Quantum Criticality and Superconductivity in the Heavy Fermion Compound $CeCoIn_5$

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In the Ce-based compounds CeMIn$_5$ (M = Co, Rh, Ir), the *f*-electrons are subject to a competition of the RKKY interaction and the Kondo effect. The former one favors long-range magnetic order (typically antiferromagnetic), whereas in the latter case the conduction electrons quench the magnetic moment of the localized *f*-electrons giving rise to a heavy fermion (HF) state below the so-called coherence temperature T^*. This results in the well-known phase diagram by Doniach [1]. At the point where the two energy scales match, a quantum critical point (QCP) is expected. However, superconductivity (SC) often emerges in the vicinity of this critical point [2]. Therefore, these materials are ideally suited to study the mutual interplay of magnetic fluctuations and superconductivity.

The tetragonal crystal structure of CeMIn$_5$ can be thought of as a sequence of $CeIn_3$ and MIn$_2$ layers stacked along the *c*-axis. Even though the material cannot be regarded as truly two-dimensional (2D) this structural anisotropy certainly influences the magnetic and superconducting properties. As one likely consequence, the superconducting transition temperature of $CeCoIn_5$ is enhanced (with respect to the cubic parent compound $CeIn_3$) to $T_c = 2.3$ K [3], the highest value among the Ce-based HF systems (at ambient pressure) known to date. Another consequence of the layered crystal structure may be anisotropic spin fluctuations near magnetic ordering as evidenced from NQR experiments. Low-temperature transport and specific-heat experiments also point at the existence of a field-induced QCP in $CeCoIn_5$ with the antiferromagnetic ground state superseded by superconductivity [4,5]. Even more, H_{c2} and the quantum critical field seem to coincide.

Fulde-Ferrell-Larkin-Ovchinnikov state in $CeCoIn_5$

As is well known, type-II superconductivity in the presence of a magnetic field is suppressed by two main mechanisms: the orbital effect and/or the Pauli effect. If orbital pair breaking is negligible relative to the Pauli limiting effect, a spatially periodic modulation of the superconducting order parameter $\Delta(\mathbf{r})$ will take place for $T \leq 0.55\ T_c$ in sufficiently clean systems. This periodic state (the FFLO state) was predicted 40 years ago by Fulde and Ferrell [6] and Larkin and Ovchinnikov [7]. However, the realization of such a state in conventional *s*-wave superconductors is almost impossible.

The appearance of the unconventional superconductor $CeCoIn_5$ opens up a new window for exploration of the FFLO state. The reduced electronic dimensionality provides a path to substantially reduce the orbital limiting effect. Technical advances in single-crystal growth allow one to obtain samples with an electronic mean free path of the order of microns which favors the FFLO state. Additionally, for *d*-wave SC the FFLO state has a more extended stability region and is more robust against impurities than for the *s*-wave superconductors. Furthermore, the Maki parameter α takes the value 5.8 for $H \parallel ab$, which is significantly larger than the minimum value ($\alpha = 1.8$) required for *s*-wave superconductors. Indeed, there are several reports providing strong evidence for the realization of the FFLO state in CeCoIn5 and/or a first order phase transition to the superconducting state for $T \leq 0.7$ K [8-14].

We conducted specific heat measurements on $CeCoIn_5$ under applied pressure and in high magnetic fields that reveal the pressure evolution of the low-temperature anomaly ascribed to the FFLO state [15]. In order to rule out the magnetic QCP related origin of this anomaly, one has to drive the system away from the influence of magnetic fluctuations. This is accomplished by applying hydrostatic pressure: $CeCoIn_5$ moves away from quantum criticality and enters a Fermi liquid state at high pressure [16-19]. Therefore, pressure studies are an ideal tool to investigate the origin of the second anomaly in the SC state.

We used a newly developed miniature pressure cell (machined completely from CuBe) for specific heat (C) measurements on high quality single crystals of $CeCoIn_5$ [20,21]. The experiments were carried out for magnetic fields applied parallel to the tetragonal *ab*-plane as well as parallel to the *c*-axis in a dilution cryostat ($T \geq 100$ mK, $\mu_0 H \leq 12$ T) and a PPMS (Quantum Design, $T \geq 350$ mK, $\mu_0 H \leq 14$ T). A comparison of the specific heat data at zero field, taken in the new miniature pressure cell, to previous measurements confirms the quasi-hydrostatic conditions of the recent setup.

The specific-heat data were collected at $p = 0$, 0.45 and 1.34 GPa. In the following, we focus on data obtained with magnetic field applied in the basal plane, where the possible existence of the FFLO state has recently attracted much attention. T_c increases from $T_c = 2.24$ K at zero pressure to $T_c = 2.43$ K at 0.45 GPa, and to $T_c = 2.58$ K at 1.34 GPa, in good agreement with T_c determined from resistivity data [22] and previous specific heat and susceptibility measurements [17] under pressure.

The large nuclear Schottky-contribution, C_{Schottky}, coming from both pressure cell and sample, causes a relatively high scattering in the low-temperature electronic specific heat, $\Delta C = C - C_{\mathrm{Schottky}}$ (Fig. 1), in magnetic field. At low magnetic fields the specific heat at the SC transition (main peak) reveals a mean-field like shape. With increasing field the anomaly sharpens, despite the phase transition line $H_{c2}(T)$ being crossed at a glancing angle at high magnetic fields. In the case of a second order phase transition one expects a significant broadening of the peak in this field range. However, the peak becomes more symmetrical, indicating the change from a second to a first order phase transition at the magnetic field H_0 corresponding to $T_c = T_0$. Additionally, we observed a minimum of the height of the anomaly at T_0, typically seen at the crossover from a second to a first order phase transition (not shown). The specific heat results, together with magnetization data [23], provide strong evidence for the phase transition to the SC state (at high magnetic fields both at 0.45 GPa and 1.34 GPa) being of first order as already observed at ambient pressure.

At ambient pressure, ΔC in high magnetic fields exhibits a second anomaly inside the SC state at low-T (which we denote T_{FFLO}), visible even if the sample is measured inside the pressure cell. The $T_{\mathrm{FFLO}}(H)$ dependency observed for $p = 0$ GPa is in very good agreement with [8]. This feature can be traced under pressure as well, at $p = 0.45$ GPa and

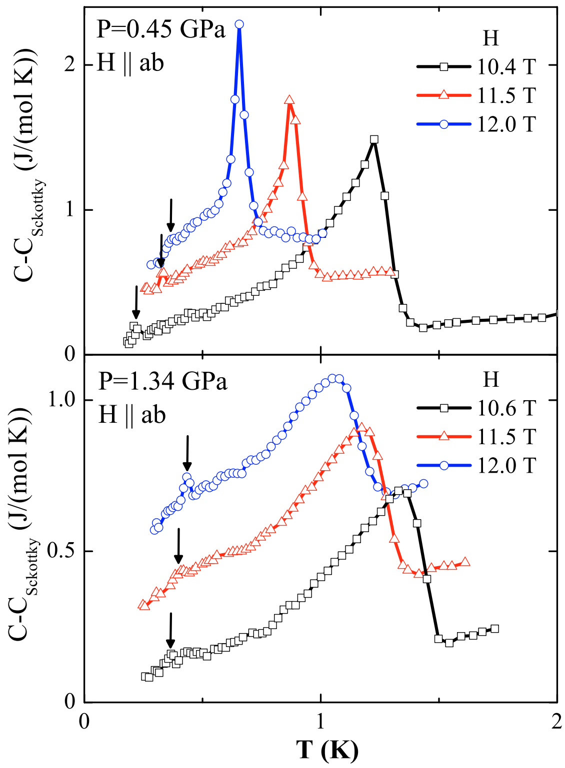

Fig.1: Electronic contribution of the low temperature specific heat, C - $C_{Schottky}$, for selected magnetic fields H close to $H_{c2}(0)$ at p = 0.45 GPa (upper panel) and p = 1.34 GPa (lower panel). Data at 11.5 T and 12 T are shifted by 0.25 J/(mol K) and 0.5 J/(mol K) for clarity. The arrows indicate T_{FFLO}.

$p = 1.34$ GPa (Fig. 1). The tiny anomaly is comparable in size to the one found at ambient pressure. $C(T)$ at $p = 0.45$ GPa (Fig. 1, upper panel) shows the evolution of T_{FFLO} with magnetic field. For this pressure, at 10.4 T the transition from the normal to the SC state is still of second order, but a second anomaly is already observable at low T. Only for fields higher than 11.2 T (11.5 T and 12 T depicted in Fig. 1) the SC transition is of first order. This behavior is different from results at ambient pressure. Here, at the field where the second anomaly is found, the transition from the normal to the SC state is already of first order. We obtain similar results for $p = 1.34$ GPa, where, at fixed field, a normal to SC state phase transition, of a second order, is followed by a second anomaly in $C(T)$.

Figure 2 displays the H - T phase diagram for $p = 0$, 0.45 and 1.34 GPa for $H \parallel ab$ and for $H \parallel c$. At ambient pressure we have established an $H - T$ phase diagram for $CeCoIn_5$ very similar to those observed previously [9, 10]. We note the increasing anisotropy between $H_{c2}(0) \parallel ab$ and $H_{c2}(0) \parallel c$ upon

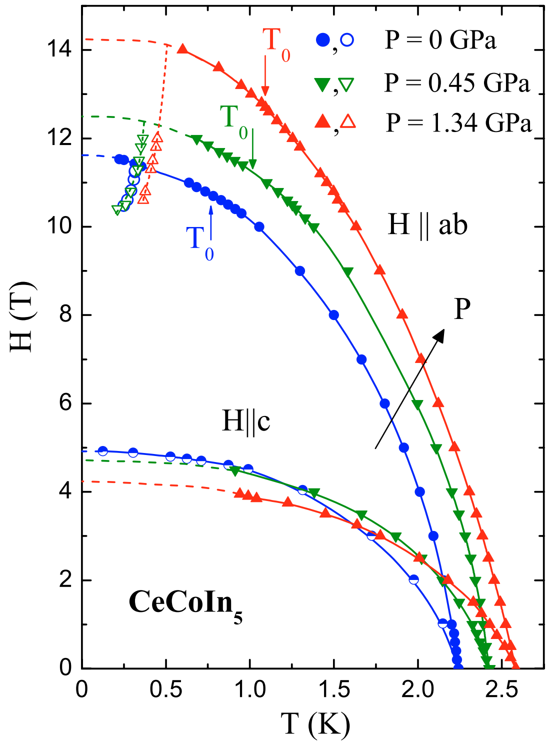

Fig. 2: H - T phase diagram for magnetic field H || c and H || ab. Arrows mark the crossover temperature T_0 from a second to a first order phase transition into the SC state. Closed symbols (half-filled symbols represent data taken from [8]) indicate $H_{c2}(T,p)$ and open symbols the second anomaly inside the SC phase.

applying pressure. The anomaly at T_{FFLO} appears first at almost the same magnetic field ($\approx$ 10.5 *T*) independent of pressure. With increasing field, $T_{FFLO}(H)$ shifts to higher temperatures for all pressures but is almost unaffected by applying only a small pressure. Increasing the pressure to p = 1.34 GPa, however, moves $T_{FFLO}(H)$ to higher temperatures, and $H_{c2}(0)$ increases considerably. Under finite pressure, with our setup, we are not able to follow $T_{FFLO}(H)$ all the way to the tricritical point in the phase diagram, because our maximum magnetic field is limited to 12 T at lowest *T*. Like $T_{FFLO}(H)$ at 0 and 0.45 GPa, the initial slope of the upper critical field, $H'_{c2} = dH_{c2}/dT|_{T=T_c}$ of –30.5 T/K at p = 0 GPa and –29.4 T/K at 0.45 GPa also remains roughly the same. Correspondingly, the orbital critical field $H_{orb} = 0.7T_c|H'_{c2}|$ does not change significantly (H_{orb}(0 GPa) = 47.9 T and H_{orb}(0.45 GPa) = 49.9 T). However, at p = 1.34 GPa, H'_{c2} decreases drastically, by nearly one half to –16.4 T/K, and consequently H_{orb}(1.34 GPa) = 29.7 T. The value of the Maki parameter α is estimated to 5.8, 5.7 and 2.9 at 0, 0.45 and 1.34 GPa, respectively, still sufficiently large compared to the required minimum value α = 1.8 for *s*-wave superconductors [7] to realize the FFLO state.

In conclusion, the FFLO anomaly inside the SC state appears to be present at all pressures, reinforcing the existence of the FFLO state at low-*T* close to $H_{c2}(0)$. Our result is the first evidence of the existence of this state away from the influence of the strong magnetic fluctuations clearly suggesting its genuine FFLO nature. Our results can be analyzed by the model recently proposed in [24]. The reduction of the effective mass and the rise of the Fermi velocity with increasing p indicate a decrease of the quasiparticle-quasiparticle interaction.

Hall effect measurements

Recently, Hall effect measurements have proven useful in studying HF materials close to a QCP [25]. Therefore, we investigated the Hall effect of high-quality single crystalline $CeCoIn_5$. It should be noted in this context that measurements of the de Haas-van Alphen (dHvA) effect in $CeCoIn_5$ revealed essentially two Fermi surfaces (FS) of quasi-2D character [26,27] related to the layered structure of this compound. Band structure calculations mainly showed a roughly cylindrically shaped FS of electron character and a complicated hole-like FS [26,28]. Moreover, these investigations revealed that the electron and hole FS volumes match and hence, this material is a (nearly) compensated metal.

For the Hall measurements, isothermal magnetic field sweeps (applied magnetic field parallel to the crystallographic *c*-axis) were conducted at temperatures down to 0.05 K. The Hall voltage was obtained as the asymmetric contribution under field reversal. The symmetric contribution (much smaller than the asymmetric one for well aligned contacts) was compared to the simultaneously measured transversal magnetoresistance as a consistency check. The results of Hall measurements at selected temperatures are shown in Fig. 3. Our Hall resistivity data ρ_{xy} can favorably be compared to those reported for temperatures down to 2 K [29] and 1 K [30].

The Hall coefficient $R_H = \rho_{xy} / \mu_0 H = R_0 + R_a$ is composed of the normal contribution R_0 (related to the FS topology) and the anomalous part usually

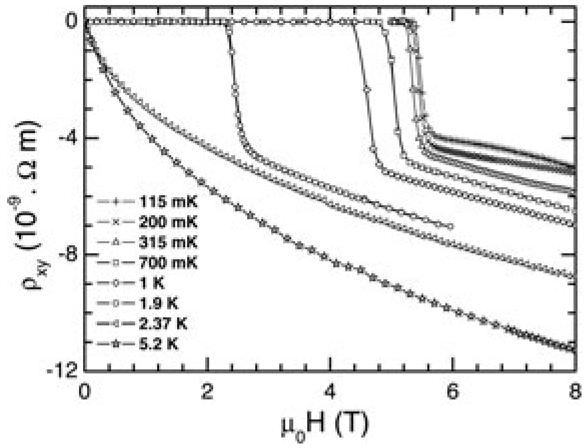

Fig. 3: Isothermally measured Hall resistivity of $CeCoIn_5$ for selected temperatures. Superconductivity at low temperatures and field-dependent Hall coefficients can be well recognized.

ascribed to skew scattering. In an impurity model [31], $R_a \propto \rho\chi$ where ρ is the magnetic contribution to the electrical resistivity and χ is the magnetic susceptibility. In the coherent regime of HF metals, however, an impurity model should not be applicable, rather it was argued [32] based upon an Anderson lattice model that $R_a \propto \chi$. Therefore, R_a usually assumes a positive maximum at around T^* and dominates R_H but drops rapidly at low temperatures. In $CeCoIn_5$, T^* is estimated to about 40 K. The facts that i) such a maximum is not observed and ii) the investigated T-range of Fig. 3 is well below T^* substantiate a negligible contribution of R_a to R_H in our case. Hence, R_0 mainly probes the FS volume of $CeCoIn_5$ at low-T. The above mentioned properties of the FS of $CeCoIn_5$, however, complicate an analysis substantially. In case of multiple bands residing at the FS, the net R_H is determined by a mobility-weighted (and hence, carrier-mass dependent) sum of the band contributions.

As seen from Fig. 3, $\rho_{xy}(H)$ shows a considerable change in slope at all temperatures. This holds even true for $T < T_c$ as any reasonable extrapolation of the high-field data would *not* intercept the origin of the ρ_{xy}-H plot without distinct change of R_H. Often, the initial Hall coefficient R_H^0 is analyzed. In our case, however, this is complicated i) by the onset of superconductivity at a critical field $H_{c2}(T)$ and ii) in a multi-band material R_H^0 also depends on the individual-band mobilities. The Hall coefficient in the high field limit, $R_H^\infty = \lim_{H\to\infty} R_H$, on the other hand, is difficult to obtain in our maximum field of 8 T: We estimate $\omega_c\tau \approx 3$ at 8 T (ω_c: cyclotron frequency, τ: average time between scattering). Nonetheless, if we take the values at maximum field we obtain a constant value of $R_H^{8T} \approx -6 \times 10^{-10}$ m^3/C for $T \geq$ 300 mK. Only at 5.2 K, R_H^{8T} is slightly increased most likely due to the fact that the high-field limit is not yet reached. We interpret this as a constant effective carrier concentration in the considered temperature range. The decrease in R_H^0 with falling temperature could then be thought of as a change of the individual-band mobilities. Considering the values of ρ_{xy} for $T < T_c$ and $H > H_{c2}$ one might even speculate this process to continue if it was not masked by superconductivity. Note that dHvA [26] shows a field-dependent effective carrier mass which may also contribute to the field dependence of R_H.

At $T \leq 250$ mK, we find marked deviations from the behavior at higher temperatures which may be related to the onset of Landau Fermi liquid behavior [4,5]. Here, further detailed research is in progress.

Low-temperature thermal expansion and Grüneisen ratio

Measurements of the thermal expansion are especially suitable to study quantum criticality since they directly probe the sensitivity of thermodynamics resulting from the QCP to pressure-tuning. Particularly, near any pressure-tuned QCP, the thermal expansion coefficient α is more singular than the specific heat C. The resulting divergence of the Grüneisen ratio $\Gamma \sim \alpha/C$ can be used to characterize the nature of QCPs [33,34]. In $CeCoIn_5$, low-temperature measurements of the electrical resistivity [4], specific heat [5] and thermal expansion [35] have found strong non-Fermi liquid effects that hint at a QCP coinciding with the upper critical field H_{c2} for unconventional superconductivity. Thus far, any attempt to separate both phenomena has failed. In $CeCoIn_{5-x}Sn_x$, H_{QCP} is pinned to H_{c2} if superconductivity is weakened by Sn substitution, suggesting that superconductivity acts as a veil over a magnetically ordered state [36]. In order to investigate the nature of quantum criticality in this system, we have performed a detailed and systematic study of the low-temperature thermal expansion and Grüneisen ratio. Single crystals of $CeCoIn_{5-x}Sn_x$ with x = 0, 0.03, 0.06, 0.09 and 0.12,

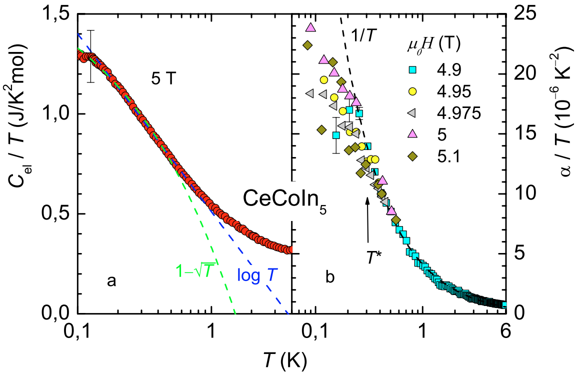

Fig. 4: Electronic specific heat of $CeCoIn_5$ as C_{el}/T vs $\log T$ at 5 T applied parallel to the c-axis (a). Corresponding c-axis linear thermal expansion as α_c/T vs $\log T$ for selected fields close to 5 T (b). Arrow indicates characteristic temperature (see text).

grown at Los Alamos National Laboratory have been studied at their respective upper critical fields which vary from 4.9 T (x=0) to 2.75 T (x=0.12).

Fig. 4 compares our thermal expansion data on the undoped system at magnetic fields close to the critical field with previous specific heat measurements [3]. In order to estimate the electronic part of the low-temperature specific heat $C_{el} = C - C_n$ a large Indium-hyperfine contribution C_n has been subtracted below 0.2 K giving rise to substantially large error bars at low temperatures, see Fig. 4a. The strong increase of C_{el}/T upon cooling from high temperatures could either be described by a logarithmic behavior below 1 K (blue dashed line) or a $1-\sqrt{T}$ dependence below 0.5 K (green dashed line). According to the itinerant model for an AF QCP, such temperature dependences are expected for 2D and 3D critical spin fluctuations, respectively [37]. However, due to the large error bars at low temperatures, a possible saturation of C_{el}/T below 0.2 K, that would indicate the cross-over to a Landau Fermi liquid (LFL) ground state, cannot be excluded. Thermal expansion may help to clarify the situation since in the quantum critical regime power-law divergences for α/T are expected (T^{-1} and $T^{-0.5}$ for the 2D and 3D case, respectively) that easily can be distinguished from $\alpha/T = const.$ for the LFL regime. Fig. 4b shows our corresponding thermal-expansion measurements at various fields close to the critical field of 5 T. Over a large temperature range 0.3 K $\leq T \leq$ 6 K, α/T follows a $1/T$ dependence predicted for 2D AF critical spin fluctuations. At lower temperatures α/T deviates from the $1/T$ dependence and shows a much weaker increase upon cooling. This characteristic deviation cannot be related to the sharp first-order superconducting transition at H_{c2} and slight variations of the applied field do not lead to changes in α/T at low temperatures (compare Fig. 4b). However, it remains unclear whether this observation indicates the precursor of a cross-over to LFL behavior at even lower T, or a change of the exponent in the α/T divergence, e.g. towards $T^{-0.5}$ expected for the 3D AF case.

In order to obtain further information, we have systematically investigated the low-temperature thermal expansion of various $CeCoIn_{5-x}Sn_x$ single crystals [38] at their respective upper critical fields H_{c2}. The substitution of In with Sn has a twofold effect. First, the introduced atomic disorder weakens the unconventional superconductivity, which becomes completely suppressed for $x_c = 0.18$ [36]. Second, disorder is expected to lead to an increase of the 4f-conduction electron hybridization that tunes the system towards the paramagnetic side of the QCP, similar found e.g. for $CeIn_{3-x}Sn_x$ [39]. We observe an increase of the characteristic temperature T^* below which thermal expansion deviates from $\alpha/T \sim T^{-1}$ with increasing x towards T^* = 0.7 K for x = 0.09. Data below T^* could satisfactory be described by $\alpha/T \sim T^{-0.5}$ expected in the quantum critical regime for the 3D AF case. Supposed that T^* marks the temperature at which the effective dimensionality of the critical fluctuations changes from 2D to 3D, the increase of T^* with x would be compatible with disorder scattering, smearing out the anisotropy of the critical spin

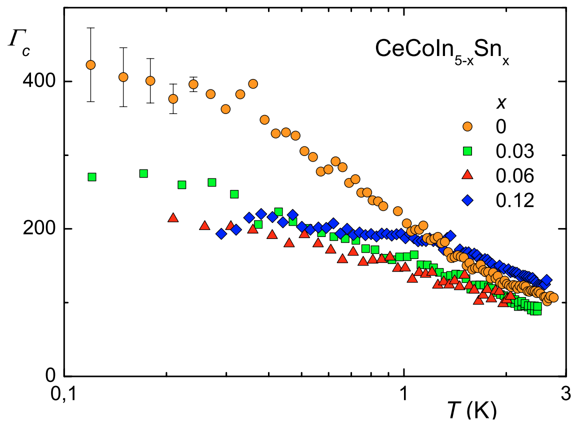

Fig. 5: Temperature dependence of the uniaxial Grüneisen parameter $\Gamma_c = V_{mol}/\kappa_T \cdot \alpha_c/C$ for various single crystals of $CeCoIn_{5-x}Sn_x$ at their respective upper critical fields [32]. V_{mol} and κ_T denote the molar volume and isothermal compressibility, respectively.

fluctuations. On the other hand, Sn-substitution of In atoms is also expected to tune the system towards the paramagnetic LFL regime. In Fig. 5, we compare the uniaxial Grüneisen parameter $\Gamma_c = V_{mol}/\kappa_T \cdot \alpha_c/C$ for the various $CeCoIn_{5-x}Sn_x$ single crystals, each at its respective upper critical field, determined from specific-heat measurements [36]. A clear trend is visible indicating less divergent behavior with increasing Sn content. In fact, for the $x = 0.12$ crystal a saturation in $\Gamma(T)$ is observed for temperatures below about 0.8 K, indicative for a LFL ground state. This proves that it is impossible to uncover the suggested hidden QCP in $CeCoIn_5$ by Sn doping as the latter moves the system away from quantum criticality before superconductivity is completely suppressed.

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