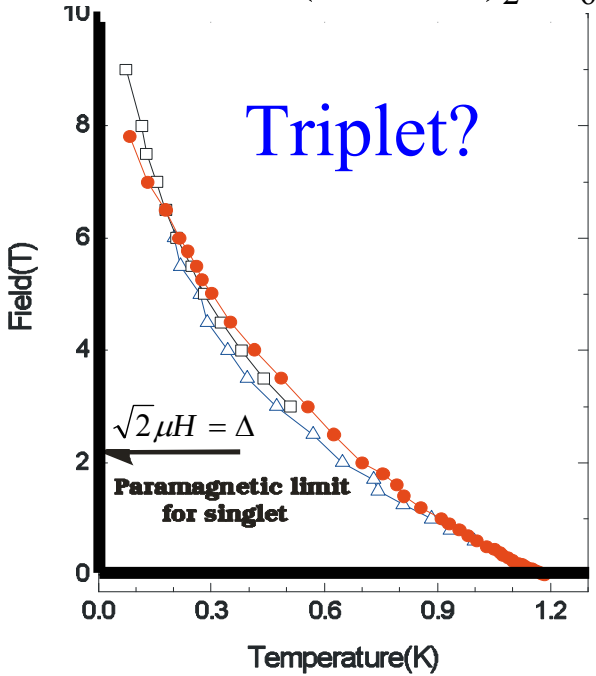
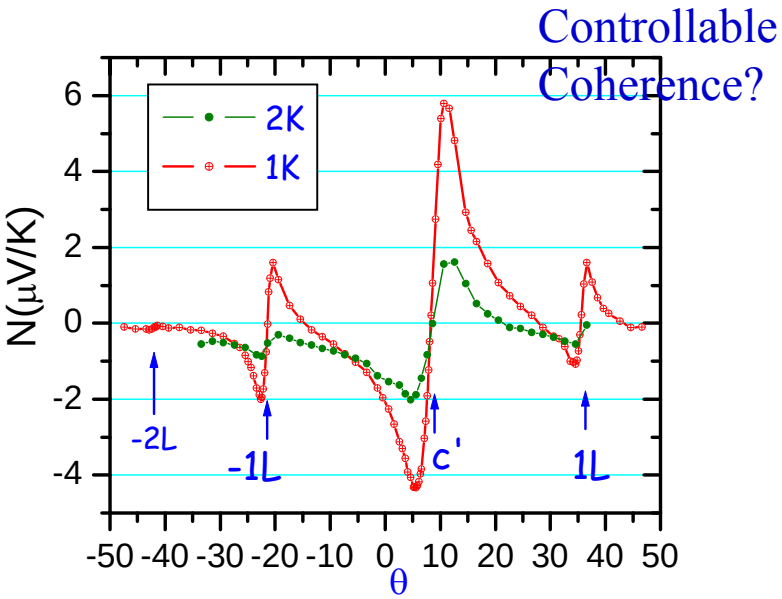
Organic Superconductivity

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 Gilles Holst

1957

Superconductivity Explained BCS

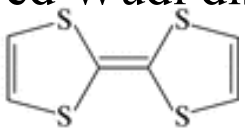
1963

Bill Little proposes Excitonic, Organic, Polymeric Superconductor

Schegolev, Bloch, Heeger,….
Work on "1D" metals, TCNQ's

1970

Fred Wudl discovers TTF



TTF-TCNQ first organic metal
(not superconductor)

1973

Alan Heeger, others

Rick Greene, $(SN)_x$, first (and only) polymeric superconductor Tc~0.3K

1975

Bechgaard and Jerome First Organic Superconductor $TMTSF_2$ PF_6 Tc~1.2K

1979

G. Saito, $(ET)_2Cu[N(CN)_2Br]$ Tc~13K

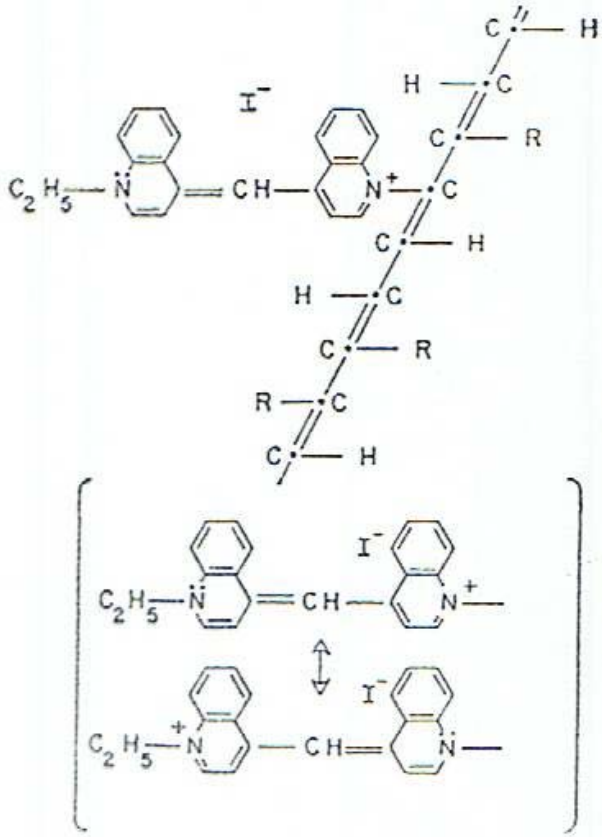


FIG. 3. Chemical structure of the proposed superconducting organic polymer. At each point R on the spine a similar side chain to the one shown is attached. These side chains are resonating hybrids of the two extreme structures shown in the inset. The positive charge resonates between the two nitrogen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

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

1911

Superconductivity Discovered by Gilles Holst

1957

Superconductivity Explained BCS

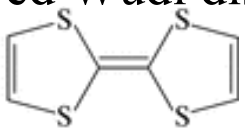
1963

Bill Little proposes Excitonic, Organic, Polymeric Superconductor

Schegolev, Bloch, Heeger,….
Work on "1D" metals, TCNQ's

1970

Fred Wudl discovers TTF



TTF-TCNQ first organic metal
(not superconductor)

1973

Alan Heeger, others

Rick Greene, $(SN)_x$, first (and only) polymeric superconductor Tc~0.3K

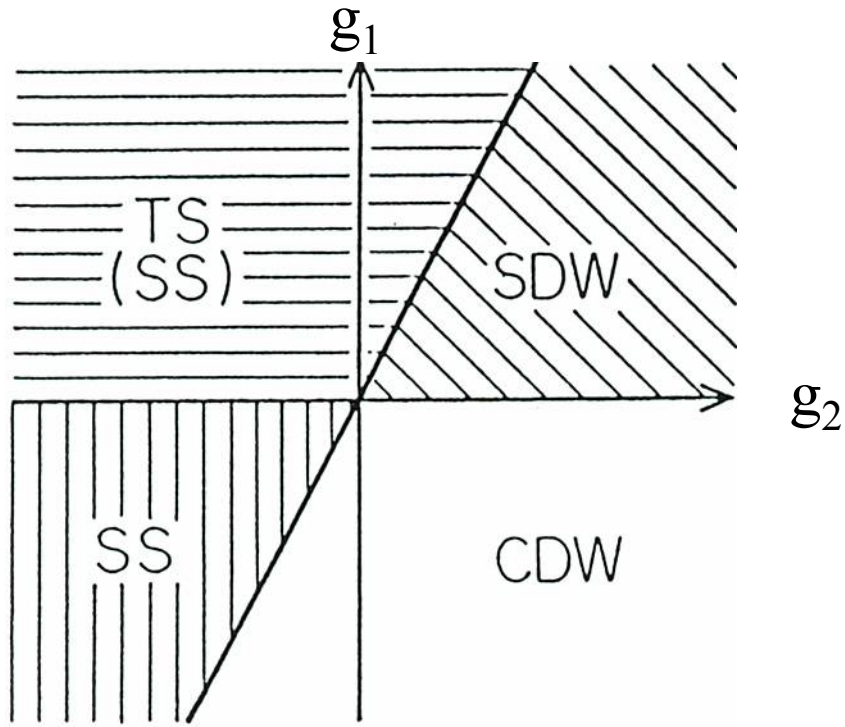
1975

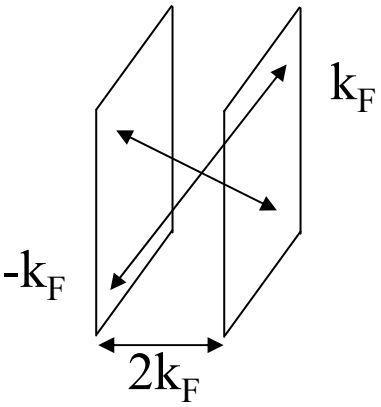
Bechgaard and Jerome First Organic Superconductor $TMTSF_2$ PF_6 Tc~1.2K

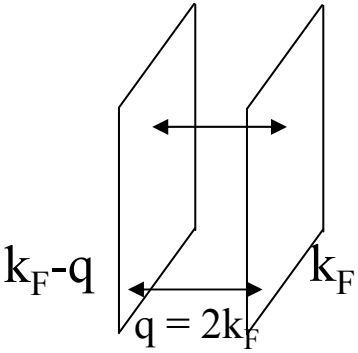
1979

G. Saito, $(ET)_2Cu[N(CN)_2Br]$ Tc~13K

“g-ology Phase Diagram 1D electrons

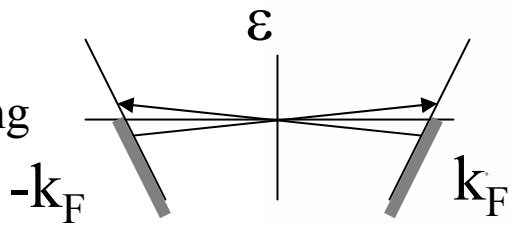




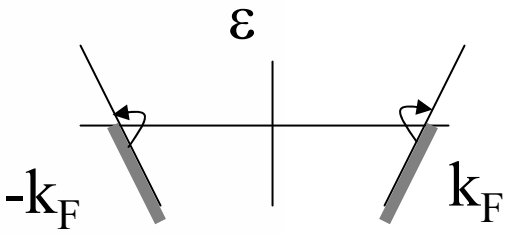


Only two interactions important

backscattering



$g_1(q=2k_F)$



forward scattering

$g_2(q=0)$

1911

Superconductivity Discovered by Gilles Holst

1957

Superconductivity Explained BCS

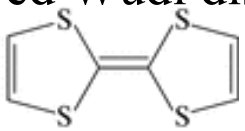
1963

Bill Little proposes Excitonic, Organic, Polymeric Superconductor

Schegolev, Bloch, Heeger,….
Work on "1D" metals, TCNQ's

1970

Fred Wudl discovers TTF



TTF-TCNQ first organic metal
(not superconductor)

1973

Alan Heeger, others

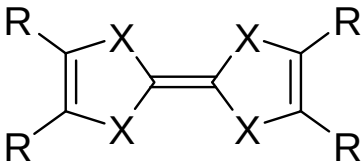
Rick Greene, $(SN)_x$, first (and only) polymeric superconductor Tc~0.3K

1975

Bechgaard and Jerome First Organic Superconductor $TMTSF_2$ PF_6 Tc~1.2K

1979

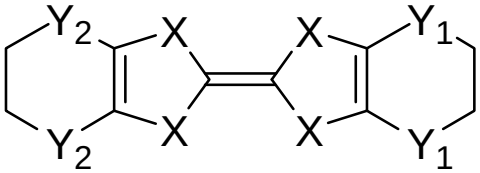
G. Saito, $(ET)_2Cu[N(CN)_2Br]$ Tc~13K



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

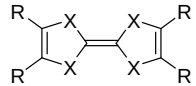
Quasi 1D



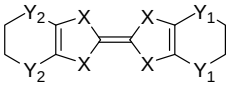
ET(BEDT-TTF) : X=Y_1=Y_2=S
BO(BEDO-TTF) : X=S,Y_1=Y_2=O
BETS(BEDT-TSF) : X=Se,Y_1=Y_2=S
EOET : X=S,Y_1=S,Y_2=O

Quasi 2D

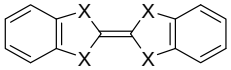
Yagubski



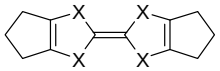
TTF : X=S, R=H
TSF : X=Se, R=H
TTeF : X=Te, R=H
TMTSF : X=Se, R=Me
TMTTF : X=S, R=Me



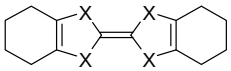
ET(BEDT-TTF) : X=Y_1=Y_2=S
BO(BEDO-TTF) : X=S,Y_1=Y_2=O
BETS(BEDT-TSF) : X=Se,Y_1=Y_2=S
EOET : X=S,Y_1=S,Y_2=O



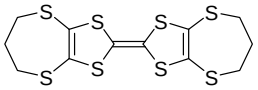
DBTTF : X=S
DBTSF : X=Se



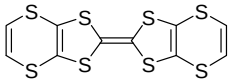
HMTTF : X=S
HMTSF : X=Se
HMTTeF : X=Te



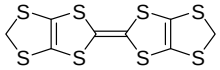
OMTTF : X=S
OMTSF : X=Se



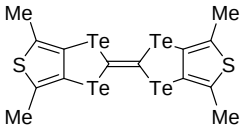
BPDT-TTF



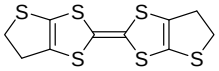
BVDT-TTF



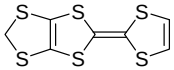
BMDT-TTF



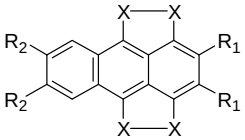
BDMT-TTeF



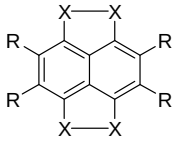
BET-TTF



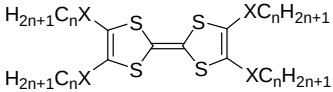
MDT-TTF



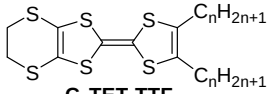
DMTTA : X=S, R_1=H, R_2=Me
TMTTA : X=S, R_1=R_2==Me
6,7-DMTTA : X=S, R_1=H, R_2=Me
TSA : X=Se, R_1=R_2=H
DMTSA : X=Se, R_1=Me, R_2=H
6,7-DMTSA : X=Se, R_1=H, R_2=Me
TMTSA : X=Se, R_1=R_2=Me
DMTTeA : X=Te, R_1=Me, R_2=H



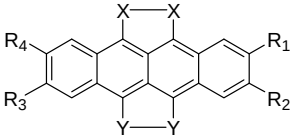
TTN : X=S, R=H
TSN : X=Se, R=H
TMTTeN : X=Te, R=Me



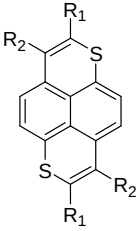
TTC_n-TTF : X=S
$TSeC_n$-TTF : X=Se
$TTeC_n$-TTF : X=Te



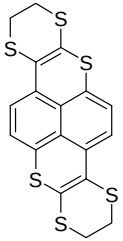
C_nTET-TTF



TTT : X=Y=S, R_1=R_2=R_3=R_4=H
F_2TTT : 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

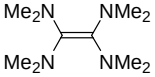


DTPY : R_1=R_2=H
MSDTPY : R_1=SeMe,R_2=H
MTDTPY : R_1=SMe,R_2=H
Ph_2DTPY : R_1=Ph,R_2=H
3,8-$(MeO)_2$DTPY : R_1=H, R_2=MeO



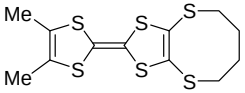
ETDTPY

Saito



TDAE

TMPD



TMDTDM-TTF

1911

Superconductivity Discovered by Gilles Holst

1957

Superconductivity Explained BCS

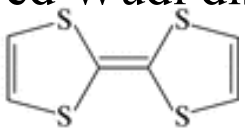
1963

Bill Little proposes Excitonic, Organic, Polymeric Superconductor

Schegolev, Bloch, Heeger,….
Work on "1D" metals, TCNQ's

1970

Fred Wudl discovers TTF



TTF-TCNQ first organic metal
(not superconductor)

1973

Alan Heeger, others

Rick Greene, $(SN)_x$, first (and only) polymeric superconductor Tc~0.3K

1975

Bechgaard and Jerome First Organic Superconductor $TMTSF_2$ PF_6 Tc~1.2K

1979

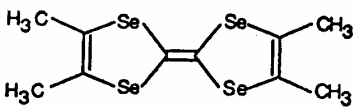
G. Saito, $(ET)_2Cu[N(CN)_2Br]$ Tc~13K

Observed and hinted at ground states

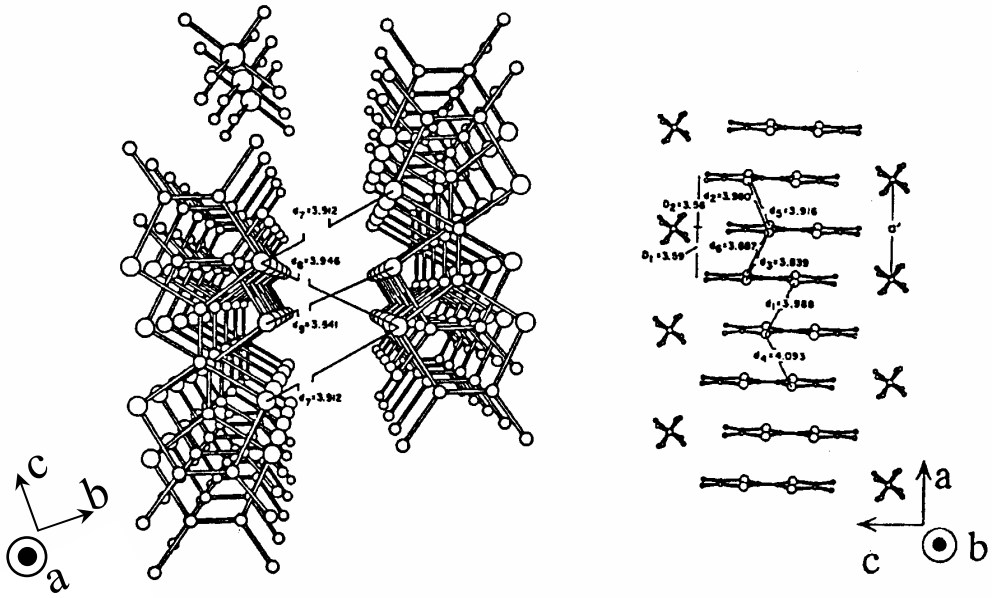
BEDT-TTF family	$(TMTSF)_2PF_6$
Supercond – singlet	Supercond – triplet?
- d-wave?	SDW
- LOFF?	CDW
Ferromagnetic	Field Induced SDW
SDW	Quantum Hall
CDW	Fermi-Liquid
Quantum Hall?	Non – Fermi, Luttinger? Liq
Fermi-Liquid	Mott Insulator?

Crystal Structure of Bechgaard Salts $(TMTSF)_2X$

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



TMTSF = tetramethyltetraselenafulvalene



Triclinic

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

$$a = 7.297\,\text{Å}, b = 7.711\,\text{Å}, c = 13.522\,\text{Å}$$

- 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

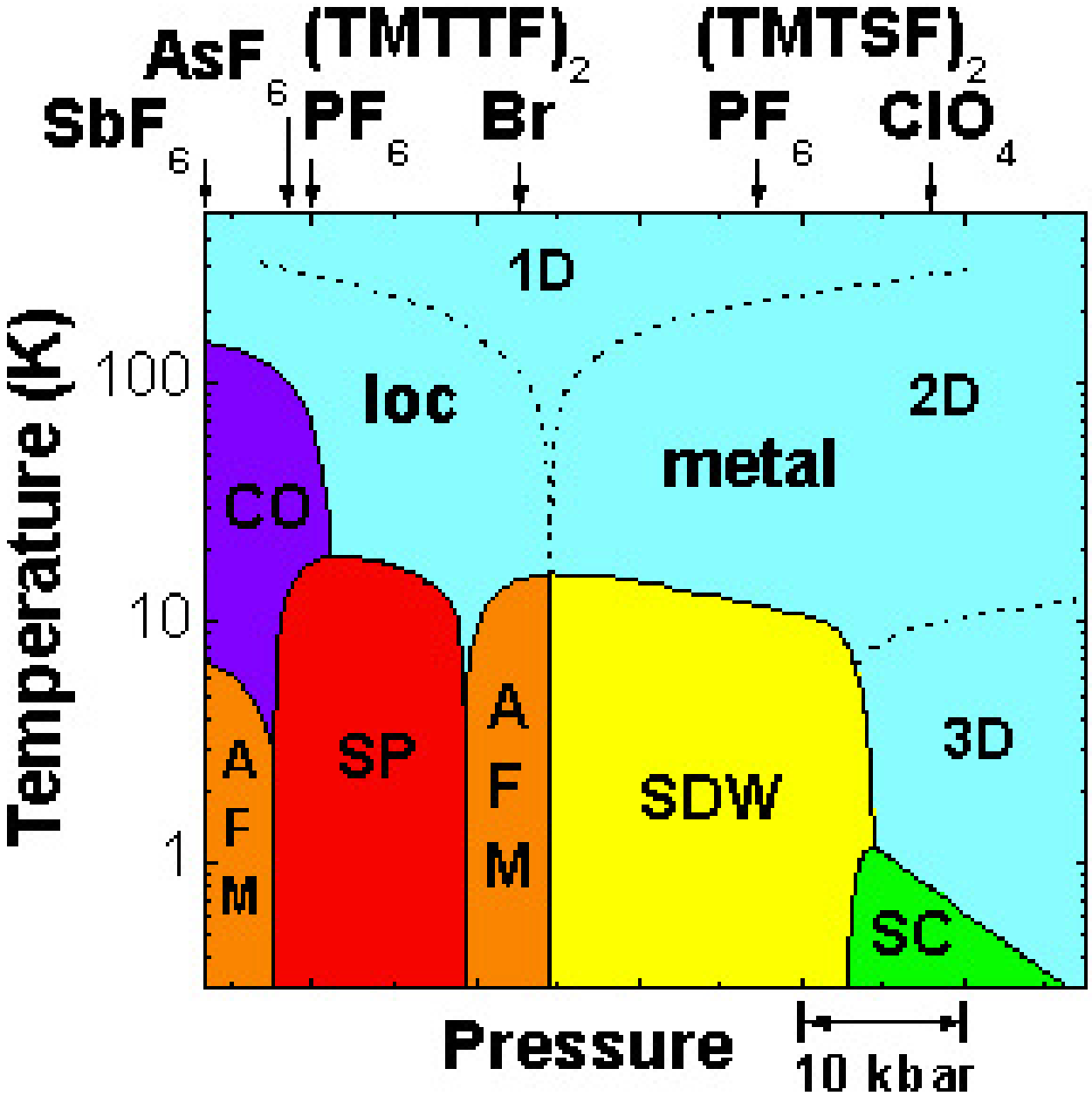
(ρ (Cu) ~ 1$\mu\Omega$cm at 300K).

- Extremely clean

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

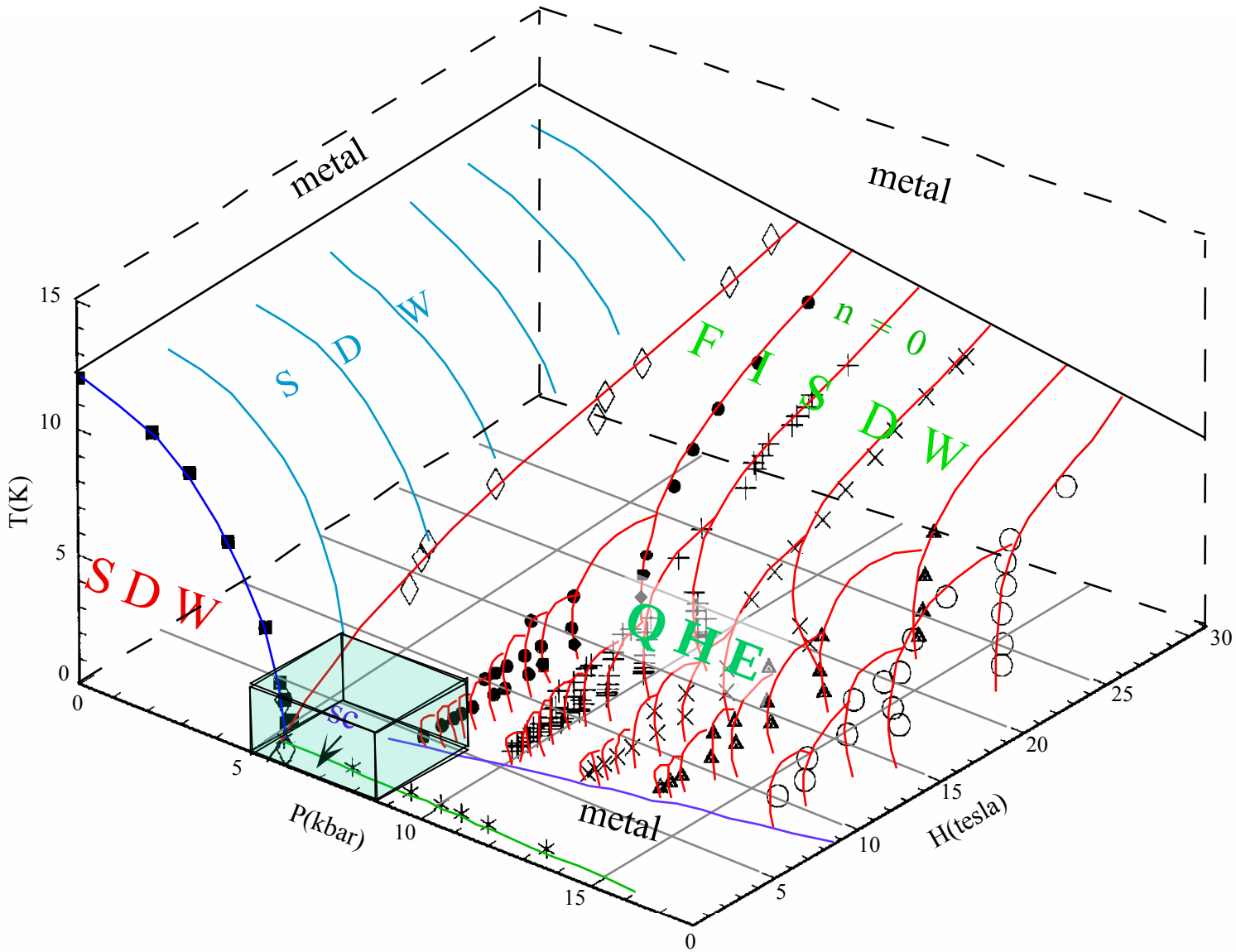
- ¼ Filled, Slightly Dimerized

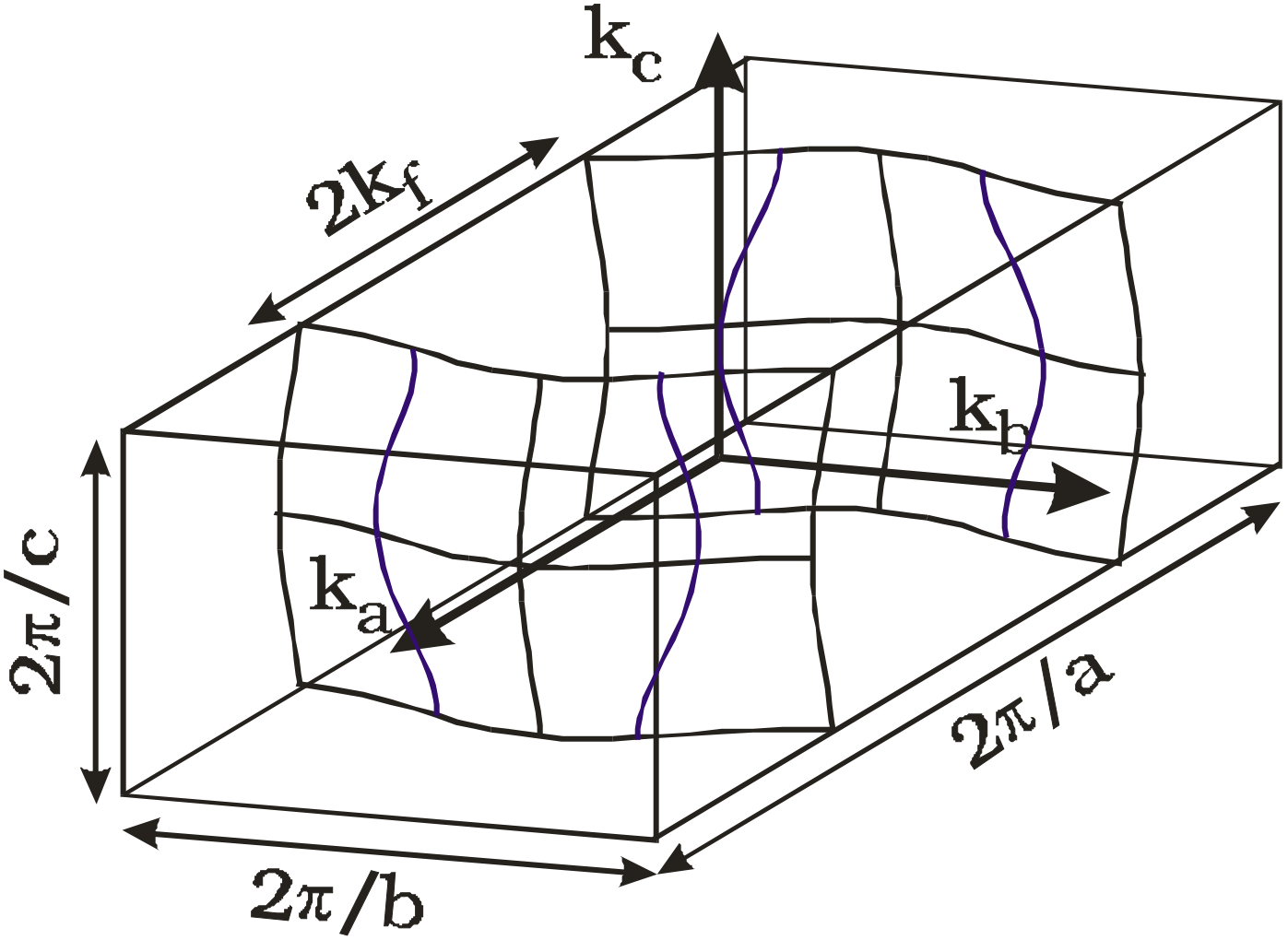
Single chain has charge gap.


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

Phase Diagram $(TMTSF)_2PF_6$

Woowon Kang

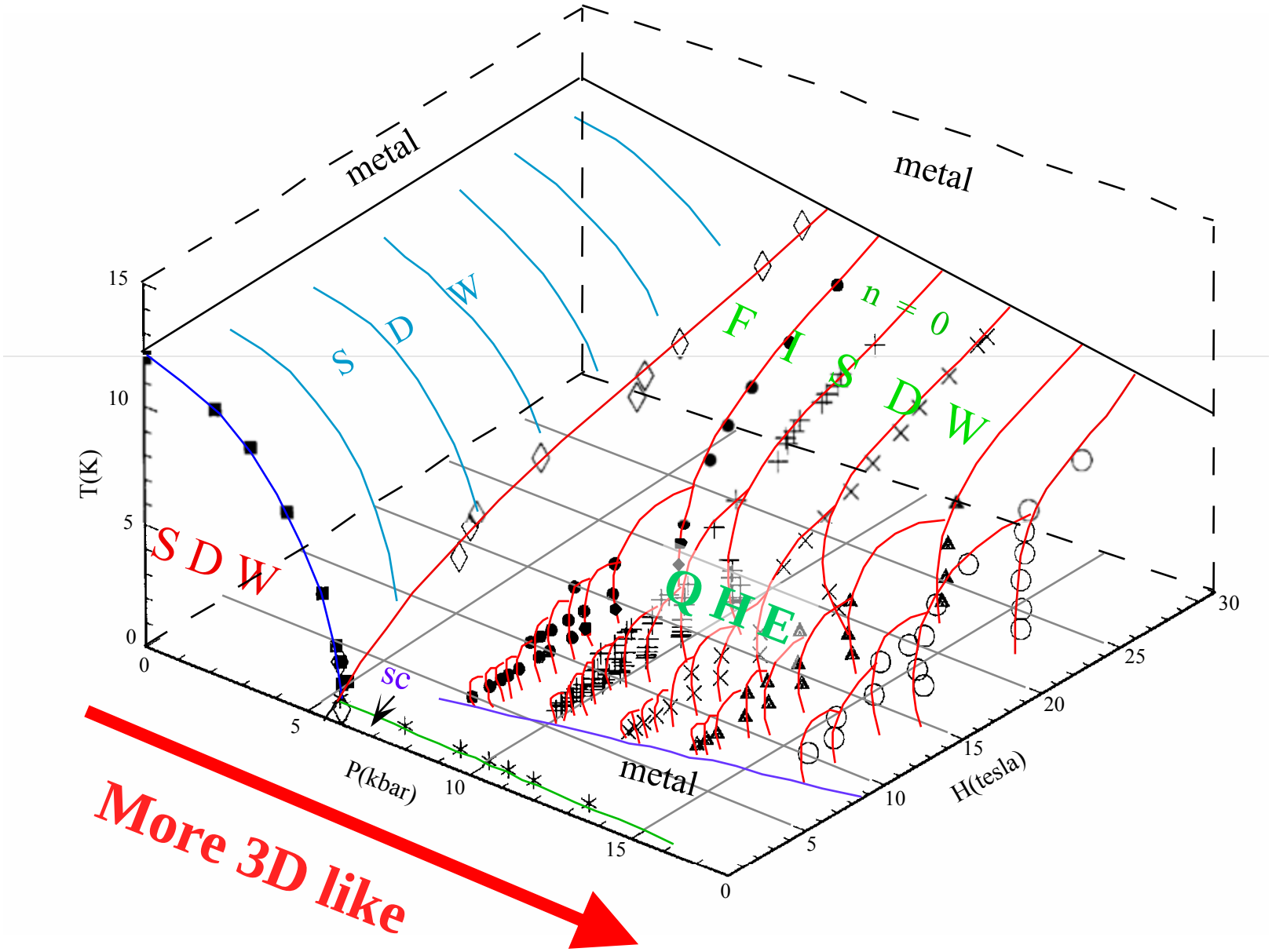




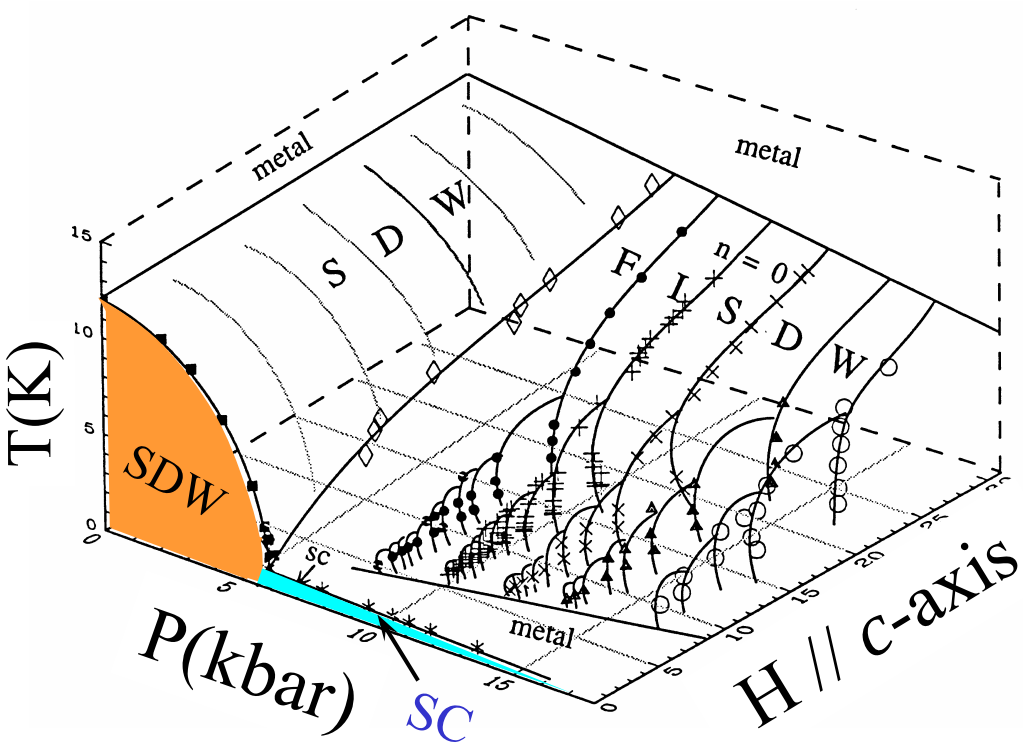
1D metals are unstable – Fermi Surfaces Nest

Interchain hopping – warped Fermi Surface – regain metal

Pressure increases interchain hopping – more 3D

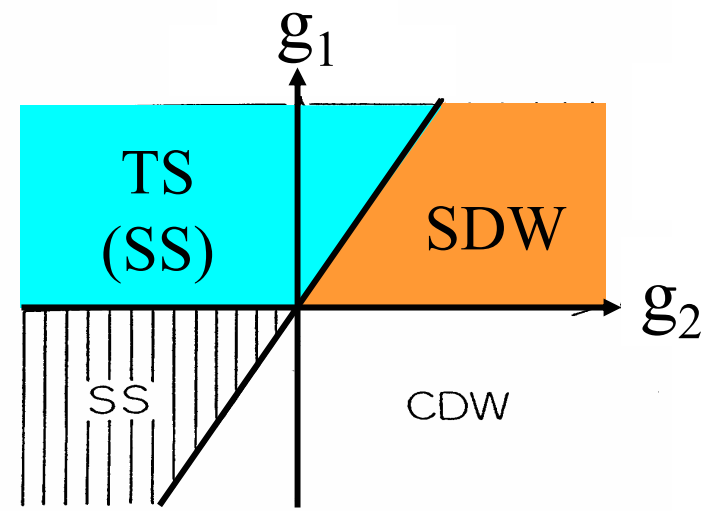

metal
metal
metal
SDW
SDW
FISDW
n = 0
QHE
sc
T(K)
P(kbar)
H(tesla)
More 3D like

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

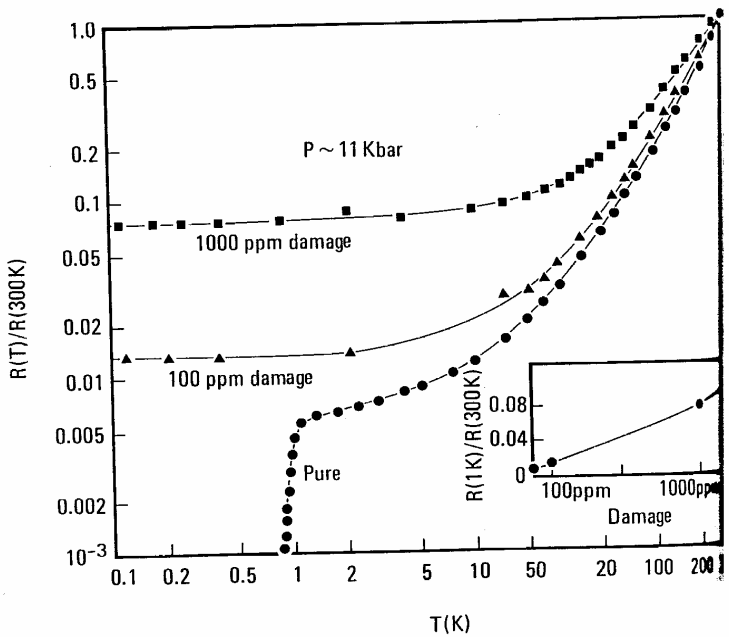


FIGURE 7 Temperature dependence of resistivity of $(TMTSF)_2PF_6$ at 11 kbar pressure for various amounts of radiation induced damage. Insert shows damage dependence of resistivity at T=1K.

Non s-wave

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

Resistive upper critical fields

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

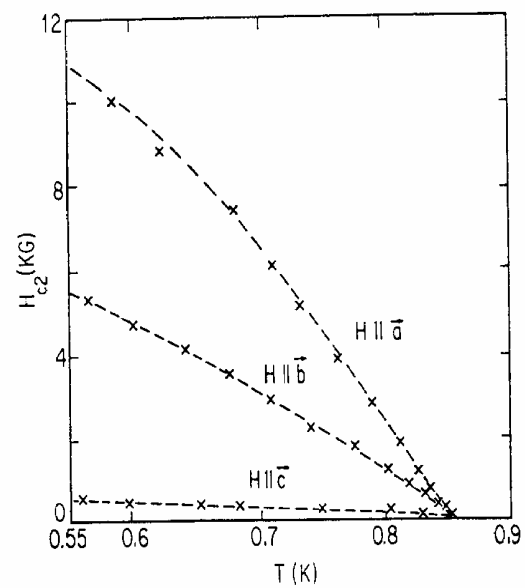


Fig. 1. Anisotropic critical field for $(TMTSF)_2ClO_4$. Fields were varied in three perpendicular directions to attain the maximum critical field along the *a* axis.

H_p=16 KG

Singlet (s,d-wave)?

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

Proton spin-lattice relaxation experiments

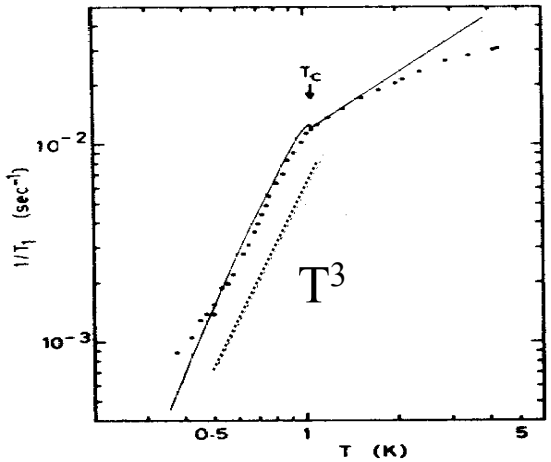


Fig. 3. Temperature dependence of $1/T_1$ of protons at zero field. The solid curve shows the calculation for the $s2$ or $t2$ state in ref. 23 normalized to the experimental data at $T_c = 1.06$ K. The dashed line indicates the T^3 dependence.

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.

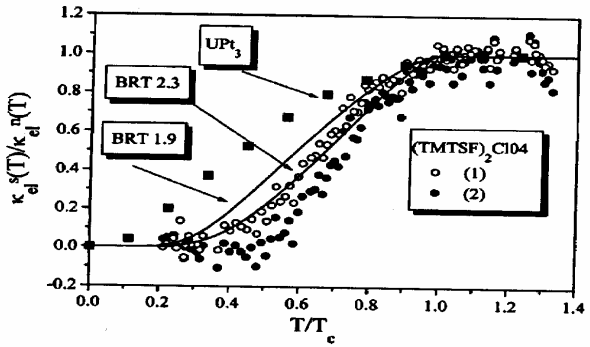


FIG. 3. Normalized electronic thermal conductivity vs normalized temperature for $(TMTSF)_2ClO_4$ in two different scenarios (see text). The results are compared with the predictions of BRT theory for two different ratios of $\Delta(0)/k_BT_c$ and with the published data on UPt_3 for a heat current along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

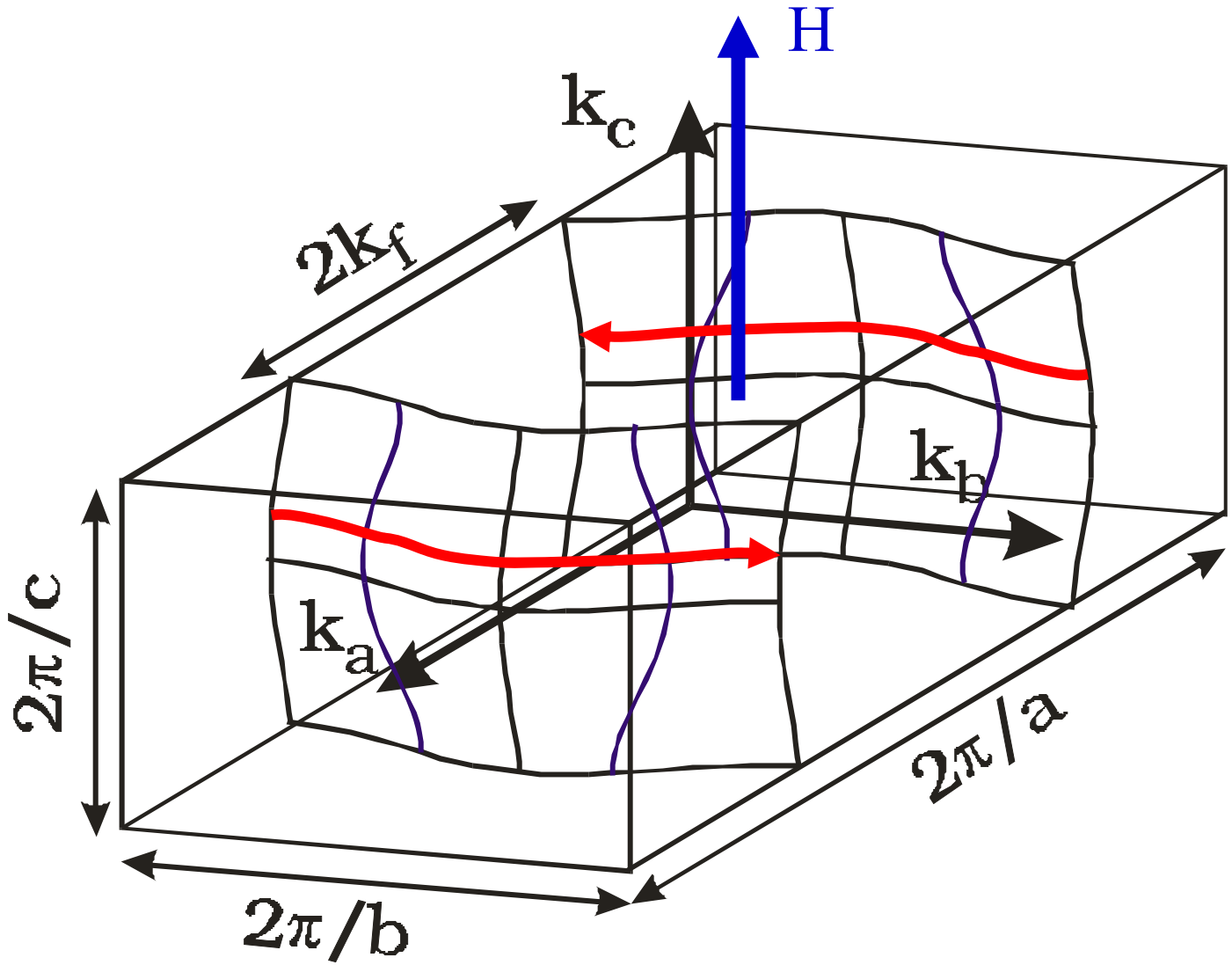
Thermal conductivity

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**

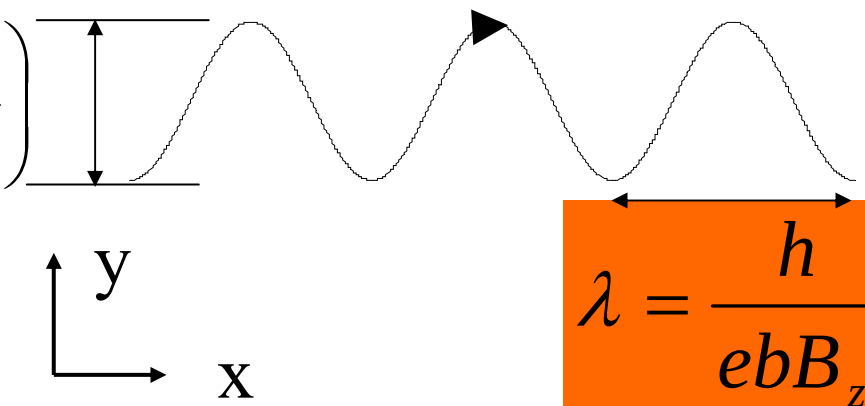


One-Dimensionalized by Magnetic field

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

Real Space

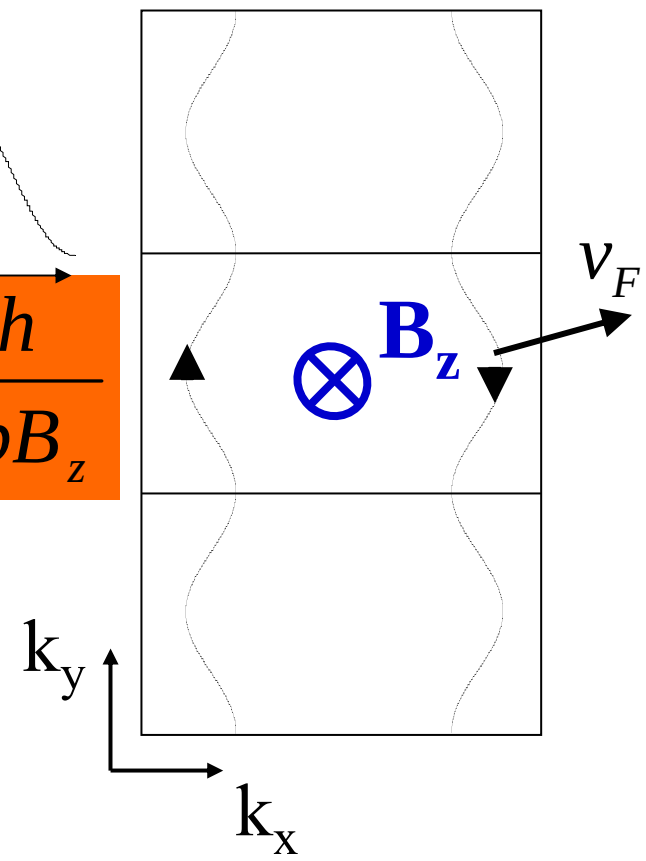
$$w_b = b\left(\frac{4t_b}{ev_F B_z}\right)$$



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

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

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

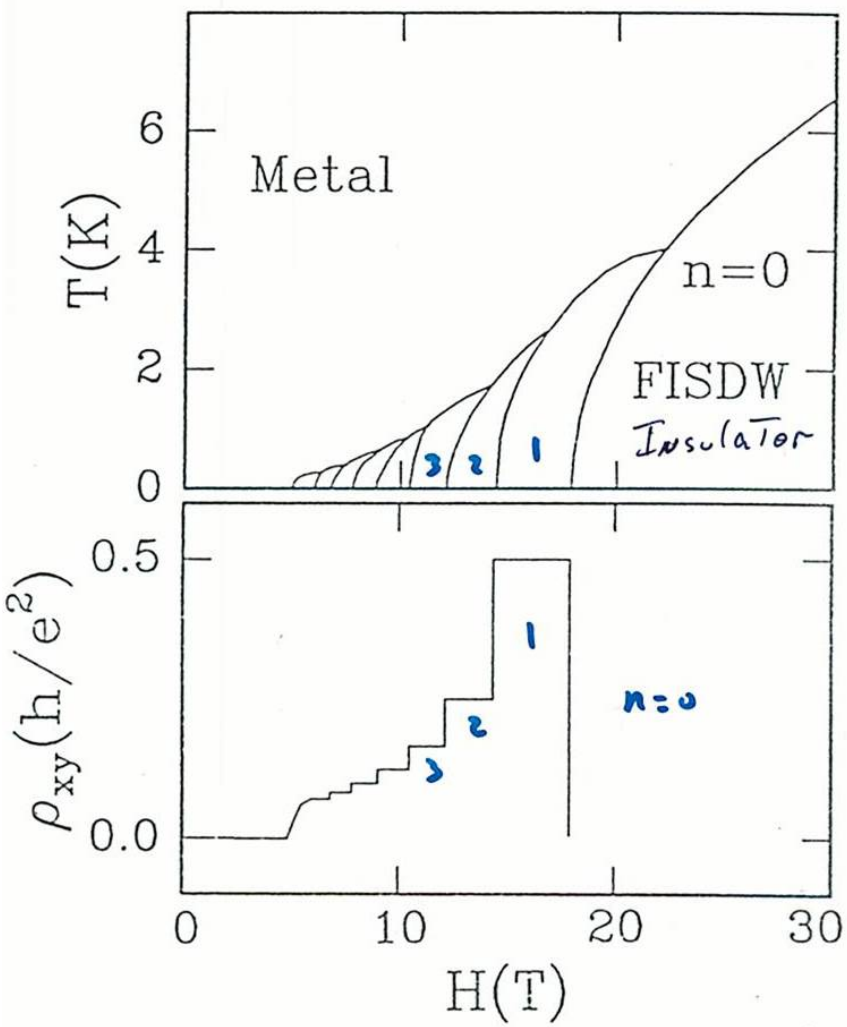
But nesting at $q=2k_F$ +/- nG, $G=2\pi/\lambda$

⇒Spectrum with multiple gaps

⇒Cascade of transitions

⇒Quantum Hall $\rho_{xy} = h/ne^2$

Cascade of Field Induced Spin Density Waves

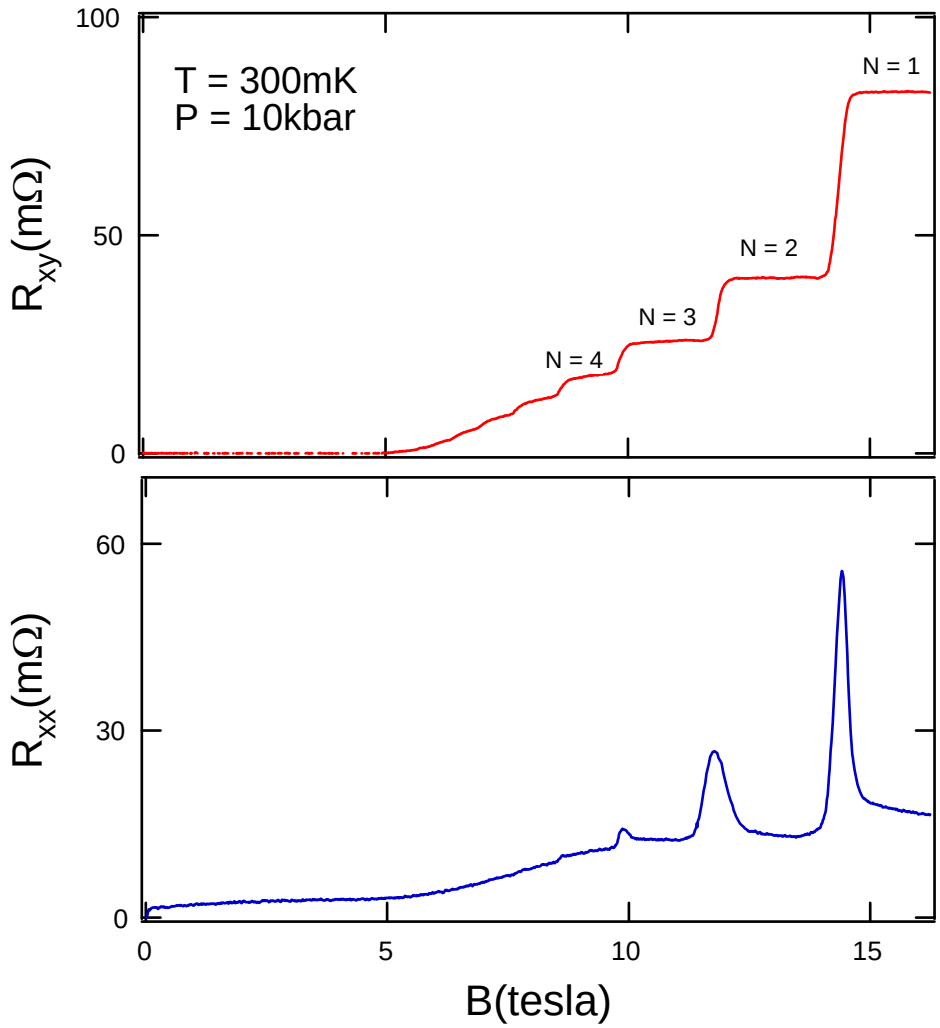


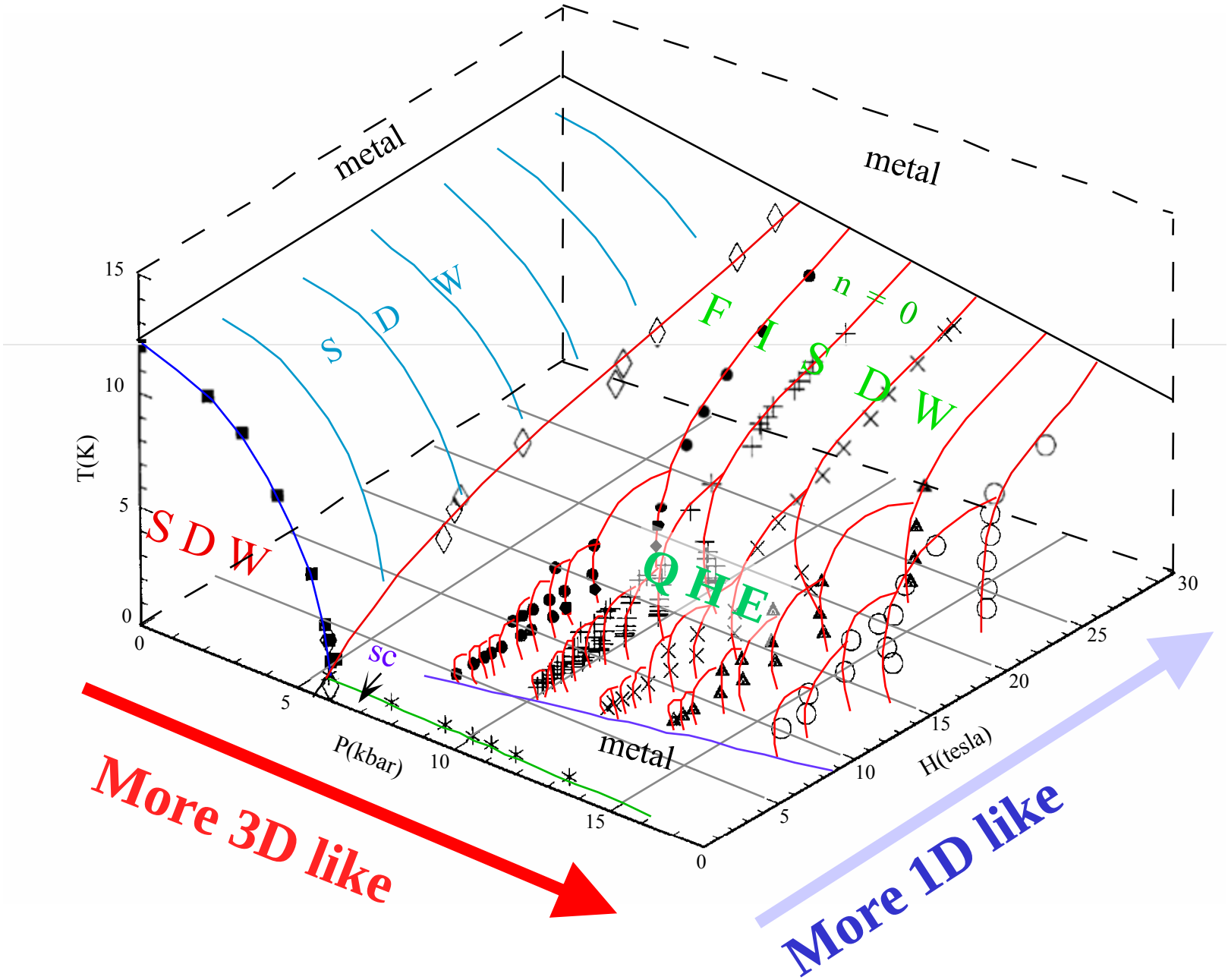
$\rho_{xy} = \frac{h}{2ne^2}$

with Quantum Hall Effect

Woowon Kang

Integer Quantum Hall Effect in $(TMTSF)_2PF_6$

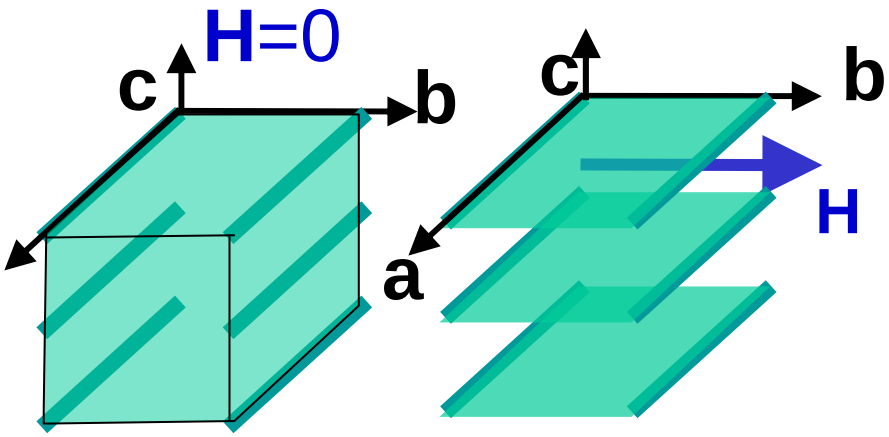



metal
metal
metal
SDW
SDW
FISDW
n = 0
QHE
sc
T(K)
P(kbar)
H(tesla)
More 3D like
More 1D like

Main lesson:

Magnetic field perpendicular to the chains reduces electronic dimension

Does this decouple chains/planes?

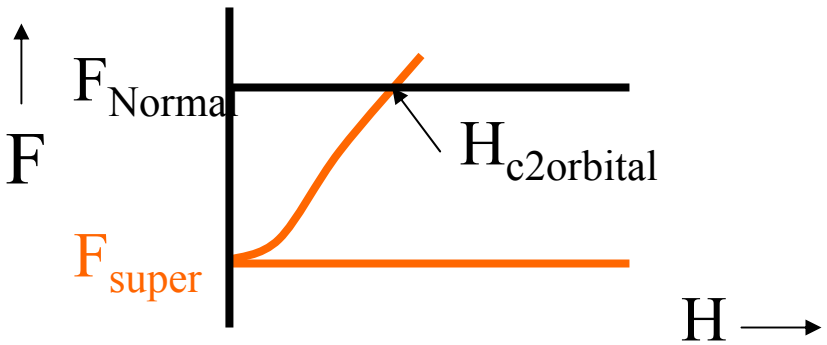


3D coherent Coherent planes

Two Contributions to Magnetic Critical Field - Orbital and Spin

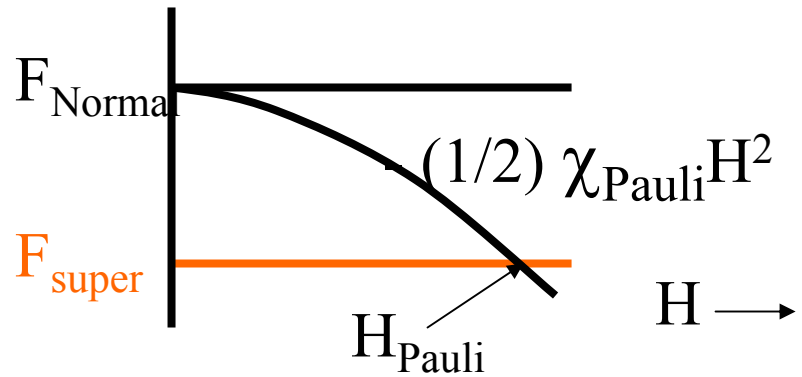
Orbital term derives from Field Expulsion
e.g. Meisner Effect

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

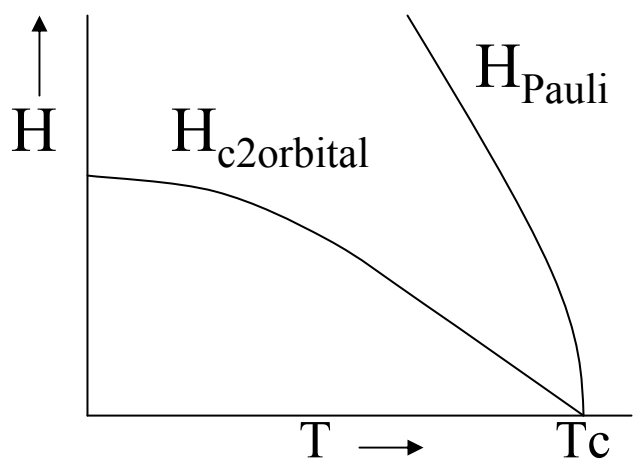


Spin derives from susceptibility
of spin paired state

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



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



Clogston-Pauli Limit to Hc_2

Normal Metal

$\uparrow\downarrow$ $\chi_{spin}=\chi_{Pauli}=\mu_0^2 N(E_F)$

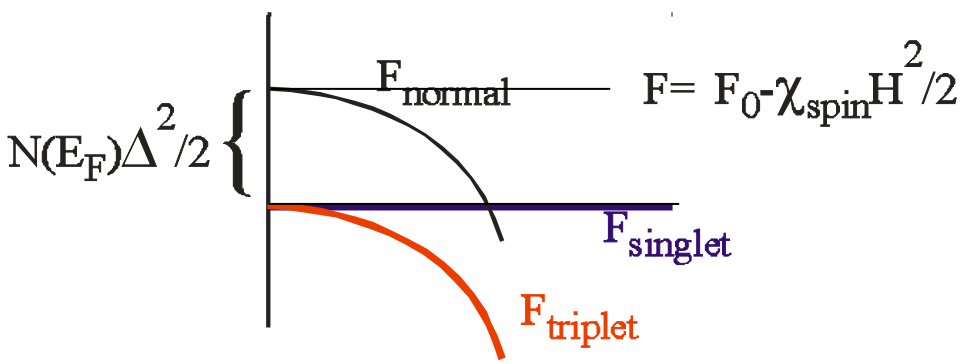
Singlet Superconductor

$\uparrow\downarrow$ $\chi_{spin}=0$

Triplet Superconductor

$\uparrow\uparrow$ $\downarrow\downarrow$ $\chi_{spin}=\chi_{Pauli}$

H ↑↓>



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

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

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

Note: When

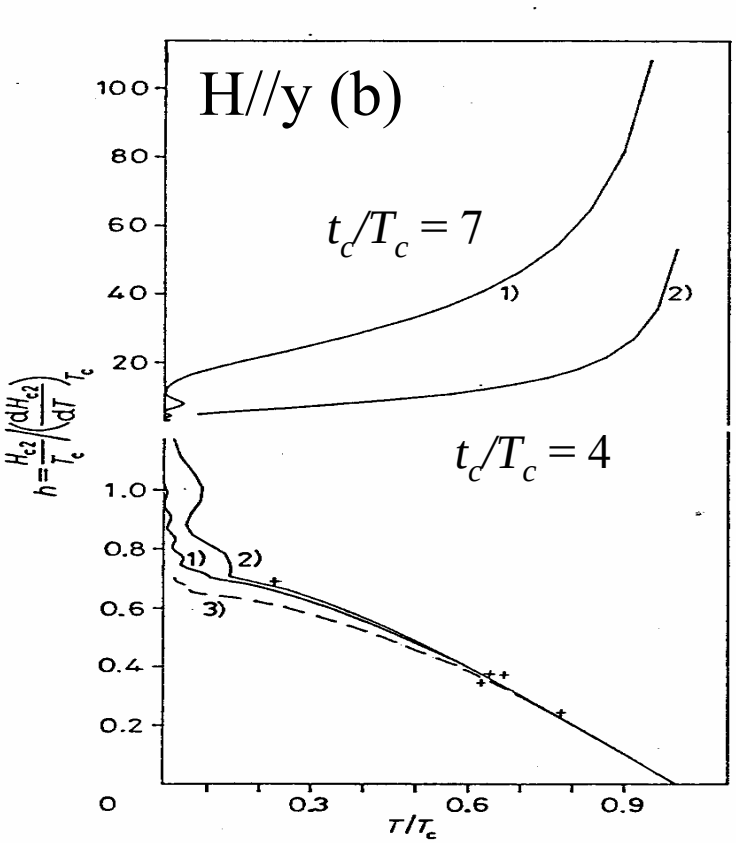
$$\mu_0 H > \Delta$$

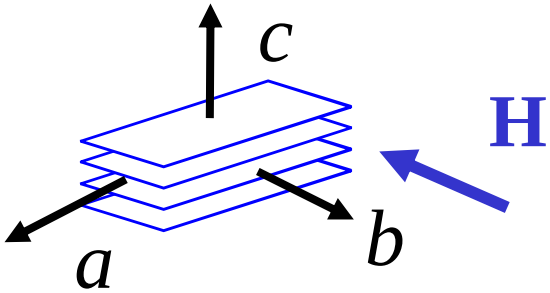
$\uparrow\downarrow \rightarrow \uparrow\uparrow$ $\uparrow$ H

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)





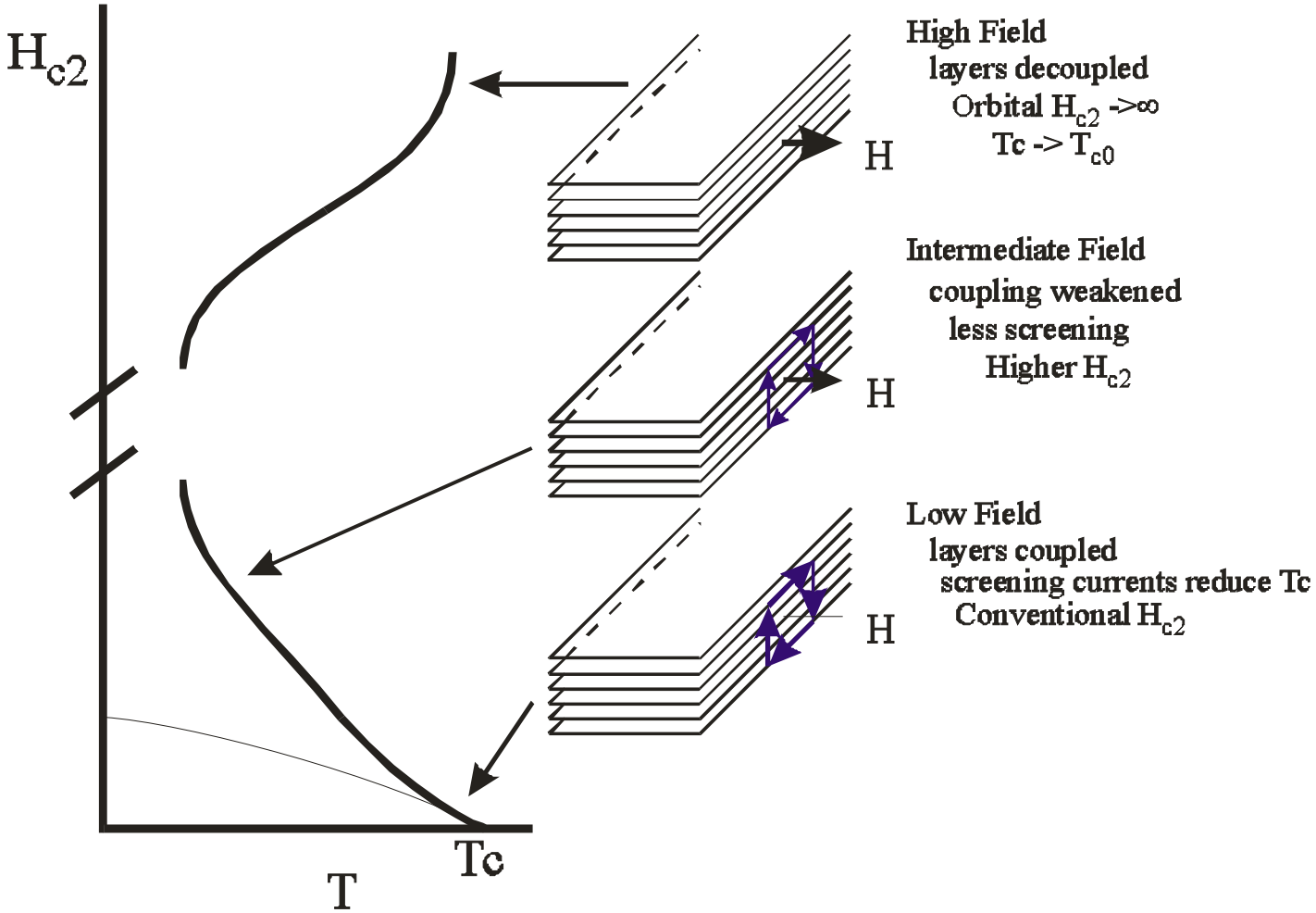
Test for the triplet superconducting pairing?

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

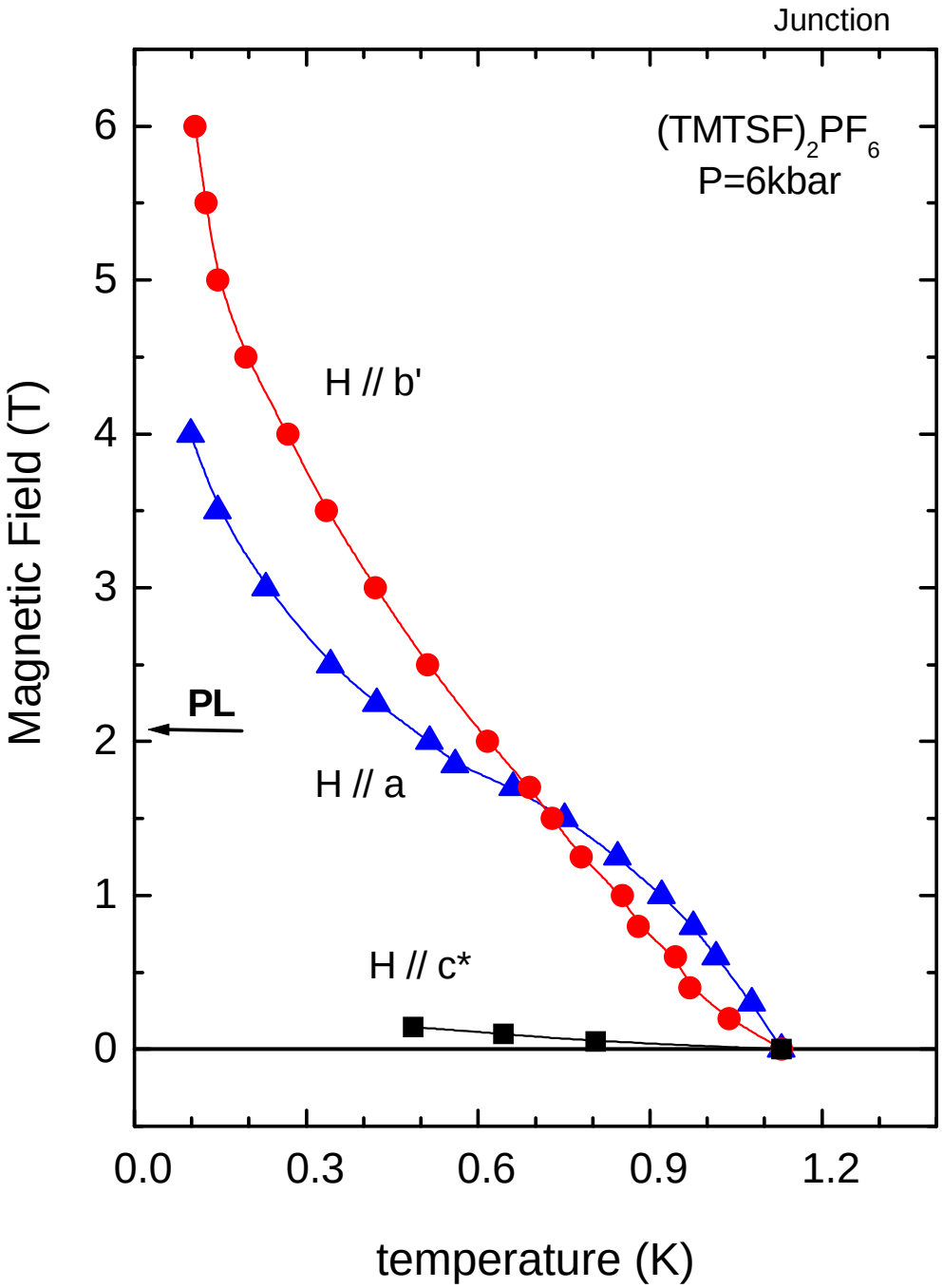
L.I. Burlarchkov, L.P. Gor'kov and A.G. Lebed'
Europhys. Lett., 4 941 (1987)

Critical Field with decoupling

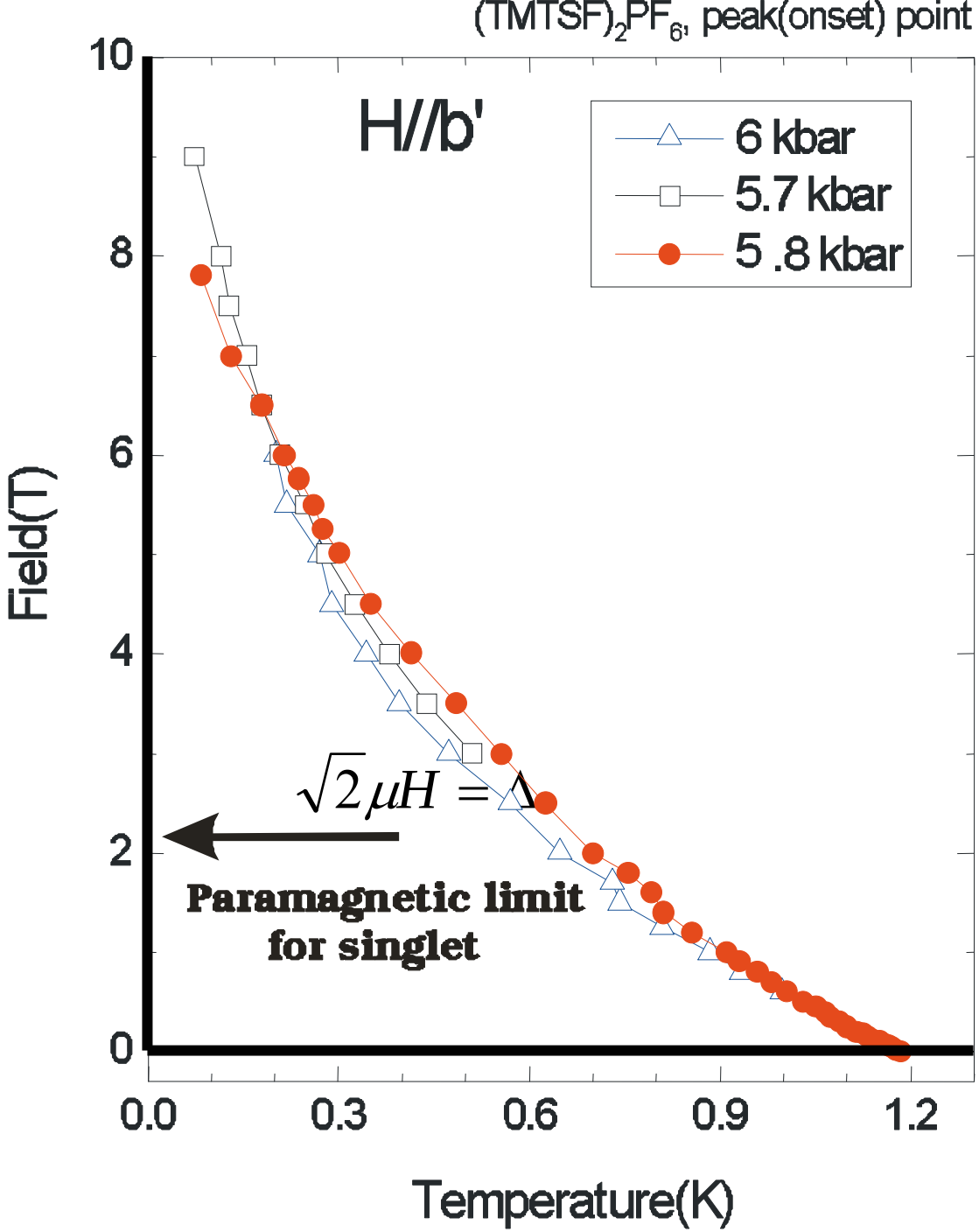
ala Lebed, Montambaux, Dupuis, Sa de Melo



Injae Lee


Junction
(TMTSF)2PF6
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

Injae Lee


(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

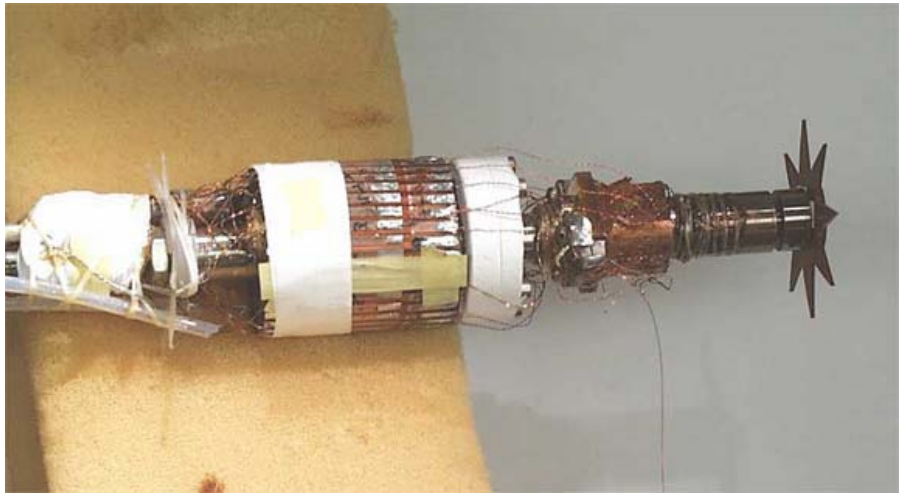
$H_{C2} > 4 \times H_{Pauli}$ ***proves*** triplet (equal spin paired)

↑↑ *or* ↓↓

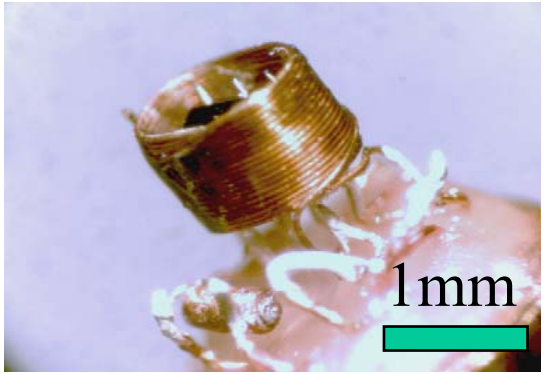
But people are more used to seeing NMR Knight Shift

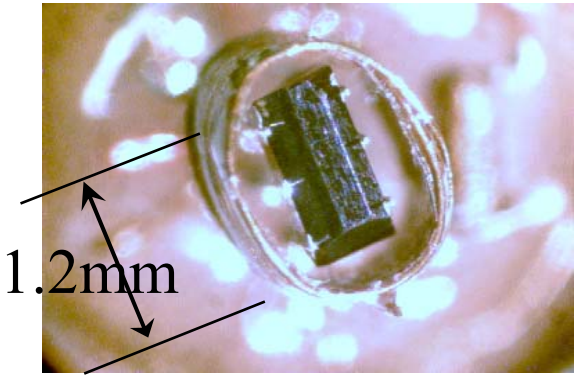
Setup for ^{77}Se NMR Knight Shift experiments

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

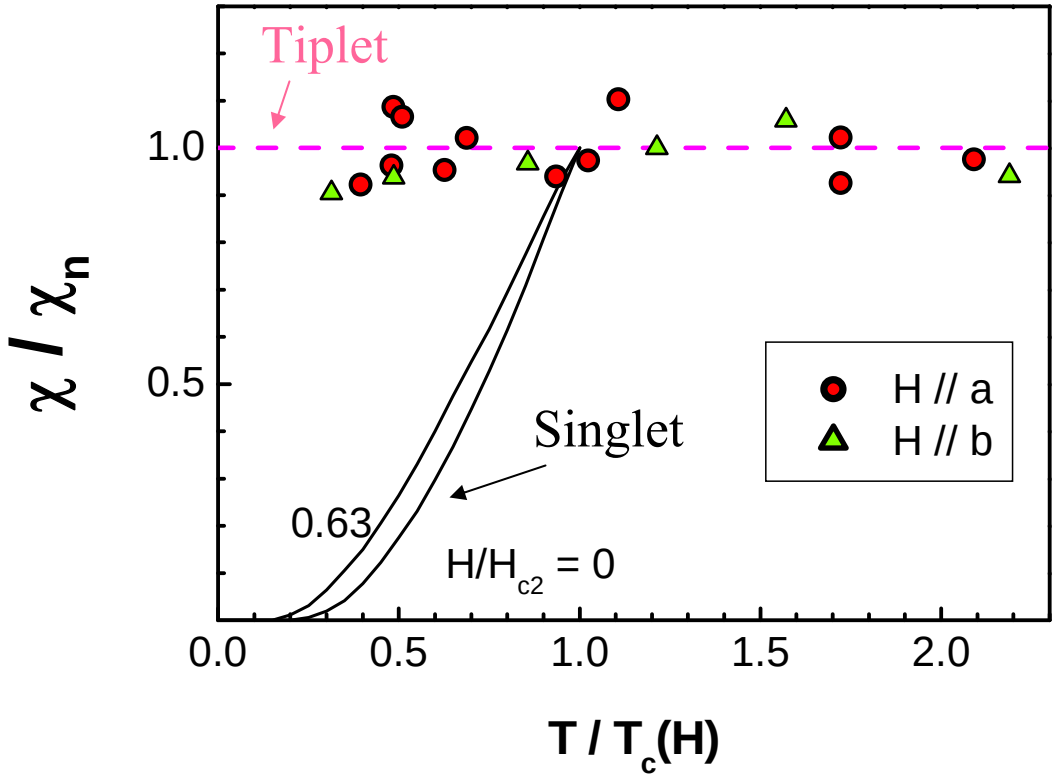


Miniature pressure cell mounted on the bottom of mixing chamber





Spin susceptibility in $(TMTSF)_2PF_6$



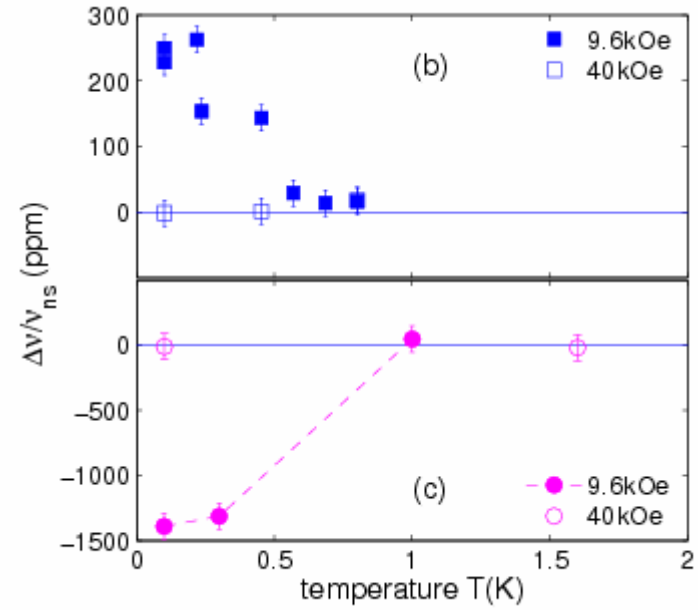
$$\frac{\chi}{\chi_n} = \frac{\langle \omega \rangle - \overline{\langle \omega \rangle}_n}{Ks}$$

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)

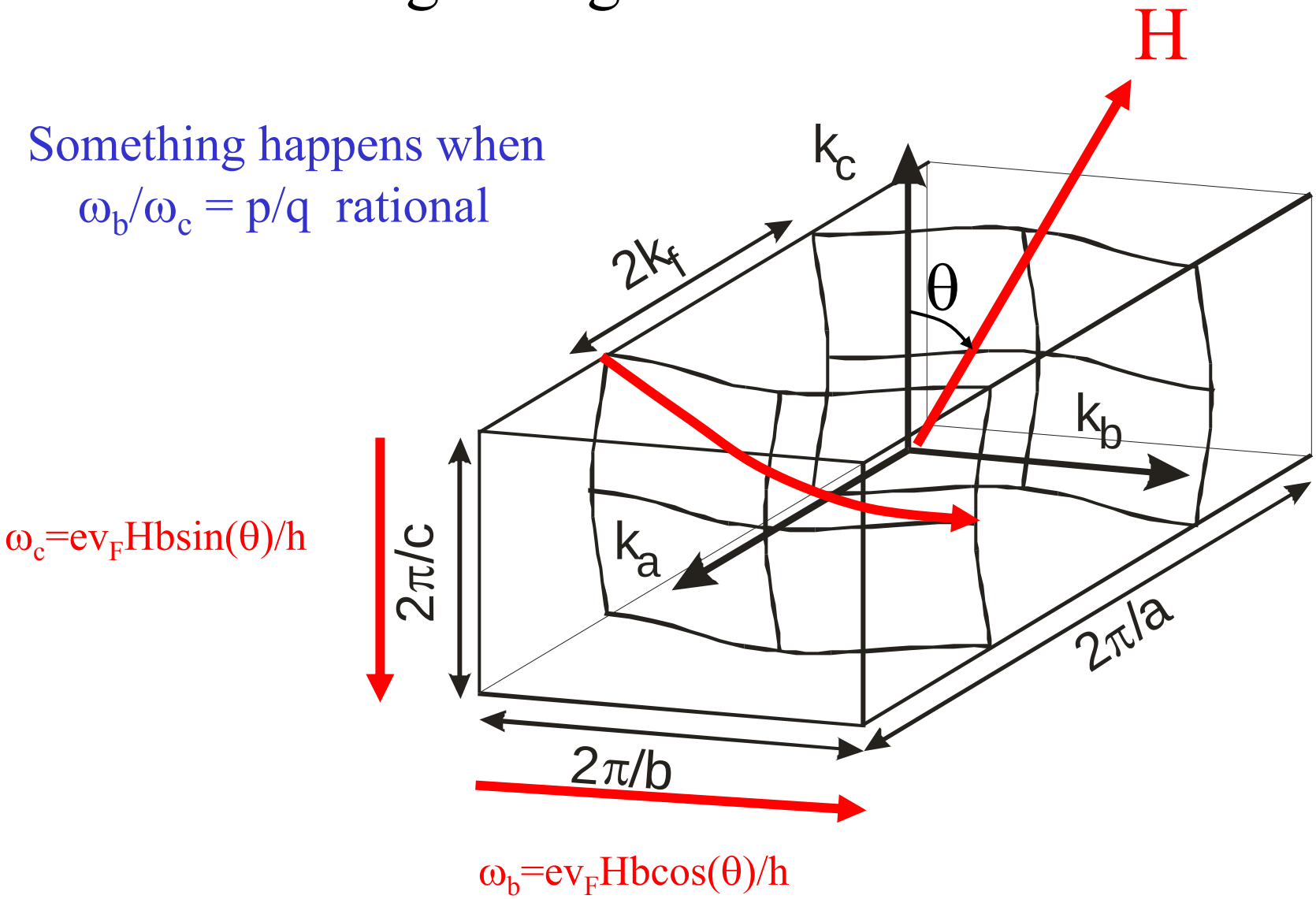
(TMTSF)2ClO4 is a quasi-one dimensional organic conductor and superconductor with Tc = 1.4K, and one of at least two Bechgaard salts observed to have upper critical fields far exceeding the paramagnetic limit. Nevertheless, the 77Se NMR Knight shift at low fields reveals a decrease in spin susceptibility 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?

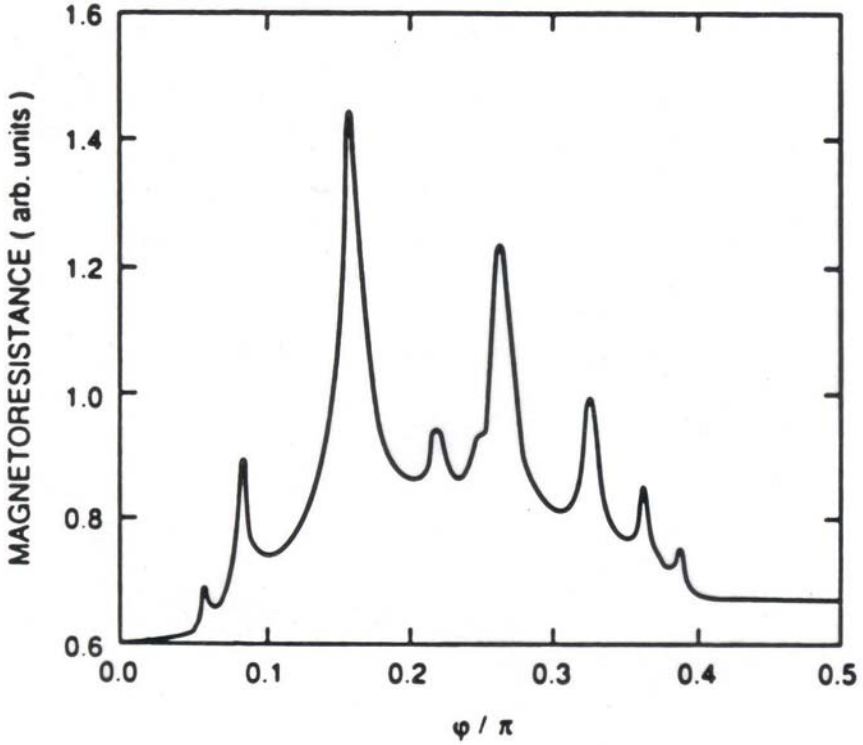
Back to Magnetic Field Induced Decoupling/Decoherence

Lebed's magic Angles

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



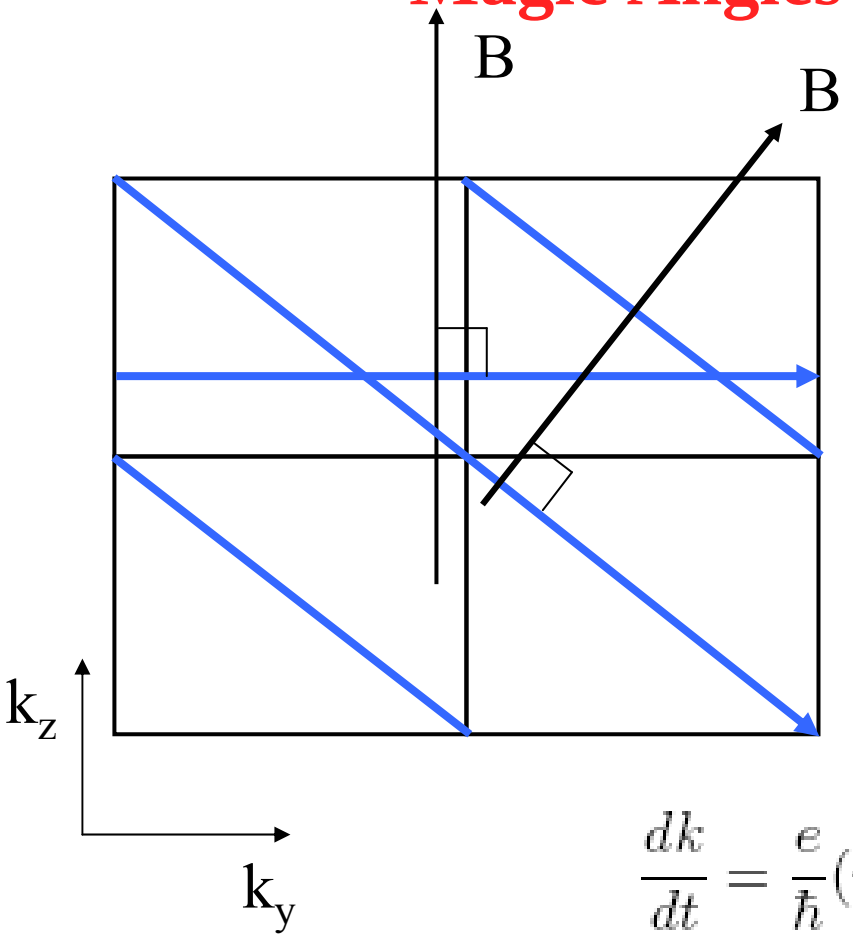
Lebed Magic Angle Effects

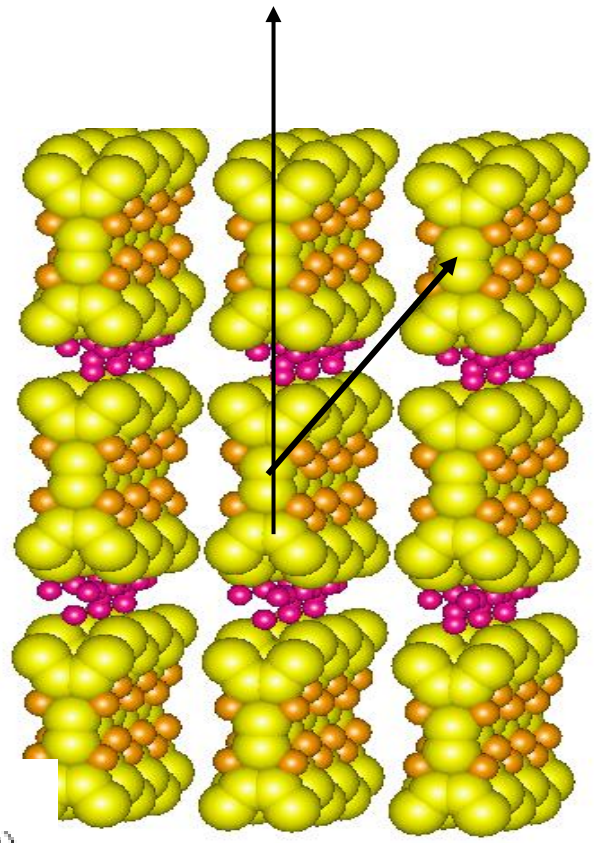


A.G. Lebed, "Anisotropy Of An Instability For A Spin-Density Wave-Induced By A Magnetic-Field In A Q1D Conductor", JETP Lett. **43**, 174 (1986).
A. G. Lebed, P. Bak, "Theory Of Unusual Anisotropy Of Magnetoresistance In Organic Superconductors", Phys Rev Lett **63**, 1315 1989

Commensurate Orbits correspond to field directed between real space chains

Magic Angles → Lattice Vectors

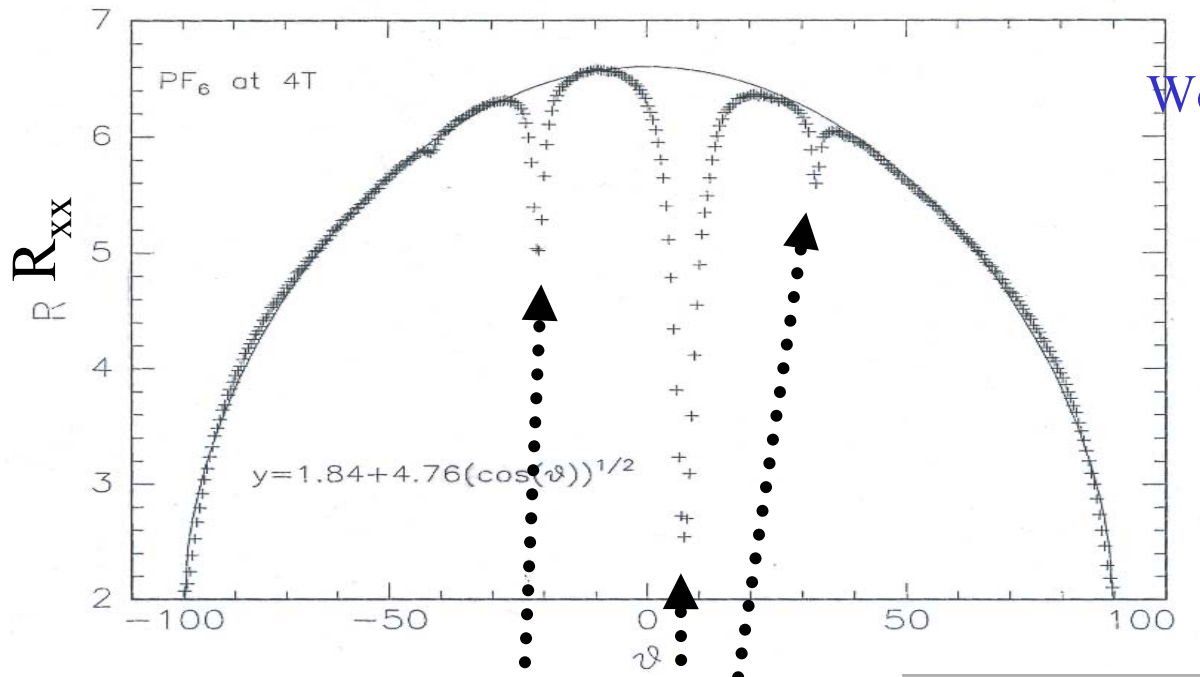




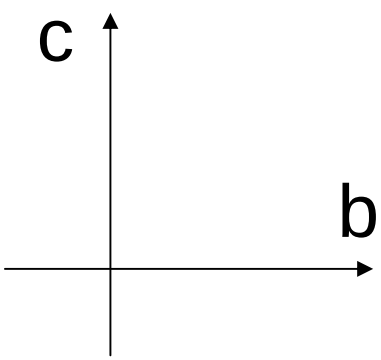
$$\frac{dk}{dt} = \frac{e}{\hbar}(v \times B)$$

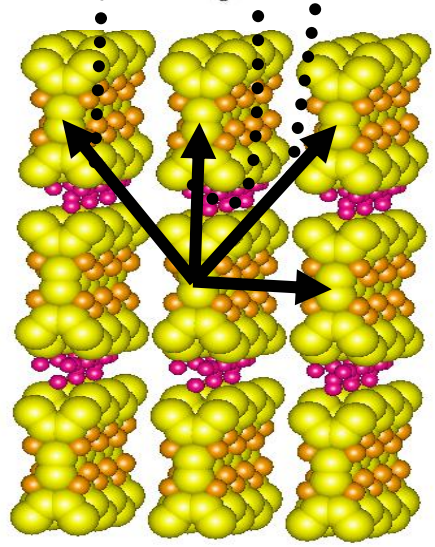
Recip space ⟷ Real space

Quasi-particle coherence



Woowon Kang





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

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

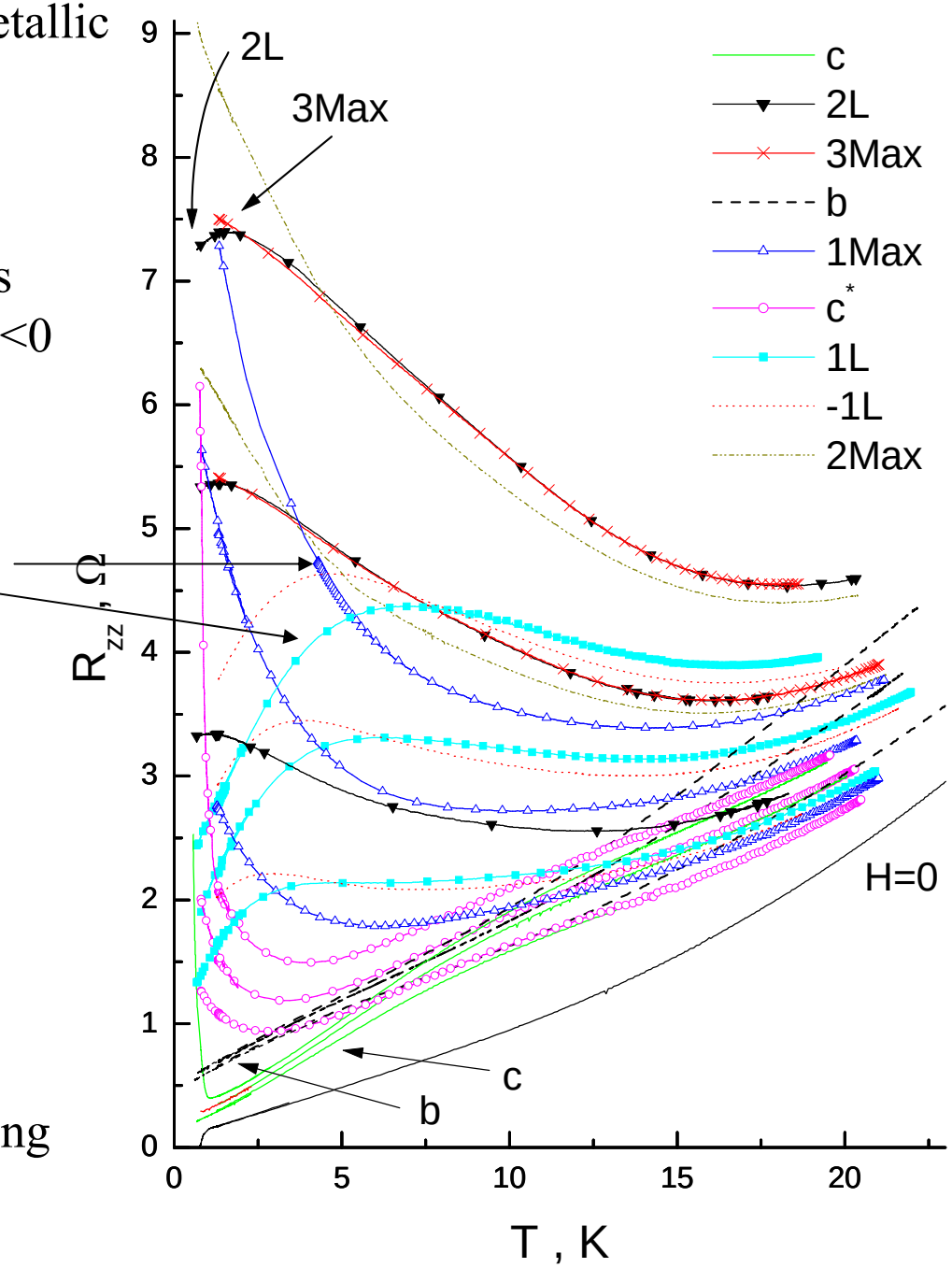
Чашечкина

At magic angles metallic dR/dT>0

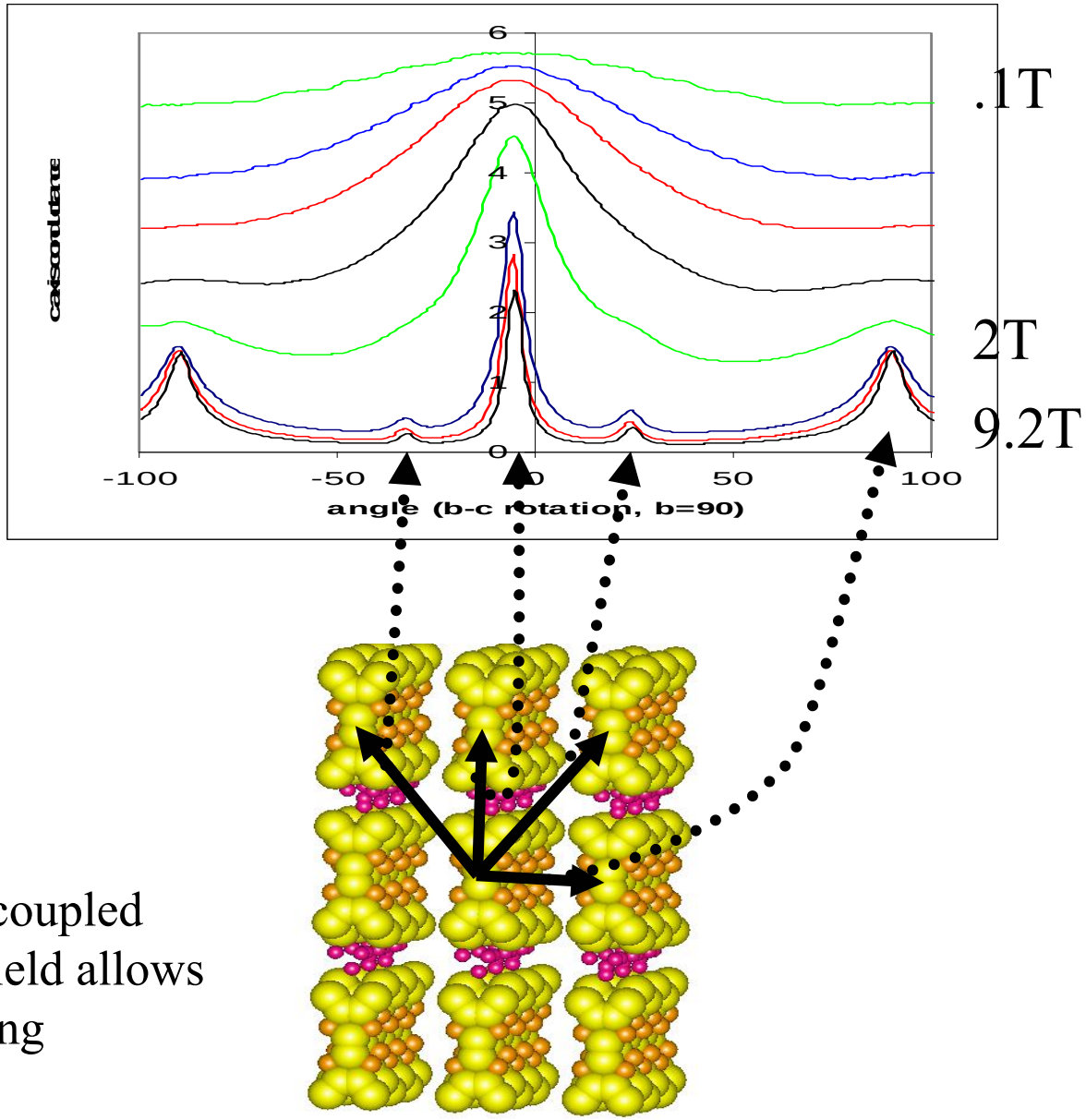
At nonmagic angles Nonmetallic dR/dT<0

These differ by 6°

Similar effect along a,b,c axes



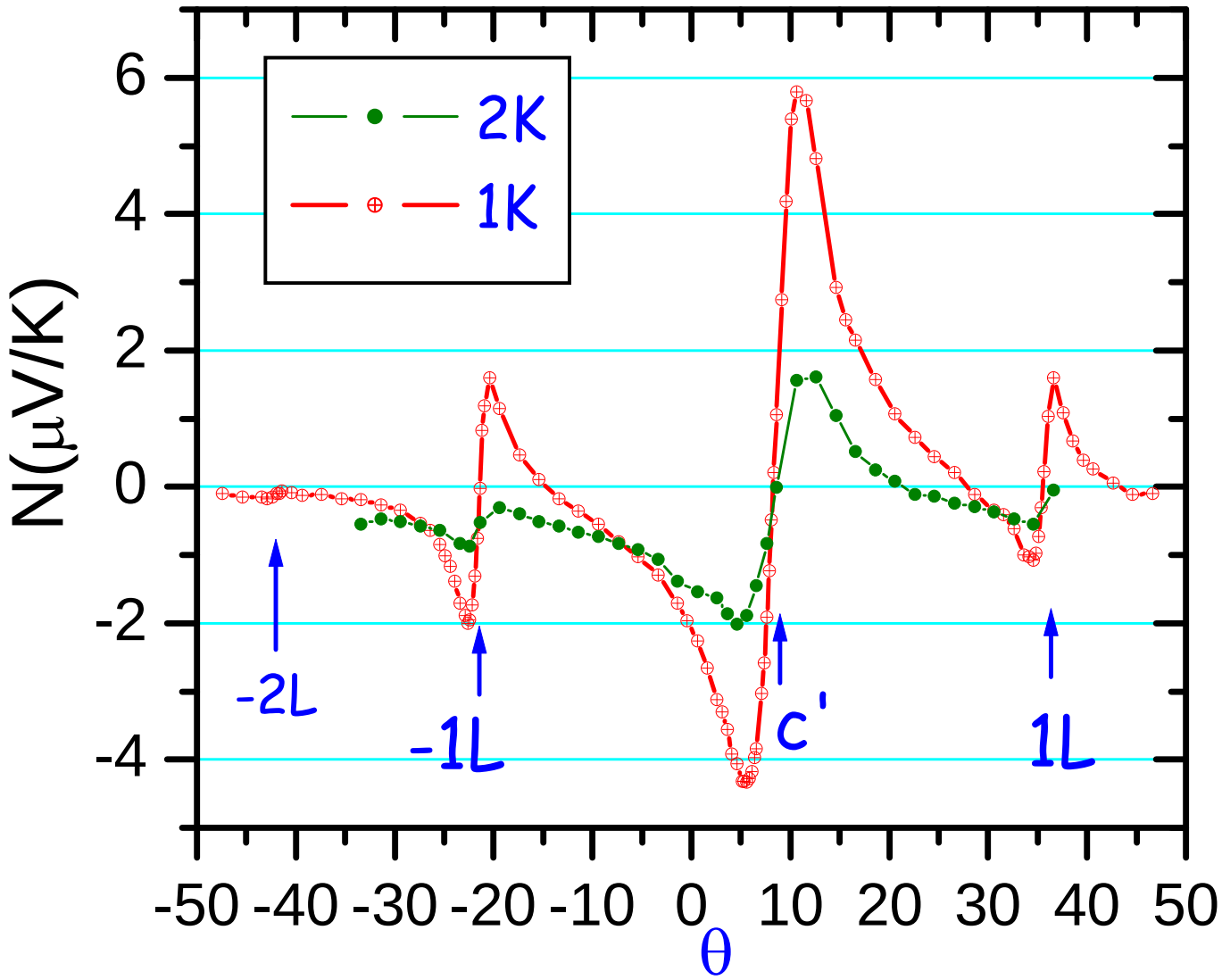
Look at Conductivity instead of resistivity



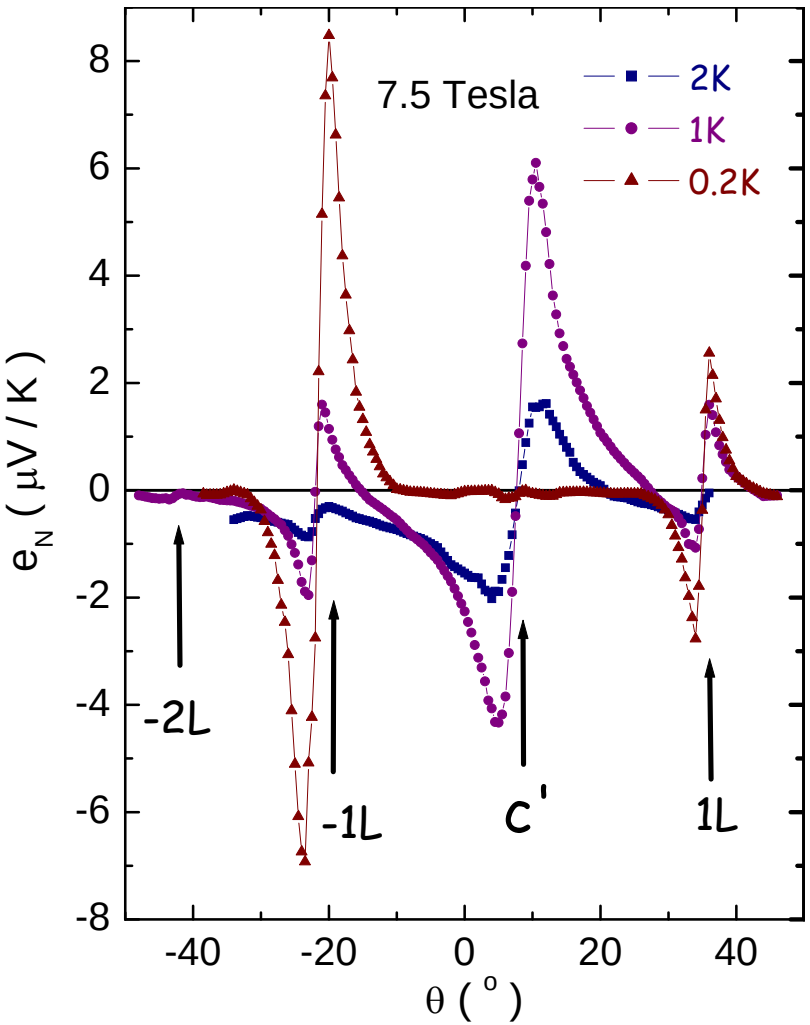
Insulating when decoupled
Conducting when field allows
interchain tunneling

Angular dependent Nernst

Weida Wu



Giant Nernst Signal



Drude, Boltzmann:

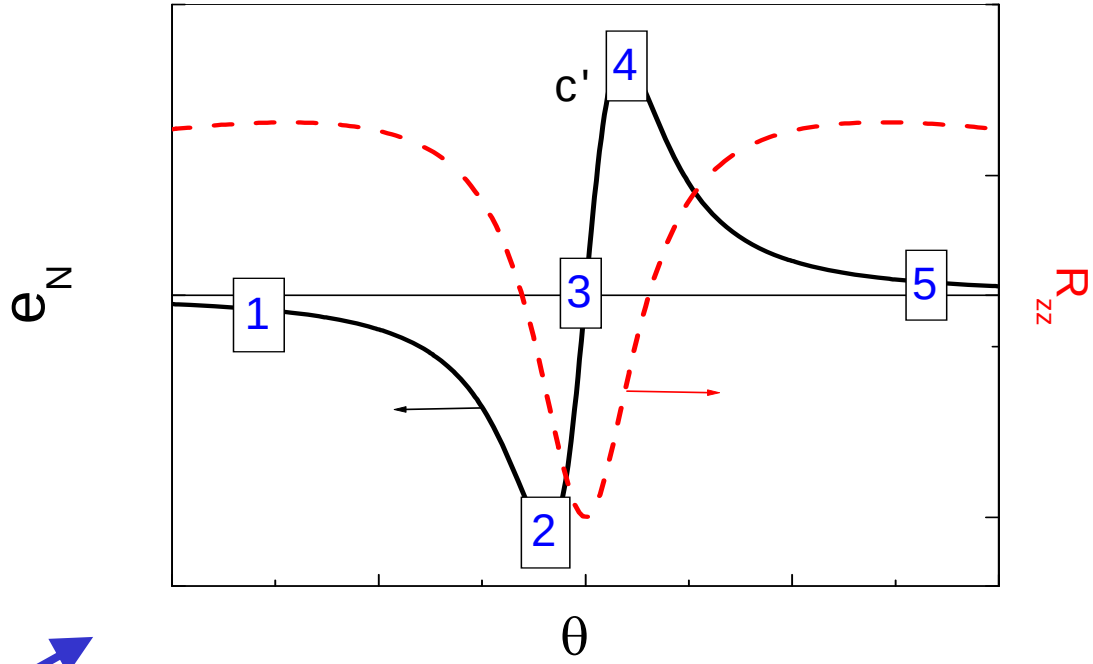
$$e_N \propto T \bullet B \sin\theta$$

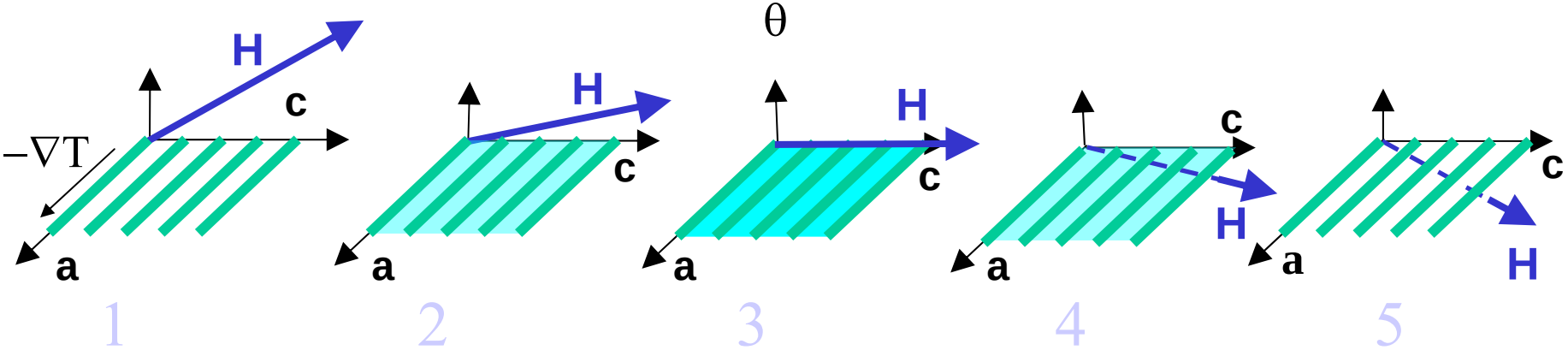
$$\sim \frac{k_B}{e}\frac{T}{T_F}\omega_c \tau$$

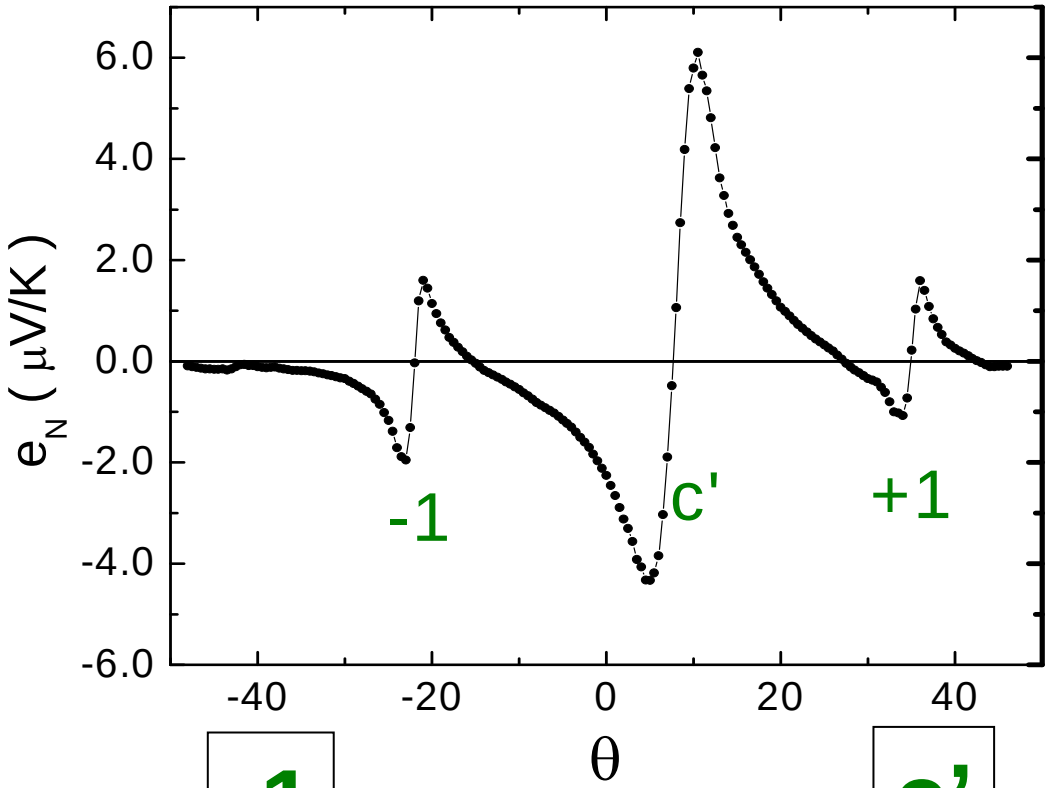
$$\approx 1 nV / K$$

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

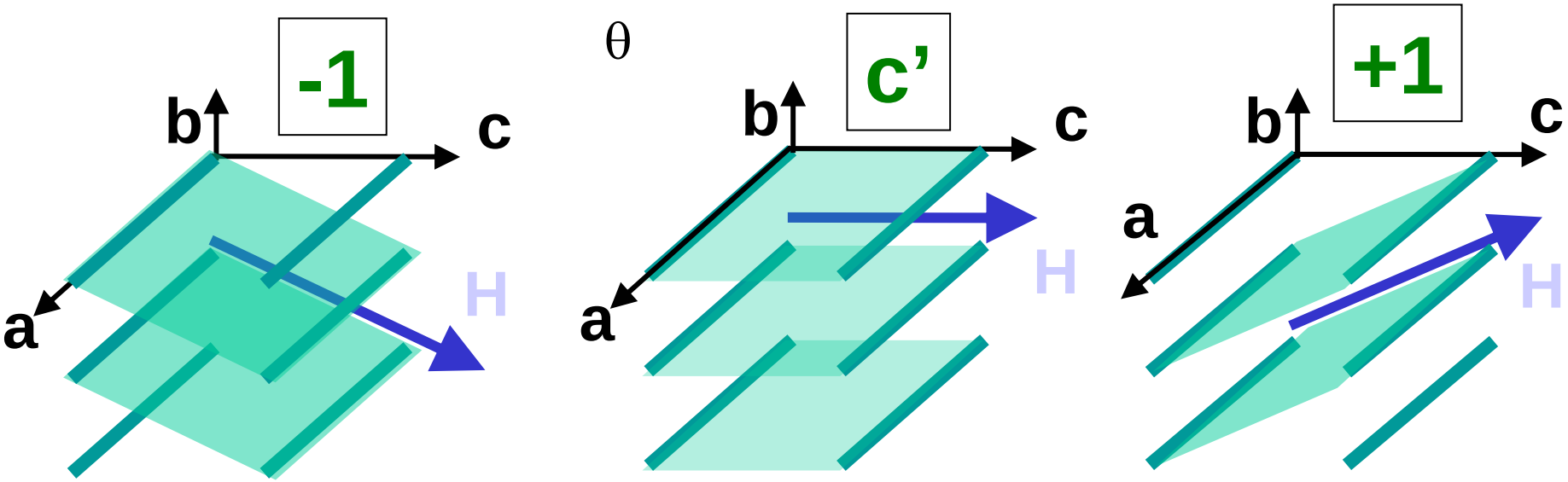
Field induced inter-chain decoupling





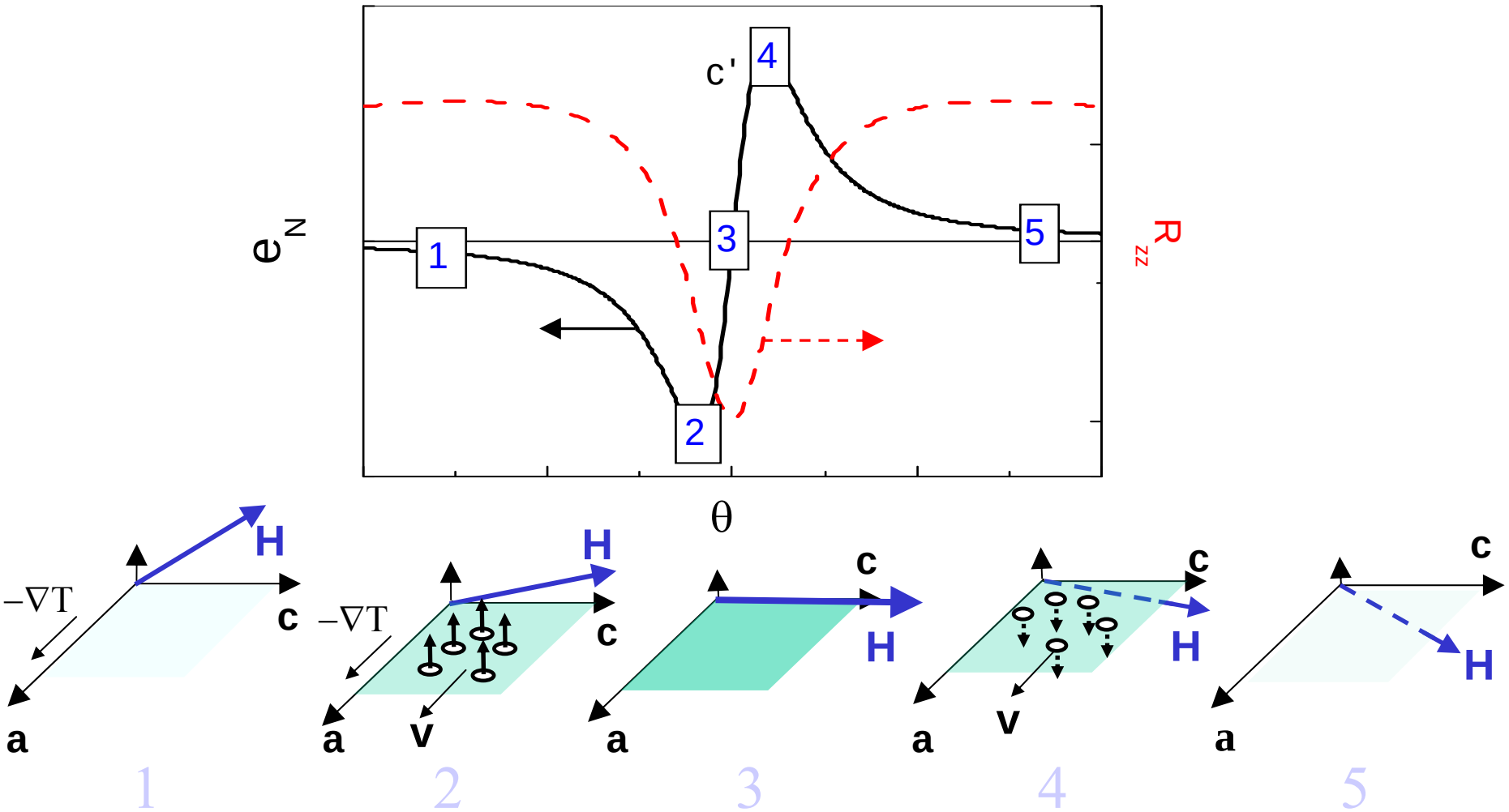


Transport:
Only coherent
at planes // **H**



What is the coherence?

SC Phase coherence at Magic Angle Planes

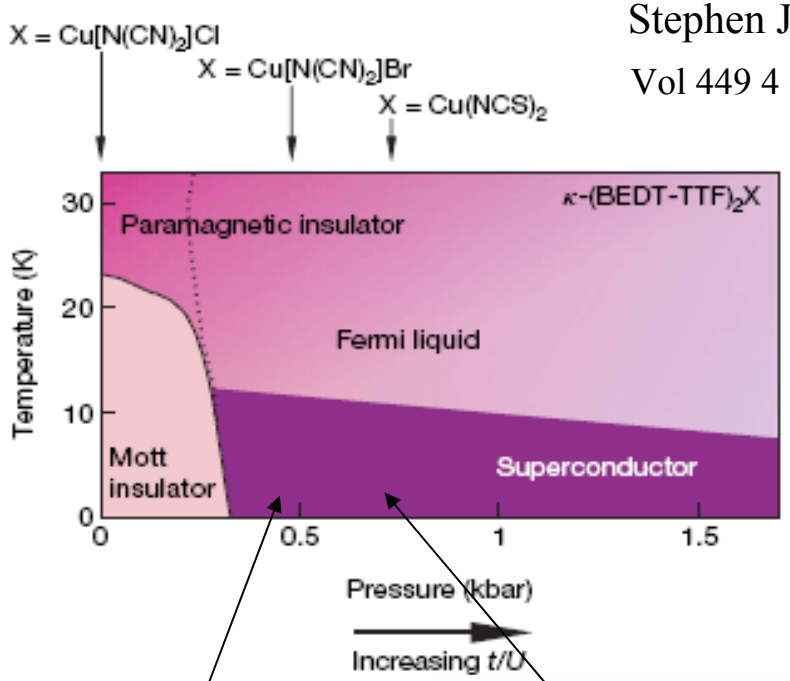


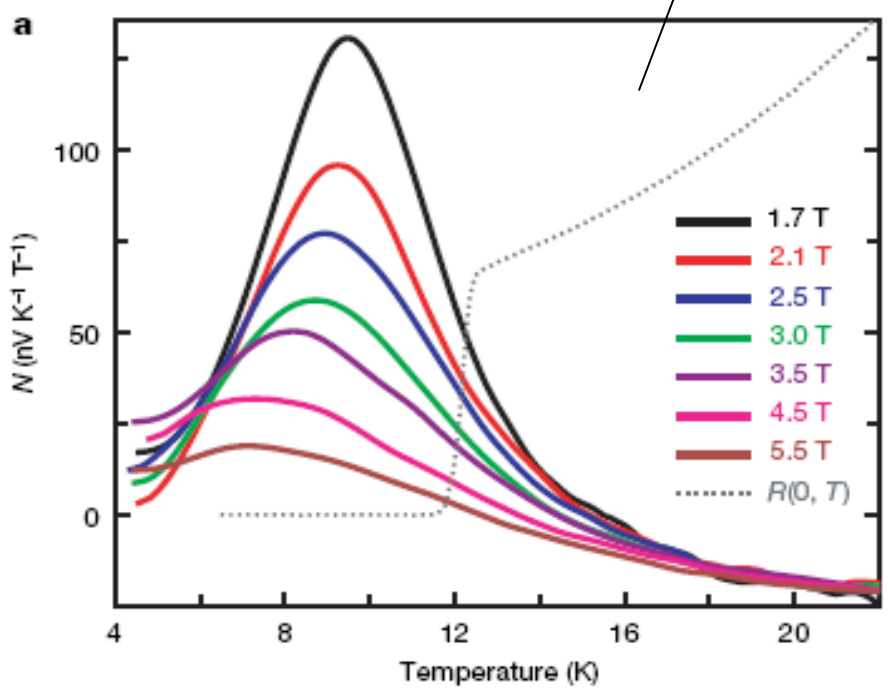
N.P. Ong, W. Wu, P. M. Chaikin and P. W. Anderson, EuroPhys. Lett. **66** (4) 579 (2004)

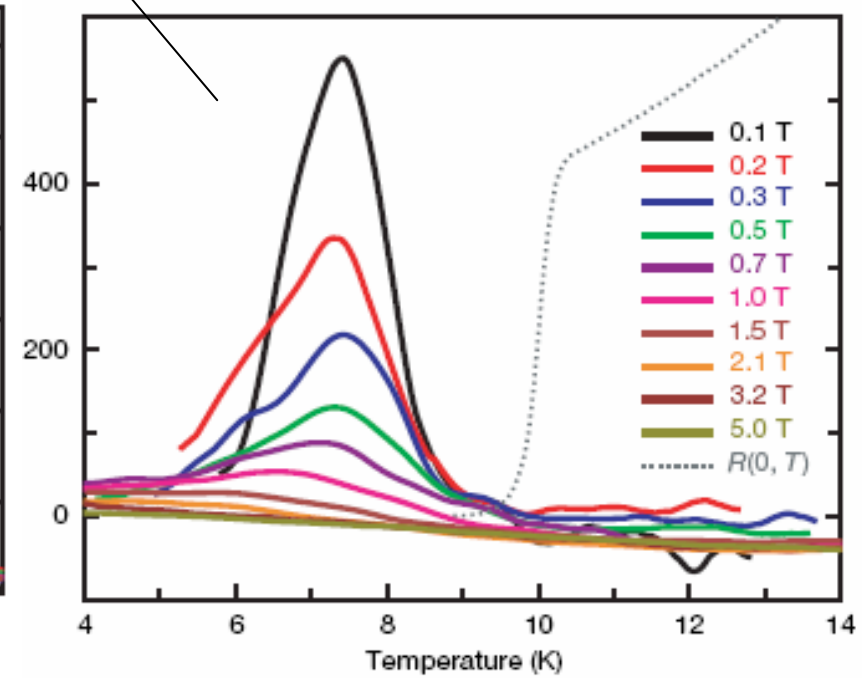
Moon-Sun Nam, Arzhang Ardavan,
Stephen J. Blundell & John A. Schlueter

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?