Thanks to :
Prof. Roman Swietlik,
Dr. Iwona Olejniczak,
Organizing Committee members

Ten years of the electronic ferroelectricity in organic materials: from critical dynamics of domain walls to optics of solitons.

S. Brazovski[1], N. Kirova[2], P. Monceau[3] and **F. Nad**[4]

[1]*LPTMS - CNRS, Univ. Paris-Sud, Orsay, France*
[2]*LPS - CNRS, Univ. Paris-Sud, Orsay, France*
[3]*Institute Neel, CNRS, Grenoble, France*
[4]*IREE, RAS, Moscow, Russia.*

Nad' Felix Ya. died
21 September 2011, age 73

Inst. for Radio-Electronics and Engineering, Moscow
Frequently in Grenoble, France with Pierre Monceau.

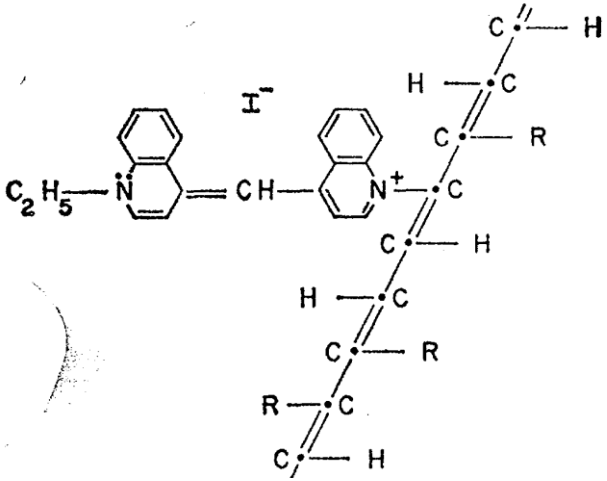
60's : Optics of defects in semiconductors
70's : weak superconductivity, Josephson devices for MW reception
80's : CDWs – optics, conductivity ----- solitons, phase slips
90's : CDWs in Grenoble – space-resolved X-ray, glassy state of CDWs.
2000's : Bringing the methods for sliding CDWs to organic conductors.
Clarifying the anomaly near "structurless transitions"
stimulated discovery of the charge orderings/disproportionation
Further spectacular refinement – 2001 discovery of the never expected Ferroelectricity of electronic origin in organic conductors; more subsequent progress through the last decade.

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

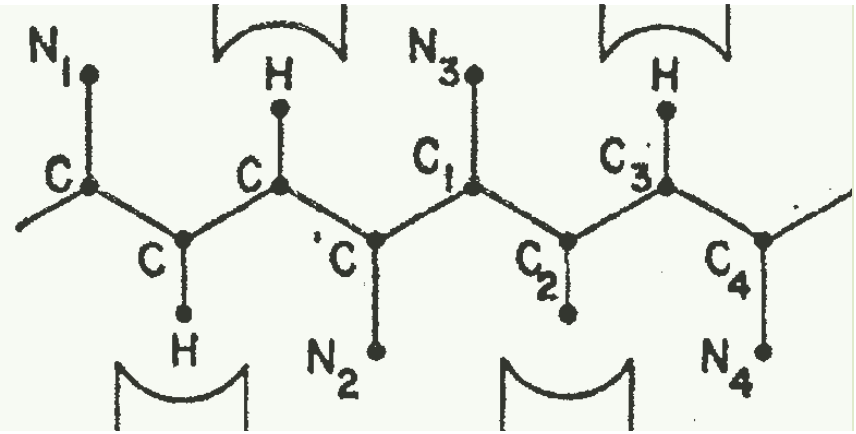
Physical Review 1964
W.A. Little
POSSIBILITY OF A SYNTHESIZING AN ORGANIC SUPERCONDUCTOR.

Scientific America 1965
"… theoretical studies suggest that it is possible to synthesize organic materials ... without resistance"

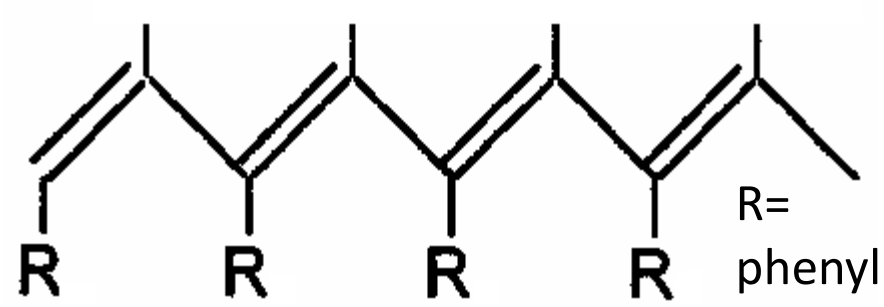
"Little" mystification: did he actually mean **ferroelectricity**?



Was “organic superconductivity” the only promised land?
Not quite : some of the prophet's visions actually imply a frozen/spontaneous electric polarization, hence they are Pyro/Ferro-Electics.



Drawing - PRB 1964 - **pyroelectric**



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

Certificate of reality: Ferroelectric Mott-Hubbard phase and charge ordering in organic conductors.

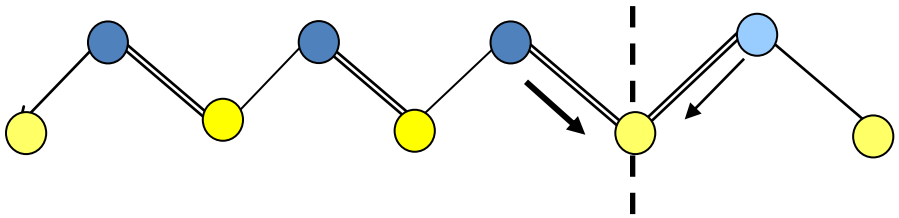
Closing the "Little" loop:

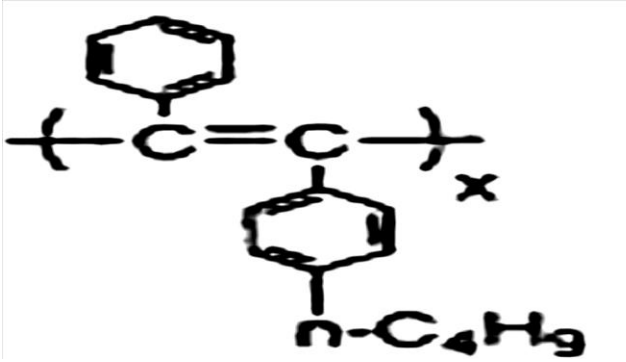
Expectations of electronic ferroelectricity in conjugated polyenes.

The first coming unrecognized to Utah from Kyoto-Osaka, now + Nanjing.

Instructions for the ferroelectric design: Combined symmetry breaking.

- *Lift* the inversion symmetry: remove the mirror and glide planes.
- *Keep* the double degeneracy to get a switchable polarization.





Di-substituted polyacetylene $(CR_1CR_2)_x$ below the Peierls transition

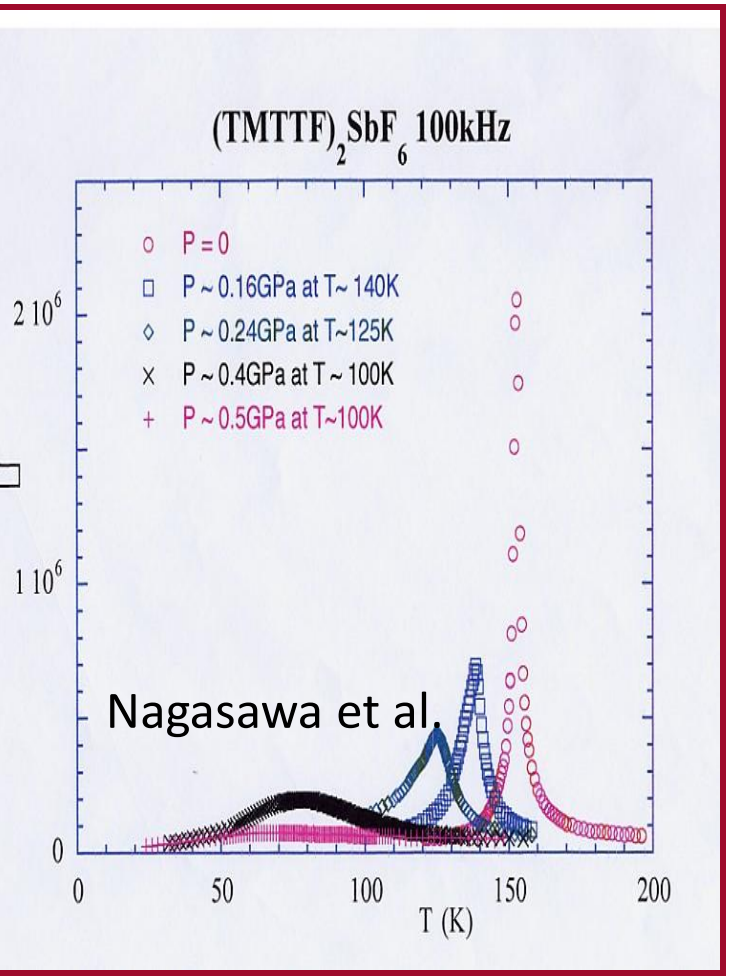
Same principle scheme – the $(TMTTF)_2X$ with the charge ordering

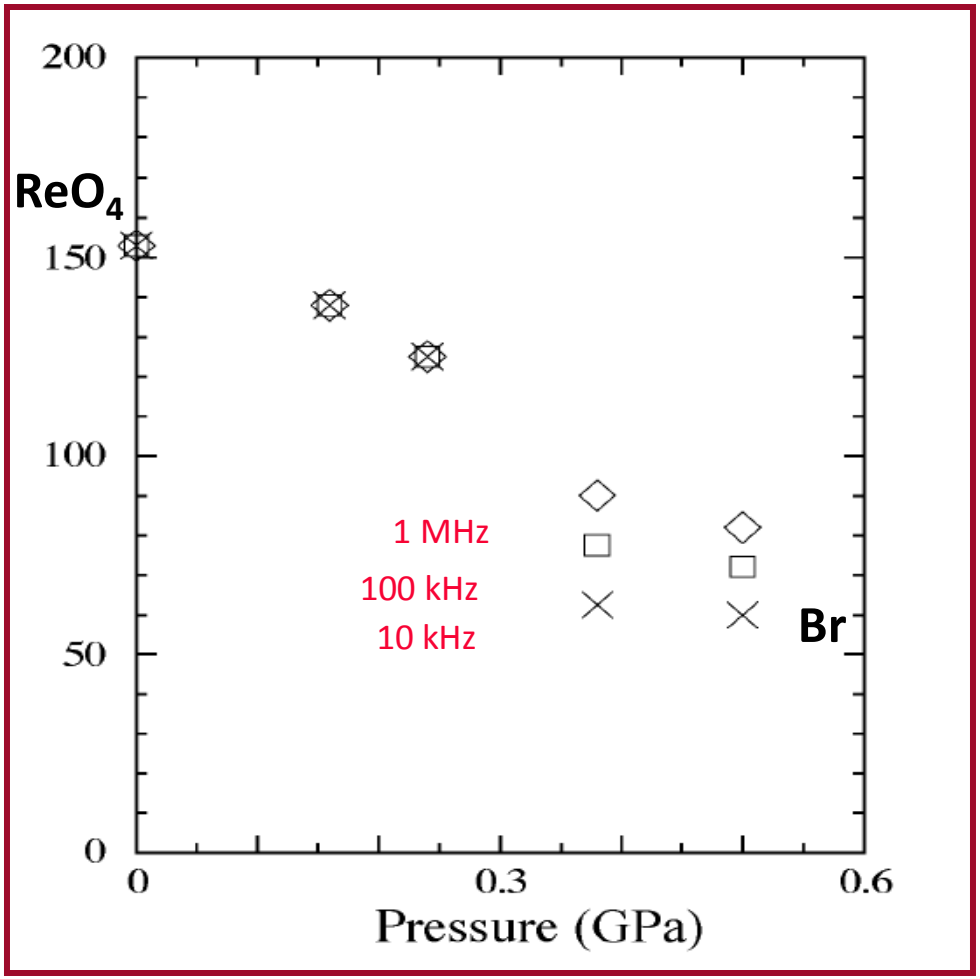
T_{CO} vs pressure in $(TMTTF)_2SbF_6$ as a model phase diagramme

(adding limiting cases of ReO4 and Br at ambient P)

FE anomaly is the precise tool to identify the CO which spreads over the whole non-metalic (TMTTF) part of the phase diagram

– opposing the other methods' view.





After publications by Monceau, Nad et al.

T_{CO} = 230K (ReO_4) -30K (Br) - From FE

No spin gaps except at after additional low T transitions.
Gaps from activation or optics: 1500-600K (TMTTF) , 500K – $(TMTSF)_2$

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

T_c = 230K (ReO_4) -30K (Br)

Gaps from activation or optics:
2000K (ReO_4) , 600K (Br) , 500K – $(TMTSF)_2X$!

TMTSF		NA		??	500	25			AFM,SC

Anion X	σ (S/cm)	T_ρ (K)	Δ_1 (K)	T_{CO} (K)	Δ_2 (K)	T_{AO} (K)	Δ_3 (K)	LT state
Br	100	≈ 200	75	28	–	–	–	AFM
PF_6	40	250	300	70	370	–	–	SP
AsF_6	20	230	175	100.6	360	–	–	SP
SbF_6	10	≈170	–	154	500	–	–	AFM
ReO_4	20	290	800	227.5	1400	154	2000	–
SCN	40	265	500	–	–	169	2000	AFM

Anti FE

BF_4		220		83		39			

SUBSEQUENT DEVELOPMENTS IN FERROELECTRICITY:

Enrichment of the quasi-1D family:

$(EDT\text{-}TTF\text{-}CONMe_2)_2X$ - *Batail, Brown, Pasquier Pouget, Zorina, et al*

$(DI\text{-}DCNQI)_2Ag$ - *Furukawa, Hiraki, Monceau, Nad, Nakamura, Takahashi*

Generalizations to quasi-2D family:

θ- $(BEDT\text{-}TTF)_2RbZn(SCN)_4$ *Monceau, Nad, H.Yamamoto*

α-$(ET)_2I_3$, etc. –

Kowalska, Kawamoto, Nakano, Uruichi, Yakushi, K.Yamamoto , Yue

More distant new relative:

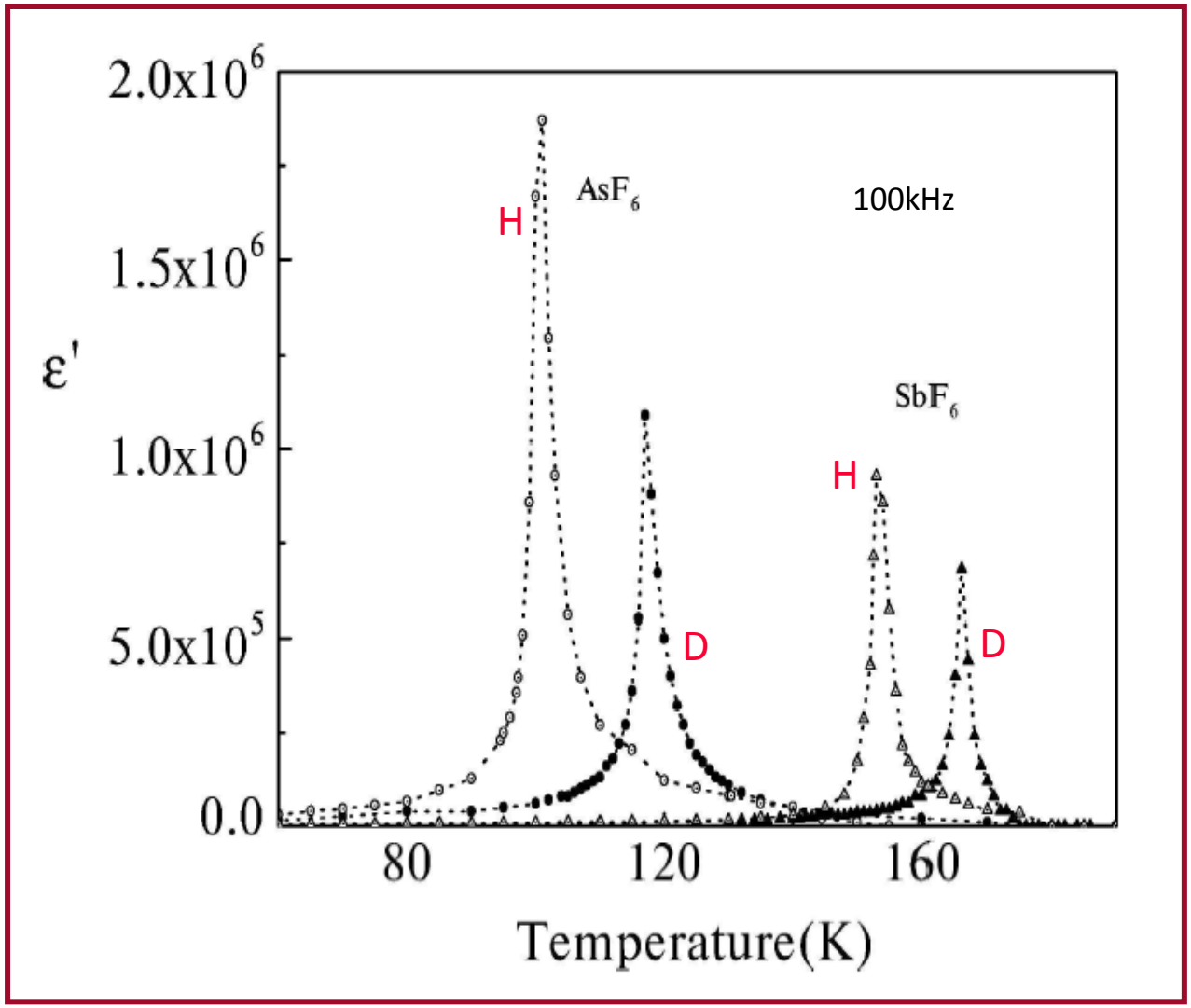
organic charge-transfer salt TTF–BA as a spin–Peierls ferroelectric

Kagawa, Horiuchi, Tokunaga, Fujioka & Tokura

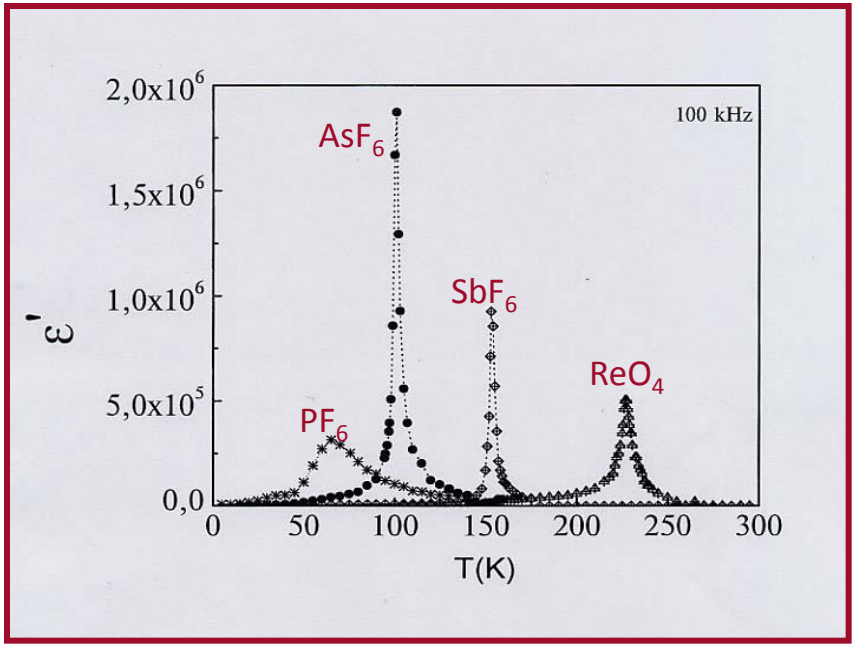
Towards applications and integrity of "synthetic metals":

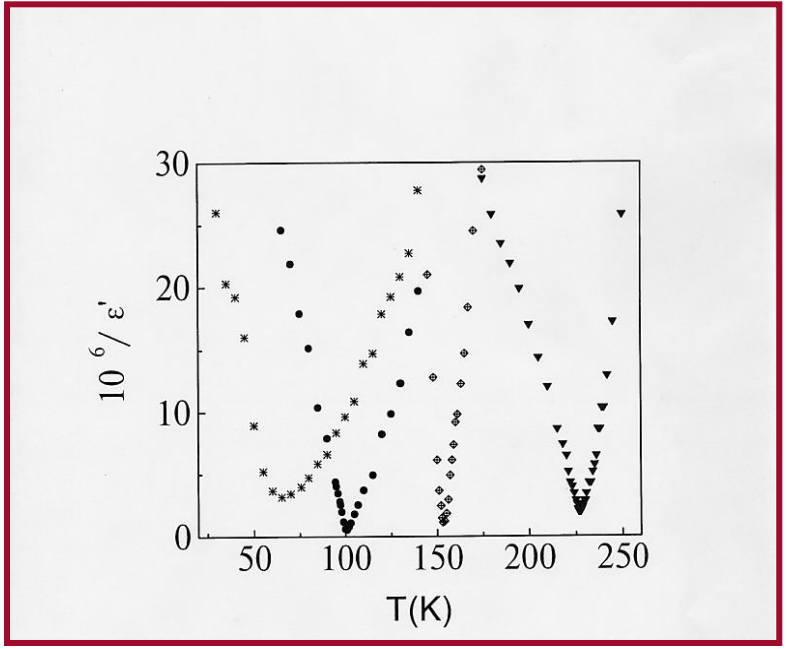
proposal for a ferroelectric conjugated polymer (N. Kirova and SB 2007)

Real part of the dielectric permittivity - effect of deuteriation



This and a few other plots are due to courtesy of P. Monceau



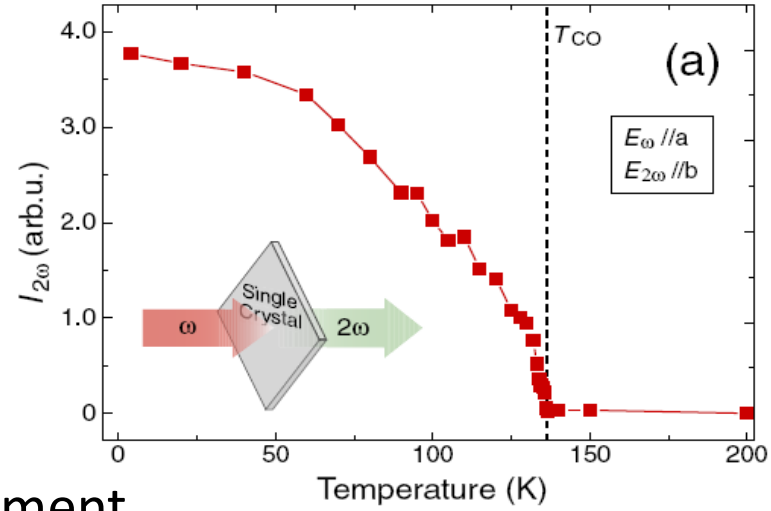


Real part of dielectric constant of $(TMTTF)_2X$ P. Monceau, F. Nad', S. Brazovskii (2001)

Second order phase transition with the Curie-Landau law $\varepsilon' = A/|T-T_{CO}|$, width 30K !

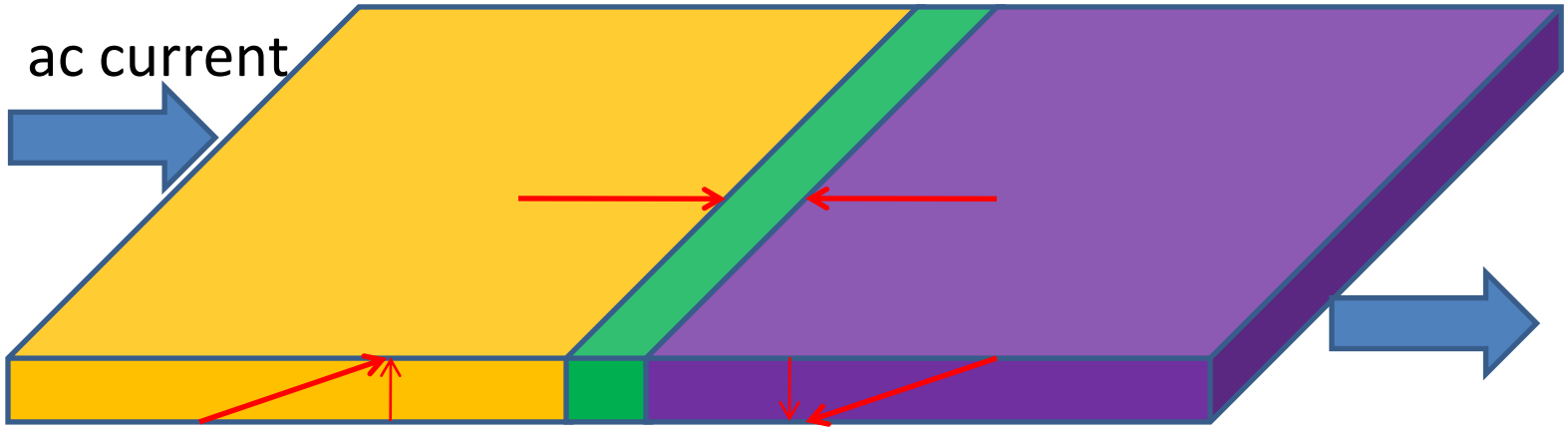
Direct proof for the FE state:
Second harmonic generation , α-$(ET)_2I_3$
K. Yamamoto et al. (2008-11)

$$P = \varepsilon E + \chi_2 E^2$$

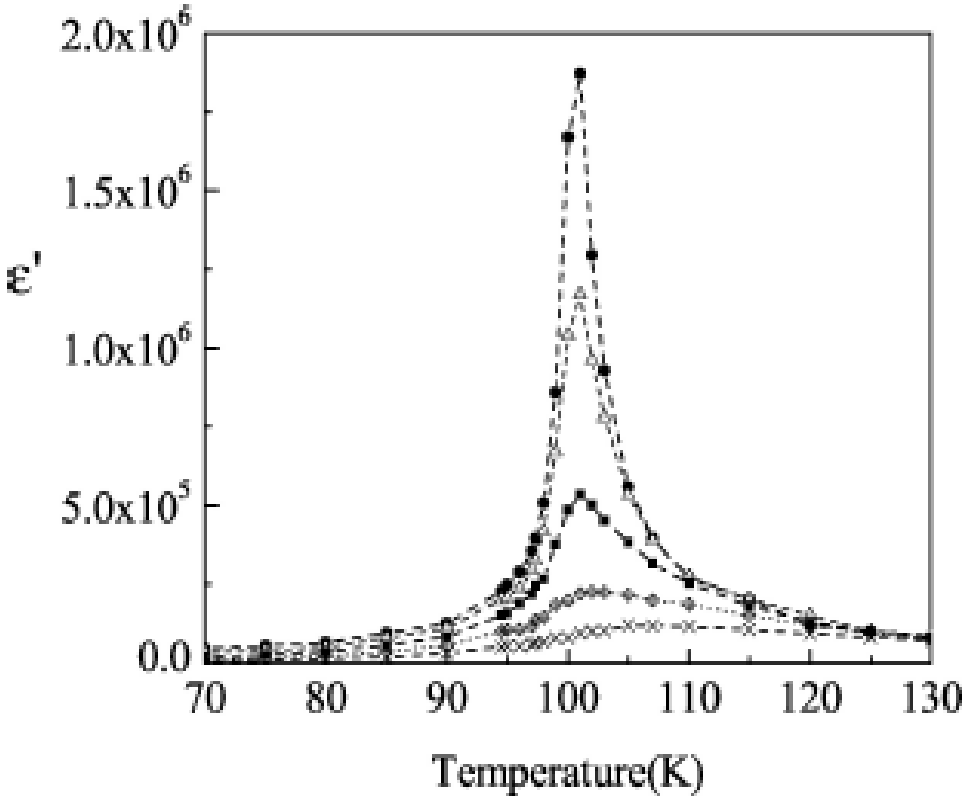


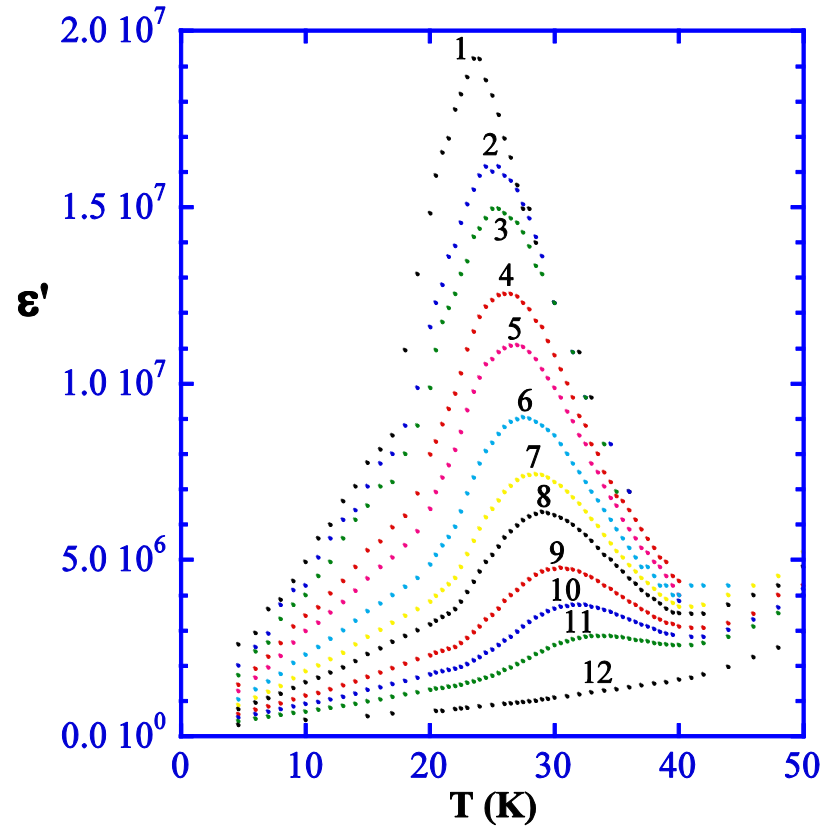
"Third Evidence" H. Sawa 2011 – X-ray refinement

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', + χ_2 (global symmetry breaking)



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.
v. v. : domain wall concentrates carriers, effecting ∥ & ⊥ conduction
- Call for combined methodics.





Frequency from 100 kHz to 10MHz

Need the imaginary part ε″(f)

Provoked to access the critical dynamics

The way all started

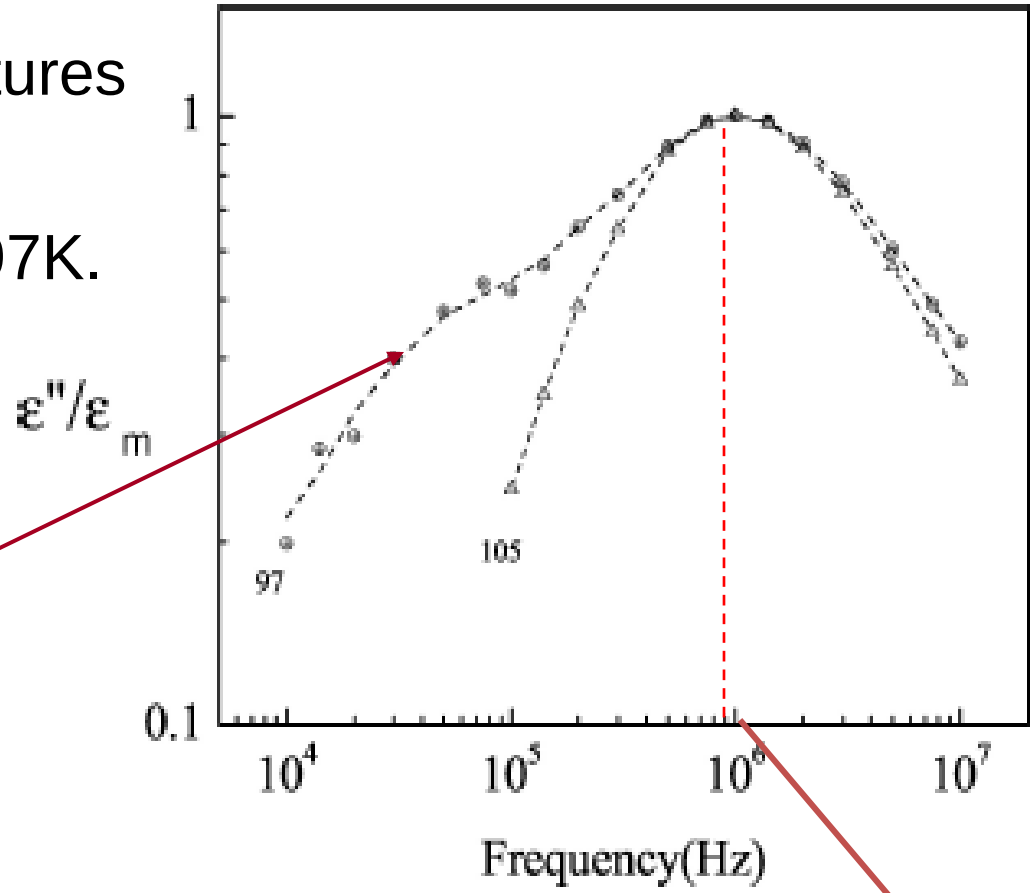
Response of pinned CDWs and SDWs

Monceau and Nad 1990's

Exploit the X=AsF_6 – the best critical singularity Nad & Monceau

frequency f dependence of imaginary part ε"

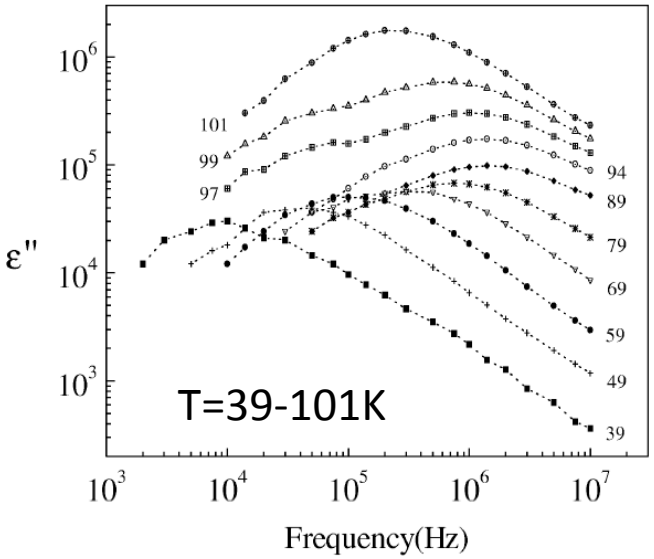
ε″(f) curves at two temperatures around T_c=102K, above - 105K and below - 97K.



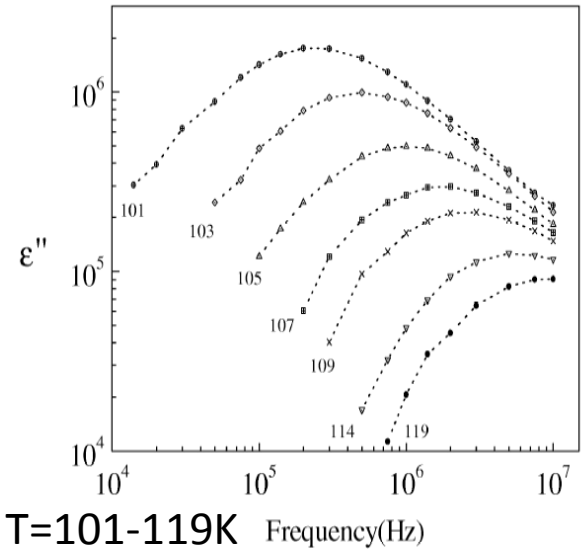
Low frequency shoulder – only at T<Tc : pinning of FE domain walls i.e. hidden hysteresis ?

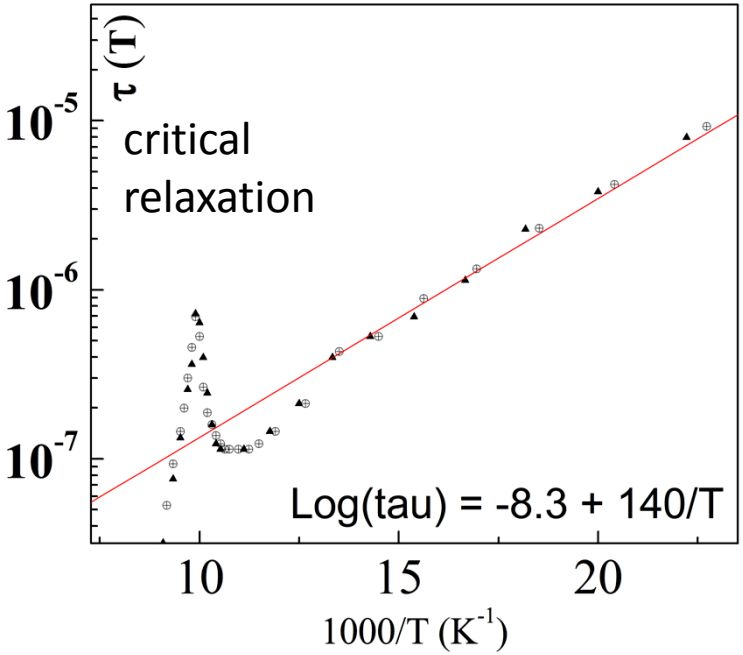
$\tau(T) = 1/f_m$

Relaxation time τ(T) in a wide temperature range.



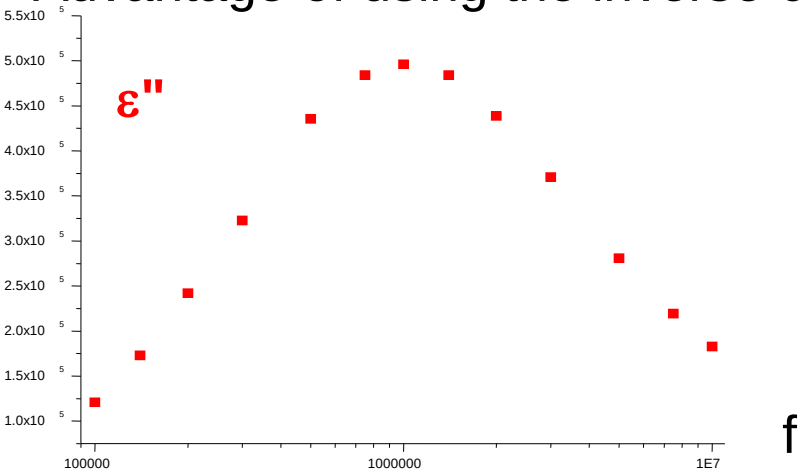
$\tau(T) = 1/f_m$ given by maximum position f_m of $\varepsilon''(f)$

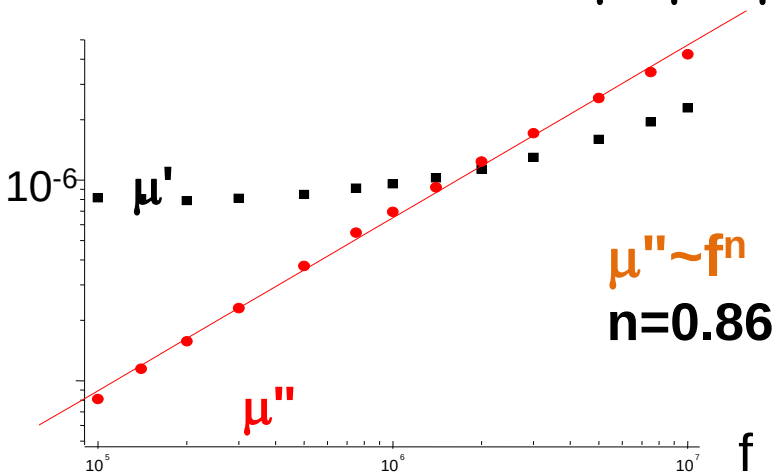




Perfect low T activation law.
Activation energy Δ_τ**=322K**
well correlates with the
conductivity activation Δ_σ**≈350K**
➔ ferroelectric polarization
dissipates via charge carriers
-spinlesss solitons (holons).
Proof for the FE- IV interference

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 $\mu'' \sim f^n$ with **n=0.86**±0.01.

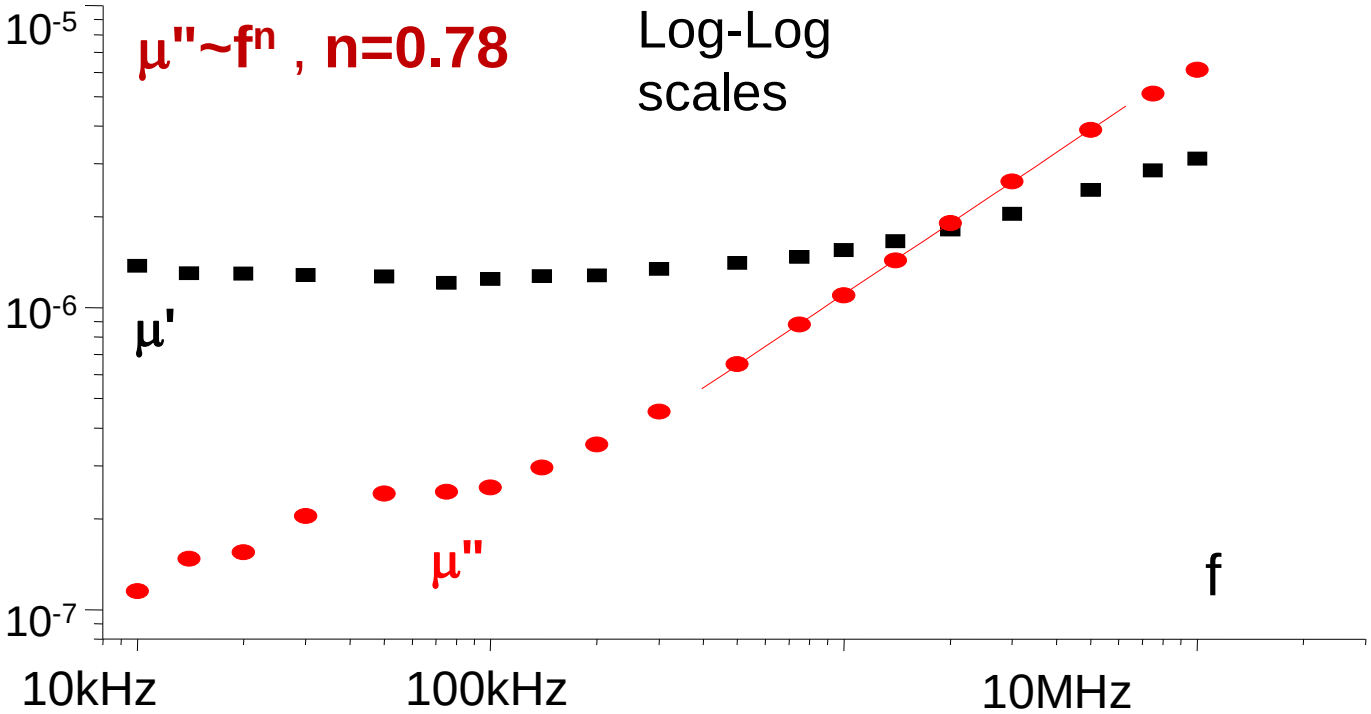
The exponent **0.86** is not **1** as in mean field theory of critical relaxation

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

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

Real part μ' is frequency dependent (should not), with a similar law.
But the variation is much smaller than for μ'' –
may be an experimental interference between the two?

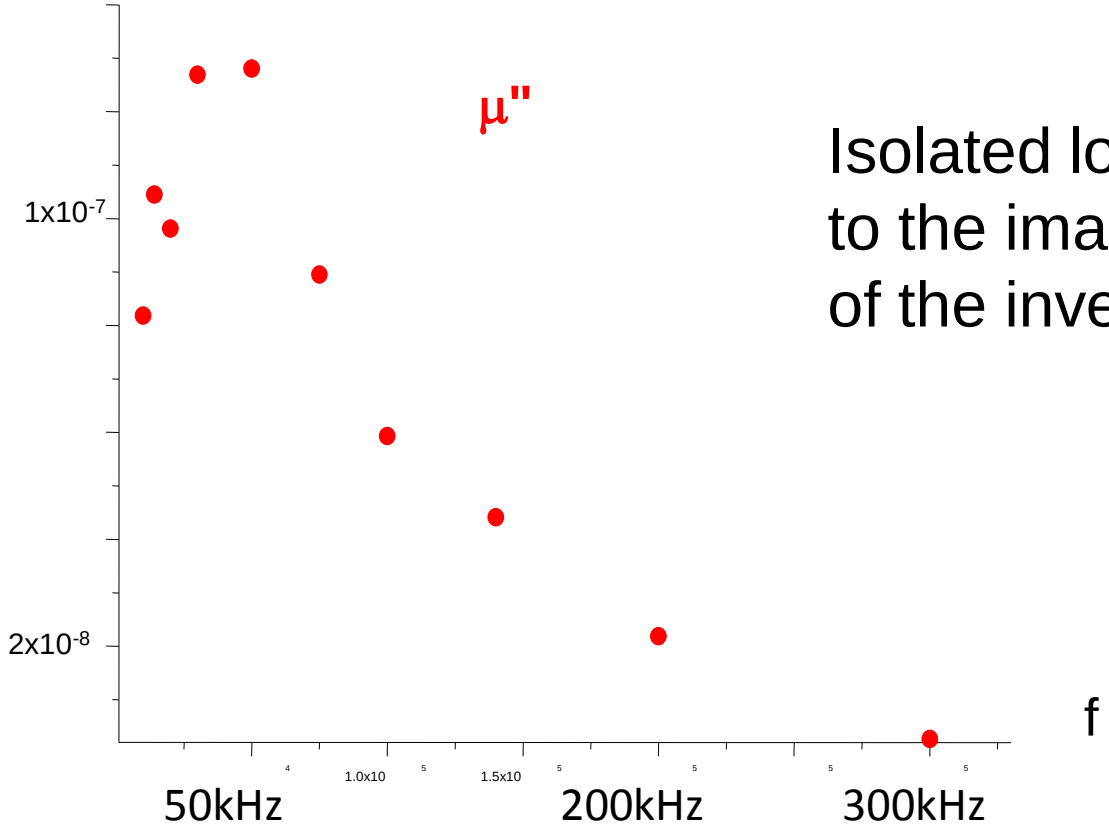
Below **Tc – T=97K**



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 beyond our 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.

Presumably: pinning of sweeping domain walls, weak hysteresis.
What is so special about the peak position at 50kHz?
A wide range of lower T needs to be explored.

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.

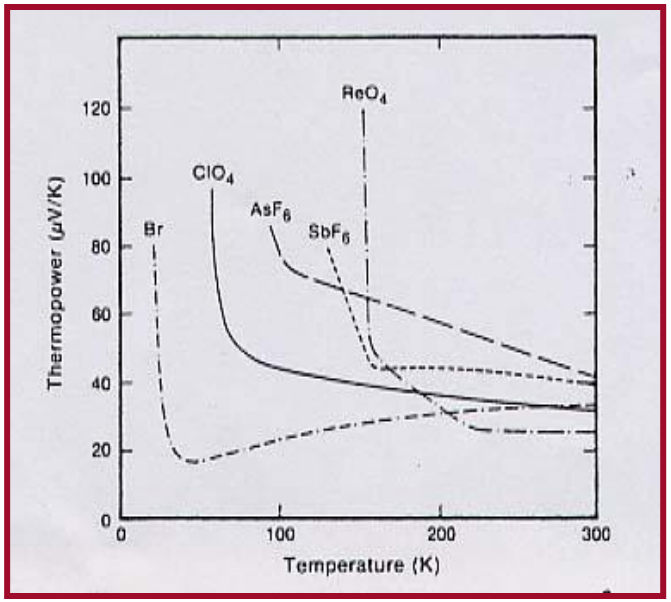
Combined methods – *success in conjugated polymers*:

Microscopic probes depending on the state or evolution of the FE.

Why always FE? Only $(TMTTF)_2SCN$ shows the anti-FE case !

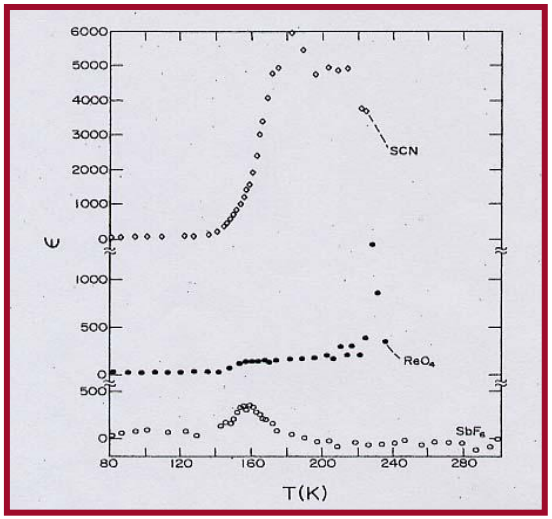
« Structureless » transitions

Thermopower of some $(TMTTF)_2X$ salts

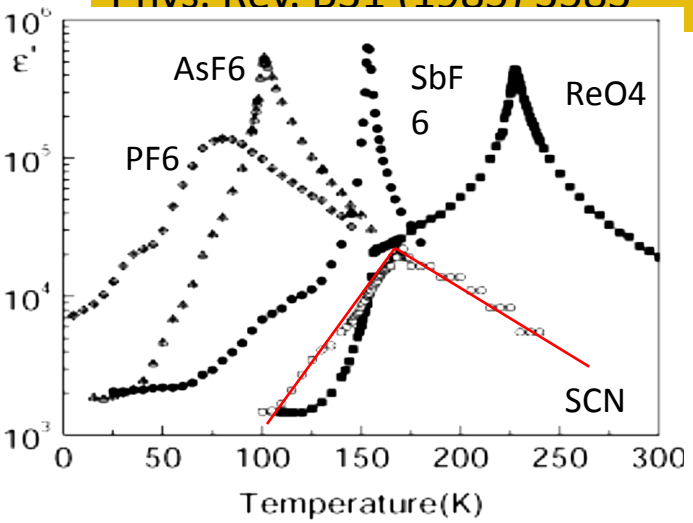


C. Coulon, S.S.S. Parkin and R. Laversanne, Phys. Rev. B31 (1985) 3583

Dielectric constant of some $(TMTTF)_2X$ salts



H. Javadi, R. Laversanne and A.J. Epstein Phys. Rev. B37 (1988) 4280



More general remaining challenges to elucidate the nature of the spontaneously formed Charge-Ordered Mott state:

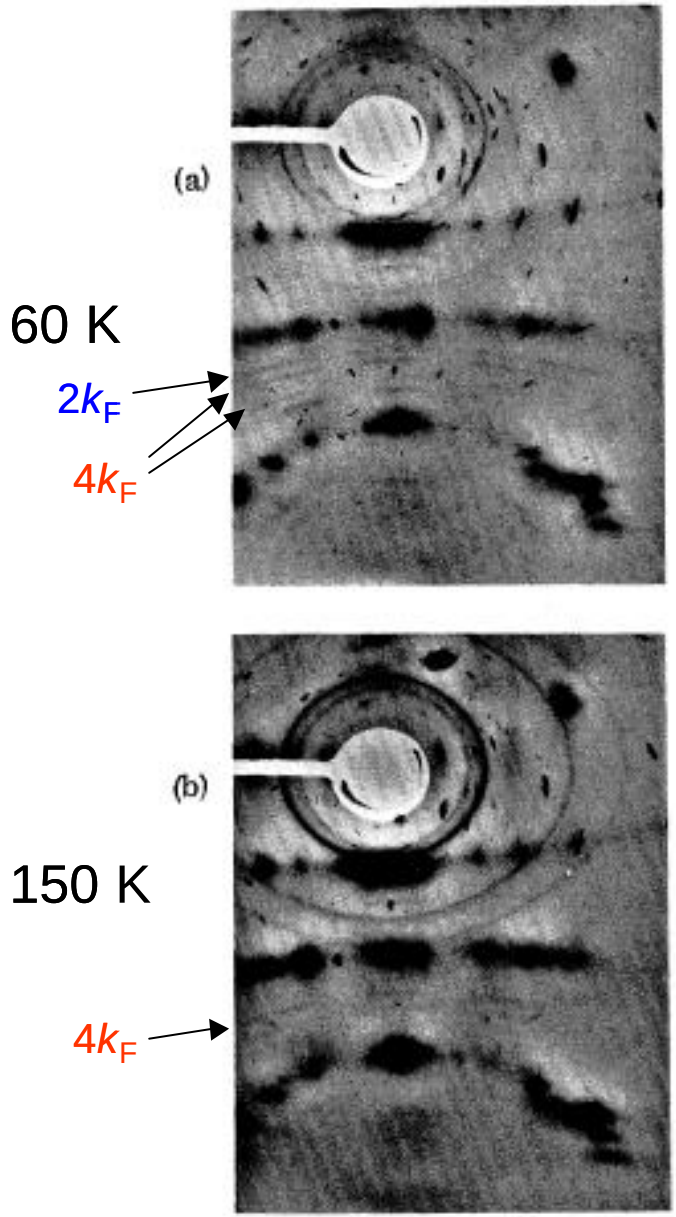
Solitons via conductivity, optics, NMR; photoconductivity.
Optical identification of gaps and soft modes
Hidden existence of CO/FE in the metallic *Se* subfamily;

Links to inorganic worlds: cuprates and TMO
recent discovery of charge ordering in cobaltides (Orsay)
latest discovery of charge ordering in cuprates (Grenoble);
high-T crossover line becomes a true transition (California, Saclay)

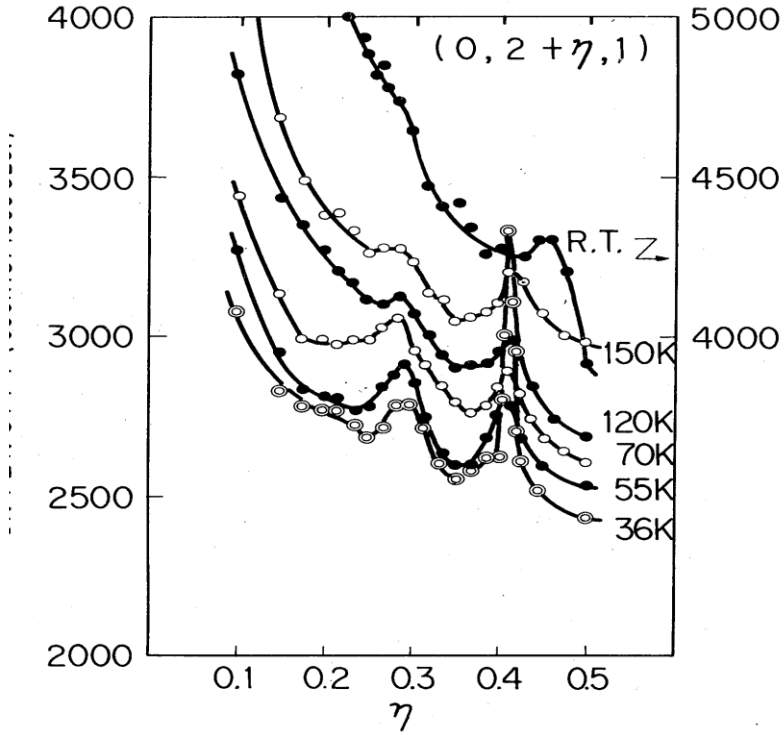
Q. Is the 1:4 formula an intelligent design, giving special properties?

A. No, it is human chemists' design; effects are general. Recall 1970's $4K_F$ stories

B. - next 2 slides



J. P. Pouget et al. (1976)



S. Kagoshima et al. (1976)

$4K_f$ lines exist since the RT but never condense

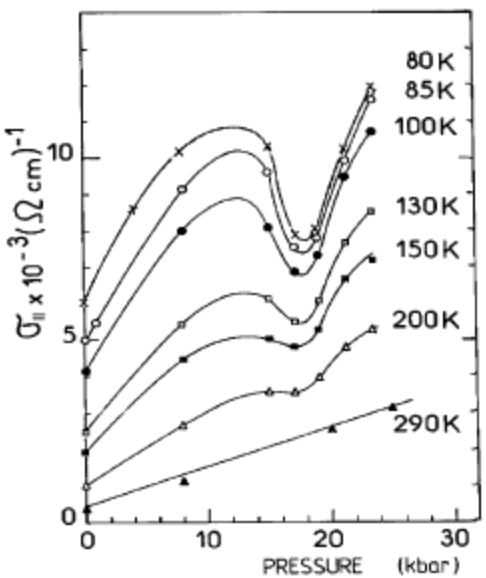
$2K_f$ appear at lower T

but condense into true Braggs.

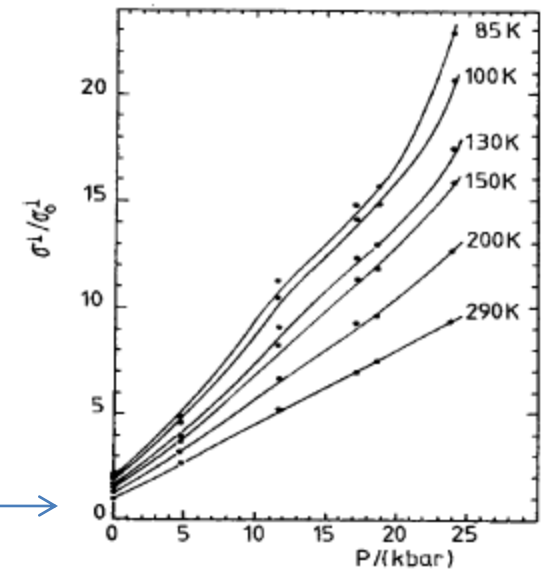
$4K_f$ CDW = Wigner crystal ever coexists with both metallic and CDW phases.

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

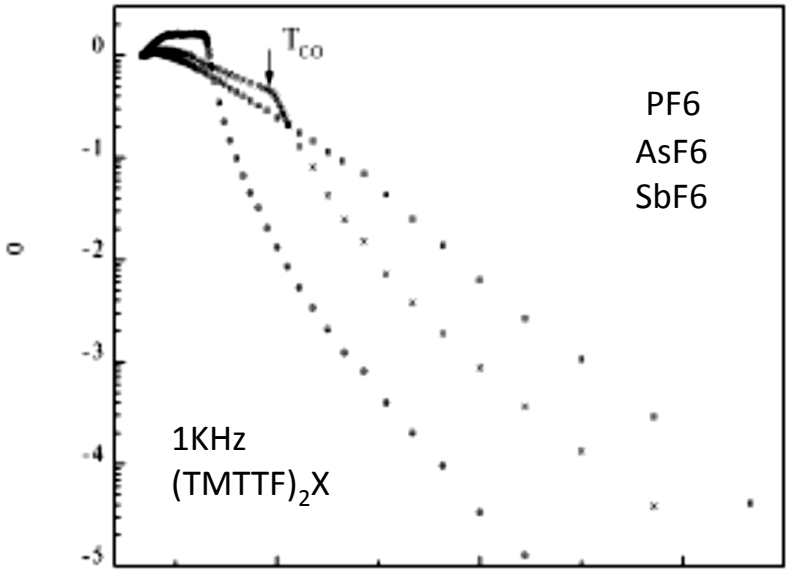


On-chain conductivity
drops at the 3:1 lock-in

Inter-chain conductivity
does not feel the lock-in

Q. Why did we invoked SOLITONS as charge carriers?

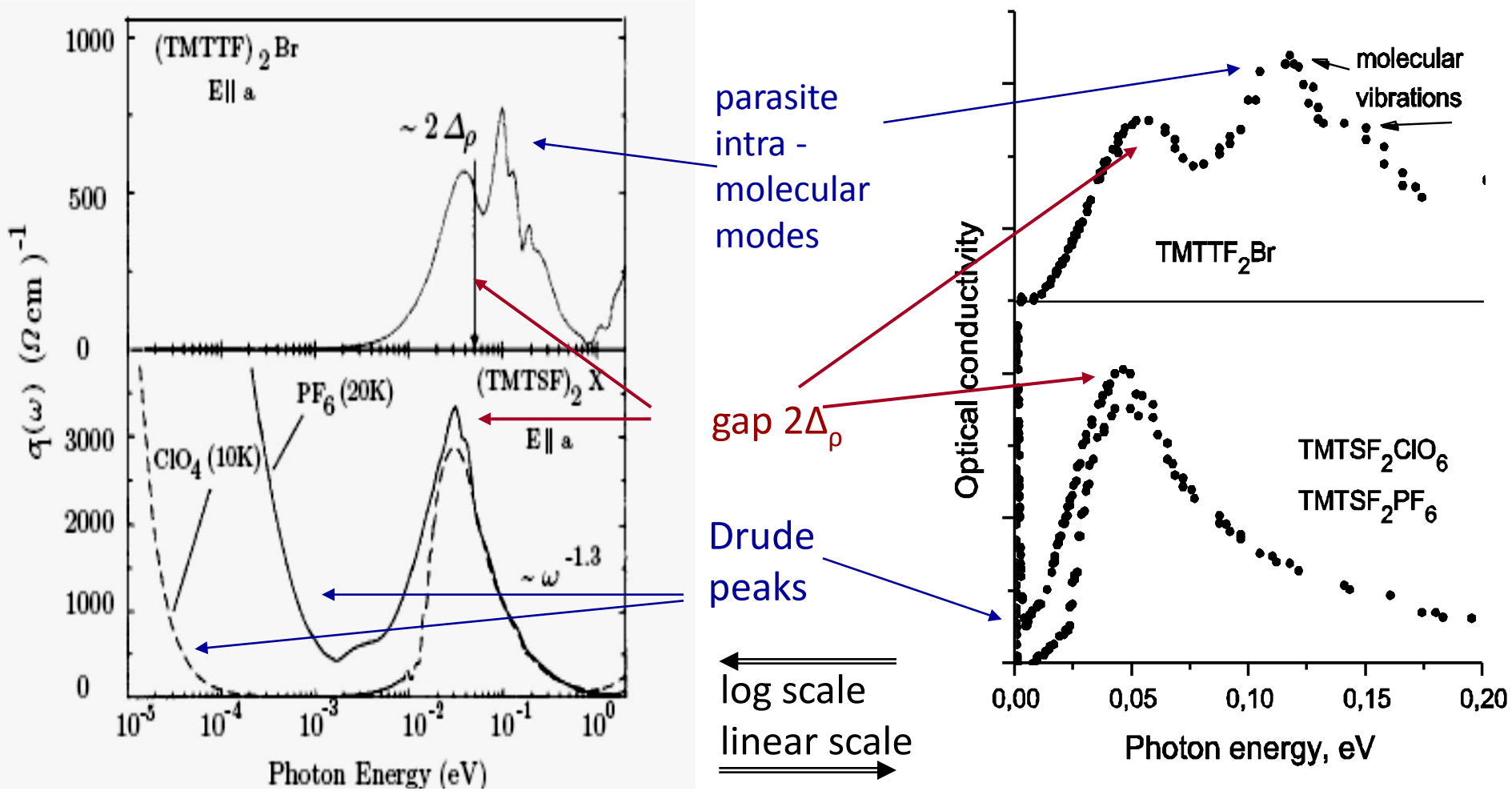
The earliest intrigue: What does conduct in these "narrow gap ferroelectric semiconductors" ? NOT the electrons !



Conductance G , normalized to RT
- Ahrenius plot Log G(1/T).
Gaps for thermal activation Δ
range within 500-2000K.

Contrarily to normal semiconductors -
no gap in spin susceptibility : χ(T) stays flat as for metal.
Clearlest example for conduction by charged spinless solitons - holons .

Q. Do we excite the same in optics? Can we test the metallic state?
A. – next slide



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 case, c.f. polymers

- role of the $4k_F$ umklapp scattering in the Mott-Hubbard localization

- possibility of a Mott insulator in a quarter-filled uniform system

  - $(EDT\text{-}TTF\text{-}CONMe_2)_2AsF_6$ K. Heuzé et al. Adv. Mater. (2003)

  - $(DMtTTF)_2X$ with X= ClO_4, ReO_4 C. Coulon ISCOM (2003); S. Sylvain et al. (ISCOM 2003)
    - Electronic localisation at 150K with appearance of a short range incommensurate
    - modulation with q= (-0.58, 0, 0.275)

  - DI-DCNQI)$_2$Ag Wigner crystal type of charge ordering
  - K.Hiraki and K. Kanoda, Phys. Rev. Lett. 80 (1998) 4737

Quarter-filled systems with a uniform stacking show the universal CO but were thought to have no FE - having no bonds dimerization,
the CO preserves the inversion or mirror symmetries preventing the FE polarization.
Latest results: subtle symmetry lowering still gives rise to weak FE anomalies.

CONCLUSIONS - main challenges:

Identification of gaps and soft modes;

Solitons via conductivity, optics, NMR.

FE hysteresis, relaxation, domains.

Interference of the FE state and its response with the conductions.

Origin of the guiding parameter – the LL const K_ρ :

local U,V's **or** long range Coulomb **or** 4KF joint lattice mass ?

Hidden existence of CD/FE in the metallic *Se* subfamily – related mysteries of the optical gap, low intensity Drude, low ω_p

Politically incorrect Q: merge strong correlations views and an amazing success of free band theories explaining numerous types of magnetic oscillations