Evolution of crystalline electric field effects, superconductivity, and heavy-fermion behavior in the specific heat of $Pr(Os_{1-x}Ru_x)_4Sb_{12}$

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Specific heat $C(T)$ measurements were made on single crystals of the superconducting filled skutterudite series $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ 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 $x=0$ ($PrOs_4Sb_{12}$), and with exponential behavior for $0.05 \leqslant x \leqslant 0.2$. An enhanced electronic specific heat coefficient γ was observed for $x \leqslant 0.4$, 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 observed only for $x=0$ and 0.05.

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I. INTRODUCTION

The filled skutterudite compound $PrOs_4Sb_{12}$ has proven to be an intriguing and unusual material since its discovery as the first Pr-based heavy-fermion superconductor a few years ago.[1,2] Both the heavy-fermion ($m^* \sim 50m_e$) and the superconducting ($T_c=1.85$ K) states display very unusual properties. The ground state of the Pr^{3+} ion in $PrOs_4Sb_{12}$ that arises from the splitting of the Pr^{3+} $J=4$ multiplet in a crystalline electric field (CEF) is nonmagnetic, and is either a Γ_1 singlet or a Γ_3 doublet. The Γ_5 triplet first excited state is $\sim$10 K above the ground state, with the other excited states following at $\sim$100 K (Γ_4 triplet) and $\sim$300 K (Γ_3 or Γ_1, respectively). In the superconducting state, $PrOs_4Sb_{12}$ exhibits multiple transitions in specific heat[2,3] and magnetic penetration depth,[4] and may also contain multiple superconducting phases.[5] The nature of the superconducting energy gap is also not clear: muon spin rotation[6] (μSR) and Sb-nuclear quadrupole resonance[7] (Sb-NQR) measurements indicate isotropic and strong-coupling superconductivity, tunneling spectroscopy measurements support a nearly fully gapped but unconventional superconducting order parameter,[8] and data from thermal conductivity in a magnetic field[5] and magnetic penetration depth[9] are consistent with point nodes in the energy gap. Additional μSR measurements reveal possible time-reversal symmetry breaking in the superconducting state, further suggesting that the superconducting state does not have s-wave symmetry.[10]

$PrRu_4Sb_{12}$ is a much simpler compound than $PrOs_4Sb_{12}$. It is also superconducting ($T_c=1.1$ K), but displays more conventional properties.[11] From Sb-NQR measurements, the superconductivity appears to be weak coupling with an isotropic energy gap.[12] Magnetic penetration depth measurements yield moderate coupling and a fully gapped order parameter.[13] In addition, $PrRu_4Sb_{12}$ is not a heavy-fermion compound; it has an electronic specific heat coefficient $\gamma \sim 10$ times smaller than that of $PrOs_4Sb_{12}$. Features in the physical properties of $PrRu_4Sb_{12}$ could be described by a CEF model with a Γ_1 ground state and a Γ_4 first excited state separated by $\sim$70 K.[11,14]

The $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ series of compounds was previously studied through measurements of magnetic susceptibility $\chi(T)$ and electrical resistivity $\rho(T)$.[15] 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 $PrOs_4Sb_{12}$ ($x=0$) and the BCS superconductivity of $PrRu_4Sb_{12}$ ($x=1$). Based on theoretical models, it has recently been suggested that there may be a mixed-parity superconducting state near this minimum in T_c.[16] 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 1. For $\chi(T)$, fits with a Γ_3 ground state were consistent with the data for all values of x, while fits with a Γ_1 ground state were satisfactory only near the extremal values of the $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ series. The $\rho(T)$ data were also fitted 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 $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ 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 $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ investigated in this work were identical to those previously studied.[15] 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

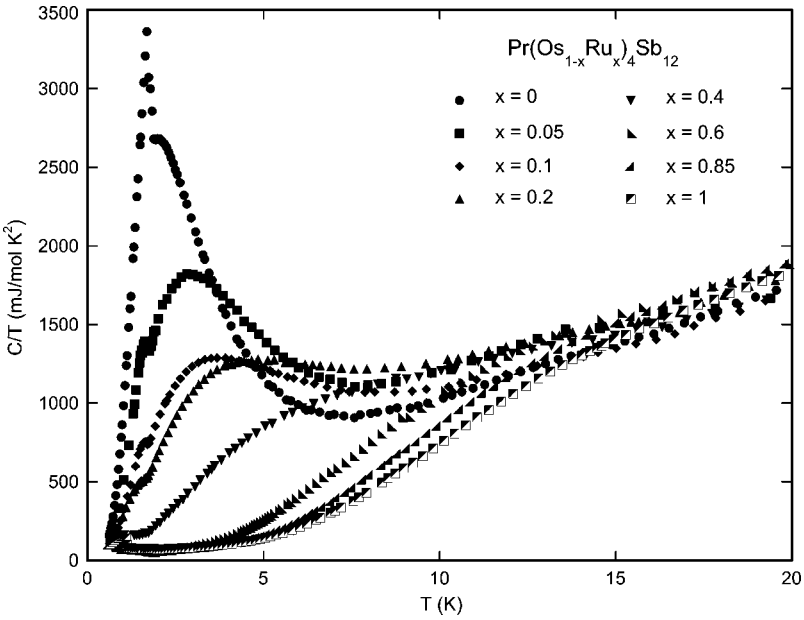

FIG. 1. Specific heat divided by temperature C/T below 20 K for single-crystal samples of $Pr(Os_{1-x}Ru_x)_4Sb_{12}$.

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.[15] 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 $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ 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 x. All of the $C(T)$ data for $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ were fitted between their superconducting transitions T_c and 10 K by an equation including electronic, lattice, and Schottky terms:

$$C/T = \gamma + \beta T^2 + rC_{\mathrm{Sch}}/T. \quad (1)$$

Here γ is the electronic specific heat coefficient, $\beta \propto \Theta_D^{-3}$ is the lattice specific heat coefficient (where Θ_D is the Debye temperature), and $C_{\mathrm{Sch}}(T)$ 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 Θ_D for the end member compounds comparable to other single-crystal results of 165 K for $PrOs_4Sb_{12}$ (Ref. 17) and 232 K for $PrRu_4Sb_{12}$.[11]

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

TABLE I. Physical properties of samples of $Pr(Os_{1-x}Ru_x)_4Sb_{12}$, determined from normal state specific heat data. The parameter δ 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, γ is the estimated electronic specific heat coefficient, and Θ_D is the estimated Debye temperature. The errors in the parameters were determined by allowing Θ_D to vary by ±10 K within the fits (see text for details).

	Γ_3 ground state				Γ_1 ground state			
x	δ (K)	r	γ (mJ/mol K^2)	Θ_D (K)	δ (K)	r	γ (mJ/mol K^2)	Θ_D (K)
0	6.72±0.06	1.0±0.03	421±58	186	7.36±0.04	0.56±0.01	586±33	211
0.05	9.49±0.04	0.75±0.03	617±43	199	10.2±0.01	0.39±0.01	775±25	224
0.1	11.9±0.2	0.55±0.02	565±38	200	12.8±0.2	0.29±0.01	629±34	203
0.2	13.1±0.6	0.63±0.02	393±43	152	13.8±0.6	0.34±0.01	418±48	146
0.4	16.9±1.4	0.45±0.09	138±31	139	17.3±1.6	0.23±0.05	140±36	135
0.6	38.3±0.1	1.22±0.20	35.8±7.6	181	38.9±0.2	0.62±0.12	34.2±8.5	178
0.85	48.7±0.6	2.23±0.09	49.3±4.7	218	49.1±0.6	1.15±0.05	48.7±4.9	216
1.0	53.4±1.0	2.45±0.02	59.1±4.0	232	53.7±1.0	1.26±0.01	58.9±4.1	231

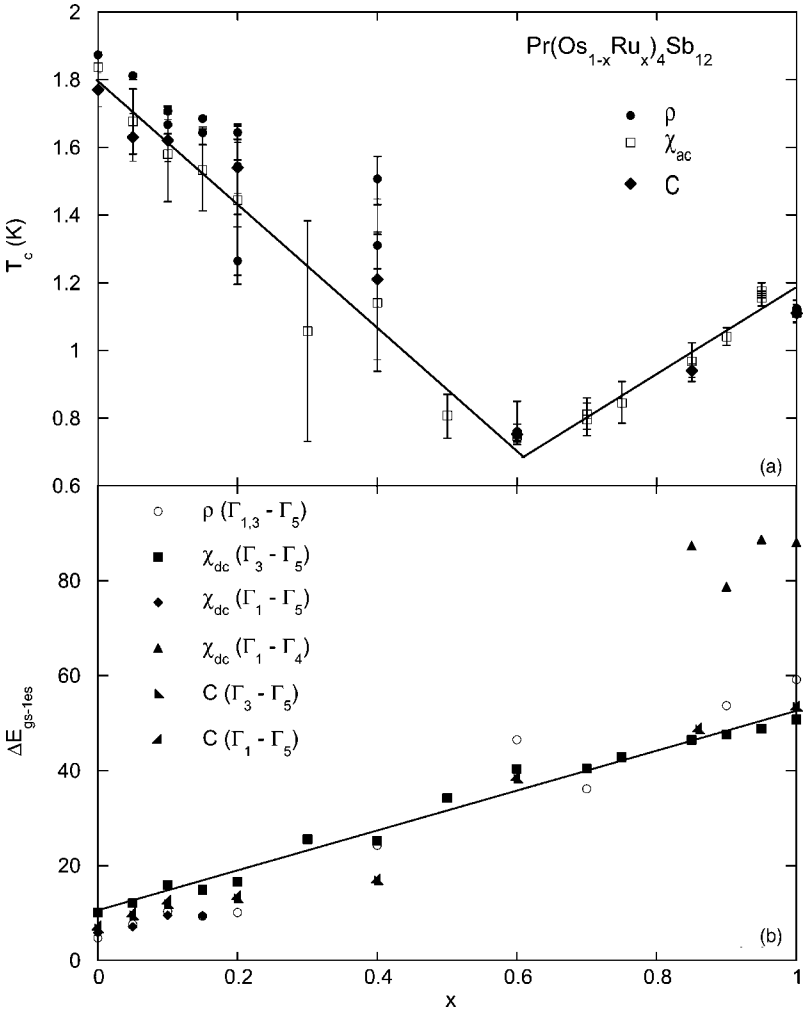

FIG. 2. (a) Superconducting critical temperature T_c vs Ru concentration x for $Pr(Os_{1-x}Ru_x)_4Sb_{12}$, including data from measurements of $\rho(T)$, $\chi_{ac}(T)$, and $C(T)$. The straight lines are guides to the eye. (b) The splitting between the ground state and first excited state $\Delta E_{gs\text{-}1es}$ vs Ru concentration x for $Pr(Os_{1-x}Ru_x)_4Sb_{12}$, 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 (Ref. 15).

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

where δ 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 symmmetry 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. (1) 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 γ 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. (1), with r only modifying the Schottky anomaly term.

The normal state fits were only performed up to 10 K so that the $C_{\mathrm{lattice}} \approx \beta T^3$ 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 0.4, where Θ_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 Θ_D, the error in the other parameters was estimated by varying Θ_D by ±10 K and refitting the data. The largest error in the normal state arises in γ, while the errors in δ and r are much smaller. These errors are represented in Table I and in the figures where appropriate.

The question of whether or not the ground state in $PrOs_4Sb_{12}$ is a Γ_3 doublet or a Γ_1 singlet has been contentious since the heavy-fermion superconductivity of $PrOs_4Sb_{12}$ was discovered. In our original reports of heavy-fermion superconductivity in $PrOs_4Sb_{12}$,[1,2] fits to the magnetic susceptibility yielded two possible Pr^{3+} crystalline electric field splittings, both with a Γ_5 first excited state and either a Γ_1 singlet ground state or a Γ_3 nonmagnetic doublet ground state with a quadrupole moment. At the present time, it appears that the overall data are better explained by a Γ_1 singlet ground state.[19–21] Nevertheless, it was felt that fits to the $C(T)$ data for both possibilities should be made. As can be seen from Table I and Fig. 2(b), when fitting the normal state data up to 10 K, both possible ground state fits result in

TABLE II. Physical properties of samples of $Pr(Os_{1-x}Ru_x)_4Sb_{12}$, determined from superconducting state specific heat data. The parameter T_c is the superconducting transition temperature, ΔC is the jump in $C(T)$ at T_c, γ_s is the electronic specific heat coefficient in the superconducting state, n is the exponent of the power-law fit below T_c, Δ_e is the parameter in the exponential fit below T_c that is proportional to the energy gap, and $\%_{Sch}$ indicates the maximum percentage of the data in the fit range below T_c subtracted due to the Schottky anomaly. The errors in the parameters were determined in the same manner as Table I, by propagating an error in Θ_D, with the exception of T_c and $\Delta C/T_c$ (whose errors are represented graphically; see text for details).

			Γ_3 ground state				
x	T_c (K)	$\Delta C/T_c$ (mJ/mol K^2)	γ_s^p (mJ/mol K^2)	n	γ_s^e (mJ/mol K^2)	Δ_e (K)	$\%_{Sch}$
0	1.77	1021	101±1	4.55±0.40	114±1	6.46±0.43	78
0.05	1.63	339	0	2.57±0.02	48.2±2.0	3.57±0.04	19
0.1	1.62	179	23.0±1.9	2.59±0.04	73.2±1.0	4.15±0.03	3.9
0.2	1.54	131	0	2.11±0.02	53.5±2.4	3.39±0.03	1.0
0.4	1.21	165					
0.6	0.75	75					
0.85	0.94	89					
1.0	1.11	88					
			Γ_1 ground state				
x	T_c (K)	$\Delta C/T_c$ (mJ/mol K^2)	γ_s^p (mJ/mol K^2)	n	γ_s^e (mJ/mol K^2)	Δ_e (K)	$\%_{Sch}$
0	1.77	1029	0	2.27±0.01	93.2±3.1	3.97±0.07	60
0.05	1.63	327	0	2.71±0.01	55.2±0.7	3.79±0.01	12
0.1	1.62	177	26.8±1.3	2.69±0.02	74.7±0.9	4.23±0.02	2.1
0.2	1.54	127	0	2.13±0.02	52.9±2.7	3.42±0.02	0.6
0.4	1.21	167					
0.6	0.75	74					
0.85	0.94	89					
1.0	1.11	88					

reasonable values that agree well with those previously published for $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ based on $\chi(T)$ and $\rho(T)$ measurements.[15] However, for $x \leqslant 0.4$, the scaling factor r is much closer to 1 for a Γ_3 ground state compared to Γ_1. In fact, the best Γ_3 ground state fit for $x=0$, pure $PrOs_4Sb_{12}$, 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 $r_{\Gamma_1} \sim 0.5$.[17] As x increases, the scaling factor decreases, indicating a suppression of the Schottky anomaly. At face value, the fact that r_{Γ_3} is always closer to 1 than r_{Γ_1} for $x \leqslant 0.4$ could be considered as support for a Γ_3 ground state. It has been suggested that the suppression of the Schottky anomaly, especially for a Γ_1 ground state fit for $PrOs_4Sb_{12}$, 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 $x \leqslant 0.4$ appear unable to discern between Γ_1 and Γ_3 ground states.

For $x > 0.4$, the scaling factor r increases rapidly. $PrRu_4Sb_{12}$ exhibits a situation complementary to that of $PrOs_4Sb_{12}$: while r_{Γ_3} is still 1.8–1.9 times larger than r_{Γ_1}, it is r_{Γ_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 δ for the different ground states agree very well overall with the values previously measured,[15] supporting the monotonic increase of the splitting between the ground state and the first excited state throughout the $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ 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 Γ_3 and the Γ_1 ground state CEF fits, including those due to the variation of Θ_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 $PrOs_4Sb_{12}$ (i.e., for $x>0$), the shapes of the measured $C(T)$ curves below T_c were nearly the same for either Γ_1- or Γ_3-based subtraction. However, for $PrOs_4Sb_{12}$, a significant

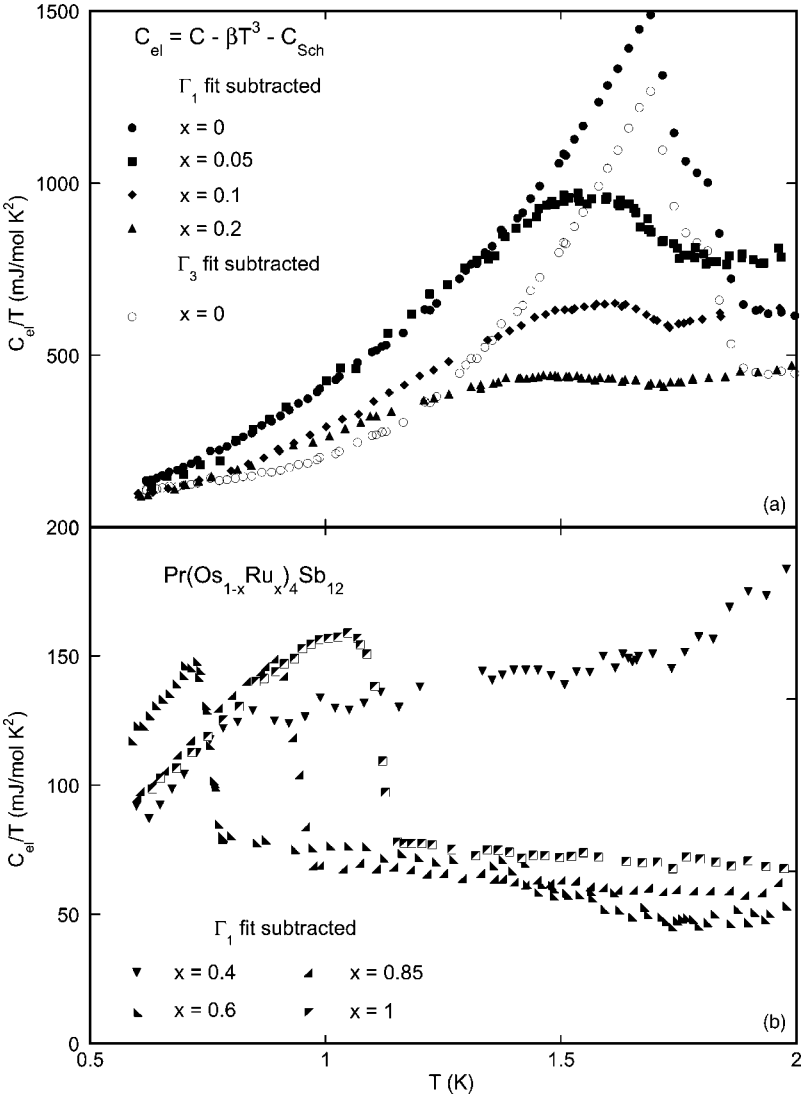

FIG. 3. The electronic specific heat divided by temperature C_{el}/T ($C_{\mathrm{el}}=C-C_{\mathrm{lat}}-C_{\mathrm{Sch}}$) of $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ below 2 K for (a) $0\leqslant x\leqslant 0.2$ and (b) $0.4\leqslant x\leqslant 1$. The data that were subtracted came mostly from fits including a Γ_1 ground state. The data from subtracting a Γ_3 ground state fit were included only for $x=0$ due to large differences that are not present for other concentrations.

difference can be seen in the slope of the data below T_c for the two different subtractions. This is due to the proximity of the Schottky anomaly to the superconducting state, and the difference in slopes between the two fits. As listed in the $\%_{\mathrm{Sch}}$ column in Table II, the Schottky anomaly accounts for a very large percentage of the data below T_c for $x=0$. As x increases, however, this percentage drops rapidly to $\sim$1% for $x=0.2$. The higher accuracy of the $x=0$ fits in the normal state, due to the lower splitting of the Schottky anomaly, mitigates the possible error after subtracting the fits in the superconducting state. The $C(T)$ data after subtraction of $C_{\mathrm{lat}}(T)$ and $C_{\mathrm{Sch}}(T)$ for a Γ_1 or Γ_3 ground state, $C_{\mathrm{el}}(T)$, are shown in Fig. 3. All the concentrations are shown for the Γ_1 ground state subtraction, and the Γ_3 ground state subtraction is also shown for $x=0$.

The data below T_c, after the lattice and CEF terms were subtracted, were fitted 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., Ref. 25 and 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.[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 $0\leqslant x\leqslant 0.2$ 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

$$C/T=\gamma_s^p+AT^n, \tag{3}$$

suggested for energy gaps containing nodes,[27] and the exponential fit was of the BCS form[18]

$$C/T=\gamma_s^e+\frac{B}{T}\exp\left(-\frac{\Delta_e}{T}\right), \tag{4}$$

where γ_s represents an electronic specific heat coefficient in the superconducting state, A and B are fitting constants, and Δ_e is proportional to the energy gap in the BCS theory of

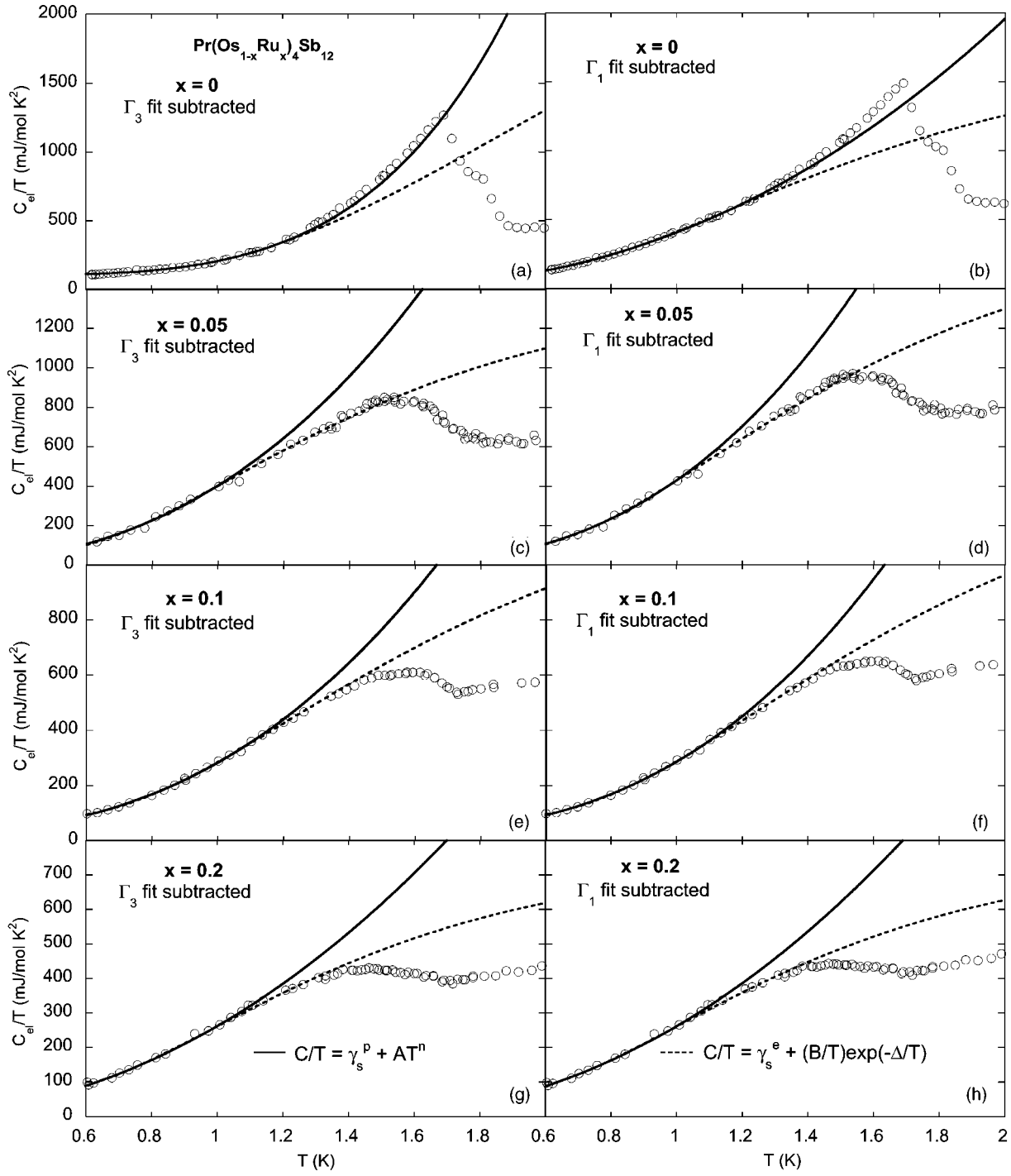

FIG. 4. Comparison of exponential (dashed line) and power-law (solid line) fits, subtracting data for either Γ_3 [(a), (c), (e), and (g)] or Γ_1 [(b), (d), (f), and (h)] ground states below T_c, for $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ with $x=0$ [(a) and (b)], 0.05 [(c) and (d)], 0.1 [(e) and (f)], and 0.2 [(g) and (h)]. The $x=0$ fits only extend up to ~1.2 K, the $x=0.05$ and 0.1 fits only extend up to ~1.1 K, and the $x=0.2$ fits only extend up to ~1.0 K, as described in the text.

superconductivity. The results of the application of these fits to the $0 \leqslant x \leqslant 0.2$ 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 ~1.2 K all the way up to the transition, while the exponential fits deviate from the data right above 1.2 K. For $x \geqslant 0.05$, the converse is true, as the exponential fits extrapolate to the higher-temperature data (above ~1.1 K for $x=0.05$ and 0.1, and above ~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 to be more appropriate.

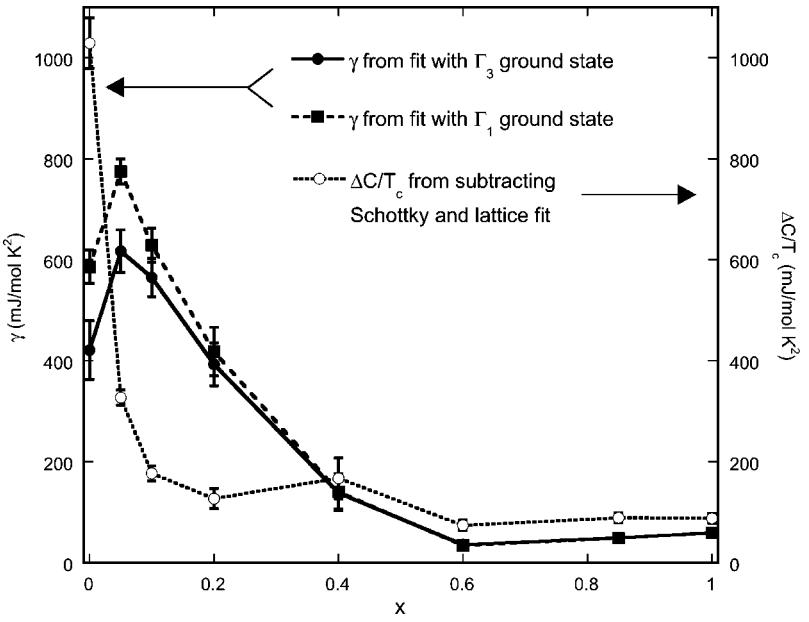

FIG. 5. Electronic specific heat coefficient γ (left axis, closed circles and squares) and $\Delta C/T_c$ (right axis, open circles) as a function of Ru concentration x for $Pr(Os_{1-x}Ru_x)_4Sb_{12}$.

The constants from the fits below T_c are also listed in Table II. The listed errors are due to the variation of Θ_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. 2(a); the error in $\Delta C/T_c$ from the variation of Θ_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 $PrOs_4Sb_{12}$, the Γ_3 ground state subtraction results in fits that are much different from the Γ_1 ground state subtraction results. The other concentrations have similar fit parameters for the two different ground states. In addition, the values for n and Δ_e, and the errors associated with them, are much larger for the Γ_3 $x=0$ fits than for the other Γ_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 Γ_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.[27] n is also between 2 and 3 for $x \geqslant 0.05$, but the exponential fits appear to be more accurate for these concentrations. The values of Δ_e for the Γ_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 Δ_e in units of K). The parameter γ_s can be interpreted as a portion of the sample that is normal or gapless; however, the values of γ_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 $PrOs_4Sb_{12}$, even if the absolute values are not entirely accurate, does lend phenomenological support for Γ_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 Γ_1 or Γ_3 for the Pr^{3+} ground state.

Figure 5 shows a comparison between the electronic specific heat coefficient γ 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 $PrOs_4Sb_{12}$. However, it is expected that there will be some proportional relation between $\Delta C/T_c$ and γ (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 γ determined from the normal state data and calculated from the superconducting transition is an interesting one. The minimum in γ at $x=0.6$ for the measured γ, 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 0.05 implies that strong-coupling superconductivity is only present for these two concentrations. Taken at face value, this could mean that for $0.1 \leqslant x \leqslant 0.4$, the heavy electrons are *not* participating in the superconductivity, which would imply that the superconductivity is nearly conventional for $x \geqslant 0.1$ (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 $0.05 \leqslant x \leqslant 0.4$, however, as the superconducting transitions for $x=0.6$ and 0.85 are as sharp as or sharper than that 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 $PrOs_4Sb_{12}$ 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.[13] 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 $PrOs_4Sb_{12}$, preliminary results suggest that only the lower transition of $PrOs_4Sb_{12}$ is suppressed for small La concentrations.[24] 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 $PrOs_4Sb_{12}$, where the two bands are coupled by Josephson pair tunneling, which requires the two order parameters to have the same symmetry.[4] The difference in the behavior below T_c between $PrOs_4Sb_{12}$ 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 under way 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 $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ 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 $PrOs_4Sb_{12}$, but an exponential fit associated with an isotropic energy gap was more appropriate for the data with $0.05 \leqslant x \leqslant 0.2$. The electronic specific heat γ was inferred from both normal state data and the ratio $\Delta C/T_c$. The normal state fits revealed an enhanced γ for $x \leqslant 0.4$, reaching a minimum value at $x=0.6$, the same concentration as the minimum in T_c. However, $\Delta C/T_c$ was significantly enhanced only for $x=0$ and 0.05.

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[1] E. D. Bauer, N. A. Frederick, P.-C. Ho, V. S. Zapf, and M. B. Maple, Phys. Rev. B **65**, 100506(R) (2002).
[2] M. B. Maple, P.-C. Ho, V. S. Zapf, N. A. Frederick, E. D. Bauer, W. M. Yuhasz, F. M. Woodward, and J. W. Lynn, J. Phys. Soc. Jpn. **71**, Suppl., 23 (2002).
[3] M. B. Maple, P.-C. Ho, N. A. Frederick, V. S. Zapf, W. M. Yuhasz, E. D. Bauer, A. D. Christianson, and A. H. Lacerda, J. Phys.: Condens. Matter **15**, S2071 (2003).
[4] D. M. Broun, P. J. Turner, G. K. Mullins, D. E. Sheehy, X. G. Zheng, S. K. Kim, N. A. Frederick, M. B. Maple, W. N. Hardy, and D. A. Bonn, cond-mat/0310613 (unpublished).
[5] 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).
[6] 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. Lett. **89**, 157001 (2002).
[7] H. Kotegawa, M. Yogi, Y. Imamura, Y. Kawasaki, G. q. Zheng, Y. Kitaoka, S. Ohsaki, H. Sugawara, Y. Aoki, and H. Sato, Phys. Rev. Lett. **90**, 027001 (2003).
[8] H. Suderow, S. Vieira, J. D. Strand, S. Bud'ko, and P. C. Canfield, Phys. Rev. B **69**, 060504(R) (2004).
[9] E. E. M. Chia, M. B. Salamon, H. Sugawara, and H. Sato, Phys. Rev. Lett. **91**, 247003 (2003).
[10] Y. Aoki, A. Tsuchiya, T. Kanayama, S. R. Saha, H. Sugawara, H. Sato, W. Higemoto, A. Koda, K. Ohishi, K. Nishiyama, and R. Kadono, Phys. Rev. Lett. **91**, 067003 (2003).
[11] N. Takeda and M. Ishikawa, J. Phys. Soc. Jpn. **69**, 868 (2000).
[12] M. Yogi, H. Kotegawa, Y. Imamura, G. q. Zheng, Y. Kitaoka, H. Sugawara, and H. Sato, Phys. Rev. B **67**, 180501(R) (2003).
[13] E. E. M. Chia, M. B. Salamon, H. Sugawara, and H. Sato, Phys. Rev. B **69**, 180509(R) (2004).
[14] K. Abe, H. Sato, T. D. Matsuda, T. Namiki, H. Sugawara, and Y. Aoki, J. Phys.: Condens. Matter **14**, 11757 (2002).
[15] N. A. Frederick, T. D. Do, P.-C. Ho, N. P. Butch, V. S. Zapf, and M. B. Maple, Phys. Rev. B **69**, 024523 (2004).
[16] I. A. Sergienko, Phys. Rev. B **69**, 174502 (2004).
[17] R. Vollmer, A. Faiβt, C. Pfleiderer, H. v. Löhneysen, E. D. Bauer, P.-C. Ho, V. S. Zapf, and M. B. Maple, Phys. Rev. Lett. **90**, 057001 (2003).
[18] E. S. R. Gopal, *Specific Heat at Low Temperatures* (Plenum Press, New York, 1966).
[19] M. Kohgi, K. Iwasa, M. Nakajima, N. Metoki, S. Araki, N. Bernhoeft, J.-M. Mignot, A. Gukasov, H. Sato, Y. Aoki, and H. Sugawara, J. Phys. Soc. Jpn. **72**, 1002 (2003).
[20] C. R. Rotundu, H. Tsujii, Y. Takano, B. Andraka, H. Sugawara, Y. Aoki, and H. Sato, Phys. Rev. Lett. **92**, 037203 (2004).
[21] E. A. Goremychkin, R. Osborn, E. D. Bauer, M. B. Maple, N. A. Frederick, W. M. Yuhasz, F. M. Woodward, and J. W. Lynn, Phys. Rev. Lett. **93**, 157003 (2004).
[22] M. B. Maple, P.-C. Ho, N. A. Frederick, V. S. Zapf, W. M. Yuhasz, and E. D. Bauer, Acta Phys. Pol. B **34**, 919 (2003).
[23] Y. Aoki, T. Namiki, S. Ohsaki, S. R. Saha, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **71**, 2098 (2002).
[24] C. R. Rotundu, P. Kumar, and B. Andraka, cond-mat/0402599 (unpublished).
[25] G. R. Stewert, Rev. Mod. Phys. **56**, 755 (1984).
[26] J. P. Brison, N. Keller, P. Lejay, A. Huxley, L. Schmidt, A. Buzdin, N. R. Bernhoeft, I. Mineev, A. N. Stepanov, J. Flouquet, D. Jaccard, S. R. Julian, and G. G. Lonzarich, Physica B **199&200**, 70 (1994).
[27] M. Sigrist and K. Ueda, Rev. Mod. Phys. **63**, 239 (1991).