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Tuning the magnetic dimensionality by charge ordering in the molecular TMTTF salts

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We theoretically investigate the interplay between charge ordering and magnetic states in quasi-one-dimensional molecular conductors TMTTF₂X, motivated by the observation of a complex variation of competing/coexisting phases. We show that the ferroelectric-type charge order increases two-dimensional antiferromagnetic spin correlation, whereas in the one-dimensional regime two different spin-Peierls states are stabilized. By using first-principles band calculations for the estimation for the transfer integrals and comparing our results with the experiments, we identify the controlling parameters in the experimental phase diagram to be not only the inter-chain transfer integrals but also the amplitude of the charge order.

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Low-dimensional molecular conductors provide a fruitful stage to study strong electron correlations in the presence of large quantum fluctuations and coupling to lattice degrees of freedom [1]. The observed phase transitions involving spin, charge, and lattice degrees of freedom are summarized in the form of pressure (P)-temperature (T) phase diagrams for different families. It is common to stabilize a different ground state even for relatively small pressure variations. Presumably, these changes are triggered by small variations in lattice constants for a given material while maintaining the same geometry of constituent molecules at room T (isostructural) [2]. A general goal is to identify the parameters controlling the ground states and trends in the nature of the elementary excitations. An example of interest is the TMTTF₂X (TMTTF: tetramethyl-tetrathiafulvalene, X : monovalent anion) family of molecular solids [3], in which the tuning of charge order, by way of applying pressure, appears to play a role controlling the magnetic states [4]. Specifically, decreasing the charge order amplitude by use of applied pressure is associated with the antiferromagnetic (AF) transition $T_N \rightarrow 0$, and clarifying the relevant physics for this behavior is of interest in the field of quantum magnetism.

In the quasi-one dimensional family of TM₂X (TM: TMTTF or tetramethyl-tetraselenafulvalene TMTSF), the key parameter has been widely accepted as the dimensionality (D) tuned by the relative increase of inter-chain transfer integrals by P [3, 5, 6]. Figure 1 shows the recently updated phase diagram [3, 4, 7, 8]. Amazingly, a wide variety of phase transitions appear by applying P or replacement of X (chemical P). The phases latest revealed are in the left side where a ferroelectric-type charge ordering (FCO) transition was found [7, 9]; it has a strongly correlated nature [10], leading to magnetic transitions at low T . Prior to discovery of the FCO phases, the P - D correspondence was invoked to describe the phases and transitions appearing at higher P : transport experiments indicate that the

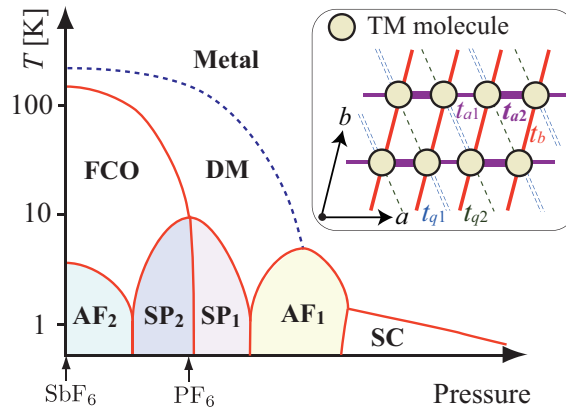


FIG. 1: (Color Online) A schematic phase diagram for TM salts [4]. The ambient pressures for TMTTF₂SbF₆ and TMTTF₂PF₆ are shown. DM, FCO, AF, SP, SC represent dimer Mott, ferroelectric charge ordering, antiferromagnetic, spin-Peierls, and superconducting states. The dashed line is a crossover while the solid lines are phase transitions. The inset shows the arrangement of TM molecules in the conducting plane.

correlation gap is reduced with P , interpreted as driven by the transverse hopping process [11], and the system shows a dimensional crossover [3]. The low- T spin-Peierls (SP) state (SP₁ in Fig. 1) is destabilized in favor of an AF state (AF₁) [12], which is consistent with the increase in the transverse spin exchange couplings [13, 14].

Difficulties come about when one attempts to apply the relation to the left side, the region with FCO. First, a discrepancy is easily seen since another AF phase (AF₂) appears at the lowest P and turns into the SP phase (SP₂) by applying P , opposite to the SP₁ \rightarrow AF₁ variation; the AF₂ and SP₂ states both coexist with FCO. Another point is that the FCO and AF₂ transitions behave cooperatively, namely, their transition temperatures both develop at low P [4, 15]. This is peculiar in the sense that, in general, charge ordering tends to decrease the effective spin exchange couplings [10, 16], and therefore would diminish transitions subject to spin couplings; in fact, the SP₂ phase shows such behavior [7, 8] which is reproduced in theoretical works [17, 18].

In this Letter, we theoretically elucidate the origin for such variations which apparently do not fit to the conventional practice. Starting by evaluation of transfer integrals using first principles band calculations (FPBC), we then investigate the roles of electronic correlation and electron-lattice couplings on the basis of the effective quarter-filled extended Hubbard model (EHM). We will show that the complex sequence of phases observed experimentally can be reproduced naturally when we add the inter-site Coulomb interaction as another essential parameter, in addition to the inter-chain transfer integrals.

The inclusion of the newly found phases in the low- P side of the phase diagram was proposed based on NMR measurements [4, 8], and the continuous connection of phases has been shown by different experiments [19–22]. First we address this in terms of electronic structure. We calculate the electronic band dispersions for two (TMTTF)₂ X members situated in the FCO region, $X=\text{PF}_6$ (SP₂ phase) and $X=\text{SbF}_6$ (AF₂ phase), within FPBC using the computational code QMAS (Quantum Materials Simulator) [23] based on the projector augmented-wave method [24] with the generalized gradient approximation [25].

By tight binding fitting to the electron bands near the Fermi level we obtain the values of transfer integrals in the unit of meV as $\{t_{a1}, t_{a2}, t_b, t_{q1}, t_{q2}\} = \{-155, -203, 26.2, -1.31, -3.29\}$ for the former and $\{-149, -207, 16.4, -16.4, -9.73\}$ for the latter salt (notations are shown in the inset of Fig. 1). The absolute values of t_{a1} and t_{a2} are about 10 times larger than the other transfer integrals: both salts form a quasi-one dimensional electronic structure along the a axis with dimerization. A measure for the D effect is given by $|t_b/t_{a2}|$ whose values are given as 0.129 for the PF₆ salt and 0.080 for the SbF₆ salt. From this point, as far as the transfer integrals are concerned, the 2- D in the PF₆ salt is indeed more higher than that in the SbF₆ salt. This is consistent with the semi-empirical extended Hückel calculations as well as considerations based on their crystal structures [26].

Next we investigate the role of Coulomb repulsions on top of such electronic structure, by considering the quasi-one dimensional EHM at quarter-filling in terms of holes. The Hamiltonian is given by

$$\begin{aligned} \mathcal{H}_{\text{EHM}} = & - \sum_{\langle ij \rangle, \sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) \\ & + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{\langle ij \rangle} V_{ij} n_i n_j, \end{aligned} \quad (1)$$

where t_{ij} is the transfer integral between the neighboring sites denoted by $\langle ij \rangle$, $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) is the creation (annihilation) operator of a hole on the i th site with spin $\sigma = \uparrow$ or \downarrow , and $n_i = n_{i\uparrow} + n_{i\downarrow}$ with $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$. U and V_{ij} are the on-site and the inter-site Coulomb interactions, respectively. From the results of FPBC, we hereafter set the transfer integrals as $t_{a1} = -0.8$, $t_{a2} = -1$, $t_{q1} = 0$, $t_{q2} = 0$ [27] and choose the inter-chain transfer integral t_b as a parameter, as inferred from the results above. We choose the on-site Coulomb interaction to be a typical value for this class of materials [10], as $U = 4$ (~ 1 eV) and impose a constraint on V_{ij} as $V_{a1} = V_{a2} = V_{q1} = V_{q2} = V$ and $V_b = 0$ to realize the FCO pattern observed in experiments (see Fig. 3).

Numerical exact diagonalization on a 4×4 sites cluster under periodic boundary conditions is performed, where we introduce inter-dimer/intra-dimer charge and spin structure factors given by $C_\pm(\mathbf{q}) = N_d^{-1} \sum_{i,j} \langle n_i^\pm n_j^\pm \rangle e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)}$ and $S_\pm(\mathbf{q}) = N_d^{-1} \sum_{i,j} \langle m_i^\pm m_j^\pm \rangle e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)}$, respectively, where N_d is the total number of dimers and \mathbf{r}_i denotes the center position of the i th dimer. Here, the inter-dimer/intra-dimer (+/-) correlations are detected by the summation/difference in charge and spin densities within each dimer, $n_i^\pm = (n_{2i} \pm n_{2i+1})/2$ and $m_i^\pm = (m_{2i} \pm m_{2i+1})/2$ with $m_i = n_{i\uparrow} - n_{i\downarrow}$, respectively, where even (odd) number is labeled as the site for the left (right) side in a dimer.

Figure 2 shows $C_\pm(\mathbf{q})$ and $S_\pm(\mathbf{q})$ for $t_b = 0.1$, at $V = 0$ (a) and $V = 2$ (b) [28]. At $V = 0$, there is no pronounced peak in $C_\pm(\mathbf{q})$; the system is in the dimer-Mott (DM) insulating state, where the intra-chain dimerization together with U lead to a Mott insulator [10]. The enhanced $S_+(\pi, q_b)$ and featureless behavior in $S_-(\mathbf{q})$ indicate that the AF correlation is developed between dimers, but only in the a -direction due to the 1- D . On the other hand, at $V = 2$,

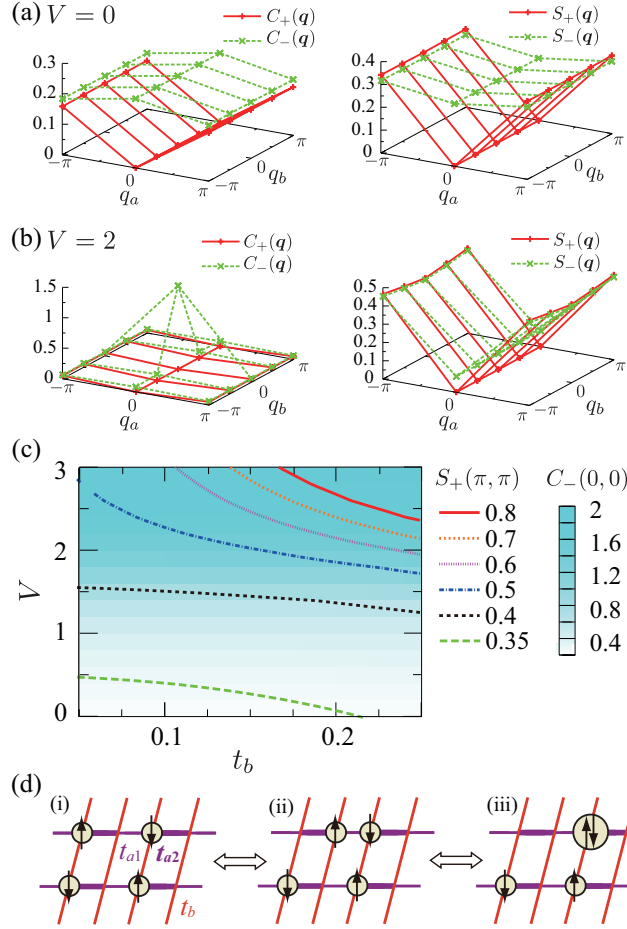


FIG. 2: (Color Online) Inter-dimer/intra-dimer charge and spin structure factors $C_{\pm}(\mathbf{q})$ and $S_{\pm}(\mathbf{q})$ at (a) $V = 0$ and (b) $V = 2$, for $U = 4$ and $t_b = 0.1$. (c) $C_-(0,0)$ (background color) and $S_+(\pi, \pi)$ (contour) on the (t_b, V) plane: The two-dimensional AF correlation is developed by both t_b and V . (d) The leading spin-exchange process from the fourth-order perturbation in the presence of FCO.

$C_-(\mathbf{q})$ has a clear peak at $\mathbf{q} = (0,0)$, i.e., the FCO correlation, and $S_{\pm}(\mathbf{q})$ both have peaks at $\mathbf{q} = (\pi, \pi)$. This shows that the development of FCO due to the inter-site Coulomb interaction induces the two-dimensional AF correlation between the charge rich sites. Note that this happens in spite of the fact that the transfer integrals are unchanged from Fig. 2 (a).

The emergence of 2-D AF correlation is balanced by the degree of FCO and the inter-chain transfer integral, as seen from Fig. 2 (c), where $C_-(0,0)$ and $S_+(\pi, \pi)$ are plotted on the (t_b, V) plane. $C_-(0,0)$ sharply develops with increasing V while $S_+(\pi, \pi)$ increases with increasing t_b , expected from the inter-chain spin exchange. The noticeable point is that the $S_+(\pi, \pi)$ peak is rapidly developed at large V when FCO is stabilized: the FCO state assists in stabilizing the AF state. As a result, the one-dimensional regime in the spin sector is limited to the region where *both* parameters t_b and V are small.

The origin of the magnetic properties seen in Fig. 2 (c) can be understood by a simplified strong-coupling analysis estimating the leading terms of the spin-exchange couplings by perturbation calculations with respect to the transfer integrals. In the DM state, the spin-exchange couplings between dimers along a -axis is simply given by $J_a = -t_{a1}^2/U_d$, while that along b -axis is given by $J_b = -4t_b^2/U_d$, where U_d is the effective on-site Coulomb interaction for the dimer units [10]. Thus, the 2-D is enlarged toward $|t_{a1}| \sim 2t_b$, namely, $t_b \sim 0.4$; in fact $S_+(\pi, \pi)$ shows a maximum around this value for $V = 0$ (large t_b region is not shown). On the other hand, in the basis of the FCO state in the limit of large U and V , the charge localizes on every other site along the intra-chain a -axis, and on the nearest-neighbor sites along the b -axis (see Fig. 2 (d)); then the spin exchange coupling between these sites for the former is given by $J_a \sim -4t_{a1}^2 t_{a2}^2 / (9UV^2)$ from the forth-order perturbation whose spin-exchange process is shown in Fig. 2 (d) [29], while for the latter $J_b \sim -4t_b^2/U$ from the second-order perturbation. Although t_b is small compared to t_{a1} and t_{a2} , J_b can become the same order compared to J_a due to the effect of V . Then the 2-D in the magnetic state increases

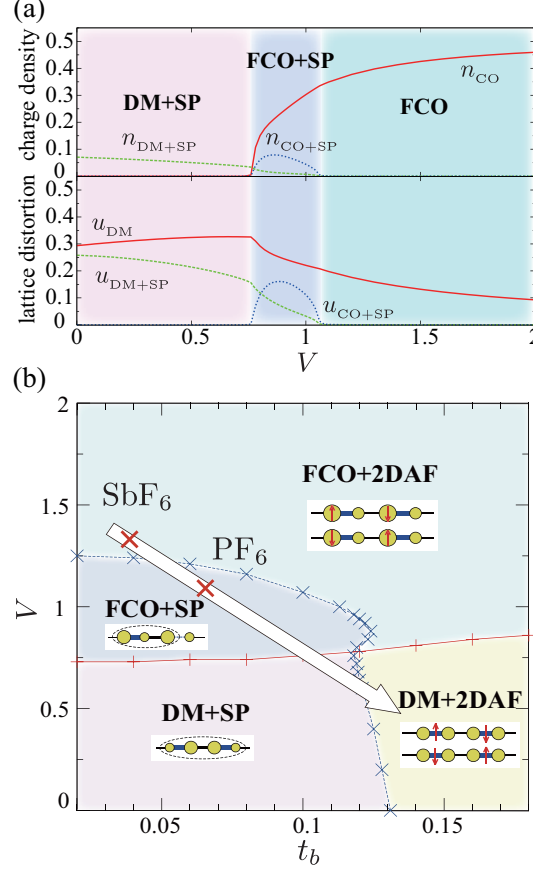


FIG. 3: (Color Online) (a) V -dependence of the order parameters in the charge densities and lattice distortions for $U = 4$, $t_b = 0.1$, $K_1 = 0.8$, and $K_2 = 1$. (b) Ground state phase diagram on (t_b, V) plane for $U = 4$, $K_1 = 0.8$, and $K_2 = 1$. “2DAF” stands for the enhanced two-dimensional AF correlation while the other abbreviations (see text) represents ordered phases. The proposed trajectory for the pressure axis in the phase diagram Fig. 1 is shown by the arrow.

and the AF state is induced.

It is known that electron-lattice couplings invoke the SP transition and various types of phase transitions with lattice modulations within one-dimensional models [17, 18, 30]. Here we investigate such effects in our quasi-one dimensional system by considering both Peierls- and Holstein-type electron-lattice interactions coupled to the EHM, given in addition to eq. (1) as

$$\mathcal{H}_P = - \sum_{\langle ij \rangle_a, \sigma} t_{ij} u_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + \frac{K_1}{2} \sum_{\langle ij \rangle_a} u_{ij}^2, \quad (2)$$

$$\mathcal{H}_H = - \sum_i v_i n_i + \frac{K_2}{2} \sum_i v_i^2, \quad (3)$$

where u_{ij} and v_i are the renormalized lattice distortions treated here as classical values and the corresponding spring constants are given by K_1 and K_2 , respectively. The Peierls distortions are treated along the a axis (written as $\langle ij \rangle_a$ pairs in eq. (2)), namely only intra-chain couplings are considered, to account for the one-dimensional quantum effects. Using the Hellman-Feynman theorem under the constraint $\sum_{\langle ij \rangle_a} u_{ij} = 0$, we can obtain u_{ij} and v_i ($= \langle n_i \rangle / K_2$) self-consistently using the ground state expectation values for bond operators and charge densities [17, 18, 30]. In the following we show results for an 8×2 site-cluster [31] at $K_1 = 0.8$ and $K_2 = 1$, under the anti-periodic and periodic boundary conditions along a - and b -axis, respectively. From the four-lattice periodicity modulations along the a axis, we can define order parameters following Ref. [17] as, for the FCO state: n_{CO} , for the coexistence of FCO and SP tetramerization (FCO+SP): $\{u_{CO+SP}, n_{CO+SP}\}$ and for the SP state without FCO (DM+SP): $\{u_{DM+SP}, n_{DM+SP}\}$ [32] (see Fig. 3 (b) for schematic representations). Due to intrinsic dimerization (t_{a1}, t_{a2}), two-fold lattice distortion u_{DM} always exists.

Figure 3 (a) shows the results for $t_b = 0.1$ (same as Figs. 2 (a) and (b)), as a function of V . As V increases, first a

phase transition occurs as DM+SP \rightarrow FCO+SP due to the effect of V [17], and then to the FCO state without SP tetramerization; the SP state becomes unstable by the development of the two-dimensional AF correlation controlled by the FCO that we have seen above. The ground state phase diagram on the (t_b, V) plane is shown in Fig. 3 (b). The two kinds of SP states are suppressed with increasing t_b , due to the increase in the inter-chain spin exchange, while, as we have seen in Fig. 3 (a), V also diminishes the SP states. We confirm that both $S_{\pm}(\mathbf{q})$ have sharp peaks at $\mathbf{q} = (\pm\pi, \pm\pi)$ in FCO state, while only $S_{+}(\mathbf{q})$ has peaks at $\mathbf{q} = (\pm\pi, \pm\pi)$ in DM state: these tendencies are the same for the case without electron-phonon couplings shown in Fig. 2.

Based on the above results, we finally discuss our results in relation with the complex variation of phases in the phase diagram in Fig. 1. To establish a correspondence between t_b in our calculation in Fig. 3 and our estimations based on FPBC mentioned above, we need to divide the latter by two due to the 8×2 cluster having a “ladder” geometry; then for the PF_6 and SbF_6 salts, this gives $t_b = 0.065$ and $t_b = 0.040$. By considering the experimental ground states for the PF_6 salt (FCO+SP) and the SbF_6 salt (FCO+2DAF), we can deduce that they are positioned as indicated in Fig. 3 (b), where the SbF_6 salt has larger value of V . This is consistent with the fact that the SbF_6 salt has larger transfer integrals along the diagonal q_1 and q_2 bonds, namely, larger overlap between the molecular orbitals, which results in larger values of intersite Coulomb repulsions [33], V_{q_1} and V_{q_2} , favoring the FCO pattern. The smooth evolution of phases with applied P suggests that the system follows along the arrow in Fig. 3 (b). Specifically, with applied P , transfer integrals reflecting the overlap between the molecular orbitals are more sensitive compared to the inter-site Coulomb repulsions, which are approximately a function of inter-molecular distance [33]. Then, the variation of ground state with P is now given by FCO+2DAF (AF_2) \rightarrow FCO+SP (SP_2) \rightarrow DM+SP (SP_1) \rightarrow DM+2DAF (AF_1) states, which agrees with the variation in Fig. 1. As for the case of chemical P , namely, with the variation among different X other than PF_6 and SbF_6 , our work suggests that a careful reconsideration for each compound should be made how to allocate “ambient P ” positions, where the anisotropic parameters sensitively reflect the ground state; we leave them as a future problem. Our results indicate that the dimensional crossover in magnetic states is controlled by not only t_b but also V , inducing the FCO state is essential to understand the sequence of phase transitions in TMTTF salts. The apparently confusing cooperative behavior in the FCO and AF_2 states, is naturally understood based on our scenario.

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