FERROELECTRIC MOTT-HUBBARD PHASE IN ORGANIC CONDUCTORS AND ITS IMPACT.

Felix Nad', **Serguei Brazovskii**, Pierre Moncea

Laboratoire de Physique Théorique et Modèles Statistiques,
CNRS and Univ. Paris-Sud, Orsay, France

OUTLINE.

- Interplay of electronic and structural properties.
- Subtle anionic transitions as the gift of magicians.
- The abandoned "structurless" transitions take a revenge.
- Discovery of the ferroelectric anomaly (Nad, et al).
- Discovery of the charge disproportionation (Brown et al).
- First clear prove for the conductivity by holons (π-solitons).
- MF theory for charge disproportionation (Seo, Fukuyama).
- Combined Mott-Hubbard state and ferroelectricity (S.B.et al).
- The 20 years anniversary picture revised.
- A provocation: will the *Se* subfamily stay intact?
- Ferroelectric dipole mode as the reason for optical features.
- S.B.& V.Y. theory for the universal phase diagram revived.

"Vingt ans après":

- F. Nad, P. Monceau and S. Brazovskii, PRL, **86** (2001) 4080. *Ferroelectric Mott-Hubbard phase of organic conductors.*
- S. Brazovskii, V. Yakovenko, J. de Physique **47** (1986) 175. *On the theory of superconducting phase in organic superconductors.*
- S. Brazovskii, V. Yakovenko: JETP Letters **43** (1986) 134. *Magnetic oscillations in organic superconductors (theory).*
- S. Brazovskii, V. Yakovenko: JETP **62** (1985) 1340. *On the theory of the organic superconducting materials.*
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- S. Barisic, S. Brazovskii. Recent Developments in Cond Matt. Phys., Pl. Pr, **1** (1981) 142. *Superconductivity and repulsive interactions in linear chain materials.*
- S. Brazovskii, S. Gordyunin, , JETP Letters **31** (1980) 371. *Weak two - fold commensurability in a Peierls system..*

minimal others' quotations:

Experiment S. Brown group UCLA

Theory Seo & Fukuyama Tokyo

Main quotations:

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  J. de Phys. IV, **9** (1999) Pr10-361. Phys. Rev. B **62** (2000) 1753;
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- R. Lawersanne et al, J. Physique. Lett. **45** (1984) L393.
  Phys. Rev. B 37, 4280 (1988) ;Phys. Rev. B, **31** (1985) 3583.
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V. Ilakovac et al PRB 50 (1994) 7136

TMTTF/TMTSF-X **family**

Tc ~ 1-15K almost all known electronic phases

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

At higher T= T_0 - ``structureless`` transitions, mysterious origin

Recent discoveries:
the huge dielectric anomaly (Monceau group)
the charge disproportionation seen by the NMR (Brown group).

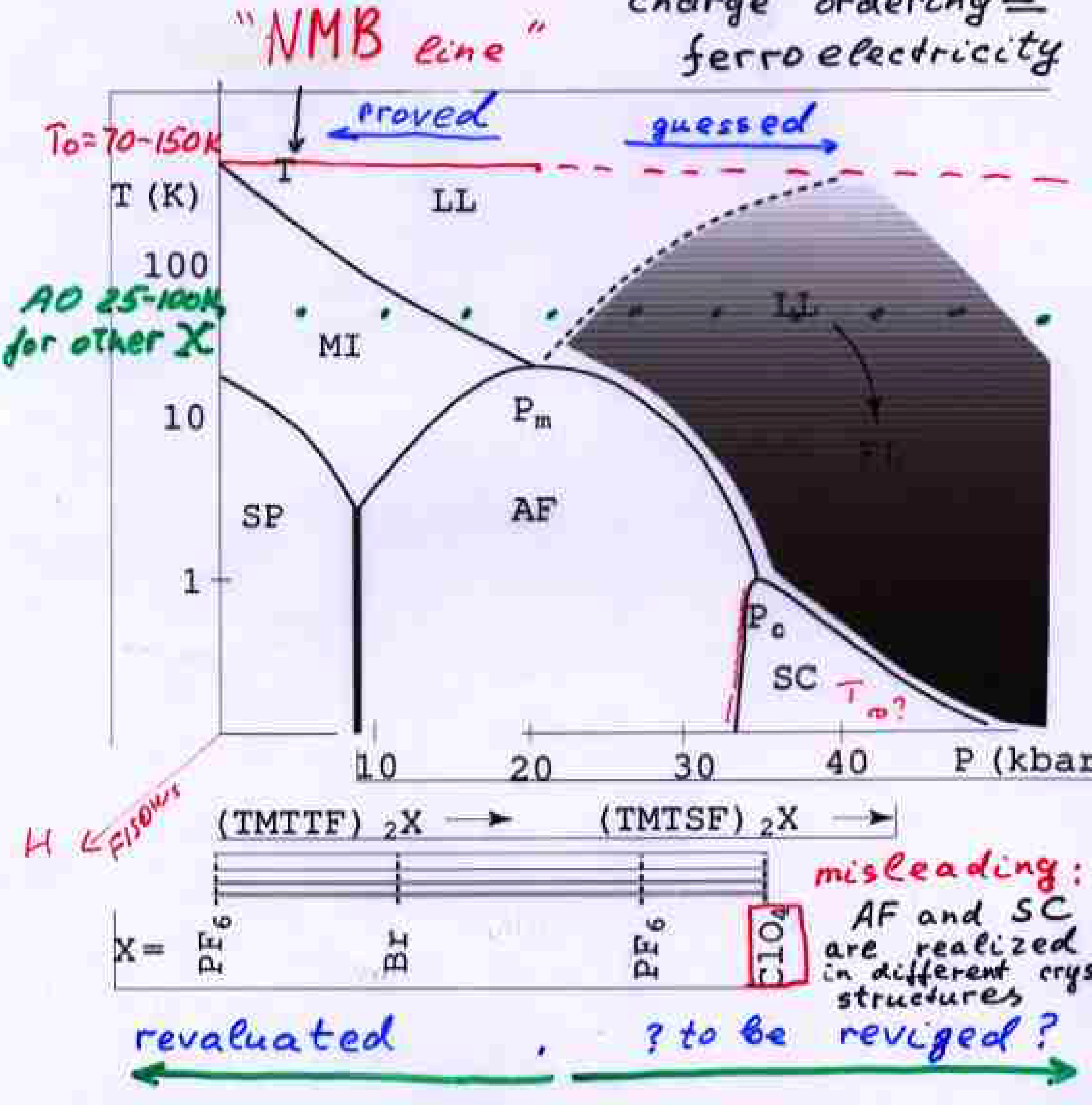
Our interpretation: the ferroelectric FE state. triggered by the uniform shift of ions yielding a macroscopic FE polarization.

Our theory : *combined Mott-Hubbard state,* a strongly fluctuating $4K_F$ density wave, i.e. the local Wigner crystal, subjected to a weak two fold commensurability potential.

New ingredient - an account for the 'orthogonal' contributions from two symmetry breaking effects:
•build in nonequivalence of bonds
•spontaneous nonequivalence of sites.

Our approach - complementary to the one by Seo and Fukuyama.

The experimental discoveries together with the supplied theory call for revaluation of studies in what was thought to be the "abnormal metallic state" (Bourbonnais and Jerome) and return us to concept of universal phase diagram developed in mid 80's by S. B. and V.Yakovenko based upon effects of interference between electronic properties and fine symmetry changes due to the AOs or external fields.



charge ordering = ferroelectricity

"NMB line"

T_0=70-150K

proved ⟵

guessed ⟶

AO 25-100K for other X

T_{co}?

H ⟵ FISDWs

misleading: AF and SC are realized in different crys structures

revaluated , ? to be revised ?

Electronic phases of the $(TMTCF)_2X$ families:

- the normal and the superconducting SC metals,
- the regime of the Mott-Hubbard charge localization,
- the spin-Peierls state (i.e. the charge density wave –CDW in frame of repulsion),
- several types of spin density waves - SDW, FISDW.

Usual frame:

Several weakly different structural types due to the *anion ordering* -AO which are fine arrangements, with $\mathbf{q} \neq 0$, of singly charged counter-ions *X* [Pouget and Ravy, review 96].

Their energy scale $T_{ao} \approx 100K$, is much higher than scales of electronic transitions $Tc \sim 1 \div 20K$

Occasionally, as it seemed, there were *"structureless transitions"* at temperatures $T_0 > T_{ao}$ which nature was unknown till recently. They were weakly seen in high (~ GHz) frequency dielectric susceptibility ε, in resistivity and in thermo power, also very poorly in the $\mathbf{q}=0$ scattering.

Recent successes in resolving the mystery of T_0

- the gigantic anomaly in low frequency permitivity ε (Nad et al - P. Monceau group, Grenoble),
- the charge disproportionation seen by the NMR (Chow et al - S. Brown group, UCLA).

Adventure of the NMR:
clear detection of the site nonequivalence.

Its constraint:
the 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 known from the structural studies.

The conductivity from JmE

A clearest example of charge transport by Sine-Gordon solitons ≡ holons.

[redacted]

$T \gg T_{d.\,ordering}$ (SDW, SC)

$(TMTTF)_2SbF_6$

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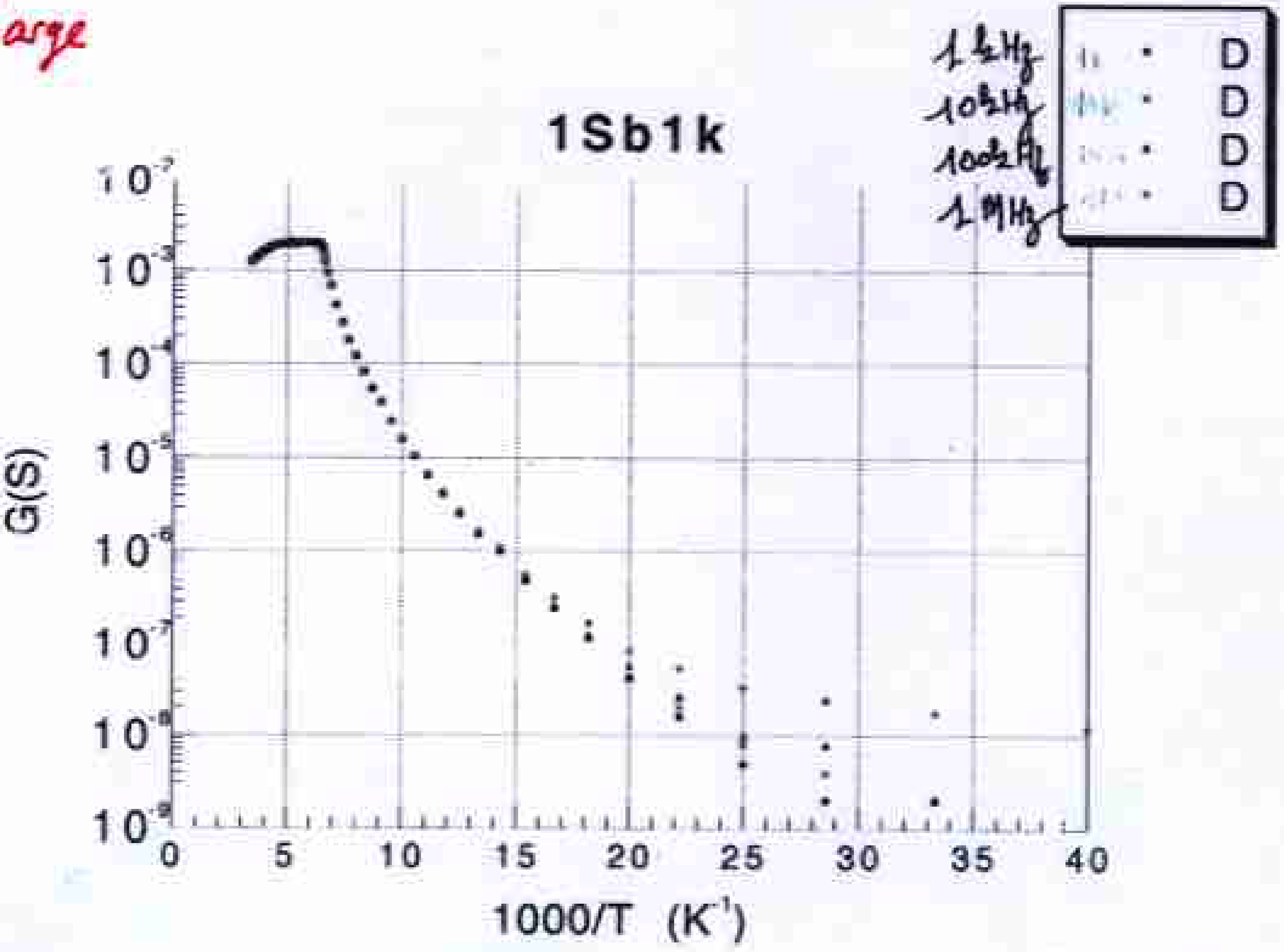
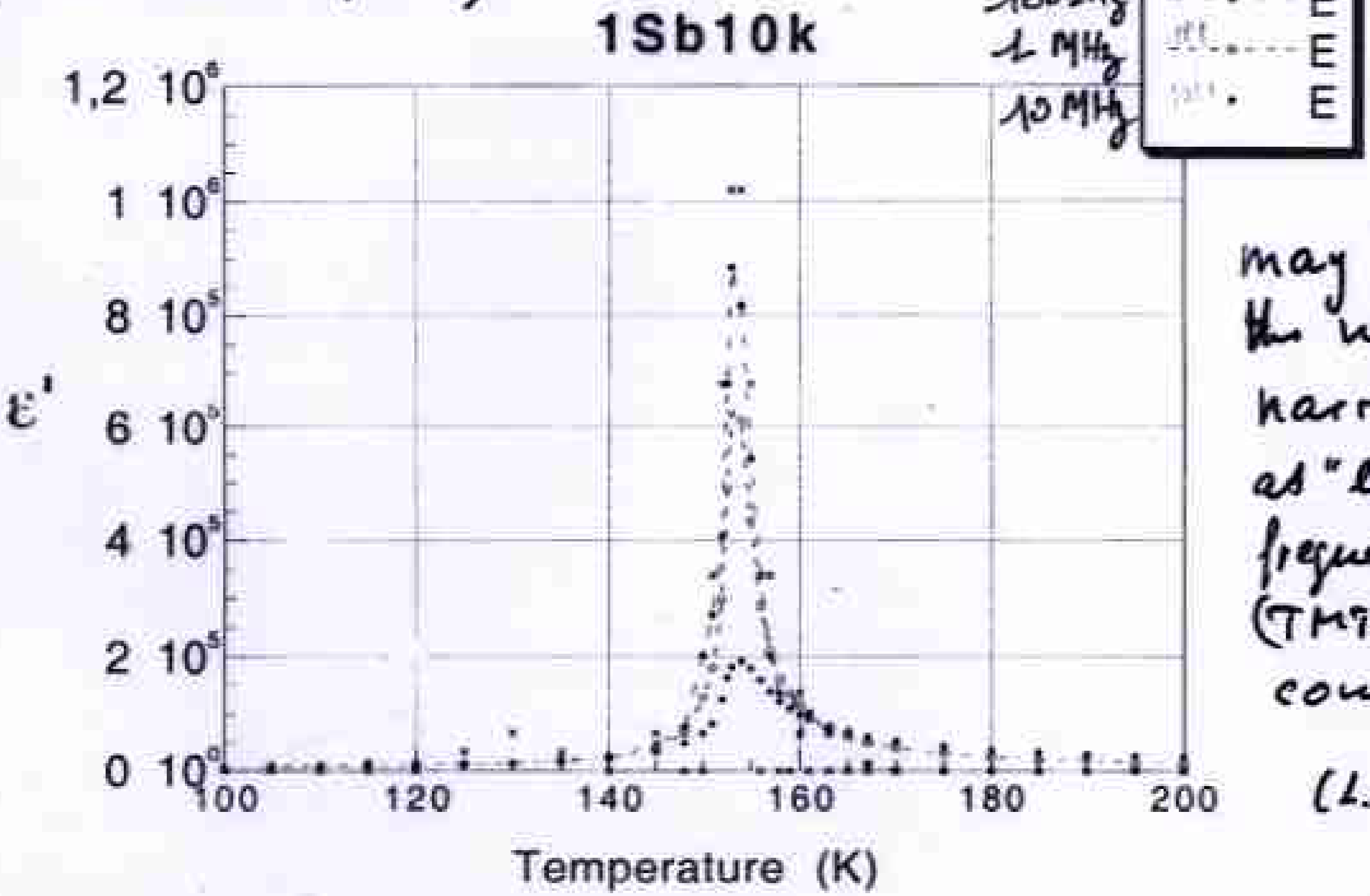


$\Delta \simeq 520K$

greatly improved quality,
perfectly sharp gigantic anomaly
understanding the dualism:
Charge ordering — Ferroelectricity

$(TMTTF)_2SbF_6$

are 10^2-10^5 lower
than the lowest ones
in optics



may also explain
the misterious
narrow peak
at "low" optical
frequency in
$(TMTSF)_2X$
compounds

(L. Degiorgi et al)

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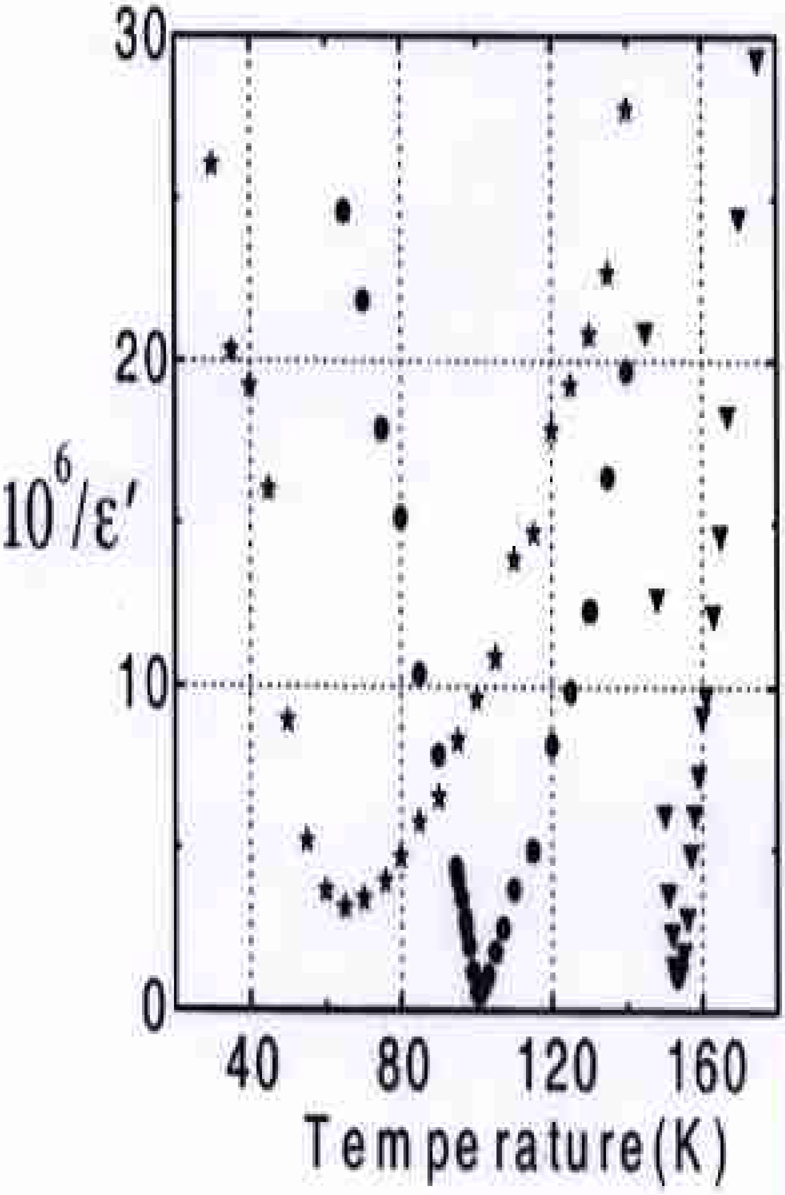
NAD - MONCEAU



The electric permitivity experiments (Nad et al, 99 - 01) provided an unique access to the brightly manifested anomalous collective property of the mysterious T_0 transition. A clear cut fitting of the anomaly in ε(T) to the Curie law suggests that we are dealing with the least expected case of the *ferroelectric* phase. Even more curiously is that it is the ferroelectric version of the Mott-Hubbard state

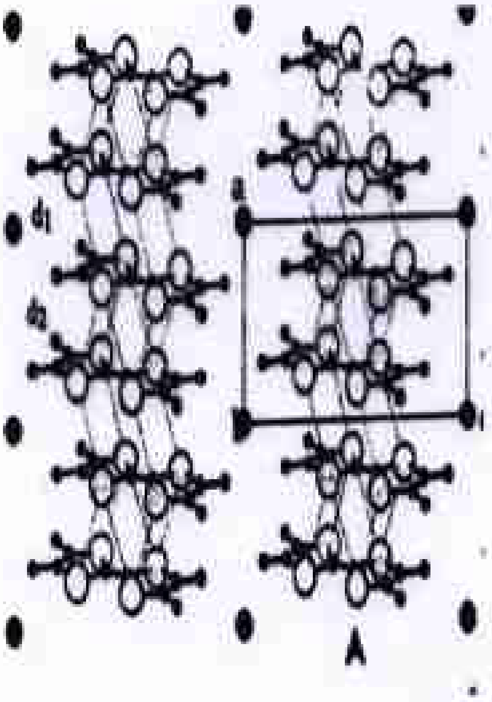
Fig. Temperature dependence of the inverse of the real part of the dielectric permitivity ε' $(TMTTF)_2PF_6$, $(TMTTF)_2AsF_6$, and $(TMTTF)_2SbF_6$ at the frequency of 100Hz.

$T < T_0$:

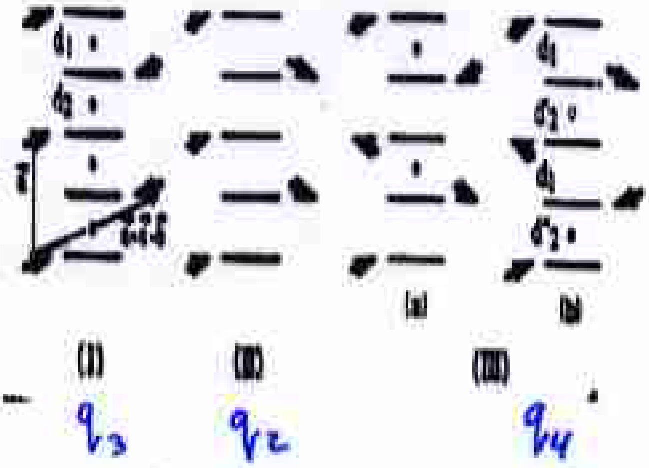
$\varepsilon^{-1} \sim (CO)^2$

Wide $T-T_0$ anomal dominates the wha regime of what was thought to be the non-FL metal.

Figures from the review by Pouget and Ravy, 1996



The nonperturbed crystal structure. The dimerization of intermolecular distances $d_1 \neq d_2$ doubles the on-stack unit cell, hence changing the mean electronic occupation from ½ per molecule 1 per dimer. It originates the Umklapp scattering g_3 which opens (Dzyaloshinskii and Larkin, Luther and Emery) the route to the Mott-Hubbard insulator.



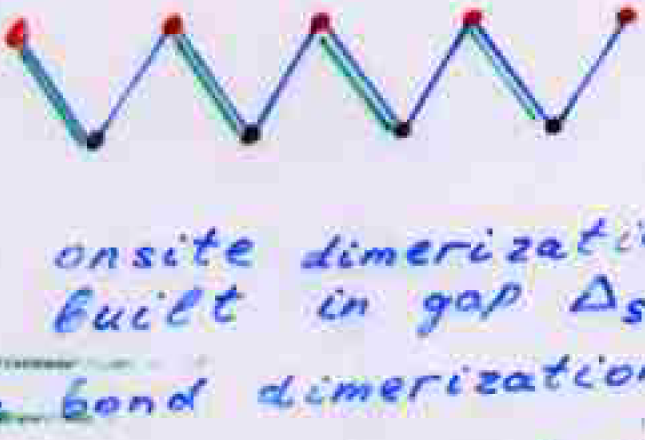
Basic types of anion ordering with correspondence to the classification of S.B.& V.Y: I⇒ q_3, II ⇒ q_2, III(a,b) ⇒ q_4. The structure q_2 already demonstrates the common ionic polarization of each anionic chain, hence the electronic dipole moment of each stack. But they alternate in perpendicular direction forming the antiferroelectric state.

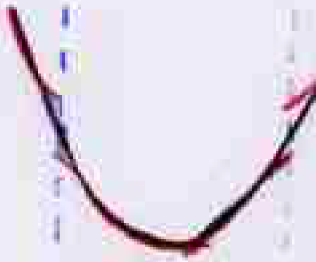
The key hypothesis: the ferroelectric state **q**=0 is built by similar structure but with all displacements being identical both along and among the chains/stacks thus leading to the FE state.

From polymers to organic crystals.

The idea of the hidden ordering comes from the "combined Peierls state" S.B.+N.K. 1981 [6] in polymers. It describes the joint effect of *extrinsic* Δ_{ex} and *intrinsic*_Δ_{in} contributions to the dimerization, hence to the electronic gap Δ. We need the case of the "orthogonal mixing" relevant to polymers of the $(AB)_x$ type like the modified polyacethylene $(CRCR')_x$. Δ_{in} comes from the build-in site dimerization Δ_{ex} due to the AB alternation. The additional intrinsic contribution Δ_{in} to the total gap $\Delta=(\Delta_{in}{}^2 + \Delta_{ex}{}^2)^{1/2}$ comes from the spontaneous dimerization of bonds $\Delta_{in}= \Delta_b$ like in the generic Peierls effect.

Combined Peierls state in $(AB)_x$ polymer





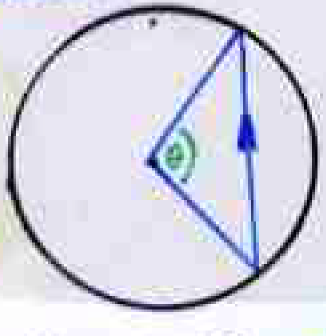
● ● onsite dimerization built in gap Δ_s

— ═ bond dimerization gap Δ_c

Δ_s, Δ_c - orthogonal matrix elements

$$\Delta = \Delta_s + i\Delta_b$$

$$|\Delta|^2 = \Delta_s^2 + \Delta_b^2$$



$\Delta_s \pm i\Delta_b$

$e\frac{\theta}{\pi} \neq e$

Solitons: chiral Gross-Neveu with constrains

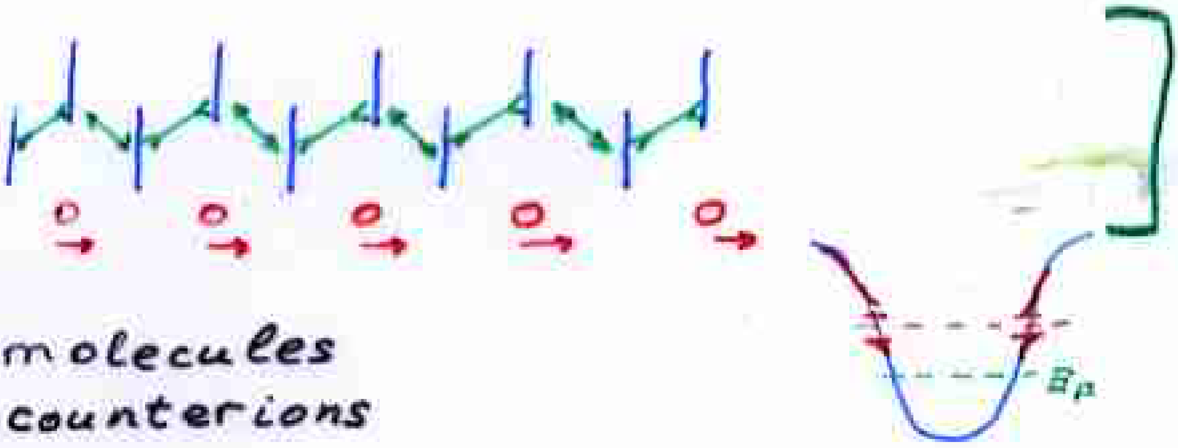
System adds a spontaneous Δ_b dimerization if: $\Delta_s < \Delta_0$ = optimum

THE Theory

Organic superconductor / $(MTTCF)_2X$

$\uparrow C = S, Se$

Mott insulator



| molecules

o counterions

Built-in weak bond dimerization let electrons know that they fill $1/2$, not $1/4$ of the band → obey Mott-Hubbard rools.

Dilemma: if this M.-H. gap Δ_B < optimal (?) site dimerization will be added.

M-H ⇒ M-H instability

For the particular zig-zag structure of $(MTTCF)_2X$ realized by $Q=0$ displacements of anyons ⇒

Ferroelectricity.

Modifications for the charge ordering:

- Substitute the Peierls effect by the Mott-Hubbard one.
- Interchange the build in and the spontaneous effects.

Now the build-in one comes from nonequivalence of bonds while the spontaneous one comes from non equivalence of sites. Both contributions can be of the build in type in the particular case of the $(TMTSF)_{0.5}(TMTTF)_{0.5}$ mixture (Ilakovac).

The 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

$$U=(U_s^2+U_b^2)^{1/2}.$$

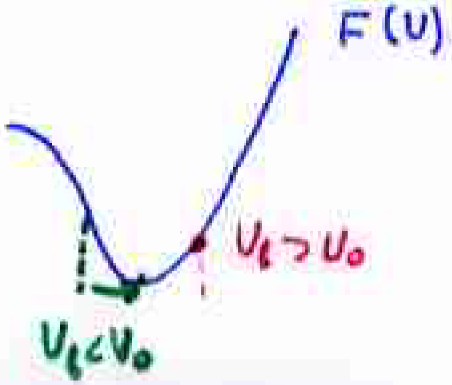
The electronic energy $\mathbf{F}_e$ depends only on Δ that is on the total U.

But the energy $\mathbf{F}_d$ of ionic displacements and of the related molecular distortions depends only on the spontaneous site component U_s: $F_d=K\,U_s^2/2$

The total energy $\mathbf{F}_{tot}$ 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 $U_0(T_0)=U_b$.



U_0 - optimum

Necessary quotations on electronic correlations

Charge degrees of freedom can be described by the phase $\varphi=\varphi(x,t)$ for the CDW and SDW order parameters developing at low T:

$k_F = \pi/2$

$$O_{dw}\sim(-1)^{x/2} \cos \varphi.$$

$\Psi_\pm \sim \exp[\pm i\varphi/2 \pm x\pi/2]$

The gapless spin degrees of freedom are split-off and not important in our context.

The bosonized Hamiltonian for φ can be written as

$\gamma \leftrightarrow K_\rho$

$$H\sim (\hbar/4\pi\gamma)\, [v_\rho (\partial_x\varphi)^2 + v_\rho{}^{-1}(\partial_t\varphi)^2] -U \cos (2\varphi)$$

ψ:

(without interactions $\gamma=1$ and $v_\rho=v_F$.)

U is the Umklapp scattering amplitude of Luther and Emery or $g_3\sim U$ of Dzyaloshinskii & Larkin. Its presence is the main feature of systems with a single electronic mean occupation of the lattice unit cell.

A generous property of the $(TMTCF)_2X$ is that U is small which opens an intriguing crossover of the charge localization - one of main subjects of contemporary studies.

Only for low enough $\gamma<1/2$ the renormalized value of U is non zero:

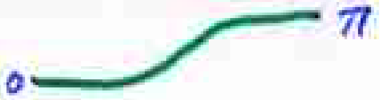
$$U\rightarrow U^*\neq 0,\ U^* =\omega_t{}^2/(8\pi\, \gamma\, v_\rho),$$

$\omega_t\leq\Delta$ is a gap in the spectrum of linear phase excitations

$\omega_k{}^2= (v_\rho k)^2+ \omega_t{}^2$

Current carriers are the $\pm\pi$ solitons with charges $\pm e$ and the energy

$\Delta \sim \omega_t$



There are standard scaling relations $F_e\sim-\Delta^2$, $\Delta \sim U^\zeta$, $\zeta=1/2(1- \gamma)$

$2\,\zeta <2$ if $\gamma <1/2$, then U can appear spontaneously: the gain of the F_e is higher than the loss $\sim KU^2$ of energy due to spontaneous deformations.

The combined Mott - Hubbard state.

Two types of dimerized systems: The two interfering sources for the weak two fold commensurability ⇒ two contributions to the Umklapp interaction.

A. ***The site dimerization.*** The symmetry $x \to x+1$ is broken;
The preserved ones are
$x \to x+2$ and $x \to -x$, hence $\varphi \to \varphi+\pi$ and $\varphi \to -\varphi$
The lowest invariant is
$\mathbf{H_U^s=-U_s \cos 2\varphi}$

B. ***The bond dimerization*** preserves the symmetries $x \to x+2$ and $x \to 1-x$,
hence $\varphi \to \varphi+\pi$ and $\varphi \to \pi/2 - \varphi$
The lowest invariant is
$\mathbf{H_U^b=-U_b \sin 2\varphi}$

***At presence of both types* A *and* B** the nonlinear Hamiltonian becomes

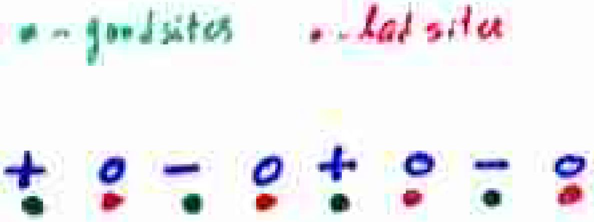
$$\mathbf{H_U= -U_s \cos 2\varphi -U_b \sin 2\varphi = -U\cos (2\varphi-2\alpha)}$$

$\mathbf{U=(U_b{}^2+ U_s{}^2)^{1/2}}$, $\mathbf{\tan 2\alpha= U_s/ U_s}$
For a given U_s the ground state is still doubly degenerate between $\varphi= \alpha$ and $\varphi= \alpha+\pi$ which allows for phase π solitons, i.e. holons with the charge *e*.

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

$U_s \neq 0$ originates the ferroelectric ground state if the same φ_0 is chosen for all stacks and the state is Anti-FE if the sign of φ_0 alternates, as for the *(TMTTF)$_2$SCN*.

The CO modulation is $\rho_{co} \sim \cos(\pi x + 2\alpha)$. It corresponds to $q=0$ since the unit cell contains two sites. Within the cell it shows the odd parity which leads to a net dipole moment of the whole stack.



$\mathcal{H}_U = -U\cos 2\varphi$

State with $\varphi = 0$

$\varphi = \pi$: interchange $+ \leftrightarrow -$
− degeneracy of GS → π-solitons

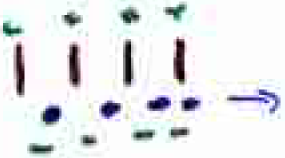
$\varphi = \pm\frac{\pi}{2}$: interchange $\pm \Leftrightarrow 0$
− maximal energy

The electric response.

Plarizability contributions :
ionic displacements, the intergap polarizability, the electronic charge ordering.

I. Ionic displacements.

U_s is originated by the polar displacement **u** of ions which leads to the macroscopic FE polarization but alone cannot explain the observed gigantic magnitude of the effect.
Indeed, the purely ionic contribution near the instability is expected to be



$$\varepsilon_i \sim 10^1\ [T_0/(T-T_0)]$$

The anomaly would develop with the weight of only 10^1 which is *three orders of magnitude below the experimental value*:

$$\varepsilon \approx 2.5\times 10^4\ [T_0/(T-T_0)]$$

Phase $\varphi \to$ polarisation $P = e\varphi/\pi$

$\Delta^2 \cos 2\varphi \to \Delta^2\varphi^2 \to \Delta^2 P^2 = \frac{1}{\varepsilon} P^2$

II. *The intergap polarizability.*

$\varepsilon_\Delta \sim (\omega_p / \Delta)^2$ where ω_p is the plasma frequency of the parent metal.
This contribution can be as large as $\varepsilon_\Delta \sim 10^4$ which just corresponds to the background upon which the anomaly at T_0 is developed.

But ε_Δ is regular, showing only a dependence on $\Delta(T)$ which starts to increase below T_0 without signs of decrease from above.

These features would only add some downward kink in ε below T_0 which is not the case.

III. *The right answer is the* anomalous contribution.

The external electric field E adds the energy $-(e/\pi)\varphi E$. Close to the CO instability we find

$$<\varphi> = 2\, U_s / U_b^{cr} = -(eE/\pi)[1/(U_b - U_b^{cr})];$$
$$\varepsilon = (4e^2/s))[1/(U_b - U_b^{cr})] = \gamma(v_\rho / v_F)[\omega_p^2/(\omega_t^2 - \omega_{cr}^2)]$$

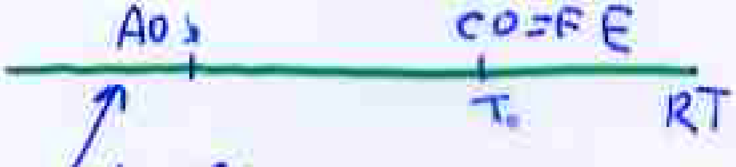
and $\varepsilon \to \infty$ at the transition point $U_b = U_b^{cr}$. gives correct $10^4/(T-T_c)$

Its divergence looks just as the zero in the frequency ω_t^2 of the purely electronic intergap contribution which provides the right order of magnitude of the observable effect.

The anomalous diverging polarizability is coming from the electronic system, even if the instability is triggered by the ions which stabilize the long range *3D* FE order.

Latest from Grenoble:

Second transition: tetramerisation AO



new Unit cell: 4 molecules.

new term in the Hamiltonian ~ cos φ

$$\mathcal{H} = (\partial\varphi)^2 - V\cos(2\varphi - 2\alpha) - V'\cos(\varphi - \beta)\cos\theta$$

$+(\partial\theta)^2$

bare π-solitons – prohibited by V'

Allowed particles:
combined topological objects

e | + $\delta\varphi = \pi$ $\cos\varphi \to -\cos\varphi$

$\frac{1}{2}$ | $\delta\theta = \pi$ $\cos\theta \to -\cos\theta$ } invarian

overlapping holon as a short Sα soliton in

and the spinon as extended one in θ

– hence reconfinement of the charge and the spi

Link to combined
Topological Defects.
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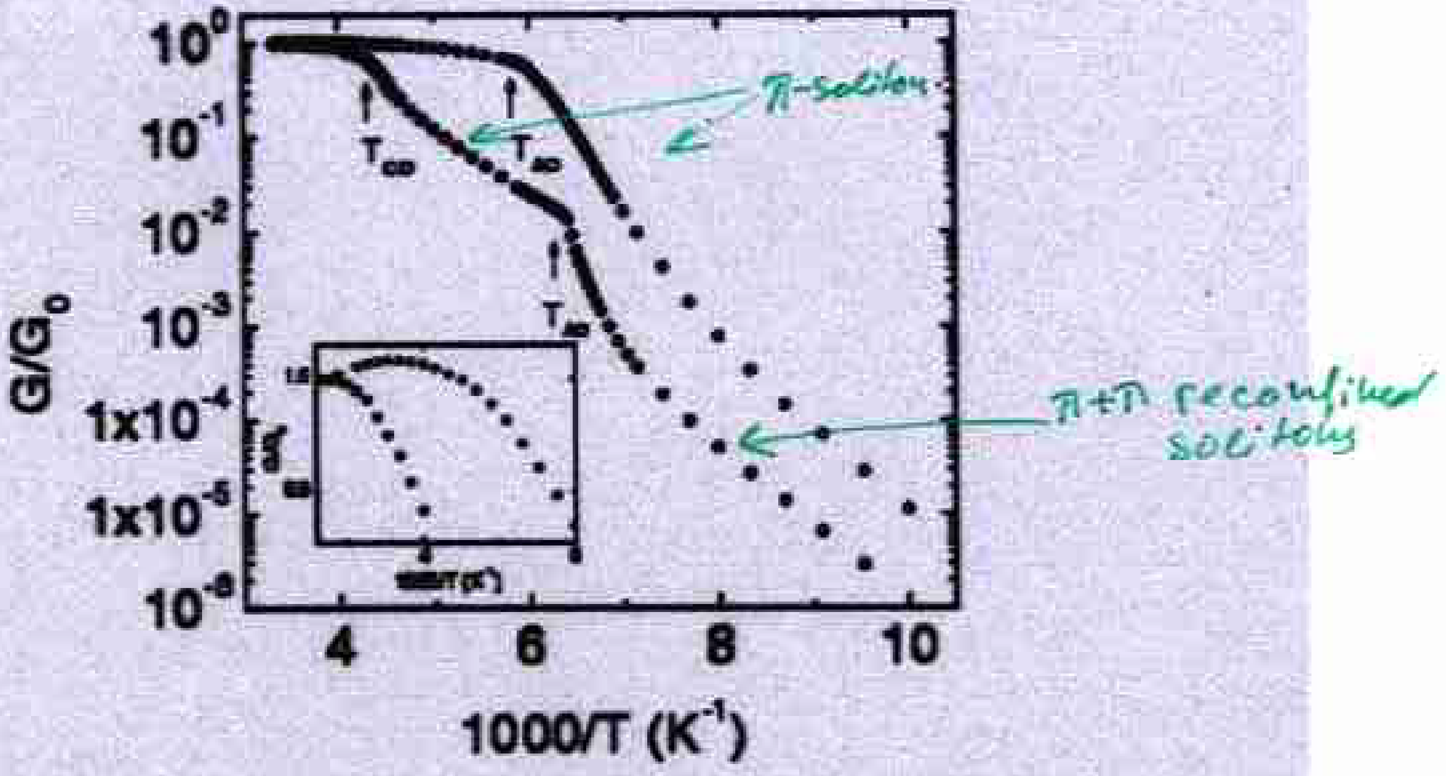


Figure 1. Variation of the real part of the conductance G normalized to its value G_0 at room temperature as a function of the inverse temperature at frequency 1 MHz for $(TMTTF)_2ReO_4$ (●) and $(TMTTF)_2SCN$ (⊕). The inset shows the temperature dependence of G/G_0 near its maximum.

SCN: Anti-FF MH insulator
ReO_4 : FFMH → FE Spin-Peierls

Relations to other models.

Among earlier theoretical studies, particularly the work by Seo and Fukuyama made the important step to predict effects of the charge disproportionation.

Providing very useful guidelines, the MF approximation for electrons requires for an AFM ordering without which any MF theory cannot provide the insulating state.

The discovered experimental regimes take place at temperatures which are by an order of magnitude higher than the ones for the AFM transitions.

We are using the bosonization procedure which is most suitable to describe low energy and collective processes. It takes into account the separation of spins and charges which is a common feature of these systems and corresponds to experimental data.

All information about basic interactions, whatever they are, is concentrated in the single parameter γ.

This approach allows to efficiently use the symmetry arguments and classification. It allows to deal with the solitonic spinless nature of thermally activated charge carriers. Most important for our goals is the direct access to the collective dielectric susceptibility.

Finally it provides a physically transparent phenomenological interpretation in terms of strongly fluctuating $4K_F$ density wave, i.e. a local Wigner crystal, subjected to a weak two fold commensurability potential, in accordance with the picture of (Hiraki and Kanoda 98).

Perspectives: fate of superconducting TMTSF subfamily?

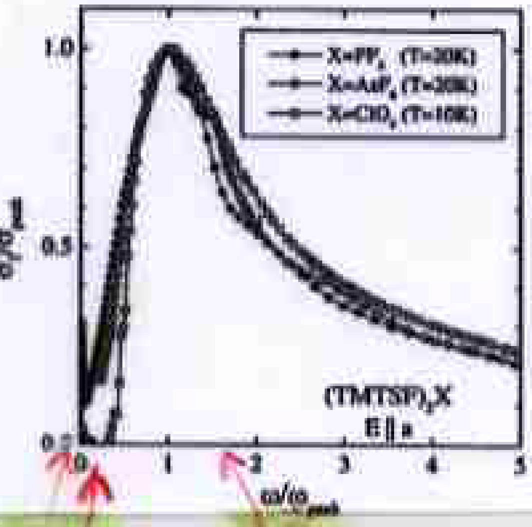
By now the revaluation concern the TMTTF subfamily which usually by the temperature T_0 is already in the Mott-Hubbard regime. The wide temperature range of the Curie anomaly in $\varepsilon(T)$ tells that the developing of the charge disproportionation seen as the ferroelectricity determines the major properties of the high temperature region.

The TMTSF compounds are highly conductive in this temperature range which today does not allow for these very particular studies of ε at very low frequencies and of the NMR with very weak line splitting.

Nevertheless *the transition may be their*, just being hidden or existing in a fluctuational regime like for stripes in High-Tc cuprates. When it is confirmed, then the whole analyses of intriguing abnormal metallic state will be revised as it already should be done for the PI phase of the TMTTF case.

A. Schwartz et al, Phys.Rev. B, 15 June 1998

almost like
the 1D semiconductor
singularity
$\omega \rightarrow e + h$
$\sigma \sim \frac{1}{(E - E_g)^{1/2}}$

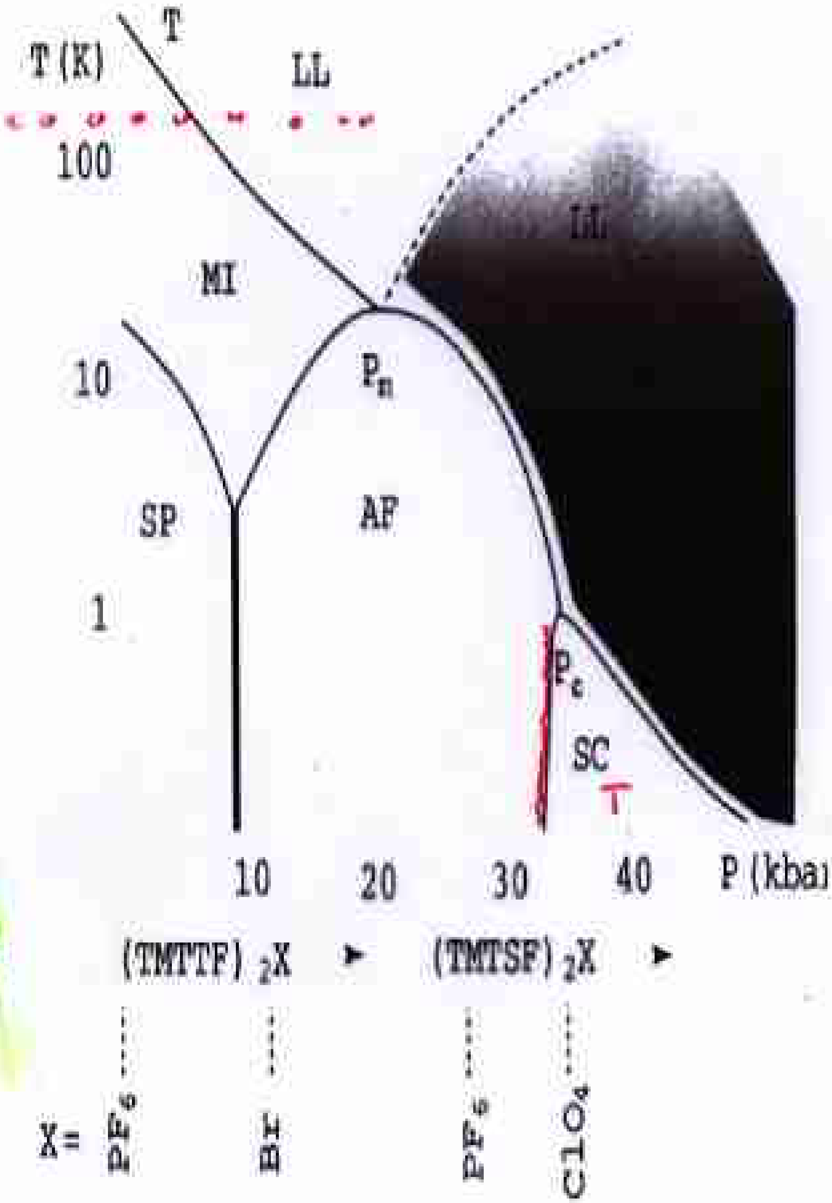


usually presente
in ln-ln scale

The frequency dependent conductivities of (TMTSF)$_2$X

The signature of the CO state may have been already seen in optical experiments by Digeorgi et al. Indeed they observe the Drude like peak with a surprisingly low oscillation strength appearing within the pseudogap.

We can interpret the peak as the optically active mode which must appear as oscillations of the FE polarization, already at the level of uncorrelated chains $T > T_0$. Even the pseudogap itself, being unexpectedly big for MTSF compounds with their less pronounced dimerization of bonds, could be enlarged by the spontaneous dimerization of sites as it was seen explicitly in TMTTF compounds. Vice versa, one can look for the FE mode in TMTTF compounds where it is probably located below the optically accessible range of frequencies.



The picture developed by the 20'th anniversary of organic superconductivity, Bourbonnais and Jerome.

The sequence of electronic phases follows a smooth variation of basic parameters. They are equally produced by substitutions of molecules, ions and reduced to the effective pressure. The compounds with NCS anions are abandoned, presumably their AOs exhort ill defined or undesirable complications.

Its advantages:

- The concentration on simplest examples of centrosymmetric - CS avoiding structural effects.
- A generality in a common frame of strongly correlated systems driven mostly by ratios of bandwidths and basic interactions.
- Extensive use of experiments under pressure and the NMR.

Its disadvantages:

- Concentration on only simplest examples avoiding the very rich information on correlation of electronic and structural properties. The fatal missing of "structureless" transitions just in these selected compounds with CS anions.
- The accent upon pressure as a universal parameter and missing the NMR splitting at the"structureless" transition.
- The contradictory necessity to introduce the case of the non CS ClO_4 case to demonstrate the appearance of the SC under pressure.

(The logic of the "effective pressure" demands to show for this compound only the nonrelaxed phase with the SDW rather than the relaxed phase where the SC appears only after the particular structural transition of the AO.)

The specific picture was mainly developed in early 80's by S.B. & V.Yakovenko.

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:

- The displacive, rather than orientational, mechanisms drive the AOs.
- Symmetrically defined effects of fine structural changes switch electronic state.
- The 1D "g-ological" phase diagram of the LL results in *2D, 3D* phase transitions only with the backup of special symmetry lowering effects.
- The accent on the charge disproportionation with the AFE arrangement in the $(TMTTF)_2SCN$.
- The SC appears only if the system is drawn away from the half filling thus 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".
- The magnitude of this "internal doping" that is the "interchain charge disproportionation" was exactly determined from data on fast magnetic oscillations.

Major difficulties of this picture.

In applications to Se compounds there are common problems of any quasi 1D approach especially in view of mostly successful band theory of the FISDWs.

There are cases of the SC state without observation of the particular **Q3** type of the AO.

The recent views on independent AOs allows to suggest that the **Q3** structure is still their,

at least in local or dynamical form without the long range order.

Q_3:

chain nonequivalence →
charge transfer $\frac{1}{2} \to \frac{1}{2} \pm \delta$
→ drive out from the MI point

CONCLUSIONS.

Discovery of the ferroelectric anomaly (Nad, Monceau, et al) and of the related charge disproportionation (S. Brown et al) call for a revaluation of the phase diagram of the (TMTTF)$_2$X compounds and return the attention to the interplay of electronic and structural properties.

We have described a concept of the combined Mott-Hubbard state as a source for the ferroelectricity.

We demonstrated the existence of two types of spinless solitons:

π - solitons (the holons) are observed via the activated conductivity; noninterger α - solitons are responsible for the depolarization of the ferroelectric order.

We proposed that the (anti) ferroelectricity does exists hiddenly even in *Se* subfamily, giving rise to the unexplained yet optical peak.

We reminded the theory by S.B. and Yakovenko from mid 80's for the universal phase diagram which we contrast with the recent summary of the 20 years anniversary of organic superconductivity.

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**, its influence upon the electronic system.

- Unperturbed structure. Bonds are dimerized. PD: M→MI →SDW.
  The last two phases are clearly separated only in TMTTF subfamily.

- $\mathbf{q}_2$ =(0,1/2,1/2). The molecules are not equivalent.
  PD: M → MI → SDW or CDW (Spin-Peierls).
- T_{MI} and T_{SDW} are well separated in *X=SCN*:
- T_{MI}=160K while T_{SDW}=7K
- $\mathbf{q}_3$ =(0,1/2,0). The neighboring stacks are not equivalent. PD: M → SC → FISDW.
- $\mathbf{q}_4$ =(1/2,1/2,1/2). The tetramerization. PD: M → 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:

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

Aassuming 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)$_2$PF$_6$ 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
(the last was the picture proposed by Jerome and Schultz).

... 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.