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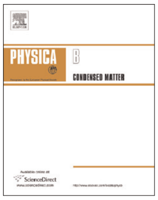

Review

# Interplay between electronic and structural degrees of freedom in quarter-filled low dimensional conductors

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ABSTRACT

We review the basic aspects of the charge density wave (CDW) and bond order wave (BOW) instabilities observed in one dimension (1D) organic conductors at either the $2k_F$ and/or $4k_F$ critical wave vectors. We start by recalling the main features of the coupled structural/electronic Peierls instabilities observed in donor–acceptor (D–A) charge transfer (CT) salts. Then we consider the specific case of 2:1 salts $D_2X$ where X is a monovalent anion. We show that the incipient CDW/BOW instabilities of the Bechgaard and Fabre salts are those of the parent quarter-filled CT salts TMTSF-DMTCNQ and TMTTF-DMTCNQ respectively. We also consider more specifically the influence of specific features of $D_2X$ salts such as the stack dimerization, the Fermi surface warping and the coupling to the anions. Then we discuss more generally the role of the anions in the Bechgaard and Fabre salts by pointing out the influence of polarization and charge displacement induced by the anion shift. Finally we show that some of these features are also relevant to understand the subtle interplay between structural and electronic degrees of freedom in 2D quarter-filled organic salts such as the $(BEDT\text{-}TTF)_2X$ series.

## 1. Introduction

Studies of 1D organic conductors such as CT salts of the TTF-TCNQ family, undergoing a Peierls transition (at $T_p$), have shown that electronic and structural degrees of freedom are intimately coupled. Such a coupling leads to the formation in a large temperature range above $Tp$ of $2k_F$ and/or $4k_F$ CDW instabilities accompanied by a BOW instability leading to the formation of a Kohn anomaly in the acoustic phonon branches ($k_F$ is the Fermi wave vector of the 1D electron gas which amounts in reciprocal chain unit, $d^*$, to one quarter of the charge $\rho$ per molecule) [1].

The role of the lattice degrees of freedom was less apparent in the literature devoted to 2:1 salts $D_2X$ where D is a donor molecule and X is a monovalent anion. For example the temperature–pressure/anion phase diagram of the so-called Bechgaard and Fabre salts, respectively $(TMTSF)_2X$ and $(TMTTF)_2X$ with centro-symmetrical anions, has been rationalized by assuming that the only role of the pressure or of the anion size is to change the electronic interactions of the quasi-1D electronic system [2]. Similarly it has been proposed [3] that the various ground states observed in several families of the 2D organic salt $(BEDT\text{-}TTF)_2X$ are controlled by tiny variations of the electronic interactions in the BEDT-TTF layers.

Although it has been noticed long time ago that order–disorder transitions of non-centro-symmetric anion X in $(TMTSF)_2X$ and $(TMTTF)_2X$ or of ethylene terminal groups of BEDT-TTF control also the phase diagrams [4], it was recently found that monovalent anions X not only provides the charge transfer of one $\pi$ hole every two donors ($\rho = 1/2$) but are an essential actor to promote CDW/BOW and charge order (CO) instabilities in the $D_2X$ salts [5,6].

In this lecture after recalling some basic aspects of the CDW and BOW instabilities of CT salts we show how these instabilities, although modified by the characteristic features of $D_2X$ salts, are also relevant to deeply understand the phase diagram of the $D_2X$ salt. This will allow us to precise the specific role of the anions which is largely ignored in the literature.

## 2. Charge transfer salts

CT salts are built with relatively well decoupled and segregated uniform stacks of donors (D) and acceptors (A). Thus with respect to Bechgaard and Fabre salts the stacks are not dimerized and there is no anion whose internal degrees of freedom can be coupled to the 1D electronic system. In addition there is no sizeable inter-stack electronic coupling (i.e. the transfer integral $t_\perp$ is smaller than $\pi Tp$) so that the 3D CDW ordering at $Tp$, the Peierls transition, is achieved through Coulomb coupling between CDWs.

Since in stack direction the inter-molecular distances are comparable to the intra-molecular ones and since intra-molecular $U$ and $m$th ($\leq 3$) neighbor Coulomb repulsions $V_m$ are significantly larger than the first neighbor transfer integral $t$, the 1D electron gas of organic conductors must be described by the extended Hubbard Hamiltonian

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$$H = \sum_i \varepsilon(i) n_i + \sum_i t(i)(c_i^{+} c_{i+1} + h.\,c.\,) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{i,m>0} V_m n_i n_{i+m} \qquad (1)$$

Quantum chemistry calculations on clusters of TTF molecules show than the $V_m$ decay as ~1/m [7], which corresponds to a convex repulsive Coulomb potential ($V_1 - V_2 > V_2 - V_3$). When the screening due to molecular polarizability is considered on obtains for the two types of stacks of TTF-TCNQ: $U$~2 eV ( ≈ 10$t$), $U$~ $2V_1$~$4V_2$ [8] .

A 1D electron gas with repulsive interactions exhibits a $2k_F$ CDW and/or a $2k_F$ spin density wave (SDW) instability and for important Coulomb repulsions a $4k_F$ CDW instability [9]. All these instabilities are caused by the low temperature divergence of the electron–hole response function (in power law of the temperature with an exponent involving the charge stiffness parameter $0 \leq K_\rho \leq 1$, function of $\rho$, $U/t$ and $V_m/t$, which decreases when the strength and range of the Coulomb repulsions increase [9]). The $2k_F$ CDW instability, leading to the Peierls transition, already occurs in a weakly interacting 1D electron gas for which $K_\rho$~1, while the $4k_F$ CDW instability, occurring for $K_\rho \leq 1/2$, requires the presence of strong and long range enough Coulomb repulsions. The $4k_F$ CDW corresponds to the first Fourier component of a 1D Wigner lattice of localized charges. For strong interactions the dominant $4k_F$ CDW is also accompanied by divergent $2k_F$ CDW (or spin-Peierls, SP) and $2k_F$ SDW instabilities. The quarter-filled ($\rho = 1/2$) electron gas exhibits both $2k_F$ and $4k_F$ CDW divergences at low temperature already when $U = 2V_1$[10].

When the Hamiltonian (1) is coupled to phonons, the electron–hole instability of the 1D electron gas drives a concomitant modulation of the bond distance and of the charge density forming respectively the so-called BOW and CDW [11]. The BOW which modulates the inter-molecular distances, $u(x)$, is in quadrature with the CDW where the charge modulation can be expressed as $\delta\rho(x) \propto \text{-}\partial u(x)/\partial x$. The modulation of charge on the molecular site $i$,$\rho + \delta\rho(x_i)$, is accompanied by an intra-molecular bond deformation $d(x_i) \propto \delta\rho(x_i)$. The BOW is basically achieved by the electron–phonon coupling with acoustic phonons which, via a change of the inter-molecular distances, modulate the transfer integral $t(i)$ and $V_m$ in expression (1). The site CDW is achieved by the electron–phonon coupling with intra-molecular modes which, via a change of the intra-molecular distances, modulate the site energy $\varepsilon(i)$ and $U$ in expression (1). In $D_2X$ salts the CDW can be also triggered by the Coulomb coupling of the 1D electron gas to the anions X whose displacement modulates the Hartree potential [12].

The divergence of the $2k_F$ and $4k_F$ BOW and CDW response functions which is controlled by the charge stiffness parameter $K_\rho$ thus depends on the molecular polarizability and on the electron density (i.e. of the screening by mobile charges). The response of the lattice degrees of freedom depends also on the electron–phonon coupling. Since X-ray diffuse scattering experiments mostly probe the coupling to acoustic phonons, the BOW response is generally measured. Such measurements were able to show that the $2k_F$ and $4k_F$ instabilities depend on the molecular polarizability (see Fig. 7 in reference [1]) and on the electron density [13]. Such dependences are also well illustrated in Fig. 1 which gives the thermal dependence of the $2k_F$ and $4k_F$ X-ray diffuse scattering measured in several CT salts built with either the TMTTF or the TMTSF donor and for charge transfer decreasing from 0.57 to 0.5 when the acceptor changes from TCNQ to DMTCNQ [14]. Note that with four Se atoms replacing the four S atoms of TMTTF, TMTSF has a stronger molecular polarizability.

Fig. 1 clearly shows that the decrease of molecular polarizability or/and of the charge transfer ρ enhances the $4k_F$ BOW instability with respect to the $2k_F$ BOW instability. TMTSF-TCNQ exhibits only the $2k_F$ BOW instability while TMTTF-DMTCNQ presents a dominant $4k_F$ BOW instability (the residual $2k_F$ BOW instability detected below 100 K reflects the tendency toward a SP pairing of the spin degrees of freedom of the Wigner lattice of localized charges). TMTSF-DMTCNQ exhibits less divergent $4k_F$ BOW instability and a $2k_F$ BOW instability is present on a larger temperature range than in TMTTF-DMTCNQ. Since the TMTSF or TMTTF stacks of $D_2X$ and CT salts have a similar 1D band structure, it is expected that the Bechgaard and Fabre salts will exhibit $2k_F$ and $4k_F$ BOW instabilities resembling those of the D stack of TMTSF-DMTCNQ and TMTTF-DMTCNQ.

The continuous lines in Fig. 1 fit the thermal divergence of the $Q = 2k_F$ and/or $4k_F$ BOW structural response $\chi(Q, T)$ using a complete theoretical treatment [15,16] taking into account the acoustic phonon fluctuations via a generalized Landau–Ginzburg formalism where constants depend on the spin and charge Luttinger liquid parameters of the correlated electron gas. The divergence of $\chi(Q, T)$ which depends on microscopic interactions is not an universal function at the difference of the intra-stack correlation length $\xi_Q(T)$ whose temperature dependence is only controlled by the thermal width of the Ginzburg critical region [17]. More precisely the fit of the thermal divergence of both $\chi(2k_F, T)$ and $\chi(4k_F, T)$ allows to obtain a charge stiffness $K_\rho$~1/4 for the D stack of TMTSF-DMTCNQ [16,18].

## 3. Quarter-filled organic salts

Fig. 2 classifies several quarter-filled organic salts according to the critical wave vector of their dominant BOW instability. Most of the CT salts, donor-based $D_2X$ and acceptor-based $A_2Y$ salts present regular stacks and no relevant inter-stack interactions $t_\perp$. Some exceptions exist among the $D_2X$ salts as indicated.

$D_2X$ salts built with TSeT and Fluorenthene donors having the strongest molecular polarizability exhibit only a $2k_F$ BOW instability which drives a Peierls transition. The quarter-filled salts built with TTF or TCNQ derivatives exhibit dominant $4k_F$ BOW instability. TMTSF-DMTCNQ and the Bechgaard salts, which will be compared below, exhibit a sizeable $2k_F$ BOW instability.

### 3.1. *The $2k_F$ instabilities in the Bechgaard salts*

Fig. 3 compares the thermal dependence of the 1D $2k_F$ BOW fluctuations measured on the TMTSF stack of TMTSF-DMTCNQ and of $(TMTSF)_2PF_6$. Above 100 K the $2k_F$ fluctuations behave similarly in temperature. Below 100 K the $2k_F$ BOW fluctuations of TMTSF-DMTCNQ diverge on approaching the 42 K Peierls transition while the $2k_F$ BOW fluctuations of $(TMTSF)_2PF_6$ saturate. Below 100 K ($T^*$) the divergence of the 1D $2k_F$ BOW fluctuations is stopped by the warping of the Fermi surface (FS) of $(TMTSF)_2PF_6$. Optical measurements [19] show that below $T^* \approx t_\perp/\pi$, $t_\perp$ becomes thermally relevant so that the $2k_F$ longitudinal FS nesting process is stopped. Below 50 K the $2k_F$ BOW fluctuations of $(TMTSF)_2PF_6$ vanish when the 12 K ($T_{SDW}$) SDW transition is approached. Differently, the $2k_F$ SDW fluctuations of $(TMTSF)_2PF_6$ diverge at $T_{SDW}$ at the critical wave vector $\mathbf{q_{SDW}} = (2k_F = 1/2,\ q_b = 0.22(4), ?)$ [20a, b] which achieves the best nesting $\mathbf{q_{nest}}$, of the warped FS of $(TMTSF)_2PF_6$ shown in Fig. 4a [20c]. These features mean that the density wave instability of $(TMTSF)_2PF_6$ is the one expected for a standard quarter-filled band system and that differently of the Fabre salts the stack dimerization does not seem to play a relevant role, probably because the inter-stack coupling $t_\perp$ allows avoiding the 1D charge localization due to $4k_F$ correlation effects.

An interesting question to address is why the FS nesting does not promote a $\mathbf{q_{nest}}$ BOW or CDW ground state? A possible explanation illustrated in Fig. 4b, could rely on the existence for