

Theory of Coexisting Charge and Spin-Density Waves in (TMTTF)₂Br, (TMTSF)₂PF₆ and α -(BEDT-TTF)₂MHg(SCN)₄

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Recent experiments indicate that the spin-density waves (SDWs) in (TMTTF)₂Br, (TMTSF)₂PF₆ and α -(BEDT-TTF)₂MHg(SCN)₄ are highly unconventional and coexist with charge-density waves (CDWs). We present a microscopic theory of this unusual CDW-SDW coexistence. A complete understanding requires the explicit inclusion of strong Coulomb interactions, lattice discreteness, the anisotropic two-dimensional nature of the lattice, and the correct bandfilling within the starting Hamiltonian.

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Organic charge transfer solids (CTS) exhibit a bewildering array of exotic phases at low temperature, including superconductivity (SC), SDW, CDW, and bond-order wave (BOW) and (related) spin-Peierls (SP) phases. Among the intriguing parallels between organic and high temperature superconductors is the proximity of the SC phase to the SDW [1,2]. Given the enormous focus on understanding the “normal” state of high temperature superconductors, it seems clear that an analogous effort should be made to understand the “normal” state of organics that exhibit SC. The SC-SDW proximity then suggests that it is crucial to understand the precise nature of the SDW and the mechanism of its formation, as well as the roles played by dimensionality effects and strong Coulomb interactions [1,2]. Very recent experiments on several materials indicate that the SDWs in the organics are highly unconventional in nature [3,4,5,6,7,8,9], imposing strict requirements of any theory of the SDWs.

In this Letter, we present a unified theory of SDW formation in a large class of 2:1 cationic CTS. While we believe that our theory is general, we focus on the specific materials (TMTSF)₂PF₆, (TMTTF)₂Br and (BEDT-TTF)₂MHg(SCN)₄ (M = K, Rb, Tl), in which the unconventional nature of the SDW has been demonstrated recently. In the past, experiments by several groups have established that the low temperature insulating phases in (TMTSF)₂PF₆ [10] and (TMTTF)₂Br [11] are SDWs. Surprisingly, recent X-ray scattering experiments [3,4] have revealed features associated with CDW in both materials even for $T < T_{SDW}$. In (TMTTF)₂Br, the experiment finds signatures of even a $4k_F$ lattice displacive instability (k_F = Fermi wavevector), along with the more usual $2k_F$ charge instability *within* the SDW phase [3,4]. The status of the experiments in (BEDT-TTF)₂MHg(SCN)₄ is very similar: while early magnetic susceptibility [12] and μ sr [13] measurements provided clear evidence for a SDW, measurement of angle-dependent magnetoresistance oscillations [5,6,7,8] have engendered the view that the insulating phase here is a “mysterious” state that is a “SDW accompanied by CDW” or a “CDW accompanied by SDW” [12]. The

authors of a recent ¹³C-NMR study have concluded that the insulating state here is not a SDW at all, but is a CDW [9]. The authors, however, also state that they have “no idea which kind of CDW reconciles the susceptibility anisotropy ... and other magnetic properties.”

Coexistence of CDW-SDW *of the same periodicity* is outside the scope of standard theories of density waves in the organic CTS [14,15], which emphasize the nesting associated with the quasi-one dimensional (quasi-1d) Fermi surface of these materials. Although CDW, SDW and SP instabilities are possible within these theories, these instabilities occur in *nonoverlapping* parameter regions, making coexistence impossible. The microscopic theory we present here explains the puzzling CDW-SDW coexistence in a natural fashion. The attractive features of our theory include: (i) our Hamiltonian is the standard strongly correlated model for quasi-1d organic conductors [16], and although the manifestations are novel, no exotic interactions are necessary to generate them; (ii) the theory can explain the differences between structurally similar quasi-1d systems that exhibit the SP phase and quasi-2d systems that exhibit the SDW; and finally, (iii) the theory clarifies the limitations of single-particle nesting concepts [15] and of the theoretical bias that SDW exists only at or near the 1/2-filled band.

We posit that the Hamiltonian appropriate for the materials considered here is the quasi-2d extended Hubbard model,

$$H = H_0 + H_{ee} + H_{inter} \quad (1a)$$

$$H_0 = - \sum_{j,M,\sigma} [t - \alpha(\Delta_{j,M})] B_{j,j+1,M,M,\sigma} + \beta \sum_{j,M} v_{j,M} n_{j,M} + K_1/2 \sum_{j,M} (\Delta_{j,M})^2 + K_2/2 \sum_{j,M} v_{j,M}^2 \quad (1b)$$

$$H_{ee} = U \sum_{j,M} n_{j,M,\uparrow} n_{j,M,\downarrow} + V \sum_{i,M} n_{j,M} n_{j+1,M} \quad (1c)$$

$$H_{inter} = -t_{\perp} \sum_{j,M,\sigma} B_{j,j,M,M+1,\sigma} \quad (1d)$$

In the above, j is a site index while M is a chain index, $B_{j,k,L,M,\sigma} \equiv [c_{j,L,\sigma}^\dagger c_{k,M,\sigma} + h.c.]$, $\Delta_{j,M} = (u_{j,M} - u_{j+1,M})$, where $u_{j,M}$ is the displacement of the molecular site from its equilibrium position, and $v_{j,M}$ represents an intramolecular vibration. The total Hamiltonian describes coupled chains, with on-site Coulomb interaction U , intrachain nearest-neighbor Coulomb interaction V , and intra- and interchain nearest-neighbor hoppings $t_j = t - \alpha(u_{j,M} - u_{j+1,M})$ and t_\perp . For simplicity, we assume a rectangular lattice. We are interested in the realistic parameter regime $t_\perp \sim 0.1$, $V \sim 2|t|$, $U > 4|t|$.

A critical implicit parameter in the Hamiltonian of Eq. (1) is the bandfilling. Charge-transfer from the cations to the inorganic anions in the 2:1 CTS of interest leads to one hole per two organic molecules, i.e., a $1/4$ -filled band of holes. This is the bandfilling we consider. Based on the weak dimerization along the stack axis (observed even *above* the metal-insulator transition temperature T_{MI} [1,2]), it is commonly argued that 2:1 cationic CTS can be modeled as *effective* quasi-1d $1/2$ -filled band systems [14,15] with Fermi surface nesting. We show that although some aspects of the physics of the *strongly correlated* $1/4$ -filled band *can* be understood within the *weak coupling* effective $1/2$ -filled theory, others simply cannot. In particular, since the coexistence of CDW-SDW with the same periodicity is impossible within the $1/2$ -filled band [17], the recent observations [3,4,5,6,7,8,9] clearly preclude this scenario as a consistent description of the normal state of these CTS. We postpone further discussion of this issue until later, when we show that both from theoretical and experimental perspectives, the weak high temperature dimerization cannot lead to a modulation of t_j .

An intuitive understanding of the broken symmetry coexistence within Eq. (1) can be obtained in the 1d limit, $t_\perp = 0$. Since long-range SDW does not occur here, the relevant order parameters are the site charge density and the bond-order $B_{j,j+1,M,\sigma}$. Periodic modulations of the charge density lead to the CDW, and of the bond-order to the BOW. Previous work has established [18] that the periodic lattice distortion arising from the BOW has the form $u_j = u_0[r_2 \cos(2k_F j - \theta_2) + r_4 \cos(4k_F j - \theta_4)]$, where r_2 and r_4 are the relative weights of the $2k_F$ and $4k_F$ components, and θ_2 and θ_4 are the corresponding phase angles [18]. In contrast, the CDW can have *either* the $2k_F$ *or* the $4k_F$ modulation *but not both*, so $n_j = 1/2 + n_0(\cos Qj - \phi)$, where $Q = 2k_F$ or $4k_F$ [18,19]. For comparison with what follows, we sketch in Figs. 1(a) and (b) the familiar BOW and SDW configurations for the $1/2$ -filled band. A crucial feature of non- $1/2$ -filled commensurate bands is the *symbiotic* coexistence between the BOW and CDW [18,19]; as shown in these references, this coexistence also enables one to understand the general case from the $\beta = 0$ limit, which we henceforth adopt. Importantly, the $1/4$ -filled band is

unique among the non- $1/2$ -filled bands in that Coulomb interactions can drive BOW-CDWs that are *different* from that driven by electron-phonon interaction. For instance, as the Hubbard U is increased from zero, the phase angles (θ_2, ϕ) of the $2k_F$ BOW-CDW switch from $(0, \pi/4)$ to $(\pi/4, 0)$ [18]. We show the uncorrelated and correlated $2k_F$ BOW-CDWs in Figs 1(c) and (d), respectively. For nonzero $V < V_c$ (where $V_c = 2|t|$ for $U \rightarrow \infty$, and is larger for finite U) the absolute ground state acquires a $4k_F$ BOW character [$r_4 \neq 0$, $\theta_4 = 0$, see Fig. 1(e)], but the CDW continues to have periodicity $2k_F$ [18,20]. Our numerical results will establish that the BOW-CDWs of Figs. 1(d) and (e) can coexist with the particular SDW shown in Fig. 1(f), consistent with the experimental data.

We begin our numerical analysis in the 1d limit. Since a true long-range SDW cannot occur here, we incorporate an additional (external field-like) term $H_{SDW} = -\sum_j \epsilon [n_{j,\uparrow} \cos(2k_F j) + n_{j,\downarrow} \cos(2k_F j + \psi)]$ and consider the ground state of $H + H_{SDW}$. H_{SDW} imposes a SDW in the $1/2$ -filled band for $\psi = \pi$ and the SDW of Fig. 1(f) in the $1/4$ -filled band for $\psi = \pi/2$, with the amplitude of the SDW increasing with ϵ . We examine the BOW-SDW coexistence using exact finite size calculations. Specifically, we calculate the exact electronic ground state energies $E(\alpha u_0, \epsilon)$ of finite periodic rings as functions of ϵ , where αu_0 is a rigid bond modulation parameter. The quantity $\Delta E(\alpha u_0, \epsilon) = E(\alpha u_0 = 0, \epsilon) - E(\alpha u_0 \neq 0, \epsilon)$ is a direct measure of the energy gained on bond distortion. For the $1/4$ -filled band, it is also necessary to specify r_2/r_4 . While we have confirmed that our results are valid for many different r_2 and r_4 , we show in the following the specific cases of $r_2 = 0$ ($2k_F$ BOW-CDW only) and $r_2 = r_4$ (both $2k_F$ and $4k_F$, contributing equally).

In Fig. 2 we show the behavior of $\Delta E(\alpha u_0, \epsilon)$ for a $1/2$ -filled band of 10 sites and a $1/4$ -filled band of 16 sites, for $U = 6$, $V = 1$. Because of the larger energy gain the $1/2$ -filled band, the nonzero values of αu_0 are 0.05 (in units of $|t|$) in the $1/2$ -filled case and 0.1 in the $1/4$ -filled case, respectively. $\Delta E(\alpha u_0, \epsilon)$ decreases rapidly with ϵ in the $1/2$ -filled band, in agreement with the known result that the SDW and the BOW are mutually exclusive here [17]. In contrast, we find that $\Delta E(\alpha u_0, \epsilon)$ *increases* with ϵ in the $1/4$ -filled band for both the cases studied, indicating a *cooperative* interaction between the BOW and the SDW. Since the BOWs we have studied coexist with the correlated $2k_F$ CDW, the ground state of $H + H_{SDW}$ is an admixture of $(2k_F + 4k_F)$ -BOW, $2k_F$ CDW and $2k_F$ SDW for the $1/4$ -filled band. We have further determined that the bond orders for nonzero ϵ show a modulation of the type shown in Fig. 1(e) for the $1/4$ -filled band *even for zero lattice distortion* ($u_0 = 0$), indicating a tendency for *spontaneous* BOW distortion in the presence of the SDW.

For $H_{SDW} = 0$ a true SDW can occur only for $t_\perp \neq 0$. We have therefore performed calculations of spin-spin

correlations, site charge densities and bond-orders in the ground state of H alone for coupled chains. These calculations were done using the constrained path quantum Monte Carlo (CPMC) approach [21]. In CPMC a constraining wavefunction (in this case the free-electron solution) is used to approximate nodal boundaries and avoid the sign problem present in 2D calculations. We expect that sign problems are less severe for the 1/4 filled band and for the small t_{\perp} we have used. All calculations were checked against exact results for a 4×4 lattice. The CPMC calculations are for four coupled chains of length twelve sites each, with the same values of U , V , αu_0 as in 1d and $t_{\perp} = 0.1$. The 12×4 lattice is taken to be periodic along both directions. We incorporate a phase difference of π between the BOWs on neighboring chains, based on calculations (a) in the noninteracting limit, and (b) for the 4×4 lattice in the interacting cases, that indicate that this particular phase difference gives the lowest total energy [22]. A SDW coexisting with the BOW-CDW requires now antiferromagnetic *interchain* spin-spin correlations. In Fig. 3 we show the spin-spin correlations between consecutive sites 2,3,4,5 on the first chain and sites 1–12 on the second chain for the case $r_2 = 0$ only. As seen from the figure, (a) The $2k_F$ bond distortion leads to antiferromagnetic interchain spin-spin correlations, (b) there is a simultaneous intrachain antiferromagnetic spin-spin correlation, - the spin densities on sites 3 and 4 are opposite to those on sites 2 and 5, and (c) the magnitude of the interchain spin-spin correlation for a given site on the second chain does not simply decrease with the separation from the site on the first chain, but is also determined by the charge density on the particular site on the second chain. This is a signature of long range SDW within the distorted lattice. With our choice of t_{\perp} , the CPMC technique does not allow us to obtain sufficiently accurate spin-spin correlations between sites two chains apart. However, with a slightly larger t_{\perp} (0.2), these more distant interchain spin-spin correlations are also in agreement with antiferromagnetic interchain correlations. Finally, as in 1d, we have also performed the calculations for $r_2 = r_4$ and find that the interaction between the BOW-CDW and the SDW remains cooperative, decreasing (increasing) αu_0 decreases (increases) the strength of the interchain antiferromagnetic correlations [22].

In Fig. 4 we sketch the ground state broken symmetry that emerges from the CPMC results: two adjacent sites with unequal charge but parallel spins are surrounded by other such pairs with opposite spins. Viewing the pairs of sites as a single effective sites, this appears similar to the SDW of the effective 1/2-filled band scenario [14,15], but there is the critical distinction that there are different charge and spin densities on the individual molecules within the pairs, and this internal structure will show up in experiments. In their X-ray diffraction experiment, Pouget and Ravy find strong evidence only for the $2k_F$ CDW in the so-called SDW phase of $(\text{TMTSF})_2\text{PF}_6$, and

perhaps both the CDW as well as a $2k_F$ or $4k_F$ BOW in the SDW phase of $(\text{TMTTF})_2\text{Br}$ [3,4]. Our results indicate that the CDW-SDW necessarily drives a modulation of the t_j . Whether or not an *observable* lattice distortion accompanies this merely depends on the strength of α .

We now revisit the issue of the bandfilling. The parameters in Eq.(1) should be derived from the overall Hamiltonian describing both the organic cations and the inorganic anions. The crystal structures of $(\text{TMTTF})_2\text{X}$ and $(\text{TMTSF})_2\text{X}$ indicate that the anions face the “stronger bonds” between consecutive organic molecules [3]. The anions therefore introduce a nonnegligible “anionic potential,” the leading term in which takes the form $\nu[c_{j,M,\sigma}^{\dagger}c_{j+1,M,\sigma} + h.c.]$, where ν ($=1$) is the number of (extra) electrons on the anion. This interaction modifies the intrachain t_j , *decreasing* the effective hopping integral between the particular pair of organic molecules, equalizing consecutive t_j , and stabilizing a metallic phase. Very similar conclusions have been reached by Fritsch and Ducasse [23], who actually demonstrated the decrease in the hopping integral in question by taking the anion potential into account. Note that equal effective hopping integrals at $T > T_{MI}$ is *essential* for explaining the high temperature metallic conductivity if Coulomb correlations are strong: any dimerization of the hopping integrals leading to an effective 1/2 filled upper subband should have, in the presence of a nonzero U , opened a Mott-Hubbard gap, leading to an insulator.

In conclusion, we have shown that the “normal” ground state of the 2:1 cationic CTS is a complex mixture of density waves. In particular, we have discovered a *cooperative* interaction among the CDW-BOW and the SDW, which emerges naturally when lattice discreteness, Coulomb interactions and actual bandfilling are taken properly into account. Three final comments are in order. First, in the appropriate small t_{\perp} regime, our theory correctly describes the existence of highly 1d systems (such as $(\text{TMTTF})_2\text{X}$, where $\text{X} \neq \text{Br}$) which exhibit only SP/BOW and CDW coexistence (*i.e.*, no long-range SDW) [22]. Second, although lack of space precludes detailed consideration of the important magnetic field-induced SDW phenomena [24], the discussion surrounding Fig. 4 suggests that key features of the previous approaches [15] remain true within the 1/4-filled, strongly correlated framework. In addition, however, interesting effects due to unequal charge and spin densities on the paired sites may emerge. Third, since SC appears in these CTS only upon the melting of the SDW, it seems that any theory of organic SC should take into consideration the important roles of bandfilling and strong Coulomb interactions that are established by the present work.

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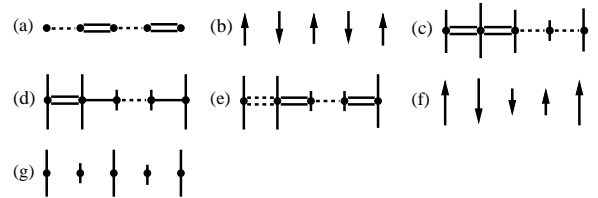


FIG. 1. Schematics of the 1d (a) 1/2-filled BOW, (b) 1/2-filled SDW, (c) 1/4-filled uncorrelated $2k_F$ BOW-CDW, (d) 1/4-filled correlated $2k_F$ BOW-CDW (the $4k_F$ BOW is the same as (a)), (e) 1/4-filled BOW-CDW that is a superposition of $4k_F$ (Fig. 1(a)) and $2k_F$ (Fig. 1(d)) periodicities, and that occurs for nonzero $V < V_c$, (f) 1/4-filled $2k_F$ SDW investigated here, and (g) the $4k_F$ site-diagonal CDW that occurs only for $V > V_c$. The double (dotted) bonds are strong (weak), the single bond is of intermediate strength, and the double dotted bond in (e) is a weak bond that is stronger than the single dotted bond. The heights of the vertical bars (arrows) on sites give their relative charge (spin) densities.

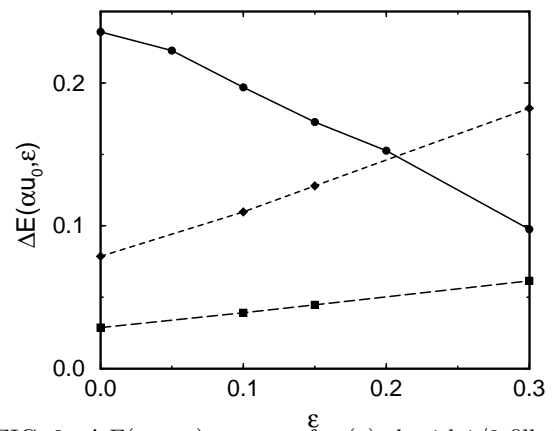


FIG. 2. $\Delta E(\alpha u_0, \epsilon)$ versus ϵ for (a) the 1d 1/2-filled band (solid line), (b) the 1d 1/4-filled band with the bond distortion of Fig. 1(d) (long dashed line), and (c) the 1d 1/4-filled band with the bond distortion of Fig. 1(e) (short dashed line).

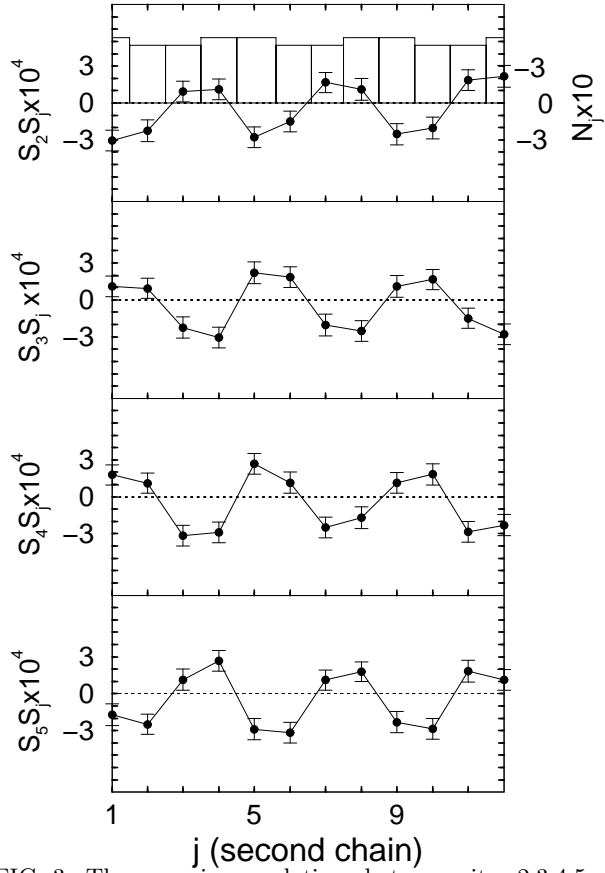


FIG. 3. The z-z spin correlations between sites 2,3,4,5 on the first chain and sites 1 – 12 on the second chain (see text). The bars in the top panel show the charge densities N_j on the sites of the second chain.

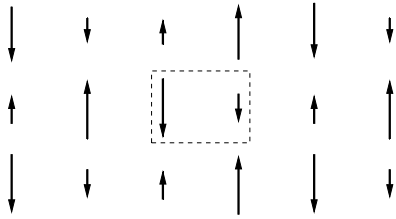


FIG. 4. Schematic of the quasi-2d SDW in the correlated 1/4-filled band. The heights of the arrows have the same meaning as in Fig. 1(f).