Competing magnetic interactions in $\mathrm{CeNi}_{9-x}\mathrm{Co}_x\mathrm{Ge}_4$

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Abstract. $\mathrm{CeNi}_9\mathrm{Ge}_4$ exhibits outstanding heavy fermion features with remarkable non-Fermi-liquid behavior which is mainly driven by single-ion effects. The substitution of Ni by Cu causes a reduction of both, the RKKY coupling and Kondo interaction, coming along with a dramatic change of the crystal field (CF) splitting. Thereby a quasi-quartet ground state observed in $\mathrm{CeNi}_9\mathrm{Ge}_4$ reduces to a two-fold degenerate one in $\mathrm{CeNi}_8\mathrm{CuGe}_4$. This leads to a modification of the effective spin degeneracy of the Kondo lattice ground state and to the appearance of antiferromagnetic (AFM) order. To obtain a better understanding of consequences resulting from a reduction of the effective spin degeneracy, we stepwise replaced Ni by Co. Thereby an increase of the Kondo and RKKY interactions through the reduction of the effective d-electron count is expected. Accordingly, a paramagnetic Fermi liquid ground state should arise. Our experimental studies, however, reveal AFM order already for small Co concentrations, which becomes even more pronounced with increasing Co content x. Thereby the modification of the effective spin degeneracy seems to play a crucial role in this system.

1. Introduction

Due to the wide variety of their ground states, Ce based ternary intermetallic compounds have attracted large attention during the last years. Inherent to these materials is the existence of localized $4f$ electrons (Ce^{3+}) at high temperatures. In the low temperature limit, the competition between Kondo and RKKY interactions results in different ground states depending on their relative magnitudes [1]: The formation of long-range magnetic order depends quadratically on the dimensionless coupling parameter $N(E_\mathrm{F})J_0$, while the development of a local Kondo ground state depends exponentially on $N(E_\mathrm{F})J_0$ [2]. The dimensionless effective exchange coupling parameter $N(E_\mathrm{F})J_0$ correlates the exchange interaction, J_0, between $4f$ localized magnetic moments and conduction electrons with the electronic density of states at the Fermi level, $N(E_\mathrm{F})$. Accordingly, small values of $N(E_\mathrm{F})J_0$ favor long range magnetic order, while for large values of $N(E_\mathrm{F})J_0$ a paramagnetic Kondo-screened ground state is anticipated. At the borderline between these two regimes non Fermi-liquid (NFL) behavior has been observed.

Apart from this classical scenario other mechanisms, e.g., via a change of the effective spin degeneracy N may occur. The latter was analyzed by Coleman [3]. This additional mechanism seems to be relevant for the ground state of the heavy fermion system $\mathrm{CeNi}_9\mathrm{Ge}_4$ [4]. In the substitution series $\mathrm{CeNi}_{9-x}\mathrm{Cu}_x\mathrm{Ge}_4$ a reduction from a quasi-quartet ground state in $\mathrm{CeNi}_9\mathrm{Ge}_4$ to a two-fold degenerated one in $\mathrm{CeNi}_8\mathrm{CuGe}_4$ leads to antiferromagnetic (AFM) order[4]. This is also benefitted by a reduction of the effective exchange coupling $N(E_\mathrm{F})J_0$ due to an enhanced effective d-electron count.

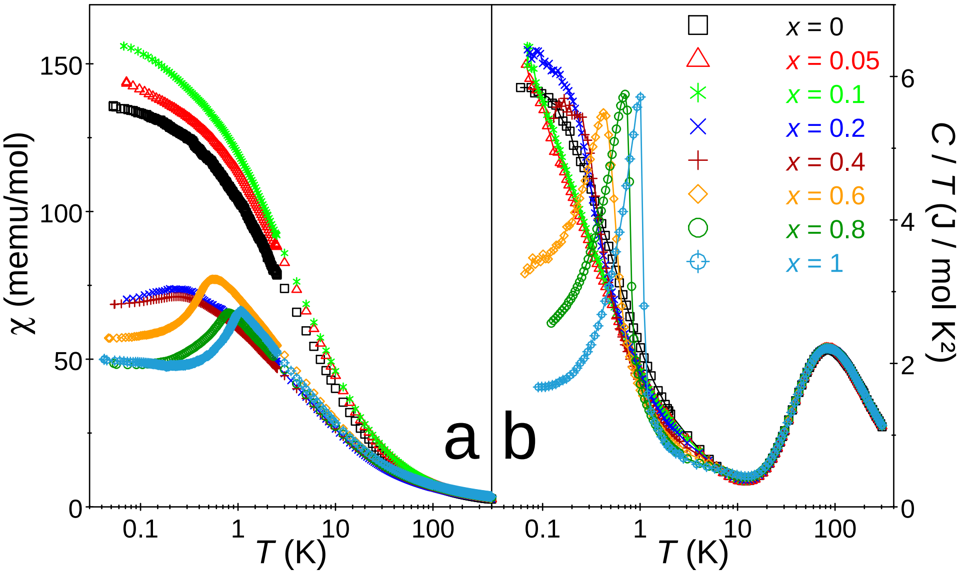

Figure 1. (Color online) (a) The magnetic susceptibility χ and (b) the specific heat divided by temperature C/T of $\mathrm{CeNi}_{9-x}\mathrm{Co}_x\mathrm{Ge}_4$ in semi-logarithmic plots. AFM transitions are evident for $x \geq 0.2$.

In the present work, the hybridization strength in $\mathrm{CeNi}_9\mathrm{Ge}_4$ is tuned contrary through non-isoelectronic Ni/Co substitution to study the influences of the effective spin degeneracy in more detail.

2. Sample preparation and characterization

For the synthesis of the samples of $\mathrm{CeNi}_{9-x}\mathrm{Co}_x\mathrm{Ge}_4$ materials of high purity were used: Ce: 4N; La: 3N8 (Ames MPC); Ni: 4N5; Co: 4N8; Ge: 5N. They were prepared by arc melting under argon atmosphere followed by an annealing process at 950° C for two weeks inside an evacuated quartz tube. Less than 0.5 % weight loss occurred during the melting process. Optical emission spectroscopy in an inductively coupled plasma (ICP-OES) and energy dispersive X-ray spectroscopy (EDX) analysis indicated that the samples used in this work are essentially single phase. X-ray powder diffraction experiments revealed that all samples crystallize in the $\mathrm{LaFe}_9\mathrm{Si}_4$-type structure (tetragonal spacegroup $I4/mcm$). For the whole concentration range, the replacement of Ni by Co does not lead to any significant changes in the lattice parameters and therefore also not in the unit cell volume. Thus, volume effects in $\mathrm{CeNi}_{9-x}\mathrm{Co}_x\mathrm{Ge}_4$ due to the substitution, i.e. chemical pressure, are hardly relevant.

3. Experimental results

Figure 1 a presents the temperature dependent magnetic susceptibility χ of $\mathrm{CeNi}_{9-x}\mathrm{Co}_x\mathrm{Ge}_4$. The magnetic behavior of the parent compound $\mathrm{CeNi}_9\mathrm{Ge}_4$ is discussed in more detail in [5]. The Co substituted samples follow a simple modified Curie-Weiss-type law, $\chi(T) = C/(T - \Theta) + \chi_0$, above 100 K . From a least-square fit the following parameters were obtained: i) the paramagnetic Curie-Weiss temperature Θ around -40 K, ii) the temperature independent susceptibility contribution χ_0 between 0.9 memu mol^{-1} for $x = 0.05$ and 1.6 memu mol^{-1} for $x = 1$, iii) the Curie constant C corresponding to an effective paramagnetic moment between 2.5 μ_B and 2.6 μ_B,

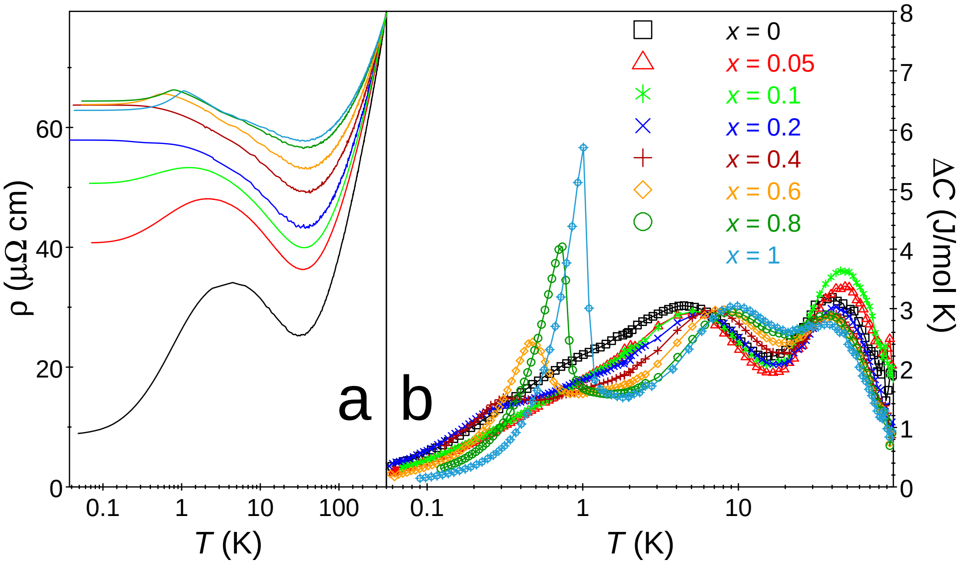

Figure 2. (Color online) (a) The electrical resistivity $\rho(T)$ of $\mathrm{CeNi}_{9-x}\mathrm{Co}_x\mathrm{Ge}_4$ normalized at 300 K to that of $\mathrm{LaNi_9Ge_4}$ in a semi-logarithmic plot. (b) Temperature dependence of the magnetic specific heat ΔC of $\mathrm{CeNi}_{9-x}\mathrm{Co}_x\mathrm{Ge}_4$ in semi-logarithmic representation.

which is in line with the theoretical value of $2.54\,\mu_\mathrm{B}$ for a Ce^{3+} ion. An itinerant paramagnetic Co sublattice as observed in La- and $\mathrm{CeCo_9Ge_4}$ [6] is not observed. For smallest Co concentrations $x \leq 0.1$ the substitution of Ni by Co causes a moderate increase of the low temperature susceptibility as compared to the parent compound $\mathrm{CeNi_9Ge_4}$. This may be caused by the influence of substitutional disorder leading to partial reduction of the AFM intersite coupling or to some ferromagnetic correlations. Between $x = 0.1$ and $x = 0.2$ the low temperature susceptibility decreases dramatically. This huge change in the magnetic properties can not only be caused by a marked increase of the Kondo screening but also by a reduction of the effective spin degeneracy. On further increasing x the development of sharp cusps in $\chi(T)$ finally indicates phase transitions towards AFM order. $\mathrm{CeNi_8CoGe_4}$ exhibits magnetic ordering below $T_\mathrm{N} \approx 1$ K. These observations are corroborated by specific heat results. Figure 1 b shows the specific heat divided by temperature C/T of $\mathrm{CeNi}_{9-x}\mathrm{Co}_x\mathrm{Ge}_4$ between 60 mK and 300 K on a semi-log scale. Already a small amount of Co ($x \leq 0.1$) causes a $C/T \propto -\ln(T)$ divergence of the Sommerfeld coefficient which holds over more than one decade in temperature down to $T = 70$ mK. This reveals a temperature dependent Sommerfeld-Wilson ratio, $R \propto \chi_0/\gamma$, which has been discussed in terms of crystal field effects and a fourfold degenerated ground state in the case of $\mathrm{CeNi_9Ge_4}$ [7, 8]. In addition, the divergence of the Sommerfeld coefficient indicates the vicinity to a QCP transition which may occur around $x = 0.15$. At higher Co concentrations susceptibility and specific heat reveal, initially a flattening ($x = 0.2; 0.4$) and then a peak $x \geq 0.6$ indicating an AFM transition. Additionally, the low temperature limit of C/T decreases with higher x values, indicating an enhancement of the Kondo coupling.

In Figure 2 a the electrical resistivity of $\mathrm{CeNi}_{9-x}\mathrm{Co}_x\mathrm{Ge}_4$ is displayed. The classical Kondo lattice behavior of $\mathrm{CeNi_9Ge_4}$ which is observed, is explicit illustrated in [4]. The two samples with a small Co concentration ($x = 0.05$ and $x = 0.1$) exhibit a similar behavior but with enhanced residual resistances at low temperature. Additionally, with increasing Co content, substitutional disorder shifts the Kondo coherence maximum to lower temperatures. On further increase of x the Kondo lattice behavior disappears and the residual resistance increases further. The cusps in the electrical resistivity for $x \geq 0.6$ indicate the AFM transition, already observed in magnetic susceptibility and specific heat data.

In order to study the crossover from single-ion Kondo behavior towards long range AFM order, the magnetic contribution to the specific heat ΔC (Fig 2 b) was extracted by subtracting the total specific heat of the corresponding La compounds with unoccupied $4f$ states. For $\mathrm{CeNi_9Ge_4}$ two pronounced maxima around 5 und 35 K are obtained. The first Schottky-like anomaly is associated with a quasi-quartet ground state characterized by a subtle splitting into two doublets $\Gamma_7^{(1)}$ and $\Gamma_7^{(2)}$ which interacts with the Kondo screening on the same energy scale [5]. The second maximum is associated with the Γ_6 CF doublet. With increasing Co concentration the upper maximum remains almost constant, while the lower maximum shifts to higher temperatures (10 K for $x = 1$). This refers to a reduction of the effective spin degeneracy N like it was found in $\mathrm{CeNi_{9-x}Cu_xGe_4}$ [4] and appears to be the driving force for the AFM ordering. For $x \geq 0.2$ the AFM phase transition at low temperatures is observed.

4. Conclusions

Studying the ground state evolution in $\mathrm{CeNi_{9-x}Co_xGe_4}$, we found already for small Co concentrations $x \leq 0.1$ a logarithmic divergence of the Sommerfeld coefficient $\gamma \simeq C/T$, as it is typical for a QCP transition. In contrast, the magnetic susceptibility of these compounds shows a flattening instead of the logarithmic divergence which would be expected in case of a temperature independent Sommerfeld-Wilson ratio χ_0/γ. A further increase of the Co content $x \geq 0.2$ leads to a significant pronounced increase of the Kondo temperature but nonetheless AFM order appears in this system. The latter is counter-intuitive to the usual Doniach picture and seems to result from a reduction of the effective spin degeneracy N. The fact that a similar scenario is observed also in $\mathrm{CeNi_{9-x}Cu_xGe_4}$ [4], where the $3d$ electron count changes in the opposite way, clearly suggests that the reduction of the effective spin degeneracy away from the paramagnetic quasi-quartet ground state in $\mathrm{CeNi_9Ge_4}$ plays a crucial role in the formation of long range AFM order in the system $\mathrm{CeNi_{9-x}}TM_x\mathrm{Ge_4}$ (TM = Cu, Co).

5. Acknowledgments

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