Multiple Superconducting Phases in New Heavy Fermion Superconductor $PrOs_4Sb_{12}$

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The superconducting gap structure of recently discovered heavy fermion superconductor $PrOs_4Sb_{12}$ was investigated by using thermal transport measurements in magnetic field rotated relative to the crystal axes. We demonstrate that a novel change in the symmetry of the superconducting gap function occurs deep inside the superconducting state, giving a clear indication of the presence of two distinct superconducting phases with twofold and fourfold symmetries. We infer that the gap functions in both phases have a point node singularity, in contrast to the familiar line node singularity observed in almost all unconventional superconductors.

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In almost all superconducting (SC) materials known to date, once the energy gap in the spectrum of electrons opens at the SC transition, only its overall amplitude, and not the shape and symmetry around the Fermi surface, changes in the SC phase [1]. The vast majority of superconductors have conventional *s*-wave pairing symmetry with an isotropic SC gap which is independent of directions over the entire Fermi surface. Over the past two decades, unconventional superconductivity with gap symmetries other than the *s* wave has been found in several classes of materials, such as heavy fermion (HF) compounds [2], high-T_c cuprates [3], ruthenate [4], and organic compounds [5]. There, the strong Coulomb repulsion leads to a notable many-body effect and often gives rise to Cooper pair states with angular momentum greater than zero. Unconventional superconductivity is characterized by anisotropic SC gap functions belonging to nontrivial representations of the crystal symmetry group which are not invariant under all symmetry elements. The gap function may also have zeros (nodes) along certain directions in the Brillouin zone. The nodal structure is closely related to the pairing interaction of the electrons. It is widely believed that the presence of nodes in almost all unconventional superconductors discovered until now are a signature of a magnetically mediated interaction, instead of a conventional electron-phonon mediated interaction. A common feature in the HF superconductors discovered until now is that they all have *line* nodes in the gap functions, parallel or perpendicular to the basal planes, except the *B* phase of UPt_3 in which point nodes may coexist with line nodes [6,7].

Recently a new HF superconductor $PrOs_4Sb_{12}$ with filled skutterudite structure has been discovered [8]. This material should be distinguished from the other unconventional superconductors, in that it has a nonmagnetic ground state of the localized *f* electrons in the crystalline electric field (most likely doublet Γ_3 state) [8–10]. The origin of HF behavior in this compound was discussed in light of the interaction of the electric quadrupole moments of Pr^{3+}, rather than local magnetic moments as in the other HF superconductors, with the conduction electrons. Therefore the relation between the superconductivity and the orbital fluctuation of *f*-electron state (i.e., quadrupole fluctuation) has aroused great interest; $PrOs_4Sb_{12}$ is a candidate for the first superconductor mediated neither by electron-phonon nor magnetic interactions. Hence it is of the utmost importance to determined the symmetry of the SC gap. Very recently heat capacity jump at T_c in zero field was reported to be broad even in high quality samples [9,12]. This behavior was attributed to the double superconducting transition, implying a possible novel feature of the superconducting state of $PrOs_4Sb_{12}$.

Here we studied the SC gap structure of $PrOs_4Sb_{12}$ by the thermal transport measurements. Thermal conductivity is a powerful probe of the low energy excitations of unpaired quasiparticles (QPs). Especially the measurements of the angular variation of the thermal transport in a magnetic field rotated relative to the crystalline axes proved to be a uniquely powerful probe for determining the location of nodes [13–24]. We report on what seems to be an exception to the well-known observation concerning the robustness of the symmetry of the SC gap function and the presence of line nodes, providing compelling evidence for the novelty of the SC state of $PrOs_4Sb_{12}$.

Our $PrOs_4Sb_{12}$ single crystals were grown by the Sb-flux method and had $T_c = 1.82$ K. Clear de Haas–van Alphen oscillations were observed at 0.4 K, confirming the high quality of the sample [25]. We measured the *c*-axis thermal conductivity κ_{zz} (the heat current $\boldsymbol{q} \parallel c$) on the sample with a rectangular shape ($0.40 \times 0.37 \times 2.20$ mm^3) by the steady-state method. By computer controlling the two SC magnets and rotating stage, we were able to rotate $\boldsymbol{H}$ with a misalignment of less than 0.5° from each axis, which we confirmed by the simultaneous measurements of the resistivity.

Figure 1 shows the T dependence of κ_{zz}/T in zero field and above H_{c2} ($\simeq 2.2$ T at $T = 0$ K). In this temperature region, the electronic contribution to κ_{zz} dominates the phonon contribution. In the upper inset of Fig. 1, $\kappa_{zz}(H = 0\ \mathrm{T})$ normalized by $\kappa_{zz}(H = 2.5\ \mathrm{T})$ is plotted. Upon entering the SC state, a double shoulder structure is seen at $T \sim 1.6$ and 1 K. This structure may be related to the double SC transitions [9,12], though the further detailed analysis is required. The lower left inset of Fig. 1 shows the H dependence of κ_{zz}. κ_{zz} is nearly linear in H below H_{c2}. This behavior is in a marked contrast to the exponentially slow increase of the thermal conductivity with field observed in s-wave superconductors at $H \ll H_{c2}$. The steep increase of κ_{zz} in $PrOs_4Sb_{12}$ is a strong indication that the thermal transport is governed by the delocalized QPs arising from the gap nodes [26].

Strong additional evidence for the existence of the nodes is provided by the angular variation of κ_{zz} in $\boldsymbol{H}$ rotated within the ab plane. The theoretical understanding of the heat transport for superconductors with nodes has made significant advances during the past few years [27]. The most significant effect on the thermal transport for such superconductors comes from the Doppler shift of the QP energy spectrum [$\varepsilon(\boldsymbol{p}) \rightarrow \varepsilon(\boldsymbol{p}) - \boldsymbol{v}_s \cdot \boldsymbol{p}$] in the circulating supercurrent flow $\boldsymbol{v}_s$ [28]. This effect becomes important at such positions where the local energy gap becomes smaller than the Doppler shift term ($|\Delta| < |\boldsymbol{v}_s \cdot \boldsymbol{p}|$), which can be realized in the case of superconductors with nodes. The maximal magnitude of the Doppler shift at a particular point strongly depends on the angle between the node direction and $\boldsymbol{H}$. For instance, when $\boldsymbol{H}$ is rotated within the basal plane in quasi-two-dimensional d-wave superconductors, the Doppler shift gives rise to the fourfold oscillation of the density of states (DOS). In this case, the DOS shows the maximum (minimum) when $\boldsymbol{H}$ is applied to the antinodal (nodal) directions [18,21]. This fourfold pattern is also present in the transport properties. In fact, a clear fourfold modulation of the thermal conductivity, which reflects the angular position of nodes, has been observed in high-T_c cuprate $YBa_2Cu_3O_7$ [13,14], HF $CeCoIn_5$ [15], organic κ-$(ET)_2Cu(NCS)_2$ [16], and borocarbide YNi_2B_2C [17], while it is absent in the fully gapped s-wave superconductors [14].

In the present experiments, κ_{zz} was measured by rotating $\boldsymbol{H} = H(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ conically around the c axis as a function of ϕ, keeping θ constant [17]. Here $\theta = (\boldsymbol{q}, \boldsymbol{H})$ is the polar angle and ϕ is the azimuthal angle measured from the a axis (see lower right inset of Fig. 1). Figures 2(a) and 2(b) display the angular variation of $\kappa_{zz}(\boldsymbol{H}, \phi)$ in $\boldsymbol{H}$ rotating within the ab plane ($\theta = 90°$) at $T = 0.52$ K. The measurements have been done in rotating $\boldsymbol{H}$ after field cooling at $\phi = -90°$. The open circles show $\kappa_{zz}(\boldsymbol{H}, \phi)$ at $H = 1.2$ and 0.5 T which are obtained under the field cooling condition at each angle. Values of $\kappa_{zz}(\boldsymbol{H}, \phi)$ obtained by different procedures of field cooling are nearly identical, indicating that the field trapping effect related to the vortex pinning is negligibly small. Above H_{c2}, $\kappa_{zz}(\boldsymbol{H}, \phi)$ is essentially independent of ϕ. A clear fourfold variation is observed just below H_{c2} down to $H \sim 0.8$ T. However, a further decrease of H below 0.8 T causes a rapid decrease of the amplitude of the fourfold symmetry and eventually a discernible fourfold symmetry is not observed below 0.7 T. At the same time, the twofold symmetry grows rapidly.

Figure 3(a) shows the H dependence of the amplitudes of twofold and fourfold symmetries. The amplitudes are obtained by decomposing $\kappa_{zz}(\boldsymbol{H}, \phi)$ into three terms with

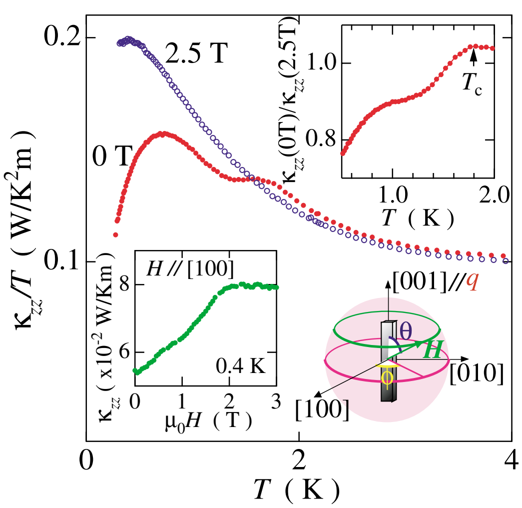

FIG. 1 (color). Main panel: T dependence of κ_{zz}/T in zero field and above H_{c2} ($\boldsymbol{H} \parallel [100]$). Upper inset: T dependence of $\kappa_{zz}(H = 0)/\kappa_{zz}(H = 2.5\ \mathrm{T})$ near T_c. Lower left inset: H dependence of $\kappa_{zz}(\boldsymbol{H} \parallel [100])$ at 0.4 K. Lower right inset: schematic figure of the $\boldsymbol{H} = H(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ rotation.

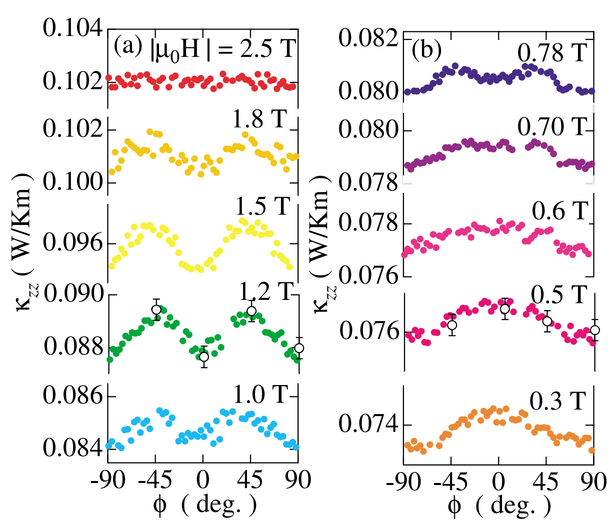

FIG. 2 (color). (a),(b) Angular variation of κ_{zz} in $\boldsymbol{H}$ rotating within the ab plane ($\theta = 90°$ in the lower right inset of Fig. 1) at 0.52 K above and below H_{c2}($\simeq 2.0$ T).

different symmetries; $\kappa_{zz}(\boldsymbol{H}, \phi) = \kappa_0 + \kappa_{2\phi} + \kappa_{4\phi}$, where κ_0 is a ϕ-independent term, $\kappa_{2\phi} = C_{2\phi}\cos 2\phi$, and $\kappa_{4\phi} = C_{4\phi}\cos 4\phi$ are terms with twofold and fourfold symmetry with respect to ϕ rotation. We attempted to fit $\kappa_{zz}(\boldsymbol{H}, \phi)$ using functions which possess the twofold and fourfold symmetries other than $\cos 2\phi$ and $\cos 4\phi$ and found that the H dependence of both amplitudes are insensitive to the choice of the functions. It is apparent that the transition from the fourfold to twofold symmetry in ϕ rotation occurs in a narrow field range at $H/H_{c2} \simeq 0.4$, which is deep inside the SC state. Both symmetries coexist in a narrow field range, possibly due to the inhomogeneity.

It should be emphasized that the fourfold anisotropy of the Fermi velocity v_F, which is inherent to the cubic band structure of $PrOs_4Sb_{12}$, is quite unlikely to be an origin of the observed twofold and fourfold symmetries because of the following reasons. First, the fact that $\kappa_{zz}(\boldsymbol{H}, \phi)$ is ϕ independent above H_{c2} strongly indicates that anisotropy of the Fermi surface does not produce a discernible anisotropy in the thermal transport. Second, the observed twofold symmetry at lower field is lower than the symmetry of the Fermi surface. Third, the in-plane anisotropy of $H_{c2}(\phi)$ which may cause the fourfold variation of $\kappa_{zz}(\boldsymbol{H}, \phi)$ just below H_{c2} is too small to explain the observed $\kappa_{4\phi}$ [29]. Moreover, the fourfold variation of $\kappa_{zz}(\boldsymbol{H}, \phi)$ arising from the anisotropy of H_{c2} is incompatible with the nonmonotonic H dependence of $C_{4\phi}$ shown in Fig. 3(a). Fourth, the calculations based on the Kubo formula indicate that anisotropy of v_F will enter only as a secondary effect in the thermal conductivity. These considerations lead us to conclude that *the observed symmetries originate from the gap nodes.* Therefore the change from fourfold to twofold symmetry

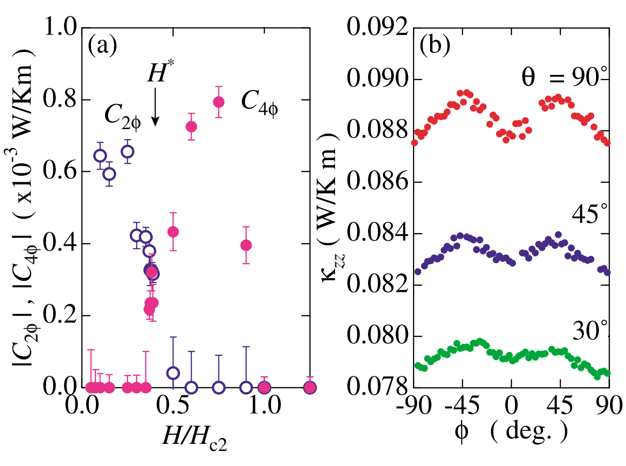

FIG. 3 (color). (a) The amplitude of twofold (open circles) and fourfold (filled circles) symmetries plotted as a function of H/H_{c2} at $T = 0.52$ K. For details, see the text. H^* indicates the phase boundary (see Fig. 4). (b) Angular variation of $\kappa_{zz}(\boldsymbol{H}, \phi)$ at $\theta = 90°$, $45°$, and $30°$ measured by rotating $\boldsymbol{H}$ ($|\mu_B \boldsymbol{H}| = 1.2$ T) conically around the c axis as a function of ϕ.

provides a direct evidence for *the change of the gap symmetry.* The fact that $\kappa_{zz}(\boldsymbol{H}, \phi)$ possesses minima at $\phi = \pm 90°$ and $0°$ at high field phase and at $\phi = \pm 90°$ for low field phase immediately leads to the conclusion that the nodes are located along the [100] and [010] directions in the high field phase, while they are located along only the [010] direction in the low field phase.

We discuss here why the lower twofold symmetry appears in the cubic lattice with higher symmetry. The twofold symmetry indicates the absence of a double domain structure, suggesting a mechanism which fixes a single domain. As shown in Fig. 2(b), the same twofold symmetry is observed in $\kappa_{zz}(\boldsymbol{H}, \phi)$ measured under the field cooling condition at each angle. This fact excludes the possibility in which the magnetic field fixes the domain. Another mechanism, such as one-dimensional dislocations produced in the process of the crystal growth, may be a possible origin for the single domain structure. Further study is required to clarify its origin.

Having established the presence of nodes, the next question is their classification. As demonstrated in Refs. [17,23,24], the angular variation of κ_{zz} can distinguish between the point and line nodes, by rotating $\boldsymbol{H}$ conically around the c axis with a tilted angle from the ab plane. In this case, with decreasing θ from 90° to 45°, the amplitude of the fourfold and twofold symmetries decrease for point nodes, while they increase for the line nodes [23]. This can be explained by noting that rotating $\boldsymbol{H}$ tilted from the ab plane does not point to the nodes for the point node case, while it always crosses the nodes for the line node case. Figure 3(b) displays the angular variation of κ_{zz} at fixed θ. The amplitudes at $\theta = 45°$ and $30°$ are smaller than that at $\theta = 90°$ [30]. Similar results were obtained for the twofold symmetry. These results are in favor of *point nodes.* We note that these results are consistent with the recent NQR experiments which show the absence of Hebel-Slichter peak and exclude the presence of the line nodes [31].

We next discuss the nodal structure inferred from the present results. Unfortunately whether the point nodes are present along the [001] direction remains unresolved. This is because the measurements of κ_{zz} as a function of the angle θ rotated across the c axis is necessary to identify the nodes along the [001] direction. In such measurements, however, the dominant twofold oscillation in $\kappa_{zz}(\theta)$, arising from the difference in transport lifetime of QPs traveling parallel to and normal to the vortices [18,19,21,22], obscures the part of the signal coming from the nodal structure along the [001] direction. We shall therefore be content here with a discussion of the nodal structure based on a group theoretical consideration. It is unlikely that the SC gap function has four point nodes in the cubic T_h crystal symmetry without taking into account the accidental mixing between the different basis functions in the SC wave function, regardless of spin singlet or triplet symmetry. This naively suggests that the

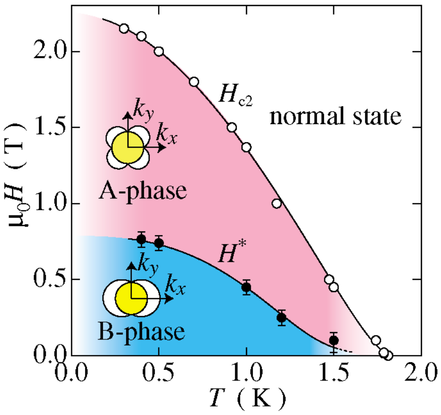

FIG. 4 (color). The phase diagram of the superconducting gap symmetry determined by the present experiments. The filled circles represent the magnetic field H^* at which the transition from fourfold to twofold symmetry takes place. The open circles represent H_{c2}. The area of the gap function with fourfold symmetry is shown by pink (A phase) and the area of the gap function with twofold symmetry is shown by blue (B phase).

gap function at high field phase has six point nodes, while that at low field phase has two point nodes. More detailed study is necessary to clarify the nodal structure along the [001] direction.

The H-T phase diagram of the SC symmetry determined by the present experiments is displayed in Fig. 4. The filled circles represent the magnetic field H^* at which the transition from fourfold to twofold symmetry takes place. Near T_c the amplitudes of both symmetries were strongly reduced but were sufficient to resolve H^*. The H^* line which separates two SC phases (high field A phase and low field B phase) lies deep inside the SC state. This line seems to terminate at a temperature slightly below T_c. It is tempting to consider that the end point coincides with a lower transition temperature of the double transitions discussed in Ref. [9]. Its clarification motivates further investigations. The only example of a superconductor with multiple phases of different gap symmetry so far has been UPt_3 [6,7]. However, the gap functions of UPt_3, in which the interaction leading to superconductivity is magnetic and the antiferromagntic symmetry breaking field reduces the symmetry from hexagonal to orthorhombic, are known to be very complicated. On the other hand, the SC gap functions of $PrOs_4Sb_{12}$ are expected to be much simpler owing to the cubic lattice symmetry.

In summary, we investigated the gap structure of heavy fermion superconductor $PrOs_4Sb_{12}$ using thermal transport measurements. Two distinct SC phases with different symmetries, the phase transition between them, and the presence of point nodes—all these highly unusual natures highlight the unconventional superconductivity in $PrOs_4Sb_{12}$ and open up a new realm for the study of the superconductivity with multiple phases. They also impose significant restrictions on possible theoretical models, including those with a novel mechanism of neither phonon nor magnetic origin of pairing.

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[29] The amplitude of H_{c2} is less than 1%; $H_{c2}(\phi)/H_{c2}(0) = 1 + p\cos 4\phi$ with $p \simeq 0.0085$ at 0.5 K. The fourfold variation of $\kappa_{zz}(\boldsymbol{H}, \phi)$ arising from the in-plane anisotropy of $H_{c2}(\phi)$ is roughly calculated from $C_{4\phi} = pHd\kappa(H)/dH$. Using $d\kappa(H)/dH = 0.016$ W/Km $\cdot$ T at 1.5 T, the magnitude of $C_{4\phi}/\kappa_n$ is estimated to be less than 0.2% below H_{c2}, which is much smaller than the observed $C_{4\phi}/\kappa_n(\sim 1\%)$ below H_{c2} as shown in Fig. 2.
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