Electric Conductivity of the Zero Gap Semiconducting State in \(\alpha-(BEDT-TTF)_2I_3\) Salt

Shinya Katayama, Akito Kobayashi and Yoshikazu Suzumura

Department of Physics, Nagoya University, Nagoya 464-8602

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The electric conductivity which reveals the zero gap semiconducting (ZGS) state has been investigated as the function of temperature \(T\) and life time \(\tau\) in order to understand the ZGS state in quarter-filled \(\alpha-(BEDT-TTF)_2I_3\) salt with four sites in the unit cell. By treating \(\tau\) as a parameter and making use of the one-loop approximation, it is found that the conductivity is proportional to \(T\) and \(\tau\) for \(k_BT \gg h/\tau\) and independent of \(T\) and \(\tau\) for \(k_BT \ll h/\tau\). Further the conductivity being independent of \(T\) in the ZGS state is examined in terms of Born approximation for the impurity scattering.

KEYWORDS: organic conductor, electric conductivity, zero gap semiconductor, Dirac cone, multi-band, uniaxial pressure, \(\alpha-(BEDT-TTF)_2I_3\)

In quasi-two-dimensional organic conductors, bis(ethylene dithiolo)tetrathiofulvalene (abbreviated as BEDT-TTF) salts, several electronic states, such as Mott insulator, charge ordering and superconductor,\(^1,2\) have been obtained by varying temperature, hydrostatic pressure and uniaxial strain. Especially, the unconventional behavior with decreasing temperature has been found in the \(\alpha-(ET)_2I_3\) salt (\(\alpha\) phase of BEDT-TTF tri-iodide), which consists of four molecules per unit cell and 3/4-filled band (quarter filling of hole) with eight transfer energies.\(^3\) For ambient pressure, \(\alpha-(ET)_2I_3\) shows a metal-insulator transition at \(T_{MI} = 135\) K followed by the charge ordering.\(^4\) Under hydrostatic pressure, \(T_{MI}\) decreases and vanishes where, at 20 kbar,\(^5\) the resistivity becomes almost temperature-independent from 300 K to 1.5 K. The carrier density decreases from \(10^{21}\) cm\(^{-3}\) (at 300 K) to \(10^{15}\) cm\(^{-3}\) (at 1 K) while the carrier mobility is interpreted to move from \(10^{-1}\) cm\(^2\)/V·s (at 300 K) to \(10^5\) cm\(^2\)/V·s (at 1 K). It has been maintained that such a temperature-dependence of the carrier indicates a narrow gap semiconducting (NGS) state with the gap \(E_g \sim 1\) meV.\(^5\) The NGS state is also obtained at 10 kbar,\(^6\) under the uniaxial strain\(^7\) along \(\alpha\)-direction.

The band calculation of \(\alpha-(ET)_2I_3\) shows a zero gap semiconducting (ZGS) state\(^8,9\) instead of the NGS state when the uniaxial pressure along \(\alpha\)-axis, \(p_\alpha\), becomes large. The Fermi surface of \(\alpha-(ET)_2I_3\) salt at ambient pressure shows a semi-metallic state with the hole and the electron pocket,\(^5\) and the band spectrum has the degeneracy at the bottom of the electron pocket with an incommensurate wave number \(\pm k^0\).\(^10\) Since \(k^0\) is different from the location corresponding to the symmetry of the Hamiltonian, such a degeneracy is called as accidental one according to Herring.\(^11\) With increasing \(p_\alpha\), the hole and electron pockets are reduced\(^12\) and diminish, for \(p_\alpha > 3\) kbar, with the resultant band dispersion, showing Dirac cones centered on \(\pm k^0\).\(^10\) Such a band dispersion and the corresponding density of states per spin and per volume are given respectively by

\[
\xi_k = \pm \hbar v |k - k^0|, \quad D(\epsilon) = \frac{|\epsilon|}{\pi \hbar^2 v^2}, \quad (1)
\]

close to the Fermi energy \(\epsilon_F\), where \(v\) is the average of the velocity and \(\epsilon\) is the energy measured from \(\epsilon_F\).

In terms of eq. (1), the carrier density \(n\) of the ZGS state at low temperatures is calculated as

\[
n = 2 \int_{-\infty}^{\infty} D(\epsilon) f(\epsilon) d\epsilon = \frac{\pi^2 (k_BT)^2}{3} \frac{1}{\pi \hbar^2 v^2}, \quad (2)
\]

where \(f(\epsilon) = (e^{\epsilon/k_BT} + 1)^{-1}\) and \(T\) is the temperature. Equation (2) is consistent with that of the experiment.\(^5,6\) However, it is unclear if the increase of the carrier density is canceled by the decrease of the carrier mobility when the conductivity keeps constant with increasing temperature. In the present paper, the conductivity as the function of \(T\) and \(\tau\) is examined for the ZGS state of \(\alpha-(ET)_2I_3\). The calculation is performed by using the Green’s function without the vertex corrections where the life time \(\tau\) in the self energy is treated as a parameter.

In the system with multi-sites, we consider explicitly \(H_0\) for the transfer energy which is crucial to obtain the ZGS state, but treat implicitly \(H_{int}\) for the interaction which gives rise to the life time. The coupling to the external field, \(H_{ext}\) is also added to calculate the conductivity. The total Hamiltonian is written as

\[
H = H_0 + H_{int} + H_{ext}, \quad (3)
\]

\[
H_0 = \sum_{\alpha,\beta} t_{\alpha;\beta} a^\dagger_{\alpha} a_{\beta}, \quad (3)
\]

\[
H_{ext} = -e \sum_{\alpha} r_i \cdot E a^\dagger_{\alpha} a_{\alpha} = -A, \quad (4)
\]

and \(i, j = 1, \cdots, N_L\) denotes indices for the unit cell, forming a square lattice. The indices \(\alpha, \beta\) denote the site in the unit cell. The quantity \(t_{\alpha;\beta}\) is the transfer energy for the nearest neighbor (n.n.) sites between \((i, \alpha)\) and \((j, \beta)\).
(j, β), and $a_{iα}$ is the annihilation operator of the conduction electron at (i, α) site. In eq. (4), $r_i$ is the position vector of the unit cell coupled with the electric field $E$ where $e$ is the electric charge. Since the equation of motion for $A$ is written as $A = (i\hbar)[H, A] = J \cdot E$, the current density $J_μ$ (μ being the direction of $J$) is given as

$$J_μ = \frac{e}{h} \sum_{kαβ} \frac{\partial ε_αβ(k)}{\partial k_μ} a^α_κ a^β_κ = \frac{e}{h} \sum_{kγγ'} ν^μγγ'(k)c^ε_κ c^ε_κ,$$

where

$$ε_αβ(k) = \frac{1}{V} \sum_{n.m.} t_{iαjβ} e^{ik(r_i-r_j)},$$

$$ν^μγγ'(k) = \frac{4}{\alphaβ} d^α_κ(k) \frac{\partial ε_αβ(k)}{\partial k_μ} d_βγ(k),$$

and $V$ is the area of a system. The directions $x$ and $y$ correspond to $a$ and $b$ in the Mori’s notation, respectively (inset of Fig. 1). The quantities $a^α_κ$ and $c^κ$ denote the Fourier transform, $a^α_κ = V^{-1/2} \sum_{ε=1}^{N_L} a^ε_α e^{-ikr_κ}$, $c^κ = \sum_{α=1}^4 d^α_κ(a^α_κ)$, where the band index $γ = 1, 2, 3, 4$. The quantity $d_αγ(k)$ is the component of the eigenvector obtained by

$$\sum_{β=1}^4 (ε_αβ(k) - ε_F) d_βγ(k) = ξ_κγ d_αγ(k),$$

where $ξ_κγ$ is the eigenvalue of the multi-band with the state $(κ, γ)$. The matrix element $ε_αβ(k)$ is given by eq. (6), which depends on the transfer energies, $t_A$, as shown in the inset of Fig. 1. The indices $A = c_1, c_2, c_3, c_4, p_1, p_2, p_3, p_4$ correspond to $a_2, a_3, a_1, a_1, b_2, b_1, b_4, b_3$, respectively, in the definition by Mori et al. Since the ZGS state is 3/4-filling, the band of $ξ_κ1$ is empty and the others are filled at $T = 0$.

In terms of the linear response theory, the electric conductivity $σ^{μν}$, $(μ, ν = x, y)$ is expressed as

$$σ^{μν} = i[(Q^R_{μν}(ω) - Q^R_{μν}(0))/ω]_{ω→0}.$$

The retarded Green’s function $Q^R_{μν}(ω)$ is obtained from the analytical continuation of $Q_{μν}(iω_0)$ where $Q_{μν}(iω_0)$ is the two-body Green’s function ($T_0$ is the ordering operator) of imaginary time $t_i$, given by

$$Q_{μν}(iω_0) = -\frac{1}{V} \int^β 0 \langle T_1 J_μ(t_1) J_ν(t_0) e^{iω_0 t_1} dt_1,\]$$

where $ω_0 = 2πk_BT l$ with $l$ being an integer.

Equation (10) is calculated by adopting one-loop approximation, i.e. without vertex correction. We treat the effect of $H_{int}$ as a lifetime, $τ$, in the Green’s function,

$$G^{γγ'(k, iε_m)} = -\int^β 0 \langle T_1 c^γγ'(t_1) c^ε_κ(0) \rangle e^{iε_m t_1} dt_1$$

$$\propto (iε_m - ξ_κγ - (S(iε_m))^{-1} δ_γγ',$$

$$\Sigma(iε_m) = -i\hbar (sgn(ε_m)/2τ),$$

where $ε_m = (2m + 1)πk_BT$ with $m$ being an integer. The life time, $τ$, is naively taken as a parameter where $τ$ may come from the processes such as the scattering by electron-phonon interaction, impurity, and fluctuation. Within the above approximation, eq. (10) is expressed as

$$Q_{μν}(iω_0) = \frac{e^2}{\pi\hbar^2 V} \sum_{kγγ'/m} ν^μγγ'(k)c^ε_κ c^ε_κ,$$

$$\times G^{γγ'(k, i(ε_m + ω))}G^{γγ'(k, iε_m)},$$

$$= \frac{e^2}{\pi\hbar V} \sum_{kγγ'} ν^{γγ'}(k)c^ε_κ(k) \int_{-∞}^{∞} dε f(ε)$$

$$\times \frac{1}{(ε + iω - ξ_κγ + (i\hbar/2τ))(ε - ξ_κγ)^2 + (i\hbar/2τ)^2}$$

$$+ \frac{1}{(ε - iω - ξ_κγ - (i\hbar/2τ))(ε - ξ_κγ)^2 + (i\hbar/2τ)^2}. (13)$$

After the analytical continuation (i.e., $iω_0 → ω + i0$), the real part of $σ^{μν}$ $(μ = ν = x, y)$ per spin is calculated as,

$$σ^{μν} = Re(σ^{μν}) = ε^{μγ} σ^{γν},$$

$$σ^{μν} = \frac{e^2}{π\hbar V} \sum_{k} |ν^{γγ'}(k)|^2 \int_{-∞}^{∞} dε \left( -\frac{∂ f(ε)}{∂ε} \right)$$

$$\times \frac{(h/2τ)^2}{(ε - ξ_κγ)^2 + (h/2τ)^2}. (14)$$

Based on the experimental data, we use the interpolation formula for the transfer energy, where $t_A$ (eV) at $p_a$ (kbar) is given by

$$t_A(p_a) = t_A(1 + K_A p_a). (15)$$

The units of the energy and the pressure are taken as eV and kbar, respectively. In eq. (15), $t_{c1} = 0.048, t_{c2} = 0.020, t_{c3} = 0.028, t_{c4} = -0.028, t_{p1} = 0.140, t_{p2} = 0.123, t_{p3} = -0.025, t_{p4} = -0.062, K_{c1} = 0.167, K_{c2} = -0.025, K_{c3} = 0.089, K_{c4} = 0.089, K_{p1} = 0.011, K_{p2} = 0.000, K_{p3} = 0.000$ and $K_{p4} = 0.032$. The ZGS state is obtained for $p_a > 3.10$. We calculate $σ$ as the function of $T$ and $τ$ where the area of an unit cell $V/N_L$, the electric charge $e$, Plank constant $h$, and Boltzmann constant $k_B$ are set unity.

Figure 1 depicts the temperature dependence of $σ$ for $1/τ = 0.001$ and $p_a = 10$ (ZGS state). The difference between $σ^x$ and $σ^y$ comes from the anisotropy of $t_A$, where $σ^x$ is larger (smaller) than $σ^y$ for $T ≥ 0.14 (T ≤ 0.14)$ in the present choice of parameters. In Fig. 1, one finds $σ^μ ∝ T$ at low temperatures in contrast to the conventional conductivity given by the Drude’s formula (i.e., $σ = ne^2τ/m$ with $m$ being the electron mass). Thus it is incorrect that $σ^μ$ in the ZGS state is proportional to the carrier number with $n(\propto T^2)$. The decrease of $σ^μ$ at low temperatures comes from the density of states $D(ε)$, which is given by eq. (1) near the Fermi energy.

Figure 2 shows the temperature dependence of $σ^y$ for several choices of life time $1/τ$. In the high temperature region, the conductivity increases monotonically up to
Fig. 1. Temperature dependence of \( \sigma^x \) and \( \sigma^y \) for ZGS state at \( p_a = 10 \) (kbar), where \( 1/\tau = 0.001 \) (eV). The inset shows the structure of \( \alpha-(ET)_{2}I_{3} \) on the conducting plane.

Fig. 2. Temperature dependence of \( \sigma^y \) at \( p_a = 10 \) where the inset shows the \( 1/\tau \) dependence of \( \sigma^y \) at the temperature \( T = 0.01 \) (i), 0.003 (ii), 0.001 (iii), and 0.0003 (iv) respectively.

\( T = 0.1 \), and is large for small \( 1/\tau \). In the low temperature region, \( \sigma^y \) is independent of the temperature. This region is wider when \( 1/\tau \) is larger. In the inset the \( 1/\tau \) dependence of \( \sigma^y \) is shown for \( T = 0.01, 0.003, 0.001 \) and 0.0003. The \( \sigma^y \) is flat for large \( 1/\tau \) and the gradient of \( \sigma^y \) is about 1 for small \( 1/\tau \) indicating that \( \sigma^y \) is proportional to \( \tau \). The above result is different from the conventional metallic state in which the conductivity is always given by \( \sigma = ne^2\tau/m \). The region in which the conductivity is independent of the life time is wide when the temperature is low.

In Fig. 3, the temperature dependence of the components of \( \sigma^y \), with \((\gamma, \gamma') = (1, 1), (1, 2), (2, 2) \) and \( \sigma^y \) are shown for \( p_a = 10 \) and \( 1/\tau = 0.001 \). The corresponding conductivity as the function of \( 1/\tau \) (\( T = 0.001 \)) is also depicted in the inset. The diagonal components of \( \sigma_{11}^y \) and \( \sigma_{22}^y \) mainly contribute to \( \sigma^y \), whereas the off-diagonal component \( \sigma_{12}^y = \sigma_{21}^y \) contributes only at the low temperatures. The fact that \( \sigma_{12}^y \) decreases monotonically in contrast to \( \sigma_{11}^y \) and \( \sigma_{22}^y \) in the region of high temperature is understood as follows. The carriers excited thermally can participate in \( \sigma_{11}^y \) and \( \sigma_{22}^y \) while only carriers close to Fermi surface give rise to \( \sigma_{12}^y \) and \( \sigma_{21}^y \). For the \( 1/\tau \) dependence, \( \sigma_{11}^y \) and \( \sigma_{22}^y \) are proportional to \( \tau \), and \( \sigma_{12}^y \) decreases for small \( 1/\tau \). Such a behavior of \( \sigma_{12}^y \) is also understood by noting that the corresponding height in the r.h.s. of eq.(14) at \( \varepsilon = 0 \) becomes large for large \( 1/T \) and large \( 1/\tau \). Thus \( \sigma_{12}^y \) can contribute in the dirty case of \( T \tau \ll 1 \). Compared with these four components of \( \sigma_{11}^y, \sigma_{22}^y, \sigma_{12}^y \), and \( \sigma_{21}^y \), the other twelve components of \( \sigma_{\gamma\gamma'} \) are negligibly small.

The behavior of the conductivity in Fig. 2 can be explained from the property of the density of states in eq. (14). Since \( D(\omega) = \sum_{k} \delta(\omega - \xi_k) = (|v|/2\pi\nu^2) \) with \( \pm \xi_k = v\sqrt{k_x^2 + k_y^2} \) (\( v \) is an averaged velocity), eq. (14) with only the diagonal component of \((\gamma, \gamma') = (1, 1) \) and \((2, 2) \) is calculated as \((x = \beta\varepsilon)\)

\[
\sigma \sim \frac{\nu^2}{\pi} \int_{-\infty}^{\infty} d\omega \varepsilon D(\omega) \left( -\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) \left[ \frac{(1/2\tau)}{(\varepsilon - \omega^2 + (1/2\tau)^2)} \right]^2 \\
= 1 \int_{-\infty}^{\infty} dx \frac{1 + (2T\tau|x|)\tan^{-1}(2T\tau|x|)}{\cosh x + 1} \tag{16}
\]

When \( T \gg 1/\tau \), one can replace \( \tan^{-1}(2T\tau|x|) \) by \( \pi/2 \) and estimate eq. (16) as

\[
\sigma \sim (\log 2/\pi)T \tau \simeq 0.220T \tau. \tag{17}
\]
Thus $\sigma$ is proportional to the temperature and the life time for $T \gg 1/\tau$. The results of eq. (17) is also derived by using Boltzmann’s equation where the conductivity, $\sigma_B$, is expressed as

$$\sigma_B = \int_{-\infty}^{\infty} v^3 T D(\varepsilon)(-\frac{\partial f(\varepsilon)}{\partial \varepsilon}) d\varepsilon. \tag{18}$$

Actually eq. (16) becomes equal to eq. (18) for $|e| \gg 1/\tau$, indicating that the case $T \gg 1/\tau$ corresponds to the classical limit. When $T \ll 1/\tau$, eq. (16) is calculated as

$$\sigma \sim 1/(2\pi^2) = 0.051, \tag{19}$$

which shows $\sigma$ being independent of both temperature and life time. In both cases of $T \gg 1/\tau$ and $T \ll 1/\tau$, the conductivity does not depend on the velocity $v$. These two regions of $\sigma \sim const$. and $\sigma \sim T\tau$ are seen in Fig. 2. The boundary between two the region of $\sigma \sim const.$ and that of $\sigma \sim T\tau$ is obtained as $1/\tau \simeq 0.7 T$ at $p_a = 10$ and $1/\tau \simeq 0.8 T$ at $p_a = 6$. 

Equations (17) and (19) exhibit the universal coefficient of $T\tau$ and the universal constant, respectively. These values multiplied by 2 are compared with those of Fig. 2, because eqs. (17) and (19) are calculated in a single Dirac cone. For $0.001 < T < 0.005$, the coefficient of $T\tau$ in Fig. 2 corresponds well to the universal coefficient. At low temperature, however, the conductivity in Fig. 2 is somewhat larger than the universal constant, because the former contains the contribution from the off-diagonal components, $(\gamma, \gamma') = (1, 2), (2, 1)$.

Now we discuss the relevance of the ZGS state to the conductivity of $\alpha$-(ET)$_2$I$_3$, which is almost independent of temperature. In terms of the mobility and the carrier, the bulk conductivity is estimated as $\sigma \simeq 3.2 \times 10^2 \Omega^{-1}$ cm$^{-1}$. Then one obtains $1/\tau \simeq 1K$ at room temperature by using naively the formula $\sigma = ne^2\tau/m$ with the bare mass $m$. Since the present result of the temperature dependence for $T > 10 K$ (i.e., $T\tau \gg 1$) is not consistent with that of the experiment, we calculate the life time of the impurity scattering by taking account of the ZGS state. In terms of the self-consistent Born approximation, the self-energy in eq. (12) is replaced by

$$\Sigma(i\varepsilon_m) = -i\hbar\varepsilon_m/(2\tau W_D). \tag{20}$$

for $|\varepsilon_m| < W_D$, where $W_D \sim 0.01$ at $p_a = 10$ kbar denotes the band width of the Dirac cone. Note that the frequency dependence similar to eq. (20) has been obtained for the calculation in the graphite at $T = 0$. Thus we obtain the conductivity in which the temperature dependence is reduced as shown in Fig. 4 indicating a tendency being consistent with the experiment. However there remains a problem of the magnitude of $\sigma$ which comes from the stacking of the two-dimensional sheet of the ET salt. From the bulk conductivity and the lattice constant of $c$-axis (as $1.7 \times 10^{-7}$ cm), the conductivity per one sheet and spin, is estimated as 0.11 in the unit of $e^2/h (= 2.44 \times 10^{-5} \Omega^{-1})$, which is utilized for the conductivity in the present calculation. This magnitude is much smaller than the numerical result of Fig. 4 although the origin of such a discrepancy is not clear for the moment.

Here, we show the validity of the extrapolation formula eq. (15) even for 10 kbar by comparing the coefficients of the density of states in eq. (1). The experimental value of the carrier density at $T$ is given by $n \simeq 10^{13}T^2$ cm$^{-3}$ and then the density per sheet is given by $n \simeq 1.7 \times 10^{6}T^2$ cm$^{-2}$. By comparing the coefficient with that of eq. (2) (lattice constants are $a = 9.2 \times 10^{-8}$ cm and $b = 10.8 \times 10^{-8}$ cm), the coefficients of $\varepsilon$ in eq. (1) is estimated as $8 \times 10$ eV$^{-2}$, which corresponds well to that the present calculation $\sim 6 \times 10$ eV$^{-2}$.

Finally we note that the three dimensional effect on the ZGS state. Since the small interplane hopping is expected in the $\alpha$-(ET)$_2$I$_3$ salt from the first principle calculation, the metallic state with small Fermi surface appears. Then the property of the ZGS state could be found at temperature larger than the interplane hopping.

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1. T. Ishiguro, K. Yamaji and G. Saito: *Organic Superconductors* (Springer-Verlag, Berlin, 1998) 2nd ed.
2. H. Seo, C. Hotta and H. Fukuyama: Chem. Rev. **104** (2004) 5005.
3. T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito and H. Inokuchi: Chem. Lett. (1984) 957.
4. Y. Takano, K. Hiraki, H. M. Yamamoto, T. Nakamura and T. Takahashi: J. Phys. Chem. Solids **62** (2001) 393.
5. N. Tajima, M. Tamura, Y. Nishio, K. Kajita and Y. Iye: J. Phys. Soc. Jpn. **69** (2000) 543.
6. N. Tajima, A. Ehina-Tajima, M. Tamura, Y. Nishio and K. Kajita: J. Phys. Soc. Jpn. **71** (2002) 1832.
7. M. Maesato, Y. Kaga, R. Kondo and S. Kagoshima: Rev. Sci. Instrum. **71** (2000) 176.
8. A. Kobayashi, S. Katayama, K. Noguchi and Y. Suzumura: J. Phys. Soc. Jpn. **73** (2004) 3135.
9) A. Kobayashi, S. Katayama and Y. Suzumura: J. Phys. Soc. Jpn. 74 (2005) 2897.
10) S. Katayama, A. Kobayashi and Y. Suzumura: preprint.
11) C. Herring: Phys. Rev. 52 (1937) 365.
12) R. Kondo, S. Kagoshima and J. Harada: J. Phys. IV (Paris) 114 (2004) 523; Rev. Sci. Instrum. 74 (2005) 093902.
13) A. A. Abrikosov, L.P. Gor’kov and I. Ye. Dzyaloshinskii, Quantum Field Theoretical Method in Statistical Mechanics (Pergamon Press, 1965).
14) J. Gonzalez, F. Guinea, and M. A. H. Vozmediano: Phys. Rev. Lett. 77 (1996) 3589.
15) N. H. Shon and T. Ando: J. Phys. Soc. Jpn. 67 (1998) 2421.
16) H. Kino, T. Miyazaki and S. Ishibashi: in preparation.
17) G. P. Mikitik and Y. V. Sharlai: Phys. Rev. Lett. 82 (1999) 2147.