Quantum Criticality and Superconductivivty in $CeCoIn_5$

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One of the most fascinating fields in solid state physics is the experimental exploration of the ground state properties of metals, especially, where correlations among the charge carriers are not weak. Since theories based on weakly interacting charge carriers (electron gas model), even in a renormalized form (Landau-Fermi-Liquid (FL) theory), no longer adequately describe such systems, our understanding of the observed phenomena awaits a more microscopic picture. Charge carriers always involve a spin (magnetic) degree of freedom leading to an intimate relation with complex forms of magnetism and unconventional types of superconductivity (SC). The later includes the intriguing possibilities of purely electronically mediated superconductivity. All of this can be ideally studied within the class of heavy-fermion (HF) materials. The first and to date only clear cut example of the existence of a non phononic coupling mechanism is given by the HF-compound UPd_2Al_3 (cf. ***"Nodal Superconductors"***). However, this particular mechanism cannot account for SC in Ce-based heavy Fermion systems, since there a dual $\boldsymbol{f}$-electron nature does not exist. Even more surprisingly then appear those Kondo-lattice antiferromagnets like $CeCu_2Ge_2$ [1], $CePd_2Si_2$ [2], $CeRh_2Si_2$ [3] and $CeIn_3$ [4], which adopt a HF superconducting state at pressures $p \approx p_c$, where p_c is the critical pressure necessary to suppress long-range antiferromagnetic order ($T_N \rightarrow 0$). The occurrence of SC in the vicinity of a zero-temperature magnetic instability (quantum critical point: QCP) support another kind of theories in which Cooper pairs form through the exchange of antiferromagnetic spin fluctuations carried solely by itinerant heavy quasiparticles [5-7]. A hallmark of such spin fluctuations, which become temporally and spatially extended on approaching the QCP, are strong deviations of the normal state properties from the expected behavior for a Landau-Fermi-liquid (NFL: $\Delta C_{el}/T|_{T\rightarrow 0} \neq$ const.). Within these theories, favorable conditions for SC are i) the closeness to a quantum critical point, ii) antiferromagnetic spin fluctuations, iii) a two dimensional (2D) electronic structure, iv) a high spin fluctuation temperature $T_{SF} \propto k_F^2/m_{eff}$ and v) a $\boldsymbol{d}$-wave (singlet) pairing state [7]. However, tests of these theories have been limited, because, only a few physical properties can be examined at the high pressures needed to suppress long-range magnetic order (despite continuous efforts to overcome these limits -including ours: cf. ***"Research at High Pressures"***). Interestingly, all but one of the Ce-based HF superconductors named above form in the same structure as $CeCu_2Si_2$ (tetragonal $ThCr_2Si_2$-type). Only for the case of $CeIn_3$ the crystal structure is different (cubic) [4].

The discovery of another series of Ce-based HF-superconductor compounds ($Ce\boldsymbol{TM}In_5$), which all inhibit the tetragonal $HoCoGa_5$ structure, may appear as a consequence of the structure argument raised above, since $Ce\boldsymbol{TM}In_5$ ($\boldsymbol{TM}$ = Co, Rh, Ir) can be regarded as a variant of $CeIn_3$. $Ce\boldsymbol{TM}In_5$ consists of alternating layers of $CeIn_3$ and $\boldsymbol{TM}In_2$, stacked sequentially along the crystallographic $\boldsymbol{c}$-axes. $CeRhIn_5$ is a HF antiferromagnet (T_N = 3.8 K, C/T ($T\rightarrow 0$) = 0.4 J/molK^2) which becomes a superconductor below T_c = 2.1 K at a moderate pressure of $p \geqq$ 1.6 GPa [8]. For the ambient pressure superconductors $CeIrIn_5$ and $CeCoIn_5$, nuclear-quadrupole-resonance (NQR) experiments [9] suggest that both are located close to a T = 0 magnetic instability, while an analysis of the temperature dependences of their specific heat and thermal conductivity for $T < T_c$ indicates unconventional SC of most likely $d_{x^2-y^2}$ symmetry [10]. For $CeIrIn_5$ T_c = 0.4 K, above which C/T = 0.72 J/molK^2 [11]. $CeCoIn_5$ reveals no long range magnetic order down to T = 20 mK, but exhibits a record high value of T_c = 2.3 K among HF-superconductors at ambient pressure with C/T = 0.36 J/molK^2 [12].

In a working hypothesis based on theories of a nearly antiferromagnetic Fermi-liquid (NAFFL) [5-7] a scenario of spin-fluctuation mediated superconductivity (SFMS) is proposed. The large increase of T_c in $CeCoIn_5$ with respect to that of $CeIn_3$ (T_c = 0.15 K, p_c = 2.55 GPa) [4] is attributed mainly to the reduced effective electronic dimensionality introduced by the ***TM***In_2 layers, which are regarded to act like "inert" spacers.

Experiment

All samples have been supplied by MST-10, Los Alamos National Laboratory, U.S.A. through Dr. J.L. Sarrao. Single crystals of Ce***TM***In_5 were grown from In flux by combining stoichiometric amounts of high purity elements of Ce and ***TM*** with excess In in an aluminum crucible. The crucible was encapsulated in a quartz ampoule. After the growth of the crystals, the excess flux was removed at T = 720 K by a centrifuge [12]. Powder x-ray patterns obtained on crushed single crystals show that $CeIrIn_5$ (a = 0.4668(1) nm, c = 0.7515(2) nm [11]), $CeCoIn_5$ (a = 0.4614 nm, c = 0.7552 nm [12]) and $CeRhIn_5$ (a = 0.4652 nm, c = 0.7542 nm [8]) are phase pure and crystallize in the proper tetragonal $HoCoGa_5$ structure. Measurements of the heat capacity under hydrostatic pressure have been performed in our ^{3}He-evaporation cryostat by a quasi-adiabatic compensated heat-pulse technique utilizing a high-purity Cu(Be) piston-cylinder pressure cell with Flourinert as pressure transmitting medium (CG-HP, for details, see report 2000). Several single crystals with a total sample mass of about 400 mg were used to perform the experiments. The coefficient of thermal expansion, $\alpha(T) = l^{-1}\, dl\, /\, dT$, was determined down to 50 mK by utilizing our ultrahigh-resolution capacitive dilatometer (CG-LT).

Results

Figure 1 shows the specific heat of $CeCoIn_5$ at ambient pressure and at p = 1.5 GPa. At ambient pressure, just above T_c, the specific heat coefficient $C/T \approx 0.36$ J/molK^2. A very large jump in the specific heat is observed when entering the superconducting state ($\Delta C/\gamma T_c \approx 5$). This value is one of the largest found among all superconductors (BCS-value: $\Delta C/\gamma T_c \approx 1.43$). It confirms that the Cooper pairs consist of the heavy quasiparticles. However, the shape of the data for $T < T_c$ can not simply be calculated within a strong-coupling theory. This raises a very important question about the mechanism which transfers the electronic normal state entropy into the system of Cooper pairs.

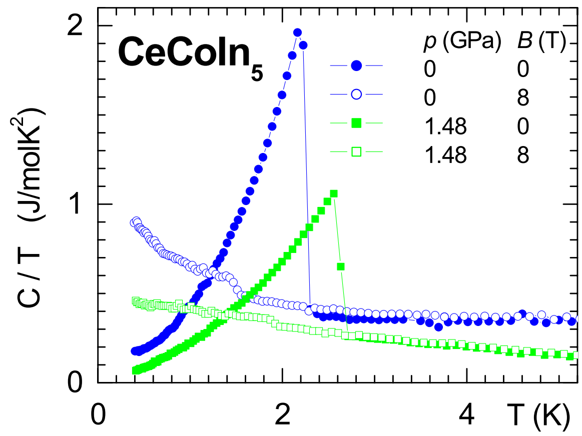

***Fig. 1:** Specific heat of $CeCoIn_5$ as C/T vs T for p=0 and p = 1.5 GPa both at B = 0 and B = 8 Tesla.*

With increasing pressure T_c raises at an initial rate of $dT_c/dp \approx 0.4$ K/GPa (Fig. 2a), which is close to what was calculated from our thermal expansion measurements applying the Ehrenfest relation (dT_c/dp ($p\rightarrow 0$) = 0.64 K/GPa) [13], while the ratio C/T at T = 3 K decreases linearly with a rate of $d\ln(C/T)/dp \approx -0.25$/GPa. Qualitatively, this is typical for Ce-based HF compounds and consistent with an increasing hybridization between the Ce-4f- and the conduction-band electrons usually characterized by the single-ion Kondo temperature T_K.

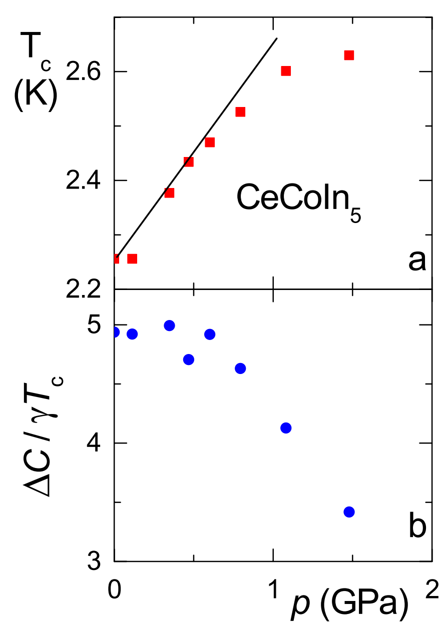

***Fig. 2:** T_c vs. p (a) and $\Delta C/\gamma T_c$ vs. p (b) of $CeCoIn_5$. Straight line marks initial slope $dT_c/dp \approx 0.4$ K/GPa.*

A qualitatively very similar behavior is found for the pressure dependence of the heat capacity of $CeIrIn_5$. The data can be found in detail in [14-16]. In the framework of spin fluctuation theory, the decrease of the quasiparticle mass indicates an increase of the characteristic spin-fluctuation temperature $\boldsymbol{T}_{SF}$, ($\boldsymbol{T}_{SF} \propto \boldsymbol{k}_F^2/\boldsymbol{m}_{eff}$), which is held responsible for the increase of $\boldsymbol{T}_c$ [7]. At higher $\boldsymbol{p}$, however, $\boldsymbol{T}_c(\boldsymbol{p})$ seems to approach a maximum ($\boldsymbol{T}_c \approx 2.7$ K, $\boldsymbol{p} \approx 1.5$ GPa) (Fig. 2a), the existence of which was confirmed by measurements of the electrical resistivity at pressures up to $\boldsymbol{p}$ = 4.2 GPa, where $\boldsymbol{T}_c < 1$ K [17].

Interestingly, the ratio $\Delta\boldsymbol{C}/\gamma\boldsymbol{T}_c$ starts to decrease more rapidly at about the same pressure value at which $\boldsymbol{T}_c(\boldsymbol{p})$ deviates from linear dependence ($\boldsymbol{p} \approx 0.8$ GPa), revealing $\Delta\boldsymbol{C}/\gamma\boldsymbol{T}_c = 3$ at the highest pressure reached in our experiments (Fig. 2b). The existence of a maximum in $\boldsymbol{T}_c$ as well as the loss in entropy transfer between normal- and superconducting state give a hint towards a yet unidentified mechanism which competes with the effect of increasing $\boldsymbol{T}_{SF}$.

Applying a magnetic field $\boldsymbol{B}$ = 8 T is sufficient to suppress SC in those crystals whose basal plane is oriented perpendicular to $\boldsymbol{B}$, but a phase transition anomaly is still observed at $\boldsymbol{T}_{c2} \approx 1.48$ K for crystals for which the field direction lies within the basal plane (Fig. 1). The values of $\boldsymbol{B}_{c2}$ (||) and $\boldsymbol{B}_{c2}$ ($\perp$) at ambient pressure agree well with the anisotropy of the upper critical fields as determined in [13].

At ambient pressure and $\boldsymbol{B}$ = 8 T, $\boldsymbol{C}/\boldsymbol{T}$ is proportional to $-\ln\boldsymbol{T}$ for $\boldsymbol{T} < 1$ K, indicating deviations from Landau-Fermi-Liquid behavior (NFL-behavior) at a surprisingly high value of $\boldsymbol{B}$ (compared to, e.g., $CeNi_2Ge_2$ [18]) and demonstrating that $CeCoIn_5$ is located close to a QCP (Fig. 1). At high pressure, however, $\boldsymbol{C}/\boldsymbol{T}$ no longer increases logarithmically with decreasing temperature, but rather tends to level off, approaching a constant value of $\boldsymbol{C}/\boldsymbol{T} \approx 0.5$ J/molK^2 below $\boldsymbol{T}$ = 0.5 K (Fig. 1). Thus, by applying hydrostatic pressure, the physical properties of $CeCoIn_5$ can be tuned from NFL- to FL behavior through increasing the distance to the QCP.

Looking in more detail at our thermal expansion data, we found that the signature of the superconducting phase transition of $CeCoIn_5$ becomes first-order like when the magnetic field $\boldsymbol{H}$ || [001] is larger than $\boldsymbol{H}$ = 4.7 T, i.e., close to the upper critical field of the superconductor $\boldsymbol{H}_{c2}$ ($\boldsymbol{T}\rightarrow 0$) = 4.95 T

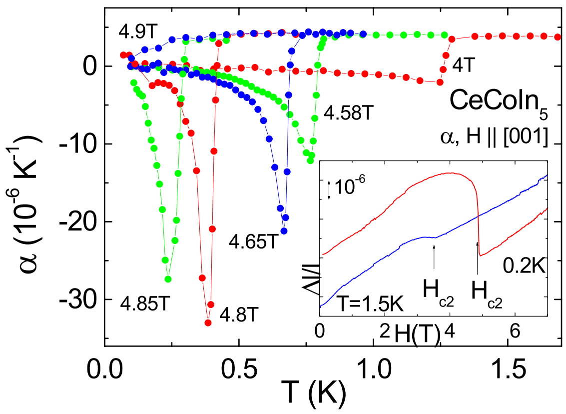

Fig. 3: Thermal expansion coefficient α vs. T of $CeCoIn_5$ for fields 4T $\leq$ H $\leq$ 4.9T applied along [001]. The inset shows the relative length change $\Delta l/l$ vs. H at T = 1.5 K and T = 0.2 K. The arrows indicate anomalies at H_{c2}.

(Fig. 3) [13]. Here, the transition temperature is below $\boldsymbol{T} = 0.31\ \boldsymbol{T}_c$ ($\boldsymbol{B}$=0). The change from second order at lower fields is reflected in a strong sharpening of both specific heat and thermal expansion anomalies associated with the phase transition, a strong magnetocaloric effect, and a step-like change in the sample volume. This effect was predicted theoretically in the mid-1960s but yet eluded experimental confirmation. It was shown that, when the Pauli effect is sufficiently strong relative to the orbital effect, the superconducting phase transition may change from second order (BCS result for zero field) to first order [19-21]. This is due to the competition between the pair-condensation energy and the magnetic energy of the normal electron spins due to Pauli paramagnetism.

Thermal expansion along the crystallographic [001] direction was measured for two different plate-like single crystals in magnetic fields up to $\boldsymbol{H}$ = 8 T applied along [001]. For one of the crystals, isothermal magnetostriction measurements were performed as well at $\boldsymbol{T}$ = 0.2 K and at $\boldsymbol{T}$ = 1.5 K. In the low field range $\boldsymbol{H} \leq 4$ T, a step-like anomaly in $\alpha(\boldsymbol{T})$, indicative of a second-order transition, is observed, which shifts towards lower temperatures upon increasing $\boldsymbol{H}$. With increasing fields (Fig. 3) the signature sharpens anomalously and becomes peak-like, with extremely high absolute values of α. This again indicates a change of the nature of the superconducting transition from second order to first order for magnetic field about of $\boldsymbol{H}$ = 4.6 T. A first-order transition results in a jump in the sample length, corresponding to a divergence of α. Thus, the peak-like signature in α indicates a broadened first-order transition. We also measured the isothermal magnetostriction of $CeCoIn_5$, which is shown in the inset of Fig. 3. Whereas at $\boldsymbol{T}$ = 1.5 K the kink in $\Delta\boldsymbol{l}/\boldsymbol{l}$ at $\boldsymbol{H}$ = 3.55 T indicates a second-order phase transition, the jump in $\Delta\boldsymbol{l}/\boldsymbol{l}$, observed for $\boldsymbol{T}$ = 0.2 K at $\boldsymbol{H}$ = 4.86 T, provides clear evidence for the first-order nature of the transition.

Summary and outlook

The first-order phase transition observed in $CeCoIn_5$ close to $\boldsymbol{H}_{c2}$ ($\boldsymbol{T}\rightarrow 0$) can be regarded as the first experimental observation of a particular effect of the Pauli limiting in a type-II superconductor as it was predicted in the mid-1960s. The experimental finding that $\boldsymbol{T}_c$ of $CeCoIn_5$ increases while its heat capacity $\boldsymbol{C}/\boldsymbol{T}$ decreases with increasing pressure supports a picture of spin-fluctuation mediated SC as laid out on the basis of the itinerant spin-fluctuation theory. At elevated pressures a crossover from NFL- to FL-behavior is observed in $CeCoIn_5$ which is accompanied by a saturation of $\boldsymbol{T}_c$ and a loss in entropy transfer between normal- and superconducting state. To date, this is interpreted as a weakening of the superconducting state due to the growing distance from the QCP. Without doubt this interpretation is unsatisfactory. It does not account for the discrepancy found between $CeIrIn_5$ and $CeCoIn_5$ where the pressure dependence of $\boldsymbol{T}_c$ does not simply scale with the pressure dependence of $\boldsymbol{T}_{SF}$ as determined by the ratio $\boldsymbol{C}/\boldsymbol{T}(\boldsymbol{p})$. A similar scaling problem exists for the case of $CeCu_2Si_2$ ($\boldsymbol{p}$ = 0: $\Delta\boldsymbol{C}/\gamma\boldsymbol{T}_c \approx 1.45$ but $CeCu_2(Si_{0.9}Ge_{0.1})_2$: $\Delta\boldsymbol{C}/\gamma\boldsymbol{T}_c \approx 0.15$ only). In addition, within the scenario of spin-fluctuation mediated SC, the existence of SC should be restricted to the vicinity of the QCP. However, in contrast to $CeIn_3$ and $CePd_2Si_2$, SC in $CeCoIn_5$ exists over a surprisingly large regime in $\boldsymbol{p}$ [17], similar to what is found for $CeCu_2Si_2$ [22] and $CeCu_2Ge_2$ [1]. Applying such high pressures implies introducing a large variation of the unit cell volume which causes a non-negligible change in the Ce-4$\boldsymbol{f}$- to conduction electron hybridization. How such a dramatic change of the parameters determining the underlying heavy quasiparticle state can be incorporated into the existing electronic-coupling scenarios has to be demonstrated yet [23]. Measurements of the specific heat to higher pressures (new CrNiAl-piston-cylinder cell, new Bridgman-cell) and lower temperatures (new dilution refrigerator) are scheduled to explore the properties of the superconductor once $CeCoIn_5$ truly adopts a FL ground state as already indicated by electrical resistivity measurements for $\boldsymbol{p}$ > 1.5 GPa [17]. Utilizing the Bridgman-cell, we want to explore the power law of electrical resistance at pressures in excess of $\boldsymbol{p}$ = 4 GPa and in the mK-regime to characterize the ground state properties in the crossover regime between NFL- and FL-state. All these efforts will be complemented by our high pressure studies on the new single crystals of $CeCu_2Si_2$ and $CeCu_2(Si_{1-\boldsymbol{x}}Ge_{\boldsymbol{x}})_2$ where we expect very similar physics. With respect to the discovery of superconductivity at $\boldsymbol{T}_c$ = 18.5 K in the isostructural compound $PuCoGa_5$ [24], which is as unexpectedly high as was $\boldsymbol{T}_c$ of MgB_2 [25], the multiband nature of itinerant charge carriers may play a key role in developing a more microscopic picture of these compounds. On this basis one might be able to account for the large variations in the values of $\boldsymbol{T}_c$ as well as the changes in entropy involved in the phase-transition anomaly of the superconductor, where only certain parts of the Fermi surface might be involved in Cooper-pair formation.

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