Interplay between structural and electronic degrees of freedom in quarter-filled low dimensional organic conductors

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Outline of the lecture

From bond and charge instabilities in charge transfer salts of the TTF-TCNQ family to those of D_2X salts

Influence of some specific features of D_2X salts :

- Fermi surface warping
- stack dimerization

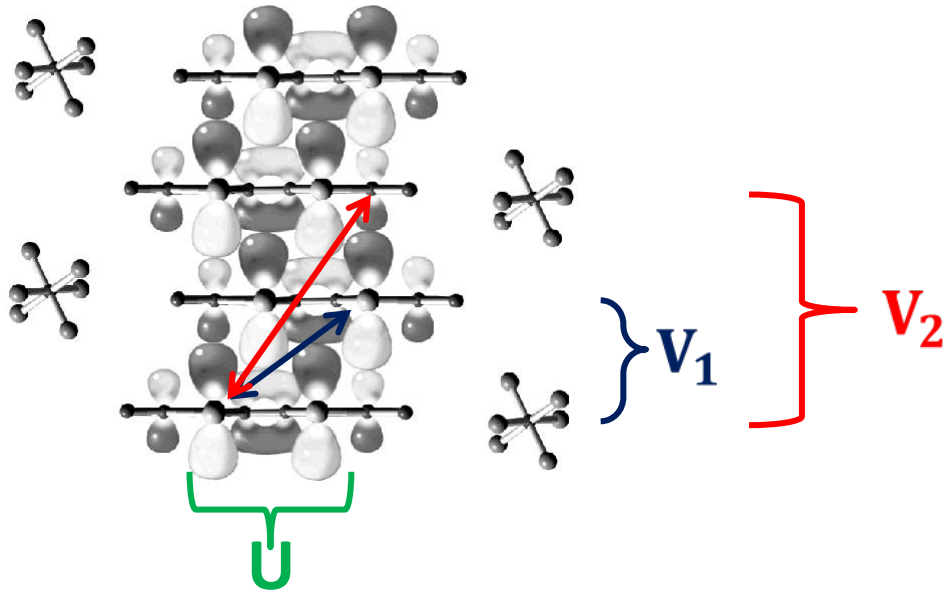
What is the role of the anions X?

mostly in $(TMTSF)_2X$'s and $(TMTTF)_2X$'s

+ some comments concerning the $(BEDT\text{-}TTF)_2X$'s

This lecture follows an earlier lecture given at ECYS 2011 and published in Physica B **407** (2012) 1762–1770

Organic conductors



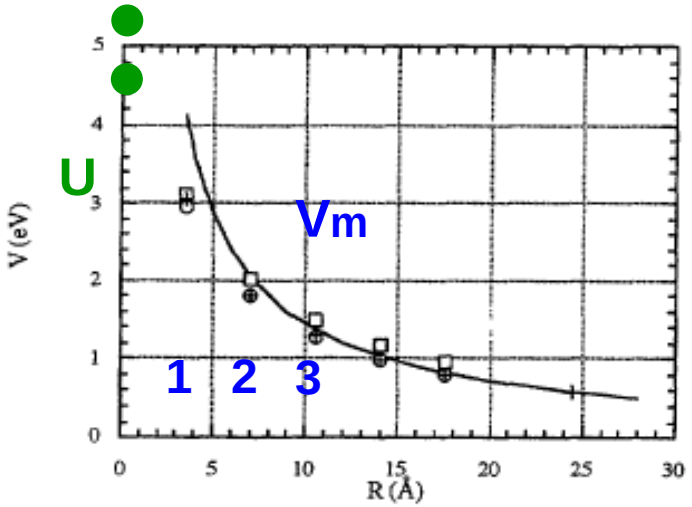
Extended Hubbard Model

$$H = H_0 + U\sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{i,m>0} V_m n_i n_{i+m}$$

Large molecules: V_1 is not too small compared to U

V_2 is a sizeable fraction of V_1

- Bare Coulomb repulsions



Quantum chemistry calculations on clusters of TTF molecules
F. Castet et al J. Phys. I **6**, 583 (1996)

Similar Vm are found for TMTTF

$V_m \propto 1/m$

- Screened Coulomb repulsion by molecular polarizability: $V_m \propto 1/\epsilon m$

U, Vi reduced by a factor 2.5-4 (TTF-TCNQ L. Cano-Cortés et al EPJB 56, 173 (2007))

U ~2 - 1.7 eV
V1~ 1 - 0.9 eV
V2 ~ 0.55 - 0.4 eV
V3 ~ 0.4 - 0.3 eV

U ~ 2V1
V1 ~ 2V2

$V_1 - V_2 \geq V_2 - V_3$ (or $V_1+V_3 \geq 2V_2$) convex Coulomb potential

t ~0.15 - 0.2 eV

U~ 2 bandwidths (4t)

Interstack (screened) Coulomb repulsions (TTF-TCNQ)

$V_\perp$~0.4eV comparable to screened V2 , V3

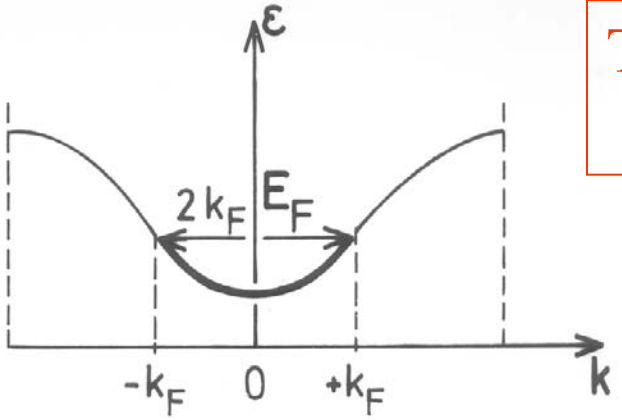
1D stack: regular (no dimerization)

no relevant interchain coupling $t_\perp$

no anion potential

Case of charge transfer salts of the TTF-TCNQ family

1D electron gas with repulsive interactions exhibits a $2k_F$ CDW/SDW instability and for strong enough repulsion a $4k_F$ CDW instability due to a (low temperature) divergence of the electron-hole response function

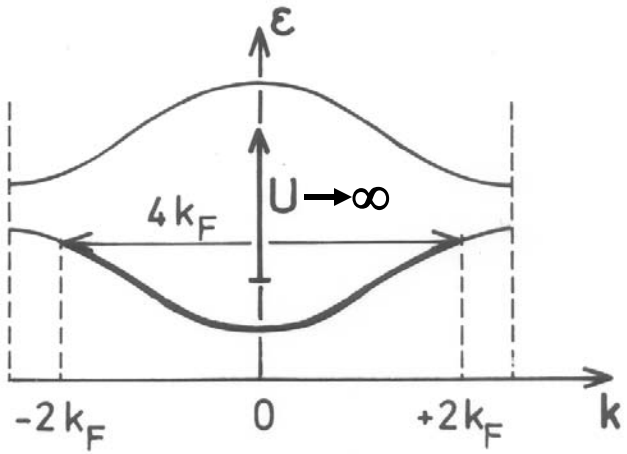


T= 0°K ground state in electron-phonon coupled systems

$2k_F$ Peierls transition for non (weakly) interacting fermions

Spin degree of freedom

$\rho = (2) \times 2k_F$: charge per molecule with $2k_F$ expressed in reciprocal unit



if U>>t no double site occupancy

$4k_F$ Peierls transition for spinless fermions or strongly interacting fermions

No spin degree of freedom

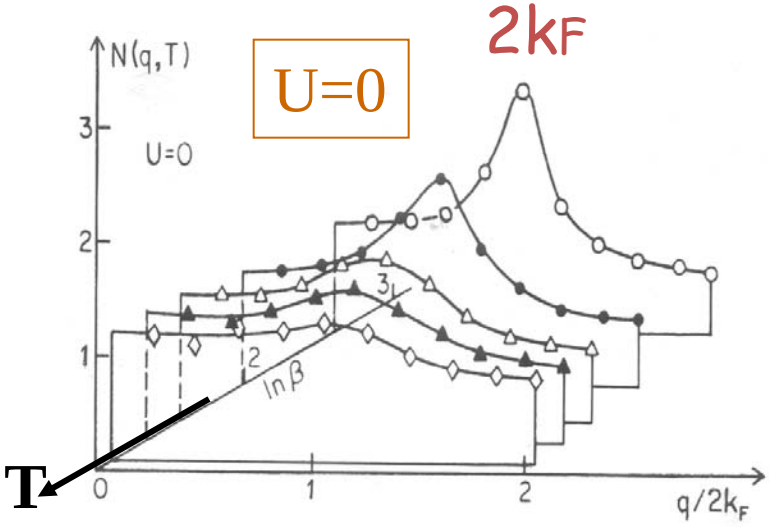
$\rho = 4k_F$ ⟶ Average distance between charges: $1/\rho=(4k_F)^{-1}$

The $4k_F$ CDW corresponds at the first Fourier component of a 1D Wigner lattice of localized charges

J. Hubbard, J. Kondo & K. Yamaji

CDW electron-hole response function ($U, V_1 \geq 0$ case)

Non interacting electron gas

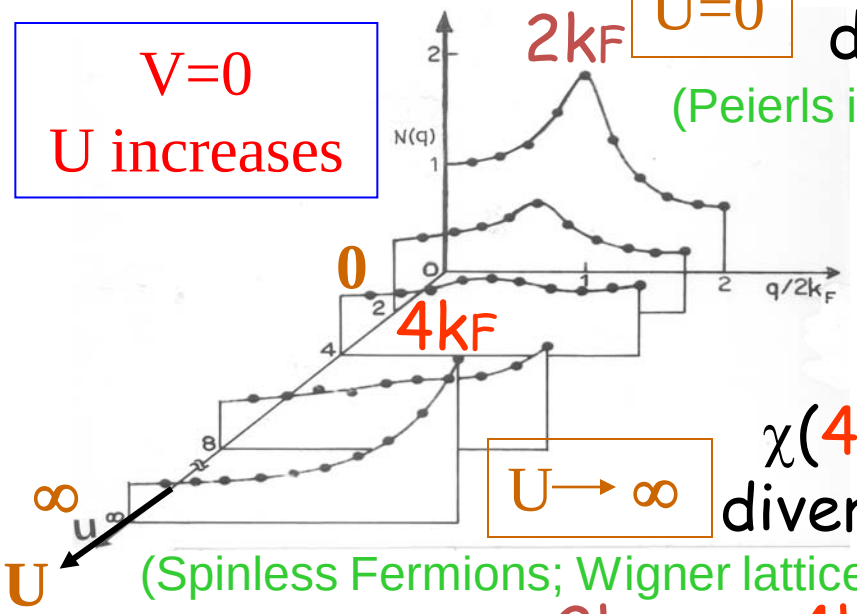


$T \rightarrow 0$: $\chi(2k_F)$ diverges

(Peierls instability)

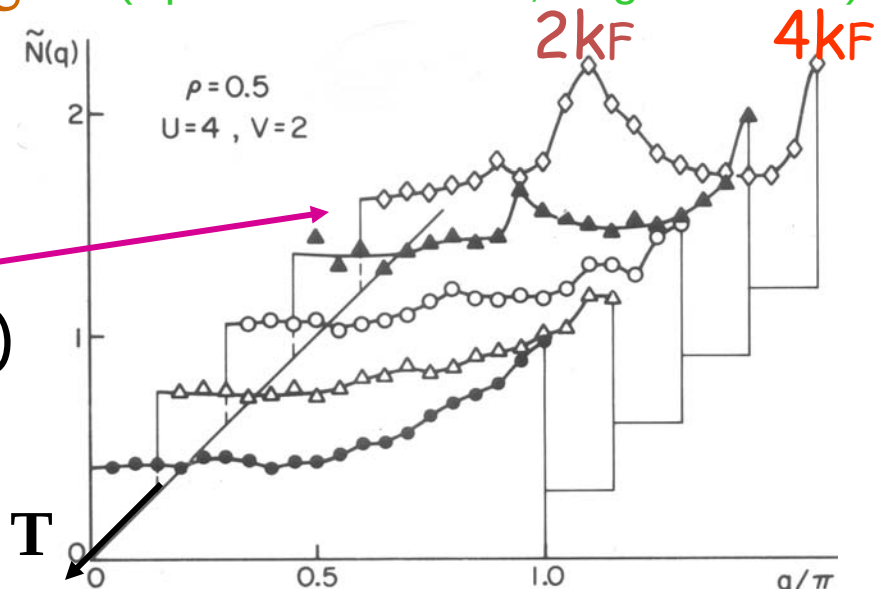
V=0

U increases



V ~ U/2

$T \rightarrow 0$: both $\chi(2k_F)$ and $\chi(4k_F)$ diverge



J.E.Hirsch and D.J.Scalapino PRB **29**, 5554 (1984)

The **electronic instability** coupled to the lattice (via the electron-phonon coupling) leads to a concomitant* **structural instability** on the bond (BOW) and on the molecular site (CDW)

General situation:

$2k_F$ **inter-molecular bond modulation** (BOW): u(x)

together with a **modulation of the charge on the bonds** shifted by $\pi/2$:

$\rho(x) = \rho_0 + \delta\rho(x)$ with $\delta\rho(x) \approx -\partial u(x)/\partial x$

as well as the charge on molecular sites i (**intra-molecular bond deformation**) $d(x_i) \propto \delta\rho(x_i)$*

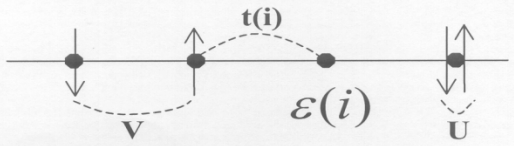
A modulation of the charge on the site does not necessarily mean the presence of a ($4k_F$) charge ordering!

*when $2k_F$ or $4k_F$ are different of $a^*/2$

If $2k_F$ or $4k_F$ are equal to $a^*/2$ the BOW and the CDW are of different symmetry (i.e. decoupled)

1D Hubbard model
coupled with classical phonon field

$$H_{1D} = \sum_i \varepsilon(i) n_i + \sum_{i,\sigma} t(i)(c^{\dagger}_{i;\sigma} c_{i+1;\sigma} + h.c.) + U \sum_i n_{i;\uparrow n_i;\downarrow}$$
$$+ V \sum_i n_i n_{i+1} + H_{ph}$$



Electron – phonon coupling

$H_{el\ ph}$

$$\varepsilon(i) = \varepsilon(1 - \alpha\delta_i^S) \Rightarrow H_{Holstein}$$

« Internal » phonon mode

local deformation of the molecule i changes the on site energy $\varepsilon(i)$ at a cost of

$$H_{elas} = \frac{1}{2} K_S \sum_i (\delta_i^S)^2$$

idem for U

Modulation of the charge on site i: **CDW**

$$t(i) = t(1 - \beta\delta_i^B) \Rightarrow H_{SSH}$$

« External » phonon mode

change of the inter stack distances modulates the single particle hopping integral t(i) at a cost of an elastic energy

$$H_{ph} \equiv H_{elas} = \frac{1}{2} K_B \sum_i (\delta_i^B)^2$$

idem for V

Modulation of the bond length i-i+1: **BOW**

$$n_{i,\sigma} = C^{\dagger}_{i\sigma} C_{i\sigma}$$

$$n_i = n_{i\uparrow} + n_{i\downarrow}$$

U and Vi which condition the divergence of the $2k_F$ and $4k_F$ instabilities are controlled by:

- the molecular polarizability
- the electron density (screening by the mobile electrons)

Experimental $2k_F$ and $4k_F$ structural instabilities:

TMTTF

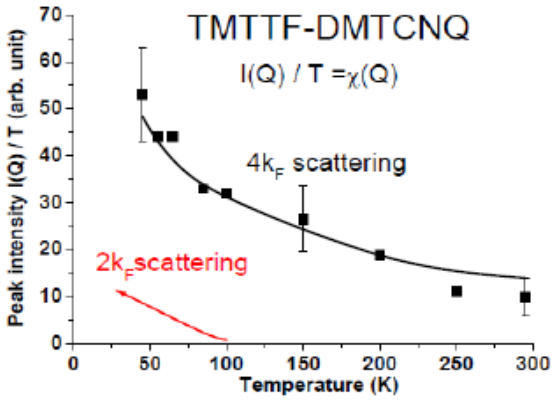
TMTSF

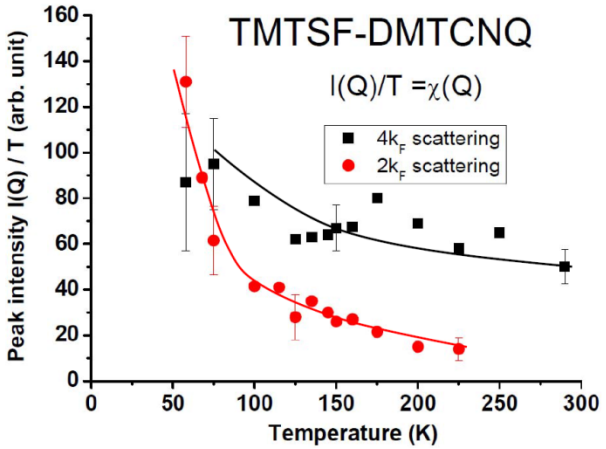
Molecular polarisability

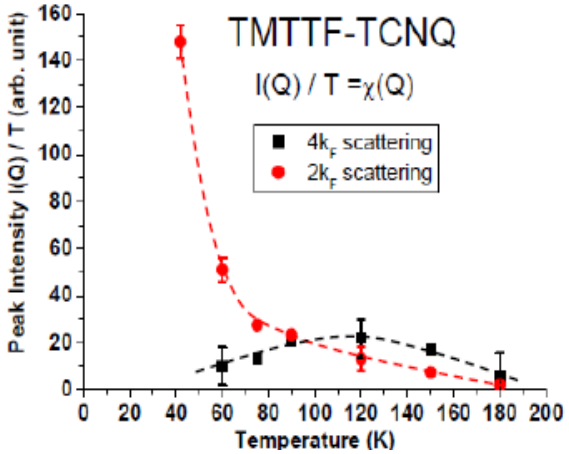
0.5

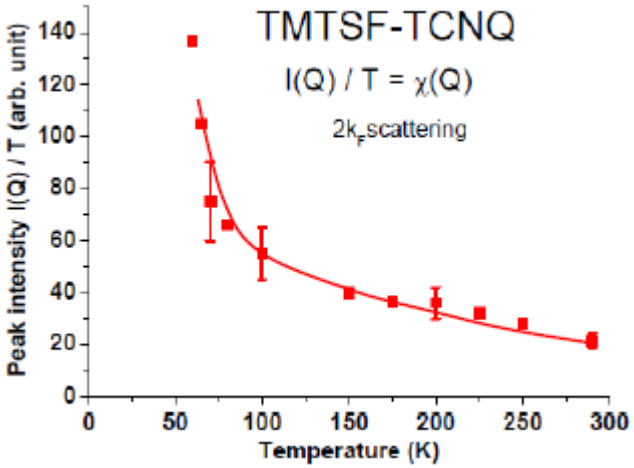
0.57

Electron (hole) density

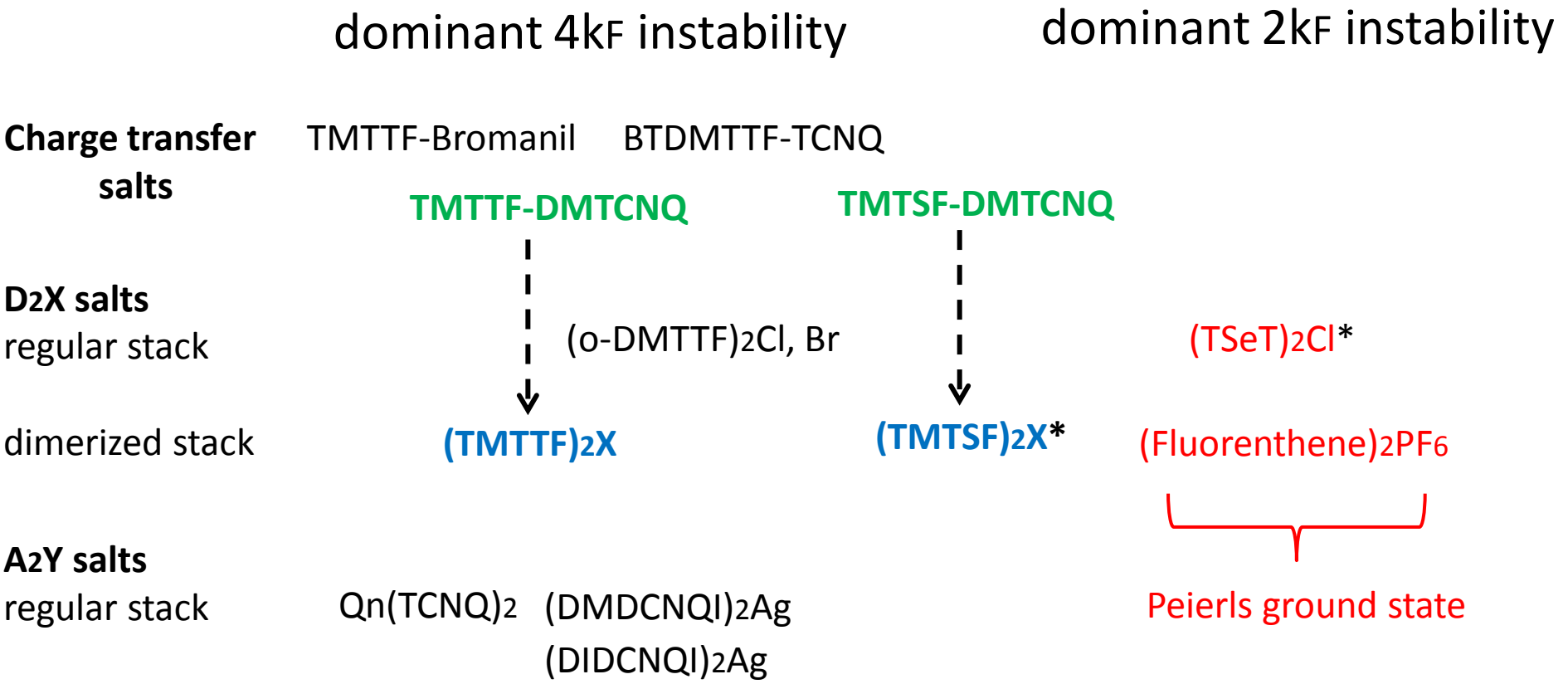








Summary of quarter-filled band 1D systems



* warped Fermi surface at low T

Specific features of the D_2X salts:

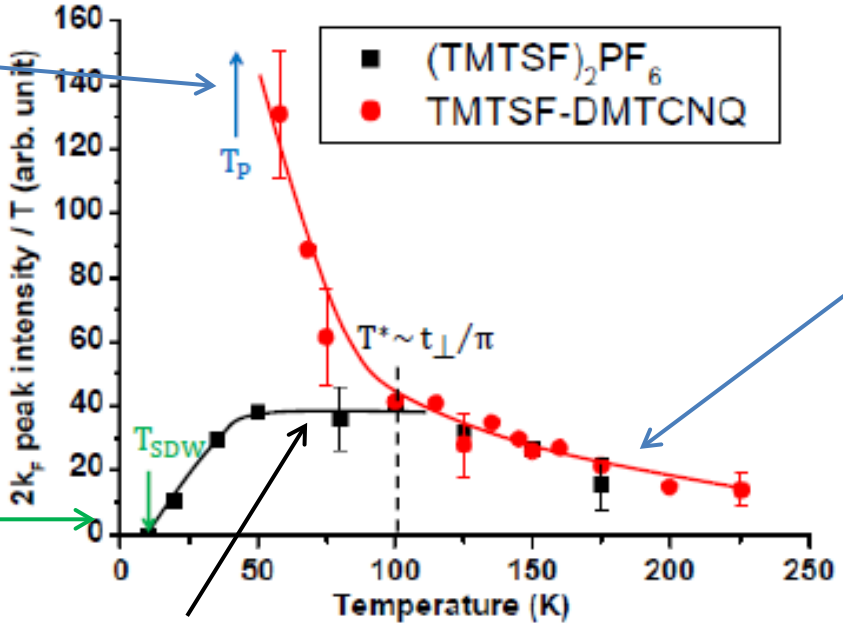
Role of the warping of the Fermi surface on the $2k_F$ density wave instability

Role of the stack dimerization (presence of an incipient static $4k_F$ BOW distortion)

Coulomb interactions of the BOW/CDW with the charged anion sublattice

$2k_F$ BOW fluctuations on the TMTSF stack*

divergence at the 42K Peierls transition

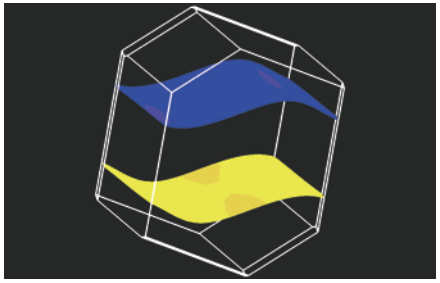


Same behavior above 100K as the quarter-filled TMTSF-DMTCNQ

Vanishing at low T when the $2k_F$ SDW is set

Saturation of the $2k_F$ response function below $T^* \approx 100K$ ($\approx t_\perp/\pi$)
1D divergence stopped by the warping $t_\perp$ of the Fermi surface

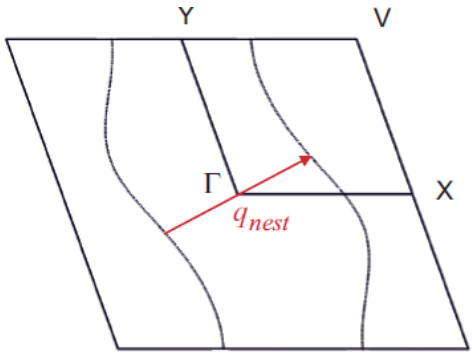
No divergent $2k_F$ longitudinal nesting



$2k_F$ SDW fluctuations are also present on all the temperature range in $(TMTSF)_2PF_6$

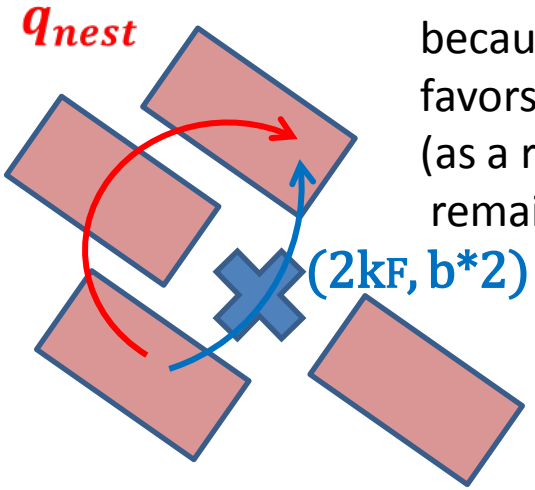
Note that 1D $2k_F$ SDW fluctuations exist also for an incommensurate band filling on the TTF stack of TTF-TCNQ (around 100-150K) and of TTF-$[Ni(dmit)_2]_2$

T<100K: warped fermi surface



$2k_F$ Fermi surface nesting implies an (incommensurate $q_b \approx b^*/4$) transverse coupling of density waves along b.

This mechanism stabilizes the $2k_F$ SDW ground state



1- Why nesting does not promote the $2k_F$ BOW instability?

because there is an additional coupling via the anion sublattice which favors a different b*/2 transverse coupling

(as a result there is a frustated transverse coupling. The BOW fluctuations remain short ranged)

2- Also the $2k_F$ instability differs from that of a quarter-filled standard Peierls system.

The interaction with the anions leads to a decoupling between the $2k_F$ BOW and the $2K_F$ CDW.

In that case the Fermi surface nesting alone can promote a $\mathbf{q}_{nest}$ CDW independently of the BOW.

(This could explain the coexistence of $2k_F$ SDW and CDW below T_{SDW})

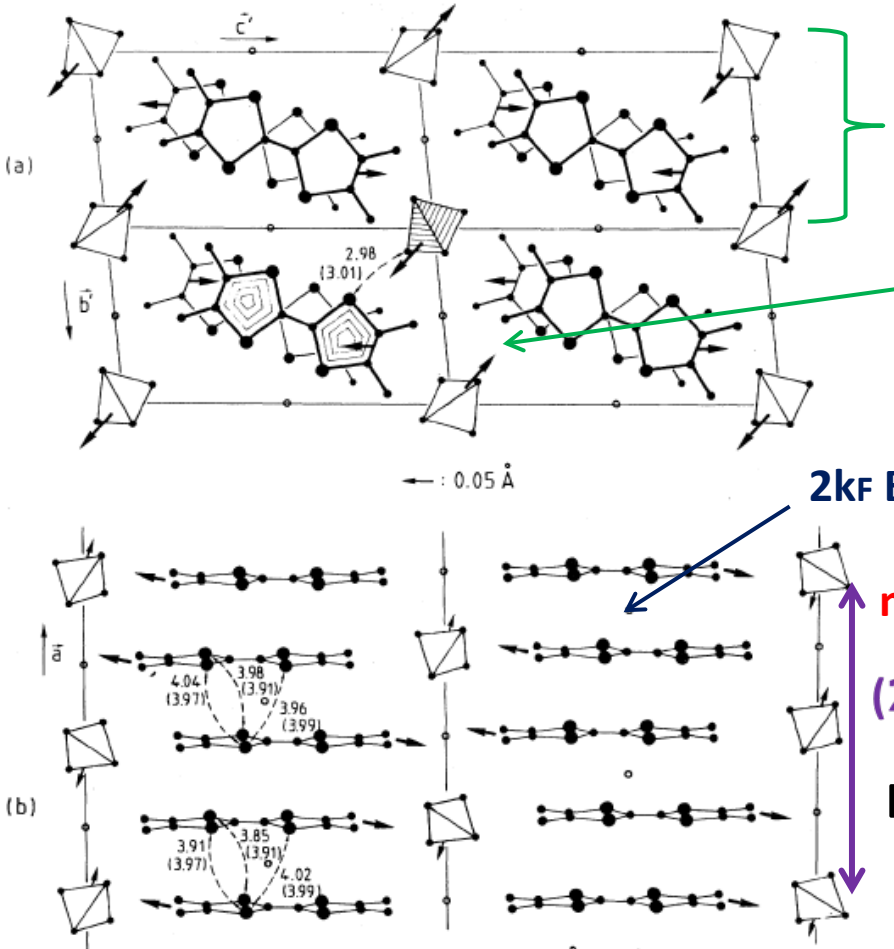
These features are well illustrated by the anion ordering transition of $(TMTSF)_2ReO_4$

The **$2k_F$ BOW ground state** alone is stabilized via the ordering of non-centrosymmetric anions: **$(TMTSF)_2ReO_4$**

ReO_4 is disordered in its methyl group cavity at 300K

For entropy reasons **ReO_4 orders** in a **2a** x 2b x 2c superstructure at 180K (in the 1D electronic regime). For a dimerized stack: 2a corresponds to the $2k_F$ wave length

Thus the anion ordering transition is accompanied by a $2k_F$ Peierls like metal-insulator transition



Staggered order of the ReO_4 in all the directions

Shift of the anion towards the Se:
short contact ReO_4----Se distance.
The shift induces $2k_F$ modulation of the Hartree anion potential on the TMTSF stacks

$2k_F$ BOW modulation of inter-molecular distances u(x)

but

no modulation of intra-molecular distance d(x)=0

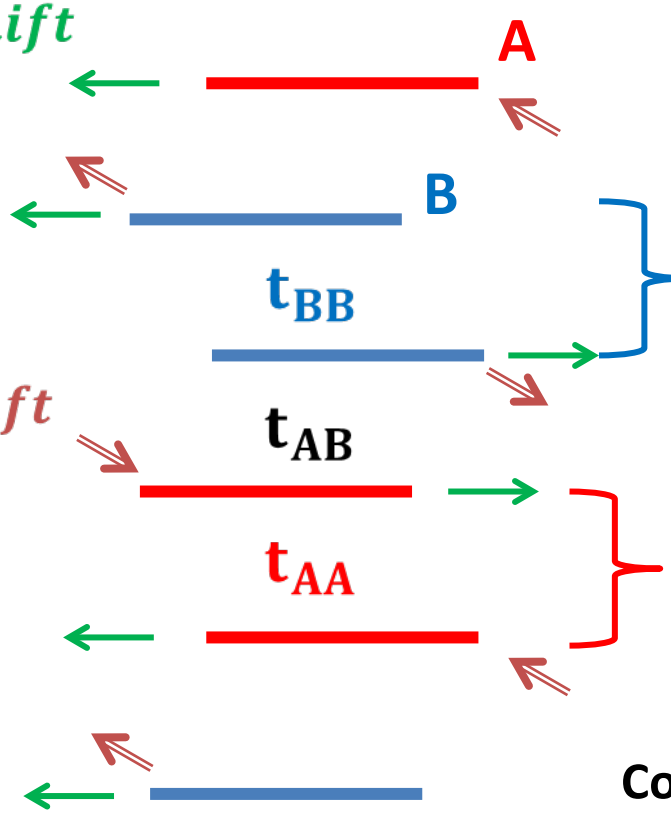
no CDW modulation (δρ<±0.01)!

$(2k_F)^{-1}$

Different from a standard Peierls transition!

R. Moret et al PRL **49**, 1008 (1982)

Why is there a decoupling between the $2k_F$BOW and CDW modulations?

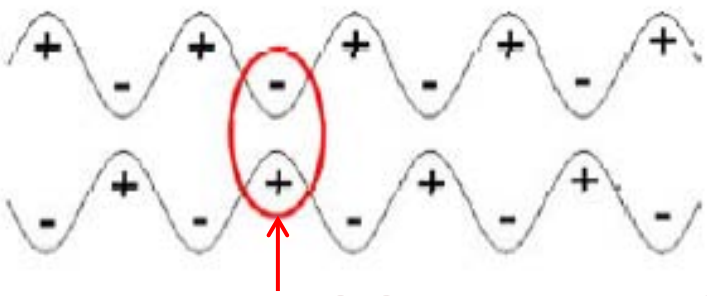


BOW modulation + staggered anion shift

decrease of t_{BB} : increase of hole density
Shift of the ReO_4 away from TMTSF B
(decrease of ε_B):
decrease of hole density

increase of t_{AA} : decrease of hole density
Shift of the ReO_4 towards TMTSF A
(increase of ε_A):
increase of hole density

Compensation: equal charges on TMTSF A and B
(no Coulomb forces induced at the AO transition)



CDW accompanying the $2k_F$BOW modulation of the inter − molecular TMTSF distances

out of phase site CDW induced by the staggered anion shift

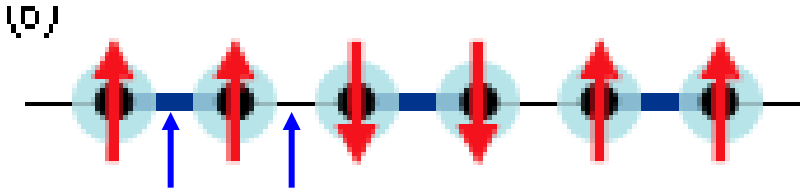
Compensation of the two types of CDW

For a quarter filled band (ρ=1/2) $4k_F$ BOW and CDW have different inversion symmetries

- The corresponding order parameters are of different symmetry with respect to the inversion

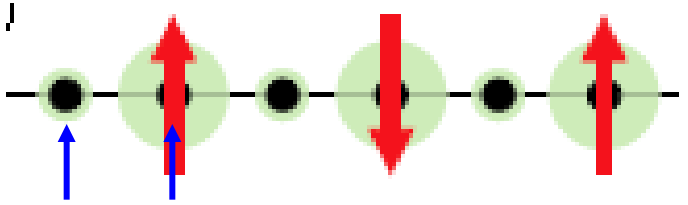
- In the corresponding $4k_F$ ground states the electrons are localized:

- on one bond out of two
  ($4k_F$ BOW: Mott Dimer)

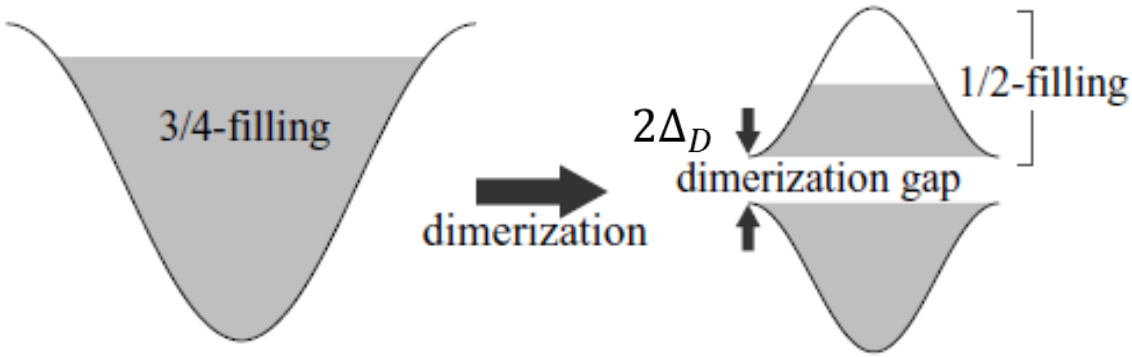


Inversion centres are at mid-bond positions

- on one site out of two
  ($4k_F$ CDW: Charge Ordering)



Inversions centres are on the sites



In presence of an important $4k_F$ BOW response function of the regular stack (χ_{BOW}) the bond dimerization potential ${\Delta_D}^B$ induces a gap of charge ${\Delta_\rho}^B$.*

$\Delta\rho$ is a function of U, Vi and of Δ_D (K. Penc and F. Mila, PRB **50**, 11429 (1994))

The induced $4k_F$ BOW corresponds to the preferential localization of one hole per dime

Alternatively the stack dimerization promotes a $4k_F=a^*$ Umklapp electron-electron scattering term (g_3) in the 1D electron gas which helps the charge localization on the dimers (Brazovskii, Barisic, Emery)

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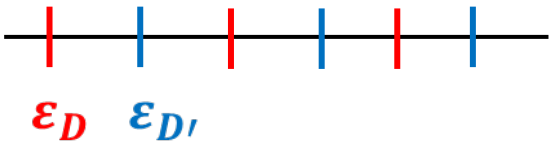
*for a linear response: $({\Delta_\rho}^B - {\Delta_D}^B) \approx \chi_{BOW}(4k_F, {\Delta_\rho}^B)\, {\Delta_\rho}^B$

Similar features are expected for mixed DD'-X compounds



In presence of an important $4k_F$ CDW response function of the regular stack (χ_{CDW}) the site staggered potential $2\Delta_D{}^S = \varepsilon_D - \varepsilon_{D'}$ induces a gap of charge $\Delta_\rho{}^S$.

The induced CO corresponds to the preferential localization of the hole per site (the one with the largest ε).

Case of $[(TMTTF)_x(TMTSF)_{1-x}]_2X$ with x~0.5

For $X=ReO_4$ with x~0.55: $\Delta_\rho{}^S \sim 750K$ and Tρ >300K (larger values than for x=1)
(V. Ilakovac et al PRB **50**, 7136 (1994))

(This result means that the mixed TMTCF stack exhibits a significant $4k_F$ CDW response function)

Interplay between the $4k_F$ BOW (Dimer Mott) localization and the $4K_F$ CDW (Charge ordering)

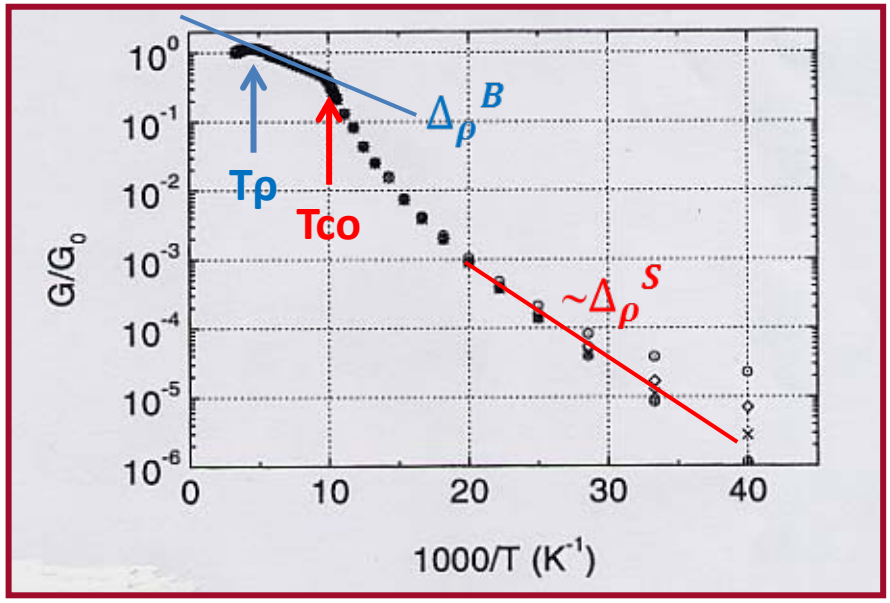
Is it possible to have successively a charge localization on the dimers (opening $\Delta_\rho{}^B$) then a charge ordering on one site out of two (opening $\Delta_\rho{}^S$)?

If the intrinsic CO gap $\Delta_\rho{}^S$ is larger than the pre-existing bond gap $\Delta_\rho{}^B$ there is an energy gain to stabilize a CO ground state (Brazovskii)

Case of $(TMTTF)_2X$ where:

$\Delta_\rho{}^B$ ~200-500K < $\Delta_\rho{}^S \sim 750K$ (gap of SbF_6 salt having no appreciable charge localization above Tco)

X=AsF_6



(Nad and Monceau)

If $\Delta_\rho{}^B > \Delta_\rho{}^S$ the CO gap opening does not occur

The intra-dimer charge degrees of freedom are not relevant.

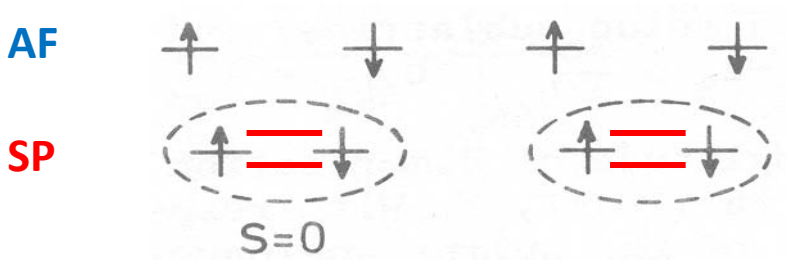
One has an effective half filled electronic system with one hole per « site » (i.e. per dimer)

The instabilities of this system are those of the S=1/2 AF Heisenberg chain :

- antiferromagnetism

or

- spin-Peierls ground state (in case of important magneto-elastic coupling)



Case of $(BCPTTF)_2X$ where $\Delta_\rho{}^B \sim 1000K$ and $T\rho >> 300K$

Spin-Peierls ground state at $T_{SP}=35K$

CO and PEC/SP ground states

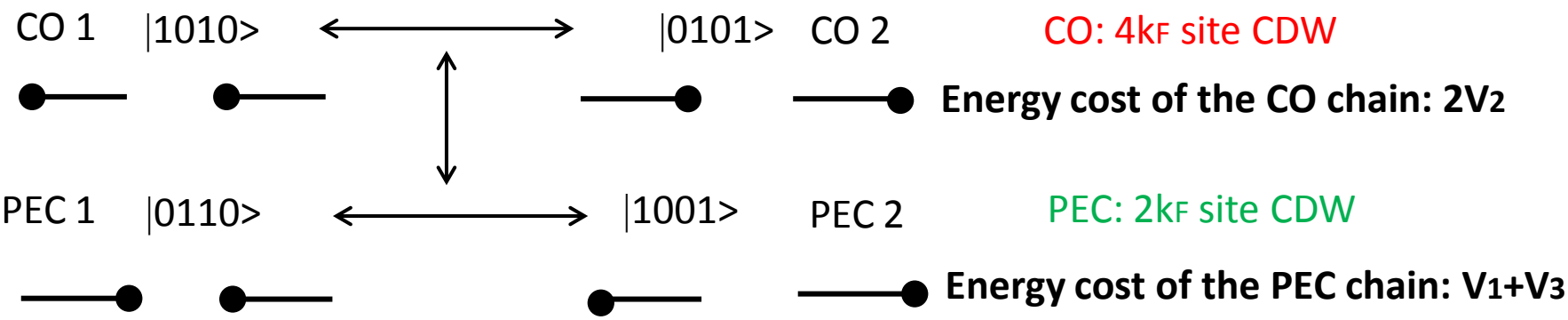
one electron localized per dimer  $|10\rangle + |01\rangle$

U large no double site occupancy

2 dimers wave function:

 $(|10\rangle + |01\rangle)_i \otimes (|10\rangle + |01\rangle)_{i+1}$

Chain of dimers is a resonant mixture of CO and PEC configurations of different symmetries



For a convex potential $V_1-V_2>V_2-V_3$ the CO ground state is favored
(with a S=1/2 par site the magnetic excitations are those of a gapless Heisenberg chain)

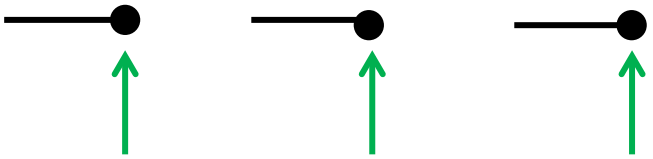
In presence of a $2k_F$ BOW achieving an attractive interaction between neighboring electrons V_1 can be reduced so that the PEC ground state can be stabilized

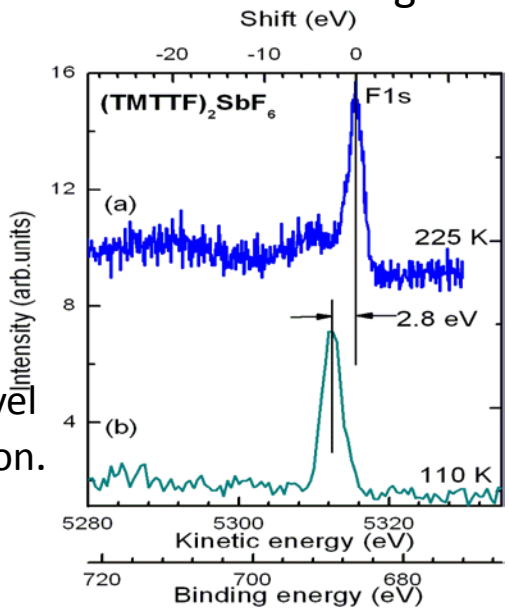
Gapped S=0 Spin-Peierls non magnetic ground state

CO 1 ⟷ **CO 2**

The CO transition stabilizes a single CO configuration by a staggerred modulation of the site energy, via a deformation of the anion sublattice creating short contacts towards the charge rich TMTTF :

- uniform anion shift (X=MF_6; M=P, As, Sb)
- anion orientational ordering process (X=SCN)

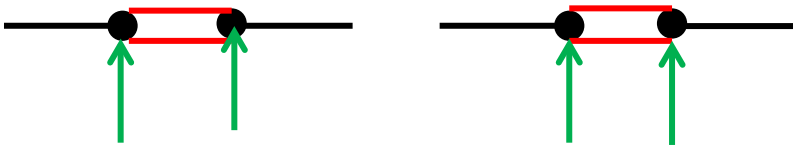


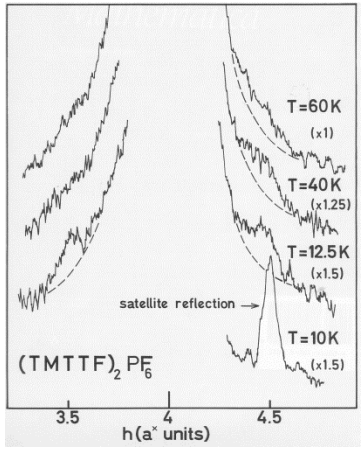


Shift of the F1s HAXPES core level spectra through the CO transition. (K. Medjanik et al)

PEC 1 ⟷ **PEC 2**

The SP transition stabilizes a single PEC configuration by setting of a $2k_F$ BOW lattice modulation* (together with a $2k_F$ CDW energy site modulation through a deformation of the anion sublattice)



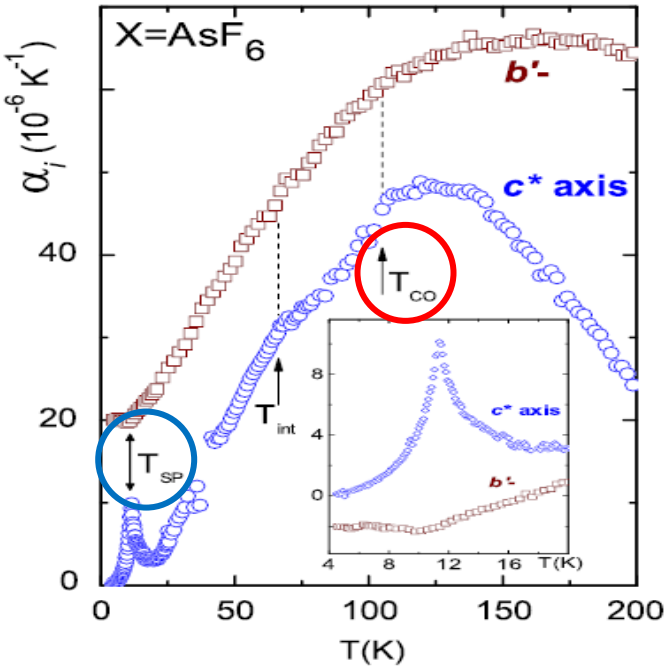


*TMTTF-DMTCNQ is already subject to a $2k_F$ BOW instabilty below 100K

SP- $2k_F$ BOW lattice fluctuations are observed below 60K in $(TMTTF)_2PF_6$

Lattice and anion effets at the CO and SP transitions

Thermal expansion

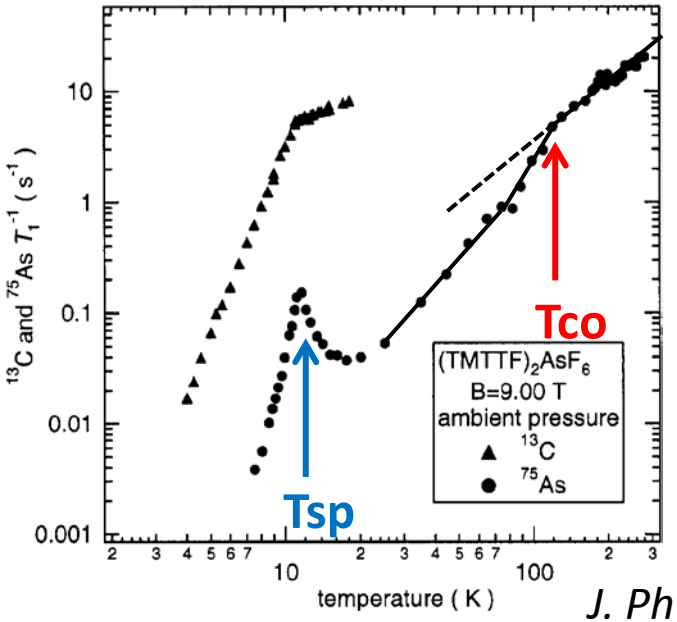


(TMTTF)2AsF6

M. De Souza et al
PRL 101, 216403 (2008)

$^{75}As \quad T_1^{-1}$

probe of EFG fluctuations



Anomaly at the CO + critical divergence at the SP transition

F. Zamborszky et al
J. Phys. IV France **12** (2002) Pr9-139

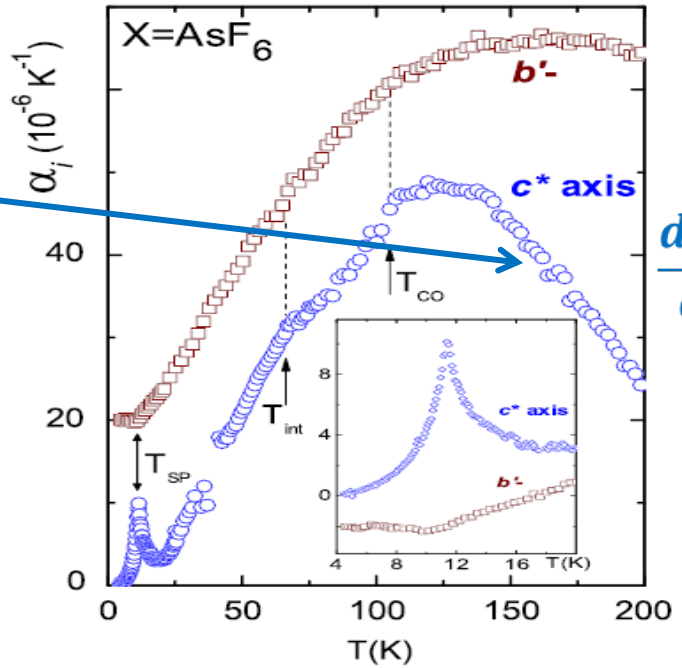
Coupling of charges with the anion sublattice

Charge fluctuation inside the dimer

Coupled sub-system

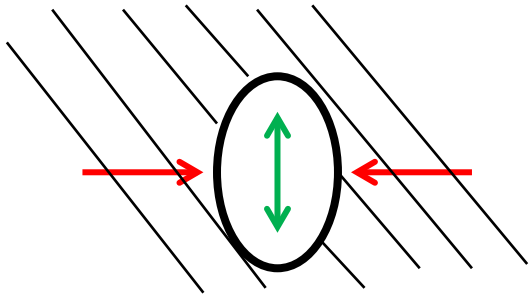
Positional anion fluctuations

Negative thermal expansion*



$$\frac{d\alpha_{c*}}{dT} < 0$$

Signature of an unconventional lattice dynamics (coming the shrinking of the CH_3 cavity due to high T positional fluctuations of the anion)

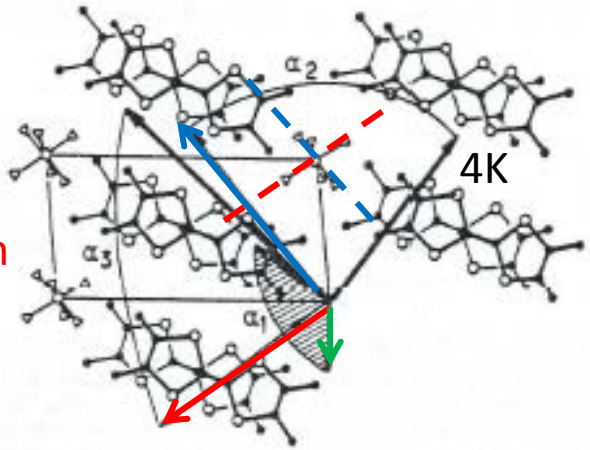


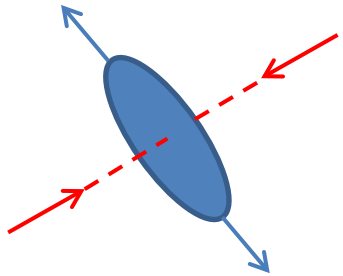
* along c*: interlayer direction
not an eigen direction of the dilatation tensor

Eigen-values and eigen-direction of the dilatation tensor of $(TMTTF)_2PF_6$

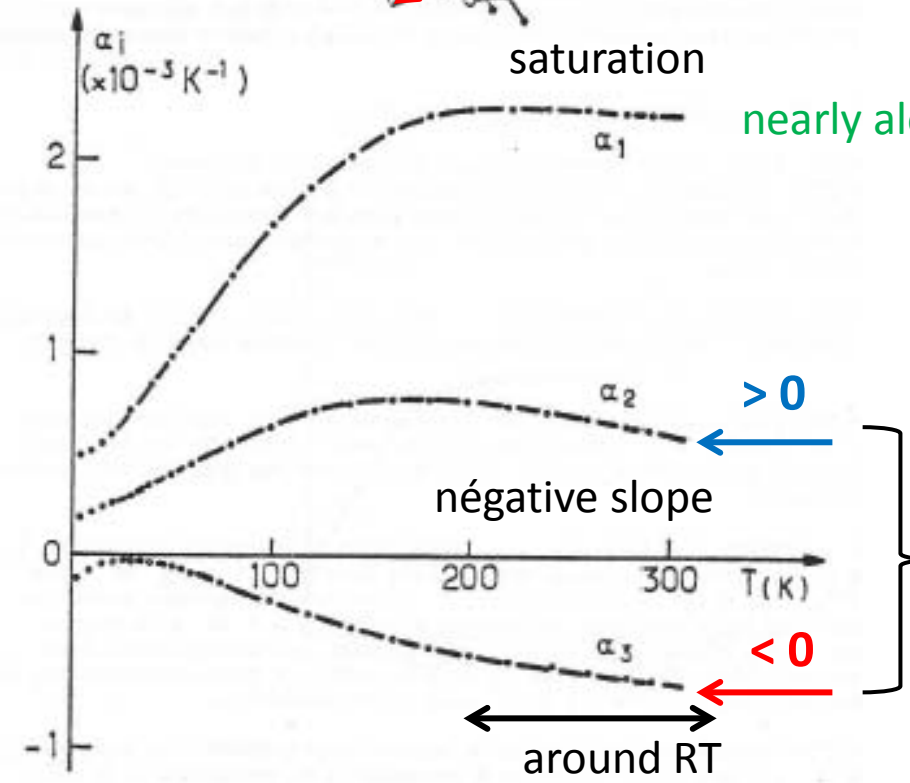
Direction of lattice dilatation upon heating around RT (close to CH_3-anion direction)

Direction of lattice contraction upon heating around RT (close to S-anion direction)





Anion rotation/translation



saturation

nearly along a

> 0

négative slope

< 0

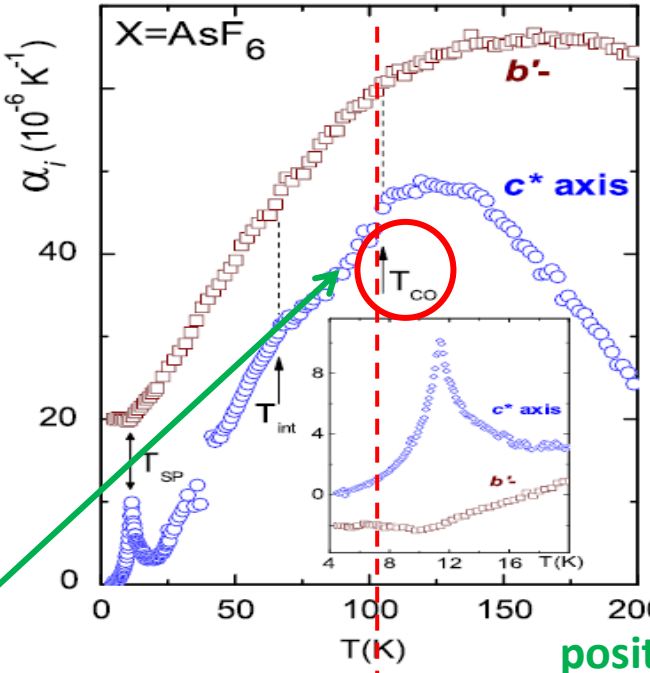
around RT

nearly in the (b,c) plane

(B. Gallois PhD thesis Bordeaux 1987)

Back to anion fluctuations: $(TMTTF)_2AsF_6$

Thermal expansion



Above Tco

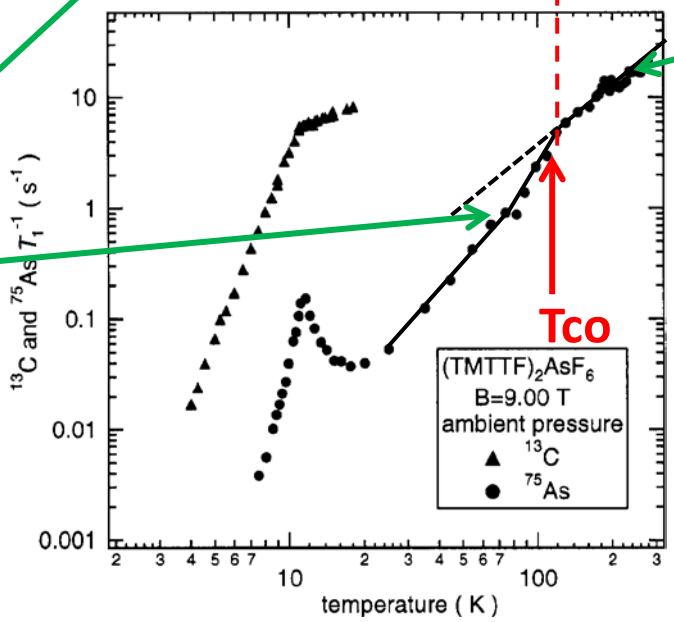
$$\frac{d\alpha_{c*}}{dT} < 0$$

^{75}As T_1^{-1}

probe of EFG fluctuations

positional fluctuations of the anions giving rise to EFG fluctuations on the As site

Below Tco reduction of anion fluctuations: « linkage » of the anions to the charge rich TMTTF?

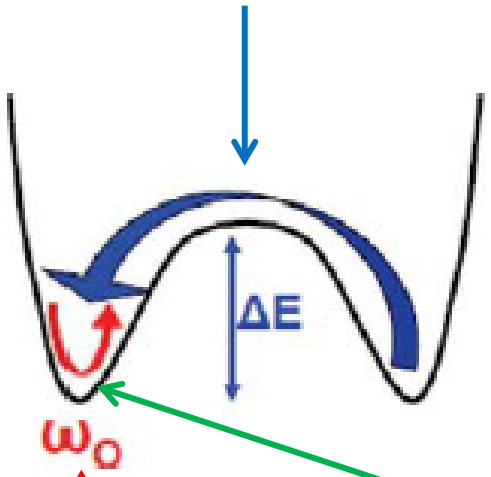


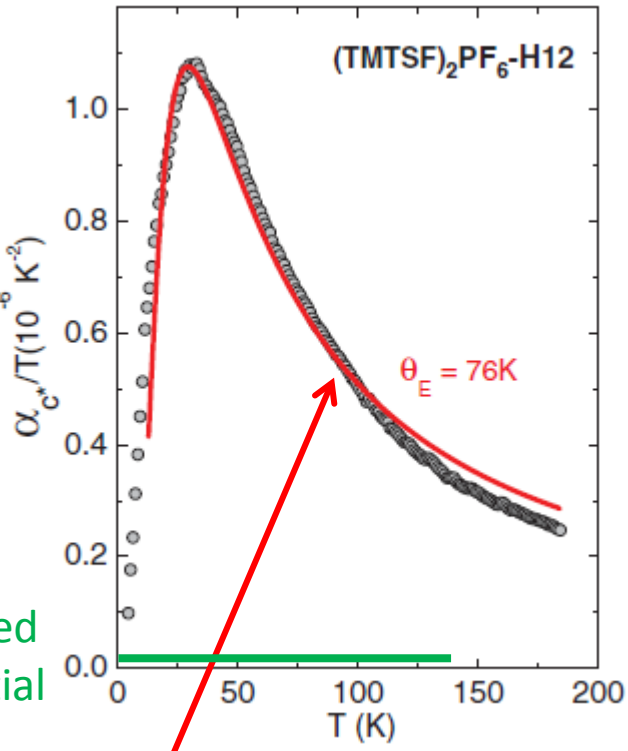
Back to anion dynamics : $(TMTSF)_2PF_6$

^{19}F NMR studies

T>140K
activated thermal jump of PF_6

$$\alpha_{c*}(T) \propto C_V(T)$$





Rotation of PF_6 starts above 70K ($\approx \Theta_E$)

T<140K
anion located in its potential well

Low T thermal expansion accounted by a thermally populated Einstein oscillator with ω_0=76K
(frequency of rotation of PF_6 in its cavity)

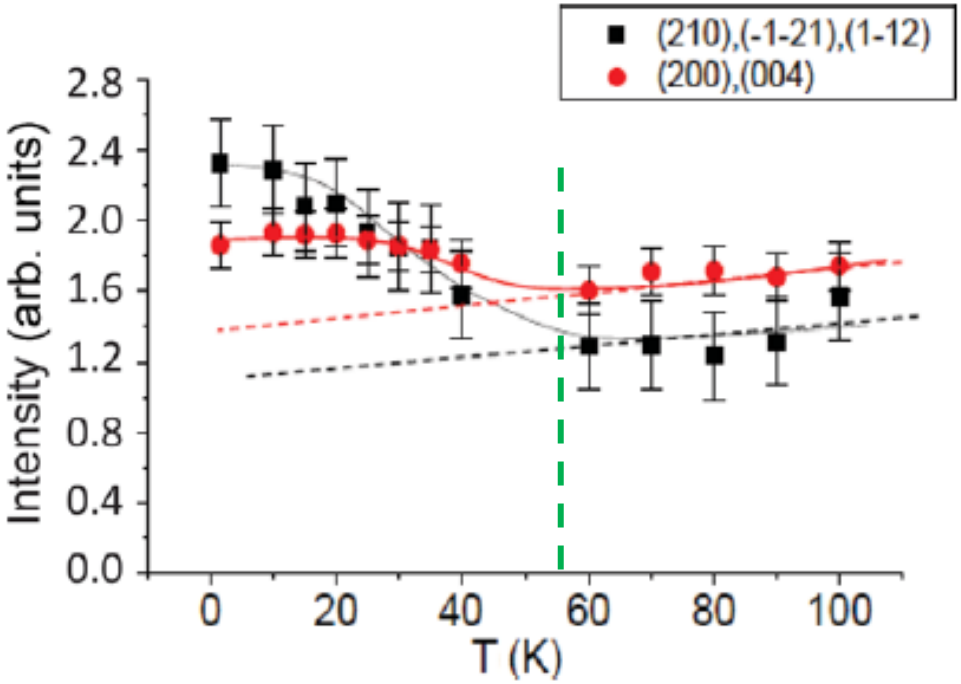
P. Foury-Leylekian et al
PRB **88**, 024105 (2013)

Anion rotation controls the low temperature thermal expansion!

Anion + methyl groups dynamics

Thermally activated motion of methyl groups is frozen below 55K and 74K ($^1H\ NMR$)

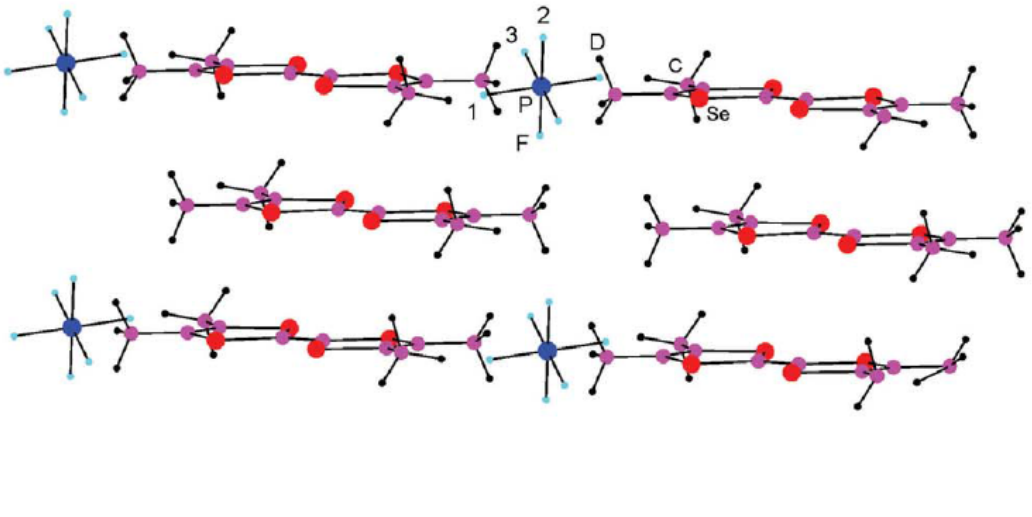
At ~55K: H bond linkage of PF_6 to methyl groups

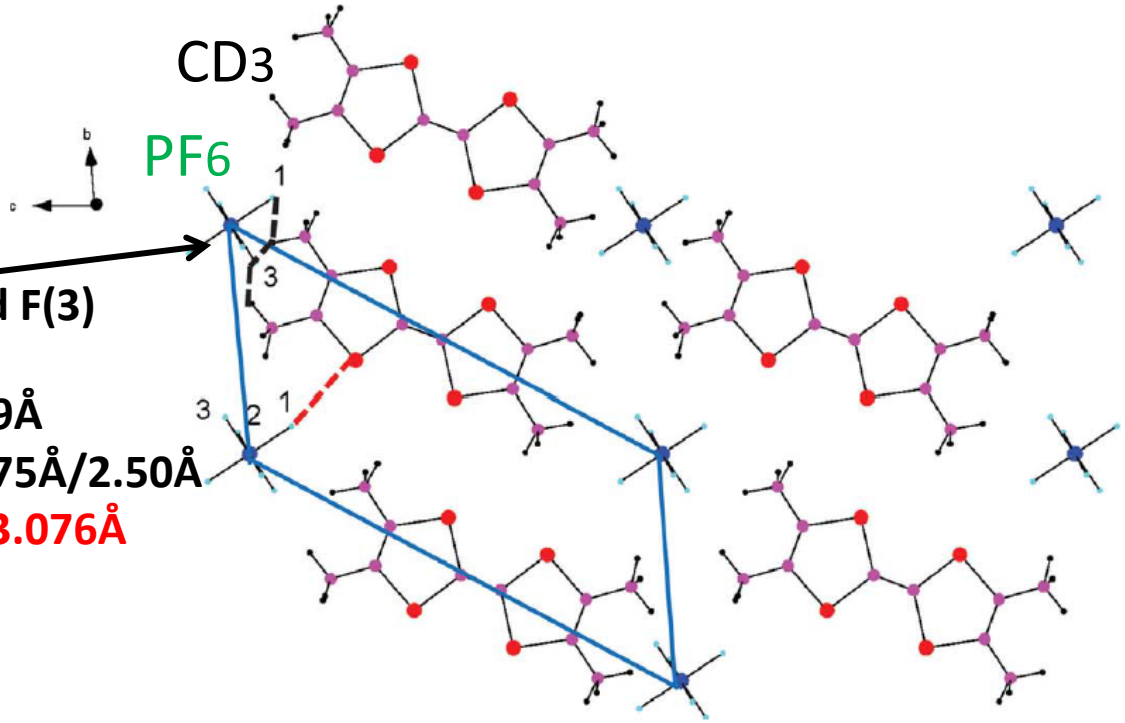


Saturation of the response function below 100K ($\approx t_\perp/\pi$)
1D divergence stopped by the warping $t_\perp$ of the Fermi surface
Then vanishing of the response function near T_{SDW}

P. Foury-Leylekian et al
PRB **88**, 024105 (2013)

4K neutron scattering structure of $D_{12}-(TMTSF)_2PF_6$



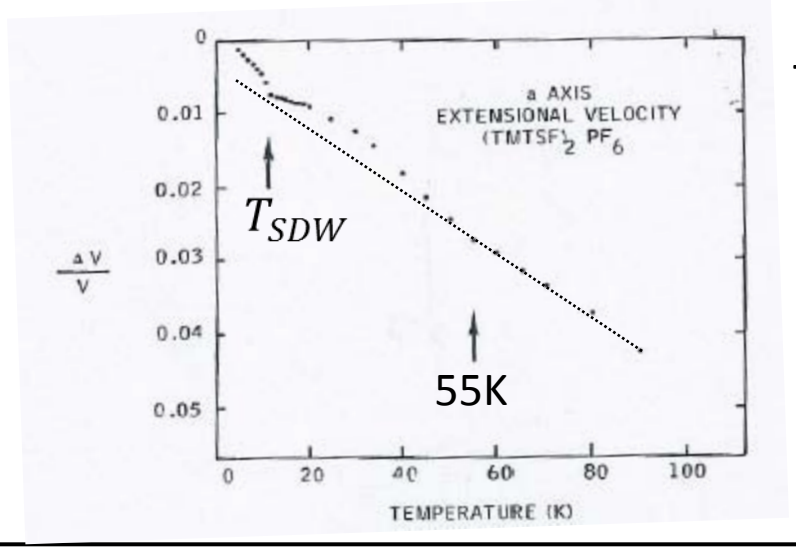


H bonds with F(1) and F(3)

F(1)----D : 2.49Å
F(3)----D : 2.475Å/2.50Å
F(1)----S(12): 3.076Å

P. Foury-Leylekian et al
PRB **88**, 024105 (2013)

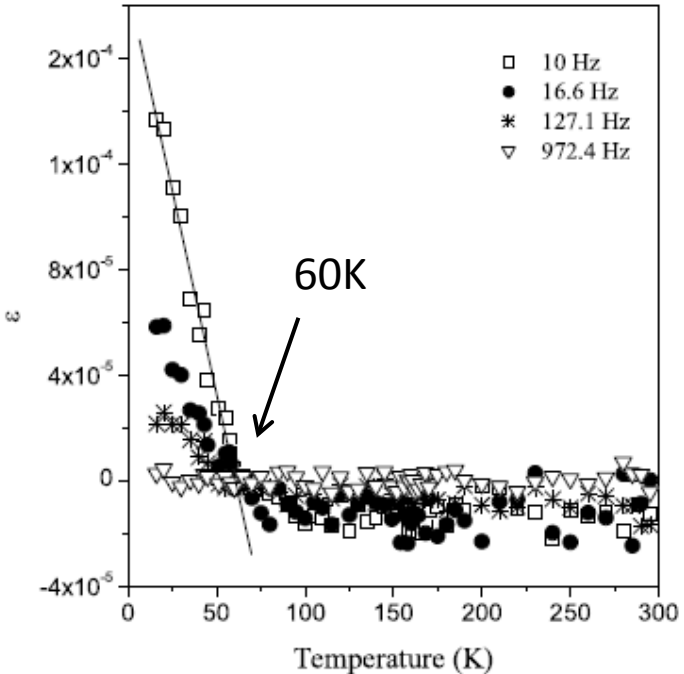
H bonding leads to an hardening of the $(TMTSF)_2PF_6$ structure below 55K



Thermal enhancement of the sound velocity of the LA mode polarized in stack direction

P. M. Chaikin et al SSC 41, 739 (1982)

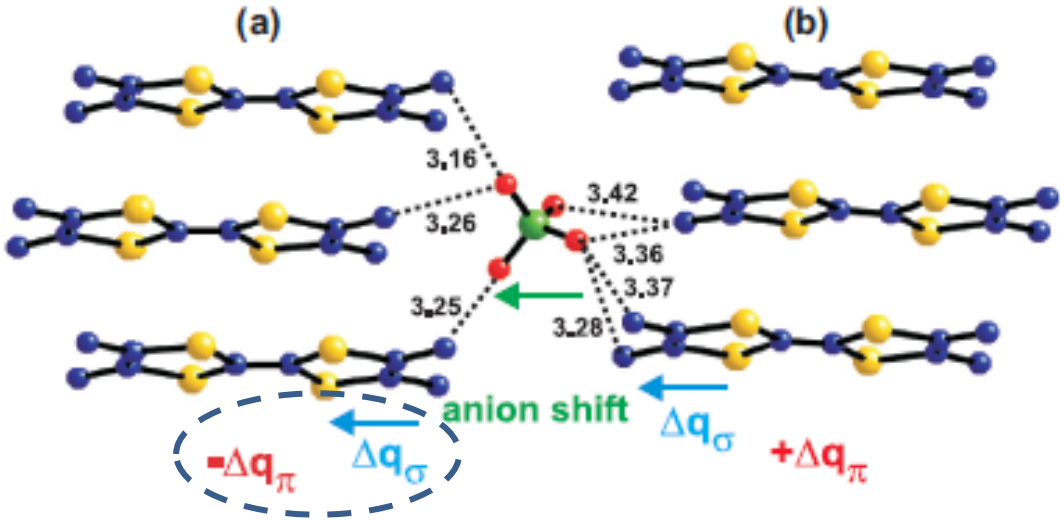
Anion linked to methyl groups forms a polarizable medium below 60K



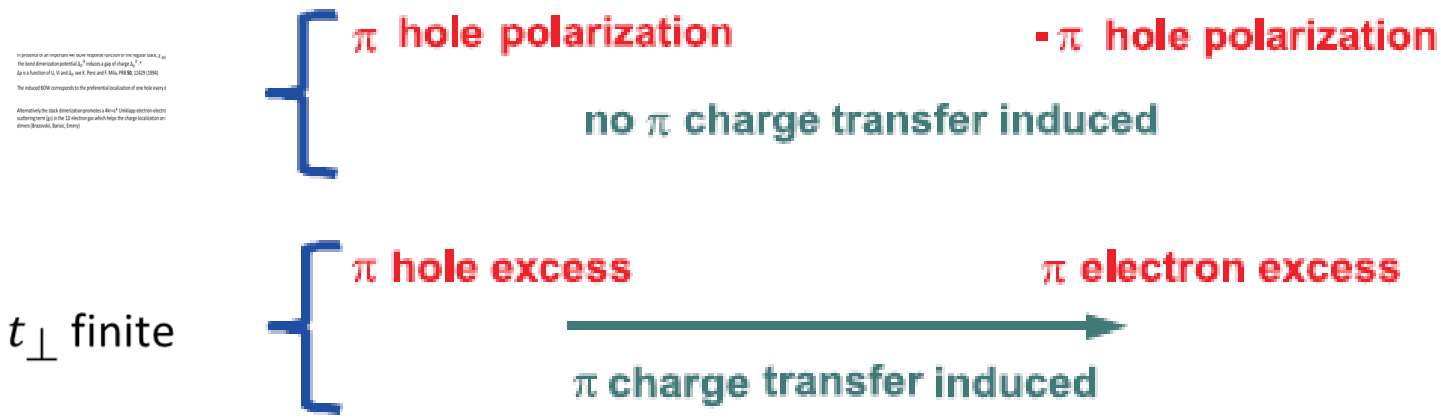
Dielectric constant in the interlayer (less conducting) c* direction

K. W. Lee et al Current Applied Physics **9**, 524 (2009)

Shift of the anion induces charge displacement/polarization



Increase of H bonding between anion and terminal groups of the donor makes their H more positively charged. This induces a negative σ charge shift towards the inner part of the donor. Consequently a more positive charge is stabilized in the inner π system .

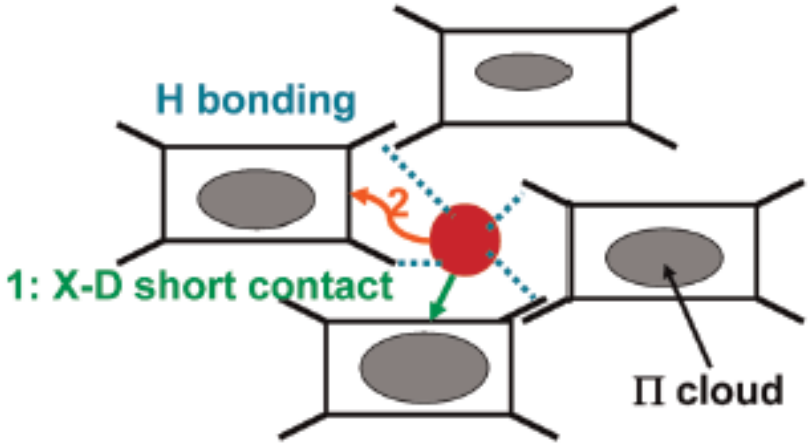


P. Alemany et al
PRB **89**, 155124 (2014)

Anion shift in $(TMTSF)_2X$ and $(TMTTF)_2X$

Polarization of the π electron density of the donors

1. ***By direct Anion-Donor interaction via the Coulomb potential***
2. ***By hydrogen bond mediated interaction***



Polarized TMTSF/TMTTF molecule depends of the direction of shift of the anion:

1- towards the Se/S

2- towards the metyl groups

J.-P. Pouget et al
Phys. Status Solidi B **249**, 937 (2012)

Polarized or charge rich TMTSF/TMTTF depends of the direction of shift of the anion:

1- towards the Se/S for:

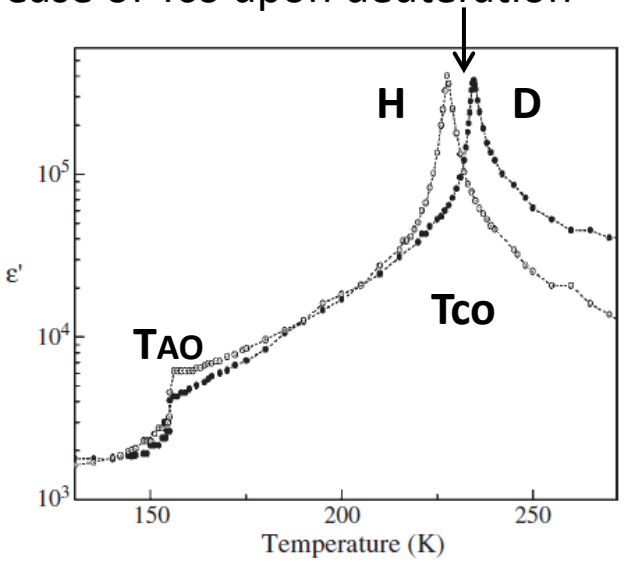
(1/2, ½, ½) anion ordering transition of the ReO4 salts
(0, ½, ½) coupled anion/charge ordering transition of (TMTTF)2SCN

2- towards the metyl groups for:

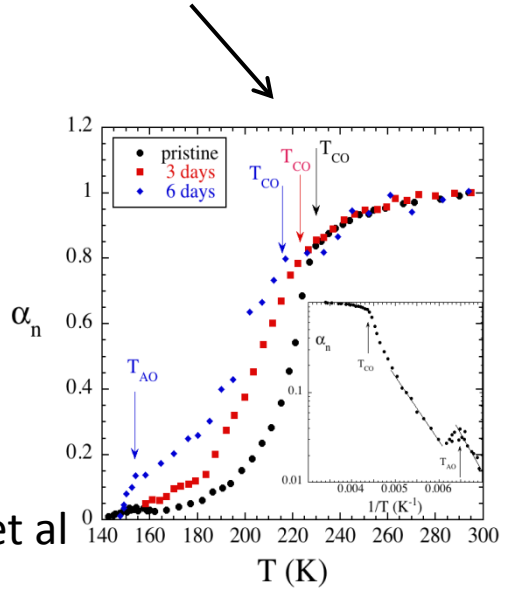
(1/2, 0,0) anion ordering transition of (TMTSF)2NO3
(0, 1/2, 0) anion ordering transition of (TMTSF)2ClO4
Charge ordering/ferroelectric transition?*

*shift towards some methyl groups explain:
- the strong sentivity of the CO to irradiation (which disorders the methyl groups)
- the strong increase of Tco upon deuteration

(TMTTF)2ReO4



F. Nad et al 2005

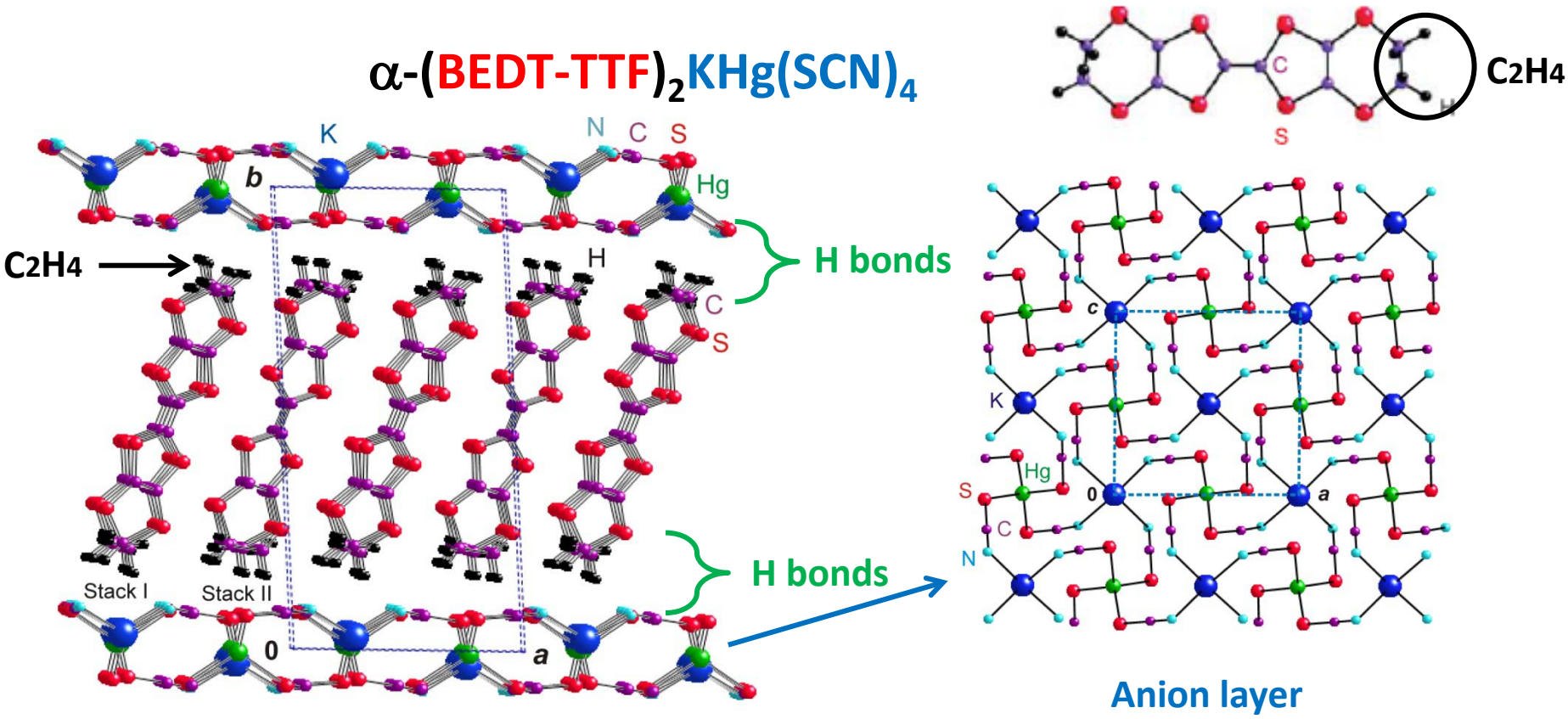


C. Coulon et al 2014

(BEDT-TTF)$_2$X series

layered organic conductors

polymorphism: several types of BEDT-TTF packing

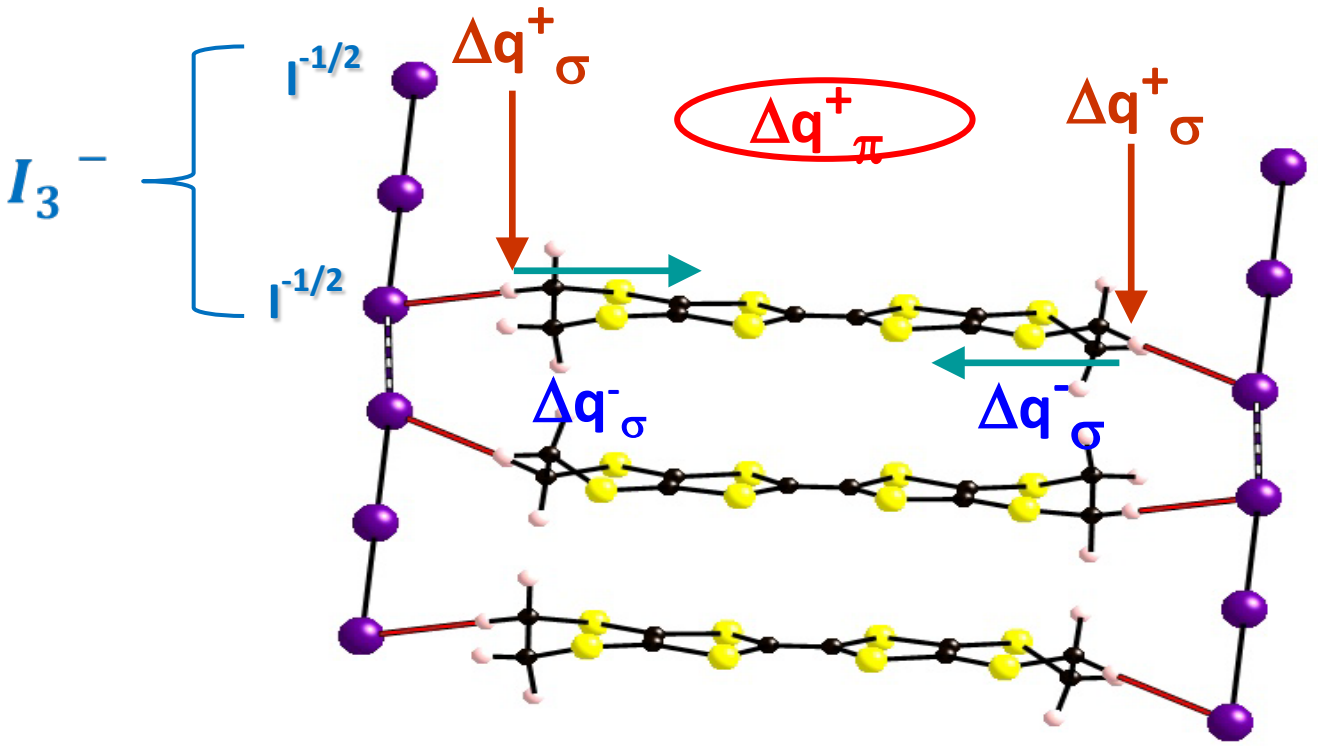


H bonds between SCN and terminal ethylene groups of the BEDT-TTF

CO transition accompanied by a strengthening of H-bonding between the anions and the ethylene groups of the charge rich BEDT-TTF: this stabilizes the hole excess

α-$(BEDT\text{-}TTF)_2I_3$

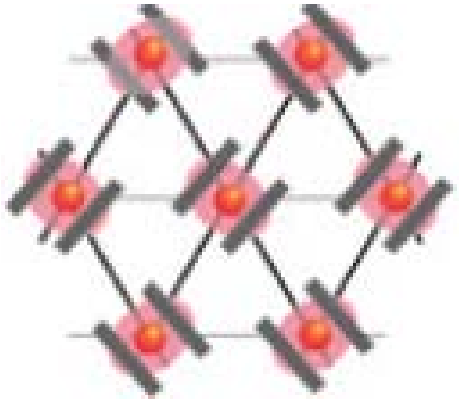
I_3^- induces effect on the π charge distribution via the polarization of the σ electrons

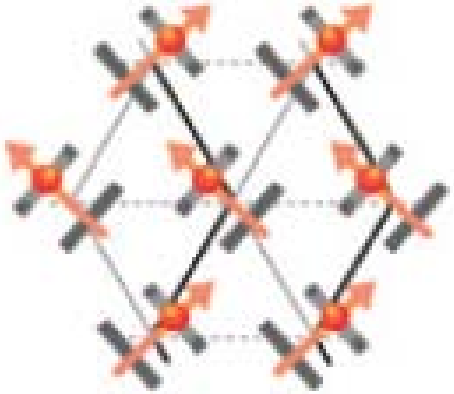


The increase of H bonding of molecule A makes the terminal hydrogens more positive Δq^+_σ. This induces a negative σ charge shift Δq^-_σ which stabilizes a positive π charge Δq^+_π in the core of the ET

(P. Alemany et al PRB **85**, 195118 (2012))

Layer of dimers in κ-(BEDT-TTF)2X





1 hole per dimer at high T

Charge fluctuations inside each dimer

Polar dimer
Charge disproportion?
Ferroelectricity?

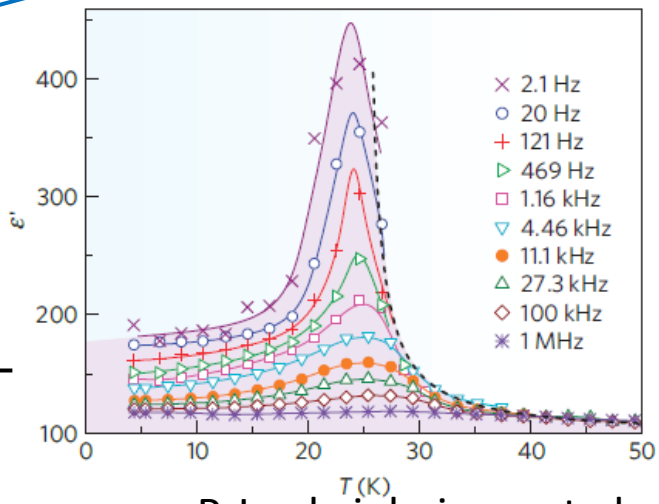
1 dimer = 1 occupied site
Effective half filled system

?

X=Cu[N(CN)2]Cl

Freezing of mobile carriers
Mott localization X=Cu[N(CN)2]Cl

Spin degree of freedom only interesting
Magnetism, Quantum spin liquid [X=Cu2(CN)3]



P. Lunkeinheimer et al
Nature Materials, **11**, 755 (2012)

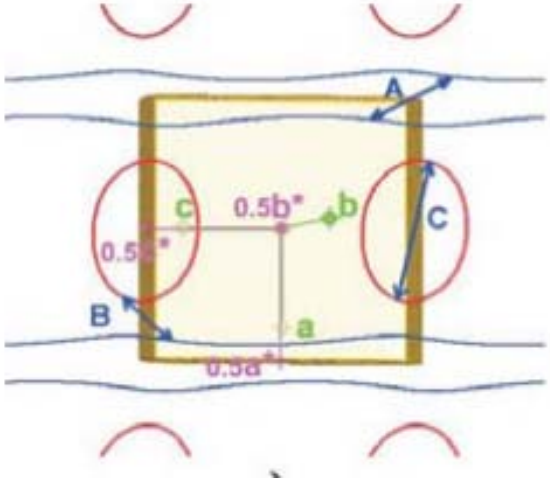
Relevance of the charge degrees of feedom?
Coupling to anions?

See the lecture of S. Tomic

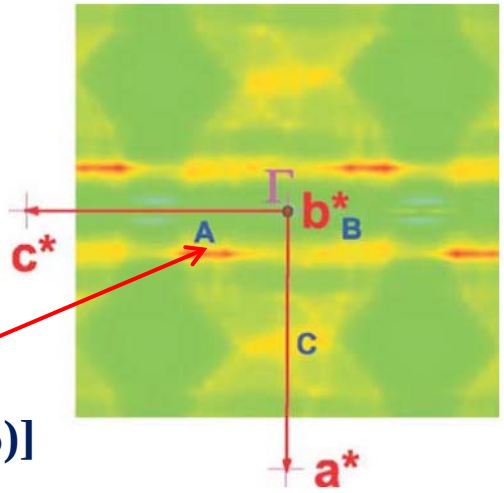
CDW trigered by the anion layer in α-(BEDTTTF)2KHg(SCN)4

Structural instability of the anion layer coupled to the electron gas via the H bonds

Fermi surface of the BEDT-TTF layer



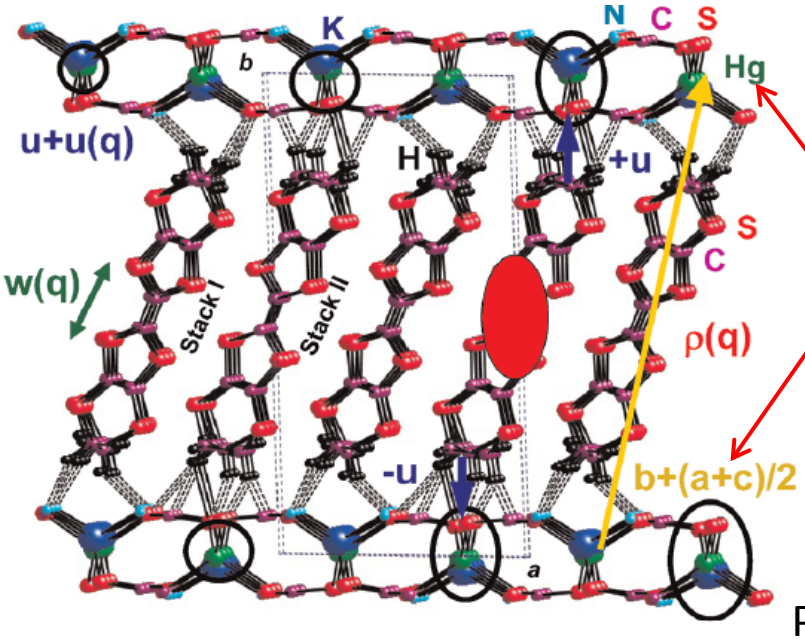
Lindhard response function



q nest=0.17 *a + (0.38-0.24) *c*** selects

q_{CDW} = [0.13(5), 0.15(5), 0.42(5)] such that

$q_{CDW}[(b+(a+c)/2]=\pi$

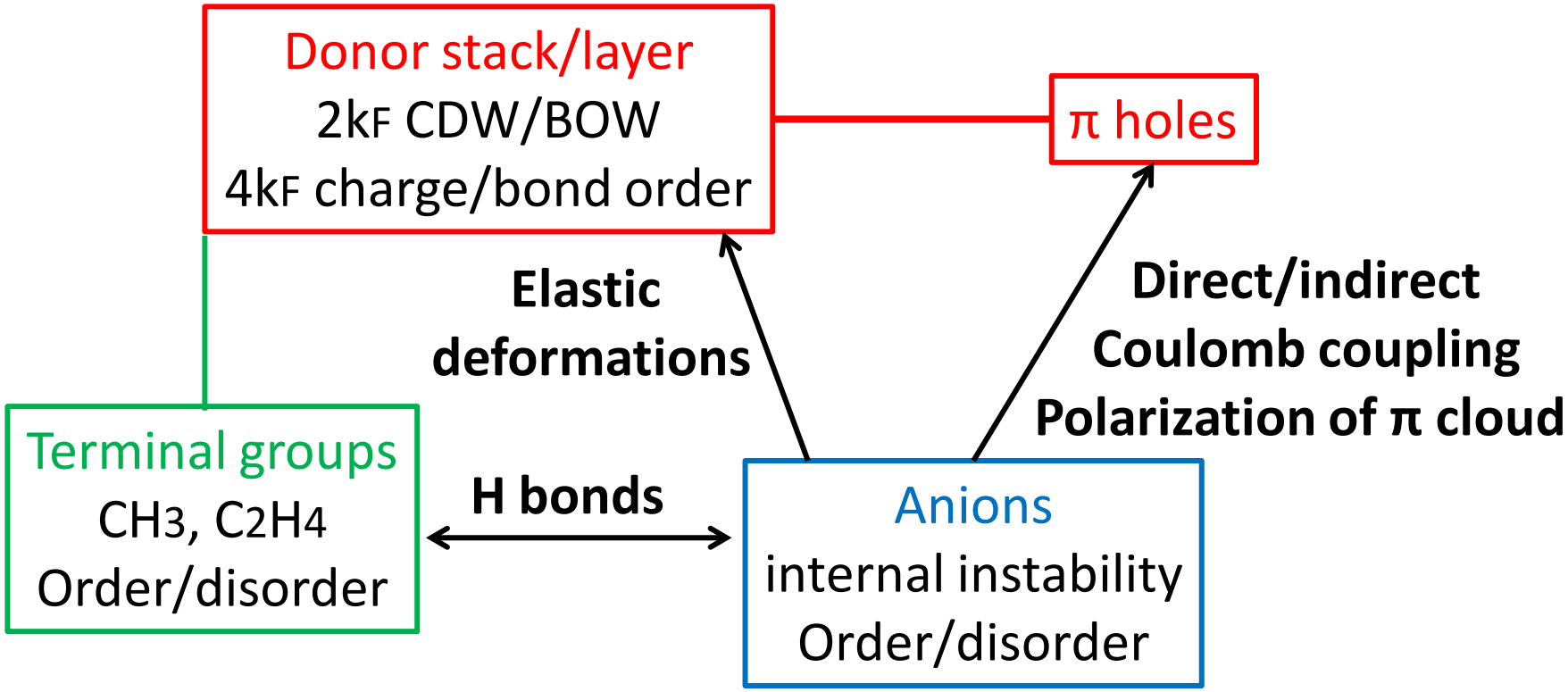


staggered deformation (±u) of adjacent anions layers

Via the H bonds this cooperatively modulates the π charge density on the BEDT-TTF layer. This forms the 2kF CDW.

P. Foury-Leylekian Phys. Rev. B **82**, 134116 (2010)

Summary of anion couplings



Anions provide interactions not yet considered until now!

Collaborations for recent work

P. Foury-Leylekian, A. Moradpour† (LPS Orsay)
P. Alemany and E. Canadell (Barcelona)
M. de Souza and M. Lang (Frankfurt)
C. Coulon (Bordeaux)

+ use of neutron scattering facilities (ILL, LLB)

Supplementary material

Anions control the donor packing and the thermal expansion

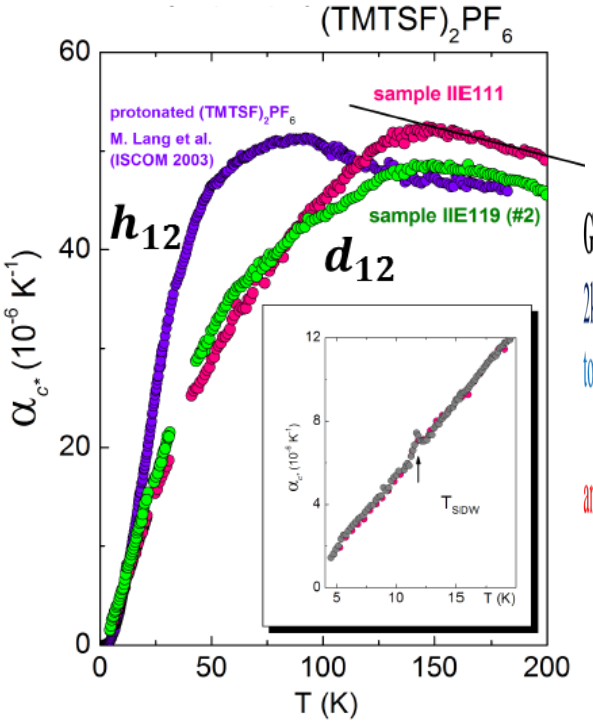
Via H bond linkage between anions and the terminal groups of donors (BEDT-TTF family)

Thermal excitations of the anion internal degrees of freedom control the lattice deformation

Thermal expansion of (TMTSF)2PF6 controlled by the anion cavity

$$\alpha_i = \frac{1}{l_i}\frac{dl_i}{dT}$$

α_{c*} in the interlayer direction c*



$$\frac{d\alpha_{c*}}{dT} < 0!$$

General situation:

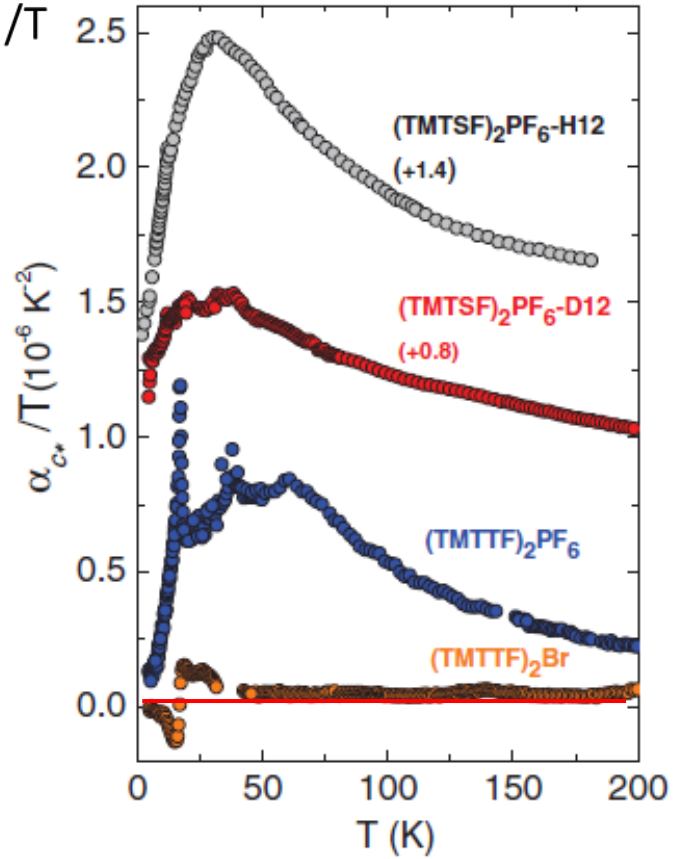
2k_F inter-molecular bond modulation (BOW): u(x)

together with a modulation of the charge on the bonds shifted by π/2 :

$\rho(x) = \rho_0 + \delta\rho(x)$ with $\delta\rho(x) \sim -\partial u(x)/\partial x$

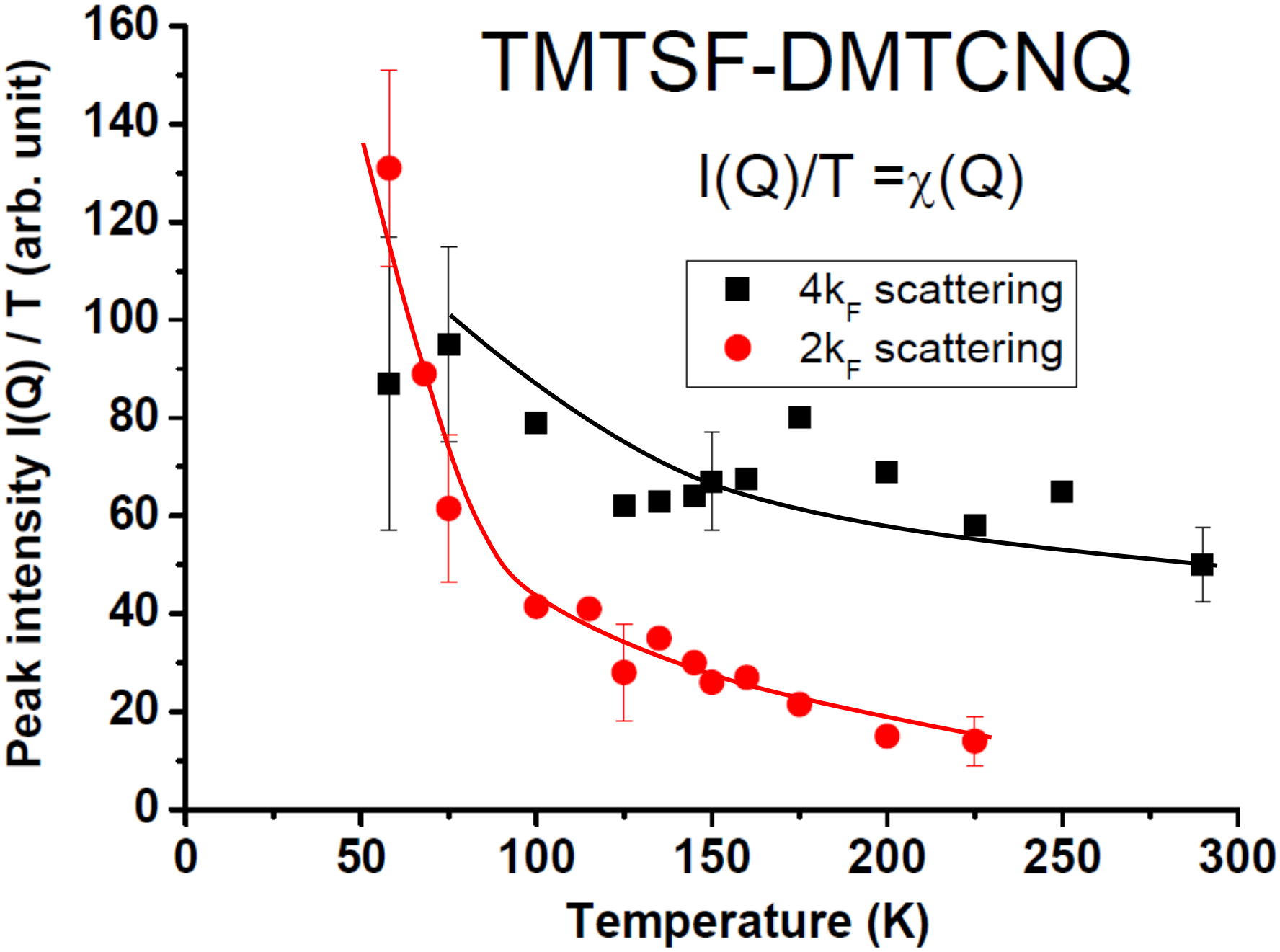
and of the charge on molecular sites (intra-molecular bond deformation) $d(x) \propto \delta\rho(x)$*

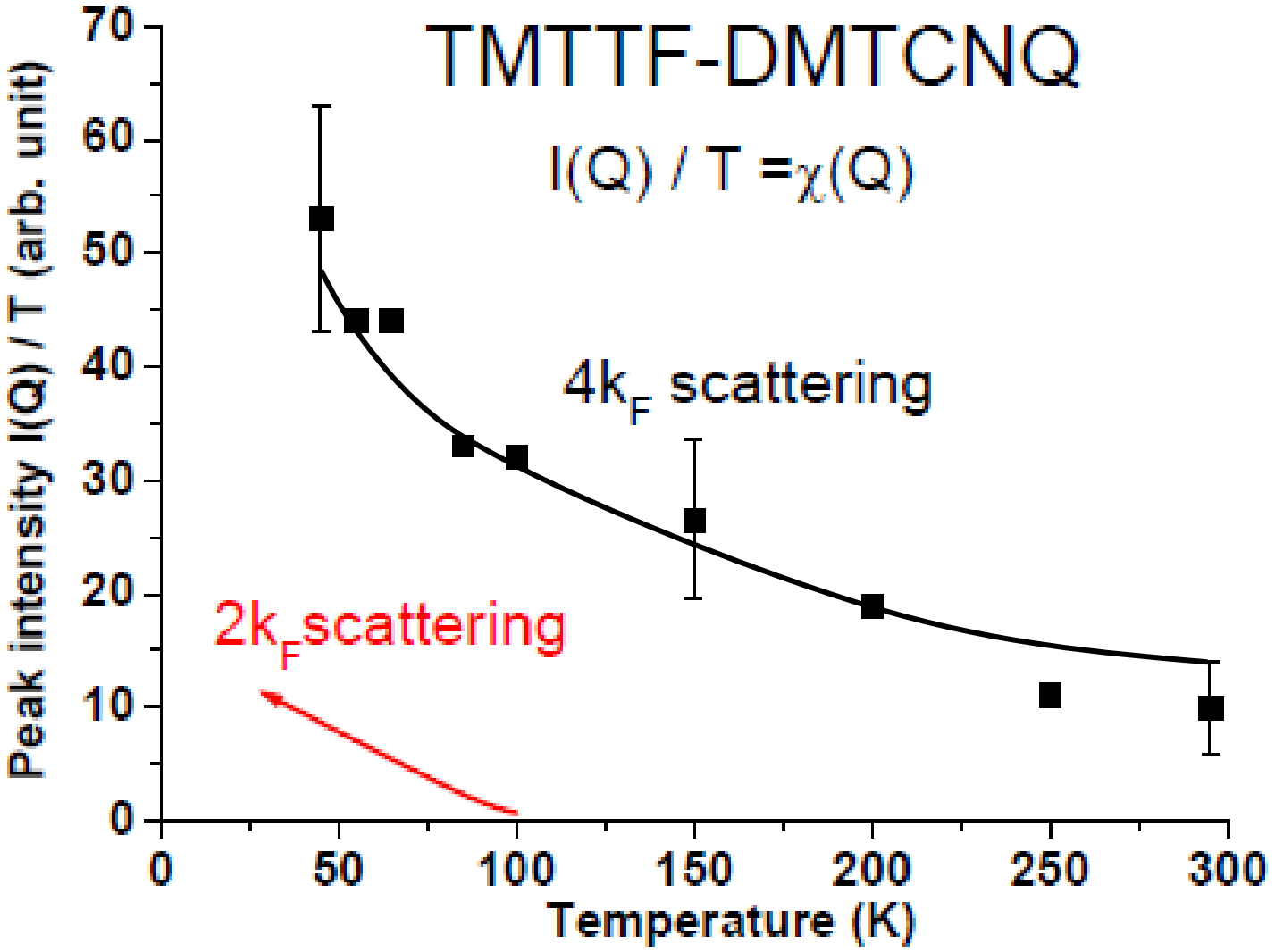
α_{c*}/T

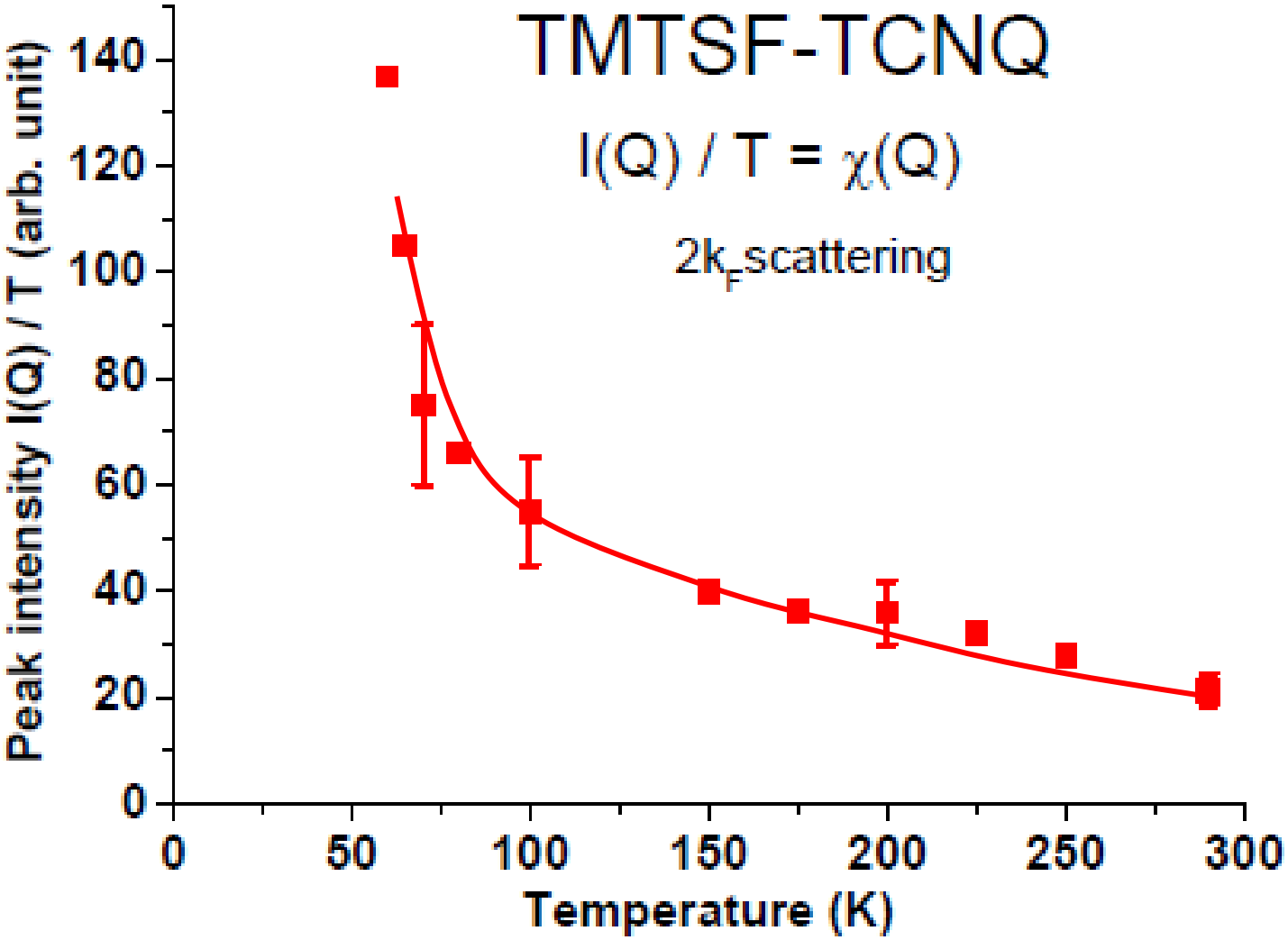


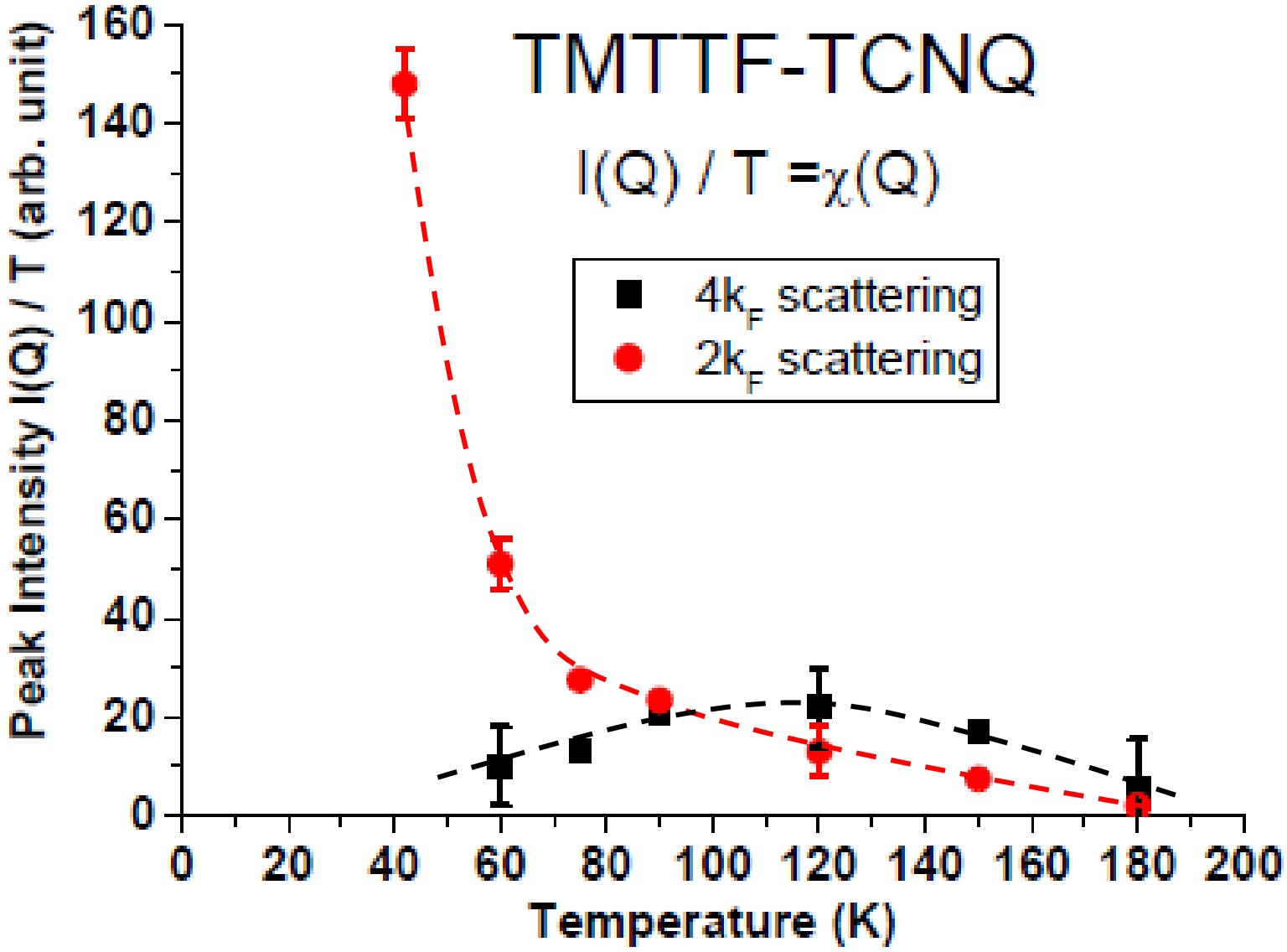
$\alpha_{c*}(T)$ depends upon the "effective volume" of the metyl group cavities ($CH_3 \rightarrow CD_3$)

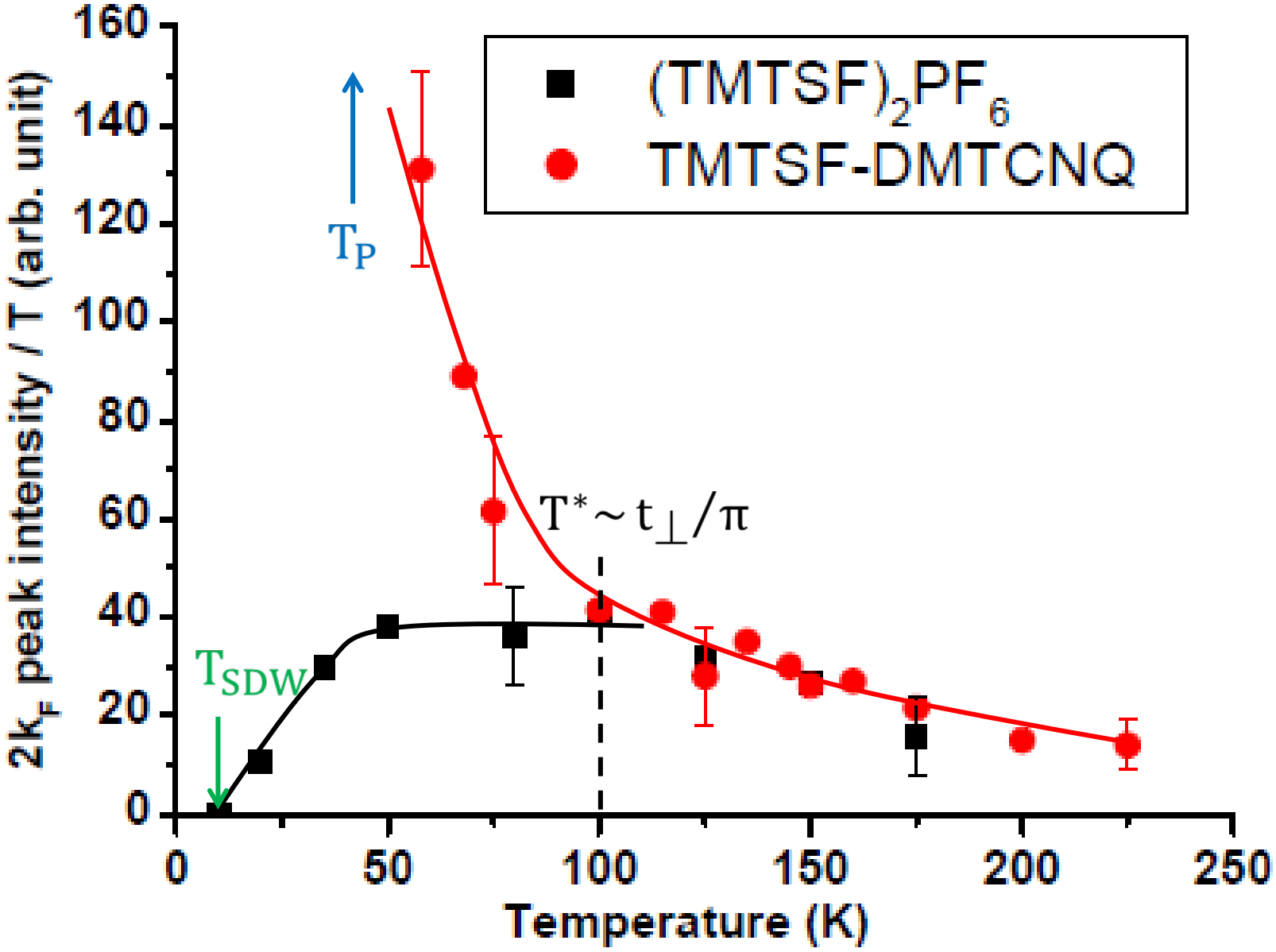
α_{c*} very small fo X=Br which has no rotation degree of freedom!


TMTSF-DMTCNQ
I(Q)/T =χ(Q)
4k_F scattering
2k_F scattering
Peak intensity I(Q) / T (arb. unit)
Temperature (K)
0
20
40
60
80
100
120
140
160
0
50
100
150
200
250
300


TMTTF-DMTCNQ
I(Q) / T =χ(Q)
4k_F scattering
2k_F scattering
Peak intensity I(Q) / T (arb. unit)
Temperature (K)
0
10
20
30
40
50
60
70
0
50
100
150
200
250
300


TMTSF-TCNQ
I(Q) / T = χ(Q)
2k_F scattering
Peak intensity I(Q) / T (arb. unit)
0
20
40
60
80
100
120
140
0
50
100
150
200
250
300
Temperature (K)


TMTTF-TCNQ
I(Q) / T =χ(Q)
4k_F scattering
2k_F scattering
Peak Intensity I(Q) / T (arb. unit)
Temperature (K)
0
20
40
60
80
100
120
140
160
180
200


(TMTSF)2PF6
TMTSF-DMTCNQ
TP
T*~t⊥/π
TSDW
2kF peak intensity / T (arb. unit)
Temperature (K)
0
20
40
60
80
100
120
140
160
0
50
100
150
200
250

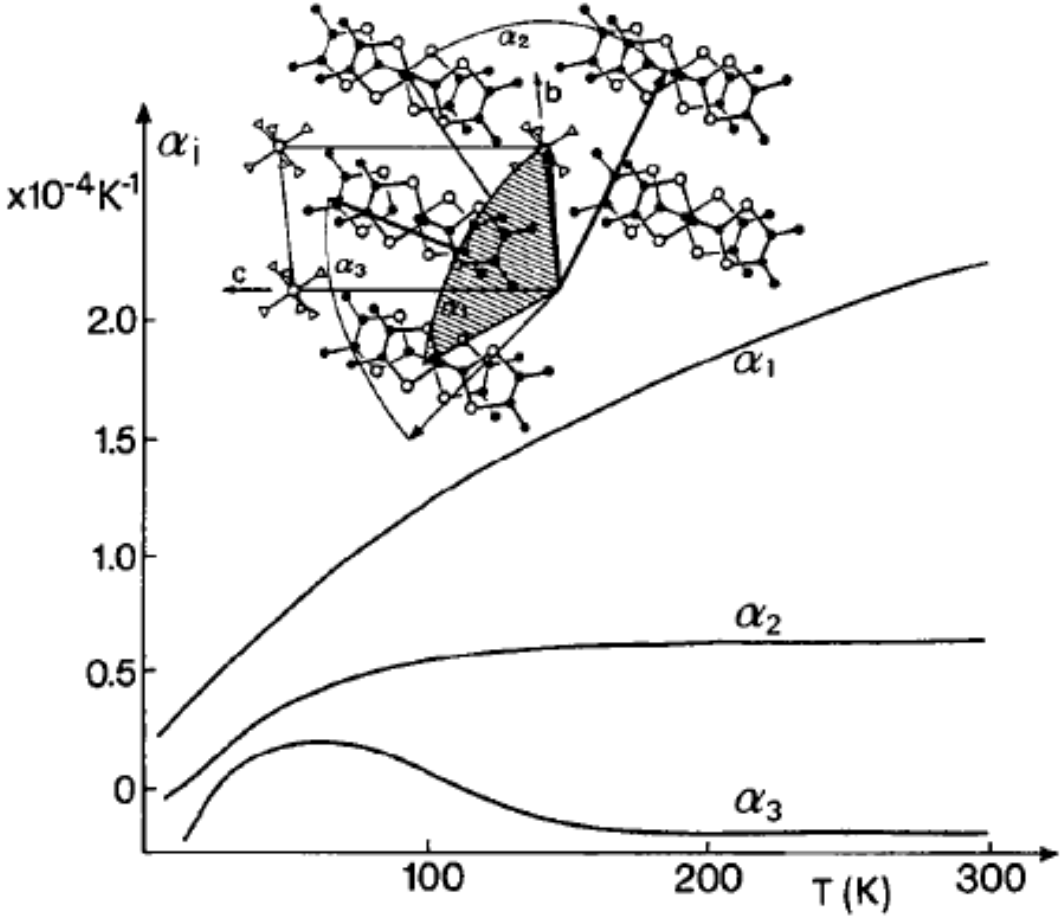


Fig. 5. Magnitudes $[\alpha_i = (1/l_i)(\partial l_i/\partial T)_P]$ and directions of the principal thermal expansions in $(TMTSF)_2PF_6$. The directions are indicated in the inset by vectors of equal arbitrary modulus (thin vectors: 100 K, thick vectors: 15 K).

B. Gallois et al *Acta Cryst.* (1986). **B42,** 564–575