Introduction to the physics of organic conductors and superconductors

Part I

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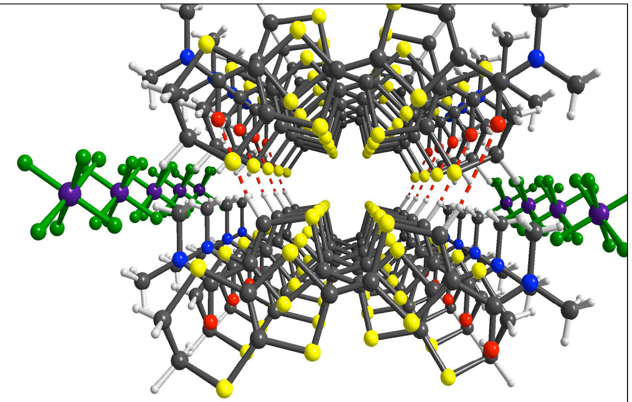
Summer school Boulder July 2008

UNIVERSITÉ DE SHERBROOKE

Molecular organic conductors



Variety of *quasi-one*-dimensional materials

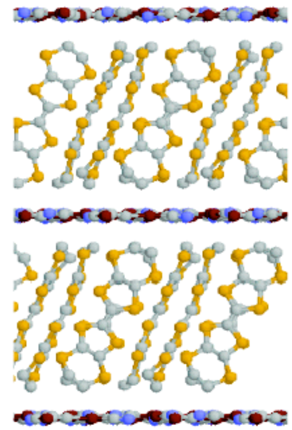
Rich phenomenology:

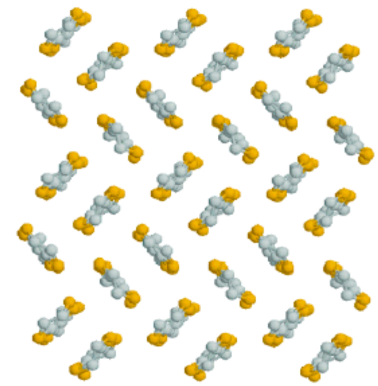
LRO: Charge-density-wave, spin-Peierls, Néel AF, spin-density-wave, charge order, ferroelectricity, quantized spin-density-wave, ... superconductivity ... sliding CDW, SDW

'normal phase': Luttinger liquid, Luther-Emery liquid, Mott, confinement, ...

Fermiology: Quantum oscillations, quantized Hall effect, AMRO resonances ....

Spin Ladders ...





Variety of *quasi-two*-dimensional materials

LRO: Néel, superconductivity, Mott transition line and critical point, charge order, Jaccarino-Peter SC phases, FFLO (?) ...

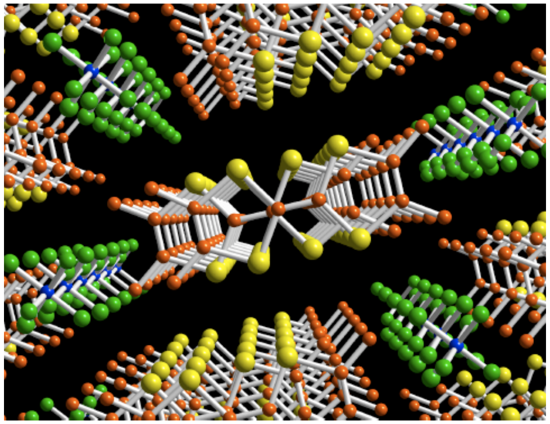
Pseudo-gap, spin liquid (RVB ?), Dirac cones (~ graphene)

Fermiology: SdH, dvH, ...

Outline

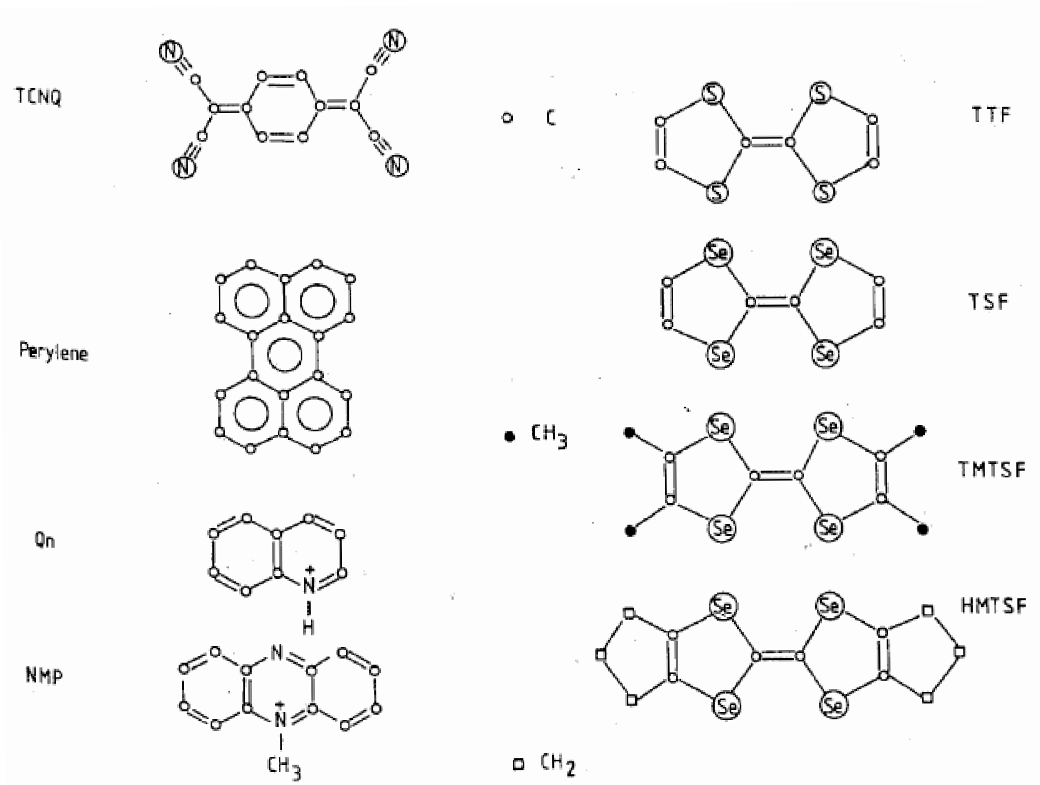
I-Quasi-1D materials: Era of Peierls like materials (70's), The route towards the synthesis of first organic superconductors $(TMTSF)_2X$ and $(TMTTF)_2X$.
One dimensional quantum features, application of the renormalization group to the normal phase.

II-Quasi-1D materials: electronic confinement, ordered phase, supercondcutivity and antiferromagnetism

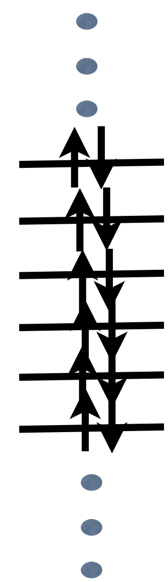


Organic molecular crystals : packing of flat molecules

Texte



Closed shell molecules
HOMO filled (2e)



One component molecular compound: band insulator
(one exception)

Recipe for a metal: combination of two different molecular species

good donnor (of e^-) good acceptor

D A

$\xrightarrow{\delta e}$

D A ⇨ $D^{+\delta}$ $A^{-\delta}$

D A $D^{+\delta}$ $A^{-\delta}$

D A $D^{+\delta}$ $A^{-\delta}$

D A $D^{+\delta}$ $A^{-\delta}$

D A $D^{+\delta}$ $A^{-\delta}$

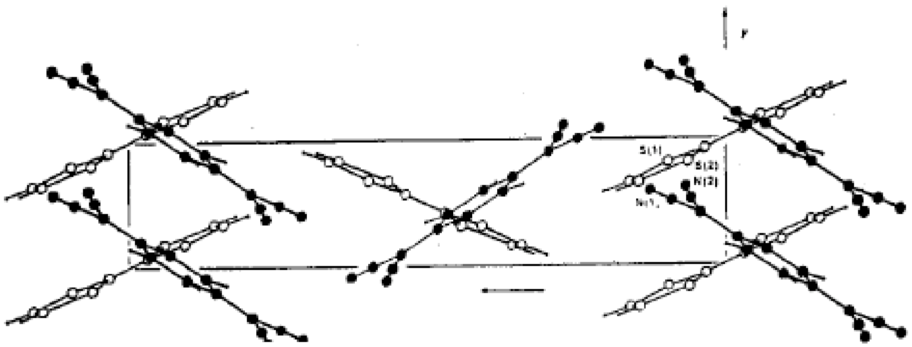
$HOMO^{+\delta}$ $LUMO^{-\delta}$

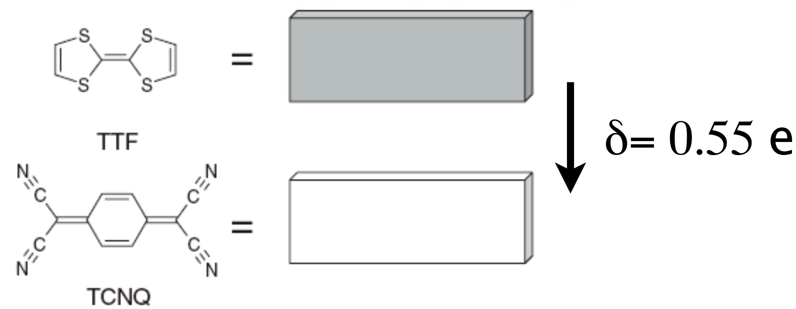
Partly filled band formation ⟶ metal

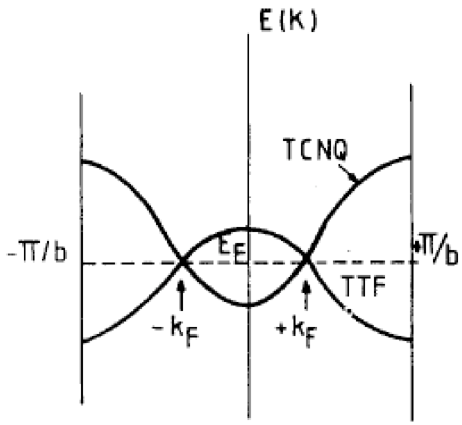
Lucky marriage of TTF (donor, 1972) and TCNQ (acceptor)

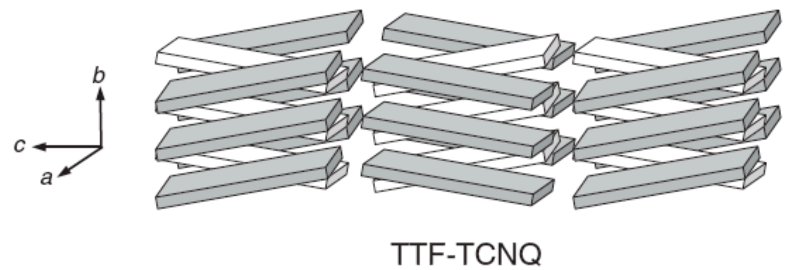
F. Wudl

TTF-TCNQ charge transfer salt (1973)





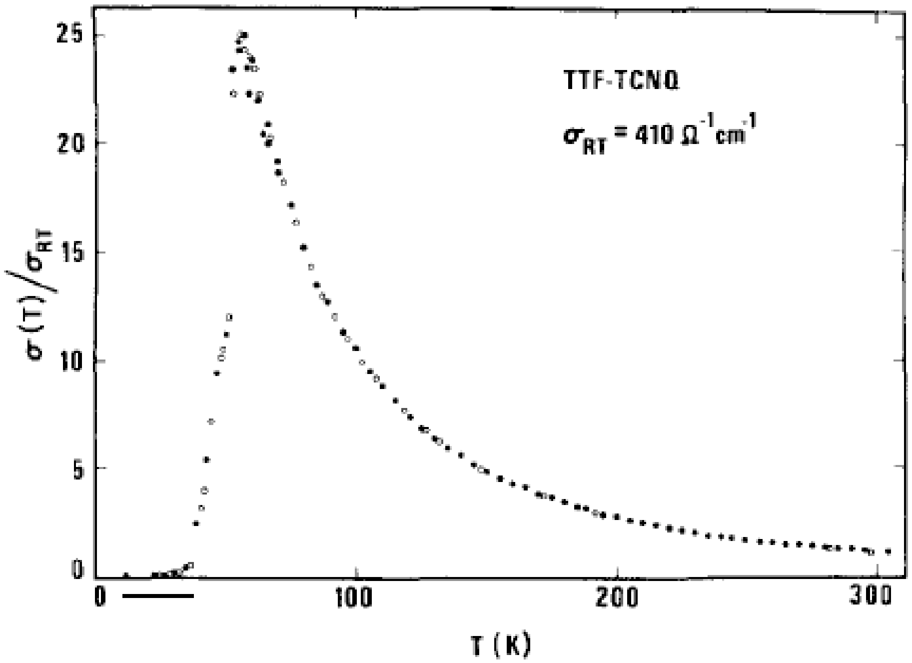




Pancake like piling, stronger elect. overlap in chain b direction

Much weaker interstack overlap: close realization of a 1D metal (quasi -1D)

TTF-TCNQ

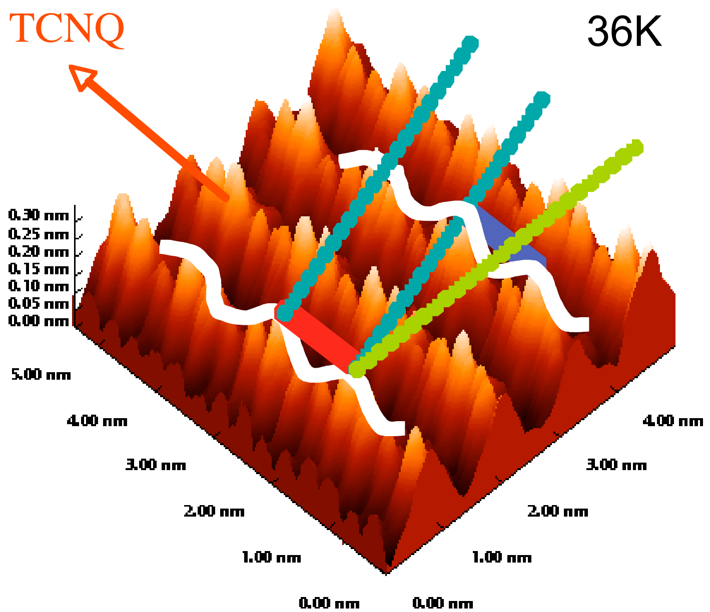


Coleman *et al*., Sol. State Comm. **12**, 125 (1973)
Ferraris *et al*., Sol. State Comm. **18**, 1169, (1976)

Large peak of conductivity $\sigma \sim 10^4(\Omega \cdot \mathrm{cm})^{-1}$

Initially interpreted by precursor of high temperature superconductivity !!

Sharp metal-insulator $T_c = 54\mathrm{K}$, CDW superstructure



STM-UHV study

Real space representation of the CDW

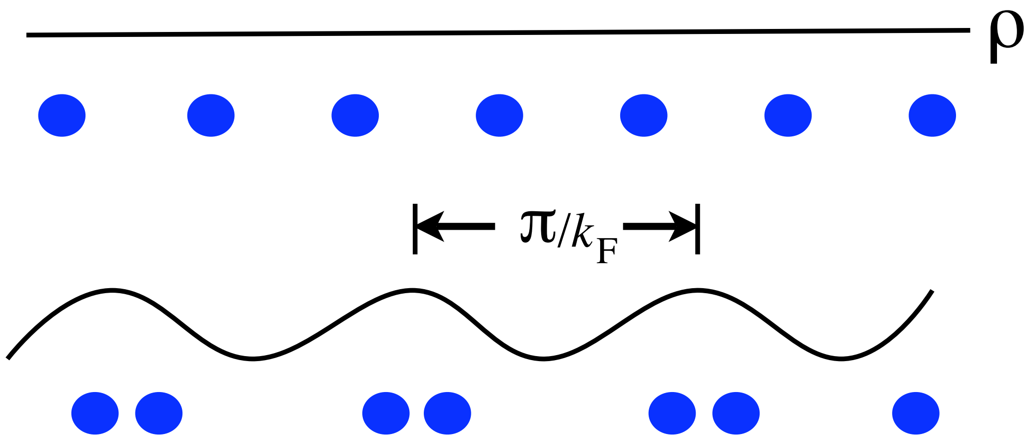
Charge density wave below 38 K

ordering λ_b=3.39b, λ_a=4a

Z.Z.Wang, et-al

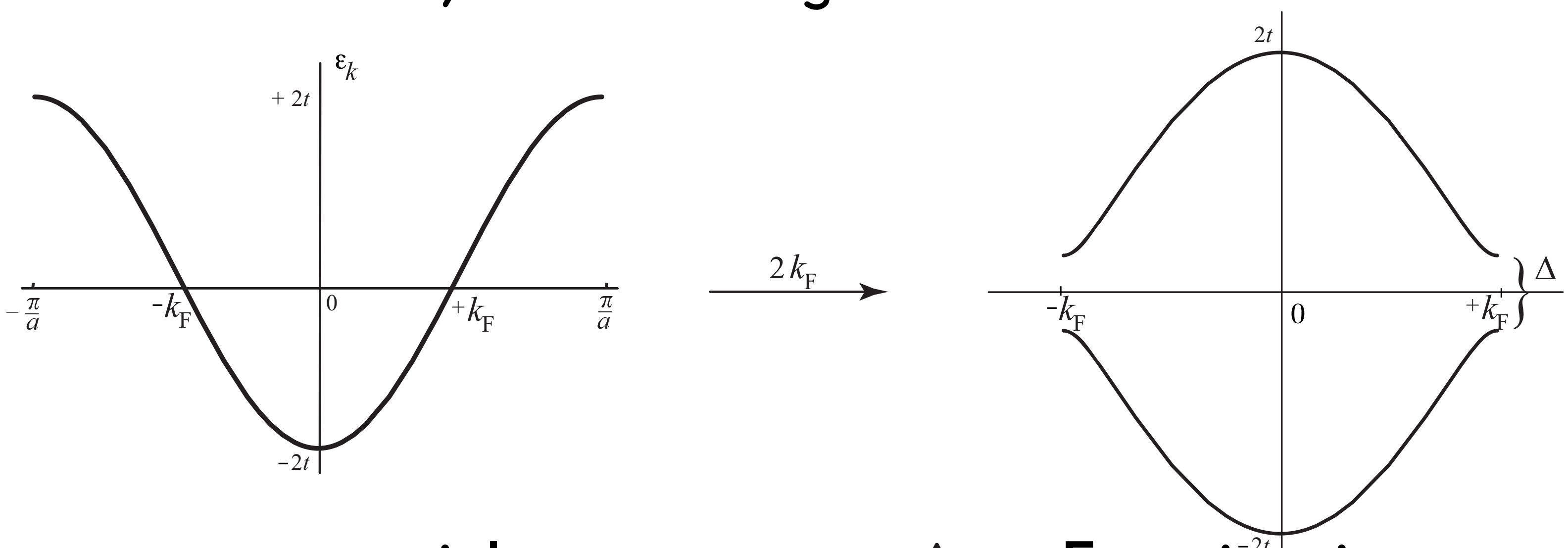
Phys.Rev.B,67, R121401 (2003)

Peierls mechanism of the CDW superstructure:



Rudolf E. Peierls

"A 1D metal always unstable against the formation of $2k_F$ CDW"



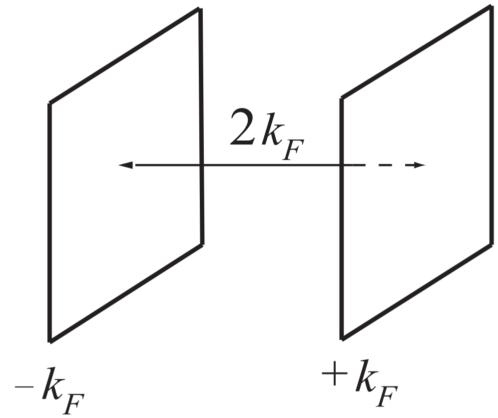
$2k_F$ potential opens a gap Δ at Fermi points

Mechanism of the Peierls instability in 1D

The driving force of the instability of the metallic state : *nesting*

Density response of free electrons (lindhard)

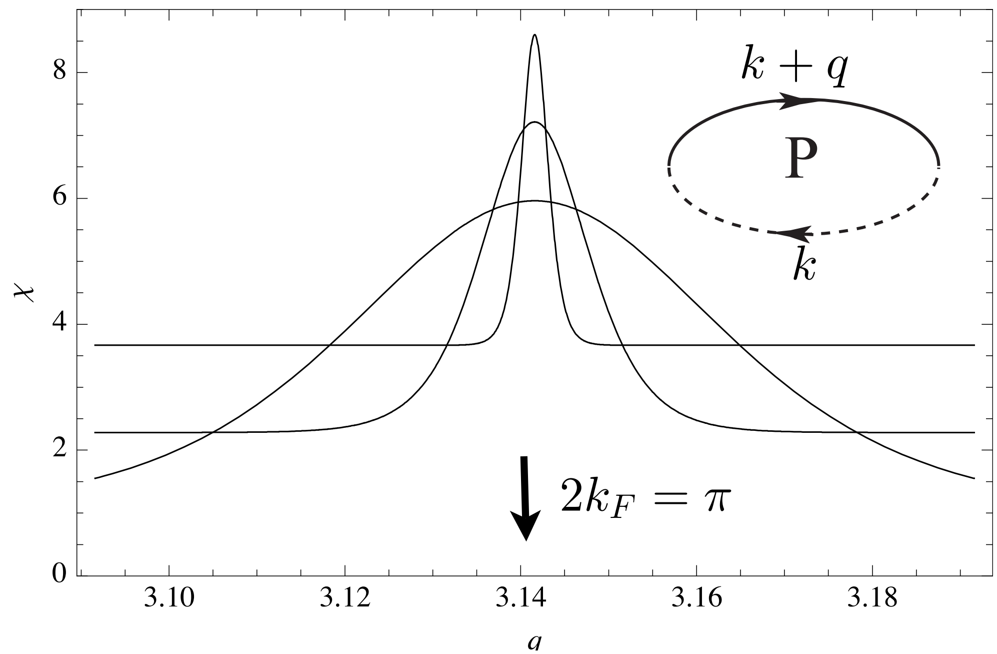
$$\chi_P^0(q,T) = \frac{1}{\pi}\int dk\, \frac{n(\epsilon_k) - n(\epsilon_{k+q})}{\epsilon_{k+q} - \epsilon_k}$$



$$\epsilon_k = -\epsilon_{k+2k_F} \quad \text{(e-h symmetry, } \forall \text{ k)}$$

$$\chi_P^0(2k_F,T) \sim \frac{1}{\pi v_F} \ln \frac{E_F}{T}$$

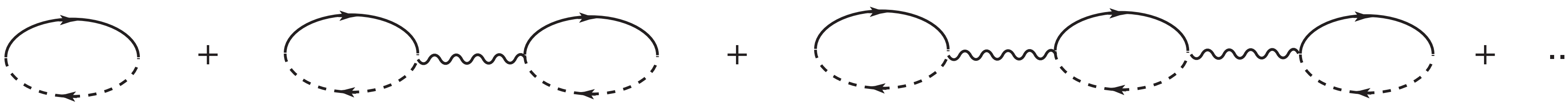
Singular response to CDW formation !



Electron-phonon interaction and the Peierls instability of the metallic state in one dimension

$$H = \sum_{k,\sigma} \epsilon_k \, c^\dagger_{k,\sigma} c_{k,\sigma} + \sum_q \omega_q b^\dagger_q b_q + \frac{g}{\sqrt{L}} \sum_{k,q,\sigma} c^\dagger_{k+q,\sigma} c_{k,\sigma} \left(b^\dagger_q + b_{-q} \right)$$

RPA series:



$$\begin{aligned} \chi_P(q,T) &= \chi^0_P(q,T) + \chi^0_P(q,T)\lambda\chi^0_P(q,T) + \chi^0_P(q,T)\lambda\chi^0_P(q,T)\lambda\chi^0_P(q,T) + \ldots \\ &= \frac{\chi^0_P(q,T)}{1-\lambda\chi^0_P(q,T)}, \qquad \lambda = g^2/\omega_D \end{aligned}$$

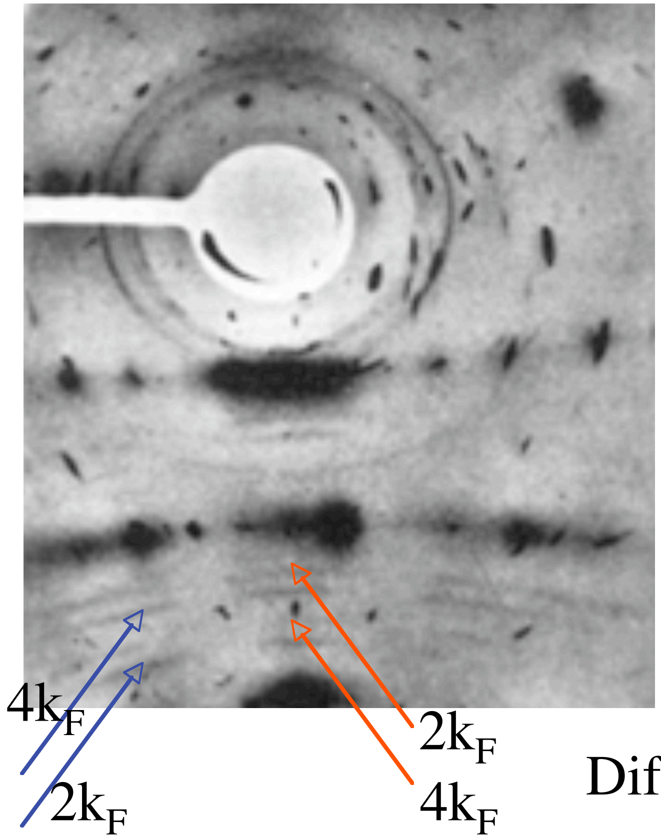
At $q = 2k_F$ $\quad \chi^0_P(2k_F,T) \sim \ln E_F/T \longrightarrow T^0_P = 1.13 E_F \, e^{-1/\tilde{\lambda}}$

'Critical' scale for the Peierls instability

MF-RPA theory: Caveat

No phase transition in 1D $\longrightarrow$ T_P^0 is a scale for fluctuations

1D Peierls Fluctuations seen by X-ray diffuse scattering



Diffuse lines above T_P

J.P. Pouget et-al, PRL, 37, 437, 1976

CDW Peierls state : the common fate of two chain molecular conductors syntheiszed in the 70's

TTF-TCNQ, TSeF-TCNQ, HMTSF-TCNQ, HMTTF-TCNQ, ...

But CDW organic (and inorganic !) systems give rise to a very rich phenomenology

- Sliding CDW (Frölich mode of coduction [1953-4]), found e.g in TTF-TCNQ

- Pinning, commensurability, glass behaviour, memory effects, ...

Mobilized the attention of chemists, experimentalists and theorists in the 70's and the begining of 80's

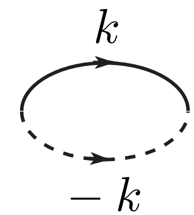
Is (organic) superconductivity possible ?

Why the Peierls instability apparently wins ?

A closer look to Cooper e-e pairing channel ...

Cooper pairing response of free electrons ($\epsilon_k = \epsilon_{-k}$)

$$\chi_C^0(q,T) \;=\; \frac{1}{\pi}\int dk\,\frac{n(-\epsilon_k)-n(\epsilon_{-k+q})}{\epsilon_{-k+q}+\epsilon_k} \;\xrightarrow{q\,=\,0}\; \frac{1}{\pi v_F}\ln 1.13 E_F/T$$



As singular as the Peierls response !

True in any dimension (c.f. BCS instability)

The Cooper response coupled to phonons

Ladder summation:

$$g^2\ \mathcal{D}(q,\omega_m) \sim \frac{-g^2}{\omega_m^2+\omega_D^2}$$

Intermediate frequency summation and retarded interaction
(e-e mediated by phonons)

$$\chi_C(q=0,T) = \frac{\chi_C^0(T)}{1-\frac{1}{2}\tilde{\lambda}\ln\frac{1.13\omega_D}{T}}$$

BCS: $$T_C^0 = 1.13\omega_D\, e^{-2/\tilde{\lambda}} \quad \ll \quad T_P^0$$

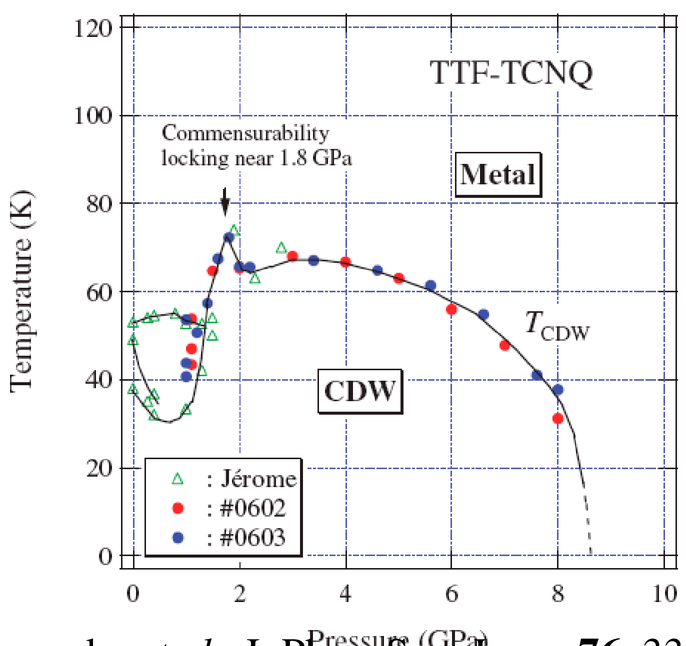
Typically : $\omega_D \sim 5\mathrm{meV}$ $\quad E_F \sim 0.5\mathrm{eV}$

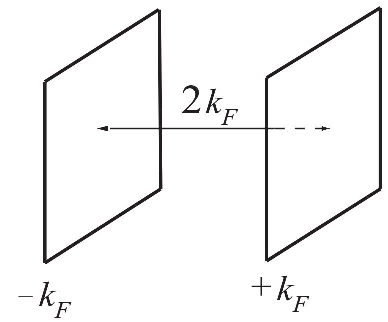
Getting rid of the Peierls instability ...

From experimental physics : Pressure studies

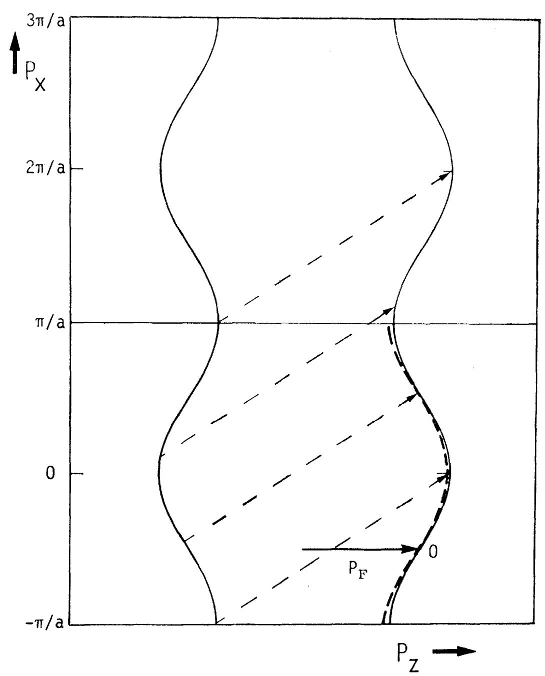
Increase of inter stack overlap
nesting mismatch grows

TTF-TCNQ up to 80 kbar





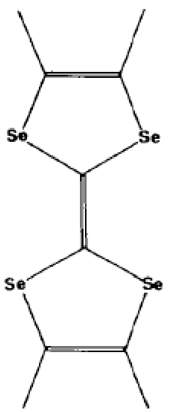
1D



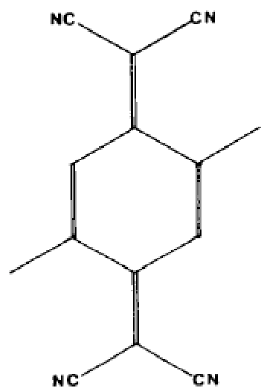
Q-1D

Yasuzuka *et al.*, J. Phys. Soc. Japan **76**, 33701(2007).
R. H. Friend *et al.*, PRL **40**, 1048, (1978)

The chemistry route : the synthesis of TMTSF-DMTCNQ

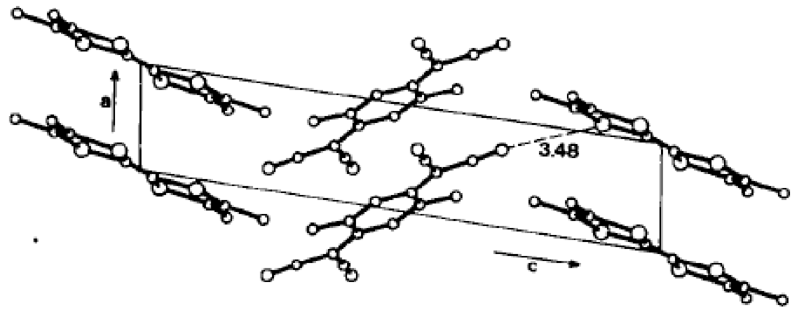


TMTSF



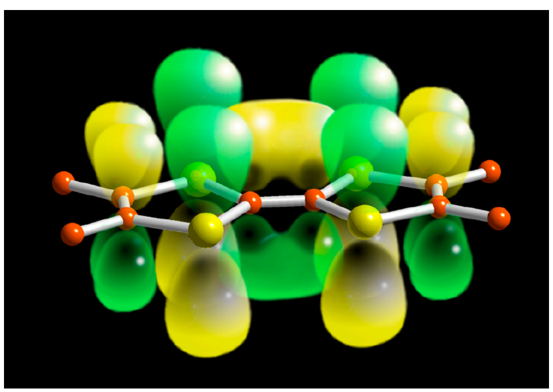
DMTCNQ

Endersen et al., Acta crystal.   (1978)



1/4-filled band conductor, δ= 0.5e, closer Se-Se (interchain) contacts

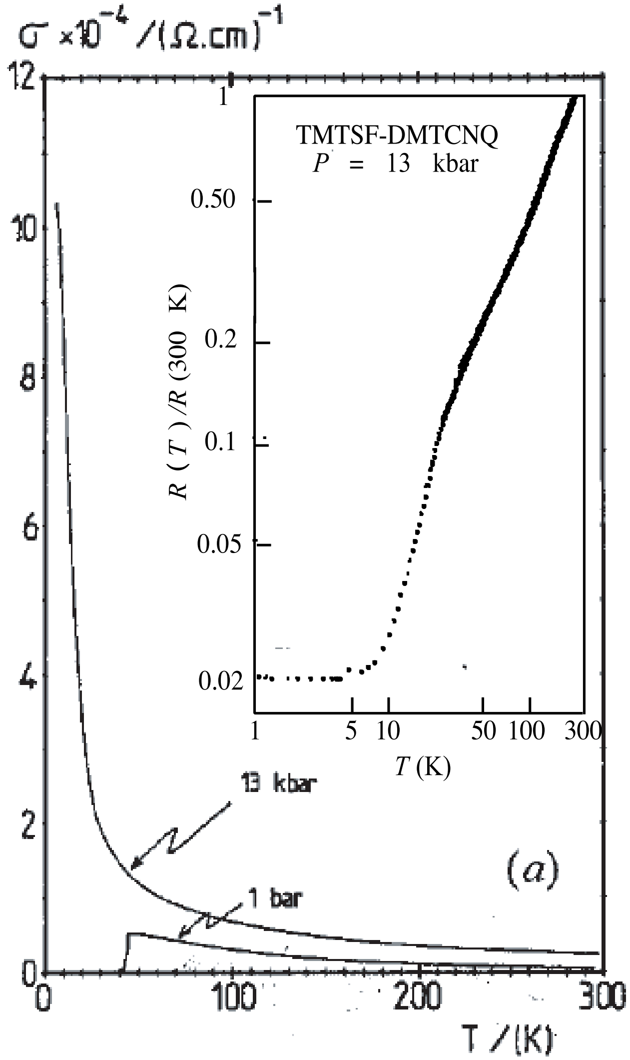
From the new donnor molecule : TMTSF (born from TTF)

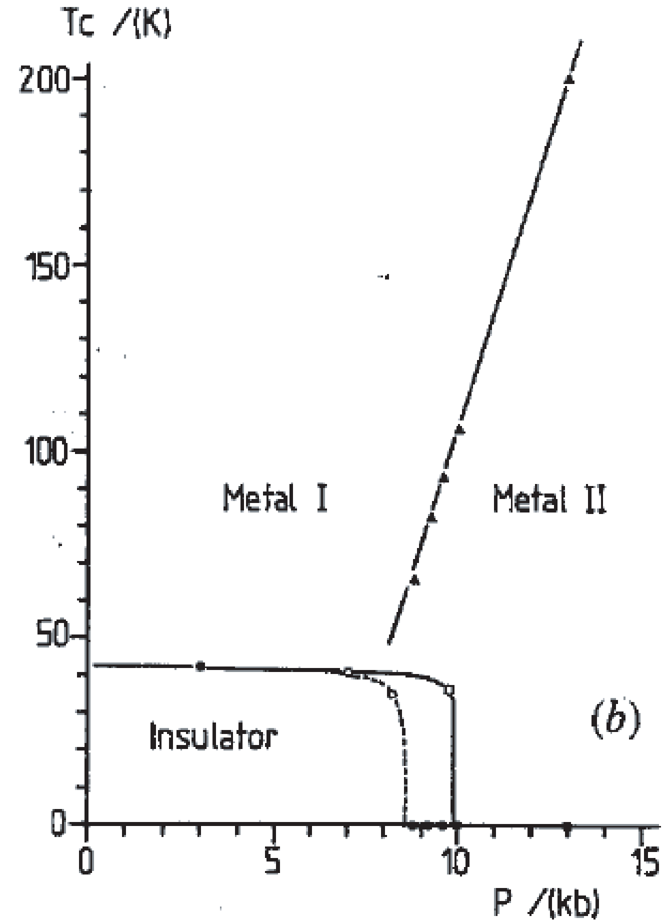


K. Bechgaard *et al.*, Chem. Comm. **22**, 937 (1974)

K. Bechgaard

TMTSF-DMTCNQ : the first stable organic metal





- 1bar : a Peierls insulator below 43 K (Jacobsen *et al*., PRB **18**, 905 (1978))
- 13 kbar: an excellent metal (Andrieux *et al*., J. Physique Lett. **40**, 381 (1979))

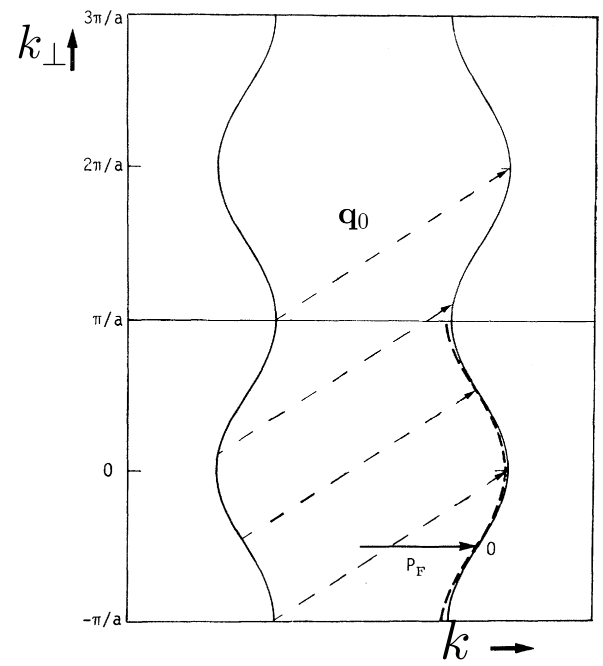
Nesting frustration and T_P

$$\epsilon_k \to E(\mathbf{k}) = \epsilon_k - 2t_\perp \cos(k_\perp) - 2t_{\perp 2}\cos(2k_\perp)$$

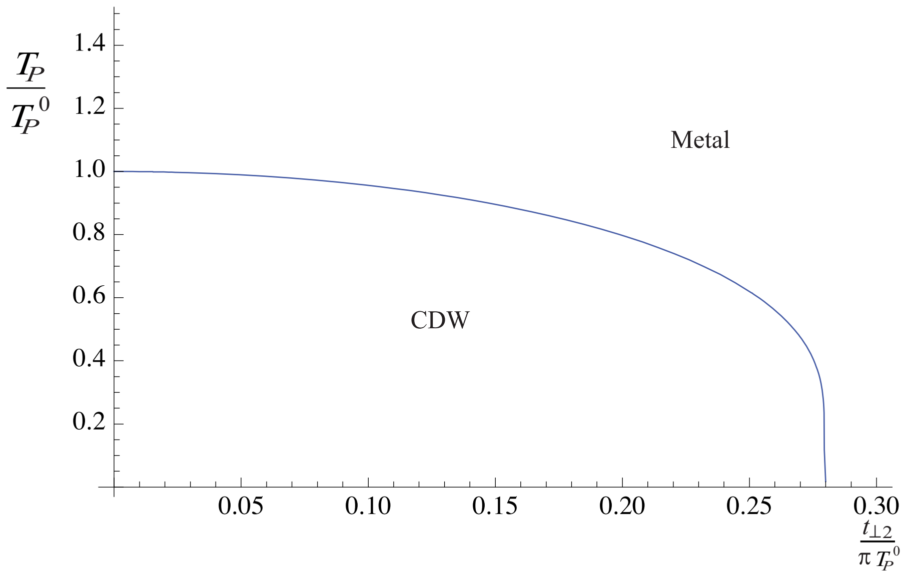
Nesting relation:

$$E(\mathbf{k}+\mathbf{q}_0) = -E(\mathbf{k}+\mathbf{q}_0) + \underbrace{4t_{\perp 2}\cos 2k_\perp}_{k_\perp \text{ - dep. deviations}}$$

$$\ln \frac{T_P}{T_P^0} = \psi\Big(\frac{1}{2}\Big) - \Big\langle \psi\Big(\frac{1}{2} - i\frac{t_{\perp 2}\cos 2k_\perp}{\pi T_P}\Big)\Big\rangle_{k_\perp}$$



Horovitz et al., Phys. Rev. B. ***12****, 3174 (1975)*



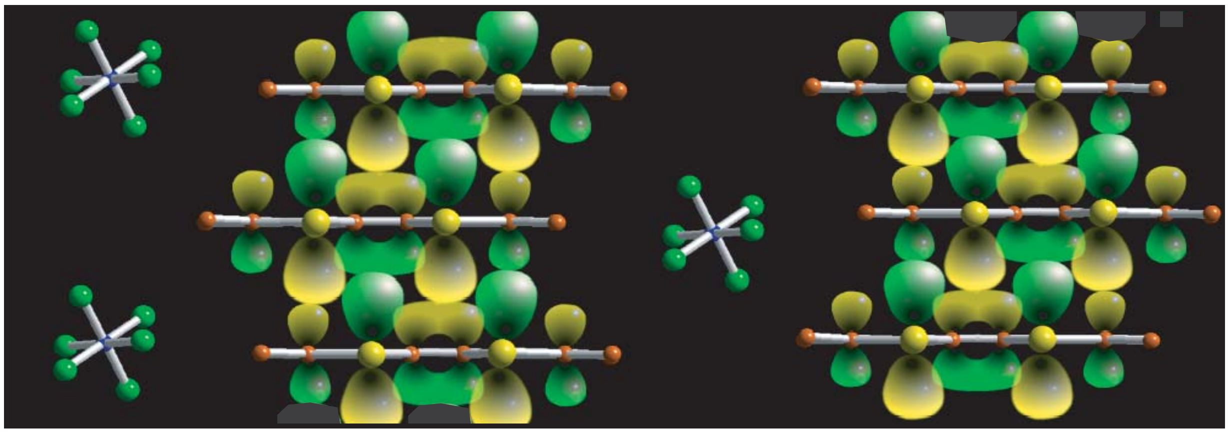
$t_{\perp 2}$ simulates pressure

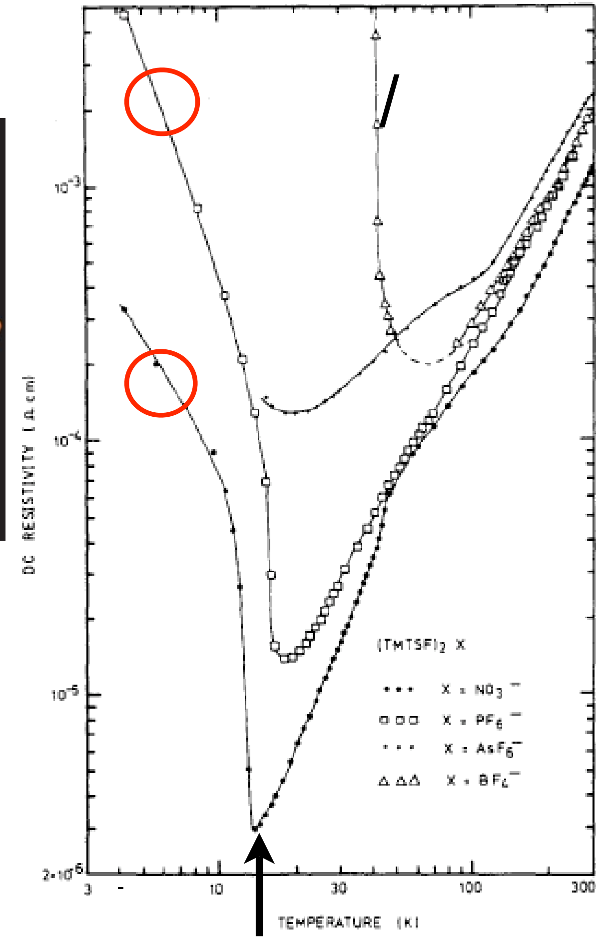
T_P suppressed at $t_{\perp 2} \sim 20$ K

Synthesis of a new series one-chain cation-radical salts

$(TMTSF)_2X$ $X = PF_6$, AsF_6, ClO_4, ... (radicals)

The Bechgaard salts





Very high conductivity $\sigma \sim 10^5 (\Omega \cdot \mathrm{cm})^{-1}$

Metal-Insulator transition at ~ 12K

K. Bechgaard *et al.*, Solid State Comm. **33**, 1119 (1980)

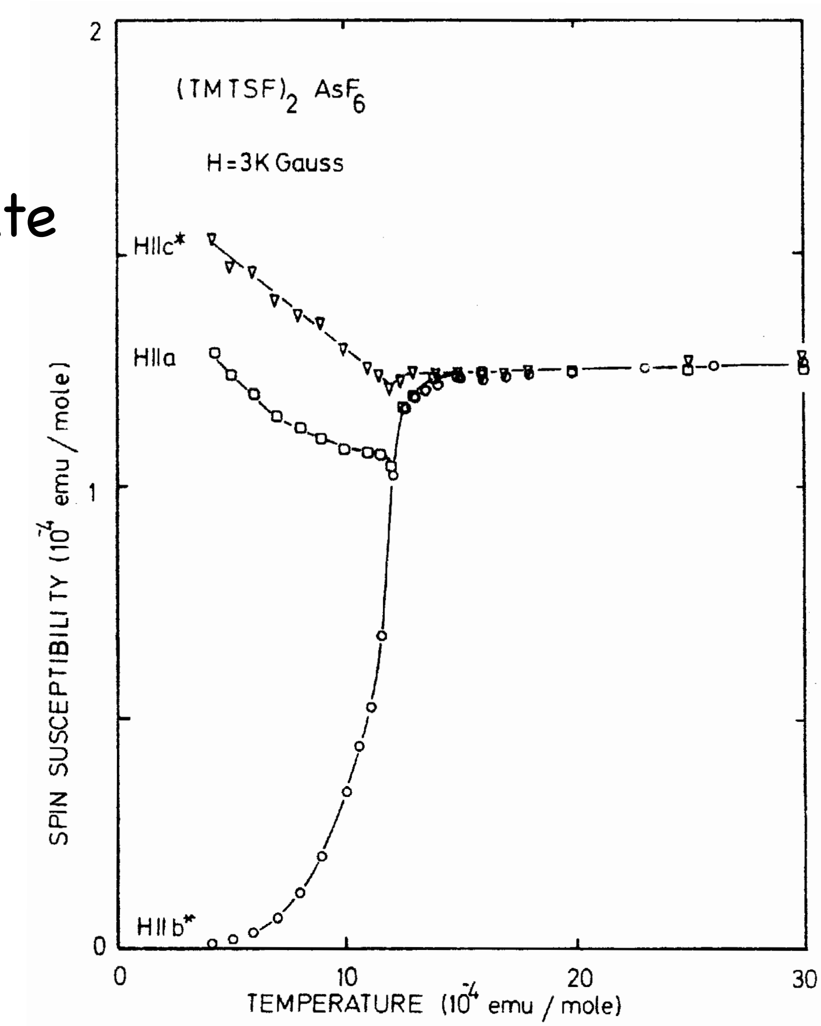
Nature of the insulating state: magnetic !

Itinerant antiferromagnet : SDW state

Confirmed by NMR:

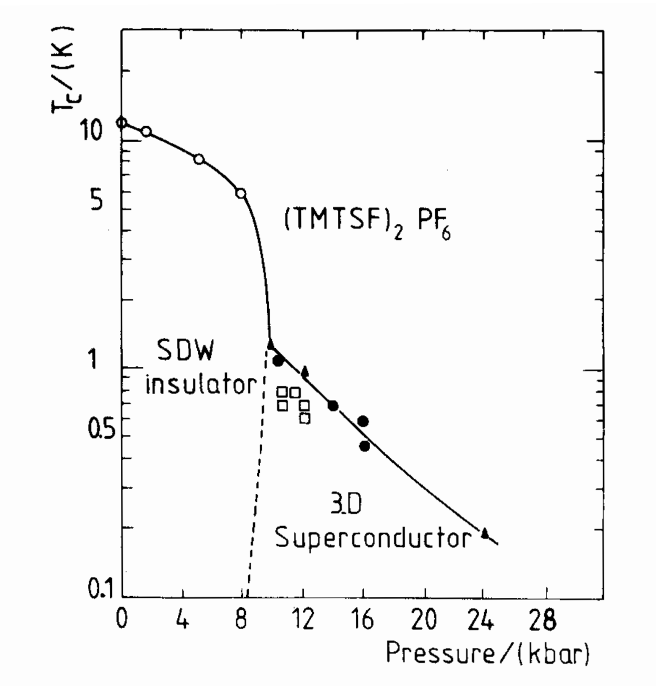
$$T_1^{-1}$$

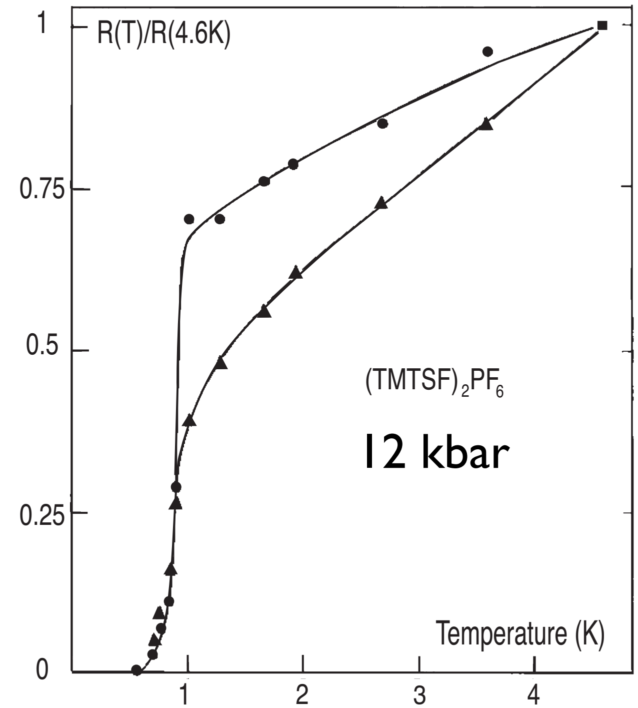
Line shape -> SDW modulation vector q_0



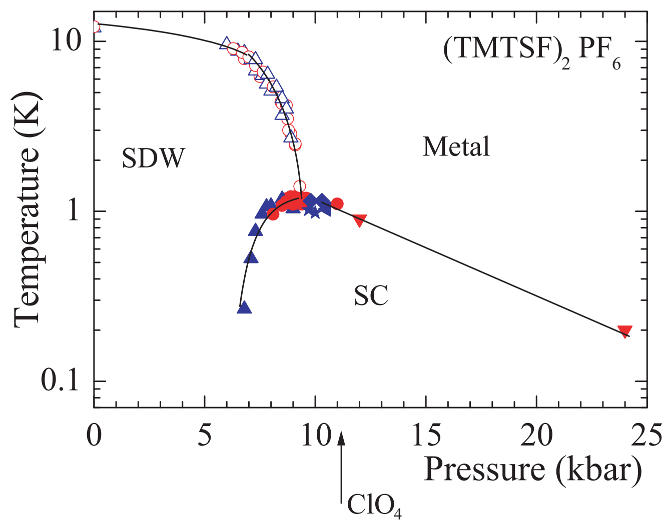
Mortensen et al., Phys. Rev. B

$(TMTSF)_2PF_6$ under pressure: the first organic superconductor





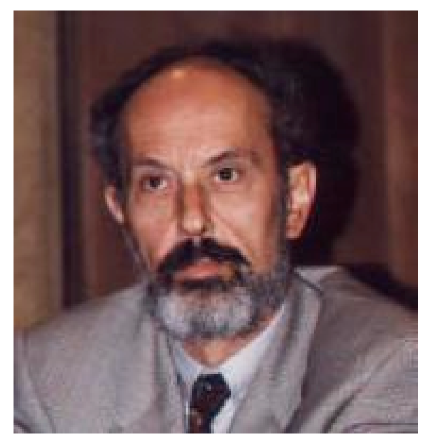
D. Jerome et al., J. Physique Lett. **41**, L-95 (1980)



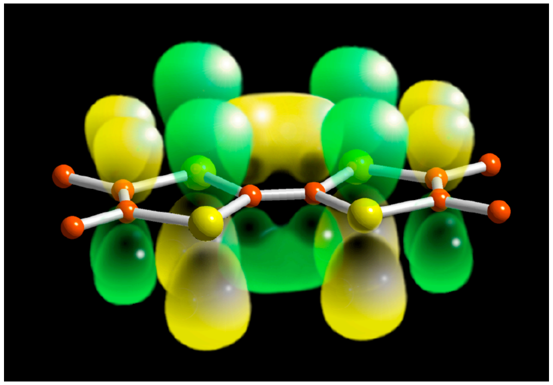
SDW- SC proximity

Max. T_c (boundary)

Unconventional SC ?



The Fabre salts: $(TMTTF)_2X$, X = PF_6, AsF_6, ClO_4 ...



TMTTF
sulfur instead of selenium

Brun *et al.*, C.R. Acad. Sc. (Paris) **284** C, 211 (1977)

J. M. Fabre

Isostructural to $(TMTSF)_2X$

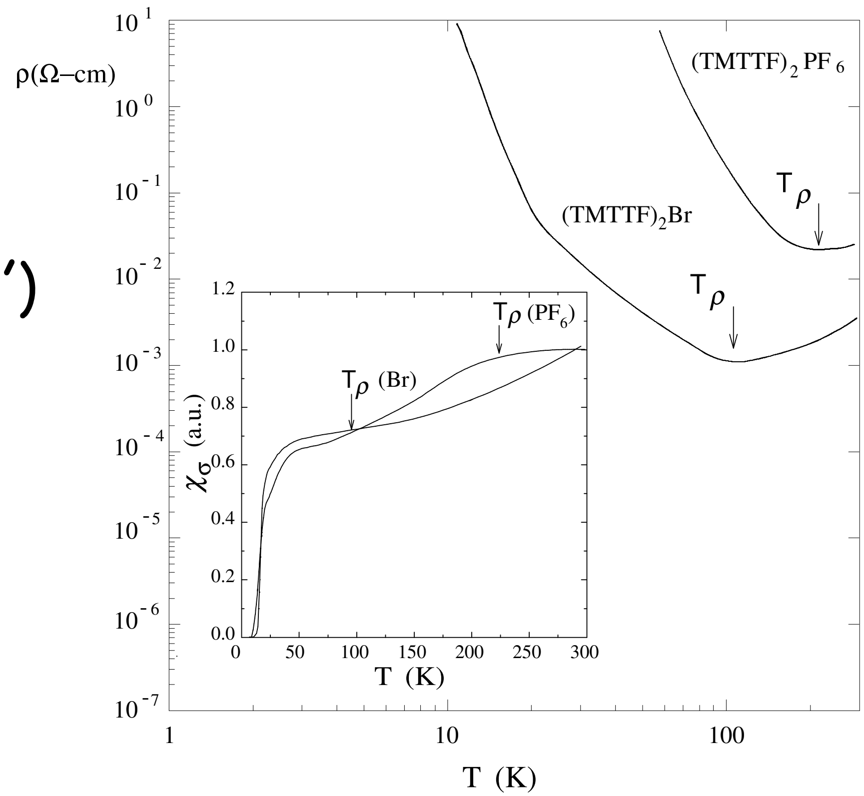
S-S > Se-Se distances ('More 1D')

Insulating at below T_ρ

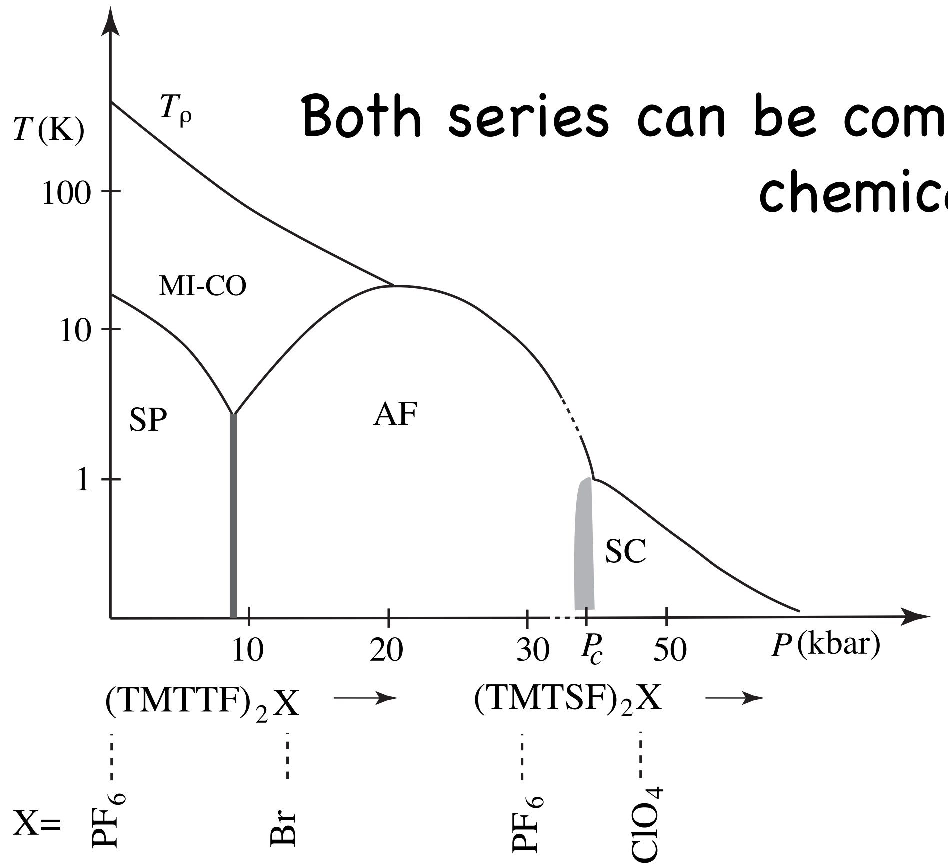
but spins are gapless !

Mott insulating !! (1D)

Coulomb int. dominates



Universal phase diagram of $(TMTTF)_2X$ and $(TMTSF)_2X$



Both series can be combined on the hydrostatic or chemical pressure

SP: spin-Peierls

AF: antiferromagnet

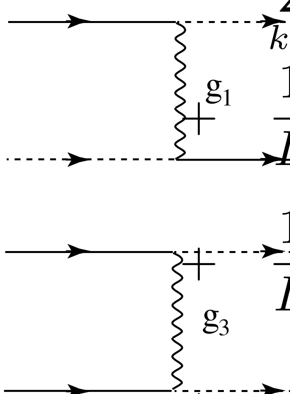
SC: superconductor

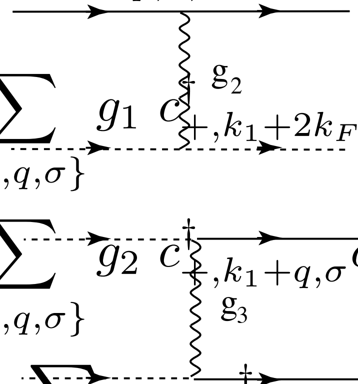
MI: Mott insulator

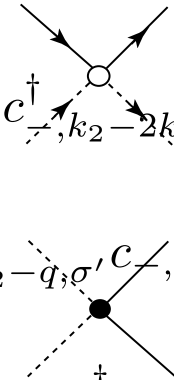
CO: charge ordered

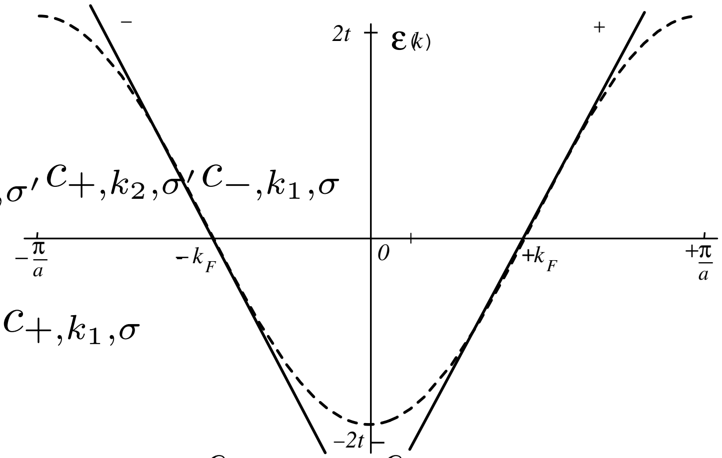
1D electron gas model and the non ordered phase of $(TMTTF)_2X$

$$
\begin{aligned}
H &= \sum_{k,p,\sigma} \epsilon_p(k) c^\dagger_{p,k,\sigma} c_{p,k,\sigma} \\
&+ \frac{1}{L}\sum_{\{k,q,\sigma\}} g_1\, c^\dagger_{+,k_1+2k_F+q,\sigma} c^\dagger_{-,k_2-2k_F-q,\sigma'} c_{+,k_2,\sigma'} c_{-,k_1,\sigma} \\
&+ \frac{1}{L}\sum_{\{k,q,\sigma\}} g_2\, c^\dagger_{+,k_1+q,\sigma} c^\dagger_{-,k_2-q,\sigma'} c_{-,k_2,\sigma'} c_{+,k_1,\sigma} \\
&+ \frac{1}{2L}\sum_{\{p,k,q,\sigma\}} g_3\, c^\dagger_{p,k_1+p2k_F+q,\sigma} c^\dagger_{p,k_2-p2k_F-q+pG,\sigma'} c_{-p,k_2,\sigma'} c_{-p,k_1,\sigma},
\end{aligned}
$$





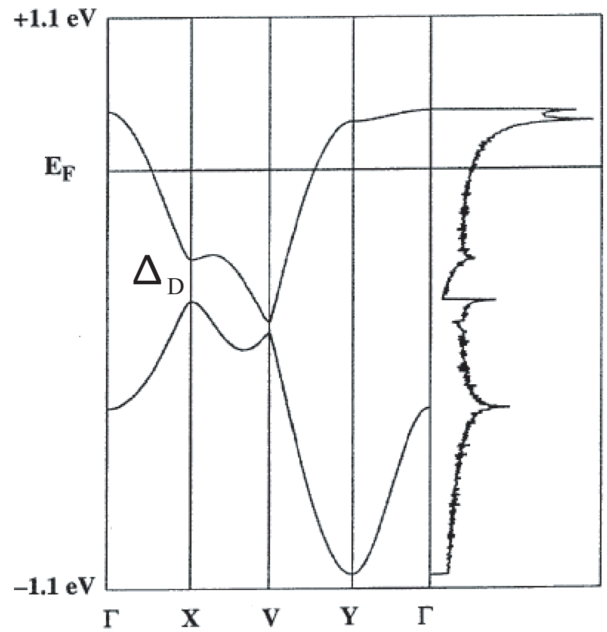




Hubbard case : $g_1 = g_2 = U$

Weakly dimerized organic stacks $\rightarrow$
'half-filled' band with small Umklapp

$$g_3 \approx g_1 \frac{\Delta_D}{E_F}$$



One-loop RG at a glance ...

$$Z = \mathrm{Tr}\ e^{-\beta(H_0+H_I)}$$

$$\rightarrow \iint \mathcal{D}\psi^*\mathcal{D}\psi\ e^{S_0[\psi^*,\psi]+S_I[\psi^*,\psi,\ g_{1,2,3}]}$$

$$= \iint \mathcal{D}\psi^*\mathcal{D}\psi\ \exp\Big[\sum_{p,k,\omega_n,\sigma} \psi^*_{p,\sigma}(k,\omega_n)[i\omega_n - \epsilon_p(k)]\psi^*_{p,\sigma}(k,\omega_n) + S_I[\psi^*,\psi,\ g_{1,2}$$

Parameterization of the bare action:

$$\mu_S = (G^0_p, g_1, g_2, g_3)$$

At the one-loop level, from ℓ to $\ell + d\ell$ ($E_0(\ell) = E_0 e^{-\ell}$),

$$Z \ \sim \iint_< \mathcal{D}\psi^*\mathcal{D}\psi\ e^{(S_0+S_I)_<} \iint_{o.s} \mathcal{D}\bar{\psi}^*\mathcal{D}\bar{\psi}\ e^{S_0[\bar{\psi}^*,\bar{\psi}]+S_{I,2}+(S_{I,3}+S_{I,4}+S_{I,1})}$$

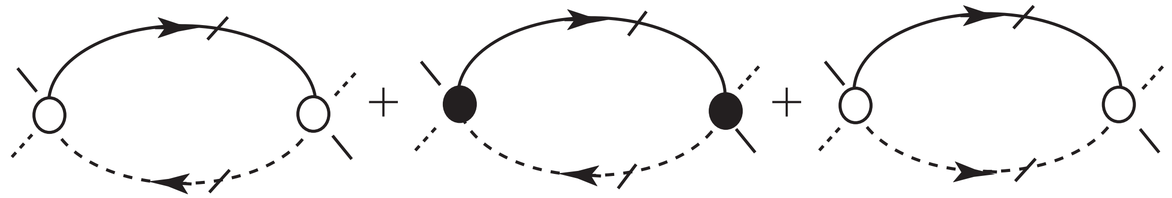
$$= Z^0_{o.s} \iint_< \mathcal{D}\psi^*\mathcal{D}\psi\ e^{(S_0+S_I)_<} \frac{1}{Z^0_{o.s}} \iint_{o.s} \mathcal{D}\bar{\psi}^*\mathcal{D}\bar{\psi}\ e^{S_0[\bar{\psi}^*,\bar{\psi}]+S_{I,2}+(S_{I,3}+S_{I,4}+S_{I,1})}$$

$$\propto \iint_< \mathcal{D}\psi^*\mathcal{D}\psi\ e^{(S_0+S_I)_<}\ e^{\frac{1}{2}\langle (S_{I,2})^2\rangle_{o.s,C}} \ + \ ....$$

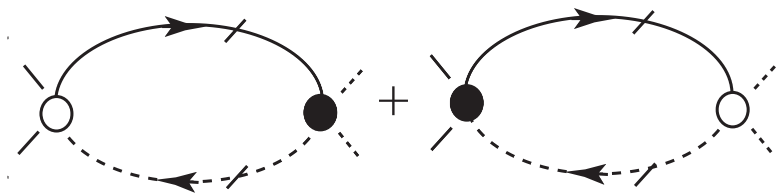
The RG transformation becomes

$$\mathcal{R}_{d\ell}\ \mu_S(\ell) = \ \big(G_p^0, g_1(\ell + d\ell), g_2(\ell + d\ell), g_3(\ell + d\ell)\big)$$

$$g_{1,2}(\ell + d\ell) \ = \ g_{1,2}(\ell) +$$



$$g_3(\ell + d\ell)) \ = \ g_3(\ell) +$$



$$\begin{aligned} g_1' &= \ -g_1^2, \\ (2g_2 - g_1)' &= \ g_3^2, \\ g_3' &= \ g_3(2g_2 - g_1) \end{aligned}$$

RG flow:

$$\left.\begin{aligned}\tilde{g}_1' &= -\tilde{g}_1^2,\end{aligned}\right\}\sigma$$
$$\left.\begin{aligned}(2\tilde{g}_2-\tilde{g}_1)' &= \tilde{g}_3^2,\\ \tilde{g}_3' &= \tilde{g}_3(2\tilde{g}_2-\tilde{g}_1)\end{aligned}\right\}\rho$$

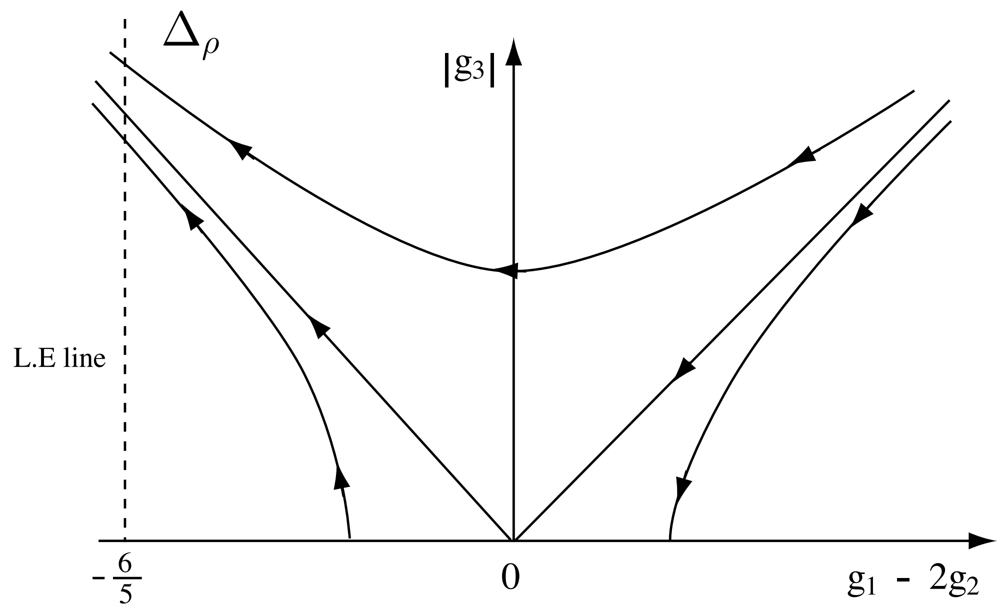
σ- sector

$$g_1(\ell) = \frac{g_1}{1+g_1\ell} \quad \rightarrow \quad 0$$

Regular spin susceptibility

$$\chi_\sigma(T) = \frac{2\mu_B^2(\pi v_\sigma)^{-1}}{1-\frac{1}{2}\tilde{g}_1(T)}$$

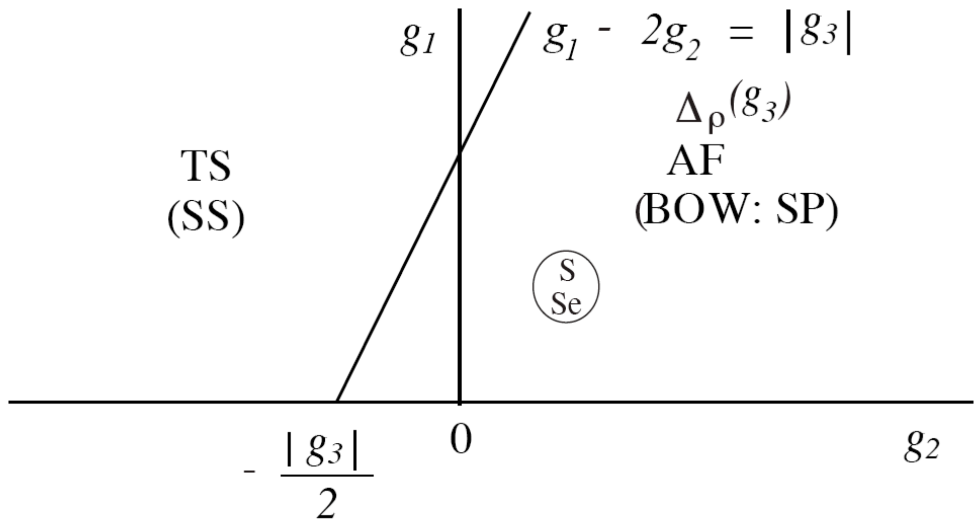
ρ- sector



Insulating behavior for resistivity

$$\rho(T) \propto T\, g_3^2(T)$$

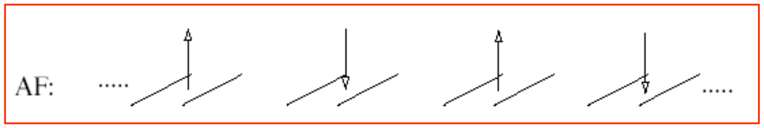
Phase diagram of the 1D electron model: repulsive sector



$\gamma = \gamma_{\mathrm{BOW}} = 1$ (L-E liquid)

Singular AF response

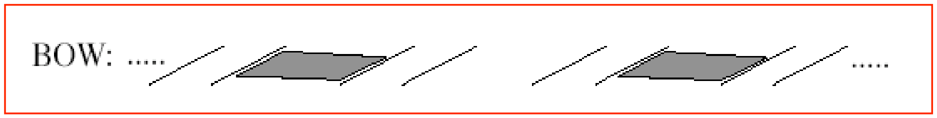
$$\chi_{\mathrm{AF}}(2k_F, T) \propto (\pi v_F)^{-1}(T/\Delta_\rho)^{-\gamma}$$



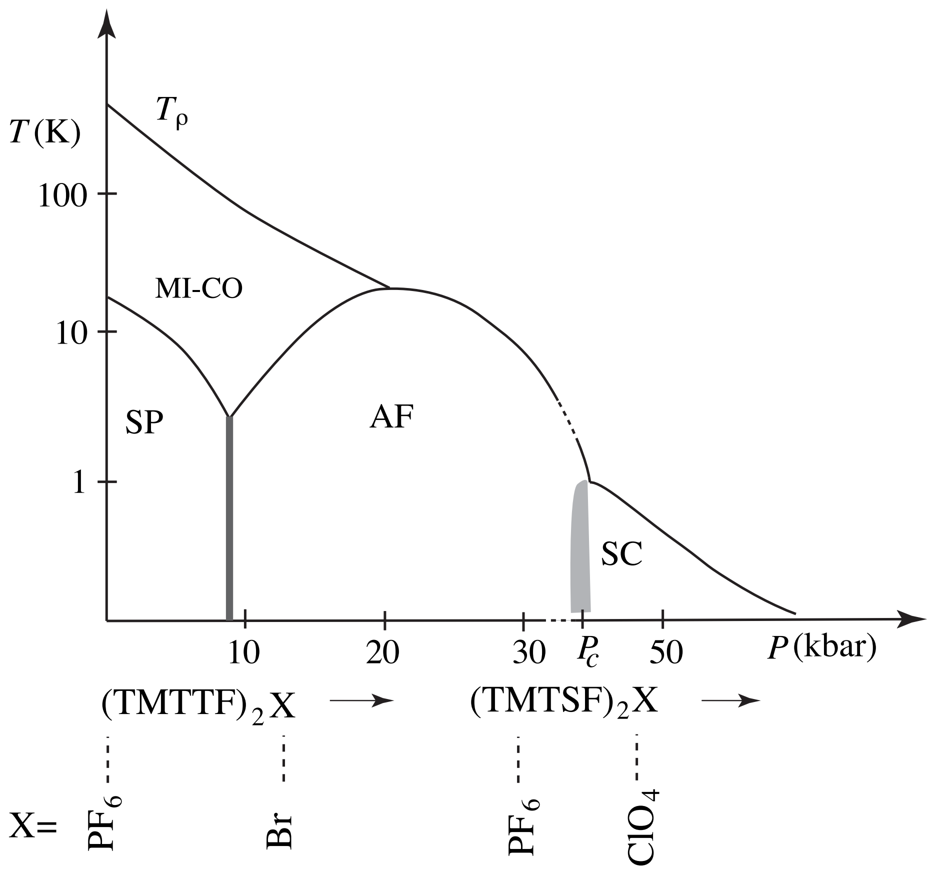
Singular Bond-Order-Wave response ~ with phonons

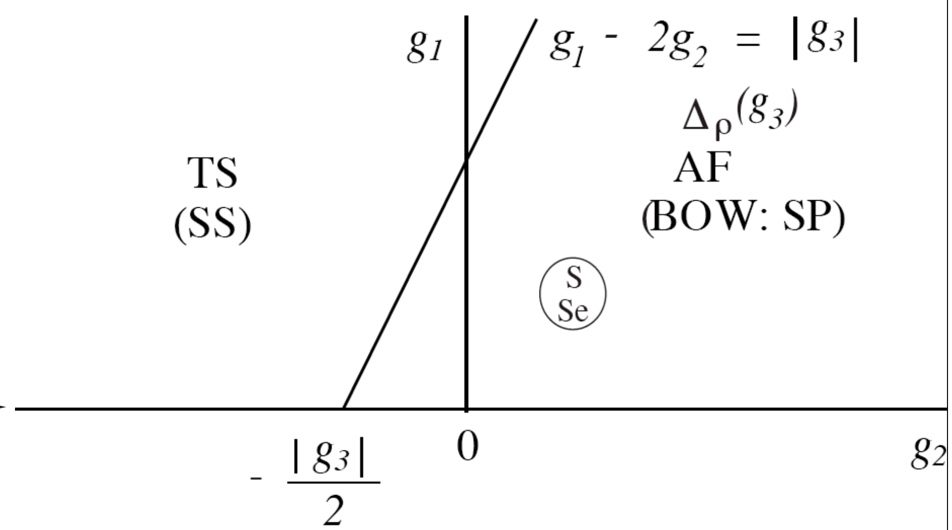
-> spin-Peierls correlations

$$\chi_{\mathrm{BOW}}(2k_F, T) \propto (\pi v_F)^{-1}(T/\Delta_\rho)^{-\gamma_{\mathrm{BOW}}}$$



Qualitative features qualitatively match with experiments





Nuclear relaxation rate as a probe of 1D confinement

$$T_1^{-1} = |A|^2\, T \underbrace{\int_{\mathcal{D}} d^D q}_{q \sim 0 \,+\, q \sim 2k_F} \frac{\mathrm{Im}\chi(\boldsymbol{q},\omega)}{\omega}$$

(Moriya, 1963)

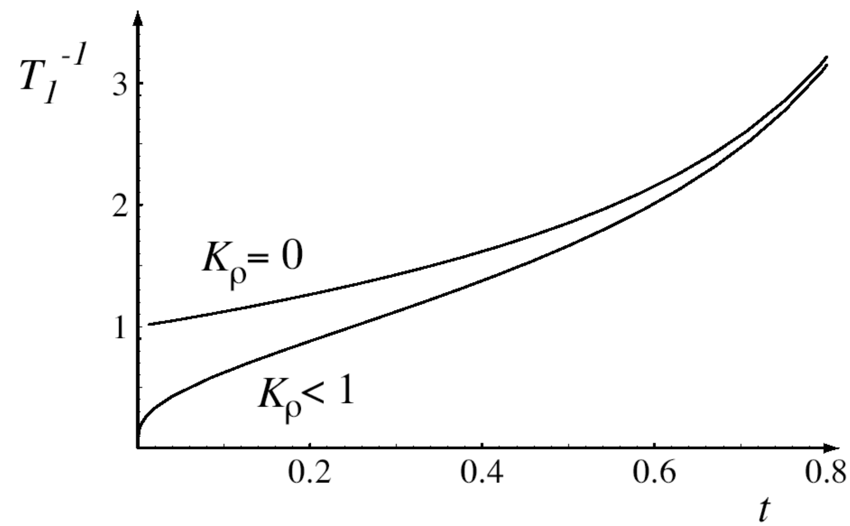
(c.f. Mitrovic talks)

$$T_1^{-1} = \; C_0\, T\, \chi_\sigma^2(T) \; + \; C_1\, T^{K_\rho}\,, \qquad (\, D \,=\, 1\,)$$

Luttinger liquid: $0 \,<\, K_\rho \,<\, 1$

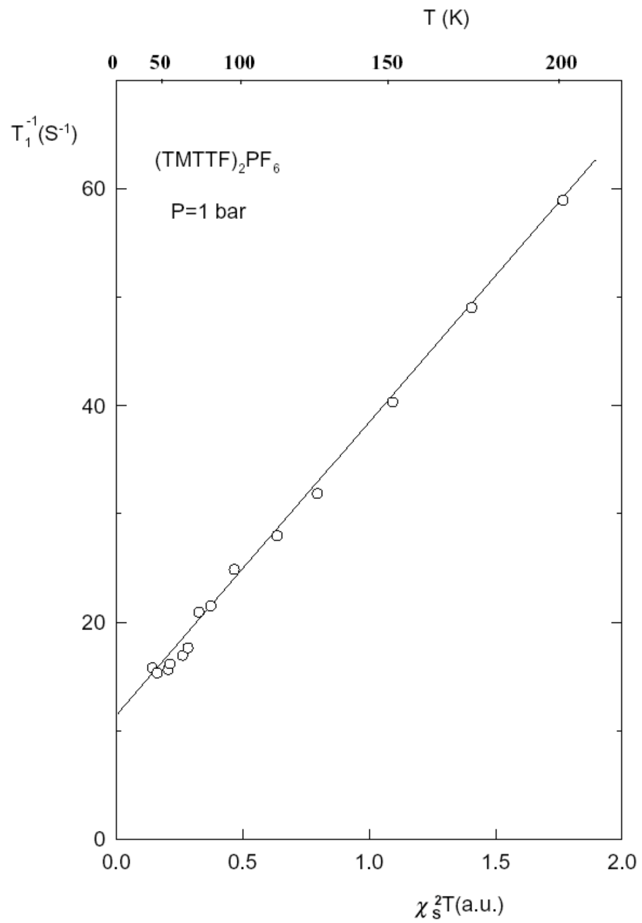
Luther-Emery liquid: $K_\rho \,=\, 0$

$$\chi(2k_F, T) \sim T^{-\gamma}\, (\gamma = 1 - K_\rho)$$



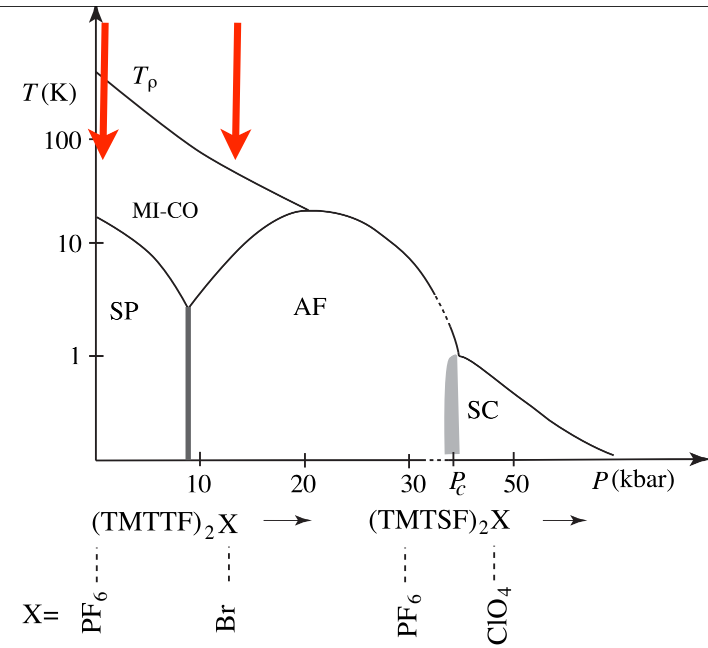
C. Bourbonnais *et al.*, PRL, **62** 1532 (1989)
J. Physique I **3**, 170 (1993).

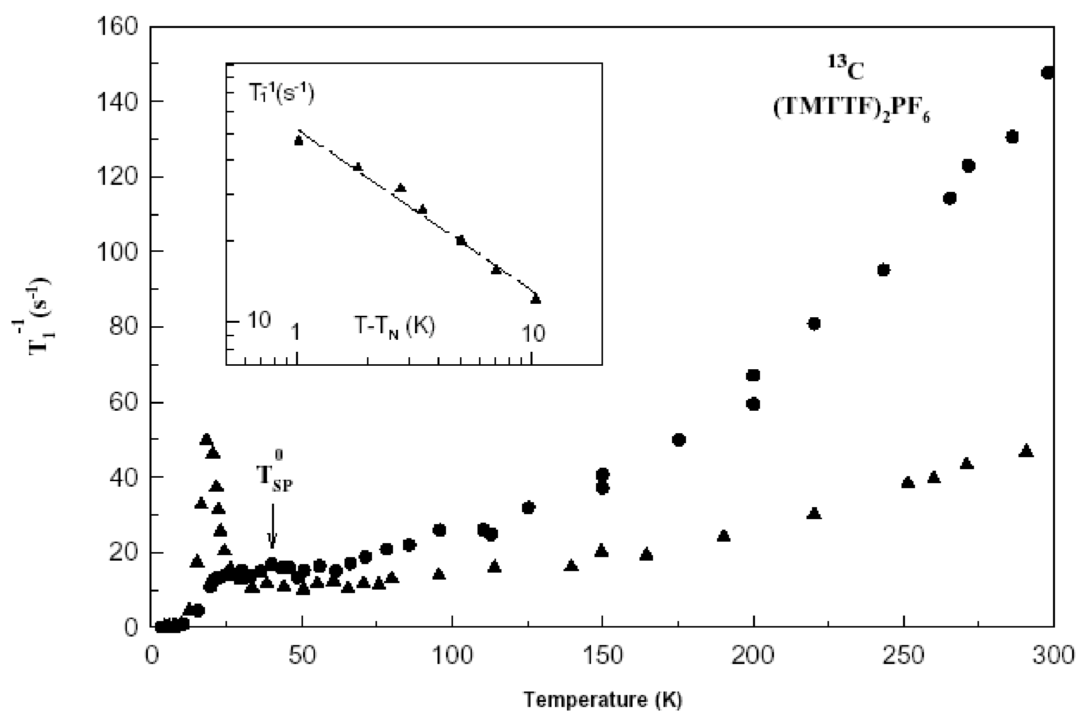
$(TMTTF)_2PF_6$



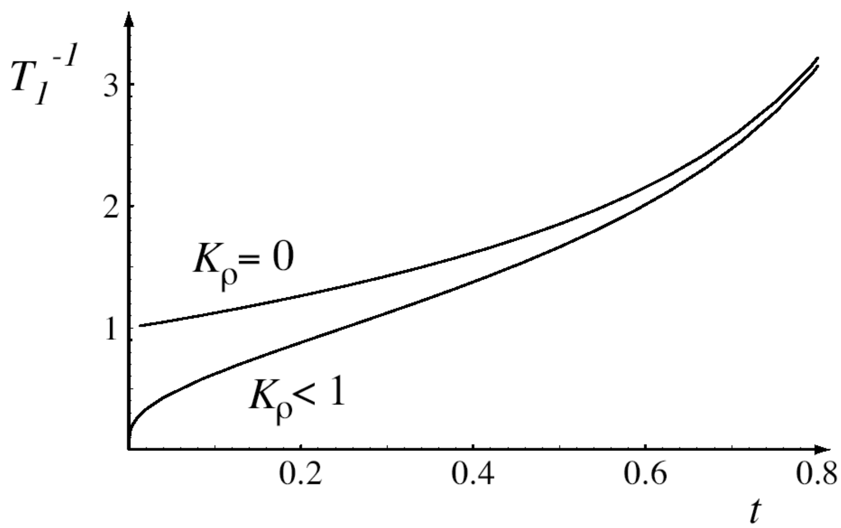
$$T_1^{-1} = C_0 T \chi^2(T) + C_1$$

$$\gamma = 1 \quad \text{or} \quad K_\rho = 0$$

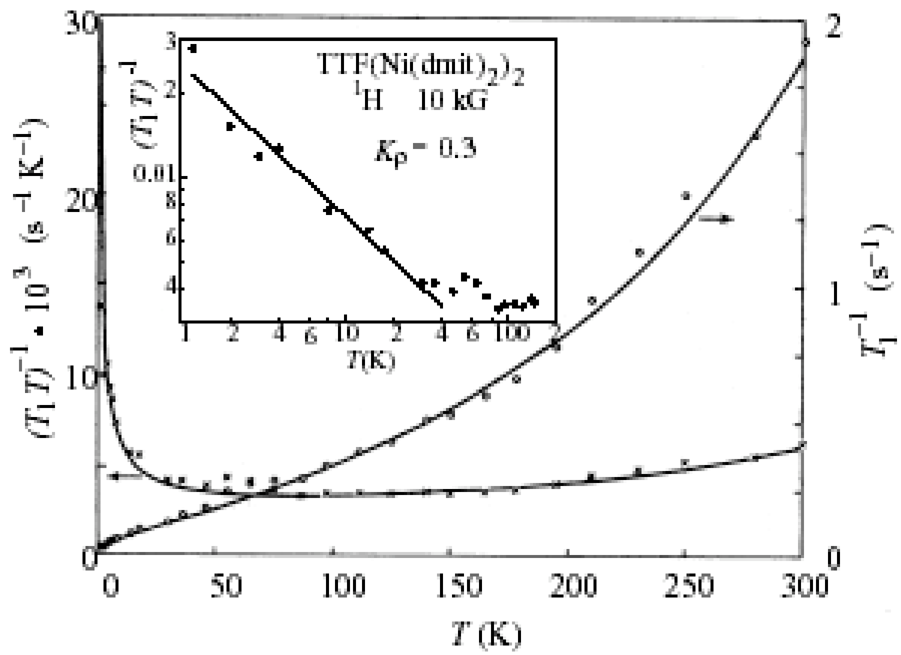




A disgression on TTF[Ni(dmit)$_2$]$_2$: one-dimensional metal (TTF chains)



TTF[Ni(dmit)$_2$]$_2$ = incommensurate



P. Wzietek *et al.*, Europhys. Lett. **6**, 177 (1988)

$$T_1^{-1} = C_0\,T\,\chi_\sigma^2(T) + C_1\,T^{K_\rho}\,,$$

$$K_\rho = 0.3$$