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Inhomogeneous electronic states resulting from entangled spin, charge, and lattice degrees of freedom are hallmarks of strongly correlated electron materials; such behavior has been observed in many classes of d-electron materials, including the high-Tc copper-oxide superconductors, manganites, and most recently the iron-pnictide superconductors. The complexity generated by competing phases in these materials constitutes a considerable theoretical challenge—one that still defies a complete description. Here, we report a manifestation of electronic inhomogeneity in a strongly correlated f-electron system, using CeCoIn5 as an example. A thermodynamic analysis of its superconductivity, combined with nuclear quadrupole resonance measurements, shows that nonmagnetic impurities (Y, La, Yb, Th, Hg, and Sn) locally suppress unconventional superconductivity, generating an inhomogeneous electronic “Swiss cheese” due to disrupted periodicity of the Kondo lattice. Our analysis may be generalized to include related systems, suggesting that electronic inhomogeneity should be considered broadly in Kondo lattice materials.

Kondo effect | heavy fermion

Electronic inhomogeneity is commonplace in materials in which strong correlations among electrons produce electronic states that compete with one another on multiple length scales (1). One early indication of such heterogeneity came from studies of the high-Tc cuprate superconductors in which nonmagnetic Zn impurities were introduced into the CuO2 planes of YBa2Cu3O7 (YBCO) and La2−xSrxCuO4 (LSCO); the anomalous suppression of the superfluid density of the superconducting condensate was explained within a Swiss cheese model comprised of normal regions around the impurity that healed over a (short) coherence length of order 20 Å within a superconducting matrix (2), later verified by scanning tunneling spectroscopy (3). Not only is superconductivity locally suppressed in the normal state Sommerfeld coefficient γN follows a logarithmic temperature dependence, indicating proximity to a quantum critical point (9) for all dopants. An extrapolation of the infeld C/T data to T = 0 K, such that the extrapolation conserves entropy between the normal and superconducting states at Tc, yields γÑ > 1.2 μJ mol−1 K−2 for all concentrations. We make the ansatz that there is an additional normal component to C/T below Tc given by γÑ/γN and compare this normal component to the reduction of the superconducting condensation energy RU = [UC/γN(Tc)2]/[UC(0)/Tc(0)2] (properly normalized relative to the condensation energy of pure CeCoIn5), where UC = 1/2∫γdTγN(γN−SC)/dT. As shown in Fig. 24, the doping-induced normal state fraction comes precisely at the expense of the superconducting state fraction as evidenced by a common linear variation of RU = γÑ/γN vs. 1 − Rρ, for all substituents (Y3+, La3+, Th4+, Yb2+, Hg, and Sn—see Fig. 2B and S1), regardless of valence or size of the impurity atom. This unexpected result provides compelling evidence for electronic inhomogeneity in an f-electron Kondo lattice. Furthermore, the linear dependence of γÑ/γN on impurity concentration (Fig. 24, Inset) does not follow the expectation for creating electronic states in superconducting nodes through disorder in a “dirty” d-wave scenario in the strong scattering (unitary) limit (for which γÑ/γN ∼ 1/2) or in the weak scattering (Born) limit (Fig. 34), implying that the impurities suppress the superconducting energy gap through the creation of intragap states, much like Zn impurities in YBCO and Bi2Sr2CaCu2O8+δ (Fig. 3B) (4, 10). In this analysis, we have used the simple Bardeeen–Cooper–Schrieffer expression for the condensation energy USC = N(0)Δ2/(2Tc2), where N(0) is the density of states at the Fermi level, to allow a comparison of the different dopants substituted into the heavy fermion superconductors. More complete calculations of USC for unitary scatterers is plotted as γÑ/γN vs. 1 − U(SC)/USC(0) in Fig. 82, where U is the impurity scattering rate. These calculations do not reproduce the universal linear relation of RU vs. 1 − RU (Fig. 2B), furthering a scenario of electronic inhomogeneity in which the dopants locally suppress superconductivity.

Results and Discussion

Substitutions for Ce (or In) in CeCoIn5 by nonmagnetic elements R(or Hg, Sn) rapidly suppress Tc, with Tc → 0 K typically in the range of 10–15% substitution for Ce (In). Fig. 1 shows that, concomitant with the depression of Tc, there is a systematic increase in the value of C/T (T → 0 K) ≈ γÑ that is a measure of a non-superconducting electronic contribution to specific heat in the superconducting state. In a magnetic field of H = 5 T (H||c axis), the normal state Sommerfeld coefficient γN follows a logarithmic temperature dependence, indicating proximity to a quantum critical point (9) for all dopants. An extrapolation of the infeld C/T data to T = 0 K, such that the extrapolation conserves entropy between the normal and superconducting states at Tc, yields γÑ > 1.2 μJ mol−1 K−2 for all concentrations. We make the ansatz that there is an additional normal component to C/T below Tc given by γÑ/γN and compare this normal component to the reduction of the superconducting condensation energy RU = [UC/γN(Tc)2]/[UC(0)/Tc(0)2] (properly normalized relative to the condensation energy of pure CeCoIn5), where UC = 1/2∫γdTγN(γN−SC)/dT. As shown in Fig. 24, the doping-induced normal state fraction comes precisely at the expense of the superconducting state fraction as evidenced by a common linear variation of RU = γÑ/γN vs. 1 − Rρ, for all substituents (Y3+, La3+, Th4+, Yb2+, Hg, and Sn—see Fig. 2B and S1), regardless of valence or size of the impurity atom. This unexpected result provides compelling evidence for electronic inhomogeneity in an f-electron Kondo lattice. Furthermore, the linear dependence of γÑ/γN on impurity concentration (Fig. 24, Inset) does not follow the expectation for creating electronic states in superconducting nodes through disorder in a “dirty” d-wave scenario in the strong scattering (unitary) limit (for which γÑ/γN ∼ 1/2) or in the weak scattering (Born) limit (Fig. 34), implying that the impurities suppress the superconducting energy gap through the creation of intragap states, much like Zn impurities in YBCO and Bi2Sr2CaCu2O8+δ (Fig. 3B) (4, 10). In this analysis, we have used the simple Bardeeen–Cooper–Schrieffer expression for the condensation energy USC = N(0)Δ2/(2Tc2), where N(0) is the density of states at the Fermi level, to allow a comparison of the different dopants substituted into the heavy fermion superconductors. More complete calculations of USC for unitary scatterers is plotted as γÑ/γN vs. 1 − U(SC)/USC(0) in Fig. 82, where U is the impurity scattering rate. These calculations do not reproduce the universal linear relation of RU vs. 1 − RU (Fig. 2B), furthering a scenario of electronic inhomogeneity in which the dopants locally suppress superconductivity.


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Our thermodynamic analysis of impurities introduced into CeCoIn₅ further implies that the electronic inhomogeneity arises from disruption of the coherent Kondo lattice by Kondo holes. We estimate the characteristic energy scale of these Kondo holes through a simple binary alloy model, consistent with the creation of Swiss cheese holes, in which the specific heat is composed of a superconducting and normal component:

\[ C_{\text{tot}} = xC_N + (1-x)C_{\text{SC}}. \]  

Because \( C_{\text{tot}} \sim \ln(T/T') \) remains virtually unchanged with a Kondo lattice coherence temperature \( T' \sim 40 \text{ K} \) up to approximately 40% La in CeCoIn₅, the large contribution to electronic specific heat from these Kondo holes \( (\gamma_0 - 9.5) \text{ J/mol La K}^2 \) for \( x = 0.1 \); see Fig. 1) indicates that their effective mass is huge or, equivalently, that their characteristic energy scale is small, \( T_{\text{KHI}} = \pi R T' / 6 \gamma_0 \sim 0.3 \text{ K} \) for an effective “spin-1/2” La impurity, where \( R \) is the gas constant (12); strong scattering from these massive Kondo holes leads to the loss of quantum oscillations (13), even for <1% La impurities in CeCoIn₅. Breaking the translational invariance of the Kondo lattice locally suppresses the superconducting gap significantly as seen in the strong reduction of the specific heat jump \( \Delta C \) at \( T_c \) (Fig. 3A) of doped CeCoIn₅, analogous to the strong temperature-dependent pair-breaking effects when Ce Kondo impurities, characterized by \( T_K \sim 0.1 \text{ K} \) are introduced into the 3.3 K \( s^\pm \)-wave superconductor LaAl₄ (14); indeed, the suppression of \( \Delta C \) in these two systems is very similar (Fig. 3A). Substitutions on the In site lead to either weaker suppression (Sn) of the gap, or stronger suppression (Cd, Hg) possibly due to additional spin-flip pair-breaking effects caused by the local nucleation of magnetism near the Cd or Hg sites (15). Further support for the local suppression of superconductivity around the Kondo holes is provided by analysis of the effective size of an impurity bound state in a \( d^\pm \)-wave superconductor (4), given by \( R_{\text{imp}} = \xi_0 / (1 - e^{-\Delta_0})^{1/2} \), where \( \xi_0 = 4.9 \text{ nm} \) is the superconducting coherence length for the Ce₀.₉₅La₀.₀₅CoIn₅ sample, determined from the initial slope of the upper critical field \( dH_{c2}/dT \) (16). The ratio of the energy of the impurity state (or resonance) to the superconducting gap \( \Delta_0 = \psi_0 = [(1 - (T_{\text{KHI}}/0.3\Delta_0)^2)]/[1 + (T_{\text{KHI}}/0.3\Delta_0)^2] \) following ref. 17, where the strong-coupling value \( \Delta_0 = 2.25T_c \) was used (6). From this formula, we find that \( R_{\text{imp}} = 5.8 \text{ nm} \) is comparable to \( \xi_0 \), using \( T_{\text{KHI}} = 0.3 \text{ K} \) for Ce₀.₉₅La₀.₀₅CoIn₅, consistent with local suppression of superconductivity near the La impurities. [Similar impurity length scales \( R_{\text{imp}} \sim \xi_0 \) are obtained for other La concentrations \( x = 0.02 \) and 0.15, which have nearly identical Kondo hole energy scales \( T_{\text{KHI}} \sim 2-0.3 \text{ K} \) (12) and values of \( dH_{c2}/dT \) (16).] Recent scanning-tunneling spectroscopy on Th impurities in UR₈S₈ (18) reveals a strong local change of the density of states in this Kondo lattice, demonstrating that Kondo holes significantly affect the normal state as well (19). Our results further strengthen the connection between the heavy fermion superconductors and the cuprates, as the suppression of \( \Delta C \) of Zn-doped YBCO is similar to that of Ce₀.₉₅R₀.₀₅CoIn₅ (Fig. 3A), and also to the iron-pnictide superconductors (20, 21), in which electronic inhomogeneity has been observed recently (22).

In nuclear quadrupole resonance (NQR) measurements further characterize the doping distribution of Ce₁₋ₓLaₓCoIn₅ and provide insight into the nature of the resulting electronic state. Fig. 4 shows the NQR signal for the 4\( _{17} \)Co quadrupolar \( (\pm 9/2 \leftrightarrow \pm 7/2) \) transition for the in-plane In(1), as well as the temperature dependence of the spin-lattice relaxation rates \( (T^{1/4}) \) for \( x = 0.0, 0.1, \) and 1. The NQR peaks are relatively sharp in the pure compound (Fig. 4B) with the LaCoIn₅ frequency \( (\nu_0 \sim 8.0 \text{ MHz}) \) smaller than that of Ce₁₋ₓLaₓCoIn₅ \( (\nu_0 \sim 8.17 \text{ MHz}) \), in good agreement with previous reports (23, 24). The NQR spectrum in the normal state at \( T = 3 \text{ K} \) is significantly broadened for the \( x = 0.1 \) sample, with the main peak (labeled A) virtually at the same frequency as in CeCoIn₅ and with two adjacent peaks (labeled B and C) resolved. There is no additional broadening or shift in the spectra as the sample becomes superconducting below \( T_c = 0.9 \text{ K} \), confirming that the heterogeneous electronic state below \( T_c \) has its origin in the normal state, as a result of doping. The lack of any intensity at the frequency corresponding to pure LaCoIn₅ and the similar temperature dependence of the spin-lattice relaxation rates of the three peaks—all with essentially the same onset \( T_c \)—rule out chemical segregation.

This thermodynamic analysis extends to other heavy fermion superconductors, as presented in Fig. 2B, and such electronic inhomogeneity may provide a framework for resolving several outstanding issues. In the 18.5 K superconductor PuCoGa₅, the radioactive decay of Pu-239 produces defects and/or dislocations, mimicking the Swiss cheese hole in Ce₁₋ₓR₀.₀₅CoIn₅. Analysis of the specific heat data of a “fresh” (approximately 2-wk old)
and “aged” (approximately 3-mo old) PuCoGa$_3$ sample (Figs. S3 and S4), reveals that the induced normal state fraction is comparable to the superconducting state fraction as radiation damage accumulates, in agreement with self-consistent $T$-matrix calculations describing the rate of suppression of $T_c$ (20). Furthermore, the observed anomalous reduction in superfluid density (25) with time in this strong-coupling $d$-wave superconductor is similar to the reduction observed in the Zn-doped YBCO and LSCO cuprates (2). Likewise, nonmagnetic Y and Th impurities (26) introduced into the exotic (odd-parity, ref. 27) superconductor

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The 115In NQR measurements were performed using a phase coherent pulsed NMR/NQR spectrometer. Several crystals with similar $T_c$ previously investigated by specific heat measurements were gently crushed into powder to improve the signal probed by the rf measurement. The frequency-swept 115In NQR spectra ($I = 9/2, \gamma /2\pi = 9.3295 \text{MHz/T}$) were obtained using an auto-tuning probe in a $\text{He}$ cryostat. The spectra were obtained by stepwise summing the Fourier transform of the spin-echo signal. The values of the spin-lattice relaxation time $T_1$ were obtained by fits of the recovery of the nuclear magnetization $M(t)$ after a saturation pulse. The self-consistent $T$-matrix calculations of the specific heat jump are described in detail in ref. 32.

In our thermodynamic analysis, estimates of the normal state electronic specific heat coefficient $\gamma_N$ were obtained by linear extrapolation to $T = 0 \text{K}$ (a determination of $\gamma_N$ obtained by fits of the data to the model of Moriya and Takimoto, ref. 33, for critical fermions yields similar values within 5–10%) and requiring entropy balance at 1.6 K. The entropy difference gives the error bars for $R_N$, these samples in Fig. 2, and the entropy balance at $T_c$ indicates this approximation is reasonable. In a few cases ($x = 0.05 \text{La, } 0.01 \text{Sn, } 0.03 \text{Yb}$), the entropy balance was not satisfied in all available datasets (see Fig. 1); therefore, we added a small linear term (approximately 3–5% of $\gamma_N$) to correct the entropy balance and obtain two different values of $U_c$ before and after the correction for a better relative comparison within each doping series. We take the average and their difference gives the error bars for $R_N$ of these samples in Fig. 2.

In our analysis of $C_{\text{CeCoIn}_3} = R_N(0)/T_c(0)$ we have taken approximately $R_N = U_c(0)/T_c(0)^2$ from the pure compound CeCoIn$_5$. This analysis, together with the experimental fact $R_N = R_0 = 1$ in Fig. 2, indicates that the pure compound of CeCoIn$_5$ has a negligible amount of impurities (i.e., comparing $\gamma_N = 0.04 \text{ J/mol Ce K}^2$ to $\gamma_N = 2 \text{ J/mol Ce K}^2$). However, in some heavy fermion compounds such as $U_x\text{Mn}_3\text{Pt}_5$ and PuCoGa$_5$, even the pure compounds have a significant number of defects or a large intrinsic $\gamma_N$. In this case, it is necessary to define a parameter $R_N$, which corrects the normalization by $U_c(0)/T_c(0)^2$ for additional disorder and/or systematic errors (see Table S1), to best fit all the doped data of a given system. For example, in PuCoGa$_5$, $R_N \approx 0.2$ even in the fresh sample, suggesting a large amount of defects caused by radiation damage, which is consistent with theoretical calculations that indicate $T_c = 19.1 \text{ K}$ in an undamaged material and account for the decrease in $T_c$ with time (20, 25). In the case of UPt$_3$, the pure material has a different condensation energy from the doped compounds (Fig. 2B), reflecting the double superconducting transition and also the sensitivity of this exotic odd-parity superconductor to impurities.

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Materials and Methods
Single crystals of $\text{Ce}_x\text{La}_y\text{In}_5$ ($R = $ Y$^{\text{III}}$, La$^{\text{III}}$, Gd$^{\text{III}}$, Tb$^{\text{III}}$, Th$^{\text{III}}$; $M = $ Sn, Cd, Hg) were grown from In flux, whereas single crystals of PuCoGa$_5$ were grown from Ga flux. Specific heat measurements were carried out in a Quantum Design Physical Properties Measurement System from 0.4 to 20 K (or from 5 to 25 K for PuCoGa$_5$), or in a $\text{He}$ cryostat dilution refrigerator from 50 mK to 3 K in magnetic fields up to 9 T. The concentrations of the impurities were determined from energy-dispersive X-ray spectroscopy.

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