Charge-Ordered State versus Dimer-Mott Insulator at Finite Temperatures

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We theoretically investigate the competition between charge-ordered state and Mott insulating state at finite temperatures in quarter-filled quasi-one-dimensional electron systems, by studying dimerized extended Hubbard chains with interchain Coulomb interactions. In order to take into account one-dimensional fluctuations properly, we apply the bosonization method to an effective model obtained by the interchain mean-field approximation. The results show that lattice dimerization, especially in the critical region, and frustration in the interchain Coulomb interactions reduce the charge-ordering phase transition temperature and enlarge the dimer-Mott insulating phase. We also derive a general formula of the Knight shift in the charge-ordered phase and its implication to experiments is discussed.

KEYWORDS: charge-ordering, quarter filling, quasi one-dimension, extended Hubbard model, lattice dimerization, Mott insulator, molecular conductors

Fig. 1. Schematic illustration of the model investigated in the present study. Each ellipse denotes a molecular site and the a (b) axis shows the chain (interchain) direction. The thick (thin) lines along the a-axis shows the lattice dimerization of the stronger (weaker) bonds. The solid and dashed lines connecting the chains represent the interchain interactions, \( V_{\perp} \) and \( V'_{\perp} \), respectively.

Since the experimental observations of the charge-ordered (CO) state in quasi-one-dimensional (1D) organic 2:1 compounds, e.g., (DI-DCNQI)_2Ag and (TMTTF)_2X (X: a monovalent counter anion), in which the charge distribution becomes disproportionated in a regular way due to the electron-electron Coulomb repulsion, these systems have been extensively studied, experimentally as well as theoretically. In (TMTTF)_2X, the CO state is easily destroyed by external pressure but nevertheless the system remains insulating, which is due to a competing state, i.e., the so-called dimer-Mott insulating state where the charge localizes on each lattice-dimerized bond. On the other hand, in (DI-DCNQI)_2Ag, a recent X-ray structural analysis revealed the existence of a three-dimensional mixed pattern of CO and bond dimerization in the “CO phase”. In this paper, we theoretically investigate such interplay between the CO state and the lattice dimerization based on a quasi-one-dimensional model, especially their properties at finite-temperatures.

Previous theoretical studies on the CO phenomena in these quasi-1D materials have mainly been devoted to ground-state properties of the 1D quarter-filled extended Hubbard model (EHM) with the on-site and nearest-neighbor Coulomb repulsions \( U \) and \( V \) as a minimal model. In this model, CO insulator (COI) is stabilized at \( T = 0 \) in the large \( U \) and \( V \) region, while the system is in the metallic state described by the Tomonaga-Luttinger liquid (TLL) otherwise (for positive \( U \) and \( V \)). When the lattice dimerization is included by alternation in the transfer integrals, the TLL phase is transformed to the dimer-Mott insulating phase, and this competes with the CO state. There, the fluctuation effects in the competing region have been focused based on the bosonization theory and critical fluctuation appears on the boundary between the two competing states where its universality class is the two-dimensional Ising-type.

However, these results cannot be directly applied to the analysis of the actual materials, since purely 1D electronic models do not show any phase transition at finite temperatures. In our previous work, in addition to the 1D quarter-filled EHM, we have taken into account the interchain Coulomb interaction \( V_{\perp} \) and investigated the CO phase transition whose transition temperature \( T_{CO} \) becomes always finite due to the dimensionality effect. We found that the inter-chain interaction can transform the system from TLL metallic at \( V_{\perp} = 0 \) to CO insulating by infinitesimal \( V_{\perp} \neq 0 \) in the critical region and thus the interchain interaction greatly enhances the COI phase in the \( U-V \) plane.

In the present study, we consider a system shown schematically in Fig. 1, which is adopted from the crystal structure of (TMTTF)_2X. This is an extension of the model studied in our previous work to include the lattice dimerization along the chain direction, as well as different Coulomb interactions in the interchain direction. As in Ref. 20, in order to take full account of the 1D fluctuation effects, we treat an effective 1D model by the bosonization theory, by applying mean-field approximation to the interchain interactions. Our main results are summarized as follows. (i) By deriving an analytical expression of \( T_{CO} \) and computing it by the renormalization group (RG) approach, we find that the lattice dimerization largely suppresses the COI phase and results in the dimer-
Mott insulating phase, especially in the critical region. (ii) The different interchain Coulomb interactions act as geometrical frustration for the CO state, therefore the COI phase is suppressed when these are comparable to each other, consistent with previous works. (iii) A general formula for the Knight shift below the CO phase transition temperature is derived as a function of the magnitude of order parameter.

We start with the model Hamiltonian $H_{Q1D} = \sum_j H_{1D}^j + H_{\perp}$, where $H_{1D}^j$ represents the $j$th extended Hubbard chain with finite lattice dimerization $\delta_d$:

$$H_{1D}^j = -t \sum_{i,s} [1 + (-1)^i\delta_d] \left( c_{i,j,s}^\dagger c_{i+1,j,s} + \text{h.c.} \right) + U \sum_i n_{i,j} n_{i,j+1} + V \sum_i n_{i} n_{i+1}, \quad (1)$$

where $c_{i,j,s}$ is the creation operator of an electron with spin $s(=\uparrow,\downarrow)$ at the $i$th site on the $j$th chain. The density operators are $n_{i,j,s} = c_{i,j,s}^\dagger c_{i,j,s} - \frac{1}{2}$ and $n_{i,j} = n_{i,j,\uparrow} + n_{i,j,\downarrow}$. The second term $H_{\perp}$ expresses the interchain interactions, given by

$$H_{\perp} = V_{\perp} \sum_i n_{i,j} n_{i,j'} + V_{\perp} ' \sum_i n_{i} n_{i+1,j'}, \quad (2)$$

where the $V_{\perp}$-term denotes the interchain interaction between electrons on the nearest-neighbor sites (along the solid horizontal lines in Fig. 1) and the $V_{\perp} '$-term denotes the interaction for the next-nearest-neighbor sites (along the dotted diagonal lines). When $V_{\perp} = V_{\perp} ' = 0$ the model reproduces the above-mentioned 1D dimerized EHM.

As in Ref. 20, we assume the Wigner crystal-type CO pattern with a 2-fold periodicity along the chain direction, and apply the interchain mean-field approach to $H_{\perp}$ [eq. (2)]. The two interchain Coulomb interactions favor different CO along the interchain direction, namely, $V_{\perp}$ favors the antiphase pattern, $\langle n_{i,j} \rangle = (-1)^{i+j+n}$, while $V_{\perp} '$ favors the inphase CO with $\langle n_{i,j} \rangle = (-1)^n$, where $n(>0)$ is the amplitude of CO to be determined self-consistently. This result in geometrical frustration arising from a competition between two types of CO states. The resultant effective 1D Hamiltonian can be written for both cases as

$$H = -t \sum_{i,s} [1 + (-1)^i\delta_d] \left( c_{i,s}^\dagger c_{i+1,s} + \text{h.c.} \right) + U \sum_i n_{i} n_{i+1} + V \sum_i n_{i} n_{i+1} + zV_{\perp} n \sum_i [1 + (-1)^i] n_i + \frac{1}{2}zN^2V_{\perp} n^2, \quad (3)$$

where the chain index $j$ is omitted and $N$ is the total number of sites in a chain. The coordination number of adjacent chains, which is given by 2 in the system of Fig. 1, is written as $z$. The effective interchain interaction $V_{\perp}$ is given by $V_{\perp} = V_{\perp} - V_{\perp} '$, then the interchain frustration simply reduces the effective interchain interaction in the present scheme, therefore acts as destabilizing the CO state, similarly to previous studies on different models.

In order to take fully into account the 1D fluctuation effects, we treat the Hamiltonian (3) based on the bosonization theory. First, we focus on low-energy excitations near the Fermi wavenumber $\pm k_F = \pm \pi/(4a)$ (a: lattice spacing), by integrating out the high-energy states. Next, following the standard bosonization theory, we express the Hamiltonian in the bosonic phase variables and separate it into the charge and spin parts, $H = H_q + H_s$. The spin part $H_s$ takes the same form of the effective theory of the 1D isotropic $S = 1/2$ Heisenberg chain, in which the coupling constants depend on $\delta_d$ as well as $n$. This indicates that the spin excitation is gapless in the both insulating states, and the competition between the CO phase and the dimer-Mott state is characterized solely by the charge part of the Hamiltonian, $H_q$.

Let us first focus on the CO transition temperature $T_{CO}$. Although the phase Hamiltonian is derived for the full order of $n$ by the above operation, in order to evaluate $T_{CO}$ the expression up to the first order in $n$ is sufficient, since a recent numerical study shows that the transition is continuous. In this order, the charge part is given by $H_q = \int dx (H_{\rho0} + H_{\rho1})$ where

$$H_{\rho0} = \frac{\nu_p}{4\pi} \left[ -\frac{1}{K_p} \partial_\rho(\partial_\rho \rho^2) + K_p \partial_\rho \rho^2 \right] - \frac{g_1/2}{(\pi\alpha)^2} \sin 2\theta_p + \frac{g_1/4}{2(\pi\alpha)^2} \cos 4\theta_p, \quad (4)$$

$$H_{\rho1} = \frac{c_2}{\pi a} D \tilde{V}_\perp n \cos 2\theta_p + \frac{z}{2a} \tilde{V}_\perp n^2, \quad (5)$$

with $D = (2 - \sqrt{1 + \delta_d^2})/(1 + \delta_d^2)$ and $c_2 = [U/(\sqrt{2\pi}t)] (a/\alpha)^2$. The quantity $\alpha$ is a short-length cutoff of the order of the lattice constant $a$. The first term (4) is the 1D part and takes the same form of the phase Hamiltonian for the 1D dimerized EHM at quarter-filling, derived in Ref. 16. Here, the effects of finite lattice dimerization, compared with our previous work for $\delta_d = 0$, are (i) the appearance of the sin $2\theta_p$ potential, and (ii) the modifications of the coupling constants (e.g., the factor $D$ in the cos $2\theta_p$ potential). The order parameter $n$ is determined by the self-consistency condition

$$n = -\frac{c_2}{\pi} D(\cos 2\theta_p), \quad (6)$$

where (\cdots) denotes the expectation value with respect to $H_q$. Equation (6) is obtained from the stationary condition of eq. (5) and takes the same form of eq. (14) in Ref. 20 except the appearance of the factor $D$. The equation to determine $T_{CO}$ is given by

$$1 = \frac{c_2}{\pi^2 a} D^2 \tilde{V}_\perp \int dx \int_{0}^{1/T_{CO}} d\tau F_{CO}(x,\tau) |_{T=T_{CO}}, \quad (7)$$

where $F_{CO}(x,\tau) \equiv \langle T_x \cos 2\theta_p(x,\tau) \cos 2\theta_p(0,0) \rangle_0$ is the correlation function of the CO order parameter and (\cdots) is the expectation value with respect to $H_{\rho0}$, i.e., the Hamiltonian of the purely 1D system.

Here we calculate the correlation function based on the RG treatment. We also evaluate $F_{BO}(x,\tau) \equiv \langle T_x \sin 2\theta_p(x,\tau) \sin 2\theta_p(0,0) \rangle_0$, which corresponds to the correlation function of the bond-order parameter. Based on the conventional RG treatment, these are given by

$$F_{CO}(\ell) = \frac{1}{2} \exp \left[ -\int_0^\ell d\ell' \left( 4K_p(\ell') + 2G_{1/4}(\ell') \right) \right], \quad (8)$$

$$F_{BO}(\ell) = \frac{1}{2} \exp \left[ -\int_0^\ell d\ell' \left( 4K_p(\ell') - 2G_{1/4}(\ell') \right) \right], \quad (9)$$
temperature as a function of procedure, we evaluate parameter satisfy finite amount of transition temperature assume that, in the low-energy limit.

In Fig. 2, we show the transition temperature is expressed as to the excitation gap in the ground state where

dimer-Mott insulating state is obtained for small intersite Coulomb repulsion (i.e., for $V < V^1_{c}$), the dimer-Mott insulating state is obtained

Again, the dimerization suppresses for small $V < V^1_{c}$ case. For $\delta_1 = 0$, the critical value $V^1_{c}$ is shown in the inset of Fig. 2. For $V^1_{c} \geq V^1_{l}$, the $V^1_{l}$ dependence of the transition temperature is expressed as

$$ T^{\text{CO}}_{\perp} \sim \frac{\Delta_{\text{Mott}}}{\ln \left( \frac{V^1_{c}}{V^1_{l} - V^1_{c}} \right)}, \quad (10) $$

where $\Delta_{\text{Mott}}$ is the Mott gap in the absence of the interchain interaction. This formula can be derived by noting that $F_{\text{CO}}$ decays exponentially.

In Fig. 3, $T^{\text{CO}}_{\perp}$ for the $V > V^1_{c}$ case is shown, where, on the other hand, the COI state is stabilized even for $V^1_{l} = 0$. Again, the dimerization suppresses $T^{\text{CO}}_{\perp}$. However, for a fixed value of $\delta_1$, the critical value $V^1_{c}$ of the effective interchain interaction $\tilde{V}^1_{l}$ for the appearance of the CO state is now always zero, i.e., infinitesimal interchain interaction leads to finite $T^{\text{CO}}_{\perp}$. The $\tilde{V}^1_{l}$ dependence of the transition temperature is now given by $T^{\text{CO}}_{\perp} \propto \tilde{V}^1_{l}$ as long as $T^{\text{CO}}_{\perp} \ll \Delta_{\text{CO}}$ with $\Delta_{\text{CO}}$ being the charge gap of the purely 1D COI.

Summarizing the above results, schematic phase diagrams on the $V_{l} - V^1_{l}$ plane are shown in Fig. 4 where the shaded CO regions denote $T^{\text{CO}}_{\perp} > 0$. In the $V < V^1_{c}$ case (a), between the anti-phase and in-phase CO states, there appears the dimer-Mott insulating phase where CO is absent. On the other hand, in the $V > V^1_{c}$ case (b), there is a direct transition between the two CO states; at the boundary, $T^{\text{CO}}_{\perp} = 0$, i.e., CO is realized only at the ground state.

Next, we focus on the critically fluctuating line, $V = V^1_{c}$. The quantum phase transition in the 1D case (i.e., $V^1_{l} = 0$) is known to be the Ising-type, as mentioned. On this line the finite-temperature CO phase transition for $V^1_{l} \neq 0$ shows nontrivial behavior, since the correlation function of the CO order parameter $F_{\text{CO}}(x, \tau)$ exhibits a power-law of $x^{-1/4}$. At finite temperature, the analytical form can be obtained as

$$ F_{\text{CO}}(x, \tau) = \langle T_{\tau} \cos \theta_\rho(x, \tau) \cos \theta_\rho(0, 0) \rangle$$

$$ \propto \left[ \frac{\sinh[\pi T(x - i\tau)] \sinh[\pi T(x + i\tau)]}{\sinh[\pi T(x - \tau)] \sinh[\pi T(x + \tau)]} \right]^{1/8}. \quad (11) $$

By inserting this into eq. (7), we find that the $V^1_{l}$ dependence of the transition temperature is given by $T^{\text{CO}}_{\perp} \propto V^1_{l}$. Now we turn to the COI phase below the transition temperature $T^{\text{CO}}_{\perp}$ and derive a useful formula for the relation be-

Fig. 2. (Color online) Charge-ordering transition temperature, $T^{\text{CO}}_{\perp}$ as a function of $zV^1_{l}/t$ for $\delta_1 = 0$ and $\delta_3 = 0.15$ for $V < V^1_{c}$. The inset shows the critical interchain interaction $zV^1_{l}/t$ as a function of the dimerization $\delta_1$.

Fig. 3. (Color online) Charge-ordering transition temperature, $T^{\text{CO}}_{\perp}$ as a function of $zV^1_{l}/t$ for $\delta_1 = 0$ and $\delta_3 = 0.15$ for $V > V^1_{c}$.

Fig. 4. (Color online) Schematic phase diagrams of model (3) on the plane of the interchain interactions $V^1_{l}$ and $V^1_{l}$ for the $V < V^1_{c}$ case (a) and for the $V > V^1_{c}$ case (b). CO and dimer-Mott stand for charge-ordered insulating phase with $T^{\text{CO}}_{\perp} > 0$ and dimer-Mott insulating phase, respectively.
tween splitting in the NMR spectrum and the CO amplitude. In the presence of the Wigner crystal-type CO, an effective alternating site potential \( zV_{\perp}n(-1)^{n_{i}} \) (its wavenumber is \( q = \pi/a = 4kF \)) is applied to the system [see, eq.(3)] and results in folding of the one-particle dispersion relation. Then the \( 4kF \)-component of the density operators is expressed in part by the Knight shift. In the phase representation, the staggered component of the spin density \( m_{4kF}(x) \) is proportional to the slowly varying component of the spin density \( m_{0}(x) = \partial_{x}\theta_{\parallel}(x)/\pi \) as

\[
m_{4kF}(x) = (-1)^{i}\frac{z\tilde{V}_{\perp}n}{\sqrt{2t^{2}(1 + \delta_{q}^{2}) + (z\tilde{V}_{\perp}n)^{2}}} \frac{\partial_{x}\theta_{\parallel}(x)}{\pi}.
\]

(12)

From this relation, the Knight shift at the \( i \)th site can be expressed as

\[
S_{i}(T) \propto \chi_{\sigma}(T) \left[ 1 - (-1)^{i}\frac{z\tilde{V}_{\perp}n}{\sqrt{2t^{2}(1 + \delta_{q}^{2}) + (z\tilde{V}_{\perp}n)^{2}}} \right],
\]

(13)

where \( \chi_{\sigma}(T) \) is the magnetic susceptibility. This verifies that the average of the Knight shift is proportional to the magnetic susceptibility as observed experimentally. Furthermore, we find that the “relative shift” \( (S_{i} - S_{0})/(S_{1} + S_{0}) \) can be expressed as

\[
\frac{S_{i} - S_{0}}{S_{1} + S_{0}} = \frac{z\tilde{V}_{\perp}n}{\sqrt{2t^{2}(1 + \delta_{q}^{2}) + (z\tilde{V}_{\perp}n)^{2}}}
\]

(14)

We note that the intrachain interactions do not explicitly appear in this expression, but they are embedded in the magnitude of the order parameter \( n \). Experimentally, the order parameter of the CO phase has been sometimes estimated so far by simply assuming that the Knight shift is proportional to an amount of the charge located on the site, i.e., \((S_{i} - S_{0})/(S_{1} + S_{0}) \rightarrow 2n^{2}\). However, the value of \( n \) obtained in such a way can have been misestimated.

We compare the present results with recent experimental observations by dielectric permittivity and ESR, which \( T_{CO} \) for some (TMTTF-\( d_{12} \)) \( X \) salts composed of the perdeuterio-TMTTF are increased. The X-ray analysis for the TMTTF-\( d_{12} \) and TMTTF-\( H_{12} \) compounds has revealed that the deuteration leads to suppression of the lattice dimerization, which is consistent with the present results. The rather large rise in \( T_{CO} \) of about 10 percent compared to the small change in dimerization suggests that the systems are in the critical region, \( V < V_{c}^{1D} \).

The anomalous behavior of the dielectric constant, proportional to \( (T - T_{CO})^{-1} \), observed in the TMTTF compounds has been theoretically discussed based on the dimerized EHM in the purely 1D case. It is suggested that at \( T = 0 \) the dielectric constant shows a divergent behavior at the boundary between the Mott insulator and the COI, i.e., \( V = V_{c}^{1D} \). If the interchain coupling is taken into account as in our work here, this quantum phase transition would be changed into a finite-temperature transition and we expect that the dielectric constant should show a similar anomalous behavior at \( T_{CO} \). The investigation of such a possibility in the present scheme remains for a future study.

In conclusion, we have discussed the competition between the charge-ordered insulating state and the dimer-Mott insulator at finite temperatures in a quasi-one-dimensional extended Hubbard model at quarter filling. Frustration in the interchain Coulomb repulsion reduces the effective interchain interaction and therefore decreases the charge-ordering transition temperature \( T_{CO} \). The lattice dimerization also reduces \( T_{CO} \), while a finite strength of the effective interchain interaction is necessary to transform the system from the dimer-Mott insulating state into the charge-ordered insulating state. Based on the present analysis, we have derived a useful formula for estimating the magnitude of the order parameter of the CO phase experimentally.

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We do not consider the $2k_F$-CDW state with a 4-fold periodicity along the chains since we are interested in stability of Wigner crystal-type charge ordering.

The notation of the coupling constant $g_{1/2}$ differs from that in Ref. 16. The coefficient of $\sin 2\theta_{\rho}$ in eq. (4), should be multiplied by $-\frac{1}{2}$ in order to reproduce the Hamiltonian in Ref. 16. The change in the sign is due to the choice of the Klein factor.