Specific heat in high magnetic fields and non-Fermi-liquid behavior in $CeMIn_5$ (M=Ir, Co)

J. S. Kim, J. Alwood, and G. R. Stewart
Department of Physics, University of Florida, Gainesville, Florida 32611-8440

J. L. Sarrao and J. D. Thompson
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 8 February 2001; revised manuscript received 14 May 2001; published 12 September 2001)

The low-temperature specific heat, in magnetic fields to 32 T, and the magnetic susceptibility are reported on single crystals of the new heavy-fermion superconductors $CeMIn_5$, M=Ir and Co, as well as the new heavy-fermion antiferromagnet $CeRhIn_5$. The absence of a pronounced field dependence to the specific heat of the Ir and Co systems suggests that the large Sommerfeld coefficients of these compounds are due to correspondingly large effective electron masses. In addition, the indicated non-Fermi-liquid behavior previously suggested from the temperature dependence of the resistivity of $CeIrIn_5$ has been confirmed in our measurements of the susceptibility and specific heat for this compound, as well as in the susceptibility and specific heat of $CeCoIn_5$. The existence of superconductivity in these systems that appears, based on their non-Fermi-liquid behavior, to develop near a quantum critical point is further support for this superconductivity being of unconventional nature.

DOI: 10.1103/PhysRevB.64.134524 PACS number(s): 71.10.Hf, 71.27.+a, 74.25.Bt, 74.70.Tx

I. INTRODUCTION

Recently, a family of heavy-fermion compounds has been discovered that crystallize in a layered, tetragonal structure[1] with chemical composition $CeMIn_5$, where M=Ir, Co, and Rh. Characteristic of heavy-fermion systems, each member exhibits a large Sommerfeld coefficient γ ($\equiv C/T$ as $T\rightarrow 0$) in the specific heat C. $CeIrIn_5$ (Ref. 2) and $CeCoIn_5$ (Ref. 3) are bulk superconductors with transition temperatures at T_c =0.4 and 2.3 K and normal-state values of γ $\approx$750 mJ/mol K^2 and $\approx$1200 mJ/mol K^2, respectively. $CeRhIn_5$ displays heavy-fermion antiferromagnetism with[4] T_N=3.8 K. A precise value of γ is difficult to establish unambiguously because of the Néel order, but a lower limit is approximately[5,6] 400 mJ/mol K^2.

There is a transition[2] in $CeIrIn_5$ to a zero-resistance state at 1.2 K that is significantly above the bulk T_c, as determined by specific heat and susceptibility, and the resistivity[2] varies as $\rho=\rho_0+AT^{1.3}$ up to 5 K (and down to 0.06 K in a magnetic field sufficient to suppress superconductivity). This non-Fermi-liquid (NFL)-like temperature dependence of the resistivity suggests that superconductivity in $CeIrIn_5$ develops near or at a quantum critical point, with associated spin fluctuations that are conducive to magnetically mediated Cooper pairing.[7] Additional evidence for unconventional superconductivity has been reported for M=Ir,[2,8] Co,[3,8] and Rh,[6,9] which is superconducting under pressure.[5]

The present work has two principal goals. First, specific-heat measurements in high (up to 32 T) magnetic fields provide information[10] on the heavy-fermion ground state as well as allowing an intercomparison[10,11] of the field response of other heavy-fermion systems. Second, the temperature dependences of the specific heat and low-field ($\leqslant$5 T) magnetization will be examined for non-Fermi-liquid behavior in light of the NFL behavior observed[2] in the resistivity of $CeIrIn_5$ and the indications[2,3,8,12] of unusual superconductivity observed in both $CeIrIn_5$ and $CeCoIn_5$. Typical of a Landau Fermi liquid are C/T and χ being constants as $T\rightarrow 0$ and the resistivity behaving as $\rho=\rho_0+AT^2$, independent of the strength of electron-electron interactions so long as the concept of a quasiparticle remains valid. Various theoretical models[13–15] for NFL behavior predict particular temperature dependences, e.g., $C/T\sim -\ln T$ or $C/T\sim\gamma-AT^{1/2}$. One problem with providing precise temperature dependences for C/T in these compounds is the large nuclear quadrupole moment of In, which splits otherwise degenerate nuclear energy levels and creates[3] a small low temperature (visible in our zero-field specific-heat data for $CeCoIn_5$ below 0.5 K) Schottky anomaly. Also, applying a magnetic field to suppress superconductivity splits nuclear magnetic-moment degenerate levels ($I=\frac{9}{2}$ in ln) which also will lead to a low-temperature Schottky anomaly. The applied field (5 T) necessary to suppress superconductivity in $CeIrIn_5$ and $CeCoIn_5$ causes a Schottky anomaly due to splitting of nuclear magnetic levels with approximately a 10% contribution to C/T at 0.3 K which must be subtracted in order to probe the temperature dependence of the electronic specific heat at low temperatures.

Last, the zero-field specific heats of these (differently prepared) samples of $CeMIn_5$ crystals will serve as a look at possible sample dependence in these materials, since sample dependence is certainly well known[11,16] and, in some cases, of crucial importance for understanding other heavy-fermion systems.

II. EXPERIMENT

Rather flat platelet crystals of up to 20 mm^2 were obtained in our sample preparation facility at the University of Florida by heating stoichiometric amounts of the component elements, but with a 50%-In excess (In flux method[17,18]), in an outgassed BeO crucible with lid, sealed under purified Ar in a Ta containment to 1200 °C. The Ce was from Ames Laboratory (purity 99.95%), the Ir was from Colonial Metals (purity 99.95%), while the Co, Rh, and In were from Johnson Mathey/Aesar and had purities of 99.9975, 99.95, and 99.9999%, respectively. The melt was then allowed to homogenize for 2 h, followed by a slow cool (10 °C/h) down to 600 °C (75 °C/h down to 750 °C, followed by 5 °C/h to 300 °C for $M=$Co), followed by reducing the furnace to room temperature at a cooling rate of 75 °C/h. Crystals were separated by heating the contents of the crucible to the melting point of In and then extracting individual crystals from the melt using a small soldering iron and tweezers. Excess In was removed from the crystal surfaces using an H_2O:HF:H_2O_2 4:1:1 etch; crystals after etching exhibited silvery, flat mirror surfaces. Due to the comparison (discussed later) of the specific heat jump at T_c with that in the discovery report,[2] some crystals of $CeIrIn_5$ were powdered and x-rayed. A slight, unidentified second phase constituting circa 5–10 % of the sample was detected; powder-diffraction experiments on crushed crystals grown at Los Alamos find no evidence for unidentified second phases to within the resolution of the data, which sets an upper limit of about 5% on second phase content.

The specific heat in fields to 13 T and down to 0.3 K was measured in house, while the specific heat to 32 T down to 1.4 K was measured at the NHMFL in Tallahassee using established[10,19] calorimetry techniques. The magnetization in fields up to 5 T and down to 1.8 K was measured in a Quantum Design superconducting quantum interference device (SQUID) magnetometer. Temperature dependences were analyzed for possible non-Fermi-liquid behavior following the analysis in a recent review.[13]

III. RESULTS AND DISCUSSION

A. $\gamma(B)$

The specific heats of single-crystal $CeMIn_5$ $M=$Ir, Co, and Rh are shown in Figs. 1–3 respectively, with the field aligned perpendicular to the platelet flat faces, i.e., perpendicular to the basal plane. (A somewhat different temperature dependence is found for $M=$Ir when a field of 6 T is applied in the basal plane and will be discussed in Sec. III B.) As shown in Fig. 1 for $CeIrIn_5$, a field of 13 T still results in C/T continuing to rise slightly (~6% from 2 K down to 1 K) with decreasing temperature, i.e., to show continuing development of the heavy-fermion ground state. In contrast, Fig. 2 for $M=$Co shows that a 13-T field effectively suppresses the heavy-fermion upturn (the data remain flat from 2 K down to 1 K) in C/T with decreasing temperature, as is the case[20] for $CeCu_6$. By 23 (20) T, C/T for $M=$Ir (Co) no longer shows a heavy-fermion upturn at low temperatures, but rather normal metallic behavior where $C/T=\gamma+\beta T^2$, with the second term due to the lattice specific heat and a γ that is still rather large. One sees in Figs. 1 and 2 that with increasing field the further suppression of γ ($\equiv C/T$ as $T\rightarrow 0$) is rather minimal, with $\gamma(28.5\ \mathrm{T})\sim 400\,(175)$ mJ/mol K^2 for $M=$Ir (Co). These 28.5-T results correspond to decreases in C/T at 1.5 K

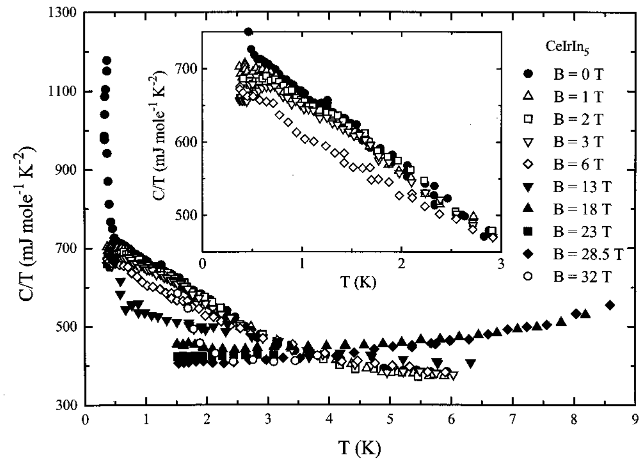

FIG. 1. Specific heat divided by temperature C/T vs temperature for single-crystal $CeIrIn_5$ at fields between 0 and 32 T, with field perpendicular to the basal plane. At zero field, the superconducting transition at 0.4 K is visible at the lowest temperatures. The data for fields above 13 T were taken down to 1.4 K at the NHMFL. The data below 0.7 K for $B=13$ T shown an upturn due primarily to the field splitting of the nuclear levels in In.

of ~33 and 52% for $M=$Ir (Co), respectively, compared to their zero-field values. Thus, at least in this sense, $CeIrIn_5$ and $CeCoIn_5$ are similar[10] to other Ce heavy fermion systems, which show suppression of the heavy-fermion upturn in C/T with decreasing temperature at comparable fields, while U-based heavy-fermion systems such as UBe_{13} and UPt_3 still show[21,22] increasing C/T values as $T\rightarrow 0$ in 30 T. This difference in field dependences of C/T in superconducting Ce- and U-based systems may be related to what happens below the Néel temperature of heavy-fermion antiferromagnets. In Ce systems, the large C/T above T_N is almost completely lost as $T\rightarrow 0$, but in U-based systems, typically one-

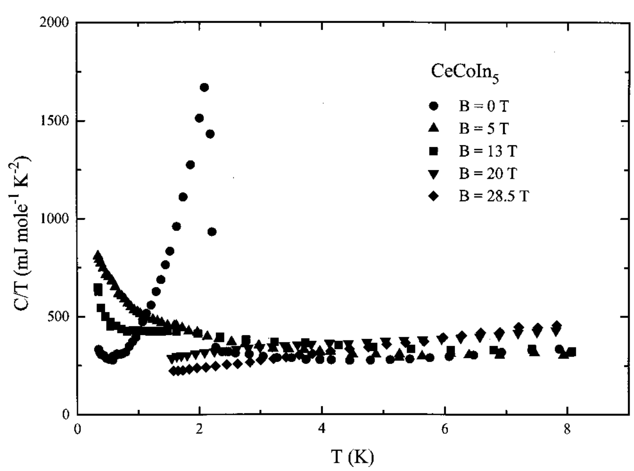

FIG. 2. Specific heat divided by temperature vs temperature for single-crystal $CeCoIn_5$ at fields between 0 and 28.5 T, with field perpendicular to the basal plane. The superconducting transition is clearly visible at 2.3 K. The sharp upturn in the 13-T data at the lowest temperatures is due to the field splitting of the nuclear levels in In and Co.

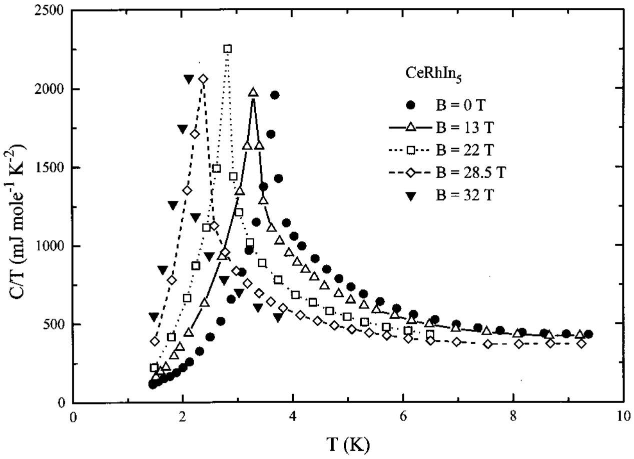

FIG. 3. Specific heat divided by temperature vs temperature for single-crystal $CeRhIn_5$ at fields between 0 and 32 T, with field perpendicular to the basal plane. The antiferromagnetic transition at 3.8 K decreases in temperature with applied field rather slowly. Note that the upturn in C/T with decreasing temperature for $T>T_N$ is still quite marked even in 32 T, as discussed in the text.

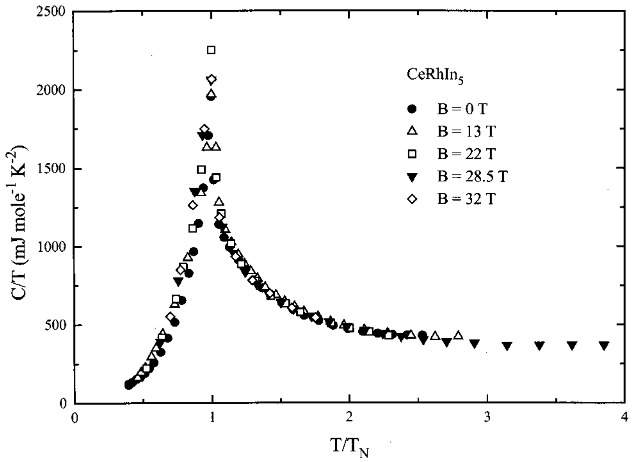

FIG. 4. Specific heat divided by temperature at various fields for $CeRhIn_5$, field perpendicular to the basal plane, plotted vs T/T_N, where T_N is the temperature of the antiferromagnetic transition in the particular field. This plot shows clearly that, as field suppresses the antiferromagnetic transition, the upturn in C/T with decreasing temperature scales precisely with T_N and therefore appears to be primarily associated with the antiferromagnetism. If the data above (below) T_N are investigated for power-law behavior following $C/T \sim 1/(|1-T/T_N|)^{\alpha}$, $\alpha \sim 2(0.3)$ for $T>(<)T_N$.

third of the high-temperature C/T survives to lowest temperatures.[11] The survival of such large γ values to 28.5 T for $CeIrIn_5$ and, to a lesser extent, $CeCoIn_5$ is strong evidence that these systems owe their large C/T values to large electron effective masses and not to magnetic correlations that strengthen with lower temperature and mimic the heavy-fermion upturn in C/T as $T \rightarrow 0$. As a comparison, γ in $CeCu_6$ decreases from 1600 mJ/mol K^2 in zero field to 500 mJ/mol K^2 in only 14.5 T.[23]

Considering now the field data, field aligned perpendicular to the basal plane, for $CeRhIn_5$ shown in Fig. 3, two things become clear. First, a magnetic field does not suppress T_N very rapidly. This weak-field dependence of T_N is somewhat surprising, even given[4] the small ordered moment $\mu_0 = 0.37\,\mu_B$ in $CeRhIn_5$. 30 T acting on this small moment corresponds (via $\mu_0 B = k_B T$) to approximately 7.5 K, which exceeds T_N by almost a factor of 2; however, Fig. 3 shows that T_N is depressed by less than 50% at 30 T. As a comparison, although most antiferromagnets show a much more rapid suppression of T_N with field, $CePd_2Si_2$ with[24] $T_N = 10$ K and a local moment of $0.7\mu_B$ shows[25] only a 30% suppression of T_N with the application of 29 T. Second, the strongly temperature-dependent C/T above T_N in zero field does not show a strong field dependence. Although it is often the case that a strong-field dependence in the upturn in C/T in a system is evidence that the upturn is due to magnetic correlations and not to the formation of a large m^* heavy fermion ground state [e.g., in $CeCu_6$ (Ref. 23) and in $UIn_{3-x}Sn_x$ (Ref. 26)], the inverse can be shown as follows not to be the case here.

One way to estimate how much of the C/T value at 4 K in $CeRhIn_5$ is due to a heavy fermion ground state forming as temperature is lowered below 10 K (as happens for $M = $ Ir and Co, see Figs. 1 and 2) is to do an entropy, *S*, calculation. One uses the *measured* C/T below some temperature above both the magnetic anomaly and any magnetic correlations extending above T_N (from Fig. 3, this would be roughly 8 K) to calculate the magnetic state entropy (=integral of $C/T\ dT$) at that temperature and, assuming the antiferromagnetic transition is second order, *extrapolates* the C/T data from above this temperature down to $T=0$, choosing as the intercept (i.e., C/T as $T \rightarrow 0$, or γ) the value that gives $S_{mag}(T) = S_{extrap}(T)$ for the chosen temperature T. Using a linear extrapolation from 8 K, this procedure gives a γ for $CeRhIn_5$ of less than roughly 750 mJ/mol K^2. This value implies that the lack of strong-field dependence in the strong upturn observed in C/T above T_N in $CeRhIn_5$ (Fig. 3) that already reaches $C/T = 1000$ mJ/mol K^2 at 4 K (and extrapolates to much higher values at $T=0$) is *not* a sign of a large electron effective mass. In order to compare the field dependence of this upturn above T_N in C/T with decreasing temperature in $CeRhIn_5$ with the field dependence of T_N itself, Fig. 4 shows the specific-heat data for all fields plotted versus a temperature scaled to the T_N for each respective field. As may be immediately seen, all the sets of data for fields up to 32 T lie essentially on a universal curve, i.e., the upturn above T_N in C/T appears to be largely associated with the magnetic order and not with a field-dependent m^*. Thus the expected effective mass in $CeRhIn_5$ should be related to a γ of less than or equal to 750 mJ/mol K^2 (i.e., like that of $CeIrIn_5$) and not the numbers in excess of 1500 mJ/mol K^2 that would come from extrapolating to $T=0$ the C/T just above T_N.

B. Possible NFL temperature dependence in *M* and *C/T*

Before beginning a discussion of possible evidence for NFL behavior in these materials, it is worthwhile to summarize briefly what might be expected and what might be believed. As mentioned in the Introduction, the temperature dependences of C/T, χ, and ρ as $T\rightarrow 0$ are expected to be qualitatively different for a NFL relative to those of a Landau Fermi liquid. A rather wide range of temperature dependences has been predicted in these properties in cases where NFL behavior arises from proximity to a quantum critical point, and there is experimental support for some of these predictions even to temperatures much higher than the expected validity of the theory.[13] In some cases, an "effective susceptibility" $1/\chi_{\mathrm{eff}}=(1/\chi-1/\chi_0)$, with χ_0 a system-specific parameter, also is analyzed for its temperature dependence. There, $1/\chi_{\mathrm{eff}}\propto T^{\alpha}$ and $\alpha<1$ is taken[27] as an indication of proximity to a quantum critical point, for which there is some theoretical justification.[27,28] As a note of caution, experimentally there can be complicating factors that make a direct comparison to theory ambiguous, e.g., the presence of low-lying crystal-field levels, a situation (perhaps as in the $\mathrm{CeMIn_5}$ family) where the electronic system is neither clearly two dimensional (2D) nor 3D, and inability to reach sufficiently low temperatures where theory is expected to be tested most critically. In this regard, specific-heat measurements[29] on the $\mathrm{CeMIn_5}$ family at temperatures much higher than shown here suggest that splitting between the crystal-field ground-state doublet and next higher doublet is on the order of 40–80 K in these materials. Further, as discussed below, there is a shoulder in the magnetic susceptibility of $\mathrm{CeIrIn_5}$ and $\mathrm{CeCoIn_5}$ near 40 K when a field is applied along the c axis (perpendicular to the basal plane). These shoulders appear to be due to crystal-field effects.[30] In the following, we discuss fits of C/T and χ to various functional forms anticipated by theory or found empirically in other materials thought to be NFL systems. Finally, besides proximity to a quantum critical point, another mechanism that can produce NFL behavior is hybridization disorder.[31] The electrical resistivities of the $\mathrm{CeMIn_5}$ family are small at low temperatures, of order one to a few $\mu\Omega$ cm, suggesting a high degree of crystalline order. Consequently, hybridization disorder effects should be minimal, and we do not consider this possibility further.

1. *CeIrIn*$_5$

The magnetic susceptibility, $\chi(\equiv M/B)$, versus temperature of $\mathrm{CeIrIn_5}$ for the two field directions is shown in Fig. 5. Considering first the low-temperature dependence for a field in the basal plane, the data can be fit by $\chi\sim\ln T$ only up to $\sim$6 K, and as $\chi\sim T^{-\alpha}$ also only in a similarly restricted temperature range (not shown). However, when the data are replotted as $1/\chi$ vs T in Fig. 6, it is apparent that a fit to the data that includes a constant term in $1/\chi$ matches the data rather well over a surprisingly large temperature range, with $\alpha\approx 0.84$. Such a dependence of $1/\chi$ $(=1/\chi_0+AT^{\alpha},\ \alpha<1)$ suggests[13,27,32,33] a local deviation from Fermi-liquid behavior, i.e., this is quite consistent with the observed[2] NFL behavior between 0.06 and 5 K in the resistivity. Quite similar behavior in $1/\chi$ is observed,[13] e.g., in the well-known NFL system $\mathrm{UCu_{3.5}Pd_{1.5}}$.

Considering now data obtained with a field perpendicular to the basal plane, the shoulder in $\chi(T)$ (see Fig. 5) prevents

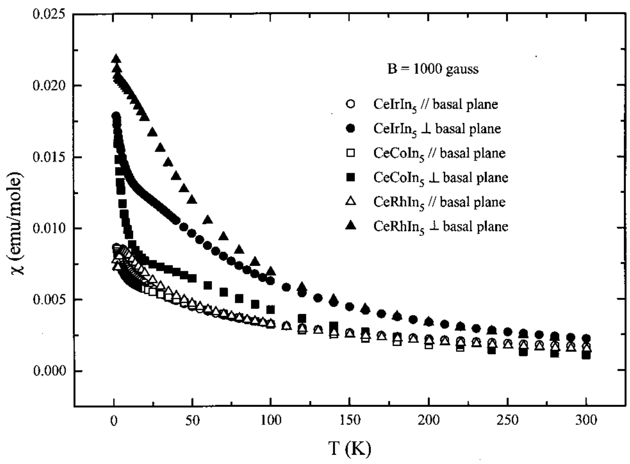

FIG. 5. Magnetic susceptibility χ vs temperature of single-crystal $\mathrm{Ce}M\mathrm{In_5}$, $M=\mathrm{Ir}$, Co, and Rh, with field in the basal plane (open symbols) and perpendicular to the basal plane (closed symbols). Note the shoulder feature in the latter direction which extends between about 15 and 40 K. Note also the similarity in the χ data for all three compounds for field in the basal plane.

a fit over a temperature range that includes 20–40 K to any particular temperature dependence, although up to about 15 K $1/\chi$ can be fit (not shown) to a constant term plus AT^{α}, with $\alpha\approx 0.33$. (If the temperature range of the fit shown in Fig. 6 for field in the basal plane is restricted to 1.8–15 K, the "best-fit" α is reduced from 0.84 to 0.61, i.e., the two directions give definitely different exponents.) χ for field perpendicular to the basal plane can also be, however, well-fit between 1.8 and 12 K to a $-\ln T$ temperature dependence (another well-known[13] NFL behavior). The limitation of the temperature range over which the data can be fit is known[13] to make a definitive determination of the temperature dependence difficult. If the $T>50$-K data are fit (not shown) for field perpendicular to the basal plane, $1/\chi=\mathrm{const}+T^{\alpha}$, α

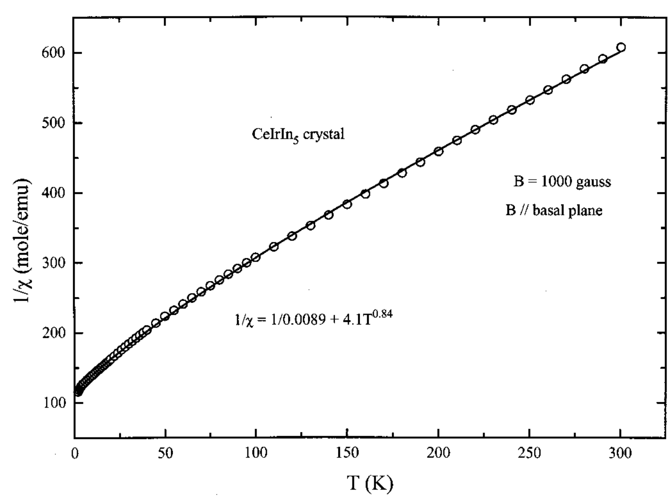

FIG. 6. Inverse magnetic susceptibility $1/\chi$ vs temperature for single-crystal $\mathrm{CeIrIn_5}$, field in the basal plane, showing that $1/\chi$ can be fit to a constant plus T^{α}, $\alpha=0.84$, over the whole temperature range of measurement.

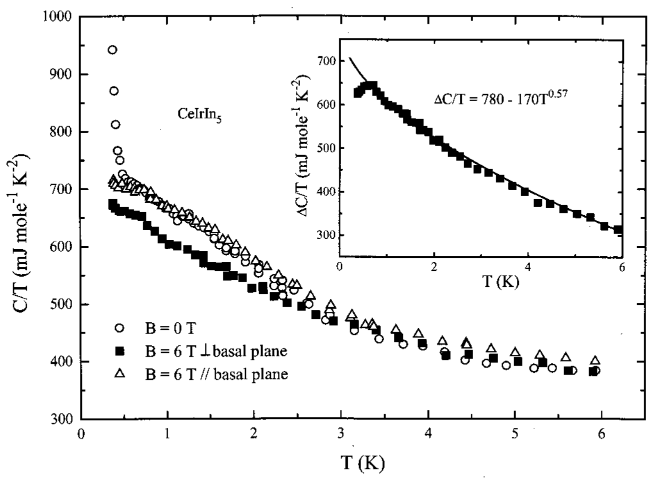

FIG. 7. Specific heat divided by temperature C/T vs temperature for single-crystal $CeIrIn_5$ in zero field and in 6 T in both field directions. For field parallel to the basal plane the quasilinear with temperature decrease in C/T above the superconducting transition persists to 6 T, while for field perpendicular to the basal plane the decrease in C/T in 6 T at low temperatures is qualitatively different. (Data for field in the basal plane in 3 T, not shown, also show the quasilinear with temperature decrease in C/T as seen in zero field and 6 T.) As shown in the inset, the 6-T data for field perpendicular to the basal plane, with the lattice and the nuclear Schottky contributions to the specific heat subtracted as discussed in the text, behave approximately (the best fit, represented by the solid line through the data gives an exponent of 0.57) as $\gamma_0 - AT^{1/2}$ over the decade in temperature between 0.6 and 6 K.

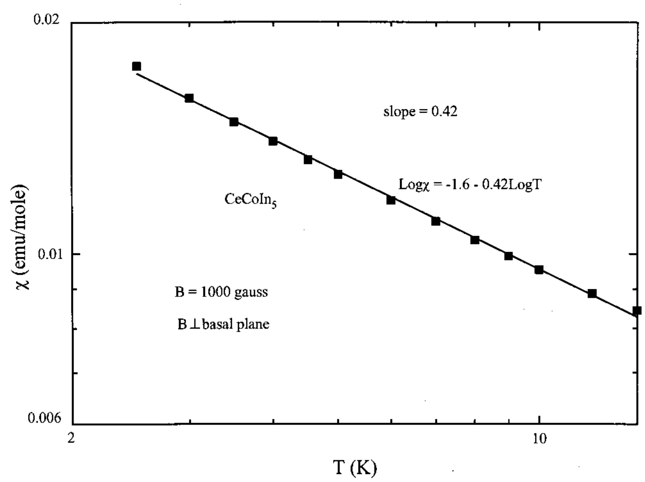

FIG. 8. The logarithm of the magnetic susceptibility vs log (temperature) for single-crystal $CeCoIn_5$, field perpendicular to the basal plane, showing a power-law temperature dependence $\chi = \chi_0 T^{-0.42}$ for temperatures up to where the shoulder in χ vs T starts, see Fig. 5.

$\sim$1.24. Although it is the low-temperature dependence of χ that must be known to investigate non-Fermi-liquid behavior, this fit to the higher temperature χ data serves to further strenghten the statement that the behavior in the two different field directions for χ in $CeIrIn_5$ is in fact different.

C/T for $CeIrIn_5$ in zero field and in 6 T with the field parallel to the basal plane (Fig. 7) can be fit in the temperature range $0.4 < T < 2.5$ K to γ-AT—certainly not a Fermi-liquid-like temperature dependence but one neither predicted theoretically nor of any particular uniqueness when compared to other heavy-fermion systems, such as UBe_{13}.[11] For field perpendicular to the basal plane, the $\Delta C/T$ data in 6 T shown in Fig. 7, where $\Delta C = C_{\text{measured}} - C_{\text{lattice}} - C_{\text{Schottky}}$ compare well between 0.6 and 6 K to the weak fluctuation NFL theory for three-dimensional antiferromagnetic fluctuations of Millis[14] and Moriya and Takimoto[15] where C/T is predicted to vary as $\gamma_0 - AT^{1/2}$; see Fig. 7 inset. C_{Schottky}, the nuclear magnetic moment and quadrupolar level splitting contributions[34] to the specific heat, decreases with increasing temperature as $1/T^3$ and is negligible above 0.6 K. The lattice contribution is obtained from fitting the 28.5-T data in Fig. 1 to the Debye model [$C/T = \gamma + \beta T^2$, with $\beta \propto 1/\Theta_D{}^3$] for the lattice specific heat, which gives $\beta \sim 1.98$ mJ/mol K^4 and a Debye temperature Θ_D of 190 K. At 6 K, the lattice contribution is $\sim$20% of the total specific heat, decreasing to $<$2% below 2.5 K. However, it should be stressed that the fit is not sensitive to the choice for Θ_D; if Θ_D is taken to be 230 K, the best-fit exponent changes to 0.50 instead of 0.57, and the standard deviation of the fit to the data over the decade of temperature between 0.6 and 6 K increases by only 10%. Thus, the $T^{1/2}$ temperature dependence does not depend critically on either what is used either for C_{lattice} or for C_{Schottky}. Below 0.6 K, as shown in the inset to Fig. 7, the substraction of the nuclear-magnetic-moment splitting in field and the quadrupolar level splitting[34] from C_{measured} causes the data to deviate from the fit.

Such NFL behavior in χ *and* C/T in superconducting $CeIrIn_5$, even though the temperature dependence seen in $C/T(\sim \gamma_0 - AT^{1/2})$ is more indicative of weak rather than strong magnetic interactions between the electrons, coupled with the already known[2] NFL behavior in ρ, strongly suggests[13,35] that $CeIrIn_5$ is near an antiferromagnetic quantum-critical point, as also implied[36] by spin-lattice relaxation studies.

2. $CeCoIn_5$

Considering now χ vs T for $CeCoIn_5$ (see Fig. 5), the data for field perpendicular to the basal plane differ from those for $CeIrIn_5$ both in magnitude and in temperature dependence, although both samples show a shoulder in χ vs T. Fitting these χ ($B\perp$ basal plane) data for $CeCoIn_5$ as shown in Fig. 8 in the temperature range below the shoulder, the best fit gives the NFL behavior $\chi = \chi_0 T^{-0.42}$—i.e., no constant term is needed. For field in the basal plane, neither a power law nor $\chi \sim -\ln T$ will fit the low-temperature χ data. Instead, Fig. 9 shows that—just as for $CeIrIn_5$—$1/\chi = \text{const} + AT^{\alpha}$, with the differences that the temperature range of this behavior is limited to low temperatures for $CeCoIn_5$ and $\alpha = 0.10$ rather than the value of 0.84 found for $CeIrIn_5$.

The 5-T C/T data (field$\perp$basal plane) for $CeCoIn_5$ between 0.35 and 8 K from Fig. 2 are replotted in Fig. 10 with a background subtraction ($= C_{\text{lattice}} + C_{\text{Schottky}}$) to show the temperature dependence of only the electronic contribution. As discussed above for $CeIrIn_5$, the lattice background sub-

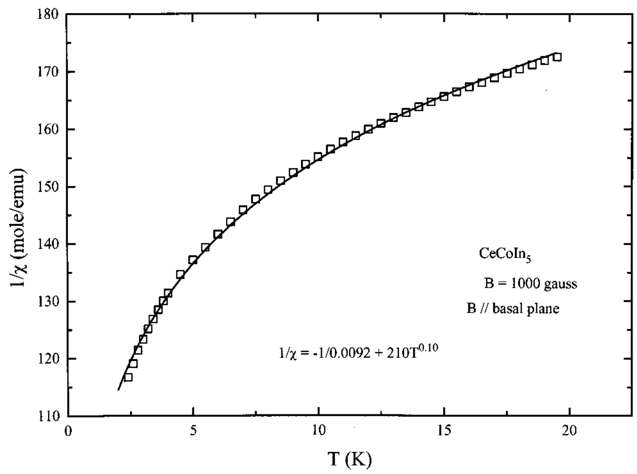

FIG. 9. Inverse magnetic susceptibility $1/\chi$ vs temperature for single-crystal $CeCoIn_5$, field in the basal plane, showing that $1/\chi$ can be fit to a constant plus T^{α}, $\alpha = 0.10$, in the low-temperature regime. A separate fit (not shown) to the data between 20 and 300 K show the same qualitative temperature dependence but with $\alpha = 1.4$. As seen in Fig. 5, the χ data for $CeCoIn_5$, field in the basal plane, show a change in slope at low temperatures (not seen in the comparable data for the same field direction for $CeIrIn_5$ and $CeRhIn_5$) that forces this separation for fitting into two temperature regimes.

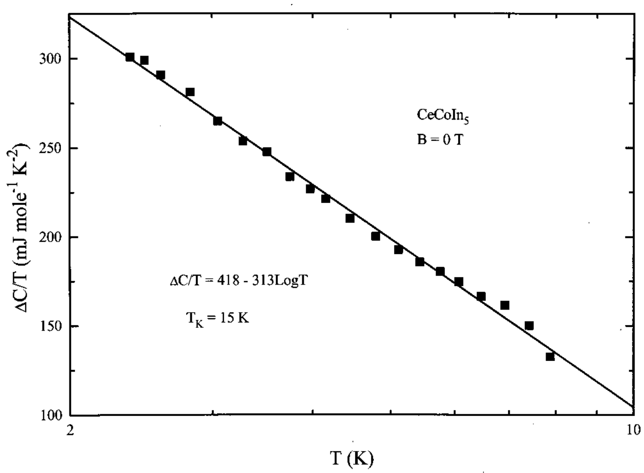

FIG. 11. Plotted is $\Delta C/T$, where $\Delta C = C_{\mathrm{measured}} - C_{\mathrm{lattice}}$ with $\Theta_D = 161$ K, in zero field above T_c in single-crystal $CeCoIn_5$ showing that $\Delta C/T \sim \ln T$ between 2.3 and 8 K.

traction is based on extracting the lattice term from the high- (28.5 T) field data for $CeCoIn_5$ in Fig. 2 where the upturn in C/T with decreasing temperature has been suppressed. The Debye temperature obtained from these high-field data was 161 K, which gives a lattice contribution $<10\%$ of C_{measured} up to 3.5 K, i.e., over a whole decade of temperature dependence starting at 0.35 K. It should be stressed that the $\Delta C/T \sim -\ln T$ temperature dependence seen in Fig. 10 is not strongly dependent on this assumption for the Debye temperature. For example, if Θ_D were 200 K for $CeCoIn_5$, the fit of $\Delta C/T$ to the $\ln T$ dependence (see Fig. 10) still looks convincing, although the standard deviation is larger by 50%. Also, the contribution[34] to C/T from the nuclear Schottky anomaly, which is $\sim$13% at the lowest temperatures, decreases with increasing temperature as $1/T^3$ so that the correction is already negligible by 0.6 K. The data clearly follow the canonical NFL behavior ($\Delta C/T \sim -\ln T$) observed[13] in over 50 NFL systems. The characteristic temperature T_0 calculated from[13] $(1/R)(d\ C/T/d\ln T) = -0.25/T_0$ (where R is the gas constant) is $\sim$11 K, which is consistent with the measured C/T value at 1.5 K of approximately 500 mJ/mol K^2.

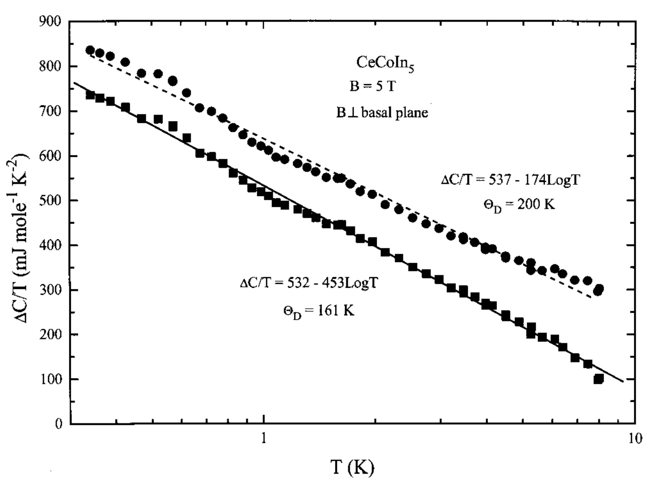

FIG. 10. Plotted is the difference ΔC between the measured data and the lattice background plus nuclear magnetic and quadrupole contributions, divided by temperature vs $\log T$ for single-crystal $CeCoIn_5$ for 5 T, field $\perp$ basal plane, for $\Theta_D = 161$ K (lower curve) and 200 K (upper curve, shifted by 100 mJ/mol K^2) showing that $\Delta C/T$ behaves as $-\ln T$ over more than a decade in temperature independently of the precise choice for the Debye temperature as discussed in the text.

One might ask, after learning of this result for the 5-T (field$\perp$basal plane) C/T data for $CeCoIn_5$ and upon inspection of Fig. 2, what about the temperature dependence of the *zero-field* C/T data above T_c? Using $\Theta_D = 161$ K from the fit to the 28.5-T data, $\Delta C/T$ in zero field above T_c is shown in Fig. 11 plotted vs $\log T$, where C_{measured} must only be corrected for C_{lattice} since C_{Schottky} is negligible in zero field above 0.5 K. The characteristic temperature T_0 is 15 K, which is comparable to the 5-T result. The 13-T data, corrected for C_{lattice} and C_{Schottky}, can also be fit to a $\ln T$ dependence (with $T_0 = 33$ K, i.e., out of sequence with the 0- and 5-T results) but—as may be inferred from Fig. 2—the $\Delta C/T$ data flatten out below 1.5 K.

We have also measured the specific heat of $CeCoIn_5$ for field in the basal plane (not shown). Unlike the perpendicular field direction, superconductivity is rather slowly suppressed[37] in the basal plane field direction in $CeCoIn_5$, with T_c in 9 T still $\sim$1.3 K. By 13 T, superconductivity has been suppressed below our lowest temperature of measurement (0.3 K). Correcting for a nuclear Schottky anomaly caused by field splitting of the nuclear magnetic moments below 1 K in 13 T, both the 9- and 13-T specific-heat data agree in their temperature range of overlap (1.3–8 K) and obey $C/T \sim -\ln T$ between 0.3 and 8 K, with the same T_0 as

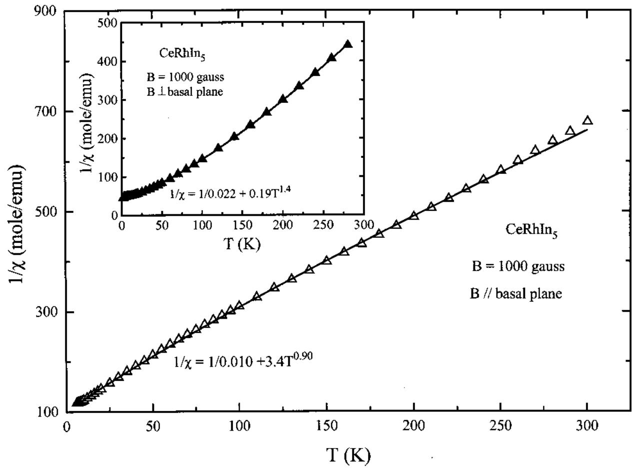

FIG. 12. Inverse magnetic susceptibility $1/\chi$ vs temperature for single-crystal $CeRhIn_5$, field in the basal plane, open symbols and field perpendicular to the basal plane, closed symbols show the $1/\chi=\mathrm{const}+T^{\alpha}$ behavior over almost the whole temperature range of measurement just as seen in Fig. 6 for field in the basal plane for $CeIrIn_5$. Note that for field perpendicular to the basal plane, $\alpha>1$ which is outside of the theory for local deviations from Fermi-liquid behavior.[27]

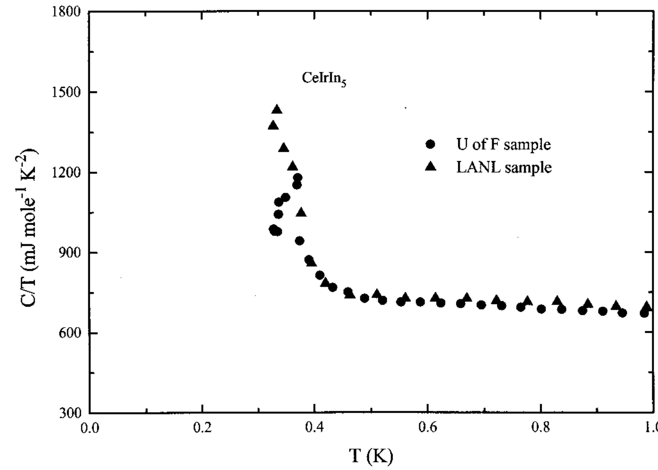

FIG. 13. Specific heat divided by temperature vs temperature for two different preparations of single-crystal $CeIrIn_5$ as discussed in the text. Note that C/T in the normal state is the same for both samples within our $\pm3\%$ error bar, while the jump ΔC at the superconducting transition is quite different for the two samples, arguing against a second phase explanation and rather for a significant sample dependence.

for the perpendicular field direction, i.e., just as for the field$\perp$basal plane data, $\ln T$ behavior over a range of about 5 T with approximately the same T_0 is observed.

This $C/T\sim-\ln T$ behavior is strong evidence for non-Fermi-liquid behavior arising from proximity to an antiferromagnetic quantum critical point.[36] Such a situation appears to be favorable for unconventional superconductivity, see, e.g., Refs. 13 and 35. In order to investigate further, it would be of interest to examine possible sources for magnetism in the phase diagram near in concentration to $CeCoIn_5$, as well as to investigate the specific heat to lower temperatures.

Concerning this latter point, low-temperature C/T data down to $\sim$0.15 K taken in 5 T and corrected for the Schottky anomaly were in fact presented in Ref. 3, although they were plotted versus temperature and not analyzed for $\ln T$ dependence. These data, except for some slight structure apparent at $\sim$0.27 K, appear to be consistent with the data in the present work as shown in Fig. 10.

3. $CeRhIn_5$

Susceptibility data for field in the basal plane above 4 K for $CeRhIn_5$ (see Fig. 5) fit the $1/\chi=1/\chi_0+AT^{\alpha}$ temperature dependence up to 250 K as shown in Fig. 12, very similar to the behavior shown in Fig. 6 for the same field direction for $CeIrIn_5$. For field in the other crystalline direction, $B\perp$ basal plane, the χ data for $CeRhIn_5$ also can be fit over a wide temperature range to $1/\chi=\mathrm{const}+AT^{\alpha}$, see inset to Fig. 12, just as found for field in the basal plane for $CeIrIn_5$ and $CeRhIn_5$, but in this case $\alpha>1$, which is outside of the theory[27] of a local deviation from Fermi-liquid behavior. Caution must be taken in interpreting these susceptibility results as being associated with NFL effects since, unlike the other cases, $CeRhIn_5$ is ordered magnetically and precisely how close it is to a quantum critical point requires further study.

The specific-heat data above T_N in 0 and 13 T can be fit (not shown) up to 10 K to $\Delta C/T\sim T^{\alpha}$, where ΔC is $C_{\mathrm{measured}}-C_{\mathrm{lattice}}$ and $\alpha\sim1.8$. Although $\Delta C/T\sim T^{\alpha}$ is not Fermi-liquid behavior, such a temperature dependence also is not characteristic[13] of systems classed as showing NFL behavior in their general properties. Measurements of the temperature dependence of C/T to lower temperatures (i.e., as shown in Fig. 3 in much higher fields than 32 T) would be required to make any definitive statement about NFL behavior in C/T in $CeRhIn_5$.

C. Sample dependence

Shown in Fig. 13 are specific-heat data for the sample of $CeIrIn_5$ prepared at the University of Florida (previously shown in Fig. 1), plus data for a sample made at Los Alamos National Laboratory. All data were taken at University of Florida to avoid any intercomparison errors due to absolute accuracy in the respective calorimeters (estimated from a comparison of Fig. 13 with data from Ref. 2 to be $\pm5\%$). The $\Delta C/\gamma T_c$ value for the sample prepared at the University of Florida is only about 65% of that prepared at Los Alamos National Laboratory. The bulk superconducting transition appears to have exactly the same onset temperature (certainly one of the significant sample variations observed[11] in, e.g., the heavy-fermion superconductor $CeCu_2Si_2$) in both samples and the transition width is somewhat sharper in the smaller $\Delta C/\gamma T_c$ sample. Because a narrow transition width and large ΔC are generally considered to be both indicative of sample quality, and because the phase purity of both

TABLE I. Temperature dependences of C/T and χ in $\mathrm{Ce}M\mathrm{In}_5$, $M=\mathrm{Ir}$, Co, Rh

C/T/Temperature range (K)	χ/Temperature range (K)
CeIrIn_5	
B in basal plane $\gamma_0 - AT$/0.4–2.5	$\chi^{-1}=\chi_0^{-1}+AT^{0.84}$/1.8–300[a]
$B\perp$ basal plane $\gamma_0 - AT^{1/2}$/0.3–6[a]	$\chi^{-1}=\chi_0^{-1}+AT^{0.33}$ or $\chi\sim -\ln T$/1.8–12[b]
CeCoIn_5	
B in basal plane $-\ln T$/0.3–8[a]	$\chi^{-1}=\chi_0^{-1}+AT^{0.10}$/1.8–20
$B\perp$ basal plane $-\ln T$/0.3–8[a]	$\chi=\chi_0 T^{-0.4}$/1.8–15[b]
CeRhIn_5	
B in basal plane $\sim T^{-1.8}$/4–10[a]	$\chi^{-1}=\chi_0^{-1}+AT^{0.90}$/4–250
$B\perp$ basal plane	$\chi^{-1}=\chi_0^{-1}+AT^{1.35}$/4–280[a]

[a]Highest temperature of measurement.

[b]The temperature range of the fit to χ is limited by a shoulder in χ at ~15 K.

samples is within 5–10 % of each other, this intercomparison of the superconducting transition is somewhat puzzling. In any case, there does seem to be significant variation in ΔC (both γ and T_c are, within error bars, identical) in CeIrIn_5, as has been seen, for example, strongly in UPt_3.[11,16] Measurements (not shown) of the resistive transition seen at ~1.2 K in the discovery work[2] in a crystal from the same batch of CeIrIn_5 as used here for the C and χ measurements find an onset temperature of 0.9 K—still well above the bulk T_c (C or χ)—and a much larger transition width than reported in Ref. 2, also indicating important sample dependence. In this regard, the resistivity ratio ρ (300 K)/ρ (2 K) of the crystal used in Ref. 2 was greater than 50; whereas, this ratio for the present crystal is about 22. Since the crystals in the present work had the excess In removed by etching, rather than by the centrifuge technique used in Ref. 2, this resistive transition being a spurious surface effect appears to be ruled out.

Comparing the superconducting transition in the specific heat for the sample made at the University of Florida of CeCoIn_5 shown in Fig. 2 with data[3,8] for the sample made at the Los Alamos National Laboratory, the onsets and the transition widths appear equivalent, and the ΔC values are only ~8% different.

Although samples of heavy-fermion antiferromagnets are not known[11] to be strongly sample dependent in their properties, for completeness the C/T data shown in the present work in Fig. 3 are compared here with the published[5] data. The onsets and the widths of the transitions are similar, with less than a 5% difference in the ΔC values.

IV. SUMMARY AND CONCLUSIONS

Specific-heat data in high magnetic fields on the heavy-fermion compounds $\mathrm{Ce}M\mathrm{In}_5$, $M=\mathrm{Ir}$, Co, and Rh, show that the electronic specific heat, proportional to the $dHvA$ measurable electron effective masses m^*, are relatively field independent in fields to 13 T and show a more metallic, $C/T=\mathrm{const}+\beta T^2$ behavior for $B\geqslant 20$ T for $M=\mathrm{Ir}$ and Co. These observations appear to be fully consistent with (and generalize results of) a recent $dHvA$ study[37] of CeIrIn_5 that finds the cyclotron mass of one particular hole orbit to decrease from $24m_0$ in fields of 9–11.7 T to $20m_0$ in 11.7–16.9 T. The rate of the suppression of γ with field for $M=\mathrm{Ir}$ and Co indicates large m^* values in zero field, with the values for CeRhIn_5, based on scaling of $C/T(B)$ to T/T_N (Fig. 4) as well as an entropy argument, being approximately like those found in CeIrIn_5.

The non-Fermi-liquid-like temperature dependences in the specific heat and susceptibility of $\mathrm{Ce}M\mathrm{In}_5$ for $M=\mathrm{Ir}$ and Co are strongly suggestive of NFL behavior in these compounds This evidence for NFL behavior, which argues for a nearby quantum-critical point in superconducting CeIrIn_5 and CeCoIn_5 and therefore for unconventional superconductivity, is summarized in Table I. Why C/T behaves as $\gamma_0 - AT^{1/2}$ (a temperature dependence associated[14–15] with weakly interacting spin fluctuations) in CeIrIn_5 for $B\perp$ basal plane and $-\ln T$ (a temperature dependence associated[13] with strong spin fluctuations) in CeCoIn_5 for both field directions may be connected to a fundamental difference in the fluctuation spectrum in the two compounds. Considering the speculations raised[2,3,8] about unconventional superconductivity in these two compounds, the fact that the Co compound, with its factor of 5 higher superconducting transition temperature, has stronger magnetic fluctuations as revealed by its NFL behavior in the specific heat than the Ir compound is certainly an interesting fact to consider. Concerning the NFL behavior reported here for the magnetic susceptibility, at present the status[13] of the theory for NFL behavior in χ is that the theory in still under development. It is tempting to draw conclusions based on the broad temperature range where NFL behavior is observed in the Ir compound, B in the basal plane, and possibly in both field directions in CeRhIn_5, but such conclusions require further theoretical understanding first, as well as further investigation of the possible cause(s) of the shoulder feature in χ. The theories[27,32,33] of a strong local deviation in Fermi-liquid behavior do appear to be consistent with our results. Further work on the NFL behavior of the resistivity in CeCoIn_5 and CeRhIn_5, as well as neutron-scattering investigation of the fluctuation spectra of all three $\mathrm{Ce}M\mathrm{In}_5$ compounds, are obviously of considerable interest.

Finally, it is worth noting that the combination of NFL behavior that is field and crystalline-direction dependent in $CeIrIn_5$, where for $B\perp$ basal plane $C/T=\gamma_0-AT^{1/2}$ *and* for B in the basal plane χ exhibits NFL behavior over a broad temperature range, is unique[13] among currently known NFL systems and—even without the excitement about possible unconventional superconductivity—makes this and its related compounds of extreme interest for further study.

ACKNOWLEDGMENTS

Work at the University of Florida was performed under the auspices of the U.S. Department of Energy, Contract No. DE-FG05-86ER45268. Work at Los Alamos was performed under the auspices of the U.S. Department of Energy. The authors gratefully acknowledge helpful conversations with P. Kumar, R. Movshovich, and Q. Si.

[1] E. G. Moshopoulou, Z. Fisk, J. L. Sarrao, and J. D. Thompson, J. Solid State Chem. **158**, 25 (2001).

[2] C. Petrovic, R. Movshovich, M. Jaime, P. G. Pagliuso, M. F. Hundley, J. L. Sarrao, Z. Fisk, and J. D. Thompson, Europhys. Lett. **53**, 354 (2001).

[3] C. Petrovic, P. G. Pagliuso, M. F. Hundley, R. Movshovich, J. L. Sarrao, J. D. Thompson, and Z. Fisk, J. Phys.: Condens. Matter **13**, L337 (2001).

[4] N. J. Curro, P. C. Hammel, P. G. Pagliuso, J. L. Sarrao, J. D. Thompson, and Z. Fisk, Phys. Rev. B **62**, 6100 (2000); W. Bao, P. G. Pagliuso, J. L. Sarrao, J. D. Thompson, Z. Fisk, J. W. Lynn, and R. W. Irwin, *ibid.* **62**, 14 621 (2000); **63**, 219901(E) (2001).

[5] H. Hegger, C. Petrovic, E. G. Moshopoulou, M. F. Hundley, J. L. Sarrao, Z. Fisk, and J. D. Thompson, Phys. Rev. Lett. **84**, 4986 (2000).

[6] R. A. Fisher, F. Bouquet, N. E. Phillips, M. F. Hundley, P. G. Pagliuso, J. L. Sarrao, Z. Fisk, and J. D. Thompson (unpublished).

[7] N. D. Mathur, F. M. Grosche, S. R. Julian, I. R. Walker, D. M. Freye, R. K. W. Haselwimmer, and G. G. Lonzarich, Nature (London) **94**, 39 (1998).

[8] R. Movshovich, M. Jaime, J. D. Thompson, C. Petrovic, Z. Fisk, P. G. Pagliuso, and J. L. Sarrao, Phys. Rev. Lett. **86**, 5152 (2001).

[9] J. D. Thompson, R. Movshovich, Z. Fisk, F. Bouquet, N. J. Curro, R. A. Fisher, P. C. Hammel, H. Hegger, M. F. Hundley, M. Jaime, P. G. Pagliuso, C. Petrovic, N. E. Phillips, and J. L. Sarrao, J. Magn. Magn. Mater **266**, 5 (2001).

[10] B. Andraka, G. Fraunberger, J. S. Kim, C. Quitmann, and G. R. Stewart, Phys. Rev. B **39**, 6420 (1989).

[11] G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).

[12] P. G. Pagliuso, C. Petrovic, R. Movshovich, D. Hall, M. F. Hundley, J. L. Sarrao, J. D. Thompson, and Z. Fisk, Phys. Rev. B **64**, 100503(R) (2001).

[13] G. R. Stewart (unpublished).

[14] A. Millis, Phys. Rev. B **48**, 7183 (1993).

[15] T. Moriya and T. Takimoto, J. Phys. Soc. Jpn. **64**, 960 (1995).

[16] N. Grewe and F. Steglich, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (Elsevier, Amsterdam, 1990), Vol. 14, p. 343.

[17] P. C. Canfield and Z. Fisk, Philos. Mag. B **65**, 1117 (1992).

[18] J. Remeika and Z. Fisk, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneider, Jr. and L. Eyring (Elsevier, Amsterdam, 1989), Vol. 12, p. 53.

[19] G. R. Stewart, Rev. Sci. Instrum. **54**, 1 (1983).

[20] A. Edelstein, B. N. Das, W. W. Fuller, B. Andraka, and G. R. Stewart, Physica B **163**, 504 (1990).

[21] J. S. Kim and G. R. Stewart (unpublished).

[22] J. S. Kim, D. Hall, K. Heuser, and G. R. Stewart, Solid State Commun. **114**, 413 (2000).

[23] G. R. Stewart, B. Andraka, C. Quitmann, B. Treadway, Y. Shapira, and E. J. McNiff, Jr., Phys. Rev. B **37**, 3344 (1988).

[24] F. M. Grosche, S. R. Julian, N. D. Mathur, and G. G. Lonzarich, Physica B **223&224**, 50 (1996).

[25] K. Heuser, J. S. Kim, E.-W. Scheidt, T. Schreiner, and G. R. Stewart, Physica B **259–261**, 392 (1999).

[26] L. W. Zhou, C. L. Lin, J. E. Crow, S. Bloom, R. P. Guertin, S. Foner, and G. R. Stewart, Physica B & C **135B**, 99 (1985).

[27] Q. Si, S. Rabello, K. Ingersent, and J. L. Smith cond-mat/0011477 (unpublished).

[28] A. Schröder, G. Aeppli, E. Bucher, R. Ramazashvili, and P. Coleman, Phys. Rev. Lett. **80**, 5623 (1998).

[29] P. G. Pagliuso (unpublished).

[30] N. J. Curro, B. Simonvic, P. C. Hammel, P. G. Pagliuso, G. B. Martins, J. L. Sarrao, and J. D. Thompson, cond-mat/0105175 (unpublished).

[31] O. O. Bernal, D. E. MacLaughlin, H. G. Lukefar, and B. Andraka, Phys. Rev. Lett. **75**, 2023 (1995).

[32] P. Coleman, Physica B **259–261**, 353 (1999).

[33] Q. Si, J. L. Smith, and K. Ingersent, Int. J. Mod. Phys. B **13**, 2331 (1999).

[34] The contribution of the nuclear quadrupolar splitting to the low-temperature specific heat, which is negligible in our measured temperature range, was communicated to us by R. Movshovich and is calculated from NQR data from N. Curro (unpublished; see also Ref. 4 for data for $CeRhIn_5$) and is the same as used for Refs. 2 and 8. The contribution of the splitting of the nuclear magnetic moment levels by an applied magnetic field, which is *almost* negligible in our measured temperature range, was calculated from fits to the low-temperature specific-heat data in field by R. Movshovich and was communicated to us by him.

[35] S. S. Saxena, P. Agarwal, K. Ahilan, F. M. Grosche, R. K. W. Haselwimmer, M. J. Steiner, E. Pugh, I. R. Walker, S. R. Julian, P. Monthoux, G. G. Lonzarich, A. Huxley, I. Sheikin, D. Braithwaite, and J. Flouquet, Nature (London) **406**, 587 (2000).

[36] Y. Kohori, Y. Yamato, Y. Iwamoto, T. Kohora, E. D. Bauer, M. B. Maple, and J. L. Sarrao (unpublished).

[37] Y. Haga, Y. Inada, H. Harima, K. Oikawa, M. Murakawa, H. Nakawaki, Y. Tokiwa, D. Aoki, H. Shishido, S. Ikeda, N. Watanabe, and Y. Onuki, Phys. Rev. B **63**, 060503 (2001).