Wilson ratio in Yb-substituted CeCoIn5

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Abstract – We have investigated the effect of Yb substitution on the Pauli-limited, heavy-fermion superconductor, CeCoIn5. Yb acts as a non-magnetic divalent substituent for Ce throughout the entire doping range, equivalent to hole doping on the rare-earth site. We found that the upper critical field in (Ce,Yb)CoIn5 is Pauli limited, yet the reduced (H,T) phase diagram is insensitive to disorder, as expected in the purely orbitally limited case. We use the Pauli-limiting field, the superconducting condensation energy and the electronic specific-heat coefficient to determine the Wilson ratio (RW), the ratio of the specific-heat coefficient to the Pauli susceptibility in CeCoIn5. The method is applicable to any Pauli-limited superconductor in the clean limit.

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Introduction. – Heavy-fermion (HF) systems have been an ideal playground for investigating unconventional superconductivity (SC) since the discovery of SC in this class of materials [1,2]. Much of the attention has been focused on the symmetry of the superconducting order parameter and the interplay/competition between SC and magnetism [3]. Such investigations laid ground for magnetism as the origin of Cooper pairing, since SC in HF seems to occur invariably in close proximity to a T = 0 magnetic instability [4]. Their large specific-heat (C) anomaly at the SC transition and the absence of SC in the non-magnetic La analogs imply that Cooper pairs form out of heavy quasiparticles (QP). Thus, the heavy mass and SC appear to originate from the same mechanism. Yet, the relationship between SC and the Kondo lattice physics, at the heart of the HF problem, has only recently come to spotlight. In particular, a new model of superconductivity for the 115 family of heavy fermions shows that the composite heavy quasiparticles form only when the system becomes superconductor [5].

CeCoIn5 is an ambient pressure SC with TC = 2.3 K [6] and has the unique feature of an antiferromagnetic (AFM) quantum critical point located near the upper critical field Hc2, indicating that AFM is superseded by SC [7,8].

Moreover, the change of the SC transition from second to first order for transition temperatures TC ≤ T* ~ 0.7 TC0 [9] combined with the discovery of a second SC phase in the large B/T region of the phase diagram lead to the suggestion that CeCoIn5 is the first realization [10,11] of a Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state [12,13]. Subsequent NMR measurements have shown that only some of the NMR lines broadened within the second SC phase, consistent with local moment ordering [14]. A more recent neutron diffraction experiment has found that this second SC phase carries AFM order that collapses at the same upper critical field at which SC is destroyed [15]. CeCoIn5 is thus the first example of magnetic order being stabilized by superconductivity, suggesting a ground state differing from the one proposed by FF and LO.

The unconventional dxy gap symmetry in CeCoIn5 has been established based on the angular dependence of C [16] and thermal conductivity [17,18], as well as point contact spectroscopy [19]. Recently, a resonance peak has been discovered below TC in inelastic neutron scattering [20], suggesting a magnetically mediated pairing in analogy with the high-Tc cuprates. CeCoIn5 has also been a model system for investigating the emergence of coherence in a Kondo lattice. A phenomenological two-fluid model has been successfully used to describe the crossover from single-ion Kondo behavior to coherent heavy-fermion ground state in Ce1−xLaxCoIn5 [21].
Here we report a specific-heat investigation of CeCoIn$_5$ as a function of Yb substitution to Ce. Yb acts as a non-magnetic divalent substituent for Ce throughout the entire doping range, equivalent to hole doping on the rare-earth site. The divergence of the specific heat in the normal state (at $H = 5$ T) is moderately suppressed with Yb doping, as a result of the Ce Kondo-lattice dilution. The upper critical field in (Ce,Yb)CoIn$_5$ appears to be Pauli limited, as in the pure compound, yet it exhibits a scaling expected in the purely orbital limit. To the best of our knowledge, this is the first report that the upper critical field is insensitive to the amount of doping as a function of Yb substitution to Ce. Yb acts as a scaling expected in the purely orbital limit. To the best of our knowledge, this is the first report that the upper critical field is insensitive to the amount of doping.

Crystal growth and characterization. – CeCoIn$_5$ crystallizes in the tetragonal HoCoGa$_5$ structure. Single crystals of Ce$_{1-x}$Ln$_x$CoIn$_5$ ($Ln =$ Yb, Lu) were grown from excess In flux [6]. The lattice parameters were determined from Rietveld refinement of powder X-ray diffraction patterns, using Si standard. The effective concentrations were determined with energy dispersive X-ray spectroscopy (EDS) on the measured single crystals, as well as proton-induced X-ray emission microscope (PIXE) on a mosaic of crystals from the same batches. The magnetic susceptibility was measured using a vibrating sample SQUID magnetometer in a field of 1T or higher applied perpendicular to [001]. The heat capacity was measured using the standard adiabatic heat pulse technique in a $^3$He-PPMS. The resistivity ($\rho$) was measured using the standard four wire technique with an AC resistance bridge. Low resistance contacts were obtained by spot-welding Au wires.

Figure 1 shows the doping evolution of characteristic parameters in Ce$_{1-x}$Ln$_x$CoIn$_5$ ($Ln =$ Yb, Lu). The effective Yb concentrations, as determined with either EDS or PIXE, are close to the nominal values for small $x_{nom}$ but show large distribution around $x_{nom} = 0.5$, as indicated by the error bars in fig. 1(a). Phase separation between pure YbCoIn$_5$ and Ce$_{1-x}$Yb$_x$CoIn$_5$ is likely the reason why we could not reach effectively $x_{Yb} \geq 0.3$. In fact, for $x_{nom} \geq 0.7$, the batches yield essentially pure YbCoIn$_5$, with very few Yb-substituted CeCoIn$_5$ crystals. The difference between EDS and PIXE values reflects this difference between a single crystal and the average concentration of the mosaic of crystals. For simplicity, nominal concentrations will be used in the rest of the paper. The lattice volume decreases systematically with Yb and Lu doping due to the lanthanide contraction (see fig. 1(c)). The Curie-Weiss moment $\mu_{eff}$ (per formula unit), obtained from linear fits to inverse magnetic susceptibility is suppressed below the Ce$^{3+}$ moment (2.54 $\mu_B$) with Yb as with Lu doping (see fig. 1(d)). This indicates that Yb substitutes as a non-magnetic Yb$^{2+}$ ion, resulting in a dilution of the Ce lattice. As such, the Yb doping is not an isoelectronic substitution, unlike La or Lu, but is equivalent to hole doping. The absence of Curie-Weiss behavior in pure YbCoIn$_5$ and its small Sommerfeld coefficient ($\simeq 11$ mJ/K$^2$ mol) shows that it is not a heavy fermion.

Results and discussion. – Figures 2(a) and (b) show the zero-field superconducting transition in $\rho$ and $C$ for various Yb (EDS) concentrations. The transitions in $\rho$ are sharp, except for $x = 0.6$ which shows a double jump, indicative of an inhomogeneous sample, consistent with the large error bars found in the EDS (see fig. 1(a)). Two different crystals have been measured in $\rho$ from most batches and they exhibit very similar $T_c$’s, determined...
from the onset of non-zero resistance, and shown in fig. 1(b). A fairly sharp, \(\lambda\)-like anomaly is observed in \(C\), measured on the same single crystals for \(x = 0.1, 0.2\) and 0.3, also shown in fig. 2(b). The SC anomaly is smaller and broader for \(x = 0.55\) and 0.8. The onset of the jump in \(\frac{C}{T}\) defines \(T_c\) for all samples. Two samples have been measured for \(x = 0.55\) and both exhibit a broad jump (but with similar \(T_c\)'s) possibly due to the doping inhomogeneity. Overall, the resistive \(T_c\) in good agreement with the thermodynamic \(T_c\) determined from \(\frac{C}{T}\) and \(\chi\), as shown in fig. 1(b), except for \(x = 0.8\) with \(T_c^p > T_c^C\). The ratio \(\frac{\Delta C}{\gamma_0 T_c}\) has been determined with \(\gamma_0\) taken as the \(\frac{C}{T}\) value linearly extrapolated to \(T = 0\) in the normal state at \(H = 5\) T. In the standard BCS theory, this ratio is expected to be 1.43 in the weak coupling regime. For Yb concentrations \(x = 0.1, 0.2, 0.3\) and 0.8, the SC appears to be bulk, in contrast to \(x = 0.55\) and 0.8 with significantly smaller \(\frac{\Delta C}{\gamma_0 T_c}\) values.

The temperature (and field) dependence of the electronic specific heat \(\frac{C}{T}\) in Yb-doped CeCoIn\(_5\) is shown in fig. 3, for \(x_{Yb} = 0.1, 0.3, 0.55\) and 0.8 (nominal). The electronic contribution is obtained by subtracting the phonon contribution, determined from \(C\) of YbCoIn\(_5\). \(\frac{C}{T}\) has a divergent \(T\)-dependence down to \(T_{c2}(H)\) for all Yb concentrations, with little change in slope with increasing magnetic field. Moreover, the divergence of \(\frac{C}{T}\) extends down to lowest \(T \approx 0.5\) K at \(H = 5\) T in these samples, a characteristic shared with the pure CeCoIn\(_5\). This divergence has been attributed to a field tuned QCP near \(H_{c2}^0\) in CeCoIn\(_5\) [7,8]. As seen in fig. 2(b) and fig. 3, the divergence of \(\frac{C}{T}\) becomes weaker with increasing Yb concentration and the corresponding \(\gamma_0\), obtained from linear extrapolation of \(\frac{C}{T}\) vs. \(T\) at \(H = 5\) T, decreases systematically with \(x_{Yb}\), consistent with a dilution of the Kondo lattice (see table 1).

Figure 3 also shows the magnetic field suppression of the superconducting transition, for magnetic field applied parallel to the [001] axis, with a broader and smaller jump as the field is increased, due to the presence of vortices. Unlike in the pure case, the SC transition in the Yb-doped compounds does not sharpen into a first-order anomaly in the \(T = 0\) limit, as seen in fig. 3, likely due to disorder introduced by doping [22]. The corresponding \(H-T\) phase diagrams (deduced from \(C\)) are shown in figs. 4(a) and (b). The upper critical field \(H_{c2}\) vs. \(T\) for various Yb concentrations (nominal). (b) Upper critical field \(H_{c2}\) vs. temperature.

### Table 1: Doping dependence of characteristic parameters in Ce\(_{1-x}\)Yb\(_x\)CoIn\(_5\). \(x_{Yb}\): nominal Yb concentration, \(T_c\): critical temperature at \(H = 0\) from heat capacity, \(\gamma_0\): the \(T = 0\) linear extrapolation of \(\frac{C}{T}\) at \(H = 5\) T in \(J/K^2\) mol, \(U_c\): the superconducting condensation energy in \(J/mol\), \(H_{c2}^0\) \((\gamma_0\) fits [24] give clear evidence for a Pauli-limited \(H_{c2}\). Despite the absence of a first-order transition in Yb-doped compounds, the

<table>
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<th>(x_{Yb})</th>
<th>(T_c) (K)</th>
<th>(\gamma_0)</th>
<th>(U_c) ((\gamma_0)</th>
<th>(H_{c2}^0) (T)</th>
<th>(H_P) (T)</th>
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<td>0.53</td>
<td>8.9</td>
<td>3.5</td>
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Pauli limit [25] still applies; the extrapolation based on the standard expression [26], \(H_{c2} \approx -0.7 \frac{\mu_B H}{\Delta_{c1}} T_c\), yields an orbital critical field far in excess of the observed transition field, see table 1.

Figure 4(a) shows that the \(H_{c2}\) data for all Yb concentrations collapse onto a single curve when scaled by the initial slope at \(T_c\). Such a scaling is expected in the purely orbital limit, as the reduced critical field \(\frac{H}{T_c}\) is only weakly dependent on the disorder level in this data [26]. In the Pauli limit there is no reason to expect a similar scaling, however the orbital mechanism is still predominant in the zero-field limit. The implication of this scaling is that the ratio of the orbital critical field to the Pauli-limiting field: \(\alpha = \frac{\Delta H_{c2}}{H_{c2}}\), is independent of \(x_{Yb}\). This is not a trivial result, knowing that \(\alpha\) decreases under pressure [27]. \(\alpha\) was estimated to be 3.6 for \(H||[001]\) in pure CeCoIn\(_5\) [9]. We have used this value to determine \(H_P\) in the Yb-doped samples from \(H_{c2}\), see table 1.

In a \(d\)-wave BCS superconductor, the superconducting condensation energy, \(U_c\), is related to the specific-heat jump \(\Delta C\) at the SC transition via the standard relation [28]: \(U_c = \frac{\Delta C}{\pi T_c}\). Since \(\frac{\Delta C}{\pi T_c}\) in the normal state is divergent in CeCoIn\(_5\) and since it is likely a strong coupling superconductor [6], the use of this formula is questionable. Alternatively, we have determined \(U_c\) directly from integration of \(\int_0^{T_c} (S_n - S_s) dT\) up to \(T_c\), following extrapolation of the \(\frac{\Delta C}{\pi T_c}\) data to \(T = 0\). We have excluded the \(x = 0.55\) and 0.8 samples from the analysis since the lowest temperature (0.4 K) in the data does not allow a proper extrapolation to \(T = 0\). The results are listed in table 1. The obtained value of \(U_c\) for pure CeCoIn\(_5\) (1.43 J mol\(^{-1}\)) compares favorably with the value (1.34 J mol\(^{-1}\)) determined from magnetization [29]. For the doped samples, we found that the condensation energy decreases with increasing Yb concentration, a trend similar to the one reported for La (not shown) or Sn doping [30].

The combination of \(U_c\) and \(H_P\) then allows the determination of the Pauli paramagnetic susceptibility \((\chi_0)\). In fact, \(H_P\) is related to \(U_c\) via [25]: \(U_c = \frac{1}{3} \chi_0 H_P^2\). This expression is originally derived for an \(s\)-wave superconductor [25] and overlooks the possibility of a finite Pauli susceptibility at \(T = 0\) in the superconducting state [31]. For a \(d\)-wave superconductor, it only remains valid in the clean limit. In the presence of nodal quasiparticles in a \(d\)-wave superconductor, there should be a contribution to the free energy in the superconducting state and thus the Pauli critical field should be derived from: \(\Delta F = F_n - \chi_n H_P^2 = F_s - \chi_s H_P^2\), where the subscripts “\(n\)” and “\(s\)” refer to the normal and the superconducting states. This is equivalent to \(\Delta F = F_n - F_s = (1 - \frac{\chi_n}{\chi_s}) \chi_s H_P^2\) and thus \(U_c = \frac{1}{3} \chi_0 (1 - \frac{\chi_n}{\chi_s}) \chi_s H_P^2\). It is straightforward to assume that the fraction of excited nodal quasiparticles, \(\frac{\chi_n}{\chi_s}\), should be proportional to the Yb concentration, but since we do not have an exact determination of this ratio, we will not pursue the analysis in the Yb doped compounds. Instead, we focus on pure CeCoIn\(_5\), which is in the clean limit, implying that \(\frac{\chi_n}{\chi_s} \ll 1\). For CeCoIn\(_5\), \(\chi_0 = 10^{-4}/4\pi\) determined from \(U_c\) via this formula is close to the value of the c-axis susceptibility [6], \(\chi = 1.54 \times 10^{-7}/4\pi\) at 1.8 K. The resulting Wilson ratio is \(R_W = \frac{\chi_0}{\gamma_0} = 0.76 R_{W0}\), where \(R_{W0}\) is the free-electron value. In this method, the error on \(R_W\) essentially comes from the uncertainty on \(U_c\) (via \(\chi_0\)).

The Wilson ratio of a free-electron gas is defined as the ratio of the Pauli paramagnetic susceptibility to the electronic specific-heat (Sommerfeld) coefficient and is a universal number: \(R_{W0} = \frac{\chi_0}{\gamma_0} = \frac{3\sqrt{\pi e\hbar}}{2k_B^2}\). Despite the large mass renormalization, heavy-fermion systems exhibit Wilson ratios very close to the free-electron gas value. This is due to the fact that the mass renormalization corresponds to an enhanced density of states at the Fermi level, and the latter determines both the paramagnetic susceptibility and the specific-heat coefficient [32]. The difficulty in estimating the Wilson ratio in heavy-fermion systems is associated with the experimental determination of the low-temperature Pauli susceptibility. In fact, the magnetic susceptibility is overwhelmingly dominated by the Curie-Weiss contribution of Ce moments. Here we show that this difficulty can be overcome in the case of Pauli-limited heavy-fermion superconductors, making use of the superconducting condensation energy. The \(R_W\) we obtained from this method in pure CeCoIn\(_5\) is close to but somewhat lower than the expected value of \(R_W = \frac{2J+1}{2J} R_{W0} = 1.2 R_{W0}\) for a system of \(J = 5/2\) local moments (corresponding to Ce), confirming the validity of the method.

Conclusion. — In conclusion, we have investigated the effect of Yb substitution on the superconducting and heavy-fermion properties of CeCoIn\(_5\). Our findings can be summarized as follows: i) the suppression of the condensation energy and Sommerfeld coefficient \(\gamma_0\) with Yb doping is due to the dilution of the dense Ce Kondo lattice, ii) the upper critical field exhibits a scaling that is unusual for Pauli-limited superconductors, implying a doping-independent Maki parameter. Moreover, we introduce a new method for the determination of the Wilson ratio from the superconducting condensation energy, which is valid for any clean superconductor in the Pauli limit. The value we estimate is consistent with the expected value for pure CeCoIn\(_5\).

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REFERENCES