Ambient-pressure bulk superconductivity deep in the magnetic state of CeRhIn₅

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Specific heat, magnetic susceptibility, and electrical transport measurements were performed at ambient pressure on high quality single-crystal specimens of CeRhIn₅ down to ultralow temperatures. We report signatures of an anomaly observed in all measured quantities consistent with a bulk thermodynamic phase transition to a superconducting state at \( T_N = 110 \) mK. Occurring far below the onset of antiferromagnetism at \( T_N = 3.8 \) K, this transition appears to involve a significant portion of the available low-temperature density of electronic states, exhibiting an entropy change in line with that found in other members of the 115 family of superconductors tuned away from quantum criticality.

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With the record-high transition temperature of \( T_N = 2.3 \) K for Ce-based heavy-fermion materials,¹ superconductivity in CeCoIn₅ has been the subject of many studies, which have since revealed an exotic pairing state with several intriguing properties including unconventional (nodal) gap symmetry,² an anomalously large specific heat jump at \( T_c \),¹ an unconventional behavior in superfluid density,⁴ multiple-size energy gaps,⁵ and unpaired quasiparticles in the \( T \rightarrow 0 \) limit.⁶ Furthermore, the application of magnetic field exposes additional anomalies, including a first-order superconductor to normal state transition²,⁷ and a magnetic quantum critical point that coincides with the upper critical field \( H_{c2} \).⁸ CeRhIn₅, on the other hand, is a well-characterized anti-ferromagnet at ambient conditions with a Néel temperature \( T_N = 3.8 \) K that is gradually suppressed upon the application of pressure¹⁰,¹²–¹⁴ or Co substitution¹⁵,¹⁶ to reveal a superconducting state that is widely thought⁷ to resemble that found in CeCoIn₅. This tuning is considered to be strongly tied to the nature of Ce \( f \)-electron states since both theoretical¹⁰ and experimental¹⁵ evidence point to a localized \( f \)-electron scenario for CeRhIn₅ and a delocalized one for CeCoIn₅.

Intriguingly, signatures of a low-lying superconducting phase in CeRhIn₅ were observed even at ambient pressure by Zapf et al.¹⁵ and, more recently, by Chen et al.²⁰ as a diamagnetic drop in susceptibility measurements near 100 mK. Lacking any evidence for superconductivity in any of the La- or Y-based (non-\( f \)-electron) analogs of CeRhIn₅, this phase is unlikely to arise from the pairing of electronic \( d \) and \( p \) states but is rather associated with delocalized \( f \) states. However, a nonbulk superconducting phase cannot be ruled out as the cause of the observed low-pressure diamagnetic response. For instance, it has been predicted that superconductivity can be stabilized at the surface of a magnetic material,²¹ where the internal (spontaneous) magnetic field tends toward zero. More importantly the third member of the 115 family, CeIrIn₅, indeed exhibits a nonbulk superconducting phase with supercurrents causing a resistive transition at 1.2 K, while a thermodynamic signature only appears at a much lower temperature of 0.4 K (Ref. 22). The likely existence of filamentary²³ and/or surface²⁴ superconducting phases in CeIrIn₅ thus adds to the controversy about ambient-pressure superconductivity in CeRhIn₅.

Here, we establish the bulk nature of the transition observed deep within the antiferromagnetic state of CeRhIn₅ by presenting clear thermodynamic evidence for ambient-pressure superconductivity in this material: Deep below the onset of incommensurate magnetic order in CeRhIn₅, a significant fraction of the remaining density of electronic states undergoes a bulk superconducting transition at 110 mK. We show that the thermodynamic nature of this transition is quite similar to that found throughout the 115 series, confirming the ubiquitous presence of pairing instabilities in this family of materials even far from criticality.

Large single-crystal specimens of CeRhIn₅ were grown by the self-flux method,¹ yielding samples with unprecedentedly low impurity concentrations as evidenced by a residual resistivity \( \rho_0 = 37 \) nΩ cm and resistivity ratio \( \rho(300 \) K)/\( \rho_0 \) \( \sim 1000 \) (Ref. 11). Resistivity samples were prepared with dimensions \( 4 \times 0.1 \times 0.05 \) mm³ and measured with an ac resistance bridge, applying currents parallel to the basal plane of the tetragonal crystal structure. Both ac susceptibility and specific heat measurements were performed on a larger single-phase crystal from the same growth batch, using a conventional low-frequency drive/pickup coil method and a standard semiadiabatic heat pulse method, respectively. All experiments were performed in a dilution refrigerator.

As shown in Fig. 1, the specific heat of CeRhIn₅ is characterized by a dramatic transition into the antiferromagnetic state at 3.8 K, as evidenced by the sharp anomaly in \( C(T) \). Below \( T_N \), \( C(T) \) has been previously characterized as composed of a standard electronic contribution \( C_e(T) = \gamma T \) with \( \gamma = 56 \) mJ/mol K², in line with the universal Kadowaki-Woods ratio,¹¹ and a magnetic contribution \( C_m(T) \), which itself shows evidence of a gapped density-wave-like state with a gap magnitude of \( \sim 8 \) K.⁹ Here we reproduce the same results, but focus on the properties far below \( T_N \). In this
regime, the total specific heat can be described by the sum of several standard contributions

\[
C(T) = C_{\text{latt}} + C_e + C_m + C_n, \tag{1}
\]

including lattice, electronic, magnetic, and nuclear terms. Shown in Fig. 1 is the total measured \(C(T)\) less the lattice term, estimated using the measured specific heat of the non-f-electron analog YRhIn\(_5\) (with \(\gamma \approx 56\) mJ/mol K\(^2\)).

Below \(\sim 200\) mK, a large upturn in \(C(T)\) (Fig. 1 inset) is attributable to a low-lying Schottky anomaly arising from the splitting of the degenerate nuclear energy levels of indium by its large nuclear quadrupole moment. To analyze this low-temperature behavior, a fit of \(C(T)\) below 2 K was performed by fixing \(\gamma \approx 56\) mJ/mol K\(^2\) and fitting both the magnetic and nuclear contributions as follows. To model the magnetic contribution \(C_m\), we employed a simple power law (e.g., \(C_m(T) = b T^\beta\)) to characterize \(C(T)\) well above the temperatures where \(C_n\) is sizeable. This yields a phenomenological exponent \(\beta = 4.1\), which captures the curvature of \(C(T)\) below 2 K while essentially folding in the details of the analysis performed previously.\(^9\) To model the nuclear component \(C_n\), we include the first three terms \((i=1, 2, 3)\) of the series expansion \(C_n(T) = \sum_c T^{2i}\) to approximate the high-temperature side of the nuclear Schottky peak. This results in an adequate fit to the data at both zero field and applied magnetic fields up to 330 mT (as discussed below), which compares well with other measurements [e.g., 0.290/T\(^2\) mJ/mol K, the value of the most significant \((i=2)\) term, compares favorably with that of both CeIrIn\(_5\) and CeRhIn\(_5\)].\(^{22,23}\)

To our surprise, and in contrast to recent reports,\(^{24}\) an examination of the fit residuals reveals an anomaly in the zero-field data, which is absent in fields of 60 mT and above.

As shown in Fig. 2(a), subtracting the fitted form of \(C_n(T)\) works quite well down to the lowest temperatures for all finite-field data, leaving the same approximately \(T\)-independent contribution from \(\gamma\). However, applying the same procedure to the zero-field data reveals a distinct anomaly in \((C-C_n)/T\) near \(\sim 100\) mK, followed by a decrease toward zero. To check that this feature is not an extrinsic result of the fitting procedure, we also performed a subtraction of the finite-field raw data \(C(T, H)\) from the zero-field raw data \(C(T, 0)\), as shown in Fig. 2(b). This procedure, which does not involve any fitting procedures aside from simple data interpolation, results in an almost identical jump in the difference \([C(0) - C(H)]/T\) as that found in the nuclear fit subtraction [Fig. 2(a)].

We therefore conclude that this zero-field anomaly, reminiscent of a BCS-like phase transition that gaps the density of states and sends \(C(T)\) toward zero at lower temperatures, provides strong evidence for a bulk thermodynamic phase transition at \(T_c = 110\) mK in CeRhIn\(_5\). Moreover, this confirms the existence of a robust, ambient-pressure pairing instability in all three members of the Ce-based 115 family.

\(ac\) magnetic susceptibility \(\chi_{ac}\) measured on the same specimen reveals a diamagnetic response at \(T_c\) nearly identical to that reported previously,\(^{15,20}\) confirming the superconducting nature of the transition. As shown in Fig. 3, the drop in \(\chi_{ac}\) reaches at least 90% of \(-1/4\pi\) by 70 mK and approaches a full 100% volume fraction as \(T \to 0\), as determined by comparing to the response from a similar size
FIG. 3. Comparison of extracted specific heat transition (solid circles) [where ∆C=C(0)−C(120 mT) and γ=56 mJ/mol K²], and the diamagnetic response of the same 55 mg single-crystal specimen of CeRhIn₅ (open circles), showing the bulk full-volume nature of the ambient-pressure superconducting transition at Tc =110 mK. The superconducting transition in a similar sized single-crystal sample of RhIn₃ is also shown (triangles) for comparison.

FIG. 4. (Color online) Low temperature resistivity of CeRhIn₅ in zero and applied magnetic fields. Dashed lines are linear fits to zero-field data below the kink associated with the onset (indicated by arrow) of the superconducting transition at Tc, showing a slight dependence on excitation current. The solid line is a quadratic fit to zero-field data above the kink.
ducting ground states, as recently advocated both experimentally\textsuperscript{20} and theoretically\textsuperscript{30} for CeRhIn\textsubscript{5} and as proposed over two decades ago for the heavy-fermion superconductor URu\textsubscript{2}Si\textsubscript{2}, in which the Fermi surface is partially gapped.\textsuperscript{31}

However, a qualitative change in this scenario appears to occur in CeRhIn\textsubscript{5} once magnetism is suppressed. Rather than remaining constant upon further pressure increase, $\Delta C/T_c$ undergoes a substantial threefold growth—reaching a maximum of $\sim 1.45$ at 2.55 GPa (coincident with the maximum $T_c$) before decreasing back toward $\sim 0.5$ at much higher pressures (i.e., near 3.38 GPa, where $T_c \approx 2.0$ K).\textsuperscript{13} In other words, the superconducting state of CeRhIn\textsubscript{5} near its pressure-tuned quantum control point qualitatively differs from that found under both low- and high-pressure conditions while being strikingly similar to that of CeCoIn\textsubscript{5} at ambient pressure. Interestingly, the third member of this family, CeIrIn\textsubscript{5}, also has a small $\Delta C/T_c=0.76$ at ambient pressure,\textsuperscript{22} provoking the idea that its pairing state differs from those in the critical pressure region yet perhaps shares similarities with CeRhIn\textsubscript{5} at either low or extremely high pressures. Recent thermal conductivity measurements have, in fact, shown evidence for different (bulk) superconducting gap symmetries in CeCoIn\textsubscript{5} and CeIrIn\textsubscript{5}.\textsuperscript{32} However, the jump in CeIrIn\textsubscript{5} differs from that in both its Rh- and Co-based counterparts, exhibiting a minimal change with increasing pressure\textsuperscript{33} that suggests (at the very least) that the pairing state in CeIrIn\textsubscript{5} is much less sensitive to pressure. In any case, the evidence for multiple, distinct superconducting phases in this family is further supported by the observation of separated “domes” of superconductivity as a function of pressure in CeRh\textsubscript{1-x}Ir\textsubscript{x}In\textsubscript{5}.\textsuperscript{14} It remains to be determined whether the competition between magnetic and superconducting states for electronic density of states in this family is due to a gapped nature of magnetism, as recently proposed theoretically,\textsuperscript{30} or to a different phase space distribution for each coupling mechanism.

In conclusion, the proof of a bulk-phase superconducting state in CeRhIn\textsubscript{5} at ambient pressure is provided by the observation of a phase transition in specific heat data that occurs simultaneously with both a diamagnetic drop in magnetic susceptibility and a drop in electrical resistivity. With evidence for an ambient-pressure superconducting ground state in all three members of the Ce-based 115 materials, critical comparisons of each may play a vital role in elucidating the origins of both unconventional superconducting and normal state characteristics throughout this family.

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