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SPRING COLLEGE IN CONDENSED MATTER
ON
'PHYSICS OF LOW-DIMENSIONAL SEMICONDUCTOR STRUCTURES'
(23 April - 15 June 1990)

ELECTRON PROPERTIES OF LOW-DIMENSIONAL ORGANIC CONDUCTORS - II

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ORGANIC CONDUCTORS Lecture 2 J.R. Cooper ①

Large planar molecules π orbitals ⊥ plane.
Initially closed shells - neutral molecule diamagnetic

Conductors formed either from mixed molecules
e.g. TTF^+ $TCNQ^-$ hole and electron conduction
$\to 0.6e^-$ in parallel

generally crystals precipitated from saturated solutions

or one type of molecule and an inorganic acceptor with strong electron affinity
e.g. $(TMTSF)_2 PF_6$ or $(BEDT-TTF)_2 I_3$

generally crystals grown electrochemically - gives high purity and favours conducting modification.
PF_6^-, I_3^- ions no contribution to conductivity
In Bechgaard salts symmetry of negative ion important. Asymmetric ones such as ClO_4^-, ReO_4^-, NO_3^- (no centre of symmetry) order at low T - modify electronic properties of TMTSF stacks

- Pressure studies (D. Jérome et al - Orsay)
  Initial motivation - stabilise metallic state down to helium temperatures - organic superconductivity?

Review article D. Jérome and H. J. Schulz Adv. Phys. (1982) Vol 31 ①

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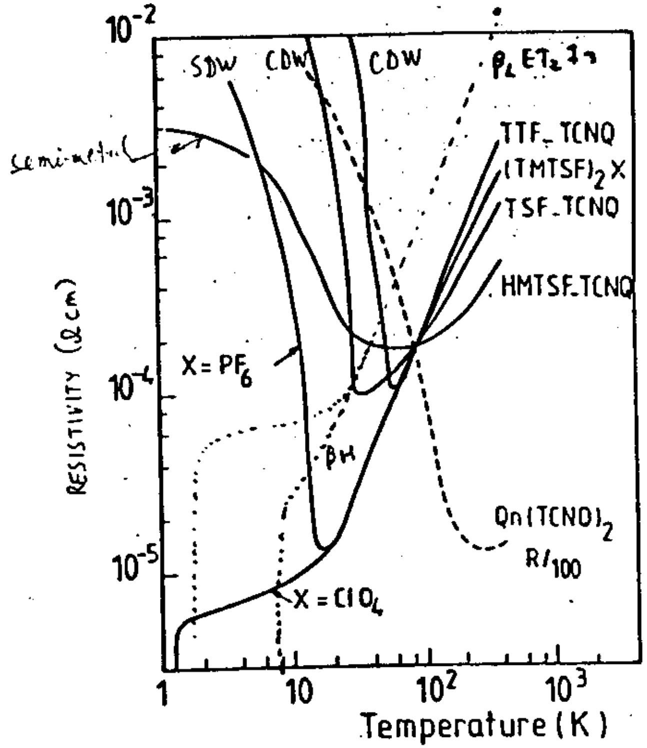
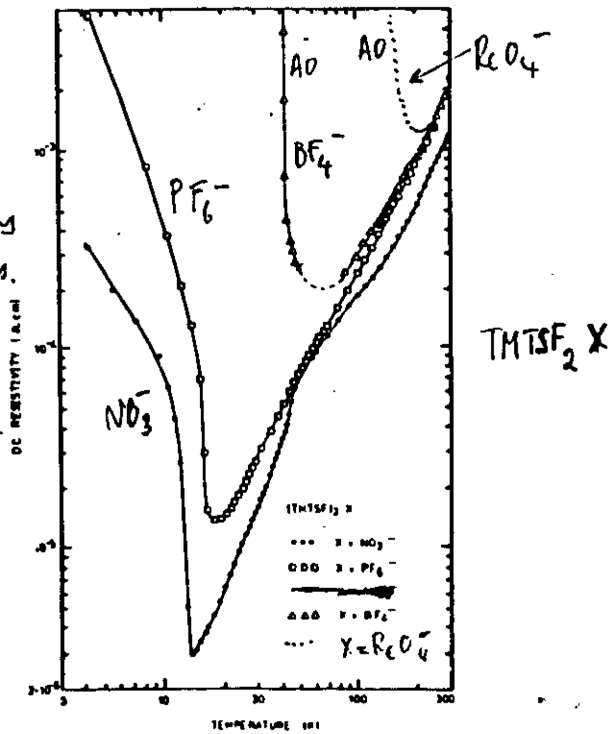


Resistivity of single crystals of various organic conductors and superconductors.



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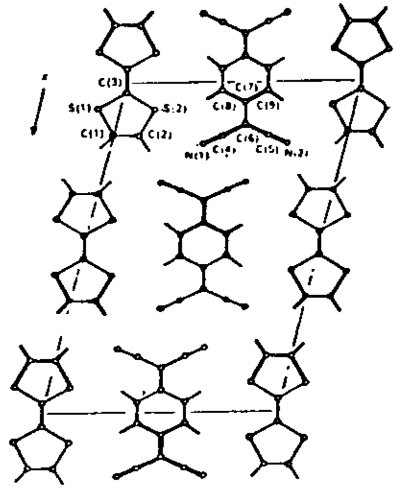
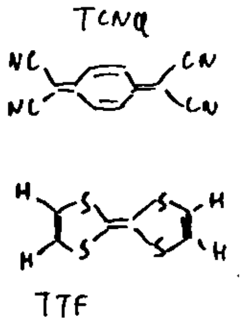
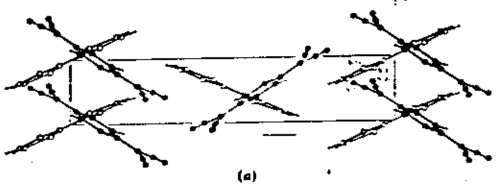
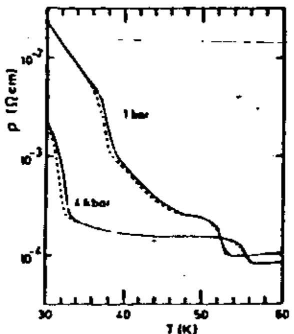


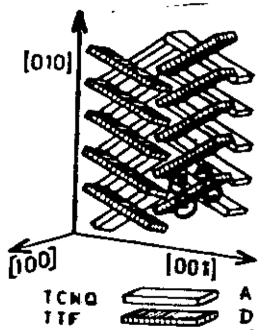




$$TTF^0 + TCNQ^0 \rightleftharpoons TTF^+ + TCNQ^-$$

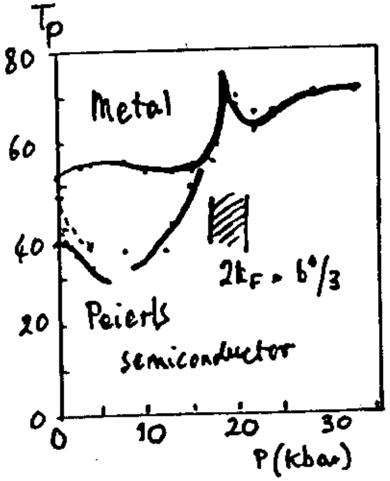
$$\langle n \rangle_{TCNQ} = 0.55\, e^-$$



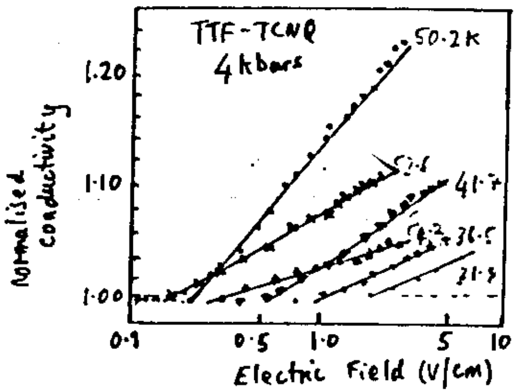


For review of structural properties

TTF-TCNQ



R. Friend et al (1978)



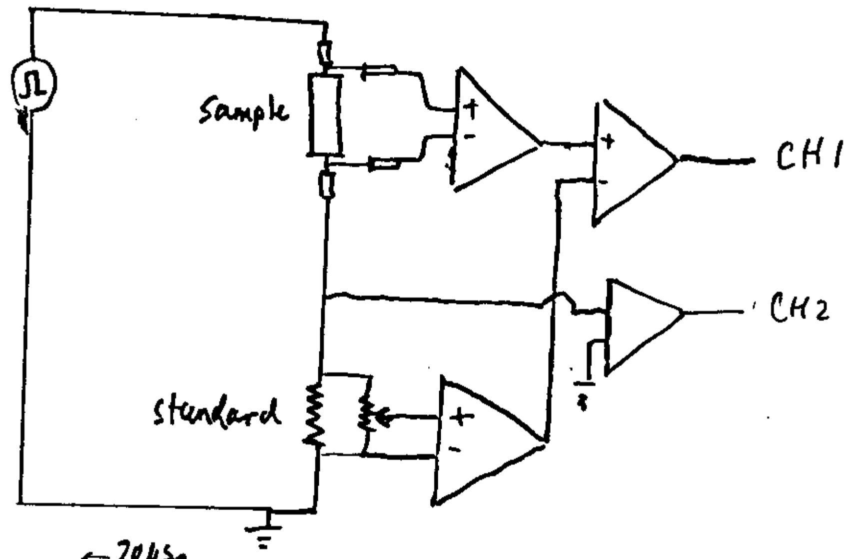
R. Lacoe et al PRL 58, 212 (1987)

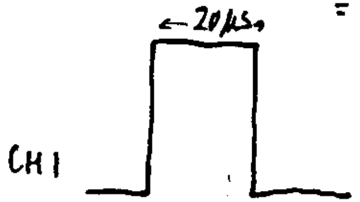
pulse method $T_D \approx 5\mu s$

CDW conduction in TTF-TCNQ

Bridge cct. used for pulsed I-V measurements. 4(a)

R. Lacoe et al (1985)



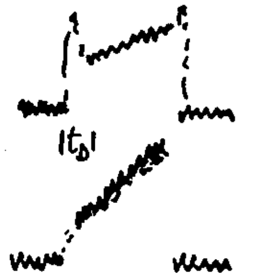


CH1 - channel 1 of digital storage oscilloscope

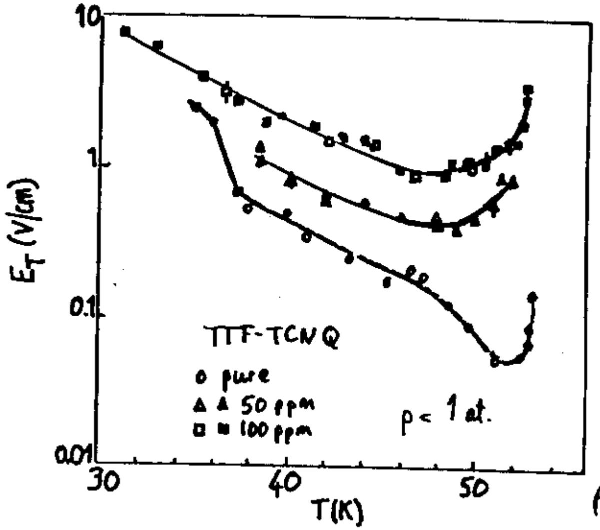
$V_1 < V_2$

V_1 — CH2 Balanced

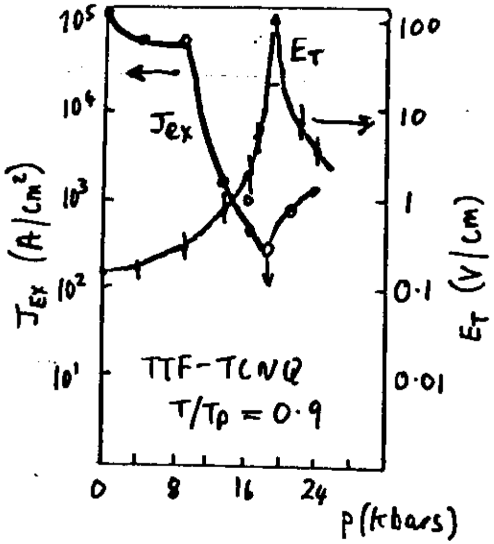
V_2 — non-linearity plus some heating



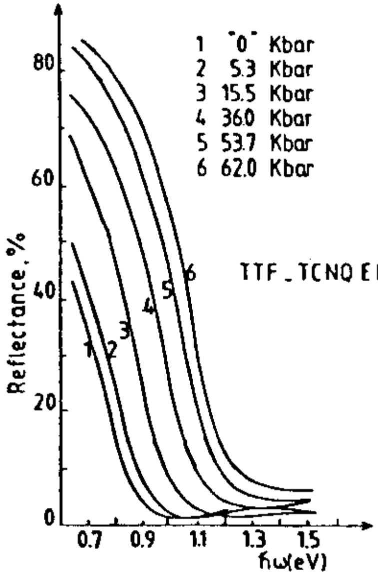
just heating



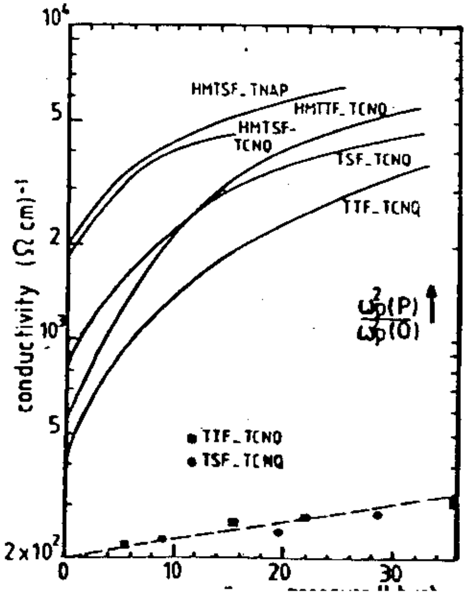
L. Ferró et al Phys. Rev. B. (1986)



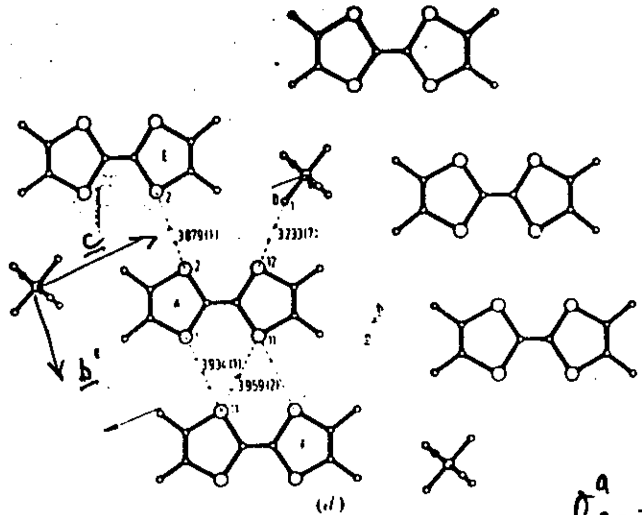
R. Lacoe et al (1986) PRL 58, 262 1987



B. Welber et al (1978)



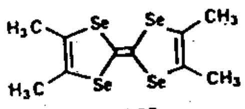
BECHGAARD SALTS $TMTSF_2X$



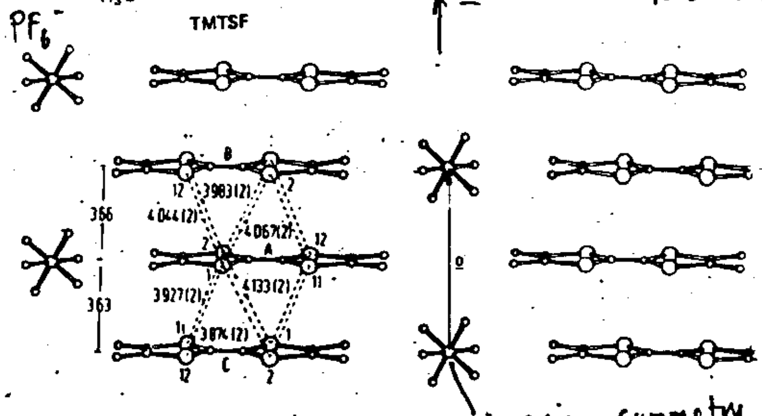
$\sigma^{a}_{RT} = 800\,(\Omega cm)^{-1}$

$\sigma^{b'}_{RT} = 10\,(\Omega cm)^{-1}$

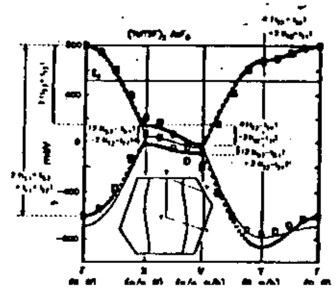
$\sigma^{c}_{RT} = 0.2\,(\Omega cm)^{-1}$ to $0.02\,(\Omega cm)^{-1}$



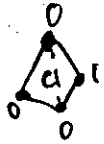
TMTSF



inversion symmetry

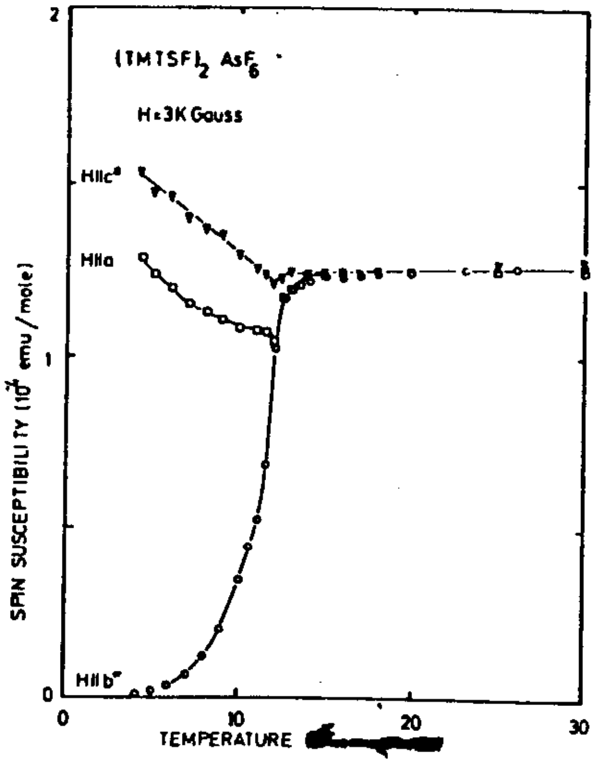


P.H. Grant (1983)



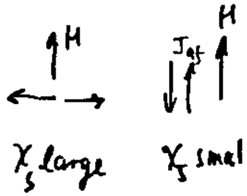
$$\varepsilon = -2t_{\parallel}\cos \underline{k}.\underline{a} - 2t_{\perp}^{b}\cos \underline{k}.\underline{b} - 2t_{\perp}^{c}\cos \underline{k}.\underline{c}$$

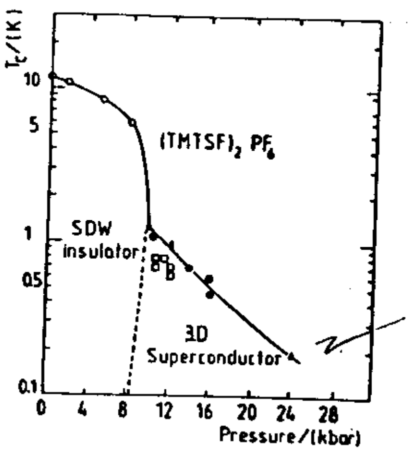
$t_{\parallel} \approx 300\ meV$ (1 meV = 12 K)



K. Mortensen et al

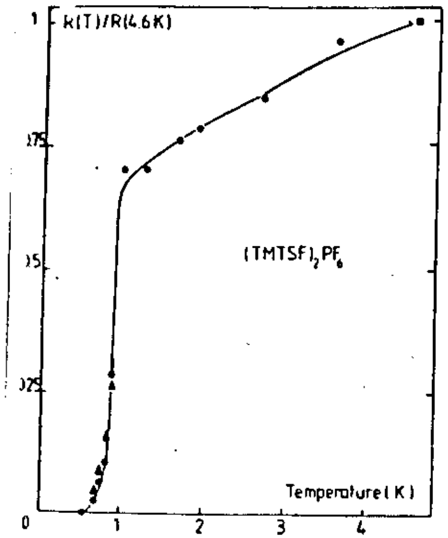
P.R. B 25, 1982 p. 3319

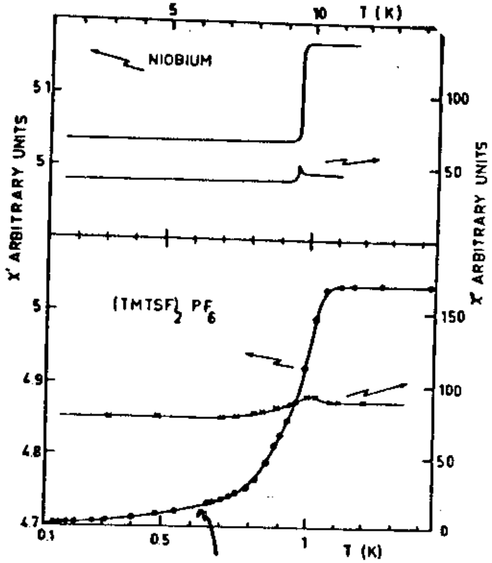




note Tc falls

D. Jérome and H. J. Schulz Loc. cit.





$\lambda(T) - \lambda(0) = AT^2$?

seen in UBe_{13} and high T_c oxides

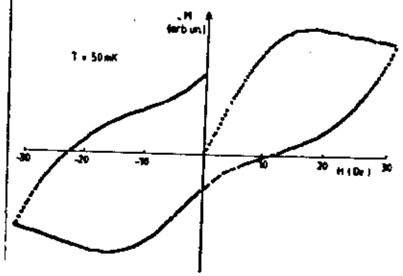
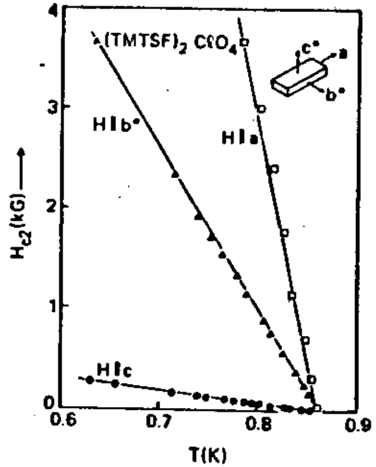


Fig. 4 : Hysteresis cycle of (TMTSF)$_2$ClO$_4$ at T = 50 mK, with the magnetic field oriented along the c* axis.

Flux trapping at molecular ie. unit cell level?



Anisotropic Superconducting Properties

from D. Jérome and H. J. Schulz Adv. Phys. Vol 31 pp 299–490 (1982)

Generally believed that electron-electron interactions important in organic conductors

(Caveat – strange behaviour arising from molecular vibrational modes & librons?)

Why? • Bandwidths small $4t_{\parallel} \simeq 1eV \rightarrow \varepsilon_F = 0.25eV$

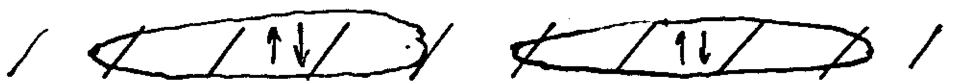
• spin susceptibility χ_s enhanced in metallic region by factor 2 – 6 (no longer believe χ_s / γ where $C_V = \gamma T$ $(T \to 0)$ is good measure of enhancement)
Instead compare χ_s with ω_p or $t_{\parallel}$ (calculated)

• In many semiconducting organic compounds activation energy for magnetic excitations much less than that for conductivity.

• X-ray diffuse scattering – sometimes see 1D lines and superlattice spots at $4k_F$ as well as or instead of $2k_F$

$k_F = \pi/4a$

e.g. for 1/4 filled band (1 carrier / 2 molecules)



$\leftarrow a \rightarrow$ $\leftarrow \lambda_F = 4a \rightarrow$ $U \lesssim 4t$

$2k_F$ instability (Peierls distortion)

t'

$\vdash \lambda_F = 2a \dashv$ U_{eff} $U \gtrsim 4t$

$4k_F$ instability $E_\chi \sim J \sim t'^2 / U_{eff}$
($k_F \times 2$ to accommodate all electrons)

• Strong pressure dependence of many physical quantities

e.g. $\frac{d \ln \sigma_{RT}}{dp} = +20 \rightarrow +70\% / \text{kbar}$ $ET_2 I_3$

$\frac{d \ln \chi_s}{dp} = -10$ (TTF-TCNQ) to $-3\% / \text{kbar}$ ($ET_2 I_3$)

e.g. S. Kotj et al Phys. Rev. B38 5878 (1988)

cf. 1 electron properties – $\frac{d \ln \omega_p}{dp} = +2\% / \text{kbar}$

calc. $\frac{d \ln t_{\parallel}}{dp} = 2\% / \text{kbar}$

• strong p dependence of phase diagram.

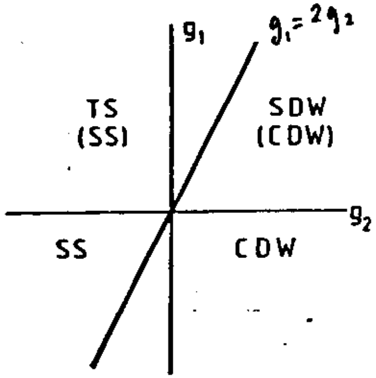
Why? Screening of el-el interaction may become more effective under pressure 1D – 2D effect?
connected with singular behaviour of χ_{2k_F} in 1D?

D. Jérome and H. J. Schulz (loc. cit.)

Fig. 1.5

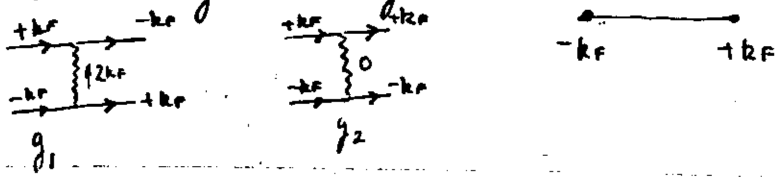
"g-ology"

ss = singlet superconductivity
ts = triplet -"-



Phase diagram of the hamiltonian (1.28).

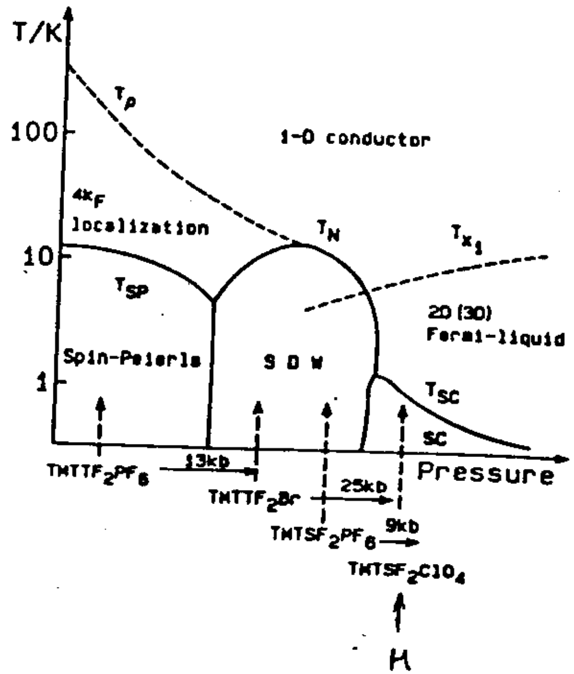
1 D interacting electron gas -



may be most appropriate picture in intermediate coupling limit $U \gtrsim 4t$

Above diagram shows most divergent response functions for different values of the two el-el coupling parameters g_1 ($2k_F$ momentum transfer) and g_2 ($\simeq 0$ momentum transfer)

For complete reviews of theory of 1D interacting gas see references given by Jérome and Schulz (loc. cit)



<u>Some evidence that superconductivity is unusual in Bechgaard salts</u>

- NMR T_1^{-1} does not show peak just below T_c
- T_1^{-1} has power law dependence not $\exp -\frac{\Delta}{kT}$ below T_c ($T_1^{-1} \propto T^3$)
- Non-magnetic impurities strongly reduce T_c
- Starting to be evidence for T^2 term in $\lambda(T) - \lambda(0)$ as $T \to 0$

D. Jérome - Vol. 6. of "Studies of High Temperature Superconductors"
Dr. A.V. Narlikar (Ed.) Nova Science Publ. Inc. New York

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Summary

In TTF-TCNQ and close relatives TSeF-TCNQ HMTSF-TCNQ T_P was increased by pressure - unable to stabilise metallic state to low temperatures.
However TTF-TCNQ did show some interesting properties CDW sliding, commensurability under pressure.
E_T increased at commensurability
Believe that decrease above 19 kbar showed that it was genuine commens. effect and not TCNQ - TTF chain interaction.

$TMTSF_2X$ - No Peierls transition!
- weak $2k_F$ anomaly in Xrays gets even weaker as T falls - Why? 1D interacting electron gas picture.
- instead SDW or sometimes anion ordering
- SDW suppressed by pressure - but can be resurrected by a magnetic field - FISDW.
- s/c state anisotropic - some unusual properties

$BEDT\text{-}TTF_2I_3$ Higher T_c 8K for β_H phase
1.5K for β_L phase
only small differences between them - CH_2 groups less disorder
t_c 0.75meV vs. 0.5meV

Next time (Wed.) FISDWs in $(TMTSF)_2X$
Type of Quantum Hall Effect
High Field re-entrance to Metallic State
Anomalous magnetoresistance in low field (metallic

A Peierls distortion is a type of 'nesting' instability

$$\chi(q) = \sum_k f_{k+q} - f_k / (\varepsilon_{k+q} - \varepsilon_k)$$

is large for any q value which connects or "nests" appreciable regions of the Fermi surface

"nesting" is responsible for weak itinerant antiferromagnetism in Cr and also for unusual spiral magnetic ordering in some rare earth metals.
For magnetic instabilities, mean field criterion for a phase transition is that $I_q \chi^s(q) \geq 1$
I_q is exchange interaction, in def^n of χ^s have $\varepsilon_{k+q\uparrow} - \varepsilon_{k\downarrow}$

Tight binding Fermi surface

$$\varepsilon = -2t_{\parallel} \cos k_x a - 2t_{\perp}^b \cos k_y b - 2t_{\perp}^c \cos k_z c$$