## 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  $p_x+ip_y$  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.

DOI: 10.1103/PhysRevB.78.224504

PACS number(s): 74.20.Rp, 74.20.Mn, 74.72.-h

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<sup>1</sup> 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.<sup>2,3</sup> Singlet d-wave superconductivity has been firmly established in quasi-two-dimensional (Q2D) high-temperature<sup>4</sup> and organic<sup>5</sup> materials. On the other hand, heavy fermion,<sup>6,7</sup> Sr<sub>2</sub>RuO<sub>4</sub>,<sup>8</sup> ferromagnetic,<sup>9</sup> and tetramethyltetraselena-fulvalene (TMTSF)<sub>2</sub>X (Ref. 10) compounds are candidates for a triplet superconducting pairing. Recently, it has been demonstrated<sup>11</sup> 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,<sup>2,3</sup> a time-reversal symmetry of the internal orbital order parameter may be broken for multicomponent order parameters. The corresponding chiral Cooper pairs possess nonzero spontaneous orbital magnetic momenta. Experimentally, such situation is realized in superfluid <sup>3</sup>He, where the so-called A and  $A_1$  phases are characterized by superfluid Cooper pairs with nonzero magnetic orbital momenta. A possibility of a chiral triplet order parameter  $p_x + ip_y$  to exist in an unconventional superconductor Sr<sub>2</sub>RuO<sub>4</sub> is widely discussed,<sup>8</sup> in particular, in connection with the recent remarkable measurements on the Kerr effect.<sup>13</sup> Nevertheless, in our opinion, the chiral triplet order parameter  $p_x + ip_y$  has not been firmly established in Sr<sub>2</sub>RuO<sub>4</sub> since it seems to contradict to some other experimental data.14-16

The purpose of our paper 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 spinrotational 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<sup>11</sup> due to a special (parallel) orientation of a magnetic field. Under such condition, only one triplet component was generated in the Abrikosov vortex phase and, thus, time-reversal symmetry of the internal orbital wave function of the Cooper pairs was not broken. Though the theory suggested in this paper 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,<sup>2,3</sup>

$$\begin{split} H &= \sum_{\vec{p},\sigma} \epsilon_{\sigma}(\vec{p}) a^{\dagger}_{\vec{p},\sigma} a_{\vec{p},\sigma} \\ &+ \frac{1}{2} \sum_{\vec{p},\vec{p}',\vec{q},\sigma} V(\vec{p},\vec{p}') a^{\dagger}_{\vec{p}+\vec{q}/2,\sigma} a^{\dagger}_{-\vec{p}+\vec{q}/2,-\sigma} a_{-\vec{p}'+\vec{q}/2,-\sigma} a_{\vec{p}'+\vec{q}/2,\sigma}, \end{split}$$

$$(1)$$

where the effective electron interactions do not depend on electron spins  $s = \sigma/2(\sigma = \pm 1)$ . In Eq. (1), two-dimensional (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<sup>17</sup> to derive Ginzburg-Landau (GL) equations to the case of a singlet-triplet mixed order parameter. In particular, we represent effective electron interaction 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 the Gor'kov Green's functions,<sup>18</sup>

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

$$F_{\sigma,-\sigma}(\vec{p},\vec{p}';\tau) = \langle T_{\tau}a_{\sigma}(\vec{p},\tau)a_{-\sigma}(-\vec{p}',0)\rangle,$$

$$F_{\sigma,-\sigma}^{\dagger}(\vec{p},\vec{p}';\tau) = \langle T_{\tau}a_{\sigma}^{\dagger}(-\vec{p},\tau)a_{-\sigma}^{\dagger}(\vec{p}',0)\rangle.$$
(2)

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

$$\Delta_{s}(\vec{p},\vec{q}) = -\frac{1}{2} \sum_{\vec{p}'} V_{s}(\vec{p},\vec{p}') T \sum_{\omega_{n}} \left[ F_{+,-} \left( \vec{p}' + \frac{\vec{q}}{2}, \vec{p}' - \frac{\vec{q}}{2}; i\omega_{n} \right) - F_{-,+} \left( \vec{p}' + \frac{\vec{q}}{2}, \vec{p}' - \frac{\vec{q}}{2}; i\omega_{n} \right) \right],$$
(3)

$$\Delta_{t}(\vec{p},\vec{q}) = -\frac{1}{2} \sum_{\vec{p}'} V_{t}(\vec{p},\vec{p}') T \sum_{\omega_{n}} \left[ F_{+,-} \left( \vec{p}' + \frac{\vec{q}}{2}, \vec{p}' - \frac{\vec{q}}{2}; i\omega_{n} \right) + F_{-,+} \left( \vec{p}' + \frac{\vec{q}}{2}, \vec{p}' - \frac{\vec{q}}{2}; i\omega_{n} \right) \right],$$
(4)

where  $\omega_n = (2n+1)\pi T$  is the Matsubara frequency.<sup>18</sup>

In this paper, 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,

$$\Delta_s(\vec{p}, \vec{q}) = \sqrt{2\Delta_s(\vec{q})\cos(2\phi)},\tag{5}$$

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

$$\Delta_t(\vec{p}, \vec{q}) = \sqrt{2} [\Delta_t^1(\vec{q}) \cos(\phi) + \Delta_t^2(\vec{q}) \sin(\phi)], \qquad (6)$$

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 (5) at H=0, we obtain

$$\frac{\Delta_{s}(\vec{q})}{g_{s}} = A_{1}\Delta_{s}(\vec{q}) + D_{1}\Delta_{t}^{1}(\vec{q}) + D_{2}\Delta_{t}^{2}(\vec{q}),$$

$$\frac{\Delta_{t}^{1}(\vec{q})}{g_{t}} = A_{2}\Delta_{t}^{1}(\vec{q}) + C\Delta_{t}^{2}(\vec{q}) + D_{1}\Delta_{s}(\vec{q}),$$

$$\frac{\Delta_{t}^{2}(\vec{q})}{g_{t}} = A_{3}\Delta_{t}^{2}(\vec{q}) + C\Delta_{t}^{1}(\vec{q}) + D_{2}\Delta_{s}(\vec{q}),$$
(7)

where

$$A_{1} = \pi T \sum_{n \ge 0} \left[ \frac{2}{\omega_{n}} - \frac{v_{F}^{2}}{4\omega_{n}^{3}} (q_{x}^{2} + q_{y}^{2}) \right],$$

$$A_{2} = \pi T \sum_{n \ge 0} \left[ \frac{2}{\omega_{n}} - \frac{v_{F}^{2}}{4\omega_{n}^{3}} \left( \frac{3}{2} q_{x}^{2} + \frac{1}{2} q_{y}^{2} \right) \right],$$

$$A_{3} = \pi T \sum_{n \ge 0} \left[ \frac{2}{\omega_{n}} - \frac{v_{F}^{2}}{4\omega_{n}^{3}} \left( \frac{1}{2} q_{x}^{2} + \frac{3}{2} q_{y}^{2} \right) \right],$$

$$C = -\pi T \left( \sum_{n \ge 0} \frac{1}{4\omega_{n}^{3}} \right) \frac{v_{F}^{2} (q_{x} q_{y} + q_{y} q_{x})}{2},$$

$$D_{1} = -\mu_{B} H(\pi T) \left( \sum_{n \ge 0} \frac{1}{\omega_{n}^{3}} \right) (v_{F} q_{x}),$$

$$D_{2} = \mu_{B} H(\pi T) \left( \sum_{n \ge 0} \frac{1}{\omega_{n}^{3}} \right) (v_{F} q_{y}),$$
(8)

with  $v_F$  being the Fermi velocity. [Note that the principle difference between our Eqs. (7) and (8) and the results of Ref. 11 is that the singlet component (5) is coupled to two triplet components (6), which, as shown below, results in a time-reversal symmetry breaking.]

In the presence of a magnetic field, the gauge transformation  $\vec{q} \rightarrow \vec{\Pi} \equiv -i\vec{\nabla} - (2e/c)\vec{A}$ , where 2e is the charge of the Cooper pair, results in the following GL equations:

$$\begin{bmatrix} t - \xi_{\parallel}^{2} (\Pi_{x}^{2} + \Pi_{y}^{2}) ] \Delta_{s}(x, y) - \sqrt{\frac{7\zeta(3)}{2}} \frac{\mu_{B}H}{\pi T} \xi_{\parallel} [\Pi_{x} \Delta_{t}^{1}(x, y) - \Pi_{y} \Delta_{t}^{2}(x, y)] = 0, \qquad (9)$$

$$\begin{bmatrix} 1 - \frac{g_{t}}{g_{s}} - \frac{\xi_{\parallel}^{2}}{2} (3\Pi_{x}^{2} + \Pi_{y}^{2}) \end{bmatrix} \Delta_{t}^{1}(x, y) - \frac{\xi_{\parallel}^{2}}{2} [\Pi_{x}\Pi_{y} + \Pi_{y}\Pi_{x}] \Delta_{t}^{2}(x, y) + g_{t} \sqrt{\frac{7\zeta(3)}{2}} \frac{\mu_{B}H}{\pi T} \xi_{\parallel} \Pi_{x} \Delta_{s}(x, y) = 0, \qquad (10)$$

$$\begin{bmatrix} 1 - \frac{g_t}{g_s} - \frac{\xi_{\parallel}^2}{2} (\Pi_x^2 + 3\Pi_y^2) \end{bmatrix} \Delta_t^2(x, y) - \frac{\xi_{\parallel}^2}{2} [\Pi_x \Pi_y + \Pi_y \Pi_x] \Delta_t^1(x, y) - g_t \sqrt{\frac{7\zeta(3)}{2}} \frac{\mu_B H}{\pi T} \xi_{\parallel} \Pi_y \Delta_s(x, y) = 0, \qquad (11)$$

where we also perform the Fourier transformation with respect to  $\vec{q}$ . Note that, in Eqs. (9)–(11),  $g_s > g_t$  are effective electron coupling constants in singlet and triplet channels, respectively;  $\xi_{\parallel} = \sqrt{7\zeta(3)}v_F/4\sqrt{2}\pi T_c$  is in-plane GL coherence length, and  $t = (T_c - T)/T_c \ll 1$ . Equations (9)–(11) directly demonstrate instability of singlet superconductivity with respect to a generation of two triplet components (6) since they do not have a solution for  $\Delta_t^1(x, y) = \Delta_t^2(x, y) = 0$ .

*High-Tc Superconductors*. For  $|g_t| \leq g_s$ , Eq. (9) transforms to the conventional equation to determine the superconduct-

ing nucleus  $[t - \xi_{\parallel}^2 \Pi^2] \Delta_s(x, y) = 0$ , with  $\Pi^2 = \Pi_x^2 + \Pi_y^2$ . The GL Eqs. (10) and (11) for two triplet order parameters (6) were simplified to

$$\Delta_t^1(x,y) + g_t \sqrt{\frac{7\zeta(3)}{2}} \left(\frac{\mu_B H}{\pi T}\right) \xi_{\parallel} \Pi_x \Delta_s(x,y) = 0,$$
  
$$\Delta_t^2(x,y) - g_t \sqrt{\frac{7\zeta(3)}{2}} \left(\frac{\mu_B H}{\pi T}\right) \xi_{\parallel} \Pi_y \Delta_s(x,y) = 0.$$
(12)

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 approximately given by the conventional formula  $H_{c_2,0}^{\perp} = t\phi_0/2\pi\xi_{\parallel}^2$ . For magnetic fields  $H \leq H_{c_2}$  in gauge  $\vec{A} = (0, Hx, 0)$ , the order parameter of the superconducting nucleus is given by

$$\begin{bmatrix} \Delta_{s}(x) \\ \Delta_{t}^{1}(x) \\ \Delta_{t}^{2}(x) \end{bmatrix} = \begin{bmatrix} \exp\left(-\frac{tx^{2}}{2\xi_{\parallel}^{2}}\right) \\ -ig_{t}\sqrt{t}\alpha(H)\left[\frac{\sqrt{t}x}{\xi_{\parallel}}\right]\exp\left(-\frac{tx^{2}}{2\xi_{\parallel}^{2}}\right) \\ -g_{t}\sqrt{t}\alpha(|H|)\left[\frac{\sqrt{t}x}{\xi_{\parallel}}\right]\exp\left(-\frac{tx^{2}}{2\xi_{\parallel}^{2}}\right) \end{bmatrix}, \quad (13)$$

where  $\alpha(H) = \sqrt{7\xi(3)/2} (\mu_B H / \pi T_c)$ .

To find a change in the upper critical field due to the appearance of the triplet components, we substitute Eq. (12) in Eq. (9). As a result, we obtain,

$$\{t - \xi_{\parallel}^2 [1 - g_t \alpha^2 (H_{c_2}^{\perp}) \Pi^2] \} \Delta_s(x, y) = 0.$$
 (14)

Solution of Eq. (14) defines the corrected value of the upper critical field,

$$\frac{H_{c_2}^{\perp}}{H_{c_2,0}^{\perp}} = 1 + g_t \alpha^2 (H_{c_2}^{\perp}).$$
(15)

[Note that the recent measurements of the upper critical fields in high-*Tc* superconductors<sup>19</sup> give  $H_{c_2} \sim H_P \sim T_c / \mu_B$ , 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 in Eq. (13) is associated with angular momentum,

$$L = \operatorname{sgn}(H)g_t^2 \alpha^2(H_{c_2}) \left[ \frac{(T_c - T)x}{T_c \xi_{\parallel}} \right]^2 \exp\left[ -\frac{(T_c - T)x^2}{T_c \xi_{\parallel}^2} \right],$$
(16)

which is directed along the applied magnetic field and possesses a nontrivial coordinate dependence. It is instructive to rewrite superconducting order parameter (13) in a form, where its spin structure and chirality are shown explicitly,

$$\Delta(x, y; p) = \Delta_s(x, y) \cos(2\phi) * (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) + i \frac{\Delta_t(x, y)}{2} [\operatorname{sgn}(H)p_x + ip_y] * (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle),$$
(17)

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

The presence of both singlet and triplet components in Eq. (17) 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 counterclockwise 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:

$$M \sim - \left|\Delta_s(x,y)\right| \left[ \left(\frac{\partial |\Delta_s(x,y)|}{\partial y}\right) v_x - \left(\frac{\partial |\Delta_s(x,y)|}{\partial x}\right) v_y \right],$$
(18)

where  $v_x = \frac{1}{2m} \left[ \frac{\partial \Phi(x,y)}{\partial x} - \frac{2e}{c} A_x \right]$  and  $v_x = \frac{1}{2m} \left[ \frac{\partial \Phi(x,y)}{\partial y} - \frac{2e}{c} A_y \right]$  are the corresponding components of the superfluid velocity. We propose to measure the spatial distribution of the magnetic moment (18), which is different from the spatial distribution of a magnetic moment due to the Meissner currents, to prove the symmetry-breaking effect suggested in this paper.

*Structure of a Single Vortex.* The order parameter of the Abrikosov vortex in a singlet superconductor is known<sup>1</sup> to be well approximated by

$$\Delta_s(x,y) = \Delta_0 \tanh\left(\frac{r}{\xi_{\parallel}}\right) \exp[i\Phi(x,y)], \qquad (19)$$

where  $r = \sqrt{x^2 + y^2}$  and the phase  $\Phi(x, y) = \tan^{-1}(y/x)$ . Equation (19) defines a single vortex with the Cooper pairs being rotating counterclockwise, which corresponds to a magnetic field directed along the *z* direction. Inserting the singlet order parameter (19) into Eq. (12), we obtain,

$$\frac{\Delta_t^1(x,y)}{\Delta_0} = g_t \alpha(H) \frac{\xi_{\parallel}}{r} \bigg[ \tanh\bigg(\frac{r}{\xi_{\parallel}}\bigg) \frac{y}{r} + i \operatorname{sech}^2\bigg(\frac{r}{\xi_{\parallel}}\bigg) x \bigg] \exp[i\Phi(x,y)],$$
$$\frac{\Delta_t^2(x,y)}{\Delta_0} = g_t \alpha(H) \frac{\xi_{\parallel}}{r} \bigg[ \tanh\bigg(\frac{r}{\xi_{\parallel}}\bigg) \frac{x}{r} - i \operatorname{sech}^2\bigg(\frac{r}{\xi_{\parallel}}\bigg) y \bigg] \exp[i\Phi(x,y)].$$
(20)

For further development, it is convenient to rewrite Eqs. (19) and (20) in the following form:



FIG. 1. Relative magnitudes of the singlet (solid line) and the two triplet components  $\Delta_t^-$  (dashed line) and  $\Delta_t^+$  (dash-dotted line) of an isolated vortex calculated using Eqs. (19)–(22) are shown.

$$\begin{aligned} \Delta(x,y;p) &= \Delta_s(x,y)\cos(2\phi) * (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \\ &+ \frac{i}{2} [\Delta_t^+(x,y)(p_x + ip_y) \\ &+ \Delta_t^-(x,y)(p_x - ip_y)] * (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \end{aligned} \tag{21}$$

where

$$\Delta_{t}^{+}(x,y) = \frac{\left[\Delta_{t}^{1}(x,y) - i\Delta_{t}^{2}(x,y)\right]}{2}$$
$$\Delta_{t}^{-}(x,y) = \frac{\left[\Delta_{t}^{1}(x,y) + i\Delta_{t}^{2}(x,y)\right]}{2}.$$
(22)

We stress that unlike the case where magnetic field is close to  $H_{c_2}$  [given in Eq. (17)], a single vortex state prominently consists of a chiral order parameter  $p_x - ip_y$  at small values of r (see Fig. 1). For large values of r, both triplet components in Eq. (22) have almost equal magnitudes. The corresponding internal orbital magnetic moment of the Cooper pairs in chiral vortex state (19)–(22) is given by  $|M|=-2\mu_B[|\Delta_t^+(x,y)|^2-|\Delta_t^-(x,y)|^2]$  and shown in Fig. 2. Note that the magnetic moment is directed parallel to the external magnetic field.

Layered Organic Superconductors. In a typical Q2D organic material,<sup>5</sup> the upper critical field perpendicular to the conducting layers  $H_{c_2}^{\perp} \ll H_P$ , whereas the parallel upper critical field  $H_{c_2}^{\parallel} \gg H_P$ , where  $H_P$  is the Clogston paramagnetic limit.<sup>3</sup> Under such conditions, we suggest experiments in an inclined magnetic field, where only the 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 experiment shows that the suggested symmetrybreaking 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  $\theta^* \sim H_{c_2}^{\perp}/H_P \ll 1$  (see Fig. 3). We propose de-



FIG. 2. Spatial profile of the internal orbital magnetic moment of the Cooper pairs in a chiral single vortex state (19)-(22).

tailed 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 paper.

In conclusion, we point out that the phenomenon suggested in this paper is different from the singlet-triplet mixing effects in noncentrosymmetric superconductors.<sup>3,12,20-22</sup> It is also different from a generation of a triplet component in centrosymmetric superconductors due to the relativistic spinorbital coupling.<sup>23</sup> Note that in Ref. 20, the singlet-triplet mixing effects due to the phenomenological Lifshitz invariant are considered. We stress that the Lifshitz invariant, corresponding to the phenomenon suggested in our paper, is proportional to a magnitude of a magnetic field and, thus, cannot be introduced without microscopic calculations. In other words, the main message of this paper 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 due to



FIG. 3. Schematic diagram of the suggested angular dependence of the upper critical field for a highly anisotropic Q2D organic superconductor. The dash-dotted line denotes the region where the Pauli paramagnetic effect destroys superconductivity. Due to the singlet-triplet mixing effects the normalized upper critical field is higher (lower) than one depending on a sign of the effective electron interactions in a triplet channel.

the spin-splitting paramagnetic effects. In Q2D organic and high- $T_c$  superconductors, these effects are expected to be of the order of unity.

One of us (A.G.L.) is thankful to N. N. Bagmet, V. V. Kabanov, and Z. Tesanovic for useful discussions. This work was supported by the NSF under Grant No. DMR-0705986.

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