Can Competition between the Crystal Field and the Kondo Effect Cause Non-Fermi-Liquid-Like Behavior?

Frithjof B. Anders[1] and Thomas Pruschke[2]

[1]*Theoretical Physics, University of the Saarland, 66041 Saarbrücken, Germany*
[2]*Institute for Theoretical Physics, University of Göttingen, D-37077 Göttingen, Germany*

(Received 14 November 2005; published 1 March 2006)

The recently reported unusual behavior of the static and dynamical magnetic susceptibility as well as the specific heat in $Ce_{1-x}La_xNi_9Ge_4$ has raised the question of a possible non-Fermi-liquid ground state in this material. We argue that for a consistent physical picture the crystal-field splitting of two low-lying magnetic doublets of the Ce $4f$-shell must be taken into account. Furthermore, we show that for a splitting of the order of the low temperature scale T^* of the system a crossover behavior between an SU(4) and an SU(2) Kondo effect is found. The screening of the two doublets occurs on different temperature scales leading to a different behavior of the magnetic susceptibility and the specific heat at low temperatures. The experimentally accessible temperature regime down to 50 mK still lies in the extended crossover regime into a strong-coupling Fermi-liquid fixed point.

DOI: 10.1103/PhysRevLett.96.086404 PACS numbers: 71.27.+a, 71.10.Hf, 72.15.Qm, 75.20.Hr

Introduction.—The investigation of thermodynamic and transport properties of strongly correlated electron systems is of fundamental importance for our understanding of elementary excitations in solid state physics. Especially measurements on the metallic heavy fermion (HF) compounds [1] challenge the paradigm of Landau's Fermi-liquid concept which incorporates all lattice and Coulomb correlations into a renormalized quasiparticle mass m^* and a few Fermi-liquid parameters.

In many cases, the presence of localized moments in the HF compounds leads to magnetic or superconducting phase transitions, which either compete with each other in Ce based compounds or possibly even coexist as in uranium based materials. The experimental evidence [2,3] compiled over the past ten years also indicates that even for HF systems with paramagnetic ground state, the temperature dependence of the specific heat and the magnetic susceptibilities often does not agree with the predictions of the Fermi-liquid theory, in particular, when subject to pressure or ion substitution [4]. Therefore, the phenomenological term non-Fermi liquid (nFL) was attributed to such regimes appearing in a large variety of different materials [2,3].

The understanding of the observed nFL behavior is one of the most challenging and unsolved theoretical puzzles. In many materials, it is ascribed to a quantum critical point (QCP) at which a transition temperature is suppressed to $T = 0$ by an external control parameter such as pressure or doping [4,5]. It is believed that in the vicinity of such a QCP, quantum fluctuations dominate over thermal ones even at finite temperatures as shown by Hertz [6] and Millis [7] in a renormalized quasiparticle picture. Despite a tremendous experimental and theoretical effort, it is, however, still not clear whether the nFL effects observed in HF compounds are related to novel low-lying nonlocal excitations in concentrated systems, true local nFL physics, or simply due to competing local energy scales.

Recently, the experiments showing unusual specific heat, magnetic susceptibility, and resistivity data for $Ce_{1-x}La_xNi_9Ge_4$ for various concentrations have drawn a lot of attention since this material has the "largest ever recorded value of the electronic specific heat at low temperature" [8] of $\gamma(T) = \Delta C/T \approx 5\ \mathrm{J\,K^{-2}\,mol^{-1}}$. While the γ coefficient continues to rise at the lowest experimentally accessible temperature, the magnetic susceptibility apparently tends to saturate at low temperatures. Experimentally, the quantum critical [7] and Kondo disorder scenario [9] were ruled out [8].

In this Letter, we propose a local scenario for the observed nFL behavior in $Ce_{1-x}La_xNi_9Ge_4$. This is backed by the experimental findings that the electronic contribution to the specific heat as well as the magnetic susceptibility normalized to the Ce concentration remains almost independent of the La concentration [8]. We will show that the competition of Kondo and crystal-field effects leads to a crossover regime connecting incoherent spin scattering at high temperatures and a conventional strong-coupling Fermi-liquid regime at temperatures much lower than the experimentally accessible 30 mK.

Crystal-field scheme for $CeNi_9Ge_4$.—The Hund's rule ground state of Ce^{3+} with $j = 5/2$ is split in a tetragonal symmetry [8] in three Kramers doublets. If the crystal electric field (CEF) parameters are close to those of cubic symmetry, the two low-lying doublets $\Gamma_7^{(1)}$ and $\Gamma_7^{(2)}$, originating from the splitting of the low-lying Γ_8 quartet, are well separated from the higher lying Γ_6 doublet. Ignoring this Γ_6 doublet, we can discuss two extreme limits. In a cubic environment, the CEF splitting vanishes and the low temperature physics is determined by an SU(4) Anderson model described by a strong-coupling fixed point plus a marginal operator responsible for the particle-hole asymmetry [10]. In a strongly tetragonally distorted crystal, on the other hand, the crystal-field splitting of the quartets is expected to be large. In this case, the low temperature properties are determined by an SU(2) Anderson model which has a significantly lower Kondo scale since the degeneracy N enters the denominator of the exponential $T_K \propto \exp[-1/NJ]$. Then the second doublet at higher energies is screened at temperature $T \approx \Delta = E_{\Gamma_7^{(2)}} - E_{\Gamma_7^{(1)}}$ and contributes little to the magnetic susceptibility. Thus, the experimental response would be that of a simple SU(2) Anderson model which was ruled out by the experiments [8]. Therefore, we propose that the material parameters lie in the crossover regime where the effective low temperature scale T^* is of the order of the crystal-field splitting Δ. Then, the excited doublet will have significant weight in the ground state so that the total magnetic response differs from a simple SU(N) Anderson model.

Formulation.—Our calculation is based on an SU(N) Anderson model with infinite-U [11] whose Hamiltonian is given by

$$H = \sum_{k\alpha} \varepsilon_{k\alpha\sigma} c^\dagger_{k\alpha\sigma} c_{k\alpha\sigma} + \sum_{\alpha\sigma} E_{\alpha\sigma} |\alpha\sigma\rangle\langle\alpha\sigma| + \sum_{k\alpha\sigma} V_{\alpha\sigma}(|\alpha\sigma\rangle\langle 0| c_{k\alpha\sigma} + c^\dagger_{k\alpha\sigma}|0\rangle\langle\alpha\sigma|), \quad (1)$$

where $|\alpha\sigma\rangle$ represents a state with energy $E_{\alpha\sigma}$ on the Ce $4f$ shell of the αth irreducible representation (irrep) with spin σ and $c_{k\alpha\sigma}$ annihilates a conduction electron state with energy $\varepsilon_{k\alpha\sigma}$ transforming according to the irrep α of the tetragonal magnetic point group [12]. This allows locally only fluctuations between an empty and a singly occupied Ce $4f$ shell.

We accurately solve the Hamiltonian (1) using Wilson's numerical renormalization group (NRG) [13,14] best suited to deal with the competition between Kondo effect and CEF field splittings. The key ingredient in the NRG is a logarithmic discretization of the continuous bath, controlled by the parameter $\Lambda > 1$ [13]. The Hamiltonian is mapped onto a semi-infinite chain, where the Nth link represents an exponentially decreasing energy scale $D_N \sim \Lambda^{-N/2}$. Using this hierarchy of scales the sequence of finite-size Hamiltonians $\mathcal{H}_N$ for the N-site chain is solved iteratively, truncating the high-energy states at each step to maintain a manageable number of states. The reduced basis set of $\mathcal{H}_N$ thus obtained is expected to faithfully describe the spectrum of the full Hamiltonian on the scale of D_N, corresponding to a temperature $T_N \sim D_N$ [13] from which all thermodynamic expectation values are calculated.

In order to obtain the impurity contribution to the specific heat, we calculate the difference between the entropy of the full model (1) and the corresponding free electron gas $S_{\rm free}(T)$, i.e., $\Delta S(T) = S_{\rm tot}(T) - S_{\rm free}(T)$ [13]. The Sommerfeld coefficient $\gamma(T) = \Delta C(T)/T$ of the Ce contribution to the specific heat is directly obtained by differentiating $\Delta S(T)$ with respect to T:

$$\Delta C(T) = T \frac{\partial S(T)}{\partial T}. \quad (2)$$

Since $\Delta C(T)/k_B$ is a dimensionless quantity, the NRG predicts the absolute magnitude of $\Delta C(T)$ per Ce without any further fitting parameter. The experiment, however, is needed to provide the absolute scale of the temperature axis. Since γ has the dimensions of an inverse energy, we obtain an estimate of the Anderson width $\Gamma_0 = V^2\pi\rho(0)$ by comparison with the experiment [15] [$\rho(0)$ is the density of states of the conduction electrons at the chemical potential]. While the calculation allows for different values of the hybridization matrix element V_α to incorporate different coupling strength of the multiplets to the conduction band, we used the same matrix element V for all calculations to keep the number of free parameter as small as possible.

Assuming a Zeeman splitting of the multiplet energy $E_{\alpha\sigma}$ as $E_{\alpha\sigma} = E_\alpha - \sigma g_\alpha \mu_B H$, the Ce contribution to the magnet susceptibility is given by

$$\Delta\chi = \mu_B^2 \sum_\alpha g_\alpha^2 \frac{\partial\langle S^z_\alpha\rangle}{\partial \bar{H}_\alpha} = \mu_B^2 \sum_\alpha g_\alpha^2 \chi_\alpha, \quad (3)$$

where the magnetic field $\bar{H}_\alpha$ is the Zeeman splitting energy $\bar{H}_\alpha = g_\alpha \mu_B H$. While the g factor is determined by the CEF states of the multiplets, we view them as adjustable parameters and calculate χ_α by applying a very small external magnetic field of the order of $\bar{H}/\Gamma_0 = 10^{-9}$ and estimate the values of g_α by comparing with the experiment [15]. As a consequence, the dynamical susceptibility $\chi''(\omega)$ presented later does not contain any adjustable parameter and the q integrated dynamical structure factor $S(\omega)$ can be obtained by the dissipation fluctuation theorem,

$$S(\omega)[1 - e^{-\beta\omega}] = \chi''(\omega) = \mu_B^2 \sum_\alpha g_\alpha^2 \chi_\alpha(\omega), \quad (4)$$

where $\chi''_\alpha(\omega)$ is given by the imaginary part of the spin susceptibility $\chi_\alpha(\omega) = \langle\langle S^z_\alpha | S^z_\alpha \rangle\rangle(\omega)$. Since the two doublets contribute differently to $S(\omega)$ for temperatures comparable or lower than the CEF splitting Δ, the proposed fit by a simple Lorentzian for $\chi''(\omega)$ must obviously fail [16]. At temperatures well above the splitting, the magnetic response of the two doublets is this of a quartet, and in that regime a single Lorentzian fit is justified. At $T < \Delta$, $S(\omega)$ cannot be approximated by a Lorentzian consistent with the reported neutron scattering data [16].

Results.—The impurity contribution to the entropy is plotted as function of temperature for various CEF splittings Δ in Fig. 1. A symmetric band of $D = 50\Gamma_0$ with a constant density of states $\rho_0 = 1/2D$ is used in all calculations. While the entropy curves are very similar for small splitting, for larger $\Delta/\Gamma_0 > 0.05$ the decrease of the en-

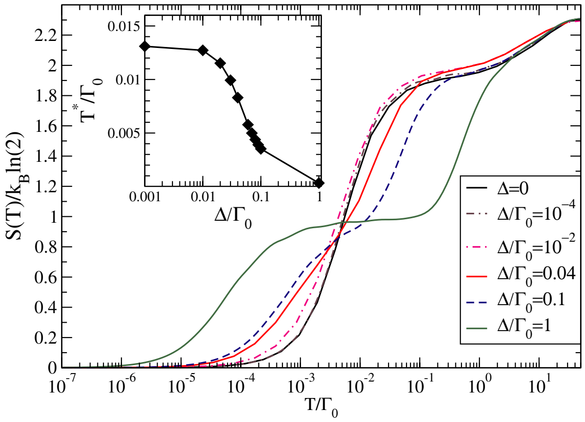

FIG. 1 (color online). The impurity contribution to the entropy in units $k_B \ln(2)$ for a ground state doublet $E_{\Gamma_7^{(1)}} = -8\Gamma_0$ and a bandwidth of $50\Gamma_0$ as function of the CEF splitting Δ. The inset shows the splitting dependent low temperature scale $T^*(\Delta)$. The calculations were performed with NRG discretization parameter $\Lambda = 4$, keeping $N_s = 1500$ states at each NRG step.

tropy occurs in two steps from $\ln(4) \rightarrow \ln(2)$ and from $\ln(2) \rightarrow 0$ when decreasing the temperature. This implies that the screening of the two doublets occurs at two separate energy scales once the splitting Δ exceeds the low temperature scale $T^*(\Delta)$. We have defined the scale $T^*(\Delta)$ [13] as the temperature at which the impurity contribution to the effective spin moment $\Delta\langle S_z^2\rangle = \langle S_z^2\rangle_{\rm tot} - \langle S_z^2\rangle_{\rm free}$ is reduced by a factor of 2 compared to its local moment value of $1/4$. The inset shows the splitting dependency of this low temperature scale. Once the splitting reaches a value comparable to $T^*(0)$, the low temperature scale is rapidly reduced. For splittings slightly larger than $T^*(0)/\Gamma_0 = 0.0131$, the crossover region of the entropy from $\ln(4) \rightarrow 0$ is significantly extended compared to the SU(4) curve as shown by the solid red (online) curve for $\Delta/\Gamma_0 = 0.04$. The onset occurs at higher temperature due to earlier screening of the upper doublet while the strong-coupling Fermi-liquid fixed point is reached at much lower temperatures compared to a simple Kondo model. In $Ce_{1-x}La_xNi_9Ge_4$ this temperature regime was phenomenologically attributed to a nFL behavior [8]. Based on our calculations, we, however, argue that a rather extended crossover regime to a Fermi-liquid fixed point is observed in the experiments.

We achieved the best agreement between theory and experiment in the Kondo regime of (1) using a ground state doublet energy of $E_{\Gamma_7^{(1)}}/\Gamma_0 = -8.5$ and a splitting of $\Delta/\Gamma_0 = 0.015$. We have used the comparison of the dimensionless experimental and theoretical specific heat to obtain the absolute scaling factor for the temperature axis, and the $\gamma(T)$ coefficient to assign an explicit value to Γ_0. Both procedures gave $\Gamma_0 \approx 714$ K $= 61.6$ meV and, therefore, a bare CEF splitting of $\Delta = 10.7$ K was used in the calculations. The corresponding entropy curve would be located between $\Delta/\Gamma_0 = 0.01$ and $\Delta/\Gamma_0 = 0.04$ in Fig. 1. No lattice renormalization effects have been taken into account since the experiments indicate very good scaling with the Ce concentration [8]. The additional Schottky peak observed at $T \approx 60$ K in the experimental data stems from the third doublet neglected in our calculation.

The comparison between the temperature dependence of $\gamma(T)$ and $\chi(T)$ is shown in Fig. 2 assuming a ratio of $g_2^2/g_1^2 = 2$ for a good fit to the experimental data [15]. The ground state doublet dominates the magnetic response at low temperature and tends to saturate at temperatures higher than the γ coefficient, consistent with the experiments [8]. We find this behavior only for CEF splittings $\Delta \approx T^*(\Delta)$ while for much larger or much smaller values $\chi(T)$ and $\gamma(T)$ saturate simultaneously.

Having obtained a reasonable estimate for the ratio between the g values of the doublets, we can predict the temperature dependence of the imaginary part of the local magnetic susceptibility $\chi(\omega)$. Our results are shown in Fig. 3 for (a) $T = 4$ K and (b) at $T = 160$ K for the parameter set of Fig. 2. While for high temperatures [panel (b)] the contributions to $\chi''(\omega)$ are identical for both doublets and can be fitted by a Lorentzian $\chi''(\omega) \approx A_0 \frac{\omega\Gamma(T)}{\omega^2+\Gamma^2(T)}$ of width $\Gamma(T) = 13$ meV, this is not possible for $0.1\ {\rm K} < T < 40$ K as seen in (a). Only at temperatures below 0.1 K, $\chi_1''(\omega)$ might be described by a Lorentzian using a Γ of 1 meV. An effective linewidth of $\Gamma = 1.2$ meV was used to obtain the dotted (blue online) line in (a) fitting $\chi''(\omega)$. In contrast to a naïve ionic picture, the ground state contains significant contributions from the first excited doublet.

Our findings naturally explain the failure of the attempt to fit recently reported neutron scattering data on power samples of concentrated $CeNi_9Ge_4$ with a simple Lorentzian for temperatures below 30 K [16]. The change of slope in $\chi''(\omega)$ yields a small peak for $\omega < 0$ in $S(\omega, T = 4\ {\rm K})$ shown in Fig. 4. Note that the unusual behavior of $\chi_\alpha(\omega)$ in the crossover regime can also not be explained as originating from a distribution of Lorentzians [17] used to fit $S(\omega)$ in [16]. Such phenomenological approaches contain obviously limited amount of

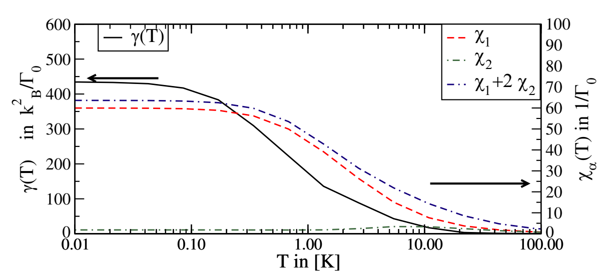

FIG. 2 (color online). Comparison between $\gamma(T) = C(T)/T$ vs T and the susceptibility contributions of the two doublet vs T for $E_{\Gamma_7^{(1)}}/\Gamma_0 = -8.5$, $\Delta/\Gamma_0 = 0.015$. The contribution of the lower doublet, χ_1, is much larger than the one of the upper doublet, χ_2. NRG parameters as in Fig. 1.

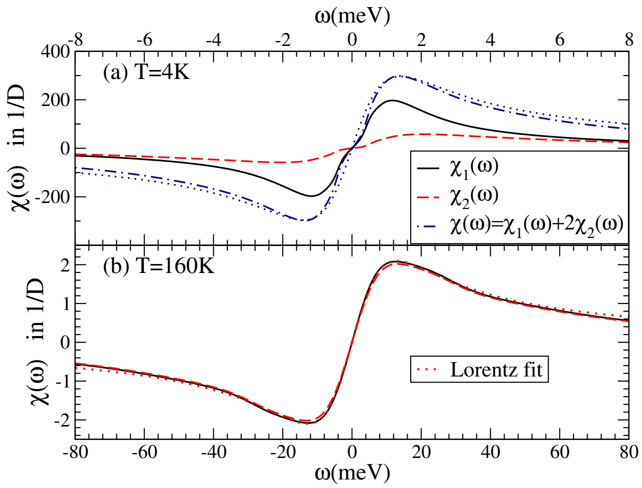

FIG. 3 (color online). Comparison of the contributions to $\chi''(\omega)$ at (a) $T = 4$ K and (b) $T = 160$ K for the model parameters of Fig. 2. The dotted lines present a Lorentzian fit. Calculations were done with NRG discretization $\Lambda = 2.5$ keeping $N_s = 6400$ states at each step.

information if no consistent physical picture for *all* physical properties emerges. A rough estimate of $\Gamma(T)$ plotted as inset to Fig. 4 indicates $\Gamma \propto T$ as in the experiment [16] before it saturates below 100 mK. Our absolute values for $\Gamma(T)$ are roughly a factor of 2 larger than those reported in [16]. This is consistent with the fact that T^* for $Ce_{0.5}La_{0.5}Ni_9Ge_4$, the material we used to fix our model parameters, is larger than T^* for $CeNi_9Ge_4$. In addition, our error in the estimate of the CEF splitting Δ sensitively determines the low temperature scale T^* as depicted in the inset of Fig. 1 and therefore our absolute energy scale.

Summary and discussion.—A simple physical picture of the competition between Kondo effect and CEF splitting leads to an extended crossover region from the high temperature free multiplet to the low temperature strong-coupling fixed point if the crystal-field splitting is of the order of the low temperature scale T^*. Both doublets contribute significantly to the magnetic response at the fixed point yielding *different* contributions to the static and dynamic susceptibility. We propose that the origin of the nFL behavior in $Ce_{1-x}La_xNi_9Ge_4$ is related to this extended crossover region compared to a simple Kondo model or a two channel Kondo lattice scenario [18,19]. This provides a consistent picture for the temperature dependence of specific heat and the magnetic response in agreement with *all* experimental data in all regimes. We hope to include lattice coherence effect in future calculations to explain the transport properties as well.

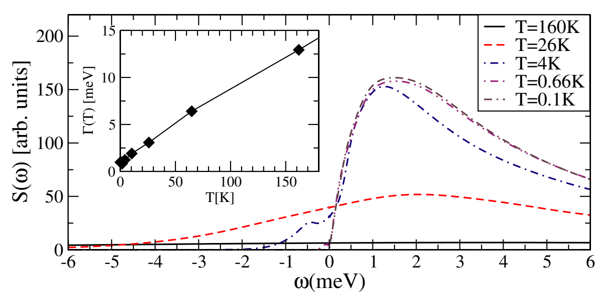

FIG. 4 (color online). The q-integrated dynamical structure factor $S(\omega)$ for different temperatures vs frequency for NRG parameters as in Fig. 3. The inset shows an estimate for temperature dependent relaxation rate $\Gamma(T)$ fitted to the lower doublet only.

We have benefited from discussions with E. W. Scheidt. F. B. A. acknowledges funding of the NIC, Forschungszentrum Jülich, under Project No. HHB000, T. P. financial support by the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 602 and supercomputer support by the Gesellschaft für wissenschaftliche Datenverarbeitung Göttingen and the Norddeutsche Verbund für Hoch- und Höchstleistungsrechnen.

[1] N. Grewe and F. Steglich, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by J. K. A. Gschneidner and L. Eyring (North-Holland, Amsterdam, 1991), Vol. 14, p. 343.
[2] M. B. Maple *et al.*, J. Low Temp. Phys. **99**, 223 (1995).
[3] G. R. Stewart, Rev. Mod. Phys. **73**, 797 (2001).
[4] H. von Löhneyen, J. Phys. Condens. Matter **8**, 9689 (1996).
[5] F. Steglich *et al.*, J. Phys. Condens. Matter **8**, 9909 (1996).
[6] J. A. Hertz, Phys. Rev. B **14**, 1165 (1976).
[7] A. J. Millis, Phys. Rev. B **48**, 7183 (1993).
[8] U. Killer *et al.*, Phys. Rev. Lett. **93**, 216404 (2004).
[9] O. O. Bernal *et al.*, Phys. Rev. Lett. **75**, 2023 (1995).
[10] H. R. Krishna-murthy, J. W. Wilkins, and K. G. Wilson, Phys. Rev. B **21**, 1044 (1980).
[11] G. Toulouse, Phys. Rev. B **2**, 270 (1970).
[12] D. L. Cox, Phys. Rev. Lett. **59**, 1240 (1987).
[13] K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975).
[14] H. R. Krishna-murthy, J. W. Wilkins, and K. G. Wilson, Phys. Rev. B **21**, 1003 (1980).
[15] E.-W. Scheidt *et al.*, cond-mat/0506163 [Physica B (to be published)].
[16] H. Michor *et al.*, "Proceedings of the SCES 05" [Physica B (to be published)].
[17] N. Bernhoeft, J. Phys. Condens. Matter **13**, R771 (2001).
[18] F. B. Anders, M. Jarrell, and D. Cox, Phys. Rev. Lett. **78**, 2000 (1997).
[19] D. L. Cox and A. Zawadowski, Adv. Phys. **47**, 599 (1998), for a review on the multichannel models.