Electronic Tuning and Uniform Superconductivity in $CeCoIn_5$

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We report a globally reversible effect of electronic tuning on the magnetic phase diagram in $CeCoIn_5$ driven by electron (Pt and Sn) and hole (Cd, Hg) doping. Consequently, we are able to extract the superconducting pair breaking component for hole and electron dopants with pressure and codoping studies, respectively. We find that these nominally nonmagnetic dopants have a remarkably weak pair breaking effect for a *d*-wave superconductor. The pair breaking is weaker for hole dopants, which induce magnetic moments, than for electron dopants. Furthermore, both Pt and Sn doping have a similar effect on superconductivity despite being on different dopant sites, arguing against the notion that superconductivity lives predominantly in the $CeIn_3$ planes of these materials. In addition, we shed qualitative understanding on the doping dependence with density functional theory calculations.

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In a superconductor whose order parameter changes sign, nonmagnetic impurities are expected to be strongly pair breaking and will suppress T_c rapidly, similar to the effect of magnetic impurities in conventional superconductors [1]. Indeed, a few percent of Zn impurities in YBCO causes a dramatic suppression of T_c [2]. However, the lack of T_c suppression by various dopants in Fe-based superconductors has been argued as evidence that the order parameter does not change sign [3]. The heavy fermion superconductors $CeTIn_5$ (T = Co, Rh, Ir) are prototypical of a general class of strongly correlated systems in which unconventional superconductivity (SC) emerges in close proximity to an antiferromagnetic quantum critical point (QCP) as in the cuprates and pnictides. The pure compound $CeCoIn_5$ is a high temperature (relative to E_F) *d*-wave superconductor [4], and consequently provides a great opportunity to study the effects of impurities on an unconventional superconductor.

Due to the small energy scales, however, heavy fermions are also easily tuned electronically. Indeed, hole doping with only 1% of Cd or Hg induces an antiferromagnetic ground state in $CeCoIn_5$ [5,6], while electron doping with Sn has the opposite effect to hole doping, suppressing T_c, and eventually recovering a Fermi liquid ground state [7–11]. It has been argued that the reason for the strong doping dependence is due to the fact that the dopant atoms Sn, Cd, and Hg preferentially substitute on the In(1) site in the "active" $CeIn_3$ planes [8] [see structure in Fig. 1(a)]. Indeed, in $CeCo_{1-x}Rh_xIn_5$, superconductivity persists up to 75% Rh [12]. However, the only substitutions that have been made in the TIn_2 "buffer"layers have been isoelectronic.

In this Letter, we show that Pt doping on the transition metal site is similar to Sn doping, both of which nominally contribute 1 electron per dopant atom. Thus, the strength of pair breaking created by electron doping is roughly independent of the dopant location within the unit cell. By pressure [5] and by codoping with Hg [this work] we find that the magnetic phase diagram and the coherence temperature T^* are reversible via local electronic tuning, enabling a determination of the pair breaking scattering rates. While the pair breaking for electron dopants is stronger than for hole dopants, both are strikingly much weaker than expected for nominally nonmagnetic impurities in a *d*-wave superconductor [13]. In addition, we show that density functional theory calculations qualitatively describe the observed doping dependence in this Ce-based heavy fermion system.

All single crystals were synthesized using an indium self-flux method [4,9,14]. The doping levels were determined by single crystal x-ray diffraction and by microprobe analysis. For the physical properties measurements of $CeCoIn_{5-x}Sn_x$, crystals from the same batch as in Ref. [9] have been used. For Pt and Hg doping the actual concentrations have been established to be 85% and 16% of the nominal concentrations, respectively. The actual concentrations are used in this Letter. The electrical resistivity were measured using a four wire (AC) method, implemented in a Quantum Design PPMS-9 device.

The main panels in Figs. 1(a) and 1(b) show the temperature dependencies of the electrical resistivity of selected samples of $CeCo_{1-x}Pt_xIn_5$, $CeCo_{0.91}Pt_{0.09}In_{5-y}Hg_y$, $CeCoIn_{5-x}Sn_x$, and $CeCo(In_{4.91}Sn_{0.09})_{1-(y/5)}Hg_y$. All the curves show behavior typical of heavy-fermion materials

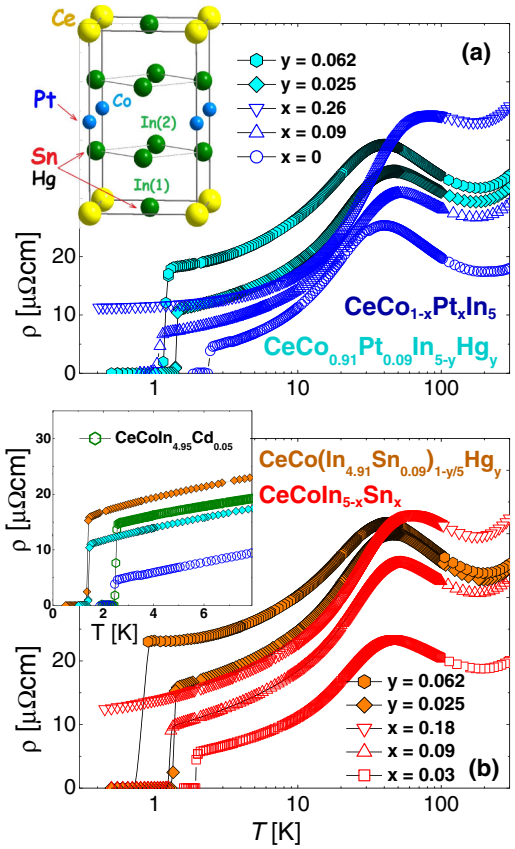

FIG. 1 (color online). (a),(b): The temperature dependence of the electrical resistivity of $CeCoIn_{5-x}Sn_x$, $CeCo_{1-x}Pt_xIn_5$, $CeCo_{0.91}Pt_{0.09}In_{5-y}Hg_y$ and $CeCo(In_{4.91}Sn_{0.09})_{1-(y/5)}Hg_y$. Inset to (a) crystal structure of $CeCoIn_5$ which can be viewed as an alternating series of active $CeIn_3$ and buffer TIn_2 layers; and (b) low temperature resistivity of $CeCoIn_5$ and the optimally tuned codoped samples. Also shown is $CeCoIn_{4.95}Cd_{0.05}$ at $P = 1.6$ GPa.

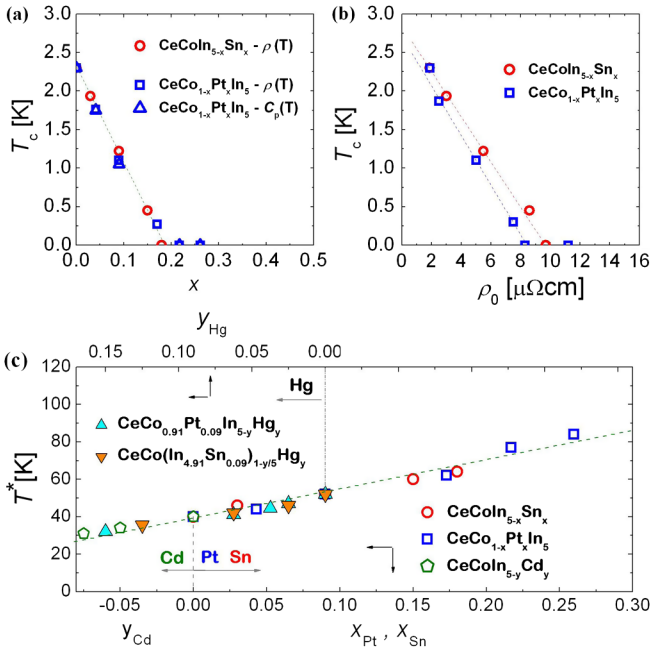

FIG. 2 (color online). (a) Temperature-composition phase diagram and (b) T_c vs ρ_0 for $CeCoIn_{5-x}Sn_x$ and $CeCo_{1-x}Pt_xIn_5$. (c) T^* vs x and y for $CeCoIn_{5-x}Sn_x$, $CeCoIn_{5-y}Cd_y$ $CeCo_{1-x}Pt_xIn_5$, $CeCo_{0.91}Pt_{0.09}In_{5-y}Hg_y$, and $CeCo(In_{4.91}Sn_{0.09})_{1-(y/5)}Hg_y$.

as characterized by a pronounced maximum at the coherence temperature T^*. Such behavior is related to the onset of coherent Kondo screening of the magnetic moments by the conduction electrons at T^*. For superconducting samples the superconductivity is clearly visible as marked by a sharp drop of ρ to zero at T_c which agree with the bulk transitions measured by specific heat (not shown). As can be seen from Figs. 1 and 2(a), the substitution with Pt leads to a T_c suppression similar to the one observed in Sn doping [7–11]. As seen from Fig. 2(b), superconductivity is completely suppressed at about 10 $\mu\Omega$ cm which is about half that observed for rare-earth doped $CeCoIn_5$ [15].

All dopants of $CeCoIn_5$ have a pair breaking and an electronic tuning component. The electronic tuning is evident in Fig. 2(c) where electron doping (both Pt and Sn) increases the coherence temperature T^* while hole doping (Cd and Hg) has the reverse effect. The electronic tuning is also reflected in the low temperature magnetic phase diagram where electron doping drives the system away from quantum criticality towards a paramagnetic state while hole doping pushes the system into a long range antiferromagnetically ordered state [5,6].

Our density functional theory (DFT) calculations reveal that this electronic tuning effect arises from a local change in the hybridization strength of the Ce f electrons to the conduction electrons caused by the dopant atoms. We use a supercell which is eight times the size of the conventional unit cell (see the Supplemental Material [16] for details). Figure 3 shows the resulting partial density of states (PDOS) for $CeCoIn_5$ doped with 2.5% of Cd, Hg, and Sn. The PDOS of In and Ce sites which lie far from the impurity atom are virtually identical to that of pure $CeCoIn_5$. Meanwhile, the Sn (Cd,Hg) p states possess a larger (smaller) bandwidth and are shifted down (up) in energy relative to the In states they replaced. A larger bandwidth reflects a larger hybridization. When one compares the Ce f-orbital PDOS for undoped and doped cases, it can be seen that the PDOS for Ce close to the impurity (labeled Ce1) is slightly broader (narrower) with Sn (Cd) doping relative to the Ce sites further away from the dopant atom (labeled Ce2), suggestive of an enhanced hybridization in the Sn doped case. While these calculations do not capture the many-body physics necessary to describe the low energy properties of Ce-based heavy fermions, they provide a qualitative understanding of the doping trends. In the Doniach picture as the Kondo coupling grows the coherence temperature is expected to rise and simultaneously magnetic order becomes suppressed [17]. The expression for the Kondo coupling is $J_K = V^2/(\epsilon_f - E_F)$

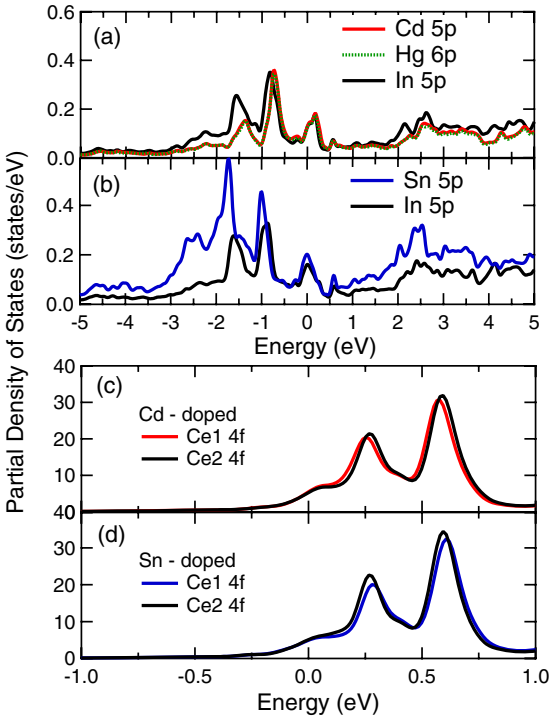

FIG. 3 (color online). DFT results from three supercell calculations of Cd, Sn, and Hg doping in $CeCoIn_5$. (a) Comparison of the PDOS of the Cd impurity to a well removed In(1) site. Also shown is the PDOS from an identical calculation with Hg (dotted line) overlapping with the Cd curve. (b) Same as (a) but for the calculation done with Sn doping. (c) and (d) PDOS of Ce1 atoms which neighbor the dopant atom, and Ce2 which are furthest from the Cd and Sn dopant atom, respectively.

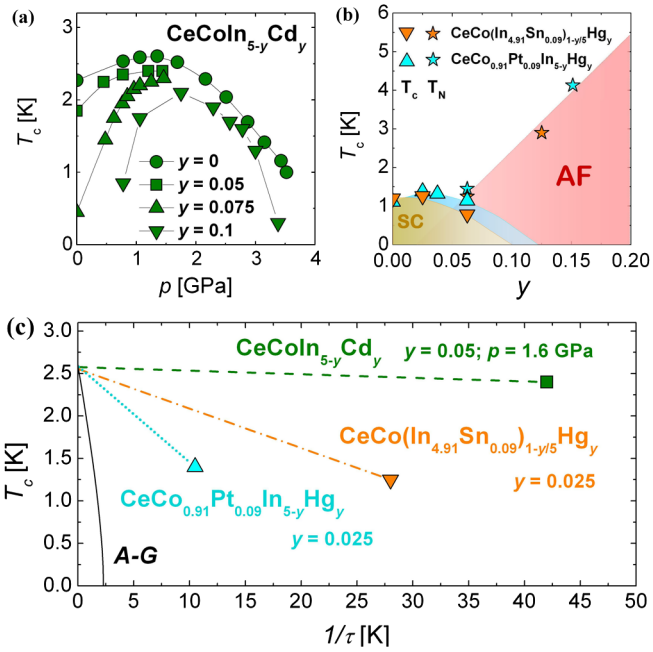

FIG. 4 (color online). (a) Pressure dependence of T_c of $CeCoIn_{5-y}Cd_y$ samples. (b) Temperature-composition phase diagram of $CeCo_{0.91}Pt_{0.09}In_{5-y}Hg_y$ and $CeCo(In_{4.91}Sn_{0.09})_{1-(y/5)}Hg_y$. (c) T_c suppression vs conservative estimates of the scattering rate for $CeCoIn_{4.95}Cd_{0.05}$, $CeCoIn_{4.88}Sn_{0.09}Hg_{0.026}$ and $CeCo_{0.91}Pt_{0.09}In_{4.97}Hg_{0.026}$ (see text). The latter two have had the contribution to the scattering rate and T_c suppression from Hg subtracted to isolate the effects due to the electron dopants (Sn and Pt). The solid black line is the expectation for a d-wave SC based on AG theory.

where V is the hybridization to the bare f level with energy ϵ_f and E_F is the Fermi energy [18]. The increased (decreased) hybridization seen for Sn (Cd, Hg) doping is consistent with the increased (decreased) coherence temperature and suppression (onset) of magnetism observed experimentally. It is also interesting to note that the calculations report a near identical bare electronic structure for Cd and Hg doped $CeCoIn_5$, consistent with the experimentally identical phase diagrams [5,6]. To uncover the full microscopic physics underlying the electronic tuning effects, a more quantitative theoretical analysis of hybridization between Ce and ligand atoms is required, and left for future work.

T_c is affected simultaneously by pair breaking and electronic tuning. To isolate the pair breaking component, we utilize pressure and codoping to eliminate the electronic tuning contribution. For hole doped samples with Cd it has been shown that pressure reversibly tunes the global magnetic phase diagram [5]. Consequently, for any $CeCoIn_{5-y}Cd_y$ sample pressure can be used to tune to its optimal T_c [see Fig. 4(a)]. From this maximal T_c with pressure the pair breaking component $\frac{dT_c}{dCd} = -5$ K/Cd can be extracted [16]. We assume that the effect of Hg and Cd doping is the same. This is supported by almost identical phase diagrams and our DFT calculations in Fig. 3(a).

To isolate the pair breaking component for the electron doped samples with Sn and Pt we utilize codoped samples with Hg for which we now know the pair breaking component. We have chosen Pt and Sn doped $CeCoIn_5$ samples at concentrations such that $T_c \sim 1.2$ K ($x = 0.09$). Then we have doped these two systems with Hg (substitution on the In site) which is a hole dopant. Figure 2(c) demonstrates that the coherence temperature is reversibly tuned by this procedure. Moreover, for both systems upon Hg doping, superconductivity initially increases (see Fig. 1)—clear evidence of the reversible electronic tuning—and forms a superconducting dome seen in Fig. 4(b). For higher Hg concentrations long-range antiferromagnetic ordering occurs as observed previously in $CeCoIn_{5-x}M_x$ studies where $M =$ Hg or Cd [5,6,19,20]. Note that the extra electrons from doping with Pt or Sn is nearly perfectly compensated by the holes from the Hg dopants with respect to the global phase diagram and T^*. The maximal T_c in the codoped samples with $x = 0.09$ occurs at $y = 0.025$. At this point electronic tuning is again optimized. The expected decrease in T_c due to Hg doping is only 0.125 K. The remaining T_c suppression relative to the maximal T_c

of $CeCoIn_5$ under pressure ($T_c \approx 2.6$ K [21]) can then be attributed to pair breaking by Pt and Sn. We find $\frac{dTc}{dPt} = -11.2$ K/Pt and $\frac{dTc}{dSn} = -13.3$ K/Sn. The fact that the pair breaking strength of Pt substituted on the Co site is comparable to Sn substituted primarily on the in-plane In site indicates a similar impurity potential effect independent of the dopant location. This demonstrates that the 115 structure *cannot* be thought of as active $CeIn_3$ layers separated by TIn_2 buffer layers. Interestingly, the pair breaking strength of electron doping matches that of rare-earth substitution $\frac{dTc}{dR} \approx -10$ K/R [22], possibly reflecting an equivalence between physically removing Ce moments and quenching the Ce moments through increased local hybridization, although we note that the normal state scattering rates are different.

These pair breaking rates reflect the remarkable robustness of superconductivity to non-magnetic impurities in $CeTIn_5$. To quantify this we estimate the scattering rate caused by our various dopants. $1/\tau = ne^2\Delta\rho/m^* = \Delta\rho/\mu_0\lambda^2$. From the inset of Fig. 1 we can see that $\Delta\rho =$ 12, 14 and 9 $\mu\Omega$ cm for optimally tuned Cd = 0.05, (Sn = 0.09, Hg = 0.025), and (Pt = 0.09, Hg = 0.025) samples, respectively. Values of the penetration depth λ range from 190 to 550 nm [23–25]. Thus, the largest reported penetration depth gives conservative estimates for the minimum scattering rate. According to Abrikosov-Gorkov (AG) theory for a d-wave superconductor with unitary scattering of non-magnetic impurities the initial rate of T_c suppression should be $dT_c/d(1/\tau) = -\pi/4 \approx -1$ [13]. Our conservative estimates for the maximal $dT_c/d(1/\tau)$ are -0.006, -0.04, and -0.09 for Cd, Sn, and Pt doping, respectively. To obtain the values for Sn and Pt doping we have subtracted Hg's contribution to the scattering rate in the codoped samples in the same way as the T_c suppression was determined above. As shown in Fig. 4(c) this demonstrates that the pair breaking by nominally nonmagnetic dopants in $CeCoIn_5$ is more than one order of magnitude weaker than expected on the basis of AG theory for d-wave superconductors.

Anomalously small T_c suppression from nominally non-magnetic impurities in pnictides has controversially been argued to imply a conventional order parameter which does not change sign [3,26]. Meanwhile, weak T_c suppression by non-magnetic impurities in cuprates has led to the realization that this can arise from small coherence lengths leading to spatial inhomogeneity, anisotropic scattering, strong coupling superconductivity, and induced magnetic moments [27–30]. Many of the explanations for cuprates are likely applicable here as well. $CeCoIn_5$ is a well established strong-coupling d-wave superconductor with a short coherence length [4]. Spatial inhomogeneity by dopant atoms in $CeCoIn_5$ reveals the extended nature of the impurities [19,31]. For instance, Cd dopants are known to create antiferromagnetic droplets [19] similar to the case of Zn doping in cuprates [2,32].

In summary, we have observed the effects of both reversible electronic tuning and superconducting pair breaking in the unconventional superconductor $CeCoIn_5$ driven by electron (Pt and Sn) and hole (Hg, Cd) doping. DFT calculations reveal the doping dependence is qualitatively understood from the local increase (decrease) in hybridization caused by Sn (Cd) dopants. In addition, the equivalence of doping with Cd and Hg is demonstrated, thereby illustrating the utility of DFT calculations for understanding doping trends in heavy fermions. We have further shown that pair breaking by electron dopants is roughly independent of their location within the unit cell and is stronger than with hole dopants which induce antiferromagnetic droplets. Conservative estimates for the minimal scattering rate reveal that we can add $CeCoIn_5$ to the list of unconventional superconductors for which T_c suppression by nonmagnetic impurities is significantly weaker than expected by Abrikosov-Gorkov theory.

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