Emergence of Dirac Electron Pair in Charge Ordered State of Organic Conductor
\(\alpha-(BEDT-TTF)_2I_3\)

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We re-examine the band structure of the stripe charge ordered state of \(\alpha-(BEDT-TTF)_2I_3\) under pressure by using an extended Hubbard model within the Hartree mean-field theory. By increasing pressure, we find a topological transition from a conventional insulator with a single-minimum in the dispersion relation at the M-point in the Brillouin zone, towards a new phase which exhibits a double-minimum. This transition is characterized by the appearance of a pair of Dirac electrons with a finite mass. Using the Luttinger-Kohn representation at the M-point, it is shown that such a variation of the band structure can be described by an effective \(2 \times 2\) low energy Hamiltonian with a single driving parameter. The topological nature of this transition is confirmed by the calculation of the Berry curvature which vanishes in the conventional phase and has a double peak structure with opposite signs in the new phase. We compare the structure of this transition with a simpler situation which occurs in two-component systems, like boron-nitride.

I. INTRODUCTION

Two-dimensional molecular conductor \(\alpha-(BEDT-TTF)_2I_3\) has brought much interest by the variety of electronic states, such as an insulating stripe Charge Ordered (CO) state, a superconducting state in the presence of charge ordering, and a Zero Gap State (ZGS) with a massless Dirac spectrum\(^3\).

The stripe CO state\(^4,5,6\), which was suggested to explain an insulating phase below 135K at ambient pressure, was confirmed by NMR experiment\(^7\). The superconducting state, found under uniaxial pressure along stacking axis (\(a\)-axis)\(^8\), was investigated theoretically by using an extended Hubbard model\(^9\). A narrow gap state was suggested by Kajita to explain anomalous increase of Hall coefficient at high pressures\(^10\). The existence of massless Dirac electrons was predicted theoretically\(^11\) based on a tight-binding calculation using the transfer energies of ref. \(^12\). Thus it has been revealed that this narrow gap state is indeed a zero gap state, as also confirmed by a first principle calculation\(^13,14\). In this state, the energy spectrum near the Fermi energy consists of two cones described by a tilted Weyl equation for massless Dirac electrons\(^15,16\). This has been confirmed by a comparison between the theoretical and experimental results for the temperature dependence of the Hall coefficient\(^17,18\) and the angular dependence of the magnetoresistance\(^19,20\).

The two tilted Dirac cones were predicted to merge and disappear at the \(\Gamma\) point under extremely high pressure\(^21\). This merging transition was also studied in the context of deformed graphene with a variation of transfer integrals, and was described using a generalized two-component Hamiltonian for Dirac electrons. This effective Hamiltonian describes the merging of two Dirac cones and the opening of a gap at the transition\(^20,21,22\).

In the present paper, we show that another type of transition may also occur in the CO state of \(\alpha-(BEDT-TTF)_2I_3\). In this state, the energy spectrum exhibits a gap between the conduction and valence bands at the M-point, with a single minimum. By increasing pressure, it is demonstrated that new electronic phases emerge in the CO state with a double-minimum structure in the vicinity of the M-point. This double-minimum corresponds to the emergence of a pair of massive Dirac electrons, whose study is the main goal of this paper. This qualitative change of the band structure is described by an effective Hamiltonian with a single driving parameter.

The paper is organized as follows. In section 2, a tight binding model for \(\alpha-(BEDT-TTF)_2I_3\) is described where the repulsive interactions between molecules are treated within Hartree mean-field theory. When varying pressure and the intersite repulsive interaction, a new phase diagram is obtained, and is described in section 3, where new phases characterized by a Dirac electron pair are obtained in the CO state. In section 4, using the Luttinger-Kohn representation at the M-point of the Brillouin zone, we construct a \(2 \times 2\) effective Hamiltonian to describe the low energy band structure near this point, and the emergence of a pair of Dirac points. The general structure of this effective Hamiltonian also describes the emergence of Dirac points in a simple toy-model related to the physics of boron nitride (BN). In section 5, we show that this Dirac pair is revealed by two sharp peaks of opposite sign in the Berry curvature\(^23\). Then each Dirac point is characterized by an appropriate Berry phase calculated by using a method already applied to the physics of Dirac points in boron nitride\(^24\). The last section is devoted to summary and discussion.
The model used to describe the two-dimensional electronic system in α-(BEDT-TTF)$_2$I$_3$ is shown in Fig. 1. The unit cell consists of four BEDT-TTF molecules A, A', B and C with seven transfer energies. The nearest neighbor repulsive interactions are given by $V_a$ and $V_b$. The α- and β-axis in the conventional notation correspond to the y- and x-axis in the present paper.

II. TIGHT-BINDING MODEL FOR α-(BEDT-TTF)$_2$I$_3$

A. The Hamiltonian

The transfer energies $t_{X}$ and the coefficients $K_X$ are obtained from the numerical data at $P_a = 0$ kbar and at $P_a = 2$ kbar, such that $t_{a1}(0) = -0.28$, $t_{a2}(0) = 0.048$, $t_{a3}(0) = -0.020$, $t_{b1}(0) = 0.123$, $t_{b2}(0) = 0.140$, $t_{b3}(0) = -0.062$, $t_{b4}(0) = -0.025$, [eV] and $K_{a1} = 0.089$, $K_{a2} = 0.167$, $K_{a3} = -0.025$, $K_{b1} = 0.011$, $K_{b2} = 0.032$, $K_{b3} = 0$ [eV/kbar]. We use the parameter $U = 0.4$ and the $V_{a,b}$ take two different values, $V_a = 0.17 \sim 0.18$ eV along the stacking direction, and $V_b = 0.05$ eV along the perpendicular direction. With this choice of parameters, we obtain a pressure dependence of the electronic spectrum consistent with experimental results. Moreover the results of the mean-field theory coincide with the experimental results for the charge disproportionation in the ZGS and the charge ordering in the CO phase. By "charge disproportionation", we mean that the A, B and C sites in a unit cell are inequivalent but the inversion symmetry between A and A' remains. By "charge ordered" state, we mean that the inversion symmetry between A and A' is broken. Throughout the paper, $\hbar$ and the lattice constant $a$ are taken as unity.

B. Hartree mean-field theory

As in previous work, we restrict ourselves to a Hartree mean field theory which implies that the mean field Hamiltonian is diagonal in spin space. In addition we only consider mean field solutions that do not break the underlying Bravais lattice symmetry; this further implies that for a given spin $\sigma$ the mean field Hamiltonian $H_{MF}(k)$ is a $4 \times 4$ matrix in the Bloch-basis $a_{k\alpha\sigma}$. In second quantized form, the mean-field Hamiltonian reads:

$$H_{MF} = \int_{BZ} \frac{dk}{(2\pi)^2} \sum_{\alpha} H_{\sigma}(k),$$

$$H_{\sigma}(k) = \sum_{\alpha} \epsilon_{\alpha\beta}(k)a_{k\alpha\sigma}^d a_{k\beta\sigma},$$

$$\epsilon_{\alpha\beta}(k) = I_{\alpha\sigma} \delta_{\alpha\beta} + \epsilon_{\alpha}(k),$$

$$I_{\sigma} = U_{\sigma} \langle n_{\sigma^-} \rangle + \sum_{\beta'\sigma'} V_{\beta'\sigma'} \langle n_{\beta'\sigma'} \rangle,$$

$$\epsilon_{\alpha}(k) = \sum_{\delta} t_{\alpha\delta} e^{ik\delta},$$

where $\langle n_{\sigma\alpha} \rangle = \langle a_{\alpha\sigma}^d a_{\alpha\sigma} \rangle$ is the mean field local density of spin $\sigma$ for the molecular state $\alpha$ in unit cell $i$; $\langle n_{\sigma\alpha} \rangle$ is assumed to be independent of the unit cell $i$. $\delta$ denotes the vectors connecting nearest neighbors sites. The spin dependent site potential $I_{\alpha\sigma}$ represents the Hartree mean field which comes from the on-site Hubbard $U$ and nearest-neighbor Coulomb interactions $V_a$, $V_b$. 

\[ t_X(P_a) = t_X(0)(1 + K_X P_a). \]
Note that off-diagonal elements $\epsilon_{\alpha\beta}(k)$ are independent on spin index $\sigma$ and on interaction strength but depend on $k$ and $P_a$. Moreover these off-diagonal elements $\epsilon_{\alpha\beta}(k)$ have the time reversal symmetry $\epsilon^*_{\alpha\beta}(k) = \epsilon_{\alpha\beta}(-k)$. In this representation, only the self-consistent diagonal elements may explicitly exhibit the breaking of time reversal and/or inversion symmetries.

To obtain the mean-field phase diagram, the Hamiltonian is diagonalized numerically for a given $k$ in each spin subspace, according to

$$\sum_{\beta=1}^{4} \xi_{\alpha\beta\sigma}(k) d_{\beta\gamma\sigma}(k) = \xi_{\gamma\sigma}(k) d_{\alpha\gamma\sigma}(k), \quad (2.8)$$

where $\xi_{\gamma\sigma}$ are the eigenenergies ordered such that, $\xi_{1\sigma}(k) > \xi_{2\sigma}(k) > \xi_{3\sigma}(k) > \xi_{4\sigma}(k)$ ($\gamma = 1, 2, 3, 4$ is the band index), and $d_{\alpha\gamma\sigma}(k)$ are the corresponding eigenvectors. In terms of eq. (2.8), the average number $\langle n_{\alpha\sigma} \rangle$ of electrons with spin $\sigma$ on $\alpha$ type of site is expressed as

$$\langle n_{\alpha\sigma} \rangle = \int_{BZ} \frac{dk}{(2\pi)^2} \sum_{\gamma=1}^{4} d_{\alpha\gamma\sigma}(k) d_{\alpha\gamma\sigma}(k) n_F(\xi_{\gamma\sigma}(k)), \quad (2.9)$$

where $n_F(\xi_{\gamma\sigma}(k)) = 1/\{\exp[(\xi_{\gamma\sigma}(k) - \mu)/T] + 1\}$ is the Fermi factor at temperature $T$ ($k_B = 1$) and $\mu$ is the chemical potential determined from the condition of a 3/4 filled system:

$$\frac{3}{4} = \frac{1}{8} \sum_{\alpha\sigma} \langle n_{\alpha\sigma} \rangle = \frac{1}{8} \int_{BZ} \frac{dk}{(2\pi)^2} \sum_{\gamma\sigma} n_F(\xi_{\gamma\sigma}(k)). \quad (2.10)$$

Equation (2.9) constitutes the self-consistent relation for the mean field quantities $\langle n_{\alpha\sigma} \rangle$. A high accuracy in fulfilling these constraints requires a very fine mesh of the reciprocal space which constitutes the main numerical difficulty. When convergence is achieved, the mean field energy per unit cell of a given state is then calculated as

$$E_{MF} = \int_{BZ} \frac{dk}{(2\pi)^2} \sum_{\gamma} n_F(\xi_{\gamma\sigma}(k))\xi_{\gamma\sigma}(k) - \sum_{\alpha} U_{\alpha} \langle n_{\alpha\uparrow} \rangle \langle n_{\alpha\downarrow} \rangle - \sum_{(\alpha,\beta),\sigma,\sigma'} V_{\alpha\beta} \langle n_{\alpha\sigma} \rangle \langle n_{\beta\sigma'} \rangle. \quad (2.11)$$

The ground state is obtained from minimization of $E_{MF}$.

### III. PHASE DIAGRAM

The $(P_a, V_a)$ phase diagram obtained from the self-consistent Hartree approximation described above is presented in Fig. 2. $P_a$ is the uniaxial pressure along the $a$-axis and $V_a$ is the repulsive interaction between nearest-neighbor sites along the $a$-axis. This figure exhibits three

![FIG. 2: The phase diagram on the uniaxial pressure along a-axis ($P_a$ [kbar]) and the repulsive interaction between nearest-neighbor sites along $a$-axis ($V_a$ [eV]) where $U = 0.4$ eV, and $V_b = 0.05$ eV. The CO and COM denote insulating and metallic states respectively. In addition to the phase (I) of the previous work, there exists a new phase (II), which is characterized by a double minimum in the up spin band.](image)

![FIG. 3: Schematic behavior of the energy spectrum close to the Fermi energy (horizontal line), in the different sub-phases of the CO phase: (a)CO(I), (b)CO(II), (c)COM(I), (d)COM(II). The red and blue bands correspond respectively to $\uparrow$ and $\downarrow$ spins. The center of the horizontal line corresponds to the M point ($k_M = (\pi, \pm \pi)$).](image)
transition lines. Two of them (the continuous and dashed lines) were already found in previous works \(^{11,13}\) and the third one (dotted line) is a novel transition that constitutes the main object of this work. The schematic band spectrum close to the Fermi surface is shown in Fig. 3 and is discussed below. Before describing this last transition in more details, we remind the qualitative picture associated to the two other transitions.

In Fig. 2, the solid line marks a charge ordering transition resulting from the simultaneous breaking of time reversal and inversion symmetries. It separates the charge ordered metallic state (COM) from the Zero Gap state (ZGS). In the ZGS phase, energy bands are spin degenerate and inversion symmetry is preserved such that a conduction band \(\xi_{\uparrow}\sigma(k)\) and valence band \(\xi_{\downarrow}\sigma(k)\) touch each other at two Fermi points (Dirac points) \(k_{\pm}\). These Dirac points move in the Brillouin zone when varying parameters \(P_a\) and \(V_a\). Around each point \(k_{\pm}\), the dispersion relation is linear. In addition there is a large anisotropy in the Fermi velocities (a factor \(\sim 10\) between the highest and lowest velocity values \(^{11,13}\) ), this appears as a tilt in the Dirac cones.\(^{11,13}\) Coming from this high pressure ZGS phase and traversing the continuous line, the inversion symmetry is spontaneously broken by the electronic interactions. As consequence, for a given spin \(\sigma\), a gap opens between bands \(\xi_{\uparrow}\sigma(k)\) and \(\xi_{\downarrow}\sigma(k)\), leading a priori to an insulating phase. However the time reversal symmetry is also spontaneously broken by the interactions so that the degeneracy between \(\uparrow\) and \(\downarrow\) bands is now lifted. Therefore the simultaneous breaking of time reversal and inversion symmetries results in a semi-metallic phase (COM) with band overlap leading to small electrons and holes pockets of opposite spin orientations (Fig. 3).

In striking contrast with the continuous line, the dashed line marks a metal-insulator transition from a charge ordered metallic (COM) phase to a charge ordered insulator (CO) without breaking of any symmetry. In traversing this transition line, the dispersion relations of the four energy bands \(\xi_{\uparrow}\sigma(k)\) and \(\xi_{\downarrow}\sigma(k)\) stay similar but their relative positions to the Fermi level vary in such a way that, in the CO phase, the Fermi level falls in a true charge gap that separates a valence band and a conduction band of equal spin orientation (Fig. 4). We stress that, at the metal-insulator transition, the electron density \(\langle n_{\alpha\sigma}\rangle\) and therefore the resulting mean field potential \(I_{\alpha\sigma}\) exhibit a cusp on respective sites.

In this work, by a more detailed analysis of the COM and CO phases, we find a new topological transition (dotted line in Fig. 2) that further splits each of the COM and CO phase into two phases: COM(II) and CO(II). The electronic spectrum in each phase is represented schematically in Fig. 3. The band structure of both \(\uparrow\) band and \(\downarrow\) band in CO (II) state is explained in Appendix A. This transition concerns a modification in the two energy bands close to the Fermi energy. They correspond to a given value of the spin, that we choose to denote by \(\uparrow\). The two other bands (\(\downarrow\)) are not concerned by this transition. As illustrated in Fig. 4 the transition from CO(I) (Fig. 4a) to CO(II) (Fig. 4b) is characterized by a change in the form of the dispersion relation of the valence and conduction bands. In the CO(I) phase, there is a single minimum of charge gap whose position in \(k\) space stays at the M-point \(k_M = (\pi, \pm \pi)\), independently of the parameters \(P_a, V_a\). Around this point \(k_M\), valence and conduction bands disperse quadratically. In the CO(II) phase, the single charge gap separates in two points at symmetrical positions (For example, \(k_{\pm} = (0.95, -0.71)\pi\) for \(P_a = 5.4\) kbar and \(V_a = 0.18\) eV) from the M-point, and \(k_{\pm}\) move continuously with parameters \(P_a, V_a\). There is now a double-well structure in the dispersion relation. The aim of this work is to describe this topological transition in the framework of a universal Luttinger-Kohn Hamiltonian.

As a last remark concerning the phase diagram of Fig. 2 we note an intersection of the dashed line and the dotted line, at the critical point of coordinates \((P_a^*, V_a^*)\) =\((4.75\) kbar, \(0.175\) eV). Such crossing implies the proximity of several minima of the total energy in its neighborhood. Therefore in this region of the phase diagram one may need to go beyond Hartree mean-field approximation. This might be an important issue since this critical point \(P_a^*, V_a^*\) is in a region of parameters value that is reachable experimentally.

IV. TOPOLOGICAL TRANSITION AROUND THE M-POINT

A. Low energy \(2 \times 2\) effective Hamiltonian at the M-point

In order to analyze the band structure in the CO state, we expand the mean-field Hamiltonian up to the second order in momentum around the M-point, writing \(k = k_M + \mathbf{q}\). The Hamiltonian is diagonal in spin space and it has the \(4 \times 4\) structure, for each spin direction \(\sigma\):

\[
H_{\alpha\beta\sigma}(k) = H_{\alpha\beta\sigma}(k_M) + q^\mu \partial_\mu H_{\alpha\beta\sigma}(k)|_{k_M} + \frac{1}{2} q^\mu q^\nu \partial_\mu \partial_\nu H_{\alpha\beta\sigma}(k)|_{k_M} + \delta H_{\alpha\beta\sigma}(\mathbf{q}).
\]

We wish to restrict ourselves to the two bands which are close to the Fermi level (\(\sigma = \uparrow\)). This can be done by using the Luttinger-Kohn representation\(^{12}\) at the M-point, and we obtain an effective \(2 \times 2\) Hamiltonian with the matrix elements \(\langle \nu, \nu'\rangle = 1, 2\) up to \(O(q^2)\) \(\Longrightarrow\):

\[
H_{\nu,\nu'} = \xi_{\nu}^0 \delta_{\nu,\nu'} + \langle \nu | H(\mathbf{q}) | \nu' \rangle + \frac{1}{2} \sum_{\nu'' = 3, 4} \langle \nu | \delta H(\mathbf{q}) | \nu'' \rangle \langle \nu'' | H(\mathbf{q}) | \nu' \rangle \left( \frac{1}{\xi_{\nu''}^0 - \xi_{\nu}^0} + \frac{1}{\xi_{\nu}^0 - \xi_{\nu''}^0} \right),
\]

where \(\xi_{\nu}^0\) and \(\langle \nu \rangle\) are respectively the eigenvalues and the eigenvectors of \(H(k_M)\). Thus the effective Hamiltonian
a) Spectrum of the CO(I) phase.

The Hamiltonian has the symmetry of the original Hamiltonian, the Luttinger-Kohn (L-K) Hamiltonian $H(k)$ where, by construction, $H(k)$ is rewritten as

$$H(k) = H(k_M) + iq \cdot V(k_M) + \sum_{ij} W_{ij}(k_M) q_i q_j,$$

where, by construction, $H(k_M)$ is diagonal. Like the original Hamiltonian, the Luttinger-Kohn (L-K) Hamiltonian has the symmetry $H^*(k) = H(-k)$. Therefore, near the M-point as well as in the vicinity of the other so-called time-reversal points of position $\mathbf{G}/2$ where $\mathbf{G}$ is a reciprocal lattice vector, the energy bands $\xi_\alpha(k)$ have peculiar properties: for any band $\xi_\alpha(k)$, the particular values $\xi_\alpha(\mathbf{G}/2)$ are either a local extremum or a saddle point. As a consequence, the gap between two consecutive bands at these symmetry points is also either a local extremum or a saddle point. This picture explains the topological transition from the CO(I) phase where the gap at M is a local minimum to the CO(II) phase where the gap at M is a local saddle point. To be more precise, let us focus on the structure of the Luttinger-Kohn Hamiltonian. A strong consequence of the symmetry $H^{LK*}(k) = H^{LK}(-k)$ is that at the M-point, like at the other symmetry points, $W_{ij}(k_M)$ are real symmetric matrices and $V_i(k_M)$ are real antisymmetric matrices. We deduce that the minimal form of the $2 \times 2$ matrix $H^{LK}(k_M + q)$ to order $q_i q_j$ can be recast as:

$$H^{LK}(k_M + q) = f_0(q) \sigma_0 + f_1(q) \sigma_1 + f_2(q) \sigma_2 + f_3(q) \sigma_3,$$

where we have used a representation in terms of Pauli matrices $\sigma_i$ and

$$f_0(q) = \mu + \sum_{ij} w_{ij} q_i q_j,$$

$$f_1(q) = \sum_{ij} w_{ij} q_i q_j,$$

$$f_2(q) = v \cdot q,$$

$$f_3(q) = \Delta + \sum_{ij} w_{ij} q_i q_j.$$  

with $\Delta > 0$. The eigenenergies near the M-point are given by

$$\xi_\pm(q) = f_0(q) \pm \sqrt{f_1(q)^2 + f_2(q)^2 + f_3(q)^2}.$$  

The local band structure around M has the symmetry $\xi_\pm(q) = \xi_\pm(-q)$. Moreover these expressions also imply that $\partial_{q_i} \xi_\pm(q)|_{q=0} = 0$ so that, as anticipated, M is either a local extremum or a saddle point of the dispersion relation of each band. The same properties are also valid for the gap $\Delta(q) = \frac{1}{2} (\xi_+(q) - \xi_-(q))$ separating the two bands.

B. CO(I)-CO(II) transition: phase boundary

Within the framework of this Luttinger-Kohn representation, we now determine the condition for a transition from a minimum to a saddle point at the M-point. For this purpose, it is useful to define the $2 \times 2$ stability (Hessian) matrix $S_M$. We have

$$\Delta(q) = \frac{\xi_+(q) - \xi_-(q)}{2} \simeq \Delta + \frac{1}{2} (q_x q_y) S_M \begin{pmatrix} q_x \\ q_y \end{pmatrix} + \cdots,$$

FIG. 4: The $q$-dependence of the conduction and valence bands for $\uparrow$ spin where $q = k - k_M$, and the center denotes the M point ($k_M = (\pi, \pm \pi)$). a) Spectrum of the CO(I) phase with a single minimum at the M point. b) Spectrum of the CO(II) phase with a double minimum around the M point. Here the parameters are $V_a = 0.18$ eV and $V_b = 0.05$ eV, and the pressures are respectively $P_a = 4.5$ kbar and $P_b = 5.4$ kbar, for the CO(I) and CO(II) phases.

is rewritten as

$$H^{LK}(k) = H^{LK}(k_M) + i\mathbf{q} \cdot \mathbf{V}(k_M) + \sum_{ij} W_{ij}(k_M) q_i q_j.$$
where

\[ S_M = \begin{pmatrix} \frac{\partial^2 \Delta(q)}{\partial q^2} & \frac{\partial^2 \Delta(q)}{\partial q \partial \sigma_3} & \frac{\partial^2 \Delta(q)}{\partial q \partial \sigma_1} \\ \frac{\partial^2 \Delta(q)}{\partial \sigma_1 \partial q} & \frac{\partial^2 \Delta(q)}{\partial \sigma_1^2} & \frac{\partial^2 \Delta(q)}{\partial \sigma_1 \partial \sigma_3} \\ \frac{\partial^2 \Delta(q)}{\partial \sigma_3 \partial q} & \frac{\partial^2 \Delta(q)}{\partial \sigma_3 \partial \sigma_1} & \frac{\partial^2 \Delta(q)}{\partial \sigma_3^2} \end{pmatrix} \]

(4.11)

with \( w_{ij} = w_{ij}^{\sigma_3} + c_{ij} \). The determinant of this matrix:

\[ \det S_M = w_{33}^{\sigma_3} - (w_{33}^{\sigma_3})^2, \]

(4.12)

governs the stability of the M-point. There is an extremum when \( \det S_M > 0 \) and a saddle point when \( \det S_M < 0 \). Therefore the transition line is given by the condition \( \det S_M = 0 \), that is

\[ \left( w_{33}^{\sigma_3} + \frac{v^2}{2 \Delta} \right) \left( w_{33}^{\sigma_3} + \frac{v_y^2}{2 \Delta} \right) = \left( w_{33}^{\sigma_3} + \frac{v_x v_y}{2 \Delta} \right)^2. \]

(4.13)

We emphasize that the stability matrix \( S_M \) is totally independent of the terms \( w_{ij}^{\sigma_3} \). Nevertheless, these terms are important to determine the position of the Dirac points and the size of the gap at the Dirac points in the CO(II) phase. They also play a crucial role in determining the topological properties of the band structure (Berry curvature). Therefore, among the 9 initial parameters of Eqs. (4.6), (4.7) and (4.8), only 6 are pertinent to determine the transition line. They enter the combination \( \det S_M \) which is the single driving parameter for the CO(I) - CO(II) transition.

C. Minimal form of the effective Hamiltonian for the merging transition

In order to analyse the local structure of the Hamiltonian near a time-reversal point, it is convenient to parametrize it using polar coordinates of the wave vector \( q \). We write:

\[ q_x = q \cos \theta, \quad q_y = q \sin \theta, \]

(4.14)

so that the Hamiltonian describing the CO(I)-CO(II) transition can be written in the form (since the component \( \sigma_0 \) plays no role in our discussion, we define the effective Hamiltonian as \( h(q) = H_{KK}(k_M + q) - f_0(q) \sigma_0 \)):

\[ h(q) = \begin{pmatrix} \Delta + w^0 q^2 & -i v_y q + w^0 q^2 \\ i v_y q + w^0 q^2 & -\Delta - w^0 q^2 \end{pmatrix}, \]

(4.15)

where

\[ w^0 = w^{\sigma_3} \sin^2 \theta + w^{\sigma_3} \cos^2 \theta + 2 w^{\sigma_3} \cos \theta \sin \theta, \]
\[ w^y = w^{\sigma_3} \sin^2 \theta + w^{\sigma_3} \cos^2 \theta + 2 w^{\sigma_3} \cos \theta \sin \theta, \]
\[ v_y = v_x \cos \theta + v_y \sin \theta. \]

(4.16)

To lowest order in \( q \), the gap function can be expanded as:

\[ \Delta(q) \simeq \Delta + (w_3^0 + \frac{v_y^2}{2 \Delta}) q^2. \]

(4.17)

In the CO(II) phase, the function \( \Delta(q) \) has a saddle point. This corresponds to the case where \( \det S_M \leq 0 \) or equivalently \( w_{33}^{\sigma_3} - (w_{33}^{\sigma_3})^2 \leq 0 \). There is an angular region where \( \Delta(q) < \Delta \). This happens in an interval \( \theta_{\text{min}} \leq \theta \leq \theta_{\text{max}} \) such that \( (w_3^0 + \frac{v_y^2}{2 \Delta}) < 0 \). The two angles \( \theta_{\text{min}}, \theta_{\text{max}} \), chosen in the range \([0, \pi]\), are determined by the condition \( (w_3^0 + \frac{v_y^2}{2 \Delta}) = 0 \), which gives

\[ \tan \theta_{\text{max, min}} = \frac{-w_{33}^{\sigma_3} \pm \sqrt{\det S_M}}{w_{33}^{\sigma_3}}. \]

(4.18)

The gap function can be rewritten in terms of these angles as

\[ \Delta(q) = \Delta + \frac{w \sin(\theta - \theta_{\text{max}}) \sin(\theta - \theta_{\text{min}})}{2 \Delta} q^2, \]
\[ = \Delta + \frac{w}{2} \left[ \cos(\theta_{\text{max}} - \cos 2(\theta - \theta_{\text{max}}) \right] q^2 \]

(4.19)

where \( w \) can be rewritten conveniently as

\[ w = \left[ w_{33}^{\sigma_3} - 4 \det S_M \right]^{1/2}, \quad w_{33}^{\sigma_3} = \left[ w_{33}^{\sigma_3} + w_{33}^{\sigma_3} \right]. \]

(4.20)

The angles \( \theta_{\text{max, min}} \) are defined as

\[ \theta_{\text{+}} = \frac{1}{2}(\theta_{\text{max}} + \theta_{\text{min}}), \]
\[ \theta_{\text{-}} = \theta_{\text{max}} - \theta_{\text{min}}. \]

(4.21)

They represent respectively the most unstable direction and the angular aperture of the region \( \Delta(q) < \Delta \). Fig. 2a) shows the gap function in the CO(II) phase at \( P_a = 5.4 \text{ kbar} \). Their expression is

\[ \theta_{\text{+}} = \frac{\pi}{2} + \frac{1}{2} \arctan \left( \frac{2 w_{33}^{\sigma_3} - w_{33}^{\sigma_3}}{w_{33}^{\sigma_3}} \right), \]
\[ \theta_{\text{-}} = \arctan \left( \frac{2 \sqrt{-\det S_M}}{w_{33}^{\sigma_3}} \right). \]

(4.22)

Near the merging transition, when \( P_a \geq P_M, \theta_{\text{+}} \rightarrow \theta \) where the angle \( \theta_M \) given by

\[ \theta_M = \pi - \arctan \left( \frac{2 w_{33}^{\sigma_3}}{w_{33}^{\sigma_3}} \right), \]

(4.23)

defines the direction of emergence of the two Dirac points. Moreover \( w \rightarrow w_M = \left| w_{33}^{\sigma_3} + w_{33}^{\sigma_3} \right| \) and the angular aperture \( \theta_- \) vanishes as \( \theta_- \) reaches \( 2 \sqrt{-\det S_M}/w_M \).

Near the transition, we define a new set of coordinates along the direction of emergence and the perpendicular direction. Writing \( q_x' = q \cos(\theta - \theta_M) \) and \( q_y' = q \sin(\theta - \theta_M) \), the gap function can be expanded as

\[ \Delta(q) \simeq \Delta + w_M \left( q_y'^2 - \frac{\theta^2}{4} q_x'^2 \right). \]
FIG. 5: (a) Contours of the gap function $\Delta_k = [\xi_+(k) - \xi_-(k)]/2$ for $P_a = 5.4$ kbar in CO (II) phase where $0 < k_y < 2\pi$ and $0 < k_x < 2\pi$. The two Dirac points emerge from the M point $k_M = (\pi, \pm \pi)$. Points O, X and Y denote (0,0), $(\pi,0)$ and $(0,\pi)$, respectively. (b) The same contour $\Delta_q$ in the vicinity of the M point, which is taken as the origin ($q = k - k_M$). The red curve represents the energy contour $\Delta_q = \Delta$. The two red lines denote the angles $\theta_{\text{min}}$ and $\theta_{\text{max}}$ defined in the text (4.18). Note that on Fig. (b), the scales are different along the two axes.

\[ \Delta \approx \Delta + \frac{\det S_M}{w_M} q_x^2 + w_M q_y^2. \]  
(4.24)

This explicitly shows that $\det S_M$ is the single parameter for the merging condition.

The $P_a$-dependence of $\Delta$, $v_j$, $w_{ij}^3$ and $\det S_M$ for $V_a = 0.18$ eV and $V_b = 0.05$ eV are shown in Fig. 6. The merging pressure, calculated from $\det S_M = 0$, is found to be $P_a^{\text{M}} \approx 5.07$ kbar, which almost coincides with that obtained from the direct calculation of energy bands. The merging axis $q_y'$-axis is very close to the $q_y$ axis, $\theta_{\text{M}} = 1.73$ as shown in Fig. 5(a).

D. Relation between effective Hamiltonians for $\alpha$-(BEDT-TTF)$_2$I$_3$ and two-component systems

In this section, we compare the physics of the emergence of Dirac points in $\alpha$-(BEDT-TTF)$_2$I$_3$, with a possible similar transition in two-component systems such as graphene or boron nitride (BN) under stress. Near the M-point, the electronic spectrum of these two systems can be described by the following Hamiltonians:

In graphene $M = 0$, and in boron nitride $M \neq 0$ is proportional to the energy difference between sites B and N. The parameter $\Delta_*$ drives the transition from a phase with two Dirac points ($\Delta_* < 0$) separated by $\delta q = 2\sqrt{-2m\Delta_*}$ to an insulating phase with a gap $\Delta_* > 0$. This transition has been studied in refs. 21,22,23.

Here we show that this transition has the same structure as the transition described above in $\alpha$-(BEDT-TTF)$_2$I$_3$. To do this, we have to compare the Luttinger-
Kohn Hamiltonian (4.15) and the "boron-nitride" Hamiltonian (4.25). This is possible after a rotation of angle $-\varphi$ where
\[
\tan \varphi = \frac{\Delta}{M},
\] (4.26)
from which we obtain a new Hamiltonian:
\[
h_{BN}^I(q) = \exp^{i\frac{\varphi}{2} \sigma^z} h_{BN}(q) \exp^{-i\frac{\varphi}{2} \sigma^z}.
\] (4.27)
This Hamiltonian has the form
\[
h_{BN}^I(q) = \left( \begin{array}{cc}
\Delta + w_3 q^2 & w_1 q^2 - iv_x q_x \\
w_1 q^2 - iv_x q_x & \Delta + w_3 q^2
\end{array} \right)
= (\Delta + w_3 q^2) \sigma^z + w_1 q^2 \sigma^x + v q \sigma^y,
\] (4.28)
with the parameters $w_1, w_3$ and $\Delta$ given by
\[
w_1 = \frac{1}{2m} \cos \varphi = \frac{1}{2m} \sqrt{M^2 + \Delta^2},
\] (4.29)
\[
w_3 = \frac{1}{2m} \sin \varphi = \frac{1}{2m} \frac{\Delta}{\sqrt{M^2 + \Delta^2}},
\] (4.30)
\[
\Delta = \sqrt{\Delta^2 + M^2}.
\] (4.31)

This Hamiltonian therefore appears as a peculiar case of the general Hamiltonian (4.15), with the following parameters $\Delta, v_x, w_1 w_3 = w_1, w_3^2 = w_3$ and all other parameters being zero ($w_1^\theta = w_1 \sin^2 \theta, w_3^\theta = w_3 \sin^2 \theta, v_\theta = v_x \cos \theta$). In this case, the determinant of the stability matrix is simply $\det S_M = \frac{\sigma^z}{\Delta^2} w_3$. The merging transition has the same structure as the one described above. Here we have simply
\[
\theta_{\min} = \arctan \sqrt{\frac{v_x^2}{-2\Delta w_3}} = \arctan \sqrt{\frac{m v_x^2}{-\Delta}},
\] (4.32)
and $\theta_{\max} = \pi - \theta_{\min}$, so that $\theta_+ = \frac{\pi}{2}$ and
\[
\theta_- = \arctan \frac{2 \sqrt{2\Delta w_3}}{1 + 2 \Delta w_3} = \arctan \frac{2 \sqrt{\Delta}}{1 + \Delta w_3^{-1}}.
\] (4.33)

In this simple case, the direction of the merging stays constant and perpendicular to the velocity (see Fig. 7). The BN Hamiltonian is interesting since it explicitly reveals the role of the different parameters. Whereas $w_3$ drives the topological transition, the parameter $w_1$ controls the opening of a gap in both phases. The situation in $\alpha$-(BEDT-TTF)$_2$I$_3$ is more involved since there are 9 parameters but the main features of the topological transition can be understood within a simplified Hamiltonian with only 4 parameters.

V. BERRY CURVATURE ASSOCIATED WITH THE TOPOLOGICAL TRANSITION

In this section we show that the emergence of the Dirac pair is well characterized by the appearance of a non trivial Berry curvature $B_{17}(k)$ for the conduction band. This Berry curvature, which plays the role of a $k$ dependent effective magnetic field in the Brillouin zone, appears to be sharply peaked around the two massive Dirac points (see Fig. 7b). We then show how to associate a Berry phase to each Dirac point.

A. Full Brillouin zone computation of the Berry curvature within the four-band model

For a multiband system, the Berry curvature $B_n(k)$ of the $n^{th}$ band is given by:
\[
B_n(k) = \text{rot}_k A_n(k).
\] (5.1)
where $A_n(k)$ denotes the so-called Berry connection and is written as
\[
A_n(k) = -i \langle n(k) | \partial_k | n(k) \rangle,
\] (5.2)
and $| n(k) \rangle$ is an eigenvector of Eq. (2.23).

For our model Hamiltonian (2.25) which is diagonal in spin index and with non degenerate bands $\xi_{n \sigma}(k)$ that never cross for any $k$, the Berry curvature $B_{n \sigma}(k) \equiv B_{n \sigma}(k) u_z$ can be computed from
\[
B_{n \sigma}(k) = -i \sum_{m \neq n} \frac{v_{n m \sigma}(k) v_{m n \sigma}^*(k) + c.c.}{(\xi_{n \sigma}(k) - \xi_{m \sigma}(k))^2},
\] (5.3)
where

\[ \psi^\alpha_{nm\sigma}(\mathbf{k}) = < n\sigma(\mathbf{k})| \partial_{k_x}\partial_{k_y} \mathcal{H}(\mathbf{k}) | m\sigma(\mathbf{k}) > = \sum_{\alpha\beta} \delta_{n\alpha\sigma}(\mathbf{k}) \delta_{m\beta\sigma}(\mathbf{k}) \partial_{k_x} \partial_{k_y} \epsilon_{\alpha\beta}(\mathbf{k}), \quad (5.4) \]

are the nm interband matrix elements of the velocity operator. \( n, m = 1, 2, 3, 4 \) are Bloch bands indices and \( \alpha, A, A', B, C \) are sites in \( \alpha \)-BEDT-TTF\_2I\(_3\). Note that since \( \psi^\alpha_{nm\sigma}(\mathbf{k}) = (\psi^\alpha_{nm\sigma}(\mathbf{k}))^* \), we immediately obtain that \( B_{n\sigma}(\mathbf{k}) = -\sum_{m\neq n} B_{m\sigma}(\mathbf{k}) \). Therefore computing \( B_{n\sigma}(\mathbf{k}) \) fully characterizes our 3/4 filled system.

Fig. 8 shows the typical result for \( B_{1\uparrow}(\mathbf{k}) \) in the insulating CO(I) (\( P_a = 4.4 \) kbar) and CO(II) (\( P_a = 5.4 \) kbar) phases. In the CO(II) phase, there is a pair of massive Dirac particles and consequently the Berry curvature is sharply peaked around the position of the Dirac points \( \mathbf{k}_\pm \). The peaks at \( \mathbf{k}_\pm \) are strongly anisotropic and have the same magnitude but opposite sign, reflecting the so-called opposite chirality associated to the two Dirac particles. Conversely, in the CO(I) phase, the intensity of the Berry curvature becomes small owing to cancelation of the positive and negative peaks.

In order to understand in a more quantitative way these numerical results, we show here how the Berry curvature \( B_{1\uparrow}(\mathbf{k}) \) can be computed directly from the low energy effective \( 2 \times 2 \) Luttinger-Kohn reduced Hamiltonian \( \mathcal{H}_{\mathbf{K}\mathbf{L}}(\mathbf{k}_\mathbf{M} + \mathbf{q}) = f_0(\mathbf{q}) \mathcal{H}_0(\mathbf{q}) \cdot \mathbf{f}(\mathbf{q}) \cdot \sigma \). \( \mathbf{f} \) is the vector of components \( (f_1, f_2, f_3) \) (Eq. 4.13). For this \( 2 \times 2 \) Hamiltonian, the Berry curvature \( B_{1\uparrow}(\mathbf{q} = \mathbf{k} - \mathbf{k}_\mathbf{M}) \) (in cartesian and polar coordinates) reads

\[ B_{1\uparrow}(\mathbf{q}) = \frac{(\partial_{k_x} \mathbf{f} \times \partial_{k_y} \mathbf{f}) \cdot \mathbf{f}}{2q \Delta^3(\mathbf{q})}, \quad (5.5) \]

From Eq. (4.15) we obtain:

\[ B_{1\uparrow}(\mathbf{q}, \theta) = \frac{\Delta (2w^{\theta}_1 w'^{\theta}_1 - w^{\theta}_1 w'^{\theta}_1)q + v_g (w'^{\theta}_1 w'^{\theta}_1 - w^{\theta}_1 w'^{\theta}_1)q^3}{2 [\Delta + w^{\theta}_3 q^2]^2 + v^2_0 q^2 + (w'^{\theta}_1 q^4)^{3/2}}, \quad (5.6) \]

where we have defined the derivatives

\[
\begin{align*}
  w^{\theta}_1 &= (w^{yy}_1 - w^{xx}_1) \sin 2\theta + 2w^{xy}_1 \cos 2\theta, \\
  w'^{\theta}_1 &= (w'^{yy}_1 - w'^{xx}_1) \sin 2\theta + 2w'^{xy}_1 \cos 2\theta, \\
  v_g &= -v_x \sin \theta + v_y \cos \theta.
\end{align*}
\]

The expression Eq. (5.6) shows that the \( w^{\theta}_1 \) F term is essential to have a non-vanishing Berry curvature. We note that this expression is quite general. In particular, for the boron nitride Hamiltonian described in previous section, we obtain

\[ B_{BN}^{3}(\mathbf{q}) = \frac{-\Delta w_1 v_x q_y}{(\Delta + w_3 q_y^2 + v_2 q_x^2 + w'^{\theta}_1 q_y^4)^2}, \quad (5.8) \]

The \( q^3 \) term in the numerator (that determines the large \( q \) tail of the Berry curvature) vanishes here because \( w^{\theta}_1 \) and \( w'^{\theta}_1 \) have identical \( \theta \) dependences.

**C. Berry phase associated to Dirac points**

The integral of the Berry curvature \( B_{1\uparrow}(\mathbf{k}) \) over the full Brillouin zone (BZ) is a topological quantity called a Chern number \( ^{24} \),

\[ \text{Ch}_{1\uparrow} = \frac{1}{2\pi} \int_{BZ} dSB_{1\uparrow}(\mathbf{k}). \quad (5.9) \]

In our system, \( \text{Ch}_{1\uparrow} = 0 \) since the curvatures associated to the two Dirac points exactly compensate. In order to characterize the contribution of each Dirac point, we define a Berry phase which is the integral over an appropriate region in \( \mathbf{k} \) space around a given Dirac point as explained in \( ^{24} \),

\[ \Gamma(\mathbf{k}_\pm) = \frac{1}{2\pi} \int_{S(\mathbf{k}_\pm)} dSB_{1\uparrow}(\mathbf{k}). \quad (5.10) \]
The area \( S(k_{\pm}) \) denotes the region around a given Dirac point \( k_{\pm} \) where \( \Delta(k) \) contours are closed (\( \Delta(k) < \Delta \)). This is the region inside the red curve in Figures 5 and 7.

Here we compare \( \Gamma(k_{\pm}) \) with the following expression \( \Gamma_{\pm} \):

\[
\Gamma_{\pm} = \mp \frac{1}{2} \left( 1 - \frac{\Delta(k_{\pm})}{\Delta(k_M)} \right). \tag{5.11}
\]

This expression was obtained in Ref. 24 for a general class of \( 2 \times 2 \) Hamiltonians that include the BN model for which we find

\[
\Gamma_{\pm} = \mp \frac{1}{2} \left( 1 - \frac{w_1}{\sqrt{w_1^2 + w_3^2}} \right) = \mp \frac{1}{2} \left( 1 - \frac{M}{\sqrt{M^2 + \Delta^2}} \right). \tag{5.12}
\]

Therefore in the vicinity of the transition \( (w_3 \to 0_-) \), \( \Gamma_{\pm} \) varies as

\[
|\Gamma_{\pm}| \simeq \frac{1}{4} \frac{w_2^2}{w_1^2}. \tag{5.13}
\]

At the same time, the separation \( \delta q \) between Dirac points varies as

\[
\delta q \simeq \frac{(-\Delta w_3)^{1/2}}{w_1}. \tag{5.14}
\]

The \( \rho_a \)-dependence of \( \Gamma(k_{\pm}) \) is compared with that of \( \Gamma_{\pm} \) in Fig. 9. Although the behavior of \( \Gamma(k_{\pm}) \) is qualitatively similar to \( \Gamma_{\pm} \), there is a slight difference between these two quantities, which may come from the effect of the other bands in Eq. (5.3). This multi-band effect is discussed in a separate paper. Both quantities \( \Gamma(k_{\pm}) \) and \( \Gamma_{\pm} \) vanish below a critical pressure which coincides with the merging pressure \( P_M^a \) found in Fig 6, within numerical accuracy. This is consistent with the effective Hamiltonian which leads to \( |\Gamma(k_{\pm})| \propto (\rho_a - P_M^a)^2 \) and \( q_{+y} \propto (\rho_a - P_M^a)^{1/2} \). This is also seen quite simply in the BN model for which we obtain, from Eqs. (5.13) and (5.14), \( |\Gamma_{\pm}| \propto w_2^2 \propto (\text{det}S_M)^2 \) and \( q_{+y} \propto w_3^{1/2} \propto (\text{det}S_M)^{1/2} \).

**VI. SUMMARY AND DISCUSSION**

In this paper, we re-examined the electronic properties in the stripe charge ordered states in the organic conductor \( \alpha-(\text{BEDT-TTF})_2I_3 \). With increasing pressure, a transition occurs from an insulating charge ordered (CO) state to a metallic charge ordered (COM) state. In this work, we have found a new topological transition which further splits each of the CO and COM phases into two phases, respectively CO(I)-CO(II) and COM(I)-COM(II). We specifically consider the CO(I)-CO(II) transition which separates a phase (CO(I)) with a usual gap at the M-point of the Brillouin zone from a phase (CO(II)) where the gap exhibits a double minimum with a local maximum at the M-point. This transition corresponds to the emergence of a pair of Dirac points.

This modification of the band structure is described by an effective \( 2 \times 2 \) low energy Luttinger-Kohn Hamiltonian with 9 parameters that can be extracted from a numerical Hartree calculation. From a detailed study of this Hamiltonian and the corresponding energy spectrum, we show that the transition is driven by a single quantity \( \text{det}S_M \) (Eq. (4.12)) which is an appropriate combination of these parameters and whose sign changes at the transition. A similar scenario occurs for the COM(I)-COM(II) transition. The Hartree contribution, which induces on-site potentials, is crucial to break inversion and time-reversal symmetries, leading to the CO state. The exchange (Fock) term modifies the hopping energies but does not break the symmetry, so that it is not responsible for the CO state. It may only modify the relative stability of the different phases. Moreover, in the ZGS phase, it does not disturb the Dirac spectrum as shown by first principle calculations\(^{13,14}\). Similarly we believe that going beyond the mean field approximation does not change qualitatively the topological transition around the M point but may only modify the parameters of the Luttinger-Kohn Hamiltonian.

We compare the structure of this transition with a similar situation which occurs in a simple model for boron nitride\(^{21,22,24}\), where the emergence of a pair of Dirac points is quite comparable, although the driving forces are different.

The existence of a pair of Dirac points is characterized by a special structure of the the Berry curvature inside the Brillouin zone. In the CO(II) and COM(II) states, the latter shows two sharp peaks with opposite signs. On the other hand, in CO(I) and COM(I) phases, the Berry curvature becomes very small owing to cancelation.
of the positive and negative contributions. The existence of the Dirac point is also verified by integrating the Berry curvature over a region limited by a closed energy contour around a single point.

It would be interesting to observe directly the modification of the energy spectrum associated to the topological transition by angle-resolved photoelectron spectroscopy experiments. Moreover this topological transition could be probed in a magnetic field by the modification of the Landau level structure, therefore by e.g. magnetoresistance and Hall experiments, in a range of pressure which is accessible experimentally. Finally we mention the existence of another conductor, α-(BETS)$_2$I$_3$ which is also a good candidate for a Dirac-like electron spectrum. Moreover, since the BETS molecule contains relatively heavy atoms, the spin-orbit interaction may be effective leading to non-zero Chern number as shown in the Weyl Hamiltonian with the spin-orbit interaction.

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Appendix A: Band Structure in the stripe Charge Ordered state

In the stripe CO state, the energy band with ↑ spin is different from that with ↓ spin owing to inversion symmetry breaking and time reversal symmetry breaking. For the CO(I) phase (V$_a$ = 0.17 eV, and P$_a$ = 3 kbar in Fig. 2), the minimum point of the energy gap is located at k$_{0↑}$ = k$_M$ = (π, ±π) (the M-point ) for ξ$_{1↑}$($\mathbf{k}$), and at k$_{0↓}$ = ±(0.36π, −0.62π) for ξ$_{1↓}$($\mathbf{k}$). The ↑ spin band has a small gap $\Delta_↑$ = 0.0033 eV at the M-point and is very anisotropic in its vicinity. The ↓ spin band has a large gap $\Delta_↓$ = 0.0171 eV and is more isotropic. In the CO(II) phase (Fig. 2), on the other hand, there is a pair of minima of the gap in the ↑ spin band as shown in Fig. 10. The gap-minima of the ↑ spin band are located at k$_{0↑}$ = ±(0.95π, −0.71π) for P$_a$ = 5.4kbar, V$_a$ = 0.18 eV and V$_b$ = 0.05 eV.

FIG. 10: The energy bands of ξ$_{1σ}$ and ξ$_{2σ}$ for ↑ spin band (a) and the ↓ spin band (b) in the CO(II) for P$_a$ = 5.4kbar, V$_a$ = 0.18 eV and V$_b$ = 0.05 eV. The center denotes the M point.

The energy dispersion in COM(II) is similar to that of CO(II). However, for COM(II), the Fermi level is located in the conduction band for the ↑ spin band, and in the valence band for the ↓ spin band (Fig 3 d). When the pressure is decreased, those two minimum points of the ↑ spin bands merge at the M-point while the quantity ξ$_{1↑}$ − ξ$_{2↑}$ (ξ$_{1↓}$ − ξ$_{2↓}$) remains finite on the boundary line between COM(I) and COM(II).

1 N. Tajima and K. Kajita K, Sci. Tech. Adv. Mater. 10, 024308 (2009).
2 H. Seo, C. Hotta, and H. Fukuyama H, Chem. Rev. 104,
3. A. Kobayashi, S. Katayama, and Y. Suzumura, Sci. Tech. Adv. Mater. 10, 024309 (2009).
4. H. Kino and H. Fukuyama, J. Phys. Soc. Jpn. 64, 4523 (1995).
5. H. Seo, J. Phys. Soc. Jpn. 69, 805 (2000).
6. C. Hotta, J. Phys. Soc. Jpn. 72, 840 (2003).
7. T. Takahashi, Synth. Met. 133-134, 26 (2003).
8. N. Tajima, A. Ebina-Tajima, M. Tamura, Y. Nishio, K. Kajita, J. Phys. Soc. Jpn. 71, 1832 (2002).
9. A. Kobayashi, S. Katayama, and Y. Suzumura, J. Phys. Soc. Jpn. 74, 2897 (2005).
10. K. Kajita, T. Ojiro, H. Fujii, N. Nishio, H. Kobayashi, A. Kobayashi, R. Kato, J. Phys. Soc. Jpn. 61, 23 (1992).
11. S. Katayama, A. Kobayashi, and Y. Suzumura, J. Phys. Soc. Jpn. 75, 054705 (2006).
12. R. Kondo, S. Kagoshima, and J. Harada, Rev. Sci. Instrum. 76, 093902 (2005).
13. H. Kino and T. Miyazaki, J. Phys. Soc. Jpn. 75, 034704 (2006).
14. S. Ishibashi, T. Tamura, M. Kohyama, and K. Terakura, J. Phys. Soc. Jpn. 75, 015005 (2006).
15. A. Kobayashi, S. Katayama, Y. Suzumura, and H. Fukuyama, J. Phys. Soc. Jpn. 76, 034711 (2007).
16. M.O. Goerbig, J.-N. Fuchs, G. Montambaux, and F. Piéchon, Phys. Rev. B 78, 045415 (2008).
17. A. Kobayashi, Y. Suzumura, and H. Fukuyama, J. Phys. Soc. Jpn. 77, 064718 (2008).
18. N. Tajima, S. Sugawara, R. Kato, Y. Nishio, and K. Kajita, Phys. Rev. Lett. 102, 176403 (2009).
19. K. Morinari, T. Himura, and T. Tolyama, J. Phys. Soc. Jpn. 78, 023704 (2009).
20. P. Dietl, F. Piéchon, and Montambaux G Phys. Rev. Lett. 100, 236405 (2008).
21. G. Montambaux, F. Piéchon, J.-N. Fuchs, and M.O. Goerbig, Eur. Phys. J. B 72, 509 (2009).
22. G. Montambaux, F. Piéchon, J.-N. Fuchs, and M.O. Goerbig, Phys. Rev. B 80, 153412 (2009).
23. M. V. Berry, Proc. Roy. Soc. London A 392, 45 (1984).
24. J.-N. Fuchs, F. Piéchon, M.O. Goerbig, and G. Montambaux, Eur. Phys. J. B 77, 351 (2010).
25. T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, Chem. Lett. 957 (1984).
26. T. Mori, H. Mori, and S. Tanaka, Bull. Chem. Soc. Jpn. 72, 179 (1999).
27. T. Kakiuchi, Y. Wakabayashi, H. Sawa, T. Takahashi, and T. Nakamura, J. Phys. Soc. Jpn. 76, 113702 (2007).
28. Y. Takano, K. Hiraki, T. Takahashi, and H.M. Yamamoto, J. Phys. Soc. Jpn. 79, 104704 (2010).
29. A. Kobayashi, S. Katayama, K. Noguchi, and Y. Suzumura, J. Phys. Soc. Jpn. 73, 3135 (2004).
30. A. Kobayashi, S. Komaba, S. Katayama, and Y. Suzumura, J. Phys., Conf. Ser. 132, 012002 (2008).
31. J.M. Luttinger and W. Kohn W Phys. Rev. 97, 869 (1955).
32. S. Katayama, A. Kobayashi, and Y. Suzumura, Eur. Phys. J. B 67, 139 (2009).
33. The possibility of a transition towards a local maximum is also possible, but does not correspond to the physical situation discussed in this paper.
34. D.J. Thouless, Topological Quantum Numbers in Nonrelativistic Physics (World Scientific, Singapore, 1998) (1998).
35. Y. Suzumura and A. Kobayashi, private communication.
36. K. Hiraki, S. Harada, K. Arai, Y. Takano, T. Takahashi: J. Phys. Soc. Jpn. 80, 014715 (2011).
37. C.L. Kane and E.J. Mele, Phys. Rev. Lett. 95, 226801 (2005).