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Thermal expansion and Grüneisen ratio near quantum critical points

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Abstract

Recently it has been shown that at any quantum critical point (QCP) thermal expansion is more singular than specific heat and that the resulting Grüneisen ratio divergence characterizes the nature of the critical fluctuations. Here, we report a comparative study on heavy fermion and d-metal systems. In $Ce_{0.98}Ni_{2+x}Ge_{2-x}$ polycrystals ($0 \leqslant x \leqslant 0.015$) an extreme sensitivity of the ground-state behavior on small changes of composition is observed. For $YbRh_2(Si_{1-x}Ge_x)_2$ the Grüneisen ratio changes sign between the antiferromagnetic and paramagnetic state and diverges with a fractional exponent in the quantum critical regime. In the alloy Ni_xPd_{1-x} the absence of a Grüneisen ratio divergence is incompatible with a ferromagnetic QCP.

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1. Introduction

The strong fluctuations between different ground states close to magnetic quantum critical points (QCPs) in f- and d-electron metals lead to a breakdown of Landau's Fermi liquid (LFL) theory. Recently, it has been shown that dilatometric studies are of particular interest, because thermal expansion, β, probing the pressure dependence of the entropy being accumulated close to the instability, is more singular than specific heat, C [1]. Consequently, the critical Grüneisen ratio $\Gamma^{cr} \sim \beta^{cr}/C^{cr}$, where β^{cr} and C^{cr} denote the critical contributions, must diverge at any QCP being sensitive to pressure.

We have recently observed divergences $\Gamma^{cr} \propto 1/T^x$ in the two quantum critical heavy fermion systems $CeNi_2Ge_2$ and $YbRh_2(Si_{0.95}Ge_{0.05})_2$ [2]. For the Ce-system, $x = 1$ in accordance with the expectation from scaling analysis for a spin-density wave (SDW) QCP [1] has been found. By contrast, the fractional exponent $x = 0.7$ observed in the Yb-system is incompatible with this scenario [2]. Furthermore, a weak logarithmic divergence of $\Gamma(T)$ has been found at the QCP in $CeCu_{6-x}Ag_x$ which excludes an itinerant description for quantum criticality in this latter system as well [3].

In this paper, we report a systematic investigation of different heavy fermion and d-metal systems close to quantum phase transitions by means of thermal expansion and Grüneisen ratio using the technique described in Ref. [2]. In Section 2, new results on slightly off-stoichiometric $Ce_{0.98}Ni_{2+x}Ge_{2-x}$ polycrystals are discussed. As shown in Section 3 for undoped ($x = 0$) and Ge-doped ($x = 0.05$) $YbRh_2(Si_{1-x}Ge_x)_2$, the Grüneisen ratio changes sign between the ordered and quantum critical regime. For the solid solution Ni_xPd_{1-x} a ferromagnetic QCP at $x_c = 0.025$ has been proposed previously [4,5]. In Section 4, we report thermal expansion and Grüneisen ratio measurements on this system.

2. $CeNi_2Ge_2$

$CeNi_2Ge_2$ is a paramagnetic heavy fermion system with a single-ion Kondo scale of $T_K = 30\,K$ [6]. At zero magnetic field, pronounced non-Fermi liquid (NFL) effects have been observed in thermodynamic and electrical

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transport experiments [7] related to a nearby magnetic instability. Indeed, the substitution of Ni with the larger Pd in $Ce(Ni_{1-x}Pd_x)_2Ge_2$ induces long-range antiferromagnetic (AF) ordering below $T_N = 2\,K$ for $x = 0.2$ (Ref. [8]). Furthermore, by applying magnetic fields, a LFL state is induced with a coefficient $A(B)$ derived from the electrical resistivity $\Delta\rho = AT^2$ that diverges for $B \to 0$ [7]. Nevertheless, there are conflicting specific heat results about whether NFL behavior is held down to lowest temperatures or whether a cross-over to LFL behavior occurs. The earliest measurements show a small cusp in $C(T)/T$ at 0.3 K [6] and more recent work revealed a cross-over from a logarithmic increase above 0.3 K to a saturation at lower temperatures [9]. By contrast, $C(T)/T$ of a high-quality sample with very low residual resistivity does not saturate but shows an upturn at lowest temperatures [10]. Finally, for the single crystal investigated in Ref. [2], the observed T dependencies of both the thermal expansion and the critical Grüneisen are, down to the lowest measured temperature of 50 mK, in full agreement with the 3D SDW prediction for a system at an AF QCP.

These varying results point to a strong dependence of the physical properties on composition. In order to understand the unclarified nature of the groundstate of $CeNi_2Ge_2$, we performed a systematic study of the thermal expansion $\beta(T)$ on slightly off-stoichiometric $CeNi_2Ge_2$ polycrystalline samples. The chemical composition is described by the formula $Ce_{0.98}Ni_{2+x}Ge_{2-x}$ with $0 \leqslant x \leqslant 0.015$. Because of the particularities of the Ce–Ni–Ge ternary chemical phase diagram [11], the $x = 0$ sample has a Ge-rich 122-phase, whereas in the $x = 0.015$ sample the stoichiometric 122 phase is expected. This is in accordance with the lowest residual resistivity ($\rho_0 \approx 0.16\,\mu\Omega\,cm$) for $x = 0.015$ and enhanced values ($\rho_0 \approx 2$–$3\,\mu\Omega\,cm$) for $x = 0$ and 0.005 samples.

Fig. 1 compares the T dependence of the volume expansion for the three different polycrystals with that of the single crystal studied in Ref. [2]. Above 0.3 K, all samples show a $\beta(T) = a\sqrt{T} + bT$ dependence, expected at a 3D AF QCP [1]. Below 0.3 K, similar as already observed in specific heat measurements on the same polycrystals [12], an extreme sensitivity against small variations of the Ni–Ge composition is observed. In particular, β/T for the $x = 0.015$ crystal passes a sharp cusp around 0.2 K and saturates at lowest temperatures.

To get further information, measurements of the linear thermal expansion have been performed at various magnetic fields (see Fig. 2). For the $x = 0$ crystal, a field-induced LFL behavior $\alpha/T = a_0(B)$ with diverging coefficient $a_0 \sim B^{-0.5}$ is observed. By contrast, more complicated behavior is found for $x = 0.015$. Contrary to the zero-field saturation of α/T, a divergence is observed at 0.5 and 0.6 T. LFL behavior is only observed for $B \geqslant 1\,T$ in agreement with corresponding specific heat measurements [13].

Remarkably, this complicated behavior is found only for the polycrystal with the lowest residual resistivity that

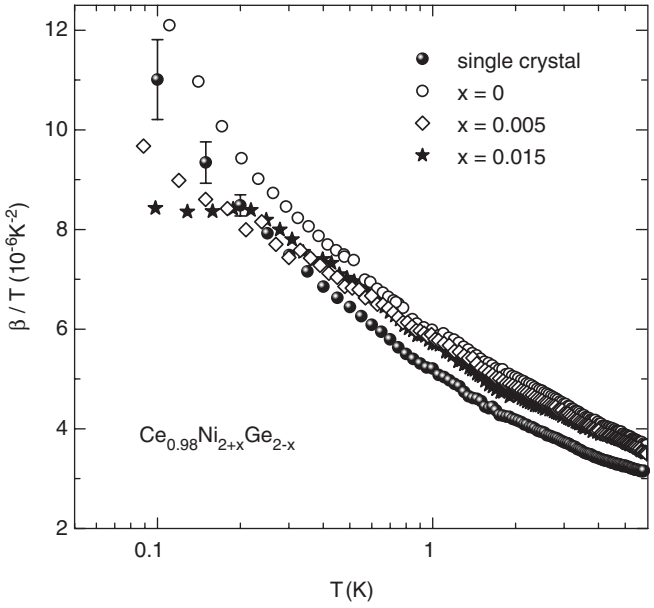

Fig. 1. Volume thermal expansion coefficient for the $CeNi_2Ge_2$ single crystal studied in Ref. [2] as well as various polycrystals with nominal composition $Ce_{0.98}Ni_{2+x}Ge_{2-x}$ as β/T vs. T.

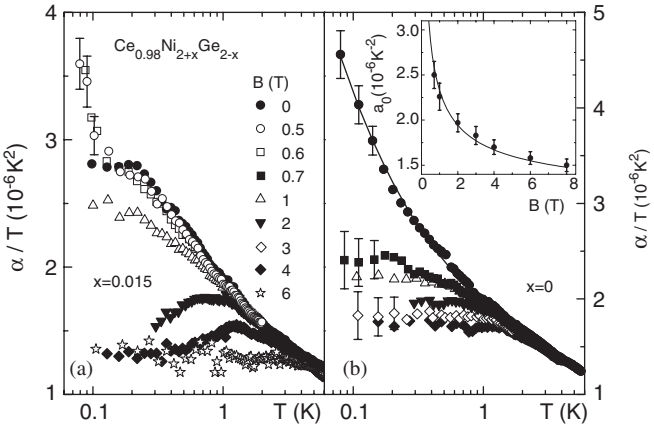

Fig. 2. Linear thermal expansion coefficient for $Ce_{0.98}Ni_{2+x}Ge_{2-x}$ polycrystals (a: $x = 0.15$, b: $x = 0$) at different magnetic fields as α/T vs. T. Line represents $T^{-0.5}$ dependence. Inset in (b) displays field dependence of Fermi liquid coefficient, see text.

should be located closest to the stoichiometric 1:2:2 composition. This raises the question whether the observed behavior might indicate an AF ground state below $T_N \approx 0.2\,K$ in that sample, suppressed by a critical magnetic field of about 0.7 T. Further measurements, in particular on single-crystalline samples are needed for clarification.

3. $YbRh_2(Si_{1-x}Ge_x)_2$

In $YbRh_2Si_2$ pronounced NFL behavior is observed above a weak AF ordering at $T_N = 70\,mK$ [14]. The ordering is further weakened by a tiny volume expansion induced by the substitution of nominally 5 at% of Si with the larger but isoelectronic Ge in $YbRh_2(Si_{0.95}Ge_{0.05})_2$ [15].

For this latter system, $T_N = 20\,\mathrm{mK}$ and a field-induced QCP occurs at about 0.025 T applied in the tetragonal plane. For temperatures above 50 mK, no effect of the AF transition is detected and zero-field measurements probe the quantum critical behavior [15]. The latter is characterized by a $T^{-0.7}$ divergence of the critical Grüneisen ratio being incompatible with the prediction of the itinerant SDW theory for an AF QCP [2]. By contrast, such a fractional exponent has been predicted for the locally-critical scenario [16,2]. Interestingly, a critical exponent of $\frac{2}{3}$ would also be expected for a ferromagnetic (FM) instability [1]. Indeed, recent susceptibility measurements have provided evidence for the importance of both AF and FM quantum critical fluctuations in $YbRh_2(Si_{0.95}Ge_{0.05})_2$ [17]. Quantum critical fluctuations that exist in an extended part of q-space could result in a breakup of the heavy fermions at a locally-critical QCP, suggested by the dramatic change of the Hall coefficient [18].

Below, we focus on the comparison of the Grüneisen ratio for pure and 5% Ge doped $YbRh_2Si_2$. Data for $x = 0$ have been calculated from published thermal expansion [19] and specific heat [15] measurements. As shown in Fig. 3, for $x = 0$, the Grüneisen ratio $\Gamma(T)$ changes sign upon entering at 0.1 K the critical Ginzburg regime close to the AF phase transition. This is in full agreement with the very recent theoretical predictions [20] and indicates the accumulation of entropy close to the phase boundary. Thermodynamically, $\Gamma = (V_m T)^{-1}(\mathrm{d}T/\mathrm{d}p)_S$ measures the slope of temperature vs. pressure traces at constant entropy. The minima of these isentropes thus mark the accumulation points of entropy.

The *positive* Grüneisen ratio, $\Gamma > 0$, indicates a dominating energy scale, here the strength of the AF coupling, that increases with pressure. On the other hand, the *negative* Grüneisen ratio in the paramagnetic state is compatible with the negative pressure dependence of the Kondo temperature in Yb-based HF systems.

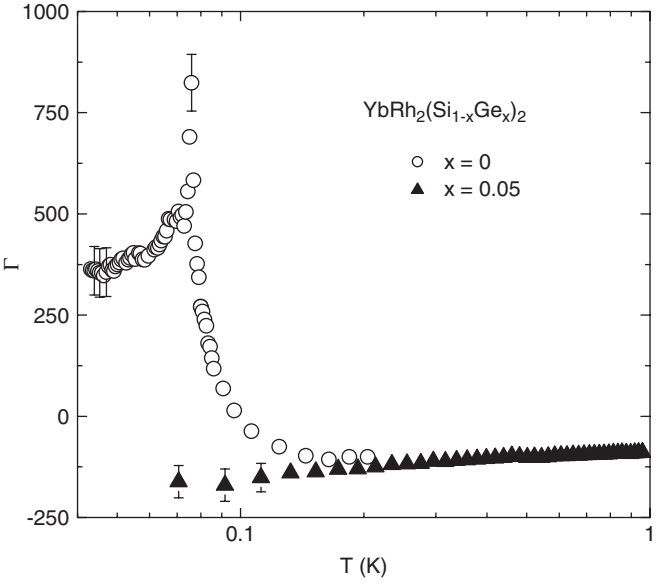

Fig. 3. Temperature dependence of the Grüneisen ratio $\Gamma = V_m/\kappa_T\beta/C$ of $YbRh_2(Si_{1-x}Ge_x)_2$ ($x = 0, 0.05$). V_m and κ_T denote the molar volume and isothermal compressibility, respectively.

The record value of $\Gamma \approx 350$ in the LFL regime within the AF ordered state results from the closeness to the QCP similar as huge values of the specific heat coefficient $\gamma_0 \approx 1.7\,\mathrm{J/K^2\,mol}$ and the coefficient $A \approx 22\,\mu\Omega\,\mathrm{cm/K^2}$ of the electrical resistivity $\Delta\rho = AT^2$ [21].

4. Ni_xPd_{1-x}

Recent experiments on clean and stoichiometric itinerant ferromagnets like $ZrZn_2$ or MnSi have revealed a first-order instead of continuous suppression of the FM ordering [22]. For doped systems, on the other hand, one might expect that disorder leads to a rounding of the phase transition [23]. This raises the question, whether FM QCPs could exist in any material. Here, we focus on the alloy Ni_xPd_{1-x}. It has long been known that about 2.5% of nickel ions doped into palladium induce long-range FM order [24]. A more recent study for concentrations at the border of long-range order has revealed evidence for a FM QCP at a nickel concentration $x_c = 0.025 \pm 0.002$ [4,5]. In particular for $x = 0.024$ and 0.026, a logarithmic divergence of the specific heat coefficient has been observed between 0.3 and 10 K while the electrical resistivity follows $\Delta\rho \propto T^{5/3}$ over more than two decades in temperature [4]. These observations perfectly agree with the predictions of the Hertz–Millis itinerant scenario for a three-dimensional FM QCP. For this case, a $(T^{2/3}\log(1/T))^{-1}$ divergence of the critical contribution to the Grüneisen ratio would be expected. In particular, the thermal expansion coefficient α/T should diverge with a dominating $T^{-2/3}$ contribution [1].

Fig. 4 shows the low-temperature thermal expansion of the same $x = 0.024$ polycrystal studied in Ref. [5]. In contrast to the specific heat coefficient, α/T does not increases with decreasing temperature but remains constant below 3 K within the scatter of the measurement. Compared to pure palladium, there is a four-fold enhancement but most remarkably, no signature of quantum critical behavior is observed. This is also reflected in the temperature dependence of the Grüneisen ratio shown in the inset of Fig. 4. Instead of showing a divergence, $\Gamma(T)$ stays constant below 2 K. This excludes a pressure-sensitive QCP in this system. An alternative scenario would be that in Ni_xPd_{1-x} for small concentrations x of magnetic moments, the long-range ordering transforms to a short-range ordered state which shows the characteristics of a spin-glass. We note that DC-magnetization measurements above 2 K have indeed observed spin-glass anomalies for $0.025 \leqslant x \leqslant 0.028$ [5].

5. Conclusion

We have studied the thermal expansion and Grüneisen ratio for different f- and d-electron systems located close to

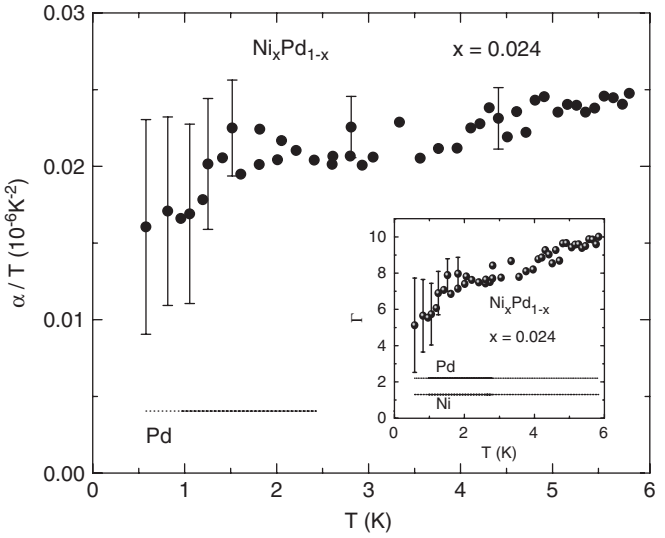

Fig. 4. Linear thermal expansion of Ni_xPd_{1-x} for $x = 0.024$ (closed circles) and $x = 0$ (line) [25] as α/T vs. T. The inset compares the temperature dependence of Grüneisen parameter for $x = 0.024$, calculated using specific heat data obtained on same sample [4] with data for pure Ni and Pd [25].

magnetic quantum phase transitions. Thermal expansion is a very sensitive probe because it directly measures the sensitivity of thermodynamics to pressure tuning. For any QCP being sensitive to pressure tuning, $\Gamma(T)$ has to diverge and this divergence is characterized only by the symmetry of the interaction and dimensionality of the critical fluctuations [1].

For $CeNi_2Ge_2$ we have observed the first-ever Grüneisen ratio divergence in a high-quality single crystal which proves that this system is located at an AF QCP of itinerant (spin-density-wave) type. In this paper, we have shown that the ground state of this system is extremely sensitive against small changes of stoichiometric composition.

For $YbRh_2(Si_{0.95}Ge_{0.05})_2$ the fractional exponent of the Grüneisen ratio divergence hints at a locally-critical QCP in this system. The sign change of $\Gamma(T)$ in $YbRh_2Si_2$, that occurs in the classical critical regime, indicates the accumulation of entropy at the phase boundary.

In Ni_xPd_{1-x} the absence of a Grüneisen ratio divergence is incompatible with a FM QCP. Most likely, long-range ordering transforms into short-range correlated regions upon diluting the concentration of magnetic moments.

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