FERROELECTRIC MOTT-HUBBARD PHASE and CHARGE DISPROPORTIONATION in QUASI 1D ORGANIC CONDUCTORS from physics of solitons to optics

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After collaboration with	Felix Nad	Moscow and Grenoble
	Pierre Monceau	Grenoble and Saclay
	J.M. Fabre & C. Carcel	Montpellier

Publications: ISCOM 2001, ICSM 2002, ECRYS 2002, ISCOM 2003

References: cond-mat/0012237/0304076/0304483/0306006/ 0401309

Japan connections:

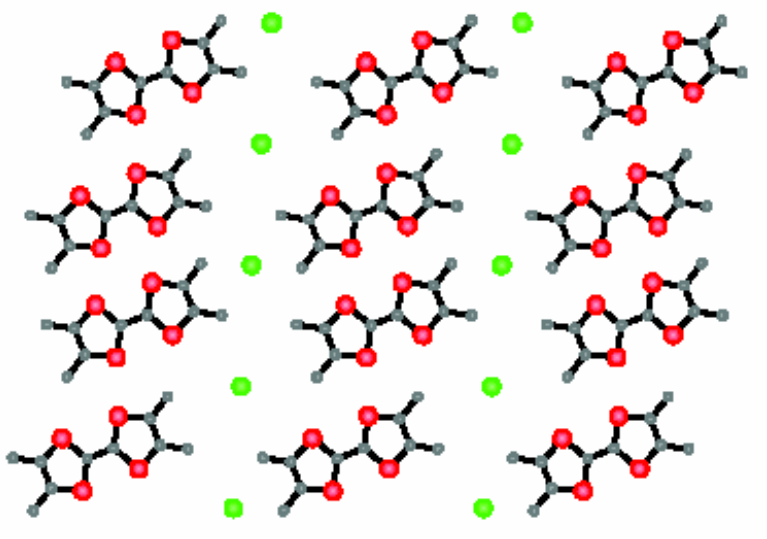
H.Fukuyama and H.Seo, K.Hiraki and K.Kanoda, S.Kagoshima and Y.Nogami, H.Fujiyama and T.Takahashi, H.Mori and H.Tajima, ….

HISTORY and EVENTS.

- $4K_F$ anomaly and its condensation — *Comes & Pouget, Kagoshima, ...*
- $4K_F + 2K_F$ lock-in — Jerome
- Subtle anionic transitions as magicians' gifts — *Moret, Pouget, Ravy...*
- Interplay of electronic and structural properties — *S.B.& Yakovenko*
- Abandoned structureless transitions wait for revenge — *Coulon, Lawersonne...*
- Theory predictions for charge disproportionation — *Seo and Fukuyama*
- Ferroelectric anomaly — *Nad, Monceau, S.B.,...*
- Charge Disproportionation in Quasi 1D — *Kanoda…,Brown…., Fujiyama...*

FACTS and VIEWS

- Combined Mott-Hubbard state
- Solitons in conductivity and optics
- Ferroelectricity and collective modes
- Subsequent transitions and spin-charge reconfinement
- Provocation: will the *Se* subfamily stay intact?
- Compounds without build-in dimerization
- Routs to microscopics: where we are?
- The univers of universal phase diagrams

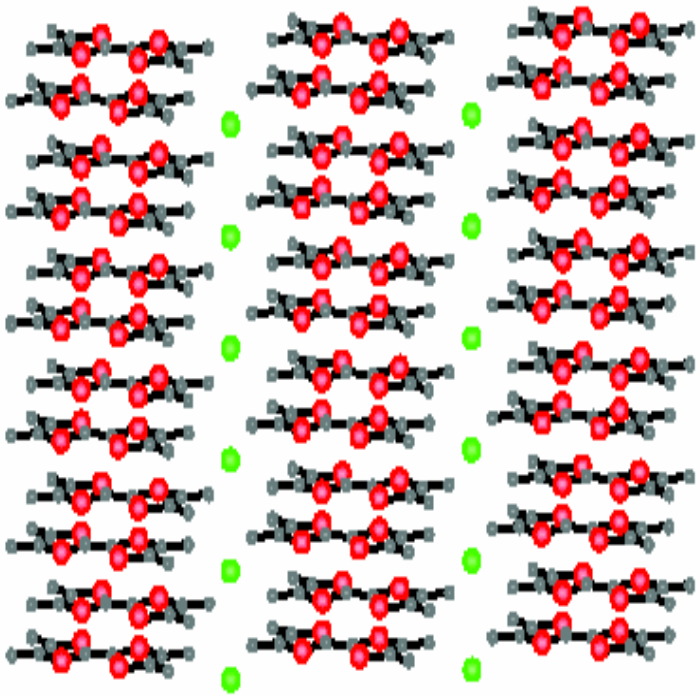


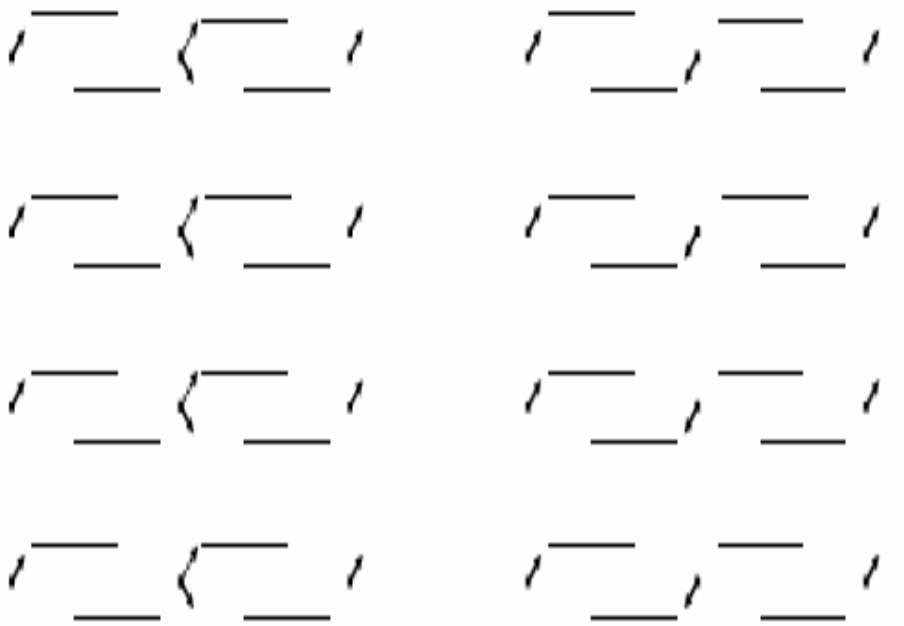
TMTCF molecules, their stacks, and columns of counterions X

LEFT : top view

BOTTOM : side views

BOTTOM RIGHT : tiny structural Transitions of anion orderings





Exceptional richness TMTTF/TMTSF-X family

Tc ~ 1-15K almost all known, + unknown, electronic phases

T_{ao} ~25-100K - set of weak structural transitions of the anion orderings AOs: slight arrangements of chains of counterions **X**.

$T \approx T_0$>100K – "structureless" transitions of a mysterious origin

Recent insights to the nature of the **T_0** transitions in **TMTTF:**

Huge anomaly of dielectric susceptibility (Grenoble group)

Charge disproportionation from the NMR (UCLA group)

Views and interpretations (equivalent):

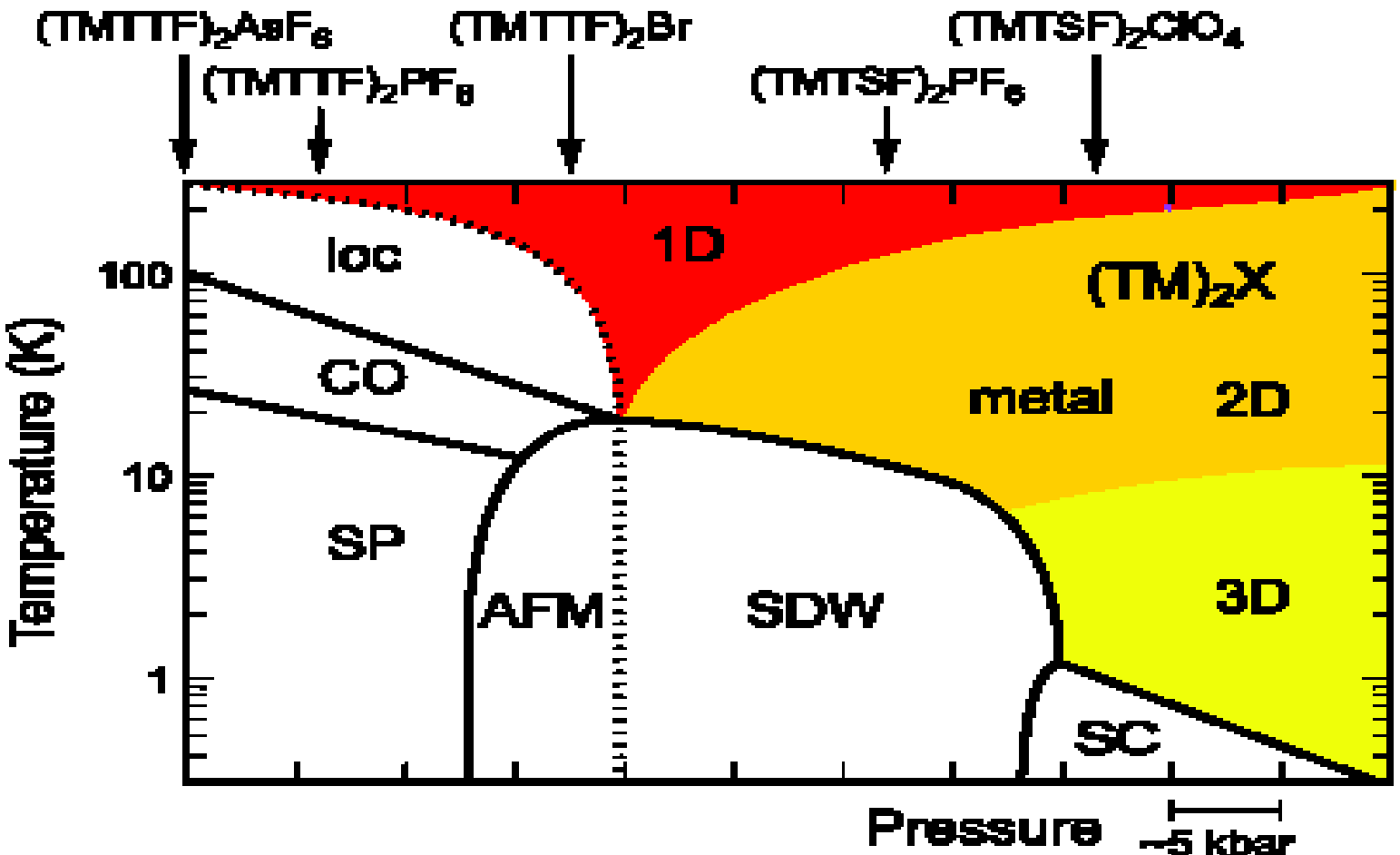
FerroElectric version of Mott-Hubbard state, mixed site/bond 4KF CDW, Nonsymmetrically pinned Wigner crystal.

Theory views combined Mott-Hubbard state; **$4K_F$** density wave or Wigner crystal, subjected to weak two fold commensurability or showing 3D ordering.

Main theory ingredient - interference of two types of Umklapp scattering of electrons from two symmetry breaking effects: build in nonequivalence of bonds (if present) and spontaneous nonequivalence of sites.

ELECTRONIC PHASES OF *(TMTCF)2X* FAMILIES:

Superconductor SC, METAL versus charge localisation LOC,
Charge Ordering CO, Spin-Peierls SP,
Spin Density Waves SDW, AntiFerroMagnet AFM,
add Magnetic Field Induced Spin Density Waves FISDW,
1D,2D,3D – dimension crossovers



ELECTRONIC PHASES OF $(TMTCF)_2X$ FAMILIES:

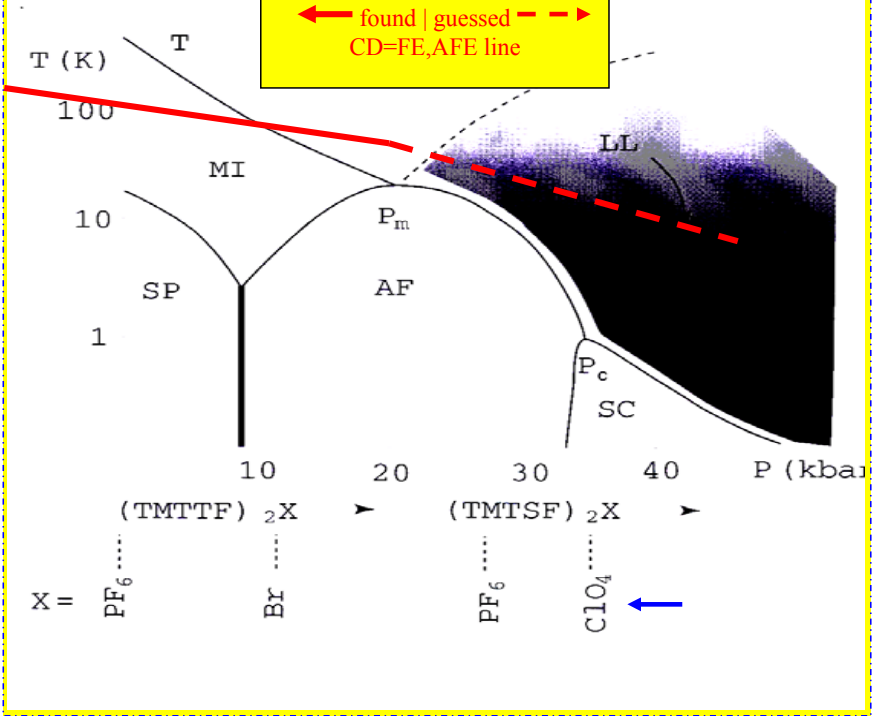
- Normal N and Superconducting SC metals,
- Paramagnetic Insulator (Mott-Hubbard state),
- Several types of spin density waves - SDW, FISDW.
- Charge Density Waves
- Spin-Peierls state (CDW in the frame of repulsions)

Their usual background:

Several weakly different structural types due to build-in effects of counterions and, much more, from additional ***anion orderings*** AO --
fine arrangements, with $\mathbf{q \neq 0}$, of singly charged counter-ions *X* .
AO temperatures $\mathbf{T_{ao} \approx 100K}$, are typically much higher than scales of electronic transitions $\mathbf{T_c \sim 1 \div 20K.}$

Occasionally as it seemed: also *"structureless transitions"* at even higher $\mathbf{T_0 > T_{ao}}$ which nature was unknown till recently (Coulon et al).
They were weakly seen in high (~ GHz) frequency dielectric susceptibility ε, in resistivity and in thermopower, but never, it was thought, in X ray scattering.
Their 15 years long fate: unexplained, unattended, abandoned.
Recent breakthrough (Grenoble-Moscow):

Low frequency methods for Reε were designed for pinned CDWs, applied to SDWs and finally to structurless transitions.



$(TMTCF)_2X$, 1980-2002

Black and white: Anniversary picture 1999

SC- superconductivity

AF- AFM = SDW

SP- Spin-Peierls

LL- Luttinger liquid

MI- Mott insulator

Red line T_0 - 2000 revolution:

Structurless transitions (*Coulon et al 1985*)

= Ferroelectricity (*Monceau et al*)

= Charge disproportionation (*Brown et al*)

15 years long fate of structurless transitions :
unexplained, unattended, abandoned.

Recent insights to their nature:

Huge anomaly of dielectric susceptibility (Grenoble group)

Charge disproportionation from the NMR (UCLA group)

The breakthrough (Grenoble-Moscow):

Low frequency methods for the dielectric permittivity $Re\varepsilon=\varepsilon'$:
designed for pinned CDWs, applied to SDWs
and finally to structurless transitions.

Resolving the mystery of structureless transitions: *since **Coulon et all, 1985***

Gigantic anomaly in permitivity of $\varepsilon'(T)$ (*Nad et al, Grenoble - Moscow*)

•Charge Disproportionation seen by the NMR (*Brown - UCLA, Fujiyama -IMS*)

Views and interpretations (equivalent):

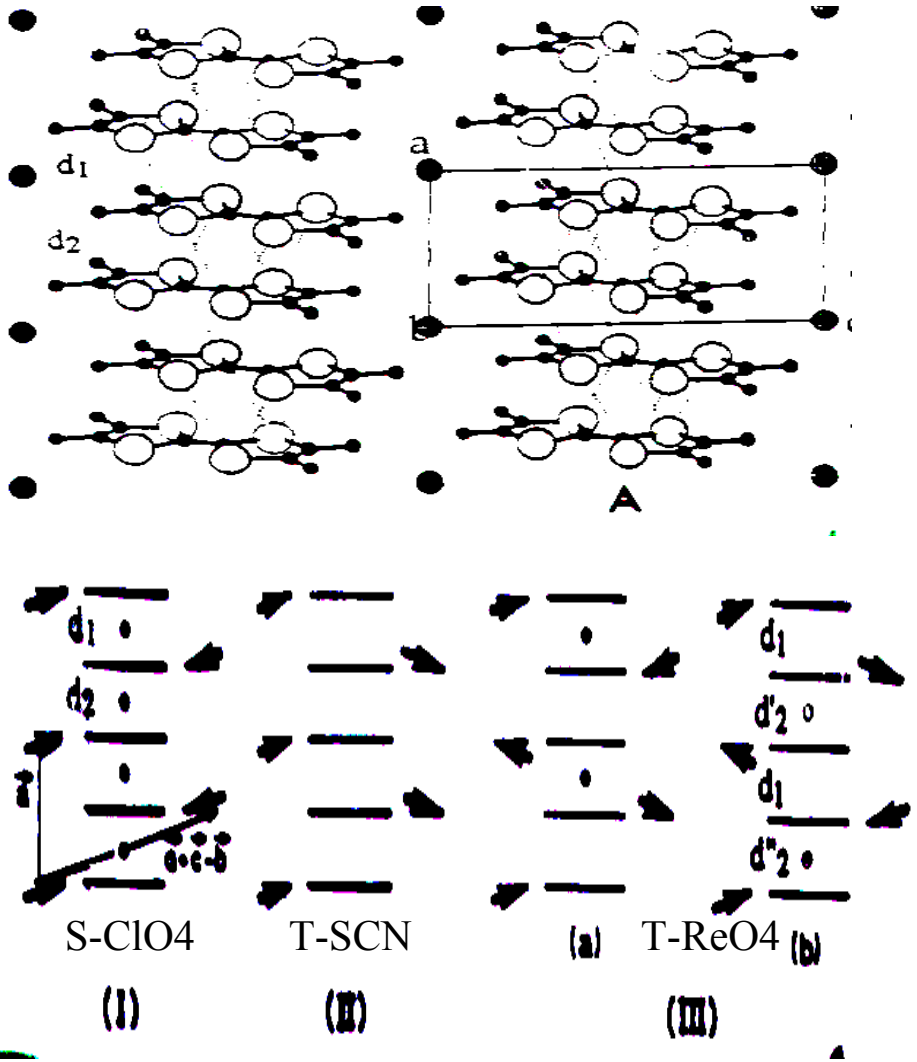
FerroElectric version of Mott-Hubbard state,
mixed site/bond $4K_F$ CDW,
nonsimmetrically pinned Wigner crystal

Special facility to see Solitons:
Purely 1D regime for electrons -
$T_0 \approx 150$ is 10 times above 3D electronic transitions.

NMR: Clear detection of the site nonequivalence.

NNR and conductance G: same observation both for the ‘structureless’ transition and for the AO already known as a very rare structure of the type (0,1/2,1/2) in $(TMTTF)_2SCN$ where the site non equivalence was already detected by structural studies. Hence at the on-chain level the FE was already seen in X-rays. As an anti-FE state, the SCN case is a cone shared by domains of AOs and CDs.

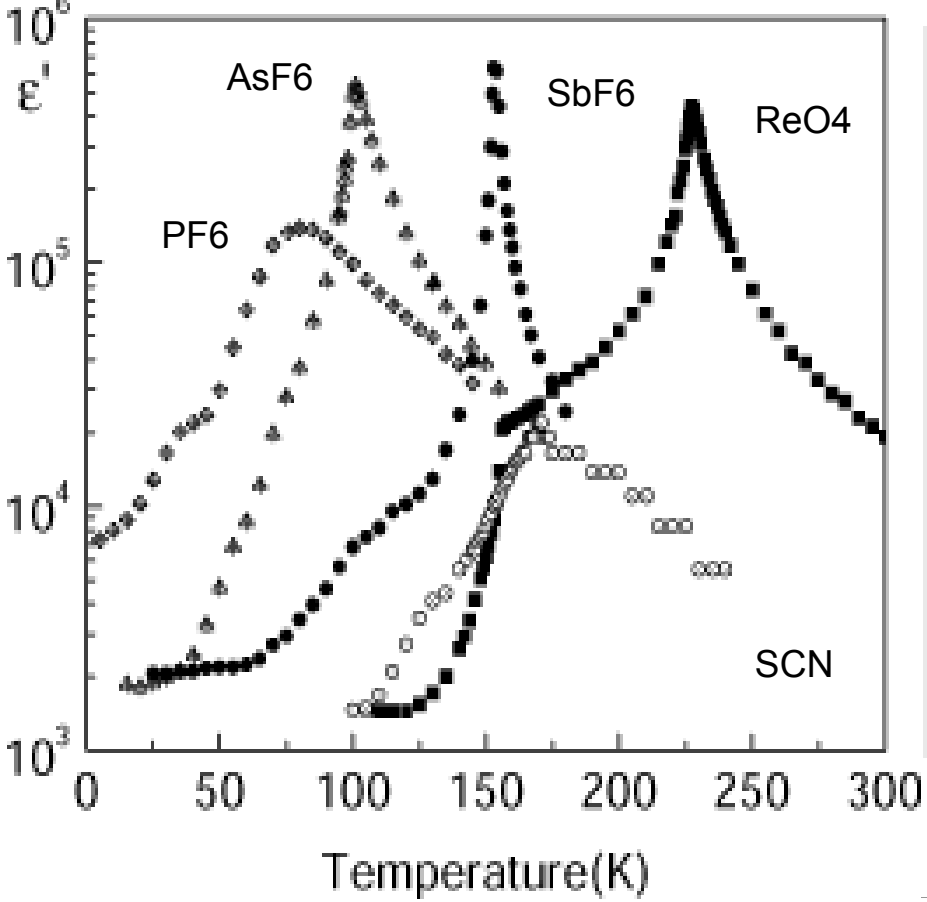
Figures from review by Pouget & Ravy

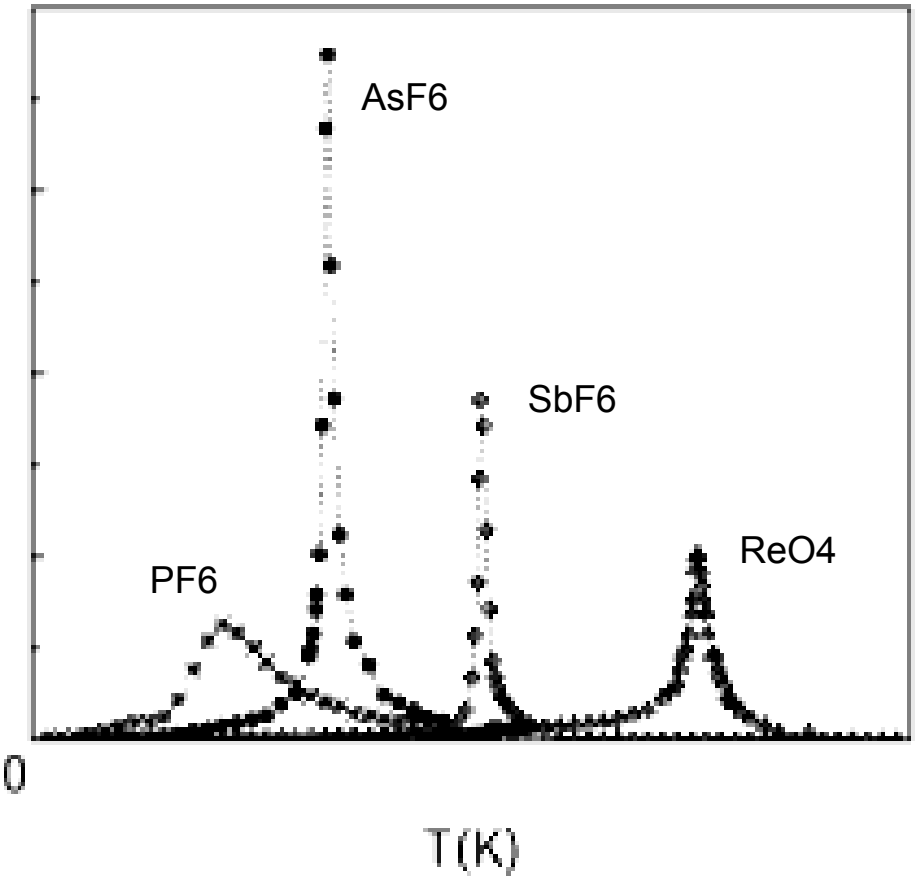


Nonperturbed crystal structure.
Bond dimerization $d_1 \neq d_2$ changes the mean electronic occupation from ½ per molecule to 1 per dimer. It originates the Umklapp scattering g_3 which opens (*Dzyaloshinskii & Larkin, Luther & Emery*) the route to the Mott-Hubbard insulator (*Barisic & S.B. 1981*).

Basic anion orderings: structure II already demonstrates the net ionic polarization of each anionic chain, hence the electronic dipole moment of each stack. But they alternate in perpendicular direction forming the Anti-FE state.
SCN case: shares membership in calsses of AO and CD transitions.
New more complex AFE structures:
$(DMtTTF)_2X$ (*Ravy et al*)

Key hypothesis: ferroelectric state **q**=0 is built by a similar structure II but with all displacements being identical both along and among the stacks.





Dielectric anomaly ε′(T) in (TMTTF)2X, after Nad & Monceau, LT 2002

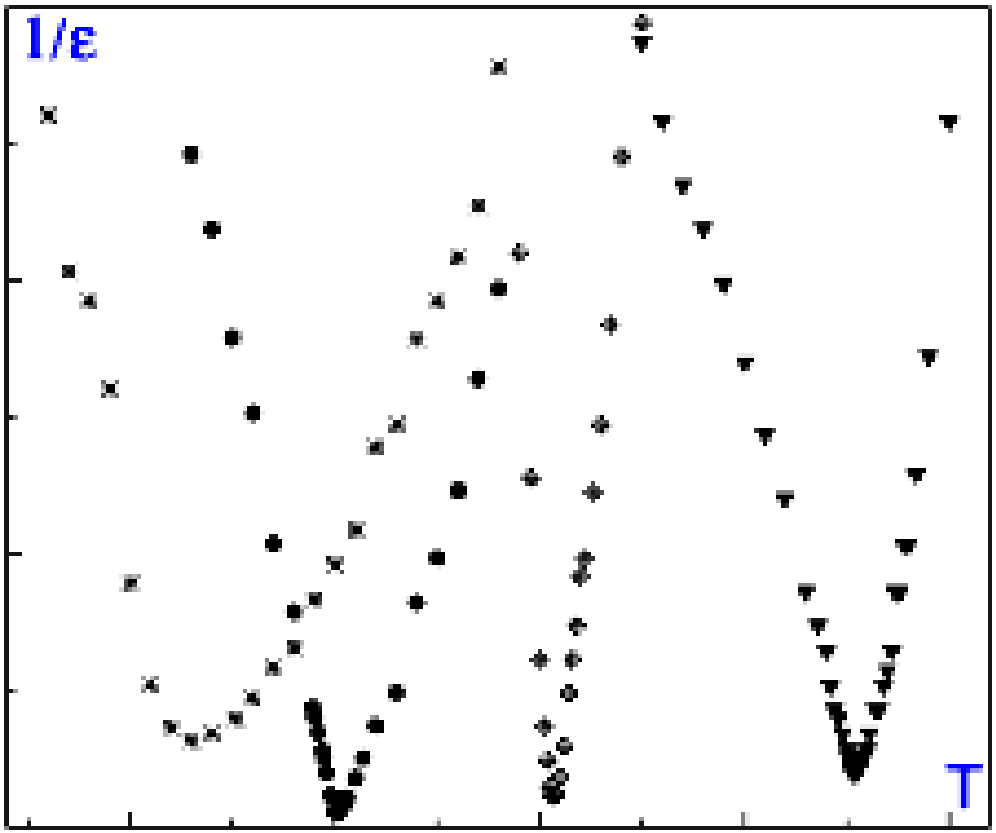
Left: at f=1MHz in *semi logarithmic scale* | Right: at f=100 kHz in *linear* scale

Anti FE case of SCN shows only a kink as it should be.

Smoothened anomaly in PF6 correlates with its weak frequency dispersion

- DE domain walls and hidden hysteresis ?.

Other cases - pure mono-domain “initial” FE susceptibility.



T dependence of the inverse of the real part of **ε'** at ***f=100Hz***,

$X=PF_6, AsF_6, SbF_6, ReO_4$

$1/\varepsilon' = C(T-T_0)$

Typically $C \sim 10^4/T_0$

$C_< = 2C_>$ --

exact Landau theory !

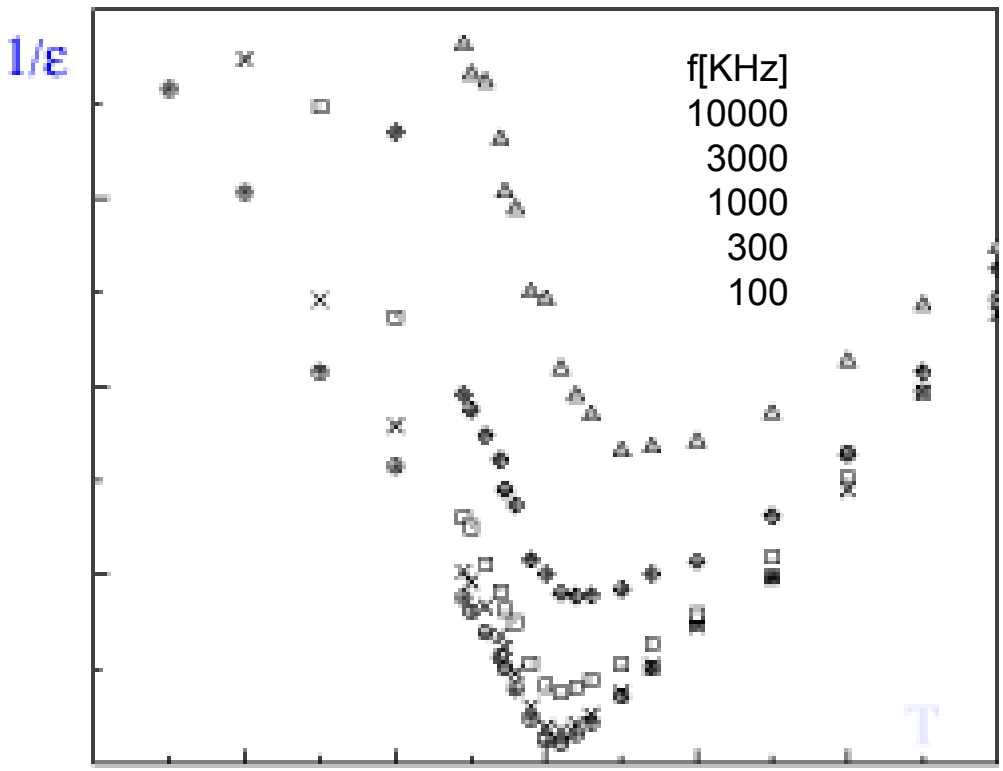
Complication: PF_6

Clear cut fitting of the anomaly in ε(T) to the Curie law prooves the <u>least expected</u> case of the ferroelectric phase.
Even more curiously, it is the ferroelectric version of the Mott-Hubbard state and of the Charge Disproportionation.

Frequency dependent depolarization of the mono domain conducting ferroelectric instead of the long time hysteresis of domains in usual nonconducting ferroelectrics.

Normal carriers may screen surface charges of the FE polarisation, hence no reason for domain structure.

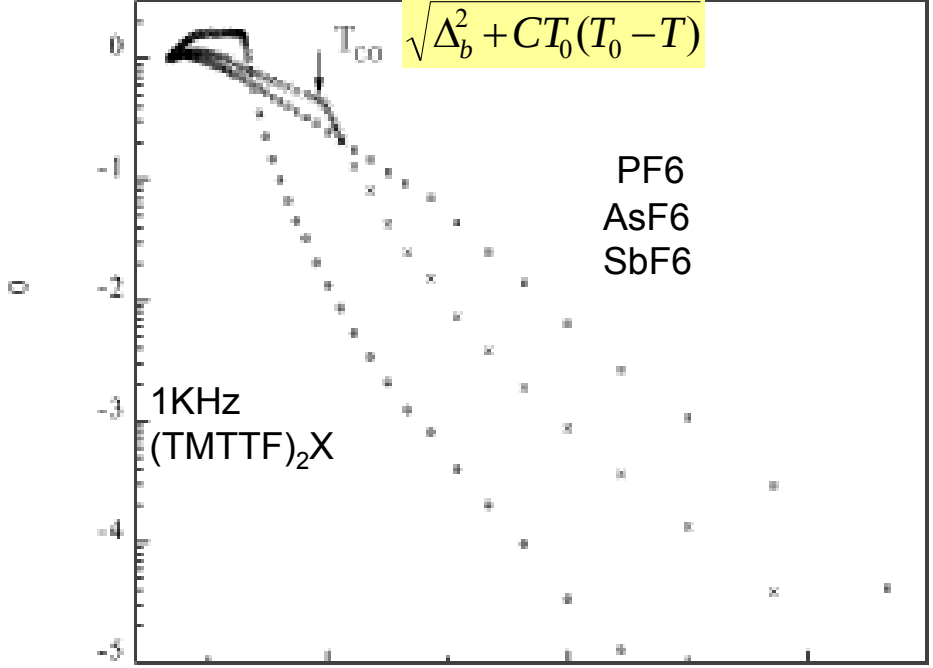
True low T or radiational/alloying damage are necessary to pin FE domain walls and enforce the remnant polarization, the hysteresis.

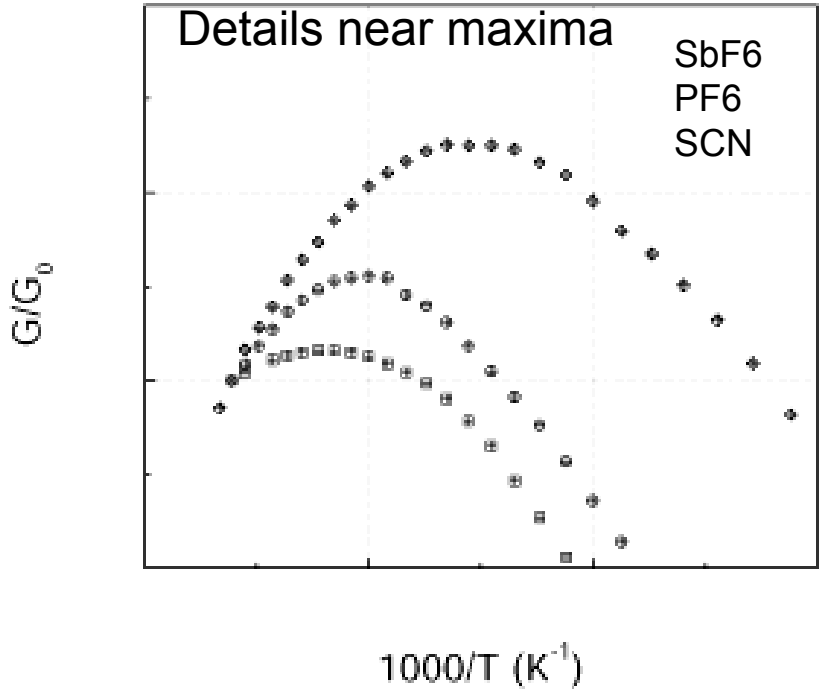


$(TMTTF)_2AsF_6$:

$1/\varepsilon'(T)$

after Nad and Monceau





Conductance G (normalized to RT, Ahrenius plot Log G versus 1/T).

Conrarily to normal semiconductors, there is no gap in spin susceptibility.

Gaps for thermal activation Δ range within 500-2000K.

Similar to data from 80's (Javadi et al) but with new insights:

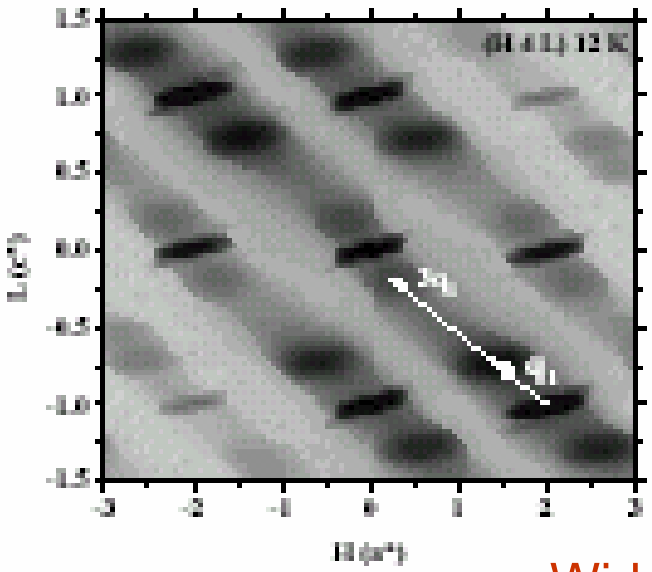
i. Clearlest example for conduction by charged spinless solitons - holons .

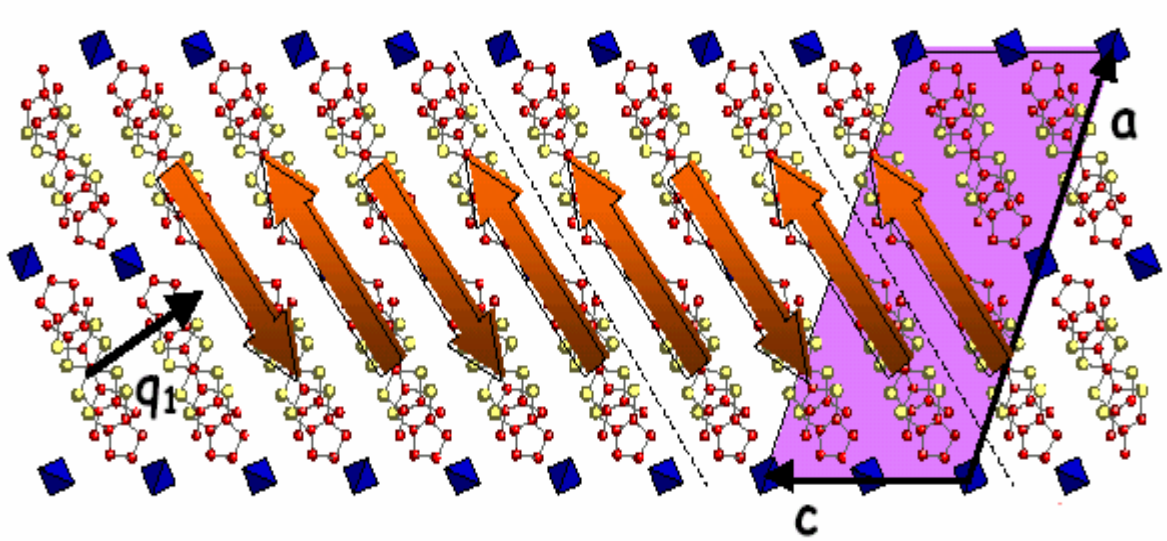
ii. Inspite of the IInd order character of T_0, site dimerization contribution to the gap develops very fast and soon dominates over the bond dimerization gap: hence no necessity for the build-in dimerization,

hence a route to compounds with equivalent bonds (*Kanoda, Coulon, Ravy*) (DI-DCNQI), (EDT-TTF-$CONMe_2$), (DMtTTF) --

waiting to be tested for ε anomaly (all three) and NMR splitting (last two).

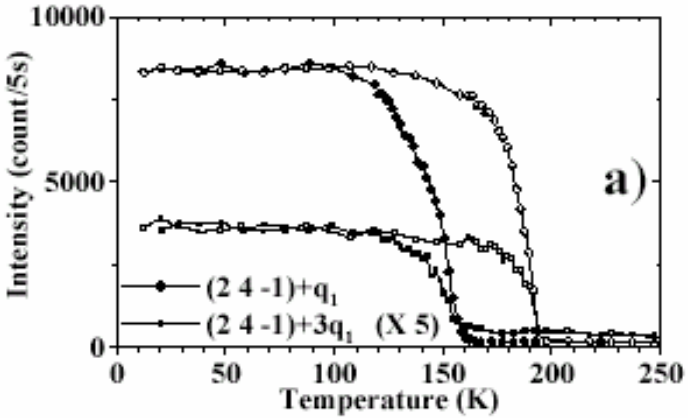
S. Ravy, P. Foury-Leylekian, D. Le Bolloc'h, J.-P. Pouget, J.M. Fabre, R. J. Prado and P. Lagarde

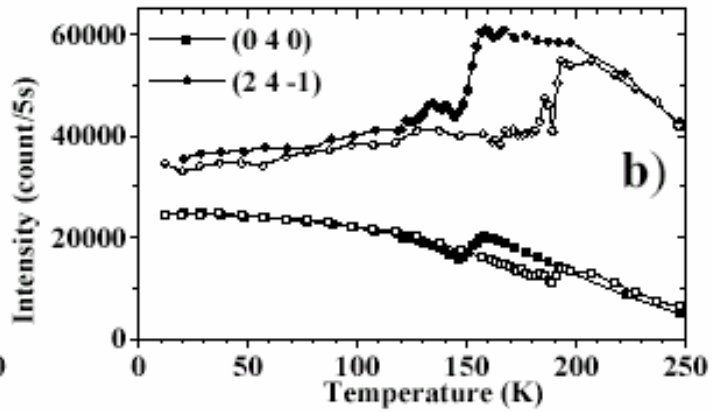




$(DMtTTF)_2ClO_4$

Wide arrows: displacements in (**a**+2**c**,**b**) planes.
Dashed lines: π walls of AFE order parameter.
statistical distribution of 3 and 4 AFE ordered domains.





a) (2 4 -1)+**q**1- and (2 4 -1)+3**q**1-diffuse spots intensities.
b) (2 4 -1) and (0 4 0) Bragg reflections intensity.

Hysteresis,
Ist order
transitions

Symbols:
Full (open) --
cooling down
(heating up).

ANION ORDERINGS: ROTATIONS or DISPLACEMENTS ?

Already at $\mathbf{T > T_0}$,$\mathbf{T_{ao}}$, the ions already exhort a profound effect on electronic properties: they dimerize intramolecular spacings lifting up the glide plane symmetry. The electronic band is folded, the mean occupation changes from 1/2 per molecule to *1* per unit cell which brings to the game particular effects of the Mott-Hubbard charge localization.

Usual $\mathbf{q} \neq 0$ AOs were always observed for non centrosymmetric -NCS anions, and the orientational ordering, related to establishing short contacts to *Se* or *S* atoms, was supposed to be the principle mechanism with positional displacements being its consequences.

The accent upon the orientational ordering could be the reason not to appreciated the $\mathbf{q}=0$ transitions which were registered, until very recently, only for the centrosymmetric ions. But today we should think about a universal mechanism related only to the positional instability. Mechanisms for displacive and orientational orderings seem to be independent as it is supported by finding of a sequence of $\mathbf{q}=0$ and $\mathbf{q} \neq 0$ transitions in $(TMTTF)_2ReO_4$.

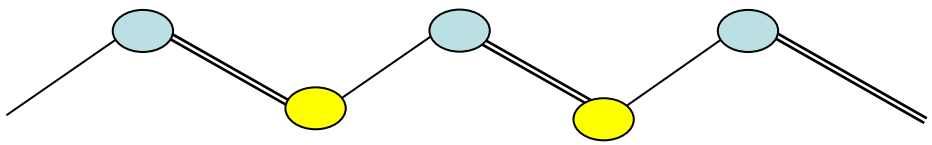
From POLYMERS to ORGANIC CRYSTALS

Combined Peierls state in conjugated polymers of the (AB)x type: modified polyacetylene $(CRCR')_x$ from Akagi (Tsukuba) or W.Little imagination. (S.B. & N.Kirova 1981, also E.Mele and M.Rice)

Joint effect of extrinsic Δ_{ex} and intrinsic Δ_{in} contributions to dimerization gap Δ.

Δ_{ex} comes from the build-in site dimerization – inequivalence of sites A and B.

Δ_{in} - from spontaneous dimerization of bonds $\Delta_{in}=\Delta_b$ - generic Peierls effect,



$$\Delta = \sqrt{\Delta_{ex}^2 + \Delta_{in}^2}$$

Modifications for the charge ordering:

Substitute the Peierls effect by the Mott-Hubbard one.

Interchange the build extrinsic in and the spontaneous intrinsic effects.

Now the build-in effect comes from the nonequivalence of bonds while the spontaneous one comes from the nonequivalence of sites.

Both can be of the build in type, rem.$(TMTSF)_{0.5}(TMTTF)_{0.5}$ (Ilakovac). In any case (organic crystals or polymers) this combination lifts the inversion symmetry, hence the Ferroelctricity.

Charge gap $\Delta = \Delta(U)$ appears as an interference of both contributions U_s and U_b to the Umklapp scattering and it is a function of the total amplitude $U=(U_s^2+ U_b^2)^{1/2}$.

Electronic energy F_e depends only on Δ hence the total U.

Energy F_d of ionic displacements or molecular distortions depends only on the spontaneous site component U_s: $F_d=K U_s^2 /2$

Total energy F_{tot} must be minimal over U under the restriction $U>U_b$.

$F_{tot}=F_e(U)+(1/2)KU^2-(1/2)KU_b^2$

The ground state will change if the minimum appears at some $U=U_0>U_b$.

Since $U_0=U_0(T)$ increases with decreasing T, there will be a phase transition at $T=T_0$ such that $U_0(T_0)=U_b$.

$\gamma<1$: renormalized $U\neq0$ - gap originated by build-in dimerization.

$\gamma <1/2$: spontaneous U is formed = $4K_F$ condensed, no nead for bare U.

-- electronic energy gain $\delta F_e \sim -\Delta^2 \sim -U^\zeta$ ($\zeta=1/(1-\gamma)<2$) becomes higher than the energy lost $\sim U^2$ to pay spontaneous deformations.

1D Mott-Hubbard state. 1 electron per site i.e. the half filled band.

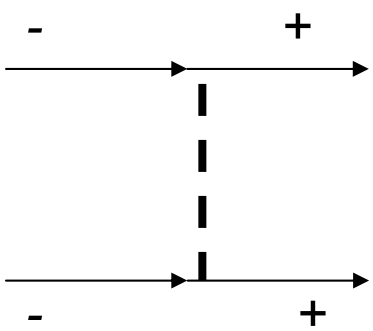
Spin degrees of freedom are split-off and gapless (free spin rotation phase θ).

Charge degrees of freedom can be gapful.

Chiral phase $\varphi=\varphi(x,t)$ for electrons near +/-K_F:

$$\Psi_{\pm} \sim \exp[\pm i\varphi/2]$$

Origine: Umklapp scattering (Luther & Emery,Dzyaloshinskii & Larkin).



$U\exp[i2\varphi]$ *: amplitude of the Umklapp scattering of electrons* $(-K_F, -K_F) \rightarrow (+K_F, +K_F)$ is allowed here.

Momentum deficit $4K_F$ is just compensated by the reciprocal lattice period. Continuous chiral symmetry lifting: arbitrary translations are forbidden on the lattice.

Remnant symmetry: Allowed translations

$x \rightarrow x+2$ hence $\varphi \rightarrow \varphi+\pi$ is preserved.

$$H \sim (\hbar/4\pi\gamma)\,[v_\rho\,(\partial_x\varphi)^2 + (\partial_t\varphi)^2/v_\rho] - U\cos(2\varphi)$$

Hamiltonian degeneracy $\varphi \rightarrow \varphi+\pi$ originates current carriers:

$\pm\pi$ solitons with charges $\pm e$, energy Δ

(= holon = $4K_F$ CDW discommensuration = Wigner crystal vacancy)

Stability conditions:

$\gamma<1$: U is not renormalized to zero, common case

$\gamma<1/2$: U can be spontaneously generated, new circumstances

Collective description for generic 1D Mott state = $4K_F$ CDW.

Spin degrees of freedom are gapless, split-off and not important for a while.

Charge degrees of freedom: phase $\varphi=\varphi(x,t)$

$2K_F$ CDW/SDW ~cos $(\varphi+x\pi/2a)$ 4KF CDW~ cos $(2\varphi+x\pi/a)$

Two fold commensurability: pinning potential potential and its degeneracy.

Wave function Ψ distriburtion at E_F (for the site dimerisation):

+ o - o + o - o

▽▼▽▼▽▼▽▼

$\varphi=0,\pi$: $\Psi=\pm1$ at good sites ▽ and $\Psi=0$ at bad sites ▼

$\varphi=\pi/2$: $\Psi=0$ at good sites ▽ and $\Psi=\ =\pm1$ at bad sites ▼

$$H\sim (\hbar/4\pi\gamma)\,[v_\rho\,(\partial_x\varphi\,)^2+(\partial_t\varphi\,)2\,/v_\rho\,]-U\cos(2\varphi)$$

U is the Umklapp scattering amplitude of Luther and Emery or $\mathbf{g_3}\sim\mathbf{U}$ of Dzyaloshinskii & Larkin. Its presence is the main feature of systems with a single electronic mean occupation. The generosity of $(TMTCF)_2X$ - small **U**, hence the “charge localization” crossover (S.Barisic and S.B. 1981).

without interactions $\gamma=1$ *and* $v_\rho=v_F$

COMBINED MOTT - HUBBARD STATE

2 types of dimerization $\Rightarrow$2 interfering sources for two-fold commensurability

$\Rightarrow$ 2 contributions to the Umklapp interaction.

x $\rightarrow$ x+1 translational symmetry is broken, but

Site dimerization. preserved symmetries:

x $\rightarrow$ x+2 and **x $\rightarrow$ -x** , hence $\varphi \rightarrow \varphi+\pi$ and $\varphi \rightarrow -\varphi$

The lowest invariant: $\mathbf{H_U^s=-U_s \cos 2\varphi}$

Bond dimerization preserves symmetries

x $\rightarrow$ x+2 and **x $\rightarrow$ 1-x**, hence $\varphi \rightarrow \varphi+\pi$ and $\varphi \rightarrow \pi/2 - \varphi$

The lowest invariant: $\mathbf{H_U^b=-U_b \sin 2\varphi}$

At presence of both site and bond types

$$H_U= -U_s \cos 2\varphi -U_b \sin 2\varphi = -U\cos (2\varphi-2\alpha)$$

$$U=(U_b{}^2+ U_s{}^2)^{1/2} , \quad \tan 2\alpha= U_s/ U_s$$

CO modulation $\rho_{co} \sim \cos(\pi x+2\alpha)$

corresponds to q=0 since the unit cell contains two sites.

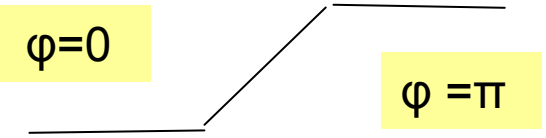
Parity breaking $\alpha \neq 0$ leads to a net dipole moment of the whole stack.

$U_s \neq 0$ originates the ferroelectric ground state if

the same α is chosen for all stacks and the state is

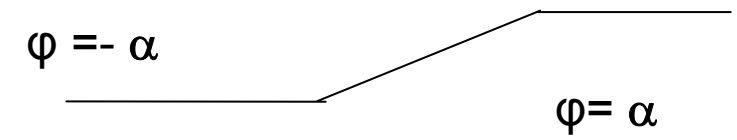
Anti-FE if the sign of α alternates as for the $(TMTTF)_2SCN$.

For a given U_s the ground state is still doubly degenerate between $\varphi = \alpha$ and $\varphi = \alpha + \pi$. $\mathbf{H_U = -U\cos(2\varphi - 2\alpha)}$
It allows for phase π solitons, i.e. holons with the charge *e*.



Purely on-chain solitons, exist as conducting quasiparticles both above and below the $\mathbf{T_{FE}}$.

Spontaneous U_s itself can change sign between different FE domains.
Then electronic system must also adjust its ground state from α to $-\alpha$.
Hence the domain boundary $\mathbf{U_s \leftrightarrow -U_s}$ requires for the phase soliton of the increment $\delta = -2\alpha$
which will concentrate the *non integer* charge $\mathbf{q = -2\alpha/\pi}$ per chain.



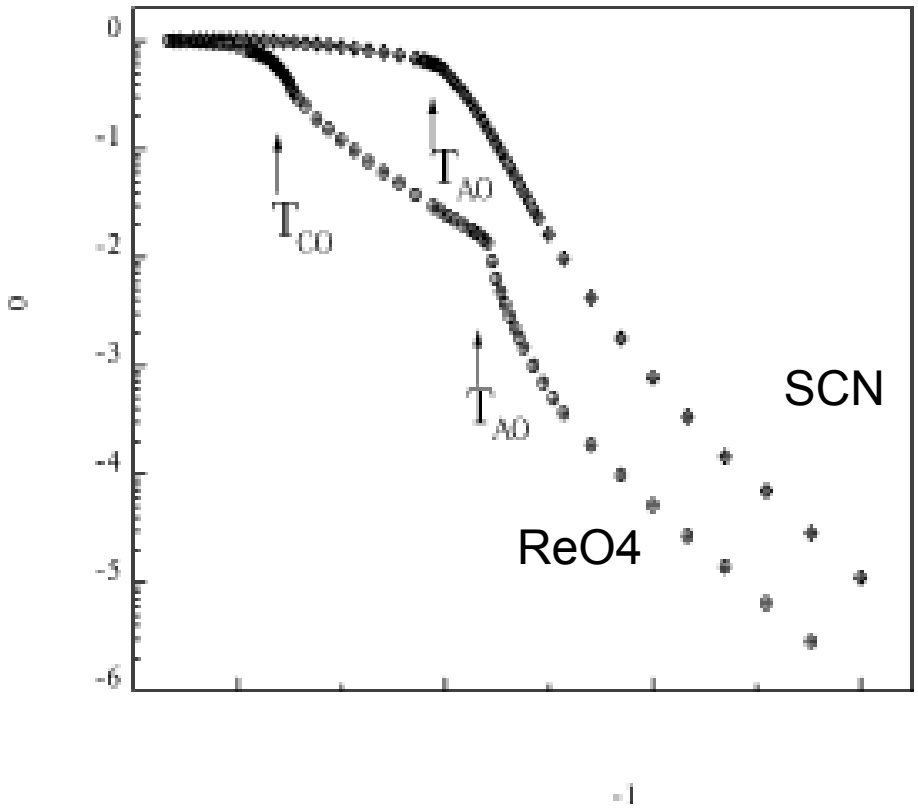
alpha- solitons are walls between domains of opposite FE polarizations

They are on-chain conducting particles only above $\mathbf{T_{FE}}$.
Below $\mathbf{T_{FE}}$ they aggregate into macroscopic walls.
They do not conduct any more,
but determine the FE depolarization dynamics.

Effects of subsequent transitions.

Combined solitons. Spin-Charge reconfinement.

Another present from the Nature:
tetramerization in $(TMTTF)_2ReO_4$ at $T_{AO}<T_0$



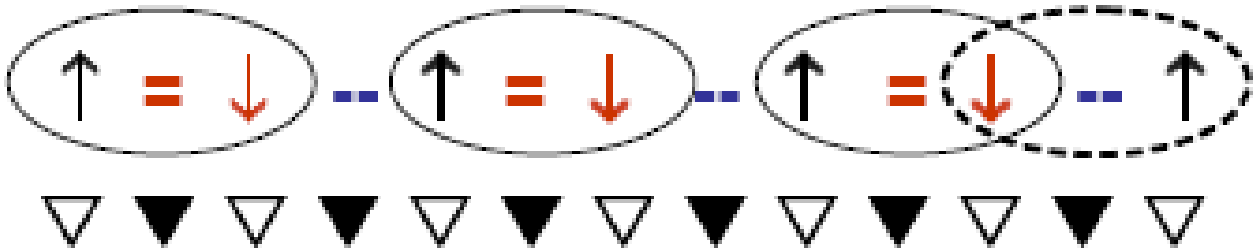
Spin-charge reconfinement below T_{AO} of tetramerisation. Enhanced gap Δ comes from topologically coupled **π**- solitons in both sectors of the charge and the spin. The last is weakly localized.

What does it mean ?

Spin degrees of freedom enter the game:

$$\Psi_{\pm\sigma} \sim \exp[\pm i(\varphi + \sigma\theta/2]$$

θ - spin phase, θ′/ π = smooth spin density



Schematic illustrations for effects of the tetramerization

Inequivalence of bonds **=** , **--** between good sites ▽ endorses ordering of spin singlets.

Also it prohibits translations by one ▽ ▼ ▽ distance which were explored by the $\delta\varphi=\pi$ soliton.

But its combination with the defected unpaired spin ($\delta\theta=\pi$ soliton which shifts the sequence of singlets) is still allowed as the selfmapping – connction of equivalent ground states

Further symmetry lifting of tetramerization mixes charge and spin:
additional energy **$V\cos(\varphi-\beta)\cos\theta$** – on top of **$\sim V\cos(2\varphi)$**
φ and θ -- chiral phases counting the charge and the spin
φ'/π and θ'/π = smooth charge and spin densities
cos θ sign instructs the CDW to make spin singlets over sorter bonds

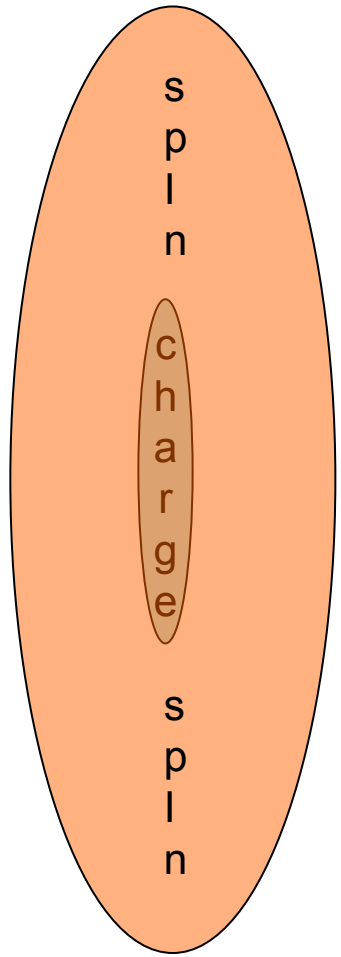
Major effects of V-term :

Opens spin gap $2\Delta_\sigma$:
triplet pair of $\delta\theta=\pi$ solitons at $\varphi=const$

- Prohibits $\delta\varphi=\pi$ solitons –
  now bound in pairs by spin strings
- Allows for combined spin-charge
  topologically bound solitons:

$\{\delta\varphi=\pi + \delta\theta=\pi\}$ – leaves the **V** term invariant

Quantum numbers of the compound particle --
charge **e** , spin ½ but differently localized:
charge **e** , $\delta\varphi=\pi$ sharply within $\hbar v_F/\Delta_\rho$
spin ½ , $\delta\theta=\pi$ loosely within $\hbar v_F/\Delta_\sigma$



Optical Conductivity $\sigma(\omega)$ and Electric Permittivity $\varepsilon(\omega)$

2Δ - 2-particle gap (photoconductivity) – kinks= π- solitons

Eg - optical absorption edge (exciton = bound kink+antikink)

Regime change just at the borderline CD instability $\gamma = 1/2$

Fermi gas side $1/2 < \gamma < 1$: $E_g = 2\Delta$ - no bound states

$4K_F$ CDW side $\gamma < 1/2$: $E_g < 2\Delta$ - collective mode at $E_g = \omega_t = \pi \gamma \Delta < 2\Delta$.

Region $\omega < \omega_t < 2\Delta$ support quantum breathers – bound states of solitons.

Access to $\gamma \sim \Delta/\omega_t$: Δ is well known from $\sigma(T)$ and ω_t is measurable

but not yet - complicated by phonon lines present in the same region.

Not in vain - another indication for the CD.

Surprisingly high intensity of molecular vibrations in TMTTF

(already since Jacobsen et al, 1982)

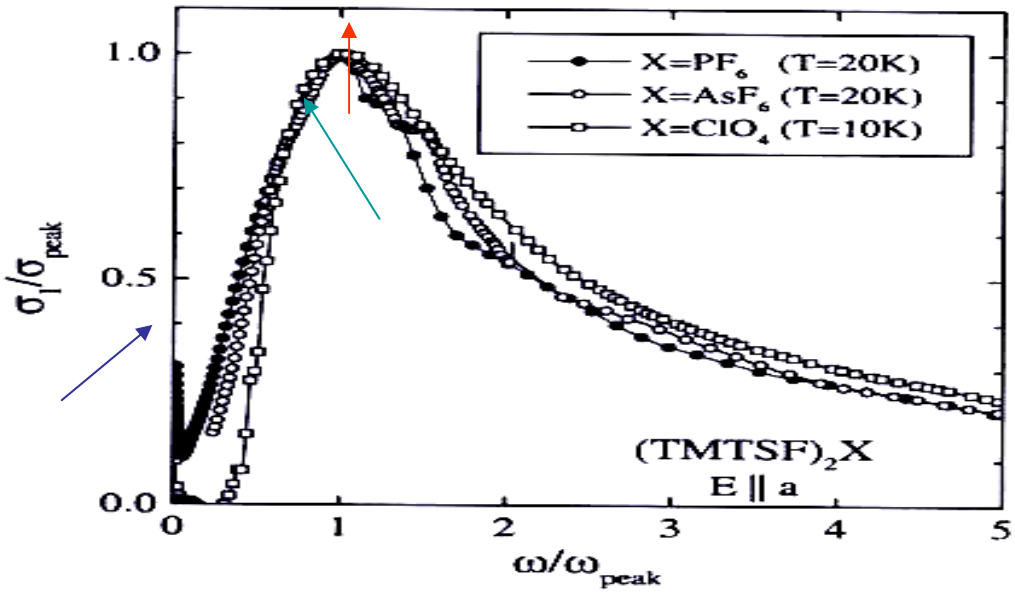
may be just due to the lack of the inversion symmetry lifted by the CD.

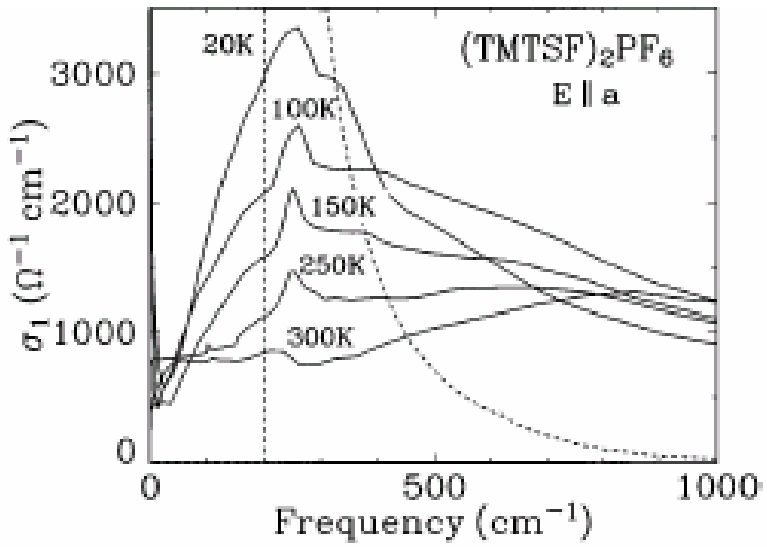
Poorly resolved but still strong sometimes, phonon lines in TMTSF

tell in favour of a fluctuational regime of the CD – agrees with the pseudogap,

rather than a true gap, in electronic optical transitions

$\sigma(\omega)$: Optical Conductivity *Digeorgi group* *Dressel et al, PRL 96*





PSEUDOGAP REGION IN TMTSF SUBFAMILY - interpretations:

Low ω rise: optically active FE mode of the FE rather than Drude peak.

Sharp peak at ω_{peak} : Collective phason mode =exciton= bound pair of kinks

Shoulder above ω_{peak}: $E_g=2\Delta$ - 2-particle gap: pair of kink –
call for photoconductivity experiments at $T<T_{SDW},T_{SP}$.

Pseudogap itself $\omega<\omega_{peak}$, unexpectedly big for TMTSF's small dimerization of bonds, might be enlarged by the fluctuational dimerization of sites similar to staic effect in TMTTF.

APPEAL for optics in TMTTF's with small magnitude of CD
(to send the gap below the mess of molecular phonons)

OPTICAL PERMITTIVITY $\varepsilon(\omega)$ IN FERROELECTRIC CASE.

Mixed electron-phonon contribution at $T>T_{CD}$:

ω_p^* - renormalized metallic plasma frequency,

ω_0 - bare frequency of the molecular vibration associated to CD,

$\omega_{cr}(T)$ - critical value of the optical gap $\omega_t(T)$:

spontaneous CD at $\omega_t < \omega_{cr}$ -- at the criticality $Z(T_0)=1$

$$\varepsilon(\omega) = \frac{(\omega_p^*/\omega_t)^2(1-(\omega/\omega_0)^2)}{(1-(\omega/\omega_0)^2)(1-(\omega/\omega_t)^2)-Z} \quad ....Z = \left(\frac{\omega_{cr}}{\omega_t}\right)^{2-4\gamma} \leq 1$$

1. Fano antiresonance at ω_0

2. combined electron-phonon resonance at $\omega_{0t}^2 \approx \omega_0^2 + \omega_t^{\,2}$

3. FE soft mode at $\omega_{fe}^2 \approx (1-Z)/\left(\omega_0^{-2} + \omega_t^{\,-2}\right)$

-overdamped near T_0 , at $T<T_0$ the FE mode frequency follows the order parameter as $\omega_{fe} \sim \varepsilon^{-1/2} \sim (T_0 - T)^{1/2}$ to become finally comparable with ω_{0t}.

The two modes share the total weight ω_p^{*2} as $(\omega_t/\omega_0)^2$

Optics: collective and mixed modes, solitons. Main expected features.

I. *In any case of the CD*, for both FE or Anti-FE orders, we expect:

Ia) Strongest absorption feature comes from the phase mode,
analogy of the exciton as the bound kink-antikink pair;

Ib) Two-particle gap 2D (photoconductivity e.g.) lies higher,
it is given by free pairs of π-solitons=kinks;

Ic) Spectral region $\omega_t < \omega < 2D$ may support also quantum breathers –
higher bound states of solitons.

II. *In case of the FE order* we expect additionally or instead of **I**:

IIa) Fano antiresonance at the bare a phonon mode coupled to the CD;

IIb) Combined electron-phonon resonance at $\omega_{0t} > \omega_0$, ω_t substitutes for Ia;

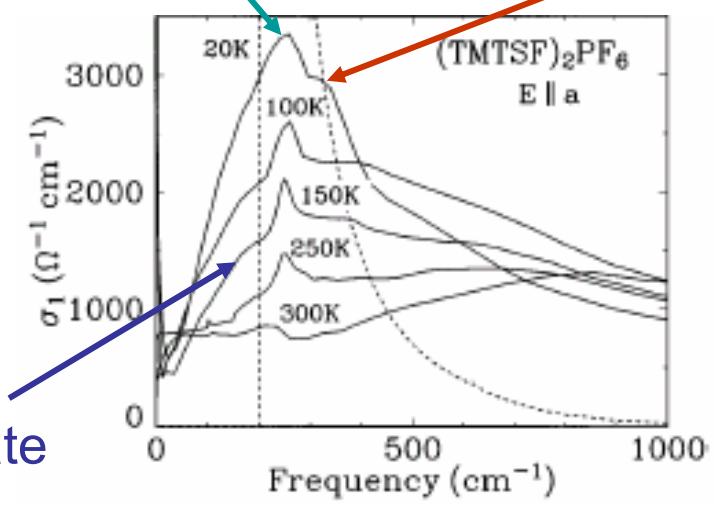
IIc) FE soft mode at ω_{fe} (it increases with the FE order parameter).

TMTTFs: multiple phonon lines filling just the relevant region.
This obstacle is not in vain -- another indication for the CD.
Surprisingly (since 80's, Jacobsen et al) high intensity of molecular vibrations --
Just due to the inversion symmetry lifting by the CD.
TMTSF: weaker phonon lines -- fluctuational CD, pseudogap for electrons.

Do we see solitons in optics ?

collective mode or exciton
= two kinks bound state

Eg=2Δ - pair of free kinks.
Only that will contribute
to photoconductivity



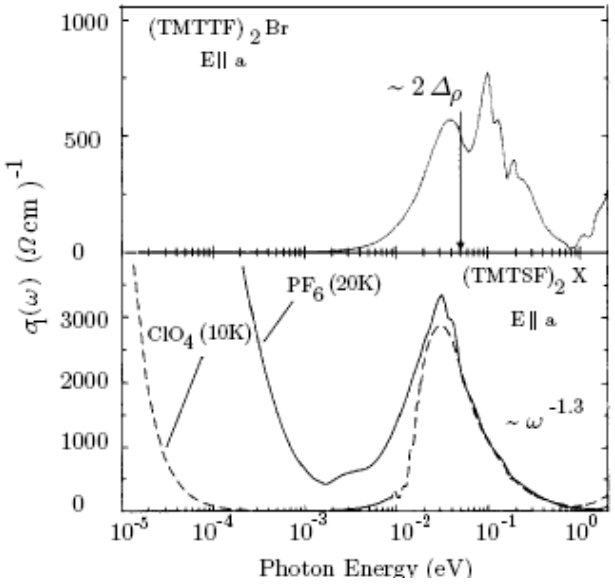
Optical Conductivity,
ETH group
Dressel et al, PRL 96

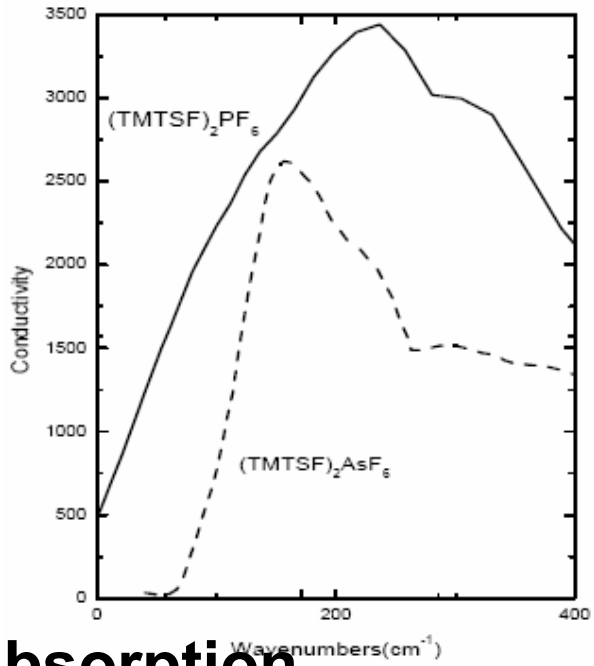
optically active
phonon of FE state

Illustrative interpretation of optics on TMTSF in terms of firm expectations for CO/FE state in TMTTF's

For the Mott state without CO
-no collective mode peak below E_g – need photoconductivity !

Call for experiments on low gap CO states like in $(TMTTF)_2Br$
Recall a great experience of optics in conjugated polymers.





Optical Conductivity $\sigma(\omega)$ = absorption

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Regime change just at the borderline CD instability $\gamma = 1/2$

Fermi gas side ½< γ <1: $E_g = 2\Delta$ - no bound states

$4K_F$ CDW side γ <1/2:

Eg<2Δ - collective mode at Eg= $\omega t = \pi \gamma \Delta < 2\Delta$.

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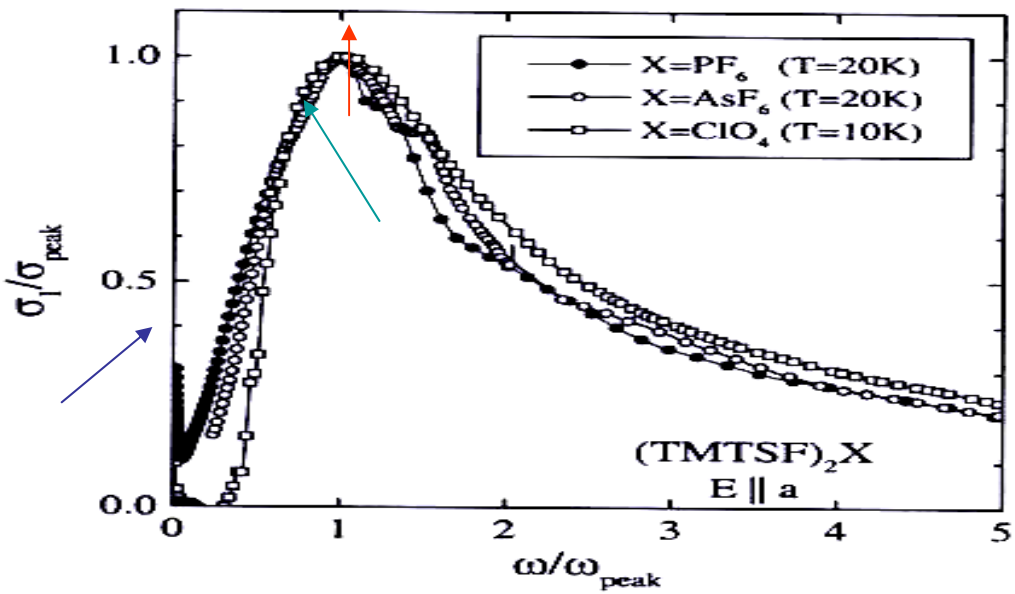

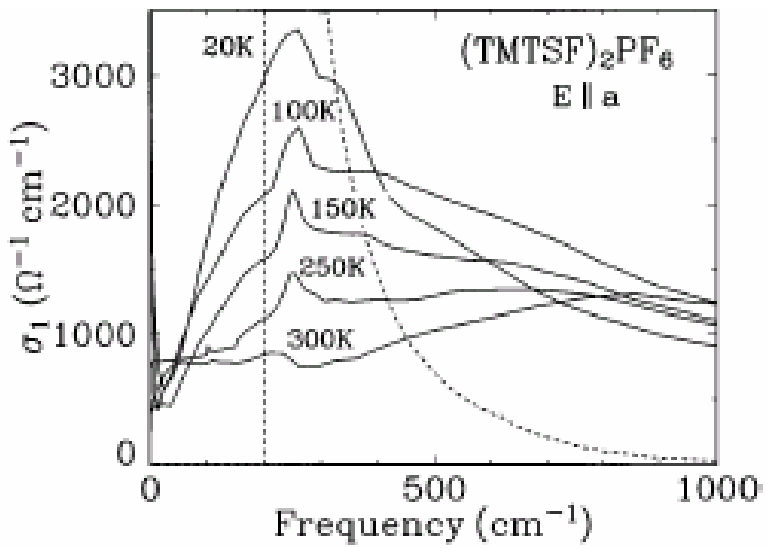

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APPEAL for optics in TMTTF's with small magnitude of CD
(to send the gap below the mess of molecular phonons)

PERSPECTIVES: THE FATE OF METALLIC TMTSF SUBFAMILY?

Nonmetallic TMTTF subfamily: High CD gaps, up to 2000K, at low T;

Mott gap well above T_0, Wide range ($T_0 \pm 30K$) of the FE anomaly;

remind also TTF-TCNQ with ever present $4K_F$ fluctuations.

This is the "Grand Unification" scale, with no differences from interchain couplings, AOs, FE and AFE types, and between *Sulphur* and *Selenium* subfamilies.

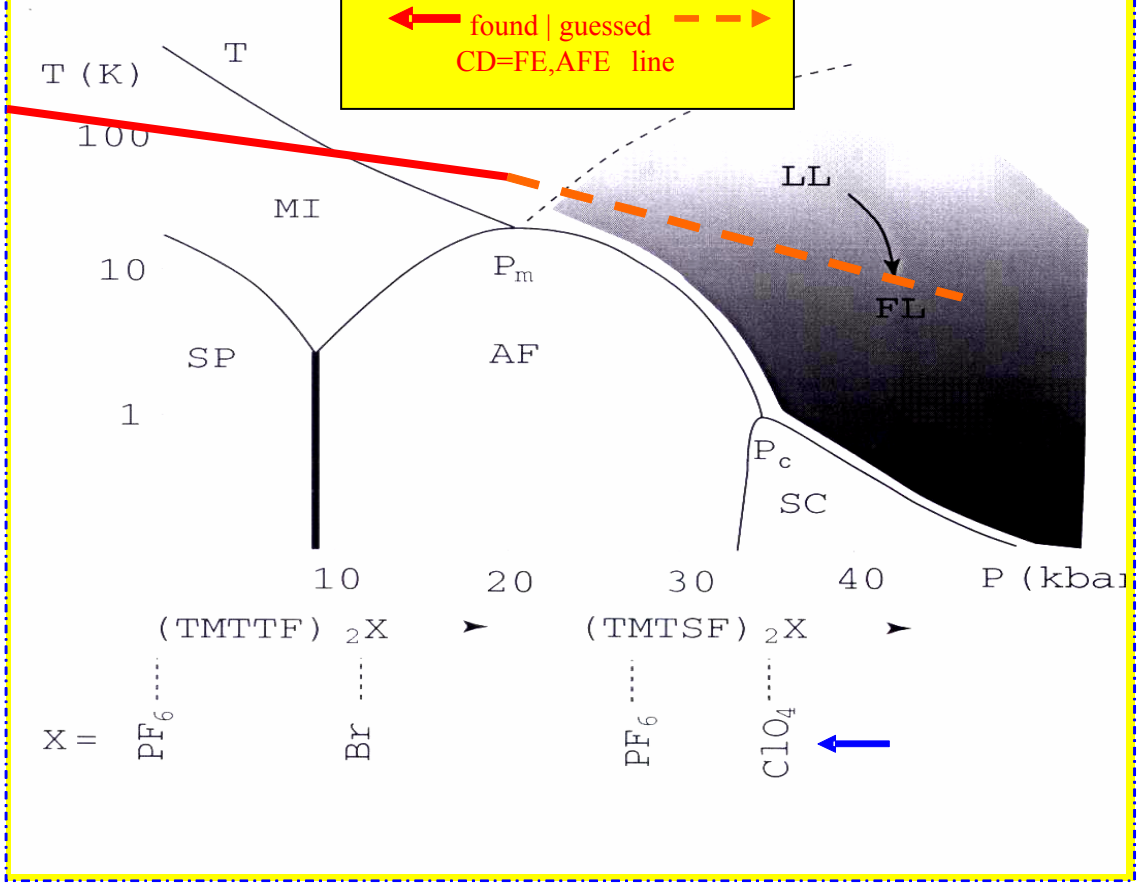
Metallic TMTSF do not allow for studies of ε at very low frequencies and of the NMR with probably very weak line splitting.

Nevertheless *the CD must be their*, just hidden or existing in a fluctuational regime, like stripes in High-T_c cuprates.

The signature may have been already seen in optical experiments.

Natural features to guess and try:

- Optical creation of kink-antikink pairs at 2Δ -- the photoconductivity edge;
- Optical activation of the gapped phase mode at $\omega_t < 2\Delta$;
- T evolution of the FE mode from the overdamped critical one at T_0 to the particularly strong optical phonon mode at low T;
- Activation or enhancement of generic molecular vibrations (both an obstacle and a tool).



Anniversary picture,
Bourbonnais…1999

Message: sequence of electronic phases follows a smooth variation of basic parameters. Substitutions of molecules, ions are equivalent and reduced to the effective pressure. Compounds with NCS anions are abandoned, their AOs were thought to exhort ill defined or undesirable complications. First warning even before CD is noticed: relaxed $(TMTSF)_2ClO_4$ with AO had to be placed to bring the SC. *Logics of effective pressure requires for the quenched phase with no AO, but it yields SDW, not SC.*
Are we on the route from a special interchain charge disproportionation to superconductivity?

Specific picture by S.B. & V.Yakovenko from 1985,86.

The synthesis of structural and electronic phase transitions;
the accent upon major compounds with AOs.
It includes already the AFE case of charge disproportionation.

Its main statements:

Displacive, rather than orientational, mechanisms drive the AOs.
Symmetrically defined effects of fine structural changes switch electronic state.
1D "g-ological" phase diagram of the LL results in *2D, 3D* phase transitions only with the backup of special symmetry lowering effects.
Accent on the charge disproportionation with the AFE arrangement in $(TMTTF)_2SCN$.
SC appears only if the system is drawn away from half filling avoiding the Mott state.
It happens in $(TMTSF)_2ClO_4$ thanks to the particular AO leading to inequivalence of chains. This is a purely defined case of what today is called the "internal doping". Its magnitude, I.e. the "interchain charge disproportionation" was exactly determined from data on fast magnetic oscillations.

Major difficulties of this picture.

In applications to Se compounds: common problems of any quasi 1D approach in view of mostly successful band theory of the FISDWs.
Cases of the SC state without observation of the particular **Q**3 AO.
The recent views on independent AOs allows to suggest that the **Q**3 *structure is still their, at least in local or dynamical form without the long range order.*

WHERE WE ARE? Routes to microscopics.

$H\sim=(\hbar/4\pi\gamma)\,[v_\rho(\partial_x\varphi)^2 + (\partial_t\varphi)^2/v_\rho] - U\cos(2\varphi) - W\cos(4\varphi)$

U- dimerization, build-in or spontaneous

W- effect of ¼ filling, octamerization

$\gamma \equiv K_\rho$ controls renormalization of U and W,

without interactions $\gamma=1$ *and the velocity* $v_\rho=v_F$

Only negligible 3D coupling may allow to pass by CD at $\gamma<1/2$.

Prove:

$\gamma<1$: renormalized $U\neq0$ - gap originated by build-in dimerization.

$\gamma<1/2$: spontaneous U is formed = $4K_F$ condensed, no need for bare U.

-- electronic energy gain $\delta F_e\sim -\Delta^2 \sim -U^\zeta$ ($\zeta=1/(1-\gamma)<2$)

overcomes the energy lost $\sim U^2$ to pay spontaneous deformations.

Optical signature: collective mode drops below two-particle gap.

$\gamma<4/9 = 0.39$ trimerization lock-in (TMTTF-TCNQ case, Jerome 78)

$\gamma<1/4 = 0.25$ renormalized $W\neq0$ - gap originated by generic ¼ filling.

$\gamma<\sqrt{5}-2=0.24$ ultimate 3D SDW instability.

$\gamma<2/9 = 0.20$ spontaneous trimerization.

$\gamma<3-\sqrt{2}=0.17$ last features (PES,ARPES) of electrons disappear.

$\gamma=1/8=0.125$ spontaneous W is formed, close to estimate from optical tails

What makes γ and ω^*_p small enough: interactions or phonons?

$$\frac{\hbar v_F}{4\pi}\left\{(\partial_t\varphi)^2 C_{kin}/v_F^2 + (\partial_x\varphi)^2 C_{pot}\right\} \equiv \frac{1}{4\pi\gamma}\left\{(\partial_t\varphi)^2/v_\rho + (\partial_x\varphi)^2 v_\rho\right\}$$

$$\gamma = \frac{1}{C_{pot}C_{kin}}\,,\quad \frac{\omega_p^*}{\omega_p} = \left(\gamma\frac{v_\rho}{v_F}\right)^{1/2} = \frac{1}{C_{kin}}\,,\quad \frac{v_\rho}{v_F} = \frac{C_{pot}}{C_{kin}}$$

Lowering of ω^*_p singles out effctive mass enhancement $C_{kin} > 1$ – coupling of the phase mode with acoustic phonons like in CDWs.

Coulomb hardening factor $C_{pot} > 1$ acts upon γ and velocity v_ρ

but cancels in their product which gives ω^*_p

Mass enhancement is not effective above acoustic frequencies.

It explains the divergence in extracting values of ω^*_p from very high and from intermediate frequency ranges.

If true, then the CD state resembles CDWs or another Wigner crystal: electrons on the He surface where selftrapped electrons gain the effective mass from surface deformations - the riplons.

CONCLUSIONS

Discovery of the ferroelectric anomaly (Nad, Monceau) and of the charge disproportionation (S. Brown et al) call for a revaluation of the phase diagram of the $(TMTCF)_2X$ compounds and return the attention to the interplay of electronic and structural properties (S.B. and V. Yakovenko).

Theory versions:

Charge Disproportionation (Seo and Fukuyama)

Combined Mott-Hubbard state + FE, solitons (S.B.).

Links:

$4K_F$ anomalies (Kagoshima, Pouget), Wigner Xs (Kanoda et al)

BEDT family (rem. Mori with Tanaka, Tajima; Fukuyama); charge segregation in transition metals oxides, stripes (Nagaev since 70's + Oxford book 2003)

Main challenges:

Hidden existence of CD/FE in the metallic *Se* subfamily;

Optical identification of gaps and soft modes;

Solitons via conductivity, optics, NMR.

FE hysteresis, relaxation, domains.

The state of world of organic conductors in the IIId millennium:
DISPROPORTIONATED and POLARIZED

Appendix: History Excursions.

The described events call again for the role of AOs upon electronic phases. It returns us to suggestions already made about two decades ago. In the following we quote from publications written in early-mid 80' which views usually have been ignored by now.

Some extracts from S.B. & V. Yakovenko (1985).

…We suggest a general model for the phase diagram of the Bechgaard salts in a way that the variation of electronic states is mainly determined by the crystal symmetry changes.

…A complicated phase diagram PD includes the states:
Metal M, insulator I, Peierls insulator CDW, magnetic (paramagnetic) insulator MI (PI), antiferromagnetic AF insulator SDW, field induced SDW,
superconductivity SC of singlet or, not excluded yet, triplet TS types.

…The variation of phases follows the change of an anion type *X*, anion structure, pressure, temperature, magnetic field. We suggest a simple general model where details of the PD are uniquely determined by the anion structure changes.

…Experimental data show us the following correlation between the anionic structure characterized by the wave vector **q**, it's influence upon the electronic system.

q2 =(0,1/2,1/2). The molecules are not equivalent.

Phase sequence: M $\rightarrow$ MI $\rightarrow$ SDW or CDW (Spin-Peierls).

Unperturbed structure. Bonds are dimerized. PD: M$\rightarrow$MI $\rightarrow$SDW.

The last two phases are clearly separated only in TMTTF subfamily.

TMI and TSDW are well separated in *X*=*SCN*: TMI=160K while TSDW=7K

q3 =(0,1/2,0). The neighbouring stacks are not equivalent.

Phase sequence : M $\rightarrow$ SC $\rightarrow$ FISDW.

q4 =(1/2,1/2,1/2). The tetramerization.

Phase sequence : M $\rightarrow$ I transition being driven by the AO.

The rare case 2.

helps us to fix the model for the whole family: a strongly correlated 1D state with the separation of charge- and spin degrees of freedom.

The typical case 1. Qualitatively corresponds to the same model while the separation is less pronounced and interpretation may be controversial.

The most important for appearance of the SC is the case 3.:

the alternating potentials lead to some redistribution of the charge between the two types of stacks, hence their system is driven from the two fold commensurability which removes the Umklapp scattering, destroys the Mott-Hubbard effect and stabilizes the conducting state down to lower temperatures where the SC can appear.

Some extracts from S. Barisic & S.B. (1981):

...we propose an alternative explanation of (TMTSF)2PF_6, based on the fact that this material possesses a weak dimerization gap Δ.

…This gap is due to the environment of the given chain, which, unlike the chain itself, does not posses a screw symmetry along the chain axis.

…Without the effect of the environment the band is quarter-filled.

…The environment (PF_6, etc.) opens a small gap Δ in the middle of this band which therefore becomes half-filled. Hence also small are the corresponding constant for Umklapp scattering and the characteristic temperature:

$$\mathbf{g_3 \sim g_1 \Delta / E_F .\ T_3 \sim E_F\, g^{1/2} (g_3/g)^{1/g}\ ;\ g = 2g_2 - g_1}$$

…Assuming the pressure suppresses g_3 and with it T_3, the Josephson coupling J of superconducting fluctuation will finally overcome the Umklapp scattering.

…This interpretation explains observations in $(TMTSF)_2PF_6$ as a result of competition of two small (off-chain) parameters, g_3 and J, rather than as a result of the accidental cancellation of the large coupling constants $2g_2$ and g_1 *(as just proposed at Orsay)*.
In this way there appears a region in the phase diagram where the superconductivity exists in absence of g_3 , but where the CDW is introduced by g_3

… A closer examination of the model shows that it is the triplet superconductivity TS which becomes more stable than the CDW.

History Excursion. *Some extracts from S.B. & V. Yakovenko (1985).*

...Variation of electronic states is determined by crystal symmetry changes…

…Experimental correlation between electronic phases and anionic structures characterized by the wave vector **q**….

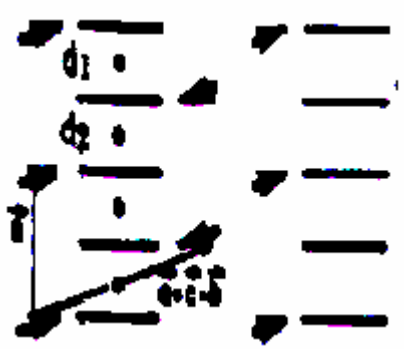
Most important for appearance of the SC is the case of relaxed $(TMTSF)_2ClO_4$

$\mathbf{q_3}$ =(0,1/2,0) (T_{AO}=24K only). Phase sequence : M $\rightarrow$ SC $\rightarrow$ FISDW.

Neighbouring stacks are not equivalent.

Alternating potentials redistribute the charge between two types of stacks, hence the system is driven away from the two fold commensurability

Umklapp scattering is removed, Mott-Hubbard effect is destroyed conducting state is preserved down to lower temperatures where the SC can appear.



Major difficulties of this picture: Cases of the SC state under pressure without observation of particular $\mathbf{Q}_3$ AO.

But *recent views on independent AOs suggest that the* **Q**3 *structure is still their, at least in local or dynamical form without the long range order. Low T structures in under pressure are necessary. In case of failure, we need two models for SC in* $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$