Exotic properties of zerogap state in
α-(BEDT-TTF)$_2$I$_3$

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Abstract. We investigate effects of a non-magnetic impurity on zerogap state of molecular conductor α-(BEDT-TTF)$_2$I$_3$ and predict theoretically incommensurate oscillations of charge density. These oscillations reflect unique properties of the massless Dirac fermions, which are characterized by the incommensurate momenta $\pm k_0$ of the contact points and the singular momentum distributions of the charge density. We examine an effective Hamiltonian in the presence of stripe charge ordering, neighboring the zerogap state. The energy bands are divided into two parts, having one-dimensional fermions and two-dimensional fermions. The one-dimensional-like bands exhibit a unique anisotropic dispersion which is linear along b-axis (parallel to the stripe) and parabolic along the a-axis (the stacking axis). Thus we expect anomalous magnetoresistance in stripe charge ordering state, since such an anisotropic dispersion indicates the unconventional Landau quantization.

1. Introduction

Two-dimensional molecular conductor α-(BEDT-TTF)$_2$I$_3$ has attracted many interests by a rich phase diagram on uniaxial pressure and temperature, which consists of insulating state with stripe charge ordering, superconducting state in the presence of charge ordering, and narrow gap state. The stripe charge ordering state was suggested by the mean-field theories[1, 2, 3] to explain insulating phase below 135K at ambient pressure, and was confirmed by NMR[4]. The superconducting state, which was found under uniaxial pressure along stacking axis (a-axis)[5], was investigated by using the extended Hubbard model.[6] The pairing mechanism mediated by the spin fluctuation was maintained and interpreted in terms of the self-doped pseudo-one-dimensional Heisenberg chain.

The narrow gap state was suggested by Kajita[7] to explain anomalous increase of Hall coefficient at high pressures. The existence of massless Dirac fermion was discovered theoretically[8] by using the transfer energies[9] which were calculated from the experimental data under uniaxial strain. It was revealed that such a narrow gap state is the zerogap state (ZGS), where the chemical potential coincides with the contact point. Existence of the ZGS was also verified by the first principle calculation.[10, 11] Motion of the massless Dirac fermion obeys the tilted Weyl equation.[12] The Hall conductivity, the conductivity and the orbital susceptibility were investigated theoretically by using the equation.[13] These results and temperature dependence of the chemical potential in α-(BEDT-TTF)$_2$I$_3$ elucidated a long...
standing puzzle on transport phenomena, i.e. strong increase of Hall coefficient and weak temperature dependence of resistivity with decreasing temperature. Moreover, the sharp but continuous reversal of the sign of the Hall coefficient was observed by N. Tajima (2007).[14] Such a phenomena is possible at low temperatures if the extremely small amount of electron doping exists[13]. The orbital diamagnetism is expected to have a peak at the temperatures where the Hall coefficient changes the sign. All these strong temperature dependences of both the Hall coefficient and the orbital diamagnetism are due to the inter-band effects of magnetic field[15, 16].

The ZGS in α-(BEDT-TTF)2I3 exhibits several unique features distinguished from those of other materials with Dirac fermions. The contact points are located at incommensurate momenta $\pm k_0$ which move continuously in the Brillouin zone with varying pressure.[8] The charge densities, $n_\alpha(k)$ on each organic molecule BEDT-TTF sites ($\alpha =$B, C among four sites A, A', B, C in the a cell), exhibit singular momentum distribution around the contact points.[12] Those singularities come from both the angle-dependent wave functions of the massless Dirac fermion and the inequivalent sites of B and C. Charge disproportionation which comes from inequivalency of the BEDT-TTF sites has been observed in the ZGS.[17, 18] We note the charge disproportionation is different from the charge ordering which originates from electron correlation. Further, the pattern of the charge disproportionation has been investigated using the mean-field approximation for the extended Hubbard model, and the consistency between the charge disproportionation obtained from the model and that observed by NMR spectrum has been clarified[19]. Those unique properties must affect electronic states near an impurity violating translational symmetry. In a conventional metal, electron density near an impurity exhibits spatial oscillation reflecting Fermi wave number, i.e. the Friedel oscillation. Correlation function of electron-hole excitation (exciton), however, remains finite even at zero temperature, although there are only two Fermi points (the contact points), and density of states (DOS) vanish at the crossing point. In the ZGS in graphene, impurity effects have been investigated intensively indicating commensurate oscillation reflecting wave number between two Dirac points $K$ and $K'$.[20, 21, 22, 23, 24, 25, 26]

In the present paper, we propose a way to observe these unique properties of the ZGS in α-(BEDT-TTF)2I3 by investigating the electronic states in the vicinity of a non-magnetic impurity. Further, an effective Hamiltonian for the stripe charge ordering state neighboring the zero-gap state is investigated to understand how the energy bands in the stripe charge ordering state have an aspect of Dirac fermion with finite mass.

2. Electronic states in ZGS

In this section, before studying the impurity effects, we summarize the unique properties of the ZGS in the α-(BEDT-TTF)2I3. A model describing the two-dimensional electronic system in the α-(BEDT-TTF)2I3 is shown in Fig. 1.[10, 28] The unit cell consists of four BEDT-TTF molecules with sites A, A’, B and C. The sites A, B and C are inequivalent, although there is the inversion symmetry with equivalence of A and A’. There are six electrons in the four molecules, i.e., the 3/4-filled band. The electronic states are described by the extended Hubbard model with the on-site repulsive interaction $U$ and the anisotropic nearest-neighbor repulsive interaction $V_{\alpha\beta}$ based on the HOMO orbitals of these sites.[1, 2]

$$
H = \sum_{(i\alpha,j\beta),\sigma} (t_{i\alpha,j\beta} a_{i\alpha\sigma}^\dagger a_{j\beta\sigma} + \text{h.c.}) + \sum_{i\alpha} U a_{i\alpha\uparrow}^\dagger a_{i\alpha\downarrow} + \sum_{(i\alpha,j\beta),\sigma,\sigma'} V_{\alpha\beta} a_{i\alpha\sigma}^\dagger a_{j\beta\sigma'}^\dagger a_{j\beta\sigma} a_{i\alpha\sigma},
$$

(1)
Figure 1. The model describing the electronic system of $\alpha$-(BEDT-TTF)$_2$I$_3$.[10] The unit cell consists of four BEDT-TTF molecules A, A’, B and C with ten transfer energies. The nearest neighbor repulsive interactions are given by $V_a$ and $V_b$. The $a$- and $b$-axis in the conventional notation correspond to the $y$- and $x$-axis in the present paper.

where $i,j$ denote site indices of the unit cell, and $\alpha, \beta (= A, A’, Band C)$ are indices of BEDT-TTF sites in the unit cell. Hereafter, we take eV as the unit of the energy. In the first term, $a^\dagger_{i\alpha\sigma}$ denotes a creation operator with spin $\sigma (= \uparrow, \downarrow)$ and $t_{i\alpha\beta}$ is the transfer energy between the $(i, \alpha)$ site and the $(j, \beta)$ site.

In this paper we use the transfer energies given by fitting to reproduce the band structure obtained by the first principle calculation, where $t_{i\alpha j\beta} = a1 = -0.0267$, $a2 = -0.0511$, $a3 = 0.0323$, $b1 = 0.1241$, $b2 = 0.1296$, $b3 = 0.0513$, $b4 = 0.0152$, $a1’ = 0.0119$, $a3’ = 0.0046$, and $a4’ = 0.0060$,[10] because the result given by Kino is applicable to explain the fact that the Hall coefficient is always positive at high temperatures.[13, 14]

The mean-field Hamiltonian is given by

$$H_{MF} = \sum_{k\alpha\beta\sigma} \tilde{\epsilon}_{\alpha\beta\sigma}(k) d_{k\alpha\sigma}^\dagger d_{k\beta\sigma}$$

$$- \sum_{\alpha} U_{\alpha} \langle n_{\alpha\uparrow} \rangle \langle n_{\alpha\downarrow} \rangle - \sum_{(\alpha, \beta)\sigma, \sigma’} V_{\alpha\beta} \langle n_{\alpha\sigma} \rangle \langle n_{\beta\sigma’} \rangle,$$

$$\tilde{\epsilon}_{\alpha\beta\sigma}(k) = \delta_{\alpha\beta} [U_{\alpha} \langle n_{\alpha\bar{\sigma}} \rangle + \sum_{\beta’\sigma’} V_{\alpha\beta’} \langle n_{\beta’\sigma’} \rangle] + \epsilon_{\alpha\beta}(k),$$

$$\epsilon_{\alpha\beta}(k) = \sum_{\delta} t_{\alpha\beta} e^{i\delta}$$

where $n_{\alpha\sigma} = a_{i\alpha\sigma}^\dagger a_{i\alpha\sigma}$ (i.e. independent of the site $i$), $\bar{\sigma} = -\sigma$, and $\delta$ denotes the vector representing the nearest neighbor of the unit cell. The mean-field Hamiltonian is diagonalized by

$$\sum_{\beta=1}^{4} \tilde{\epsilon}_{\alpha\beta\sigma}(k) d_{\beta\gamma\sigma}(k) = \xi_{\gamma\sigma}(k) d_{\alpha\gamma\sigma}(k),$$
The energy dispersions of the conduction band \( \xi_1 \) and the valence band \( \xi_2 < \xi_1 \), where the vertical axis represents the band energy in unit of eV, on the \( k_x-k_y \) plane in unit of radian. (b) The energy dispersions in the vicinity of the contact point \( k_0 = (1.90, 1.42) \).

where \( \xi_{\gamma\sigma} \) are eigenvalues with a descending order, \( \xi_1\sigma(k) > \xi_2\sigma(k) > \xi_3\sigma(k) > \xi_4\sigma(k) \), and \( d_{\alpha\gamma\sigma}(k) \ (\gamma = 1, 2, 3, 4) \) are the corresponding eigenvectors. In terms of eq. (5), the number of electrons on \( \alpha \)-site with spin \( \sigma \), \( \langle n_{\alpha\sigma} \rangle \), is expressed as

\[
\langle n_{\alpha\sigma} \rangle = \frac{1}{4} \sum_{\gamma=1}^{4} d_{\alpha\gamma\sigma}^*(k) \ d_{\alpha\gamma\sigma}(k) \ \frac{1}{\exp \left[ \frac{(\xi_{\gamma\sigma}(k) - \mu)}{T} \right] + 1},
\]

where \( T \) is the temperature (\( k_B = 1 \)). Equation (6) is the self-consistency equation for \( \langle n_{\alpha\sigma} \rangle \).

The quantity \( \mu \) is the chemical potential determined from a condition

\[
\frac{3}{2} = \frac{1}{4} \sum_{\alpha\sigma} \langle n_{\alpha\sigma} \rangle.
\]

which gives the electron with 3/4 filling per each molecule.

Figure 2 shows the energy dispersions of the conduction band \( \xi_1 \) and the valence band \( \xi_2 \) with \( U = 0.4, V_a = 0.17, \) and \( V_b = 0.05 \), where the unit of energy is electron volt (eV), and we take the Planck constant \( \hbar \) and the lattice constant \( a \) as \( \hbar = a = 1 \). The entire structure is similar to the result of the previous study[8] using the transfer energies given by the extended Hückel method on the basis of the data of the X-ray experiment.[9] The chemical potential coincides with the contact point at \( T = 0 \). There are two contact points \( \pm k_0 \) because of the inversion symmetry. The linear dispersion exists within about 100meV around the contact point. Velocity in the vicinity of the contact points is extremely anisotropic because of tilting of the cone, i.e. the highest velocity is about ten times larger than the lowest velocity. The directions of the highest and the lowest velocities are opposite each other.

The parameters \( U = 0.4, V_a = 0.17, \) and \( V_b = 0.05 \) used in previous studies[6, 12] are also chosen in this paper, because the results of the mean-field theory coincide with the experimental
results of charge disproportionation, \(n_C > n_A = n_{A'} > n_B\), which have been observed in the zerogap states.[17, 18] The gap does not open in the presence of the charge disproportionation when we vary the parameters continuously with keeping the inversion symmetry, excepting the case that two contact points merge with each other.[12] The charge disproportionation is essentially due to the inequivalency of the BEDT-TTF sites in a unit cell, but both \(V_a\) and \(V_b\) are indispensable for reproducing the experimental results, although the transfer energies given by the first principle calculation[10] include effects of the energy levels of the HOMO orbitals, the Coulomb potential of the anions \(I_3^−\), and some part of the electron-electron correlations.

It is found that the density of states (DOS) also reflect the inequivalence of the BEDT-TTF sites A (A’), B and C. Figure 3 shows the DOS, \(\rho_\alpha(\omega)\), on each BEDT-TTF sites \(\alpha = A, A', B, C\) in a unit cell. These four components exhibit linear energy dependences in the vicinity of the contact point within about 100mev. However, the inclination of \(\rho_C(\omega)\) is much higher than that of \(\rho_B(\omega)\), and that of \(\rho_A(\omega)\) (= \(\rho_{A'}(\omega)\)) has an intermediate value. It indicates that the site C mainly contributes the massless Dirac fermions. We note that the order of magnitudes of the inclinations of \(\rho_\alpha(\omega)\) is generally independent of that of the electron numbers \(n_\alpha\), although these coincide with each other in the present case, because the electron numbers are given by integration on energy in energy bands below the chemical potential.

The momentum distributions of the charge density \(n_\alpha(k)\) also reflect the inequivalence of the BEDT-TTF sites A (A’), B and C, where

\[
n_\alpha(k) = \sum_\gamma d_{\alpha\gamma}^*(k)d_{\alpha\gamma}(k)\frac{1}{\exp(\xi_{\gamma}(k)/T) + 1}.
\] (8)

The momentum distributions of the charge density for a single-band metal, a band insulator, and the graphene are shown in Fig. 4. In a single-band metal, \(n(k)\) is finite inside the Fermi surface, and zero outside the Fermi surface. In a band insulator, \(n(k)\) is independent of \(k\). In the graphene, both components for sublattice A and B are equivalent and independent of \(k\).
It has been pointed out that $n_\alpha(k)$ have anomalous momentum dependences which are the functions of the angle around the contact points in the vicinity of the contact points. This singularity comes from the angle-dependent wave functions of the massless Dirac fermions on these inequivalent BEDT-TTF sites, $d_{\alpha\gamma\sigma}(k)$, although the inversion symmetry exists with the equivalence of A and A'. Figure 5 shows the momentum-dependence of $n_A(k)$, $n_B(k)$ and $n_C(k)$ in the vicinity of the contact points. The anti-symmetric components are found in $n_B(k)$ and $n_C(k)$. The tendency of the momentum-dependence in $n_B(k)$ is opposite to that of $n_C(k)$. On the other hand, $n_A(k)$ (or $n_{A'}(k)$) is almost independent of $k$. The total charge density $n(k) = \sum_{\alpha} n_\alpha(k)$ is independent of $k$ at $T = 0$. In the vicinity of another contact point $k = -k_0$, the momentum dependences of $n_\alpha(k)$ are opposite to those of Fig. 5 as functions of $k + k_0$. We emphasize that these singular momentum distributions of the charge density are remarkable features of the massless Dirac fermions of the molecular conductors in marked contrast to the case of graphene.

3. Impurity effects in ZGS

In order to propose a way to observe the unique properties of the massless Dirac fermions in the molecular conductors shown in the previous section, we investigate the electronic states in the vicinity of a non-magnetic charged impurity. In the $\alpha$-(BEDT-TTF)$_2$I$_3$, the possible charged impurity is assumed to be the lack of $I_3^-$ or the change of $I_3^-$ into different molecule. The locations of $I_3^-$ are shown in Fig. 6. There are two kinds of $I_3^-$, above the C site and between A and A' sites, where $I_3^-$ exist at the center of the space between the BEDT-TTF layers.

In this paper, we put a non-magnetic charged impurity between A and A' in the unitcell
Figure 5. The momentum-dependence of $n_A(k) (= n_A'(k))$ (a), $n_B(k)$ (b) and $n_C(k)$ (c) in the vicinity of the contact point $k = k_0$. Contour plot of $n_C(k)$ in the Brillouin zone (d), where red square corresponds to the region shown in (c).
Figure 6. The locations of the $I_3^-$ ions (green filled circles), which are projected on the two-dimensional BEDT-TTF plane. The dotted rectangular denotes the unit cell. [29, 28]

$i = 0$. Hamiltonian for the impurity potential is given by

$$H^1 = \sum_{i\alpha\sigma} v_{i\alpha\sigma} a_{i\alpha\sigma}^\dagger a_{i\alpha\sigma}$$

(9)

with $v_{i\alpha\sigma} = v_{0}\delta_{i,0}\delta_{\alpha,\Lambda}$ and $v_{0} = -1.58eV$ obtained by a point-charge approximation in the absence of screening effects. The electron numbers are given by

$$n_{i\alpha} = \frac{1}{N}\sum_{k'\kappa} T \sum_{\iota\varepsilon_n} G_{\alpha\alpha,\sigma}(k', k; i\varepsilon_n)e^{-i\varepsilon_n\tau} |_{\tau \to 0^+} e^{-i(k-k')r_i},$$

(10)

where $G_{\alpha\alpha,\sigma}(k', k; \tau) = -\langle T_{\tau}a_{i\alpha\sigma}(\tau)a_{k'\alpha\sigma}(0)\rangle$ is the Green’s function in the site-representation. By perturbation on $H_{imp}$ up to infinite order, the electron numbers are given by

$$n_{i\alpha} = n_{i\alpha}^{(0)} + T \sum_{i\varepsilon_n} v_{0} N^2 \sum_{k'k\kappa} G_{\alpha\beta,\sigma}^0(k', i\varepsilon_n)G_{\beta\alpha,\sigma}^0(k, i\varepsilon_n)e^{-i(k-k')r_i} \sum_{n=1}^{\infty} (I_{\beta}(i\varepsilon_n)^{n-1}) e^{-i\varepsilon_n} |_{\tau \to 0^+},$$

(11)

where $n_{i\alpha}^{(0)}$ is the electron number in the absence of the impurity potential, $G_{\alpha\beta,\sigma}^0(k', i\varepsilon_n)$ is the Green function in the absence of the impurity potential, and $I_{\beta}(i\varepsilon_n)$ is given by

$$I_{\beta}(i\varepsilon_n) = \frac{v_{0}}{N} \sum_{k\gamma} \frac{d_{\gamma\beta}^*(k)d_{\beta\gamma}(k)}{i\varepsilon_n - \xi_{\gamma}(k)}.$$  

(12)

The impurity potential induces a quasi-bound state with small but finite imaginary part in the vicinity of the contact point. Thus we define an integrated DOS in the vicinity of the contact point to detect the oscillation of the electron density,

$$\Delta\rho_{i\alpha} = -\frac{1}{\pi} \text{Im} \int_{-\omega_c}^{\omega_c} d\omega | \frac{v_{0}}{N^2} \sum_{k'k\kappa} G_{\alpha\beta,\sigma}^0(k', \omega + i\delta)G_{\beta\alpha,\sigma}^0(k, \omega + i\delta)e^{-i(k-k')r_i} \frac{1}{1 - I_{\beta}(\omega + i\delta)} |$$

(13)

with $\omega_c = 0.01eV$ which is a energy range of the linear dispersions. Contribution of fluctuation due to electron-hole excitation remains finite at $T = 0$, although the DOS at the contact point
Figure 7. Two-dimensional images of the integrated DOS for site C. Left figures ((a) and (c)) are described in the real space, where the impurity is located at the center of the figures. Right figures ((b) and (d)) are shown in the Fourier space. Upper figures ((a) and (b)) are due to the inter-valley scattering, and lower figures ((c) and (d)) are due to the intra-valley scattering.

is zero. The component of site C is the largest and that of site B is the smallest reflecting the proportion of the DOS of each sites shown in Fig 3.

Figure 7 shows two-dimensional images of the integrated modification of DOS for site C. Left figures ((a) and (c)) are of real space, where the impurity is located at the center of the figures. Right figures ((b) and (d)) are of Fourier space. Upper figures ((a) and (b)) are due to the inter-valley scattering which means the scattering the left Dirac cone to the right Dirac cone. Lower figures ((c) and (d)) are due to the intra-valley scattering.

Inter-valley scattering gives an incommensurate oscillation with wave number $2k_0$, although a commensurate oscillation exists in graphene. The contribution of intra-valley scattering is much smaller than that of the inter-valley scattering, but unique anisotropy due to angular dependence of the wave function which is related to Berry phase appears in Fourier space.

4. Electronic states in stripe charge ordering state

An effective Hamiltonian in the stripe charge ordering state neighboring the zerogap state is investigated in this section to show that the energy bands have an aspect of extremely anisotropic Dirac fermion with finite gap. We have the mean-field solution of the ZGS with the charge disproportionation with $n_A = n_{A'} 
eq n_B 
eq n_C$ at high pressures, and have the stripe charge ordering state with staggered magnetic moments at lower pressures than $P_a = 4$ kbar, by using
the transfer energies[9] calculated from the experimental data under uniaxial strain.[6] In the stripe charge ordering state, \( n_A \) does not equal \( n_{A'} \) breaking inversion symmetry. The component of Hamiltonian breaking inversion symmetry is given by

\[
H_{\sigma}^{\text{BIS}} = \begin{bmatrix}
U\delta n_{A\sigma} + V_C \sum_{A'\sigma} \delta n_{A'\sigma} & 0 & 0 & 0 \\
0 & U\delta n_{A'\sigma} + V_C \sum_{A\sigma} \delta n_{A\sigma} & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{bmatrix},
\]

(14)

where \( n_{A\sigma} = n_0 + \delta n_{A\sigma} \) and \( n_{A'\sigma} = n_0 + \delta n_{A'\sigma} \) with \( n_0 = \frac{1}{4} \sum_s (n_{4s} + n_{4s'}) \). This inversion-breaking term induces finite gap between the conduction and the valence bands. Here we note that spin-singlet have been observed at ambient pressure[30]. But we assume the singlet may melt under pressure, since the resistivity decreases and the superconductivity occurs as pressure increases.

By expanding the mean-field Hamiltonian by momentum up to second order based on the Luttinger-Kohn representation at the minimum point of the gap, we have a generalized effective Hamiltonian of a \( 2 \times 2 \) matrix on the bases of the conduction and valence bands.

\[
H_{\gamma,\gamma'}^{\text{Eff}} = \sum_{\alpha\beta} d_{\alpha\gamma}^* (k_s) d_{\beta\gamma'} (k_s) H_{\alpha\beta\gamma\gamma'} (k)
\]

(15)

\[
= \epsilon_\sigma \delta_\sigma + \frac{\Delta_s}{2} \sigma_z + \delta k_\mu v_{\mu\rho}^\sigma \sigma_\rho + \delta k_\nu \delta k_\nu' w_{\mu\nu\rho}^\sigma \sigma_\rho
\]

(16)

\[
= \begin{bmatrix}
\epsilon_\sigma + \frac{\Delta_s}{2} & 0 & 0 & 0 \\
0 & \epsilon_\sigma - \frac{\Delta_s}{2} & 0 & 0 \\
0 & 0 & \epsilon_\sigma + \frac{\Delta_s}{2} \\
0 & 0 & 0 & \epsilon_\sigma - \frac{\Delta_s}{2}
\end{bmatrix} + \delta k_\mu \delta k_\nu \begin{bmatrix}
v_{10s}^\mu + v_{2s}^\mu & v_{1s}^\mu & v_{10s}^\mu - iv_{2s}^\mu \\
v_{1s}^\mu & v_{1s}^\mu - iv_{2s}^\mu & v_{1s}^\mu \\
v_{10s}^\mu - iv_{2s}^\mu & v_{10s}^\mu & v_{10s}^\mu + iv_{2s}^\mu \\
v_{10s}^\mu & v_{1s}^\mu & v_{1s}^\mu - iv_{2s}^\mu
\end{bmatrix}
\]

(17)

where

\[
H_{\alpha\beta\gamma\gamma'} (k) \equiv H_{\alpha\beta\gamma\gamma'} (k_s) + \delta k_\mu \delta k_\nu \partial_{\mu\nu} H_{\alpha\beta\gamma\gamma'} (k_s)
\]

(18)

is a \( 4 \times 4 \) matrix on the bases of the sites, \( \epsilon_\sigma \) is middle point of the energy gap of the spin-\( s \) band, and \( \Delta_s \) is the energy gap. First order term on momentum is equivalent with the tilted Weyl equation[12], which gives linear dispersion. The second order term on momentum gives parabolic dispersion. There is no off-diagonal component to mix the up-spin with down-spin bands. The effective potential for a up-spin electron is different from that of a down-spin electron generally, because all four sites are inequivalent each other in the stripe charge ordering state in \( \alpha-(\text{BEDT-TTF})_2\text{I}_3 \). Thus, the conduction and valence bands are reconstructed into four bands, although we can exchange the up-spin with down-spin.

There are two pairs of energy bands in the stripe charge ordering state at \( P_a = 3 \text{kbar} \), which are one-dimensional-like bands and two-dimensional-like bands as shown in Fig. 8. The minimum points of the energy gap are located at \( (\pi, \pi) \) for the former, and at \( (0.36\pi, -0.62\pi) \) for the latter.

The effective Hamiltonian of the one-dimensional-like bands is approximately given by

\[
H_C = \begin{bmatrix}
\epsilon_C + \frac{\Delta_C}{2} + w_{\alpha\gamma} \delta k_y^2 & v^x \delta k_x \\
v^x \delta k_x & \epsilon_C - \frac{\Delta_C}{2} - w_{\alpha\gamma} \delta k_y^2
\end{bmatrix}
\]

(19)

with \( \Delta_C = 0.0066 \text{eV} \), \( v^x = 0.092 \text{eV}/\text{rad} \), \( w_{\alpha\gamma} = 0.055 \text{eV}/\text{rad}^2 \), where “effective mass” \( m_{\alpha\gamma} = 1/2m_0 \) is \( 0.91 \text{rad}^2/\text{eV} \). It consists of \( k_x \)-linear terms in off-diagonal components and \( k_y \)-square terms in diagonal components, and then it exhibits the linear dispersion along \( b \)-axis (parallel to the stripe) and the parabolic dispersion along \( a \)-axis (the stacking axis).
Figure 8. One-dimensional-like bands (a) and two-dimensional-like bands (b) in the stripe charge ordering state at $P_a = 3$ kbar in $\alpha$-(BEDT-TTF)$_2$I$_3$, where $k_x$-axis and $k_y$-axis are shown in the unit of $\pi$.

In the two-dimensional-like bands, on the other hand, 2nd order term of momentum in the effective Hamiltonian is much smaller than that of the first order term as shown by

$$H_D = \begin{bmatrix}
\epsilon_D + \frac{\Delta_D}{2} & \delta k_\mu v_{1D}^\mu \\
\delta k_\mu (v_{1D}^\mu + iv_{2D}^\mu) & \epsilon_D - \frac{\Delta_D}{2} + \delta k_\mu v_{0D}^\mu
\end{bmatrix},$$

(20)

with $\Delta_D = 0.0342\text{eV}$. It is a tilted Weyl equation which consists of $\sigma_0$, $\sigma_x$ and $\sigma_y$, and the finite gap. This is not good Dirac fermion, since the energy gap is larger than the energy range of linear dispersion. The low energy excitations in stripe charge ordering state are described by $H_C$, since $\Delta_D$ is much larger than $\Delta_C$.

The minimum points of the one- and two-dimensional-like bands move as the magnitude of inversion-symmetry-breaking increases. To examine this tendency, we change the mean-field solution of ZGS to that of charge ordering state continuously, since the phase boundary between the charge ordering state and the ZGS is of the 1st order. In the ZGS, there are the contact points at $\pm k_0$. When inversion symmetry is broken, $k_0$ is split into the two minimum points of the energy gaps of both the one- and two-dimensional-like bands. The minimum points of the one-dimensional-like bands go to the symmetry point, although those of the two-dimensional-like bands remain incommensurate, as shown in Fig. 9.

5. Summary and discussion

We have investigated effects of a non-magnetic impurity in the ZGS of molecular conductor $\alpha$-(BEDT-TTF)$_2$I$_3$. The inter-valley scattering gives an incommensurate oscillation with wave number $2k_0$, although a commensurate oscillation exists in graphene. The contribution of intra-valley scattering exhibits unique anisotropy due to angular dependence of the wave function which is related to the Berry phase. Thus STM experiment is expected to observe these properties if a new material with the ZGS at ambient pressure is discovered. Further, we have
studied an effective Hamiltonian in stripe charge ordering state. The energy bands in the stripe charge ordering state have an aspect of extremely anisotropic Dirac fermion with finite gap. The one-dimensional-like bands are relevant for low energy excitations and exhibit an unique anisotropic dispersions which are linear along b-axis (parallel to the stripe) and parabolic along the a-axis (the stacking axis).

Recently an effective Hamiltonian has been proposed in a modified graphene model with $t' = 2t$.\cite{31} It exhibits similar anisotropic dispersions except that is gapless. Interestingly, an unconventional Landau quantization, $\epsilon_n \propto ((n + 1/2)B)^{2/3}$, has been proposed in such a dispersion. Thus anomalous magnetoresistance could be expected for the present material in the stripe charge ordering state under pressure.

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