Coexistence of charge-density waves, bond-order waves, and spin-density waves in quasi-one-dimensional charge-transfer salts

J. Riera[1,2] and D. Poilblanc[1]

[1]*Instituto de Física Rosario, Consejo Nacional de Investigaciones Científicas y Técnicas, y Departamento de Física,
Universidad Nacional de Rosario, Avenida Pellegrini 250, 2000-Rosario, Argentina*

[2]*Laboratoire de Physique Quantique & UMR–CNRS 5626, Université Paul Sabatier, F-31062 Toulouse, France*

Charge, spin, as well as lattice instabilities are investigated in isolated or weakly coupled chains of correlated electrons at quarter filling. Our analysis is based on extended Hubbard models including nearest-neighbor repulsion and Peierls coupling to lattice degrees of freedom. While treating the electronic quantum fluctuations exactly, the lattice structure is optimized self-consistently. We show that, generically, isolated chains undergo instabilities towards coexisting charge-density waves (CDW's) and bond order waves (BOW's) insulating spin-gapped phases. The spin and charge gaps of the BOW-CDW phase are computed. In the presence of an interchain magnetic coupling spin-density waves phases including a CDW or a BOW component are also found. Our results are discussed in the context of insulating charge-transfer salts.

Quasi-one-dimensional correlated electrons systems at quarter filling show fascinating physical properties. A widely studied class of such materials are the so-called organic charge transfer salts like the Bechgaard salts $(TMTSF)_2X$ or their sulfur analogs $(TMTTF)_2X$ $(X=PF_6, AsF_6)$.[1–3] These systems, which consist of stacks of organics molecules forming weakly coupled one-dimensional (1D) chains, exhibit, at low temperature, a large variety of exotic phases such as triplet superconducting,[4] spin-density wave (SDW), charge-density wave (CDW), and spin-Peierls (SP) phases.[5] The compounds of the sulfur $(TMTTF)_2X$ series show strong charge localization at rather high temperature T_ρ (as signaled, e.g., by transport measurements) as well as a weak (to moderate) dimerization along the stacks.[1,2] The insulating behavior observed in this regime has been interpreted as 1D CDW fluctuations[3] or using a Hubbard chain Hamiltonian with an explicit dimerization.[6] At a significantly lower temperature T_{SP} (typically $T_{SP} \sim 15$ K) an SP transition occurs together with a tetramerization along the chains.[1,5] In this system the interplay between charge ordering and lattice instability is poorly understood. In particular whether the tetramerization (connected to the spin gap) is occurring simultaneously with a CDW transition is still controversial. So far the existing theory of the SP phase[7] do not consider the possibility of a coexisting $2k_F$ CDW. Interestingly enough, CDW fluctuations were seen by x-ray diffuse scattering[8] in the SDW phase of the (more metallic) $(TMTSF)_2PF_6$ compound.

In this paper, our aim is to investigate by numerical exact diagonalization (ED) techniques, the interplay between the electron repulsion and the electron-phonon coupling in the case of an adiabatic lattice. We focus on the competition or the cooperative behavior between charge ordering and lattice instabilities. Such a problem has been addressed in a number of previous studies[9,10] where several interesting modulated phases have been proposed. However, so far, no systematic investigation of the full phase diagrams has been carried out. Indeed, the suggested translation symmetry broken states[10]

were found in a restricted variational space. We shall here re-examine these issues in order to determine the absolute stability of the various competing phases.

We use extended 1D Hubbard models at quarter filling ($\bar{n}=1/2$) coupled with some (classical) phonon field,

$$H_{1D}=\sum_{i,\sigma} t(i)(c_{i;\sigma}^\dagger c_{i+1;\sigma}+\text{H.c.})+U\sum_i n_{i;\uparrow}n_{i;\downarrow}$$
$$+V\sum_i n_i n_{i+1}+H_{\text{ph}}, \qquad (1)$$

where $n_{i;\sigma}=c_{i;\sigma}^\dagger c_{i;\sigma}$ and $n_i=n_{i;\uparrow}+n_{i;\downarrow}$. We have included a nearest-neighbor (NN) interaction V as its role will become clear in the following. Local deformations of the molecules can produce changes of the on-site (or molecular) orbitals energies and can simply be taken into account by a Holstein term $\Sigma_i n_i \delta_i$ while assuming a constant hopping integral $t(i)=t$ and an elastic energy cost $\frac{1}{2}K\Sigma_i \delta_i^2$. This effect has been studied numerically in a different context[11] but it is relatively small in the case of the organic systems here considered. In contrast to the above on-site deformation, the positions of the intercalated anions can couple strongly to the electrons especially through modulations of the single-particle hoppings along the chains of the Peierls type,

$$t(i)=t(1+\delta_i^B) \qquad (2)$$

with an elastic energy

$$H_{\text{ph}}\equiv H_{\text{elas}}=\frac{1}{2}K_B\sum_i (\delta_i^B)^2. \qquad (3)$$

The electron-lattice couplings have been absorbed in the redefinition of the displacements δ_i^B so that the strength of the lattice coupling scales like $1/K_B$ (also t is set to 1). We first consider the case of the *isolated* Hubbard chain and, next, the role of an interchain magnetic coupling (in the mean field).

In contrast to previous treatments[10] our numerical method enables us to obtain the lowest energy equilibrium lattice configuration without making any assumption on the broken symmetry ground state (GS). In particular, no super-cell order is imposed *a priori* and the GS configuration is obtained through a self-consistent procedure. Indeed, the total-energy functionals $E(\{\delta_i^B\})$ can be minimized with respect to the sets of distortions $\{\delta_i^B\}$ by solving the following nonlinear coupled equations:

$$K_B \delta_i^B + t \langle c_{i;\sigma}^\dagger c_{i+1;\sigma} + \text{H.c.} \rangle = 0. \qquad (4)$$

Here $\langle \ldots \rangle$ is the GS mean value obtained by ED (using the Lanczos algorithm) of Hamiltonian (1) on cyclic L-site rings (with L up to 16 sites). Since the second term depends implicitly on the distortion pattern $\{\delta_i^B\}$, Eq. (4) can be solved by a regular iterative procedure.[12] A similar approach has been applied to the case of the on-site Holstein coupling.[11] We should stress here that within the intrinsic limitations of the method (adiabatic lattice and finiteness of the system) our resolution of the problem is basically exact (numerical accuracy better than 10^{-7}). Note also that once a small adiabatic lattice coupling is included finite-size effects become quite small.

Before discussing our main results on the Hubbard-Peierls chain, let us briefly describe the phase diagram of the Hubbard-Holstein chain[11] in order to introduce the generic types of CDW states. At quarter filling, the Fermi wave vector is given by $q_{2k_F} = \pi/2$ so that, at small U, one expects an instability towards a $2k_F$ CDW state of wave vector $\lambda_{2k_F} = 4a$ (a is the lattice spacing) mediated by the electron-lattice coupling. In contrast, for large U, the system becomes more similar to a gas of interacting spinless fermions (SF's) and the instability is likely to occur at wave vector $2k_F^{SF} = 4k_F$. More generally, we can parametrize the relative charge-density modulation as

$$\frac{\Delta n_i}{\bar{n}} = \rho_{4k_F} \cos\left(2\pi \frac{r_i}{2a}\right) + \rho_{2k_F} \cos\left(2\pi \frac{r_i}{4a} + \Phi_{2k_F}\right), \qquad (5)$$

where $\Delta n_i = \langle n_i \rangle - \bar{n}$. Complete phase diagrams of the Hubbard-Holstein chain have been established in Ref. 11 and we briefly summarize them here. For $V=0$ the metallic uniform U phase ($\rho_{2k_F} = \rho_{4k_F} = 0$) is restricted to a region at small lattice coupling. Above a critical line $(1/K)_U$, three different insulating CDW phases can be distinguished; (i) at small U, a $2k_F$ CDW phase ($\rho_{4k_F} = 0$) centered on the sites, i.e., with $\Phi_{2k_F} = 0$; (ii) at intermediate U (in the range 4–8), a *bond-centered* $2k_F$ CDW phase (i.e., with $\Phi_{2k_F} = \pi/4$); (iii) at large U, a $4k_F$ CDW ($\rho_{2k_F} = 0$). As discussed in Ref. 11, a small NN repulsion suppresses completely the intermediate phase and enlarges the region of stability of the $4k_F$ CDW phase. Although these CDW might have some relevance to the low-temperature phase of the (TMTTF)$_2$X family, their charge modulations should couple strongly to the anion potential. Therefore, we investigate next the role of a Peierls coupling.

The phase diagrams as a function of the on-site repulsion U/t and the Peierls coupling $1/K_B$ are shown in Figs. 1(a)
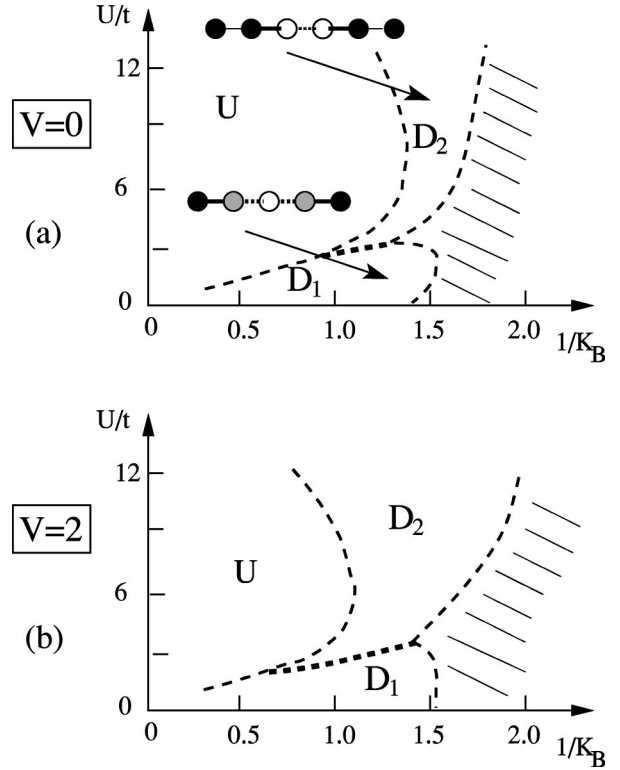

FIG. 1. Typical $(U/t, 1/K_B)$ phase diagrams of a $\frac{1}{4}$-filled Hubbard-Peierls chain without (a) or with a nearest-neighbor Coulomb repulsion V (b) obtained from ED of small periodic chains. Hashed regions are unphysical.

and 1(b) for $V=0$ and $V=2$. For too large electron-lattice coupling the linear coupling approximation breaks down and our model becomes unphysical (hashed regions) so that we shall restrict to small and intermediate values of $1/K_B$. For intermediate values of $1/K_B$, the uniform state is unstable towards translation symmetry broken states. Such bond order wave (BOW) states are characterized by a modulation of the hopping amplitudes of the form

$$\delta_i^B = \delta_{4k_F}^B \cos\left(2\pi \frac{r_i}{2a}\right) + \delta_{2k_F}^B \cos\left(2\pi \frac{r_i}{4a} + \Phi_{2k_F}^B\right). \qquad (6)$$

Generically, we find that BOW coexist with weaker charge modulations (CDW) given by Eq. (5). The amplitudes of the bond and charge modulations are shown in Fig. 2(a) for a fixed electron-lattice coupling $K_B = 0.8$. Very small finite-size effects are observed and calculations on 12- and 16-site rings give almost identical results. Two different types of structures are stable; (i) in the weak-coupling regime (let us say $U/t < 3$), a strong $2k_F$ BOW with $\Phi_{2k_F}^B = \pi/4$, i.e., corresponding to a X-X-Y-Y type of sequence of the bonds occurs. This modulation coexists with a weaker $2k_F$ site-centered CDW (A-B-$\bar{A}$-B type of sequence of the on-site charge densities, A and $\bar{A}$ corresponding to opposite values of Δn_i) and an even weaker $4k_F$ (i.e., A-B-A-B) CDW component (D_1 phase); (ii) at larger U/t, the D_2 phase corresponds to the superposition of a lattice dimerization ($4k_F$ BOW) together with a tetramerization ($2k_F$ BOW with $\Phi_{2k_F}^B = 0$). In other words, among the, say, weak bonds of the dimerized state, one every two becomes weaker (or stron-
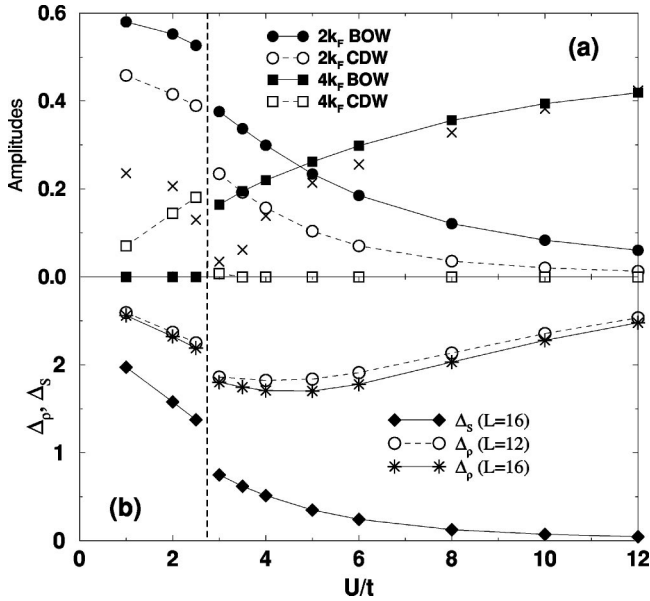
FIG. 2. (a) Amplitudes of the CDW (ρ_{2k_F} and ρ_{4k_F}) and BOW ($\delta^B_{2k_F}$ and $\delta^B_{4k_F}$) components versus U/t for $(K_B)^{-1}=1.25$ and $V=2$ (computed on a 16-site ring). Open (close) symbols correspond to CDW (BOW). Note that, although identical symbols have been used, the $2k_F$ orders are in fact *different*, i.e., have different phases Φ_{2k_F} and $\Phi^B_{2k_F}$ in the D_1 and D_2 phases (see text). The crosses indicate the energy difference (in absolute value) between the states with these two patterns. (b) Charge (Δ_ρ) and spin (Δ_S) gaps in unit of t vs U/t computed on 12- and 16-site rings (Δ_S on $L=12$ and $L=16$ are undistinguishable).

ger) so that electrons become weakly bound in singlet pairs on next NN bonds. The D_2 phase is therefore a simple realization of the above-mentioned SP phase.[13] Interestingly enough, we observe that the tetramerization leads to a weak coexisting $2k_F$ CDW component corresponding to a A-A-B-B charge modulation (i.e., with $\Phi_{2k_F}=\pi/4$). Note also that the boundary between the D_1 and D_2 phases is a first-order transition line as it is clear from the discontinuity of the various order parameters seen in Fig. 2(a). We have also included in this plot the energy difference between the states corresponding to $D1$ and $D2$ patterns. This difference is, in general, (except at large U) considerably smaller than charge and spin excitations (see below).

To complete our study we have also computed the charge (Δ_ρ) and the spin (Δ_S) gaps in the D_1 and D_2 phases for the same set of parameters as shown in Fig. 2(b). As for the Fourier amplitudes, finite-size effects are almost negligible especially for Δ_S. Clearly Δ_S follows closely the magnitude of the $2k_F$ BOW-CDW. For large-U (and large dimerization) the system behaves qualitatively like a spin-1/2 antiferromagnet (since the electrons are localized on the strong bonds) and the spin gap is expected to vanish in this limit. In contrast, in the D_1 phase, electrons are strongly localized in pairs on two adjacent strong bonds (i.e., on three sites) so that $\Delta_S \sim t$. The charge gap, also shown in Fig. 2, has a minimum at intermediate U in the region corresponding to the crossover from dominant $2k_F$ to dominant $4k_F$ BOW-CDW. Note that both charge and spin gaps are discontinuous at the first-order transition between D_1 and D_2.
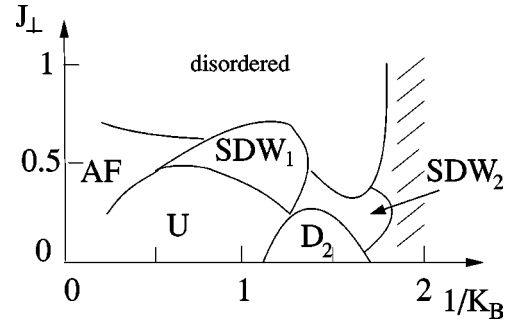

FIG. 3. Phase diagram of weakly coupled $\frac{1}{4}$-filled Hubbard-Peierls chains as a function of $1/K_B$ and $J_\perp$ for $U=6$, $V=2$. Hashed regions are unphysical.

Our study shows that the electronic correlations (both U and V) are essential to stabilize the D_2 phase which, we believe, is a fair realization of the SP phase of the $(TMTTF)_2X$ material. Note that the $2k_F$ ($4k_F$) Fourier components are suppressed (increased) as U/t increases as seen in Fig. 2(a) and in agreement with previous numerical calculations of the on-site charge-density and NN charge-transfer response functions of the extended Hubbard model.[14]

Lastly, we investigate the role of an interchain coupling which is relevant, e.g., in the case of $(TMTTF)_2Br$ [or $(TMTTF)_2PF_6$ under pressure]. These systems which are less anisotropic than $(TMTTF)_2PF_6$ at ambient pressure exhibit an antiferromagnetic (AF) phase at low temperature. In an insulating regime, due to the presence of a charge gap Δ_ρ, the interchain single-particle hopping $t_\perp$ is believed to be irrelevant.[3] Therefore, we only consider a transverse magnetic coupling $J_\perp$ (typically $J_\perp \sim t_\perp^2/\Delta_\rho$) in the mean-field approximation. Our previous method can be straightforwardly extended to include this interchain coupling by adding to Eq. (1) an extra term such as

$$H_\perp = \frac{1}{2} \sum_i H_i(n_{i;\uparrow}-n_{i;\downarrow}), \qquad (7)$$

where the local fields H_i are determined self-consistently (simultaneously with the δ^B_i bond modulations) from an additional set of nonlinear equations,

$$H_i = \frac{J_\perp}{2}\langle(n_{i;\uparrow}-n_{i;\downarrow})\rangle. \qquad (8)$$

Our results on coupled Hubbard-Peierls chains are summarized in Fig. 3. Besides the D_2 phase [Fig. 4(a)] which is stable at small $J_\perp$ new magnetic phases depicted in Figs. 4(b) and 4(c) appear; (i) at small electron-lattice coupling an antiferromagnetic phase consisting of a site-centered $4k_F$ CDW with a finite spin density on the sites carrying an excess charge [see Fig. 4(c)]; (ii) at larger values of $1/K_B$, a superposition of a dimerization ($4k_F$ BOW) with a $2k_F$ *bond-centered* SDW order[15] [see Fig. 4(b)]. Note that only the spin densities of these two magnetic phases could be obtained by adding two out-of-phase $2k_F$ CDW for the spins up and down so that the $4k_F$ CDW and BOW components should really be considered as extra coexisting orders. In a small region of the parameter space, a more exotic magnetic SDW_2 phase (not shown) has been stabilized on our clusters. This phase contains all three CDW, SDW, and BOW components
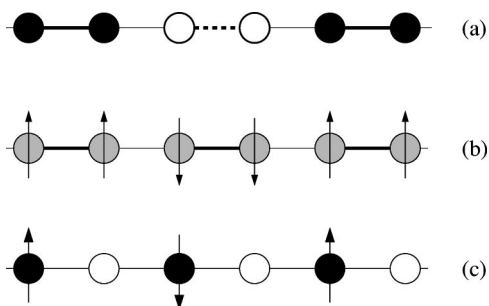
FIG. 4. Pictures of the various phases of antiferromagnetically coupled chains showing the bond modulation (thick lines are strong bonds, dashed lines are weak bonds), the charge modulation (full and open circles correspond to excess and depression of charge, respectively), and the local spin densities (arrows). (a) dimerized/tetramerized D_2 phase; (b) Spin-density wave SDW_1 phase; (c) antiferromagnetic phase.

with large supercells of the order of our chain lengths. Finally, we note that the region of stability of the D_2 phase should be extended by a small interchain bond coupling.[13]

To summarize, the role of Peierls electron-lattice couplings has been investigated in the adiabatic approximation in quarter-filled isolated or weakly coupled one-dimensional Hubbard chains. A numerical method based on ED techniques supplemented by a self-consistent procedure has been used to determine the various phase diagrams as a function of the strengths of the lattice coupling and the Coulomb repulsion. We have shown that, generically, lattice modulations (BOW) are always accompanied by CDW's of weaker amplitudes. In addition, at intermediate and large on-site Coulomb repulsion, the lattice modulation consists of a superposition of a $4k_F$ (dimerization) and a $2k_F$ (tetramerization) BOW. Interestingly enough, we found that a NN electronic repulsion further stabilizes this lattice/charge modulated phase. Under the application of an interchain AF coupling, we found long-range spin-order phases showing coexisting $4k_F$ CDW or BOW (i.e., dimerization). It is argued that such a simple model can well describe the various low-temperature SP, AF, and SDW phases of the insulating charge-transfer salts of the sulfur series.[5]

[1] D. Jérome and H.J. Schulz, Adv. Phys. **31**, 299 (1982); C. Bourbonnais and D. Jerome, in *Advances in Synthetic Metals, Twenty Years of Progress in Science and Technology*, edited by P. Bernier, S. Lefrant, and G. Bidan (Elsevier, New York, 1999), pp. 206–261.

[2] T. Ishiguro, K. Yamaji, and G. Saito, in *Organic Superconductors*, 2nd ed., Springer Series in Solid-State Sciences, Vol. 88 (Springer-Verlag, Berlin, 1998).

[3] C. Bourbonnais, cond-mat/0004470 (unpublished).

[4] I.J. Lee *et al.*, Phys. Rev. Lett. **78**, 3555 (1997).

[5] M. Dumm *et al.*, Phys. Rev. B **61**, 511 (2000), and references therein.

[6] Karlo Penc and Frédéric Mila, Phys. Rev. B **50**, 11 429 (1994).

[7] B. Dumoulin *et al.*, Phys. Rev. Lett. **76**, 1360 (1996).

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

[9] K.C. Ung, S. Mazumdar, and D.K. Campbell, Solid State Commun. **85**, 917 (1993); K.C. Ung, S. Mazumdar, and D. Toussaint, Phys. Rev. Lett. **73**, 2603 (1994).

[10] S. Mazumdar, S. Ramasesha, R. Torsten Clay, and D.K. Campbell, Phys. Rev. Lett. **82**, 1522 (1999); S. Mazumdar, R.T. Clay, and D.K. Campbell, cond-mat/0003200.

[11] J. Riera and D. Poilblanc, Phys. Rev. B **59**, 2667 (1999).

[12] A. Dobry and J. Riera, Phys. Rev. B **56**, 2912 (1997).

[13] Note that extrinsic causes to the $4k_F$ dimerization (such as anion potential, etc.) have also been invoked; see, e.g., L. Caron *et al.*, J. Phys. I **6**, 1727 (1996); Synth. Met. **19**, 69 (1987). In that case, a weaker lattice coupling is sufficient to produce a similar $2k_F$ instability.

[14] J.E. Hirsch and D.J. Scalapino, Phys. Rev. B **29**, 5554 (1984).

[15] Note that these SDW Mott insulators should not be confused with the weak-coupling SDW phases of the quasi-1D $(TMTSF)_2X$ metals.