Systematic Study of the Grüneisen-Ratio near Quantum Critical Points

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The nature of the quantum critical point (QCP) at which long-range magnetic order gradually develops in heavy-fermion (HF) systems has been the focus of one of the main research activities at the institute during the past years. QCPs are of extensive current interest, as the electronic properties close to a QCP deviate strongly from the predictions of the standard theory of metals — Landau's Fermi liquid theory [1]. The understanding of such non-Fermi liquid (NFL) behavior that occurs close to the antiferromagnetic (AF) QCP in HF systems represents a basic challenge to modern quantum condensed matter physics. Two different scenarios for the QCP, where long-rang AF order emerges from the HF state, have been proposed: a spin density wave (SDW) and a localized moment (LM) scenario. In the traditional SDW-picture [2,3,4] the quasiparticles retain their itinerant character if these materials are tuned into the long-range magnetically ordered state and, as a consequence, form a SDW- type of AF order. Recent experiments have shown that at least in some HF systems this picture fails [5,6]. Consequently, a new type of QCP has been proposed at which the quasiparticles break up into their components: conduction electrons and local 4f moments forming magnetic order. This locally critical scenario arises due to the destruction of the Kondo resonance at the QCP [7,8].

At a classical critical point, many thermodynamic quantities — such as specific heat — diverge; historically, the measurements of the associated critical exponents were the decisive factor leading to the eventual understanding of universality and renormalization group. Such divergences, however, typically disappear at a QCP due to the very fact that a quantum phase transition takes place at zero temperature, making experimental studies of QCPs difficult. Our experimental results represent the first observation of the divergence of the Grüneisen ratio at QCPs. While the Grüneisen ratio has long been used to describe the volume dependence of various physical processes [9], our results establish this quantity for a totally new usage, viz to characterize QCPs. As shown in [10], the temperature exponent of the Grüneisen ratio is expected to diverge as $\Gamma^{cr} \sim \beta^{cr} / C^{cr} \sim 1/T^{1/vz}$ (β^{cr} and C^{cr} are the thermal expansion and specific heat with the background contributions subtracted) and therefore, provides a direct means to i) check the very existence of the QCP and ii) measure the scaling dimensions *vz* and, as a result, characterize a QCP. By means of our dilatometric study and the systematic comparison with the theory we could identify the two different classes of quantum phase transitions through the diverging Grüneisen ratio in three prototype strongly correlated electron materials.

For our study we have chosen $CeNi_2Ge_2$ [11] and $YbRh_2(Si_{0.95}Ge_{0.05})_2$ [12,13] as well as $CeCu_{5.8}Ag_{0.2}$ [14] since they are located very close to quantum critical points, and since the effect of disorder is minimized in high quality crystals with low residual resistivities.

$CeNi_2Ge_2$ is a paramagnetic heavy fermion system with a single-ion Kondo scale of T_K = 30 K [15]. At zero magnetic field, pronounced non-Fermi liquid (NFL) effects have been observed in thermodynamic and electrical transport experiments [11] 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 AF order below T_N = 2 K for x = 0.2 [16]. Furthermore, by applying magnetic fields, a Landau-Fermi liquid (LFL) state is induced with a coefficient *A(B)* derived from the electrical resistivity $\Delta\rho = AT^2$ that diverges for $B \rightarrow 0$ [11]. 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 [15] and more recent work revealed a cross-over from a logarithmic increase above 0.3 K to a saturation at lower temperatures [17]. 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 [18]. We measured low-temperature volume thermal expansion, β, and specific heat, C, on high-quality single crystals with a residual resistivity of 5 μΩcm. Fig 1b displays the volume expansion coefficient β, plotted as $\beta(T)/T$. $\beta(T)$ has been cal-

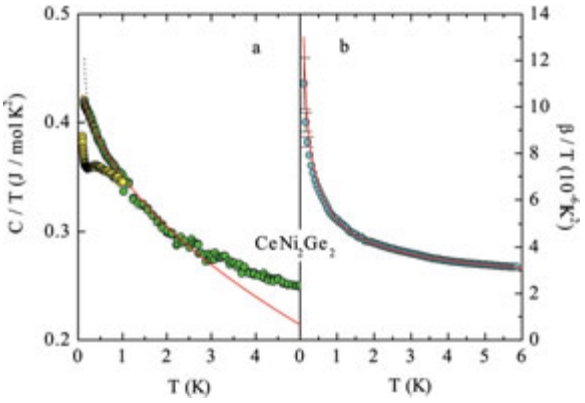

Fig. 1: Low-temperature specific heat as C/T vs T (a) and volume thermal expansion as β/T vs T (b) of a $CeNi_2Ge_2$ single crystal. Red solid lines represent fits according to the 3D SDW scenario. Dotted line in (a) represents the raw data, from which a contribution $C_n = a/T^3$ with a = 102 μJK/mol has been subtracted. Yellow symbols shows data at B = 2 T.

culated from the linear thermal expansion coefficients of $CeNi_2Ge_2$ measured along the tetragonal *a*- and *c*-axis: $\beta = 2\ \alpha_a + \alpha_c$. $\beta(T)/T$ is not constant upon cooling, as expected for a Fermi liquid, but shows a divergence over more than two decades in temperature from 6 K down to at least 50 mK. This is one of the cleanest observations of NFL behavior in a thermodynamic property made in any system so far and provides striking evidence that the single crystal of $CeNi_2Ge_2$ is located very close to a QCP. As shown by the solid red line, the data can be described in the entire *T* range investigated by the temperature dependence predicted by the three-dimensional (3D) SDW scenario [10], i.e., the sum of a (singular) one over square-root and a (normal) constant contribution. The corresponding fit function is described by $\beta(T)/T = a/T^{1/2} + b$, with $a = 3.5\times10^{-6}K^{-1.5}$ and $b = 1.7\times10^{-6}\ K^{-2}$.

In the following we discuss the specific heat (Fig. 1a) measured on the same sample that has been used for the thermal expansion study. Below 3 K the electronic contribution of the specific heat (green curve in Fig 1a) could be described by $C(T)/T = \gamma_0 - c\,T^{1/2}$ (red line), which is also expected in the 3D-SDW scenario. Here we assumed that the low temperature upturn $C/T \sim a/T^3$ (dotted line), present in this single crystal, could be ascribed by the high-temperature tail of a (nuclear) Schottky anomaly. The origin of the latter is yet unclear, since internal magnetic fields of the order of 30 T acting on the nuclear ^{61}Ni or ^{73}Ge spin states would be necessary to produce this contribution to our *B* = 0 data [18]. Of particular importance is the very fact that this upturn can't be part of the quantum critical behaviour: It remains in a magnetic field of about 2 T (yellow curve) which, at $T < 0.7$ K, is outside the quantum critical regime. For $B = 2$ T a crossover to a constant value in both β/T and C/T is observed at low temperatures indicating the entrance into the FL state.

The influence of the low-T upturn in $C(T)/T$ on the Grüneisen ratio is also smaller than 5% at 0.1 K and therefore not visible in the $\Gamma(T)$ plot shown in Fig. 2. This is the first observation of a divergent $\Gamma(T)$ for $T \to 0$ in any material and confirms the theoretical expectation that $\Gamma(T)$ has to diverge at any pressure-induced QCP [10]. Therefore, the Grüneisen ratio provides a novel thermodynamic means of probing quantum phase transitions.

To interpret our results, we discuss the Grüneisen exponent ε in terms of the critical component of the Grüneisen ratio $\Gamma^{cr} \propto \beta^{cr} / C^{cr} \propto 1 / T^{\varepsilon}$. It is proposed in [7] that, for magnetically three-dimensional systems without frustration the SDW picture should apply. This is consistent with our finding that both the thermal expansion and specific heat

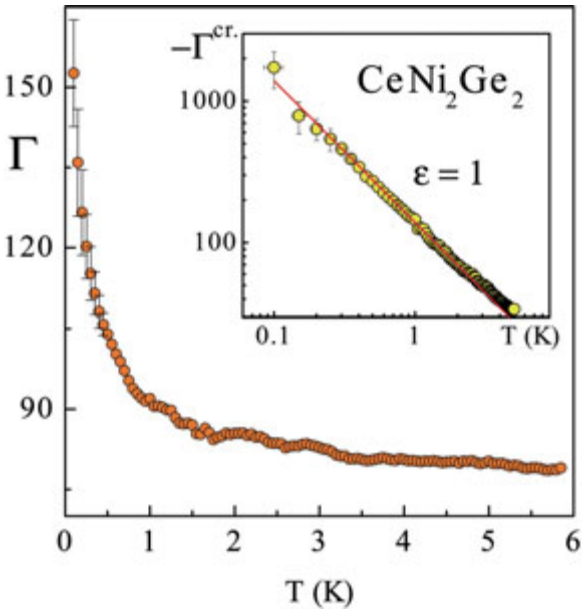

Fig. 2: Temperature dependence of the Grüneisen-ratio $\Gamma = V_{mol}\ \kappa_T^{-1}\ \beta/C$ where V_m and κ_T are the molar volume and isothermal compressibility, respectively. Since the latter has not been measured for $CeNi_2Ge_2$, we use $\kappa_T = 8.33 \times 10^{-12}\ Pa^{-1}$ obtained for the isostructural and related HF compound $CeCu_2Si_2$ [19]. Inset shows the critical component of Grüneisen ratio $\Gamma^{cr} = V_{mo}/\kappa_T^{-1}\ \beta^{cr}/C^{cr}$ as log Γ^{cr} vs log T (at B = 0) with $\beta^{cr} = \beta(T) - bT$ and $C^{cr} = C(T) - (\gamma T + a/T)^2$. Solid red line represents $\beta^{cr} \propto 1/T^{\varepsilon}$ with $\varepsilon = 1$.

results in $CeNi_2Ge_2$ can be fit by the respective expressions for a 3D-AF-SDW theory. Our results correspond to $\beta^{cr} \propto T^{1/2}$ and $C^{cr} \propto T^{3/2}$, leading to $\Gamma^{cr} \propto 1/T$. In other words, the Grüneisen exponent $\varepsilon = 1$ (with error bars +0.05/ –1, as determined from the log-log plot shown in the inset of Fig 2). The observed T dependence is therefore again in full agreement with the 3D SDW prediction [1].

We now turn to the second system which we have studied. In $YbRh_2Si_2$, pronounced NFL behavior is observed above a weak AF ordering at $T_N = 70$ mK [12]. 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 $YbRh_2(Si_{0.95}Ge_{0.05})_2$ [16]. For this latter system, $T_N = 20$ mK and a field-induced QCP occurs at a magnetic field of 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 data above 50 mK probe the quantum critical behavior [16]. In $YbRh_2Si_2$ the volume thermal expansion coefficient $\beta(T)$ has a negative sign reflecting the decrease of the Kondo temperature with pressure, which is opposite as in the case of Ce-based HF systems. In Fig. 3, we compare the

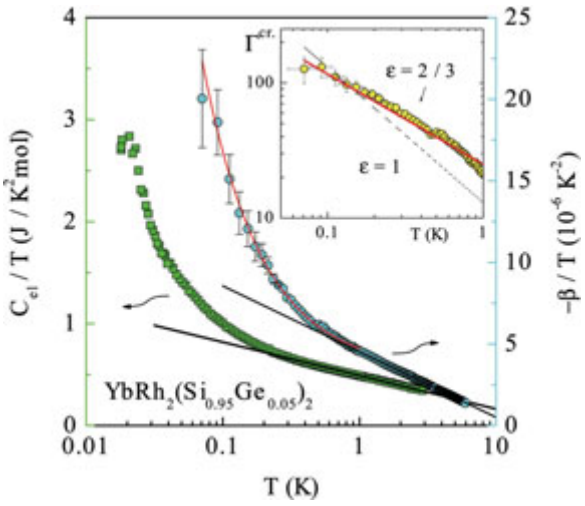

Fig. 3: Electronic specific heat as $C_{el}/T = (C - C_Q)/T$ (left axis) and volume thermal expansion as $-\beta/T$ (right axis) vs T (on a logarithmic scale) for $YbRh_2(Si_{0.95}Ge_{0.05})_2$ at $B = 0$. Black solid lines indicate $\log(T_0/T)$ dependences with $T_0 = 30$ K and 13 K for C_{el}/T and $-\beta/T$, respectively. Red solid line represents $-\beta/T = a_0 + a_1/T$ with $a_0 = 3.4 \times 10^{-6}$ K^{-2} and $a_1 = 1.34 \times 10^{-6}$ K^{-1}. The inset displays the log-log plot of $\Gamma^{cr}(T)$ with $\Gamma^{cr} = V_{mol}/\kappa_T \beta^{cr}/C^{cr}$ using $\kappa_T = 5.3 \times 10^{-12}$ Pa^{-1} [20], $\beta^{cr} = \beta(T) + a_0 T$ and $C^{cr} = C_{el}(T)$. The solid red and the dotted black lines represent $\beta^{cr} \propto 1/T^{\varepsilon}$ with $\varepsilon = 0.7$ with $\varepsilon = 1$, respectively.

temperature dependence of the electronic specific heat C_{el}/T with that of the volume expansion coefficient β/T. At $T > 1$ K, $\beta(T)$ can be fit by $-T \log(T_0/T)$ with $T_0 \approx 13$ K (see solid black line in Fig. 3). At $T < 1$ K, the best fit is given by $a_1 + a_0 T$. Both are not only different from the expected 3D-SDW results discussed earlier, but also weaker than the *log log T* form [10] expected in a 2D-SDW picture. The maximum at 20 mK in $C_{el}(T)/T$ marks the onset of a very weak AF order [6]. This is suppressed by a tiny critical magnetic field of $B_c = 0.027$ T applied in the easy plane. At $B = B_c$, a power law divergence $C_{el}(T)/T \propto T^{-1/3}$ is observed, which is clearly incompatible with the 2D-SDW picture [6]. At higher temperatures the zero-field specific heat coefficient also varies logarithmically [12]. Because of the different slope compared to β/T the Grüneisen ratio is strongly temperature dependent above 1 K. Most importantly, below 1 K the critical Grüneisen ratio (see the inset of Fig. 3) diverges as $T^{-2/3}$, incompatible with the prediction of the itinerant SDW theory for an AF QCP. By contrast, such a fractional exponent would be consistent with the locally quantum critical picture [7,21]. The latter has also been deduced from the dramatic change of the Hall coefficient observed when tuning the system by magnetic field across the QCP [22] (see *"Hall-Effect Evolution across a Heavy-Fermion Quantum Critical Point"*). As such a locally critical scenario has first been proposed on the basis of neutron scattering experiments on $CeCu_{6-x}M_x$ (M = Au) [5]; it has been particular interesting to determine the critical exponent of the Grüneisen ratio divergence in this system at the critical concentration x_c.

In the following we show first that the QCP in $CeCu_{6-x}Au_x$ ($x_c = 0.2$) is phenomenologically related to that in $CeCu_{6-x}Au_x$ ($x_c = 0.1$) and afterwards we investigate the nature of this QCP by means of a Grüneisen ratio analysis. Figure 4 displays the low-temperature specific heat divided by temperature, $C(T)/T$, of various $CeCu_{6-x}Ag_x$ samples on a logarithmic temperature scale. Long-range AF order is observed for $x \geq 0.3$ and manifests itself by broadened jumps in $C(T)/T$. The inset shows $T_N(x)$ as determined by (entropy-conserving) equal-areas constructions and the maximum of the derivative $d\rho(T)/dT$ in corresponding electrical resistivity measurements [23]. Extrapolation of T_N to zero temperature yields a critical concentration $x_c = 0.2$ (see inset Fig. 4). $CeCu_{5.8}Ag_{0.2}$ belongs to

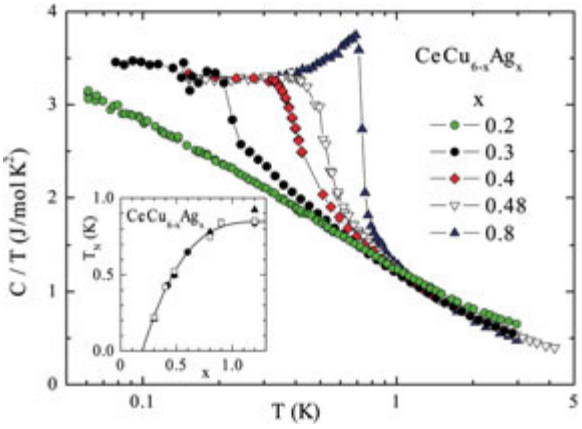

Fig. 4: Specific heat as C/T vs T (on a logarithmic scale) for different $CeCu_{6-x}Ag_x$ polycrystals. Inset shows the evolution of the antiferromagnetic phase transition temperature T_N vs x as derived from specific heat (squares: this study, circles [24]) and electrical resistivity [23]) results.

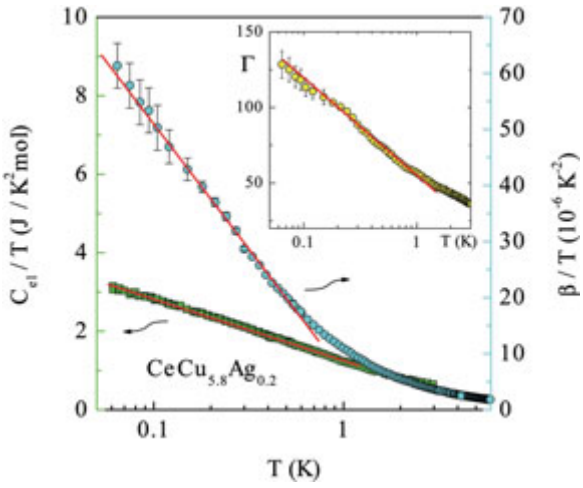

Fig. 5: Electronic specific heat as C_{el}/T vs T (left axis) and volume thermal expansion as β/T (right axis) vs T (on a logarithmic scale) for $CeCu_{5.8}Ag_{0.2}$ at B = 0. Red solid lines indicate log T dependences for C_{el}/T and β/T. The inset shows the temperature dependence of the Grüneisen-ratio $\Gamma = V_{mol}\kappa_T^{-1}\beta/C$ with molar volume $V_{mol} = 6.37 \times 10^{-5}$ m^3mol^{-1} and isothermal compressibility $\kappa_T = 1 \times 10^{-11}$ Pa^{-1} [28] on a logarithmic temperature scale. Solid red line represents a log(T) dependence.

a class of $CeCu_6$-based HF systems in which the AF QCP is reached by doping the Cu-site [25,26]. Common to all of these systems is a universal $C/T \propto log(T_0/T)$ dependence ($T_0 \approx 6$ K) of the specific heat coefficient over nearly two decades in temperature down to 50 mK (see green curve in Fig 4). This behavior would be compatible with theoretical predictions of the itinerant scenario for an AF QCP in the presence of 2D critical spin-fluctuations [10]. Indeed, inelastic neutron scattering experiments on $CeCu_{5.9}Au_{0.1}$ revealed rod-like structures of high intensity in *q*-space translating to quasi-2D fluctuations in real space [27]. The 2D SDW picture, however, has been questioned by the observation of energy over temperature scaling in the dynamical susceptibility with an anomalous fractional exponent virtually independent of wave vector [5]. To disprove from thermodynamics the correctness of the 2D version of the itinerant picture we now turn to the thermal expansion, measured along three perpendicular orientations, on the same polycrystal studied by specific heat (Figure 5). The volume expansion coefficient β is determined by the sum of the three linear expansion coefficients α_i all showing a similar temperature dependence. Upon cooling to the lowest temperatures, $\beta(T)/T$ increases strongly and diverges logarithmically for $T \leq 0.8$ K (see Fig 5). Although the observed $\beta(T)/T$ divergence is steeper than in C/T, indicating that the NFL behavior is caused by a QCP, it is much weaker than the temperature dependence expected in the 2D-SDW scenario [10]. At last, we discuss the temperature dependence of the Grüneisen ratio $\Gamma(T)$ calculated from the specific heat and thermal expansion data shown in Figure 5. In the entire temperature range, the divergence is weaker than $\Gamma \propto 1/T$ and thus, incompatible with the predictions of the itinerant scenario for both 3D or 2D critical spin fluctuations [10]. As shown in the inset of Fig 5, $\Gamma(T)$ roughly follows a logarithmic increase upon cooling from below 1 K.

To summarize, we have shown that at any QCP thermal expansion is more singular than specific heat and that the resulting Grüneisen ratio divergence characterizes the nature of the critical fluctuations. We have reported the first experimental observation of a divergent Grüneisen ratio in the heavy fermion systems $CeNi_2Ge_2$, $YbRh_2(Si_{0.95}Ge_{0.05})_2$ [21] and $CeCu_{5.8}Ag_{0.2}$ [29], all of them located close to AF quantum critical points. For $CeNi_2Ge_2$ the divergence is in accordance with the expectation from scaling analysis for a SDW QCP [21]. By contrast, the fractional exponent observed in the Yb-system is incompatible with this scenario [21]. Furthermore, a weak logarithmic divergence of $\Gamma(T)$ has been found at the QCP in $CeCu_{5.8}Ag_{0.2}$ which excludes an itinerant description for quantum criticality in this latter system as well [29].

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