Quantum melting of charge order due to frustration in two-dimensional quarter-filled systems

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The effect of geometrical frustration in a two-dimensional 1/4-filled strongly correlated electron system is studied theoretically, motivated by layered organic molecular crystals. An extended Hubbard model on the square lattice is considered, with competing nearest-neighbor Coulomb interaction V, and that of next-nearest neighbor along one of the diagonals V', which favor different charge ordered states. Based on exact diagonalization calculations, we find a metallic phase stabilized over a broad window at $V' \sim V$ even for large Coulomb repulsion strengths as a result of frustrating the charge ordered states. Slightly modifying the lattice geometry relevant to the actual organic compounds does not alter the results, suggesting that this "quantum melting" of charge order is a robust feature of frustrated strongly correlated 1/4-filled systems.

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Effects of geometrical frustration in strongly correlated systems have been studied actively, where exotic states may arise as a result of competition between different "conventional" ordered phases. Such possibilities have been explored extensively in spin systems, for example, in spin-1/2 models with frustrated antiferromagnetic (AF) exchange interactions of nearest neighbor (NN) and of next-nearest neighbor (NNN).[1] There, conventional Néel states can be destabilized due to the competition between different AF patterns and quantum fluctuations lead to exotic states such as spin liquids. In contrast, works devoted to the charge degrees of freedom are limited and little is known on such situations. One can consider an analogy between the classical spin systems, i.e., Ising systems, and the charge ordering (CO) systems.[2] However, when CO melts due to quantum fluctuation, the nature of this transition will be different from spin systems because of Fermi statistics. Furthermore, "quantum melting" of CO is of particular interest since CO states have now been found in various materials, such as transition metal oxides[3] and organic conductors,[4] including systems susceptible to frustration such as a triangular lattice system Na_xCoO_2, which has recently been attracting interest.[5]

Our motivation here is CO systems having frustrated lattice structures, namely, quasi-two-dimensional (2D) organic conductors θ- and α-$(ET)_2X$ (ET=BEDT-TTF, X: monovalent anion). These systems have recently been studied extensively, displaying a subtle competition among CO, metallic, and superconducting phases.[6–8] Their electronic states have been studied theoretically by using 2D extended Hubbard models, which include Coulomb repulsions of not only on-site (U), but also intersite (V_{ij}). The latter plays a crucial role for CO at 3/4-filling (or equivalently 1/4-filling of holes).[9,10] So far, these kinds of models have been studied for simple lattice structures such as one-dimensional (1D) chain,[11] ladder,[12] 2D square lattice,[13,14] and so on. In all of these works, Wigner crystal-like CO states become stabilized, in general, due to the effect of V_{ij} between NN sites when U is large.

Recently, however, there appear experiments in these organic materials which are difficult to interpret within naive understandings of such CO phase transitions. In θ-$(ET)_2RbZn(SCN)_4$, when CO was quenched by rapid cooling, a glassy CO state is found.[6,15] Even above the transition temperature, where the system shows metallic resistivity,[6,8] the dielectric constant is unexpectedly found to have a frequency-dependence characteristic of insulators in members of θ-$(ET)_2X$,[16] while an extremely slow dynamics of CO is found in ^{13}C-NMR in the above θ-type compound as well as in α-$(ET)_2I_3$.[17] These suggest effects of geometrical frustration in the charge degree of freedom, which we investigate in this paper.

Fortunately, the modeling of organic systems is very simple and reliable. The transfer integrals between the molecules (t_{ij}) can be obtained from the extended Hückel method.[18] In the θ- and α-type structures, the ET molecules are arranged in 2D planes that are close to triangular lattices. However, the network of t_{ij} can be approximately described by a square lattice.[9] On the other hand, the values of V_{ij} are comparable on every bond of this triangular lattice,[18] which introduce frustration in this system. In the previous calculations on 2D extended Hubbard models for these materials,[10] U and V_{ij} were treated at the mean-field level and only insulating phases were found for large interactions. However, we expect that a quantum melting of CO takes place due to frustration, and that a metallic region is stabilized even in the strongly correlated regime. Actually, in a frustrated 1D model, destabilization of CO state due to quantum fluctuation was shown numerically.[19] Therefore, it is of fundamental interest to proceed beyond the mean field in those 2D models.

To study this problem, we first consider a simplified

model for the 2D organic systems based on the considerations above; i.e., the 1/4-filled extended Hubbard model on a square lattice with NN and NNN Coulomb repulsions:

$$H = -t\sum_{\langle ij\rangle,\sigma}(c^{\dagger}_{i\sigma}c_{j\sigma}+c^{\dagger}_{j\sigma}c_{i\sigma}) + U\sum_{i} n_{i\uparrow}n_{i\downarrow} + V\sum_{\langle ij\rangle} n_i n_j + V'\sum_{\langle ij\rangle'} n_i n_j. \quad (1)$$

Here, $c^{\dagger}_{i\sigma}$ and $(c_{i\sigma})$ creates (eliminates) an electron of spin σ at site i, $n_{i\sigma}=c^{\dagger}_{i\sigma}c_{i\sigma}$ and $n_i=n_{i\uparrow}+n_{i\downarrow}$. t and V are the transfer integrals and the NN Coulomb repulsion along the bonds of the square lattice $\langle ij\rangle$, respectively, and V' is the NNN Coulomb repulsion along one of the diagonals $\langle ij\rangle'$.

Some insight of the CO states in the above model can be attained by considering the following two limits for $U/t \gg 1$, where doubly occupied sites are suppressed.

Case A. $V/V' \gg 1$: An insulating state due to a checkerboard pattern of CO with alternating charge in every other site [wave vector $\mathbf{q}=(\pi,\pi)$] is realized. The effective model for the spin degrees of freedom on the sites occupied by an electron is a 2D spin-1/2 AF Heisenberg model with NN J and NNN J' along both the diagonals. The estimated exchange couplings from a fourth-order perturbation in t show $J \gg J'$, and then $\mathbf{q}=(\pi/2,\pi/2)$ spin ordering is expected.[7,13]

Case B. $V'/V \gg 1$: The system is insulating, but with $\mathbf{q}=(0,\pi)$ CO forming rows or columns of occupied sites alternating with empty ones in a stripe-type manner. The spin degrees of freedom is described by a quasi-1D AF Heisenberg model with J along the chains coupled through the interchain interaction J'. Therefore, the AF spin ordering of $\mathbf{q}=(\pi,\pi/2)$ is expected.

When $V'/V \sim 1$, the frustration is expected to play a major role. Actually, if $t=0$ and U is large enough, the model is equivalent to the 2D Ising model with couplings $V/2$ and $V'/2$, as can be easily seen from Eq. (1). In this case, the ground state for exactly $V=V'$ is always gapless, which corresponds to the metallic state in the present model. Below we will analyze Eq. (1) by Lanczos exact diagonalization on an $L=16$ cluster to take account of quantum fluctuation.

In order to determine whether the system is insulating or not, we have calculated the Drude weight:[20]

$$\frac{D}{2\pi e^2} = -\frac{\langle 0|T|0\rangle}{4L} - \frac{1}{L}\sum_{n\neq 0}\frac{|\langle n|j_x|0\rangle|^2}{E_n - E_0}, \quad (2)$$

where E_0 and E_n are the ground state and excited state energies of the system, respectively. T is the kinetic energy operator [first term in Eq. (1)], j_x is the current operator in the x direction, and e is the electron charge. To explore the electronic states we have also calculated the charge and spin structure factors, $C(\mathbf{q})=(1/L)\Sigma_{ij}e^{i\mathbf{q}\cdot\mathbf{R}_{ij}}\langle n_i n_j\rangle$ and $S(\mathbf{q})=(1/L)\Sigma_{ij}e^{i\mathbf{q}\cdot\mathbf{R}_{ij}}\langle S^z_i S^z_j\rangle$, respectively, where $\mathbf{R}_{ij}$ is the vector connecting two different sites and S^z_i is the z component of the spin operator.

The ground state phase diagram on the $V-V'$ plane for a fixed $U=10t$ is shown in Fig. 1, which includes CO insulating phases and a metallic phase. At weak coupling with small $(V/t, V'/t)$ a metallic phase is stabilized, as expected from the large fraction of charge carriers available in the system. Fixing $V'=0$ and increasing V induces a metal-insulator transition at $V \sim 2t$ to the checkerboard CO phase (*Case A* discussed above).[14] On the other hand, if we fix $V=0$ and vary V', a metal-insulator transition to the stripe CO phase occurs at $V' \sim 4t$ (*Case B*). Interestingly, the metallic phase appearing at weak coupling extends out along the $V'=V$ line up to strong coupling in a robust manner.

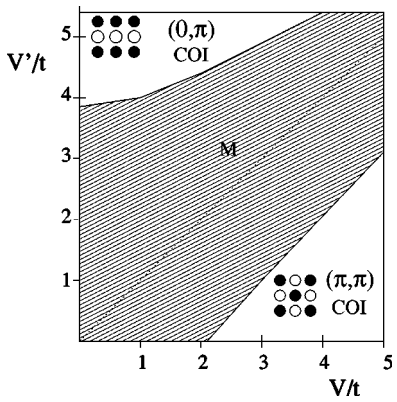

FIG. 1. Ground state phase diagram of the 1/4-filling extended Hubbard model Eq. (1) for $U=10t$. The boundaries are extracted from exact diagonalization calculations of the Drude weight on $L=16$ site cluster (see Fig. 2). The label M stands for metallic, and COI for a charge ordered insulator.

In Fig. 2 the Drude weight for different values of V and in Fig. 3 the structure factors for $V=3t$ as a function of V', both for fixed $U=10t$, are plotted. Fixing V to a large value $(V>3t)$, we find that the checkerboard CO state with AF ordering is stabilized for small values of V', as observed from a negligibly small Drude weight and the large values of $C(\pi,\pi)$ and $S(\pi/2,\pi/2)$. This insulating phase is destabilized with increasing V' and a transition from the CO insulating phase to a metallic phase occurs as can be seen from

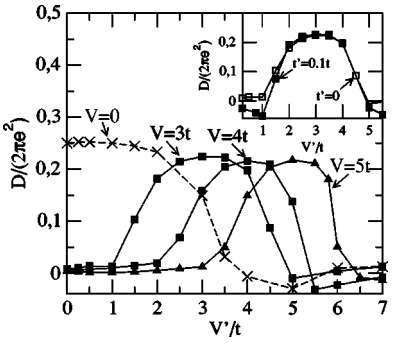

FIG. 2. The Drude weight calculated by exact diagonalization on $L=16$ for the 1/4-filled extended Hubbard model Eq. (1) for $U=10t$ and different values of V. It is rapidly enhanced as V' is increased with V fixed, signaling the presence of a metallic phase. The inset shows, for $V=3t$, the variation when a diagonal hopping, $t'=0.1t$, is included in the model, where the change is small.

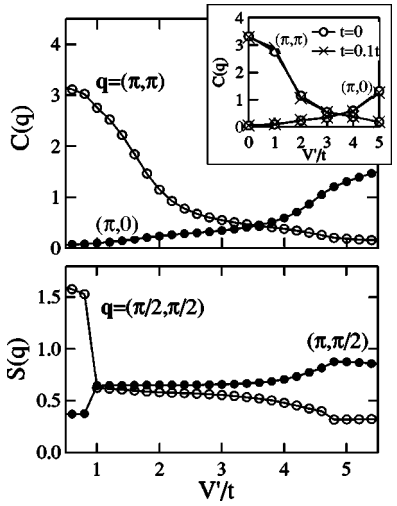

FIG. 3. The charge and spin structure factors, $C(\mathbf{q})$ and $S(\mathbf{q})$, for $U=10t$ and $V=3t$ as a function of V' for wave vectors relevant for the two CO states. A crossover corresponding to the Drude weight is seen. The inset shows the variation of $C(\mathbf{q})$ when small diagonal $t'=0.1t$ is included in the model, where the change is small.

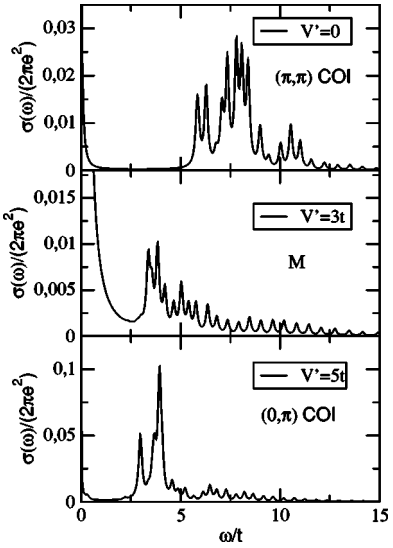

FIG. 4. Evolution of optical conductivity $\sigma(\omega)$ of the model Eq. (1), for $U=10t$ and $V=3t$, as the system is driven across the frustration-induced metallic phase from the checkerboard to the stripe CO phases. Spectral weight is transfered from high to low energies as the system is driven through the metallic phase, forming a mid-infrared band with a feature appearing at its lower band edge and a strong Drude component. A Lorentzian broadening of $\eta=0.1t$ is used to smoothen out the delta peaks.

the rapid increase of the Drude weight with V'. In this region, $C(\pi,\pi)$ and $S(\pi/2,\pi/2)$ are suppressed with V' and a crossover to the stripe CO state is seen, characterized by the large value of $C(0,\pi)$ and $S(\pi,\pi/2)$ at large V'. When $V' \sim V$, $C(\mathbf{q})$ becomes featureless, indicating that neither the checkerboard nor the stripe CO state is preferred, as expected.

The existence of the intermediate metallic phase found here should be robust enough in the thermodynamic limit, although the cluster size investigated is limited to $L=16$.[21] Whether the CO quantum phase transition is always accompanied with a metal-insulator transition or not is not clear from our results. As a matter of fact, sudden changes of $S(\pi/2,\pi/2)$ and the Drude weight at $V'/t=1$ indicate a level crossing to a metallic state. However, $C(\pi,\pi)$ still dominates over the other $\mathbf{q}$ values, suggesting the presence of CO metallic states near the boundary. Calculations on larger systems and finite size scaling are neccesary to determine the CO transition lines more accurately.

This frustration induced metallic phase is found to be robust against introducing a small hopping amplitude t' along the diagonal direction $\langle ij\rangle'$, relevant to the actual θ- and α-$(ET)_2X$ materials.[6,8] In the insets of Figs. 2 and 3, a comparison between the square lattice case Eq. (1) and the results for the model where $t'=0.1t$ is added are shown. The metallic phase is stabilized in a similar V' range, and $C(\pi,\pi)$ $[C(0,\pi)]$ diplays similar suppression (enhancement) as V' is increased.

Finally, we discuss the evolution of the optical spectra[20] upon these crossovers, as shown in Fig. 4 for fixed $U=10t$ and $V=3t$ for different values of V'. In the case of $V'=0$ (top frame), the system is in the checkerboard CO insulating phase, and a gap in the spectra with a peak position centered around $8t$ is observed. This is naturally expected since moving a charge from the checkerboard CO state costs energy of $3V$ (=$9t$ in this case) in the atomic limit.[14] On the other hand, in the stripe CO insulating phase, there are two possible ways of moving a charge, which are perpendicular and along the stripes, with the estimated energy costs of $2V'-V$ and $U-V$, respectively. These lead to a rather broad incoherent band around $7t$ in the bottom frame of Fig. 4, in the case of $V'=5t$, as expected. Apart from this, sharp peaks at about $4t$ appear, which can be attributed to the 1D nature of the stripes. Indeed, excitonic features appear inside the Mott gap in the optical spectra of a $1/2$-filled 1D extended Hubbard chain for $V<U/2$,[22] which should be an effective model for each stripe.

In the metallic phase at intermediate V'/V (see middle frame of Fig. 4), a redistribution of the spectral weight occurs. Spectral weight associated with incoherent transitions due to U and V_{ij} is transfered to lower energies giving rise to the Drude peak and a mid-infrared band together with a low energy feature appearing at its lower edge. The overall appearance of the optical conductivity is similar to the one observed for a $1/4$-filled metal close to the checkerboard CO transition[14] induced by V $(V'=0)$. We stress again that this is nontrivial since the interaction strengh is much larger here in the frustration-induced case. However, interestingly, the mid-infrared band reaches higher energies making the spectrum somewhat broader while the feature at its lower edge appears at larger energies. All these "exotic" features appearing in the frustrated metallic phase can be attributed to the dynamics of quasiparticles immersed in a charge fluctuating background and would be missed in a mean-field analysis.

In the actual organic compounds, θ- and α-$(ET)_2X$, $U\sim 1$ eV and $t\sim 0.1$ eV, which correspond to $U\sim 10t$, and $V'\sim V$ with the value of $\sim U/3$ is realized;[18] therefore, the

system is inherently located in or near to the frustration-induced metallic phase. In reality, however, the lower symmetry for t_{ij} and/or the coupling to the lattice degree of freedom, which we do not include in our model, would push the system toward CO states. As a matter of fact, large displacements of the molecules are observed in α-$(ET)_2I_3$ at the CO transition temperature, and in θ-$(ET)_2X$ a structural change lowering the crystal symmetry takes place concommitantly with the CO phase transition.[4] One may consider these experimental facts as suggesting that the CO phase is realized by relaxing the frustration effect seen in our calculations, since the interaction strength is already strong enough to drive the CO state. Another aspect worth considering when comparing our results to experimental data is that the CO states actually observed in ET compounds have a different charge pattern as the ones discussed here,[4] corresponding to a "zigzag"-type pattern in our model. We mention that this phase is also found in our exact diagonalization study; e.g., for appreciably large V', larger than $6t$ for $U=10t$ and $V=3t$. We also note that the CO pattern corresponding to the checkerboard pattern has been observed in a similar material with the θ-type structure; i.e., θ-$(BDT\text{-}TTP)_2Cu(NCS)_2$.[23] The precise determination of the phase diagram including such different CO states in comparison with each material, as well as more detailed investigation of the frustration-induced metallic phase are left for future studies.

In conclusion, we have found a metallic phase induced by frustration in 2D 1/4-filled systems that is robust against changing the lattice geometry from a square to an anisotropic triangular lattice relevant to layered organic conductors. Our phase diagram is similar to that of the extended Hubbard model on the 1D zigzag chain structure,[19] as well as to that of a frustrated 2D Bose-Hubbard Hamiltonian where a superfluid phase is stabilized between two charge modulated phases.[24] From our findings, it is natural to conjecture that quantum melting of CO states due to geometrical frustration is rather general and that the metallic phase near the CO phase in the actual compounds with geometrically frustrated structure is relevant to such a situation. An interesting issue to address in future is whether superconductivity can exist between the frustration-induced metallic phase and the CO phase mediated by charge fluctuations appearing at the phase boundary. This kind of possible superconductivity has been studied in connection to organic conductors[25] and to Na_xCoO_2.[26]

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[1] For instance, see *Magnetic System with Competing Interactions*, edited by H. T. Diep (World Scientific, Singapore, 1994).
[2] P. W. Anderson, Phys. Rev. **102**, 1008 (1956).
[3] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998), Chap. IV E.
[4] H. Seo, C. Hotta, and H. Fukuyama, Chem. Rev. (Washington, D.C.) **104**, 5005 (2004), and references therein.
[5] M. L. Foo, Y. Wang, S. Watauchi, H. W. Zandbergen, T. He, R. J. Cava, and N. P. Ong, Phys. Rev. Lett. **92**, 247001 (2004).
[6] H. Mori, S. Tanaka, and T. Mori, Phys. Rev. B **57**, 12 023 (1998); K. Miyagawa, A. Kawamoto, and K. Kanoda, *ibid.* **62**, R7679 (2000).
[7] R. H. McKenzie, J. Merino, J. B. Marston, and O. P. Sushkov, Phys. Rev. B **64**, 085109 (2001).
[8] N. Tajima, A. Ebina-Tajima, M. Tamura, Y. Nishio, and K. Kajita, J. Phys. Soc. Jpn. **71**, 1832 (2002); R. Wojciechowski, K. Yamamoto, K. Yakushi, M. Inokuchi, and A. Kawamoto, Phys. Rev. B **67**, 224105 (2003).
[9] H. Kino and H. Fukuyama, J. Phys. Soc. Jpn. **65**, 2158 (1996).
[10] H. Seo, J. Phys. Soc. Jpn. **69**, 805 (2000).
[11] F. Mila and X. Zotos, Europhys. Lett. **24**, 133 (1993); K. Penc and F. Mila, Phys. Rev. B **49**, 9670 (1994).
[12] M. Vojta, A. Hübsch, and R. M. Noack, Phys. Rev. B **63**, 045105 (2001).
[13] Y. Ohta, K. Tsutsui, W. Koshibae, and S. Maekawa, Phys. Rev. B **50**, 13 594 (1994).
[14] M. Calandra, J. Merino, and R. H. McKenzie, Phys. Rev. B **66**, 195102 (2002); M. Dressel, N. Drichko, J. Schlueter, and J. Merino, Phys. Rev. Lett. **90**, 167002 (2003); J. Merino, A. Greco, R. H. McKenzie, and M. Calandra, Phys. Rev. B **68**, 245121 (2003).
[15] K. Miyagawa and K. Kanoda (private communications).
[16] K. Inagaki, I. Terasaki, and H. Mori, Physica B **329**, 1162 (2003); K. Inagaki, I. Terasaki, H. Mori, and T. Mori, J. Phys. Soc. Jpn. **73**, 3364 (2004).
[17] T. Takahashi, R. Chiba, K. Hiraki, H. M. Yamamoto, and T. Nakamura, J. Phys. IV **114**, 269 (2004).
[18] T. Mori, Bull. Chem. Soc. Jpn. **73**, 2243 (2000).
[19] H. Seo and M. Ogata, Phys. Rev. B **64**, 113103 (2001); S. Nishimoto and Y. Ohta, *ibid.* **68**, 235114 (2003).
[20] The exact diagonalization calculation of quantities in this work is now standard, as can be found in, e.g., W. Stephan and P. Horsch, Phys. Rev. B **42**, 8736 (1990), and Refs. 13 and 14.
[21] Previous calculations (Ref. 14) at $V'=0$ show that the behavior of the Drude weight and the critical value for the metal-insulator transition is robust against an increase of the size cluster from $L=16$ to $L=20$. Furthermore, finite size scaling of the charge gap in a two-leg ladder system where one can reach larger sizes indicates the presence of a metallic phase when $V' \sim V$ (see Ref. 19).
[22] S. S. Kancharla and C. J. Bolech, Phys. Rev. B **64**, 085119 (2001).

[23] K. Yakushi, K. Yamamoto, M. Simonyan, J. Ouyang, C. Nakano, Y. Misaki, and K. Tanaka, Phys. Rev. B **66**, 235102 (2002).
[24] G. G. Batrouni, R. T. Scalettar, G. T. Zimanyi, and A. P. Kampf, Phys. Rev. Lett. **74**, 2527 (1995).
[25] J. Merino and R. H. McKenzie, Phys. Rev. Lett. **87**, 237002 (2001); A. Kobayashi, Y. Tanaka, M. Ogata, and Y. Suzumura, J. Phys. Soc. Jpn. **73**, 1115 (2004); Y. Tanaka, Y. Yanase, and M. Ogata, *ibid.* **73**, 2053 (2004).
[26] Y. Tanaka, Y. Yanase, and M. Ogata, J. Phys. Soc. Jpn. **73**, 319 (2004).