Non-Fermi liquid states in the pressurized CeCu$_2$(Si$_{1-x}$Ge$_x$)$_2$ system: two critical points

H. Q. Yuan,$^1$ F. M. Grosche,$^2$ M. Deppe,$^1$ G. Sparn,$^1$ C. Geibel,$^1$ and F. Steglich$^1$

$^1$Max-Planck-Institute for Chemical Physics of Solids, Nöthnitzer Straße 40, 01187 Dresden, Germany
$^2$Department of Physics, Royal Holloway, University of London, Egham TW20 0EX, UK

(Dated: March 23, 2022)

In the archetypal strongly correlated electron superconductor CeCu$_2$Si$_2$ and its Ge-substituted alloys CeCu$_2$(Si$_{1-x}$Ge$_x$)$_2$ two quantum phase transitions – one magnetic and one of so far unknown origin – can be crossed as a function of pressure [1]. We examine the associated anomalous normal state by detailed measurements of the low temperature resistivity ($\rho$) power law exponent $\alpha$. At the lower critical point (at $p_{c1}$, $1 \leq \alpha \leq 1.5$) $\alpha$ depends strongly on Ge concentration $x$ and thereby on disorder level, consistent with a Hlubina-Rice-Rosch scenario of critical scattering off antiferromagnetic fluctuations. By contrast, $\alpha$ is independent of $x$ at the upper quantum phase transition (at $p_{c2}$, $\alpha \approx 1$) suggesting critical scattering from local or $Q = 0$ modes, in agreement with a density/valence fluctuation approach.

PACS numbers: 71.10.Hf, 71.27.+a

Amongst the cerium based f-electron compounds, the superconductor CeCu$_2$Si$_2$ takes a special place. The difficulty in growing high quality samples with reproducible properties and the diversity of observed low temperatures states have long complicated and delayed a theoretical description of this intriguing material. After more than 25 years of intensive study, its key properties are gradually being understood. Initial confusion about the ground state properties of CeCu$_2$Si$_2$ samples – some magnetic, some superconducting – can now be attributed unambiguously to the delicate positioning of this material close to a magnetic quantum critical point (QCP) [3]. The precise nature of the incipient magnetism in ambient-pressure CeCu$_2$Si$_2$ has recently been determined as incommensurate spin density wave order [4].

Superconductivity in low pressure CeCu$_2$Si$_2$ now appears amenable to an analysis along the same lines as in other Ce-based heavy fermion (HF) compounds on the threshold of magnetism [3], in terms of magnetically mediated pairing. The evolution of CeCu$_2$Si$_2$ under high pressure, however, has opened up new questions.

The pressure dependence of the superconducting transition temperature $T_c$ in CeCu$_2$Si$_2$ [3,5] and in its iso-electronic sister compound CeCu$_2$Ge$_2$ [6] is very different from that observed in other Ce-based HF compounds, such as CePd$_2$Si$_2$ and CeIn$_3$. In CeCu$_2$Si$_2$, $T_c$ is nearly pressure independent up to about 2 GPa away from the antiferromagnetic (AFM) QCP (at $p_{c1}$) and then increases to a maximum value about 3-4 times that at $p_{c1}$.

To understand the origin of this phase diagram, we have recently performed a study on a series of partially Ge-substituted single crystals CeCu$_2$(Si$_{1-x}$Ge$_x$)$_2$. Due to the weakening of superconductivity by the increased impurity scattering associated with Ge substitution [8] (which widens the lattice and is counterbalanced by applying hydrostatic pressure), the broad and continuous superconducting range previously observed in the $p-T$ phase diagram of pure CeCu$_2$Si$_2$ and CeCu$_2$Ge$_2$ breaks up into two disconnected superconducting domes [1].

The low-pressure superconducting dome occurs around an AFM QCP, suggesting magnetically mediated pairing, while the high-pressure superconducting dome straddles a weak first-order volume collapse (Fig. 1) indicative of a second quantum phase transition (QPT) at high pressure. In this letter, we elucidate the nature of the two QPTs by studying their anomalous normal-state behavior.

Single crystals of CeCu$_2$(Si$_{1-x}$Ge$_x$)$_2$ have been prepared by a flux growth method in excess Cu. High sensitivity, AC four-point measurements of the electrical resistivity were carried out in Bridgman anvil ($p < 10$ GPa) and piston-cylinder ($p < 3.5$ GPa) devices down to 200

![FIG. 1: The combined $p-T$ phase diagram for CeCu$_2$(Si$_{1-x}$Ge$_x$)$_2$ ($TN$: $x=0.25$ ($\bigcirc$), 0.1 ($\triangle$), 0.05 ($\bigtriangleup$), 0.01 ($\square$); $T_c$: $x=0.1$ ($\bullet$)).](image-url)
mK in an adiabatic demagnetization cooler and down to 50 mK in an Oxford Instruments dilution refrigerator. The normal state behavior of our samples has been analyzed by fitting the low temperature normal state resistivity as $\rho = \rho_0 + AT^\alpha$ up to an adjustable maximum temperature $T_{max}$. The resulting residual resistivity $\rho_0$ can be used to extract the temperature dependence of $\alpha$ by taking the logarithmic derivative $\alpha(T) = d\ln(\rho(T) - \rho_0)/d\ln T$, as illustrated in Fig. 2. Both methods are iterated until convergence in $\alpha$ and $T_{max}$ is achieved. We note that $T_{max}$ – which represents the range of validity of the asymptotic low-$T$ power law behavior – depends on Ge concentration and on external pressure. It increases from about 2 K at low $p$ to 10 K at $p_{c2}$ (indicated by darkness of shading in Fig. 1).

Fig. 1 summarizes our present knowledge of the ordered phases of the CeCu$_2$(Si$_{1-x}$Ge$_x$)$_2$ system. It has been constructed by shifting the pressure scale for each Ge concentration by the respective lower critical pressure, $p_{c1}$, at which the AFM transition temperature $T_N$ extrapolates to zero. The critical pressure $p_{c1}$ is about 1.4, 1.5, 1.5 and 2.4 GPa for $x = 0.01, 0.05, 0.1$ and 0.25, respectively. Due to Cu/Si site exchange and possible sample inhomogeneities, the value of $p_{c1}$ becomes less regular for small $x$. Following such a pressure shift, the abscissa can be approximately regarded as a volume scale.

This observation is consistent with the existence of an AFM QCP in CeCu$_2$(Si$_{1-x}$Ge$_x$)$_2$, and indicates that the magnetic QCP exists at a unique volume of the unit cell. At very high pressures, as the system is tuned out of the HF state and into an intermediate valence state, it undergoes an isostructural first-order volume collapse, possibly analogous to the $\gamma - \alpha$ transition in elemental Ce. The likely pressure dependence of this transition is schematically indicated by a dashed line in Fig. 1. Indeed, a weak first-order volume-collapse line with an apparently low-lying critical end point have been observed around a second QPT in CeCu$_2$Ge$_2$, where $T_c$ reaches a maximum value.

The pressure dependence of the Néel temperature $T_N$ and the volume collapse transition divide the phase diagram into three regions: the antiferromagnetically ordered state below $p_{c1}$, the intermediate valence range above $p_{c2}$, and the more complex region in between the two QPTs.

Focussing initially on the normal state around the low pressure AFM QCP, we note that different low temperature states can be obtained in ambient pressure CeCu$_2$Si$_2$ by deliberately choosing the composition of the melt to be slightly off stoichiometry or by suitable heat treatments. On the other hand, very similar ground states can be achieved in slightly Ge-substituted samples by applying hydrostatic pressure. This allows us to study the magnetic QCP in greater detail. As an example, Fig. 3 shows three possible cases: (a) Magnetic ($T_N > T_c$). At $p = 0.34$ GPa, CeCu$_2$(Si$_{0.9}$Ge$_{0.1}$)$_2$ experiences a magnetic reorientation transition at $T_1 \simeq 1$ K (the initial AFM transition is at $T_N \simeq 1.4$ K), followed by a superconducting transition at $T_c \simeq 0.2$ K. Upon applying a magnetic field, superconductivity is quickly suppressed, but the magnetism is much more robust (in-
The magnetic field (Fig. 3c). When the magnetic field exceeds the volume collapse QPT at high pressure.

Examining the evolution of the resistivity exponent $\alpha$ across the $p-T$ phase diagram (Fig. 4a), we note the following key points: (i) At the AFM QCP (at $p_{c1}$), the exponent $\alpha$ at $p_{c1}$ ranges between 1 and 1.5 and increases with increasing Ge-content $x$. (ii) The exponent $\alpha$ reaches a second minimum in the high-pressure superconducting regime, approaching $\alpha \approx 1$ around the volume collapse transition at $p_{c2}$ ($\Delta p \sim 4$ GPa). Maximum $T_c$ is accompanied in CeCu$_2$Si$_2$ and its Ge-substituted alloys by an extended $T$-linear form of the resistivity – independent of Ge content (and of the associated disorder). Upon further increasing pressure above $p_{c2}$, Fermi-liquid behavior ($\alpha = 2$) is rapidly recovered. (iii) In between the two QPTs, for $p_{c1} < p < p_{c2}$, NFL behavior with $1 \leq \alpha < 2$ survives over a broad range in pressure (about 4 GPa). For small Ge concentrations (e.g. $x = 0, 0.01$ and 0.05), $\alpha$ is nearly pressure independent above $p_{c1}$. However, $\alpha$ goes through a local maximum at intermediate pressure for larger $x$ ($x = 0.1$ and 0.25).

As in other quantum critical HF compounds, current theories can only account qualitatively for the anomalous normal state observed in CeCu$_2$(Si$_{1-x}$Ge$_x$)$_2$. At the AFM QCP, spin-fluctuation theories predict $\alpha = 1.5$ and $\alpha = 1$ for 3D- and 2D- spin fluctuations, respectively, while our measured exponents are sample dependent and lie between these two extremes. The observed increase of $\alpha$ with increasing disorder ($1 \leq \alpha \leq 1.5$) may, however, be explained within a generalised Hlbubina-Rice type hot-spot/cold-spot scenario, e.g. [19]. Such an approach takes into account both the short-circuiting of critical scattering at large wavevector $q = Q$ (connecting “hot” regions of the Fermi surface) by “cold” regions, and the influence of impurity scattering, which is present at all $q$.

The presence of a second QPT at $p_{c2}$ holds the key for understanding the unusual pressure dependence of the resistivity exponent in between $p_{c1}$ and $p_{c2}$. In Figs. 4b and 4c, the pressure dependence of the $A$ coefficient in $\Delta \rho = AT^\alpha$ and the resistivity isotherms $\Delta \rho_T(p)$ ($= \rho(p,T) - \rho_0(p)$) at various temperatures are shown for the samples with $x = 0.1$ and $x = 0.25$. The collapse of $\Delta \rho_T(p)$ (at $T < 10$ K) and of $A(p)$ on crossing the upper critical pressure $\Delta p = p_{c2} - p_{c1} (x) \approx 4$ GPa, indicates a transition from the HF state to an intermediate valence state at $p_{c2}$. This valence transition may be accompanied by an isostructural, weak first-order volume collapse, as suggested by x-ray diffraction experiments on CeCu$_2$Ge$_2$ [11]. At temperatures exceeding 10 K, the drop in the resistivity isotherms at $p_{c2}$ weakens (Fig. 4d), and it vanishes below 50 K. These data suggest that the first order transition line associated with the putative density/valence change at $p_{c2}$ reaches its critical end point at a very low temperature, less than 50 K, explaining also why various past attempts to observe the volume collapse in CeCu$_2$(Si/Ge)$_2$ by high pressure
x-ray diffraction at room temperature have remained unsuccessful.

A weak volume collapse transition at \( p_{c2} \) is expected to be accompanied by large amplitude fluctuations of the lattice density and consequently of the local charge distribution (i.e. the valence). Charge carrier scattering is modified in the presence of these fluctuations, giving rise to an anomalous temperature dependence of \( \rho(T) \), provided that the fluctuation relaxation rate reaches down to low enough energies. In the most detailed scenario so far, proposed by Miyake [20], non-dispersive (local), but nearly critical valence fluctuations are invoked to explain the linear \( T \)-dependence of \( \rho(T) \) at \( p_{c2} \), essentially as a consequence of the equipartition theorem. It is as yet unclear whether this approach can also explain the absence of a giant heat capacity or \( A \)-coefficient peak, which would be expected in the presence of very low-lying excitations spread over large portions of the Brillouin zone, as well as the occurrence of superconductivity, which usually requires a non-local pair-forming interaction. Density or valence fluctuations peaked at \( q = 0 \), whether dispersive or nearly local, would however offer an explanation for the observed disorder-level independent power-law exponent at \( p_{c2} \), because in this case the entire Fermi surface can be considered “hot.” In contrast to the AFM QCP at \( p_{c1} \), where a hot-spot/cold-spot scenario accounted at least qualitatively for the impurity-level dependence of \( \alpha \), the \( T \)-linear resistivity obtained from a density or valence-fluctuation model should then be robust against the level of disorder – in agreement with our experimental findings.

Second to superconductivity, arguably the most dramatic phenomenon in the CeCu\(_2\)(Si/Ge)\(_2\) system is the enormous enhancement of the residual resistivity \( \rho_0 \) around \( p_{c2} \) (Fig. 4b), which contrasts starkly with the weak minimum in \( \rho_0 \) at \( p_{c1} \). The origin of this distinct peak in \( \rho_0(p) \) has been proposed to lie in a strongly pressure-dependent impurity scattering cross-section, as \( p_{c2} \) is approached. Here, the problem lies in the computed logarithmic dependence of \( \rho_0 \) on distance from the critical point [21], coupled with the first order nature of the volume collapse transition at low \( T \). An alternative approach to the state of CeCu\(_2\)(Si/Ge)\(_2\) near \( p_{c2} \) may consider the likely phase separation into low-density (HF) and high-density (intermediate valent) domains, populated by heavy and light carriers, respectively, in distant analogy with the mechanism underlying Giant Magnetoresistance. On the assumption that light quasi-particles cannot propagate in heavy-fermion domains and conversely, heavy quasi-particles scatter strongly in the intermediate-valent (high density) domains, CeCu\(_2\)Si\(_2\) is expected to turn opaque to electrical transport over a narrow region surrounding \( p_{c2} \), leading to the observed pronounced maximum in \( \rho_0(p) \).

In contrast to stoichiometric CeCu\(_2\)Si\(_2\), in which a quasi-linear \( T \)-dependence of the resistivity extends over the entire region between \( p_{c1} \) and \( p_{c2} \), the resistivity exponent \( \alpha \) in Ge-substituted CeCu\(_2\)Si\(_2\) single crystals reaches two distinct minima at \( p_{c1} \) and \( p_{c2} \). These results indicate that the apparent critical region in the \( p-T \) phase diagram of stoichiometric CeCu\(_2\)Si\(_2\) is a result of two critical points, each surrounded by a pressure range in which \( \alpha \) is low. We arrive, then, at a picture analogous to the explanation for the wide superconducting range in stoichiometric CeCu\(_2\)Si\(_2\), which is attributed to the merger of the two superconducting domes in Ge-substituted CeCu\(_2\)(Si/Ge)\(_2\): the interplay of two QPTs results in the unusual pressure dependence of both superconductivity and normal state behavior in CeCu\(_2\)Si\(_2\). While the AFM critical point at \( p_{c1} \) is similar in nature to that in other Ce based HF compounds, the precise nature and origin of the QPT at \( p_{c2} \) is still unclear. Some of its consequences – the colossal pressure dependence of \( \rho_0 \) and the linear, disorder-level independent \( T \)-dependence of \( \rho \) – are, however, clearly established and invite further theoretical investigation.

We thank P. Gegenwart, G. G. Lonzarich, K. Miyake, P. Monthoux, J. A. Mydosh, and M. B. Salamon for useful discussions. HQY also acknowledges the ICAM post-doctoral fellowship.

* Present address: Department of Physics, University of Illinois at Urbana and Champaign, 1110 West Green Street, Urbana, IL 61801; Electronic address: yuan@nrl.uiuc.edu

[1] H. Q. Yuan et al, Science 302, 2104 (2003); H. Q. Yuan et al, Acta Physica Polonica B 34, 533 (2003).
[2] F. Steglich et al, Phys. Rev. Lett. 43, 1892 1979.
[3] P. Gegenwart et al, Phys. Rev. Lett. 81, 1501 (1998).
[4] O. Stockert et al, Phys. Rev. Lett. 92, 136401 (2004).
[5] N. D. Mathur et al, Nature 394, 39 (1998).
[6] F. Thomas et al, Physica B 186-188, 303 (1993).
[7] B. Bellarbi et al, Phys. Rev. B 30, 1182 (1984).
[8] D. Jaccard et al, Physica B 259-261, 1 (1999)
[9] H. Q. Yuan et al, New J. Phys. 6, 132 (2004).
[10] H. Q. Yuan, PhD thesis, TU-Dresden, 2003.
[11] A. Onodera et al, Solid State Commun. 123, 113 (2002).
[12] F. Steglich et al, J. Phys.: Condens. Matter 8, 9909 (1996).
[13] F. Steglich et al, Physica B 223-224, 1 (1995).
[14] M. Lang et al, in Electron Correlations and Materials Properties, Edited by Goni et al. (Kluwer Academic/Plenum Publishers, 1999), p.153.
[15] J. A. Hertz, Phys. Rev. B 14, 1165 (1976).
[16] A. J. Millis, Phys. Rev. B 48, 7183 (1993).
[17] T. Moriya et al, J. Phys. Soc. Jpn. 64, 960 (1995).
[18] G. G. Lonzarich, in Electron, Edited by M. Springford (Cambridge University Press, 1997).
[19] A. Rosch, Phys. Rev. Lett. 82, 4280 (1999).
[20] A. T. Holmes et al, Phys. Rev. B 69, 024508 (2004).
[21] K. Miyake et al, J. Phys. Soc. Jpn. 71, 1007 (2002).