Finite-Temperature Charge-Ordering Transition and Fluctuation Effects in Quasi-One-Dimensional Electron Systems at Quarter Filling

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Finite-temperature charge-ordering phase transition in quasi one-dimensional (1D) molecular conductors is investigated theoretically, based on a quasi 1D extended Hubbard model at quarter filling with interchain Coulomb repulsion $V$\textsubscript{f}. The interchain term is treated within mean-field approximation whereas the 1D fluctuations in the chains are fully taken into account by the bosonization theory. Three regions are found depending on how the charge ordered state appears at finite temperature when $V$\textsubscript{f} is introduced: (i) weak-coupling region where the system transforms from a metal to a charge ordered insulator with finite transition temperature at a finite critical value of $V$\textsubscript{f}, (ii) an intermediate region where this transition occurs by infinitesimal $V$\textsubscript{f} due to the stability of inherent 1D fluctuation, and (iii) strong-coupling region where the charge ordered state is realized already in the purely 1D case, of which the transition temperature becomes finite with infinitesimal $V$\textsubscript{f}. Analytical formula for the $V$\textsubscript{f} dependence of the transition temperature is derived for each region.

KEYWORDS: charge-ordering transition, quarter filling, quasi one-dimension, extended Hubbard model

Charge-ordering (CO) phenomenon has been one of the central research subjects in quasi-one-dimensional (1D) organic 2:1 salts such as (DCNQI)$_2$X\textsuperscript{1-3} and (TMTTF)$_2$X\textsuperscript{4-6} ($X$: monovalent counter ion). Some members of them having a quarter-filled electron or hole band exhibit insulating behavior due to CO. For example, in (DI-DCNQI)$_2$Ag, an NMR measurement clarified the CO phase transition at $T\textsubscript{CO} = 220$ K\textsuperscript{1} above which non-metallic behavior is already seen even from room temperature interpreted as due to CO fluctuation.\textsuperscript{3} In (TMTTF)$_2$X, CO is found by NMR as well\textsuperscript{4,5} and the dielectric constant shows a divergence toward $T\textsubscript{CO}$, where $T\textsubscript{CO} = 70 - 160$ K depending on $X$.\textsuperscript{5}

Theoretical studies showed that a minimal model for describing such CO is the 1D quarter-filled extended Hubbard model (EHM) with not only the on-site Coulomb repulsion $U$ but also the intersite repulsion $V$.\textsuperscript{7} This model has been intensively studied and the ground-state properties have been revealed. Using different numerical techniques, the $T = 0$ phase diagram on the ($U, V$) plane has been obtained with high accuracy.\textsuperscript{8} The CO insulator (COI) appears in the large ($U, V$) region. Analytical approaches based on the bosonization theory clarified the mechanism of the transition from a Tomonaga-Luttinger liquid (TLL) metallic phase to the COI.\textsuperscript{9-12}

It is useful to consider the TLL parameter $K$ depending on ($U, V$) in the metallic phase of this 1D EHM. It takes $K > 1=4$ and approaches to $K = 1=4$ at the boundary between the TLL and the COI. Based on the TLL theory, CO fluctuation is known to develop as $c \sim (\Gamma)\sim T^{2K-2}$, which implies that for $1=2 > K > 1=4$ it diverges at low temperatures. This divergence does not immediately point to the appearance of long range order of CO in the purely 1D systems. The COI is achieved for larger ($U, V$), only at $T = 0$. These features are schematically illustrated in Fig. 1 (a). When $U$ is fixed at a large value (e.g., $U \geq 4t$; see Fig. 2 later) and $V$ is increased, $K$ decreases, and the system transforms through three regions bounded by $V_c = V_{c1D}$ and $V = V_c$ defined by the values where $K = 1=2$ and 1=4, respectively. The system is the TLL for (i) $V < V_c$ and (ii) $V_{c1D} < V < V_c$, where in the latter CO fluctuation develops at low-$T$, and it is the COI for (iii) $V_{c1D} < V$.

In order to examine the finite-temperature CO transition in the quasi 1D materials, in addition to such 1D fluctuation we need to take into account the dimensionality effect by the interchain coupling. In these systems two types of interchain coupling exist in the electronic sector; one is the single-particle interchain hopping and the other is the Coulomb interaction between electrons in the different chains. In this letter, we consider the latter and discuss the critical temperature of CO, $T\textsubscript{CO}$, by treating the interchain interaction within the mean-field approximation, whereas taking full account of the 1D fluctuations in the chains by the bosonization theory. We will find distinct behavior for the three regions defined above: in region (i) the system transforms from TLL metal to

![Fig. 1. Schematic illustration of the finite-temperature phase diagram for purely 1D case (a) and quasi-1D case with finite $V_c$ (b), where the CO fluctuation develops in the shaded regions. Here $V_c^{1D}$ express the critical value of $V$ for the COI appearing in the quasi-1D case. The quantities $V_c^{1D}$ and $V_{c1D}$, and the regions, (i), (ii) and (iii) are defined in the text.](image-url)
COI with finite $T_{COI}$ at a finite critical value of $V_\gamma$, in (ii) this transition occurs by infinitesimal $V_\gamma$, and in (iii) COI in the purely 1D case always has finite $T_{COI}$ when $V_\gamma$ is turned on. A schematic phase diagram in the presence of $V_\gamma$ is summarized in Fig. 1 (b).

Our Hamiltonian is given by $H = H_{\text{1D}} + H_\gamma$. Here $H_{\text{1D}}$ represents the $\gamma$-th isolated extended Hubbard chain:

$$H_{\text{1D}} = \sum_{i} \left( t_{ij} c_{i \uparrow}^\dagger c_{j \uparrow} + h.c. + U n_{ij \uparrow} n_{ij \downarrow} + V \sum_{s} n_{ij \uparrow} n_{ij \downarrow} \right) \quad (1)$$

and $H_\gamma$ expresses the interchain coupling:

$$H_\gamma = \sum_{i} \left( U n_{i \uparrow} n_{i \downarrow} \right) \quad (2)$$

where $c_{i \uparrow}$ is the creation operator of an electron with spin $\uparrow$ at the $i$-th site in the $\gamma$-th chain, $n_{ij}$ the pair of adjacent chains and the strength of interchain Coulomb repulsion is expressed by $V_\gamma$. The number of adjacent chains, $z$, for (DCNQI)$_2$X and (TMTCF)$_2$X would be $z = 4$ and $z = 2$ judging from the crystal structures, although their interchain networks are rather complicated, as we will discuss later. We do not take into account the interchain hopping which should not yield qualitative changes to the present analysis at the temperature above the crossover energy scale due to the interchain hopping.

We treat eq. (2) in the interchain mean-field approach, which is known to be effective in the weak $V_\gamma$ region, by considering the Wigner-crystal-type CO pattern stabilized in the 1D EHM. We assume the CO pattern to be anti-phase between adjacent chains, which is naturally expected to gain the $V_\gamma$ term. The resulting effective 1D Hamiltonian is written as

$$H = \sum_{i} \left( t_{ij} c_{ij \uparrow}^\dagger c_{ij \downarrow} + h.c. + \sum_{s} n_{ij \uparrow} n_{ij \downarrow} \right) \quad (3)$$

where the chain index $\gamma$ is suppressed and $N$ is the total number of sites in a chain. The amplitude of CO is written as $n$.

To obtain a qualitative insight of this model we first discuss the $U = 1$ limit, where some exact results for the 1D model based on the Bethe ansatz can be used. In this case, we can neglect the spin degree of freedom which acts freely, and the charge degree of freedom is reduced to a half-filled spinless fermion model:

$$H_{U = 1} = \sum_{i} \left( t_{ij} c_{ij \uparrow}^\dagger c_{ij \downarrow} + h.c. + \sum_{s} n_{ij \uparrow} n_{ij \downarrow} \right) \quad (4)$$

where the creation operator of the spinless fermion is expressed by $c_{ij}$ and $n_{i}$. This model is equivalent to the $S = 1/2$ XXZ spin-chain coupled by the interchain exchange interaction $J_\gamma$ treated in the interchain mean-field approach. Several authors have performed such approach to the Heisenberg limit (i.e., $V = 2t$). Bhaseen and Tsvelik discussed a nontrivial spectrum of eq. (4) in a parameter region $V > 2t$, where the system is the COI and has a finite excitation gap even for $V_\gamma = 0$. We restrict ourselves to a parameter region $0 < V < 2t$, where the system is known to be metallic if $V_\gamma = 0$, and show that infinitesimally small $V_\gamma$ makes the system insulating and gives rise to finite $T_{COI}$.

We apply the bosonization method to eq. (4). The density operator is given by $n_{i} = \frac{1}{2} \left( (\hat{\sigma}_{x}^\dagger \hat{\sigma}_{x} + 1 \right)$, which becomes irrelevant but has an effect to renormalize the velocity, the TLL parameter, and the prefactor of the bosonized density operator. By taking into account these effects properly, the density operator is given by $n_{i} = \frac{1}{2} \left( (\hat{\sigma}_{x}^\dagger \hat{\sigma}_{x} + 1 \right)$, which is given by $\cos^{2} \frac{\pi}{2K} V_\gamma n_{i}^{\gamma} = \frac{1}{2} \left( (\hat{\sigma}_{x}^\dagger \hat{\sigma}_{x} + 1 \right)$, where $\hat{\sigma}_{x}$ is a nonuniversal constant depending on $V=0$ and its exact value has been suggested. We will use the renormalized velocity and the TLL parameter, and neglect the $\cos \frac{\pi}{2K} V_\gamma$ term. After this procedure, we switch on the $V_\gamma$ term, and then the effective Hamiltonian density reads

$$H_{U = 1} = \frac{V}{4} \sum_{i} \left( \hat{\sigma}_{x}^\dagger \hat{\sigma}_{x} + 2K \right) \quad (5)$$

where $V = \frac{1}{2} \left( (\hat{\sigma}_{x}^\dagger \hat{\sigma}_{x} + 1 \right)$, and $g_{\gamma} = 2 \alpha_{\gamma} n_{\gamma}$. The TLL parameter $K$ determines the nonuniversal constant $c = c(K)$. Since the $g_{\gamma}$ term in eq. (5) is a relevant perturbation, when $n < 0$ the system is not the TLL but has an excitation gap.

$$m(\gamma) = \frac{V}{a} \sum_{i} \left( \hat{\sigma}_{x}^\dagger \hat{\sigma}_{x} \right) \quad (6)$$

where $a = (\gamma + 1) \frac{1}{2} \left( (\gamma + 1) \right)$ $= \frac{1}{2} \left( (\gamma + 1) \right)$. The ground-state energy per site is given by

$$E(\gamma) = \frac{a}{4} m(\gamma) n + z V_\gamma n_{\gamma}^{\gamma} = \frac{1}{2} \left( (\gamma + 1) \right)$$. The optimized magnitude $n$ is given by

$$n = \frac{1}{2} \left( (\gamma + 1) \right) \quad (7)$$

The CO amplitude $n$ is determined from the condition to minimize eq. (7). The optimized magnitude $n$ is given by

$$n = \frac{1}{2} \left( (\gamma + 1) \right) \quad (8)$$
Inserting this expression to eqs. (6) and (7), the excitation gap and the ground-state energy are given by

$$m = m (n) \sim V_7^{-1/2} \delta \left( \frac{2}{2} \right)$$

and

$$E = E (n) \sim V_7^{-1/2} \delta \left( \frac{2}{2} \right).$$

Thus, an infinitesimal value of interchain interaction transforms the system from TLL in the 1D case to the COI for all values of $0 < V < 2t$. $T_{CO}$ can also be estimated in a similar way. The free energy up to $n^2$ is given by

$$f (n) = \frac{T^2}{6a} b (K) \frac{Z^2V_7^2n^2}{2a} + \frac{ZV_7n^2}{2a},$$

where $b (K) = \frac{c^2(K)}{z(2K)} \sin (2K) B^2 (K; 1, 2K)$ with $B (x; y) = (x) (y) = (x + y)$. From the condition where the coefficient of $n^2$ in eq. (9) vanishes, $T_{CO}$ is determined as

$$T_{CO} = \frac{\sqrt{2}}{2} \frac{z_b(K)}{z(2K)} V_7 a.$$  

At $V = 2t$, $T_{CO}$ is proportional to $V_7$. In this case, the ratio of the gap at $T = 0$ and the transition temperature becomes

$$m = T_{CO} \frac{1}{2} = 2t,$$

which reproduces the result obtained in Ref. 23. The formulas of the amplitude $n$ [eq. (8)] and the transition temperature $T_{CO}$ [eq. (10)] are valid for $V < V_7$, since these diverge when $V > 0$ due to the ultraviolet divergence in eqs. (7) and (9). This problem could be resolved simply by introducing an ultraviolet cutoff.

Now we consider the case of finite $U$. An effective Hamiltonian for low-energy states ($k = 0$) can be obtained by integrating out high-energy states. The Hamiltonian is separated into the charge part describing the CO transition and the spin part. The latter is essentially the same as the Hamiltonian of 1D isotropic Heisenberg model and leads to gapless excitations both in the TLL and the COI. The density operator can be bosonized as

$$n_1 = \frac{a}{\theta_x} (\kappa) + \frac{2 \phi}{(2K) x} \cos (2K) + \frac{1}{a} \cos 2 (\kappa);$$

where $(\kappa)$ and $(\kappa)$ are the bosonic phase variables for the charge and spin degrees of freedom. $c_1$ and $c_2$ are nonuniversal numerical constants. In the absence of $n$, the charge part is written by the following phase Hamiltonian,

$$H = \frac{\sqrt{2}}{4} \frac{1}{\theta_x} (\kappa) + \frac{2 \phi}{(2K) x} \cos (2K) + \frac{g_{1n+4}}{g} \cos 4 (\kappa);$$

where $[\kappa); \theta_x; \phi] = (2 \phi), = (\kappa \phi)$. The charge velocity $v$, the parameter $K_0$, and the magnitude of the 1/4-filled Umklapp scattering $g_{1n+4}$ are nonuniversal and its expressions obtained perturbatively are given in Ref. 12. In the presence of the interchain mean-field $n$, the additional Umklapp scattering appears, as in the last two terms in eq. (5),

$$H^0 = \frac{Zc''_G}{a} V_7 n \cos 2 (\kappa) + \frac{Z}{2a} V_7 n^2;$$

By minimizing $H$, with respect to $n$, the amplitude $n$ is determined as

$$n = - \frac{2a}{g} \cos 2 (\kappa);$$

where $n$ denotes the finite-T expectation value with respect to $H$. By note that the parameter $c_2$ is proportional to the on-site interaction, $c_2 = U/(2t)$ within the perturbative treatment. This implies that the CO fluctuation with 2-fold periodicity can emerge due to the correlation effect.

In order to estimate the second-order transition temperature, the lowest-order perturbation theory in $n$ is sufficient. By expanding the r.h.s. of eq. (14) with respect to $H^0$, the equation to determine $T_{CO}$ is obtained as

$$1 = \frac{Zc''_G}{a} V_7 \frac{Z_1}{Z_{1=CO}}$$

$$\frac{1}{2} \exp \left( \frac{1}{2} V_7 n \right) = \frac{Z_1}{Z_{1=CO}}$$

where $h_{ab}$ is the expectation value with respect to $H$. In the following, we employ naive renormalization group (RG) arguments to estimate $T_{CO}$. By neglecting the anisotry in space and time, the correlation function

$$\frac{1}{2} \exp \left( \frac{1}{2} V_7 n \right) = \frac{Z_1}{Z_{1=CO}}$$

where $r = \frac{P}{2} x^2 + \frac{y^2}{2}$ and $v = \nabla = (\nabla)$ is the characteristic thermal coherence length. The quantities $K$ and $G_{1n+4}$ are the solution of the RG equations,

$$dK (\nabla) = \frac{8g_{1n+4}(\nabla) \delta K (\nabla)}{g};$$

$$dG_{1n+4}(\nabla) = \frac{g_{1n+4}(\nabla) \delta G_{1n+4}(\nabla)}{g};$$

where the initial conditions are $K (0) = K_0$ and $G_{1n+4}(0) = g_{1n+4}(0)$. These RG equations have two kinds of fixed points for realistic parameters. One is $(K (1); G_{1n+4}(1)) = (0; 1)$ and the other is $(K (1); G_{1n+4}(1)) = (0; 0)$. For $V_7 = 0$, the former corresponds to the COI at $T = 0$, while the latter to the metallic TLL state. From eqs. (15) and (16), $T_{CO}$ can be estimated by

$$\frac{2}{2} \frac{z_b(K)}{z(2K)} V_7 a = \frac{2}{2} \frac{z_b(K)}{z(2K)} V_7 a.$$

and $z$ is a positive numerical constant.

Concerning the realization of the COI at finite-$T$, we find three distinct regions on the $(U, V)$ plane shown in Fig. 2. In region (ii) where the COI is already realized in the purely 1D case, infinitesimal $V_7$ makes $T_{CO}$ finite, as is naturally expected. In addition, there is a region (ii) with $1 < K$.

![Fig. 2. Three distinct regions classified by appearance of the COI at the finite temperature.](image-url)
1=4 where infinitesimal $\nu_T$ also gives rise to finite $T_{\text{CO}}$ even in the metallic region for $\nu_T = 0$, since $F(\nu_T)$ diverges due to the divergence of CO fluctuation while $G_{1=4}(\nu_T) = 0$. This is consistent with the case of $U = 1$ discussed above, where $0 < V < 2t$ correspond to region (ii) in this limit, as mentioned. Moreover, even in the region (i) without divergence of CO fluctuation, finite amount of $\nu_T$ makes the system COI. The obtained expressions for $T_{\text{CO}}$ as a function of $\nu_T$ is summarized in Table I. The critical value of $\nu_T$ for appearance of the COI in the region (i) is proportional to $4K - 2$. We note that $\nu_T$ = $\exp(A = \nu_T)$ at $K = 1 = 2$, and $T_{\text{CO}} / \nu_T$ for $K = 1 = 4$, also consistent with the $U = 1$ case.

Now let us discuss the relevance of our results to the experiments. In (DI-DCNQI)$_2$Ag, the non-metallic behavior above $T_{\text{CO}} = 220 K$ might be due to the 1=4-allowed Umklapp scattering described in eq. (12). The peak at $T = T_{\text{CO}}$ in the derivative of the resistivity as a function of $T$ in Ref. 3 seems to be triggered by the generation of additional Umklapp scattering $\cos2\theta$ in eq. (13) due to the appearance of the CO. In (TMTTF)$_2$X, the system is also insulating already above $T_{\text{CO}} = 220 K$ and a change in the slope of the resistivity curve is observed.\(^{24}\) However, in this case the slight dimerization in the chain direction gives rise to another relevant 1=2-allowed Umklapp scattering.\(^{12}\) Whether or not the 1=4-filled Umklapp scattering is effective above $T_{\text{CO}}$ is difficult to judge, but the change in the slope should be due to the additional Umklapp scattering by CO as discussed above.

In these quasi 1D compounds, the interchain Coulomb interaction is in fact considered to be fairly large. For example in some members of (TMTTF)$_2$X it is even estimated to be comparable to the intrachain ones in quantum chemistry calculations.\(^{25}\) This is noticeable since the interchain electron hopping is one order of magnitude smaller than that in the intrachain direction due to the anisotropic shape of the HOMO of the TMTTF molecule. However we should note also that the actual interchain networks are rather complicated. In the structure of (DCNQI)$_2$X, it has a spiral symmetry when rounding each plaquette in the network. It is pointed out that this gives rise to frustration for the Wigner-crystal-type CO since the periodicity of the spiral does not fit the 2-fold period along the DCNQI chains.\(^{26}\) In (TMTTF)$_2$X, such frustration is more straightforwardly expected since the interchain coupling is zigzag-like therefore anti-phase and in-phase CO patterns would have close energy. These should reduce the effective interchain interaction to a smaller value at a first approximation.

In the present analysis, we considered the Wigner-crystal-type CO with a 2-fold periodicity only, namely, the “4k$_F$” CDW state. In the small $\nu$ region, however, the 2k$_F$ CDW state having a 4-fold periodicity may also be stabilized, since its fluctuation develops as $e^{-2k_Fr}(T) / T^K$. From the simple power counting, one finds that 2k$_F$ fluctuation becomes dominant if $K > 1$. Thus in the phase diagram where $1=3 < K < 1=2$, competition and/or coexistence of the CO and the 2k$_F$ CDW may be possible. This problem needs further investigation.

In conclusion, we investigated the finite-temperature CO transition in the quasi-1D electron system at quarter filling coupled by the interchain Coulomb repulsion $V_T$, by using the interchain mean-field theory and the bosonization method. It was shown that the interchain interaction gives rise to finite transition temperature $T_{\text{CO}}$, with different behavior depending on the parameter in the 1D limit. When it is in the COI, $\nu_T$ gives rise to finite temperature phase transition. In the TLL phase, in the parameter region where the charge-fluctuation develops, i.e., $1=2 > K > 1=4$, infinitesimally small $\nu_T$ also produces the COI with finite $T_{\text{CO}}$, while for $K < 1=2$, at a finite critical value of $\nu_T$, the system transform from the TLL to the COI.

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