Coexistence of Charge Order and Spin-Peierls Lattice Distortion in One-Dimensional Organic Conductors

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The electronic properties of quarter-filled organic materials showing spin-Peierls transition are investigated theoretically. By studying the one-dimensional extended Peierls-Hubbard model analytically as well as numerically, we find that there is a competition between two different spin-Peierls states due to the tetramized lattice distortion in the strongly correlated regime. One is accompanied by lattice dimerization which can be interpreted as a spontaneous Mott insulator, while the other shows the existence of charge order of Wigner crystal-type. Results of numerical density matrix renormalization group computations on sufficiently large system sizes show that the latter is stabilized in the ground state when both the on-site and the inter-site Coulomb interactions are large.

KEYWORDS: organic conductors, spin-Peierls transition, charge order, one-dimensional system, density matrix renormalization group, bosonization

Quasi-one-dimensional (1D) organic conductors exhibit a variety of electronic states with spatially inhomogeneous charge, spin, and lattice structures. A typical example is the family of TMTSF2X and TMTTF2X,1) where X denotes different anions. Recently, the existence of charge ordering (CO) has been identified in several of such quasi-1D compounds, which has renewed interest in these systems. It was first found in DI-DCNQI2Ag, a member of the R1R2-DCNQI2X family, with X = Ag or Li, and R1 and R2 taking different substitution groups to modify the DCNQI molecule itself, in which the charge pattern has been identified as a Wigner crystal-type one.2,3) Independently, analogous CO was predicted theoretically to also exist in TMTTF2X based on the result of mean field calculations,4) and soon after it was confirmed experimentally.5,6)

In the two families mentioned above, the 1D π-band is quarter-filled in terms of electrons or holes. The wave vector along the chain direction for the CO state mentioned above is 4kF, corresponding to the period of two molecules, which suggests the origin of this phenomenon to be the long range nature of Coulomb interaction as theoretically studied in the past.7) Further studies have been performed on explicit models appropriate for the description of the electronic properties of DCNQI/TMTTF molecules, i.e., 1D extended Hubbard models of quarter filling with on-site and nearest-neighbor Coulomb interactions, U and V, respectively.4,8-11) In those models, the CO insulating ground state is actually stable, in general, when both U and V are appreciably large compared to the transfer integrals.
Fig. 1. Schematic views of the ground states in quasi-one-dimensional organic conductors. Coexisting states of (a) charge ordering and Néel ordering, (b) charge ordering and spin-Peierls lattice distortion, and (c) dimer Mott insulating state and spin-Peierls lattice distortion. The grey area represents where the charge localizes, and the arrows and the ellipses represent the ordered spins and the spin singlet formation, respectively. The lattice distortions are also shown schematically by the thickness of the bonds.

In the above compounds showing CO, below the CO transition temperature which is typically of the order of 100 K, magnetic phase transitions take place, to either antiferromagnetic (AF) or spin-Peierls (SP) state. These can be understood since in this CO state each charge is localized on every other site so that the spin degree of freedom acts as a quasi-1D spin 1/2 system. Then a competition arises between the AF state stabilized by the interchain exchange interaction and the SP state due to the 1D instability coupled to the lattice degree of freedom. In fact, the mean field calculations mentioned above, expected to be relevant for the former case with sufficient three-dimensionality, show the coexistence of CO and AF for the ground state when $V$ exceeds a critical value. This state is schematically shown in Fig. 1 (a), which is consistent with the low temperature AF states observed in DI-DCNQI$_2$Ag, and TMTTF$_2$X with $X =$ Br and SCN.

On the other hand, in a recent experiment on TMTTF$_2$X with $X =$ PF$_6$ and AsF$_6$, the CO is actually found to also persist in the SP phase with lattice tetramization. Then this coexistence state can be schematically drawn as in Fig. 1 (b), which we call the CO-SP state. However, existing theoretical studies, mainly numerical ones, have failed to reproduce this CO-SP state within the so-called 1D extended Peierls-Hubbard model, which is a natural extension of the extended Hubbard model to include the electron-lattice coupling. In these studies, only one other SP state is found, in which the lattice dimerization and the lattice tetramization both occur, as schematically shown in Fig. 1 (c). The lattice dimerization produces a spontaneous ‘dimer Mott insulating’ (DM) state, as will be discussed later, so we call this state the DM-SP state. This state is relevant to several DCNQI compounds and to a classical example of SP compounds, MEM-(TCNQ)$_2$.

In this paper, we will show that the coexistent state of CO and SP is stable in the strongly correlated regime, i.e., with large $U$ and $V$, in contrast to previous studies. This explains naturally the experimental facts noted above, and provides a unified view for the ground-state properties of the strongly correlated quarter-filled 1D organic compounds on the basis of the CO
phenomenon.

The 1D extended Peierls-Hubbard model as in refs. 14 and 15 is expressed as

$$ H = \sum_{i,\sigma} t(1 + u_i) \left( c_{i\sigma}^\dagger c_{i+1\sigma} + h.c. \right) + \frac{K}{2} \sum_i u_i^2 $$

$$ + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_i n_{i\uparrow} n_{i+1\uparrow}, \quad (1) $$

where $\sigma$ is the spin index which takes $\uparrow$ or $\downarrow$, $n_{i\sigma}$ and $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) denote the number operator and the creation (annihilation) operator for the electron of spin $\sigma$ at the $i$th site, respectively, and $n_i = n_{i\uparrow} + n_{i\downarrow}$. $U$ and $V$ are the on-site and nearest-neighbor Coulomb energies, respectively. The electron-lattice interaction is included in the Peierls-type (or sometimes called the Su-Schrieffer-Heeger-type) coupling where the intermolecular motions result in the change of the transfer integral from $t$ to $t(1 + u_i)$, while it expends the elastic energy $Ku_i^2/2$, with $K$ being the spring constant. Here $u_i$’s are the normalized displacements which we treat as classical variables, and these are to be determined self-consistently to minimize the free energy of the system.

First, let us analyze this model within the bosonization scheme\textsuperscript{18,19} following the treatment of Yoshioka et al.\textsuperscript{10} The lattice distortion can be parametrized as $u_i = u_d \cos (\pi x_i / a) + u_t \cos (\pi x_i / 2a + \chi_t)$,\textsuperscript{14} where $x_i$ and $a$ are the position of the $i$th site and the lattice constant, respectively, and $\chi_t$ is a phase factor which is determined in the following. We only consider the lattice dimerization $u_d$ and lattice tetramization $u_t$, which will be confirmed afterwards in the numerical calculations that only these modulations are relevant in the ground state. The resulting phase Hamiltonian for the low-energy properties of this model is given by $\mathcal{H} = \mathcal{H}_\rho + \mathcal{H}_\sigma + \mathcal{H}_{1/4} + \mathcal{H}_d + \mathcal{H}_t + \mathcal{H}_{el}$, where

$$ \mathcal{H}_\rho = \frac{v_\rho}{4\pi} \int dx \left\{ \frac{1}{K_\rho} \left( \partial_x \theta_+ \right)^2 + K_\rho \left( \partial_x \theta_- \right)^2 \right\}, \quad (2) $$

$$ \mathcal{H}_\sigma = \frac{v_\sigma}{4\pi} \int dx \left\{ \frac{1}{K_\sigma} \left( \partial_x \phi_+ \right)^2 + K_\sigma \left( \partial_x \phi_- \right)^2 \right\}, \quad (3) $$

$$ \mathcal{H}_{1/4} = g_{1/4} \int dx \cos 4\theta_+, \quad (4) $$

$$ \mathcal{H}_d = -g_d \int dx \sin 2\theta_+, \quad (5) $$

$$ \mathcal{H}_t = -g_t \int dx \left( \theta_+ - \chi_t - \frac{\pi}{4} \right) \cos \phi_+, \quad (6) $$

and $\mathcal{H}_{el}$ is the elastic energy term. $\theta_+$ and $\phi_+$ are the phase variables for the local density fluctuations of the charge and spin with a long wavelength, respectively, and $\Pi_\theta = -\partial_x \theta_- / 2\pi$ and $\Pi_\phi = -\partial_x \phi_- / 2\pi$ are the corresponding “momenta” satisfying $[\theta_+(x), \Pi_\theta(x')] = i\delta(x - x')$ and $[\phi_+(x), \Pi_\phi(x')] = i\delta(x - x')$. Here, we neglected higher order nonlinear terms for the phase variables as in ref. 10, since these terms have higher scaling dimensions.
The first two terms, $H_ρ$ and $H_σ$, describe the Tomonaga-Luttinger liquid where $v_ρ, K_ρ$ and $v_σ, K_σ$ are the so-called Tomonaga-Luttinger parameters for the charge and spin parts, respectively. The $SU(2)$ symmetry of the nondistorted model with $u_i = 0$ requires $K_σ = 1$.

The next two terms, $H_{1/4}$ and $H_d$, are the quarter-filled and the half-filled Umklapp scattering terms, which are potential energies in favor of the phase variable to be fixed at $θ_+ = 0$ (or $π/2$) corresponding to the CO state and at $θ_+ = π/4$ to the DM state, respectively. The coupling constants are calculated in refs. 10 and 11 perturbatively from the weak-coupling regime as $g_{1/4} ∝ U^2(U − 4V)/t^2$ and $g_d ∝ U − AU(U − 2V)/t$ where $A$ is some numerical constant, thus they become prominent in the strongly correlated regime. The DM state is analogous to that in strongly dimerized quarter-filled organic compounds such as $κ$-ET$_2$X, where the dimerization results in an effectively half-filled band. However we should note that our DM state is possible only when the spontaneous dimerization $u_d$ is finite, thus it is a consequence of both the strong correlation and the 1D instability toward lattice distortion.

The $H_t$ term is derived directly from the kinetic energy term in the presence of the lattice tetramization $u_t$, where the coupling constant $g_t$ is proportional to $t$. In the small $U/t$ and $V/t$ limits, this term produces the conventional weak coupling $2k_F$-CDW state due to Peierls instability, which fixes the phase variables at $θ_+ = π/4, φ_+ = 0$, and $χ_t = 0$. Thus in our case, the lattice tetramization $u_t$ always occurs once the electron-lattice coupling (and consequently, spin-lattice coupling) is included, then the phase variable of the spin is fixed at $φ_+ = 0$ and the spin gap opens. Namely, the CO state and the DM state result in the CO-SP state and the DM-SP state, respectively. We note that additional $2k_F$-CDW appears in the presence of finite $u_t$ where the order parameter is proportional to $\cos(2k_Fx_i + θ_+) \cos φ_+$, which is equal to $\cos(πi/2)$ and $\cos(πi/2 + π/4)$ for the CO-SP state and the DM-SP state, respectively.

To compare the relative stability of these states, the above bosonization procedure is not appropriate, not only since the coupling constants are obtained perturbatively from the weak coupling regime, but also because the treatment of the three nonlinear terms together with the lattice degree of freedom is a very subtle problem. Instead, we use the numerical density matrix renormalization group (DMRG) method directly to model (1), which is essentially exact. The
periodic boundary condition is adopted and the lattice distortions $u_i$ are calculated self-consistently as in ref. 14. We take the number of the states kept in the DMRG method, $m$, up to 250 and check that the $m$-dependence is very small in this region.

The obtained results are summarized in Fig. 2, which shows the ground-state phase diagram on the plane of $U/t$ and $V/t$ for fixed values of $1/K = 1$. For comparison, the phase diagram for the case of $1/K = 0$ corresponding to the purely electronic extended Hubbard model$^8$ is also shown, where there are two phases, the Tomonaga-Luttinger liquid metallic phase and the CO insulating phase$^{8,10}$. The presence of the finite electron-lattice coupling $1/K = 1$ makes three phases appear, the weak coupling CDW state, the DM-SP state, and the CO-SP state. One can see that the CO-SP state is stabilized in a rather wide range of parameters. We have noticed that the relative values of the ground-state energies for these states, and consequently their phase boundaries, are rather sensitive to the cluster size $N$ when it is small such as $N \lesssim 20$ as in refs. 14 and 15. Thus we show in Fig. 2 the result for $N = 36$ where such finite size effect is almost negligible, which provides qualitatively different results from those in the literature, especially in terms of the stability of the CO-SP state.

To observe the property of the CO-SP state in more detail, we show the lattice tetramization $u_t$ ($u_d$ is 0), and the electron density on each site in the CO-SP state as a function of $V/t$ for a fixed value of $U/t = 6$ in Fig. 3 (a), and as a function of $U/t$ for fixed $V/t = 5$ in Fig. 3 (b), both with $1/K = 1$. The electron density is parametrized as $\langle n_i \rangle = 1/2 + n_{4k_F} \cos(\pi x_i/a) + n_{2k_F} \cos(\pi x_i/2a)$, where $n_{4k_F}$ and $n_{2k_F}$ are the order parameters for the $4k_F$ CDW, i.e., the Wigner crystal-type CO and the $2k_F$ CDW, respectively. One can see that in the both cases of increasing the value of $V/t$ and $U/t$, $n_{4k_F}$ increases while $u_t$ and $n_{2k_F}$ decrease. These results can be interpreted as
follows. It is natural that the degree of CO is enhanced when the degree of correlation, \( U/t \) or \( V/t \) is increased, thereby increasing \( n_{4k_F} \). In such a case, the decrease in \( u_t \) and \( n_{2k_F} \), representative of the spin singlet formation due to the SP state, can be explained by the strong \( U/t \) limit, where the effective spin exchange is proportional to the expectation value for both the nearest-neighbor sites to be occupied, \( \langle n_i n_{i+1} \rangle \).\(^{24}\) Then the spin singlet formation energy decreases as the tendency toward CO is increased, since in the CO state the electron tends to occupy every other site. This result that \( n_{4k_F} \) and \( u_t \) vary in an opposite way is consistent with the experimental observation that the CO and SP states ‘compete’ with each other, which is deduced from the variation of their transition temperatures as the pressure is applied.\(^6\)

\[ \begin{align*}
\text{(a) } 1/K = 1, \ U/t = 6 & \quad \text{(b) } 1/K = 1, \ V/t = 5 \\
\end{align*} \]

Fig. 3. Plot of the lattice tetramization \( u_t \), and the order parameter for CO and \( 2k_F \) CDW, \( n_{4k_F} \) and \( n_{2k_F} \), respectively, for the CO-SP state, as a function of (a) \( V/t \) for a fixed value of \( 1/K = 1 \) and \( U/t = 6 \), and (b) \( U/t \) for a fixed value of \( 1/K = 1 \) and \( V/t = 5 \).

The values of \( U/t \) for the actual compounds are believed to be approximately 5 ~ 7.\(^1,2\) Therefore the critical value of \( V/t \sim 4 \) in our calculations necessary to stabilize the CO-SP state is apparently very large. Actually, a reliable estimate yields \( V/t \) of about 2~3,\(^{25}\) which indicates the region of DM-SP in our phase diagram. However, this estimated value for \( V/t \) is the Coulomb interaction between the neighboring molecules of the intrachain. The interchain Coulomb inter-
action should also be large, since the distance between the chains are rather close, especially in TMTTF compounds,\textsuperscript{1)} although the interchain transfer integrals are small due to the anisotropy of the $\pi$-orbital. Thus, one should consider the parameter $V/t$ in our 1D model to be an effective one, which is possibly large enough to stabilize the CO-SP state.

Finally, let us discuss some effects which we have not included in our model. Coupling to anions\textsuperscript{14)} and/or the so-called electron-molecular vibration (e-mv) coupling,\textsuperscript{15)} both of which result in the Holstein-type electron-lattice coupling modulating the on-site energy, help the stabilization of the CO-SP state as is studied in refs. 14 and 15. However, these effects should be small compared with the Coulomb interactions and also with the Peierls-type electron-lattice coupling due to the molecular displacements which we have studied. Therefore we believe that these effects are secondary.

As for the alternation in the transfer integral which exists in TMTTF compounds,\textsuperscript{1)} as $t(1 + u_i) \rightarrow t(1 + (-1)^i\Delta_d)(1 + u_i)$, where $\Delta_d$ is the degree of alternation, we expect it to be slightly disadvantageous for the CO-SP state. This is because the alternation results in modifying $H_d$ in Eq. (5), as $u_d \rightarrow u_d + \Delta_d$ for the first order, and the gain in the energy by $H$ compared to the loss in the lattice elastic energy $\Sigma_i u_d^2$ becomes larger for the DM-SP state.

On the other hand, the value of $1/K$ has been chosen to be fairly large in the DMRG calculations, in order to stabilize the numerical convergence. When we choose realistic values of $1/K$, the phase boundary in Fig. 2 approaches that for $1/K = 0$. This indicates the stability of the CO-SP state. However, this again is a subtle problem so numerical calculations should be pursued to be conclusive.

In summary, we have argued that the coexistence of charge order and spin-Peierls lattice distortion observed in quasi-1D organic compounds is naturally reproduced by the effects of on-site as well as nearest-neighbor Coulomb interaction, together with the electron-lattice coupling of Peierls-type. Our results show that there is a competition between another spin-Peierls state coexisting with the spontaneous dimer Mott insulating state and that showing the existence of the charge order of Wigner crystal-type. The parameters for the actual compounds seems to be in the region near the phase boundary between the two states, so that by applying external fields such as pressure the ground state is expected to vary, from one to another, which is actually observed in TMTTF$_2$AsF$_6$.$^6)$

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