Origin of the Superconductivity in $\beta'$(BEDT-TTF)$_2$ICl$_2$ under High Pressure and $\beta$-(BEDT-TTF)$_2$X at Ambient Pressure

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We present a theoretical study on the superconductivity in $\beta'$-(BEDT-TTF)$_2$ICl$_2$ at $T_c = 14.2$K under high hydrostatic pressure found by Taniguchi et al., which is the highest record among organic superconductors. Its electronic structure is well expressed by the anisotropic triangular lattice Hubbard model at half filling. In the present work, we study this effective model by using the fluctuation-exchange (FLEX) approximation. In the obtained phase diagram, the superconductivity with $d_{x^2-y^2}$ like symmetry is realized next to the antiferromagnetic (AF) insulating phase, as a result of the 1D-2D dimensional crossover driven by the pressure. The obtained maximum $T_c$ is 16−18K. In addition, the superconductivity in $\beta$-(BEDT-TTF)$_2$X is also understood in the same framework.

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Up to now, many kinds of organic superconductors composed of BEDT-TTF (abbreviated as ET) molecules have been discovered and studied intensively. Especially, $\kappa$-(ET)$_2$X compounds attract much attention because it shows the maximum superconducting (SC) transition temperature ($T_c \approx 12$K) among them [1]. Recently, the temperature-pressure phase diagram of $\kappa$-(ET)$_2$X salt could be produced by the fluctuation-exchange (FLEX) approximation [2–4]. It is a kind of the self-consistent spin-fluctuation theory [5,6]. According to the FLEX approximation, d-wave superconductivity is expected which is mediated by the strong antiferromagnetic (AF) fluctuations due to the Coulomb interaction.

Quite recently, Taniguchi et al. found the superconductivity at $T_c = 14.2$K in $\beta'$-(ET)$_2$ICl$_2$ under high hydrostatic pressure ($P \gtrsim 8.2$GPa), which established the new record of $T_c$ among the organic superconductors [7]. At ambient pressure, $\beta'$-(ET)$_2$ICl$_2$ shows a semiconducting conductivity below the room temperature, and indicates a magnetic transition at $T_N=22$K. As the pressure is applied, the resistivity decreases gradually, and the metallic behavior ($d\rho/dT > 0$) is observed above $T_{\text{MIT}}$ under 6.5GPa. Note that $T_{\text{MIT}}$, which is a crossover temperature, is expected to be higher than $T_N$. At 8.2GPa, insulating phase (or $T_{\text{MIT}}$) disappears and the SC transition occurs at $T_c = 14.2$K at the same time.

According to the band calculation, the Fermi surface (FS) of $\beta'$-(ET)$_2$X (X=ICl$_2$, BrCl, AuCl$_2$) compound is quasi one-dimensional (Q1D) [8,9]. It is contrastive that the FS of $\beta$-(ET)$_2$X is almost round, which shows the superconducting transition at $T_c = 2.7$K for X=IBr$_2$, at $T_c = 3.8$K for X=AuI$_2$ and at $T_c = 1.5$K (or 8K) for X=I$_3$. The difference of the crystal structure between $\beta$ and $\beta'$ compounds arises from the fact that the anion size in $\beta'$ compounds is too small to retain the $\beta$-type structure [8]; in fact, the bond lengths for I-Cl and Au-Cl are 2.52Å and 2.27Å respectively, which are smaller than the I-Br bond length in $\beta$-(ET)$_2$IBr$_2$, 2.58Å [8,9].

Until now, the deformation of the structure of $\beta'$-(ET)$_2$ICl$_2$ at $P = 8.2$GPa has not been determined experimentally. In the present study, however, we naturally assume that its structure (gradually) approaches to that of $\beta$-(ET)$_2$X as the cell volume decreases under hydrostatic high pressure, because the anion size becomes larger compared with the cell length. Note that the shape of the unit cells for $\beta$- and that for $\beta'$-structures are almost same.

In the present work, we study the origin of the superconductivity in $\beta'$-(ET)$_2$ICl$_2$ on the assumption that the crystal structure approaches to $\beta$-type under hydrostatic pressure. We use the FLEX approximation by noticing the fact that the SC phase appears by destroying the AF phase by pressure. Our theory can reproduce a reasonable value of $T_c$ in $\beta'$-(ET)$_2$ICl$_2$ under high pressure, as well as a low $T_c$ in $\beta$-(ET)$_2$X at ambient pressure.

The schematic structures of $\beta'$-(ET)$_2$X and $\beta$-(ET)$_2$X

FIG. 1. Microscopic structures for $\beta'$-(ET)$_2$X and for $\beta$-(ET)$_2$I$_3$. They are well approximated as the dimer Hubbard model ($t_0$, $t_1$, $t_2$, $U_{\text{eff}}$) at half filling. In the present simplified figure, $\beta'$-type structure is given by rotating each dimer in $\beta$-type structure slightly in a clockwise direction.

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are shown in Fig. 1. Each ellipse represents the ET molecule, and each highest occupied molecular orbital (HOMO) of the ET molecule possesses 1.5 electrons on average. The hopping parameters obtained by the band calculation are given in Table I: The hopping parameters for β-(ET)$_2$AuCl$_2$ and those for β-(ET)$_2$I$_2$ are similar. Whereas, they are very different from the parameters for β-(ET)$_2$AuCl$_2$ although their crystal structures differ slightly. This comes from the fact that the overlap integral between two ET molecules is very sensitive to the angle between them (φ): It takes the local maximum (positive) values for φ = 0°, 60°, and the local minimum (negative) values for φ = 30°, 90° [10].

As a good approximation, we take account of only the anti-bonding orbit of each pair of the ET molecules connected by t(p1), which is more than 2.5 times larger than other hopping parameters [11]. Then, the original systems is mapped onto the “dimer model” at half filling, which is anisotropic triangular lattice Hubbard model with four parameters (t$_0$, t$_1$, t$_2$, U$_{\text{eff}}$) as shown in Fig. 1. Note that the x-y coordinate in the present model does not correspond to that for the original systems. The corresponding hopping parameters for β-(ET)$_2$I$_2$ and for β-(ET)$_2$I$_3$ are given in Table II.

Table I: Hopping integrals for each systems. They are given by the well known empirical relation $t = -10S$ (eV), where $S$ is the overlap integral given by the band calculation [8,9].

| x = 0 | β-(ET)$_2$I$_2$ | β-(ET)$_2$AuCl$_2$ | β-(ET)$_2$I$_3$ |
|-------|-----------------|-------------------|-----------------|
| $t(p1)$ | -0.272 (eV) | -0.264 (eV) | -0.245 (eV) |
| $t(p2)$ | 0.016 | 0.020 | -0.084 |
| $t(q1)$ | -0.100 | -0.100 | -0.127 |
| $t(q2)$ | -0.066 | -0.065 | -0.068 |
| $t(c)$ | -0.016 | -0.023 | 0.050 |

Table II: Hopping integrals in the dimer model for $x = 0$ and $x = 1$, respectively.

Non-linear terms with respect to x are dropped in eq.(1). The $x$ dependence of the FS for $U_{\text{eff}} = 0$ is shown in Fig. 2. We see that the FS becomes round around $x \approx 0.7$.

FIG. 2. $x$ dependence of $t_0$, $t_0$, $t_0$, as well as the corresponding FS's. $x$ is expected to approach from $x = 0$ [β-type] to $x = 1$ [β-type] as the applied pressure increases.

Here, we calculate the self-energy for the dimer model for $U_{\text{eff}} = 0.4 \sim 0.5\text{eV}$ by using the FLEX approximation [5]. Hereafter, we write $U_{\text{eff}}$ as $U$ for simplicity. To obtain the magnetic transition temperature $T_N$, we calculate the Stoner factor without vertex corrections (VC’s), $\alpha_S$, given by

$$\alpha_S = \max_k \left\{U \cdot \chi^0(k, \omega = 0)\right\}, \quad (2)$$

where $\chi^0(q, \omega_l)$ is given by

$$\chi^0(q, \omega_l) = -T \sum_{k,n} G(q + k, \omega_l + \epsilon_n) G(k, \epsilon_n), \quad (3)$$

where $G(q + k, \omega_l + \epsilon_n)$ is the Green function given by the FLEX approximation, and $\omega_l (\epsilon_n)$ is the Matsubara frequency for boson (fermion). $T_N$ is determined by the Stoner criterion: $\alpha_S = 1$. In the FLEX approximation, however, $\alpha_S$ does not exceed 1 at finite temperatures in two dimensional systems, which is consistent with the Mermin and Wagner theorem. So we determine $T_N$ by the condition $\alpha_S = \alpha_N$, where we set $\alpha_N$ as $(1 - \alpha_N)^{-1} \sim O(100)$. The AF state will occur through the weak coupling between layers, $J_\perp$ [13].

Next, we solve the linearized Eliashberg equation to obtain the SC transition temperature $T_c$. For a singlet-pairing case $|\phi(-k, \epsilon_n) = +\phi(k, \epsilon_n)|$, it is given by [12].
\[ \lambda \cdot \phi(\mathbf{k}, \epsilon_n) = -T \sum_{\mathbf{q}, \epsilon_m} V(\mathbf{k} - \mathbf{q}, \epsilon_n - \epsilon_m) \]
\[ \times G(\mathbf{q}, \epsilon_m) G(-\mathbf{q}, -\epsilon_m) \cdot \phi(\mathbf{q}, \epsilon_m), \]
where \( V(\mathbf{k}, \omega_n) = \frac{3}{2} \frac{U^2}{1 - U^2} \) for \( \lambda = 1 \). In the FLEX approximation, a finite \( T_c \) is obtained even in two dimensional systems irrespective of the Hohenberg theorem. However, this approximation gives reasonable \( T_c \)'s for \( \kappa-(ET) \) organic compounds and high-\( T_c \) cuprates [2–4,12]. Note that we could not find parameters where the triplet pairing is dominant in the present model.

The obtained phase diagram is given in Fig. 3. 64×64 \( k \)-points and 512 Matsubara frequencies are used. The maximum \( T_c \) under the condition of \( T_c > T_N \) is about 16K (18K) at \( x = 0.8 \) (\( x = 0.7 \)) for \( U = 0.5eV \) (\( U = 0.4eV \)). \( T_c \) decreases as \( x \) increases, and \( T_c \sim 6K \) at \( x = 1 \) for \( U = 0.5eV \), which is consistent with the observed \( T_c \) in several \( \beta-(ET)_2 \) \( X \) compounds. The present study also explains the low \( T_c \) in \( \beta-(ET)_2 \) \( X \) at ambient pressure, which corresponds to \( x = 1 \) in Fig. 3. On the other hand, we could not find the SC phase in the metallic region for \( x < 0 \). We comment that \( T_c \sim 4K \) is obtained at \( x = 0 \) for \( U = 0.4eV \) as shown in Fig. 3. However, it should be covered with the AF phase because of \( T_N \gg T_c \).

Actually, the Stoner factor at 4K is extremely close to 1; \( \alpha_S \approx 0.999 \).

On the other hand, the Néel temperature for \( U = 0.5eV \) at \( x = 0 \) is 28K (20K) under the condition of \( \alpha_N = 0.99 \) (\( \alpha_N = 0.995 \)), which is also consistent with \( T_N = 22K \) in \( \beta^\prime-(ET)_2 \) \( ICN \) at ambient pressure. The obtained magnetic order is commensurate \( \{Q = (\pi, \pi)\} \) for \( x \leq 0.7 \) at \( U = 0.5eV \), and it becomes incommensurate for \( x \geq 0.8 \) at lower temperatures. The obtained \( T_N \) increases as \( x \) departs from 0, which is interpreted as a natural consequence of the dimensional increase. It is highly demanded to experiment on the pressure dependence of \( T_N \). We note that the crossover temperature \( T_{MIT} \) determined by the condition \( df/dT = 0 \) will be higher than \( T_N \) because \( T_{MIT} \) reflects the Mott transition, which is beyond the scope of the FLEX approximation.

Figure 4 shows the solution of eq.(4) at \((k_x, k_y)\) on the Fermi surface, where \( \theta_k = \tan^{-1}(k_x/k_y) \). Thus, the obtained SC order parameter is \( \Delta_{x-y^2} \)-wave like, as in the high-\( T_c \) cuprates and the \( \kappa-(ET) \) compounds. Note that the present \( x-y \) coordinate is different from that of the original crystal; see Fig. 1.

Finally, we study the resistivity \( \rho \) and the Hall coefficients \( R_{HI} \). Considering that the present model lacks the four-fold rotational symmetry, we define \( \rho \) and \( R_{HI} \) as \( \rho = \sqrt{2(\sigma_{xx}^2 + \sigma_{yy}^2)} \) and \( R_{HI} = (\sigma_{xy}/B_z) \cdot \rho^2 \) respectively: They are independent of the choice of the \( x-y \) coordinate. We calculate them by including the VC's for the current to maintain the conservation laws [14]. The role of the VC for the current, which is totally dropped in the relaxation time approximation, is very important in strongly correlated systems. For example, the anomalous behaviors of \( R_{HI} \) in high-\( T_c \) cuprates and in \( \kappa-(ET)_2 \) \( X \) compounds are reproduced only when the VC for the current is taken into account adequately [15–17].

![FIG. 3. Obtained phase diagram by the FLEX approximation.](image_url)

![FIG. 4. Obtained FS as well as \( \phi(\theta_k, i\pi T) \) on the FS \((U = 0.5eV, x = 0.8, T = 15K)\).](image_url)
In more detail, however, it might be better to analyze the original tight-binding model in Fig.1, instead of the dimer model, because a transport coefficient is in general sensitive to the shape of the FS.

Here, we discuss the validity of the pressure induced dimensional crossover in $\beta'-(ET)_2ICl_2$. According to Taniguchi, the resistivity along the less-conductive direction (i.e., $c$-axis direction) decreases very rapidly as the pressure increases, which suggests the system becomes 2D-like [18]. In fact, the Q1D nature in $\beta'$-compound is ascribed to the accidental cancellation of $t_1$ in the dimer model although $|t(q_2)|$ and $|t(c)|$ are not so small; see Fig. 1 and Table I. It suggests that the dimensional crossover easily occurs. Moreover, $\beta'-(ET)_2AuCl_2$ remains semiconducting even at 9GPa [18], which means that the $\beta'$-type structure in $\beta'-(ET)_2AuCl_2$ is more robust against the pressure. It is natural because Au-Cl bond length is around (2.5 Å) under the condition that $T \sim 5K$ under the condition that $T_c > T_N$ by the slight modification of the original parameters for $\beta'-(ET)_2ICl_2$, as far as the FS is Q1D. We note that $T_c$ in a Q1D system, TMTSF, is very low ($\approx 1K$), which is recognized by the FLEX approximation [19].

In summary, we studied the origin of the superconductivity in $\beta'-(ET)_2ICl_2$ based on the FLEX approximation, by assuming that the structure approaches to $\beta$-type under the hydrostatic pressure. Our theory predicts that the $d$-wave superconductivity occurs in $\beta'-(ET)_2ICl_2$ as a result of the 1D-2D dimensional crossover owing to the crystal structure change under high pressure. Moreover, both $\rho$ and $R_H$ were studied in terms of the conserving approximation. Experimental studies on the structure of $\beta'-(ET)_2ICl_2$ as well as the band calculations under the condition of high pressure are highly demanded. In addition, the superconductivity in $\beta'-(ET)_2X$ compound is also understood in the same framework.

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FIG. 5. Obtained temperature dependences of $\rho$ and $R_H$ with including the VC’s for the current.

In the present analysis, we might have underestimated the enhancement of the ratio $W_{band}/U$ ($W_{band}$ being the band width) due to the applied pressure. Actually, the hydrostatic pressure not only distorts the structure ($\beta' \rightarrow \beta$), but also shortens the cell volume, which enhances each overlap integral. Then, the enhancement of $t(p1)$, which is proportional to $U_{eff}$, is weaker than other hopping parameters [11].

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