Searching for gap zeros in Sr$_2$RuO$_4$
via field-angle-dependent specific-heat measurement

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The gap structure of Sr$_2$RuO$_4$, which is a longstanding candidate for a chiral $p$-wave superconductor, has been investigated from the perspective of the dependence of its specific heat on magnetic field angles at temperatures as low as 0.06 K ($\sim 0.04 T_c$). Except near $H_{c2}$, its fourfold specific-heat oscillation under an in-plane rotating magnetic field is unlikely to change its sign down to the lowest temperature of 0.06 K. This feature is qualitatively different from nodal quasiparticle excitations of a quasi-two-dimensional superconductor possessing vertical lines of gap minima. The overall specific-heat behavior of Sr$_2$RuO$_4$ can be explained by Doppler-shifted quasiparticles around horizontal line nodes on the Fermi surface, whose in-plane Fermi velocity is highly anisotropic, along with the occurrence of the Pauli-paramagnetic effect. These findings, in particular, the presence of horizontal line nodes in the gap, call for a reconsideration of the order parameter of Sr$_2$RuO$_4$.

Sr$_2$RuO$_4$, a layered-perovskite superconductor with $T_c=1.5$ K,$^{1,2}$ has attracted enormous attention ever since Knight-shift experiments provided favorable evidence that it exhibits spin-triplet pairing.$^{2-5}$ Numerous experiments have demonstrated that Sr$_2$RuO$_4$ has non-$s$-wave properties,$^{6,7}$ and some of the experimental reports indicate a degenerate order parameter.$^8$ The simple Fermi-surface topology of Sr$_2$RuO$_4$ comprising of three cylindrical sheets ($\alpha$, $\beta$, and $\gamma$)$^{10,11}$ together with its well-characterized Fermi-liquid behavior has led to the construction of several theoretical models to describe superconductivity.$^9$ Among these models, a spin-triplet chiral $p$-wave pairing characterized by $d = \Delta_0 \hat{z}(k_x \pm ik_y)$ has been considered to be a promising candidate. However, several experimental facts exist that cannot be explained in the framework of this spin-triplet scenario.$^{12}$ A serious controversy is the mechanism of the first-order superconducting transition along with the $H_{c2}$ limit induced by the in-plane magnetic field.$^{13-16}$ It is reminiscent of the Pauli-paramagnetic effect that is not allowed in the spin-triplet scenario. The superconducting gap structure of Sr$_2$RuO$_4$ is also a contentious issue. In general, a chiral $p$-wave gap opening on the cylindrical Fermi-surface sheets has no symmetry-protected node. Nevertheless, the gap amplitude of Sr$_2$RuO$_4$ has been widely accepted to be modulated, and lines of deep minima (or nodes) are suggested to be present somewhere in the gap because of the power-law temperature dependence of various physical quantities.$^{17-20}$ Furthermore, universal heat transport has raised the possibility of a nodal gap.$^{18}$ Various gap structures including vertical and horizontal line node gaps have been proposed so far,$^{21-25}$ however, the location of gap minima has not yet been established.

During this decade, field-angle-dependent measurements that probe quasiparticle density of states, $N(E)$, have been developed as powerful tools for determining the position of gap zeros.$^{26-29}$ This technique takes advantage of the Doppler energy shift, $\delta E = m_v^2 \sin^2 \phi$, of $N(E)$ in the mixed state. Here, $m_v$ is the effective mass, $v_F$ is the Fermi velocity, and $v_s (\perp H)$ is the velocity of the supercurrent circulating around vortices. If the gap has zeros somewhere on the Fermi surface, $N(E = 0)$ becomes finite in those areas because of the Doppler shift and varies with the angle between the field ($\perp v_s$) and the nodal ($v_F$) directions. Therefore, the field-angle dependence of $N(E = 0)$ provides key information about the gap structure.

In 2004, Deguchi et al. reported the in-plane field-angle $\phi$ dependence of the specific heat, $C(\phi)$, of Sr$_2$RuO$_4$ in the temperature range 0.12 $\leq T \leq 0.51$ K.$^{23,24}$ They proposed that the gap has fourfold anisotropy within the $ab$ plane, i.e., four vertical lines of gap minima, based on the assumption that $C(\phi) \propto N(\phi, E = 0)$. However, recent theoretical studies$^{28,29}$ have suggested that the Doppler-predominant condition $[C \propto N(E = 0)]$ is restricted in the low-temperature region Because $C(T)$ at a finite temperature mainly reflects $N(E)$ at $E \sim 2.4k_BT$. In other words, the reversed $\phi$ dependence of $N(E \neq 0)$ changes the sign of the $C(\phi)$ oscillation, e.g., approximately at 0.1$T_c$ in the case of quasi-two-dimensional $d_{x^2-y^2}$-wave superconductors.$^{28,29}$ Such a sign change was indeed observed in nodal superconductors CeCoIn$_5$,$^{30}$ and KFe$_2$As$_2$,$^{31}$ though it has not yet been detected in Sr$_2$RuO$_4$,.
at least above 0.12 K (\( \sim 0.08 T_c \) \(^{23, 24} \)).

Here, we report the results of high-precision \( C(\phi) \) measurements at temperatures as low as 0.06 K (\( \sim 0.047 T_c \)). We reveal that, well below \( H_{c2} \), the normalized amplitude of the \( C(\phi) \) oscillation, \( A_d(T, H) \), monotonically varies with \( T \) and \( H \) without a sign change. By comparing our results with microscopic calculations, we find that the observed features in \( C(T, H, \phi) \) can be qualitatively reproduced by a horizontal line node gap on a Fermi-surface sheet, which exhibits a strong in-plane anisotropy in the Fermi velocity, along with the Pauli-paramagnetic effect.

High-quality single crystals of \( \text{Sr}_2\text{RuO}_4 \) were grown by a floating-zone method,\(^{22}\) and a single 11.2-mg piece was used. The crystal was oriented using the backscattering X-ray Laue method. The angle-resolved specific heat \( C(T, H, \phi, \theta) \) was measured by the quasi-adiabatic heat-pulse method using a dilution refrigerator. Here, \( \phi (\theta) \) denotes an azimuthal (polar) field angle relative to the [100] ([(001)]) axis, as represented in Fig. 1(b). The addenda of our calorimeter mainly consisted of a stage (silver foil), thermometer, and heater. A ruthenium-oxide chip resistor (Panasonic, ERJ-XGN1, 8.2 k\( \Omega \)) was used as a thermometer; it was cut into thirds (resulting in reducing the resistance to 3.3 k\( \Omega \)) and whose substrate was polished to reduce its heat capacity. A ruthenium-oxide chip resistor (ROHM, MCR004, 240 \( \Omega \)) was used as a heater, whose substrate was also polished. In this study, we have measured the addenda heat capacity carefully and subtracted its contribution, as depicted in the lower inset of Fig. 1(b). The magnetic field was generated using a vector magnet; the field was up to 3 T along the \( z \)-axis and 5 T along the \( x \)-axis. By using a stepper motor mounting on top of the Dewar, the refrigerator could be rotated around the \( z \)-axis. Thus, the orientation of the magnetic field was controlled three-dimensionally with high accuracy (better than 0.05\(^\circ\)).

Figure 1(a) shows the temperature dependence of \( C/T \) at 0 and 2 T in \( H \parallel [100] \). In zero field, a clear specific-heat jump is observed at \( T_c \) of 1.505 K (midpoint), which is as high as the highest \( T_c \) of \( \text{Sr}_2\text{RuO}_4 \).\(^{33}\) At 2 T (\( H > H_{c2} \)) and at low temperatures, \( C/T \) shows a gradual increase with decreasing temperature. This can be attributed to the nuclear specific heat. To explore the electronic contribution \( C_e \), the phonon and nuclear contributions, \( C_{ph} \) and \( C_N \), respectively, are subtracted from the data shown below. Here, the Debye temperature is 410 K, and \( C_N \) is \((0.08 + 0.14 H^2)/T^2\) \( \mu \text{J}/(\text{mol K}^2) \). The latter is calculated using a nuclear spin Hamiltonian with the nuclear quadrupole resonance parameters of \( ^{90}\text{Ru} \), \(^{101}\text{Ru} \), and \(^{87}\text{Sr} \).\(^{34, 35}\) The resulting \( C_e/T = (C - C_{ph} - C_N)/T \) at 2 T still shows a slight upturn at low temperatures (not shown), implying insufficient subtraction of the non-electronic contributions. Nevertheless, we adopt this definition to avoid uncertainty.

In Fig. 1(b), \( C_e/T \) at 0.06 K is plotted as a function of \( H \) applied parallel to the [100] and [110] axes. The increase in \( C_e(H)/T \) from 0 T to \( H_{c2} \) is 33 \( \mu \text{J}/(\text{mol K}^2) \), which is comparable to results of a previous study,\(^{33}\) although the absolute value is enhanced due to the difference in the definition of \( C_e \).\(^{36}\) This fact indicates that the superconducting volume fraction of the present sample is above 90\%, and that an offset of \( \sim 6 \text{ mJ}/(\text{mol K}^2) \) is given to \( C_e/T \) in Fig. 1(b) by the remaining non-electronic contributions. In the high-field region, \( C_e(H) \) shows a single, sharp jump at \( \mu_0 H_{c2} \) of 1.52 (1.56) T in \( H \parallel [100] \) (\( \parallel [110] \)). In Fig. 1(c), the in-plane \( H_{c2} \) shows fourfold anisotropy, which is consistent with the results of previous reports.\(^{34, 37, 38}\) At low fields, \( C_e(H) \) is nearly proportional to \( \sqrt{H} \), as indicated with a dashed line in the upper inset of Fig. 1(b). This line \( \sqrt{H} \) behavior supports the occurrence of low-energy quasi-particle excitations around lines of deep gap minima or nodes.\(^{39}\)

In previous reports,\(^{17, 23}\) a shoulder anomaly was detected in the low-temperature \( C_e(H) \) around \( \mu_0 H \sim 0.15 \) T, which was attributed to the abrupt suppression of minor gaps in a weakly-coupled multiband superconductor. This is similar to the cases of \( \text{MgB}_2 \)\(^{40}\) and \( \text{KF}_2\text{As}_2 \)\(^{31, 14} \). However, no such anomaly is observed in our data after precise subtraction of the addenda contribution. It is noted that the total heat capacity shows a shoulder anomaly which can be attributed to the addenda contribution [the lower inset of Fig. 1(b)]. The lack of the multigap feature indicates relatively strong coupling between the three gaps on the \( \alpha, \beta \), and \( \gamma \) bands; all three gaps survive up to relatively high fields.

To examine the in-plane gap anisotropy, \( C_e(\phi) \) was measured in several magnetic fields (\( 0.07 \leq \mu_0 H \leq 1.45 \) T) that were rotated within the \( ab \) plane. The results of \( C_e(\phi)/T \) at 0.06, 0.1, and 0.2 K are shown in Fig. 2(a). In the wide field range, \( C_e(\phi) \) shows a clear fourfold oscillation that fits the
function $C_\phi(\phi) = C_0 + C_H(1 - A_4 \cos 4\phi)$ [dashed lines in Fig. 2(a)].$^{22}$ Here, $C_0$ is the zero-field value of $C_\phi$, $C_H$ is the field-dependent part of $C_\phi$, and $A_4$ is the amplitude of the fourfold oscillation normalized by $C_H$. In Fig. 2(b), $A_4(H)$ obtained from the fit in the entire range is plotted at each temperature along with somewhat overestimated error bars; the error bars represent minimum and maximum values of $A_4(H)$ obtained from the partial fit in the range $30^\circ - 0^\circ \leq \phi \leq 30^\circ + 0^\circ$, where the central angle $\phi_0$ is changed from $30^\circ$ to $60^\circ$ approximately. In the present temperature range, $A_4(H)$ stays roughly 1% below 1 T (yellow shaded area). Importantly, a sign change of $A_4$ is unlikely to occur at low fields; e.g., $A_4$ including the error bars is always positive for $0.06 \, K \leq T \leq 0.2 \, K$ at a low field of 0.3 T. With increasing field, $A_4(H)$ suddenly decreases and becomes nearly zero around 1.3 T (blue shaded area). In high fields close to $H_{c2}$, the sign of $A_4(H)$ is reversed due to the anisotropy of $H_{c2}(\phi)$.

In order to explore the out-of-plane gap anisotropy, we investigated the polar-angle $\theta$ dependence of the specific heat at 0.06 K under a rotating field within the (010) plane ($\phi = 0^\circ$). As demonstrated in Supplemental Material$^{23}$ (I), however, little information on the out-of-plane gap anisotropy can be extracted from $C_\phi(\theta)$ because $C_\phi(\theta, H)$ is dominated by $H_{c2}$ because of the large anisotropy ratio of the coherence length ($\xi_L/\xi_C \sim 60$).$^{15}$ This fact, however, suggests that the previously reported steep suppression of $A_4(H)$ under a conically-rotating field$^{24}$ is not due to the compensation of antiphase gap anisotropies between active and passive bands but due to this scaling by $H_{c2}$.

Let us discuss the origin of the $C_\phi(\phi)$ oscillation in $\text{Sr}_2\text{RuO}_4$. By combining the present $A_4(H)$ data at 0.06, 0.1, and 0.2 K with $A_4 = 0$ at 0.51 K below 0.9 T,$^{23}$ a contour plot of $A_4(T, H)$ is depicted in Fig. 3(a). Clearly, this map is very different from $A_4(T, H)$ calculated for $d_{x^2-y^2}$- and $d_{y^z-z^y}$-wave gaps on a rippled cylindrical Fermi surface [Fig. 3(b)].$^{29}$ In particular, Fig. 3(b) shows a sign change of $A_4$ at $T \approx 0.12T_C$ in low fields below $\sim 0.3H_{c2}$. On theoretical grounds, the sign-changing line in Fig. 3(b) moves by warping the cylindrical Fermi-surface shape,$^{43}$ the line is shifted toward a lower (higher) field and a lower (higher) temperature if vertical line nodes are present on large (small) curvature parts of the warped Fermi surface.$^{46}$ For $\text{Sr}_2\text{RuO}_4$, the quasi-two-dimensional $\gamma$ band is nearly cylindrical, which yields the sign-changing line around approximately 0.1$T_C$. By contrast, quasi-one-dimensional $\alpha$ and $\beta$ bands have flat and high-curvature parts in the (100) and (110) direction, respectively. If the $d_{xy}$-type vertical lines of deep gap minima exist on the $\alpha$ and/or $\beta$ bands and dominantly contribute to the $C_\phi(\phi)$ oscillation, the observed $A_4(T, H)$ map might be reproduced to some extent. However, this is not guaranteed because fine-tuning of multiband parameters is essential.

An alternative, more promising scenario is to assume a horizontal line node gap. According to the recent band-structure calculation,$^{49}$ the in-plane $v_T$-anisotropy ratio, $v_{\parallel}([110])/v_{\parallel}([100])$, is estimated to be roughly 4 (0.8$^{50}$) for the $\gamma$ band ($\alpha$ and $\beta$ bands). If the in-plane anisotropy of the Fermi velocity, $v_T(\phi_L)$, is sufficiently large, a prominent $C_\phi(\phi)$ oscillation is expected because of an anisotropic Doppler shift $[\delta E(\phi_L) \approx v_T(\phi_L) \sin(\phi - \phi_L)]$ at $\phi_L$ around the horizontal line nodes.$^{49}$ To examine this possibility, microscopic calculations were performed by assuming a horizontal line node gap $\Delta(k) = \Delta_0 \cos c_k c$ and $v_T(\phi_L) = v_T(0)(1 - b \cos 4\phi_L)^{46}$ on the rippled cylindrical Fermi surface; this method was similar to that used in previous reports.$^{29,50,51}$ Here, we use the anisotropic parameter $b = 0.5$ (for the $\gamma$ band) and the Maki parameter $\mu = 0.04$; the latter is adopted to reproduce the $H_{c2}$ limit.

The calculated result of $N(E = 0, H)$ in $H \parallel [110]$ is shown in Fig. 1(b) with squares that match $C_\phi(H)$ sufficiently owing to the nodal gap with the finite Maki parameter.$^{52,53}$ Slight mismatch at low fields can be attributed to thermal excitations of quasiparticles in $C_\phi(T$ at 0.06 K which are absent in $N(E = 0)$; note that the origin of $N(E = 0)$ is vertically shifted so that in zero field $N(E = 0)$ corresponds to $C_\phi(T$ at 0 K estimated by the extrapolation of the $C_\phi(T$ data to 0 K. In Fig. 3(c), the calculated $A_4(H)$ (squares)$^{46,54}$ is compared with the experimental result at 0.1 K (circles). The absence of a sign change in $A_4(H)$ at low fields and its steep decrease in high fields are captured by this model. The latter is caused by the Pauli-paramagnetic effect; without this, $A_4(H)$ starts to decrease at a relatively low field ($\sim H_{c2}/3$) [refer to Supplemental Material$^{53}$ (II)] and the low-temperature $C_\phi(\theta, H)$ behavior as well as the $H_{c2}$ limitation cannot be reproduced. A slight mismatch above $\sim 1$ T might suggest the occurrence of an extra phase that is not considered in the present calculation. A possible one is the Fulde-Ferrell-Larkin-Ovchinnikov phase.$^{55}$ This phase might be the origin of the strange $A_4(H) \sim 0$ region around 1.3 T and in-plane $H_{c2}$ anisotropy ($H_{c2}(\parallel [100]) < H_{c2}([110])$) developing below 0.8 K (above 1.2 T),$^{37,56}$ which is inverted to the anisotropy expected from $v_T(\phi_L)$ of the $\gamma$ band. Figure 3(d) shows a contour map of the
in-plane anisotropy of $C_\nu(H, \phi)$ does not change its sign even at 0.06 K. In addition, an abrupt change in the normalized oscillation amplitude $A_\nu(H)$ is observed around $\mu_0 H \sim 1.2$ T. These features can be understood by considering a horizontal line node gap along with large in-plane anisotropy in $\nu_F$ and the Pauli-paramagnetic effect. The present results shed fresh light on a possibility that the gap symmetry possesses horizontal line nodes and challenge the current view of the order parameter of Sr$_2$RuO$_4$.

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From the present data, we cannot distinguish the oscillation pattern in...
Supplemental Material for

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1. Out-of-plane field-angle dependence of the specific heat for Sr$_2$RuO$_4$

Figure S1 shows $C_v(H)/T$ of Sr$_2$RuO$_4$ measured at 0.06 K in $H || [001]$. At low fields, $C_v(H)$ measured after the zero-field-cooling process is nearly unchanged up to $\mu_0 H_{c1} \sim 7$ mT for $H || [001]$ and rapidly increases above $H_{c3}$. By contrast, $C_v(H)$ measured in the each-point-field-cooling (EPFC) process varies proportionally from 0 T to $H$. This $H$-linear behavior is probably due to an increase of trapped fluxes inside the sample. These effects unfortunately mask low-energy quasiparticle excitations in $H || [001]$, in sharp contrast to the experimental result at 0.1 K, not in the EPFC process. Then, we found that the results strongly depend on the rotational direction of $H$; this is indicated in Fig. S2(a) by solid and dashed lines that represent the data taken in increasing and decreasing $\theta$ sweeps, respectively. The dependence on the rotational direction becomes prominent at lower fields. This can be attributed to the strong trap of the magnetic flux, which is illustrated in Fig. S1. Therefore, to align the trapped fluxes with the applied field orientation, we then performed EPFC measurements of $C_v(H)$; i.e., the sample temperature once increases well above $T_c$ after each field rotation. EPFC data of $C_v(\theta)$ [symbols in Fig. S2(a)] become symmetric around $\theta = 90^\circ$ with no rotational-direction dependence.

In Fig. S2(b), the EPFC data of $C_v(\theta)$ at various fields are plotted as a function of $H_{lc} = H \cos \theta$, together with the EPFC data of $C_v(\theta = 0, H)$. Except near $H_{lc} \sim 0$, all $C_v(\theta, H)$ data are scaled by $H_{lc}$, and the scaling function matches $C_v(\theta = 0, H)$ well. This means that it is difficult to investigate the out-of-plane gap anisotropy of Sr$_2$RuO$_4$ from $C_v(\theta)$ measurements because of the large anisotropy of the coherence length.

2. Pauli-paramagnetic effect on $A_4(H)$

Figure S3 compares $A_4(H)$ obtained from calculations with (squares; $\mu = 0.04$) and without (triangles; $\mu = 0$) the Pauli-paramagnetic effect by assuming a horizontal line node gap and a large in-plane $v_F$ anisotropy. Inclusion of the Pauli-paramagnetic effect tends to shift a hump in $A_4(H)$ toward a higher field. In the case of no Pauli-paramagnetic effect, $A_4(H)$ starts to decrease when the magnetic field exceeds $\sim 0.3 H_{c2}$. This behavior is in contrast to the experimental result at 0.1 K (circles in Fig. S3). In addition, a rapid increase in $C_v(H)$ with approaching $H_{c2}$ cannot be reproduced if $\mu = 0$ is adopted. Thus, the Pauli-paramagnetic effect is favorable to explain the specific-heat behavior under a magnetic field.

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**Fig. S1.** $C_e(H)/T$ at 0.06 K in $H \parallel [001]$ measured in the zero-field-cooling (ZFC; circles) and each-point-field-cooling (EPFC; crosses) processes.

**Fig. S2.** (a) Field-angle $\theta$ dependence of $C_e/T$ at 0.06 K in a rotating magnetic field within the (010) plane. Here, $\theta$ denotes the field angle with respect to the [001] axis. Symbols are the data taken in the EPFC process. Solid and dashed lines are the data (8, 75, and 150 mT) taken in the increasing and decreasing $\theta$ sweeps, respectively, without increasing the sample temperature significantly. (b) The same data (symbols), as in (a), plotted as a function of the magnetic-field component along the [001] axis, $H_{||c} (= H \cos \theta)$. The EPFC $C_e(H)/T$ data in $H \parallel [001]$ ($\theta = 0$; crosses) are also plotted for comparison.
Fig. S3. Field dependence of $A_4$ calculated with $\mu = 0$ (triangles) and $\mu = 0.04$ (squares) by assuming a horizontal line node gap and a large in-plane $v_F$ anisotropy ($b = 0.5$). Circles are the experimental data at 0.1 K.