Anisotropic Effect of Cd and Hg Doping on the Pauli Limited Superconductor CeCoIn$_5$

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We studied the effect of impurity on the first order superconducting (SC) transition and the high field-
low temperature (HFLT) SC state of CeCoIn$_5$ by measuring the specific heat of CeCo(In$_{1-x}$Cd$_x$)$_5$ with
$x = 0.0011$, 0.0022, and 0.0033 and CeCo(In$_{1-x}$Hg$_x$)$_5$ with $x = 0.00016$, 0.00032, and 0.00048 at
temperatures down to 0.1 K and fields up to 14 T. Cd substitution rapidly suppresses the crossover
temperature T_0, where the SC transition changes from second to first order, to $T = 0$ K with $x = 0.0022$
for $H \parallel [100]$, while it remains roughly constant up to $x = 0.0033$ for $H \parallel [001]$. The associated anomaly
of the proposed FFLO state in Hg-doped samples is washed out by $x = 0.00048$, while remaining at the
same temperature, indicating high sensitivity of that state to impurities. We interpret these results as
supporting the nonmagnetic, possibly FFLO, origin of the HFLT state in CeCoIn$_5$.

In most type-II superconductors (SC) the superconduct-
ing upper critical field H_{c2} is largely determined by the
orbital limiting field H_{c2}^0, when the opposite forces that the
magnetic field applies to the electrons with opposite mo-
menta break up the Cooper pair. The Zeeman energy of the
electron spin in a magnetic field also influences H_{c2}, and in
some cases, such as two-dimensional (2D) SC (e.g. organ-
ics) with the magnetic field applied within the 2D planes,
or heavy-fermion compounds, with large H_{c2}^0, can be the
dominant mechanism of suppression of SC. In the normal
state, electron spins align preferentially with the magnetic
field, lowering their total energy, and leading to the
temperature-independent Pauli susceptibility. In spin-
singlet superconductors, the superconducting pairs are
formed by electrons with opposite spins, which therefore
can not take advantage of the Zeeman energy. When
Zeeman energy in the normal state is greater than the
superconducting condensate energy, superconductivity is
destroyed. This effect leads to an upper bound on H_{c2},
called the Pauli limiting field H_P [1]. The relative strength
of the orbital and Pauli limiting is reflected by the Maki
parameter $\alpha = \sqrt{2}H_{c2}^0/H_P$. When orbital limiting is ne-
glected ($\alpha = \infty$), and Pauli limiting is the only effect
leading to suppression of superconductivity, the SC tran-
sition is expected to become first order below a cross over
temperature $T_0 = 0.56T_c$ [2,3]. A large Zeeman energy in
the normal state should also lead to a peculiar SC state.
Fulde and Ferrell [4] and Larkin and Ovchinnikov [5]
(FFLO) predicted that a spatially modulated SC state,
that takes advantage of the electron's Zeeman energy,
will be stabilized in high fields for Pauli limited super-
conductors. Gruenberg and Gunther [6] later put a lower
bound on the Maki parameter ($\alpha > 1.8$) for the existence
of the FFLO state.

The discovery of heavy-fermion unconventional super-
conductivity in CeCoIn$_5$ [7,8] has lead to numerous inves-
tigations of its unusual properties. CeCoIn$_5$ is in a strong
Pauli limiting regime, with a Maki parameter α anisotropic
with respect to the magnetic field, ranging between
3.5($H \parallel [001]$) and 4.5($H \perp [100]$). CeCoIn$_5$ provided
the first example of a first-order SC transition in a bulk
superconductor, in accord with the above mentioned theo-
retical expectations, revealed in the specific heat and mag-
netization anomalies at high fields [9,10]. The specific heat
anomaly, associated with the SC transition, sharpens and
becomes more symmetric as the field is increased, and
magnetization as a function of field shows a step at T_c
with hysteresis. In high magnetic fields within the basal
plane of the tetragonal crystal structure of CeCoIn$_5$, spe-
cific heat shows an anomaly inside the SC state, reflecting
the formation of an additional phase in the high-field, low-
temperature (HFLT) corner of the SC phase of the $H - T$
diagram [11,12]. In addition, CeCoIn$_5$ is in the clean limit,
with an electron mean free path on the order of a few
microns within the superconducting state at low tempera-
ture [8]. Because of these favorable conditions (FFLO was
traditionally expected to be readily destroyed by impuri-
ties), it was suggested that the additional HFLT SC phase
might indeed be a realization of a long sought after FFLO
state.

There have been a number of thermodynamic, transport,
and microscopic investigations of the HFLT phase in
CeCoIn$_5$ (for a recent review see Ref. [13]). Many studies
have been interpreted as supporting the FFLO nature of the
HFLT phase. A recent NMR investigation [14] concluded,
however, that there is a long-range antiferromagnetic order
within the HFLT phase, making it at least a more compli-
cated version of an FFLO state. Regardless of whether the

HFLT state is of purely magnetic origin or magnetism accompanies a fundamentally FFLO state, the magnetism is stabilized in the superconducting state only and does not extend into the normal state. This is a highly unique situation, exactly opposite to the canonical picture of the competition between superconductivity and magnetism, and is worthy of detailed experimental and theoretical studies. Additional investigations of the HFLT state in CeCoIn$_5$ are required before a firm case can be made for its nature.

Pressure has proven to be a very useful tuning parameter in the quest to elucidate the connection between magnetism and superconductivity in CeCoIn$_5$. It was shown [15] that pressure enhances both T_0 and the extent of the HFLT state, while it suppresses the QCP [16] suggested to arise from a nearby AFM ground state [17]. The opposite effect of pressure on the HFLT and AFM lead the authors to conclude that the HFLT state is of an FFLO origin [15]. Recently, it was shown that Cd doping in CeCoIn$_5$ suppresses superconductivity and stabilizes antiferromagnetism, finally exposing the AFM state [18] that might be responsible for the QCP at H_{c2} in CeCoIn$_5$. The authors also demonstrated that Cd doping effect can be reversed by pressure, which drives the system back from the AFM to the SC ground state. Since Cd doping stabilizes the AFM state, while pressure suppresses it and instead stabilizes the HFLT phase, investigation of the effect of Cd impurities on the HFLT can provide important clues about its nature.

In this Letter, we present the results of the specific heat measurements on CeCo(In$_{1-x}$Cd$_x$)$_5$ and CeCo(In$_{1-x}$Hg$_x$)$_5$ with low Cd ($x = 0.0011$, 0.0022 and 0.0033) and Hg (0.000 16, 0.000 32, and 0.000 48) concentrations, which directly address the stability of the first-order nature of the SC transition and the HFLT phase of CeCoIn$_5$ with respect to impurities. Single crystals of CeCo(In$_{1-x}$Cd$_x$)$_5$ and CeCo(In$_{1-x}$Hg$_x$)$_5$ were grown from In-flux. Single platelike samples with a typical weights of 1–3 mg were used for specific heat measurements. Initial sample characterization via microprobe analysis, using wavelength dispersive spectroscopy, showed uniform distribution of the dopants. The actual Cd concentration, shown in Fig. 1(a), is linear with respect to the nominal concentration, with zero offset. The actual to nominal concentration ratio of 0.11 is in good agreement with that of 0.1 reported by L. D. Pham *et al.* [18]. The actual concentrations, rather than the nominal ones, are referred to in the rest of this Letter. Specific heat at temperatures down to 100 mK and high fields up to 14 T was measured in a dilution refrigerator and a superconducting magnet, employing the quasiadiabatic method. The Physical Property Measurement System (PPMS) from Quantum Design was used to measure specific heat at low fields in the vicinity of the SC anomaly.

The main panel of Fig. 1 shows the zero field specific heat of CeCo(In$_{1-x}$Cd$_x$)$_5$, with $x = 0.0011$, 0.0022, and 0.0033, against the reduced temperature $T - T_c$ in the vicinity of the SC transition. With increasing x, the jump
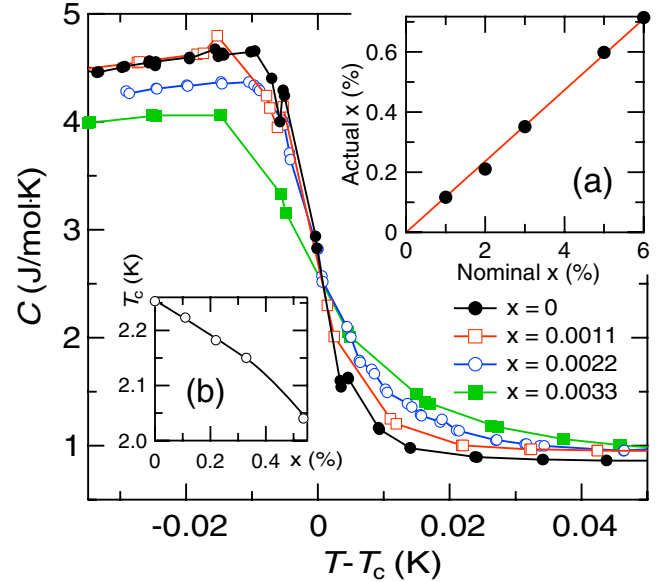

FIG. 1 (color online).   Specific heat of CeCo(In$_{1-x}$Cd$_x$)$_5$ ($x = 0.0011$, 0.0022, and 0.0033) around T_c, plotted against reduced temperature $T - T_c$. (a) Actual vs nominal Cd concentration. Red solid line is a fit to the data through the origin. (b) T_c as a function of actual Cd concentration x. The line is a guide to the eye.

decreases and the width of the specific heat anomaly at SC transition increases monotonically, while T_c decreases linearly [inset (b)]. These monotonic changes in SC properties indicate a gradual variation of the actual Cd concentration with x, consistent with the results of the microprobe analysis. These results show good control of the amount of the Cd dopants and their homogeneous distribution in our samples.

Figure 2 shows the effect of Cd doping on the SC anomaly in specific heat at high magnetic field. The specific heat of CeCo(In$_{0.9978}$Cd$_{0.0022}$)$_5$ at low temperatures and fields close to H_{c2} is shown in the main panels after subtraction of the low-temperature tail due to a nuclear Schottky anomaly. Figure 2(a) shows the specific heat for $H \parallel [001]$. The jump in the second-order-like SC anomaly initially decreases with increasing field, but above 4.8 T the height of the anomaly increases, its width narrows, and the shape becomes more symmetric, indicating the change in the order of the SC transition from second to first for $H > 4.8$ T. This is in contrast to the evolution of the SC anomaly for $x = 0.0022$ with $H \parallel [100]$, shown in the main panel of Fig. 2(b), where the size of the jump at T_c decreases monotonically with increasing field. These data indicate that the first-order character of the SC transition at low temperatures is suppressed already with 0.22% Cd doping for $H \parallel [100]$. Similar data for different levels of Cd doping are summarized in the insets of Fig. 2, where we plot the jump in specific heat at T_c, with magnetic field as an implicit variable via $H_{c2}(T_c)$. ΔC is monotonic for $x \geq 0.0022$ and $H \parallel [100]$ [inset of Fig. 2(b)] (no first-order
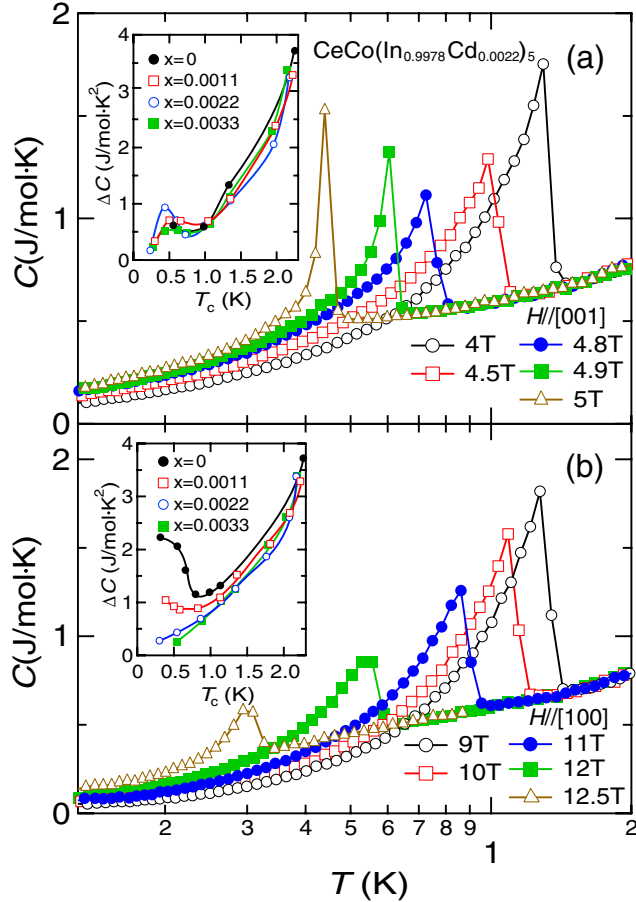
FIG. 2 (color online). Electronic specific heat of $CeCo(In_{0.9978}Cd_{0.0022})_5$ vs temperature for (a) $H \parallel [001]$ and (b) $H \parallel [100]$. Insets: Jump height at T_c vs $T_c(H_{c2})$. All solid lines are guide to the eye.

FIG. 3 (color online). Electronic specific heat divided by temperature C/T for $CeCo(In_{0.99968}Hg_{0.00032})_5$ as a function of temperature at magnetic field 11 T applied along [100]. Arrow indicates an anomaly within the SC state. Inset: Expanded plot of C/T around the transition temperature into the HFLT SC phase. Data are shifted vertically for clarity. Dotted line is a smooth background between the high and low-temperature data.

transition), while all other curves are nonmonotonic (signature of the first-order phase transition). Cd doping is therefore more effective in suppressing the first-order nature of the SC transition when the field is applied within the $a - b$ plane of $CeCo(In_{1-x}Cd_x)_5$, in spite of the fact that the height of the anomaly in pure $CeCoIn_5$ is greater for this field orientation.

There is no indication of an additional specific heat anomaly within the SC phase (as the one defining the HFLT phase in pure $CeCoIn_5$) for the Cd-doped samples studied. Given that the lowest Cd concentration studied is only $\approx 0.1\%$, the proposed FFLO state appears to be extremely susceptible to impurities, in agreement with the theoretical work by Adachi, *et. al.* [19].

To probe the effect of even lower impurity concentrations, we conducted specific heat investigation of Hg-doped samples $CeCo(In_{1-x}Hg_x)_5$, with Hg concentrations of $x = 0.00016$, 0.00032, and 0.00048. The specific heat data for a sample with $x = 0.00032$ at $H = 11$ T are displayed in Fig. 3 after subtraction of the nuclear contribution. In addition to the first-order SC anomaly, the anomaly associated with the lower temperature phase tran-
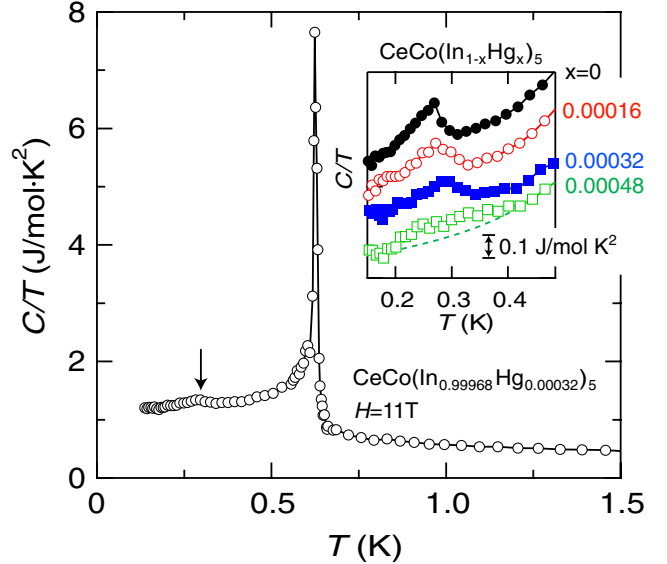
sition into the HFLT state is clearly resolved. Such anomalies at $H = 11$ T for all the Hg-doped samples are displayed in the inset of Fig. 3. The anomaly does not shift substantially in temperature with increase in Hg-doping level, but it is suppressed in an unusual way. The temperature of the anomaly is not driven to $T = 0$, but, instead, the anomaly gradually broadens and eventually washes out.

Figure 4 summarizes our results for both the first-order SC phase transition, the HFLT anomaly, and a zero field SC transition temperature T_c as a function of both Cd and Hg dopant concentration. The narrow region where T_c is independent of doping concentration ($x < 0.05\%$) is most likely due to the break down of the homogeneous Abrikosov-Gorkov (AG) model of the impurity suppression of T_c, which starts out with a linear slope of T_c vs x. When the interimpurities distance $d > 2\xi$, the AG model is expected to break down (inhomogeneous SC limit). Superconductivity will be suppressed only within the region on the order of the coherence length ξ and T_c should become independent of impurity concentration. We can estimate $d = (V/5 \times 5 \times 10^{-4})^{1/3} = 40$ Å, where $V = 161$ Å^3 is the unit cell volume of $CeCoIn_5$ [7] and 5×10^{-4} is the approximate upper limit of concentration for the constant T_c region. The estimated d compares well with $2\xi \approx 70$ Å obtained by previous thermodynamic measurements [20], and, most importantly, the HFLT phase exists only in the constant T_c region of impurity concentration, demonstrating that ξ is the relevant length scale for the HFLT state. Therefore, the HFLT state is likely to be of the superconducting, nonmagnetic origin.
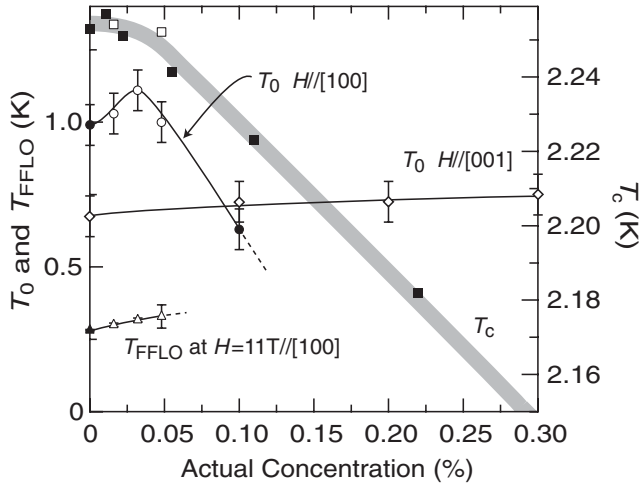
FIG. 4. Doping dependence of the onset of first-order phase transition T_0, T_{FFLO} at magnetic field $H = 11$ T applied along [100] and superconducting transition temperature T_c at zero field. Solid symbols: $CeCo(In_{1-x}Cd_x)_5$ ($x = 0$, 0.0011, 0.0022 and 0.0033). Open symbols: $CeCo(In_{1-x}Hg_x)_5$ ($x = 0.00016$, 0.00032 and 0.00048). ●, ○: T_0 for $H \parallel [100]$, ◇: T_0 for $H \parallel [001]$, ■, □: T_c, △, ▲: T_{FFLO}. All curves are guides to the eye.

Earlier theoretical studies of impurity effects on the first-order SC transition by Maki and Tsuneto [2] used microscopic theory to show that for an s-wave SC in a strong Pauli limit, the SC transition remains first-order below $T_0 = 0.56T_c$ for nonmagnetic impurities. Conversely, it was widely accepted that an FFLO state is easily suppressed by small amount of impurities, perhaps based on the results of the early theoretical investigations of FFLO in s-wave superconductors [21]. Recent theoretical studies of impurity effects on FFLO states in d-wave superconductors came down on both sides of the issue, some suggesting a moderately sensitive nature of FFLO state [19], and some concluding that an FFLO state is robust against impurites [22,23]. If the HFLT state is indeed of an FFLO origin, as suggested by this work, our results support a very fragile nature of the FFLO state with respect to impurities.

If the HFLT state was of magnetic origin, we would expect the enhancement of such a state with Cd and Hg impurities, since higher concentrations of $\approx 0.5\%$ stabilize an AFM ground state. Instead, the HFLT is suppressed at very low concentrations, suggesting competition of the AFM and the HFLT state. This competition may provide an avenue for suppression of the FFLO state in addition to a simple impurity scattering effect, and may be responsible for the high sensitivity of the HFLT state to Cd impurities. This effect was not taken into account by recent theoretical investigations [22,23], which may reconcile them with our experimental results.

In conclusion, we have measured the specific heat of $CeCo(In_{1-x}Cd_x)_5$ with $x = 0.0011$, 0.0022 and 0.0033 and $CeCo(In_{1-x}Hg_x)_5$ with $x = 0.00016$, 0.00032, and

0.00048 to study the doping effect on high-field low-temperature SC state of $CeCoIn_5$. We found that roughly 0.05% of Hg-doping is sufficient to suppress the HFLT state. Thus, the HFLT state is extremely sensitive to impurities, suggesting a nonmagnetic, FFLO origin of this state. The first-order character of the SC transition is less susceptible to impurities, with an anisotropic response to Cd doping. The crossover temperature T_0, where SC transition changes its character from first to second order, decreases rapidly with increasing Cd doping for $H \parallel [100]$, while it remains roughly the same up to $x = 0.003$ for $H \parallel [001]$. The relative robustness to impurities of the first-order transition compared to the HFLT state is in agreement with the theoretical calculations of Ref. [19] for the FFLO state.

[1] A. M. Clogston, Phys. Rev. Lett. **9**, 266 (1962).
[2] K. Maki and T. Tsuneto, Prog. Theor. Phys. **31**, 945 (1964).
[3] G. Sarma, J. Phys. Chem. Solids **24**, 1029 (1963).
[4] P. Fulde and R. A. Ferrell, Phys. Rev. **135**, A550 (1964).
[5] A. I. Larkin and Y. N. Ovchinnikov, Zh. Eksp. Teor. Fiz. **47**, 1136 (1964); Sov. Phys. JETP **20**, 762 (1965).
[6] L. W. Gruenberg and L. Gunther, Phys. Rev. Lett. **16**, 996 (1966).
[7] C. Petrovic *et al.*, J. Phys. Condens. Matter **13**, L337 (2001).
[8] R. Movshovich *et al.*, Phys. Rev. Lett. **86**, 5152 (2001).
[9] A. Bianchi *et al.*, Phys. Rev. Lett. **89**, 137002 (2002).
[10] T. Tayama *et al.*, Phys. Rev. B **65**, 180504 (2002).
[11] A. Bianchi *et al.*, Phys. Rev. Lett. **91**, 187004 (2003).
[12] H. A. Radovan *et al.*, Nature (London) **425**, 51 (2003).
[13] Y. Matsuda and H. Shimahara, J. Phys. Soc. Jpn. **76**, 051005 (2007).
[14] B. L. Young *et al.*, Phys. Rev. Lett. **98**, 036402 (2007).
[15] C. F. Miclea *et al.*, Phys. Rev. Lett. **96**, 117001 (2006).
[16] F. Ronning *et al.*, Phys. Rev. B **73**, 064519 (2006).
[17] A. Bianchi *et al.*, Phys. Rev. Lett. **91**, 257001 (2003).
[18] L. D. Pham *et al.*, Phys. Rev. Lett. **97**, 056404 (2006).
[19] H. Adachi and R. Ikeda, Phys. Rev. B **68**, 184510 (2003).
[20] S. Ikeda *et al.*, J. Phys. Soc. Jpn. **70**, 2248 (2001).
[21] L. G. Aslamazov, Zh. Eksp. Teor. Fiz. **55**, 1477 (1968).
[22] D. F. Agterberg and K. Yang, J. Phys. Condens. Matter **13**, 9259 (2001).
[23] A. Vorontsov, I. Vekhter, and M. Graff (private communication).