

Spiral Charge Frustration in the Molecular Conductor (DI-DCNQI)₂Ag

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We theoretically study the effect of spiral-type charge frustration in a quasi-one-dimensional molecular conductor (DI-DCNQI)₂Ag. We clarify how the spiral frustration in the interchain Coulomb repulsion is relieved and leads to a self-organization of complex charge-lattice ordered chains, in agreement with the recent synchrotron x-ray study [T. Kakiuchi *et al.*, Phys. Rev. Lett. **98**, 066402 (2007)]. In addition, we find that a keen competition between charge and lattice degrees of freedom under the frustration gives rise to a characteristic temperature within the ordered phase, below which a drastic growth of molecular displacements occurs. Our results enlighten the relevance of the spiral frustration and provide a possible reconciliation among puzzling experimental data.

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Geometrical frustration in charge degree of freedom, i.e., charge frustration, has been a fundamental problem in condensed matter physics, since Anderson argued its importance in the Verwey transition in magnetite [1]. Recently, it is attracting renewed interests partly because exotic behaviors are found in several molecular conductors, where frustrated lattice structures are often formed. A typical example is the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) based compounds, in which strong frustration in the two-dimensional triangular lattice makes the charge ordering (CO) unstable [2] and intriguing transport phenomena are observed in the critical region [3,4].

Quasi-one-dimensional (Q1D) molecular conductors, however, have been less examined from the viewpoint of frustration; it is usually supposed that the 1D chains are well decoupled, offering canonical systems to study 1D physics such as Tomonaga-Luttinger liquids, charge and spin density waves, and so on [5]. Nevertheless, the Q1D compounds also often retain a “hidden” three-dimensional (3D) frustration in packing the 1D chains. Such interchain frustration effect has been studied within extended Hubbard-type models on frustrated zigzag ladders [6–8].

We consider here a typical Q1D molecular conductor (DI-DCNQI)₂Ag [9], which provides a different avenue to interchain frustration. This compound consists of 1D chains of DI-DCNQI (2,5-diiodo-*N,N'*-dicyanoquinonediimine) molecules whose electronic structure near the Fermi level is described by a Q1D band at quarter filling [10]. A prominent feature of this system is the phase transition at $T_c \approx 220$ K. It was observed that the ¹³C-NMR line splits below T_c , which was ascribed to a Wigner-crystal-type CO with a twofold period along the chains [11]. Although the simple CO scenario was supported by theoretical studies in 1D models [12], there have been many puzzling behaviors found in experiments.

One is the lattice displacements suggested by optical spectra analyses [13,14]: The IR and Raman spectra are

complicated and not well fitted by such simple CO without assuming any lattice distortions. Another unaccountable behavior is seen in the NMR line shape [11]. There appears an extraordinarily wide broadening below ~ 100 K in the outer line with a larger shift, which can hardly be ascribed to critical fluctuations related to the magnetic ordering at a considerably lower temperature (T) of 5 K. Furthermore, a small peak starts to grow at around zero shift in a similar T range. Such a characteristic T range within the ordered phase was also observed in transport properties. The $1/T$ derivative of the log of resistivity shows, in addition to a peak structure at T_c , a broad hump centered at around 100 K [15]. In the same region, the dielectric permittivity exhibits a peak and large frequency dependence [16]. All these behaviors, implying intrinsic changes at a much lower T than T_c , are difficult to understand from the simple 1D CO picture.

A clue to a possible origin of these features was found by a recent experimental study based on synchrotron x-ray crystal structure analysis at 50 K [17]. It was claimed that the ordered structure is not a simple CO: Instead it is a periodic array of DI-DCNQI chains with mixed patterns of charge-lattice symmetry breaking as shown in Fig. 1, which we call the “mixed state.” The importance of frustration in the lattice structure was pointed out; if all the chains exhibit the simple twofold CO, they would suffer from a spiral-type charge frustration among neighboring chains, since the DI-DCNQI molecules are displaced with each other by $1/4$ of lattice spacing along the chain as shown in Fig. 1(b) (see also Fig. 4 of Ref. [17]). However, it is not clear how the mixed state is stabilized and, furthermore, what causes the peculiar T dependences in the ordered phase mentioned above.

Theoretically, interplay between charge and lattice degrees of freedom in Q1D molecular conductors has been studied on the basis of 1D or Q1D extended Hubbard models at quarter filling [12]. In particular, recent studies showed that CO and lattice dimerization (LD) compete

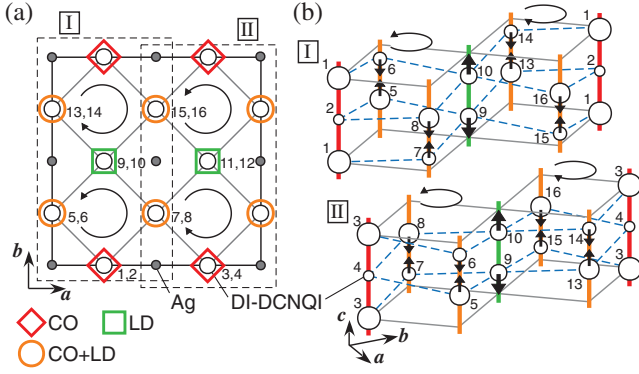


FIG. 1 (color). The charge-lattice ordered state (the mixed state) in $(\text{DI-DCNQI})_2\text{Ag}$ [17]. (a) DI-DCNQI and Ag sites viewed from the chain direction (c axis), where the arrangement of chains with different orders are indicated; CO and LD represent charge order and lattice dimerization, respectively. (b) Side view of the DI-DCNQI sites where the size of circles and arrows represent the charge density and the lattice displacement, respectively. The blue dotted lines in (b) are the spiral V' bonds in Eq. (1).

with each other but they coexist in some cases [18]. These three states, CO, LD, and their coexistence, are in fact realized but in different chains in the mixed state shown in Fig. 1. The spiral frustration is expected to be a key factor for the nontrivial mixture of orderings out of uniform and equivalent chains; however, theoretical studies taking account of it have not been done so far.

In this study, we investigate the effect of the interchain spiral frustration in Q1D systems for a model of $(\text{DI-DCNQI})_2\text{Ag}$. We clarify how the mixed state in Fig. 1 is stabilized under the charge frustration. We also calculate finite- T properties of the charge-lattice coupled phenomena and propose a possible scenario to reconcile the puzzling experimental data in this compound.

We consider a Q1D model which takes account of the 3D interchain spiral structure in the actual compound. Each 1D chain is represented by the extended Peierls-Hubbard model at quarter filling [12]. Here, in order to concentrate on the competition between charge and lattice degrees of freedom, we take the limit of strong on site Coulomb interaction and leave out the spin degree of freedom [19]. Namely, we study a half-filled spinless fermion model coupled to the lattice, whose Hamiltonian reads

$$\mathcal{H} = \sum_{\langle i,j \rangle_{1D}} \{t_{ij}(a_i^\dagger a_j + \text{H.c.}) + V_{ij}n_i n_j\} + \sum_{\langle i,j \rangle'_\perp} V'_{ij}n_i n_j + \sum_{\langle i,j \rangle''_\perp} V''_{ij}n_i n_j + \frac{K}{2} \sum_i u_i^2, \quad (1)$$

where a_i^\dagger (a_i) is the creation (annihilation) operator for a spinless fermion at the i th DI-DCNQI site, and $n_i = a_i^\dagger a_i$. Here, the first term is the 1D part where the sum on $\langle i,j \rangle_{1D}$ is taken for nearest-neighbor sites along the chains. The next two terms are the interchain Coulomb interactions

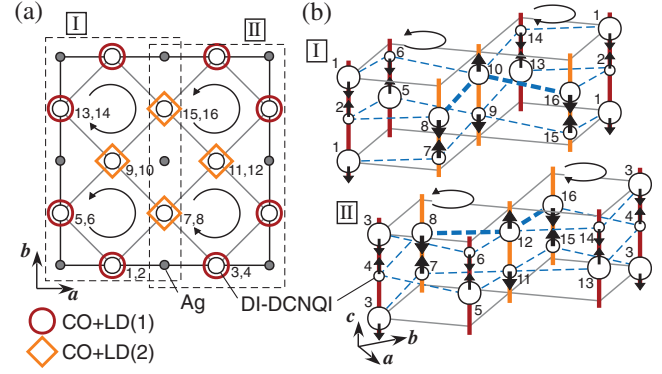


FIG. 2 (color). The CO + LD state. Notations are the same as in Fig. 1, whereas CO + LD(1) and CO + LD(2) in (a) indicate the two kinds of chains, both with charge order as well as lattice dimerization but with different degrees. The thick V' bonds in (b) suffer from frustration in Coulomb repulsion between charge rich sites.

where $\langle i,j \rangle'_\perp$ are the nearest interchain site pairs shown by the blue dotted lines in Fig. 1(b), and $\langle i,j \rangle''_\perp$ are the next-nearest interchain pairs such as sites 1–8, 2–7, etc., while interactions of farther range are neglected for simplicity. Note that both terms undergo the spiral frustration. The transfer integrals and the Coulomb repulsions are coupled with the lattice displacement u_i of each molecule, as $t_{ij} = t(1 + \alpha \delta u_{ij})$, $V_{ij} = V(1 + \beta \delta u_{ij})$, $V'_{ij} = V'(1 + \beta' \delta u_{ij})$, and $V''_{ij} = V''(1 + \beta'' \delta u_{ij})$, where $\delta u_{ij} = u_i - u_j$ [20]. The last term in Eq. (1) is the elastic energy, and the displacements u_i are treated as classical variables within the adiabatic approximation. In the following, we restrict ourselves to u_i being uniaxial, i.e., the molecules are allowed to move only in the chain direction, by considering the experimental results [17].

We treat the Coulomb interaction within Hartree-Fock approximation. The size of unit cell we consider is the experimental one which contains eight chains with two sites each, namely, 16 sites as shown in Fig. 1. The order parameters, $\langle n_i \rangle$, $\langle a_i^\dagger a_j \rangle$, and u_i are self-consistently determined with the precision of 10^{-6} . We set $t = 1$ and $\alpha = 1$ (absorbed in the notation of u_i), and fix $V = 1.5$, $V' = 0.75$, $V'' = 0.15$, $\beta = 0.5$, $\beta' = 0.0325$, and $\beta'' = 0.0975$ [21], while varying K^{-1} , which represents the softness of the lattice. We will comment on the choice for the intersite Coulomb repulsions later.

First let us discuss the results for the ground state properties. We find that the charge-lattice ordering equivalent to the mixed state pattern in Fig. 1 is indeed stabilized over others in a certain range of K^{-1} , among the several solutions self-consistently obtained. Otherwise, another solution gives the lowest energy: In this state, all chains show both CO and LD as shown in Fig. 2, which we call here the CO + LD state. Both of these states are insulating. Figure 3 shows the ground state energies as well as the charge disproportionations $\delta_i = \langle n_i \rangle - 1/2$ and the lattice displacements u_i for these two solutions as a function of

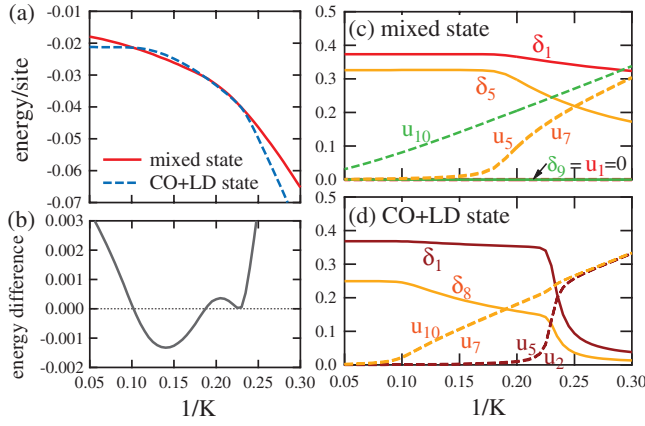


FIG. 3 (color). The ground state properties of the mixed state and the CO + LD state. K^{-1} dependences of (a) the ground state energies, (b) energy difference between the two states, and (c),(d) charge disproportionations $\delta_i = \langle n_i \rangle - 1/2$ and lattice displacements u_i for representative sites in the two solutions. δ_i and u_i for other sites are equal or have opposite sign with equal absolute value to the plotted ones (see Figs. 1 and 2). Note that (u_5, u_7) in (c) and (u_2, u_5) and (u_7, u_{10}) in (d) take almost the same but not identical values [see also the insets of Figs. 4(c) and 4(d)].

K^{-1} . For $K^{-1} < 0.10$, the CO + LD state is the ground state: As shown in Fig. 3(d), the lattice displacements u_i are almost negligibly small in this region; therefore, it is essentially regarded as a bundle of 1D CO states stabilized by the intrachain Coulomb repulsion V . This state suffers from the charge frustration in the thick V' bonds in Fig. 2(b). On the other hand, for $K^{-1} > 0.19$, the CO + LD state is the ground state as well [22]; when K^{-1} is large, the charge disproportionations δ_i become small, and hence, it is essentially a LD state stabilized by the intrachain charge-lattice coupling. In between these two, the mixed state gives a lower energy for $0.10 < K^{-1} < 0.19$. This state emerges in the transient regime from the CO-dominant state for small K^{-1} to the LD-dominant state for large K^{-1} , both of which undergo frustration. There, the system finds a way to relieve the frustration by self-organizing arrays of the CO, LD, and coexisting chains.

Next we show how these coexistences and competitions evolve at finite T . In Fig. 4(a), T dependences of the free energies for the two solutions are shown at $K^{-1} = 0.15$, for which the ground state is the mixed state. As increasing T , the free energy difference between the two states becomes smaller, and at $T_c^{1st} = 0.66$, a first-order transition takes place above which the CO + LD state gives lower free energy [see also Fig. 4(b)]. Finally, for $T > T_c^{CO+LD} = 0.91$ the system turns into the uniform metallic state. The sequence of the phase transitions is summarized in Fig. 5(a).

An important point is that the free energy difference is extremely small for $T_c^{1st} < T < T_c^{CO+LD}$, much less than 10^{-4} as shown in Fig. 4(b). Another key observation is that T dependences of δ_i and u_i are similar between these two

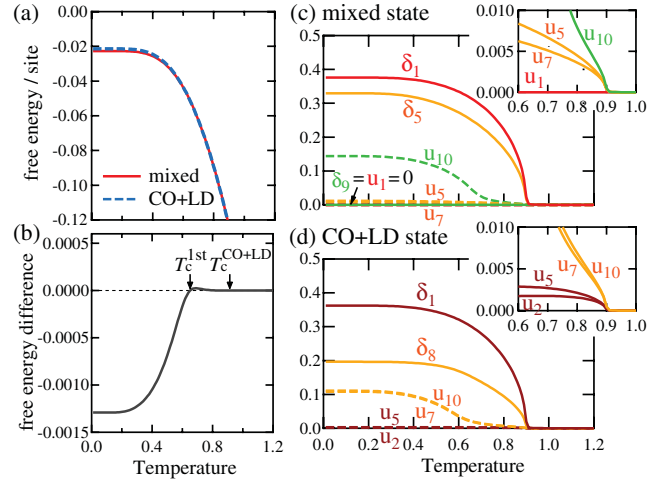


FIG. 4 (color). Temperature dependences of (a) the free energies, (b) free energy difference, and (c),(d) charge disproportionations $\delta_i = \langle n_i \rangle - 1/2$ and lattice displacements u_i for the two solutions for $K^{-1} = 0.15$. Insets show enlarged view for u_i near the transition temperatures.

solutions as plotted in Figs. 4(c) and 4(d). Their transition temperatures from the high- T uniform phase are almost the same ($T \approx 0.91$), and by decreasing T , charge disproportionations δ_i develop first while lattice distortions u_i remain suppressed. When T is decreased down to $T^* \approx 0.7$, the u_i rapidly develop. Note that this crossover temperature T^* almost coincides with T_c^{1st} . The first-order phase transition as well as the finite- T features described above are always seen in our calculations when the mixed state is the ground state.

From these results at finite T , we propose two different scenarios for what is taking place in the actual compound (DI-DCNQI)₂Ag. One is that, as in our calculation, the system exhibits two phase transitions. The first one is the transition at $T_c = 220$ K, which corresponds to $T = T_c^{CO+LD}$, and the second occurs at T_c^{1st} well below T_c as indicated in Fig. 5(a); yet this latter transition has not been observed in experiments so far. The other scenario is that the CO + LD state in our calculation is destabilized if fluctuations are taken into account beyond the mean-field level, and the mixed state gives a lower free energy in the entire T range within the ordered phase. Then, we predict that there is only one transition to the mixed state; $T_c = 220$ K corresponds to T_c^{mixed} , which is followed by a crossover behavior at T^* , instead of the successive transitions, as illustrated in Fig. 5(b). This latter scenario is based on the observation that CO suffering from frustration is often destabilized by fluctuations [12,23], and the free energy

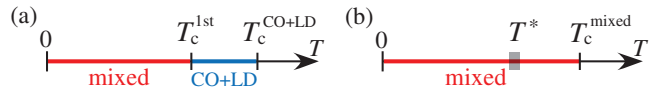


FIG. 5 (color). Schematic illustration of the proposed two scenarios for the phase transition(s) in (DI-DCNQI)₂Ag.

difference is already very tiny in the present mean-field results.

In both of these scenarios, an additional characteristic temperature is predicted: T_c^{1st} in the former and T^* in the latter. In either case, the system undergoes drastic changes there in the lattice sector, i.e., a rapid development of the lattice displacements within the ordered phase. This is suggestive in considering the puzzling experimental results mentioned above. The rapid growth and the expected large fluctuations in the lattice displacements may explain a peak and frequency dependence of the dielectric permittivity [16] as well as the anomalous broadening and an additional peak in the NMR spectra [11]. A hump in the $1/T$ derivative of the log of resistivity [15] can also be related to the drastic changes at the characteristic temperature. To confirm our proposal, systematic measurements of T dependence of x-ray diffraction as well as NMR for single crystals are highly desired.

Let us comment on the values of interchain Coulomb repulsions used in our calculations. By investigating several sets of parameters with varying K^{-1} , we have found that the mixed state is robust particularly for $V' \gg V''$, while the region becomes small when V' is compatible with V'' . The results imply that, since the center-to-center distances between two DI-DCNQI molecules are not much different for V' and V'' , other factors are also important in determining the (effective) interchain Coulomb repulsions, such as the cation environment and the anisotropy of molecular orbitals. In particular, the displacements of Ag^+ cations to positions along the V' bonds [17] can be relevant by enhancing the values of V' (and reducing V'') in our model, since the cation with positive charge enhances charge disproportionations between the neighboring DI-DCNQI molecules. A similar effect was discussed in another Q1D molecular conductor $(\text{TMTTF})_2\text{X}$ [24,25].

Finally we make a remark on the spin degree of freedom. Experimentally, an antiferromagnetic transition is observed by NMR [9] and ESR [26] at $T \approx 5$ K. In the mixed state, we expect localized spins to appear on the charge rich sites in the CO chains, on the dimers in the LD chains, and on the dimers in the coexisting chains but with more spin density on the charge rich sites. Both intrachain and interchain exchange couplings depend on the degree of CO as well as LD, which show characteristic T dependences as discussed above; hence, it is highly nontrivial how the spin degree of freedom acts under such condition. This should be a reason why simple Bonner-Fisher-type analysis fails to understand the magnetic susceptibility [9] and specific heat data [27]. Calculations including spins are left for future study.

In summary, we have studied a charge-frustrated spinless fermion model coupled to the lattice degree of freedom to understand the charge-lattice coupled phenomena in the quasi-one-dimensional molecular conductor $(\text{DI-DCNQI})_2\text{Ag}$. We have shown that a peculiar mixed state, where charge ordered, lattice dimerized, and their

coexisting chains arrange periodically, is self-organized so as to relieve the spiral frustration between the chains. We have proposed two scenarios for the finite-temperature properties, and in both of them there is a characteristic temperature where lattice distortions develop rapidly. This drastic change provides a key to understand the puzzles remaining in experiments. Similar interchain frustration is seen in other quasi-one-dimensional compounds, and, therefore, our results indicate the necessity to examine its effect to obtain deeper understanding of these systems.

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