Evolution of crystalline electric field effects, superconductivity, and heavy fermion behavior in the specific heat of

$$\text{Pr(Os}_{1-x}\text{Ru}_x\text{)}_4\text{Sb}_{12}$$

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Abstract

Specific heat $C(T)$ measurements were made on single crystals of the superconducting filled skutterudite series $\text{Pr(Os}_{1-x}\text{Ru}_x\text{)}_4\text{Sb}_{12}$ down to 0.6 K. Crystalline electric field fits in the normal state produced parameters which were in agreement with previous measurements. Bulk superconductivity was observed for all values of the Ru concentration $x$ with transition temperatures consistent with previous experiments, confirming a minimum in $T_c$ at $x = 0.6$. The $C(T)$ data below $T_c$ appear to be more consistent with power law behavior for $x = 0$ (PrOs$_4$Sb$_{12}$), and with exponential behavior for $0.05 \leq x \leq 0.2$. An enhanced electronic specific heat coefficient $\gamma$ was observed for $x \leq 0.4$, further supporting $x \simeq 0.6$ as a critical concentration where the physical properties abruptly change. Significant enhancement of $\Delta C/T_c$ above the weak coupling value was only observed for $x = 0$ and $x = 0.05$.

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The filled skutterudite compound PrOs$_4$Sb$_{12}$ has proven to be an intriguing and unusual material since its discovery as the first Pr-based heavy fermion superconductor a few years ago. Both the heavy fermion ($m^* \sim 50 m_e$) and the superconducting ($T_c = 1.85$ K) states display very unusual properties. The ground state of the Pr$^{3+}$ ion in PrOs$_4$Sb$_{12}$ that arises from the splitting of the Pr$^{3+} J = 4$ multiplet in a crystalline electric field (CEF) is nonmagnetic, and is either a $\Gamma_1$ singlet or a $\Gamma_3$ doublet. The $\Gamma_5$ triplet first excited state is $\sim 10$ K above the ground state, with the other excited states following at $\sim 100$ K ( $\Gamma_4$ triplet) and $\sim 300$ K ( $\Gamma_3$ or $\Gamma_1$, respectively). In the superconducting state, PrOs$_4$Sb$_{12}$ exhibits multiple transitions in specific heat and magnetic penetration depth and may also contain multiple superconducting phases. The nature of the superconducting energy gap is also not clear: muon spin rotation ($\mu$SR) and Sb-nuclear quadrupole resonance (Sb-NQR) measurements indicate isotropic and strong-coupling superconductivity, tunneling spectroscopy measurements support a nearly fully gapped but unconventional superconducting order parameter and data from thermal conductivity in a magnetic field and magnetic penetration depth are consistent with point nodes in the energy gap. Additional $\mu$SR measurements reveal possible time-reversal symmetry breaking in the superconducting state, further suggesting that the superconducting state does not have s-wave symmetry.

PrRu$_4$Sb$_{12}$ is a much simpler compound than PrOs$_4$Sb$_{12}$. It is also superconducting ($T_c = 1.1$ K), but displays more conventional properties. From Sb-NQR measurements, the superconductivity appears to be weak-coupling with an isotropic energy gap. Magnetic penetration depth measurements yield moderate coupling and a fully gapped order parameter. In addition, PrRu$_4$Sb$_{12}$ is not a heavy fermion compound; it has an electronic specific heat coefficient $\gamma \sim 10$ times smaller than that of PrOs$_4$Sb$_{12}$. Features in the physical properties of PrRu$_4$Sb$_{12}$ could be described by a CEF model with a $\Gamma_1$ ground state and a $\Gamma_4$ first excited state separated by $\sim 70$ K.

The Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ series of compounds was previously studied through measurements of magnetic susceptibility $\chi(T)$ and electrical resistivity $\rho(T)$. Superconductivity was found to persist for all values of the Ru concentration $x$, with a minimum in the $T_c - x$ phase diagram at $x = 0.6$ where $T_c = 0.75$ K. This minimum may arise from a competition between the heavy fermion superconductivity of PrOs$_4$Sb$_{12}$ ($x = 0$) and the BCS supercon-
ductivity of PrRu$_4$Sb$_{12}$ ($x = 1$). Based on theoretical models, it has recently been suggested that there may be a mixed-parity superconducting state near this minimum in $T_c$. CEF effects were also observed for all values of $x$ in the normal state of $\chi(T)$ and $\rho(T)$, with the splitting between the ground state and the first excited state increasing monotonically with $x$ between $x = 0$ and $x = 1$. For $\chi(T)$, fits with a $\Gamma_3$ ground state were consistent with the data for all values of $x$, while fits with a $\Gamma_1$ ground state were only satisfactory near the extremal values of the Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ series. The $\rho(T)$ data were also fit with CEF equations, and although the fits were insensitive to the degeneracy of the ground state, they were still able to provide level splittings consistent with those derived from the $\chi(T)$ data. In the present study, the specific heat $C(T)$ of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ was measured down to $\sim 0.6$ K, to further investigate the normal and superconducting state properties of this extraordinary system.

II. EXPERIMENTAL DETAILS

The single crystal specimens of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ investigated in this work were identical to those previously studied. Specific heat $C$ was measured as a function of temperature between 0.6 and 50 K in a $^3$He semiadiabatic calorimeter by using a standard heat pulse technique. The samples were attached to a sapphire platform with Apiezon N grease. The data presented in this work were taken from experiments on collections of single crystals with total masses between 11 and 114 mg. X-ray measurements show no signs of multiple phases in the doped materials; however, there was some sample dependence of the superconducting transition in electrical resistivity, especially on the doped materials. Thus, the $C(T)$ data, especially at the superconducting transitions, are expected to be slightly broadened by the sample dependence of the crystals.

III. RESULTS AND DISCUSSION

Displayed in Fig. 1 are specific heat divided by temperature $C/T$ vs $T$ data for various Ru concentrations $x$ of the Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ series for temperatures between 0.6 and 20 K. The maximum of the Schottky anomaly, associated with the CEF splitting of the Pr$^{3+}$ energy levels, noticeably decreases in magnitude and shifts to higher temperatures with increasing
All of the $C(T)$ data for Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ were fitted between their superconducting transitions $T_c$ and 10 K by an equation including electronic, lattice, and Schottky terms:

$$C/T = \gamma + \beta T^2 + r C_{Sch}/T.$$  \hspace{1cm} (1)

Here $\gamma$ is the electronic specific heat coefficient, $\beta \propto \Theta_D^3$ is the lattice specific heat coefficient (where $\Theta_D$ is the Debye temperature), and $C_{Sch}(T)$ is the Schottky specific heat anomaly for a two level system arising from the energy difference between the CEF ground state and the first excited state, scaled by a factor $r$. The results of these fits are listed in Table I. These fits find values of $\Theta_D$ for the end member compounds comparable to other single crystal results of 165 K for PrOs$_4$Sb$_{12}$\(^{17}\) and 232 K for PrRu$_4$Sb$_{12}$.\(^{11}\)

The Schottky specific heat anomaly $C_{Sch}(T)$ for a two-level system is given by

$$C_{Sch}(T) = R \left(\frac{\delta}{T}\right)^2 \frac{g_0}{g_1} \frac{\exp(\delta/T)}{[1 + (g_0/g_1) \exp(\delta/T)]^2}, \hspace{1cm} (2)$$

where $\delta$ is the energy difference in units of K between the two levels, and $g_0$ and $g_1$ are the degeneracies of the ground state and excited state, respectively.\(^{18}\) In zero magnetic field, this equation is independent of whether or not the local symmetry of the Pr$^{3+}$ ions is cubic or tetrahedral. It was found during the fitting procedure that in order for the fits to be accurate, one or more of the terms in Eq. I had to be scaled. Fits were done both with $r$ modifying the Schottky term, and with $r$ multiplying the entire equation. The former case would be interpreted as some internal broadening of the energy levels or as an overall transfer of entropy to the itinerant electrons due to hybridization, while the latter case would imply impurity phases (most likely free Sb) causing an overall overestimate of the sample mass. While both possibilities produced good qualitative fits, the values for $\gamma$ resulting from assuming an overall scaling were extremely large and not physically reasonable. Therefore, all the fits presented here were exactly as shown in Eq. I with $r$ only modifying the Schottky anomaly term.

The normal state fits were only performed up to 10 K so that the $C_{lattice} \approx \beta T^3$ approximation would more likely be accurate; however, the lattice terms are clearly the smallest in this temperature range compared to the other terms, and are thus difficult to accurately fit. This appears to especially be true for $x = 0.2$ and $x = 0.4$, where $\Theta_D$ is suppressed compared to the end member compounds, and which may be due to the disorder inherent in the substituted compounds. Because of the uncertainty in the accuracy of the fit values
for \( \Theta_D \), the error in the other parameters was estimated by varying \( \Theta_D \) by \( \pm 10 \) and refitting the data. The largest error in the normal state arises in \( \gamma \), while the errors in \( \delta \) and \( r \) are much smaller. These errors are represented in Table II and in the figures where appropriate.

The question of whether or not the ground state in PrOs\(_4\)Sb\(_{12}\) is a \( \Gamma_3 \) doublet or a \( \Gamma_1 \) singlet has been contentious since the heavy fermion superconductivity of PrOs\(_4\)Sb\(_{12}\) was discovered. In our original reports of heavy fermion superconductivity in PrOs\(_4\)Sb\(_{12}\),\(^1\)\(^2\) fits to the magnetic susceptibility yielded two possible Pr\(^{3+}\) crystalline electric field splittings, both with a \( \Gamma_5 \) first excited state and either a \( \Gamma_1 \) singlet ground state or a \( \Gamma_3 \) nonmagnetic doublet ground state with a quadrupole moment. At the present time, it appears that the overall data are better explained by a \( \Gamma_1 \) singlet ground state.\(^{19,20,21}\) Nevertheless, it was felt that fits to the \( C(T) \) data for both possibilities should be made. As can be seen from Table II and Fig. 2(b), when fitting the normal state data up to 10 K, both possible ground state fits result in reasonable values that agree well with those previously published for Pr(Os\(_{1-x}\)Ru\(_x\))\(_4\)Sb\(_{12}\) based on \( \chi(T) \) and \( \rho(T) \) measurements.\(^{15}\) However, for \( x \leq 0.4 \), the scaling factor \( r \) is much closer to 1 for a \( \Gamma_3 \) ground state compared to \( \Gamma_1 \). In fact, the best \( \Gamma_3 \) ground state fit for \( x = 0 \), pure PrOs\(_4\)Sb\(_{12}\), results in almost no scaling whatsoever. (The present fits were performed on data from a measurement of single crystals, while some previously published fits were performed on data from a measurement of a pressed pellet.\(^1\)\(^2\)\(^22\)) These results of \( r_{\Gamma_3} = 1.01 \) and \( r_{\Gamma_1} = 0.56 \) for \( x = 0 \) are very consistent with fits performed on data from measurements of single crystals by Vollmer et al., which resulted in the values \( r_{\Gamma_3} \approx 0.99 \) and \( r_{\Gamma_1} \approx 0.5 \).\(^{17}\) As \( x \) increases, the scaling factor decreases, indicating a suppression of the Schottky anomaly. At face value, the fact that \( r_{\Gamma_3} \) is always closer to 1 than \( r_{\Gamma_1} \) for \( x \leq 0.4 \) could be considered as support for a \( \Gamma_3 \) ground state. It has been suggested that the suppression of the Schottky anomaly, especially for a \( \Gamma_1 \) ground state fit for PrOs\(_4\)Sb\(_{12}\), could result from an energy dispersion due to Pr-Pr interactions\(^{23}\) or hybridization between the Pr f-electrons and ligand states.\(^{24}\) As these arguments can apply equally well to either ground state, these normal state results for \( x \leq 0.4 \) appear unable to discern between \( \Gamma_1 \) and \( \Gamma_3 \) ground states.

For \( x > 0.4 \), the scaling factor \( r \) increases rapidly. PrRu\(_4\)Sb\(_{12}\) exhibits a situation complementary to that of PrOs\(_4\)Sb\(_{12}\): while \( r_{\Gamma_3} \) is still \( 1.8 - 1.9 \) times larger than \( r_{\Gamma_1} \), it is \( r_{\Gamma_1} \) that is closer to 1. The accuracy of these results could be affected by the temperature limits of the fits; for these large splittings, the maximum of the Schottky anomaly is well above 10
K. However, the calculated values of $\delta$ for the different ground states agree very well overall with the values previously measured,\textsuperscript{15} supporting the monotonic increase of the splitting between the ground state and the first excited state throughout the Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ series (Fig. 2(b)).

In order to get a more accurate determination of $T_c$ and the specific heat jump at $T_c$, $\Delta C/T_c$, the CEF and lattice fit results were subtracted from the data at low temperatures, leaving only the electronic specific heat. The subtractions were carried out using both the $\Gamma_3$ and the $\Gamma_1$ ground state CEF fits, including those due to the variation of $\Theta_D$ in order to further estimate the error of the parameters. All the subtractions resulted in exactly the same $T_c$ values, and very similar (within experimental error) $\Delta C/T_c$ values, which are both listed in Table II. These values of $T_c$ are plotted as a function of $x$ in Fig. 2(a), along with previously measured values; the error bars for the $T_c$ points represent the width of the transitions in the respective measurements. All the data agree very well, and the minimum at $x = 0.6$ is also reproduced in the current data. With the exception of pure PrOs$_4$Sb$_{12}$ (i.e., for $x > 0$), the shapes of the measured $C(T)$ curves below $T_c$ were nearly the same for either $\Gamma_1$ or $\Gamma_3$-based subtraction. However, for PrOs$_4$Sb$_{12}$, a significant difference can be seen in the slope of the data below $T_c$ for the two different subtractions. The $C(T)$ data after subtraction of $C_{\text{lat}}(T)$ and $C_{\text{Sch}}(T)$ for a $\Gamma_1$ or $\Gamma_3$ ground state, $C_{\text{el}}(T)$, are shown in Fig. 3. All the concentrations are shown for the $\Gamma_1$ ground state subtraction, and the $\Gamma_3$ ground state subtraction is also shown for $x = 0$.

The data below $T_c$, after the lattice and CEF terms were subtracted, were fit to both power-law and exponential functions, for energy gaps with and without nodes, respectively. These functions are typically considered to be valid only at very low temperatures. However, there are several examples of heavy fermion superconductors which appear to display power-law behavior up to near $T_c$ (e.g.,\textsuperscript{25,26}). The current experiment had a low-temperature limit of 0.6 K, which is effectively a base temperature due to the large nuclear Schottky contribution at lower temperatures.\textsuperscript{17,23} The high temperature limit of the fit was chosen to be $\frac{2}{3}T_c$ in light of the above referenced examples, and also to avoid possible spurious effects due to the width of the superconducting transitions. Because of these constraints, only the samples with $0 \leq x \leq 0.2$ could be fitted below $T_c$, as there were not enough data points at the other
concentrations to give a reliable fit. The power-law fit was of the form

\[ \frac{C}{T} = \gamma_s^p + AT^n, \]  

(3)
suggested for energy gaps containing nodes, and the exponential fit was of the BCS form

\[ \frac{C}{T} = \gamma_s^e + \frac{B}{T} \exp \left( \frac{-\Delta_e}{T} \right), \]  

(4)

where \( \gamma_s \) represents an electronic specific heat coefficient in the superconducting state, \( A \) and \( B \) are fitting constants, and \( \Delta_e \) is proportional to the energy gap in the BCS theory of superconductivity. The results of the application of these fits to the \( x = 0 \) and \( x = 0.05 \) data, for both ground state subtractions, are shown in Fig. 4, where the solid lines correspond to the power law fits and the dashed lines represent the exponential fits. For \( x = 0 \), the power-law fits extrapolate from the highest fit temperature of \( \sim 1.2 \) K all the way up to the transition, while the exponential fits deviate from the data right above 1.2 K. For \( x = 0.05 \) and higher, the converse is true, as the exponential fits extrapolate to the higher temperature data (above \( \sim 1.1 \) K for \( x = 0.05 \) and \( x = 0.1 \), and above \( \sim 1.0 \) K for \( x = 0.2 \)) much more accurately than the power law fits. While these extrapolations cannot be taken by themselves as proof of the superiority of one fit over the other, they are certainly suggestive and intriguing. The broadened superconducting transitions in the Ru-doped samples in particular may make the exponential fit appear more appropriate.

The constants from the fits below \( T_c \) are also listed in Table II. The listed errors are due to the variation of \( \Theta_D \) in the normal state fits. The error in \( T_c \) was taken to be the width of the superconducting transition and is presented graphically in Fig. 2a; the error in \( \Delta C/T_c \) from the variation of \( \Theta_D \) was negligibly small compared to the error inherent in the equal area construction for determining \( \Delta C/T_c \), which is represented graphically in Fig. 5. Since these fits are phenomenological, the absolute values of the resulting parameters should not necessarily be trusted. However, comparing the fits and the samples to one another can prove instructive. For pure PrOs\(_4\)Sb\(_{12}\), the \( \Gamma_3 \) ground state subtraction results in fits that are much different from the \( \Gamma_1 \) ground state subtraction results. The other concentrations have similar fit parameters for the two different ground states. In addition, the values for \( \gamma_s^p \), \( n \), and \( \Delta_e \), and the errors associated with them, are much larger for the \( \Gamma_3 \) \( x = 0 \) fits than for the other \( \Gamma_3 \) fits, falling well outside the spread of the other three data points. If the fits are indeed accurate, then the value of \( n \) for the \( \Gamma_1 \) \( x = 0 \) data is comparable with the
$n = 2$ expected in $C/T$ for a heavy fermion compound with point nodes in the energy gap.\textsuperscript{27} The values of $\Delta_e$ for the $\Gamma_1$ data of $\Delta_e/T_c \approx 2.2 - 2.6$ are moderately enhanced compared to the weak-coupling value of $\Delta_e/T_c = 1.76$ (for $\Delta_e$ in units of K). The parameter $\gamma_s$ can be interpreted as a portion of the sample that is normal or gapless; however, the values of $\gamma_s$ could also simply be artifacts of the fit, especially in the case of the power law fit for $x = 0.1$. The large discrepancy between the fits below $T_c$ for PrOs$_4$Sb$_{12}$, even if the absolute values are not entirely accurate, do lend phenomenological support for $\Gamma_1$ being the ground state in this compound. It is interesting that the analysis of $C(T)$ in the superconducting state for samples containing a small amount of Ru shows only small sensitivity to the choice of $\Gamma_1$ or $\Gamma_3$ for the Pr$^{3+}$ ground state.

Fig. 5 shows a comparison between the electronic specific heat coefficient $\gamma$ calculated from the fits of the normal state $C/T$ data and a value estimated from $\Delta C/T_c$. In the BCS theory of superconductivity, $\Delta C/\gamma T_c = 1.43$. This is not likely to be true in the case of the unconventional superconductivity in PrOs$_4$Sb$_{12}$. However, it is expected that there will be some proportional relation between $\Delta C/T_c$ and $\gamma$ (e.g., $\Delta C/T_c \propto \gamma$), and so it can still be instructive to view this graphically. It can be seen in Table II and Fig. 5 that $\gamma(x)$ derived from the normal state fits exhibits a peak at $x = 0.05$, decreases with $x$ to a minimum at $x = 0.6$, and then slowly rises with $x$ to $x = 1$. In contrast, $\Delta C/T_c$ starts out extremely large for $x = 0$ and decreases very quickly, again to a minimum value at $x = 0.6$. The “hump” in the data at $x = 0.4$ is due to the extremely broad superconducting transition at this concentration.

The discrepancy between the values of $\gamma$ determined from the normal state data and calculated from the superconducting transition is an interesting one. The minimum in $\gamma$ at $x = 0.6$ for the measured $\gamma$, along with the minimum in $T_c$, strongly suggests that something unusual is happening with the physical properties at this concentration. In contrast, the enhanced $\Delta C/T_c$ for $x = 0$ and $x = 0.05$ imply that strong-coupling superconductivity is only present for these two concentrations. Taken at face value, this could mean that for $0.1 \leq x \leq 0.4$, the heavy electrons are not participating in the superconductivity, which would imply that the superconductivity is nearly conventional for $x \geq 0.1$ (and possibly also for $x = 0.05$ if the exponential behavior below $T_c$ is appropriate). A more conventional explanation could be that the Ru substitution broadens the superconducting transitions in $C(T)$ enough to result in an underestimate for $\Delta C/T_c$. This would only appear to be
the case for $0.05 \leq x \leq 0.4$, however, as the superconducting transitions for $x = 0.6$ and $x = 0.85$ are as sharp or sharper than for $x = 1$. It would be unusual for disorder to play a strong role only for low Ru concentrations.

In Figs. 3 and 4 it can be seen that the sharp double superconducting transition present in pure PrOs$_4$Sb$_{12}$ is not obviously apparent in the Ru-doped samples, although this may be obscured by the width of the transitions. Chia et al. have recently suggested that this double transition may arise from two superconducting phases which react differently to Ru substitution; i.e., one is unconventional and is quickly destroyed by impurities, while the other is more conventional and persists throughout the entire series. It will be interesting to see whether or not this conjecture can tie together the seemingly contradictory results obtained through experiments over the past few years. Indeed, in studies on the specific heat of La-doped PrOs$_4$Sb$_{12}$, preliminary results suggest that only the lower transition of PrOs$_4$Sb$_{12}$ is suppressed for small La concentrations. This could also be the case for the present Ru substitution studies. On the other hand, measurements of magnetic penetration depth suggest two-band superconductivity in PrOs$_4$Sb$_{12}$, where the two bands are coupled by Josephson pair tunnelling, which requires the two order parameters to have the same symmetry. The difference in the behavior below $T_c$ between PrOs$_4$Sb$_{12}$ and the Ru-doped samples could perhaps be accounted for by the suppression of one of the superconducting bands. Measurements on samples with small Ru concentrations are underway in order to more closely track the evolution of the superconducting properties in this remarkable series of compounds.

IV. SUMMARY

The specific heat of single crystal samples of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ was measured down to 0.6 K. Fits to the normal state data resulted in CEF parameters that monotonically increase with $x$, in agreement with previously reported data. The superconducting transitions in $C(T)$ were also consistent with previously reported $\chi(T)$ and $\rho(T)$ data, confirming the minimum in $T_c$ at $x = 0.6$. Below $T_c$, a power law fit possibly corresponding to point nodes in the energy gap could better describe the data for PrOs$_4$Sb$_{12}$, but an exponential fit associated with an isotropic energy gap was more appropriate for the data with $0.05 \leq x \leq 0.2$. The electronic specific heat $\gamma$ was inferred from both normal state data and the ratio $\Delta C/T_c$. The
normal state fits revealed an enhanced $\gamma$ for $x \leq 0.4$, reaching a minimum value at $x = 0.6$, the same concentration as the minimum in $T_c$. However, $\Delta C/T_c$ was only significantly enhanced for $x = 0$ and $x = 0.05$.

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TABLE I: Physical properties of samples of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$, determined from normal state specific heat data. The parameter $\delta$ is the splitting between the ground state and the first excited state in the Schottky anomaly, $r$ is the scaling factor for the Schottky anomaly, $\gamma$ is the estimated electronic specific heat coefficient, and $\Theta_D$ is the estimated Debye temperature. The errors in the parameters were determined by allowing $\Theta_D$ to vary by $\pm 10$ K within the fits (see text for details).

| $x$ | $\delta$ (K) | $r$ (mJ/mol K$^2$) | $\gamma$ (K) | $\Theta_D$ (K) |
|-----|---------------|-------------------|--------------|--------------|
| 0   | 6.72±0.06     | 1.01±0.03         | 216          | 186          |
| 0.05| 9.49±0.04     | 0.75±0.03         | 199          | 10.2±0.01    |
| 0.1 | 11.9±0.2      | 0.55±0.02         | 200          | 12.8±0.2     |
| 0.2 | 13.1±0.6      | 0.63±0.02         | 152          | 13.8±0.6     |
| 0.4 | 16.9±1.4      | 0.45±0.09         | 139          | 17.3±1.6     |
| 0.6 | 38.3±0.1      | 1.22±0.20         | 181          | 38.9±0.2     |
| 0.85| 48.7±0.6      | 2.23±0.09         | 218          | 49.1±0.6     |
| 1.0 | 53.4±1.0      | 2.45±0.02         | 232          | 53.7±1.0     |

FIG. 1: Specific heat divided by temperature $C/T$ below 20 K for single crystal samples of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$. 
TABLE II: Physical properties of samples of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$, determined from superconducting state specific heat data. The parameter $T_c$ is the superconducting transition temperature, $\Delta C$ is the jump in $C(T)$ at $T_c$, $\gamma_s$ is the electronic specific heat coefficient in the superconducting state, $n$ is the exponent of the power-law fit below $T_c$, and $\Delta_e$ is the parameter in the exponential fit below $T_c$ that is proportional to the energy gap. The errors in the parameters were determined in the same manner as Table I by propagating an error in $\Theta_D$, with the exception of $T_c$ and $\Delta C/T_c$ (whose errors are represented graphically; see text for details).

| $x$  | $T_c$ (K) | $\Delta C/T_c$ (mJ/mol K$^2$) | $\gamma_s^p$ (mJ/mol K$^2$) | $n$ | $\gamma_s^e$ (mJ/mol K$^2$) | $\Delta_e$ (K) |
|------|----------|-------------------------------|---------------------------|-----|---------------------------|---------------|
| 0    | 1.77     | 1021                          | 101±1                     | 4.55±0.40 | 114±1                    | 6.46±0.43     |
| 0.05 | 1.63     | 339                           | 0                         | 2.57±0.02 | 48.2±2.0                | 3.57±0.04     |
| 0.1  | 1.62     | 179                           | 23.0±1.9                  | 2.59±0.04 | 73.2±1.0                | 4.15±0.03     |
| 0.2  | 1.54     | 131                           | 0                         | 2.12±0.02 | 53.5±2.4                | 3.39±0.03     |
| 0.4  | 1.21     | 165                           |                           |       |                          |               |
| 0.6  | 0.75     | 75                            |                           |       |                          |               |
| 0.85 | 0.94     | 89                            |                           |       |                          |               |
| 1.0  | 1.11     | 88                            |                           |       |                          |               |

| $x$  | $T_c$ (K) | $\Delta C/T_c$ (mJ/mol K$^2$) | $\gamma_s^p$ (mJ/mol K$^2$) | $n$ | $\gamma_s^e$ (mJ/mol K$^2$) | $\Delta_e$ (K) |
|------|----------|-------------------------------|---------------------------|-----|---------------------------|---------------|
| 0    | 1.77     | 1029                          | 0                         | 2.27±0.01 | 93.2±3.1                  | 3.97±0.07     |
| 0.05 | 1.63     | 327                           | 0                         | 2.71±0.01 | 55.2±0.7                 | 3.79±0.01     |
| 0.1  | 1.62     | 177                           | 26.8±1.3                  | 2.69±0.02 | 74.7±0.9                 | 4.23±0.02     |
| 0.2  | 1.54     | 127                           | 0                         | 2.13±0.02 | 52.9±2.7                 | 3.42±0.02     |
| 0.4  | 1.21     | 167                           |                           |       |                          |               |
| 0.6  | 0.75     | 74                            |                           |       |                          |               |
| 0.85 | 0.94     | 89                            |                           |       |                          |               |
| 1.0  | 1.11     | 88                            |                           |       |                          |               |
FIG. 2: (a) Superconducting critical temperature $T_c$ vs Ru concentration $x$ for Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$, including data from measurements of $\rho(T)$, $\chi_{ac}(T)$, and $C(T)$. The straight lines are guides to the eye. (b) The splitting between the ground state and first excited state $\Delta E_{gs-1es}$ vs Ru concentration $x$ for Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$, calculated from fits of CEF equations to $\chi_{dc}(T)$, $\rho(T)$, and $C(T)$ data. The data points derived from $\rho(T)$, $\chi_{ac}(T)$, and $\chi_{dc}(T)$ are from previous work.\textsuperscript{15}
FIG. 3: The electronic specific heat divided by temperature $C_{el}/T$ ($C_{el} = C - C_{\text{lat}} - C_{\text{Sch}}$) of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ below 2 K for (a) $0 \leq x \leq 0.2$ and (b) $0.4 \leq x \leq 1$. The data that were subtracted came mostly from fits including a $\Gamma_1$ ground state. The data from subtracting a $\Gamma_3$ ground state fit were only included for $x = 0$ due to large differences that are not present for other concentrations.
FIG. 4: Comparison of exponential (dashed line) and power law (solid line) fits, subtracting data for either $\Gamma_3$ ((a) and (c)) or $\Gamma_1$ ((b) and (d)) ground states below $T_c$, for PrOs$_4$Sb$_{12}$ ((a) and (b)) and Pr(Os$_{0.95}$Ru$_{0.05}$)$_4$Sb$_{12}$ ((c) and (d)). The PrOs$_4$Sb$_{12}$ fits only extend up to $\sim 1.2$ K, and the Pr(Os$_{0.95}$Ru$_{0.05}$)$_4$Sb$_{12}$ fits only extend up to $\sim 1.1$ K, as described in the text.

FIG. 5: Electronic specific heat coefficient $\gamma$ (left axis, closed circles and squares) and $\Delta C/T_c$ (right axis, open circles) as a function of Ru concentration $x$ for Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$. 