Charge ordering and coexistence of charge fluctuations in quasi-two-dimensional organic conductors $\theta$-(BEDT-TTF)$_2X$

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We present a scenario for the peculiar coexistence of charge fluctuations observed in quasi-2D $1/4$-filled organic conductors $\theta$-(BEDT-TTF)$_2X$ in the quantum critical regime where the charge ordering is suppressed down to zero temperature. The scenario is explored in the extended Hubbard model including electron-phonon couplings on an anisotropic triangular lattice. We find that the coexisting fluctuations emerge from two different instabilities, the “Wigner crystallization on lattice” driven by the off-site Coulomb repulsion and the charge-density-wave formation due to the nesting of the Fermi surface, not from phase competition or real-space inhomogeneity. This mechanism explains the contrastive temperature dependence of two fluctuations in experiments.

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Charge ordering (CO) is a periodic arrangement of electrons which drives a metal-insulator transition. It is often found in organic conductors as well as transition metal compounds, and it plays a key role in electronic properties such as transport phenomena. Careful control of chemical substitutions and/or the external pressure has revealed a systematic change of the electronic states, and has opened up the possibility of a comprehensive understanding of the correlated electron systems [1, 2].

Among them, quasi-2D organic conductors $\theta$-(ET)$_2X$ are intriguing systems, where ET is an abbreviation for BEDT-TTF and X represents monovalent closed-shell unit. The crystal structure consists of an alternating stack of ET and X layers; ET molecules constitute conducting layers of an anisotropic triangular structure as schematically shown in Fig. 1 and anions $X^-$ form insulating layers. The charge transfer between ET and $X^-$ layers leads to hole doping at $1/4$ filling in the ET layers (one hole per two ET molecules on average). By changing X units and/or by applying pressure, the compounds exhibit a rich variety of electronic phases at low temperatures ($T$), such as CO insulator, spin-Peierls state, and superconductivity. It was proposed that the variety is summarized in a systematic way by using the angle between neighboring ET molecules, i.e., the dihedral angle $\phi$ (Fig. 1) [3, 4]. It is considered that $\phi$ modifies the transfer integrals between ET molecules, $t_p$ and $t_c$, in particular, the ratio between them, $t_c/t_p$. In fact, in the series of $X = MM'(SCN)_4$ with $M' = Co$ or Zn, a stripe-type CO takes place in compounds with $M$ = Tl and Rb [5-8], and the transition temperature is decreased from $T_{CO} = 250$ K for Tl to 190 K for Rb, as $\phi$ decreases from $116^\circ$ to $111^\circ$ and correspondingly $t_c/t_p$ decreases from 0.5 to 0.4. Finally, $T_{CO}$ is suppressed down to the lowest $T$ for $M = Cs$ with $\phi = 104^\circ$ and $t_c/t_p \sim 0.1$.

The marginal compound with $M = Cs$, close to the quantum critical point where $T_{CO} \rightarrow 0$, has attracted special attention because of its peculiar low-$T$ properties. A striking feature was found in X-ray scattering results: two diffuse peaks were observed at different wave numbers [9, 10]. One appears at the same wave number as that of the stripe-type CO in Tl and Rb compounds, which has a twofold period along the $c$ axis. The other peak corresponds to a threefold period both in the $a$ and $c$ axes. It is remarkable that charge fluctuations with different wave numbers coexist. Moreover, these diffuse peaks exhibit contrastive $T$ dependence: The peak for the twofold period grows rapidly below $T \sim 90$ K, while the threefold one shows little $T$ dependence [3, 10].

Recently, anomalous transport properties were also observed [11, 12, 13], and their relation to the characteristic charge fluctuations has been issued. In fact, it was found that the peak for the two-fold period is suppressed under the electric current, while the threefold one is not [12].

A scenario to understand the peculiar behaviors is phase competition among different CO states. Several different CO states are stabilized due to strong Coulomb repulsion [14-17], which are sometimes considered as generalization of “Wigner crystals” [18]. It was shown that, in a certain parameter regime, some of the CO states are energetically degenerate, and a keen competition among them may suppress long-range CO and even lead to metallic behavior [15, 21, 22, 23]. It was spec-

FIG. 1: Schematic picture of BEDT-TTF layer. Ellipses represent BEDT-TTF molecules, which form an anisotropic triangular lattice. $\phi$ is the dihedral angle, and $t_p$ and $t_c$ are the transfer integrals for the nearest-neighbor molecules used in the tight-binding Hamiltonian. See the text for details.
ulated that the phase competition leads to an inhomogeneous state where the competing phases are mixed in the real space by forming domainlike structure \[11, 12\]. However, it is not obvious how such inhomogeneity emerges in the clean system almost free from impurities and why different domains grow with the contrastive $T$ dependence. Furthermore, there is no experimental evidence for the domainlike state so far.

In this letter, we present an alternative scenario for the puzzling coexistence of charge fluctuations as well as the systematic change of the CO phase diagram in $\theta$-(ET)$_2$X by focusing on different roles of the off-site Coulomb repulsion and the kinetic energy of electrons.

Our Hamiltonian consists of two contributions as $\mathcal{H} = \mathcal{H}_{\text{EHM}} + \mathcal{H}_{\text{el-ph}}$. The former term represents the extended Hubbard model in the form

$$\mathcal{H}_{\text{EHM}} = t_p \sum_{\langle i,j \rangle, \sigma} (c_{i \sigma}^\dagger c_{j \sigma} + \text{H.c.}) + t_c \sum_{\langle i,j \rangle, \sigma} (c_{i \sigma}^\dagger c_{j \sigma} + \text{H.c.}) + U \sum_i n_{i \uparrow} n_{i \downarrow} + V \sum_{\langle i,j \rangle} n_{i \sigma} n_{j \bar{\sigma}}. \quad (1)$$

Here, the summations with $\langle i,j \rangle_{p(c)}$ are taken over the nearest-neighbor sites along the $x, y$ axes ($c$ axis) (Fig. 1). The off-site Coulomb interaction $V$ is taken to be isotropic because of the almost equal distances between neighboring ET molecules. We consider the case of $t_p, t_c > 0$ and the average electron density at 1/4 filling, which corresponds to $\theta$-(ET)$_2$X by the electron-hole transformation. We take $t_p = 1$ as an energy unit, and set the Boltzmann constant $k_B = 1$.

The latter term $\mathcal{H}_{\text{el-ph}}$ describes the electron-phonon coupling which are necessary because CO appears with a change of the lattice structure [11, 12, 24]. Although realistic phonon modes are complicated, here we simply incorporate the Holstein type and the Su-Schrieffer-Heeger (SSH) type phonons in the model as $\mathcal{H}_{\text{el-ph}} = \mathcal{H}_{\text{Holstein}} + \mathcal{H}_{\text{SSH}}$ with

$$\mathcal{H}_{\text{Holstein}} = g \sum_i u_i n_i + \sum_i \left\{ \frac{M \omega_0^2}{2} u_i^2 + \frac{1}{2M} \Pi_i^2 \right\}, \quad (2)$$

$$\mathcal{H}_{\text{SSH}} = g_p \sum_{\langle i,j \rangle, \sigma} (u_{a,j} - u_{a,i})(c_{i \sigma}^\dagger c_{j \sigma} + \text{H.c.}) + g_c \sum_{\langle i,j \rangle, \sigma} (u_{c,j} - u_{c,i})(c_{i \sigma}^\dagger c_{j \sigma} + \text{H.c.}) + \sum_i \left\{ \frac{M' \omega_0^2}{2} (u_{a,i}^2 + u_{c,i}^2) + \frac{1}{2M'}(\Pi_{a,i}^2 + \Pi_{c,i}^2) \right\}. \quad (3)$$

In $\mathcal{H}_{\text{Holstein}}$, $g$ is the coupling constant; $u_i$ and $\Pi_i$ denote the lattice distortion and its conjugate momentum at site $i$, respectively. In $\mathcal{H}_{\text{SSH}}$, we describe the displacements of $\text{r}$th site in the $a$ and $c$ directions by $u_{a,i}$ and $u_{c,i}$, respectively, and we assume that they modulate the transfer integrals $t_p$ and $t_c$ independently with the coupling constants $g_p$ and $g_c$; the summations are taken in a manner that an elongation (shrinkage) of the bond length decreases (increases) the transfer integrals. $\Pi_{a,i}$ and $\Pi_{c,i}$ are the conjugate momenta of $u_{a,i}$ and $u_{c,i}$, respectively. $M$, $M'$ and $\omega_0$, $\omega_0'$ are mass and eigen-frequency of the corresponding phonons, respectively.

To study CO phenomena in our model, we mainly analyze the charge susceptibility $\chi_c(q, \omega)$ by RPA. For instance, in the case of the model with the Holstein phonons ($\mathcal{H}_{\text{SSH}} = 0$), $\chi_c$ is given in the form

$$\chi_c(q, \omega) = \frac{\chi^{(0)}(q, \omega)}{1 + W(q, \omega) \chi^{(0)}(q, \omega)}, \quad (4)$$

and $\chi^{(0)}$ is the bare susceptibility given by $\chi^{(0)}(q, \omega) = \frac{1}{N} \sum_p \{ f(\varepsilon_{p+q} - \varepsilon_p) - f(\varepsilon_p) \}$ ($\varepsilon_p$ is the Fermi distribution function, and $N$ is the number of sites), $f$ is the Fourier transform of the off-site Coulomb interaction, $V(q) = 2V \{ \cos q_x + \cos q_y + \cos(q_x + q_y) \}; D^{(0)}$ is the bare phonon Green’s function given by $D^{(0)}(q, \omega) = -2\omega_q/\omega_q^2 + \gamma^2$, and $\gamma = g/\sqrt{2M\omega_q}$. The expression becomes more complicated when $\mathcal{H}_{\text{SSH}}$ is included, but the main features of our results below are retained.

Now we discuss RPA results, mainly for the model without the SSH-type coupling ($\mathcal{H}_{\text{SSH}} = 0$) for simplicity. Figure 2(a) shows the phase diagram in the $t_c/t_p$-$T$ plane for a typical set of parameters. $T_{\text{CO}}$ is determined by the divergence of the static charge susceptibility, $\chi_c(q, 0)$. The divergence appears at $q = Q_2 \sim (\pi, 0)$ [and (0, 0)] although $Q_2$ weakly depends on $t_c/t_p$. $Q_2$ corresponds to a stripe-type CO pattern with period two along the $c$ axis as in the left inset of Fig. 2(b) (diagonal-type CO [13]). $T_{\text{CO}}$ is lowered as decreasing $t_c/t_p$ and goes to zero at $t_c/t_p \sim 0.1$, a parameter corresponding to the Cs compound in which $T_{\text{CO}} \rightarrow 0$ is experimentally observed. Here, we note that the Holstein phonon stabilizes CO by effectively reducing the on-site repulsion $U$ [23].

In the quantum critical regime at $t_c/t_p \sim 0.1$ where $T_{\text{CO}} \rightarrow 0$, $\chi_c(q, 0)$ shows two broad peaks at different wave numbers as shown in Fig. 2(b): One is at $Q_1 \simeq (2\pi/3, 2\pi/3)$ and the other is at $Q_2 \sim (\pi, 0)$ [and (0, $\pi$)]. Here the $Q_1$ peak corresponds to CO pattern with period three, as shown in the right inset of Fig. 2(b) [17]. These two peaks exhibit contrastive $T$ dependences as shown in Fig. 2(c): The $Q_1$ peak shows little $T$ dependence in this $T$ range, while the $Q_2$ peak grows rapidly as $T$ decreases. The behaviors are consistent with the X-ray scattering data in the Cs compound [8, 10].

What is the origin of the coexistence of two charge fluctuations and their contrastive $T$ dependence? The charge fluctuations at $Q_1$ and $Q_2$ have different origins, the off-site Coulomb interaction $V$ and the nesting property of the Fermi surface, respectively, as explained below. From eqs. (4) and (5), it is clear that $\chi_c(q, 0)$ is enhanced at the wave numbers where the Fourier transform of the off-site Coulomb interaction $V(q)$ is minimized or the
bare susceptibility $\chi(q,0)$ is maximized. Figure 2(d) plots $-V(q)$ and $\chi^{(0)}(q,0)$. Obviously, the $Q_1$ peak corresponds to the minimum of $V(q)$, indicating that this peak originates from the off-site Coulomb repulsion. On the other hand, the $Q_2$ peak corresponds to the maximum of $\chi^{(0)}(q,0)$, and hence this originates from the noninteracting electronic state, i.e., the nesting property of the Fermi surface. These assignments explain the contrastive $T$ dependence of the two peaks: The $Q_1$ peak is of the Coulomb origin, and hence its height is weakly dependent on $T$ in the present $T$ range much lower than the energy scale of $V$. On the other hand, the Fermi degeneracy at low $T \ll t_p$ enhances $\chi^{(0)}(q,0)$ at the nesting vector $q = \mathbf{Q}_3$, which leads to the rapid increase of the $Q_2$ peak. In the inset of Fig. 2(c), we show $T$ dependencies of the peak heights in a wider $T$ range. The $Q_2$ peak steeply grows at low $T$ with a concave $T$ dependence, while the $Q_1$ peak has a weak, convex $T$ dependence and saturates at $T \sim 0.1$. Thus, our RPA results successfully reproduce the experimental features in $\theta$-(ET)$_2$X, i.e., the coexisting charge fluctuations and their contrastive $T$ dependencies as well as the systematic change of phase diagram in terms of $t_c/t_p$. The coexistence of charge fluctuations comes from the fact that the off-site Coulomb energy and the kinetic energy (the Fermi surface nesting) favor the different types of CO: the former induces an instability toward the “Wigner crystal” formation, whereas the latter leads to the charge-density-wave instability. The mechanism is intrinsic in the correlated electron systems, and it holds for the model including $H_{\text{SSH}}$.

There remain some issues to be clarified. One is the order of CO phase transition. The transition is always of second order in RPA, while it is of first order with a structural change in experiments. An interesting experimental observation is that a diffuse peak for the three-fold period appears above $T_{\text{CO}}$. With an unusual critical behavior in spite of the first-order transition, a corresponding behavior is found in our RPA results; the threefold $Q_1$ peak develops above $T_{\text{CO}}$ since the peak is induced by $V$ much larger energy scale than $T_{\text{CO}}$. However, in order to describe the first-order nature of the transition, it is necessary to go beyond RPA. Anharmonic contributions from phonons may play a role as well. This is left for future study.

Another issue is the wave numbers of CO and fluctuations. In our results, the coexisting charge fluctuations appear at $Q_1 \simeq (2\pi/3, 2\pi/3)$ and $Q_2 \simeq (\pi, 0)$. Whereas, in experiments, they are found at $q_1 \simeq (\pi, -\pi/3)$ and $q_2 \simeq (\pi/2, \pi/2)$. Accordingly, the stabilized CO pattern below $T_{\text{CO}}$ is also different; our result in Fig. 2(a) predicts the diagonal-type CO with $Q_2 \sim (\pi, 0)$, while the experimental one is the horizontal type with $q_2 \sim (\pi/2, \pi/2)$. We consider that these discrepancies are not fundamental and can be reconciled without modifying the essential part of our results in the following reasons. As to the $Q_1$ peak, the wave number is determined by the minimum of $V(q)$, and it locates at $q = Q_1$ because we assume the simplest form of the off-site Coulomb interaction, i.e., the isotropic one for the nearest-neighbor sites only. If we include longer-range parts of and/or an anisotropy in the Coulomb interaction, $V(q)$ takes its minimum at a different wave number, which may coincide with $q_1$. On the other hand, the $Q_2$ peak comes from the maximum of $\chi^{(0)}$, and hence, its wave number is dependent on the form of transfer.
integrals which modifies the Fermi surface nesting. In fact, we observe a shift of the peak when we include the SSH-type coupling which directly couples to the transfer integrals. To demonstrate how the SSH-type coupling affects the ordering vector \( \mathbf{Q}_2 \), we study the low-\( T \) phase diagram for the model including \( \mathcal{H}_{\text{SSH}} \). We decouple Coulomb interactions and electron-phonon couplings by using the mean fields, \( \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle, \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle, \langle u_q \rangle \) and \( \langle u_{a(c),i} \rangle \), and obtain a solution by minimizing the free energy among various mean-field configurations within a unit cell of up to 4 \( \times \) 4 sites in the \( x \) and \( y \) coordinates. Figure 1 shows the result at \( T = 0.01 \) by changing the SSH couplings \( \gamma_p = g_p / \sqrt{2M\omega_0} \) and \( \gamma_c = g_c / \sqrt{2M\omega_0} \). To focus on the effect of \( \mathcal{H}_{\text{SSH}} \), here we omit the Holstein coupling and take \( U = V = 0 \). A variety of phases emerges as shown in the figure; in particular, in a region where both \( \gamma_p \) and \( \gamma_c \) are substantial, the horizontal-type CO is stabilized whose wave vector is consistent with \( \mathbf{q}_0 \) observed in TI and Rb compounds [26]. We confirmed that the horizontal CO remains robust against finite \( U \) and \( V \) within the Hartree-Fock approximation. Thus, the SSH-type electron-phonon coupling plays an important role in determining an actual CO instability induced, which suggests possibility to shift \( \mathbf{Q}_2 \) to \( \mathbf{q}_2 \). For further comparison, detailed information is indispensable on realistic electron-phonon couplings, which are possibly more complicated than our model.

In summary, we have theoretically investigated the origin of puzzling features in charge ordering and fluctuations in \( \theta-(\text{BEDT-TTF})_2X \). The peculiar coexisting fluctuations are ascribed to two different instabilities, the “Wigner crystalization” driven by the Coulomb repulsions and the charge-density-wave instability due to the Fermi surface nesting. Our scenario does not need to suppose either a competition among different “Wignercrystal-type” CO in the strong-correlation regime nor real-space inhomogeneity. Our results provide a key toward understanding the low-\( T \) transport phenomena related to the charge fluctuations.

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