Title
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Permalink
https://escholarship.org/uc/item/2rj0q65w

Journal
Journal of the Physical Society of Japan, 81(1)

ISSN
0031-9015

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Publication Date
2012-01-15

DOI
10.1143/jpsj.81.011002

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Peer reviewed
Progress in Heavy-Fermion Superconductivity: 
Ce115 and Related Materials

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(Received February 18, 2011; accepted April 25, 2011; published online December 26, 2011)

Ce115 and related Ce compounds are particularly suited to detailed studies of the interplay of antiferromagnetic order, unconventional superconductivity and quantum criticality due to their availability as high quality single crystals and their tunability by chemistry, pressure and magnetic field. Neutron-scattering, NMR and angle-resolved thermodynamic measurements have deepened the understanding of this interplay. Very low temperature experiments in pure and lightly doped CeCoIn\(_5\)s have elaborated the FFLO-like magnetic state near the field-induced quantum-critical point. New, related superconducting materials have broadened the phase space for discovering underlying principles of heavy-fermion superconductivity and its relationship to nearby states.

KEYWORDS: CeCoIn\(_5\), CeRhIn\(_5\), CeIrIn\(_5\), CePt\(_3\)In\(_7\), Ce\(_2\)PdIn\(_8\), unconventional superconductivity, quantum criticality

1. Introduction

Superconductivity continues to fascinate the imagination even though it has been found in thousands of materials and in over half the elements. Irrespective of whether their superconducting transition temperature \(T_c\) is milliKelvin or tens of Kelvin, superconductivity in the vast majority of these can be understood within the weak coupling theory of Bardeen, Cooper, and Schrieffer (BCS) who showed that itinerant electrons form pairs due to an attractive interaction provided by phonons.\(^3\) Though this theory has had little success predicting where new examples might be found, its ability to account for a broad spectrum of experimental observations is very powerful. For nearly 60 years, from Onnes’ original discovery in 1911 until the late 1970’s, superconductivity in all examples could be understood within the BCS framework. This changed, however, with the discovery of superconductivity in CeCu\(_2\)Si\(_2\).\(^2\) Contrary to prior examples, superconductivity emerged at low temperatures from a normal state with strong temperature-dependent paramagnetism, and, further, \(T_c\) was a substantial fraction of the degeneracy temperature \(T_F\) of massive electrons that formed Cooper pairs. Neither of these observations, and especially the hierarchy of energy scales \(k_B T_c < k_B T_F < k_B \Theta_D\), where \(k_B \Theta_D\) is a characteristic phonon energy, was consistent with BCS. These observations by Steglich and coworkers led them to suggest that CeCu\(_2\)Si\(_2\) was a “high temperature” superconductor that could not be described by conventional ideas.\(^2\)

Subsequent discoveries of superconductivity in UBe\(_{13}\)\(^3\) and UPt\(_3\),\(^1\) both with large Sommerfeld coefficients of specific heat and strongly paramagnetic susceptibilities, established that CeCu\(_2\)Si\(_2\) was not a singular example. Like CeCu\(_2\)Si\(_2\),\(^5\) physical properties that depend on the electronic density of states exhibited power laws in the superconducting state of these U-based heavy-fermion materials, suggesting an unconventional form of superconductivity in which the superconducting energy gap was zero at points or lines on the Fermi surface.\(^5\) Such nodal superconductivity was counter to expectations of conventional phonon-mediated superconductivity in which the gap is finite over the entire Fermi surface and hence preserves symmetry of the underlying crystal lattice. Analogies to superfluid states in nearly magnetic \(^{3}\)He suggested that heavy-fermion superconductivity might have a magnetic origin,\(^7\) but stronger evidence for this possibility came from discoveries of superconductivity in several Ce-based heavy-fermion antiferromagnets as their Neél temperature \(T_N\) was tuned to zero by applied pressure.\(^8-10\) In these cases, the emergence of a dome of superconductivity centered at the critical pressure where \(T_N\) extrapolated to zero led to the suggestion that quantum fluctuations of the antiferromagnetic order parameter might assume the role of phonons in creating an attractive pair interaction.\(^9\) This, however, has been difficult to prove, especially because of challenges posed by performing a variety of measurements under high pressure conditions and the relatively low (\(<0.5\,\text{K}\)) \(T_c\)’s of these materials.

New opportunities to explore the relationship among magnetism, quantum criticality and unconventional superconductivity in heavy-fermion materials opened with the discovery of the “Ce115” family CeCoIn\(_5\),\(^{10}\) CeRhIn\(_5\),\(^{12}\) and CeIrIn\(_5\).\(^{13}\) Not only were CeCoIn\(_5\) and CeIrIn\(_5\) the first Ce-based heavy-fermion systems since CeCu\(_2\)Si\(_2\) to exhibit superconductivity at atmospheric pressure, the transition temperature of pressure-induced superconductivity in the isostructural, antiferromagnetic member CeRhIn\(_5\) was 2.3 K, much higher than prior examples. These materials are \(n = 1\), \(m = 1\) members of the larger family Ce\(_n\)M\(_n\)\(_{3n}\)B\(_{3n}\), where \(M\) is a transition metal element Co, Rh, Ir, Pd, and Pt, \(n\) and \(m\) = 1 or 2 and in which \(n\) layers of CeIn\(_3\) are a common structural unit. For reasons that still are not understood fully, this family of heavy-fermion materials likes to support superconductivity, with eight members (the three Ce115s, Ce\(_2\)RhIn\(_8\), Ce\(_2\)CoIn\(_8\), Ce\(_2\)PdIn\(_8\), Ce\(_2\)PtIn\(_7\), and Ce\(_3\)Pt\(_2\)In\(_7\)) superconducting either at atmospheric or higher pressure. Many properties of the Ce115s have been reviewed in several articles in ref. 18 and particularly in ref. 19. Here, we focus on recent experimental progress in revealing the nature and relationship of magnetism, superconductivity and quantum criticality in Ce115 crystals as well as in related Ce\(_2\)PdIn\(_8\) and Ce\(_2\)PtIn\(_7\).
As will be discussed, this progress has raised several questions for future study as well as pointed out similarities but also differences between these systems and other strongly correlated electron superconductors.

2. **Ce115’s**

2.1 **CeCoIn5**

Superconductivity in CeCoIn$_5$ develops at 2.3 K out of an anomalous normal state in which physical properties are not those of a Landau Fermi liquid. For example, the longitudinal resistivity $\rho_{xx} \sim T^n$, with $n \approx 1.0$, 30) the ratio of longitudinal to transverse resistivity ($\rho_{xx}/\rho_{xy}$) increases as $-T^2$; 21) the nuclear spin relaxation rate $1/T_1 \sim T^{1/4}$; 22) the specific heat divided by temperature $C/T \sim -\ln T/T_0$ 11) and volume thermal expansion coefficient $\beta/T$ diverges as $1/T$. 23) In contrast, at sufficiently high magnetic fields [just below to far above the $T = 0$ upper critical field $H_{c2}(0)$] or at high pressures, Landau Fermi-liquid behaviors ($\rho_{xx} \sim T^2$; 20, 24) $1/T_1 \sim T^{25}$, $\beta/T$, and $C/T = \text{constant}^{23}$) emerge that indicate a reduced but still large mass of itinerant electrons. Various interpretations have been given for the origin of the anomalous temperature dependences of physical properties, but all are consistent with CeCoIn$_5$ being close to an antiferromagnetic quantum-critical point from which excitations dominate properties over broad ranges in temperature, magnetic field and pressure.

Though theory has raised the possibility that fluctuations from an antiferromagnetic quantum-critical point might mediate Cooper pairing, 9, 26) experiments on CeCoIn$_5$ are only suggestive but not definitive in this regard. On the other hand, inelastic neutron scattering measurements reveal the presence of magnetic fluctuations of relative large moments ($\sim 0.6 \mu_B$) at the commensurate wavevector $Q = (1/2, 1/2, 1/2)$. 27) In the temperature range $T_n < T < \sim 20 \text{K}$, where electrical transport exhibits non-Fermi-liquid temperature dependences, the dynamical spin susceptibility of CeCoIn$_5$ has a Lorentzian response. Upon cooling below $T_n$, magnetic spectral weight at low energies is shifted to higher energies to create a spin resonance centered near 0.6 meV. See Fig. 1.

A similar resonance appears in the high-$T_n$ cuprate and iron-pnictide superconductors as well as in the heavy-fermion superconductors UPd$_2$Al$_3$ and CeCu$_2$Si$_2$. 28) A recent analysis of the dynamical spin response and thermodynamic properties of CeCu$_2$Si$_2$ near its quantum-critical point is consistent with antiferromagnetic excitations being the primary pairing mechanism; 29) but more generally a sign change in the superconducting gap function, such that $\Delta(q) = -\Delta(q + \mathbf{Q})$, will produce a spin resonance. 30) Such a sign change is expected for a gap with d-wave symmetry, which is known to be present in the cuprates and in CeCoIn$_5$. In particular, tunneling spectra; 31) a four-fold modulation in the angular dependence of thermal conductivity (22) and specific heat (33) and power-law temperature dependences of thermal conductivity $1/T_1^{25}$ and $C/T^{23}$ below $T_n$ are all consistent with $d_{x^2-y^2}$ symmetry of the superconducting gap in which line nodes extend along the c-axis in CeCoIn$_5$. The ratio of the spin resonance energy $E_s$ to $2\Delta_0(T = 0)$ is 0.62 in CeCoIn$_5$, 27) which is similar to $E_a/2\Delta_0$ in CeCu$_2$Si$_2$ ($=0.73$) 29) and UPd$_2$Al$_3$ ($=0.74$). 35) Although $2\Delta_0/k_B T_n$ varies from $\sim 2$ to over 6, $T_n$ ranges from 0.6 to over 100 K, and a resonance appears in the presence or absence of long range antiferromagnetic order, $E_a/2\Delta_0$ clusters around 0.68 ± 0.06 for the cuprates, iron-pnictides and these heavy-fermion superconductors.

In a magnetic field of 5 T applied in the tetragonal basal plane, the spin resonance in CeCoIn$_5$ broadens and $E_a$ decreases to $\sim 0.35 \text{meV}$ (Fig. 1 inset). 36) A similar field response has been reported in La$_1.85$Sr$_0.15$CuO$_4$ in which the resonance energy is suppressed to zero near 7 T, above which magnetic scattering appears in the elastic channel associated with the development of long range antiferromagnetism in the superconducting state. 37) Depending on the functional form assumed to extrapolate $E_a(q)$ to zero, an estimate of the critical field required to suppress completely the resonance in CeCoIn$_5$ is $\sim 7–14 \text{T}$, comparable to its in-plane $H_{c2}(0) = 11.8 \text{T}$. In analogy with results on Sr-doped La$_2$CuO$_4$, this crude estimate raises the possibility of field-induced magnetic order in the superconducting state of CeCoIn$_5$. Indeed, neutron diffraction experiments find field-induced small moment ($\sim 0.15 \mu_B$) order at the incommensurate wavevector $Q = (0.45, 0.45, 1/2)$. 38) This order exists only in the superconducting state at low temperatures and high magnetic fields, bounded by the Pauli-limited, first-order upper critical field $H_{c2}(T)$ and a line of second-order transitions $T_c(T)$ within the Abrikosov state, as shown in Fig. 2. 39) An analysis of the magnetic diffraction peaks gives a magnetic correlation length in the $(0, k, l)$ plane that is longer than 300 nm, which is considerably greater than the superconducting coherence length of $\sim 8 \text{nm}$; consequently, magnetic order extends well outside the normal core of vortices and coexists with d-wave superconductivity.

The region of the $H–T$ plane where field-induced order appears coincides precisely with that where specific heat 39) and NMR 40–44) experiments reveal a phase that is consistent with a Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) state. The field-induced order were only a consequence of shifting magnetic spectral weight from high to low energies as the spin resonance is suppressed, we might expect, as in Sr-doped La$_2$CuO$_4$, that the propagation wavevector of antiferromagnetic order would be the $\mathbf{Q}$ of the spin resonance, but it is not. This raises the possibility that the...
The Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) phase in the \(\frac{1}{2}\) parallel to [100] and \(T\) incommensurate antiferromagnetic order is detected. Note that field-induced neutron diffraction. Closed circles in the inset represent points at which the line of field-induced second order phase transitions, labeled \(T\) (first) order, as indicated by open (half-filled) symbols. Open triangles define a line of field-induced second order phase transitions in CeCoIn\(_3\). Circles denote the upper critical field boundary that is second (first) order, as indicated by open (half-filled) symbols. Open triangles define a line of field-induced second order phase transitions, labeled \(T_2\), inside the superconducting state and that are consistent with the appearance of a Fulde–Ferrell–Larkin–Ovchinnikov phase in the \(H-T\) plane defined by \(H_2(T)\) and \(T_2\) boundaries. Data after ref. 59. The inset is an expanded view of the low-\(T\), high-\(H\) part of the phase diagram and includes results from neutron diffraction. Which, if any, of these ideas is correct in detail remains to be determined, but four experimental observations are relevant to this debate. (1) In Ce-based heavy-fermion materials, a paramagnetic state is favored with applied pressure relative to small moment antiferromagnetism, and, consequently, we might expect the region of the \(H-T\) plane occupied by field-induced order to shrink when pressure is applied. Experiments, however, show the contrary. (2) Evidence for field-induced magnetic order disappears in neutron diffraction measurements when the magnetic field is rotated out of the tetragonal basal plane by more than \(\sim 17^\circ\). Consequently, anomalies in bulk measurements in the superconducting state for \(H=0\) may not be magnetic in origin. (3) Theory predicts a strong sensitivity of an FFLO state to impurities; whereas, magnetic order should be affected relatively little. Specific heat measurements on very lightly doped CeCo\((\text{In}_{1-x}\text{Cd}_x)\)\(_3\), where \(T=\text{Sn}\), Hg, and Cd, find that thermodynamic evidence for the field-induced state at low temperatures and high fields disappears for \(x<0.008\), an extreme response to disorder. (Finally) At slight higher Cd or Hg substitutions (\(\sim 0.0075 \leq x \leq \sim 0.015\)), rather large (\(\sim 0.7 \mu_B\)) moment antiferromagnetic order coexists with bulk superconductivity in zero applied field. In this case, the doping-induced antiferromagnetic \(Q=(1/2, 1/2, 1/2)\) is the same as at which the spin resonance appears. Singly and collectively, these observations point to the possibility of an FFLO state in CeCoIn\(_3\). This conclusion is supported by an analysis of recent NMR experiments that reveal a quasiparticle density of states consistent with coexisting FFLO nodal planes and long range antiferromagnetic order.

Besides determining the ordering wavevector in the more heavily Cd-doped CeCoIn\(_3\), neutron diffraction measurements also find that the magnetic correlation length is approximately three times longer than the superconducting coherence length, again implying microscopic coexistence of these two broken symmetries that also is concluded from NMR. At these Cd concentrations, antiferromagnetic order sets in at a temperature above the onset of superconductivity. As shown in Fig. 3, magnetic elastic scattering develops in a mean-field way below \(T_N\), but the growth in intensity with decreasing temperature is arrested abruptly at \(T_c\) and remains nearly constant to the lowest temperatures of these measurements. As with field-induced antiferromagnetism in the superconducting state of undoped CeCoIn\(_3\), these experiments indicate a coupling between superconducting and antiferromagnetic order parameters. Further, the relation between magnetic and superconducting order remains unchanged in a magnetic field. A question raised by the results of Fig. 3 is what happens to the “missing” magnetic spectral weight in the elastic scattering channel below \(T_c\). One possibility is that it appears at finite frequencies in the form of a spin resonance.

Similar neutron diffraction experiments have been made on CeCu\(_2\)Si\(_2\) and Co-doped BaFe\(_2\)As\(_2\) in which antiferromagnetic order and superconductivity, with \(T_N > T_c\), arise in the same crystal. Results, especially on CeCu\(_2\)Si\(_2\), are qualitatively different from those plotted in Fig. 3. In CeCu\(_2\)Si\(_2\), elastic magnetic scattering intensity reaches a maximum at \(T_c\) below which it drops to zero, an indication that superconductivity expels magnetic order such that they do not coexist well below \(T_c\). On the other hand, elastic magnetic intensity in BaFe\(_{1.92}\)Co\(_{0.08}\)As\(_2\) decreases only by
about 6% below $T_c$, which is more similar to what is found in CeCo(T0.925Cd0.075)$_5$. In this sample of Co-doped \(\text{BaFe}_2\text{As}_2\), the “missing” elastic intensity reappears as an inelastic spin resonance. It remains to be seen if this also is the case in Cd-doped CeCoIn$_5$.

An analysis of NMR spectra of Cd-doped CeCoIn$_5$ is consistent with magnetism nucleating as droplets around Cd impurities.\(^{54}\) When the magnetic correlation length becomes of the order a few lattice spacings, as found in neutron diffraction, the droplets overlap neighboring Cd sites to form long range order. This view of inhomogeneous nucleation of magnetic order out of the anomalous normal state of CeCoIn$_5$ begs the corollary of how we should view the role of impurities in the superconducting state. In conventional s-wave superconductors, Abrikosov and Gor’kov showed that very small amounts of magnetic impurities break time-reversal symmetry of the phase-coherent superconducting condensate and globally suppress $T_c$ rapidly to zero; whereas, in d-wave superconductors non-magnetic impurities should behave as magnetic impurities in s-wave systems.\(^{57}\) A strikingly different interpretation has come from a thermodynamic analysis of the superconducting condensation energy of CeCoIn$_5$ doped with non-magnetic impurities, such as \(\text{Yb}^{2+}, \text{La}^{3+}, \text{Y}^{3+}\), and \(\text{Th}^{3+}\).\(^{58}\) This study suggests that impurities create an electronically inhomogeneous superconducting state, effectively “digging a hole” in the condensate and forming a normal state volume that grows precisely at the expense of a decreasing superconducting volume. A similar scenario has been proposed to account for the loss of superfluid density in Zn-doped \(\text{CeRhIn}_5\) (Color online) (a) Temperature-pressure phase diagram of CeRhIn$_5$. Red filled circles denote the Néel temperature below which incommensurate long-range order appears. Solid stars and filled blue circles are superconducting transition temperatures defined by resistivity ($\rho$) and heat capacity ($C_p$) measurements, respectively. The pressure $P$ is the point at which $T_N = T_c$ and above which there is no evidence for magnetic order in the absence of an applied magnetic field; whereas, $P_2$ is the pressure at which $T_N(P)$ extrapolates linearly to zero. The vertical line at $P_1$ is a guide to the eye. Data after ref. 64. (b) Elastic magnetic scattering intensity $I$ versus temperature for CeRhIn$_5$ at 1.48 GPa. Open circles correspond to the onset of magnetic order at wavevector $Q_1$, and open triangles represent order at a slightly different wavevector $Q_2$. Data after ref. 66. Note that the resistively measured superconducting temperature $T_c(P)$ appears once there is scattering at $Q_2$. Bulk superconductivity $T_c[C_1]$, measured by specific heat, correlates with the disappearance of scattering at $Q_1$.

2.2 CeRhIn$_5$

Under ambient conditions, CeRhIn$_5$ orders antiferromagnetically at 3.8 K with an ordered moment of $\sim 0.8 \mu_B$ that lies in the basal plane and spirals along the c-axis with $Q = (1/2, 1/2, 0.297)$.\(^{60}\) Application of pressure produces a non-monotonic variation in $T_N(P)$ and induces bulk superconductivity near 0.6 GPa where $T_N$ reaches a maximum. With increasing pressure, $T_N$ decreases, $T_c$ increases and they meet at $P_1 \approx 1.75$ GPa. Above $P_1$ evidence for magnetic order disappears and only superconductivity remains with a maximum $T_c$ of $\sim 2.3$ K.\(^{61,62}\) Consequently, evidence for a potential magnetic quantum-critical point is hidden by superconductivity. In the pressure range below $P_1$, NMR experiments are consistent with microscopic coexistence of long-range antiferromagnetic order and unconventional superconductivity.\(^{63}\) At $T < T_c(P)$, field-angle-dependent specific heat measurements show the same four-fold modulation when a magnetic field is rotated in the basal plane for pressures greater and less than $P_1$, which indicates that the coexisting antiferromagnetic does not influence the d-wave gap symmetry.\(^{64}\)

Once magnetic order disappears, the superconducting transition at $P \geq P_1$ is sharp and coincident in both specific heat and electrical resistivity measurements; however, for $P \leq P_1$, the resistively measured $T_c$ is higher than the bulk $T_c$ from specific heat and this difference grows with decreasing pressures.\(^{65}\) These differences are illustrated in Fig. 4(a). Results of neutron diffraction experiments, plotted in Fig. 4(b), suggest a possible origin for this difference.\(^{66}\) On cooling initially below $T_N$, magnetic scattering intensity appears at $Q_1$, which is associated with the propagation wavevector at ambient pressure, but with further cooling, intensity at $Q_1$ begins to decrease and scattering grows at a slightly different $Q_2$. The temperature at which scattering
becomes finite at $Q_2$ corresponds to the onset of a resistive transition to superconductivity; whereas, a bulk transition to superconductivity occurs at the temperature where scattering at $Q_1$ vanishes.

Theoretical calculations show that the incommensurate $c$-axis spiral in CeRhIn$_5$ is stabilized by an energy gain of only about 0.15 meV ($\sim$1.6 K).$^{[67]}$ Consequently, a change in ordering wavevector with decreasing temperature might not be surprising nor should it be a surprise that conclusions about the precise nature of magnetic order in CeRhIn$_5$ appear to depend sensitively on sample and/or pressure environment.$^{[68–70]}$ Additional neutron diffraction studies at other pressures and under as-close-as-possible hydrostatic conditions would be useful to establish more definitively the apparent correlation between a change in magnetic structure and onset of bulk superconductivity. Assuming this correlation is supported, these results imply a coupling between magnetism and superconductivity and raise the question of whether the change in magnetic structure is allowing bulk superconductivity or whether superconducting correlations are driving the change in magnetic structure. From existing data, there appears to be little or no “missing” elastic intensity below the bulk $T_c$, which is contrary to results on Cd-doped CeCoIn$_5$$^{[52]}$ as well as on CeCu$_2$Si$_2$$^{[55]}$ and Co-doped BaFe$_2$As$_2$$^{[56]}$ and could imply the absence of an inelastic spin resonance. On the other hand, a $T^3$ dependence of the spin relaxation rate$^{[63]}$ and four-fold modulation of field-angle specific heat$^{[64]}$ are consistent with a d-wave gap, in which case a resonance is expected. Extending neutron experiments to temperatures much lower than the pressure-induced bulk $T_c$ would be worthwhile.

Before discussing the relationship between superconductivity and quantum criticality, it is useful to comment on what is known about the nature of magnetic order and the Ce-4f configuration in CeRhIn$_5$. The relatively large ordered moment in CeRhIn$_5$ at atmospheric pressure is a substantial fraction of the moment expected (0.92 $\mu_B$) in the crystal-field doublet ground state of Ce$^{3+}$. This, together with a favorable comparison of de Haas–van Alphen frequencies to band structure calculations that assume the 4f electron of Ce is localized in the ionic core,$^{[71,72]}$ has led to the nomenclature of 4f-localized magnetic order. Relative to the much smaller ordered moment ($\approx 0.1 \mu_B$) in the spin-density-wave variant of CeCu$_2$Si$_2$,$^{[73]}$ the moment in CeRhIn$_5$ is indeed “large” but it does not arise from a strictly localized 4f electron. Hybridization of the 4f electron with ligand states is essential for producing the large Sommerfeld coefficient of CeRhIn$_5$ and an ordered moment reduced from that expected for a crystal-field doublet. Further, some (small) mixing of 4f and ligand states is necessary to account for the incommensurate $c$-axis spiral of the ordered moment.$^{[67]}$ Thus, a more realistic interpretation of the magnetism in CeRhIn$_5$ is that it arises from “nearly localized” 4f electrons that hybridize weakly with p,d band electrons to give a density of states at the Fermi energy with some 4f character. With applied pressure, the ordered moment decreases by $\sim 25\%$ as the critical pressure $P_1$ is approached, implying additional band mixing. At a higher pressure of $\sim 2.3$ GPa, de Haas–van Alphen frequencies jump sharply to larger values and the mass of electrons diverges.$^{[74]}$ This jump in dHvA frequencies is consistent with an increase in the Fermi volume due to more complete incorporation of 4f electrons and with an associated increase in Ce valence. Already, however, new dHvA frequencies appear for pressures $P_1 < P < 2.3$ GPa, suggesting a change in Fermi surface topology in this intermediate pressure region.$^{[74]}$ This change in electronic structure may be related to the observation of a reversal in upper critical field anisotropy: for $P < P_1$, $H_{c2} \parallel [100] > H_{c2} \parallel [001]$ but above $P_1$, $H_{c2} \parallel [100] < H_{c2} \parallel [001].$$^{[75,76]}$

As mentioned, once pressure exceeds $P_1$, evidence for magnetic order disappears; however, with an applied magnetic field, magnetic order reappears in the superconducting state.$^{[61,62]}$ The nature of the field-induced order remains undetermined. Unlike CeCoIn$_5$, the field-induced order [Fig. 5(a)] extends into the normal state above $H_{c2}(0, P > P_1)$, and so far there is no evidence for an FFLO-phase. At 0.35 K, the lowest temperature of these
specific heat measurement, there is a line of field-induced magnetic transitions in the superconducting state that extends from $P_1$ at $H = 0$ and terminates at $P_2 \approx 2.3$ GPa when $H = H_{c2}(0.35 \text{ K}, P_2)$, where $P_2$ is the critical pressure at which $T_N(P)$ extrapolates linearly to zero.\(^{61}\) Assuming the line of field-induced transitions persists at $T = 0$, then it defines a line of quantum phase transitions that end at a quantum tetracritical point $P_2$ where four phases meet: a phase of d-wave superconductivity coexisting with magnetic order, a purely d-wave superconducting state, a paramagnetic phase and an antiferromagnetically ordered phase. These relationships are illustrated in Fig. 5(b). A quantum tetracritical point revealed experimentally in CeRhIn$_5$ has been proposed theoretically to exist in the $T = 0$, field-doping phase diagram of the cuprates,\(^{77}\) but it has not been confirmed experimentally in that case nor in any other example.

Measurements of electrical resistivity with current flow parallel and perpendicular to the c-axis of CeRhIn$_5$ find that the resistivity just above $T_c(P)$ reaches a pronounced maximum at $P_2$, where it exceeds $20 \mu\Omega$ cm.\(^{78}\) The scattering rate inferred by this resistivity is larger than that at which superconductivity is suppressed completely in CeCoIn$_5$ by chemical substitutions.\(^{60}\) Instead of suppressing pressure-induced superconductivity in CeRhIn$_5$, strong scattering at $P_2$ coincides with a maximum in $T_c(P)$ and suggests that fluctuations emerging from the quantum-critical point at $P_2$ are responsible for strongly enhanced scattering and are beneficial to superconductivity.\(^{78}\)

The conventional view of a magnetic quantum-critical point, due to Hertz,Millis, and Moriya, is based on a quantum extension of the theory of classical phase transitions to include time as a relevant dimension.\(^{80}\) When the spin-density-wave transition is tuned by a non-thermal parameter to $T = 0$, hot spots on the Fermi surface spanned by the SDW wavevector produce long-range, long-lived fluctuations of the magnetic order parameter that dominate physical properties at finite temperatures, inducing distinctly non-Fermi-liquid temperature dependences. There is no discontinuity of the $T = 0$ Fermi volume upon tuning through the critical point and scattering from hot spots could lead to new anisotropy in resistivity. In contrast to these expectations of a conventional SDW-type quantum-phase transition, the Fermi volume of CeRhIn$_5$ appears to change discontinuously at $P_2$;\(^{79}\) there is no new anisotropy in resistivity at pressures around $P_2$;\(^{78}\) and, the temperature dependence of the resistivity over a broad range above $T_c(P_2)$ is weaker than predicted to arise from a $T = 0$ SDW transition.\(^{88}\) These observations and the nearly local-moment character of antiferromagnetism in CeRhIn$_5$ raise the possibility that quantum criticality at $P_2$ is not of the conventional type. Various alternatives include a form of local, Kondo destroying quantum criticality,\(^{61}\) a $T = 0$ selective Mott transition\(^{82}\) and a quantum valence transition.\(^{83}\) Model calculations of these alternative scenarios capture aspects of experimental observations on CeRhIn$_5$, and the first two models have been applied to account for quantum-critical properties of other heavy-fermion systems, such as CeCu$_{6-y}$Au$_y$ and YbRh$_2$Si$_2$.\(^{84}\) Unlike CeRhIn$_5$, however, neither of these other systems becomes superconducting, which can be understood within the related local or Mott-type models because both exclude a momentum-dependent divergence of magnetic fluctuations that favor d-wave superconductivity. Strictly, a valence transition is a local effect, and by this reasoning, associated valence fluctuations also should not favor pairing in a d-wave channel. As shown theoretically, however, critical valence fluctuations become “almost” local due to particle-particle scattering.\(^{85}\) The resulting pairing interaction is strongly repulsive on-site but attractive at near-neighbor sites, which is favorable for d-wave pairing. This model has been invoked to account for a second dome of pressure-induced superconductivity in CeCu$_2$Si$_2$. Besides providing a plausible mechanism for Cooper pairing, a pressure-induced valence transition would account for a first-order change in Fermi volume and strongly enhanced scattering at $P_2$.\(^{85}\)

In this regard, it should be noted that a Kondo-destroying quantum critical transition also predicts a sharp change in Fermi volume and strong fluctuations of the Fermi volume, between large and small or equivalently between non-integral and integral Ce valence states.\(^{86}\) Presently, experiments on CeRhIn$_5$ cannot distinguish between valence-driven or Kondo-destroying types of quantum-critical point at $P_2$. To help resolve this debate, it will be important to determine directly the pressure evolution of Ce’s valence and the nature of field-induced magnetic order. In any event, it seems clear that fluctuations emerging from the critical point at $P_2$ are connected intimately to the presence of pressure-induced superconductivity.

### 2.3 CeIrIn$_5$

Of the Ce115’s, CeIrIn$_5$ is least studied but just as interesting as other members. Like CeCoIn$_5$ and CeRhIn$_5$, superconductivity in CeIrIn$_5$ develops from a heavy-fermion normal state, and the specific heat jump at $T_c = 0.4$ K shows that bulk superconductivity arises from pairing of very heavy quasiparticles.\(^{13}\) Power-law temperature dependences of the specific heat, thermal conductivity\(^{34}\) and spin relaxation rate below $T_c$\(^{87}\) are consistent with d-wave superconductivity. On the other hand, anisotropy in thermal conductivity measurements, with heat flow parallel and perpendicular to the c-axis, would rule out a line of gap nodes along the c-axis and, instead, suggest a hybrid gap structure with a line of nodes in the basal plane and two point nodes along the c-axis, a gap structure also proposed for UPt$_3$.\(^{88}\) This conclusion, however, remains controversial. Subsequent superconducting penetration depth\(^{89}\) as well as field-angle-dependent thermal conductivity\(^{90}\) and specific heat measurements argue that the nodal topology is d-wave, specifically $d_{x^2-y^2}$.

Proper identification of the nodal gap structure, the nature of the normal state out of which superconductivity develops and the mechanism of Cooper pairing are interrelated issues. A peculiar property of CeIrIn$_5$ is that its bulk $T_c$ is $0.4$ K; whereas, the resistive transition temperature, though somewhat sample dependent, is robust and ranges between $\sim 1.2$ and $1.4$ K.\(^{13}\) Anisotropy in the critical fields $H_{c2}(T)$, determined by specific heat and resistivity, scale with the respective transition temperatures, suggesting that both transitions arise from a common underlying electronic structure. With applied pressure, the bulk $T_c$ increases and approaches the essentially pressure-independent resistive
transition temperature at a pressure of \( \sim 3 \) GPa above which \( T_c \) decreases.\(^{91-93}\) This pressure response, plotted in Fig. 6, is reminiscent of that in CeRhIn\(_5\), but in CeIrIn\(_5\) there is no long range magnetic order nor any other identified broken symmetry competing with superconductivity. Nevertheless, at atmospheric pressure, the nuclear spin relaxation rate \( 1/T_1^{\text{sp}} \) as well as longitudinal and transverse resistivities have non-Fermi-liquid temperature dependences\(^{94}\) and momentum-dependent spin damping \( \Gamma(Q) \) at low temperatures to \( T^{-3/2} \), \( T^{-3/4} \), and \( T^{3/2} \), respectively.\(^{34}\) These dependences are anticipated for proximity to a three-dimensional SDW quantum-critical transition.\(^{35,36}\) Field-dependent thermal conductivity measurements of Ce\(_2\)PdIn\(_8\) also suggest that its \( H_{c2}(0) \approx 6.8 \) T is about three times larger than the measured \( H_{c2} = 2.32 \) T at 50 mK.\(^{100}\) In CeCoIn\(_5\), although there is an even larger difference that has been established to arise from strong Pauli limiting, an associated first-order transition from Abrikosov to normal states, as illustrated in Fig. 2.\(^{39}\)

2.4 Related materials Ce\(_2\)PdIn\(_8\) and CePt\(_2\)In\(_7\)

Until recently, all \( n = 1, m = 1 \) and \( n = 2, m = 1 \) superconducting members of the family, including their Pu-based analogs,\(^{98,99}\) were formed with a transition metal from the Co column. This changed with the discovery of superconductivity in Ce\(_2\)PdIn\(_8\) with \( T_c = 0.68 \) K.\(^{100}\) Structurally, Ce\(_2\)PdIn\(_8\) is the same as other \( n = 2, m = 1 \) members, crystallizing with a double layer of Ce\(_2\)In\(_5\) separated by a single PdIn\(_2\) layer. So far, Ce\(_2\)PdIn\(_8\) has been studied relatively little, but it may share some characteristics in common with CeCoIn\(_5\). Both have a large initial slope of their upper critical field that would imply an orbitally derived \( H_{c2} \) considerably higher than the measured critical field. Specifically, for Ce\(_2\)PdIn\(_8\) the estimated orbital \( H_{c2}(0) \approx 6.8 \) T is about three times larger than the measured \( H_{c2} = 2.32 \) T at 50 mK.\(^{100}\) In CeCoIn\(_5\), there is an even larger difference that has been established to arise from a strong Pauli limiting, but these measurements need to be extended to lower temperature for a more definitive statement.\(^{100}\) Field-dependent thermal conductivity measurements of Ce\(_2\)PdIn\(_8\) also suggest that its \( H_{c2}(T) \) may be first order very near the \( T \approx 0 \) critical field.\(^{100}\) Whereas any evidence points to line nodes in the superconducting gap of CeCoIn\(_5\), this is less clear in Ce\(_2\)PdIn\(_8\). Zero-field thermal conductivity measurements find \( \kappa/T \sim T \) in a limited temperature range \( \sim 0.1T_c < T < \sim 0.3T_c \), which has been suggested to be evidence for a nodal gap, but these measurements need to be extended to lower temperature for a more definitive statement.\(^{100}\) Finally, in-plane resistivity measurements on Ce\(_2\)PdIn\(_8\) show that \( \rho(T) \) is linear in temperature from \( T_c \) to about 2 K. This dependence persists in magnetic fields below 2.3 T, above which \( \rho(T) \sim A T^2 \) with the \( T^2 \) coefficient decreasing with increasing field.\(^{100}\) The evolution of resistivity with temperature and
field is similar to that in CeCoIn$_5$\textsuperscript{24} and has been used to argue for a field-tuned quantum-critical point in Ce$_2$PdIn$_8$. With the recent availability of phase-pure single crystals of Ce$_2$PdIn$_8$, additional studies on this new member should clarify these issues as well as reveal more of its still hidden physics.

Like Ce$_2$PdIn$_8$, the newest member of the family CePt$_3$In$_7$ forms with an element from the Ni-column, but it is the first with $n = 1$, $m = 2$ member of the series.\textsuperscript{17} This compound has two transition metal–indium layers of PtIn$_2$ between each CeIn$_3$ layer and, as such, is crystallographically more anisotropic than the Ce115s. It also is electronically more anisotropic, which is borne out in de Haas–van Alphen measurements and band structure calculations that find five nearly cylindrical nested Fermi-surface sheets.\textsuperscript{101} A potential important distinction between CePt$_3$In$_7$ and others in the series is that its structure is body-centered I4/mmm; whereas, the $n = 1$, $m = 1$ and $n = 2$, $m = 1$ members crystallize in the primitive P4/mmm structure. This difference in structure can be viewed as a shift of alternating Ce-planes by half a lattice constant along [110].

At ambient pressure CePt$_3$In$_7$ orders antiferromagnetically at 5.4 K but develops only $\sim 0.3 R\ln 2$ entropy up to $T_N$, which suggests reduced ordered moments on the Ce in the antiferromagnetic state. Applying pressure to a polycrystalline sample induces a broad dome of superconductivity (Fig. 7) as in CeRhIn$_5$, with a maximum $T_c = 2.1$ K near 3.4 GPa where the Néel boundary extrapolates to $T = 0$.\textsuperscript{17} As also shown in Fig. 7, $T_N(P)$ is reproduced in a single crystal, but the onset of pressure-induced superconductivity is delayed until much higher pressures.\textsuperscript{102} Once pressure exceeds $\sim 3$ GPa, $T_c(P)$ is the same for polycrystal and single crystal samples. The different pressure dependences of $T_c$ when magnetic order is present indicates an interplay between magnetic order and superconductivity that is supported by NQR studies. Initial NQR measurements on a polycrystalline sample at ambient pressure reveal only commensurate antiferromagnetic order.\textsuperscript{103} On the other hand, NQR on a single crystal is consistent with incommensurate order coexisting with a small volume fraction of a commensurate phase; however, lightly grinding the crystals produces an NQR power pattern that was found in polycrystalline material, implying that the nature of magnetism and its relationship to superconductivity is strain dependent.\textsuperscript{104} Applying pressure to single crystals induces an increasing volume fraction of commensurate antiferromagnetism such that it is essentially 100% of the volume at 2.4 GPa, which may account for the near coincidence of $T_c(P)$ at this pressure for both polycrystal and single crystal samples. Extending these NQR measurements to higher pressures and lower temperatures will be important for establishing microscopic coexistence of magnetism and superconductivity as well as for indicating the gap symmetry of pressure-induced superconductivity.

It is not known if a magnetic field will induce magnetic order in the superconducting phase of CePt$_3$In$_7$ at pressures above 3 GPa, but, like CeRhIn$_5$, its residual resistivity and temperature coefficient $A$ of $\rho \sim AT^n$ peak sharply at a pressure where $T_N$ extrapolates to $T = 0$. These, combined with a decrease in the temperature exponent $n$ to a value close to unity at this pressure, would be consistent with a magnetic quantum-critical point near 3.4 GPa that is hidden by the dome of superconductivity.\textsuperscript{102}

It is interesting that the maximum $T_c$ of CePt$_3$In$_7$ is very close to the $T_c$ of CeCoIn$_5$ and CePdIn$_8$ under pressure. From a simple model of magnetically mediated superconductivity, we might expect that the stronger crystallographic and electronic two-dimensionality of CePt$_3$In$_7$ might lead to a higher $T_c$ than in the Ce115s.\textsuperscript{103} Of course, there are other factors, such as the extent of f–p,d hybridization and nature of the magnetic fluctuations, that also influence $T_c$. Unraveling these other factors and, indeed, establishing that superconductivity is magnetically mediated must await further study.

3. Summary and Perspective

The interesting questions which the detailed studies on the Ce115 materials address concern both the appropriate description of their quantum criticality and what the deep connections between magnetism and superconductivity really are. We actually know very little about this at present. It appears that more is involved than the simple competition between phases that characterizes the ternary moly-selenides, rhodium borides and nickel boro-carbides. The expansion of the materials phase space is particularly interesting, and holds the hope of ultimately understanding why heavy-fermion superconductivity occurs in one set of materials and not another and what limits the $T_c$’s so far to $\sim 2$ K for the Ce-based heavy fermions. The Pu-based heavy-fermion superconductors crystallizing in the same space group as the Ce115s approach $T_c$ of 20 K and offer promise of helping to answer these questions. In this regard, the recent discovery of superconductivity in the volume-expanded variant of PuCoGa$_5$, PuCoIn$_5$, has both proximity to magnetism and a much lower $T_c$ of $\sim 2.5$ K.\textsuperscript{106}

In the phase of coexisting superconductivity and magnetism in CeRhIn$_5$ and CePt$_3$In$_7$ as well as in Cd-doped CeCoIn$_5$, the resistively determined $T_c$ is always higher than that found in specific heat. But, once magnetism is suppressed by pressure, the resistive and bulk transitions coincide. Where data exist, these trends are found in other Ce-based heavy-fermion materials in which there is both
magnetism and superconductivity. Though there is no evidence for a coexisting broken symmetry in CeIrIn$_3$, its resistive and bulk $T_c$’s also merge at high pressure, suggesting that some competing electronic state is being suppressed. At face value, these observations imply a form of electronic inhomogeneity that also is deduced from an analysis of the condensation energy in chemically disordered CeCoIn$_5$ and other heavy-fermion superconductors. The possibility that electronic inhomogeneity might be a ubiquitous feature of strongly correlated superconductors merits some attention.

Acknowledgments

We thank the many collaborators at Los Alamos and elsewhere who have contributed invaluable to exposing the richness of Ce115s and related materials and who have shared their insights with us. Work at Los Alamos was performed under the auspices of the U.S. Department of Energy, Support from the DOE Office of Basic Energy Science, Division of Materials Sciences and Engineering (JDT) and from the National Science Foundation under grant NSF-DMR-0801253 (ZF) is gratefully acknowledged.

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