Possible mechanism to enhance spin-fluctuation-mediated superconductivity in two-dimensional organic conductor

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Abstract. Mechanisms of superconductivity in quasi-two-dimensional organic conductors have been investigated using an extended Hubbard model by using the transfer energies between BDA-TTP molecules for β-(BDA-TTP)₂I₃ based on the X-ray experiment data and the extended Hückel calculation. We obtain several mean-field solutions with charge orderings which may represent short-range orderings or low-energy fluctuations in the low-dimensional electronic system. In the pressure-temperature phase diagram, a charge ordered metal state almost degenerates with a normal metal state between an insulating phase with charge ordering and the normal metal phase. Using the random phase approximation (RPA) and the linearized gap equation, the transition temperature of the superconducting state is estimated for the charge-ordered metal state and the normal metal state. It is found that transition temperature of the superconductivity induced by spin fluctuations in the charge-ordered metal state is much higher than that of the normal metal state and that the superconductivity in the charge-ordered metal state is the gapless d-wave. This suggests that the short range charge ordering may also contribute to an enhancement of spin-fluctuation-mediated superconductivity. The difference in the superconducting states between β-(BDA-TTP)₂I₃ and β-(BDA-TTP)₂SbF₆ are briefly discussed.

1. Introduction

Quasi-two-dimensional organic conductors with a quarter-filled band reveal various kinds of superconductors, which may originate from fluctuations associated with magnetic ordering or charge ordering (CO). The superconductivity of κ-BEDT-TTF salts [4, 5, 6, 7] and β'-BEDT-TTF salts [8, 9] which occur in the vicinity of the magnetic ordering has been claimed that the pairing is due to the spin fluctuation. On the other hand, superconductors associated with the CO could be expected. Possible cases are the superconductor in the presence of CO as found in α-(BEDT-TTF)₂I₃[10] and the superconductor located in the vicinity of the charge order phase, e. g. θ-BEDT-TTF salts[11] and β''-(DODHT)₂PF₆[12]. One may also expect the superconductor like α-(BEDT-TTF)₂NH₄Hg(SCN)₄[13] which exists in the normal metal phase and is slightly away from the charge density wave phase.
The CO states have been investigated using the extended Hubbard models for organic conductors theoretically [2, 14, 15, 16, 17]. It is shown that the anisotropic repulsive interactions between the nearest-neighbor sites induce the stripe CO. The mechanisms of the superconductivity related with the CO state have been suggested for several salts. It has been shown that the superconductivity in the presence of the CO is induced by the spin fluctuation in the charge ordered metal (COM) for α-(BEDT-TTF)₂I₃. This COM is interpreted as the self-doped Heisenberg chain in the stripe CO weakened by the uniaxial pressures. [17] The COMs have been also investigated in the square lattice model[18] and in a model for θ-(BEDT-TTF)₂X.[19] These states are located between insulator with the CO and the normal (homogeneous) metal. The superconductivity in a quasi-two-dimensional organic conductor, β"-(DODHT)₂PF₆ salt, which is expected to appear after the melting of a stripe CO state, has been investigated [20]. When pressure is applied, an insulating state with the stripe CO changes into a metallic state with the weakened nonmagnetic CO at an intermediate pressure, and the normal state without the CO emerges at higher pressures. For the COM state at the intermediate pressure, the COI state and the normal state also exist as metastable states, and their free energies are nearly the same within a narrow energy range of 10⁻³ eV. Thus these three states may coexist each other by forming the phase separation at finite temperature. We find that the spin fluctuation around such a mean-field COM state gives rise to the superconducting state with a full gap. The organic superconductors, which occur in the normal state in the vicinity of the CO, have been also investigated, [19, 20, 21, 22, 23, 24, 25, 26, 27] showing that the mechanism may be ascribed to the charge fluctuation.

In the previous paper we have examined the superconductivity of β-(BDA-TTP)₂SbF₆, which comes from the spin fluctuation in the normal state. In order to examine a mechanism to enhance transition temperature of spin-fluctuation-mediated superconductivity, we examine the quasi-two dimensional organic conductors β-(BDA-TTP)₂I₃, which exhibit the superconductivity with rather higher critical temperature T_c of 8.2K at the pressure of 10.3 kbar [28] compared with that of β-(BDA-TTP)₂SbF₆. For β-(BDA-TTP)₂I₃ at lower pressures, the resistivity increases strongly as T decreases. The band structure shows finite overlap between the conduction and valence bands [28], indicating effectively quarter-filled electronic system. Then we examine CO in the mean-field theory. The solution with stripe CO is compatible with a fact that a finite residual magnetic susceptibility has been observed [28]. The purpose of the present paper is to find a possible mechanism to enhance spin-fluctuation-mediated superconductivity in the presence of (short range) CO which could exist widely in two-dimensional organic conductors.

2. Formulation

2.1. Extended Hubbard model

We consider an extended Hubbard model with the Coulomb interactions between each molecules, which is given by

\[ H = \sum_{\text{n.n.}, \sigma} \left[ t_{i\alpha,j\beta} C_{i\alpha\sigma}^\dagger C_{j\beta\sigma} + h.c. \right] + \sum_{i\alpha} U n_{i\alpha\uparrow} n_{i\alpha\downarrow} + \sum_{n.n., \sigma, \sigma'} V_{i\alpha,j\beta} n_{i\sigma\alpha} n_{j\beta\sigma}, \]  

(1)

where \( i, j = (1, \ldots, N_L) \) are indices of the unit cell of 2D square lattice and \( \alpha, \beta = (1,2) \) are indices of molecules in the unit cell. The first term denotes the kinetic energy with \( C_{i\alpha\sigma}^\dagger \) being creation operator with spin \( \sigma = (\uparrow, \downarrow) \). The quantity \( t_{i\alpha,j\beta} = (t_{p1}, t_{p2}, t_c, t_{q1}, t_{q2}) \) denote the transfer energy between nearest neighbor (n.n.) sites, \( (i, \alpha) \) and \( (j, \beta) \). The second and the third terms denote the on-site repulsive interaction \( U \), and the nearest-neighbor one \( V_{i\alpha, j\beta} \). By using Fourier transform

\[ C_{i\alpha\sigma}^\dagger = \frac{1}{\sqrt{N_L}} \sum_{k} e^{-ik \cdot r_i} C_{k\alpha\sigma}^\dagger, \]  

(2)
eq.(1) is written as

\[ H = \sum_{k\sigma} \varepsilon_{\alpha\beta\sigma}(k) C_{k\alpha\sigma}^{\dagger} C_{k\beta\sigma} + \frac{1}{N_L} \sum_{kk'q_0} U C_{k-q_0\alpha}^{\dagger} C_{k'+q_0\alpha}^{\dagger} C_{k'\beta\sigma} C_{k\alpha\sigma} \]

\[ + \frac{1}{N_L} \sum_{kk'q_0\alpha\beta} V_{\alpha\beta}(q) C_{k-q_0\alpha}^{\dagger} C_{k'+q_0\beta}^{\dagger} C_{k'\beta\sigma} C_{k\alpha\sigma}, \]  

(3)

where \( r_i \) denotes the position at the \( i \) unit cell and \( r \) denotes the vector between two unit cells.

The structure of the \( \beta \)-(BDA-TTP)\(_2\)I\(_3\) in the 2D conducting plane is shown in Fig. 1, where ET molecules stack along the vertical direction of the \( a \)-axis. The \( c \)- and \( a \)-axis in the conducting plane correspond to \( x \) - and \( y \)-axis in our formulation. The unit cell consists of two BDA-TTP molecules numbered by 1 and 2 with five transfer energies between molecules shown by \( p_1, p_2, q_1, q_2 \) and \( c \). Further we consider three kinds of nearest neighbor repulsive interaction, \( V_p, V_c \) and \( V_q \).

For \( \beta \)-(BDA-TTP)\(_2\)I\(_3\), eq. (4) on the basis of the site representation [eq. (2)] is written as

\[ \varepsilon^{\sigma} = \begin{pmatrix}
    t_c e^{i k_x} + t_c e^{-i k_y} \\
    t_{p1} + t_{q2} e^{-i k_y} + t_{q2} e^{-i k_x} + t_{q1} e^{i(k_x+k_y)} \\
    t_{c} e^{i k_x} + t_c e^{-i k_y}
\end{pmatrix}.
\]

(6)

We assume the pressure \( P \) dependence of transfer energies \( t_{\alpha\beta}(P) \) as follows.

\[ t_A(P) = t_A(0) + K_A P, \]

(7)

where \( A = p_1, p_2, q_1, q_2, c \).

We use eV and kbar as the units of energy and pressure, respectively. The coefficients \( K_A \) are estimated in Table 1 by using the data of \( \beta \)-(BDA-TTP)\(_2\)I\(_3\) salt at \( P = 0 \) (ambient pressure)\([28]\) and \( P = 7.5 \).

| \( A \) | \( p_1 \) | \( p_2 \) | \( q_1 \) | \( q_2 \) | \( c \) |
|---|---|---|---|---|---|
| \( t_A(0) \) | -0.140 | -0.0528 | -0.0010 | 0.0516 | 0.0668 |
| \( K_A \) | -0.0023 | -0.0028 | -0.00024 | -0.000027 | 0.0016 |

Table 1. Transfer energy \( t_A(0) \) and coefficient \( K_A \).

2.2. Mean field theory

When considering the CO states, the unit cell consists of four BDA-TTP molecules (Fig. 1). Applying Hartree-Fock approximation to the interactions, \([14]\) the mean field Hamiltonian is described as

\[ H_{MF} = \sum_{k\sigma} \varepsilon_{\alpha\beta\sigma}(k) C_{k\alpha\sigma}^{\dagger} C_{k\beta\sigma} - N_L \sum_{\alpha} U \langle n_{\alpha\uparrow} \rangle \langle n_{\alpha\downarrow} \rangle - N_L \sum_{\alpha\beta \langle r \rangle \sigma \sigma'} V_{\alpha\beta}(q) \langle n_{\alpha\sigma} \rangle \langle n_{\beta\sigma'} \rangle, \]

(8)
Figure 1. The structure of the β-(BDA-TTP)_2I_3 corresponding to solutions of CO . The unit cell consists of four BDA-TTP molecules with five transfer energies, \( t_{i\alpha:j\beta} \), and three kinds of nearest neighbor repulsive interaction, \( V_p, V_c \) and \( V_q \). In the normal state, the unit cell divides into two sections in the dotted line.

\[
\tilde{\varepsilon}_{\alpha\beta\sigma}(k) = \varepsilon_{\alpha\beta\sigma}(k) + U\langle n_{\alpha(-\sigma)} \rangle \delta_{\alpha\beta} + \sum_{\beta'} V_{\alpha\beta'} \langle n_{\beta'\sigma'} \rangle \delta_{\alpha\beta}.
\]  

Equation (9) is diagonalized by

\[
\sum_{\beta} (\tilde{\varepsilon}_{\alpha\beta\sigma}(k) - \mu \delta_{\alpha\beta}) d_{\beta\sigma}(k) = \xi_{r\sigma}(k) d_{\alpha\sigma}(k),
\]  

where \( \xi_{r\sigma}(k) \) and \( d_{\alpha\sigma}(k) \) \((r = 1, 2, 3, 4)\) are the eigen value \((\xi_{1\sigma}(k) > \xi_{2\sigma}(k) > \xi_{3\sigma}(k) > \xi_{4\sigma}(k))\) and the eigen vector with momentum \( k \) and spin \( \sigma \). The quantity \( \mu \) is the chemical potential determined by the condition of the 3/4-filled band. Using \( d_{\alpha\sigma}(k) \), \( \langle n_{\alpha\sigma} \rangle \) is written as

\[
\langle n_{\alpha\sigma} \rangle = \frac{1}{N_L} \sum_{k} \sum_{r} \frac{e^{\xi_{r\sigma}(k)/T}}{e^{\xi_{r\sigma}(k)/T} + 1} d_{\alpha\sigma}^*(k)d_{\alpha\sigma}(k),
\]  

where \( T \) is the temperature \((k_B = 1)\). Helmholtz free energy is expressed as

\[
F = -T \sum_{k_{\tau\sigma}} \ln \left(1 + e^{-\xi_{r\sigma}(k)/T}\right) - N_L \sum_{\alpha} U \langle \langle n_{\alpha\uparrow} \rangle \langle n_{\alpha\downarrow} \rangle \rangle - N_L \sum_{\alpha\beta} V_{\alpha\beta} \langle \langle n_{\alpha\sigma} \rangle \langle n_{\beta\sigma} \rangle \rangle + 6\mu N_L.
\]

### 2.3. Charge and spin susceptibilities

We calculate the susceptibility of the model with the multi-site for the nonmagnetic state. In terms of linear response theory, the charge susceptibility \( \chi^c \), the longitudinal spin susceptibility
The operators $O^{(\nu)}_{q}(\tau)$ ($\nu = 0, 1, 2, 3$) are defined by

$$O^{(\nu)}_{q}(\tau) = \sum_{k, \sigma, \sigma'} C_{k, \sigma}^{\dagger}(\tau) C_{k+ q, \sigma'}(\tau),$$

and

$$O^{(\pm)} = \left(O^{(1)} \pm iO^{(2)}\right)/2,$$

where $\tau$ is the imaginary time, $\sigma^{(0)}$ is the unit matrix and $\sigma^{(\nu)}$ ($\nu = 1, 2, 3$) is the Pauli matrices acting on the spin space. In eqs. (13)-(15), $\omega_{m}$ is the Matsubara frequency for boson and the susceptibility, $\chi^{s_{\nu}}$, is defined by

$$\chi^{s_{\nu}}_{\alpha\beta}(q, i\omega_{m}) = \frac{1}{N_{L}} \int_{0}^{1/T} d\tau \left\langle O^{(\nu)}_{q}(\tau) O^{(\nu)}_{-q}(0) \right\rangle e^{i\omega_{m}\tau}$$

$$= \frac{1}{2} \left( \chi^{\uparrow\uparrow}_{\alpha\beta}(q, i\omega_{m}) + \chi^{\downarrow\downarrow}_{\alpha\beta}(q, i\omega_{m}) + \chi^{\uparrow\downarrow}_{\alpha\beta}(q, i\omega_{m}) + \chi^{\downarrow\uparrow}_{\alpha\beta}(q, i\omega_{m}) \right),$$

$$\chi^{s_{\nu}}_{\alpha\beta}(q, i\omega_{m}) = \frac{1}{N_{L}} \int_{0}^{1/T} d\tau \left\langle O^{(\nu)}_{q}(\tau) O^{(\nu)}_{-q}(0) \right\rangle e^{i\omega_{m}\tau}$$

$$= \frac{1}{2} \left( \chi^{\uparrow\uparrow}_{\alpha\beta}(q, i\omega_{m}) - \chi^{\downarrow\downarrow}_{\alpha\beta}(q, i\omega_{m}) - \chi^{\uparrow\downarrow}_{\alpha\beta}(q, i\omega_{m}) + \chi^{\downarrow\uparrow}_{\alpha\beta}(q, i\omega_{m}) \right),$$

$$\chi^{s_{\nu}}(q, i\omega_{m}) = \frac{1}{N_{L}} \int_{0}^{1/T} d\tau \left\langle O^{(+)}_{q}(\tau) O^{(-)}_{-q}(0) \right\rangle e^{i\omega_{m}\tau}.$$

The operators $O^{(\nu)}_{q}(\tau)$ ($\nu = 0, 1, 2, 3$) are defined by

$$O^{(\nu)}_{q}(\tau) = \sum_{k, \sigma, \sigma'} C_{k, \sigma}^{\dagger}(\tau) C_{k+ q, \sigma'}(\tau),$$

and

$$O^{(\pm)} = \left(O^{(1)} \pm iO^{(2)}\right)/2,$$

where $\tau$ is the imaginary time, $\sigma^{(0)}$ is the unit matrix and $\sigma^{(\nu)}$ ($\nu = 1, 2, 3$) is the Pauli matrices acting on the spin space. In eqs. (13)-(15), $\omega_{m}$ is the Matsubara frequency for boson and the susceptibility, $\chi^{s_{\nu}}$, is defined by

$$\chi^{s_{\nu}}_{\alpha\beta}(q, i\omega_{m}) = \frac{1}{N_{L}} \int_{0}^{1/T} d\tau \sum_{kk'} \left\langle C_{k- q, \sigma}^{\dagger}(\tau) C_{k, \sigma}(\tau) C_{k+ q, \sigma'}^{\dagger}(0) C_{k', \sigma'}^{\dagger}(0) \right\rangle e^{i\omega_{m}\tau}.$$

For the calculation of the diagram of the susceptibility, we introduce the following irreducible susceptibility, $\chi^{0}_{\alpha\beta}$, which is obtained in the absence of interaction.

$$\chi^{0}_{\alpha\beta}(q, i\omega_{m}) = -\frac{T}{N_{L}} \sum_{p, \epsilon_{n}} \left[C^{0}_{\alpha\beta}(p+q, i\omega_{m} + i\epsilon_{n}) M^{0}_{\beta\alpha}(p, i\epsilon_{n}) \right],$$

where the single particle Green function, $G^{0}_{\alpha\beta}(k, i\epsilon_{n})$, is given by

$$G^{0}_{\alpha\beta}(k, i\epsilon_{n}) = \sum_{\nu} d_{\alpha\nu}(k) d_{\beta\nu}(k) \frac{1}{i\epsilon_{n} - \epsilon_{\nu}(k)},$$

and $\epsilon_{n}$ is the Matsubara frequency for the fermion.

By applying RPA, Eq. (18) is evaluated as

$$\chi = \overline{\chi} - \overline{\chi}^{0}(U \otimes \sigma^{(1)}) \overline{\chi} - \overline{\chi}^{0} \left\{ V \otimes \left( \sigma^{(0)} + \sigma^{(1)} \right) \right\} \overline{\chi},$$

where $\overline{\chi}$ and $\overline{\chi}^{0}$ are given by

$$\overline{\chi} = \begin{pmatrix} \chi^{\uparrow\uparrow} & \chi^{\downarrow\downarrow} \\ \chi^{\uparrow\downarrow} & \chi^{\downarrow\uparrow} \end{pmatrix},$$

$$\overline{\chi}^{0} = \begin{pmatrix} \chi^{0} & 0 \\ 0 & \chi^{0} \end{pmatrix}.$$
Equation (21) is expressed as
\[
\chi^{\sigma\sigma} = \frac{1}{2}(I - \chi^0 U)^{-1}\chi^0 + \frac{1}{2}(I + \chi^0 U + 2\chi^0 V)^{-1}\chi^0 ,
\]
(24)
\[
\chi^{(-\sigma)\sigma} = \frac{1}{2}(I + \chi^0 U + 2\chi^0 V)^{-1}\chi^0 - \frac{1}{2}(I - \chi^0 U)^{-1}\chi^0 .
\]
(25)

By using eqs.(13)(14)(24)(25), \(\chi^c\) and \(\chi^s\) are calculated as
\[
\chi^c = \chi^{\sigma\sigma} + \chi^{(-\sigma)\sigma} = (I + \chi^0 U + 2\chi^0 V)^{-1}\chi^0 ,
\]
(26)
\[
\chi^s = \chi^{\sigma\sigma} - \chi^{(-\sigma)\sigma} = (I - \chi^0 U)^{-1}\chi^0 .
\]
(27)
The susceptibility for the ladder type diagram, \(\chi^L\), is given by
\[
\chi^L = (I - \chi^0 U)^{-1}\chi^0 = \chi^s .
\]
(28)

2.4. Pairing interaction
We calculate the pairing interaction within RPA in a way similar to the previous work.[17]

The interaction for the singlet pairing is given by the diagram consisting of both the bubble term, \(p^B\), and the ladder term, \(p^L\):
\[
p^{\text{Singlet}} = p^B + p^L ,
\]
(29)
where
\[
p^B = U + V - U\chi^{(-\sigma)\sigma}U - U\left\{\sum_{\sigma'}\chi^{(-\sigma')\sigma'}\right\}V - V\left\{\sum_{\sigma'}\chi^{\sigma'\sigma}\right\}U - V\left\{\sum_{\sigma_1,\sigma_2}\chi^{\sigma_1\sigma_2}\right\}V ,
\]
(30)
\[
p^L = U\left(I - \chi^0 (-\sigma)U\right)^{-1}\chi^0 U .
\]
(31)

By using eqs. (26) (27) and (28), the pairing interaction for the singlet state is rewrited by
\[
p^{\text{Singlet}} = p^B + p^L = U + V + \frac{3}{2}U\chi^s U - \frac{1}{2}(U + 2V)\chi^c (U + 2V) ,
\]
(32)
where
\[
p^B = U + V + \frac{1}{2}U\chi^s U - \frac{1}{2}(U + 2V)\chi^c (U + 2V) ,
\]
(33)
\[
p^L = U\chi^L U = U(I - \chi^0 U)^{-1}\chi^0 U = U\chi^s U .
\]
(34)

This pairing is also expressed as
\[
p^{\text{Singlet}} = p^c + p^s ,
\]
(35)
where \(p^c\) and \(p^s\) represent the pairing interaction induced by the charge fluctuation and the spin fluctuation, respectively, and defined by
\[
p^c \equiv V - \frac{1}{2}(U + 2V)\chi^c (U + 2V) ,
\]
(36)
\[
p^s \equiv U + \frac{3}{2}U\chi^s U .
\]
(37)
By using these pairing interactions, the linearized gap equation for the SC state is obtained as

$$
\lambda \Sigma_{\alpha \beta}(k) = -\frac{T}{N_L} \sum_{k'_{\max}} \left\{ P_{\alpha \beta}^R(k - k') G_{\alpha \alpha'}^0(k', i\varepsilon_m) G_{\beta \beta'}^0(-k', -i\varepsilon_m) + P_{\alpha \beta}^L(k + k') G_{\beta \alpha'}^0(k', i\varepsilon_m) G_{\alpha \beta'}^0(-k', -i\varepsilon_m) \right\} \Sigma_{\alpha' \beta'}(k') .
$$

(38)

where $\Sigma_{\alpha \beta}$ is the anomalous self-energy corresponding to the SC order parameter and $\lambda$ is the eigen value obtained by diagonalizing eq. (38). The transition temperature, $T_c$, for the SC state is determined by $\lambda = 1$.

The pairing interaction for the triplet state is also given by

$$
P_{\text{Triplet}} = V - U \chi_{(-\sigma)(-\sigma)} U - U \left\{ \sum_{\sigma'} \chi_{(-\sigma)\sigma'} \right\} V - V \left\{ \sum_{\sigma' \sigma''} \chi_{\sigma' \sigma''} \right\} U - U \left\{ \sum_{\sigma' \sigma''} \chi_{\sigma' \sigma''} \right\} V
$$

\[= V - \frac{1}{2} U \chi U - \frac{1}{2} (U + 2V) \chi \left( U + 2V \right),
\]

(39)

and the linearized gap equation for the SC state is described as

$$
\lambda \Sigma_{\alpha \beta}(k) = -\frac{T}{N_L} \sum_{k'_{\max}} P_{\alpha \beta}^{\text{Triplet}}(k - k') G_{\alpha \alpha'}^0(k', i\varepsilon_m) G_{\beta \beta'}^0(-k', -i\varepsilon_m) \Sigma_{\alpha' \beta'}(k') .
$$

(40)

where $\lambda$ is the eigen value obtained by diagonalizing eq. (40).

In the present choice of parameters, the anomalous self-energy, $\Sigma_{\alpha \beta}$ depends mainly on $k$, while it does not nearly depend on $\varepsilon_n$. Therefore we ignore the $\varepsilon_n$ dependence in the pairing interaction. In this case, eqs. (38) and (40) is called linearized gap equation.

3. Phase diagram of charge order

![Figure 2](image_url). The phase diagram on the plane of $V_p$ and $V_c$ (= $V_q$) with the fixed $U = 0.40$ and $T = 0.03$. 


Considering the CO solution, we start from a unit cell consisting of four BDA-TTP molecules. The CO pattern is determined by calculating Helmholtz free energy \[eq. (12)\].

Figure 2 shows a phase diagram on the plane of \(V_p\) and \(V_c\) \((= V_q)\) with the fixed \(U = 0.40\) and \(T = 0.03\). Antiferromagnetic metal state appears in the region where both \(V_p\) and \(V_c\) are small. Stripe CO along \(c\)-axis appears in the region where \(V_p\) is large and \(V_c\) is small. Stripe CO along \(a+c\)-axis appears in the region where \(V_p\) is small and \(V_c\) is large. Charge ordering with three charge rich sites and one hole rich site appears in the region where both \(V_p\) and \(V_c\) are large. Since CO pattern which corresponds to the experiment \([28]\) is stripe CO along \(c\)-axis, we choose the parameter \(V_p = 0.25\) and \(V_c = V_q = 0.15\).

\[\text{(a) } T = 0.056, \text{ (b) } T = 0.056, \text{ (c) } T = 0.056.\]

Figure 3 shows the temperature dependence of the electron number \(n_\alpha\), the magnetic moment \(m_\alpha\) and the gap at the ambient pressure where \(\alpha\) is the site indices in the unit cell. For \(T < 0.056\), the gap is positive. The electron is rich and the magnetic moment is small at the sites 1 and 3 while the hole is rich and staggered moment exists at the sites 2 and 4. Therefore this state is regarded as the charge ordered insulator along \(c\)-axis. For \(0.064 < T\), the state is normal, since the gap is negative, the electron number is 1.5 in the all sites, and the magnetic moments is 0 in all sites. For \(0.056 < T < 0.064\), following two states are almost degenerate. One state is the COM along \(c\)-axis where the gap is negative, the sites 1 and 3 (2 and 4) are electron-rich (hole-rich) and the magnetic moments is 0 in all the sites. Another state is the normal state which is the same as that at \(T > 0.064\). In Fig. 3, only COM state is shown at \(0.056 < T < 0.064\). The phase transition from the charge ordered insulator to the COM at the temperature \(T = 0.056\) is of the first order while that from the normal state to the COM at the temperature \(T = 0.064\) is of the second order.

The pressure-temperature phase diagram is shown in Fig. 4. The transition temperature for the charge order insulator (COI) decreases with increasing pressure. The charge order metal (COM) emerges as the intermediated state between the COI and the normal state with varying temperature and also pressure. The phase where the COM almost degenerates with normal state exist between the charge ordered insulator phase and the normal phase. In this charge order metal phase, the magnetic moment is zero in all sites and the CO pattern is stripe along
Figure 4. Phase diagram on the plane of $P$ and $T$ with $U = 0.40$, $V_p = 0.25$ and $V_c = V_q = 0.15$. The solid (the short-dashed) line corresponds to the first (second) order transition.

$c$-axis. Therefore, the number of sites in a unit cell becomes two.

4. Spin-fluctuation mediated superconductivity

Figure 5. (a) The pairing interaction $P_{22}^c$ with $P = 11.0$, $U = 0.40$, $V_p = 0.25$, $V_c = V_q = 0.15$ and $T = 0.03$. (b) The pairing interaction $P_{22}^s$ with $P = 11.0$, $U = 0.40$, $V_p = 0.25$, $V_c = V_q = 0.15$ and $T = 0.03$.

Figure 5 shows the momentum dependence of the pairing interaction in the charge ordered metal state, where both the charge fluctuation $P_{22}^c$ and the spin fluctuation $P_{22}^s$ are calculated for $P = 11.0$, $U = 0.40$, $V_p = 0.25$, $V_c = V_q = 0.15$ and $T = 0.03$ is shown in The peak of $P_{22}^s$ is located at $q = (±\pi, ±\pi)$ and the maximum of $P_{22}^s$ is the largest among the other pairing interactions. The maximum of $P_{11}^s$ is about 40 percent and those of $P_{12}^s$ and $P_{21}^s$ are about 60 percent compared with the largest one. The wave number of the peak of other components
of $P^s$ is the same as $P^s_{22}$. The maximum of $P^s_{22}$ is the largest among $P^c$. Note that the spin susceptibility is much larger than the charge susceptibility. The maximum of $P^s_{22}$ in the normal state is less than 10 percent of that in the charge ordered metal state. The wave number of the peak of $P^s_{22}$ in the normal state is the same as that in the COM state.

The momentum dependence of the charge susceptibility $\chi^c$ and the spin susceptibility $\chi^s$ in the site representation with $P = 11.0$, $U = 0.40$, $V_p = 0.25$, $V_c = V_q = 0.15$ and $T = 0.03$ in the COM state is almost the same as that of $P^c$ and $P^s$, respectively.

![Figure 6. The Fermi surface (solid line) and the node of the gap (dotted line) with $P = 11.0$, $U = 0.40$, $V_p = 0.25$, $V_c = V_q = 0.15$ and $T = 0.03$.](image)

The node of the gap is calculated in a way similar to the previous work.[27] In Fig. 6, the node of the gap is shown by the dotted line together with the Fermi surface (solid line). It is found that the SC state is a gapless state of the d-wave, since the node crosses with the Fermi surface four times.

In Fig. 7, the pressure dependence of the eigen value $\lambda$ for the singlet SC state in the charge order metal phase (solid line) and the normal phase (dotted line) with $U = 0.40$, $V_p = 0.25$, $V_c = V_q = 0.15$ and $T = 0.03$ is shown. The eigen value $\lambda$ in the nonmagnetic COM phase is larger than that in the normal metal phase. So the nonmagnetic COM phase becomes superconductivity more easily than the normal phase. Therefore the superconductivity appears in the nonmagnetic COM phase.

In Fig. 8, the phase diagram on the plane of $U$ and $V$ with $P = 0.0$ and $T = 0.001$ for $\beta$-(BDA-TTP)$_2$I$_3$ and $\beta$-(BDA-TTP)$_2$SbF$_6$. For $\beta$-(BDA-TTP)$_2$SbF$_6$, the charge ordered metal state does not appear and the range of the normal metal state in the $U$-$V$ phase diagram is larger than that for $\beta$-(BDA-TTP)$_2$I$_3$. So the superconductivity of $\beta$-(BDA-TTP)$_2$SbF$_6$ is the superconducting state in the normal metal state corresponding to the superconducting state of $\beta$-(BDA-TTP)$_2$I$_3$ in the normal metal state.

5. Summary and discussion

We investigated a possible mechanism to enhance spin-fluctuation-mediated superconductivity in organic conductors. By using the transfer integrals of $\beta$-(BDA-TTP)$_2$I$_3$, we have examined the
mean-field solutions of CO and the fluctuation-mediated superconductivity where the present CO may become short range in actual two-dimensional electronic systems. Increasing the pressure or the temperature, the nonmagnetic COM state which almost degenerates with the normal state exist between the stripe charge ordered state and the normal state. The eigen value \( \lambda \) in the charge ordered metal state is larger than that in the normal state, since the effective magnetic moments in the hole-rich sites moves from \( 1/4 \) to \( 1/2 \) due to CO. Thus spin-fluctuation-induced superconductivity in the presence of CO is more relevant than that in the normal state.

We note that there is a recent experiment indicating the absence of CO.[29] The possible state could be the Mott insulator, although such a state is incompatible with the band structure obtained from the transfer integrals.[28] It remains an interesting problem in the future to examine the origin of insulating phase and possible short range CO.
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