Evolution of quantum criticality in CeNi$_{9-x}$Cu$_x$Ge$_4$

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Abstract
Crystal structure, specific heat, thermal expansion, magnetic susceptibility and electrical resistivity studies of the heavy fermion system CeNi$_{9-x}$Cu$_x$Ge$_4$ (0 $\leq$ x $\leq$ 1) reveal a continuous tuning of the ground state by Ni/Cu substitution from an effectively fourfold-degenerate non-magnetic Kondo ground state of CeNi$_9$Ge$_4$ (with pronounced non-Fermi-liquid features) towards a magnetically ordered, effectively twofold-degenerate ground state in CeNi$_8$CuGe$_4$ with $T_N$ = 175 $\pm$ 5 mK. Quantum critical behavior, $C/T \propto \chi \propto -\ln T$, is observed for x $\approx$ 0.4. Hitherto, CeNi$_{9-x}$Cu$_x$Ge$_4$ represents the first system where a substitution-driven quantum phase transition is connected not only with changes of the relative strength of the Kondo effect and RKKY interaction, but also with a reduction of the effective crystal field ground state degeneracy.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Since the discovery of non-Fermi-liquid (nFL) behavior in U$_{0.2}$Y$_{0.8}$Pd$_3$ characterized by a logarithmic divergence of the Sommerfeld coefficient $\gamma \simeq C/T \propto -\ln(T/T_0)$ [1], the research activity in the field of nFL physics has been very active [2]. Therefore, a great deal of attention was devoted to Kondo systems, in particular to those where nFL behavior appears to originate from critical magnetic fluctuations. The latter may emerge near a magnetic phase transition when a subtle balancing of competing interactions shifts a magnetic phase transition towards 0 K. In this quantum critical phase (QCP) scenario [3–5], Kondo interactions, favoring a paramagnetic Fermi-liquid ground state, compete with RKKY interactions, favoring a magnetically ordered ground state (for recent reviews, see [6, 7]).

The relative strength of competing Kondo and RKKY interactions, e.g. in Ce or Yb intermetallics, can be tuned by parameters such as: (i) pressure [8], (ii) substitutions [9] or (iii) external magnetic fields [10]. Besides these tuning parameters controlling the relative strength of Kondo and RKKY interactions, there is another interesting aspect of heavy fermion quantum criticality which was considered in theoretical studies, but hardly explored experimentally, namely the relative magnitudes of Kondo energy and crystal field (CF) level splittings, i.e. the effective number of the total angular momentum degrees of freedom relevant for the Kondo ground state formation. This parameter, abbreviated as effective spin degeneracy $N$, is the number of crystal field states with energies comparable to the Kondo energy or lower. Its variation may also drive a system through a QCP. Coleman [11] has shown that the critical value of the Kondo coupling constant above 0953-8984/09/235604+09$\$30.00 © 2009 IOP Publishing Ltd Printed in the UK.
which a spin-compensated ground state is stable tends to zero by $1/N$ as $N$ increases, i.e. systems having a large effective spin degeneracy $N$ are less likely to order magnetically.

In this respect, the heavy fermion CeNi$_9$Ge$_4$ represents a suitable model system to study the role of effective spin degeneracy since it displays larger $N$ values than the usual twofold one in classical nFL systems. Recently, single-ion nFL behavior of the specific heat and magnetic susceptibility has been discussed for this system. Here, CeNi$_9$Ge$_4$ shows the largest ever recorded value of the electronic specific heat coefficient $\gamma = C/T \approx 5.5 \text{ J K}^{-2} \text{ mol}^{-1}$ at 0.08 K for paramagnetic Kondo lattices [12, 13]. The dilution of the $f$ moments via Ce/La substitution, i.e. Ce$_{1-\delta}$La$_\delta$Ni$_9$Ge$_4$, revealed an approximate scaling of the magnetic specific heat contribution and magnetic susceptibility with the cerium ions’ fraction, thus indicating that the huge Sommerfeld coefficient $\gamma$ of CeNi$_9$Ge$_4$ is mainly due to Ce single-ion effects, i.e. crystal field and Kondo interactions [12]. Another remarkable feature in CeNi$_9$Ge$_4$ is its strongly temperature-dependent Sommerfeld–Wilson ratio, $R \propto \Theta_0/\gamma$, which is revealed by the distinct different temperature dependencies of specific heat and magnetic susceptibility below 1 K [12].

The origin of this behavior is illuminated by CeNi$_9$Ge$_4$ single-crystal susceptibility and polycrystal magnetic entropy data revealing a crystal field scheme of Ce$^{3+}$ with a quasi-quartet ground state below 20 K. Thereby, a fourfold effective spin degeneracy of the Ce ions is based on two doublets with an energy splitting of only 0.5 meV, i.e. of the same order of magnitude as the Kondo energy in this system, which is about 0.3 meV [14]. Numerical renormalization group (NRG) calculations by Anders and Pruschke [15, 16] using the SU(4) Anderson impurity model which also accounted for crystal field splitting demonstrated that the Kondo effect in combination with a quasi-quartet CF ground state leads to a SU(2) to SU(4) crossover regime with a significant variation of the Sommerfeld–Wilson ratio as experimentally observed in Ce$_{1-\delta}$La$_\delta$Ni$_9$Ge$_4$.

In this work we study the solid solution CeNi$_{9-x}$Cu$_x$Ge$_4$, where Ni is gradually replaced by Cu ions up to $x = 1$. This substitution modestly changes the 3d electron number and as a consequence the position of the Fermi level relative to the Ce 4f$^1$ state. Replacing Ni by Cu is thus expected to influence the Kondo and RKKY interactions. Usually such a substitution should lower the Kondo temperature and support the formation of long range magnetic order. The latter effect is also expected as a consequence of an increasing unit cell volume. Even in the absence of any lattice expansion, Ni/Cu substitution reduces the local point symmetry at Ce sites and thus cancels the quasi-fourfold degeneracy of the CF ground state.

It is important to mention that isostructural and isoelectronic CeNi$_9$Si$_4$ with an almost 4% smaller unit cell volume exhibits typical Kondo lattice behavior with a Kondo temperature, $T_K \approx 80$ K [17], being about one order of magnitude larger than $T_K$ of CeNi$_9$Ge$_4$. X-ray photoelectron spectroscopy on CeNi$_9$Si$_4$ revealed a cerium valence being close to 3+$/2$ (Ce$^{3+0.5}$ with $\delta < 0.1$) [18], thus indicating cerium in CeNi$_9$Ge$_4$ with one order of magnitude lower $T_K$ is Ce$^{3.0+\gamma}$ with $\gamma \ll 0.1$.

![Figure 1](image1.png)

Figure 1. Observed and calculated (Rietveld refinement) x-ray powder diffraction pattern of annealed CeNi$_9$CuGe$_4$. The dotted line displays the difference plot. The inset shows the variation of the lattice parameters of CeNi$_{9-x}$Cu$_x$Ge$_4$ with respect to the Cu concentration $x$.

2. Sample preparation and structural characterization

Polycrystalline samples of CeNi$_{9-x}$Cu$_x$Ge$_4$ and LaNi$_{9-x}$Cu$_x$Ge$_4$ were prepared by arc-melting of pure elements, Ce: 4N, La: 3N8 (Ames MPC [19]), Ni: 4N5; Cu: 6N; Ge: 5N, under a highly purified argon atmosphere. To obtain the highest possible homogeneity, the samples were flipped over several times and remelted. Subsequently, the samples were annealed in evacuated quartz-glass tubes for two weeks at 950°C. Inductively coupled plasma spectroscopy (ICP-OES) studies were carried out and confirmed Ni to Cu ratios in good agreement with the relative amount of the starting materials.

Standard x-ray diffraction techniques using Cu K$\alpha$ radiation were performed on carefully prepared sieved powdered samples (grain size 40 $\mu$m). CeNi$_9$Ge$_4$ crystallizes in the tetragonal space group I$4/mcm$ with lattice parameters $a = b = 7.9701(1)$ Å and $c = 11.7842(3)$ Å (for structural details, see [12, 13]). From Rietveld analysis (see as one example the CeNi$_9$CuGe$_4$ pattern in figure 1) precise lattice parameters of the solid solutions were determined. The high quality of the refinement ($R_f = 4.14$) is reflected in the difference plot. The analysis indicates that replacement of the Ni ions by Cu leads to a modest volume expansion, increasing linearly up to 0.8% for $x = 1$ (inset of figure 1). Lattice parameters of CeNi$_9$CuGe$_4$ are $a = b = 7.9816(7)$ Å and $c = 11.8441(2)$ Å. Total energy calculations based on the new full-potential augmented spherical wave method [20] suggest some degree of preferential occupation of the three inequivalent Wyckoff positions 16k, 16l, and 4d by Cu: $E$(16k) < $E$(4d) < $E$(16l). Indeed, the energy increases for Cu placed on 4d and 16l sites relative to the 16k site are about 0.1 eV and 0.2 eV, respectively.
3. Experimental results

3.1. Susceptibility and specific heat

The temperature dependence of the dc magnetic susceptibility was measured between 2 and 400 K in an applied magnetic field of 0.5 T with a commercial SQUID magnetometer (MPMS7). In the low temperature region (0.06 K < T < 2.5 K) these measurements were completed by a self-designed ac susceptibility device (B < 0.3 mT) installed in a 3He/4He-dilution refrigerator. The absolute values of the low temperature data were obtained by normalizing the ac-χ data to the dc-χ data between 1.8 and 2.5 K. The specific heat experiments were performed with a commercial equipment (PPMS) between 2 and 300 K and in a 3He/4He-dilution refrigerator down to a base temperature (BT) of 60 mK using a standard relaxation method [21].

Figure 2 shows the susceptibility χ(T) for various compositions of CeNi0.6−xCu1.6Ge4. Above 100 K all samples follow a simple modified Curie–Weiss-type law, χ(T) = C/(T − Θ) + χ0, yielding a paramagnetic Curie–Weiss temperature Θ around −14 K, χ0 ≈ 0.9 memu mol⁻¹, in reasonable agreement with the Pauli susceptibility of LaNi5Ge4 and a Curie constant C corresponding to an effective paramagnetic moment of ≈2.5 μB, which is in line with the theoretical value of 2.54 μB for a Ce³⁺ ion. Starting from the parent compound CeNi5Ge4, Ni/Cu substitution initially increases the low temperature susceptibility and reduces the temperature below which it tends to flatten (from ≈1 K for x = 0 to ≈0.2 K for x = 0.2). For CeNi5.6Cu0.4Ge4 we finally observe a χ(T) ∝ −ln(T) behavior down to the BT of 60 mK (see the inset of figure 2(a)) which is indicative of quantum criticality. At higher Cu concentrations, x > 0.4, sharp cusps in χ(T) indicate phase transitions towards antiferromagnetic (AFM) order. Finally, CeNi5CuGe4 exhibits magnetic ordering below T_N ≈ 175 ± 5 mK.

These observations are corroborated by specific heat results shown as C/T versus T plots for the same compositions of CeNi0.6−xCu1.6Ge4 in figure 2(b). In comparison to CeNi5Ge4, the initial substitution of Ni by Cu, x = 0.2, reduces the C/T values, and the observed deviation from C/T ∝ −ln(T) behavior (which starts below 250 ± 10 mK for x = 0) shifts to 150 ± 10 mK. For CeNi5.6Cu0.4Ge4, a C/T ∝ −ln(T) divergence of the Sommerfeld coefficient holds over more than one decade in temperature down to the BT of 60 mK (see the inset of figure 2(b)). We note that, despite the common −ln(T) behavior of specific heat and susceptibility of CeNi5.6Cu0.4Ge4, a simple proportionality χ ∝ C/T is not observed. Rather, these quantities reveal a temperature-dependent Sommerfeld–Wilson ratio, R ∝ χ0/γ, which has been discussed in terms of CF effects in the case of CeNi5Ge4 [15, 16]. Above x = 0.4, magnetic phase transitions are clearly indicated by specific heat anomalies superimposed on a huge background due to heavy electrons with Sommerfeld values C/T exceeding 9 J mol⁻¹ K⁻² for CeNi5Cu0.6Ge4.

To check whether the nature of magnetic ordering of CeNi5CuGe4 is long range AFM or of spin-glass type, we performed low temperature ac susceptibility measurements for two different frequencies (95 and 995 Hz) which are shown in figure 3. The absence of any significant frequency dependence of the sharp cusp of χ′ ac(T) rules out a spin-glass type of magnetic transition. Rather, it is a strong hint towards long range AFM order (compare, for example, [22]). The AFM nature of the magnetic transition in CeNi5CuGe4 is further supported by local probe muon spin relaxation (μSR) studies which will be published elsewhere [23]. μSR signals compatible with the spin-glass or cluster-glass type of magnetism have not been observed for CeNi5CuGe4 nor for CeNi5.6Cu0.4Ge4 or CeNi5Ge4 for measurements down to 40 mK.

3.2. Volume thermal expansion

The volume thermal expansion α(T) = 1/V (∂V/∂T) is ideally suited to study nFL behavior that results from a
QCP, because $\alpha(T) \propto (\partial S/\partial p)$ directly probes the pressure dependence of the entropy which is accumulated close to the instability. A theoretical study in terms of a scaling analysis suggested that the thermal expansion is far more singular than the specific heat $C(T)/T$ at any pressure-sensitive QCP [24].

We obtained $\alpha(T)$ by means of a high-resolution capacitive dilatometer (redesigned after Pott and Schefzyik [25]) attached to a $^3$He/$^4$He-dilution refrigerator. Measurements on selected compositions CeNi$_8$CuGe$_4$ with $x = 0, 0.4$ and 0.5 were carried out between 0.08 K $< T < 4$ K and in applied magnetic fields up to 4 T. The volume thermal expansion $\alpha$ is given by the sum of the linear thermal expansion coefficients along three perpendicular directions $a$, $b$ and $c$, i.e. $\alpha = \alpha_a + \alpha_b + \alpha_c$. Assuming isotropic behavior in our polycrystalline samples, we have obtained the volume expansion as $\alpha = 3\alpha_c$. For the data in a magnetic field, the linear expansion coefficient along the direction of the applied magnetic field has been determined and denoted as $\alpha_c$ in the following. This estimate does not take into account that texture may play a role in particular for CeNi$_8$Ge$_4$.

Figure 4 shows the volume thermal expansion $\alpha(T)/T$ versus $T$ for various concentrations $x = 0, 0.4$ and 0.5 for CeNi$_8$Cu$_{1-x}$Si$_x$. It reaches remarkably high values of the order of $10^{-6}$ K$^{-2}$, typical for heavy fermion compounds. In agreement with the susceptibility data of the undoped sample, we find $\alpha(T)/T = \text{constant}$ for $T < 1$ K, indicative for an FL ground state. Substituting Cu for Ni generates singular behavior in $\alpha(T)/T$ which is most pronounced for $x = 0.4$. Further increasing the Cu content causes a saturation of $\alpha(T)/T$ at lowest temperatures $T < 0.2$ K for $x = 0.5$. A suppression of the critical fluctuation is also observed by applying a magnetic field, which is demonstrated for CeNi$_{8.5}$Cu$_{0.5}$Ge$_4$ in the inset of figure 4. While for $B = 0$ T, FL behavior, i.e. $\alpha_c(T)/T = \text{const.}$ is found only up to $T \approx 0.2$ K, this behavior extends until $T \approx 0.8$ K for $B = 4$ T. At the same time, the linear coefficient $a_1$ of the FL contribution to the thermal expansion coefficient $\alpha(T) \approx a_1T$ varies by an order of magnitude from $a_1(B = 0) = 9 \times 10^{-6}$ K$^{-2}$ to $a_1(B = 4) = 4 \times 10^{-7}$ K$^{-2}$, indicating that $\alpha_c/T$ is strongly suppressed in a magnetic field. Such behavior is found in many quantum critical systems [26, 27].

3.3. Electrical resistivity

The concentration-dependent crossover from Kondo lattice behavior with unusual single-ion NFl features of the specific heat and magnetic susceptibility in CeNi$_8$Ge$_4$ to long range magnetic order in CeNi$_{8-x}$Cu$_x$Ge$_4$ is also revealed by resistivity measurements (figure 5(a)). While the LaNi$_9$Ge$_4$ reference sample exhibits a normal metallic Bloch–Grüneisen behavior with a very low residual resistivity of 5 $\mu$Ω cm, CeNi$_8$Ge$_4$ seems to represent a classical Kondo lattice, with a residual resistivity $\rho_0 \approx 9 \mu$Ω cm of a very pure sample. After passing a minimum around 30 K and a logarithmic increase, the resistivity follows a $1 - T^2$ law, as is known for Kondo systems. At lower temperatures the resistivity passes through a maximum at a temperature $T^* \approx 3$ K and follows a $T^2$-behavior below the Fermi liquid temperature $T_{FL} = 160 \pm 20$ mK. While $T_{FL}$ is close to the temperature where $C/T$ deviates from the $C/T \propto -\ln T$ trend, $T^*$ coincides approximately with the temperature below which the susceptibility of CeNi$_8$Ge$_4$ deviates from the $\chi \propto -\ln T$ behavior of CeNi$_{8.5}$Cu$_{0.5}$Ge$_4$.

The drastic initial rise of the residual resistivity between $x = 0$ and 0.2 is also observed in the solid solution CeNi$_8$Ge$_{1-x}$Si$_x$ for $x < 0.1$ [28]. This increase seems to be related to the reduction of the local site symmetry of the cerium ions which again leads to modified crystal field effects and Kondo coherence. In the same concentration range the corresponding LaNi$_9$Ge$_{1-x}$Si$_x$ series simply follows the
measured with the Van der Pauw method. The solid lines depict therefore synthesized the 4f^0 reference compounds LaNi_{9-x}Ge_{4} with unoccupied 4f states. We exhibit Kondo lattice behavior. (b) In a linear plot of ρ versus T the development of a long range ordered AFM phase transition is observed for x ≥ 0.5, while the resistivity for CeNi_{8-6}Cu_{6-x}Ge_{4} is linear down to 80 mK (solid line).

Nordheim law [29] describing the variation of the residual resistivity upon substitutional disorder.

For the Cu substituted samples the resistivity ρ(T) passes through a Kondo minimum around 30 K, followed by a logarithmic increase at lower temperatures. For x = 0.4 the resistivity increases linearly below 1 K, indicating nFL behavior (figure 5(b)). This particular behavior was observed for so-called disordered Kondo systems [30, 31]. For x ≥ 0.5 the resistivity exhibits a bending at lower T for some samples and a maximum for CeNi_{9}Cu_{6}Ge_{4} denoting long range magnetic order. This is in line with the evolution of the AFM transition observed in C/T and χ measurements.

4. Discussion

4.1. Analysis of the high temperature specific heat

To track the mechanism driving the system from Kondo lattice behavior with unusual nFL features towards RKKY antiferromagnetism, we extract the magnetic contribution of the specific heat by subtracting the total specific heat of the system LaNi_{9-x}Cu_{6-x}Ge_{4} with unoccupied 4f states. We therefore synthesized the 4f^0 reference compounds LaNi_{9}Ge_{4} and LaNi_{8-x}Cu_{6-x}Ge_{4} and interpolated the total specific heat data of the corresponding La sample for each respective composition linearly.

The magnetic contribution to the specific heat ΔC of all CeNi_{9-x}Cu_{6-x}Ge_{4} samples is depicted in figure 6. The reliability of ΔC is indicated by vertical error bars which become larger at high temperature because of the relatively large phonon background. For CeNi_{9}Ge_{4}, two pronounced maxima occur around 5 and 35 K. The former is associated with the effectively fourfold-degenerate Kondo lattice ground state which is composed by Γ_1^{(1)} and Γ_2^{(2)} CF doublets with an energy splitting of comparable magnitude as the Kondo energy [15, 16]. Thus, a broad Kondo-like contribution rather than a CF Schottky anomaly becomes visible. The second Schottky-like maximum at about 35 K is associated with a third CF doublet (Γ_6). With increasing Cu concentration this specific heat maximum gains in height, but remains roughly at the same position near 35 K. In contrast, the lower Kondo-like maximum decreases and broadens. At a Cu concentration of x = 0.4 a clear separation is observed dividing the broad hump into a low lying anomaly around 0.8 K, while the upper anomaly is shifted towards higher temperature. Finally, for x = 1, the latter merges with the Schottky contribution centered at about 35 K. The appearance of two separated maxima upon Ni/Cu substitution, originating from the initially single but broad low temperature maximum of pure CeNi_{9}Ge_{4}, indicates a reduction of the effective spin degeneracy of the Ce

Figure 5. (a) A semi-logarithmic plot of the electrical resistivity ρ(T) of CeNi_{9-x}Cu_{6-x}Ge_{4} normalized at 300 K to that of LaNi_{9}Ge_{4} which was measured with the Van der Pauw method. The solid lines depict T^2 fits for CeNi_{9}Ge_{4} and a Bloch–Grüneisen fit for LaNi_{9}Ge_{4}. CeNi_{9}Ge_{4} exhibits Kondo lattice behavior. (b) In a linear plot of ρ versus T the development of a long range ordered AFM phase transition is observed for x ≥ 0.5, while the resistivity for CeNi_{8-6}Cu_{6-x}Ge_{4} is linear down to 80 mK (solid line).

Figure 6. Temperature dependence of the magnetic specific heat ΔC of CeNi_{9-x}Cu_{6-x}Ge_{4} in semi-logarithmic representation. The errors are indicated by vertical bars exemplary for CeNi_{9}Cu_{6}Ge_{4}. The resulting temperatures where the entropy reaches R ln 2 and R ln 4 with respect to the Cu concentration x are plotted in the inset.
ions from fourfold in the case of CeNi₈Ge₄ to a twofold one for CeNi₈₋ₓCuₓGe₄.

The evolution of the temperature-dependent magnetic entropy gain, ΔS(T), further supports a change of energy scales. The inset in figure 6 shows those temperatures where the entropy approaches R ln 2 and R ln 4 in dependence on the Cu concentration. Both values, T(S = R ln 2) and T(S = R ln 4), increase significantly from CeNi₈Ge₄ to CeNi₈₋ₓCuₓGe₄, thus indicating a distinct change of the CF scheme and/or Kondo energy scale. An increase of the Kondo energy may be anticipated from the observed increase of T(K) with increasing Cu concentration, and T(S = R ln 2) increases almost twice as large as for CeNi₉Ge₄ (inset of figure 6).

4.2. Discussion of the low temperature specific heat

To obtain a more reliable estimate for the trend of the Kondo energies in CeNi₉₋ₓCuₓGe₄ we utilized the resonant-level model by Schotte and Schotte [32] in combination with a molecular field approach to account for long range magnetic order [33, 34].

For a spin-1/2 system the magnetic contribution of the specific heat Cₘₐ₉g(T) follows in this model from

\[ C_{\text{mag}}(T) = 2k_B \text{Re} \left\{ \frac{z}{T} \left[ 1 - \left( \frac{z}{T} - \frac{\partial z}{\partial T} \right) \psi \left( \frac{1}{2} - \frac{z}{T} \right) \right] \right\}, \tag{1} \]

where z = T_K + i E(T)/2π k_B, with T_K the Kondo temperature, E the Zeeman energy and ψ the derivative of the digamma function. By factoring the mean-field theory into the resonant-level model, E gets temperature-dependent with

\[ E(T) = g\mu_B \lambda M(T) = J \frac{M(T)}{g\mu_B}. \tag{2} \]

Here g is the Landé factor (for Ce³⁺: g = 6/5), λ is the molecular field constant, J describes the s–f exchange interaction and \( M(T) \) is the simple magnetization for a two-level system. Since the levels are broadened by the Kondo effect the simple Brillouin function becomes modified and \( M(T) \) is

\[ M(T) = \frac{g\mu_B}{\pi} \text{Im} \left[ \psi \left( \frac{1}{2} + \frac{T_K + i E(T)}{2\pi k_B T} \right) \right]. \tag{3} \]

Finally, while equations (2) and (3) are implicit equations for \( E(T) \) and \( M(T) \), respectively, we have to calculate the specific heat (equation (1)) numerically.

Model calculations for specific heat data were done for all samples with \( x \geq 0.5 \). In this composition range, T(S = R ln 2) and T(S = R ln 4) are roughly constant at values almost twice as large as for CeNi₉Ge₄ (inset of figure 6).

The results are plotted in figure 7. The simple molecular field model plus the Kondo effect within a doublt ground state, of course, does not account for any kind of short range magnetic correlations or fluctuations. Therefore it cannot be taken into account for the experimental data over an extended temperature range. Nevertheless, it qualitatively reproduces the evolution of the magnetic specific heat anomalies and Kondo contributions of CeNi₉₋ₓCuₓGe₄ for \( x > 0.5 \). The exchange interactions J and the Kondo temperatures T_K obtained from the resonant-level model are recorded in figure 7(b). In addition, T_K is depicted in a magnetic phase diagram of CeNi₉₋ₓCuₓGe₄ (see section 4.4). A linear extrapolation of the T_K values above \( x = 0.5 \) results in a T_K = 3.5 K for CeNi₉Ge₄, which is in line with T_K revealed by the quasi-elastic linewidth observed by quasi-elastic neutron scattering [14]. The substantial reduction of T_K with increasing Cu concentration is in accordance with the usual trend observed in the case of Ni/Cu substitution in other cerium heavy fermion systems [35]. In addition, the drop of
The Kondo temperature $T_K$ combined with the lowering of the exchange interaction parameter $J$ is in agreement with the Doniach picture [36]. Therefore, the change of the magnetic entropy gain observed from $x = 0$ to 0.5 is attributed to CF effects causing a reduction of the effective spin degeneracy of Ce ions from fourfold in the case of CeNi$_9$Ge$_4$ to a twofold one for CeNi$_{8.6}$Cu$_{0.4}$Ge$_4$.

4.3. Thermal expansion and Gr"uneisen ratio

To analyze the nature of the QCP indicated by the thermodynamic data of CeNi$_{8.6}$Cu$_{0.4}$Ge$_4$ we calculate the dimensionless Gr"uneisen ratio $\Gamma(T) = (V_m/kT)\times\alpha(T)/C(T)$ displayed in figure 8 for CeNi$_{9-x}$Cu$_x$Ge$_4$ with $x = 0, 0.4$ and 0.5. In this calculation of $\Gamma(T)$, the molar volume is $V_m = 7.485 \times 10^{-28}$ m$^3$ and the isothermal compressibility is assumed to be $kT = 1 \times 10^{-11}$ Pa$^{-1}$, which is a typical value for heavy fermion systems. The temperature-independent Gr"uneisen ratio of CeNi$_{9}$Ge$_4$ $[\Gamma(T) = \text{const.}]$ below 200 mK and the enhanced values of $\Gamma$ compared to the usual metals characterize CeNi$_{9}$Ge$_4$ as a Kondo lattice system [37]. In contrast to the latter system, both CeNi$_{8.6}$Cu$_{0.4}$Ge$_4$ and CeNi$_{8.5}$Cu$_{0.5}$Ge$_4$ exhibit an order of magnitude higher $\Gamma$ value which is typical for heavy fermion systems close to a magnetic instability [26, 38, 39]. For the antiferromagnetic system CeNi$_{8.5}$Cu$_{0.5}$Ge$_4$, a negative Gr"uneisen ratio is expected below the Néel temperature ($T_N = 55$ mK). The decrease of $\Gamma(T)$ below 0.2 K may indicate short range order above $T_N$. In particular for CeNi$_{8}$Cu$_{0.4}$Ge$_4$ the high $\Gamma$ values $[\Gamma(0.35 \text{ K}) = 340]$ and the strong temperature dependence of $\Gamma(T)$ above 0.35 K are quite different to the parent compound CeNi$_9$Ge$_4$ and suggest the vicinity of a QCP. Below 0.35 K, $\Gamma(T)$ saturates and passes a broad maximum, indicating that quantum critical behavior, i.e. the divergence of $\Gamma(T \to 0)$ suggested by Zhu et al [24], is vanishing at very low temperatures. This could be explained by assuming that either the $x = 0.4$ system is located somewhat away from the QCP or that the quantum phase transition is slightly rounded by disorder in line with the results of the electrical resistivity. Above 0.35 K the Gr"uneisen ratio follows, within experimental resolution, a logarithmic dependence, which clearly deviates from the scaling prediction for a standard QCP by Zhu et al [24]. We speculate that the reduction of the effective crystal field ground state degeneracy near the quantum phase transition may modify quantum criticality in our system.

4.4. Evolution of quantum criticality and crystal field

The phase diagram of CeNi$_{9-x}$Cu$_x$Ge$_4$ illustrates the presence of a quantum phase transition near $x = 0.4$ (figure 9). The FL temperature $T_{FL}$ of CeNi$_9$Ge$_4$ is estimated from the deviation from $T^2$ behavior of the resistivity at low temperature (see figure 5). In addition, the Néel temperature $T_N$ is derived from the sharp kink of $C/T$ and the susceptibility found in the AFM region. At the critical composition, CeNi$_{8.6}$Cu$_{0.4}$Ge$_4$, $C/T$ and $\chi(T)$ display a logarithmic temperature dependence over more than one decade in temperature at least down to 60 mK and the thermal expansion coefficient $\alpha/T$ diverges. These results signify the presence of a heavy fermion QCP. In CeNi$_{8}$Cu$_{0.4}$Ge$_4$, the nFL state develops from a crossover between a Kondo state ($x \ll 0.4$) to an antiferromagnetic coherent state ($x \geq 0.4$) starting from $T_N = 0$ K at $x \approx 0.4$. The question arises whether this crossover is mainly driven by ‘disorder’ in the energy phase space (originated by substitutional disorder) or mainly by the reduction of the effective ground state degeneracy in combination with a reduction of the Kondo energy. The latter scenario implies that the crossover from the paramagnetic to the AFM ground...
state is connected with a QCP similar to the one discussed for CeCu_{6-x}Au_x [40].

To elucidate the change of the CF scheme in the solid solution from CeNi_{8}Ge_{4} with a quasi-fourfold ground state [12, 14] to CeNi_{8}CuGe_{4} we have quantitatively analyzed the magnetic contribution to the specific heat \( \Delta C \) of CeNi_{8}CuGe_{4} by model calculations combining specific CF schemes with an energy-split ground state doublet as considered above in the resonant-level model for CeNi_{8}CuGe_{4} we have quantitatively analyzed the magnetic contribution to the specific heat \( \Delta C \) of CeNi_{8}CuGe_{4} by model calculations combining specific CF schemes with an energy-split ground state doublet as considered above in the resonant-level model for CeNi_{8}CuGe_{4} with \( J = 2.3 \) K and \( T_K = 1.3 \) K (see figure 7(b)). The bases for these calculations are preliminary inelastic neutron scattering (INS) data, where two crystal field transitions at 8.7 meV (\( \approx 101 \) K) and 12.0 meV (\( \approx 139 \) K) were obtained from energy-loss spectra (inset, figure 10). In figure 10 two model cases considering different crystal field tuning mechanisms are displayed. The first one is based on a unique crystal field environment for each cerium atom using the CF level extracted from the INS experiment. Here the CF splitting of the \( j = 5/2 \) state, \( \Delta_1 = 101 \) K, is significantly larger than \( \Delta_1 \approx 6 \) K of the undoped CeNi_{9}Ge_{4}, whereas \( \Delta_2 = 139 \) K is of similar magnitude [14] (see the dashed line in figure 10). The second model scenario considers two or more different CF environments arising from a stochastic occupation of the Cu atoms on the Ni1 site (Wyckoff position 16k; section 2). For example, the solid line in figure 10 represents a model calculation based on two weighted CF schemes consisting of \( \Delta_1 = 26 \) K, \( \Delta_2 = 101 \) K (40%) and \( \Delta_1 = 71 \) K, \( \Delta_2 = 139 \) K (60%). Here the two CF transitions from the INS studies were utilized to describe each upper CF level \( \Delta_2 \) of the two different environments. The latter model is in better agreement with the experimental specific heat data of CeNi_{9}CuGe_{4}, thus indicating some variability of the local CF level schemes due to substitutional disorder, but nevertheless, relatively defined excitation energies and a twofold degenerate CF ground state.

The nFL behavior of CeNi_{8.6}Cu_{0.4}Ge_{4} is thus attributed to a QCP caused by a reduction of the Kondo temperature in combination with a disorder-induced reduction of the local site symmetry of cerium ions which alters the effective ground state degeneracy. While the Kondo disorder model considers a Kondo singlet ground state with varying local coupling strength, a different aspect is more relevant in the present case, namely the reduction of the local site symmetry of cerium ions which changes the local ground state from effectively fourfold- to twofold-degenerate. Such symmetry changes would generally be expected to be very susceptible to disorder: as we have seen above, this kind of scenario could consistently explain our experimental results.

5. Summary

In conclusion, in the system CeNi_{9-x}Cu_xGe_{4} (0 \( \leq x \leq 1 \)) the change from an effectively fourfold-degenerate to a twofold-degenerate ground state is accompanied by a quantum phase transition near CeNi_{8.6}Cu_{0.4}Ge_{4} which separates CeNi_{9}Ge_{4}, a Kondo lattice with unusual nFL features, from the antiferromagnetically ordered state for \( x \geq 0.4 \). In this solid solution Ni/Cu substitution crucially alters the local CF environment of the Ce ions. This leads to a quantum phase transition, which is not only driven by the competition between the Kondo effect and RKKY interaction, but also by a reduction of the effective CF ground state degeneracy.

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References

[1] Seaman C L, Maple M B, Lee B W, Ghamaty S, Torikachvili M S, Kang J-S, Liu L Z, Allen J W and Cox L D 1991 Phys. Rev. Lett. 67 2882
[2] Stewart G R 2001 Rev. Mod. Phys. 73 797
Stewart G R 2006 Rev. Mod. Phys. 78 743
[3] Hertz J A 1976 Phys. Rev. B 14 1165
[4] Millis A J 1993 Phys. Rev. B 48 7183
[5] Moriya T and Takimoto T 1995 J. Phys. Soc. Japan 64 960
[6] von Löhnysen H, Rosch A, Voitja M and Wölfle P 2007 Rev. Mod. Phys. 79 1015
[7] Gegenwart P, Si Q and Steglich F 2008 Nat. Phys. 4 186
[8] Bogenberger B and von Löhnysen H 1995 Phys. Rev. Lett. 74 1016
[9] Andra B and Stewart G R 1993 Phys. Rev. B 47 3208
[10] Heuser K, Scheidt E-W, Schreiner T and Stewart G R 1998 Phys. Rev. B 57 R4198
[11] Coleman P 1983 Phys. Rev. B 28 5255
[12] Killer U, Scheidt E-W, Eickerling G, Michor H, Sereni J, Pruschke T and Kehrein S 2004 Phys. Rev. Lett. 93 216404
[13] Michor H, Bauer E, Dusek C, Hilscher G, Rogl P, Chevalier B, Etourneau J, Giester G, Killer U and Scheidt E-W 2004 J. Magn. Magn. Mater. 272–276 227
[14] Michor H et al 2006 Physica B 378–380 640
[15] Scheid E-W, Mayr F, Killer U, Scherer W, Michor H, Bauer E, Kehrein S, Pruschke T and Anders F 2006 Physica B 378–380 154
[16] Anders F and Pruschke T 2006 Phys. Rev. Lett. 96 086404
[17] Michor H, Berger S, El-Hagary M, Paul C, Bauer E, Hilscher G, Rogl P and Giester G 2003 Phys. Rev. B 67 224428
[18] Wang X, Michor H and Grioni M 2007 Phys. Rev. B 75 035127
[19] Materials Preparation Center, Ames Laboratory, US DOE Basic Energy Sciences, Ames, IA, USA available from: www.mpc.ameslab.gov
[20] Eyert V 2007 The Augmented Spherical Wave Method—A Comprehensive Treatment (Lecture Notes in Physics vol 719) (Berlin: Springer)
[21] Bachmann R et al 1972 Rev. Sci. Instrum. 43 205
[22] Körner S, Weber A, Hemberger J, Scheidt E-W and Stewart G R 2000 J. Low Temp. Phys. 121 105
[23] Michor H and Hillier A D 2006 ISIS Experimental Report RB520265 unpublished
[24] Zhu L, Garst M, Rosch A and Si Q 2003 Phys. Rev. Lett. 91 066404
[25] Pott R and Schefzyk R 1983 J. Phys. E: Sci. Instrum. 16 444
[26] Küchler R et al 2003 Phys. Rev. Lett. 91 066405
[27] Donath J G, Steglich F, Bauer E D, Sarrao J L and Gegenwart P 2008 Phys. Rev. Lett. 100 136401
[28] Gold C and Scheidt E-W 2008 unpublished
[29] Cox C L and Grewe N 1988 Z. Phys. B 71 321
[30] Bernal O, MacLaughlin D E, Lukefahr H G and Andra B 1995 Phys. Rev. Lett. 75 2023
[31] Miranda E, Dobrosavlievic V and Kotliar G 1997 Phys. Rev. Lett. 78 290
[32] Schotte K D and Schotte U 1975 Phys. Lett. A 55 38
[33] Bredl C D, Steglich F and Schotte K D 1978 Z. Phys. B 29 327
[34] Gribanov A et al 2006 J. Phys.: Condens. Matter 18 9593
[35] Nieuwenhuys G J 1995 Handbook of Magnetic Materials ed K H J Buschow (Amsterdam: North-Holland) chapter 1, p 1
[36] Doniach S 1977 Physica B+C 91 231
[37] Takke R, Nilsch M, Assmus W, Lüthi B, Pott R, Schefzyk R and Wohleben D K 1981 J. Phys.: Condens. Matter 44 33
[38] Kambe S, Flouquet J, Lejey P, Hean P and de Visser A 1997 J. Phys.: Condens. Matter 9 4917
[39] Küchler R, Gegenwart P, Heuser K, Scheidt E-W, Stewart G R and Steglich F 2004 Phys. Rev. Lett. 93 096402
[40] Löhnysen H v 1996 J. Phys.: Condens. Matter 8 9689