Motivated by the results of recent transport and optical conductivity studies, we propose a semi-infinite two-dimensional lattice model for interacting massive Dirac electrons in the pressurized organic conductor $\alpha$-(BEDT-TTF)$_2$I$_3$ and address the problem of domain wall conductivity in a charge-ordered insulating phase under realistic experimental conditions. Using the extended Hubbard model at a mean field level, we present results of extensive numerical studies around the critical region of the model, reporting on the calculated resistivity and optical conductivity by means of the Nakano-Kubo formula. We find that the activation gap extracted from resistivity data should be much smaller than the optical gap in the critical region which is induced by metallic conduction along one-dimensional domain walls, emerging at the border of two charge-ordered ferroelectric regions with opposite polarizations. The data are consistent with the observed transport gap in real $\alpha$-(BEDT-TTF)$_2$I$_3$ samples that is reduced remarkably faster than the optical gap upon suppressing charge order with pressure. At low energy inside the gap an additional shoulder-like structure appears in our optical conductivity, which is argued to be directly relevant to the metallic bound states residing on the domain walls.

I. INTRODUCTION

The quasi-two-dimensional (quasi-2D) electron system in the layered organic salt $\alpha$-(BEDT-TTF)$_2$I$_3$ has a unique pressure-temperature ($P-T$) phase diagram in which a 2D massless Dirac electron phase appears at high $P$ [1–7] adjacent to an insulating phase at low $P$ showing charge ordering. In the high-$P$ phase the space and time inversion symmetry guarantees the stability of (spin-degenerate) Dirac points in the momentum space, and the 3/4-filling of the electronic band fixes the Fermi energy at the band crossing. In contrast, the inversion symmetry is spontaneously broken in the low-$P$ insulating phase where electrons are localized and form a stripe-like charge ordering pattern along the crystalline b axis [8][11]. At ambient pressure the charge ordered phase appears below a transition temperature $T_{\text{CO}} = 135$K; an application of a hydrostatic pressure linearly reduces $T_{\text{CO}}$ and eventually suppresses the phase transition above a critical pressure $P_c = 12$kbar, stabilizing the massless Dirac electron phase at low temperature. A narrow energy bandwidth characteristic for this type of organic conductors gives rise to strong electronic correlation effects in both phases. (We recall that the low-energy effective theory in this system can be approximatively described by a 2D lattice model since inter-layer conductivity is 1000 times smaller with respect to its interlayer counterpart [11][2][12]). As theoretically predicted and also experimentally confirmed, the electron-electron Coulomb interaction plays a significant role in the stripe-type charge ordered phase, where for example recent NMR and Monte Carlo studies suggest a spin-excitation nature that is consistent with 1D alternating Heisenberg spin chains [8][9][13][14]. In the massless Dirac electron phase, not only the short-range repulsive interactions but also the long-range part of the Coulomb interaction (which appears due to the absence of metallic screening at the Dirac point) induce various anomalies in NMR spin susceptibilities, ranging from a ferrimagnetic spin polarization, and a logarithmic suppression of the Knight shift upon cooling to a simultaneous giant enhancement of the Korringa ratio; moreover, at low temperature, signatures of inter-valley excitonic spin fluctuations were also reported growing as a precursor to the transition from a massless to massive state, triggered by an intense long-range Coulomb interaction [15][18].

Recently, a surprising transport phenomena has been observed by resistivity measurements [19]; a transport gap defined by an Arrhenius plot (dubbed the resistivity gap $\Delta_p$) is much smaller than another gap defined by optical conductivity measurements (dubbed the optical gap $\Delta_O$) [20]. $\Delta_p$ is strongly suppressed as pressure is increased and becomes zero at $P \approx 7$ kbar, albeit $T_{\text{CO}}$ and $\Delta_O$ remain finite until the pressure reaches $P_c$. As a candidate of possible dc conduction mechanism, 1D conduction along a gapless bound state on the domain wall arising between two charge-ordered domains has been theoretically predicted, using the extended Hubbard model at a real-space-dependent mean-field level [21][23]. Experimentally, this charge ordering is shown to be accompanied by a formation of ferroelectric domains with a domain size of several hundred micrometers [24][26]; domain walls formed between different ferroelec-
tric domains having opposing electric polarization should therefore naturally appear in the charge ordered phase. However, the relation of this domain wall formation and the observed contrasting pressure dependence of $\Delta_\rho$ and $\Delta_\sigma$ is not yet understood.

In the vicinity of the phase boundary, it is theoretically suggested that the energy dispersion has a small charge-ordering gap at the Dirac points, i.e., the Dirac cones are massive; previous calculation using the Extended Hubbard model and assuming a uniaxial pressure along the a-direction ($P_a$) find that the two massless Dirac points move as increasing $P_a$ and end up with a merging transition at $P_a = 40$ kbar where an energy gap opens at the Fermi energy [4]. We recently analyzed this 2D motion of Dirac points in momentum space in more detail by means of a low-energy effective Hamiltonian based on the Luttinger-Kohn representation (having an effective mass term), finding that the two minima (maxima) in the conduction (valence) band move towards a time-reversal invariant momentum point [24]. Similar studies were also performed in a deformed honeycomb lattice by using an effective two component Hamiltonian, in which the merging transition was investigated in terms of the sizes of transfer integrals and some kind of driving parameters that favour the merging [25–30]. We note that in the charge-ordered phase of $\alpha$-(BEDT-TTF)$_2$I$_3$ the momentum-space topology also changes at the merging; each massive cone is characterized by a non-zero Berry curvature $B_1(k)$ having opposite signs between two cones, whereas this quantity becomes zero when two cones merge [31]. Depending on the sign of $B_1(k)$ in the left cone and the right cone, the valley Hall conductivity would yield valley dependent polarities [21, 22].

In this paper we develop a numerical approach which accounts for the distinct pressure dependence of $\Delta_\rho$ and $\Delta_\sigma$ in the pressurized $\alpha$-(BEDT-TTF)$_2$I$_3$ using a cylindrical boundary condition that naturally introduces domain walls in a space-dependent mean field theory [21–23, 32, 33]. The interaction between electrons is treated within the extended Hubbard model, where the canonical on-site interaction and the nearest-neighbor interactions are included. In our recent mean-field studies in terms of semi-infinite [21, 23] and 2D periodic [40] boundary conditions, indications were found that the influence of variations in pressure is able to be parameterized by the strength of the nearest-neighbor Coulomb interaction along the crystalline a-axis $V_a$, which varies most sensitively upon changing the applied external pressure [43, 45] and plays dominant roles in stabilizing stripe-type charge order that opens a gap in the energy spectrum at the Dirac point. Following this hypothesis, we utilize $V_a$ as our control parameter and elaborate on the mechanism that necessitates domain walls in the model, based on two different types of cylindrical boundary conditions; these models consider periodic boundary conditions in the a-direction but place edges in the b-direction. We present extensive numerical calculations of the dc resistivity and the optical conductivity, using the T-matrix approximation and the Nakano-Kubo formula [22, 36–40], which provide a novel way to understand the anomalous sizes of the gap found in experiments (i.e., $\Delta_\rho << \Delta_\sigma$ around $P \sim 7$ kbar [19, 20]) by means of domain wall conduction along the a-direction in the model’s critical region. We also find an unexpected shoulder-like structure in the optical conductivity at low energy, which is discussed in terms of a metallic bound state on the domain walls.

The remainder of the paper is organized as follows. In Sec. II, we lay out the extended Hubbard model for $\alpha$-(BEDT-TTF)$_2$I$_3$ to be studied in detail together with two kinds of cylindrical boundary conditions we use, either symmetric or asymmetric in the b-direction, and present the formalisms of the dc and optical conductivities within the T-matrix approximation using the Nakano-Kubo formula. Our numerical results are shown in Sec. III: we first focus on the temperature dependence of the dc resistivity for various sizes of the nearest neighbor interaction, and fit the data to the Arrhenius law at different temperature ranges yielding estimates for the transport gap $\Delta_\rho$ as a function of the interaction and for the type of the boundary conditions; we then evaluate the optical conductivity as a function of energy and for the boundary types, providing the optical gap $2\Delta_\sigma$ for a range of interaction sizes. We summarize our findings for the domain wall conduction in Sec. VI and also try to associate our proposed conduction mechanism to the results in real $\alpha$-(BEDT-TTF)$_2$I$_3$ by considering realistic experimental and materialistic conditions.

A range of elaboration is relegated in the Appendix. Some detailed structures of the space-resolved electronic states for the two types of boundary conditions in addition to the interaction-temperature phase diagram are presented in Appendix A.

II. MODEL AND FORMULATION

For the description of conducting mechanisms in $\alpha$-(BEDT-TTF)$_2$I$_3$ in a realistic situation, we will use a similar model as in Refs. [21, 23] in which cylindrical boundary conditions are employed in the conducting 2D plane that assume a periodic condition along the crystalline a-axis, whereas edges are introduced along the b-axis, as presented in Fig. 1(a) and (b). The 2D unit cell in the charge ordered insulating state of $\alpha$-(BEDT-TTF)$_2$I$_3$ contains four nonequivalent molecular sites [12, 11], dubbed A, A’, B and C, which form two distinct columns in the a-direction, i.e., AA’ column and BC column in Fig. 1. Because of these two columns, there are three ways to introduce edges at the two ends in the b-direction: AA’-AA’, AA’-BC and BC-BC. In our previous study [22], however, we showed that the last two have qualitatively little difference in the local electronic structures, and therefore only the edges with AA’-BC and AA’-AA’ types will be considered hereafter. These edge patterns, either asymmetric (AA’-BC) or symmet-
Our starting point is a 2D Hubbard-type model which serves as a standard framework to study interacting electrons on a lattice. In the orthodox Hubbard model one only considers a repulsive on-site interaction between electrons of opposite spin, but in this study we incorporate the nearest neighbor interactions that play one of the most essential roles in driving the charge ordering transition in \( \alpha-(\text{BEDT-TTF})_2I_3 \), as theory first suggested [9] and later NMR experiments confirmed [14]. We also introduce edge potentials following Ref. [14] to treat the effects of a surface charge recombination. (In addition, we note that the interactions between BEDT-TTF molecules and \( I_3 \) anions would also play some roles in charge order as argued in Ref. [32]. Although we do not exclude that possibility, these interactions are assumed to have only a minor influence upon our main arguments and are thus neglected.) The Hubbard-type model used in this study is described by the Hamiltonian \( H = H_{\text{kin}} + H_{\text{int}} \) which
is given by a sum of the kinetic term

\[ H_{\text{kin}} = \sum_{(i,l'),\sigma} \sum_{\sigma'} \left( t_{i,l'} a_{i\sigma}^\dagger a_{i'\sigma'} + \text{h.c.} \right), \tag{1} \]

and the interaction term

\[ H_{\text{int}} = \sum_{l} U n_{l\uparrow} n_{l\downarrow} + \sum_{(i,l'),\sigma} V_{i,l'} n_{i\sigma} n_{i'\sigma'} + \sum_{\text{edge}} V_{\text{edge}} n_{i}. \tag{2} \]

Here, \( l = (i_a, i_b, \alpha) \) represents a molecule \( \alpha = A, A', B, \) and \( C \) in the \((i_a, i_b)\)-th unit cell, for the space slices in the \(a\)-direction \( i_a = 1, \cdots, N_a \) and in the \(b\)-direction \( i_b = 1, \cdots, N_b, \) \( t_{i,l'} \) is the nearest or next nearest neighbor hopping integral between sites \( l \) and \( l' \), \( U \) is the (molecule-independent) on-site interaction, \( V_{i,l'} \) the nearest neighbor interaction between electrons at sites \( l \) and \( l' \) for which we introduce only two types at all sites (one in the \(a\)-direction \( V_a \) and the other in the \(b\)-direction \( V_b \)), \( a_{i\sigma}^\dagger \) (or \( a_{i\sigma} \)) creates (annihilates) an electron of spin \( \sigma = \uparrow, \downarrow \) at site \( l \), \( n_{i\sigma} \) is \( a_{i\sigma}^\dagger a_{i\sigma} \) is the density of electrons with spin \( \sigma \) at site \( l \), and the density \( n_l = \sum_{\sigma} n_{l\sigma} \) at site \( l \) summed over all spin projections. Following recent analyses of the high-pressure NMR data \cite{15,16}, we use the values of \( t_{i,l'} \) given by a first principle calculation in Ref. \cite{43}: \( t_{a1} = -0.0267, t_{a2} = -0.0511, t_{a3} = 0.0323, t_{b1} = 0.1241, t_{b2} = 0.1296, t_{b3} = 0.0513, t_{b4} = 0.0152, t_{a1}' = 0.0119, t_{a3}' = 0.0046, t_{a3}' = 0.0060 \) (in eV; see Fig. 1(c)). The interaction parameters are set to literature-accepted values \( U = 0.4 \) eV and \( V_b = 0.05 \text{eV} \) \cite{21,23}, and \( V_a \) is the control parameter of the model. The third (edge potential) term in \( H_{\text{int}} \) only acts on the electrons at edge sites, and we use the value of the edge potential estimated to be \( V_{\text{edge}} = 4V_b \) following Ref. \cite{22}. The system size is set as \( N_a = 200 \) and \( N_b = 60 \).

The Fourier transformation along the \(a\)-axis, with the operator \( a_{i\sigma} = N_a^{-1/2} \sum_{l} a_{l\sigma} e^{i k_a l} e^{i k_b a} \) defined for \( l = (i_b, \alpha) \) and the wavenumber vector \( k_a \), yields the Hamiltonian

\[ H_{\text{kin}} = \sum_{l_b, l_b', k_a} \varepsilon_{l_b, l_b'}(k_a) a_{l_b, k_a \sigma}^\dagger a_{l_b', k_a \sigma}, \tag{3} \]

\[ H_{\text{int}} = \frac{U}{N_a} \sum_{l_b, l_b', k_a} \sum_{\sigma'} \delta_{l_b, l_b'} a_{k_a \sigma}^\dagger a_{k_a \sigma'}^\dagger a_{k_a \sigma} a_{k_a \sigma'} + \frac{1}{N_a} \sum_{l_b, l_b', k_a} \sum_{\sigma'} V_{l_b, l_b'}(q_a) \]

\[ \times a_{k_a \sigma}^\dagger a_{k_a \sigma'}^\dagger a_{k_a \sigma} a_{k_a \sigma'} + \sum_{\text{edge}} \sum_{k_a} V_{\text{edge}} n_{l_b, k_a} a_{k_a \sigma} \tag{4} \]

where \( \varepsilon_{l_b, l_b'}(k_a) \) and \( V_{l_b, l_b'}(q_a) \) are defined as \( \varepsilon_{l_b, l_b'}(k_a) = \sum_{\delta} t_{l_b, l_b'} e^{-i k_a \delta} \) and \( V_{l_b, l_b'}(q_a) = \frac{1}{2} \sum_{\delta} V_{l_b, l_b'} \), respectively, for a momentum transfer \( q_a \) and a vector \( \delta \) connecting all possible nearest neighbor sites. Within the Hartree approximation, one obtains a mean field Hamiltonian

\[ H_{\text{MF}} = \sum_{l_b, l_b', k_a} \varepsilon_{l_b, l_b'}(k_a) a_{l_b, k_a \sigma}^\dagger a_{l_b', k_a \sigma} + \text{const.}, \tag{5} \]

\[ \varepsilon_{l_b, l_b'}(k_a) = \varepsilon_{l_b}(k_a) + \delta_{l_b l_b'} \phi_{l_b, \sigma}, \tag{6} \]

\[ \phi_{l_b, \sigma} = U(n_{l_b \downarrow} - \sigma) + \sum_{l_b' \sigma'} V_{l_b, l_b'}(n_{l_b' \sigma'}) + V_{\text{edge}}. \tag{7} \]

where \( \langle n_{l_b \sigma} \rangle = \sum_{\sigma'} a_{l_b \sigma}^\dagger a_{l_b \sigma} \) is the mean density of electrons with spin \( \sigma \) at site \( l_b \) averaged for the Fermi distribution. Diagonalization of \( H_{\text{MF}} \) leads to the energy eigenvalue \( E_{\nu \sigma}(k_a) \) and the eigenvector \( d_{l_b, \nu \sigma}(k_a) \), which results in a formation of energy band \( \nu = 1, 2, \cdots, 4N_{b} - 2 \) \((1, 2, \cdots, 4N_{b} - 1, 4N_{b})\) for the symmetric (asymmetric) edge pattern. Recalling the orthogonality \( \sum_{k_a} d_{l_b, \nu \sigma}(k_a) d_{l_b, \nu' \sigma}(k_a) = \delta_{\nu \nu'} \), the Hamiltonian becomes

\[ H_{\text{MF}} = \sum_{k_a \nu \sigma} E_{\nu \sigma}(k_a) c_{k_a \nu \sigma}^\dagger c_{k_a \nu \sigma} + \text{const.}, \tag{8} \]

\[ E_{\nu \sigma}(k_a) d_{l_b, \nu \sigma}(k_a) = \sum_{l_b'} \varepsilon_{l_b, l_b'}(k_a) d_{l_b', \nu \sigma}(k_a), \tag{9} \]

with \( E_{1 \sigma}(k_a) < E_{2 \sigma}(k_a) < \cdots < E_{4N_{b} - 2 \sigma}(k_a) \). The chemical potential \( \mu \) is determined from the quarter filling condition \( \frac{1}{2} \sum_{l_b \sigma} \langle n_{l_b \sigma} \rangle = \frac{1}{2} \). Note that we set \( h = k_B = 1 \). Using Eqs. (8) and (9), we will evaluate the electronic properties at finite temperature, in particular conductivity.

The optical conductivity along the \(a\)-axis is calculated by the Nakano-Kubo formula which is formulated in terms of a linear response theory given by

\[ \sigma^\alpha(\omega) = \frac{1}{i \omega} \left[ Q_R(\omega) - Q_R(0) \right], \tag{10} \]

\[ Q_R(\omega) = -\frac{e^2}{\Omega} \sum_{k_a \nu \sigma} \left| v_{\nu \sigma}^\alpha(k_a) \right|^2 \]

\[ \times \frac{f(E_{\nu \sigma}(k_a)) - f(E_{\nu \sigma}(k_a))}{E_{\nu \sigma}(k_a) - E_{\nu \sigma}(k_a) + \omega + i \Gamma}, \tag{11} \]

for the 2D system size \( \Omega = N_a \times N_b \) and the Fermi-Dirac distribution function \( f(E_{\nu \sigma}(k_a)) \).

The longitudinal dc conductivity \cite{22,36,39} along the \(a\)-axis is given by

\[ \sigma^\alpha = \int d\omega \left( -\frac{df}{d\omega} \right) \Phi(\omega), \tag{12} \]

\[ \Phi(\omega) = \frac{2e^2}{\pi \Omega} \sum_{k_a} \text{Tr} \left[ v^\alpha \text{Im} \hat{G}^R(\omega, k_a) v^\alpha \text{Im} \hat{G}^R(\omega, k_a) \right], \tag{13} \]

where one introduces velocity variables

\[ v_{l_b, \nu \sigma}^\alpha(k_a) = \sum_{l_b'} d_{l_b, \nu \sigma}^\alpha(k_a) v_{l_b', \nu \sigma}^\alpha(k_a) d_{l_b', \nu' \sigma}(k_a), \tag{14} \]

\[ v_{l_b, l_b'}^\alpha(k_a) = \frac{\hat{\partial}}{\partial k_a} \varepsilon_{l_b, l_b'}(k_a), \tag{15} \]
and $\hat{G}_R$ is the retarded Green function written in the T-matrix approximation as

$$G_{l_i l'_i \sigma}^R(\omega, k_a) = \sum_{\nu} \frac{d_{l_i l'_i \sigma}(k_a) d_{l'_i l \sigma}^*(k_a)}{\omega - E_{\nu \sigma}(k_a) - \Sigma_{l_i l' \nu}^R(\omega, k_a)},$$

with the retarded self energy

$$\Sigma_{l_i l' \nu}^R(\omega, k_a) = \sum_{l_b} \frac{n_{\text{imp}} V_{\text{imp}} |d_{l_i l' \nu}(k_a)|^2}{1 - \frac{V_{\text{imp}}}{\pi \rho} \sum_{l'_b} G_{l_i l' \nu}^R(\omega, k_a)},$$

and the single-particle retarded Green function

$$G_{l_i l' \nu}^0(\omega, k_a) = \sum_{l_b} \frac{d_{l_i l' \nu}(k_a) d_{l'_b l \nu}^*(k_a)}{\omega - E_{\nu \sigma}(k_a) + i0^+},$$

in terms of the impurity potential $V_{\text{imp}}$, defined by

$$H' = \frac{V_{\text{imp}}}{N_a} \sum_{l= \alpha \sigma} n_{\text{imp}}^l \rho_{\text{imp}}(q_{\alpha \sigma}) a_{l_{\alpha \sigma}}^\dagger a_{l_{\alpha \sigma}},$$

$$\rho_{\text{imp}}(q_{\alpha \sigma}) = \sum_{l_{\alpha \sigma}} e^{-i q_{\alpha \sigma} r_l},$$

for the number of impurity centers $N_{\text{imp}}$ and the density of impurities $n_{\text{imp}} = N_{\text{imp}} / N_a$ in the $a$-direction. The damping constant $\gamma_{\nu \sigma}(\omega, k_a)$ is given by the imaginary part of $\Sigma_R^R$ and is calculated as

$$\gamma_{\nu \sigma}(\omega, k_a) = -\Im \Sigma_{\nu \sigma}^R(\omega, k_a) = \sum_{l_i} \left| d_{l_i l' \sigma}(k_a) \right|^2 \left[ \pi n_{\text{imp}} V_{\text{imp}} N_{l_i \sigma}(\omega) \right] 1 + \pi V_{\text{imp}} N_{l_i \sigma}(\omega),$$

where we introduced a site resolved spectral density $N_{l_i \sigma}(\omega)$

$$N_{l_i \sigma}(\omega) = \frac{1}{N_a} \sum_{k} \left( -\frac{1}{\pi} \Im \Sigma_{l_i l' \nu}^R(\omega, k_a) \right)$$

$$= \frac{1}{N_a} \sum_{k} \delta(\omega - E_{\nu \sigma}(k_a)) \left| d_{l_i l' \nu}(k_a) \right|^2.$$

Recalling $\tau = 1/2\gamma$ defines the relaxation time, one is able to simplify $\Phi$ in Eq. (15) to the expression

$$\Phi(\omega) = \frac{4e^2}{\Omega} \sum_{k_{\alpha \nu}} |v_{\alpha \nu}^l(k_a)|^2 \tau_{\nu}(\omega, k_a) \delta(\omega - E_{\nu}(k_a)).$$

In order to see the spatial distribution of the conductivities along the $b$-direction, we define a spatially resolved conductivity

$$\sigma_{b_i}^a = \int d\omega \left( -\frac{d}{d\omega} \right) \Phi_{b_i}(\omega),$$

with a distribution function

$$\Phi_{b_i}(\omega) = \sum_{a_l l_i} \Phi_{l_i l_i l_i}(\omega),$$

$$\Phi_{l_i l_i l_i}(\omega) = \frac{4e^2}{N_a} \sum_{k_{\alpha \nu}} |v_{\alpha \nu}^l(k_a)| \left[ d_{l_i l_{\nu} l_{i}}^0(k_a) v_{l_i l_{\nu} l_{i}}^0(k_a) d_{l_i l_{\nu} l_{i}}^0(k_a) \right]$$

$$\times \tau_{\nu}(\omega, k_a) \delta(\omega - E_{\nu}(k_a)).$$

The dc conductivity $\sigma^a$ (or dc resistivity $\rho^a = 1/\sigma^a$) are derived from a summation of $\sigma_{b_i}^a$ over $i_b$. In the following section, the unit of the conductivity is set by the universal conductivity $\sigma_0 = 4e^2/\pi\hbar$, and we use eV as the unit of energy.

III. NUMERICAL RESULTS

A. Transport coefficients

Figures 2(a) and (b) present the 2D plots of the spatially resolved dc conductivity $\sigma_{b_i}^a(T)$ in the $a$-direction at $V_a = 0.21$ plotted also as a function temperature $(T)$ and the position in the $b$-direction $i_b$, for the AA'-BC asymmetric edges [Fig. 2(a)] and the AA'-AA' symmetric edges [Fig. 2(b)]. The plots reveal a very different nature in the low $T$ behaviors in each case. For the asymmetric case, $\sigma_{b_i}^a(T)$ vanishes at low $T$ in the bulk of the sample since a gap opens at the Fermi energy. For the symmetric case, by contrast, $\sigma_{b_i}^a(T)$ becomes vanishingly small at low $T$ except for the region at the center of the sample along the $b$-axis (i.e., $i_b = 30$) where a gapless one-dimensional (1D) bound state appears on the domain wall, yielding finite conductivity. (The detailed analyses of the local electronic states are discussed in Appendix A.) Note that high conductivity also survives at low $T$ on the two edges in the symmetric-edge case while it remains large only on the right end in the asymmetric-edge case, which can be explained by means of thermal edge conductance due to the edge states (see Figs. A.1 and A.2).

To have a closer look on the temperature dependence, we measured the dc resistivity $\rho^a(T)$ as a function of $T$ in the $a$-direction for several strength of interaction, using $V_a$ ranging from 0.180 to 2.30. The resulting curves for the asymmetric and symmetric edge patterns are shown in Figs 3(a) and 3(b), respectively. For the asymmetric case [Fig. 3(a)], the curves start to diverge at low $T$ above a critical value of interaction $V_a^c = 0.197$ which signals the generation of a gap via spontaneous charge ordering, in line with our recent results using a two-dimensional periodic boundary condition [40]. These data are contrasted to the symmetric case [Fig. 3(b)] in which the resistivity does not diverge but levels off at low $T$ for $V_a > V_a^c$ since the domain wall formation in the charge ordered state results in the finite conductivity along the gapless 1D bound state. The values of the resistivity gap $2\Delta_{\rho}$ can be extracted from exponential fits to the Arrhenius plot of $\rho^a(1/T)$, presented in Figs. 3(c) and 3(d) for the asymmetric and symmetric cases, respectively, together with the fitted lines. The slope of the data shows a systematic increase for $V_a \geq V_a^c$ for the asymmetric case [Fig. 3(c)], pointing to a continuous evolution of $2\Delta_{\rho}$ as $V_a$ is increased. For the symmetric case [Fig. 3(d)], however, the curves of $\rho^a(1/T)$ show a nonmonotonic behavior upon increasing $V_a$: for large values of $V_a$ there is a steep slope at high $T$ (around the transition temperature
\[ T^* \), a gradual increase at intermediate \( T \) (\( \approx T^*/2 \)) and a clear levelling-off at low \( T \) (\( T \approx 0.001 \ll T^* \)). These contrasting behaviors yield different estimates of \( 2\Delta_p \) in the charge ordered state \( V_a > V_{c}^* \) that strongly depend on the range of the fits to the data, as we shall see below.

We note here that the calculated \( \rho^a(1/T) \) in Fig. 3(d) have many features in common with the recent transport experiments at a range of pressure \( P \) \([19]\) that show strongly nonmonotonic changes in the shape of \( \rho^a(1/T) \) upon increasing \( P \). This apparent similarity motivates us to make a comparison of the calculated values of \( 2\Delta_p(V_a) \) with the experimentally obtained ones \( 2\Delta_p(P) \), albeit their control parameters are different. To this end, we experimented with fits with different fitting ranges to Figs. 3(c) and 3(d) together with fits to the previous data for the 2D periodic boundary condition \([40]\). Figure 4 plots the resulting values of \( 2\Delta_p \) against \( V_a \) for several fitting procedures, in which the horizontal axis is re-verted in order to make their comparison to the pressure-dependence data in Ref. \([19]\). The charge-ordering gap \( 2\Delta_p(V_a) \) starts to open at \( V_a = V_{c}^* \) and continues to develop almost linearly for \( V_a > V_{c}^* \). Their gap sizes well agree with each other for the 2D boundary condition and the case of asymmetric edge since the bulk appearance of charge order results in a unique definition of the gap. In contrast, the evolution of \( 2\Delta_p(V_a) \) shows a marked difference for the symmetric edge which depends on the type of the fit; the fits at high \( T \) yield the same results as the above two cases, pointing to a small influence of the in-gap bound state at high temperature. On the other hand, the gap becomes smaller for the fits at intermediate \( T \) and is almost zero for the low \( T \) fits, reflecting the presence of the metallic bound state that dominates the conductivity at low temperature.

In Ref. \([19]\) the authors examined the fits to the Arrhenius plot of the experimental resistivity \( \rho^a \) at a range of pressures \( P \) for determining \( 2\Delta_p(P) \), but the choice of their fitted temperature range was pressure dependent. For instance, the fits were done just below the transition temperature at ambient pressure, at half of the transition temperature at \( P = 4.8 \) and 6.3 kbar, and at the low-temperature limit (below 20 K) for 7 kbar < \( P < P_c \). Given the similarity of the experimental Arrhenius plots and Fig. 3(d), one is tempted to hypothesize that there is a correspondence between the \( P \)-dependent choice of the fit range mentioned above and the \( V_a \)-dependent fit range in Fig. 3(d). This allows us to deduce the corresponding curve of \( 2\Delta_p(V_a) \) that follows the experimental results (the black dash-dotted line in Fig. 4).
FIG. 4. (Color online) The resistivity gap $2\Delta \rho$ plotted as a function of $V_a$ for the 2D periodic boundary condition (phases) and the asymmetric-edge (crosses) as well as the symmetric-edge for fits to $\rho^2(1/T)$ at high $T$ (stars), mid $T$ (filled squares), and low $T$ (open squares). $V_c^\alpha$ stands for the critical point in this model at which the charge-ordering gap closes. The black dash-dotted line corresponds to the $Va$ dependence of $2\Delta \rho$ that is deduced from the experimental data in Ref. [19] following the fitting procedure discussed in the text.

B. Optical conductivity

As the next step of this study, we calculated the optical conductivity $\sigma^a(\omega)$ vs $\hbar \omega$ in the $a$-direction for the asymmetric (AA'-BC) and symmetric (AA'-AA') edges; the interaction $V_a$ was varied between 0.180 and 2.30. The representative conductivity data normalized to $\sigma_0 = 4e^2/\pi h$ deep in the charge ordered phase ($T = 0.0005$) are presented in Fig. 5, calculated at $V_a = 0.21$. The overall shape of the optical conductivity spectra is more or less similar for the two edge cases, which is characterized by a sharp drop at $2\Delta_O \approx 20meV$ signaling the opening of a direct charge-ordering gap at the Dirac point and a hump-like structure with a peak at $\hbar \omega_{\text{peak}} \approx 34meV$ above the gap. The peak is ascribed to a direct transition between different van Hove singularities in the conduction and valence bands locating at a time reversal invariant momentum (TRIM). Similar structures have been observed in our previous study using the 2D periodic boundary condition [40]. The remarkable finding here is that there is an additional bump at low energy with a kink at $\hbar \omega_{\text{DW}} \approx 6meV$ which only appears in the symmetric-edge case. This bump can be associated to a direct transition between the conduction band and the gapless band at the Fermi energy that is linked to the 1D bound state on the domain wall. In addition, we note that $\hbar \omega_{\text{DW}}$ is almost half the charge ordering gap $2\Delta_O$ since the Fermi energy locates at approximately the mid point of the gap (for details, see the inset of Fig. 5).

Figures 6(a) and 6(b) show the 2D plots of the spatially resolved optical conductivity $\sigma^a_{\nu}(\omega)$ normalized to $\sigma_0$ in the charge ordered phase ($T = 0.0005$) calculated at $V_a = 0.21$ for the asymmetric-edge [Fig. 6(a)] and the symmetric-edge [Fig.6(b)], plotted as a function of $\hbar \omega$ and the position $i_b$ in the $b$-direction. A spatially uniform optical gap is clearly visible in both plots except for the central region ($i_b \sim 30$) in the case of symmetric-edge in which the conductivity increases from a lower energy due to the bound state at the domain wall, bringing about a T-shaped structure in the profile of $\sigma^a_{\nu}(\omega)/\sigma_0$. At the edges finite conductivity resumes due to direct transitions between the edge states (Fig. A. 2) and the conduction band. The edge conductance is absent at the left end of the sample ($i_b = 60$) in Fig. 6(a) since there is no edge states in this case (see the Appendix A for detail).

In Fig. 7 we present results for both the optical gap $2\Delta_O$ and the two characteristic energy scales $\hbar \omega_{\text{peak}}$ and $\hbar \omega_{\text{DW}}$ defined in Fig. 5 at $T = 0.0005$ as a function of $V_a$. Here the horizontal axis is inverted for the sake
FIG. 6. (Color online) The 2D plot of the spatially-resolved optical conductivity $\sigma^{\text{ib}}_a(\omega)/\sigma^0$ for the asymmetric-edge pattern (a) and the symmetric-edge pattern (b).

FIG. 7. (Color online) The optical gap $2\Delta_O$ plotted against $V_a$ (crosses). Other characteristic energy scales of $\hbar\omega_{\text{peak}}$ (stars) and $\hbar\omega_{\text{DW}}$ (open circles) are also presented. Here, $\hbar\omega_{\text{peak}}$ is defined as the energy difference between the conduction and valence bands at the M-point in the first Brillouin zone.

IV. SUMMARY AND DISCUSSION

The main result in this study is that by numerical calculations, in a minimal lattice model representing interacting 2D Dirac electrons in $\alpha$-(BEDT-TTF)$_2$I$_3$, we have identified a conduction regime dominated by a gapless 1D bound state on a domain wall formed on a boundary between two interaction-induced charge-ordered domains having opposite electric polarization. We have been able to identify that the domain wall conduction is a unique feature that necessarily appears when one introduces a cylindrical boundary condition with a symmetric-edge pattern in the b-direction, as illustrated in Fig. 1(b). The most striking finding, emerging from a calculation of spatially resolved conductivities and supported by both a direct study of the bulk properties and a fit to the resistivity with a $T$-dependent fitting range, is that the resistivity saturates at low $T$ due to the gapless excitations on the domain wall. In addition, we have presented results for the optical conductivity spectra, finding evidence for an in-gap bound state that is also explained by the domain wall. These data are significantly different...
from the results obtained for an asymmetric-edge pattern and a 2D periodic boundary condition [40] possessing no domain walls, demonstrating that a domain-wall formation causes a remarkable change in the conductivity at low energy.

We have also estimated the transport and optical gaps using several means, confirming an opening of a charge-ordering gap developing spontaneously at the Dirac point for \( \nu_a > \nu_{a,c} \), experiencing a merging transition (pair annihilation) of gapped Dirac points at \( \nu_a = \nu_{a,c}^2 \), and turning into a trivial gap with no Dirac points for \( \nu_a > \nu_{a,c}^2 \) [21][23], as summarized in Fig. A.3. The Arrhenius analyses of the resistivity data provide entirely distinct gap values depending strongly on the \( T \) slice the data are fitted; the gap is identical to the bulk gap just below the transition temperature \( T^* \), whereas it is largely suppressed towards lower \( T \) and eventually becomes zero at low \( T \). We reiterate that a very similar behavior has been reported in the recent transport experiments under pressure; Fig. 1(b) of Ref. [19] highlights a levelling-off-like feature of resistivity developing upon increasing pressure at low \( T \) which draws an excellent parallel with the calculated resistivity in Fig. 3(d) showing a similar saturation at large \( V_a \). This strongly reinforces our original hypothesis that the major impact of pressurization is altering the size of \( V_a \).

We should however note that, while our model assumes semi-infinite boundary conditions and is hence different from the situation in a naturally grown \( \alpha \)-(BEDT-TTF)\(_2\)I\(_3\) bulk sample, a real crystal is a quasi-2D system consisted of a multiple stacks of 2D conducting layers that inevitably has edges in each layer of either asymmetric- or symmetric-edge types. Taking proper account of this will allow us to expect certain portions of the layers to be comprised of the symmetric-edge pattern; we therefore argue that domain wall conductance must be relevant at low temperature at least in these symmetric-edged layers. Recent experimental reports on the electronic ferroelectricity in \( \alpha \)-(BEDT-TTF)\(_2\)I\(_3\) at ambient pressure [21][20] agree with this notion, which point to the presence of multiple domain walls created between charge-ordered regions having opposing electric polarizations. Another interesting remark is that the saturation-like behavior of resistivity emerges even at ambient pressure in some samples [14] (albeit it is absent in others [19][41]). This suggests that the domain wall conductance may be present in an extended region of the charge ordered phase in the real materials. We propose that optical conductivity or real-space resolved spectroscopy would be able to confirm domain walls, which should see some bump structures at low energy inside the charge-ordering gap.

Of course, the assumption in our model is oversimplified, and in reality pressure also changes other parameters such as the electronic bandwidth as well as interactions between BEDT-TTF molecules and I\(_3\) anions [42]. In our view, however, these effects are insufficient to qualitatively reproduce the remarkable saturation of the low-\( T \) resistivity, allowing us to safely omit them as a first approximation. Unfortunately the putative model we rely on precludes us from making a more quantitative analysis of the gap sizes at this stage. In this regard a more complete calculation considering all these pressurization effects may prove interesting.

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Appendix A: Local electronic structures for (AA’-BC) asymmetric- and (AA’-AA’ symmetric-edge patterns

In the Appendix A, we present results of investigations of local electronic states in the charge-ordered state around the merging transition of two massive Dirac points (at \( \nu_a \approx \nu_{a,c}^2 = 0.212 \)), with a particular emphasis on band structures, densities of electrons on each site, and edge-state structures.

Figures A.1(a) and (b) show the mean-field energy eigenvalue \( E_F(k_a) \) around the Fermi level at the charge-ordering temperature \( T^* = 0.0075 \) for the asymmetric- and symmetric-edge patterns, respectively. In addition the corresponding mean density of electrons \( \langle \eta_i \rangle \) at site \( \nu_a = \nu_{a,c}^2 \) and the \( \langle \eta_i \rangle \) is plotted in Fig. A.1(c) for the asymmetric-edge and in Fig. A.1(d) for the symmetric-edge (see Eqs. (8) and (9)). The gapless state arising from the domain wall and crossing \( E_F \) is present in the energy spectrum for the symmetric-edge [green curve in Fig. A.1(b); band index \( \nu = 179 \)], whereas it is absent for the asymmetric-edge so that the system is fully gapped [Fig. A.1(a), where the green curve represents the top level in the valence band; band index \( \nu = 180 \)]. Note that the sizes of \( \langle \eta_i \rangle \) for the symmetric-edge coincide at \( \nu_a = 30 \) at the sites A and A’, which signifies the appearance of the domain wall as we discussed previously [21][23].

In Fig. A.2 we plot the temperature dependence of the modulus of squared A-site eigenvector at \( k_a = \pi/2 \), \( \eta_{A\nu}(\pi/2) \), by focusing on the band \( \nu = 179 \) and the unit cell \( \nu_a = 30 \) (i.e., at the center) for symmetric-edge and \( \nu = 180 \) and \( \nu_a = 3 \) (i.e., around the right end) for asymmetric-edge, respectively. The 2D plot of \( \eta_{A\nu}(\pi/2) \) at \( T = 0.011(> T^*) \) is also shown in the inset, plotted as a function of \( \nu_a \) and \( k_a \) for asymmetric [inset (a)] and symmetric [inset (b)] edges. A clear change in the temperature dependence occurs for both cases at \( T = T^* \). For \( T > T^* \) the emergence of edge states is clearly visible in both cases, while the peak
FIG. A.1. (Color online) The energy spectrum near the Fermi energy at $V_a = 0.21$ and $T = T^* = 0.0075$ plotted as a function of the wavevector in the $a$-direction ($k_a$) for the asymmetric-edge pattern (a) and the symmetric-edge pattern (b). The corresponding mean electron charge density at each molecule in the unit cell $i_b$ is also presented in (c) and (d), respectively. The green solid curves in (a) and (b) specify those bands that are important for the arguments of domain wall, labeled as $\nu = 180$ for the asymmetric-edge and $\nu = 179$ for the symmetric-edge.

FIG. A.2. (Color online) Temperature dependence of the squared A-site eigenvector at $k_a = \pi/2$ and $V_a = 0.21$ plotted for the asymmetric-edge ($\nu = 180$) and the symmetric-edge ($\nu = 179$). The results around the right edge ($i_b = 3$) and the center ($i_b = 30$) are presented. $T^*$ represents the charge-ordering transition temperature. Inset: the 2D plot of the squared A-site eigenvector at $V_a = 0.21$ and $T = 0.011 (> T^*)$, plotted as a function of $k_a$ and $i_b$ for asymmetric ($\nu = 180$) (a) and symmetric ($\nu = 179$) (b) edges.

FIG. A.3. (Color online) The $V_a - T$ phase diagram. $T_{DW}$ is calculated by fits to $\langle n_{i_b,A} \rangle$ using a hyperbolic tangent function [21, 23]. $T^*$ is defined as the temperature where the second derivative of the Helmholtz Free energy $\partial^2 F(T)/\partial T^2$ shows a discontinuous behavior. Gapless Dirac cones are present in the massless Dirac electron phase protected by the space and time inversion symmetry, whereas the inversion symmetry is broken in the colored region due to charge ordering; for $T_M < T < T^*$ (green region), a charge-ordering gap opens at the Dirac points and the cones become massive. These massive cones merge at $T = T_M$ at the M point so that the charge-ordered state becomes a trivial one without Dirac points (yellow region).

size of $|d_{i_b,A\nu}(\pi/2)|^2$ for asymmetric-edge is twice larger than that for symmetric-edge. Moreover, the edge state appears only at the right end in the former, whereas they are visible at both ends in the latter. These results suggest that electrons tend to gather more easily round charge neutral molecules that appear in the AA’ column at the edges (see Fig. 1). For $T < T^*$ in the symmetric-edge case a redistribution of electrons takes place which shifts electrons from the edge ($|d_{i_b,A\nu}(\pi/2)|^2$ at $i_b = 3$) to the center ($|d_{i_b,A\nu}(\pi/2)|^2$ at $i_b = 30$) due to the domain-wall formation and the associated bound state. In the asymmetric-edge case, by contrast, electrons do not gather round the center, but instead the population around the right edge ($|d_{i_b,A\nu}(\pi/2)|^2$ at $i_b = 3$) suddenly increases below $T^*$, signaling that electrons are bound to charge neutral molecules in the whole temperature range. These edge-bound electrons might contribute to the conductivity by thermal excitations.

Figure A.3 shows the $V_a - T$ phase diagram obtained in this study. Here, the line of $T^*$ stands for the transition temperature to the charge-ordered state which also divides the Dirac electron phase into a massless phase (with gapless Dirac cones) and a massive phase (with gapped Dirac cones). The characteristic energy scale for the domain-wall formation, $T_{DW}$, is determined from the
temperature where the domain-wall width $W_D$ at the given $V_0$ diverges (for more details, see Ref. [21][23]). The fact that $T^*$ coincides with $T_{DW}$ supports the notion that the domain wall appears only in the charge-ordered state and disappears in the massless Dirac electron phase. A merging of the gapped Dirac cones occurs at $T_M$ which transforms the massive Dirac electron phase into a trivial charge-ordered phase with no Dirac points. These two phases can be distinguished by the valley Hall effect [21] because the valley Chern number has a finite value only in the massive Dirac electron phase. (Note however that the real situation is a bit more complicated as the merging happens separately in the conduction and valence bands in $\alpha$-(BEDT-TTF)$_2$AuI, reflecting the tilt of the Dirac cones. We therefore defined $T_M$ as the temperature where the merging of two energy minima occurs in the conduction band.) We also mention that the previously discussed zero line of the B-site (C-site) wave function connecting two Dirac points in the conduction (valence) band [15] disappears when the merging transition occurs in each band.

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