Les instabilités d’ordre de charge dans les conducteurs organiques quasi-unidimensionnels

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outline

- Focus on organic conductors undergoing important electron-electron interactions
- Charge density wave electronic instability and its coupling with the lattice
- In particular: $4k_F$ CDW instability in 1D / Charge ordering (CO) / Wigner localization
- In 2:1 salts: influence of the anion sublattice*
  Quarter band filling effect?

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**ONE DIMENSIONAL CONDUCTORS**

Structural anisotropy: \(d_{//}<d_{\perp}\)

\[
d_{//} \quad \vdots \quad \vdots \quad \vdots \quad d_{\perp}
\]

Anisotropy of overlap of wave functions

- Organics: \(p\pi\)
- Inorganics: \(dz^2\)

\[
\sigma \quad \begin{pmatrix}
\pi \\
t_{\text{perp}}
\end{pmatrix}
\]

\(t_{//} \gg t_{\perp}\)

Anisotropy of electronic properties:

charge transport \(\sigma_{//}(\omega) \gg \sigma_{\perp}(\omega)\)

**real 1D conductor**: no coherent interchain electronic transfert imply: \(t_{\perp} \ll \pi k_B T\) (Fermi surface thermal broadening)
ORGANIC CHARGE TRANSFERT SALTS

2 bands crossing at $E_F$

$2k_F(A) = 2k_F(D)$

Only a single 2$k_F$ critical wave vector!

Charge transfer $\rho$: $D^+\rho A^-\rho$ $2k_F = \rho/2$
(TM)$_2$X: BECHGAARD and FABRE SALTS

TM: TMTSF or TMTTF

Se or S

zig-zag chain of TM

X centrosymmetrical: AsF$_6$, PF$_6$, SbF$_6$, TaF$_6$, Br

X non centro: BF$_4$, ClO$_4$, ReO$_4$, NO$_3$, SCN

1 hole per formula unit: $2k_F = 1/2a^*$
1D metal coupled to the lattice: unstable at 0°K towards a Periodic Lattice Distortion which provides a new $(2k_F)^{-1}$ lattice periodicity.

PLD opens a gap $2\Delta$ at the Fermi level: insulating ground state.
Charge density wave ground state

Charge density wave has two components*:

- Periodic Lattice Distortion $u(x)$ (PLD)**
  - observed by diffraction (information in reciprocal space: $u(q)$)

- Modulation of the electronic density $\rho(x)$ (electronic CDW):
  - observed by STM (information in direct space)

\[ \rho(x) = -\frac{\partial u(x)}{\partial x} \]

**in practice the PLD modulates the inter-site (bond) distance

one has a $2k_F$ bond order wave (BOW)

* not always the case if $2k_F = 1/2$: the BOW and CDW can be decoupled

- $a^*/2$ BOW: (CH)$_x$ : $\equiv\equiv\equiv\equiv\equiv$ all the C atoms have the same environment: no CDW

- idem for a $a^*/2$ CDW: O o O o all the bonds are identical: no BOW

**
CDW instability: driven by the divergence of the electron-hole response function $\chi(q)$

$$\chi_e = \sum_k \frac{f(E_{k+q}) - f(E_k)}{E_{k+q} - E_k}$$

(for non interacting electrons)

Divergence of $\chi(q)$ for $q$ such that $E_{k+q} \sim E_k$

PLD fingerprint of $q$ wave vectors at which $\chi(q)$ diverges
$2k_F$ modulated chain

Satellite lines:

Fourier transform of a modulated chain: diffuse sheets in reciprocal space detected by diffraction methods (X-ray diffuse scattering: Guinier’s school)
TSF-TCNQ: 2$k_F$ CDW / BOW* instability

Charge transfer

$\rho = 0.63$

*2$k_F$ modulation of the TSF intra-molecular distance

Yamaji et al J.Physique 42, 1327 (1981)
TTF-TCNQ: 2kF and 4kF CDW/BOW!

2kF instability on the TCNQ stack

4kF instability on the TTF stack

2k_F Peierls transition for non interacting Fermions
(exists whatever the strength of the electron-phonon coupling)

\[ \rho = (2) \times 2k_F \]

4k_F Peierls transition for spinless Fermions (no double occupancy \( U \gg t \))
(exists only if the electron-phonon coupling is strong enough)

\[ \rho = 4k_F \rightarrow \text{Average distance between charges: } 1/\rho = (4k_F)^{-1} \]

The 4k_F CDW can correspond at the first Fourier component of a 1D Wigner lattice of localized charges
$4k_F$ phase diagram for spinless fermions with long range coulomb interactions

$$\text{limit } U \to \infty.$$ $$\hat{H} = -t \hat{T} + V \hat{W} = \sum_k \epsilon_k c_k^+ c_k + \frac{1}{2L} \sum_q' V(q) \rho_q \rho_{-q}.$$ $$\epsilon_k = -2t \cos k.$$ $$V(q) = -V \ln[2(1 - \cos q)].$$ $$\rho_q = \sum_k c_{k+q}^+ c_k.$$

$4k_F = n$ (d_{\phi} *)

**FIG. 3.** Average occupation of site $l$ for different values of the interaction strength at $n = 1/8$: $V = 0.5t$ (triangles), $V = 20t$ (circles), $V = 500t$ (squares). Lines are guides to the eye.

**FIG. 5.** Phase diagram for the spinless model (9). A charge-ordered state persists for all commensurate fillings with three characteristic regimes, from top to bottom: (I) generalized Wigner lattice, (II) Wigner crystal and (III) small-amplitude charge-density wave.

**ORGANIC CONDUCTORS**

Extended Hubbard Model:

\[ H = H_0 + U \sum_i n_i \uparrow n_i \downarrow + \sum_{i,m>0} V_{m} n_i n_{i+m} \]

1D correlated fermion gas: no quasiparticle

only CDW, SDW and supraconductivity fluctuations

The most diverging fluctuation at low T depends upon:

- The strength and range of Coulomb interactions: \( K_\rho > 0 \)
  - \( K_\rho < 1 \) density waves / \( K_\rho > 1 \) superconductivity

- The sign of the 2kF Fourier transform of the Coulomb interaction:
  - \( g_1 = U + 2V_1 \cos \pi \rho \)
    - If repulsion \( (g_1 > 0) \): Tomonaga Luttinger Liquid
    - If attraction \( (g_1 < 0) \): Luther Emery Liquid

\[ U \sim 4t_{1//} \sim 1 \text{eV}; \ U/V_1 \sim 2-3; \ V_2 \text{ relevent?} \]
PHASE DIAGRAM OF THE 1D INTERACTING ELECTRON GAS

Charge sector ($K\sigma = 1$)

Coexistence of $2k_F$ and $4k_F$ CDW!

$2k_F$ incommensurate no unklapp scattering

(H. Schultz)
Divergence of the CDW electron-hole response function (U, V ≥ 0 case)

\( T \to 0: \chi(2k_F) \) diverges

\( T \to 0 \): both \( \chi(2k_F) \) and \( \chi(4k_F) \) diverge

\( U = 0 \)

\( V = 0 \)

\( U \to \infty \)

\( \chi(2k_F) \) diverges

\( \chi(4k_F) \) diverges

$2k_F$ and $4k_F$ CDW / BOW instabilities in TMTSF-DMTCNQ

Charge transfer: $\rho = 1/2$

$2k_F = 1/4a^*$  $4k_F = 1/2a^*$

$2k_F$ and $4k_F$ BOW instabilities are both located on the TMTSF stack
BOW instability on the donor stack

Increase of the polarizability of the molecule

HMTSF

2kF BOW

TSF

1/2

1

2kF + 4kF BOW

HMTTF

two more cycles

1/3

0

4kF BOW

TTF
In charge transfer salts:
the $2k_F$ BOW instability drives the Peierls transition
the $4k_F$ BOW instability is at most weakly divergent
Crossover from a dominant $2k_F$ instability to a dominant $4k_F$ instability in NMP$_{1-x}$Phen$_x$ TCNQ

Reduction of the interchain screening* promotes the divergence of the $4k_F$ instability!


*screening between electron (TCNQ) and hole (NMP) 1D gas
2\(k_F\) BOW instability on the TMTSF stack

- **diverges** in TMTSF-DMTCNQ
  - Charge transfer salt with \(\rho=0.5\)

- **vanishes** in \((TMTSF)_{2}\)PF\(_6\)
  - 2:1 cation radical salt: \(\rho=0.5\)

What about the \(4k_F\) instability in \(\frac{1}{4}\) filled single chain organic salts?
4k_F charge localization in a quarter filled band (ρ=1/2)

- U, V_1 phase diagram (Mila & Zotos EPL 24, 133 (1993))

- In the insulating phase the electrons are localized:
  - on one bond out of two (4k_F BOW: Mott Dimer)
  - on one site out of two (4k_F CDW: Charge Ordering)
4k_F BOW: Mott dimers
(all the sites are equivalent; the bonds are different)

Exemple 1:2 TCNQ salts

MEM (TCNQ)_2 : T<335K

(S. Huizinga et al PRB 19, 4723 (1979))
4K_F CDW: Wigner charge order

NMR shows that the 2 sites are different: charge disproportion

First experimental evidences in $\frac{1}{4}$ filled organic conductors D_2X or A_2Y:

- $(\text{TMP})_2X$-CH$_2$Cl$_2$ $(X=\text{PF}_6, \text{AsF}_6)$
  (Ilakovac et al PRB 52, 4108 (1995))
  but problem of disorder due to solvant

- $(\text{DI-DCNQI})_2\text{Ag}$ (uniform stack)
  1998-1999

- $(\text{TMTTF})_2X$ $(X=\text{PF}_6, \text{AsF}_6, \text{SbF}_6, \text{ReO}_4, \ldots)$ (dimerized stack)
  2000-2001

Role of the cationic/anionic sublattice in the stabilization of the CO?
NMR: inequivalent molecular sites: charge disproportion below ~210K
(K. Hiraki et al PRL 80, 4737 (1998))

4k_F = 1/2c* X-ray scattering: quasi-1D at RT
chain dimerization below ~ 220K
(Y. Nogami et al Synth. Met. 102, 1778 (1999))
4k_F CO and BOW in (DI-DCNQI)_2Ag

shift of Ag^+ towards charge rich DCNQI

charge pattern reveals 3 kinds of stack in the CO state!

Charge rich aeras form a body centered tetragonal structure

charge on the sites
charge on the bonds
intermediate situation

Charge pattern imposed by the interchain Coulomb coupling?

Kakiuchi et al PRL 98, 066402 (2007)
Charge ordering transition in (TMTTF)$_2$X

- Charge disproportion at $T_{CO}$
- 2 different molecules: NMR line splitting

Chow et al. PRL 85, 1698 (2000)

- Charge disproportion + incipient lattice dimerization (4$k_F$ BOW)
  - no inversion centers: ferroelectricity at $T_{CO}$
    Montceau et al. PRL 86, 4080 (2001)

Symmetry breaking at $T_{CO}$
- Difficulties to detect it due to:
  - the very low symmetry of the lattice
  - X-ray irradiation damages
Lattice anomaly at the CO transition (thermal expansion)

$c^*$ soft direction:
softening could be achieved by a transverse shift of the anions

$\beta/T \sim \delta^2 F/\delta T^2$

Additional transition at $T_{\text{int}}$?

Shift of the anion sublattice $X$ with respect to TMTTF sublattice

- $\rho_h = 0.5 + \delta$
- $\rho_e = 0.5 - \delta$

Shift of the anion sublattice required to break the inversion symmetry and to achieve ferroelectricity (S. Brazovski)
Hypothetical charge pattern of ferroelectric TMTTF

Anion X⁻ points towards hole rich TMTTF

3D Coulomb interactions minimized? anion shift seems to be essential to impose the charge pattern
2:1 salts with 1/4 (3/4) or 1/2 Band filling

- \((\text{DI-DCNQI})_2\text{Ag}\) - uniform stack
  ¼ filled system undergoing a 4\(k_F\) CDW instability

- \((\text{TMTT(S)}\text{F})_2\text{X}\) - zig-zag dimerized
  ½ or 3/4 filled system if the dimerization gap \(2\Delta\) is larger or smaller than \(W\perp\) or \(\pi k_B T\)

\[
\begin{align*}
\text{(TMTTF)}_2\text{PF}_6 : & 2\Delta \approx 88\text{meV} \\
W_b \approx 55\text{meV} & 1/2 \text{ filled system} \\
\text{(TMTSF)}_2\text{PF}_6 : & 2\Delta \approx 86\text{meV} \\
W_b \approx 130\text{meV} & 3/4 \text{ filled system}
\end{align*}
\]

• δ-(EDT-TTF-CONMe$_2$)$_2$Br –
  « average structure » Pmna
  approximate symmetry: non planar molecule located on the mirror m (→ no stack dimerization: approximate statement)
  glide plane a → all molecules are identical (no CO)
  close to 3/4 filled system at RT

  in fact superlattice modulation (0,1/2,0) at RT
  structural refinement → weak dimerization + CO at RT

• (DMtTTF)$_2$ClO$_4$ - uniform zig-zag (2$_1$ screw axis symmetry)
  ¾ filled
Figure 1a: Crystal structure of (DMtTTF)$_2$ClO$_4$; projection perpendicular to the stacking axis.

Figure 2: Electrical conductivity of the DMtTTF salts. Note that the low temperature activation energy is smaller than for (TMTTF)$_2$AsF$_6$ also given for comparison.

Coulon et al. J. Physique 47, 157 (1986)
X-ray diffuse scattering investigation of (DMtTTF)$_2$ClO$_4$

Short range incommensurate anharmonic Modulation \( \mathbf{q} = (-0.58, 0, 0.275) \)

Diffuse spots Main Bragg reflections

Stack periodicity

Figure 2. X-ray patterns of the (H 4 L) reciprocal plane of (DMtTTF)$_2$ClO$_4$ at 12 K (left) and 250 K (right). The complete patterns were obtained using the monoclinic symmetry from the effectively measured [001] part. Intensities are on a logarithmic greyscale. For the sake of simplicity, the monoclinic angle \( \beta \) has been set to 90°.

Figure 3. a) Temperature variation of the (2 4 -1)+\( q_y \) and (2 4 -1)+3\( q_y \) diffuse spots peak intensity. b) Temperature variations of the (2 4 -1) and (0 4 0) Bragg reflections intensity. Full/open symbols represent data obtained by cooling down/heating up.

$4k_F$ order does not involve the spin degrees of freedom which remains free to order at low $T$.

$\chi_S$ not perturbed at the CO transition.

$4k_F$ order well decoupled from the low $T$ ground state involving $S=1/2$ coupling.
Partial conclusions

• $4k_F$ or CO instability are not new in the organic conductors: known since 1976 in the charge transfer salts!
• In 2:1 salts $4k_F$ intrastack instability strengthened by the reduction of the interchain screening
• Cooperative role of the anion (cation) sublattice to stabilize the CO ground state
• Is there anything special for $\frac{1}{4}$ band filling?

more the order of commensurability $n$ of the filling increases more the $V_n$ coulomb interactions must be important to induce a Wigner charge localization in 1D
Indirect contribution to $V_2$ interaction via Coulomb coupling with the anion sublattice

**Contribution to the polarisability of the anion sublattice**

\[ V_2^{\text{eff}} \approx V_2 + (\lambda_{eA})^2 \text{FT}\left[ \chi_{A}(q,\omega) \right]_{i=j=a} \]

which can be high near a structural transition involving an anionic shift

Quantum chemistry calculations on clusters of TMTTF molecules for intrastack interactions:

\[ V_1^D \sim V_1 | \sim U/2 \]
\[ V_1 \sim 1.5 \; V_2 \]


The polarisability of the anions and the screening effects are ignored.
Explicit consideration of repulsive $V_2$

$t, U, V_1, V_2$ extended 1D Hubbard model

Ground state:

Well below this line: $4k_F$ CDW  O o O o O o O

Well above this line: $2k_F$ CDW  O O o o O O

For $V_2 \sim V_1/2$ frustration: metallic state (TLL) preserved

However frustration effects can be lifted by small perturbations (chain dimerization, anion ordering)

(Ejima et al PRB 72, 033101 (2005))