Gap Structure of the Spin-Triplet Superconductor Sr$_2$RuO$_4$

Determined from the Field-Orientation Dependence of Specific Heat

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We report the field-orientation dependent specific heat of the spin-triplet superconductor Sr$_2$RuO$_4$ under the magnetic field aligned parallel to the RuO$_2$ planes with high accuracy. Below about 0.3 K, striking 4-fold oscillations of the density of states reflecting the superconducting gap structure have been resolved for the first time. We also obtained strong evidence of multi-band superconductivity and concluded that the superconducting gap in the active band, responsible for the superconducting instability, is modulated with a minimum along the [100] direction.

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Since the discovery of its superconductivity [1], the layered ruthenate Sr$_2$RuO$_4$ has attracted a keen interest in the physics community [2]. The superconductivity of Sr$_2$RuO$_4$ has pronounced unconventional features such as: the invariance of the spin susceptibility across its superconducting (SC) transition temperature $T_c$ [3, 4], appearance of spontaneous internal field [5], evidence for two-component order parameter [6] and absence of a Hebel-Slichter peak [7]. These features are coherently understood in terms of spin-triplet superconductivity with the vector order parameter $d(k) = \hat{z}\Delta_0(k_x + ik_y)$, representing the spin state $S_z = 0$ and the orbital wave function with $L_z = +1$, called a chiral $p$-wave state.

The above vector order parameter leads to the gap $\Delta(k) = \Delta_0(k_x^2 + k_y^2)^{1/2}$, which is isotropic because of the quasi-two dimensionality of the Fermi surface consisting of three cylindrical sheets [8]. However, a number of experimental results [9, 10, 11, 12, 13] revealed the power-law temperature dependence of quasiparticle density because of quasiparticle (QP) excitations, which suggest lines of nodes or node-like structures in the SC gap. There have been many theoretical attempts (anisotropic $p$-wave or $f$-wave states) to resolve this controversy [14, 15, 16, 17, 18]. Although all these models suggest a substantial gap anisotropy, magnetothermochal conductivity measurements with the applied field rotated within the RuO$_2$ plane down to 0.35 K revealed little anisotropy [20, 21]. To explain those experimental facts as well as the mechanism of the spin-triplet superconductivity, several theories [22, 23], taking the orbital dependent superconductivity (ODS) into account, have been proposed. In these models, there are active and passive bands to the superconductivity: the SC instability originates from the active band with a large gap amplitude; pair hopping across active to passive bands leads to a small gap in the passive band. The gap structure with horizontal lines of nodes [22, 23] or strong in-plane anisotropy [24] in the passive bands was proposed.

In order to identify the mechanism of the spin-triplet superconductivity, the determination of the gap structure in the active band is currently of prime importance. The field-orientation dependent specific heat is a direct measure of the QP density of states (DOS) and thus a powerful probe of the SC gap structure [24, 25, 26, 27, 28]. In this Letter, we report high precision experiments of the specific heat as a function of the angle between the crystallographic axes and the magnetic field $H$ within the RuO$_2$ plane. We reveal that the SC state of Sr$_2$RuO$_4$ has a band-dependent gap and that the gap of its active SC band has strong in-plane anisotropy with a minimum along the [100] direction, as illustrated in Fig. 1.

Single crystals of Sr$_2$RuO$_4$ were grown by a floating-zone method in an infrared image furnace [24]. After specific-heat measurements on two crystals to confirm the reproducibility of salient characteristics such as a double SC transition [30], the sample with $T_c = 1.48$ K, close to the estimated value for an impurity and defect free specimen ($T_{c0} = 1.50$ K) [31], was chosen for detailed study. This crystal was cut and cleaved from the sin-

![FIG. 1: Left: Electronic specific heat divided by temperature $C_e/T$ for $H || [100]$, as a function of field strength and temperature. A contour plot is shown on the bottom $H-T$ plane, with the same color scale as the 3D plot. Right: Superconducting gap structure for the active band $\gamma$ deduced from the present study, corresponding to $d(k) = \hat{z}\Delta_0(sinak_x + isinak_y)$.](image-url)
crystalline rod, to a size of 2.8 x 4.8 mm$^2$ in the $ab$-plane and 0.50 mm along the $c$-axis. The side of the crystal was intentionally misaligned from the [110] axis by 16°. The field-orientation dependence of the specific heat was measured by a relaxation method with a dilution refrigerator. Since a slight field misalignment causes 2-fold anisotropy of the specific heat due to the large $H_{c2}$ misalignment ($H_{c2}^{[ab]} / H_{c2}^{[c]} \approx 20$ ②), the rotation of the field $H$ within the RuO$_2$ plane with high accuracy is very important. For this experiment, we built a measurement system consisting of two orthogonally arranged SC magnets ③ to control the polar angle of the field $H$. The two SC magnets are installed in a dewar seating on a mechanical rotating stage to control the azimuthal angle. With the dilution refrigerator fixed, we can rotate the field $H$ continuously within the RuO$_2$ plane with a misalignment no greater than 0.01° from the plane.

The electronic specific heat $C_e$ under the in-plane magnetic fields was obtained after subtraction of the phonon contribution with a Debye temperature of 410 K. The left panel of Fig. 1 shows $C_e/T$ for the [100] field direction, as a function of field and temperature. The figure is constructed from data involving 13 temperature-sweeps and 11 field-sweeps. At low temperatures in zero field, power-law temperature dependence of $C_e/T \propto T$ was observed, corresponding to the QPs excited from the line nodes or node-like structure in the gap.

Now we focus on the field dependence of $C_e/T$ at low temperature shown in Fig. 1 and Fig. 2 (a). $C_e/T$ increases sharply up to about 0.15 T and then gradually for higher fields. This unusual shoulder is naturally explained by the presence of two kinds of gaps ③. On the basis of the different orbital characters of the three Fermi surfaces ($\alpha$, $\beta$, and $\gamma$ ⑤), the gap amplitudes $\Delta_{\alpha\beta}$ and $\Delta_\gamma$ are expected to be significantly different ②. The normalized DOS of those bands are $N_{\alpha\beta}/N_{\text{total}} = 0.43$ and $N_{\gamma}/N_{\text{total}} = 0.57$ ⑥. Since the position of the shoulder in $C_e/T$ corresponds well with the partial DOS of the $\alpha$ and $\beta$ bands, we conclude that the active band which has a robust SC gap in fields is the $\gamma$-band, mainly derived from the in-plane $d_{xy}$ orbital of Ru 4$d$ electrons. Figures 2 (a) and (b) show the field and temperature dependence of $C_e/T$ under the in-plane magnetic fields $H \parallel [100]$ and $H \parallel [110]$ and indicate the existence of a slight in-plane anisotropy.

In the mixed state, the QP energy spectrum is affected by the Doppler shift $\delta \omega = \hbar \mathbf{k} \cdot \mathbf{v}_s$, where $\mathbf{v}_s$ is the superfluid velocity around the vortices and $\hbar \mathbf{k}$ is the QP momentum. This energy shift gives rise to a finite DOS at the Fermi level in the case of $\delta \omega \gtrsim \Delta(k)$ ④. Since $\mathbf{v}_s \perp \mathbf{H}$, $\delta \omega = 0$ for $\mathbf{k} \parallel \mathbf{H}$. Thus the generation of nodal QPs is suppressed for $\mathbf{H} \parallel \text{nodal directions}$ and yields minima in $C_e/T$ ⑤⑥⑦.

Figure 3 shows the field-orientation dependence of the specific heat. The absence of a 2-fold oscillatory component in the raw data guarantees that the in-plane field alignment is accurate during the azimuthal-angle rotation. Thus $C_e(T, H, \phi)$ can be decomposed into $\phi$-independent and 4-fold oscillatory terms, where the in-plane azimuthal field angle $\phi$ is defined from the [100] direction: $C_e(T, H, \phi) = C_0(T, H) + C_4(T, H, \phi)$. $C_4(T, H, \phi)/C_N$ is the normalized angular variation term, $\mathbf{H}$.
where \( C_N \) is the electronic specific heat in the normal state: \( C_N = \gamma N T \) with \( \gamma N = 37.8 \) mJ/K\(^2\)mol. There is no discernible angular variation in the normal state \((\mu_0 H = 1.7 \, T \geq \mu_0 H_c)\); possibilities of angular variation originating from experimental setup or other extrinsic contributions are excluded.

For fields near \( H_{c2} \) (1.2 \( T \leq \mu_0 H \leq 1.45 \, T \)), a sinusoidal 4-fold angular variation is observed: \( C_4(\phi) \propto f_4(\phi) = -\cos 4\phi \). This is consistent with the in-plane sinusoidal anisotropy of \( H_{c2} \) with the maximum in the [110] direction \( 21 \, 22 \) \( C_4 = H_{c2}[110]-H_{c2}[100] dC_e H \cos 4\phi \). Since \( H_{c2} \) decreases with increasing \( T \), the oscillation amplitude at 1.3 \( T \) increases strongly at 0.51 \( K \). For \( \mu_0 H < 1.2 \, T \), however, a non-sinusoidal 4-fold angular variation approximated as \( C_4(\phi) \propto f_4(\phi) = 2|\sin 2\phi| - 1 \) is observed. Importantly, a phase inversion in \( C_4(\phi) \) occurs across about \( \mu_0 H = 1.2 \, T \): \( C_4(\phi) \) takes minima at \( \phi = \pm n \) \( (\phi = \pi + \pm n, n: \text{integer}) \) for \( \mu_0 H < 1.2 \, T \) \( (\mu_0 H \geq 1.2 \, T) \), and thus the angular variation for \( \mu_0 H < 1.2 \, T \) cannot be due to the in-plane \( H_{c2} \) anisotropy. Therefore we conclude that the non-sinusoidal 4-fold oscillations originate from the SC gap structure. This result does not contradict the previous measurements of the magnetothermal conductivity down to 0.35 \( K \) \( 21 \, 22 \), which reported little in-plane anisotropy, because these clear oscillations emerge only at lower \( T \) \( (T/T_c \leq 0.2) \).

For the field range 0.15 \( T < \mu_0 H < 1.2 \, T \), where the QPs in the active band \( \gamma \) are the dominant source of in-plane anisotropy, we first deduce the existence of a node or gap minimum along the [100] direction, because \( C_e \) takes a minimum. In addition, we found that the 4-fold oscillations have a non-sinusoidal form, approximated as \( C_4(\phi) \propto 2|\sin 2\phi| - 1 \), since cusp-like features are clearly seen at the minima \( \phi = \pm \frac{\pi}{2} n \). Strong \( k_z \) dependence of the gap function would enhance the QP excitations even if \( H \) is parallel to the nodal direction, so that the cusp-like features would have been strongly suppressed \( 22 \).

Most of the proposed gap structures can be classified into four groups as summarized in Table I. #1 and #2 provide the direction of the gap minima consistent with our observation. To distinguish between #1 with gap minima and #2 with nodes, we examine the specific heat jump \( \Delta C_e/\gamma N T_c \) at \( T_c \) in zero field. The jump originates mainly from the active band with large \( \Delta \) because of \( \Delta C_e/\gamma N T_c \propto \partial^2/\partial T^2|T_c \). We estimated the contribution of \( \Delta C_e/\gamma N T_c \) from the active band for the gap structures #1 and #2: \( \Delta C_e/\gamma N T_c = (1.22 \text{ to } 1.07) \times 0.57 = 0.70 \text{ to } 0.61 \) with the gap minimum \( \Delta_{\text{min}}/\Delta_{\text{max}} = 1/2 \text{ to } 1/4 \) \( 14 \), while \( \Delta C_e/\gamma N T_c = 0.75 \times 0.57 = 0.42 \) with the line nodes \( 17 \). From the experimental result \( \Delta C_e/\gamma N T_c = 0.75 \) in Fig. I and the estimated additional contribution from the passive bands \( \Delta C_e/\gamma N T_c \sim 0.04 \) \( 24 \), \( d(k) = \hat{z}\Delta_0(\sin nk_z + i\sin k_y) \) with the gap minimum is promising for the active band.

To facilitate a comparison with theories, although they are presently available only for line-node gaps \( 26 \, 27 \), we decomposed \( C_e \) into two parts: \( C_e(T,0) \) due to the thermally excited QPs and \( \Delta C_0(T,H) \) due to the field induced QPs, consisting of an isotropic component and a 4-fold anisotropic component \( A_4(T,H) \): \( C_e(T,H,\phi) = C_0(T,0) + \Delta C_0(T,H)[1 + A_4(T,H)f_4(\phi)] \), \( A_4(T,H)f_4(\phi) = C_4(T,H,\phi) \), where \( f_4 \) was defined previously for low- and high-field ranges. Figures I (a) and (b) show the field and temperature dependence of \( A_4 \). The field dependence of \( A_4 \) with a maximum of 4\% anisotropy at 0.31 \( K \) shows a monotone decrease from the delocalized-QP dominant region at low fields to the \( H_{c2} \)-anisotropy dominant region at high fields. The temperature dependence of \( A_4 \) with 3\% anisotropy at 0.9 \( T \) shows a smooth decrease with increasing temperature. These results are in semi-quantitative agreement with recent theories \( 24 \, 27 \) which predict 4 to 1.5\% anisotropy from gap structures with vertical line nodes.

In contrast to the theoretical prediction \( 27 \), however, at combined low fields \( (\mu_0 H \leq 0.15 \, T) \) and low temperatures \( (T \leq 0.3 \, K) \) where QPs on both the active and passive bands are important for the anisotropy, \( A_4 \) rapidly decreases. This steep reduction of \( A_4 \) is primarily attributable to the non-zero gap minima \( \Delta_{\text{min}} \) of the active \( \gamma \) band (#1). In fact, at the lowest temperatures the 4-fold oscillations are suppressed below a threshold field.

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**TABLE I:** The classified order parameters with the typical gap structures for Sr\(_2\)RuO\(_4\).

| #   | \( d(k) \) | direction of node or \( \Delta_{\text{min}} \) | Ref. |
|-----|-----------|-------------------------------|-----|
| 1   | \( \hat{z}\Delta_0(\sin nk_z + i\sin k_y) \) | \[100\] tiny gap | 16  |
| 2   | \( \hat{z}\Delta_0k_zk_y(k_z + ik_y) \) | \[100\] nodes | 17  |
| 3   | \( \Delta_0(k_x^2 - k_y^2)(k_x + ik_y) \) | \[110\] nodes | 18  |
| 4   | \( \{ \Delta_0(k_x + ik_y)\cos k_x \) \( \Delta_0k_z(k_x + ik_y)^2 \) | horizontal nodes | 19  |

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**FIG. 4:** (a), (b) Field and temperature dependence of the 4-fold anisotropy \( A_4 \) in the specific heat. The points are evaluated from the fitting to the oscillatory data in Fig. I while the lines from the difference in \( C_e \) between \( H \parallel [110] \) and \( H \parallel [100] \) in Fig. I. Two methods yield consistent results.
Let us finally discuss the roles of the passive bands in the oscillations in $C_v$. While the present experimental study has resolved the directions of gap minima in the $\gamma$ band, there still remain two types of possibilities for the passive bands $\alpha$ and $\beta$ to account for the power-law QP excitations at low temperatures: (A) horizontal line nodes (#4 in Table 1) and (B) vertical gap minima along the [110] directions. The gaps (A) in the passive bands will not contribute to any oscillatory component whether they are fully developed or filled with QPs induced by $H$ and/or $T$. Thus in this case the rather complex $H$ and $T$ dependence of $A_4$ needs to be accounted for solely by the gap structure of the active band. On the other hand, the gaps (B) will give rise to 4-fold oscillations which are out of phase with those originating from the active band, so that the oscillations will be additionally suppressed. Since Fig. 4 (b) shows that $A_4$ at 0.15 $T$ decreases steeply with decreasing temperature in the temperature range where QP excitations strongly reflect the gap structure of the passive bands, the observed steep reduction of $A_4$ may be a consequence of an additional compensation by the passive bands.

In conclusion, we have for the first time revealed the in-plane anisotropy in the SC gap of the spin-triplet superconductor Sr$_2$RuO$_4$, from the field-orientation dependence of the specific heat at low temperatures. We identified the multi-band superconductivity with the active band $\gamma$, which has a modulated SC gap with a minimum along the [100] direction with little interlayer dispersion. This gap structure is in good correspondence with the $\Delta_T$ field of up to 5 T and a vertical field of up to 3 T. The results may contain decisive information and call for a more quantitative theoretical work to enable the full assignment of the gap structures in all bands.

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