A time to cast away stones, and a time to gather stones;
A time to search and a time to give up,
A time to keep and a time to throw away

Is there anything of which one can say,
“Look! This is something new”?
It was here already, long ago; it was here before our time.
Ecclesiastes 3:4-3:6

« In the beginning was the Word, …
and without him was not anything made that was made »

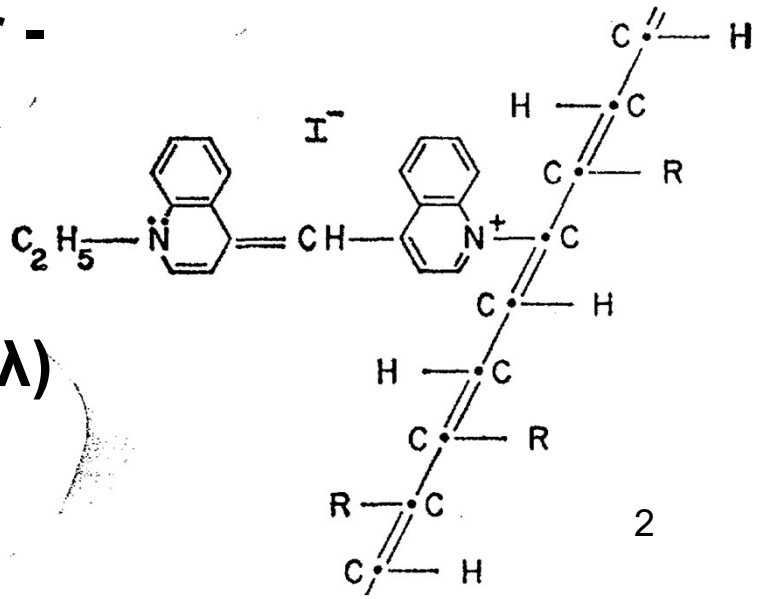
Physical Review 1964 & Scientific American 1965

W.A. Little , Stanford University

POSSIBILITY OF A SYNTHESIZING AN ORGANIC SUPERCONDUCTOR. SUPERCONDUCTIVITY AT ROOM TEMPERATURE.

It has not yet been achieved, but … it is possible to synthesize organic materials that … conduct electricity without resistance.

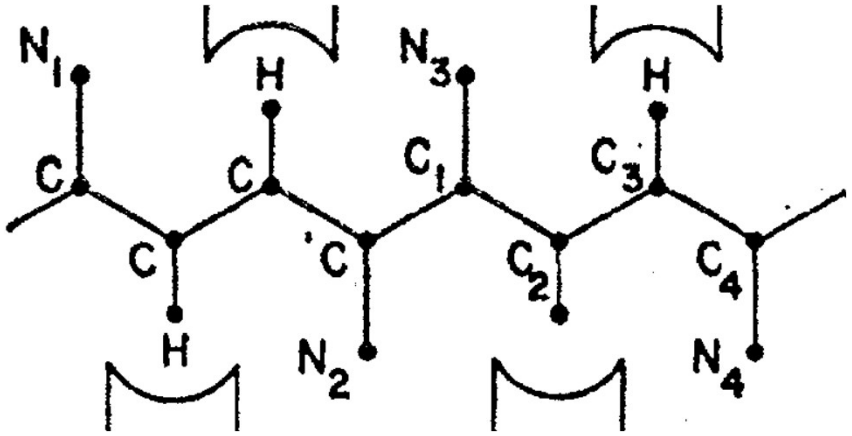
"Little" drawing: conjugated polymer - the polyene backbone with ligands R



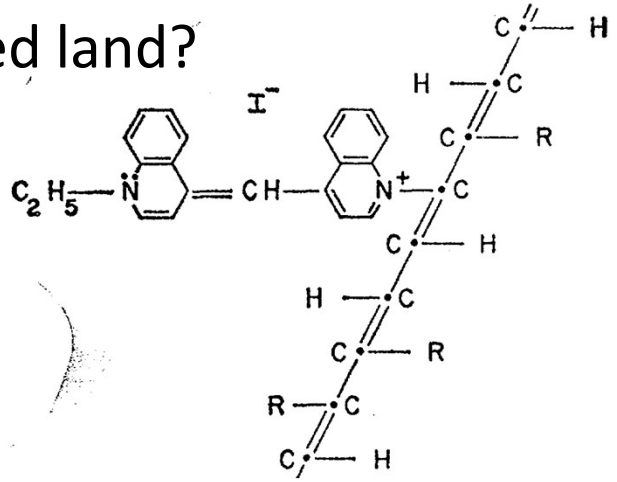
Superconductivity: $T_c \sim \hbar\omega_{ph} \exp(-1/\lambda)$

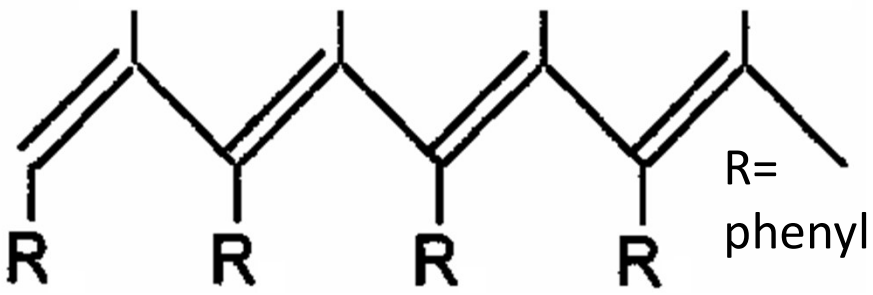
λ –coupling of electrons to vibrations with a frequency $\omega_{ph} \propto 1/M^{1/2}$

Was “organic superconductivity” the only promised land?
Not quite : some of the prophet's visions actually implied a spontaneous electric polarization, hence would be Pyro/Ferro-Electrics.



Drawing - PRB 1964 - **pyroelectric**





His later popular drawing (Sci. Am.)
Questionably a superconductor,
It must be a ferroelectric.

Funny coincidence:
Anderson and Blount 1965
- A hidden FE in a polar metal

Synthetic metals, first or main contributors

Inorganic chains, Charge and Spin density waves
T. Sambongi,
R.Comes JP Pouget
P. Monceau, G. Gruner

Conducting polymers

A.J. Heeger,
A. MacDiarmid
H. Shirakawa,
Y.W. Park, R. Friend

Organic Crystals, Superconductivity
I. Schegolev & E. Yagubskii,
D. Jérome & K. Bechgaard
T. Ishiguro, Meitzner,
Williams,

Fullerenes 1985
Smalley, Curl **&** Kroto

Carbon nanotubes 1991
S. Iijima

Graphene
A. Geim, K. Novoselov

***Looking for* : high Tc superconductivity in polymers, then organics**

***People found*:**

***Materials* : conductors, superconductors, magnetics, optically and electronically active polymers, ferroeletrics, Peierls & Mott insulators, Froehlich conductors, Wigner crystals**

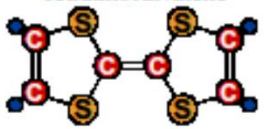
With polymer being the gap>3eV insulators,
the first successful route, to the RT metallicity at least, were molecular stacks

Organic Conductors
charge transfer salts

TTF-TCNQ

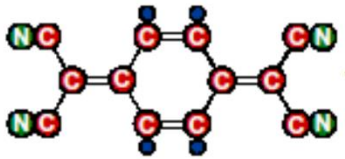
The structure consists of TTF and TCNQ stacks.
TTF is a strong electron donor,
TCNQ is an electron acceptor.

Tetrathiofulvalene

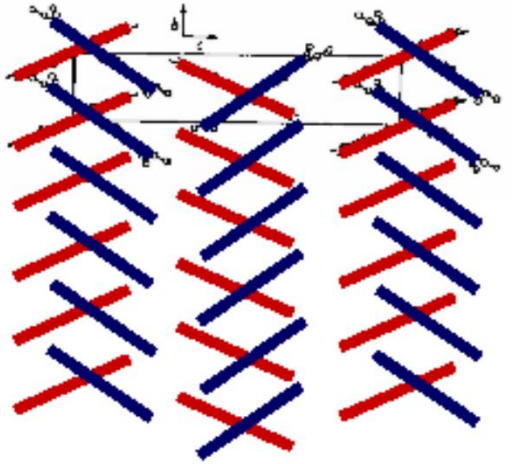


TTF

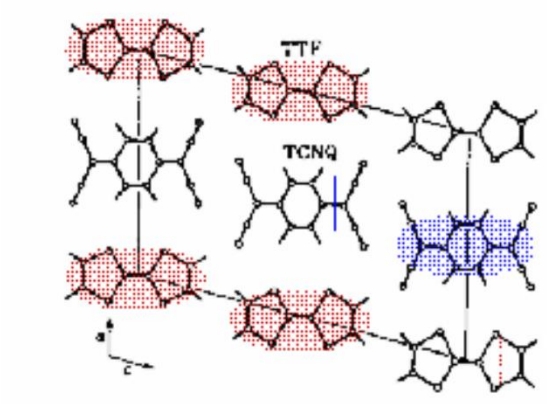
Tetracyanoquinodimethane

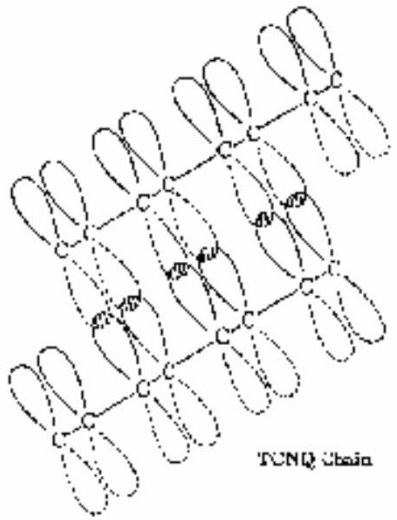


TCNQ



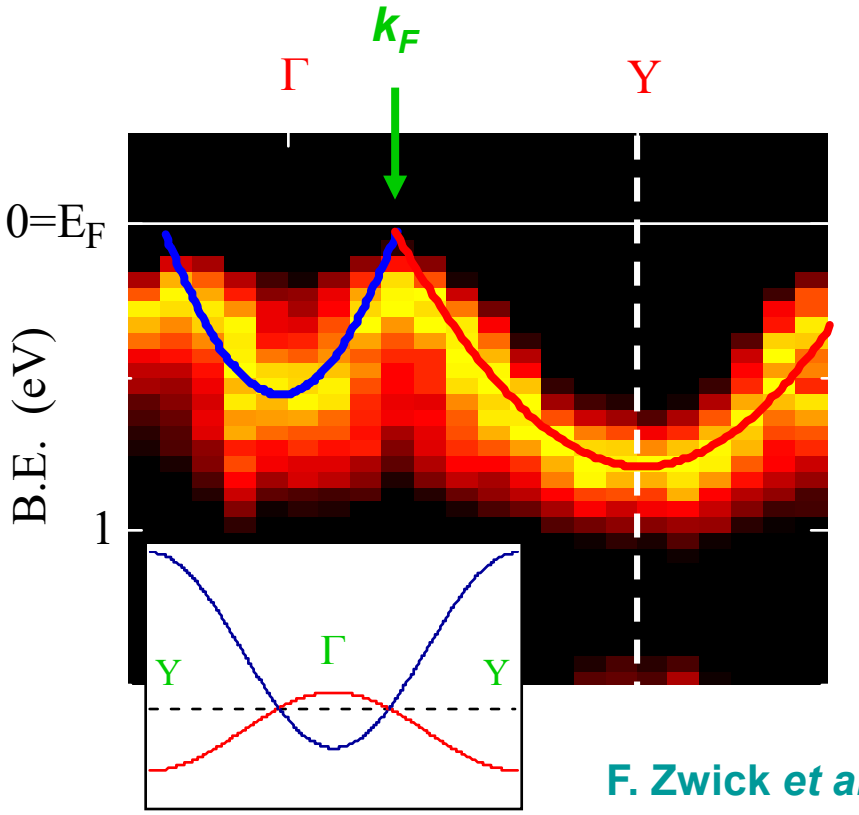
Along the stacks the π-orbitals overlap
leading to one-dimensional conductivity.



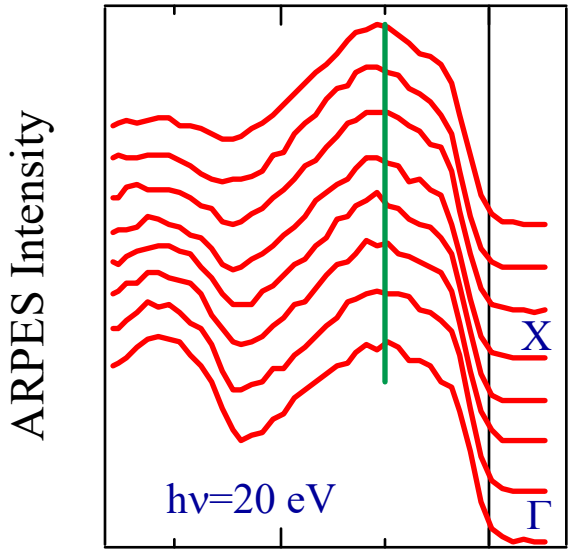


Hybridization of Pi-electrons

The organic conductor TTF-TCNQ



No perpendicular dispersion



F. Zwick *et al*, PRL (1998)

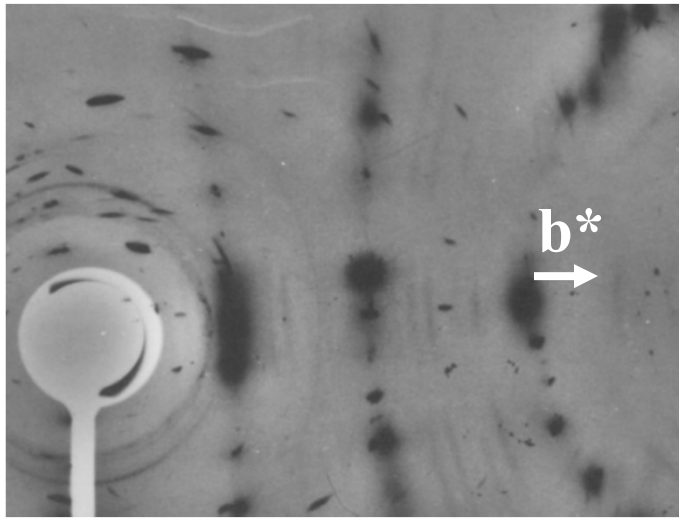
Binding energy (eV)

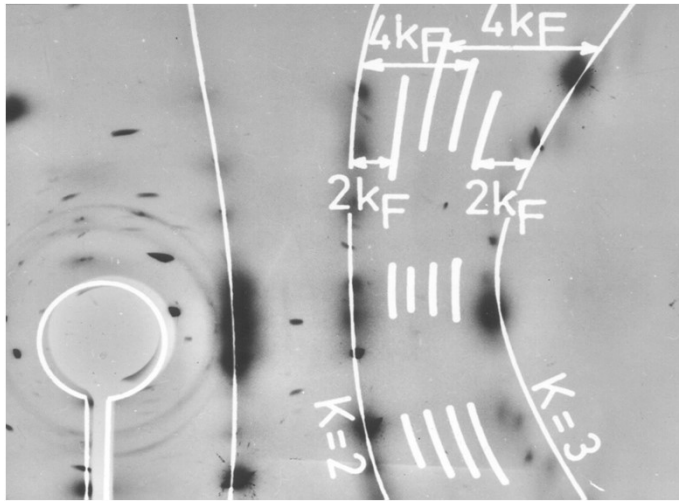
1 **0=E_F**

ARPES: conventional Quasi-1D material with two open Fermi surfaces originated by two stacks.

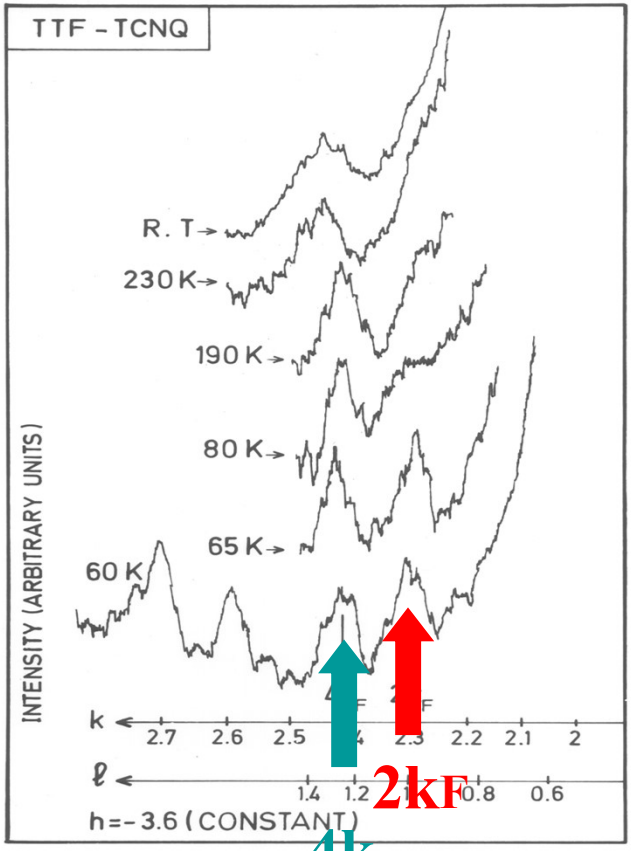
Other data: TTF at least is the strongest correlated conductor of the whole family.

TTF-TCNQ: $2k_F$ and $4k_F$ CDW/BOW!





T=60K



Charge transfer
ρ=0.59

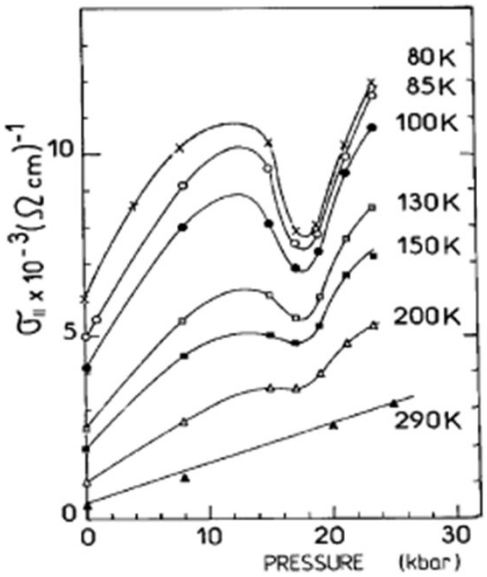
$2k_F$ instability on the TCNQ stack

$4k_F$ instability on the TTF stack

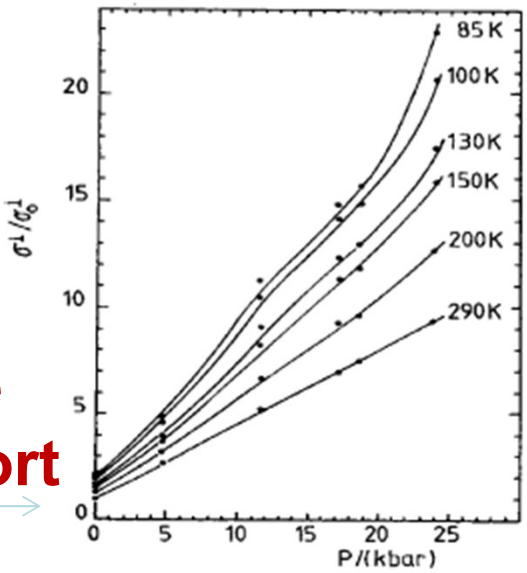
J.-P. Pouget, R. Comes, et (1975 @ BNL); S. Kagoshima et al (1976)

Charge Transfer Change at High Pressure *D. Jerome 1978*

1:3 commensurability locking and its consequences.



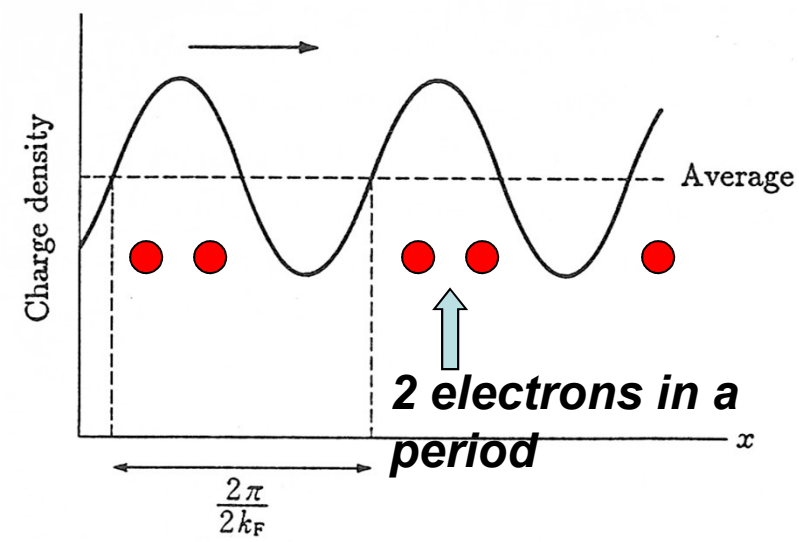
Collective nature of on-chain transport versus single-particle nature of inter-chain transport



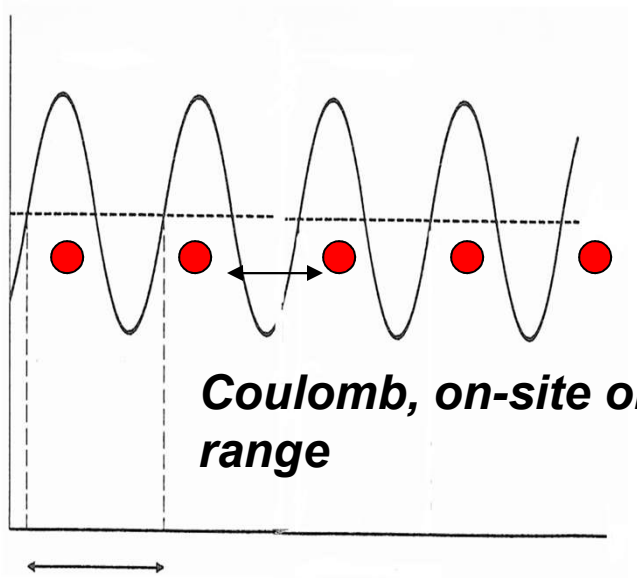
On-chain conductivity drops at the 3:1 lock-in

Inter-chain conductivity does not feel the lock-in

Coulomb Interaction to Cause $4k_F$ CDW



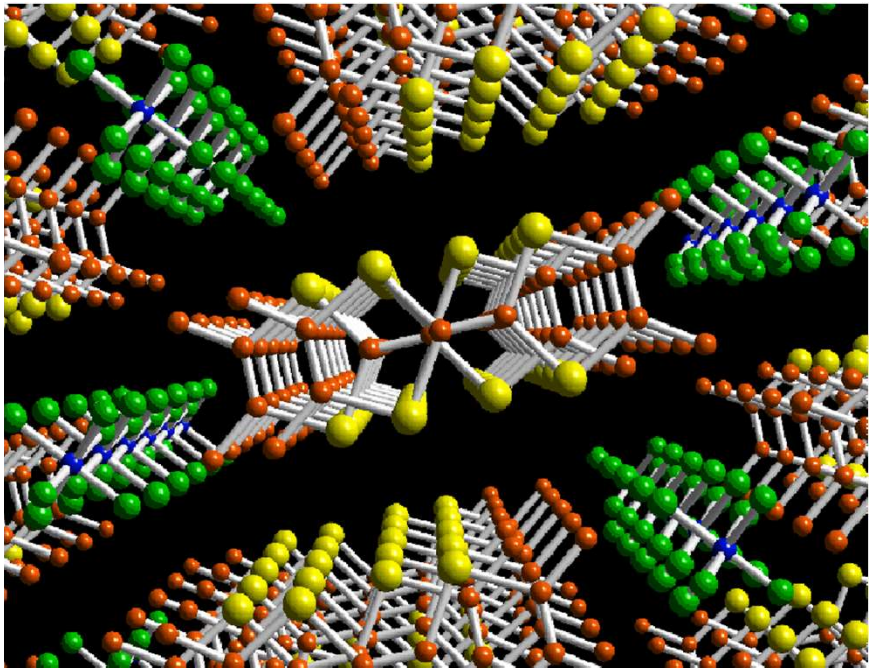
$2k_F$ CDW



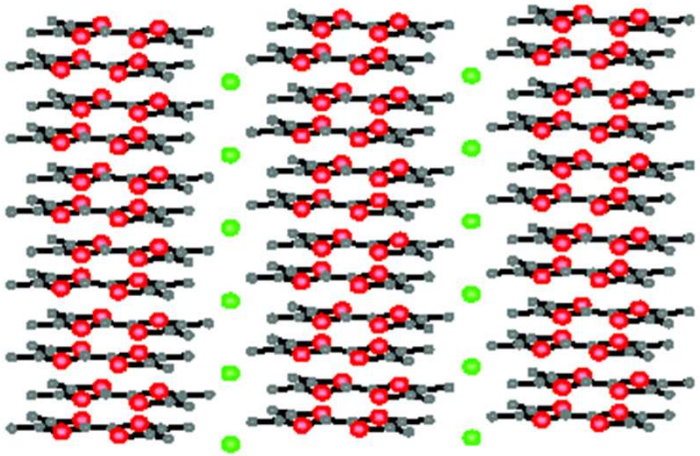
$4k_F$ CDW

The electrons have a strong correlation in their motion because of the repulsive Coulomb interaction.

$4k_F$ CDW = Wigner XI is the introduction to physics of strongly correlated electrons.

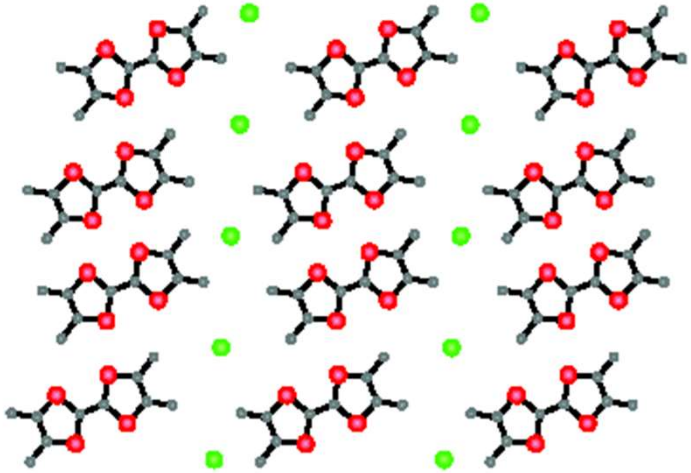


The breakthrough to the SC and later to FE



conterion
= dopant X

Molecule
TMTTF
or TMTSF



BCS@50 October 12, 2007

$(TMTSF)_2PF_6$ - Most Remarkable Electronic Material Ever Discovered

So far in ***one single crystal***:

All the usual competitions:
Metal-Insulator, Magnetic-Superconductor,
Commensurate-Incommensurate, FermiLiquid- NonFermiLiquid,
Spin Density Wave - Charge Density Wave……

Exhibits all transport mechanisms known to man:
Metallic, Sliding Density Wave, Superconducting,
Quantum Hall

Plus somethings new :
Field Induced SDW/QHE
Giant Nernst Effect, Magic Angle Effects
Triplet Superconductivity, Field Induced Slabs

Add more to this P. Chaikin list:
charge ordering, ferroelectricity, inhomogeneous inter-pase superconductivity

ELECTRONIC FERROELECTRICITY IN CARBON-BASED SYSTEMS: FROM MOLECULAR CRYSTALS AND ORGANIC CONDUCTORS TO PROMISES OF POLYMERS AND GRAPHENE NANO-RIBBONS

Serguei Brazovskii

LPTMS, CNRS & University Paris-Saclay, Orsay, France;

Three forms of the ferroelectricity:
Conventional dipoles' ordering type, Conventional ions' displacive type
New electronic ferroelectricity from redistributions of electron's density

Birth of the nick-name: Portengen, Ostreich, & Sham
Theory of electronic ferroelectricity, PRB (1996).

Its de facto observation: Ikeda, N. et al. , JPSJ (2000).
Charge frustration and dielectric dispersion in LuFe2O4.

Monceau, Nad, & Brazovskii, PRL (2001)
Ferroelectric Mott-Hubbard phase of organic TMTTF2X ***conductors.***

The nickname is brought to the real life: Ikeda, N. *et al. .* Nature (2005)*. Ferroelectricity from iron valence ordering in the charge-frustrated LuFe2O4*

Direct proofs of the electronic ferroelectricity: 2010
Yamamoto,K. et al. Direct observation of ferroelectric domains created by Wigner crystallization of electrons. *Appl.Phys.Lett.*

Kobayashi, K. *et al. PRL (2012) Electronic ferroelectricity in a molecular crystal with polarization directing antiparallel to ionic displacement*

Theory of electronic ferroelectricity
T. Portengen, Th. Östreich, and L.J. Sham
Phys. Rev. B 54, 17452 – 1996

We present a theory of the linear and nonlinear optical characteristics of the insulating phase of the Falicov-Kimball model within the self-consistent mean-field approximation. The Coulomb attraction between the itinerant d electrons and the localized f holes gives rise to a built-in coherence between the d and f states, which breaks the inversion symmetry of the underlying crystal, leading to (1) electronic ferroelectricity, (2) ferroelectric resonance, and (3) a nonvanishing susceptibility for second-harmonic generation.

Ferroelectricity from iron valence ordering in the charge-frustrated system LuFe 2 O4

Naoshi Ikeda, Hiroyuki Ohsumi, Kenji Ohwada, Kenji Ishii, Toshiya Inami, Kazuhisa Kakurai, Youichi Murakami, Kenji Yoshii, Shigeo Mori, Yoichi Horibe & Hijiri Kito

… However, an alternative model — electronic ferro-electricity — has been proposed in which the electric dipole depends on electron correlations, rather than the covalency.
Here we report experimental evidence for ferroelectricity arising from electron correlations in the triangular mixed valence oxide, LuFe2 O4 . Using resonant X-ray scattering measurements, we determine the ordering of the Fe 21 and Fe31 ions. They form a superstructure that supports an electric polarization consisting of distributed electrons of polar symmetry. The polar ordering arises from the repulsive property of electrons — electron correlations — acting on a frustrated geometry.

Charge Ordering and Ferroelectricity in organic conductors.

1964 W.A. Little mobilizes for high-Tc in polymers, but draws a ferroelectric.

1966-72 Dispute on the origin of the (Mott) gap in 1D models. g1,g2,g3. Commensurability and Umklapp scattering. *Dzyaloshinskii&Larkin, Luther&Emery*

1975/6 $2K_F$ - $4K_F$ anomalies in stacked conductors.
Breaking the weak interactions universal theory *Comes&Pouget, Kagoshima, ...*

1978 $4K_F$+ $2K_F$ lock-in at 1/3 commensurability *Jerome*

1979 Discovery of the organic superconductor *Bechgaard, Jerome, et al*

1979/80 Tiny interplay among structure and electronic state SB &S.Barisic

1982 Subtle anionic transitions as magicians' gifts *Comes, Pouget, Ravy...*

1985 Theory for interplay of electronic and structural transitions *S.B.& Yakovenko*

1985/8 Abandoned structureless transitions wait for revenge *Coulon, Lawersonne.*

1996 Optical gaps even in the metallic state Degiorgi, Dressel, et al

1997 Predictions for charge disproportionation in 1D SDW *Seo and Fukuyama*

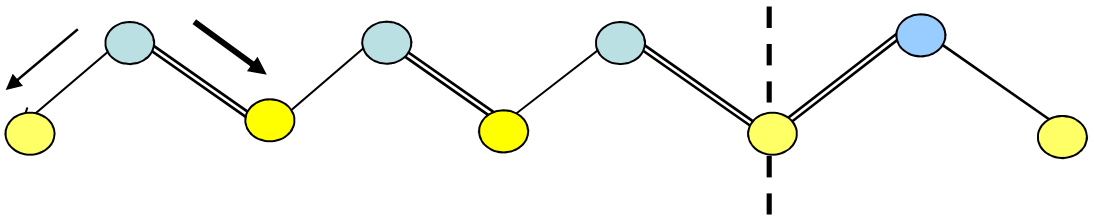
1999/2001 Huge ferroelectric anomaly at high T *Nad, Monceau, S.B.,...*

2001 Charge Ordering by NMR *Kanoda…,Brown…., Fujiyama...*

2007 Ferroelectric polymers. Closing the Little loop SB and N. Kirova

Instructions for the deterministic FE design: Combined symmetry breaking.

- ***Lift*** the inversion symmetry, remove the mirror symmetry,
- **D**o not leave a glide plane.
- ***Keep*** the double degeneracy to get a ferroelectric rather than an unflexible pyroelectric state.



A chain with the double dimerization of sites and bonds.
Alternation of bonds removes the mirror symmetry,
Alternation of sites removes the glide plane
Local view: Bonds are polar because of site dimerization.
Their dipoles are not compensated **since the lengths alternate**.

Both dimerizations are built in: alternating stacks **$TMTTF_{0.5}TMTST_{0.5}$** (*Pouget et al*) - must be pyroelectric**:** the polarization is frozen

Any one of two dimerization is spontaneous. Direction of polarization can be changed – the ferroelectric state. **Its 4 versions**:

1. *Dimerization of bonds* is built in; *dimerization of sites* is spontaneous: organic conductors $(TMTTF)_2X$. Charge ordering is endorsed by the energy gain from falling to the Mott insulator state: band filling goes from ¼ to ½) (*S.B. & Monceau**, 2000's***)

2. *Dimerization of sites is built in; dimerization of bonds is spontaneous* – Peierls dimerization: proposal for conjugated polymers of the $(AB)_x$ type, expected to be seen in substituted polyacetylene $(CRCR')_x$ (*S.B. & N.K. – 2008*)

3. *Both sites' and bonds' dimerizations are spontaneous*
-1st order neutral-ionic transition in charge transfer salts like TTF-CA (Y.Tokura et al)

4. *Spin- Peierls dimerization:*
organic quantum magnets (F. Kagawa et al, 2010)

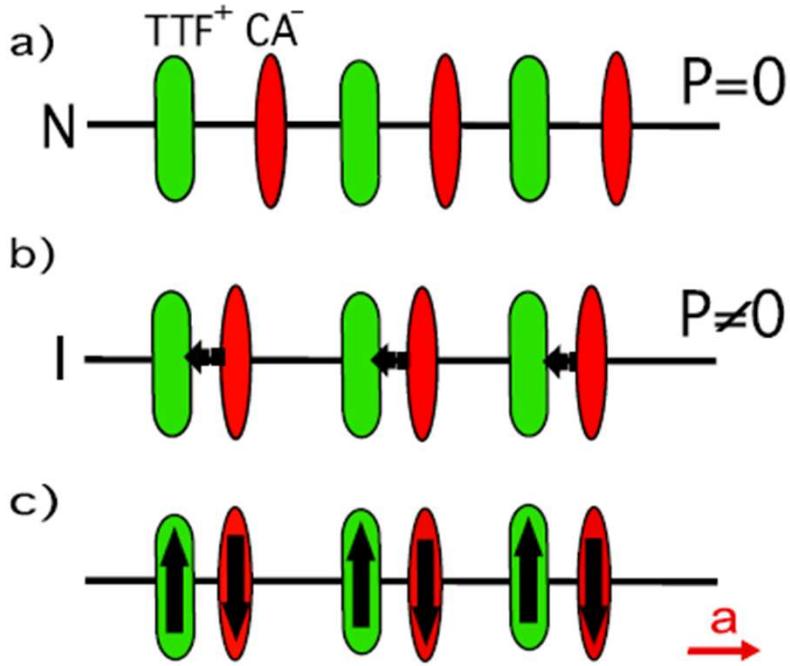
Both sites' and bonds' dimerizations are spontaneous

- 1st order neutral-ionic transition in

charge-transfer salts like TTF-CA

Neutral-Ionic Transition

TTF-CA: stacks of alternating **donors D=TTF and acceptors A=CA.**
T>Tc=81 K: molecules are weakly charged.
T=Tc: quasi-neutral to ionic transition.
Charge transfer ρ_n jumps from 0.3 to 0.7
Charged molecules shift relative to each other – interpretations as either Coulomb or spin-Peierls instabilities, creating alternating long and short bonds.
With all inversion and mirror symmetries lifted, this might be the ferroelectric.

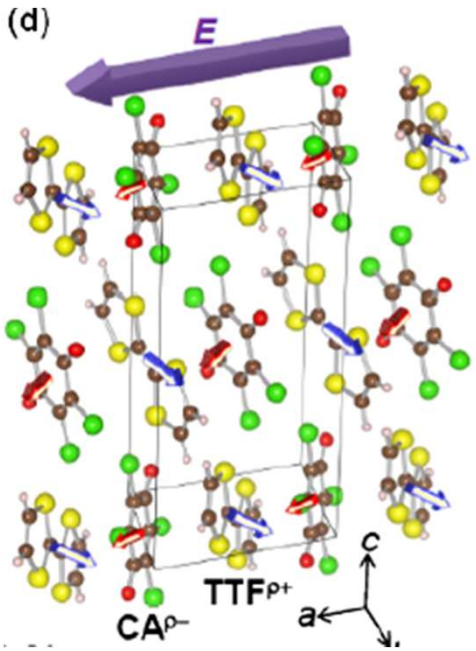


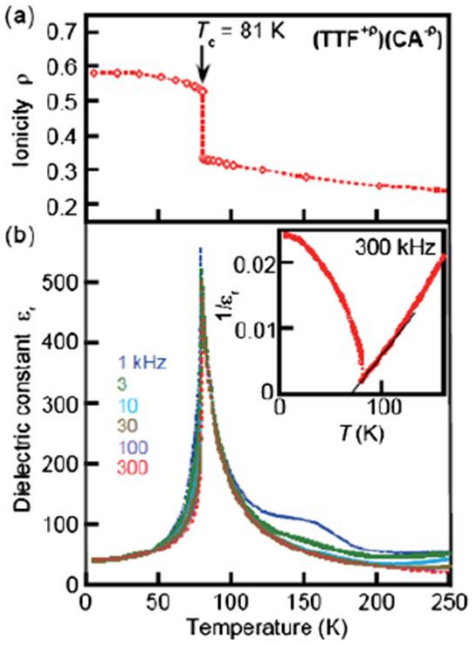
Thermodynamic CT.
Primary effect: **redistribution of the charge density ρ with no symmetry breaking, hence an isomorphic (liquid-gas class) transition described by the single real field $q=\rho-\rho_n$.**
Actually **– symmetry breaking because of complementary dimerization.**

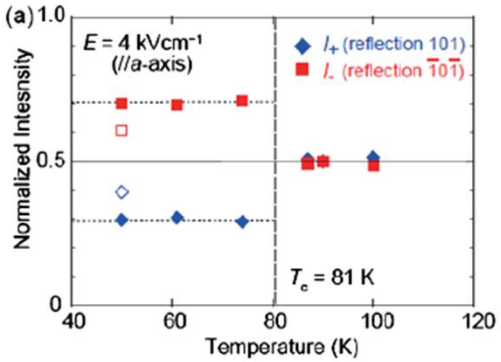
Electronic Ferroelectricity in a Molecular Crystal with Large Polarization Directing Antiparallel to Ionic Displacement

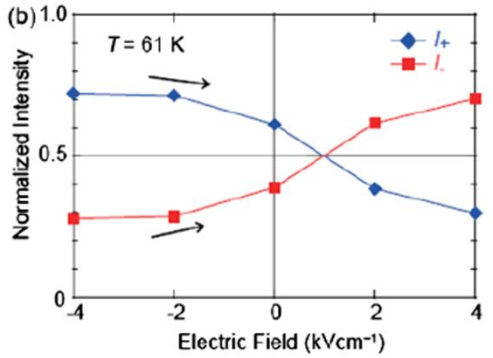
K. Kobayashi, S. Horiuchi, R. Kumai, F. Kagawa, Y. Murakami, and Y. Tokura

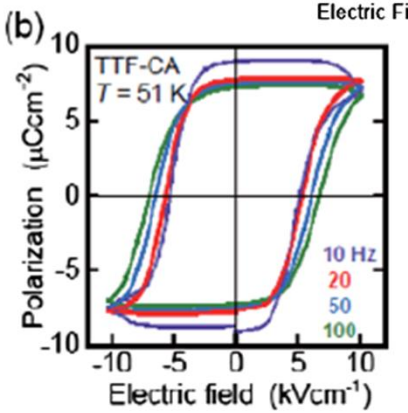
Phys. Rev. Lett. **108,** 237601 (2012)











Electronic polarizaion is 20 times of the ionic polarization
and the two point in opposite directions.

Game of principle variables.

h – dimerizational displacement of molecules
ρ - charge transfer, in neutral phase $\rho = \rho_n$,
ρ_c – monitoring parameter $\rho_c = \rho_c(T)$
The energy density:

$$W(\rho, h) = \frac{a}{2}(\rho - \rho_n)^2 + \frac{b}{3}(\rho - \rho_n)^3 + \frac{c}{4}(\rho - \rho_n)^4 + d(\rho_c - \rho)h^2 + fh^4$$

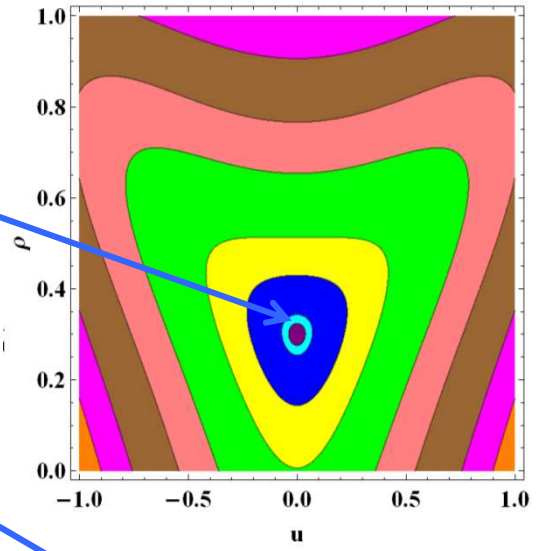
$\rho_c > \rho_n$ – critical value of ρ for instability in h:

$$h = 0 \Rightarrow h = \pm\sqrt{(\rho - \rho_c)d / 2f}$$

Changing the energy landscape by pumping excitations

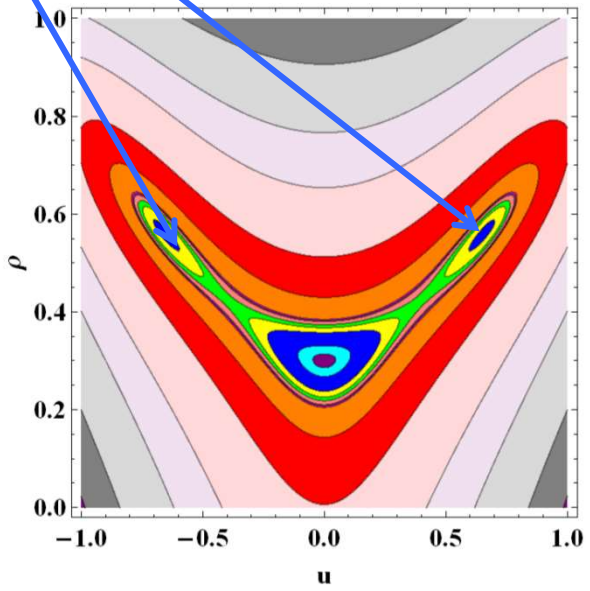
n=0.04

ρ-ρ_n



Trivial minimum at $\rho=\rho_n$, h=0

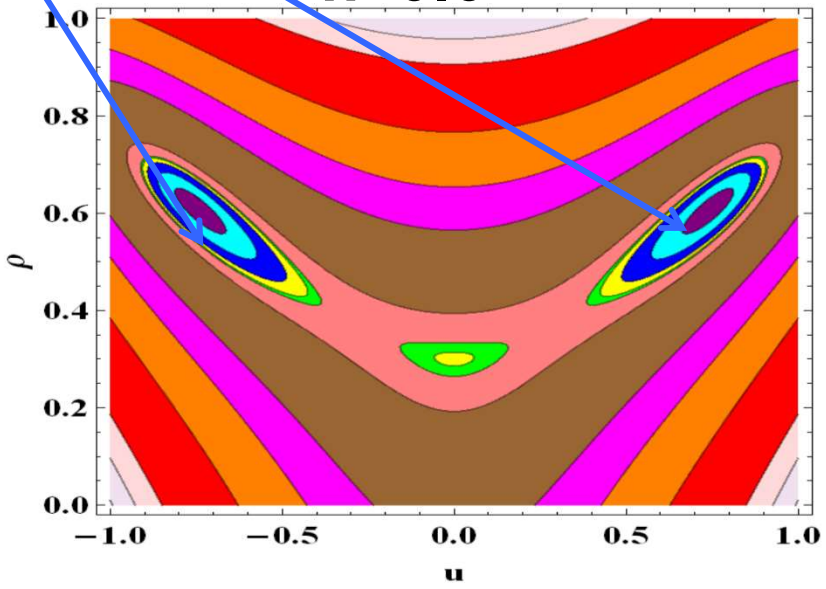
Double minima at $\rho>\rho_n$, $h=\pm h_0$ appe and evolve to the ionic state



n=0.4

u

n=0.6



. Dimerization of sites is built in;

dimerization of bonds is spontaneous

Peierls insulator – conjugated polymers of the (AB)x type

like di-substituted polyacetylene

after collaboration with Natasha Kirova

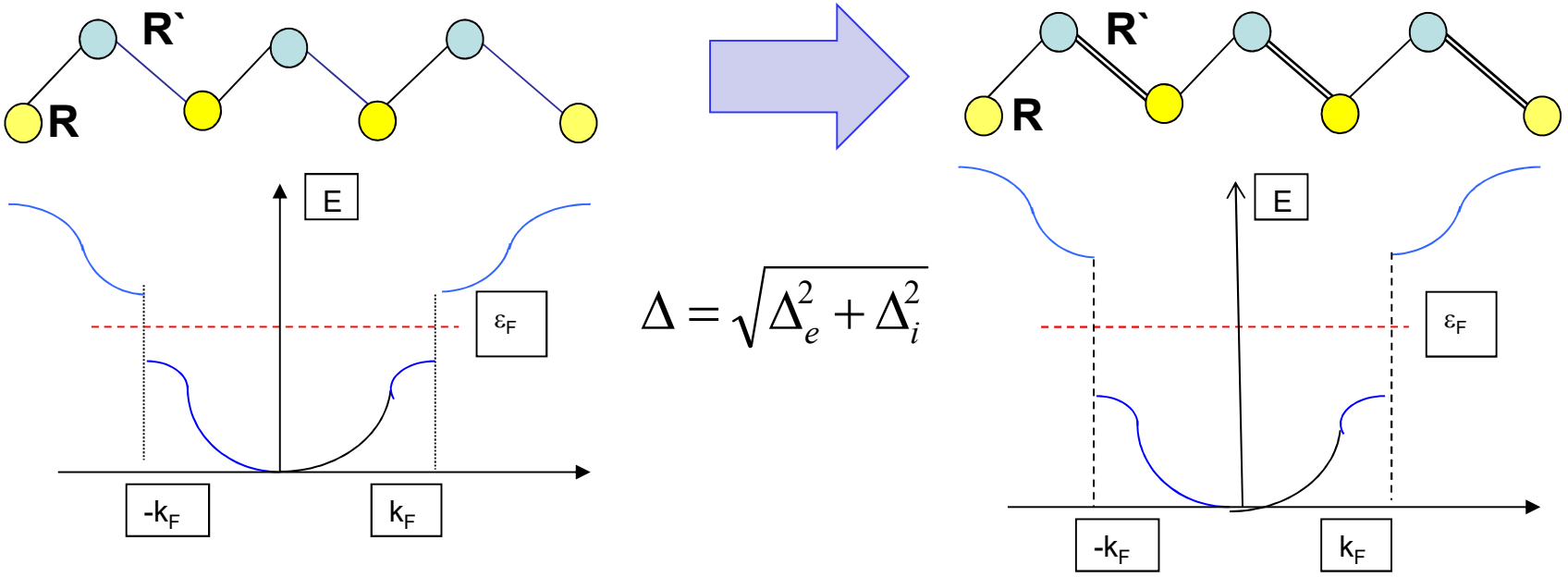
Combined Peiels effect in diatomic linear chain polymer $(C_2RR`)x$

(First theory: S.B. & N.Kirova 1981; baptized (AB)x by M.J. Rice, R.J. Mele, 1982)

Joint effect of extrinsic Δ_e and intrinsic Δ_i contributions to dimerization gap Δ.

Δ_e comes from the build-in site dimerization – non-equivalence of sites A and B.

Δ_i comes from spontaneous dimerization of bonds, the Peierls effect.



Threshold effect : **Δ_i WILL NOT be spontaneously generated –**

if Δ_e already exceeds the wanted optimal Peierls gap.

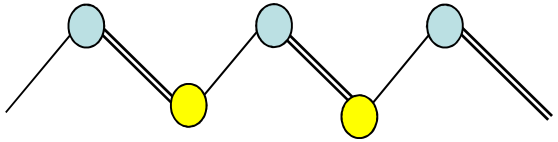
Chemistry precaution: **make a small difference of ligands R and R'**

SOILITONS WITH NONINTEGER VARIABLE CHARGES:

Orthogonal mixing of static and dynamic gap generations.

Realization: modified polyacetylene $(CRCR')_x$

Theories for solitons with variable charges: S.B. & N.K. 1981, M.Rice, J.Mele 1982

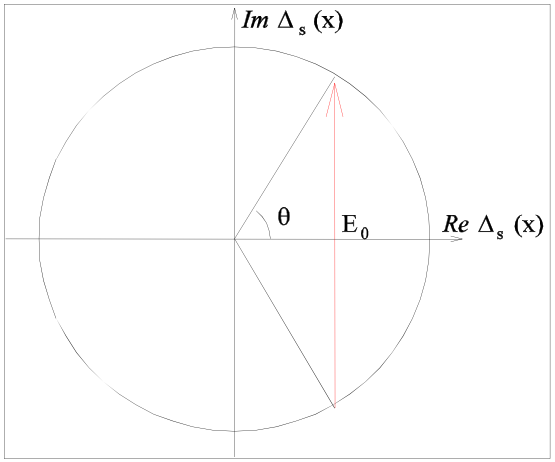


$$\Delta = \sqrt{\Delta_e^2 + \Delta_i^2}$$

Joint effect of extrinsic Δ_{ex} and intrinsic Δ_i contributions to dimerization gap Δ.
Δ_e comes from the build-in site dimerization – nonequivalence of sites A and B.
Δ_i - from spontaneous dimerization of bonds $\Delta_i=\Delta_b$ - generic Peierls effect.

$$Tr\begin{vmatrix} -i\hbar v_F\partial_x & \Delta_e + i\Delta_i \\ \Delta_e - i\Delta_i & i\hbar v_F\partial_x \end{vmatrix} + K\overline{|\Delta_i|^2}$$

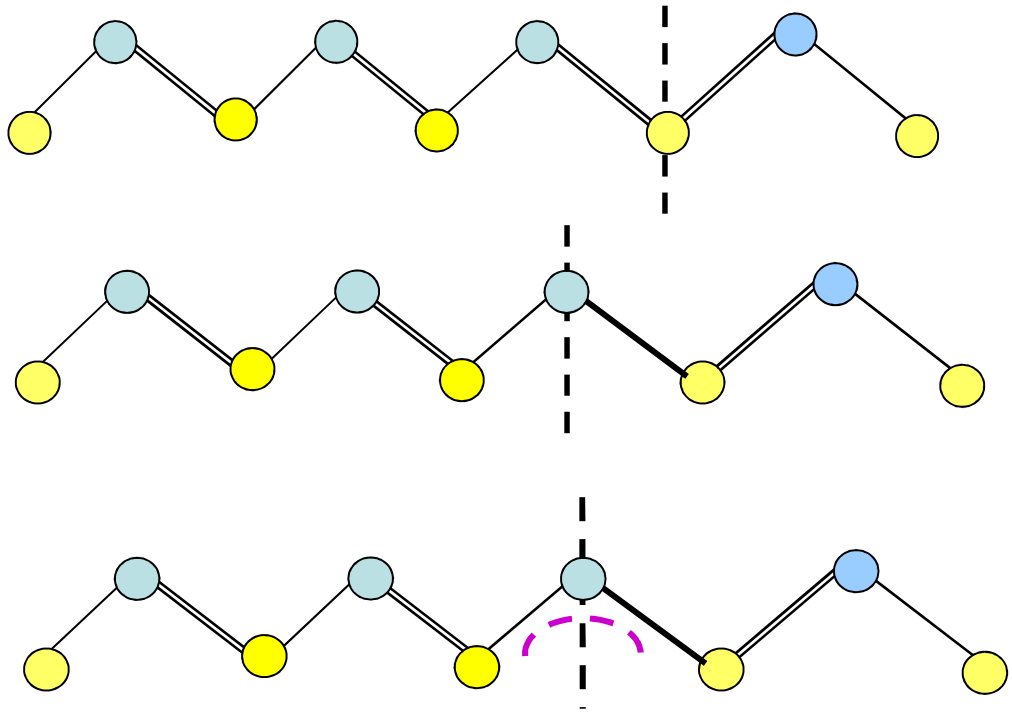
$$\Delta_e = cnst, \quad \overline{\Delta_i} = \pm\sqrt{\Delta_0^2 - \Delta_e^2}$$



Nontrivial chiral angle $0<2\theta<\pi$ of the soliton trajectory corresponds to the noninteger electric charge $q= e\theta/\pi$

Solitons with noninteger charge:

$$\Delta = \sqrt{\Delta_e^2 + \Delta_i^2}$$



S=0

$$Q = \frac{2e}{\pi} \tan^{-1} \frac{\Delta}{\Delta_e}$$

S=1/2

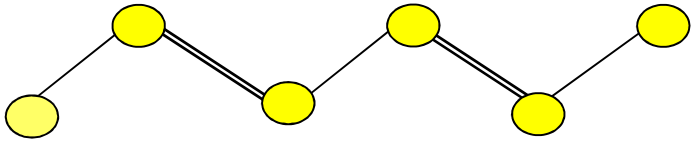
$$Q = \frac{2e}{\pi} \tan^{-1} \frac{\Delta_e}{\Delta}$$

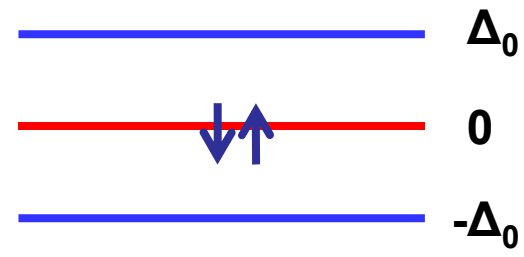
Special experimental advantage: an *ac* electric field alternates polarization by commuting the bond ordering patterns, i.e. moving charged solitons.

Through solitons' spectral features it opens a special tool of electro-optical interference.

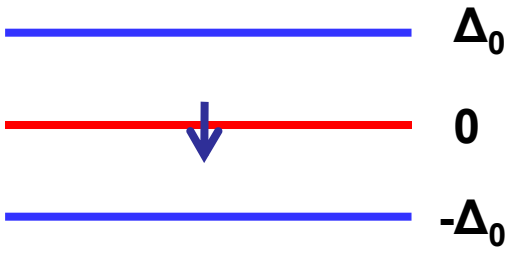
Solitonic intra-gap states

Standard (CH)x chain





Q=e

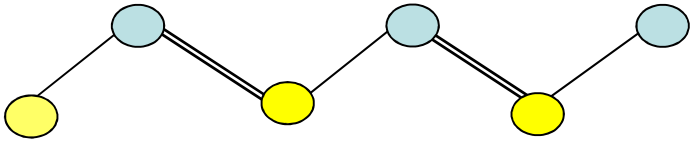


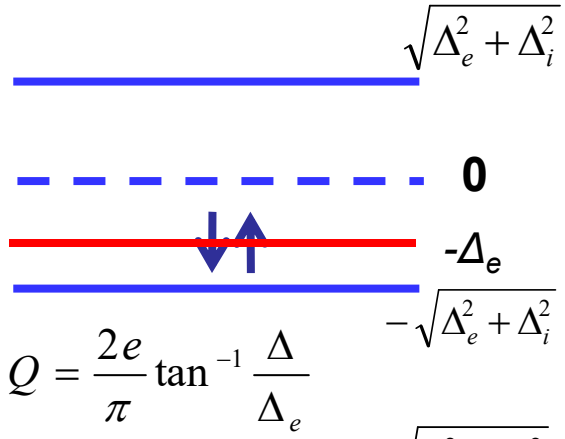
Q=0

S=0

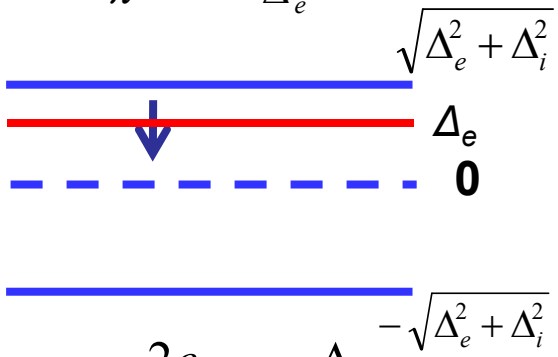
S=1/2

Diatomic ($C_2RR`$) chain – (AB)x polymer





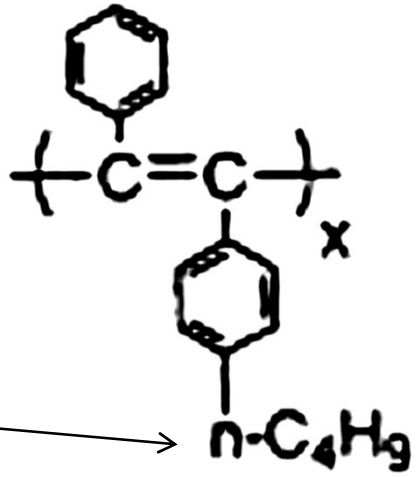
$$Q=\frac{2e}{\pi}\tan^{-1}\frac{\Delta}{\Delta_e}$$



$$Q=\frac{2e}{\pi}\tan^{-1}\frac{\Delta_e}{\Delta}$$

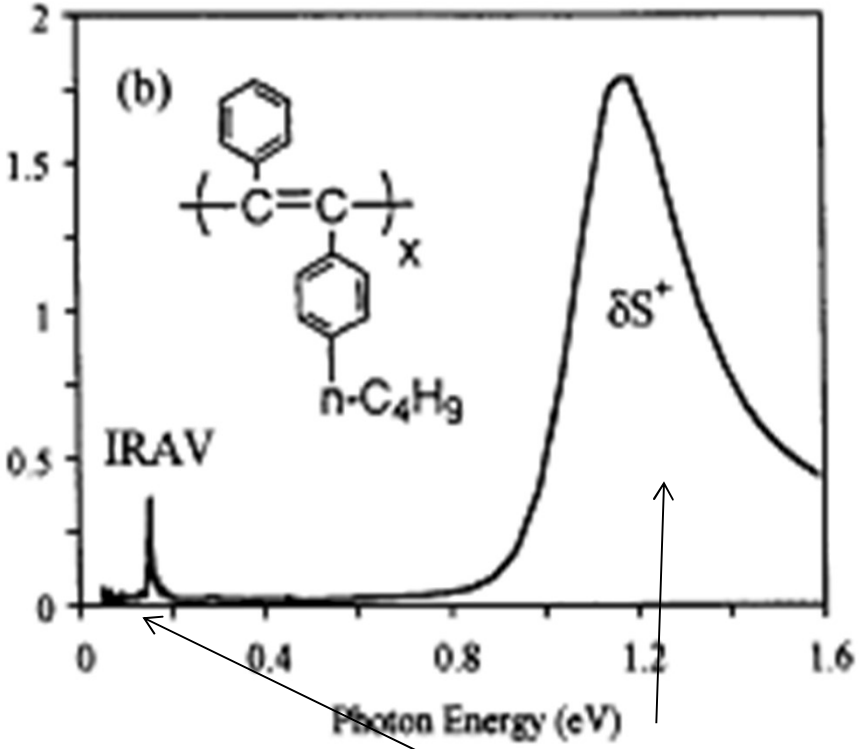
Our allusion of early 80's : $(CHCF)_x$ - vaguely reported to exist;
it may not generate bonds dimeriszation:
too strong effect of substitution H→F.
New promise: in 1999 from Kyoto-Osaka-Utah team.
By today – complete optical characterization,
indirect proof for spontaneous bonds dimerization
via spectral signatures of solitons.

"Accidental" origin of the success
to get the Peierls effect of bonds dimerization:
weak difference or radicals
– only by a distant side group.
Small site dimerisation gap provoke to add the
bond dimerisation gap.

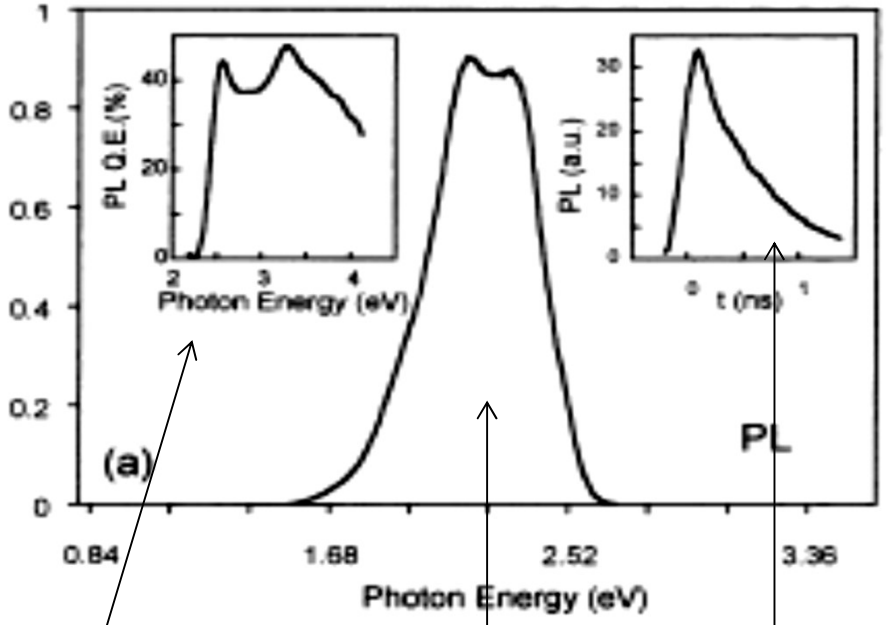


Proof for spontaneous dimerization: no X-ray experiments,
No dielectric susceptibility experiments,
but via existence of solitons.

Optical results by Vardeny group, Utah. Solitons' identification:



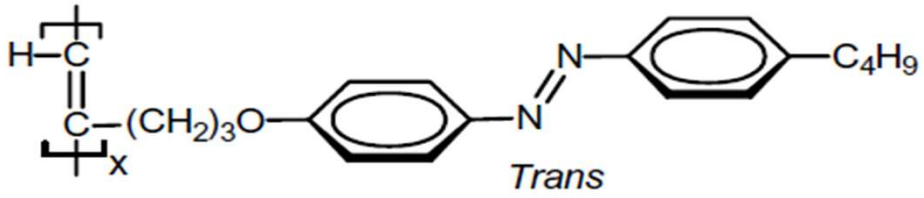
Features in IR and visible



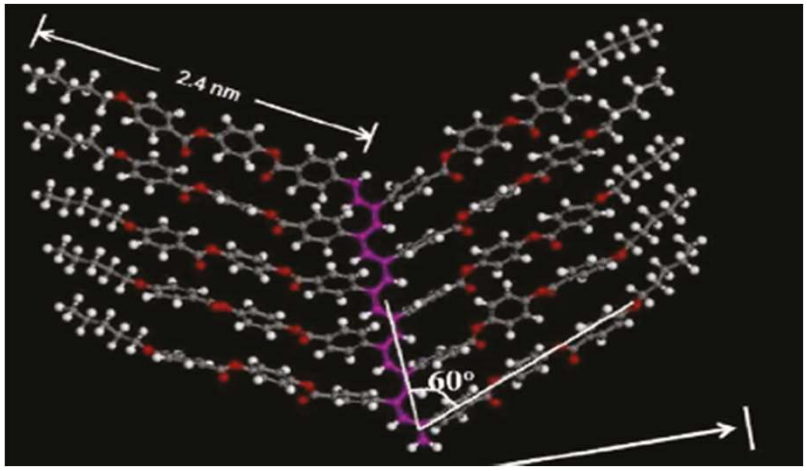
Absorption, Luminescence, Dynamics

Combined ESR - optics **experiments and IRAV (infra-red-active-vibrations):**
The spin solitons now carry some charge
- surprising from experience of the conventional **polyacetylene**

What else is promising today?
A great variety of synthesis is already demonstrated.
(the strongest activity in chemistry has moved to Hong Kong (Benzhong Tang), with some physical characterizations in Beijing.



Trans



An already existing compound might be at least the pyroelectric. The carbon backbone was suggested (?) to posssess the cis isomerization – the degeneracy of bonds' dimerization is already lifted, the polarization is weakly frozen.

Another example of the monosubstituted polyacetylene tells that there may be a ferroelectrically tunable visible-light laser**.**

(*Shantou, Guangdong, China)*

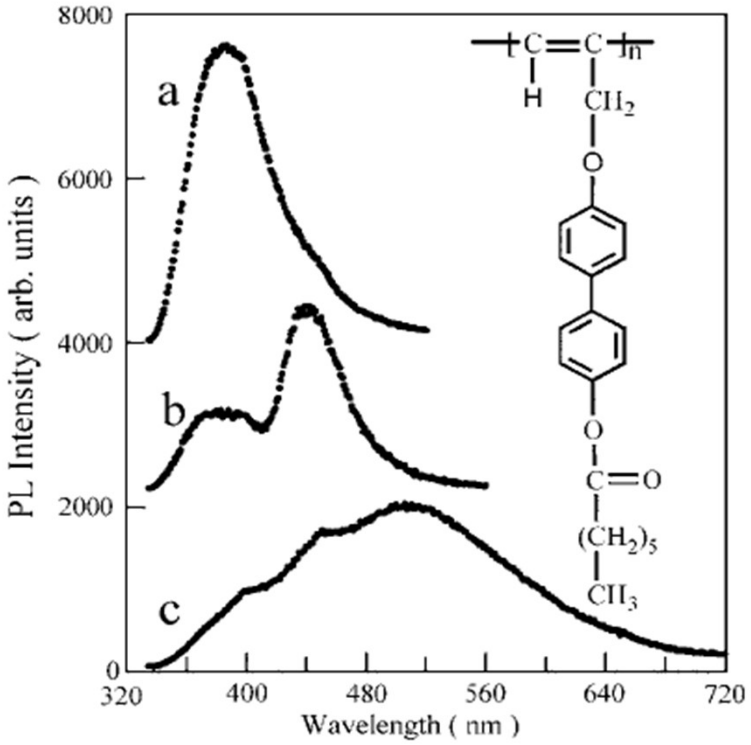
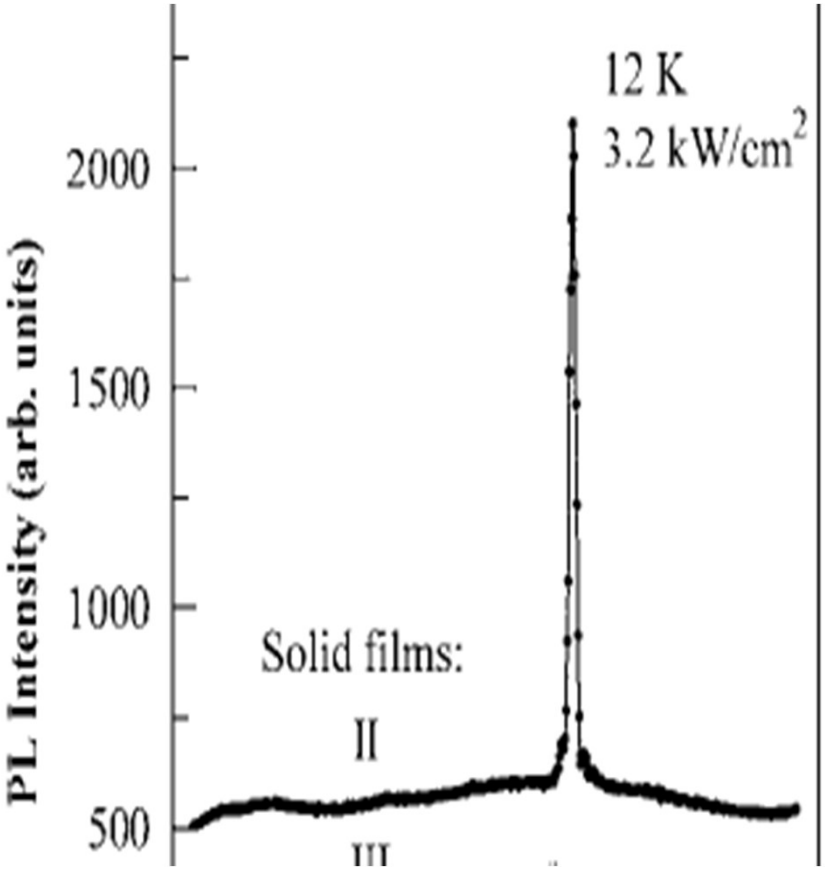
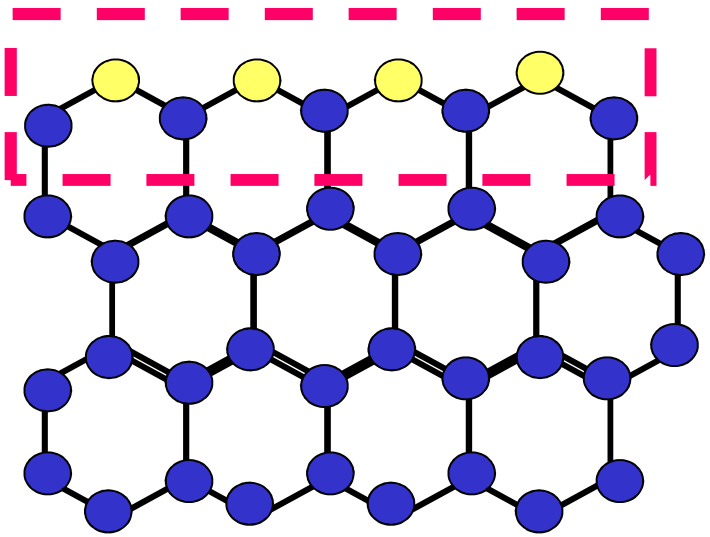


Photo-luminescence spectra at room temperature at low pumping:
a) and b) - dilute and concentrated solutions, c) **-** solid film c.

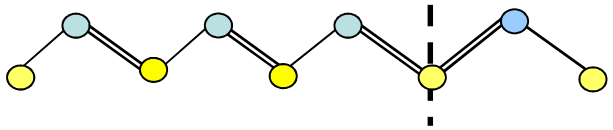


Green laser at T <200K for photo pumping ~4 kW/cm2.

Hypothesis on the spontaneous polarization at edges of the Graphene – think of nanoribons.



Analogy to the (AB)x polymer



The sites are alternating by their position.
Will the bond alternation be added at a reasonable temperature?
It depends on the coupling **λ** of the edge state with lattice deformations.
Theoretical estimations for **λ** strongly diverge: from **$\lambda \sim 10^{-2}$** to **$\lambda \sim 0.3$.**
Need a stronger localization **L** of the edge state: **$\lambda \sim 1/L$.**

Waiting for experiments.

Dimerization of bonds is built in;

dimerization of sites is spontaneous after a phase transition

to the Mott insulator state:

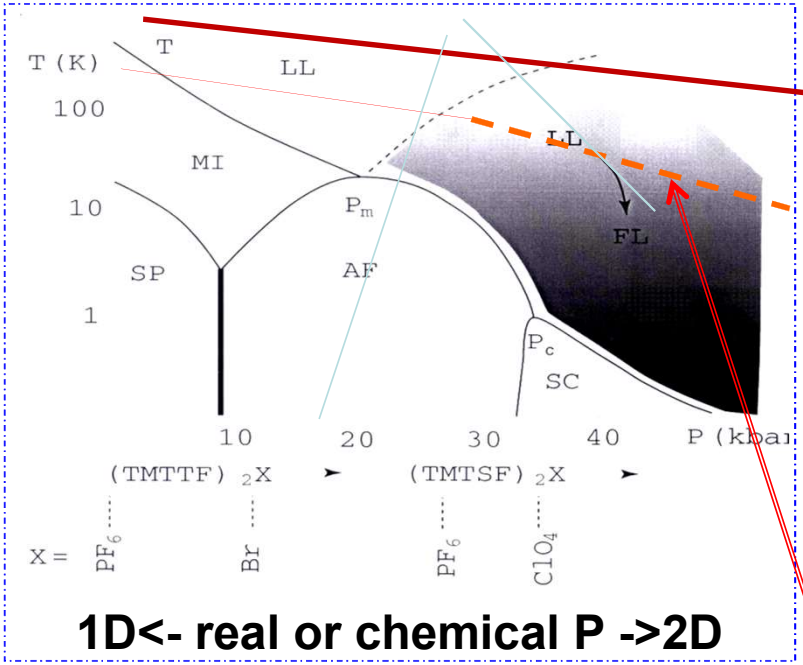
organic conductors $(TMTTF)_2X$

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, ..*
- 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?
- Larger family: electronic ferroelectrics – existing and proposed



1D<- real or chemical P ->2D

Gaps from activation or optics:

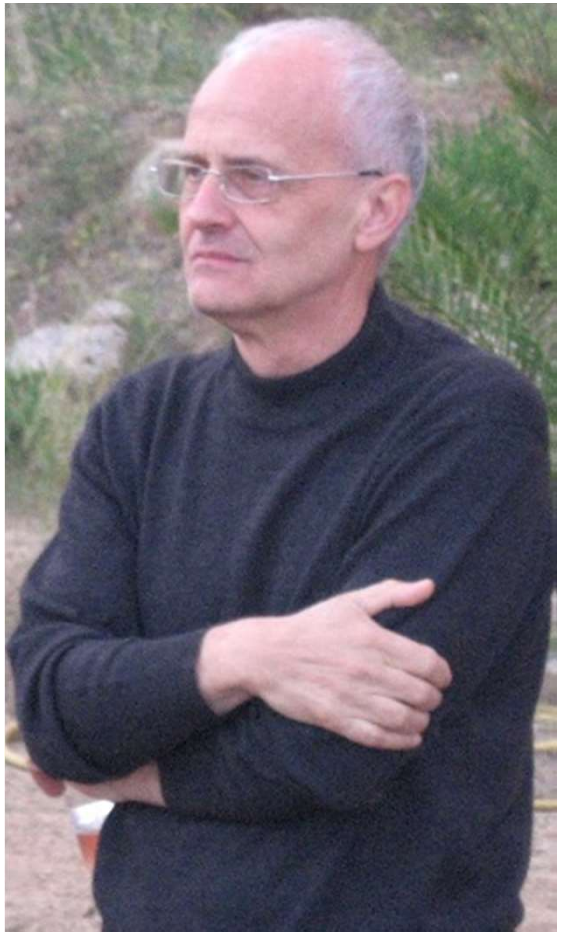
SC- superconductivity
AF= AFM = SDW, SP- Spin-Peierls
LL- Luttinger liquid, MI- Mott insulator
Red lines 2000's revaluation:
Structurless transitions = Ferroelectricity
= Charge disproportionation

Views and interpretations:
FerroElectric Mott-Hubbard state
mixed site/bond $4K_F$ CDW
pinned Wigner crystal
charge ordering

Workshop for Solitons -
3 different types identified:
spinless phase solitons,
spinless polarisation solitons,
spin+charge confined **solitons**

Major enigma:
continuation of the Charge Order and Ferroelectricity into the metallic and even superconducting state of the TMTSF, or TMTTF under pressure: strong evidences for the related optical gap.

Unloyal intervents from inorganic world of CDWs in pursue of a similar sliding of SDWs in molecular conductors



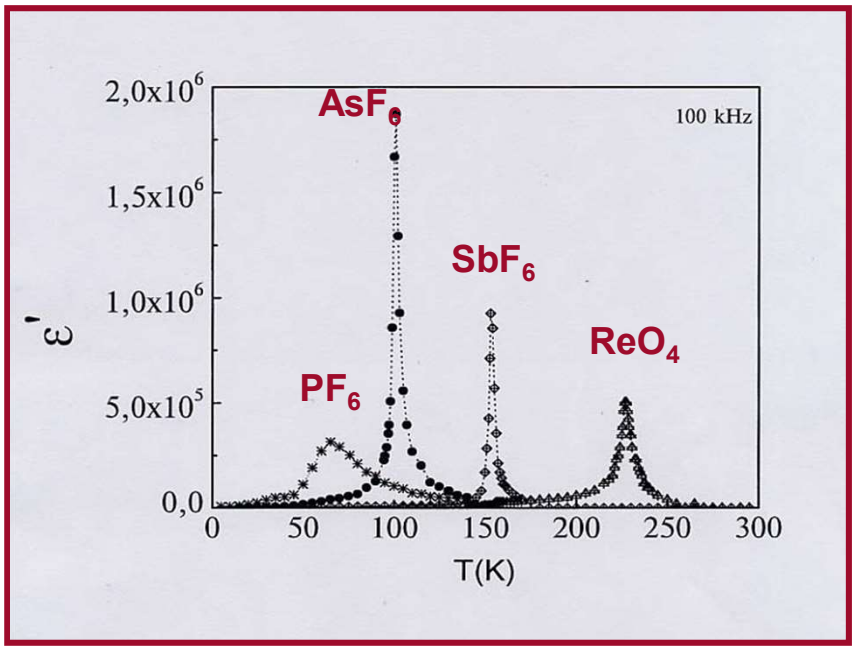
Il dit:
Que la glissance soit!
Et la glissance fut.
Ce fut le premier jour
Genesis 1976

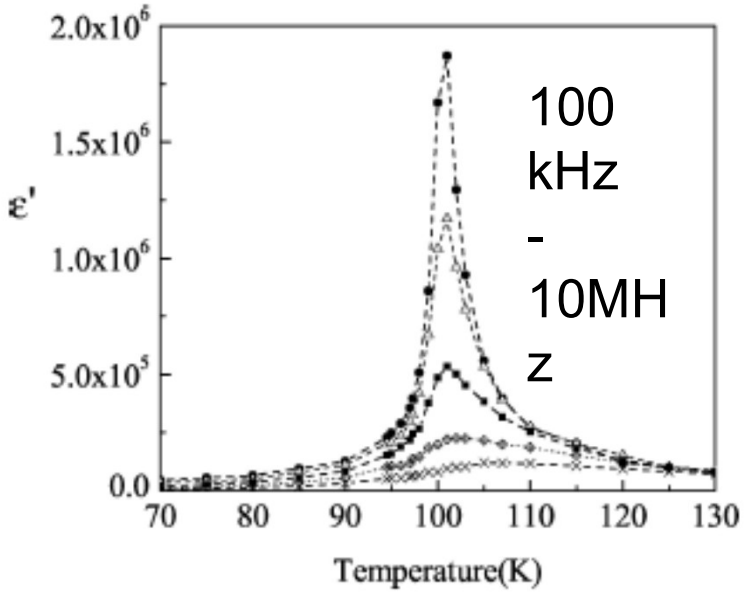
Il vit tout ce qu'il avait fait. et voici,
cela était très bon

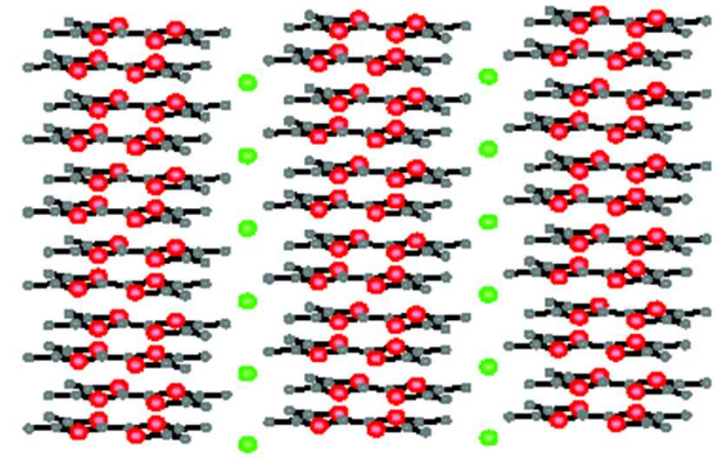
Il ne se reposa pas au jour de toute son œuvre, qu'il avait faite

Insights and problems in ferroelectricity and charge ordering in quasi-1D organic conductors.

S. Brazovskii (Orsay), P. Monceau (Grenoble, France)
and late F. Nad (Moscow, Russia)

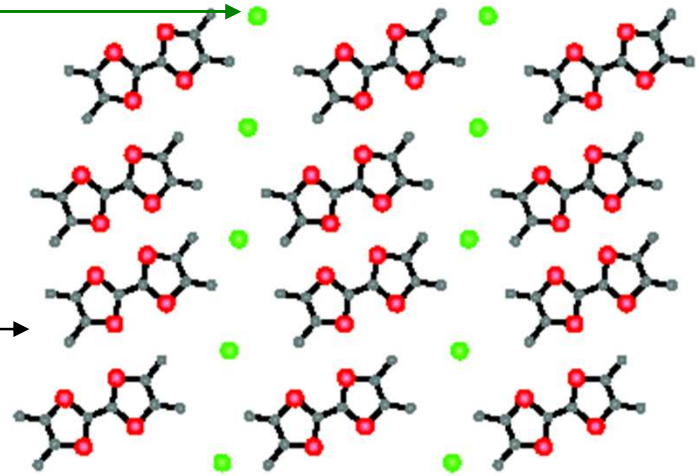


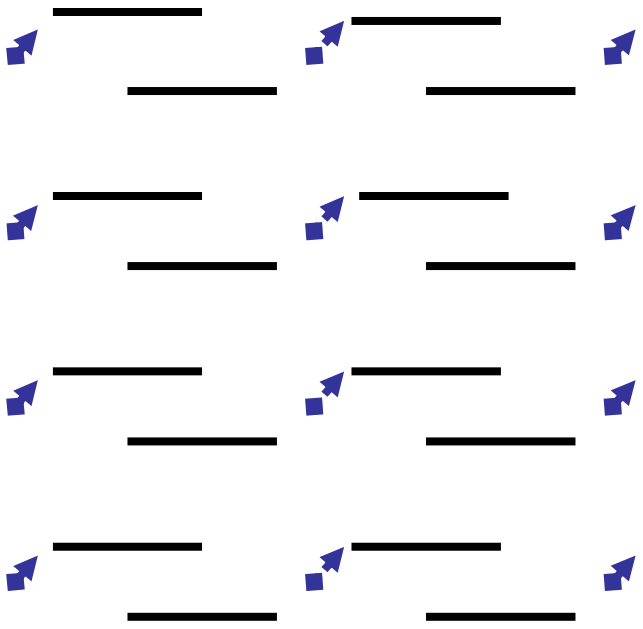




conterion
= dopant X

Molecule
TMTTF
or TMTSF





Built-in: dimerization of bonds
(the counter-ions X are placed against each second pair of molecules)

Spontaneous: displacements of ions X signify the dimerization of sites, it lifts last mirror symmetries, hence **the ferroelectricity.**
Q=0 prevents the X-ray observation

Structurless transitions (*Coulon et al 1985*)
= Ferroelectricity (*Monceau, Nad, S.B.*)
= Charge disproportionation (*Brown et al*), Dressler et al

Views and interpretations:

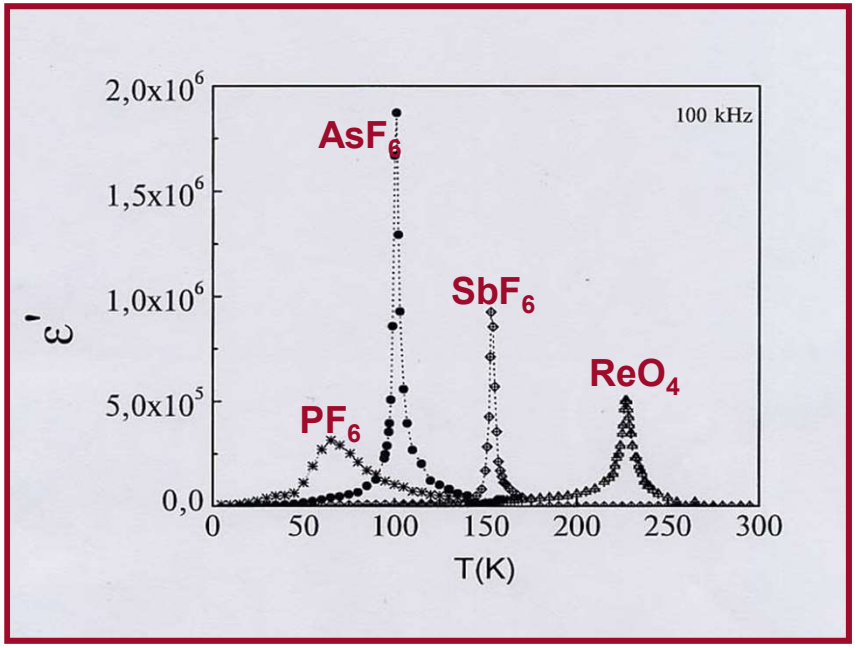
AFM with Charge ordering	***(Seo&Fukuyama)***
FerroElectric Mott-Hubbard state	**(*SB, Monceau, Nad*)**
mixed site/bond $4K_F$ CDW	**(back to *Pouget&Kagoshima* 76)**
pinned Wigner crystal	**(*Hiraki&Kanoda*)**

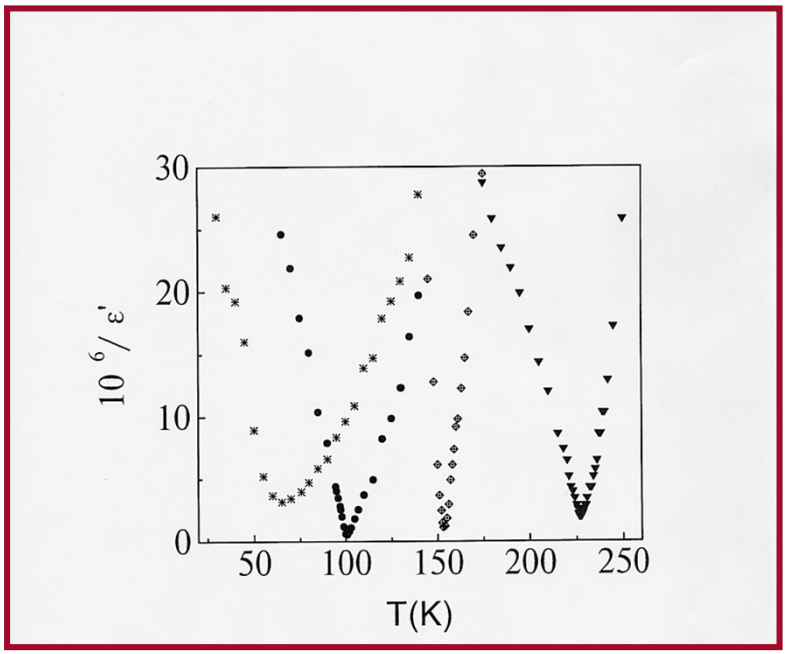
Workshop for Solitons (SB) - 3 different types identified: spinless phase solitons, spinless polarisation solitons, spin+charge reconfined solitons

Major enigma:
continuation of the Charge Order and Ferroelectricity into the metallic and even superconducting state of the TMTSF, or TMTTF under pressure: strong evidences for the related optical gap – Degeorgi & Dressel groups.

Real part of dielectric constant of $(TMTTF)_2X$ salts

P.Monceau et al. Phys. Rev. Lett. 86 (2001) 4081

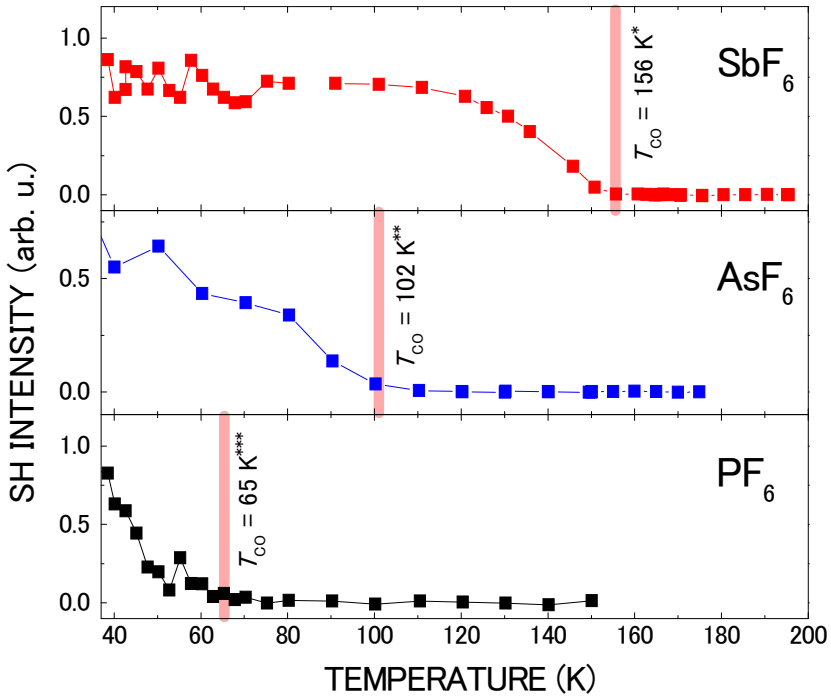




Real part of the permittivity (the dielectric constant ε')

- the second order phase transition described by the perfect Curie law

$$\varepsilon' = \frac{A}{|T - T_C|}$$



* *T. Nakamura, et al (2007)*

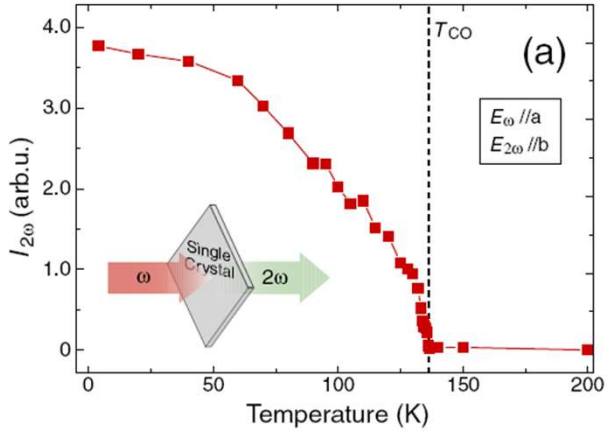
** *S. Fujiyama, et al (2006)*

*** *W. Yu et al., (2004)*

Direct proof for the FE state in a syster compound:
local measuraments of the second harmonic generation in
α-$(ET)_2I_3$ *K. Yamamoto et al. (2008-11)*

Second harmonic generation

Identification of the frozen polarization:
through anomalous optical activity
- lack of inversion symmetry



$$P = \frac{\varepsilon}{4\pi} E + \chi_2 E^2$$

E^2 is allowed only
if the inversion symmetry is lifted.

COMBINED MOTT - HUBBARD STATE

2 types of dimerization $\Rightarrow$

Site dimerization : $\mathbf{H_U^s = -U_s \cos 2\varphi}$ (spontaneous)

Bond dimerization : $\mathbf{H_U^b = -U_b \sin 2\varphi}$ (built-in)

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

$U_s \neq 0 \rightarrow \alpha \neq 0 \rightarrow$
shifts from $\varphi = 0$ to $\varphi = \alpha$ - ***the gigantic FE polarization.***

From a single stack to a crystal:

Macroscopic FerroElectric ground state: the same α for all stacks

Anti-FE state: the sign of α alternates

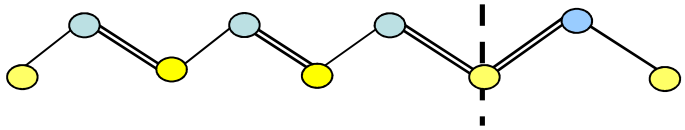
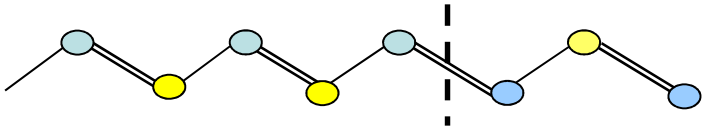
Spontaneous U_s can change sign between different FE domains.

Domain boundary $\mathbf{U_s \leftrightarrow -U_s}$ - the phase soliton $\mathbf{\Delta\varphi = -2\alpha}$

non integer charge $\mathbf{q = -2\alpha/\pi}$ per chain.

alpha- solitons - walls between domains of opposite FE polarizations

On-chain conducting particles above $\mathbf{T_{FE}}$.
Macroscopic walls below $\mathbf{T_{FE}}$ (do not conduct, but determine the FE depolarization dynamics.

$(AB)_x$ Conducting Polymers	Organic Crystals
built-in	
nonequivalence of sites	nonequivalence of bonds
spontaneous	
Peierls bonds alternation	Wigner-Mott-Hubbard charge localization
	
$\Delta = \sqrt{\Delta_e^2 + \Delta_i^2}$	
Lifting of the inversion symmetry, leading to electric polarization, hence the ferroelectricity.	

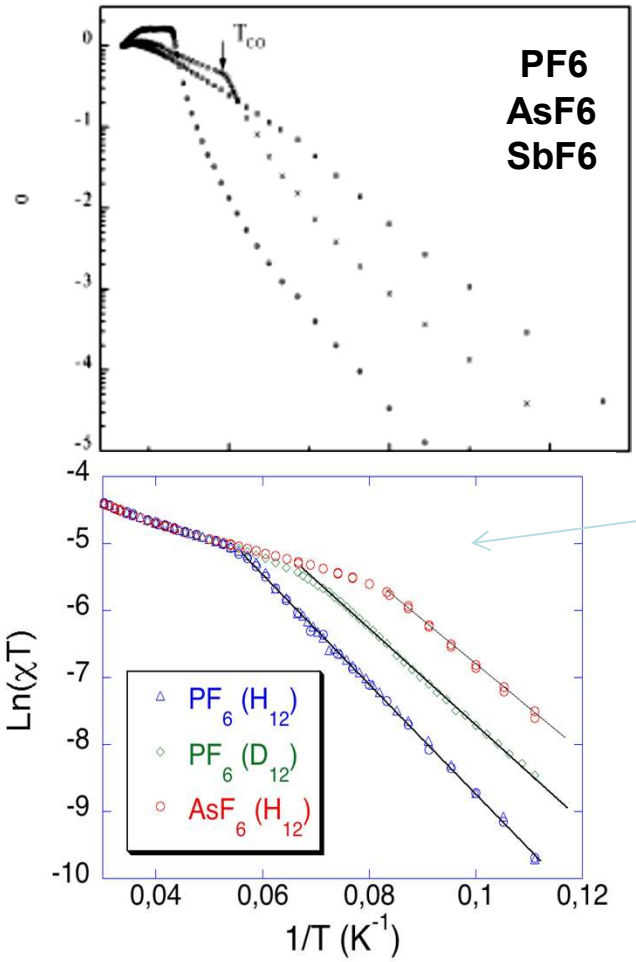
How do we know that polarization is present (X-rays are no good, q=0)?

From identification of physics of solitons.

Advantage of organic conductors: low scales of gaps allow for their determination from thermal activation, to be compared with optical features.

What does conduct in these “narrow gap semiconductors” ?

NOT the electrons, even in the polaronic version !



Conductance G , normalized to RT

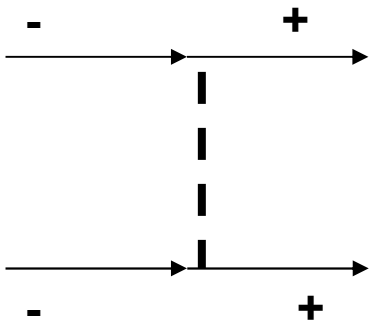
- Ahrenius plot Log G(1/T).

Gaps Δ_c for thermal activation of conductance range within 500-2000K.

$\chi \sim \exp(-\Delta_s/T)$, $\Delta_s \sim 75K$

Contrarily to normal semiconductors -NO GAP, or a very small gap Δ_s, in spin susceptibility $\chi(T)$. Clearest example for conduction by charged spinless solitons - holons.

Spin gaps, if any, are the order of magnitude smaller than the charge gaps.



Umklapp scattering amplitude, leading to the Mott state
Dzyaloshinskii & Larkin, Luther & Emery.
U from $4K_F$ or CO commensurability

Uexp[i2φ] *: 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.

COMBINED MOTT - HUBBARD STATE

2 types of dimerization $\Rightarrow$

Site dimerization :	$\mathbf{H_U^s = -U_s \cos 2\varphi}$	(spontaneous)
Bond dimerization :	$\mathbf{H_U^b = -U_b \sin 2\varphi}$	(built-in)

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

$U_s \neq 0 \rightarrow \alpha \neq 0 \rightarrow$ shifts from $\varphi = 0$ to $\varphi = \alpha$ - ***FE polarization.***

Quasi-1D Mott state = 4KF CDW= commensurate Wigner crystal

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

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

$$\mathbf{H= (\hbar/4\pi\gamma) [v (\partial_x\varphi)^2 + (\partial_t\varphi)^2 /v] - Ucos (2\varphi -2\alpha)}$$

$v\sim v_F$ – velocity $\gamma= K_\rho$ **-** in notations of "Luttinger liquid"

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)

Phase centre shift α - may appear at the ferroelectric transition T_{FE}

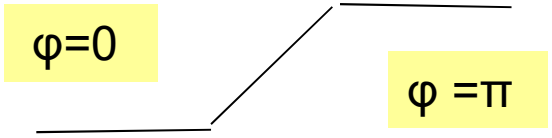
$\gamma= K\rho$ - major monitoring parameter :

$\gamma<1$: *any repulsion,* build-in **U** is not renormalized to zero, generic Mott state

$\gamma<1/2$: *strong repulsion*, then U can be spontaneously generated

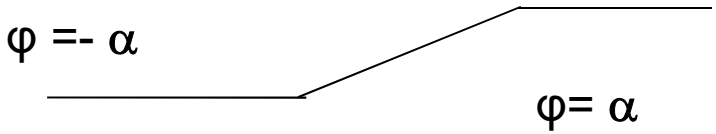
– Charge Ordering = **$4K_F$** condensation – our case

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*.



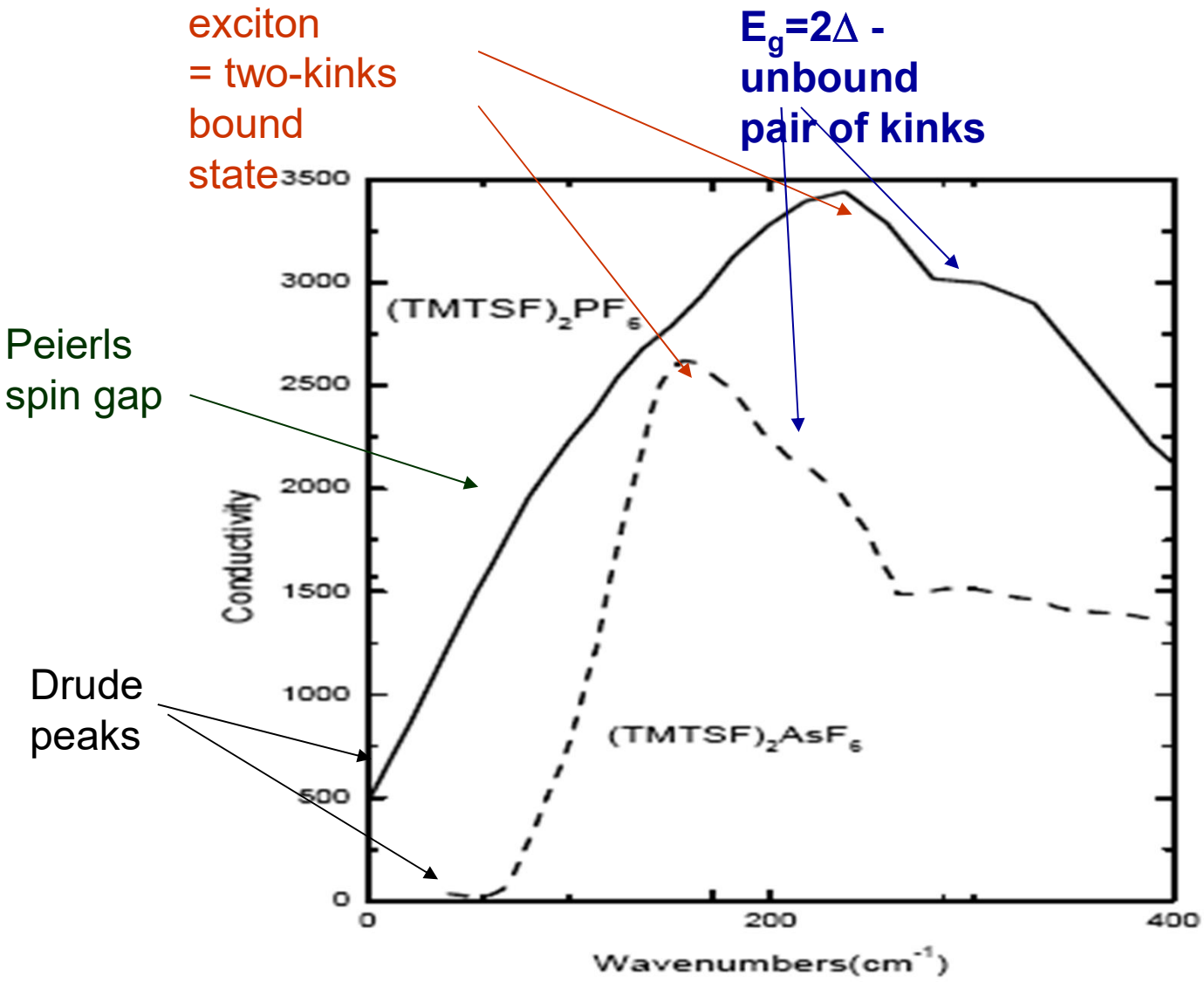
Purely on-chain solitons, exist as conducting quasiparticles both above and below the $\mathbf{T_{FE}}$.

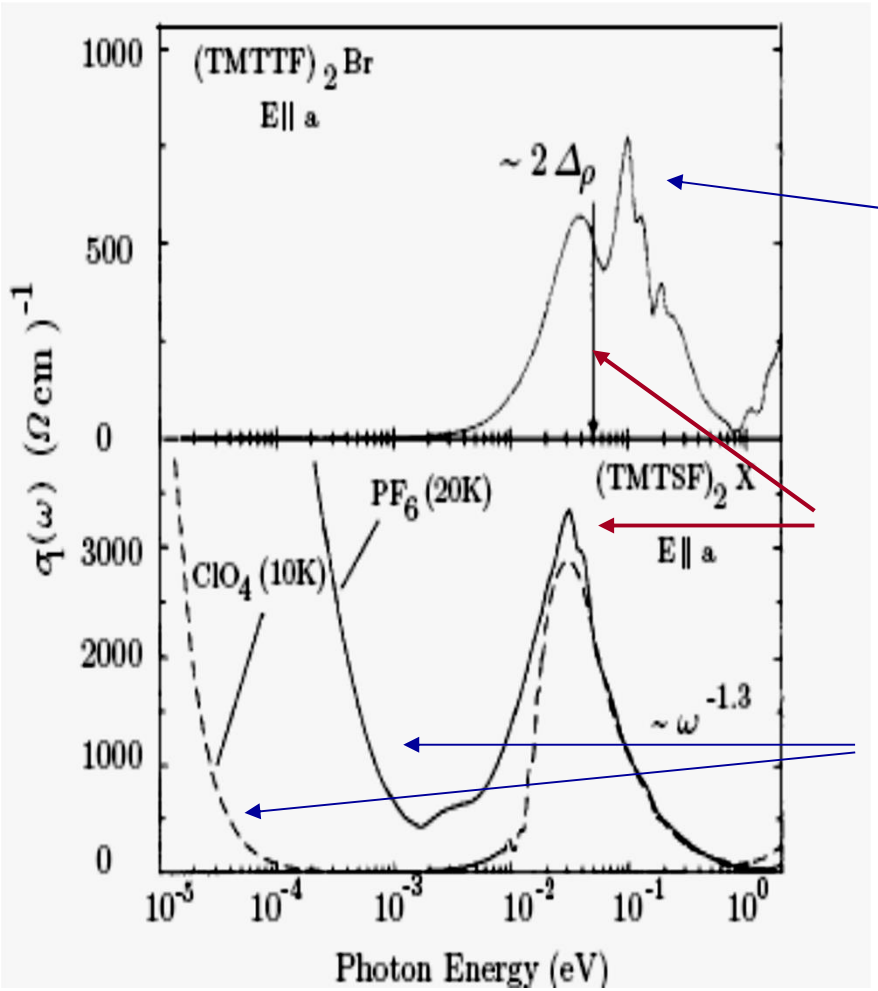
Spontaneous U_s itself can change sign between different FE domains.
Then electronic system must also adjust its ground state from α to $-\alpha$.
Hence the domain boundary $\mathbf{U_s \leftrightarrow -U_s}$ requires for the phase soliton of the increment $\delta = -2\alpha$
which will concentrate the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


exciton
= two-kinks
bound
state
$E_g=2\Delta$ -
unbound
pair of kinks
Peierls
spin gap
Drude
peaks
(TMTSF)$_2$PF$_6$
(TMTSF)$_2$AsF$_6$
Conductivity
Wavenumbers(cm^{-1})
0
500
1000
1500
2000
2500
3000
3500
0
200
400



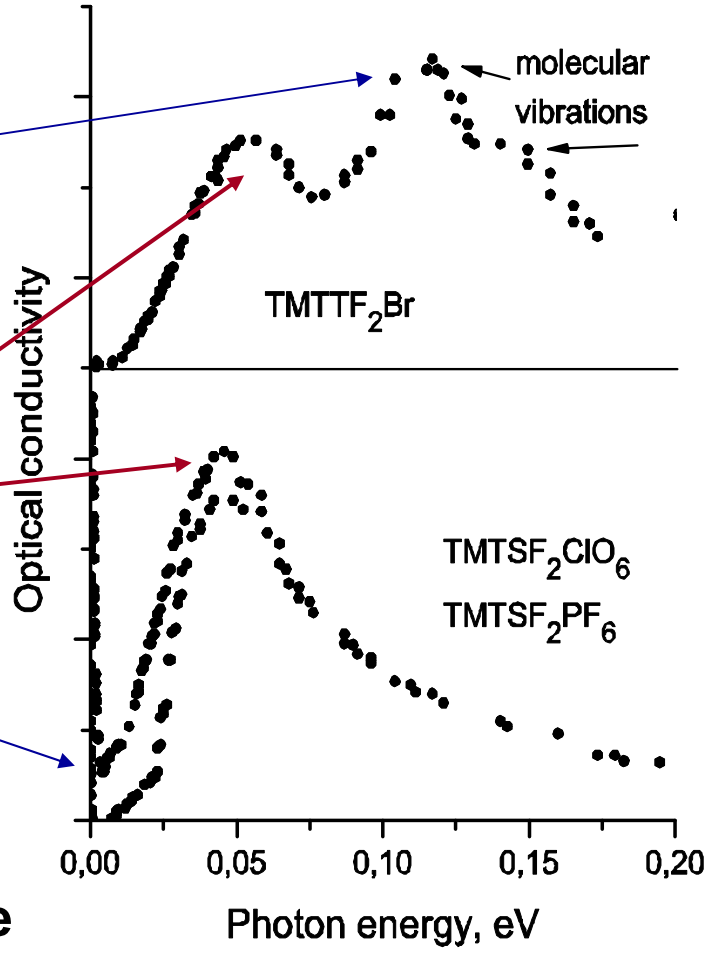
parasite intra - molecular modes

gap $2\Delta_\rho$

Drude peaks

log scale

linear scale



Comparison of optical absorption in two subfamilies:

Mott insulator TMTTF (*upper plots*) and a "metal" TMTSF (*lower plots*)

Dressel &Degiorgi

Resemblance of static (TMTTF) and fluctuational (TMTSF) Mott states

Only the weakest CO in Bromine allows to see the expected gap.

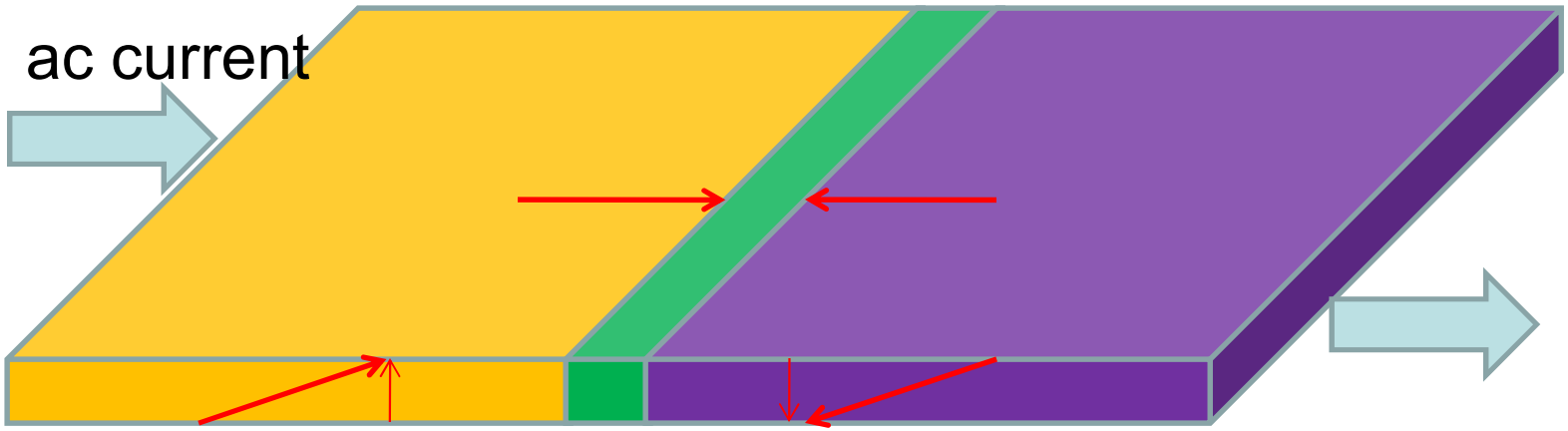
Photoconductivity may be a tool for other cases, c.f. polymers

What is so special about ferroelectricity in organic conductors?

Charge carriers screen the electric field at the sample boundaries, eliminating the usual separation into domains of opposite polarization. Hence no hysteresis, easy *ac* repolarization and the astonishingly high permittivity $\varepsilon \propto 10^6$.

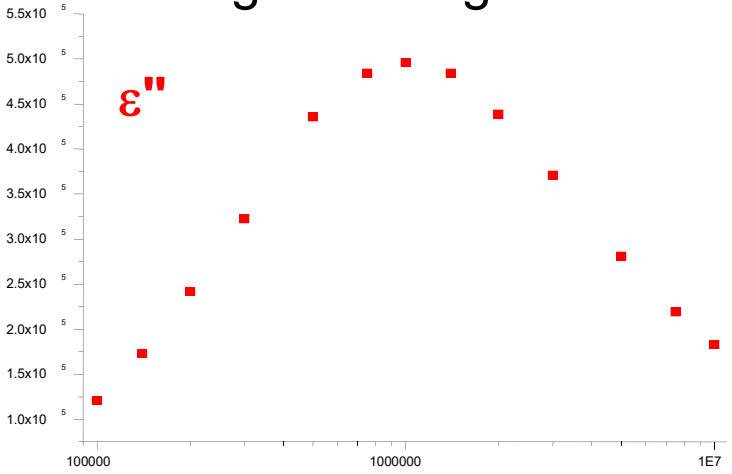
That allows us to test the dynamical scaling from critical fluctuations.

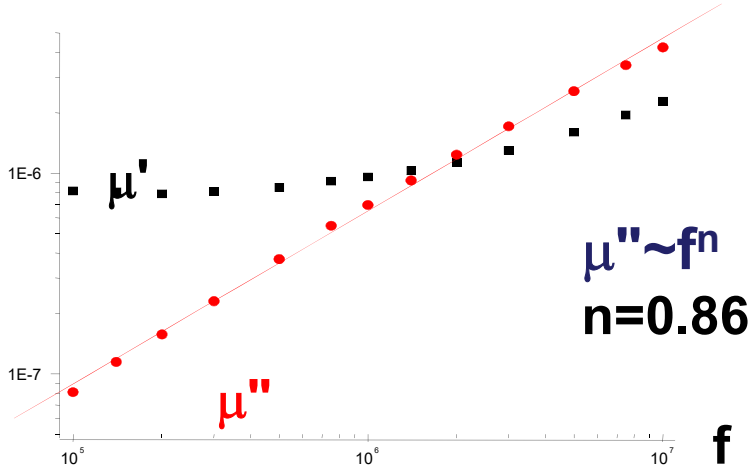
Polarizations inclined → normal component of electric field E → surface charge. Unusually, it is screened by current carriers, no field goes out of the sample → no need for a domain structure. Mono-domain state → gigantic ε'



Stil, domain walls sweep in the course of re-polarization by *ac* current. Jump of the longitudinal polarization → ← makes the wall charged. Hence the accompanying cloud of normal carriers which resistance gives rise to the observed activated damping at low T.
*D*omain wall concentrates carriers, effecting || & ⊥ conductions (interpretation of M.Dressel finding) - call for combined methods.

Advantage of using the inverse complex function: $\varepsilon=\varepsilon'+i\varepsilon'' \rightarrow 1/\varepsilon=\mu=\mu'+i\mu''$





Log-Log plots of ε'' and μ' , μ'' above Tc **- T=105K**

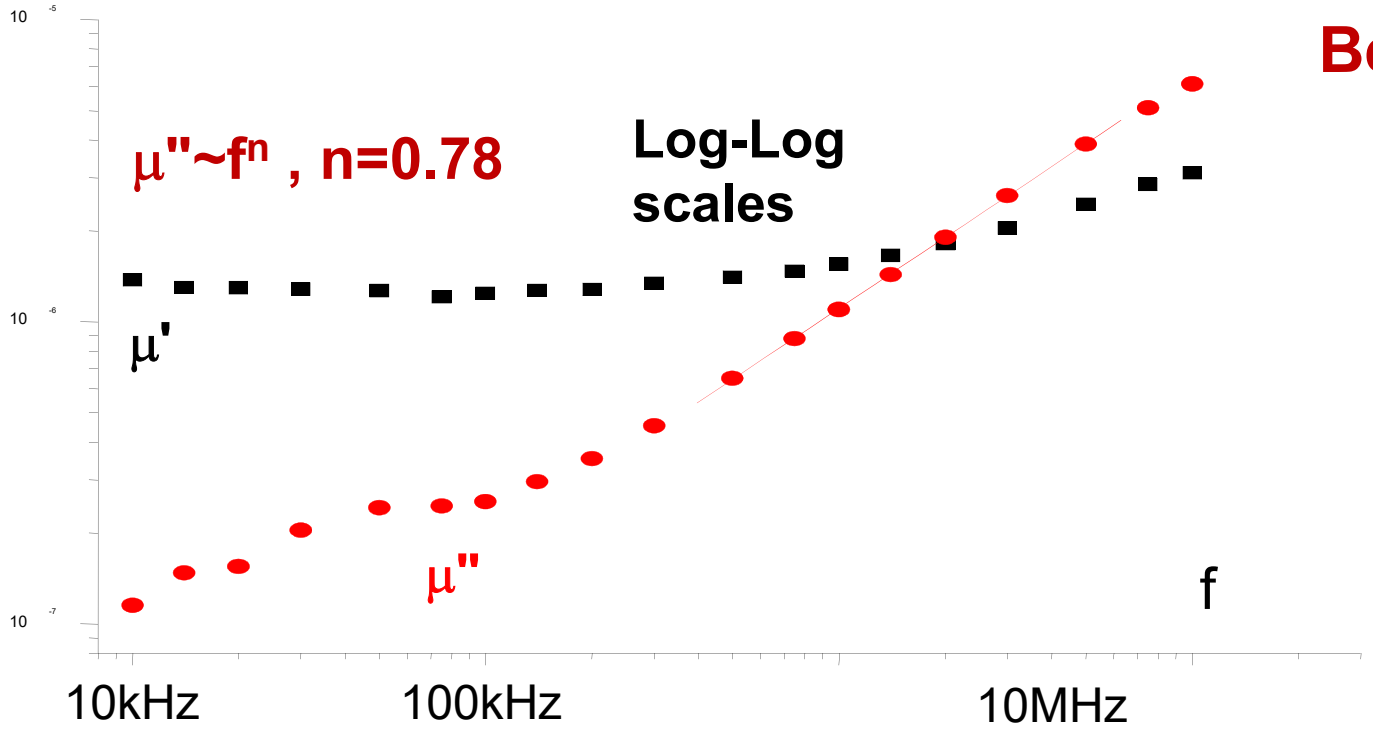
Hump in ε'' → straight line for μ'' over the whole interval of **f.**

The power law μ'' **~f^n** with **n=0.86**±0.01.

The exponent **0.86 is not 1** as in mean field theory of critical relaxation

- unexpected access to the profound dynamical scaling at the criticality.

Expect a scaling between **f** and T-Tc – need more T's to examine.



Log-Log plot still recovers a good straight line **but only at sufficiently** high f.

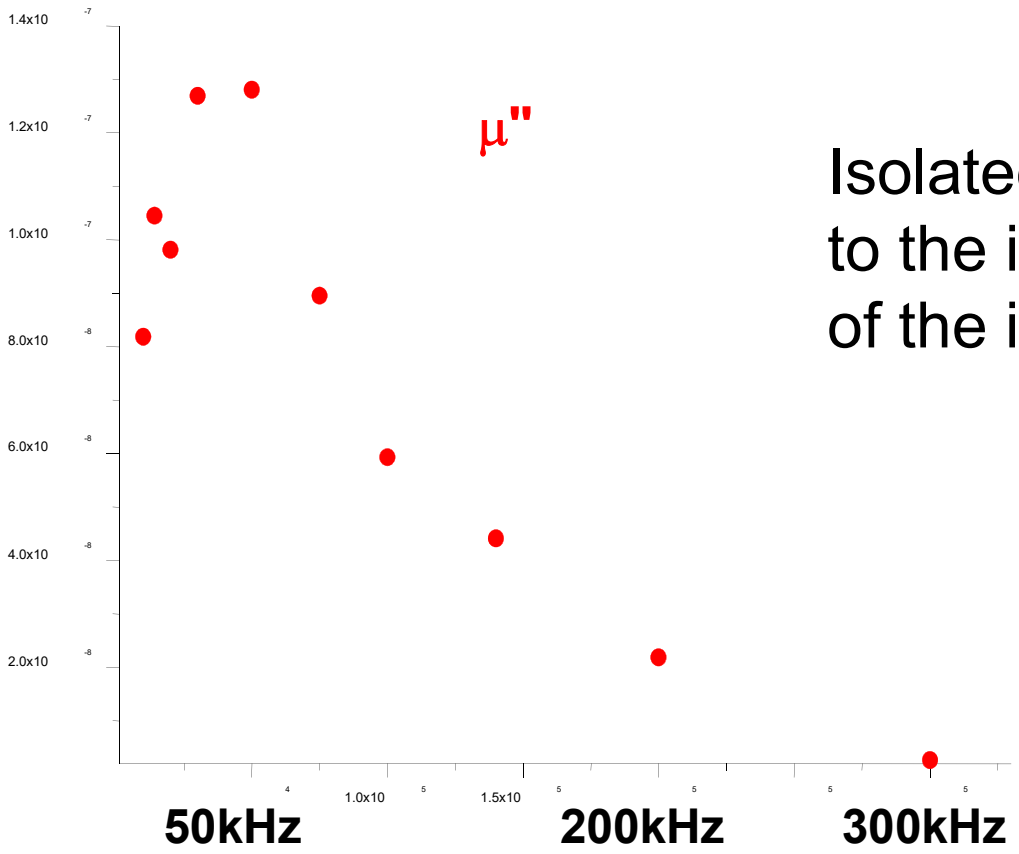
The power law is $\mu''\sim f^n$ with **n=0.78**

– not far from **n=0.86** for T=105K but the difference is beyond our quite good accuracy **0.02**.

This fit *covers symmetrically both slopes* of the maximum of ε''.

Now **we** extrapolate and subtract the straight line, **to** single out the contribution of the low **f** shoulder in μ'' and ε''.

Separation of the low *f* feature - now it shows up sharply and can be plotted in Lin-Lin scales. FINAL RESULT :



Isolated low frequency contribution to the imaginary part μ" of the inverse permittivity.

f

Presumably: pinning of sweeping domain walls, weak hysteresis.

CONCLUSIONS on dynamics of the FE conductors

Simultaneous analysis of real and imaginary parts of the inverse permittivity allows to separate several dynamic regimes.

a. critical slowing down characterized by anomalous powers 0.86 and 0.78 - above and below the phase transition.
b. low frequency response of the re-polarization, associated to sweeping of domain walls below Tc.
c. low T viscosity of the FE polarization follows the concentration of normal conducting carriers – the spinless solitons.

Remaining challenges on Ferroelectricity:
Frozen polarization, hysteresis, domains.

Softening of a responsible phonon mode above T_c.

Crossover from the overdamped critical mode below T_c to the underdamped IR active mode at low T.

Combined methods – *success in conjugated polymers*:
Microscopic probes depending on the state or evolution of the FE.
Why always FE? Only $(TMTTF)_2SCN$ shows the anti-FE case !

What is so special about ferroelectricity in organic conductors?

1. **Abundance of charge carriers (phase solitons or holons !) which screen the normal electric field at the side boundaries, hence eliminate the usual reason for the sample separation into domains of opposite polarization.**
2. **No domains, then no domain walls which pinning usually stabilizes the frozen polarization, giving rise to the hysteresis.**
3. **Free carriers screen the charge of the domain wall thus eliminating a high cost of the Coulomb energy to nucleate the domain wall.**
   Hence the easy re-polarization under the ac field of existing experiments.
4. **All that secures a pure response of the collective mode, leading to this astonishingly high permittivity $\varepsilon \sim 10^6$, allows to reach and test the regime of critical fluctuations to test the dynamical scaling.**

LESSONS and PERSPECTIVES

- π-conjugated systems can support the electronic ferroelectricity.
- Effect is registered and interpreted in two families of organic crystalline conductors (quasi 1D and quasi 2D).
- Mechanism is well understood as combined collective effects of Mott (S.B. 2001) or Peierls (N.K.&S.B. 1981) types.
- The energy is gained from the gap increase by the Mott or Peierls or spin-Peierls effects.
- An example of a must_be_ferroelectric polyene is already at hands.
- The design is symmetrically defined and can be previewed. Cases of low temperature phases should not be overlooked.
- Solitons will serve duties of re-polarization walls.

Remaining challenges on Ferroelectricity:

- **Frozen polarization, hysteresis, domains.**
- **Combined methods – *success in conjugated polymers*:**
- **Microscopic probes depending on the state or evolution of the FE.**
- **Why always FE? Only $(TMTTF)_2SCN$ shows the anti-FE case !**

Particular interest in developing of ferroelectric π-conjugated systems "electronic ferroelectrics":

- Manipulations of charged solitons by electric field. Their spectral features arrive in optics
- Gigantic ε, easy repolarization – fast response
- Conductivity and/or optical activity of π-conjugated systems will add more functionality to their ferroelectric states.
- Polarizability of chains can allow to manipulate morphology (existing hybrids of polymers and liquid crystals. K. Akagi - Kyoto).
- High and fast nonlinearity : χ_2 for the optical mixing , second harmonic generation

Ferroelectricity is a rising demand in fundamental and applied solid state physics.

R&D include:

- Active gate materials and electric RAM in microelectronics,
- Capacitors in portable WiFi communicators,
- Electro-Optical-Acoustic modulators,
- Electro-Mechanical actuators
- Transducers and Sensors in medical imaging.

Difficulties with conventional ferroelectric oxides:

Process compatibility and contamination.

Request for plasticity – polymer-ceramic composites

but weakening responses – effective ε~10.

Plastic ferrroelectrics are necessary in medical imaging – low weight : compatibility of acoustic impedances with biological tissues.