LOW-TEMPERATURE SPECIFIC HEAT OF SLIGHTLY OFF-STOICHIOMETRIC $CeNi_2Ge_2$*

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We have studied the effect of slight changes in the chemical composition on the low-temperature specific heat of $Ce_{0.98}Ni_{2+x}Ge_{2-x}$ with $0 \leq x \leq 0.015$. Above 0.3 K, the specific heat obeys a $C(T)/T$=γ_0-$\alpha T^{1/2}$ dependence for all the Ni-Ge compositions investigated. Below 0.3 K, however, the $C(T)/T$ data are strongly sample dependent. While for x=0 the quantum-critical $T^{1/2}$ behavior is masked by a low-T upturn, which follows a $C(T)$=AT^{-2} dependence with a large A parameter (62 μJK/mol), for x=0.015 a leveling off in $C(T)/T$ at $\simeq$ 380 mJ/K^{2}mol is observed. The sample with x=0.005 and small low-T upturn below 0.14 K appears to be in the vicinity to the QCP.

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The non-magnetic heavy-fermion $CeNi_2Ge_2$ compound is believed to be one of only a few undoped systems at or close to a quantum critical point (QCP). Nevertheless, there are conflicting results about whether non-Fermi-liquid (nFL) properties of $CeNi_2Ge_2$ are held down to the lowest temperature of measurement, or whether Fermi-liquid (FL) behavior is recovered below about 0.3 K. Moreover, the origin of the QCP has not been clarified up to now [1]. In an earlier work on the specific heat, $C(T)$, of $CeNi_2Ge_2$ a small cusp in $C(T)/T$ at $T \simeq 0.3$ K has been reported [2] but a recent study revealed $C(T)/T$ = const. ($\simeq$ 380 mJ/K^{2}mol) and $\sim$ log-T below and above 0.3 K, respectively [3]. On the other hand, measurements on single crystal showed the $T^{1/2}$ dependence of $C(T)/T$ between 0.25 K and 6 K [4]. Finally, in at least some samples of $CeNi_2Ge_2$ a sample-dependent anomalous upturn in $C(T)/T$ below about 0.3 K accompanied by the $T^{1/2}$ dependence at higher temperatures has been observed [5].

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In order to bring this puzzle closer to a solution, we performed systematic $C(T)$ studies on slightly off-stoichiometric $CeNi_2Ge_2$. The starting chemical composition can be described by the formula $Ce_{0.98}Ni_{2+x}Ge_{2-x}$ with $0 \leq x \leq 0.015$. Because of the particularities of the Ce–Ni–Ge ternary chemical phase diagram [6], the $x = 0$ sample has a Ge-rich 122-phase, whereas a stoichiometric 122 phase is expected in the sample $x \approx 0.015$ in accordance with results of the residual resistivity [7]. The specific heat between 0.05 and 1 K has been measured by a compensated heat-pulse method. Since we investigated relatively large samples having the similar mass ~ 170 mg, the differences between their $C(T)$ dependencies are unaffected by possible uncertainties of the addenda estimate at lowest temperatures.

In Fig. 1 we show specific-heat data, as $C(T)/T$ *vs* $T^{1/2}$, obtained below 1 K for $Ce_{0.98}Ni_{2+x}Ge_{2-x}$ polycrystals with various Ni-Ge composition. Above 0.3 K, the $C(T)/T$=γ_0-$\alpha T^{1/2}$ dependence, which is predicted for

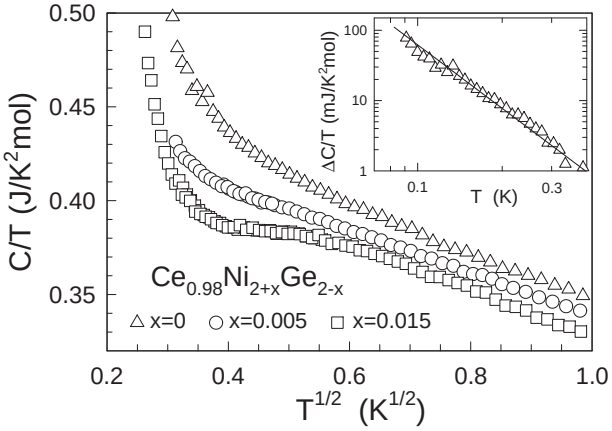

Fig. 1. Low-temperature specific heat of slightly off- stoichiometric $CeNi_2Ge_2$ polycrystals with various starting chemical composition. Inset: $\Delta C(T)/T = C(T)/T$-(γ_0-$\alpha T^{1/2}$) for the $x = 0$ sample on a double-logarithmic scale below 0.4 K. $\gamma_0 = 472$ mJ/K^{2}mol and α=125 mJ/K$^{5/2}$mol were approximated from the temperature range $0.35 \div 1$ K. The solid line displays a $\Delta C(T) = AT^{-2}$ fit with $A = 62\,\mu$JK/mol.

three-dimensional (3D) spin fluctuations (SF) in the vicinity of the antiferromagnetic (AF) QCP [8] has been clearly observed in all the samples investigated. Whereas the slope of the $C(T)/T$ curves does not change significantly with x and varies between 111 and 125 mJ/K$^{5/2}$mol, γ_0 monotonously decreases from 470 to 440 mJ/K^{2}mol with increasing Ni concentration. Below 0.3 K, $CeNi_2Ge_2$ exhibits an enormous sensitivity of $C(T)$ to a tiny variation of the chemical composition. While for $x \leq 0.005$ the quantum-critical

$T^{1/2}$ dependence is masked by a low-T upturn, for x=0.015 the low-T upturn is preceded by a levelling off in $C(T)/T$ at $\simeq$ 380 mJ/K^{2}mol. A closer inspection of the $\Delta C(T)/T$=$C(T)/T$-(γ_0-$\alpha T^{1/2}$) data at $T \leq 0.3$ K for the x=0 sample reveals a well-defined AT^{-3} behavior, where the A parameter amounts to 62 μJK/mol (see the inset of Fig. 1). If this upturn would be related to the Zeeman splitting of the nuclear ^{61}Ni or ^{73}Ge spin states an internal magnetic filed, $B_{\rm int}$, of the order of 30 T would be necessary. To date, there are no experimental evidences for such a high field. In the case of $x = 0.005$ the upturn becomes evident only below 0.14 K and, hence, a much smaller value of A (*i.e.* $B_{\rm int} \ll$ 30 T) may be deduced. A detailed analysis, however, requires additional experiments at lowest temperatures.

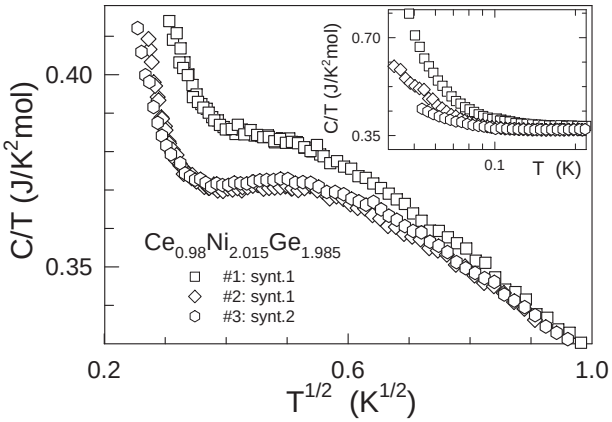

Fig. 2. The low-T heat capacity, as $C(T)/T$ *vs* $T^{1/2}$, of three $Ce_{0.98}Ni_{2+x}Ge_{2-x}$ samples with $x = 0.015$. Inset: The sample-dependent upturn in $C(T)/T$ below 0.2 K.

Since $CeNi_2Ge_2$ shows an extreme sensitivity of its specific heat against variation of the Ni–Ge composition, one can suppose that a tiny difference in the *average* occupation of the non-f sites surrounding Ce plays a key role. This conjecture is supported by the results from Fig. 2, in which the $C(T)/T$ curves for various $Ce_{0.98}Ni_{2.015}Ge_{1.985}$ polycrystals are presented. Whereas the sample ♯1 (*cf.* Fig. 1) and ♯2 were cut out from the same batch, the third one was independently synthesized keeping the same conditions. Note that a detailed X-ray analysis did not detect a difference between the $x = 0.015$ samples investigated. Except for different slope of the upturns in $C(T)/T$ below 0.1 K (see the inset of Fig. 2), no significant distinctions between the samples ♯2 and ♯3 are found. On the other hand, their $C(T)/T$ data differ distinctly from those observed for the sample ♯1, *e.g.*, both of them deviate from the $T^{1/2}$ dependence already at $\sim$ 0.36 K with $\gamma_0 \simeq$ 370 mJ/K^{2}mol and their low-T upturn becomes evident at slightly lower temperature. These

observations point to the same *average* occupation of the non-f sites in the samples ♯2 and ♯3 that, however, is different in the sample ♯1. In the latter case, the true Ni concentration appears to be smaller than in the former ones. Some distinctions between the specimens ♯2 and ♯3 below 0.1 K suggest a slightly different distribution of the Ni/Ge ratio, *i.e.* various *local* occupation of the non-f sites surrounding Ce.

An extreme sensitivity of the specific heat of $CeNi_2Ge_2$ against variations of the chemical composition close to the 1:2:2 stoichiometry point somewhat resembles the properties of $CeCu_2Si_2$. In the latter system four different ground states were identified in the homogeneity range, extending to approximately $\pm 0.5\%$ from the true stoichiometry point [5]. The pronounced nFL behavior in $CeCu_2Si_2$ with $C(T)/T = \gamma_0$-$\alpha T^{1/2}$ presumably is governed by a spin-density-wave instability at the QCP. Note that the transition from the paramagnetic state into "phase A" being well marked in both the transport and thermodynamic properties at around 0.7 K, becomes hardly detectable as $T_A \to 0$ [9]. For several slightly Ge-rich $CeNi_2Ge_2$ samples, resistivity measurements done at $B = 0$ have revealed an anomaly at 0.6 K that strongly resembles the "A-phase" transition in $CeCu_2Si_2$ [7]. Unfortunately, besides the above-mentioned singularities, no additional one is observed in our specific-heat experiments.

In summary, we have shown that a tiny increase of the Ni concentration leads to a decrease of the low-T upturn accompanied by a leveling off in $C(T)/T$. In other words, upon increasing x from 0 to 0.015 we have observed an extension of the nFL behaviors towards lower temperatures as well as a recovering of the FL properties below 0.3 K. Thus, according to specific heat experiments, the $Ce_{0.98}Ni_{2+x}Ge_{2-x}$ sample with $x = 0.005$ appears to be at or, at least, very close to the QCP. Although the origin of the QCP is not clear, the $C(T)/T \sim T^{1/2}$ dependence in all the samples investigated hints at the 3D-SF in the vicinity to the AF QCP.

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