Phase-sensitive tests of the pairing state symmetry in Sr$_2$RuO$_4$

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Exotic superconducting properties of Sr$_2$RuO$_4$ have provided strong support for an unconventional pairing symmetry. However, the extensive efforts over the past decade have not yet unambiguously resolved the controversy about the pairing symmetry in this material. While recent phase-sensitive experiments using flux modulation in Josephson junctions consisting of Sr$_2$RuO$_4$ and a conventional superconductor have been interpreted as conclusive evidence for a chiral spin-triplet pairing, we propose here an alternative interpretation. We show that an overlooked chiral spin-singlet pairing is also compatible with the observed phase shifts in Josephson junctions and propose further experiments which would distinguish it from its spin-triplet counterpart.

Unambiguous determination of the pairing state symmetry is one of the key steps towards understanding the pairing mechanism in a continuously growing class of unconventional superconductors [1]. Phase-sensitive experiments, capable of identifying angular dependence of the superconducting order parameter, have provided a crucial evidence for a dominant $d$-wave orbital symmetry in cuprate superconductors [2,3,4]. However, much less is known for other unconventional superconductors such as heavy fermions, charge transfer salts, and cobaltates. In particular, there is compelling evidence for an unconventional pairing in Sr$_2$RuO$_4$ [5,6] with the strong possibility of spin-triplet superconductivity which would be a solid-state analog of superfluid He$^3$ [7].

In superconductors with inversion symmetry an order parameter (gap matrix) can be expressed as $\Delta(\mathbf{k}) = \Delta_0(\mathbf{k})i\sigma_y$ for spin singlet and $\Delta(\mathbf{k}) = \sigma \cdot \mathbf{d}(\mathbf{k})i\sigma_y$ for spin-triplet pairing. Here $\sigma$ are the Pauli spin matrices and scalar (vector) $\Delta_0 (\mathbf{d})$ has even (odd) parity in the wavevector $\mathbf{k}$. Often the symmetry of both the orbital and the spin part of $\Delta(\mathbf{k})$ remains to be identified and the lack of related understanding comes from the difficulty in performing phase-sensitive experiments.

While numerous previous experiments probed the pairing symmetry of Sr$_2$RuO$_4$ [5,6] in this context, recent phase-sensitive experiments [8] that provide angle-resolved information are particularly important. The corresponding measurements were performed in a superconducting quantum interference device (SQUID) geometry, consisting of a pair of Au$_{0.5}$In$_{0.5}$/Sr$_2$RuO$_4$ Josephson junctions. Since Au$_{0.5}$In$_{0.5}$ is a conventional $s$-wave superconductor, the observed modulation of critical current in an applied magnetic field was interpreted as conclusive support for the phase shifts from an odd-parity spin-triplet pairing in Sr$_2$RuO$_4$ [5,6].

A similar SQUID geometry was initially proposed [9] to study possible $p$-wave pairing in heavy fermions and later also used for identifying $d$-wave pairing in cuprates [2]. The critical current $I_c$ is modulated in the applied magnetic field as [10]

$$I_c \propto \cos(\Phi/\Phi_0 + \delta_{12}/2),$$

where $\Phi$ is the flux threading the SQUID, $\Phi_0$ is the flux quantum, and $\delta_{12}$ is the intrinsic phase shift of the order parameter between the two tunneling directions. For a conventional $s$-wave SQUID $\delta_{12} = 0$ and $I_c$ has a maximum at $\Phi = 0$. In contrast, a phase shift $\delta_{12} = \pi$, characteristic of unconventional pairing [12], yields a minimum $I_c$ at $\Phi = 0$. The modulation of external flux together with the fabrication of junctions with varying tunneling directions in SQUID geometry therefore provides an angle-resolved phase-sensitive information about the superconducting pairing symmetry.

The suggested chiral $p$-wave (C$pW$) state with the triplet order parameter [13],

$$\mathbf{d}(\mathbf{k}) \propto (k_x + ik_y)\hat{z},$$

in which the spins of the Cooper pairs lie in the RuO$_2$ plane ($\perp \mathbf{d}$), is indeed compatible with the experiment [5]. However, we show here that it is not the only candidate. There exists another pairing state, allowed by the tetragonal symmetry of Sr$_2$RuO$_4$, the singlet chiral $d$-wave (C$dW$) state $^1E_g(c)$ with $\Delta_0(\mathbf{k}) \propto (k_x + ik_y)k_z$, or, more accurately [14]

$$\Delta_0(\mathbf{k}) \propto (k_x + ik_y)\sin k_z c,$$

which is equally consistent with the phase shifts observed in Ref. [5]. We use our findings to propose an experimental test which would discriminate between C$pW$ and C$dW$ pairing symmetries.

Could experimental and theoretical reasons be used to rule out C$dW$ and favor only the C$pW$ state? The two main arguments in favor of the C$pW$ come from muon spin resonance and Knight shift experiments [6,10]. The former indicate a time-reversal symmetry breaking below the transition temperature $T_c$, incompatible with the $d_{x^2-y^2}$-wave state in cuprates, but fully compatible with either C$pW$ or C$dW$ symmetry. The Knight shift ($K$) was initially interpreted as firm evidence for a triplet state with in-plane spins (like C$pW$), since no change of the in-plane spin susceptibility below $T_c$ was found.

Even in singlet superconductors (e.g., vanadium), $K$ could remain invariant below $T_c$. Such behavior is usually attributed to (a) spin-orbit induced spin-flip scattering which suppresses the effect of the superconductivity on
$K$ and (b) an accidental cancellation of the spin, dipole, and orbital contributions of the Fermi-level electrons to $K$ which leaves only superconductivity-insensitive contributions such as the Van Vleck susceptibility. However, a quantitative analysis shows that the spin-orbit coupling in Sr$_2$RuO$_4$ is too weak for scenario (a) while the accidental cancellation, required for scenario (b), does not occur. Thus, neither of the two explanations of a constant $K$ arising from singlet pairing is applicable.

This would have made the Knight shift argument for $CpW$ very convincing, if not for the recent experiment showing the same result in a field perpendicular to the plane. It was proposed that the testing field of 0.02 T may be enough to induce a phase transition from the $CpW$ in Eq. 2 to a state with d∥$\hat{x}$. However, this is highly unlikely: (i) the $d||\hat{x}$ state would have an additional horizontal line node, as compared to the $d\times(k_x+ik_y)\hat{z}$ state and therefore lose a large part of the pairing energy ($\sim \Delta$ per electron, $\Delta \gtrsim 1.4 \, K \gg \mu_B \times 0.02 \, T$); (ii) although in the $d||\hat{x}$ state the spins of the pairs lie in the $yz$ plane, there is no $y-z$ symmetry (as opposed to the $xy$ plane) and it is not a priori clear whether the magnetic susceptibility of the Cooper pair will be the same as for the normal electrons. Since $d||\hat{x}$ is not allowed for a tetragonal symmetry, it may only appear as a result of a second phase transition below $T_c$, which has never been observed in Sr$_2$RuO$_4$; (iii) the spin-orbit part of the pairing interaction, which keeps the spins in the $xy$ plane, despite $z$ being the easy magnetization axis, would have to be weaker than $\mu_B \times 0.02 \, T = 1.1 \, \mu eV = 0.013 \, K$, an energy scale much too small for the spin-orbit coupling in Sr$_2$RuO$_4$. So, neither the old theories for the lack of a Knight shift reduction below $T_c$, nor the new explanation in terms of the magnetic-field rotated order parameter withstand quantitative scrutiny; the Knight shift in Sr$_2$RuO$_4$ remains a challenge for theorists. Until this puzzle is resolved, we cannot use the Knight shift argument for the pairing symmetry determination.

We now turn to the experiments of Ref. and compare Josephson tunneling between an s-wave superconductor and either (a) an even parity (spin singlet) superconductor or (b) an odd parity (triplet) superconductor. In the first case, the Josephson current between a conventional s-wave superconductor and an unconventional spin-singlet superconductor, represented by the order parameters $\Delta_{s-wave}$ and $\Delta_0(\mathbf{k})$, respectively, can be expressed as

$$J \propto \left( \tilde{T}_k \text{Im}[\Delta^*_0(\mathbf{k})d(\mathbf{k}) \cdot (\mathbf{n} \times \mathbf{k})] \right)_{FS},$$

which depends on the relative phase between the superconducting order parameters. The averaging is over all states at the Fermi surface (FS) where the Fermi velocity, $v_F$, has a positive projection on the tunneling direction represented by the unit normal $\mathbf{n}$ (perpendicular to the interface plane, see Fig. (c) and $T_k$ is the tunneling probability. For a thick rectangular barrier of width $w$ and height $U$, we can obtain

$$T_k = \frac{16m^2\kappa^2v_Lv_R \exp[-2kw - k^2w/\kappa]}{(\kappa^2 + m^2v_L^2)(\kappa^2 + m^2v_R^2)},$$

where $\kappa = \sqrt{2m(U - \mu)}$ such that $wK \gg 1$ (in the thick barrier limit), $m$ is the free-electron mass, $\mu$ is the Fermi energy, and we set $\hbar = 1$. We use $v_{L,R}$ to denote normal components of the Fermi velocities in the two superconductors and $k_\parallel$ is the component parallel to the interface. From Eq. 10 we see that $T_k$ is sharply peaked when $v_F || \mathbf{n}$.

In the second case, the Josephson current between a singlet and a triplet superconductor becomes

$$J \propto \left( \tilde{T}_k \text{Im}[\Delta^*_0(\mathbf{k})d(\mathbf{k}) \cdot (\mathbf{n} \times \mathbf{k})] \right)_{FS},$$

where we use $\tilde{T}_k$ to denote that, unlike $T_k$, it contains matrix elements corresponding to spin-flip tunneling, for example, due to magnetic interfaces or spin-orbit coupling. For nonmagnetic barriers and in the absence of spin-orbit, there is no spin-flip scattering, therefore $\tilde{T}_k = 0$ and the Josephson current vanishes identically.

From Eqs. 11 and 21, we can directly infer that for c-axis tunneling, $\mathbf{n} || \mathbf{c}$, $J = 0$ for both CdW and Cpw states $\int d\mathbf{k}_x d\mathbf{k}_y (k_x + ik_y) = 0$. For tunneling precisely in the $ab$ plane, the current is also zero for CdW while for Cpw it only vanishes at $\mathbf{n} || \mathbf{k}$.

We consider a model of a quasi-two-dimensional (2D) layered superconductor which has a nearly cylindrical FS with a small c-axis dispersion originating from the weak inter-layer hopping. In Fig. 1(a) we show the sample geometry used Ref. and in Fig. 1(b) represent a warping of the Fermi surface. In the first approximation for...
Sr$_2$RuO$_4$ such a warping can be expressed as

$$\mu = \frac{k_F^2(z)}{2m}[1 + \varepsilon \cos k_z c], \quad (7)$$

where $|\varepsilon| \ll 1$ is the warping parameter ($\varepsilon \approx -7 \times 10^{-4}$[25]), $c$ is the lattice constant along the crystallographic $z$-direction, and $k_F(z)$ is the $z$-dependent projection of the Fermi wavevector in the $xy$ plane [see Fig. 1(c)]. It is convenient to resolve the Fermi wavevector in cylindrical coordinates ($k_F(z), \varphi, k_z$) with

$$k_F(z) = k_{F0}/[1 + \varepsilon \cos k_z c]^{1/2}, \quad (8)$$

where $k_{F0} = (2m\mu)^{1/2}$ and for $\varphi = 0$ [see Fig. 1(c)] $k_F(z) \rightarrow k_{Fx}$. Schematic representation of the SQUID geometry in Fig. 1(a) (adapted from Ref. [4]) is an oversimplification. While efforts were made to fabricate edges either precisely parallel or perpendicular to the $c$-axis, in the actual samples the direction of interface planes or their corresponding normals changes gradually from $a$ to $c$-direction. In several samples[2] an interface nearly parallel to the $ab$ plane, at Au$_{0.5}$In$_{0.5}$/Sr$_2$RuO$_4$ junction, was covered by an insulating oxide [see Fig. 1(a)]. It is then plausible to expect that the normal to such interface could deviate from the $ab$ plane. In Fig. 1(b) we depict a generalized situation in which an interface normal, $\mathbf{n} = (n_x, n_y, n_z)$ with $|n_z| \ll 1$, need not lie exactly in the crystallographic $ab$ plane of Sr$_2$RuO$_4$. We show below that the analysis of phase-sensitive measurements in terms of the two small but finite parameters, $\varepsilon$ and $n_z$, can provide a qualitatively different interpretation from those which a priori assume $\varepsilon = n_z = 0$.

For a conventional superconductor with the $FS$ larger than the one of Sr$_2$RuO$_4$, the Josephson tunneling across a thick rectangular barrier can be obtained from Eqs. 11 and 13 as

$$J \propto \int k_F^2 \delta(\varepsilon - \mu)\mathbf{v}_F \cdot \mathbf{n} \exp(-k_F^2 w/2\kappa)$$

where $k_F^2 = \mathbf{k}_F^2 - (\mathbf{k}_F \cdot \mathbf{n})^2$, $k^2 \gg m^2 v_L^2$, and the projection of the Fermi velocity in Sr$_2$RuO$_4$ along $\mathbf{n}$ is

$$\mathbf{v}_F \cdot \mathbf{n} = \frac{k_{F0}^2 [1 + \varepsilon \cos k_z c]^{1/2}}{m} - \frac{k_{F0}^2 \varepsilon \sin k_z c}{2m [1 + \varepsilon \cos k_z c]} n_z. \quad (10)$$

For a thick barrier, the integration can be simplified by noting that the dominant contribution comes from $k_{||} = 0$. The right hand side of Eq. 10, in the leading order in $\varepsilon$ and $n_z$, can be then reduced to $\sqrt{\pi \kappa/\omega k_{F0}^2 n_z (1 - \varepsilon)}$, such that

$$J \propto A n_z (1 - \varepsilon), \quad (11)$$

where $A$ characterizes the normal state barrier transparency. Thus, with a tilted interface ($n_z \neq 0$) there is a finite Josephson current even in the absence of any Fermi surface warping ($\varepsilon = 0$).

To verify that our findings of finite Josephson current in CdW state are not limited to the specific assumption of a thick rectangular barrier, we also consider the rather different case of a strong $\delta$-function barrier. The corresponding transmission probability is

$$T_k = \frac{4v_L v_R}{(v_L + v_R)^2 + 4U^2}, \quad (12)$$

where $v_{L,R}$ are the normal components of the Fermi velocities in the two superconductors and $U (\gg v_L^2)$ is the scattering strength. From Eqs. 10, 11 we obtain

$$J \propto \int k_F^2 \delta(\varepsilon - \mu)\mathbf{v}_F \cdot \mathbf{n} \exp(-k_F^2 w/2\kappa)$$

where, unlike in the case of a thick barrier, we perform $\varphi$ and $k_z$ integration. In the leading order, the right hand side of Eq. 10 is $-\pi k_{F0}^2 n_z$, and yields

$$J_\delta = -A \varepsilon n_z, \quad (14)$$

where again $A$ characterizes the normal state transparency. In contrast to the thick-barrier result, the current now vanishes in the absence of FS warping. From Eqs. 10, 11 one can conjecture that for a general case $J \approx A(s - \varepsilon)$, where $0 \leq s \leq 1$.

The presence of small parameters $\varepsilon$ and $n_z$ in Eqs. 11, 13 shows that the Josephson current in the CdW state would be reduced as compared to the conventional SQUID with $s$-wave electrodes. However, the alternative picture, based on the $CpW$ state, also contains small parameters which should be kept in mind when interpreting the experiment of Ref. [6]. In addition to the small relative strength of the spin-orbit coupling (quantified by the admixture of $S_1$ into a nonrelativistic $S$ state, or the spin-orbit induced band shift relative to the band width [27]), there can also be another small factor — a ratio of the lattice constant and the superconducting coherence length [26], approximately $6 \times 10^{-4}$.

Results from Eqs. 10, 11 confirm that the CdW state could be compatible with the phase shifts observed in Ref. [6]. Furthermore, the azimuthal dependence of an order parameter coincides for both CdW and CpW states. While the proposed symmetry arguments [6, 8] exclude most of superconducting states allowed in the tetragonal symmetry [29], these arguments alone are not sufficient to unambiguously identify the odd-pairing of CpW state. Instead, to confirm that a $CpW$ state has indeed been observed, one would need to accurately calculate the expected magnitudes of the Josephson current for both chiral states. In particular we propose a modification of the experimental configuration [6] such that the interface plane would be slanted at $\approx 45^\circ$ with the $c$-axis. If the corresponding ratio of the Josephson current to the normal state conductivity becomes substantially
larger (n_z is no longer small) than in Ref. [8], it would be strong support for the chiral singlet state in Eq. (3).

Another important distinction between the two chiral states is the presence of nodes in the superconducting gap. In contrast to the CpW state, CdW requires by symmetry a horizontal line node [see Eqs. (2), (3)]. The idea of a horizontal line node [30] has been entertained by experimentalists [31] and theorists [31] for a while, although recently it has fallen out of favor. Still, some researchers insist on the existence of a horizontal line node [32]. Moreover, in the Josephson experiments of Ref. [8] evidence was found for a substantial k_x dependence, albeit not necessarily for horizontal nodes, of the order parameter in Sr_2RuO_4 [32]. How could such a material with nearly 2D electronic structure develop a highly 3D superconducting state? To answer this question we point out the following facts: (a) practically no ferromagnetic spin fluctuations, favorable for a p-wave pairing, have been experimentally found in Sr_2RuO_4; (b) antiferromagnetic spin fluctuations at q = (2/3, 2/3, q_z) have negligible z dispersion; (c) the crystal structure of Sr_2RuO_4, as opposed to its electronic structure, is fairly 3D, so one can expect the electron-phonon coupling to be quite 3D as well (d) there is a sizeable O isotope effect in Sr_2RuO_4, which strongly changes with introduction of pair-breaking symmetries [33]. While electron-phonon coupling per se can only induce an s-wave pairing, such a pairing would be prevented by the strong antiferromagnetic spin fluctuations. However, for the proposed CdW state, any 2D interaction cancels out, including the magnetic interaction. Should the electron-phonon coupling have a maximum say, at (1/2, 1/2, 1/2), as opposed to (1/2, 1/2, 0), the CdW state would have been immediately stabilized providing a plausible scenario for spin-singlet superconductivity in Sr_2RuO_4.

In conclusion, we have revealed that a completely overlooked chiral d-wave pairing state in Sr_2RuO_4 is equally compatible with the existing body of experimental data as the generally accepted chiral p-wave state. We have proposed phase-sensitive experiments in a SQUID geometry with a variable tilting angle capable of unambiguously distinguishing between the two chiral states.

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