

Influence of the anion potential on the charge ordering in quasi-one-dimensional charge-transfer salts

José Riera¹ and Didier Poilblanc^{2,3}

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*Theoretische Physik, ETH-Hönggerberg, CH-8093 Zürich, Switzerland*

³*Laboratoire de Physique Quantique & UMR-CNRS 5626, Université Paul Sabatier, F-31062 Toulouse, France*

(Received 28 February 2001; revised manuscript received 21 March 2001; published 30 May 2001)

We examine the various instabilities of quarter-filled strongly correlated electronic chains in the presence of a coupling to the underlying lattice. To mimic the physics of the tetramethyltetrafulvene (TMTTF)₂X Bechgaard-Fabre salts we also include electrostatic effects of intercalated anions. We show that small displacements of the anion can stabilize new mixed charge-density wave–bond order wave phases in which central symmetry centers are suppressed. This finding is discussed in the context of recent experiments. We suggest that the recently observed charge ordering is due to a cooperative effect between the Coulomb interaction and the coupling of the electronic stacks to the anions. On the other hand, the Spin-Peierls instability at lower temperature requires a Peierls-like lattice coupling.

DOI: 10.1103/PhysRevB.63.241102

PACS number(s): 75.10.-b, 75.50.Ee, 71.27.+a, 75.40.Mg

Site-centered charge-density wave (CDW) or bond order waves (BOW) states are generic in one-dimensional (1D) chains at commensurate fillings. It is known that a strong enough short-range electronic repulsion leads to a ($4k_F$) charge instability.^{1,2} Molecular crystals such as quasi-1D charge transfer salts^{1,2} present a very rich physics due to the interplay between electron-electron and electron-phonon interactions. Several systems have been observed to show transitions towards charge ordered phases where the molecules of the conducting stack exhibit unequal electron densities. The sulfur series of the Bechgaard-Fabre salts family, namely (TMTTF)₂X ($X = \text{PF}_6, \text{AsF}_6$), consists of quarter-filled ($\bar{n} = 1/2$) molecular chains with very anisotropic transport properties.¹ Below the Mott localization crossover temperature³ evidences for a true transition towards a symmetry broken state have been recently provided by dielectric response measurements⁴ and NMR.⁵ This lower symmetry phase is characterized by the disappearance of all central symmetry centers in the crystal.⁴ The Spin-Peierls (SP) transition observed at lower temperature¹ is characterized by a freezing of remaining spin fluctuations (opening of a spin gap) and it is accompanied by a tetramerization of the chains.¹

The interplay between electronic correlations and lattice effects in 1D quarter filled chains have been addressed in a number of previous theoretical studies,^{6–8} where interesting modulated phases have been proposed. Generically, lattice modulations (or BOW) were shown to be always accompanied by CDW's of weaker amplitudes.⁸ However, the potential created by the intercalated anions have also been invoked⁹ as an extrinsic cause to the $4k_F$ dimerization. In that case, a weaker lattice coupling is sufficient to produce a similar $2k_F$ instability (tetramerization). In this work, we extend our previous model of Ref. 8 to include the crucial effect of the anion potential. The following approach is based on the realistic 2D structure of the charge-transfer salts depicted in Fig. 1 (for more details see also Figs. 1 and 8 of

Ref. 1 or Fig. 3.3 of Ref. 2). We only focus here on the most anisotropic compounds of the sulfur series where inter-chain charge transfer can be safely neglected.

Our model consists of a 2D array of electronic (extended) Hubbard chains (hereafter called E chains) coupled to classical lattice degrees of freedom;

$$H = \sum_{i,j,\sigma} t(i,j) (c_{i-1,j;\sigma}^\dagger c_{i,j;\sigma} + \text{H.c.}) + U \sum_{i,j} n_{i,j;\uparrow} n_{i,j;\downarrow} + V \sum_{i,j} n_{i-1,j} n_{i,j} + H_{\text{elas}} + H_{\text{anions}}, \quad (1)$$

where $i(j)$ are site (chain) labels, $n_{i,j;\sigma} = c_{i,j;\sigma}^\dagger c_{i,j;\sigma}$ and $n_{i,j} = n_{i,j;\uparrow} + n_{i,j;\downarrow}$. We have included a nearest-neighbor (NN) interaction V . Small local displacements of the mol-

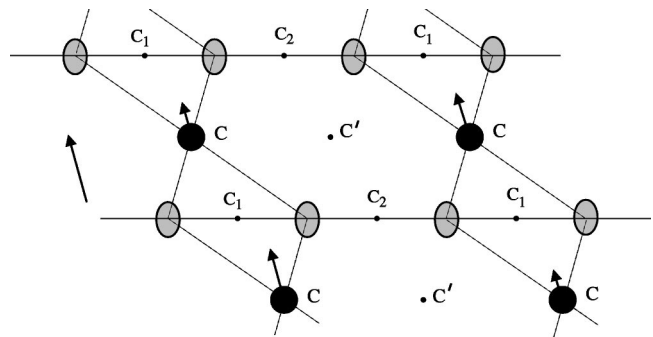


FIG. 1. Schematic structure of the ($a,b-c$) plane (see Fig. 8 of Ref. 1) used in this paper: electronic chains (gray sites) are separated by anionic chains (black sites) with one anion for two organic molecules. Due to the complete charge transfer of one electron per anion the electronic chains are quarter-filled on average. The arbitrary displacements (exaggerated for clarity) of the anions with respect to symmetric positions are shown by arrows. Central symmetry centers C , C' , C_1 , and C_2 in the high-symmetry configuration are indicated on the plot.

ecules along the E chains can couple strongly to the electrons via modulations of the single-particle hoppings of the Peierls type,

$$\begin{aligned} t(2p-1,j) &= t_1^0(1 + \delta_{2p-1,j}^B), \\ t(2p,j) &= t_2^0(1 + g \delta_{2p,j}^B), \end{aligned} \quad (2)$$

with an elastic energy

$$H_{\text{elas}} = \frac{1}{2} K_B \sum_{i,j} (\delta_{i,j}^B)^2. \quad (3)$$

The electron-lattice couplings have been (partially) absorbed in the re-definition of the bond modulations $\delta_{i,j}^B$ so that the strength of the lattice coupling scales like $1/K_B$. Let us now consider the role of the charged X^- anions located on the so-called A chains as shown in Fig. 1. They introduce a new periodicity of two lattice spacings on the E chains which, *a priori*, might lead to a dimerization of the bare electronic transfer integrals along the chain, i.e., $t_1^0 \neq t_2^0$. Hereafter, the mean value $t = (t_1^0 + t_2^0)/2$ is set to 1 and we assume $t_1^0 - t_2^0 = 0.1t$. However, the qualitative conclusions of this work do not really depend on whether t_1^0 and t_2^0 are assumed to be equal or not. For simplicity, we shall take $g = 1$. The anions can play a dominant role if they are allowed to undergo small displacements (along some arbitrary direction) leading to local changes of the on-site electronic energies. In lowest order in these displacements $\delta_{p,j}^A$, one gets

$$\begin{aligned} H_{\text{anions}} &= \sum_{p,j} \{ (\lambda \delta_{p,j}^A - \delta_{p,j+1}^A) n_{2p,j} \\ &+ (\delta_{p,j}^A - \lambda \delta_{p,j+1}^A) n_{2p+1,j} \} + \frac{1}{2} K_A \sum_{p,j} (\delta_{p,j}^A)^2, \end{aligned} \quad (4)$$

where p labels the positions of the anions in the chain direction. Note that all displacements (for molecules and anions) are defined with respect to the high-symmetry (high- T) phase shown in Fig. 1. The parameter λ ($0 \leq \lambda \leq 1$) accounts for the nonequivalent location of each given anion with respect to the two nearest molecules in each of the two neighboring chains. Hereafter, results are obtained for an intermediate value $\lambda = 0.3$.

Following the method of Ref. 8 based on exact diagonalization (ED) of small clusters supplemented by a self-consistent procedure we obtain the lowest ($T=0$) energy lattice configuration without any assumption on the supercell order of the broken symmetry ground state (GS). The condition that the energy $E(\{\delta_{i,j}^B, \delta_{p,j}^A\})$ is minimum with respect to the sets of distortions/displacements $\{\delta_{i,j}^B\}$ and $\{\delta_{p,j}^A\}$ reads,

$$\begin{aligned} K_B \delta_{i,j}^B + t \langle c_{i-1,j;\sigma}^\dagger c_{i,j;\sigma} + \text{H.c.} \rangle &= 0, \\ K_A \delta_{p,j}^A + \lambda (\langle n_{2p,j'} \rangle - \langle n_{2p+1,j'-1} \rangle) \\ &+ \langle n_{2p+1,j'} \rangle - \langle n_{2p,j'-1} \rangle = 0. \end{aligned} \quad (5)$$

Here $\langle \dots \rangle$ is the GS mean value obtained by ED (using the Lanczos algorithm) of Hamiltonian (1) on periodic $M \times L$ clusters. Typically, $M=2$ units (two electronic chains and two anionic chains) were considered in the transverse direction (so that modulated structures with $k_\perp = 0$ or π can spontaneously appear) with up to $L=12$ ($L/2=6$) electronic (anionic) sites in the E chains (A chains). The nonlinear coupled equation (5) can be solved by a generalization of the iterative procedure of Ref. 10. Note that since spin and charge are conserved in each electronic chain, each of them can be diagonalized independently. Note also that, for finite lattice coupling, finite-size effects are, in general, quite small.

Our numerical results show a very rich phase diagram with mixed CDW-BOW structures. Quite generally the largest supercell unit is four lattice spacings long along the E chains and has two basic (E chain + A chain) units in the transverse direction. Therefore, in order to discuss our results, it is convenient to parametrize the real-space behavior of the various observables in the following way:

$$\begin{aligned} \Delta n_{i,j} &= \rho_{4k_F} (-1)^i \cos(k_\perp j) + \rho_{2k_F} \cos\left(\frac{\pi}{2} i + k_\perp j + \Phi_{2k_F}\right), \\ \delta_{i,j}^B &= \delta_{4k_F}^B (-1)^i \cos(k_\perp j) + \delta_{2k_F}^B \cos\left(\frac{\pi}{2} i + k_\perp j + \Phi_{2k_F}^B\right), \\ \delta_{p,j}^A &= \delta_0^A \cos(k_\perp j) + \delta_\pi^A (-1)^p \cos(k_\perp j), \end{aligned} \quad (6)$$

where $\Delta n_{i,j} = (\langle n_{i,j} \rangle - \bar{n})/\bar{n}$ is the relative change of the electronic density. Note that the periodicity of the $4k_F$ (respectively, $2k_F$) modulation corresponds to 2 (respectively, 4) lattice spacing of the E chains while a uniform ($k_\perp = 0$) or a staggered ($k_\perp = \pi$) arrangement occur in the transverse direction. Note that both the $4k_F$ -BOW (dimerization), the $2k_F$ -BOW sequence $X-0-\bar{X}-0$ ($\Phi_{2k_F}^B = 0$) and the $2k_F$ -CDW sequence $B-B-\bar{B}-\bar{B}$ ($\Phi_{2k_F} = \pi/4$) preserve at least one of the central symmetries of Fig. 1 ($\bar{X} = -X$).

Before discussing the generic phase diagram of the model, it is interesting to comment on the special limit $K_A = \infty$, i.e., corresponding to fixed anion positions ($\delta_{p,j}^A = 0$). In that case, the E chains decouple from each other and the problem reduces to the single Peierls-Hubbard chain.^{11,8} The phase diagram of this model⁸ exhibits, for sufficiently large lattice coupling, an instability towards two different translation symmetry breaking phases D_1 and D_2 ; (i) in the weak coupling regime (let's say $U/t < 3$), a strong $2k_F$ BOW with $\Phi_{2k_F}^B = \pi/4$, i.e., corresponding to a $X-X-\bar{X}-\bar{X}$ type of sequence of the bonds occurs. This modulation coexists with a weaker $2k_F$ site-centered CDW ($A-0-\bar{A}-0$ type of sequence of the on-site relative charge densities), and an even weaker $4k_F$ (i.e., $A-\bar{A}-A-\bar{A}$) CDW component; (ii) at larger U/t , a superposition of a lattice dimerization ($4k_F$ BOW) together with a tetramerization ($2k_F$ BOW with $\Phi_{2k_F}^B = 0$) both coexisting with a weak $2k_F$ CDW component (with $\Phi_{2k_F} = \pi/4$) occurs. It is interesting to note that the

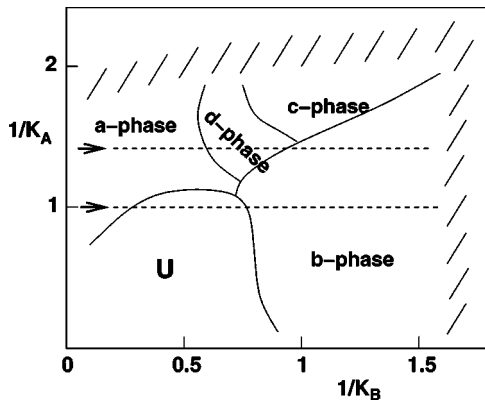


FIG. 2. Phase diagram versus the two electron-lattice couplings for $U=6$, $V=2$, and $\lambda=0.3$. Dashed regions are beyond the validity of the model. The different phases are depicted in Fig. 3. U denotes the uniform phase (with only bare dimerization). The numerical values of the order parameters along the dashed lines indicated by the arrows can be found in Fig. 4.

dimerization observed in experiments on Bechgaard-Fabre salts¹ is absent in the weak-coupling D_1 phase. In addition, the D_2 phase, a natural candidate to describe the low-temperature SP phase, still exhibits one center of symmetry (e.g., C_2) while recent experiments⁴ point towards the disappearance of *all* center of symmetries below the charge ordering transition. Therefore, we believe that the anions may play an important role in stabilizing new lower symmetry CDW-BOW phases.

The $T=0$ phase diagram of our model is shown in Fig. 2 for typical parameters in Bechgaard-Fabre salts. A rich variety of charge ordered phases are found and schematically depicted in Figs. 3. We note that (at least on finite clusters) finite values of the electron-lattice couplings are necessary to stabilize these translation symmetry breaking phases. At small Peierls coupling, the coupling to the anion displacement field generates a $\mathbf{k}_e=(4k_F,0)$ electronic CDW simultaneously with a dimerization in the chain direction (hereafter named as the *a* phase). This charge ordering is accompanied

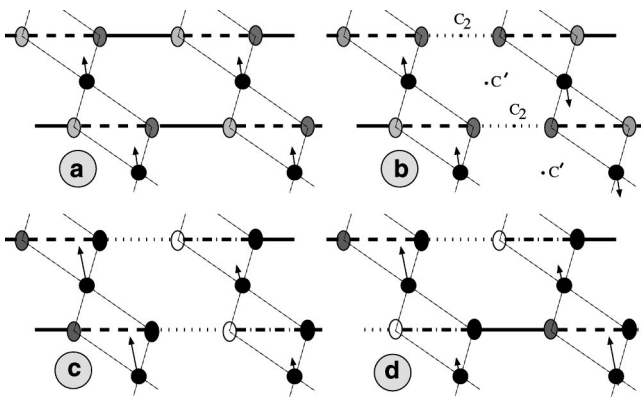


FIG. 3. Schematic representation of the various phases found in this work. Different average charge densities are indicated by different levels of gray. (a) and (b) [respectively, (c) and (d)] have two [respectively, four] nonequivalent sites. While (a) and (b) show two and three nonequivalent bonds, respectively, (c) and (d) have four.

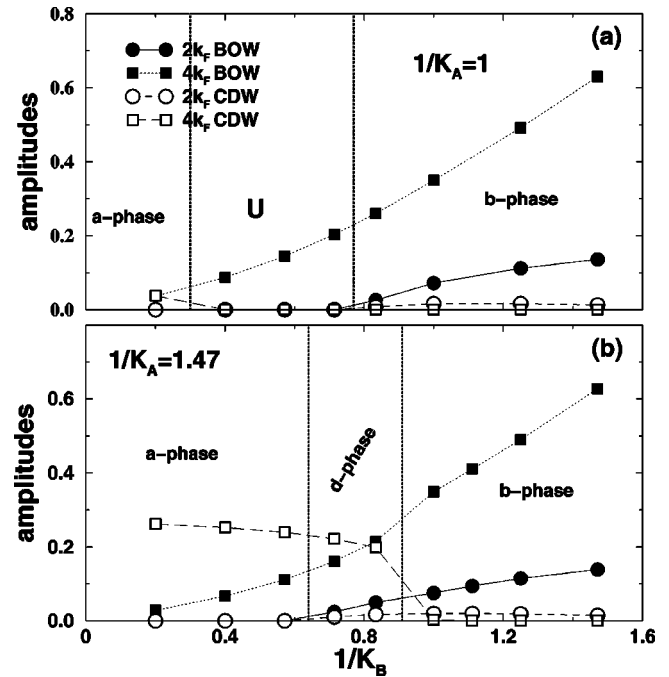


FIG. 4. Amplitudes of the various $2k_F$ and $4k_F$ CDW and BOW components (as indicated on the plot) as a function of the Peierls coupling $1/K_B$, for $U=6, V=2, \lambda=0.3$, and two different anion-electron coupling constants as indicated on the plots. The correspondence to the ordered phases of Fig. 3 is shown.

by a uniform $\mathbf{k}_A=(0,0)$ displacement of the anions with respect to their symmetric positions as shown in Fig. 3(a). On the other hand, the D_2 phase of the single chain system (see Ref. 8) at large enough $1/K_B$ coupling is weakly affected by the coupling to the anions and continuously evolves into a two-dimensional in-phase array (i.e., $k_\perp=0$) of mixed $2k_F$ -CDW/ $2k_F$ -BOW/ $4k_F$ -BOW chains (named as *b* phase here), which extends in a wide region of the phase diagram. Note that, as soon as $1/K_A$ is finite, this mixed CDW-BOW phase is accompanied by a $\mathbf{k}_A=(\pi,0)$ component of the anion displacement field [see Fig. 3(b)] so that the translation symmetry is fully preserved in the transverse direction. As for the single chain D_2 phase, the two-dimensional *b* phase arrangement preserves the symmetry centers C_2 and C' . Interesting phases are obtained in the region of intermediate $1/K_A$ and $1/K_B$ couplings. The *c* phase of Fig. 3(c) [respectively, *d* phase of Fig. 3(d)] is realized by a superposition of a uniform $\mathbf{k}_A=(0,0)$ displacement and a $\mathbf{k}_A=(\pi,0)$ [respectively, $\mathbf{k}_A=(\pi,\pi)$] modulation of the anion positions. The charge ordering is characterized by the superposition of a $4k_F$ CDW with a $2k_F$ CDW whose phase $0 < \Phi_{2k_F} < \pi/4$ depends on the model parameters. Similarly the lattice modulation contains a $4k_F$ component (dimerization) superposed with an out-of-phase (i.e., $0 < \Phi_{2k_F}^B < \pi/4$) $2k_F$ -BOW. While all the *E* chains are in-phase in the *c* phase, they are alternating in the *d* phase. It is important to note that only the uniform phase and the *b* phase preserve at least one center of symmetry of the crystal.

The modulation amplitudes are plotted vs $1/K_B$ in Figs. 4(a) and 4(b) for two characteristic values of the electron-

anion coupling constants. These plots show clearly that the Peierls coupling stabilizes BOW's while the coupling to the anions rather stabilizes $4k_F$ CDW. We believe that the competition between these two effects produces the interesting mixed four-component CDW-BOW phases at intermediate $1/K_A$ and $1/K_B$ values. In the c phase and d phase the phase of the $2k_F$ CDW [respectively, $2k_F$ BOW] increases rapidly from ~ 0 to $\sim \pi/4$ [respectively, decreases from $\sim \pi/4$ to ~ 0] for increasing Peierls coupling to eventually become locked to the value $\pi/4$ [respectively, 0] in the b phase (analogous to the 1D D_2 phase). Note that all centers of symmetries are removed by the $4k_F$ -CDW component in the a phase, c phase, and d phase and/or also by the $2k_F$ CDW and/or BOW components in the c phase and d phase as soon as $\Phi_{2k_F} \neq \pi/4$ and/or $\Phi_{2k_F}^B \neq 0$. Note also that electronic interaction (e.g., U) tends to suppress both $2k_F$ CDW and BOW components as seen in Ref. 8.

We finish by a discussion of our results in light of the recent experiments^{4,5} providing evidences of a charge modulated state in $(\text{TMTTF})_2X$ ($X = \text{PF}_6, \text{AsF}_6$). Although the spontaneously dimerized phase⁸ (D_2 phase) of the (uniform) single chain Peierls-Hubbard model is a reasonable candidate for the charge ordered state,¹² it seems in contradiction with the conclusion of the dielectric response measurements due to its remaining central symmetry center. Hence, although the single chain Peierls-Hubbard model contains most of the relevant features of the experimental system, a correct understanding is still required to consider the effective coupling of

these (electronically decoupled) chains via the anion potential. We believe that the dimerized a phase stabilized above a critical value of $1/K_A$ might be a fair description of the ordered phase with two inequivalent sites in agreement with NMR spectroscopy results.⁵ Clearly Coulomb interaction (V term) also cooperates with the electrostatic anion potential to generate the $4k_F$ CDW instability. The small additional $2k_F$ BOW and CDW components of the c phase (or d phase) might also explain the additional translation symmetry breaking (and the spin gap opening) occurring at the SP transition. Indeed, although at $T=0$ we obtain first-order lines between the various GS (by varying the parameters), continuous transitions could appear at finite temperature (and once lattice dynamics is introduced) between let us say the uniform phase and the a phase at high temperature and the a phase and the c phase (or d phase) at lower temperature. Incidentally, this scenario then implies that the charge ordering must be accompanied by a (probably quite small) global shift of the anions with respect to their symmetric locations and that the subsequent SP transition is linked to an additional (even smaller) $\mathbf{k}_A = (\pi, 0)$ or $\mathbf{k}_A = (\pi, \pi)$ modulation.

Computations were performed at the School of Computational Science & Information Technology (CSIT) and at the Academic Computing and Network Services at Tallahassee (Florida) and at IDRIS, Orsay (France). Support from ECOS-SECyT A97E05 is also acknowledged. We are indebted to S. Ravy for many useful suggestions and comments.

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

²T. Ishiguro, K. Yamaji, and G. Saito, *Organic Superconductors*, 2nd ed., Springer Series in Solid-State Sciences Vol. 88 (Springer-Verlag, Berlin, 1998); 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 (Elvesier, New York, 1999).

³R. Laversanne, C. Coulon, B. Gallois, J.-P. Pouget, and R. Moret, *J. Phys. (France) Lett.* **45**, L393 (1984).

⁴F. Nad *et al.*, *Phys. Rev. B* **62**, 1753 (2000); *J. Phys.: Condens. Matter* **12**, L435 (2000); P. Monceau, F. Nad, and S. Brazovskii, cond-mat/0012237 (unpublished).

⁵D. S. Chow *et al.*, *Phys. Rev. Lett.* **85**, 1698 (2000).

⁶K. C. Ung, S. Mazumdar, and D. K. Campbell, *Solid State Com-*

mun. **85**, 917 (1993); K. C. Ung, S. Mazumdar, and D. Tous-saint, *Phys. Rev. Lett.* **73**, 2603 (1994).

⁷S. Mazumdar *et al.*, *Phys. Rev. Lett.* **82**, 1522 (1999); J. Riera and D. Poilblanc, *Phys. Rev. B* **59**, 2667 (1999); S. Mazumdar, R. T. Clay, and D. K. Campbell, *ibid.* **62**, 13 400 (2000).

⁸J. Riera and D. Poilblanc, *Phys. Rev. B* **62**, R16 243 (2000).

⁹V. J. Emery, *J. Phys. Colloq.* **44**, C3-977 (1983); S. Brazovskii and V. Yakovenko, *J. Phys. (France) Lett.* **46**, L111 (1985); L. Caron *et al.*, *J. Phys.* **6**, 1727 (1996).

¹⁰A. Dobry and J. Riera, *Phys. Rev. B* **56**, 2912 (1997).

¹¹J. E. Hirsch and D. J. Scalapino, *Phys. Rev. B* **29**, 5554 (1984).

¹²As noticed in Ref. 8 the small extra $2k_F$ components of the D_2 phase accounts for the SP order.