Transport properties of organic Dirac electron system α-(BEDT-TSeF)$_2$I$_3$

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(Dated: July 3, 2020)

Motivated by the insulating behavior of α-(BEDT-TSeF)$_2$I$_3$ at low temperatures ($T$s), we first performed first-principles calculations based on the crystal structural data at 30 K under ambient pressure and constructed a two-dimensional effective model using maximally localized Wannier functions. As possible causes of the insulating behavior, we studied the effects of the on-site Coulomb interaction and spin-orbit interaction (SOI) by investigating the electronic state and the transport coefficient using the Hartree approximation and the $T$-matrix approximation. The calculations at a finite $T$ demonstrated that spin-ordered massive Dirac electron (SMD) appeared owing to the on-site Coulomb interaction. SMD is not a conventional spin order, but exhibits the spin-valley Hall effect. Direct current resistivity in the presence of a spin order gap divergently increased and exhibited negative magnetoresistance in the low $T$ region with decreasing $T$. The charge density hardly changed below and above the $T$ at which this insulating behavior appeared. However, when considering the SOI alone, the state changed to a topological insulator phase, and the electrical resistivity is saturated by edge conduction at quite low $T$. When considering both the SMD and the SOI, the spin order gap was suppressed by the SOI, and gaps with different sizes opened in the left and right Dirac cones. This phase transition leads to distinct changes in microwave conductivity, such as a discontinuous jump and a peak structure.

I. INTRODUCTION

Quasiparticles that have properties similar to those of relativistic particles in solids have been found in various materials such as graphene [1, 2], bismuth [3, 4], and several organic conductors [5–12]. They are called Dirac electrons in solids and exhibit exotic physical properties such as quantum transport [13]. For Dirac electrons in solids and exhibit exotic physical properties such as quantum transport [13]. For Dirac electrons in organic conductors such as α-(BEDT-TTF)$_2$I$_3$ and α-(BEDT-TSeF)$_2$I$_3$ (α-(BETS)$_2$I$_3$), which are the main focus in this study, the Coulomb interaction is relatively large owing to the narrow band width. The relationship between the Dirac electron and the electron correlation effect has been discussed. In α-(BEDT-TTF)$_2$I$_3$, it is suggested that phase transition between the Dirac electron phase and the charge-ordered insulator phase is induced by the nearest-neighbor Coulomb interaction [14–16], and anomalous behaviors associated with the electron correlation effect such as pressure dependence of the spin gap [17, 18] and transport phenomena at low temperatures ($T$s) [19–21] have been observed. It has also been shown that a long-range component of the Coulomb interaction induces reshaping of the Dirac cone [22, 23], and it enhances spin-triplet excitonic fluctuations in the massless Dirac Electron phase under high pressure and in-plane magnetic field [24].

α-(BETS)$_2$I$_3$ is a related substance of α-(BEDT-TTF)$_2$I$_3$. In the composition of the BETS molecule, the sulfur atom in the BEDT-TTF molecule is replaced with a selenium atom, and its relationship with the high-pressure phase of α-(BEDT-TTF)$_2$I$_3$ has been discussed. Direct current (DC) electrical resistivity measurements showed that properties of Dirac electron appear at $T > 50$ K [25]. On the other hand, at $T < 50$ K, the DC resistivity increases divergently. Nuclear magnetic resonance (NMR) measurements indicated that an energy gap $\sim 300$K is opened at low $T$. However, unlike in the α-(BEDT-TTF)$_2$I$_3$, the inversion symmetry is not broken, which has been revealed recently by the synchrotron X-ray diffraction experiment [27]. Thus, the electronic state at low $T$ has not been clarified.

Under hydrostatic pressure, the energy band with electron and hole pockets is obtained by band calculations using the extended Hückel method or first-principles calculation [28, 29]. A mean-field calculation using the extended Hubbard model based on the extended Hückel method suggests that the insulating state at low $T$ is a band insulator due to merging of the Dirac cones [30]. However, high-accuracy X-ray diffraction data at 30 K under ambient pressure have recently been obtained, and using first-principles calculation, it has been demonstrated that type-I Dirac electron, which has no Fermi pockets, can be realized under ambient pressure [27]. The calculation considering spin-orbit interaction (SOI) by the second-order perturbation indicated that SOI also contributed to the electronic state in α-(BETS)$_2$I$_3$ owing to the presence of selenium, and its magnitude was $5 \sim 10$ meV [31]. The results of a recent first-principles calculation with the generalized gradient approximation (GGA) also showed that the SOI had a value of approximately 2 meV, and its effect could not be neglected [32].
In this study, we investigate the effects of the Coulomb interaction and SOI as possible causes of the hidden phase transition and insulating behavior at low $T_s$. We investigate the electronic state and calculate several transport coefficients in $\alpha$-(BETS)$_2$I$_3$. The remainder of this paper is organized as follows. In Sec. II, first-principles calculations based on the X-ray data are performed to derive the transfer integrals at 30 K under ambient pressure. We obtain the on-site Coulomb interaction by the constrained random phase approximation. Using the obtained data, we construct a two-dimensional effective Hubbard model. In addition, we describe a method to calculate the DC and optical conductivities using the Nakano-Kubo formula. In Sec. III, we demonstrate the obtained electronic state at a finite $T$ and a candidate low $T$ insulator phase. Moreover, a calculation considering SOI is performed, and its contribution to the electronic state near the phase transition is estimated. Next, we calculate the $T$-dependence of the DC and optical conductivities and in-plane magnetic field $B$-dependence of the DC resistivity are also calculated and compared with the experimental results. The findings of our study are summarized in Section IV.

II. MODEL AND FORMULATION

A. Effective model based on first-principles calculations

First, we performed first-principles calculations based on the X-ray crystal structural data of $\alpha$-(BETS)$_2$I$_3$ at 30K under ambient pressure by the Quantum Espresso (QE) package. In our calculation, the GGA was used as the exchange-correlation function. As the pseudo-potentials, we used the SG15 Optimized Norm-Conserving Vanderbilt (ONCV) pseudo-potentials. The cutoff kinetic energies for wave functions and charge densities were set as 80 and 320 Ry, respectively. The mesh of the wavenumbers was set as $4 \times 4 \times 2$. After the first principles calculation, the maximally localized Wannier functions (MLWFs) were obtained using RESPACK. To construct the MLWFs, four bands near the Fermi energy were selected. Initial coordinates of the MLWFs were located at the center of each BETS molecule in the unit cell. Figure 1(a) shows the crystal structure of $\alpha$-(BETS)$_2$I$_3$ at 30K under ambient pressure (left side) and the real space distribution of the MLWFs (right) drawn by VESTA. (a) Energy bands derived from the first-principles calculation (solid red line) and Wannier interpolation (empty circle). The chemical potential is set as the energy origin.

Next, we constructed the effective model using the transfer integrals and the on-site Coulomb interactions. The on-site Coulomb interactions are evaluated by the constrained random phase approximation (cRPA) method using RESPACK. The energy cutoff for the dielectric function was set as 5.0 Ry.

Figure 2 shows a schematic lattice structure of $\alpha$-(BETS)$_2$I$_3$. The transfer integrals are considered up to almost the next nearest neighbor bonds (enclosed by the red broken line in Fig. 2). The values of the transfer integrals $t_{\alpha,\beta}$ are listed in the table shown in the right side of Fig. 2. Here, $\delta = (\delta_a, \delta_b)$ indicates the lattice vector and $\alpha$ and $\beta$ indicate the site indexes in the unit cell, i.e., A, A$, B$, and C. The cutoff energy of the transfer integrals are taken as $t_{\text{cut}} = 5.0$ [meV]. The on-site Coulomb interactions are given as $U_A = U_A' = 1.383$ [eV], $U_B = 1.396$ [eV], and $U_C = 1.359$ [eV]. Since the transfer integrals

![Figure 1](image1.png)

![Figure 2](image2.png)
between the inter planes are significantly smaller than those in the in-plane plane, this system can be considered as a two-dimensional electronic system.

In this study, we investigated the two-dimensional Hubbard model with SOI [12]:

\[ H = \sum_{R, \delta \alpha, \beta} t_{R, \alpha, \beta}^\delta c_{R, \alpha, \sigma}^\dagger c_{R+\delta, \beta, \sigma} + \sum_{R, \alpha} \lambda_0 U_{\alpha} n_{R, \alpha, \uparrow} n_{R, \alpha, \downarrow} + H_{\text{SOI}} - \mu_B B \sum_{\alpha, \sigma, R} \text{sgn}(\sigma) n_{R, \alpha, \sigma}, \] (1)

where \( R \) is the coordinate of the unit cell, and \( \alpha, \beta \) indicate the indexes of the inner-sites in the unit cell (A, A', B, and C). \( \sigma = \uparrow (\downarrow) \) indicates the index of spin. \( t_{R, \alpha, \beta}^\delta \) indicates the transfer integral between \( \alpha \) and \( \beta \) sites separated by the relative lattice vector \( \delta \), and \( U_\alpha \) indicates the on-site Coulomb interaction evaluated using cRPA method. The creation (annihilation) operator at \( \alpha \)-site in the unit cell located at \( R \) is defined as \( c_{R, \alpha, \sigma} (c_{R, \alpha, \sigma}^\dagger) \), and the number operator is defined as \( n_{R, \alpha, \sigma} = c_{R, \alpha, \sigma}^\dagger c_{R, \alpha, \sigma} \). \( \lambda_U \) \((0 < \lambda_U < 1)\) is a tuning parameter that controls the values of the on-site Coulomb interaction. \( H_{\text{SOI}} \) is the SOI term, which is generally proportional to \( (p \times \nabla U(r)) \cdot \sigma \), where \( p \) is the momentum, \( U(r) \) is the potential energy, and \( \sigma \) indicates the spin angular momentum. The specific formula of \( H_{\text{SOI}} \) is detailed in the following section. The fourth term of Eq. (1) represents the in-plane Zeeman magnetic field, where \( \mu_B \) is the Bohr magneton. In the following, the lattice constants, Boltzmann constant \( k_B \), and the Plank constant \( h \) are taken as unity. Note that electronvolt (eV) is used as the unit of energy throughout this paper.

B. Electronic state in the wavenumber space

In this study, we investigate the electronic state using the Hartree approximation. To obtain the Hamiltonian in the wavenumber representation, the Fourier inverse transformation is performed on the Hamiltonian defined in Eq. (1). Then, the Hamiltonian is given as

\[ H_{\alpha, \beta, \sigma}(k) = \sum_{\delta} t_{R, \alpha, \beta}^\delta \langle k | c_{R, \alpha, \sigma}^\dagger \delta_{k, \alpha, \sigma} c_{k, \beta, \sigma} \rangle \]

\[ + \lambda_0 U_{\alpha} \langle n_{\alpha, \uparrow} n_{\alpha, \downarrow} \rangle \delta_{k, \alpha, \sigma} c_{k, \alpha, \sigma} \]

\[ + H_{\text{SOI}}(k) - \mu_B B \sum_{\alpha, \sigma, k} \text{sgn}(\sigma) \delta_{k, \alpha, \sigma} c_{k, \alpha, \sigma}, \] (2)

where \( k = (k_x, k_y) \) indicates the wavenumber vector. Here, \( H_{\alpha, \beta, \sigma}(k) \) is the Hamiltonian of the SOI and given as the following formulas [13]:

\[ H_{\text{SOI}}^{B_{\alpha, \beta, \sigma}}(k) = i \lambda_{\text{SOI}} S_z \left( -i \left( -i \right)_{\alpha, \beta}^0 \left( -i \right)_{\alpha, \beta}^1 e^{-i k_x} \right) c_{k, \alpha, \sigma}^\dagger, \] \[ H_{\text{SOI}}^{B_{\alpha, \beta, \sigma}}(k) = i \lambda_{\text{SOI}} S_z \left( -i \left( -i \right)_{\alpha, \beta}^0 \left( -i \right)_{\alpha, \beta}^1 e^{-i k_x} \right) c_{k, \alpha, \sigma}^\dagger \] \[ H_{\text{SOI}}^{C_{\alpha, \sigma}}(k) = i \lambda_{\text{SOI}} S_z \left( -i \left( -i \right)_{\alpha, \sigma}^0 \left( -i \right)_{\alpha, \sigma}^1 e^{-i k_x} \right) c_{k, \alpha, \sigma}^\dagger \] \[ H_{\text{SOI}}^{C_{\alpha, \sigma}}(k) = i \lambda_{\text{SOI}} S_z \left( -i \left( -i \right)_{\alpha, \sigma}^0 \left( -i \right)_{\alpha, \sigma}^1 e^{-i k_x} \right) c_{k, \alpha, \sigma}^\dagger \]

where the spin \( S_z = \text{sgn}(\sigma)/2 \) and \( \lambda_{\text{SOI}} \) is the control parameter of the strength of the SOI.

Table of transfer integrals obtained from MLWFs.

\[ \delta = (\delta_{\alpha}, \delta_{\beta}) \alpha \beta \text{ Re } [\delta_{\alpha, \beta}] \text{ [meV]} \]

| \(-1, 0\) | A, B | 158.7 \( (t_{b1}) \) | \( t_{b2} \) |
| \( 0, 0 \) | A', B | 158.6 \( (t_{b1}) \) | \( t_{b2} \) |
| \( 0, -1 \) | A, C | 138.1 \( (t_{b1}) \) | \( t_{b2} \) |
| \( 0, 0 \) | A, B | 65.84 \( (t_{b3}) \) | \( t_{b4} \) |
| \( 0, 0 \) | A', A' | 51.08 \( (t_{a3}) \) | \( t_{a4} \) |
| \( 0, -1 \) | C, A | 21.92 \( (t_{a4}) \) | \( t_{a3} \) |
| \( -1, -1 \) | A, C | 18.65 \( (t_{b4}) \) | \( t_{b1} \) |
| \( 0, -1 \) | A', A | 16.31 \( (t_{a1}) \) | \( t_{a3} \) |
| \( 0, 0 \) | A | 14.19 \( (t_{b4}) \) | \( t_{b1} \) |
| \( 0, 0 \) | B | 10.12 | \( t_{b1} \) |
| \( 0, 0 \) | B, C | 9.864 \( (t_{a1}) \) | \( t_{a3} \) |
| \( -1, -1 \) | A' | 9.212 | \( t_{b1} \) |
| \( 0, -1 \) | A' | 6.737 | \( t_{a4} \) |
| \( -1, -1 \) | A, C | 6.600 | \( t_{a3} \) |
| \( 1, -1 \) | A | 6.575 | \( t_{a3} \) |
| \( -1, 0 \) | B | 5.065 | \( t_{a3} \) |
| \( -1, 0 \) | B, C | 5.010 | \( t_{a3} \) |

FIG. 2. (Color online) Schematic lattice structure of \( \alpha\)-(BETS)\(_2\)I\(_3\). The area of the unit cell is shown by the shaded blue region, and the area covered by the transfer integral from the original unit cell is shown by the pink shaded area.
$H_{\alpha,\beta,\sigma}(k)$ is diagonalized by using the eigenvector $d_{\alpha,\nu,\sigma}(k)$ about each $k$, and the energy eigenvalues $E_{\nu,\sigma}(k) = \langle \sum_{\alpha,\beta} d_{\alpha,\nu,\sigma}(k) H_{\alpha,\beta,\sigma}(k) d_{\beta,\nu,\sigma}(k) \rangle$ $(E_{1,\sigma}(k) > E_{2,\sigma}(k) > E_{3,\sigma}(k) > E_{4,\sigma}(k))$ are obtained. In the following, for convenience, we define $E_{\nu,\sigma}(k)$ as

$$E_{\nu,\sigma}(k) = \langle \sum_{\alpha,\beta} d_{\alpha,\nu,\sigma}^{*}(k) H_{\alpha,\beta,\sigma}(k) d_{\beta,\nu,\sigma}(k) \rangle - \mu,$$  (3)

where the chemical potential $\mu$ is determined to satisfy the $3/4$-filling. The charge density $\langle n_{\alpha,\sigma} \rangle$ for site $\alpha$ and spin $\sigma$ is calculated as $\langle n_{\alpha,\sigma} \rangle = \sum_{k,\nu} |d_{\alpha,\nu,\sigma}(k)|^{2} f(E_{\nu,\sigma}(k))$ using the Fermi distribution function $f(\xi) = [1 + \exp(\xi/T)]^{-1}$. The Berry curvature $B_{\nu,\sigma}(k)$ in band $\nu$ and spin $\sigma$ is obtained by

$$B_{\nu,\sigma}(k) = \sum_{\nu',\not=\nu} \frac{\epsilon^{\nu}_{\nu',\sigma}(k) \epsilon^{\nu}_{\nu',\sigma}(k)}{i(E_{\nu,\sigma}(k) - E_{\nu',\sigma}(k))^{2}} + c.c.,$$  (4)

where

$$\epsilon^{\nu}_{\nu',\sigma}(k) = \sum_{\alpha,\beta} d_{\alpha,\nu,\sigma}^{*}(k) \frac{\partial H_{\alpha,\beta,\sigma}(k)}{\partial k} d_{\beta,\nu',\sigma}(k),$$  (5)

and the Chern number is given as

$$C_{\nu} = \sum_{\sigma} C_{\nu,\sigma} = \frac{1}{2\pi} \sum_{\sigma} \int_{BZ} dk B_{\nu,\sigma}(k).$$  (6)

Here, $\int_{BZ}$ indicates that the integration is performed throughout the Brillouin zone.

### C. Conductivity

The optical conductivity in the clean limit is calculated using the Nakano-Kubo formula [13, 33–36] given as follows

$$\sigma(\omega, \theta) = \frac{1}{i \hbar \omega} \left[ Q^{R}(\omega, \theta) - Q^{R}(0, \theta) \right],$$  (7)

$$Q^{R}(\omega, \theta) = \frac{e^{2}}{N_{L}} \sum_{k,\nu,\nu',\sigma} |\epsilon_{\nu,\nu',\sigma}(k, \theta)|^{2} \chi^{0}_{\nu,\nu',\sigma}(k, \omega),$$  (8)

$$\chi^{0}_{\nu,\nu',\sigma}(k, \omega) = -\frac{f(E_{\nu,\sigma}(k)) - f(E_{\nu',\sigma}(k))}{E_{\nu,\sigma}(k) - E_{\nu',\sigma}(k) + i\omega + i0^{+}},$$  (9)

where $\theta^{+} = 5.0 \times 10^{-4}$ and the angle $\theta$ is measured from the $b$-axis direction and the projection in the $\theta$-direction of the velocity $v_{\nu,\nu',\sigma}(k, \theta)$ indicating the inter-band transition written as

$$v_{\nu,\nu',\sigma}(k, \theta) = \sum_{\alpha,\beta} d_{\alpha,\nu,\sigma}^{*}(k) v_{\alpha,\beta,\sigma}(k, \theta) d_{\beta,\nu',\sigma}(k).$$  (10)

Here, $v_{\alpha,\beta,\sigma}(k, \theta)$ is defined as

$$v_{\alpha,\beta,\sigma}(k, \theta) = \frac{1}{\hbar} \left( \frac{\partial H_{\alpha,\beta,\sigma}(k)}{\partial k_{x}} \cos \theta + \frac{\partial H_{\alpha,\beta,\sigma}(k)}{\partial k_{y}} \sin \theta \right).$$  (11)

In the limit of $\omega \to 0$ in Eq. (7), the DC conductivity is represented by the following equations:

$$\sigma(\theta) = \int d\omega \left( -\frac{d\Phi}{d\omega} \right) \Phi(\omega, \theta),$$  (12)

$$\Phi(\omega, \theta) = \frac{2e^{2}}{N_{L}} \sum_{k,\nu,\sigma} |v_{\nu,\sigma}(k, \theta)|^{2} \tau_{\nu,\sigma}(\omega, k) \times \delta(h\omega - E_{\nu,\sigma}(k)),$$  (13)

where the relaxation time $\tau_{\nu,\sigma}(\omega, k)$ is calculated within the $T$-matrix approximation using the perturbation theory for the green function. The impurity potential term is considered as

$$H_{imp} = \frac{V_{0}}{N_{L}} \sum_{i,\nu,\sigma} \sum_{q} e^{-i\mathbf{q} \cdot \mathbf{r}_{i}} c_{\mathbf{q}+k,\nu,\sigma}^{\dagger} c_{\mathbf{k},\nu,\sigma},$$  (14)

where $V_{0}$ is the intensity of the impurity potential and $\mathbf{r}_{i}$ is the coordinate of impurities. The imaginary part of the retarded self-energy $\text{Im} \Sigma_{\nu,\sigma}^{R}(\omega, k)$ gives the damping constant $\gamma_{\nu,\sigma}(\omega, k)$ and the $\tau_{\nu,\sigma}(\omega, k)$ is obtained as follows.

$$\gamma_{\nu,\sigma}(\omega, k) = \frac{\hbar}{2 \tau_{\nu,\sigma}(\omega, k)} = -\text{Im} \Sigma_{\nu,\sigma}^{R}(\omega, k)$$

$$= c_{imp} |d_{\alpha,\nu,\sigma}(k)|^{2} \left\{ \pi V_{0}^{2} N_{\sigma}(\omega) \right\}^{-1}. \quad (15)$$

Here, $c_{imp} \ll 1$ is the density of impurities and

$$N_{\sigma}(\omega) = \sum_{k,\alpha,\nu} |d_{\alpha,\nu,\sigma}(k)|^{2} \delta(h\omega - E_{\nu,\sigma}(k))$$

indicates the total density of states. In the following, the unit of conductivity is the universal conductivity $\sigma_{0} = 4e^{2}/\pi\hbar$, and the Drude term is subtracted from the optical conductivity.

### III. NUMERICAL RESULTS

#### A. Electronic state at finite temperature

In this subsection, the electronic state at a finite $T$ is investigated under the condition of $\lambda_{SOI} = 0$. Figure 3(a) shows the energy eigenvalues $E_{\nu,\sigma}(k)$ near the Fermi energy calculated using the tight-binding model ($\lambda_{U} = 0$). The conduction band ($\nu = 1$) and valence band ($\nu = 2$) form the Dirac point, and a type-I Dirac electron system that appears in the high-pressure phase of $\alpha$-(BEDT-TTF)$_{2}$I$_{3}$ is expected to be realized under ambient pressure in $\alpha$-(BETS)$_{2}$I$_{3}$.

Figure 3(b) displays the density of states $N_{\nu}(\omega)$ near the Fermi energy. The order of $N_{\nu}(\omega)$ magnitudes near the Fermi energy ($h\omega = 0$) is $N_{C}(\omega) > N_{A}(\omega) > N_{B}(\omega)$. The presence or absence of peaks of the van Hove singularity at each site is related to the property of the eigenvector $d_{\alpha,\nu,\sigma}(k)$. Figure 3(c) and (d) show the square
of the absolute value of the eigenvector $|d_{\alpha,\nu=1,\sigma=\uparrow}(k)|^2$ in $\alpha = B$ and $C$, respectively. The zero line appears in $|d_{\alpha,\nu=1,\sigma=\uparrow}(k)|^2$, which has almost the same wavenumber dependence as $\alpha$-(BEDT-TTF)$_2$I$_3$ [44]. Accordingly, the electronic state of $\alpha$-(BETS)$_2$I$_3$ in the high-$T$ phase under ambient pressure is similar to this, as demonstrated by $\alpha$-(BEDT-TTF)$_2$I$_3$ in the high-pressure phase.

Hereafter, we fixed $\lambda_U$ as 0.344, so that the phase transition $T$ matches to that observed in the experiments and investigated the effects of the on-site Coulomb interaction within the Hartree approximation. Figure 4(a) and (b) show the $T$-dependence of the charge density $\langle n_\alpha \rangle$ and magnetization density $\langle m_\alpha \rangle$ at each site in the unit cell. It is observed that with decreasing $T$ from $T = 0.006$, the charge densities hardly change, whereas the spin densities at $A$ and $A'$ sites change rapidly at the temperature $T_{C1} \approx 0.0032$. This result indicates that the system does not break the charge inversion symmetry, but breaks the spin inversion symmetry below $T_{C1}$. In the previous theoretical study [42], antiferromagnetism in the unit cell with vertical-stripe charge order was pointed out. However, the structure analysis in the experiments shows that the charge inversion symmetry is not broken in the low $T$ phase [27], and this result is consistent with our results. Figure 5(c) shows the $T$-dependence of the energy gap $\Delta$. $\Delta$ has a finite value at $T < T_{C1}$ owing to the occurrence of the spin-order phase transition.

Figure 5(a) and (b) show the energy bands at $T = 0.005 (> T_{C1})$ and $T = 0.001 (< T_{C1})$, respectively. In the spin-ordered state, $\Delta$ opens at the Dirac point, but the spin components of the energy bands do not split. On the other hand, Figs. 5(c) and (d) show the Berry curvatures $B_{\nu,\sigma}(k)$ at $\sigma = \uparrow$ and $\downarrow$. As shown in Fig. 5(c) and (d), the sign of $B_{\nu,\sigma}(k)$ inverts according to the degrees of freedom about spin $\sigma = \uparrow (+), \downarrow (-)$ and valley indices $\tau = +1(-1)$, where the right (left) Dirac cone corresponds to $\tau = +1(-1)$, respectively. Therefore, when such a spin-ordered massive Dirac electron (SMD) phase exists, it is expected that a unique spin-valley Hall effect appears. The intrinsic and side-jump terms of the valley-spin Hall conductivity on $\nu$-th band can be written in the form of

$$\sigma_{\nu,\sigma,\tau}^{\text{H, int}} = \frac{e^2}{h} \int dk f(E_{\nu,\sigma,\tau}(k)) B_{\nu,\sigma,\tau}(k),$$

and

$$\sigma_{\nu,\sigma,\tau}^{\text{H, side}} = -\frac{e^2}{h} \int dk B_{\nu,\sigma,\tau}(k) \frac{\partial f(E_{\nu,\sigma,\tau}(k))}{\partial E_{\nu,\sigma,\tau}(k)} \frac{\partial f(E_{\nu,\sigma,\tau}(k))}{\partial k},$$

where $E_{\nu,\sigma,\tau}(k)$ is the energy band at the wavenumber around the left ($\tau = -1$) or right ($\tau = +1$) Dirac point [46, 47]. The Hall conductivity $\sigma_{\nu,\sigma,\tau}^H$ is defined by $\sigma_{\nu,\sigma,\tau}^H = \sigma_{\nu,\sigma,\tau}^{\text{H, int}} + \sigma_{\nu,\sigma,\tau}^{\text{H, side}}$. The spin and valley Hall conductivities are calculated by $\sigma_{\nu,\sigma,\tau}^S = \sum_{\tau} \text{sgn}(\sigma) \sigma_{\nu,\sigma,\tau}^H$ and $\sigma_{\nu,\sigma}^V = \sum_{\tau} \text{sgn}(\tau) \sigma_{\nu,\sigma,\tau}^H$, respectively. Subsequently, the spin-valley Hall conductivity $\sigma_{\nu}^{SV}$ is obtained by $\sigma_{\nu}^{SV} = \sum_{\sigma,\tau} \text{sgn}(\sigma\tau) \sigma_{\nu,\sigma,\tau}^H$ and this value becomes finite in the

![Diagram](image-url)
FIG. 4. (Color online) T-dependence of (a) charge densities \( \langle n_\sigma \rangle \), (b) magnetization densities \( \langle m_\sigma \rangle \), and (c) energy gap \( \Delta \) at \( \lambda_U = 0.344 \). The black dotted line is plotted as a guide to show the temperature \( T = T_{C1} = 0.0032 \) where the spin-order phase transition occurs. Schematic diagrams of the magnetization density in the unit cell at \( T > T_{C1} \) and \( T < T_{C1} \) are shown in the inset of (c).

SMD phase. It is expected that the spin (valley) Hall effect depending on the degrees of freedom about valley (spin) appears [19].

FIG. 5. (Color online) Energy eigenvalues \( E_{\nu,\sigma}(k) \) for \( \nu = 1, 2 \) at (a) \( T = 0.005 (> T_{C1} = 0.0032) \) and (b) \( T = 0.001 (< T_{C1}) \), respectively. Berry curvatures \( B_{i,\sigma}(k) \) at (c) \( T = 0.005 (> T_{C1}) \) and (d) \( T = 0.001 (< T_{C1}) \), respectively.

B. Effects of SOI on the electronic state

In this subsection, the contribution of SOI to the electronic state at a finite \( T \) is examined. When only SOI is considered, i.e., \( \lambda_U = 0 \), a metallic band appears owing to the edge state, as shown in Appendix A. In this case, the insulating behavior at low \( T \) of \( \alpha \)-(BETS)\(_2\)I\(_3\) cannot be explained. In the following, we investigate the effects of SOI in the presence of Coulomb interactions. For simplicity, we set \( \lambda_{SOI} \neq 0 \) and \( \lambda_U = 0.344 \) as in the previous subsection.

Figure 6(a) and (b) show the \( T - \lambda_{SOI} \) phase diagram and the \( T \)-dependence of the energy gap \( \Delta \) at several \( \lambda_{SOI} \) values, respectively. Note that the value of the transfer integrals has the order of \( 10^{-1} \) eV (see Fig. 2), therefore, the magnitude of the SOI for \( \lambda_{SOI} = 0.01 \) is approximately 1 meV. When \( \lambda_{SOI} > 0 \) and \( T > T_{C1} = 0.0032 \), the value of \( \Delta \) is finite, and the system becomes a topological insulator (TI) as described below. It should be noted that for large \( \lambda_{SOI} (\lambda_{SOI} > 0.015) \), \( \Delta \) exhibits a \( V \)-shaped \( T \)-dependence at \( T < T_{C1} \); i.e., \( \Delta \) decreases to zero in \( T_{C2} < T < T_{C1} \), becomes zero at \( T = T_{C2} \), and is finite again in \( T < T_{C2} \).

Figure 7 shows the energy band \( E_{i,\sigma}(k) \) near the Fermi energy and Berry curvature \( B_{i,\sigma}(k) \) at \( (\lambda_U, \lambda_{SOI}) = (0.344, 0.04) \) in the following three cases: \( T = 0.005 > T_{C1} \) [Figs. 7(a) and (d)], \( T = T_{C2} = 0.0028 \) [Figs. 7(b) and (e)], and \( T = 0.001 < T_{C2} \) [Figs. 7(c) and (f)]. First, when \( T = 0.005 > T_{C1} \), the time-reversal symmetry exists, and the SOI gap opens at the Dirac point [Fig. 7(a)]. In this case, the sign of \( B_{i,\sigma}(k) \) is inverted according to the spin components, as illustrated in Fig. 7(d), and the system becomes the TI because the spin Chern number defined by \( Ch_S \equiv Ch_+ - Ch_- \) becomes 1.
FIG. 6. (Color online) (a) $\lambda_{\text{SOI}}$-$T$ phase diagram. SMD and a topological insulator (TI) indicate the SMD and topological insulator phases, respectively. Below $T_{C2}$, the spin Chern number is zero, so $\Delta$ closes once. The blue dashed line shows the points at $\Delta = 0$ in the SMD phase. (b) $T$-dependence of the energy gap $\Delta$ at several values of $\lambda_{\text{SOI}}$ ($\lambda_U = 0.344$ fixed).

Thereafter, in $T_{C2} < T < T_{C1}$ [Figs. 7(b) and (e)], the time-reversal symmetry is broken. Hence, $B_{1,\sigma}(k)$ has peaks with different magnitudes according to the left and right valleys, and the spin Chern number has a real finite value. At $T = T_{C2}$, the sign of $B_{1,\sigma}(k)$ in one valley is inverted corresponding to $\Delta = 0$ at one valley. Finally, for $T < T_{C2}$, gaps of different sizes are opened [Fig. 7(c)]. These behaviors in $T < T_{C1}$ originate from the competition between the contributions of the spin order and SOI [59, 50]. Moreover, as the sign of the $B_{1,\sigma}(k)$ in one valley has been already inverted at $T = T_{C2}$, the spin Chern number is zero in this region [Figs. 7(c) and (f)].

C. DC and optical conductivities

In this subsection, $\lambda_U$ is fixed at 0.344 as in the previous section, and the $T$ and SOI effects on the DC and optical conductivities are investigated.

The $T$-dependence of the $a$-axis DC resistivity $\rho(\theta = \pi/2)/\rho_0$ for $\lambda_U = 0$, 0.344 and $\lambda_{\text{SOI}} = 0$, 0.04 is plotted in Fig. 8(a) as solid lines. When only the SOI is considered, as indicated by the solid lines at $\lambda_U = 0$ and $\lambda_{\text{SOI}} = 0.04$, the system becomes the TI, in which the SOI gap is opened at the Dirac point and $\rho(\theta = \pi/2)/\rho_0$ increases at quite low $T$ as $T$ is decreased. Moreover, when considering the on-site Coulomb interaction, $\rho(\theta = \pi/2)/\rho_0$ increases below the phase transition temperature owing to the spin order gap. However, as a result of the finite energy width owing to $-\partial f/\partial \omega$ and the gentle function, such as $\sqrt{T}$ of the spin order gap [see Eq. (12) and Fig. 4(c)], $\rho(\theta = \pi/2)/\rho_0$ does not increase suddenly near the SMD phase transition temperature $T_{C1} = 0.0032$. When both the on-site Coulomb interaction $U$ and SOI are taken into account, the spin order gap is suppressed by the SOI. Thus, $\rho(\theta = \pi/2)/\rho_0$ is suppressed at low $T$.

Here, note that in Fig. 8(a), we also plot the $T$-dependence of $\rho(\theta = \pi/2)/\rho_0$ at $\lambda_U = 0$ for $\lambda_{\text{SOI}} = 0.08$ (dashed line) and $\lambda_{\text{SOI}} = 0.16$ (dotted chain line) obtained by the calculation using the cylindrical boundary condition. When only the SOI exists in the system with edge, the helical edge state appears, and $\rho(\theta = \pi/2)/\rho_0$ saturates, as shown by these lines. Owing to the edge conduction, the value of $\rho(\theta = \pi/2)/\rho_0$ has a finite value at frequency $\omega = 0$. At $\omega > 0$, the spin Chern number has a real value of 0, whereas that with the SOI remains zero until $\omega$ reaches approximately 10 meV when $\lambda_{\text{SOI}} = 0.16$. Therefore, we cannot explain the divergent increase of the DC resistivity observed in the experiment of $\alpha$-(BETS)$_2$I$_3$ when considering the SOI alone, and the edge state is robust (See Appendix A for details).

Figures 8(b) and (c) represent the in-plane magnetic field $B$-dependence of the energy gap $\Delta$ and $\rho(\theta = \pi/2)/\rho_0$ for several values of ($\lambda_U, \lambda_{\text{SOI}}$). The energy band is split by $-\text{sgn}(\sigma)\mu_B B$ (see Eq. (1)). Thus, $\Delta(B)$ monotonically decreases as $B$ is increased when calculating without edges. As a result, in Fig. 8(c) and the solid line in its inset, $\rho(\theta = \pi/2)/\rho_0$ decreases as $B$ is increased. This result is consistent with the negative magnetoresistance observed in $\alpha$-(BETS)$_2$I$_3$ [57]. However, when considering the edge in the system, as shown by the dashed line and dotted chain line in the inset, $\rho(\theta = \pi/2)/\rho_0$ decreases much more and nearly constant, owing to the edge conduction. Hence, we can not explain the negative magnetoresistance when considering the SOI alone.

Figures 8(a) and (b) show the real part of the optical conductivity along the $b$-axis ($\theta = 0$) direction $\text{Re}[\sigma(\omega, \theta = 0)]/\sigma_0$ for $\lambda_{\text{SOI}} = 0$ and $\lambda_{\text{SOI}} = 0.04$ around $T = T_{C1}$. $\text{Re}[\sigma(\omega, \theta = 0)]/\sigma_0$ shows clear differences depending on the presence or absence of the SOI. In $T = 0.005 > T_{C1}$, $\text{Re}[\sigma(\omega, \theta = 0)]/\sigma_0$ without the SOI has a finite value at frequency $\omega = 0$, whereas that with the SOI remains zero until $\omega$ reaches approximately 960 GHz because of the finite SOI gap. In $T < T_{C1}$, $\text{Re}[\sigma(\omega, \theta = 0)]/\sigma_0$ without the SOI becomes zero when the value of $\omega$ is smaller than the spin order gap $\Delta$, and increases abruptly in $\omega > \Delta$. However, when the SOI is considered, $\Delta$ exhibits a V-shaped $T$-dependence owing to the competition between the SMD and SOI, as indicated in Fig. 8(b). As a result, $\text{Re}[\sigma(\omega, \theta = 0)]/\sigma_0$...
increases abruptly by two times corresponding to the different $\Delta s$ in the left and right valleys. Furthermore, at $T = T_{C2}$, $\text{Re}[\sigma(\omega, \theta = 0)]/\sigma_0$ with the SOI has a finite value because $\Delta$ in the right valley is closed.

Figure 10(a) shows the $T$-dependence of the DC conductivity $\sigma(\theta)$ along the $b$-axis ($\theta = 0$) and $a$-axis ($\theta = \pi/2$) directions. $\sigma(\theta)$ decreases exponentially in $T < T_{C1}$, but a clear discontinuous jump does not appear at $T = T_{C1}$ because $\sigma(\theta)$ is influenced by the energy width of $-df/d\omega$, as indicated in Eq. (12). Figure 10(b) shows the real part of the optical conductivity $\text{Re}[\sigma(\omega = 24\text{GHz}, \theta)]$ in the absence of the SOI. As $T$ is decreased, in contrast to the DC conductivity, $\text{Re}[\sigma(\omega = 24\text{GHz}, \theta)]$ increases gradually towards $T = T_{C1}$ and decreases suddenly in $T < T_{C1}$. The optical conductivity calculated by Eqs. (7) to (9) is considered as a direct transition in the interband at the same wavenumber and frequency $\omega$. Therefore, when $\Delta$ appears in $T < T_{C1}$, the possible direct transition at the energy $\omega = 24\text{GHz} \simeq 1\text{ eV}$ disappears and $\text{Re}[\sigma(\omega = 24\text{GHz}, \theta)]$ decreases sharply. Finally, the $T$-dependence of $\text{Re}[\sigma(\omega)]$ in the presence of the SOI for several frequencies is plotted in Fig. 10(c). $\text{Re}[\sigma(\omega, \theta)]$ with the SOI has a peak at $T = T_{C2}$, where the gap of the right valley is closed.

IV. SUMMARY AND DISCUSSION

In this study, first, a Hubbard model was constructed as an effective model in the two-dimensional conduction plane of $\alpha$-(BETS)$_2$I$_3$ based on the synchrotron X-ray diffraction data at 30K under ambient pressure. We investigated the effects of the on-site Coulomb interaction $U$ and SOI at a finite temperature $T$ within the Hartree and $T$-matrix approximations to clarify the insulating behavior observed in $\alpha$-(BETS)$_2$I$_3$ in the low $T$ region.

We found the phase transition between the weak TI phase and SMD phase as a possible cause of the insulating behavior in the low $T$ region. In the SMD phase, the time-reversal symmetry is broken, but the spatial inversion and translational symmetries are conserved. The SMD phase is not a conventional spin-ordered state, but exhibits the physical properties that reflect the wave functions of Dirac electrons. It is expected that the spin-valley Hall effect occurs because the sign of the Berry curvature is reversed depending on the freedoms of the spin and valley. The SMD has the energy gap at the Dirac points, whereas the energy band in the bulk does not split in the spin degrees of freedom. The energy gaps of different sizes open in the left and right valleys owing to the competition between the SMD and SOI, as shown in the honeycomb lattice system in previous studies [49-50]. Next, we calculated the $T$- and $B$-dependences of the...
DC resistivity. When considering the SOI alone and the system has edges, the helical edge state appears in the energy gap, and the DC resistivity saturates toward low temperature. The negative magnetoresistance does not appear in this case. On the other hand, in the SMD phase, the DC resistivity increases divergently as $T$ is decreased, and there is no noticeable change near the SMD phase transition temperature $T_{C1}$. The DC resistivity exhibits the negative magnetoresistance, owing to the Zeeman split of the energy band. Finally, it was shown that the $T$-dependence of the microwave (about $10^{-4}$ eV) conductivity shows clear changes at the vicinity of $T = T_{C1}$.

In recent magnetoconductivity measurements, a positive magnetoresistance and a negative magnetoresistance were observed at $T > 50$ K under in-plane and perpendicular magnetic fields, respectively. This is the characteris-
K. The TI-SMD transition shown in the present paper is consistent with the electric transport properties and the structure analysis observed in α-(BETS)$_2$I$_3$ [26, 27, 57]. The existence of the TI-SMD transition can be directly confirmed by the microwave conductivity.

The detailed analysis of the SMD phase and physical quantities of NMR are to be reported in another paper. The nonmonotonic $T$-dependence on the Seebeck coefficient of α-(BETS)$_2$I$_3$ is also to be investigated in the future. When the time-reversal symmetry is broken by the SMD phase, the helical edge state due to the SOI is not protected, and the energy gap can open  [58, 60]. Transport properties in the presence of impurities on the edges are to be investigated in the SMD phase with the SOI. The problem of studying the effects of long-range Coulomb interaction remains unsolved [61].

ACKNOWLEDGMENTS

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Appendix A: Electrical resistivity if only spin-orbit interaction is considered

In this appendix, we show the results of the analysis of the DC resistivity of α-(BETS)$_2$I$_3$ when only the SOI is considered. To investigate the effects of the edge state on the DC resistivity, we impose the cylindrical boundary condition on the system, as illustrated in Fig. A.1(a), and consider the SOI term introduced in the main text and Ref. [13]. The Fourier inverse transform is performed in the $a$-axial direction and represented by the wavenumber $k_a$, whereas the real space structure in the $b$-axial direction is labeled by the coordinates of the unit cell $i_b$.

As a result of the numerical diagonalization, we obtain 240 energy eigenvalues $E_{\nu,\sigma}(k_a)$ ($E_{1,\sigma}(k_a) < E_{2,\sigma}(k_a) < \cdots < E_{240,\sigma}(k_a)$) and the unitary matrix $d_{i_b,\alpha,\nu,\sigma}(k_a)$. Here, we introduce the spectral weight in each unit cell defined as

$$
\rho(i_b, k_a, \omega) = \sum_{\nu, \sigma} |d_{i_b, \alpha, \nu, \sigma}(k_a)|^2 \times \delta(\hbar \omega - E_{\nu, \sigma}(k_a)).
$$

(A1)

FIG. 10. (Color online) $T$-dependence of (a) the DC conductivity $\sigma(\theta)/\sigma_0$, (b) real part of the optical conductivity $\text{Re}[\sigma(\omega = 24\text{GHz}, \theta)]/\sigma_0$ at $\lambda_{\text{SOI}} = 0$, and (c) real part of the optical conductivity $\text{Re}[\sigma(\omega, \theta = 0)]/\sigma_0$ at $\lambda_{\text{SOI}} = 0.04$ in units of the universal conductivity $\sigma_0 = 4e^2/\pi^2\hbar$ for fixed $\omega = 24, 960, 2400$ GHz.

The results indicate that the electronic states change around 50 K. The TI-SMD transition shown in the present paper is consistent with the electric transport properties and the structure analysis observed in α-(BETS)$_2$I$_3$ [26, 27, 57]. The existence of the TI-SMD transition can be directly confirmed by the microwave conductivity.

The detailed analysis of the SMD phase and physical quantities of NMR are to be reported in another paper. The nonmonotonic $T$-dependence on the Seebeck coefficient of α-(BETS)$_2$I$_3$ is also to be investigated in the future. When the time-reversal symmetry is broken by the SMD phase, the helical edge state due to the SOI is not protected, and the energy gap can open  [58, 60]. Transport properties in the presence of impurities on the edges are to be investigated in the SMD phase with the SOI. The problem of studying the effects of long-range Coulomb interaction remains unsolved [61].

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$$
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$$

(A1)
Figures A.1(b) and (c) describe the $\rho^S(i_b, k_a, \omega)$ for $i_b = 30$ (bulk) and $i_b = 1$ (left edge) for the parameters of $(T, \lambda_U, \lambda_{\text{SOI}}) = (0, 0, 0.08)$ (when considering only the SOI). Although $\rho^S(30, k_a, \omega)$ in Fig. A.1(b) is spread weakly over the whole energy range, $\rho^S(1, k_a, \omega)$ is quite large near the Fermi energy, as shown in Fig. A.1(c), owing to the existence of a helical edge state protected by the time-reversal symmetry in the system. Therefore, the conduction channel of this edge state becomes dominant at $T = 0$.

Figure A.2 shows the $T$-dependence of the DC resistivity for $\lambda_{\text{SOI}} = 0, 0.04, 0.08,$ and $0.16$. When the SOI is considered in the bulk, as calculated in the main text, the energy gap opens at the Dirac point, and the system becomes an insulator. However, when considering the SOI in a system with edges, the helical edge state appears in the vicinity of the Fermi energy owing to the band crossing between the up and down spin bands, so that it does not actually become an insulator, and the DC resistivity with the SOI is quite suppressed as compared to that without the SOI. Note that the slight increase in the resistivity at $\lambda_{\text{SOI}} = 0$ near the lowest $T$ results from the energy gap associated with the finite-size effect.

FIG. A.2. (Color online) $T$-dependence of the DC resistivity along the $a$-axis ($\theta = \pi/2$) in units of the reciprocal of the universal conductivity $\sigma_0$ at $\lambda_U = 0$ for $\lambda_{\text{SOI}} = 0, 0.04, 0.08,$ and $0.16$. 

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