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Origin of superconductivity in β'-(BEDT-TTF)$_2$ICl$_2$ under high pressure and in β-(BEDT-TTF)$_2X$ at atmospheric pressure

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We present a theoretical study on the superconductivity in β'-(BEDT-TTF)$_2$ICl$_2$ at $T_c = 14.2$ K under high hydrostatic pressure, which was recently found by Taniguchi *et al.* and is the highest recorded for organic superconductors. Its electronic structure is well expressed by the anisotropic triangular lattice Hubbard model at half filling. In the present paper, we study this effective model by using the fluctuation-exchange approximation. In the obtained phase diagram, the superconductivity with $d_{x^2-y^2}$ like symmetry is realized next to the antiferromagnetic insulating phase, as a result of the one-dimensional–two-dimensional crossover driven by the pressure. The obtained maximum T_c is 16–18 K. In addition, the superconductivity in β-(BEDT-TTF)$_2X$ 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, κ-(ET)$_2X$ compounds attract much attention because it shows a high superconducting (SC) transition temperature ($T_c \approx 12$ K) among organic superconductors.[1] Recently, the temperature-pressure phase diagram of κ-(ET)$_2X$ 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 β'-(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, β'-(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_{MIT} under 6.5 GPa. Note that T_{MIT}, which is a crossover temperature, is expected to be higher than T_N. At 8.2 GPa, insulating phase (or T_{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 β'-(ET)$_2X$ ($X=$ICl$_2$, BrICl, AuCl$_2$) compound is quasi-one-dimensional (Q1D).[8,9] It is contrastive that the FS of β-(ET)$_2X$ 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 8 K) for $X=$I$_3$. The difference of the crystal structure between β and β' compounds arises from the fact that the anion size in β' compounds is too small to retain the β-type structure;[8] in fact, the bond lengths for I-Cl and Au-Cl are 2.52 Å and 2.27 Å, respectively, which are smaller than the I-Br bond length in β-(ET)$_2$IBr$_2$, 2.58 Å.[8,9]

Until now, the deformation of the structure of β'-(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 β-(ET)$_2X$ 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 β structures and that for β' structures are almost same.

In the present paper, we study the origin of the superconductivity in β'-(ET)$_2$ICl$_2$ on the assumption that the crystal structure approaches to β 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 β'-(ET)$_2$ICl$_2$ under high pressure, as well as a low T_c in β-(ET)$_2X$ at ambient pressure.

The schematic structures of β'-(ET)$_2X$ and β-(ET)$_2X$ are shown in Fig. 1. Each ellipse represents the ET molecule and each highest occupied molecular orbital of the ET molecule possesses 1.5 electrons on an 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)$_2$ICl$_2$ are similar. Whereas, they are very

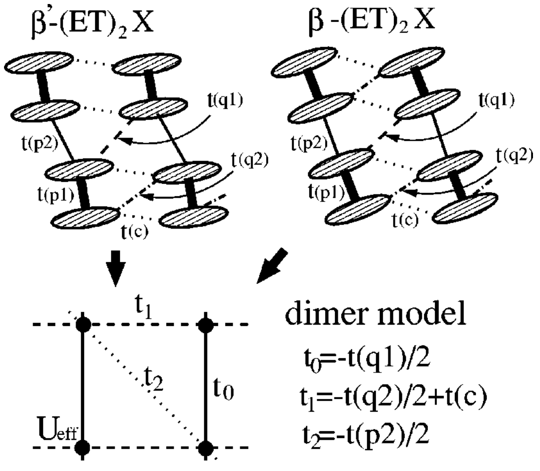

FIG. 1. Microscopic structures for β'-(ET)$_2$ICl$_2$ and for β-(ET)$_2$I$_3$. They are well approximated as the dimer Hubbard model (t_0, t_1, t_2, $U_{\rm eff}$) at half filling. In the present simplified figure, β'-type structure is given by rotating each dimer in β-type structure slightly in a clockwise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

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 calculations (Refs. 8 and 9).

	β'-(ET)$_2$ICl$_2$	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.

	$x=0$ [β'-(ET)$_2$ICl$_2$]	$x=1$ [β-(ET)$_2$I$_3$]
t_0	0.050 (eV)	0.064 (eV)
t_1	0.017	0.084
t_2	-0.008	0.042

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 $\phi=0°$, 60° and the local minimum (negative) values for $\phi=30°$, 90°.[10]

As a good approximation, we take account of only the antibonding 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 the anisotropic triangular lattice Hubbard model with four parameters (t_0, t_1, t_2, $U_{\rm eff}$) 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)$_2$ICl$_2$ and for β-(ET)$_2$I$_3$ are given in Table II. Although the original on-site Coulomb interaction on a ET molecule is $\sim$1 eV, the effective Coulomb interaction on a dimer, $U_{\rm eff}$, is limited to $\sim 2|t(p1)| \sim 0.5$ eV.[11]

Hereafter, we study the dimer model given in Fig. 1 at half filling. To analyze the pressure effect on the electronic states, we put the hopping parameters of the dimer model (t_0, t_1, t_2) as follows:

$$\begin{aligned} t_0 &= 0.05+0.014x \ \ (\text{eV}), \\ t_1 &= 0.017+0.067x \ \ (\text{eV}), \qquad (1) \\ t_2 &= -0.008+0.05x \ \ (\text{eV}), \end{aligned}$$

where $0 \leqslant x \leqslant 1$ is a free parameter. $x=0$ ($x=1$) corresponds to β'-(ET)$_2$ICl$_2$ [β-(ET)$_2$I$_3$]; see Table II. Nonlinear terms with respect to x are dropped in Eq. (1). The x dependence of the FS for $U_{\rm eff}=0$ is shown in Fig. 2. We see that the FS becomes round around $x \approx 0.7$.

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

$$\alpha_{\rm S} = \max_{\mathbf{k}} \{ U \chi^0(\mathbf{k}, \omega=0) \}, \tag{2}$$

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

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

where $G(\mathbf{q}+\mathbf{k}, \omega_l+\epsilon_n)$ is the Green function given by the FLEX approximation and ω_l (ϵ_n) is the Matsubara frequency for boson (fermion). $T_{\rm N}$ is determined by the Stoner criterion; $\alpha_{\rm S}=1$. In the FLEX approximation, however, $\alpha_{\rm S}$ does not exceed 1 at finite temperatures in the two-dimensional (2D) systems, which is consistent with the Mermin and Wagner theorem. So we determine $T_{\rm N}$ by the condition $\alpha_{\rm S}=\alpha_{\rm N}$, where we set $\alpha_{\rm N}$ as $(1-\alpha_{\rm N})^{-1} \sim O(100)$. The AF state will occur through the weak magnetic coupling between layers, $J_\perp$.[12]

Next, we solve the linearized Eliashberg equation to obtain the SC transition temperature $T_{\rm c}$. For a singlet-pairing case [$\phi(-\mathbf{k}, \epsilon_n) = +\phi(\mathbf{k}, \epsilon_n)$], it is given by[13]

$$\begin{aligned} \lambda \phi(\mathbf{k}, \epsilon_n) = -T \sum_{\mathbf{q}, m} & V(\mathbf{k}-\mathbf{q}, \epsilon_n - \epsilon_m) \times G(\mathbf{q}, \epsilon_m) \\ & \times G(-\mathbf{q}, -\epsilon_m) \phi(\mathbf{q}, \epsilon_m), \end{aligned} \tag{4}$$

where

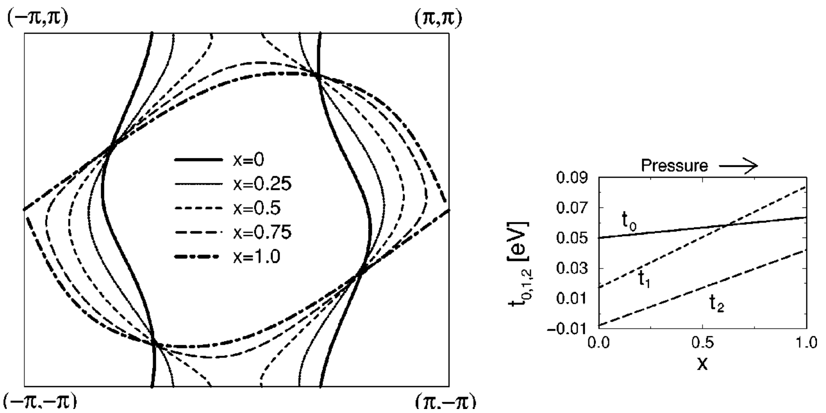

FIG. 2. x dependence of t_0, t_1, t_2, as well as the corresponding FS's. x is expected to approach from $x=0$ (β' type) to $x=1$ (β type) as the applied pressure increases.

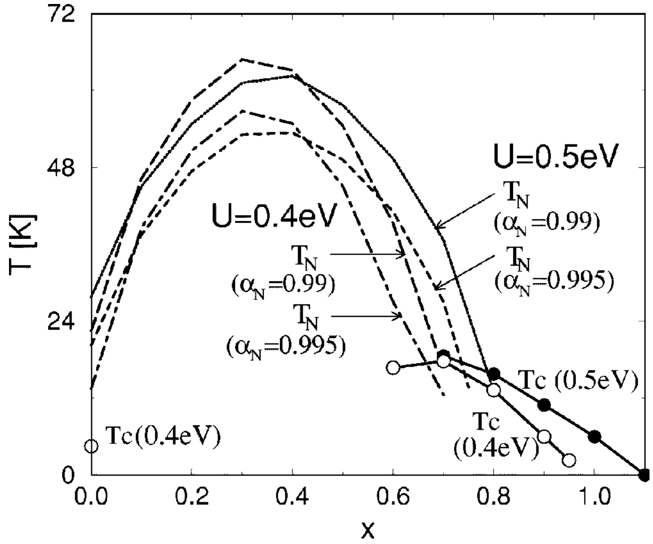

FIG. 3. Obtained phase diagram by the FLEX approximation.

$$V(\mathbf{k},\omega_l)=\frac{3}{2}U^2\frac{\chi^0(\mathbf{k},\omega_l)}{1-U\chi^0(\mathbf{k},\omega_l)}-\frac{1}{2}U^2\frac{\chi^0(\mathbf{k},\omega_l)}{1+U\chi^0(\mathbf{k},\omega_l)}+U.$$

T_c is given by the condition $\lambda=1$. In the FLEX approximation, a finite T_c is obtained even in the two-dimensional systems irrespective of the Hohenberg theorem. However, this approximation gives reasonable T_c's for κ-(ET) organic compounds and high-T_c cuprates.[2–4,13] 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 16 K (18 K) at $x=0.8$ ($x=0.7$) for $U=0.5$ eV ($U=0.4$ eV). T_c decreases as x increases, and $T_c\sim6$ K at $x=1$ for $U=0.5$ eV, which is consistent with the observed T_c in several β-(ET)$_2X$ compounds. The present study also explains the low T_c in β-(ET)$_2X$ 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 $T_c\sim4$ K is obtained at $x=0$ for $U=0.4$ eV 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; $\alpha_S\approx0.999$.

On the other hand, the Néel temperature for $U=0.5$ eV at $x=0$ is 28 K (20 K) under the condition of $\alpha_N=0.99$ ($\alpha_N=0.995$), which is also consistent with $T_N=22$ K in β'-(ET)$_2$ICl$_2$ at ambient pressure. The obtained magnetic order is commensurate [$\mathbf{Q}=(\pi,\pi)$] for $x\leqslant0.7$ at $U=0.5$ eV, and it becomes incommensurate for $x\geqslant0.8$ at lower temperatures. The obtained T_N increases as x departs from zero, 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 $T_{\rm MIT}$ determined by the condition $d\rho/dT=0$ will be higher than T_N because $T_{\rm MIT}$ 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 $\theta_{\mathbf{k}}=\tan^{-1}(k_x/k_y)$. Thus, the obtained SC order parameter is $d_{x^2-y^2}$ wavelike, as in the high-T_c cuprates and the κ-(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 ρ and the Hall coefficients R_H. Considering that the present model lacks the fourfold rotational symmetry, we define ρ and R_H as $\rho=\sqrt{2/(\sigma_{xx}^2+\sigma_{yy}^2)}$ and $R_H=(\sigma_{xy}/B_z)\rho^2$, 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_H in high-T_c cuprates and in κ-(ET)$_2X$ compounds are reproduced only when the VC for the current is taken into account adequately.[15–17]

Figure 5 shows the obtained results for $U=0.5$ eV. Experimentally, ρ under 8.2 GPa continues to increase up to 300 K approximately proportional to T, which is similar to ρ in high-T_c cuprates.[18] Such a "bad metal" behavior of ρ is well reproduced in the present study. In Fig. 5, R_H for $x=0.8$ increases below $\sim$50 K, which is caused by the VC's for the current due to the AF fluctuations. However, the obtained enhancement of R_H is rather smaller than that for high-T_c cuprates or β-(ET)$_2X$ compounds. As for $x=0.9$ and 1.0, the temperature dependence of R_H is much moderate. It is highly demanded to experiment on R_H in β'-(ET)$_2$ICl$_2$. We stress that the observed resistivity under high pressure is considered to be intrinsic free from the lattice contraction effect, which is considerably large in usual organic metals at ambient pressure.[18]

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 idea of the pressure induced dimensional crossover in β'-(ET)$_2$ICl$_2$. 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]

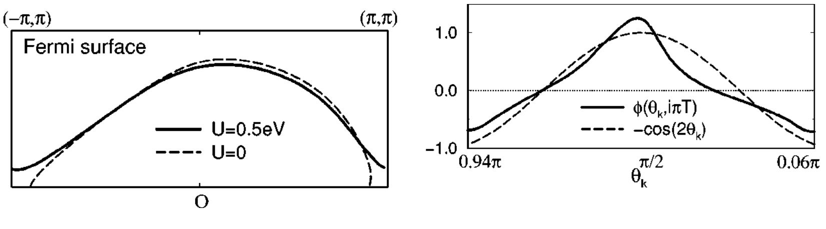

FIG. 4. Obtained FS as well as $\phi(\theta_{\mathbf{k}},i\pi T)$ on the FS ($U=0.5$ eV, $x=0.8$, $T=15$ K).

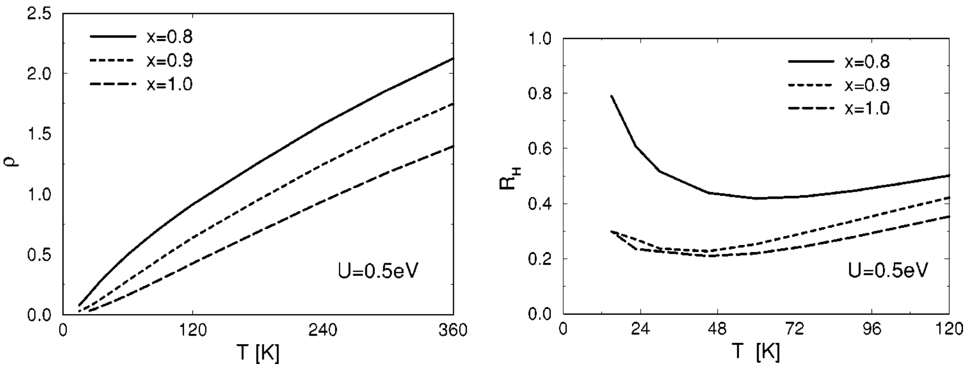

FIG. 5. Obtained temperature dependences of ρ and R_H with including the VC's for the current.

In fact, the Q1D nature in β' compound is ascribed to the accidental cancellation of t_1 in the dimer model although $|t(q2)|$ and $|t(c)|$ are not so small; see Fig. 1 and Table I. It suggests that the dimensional crossover easily occurs. Moreover, β'-(ET)$_2$AuCl$_2$ remains semiconducting even at 9 GPa,[18] which means that the β'-type structure in β'-(ET)$_2$AuCl$_2$ is more robust against the pressure. It is natural because Au-Cl bond length is about 12% smaller than the I-Cl bond length.

As a result, the obtained phase diagram, Fig. 3, as well as the concept of the SC driven by the dimensional crossover, will make sense and be reasonable, although the variable x in Eq. (1) cannot be interpreted as the pressure simply. The large density of states at the Fermi level for $x \approx 0.7$ due to the van Hove singularity around $(\pm\pi,0)$ (see Fig. 2) accounts for the high T_c in β'-(ET)$_2$ICl$_2$. Actually, we could not obtain higher T_c ($\gtrsim 5$ K) under the condition that $T_c > T_N$ by the slight modification of the original parameters for β'-(ET)$_2$ICl$_2$, as far as the FS is Q1D. We note that T_c in a Q1D system, TMTSF, is very low (≈ 1 K), which is recognized by the FLEX approximation.[19]

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

In summary, we studied the origin of the superconductivity in β'-(ET)$_2$ICl$_2$ based on the FLEX approximation, by assuming that the structure approaches to β-type under the hydrostatic pressure. Our theory predicts that the *d*-wave superconductivity occurs in β'-(ET)$_2$ICl$_2$ as a result of the 1D-2D dimensional crossover owing to the crystal structure change under high pressure. Moreover, both ρ and R_H were studied in terms of the conserving approximation. Experimental studies on the structure of β'-(ET)$_2$ICl$_2$ as well as the band calculations under the condition of high pressure are highly demanded. In addition, the superconductivity in β-(ET)$_2X$ compound is also understood in the same framework.

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