Probing the superconductivity of PrPt$_4$Ge$_{12}$ through Ce substitution

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We report measurements of electrical resistivity, magnetic susceptibility, specific heat, and thermoelectric power on the system Pr$_{1-x}$Ce$_x$Pt$_4$Ge$_{12}$. Superconductivity is suppressed with increasing Ce concentration up to $x = 0.5$, above which there is no evidence for superconductivity down to 1.1 K. The Sommerfeld coefficient $\gamma$ increases with increasing $x$ from $\sim 48$ mJ/mol K$^2$ up to $\sim 120$ mJ/mol K$^2$ at $x = 0.5$, indicating an increase in strength of electronic correlations. The temperature dependence of the specific heat at low temperatures evolves from roughly $T^3$ for $x = 0$ to $e^{-\Delta/T}$ behavior for $x = 0.05$ and above, suggesting a crossover from a nodal to a nodeless superconducting energy gap or a transition from multiband to single band superconductivity. Fermi-liquid behavior is observed throughout the series in low temperature magnetization, specific heat, and electrical resistivity measurements.

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I. INTRODUCTION

Filled skutterudite compounds have been the focus of numerous studies due to the wide variety of strongly correlated electron behavior they exhibit, including Kondo lattice behavior, valence fluctuations, metal-insulator transitions, various magnetically ordered states, spin fluctuations, heavy fermion behavior, non-Fermi liquid behavior, conventional BCS-type and unconventional superconductivity as well as being promising candidates for thermoelectric applications. Filled skutterudites have the chemical formula $MT_xX_{12}$ where $M$ can be an alkali metal, alkaline earth, or rare-earth/actinide elements, $T =$ Fe, Os, or Ru, and $X =$ Sb, As, or P. One of the most notable filled skutterudite compounds is PrOs$_4$Sb$_{12}$, the first Pr-based heavy fermion superconductor ever reported (previously reported heavy fermion superconductors were Ce- or U-based compounds). The compound has an enormous electronic specific heat coefficient $\gamma$ of $\sim 500$ mJ/mol K$^2$. The specific heat jump at the superconducting critical temperature $T_c$ shows an unusual double peak feature as observed in numerous studies. Thermal transport measurements on single crystals carried out as a function of magnetic field direction revealed two different superconducting phases. At high fields (A-phase) the energy gap has four or more point nodes while the low field (B-phase) has two point nodes. High field measurements probing the normal state properties revealed the existence of a high field ordered phase which was determined by means of neutron diffraction experiments to be an antiferroquadrupolar ordered state.

A new class of filled skutterudites of the form $R$Pt$_4$Ge$_{12}$ has recently been synthesized, opening up an entirely new direction for filled skutterudite research. Several members of this new class exhibit superconductivity ($R = $ Sr, Ba, Th, La, Pr) where the $R = $ Pr member has one of the highest values of $T_c$ at $\sim 7.9$ K. Recent investigations have suggested that PrPt$_4$Ge$_{12}$ exhibits a type of strongly-coupled unconventional superconductivity that has point nodes in the energy gap and breaks time-reversal symmetry.

The Pr-based platinum germanide and osmium antimonide filled skutterudites exhibit a number of similarities and certain differences. Both compounds exhibit evidence for time-reversal symmetry breaking from muon-spin relaxation measurements. Experiments that probe the superconducting energy gap have yielded evidence for both nodal and nodeless energy gaps in both compounds. Transverse muon spin rotation (TF-$\mu$SR) experiments revealed a temperature dependence of the penetration depth $\lambda$ for PrOs$_4$Sb$_{12}$ that is consistent with an isotropic energy gap while an NQR study reported evidence that PrPt$_4$Ge$_{12}$ is a weakly-coupled BCS superconductor. However, for PrOs$_4$Sb$_{12}$ scanning tunneling microscopy observations measured a gap that was open in large regions, discounting the possibility of zero-field microwave penetration depth measurements revealed behavior best described with point nodes in the superconducting energy gap and small angle neutron scattering experiments reported distortions in the flux-line lattice that were attributed to gap nodes. Regarding PrPt$_4$Ge$_{12}$, transverse field $\mu$SR measurements were best fit by gap nodes. More recent studies also suggest that PrOs$_{11}$Sb$_{12}$ and PrPt$_4$Ge$_{12}$ are multiband superconductors. While both compounds have a $T_1$ singlet ground state, the splitting $\Delta_{CEF}$ between the ground and first excited states differs by an order of magnitude. For PrOs$_{11}$Sb$_{12}$, $\Delta_{CEF} \approx 7$ K while for PrPt$_4$Ge$_{12}$, $\Delta_{CEF} \approx 130$ K. Furthermore, while PrOs$_4$Sb$_{12}$ is a heavy fermion compound with an electronic specific heat coefficient $\gamma \sim 500$ mJ/mol K$^2$, the electronic correlations in PrPt$_4$Ge$_{12}$ are considerably weaker as reflected in a much smaller value of $\gamma \sim 60$ mJ/mol K$^2$.

In an effort to obtain more insight into the unconventional superconductivity of PrPt$_4$Ge$_{12}$, we have performed a detailed study of the evolution of the superconducting and normal state properties of PrPt$_4$Ge$_{12}$ when Ce ions are substituted into the filler sites for Pr ions. The objective of these experiments was...
to determine the relation between the superconducting properties and the magnetic state of the Ce ions inferred from the normal state properties of the Pr$_{1-x}$Ce$_x$Pt$_4$Ge$_{12}$ system as $x$ is varied. The resultant behavior of the superconducting properties as a function of substituent concentration are correlated with the magnetic state of the substituent ions which can lead to some extraordinary types of behavior. In the limit $T^* \ll T_{c_o}$, where $T^*$ is the characteristic temperature (e.g., Kondo or spin fluctuation temperature) and $T_{c_o}$ is the critical transition temperature of the host superconductor, it has been found that the $T_c$ vs $x$ curve can exhibit reentrant behavior wherein superconductivity that occurs below a certain $T_c$ is destroyed below a second lower $T_c$, whereas, in the limit $T^* \gg T_{c_o}$, the $T_c$ vs $x$ curve has an exponential shape.

In this paper, we report electrical resistivity, magnetization, specific heat, and thermopower measurements on the Pr$_{1-x}$Ce$_x$Pt$_4$Ge$_{12}$ system as a function of Ce concentration $x$ for $0 \leq x \leq 1$. Fermi liquid behavior was observed throughout the series and a monotonic suppression of $T_c$ with $x$ is observed up to $x = 0.5$, above which there is no evidence for superconductivity down to 1.1 K. Interestingly, specific heat measurements of the superconducting state suggest either a crossover from a nodal to a nodeless superconducting energy gap or that PrPt$_4$Ge$_{12}$ is a two band superconductor and scattering of electrons by substituted Ce ions suppresses the superconductivity associated with one of the bands.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of Pr$_{1-x}$Ce$_x$Pt$_4$Ge$_{12}$ with $x = 0$, 0.05, 0.06, 0.07, 0.085, 0.1, 0.14, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.625, 0.75, 0.875, and 1 were synthesized by arc melting in an Ar atmosphere on a water cooled copper hearth using a Zr getter to minimize oxidation. The starting materials were obtained from Ce rods (Alfa Aesar 3N, ESPi 3N), Pr ingots (Alfa Aesar 99.9%), Pt sponge (99.999+%), and Ge pieces (Alfa Aesar 99.999+%). The elements were weighed in stoichiometric ratios and then arc-melted, turned over, and arc-melted again a total of five times to promote chemical homogeneity. The samples were then annealed in a sealed quartz tube (containing 200 Torr Ar at room temperature) for 336 hours at 800 °C. To determine whether Ta foil was a necessary component during the annealing process, extra batches of $x = 0.06$ and 0.07 were annealed while wrapped in Ta foil. Powder x-ray diffraction (XRD) measurements showed no noticeable difference from the batches without Ta foil.

Sample quality was characterized through analysis of powder XRD patterns collected by a Bruker D8 x-ray diffractometer using a Cu Ka source. Four-wire electrical resistivity measurements were performed from 300 K to ~1.1 K in a pumped $^4$He cryostat and down to 50 mK using a commercial Oxford Kelvinox $^3$He-$^4$He dilution refrigerator. Magnetization measurements were performed between 300 K and 2 K in a Quantum Design MPMS equipped with a 7 T superconducting magnet. Specific heat and thermoelectric power measurements were performed down to 1.8 K using a PPMS DynaCool. The heat capacity measurement employed a standard thermal relaxation technique. To measure the thermoelectric power, we applied a static temperature gradient of $\Delta T/T = 2–5\%$, where the temperature $T$ was measured using commercial Cernox 1050 thermometers and a Lakeshore 340 Temperature Controller. Copper leads were attached to the sample with silver epoxy in a two-wire configuration. The DC thermoelectric voltage generated by the sample was measured using a Keithley 2182 Nanovoltmeter and was corrected for a background contribution arising from thermal/compositional asymmetry in the wires running from the external electronics at room temperature.

III. RESULTS

Rietveld refinements were performed on powder XRD patterns for each sample using GSAS$^{35}$ and EXPGUI$^{36}$. The cubic skutterudite crystal structure with space group $Im\bar{3}$ is observed over the entire range of $x$, consistent with expectations$^{22,34}$ A representative XRD pattern (for the $x = 0.5$ sample) is shown in Fig. 1 with the theoretical peak positions represented as ticks below the XRD pattern. The agreement between patterns and their refinement with the skutterudite crystal structure was excellent for all samples (fits not shown) with typical reduced $\chi^2$ values around 10. Some samples did show evidence for trace amounts of elemental Ge with impurity concentrations up to 3%, but were otherwise phase pure. Lattice parameters, $a$, obtained for the Pr and Ce parent compounds (inset in Fig. 1) agreed with previous studies$^{22,34}$ The observed systematic linear increase of $a$ with $x$ is consistent with Vegard’s law.
Electrical resistivity, $\rho(T)$, measurements performed in zero applied magnetic field are displayed for representative concentrations in Fig. 2. Data for some concentrations were omitted for the sake of visual clarity. A metallic temperature dependence for $\rho$ was observed for all $x$ as seen in Fig. 2. Significant curvature in $\rho(T)$, which is observed near 80 K for $x = 1$, is rapidly suppressed as Pr ions are substituted for Ce so that it is no longer observed for $x = 0.75$ (25% Pr). By diluting the Ce sub-lattice with Pr ions, which generally do not allow for strong hybridization between localized and itinerant electron states, the scattering contribution related to hybridization between Ce 4$f$ electron states and the conduction band is rapidly destroyed. Gentle curvature in $\rho(T)$ remains for $0 \leq x \leq 0.75$, which may be due to Mott-Jones "s-d" type scattering. Ce substitution suppresses and broadens the superconducting transition as highlighted in Fig. 3. The onset of superconductivity was observed in samples with concentrations up to $x \sim 0.5$. The critical temperatures, $T_c$, were identified as the temperature where $\rho$ drops to half its value in the normal state right above the superconducting transition.

At low temperatures where phonons are mostly frozen out, $\rho(T)$ is dominated by impurity and electron-electron scattering. As a result, the lattice contribution to the resistivity becomes negligible, reducing the behavior of $\rho(T)$ to the function: $\rho(T) = \rho_0 + AT^n$ where $\rho_0$ is the residual resistivity. For Fermi-liquids, $n = 2$, while for non-Fermi liquids, $n$ typically lies in the range $0.5 \leq n \leq 1.5$ but is usually close to 1. For Fermi liquid systems, $A$ is proportional to the square of the electronic specific heat coefficient ($\gamma^2$), which is in turn proportional to the square of the effective mass ($m^*^2$), and inversely proportional to the square of the Fermi temperature ($T_F^2$). For typical metals, $m^4$ is comparable to the mass of the free electron and, therefore, $T_F$ is quite large (e.g., for Cu, $T_F \sim 8 \times 10^3$ K). As a result, the magnitude of $A$ is sufficiently small to make it unfeasible to observe the $T^2$ term experimentally. However, in heavy fermion systems, the strong electronic correlations enhance the effective mass and, in turn, reduce the effective values of $T_F$ so that the $T^2$ term can be readily observed.

Figure 4(a) displays $\rho$ vs $T^2$, where the selected data sets were offset for clarity. The solid lines are least squares fits to the data with $\rho(T) = \rho_0 + AT^2$ from $T_c$ up to $T^2 \sim 250$ K$^2$. It should be noted that the samples with $x = 0.45, 0.625, 0.875$ were prepared at the same time and exhibited a higher porosity than other samples (30% less dense). For this reason, they were omitted from the power law analysis. Values for $A$, extracted from the fits, are displayed in Fig. 4(b) as a function of $x$. $A$ decreases with increasing $x$, from 5.3 n$\Omega$ cm$^2$/K$^2$ for $x = 0$ to a minimum at of $\sim 0.4$ n$\Omega$ cm$^2$/K$^2$ at $x = 0.5$, after- wards increasing to 6.3 n$\Omega$ cm$^2$/K$^2$ at $x = 1$. Fig. 4(c) displays values of $\rho_0$ extracted from the fits as a function of $x$, which increases with $x$ from 1.7 $\mu$\Omega cm at $x = 0$ to a maximum of 44 $\mu$\Omega cm at $x = 0.75$. A rapid drop occurs in $\rho_0$ at $x = 1$ down to $13 \mu$\Omega cm, which is expected because it is a non-substituted compound and has less disorder, making the overall trend resemble a weighted parabola. The discrepancy of $\rho_0$ for $x = 1$ with the values reported in Ref. 39 and Ref. 40 is most likely due to sample quality as the residual resistivity ratio of the previous work was an order of magnitude higher than in the current study.

Magnetization divided by magnetic field, $M/H$, is displayed as a function of temperature in Fig. 5. The measurements were performed in applied magnetic fields of $H = 1$ T except for the $x = 0$ and $x = 1$ end-member samples which were measured in $H = 0.5$ T. The magnitude of $M/H$ decreases with Ce concentration throughout the whole series. A broad maximum at $\sim 80$ K for $x = 1$ was also observed. Such
Weiss temperature in the temperature region 75 - 300 K to determine the Curie-sents complete flux expulsion by field-induced supercurrents. Nonetheless, the is the superconducting volume fraction such that

\[ \rho = \frac{\mu_0 M}{V} \]

is the density of the compound in units of mol/cm\(^3\). The superconducting volume fraction was estimated using the (ZFC) and field-cooled (FC) data deviated from one another.

The superconducting volume fraction achieved values slightly greater than 1, which may be attributed to demagnetization factor effects; nonetheless, the volume fractions are close to 1, indicating bulk superconductivity in this series.

The \( M/H \) data were fit to a Curie-Weiss law

\[ \frac{M}{H} = C_0/(T - \Theta_{CW}), \]

in the temperature region 75 - 300 K to determine the Curie-Weiss temperature \( \Theta_{CW} \) and average effective magnetic moment \( \mu_{eff} \) of the Pr and Ce ions (\( \mu_{eff} \) extracted from the Curie constant \( C_0 = \mu_{eff}^2 N_A/3k_B \), where \( N_A \) is the number of ions that carry magnetic moments and \( k_B \) is Boltzmann’s constant). The fits were applied to the \( H/M \) data with Eq. 1 using linear least squares regression. The resulting best fit values for \( \mu_{eff} \) and \( \Theta_{CW} \) are displayed in Fig. 5 as a function of \( x \). The Pr- and Ce-based end member compounds have effective magnetic moments of 3.69\( \mu_B \) and 2.69\( \mu_B \) per lanthanide, respectively, which are consistent with previously reported values. The Curie-Weiss temperature, \( \Theta_{CW} \), is nearly constant, the following relation can be used to estimate the expected values of \( \mu_{eff} \)

\[ \mu_{eff}(x) = \sqrt{(\mu_{Pr}^{3+})^2(1-x) + (\mu_{Ce}^{4+})^2(x)}, \]

assuming that \( \mu_{Pr}^{3+} \) and \( \mu_{Ce}^{4+} \) have free ion values calculated using Hund’s rules (3.58\( \mu_B \) and 2.54\( \mu_B \), respectively). The calculated effective magnetic moment \( \mu_{eff} \) decreases as a function of \( x \) with values (dashed line) that are close to the measured values (solid circles), as can be seen in Fig. 5a.

Isothermal magnetization measurements were performed at 2 K as a function of magnetic field (not shown) up to 7 T. Superconductivity was rapidly suppressed; above 1 T, only paramagnetism was observed. Upturns in \( M/H \) at low temperature, which may be due to small concentrations of paramagnetic impurities, are most prominent for the samples with \( x = 0.1 \) and 0.14. In order to obtain a rough estimate of the concentration of paramagnetic impurities in the samples, the impurities were assumed to be Gd which would be located at the lanthanide sites where Pr and Ce reside. This choice is arbitrary, and we could have chosen another lanthanide such as Ho or Er and Fe, which would occupy the Pt sites. Also, the resulting impurity concentration takes
into account impurities on all sites, rare earth or transition metal. The impurity concentration \(N/V\) was determined from Curie law fits to the low temperature upturn using the function \(N/V = 3C_0 k_B/(N_A\mu_{eff})^2\), where \(\mu_{eff}\) is the effective magnetic moment of Gd (7.94 \(\mu_B\)), and found to be 1 atomic % of the lanthanide ions (Pr or Ce). This estimate for the paramagnetic impurity concentration is consistent with values inferred from \(M(H)\) isotherms following a procedure described in Ref. [41].

Specific heat divided by temperature, \(C(T)/T\), data are shown in Fig. 7 where panel (a) displays data for concentrations where superconductivity was observed \((x \leq 0.2)\), while panel (b) displays data for \(x > 0.2\) for which there was no evidence for superconductivity. The superconducting critical temperature \(T_c\) was defined as the mid-point of the jump in \(C(T)/T\). Consistent with the electrical resistivity and magnetization data, the specific heat data show that superconductivity is suppressed with increasing Ce concentration. The values for \(T_c\) extracted from physical properties are addressed in the discussion section.

The electronic specific heat coefficient, \(\gamma\), and the coefficient of the phonon contribution, \(\beta\), were determined from linear fits of \(C/T\) vs \(T^2\) data with the equation \(C(T)/T = \gamma + \beta T^2\). The fits were performed from the lowest non-ordered temperature up to as far as linear fits were possible in \(C/T\) vs \(T^2\). As seen in Fig. 8(a), \(\gamma\) increases with \(x\) from 48 mJ/mol K\(^2\) for \(x = 0\) up to roughly 120 mJ/mol K\(^2\) for \(x = 0.5\), after which further substitution has a negligible effect on \(\gamma\) until \(x = 1\) where it decreases to 86 mJ/mol K\(^2\). Although this shows a moderate enhancement of \(\gamma\) with increasing \(x\), when compared to PrOs\(_x\)Sb\(_{12}\) \((\sim 500\) mJ/mol K\(^2\)), these \(\gamma\) values are relatively small. \(\gamma\) for the \(x = 0\) sample deviates from values previously reported \((87\) mJ/mol K\(^2\)) [23] yet this may be explained by the differing methods of determining \(\gamma\). The authors of Ref. [22] suppressed the superconducting region by applying a magnetic field and fitted the temperature region 3-10 K, while in this work the fit was performed on zero field measurements from 7-15 K. The Debye temperature, \(\Theta_D\), was calculated using the relation: \(\Theta_D = (1944 \times (n/\beta))^{1/3}\) K where \(n = 17\), the number of atoms in the formula unit. \(\Theta_D\) increases with increasing \(x\) for all values of \(x\) as seen in Fig. 8(b).

The electronic contribution to the specific heat, \(C_e\), was calculated by subtracting the phonon contribution \((\beta T^3)\) from \(C(T)\). Figure 9(a) shows \(\log(C_e/T_c)\) vs. \(T_c/T\) with data for each concentration offset for visual clarity. The lines in Fig. 9(a) represent best fits to the data with a fit range that extends roughly up to \(T_c/T = 2\). As can be seen for samples with \(x = 0.05\) to 0.1, the data are best fit by an exponential of the form \(ae^{-(\Delta T_c)/T}\), where \(a\) is a fitting parameter and \(\Delta\) is the superconducting energy gap. As seen in Fig. 9(b-c), the parameters \(a\) and \(\Delta T_c\) show no clear variation with Ce concentration within the scatter of the data; \(a\) ranges in value between 11 and 15, while \(\Delta T_c\) ranges from 2.9 to 3.5. However, \(\Delta T_c\) is consistently above the BCS prediction of 1.76, indicating that the superconductivity in this series is in the strong-coupling region. There are no data for \(a\) and \(\Delta T_c\) with \(x = 0\) since it was not possible to fit the \(C(T)\) data with the function \(ae^{-(\Delta T_c)/T}\). However, as seen in Fig. 9(a), fits to the function \(a(T_c/T)^n\) where \(n \approx -3.0\) yielded significantly better agreement for the \(x = 0\) sample. The change from power law behavior in the \(x = 0\) sample to exponential behavior in the substituted samples could be explained by a crossover in the superconducting energy gap from a point-node structure for PrPt\(_4\)Ge\(_{12}\) \((\sim T^3)\).
the superconducting energy bands with the smaller BCS electrons by substituted Ce ions). On the other hand, if PrPt

\[ S(T) \] is roughly 0 \( \mu \text{V/K} \) for the pure Pr compound in the superconducting state below \( T_c \), as emphasized in Fig. 10(b). Applying a 2 T magnetic field suppresses superconductivity and results in a finite value for \( S \). \( S \) changes sign near 21 K and slowly increases to a broad maximum of \( \sim 6.3 \) \( \mu \text{V/K} \) near 300 K. The low magnitudes of \( S(T) \) suggests that the electronic density of states for PrPt\(_4\)Ge\(_{12}\) may be predominantly flat in the vicinity of the Fermi energy \( \epsilon_F \).

For CePt\(_4\)Ge\(_{12}\), \( S(T) \) goes through a broad peak at approximately 80 K which is consistent with previous reports. However, the peak observed in this study has a higher magnitude, and the small feature at lower temperatures (\( \sim 20 \) K) is more clearly resolved than in previous studies. The presence of this shoulder-like feature on the large peak indicates that Ce is on the border between Kondo lattice (Ce\(^{3+}\)) and intermediate valence behaviors within the context of the theory of Zlatić and Monnier.

IV. DISCUSSION

Summarized in Fig. 11 is the evolution of \( T_c \) vs \( x \) from magnetization, electrical resistivity, and specific heat measurements. All three measurements are consistent with one another in showing that \( T_c \) is suppressed with increasing \( x \); most evident from electrical resistivity is the positive curvature in the suppression of \( T_c \) with \( x \). For electrical resistivity and specific heat, the midpoints of the transition were defined as \( T_c \), whereas for magnetization the splitting between ZFC and FC was used to determine \( T_c \). It would be interesting to compare the evolution of superconductivity due to Ce substitution in PrPt\(_4\)Ge\(_{12}\) to the behavior in PrOs\(_3\)Sb\(_{12}\); an investigation of the Pr\(_{1-x}\)Ce\(_x\)Os\(_3\)Sb\(_{12}\) system is, in fact, underway.

The experiments reported in this paper were undertaken in an effort to probe the nature of the unconventional superconducting state of PrPt\(_4\)Ge\(_{12}\) through the substitution of Ce ions. In conventional superconductors, it has been shown that the behavior of \( T_c \) as a function of the concentration of substituted ions depends sensitively on the magnetic state of the substituent ion. For Ce ions that are nearly trivalent, as is apparently the case in the Pr\(_{1-x}\)Ce\(_x\)Pt\(_4\)Ge\(_{12}\) system, the 4\( f \)-electron states of the Ce ions are hybridized with conduction electron states and are expected to generate a negative intratomic exchange interaction. The negative exchange interaction should produce a Kondo effect in which the magnetic state of the Ce substituent ion depends on the Kondo temperature \( T_K \), wherein the magnetic susceptibility exhibits magnetic behavior (Curie-Weiss behavior) for \( T \gg T_K \) and non-magnetic behavior (Pauli-like behavior) for \( T \ll T_K \).

In a conventional superconductor, \( T_c \) vs \( x \) changes from a curve with negative curvature that is reentrant in the limit \( T_K \ll T_{co} \), where \( T_{co} \) is the transition temperature of the superconducting host material (in this case PrPt\(_4\)Ge\(_{12}\)), to a curve with positive curvature and nearly exponential shape for \( T_K \gg T_{co} \). The rate of the initial depression of \( T_c \) with \( x \), \( -(dT_c/dx)_{x=0} \), exhibits a pronounced maximum when \( T_K \sim T_{co} \). The dependence of \( T_c \) on Ce concentration for Pr\(_{1-x}\)Ce\(_x\)Pt\(_4\)Ge\(_{12}\)
shown in Figure 11 has positive curvature; the initial linear depression of $T_c$ with $x$ extrapolates to 0 K at $x \sim 0.15$, whereas the nearly linear region at high $x$ extrapolates to 0 K at $x \sim 0.4$. To the extent that Ce ions break superconducting electron pairs in PrPt$_4$Ge$_{12}$, which is apparently an unconventional superconductor with nodes in the energy gap, the Kondo temperature would appear to be $T_K \sim 10^{-10^{-2}} T_{co} \sim 10^{-2}-10^{-3}$ K. Borkowski and Hirschfeld have made a self-consistent theory of Kondo impurities in gapless unconventional superconductors valid in the Fermi liquid regime $T < T_K$. However, since the specific heat in the superconducting state quickly develops an exponential shape at low concentrations of Ce, indicative of nodeless superconductivity, we compare our $T_c$ vs. $x$ curves to the theory of Muller-Hartmann and Zittartz, which was developed for Kondo impurities in conventional superconductors with nodeless energy gaps. From this comparison, we estimate that the ratio $T_K / T_{co}$ lies in the range 10 - 10$^2$, suggesting that $T_K$ lies in the range 10$^2$ - 10$^3$ K. For a Kondo temperature with this value, one would expect to observe a minimum in the electrical resistivity that is produced by the sum of the lattice contribution to the resistivity, which decreases with decreasing temperature, and the contribution due to the Kondo effect, which increases with decreasing temperature. Such a minimum in the electrical resistivity is seen in many dilute alloy systems consisting of a nonmagnetic host metal containing 3d transition metal impurity ions or certain 4$f$ lanthanide (e.g., Ce, Yb) and 5$f$ actinide (e.g., U) impurity ions in which the $f$-electron states are hybridized with conduction electron states. Examples include the La$_{1-x}$Ce$_x$Al$_2$ system which has a reentrant $T_c$ vs $x$ curve ($T_K \sim 0.1$ K, $T_{co} = 3.3$ K) and Th$_{1-x}$U$_x$ which has a nearly exponential $T_c$ vs $x$ curve ($T_K \sim 100$ K, $T_c = 1.4$ K). However, no resistivity minimum is observed in the Pr$_{1-x}$Ce$_x$Pt$_4$Ge$_{12}$ system, which could be due to the fact that the system is far beyond the single impurity limit. The interactions between the Pr and Ce ions may be sufficiently strong that the normal and superconducting states are determined by the cooperative behavior of the Pr and Ce ions in Pr$_{1-x}$Ce$_x$Pt$_4$Ge$_{12}$. Thus, it may be more appropriate to think about the gradual evolution of the Pr$_{1-x}$Ce$_x$Pt$_4$Ge$_{12}$ system with increasing $x$ towards CePt$_4$Ge$_{12}$, which is a nonsuperconducting Kondo lattice system with a very large Kondo temperature, which is consistent with the saturation of the magnetic susceptibility as $T \to 0$ K.
TABLE I: Comparison of known Pr$_{4}X_{12}$ superconducting skutterudite compounds and their characteristic properties.

| $T_c$ [K] | $\mu_{eff}$ [$\mu_B$] | $\gamma$ | $\Delta/k_BT_c$ | $\Theta_D$ [K] | $\Delta C/\gamma T_c$ [mJ/mol K] | References |
|-----------|-----------------|--------|-----------------|--------------|-------------------------|-----------|
| PrOs$_4$Sb$_{12}$ | 1.85 | 2.97 | $\sim$500 | 210 | $\sim$1.5 | 2.9, 50, 51 |
| PrRu$_4$Sb$_{12}$ | 1.05 | 3.58 | 59 | 1.53 | 232 | 1.87 | 9, 51, 52 |
| PrRu$_4$As$_{12}$ | 2.5 | 3.52 | 70 | 1.44 | 344 | 1.53 | 9, 53, 54 |
| PrPt$_4$Ge$_{12}$ | 7.9 | 3.59 | 87 | 2.35 | 198 | 1.56 | 22, 32, 34 |
| PrPt$_4$Ge$_{12}$ | 7.9 | 3.69 | 48 | 193 | 2.78 | This work |

In view of the unconventional superconductivity exhibited by PrPt$_4$Ge$_{12}$, it is interesting to compare this compound to other Pr based filled skutterudite compounds. Table I displays the characteristic parameters of known Pr-based superconducting skutterudites. The values of characteristic parameters appear to be very similar when comparing the properties among the majority of these skutterudites. The effective magnetic moment $\mu_{eff}$ remains close to the Hund’s rule prediction for the Pr free ion of 3.69$\mu_B$ except for PrOs$_4$Sb$_{12}$, for which $\mu_{eff} = 2.97\mu_B$. The electronic specific heat coefficient $\gamma$ is consistently below 100 mJ/mol K$^2$ with only PrOs$_4$Sb$_{12}$ having a significantly larger value of $\gamma \approx 600$ mJ/mol K$^2$.2, 20, 50, 51 The Debye temperature $\Theta_D$ exhibits values near 200 K except in PrRu$_4$As$_{12}$ with $\Theta_D = 344$ K.9, 53, 54 While many of the Pr-based skutterudites have values of $T_c$ between 1-2 K, PrPt$_4$Ge$_{12}$ is unique with $T_c = 7.9$ K. The ratio $\Delta/k_BT_c$ is also enhanced for PrPt$_4$Ge$_{12}$ relative to the other compounds, exhibiting values of approximately 2.3. It is interesting to observe that many of the properties of these Pr-based superconducting filled skutterudites are very similar, despite the different atomic cages within which the Pr ions reside.

Illustrated in Fig. 12(a) is the Kadowaki-Woods ratio $R_{KW} = A/\gamma^2$ as a function of $x$, where $A$ is derived from power law fits to $\rho(T)$ with $n = 2$. The samples of $x = 0.45, 0.625,$ and 0.875 are omitted as there was no $A$ value to calculate $R_{KW}$ with. Figure 12(b) displays the evolution of the Sommerfeld-Wilson ratio $R$ with $\omega$, where $R = (\pi^2 k_B^2/\mu_{eff})^2 \chi_0/\gamma$. The error bars of $R_{KW}$ and $R$ in Fig. 12 were propagated through in calculations from the errors bars of $A$, $\gamma$, and $\chi_0$ employing standard error analysis.26 For many f-electron based heavy fermion compounds, $R_{KW} = 1.0 \times 10^{-5} \mu \Omega$ cm(mol K mJ$^{-1}$)$^2$.57 However, a number of heavy fermion systems that have Fermi liquid characteristics exhibit values closer to $A/\gamma^2 = 1.0 \times 10^{-6}$, which can be explained by taking into account the degeneracy of the lanthanide ions.55 Fig. 12(a) displays $R_{KW}$ vs. $x$ where $R_{KW}$ decreases with increasing $x$, from $2.6 \times 10^{-6} \mu \Omega$ cm (mol K mJ$^{-1}$)$^2$ for $x = 0$ down to $0.05 \times 10^{-6} \mu \Omega$ cm (mol K mJ$^{-1}$)$^2$ for $x = 0.5$. $R_{KW}$ then increases to $0.85 \times 10^{-6} \mu \Omega$ cm (mol K mJ$^{-1}$)$^2$ for $x = 1$. For $x = 1$, $R_{KW}$ is comparable to the value reported by Gumieniuk et al.28 However, we were unable to find a reported value for $x = 0$. $R_{KW}$ stays in the range of $10^{-6}$, suggesting that Pr$_{1-x}$Ce$_x$Pt$_4$Ge$_{12}$ behaves similarly to other heavy fermion systems even with an only modestly enhanced $\gamma \sim 110$ mJ/mol K$^2$.

For the Sommerfeld-Wilson ratio, $R$, a value of 1 is expected for a free electron gas and a value of 2 for a Kondo system.26 In Fig. 12(b), $R$ decreases with increasing $x$ down to roughly 1 at $x = 1$, suggesting that the Ce parent compound behaves as a free electron system. The higher value for small $x$ may be due to magnetic exchange enhancement.

V. CONCLUDING REMARKS

A systematic study of the system Pr$_{1-x}$Ce$_x$Pt$_4$Ge$_{12}$ was performed by electrical resistivity, magnetization, specific heat, and thermopower measurements, where Fermi liquid behavior was observed throughout the series. We find that superconductivity is suppressed with increasing Ce with positive curvature up to $x = 0.5$, above which no evidence for superconductivity was observed down to 1.1 K. The Sommerfeld
coefficient $\gamma$ increases with Ce concentration, from 48 mJ/mol K$^2$ for $x = 0$ up to a maximum of 120 mJ/mol K$^2$ for $x = 0.5$, a signature of strengthened electronic correlations. Comparisons of the $C/T$ profile in the superconducting state shows that the $C(T)/T$ data are best described by a $T^3$ dependence for $x = 0$ and an $e^{-\Delta/T}$ dependence for $x \geq 0.05$. This may be explained by a crossover from a nodal to nodeless superconducting energy gap or the suppression from multiple to single BCS type superconducting energy bands with increasing Ce concentration.

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1 B. C. Sales, in *Handbook on the Physics and Chemistry of the Rare Earths*, edited by K. A. Gschneidner Jr., J.-C. Bünzli, and M.-A. Measson, D. Braithwaite, J. Flouquet, G. Seyfarth, J. P. Brison, E. Lhotel, C. Paulsen, H. Sugawara, and H. Sato, Phys. Rev. B 70, 064516 (2004).
2 K. Izawa, Y. Nakajima, J. Goryo, Y. Matsuda, S. Osaki, H. Sugawara, H. Sato, P. Thalmeier, and K. Maki, Phys. Rev. Lett. 90, 117001 (2003).
3 Y. Aoki, T. Namiki, S. Ohhaki, S. R. Saha, H. Sugawara, and H. Sato, J. Phys. Soc. Japan 71, suppl., 23 (2002).
4 D. E. MacLaughlin, J. E. Sonier, R. H. Heffner, O. O. Bernal, B.-L. Young, M. S. Rose, G. D. Morris, E. D. Bauer, T. D. Do, and M. B. Maple, Phys. Rev. B 65, 100506(R) (2002).
5 M. B. Maple, P.-C. Ho, V. S. Zapf, N. A. Frederick, E. D. Bauer, W. M. Yuhzas, F. M. Woodward, and J. W. Lynn, J. Phys. Soc. Japan 71, suppl., 23 (2002).
6 Y. Aoki, A. Tsuchiya, T. Kanayama, S. R. Saha, H. Sugawara, H. Sato, W. Higemoto, A. Koda, K. Ohishi, K. Nishiyama, et al., Phys. Rev. Lett. 91, 067003 (2003).
7 R. Vollmer, A. Faißt, C. Pfleiderer, H. v. Löhneysen, E. D. Bauer, P.-C. Ho, V. Zapf, and M. B. Maple, Phys. Rev. Lett. 90, 057001 (2003).
8 H. Suderow, S. Vieira, J. D. Strand, S. Bud’ko, and P. C. Canfield, Phys. Rev. B 69, 060504(R) (2004).
9 M. B. Maple, N. A. Frederick, P.-C. Ho, W. M. Yuhzas, T. A. Sayles, N. P. Butch, J. R. Jeffries, and B. J. Taylor, Physica B 359, 830 (2005).
10 M. B. Maple, Z. Henkie, W. M. Yuhzas, P.-C. Ho, T. Yanagisawa, T. A. Sayles, N. P. Butch, J. R. Jeffries, and A. Pietraszk, J. Magn. Magn. Mater. 310, 182 (2007).
11 H. Sato, Y. Aoki, D. Kikuchi, H. Sugawara, W. Higemoto, K. Ohishi, T. U. Ito, R. Heffner, S. R. Saha, A. Koda, et al., Physica B 404, 749 (2009).
12 B. C. Sales, D. Mandrus, and R. K. Williams, Science 272, 1325 (1996).
13 W. Jeitschko and D. Braun, Acta Cryst. B 33, 3401 (1977).
14 M.-A. Measson, D. Braithwaite, J. Flouquet, G. Seyfarth, J. P. Brison, E. Lhotel, C. Paulsen, H. Sugawara, and H. Sato, Phys. Rev. B 70, 064516 (2004).
15 K. Izawa, Y. Nakajima, J. Goryo, Y. Matsuda, S. Osaki, H. Sugawara, H. Sato, P. Thalmeier, and K. Maki, Phys. Rev. Lett. 90, 117001 (2003).
16 Y. Aoki, T. Namiki, S. Ohhaki, S. R. Saha, H. Sugawara, and H. Sato, J. Phys. Soc. Japan 71, 2098 (2002).
17 P.-C. Ho, V. S. Zapf, E. D. Bauer, N. A. Frederick, M. B. Maple, G. Giester, P. Rogl, S. T. Berger, C. H. Paul, and E. Bauer, Int. J. of Mod. Phys. B 16, 3008 (2002).
18 P.-C. Ho, N. A. Frederick, V. S. Zapf, E. D. Bauer, T. D. Do, M. B. Maple, A. D. Christianson, and A. H. Lacerda, Phys. Rev. B 67, 180508(R) (2003).
19 T. Tayama, T. Sakakibara, H. Sugawara, Y. Aoki, and H. Sato, J. Phys. Soc. Japan 72, 1516 (2003).
20 M. Kohgi, K. Iwasa, M. Nakajima, N. Metoki, S. Araki, N. Bernhoeft, J.-M. Mignot, A. Gukasov, H. Sato, Y. Aoki, et al., J. Phys. Soc. Japan 72, 1002 (2003).
21 E. Bauer, A. Grytsiv, X. Chen, N. Melnychenko-Kobylyuk, G. Hiltscher, H. Kaldarar, H. Michor, E. Royanian, G. Giester, M. Rotter, et al., Phys. Rev. Lett. 99, 217001 (2007).
22 R. Gumeniuk, W. Schnelle, H. Rosner, M. Nicklas, A. Leithe-Jasper, and Y. Grin, Phys. Rev. Lett. 100, 017002 (2008).
23 A. Maisuradze, M. Nicklas, R. Gumeniuk, C. Baines, W. Schnelle, H. Rosner, A. Leithe-Jasper, Y. Grin, and R. Khasanov, Phys. Rev. Lett. 103, 147002 (2009).
24 A. Maisuradze, W. Schnelle, R. Khasanov, R. Gumeniuk, M. Nicklas, H. Rosner, A. Leithe-Jasper, Y. Grin, A. Amato, and P. Thalmeier, Phys. Rev. B 82, 024524 (2010).
25 F. Kanetake, H. Mukuda, Y. Kitaoka, H. Sugawara, K. Magishi, K. M. Itoh, and E. E. Haller, Physica C 470, S703 (2010).
26 E. E. M. Chia, M. B. Salamon, H. Sugawara, and H. Sato, Phys. Rev. Lett. 91, 247003 (2003).
27 A. D. Huxley, M.-A. Measson, K. Izawa, C. D. Dewhurst, R. Cubitt, B. Grenier, H. Sugawara, J. Flouquet, Y. Matsuda, and H. Sato, Phys. Rev. Lett. 93, 187005 (2004).
28 G. Seyfarth, J. P. Brison, M.-A. Méasson, J. Flouquet, K. Izawa, Y. Matsuda, H. Sugawara, and H. Sato, Phys. Rev. Lett. 95, 107004 (2005).
29 G. Seyfarth, J. P. Brison, M.-A. Méasson, D. Braithwaite,
