Non-Fermi-Liquid Effects at Ambient Pressure in a Stoichiometric Heavy-Fermion Compound with Very Low Disorder: $CeNi_2Ge_2$

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Pronounced non-Fermi-liquid (NFL) effects in thermodynamic (C, α) and transport (ρ) properties at ambient pressure (p) and zero field are reported for high-purity samples of the undoped heavy-fermion compound $CeNi_2Ge_2$. The origin of the NFL effects is not yet clear. Novel phase transitions are observed at both finite and ambient pressure. Under $p = 1.7$ GPa, a novel, perhaps spin-density-wave-type, phase transition occurs at $T_m = 0.9$ K. At $p = 0$, incipient superconductivity below $T = 100$ mK is found in the two samples with lowest residual resistivities, $\rho_0 < 0.45\ \mu\Omega$ cm. [S0031-9007(98)08329-X]

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Non-Fermi-liquid (NFL) effects in lanthanide- and actinide-based intermetallics are often considered signatures of a non-Landau (i.e., a generalized) Fermi liquid (FL), the "nearly antiferromagnetic Fermi liquid" (NAFFL): Near a magnetic instability, at which the antiferromagnetic (AFM) ordering temperature $T_N \rightarrow 0$, low-frequency and extended spin fluctuations should give rise to strongly T-dependent quasiparticle masses and quasiparticle-quasiparticle cross sections [1–3]. Two types of materials have so far been studied to check the predictions of the NAFFL concept. The first category contains heavy-fermion (HF) compounds, i.e., heavy Landau FLs like $CeCu_6$ [4] or $CeRu_2Si_2$ [5], alloyed with sizable dopands which allows one to tune these systems through their magnetic instability. However, it is not yet clear how the disorder in these alloys modifies or whether it even produces [6] the observed NFL effects. The second category contains AFM-ordered Kondo-lattice systems like $CePd_2Si_2$ [7,8] and $CeIn_3$ [8], in which hydrostatic pressure is used to tune these systems through their magnetic instability. In these cases, it is usually very difficult to perform a full thermodynamic analysis. For example, the low-temperature specific heat may not be measurable at pressure values necessary to approach the magnetic instability. In at least three prototypical *undoped* HF compounds NFL effects can be studied [9] already *at ambient pressure:* UBe_{13}, $CeCu_2Si_2$ and its homologue $CeNi_2Ge_2$. The two former compounds are HF superconductors, with extremely large quasiparticle masses ($300m_0$ to $500m_0$) and surprisingly high residual resistivities of 10 to 30 $\mu\Omega$ cm [9,10]. In both compounds, the onset of superconductivity prevents the investigation of the NFL effects in the most relevant regime of lowest temperatures and magnetic fields. No evidence of AFM order exists, to our knowledge, in UBe_{13} at $p = 0$. In $CeCu_2Si_2$, the NFL effects have been associated with the threshold of the spin-density-wave- (SDW-) type "phase A" and a rather complex phase diagram, indicating both coexistence and competition of HF superconductivity and phase A, was discussed [10].

In this Letter, we communicate the first observation of NFL behavior, in particular, at very low temperatures and magnetic fields, for an atomically well ordered HF compound: $CeNi_2Ge_2$. We shall discuss distinct deviations from Landau-FL behavior in its transport and thermodynamic properties and present evidence for novel phase transitions at both finite and ambient pressure. Our investigation will focus on a regime clearly separated from two previously studied regimes: (i) For $CeNi_2Ge_2$ the magnetic properties around $T = 30$ K were found to be dominated by apparently highly anisotropic short-range, quantum fluctuations which lead to a metamagnetic transition at $B = 42$ T [11]. (ii) Upon moderate Cu doping on Ni sites, long-range AFM order had been established at low temperatures for Cu concentrations in excess of $x_c \simeq 20$ at.% [12]. At this critical concentration NFL phenomena had, in fact, been observed [13].

From a systematic study [14] of the resistivity as a function of composition we infer that the energy necessary for the site interchange of Ni and Ge is substantially higher than, e.g., that for the Cu-Si interchange in the homologous compound $CeCu_2Si_2$. Therefore, in $CeNi_2Ge_2$ one can achieve residual resistivities 1 to 2 orders of magnitude lower than those in $CeCu_2Si_2$. Polycrystalline samples of $CeNi_2Ge_2$ from high-purity starting elements (Ce4N, Ni4N7, Ge6N) were prepared in an argon-arc furnace and subsequently annealed at 800 °C for 120 h. X-ray powder-diffraction patterns showed that all samples were single phase with the proper $ThCr_2Si_2$ structure. The samples studied here have residual resistivities ρ_0, ranging between 0.3 and 3 $\mu\Omega$ cm. The electrical resistivity was measured in a ^{3}He-^{4}He dilution refrigerator ($T \geq 10$ mK) in magnetic fields up to 15.5 T using a four-terminal low-frequency (117 Hz) lock-in technique. The coefficient of thermal expansion, $\alpha = (1/\ell)\, d\ell/dT$, was determined down to 50 mK in a ^{3}He-^{4}He dilution refrigerator by utilizing an ultrahigh-resolution capacitive dilatometer with a maximum sensitivity corresponding to $\Delta\ell/\ell \geq 10^{-11}$ [15]. The specific heat was measured in a ^{3}He cryostat utilizing a compensated heat-pulse method [16]. The

Ce increment to the specific heat, ΔC, was determined by subtracting from the measured specific heat that of $LaNi_2Ge_2$.

Figures 1 and 2(a) illustrate the existence of NFL effects in $CeNi_2Ge_2$ at zero field and down to temperatures $T \approx 0.2$ K, i.e., more than 2 orders of magnitude below the characteristic (Kondo) temperature of ≈ 30 K [11,17]. For $T \leq 2$ K, the thermodynamic quantities, plotted as $\Delta C(T)/T$ and $\alpha(T)/T$, are found to be roughly proportional to $-\ln T$. In the same temperature window, the resistivity follows a power-law dependence, $\rho(T) = \rho_0 + \beta T^{\varepsilon}$, $\varepsilon \leq 1.5$. As shown in Fig. 3, application of a magnetic field to one of the high-purity samples ($\rho_0 = 0.43\ \mu\Omega$ cm) forces the low-temperature resistivity to turn into a T^2 behavior. The slope of the low-field magnetoresistance, $d\rho/dB$, is negative for $T \geq 1.2$ K and $B \leq 2$ T but changes sign when increasing the field to $B > 2$ T. For "standard-quality" samples (ρ_0: 1.5–3 $\mu\Omega$ cm) a similar behavior was observed even at the lowest temperatures [18]. The crossover temperature below which the resistivity shows a T^2 behavior increases proportionally to $B^{0.65}$ [Fig. 4(a)]. Note that a similar observation was recently made by Grosche *et al.* [19]. At the same temperatures, at which the resistivity behavior changes, both $\Delta C(T)/T$ and $\alpha(T)/T$ show strong deviations from the $-\ln T$ dependence; cf. arrows in Figs. 1(a) and 1(b). These crossover temperatures are pushed upwards with increasing field, similar to what was first reported for $CeCu_{6-x}Au_x$ [4].

The $\Delta\rho(T) = \rho - \rho_0 = \beta T^{1.5}$ dependence observed in several $CeNi_2Ge_2$ samples with residual resistivities ρ_0 ranging between 1.5 and 3 $\mu\Omega$ cm [see, e.g., Fig. 2(a)] is in accord with the prediction by the NAFFL theory [1–3] for the asymptotic behavior (at $B = 0$) in a three-dimensional system. It characterizes a diverging quasiparticle-quasiparticle scattering cross section being proportional to $a(T) = \Delta\rho(T)/T^2 \propto T^{-0.5}$. In Fig. 4(b), we show for all samples studied the slope a of the low-T straight lines in the $\Delta\rho$ vs T^2 plots (cf. Fig. 3) as a function of the magnetic field. Our data indicate a divergence of a, i.e., the quasiparticle-quasiparticle cross section, and hint at the existence of a quantum critical point (QCP) near $B = 0$.

A closer inspection of our data, however, raises questions as to whether the NAFFL concept can be applied to $CeNi_2Ge_2$ at all: (i) Within this concept, the "crossover regime" at moderate temperatures is characterized by $\gamma(T) = \Delta C(T)/T \propto -\ln T$ and $\Delta\rho = \beta T$. However, in the temperature range where $\gamma(T)$ and $\alpha(T)/T$ show a $-\ln T$ dependence, our resistivity data are well fitted by power laws, $\Delta\rho = \beta T^{\varepsilon}$, with differing exponents ($1.37 \leq \varepsilon \leq 1.5$), depending on sample quality. (ii) Further on, in contrast to the asymptotic $\gamma_0 - \gamma(T) \propto T^{0.5}$ dependence expected [1–3] along with $\Delta\rho \propto T^{1.5}$ well below this crossover regime, the specific-heat coefficient $\gamma(T)$ was previously found [17] to exhibit a broad maximum between $T = 0.2$ K and $T = 0.3$ K. This is corroborated in Fig. 1(b) by the maximum in the $B = 0$ data for $\alpha(T)/T$ at $T = 0.2$ K. These anomalies and their shift to higher temperatures, induced by the B field, can be interpreted by a freezing out of the long-lived and long-range part of the spin-fluctuation spectrum and, thus, by establishing a FL state at low T, as illustrated in Fig. 4(a). (iii) In our $B = 0$ results for the resistivity, a corresponding change into a T^2 dependence cannot be observed, though this is theoretically expected beyond a QCP. The resistivity results rather locate this compound very close to a QCP. In this case, a low-temperature transition into a T^2 dependence was theoretically predicted, too [20]. Further on, if potential scattering in the sample is reduced and the anisotropy of the quasiparticle lifetime reinforced, an increase of the validity regime for the T^2 law is predicted in Ref. [20]: In a power-law representation of the data within a restricted temperature window this should manifest itself in an increase of the resistivity exponent with increasing perfection of the samples. Our results displayed in Fig. 2(a) are at strong variance with

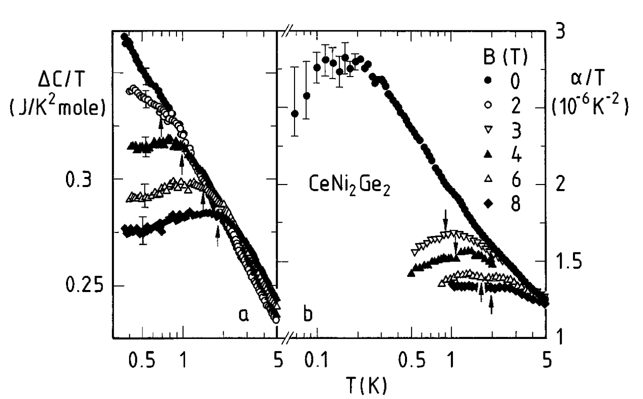

FIG. 1. Ce increment to the specific heat (a) and thermal expansion (b) of $CeNi_2Ge_2$ as C/T vs T and α/T vs T, on logarithmic temperature scales, for $B = 0$ and differing magnetic fields. Arrows indicate positions on the solid line shown in Fig. 4(a).

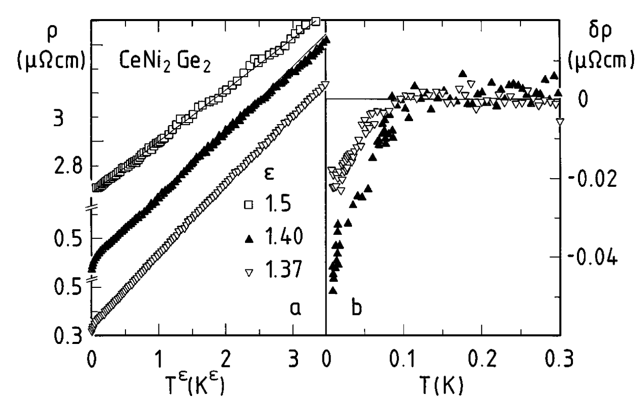

FIG. 2. Electrical resistivity as a function of temperature for three $CeNi_2Ge_2$ samples with $\rho_0 = 2.7\ \mu\Omega$ cm (□), 0.43 $\mu\Omega$ cm (▲), and 0.34 $\mu\Omega$ cm (▽) as ρ vs T^{ε} with differing exponents ε (a) and $\delta\rho = \rho - (\rho_0 + \beta T^{\varepsilon})$ vs T (b).

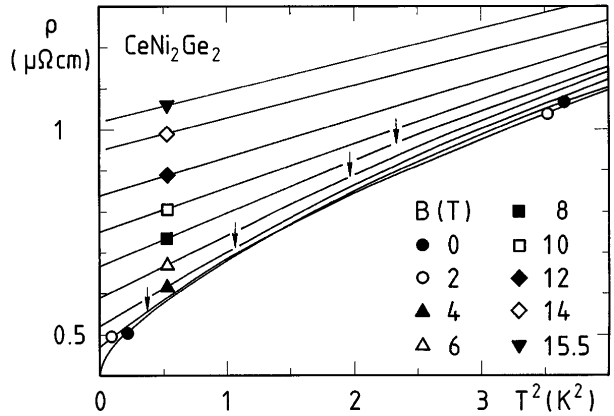

FIG. 3. Magnetic-field dependence of $\rho(T)$ of a high-quality $CeNi_2Ge_2$ sample ($\rho_0 = 0.43\ \mu\Omega$ cm) plotted as ρ vs T^2 in fields up to 15.5 T. Arrows indicate the limiting temperature of the validity range of the T^2 law.

this expectation, as the exponent clearly decreases with decreasing residual resistivity. According to the spin-fluctuation theory the resistivity exponent is given by $\varepsilon = d/z$, d being the spatial dimension and z the dynamical exponent of the spin fluctuations (AFM: $z = 2$) [1–3]. A decrease in ε upon increasing sample quality might indicate a tendency of increasing two-dimensional character [21] and/or of an increase in z. The latter, however, would require a very specific band structure [22]. A new calculation [23] including the effect of disorder revealed that ε depends very sensitively on the amount of impurity scattering. In a power-law representation ε was found to decrease from $\varepsilon = 1.5$ to $\varepsilon \approx 1$ with decreasing disorder, although $\varepsilon = 2$ is predicted for the clean case.

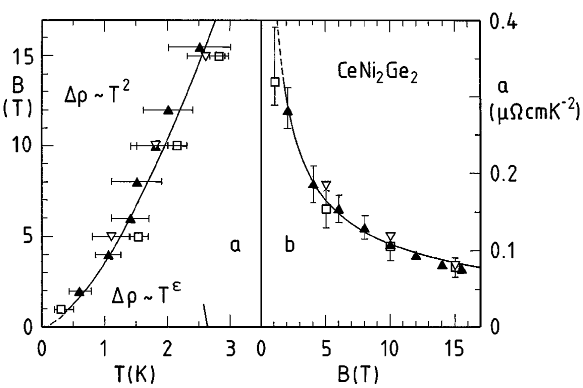

FIG. 4. (a) B-T phase diagram demonstrating, at given fields, the limiting temperatures of the low-temperature $\rho = \rho_0 + aT^2$ behavior. Symbols to characterize three $CeNi_2Ge_2$ samples are the same as in Fig. 2. The solid line through these points (as well as its extrapolation to $B \rightarrow 0$) is a guide to the eye only but can be approximated satisfactorily by $B \sim T^{1.54}$. The other solid line hitting the abscissa marks the temperature limit of the NFL regime, indicated by $\rho = \rho_0 + \beta T^{\varepsilon}$, $1.37 \leq \varepsilon \leq 1.5$ (see text). (b) Slope a of straight lines in the $(\rho - \rho_0)$ vs T^2 plots of the low-T data, taken in fixed fields, as a function of magnetic field. Symbols as in (a). Coefficient $a(B)$ diverges as $B^{-0.6}$ (solid/dashed line) for $B \rightarrow 0$.

The observed decrease of ε with decreasing residual resistivity shown in Fig. 2(a) seems to be consistent with these new theoretical results.

In summary, at $B = 0$, the thermodynamic data indicate that $CeNi_2Ge_2$ is located beyond a QCP, i.e., on its strong-coupling (high-pressure) side, while the resistivity data at $B = 0$ point to a very close vicinity of the QCP. Striking discrepancies between resistivity and specific-heat results were also found [10] for $CeCu_2Si_2$, i.e., when approaching the QCP at $T_A \rightarrow 0$. These observations had been tentatively related to a breakdown of the concept of the heavy quasiparticles [24].

Figure 2(b) shows a blow up, suitably scaled, of the resistivity data for the two samples with the lowest residual resistivities, i.e., $\rho_0 < 0.45\ \mu\Omega$ cm. Below $T = 100$ mK we observe a reduction of the resistivity which amounts to 10% and 30%, respectively. A magnetic field of less than 0.1 T is sufficient to remove the downturn in $\rho(T)$. We assign this phenomenon to the onset of superconductivity. The fact that we cannot resolve any dc-Meissner effect shows either that we are dealing with faint traces of superconductivity or, if superconductivity is a bulk effect, that its true T_c (midpoint of the full transition) has to be located close to $T = 0$ ("incipient superconductivity"). It shall be interesting to see how this new feature is related to the full superconducting transition which was found to occur at finite temperatures under hydrostatic pressure [25]. Interestingly enough, Grosche *et al.* [19] have recently observed in high-quality $CeNi_2Ge_2$ samples superconducting transitions with ≈100% reduction of the resistivity below $T = 300$ mK even at $p = 0$. These discoveries gave rise to speculations that $CeNi_2Ge_2$ might be the second Ce-based compound, following $CeCu_2Si_2$, to show HF superconductivity already at ambient pressure [19]. In order to unravel (i) the conditions for the occurrence of superconductivity and (ii) the nature of the superconducting state itself, we have initiated a detailed investigation of the chemical phase diagram, in particular, of the homogeneity range, of $CeNi_2Ge_2$. A similar study [13,26] was performed to establish the aforementioned complex physical phase diagram of $CeCu_2Si_2$ [10]. There it could be shown that the NFL effects are related to the threshold of phase A: From both specific-heat and resistivity results taken at moderate temperatures ($T > 0.2$ K) and sufficiently low magnetic fields ($B < 6$ T), the vanishing of the A-phase transition temperature $T_A \rightarrow 0$ was identified as a QCP of AFM nature in a three-dimensional system [10].

Though far from being consistent with the predictions of the NAFFL model [1–3], the NFL effects discussed above may nevertheless be regarded as indicators of some nearby AFM QCP in the magnetic phase diagram of $CeNi_2Ge_2$. One possibility could be that the Néel temperature of AFM-ordered $Ce(Ni_{1-x}Cu_x)_2Ge_2$, $x \geq 0.2$, shows a "tail" at sufficiently low temperatures, reaching into the Cu-poor regime of the composition space [27]. The possible proximity in the *undoped* compound to AFM order is highlighted by specific-heat experiments under pressure: A second-order-type phase transition was found [18] to occur at $T_m = 0.9$ K if a hydrostatic pressure of 1.7 GPa is applied to $CeNi_2Ge_2$. T_m is almost twice as large as the superconducting T_c determined at the same pressure [25]. Under this pressure, the anomalous (NFL) temperature dependence of $\gamma = \Delta C/T$ is replaced by a constant value $\gamma \simeq 0.13$ J/K^2 mole, indicating a pressure-induced medium heavy Landau-FL state [28]. Since T_m could not be changed when a magnetic field of 8 T was applied, a superconducting transition could safely be excluded [29], while an AFM transition would be compatible with this insensitivity against application of high magnetic fields. Perhaps application of pressure to $CeNi_2Ge_2$ leads to a rearrangement of the renormalized Fermi surface [30] and opens some nesting condition which may cause a SDW formation. In future work, we plan to explore the exact pressure dependence of the new transition. Preliminary studies [18] indicate a strong suppression of both the size of the anomaly at and the temperature of this transition upon decreasing the pressure. These results [18] suggest that the critical pressure p_c at which the new transition becomes suppressed ($T_m \rightarrow 0$) is substantially lower than $p = 1.3$ GPa; however, they do not allow one to determine the value of p_c more precisely.

To conclude, distinct deviations from a Landau-FL behavior have been found in a stoichiometric HF compound which shows a high degree of lattice perfection. Similar to its homologue $CeCu_2Si_2$ [10] the compound $CeNi_2Ge_2$ shows a rich variety of low-temperature properties. Whereas in the former system, the NFL effects were ascribed to the disappearance of (the as yet unidentified but presumably SDW-type) phase A, the cause of the NFL phenomena in the latter has still to be pinned down. The occurrence of (incipient) superconductivity in the atomically best-ordered samples makes $CeNi_2Ge_2$ an even more fascinating system for future studies.

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