Cooper Pairs with Broken Time-Reversal, Parity, and Spin-Rotational Symmetries in Singlet Type-II Superconductors

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We show that singlet superconductivity in the Abrikosov vortex phase is absolutely unstable with respect to the appearance of a chiral triplet component of a superconducting order parameter. This chiral component, \( p_x + i p_y \), breaks time-reversal, parity, and spin rotational symmetries of the internal order parameter, responsible for a relative motion of two electrons in the Cooper pair. We demonstrate that the symmetry breaking Pauli paramagnetic effects can be tuned by a magnetic field strength and direction and can be made of the order of unity in organic and high-temperature layered superconductors.

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Conventional superconductivity is characterized by pairs of electrons with opposite spins, known as Cooper pairs. In their relative coordinate system, the internal wave function of the conventional Cooper pair [1] is isotropic with zero total spin and zero orbital angular momentum. Among modern materials, there are two types of unconventional superconductors: singlet d-wave and triplet ones, where the latter are characterized by broken parity symmetry of the internal Cooper pairs wave function [2,3]. Singlet d-wave superconductivity has been firmly established in quasi-two-dimensional (Q2D) high temperature [4] and organic [5] materials. On the other hand, heavy fermion [6,7], Sr\(_2\)RuO\(_4\) [8], ferromagnetic [9], and (TMTSF)\(_2\)X [10] compounds are candidates for a triplet superconducting pairing. Recently, it has been demonstrated [11] that a triplet component of the internal order parameter is always generated in the Abrikosov vortex phase of singlet superconductors due to the Pauli paramagnetic spin-splitting effects. Phenomenological theory of the singlet-triplet mixed order parameters in the Abrikosov phase has been considered in Ref.[12].

In this context, the most important from physical point of view symmetry of the internal superconducting order parameter is a time-reversal one. According to a general theory of unconventional superconductivity [2,3], a time-reversal symmetry of the internal orbital order parameter may be broken for multi-component order parameters. The corresponding chiral Cooper pairs possess non-zero spontaneous orbital magnetic momenta. Experimentally, such situation is realized in super-fluid \( ^3\)He, where the so-called \( A \)- and \( A_1 \)-phases are characterized by superfluid Cooper pairs with non-zero magnetic orbital momenta. A possibility of a chiral triplet order parameter, \( p_x + ip_y \), to exist in an unconventional superconductor Sr\(_2\)RuO\(_4\) is widely discussed [8], in particular, in a connection with the recent remarkable measurements of the Kerr effect [13]. Nevertheless, in our opinion, the chiral triplet order parameter, \( p_x + ip_y \), has not been firmly established in Sr\(_2\)RuO\(_4\) since it seems to contradict to some other experimental data [14-16].

A purpose of our Letter is to show that a chiral triplet order parameter always appears in singlet superconductors in the Abrikosov vortex phase due to the Pauli spin-splitting paramagnetic effects. In some sense, this means that there are no singlet type-II superconductors. Indeed, as shown below, the internal orbital wave function of the Cooper pairs is always characterized by a singlet-chiral triplet mixed order parameter, which breaks time-reversal, parity, and spin-rotational symmetries. As a result of the time-reversal symmetry breaking, the Abrikosov vortices are shown to possess an unusual distribution of magnetization. It is important that the symmetry breaking effects exist both for attractive and repulsive effective electron interactions in a triplet channel.

To the best of our knowledge, this fundamental phenomenon has been overlooked in the past. In particular, it was not considered in our Letter [11] due to a special (parallel) orientation of a magnetic field. Though the suggested theory is applied to all type II superconductors, below, we emphasize on Q2D d-wave organic and high-Tc superconductors. In the former case, as shown, the symmetry breaking effects can be always made of the order of unity in an inclined magnetic field.

We start from a simplest generalization of the BCS Hamiltonian for the case of unconventional superconductors [2,3],

\[
H = \sum_{\vec{p},\sigma} \epsilon_\sigma (\vec{p}) a^\dagger_{\vec{p},\sigma} a_{\vec{p},\sigma} + \frac{1}{2} \sum_{\vec{p},\vec{p}',\vec{q},\sigma} V (\vec{p},\vec{p}') a^\dagger_{\vec{p}+\vec{p}',\sigma} a^\dagger_{\vec{p}+\frac{\vec{q}}{2},-\sigma} a_{\vec{p}-\vec{p}',\frac{\vec{q}}{2},-\sigma} a_{\vec{p}+\frac{\vec{q}}{2},\sigma},
\]

(1)

where the effective electron interactions do not depend on electrons spins, \( s = \sigma / 2 \) (\( \sigma = \pm 1 \)). In Eq.(1), 2D electron
energy in a magnetic field is \( \epsilon_\sigma(\vec{p}) = (p_x^2 + p_y^2)/2m - \sigma \mu_B H \), where \( \mu_B \) is the Bohr magneton; \( \vec{q} \) corresponds to motion of a center of mass of the Cooper pairs, \( \vec{p} \) and \( \vec{p}' \) correspond to relative motion of the electrons in the Cooper pairs.

Below, we extend a classical method [17] to derive Ginzberg-Landau (GL) equations to the case of a singlet-triplet mixed order parameter. In particular, we represent effective electron interactions potential as a sum of singlet and triplet parts, \( V(\vec{p}, \vec{p}') = V_s(\vec{p}, \vec{p}') + V_t(\vec{p}, \vec{p}') \), and define the finite temperature normal and Gor'kov Green functions \[18\],

\[
G_{\sigma,\sigma}(\vec{p}, \vec{p}'; \tau) = -\langle T_\tau a_\sigma(\vec{p}, \tau) a_\sigma^\dagger(\vec{p}', 0) \rangle, \\
F_{\sigma,\sigma}(\vec{p}, \vec{p}'; \tau) = \langle T_\tau a_\sigma(\vec{p}, \tau) a_{\sigma^\dagger}(\vec{p}', 0) \rangle, \\
\]

(2)

In this case, singlet and triplet order parameters can be defined by means of Gor'kov Green function as,

\[
\Delta_s(\vec{p}, \vec{q}) = \frac{1}{2} \sum_{\vec{p}} V_s(\vec{p}, \vec{p}') T \sum_{\omega_n} \left[ F_{+, -}(\vec{p}' + \frac{\vec{q}}{2}, \vec{p}' - \frac{\vec{q}}{2}; i\omega_n) - F_{-, +}(\vec{p}' + \frac{\vec{q}}{2}, \vec{p}' - \frac{\vec{q}}{2}; i\omega_n) \right], \\
\]

(3)

\[
\Delta_t(\vec{p}, \vec{q}) = \frac{1}{2} \sum_{\vec{p}} V_t(\vec{p}, \vec{p}') T \sum_{\omega_n} \left[ F_{+, -}(\vec{p}' + \frac{\vec{q}}{2}, \vec{p}' - \frac{\vec{q}}{2}; i\omega_n) + F_{-, +}(\vec{p}' + \frac{\vec{q}}{2}, \vec{p}' - \frac{\vec{q}}{2}; i\omega_n) \right],
\]

(4)

where \( \omega_n = (2n + 1)\pi T \) is the Matsubara frequency \[18\].

In the Letter, we calculate superconducting transition temperature by means of the linearized Gor'kov Eqs. (2)-(4) for the following singlet and triplet parts of the effective electron interactions, \( V_s(\vec{p}, \vec{p}') = -8\pi g_s \cos(2\phi) \cos(2\phi') \) and \( V_t(\vec{p}, \vec{p}') = -8\pi g_t \cos(\phi - \phi') \), where \( \phi(\phi') \) is an azimuthal angle corresponding to 2D electron momentum \( \vec{p}(\vec{p}') \).

Below, we consider the case, where \( d_{x^2 - y^2} \) superconducting order parameter,

\[
\Delta_s(\vec{p}, \vec{q}) = \sqrt{2} \Delta_s(\vec{q}) \cos(2\phi),
\]

(5)

corresponds to a ground state at \( H = 0 \). Whereas a triplet component of the order parameter,

\[
\Delta_t(\vec{p}, \vec{q}) = \sqrt{2} \left[ \Delta^1_s(\vec{q}) \cos(\phi) + \Delta^2_s(\vec{q}) \sin(\phi) \right],
\]

(6)

is a secondary effect and appears only in the presence of a magnetic field.

Solving Eqs.(2)-(6) at \( T_c - T \ll T_c \), where \( T_c \) is the transition temperature to singlet phase \[15\] at \( H = 0 \), we obtain

\[
\frac{\Delta_s(\vec{q})}{g_s} = A_1 \Delta_s(\vec{q}) + D_1 \Delta^1_s(\vec{q}) + D_2 \Delta^2_s(\vec{q}), \\
\frac{\Delta^1_s(\vec{q})}{g_t} = A_2 \Delta^1_s(\vec{q}) + C \Delta^2_s(\vec{q}) + D_1 \Delta_s(\vec{q}), \\
\frac{\Delta^2_s(\vec{q})}{g_t} = C \Delta^1_s(\vec{q}) + A_3 \Delta^2_s(\vec{q}) + D_2 \Delta_s(\vec{q}),
\]

(7)

where

\[
A_1 = \pi T \sum_{n \geq 0} \left[ \frac{2}{\omega_n} - \frac{\epsilon_F^2}{4\omega_n^2} \left( q_x^2 + q_y^2 \right) \right], \\
A_2 = \pi T \sum_{n \geq 0} \left[ \frac{2}{\omega_n} - \frac{\epsilon_F^2}{4\omega_n^2} \left( \frac{3}{2} q_x^2 + \frac{1}{2} q_y^2 \right) \right], \\
A_3 = \pi T \sum_{n \geq 0} \left[ \frac{2}{\omega_n} - \frac{\epsilon_F^2}{4\omega_n^2} \left( \frac{3}{2} q_x^2 + \frac{3}{2} q_y^2 \right) \right], \\
C = -\pi T \sum_{n \geq 0} \frac{1}{\omega_n^3} \left( v_F \left( q_x q_y + q_y q_x \right) \right) \frac{2}{v_F}, \\
D_1 = -\mu_B H(\pi T) \left( \sum_{n \geq 0} \frac{1}{\omega_n^3} \right) \epsilon_F q_x, \\
D_2 = \mu_B H(\pi T) \left( \sum_{n \geq 0} \frac{1}{\omega_n^3} \right) \epsilon_F q_y,
\]

(8)

with \( \epsilon_F \) being the Fermi velocity.

Note that the principle difference between our Eqs. (3) and the results of Ref. [11] is that the singlet component \[15\] is coupled to two triplet components \[16\], which, as shown below, results in a time reversal symmetry breaking.

In the presence of a magnetic field, the gauge transformation, \( \vec{q} \rightarrow \vec{q} \equiv -i \vec{\nabla} - (2e/c) A_z \), where \( 2e \) is charge of the Cooper pair, results in the following GL equations,
where we also perform the Fourier transformation with respect to $\hat{q}$. Note that, in Eqs. (9)-(11), $g_s > g_t$ are effective electron coupling constants in singlet and triplet channels respectively, $\xi_\parallel = \sqrt{\frac{7\xi(3)}{\mu B}} v/\sqrt{2}\pi T_c$ is in-plane GL coherence length, and $t = (T_c - T)/T_c \ll 1$. Eqs. (9)-(11) directly demonstrate instability of singlet superconductivity with respect to a generation of two triplet components (13) since they do not have a solution for $\Delta^k_1(x,y) = 0$.

**High Tc Superconductors:** For $|g_t| << g_s$, Eq. (3) transforms to the conventional equation to determine the superconducting nucleus $[t - \xi_\parallel^2 \Delta_s(x,y) = 0$ with $\Pi^2 = \Pi_{x}^2 + \Pi_{y}^2$. The GL Eqs. (10),(11) for two triplet order parameters (14) simplify to

\[
\begin{align*}
\Delta_{s}(x,y) &+ g_t \sqrt{\frac{7\xi(3)}{\mu B}} \frac{H}{\pi T} \xi_\parallel \Pi_{x} \Delta_{s}(x,y) = 0, \\
\Delta_{s}(x,y) &- g_t \sqrt{\frac{7\xi(3)}{\mu B}} \frac{H}{\pi T} \xi_\parallel \Pi_{y} \Delta_{s}(x,y) = 0.
\end{align*}
\]

Here, we consider the case where a magnetic field is applied perpendicular to the conducting planes of a high-Tc superconductor. Then the upper critical field is given by the conventional formula $H_{c2} = \phi_0/2\pi \xi_\parallel^2$. For magnetic fields $H \leq H_{c2}$, in gauge $\vec{A} = (0, H, 0)$, the order parameter of the superconducting nucleus is given by

\[
\begin{align*}
\Delta_{s}(x,y) &= \begin{bmatrix}
\exp \left( -\frac{t_x^2}{2\xi_\parallel^2} \right) \\
-ig_t \sqrt{g_s} \sqrt{\xi_\parallel} \sqrt{\frac{\pi B}{\xi^2}} \exp \left( -\frac{t_y^2}{2\xi_\parallel^2} \right) \\
-ig_t \sqrt{g_s} \sqrt{\xi_\parallel} \sqrt{\frac{\pi B}{\xi^2}} \exp \left( -\frac{t_x^2}{2\xi_\parallel^2} \right) \\
-ig_t \sqrt{g_s} \sqrt{\xi_\parallel} \sqrt{\frac{\pi B}{\xi^2}} \exp \left( -\frac{t_y^2}{2\xi_\parallel^2} \right)
\end{bmatrix},
\end{align*}
\]

where $\alpha(H) = \sqrt{\frac{\pi B(3)}{\mu B}} \frac{H}{\pi T_c}$. Note that the recent measurements of the upper critical field in high-Tc superconductors [19] give $H_{c2} \sim H_p \sim T_c/\mu B$, which means that the effects of the singlet-triplet mixing (13) can be made of the order of unity if $|g_t| \sim g_s$.

It is important that the chiral triplet component of the order parameter (13) is associated with angular momentum,

\[
L = \text{sgn}(H) g_t^2 \alpha^2 (H_{c2}) \left[ \frac{(T_c - T)}{T_c \xi_\parallel} \right]^2 \sqrt{\frac{\pi B}{\xi^2}} \exp \left[ -\frac{(T_c - T)x^2}{T_c \xi_\parallel^2} \right],
\]

which is directed along the applied magnetic field and possesses a non-trivial coordinate dependence. It is instructive to rewrite the superconducting order parameter (5),

\[
\begin{align*}
\Delta(x,y;x, y) &= \Delta_s(x,y) \cos(2\phi) \exp[i\phi(x,y)], \quad \Delta_{s}(x,y) = 0 \quad \text{for } \Delta_{s}(x,y) = 0, \\
+\frac{1}{2}[\Delta_{s}(x,y)] I \sin(H + ip_y) \exp[i\phi(x,y)], \quad \Delta_{s}(x,y) = 0 \quad \text{for } \Delta_{s}(x,y) = 0,
\end{align*}
\]

in a form where its spin structure and chirality are shown explicitly.

where $p_x = \cos(\phi)$ and $p_y = \sin(\phi)$.

The presence of both singlet and triplet components in Eq. (15) breaks parity and spin-rotational symmetries of the internal order parameter, whereas the chiral triplet component, $p_x + ip_y$, breaks its time-reversal symmetry. The appearance of the chiral component, $p_x + ip_y$, results in the counter clockwise relative motion of the two electrons in the Cooper pair. This leads to the appearance of orbital magnetic moment of the Cooper pair, applied exactly opposite to the direction of the external magnetic field. It is important that coordinate dependence of the above mentioned magnetic moment can be expressed through singlet superconducting gap, $\Delta_{s}(x,y) = |\Delta_{s}(x,y)| \exp[i\phi(x,y)]$, in the Abrikosov vortex phase in the following way,

\[
M \sim -|\Delta_{s}(x,y)| \left[ \frac{\partial \Delta_{s}(x,y)}{\partial y} - \left( \frac{\partial \Delta_{s}(x,y)}{\partial x} \right) \right],
\]

where $v_x = 1/2\mu B \left[ \frac{\partial \phi(x,y)}{\partial x} + 2eA_x \right]$ and $v_y = 1/2\mu B \left[ \frac{\partial \phi(x,y)}{\partial y} - 2eA_y \right]$ are the corresponding components of the superfluid velocity. We propose to measure the spatial distribution of the magnetic moment (10), which is different from the spatial distribution of a magnetic moment due to the Meissner currents, to prove the symmetry breaking effect suggested in the Letter.

**Layered Organic Superconductors:** in a typical Q2D organic material [5], the upper critical field perpendicular to the conducting layers, $H_{c2} \ll H_p$, whereas the parallel upper critical field, $H_{c2} \gg H_p$, where $H_p$ is the Clogston paramagnetic limit [3]. Under such conditions, we suggest experiments in an inclined magnetic field, where only perpendicular component of the field is important. In this case, all equations derived above are still valid if we replace $H$ by its perpendicular component, $H \rightarrow H \sin \theta$, where $\theta$ is the angle between a magnetic field and the conducting layers. An analysis of such an experiment shows that the suggested symmetry breaking effects are maximal (i.e., of the order of unity) at $H \sin \theta \sim H_p$. Therefore, we expect that angular dependence of the upper critical field has to demonstrate
deviations from the so-called "effective mass" model in the vicinity of some small angle $\theta^* \sim H_{c2}/H_P \ll 1$ (see Fig.1). We propose detailed measurements of the upper critical fields in organic superconductors to detect possible deviations from the "effective mass" model in order to prove the existence of symmetry breaking effects suggested in this Letter.

In conclusion, we point out that the phenomenon, suggested in the Letter, is different from the singlet-triplet mixing effects in non-centrosymmetric superconductors [20-22,3,12]. Indeed, the so-called Lifshitz invariant [3], responsible for the singlet-triplet mixing effects [20-22,12], does not exist in zero magnetic field in an arbitrary case. In the Letter, we show that it always appears in the Abrikosov vortex phase in any singlet type-II superconductor due to the Pauli spin-splitting effects [11]. Other words, the main message of the Letter is that the singlet-triplet mixing effects, which break time-reversal, parity, and spin-rotational symmetries of the internal order parameter, appear in any singlet type-II superconductor. In Q2D organic and high-$T_c$ superconductors, these effects are expected to be of the order of unity.

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[1] A.A. Abrikosov, *Fundamentals of the Theory of Metals* (Elsevier Science Publisher B.V., Amsterdam, 1988).