Two Distinct Superconducting Phases in $CeCu_2Si_2$

Huiqiu Q. Yuan [1], Michael Nicklas, F. Malte Grosche [2], Micha Deppe, Christoph Geibel, Günter Sparn [3], and Frank Steglich

In the last decade, a growing number of heavy-fermion compounds, especially the Ce-based systems, have been found to follow a qualitatively similar pressure-temperature (p–T) phase diagram [1–3]: At or close to a quantum critical point (QCP), where the antiferromagnetic (AFM) ordering temperature T_N is continuously suppressed by applying pressure, superconductivity (SC) appears and the behavior of the normal state deviates from Landau-Fermi liquid theory, which can nicely describe most simple metals and alloys at low temperature. These phenomena suggest that spin fluctuations contribute to the glue attracting electrons to form Cooper pairs in heavy-fermion systems [2]. However, the archetypical heavy-fermion superconductor $CeCu_2Si_2$ [4] and its isoelectronic counterpart $CeCu_2Ge_2$ revealed much more complicated behavior under pressure [5,6]. While an analogous magnetic QCP has by now been demonstrated in $CeCu_2Si_2$ at ambient pressure [7], the associated superconducting region extends to much higher pressure than in other compounds, reaching up to 10 GPa in some cases. In particular, T_c shows an unusual pressure dependence: T_c (≈ 0.7 K) is nearly constant below 2 GPa, followed by a steep increase at 2–3 GPa and reaching a maximum value of about 2.2 K around 3 GPa, far away from the magnetic QCP [5]. These properties appear to contradict the magnetic interaction model. To understand the unconventional nature of superconductivity in $CeCu_2Si_2$ we have prepared a series of Ge-substituted single crystals $CeCu_2(Si_{1-x}Ge_x)_2$. The partial substitution of Si by Ge in $CeCu_2Si_2$ has two effects: disorder and lattice expansion. The increased disorder scattering shortens the mean free path ℓ and critically affects the occurrence of unconventional superconductivity, whereas the expansion of the lattice may weaken the coupling between the conduction electrons and the localized $4f$ electrons of Ce and, therefore, favors long-range magnetic ordering at low temperature. The latter provides an opportunity to study the magnetic properties in greater detail than previously possible. Compensating this volume increase by applying hydrostatic pressure then allows us to study essentially the same material but with a higher level of impurity scattering.

Single crystals of the $CeCu_2(Si_{1-x}Ge_x)_2$ series were grown with excess Cu as flux medium in an aluminum-oxide crucible. The powder X-ray diffraction measurements demonstrated that $CeCu_2(Si_{1-x}Ge_x)_2$ crystallizes in the $ThCr_2Si_2$-structure ($I4/mmm$), in which the Ce atoms occupy body-centered tetragonal positions. The resistivity was determined by low-current ac-four-point measurements in an adiabatic demagnetization cryostat (down to T = 180 mK) and a dilution refrigerator (down to T = 50 mK). To achieve high pressure, two different pressure techniques were employed. The first one employs a piston–cylinder cell in which a 1:1 mixture of iso-pentane and n-pentane is filled as a hydrostatic pressure medium. With this technique, we can obtain a maximum pressure of about 3.5 GPa and simultaneously measure multiple samples (up to seven) in one pressure cell. To reach higher pressure, we changed to the Bridgman-type anvil cell with a solid pressure medium (steatite).

As an example, Fig. 1 shows the electrical resistivity $\rho(T)$ at various pressures for $CeCu_2(Si_{0.9}Ge_{0.1})_2$. The antiferromagnetic transitions at T_N and the reorientation transition at T_1 [10,11], determined from the kink in the derivative $d\rho(T)/dT$ (Fig. 1, inset), are gradually suppressed by applying hydrostatic pressure. Upon increasing pressure, the superconducting transition is first suppressed and then reoccurs above 3 GPa.

A systematic study on samples with different Ge-content shows that the superconducting properties of $CeCu_2Si_2$ are very sensitive to the disorder introduced by Ge substitution (Fig. 2) [12]. For the pure compounds $CeCu_2Si_2$ and $CeCu_2Ge_2$ [5, 6] superconductivity exists continuously over a broad pressure range, showing a nearly pressure-independent T_c below $\Delta p \approx 2$ GPa which is then followed by a sharp increase ($\Delta p = p - p_{c1}$, $p_{c1} \approx 0.4$ GPa for $CeCu_2Si_2$ and ≈ 11.5 GPa for $CeCu_2Ge_2$ [8]). As a small amount of Si is replaced by Ge ($0 < x < 0.1$), T_c is reduced and its pressure dependence exhibits a minimum in between two peaks. Upon further

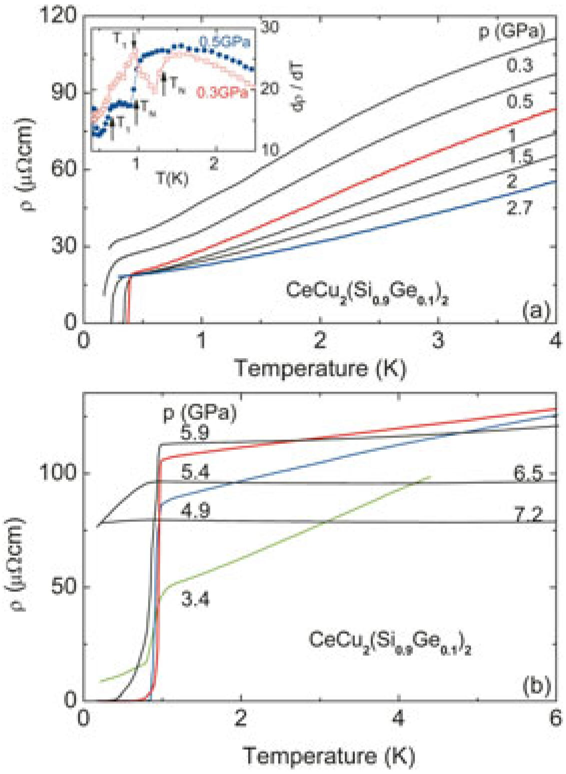

Fig. 1: Temperature dependence of the electrical resistivity ρ(T) at various pressures in $CeCu_2(Si_{0.9}Ge_{0.1})_2$ [9]: (a) p < 3 GPa. Inset dρ/dT vs. T for p = 0.3 GPa and p = 0.5 GPa. (b) p > 3 GPa.

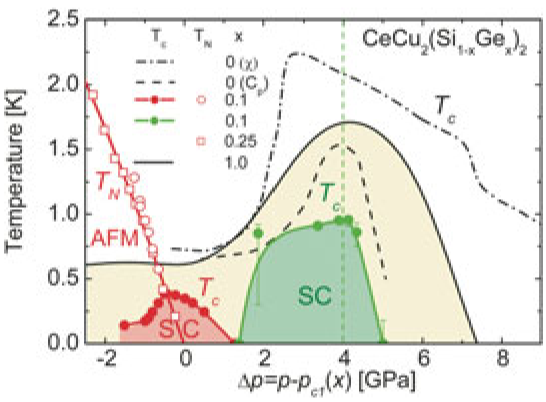

Fig. 2: The p–T phase diagram for $CeCu_2(Si_{1-x}Ge_x)_2$ [8] showing (A-phase) antiferromagnetic (T_N, open symbols) and superconducting (T_c, closed symbols) transition temperatures versus relative pressure $\Delta p = p - p_{c1}$, which reflects the inverse unit-cell volume. These transitions coincide with the magnetic transition lines for x = 0.1 (p_{c1} = 1.5 GPa, circles), x = 0.25 (p_{c1} = 2.4 GPa, squares), and x = 1 (p_{c1} = 11.5 GPa [6], T_c shown by the solid line). Pure $CeCu_2Si_2$ ([5], T_c from specific-heat measurements shown by the dotted line; [13], T_c from susceptibility experiments represented by the dashed-dotted line) is assumed to have p_{c1} = 0.4 GPa. The approximate location of the volume collapse observed in [14] is indicated by a vertical dashed line at Δp = 4 GPa.

increasing x, the continuous superconducting region breaks up into two separate superconducting domes (e.g., $x = 0.1$). Superconductivity disappears in the highly substituted materials (e.g., $x = 0.25$). These properties indicate the existence of two distinct superconducting states in $CeCu_2Si_2$ [8]. Superconductivity in the low-pressure regime occurs around a magnetic QCP at p_{c1} as observed in many other Ce-based heavy fermion systems, where $T_N \rightarrow 0$ and non-Fermi-liquid behavior is observed in the normal state, compatible with theoretical predictions of the magnetic-interaction model. Far away from the magnetic QCP, the occurrence of superconductivity in the high-pressure regime might be related to a weak first-order symmetry-conserving volume-collapse quantum phase transition, suggesting a novel pairing mechanism based on valence/charge-density fluctuations [13].

The anomalous normal-state properties found in $CeCu_2(Si_{1-x}Ge_x)_2$ further support the existence of two quantum phase transitions in $CeCu_2Si_2$ under pressure [15]. Examining the evolution of the resistivity exponent α, taken from a fit of $\rho = \rho_0 + AT^\alpha$ to the low temperature resistivity, across the p–T phase diagram (Fig. 3) we note the following key points: (i) At the AFM QCP (at p_{c1}), the exponent α reaches a local minimum. The value of α at p_{c1} ranges between 1 and 1.5 and increases with increasing Ge-content x. (ii) The exponent α reaches a second minimum in the high-pressure superconducting regime, approaching $\alpha \approx 1$ around the valence transition at p_{c2} (Δp ~ 4 GPa). The maximum T_c is accompanied in $CeCu_2Si_2$ and its Ge-substituted alloys by an extended T-linear dependence of the resistivity. Upon further increasing pressure above p_{c2}, Landau-Fermi liquid behavior ($\alpha = 2$) is rapidly recovered. (iii) In between the two quantum phase transitions, for $p_{c1} < p < p_{c2}$, non-Fermi-liquid 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), α is nearly pressure independent above p_{c1}. However, α goes through a maximum at intermediate pressure for larger x (x = 0.1 and 0.25). These results indicate that the apparent critical region in the p–T phase diagram of stoichiometric $CeCu_2Si_2$ is a result of two critical points. At the lower critical point (at p_{c1}, $1 \leq \alpha \leq 1.5$), α depends strongly on the level of disorder, consistent with a Hlubina-Rice-Rosch scenario of critical scattering off anti-

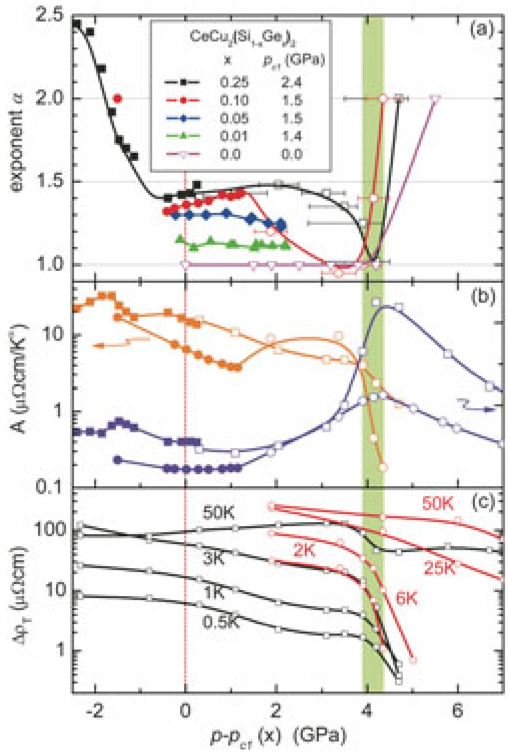

Fig. 3: The pressure dependence of (a) the resistivity exponent α (x = 0 is from Ref. [18]; (b) the resistivity A coefficient and the residual resistivity ρ_0; and (c) the resistivity isotherms $\Delta\rho_T(p)$ at various temperatures for $CeCu_2(Si_{1-x}Ge_x)_2$. Note that the same symbols are used in the figure for the same Ge-concentrations (▽: x = 0, △: x = 0.01, ◇: x = 0.05, ○: x = 0.1, □: x = 0.25). The filled symbols represent the samples measured in clamped pressure cells and the open ones are obtained from Bridgman anvil cells.

ferromagnetic fluctuations [16]. In contrast, α is independent of x at the upper quantum phase transition (at p_{c2}, $\alpha \approx 1$), suggesting critical scattering from local modes, in agreement with a density/valence-fluctuation approach [13].

The observations of a maximum T_c, a linear temperature-dependence of the electrical resistivity and a pronounced peak of the residual resistivity around p_{c2} (cf. Fig. 3) are consistent with a valence-fluctuation model [13,17], suggesting that superconductivity in the high pressure region is mediated by valence fluctuations. Evidence of a valence transition in pressurized $CeCu_2(Si_{1-x}Ge_x)_2$ can be inferred from the collapse of the A coefficient, $A(p)$, of the resistivity (Fig. 3b) and of the resistivity isotherms $\Delta\rho_T(p) = \rho(p,T) - \rho_0(p)$ (at $T <$ 10 K) (Fig. 3c) on crossing the upper critical pressure $\Delta p = p_{c2} - p_{c1}(x) \approx 4$ GPa. This valence transition may be accompanied by an isostructural, weak first-order volume collapse, as suggested by X-ray diffraction experiments on $CeCu_2Ge_2$ [14]. At temperatures exceeding 10 K, the drop in the resistivity isotherms at p_{c2} weakens and it vanishes around 50 K (Fig. 3c). 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.

In summary, we have studied the electrical resistivity $\rho(T)$ under pressure for a series of partially Ge-substituted $CeCu_2(Si_{1-x}Ge_x)_2$ (x = 0.01, 0.05, 0.1, and 0.25). Both the superconducting and normal states support the existence of two quantum phase transitions in pressurized $CeCu_2Si_2$. The occurrence of two distinct superconducting states in the p–T phase diagram of $CeCu_2(Si_{1-x}Ge_x)_2$ is associated with the corresponding quantum fluctuations — the spin-fluctuation mediated superconductivity in the low-pressure region and possibly valence-fluctuation mediated superconducting state in the high-pressure region.

References

[1] *R. Movshovich, T. Graf, D. Mandrus, J. D. Thompson, J. L. Smith, and Z. Fisk,* Phys. Rev. B **53**, 8241 (1996).

[2] *N. D. Mathur, F. M. Grosche, S. R. Julian, I. R. Walker, D. M. Freye, R. K. W. Haselwimmer, and G. G. Lonzarich,* Nature **394**, 39 (1998).

[3] *H. Hegger, C. Petrovic, E. G. Moshopoulou, M. F. Hundley, J. L. Sarrao, Z. Fisk, and J. D. Thompson,* Phys. Rev. Lett. **84**, 4986 (2000).

[4] *F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer,* Phys. Rev. Lett. **43**, 1892 (1979).

[5] *F. Thomas, J. Thomasson, C. Ayache, C. Geibel, and F. Steglich,* Physica B **186**, 303 (1993).

[6] *D. Jaccard, H. Wilhelm, K. Alami-Yadri, and E. Vargoz,* Physica B **259** 1 (1999).

[7] *P. Gegenwart et al.,* Phys. Rev. Lett. **81** 1501 (1998).

[8] *H. Q. Yuan, F. M. Grosche, M. Deppe, C. Geibel, G. Sparn, and F. Steglich,* Science **302**, 2104 (2003).

[9] *H. Q. Yuan, M. Deppe, F. M. Grosche, C. Geibel, G. Sparn, and F. Steglich,* Acta Phys. Pol. B **34**, 533 (2003).

[10] *O. Stockert, M. Deppe, C. Geibel, F. Steglich, D. Hohlwein, and R. Schneider,* Acta Phys. Pol. B, **34** 963 (2003).

[11] *O. Stockert, E. Faulhaber, G. Zwicknagl, N. Stüßer, H. S. Jeevan, M. Deppe, R. Borth, R. Küchler, M. Loewenhaupt, C. Geibel, and F. Steglich,* Phys. Rev Lett. **92**, 136401 (2004).
[12] *H. Q. Yuan, F. M. Grosche, M. Deppe, C. Geibel, G. Sparn, and F. Steglich,* New J. Phys. **6**, 132 (2004).
[13] *A. T. Holmes, A. Demuer, and D. Jaccard,* Acta Phys. Pol. B. **34**, 567 (2003).
[14] *A. Onodera et al.,* Solid State Commun. **123**, 113 (2002).
[15] *H. Q. Yuan, F. M. Grosche, M. Deppe, C. Geibel, G. Sparn, and F. Steglich*, Phys. Rev. Lett. **96** (2006) 047008.
[16] *A. Rosch*, Phys. Rev. Lett. **82**, 4280 (1999).
[17] *Y. Onishi and K. Miyake*, J. Phys. Soc. Jap. **69**, 3955 (2001); *K. Miyake and H. Maebashi*, J. Phys. Soc. Jpn. **71**, 1007 (2002).
[18] *B. Bellarbi et al.,* Phys. Rev. B **30**, 1182 (1984).

[1] Present address: University of Illinois at Urbana and Champaign, Urbana, USA.
[2] Present address: University of London, Egham, Surrey, TW20 0EX, UK.
[3] Present address: Max Planck Institute for Nuclear Physics, Heidelberg, Germany.