Quantum Phase Transition in Organic Massless Dirac Fermion System α-(BEDT-TTF)₂I₃ under Pressure

Yoshinari Unozawa, Yoshitaka Kawasugi, Masayuki Suda, Hiroshi M. Yamamoto, Reizo Kato, Yutaka Nishio, Koji Kajita, Takao Morinari, and Naoya Tajima

Quantum Phase Transition in Organic Massless Dirac Fermion System
\(\alpha\text{-}(\text{BEDT-TTF})_2\text{I}_3\) under Pressure

Yoshinari Unoaza\(^1\), Yoshitaka Kawasugi\(^1\), Masayuki Suda\(^2\), Hiroshi M. Yamamoto\(^3\), Reizo Kato\(^4\), Yutaka Nishio\(^1\), Koji Kajita\(^1\), Takao Morinari\(^5,6\), and Naoya Tajima\(^1,7\)

\(^1\)Department of Physics, Toho University, Funabashi, Chiba 274-8510, Japan
\(^2\)Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan
\(^3\)Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan
\(^4\)RIKEN, Wako, Saitama 351-0198, Japan
\(^5\)Course of Studies on Materials Science, Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

(Received September 30, 2020; accepted October 19, 2020; published online November 6, 2020)

We investigate the effect of strong electronic correlation on the massless Dirac fermion system, \(\alpha\text{-}(\text{BEDT-TTF})_2\text{I}_3\), under pressure. In this organic salt, one can control the electronic correlation by changing pressure and access the quantum critical point between the massless Dirac fermion phase and the charge ordering phase. We theoretically study the electronic structure of this system by applying the slave-rotor theory and find that the Fermi velocity decreases without creating a mass gap upon approaching the quantum critical point from the massless Dirac fermion phase. We show that the pressure-dependence of the Fermi velocity is in good quantitative agreement with the results of the experiment where the Fermi velocity is determined by the analysis of the Shubnikov-de Haas oscillations in the doped samples. Our result implies that the massless Dirac fermion system exhibits a quantum phase transition without creating a mass gap even in the presence of strong electronic correlations.

The discovery of graphene\(^1\) has opened up a new era of research on massless Dirac fermions in condensed matter physics.\(^2\) In a system with the massless Dirac fermion spectrum, the conduction and valence bands touch at discrete points called Dirac points, in the Brillouin zone, and the low-energy excitations are described by a relativistic Dirac equation, where the velocity of light is replaced by the Fermi velocity. When the Dirac points exist near the Fermi energy, the conduction electrons have extremely high mobility due to the Berry phase effect.\(^3\) Reflecting the characteristic Landau-level structure associated with Dirac fermions, a half-integer quantum Hall effect is observed under magnetic field.\(^5,5\)

Experimentally, massless Dirac fermions are realized in various systems,\(^6\) including the surfaces of three-dimensional topological insulators,\(^7\) and even in the bulk of three-dimensional systems.\(^8\)

After experimental observation of the intriguing physical properties of massless Dirac fermions, the next important question to address is the effect of electron–electron interactions on massless Dirac fermions. The interaction includes both long- and short-range parts. In contrast to conventional metals, systems hosting Dirac fermions experience long-range Coulomb interaction when the Fermi energy is close to the Dirac point because the screening effect is negligible. The renormalization group theory shows that the Fermi velocity is renormalized and logarithmically divergent due to the long-range Coulomb interaction, though the system flows to a non-interacting theory.\(^9\) Experimentally, a large enhancement in the Fermi velocity has been confirmed in graphene\(^10\) by approaching the Dirac point. Although the long-range part of the Coulomb interaction leads to reshaping of the Dirac cone, it does not lead to new phases.\(^10\)

The most enigmatic is the short-range Coulomb interaction. The analysis of excitonic and Cooper pairing instabilities suggests that a mass gap is created in the Dirac fermion spectrum when the Coulomb interaction exceeds a critical value.\(^11\) Meanwhile, theoretical analysis of the Hubbard model on a honeycomb lattice with long-range Coulomb interactions suggests that there is a quantum critical point while going from a Dirac semimetal to an antiferromagnetic Mott insulator, and that there is a decrease in the Fermi velocity due to the on-site Coulomb repulsion.\(^12\) While suspended graphene appears to be in the weak coupling regime, the interaction can be enhanced in graphene on metallic substrates.\(^12\) However, it is still challenging to drive the system into the strong coupling regime for graphene.

In order to investigate the effect of short-range interaction on massless Dirac fermions, the organic charge-transfer salt \(\alpha\text{-}(\text{BEDT-TTF})_2\text{I}_3\) under pressure forms an ideal platform.\(^13\) [Here, BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene.] A single crystal of \(\alpha\text{-}(\text{BEDT-TTF})_2\text{I}_3\) consists of conductive layers of BEDT-TTF molecules and insulating layers of \(\text{I}_3\) anions.\(^14\) There are four BEDT-TTF molecules per unit cell. According to the band calculation of this material under high pressure by Katayama et al.,\(^15\) the electronic structure is described by massless Dirac fermions. The first band (highest-energy band; valence band) and the second band (conduction band) touch each other at two points in the first Brillouin zone where the bands exhibit linear energy dispersion. There are two more bands, but they are energetically well separated from the linearly dispersing bands. Since there is one hole per two molecules, the HOMO-band is 3/4-filled. As a result, the Fermi energy is located exactly at the Dirac point.

The salient feature of this system is that one can control the electronic correlation by changing pressure. Under ambient pressure, this system exhibits a metal–insulator transition at 135 K, where the insulating state is a charge-ordered insulator with a horizontal charge stripe.\(^16,18\) The strong electronic correlations that are responsible for forming the charge stripe...
are suppressed under high pressure, and the system becomes a massless Dirac fermion system above 1.5 GPa.\textsuperscript{13,19} The interaction effect on the massless Dirac fermions in this system has been investigated theoretically and experimentally.\textsuperscript{24,25} Like in graphene, Dirac cone reshaping has been observed in $\alpha$-(BEDT-TTF)$_2$I$_3$ using site-selective nuclear magnetic resonance.\textsuperscript{24} Because of the presence of tilt of the Dirac cone, the reshaping was found to be anisotropic. The effect of the short-range Coulomb repulsion was also observed as the fermionic spin polarization. Besides, a significant violation from the Korringa law suggests that the system is in the strong coupling regime.\textsuperscript{25}

In this study, we investigate the quantum phase transition in the massless Dirac fermion system, $\alpha$-(BEDT-TTF)$_2$I$_3$. We focus on the quantum phase transition occurring upon varying the strength of the electronic correlation by controlling the pressure in this system. Applying the slave-rotor formalism,\textsuperscript{26} we theoretically show that the Fermi velocity of the massless Dirac fermions decreases upon approaching the quantum critical point without creating a mass gap. This theoretical result is in good qualitative agreement with the those obtained from the experiment where the Fermi velocity is determined by the analysis of the Shubnikov–de Haas (SdH) oscillations.

We consider an extended Hubbard model describing $\alpha$-(BEDT-TTF)$_2$I$_3$. The Hamiltonian is given by three types of transfer energies, $n_{\alpha i\beta j}$, and the on-site Coulomb repulsion, $U$. Here, $N_a$ is the number of unit cells and $k = (k_x, k_y)$ is the two-dimensional wave vector. We obtain the following Hamiltonian:

$$H = \sum_{k, \sigma} c_{k\sigma}^\dagger H_k c_{k\sigma}.$$  

Here, $c_{k\sigma}^\dagger = (c_{k\sigma}^\dagger, c_{k\sigma}^\dagger, c_{k\sigma}^\dagger, c_{k\sigma}^\dagger)$. The explicit forms of the matrix elements of $H_k$ are:

$$\langle H_k \rangle_{\alpha' \beta'} = t_{\alpha' \beta'} e^{ik\cdot r},$$

where $r$ is the atomic coordinates obtained by crystal structure analyses of $\alpha$-(BEDT-TTF)$_2$I$_3$. The diagonal matrix elements are $\langle H_k \rangle_{\alpha \alpha} = U n_{\alpha \sigma} + 2 \sum_{\beta \neq \alpha} V_{\alpha \beta} (n_{\beta \uparrow} + n_{\beta \downarrow})$. The indices for the transfer energies are defined in the inset of Fig. 1. The diagonal matrix elements are $\langle H_k \rangle_{\alpha \alpha} = U n_{\alpha \sigma} + 2 \sum_{\beta \neq \alpha} V_{\alpha \beta} (n_{\beta \uparrow} + n_{\beta \downarrow})$, where $\sigma$ denotes flipped $\sigma$ and $V_{\alpha \beta} \neq 0$ for the two nearest neighbor molecules.

The transfer energies are pressure-dependent. Their values were evaluated from the extended Hückel method using the atomic coordinates obtained by crystal structure analyses of $\alpha$-(BEDT-TTF)$_2$I$_3$ under hydrostatic pressure.\textsuperscript{28} On the other hand, the pressure dependence of the lattice constants appear to be saturated at high pressures.\textsuperscript{29} Thus, we consider the following formula for the pressure dependence of the transfer energies:

$$t_{\alpha \beta} = A_{\alpha \beta} (1 - B \tanh(Cp)),$$

where $A_{\alpha \beta}$ and $B$ are fitting parameters. The parameter $C$ is associated with the saturation of the transfer energies. The result of fitting is shown in Fig. 1 with taking $1/C = 0.3$ GPa.
Now we apply the slave-rotor theory\textsuperscript{260} to the system to investigate the effect of strong electronic correlations. The electron creation operator at molecule $\alpha$ in the $j$-th unit cell and spin $\sigma$ can be rewritten as

$$c_{\alpha j \sigma}^+ = e^{\theta_\sigma} f_{\alpha j \sigma}^+.$$  \hspace{1cm} (5)

Note that the phase field $\theta_j$ is independent of $\alpha$. When electrons are created by this operator in the vacuum, the total number of electrons is obtained by applying the operator $L_j = -i\partial/\partial \theta_j$. The advantage of this formalism is that one can distinguish between the Mott insulator phase and the metallic phase. In terms of the electron number operator, we cannot distinguish between them. However, the expectation value of $\theta_j$ vanishes for the Mott insulating phase while it is nonzero for the metallic phase.

In the slave-rotor formalism, each electron hopping term can be rewritten as $\langle h_{\alpha i \sigma} e^{\theta_\sigma} f_{\beta j \sigma}^+ \rangle_{\alpha i \sigma} f_{\beta j \sigma}$. We introduce an approximation to decouple the fermion fields and the phase fields as

$$\langle e^{i(\theta_\sigma)} f_{\alpha i \sigma}^+ \rangle_{\alpha i \sigma} f_{\beta j \sigma} + \langle f_{\alpha i \sigma}^+ \rangle_{\alpha i \sigma} f_{\beta j \sigma} e^{i(\theta_\sigma)}.$$  \hspace{1cm} (6)

In the phase field system, which is now described by a quantum XY-model, we introduce another mean field approximation\textsuperscript{260} $\langle e^{i(\theta_\sigma)} \rangle \approx \langle \cos \theta \rangle \langle \cos \theta \rangle$. As a result, the off-diagonal terms of the mean field Hamiltonian are rescaled as $(H_k)_{ij} \rightarrow Z(H_k)_{ij}$ ($i \neq j$). Here, $Z$ describes the band renormalization and is given by $Z = \eta^2$ with $\eta = \langle \cos \theta \rangle$. The final mean field Hamiltonian is $H_f = H_0 + H_\theta$, where

$$H_f = \sum_{k,a,\beta,\sigma} c_{k a \sigma}^+ [Z(H_k)]_{ab}(1 - \delta_{a\beta}) + (H_k)_{a a} \delta_{\alpha \beta}|c_{k a \sigma}|.$$  \hspace{1cm} (7)

The expectation value $\langle \cos \theta \rangle$ is computed based on the following Hamiltonian:

$$H_\theta = \frac{U_{eff}}{2} \hat{L}^2 + 2 \chi \eta \cos \theta,$$  \hspace{1cm} (8)

where $\hat{L} = -i\partial/\partial \theta$. Here, $\chi = \sum_{a \neq b} \langle f_{a \alpha}^+ f_{b \beta} \rangle/N_a$. $U_{eff}$ is the effective short-range interaction. The expectation value $\langle f_{a \alpha}^+ f_{b \beta} \rangle$ is computed based on the Hamiltonian, $H_f$. We note that there is a Lagrange multiplier enforcing the constraint on the expectation value of $\langle \hat{L} \rangle$. However, this parameter can be removed by shifting the origin of the phase field. The values $\eta$ and $\chi$ are to be determined self-consistently.

In Fig. 2(a), we show the band structure around the Dirac nodes at $\beta = p - p_0 = 0.3, 1.2$ GPa. Here, $p_0 = 0.336$ GPa denotes the shift of the pressure due to the suppression of the transfer energies associated with the strong electronic correlation effect. The Fermi velocity $v_F$ decreases as we decrease $p$ as seen in Fig. 2(b). This decrease in $v_F$ is associated with a decrease in $Z$ that reflects the effect of the strong electronic correlation, and we may adopt a simple formula $v_0 = Zv_0$ for $v_F$ with $v_0$ being a parameter. We note that the decrease in $v_F$ to the strong electronic correlation is consistent with the previous studies.\textsuperscript{224} The pressure dependence of $v_F$ is compared with the experiment in Fig. 2(c). The theory is in good quantitative agreement with the experiment. In the experiment, $v_F$ is determined by analyzing the SdH oscillations as described below. Since the tilt of the Dirac cones in this system, $v_F$ is given by the average Fermi velocity $v_F(\phi)$, defined in the direction with an azimuthal angle $\phi$, as $\int_0^{2\pi} v_F(\phi)^2 d\phi = 2\pi v_0^2$.

Now we describe the experiment. To investigate the electronic structure of the system, we observed SdH oscillations under pressure between 0.66 and 1.5 GPa at 0.5 K. To detect the SdH oscillations, we need to shift $E_F$.
from the Dirac point (DP). In this experiment, we injected holes into \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\) by the contact electrification method\(^{30,31}\) as follows. The carrier density per layer of \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\) under high pressure and at low temperatures is estimated to be approximately \(10^5\) cm\(^{-2}\). Thus, the effects of hole doping can be detected by transport measurement by fixing a thin crystal onto a polyethylene naphthalate (PEN) substrate, which is weakly negatively charged. The thickness of the crystal measured with a step profilometer is approximately 100 nm. Number of layers (pairs of BEDT-TTF molecular layers and I\(_3\) cation layers; vide infra) is estimated to be approximately 57. Note that holes are injected into a few layers and rapidly decrease from the substrate. Thus, the observed SdH oscillations are associated with the first layer on the substrate in this experiment.

The critical pressure for the quantum phase transition was determined from the resistivity, \(\rho_{xx}\), measurement. We show the temperature dependence of \(\rho_{xx}\) for different pressures in Fig. 3(a). The system evolves from the insulating state into a metallic state as we increase the pressure. From this measurement, the critical pressure is estimated to be approximately 0.75 GPa. At intermediate pressures, the system consists of the insulating phase and the massless Dirac electron phase due to the inhomogeneity of the pressure effect. The temperature-pressure phase diagram is shown in Fig. 3(b) for \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\) on the PEN substrate. This phase diagram should be compared with that of the bulk thick crystals of the same system. The softness of the PEN substrate results in a large pressure effect on the thin crystal such that the massless Dirac electron system is realized in about half of the necessary pressure needed in the case of a bulk thick crystal.

We confirmed that the system is in the Dirac electron phase from the Berry phase analysis, where the circular orbits around the DP result in the Berry phase \(\phi_B = \pi\). The magnetic field, \(B\), dependence of \(\rho_{xx}\) for different pressures is shown in Fig. 4(a). The oscillation pattern becomes clearer by taking the second-order differentials of \(\rho_{xx}\) as a function of \(B^{-1}\) as shown in Fig. 4(b). We apply the semi-classical magneto-oscillation analysis to find the phase of the SdH oscillation. We note that the maxima of the oscillations are associated with the Landau levels denoted by \(N\) in Fig. 4(b). Because of the Zeeman energy, the Landau levels with \(N = -1\) and \(-2\) are lifted. Using this splitting, we show the linear approximation formula \(B^{-1} = \frac{2\pi}{\phi_0} (N + \gamma)\) in Fig. 4(c). Here, \(S_F = 2\pi^2 B \phi_0\) is the Fermi surface cross-section area, \(B_f\) is the SdH frequency, and \(\phi_0 = h/2e\) is the fluxoid. The Onsager phase factor is defined by \(\gamma \equiv 1/2 - \phi_B/2\pi\). For the case of conventional metals, the Landau level energies are given by \(E_N = \hbar \omega_c (N + 1/2)\) with \(\omega_c\) as the cyclotron frequency and we obtain \(\gamma = 1/2\). Meanwhile, we have \(E_N = \pm \sqrt{2\hbar e B N} (N + 1/2)\) for the massless Dirac electron systems and we obtain \(\gamma = 0\). Figure 4(c) shows that \(\gamma \approx 0\). Therefore, the system is in the Dirac electron phase with \(\phi_B = \pi\) under all applied pressures.

Experimentally, the Fermi velocity, \(v_F\), is determined from the splitting of the Landau levels due to the Zeeman energy, that is, \(E_{N+1}(B) - E_N = g_B \mu_B B/2\) with \(g = 2\). For instance, \(v_F\) is obtained from the relation \(E_{-2}(B_{-2}) - E_{-2}(B_{-1})\). Here, \(B_{-2}\) and \(B_{-1}\) are magnetic field strengths, where the up- and down-spin Landau levels for \(N = -2\) cross the Fermi energy. Pressure dependence of \(v_F\) is shown in Fig. 2(b). The system approaches the quantum critical point with a rapid decrease in \(v_F\) without creating a mass gap.

To conclude, we have investigated the effect of strong electronic correlations on the massless Dirac fermion system \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\) under pressure. We have theoretically shown that the Fermi velocity \(v_F\) decreases as we increase the electronic correlation without creating the mass gap. The change in \(v_F\) was obtained by applying the slave-rotor theory. The result is in good quantitative agreement with the experimentally obtained \(v_F\), where \(v_F\) is determined from the analysis of the SdH oscillations of doped samples. Our study suggests that there is no mass gap opening at the quantum critical point between the massless Dirac fermion phase and charge ordering phase. To the best of our knowledge, there are no other massless Dirac fermion systems where one can reach the strong electron correlation.
Fig. 4. (Color online) (a) Magnetic field dependence of \( \rho_e \) under several pressures at 0.5 K. (b) Second-order differential of \( \frac{\partial \rho_e}{\partial B^2} \), as a function of \( B^{-1} \). The periodic oscillations indicate the SdH signal. The oscillation maxima are denoted by the Landau index \( N \). The Zeeman effect splits \( N = -2 \) and \(-1 \) Landau levels. (c) Landau index dependence of the value of \( B^{-1} \) for the SdH oscillation maxima. In the case of Dirac electron systems, the linear extrapolation of the data to \( B^{-1} = 0 \) should be 0.

regime. Thus, it will be interesting to further explore the physics around this quantum critical point in \( \pi \)-(BEDT-TTF)\( \text{I}_3 \).

Acknowledgments This work was supported by MEXT/JSPJ KAKENHI under Grant Nos. 16H06346 and 20K03870. The authors are grateful to the Equipment Development Center, the Institute for Molecular Science, for the technical assistance provided by the Nanotechnology Platform Program (Molecule and Material Synthesis) of the Ministry of Education Culture, Sport, Science and Technology (MEXT), Japan.

*morinari.takao.5s@kyoto-u.ac.jp
1naoya.tajima@sci.toho-u.ac.jp

7) M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. 82, 3045 (2010).