Unpaired Electrons in the Heavy-Fermion Superconductor CeCoIn$_5$

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Thermal conductivity and specific heat were measured in the superconducting state of the heavy-fermion material Ce$_{1-x}$La$_x$CoIn$_5$. With increasing impurity concentration x, the suppression of T_c is accompanied by the increase in residual electronic specific heat expected of a d-wave superconductor, but it occurs in parallel with a *decrease* in residual electronic thermal conductivity. This contrasting behavior reveals the presence of uncondensed electrons coexisting with nodal quasiparticles. An extreme multiband scenario is proposed, with a d-wave superconducting gap on the heavy-electron sheets of the Fermi surface and a negligible gap on the light, three-dimensional pockets.

Many heavy-fermion materials possess a novel form of superconductivity thought to originate from pairing by magnetic fluctuations, a mechanism most favorable in the vicinity of a continuous zero-temperature magnetic instability [1], or quantum critical point (QCP). The heavy-fermion material CeCoIn$_5$, with quantum criticality [2–4] and the highest transition temperature $T_c = 2.3$ K amongst heavy-fermion superconductors [5], is an excellent candidate to study the relationship between QCP and unconventional superconductivity.

Experimental studies of the superconducting state in CeCoIn$_5$ have revealed a plethora of unconventional properties consistent with the presence of line nodes in the superconducting gap [6–9]. The presence of a fourfold anisotropy in the thermal conductivity suggests an order parameter with $d_{x^2-y^2}$ symmetry [10]. Several observations, however, remain unexplained in this picture. Recent specific heat measurements [11] show a fourfold anisotropy which points instead to a d_{xy} nodal gap structure. The temperature dependence of the spin-relaxation rate saturates below 0.3 K [6], while that of the penetration depth does not follow the functional form expected for a d-wave gap [8].

Doping with impurities provides a powerful route to the gap structure of CeCoIn$_5$. Nonmagnetic impurities are strong pair breakers in unconventional superconductors [12], acting to both suppress T_c and generate quasiparticles in the nodal regions of the superconducting gap. Because these quasiparticles have a residual density of states (DOS) in the $T \rightarrow 0$ limit, they can be characterized by the electronic specific heat $\gamma_{0S} \equiv C_{0S}/T$ and thermal conductivity κ_{0S}/T in the $T \rightarrow 0$ limit. With increasing impurity concentration, the expectation for a gap with line nodes is:

(1) a roughly linearly increasing γ_{0S} and (2) a constant (i.e., "universal") κ_{0S}/T [13]. Observed in the d-wave superconductors YBa$_2$Cu$_3$O$_7$ [14] and Bi$_2$Sr$_2$CaCu$_2$O$_x$ [15], and the spin-triplet superconductor Sr$_2$RuO$_4$ [16], universal conductivity is considered one of the most reliable tests of nodal structure, and hence order parameter symmetry [17].

In this Letter, we report a remarkable observation: while the increase of γ_{0S} with x in Ce$_{1-x}$La$_x$CoIn$_5$ is in agreement with expectations for impurity pair breaking in a d-wave superconductor, the large residual linear term κ_{0S}/T measured at $x = 0$ is not. Instead, rather than remaining constant (universal), it is found to *decrease* upon doping, tracking the suppression of *normal-state* conductivity. We show that this contrasting behavior can be understood if a sizable fraction of conduction electrons in CeCoIn$_5$ fails to participate in the superconducting condensation, and we attribute it to a negligible superconducting gap on part of the Fermi surface.

Single crystals of Ce$_{1-x}$La$_x$CoIn$_5$ were grown by the self-flux method [5,18] for $0 < x < 0.15$. Samples for transport measurements were cut into rectangular parallelepipeds with typical dimensions $\sim 2 \times 0.2 \times 0.1$ mm^3. Four-wire contacts with ~ 5 mΩ resistance were made with indium solder. Four-probe measurements of the electrical resistivity ρ and thermal conductivity κ were performed down to 50 mK, the latter with a standard 1-heater, 2-thermometer technique. Specific heat measurements were performed down to 300 mK in a physical properties measurement system (Quantum Design PPMS).

The electronic specific heat C of Ce$_{1-x}$La$_x$CoIn$_5$ in zero field is plotted as C/T versus T in Fig. 1. For the pure sample ($x = 0$), the large jump of C/T at T_c is evidence for
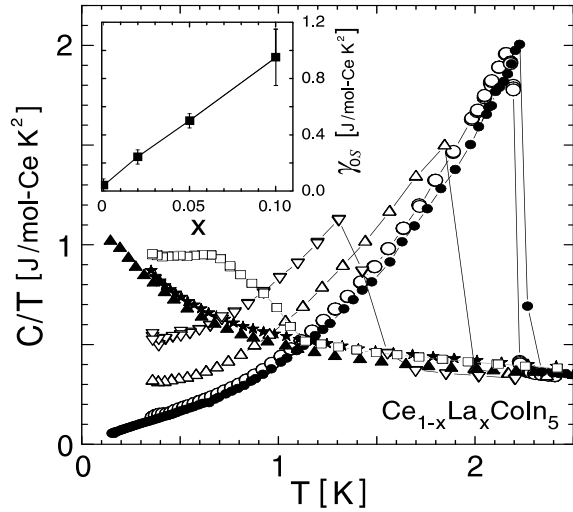
FIG. 1. Temperature dependence of specific heat C of $Ce_{1-x}La_xCoIn_5$ for $x = 0$ (open circles), 0.02 (open up-triangles), 0.05 (open down-triangles), 0.1 (open squares), and 0.15 (solid stars) in zero magnetic field plotted as C/T vs T. The data of Petrovic *et al.* [5] for pure $CeCoIn_5$ in zero field (solid circles) and at 5 T (solid up-triangles) are shown for comparison. Inset shows residual γ_{0S} as a function of x.

FIG. 2. Thermal conductivity κ of $Ce_{1-x}La_xCoIn_5$ with $x = 0$, 0.01, 0.02, 0.05, and 0.1 (top to bottom) in zero magnetic field, plotted as κ/T vs T (note logarithmic scale). Arrows indicate T_c. Inset shows determination of residual linear term κ_{0S}/T of pure ($x = 0$) samples for in-plane (squares) and interplane (triangles) heat flow directions (linear scale).

the participation of heavy-mass carriers in the superconducting condensation [5]. Upon doping, the T_c, determined from the position of the C/T peak, is gradually suppressed from 2.3 K at $x = 0$ to 0.7–0.8 K at $x = 0.10$ [18]. This is accompanied by a rapid increase in the normal-state impurity scattering: ρ_0 measured at $H = 10$ T (not shown) increases from 0.2 $\mu\Omega$ cm at $x = 0$ to ~ 10 $\mu\Omega$ cm at $x = 0.10$. Such a decrease of T_c implies a notable pair-breaking effect of nonmagnetic La impurities, which is characterized by a scattering rate $\Gamma \propto \rho_0 \propto x$ in the normal state [19,20]. (The fact that ρ_0 varies linearly with x, as confirmed in the present study, shows that the Fermi surface is unchanged with increasing x, at least up to 15%.) For comparison, we show previously published data for $x = 0$ [5], in zero field and in the field-induced normal state (5 T). The suppression of the superconducting state at $x = 0$ by field (5 T) and by 15% La substitution yield identical C/T curves. This further confirms that the normal-state density of states is unaffected by La doping, at least up to 15%. As shown in the inset of Fig. 1, γ_{0S} increases linearly with x [21], as expected for nonmagnetic impurities in unconventional superconductors [22,23].

In Fig. 2 we present the thermal conductivity of $Ce_{1-x}La_xCoIn_5$ in the superconducting state for currents directed in the basal plane, plotted as κ/T versus T on a semilog scale. In our pure sample, κ/T is roughly similar to previous reports [7,10], increasing rapidly below T_c, reaching a maximum at ~ 0.5 K, and then decreasing towards $T = 0$. However, below ~ 0.5 K the behavior of κ/T is notably different from that obtained in a previous study with $J \perp c$ [7], which found $\kappa \propto T^{3.4}$ for $T <$
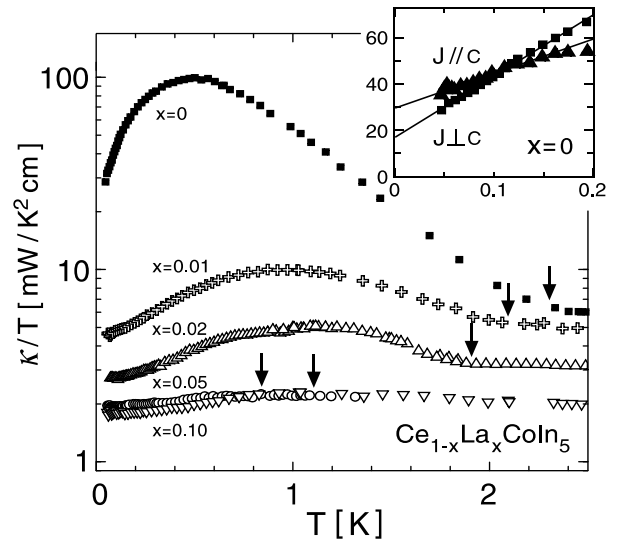
100 mK and determined κ_{0S}/T to be less than 2 mW K^{-2} cm^{-1}. In our experiment, $\kappa/T \propto T$ at low temperature and κ_{0S}/T tends to a much larger residual value of ~ 17 mW K^{-2} cm^{-1}, as shown in the inset of Fig. 2. Because it is known that the measurement of κ can be inhibited by electron-phonon decoupling [24], we have checked that our data indeed exhibit the intrinsic behavior by recovering the Wiedemann-Franz law in the normal state ($H > H_{c2}$) at $T \to 0$ [25].

Heat capacity and heat conduction are two diagnostic properties of a d-wave superconductor, and their essential interrelation is captured by simple kinetic theory applied to the residual normal fluid of nodal quasiparticles: $\kappa_{0S}/T \propto \gamma_{0S} v_F^2/\Gamma$, with $\Gamma \sim \rho_0 \sim x$, the impurity concentration. If the superconducting state has a DOS which varies linearly with energy, then one expects $\gamma_{0S} \propto x$, as is indeed observed here (see inset of Fig. 1), and the two x dependences (of γ_{0S} and Γ) cancel out to leave κ_{0S}/T universal, independent of x. A full theoretical treatment confirms this simple analysis and predicts universal heat conductivity [13]. In the normal state, the density of quasiparticle states γ_{0N} remains constant and $\kappa_{0N}/T \sim \frac{1}{x}$. In Fig. 3, we plot κ_{0S}/T and κ_{0N}/T as a function of $\rho_0(x)$ (determined for $H > H_{c2}$ in the $T \to 0$ limit) [26], and compare these to the behavior expected of a superconductor with a line node in the gap: (1) universal limit in the superconducting state (constant κ_{0S}/T) and (2) Wiedemann-Franz law in the normal state ($\kappa_{0N}/T = L_0/\rho_0$). The disagreement is dramatic. Rather than remaining roughly constant with increasing disorder, κ_{0S}/T in fact decreases by a factor 10, much like the normal-state conductivity. In Fig. 3 we show
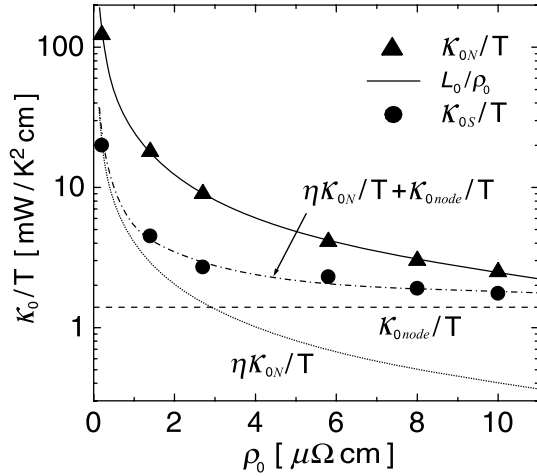
FIG. 3. Residual ($T \to 0$) electronic thermal conductivity in the normal (κ_{0N}/T, $H > H_{c2}$, triangles) and superconducting (κ_{0S}/T, $H = 0$, circles) states of $Ce_{1-x}La_xCoIn_5$ as a function of the normal-state residual resistivity ρ_0 [26]. The universal behavior expected of a superconductor with line nodes is shown as a dashed line (κ_{0node}/T). The dash-dotted line is a sum of uncondensed (dotted line) and nodal (dashed line) contributions, $\eta\kappa_{0N}/T + \kappa_{0node}/T$, with $\eta = 0.16$.

how a two-fluid scenario can capture this unusual behavior: a band of electrons remains uncondensed below T_c, while the other is gapped with a line node.

We assume that some fraction η of κ_{0N}/T is preserved in the superconducting state, in addition to the contribution of nodal quasiparticles κ_{0node}/T, so that $\kappa/T = \eta\kappa_{0N}/T + \kappa_{0node}/T$. Assuming that κ_{0node}/T obeys the universal limit and stays constant in the doping range studied [27], values of $\eta = 0.16$ and $\kappa_{0node}/T = 1.4$ mW cm^{-1} K^{-2} give a reasonable description of the data. The value we deduce for κ_{0node}/T lies between published estimates of the universal term for two-dimensional (1 mW cm^{-1} K^{-2}) and three-dimensional (1.9 mW cm^{-1} K^{-2}) superconducting states applied to CeCoIn$_5$ [7], assuming a d-wave gap [13].

The presence of uncondensed carriers suggests a multi-band scenario, whereby at least one part of the Fermi surface does not participate in superconductivity. This is an extreme version of what has been established in a number of materials recently, where multiband superconductivity occurs either as a variation in the gap magnitude from Fermi surface sheet to Fermi surface sheet, as in MgB$_2$ [28], or as a variation in nodal structure, as in Sr$_2$RuO$_4$ [29]. In the s-wave superconductor NbSe$_2$, for example, the gap maximum varies by a factor 3 or so [30,31]. However, in no case so far has the gap been seen to actually vanish all the way to zero, as observed here in CeCoIn$_5$. The possibility of such an extreme case was predicted theoretically, however, by Agterberg *et al.* [32] in their model of orbital-dependent superconductivity, in which impurities scatter electrons predominantly within one band and not between bands [33].

The value of η we deduce suggests that the conductivity of the uncondensed carriers is 16% of the total conductivity of all carriers (measured in the normal state). This is notably larger than their relative contribution to specific heat: in pure samples, $\gamma_{0S} \approx 0.04$ J mole^{-1} K^{-2} [7], or about 3% of the normal-state value in the $T \to 0$ limit (and it includes both nodal and uncondensed contributions). Therefore, the uncondensed carriers must either have a higher velocity than average, or a lower scattering rate, or both. The ratio v_F^2/Γ must be at least a factor 5 above average.

The calculated [34] and experimentally observed [35] Fermi surface of CeCoIn$_5$ allows for such large variation in carrier characteristics. The hole band 14 and electron band 15 form warped cylindrical surfaces with heavy carrier masses of $m^* \sim 30$–$100m_0$, whereas the hole band 13 (and electron band 16 which is not observed in de Haas–van Alphen experiments) forms a three-dimensional surface with order-of-magnitude lighter carrier masses of $m^* \sim 4.3$–$12m_0$. With a light mass, the contribution of the latter bands to conductivity can be much more important than their contribution to the DOS.

Consequently, our proposal is that superconductivity in CeCoIn$_5$ originates on the cylindrical sheets of the Fermi surface, with negligible transfer of the order parameter onto the three-dimensional pockets. This interpretation is supported by two further experimental results. First, the *anisotropy* of thermal transport. As shown in the inset of Fig. 2, an anomalously large residual linear term is seen not only for a current in plane, but also out of plane (along the c axis), as you would expect from an *uncondensed* 3D Fermi surface. (In fact, κ_{0S}/T is even larger for $J \parallel c$, namely, 30 mW cm^{-1} K^{-2}.) Second, de Haas–van Alphen studies show that the ϵ orbit over the band 13 sheet exhibits negligible damping in the superconducting state, persisting down to $\sim 0.2H_{c2}$ [35], in contrast with strong damping observed for the α and β orbits over band 14 and 15 sheets. In other words, holes in band 13 (and possibly electrons in band 16) do not feel the superconductivity.

The presence of a group of light, uncondensed quasi-particles in the superconducting state can explain several experimental anomalies, such as the saturation of penetration depth at low temperatures [8]. Orbital magnetoresistance of uncondensed carriers can explain the unexpectedly large difference in thermal conductivity [36] between longitudinal and transverse field orientations in the plane with respect to the heat flow. A scenario of uncondensed electrons may also help resolve the apparent contradiction in the angular field dependence of thermal conductivity [10] and specific heat [11]. Further implications of such a scenario for the nature of superconductivity in this material (and perhaps others) should be explored, e.g., the possibility of pure off-diagonal coupling [37]. Besides multiband superconductivity, other scenarios for uncondensed electrons should be considered, such as "in-

terior gap superfluidity," where a material is predicted to be simultaneously superconducting and metallic [38].

In conclusion, the qualitative contrast between low temperature specific heat and thermal conductivity in response to impurity doping in $CeCoIn_5$ has revealed the presence of a group of conduction electrons which do not participate in the superconducting condensation. This effect is naturally explained by assuming that one of the Fermi surfaces of $CeCoIn_5$ possesses a negligible superconducting gap. This is the most extreme case of multiband superconductivity encountered so far. Such an instance of complete decoupling between two groups of electrons in a single material will not only make all superconducting properties anomalous, it will also have profound implications for other cooperative phenomena, such as magnetic ordering and quantum critical behavior. It provides a fascinating new window on electron correlations in metals.

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[26] We use ρ_0 as the variable instead of x itself as this removes two sources of uncertainty, coming, respectively, from estimates of geometric factors (accurate to 10% or so) and estimates of x values. As mentioned earlier, $\rho_0 \propto x$ within error bars.
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