Angular Position of Nodes in the Superconducting Gap of Quasi-2D Heavy-Fermion Superconductor CeCoIn$_5$

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The thermal conductivity of the heavy-fermion superconductor CeCoIn$_5$ has been studied in a magnetic field rotating within the 2D planes. A clear fourfold symmetry of the thermal conductivity which is characteristic of a superconducting gap with nodes along the ($\pm \pi, \pm \pi$)-directions is resolved. The thermal conductivity measurement also reveals a first order transition at $H_{c2}$, indicating a Pauli limited superconducting state. These results indicate that the symmetry most likely belongs to $d_{x^2-y^2}$, implying that the anisotropic antiferromagnetic fluctuation is relevant to the superconductivity.

$^{74.20 Rp, 74.25 Fy, 74.25 Jb, 74.70 Tx}$

The superconductivity with unconventional pairing symmetry has been a central subject of the physics of superconductors. In the last two decades unconventional superconductivity has been found in several heavy fermion materials, such as CeCu$_2$Si$_2$, UPt$_3$, UPd$_2$Al$_3$, UBe$_13$[6] and the recently discovered UGe$_2$[7]. There, the relationship between magnetism and superconductivity is the most important theme of research, because the strong electron-electron correlation effect which originates from the magnetic interaction between 4f or 5f moment and itinerant electrons allows a non-phonon mediated pairing with unconventional symmetry. Very recently it has been reported that the family CeTIn$_5$ (T=Rh, Ir, and Co) are heavy fermion superconductors[3,4]. Especially, CeIrIn$_5$ is a heavy fermion superconductor with unconventional symmetry[3,5]. Very recently it has been reported that the family CeTIn$_5$ (T=Rh, Ir, and Co) are heavy fermion superconductors[3,4]. Especially, both CeIrIn$_5$ and CeCoIn$_5$ are ambient pressure superconductors, with transition temperature of 0.4 K and 2.3 K, respectively. Subsequent observations of power law temperature dependence of the specific heat[6], thermal conductivity[7], and NMR relaxation rate[8] have identified CeTIn$_5$ as unconventional superconductors with line nodes. The unique feature of these materials is that they bear some analogy with high- $T_c$ cuprates. For example, the superconductivity appears in the neighbor of the antiferromagnetic state[9]. Moreover, the crystal structure is tetragonal which can be viewed as layers of CeIn$_3$ separated by layers of TIn$_2$ and electronic structure is quasi-2D[3,4]. Therefore they present an uncommon opportunity to study the unconventional superconductivity in the heavy fermion materials.

Unconventional superconductivity is characterized by the superconducting gap structure which has nodes along certain directions. Since the superconducting gap function is intimately related to the pairing interaction, its identification is crucial for understanding the pairing mechanism. However, the detailed structure of the gap function, especially the direction of the nodes, is an unresolved issue in most of the unconventional superconductors. In fact, to the best of our knowledge, it is only in high-$T_c$ cuprates and the B-phase of UPt$_3$ in which the nodal direction has been successfully specified. The main reason for this is that the standard techniques to probe the unconventional superconductivity, such as penetration depth, specific heat, ultrasonic attenuation, and NMR relaxation rate do not provide direct information on the node directions. The most definitive test is a phase sensitive experiment which has been done for high-$T_c$ cuprates[3]. However, this technique appears to be available only for high-$T_c$ cuprates up to now. The situation therefore strongly confronts us with the need for a powerful directional probe.

Recently it has been demonstrated both experimentally and theoretically that the thermal conductivity $\kappa$, which responds to the unpaired quasiparticles (QPs) below $T_c$, is a powerful tool for probing the anisotropic gap structure[4,6]. An important advantage of the thermal conductivity is that it is indeed a directional probe, sensitive to the relative orientation among the thermal flow, the magnetic field, and nodal directions of the order parameter. In fact, a clear 4-fold modulation of $\kappa$ with an in-plane magnetic field which reflects the angular position of nodes of $d_{x^2-y^2}$ symmetry has been observed in YBa$_2$Cu$_3$O$_{7-\delta}$[10,11,12], demonstrating that the thermal conductivity can be a relevant probe of the superconducting gap structure. In this Letter, we have measured the thermal conductivity of CeCoIn$_5$ in magnetic field rotating within the 2D CeIn$_3$ planes. Thanks to the two dimensionality, a 4-fold symmetry of $\kappa$ which clearly demonstrates the presence of gap nodes in the ($\pm \pi, \pm \pi$)-directions is observed. We have also found the first order phase transition (FOPT) at $H_{c2}$ for the first time. On the basis of these findings, we discuss the nature of the superconducting gap function of CeCoIn$_5$.

Single crystal CeCoIn$_5$ ($T_c=2.3$ K) was grown by the self-flux method[3]. The residual resistivity ratio (RRR) was approximately 18. The thermal conductivity was measured by the steady-state method with one heater and two RuO$_2$ thermometers. The sample was cut into a rectangular shape ($3.80 \times 0.38 \times 0.12$ mm$^3$) and the heat...
current $q$ was applied along the [100] direction. In the present measurements, it is very important to rotate $H$ within the 2D CeIn$_3$ planes with high accuracy because a slight field-misalignment produces a large effect on $\kappa$ due to the two dimensionality. For this purpose, we used a system with two superconducting magnets generating $H$ in two mutually orthogonal directions and a $^3$He cryostat equipped on a mechanical rotating stage with a minimum step of 1/500 degree at the top of the Dewar [12]. Computer-controlling two magnets and rotating stage, we were able to rotate $H$ continuously within the CeIn$_3$ planes with a misalignment of less than 0.02 degree from the plane, which we confirmed by the simultaneous measurement of the resistivity $\rho$.

We first discuss the $T$- and $H$- dependences of $\kappa$. The inset of fig. 1(a) shows the $T$-dependence of $\kappa$ and $\rho$. Upon entering the superconducting state, $\kappa$ exhibits a sharp kink and rises to the maximum value at $T \sim 1.7$ K. The upturn of $\kappa$ is reminiscent of high-$T_c$ cuprates [13]. Similar $T$-dependence of $\kappa$ has been reported in Ref. [3]. Compared to Ref. [3], our $\kappa$ at the onset is slightly larger, but the enhancement below $T_c$ is smaller. The Wiedemann-Franz ratio $L = \frac{\kappa}{\rho} \simeq 1.02 L_0$ at $T_c$ is very close to the Lorenz number $L_0 = 2.44 \times 10^{-8}$ $\Omega$W/K, indicating that the electronic contribution well dominates over the phonon contribution. Therefore, the enhancement of $\kappa$ below $T_c$ is due to the suppression of the QP scattering rate, similar to the high-$T_c$ cuprates.

Figures 1(a) and (b) depict $H$-dependence of $\kappa$ for $H \parallel ab$ ($H_{ab} \simeq 11$ T) and $H \perp ab$ ($H_{ab} \simeq 5$ T) below $T_c$, respectively. At all temperatures, $\kappa$ decreases with $H$ and the $H$-dependence becomes more gradual with decreasing $T$ in both configurations. Interestingly, for $H \perp ab$, $\kappa$ jumps to the normal state value at $H_{ab}$ below 1.0 K (see also the inset of Fig. 1(b)). The magnitude of the jump in $\kappa$ increases with decreasing $T$. Since the jump in $\kappa$ most likely comes from an entropy jump, this result provides a strong evidence of the occurrence of a first-order phase transition (FOPT). As far as we know, this is the first material which shows a FOPT at $H_{ab}$, though a FOPT is predicted to occur in the Pauli paramagnetically limited superconducting state [17]. We will discuss this subject later.

The understanding of the heat transport in the mixed state of superconductors with nodes has largely progressed during the past few years [18]. There, the dominant effect in a magnetic field is the Doppler shift of the delocalized QP energy spectrum, which occurs due to the presence of a superfluid flow around each vortex, and generates a nonzero QP density of states (DOS) at the Fermi surface [19]. While the Doppler shift increases $\kappa$ with $H$ through the enhancement of the DOS, it can also lead to a decrease of $\kappa$ through the suppression of impurity scattering time and Andreev scattering time off the vortices. At high temperatures, the latter effect is predominant, while at low temperatures the former effect can exceed the latter effect, as demonstrated in high-$T_c$ cuprates [20]. The data in Figs. 1 (a) and (b), in which the $H$-dependence of $\kappa$ becomes more gradual with decreasing $T$, are consistent with the Doppler shift. Thus at least above 0.35 K, the Andreev scattering of the QPs is the main origin for the $H$-dependence of $\kappa$.

We now move on to the angular variation of $\kappa$ upon the rotation of $H$ within the CeIn$_3$ planes. Figure 2 displays

![FIG. 1. Thermal conductivity as a function of $H$ for (a) $H \parallel [010]$ and (b) $H \parallel [001]$ below $T_c$. The thermal current $q$ is applied along $[100]$-direction. Inset of (a) : $\kappa$ and $\rho$ in zero field. Inset of (b) : $H$-dependence of $\kappa$ near $H_{ab}$ at 0.45 K (solid) and 0.34 K (circle).](image)

![FIG. 2. Angular variation ($\theta = \left(\mathbf{q}, \mathbf{H}\right)$) of $\kappa(H, \theta)/\kappa_n$ at several $H$ for CeCoIn$_5$. The solid lines represent the result of the fitting by the function $\kappa(H, \theta) = C_0 + C_{2\theta} \cos 2\theta + C_{4\theta} \cos 4\theta$, where $C_0$, $C_{2\theta}$ and $C_{4\theta}$ are constants. The solid circles represent $\kappa(H, \theta)$ at $H=1$ T which are obtained under the field cooling condition at every angle. For details, see the text.](image)
κ(H, θ) as a function of θ = (q, H) at T = 0.45 K, which is measured in rotating θ after field cooling at θ = 0°. The consecutive measurement inverting the rotating direction did not produce any hysteresis in κ(H, θ). Moreover, the solid circles in Fig. 2 shows κ(H, θ) at H = 1 T which are obtained under the field cooling condition at every angle. κ(H, θ) obtained by different procedures of field cooling well coincide with each other. Thus the field trapping effect related to the vortex pinning is negligibly small. In all data, as shown by the solid lines in Fig. 2, κ(H, θ) can be decomposed into three terms with different symmetries: κ(θ) = κ₀ + κ₂₀ + κ₄₀, where κ₀ is a θ-independent term, and κ₂₀ = C₂₀ cos 2θ and κ₄₀ = C₄₀ cos 4θ are terms with 2- and 4-fold symmetry with respect to the in-plane rotation, respectively. The term κ₂₀, which has a minimum at H || q, appears as a result of the difference of the effective DOS for QPs traveling parallel to the vortex and for those moving in the perpendicular direction.

Figures 3 (a)-(d) display κ₄₀ normalized by the normal state value κₙ after the subtraction of the κ₀₀ and κ₂₀-terms from the total κ. It is apparent that κ₄₀ exhibits a maximum at H || [110] and [1,-1,0] at all temperatures. Figure 4 and the inset show the T- and H- dependences of |C₄₀|/κₙ. Below Tc, the amplitude of κ₄₀ increases gradually and shows a steep increase below 1 K with decreasing T. At low temperatures, |C₄₀|/κₙ becomes larger than 2%. It should be noted that this amplitude is more than 20 times larger than those of the 2D superconductor Sr₂RuO₄ with isotropic gap in the planes [12]. Then the most important subject is “Is the observed 4-fold symmetry a consequence of the nodes?” We here address the origin for the 4-fold symmetry. There are several possible origins for this. The first is the in-plane anisotropy of H,c. According to Ref. [1], H,c has very small but finite in-plane anisotropy; H,c || [100] is approximately 2.7% larger than H,c || [110]. However, this anisotropy is too small to explain the large amplitude of |C₄₀|/κₙ > 2% at H ≪ H,c. Further, and more importantly, if this 4-fold symmetry had come from the fact that H,c || [100] is larger than H,c || [110], the overall sign of this term should be opposite to the one actually observed in κ₄₀. The second possibility is the tetragonal band structure inherent to the CeCoIn₅ crystal. If the in-plane anisotropy of the Fermi surface is large, then the large anisotropy of κ₄₀ should be observed even above Tc. However, as shown in Fig. 4, the observed 4-fold symmetry above Tc is extremely small; |C₄₀|/κₙ < 0.2 %. Thus the anisotropies arising from H,c and the band structure are incompatible with the data. Moreover, the amplitude of the 4-fold symmetry well below Tc becomes more than 10 times larger than that above Tc. These considerations lead us to conclude that the 4-fold symmetry with large amplitude well below Tc originates from the QP structure.

We now address the sign of the 4-fold symmetry. In the presence of nodes perpendicular to the layers, the term κ₄₀ appears as a result of two effect. The first is the DOS oscillation associated with the rotating H within the ab-plane [12]. This effect arises because the DOS depends sensitively on the angle between H and the direction of the nodes of the order parameter, because the QPs contribute to the DOS when their Doppler-shifted energies exceed the local energy gap. The second effect is the the quasiparticle lifetime from the Andreev scattering off the vortex lattice, which has the same symmetry as the gap function [10,11,18]. As discussed before, the second effect is predominant in our temperature and field range. In this case, κ attains the maximum value.
when $H$ is directed to the nodal directions and becomes minimum when $H$ is directed along the antinodal directions $[10][-14]$. Thus the sign of the present 4-fold symmetry indicates the superconducting gap with nodes located along the ($\pm \pi, \pm \pi$)-directions, similar to high-$T_c$ cuprates.

A quantitative comparison of the amplitude of the 4-fold symmetry with the theory reinforces this conclusion. According to Ref. [14], the 4-fold symmetry arising from the Andreev scattering off the vortices in d-wave superconductors is roughly estimated as $\kappa_{4d}/\kappa_n = -\frac{A(T)\sqrt{\pi^2\Delta^2}}{k_BT_c} \cos \theta$. Here $\Delta$ is the superconducting gap, $\Gamma$ is the quasiparticle relaxation rate and $\varepsilon = \sqrt{2\nu_f\nu_f'}H_{c2}/h$ with $\nu_f$ and $\nu_f'$ the in- and out-of-plane Fermi velocity, respectively. According to the numerical result, $A(T)$ is nearly zero at $T/T_c > 0.4$ and shows rapid increase with decreasing $T$ at lower temperatures. Similar tendency in the $T$-dependence of $|C_{4d}|/\kappa_n$ is observed, as shown in Fig. 4. Using $\Gamma \simeq 1.3 \times 10^{11}$s$^{-1}$, $\nu_f \simeq 1 \times 10^4$m/s, $\nu_f' \simeq 5 \times 10^4$m/s $[3]$, $H_{c2} \simeq 11$ T, $2\Delta/k_BT_c = 3.54$, and $A(T) = 0.033$ at $T = 0.35$ K from Ref. [14] gives $|C_{4d}|/\kappa_n \sim 8\%$, which is in the same order to the data. Thus Andreev scattering yields $|C_{4d}|/\kappa_n$ which is consistent with the data. It is interesting to compare our results on CeCoIn$_5$ with the corresponding results on YBa$_2$Cu$_3$O$_{7-\delta}$, in which the 4-fold symmetry has been reported in the regime where the Andreev scattering predominates. The observed amplitude of 4-fold symmetry in YBa$_2$Cu$_3$O$_{7-\delta}$ is small; $\sim 0.4\%$ of total $\kappa$ at 6.8 K. However, this amplitude occupies a few $\%$ in the electronic thermal conductivity, because the phonon contribution is about 80-90% of the total $\kappa$. In YBa$_2$Cu$_3$O$_{7-\delta}$ with $d_{x^2-y^2}$ symmetry, $\kappa_{4d}$ has maxima at $H || [110]$ and $[1,-1,0]$. Thus $\kappa_{4d}$ of CeCoIn$_5$ is quantitatively in accord with $\kappa_{4d}$ of YBa$_2$Cu$_3$O$_{7-\delta}$.

We finally discuss the symmetry of CeCoIn$_5$ inferred from the present results. The fact that $H_{c2}$ is determined by the Pauli paramagnetic limit is a direct evidence of a spin singlet pairing, which is consistent with the recent Knight-shift measurements $[23]$. Together with the fact that the superconducting gap has nodes at odd multiples of 45° in $k$-space, we are naturally lead to conclude that CeCoIn$_5$ most likely belongs to the $d_{x^2-y^2}$ symmetry $[23]$. The $d_{x^2-y^2}$ symmetry strongly suggests that the anisotropic antiferromagnetic fluctuation plays an important role for the occurrence of the superconductivity. This observation is in conformity with recent NMR and neutron scattering experiments which report anisotropic spin fluctuation $[3][23]$.

In summary, we have measured the thermal conductivity of the quasi-2D heavy fermion superconductor CeCoIn$_5$ as a function of the relative orientation of the crystal axis and the magnetic field rotating within the 2D planes. A clear 4-fold symmetry of the thermal conductivity which is characteristic of a superconducting gap with nodes at odd multiples of 45° is revealed. Rather surprisingly, we also observed a first order phase transition at $H_{c2}$ at low temperatures, indicating the Pauli paramagnetically limited superconducting state. These results show that the symmetry of CeCoIn$_5$ most likely belongs to $d_{x^2-y^2}$, implying that the anisotropic antiferromagnetic fluctuation plays an important role for the superconductivity. This material is the second example followed by high-$T_c$ cuprates, in which the nodal structure in the plane is successfully specified.

Note Added. After completion of this work, we became aware of the work by T. Sakakibara et al. who observed the FOPT at $H_{c2}$ by the magnetization measurements $[24]$.

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[22] Here we disregard the the broken time reversal symmetry (BTRS). If BTRS is present in CeCoIn$_5$, the gap func-
tion should contain an additional imaginary term, such as $d_{x^2-y^2} + i\eta d_{xy}$ and $d_{x^2-y^2} + i\eta s$ with very small $\eta \ll 1$.

We note that in CeIrIn$_5$ recent $\mu$SR measurement reported a presence of the BTRS [25], while another group reported an absence of BTRS [26].

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