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# Probing the superconducting gap symmetry of $PrRu_4Sb_{12}$: A comparison with $PrOs_4Sb_{12}$

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We report measurements of the magnetic penetration depth $\lambda$ in single crystals of $PrRu_4Sb_{12}$ down to 0.1 K. Both $\lambda$ and superfluid density $\rho_s$ exhibit an exponential behavior for $T<0.5T_c$, with parameters $\Delta(0)/k_BT_c=1.9$ and $\lambda(0)=2900$ Å. The value of $\Delta(0)$ is consistent with the specific-heat jump value of $\Delta C/\gamma T_c=1.87$ measured elsewhere, while the value of $\lambda(0)$ is consistent with the measured value of the electronic heat-capacity coefficient $\gamma$. Our data are consistent with $PrRu_4Sb_{12}$ being a moderate-coupling, fully gapped superconductor. We suggest experiments to study how the nature of the superconducting state evolves with increasing Ru substitution for Os.

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The recent discovery[1,2] of the heavy fermion (HF) skutterudite superconductor (SC) $PrOs_4Sb_{12}$ has attracted much interest due to its differences from other HFSCs. Measurements of dc magnetic susceptibility, specific heat, electrical resistivity, and inelastic neutron scattering showed that the ninefold degenerate $J=4$ Hund's rule multiplet of Pr is split by the cubic crystal electric field, such that its ground state is a *nonmagnetic* $\Gamma_3$ doublet, separated from the first excited state $\Gamma_5$ by $\sim 10$ K. Hence its HF behavior, and consequently the origin of its superconductivity, might be attributed to the interaction between the electric quadrupolar moments of $Pr^{3+}$ and the conduction electrons. It is thus a candidate for the first superconductor mediated by quadrupolar fluctuations, i.e., by neither electron-phonon nor, as with other HFSCs, magnetic interactions.

Surprisingly, replacement of Os by Ru, i.e., in $PrRu_4Sb_{12}$, yields a superconductor with $T_c\approx 1.25$ K with significantly different properties. From the slope of the upper critical field[3] near $T_c$, $(-\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}=2.4$ kOe/K and using the procedure in Ref. 1, we get the effective mass of the heavy electrons $m^*\approx 20m_e$. This contrasts with the value $m^*/m_e=45$ for $PrOs_4Sb_{12}$, showing that while $PrOs_4Sb_{12}$ is clearly a heavy-fermion material, $PrRu_4Sb_{12}$ is at most, a marginal HF. Various experimental results suggest that these two materials have different order-parameter symmetry. First, there is an absence of a Hebel–Slichter peak in the nuclear quadrupole resonance (NQR) data[4] for $PrOs_4Sb_{12}$, while a distinct coherence peak was seen[5] in the Sb-NQR $1/T_1$ data for $PrRu_4Sb_{12}$. Second, the low-temperature power-law behavior seen in specific heat[1] and penetration depth,[6] and the angular variation of thermal conductivity,[7] suggest the presence of nodes in the order parameter of $PrOs_4Sb_{12}$. Specifically, Refs. 6 and 7 reveal the presence of *point* nodes on the Fermi surface (FS). For $PrRu_4Sb_{12}$, however, an exponential decrease in $1/T_1$ is observed below the Hebel–Slichter peak[5] and was fit with an isotropic gap of magnitude $\Delta(0)=1.5k_BT_c$, where $\Delta(0)$ is the magnitude of the zero-temperature superconducting gap. Third, muon spin rotation ($\mu$SR) experiments on $PrOs_4Sb_{12}$ reveal the spontaneous appearance of static internal magnetic fields below $T_c$, providing evidence that the superconducting state is a time-reversal-symmetry-breaking (TRSB) state.[8] Such experiments have not been performed on $PrRu_4Sb_{12}$.

In this paper, we present high-precision measurements of penetration depth $\lambda(T)$ of $PrRu_4Sb_{12}$ at temperatures down to 0.1 K using the same experimental conditions[6] as for $PrOs_4Sb_{12}$. Both $\lambda(T)$ and superfluid density $\rho_s(T)$ exhibit exponential behavior at low temperatures, suggesting the presence of an isotropic superconducting gap on the FS. Data are best fit by the parameters $\Delta(0)/k_BT_c=1.9$ and $\lambda(0)=2900$ Å, and thus suggest that $PrRu_4Sb_{12}$ is a moderate-coupling, fully gapped superconductor. The values of $\Delta(0)/k_BT_c$ and $\lambda(0)$ are consistent with values[3] derived from the specific-heat jump $\Delta C/\gamma T_c=1.87$, and the linear specific-heat coefficient $\gamma$.

Details of sample growth and characterization are described in Ref. 3. The observation of the de Haas–van Alphen (dHvA) effect from the same batch of samples,[9] and the large residual resistivity ratio (RRR $\sim$ 76), reflect the high quality of the samples. Measurements were performed utilizing a 21 MHz tunnel diode oscillator[10] with a noise level of two parts in $10^9$ and low drift. The magnitude of the ac field was estimated to be less than 40 mOe. The cryostat was surrounded by a bilayer Mumetal shield that reduced the dc field to less than 1 mOe. The sample was mounted, using a small amount of GE varnish, on a single crystal sapphire rod. The other end of the rod was thermally connected to the mixing chamber of an Oxford Kelvinox 25 dilution refrigerator. The sample temperature is monitored using a calibrated $RuO_2$ resistor at low temperatures ($T_{\mathrm{base}}$ to 1.8 K).

The deviation $\Delta\lambda(T)=\lambda(T)-\lambda(0.1\text{ K})$ is proportional to the change in resonant frequency $\Delta f(T)$ of the oscillator, with the proportionality factor $G$ dependent on sample and coil geometries. We determine $G$ for a pure Al single crystal by fitting the Al data to extreme nonlocal expressions and then adjust for relative sample dimensions.[11] Testing this approach on a single crystal of Pb, we found good agreement with conventional BCS expressions. The value of $G$ obtained this way has an uncertainty of $\pm 10\%$ because our sample,

 

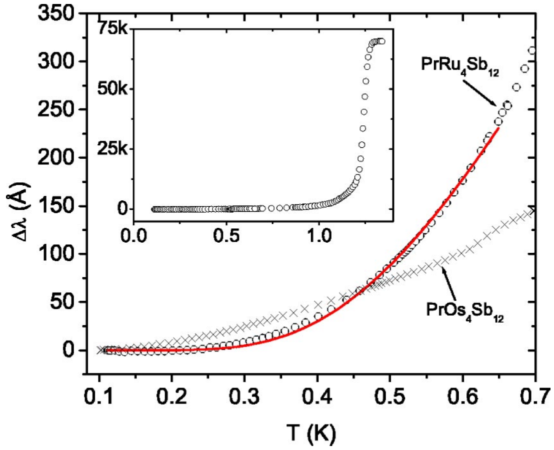


FIG. 1. (○) Low-temperature dependence of the penetration depth $\Delta\lambda(T)$ of $PrRu_4Sb_{12}$. The solid line is the fit to Eq. (1) from 0.1 to 0.65 K, with $\Delta(0)=2.4$ K$=1.9k_BT_c$. Inset shows $\Delta\lambda(T)$ of $PrRu_4Sb_{12}$ over the full temperature range. (×) $\Delta\lambda(T)$ data of $PrOs_4Sb_{12}$, taken from Ref. 6.

with approximate dimensions $0.7\times0.5\times0.25$ mm$^3$, has a rectangular, rather than square, basal area.[12]

Figure 1 (○) shows $\Delta\lambda(T)$ for $PrRu_4Sb_{12}$ as a function of temperature in the low-temperature region. The inset shows $\Delta\lambda(T)$ for the entire temperature range. The value of $T_c$, taken to be the mid-point of the transition, is 1.25 K. The data points flatten out below 0.22 K ($\sim0.18T_c$), implying activated behavior in this temperature range. Contrasting this, we superpose data for $PrOs_4Sb_{12}$ on the same figure (×), which show $\Delta\lambda$ varying strongly ($\sim T^2$) with temperature, indicative of low-lying excitations.[6] We fit the $PrRu_4Sb_{12}$ data to the BCS low-temperature expression in the clean and local limit, from $T_{\mathrm{base}}(0.1\ \mathrm{K}\approx0.08T_c)$ to 0.65 K ($\approx0.5T_c$), using

$$\Delta\lambda(T)\propto\sqrt{\frac{\pi\Delta(0)}{2k_BT}}\exp\left(-\frac{\Delta(0)}{k_BT}\right), \tag{1}$$

with the proportionality constant and $\Delta(0)$ as parameters. The best fit (solid line in Fig. 1) is obtained when $\Delta(0)=2.4$ K$=1.9k_BT_c$. This value is larger than the BCS weak-coupling value of $1.76k_BT_c$, suggesting that $PrRu_4Sb_{12}$ is in the moderate-coupling regime. To check the validity of this value of $\Delta(0)$ we make use of the strong-coupling equations[13,14]

$$\eta_\Delta(\omega_0)=1+5.3\left(\frac{T_c}{\omega_0}\right)^2\ln\left(\frac{\omega_0}{T_c}\right), \tag{2}$$

$$\eta_{Cv}(\omega_0)=1+1.8\left(\frac{\pi T_c}{\omega_0}\right)^2\left(\ln\left(\frac{\omega_0}{T_c}\right)+0.5\right), \tag{3}$$

$$\eta_\lambda(\omega_0)=\frac{\sqrt{1+\left(\frac{\pi T_c}{\omega_0}\right)^2\left(0.6\ln\left(\frac{\omega_0}{T_c}\right)-0.26\right)}}{1+\left(\frac{\pi T_c}{\omega_0}\right)^2\left(1.1\ln\left(\frac{\omega_0}{T_c}\right)+0.14\right)}, \tag{4}$$

where each $\eta$ represents the correction factor to the corresponding weak-coupling BCS value. If we take $\Delta(0)=1.9k_BT_c$, then Eq. (2) gives the characteristic (equivalent Einstein) frequency $\omega_0\approx17$ K and Eq. (3) gives $\Delta C/\gamma T_c=1.9$. This value of $\Delta C/\gamma T_c$ agrees excellently with the measured value (1.87) in Ref. 3, giving further evidence that $PrRu_4Sb_{12}$ is indeed a moderate-coupling superconductor.

To extract the superfluid density $\rho_s$ from our data, we need to know $\lambda(0)$. For a type-II superconductor, $\lambda(0)$ can be obtained from[15]

$$\lambda(0)=\frac{[\Phi_0H_{c2}(0)]^{1/2}}{\sqrt{24}\delta_{sc}T_c\gamma^{1/2}}, \tag{5}$$

where $\Phi_0=2.06\times10^9$ G Å$^2$ is the flux quantum, $H_{c2}(0)$ is the upper critical field at $T=0$, $\delta_{sc}\equiv\Delta(0)/k_BT_c$, and $\gamma$ is the electronic specific heat coefficient. Using $(-dH_{c2}/dT)_{T_c}=2.4$ kOe/K from Ref. 3 and the expression $H_{c2}(0)=0.693(-\mathrm{d}H_{c2}/\mathrm{d}T)_{T_c}T_c$, we obtain $H_{c2}(0)=2.16$ kOe. The superconducting coherence length $\xi_0$ can be estimated from the relation $H_{c2}(0)=\Phi_0/2\pi\xi_0^2$, yielding $\xi_0\approx400$ Å. The value $\gamma=59$ mJ/mol K$^2$ is also obtained from Ref. 3. We calculate $\lambda(0)$ using two methods: (1) taking $\delta_{sc}=1.9$, or (2) taking $\delta_{sc}=1.76$ along with strong-coupling corrections [Eqs. (2) and (4)]. Both methods yield $\lambda(0)\approx3200$ Å. This puts $PrRu_4Sb_{12}$ in the local limit. Furthermore, from dHvA data,[9] we estimate the mean free path $l\approx1300$ Å, implying that the sample is close to the clean limit. To calculate $\rho_s$ for an isotropic $s$-wave superconductor in the clean and local limits we use the expression

$$\rho_s=1+2\int_0^\infty\frac{\partial f}{\partial E}d\varepsilon, \tag{6}$$

where $f=[\exp(E/k_BT)+1]^{-1}$ is the Fermi function, and $E=[\varepsilon^2+\Delta(T)^2]^{1/2}$ is the quasiparticle energy. The temperature-dependence of $\Delta(T)$ can be obtained by using[15]

$$\Delta(T)=\delta_{sc}kT_c\tanh\left\{\frac{\pi}{\delta_{sc}}\sqrt{a\left(\frac{\Delta C}{C}\right)\left(\frac{T_c}{T}-1\right)}\right\}, \tag{7}$$

where $\delta_{sc}$ is the only variable parameter, $T_c=1.25$ K, $a=2/3$, and the specific heat jump $\Delta C/C\equiv\Delta C/\gamma T_c=1.87$ is an experimentally obtained value.[3]

Figure 2 shows the experimental (○) and calculated (solid and dotted lines) values of $\rho_s$ as a function of temperature. The best fit from 0.1 to 0.95 K ($\sim0.8T_c$) is obtained when $\lambda(0)=2900$ Å and $\Delta(0)=1.9k_BT_c$ (solid line). This value of $\lambda(0)$ is 10% lower than the earlier-calculated value of 3200 Å, but is acceptable because of the uncertainty in obtaining the calibration factor $G$. The value of $\Delta(0)$ once again agrees with the specific-heat jump $\Delta C/\gamma T_c$ obtained in Ref. 3 via Eqs. (2) and (3), though it disagrees with the weak-coupling value of $1.5k_BT_c$ in Ref. 5. The dotted line in Fig. 2, calculated using the weak-coupling parameters $\Delta(0)=1.76k_BT_c$ and $\Delta C/\gamma T_c=1.43$, clearly does not fit the data. Our superfluid data once again suggest that $PrRu_4Sb_{12}$ is a moderate-coupling superconductor with a superconducting gap on the entire FS.

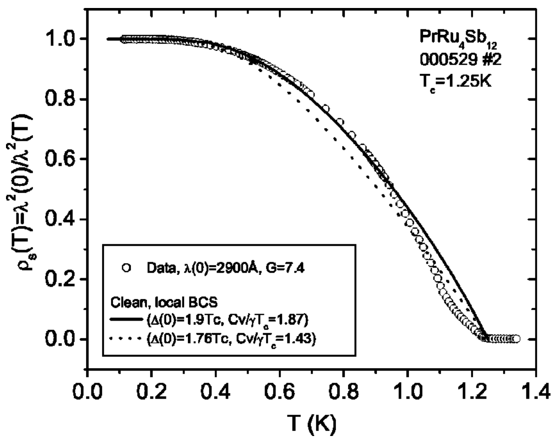


FIG. 2. (○) Superfluid density $\rho_s(T)=[\lambda^2(0)/\lambda^2(T)]$ calculated from $\Delta\lambda(T)$ data in Fig. 1. Lines: $\rho_s(T)$ calculated from Eq. (6) with parameters $\Delta(0)/k_BT_c=1.9$ and $\Delta C/\gamma T_c=1.87$ (solid line), $\Delta(0)/k_BT_c=1.76$ and $\Delta C/\gamma T_c=1.43$ (dotted line).

It is apparent in Fig. 2 that the data deviate from local BCS expression above 0.95 K. We also noticed a small hump in $\Delta\lambda$ near 1.1 K shown in Fig. 1, which shows up as a curvature change in $\rho_s$ in Fig. 2 and may explain the disagreement between data and BCS expression near $T_c$. These features may be due to inhomogeneities and/or impurity effects in the sample, because the $T_c$'s of these single crystals vary[16] between 1 and 1.3 K. The spread of $T_c$'s is not expected to affect the low-temperature exponential behavior of this BCS-like sample.

It is puzzling that the substitution of Ru for Os (same column in the periodic table) causes $PrRu_4Sb_{12}$ to differ in so many respects from $PrOs_4Sb_{12}$. Further, evidence for gap anisotropy in the latter compound is contradicted by $\mu$SR measurements[17] [suggesting either *s*- or *p*-wave pairing, with $\Delta(0)=2.1k_BT_c$], scanning tunneling spectroscopy,[18] and NQR measurements[4] (with $\Delta(0)=2.6k_BT_c$). If both $PrRu_4Sb_{12}$ and $PrOs_4Sb_{12}$ have isotropic gaps, then they are unique, especially the latter, among HFSC, suggesting the possibility of (a) an important difference in superconducting properties between HFSC with magnetic and nonmagnetic *f*-ion ground states, and (b) a correlation between pairing symmetry (isotropic or nodal gap) and mechanism (quadrupolar or magnetic fluctuations) of superconductivity.[17]

Recently, Frederick *et al.* performed x-ray powder diffraction, magnetic susceptibility and electrical resistivity measurements[19] on single crystals of $Pr(Os_{1-x}Ru_x)_4Sb_{12}$. They found that (1) the lattice constant *a* decreases approximately linearly with increasing Ru concentration, (2) the splitting between the ground and first excited state increases monotonically with *x*, with the fits consistent with a $\Gamma_3$ doublet ground state for all values of *x*, although reasonable fits can be obtained for a $\Gamma_1$ ground state for *x* near 0 and 1, and (3) $T_c$ decreases nearly linearly with substituent concentration away from $x=0$ and $x=1$, but exhibits a deep minimum (0.75 K) at $x=0.6$. The smooth evolution of *a* and $T_c$ with *x*, and the presence of superconductivity for all values of *x*, may suggest that both $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$ possess the same order-parameter symmetry. The minimum in $T_c$ at $x=0.6$ could simply mark the shift from quadrupolar-mediated heavy fermion superconductivity to phonon-mediated BCS superconductivity. On the other hand, one still has to contend with measurements[6–8,20] that indicate point-node gap structure, TRSB and double superconducting transitions in $PrOs_4Sb_{12}$. If so, the minimum in $T_c$ could be a consequence of competing order-parameter symmetries with a possible quantum critical point between them. It is also interesting to notice in Ref. 19 that the step-like structure seen in ac susceptibility data in the $x=0$ sample, i.e., $PrOs_4Sb_{12}$, indicative of an intrinsic second superconducting transition, is *not* seen for all other values of *x*.

To further elucidate the relationship between $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$, work is underway looking at the changes in penetration depth on $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ for a range of values of *x*. We want to know at which value of *x* (paying close attention to the value $x=0.6$), if any, does the isotropic superconducting gap evolve into a nodal one. Moreover, we want to know whether the second superconducting transition[20] seen in $PrOs_4Sb_{12}$ can also be seen in samples where $0<x\leqslant 1$. If we do not see the second superconducting transition in the other samples, then it is possible that the superconductivity in the two superconducting phases of $PrOs_4Sb_{12}$ respond differently to impurities (Ru substituents)—one is completely destroyed by even tiny amounts of impurities, while the other persists (though weakened) all the way to $PrRu_4Sb_{12}$. It might be useful also if the impurity introduced is of an element that would *not* produce an isostructural superconducting compound.

In conclusion, we report measurements of the magnetic penetration depth $\lambda$ in single crystals of $PrRu_4Sb_{12}$ down to 0.1 K using a tunnel-diode based, self-inductive technique at 21 MHz. Both $\lambda$ and $\rho_s$ exhibit an exponential behavior for $T<0.5T_c$, with parameters $\Delta(0)/k_BT_c=1.9$ and $\lambda(0)=2900$ Å. The value of $\Delta(0)$ is consistent with the specific-heat jump value of $\Delta C/\gamma T_c=1.87$ measured elsewhere,[3] while the value of $\lambda(0)$ is consistent with the measured value[3] of the electronic heat-capacity coefficient $\gamma$, and $\Delta(0)$. Our data are consistent with $PrRu_4Sb_{12}$ being a moderate-coupling, fully gapped superconductor. We also suggest further experiments that can be done to study how the nature of the superconducting state evolves with Ru substitution, to further elucidate the relationship among HF behavior, superconducting gap structure, and the presence of TRSB in the superconducting state.

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