Theory of Coexisting Charge and Spin-Density Waves in $(\mathrm{TMTTF})_2\mathrm{Br}$, $(\mathrm{TMTSF})_2\mathrm{PF}_6$, and α-$(\mathrm{BEDT\text{-}TTF})_2M\mathrm{Hg(SCN)}_4$

S. Mazumdar and S. Ramasesha*
Department of Physics, University of Arizona, Tucson, Arizona 85721

R. Torsten Clay and David K. Campbell
Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

(Received 10 March 1998)

Recent experiments indicate that the spin-density waves (SDWs) in $(\mathrm{TMTTF})_2\mathrm{Br}$, $(\mathrm{TMTSF})_2\mathrm{PF}_6$, and α-$(\mathrm{BEDT\text{-}TTF})_2M\mathrm{Hg(SCN)}_4$ 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 band filling within the starting Hamiltonian. [S0031-9007(99)08498-7]

PACS numbers: 71.30.+h, 71.45.Lr, 74.70.Kn, 75.30.Fv

Recent experiments have indicated that the spin-density waves (SDWs) in several organic charge–transfer solids (CTS) are highly unconventional and coexist with charge-density waves (CDWs) [1–7]. In this Letter, we present a unified theory that explains this behavior in a large class of 2:1 cationic CTS. While our theory is general, we focus on $(\mathrm{TMTSF})_2\mathrm{PF}_6$, $(\mathrm{TMTTF})_2\mathrm{Br}$ and $(\mathrm{BEDT\text{-}TTF})_2M\mathrm{Hg(SCN)}_4$ ($M =$ K, Rb, TI). Experiments by several groups have established that the low-temperature insulating phases in $(\mathrm{TMTSF})_2\mathrm{PF}_6$ [8] and $(\mathrm{TMTTF})_2\mathrm{Br}$ [9] are SDWs. Surprisingly, recent x-ray scattering experiments [1,2] have revealed features associated with CDW in both materials, even for $T < T_{\mathrm{SDW}}$. $(\mathrm{TMTTF})_2\mathrm{Br}$ exhibits signatures of a $4k_F$ lattice displacive instability (k_F is the Fermi wave vector), along with the more usual $2k_F$ charge instability *within* the SDW phase [1,2]. Similarly, while early magnetic susceptibility [10] and Muon Spin rotation (μsr) [11] measurements in $(\mathrm{BEDT\text{-}TTF})_2M\mathrm{Hg(SCN)}_4$ established the SDW, measurements of angle-dependent magnetoresistance oscillations [3–6] 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” [10]. The authors of a recent ^{13}C-NMR study have concluded that the insulating state here is actually a CDW [7], but they have “no idea which kind of CDW reconciles the susceptibility anisotropy … and other magnetic properties.”

The issue of the proper bandfilling in the 2:1 CTS has been controversial, and bandfilling of both 1/2 and 1/4 have been suggested. For non-1/2-filled bands the continuum renormalization group (“g-ology”) calculations do predict coexisting $2k_F$ CDW-SDW [12,13]. However, Monte Carlo calculations for the 1/4-filled band within an extended Hubbard model failed to find this coexistence for realistic parameters at relevant temperatures [14]. Many recent theories of the 2:1 CTS assume a weak-coupling 1/2-filled band description [15,16]. Within these effective 1/2-filled band theories, the CDW, SDW, and spin-Peierls (SP) instabilities occur within *nonoverlapping* parameter regions. The microscopic theory we present here explains the puzzling CDW-SDW coexistence in a natural fashion. The attractive features of our theory include the following: (i) Our Hamiltonian is a standard strongly correlated model for quasi-1D organic conductors [17], and although the manifestations are novel, no exotic interactions are necessary to generate them; (ii) the theory can explain the differences between quasi-1D systems that exhibit the SP phase and quasi-2D systems that exhibit the SDW; finally, (iii) the theory confirms the importance of distinguishing between the bond-order wave (an on-bond CDW) and the (on-site) CDW, and establishes the correct phase relationships among these and the SDW. Determination of the relative phases is shown to be crucial for understanding the experiments.

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

$$H = H_0 + H_{ee} + H_{\mathrm{inter}}\,, \tag{1a}$$

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

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

$$H_{\mathrm{inter}} = -t_\perp \sum_{j,M,\sigma} B_{j,j,M,M+1,\sigma}\,, \tag{1d}$$

In the above, j is a site index while M is a chain index, $B_{j,k,L,M,\sigma} \equiv [c_{j,L,\sigma}^\dagger c_{k,M,\sigma} + \mathrm{H.c.}]$, $\Delta_{j,M} = (u_{j,M} - u_{j+1,M})$, where $u_{j,M}$ is the displacement of the molecular site from its equlibrium 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 intrachain 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 $t_\perp \sim 0.1t$, $V \sim 2|t|$, $U > 4|t|$.

The composition of the 2:1 CTS suggests one hole per two organic molecules, i.e., a 1/4-filled band of holes. Based on the weak dimerization along the stack axis (observed even *above* the metal-insulator transition temperature T_{MI} [1]), it is sometimes argued that 2:1 cationic CTS can be modeled as *effective* quasi-1D 1/2-filled band systems [15,16] with Fermi surface nesting. Our results 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* in the 1/2-filled band [18], the recent observations [1–7] clearly preclude this description. A qualitative understanding of the failure of the 1/2–filled band scenario can be obtained from the following consideration. The parameters in Eqs. (1) should be determined from an overall Hamiltonian describing *both* the organic cations and the inorganic anions. The crystal structures of $(\mathrm{TMTTF})_2X$ and $(\mathrm{TMTSF})_2X$ indicate that the anions face the "stronger bonds" between consecutive molecules [1]. The anions therefore introduce a nonnegligible "anionic potential," the leading term in which takes the form $\nu[c^\dagger_{j,m,\sigma}c_{j+1,m,\sigma} + \mathrm{H.c.}]$, where $\nu(= 1)$ is the number of (extra) electrons on the anion. This interaction modifies the intrachain t_j, *decreasing* the effective hopping integral between the pair of organic molecules that are relatively close, equalizing consecutive t_j, and stabilizing a metallic phase. Thus the very small observed dimerization at high temperature is akin to a steric effect, rather than a signature of true difference in the hopping integrals. Very similar conclusions have been reached from quantum chemical calculations [19].

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 $\sum_\sigma B_{j,j+1,M,M,\sigma}$. Previous work has established [20] that the lattice distortion arising from the periodic modulation of the bond order, the bond–order wave (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 [20]. 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 $4k_F$ [20,21]. For comparison with what follows, we sketch in Figs. 1(a) and 1(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 [20,21] that enables one to understand the general case from the $\beta = 0$ limit, which we henceforth adopt. Importantly, as the Hubbard U is increased from zero, the phase angles (θ_2, ϕ) of the $2k_F$ BOW-CDW switch from $(0, \pi/2)$ to $(\pi/4, \pi/4)$ [20]. We show the uncorrelated and correlated $2k_F$ BOW-CDWs in Figs. 1(c) and 1(d), respectively. For nonzero $V < V_c$ (where $V_c = 2|t|$ for $U \to \infty$, 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 $2k_F$ [20,22]. Our numerical results will establish that the BOW-CDWs of Figs. 1(d) and 1(e) can coexist with the particular SDW shown in Fig. 1(f).

We begin our quantitative studies in the 1D limit. Since a true long-range SDW cannot occur here, we incorporate an additional (external fieldlike) term $H_{\mathrm{SDW}} = -\sum_j \epsilon[n_{j,\uparrow}\cos(2k_F j) + n_{j,\downarrow}\cos(2k_F j + \psi)]$ and consider $H + H_{\mathrm{SDW}}$. 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 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 our results for many different r_2 and r_4, we discuss only $r_4 = 0$ and $r_4 = r_2$. In Fig. 2 we show the behavior of $\Delta E(\alpha u_0, \epsilon)$ for a 1/2-filled band of 10 sites ($\alpha u_0 = 0.05$) and a 1/4-filled band of 16 sites ($\alpha u_0 = 0.1$), for $U = 6$, $V = 1$. $\Delta E(\alpha u_0, \epsilon)$ 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 [18]. In contrast, we find that $\Delta E(\alpha u_0, \epsilon)$ *increases* with ϵ in the 1/4-filled band for both cases studied, indicating a *cooperative* interaction between the BOW and the SDW. Since the BOWs we have studied

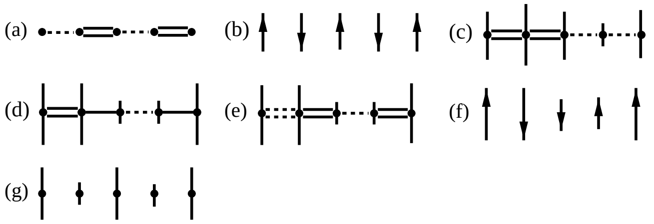

FIG. 1. Schematics of the 1D (a) 1/2-filled BOW; (b) 1/2-filled SDW; (c) 1/4-filled uncorrelated $2k_F$ BOW-CDW; (d) 1/4-filled correlated $2k_F$ BOW-CDW [the $4k_F$ BOW is the same as (a)]; (e) 1/4-filled BOW-CDW that is a superposition of $4k_F$ and $2k_F$ periodicities, and occurs for nonzero $V < V_c$; (f) 1/4-filled $2k_F$ SDW investigated here; (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 sizes of the vertical bars (arrows) on sites give their relative charge (spin) densities.

coexist with the correlated $2k_F$ CDW, the ground state of $H + H_{\rm SDW}$ is an admixture of $(2k_F + 4k_F)$-BOW, $2k_F$ CDW, and $2k_F$ SDW for the 1/4-filled band. In order to confirm that the cooperative effect is not due to finite size, we have repeated our calculations with *zero lattice distortion*; the calculated bond orders for nonzero ϵ show a modulation of the type shown in Fig. 1(e), indicating a tendency for *spontaneous* BOW distortion in the presence of the SDW.

For 2D coupled chains, we have performed calculations of spin-spin correlations, site charge densities, and bond orders in the ground state of H alone, using the constrained path quantum Monte Carlo (CPMC) approach [23] to minimize the fermion sign problem in 2D. All calculations were checked against exact results for a 4 × 4 lattice. The CPMC calculations are for 4 coupled chains of length 12 sites each, periodic along both directions, with the same values of U, V, αu_0 as in 1D and $t_\perp = 0.1t$. 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, which indicate that this particular phase difference gives the lowest total energy. In Fig. 3 we show the spin-spin correlations between consecutive sites 2, 3, 4, and 5 on the first chain and sites 1–12 on the second chain for the case $r_4 = 0$ only. As seen from the figure, (a) the $2k_F$ bond distortion leads to antiferromagnetic *inter*chain spin-spin correlations, (b) there is a simultaneous *intra*chain 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 $t_\perp = 0.1t$, the CPMC technique does not yield sufficiently accurate spin-spin correlations between sites two chains apart. However, with a slightly larger $t_\perp$ $(0.2t)$, these more distant interchain spin-spin correlations are also in agreement with antiferromagnetic interchain correlations. As in 1D, we have confirmed that the interaction between the BOW-CDW and the SDW is cooperative also for $r_2 = r_4$: Decreasing (increasing)

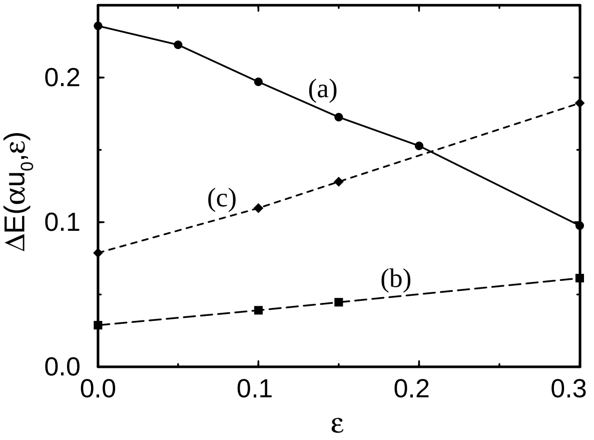

FIG. 2. $\Delta E(\alpha u_0, \epsilon)$ versus ϵ for (a) the 1D 1/2-filled band (solid line), (b) the 1D 1/4-filled band with the bond distortion of Fig. 1(d) (long dashed line), and (c) the 1D 1/4-filled band with the bond distortion of Fig. 1(e) (short dashed line).

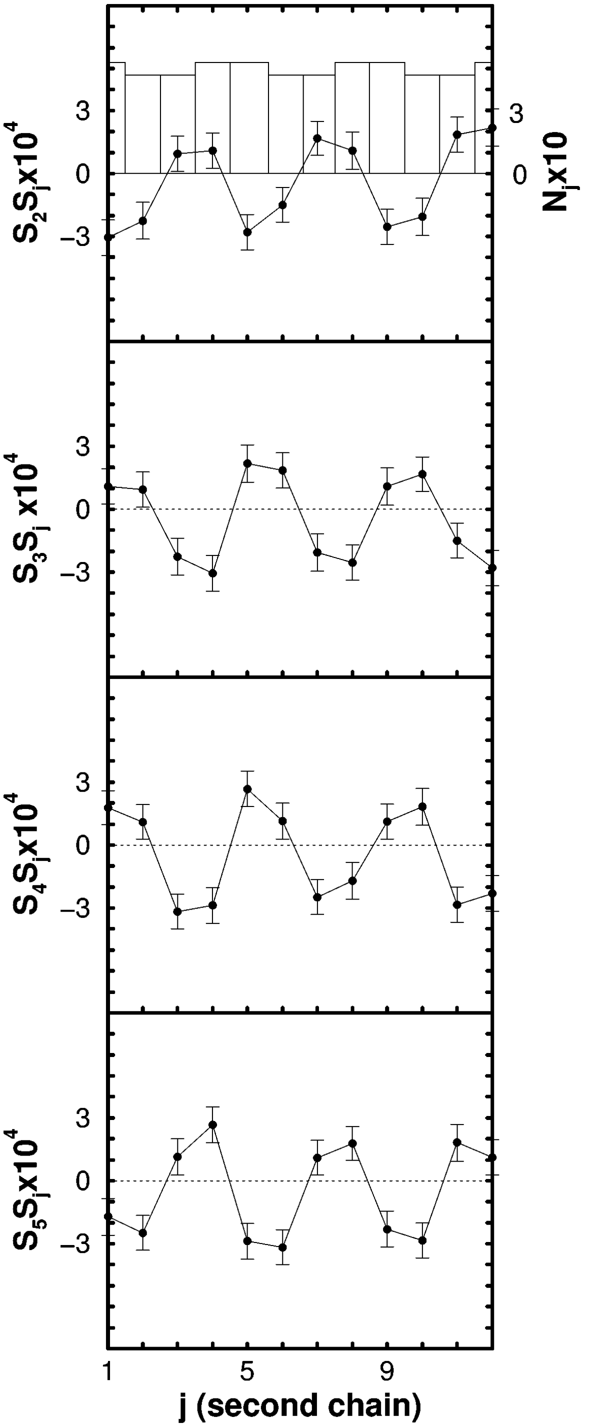

FIG. 3. The z-z spin correlations between sites 2, 3, 4, and 5 on the first chain and sites 1–12 on the second chain (see text). The bars on the top of the figure show the charge densities N_j on the sites of the second chain.

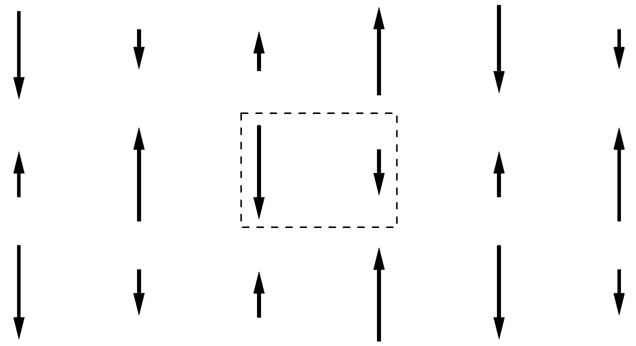

FIG. 4. Schematic of the quasi-2D SDW in the correlated 1/4-filled band. The sizes of the arrows have the same meaning as in Fig. 1(f).

αu_0 decreases (increases) the strength of the interchain antiferromagnetic correlations.

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 single effective sites, this appears similar to the SDW of the effective 1/2-filled band scenario [15,16], but the critical distinction is that there are different charge and spin densities on the individual molecules within the pairs. 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 $(\mathrm{TMTSF})_2\mathrm{PF}_6$, and perhaps both the CDW as well as a $2k_F$ or $4k_F$ BOW in the SDW phase of $(\mathrm{TMTTF})_2\mathrm{Br}$ [1,2]. Our results indicate that the CDW-SDW necessarily drives a modulation of the t_j. Whether or not an *observable* lattice distortion accompanies this depends on the strength of α.

In conclusion, we have shown that there exists a *cooperative* interaction among the CDW-BOW and the SDW in the "normal" state of cationic 2:1 CTS that 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 $(\mathrm{TMTTF})_2X$, where $X \neq \mathrm{Br}$] which exhibit only SP/BOW and CDW coexistence (i.e., no long-range SDW). 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 [16] 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.

S. M. acknowledges valuable discussions with L. Ducasse. D. K. C. acknowledges support from NSF-DMR-97-12765. R. T. C. acknowledges support of a NSF GRT Fellowship. The numerical calculations were done in part at the NCSA.

Note added.—After submission of this article, we learned of the work of Kobayashi *et al.* [25], who also posited, based on the results of [20], that the $(\uparrow, \downarrow, {\scriptstyle\downarrow}, {\scriptstyle\uparrow})$ configuration (Fig. 4) could explain the CDW/SDW coexistence in these materials. Although our calculations confirm their supposition, we believe that their use of the Hartree-Fock approximation and strictly 1D models renders their microscopic mechanisms likely incorrect and the parameter values in their models unphysical. In particular, it is not possible to explain both the SP phase in the 1D $(\mathrm{TMTTF})_2X$ ($X \neq \mathrm{Br}$) and the SDW in the weakly 2D $(\mathrm{TMTTF})_2\mathrm{Br}$ and $(\mathrm{TMTSF})_2X$ within their approach.

---

*Permanent address: Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India.

[1] J. P. Pouget and S. Ravy, J. Phys. I **6**, 1501 (1996).

[2] J. P. Pouget and S. Ravy, Synth. Met. **85**, 1523 (1997).

[3] T. Sasaki and N. Toyota, Phys. Rev. B **49**, 10 120 (1994).

[4] M. V. Kartsovnik *et al.,* Synth. Met. **70**, 811 (1995).

[5] Y. Iye *et al.,* J. Phys. Soc. Jpn. **63**, 674 (1994).

[6] J. Caulfield *et al.,* J. Phys. Condens. Matter **6**, L155 (1994).

[7] K. Miyagawa, A. Kawamoto, and K. Kanoda, Phys. Rev. B **56**, R8487 (1997).

[8] P. Wzietek *et al.,* J. Phys. I **3**, 171 (1993), and references therein.

[9] S. S. P. Parkin *et al.,* J. Phys. Colloq. **44**, C-3, 1, 111 (1983).

[10] T. Sasaki and N. Toyota, Synth. Met. **70**, 849 (1995).

[11] F. L. Pratt, T. Sasaki, N. Toyota, and K. Nagamine, Phys. Rev. Lett. **74**, 3892 (1995).

[12] J. Solyom, Adv. Phys. **28**, 201 (1979).

[13] V. J. Emery in *Highly Conducting One-Dimensional Solids,* edited by J. T. Devreese *et al.* (Plenum, New York, 1979).

[14] J. E. Hirsch and D. J. Scalapino, Phys. Rev. B **27**, 7169 (1983).

[15] C. Bourbonnais, Synth. Met. **84**, 19 (1997), and references therein.

[16] L. P. Gor'kov, J. Phys. I **6**, 1697 (1996), and references therein.

[17] S. Mazumdar and A. N. Bloch, Phys. Rev. Lett. **50**, 207 (1983).

[18] D. Baeriswyl, D. K. Campbell, and S. Mazumdar, in *Conjugated Conducting Polymers,* edited by H. Kiess (Springer-Verlag, Berlin, 1992).

[19] A. Fritsch and L. Ducasse, J. Phys. I, **1**, 855 (1991).

[20] K. C. Ung, S. Mazumdar, and D. Toussaint, Phys. Rev. Lett. **73**, 2603 (1994).

[21] K. C. Ung, S. Mazumdar, and D. K. Campbell, Solid State Commun., **85**, 917 (1993).

[22] For $V > V_c$, the ground state is a $4k_F$ CDW [Fig. 1(g)]. This state has not been observed in this class of CTS.

[23] S. Zhang, J. Carlson, and J. E. Gubernatis, Phys. Rev. B **55**, 7464 (1997).

[24] P. Chaikin, J. Phys. I **6**, 1875 (1996).

[25] N. Kobayashi *et al.,* J. Phys. Soc. Jpn. **66**, 3356 (1997); *ibid.* **67**, 1098 (1998).