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.

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The superconductivity with unconventional pairing symmetry has been a central subject of the physics of superconductors. In the past two decades unconventional superconductivity has been found in several heavy fermion materials, such as $CeCu_2Si_2$, UPt_3, UPd_2Al_3, UBe_{13} [1], and the recently discovered UGe_2 [2]. 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 the $4f$ or $5f$ moment and itinerant electrons allows a nonphonon mediated pairing with unconventional symmetry. Very recently it was 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 temperatures of 0.4 and 2.3 K, respectively. Subsequent observations of power law temperature dependence of the specific heat [3,5], thermal conductivity [6], and NMR relaxation rate [7,8] 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 [4]. Moreover, the crystal structure is tetragonal which can be viewed as layers of $CeIn_3$ separated by layers of TIn_2 and the electronic structure is quasi-2D [3–5]. 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 used 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 [9]. 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.

It was recently demonstrated both experimentally and theoretically that the thermal conductivity κ, which responds to the unpaired quasiparticles (QPs) below T_c, is a powerful tool for probing the anisotropic gap structure [10–15]. 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 fourfold modulation of κ, with an in-plane magnetic field which reflects the angular position of nodes of $d_{x^2-y^2}$ symmetry, was observed in $YBa_2Cu_3O_{7-\delta}$ [10,11,13], demonstrating that the thermal conductivity can be a relevant probe of the superconducting gap structure. In this Letter, we measured the thermal conductivity of $CeCoIn_5$ in magnetic field rotating within the 2D $CeIn_3$ planes. Thanks to the two dimensionality, a fourfold symmetry of κ which clearly demonstrates the presence of gap nodes in the $(\pm\pi, \pm\pi)$ directions is observed. We 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 [5]. 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 $\boldsymbol{q}$ was applied along the [100] direction. In the present measurements, it is very important to rotate $\boldsymbol{H}$ within the 2D $CeIn_3$ planes with high accuracy because a slight field misalignment produces a large effect on κ due to the two dimensionality. For this purpose, we used a system with two superconducting magnets generating $\boldsymbol{H}$ in two mutually orthogonal directions and a ^{3}He cryostat equipped on a mechanical rotating stage with a minimum step of $1/500°$ at the top of the Dewar [12]. By computer controlling two magnets and the rotating stage, we were able to rotate $\boldsymbol{H}$ continuously within the $CeIn_3$ planes with a misalignment of less than 0.02° from the plane, which we confirmed by the simultaneous measurement of the resistivity ρ.

We first discuss the T and H dependences of κ. The inset of Fig. 1(a) shows the T dependence of κ and ρ. Upon entering the superconducting state, κ exhibits a sharp kink and rises to the maximum value at $T \sim 1.7$ K. The upturn of κ is reminiscent of high-T_c cuprates [16]. Similar T dependence of κ was reported in Ref. [6]. Compared to Ref. [6], our κ at the onset is slightly larger, but the enhancement below T_c is smaller. The Wiedemann-Franz ratio $L = \frac{\kappa}{T}\rho \simeq 1.02L_0$ at T_c is very close to the Lorenz number $L_0 = 2.44 \times 10^{-8}\ \Omega\,\mathrm{W/K}$, indicating that the electronic contribution well dominates over the phonon contribution. Therefore, the enhancement of κ below T_c is due to the suppression of the QP scattering rate, similar to the high-T_c cuprates.

Figures 1(a) and 1(b) depict H dependence of κ for $\boldsymbol{H} \parallel ab$ ($H_{c2} \simeq 11$ T) and $\boldsymbol{H} \perp ab$ ($H_{c2} \simeq 5$ T) below T_c, respectively. At all temperatures, κ decreases with H and the H dependence becomes more gradual with decreasing T in both configurations. Interestingly, for $\boldsymbol{H} \perp ab$, κ jumps to the normal state value at H_{c2} below 1.0 K [see also the inset of Fig. 1(b)]. The magnitude of the jump in κ increases with decreasing T. Since the jump in κ most likely comes from an entropy jump, this result provides strong evidence for the occurrence of a first-order phase transition. As far as we know, *this is the first material which shows a FOPT at H_{c2},* though a FOPT is predicted to occur in the Pauli paramagnetically limited superconducting state [17]. We will discuss this subject later.

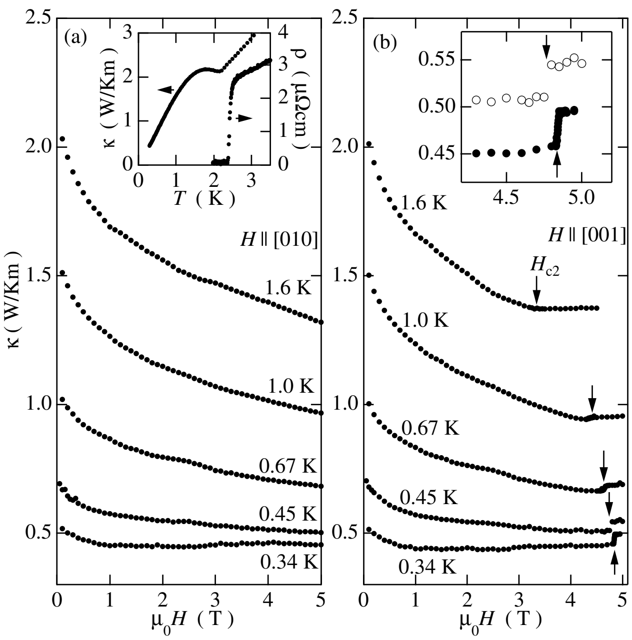

FIG. 1. Thermal conductivity as a function of H for (a) $\boldsymbol{H} \parallel [010]$ and (b) $\boldsymbol{H} \parallel [001]$ below T_c. The thermal current $\boldsymbol{q}$ is applied along the [100] direction. Inset of (a): κ and ρ in zero field. Inset of (b): H dependence of κ near H_{c2} at 0.45 K (∘) and 0.34 K (•).

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 κ with H through the enhancement of the DOS, it can also lead to a decrease of κ 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 1(b), in which the H dependence of κ 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 κ.

We now move on to the angular variation of κ upon the rotation of $\boldsymbol{H}$ within the $CeIn_3$ planes. Figure 2 displays $\kappa(H,\theta)$ as a function of $\theta = (\boldsymbol{q},\boldsymbol{H})$ at $T = 0.45$ K, which is measured in rotating θ after field cooling at $\theta = 0°$. The consecutive measurement inverting the rotating direction did not produce any hysteresis in $\kappa(H,\theta)$. Moreover, the solid circles in Fig. 2 show $\kappa(H,\theta)$ at $H = 1$ T which are obtained under the field cooling condition at every angle. $\kappa(H,\theta)$ obtained by different procedures of field cooling coincide well 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, $\kappa(H,\theta)$ can be decomposed into three terms with different symmetries; $\kappa(\theta) = \kappa_0 + \kappa_{2\theta} + \kappa_{4\theta}$, where κ_0 is a θ-independent term, and $\kappa_{2\theta} = C_{2\theta}\cos 2\theta$ and $\kappa_{4\theta} = C_{4\theta}\cos 4\theta$ are terms with twofold and fourfold symmetry with respect to the in-plane rotation, respectively. The term $\kappa_{2\theta}$, which has a minimum at $\boldsymbol{H} \perp \boldsymbol{q}$, 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)–3(d) display $\kappa_{4\theta}$ normalized by the normal state value κ_n after the subtraction of the κ_0 and $\kappa_{2\theta}$ terms from the total κ. It is apparent that $\kappa_{4\theta}$ exhibits a maximum at $\boldsymbol{H} \parallel [110]$ and $[1,-1,0]$ at all temperatures. Figure 4 and the inset show the T and H dependences of $|C_{4\theta}|/\kappa_n$. Below T_c the amplitude of $\kappa_{4\theta}$ increases gradually and shows a steep increase below 1 K with decreasing T. At low temperatures, $|C_{4\theta}|/\kappa_n$ becomes larger

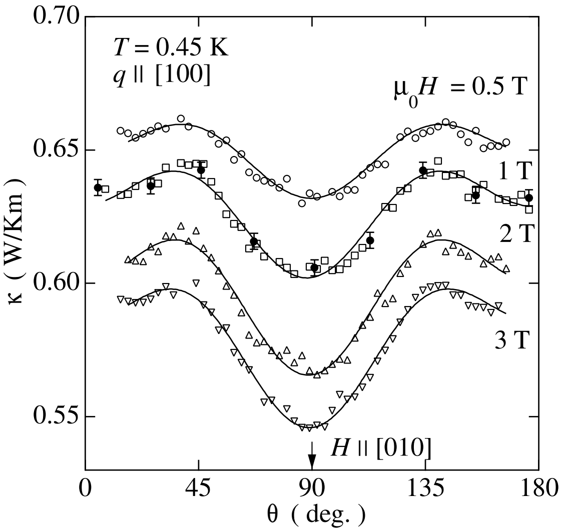

FIG. 2. Angular variation $[\theta = (\boldsymbol{q}, \boldsymbol{H})]$ of $\kappa(H, \theta)/\kappa_n$ at several H for $CeCoIn_5$. The solid lines represent the result of the fitting by the function $\kappa(H, \theta) = C_0 + C_{2\theta} \cos 2\theta + C_{4\theta} \cos 4\theta$, where C_0, $C_{2\theta}$, 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 text.

than 2%. It should be noted that this amplitude is more than 20 times larger than those of the 2D superconductor Sr_2RuO_4 with isotropic gap in the planes [12]. Then the most important subject is "Is the observed fourfold symmetry a consequence of the nodes"? We here address the origin of the fourfold symmetry. There are several possible origins for this. The first is the in-plane anisotropy of H_{c2}. According to Ref. [5], H_{c2} has very small but finite in-plane anisotropy; $H_{c2} \parallel [100]$ is approximately 2.7% larger than $H_{c2} \parallel [110]$. However, this anisotropy is too small to explain the large amplitude of $|C_{4\theta}|/\kappa_n > 2\%$ at $H \ll H_{c2}$. Further, and more importantly, if this fourfold symmetry had come from the fact that $H_{c2} \parallel [100]$ is larger than $H_{c2} \parallel [110]$, the overall sign of this term should be opposite to the one actually observed in $\kappa_{4\theta}$. The second possibility is the tetragonal band structure inherent to the $CeCoIn_5$ crystal. If the in-plane anisotropy of the Fermi surface is large, then the large anisotropy of $\kappa_{4\theta}$ should be observed even above T_c. However, as shown in Fig. 4, the observed fourfold symmetry above T_c is extremely small; $|C_{4\theta}|/\kappa_n < 0.2\%$. Thus the anisotropies arising from H_{c2} and the band structure are incompatible with the data. Moreover, the amplitude of the fourfold symmetry well below T_c becomes more than 10 times larger than that above T_c. These considerations lead us to conclude that *the fourfold symmetry with large amplitude well below T_c originates from the QP structure.*

We now address the sign of the fourfold symmetry. In the presence of nodes perpendicular to the layers, the term $\kappa_{4\theta}$ appears as a result of two effects. The first is the DOS oscillation associated with the rotating $\boldsymbol{H}$ within the *ab* plane [15]. This effect arises because the DOS depends sensitively on the angle between $\boldsymbol{H}$ 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 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 ranges. In this case, κ attains the maximum value when $\boldsymbol{H}$ is directed to the nodal directions and becomes minimum when $\boldsymbol{H}$ is directed along the antinodal directions [10,11,14]. Thus the sign of the present fourfold symmetry indicates *the superconducting gap with nodes located along the $(\pm\pi, \pm\pi)$ directions, similar to high-T_c cuprates.*

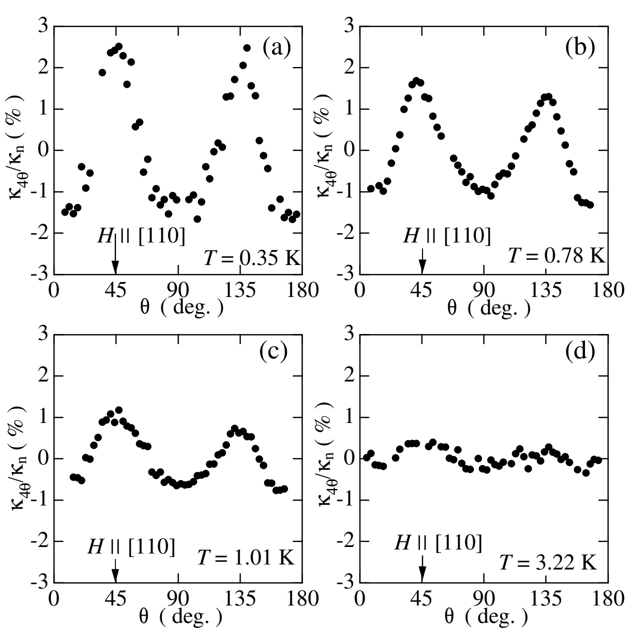

FIG. 3. (a)–(d) The fourfold symmetry $\kappa_{4\theta}/\kappa_n$ at several temperatures.

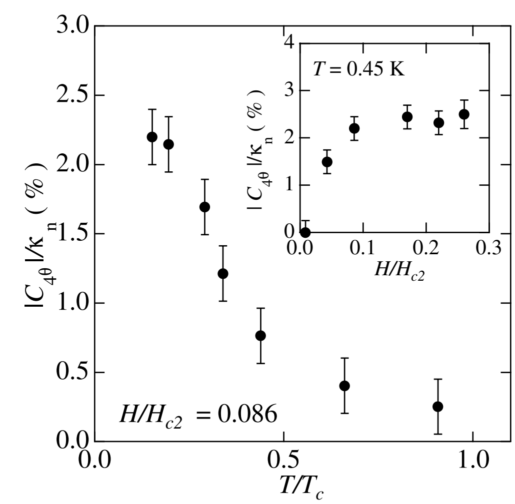

FIG. 4. Amplitude of the fourfold symmetry $|C_{4\theta}|/\kappa_n$ as a function of T/T_c. Inset: same data as a function of H/H_{c2}.

A quantitative comparison of the amplitude of the fourfold symmetry with the theory reinforces this conclusion. According to Ref. [14], the fourfold symmetry arising from the Andreev scattering off the vortices in d-wave superconductors is roughly estimated as $\kappa_{4\theta}/\kappa_n = -\frac{A(T)\sqrt{\pi}\,\Delta^2}{\hbar^2\Gamma\varepsilon}\cos 4\theta$. Here Δ is the superconducting gap, Γ is the quasiparticle relaxation rate, and $\varepsilon = \sqrt{2ev_f v_f' H_{c2}/\hbar}$ with v_f and v_f' the in-plane and out-of-plane Fermi velocities, 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. A similar tendency in the T dependence of $|C_{4\theta}|/\kappa_n$ is observed, as shown in Fig. 4. Using $\Gamma \simeq 1.3 \times 10^{11}$ s^{-1}, $v_f \simeq 1 \times 10^4$ m/s, $v_f' \simeq 5 \times 10^3$ m/s [5], $H_{c2} \simeq 11$ T, $2\Delta/k_B T_c = 3.54$, and $A(T) = 0.033$ at $T = 0.35$ K from Ref. [14] gives $|C_{4\theta}|/\kappa_n \sim 8\%$, which is in the same order to the data. Thus Andreev scattering yields $|C_{4\theta}|/\kappa_n$ which is consistent with the data. It is interesting to compare our results on $CeCoIn_5$ with the corresponding results on $YBa_2Cu_3O_{7-\delta}$, in which the fourfold symmetry was reported in the regime where the Andreev scattering predominates. The observed amplitude of fourfold symmetry in $YBa_2Cu_3O_{7-\delta}$ is small; $\sim$0.4% of total κ at 6.8 K. However, this amplitude occupies a few percent in the electron thermal conductivity, because the phonon contribution is about 80%–90% of the total κ. In $YBa_2Cu_3O_{7-\delta}$ with $d_{x^2-y^2}$ symmetry, $\kappa_{4\theta}$ has maxima at $\boldsymbol{H} \parallel [110]$ and $[1,-1,0]$. Thus $\kappa_{4\theta}$ of $CeCoIn_5$ is quantitatively in accord with $\kappa_{4\theta}$ of $YBa_2Cu_3O_{7-\delta}$.

We finally discuss the symmetry of $CeCoIn_5$ inferred from our results. The fact that H_{c2} is determined by the Pauli paramagnetic limit is direct evidence of a *spin singlet pairing*, which is consistent with the recent Knight-shift measurements [21]. Together with the fact that the superconducting gap has nodes at odd multiples of 45° in $\boldsymbol{k}$ space, we are naturally led to conclude that *$CeCoIn_5$ most likely belongs to the $d_{x^2-y^2}$ symmetry* [22]. The $d_{x^2-y^2}$ symmetry strongly suggests that the anisotropic antiferromagnetic fluctuation plays an important role in the occurrence of the superconductivity. This observation is in conformity with recent NMR and neutron scattering experiments which report anisotropic spin fluctuation [8,23].

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 fourfold 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 in 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.

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Note Added.—After completion of this work, we became aware of the works, in which the FOPT at H_{c2} is observed by the magnetization measurements [24].

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[22] Here we disregard the broken time reversal symmetry (BTRS). If BTRS is present in $CeCoIn_5$, the gap function 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 μSR measurement reported a presence of BTRS [25], while another group reported an absence of BTRS [26].
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