Multiband Order Parameters for the $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$ Skutterudite Superconductors from Thermal Conductivity Measurements

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Thermal conductivity measurements were performed on single crystal samples of the superconducting filled-skutterudite compounds $PrOs_4Sb_{12}$ and $PrRu_4Sb_{12}$ both as a function of temperature and transverse magnetic field. In a zero magnetic field, the low temperature electronic thermal conductivity of $PrRu_4Sb_{12}$ is consistent with a fully gapped Fermi surface. For $PrOs_4Sb_{12}$, residual electronic conduction in the zero-temperature limit is consistent with the presence of nodes in the superconducting energy gap. The electronic thermal conductivity for both compounds shows a rapid rise at low magnetic fields. In $PrRu_4Sb_{12}$, this is interpreted in terms of multiband effects. In $PrOs_4Sb_{12}$, we consider the Doppler shift of nodal quasiparticles and multiband effects.

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With improvements in materials science, new materials that are superconducting continue to be discovered and experimental studies on them shed light on where our knowledge about superconductivity can be enhanced. The filled-skutterudite family of materials is one such example, exhibiting many features that suggest in some variants its superconductivity may be conventional, while in others unconventional. A comparison between the superconducting properties of each type of material is certainly instructive.

Some of the more unusual properties have been seen in the heavy-fermion superconductor $PrOs_4Sb_{12}$ (POS) where, despite more than 5 yr of research activity, there is no consensus on whether the superconducting order parameter has nodes or not. For example, in angle-resolved magneto-thermal conductivity experiments [1], a change in the symmetry of the small anisotropy in the conductivity is interpreted as evidence for a multiphase superconducting phase diagram with both phases having nodes in the superconducting order parameter. More recently, the thermal conductivity has been measured to even lower temperatures [2,3]. Surprisingly, the measurements show an absence of any residual electronic conduction in zero field, which is inconsistent with the presence of nodes in the superconducting gap energy from angle-resolved measurements.

On the other hand, the isostructural but non-heavy-fermion compound, $PrRu_4Sb_{12}$ (PRS), appears to be a conventional s-wave superconductor with exponential temperature dependencies observed in specific heat [4,5] and superfluid density [6].

In this Letter, we present low temperature thermal conductivity measurements that provide evidence for a fully gapped order parameter in PRS and a nodal superconducting order parameter in POS. We also demonstrate that the field dependence of the fully gapped superconductor is consistent with multiband superconductivity. In the nodal superconductor, the field dependence immediately above H_{c1} is consistent with being due to the Doppler shift of nodal quasiparticles, with multiband effects occurring at fields above $H_{c2}/2$. Finally, we explore the possibility that multiband superconductivity is a generic feature of filled-skutterudite superconductors.

The single crystal samples were oriented using Laué x-ray backscattering. In the case of POS, the sample was then polished to a cuboid of dimension $(600 \times 100 \times 100)$ μm. The PRS sample was as-grown with dimensions $(2500 \times 188 \times 380)$ μm. In both cases, four silver wires were attached using high purity indium solder. The estimated contact resistance at $T = 0.05$ K is less than 100 mΩ. The thermal conductivity was measured using a single heater-two thermometer method. The heat current was supplied along the a-axis direction and the magnetic field applied perpendicular to this. The measurements were made in a dilution refrigerator by varying the temperature from 0.04 K to $>$1 K at fixed magnetic field. The samples were field-cooled by cycling to $T > 2$ K before changing the field. The error in the absolute value of the conductivity is estimated to be approximately 10%, with a relative error between temperature sweeps of 1%.

In Fig. 1, the temperature dependence of the zero-field thermal conductivity is plotted for both materials. Since we measure the total thermal conductivity, it is necessary to separate the contributions from electrons and phonons. Using the well-established model based on kinetic theory (see, for example, [7]), in the low temperature limit, the electronic contribution is linear in temperature, while phonons are cubic in temperature. Fitting the measured conductivity (κ) to the form

$$\frac{\kappa}{T} = \frac{\kappa_0}{T} + \beta T^2 \quad (1)$$

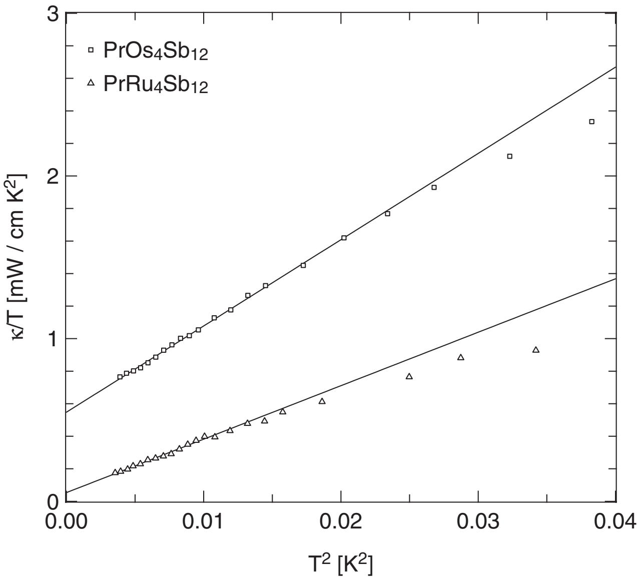

FIG. 1. Thermal conductivity divided by temperature T versus T^2 in zero field for POS and PRS. The lines are linear fits to the low temperature data ($T < 0.15$ K) which are then extrapolated to the $T = 0$ axis.

and extrapolating the fit to zero temperature we obtain a value for the residual electronic conductivity divided by T, κ_0/T. The coefficient β in the above expression represents the phonon contribution in this simple analysis. Fitting the data below $T = 0.15$ K, the values obtained for each material are 0.46 ± 0.07 mW/K^2 cm and 0.058 ± 0.007 mW/K^2 cm for POS and PRS, respectively. In contrast, the apparent phonon contribution in each material is very similar, as might be expected given the identical structure of these materials.

In PRS, the value of κ_0/T is an order of magnitude smaller than that measured in POS. In instances where κ_0/T is very small, the simplicity of the above model is exposed. Improved fitting accuracy has been demonstrated using an empirically determined variable power law for the phonon contribution [7]. In such cases the extrapolated value for the residual linear term is always found to be reduced and in this case we find $\kappa_0/T = 8 \pm 17$ μW/K^2 cm and a phonon exponent of $T^{1.6}$. Within error bars, this indicates the absence of any residual electronic conductivity and is therefore consistent with a fully gapped superconducting state.

In contrast, the observation of a significant finite value for the zero-temperature extrapolation of the linear electronic conductivity in POS is incontrovertible evidence for nodes on the Fermi surface of the superconducting order parameter.

As a consistency check, a calculation of the magnitude of the residual linear term assuming a simple d-wave symmetry of the superconducting gap and weak coupling can be made for both systems. Following [8,9], the magnitude of the residual electronic conductivity is given by

$$\frac{\kappa_0}{T} = \left(\frac{4}{\pi}\frac{\hbar\Gamma}{\Delta_0}\frac{1}{\mu}\right)\frac{\kappa_n}{T} \qquad (2)$$

where κ_n is the residual normal state thermal conductivity, Δ_0 is the maximum of the superconducting energy gap, Γ is the normal state impurity scattering rate, and $\mu = 1/\Delta_0 d\Delta(\phi)/d\phi|_{\mathrm{node}}$ is the gradient of the energy gap at the node. For d-wave symmetry, $\mu = 2$. In POS, to estimate the normal state scattering rate Γ we use the normal state conductivity (above H_{c2}) $\kappa_n/T = 8$ mW/K^2 cm combined with the Fermi velocity v_F calculated from the coherence length $v_F = 1.5 \times 10^4$ ms^{-1} [10] and the electronic specific heat $\gamma = 350$ mJ K^{-2} mol^{-1} [11]. This gives $\Gamma = 3.4 \times 10^{10}$ s^{-1}. We also use $\Delta_0 = 2.14 k_B T_c$, with $T_c = 1.85$ K. Overall, we estimate $\kappa_0/T = 0.3$ mW/K^2 cm. However, we note that such a fourfold symmetry would only be consistent with the high-field superconducting phase observed by angle-resolved magneto-thermal conductivity measurements [1]. For PRS, this simple calculation would give an even larger value because of the smaller gap magnitude, which is consistent with the very small value for κ_0/T being interpreted as evidence for a fully gapped Fermi surface.

The observation of a linear term in POS in this study directly contradicts that of other low temperature thermal conductivity measurements where the data extrapolate to zero with a rapid temperature dependence that exceeds T^3 [2,3]. Rapid temperature dependencies such as these are known to occur when electron-phonon decoupling hampers the measurement of the intrinsic electronic conductivity [12] and is thought to occur in other superconducting systems [13,14]. In $CeCoIn_5$ in particular, early measurements indicated a large $T^{3.4}$ temperature dependence and zero residual electronic conductivity [15]. Recent measurements show a large residual electronic conductivity and a lower T^2 temperature dependence [16]. Measurements in this study are clearly not affected by such a mechanism since we measure a sizable residual conductivity along with a sub-T^3 phonon conductivity. In the upper inset to Fig. 4, where we show the field dependence of the thermal conductivity at $T = 100$ mK, we also demonstrate the absence of any significant influence of the indium contacts on our result. Moreover, the measurements are benchmarked against a closely related material, PRS, where we recover no residual electronic conductivity and again a sub-T^3 phonon contribution. The use of an identical technique to measure each material with identical contacts and yet dramatically different but nevertheless consistent results is compelling. Finally, we also note that while there is an established mechanism whereby a measurement may result in the absence of any residual electronic conductivity as outlined above, we are not aware of any mechanism that gives rise to residual linear conductivity if one is not present in the material being studied.

The temperature dependence of the thermal conductivity for different magnetic fields applied perpendicular to the direction of the heat current is shown in Fig. 2 for POS and

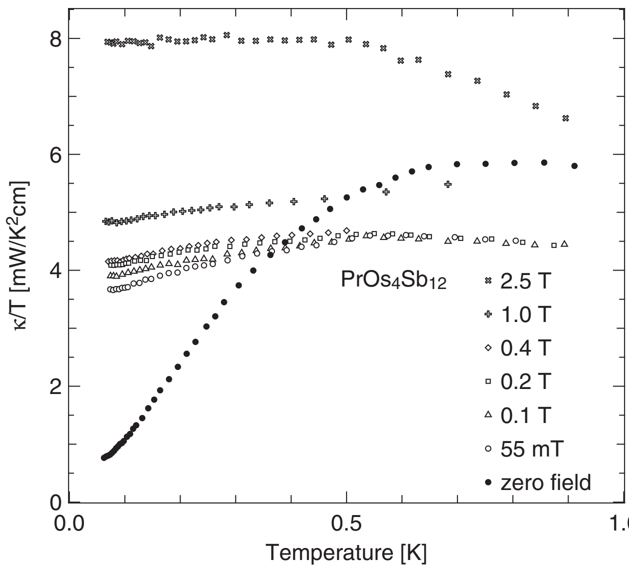

FIG. 2. Thermal conductivity divided by temperature T versus T for POS at different magnetic fields. The heat current is applied along the a axis of the single crystal sample. The magnetic field is applied perpendicular to this direction.

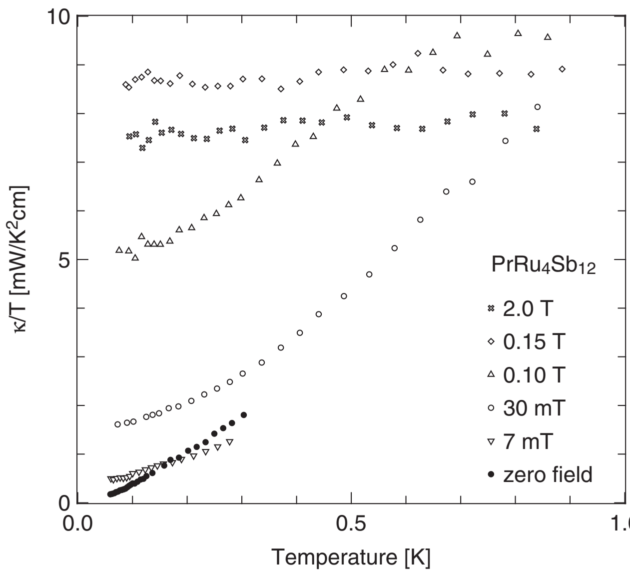

FIG. 3. Thermal conductivity divided by temperature T versus T for PRS at different magnetic fields. The heat current is applied along the a axis of the single crystal sample. The magnetic field is applied perpendicular to this direction.

Fig. 3 for PRS. The data for both materials show features that are qualitatively similar, although there are some distinct differences. In zero field, the data have the steepest temperature dependence, which in POS rises to a plateau above $T = 0.6$ K. Measurements at higher temperature show this to be a peak [17]. In both materials, as soon as a magnetic field is applied the T dependence is suppressed by a dramatic increase in κ/T at the lowest temperatures. For subsequent higher fields, the curves at low temperatures then remain approximately parallel as the field increases by orders of magnitude and the system enters the normal state.

In order to explore the magnetic field dependence more clearly, the value of the temperature dependence extrapolated to $T = 0$ K at each field is extracted, normalized to the normal state value, and then plotted in Fig. 4 as a function of magnetic field normalized to the upper critical field (H_{c2}). Values used for the upper critical field are $H_{c2} = 2$ T for POS [10] and 0.2 T for PRS [4]. In the simplest fully gapped superconductor, the field dependence of the residual electronic conduction rises exponentially with magnetic field on a scale set by H_{c2}, as has been observed experimentally in V_3Si [18]. In contrast, Fig. 4 shows the field dependence for both materials rises rapidly at low fields. Such behavior is reminiscent of that seen in multiband superconductors such as MgB_2 [19] and $NbSe_2$ [18] and has been suggested already for POS [2]. Since the zero-field behavior has already established the fully gapped nature of the superconducting order parameter in PRS, multiband effects are the most likely explanation in this material.

In POS, the picture is less clear because of the presence of nodal quasiparticles. The principal effect of magnetic field on superconductors with a nodal order parameter is the Doppler shift of the nodal quasiparticle energy spectrum through coupling to the superfluid flow around magnetic vortices. This leads to an increase in the density of states and associated properties. Using a semiclassical treatment [20], the increase in thermal transport depends on the normal state scattering rate and is given by

$$\frac{\kappa(0, H)}{T} = \frac{\kappa_0}{T}\left[\frac{\rho^2}{\rho\sqrt{1+\rho^2} - \sinh^{-1}\rho}\right]. \tag{3}$$

The parameter $\rho = \sqrt{3\Phi_0}\gamma/a\hbar v_F\sqrt{H}$ is related to the impurity bandwidth (γ) and the normal state scattering rate (Γ), $\gamma \sim \Gamma^2$. In the lower inset to Fig. 4, we plot the normalized increase in thermal conductivity at $T =$ 100 mK with magnetic field for both the data presented here and for the earlier measurements [2]. In each case, the initial increase is fitted to extract values for ρ. The values obtained are $\rho = 90$ for this study and $\rho = 183$ for the data from [2]. We note that there is some variability in exactly what range of data to fit since at higher fields there is a crossover to a field independent region. We have chosen to fit the data up to 80% of the plateau value conductivity. Adjusting the range in each case causes a shift in the values of ρ by approximately 10%. Nonetheless, the important point is that the values for ρ in each case differ by a factor of 2, which implies that the normal state scattering rates and, hence, normal state conductivity should vary by a factor of 4. Comparing our normal state conductivity value, $\kappa_0(H = 2\text{T})/T =$ 8 mW/K^2 cm, with that from Ref. [2], $\kappa_0(H = 2\text{T})/T =$ 2 mW/K^2 cm, we see that quantitatively this is exactly the case. The rapid increase with magnetic field therefore

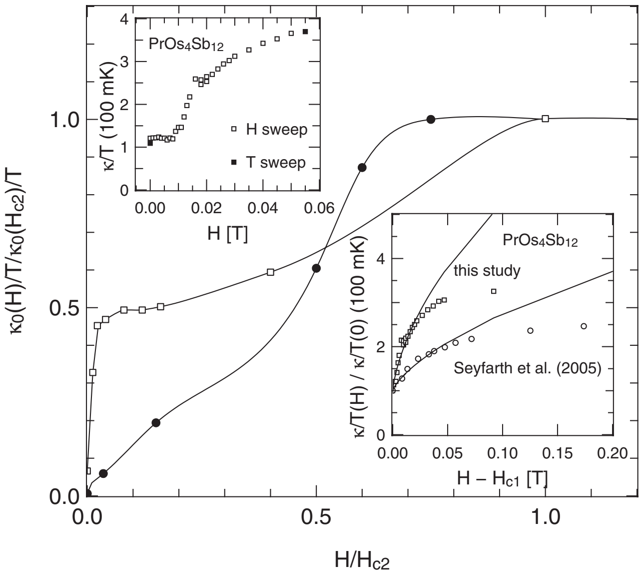

FIG. 4. Magnetic field dependence of the extrapolated $T = 0$ K thermal conductivity of POS and PRS. The lines are guides to the eye in each case. Lower inset: Field dependence of the conductivity normalized to the zero-field value for POS both from this study and from earlier work [2]. The lines result from fitting to a semiclassical theory [20] based on a Doppler shift of the nodal quasiparticle spectrum. Upper inset: Low-field dependence of the thermal conductivity divided by temperature for POS at $T = 0.1$ K. Open symbols are for sweeping the magnetic field, closed symbols are from temperature sweeps at fixed magnetic field.

scales with the normal state scattering rate in a manner that is entirely predicted by a Doppler shift of the quasiparticle energy spectrum. Unfortunately, and as has been seen in similar measurements on cuprates [21], the absolute value of Γ obtained from these fits is not in agreement with that from the normal state transport properties. This most likely reflects the limitations of the current theory.

At higher fields in POS, the conductivity exhibits a plateau and then increases in a superlinear fashion up to the normal state value at H_{c2}. This aspect is again reminiscent of the behavior seen in multiband superconductors. Consequently, we postulate that this high-field dependence results from quasiparticles associated with a second, larger superconducting gap covering a separate Fermi surface sheet. The resulting picture for POS is that it has one band with a nodal order parameter and another distinct band that is fully gapped. This scenario is appealing for a number of reasons. First, if we postulate that the gap maximum on the nodal band is somewhat smaller than the gap maximum on the fully gapped band, then our estimate for the value of the residual electronic conductivity would be revised upwards and closer to the value we measure. Second, the rapid rise of the conductivity at low fields would now be considered on a scale set by a presumably lower critical field for the band with a nodal gap. This may provide a more reasonable absolute value for the normal state scattering rate. Third, it may provide a consistent picture of the angle-resolved magneto-thermal conductivity measurements [1]. If we postulate a degree of anisotropy to the fully gapped system with a minimum orthogonal to the nodes of the other gap, then high field or high temperature measurements would pick up a fourfold symmetry due to the nodes on the gap of one band and the anisotropy on the fully gapped other band. At low fields and temperatures, only the anisotropy due to the nodal sheet would survive with quasiparticle excitations on the (anisotropic) fully gapped band exponentially suppressed. Such a system would thus have a superconducting state that is not only multiband, but also multisymmetric. The reason behind why one order parameter should have nodes and the other be fully gapped may be related to the heavy-fermion character of particular sheets of the Fermi surface. We also note that a similar multiband and multisymmetry scenario has recently been reported in URu_2Si_2 [22].

In conclusion, we have demonstrated unambiguous evidence for nodes in the superconducting energy gap of POS. This is a crucial first step in identifying the symmetry of the order parameter and ultimately the exotic mechanism that results in electronic pairing in this unconventional superconductor.

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