Is $\text{Sr}_2\text{RuO}_4$ a triplet superconductor?

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The field dependence of the specific heat $\gamma(H)$ at lower temperatures in $\text{Sr}_2\text{RuO}_4$ is analyzed by solving microscopic Eilenberger equation numerically. We find that systematic $\gamma(H)$ behaviors from a concave $\sqrt{H}$ to a convex $H^\alpha (\alpha > 1)$ under $H$ orientation change are understood by taking account of the Pauli paramagnetic effect. The magnetizations are shown to be consistent with it. This implies either a singlet pairing or a triplet one with $d$-vector locked in the basal plane, which allows us to explain other mysteries of this compound in a consistent way.

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Superconductors are classified into two distinctive groups, either spin-singlet or spin-triplet pairings. While almost all superconductors, including high $T_c$ cuprates belong to the former, the later is extremely rare and difficult to find. Only a few examples of superconductors are discussed for its possibility; In a heavy Fermion material $\text{UPt}_3$ the identification of a triplet pairing has been firmly established [1, 2]. The observed multiple phase diagram in field $(H)$ versus temperature $(T)$ plane, consisting of three phases A, B and C, is reasonably explained only in terms of triplet pairing. This situation is similar to superfluid $^3\text{He}$ where two subphases ABM and BW are identified in pressure vs. $T$ plane [3]. Knight shift (KS) experiment by NMR has played a fundamental role to confirm the theoretical predictions in $\text{UPt}_3$. It was particularly crucial that both field directions where KS is changed and unchanged below $T_c$ are found experimentally [4] as predicted [2], identifying the $d$-vector direction.

$\text{Sr}_2\text{RuO}_4$ is second prime candidate for a triplet pairing superconductor [5]. A variety of theoretical and experimental works have been devoted to establishing it, but it turns out after a decade of its discovery [6] that it is extremely difficult to identify the spin structure of a Cooper pair although the gap structure with line node is well established now. For example, it is pointed out that recent phase-sensitive experiments by Nelson et al. [7], Kidwingira et al. [8] and Xia et al. [9], all of which claim a triplet pairing, are also explained in terms of the singlet scenario by Zutic and Mazin [10] and Mineev [11]. The most direct and virtually only probe to detect its parity is the KS experiment. In fact KS experiments using various nucleus, such as $^{87}\text{Sr}$, $^{101}\text{Ru}$, $^{90}\text{Ru}$ and $^{17}\text{O}$ atoms, fail to pin down the spin direction of pairs, i.e. orientation of the $d$-vector because of the invariance of KS for both field directions of $c$- and $ab$-axes as long as $H = 200G$ [12]. There is no field direction where KS changes below $T_c$. Thus at present it is fair to say that the two scenarios either based on singlet and triplet pairings are still under debate. Note that the appearance of magnetic field below $T_c$ associated with spontaneous time reversal symmetry breaking observed by $\mu$SR experiment [13] is explained equally by spin singlet scenario as well as triplet one [14].

We examine the parity issue in $\text{Sr}_2\text{RuO}_4$ through analyses of the specific heat experiment by Deguchi et al. [15] under various $T$ and $H$. There are several outstanding problems posed by this experiment, whose understanding leads to a new clue for this debate. One of the most interesting discoveries is why the field dependence of the Sommerfeld coefficient $\gamma(H)$ is $\lim_{T \to 0} \alpha C/T$ ($C$ is the specific heat) in the basal plane shows a concave curvature in spite of the existence of the line node gap. Namely, this is quite at odd because $\gamma(H)$ is expected to be a $\sqrt{H}$-like behavior with a convex curvature due to line nodes, i.e. the so-called Volovik effect [13]. It is remarkable to see that the concave curve becomes a Volovik $\sqrt{H}$ curve with a convex curvature when the direction of the applied field moves away only by a few degrees of angle $\theta$ from the basal $ab$-plane (see inset (a) in Fig.3). In addition to analyses of the specific heat data [16], we also examine magnetization data [17] at low temperatures under a field. We explain these experiments based on an idea that strong Pauli paramagnetic effect is important in the basal $ab$ plane physics of $\text{Sr}_2\text{RuO}_4$ and establish a consistent picture for its superconductivity.

We calculate the vortex lattice state properties by quasiclassical Eilenberger theory in the clean limit [18]. This framework is valid when $k_F \xi > 1$ ($k_F$ Fermi wave number and $\xi$ coherent length), which is satisfied by $\text{Sr}_2\text{RuO}_4$. We include the paramagnetic effects due to the Zeeman term $\mu_B B(r)$. The flux density of the internal field is $B(r)$ and $\mu_B$ is a renormalized Bohr magneton [19]. The quasiclassical Green’s functions $g(\omega + i\mu B, \mathbf{k}, \mathbf{r})$, $f(\omega + i\mu B, \mathbf{k}, \mathbf{r})$ and $f^\dagger(\omega + i\mu B, \mathbf{k}, \mathbf{r})$ are calculated in the vortex lattice state by the Eilenberger equation

$$\{\omega_n + i\mu B + \mathbf{\hat{v}}(\mathbf{k}) \cdot \left[\nabla + i\mathbf{A}(\mathbf{r})\right]\} f = \Delta^*(\mathbf{r}) g,$$
$$\{\omega_n + i\mu B - \mathbf{\hat{v}}(\mathbf{k}) \cdot \left[\nabla - i\mathbf{A}(\mathbf{r})\right]\} f^\dagger = \Delta(\mathbf{r}) g,$$

where $g = (1 - f f^\dagger)^{1/2}$, $\text{Re}g > 0$, and the normalized Fermi velocity $\mathbf{\hat{v}}$ is introduced so that $\langle \mathbf{v}_n^2 \rangle = 1$ where $\langle \cdots \rangle_{\text{F}}$ indicates the Fermi surface average. The paramagnetic parameter is $\mu_B$. We consider the $d$-wave pairing for a pairing function with line
The paramagnetic parameter $\tilde{\mu} \propto H_{c2}^{orb}/H_p$, which is a key parameter to analyze $\gamma(H)$, is related to the ratio of the hypothetical orbitally limited upper critical field $H_{c2}^{\text{orb}}$ and the Pauli limiting field $H_p = \Delta_0/\sqrt{2}\mu_B$ ($\Delta_0$ is the gap amplitude at $T = 0$). $H_p$ is a material-specific bulk parameter independent of the field orientation evidenced by nearly isotropic bulk susceptibility observed [3]. The angle-dependence of the paramagnetic parameter $\tilde{\mu}(\theta)$ comes through the factor: $H_{c2}^{orb}(\theta)$. This orbital-limited $H_{c2}^{orb}(\theta)$ is sensitive to the field orientation for highly anisotropic system such as in the present layered material: Sr$_2$RuO$_4$.

The reduction of $H_{c2}$ from $H_{c2}^{orb}$ due to the paramagnetic effect is obtained by solving the Eilenberger equation as $H_{c2}(\tilde{\mu}) = H_{c2}^{orb}/\sqrt{1 + 2.4\tilde{\mu}^2}$. This is derived originally in dirty limit $s$-wave case [21], but we confirm it to be valid numerically in the present clean limit $d$-wave case too as seen from Fig. 1 where the calculated values are compared with this expression.

It is natural to consider that $H_{c2}^{orb}(\theta)$ is described by the effective mass model, namely $H_{c2}^{orb}(\theta)/H_{c2}^{orb||c||ab} = 1/\sqrt{T^2\sin^2\theta + \cos^2\theta}$ which simply embodies the fact that the orbital motion of electrons is determined by the directional cosines of the field to the basal plane. The anisotropy $\Gamma = H_{c2}^{orb||c||ab}/H_{c2}^{orb||c||ab||c}$ is an unknown parameter here. But it is assigned by the requirement that the experimental $H_{c2}(\tilde{\mu})$ be reproduced theoretically. Namely, once $\Gamma$ is determined, the angle dependence of $H_{c2}(\theta)$ is automatically known through the angle dependence of the paramagnetic parameter $\tilde{\mu}(\theta)$, which controls the reduction of the upper critical field $H_{c2}$ from the “hypothetical” orbital-limited field $H_{c2}^{orb||c||ab}$.

Having known the paramagnetic deparing effect on $H_{c2}(\tilde{\mu})$, we can calculate the angle dependence of the observed $H_{c2}(\theta)$ where we take account of the fact that $\tilde{\mu} \propto H_{c2}^{orb}/H_p$ is $\theta$-dependent through the factor $H_{c2}^{orb}(\theta)$ given above. Thus we obtain $\tilde{\mu}(\theta) = \tilde{\mu}_0/\sqrt{T^2\sin^2\theta + \cos^2\theta}$ with $\tilde{\mu}_0$ being the value at $\theta = 0$. By combining these relations, we finally obtain the $\theta$ dependence of the observed $H_{c2}(\theta)$ as $H_{c2}(\theta) = 1/\sqrt{T^2\sin^2\theta + \cos^2\theta + 2.4\tilde{\mu}_0}$. This takes account of both orbital- and paramagnetic deparing effects simultaneously. In order to reproduce the observed anisotropy $\Gamma^{\text{obs}} = 20$, we find $\tilde{\mu}_0 = 3.41$ when $\Gamma = 107$. Note that $\tilde{\mu}_0$ and $\Gamma$ are not independent parameters. As shown in Fig. 2 our effective mass model with the paramagnetic effect explains the angle dependence of $H_{c2}(\theta)$ once we fix one adjustable parameter. It is to be noted as shown in inset of Fig. 2 the $\tilde{\mu}(\theta)$ value is completely determined by the effective mass form with $\Gamma = 107$.

As for the assigned $\Gamma = 107$ we point out that the diamagnetic orbital current is determined by the perpendicular component of the average Fermi velocity to the field direction. Thus $\Gamma$ is the anisotropy ratio of the Fermi velocities, namely $\Gamma = \sqrt{\langle v_{F||c}^2 \rangle / \langle v_{F||ab}^2 \rangle}$. This quantity is determined directly by dHvA experiment; $\Gamma_\alpha = 117$, $\Gamma_\beta = 57$ and $\Gamma_\gamma = 174$ for three bands $\alpha$, $\beta$ and $\gamma$ respectively [3]. Note that a simple geometric average $\Gamma_{\text{eff}} = \frac{1}{3}(\Gamma_\alpha + \Gamma_\beta + \Gamma_\gamma) = 116$ is well compared with our assignment $\Gamma = 107$. In this sense there is virtually no adjustable parameter in our analysis. In passing we note that the observed ratio $\Gamma^{\text{obs}} = H_{c2||ab}/H_{c2||c} = 20$ is strongly reduced from $\Gamma_{\text{eff}}$, apparently suggesting some reduction mechanism. We clarified it here.

Let us now come to our main discussions on the analyses of the specific heat at a low $T$. In Fig. 3 we display $\gamma(H)$ for several values of $\tilde{\mu}$ together with the experimental data in inset (a) for various $\theta$ values. They show strikingly similar behaviors as a whole. The larger angle data exhibit a strong upward curvature, corresponding to the conventional $\gamma(H) \sim \sqrt{H}$ which is characteristic to the line node gap structure. Those are reproduced in our $\tilde{\mu} = 0.02$, or 0.41 curves. As $\theta$ becomes smaller, this changes into almost linear or concave curves near $H_{c2}$. This behavior is captured by the theoretical calculations for larger $\tilde{\mu}$’s. Thus the overall “metamorphosis” of $\gamma(H)$ from the conventional $\sqrt{H}$ to a strong convex curve is reproduced by increasing $\tilde{\mu}$. As shown in inset (b) of Fig. 3, the data are fitted well by our calculations near $H_{c2}$ where we have used the $\tilde{\mu}(\theta)$ values determined.
In Fig. 4 we display the theoretical $\gamma(H)$ behaviors (a) and the corresponding specific heat data (b), where we read off $\tilde{\mu}(\theta)$ from the inset of Fig. 2. Our theoretical curves explain these data in a consistent manner. In particular, it is noteworthy: (1) At $\theta=0^\circ$ where $\tilde{\mu}(0) = \mu_0 = 3.41$ is largest, $\gamma(H)$ shows a $\sqrt{H}$-like sharp rise in smaller $H$ region because of the presence of line nodes. But it is limited only to lower fields. (2) In the intermediate wide field region ($0.5T < H < 1T$), $\gamma(H)$ exhibits an almost linear change in $H$. This extended linear change is shown to be consistent thermodynamically with magnetization $M(T, H)$ behavior as seen shortly. (3) In the high field region ($H > 1T$) towards $H_{c2} = 1.5T$, $\gamma(H)$ displays a sharp rise with a strong concave curvature. As $H$ increases, the Pauli effect proportional linearly to $H$ becomes growingly effective, modifying $\gamma(H)$ from usual $\sqrt{H}$ to a concave $H^\alpha$-like curve with $\alpha > 1$.

The data for $\theta=3^\circ$ where $\tilde{\mu}(\theta = 3^\circ) = 0.60$ show a similar behavior to that at $\theta=0^\circ$, but the features associated with the Pauli effect, namely, the existence of the inflection point from convex to concave curves and sharp rise towards $H_{c2}$ are weaken. The $\gamma(H)$ data for higher angles ($\theta > 3^\circ$) exhibit an intermediate behavior between those at $\theta = 0^\circ$ and the ordinary $\sqrt{H}$ curve, continuously changing its shape with $\theta$. It is remarkable that the strong concaved curves of the experimental data for small angles, which were unexplained before, are reproduced by the Pauli paramagnetic effect. Physically, this effect makes the conventional Abrikosov vortex state unstable, ultimately leading to the normal state via a first order transition or the FFLO state. The sharp rise in $\gamma(H)$ near $H_{c2}$ is a precursor to it.

In Fig. 5 we show the calculated results of magnetization $M(H)$ for several $T$’s (a) together with the experimental data[17] (b) to qualitatively understand the paramagnetic effects on $M(T, H)$. We do not attempt to reproduce the data quantitatively because the data are in a qualitative nature due to hysteresis effects. It is seen from Fig. 5(a) that the magnetization with a convex curvature at lower field changes into that with a concave one towards $H_{c2}$. There is an inflection point field $H_K$ in between. The relative position of $H_K$ to each $H_{c2}$ decreases with $T$ (also see insets). In higher $T$’s $H_K$ becomes invisible because of thermal effect. These two features are observed experimentally as seen from Fig. 5(b). The inflection point field $H_K$ roughly coincides with that in $\gamma(H)$ as seen from Fig. 4, implying that these are thermodynamically related to each other.

As is seen from Fig.5 upon lowering $T$ the slope of $M(H)$ at $H_{c2}$ becomes steeper, meaning that $\kappa_2$ decreases, instead of increases as in usual superconductors[21]. This is another obvious supporting evidence that the paramagnetic effect is important in $\text{Sr}_2\text{RuO}_4$.

It is easy to derive a thermodynamic Maxwell relation $\frac{d}{dT} \frac{C}{T} = \frac{\partial^2}{\partial T^2} M(T, H)$ from which we can see at low
T, $\frac{\partial \gamma(H)}{\partial T} = \beta(H)$ with $M(T, H) = M_0(H) + \frac{1}{2} \beta(H) T^2$. We estimate $\beta(H)$ from the experimental data [17] in Fig. 5, finding that $\beta(H) \sim \text{const}$ for $0.5T < H < 1T$ and $\beta(H) \propto H^3$ for $1T < H < 1.35T$. This implies that $\gamma(H) \propto H(H^4)$ for $0.5T < H < 1T$ ($1T < H < 1.35T$). These behaviors in $\gamma(H)$ are indeed seen for the $\theta = 0^\circ$ data shown in Fig. 4. These analyses, which are free from any microscopic model, mean that the mysterious behavior of $\gamma(H)$ is supported to be true thermodynamically and comes from the intrinsic nature deeply rooted to the superconductivity in Sr$_2$RuO$_4$.

There are several known difficulties associated with the most popular two component chiral $p$-wave pairing: $\bar{z}(p_x + ip_y)$ [22] or $\bar{z}(p_x + ip_y) \cos p_y$ [23]. Experimentally these triplet states are unable to explain the paramagnetic effects mentioned above because the $d$-vector is not locked in the basal plane. Theoretically these states give a large in-plane $H_{c2}$ anisotropy [24] which is not observed. The present singlet scenario is free from it.

Let us go on considering the high field phase for $H \parallel ab$ observed as the double transition [21]. It appears in a narrow $H$-$T$ region along $H_{c2||ab}$, starting at $T_0 = 0.8K$, or $T_0 = 0.53T_c$ at which three transition lines meet, giving rise to a tricritical point in $H$ vs. $T$ plane. $T_0$ is remarkably similar to the so-called Lifshitz point $T_L = 0.56T_c$ in the FFLO phase diagram for a Pauli limited superconductor where the orbital depairing is quenched completely. This number $T_L = 0.56T_c$ is universal, valid for a variety of situations, including 3D Fermi sphere $s$-wave [23], 2D $s$-wave [26] and $d$-wave [27], and 1D $s$-wave [28] models. Our identified large paramagnetic parameter $\mu = 3.41$ means that our system is in almost Pauli limiting where the orbital effect is almost perfectly quenched because the two-dimensionality in Sr$_2$RuO$_4$ is so extreme. In fact note that the identified anisotropy $\Gamma = 107$ implies $H_{c2||ab}^{ab} \sim 7.5T$ which is reduced to $H_{c2||ab} = 1.5T$ by the Pauli effect. Thus we propose here to identify this high field phase as FFLO.

The extreme two-dimensionality is obvious: If $H$ is tilted away from the $ab$ plane only by $\theta > 0.3^\circ$, the double transition vanishes [20]. According to Nakai, et al. [29] the FFLO region at low $T$ occupies ~ 0.8% below $H_{c2}$, which is comparable with the width ~200G of the high field phase below $H_{c2||ab} = 1.5T$, a region 200G/1.5T~1.3% [20]. Guided by the known phase diagram [21], we predict that as the field orientation $\theta$ increases, $\mu$ decreasing, this high field phase survives only for $0 < \theta < 0.3^\circ$ and quickly diminishes for $\theta > 0.3^\circ$. At around $\theta \sim 1.0^\circ$ there appears a first order transition along $H_{c2}$ line instead of FFLO. Then for $\theta > 2.0^\circ$ it also disappears above which the paramagnetic effect becomes ineffective and Sr$_2$RuO$_4$ is described by a conventional singlet superconductor with line nodes. These predictions based on our analyses are all testable experimentally although the details should be further sharpened theoretically.

In conclusion, we have analyzed both specific heat at lower $T$ and magnetization $M(T, H)$ by self-consistently solving microscopic quasi-classical Eilenberger equation for the gap function with line nodes. It is seen that the Pauli paramagnetic depairing effect is essential in understanding the data in Sr$_2$RuO$_4$. This is possible only for either singlet pairing, or triplet pairing with the $d$ vector locked in the basal plane.

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