# Organic Superconductivity

P. M. Chaikin, Center for Soft Matter Research, NYU

**Brief History**

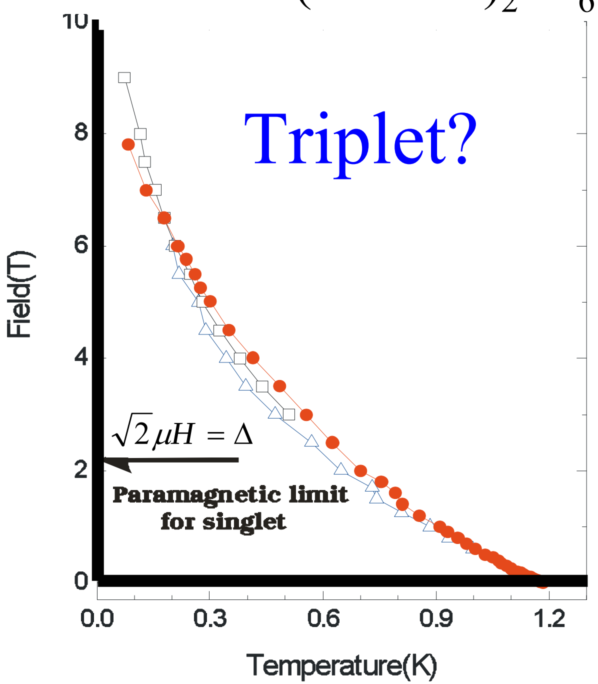
**A Remarkable Set of Materials!**

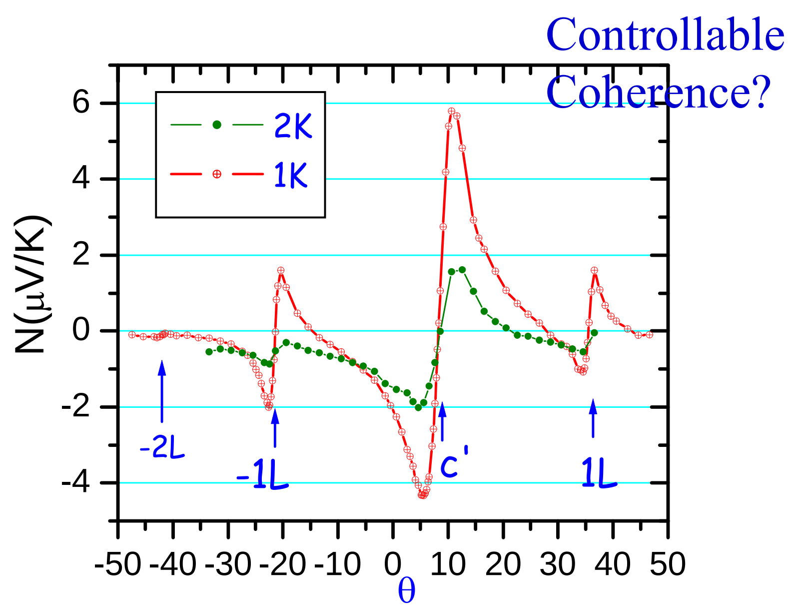
**Nature of the Superconducting State?**

**The Discovery of New Condensed Phases**

**& New Effects in High Magnetic Fields**

$(TMTSF)_2PF_6$ the first organic superconductor



# $(TMTSF)_2PF_6$ - 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

# Who's to Blame

**Princeton**
- ***InJae Lee*** (Chonbuk National University)
- ***Weida Wu*** (Rutgers)

**UCLA**
- ***Stuart Brown***
- Gil Clark
- David Chow

**Boston College**
- Mike Naughton

With Advice from: Andrei Lebed, Victor Yakovenko, Phil Anderson, David Huse, Phuan Ong

1911

Superconductivity Discovered by
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Superconductivity Explained
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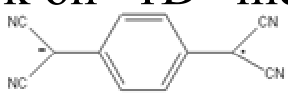
Schegolev, Bloch, Heeger,….
Work on “1D” metals, TCNQ’s

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TTF-TCNQ first organic metal
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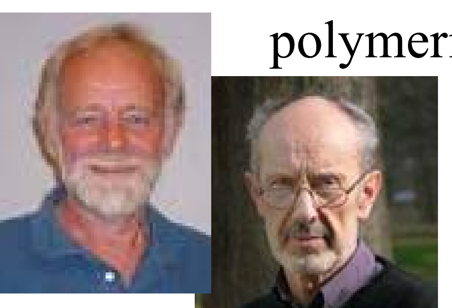

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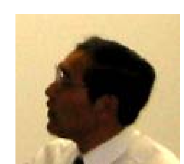

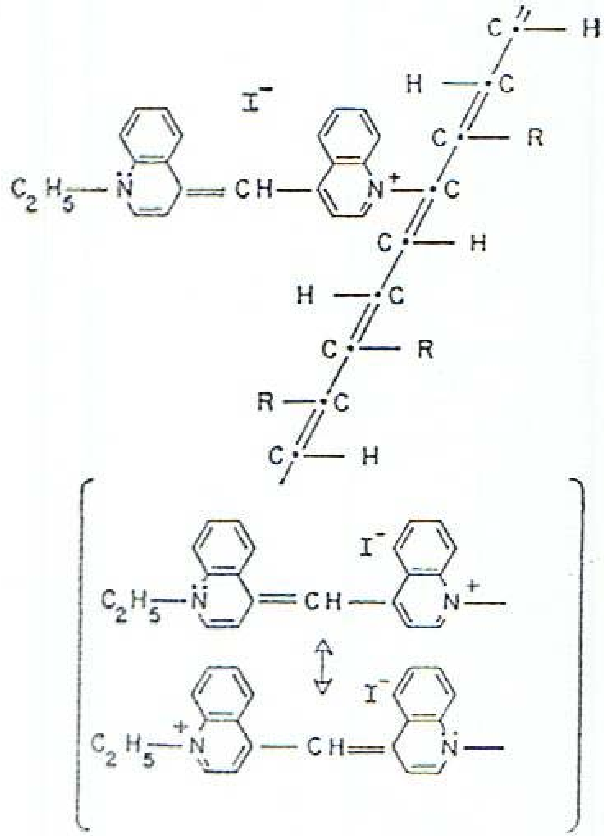


FIG. 3. Chemical structure of the proposed superconducting organic polymer. At each point $R$ on the spine a similar side chain to the one shown is attached. These side chains are resonating hybrids of the two extreme structures shown in the inset. The positive charge resonates between the two nitrogen sites as illustrated.

W. A. Little, Phys. Rev. **134**, A1416, 1964

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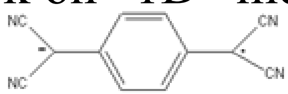


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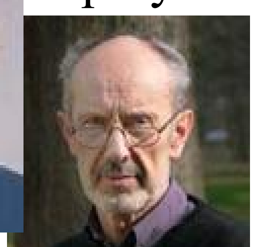

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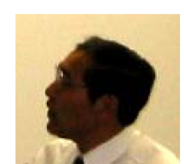
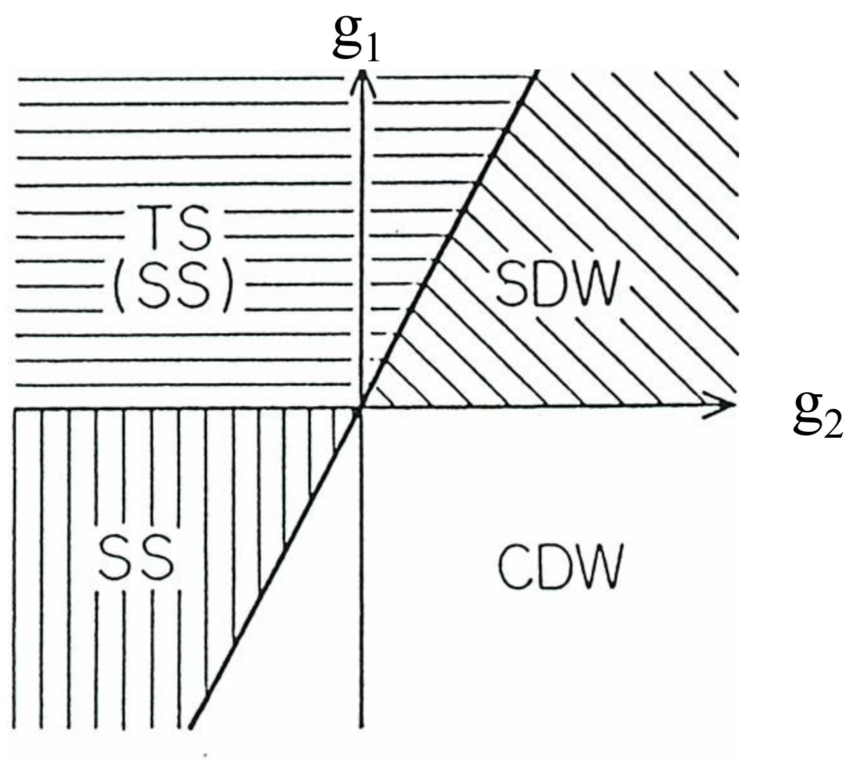
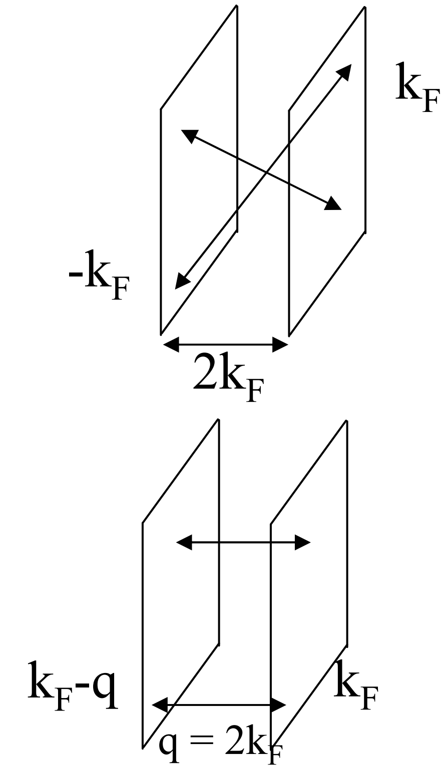


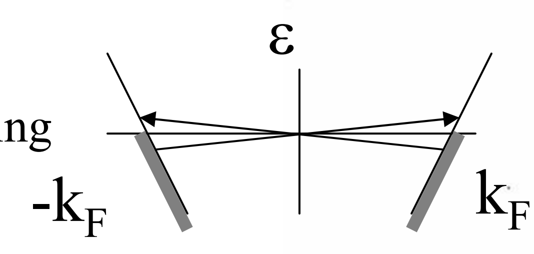
# “g-ology Phase Diagram 1D electrons



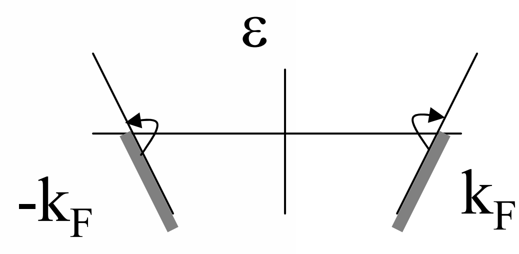




Only two interactions important

backscattering




$g_1(q=2k_F)$




forward scattering

$g_2(q=0)$

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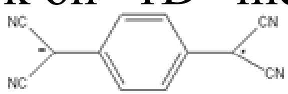

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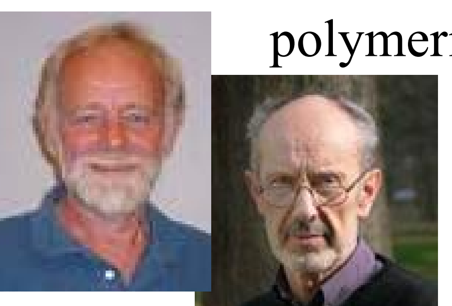

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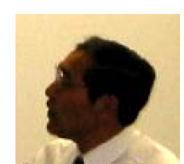
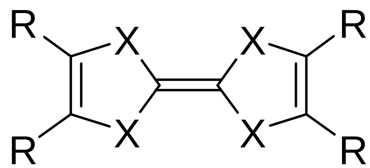
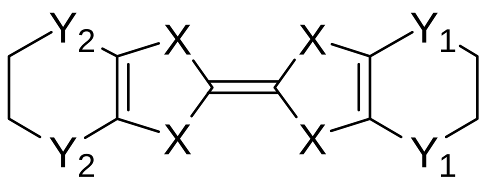




Wudl

**TTF** : X=S, R=H
**TSF** : X=Se, R=H
**TTeF** : X=Te, R=H
**TMTSF** : X=Se, R=Me
**TMTTF** : X=S, R=Me

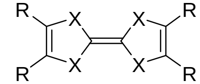
Quasi 1D



**ET(BEDT-TTF)** : X=$Y_1$=$Y_2$=S
**BO(BEDO-TTF)** : X=S,$Y_1$=$Y_2$=O
**BETS(BEDT-TSF)** : X=Se,$Y_1$=$Y_2$=S
**EOET** : X=S,$Y_1$=S,$Y_2$=O

Quasi 2D

Yagubski



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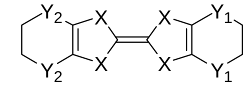

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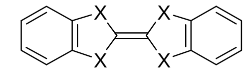
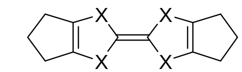
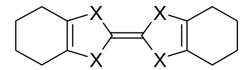


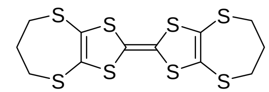
**DBTTF** : X=S
**DBTSF** : X=Se



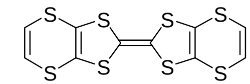
**HMTTF** : X=S
**HMTSF** : X=Se
**HMTTeF** : X=Te



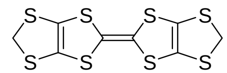
**OMTTF** : X=S
**OMTSF** : X=Se



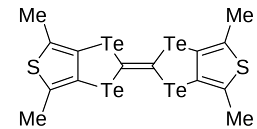
**BPDT-TTF**



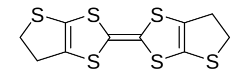
**BVDT-TTF**



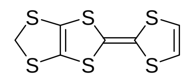
**BMDT-TTF**



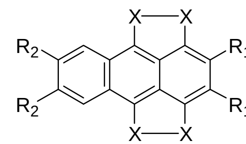
**BDMT-TTeF**



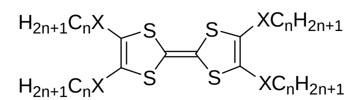
**BET-TTF**



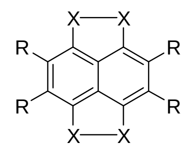
**MDT-TTF**



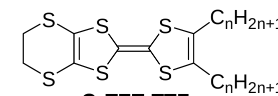
**DMTTA** : X=S, $R_1$=H, $R_2$=Me
**TMTTA** : X=S, $R_1$=$R_2$==Me
**6,7-DMTTA** : X=S, $R_1$=H, $R_2$=Me
**TSA** : X=Se, $R_1$=$R_2$=H
**DMTSA** : X=Se, $R_1$=Me, $R_2$=H
**6,7-DMTSA** : X=Se, $R_1$=H, $R_2$=Me
**TMTSA** : X=Se, $R_1$=$R_2$=Me
**DMTTeA** : X=Te, $R_1$=Me, $R_2$=H



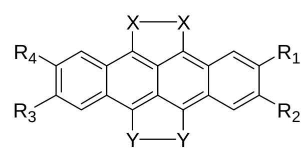
**TTC$_n$-TTF** : X=S
**TSeC$_n$-TTF** : X=Se
**TTeC$_n$-TTF** : X=Te



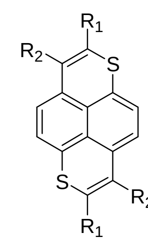
**TTN** : X=S, R=H
**TSN** : X=Se, R=H
**TMTTeN** : X=Te, R=Me



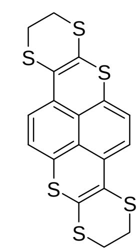
**C$_n$TET-TTF**



**TTT** : X=Y=S, $R_1$=$R_2$=$R_3$=$R_4$=H
**F$_2$TTT** : X=Y=S, $R_1$=$R_2$=$R_3$=$R_4$=H
**TST** : X=Y=Se, $R_1$=$R_2$=F, $R_3$=$R_4$=H
**TTeT** : X=Y=Te,$R_1$=$R_2$=$R_3$=$R_4$=H

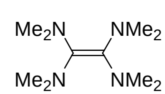


**DTPY** : $R_1$=$R_2$=H
**MSDTPY** : $R_1$=SeMe,$R_2$=H
**MTDTPY** : $R_1$=SMe,$R_2$=H
**Ph$_2$DTPY** : $R_1$=Ph,$R_2$=H
**3,8-(MeO)$_2$DTPY** : $R_1$=H, $R_2$=MeO

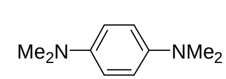


**ETDTPY**

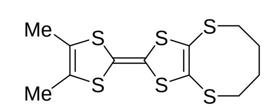
Saito



**TDAE**



**TMPD**



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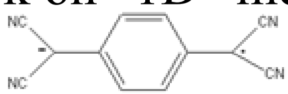


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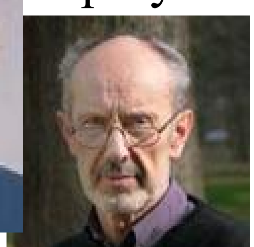

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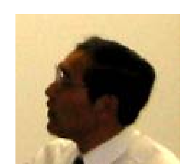
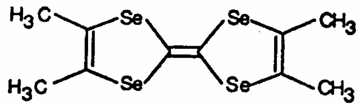


Observed and hinted at ground states

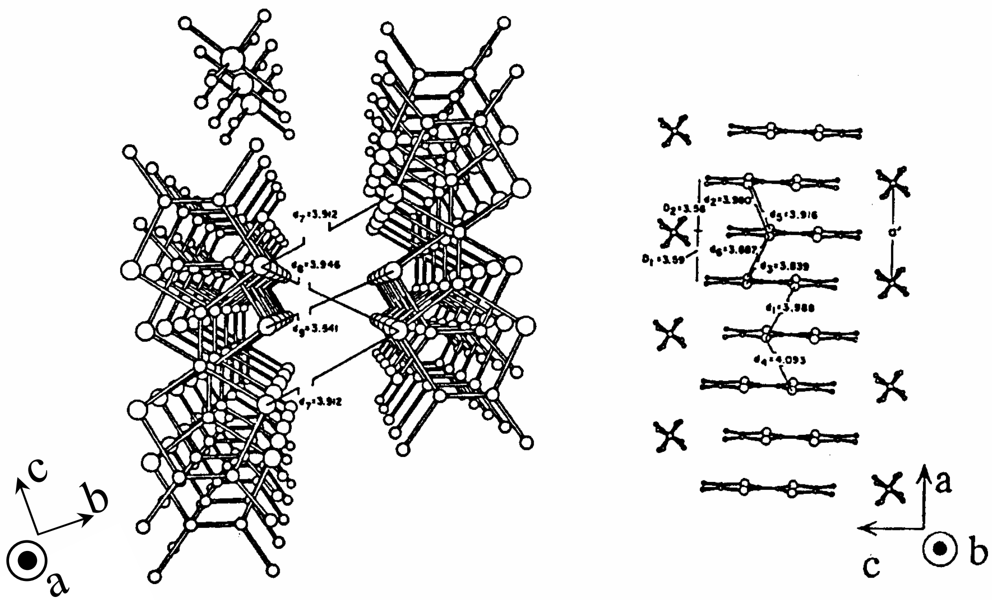
| BEDT-TTF family | $(TMTSF)_2PF_6$ |
|---|---|
| Supercond – singlet | Supercond – triplet? |
| - d-wave? | SDW |
| - LOFF? | CDW |
| Ferromagnetic | Field Induced SDW |
| SDW | Quantum Hall |
| CDW | Fermi-Liquid |
| Quantum Hall? | Non – Fermi, Luttinger? Liq |
| Fermi-Liquid | Mott Insulator? |

# Crystal Structure of Bechgaard Salts $(TMTSF)_2X$

$(TMTSF)_2X$, $X = PF_6^-, ClO_4^-, \ldots$




TMTSF = tetramethyltetraselenafulvalene




Triclinic

$$\alpha = 83.39°, \beta = 86.27°, \gamma = 71.01°$$

$$a = 7.297\,\mathring{A}, b = 7.711\,\mathring{A}, c = 13.522\,\mathring{A}$$

- Highly anisotropic

$\sigma_a : \sigma_b : \sigma_c = 1 : 10^{-2} : 10^{-5}$

$4t_a : 4t_b : 4t_c = 1 : 0.1 : 0.003$ (eV)

$\sigma_i \sim t_i^2$

- Good metal

$\rho \sim 1\ \mu\Omega$cm at 4K

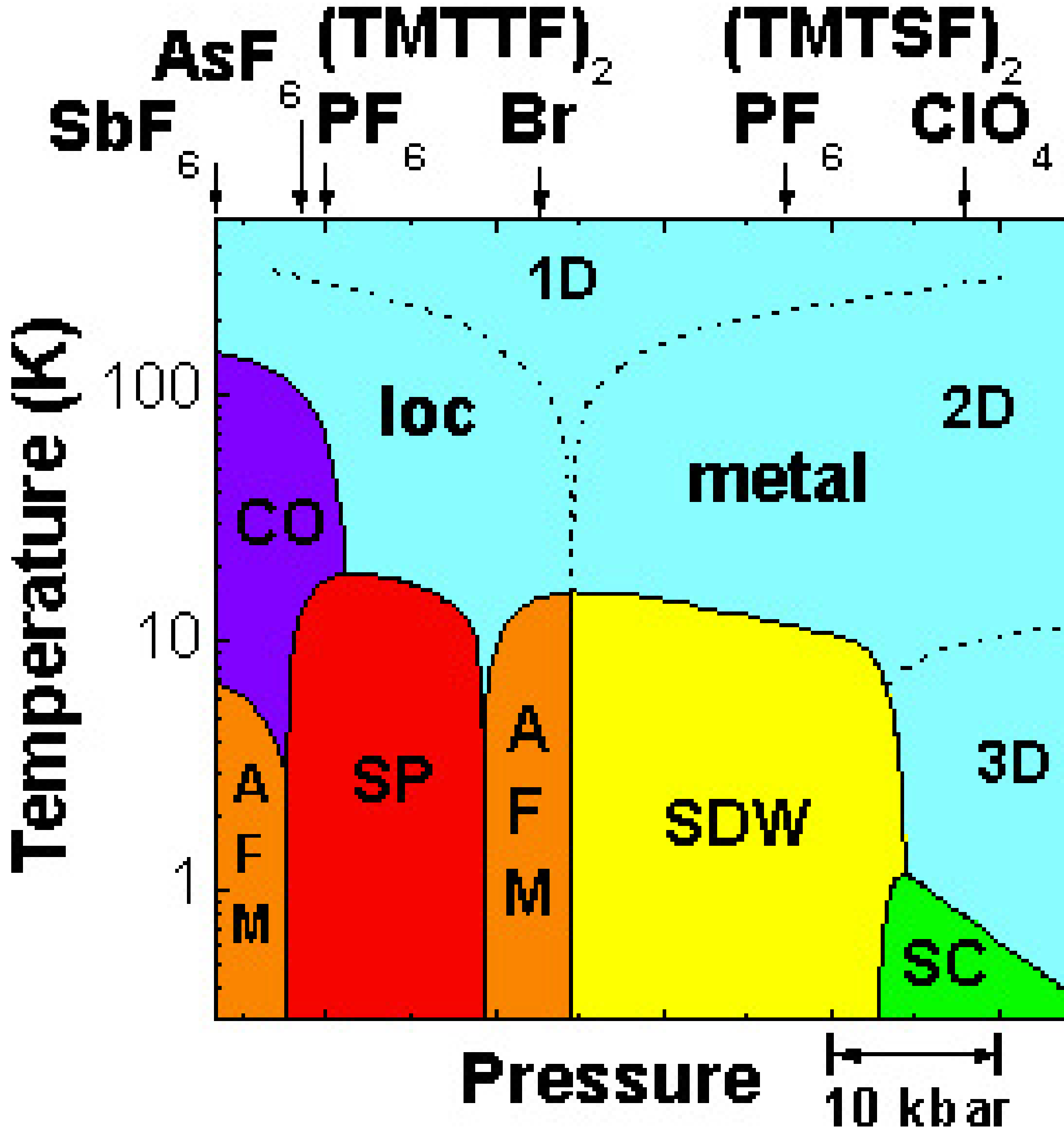
($\rho$ (Cu) ~ $1\mu\Omega$cm at 300K).

- Extremely clean

*$l$~10$\mu$ at 1K,   $h/\tau$~0.1K at 1K*

- ¼ Filled, Slightly Dimerized

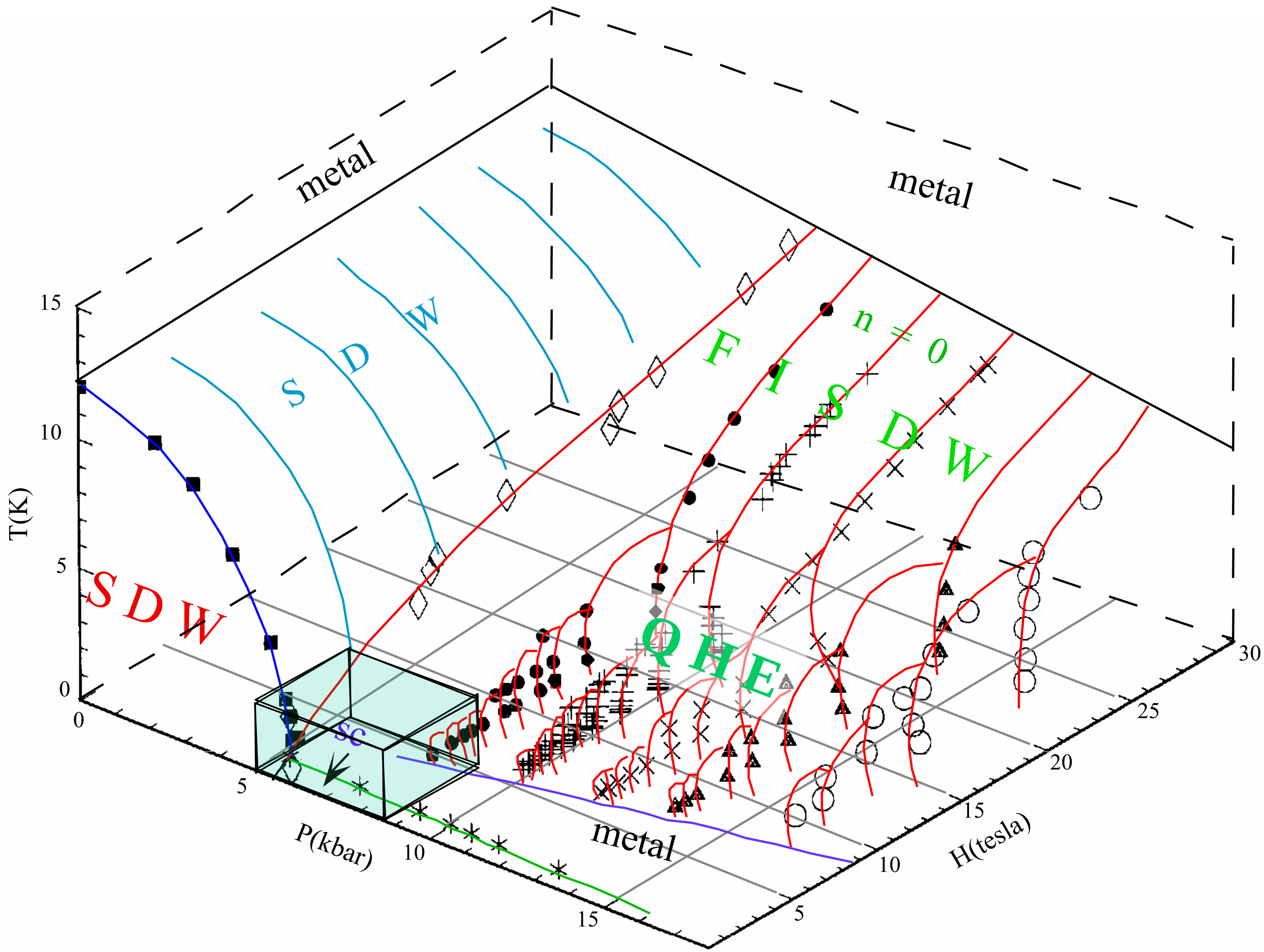
Single chain has charge gap.

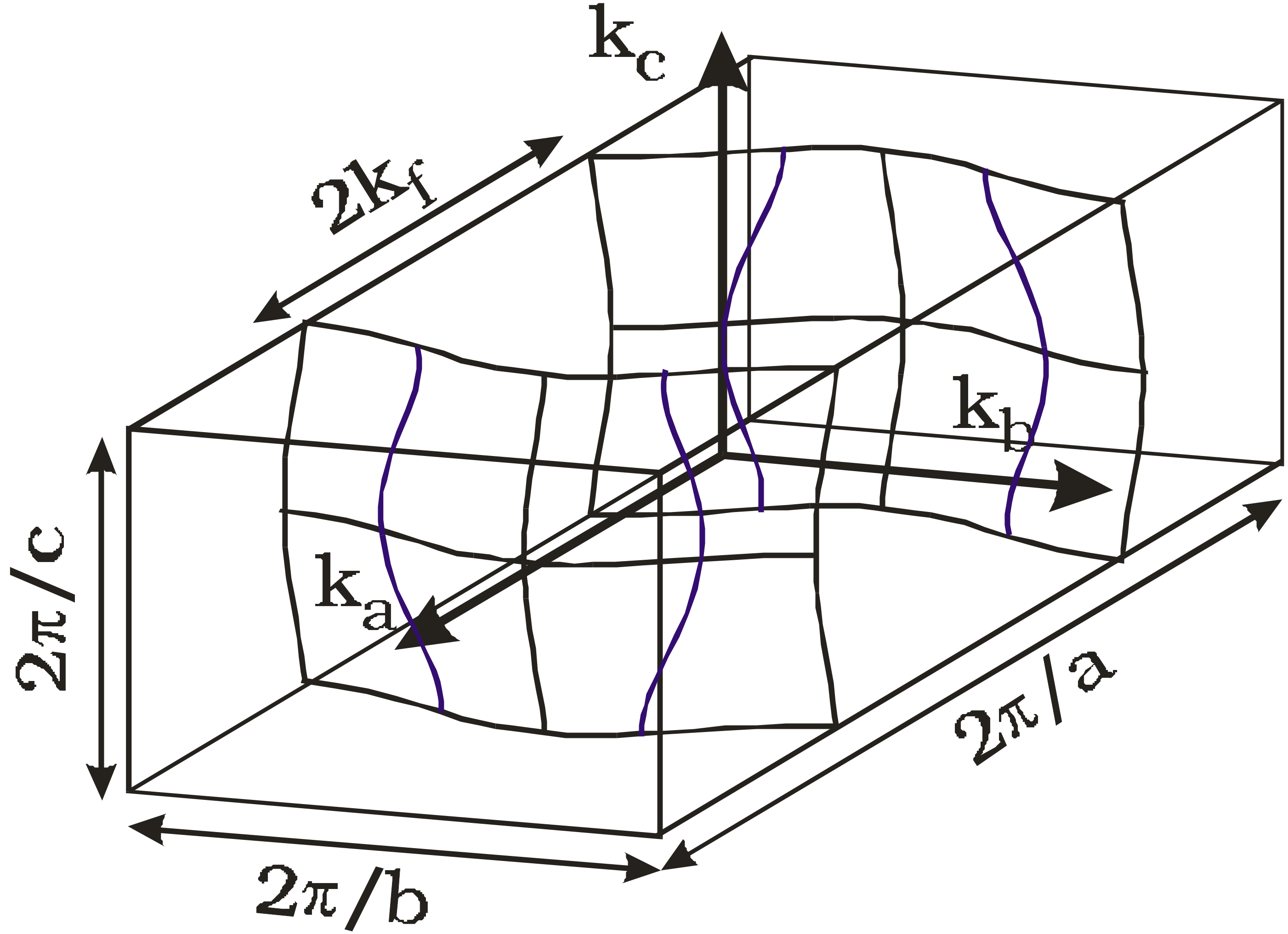


(TMTTF)2
(TMTSF)2
AsF6
SbF6
PF6
Br
PF6
ClO4
1D
2D
3D
loc
metal
CO
SP
AFM
AFM
SDW
SC
100
10
1
Temperature (K)
Pressure
10 kbar

# Phase Diagram $(TMTSF)_2PF_6$

Woowon Kang

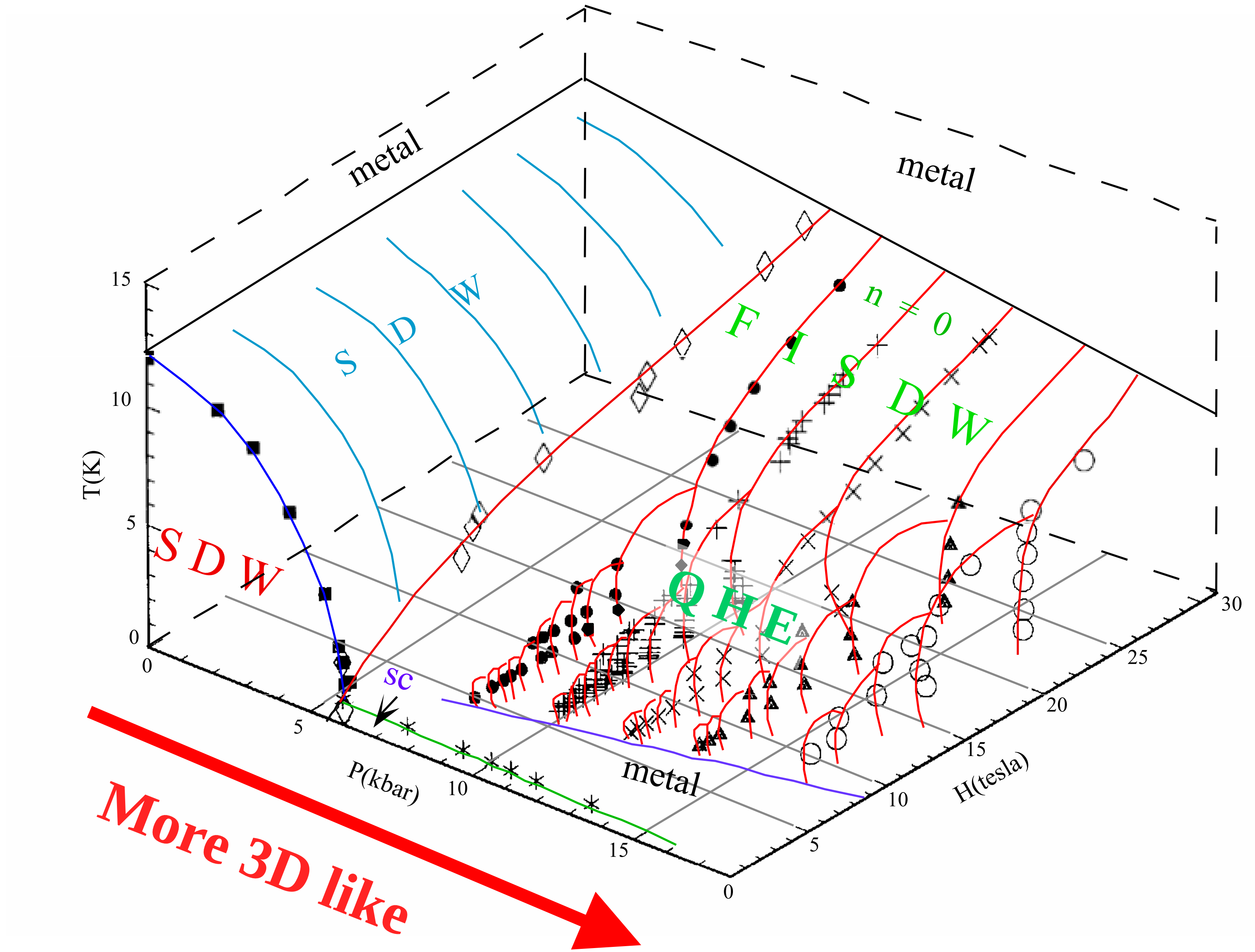





**1D metals are unstable – Fermi Surfaces Nest**

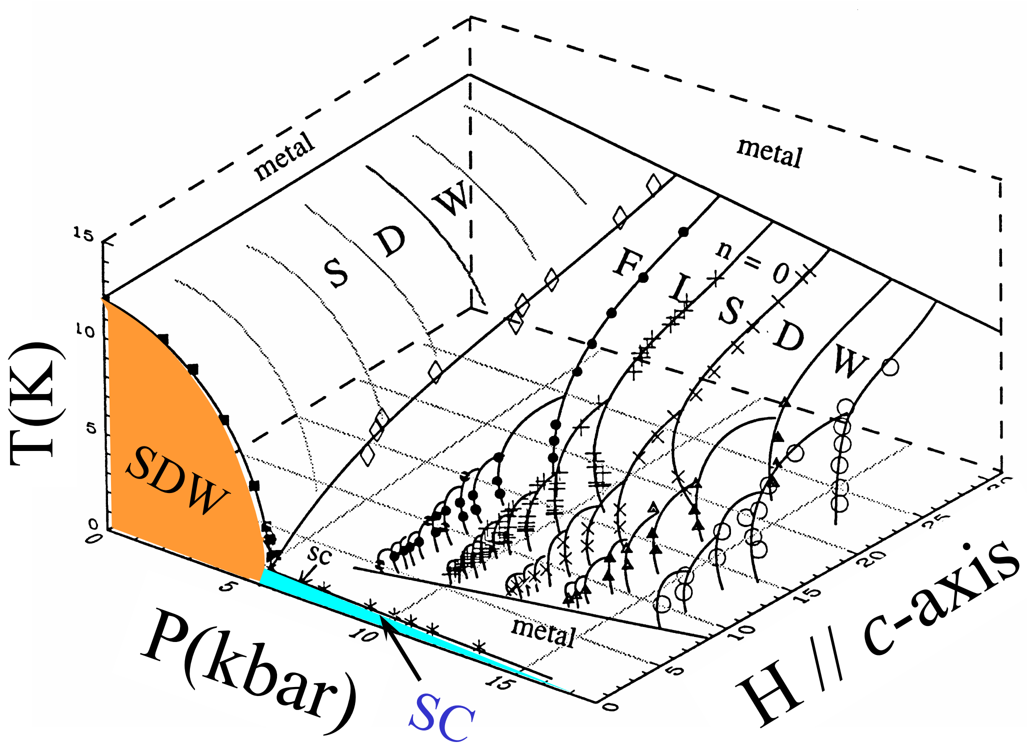
**Interchain hopping – warped Fermi Surface – regain metal**

**Pressure increases interchain hopping – more 3D**



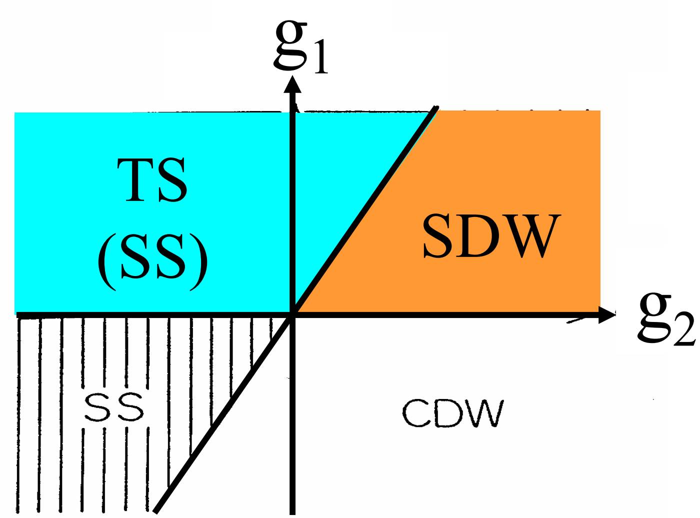
metal
metal
S D W
F I S D W
n = 0
QHE
S D W
sc
metal
T(K)
15
10
5
0
0
5
P(kbar)
10
15
0
5
10
15
20
25
30
H(tesla)
More 3D like

# 3D (P,H,T) phase diagram of $(TMTSF)_2PF_6$




Insulator-Superconductor Bechgaard, Jerome 1979

First guess from g-ology




1D-electron gas phase diagram (“g-ology”).
J. Solyom, Adv. Phys 28, 201 (1979)

# Singlet or Triplet ?

## Radiation damage experiments

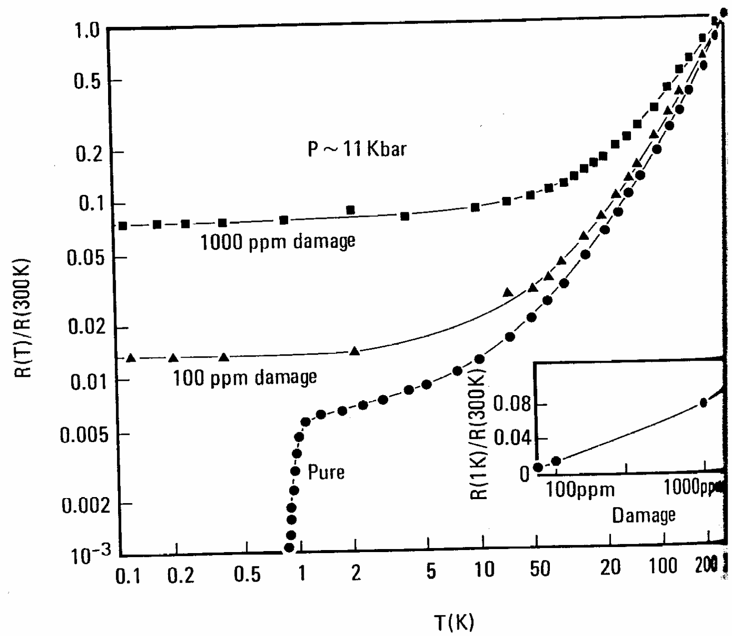



FIGURE 7 Temperature dependence of resistivity of $(TMTSF)_2 PF_6$ at 11 kbar pressure for various amounts of radiation induced damage. Insert shows damage dependence of resistivity at T=1K.

## Resistive upper critical fields

P.M. Chaikin et al. / Superconductivity and transitions in $(TMTSF)_2X$

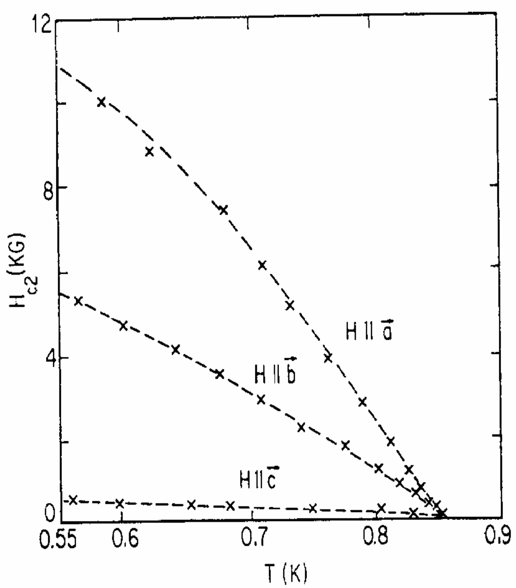



Fig. 1. Anisotropic critical field for $(TMTSF)_2ClO_4$. Fields were varied in three perpendicular directions to attain the maximum critical field along the *a* axis.

$H_p$=16 KG

Non s-wave

Singlet (s,d-wave)?

M.Y. Choi *et.al.*, Phys. Rev. B25, 6208 (1982)

P.M. Chaikin, M.Y. Choi and R.L. Greene, Mag. Mat. **31**, 1268 (1983)

# Proton spin-lattice relaxation experiments

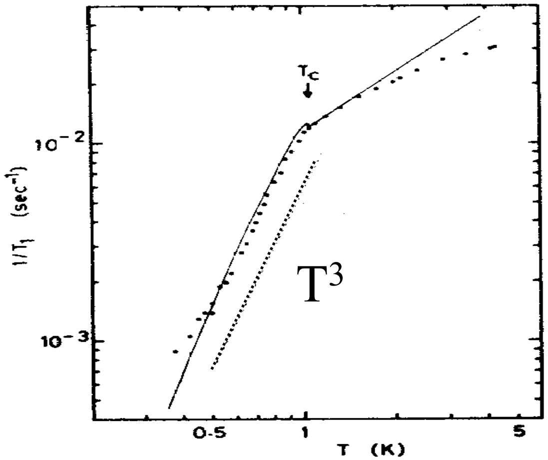



Fig. 3. Temperature dependence of $1/T_1$ of protons at zero field. The solid curve shows the calculation for the $s2$ or $t2$ state in ref. 23 normalized to the experimental data at $T_c = 1.06$ K. The dashed line indicates the $T^3$ dependence.

M. Takigawa et.al.,
J.Phys. Soc. Jpn. 56, 873 (1987)

Non S-wave
(line node on FS)

VOLUME 79, NUMBER 11 PHYSICAL REVIEW LETTERS 15 SEPTEMBER 1997

Belin et. al.

## Thermal conductivity

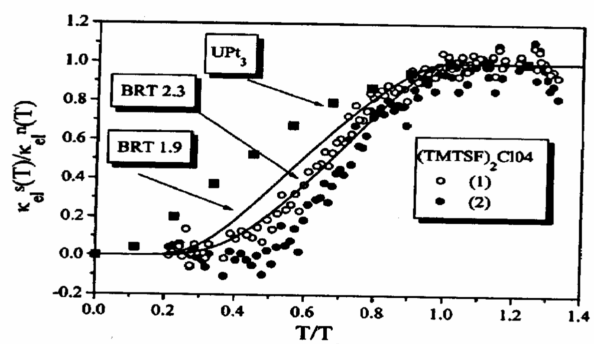


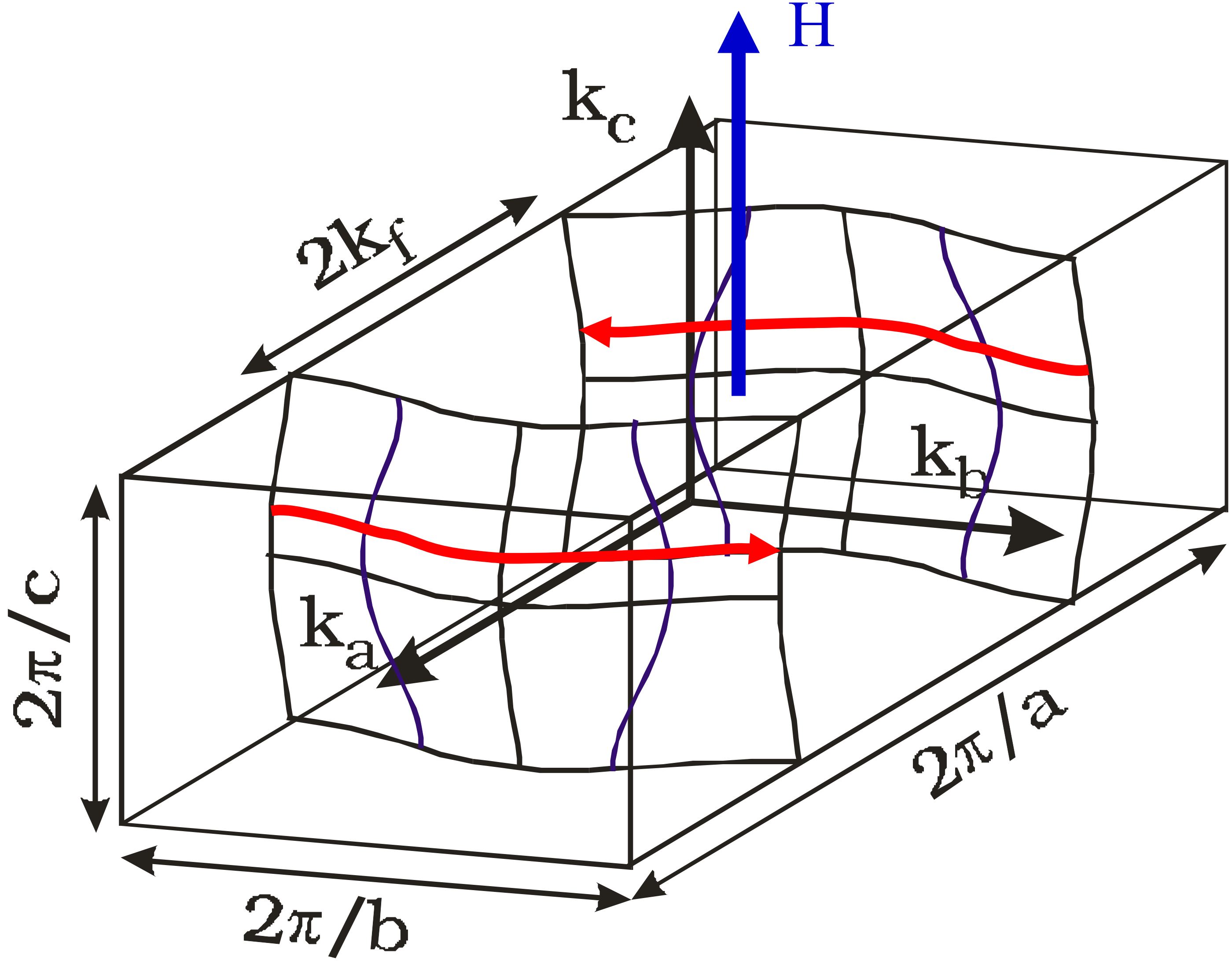

FIG. 3. Normalized electronic thermal conductivity vs normalized temperature for $(TMTSF)_2ClO_4$ in two different scenarios (see text). The results are compared with the predictions of BRT theory for two different ratios of $\Delta(0)/k_BT_c$ and with the published data on $UPt_3$ for a heat current along the $b$ axis.

S-wave (a finite gap)
(No node on FS)

# Singlet – Triplet Unresolved after ~ 12 years in 1980's

But People discovered unusual things in Magnetic Fields

# Electron Orbits for a Magnetic Field along **c**

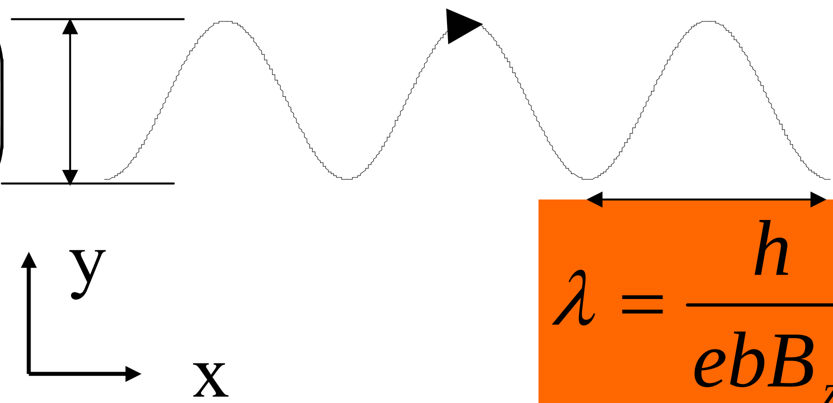


# One-Dimensionalized by Magnetic field

$$v = \frac{1}{\hbar}\frac{\partial \epsilon}{\partial k} \qquad \frac{dk}{dt} = \frac{e}{\hbar}(v \times B) \qquad \frac{dk}{dt} = \frac{e}{\hbar}\left(\frac{dr}{dt} \times B\right)$$

Real Space

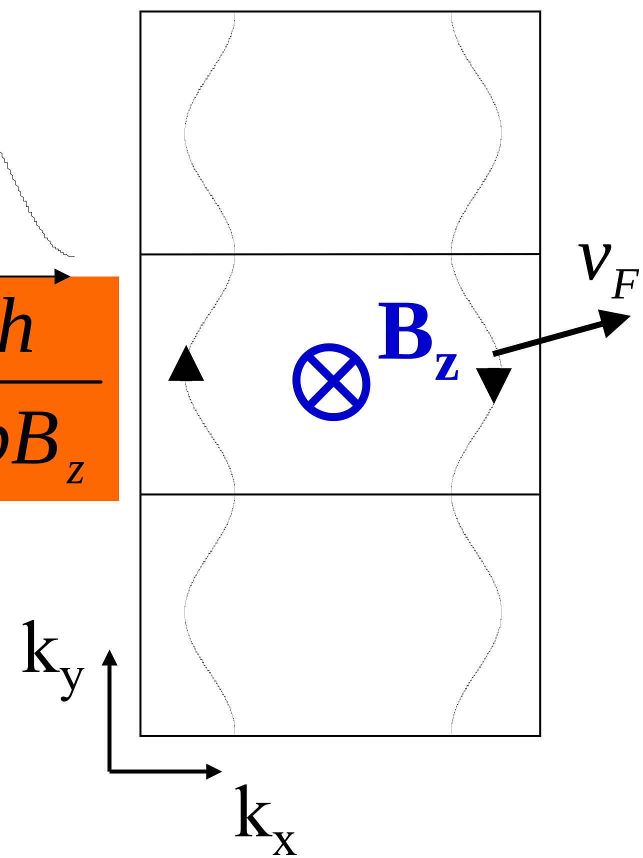
$$w_b = b\left(\frac{4t_b}{ev_F B_z}\right)$$




$$\lambda = \frac{h}{ebB_z}$$

$$\omega_b = \frac{ev_f bB_z}{\hbar}$$

k space




Chaikin, Azbel, Holstein, '83

## The Standard Model

Gor'kov, Lebed

Chaikin

Heritier, Montambaux, Lederer, Poinblanc

Yamaji

Maki, Virosztek, Chen, Chang

Azbel, Bak, Chaikin

Yakovenko

- Unnested Open Orbit Fermi Surface
- H makes system more 1-D

  ⇒Unstable to density wave

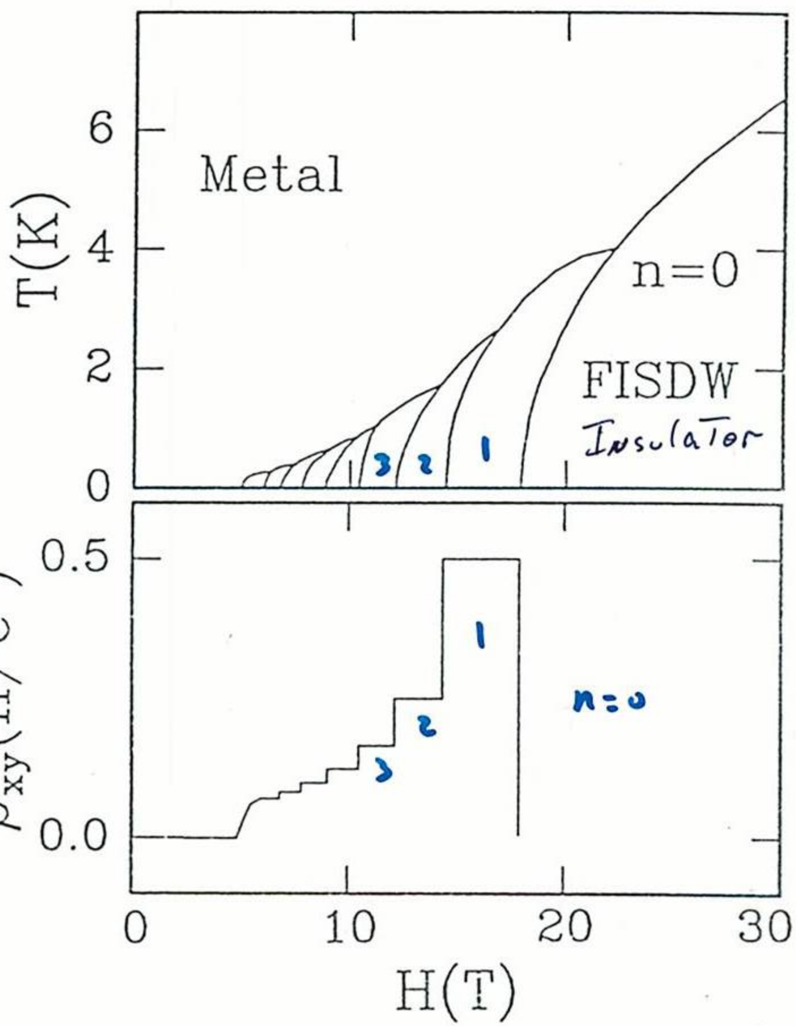
But nesting at $q=2k_F$ +/- $nG$, $G=2\pi/\lambda$

⇒Spectrum with multiple gaps

⇒Cascade of transitions

⇒Quantum Hall $\rho_{xy} = h/ne^2$

# Cascade of Field Induced Spin Density Waves

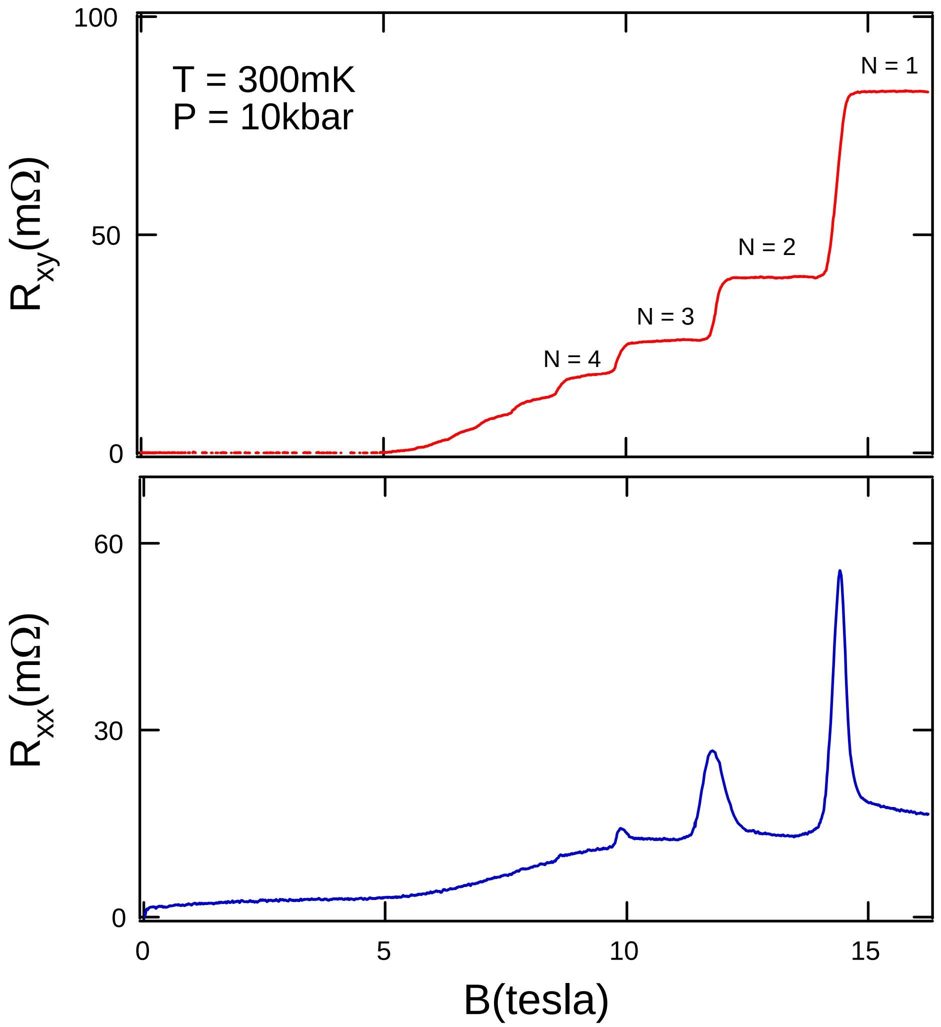


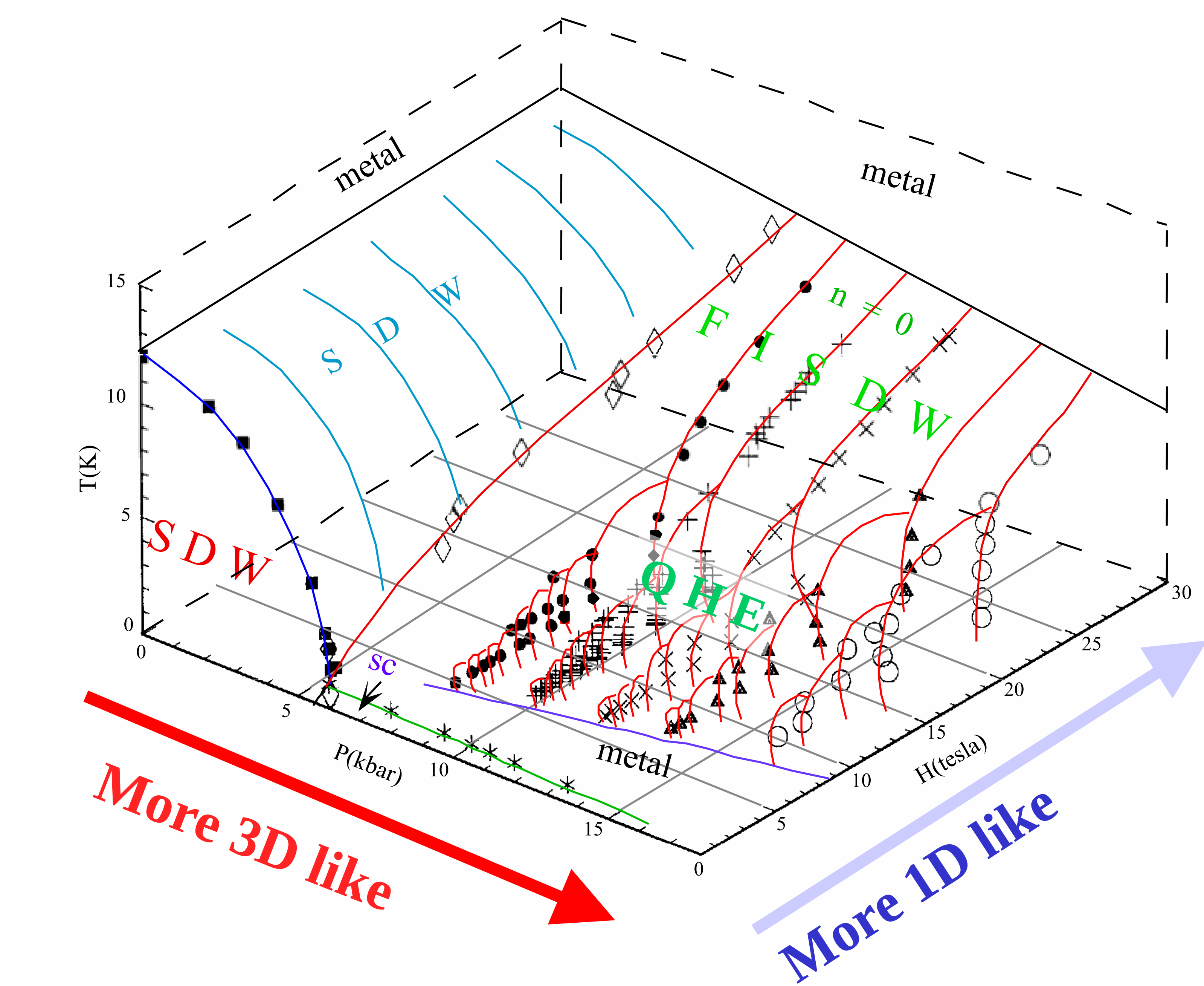

$$\rho_{xy} = \frac{h}{2 n e^2}$$

with Quantum Hall Effect

Woowon Kang

# Integer Quantum Hall Effect in $(TMTSF)_2PF_6$



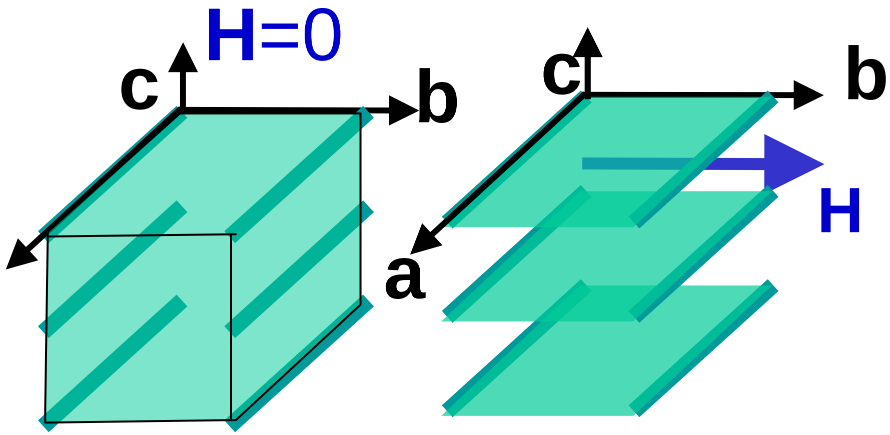


metal
metal
S D W
F I S D W
n = 0
S D W
QHE
sc
metal
T(K)
P(kbar)
H(tesla)
0
5
10
15
0
5
10
15
0
5
10
15
20
25
30
More 3D like
More 1D like

Main lesson:

Magnetic field perpendicular to the chains reduces electronic dimension

Does this decouple chains/planes?

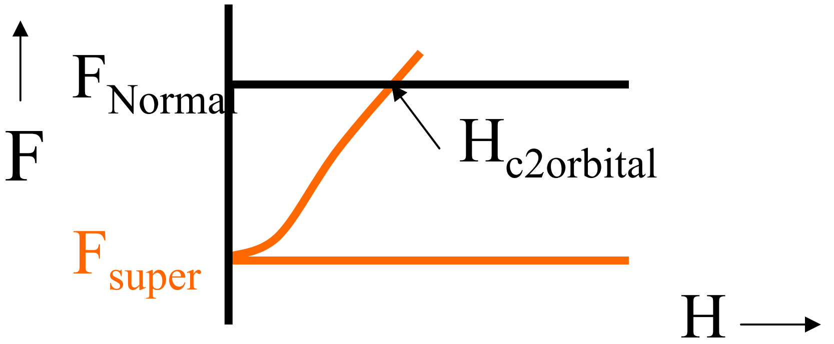



3D coherent Coherent planes

# Two Contributions to Magnetic Critical Field - Orbital and Spin

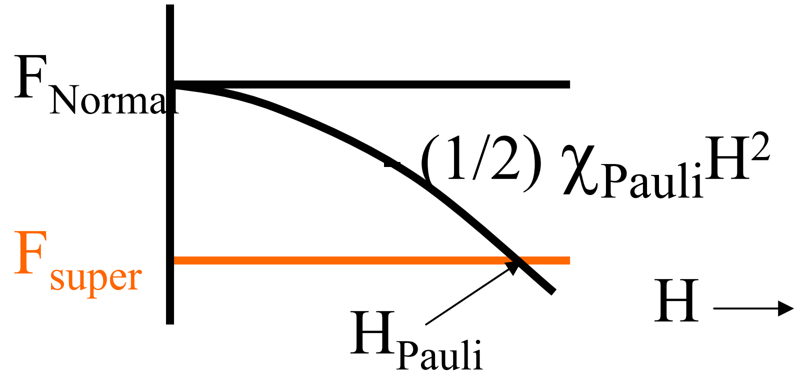
Orbital term derives from Field Expulsion
e.g. Meisner Effect

Need currents to expel field
$j \sim H$, $\Delta F \sim K.E. \sim j^2 \sim H^2$

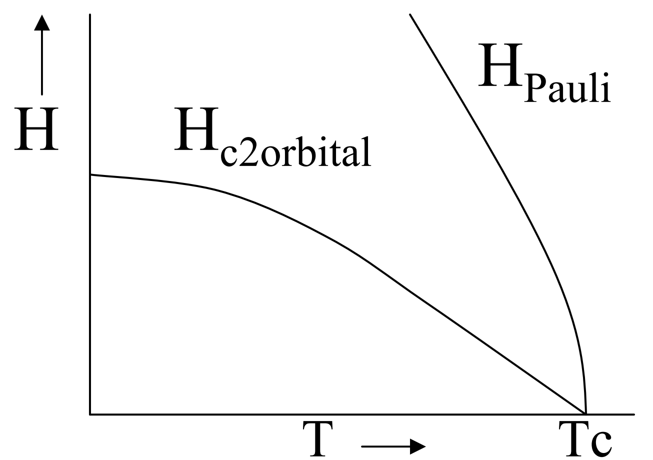



Spin derives from susceptibility
of spin paired state

$\Delta F \sim -(1/2)\Delta\chi H^2$




Usually $H_{c2orbital} << H_{Pauli}$



# Clogston-Pauli Limit to $Hc_2$

Normal Metal

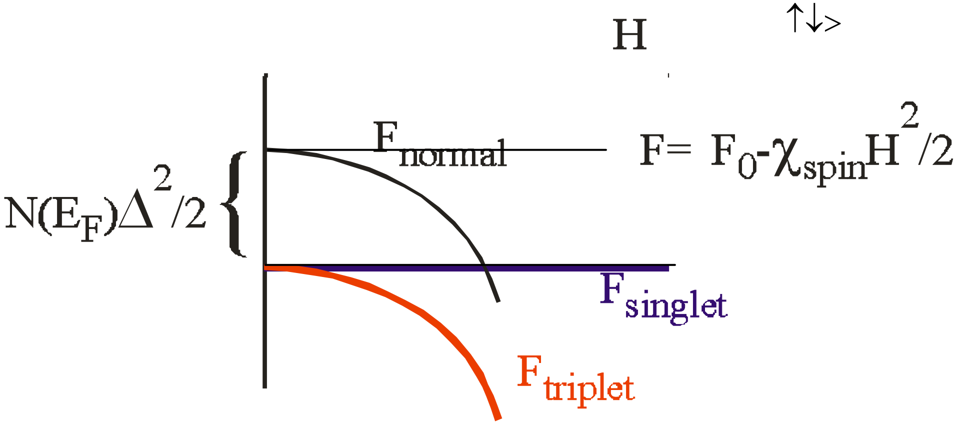
↑ ↓ $\chi_{spin} = \chi_{Pauli} = \mu_0^2 N(E_F)$

Singlet Superconductor

↑↓ $\chi_{spin} = 0$

Triplet Superconductor

↑↑ ↓↓ $\chi_{spin} = \chi_{Pauli}$



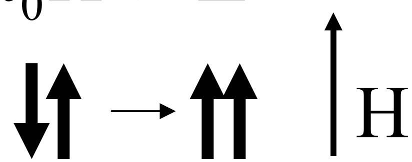

$$N(E_F)\Delta^2/2 = \chi_P H_P^2/2 = 2N(E_F)\mu_0^2 H_P^2/2$$

$$\Delta = 3.52 k_B Tc = \sqrt{2}\mu_0 H_P$$

$H_P = 1.84\ Tc$ (Tesla/K)

Note: When

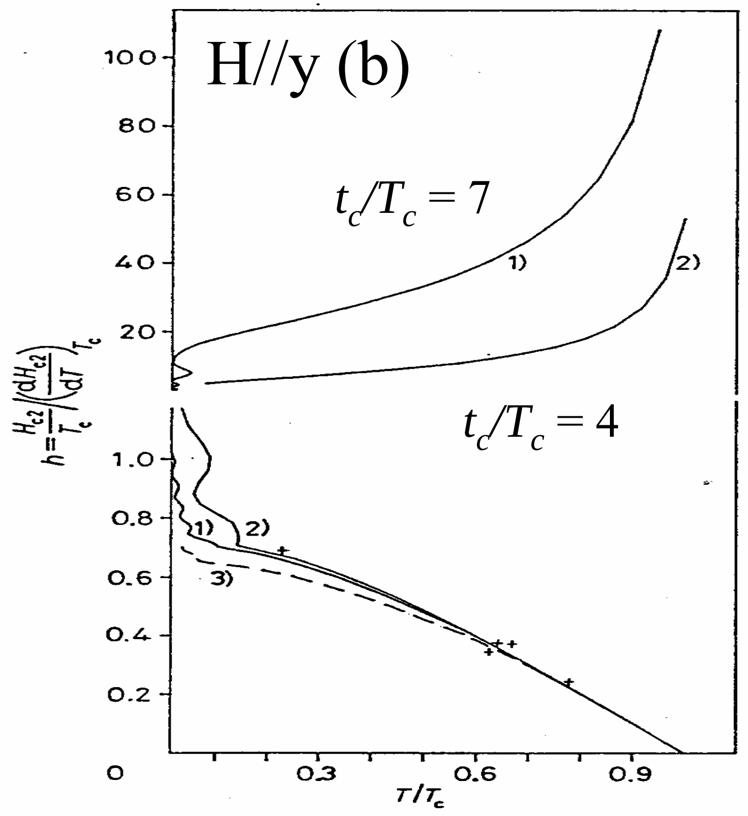
$$\mu_0 H > \Delta$$

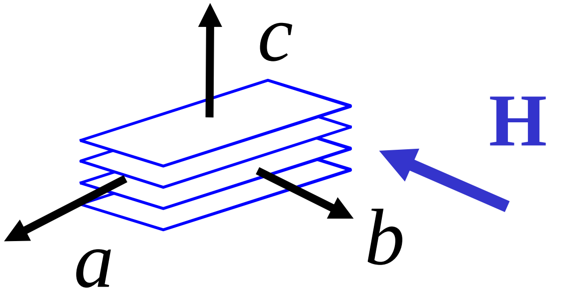



single pairs break

# A.G. Lebed'/DMS's proposal.
# Field-induced dimensional crossover quenches orbital pair breaking effect

A.G. Lebed', JETP Lett., 44, 114 (1986)
N. Dupuis, G. Montambaux and C.A.R. Sa de Melo, PRL., 70, 2613, (1993)



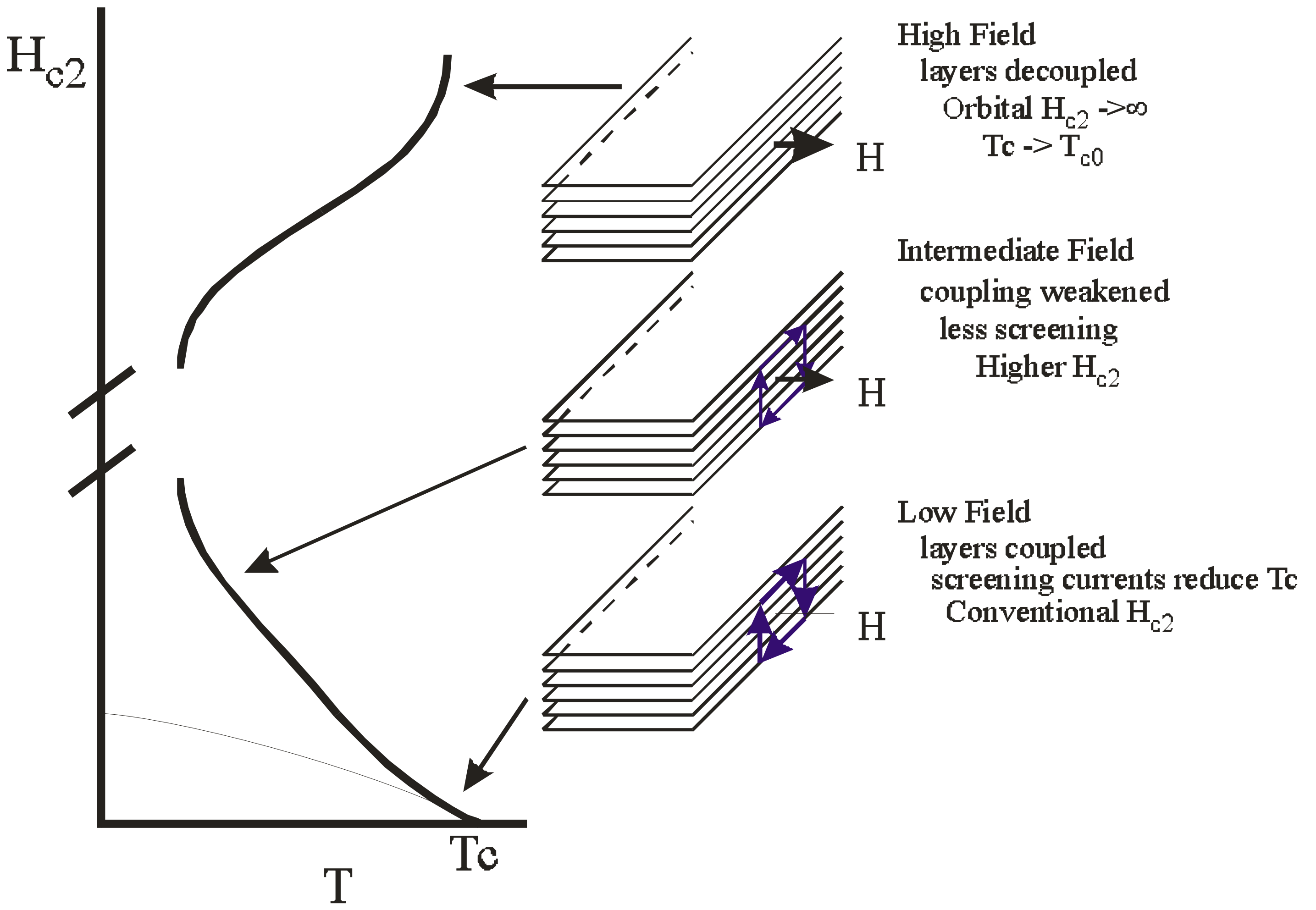

Test for the triplet
superconducting pairing?

$$H_p = \frac{\Delta}{\sqrt{2}\mu_o} = 1.84T_c[Tesla]$$

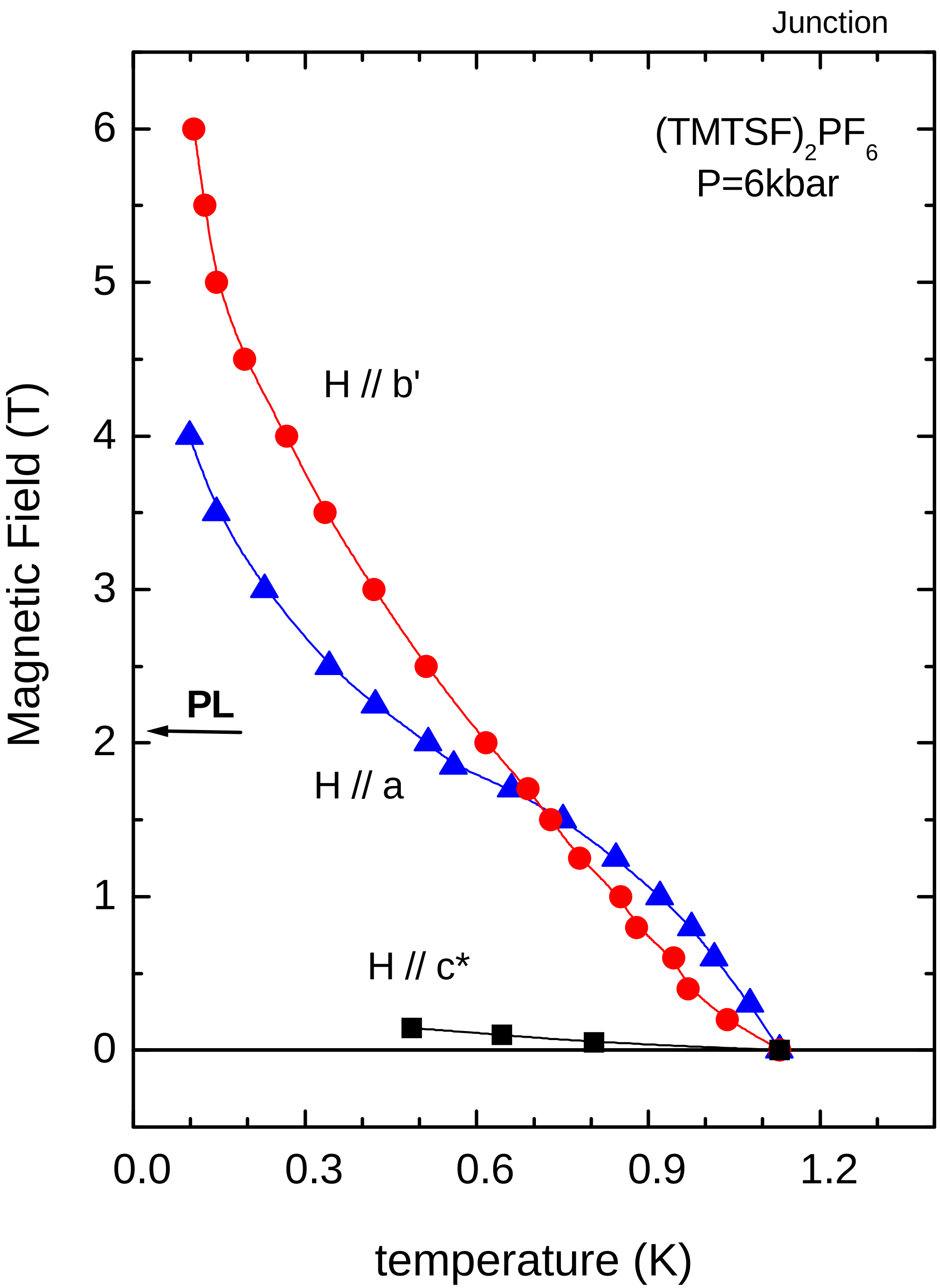
L.I. Burlarchkov, L.P. Gor'kov and A.G. Lebed'
Europhys. Lett., 4 941 (1987)

# Critical Field with decoupling

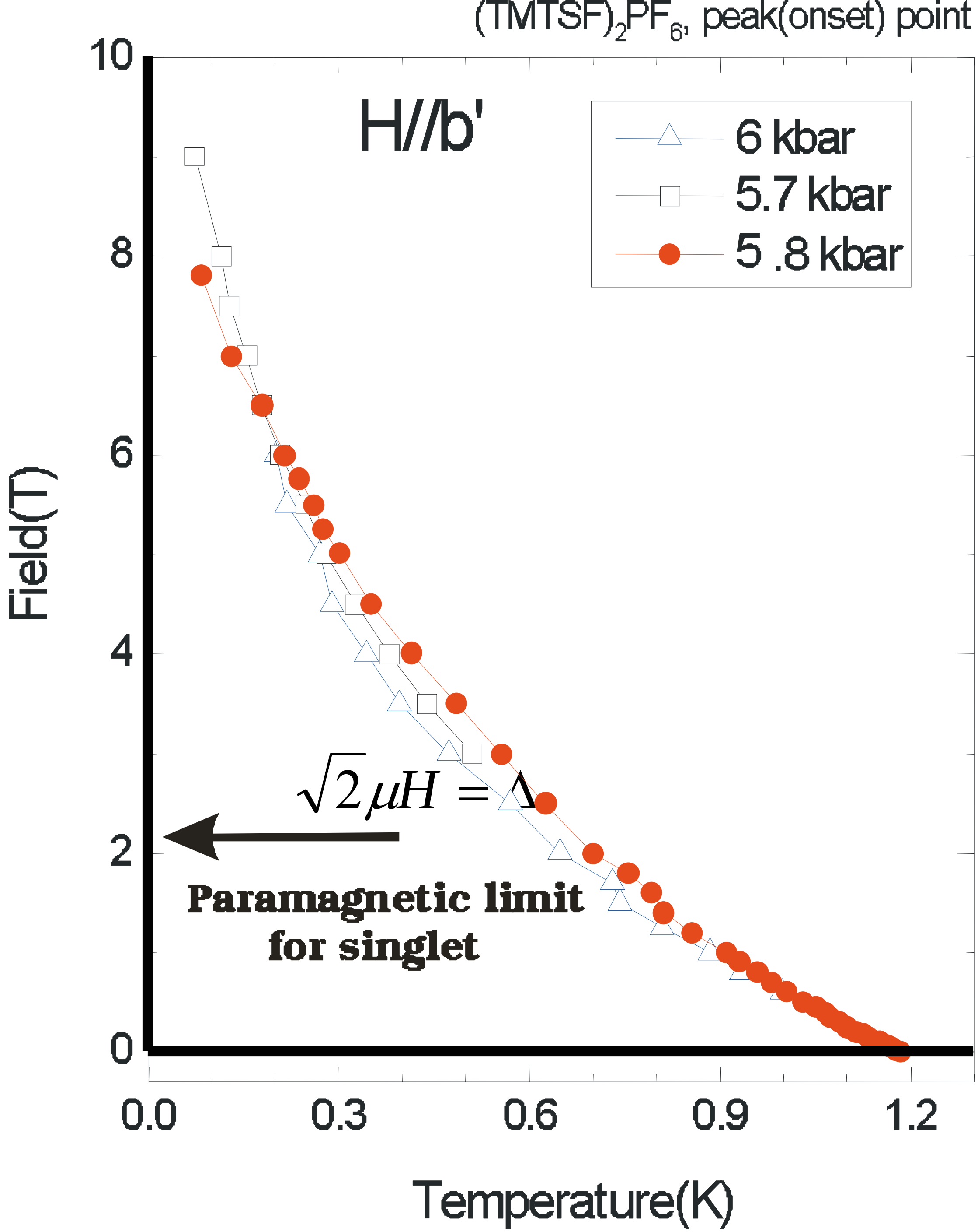
## ala Lebed, Montambaux, Dupuis, Sa de Melo



Injae Lee



Junction
(TMTSF)$_2$PF$_6$
P=6kbar
H // b'
H // a
H // c*
PL
Magnetic Field (T)
temperature (K)
0
1
2
3
4
5
6
0.0
0.3
0.6
0.9
1.2



(TMTSF)2PF6, peak(onset) point
H//b'
6 kbar
5.7 kbar
5 .8 kbar
$\sqrt{2}\mu H = \Delta$
Paramagnetic limit
for singlet
Field(T)
Temperature(K)
0
2
4
6
8
10
0.0
0.3
0.6
0.9
1.2


Injae Lee

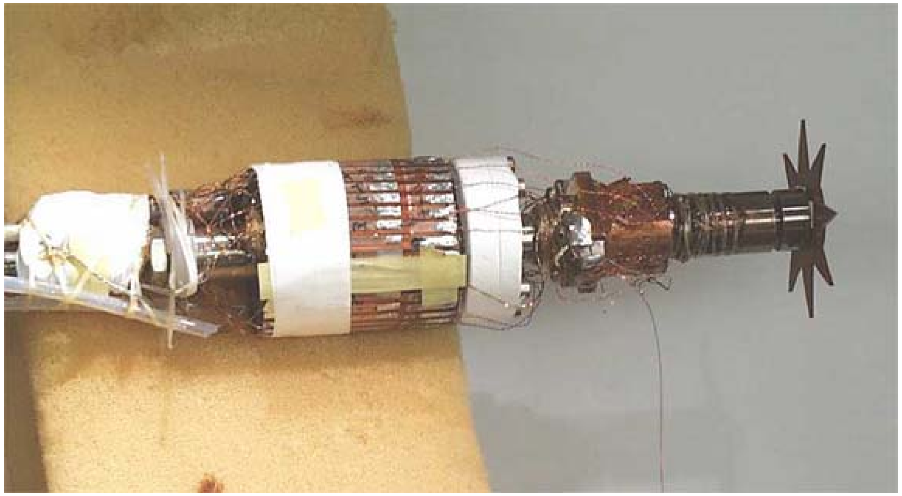
$H_{C2} > 4 \times H_{Pauli}$ ***proves*** triplet (equal spin paired)

$\uparrow\uparrow$ *or* $\downarrow\downarrow$

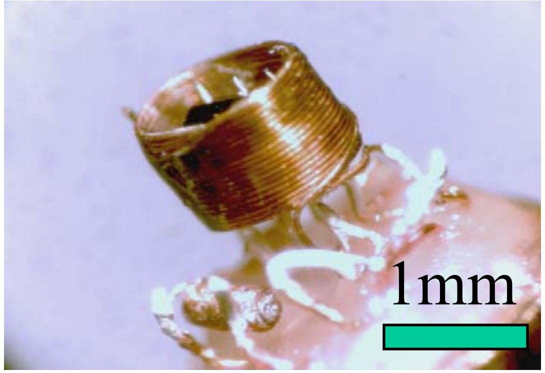
But people are more used to seeing NMR Knight Shift

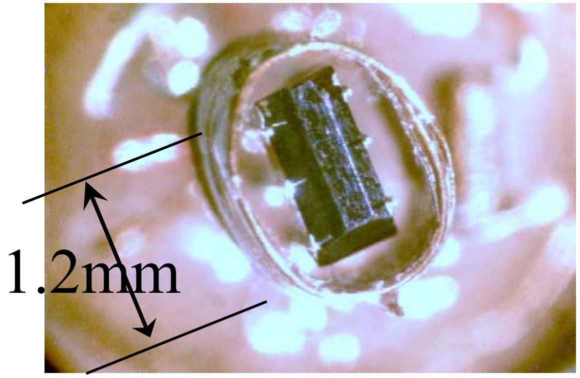
# Setup for $^{77}Se$ NMR Knight Shift experiments

- Dilution temperature (0.03 K)
- High pressure (7 kbar)
- Precise angular alignment (resolution: 0.0025°)
- Simultaneous NMR and transport measurements

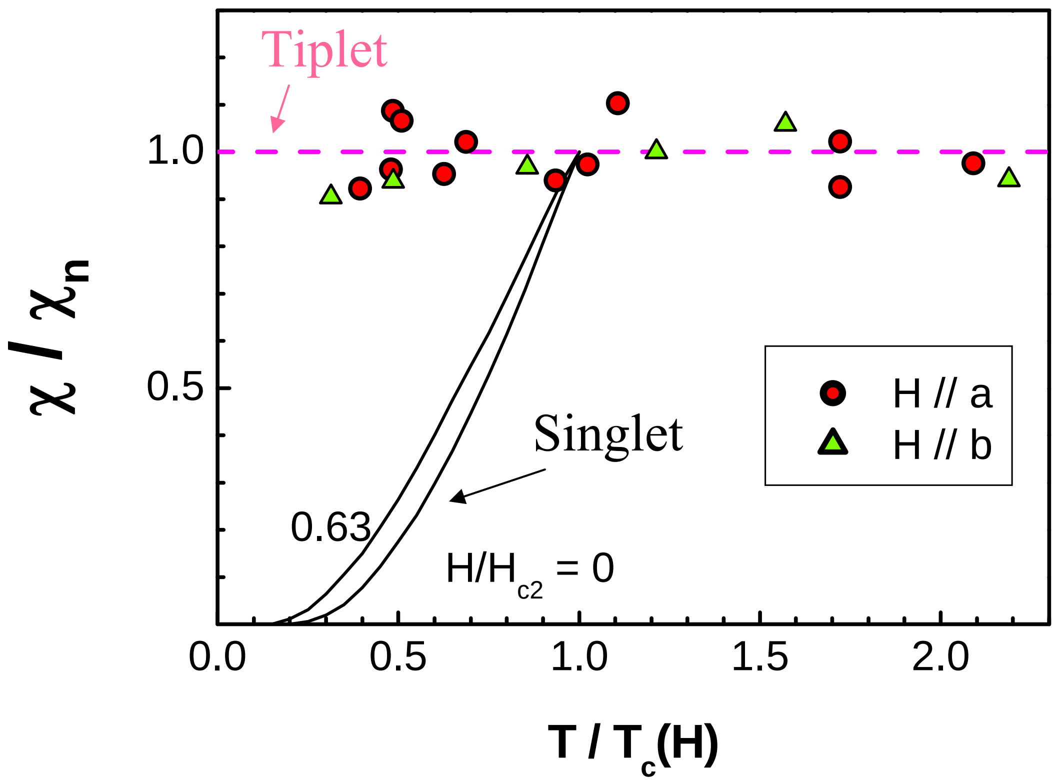


Miniature pressure cell mounted on the bottom of mixing chamber



# Spin susceptibility in $(TMTSF)_2PF_6$



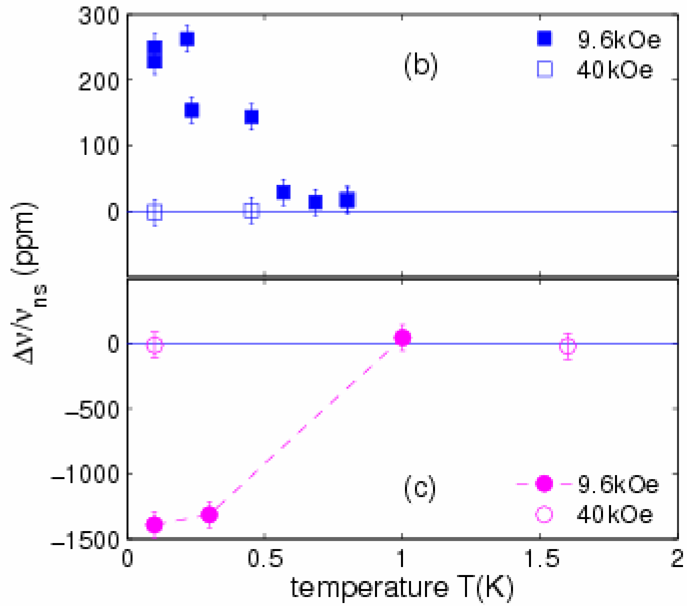

$$\frac{\chi}{\chi_n} = \frac{\langle \omega \rangle - \overline{\langle \omega \rangle}_n}{Ks}$$

P. Fulde and K. Maki,
Phys. Rev. B139, A788 (1965)

**I.J. Lee et al., PRL, 88, 17004 (2002)**

$(H=2.38T)/(H_{c2}(0)=5T) \sim 0.5$ for H // b
$(H=1.43T)/(H_{c2}(0)=3.4T) \sim 0.4$ for H // a

Spin triplet superconductivity?




On the superconducting state of the organic conductor (TMTSF)2ClO4

J. Shinagawa,1 Y. Kurosaki,1,2 F. Zhang,1 C. Parker,1,3
S. E. Brown,1 D. J´erome,4 J. B. Christensen,5 and K. Bechgaard5

(Dated: April 9, 2007)

(TMTSF)2ClO4 is a quasi-one dimensional organic conductor and superconductor with Tc = 1.4K, and one of at least two Bechgaard salts observed to have upper critical fields far exceeding the paramagnetic limit. Nevertheless, the 77Se NMR Knight shift at low fields reveals a decrease in spin susceptibility s consistent with singlet spin pairing. The field dependence of the spin-lattice relaxation rate at 100mK exhibits a sharp crossover (or phase transition) at a field Hs ~ 15kOe, to a regime where s is close to the normal state value, even though Hc2 ≫ Hs.

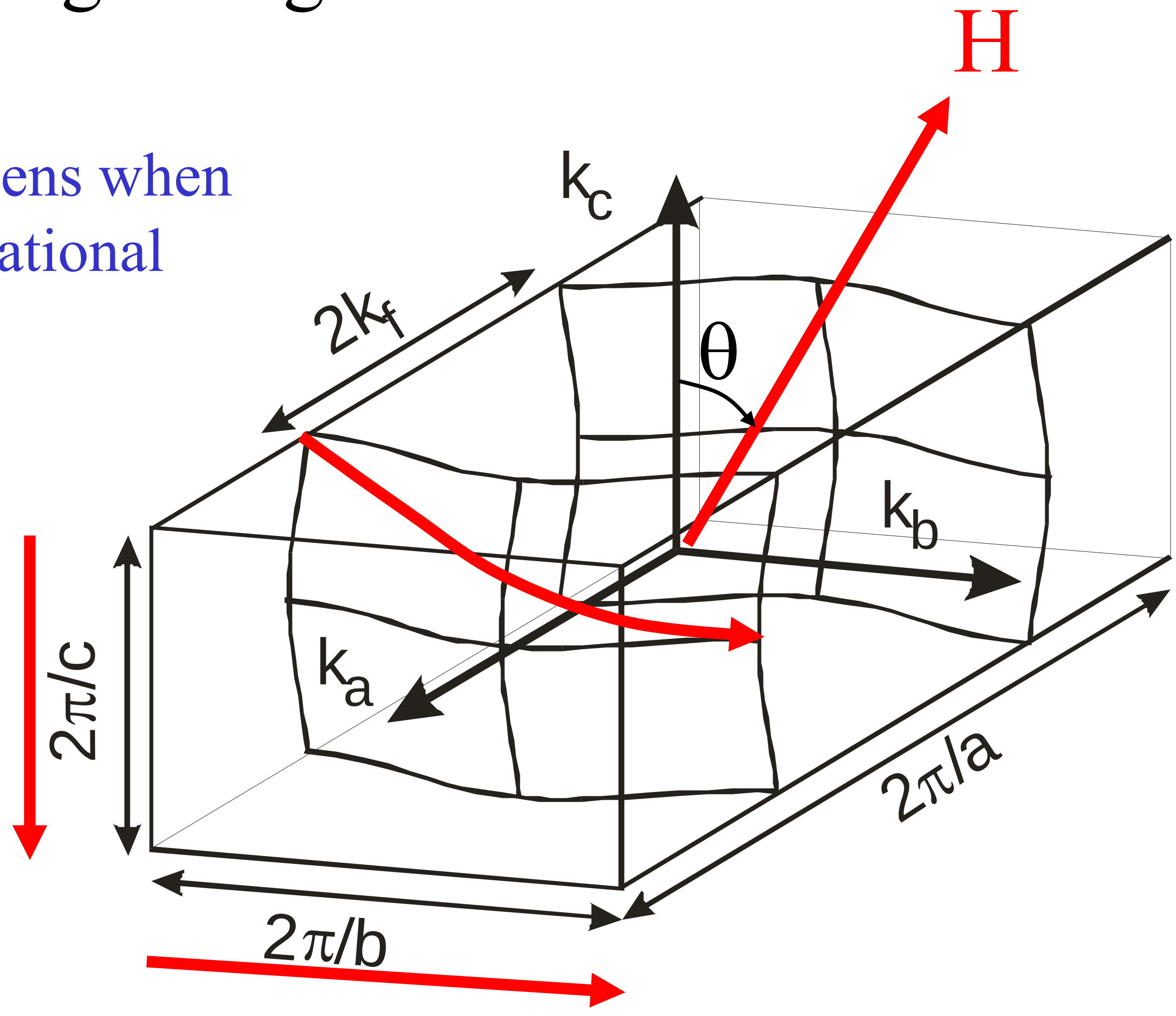
But at low field there is a Knight Shift shift?

# Back to Magnetic Field Induced Decoupling/Decoherence

# Lebed's magic Angles

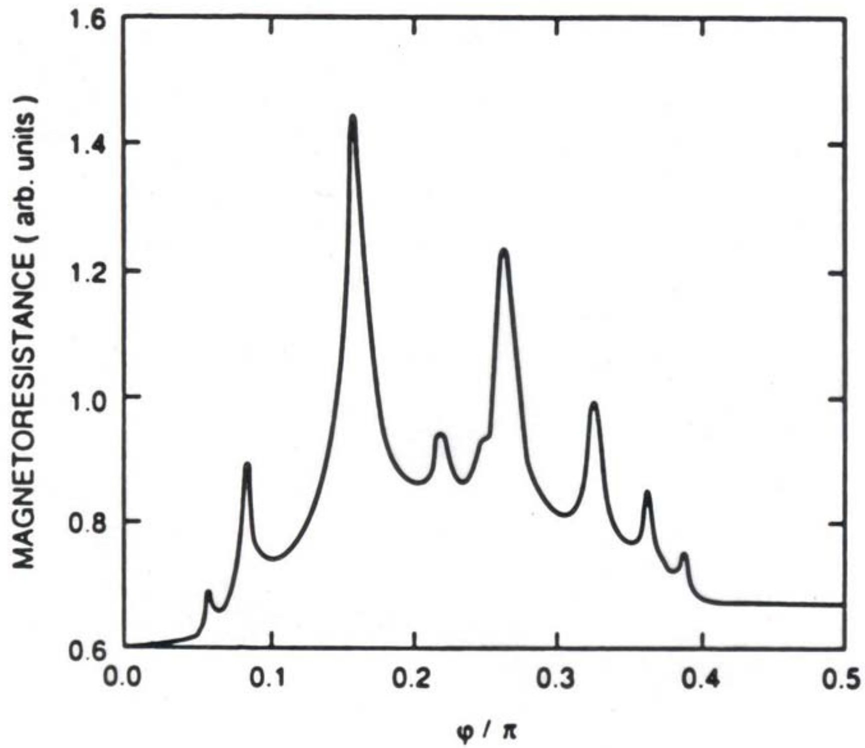
Something happens when
$\omega_b/\omega_c = p/q$ rational

$\omega_c = ev_F Hb\sin(\theta)/h$




$\omega_b = ev_F Hb\cos(\theta)/h$

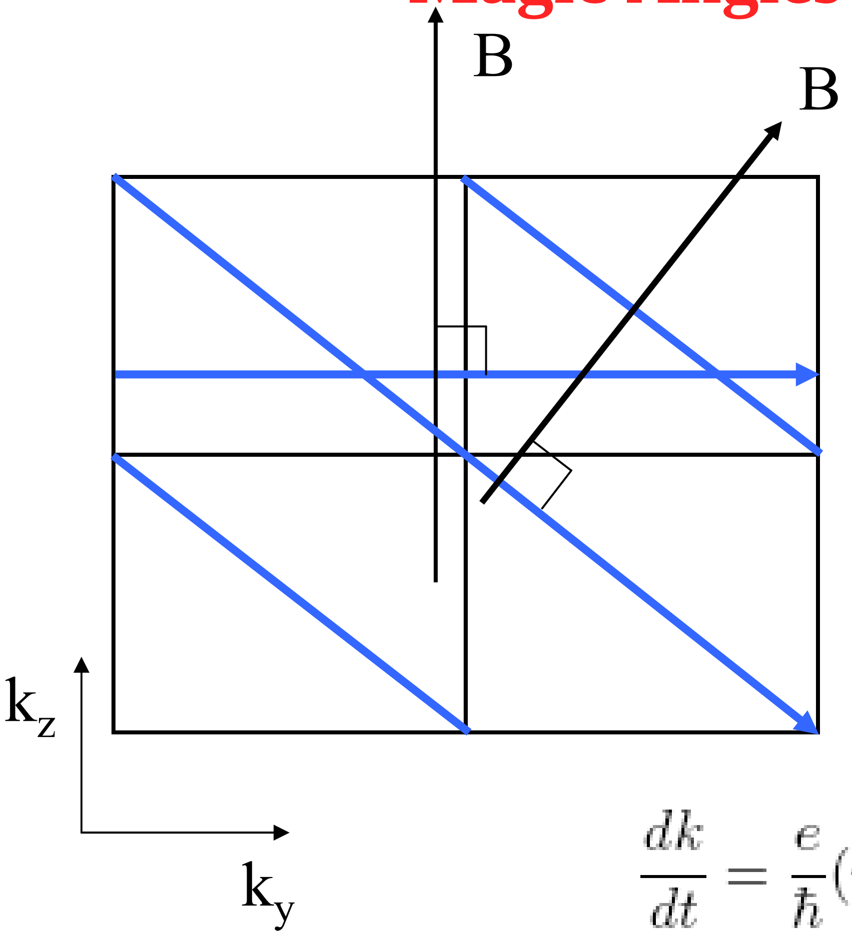
# Lebed Magic Angle Effects



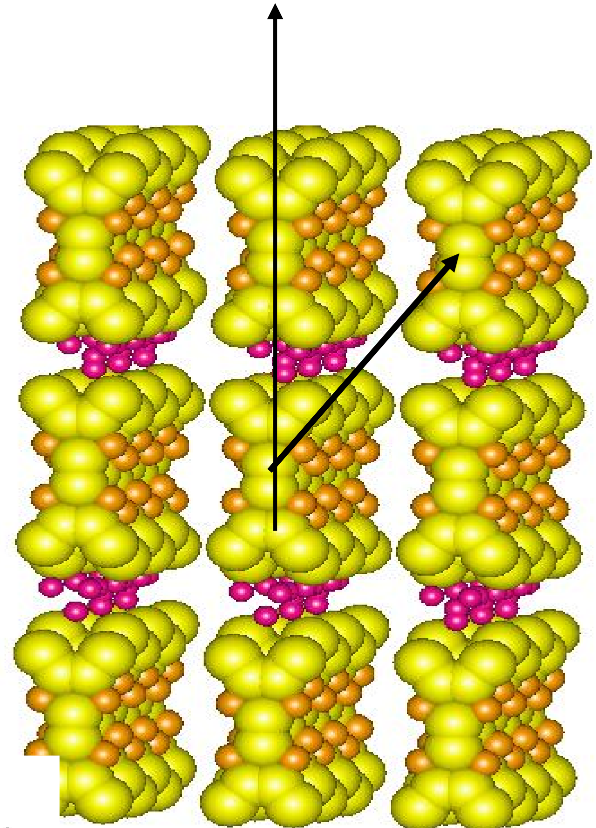

A.G. Lebed, "Anisotropy Of An Instability For A Spin-Density Wave-Induced By A Magnetic-Field In A Q1D Conductor", JETP Lett. **43**, 174 (1986).
A. G. Lebed, P. Bak, "Theory Of Unusual Anisotropy Of Magnetoresistance In Organic Superconductors", Phys Rev Lett **63**, 1315 1989

# Commensurate Orbits correspond to field directed between real space chains

## Magic Angles → Lattice Vectors

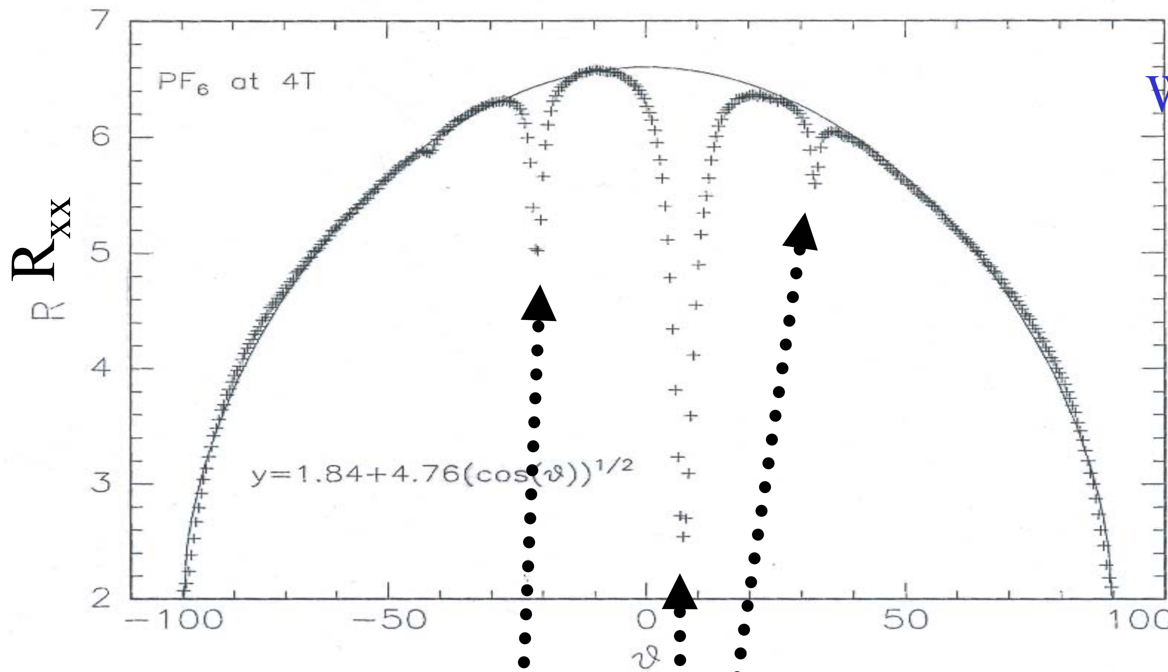


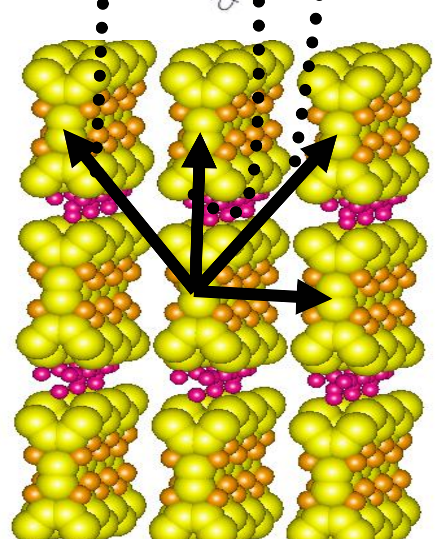

$$\frac{dk}{dt} = \frac{e}{\hbar}(v \times B)$$



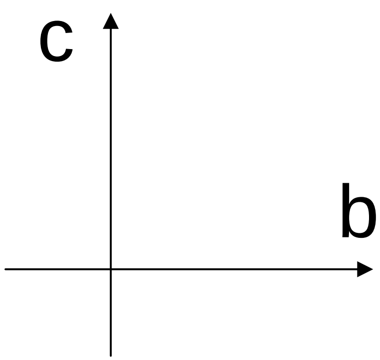
Recip space ⊥ Real space

# Quasi-particle coherence



Woowon Kang




Basic Idea:
Coherent-Incoherent Transition above Threshold $H_{perp}$ field

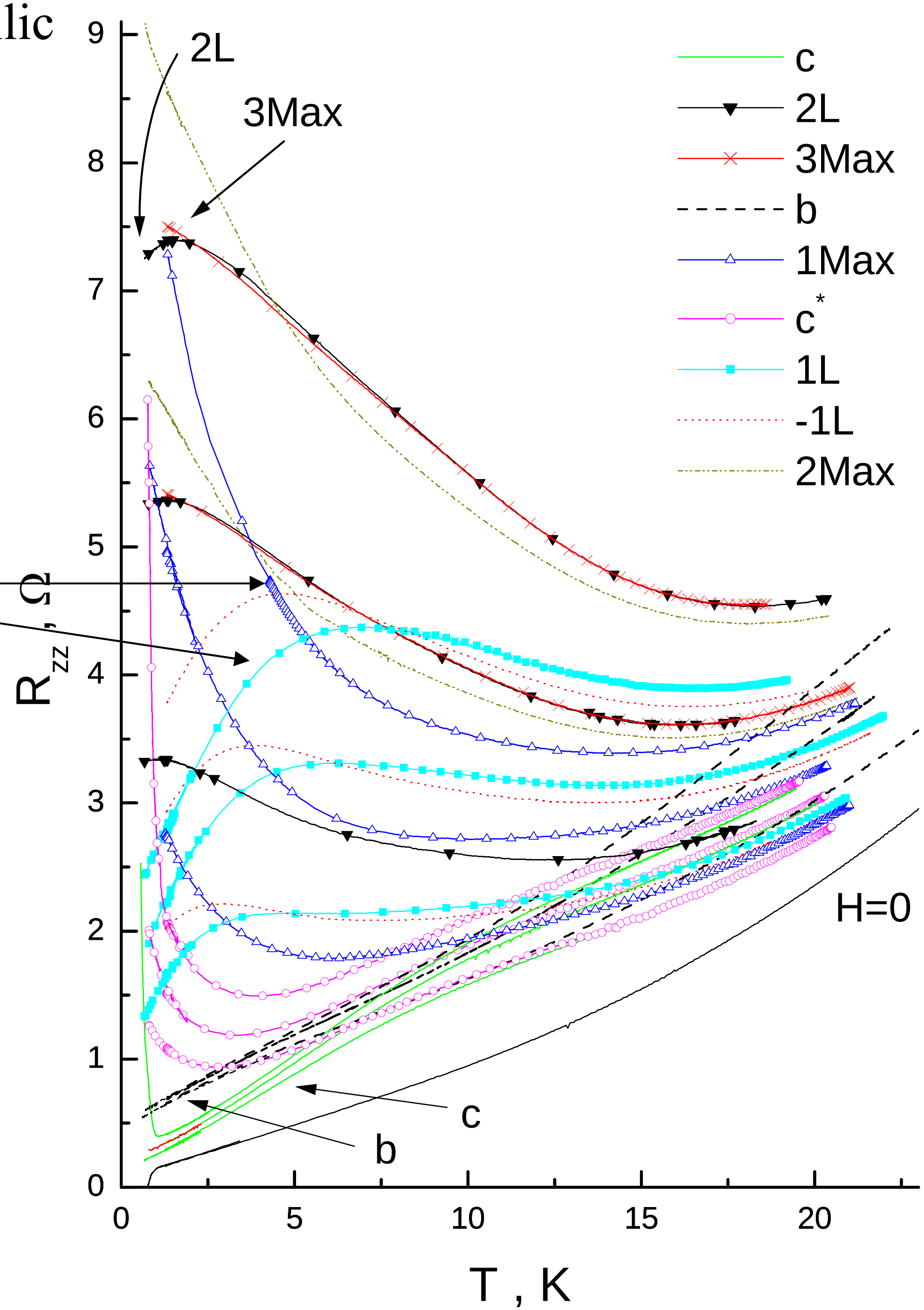
Strong, Clark, Anderson
PRL **73**, 1007 (1994)

Чашечкина

At magic angles metallic
dR/dT>0

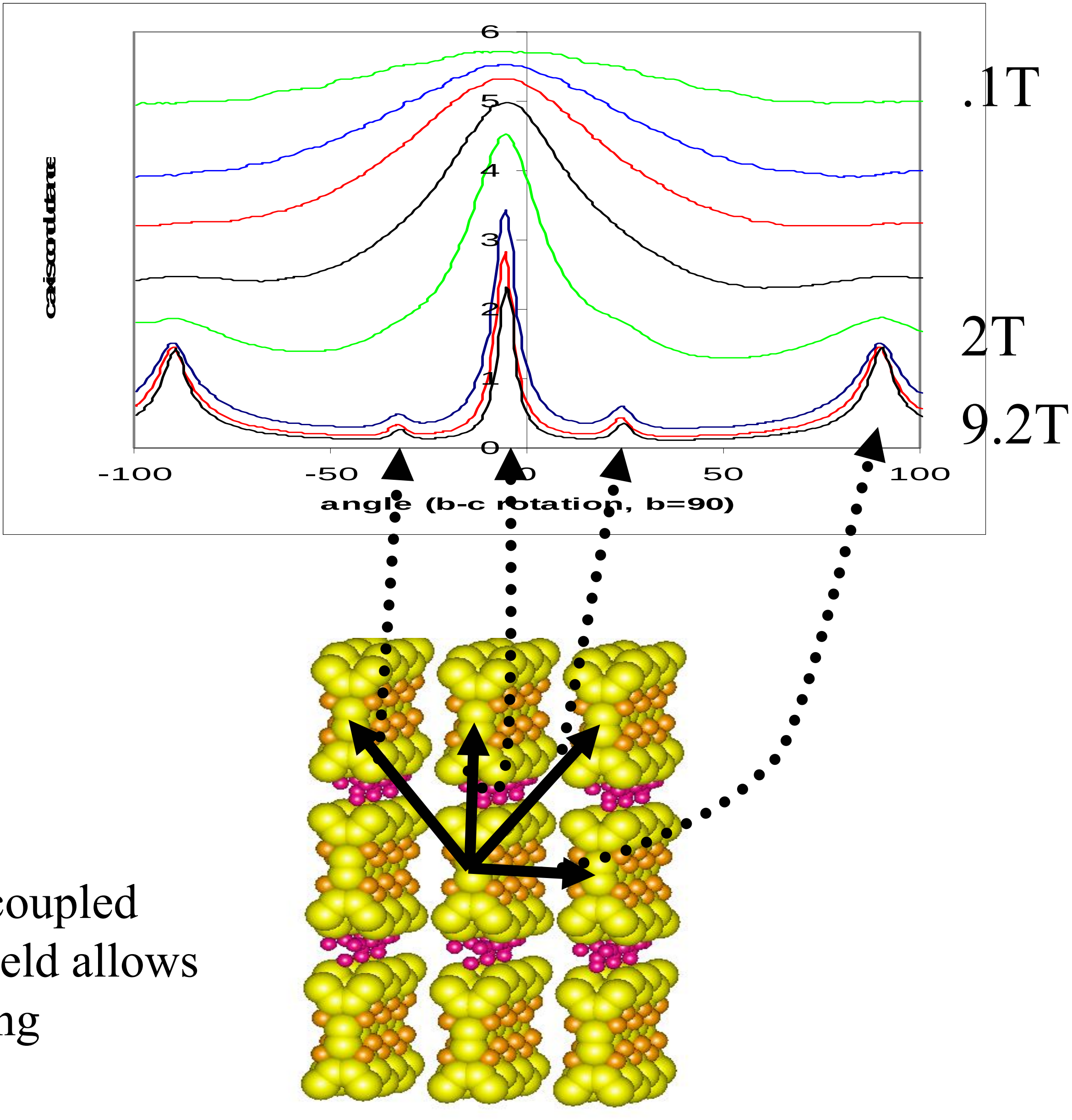
At nonmagic angles
Nonmetallic dR/dT<0

These differ by 6°




Similar effect along
a,b,c axes

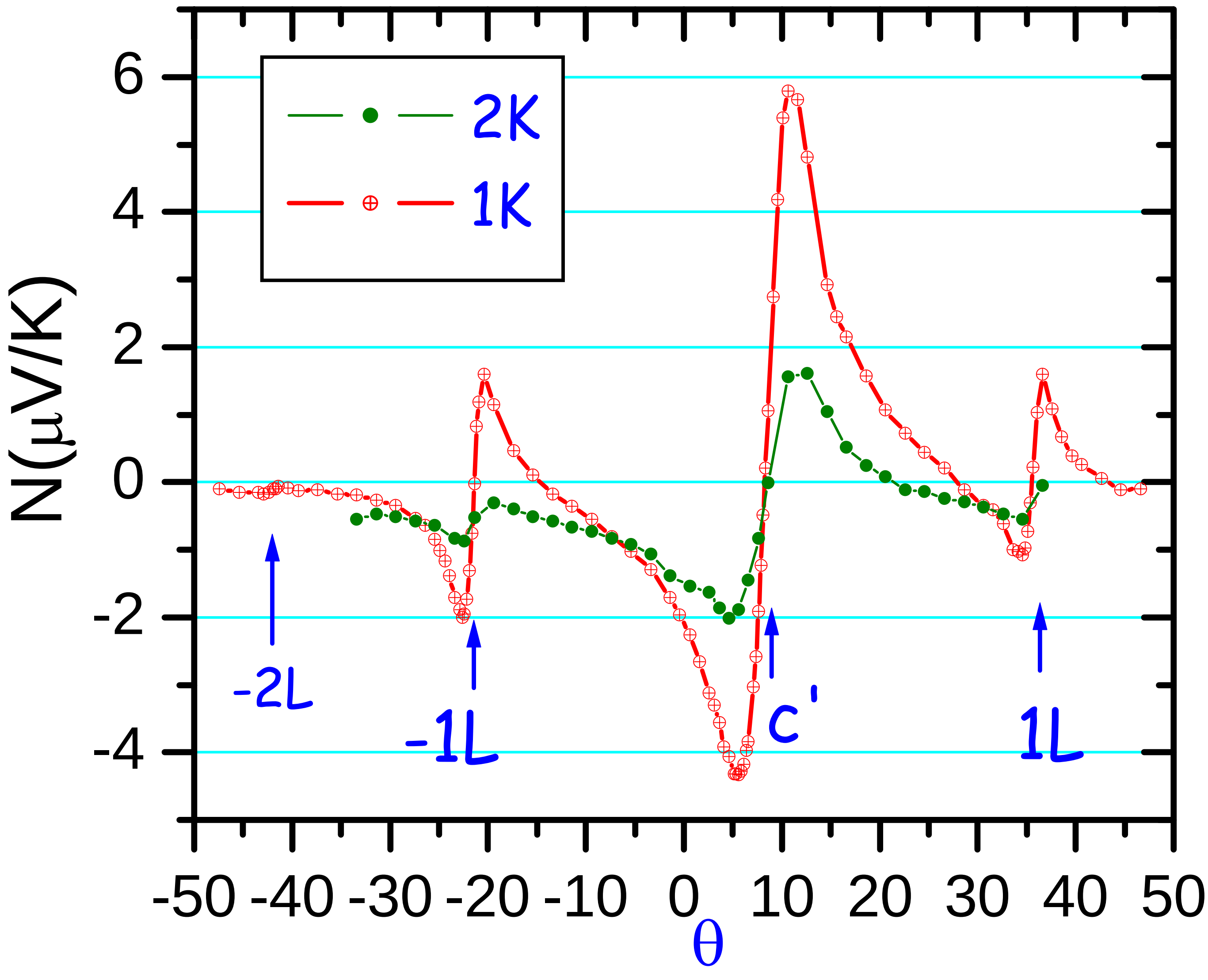
# Look at Conductivity instead of resistivity



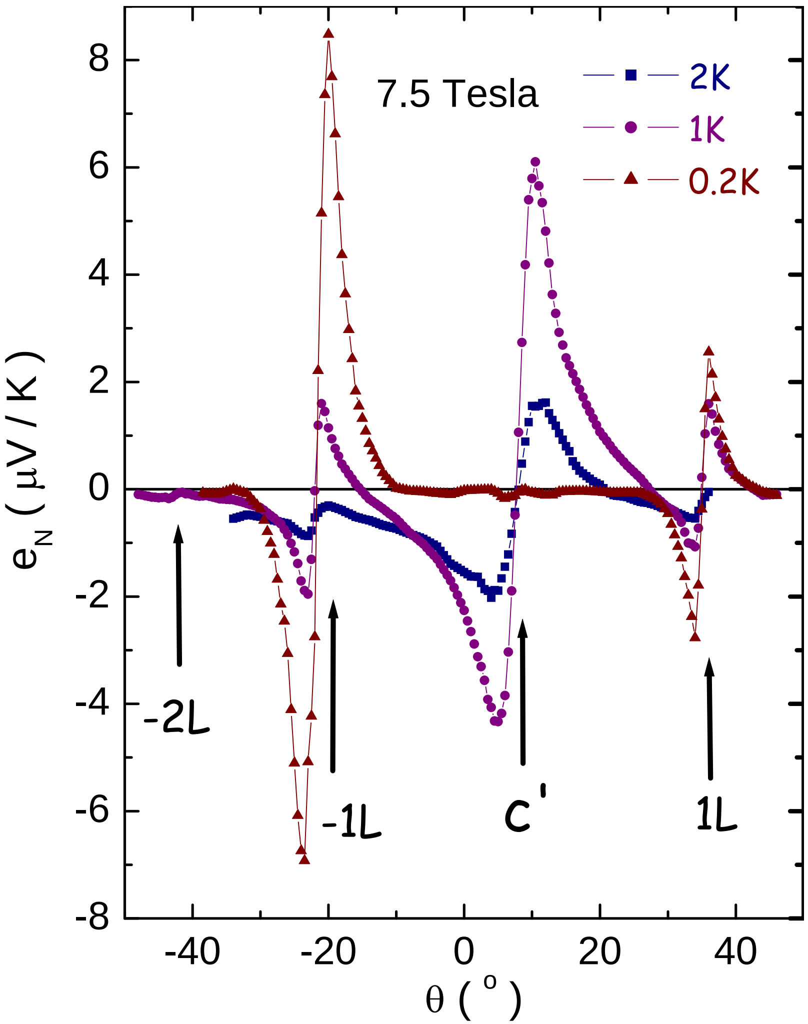

Insulating when decoupled
Conducting when field allows interchain tunneling

Angular dependent Nernst

Weida Wu



# Giant Nernst Signal




## Drude, Boltzmann:

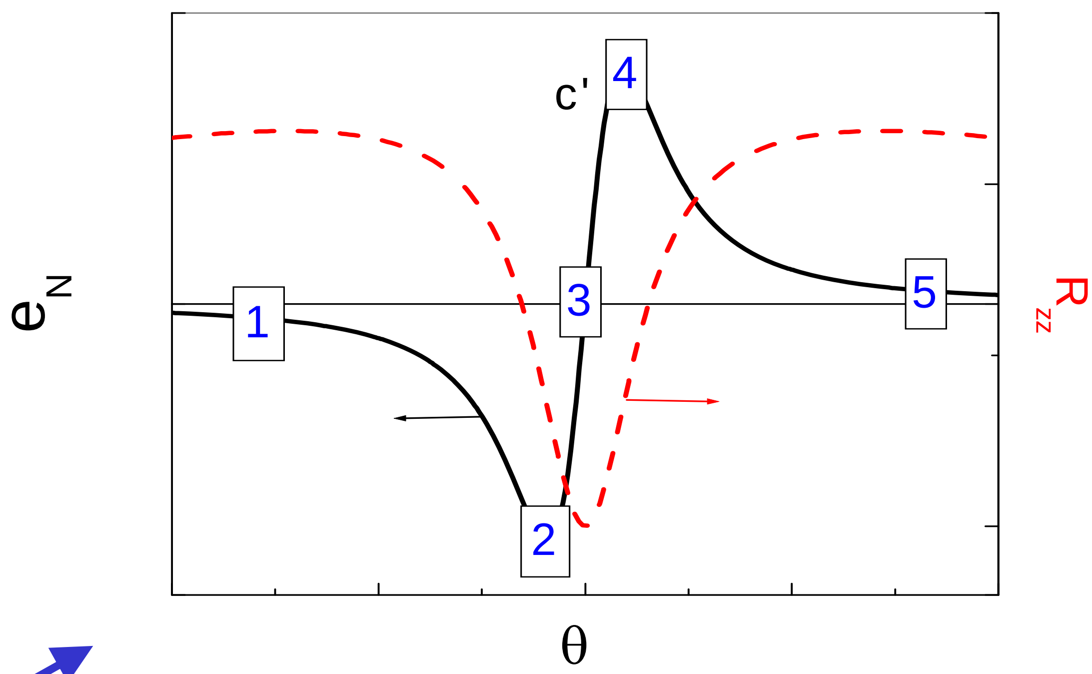
$$e_N \propto T \bullet B \sin\theta$$

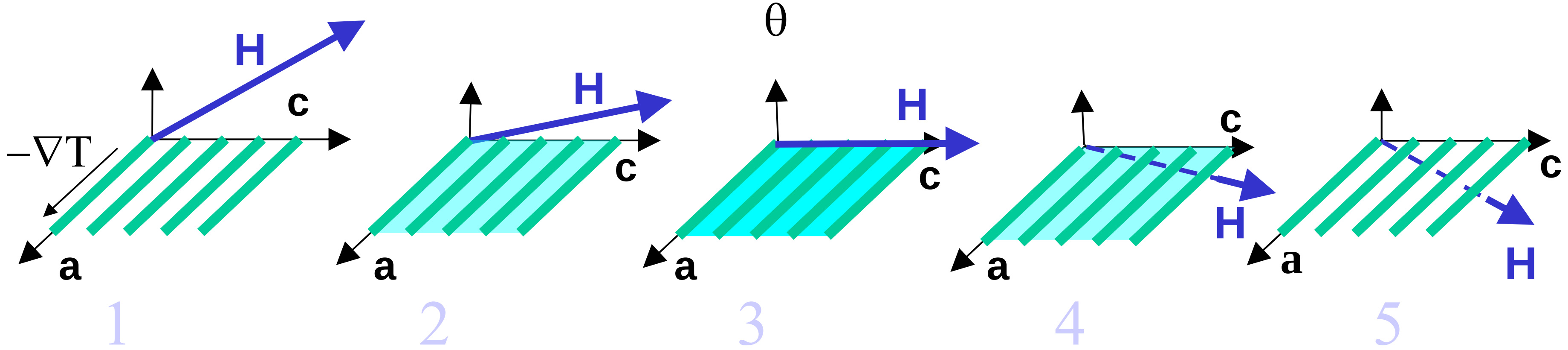
$$\sim \frac{k_B}{e}\frac{T}{T_F}\omega_c \tau$$

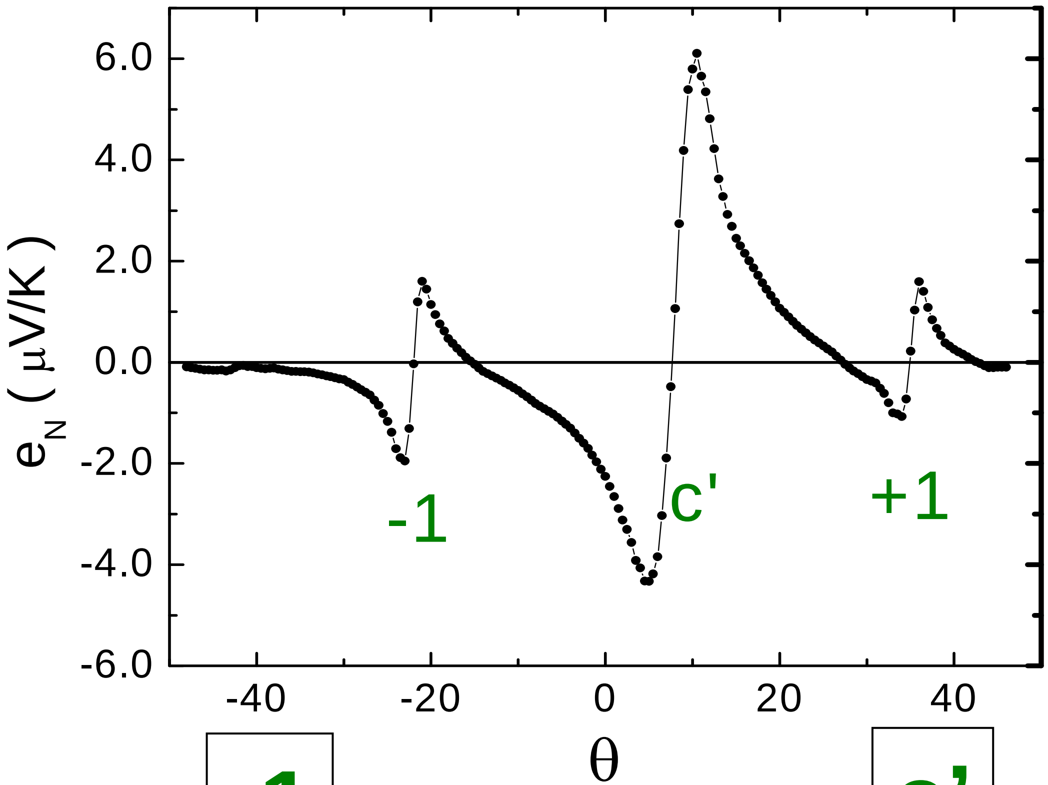
$$\approx 1nV/K$$

$(TMTSF)_2PF_6$: $e_N \sim 10\mu V/K$

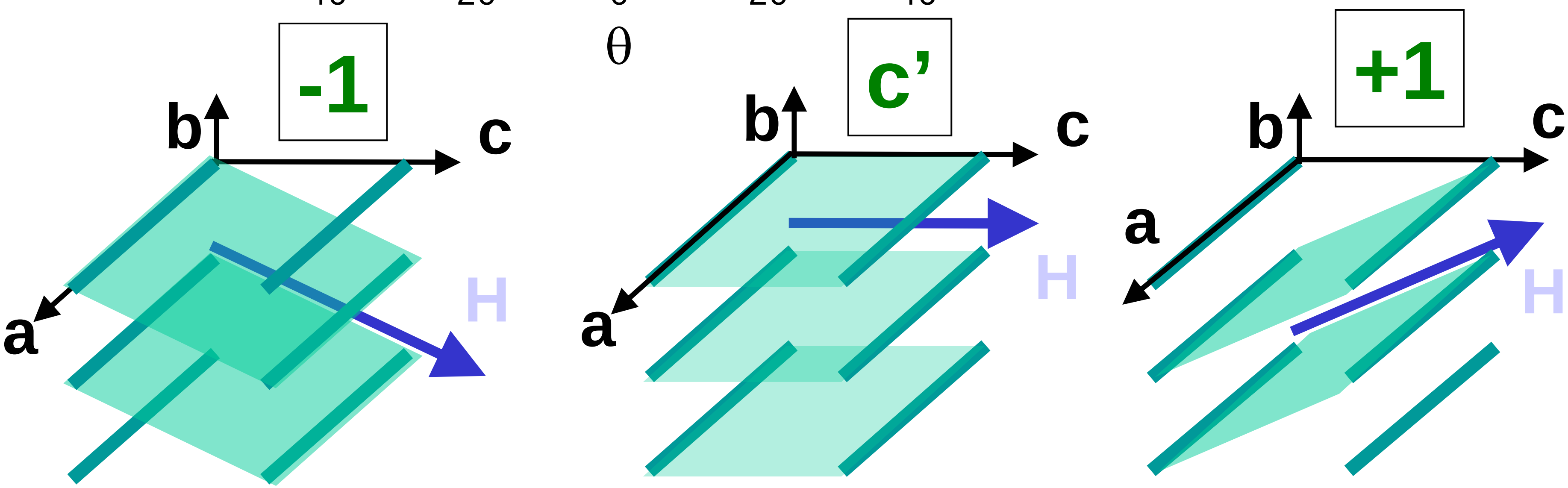
# Field induced inter-chain decoupling



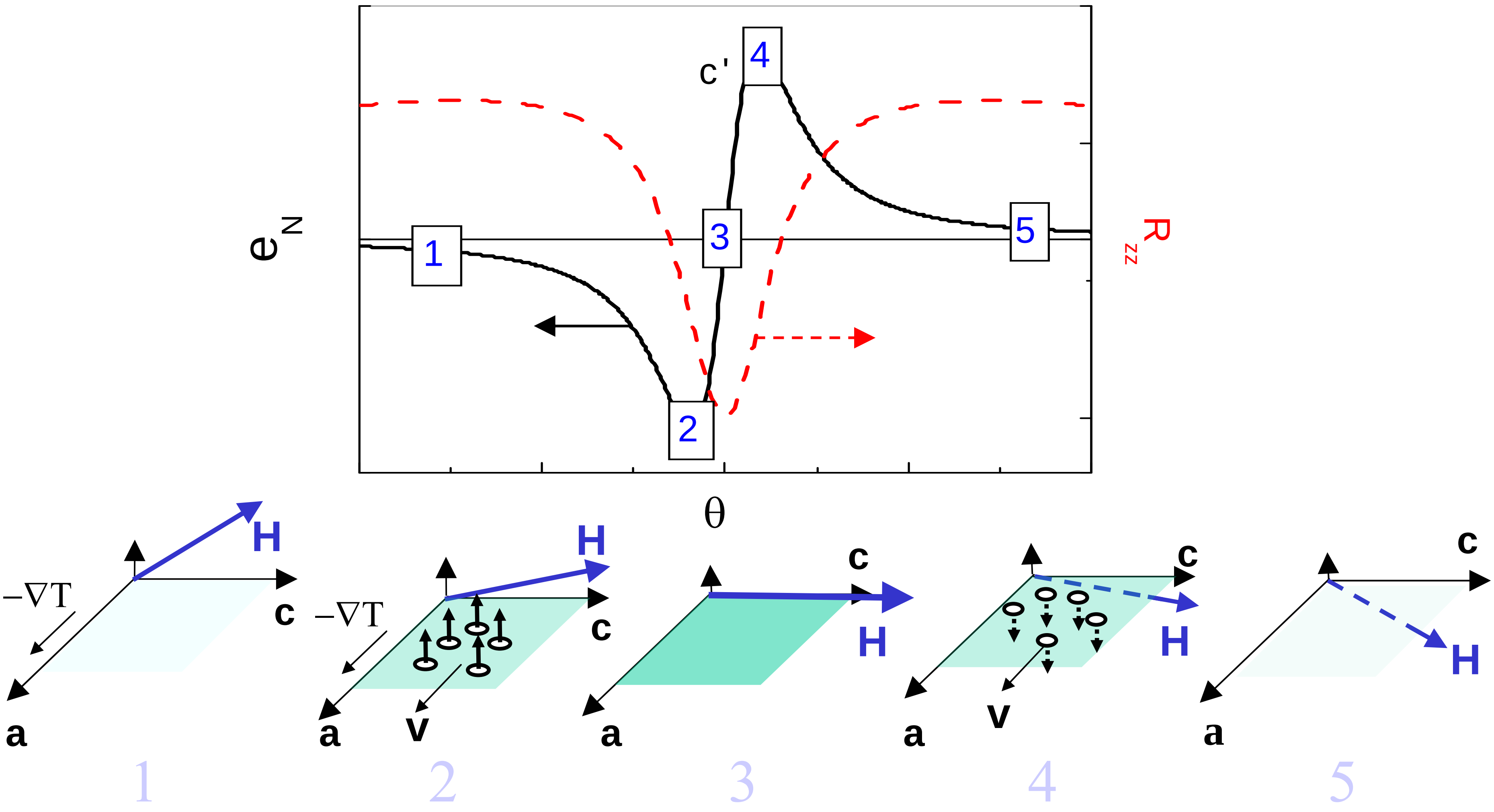



*Transport*:
Only coherent at planes // **H**




What is the coherence?

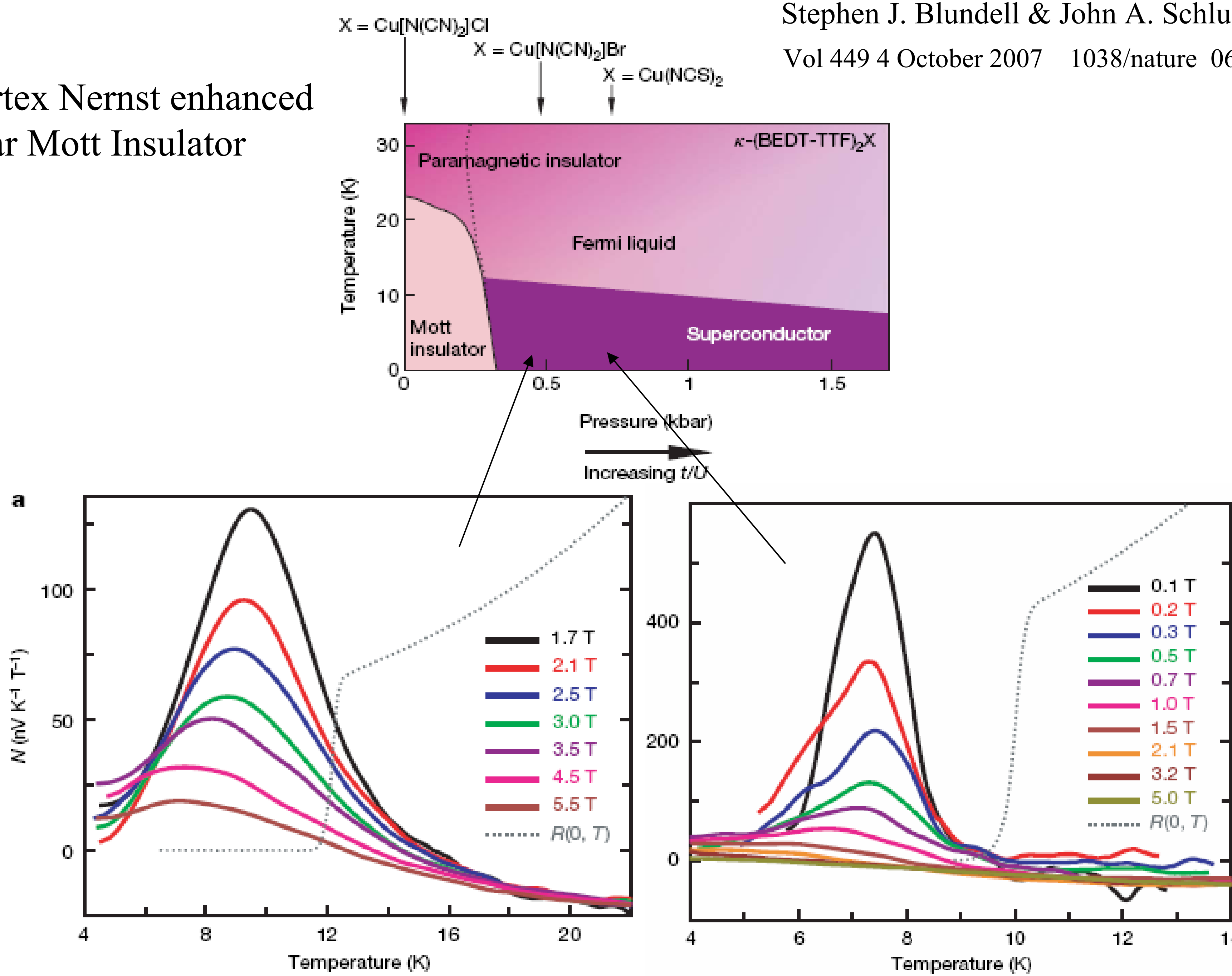
# SC Phase coherence at Magic Angle Planes




N.P. Ong, W. Wu, P. M. Chaikin and P. W. Anderson, EuroPhys. Lett. **66** (4) 579 (2004)

Moon-Sun Nam, Arzhang Ardavan,
Stephen J. Blundell & John A. Schlueter
Vol 449 4 October 2007 1038/nature 06182

# Vortex Nernst enhanced Near Mott Insulator



# Summary

- 2D organics - S and D wave Superconductors,
- 1D organics - Singlet and Triplet superconductors,
- Strong fields control dimensionality and coherence.

- ***Organic Superconductors remain an exciting testing ground for low dimensional strongly interacting electrons with characteristic energies* HTc/10**

$(TMTSF)_2PF_6$

STILL MOST REMARKABLE ELECTRONIC MATERIAL?