Sign Reversal of Field-Angle Resolved Heat Capacity Oscillations in a Heavy Fermion Superconductor $CeCoIn_5$ and $d_{x^2-y^2}$ Pairing Symmetry

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To identify the superconducting gap symmetry in $CeCoIn_5$ ($T_c = 2.3$ K), we measured the angle-resolved specific heat (C_ϕ) in a field rotated around the c axis down to a very low temperature, $0.05T_c$, and made detailed theoretical calculations. In a field of 1 T, a sign reversal of the fourfold angular oscillation in C_ϕ was observed at $T \simeq 0.1T_c$ upon entering a quasiclassical regime where the maximum of C_ϕ corresponds to the antinodal direction, coinciding with the angle-resolved density of states (ADOS) calculation. The C_ϕ behavior, which exhibits minima along the [110] directions, unambiguously allows us to conclude $d_{x^2-y^2}$ symmetry of this system. The ADOS-quasiclassical region is confined to a narrow T and H domain within $T/T_c \sim 0.1$ and 1.5 T ($0.13H_{c2}$).

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Superconductivity in strongly correlated electron systems has been a fascinating subject of investigation in the past few decades, since the realization of unconventional non-s-wave pairings can be expected due to strong electron-electron repulsion. The gap functions of these unconventional superconductors (SCs) mostly have zeros (have nodes) along certain directions in the momentum space. The existence of nodes (point or line) can be inferred from power-law dependences in physical quantities such as the specific heat (C) or the nuclear spin relaxation rate. To identify the gap structure is, however, a more formidable task. For instance, the gap symmetry d_{xy} differs from $d_{x^2-y^2}$ only in the position of line nodes (45° rotation of the latter becomes identical with the former). Phase-sensitive or direction-sensitive experiments are therefore needed to discriminate these gap structures. Very elegant phase-sensitive experiments have been done on high-T_c cuprates to establish pure $d_{x^2-y^2}$ symmetry, employing a corner SQUID [1] or sophisticated tricrystal or tetracrystal geometry [2].

Here, we address the directional thermodynamic measurements. These techniques utilize the fact that the low-lying quasiparticle excitations near the gap nodes become field orientation dependent [3,4] in the low H and T region, where the nodal quasiparticles contribute predominantly to thermodynamic quantities [5]; the angle-resolved density of states (ADOS) $N_0(\phi)$ at the Fermi energy becomes largest (smallest) when H is parallel to the antinodal (nodal) directions. The nodal directions can be determined from the angular variation of C_ϕ or the thermal conductivity κ_ϕ in a rotating H (minima of C_ϕ or κ_ϕ occur along the nodal directions). Thus, those angle-resolved bulk thermodynamic experiments provide an indispensable spectroscopic method to locate the nodal direction.

Up to now, C_ϕ experiments have been performed on various anisotropic SCs to probe the gap structures [6–11]. Among these, we concentrate here on the heavy fermion superconductor $CeCoIn_5$ ($T_c = 2.3$ K), whose gap structure has been controversial. The previous C_ϕ experiment (H rotated in the ab plane) performed down to 0.3 K ($T/T_c \geq 0.13$) revealed a fourfold angular oscillation with the minima along [100], from which d_{xy} symmetry was deduced [7]. The same symmetry was also inferred from the anisotropy in the high-field superconducting phase of $CeCoIn_5$ [12]. This conclusion was, however, in disagreement with that of the κ_ϕ measurements in which $d_{x^2-y^2}$ symmetry was derived [13]. Moreover, the instability of the vortex lattice structure observed by small-angle neutron scattering experiments [14,15] has been shown to be consistent with the $d_{x^2-y^2}$ pairing [16,17]. A point-contact Andreev reflection experiment [18] and the spin resonance observed in the superconducting state [19,20] also support $d_{x^2-y^2}$ symmetry in $CeCoIn_5$.

Recently, a resolution of this discrepancy has been put forward by Vekhter and co-workers [21,22]. They theoretically examined the phase diagram for C_ϕ of d-wave SCs in a wide H-T region and pointed out that applying H along the gap nodes may result in maxima of C_ϕ in an intermediate-T range. This is due to an inversion of the anisotropy in the finite energy DOS when the scattering of the quasiparticles off the vortices is considered. Thus, the ADOS-quasiclassical region in which C_ϕ takes minima for the nodal directions may lie at still lower temperatures. Such a crossover in C_ϕ with T has not yet been observed in nodal SCs. If this is the case for $CeCoIn_5$, then the anisotropy of C_ϕ is expected to change the sign at a temperature $\simeq 0.1T_c$ [21,22]. To explore this possibility, we have extended the C_ϕ measurements on $CeCoIn_5$ down to $0.05T_c$.

Here, we also perform more accurate C_ϕ calculations without resorting to the Pesch approximation adopted by Vorontsov *et al.* [21], and we take into account the Pauli paramagnetic effect and Fermi velocity anisotropy effect, both of which are known to be important in this system [14,16]. Those experimental and theoretical combined efforts pave the way to establish the angle-resolved thermodynamic measurements C_ϕ and κ_ϕ as important spectroscopic means to determine the pairing symmetry of unconventional superconductors.

The single crystal of $CeCoIn_5$ (23 mg weight) used in the present experiment was a thin plate whose c axis was oriented perpendicular to the largest face. C_ϕ was measured by a semiadiabatic heat pulse method. The sample was cooled using a dilution refrigerator (Oxford Kelvinox AST Minisorb) with a double sorption pump system built inside the insert (51 mm outer diameter) to allow continuous circulation of ^{3}He. Having no thick pumping tube outside, the insert could be easily rotated using a stepper motor mounted at the top of a magnet Dewar. Horizontal fields were generated by a split-pair superconducting magnet. We confirmed that the addenda contribution, which was always less than 10% of the sample specific heat, has no field-angle dependence. In a fixed field strength, we obtained C_ϕ data every 2 degrees of the H rotation in the ab plane covering the [100] through [010] directions. For each angle, the C_ϕ value was determined by the average of three successive measurements.

First, we show in Fig. 1(a) the temperature variation of C/T obtained at $H = 0$, 1, 2, and 3 T in a temperature range below 500 mK. At zero field, C/T above 300 mK is linear to T, as expected for the line node SC. At temperatures below 200 mK, an upturn in C/T shows up. This upturn is due to a quadrupole splitting of the ^{115}In ($I = 9/2$) and ^{59}Co ($I = 7/2$) nuclear spins [23,24]. The nuclear contribution significantly increases by applying H and dominates the C/T data below 0.3 K. We subtracted the nuclear Schottky contribution $C_n = a(H)/T^2$, where the coefficient $a(H)$ is determined at each field so that the resulting electronic contribution $(C - C_n)/T$ becomes linear to T at low temperatures, as shown in Fig. 1(b) [25]. Dots in Fig. 1(c) denote $a(H)$ obtained by this analysis, which show an H^2-like increase due to a nuclear Zeeman splitting. Of course, the above evaluation of $a(H)$ might have some arbitrariness. Fortunately, the manner of subtracting C_n does not strongly affect the analysis of C_ϕ below, since C_n is considered to be ϕ independent, as is discussed later. The rapid increase in C_n at low T, however, sets the lower limit of the temperature for the present C_ϕ measurements to be $\sim$0.12 K for $H = 1$ T and $T > 0.16$ K for $H = 2$ and 3 T, because of the small amplitude of the oscillation and a finite resolution ($\sim$0.5%) of the specific heat measurements.

In Fig. 2 (left panel), we show the nuclear-subtracted C_ϕ data for selected temperatures and fields. We always observed a fourfold oscillation of C_ϕ with no appreciable twofold part. We fit the data to the expression $C - C_n = C_0 + C_H(1 - A_4 \cos 4\phi)$, where C_0 and C_H are the zero field and field dependent parts of the electronic specific

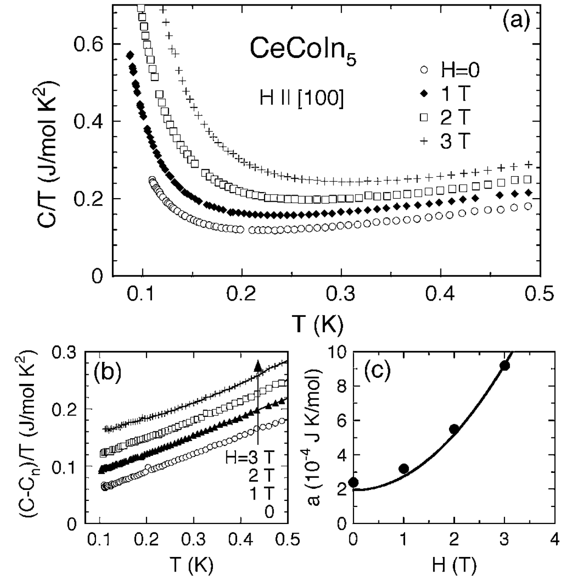

FIG. 1. (a) C/T of $CeCoIn_5$ at low temperatures measured in various fields applied along the [100] direction. (b) The electronic part $(C - C_n)/T$ obtained by subtracting the nuclear contribution. (c) Field variation of the coefficient $a(H)$ of the nuclear Schottky term. Dots and the solid line are the experimental and the calculated results, respectively.

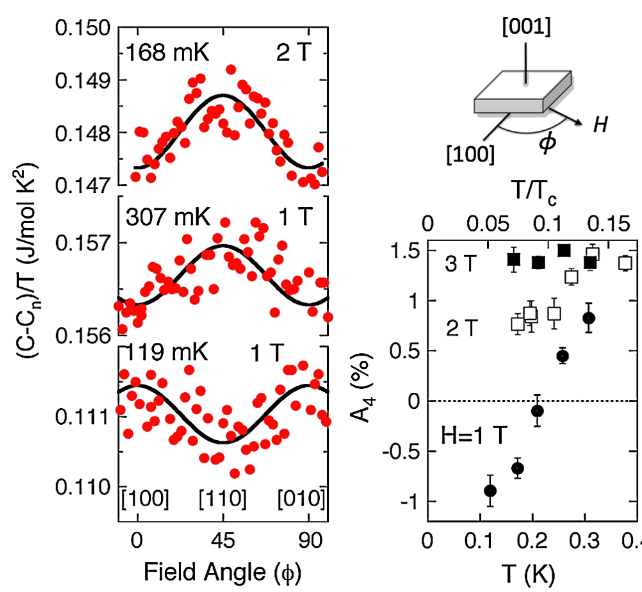

FIG. 2 (color online). Left panel: Angle-dependent specific heat data for selected fields and temperatures. Magnetic field is rotated in the ab plane. Solid lines are fits to the expression $C_0 + C_H(1 - A_4 \cos 4\phi)$. Right panel: Temperature variation of the normalized fourfold amplitude A_4 obtained for $H = 3$, 2, and 1 T.

heat, respectively, and ϕ is the angle of H measured from the [100] direction. A_4 is the normalized amplitude of the fourfold oscillation which, for nodal SCs, becomes proportional to the zero-energy DOS anisotropy $|A_4| \propto 1 - N_0(H \parallel \text{node})/N_0(H \parallel \text{antinode})$ in an ADOS-quasiclassical regime at low T and takes a nonzero value as $H \rightarrow 0$ [4]. The A_4 value thus obtained is shown in Fig. 2 (right panel) as a function of T for $H = 1$, 2, and 3 T. At $T = 300$ mK, A_4 is positive (C_ϕ minima along [100]) for all fields in agreement with the previous measurements [7]. For $H = 3$ T, A_4 is nearly T independent below 300 mK. A_4 for $H = 2$ T shows a slight decrease on cooling, although it appears to remain positive as $T \rightarrow 0$. When H is reduced to 1 T, A_4 changes the sign around 200 mK and becomes *negative* (C_ϕ minima along [110]) at lower temperatures.

In the evaluation of A_4 above, we assumed that $C_n(H)$ is isotropic in the ab plane. We confirmed the validity of this assumption by calculating $C_n(H)$ from the nuclear spin Hamiltonian [26] $\mathcal{H}_n = (h\nu_Q/6)[3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)] + \gamma\hbar \boldsymbol{I}(\mathbf{1} + \tilde{\boldsymbol{K}})\boldsymbol{H}$, where ν_Q and η are the parameters describing a quadrupole splitting, and $\tilde{\boldsymbol{K}}$ is the Knight shift tensor. In $CeCoIn_5$, there are four low-symmetry ($\eta \neq 0$) In sites (per unit cell) on the lateral faces of the unit cell. $\tilde{\boldsymbol{K}}$ also has an in-plane anisotropy in these In sites. Each of these sites then produces a twofold in-plane anisotropy in $C_n(H)$. When averaged over the four sites, however, the twofold anisotropy is cancelled, leaving no (fourfold) ϕ dependence in $C_n(H)$. The solid line in Fig. 1(c) is the field variation of $a(H)$ calculated with the parameters taken from Ref. [26], which is in good agreement with the experimentally evaluated results. We may therefore conclude that the behaviors of $A_4(T, H)$ above are the intrinsic properties in the superconducting state.

In Fig. 3, we show the contour plot of $A_4(T, H)$ obtained by the present measurements. Our present results are fully compatible with those of the previous C_ϕ experiment

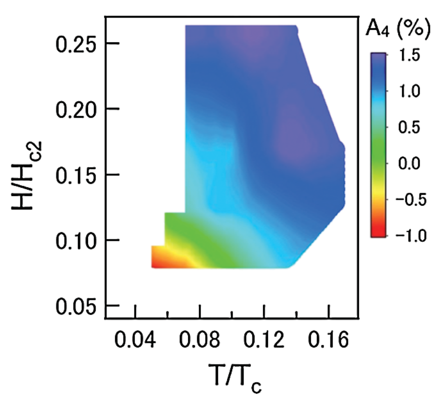

FIG. 3 (color). Contour plot of the normalized fourfold amplitude $A_4(T, H)$ of $CeCoIn_5$ obtained by the present experiment. T and H are normalized by $T_c = 2.3$ K and $H_{c2} = 11.5$ T, respectively.

performed in the region $T \geq 0.13T_c$ and $H \geq 0.17H_{c2}$, where $A_4(T, H)$ is positive and C_ϕ takes minima along [100] directions. The sign reversal in $A_4(T, H)$ is observed only at much lower temperatures ($T \leq 0.12T_c$) and lower fields ($H \leq 0.15H_{c2}$). As the following shows, the crossover temperature of the sign reversal ($\sim 0.12T_c$) well agrees with the theoretical prediction. These observations indicate that, for the first time, the low-temperature ADOS-quasiclassical region is reached experimentally. In this region, C_ϕ takes minima along the [110] directions, implying unambiguously that the gap symmetry of $CeCoIn_5$ is $d_{x^2-y^2}$.

In order to understand the above data on C_ϕ or A_4 and to help establish the angle-resolved thermodynamic measurements, we calculate the angle-resolved specific heat $C_\phi(T, H)$ accurately in the quasiclassical Eilenberger theory. The Eilenberger equations are read as

$$\{\omega_n + i\mu B + \tilde{\mathbf{v}}_F \cdot [\nabla + i\mathbf{A}(r)]\}f = \Delta(r)\bar{\phi}(k)g \quad (1)$$

$$\{\omega_n + i\mu B - \tilde{\mathbf{v}}_F \cdot [\nabla - i\mathbf{A}(r)]\}f^\dagger = \Delta^*(r)\bar{\phi}(k)g \quad (2)$$

where the quasiclassical Green functions are related to $g = (1 - ff^\dagger)^{1/2}$. The $d_{x^2-y^2}$ pairing function is given by $\bar{\phi}(k) = \cos 2\theta$ where θ is an azimuthal angle in k space. The Pauli paramagnetic parameter μ controls its strength. In the rippled cylindrical Fermi surface, $\tilde{\mathbf{v}}_F \propto (\tilde{v}\cos\theta, \tilde{v}\sin\theta, \tilde{v}_z \sin k_z)$ with $\tilde{v}_z = 0.5$ and $\tilde{v} = 1 + \beta\cos 4\theta$, where β signifies the Fermi velocity anisotropy. The anisotropy ratio of the coherent lengths $\xi_c/\xi_{ab} \sim 0.5$ by this $\tilde{v}_z$. The notation and the procedure of the calculation are the same as before [27], albeit the field direction here is in the ab plane. After solving those equations self-consistently, we evaluate the Helmholtz free energy and the entropy, which lead to the specific heat and the fourfold oscillation amplitude $A_4(T, H)$.

We have done extensive numerical computations of $A_4(T, H)$ for various μ and β values, including the previous case with $\mu = 0$ and $\beta = 0$, whose result is basically consistent with that in Ref. [21]. Here, we take into account the Pauli paramagnetic effect and the Fermi velocity anisotropy effect, both of which are known to be important in $CeCoIn_5$. In Fig. 4, we show the contour plot of $A_4(T, H)$ for $\mu = 2$ and $\beta = 0.5$. The following findings are noted. (i) The ADOS-quasiclassical region is confined to a narrow region in low H and T bounded by H_s and T_s. This region is characterized by $A_4 < 0$, where the oscillation sense coincides with the angle-resolved DOS, namely, the maximum occurs when the field direction is along the antinodal [100] direction expected by $d_{x^2-y^2}$ symmetry. (ii) The other region with $A_4 > 0$ in Fig. 4 is occupied by reversed oscillation. The maximum oscillation is located around $T/T_c \sim 0.25$ and $H/H_{c2} \sim 0.35$. (iii) The overall landscape $A_4(T, H)$ well explains the experimental data in Fig. 3. Thus, we firmly conclude that the newly discovered

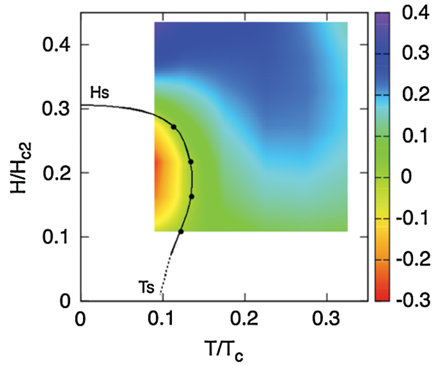

FIG. 4 (color). Topography of the specific heat oscillation amplitude A_4 (in units of percent) calculated under the paramagnetic effect parameter $\mu = 2.0$, the Fermi velocity anisotropy $\beta = 0.5$, and GL parameter $\kappa = 89$. The inside of the curved area around the origin is the ADOS-quasiclassical region bounded by H_s and T_s. The calculations are done for 6×7 grid points in (T, H) and interpolated.

sign reversal is understood as $d_{x^2-y^2}$ symmetry. (iv) We note the following: The ADOS-quasiclassical region in Fig. 4 ends at $H_s/H_{c2} \sim 0.3$ and $T_s/T_c \sim 0.1$, while the experimental data show $H_s/H_{c2} \sim 0.15$ and $T_s/T_c \sim 0.1$. There is a large discrepancy in the H_s value. Note that $H_s/H_{c2} \sim 0.4$ for the d-wave case with $\mu = \beta = 0$ and $H_s/H_{c2} \sim 0.35$ for the d-wave case with $\mu = 2$ and $\beta = 0$. Thus, the upper bound H_s is sensitive to material parameters while T_s/T_c is rather independent of them. This robustness is important when interpreting data; to find the sign change, the T sweep is more effective than the H sweep. The theoretical oscillation amplitude differs from the experimental value. Those discrepancies may be due to the material parameters which are not considered here.

A thermal conductivity experiment κ_ϕ by Izawa *et al.* [13] on $CeCoIn_5$ was done outside the ADOS-quasiclassical region ($T/T_c \geq 0.2$). They correctly conclude the $d_{x^2-y^2}$ symmetry, which is fully consistent with the present identification. We also comment on the recent C_ϕ experiment by Park *et al.* [11] on $CeRhIn_5$ under pressure taken at $H/H_{c2} \sim 0.13$ and $T/T_c = 0.14$. The data show the maximum at the [110] direction. Since that temperature is just at the boundary of the ADOS-quasiclassical region, we should be careful to conclude the gap symmetry. Based on the present result, we suggest an experiment by changing T under a fixed field to check whether the data are inside or outside that region.

In summary, we have found the sign change of the specific heat oscillation and discovered the (H, T) region, or the ADOS-quasiclassical region where the oscillation maximum coincides with the antinodal direction [100]. Except for trivial sign changes near H_{c2} (see, for example, [8]), this is the first report of this crossover. Thus, the gap symmetry in $CeCoIn_5$ is $d_{x^2-y^2}$. Those findings also help establish the angle-resolved thermodynamic measurements as a unique and indispensable spectroscopic method to identify gap locations, or pairing symmetry.

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