Phase transition to the Fulde–Ferrell–Larkin–Ovchinnikov state in a quasi-one-dimensional organic superconductor with anion order

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Abstract. A theoretical study is presented on the effect of anion order on the phase transition from the normal state to a Fulde–Ferrell–Larkin–Ovchinnikov superconducting state in a quasi-one-dimensional organic superconductor (TMTSF)_2ClO_4. The temperature dependence of the upper critical field $H_{c2}(T)$ is examined. In the absence of anion order, the $H_{c2}(T)$ curve exhibits a one- to two-dimensional crossover with decreasing temperature $T$. For a sufficiently large anion order parameter, the dimensional crossover disappears and then a kink appears in the $H_{c2}(T)$ curve.

1. Introduction
The realization of the Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) state has been suggested in low-dimensional organic superconductors [1, 2]. The low-dimensionality is advantageous to the FFLO state because the upper critical field $H_{c2}$ is not so strongly reduced by the orbital pair-breaking effect when a magnetic field is applied parallel to the conductive layer. Moreover, anisotropy of the Fermi surface helps stabilize the FFLO state [3, 4].

Recently, Yonezawa et al. reported measurements of the superconducting onset temperature $T_{c}^{\text{onset}}$ of a quasi-one-dimensional (Q1D) organic superconductor (TMTSF)_2ClO_4 in magnetic fields $H$ aligned with the conductive plane. They found a characteristic field-direction dependence of $T_{c}^{\text{onset}}$ suggestive of the transition to the FFLO superconducting phase [5]. Lebed showed that the observed $H_{c2}$ in $H$ parallel to the $b'$ axis (parallel to the conducting $ab$ plane and perpendicular to the most conductive $a$ axis) agrees in magnitude with a theory in which the FFLO state with $d$-wave pairing symmetry is assumed [6], Croitoru et al. demonstrated how the orbital magnetism in the FFLO state causes the in-plane anisotropy of $T_{c}^{\text{onset}}$ [7]. Miyawaki and Shimahara examined the temperature dependence of $H_{c2}$ with a focus on the effect of the anisotropic Fermi surface and revealed that a novel dimensional crossover of the $H_{c2}(T)$ curve appears for $q \parallel a$ [8], where $q$ is the center-of-mass momentum of Cooper pairs and $a$ is the lattice vector of the most conducting chain of (TMTSF)_2ClO_4.
In this paper, the previous theory [8] is extended to investigate $H_{c2}(T)$ in (TMTSF)$_2$ClO$_4$ on the basis of a more realistic band structure. Specifically, the effect of anion (ClO$_4^-$) order [9], which is known to cause a splitting of the Q1D Fermi surface, is taken into account. It is shown that the finite anion gap $\Delta_{AO}$ gives rise to a qualitative difference in the temperature dependence of the FFLO upper critical field $H_{c2}$.

2. Model and method

We consider the Q1D tight-binding Hamiltonian [10]

$$H_{AO} = -\sum_{i,j,\sigma} t_{ij} a_i^\dagger a_j + \sum_{i,\sigma} \epsilon_i a_i^\dagger a_i - \sum_{i,\sigma} (\mu + \sigma \mu_e H) a_i^\dagger a_i, \quad (1)$$

where $\mu$ is the chemical potential and $\sigma \mu_e H$ ($\sigma = \pm$) is the Zeeman energy. In this model, two kinds of chains (A and B) are defined in the $a$ direction. There is an energy difference between the A- and B-site due to the anion order. This energy difference is accounted for by the parameter

$$\epsilon_i = \begin{cases} \Delta_{AO} & \text{for } i \in A \\ -\Delta_{AO} & \text{for } i \in B. \end{cases} \quad (2)$$

For $t_{ij}$, only the nearest neighbor hopping is taken into account, and we define $t_{ij} = t_a$ ($t_b$) for the intra-chain (inter-chain) nearest neighbor hopping.

Diagonalizing this Hamiltonian, we obtain the dispersion [10, 11, 12]

$$\xi_s^a(k, H) = -2t_a \cos k_x - s\sqrt{(2t_b \cos k_y)^2 + \Delta_{AO}^2 + \mu - \sigma \mu_e H}, \quad (3)$$

where the momentum $k_x$ ($k_y$) is scaled by the inverse of the lattice constant $a$ ($b$). There are two electron bands in the Brillouin zone $|k_y| < \pi/2$, corresponding to $s = \pm$. In the organic conductor (TMTSF)$_2$ClO$_4$, the hole number per site is 0.5 and thus the chemical potential $\mu$ is determined by the 1/4-filled condition. The anion gap $\Delta_{AO}$ is suggested to be 25 meV by magnetoresistance measurements [11]. Another estimation based on the Hückel method gives $\Delta_{AO} \sim 100$ meV [13]. From recent first-principles calculations, however, $\Delta_{AO}$ has been claimed to be nearly zero [14] or $\sim 14$ meV [15]. We thus treat $\Delta_{AO}$ as a parameter that is less than $t_a \sim 300$ meV.

In the superconducting state, we take into account only intra-band Cooper pairing. We then obtain the following Bogoliubov-quasiparticle energy in an FFLO state with the superconducting gap function $\Delta(r, k) = \Delta(k)e^{iq \cdot r}$:

$$E_{k\sigma}^s = \sigma \zeta^s + E_k^s, \quad (4)$$

where

$$E_k^s = \sqrt{\xi_k^S(0, 0)^2 + \Delta(k)^2}, \quad (5)$$

$$\zeta^s = \frac{1}{2} v_F^s(k) \cdot q - \mu_e H. \quad (6)$$

In Eq. (6), $v_F^s(k)$ is the Fermi velocity for the $s$ band.

The gap $\Delta(k)$ is determined self-consistently from

$$\Delta(k') = \frac{1}{N} \sum_{s=\pm} \sum_k V(k', k) \frac{1 - f(E_{k\uparrow}^s) - f(E_{k\downarrow}^s)}{2E_k^s} \Delta(k), \quad (7)$$

where

$$f(x) = \frac{1}{2} \left( 1 + \frac{e^{x/T}}{1 + e^{x/T}} \right). \quad (8)$$
where $V(k',k) = V\gamma(k')\gamma(k)$ is the pairing interaction. According to Ref. [6], we assume a $d$-wave symmetry of the gap, i.e., $\Delta(k) = \Delta_0\gamma(k)$ with $\gamma(k) = \sqrt{2}\cos k_y$. The normal-superconducting phase boundary is determined by linearizing the above gap equation with respect to $\Delta_0$. From the linearized gap equation, we can obtain

$$\ln \frac{T}{T_c(0)} = -\sum_{s=\pm} \int_{-\pi/2}^{\pi/2} \frac{dk_y}{2\pi} \frac{\rho^s(0,k_y)}{N_d(0)} \gamma^2(k_y) \sinh^2 \frac{\beta \zeta^s}{2} \int_0^\infty dy \ln y$$

$$\times \left[ \frac{2\sinh^2 y}{[\cosh^2 y + \sinh^2 (\beta \zeta^s/2)]^2} - \frac{1}{\cosh^2 y[\cosh^2 y + \sinh^2 (\beta \zeta^s/2)]} \right]$$

with

$$N_d(0) = \sum_{s=\pm} \int_{-\pi/2}^{\pi/2} \frac{dk_y}{2\pi} \rho^s(0,k_y) \gamma^2(k_y).$$

Here, $\rho^s(0,k_y)$ is the Fermi surface value of the density of states defined through

$$\frac{1}{N} \sum_k (\cdots) = \int d\xi \sum_{s=\pm} \int_{-\pi/2}^{\pi/2} \frac{dk_y}{2\pi} \rho^s(\xi,k_y)(\cdots).$$

Equation (8) determines $H_{c2}$ as a function of $(T, q)$. An optimum value of $q$ is fixed such that $H_{c2}$ is maximized at a given temperature $T$, leading to an $H_{c2}(T)$ phase boundary.

The optimum $q$ occurs when it is directed along $a$, as expected from the Fermi-surface nesting consideration [3, 4, 8, 16]. For the optimum value of $q = |q|$, there are two possibilities associated with the nesting vectors $q^+$ and $q^-$ for the outer ($s = +$) and inner ($s = -$) Fermi surfaces (Fig. 1). In fact, when we plot $H_{c2}$ as a function of $q$, we find that the $H_{c2}(q)$ curve has two local maxima at low temperatures, though it has a single maximum at high temperatures. We shall denote the critical fields at the two local maxima by $H_{c2}^\pm$.

3. Results

Figure 2 shows plots of the numerical results of $H_{c2}^\pm(T)$. The FFLO state appears at low temperatures below $T^* \approx 0.56T_c(0)$, where $T_c(0)$ is the transition temperature at $H = 0$. When $\Delta_{AO} = 0$ (black solid line), $H_{c2}(T)$ curve exhibits a characteristic temperature dependence. Just below $T^*$, the $H_{c2}^+(T)$ curve has a positive curvature as in the case of the 1D system (dashed line); however, as temperature decreases, the curvature becomes negative and a shoulder appears. As temperature decreases further, the curve exhibits an upturn similar to the 2D system (dotted line). This one- to two-dimensional crossover is typical for Q1D systems [8]. As $\Delta_{AO}$ is increased, the magnitude of $H_{c2}^+(T)$ decreases, and the crossover behavior becomes less pronounced for $\Delta_{AO} \gtrsim 0.3t_a$. This is because the Fermi-surface mismatch between the up- and down-spin Fermi surfaces for $s = -$ at the nesting vector $q^-$ is larger for larger $\Delta_{AO}$.

When $\Delta_{AO} = 0$, the critical field $H_{c2}^+(T)$ is larger than $H_{c2}^-(T)$ throughout the entire temperature region. However, numerical calculations show that the reduction of $H_{c2}^-(T)$ by a finite $\Delta_{AO}$ is less significant than that of $H_{c2}^+(T)$. This is because the density of states $\rho^-(0,k_y)$ is larger than $\rho^+(0,k_y)$ on the nested Fermi surface. As a result, for $\Delta_{AO} \gtrsim 0.3t_a$, the critical field $H_{c2}^-(T)$ becomes larger than $H_{c2}^+(T)$ at low temperatures. This means that the upper critical field $H_{c2}(T)$ observed actually has a kink in its temperature dependence (Fig. 3).
Figure 1. Fermi surfaces for (a),(c) $\Delta_{AO} = 0$ and (b),(d) $\Delta_{AO} = 0.3t_a$. Red and black solid curves are the Fermi surfaces of minority-spin and majority-spin electrons, respectively. The red dotted curves represent the minority-spin Fermi surface shifted by the nesting vector $q^+$ ($q^-$) for the outer (inner) Fermi surface (where the shifted Fermi surface is shown only for the $k_x > 0$ branch).

4. Conclusion
We have examined how the FFLO upper critical field $H_{c2}(T)$ in a Q1D superconductor (TMTSF)$_2$ClO$_4$ is modified depending on the anion order. In the absence of the anion gap $\Delta_{AO}$, the $H_{c2}(T)$ curve exhibits a dimensional crossover typical for Q1D systems. For $\Delta_{AO} \gtrsim 0.3t_a$, the dimensional crossover disappears and a kink appears in the $H_{c2}(T)$ curve at a low temperature. If the anion gap $\Delta_{AO}$ is large enough, a kink of $H_{c2}(T)$ should be observed in (TMTSF)$_2$ClO$_4$.
**Figure 2.** Temperature dependence of $\mu_e H_{c2}^+ / T_c^{(0)}$ for $t_b = 0.1t_a$ and $\Delta_{AO} = 0$, $0.1t_a$, $0.2t_a$, $0.3t_a$, and $0.4t_a$. The temperature $T$ is scaled by $T_c^{(0)} = T_c(H = 0)$. For reference, the results for a 1D superconductor ($t_b = 0$ and $\Delta_{AO} = 0$) and for a 2D $d_{x^2-y^2}$-wave superconductor (with a cylindrical Fermi surface) are plotted by dashed and dotted lines, respectively. The inset shows the $T$ dependence of the optimum $v_{F0}^+ q / T_c^{(0)}$. Here, $v_{F0}^+$ denotes the Fermi velocity $|v_{F}^+(k_x, k_y = 0)|$.

**Figure 3.** Phase diagram for $t_b = 0.1t_a$ and $\Delta_{AO} = 0.3t_a$. The solid line corresponds to $H_{c2}^+$ and the dashed line to $H_{c2}^-$. The inset shows the $T$ dependence of the optimum $v_{F0}^+ q / T_c^{(0)}$. The phase boundary between the normal and superconducting states corresponds to the larger value of $H_{c2}^+$ and $H_{c2}^-$. The upper critical fields $H_{c2}^\pm$ cross each other at $T \approx 0.11T_c^{(0)}$, resulting in a kink in the phase boundary.

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References

[1] Lebed A G 2008 *The Physics of Organic Superconductors and Conductors* (Berlin: Springer) pp 687–704
[2] Ardavan A, Brown S, Kagoshima S, Kanoda K, Kuroki K, Mori H, Ogata M, Uji S, and Wosnitza J 2012 *J. Phys. Soc. Jpn.* **81** 011004
[3] Shimahara H 1994 *Phys. Rev. B* **50** 12760
[4] Shimahara H 1997 *J. Phys. Soc. Jpn.* **66** 541
[5] Yonezawa S, Kusaba S, Maeno Y, Auban-Senzier P, Pasquier C, Bechgaard K, and Jerome D 2008 *Phys. Rev. Lett.* **100** 117002
[6] Lebed A G 2011 *Phys. Rev. Lett.* **107** 087004
[7] Croitoru M D, Houzet M, and Buzdin A I 2012 *Phys. Rev. Lett.* **108** 207005
[8] Miyawaki N and Shimahara H 2014 *J. Phys. Soc. Jpn.* **83** 024703
[9] At $T = 24$ K, (TMTSF)$_2$ClO$_4$ shows the orientational order-disorder transition of anion ClO$_4^-$. Because of the structure of the anion order which is characterized by the wave vector $(0, 1/2, 0)$, the Brillouin zone becomes half. As a result, the Q1D Fermi surface splits at the boundary of the new Brillouin zone.
[10] Shimahara H 2000 *Phys. Rev. B* **61** R14936
[11] Yoshino H, Oda A, Sasaki T, Hanajiri T, Yamada J, Nakatsuji S, Anzai H, and Murata K 1999 *J. Phys. Soc. Jpn.* **68** 3142
[12] Lebed A G, Ha H I, and Naughton M J 2005 *Phys. Rev. B* **71** 132504
[13] Pevelen D L, Gauthier J, Barrans Y, Chasseau D, Castet F, and Ducasse L 2001 *Eur. Phys. J. B* **19** 363
[14] Nagai Y, Nakamura H, and Machida M 2011 *Phys. Rev. B* **83** 104523
[15] Alemany P, Pouget J P, and Canadell E 2014 *Phys. Rev. B* **89** 155124
[16] Miyawaki N and Higashitani S 2015 *Phys. Rev. B* **91** 094511