Boulder School, July 28,29, 2016

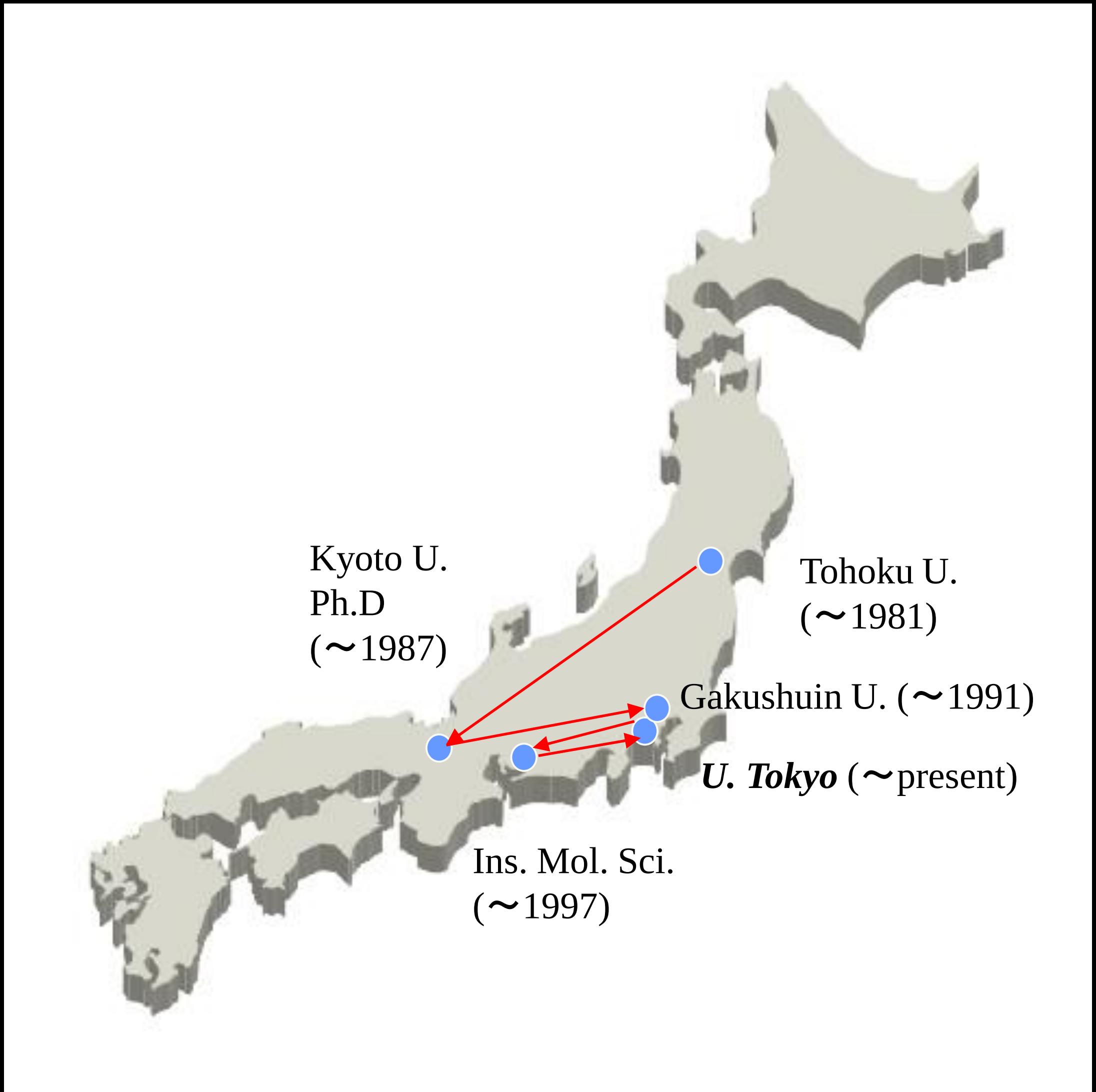
Spin liquid in organic materilas

K. Kanoda, UTokyo

References

(review article)

Yi Zhou, K. Kanoda and Ng Tai Kai
Spin liquid states
arXiv. 1607.03228

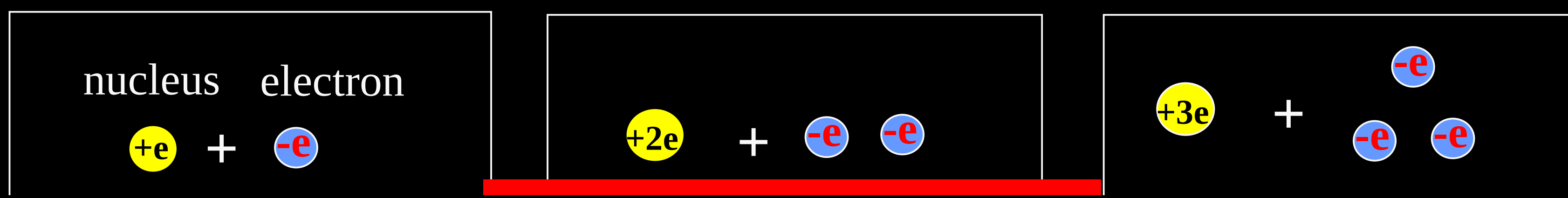

Kyoto U.
Ph.D
(〜1987)
Tohoku U.
(〜1981)
Gakushuin U. (〜1991)
U. Tokyo (〜present)
Ins. Mol. Sci.
(〜1997)

Physics of condensed matter

Understanding *low-energy state* of nucleus and electron assembly

More is *differently* different.

Hydrogen Helium Lithium

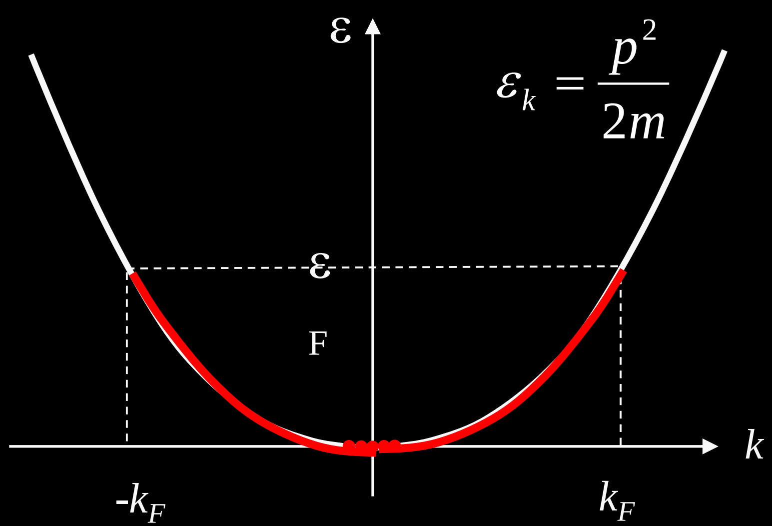


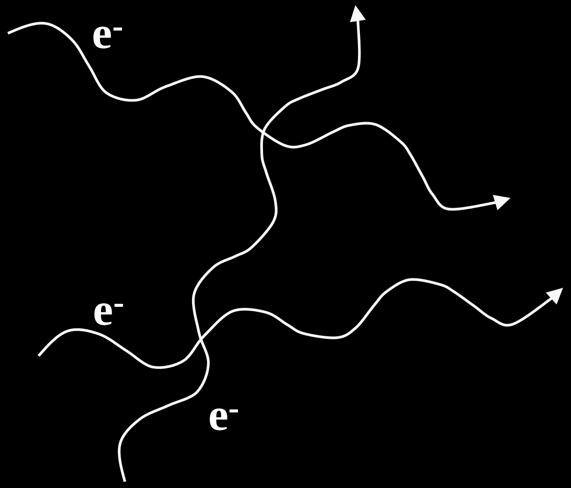
Without interaction,
electrons are free waves with Fermi surface.

$$e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$(p = \hbar k)$$

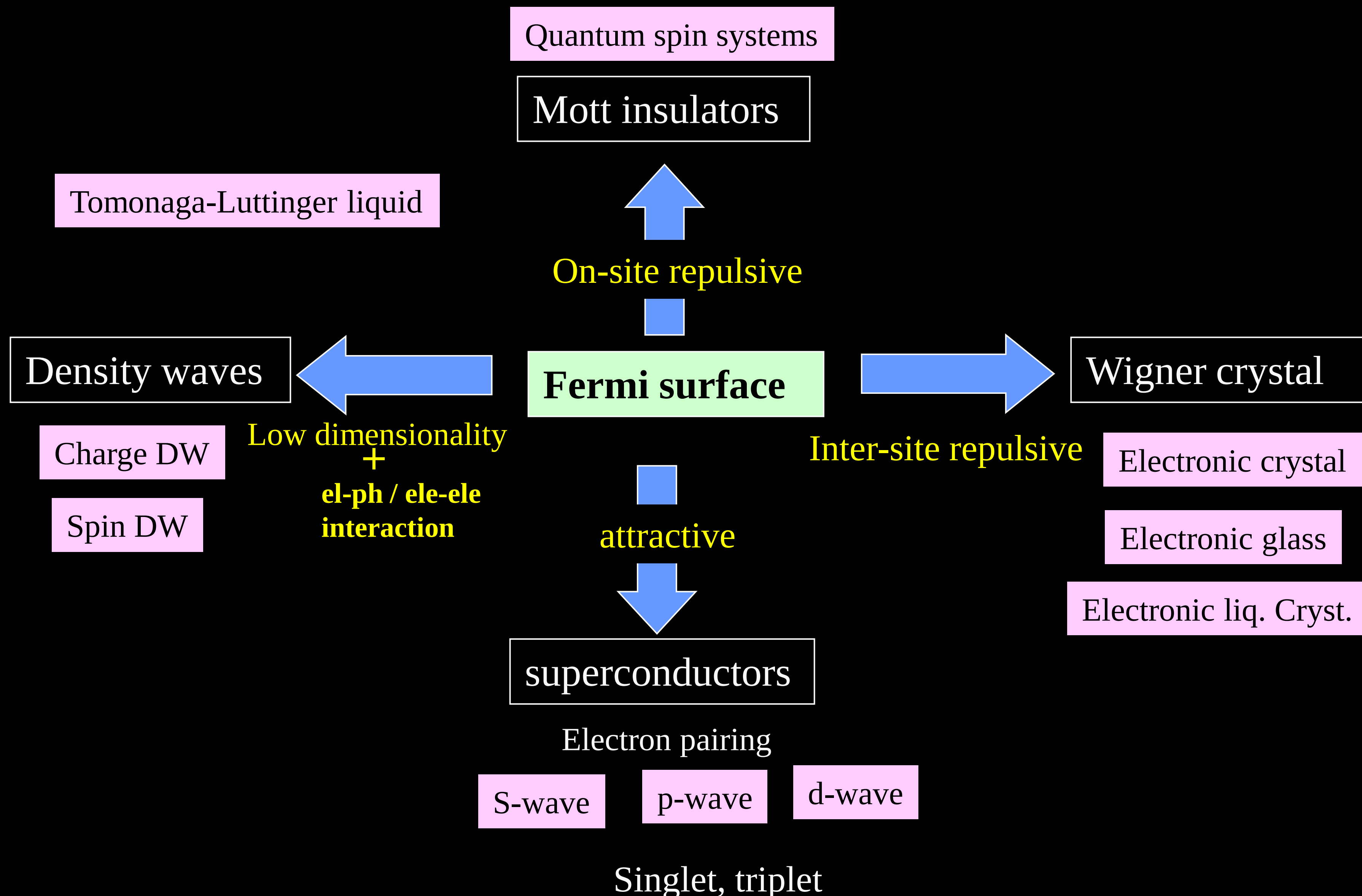
$$\varepsilon_k = \frac{p^2}{2m}$$





Fermi gas

With interaction, Fermi surface …..unstable



Contents

1. Fundamentals of organic materials

complex in real space, but simple in *k*-space

2. Electron correlation in organic materials

all-in-one systems for Mott physics

3. Spin liquid in quasi-triangular lattice

controlled frustration, correlation, disorder, doping

(Optional)

4. Massless Dirac Fermions in orhanic materials

Dirac cone reshaping and ferromagnetism

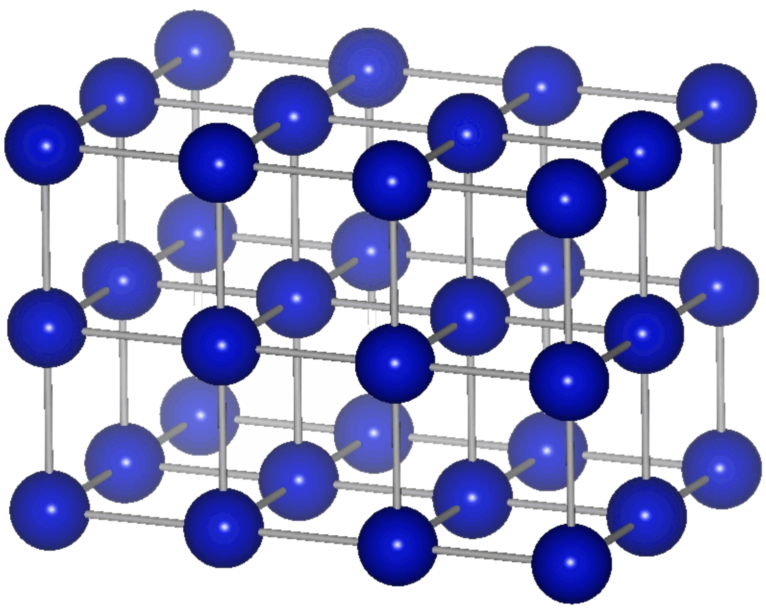
1. Molecular materials and electronic structures

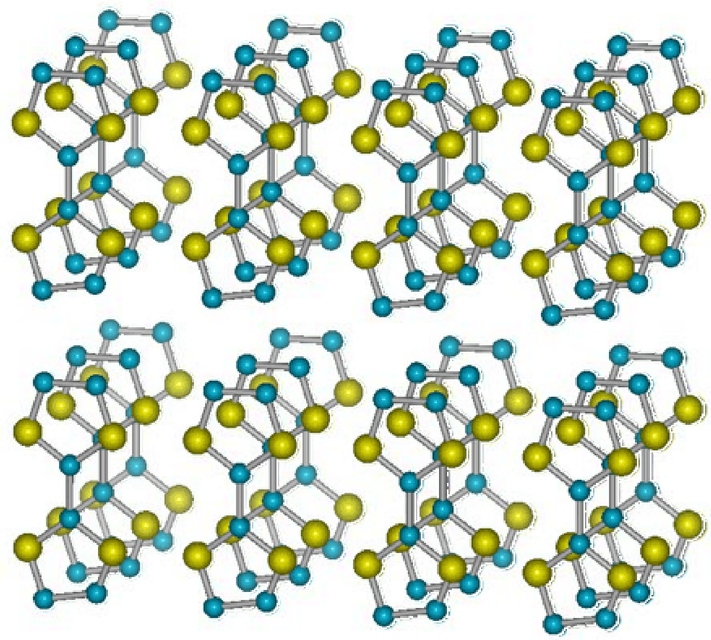
Keywords;

- a variety of lattice structures
- concept of molecular orbital
- simple band structure
- highly compressible system

Inorganic solid

Organic (molecular) solid

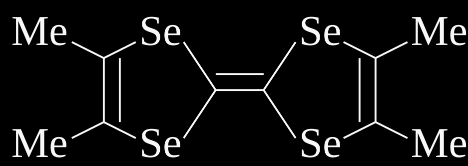




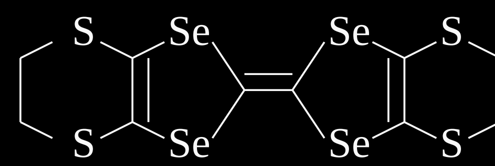
Simple metals,
oxides,….

π electron systems

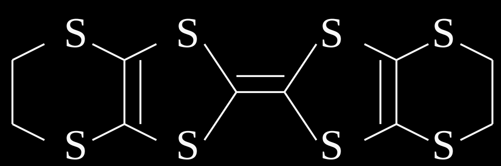
Organic molecules giving (super)conductors



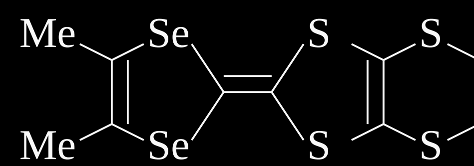
TMTSF



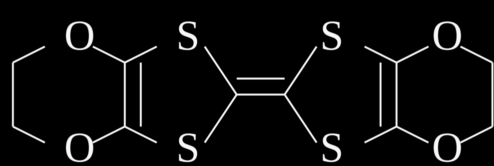
BEDT-TSF (BETS)



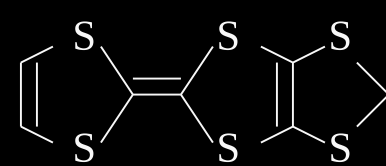
BEDT-TTF (ET)



DMET

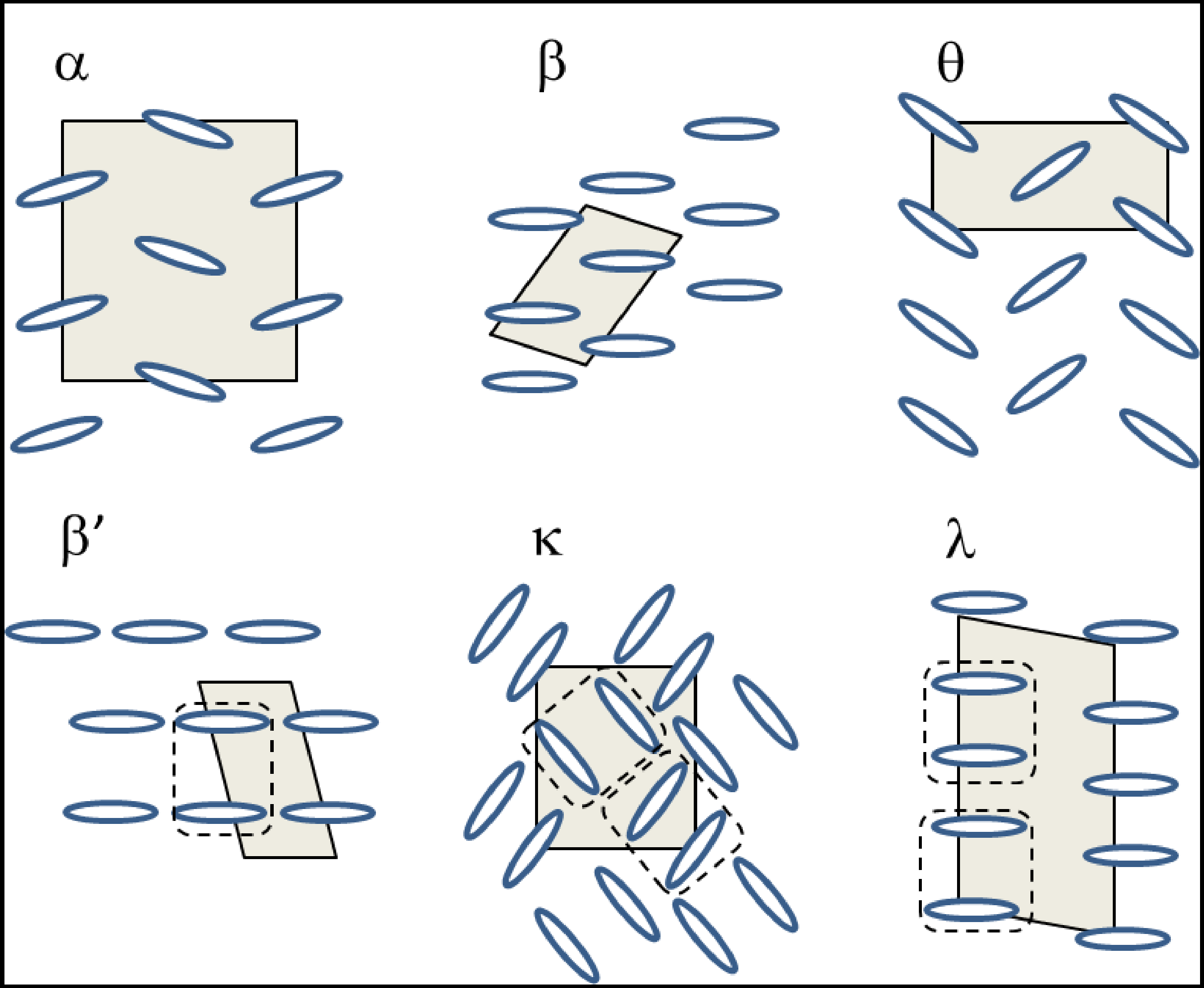


BEDO-TTF (BO)

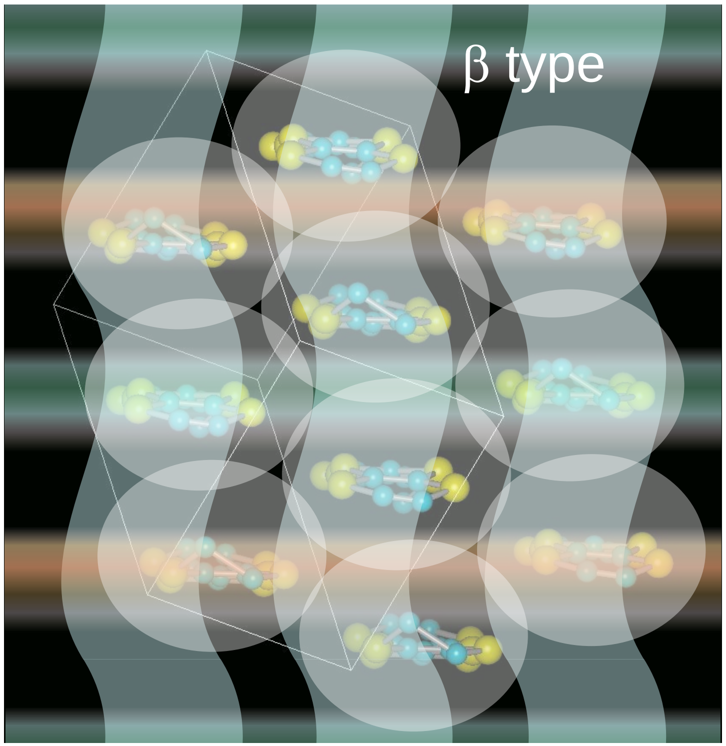


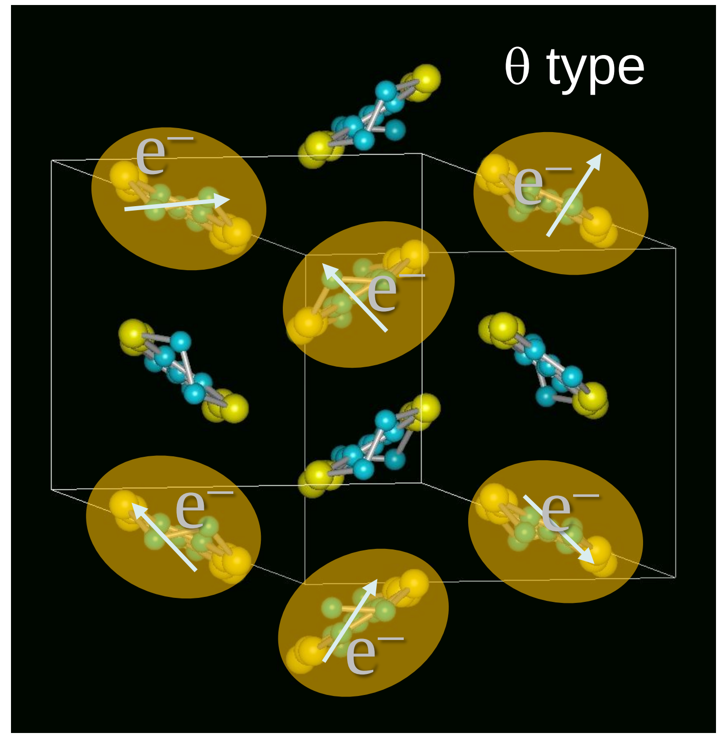
MDT-TTF

Molecular arrangement degrees of freedom

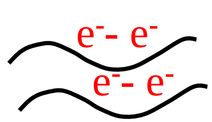


Molecular arrangement degrees of freedom

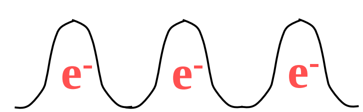




superconductivity



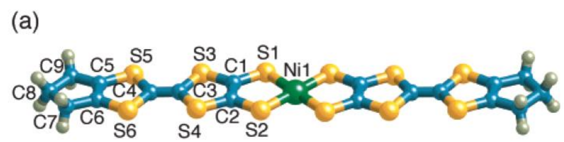
Electronic crystals

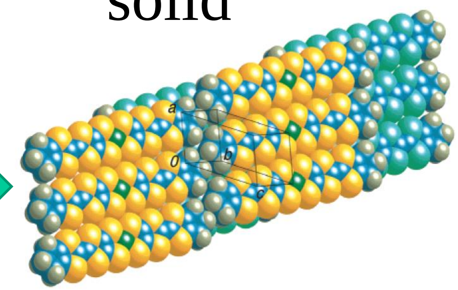


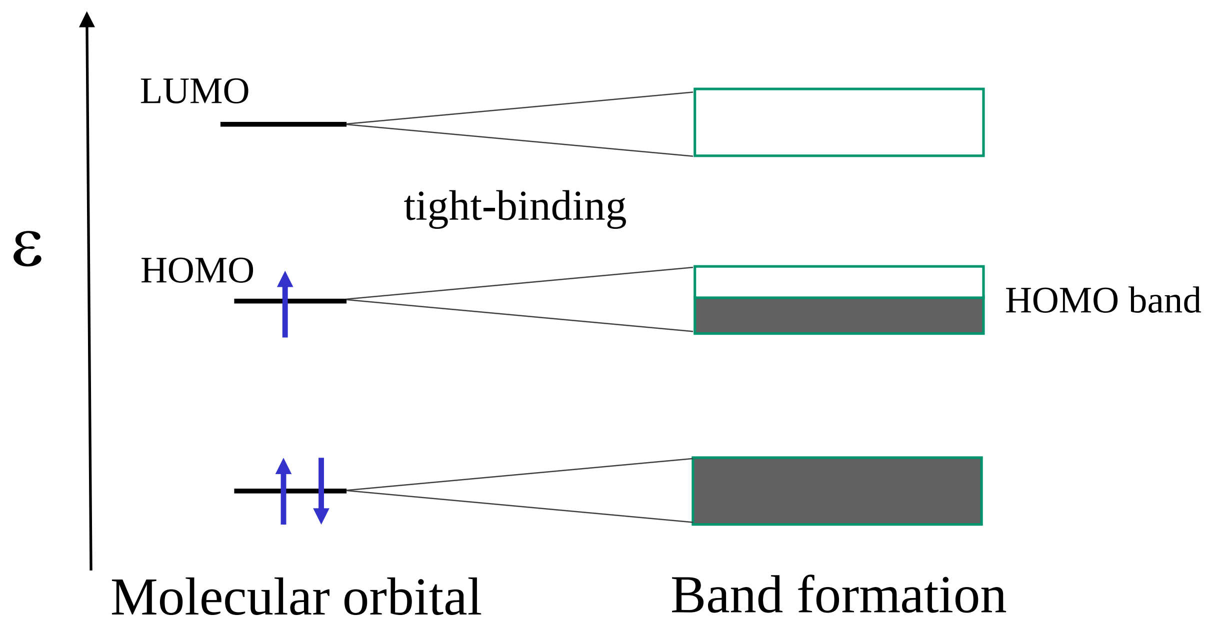
Organic conductors

complex in real space, but ***simple band structure***

atom | molecule | solid







Electronic structure

Molecular orbital is a minimum entity for electrons

No need to look into atomic orbitals in a low energy scale

Molecular material; structure is complicated in real space, but electronic structure is surprisingly simple in *k-space*

It's because of the hierarchy; atomic orbital → **molecular orbital** → electronic band

Key concept

1) The simplest non-degenarate case; hydrogen molecule

Molecular orbital   Linear combination of atomic orbitals

$$\varphi = c_a\phi_a + c_b\phi_b \qquad H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_a} - \frac{e^2}{4\pi\varepsilon_0 r_b} + \frac{e^2}{4\pi\varepsilon_0 R}$$

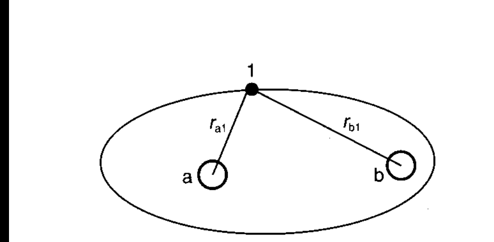


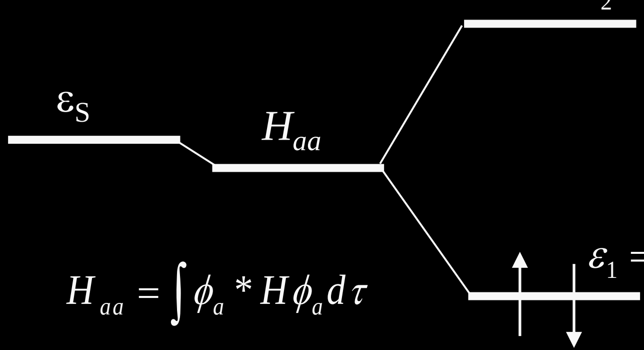
図 4.1 H_2^+の陽子 a, b と電子 1

$$\varphi_1 = \frac{1}{\sqrt{2(1+S)}}(\phi_a + \phi_b)$$ bonding orbital

$$\varphi_2 = \frac{1}{\sqrt{2(1-S)}}(\phi_a - \phi_b)$$ antibonding orbital

$$S = \int \phi_a{}^* \phi_b d\tau$$

Overlapping integral



$$\varepsilon_2 = \frac{H_{aa} - H_{ab}}{1-S}$$

$$\varepsilon_1 = \frac{H_{aa} + H_{ab}}{1+S}$$

$$H_{aa} = \int \phi_a{}^* H\phi_a d\tau$$

$$H_{ab} = \int \phi_b{}^* H\phi_a d\tau$$

Transfer integral

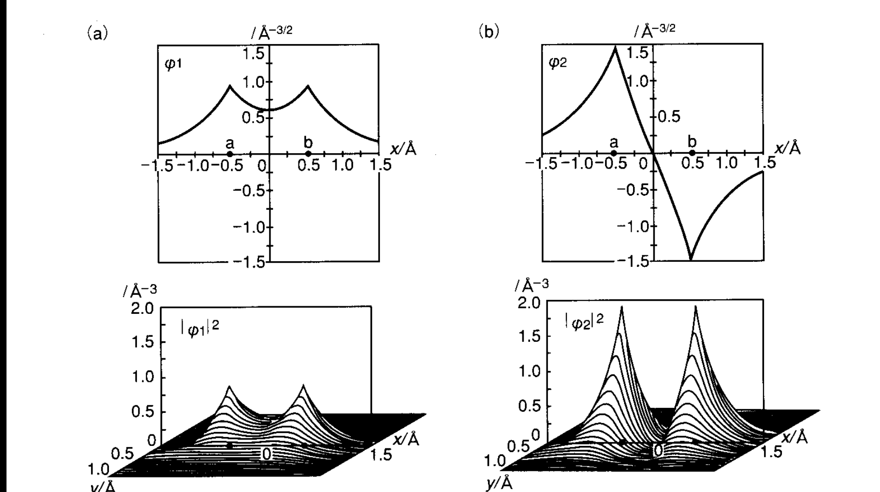


図 4.2 (a) H_2^+の対称分子軌道φ_1 と電子密度 $|\varphi_1|^2$, (b) H_2^+の非対称分子軌道φ_2 と電子密度 $|\varphi_2|^2$ [1b)]

2) The degenarate case: carbon atom

$\varphi_{lmn} = R_{nl} Y_{lm}(\vartheta, \phi)$

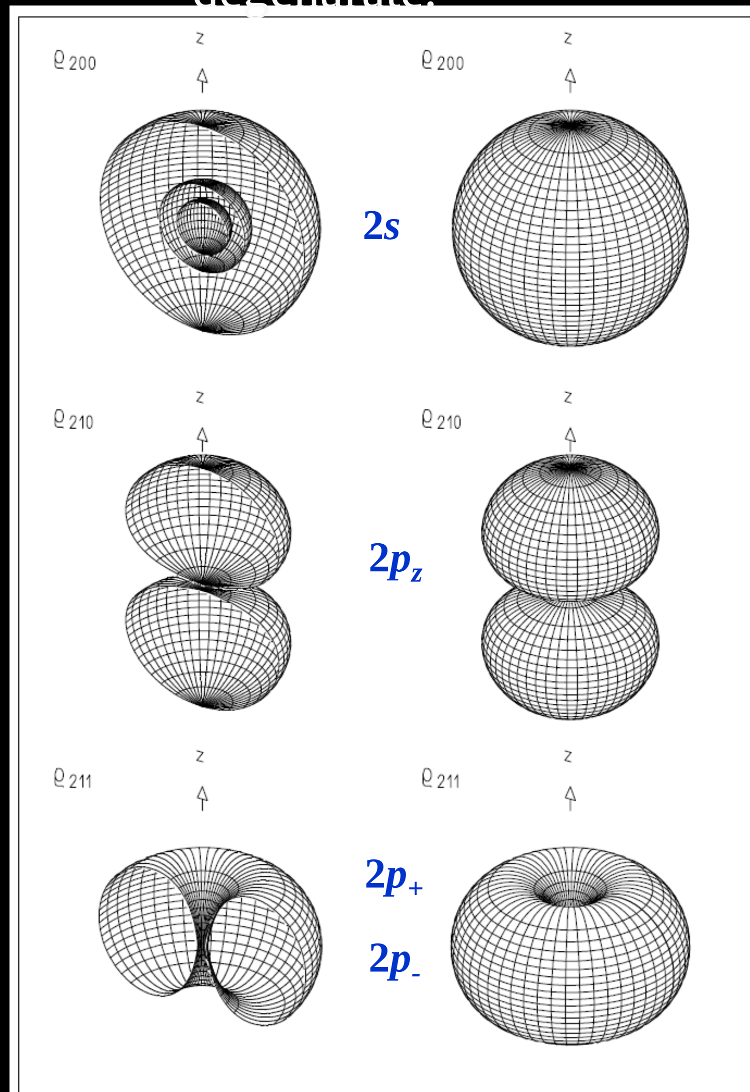
For n=2, four orbitals (2s, 2p × 3) are degenarate.

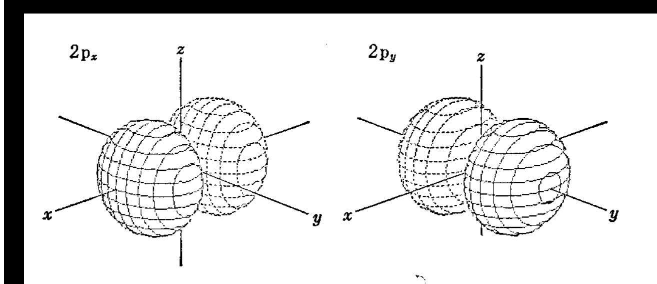
$Y_{00}(\vartheta, \phi)$

$Y_{10}(\vartheta, \phi)$

$Y_{11}(\vartheta, \phi)$

$Y_{1-1}(\vartheta, \phi)$





Atomic *p*-orbital→ molecular orbital

First, consider symmetry of coordination and reconstruct orbitals (intra-atomic hybridization)

↓

Next, reconstruct orbitals between neighbors (inter-atomic hybridization like hydrogen molecule)

↓

Finally, construct the overall molecular orbitals

i） Uniaxial 2-way coordination; sp hybridization

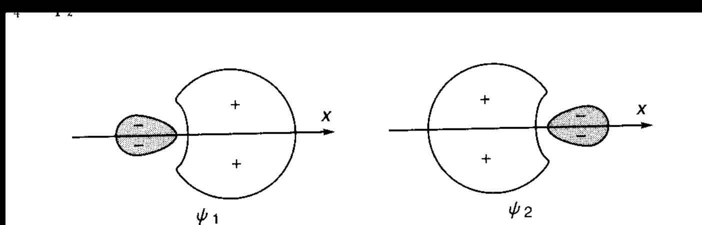
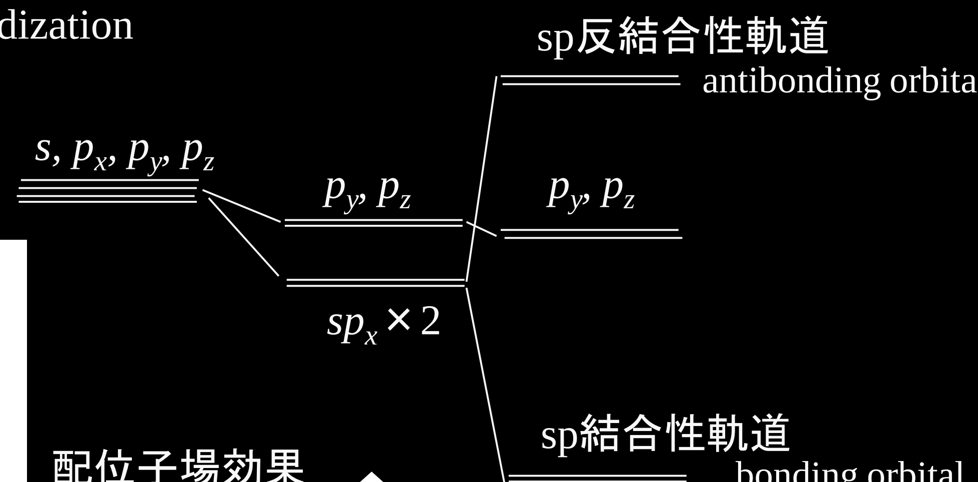


図 4.8 sp 混成軌道



配位子場効果
（原子内混成）

intra-atomic hybridization

inter-atomic hybridization
(Chemical bond)

H-C≡C-H
Acetylene

$$sp_x = \frac{1}{\sqrt{2}}(s \pm p_x)$$

Atomic *p*-orbital→ molecular orbital

Imagine alien atoms are approaching carbon → intra-atomic hybridization

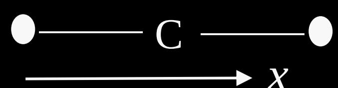
↓

When the alien atoms get close to carbon → inter-atomic hybridization like hydrogen molecule)

↓

Finally, construct the overall molecular orbitals

i) Uniaxial 2-way coordination; sp hybridization



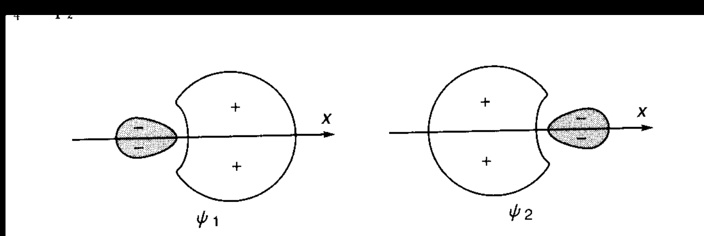
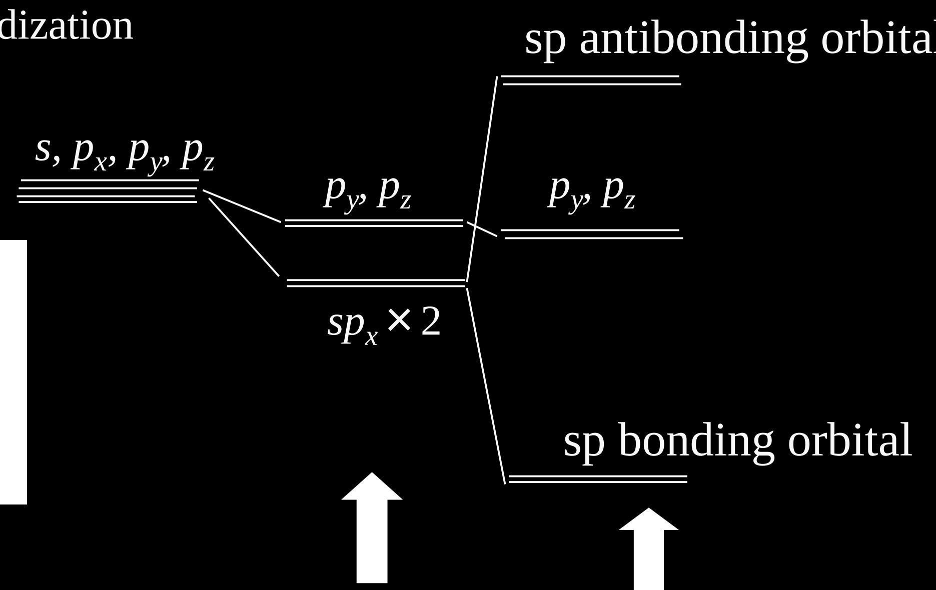


図 4.8 sp 混成軌道



H-C≡C-H
Acetylene

$$sp_x = \frac{1}{\sqrt{2}}(s \pm p_x)$$

intra-atomic hybridization

inter-atomic hybridization
(Chemical bond)

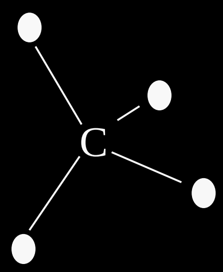
intra-atomic　　inter-atomic　　hybridization

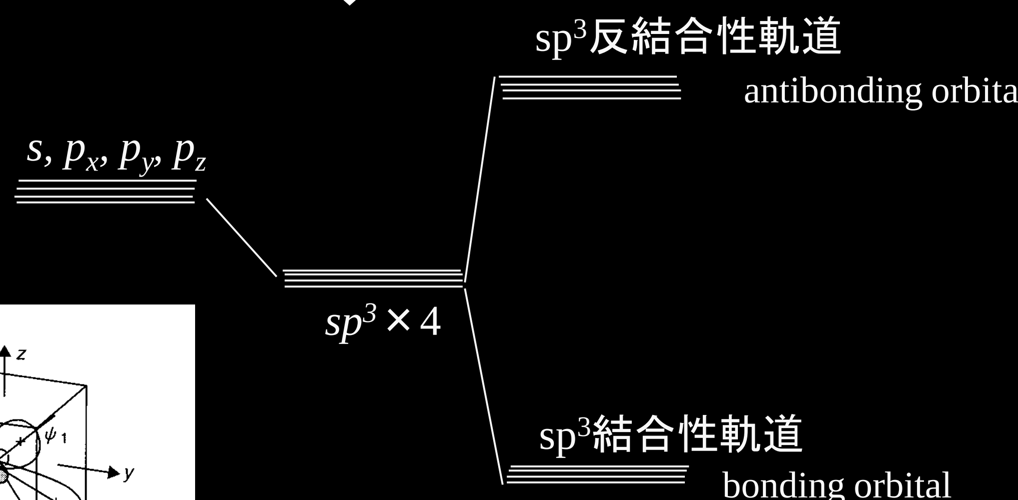
配位子場効果
（原子内混成）

化学結合
（原子間混成）

Chemical bond

Tetrahedral 4-way coordination; sp^3 hybridization





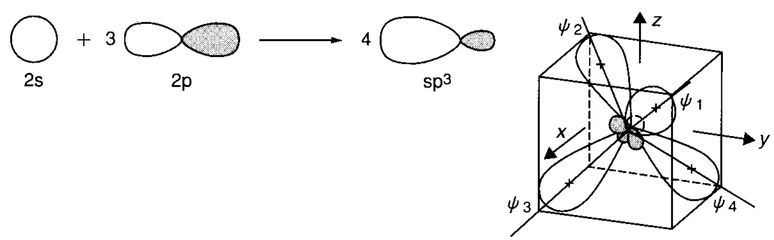


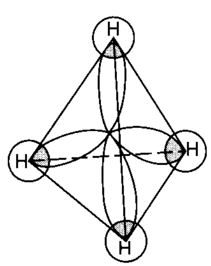
図 4.6　sp^3 混成軌道

$$sp^3 = \frac{1}{2}(s + p_x + p_y + p_z)$$

$$\frac{1}{2}(s + p_x - p_y - p_z)$$

$$\frac{1}{2}(s - p_x - p_y + p_z)$$

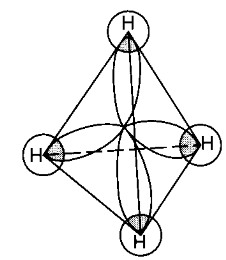
$$\frac{1}{2}(s - p_x + p_y - p_z)$$



CH_4 (sp^3)

メタン、 ダイヤモンド
methane, diamond

Tetrahedral 4-way coordination molecular orbital; the case of **CH_4 (sp3)**

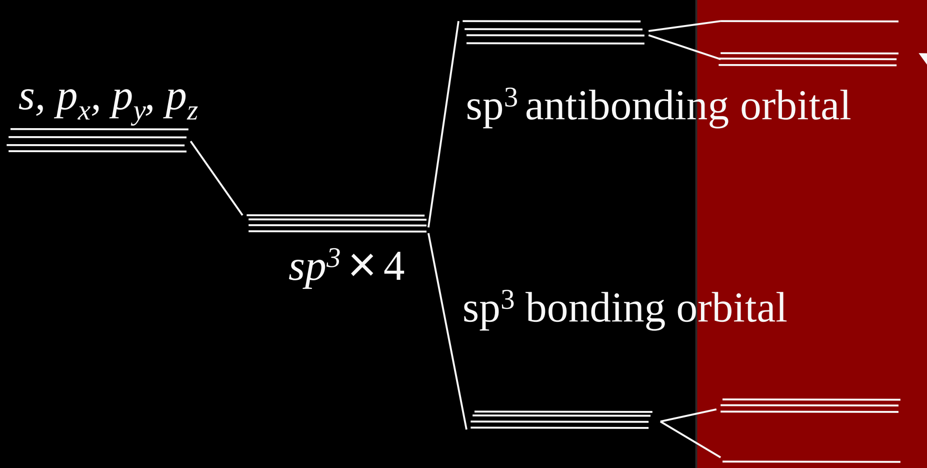


CH_4 (sp^3)

intra-atomic hybridization

inter-atomic hybridization

Molecular orbital



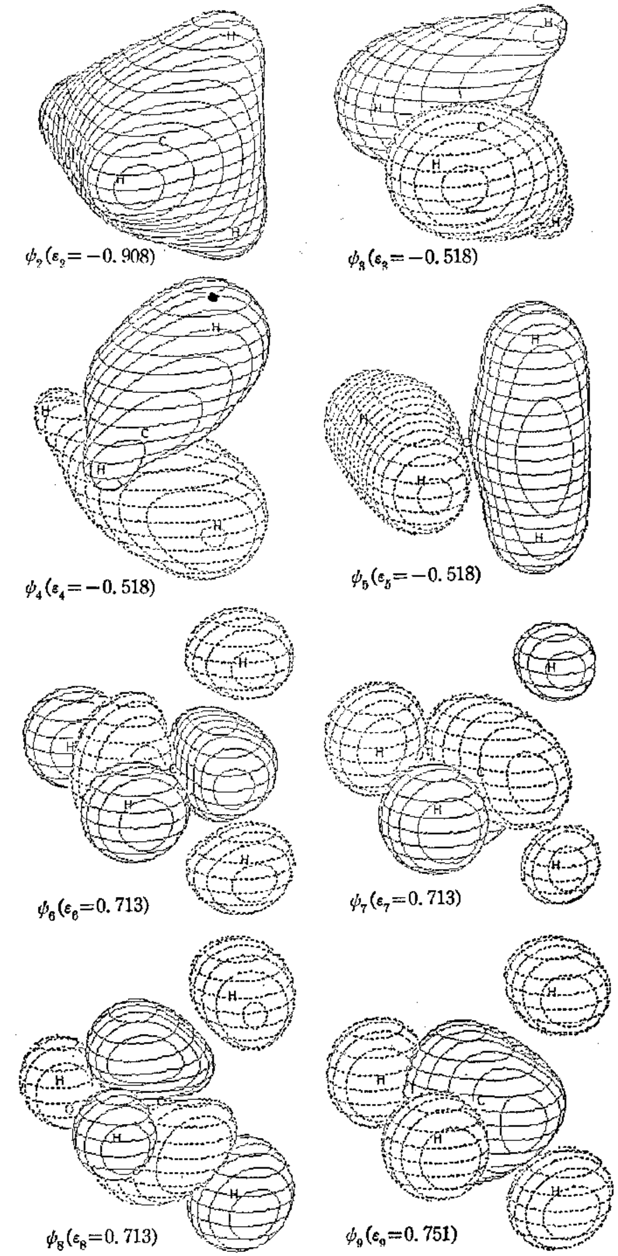
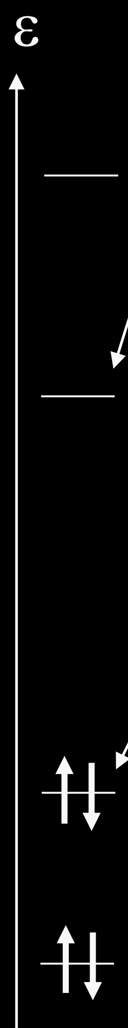
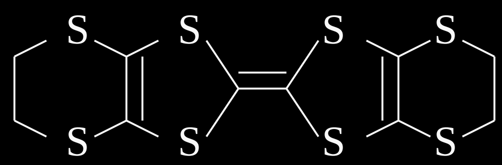


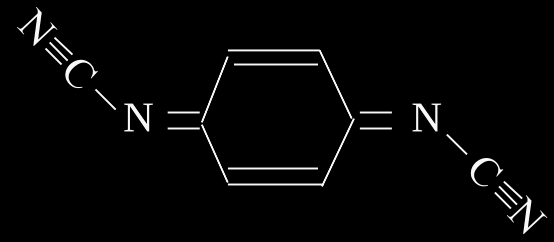
図 3.23 CH_4 の分子軌道。

Molecular orbital in molecular conductors



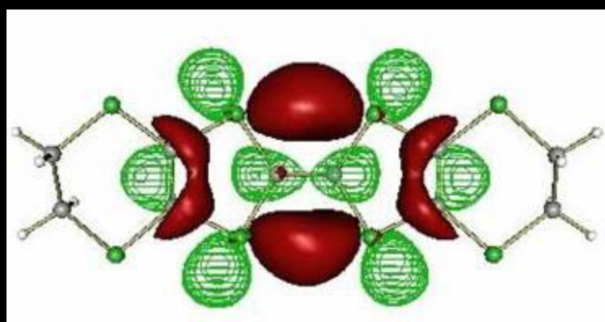


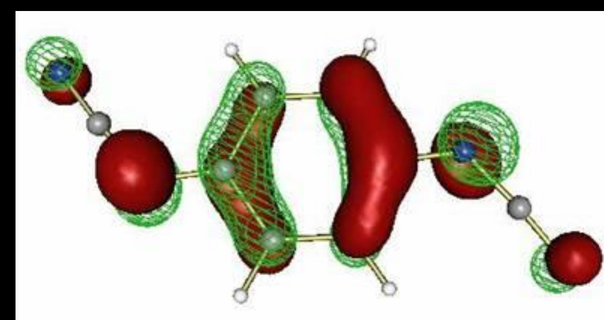
BEDT-TTF (ET)



DCNQI

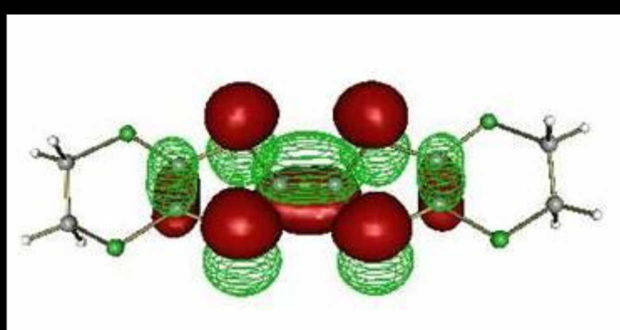
Lowest Unoccupied Molecular Orbital (LUMO)

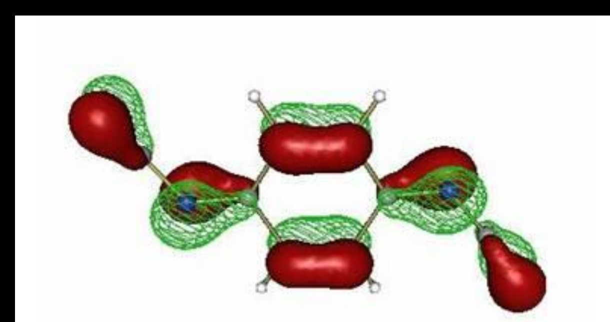




By Imamura and Tanimura

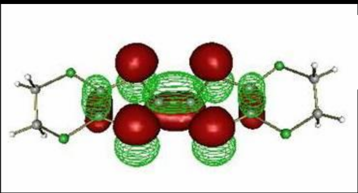
Highest Occupied Molecular Orbital (HOMO)





Band-structure calculations I; π electronic system κ-$(ET)_2X$

well described by tight-binding model of MO

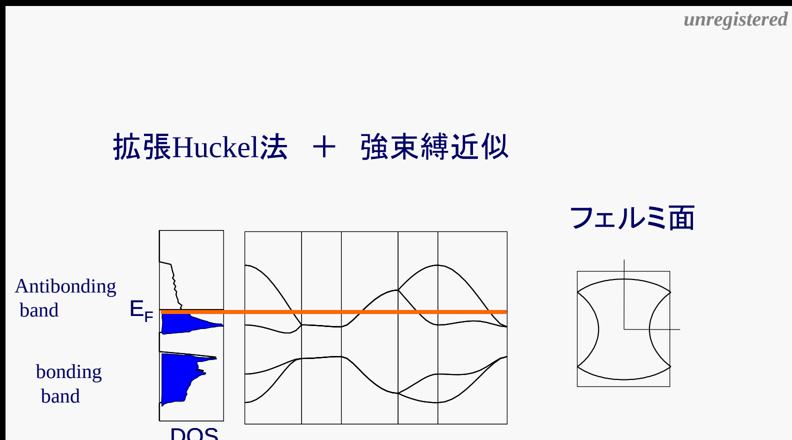


HOMO＋tight-binding approx.

T. Mori et al.,

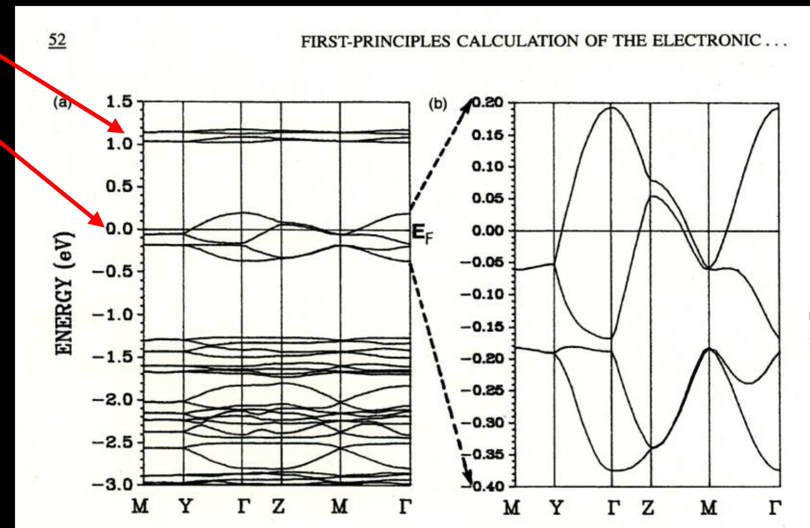
LUMO level

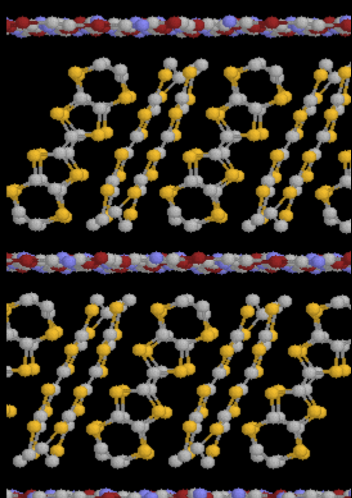
HOMO level

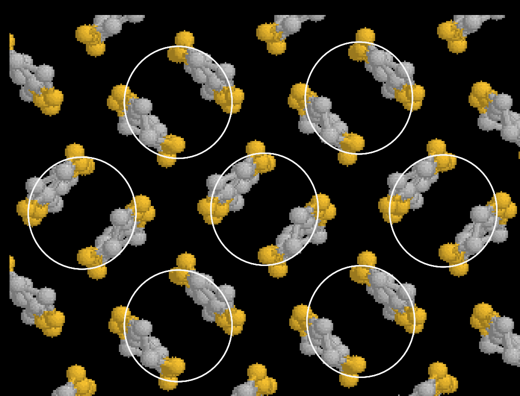


First-principles calculations

Y.-N. Xu *et al., Phys. Rev. B 52, 12946*







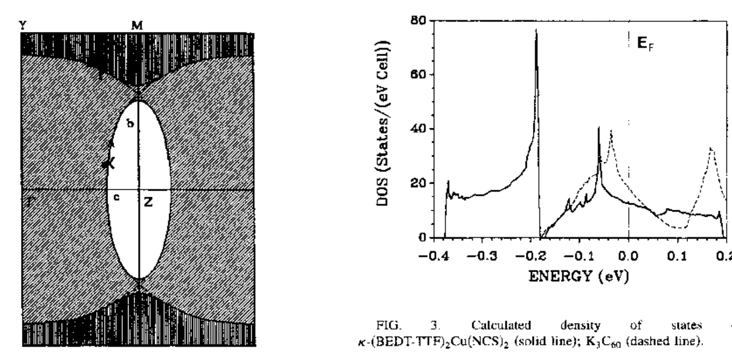
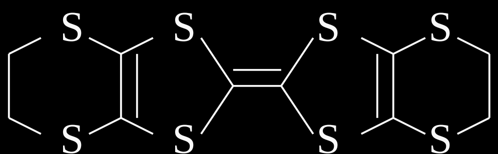

12 948 YONG-NIAN XU, W.Y. CHING, Y.C. JEAN, AND Y. LOU 52

FIG. 2. Calculated Fermi surface of the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The two orbits α and β are marked. The dashed lines indicate the path of electron in the magnetic breakdown.

FIG. 3. Calculated density of states of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (solid line); K_3C_{60} (dashed line).

lated to the saddle point of the band at M. By resolving the DOS into atomic and orbital components, we find that the DOS at E_F are exclusively derived from the C and S atoms in the ET molecules, and their orbital components are almost entirely of p character (45% of C-2p, 52% of S-3p, and 3%

Notion of molecular orbital

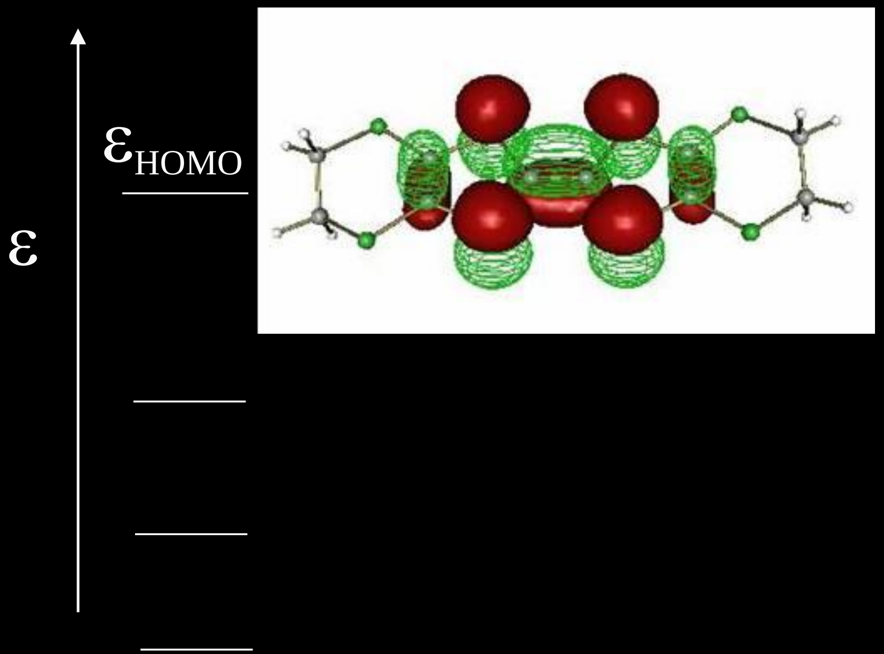


BEDT-TTF (ET)

Cu

HOMO

d orbital



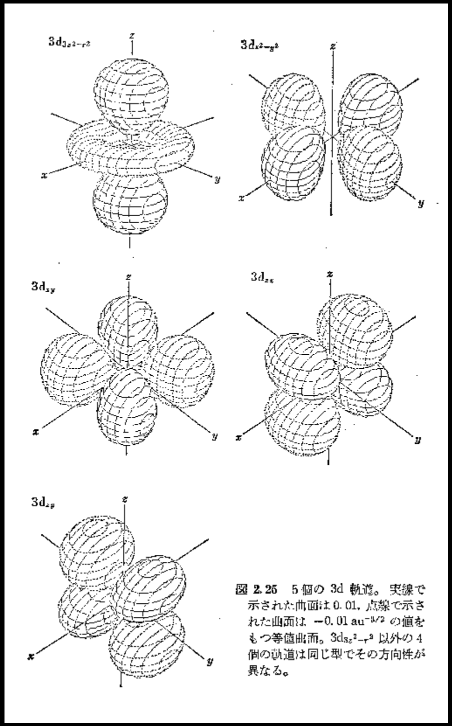


図 2.25　5 個の 3d 軌道。実線で示された曲面は 0.01，点線で示された曲面は −0.01 au$^{-3/2}$ の値をもつ等値曲面。$3d_{3z^2-r^2}$ 以外の 4 個の軌道は同じ型でその方向性が異なる。

Molecular conductors

Seemingly complicated structure in real space

but

Simple electronic structure in *k* space

(MO is a minimum electronic entity)

In many cases,

no orbital degeneracy

negligible spin-orbit interaction

Highly compressible

↓

Model systems to look into correlation effect
in simple electronic systems

Contents

1. Fundamentals of organic materials

compex in real space, but simple in *k*-space

2. Electron correlation in organic materials

all-in-one systems for Mott physics

3. Spin liquid in quasi-triangular lattice

controlled frustration, correlation, disorder, doping

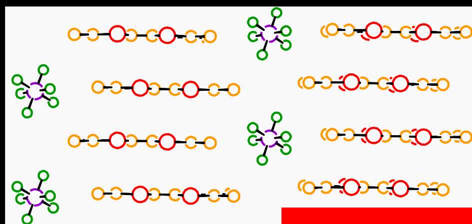
(Optional)

4. Massless Dirac Fermions in orhanic materials

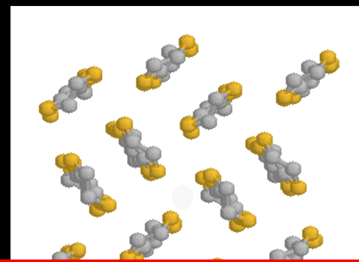
Dirac cone reshaping and ferromagnetism

Correlation-induced insulating phases everywhere in organics

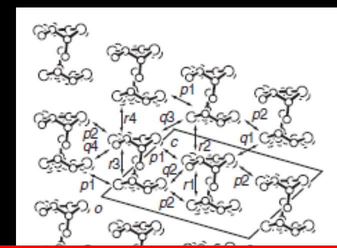
Quasi 1D 1/4-filled
$(TMTSF)_2X$



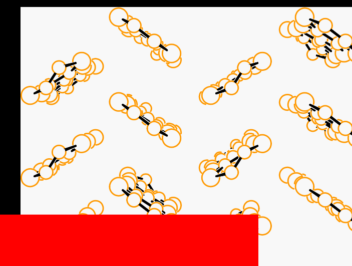
Quasi 2D 1/2-filled
κ-$(ET)_2X$



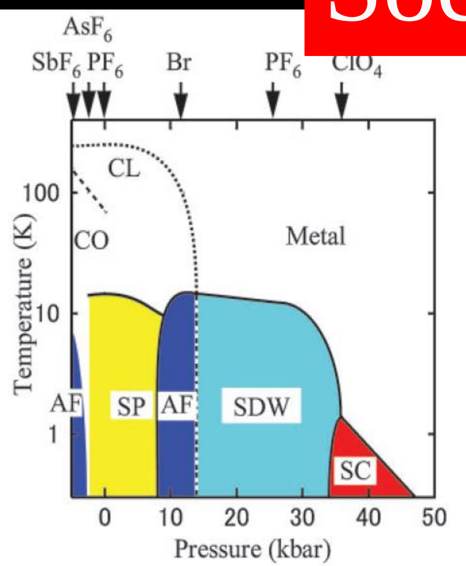
Quasi 2D ¼-filled
β-(*meso*, DMeET)$_2PF_6$



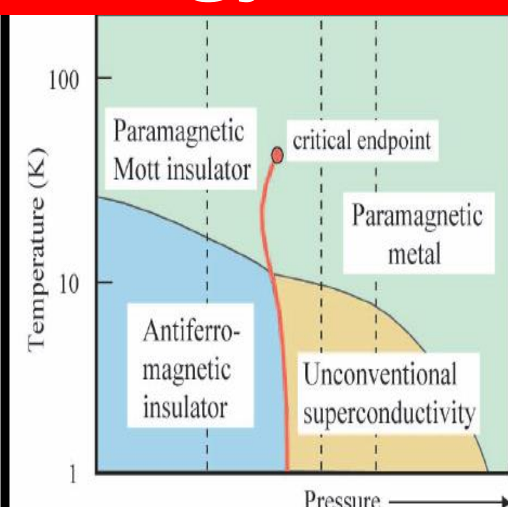
Quasi 2D ¼-filled
α-$(ET)_2X$



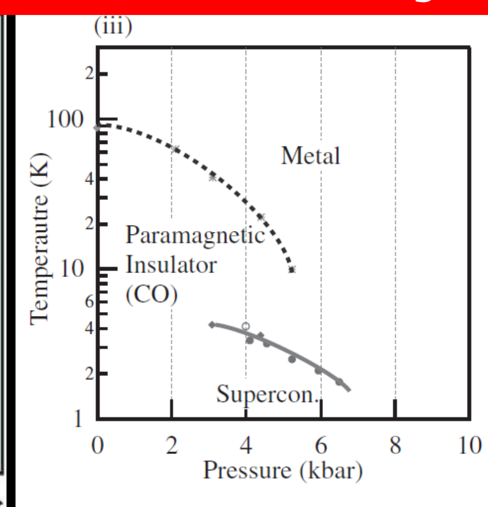
Sociology of electronic system



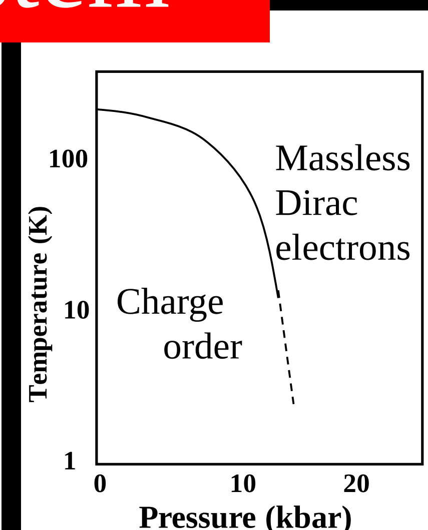
SDW/SC
Nesting



Mott/SC
On-site repulsion



CO/SC
Inter-site repulsion



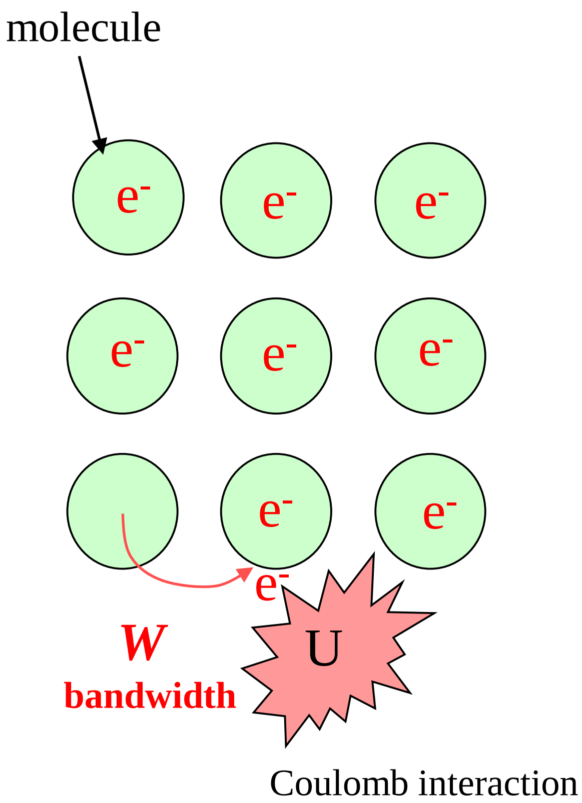
CO/DE
Inter-site repulsion

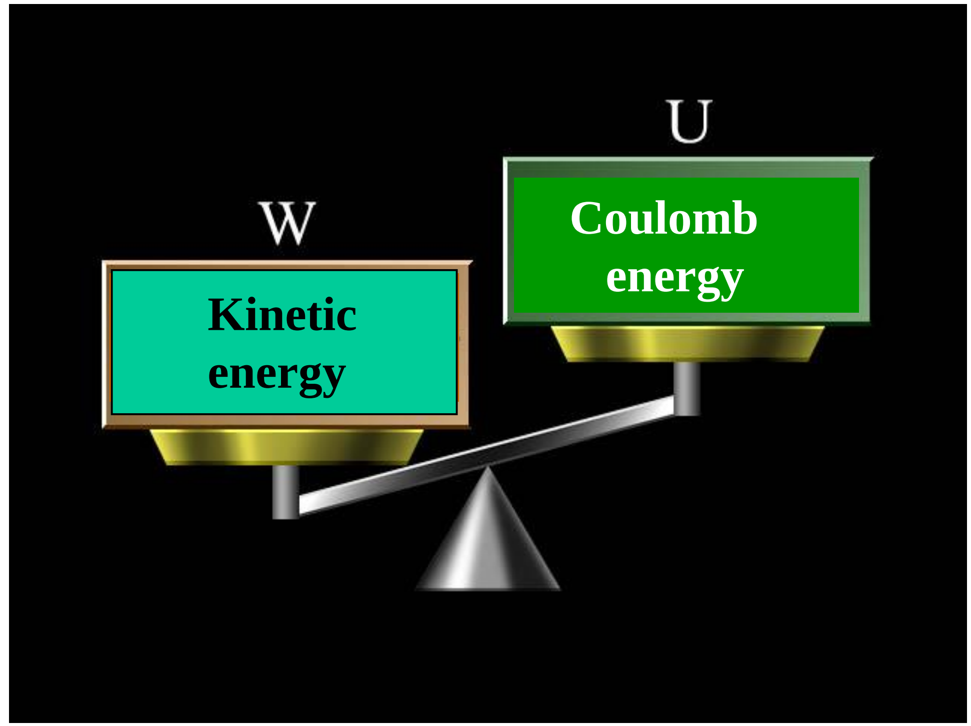
3. Mott transition

N. Mott (1949)

Mott transition

Competition between kinetic energy and Coulomb





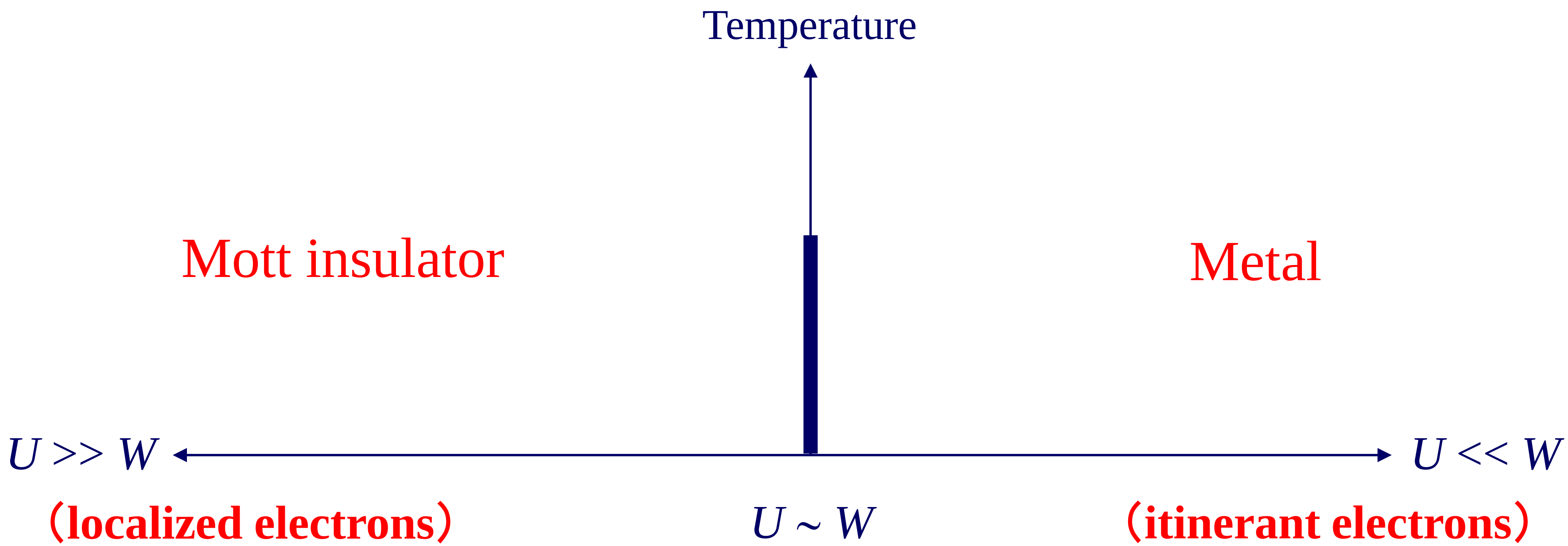
$W > U$ ↔ $W < U$

metal — insulator

Wave-like — **particle-like**

Competition between kinetic energy and Coulomb energy

(W : bandwidth) (U : Coulomb repulsion)



(localized electrons)

particlelike

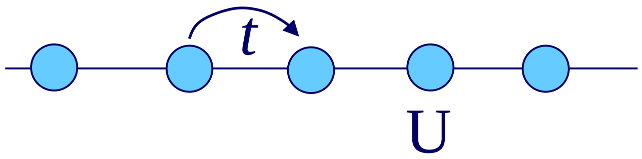
(itinerant electrons)

wavelike

Strongly interacting

Weakly interacting

Hubbard model



Hubbard Hamiltonian

1particle/site

H *H'*

$$H = \sum_{(i,j)\sigma} (t c^{+}_{i,\sigma} c_{j,\sigma} + h.c.) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}$$

off-diagonal diagonal

Wannier Bloch

$$c_{j,\sigma} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_j} c_{\mathbf{k},\sigma}$$

diagonal off-diagonal

$$H = \sum_{\mathbf{k},\sigma} \varepsilon_{\mathbf{k}} c^{+}_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + \frac{U}{N} \sum_{k_1,k_2,k_3,k_4} c^{+}_{k_1,\uparrow} c^{+}_{k_2,\downarrow} c_{k_3,\uparrow} c_{k_4,\downarrow} \delta_{k_1+k_2,k_3+k_4}$$

H *H'*

In the weak correlation regime, W~2zt >> U

Hubbard Hamiltonian

Calculate life time of Bloch electron

$$H = \sum_{\mathbf{k},\sigma} \varepsilon_{\mathbf{k}} c^{+}_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + \frac{U}{N} \sum_{k_1,k_2,k_3,k_4} c^{+}_{k_1,\uparrow} c^{+}_{k_2,\downarrow} c_{k_3,\uparrow} c_{k_4,\downarrow} \delta_{k_1+k_2,k_3+k_4}$$

H_0 $\quad$ *H'* (perturbation) $\quad$ Scattering term

Scattering rate

$$\frac{1}{\tau(k_1)} = \sum_{k_2,k_1',k_2'} \frac{2\pi}{\hbar} \left\langle k_1', k_2' \middle| H' \middle| k_1, k_2 \right\rangle^2 \delta(\varepsilon_{k_1} + \varepsilon_{k_2} - \varepsilon_{k_1'} - \varepsilon_{k_2'}) f_{k_2}(1 - f_{k_1'})(1 - f_{k_2'})$$

$$= \frac{2\pi}{\hbar} \frac{1}{N^2} \sum_{k_2,k_1',k_2'} U^2 \delta(\varepsilon_{k_1} + \varepsilon_{k_2} - \varepsilon_{k_1'} - \varepsilon_{k_2'}) \delta_{k_1+k_2,k_1'+k_2'} f_{k_2}(1 - f_{k_1'})(1 - f_{k_2'})$$

3D, $\quad \frac{1}{\tau(k_1)} \propto T^2$

2D, $\quad \frac{1}{\tau(k_1)} \propto T^2 \log \frac{\varepsilon_F}{k_B T}$

} At low-Temperatures $\quad \frac{\hbar}{\tau} << k_B T$

Fermi liquid

1D, $\quad \frac{1}{\tau(k_1)} = \frac{2\pi}{\hbar} U^2 \frac{1}{8\pi^2} \frac{a^2}{(\hbar v_F)^2} k_B T$

✕ **Non-Fermi liquid**

In the strong correration regime, W~2zt << U

Hubbard Hamiltonian

$$H = \sum_{(i,j)\sigma} (t c^{+}_{i,\sigma} c_{j,\sigma} + h.c.) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}$$

H' (perturbation) $\qquad$ H_0

Heisenberg Hamiltonian

$$H = \sum_{(i,j)} J \mathbf{S}_i \mathbf{S}_j$$

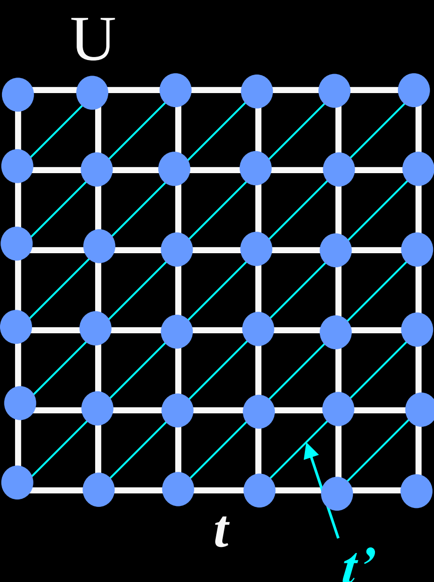
$J=4t^2/U$

Antiferromagnetic insulator

Mott transition occurs at *W~U*,
but depends on dimension and lattice geometry

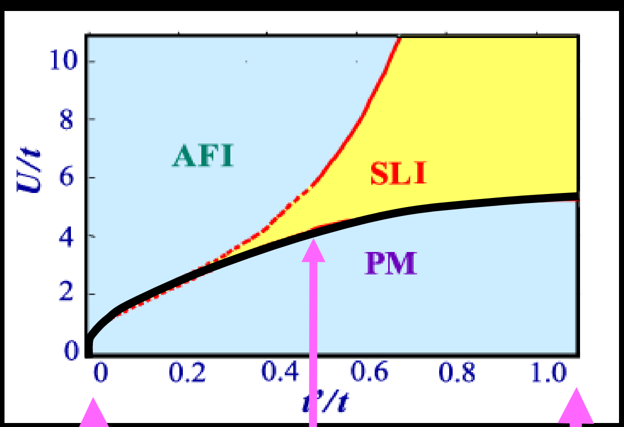
1-D Hubbard models are always Mott insulators.

2D ½-filled Hubbard model on anisotropic triangular lattice



PIRG

Imada et al. JPSJ (2003)



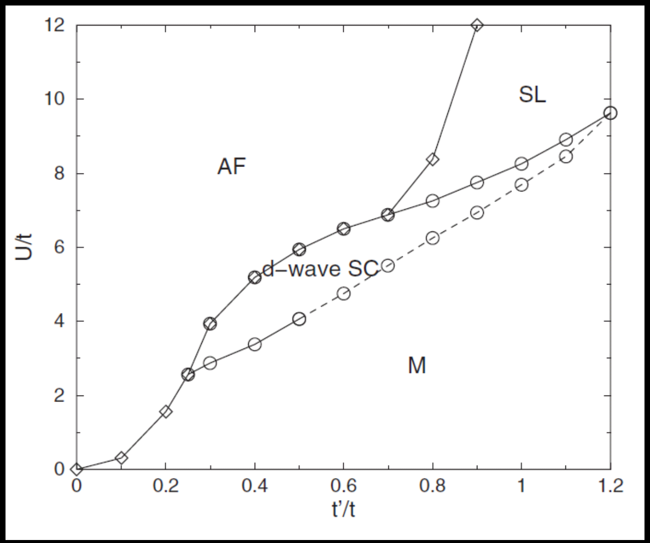
Mott transition line

Square lattice

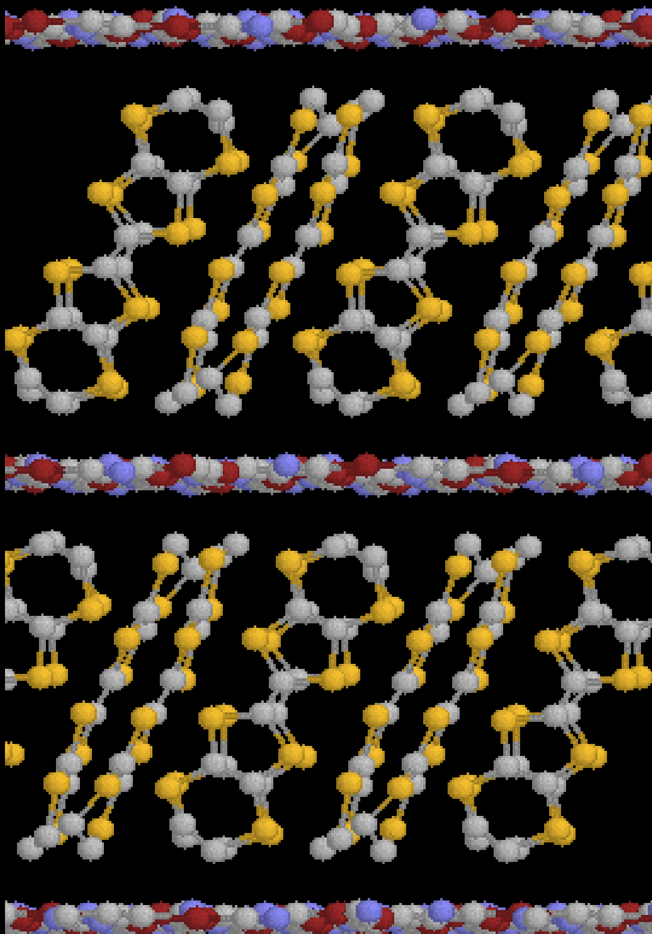
Triangular lattice

Cluster-DMFT

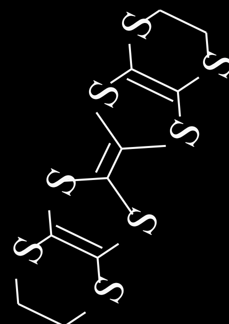
Tremblay et al. PRL (2006)



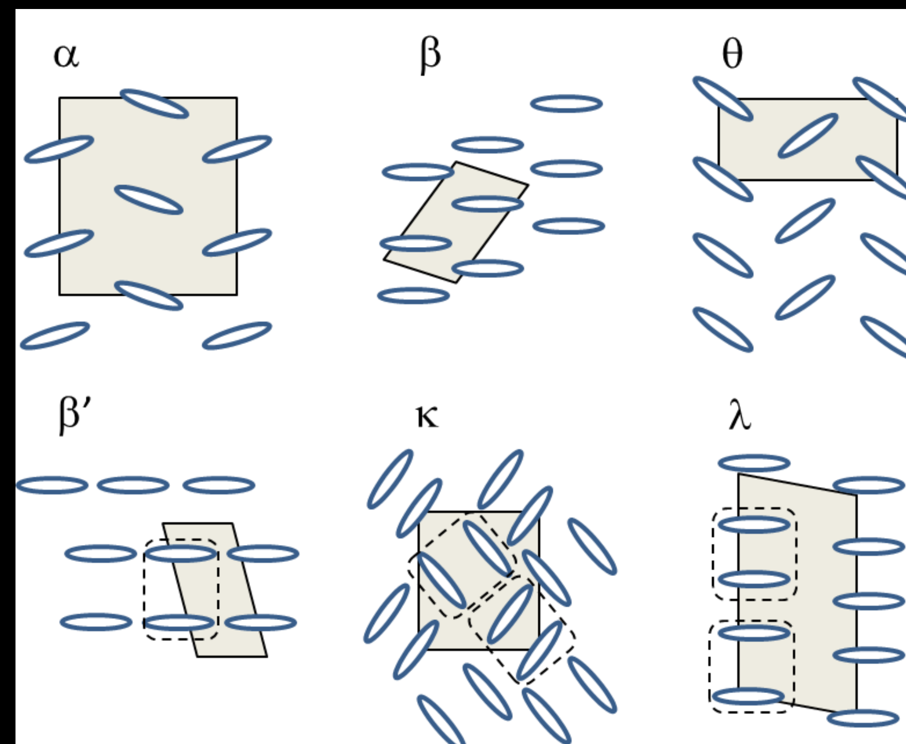
Layered molecular conductors, $(BEDT\text{-}TTF)_2X$



X

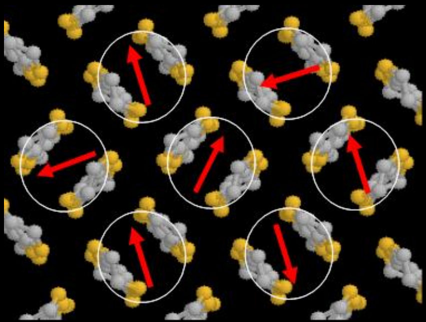


A variety of in-plane structures



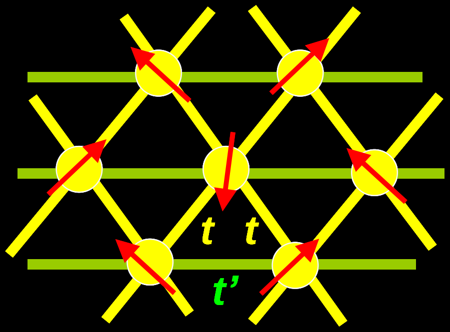
κ-(ET)$_2$X family are on the verge of Mott transition

in-plane structure



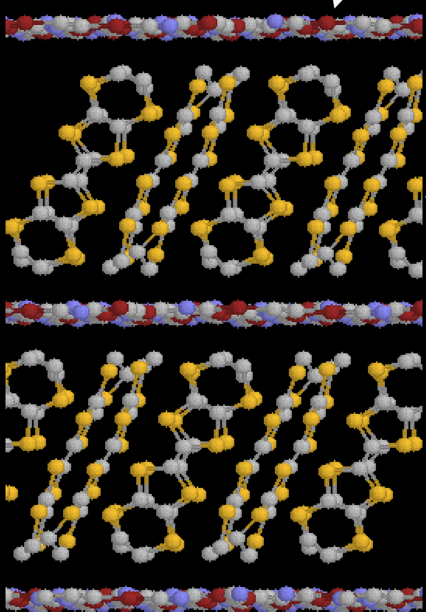
dimer model

Kino & Fukuyama

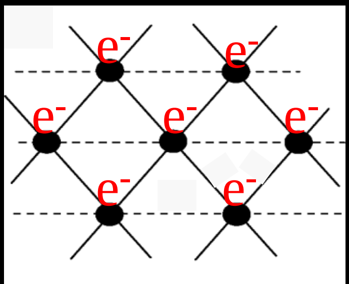


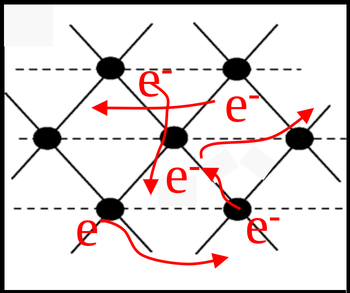
Triangular lattice
Half-filled band

t : inter-dimer transfer integral
U : on-site Coulomb

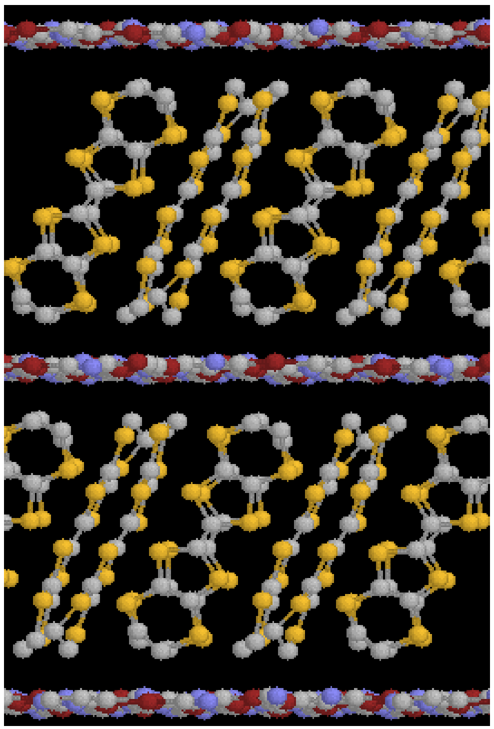


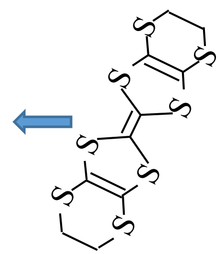
X$^-$	Gorund state	U/t	t'/t
$Cu_2(CN)_3$	Mott insulator	8.2	1.06
$Cu[N(CN)_2]Cl$	Mott insulator	7.5	0.75
$Cu[N(CN)_2]Br$	Metal (SC)	7.2	0.68
$Cu(NCS)_2$	Metal (SC)	6.8	0.84
$Cu(CN)[N(CN)_2]$	Metal (SC)	6.8	0.68
$Ag(CN)_2\ H_2O$	Metal (SC)	6.6	0.60
I_3	Metal (SC)	6.5	0.58



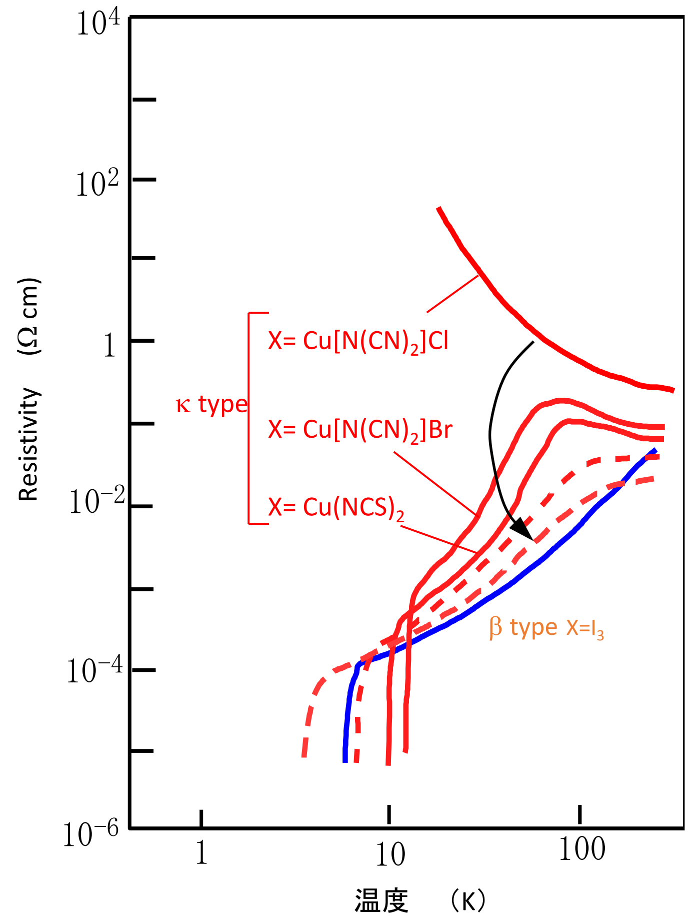


Resistivity of κ-(BEDT-TTF)$_2$X

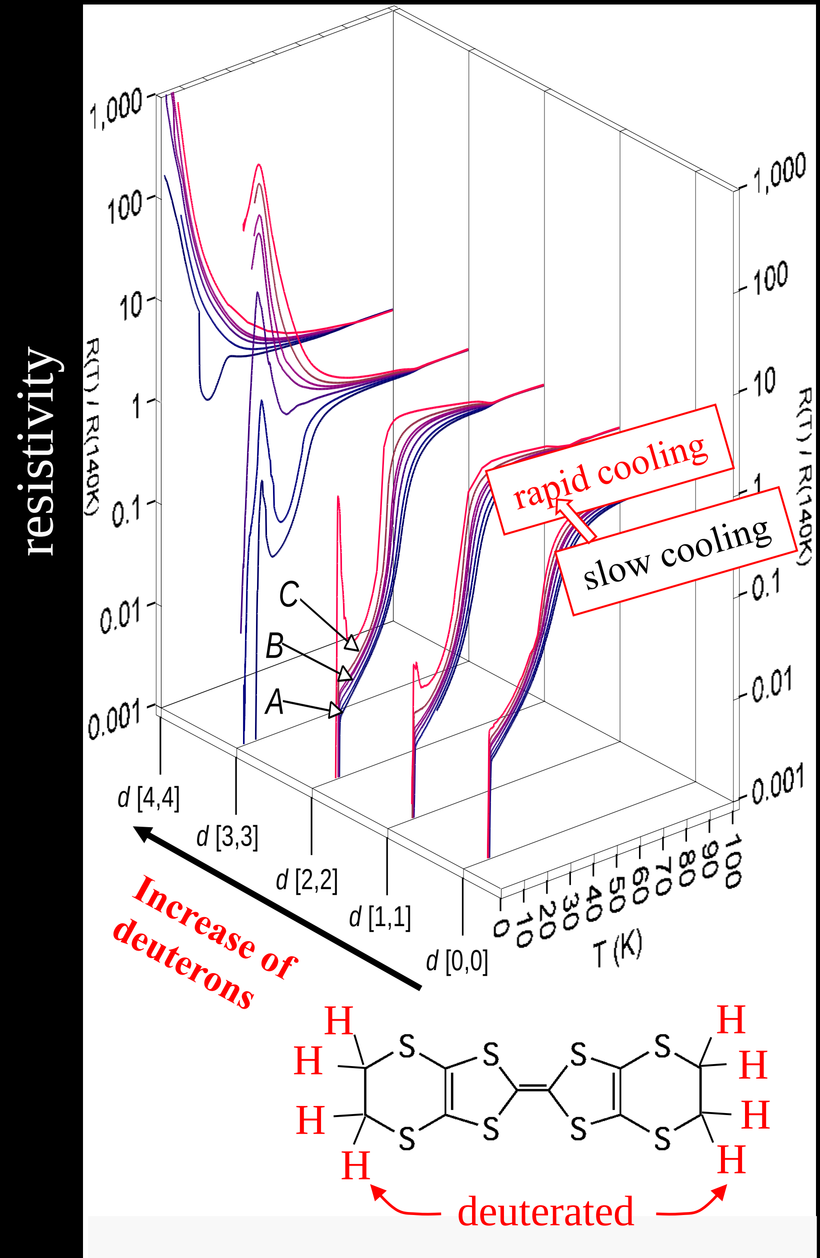




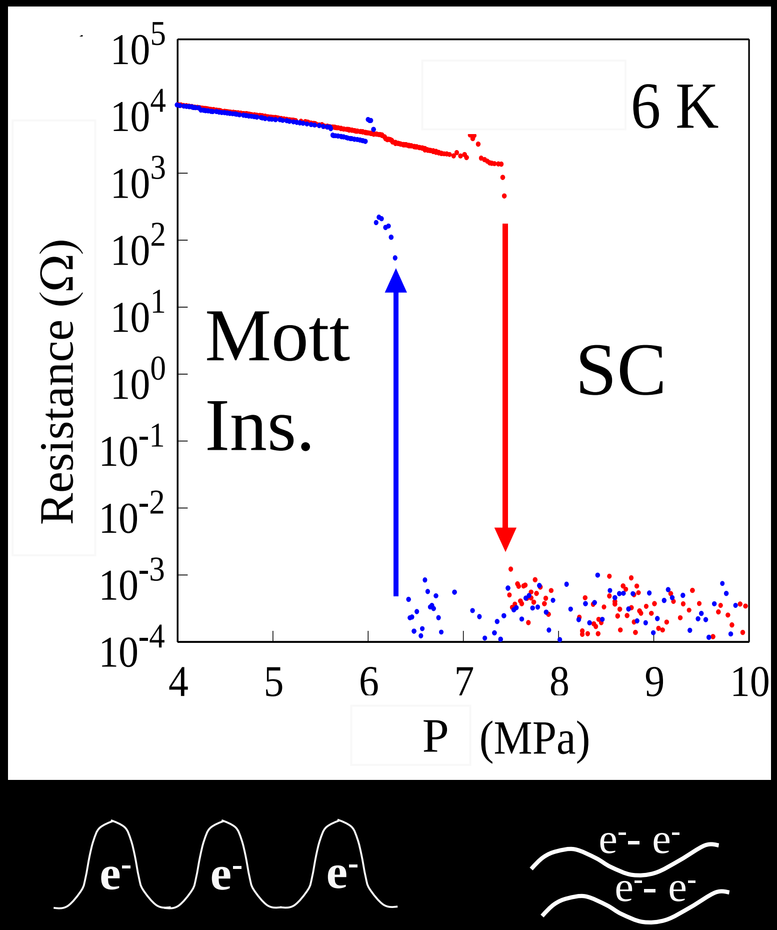
X



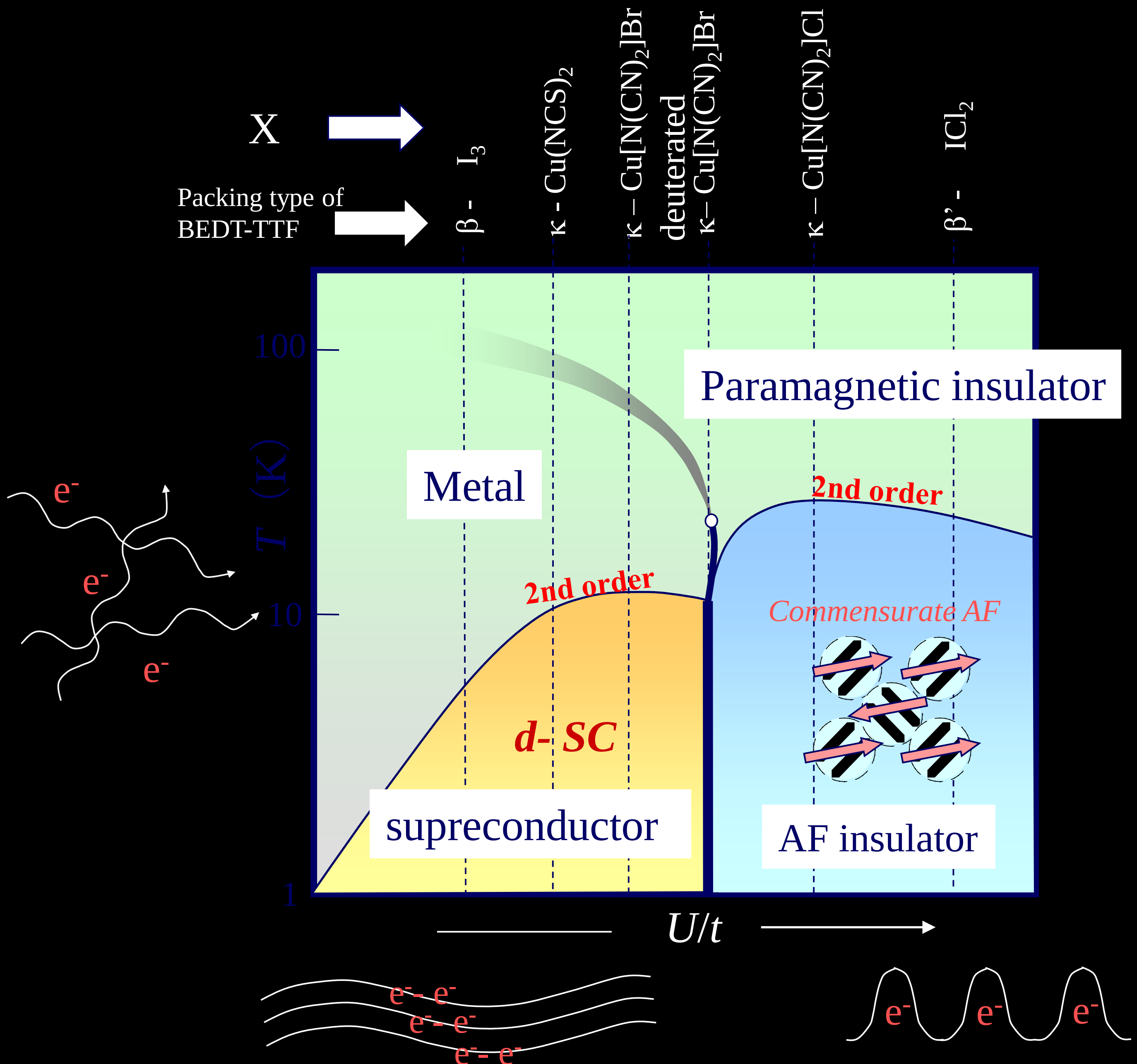
SIT by fine pressure tuning or isotope substitution



κ-(deuterated ET)$_2$Cu[N(CN)$_2$]Br

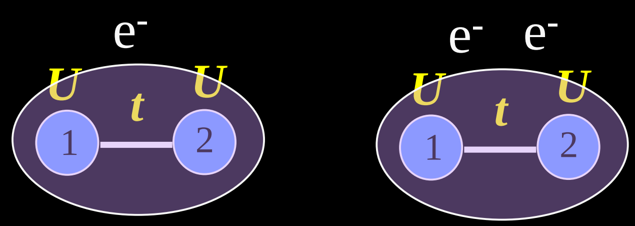


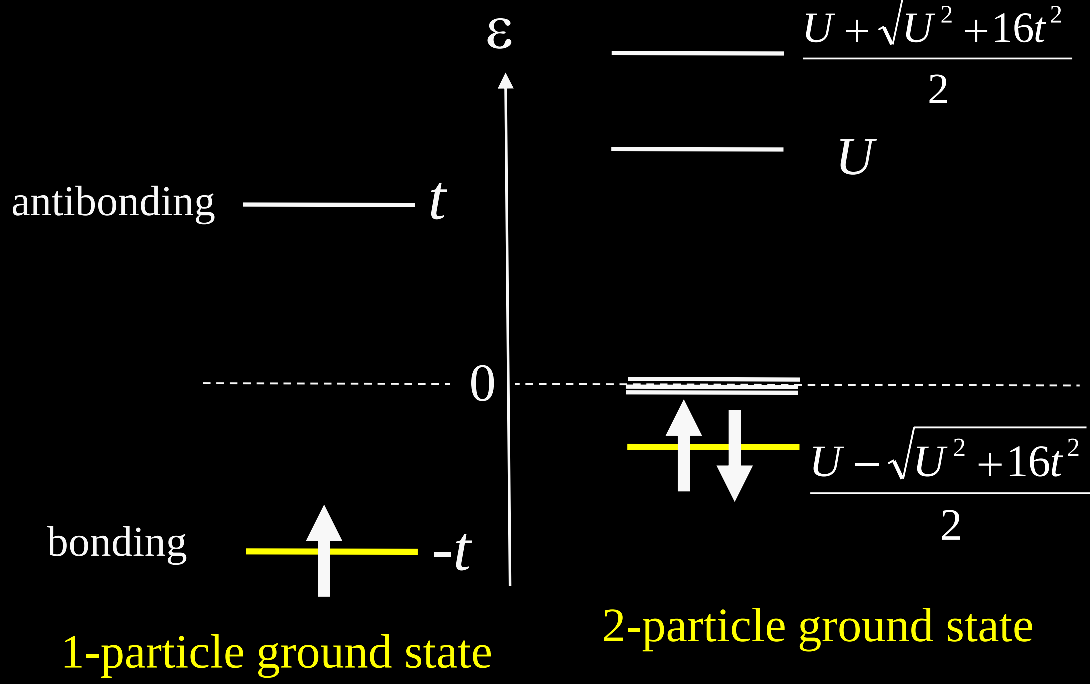
κ-$(ET)_2X$ family are on the verge of Mott transition



2 electrons/dimer with on-site Coulomb energy → Hubbard model of a hydrogen molecule

$$H = -t\sum_{\sigma}(c_{1\sigma}^{+}c_{2\sigma} + c_{2\sigma}^{+}c_{1\sigma}) + U(n_{1\uparrow}n_{1\downarrow} + n_{2\uparrow}n_{2\downarrow})$$





$$\frac{U+\sqrt{U^2+16t^2}}{2}: \quad |\uparrow\downarrow,0\rangle + |0,\uparrow\downarrow\rangle + \frac{U-\sqrt{U^2+16t^2}}{4t}(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle)$$

$$U: \quad |\uparrow\downarrow,0\rangle - |0,\uparrow\downarrow\rangle$$

$$0: \quad |\uparrow,\uparrow\rangle, \quad |\downarrow,\downarrow\rangle, \quad |\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle$$

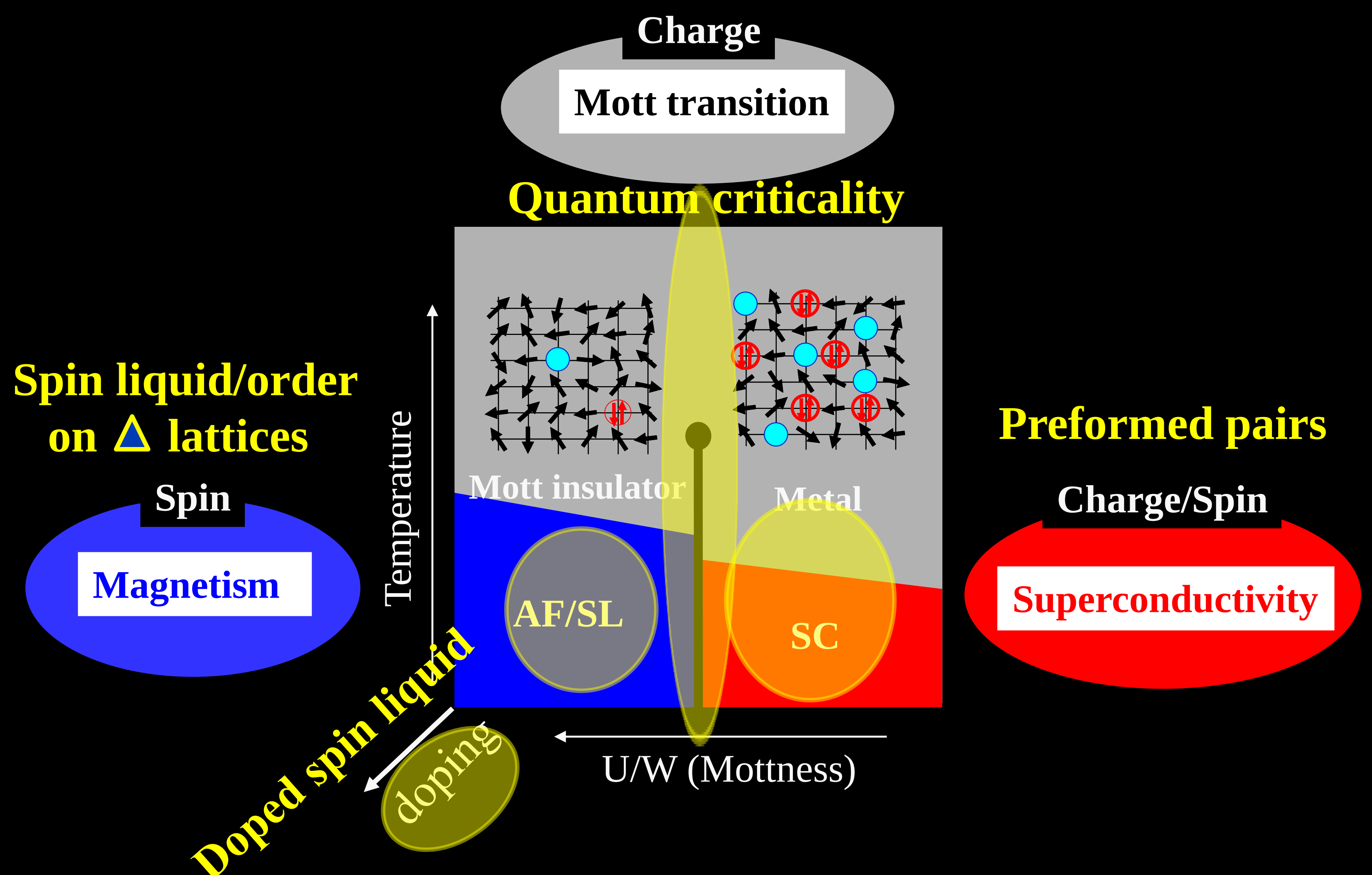
$$\frac{U-\sqrt{U^2+16t^2}}{2}: \quad |\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle + \frac{4t}{U+\sqrt{U^2+16t^2}}(|\uparrow\downarrow,0\rangle + |0,\uparrow\downarrow\rangle)$$

$$U_{eff} = \frac{U-\sqrt{U^2+16t^2}}{2} - 2(-t) = 2t + \frac{U-\sqrt{U^2+16t^2}}{2} \approx 2t$$

From band-structure calculations, $U_{eff} \sim 2t \sim$ 0.5 eV and bandwidth $W \sim$ 0.4 eV

comparable

Mott physics in 2D organics



Interacting spins → Order or not ?

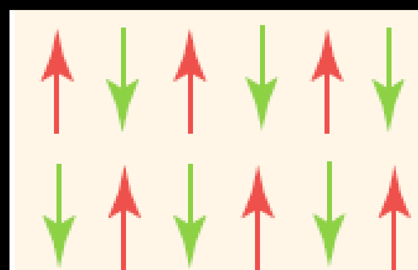
1900 — 1936 — 1949 — 1950 — 1973 — 2000

Heisenberg

$J\, \boldsymbol{S}_i \cdot \boldsymbol{S}_j$

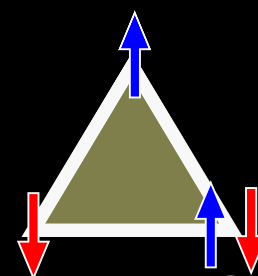
Antiparrallel interaction

1936: Neel proposed

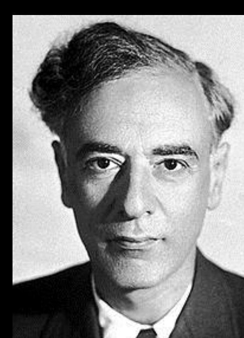


1949: proved by neutron

1973: Anderson proposed



?



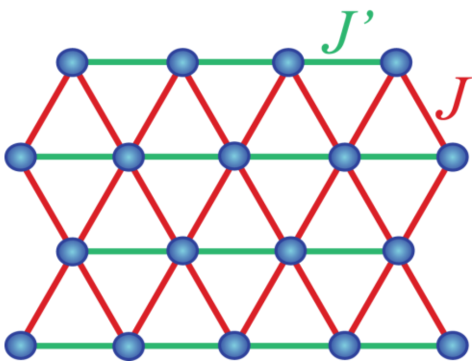
?

Landau

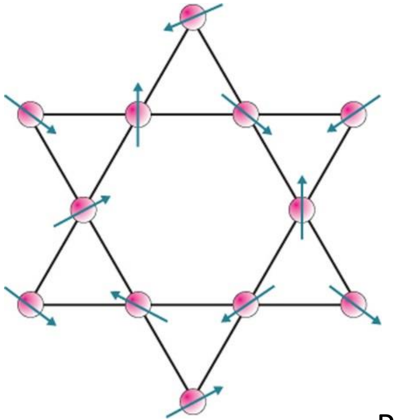
Anderson

Triangle-based lattices

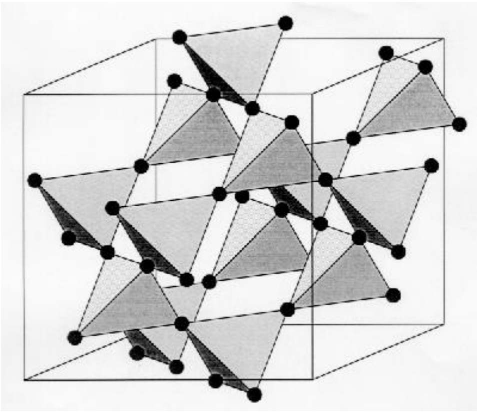
Triangular lattice

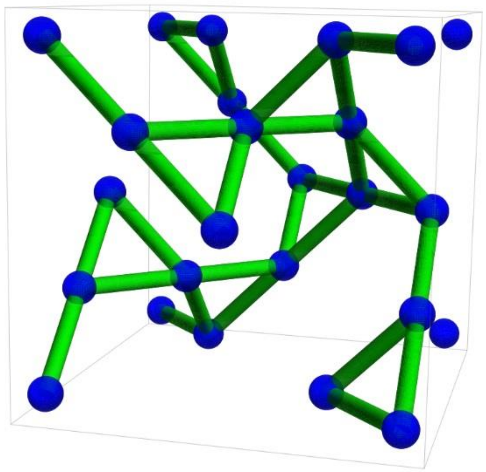


Kagome lattice



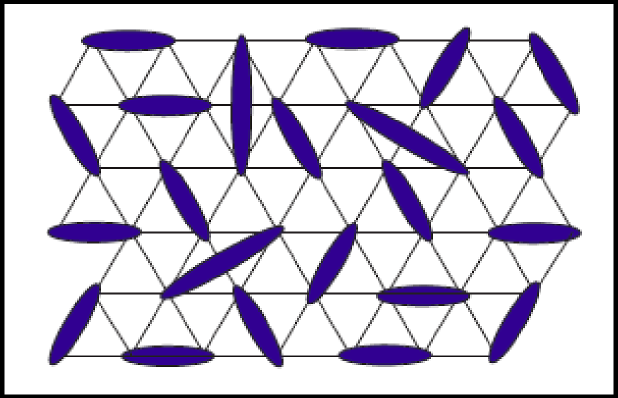
Pyrochlore lattice





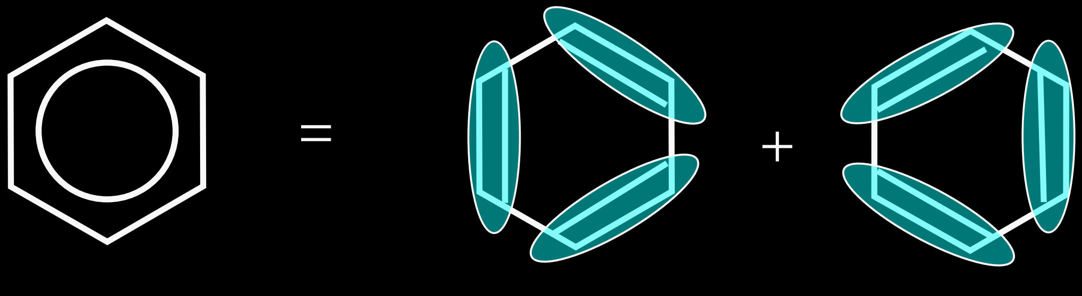
Hyper Kagome lattice

Anderson' idea of spin liquids: Resonating Valence Bond (RVB) state



\+ …… ………..

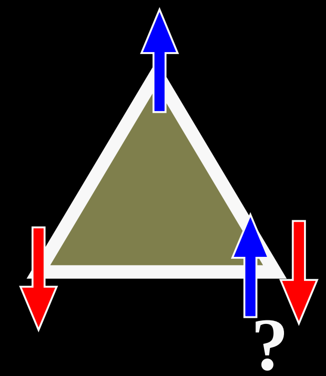
In analogy with benzene



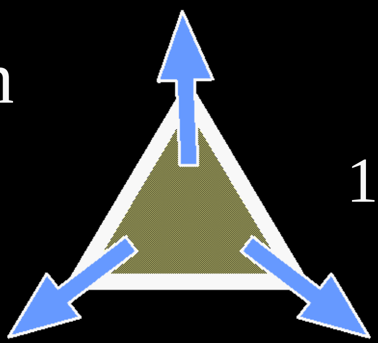
However, ……… ～1990

Heisenberg model

$$H = 2J \sum_{(i,j)} \mathbf{S}_i \cdot \mathbf{S}_j$$ on



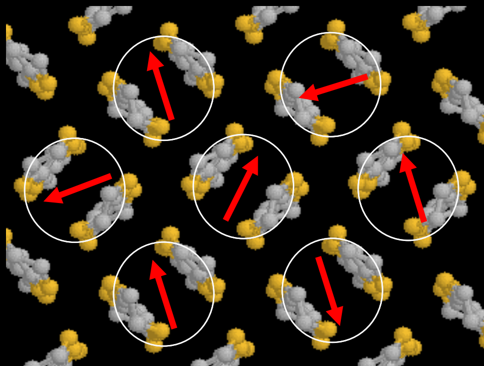
Solution



120° Neel order

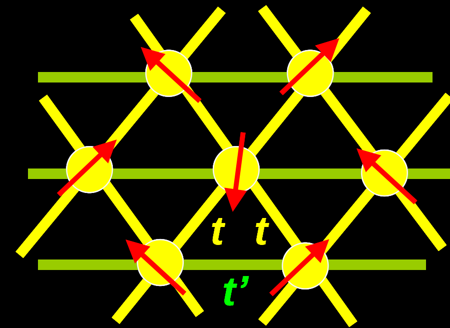
No spin liquid material in 20th century ………the end ?

Q2D organics κ-$(ET)_2X$; *spin-1/2 on triangular lattice*



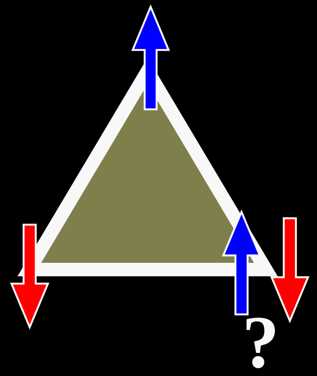
Kino & Fukuyama

dimer model



$t'/t = 0.4 \sim 1.1$

Spin frustration



Quantum spin liquid ?

Anderson (1973)

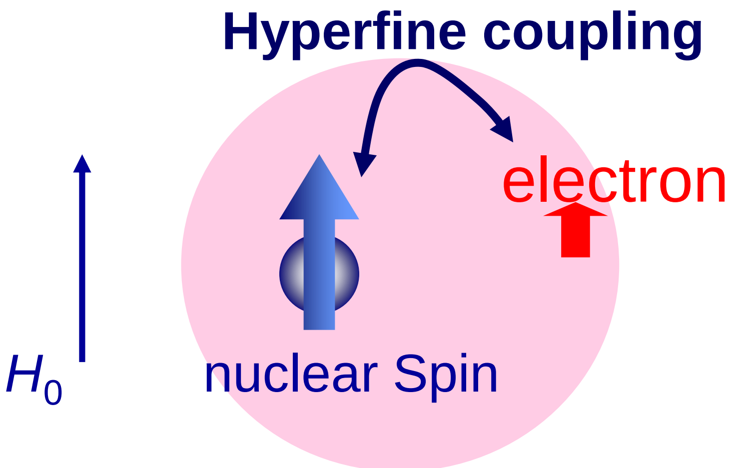
X^-	Ground State	t'/t	
$Cu_2(CN)_3$	Mott insulator	1.06	0.80
$Cu[N(CN)_2]Cl$	Mott insulator	0.75	0.44

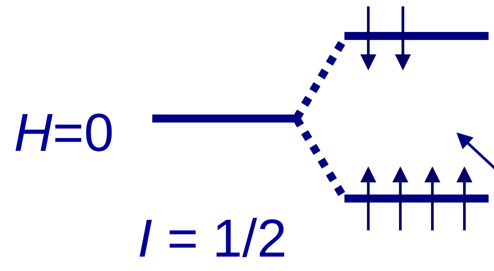
Huckel & tight binding

Ab initio; Kandpal et al. PRL (2009)
Nakamura et al. JPSJ (2009)

Magnetism

Nuclear Magnetic Resonance

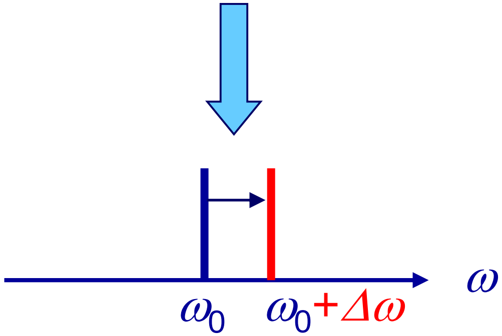




$\omega_0 = \gamma_n (H_0 + \Delta H)$

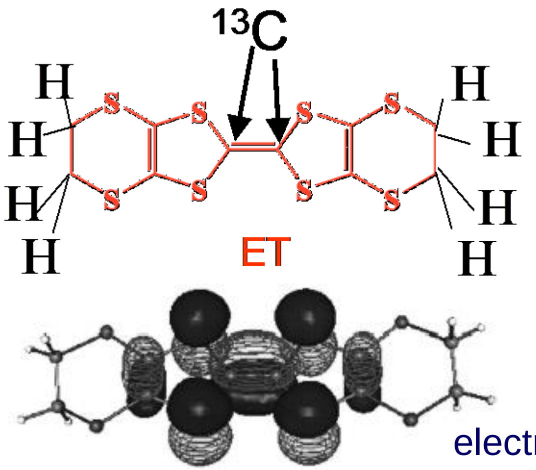
$= \omega_0 + \Delta\omega$

ω_0=10-1000 MHz



Local fields

Knight shift, $K=\Delta\omega/\omega_0$

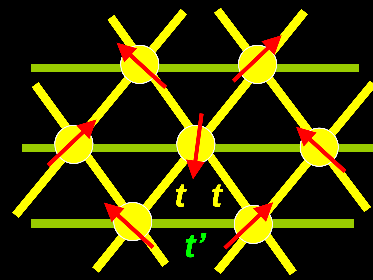


electron density of HOMO
Y. Imamura, et al., JCP**111**(1999)5986

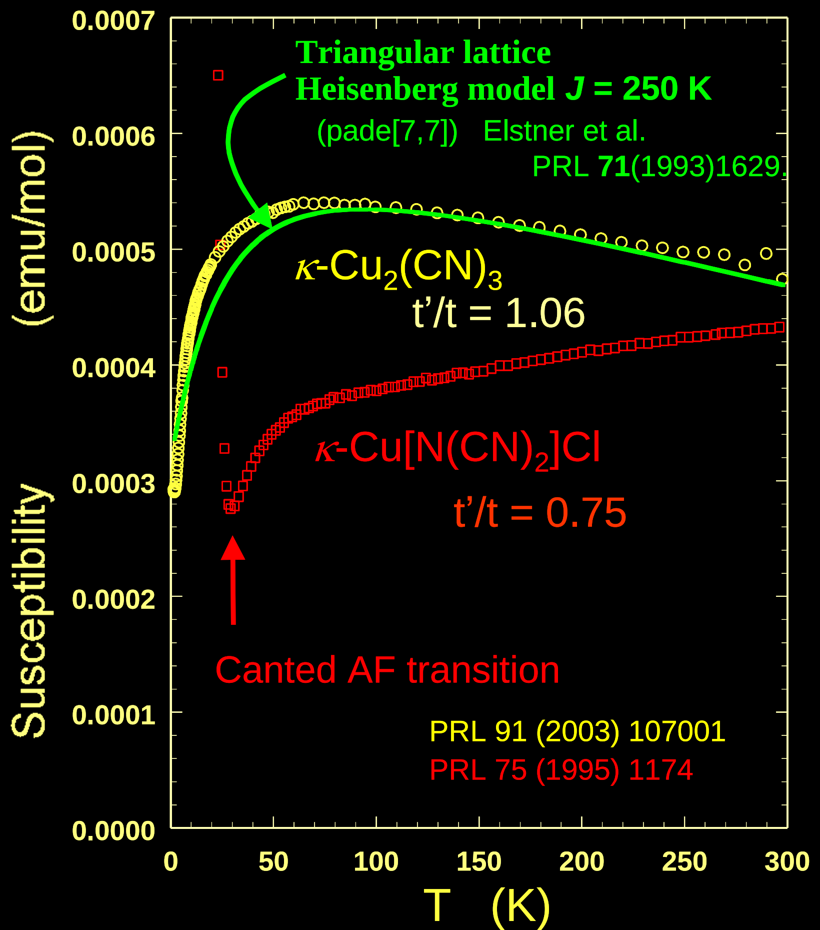
Mott insulators κ-$(ET)_2X$

Spin ordering or not ?

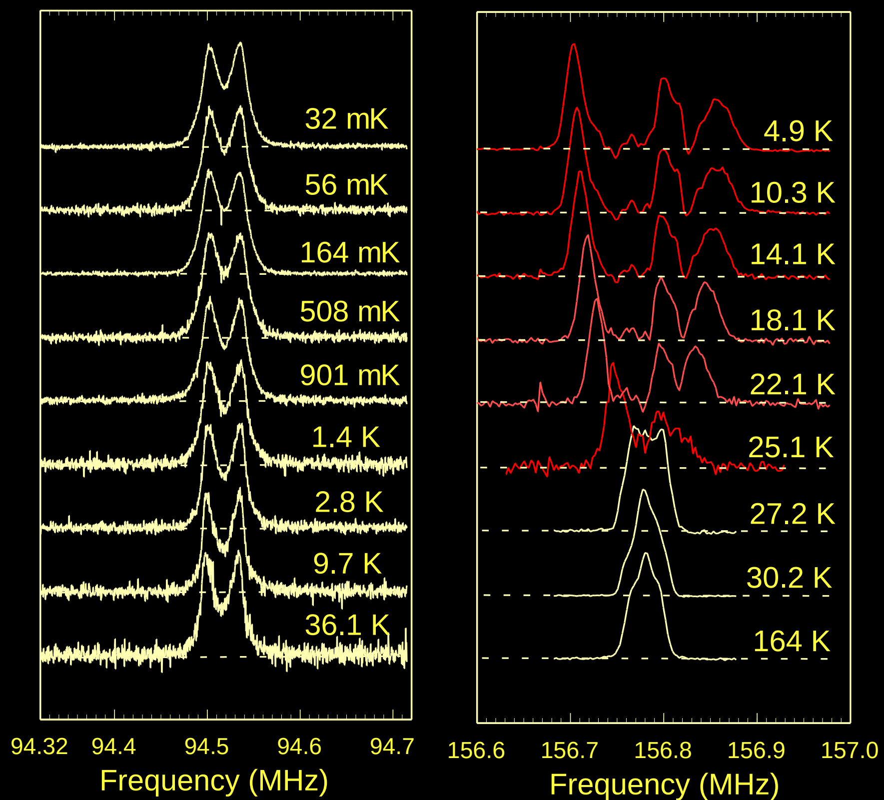
X	t'/t
$Cu_2(CN)_3$	1.06 (0.8)
$Cu[N(CN)_2]Cl$	0.75 (0.44)



Magnetic susceptibility



^{1}H NMR spectrum



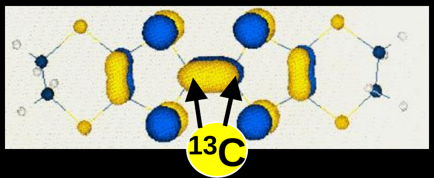
κ-$(ET)_2Cu_2(CN)_3$ κ-$(ET)_2Cu[N(CN)_2]Cl$

t'/t =1.06 t'/t =0.75

No ordering ⟺ AF ordered ($0.45\mu_B$)

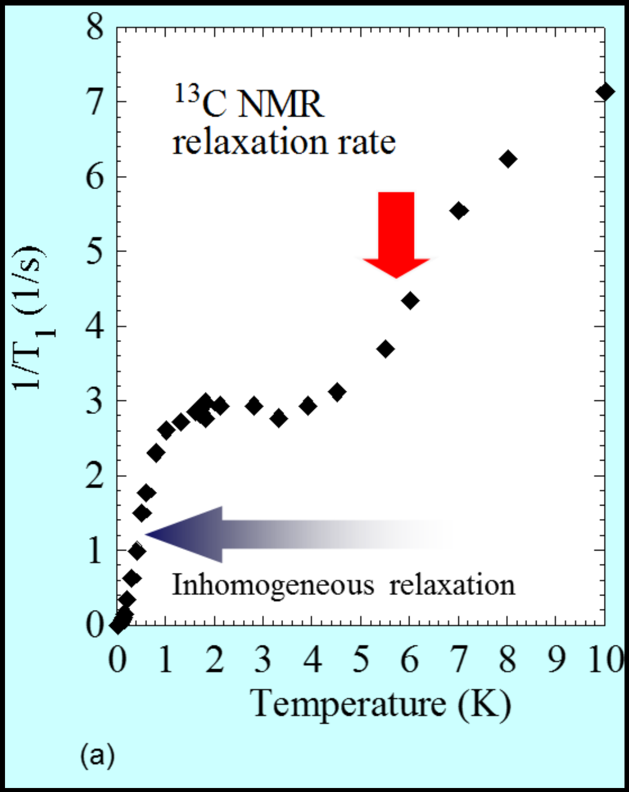
Also see Zheng et al. PRB 71 (2005) 134422

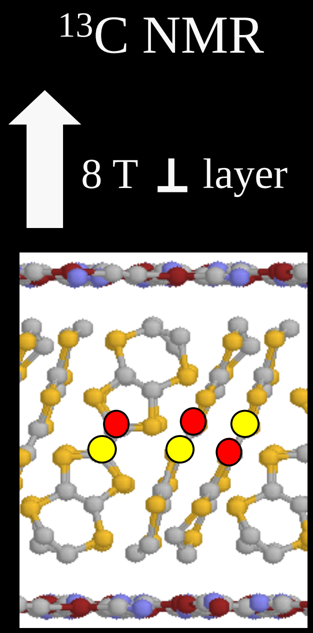
Spin anomaly around 5-6K in κ-$(ET)_2Cu_2(CN)_3$

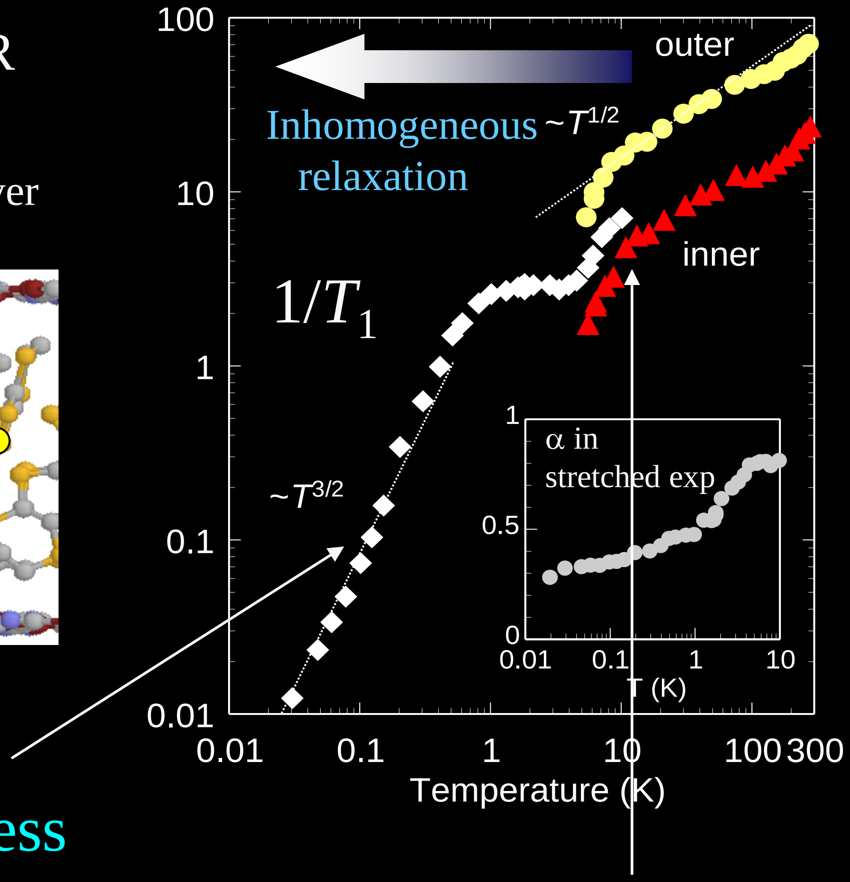


Shimizu *et al.*, PRB 70 (2006) 060510

NMR relaxation rate





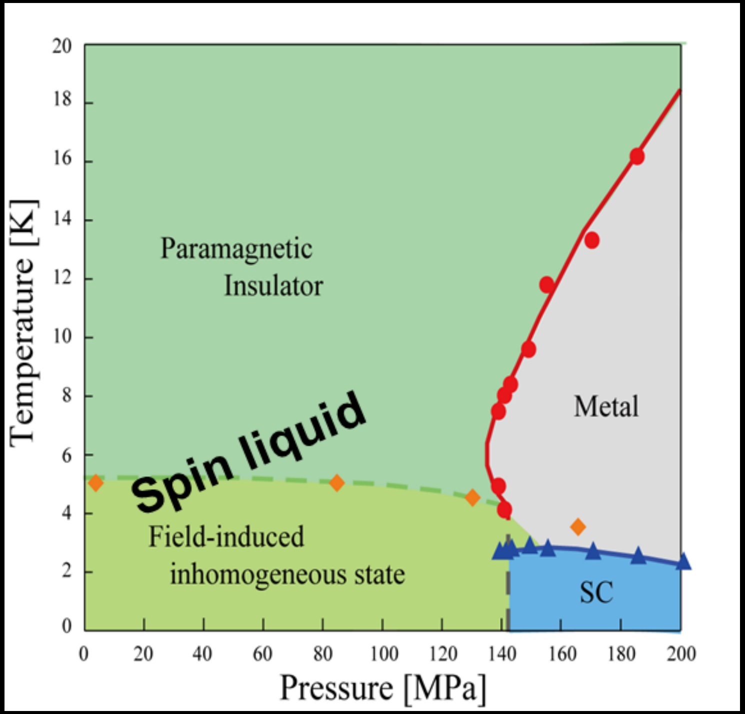


Gapless

Why a spin liquid realized instead of  expected in Heisenberg model ?

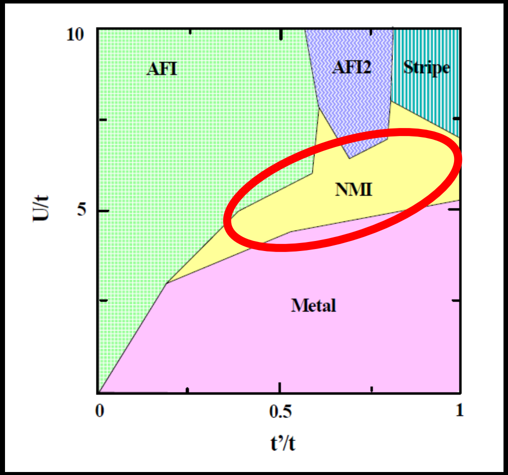
→near Mott transition

"Hubbard spin liquid"

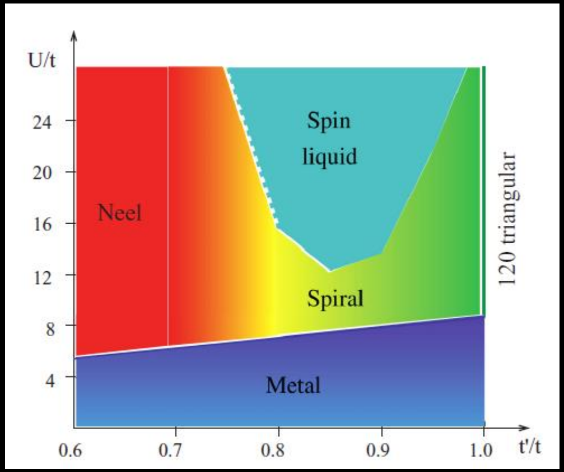


Spin liq. emerges Hubbard model ?

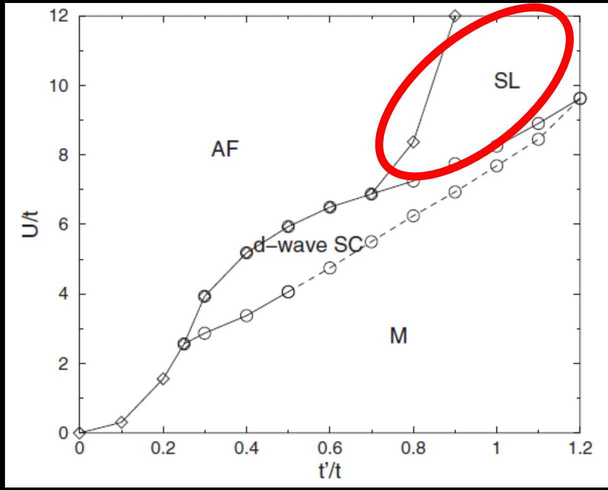
PIRG; Morita, Mizusaki, Imada (2002), (2006)



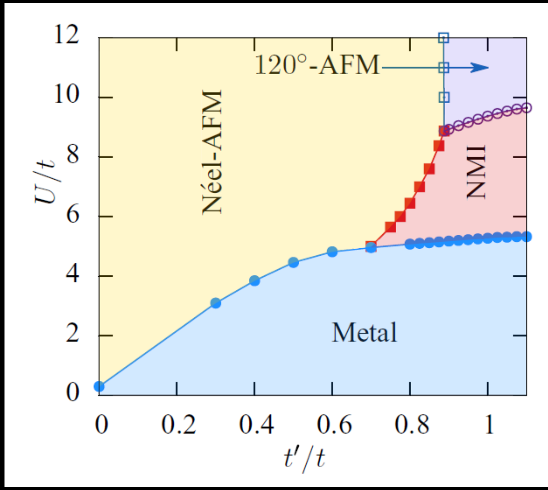
Tocchio et al. PRB (2013)



Cellular DMFT; Kyung, Tremblay (2006)



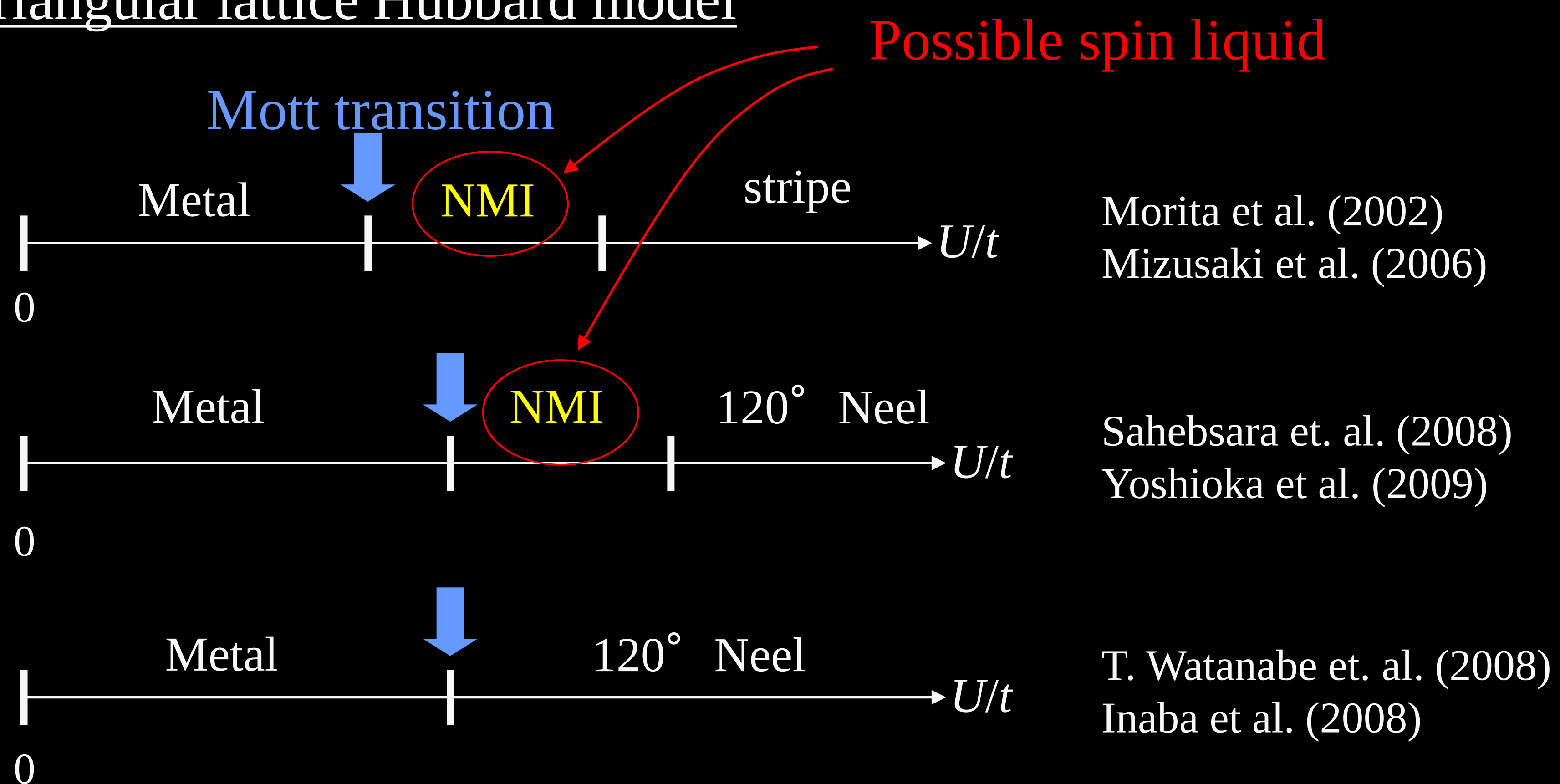
VCA + LDFA Laubach et al. PRB (2015)

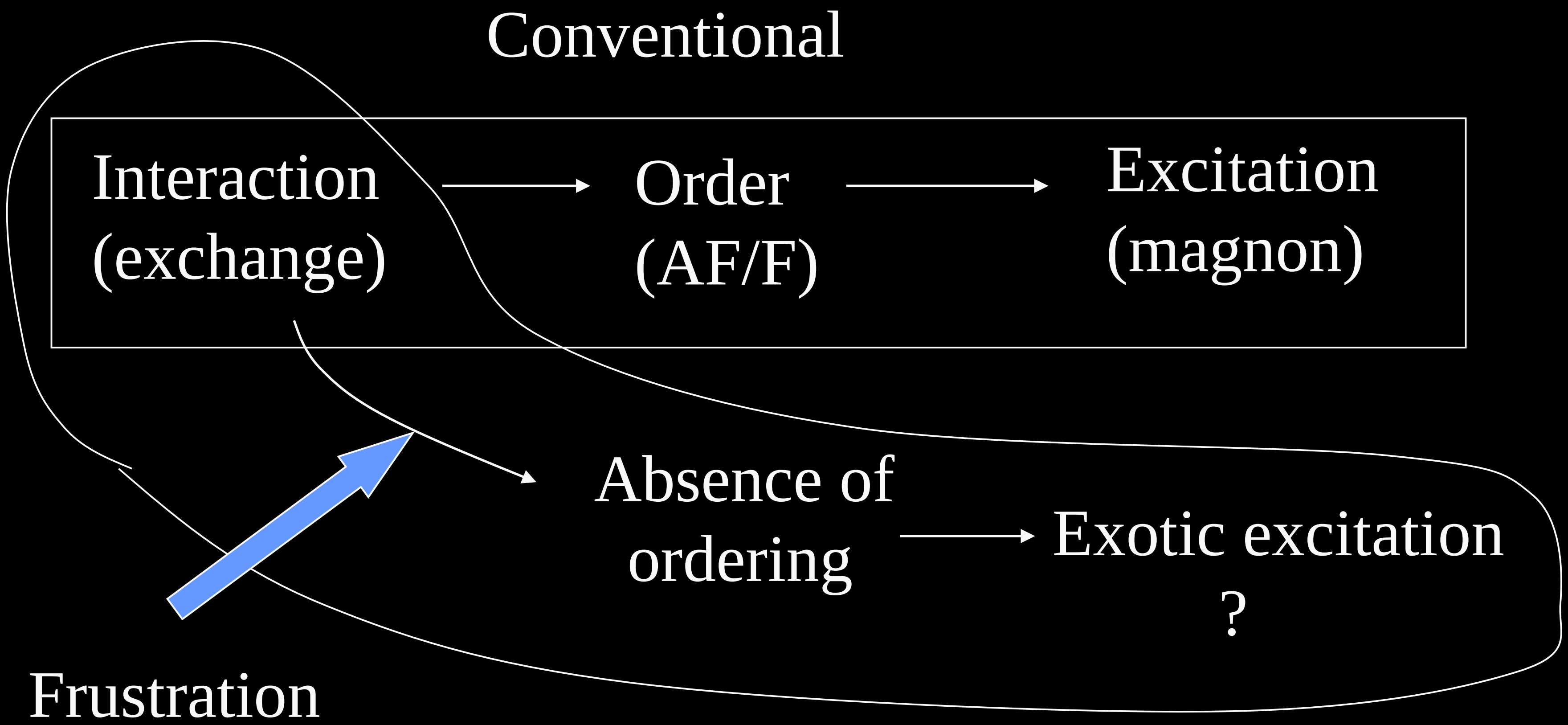


Why not  expected in Heisenberg model ?

→near the Mott transition

<u>Triangular lattice Hubbard model</u>




Conventional
Interaction
(exchange)
Order
(AF/F)
Excitation
(magnon)
Absence of
ordering
Exotic excitation
?
Frustration

Thermodynamics

Specific heat by Yamashita and Nakazawa (Osaka Univ.)

$C=\gamma T+\beta T^3$

<u>At low temperatures</u>

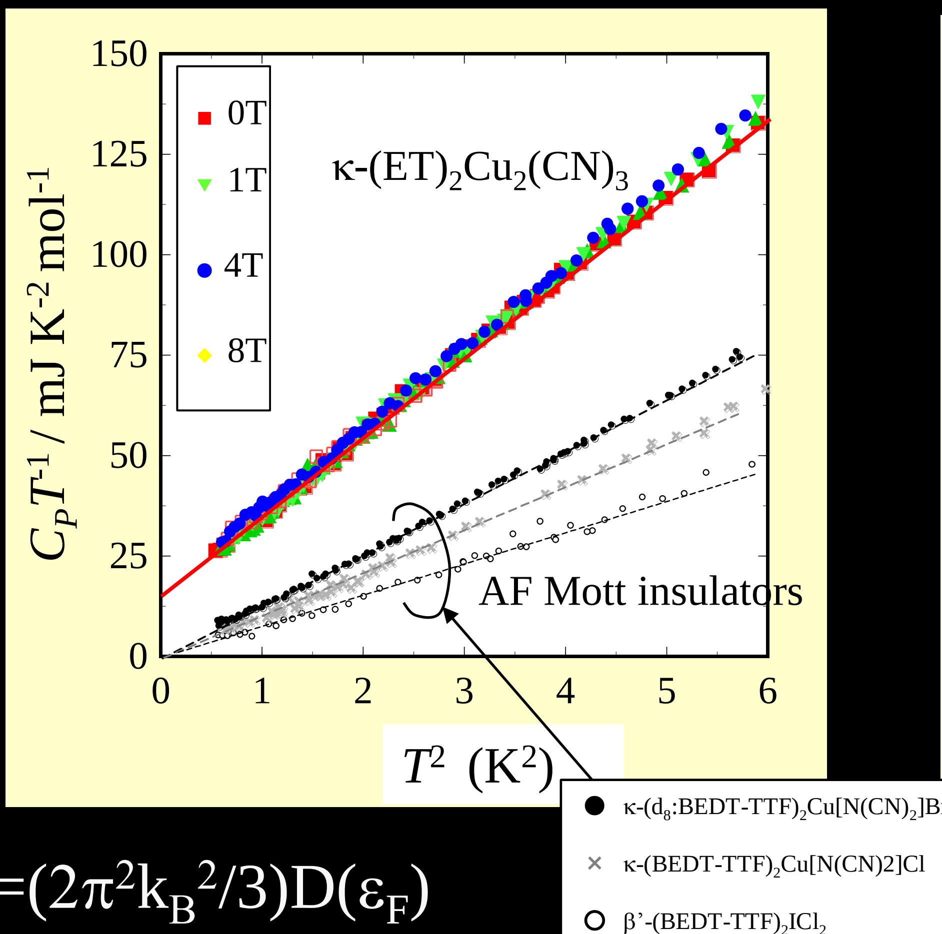
Finite γ

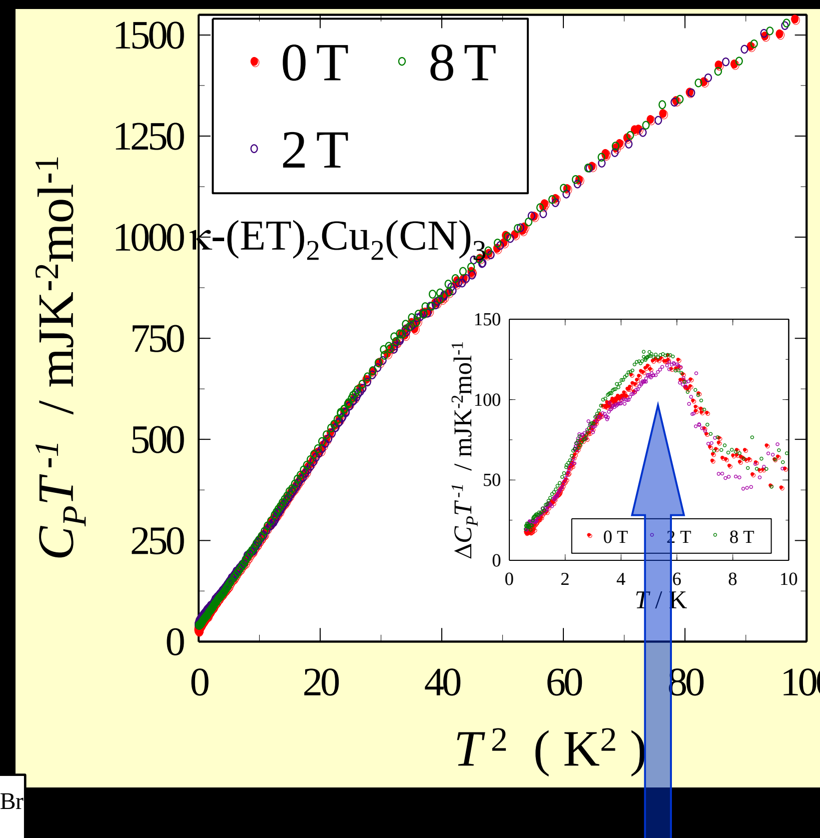
➡ Low-lying spin excitations

<u>At higher temperatures;</u>

Field-insensitive anomaly

➡ Hidden order or some crossover ?





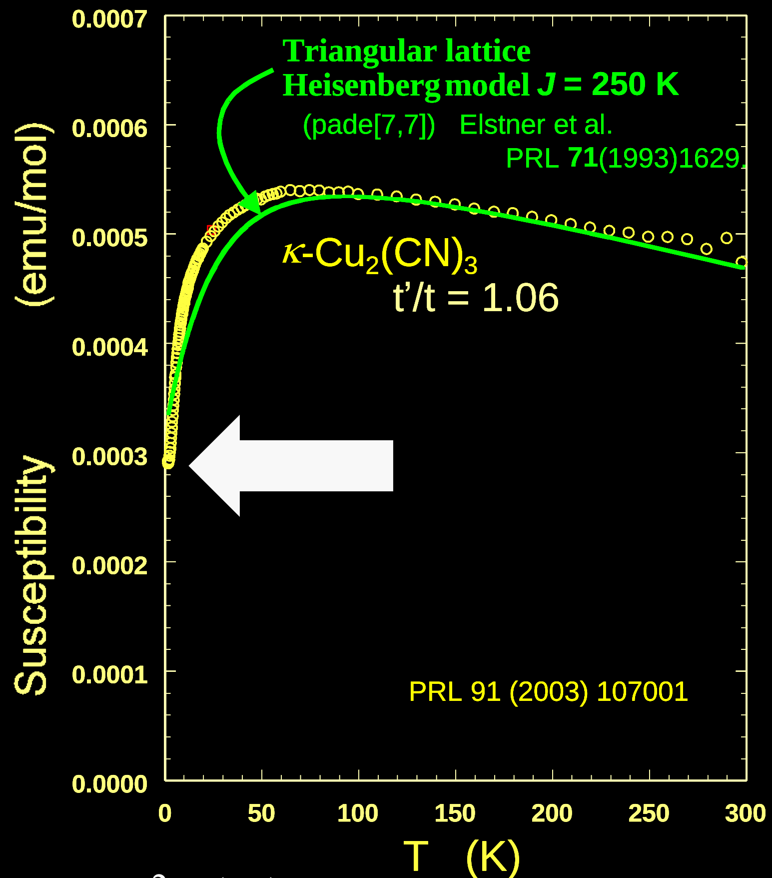
$\gamma=(2\pi^2 k_B^2/3)D(\varepsilon_F)$

Anomaly at 5-6 K

Wilson ratio $R_W = \dfrac{\{\chi/(2\mu_B{}^2)\}}{\{\gamma/(2\pi^2 k_B{}^2/3)\}}$ ~ 1.6

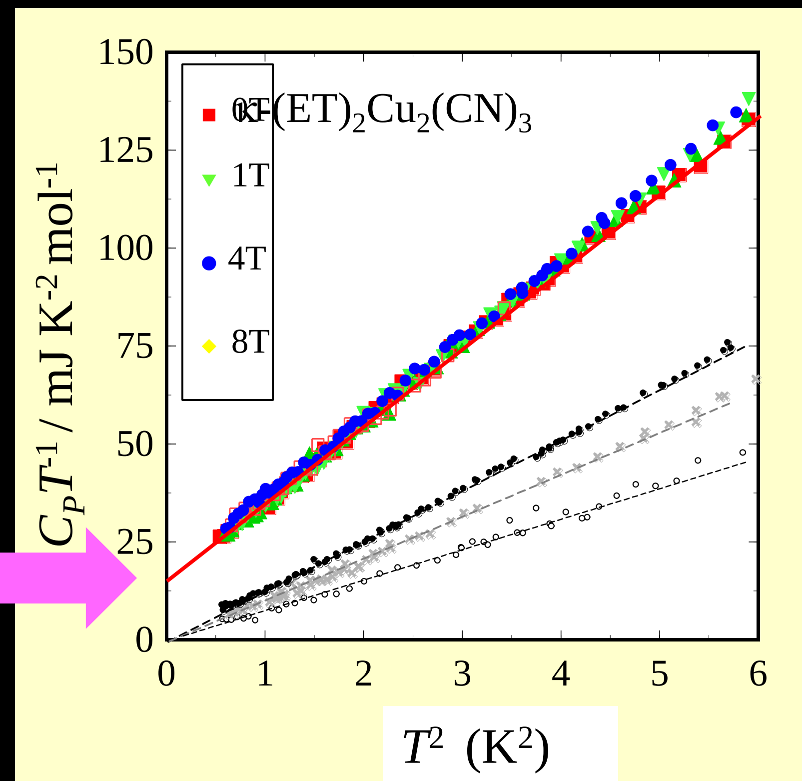
→ Degenerate Fermionic objects in Mott insulator

$\chi_{spin} = 3 \times 10^{-4}$ emu/mol



$\chi = 2\mu_B{}^2 D(\varepsilon_F)$

$\gamma = 13$ mJ/K^{2}mol



$\gamma = (2\pi^2 k_B{}^2/3) D(\varepsilon_F)$

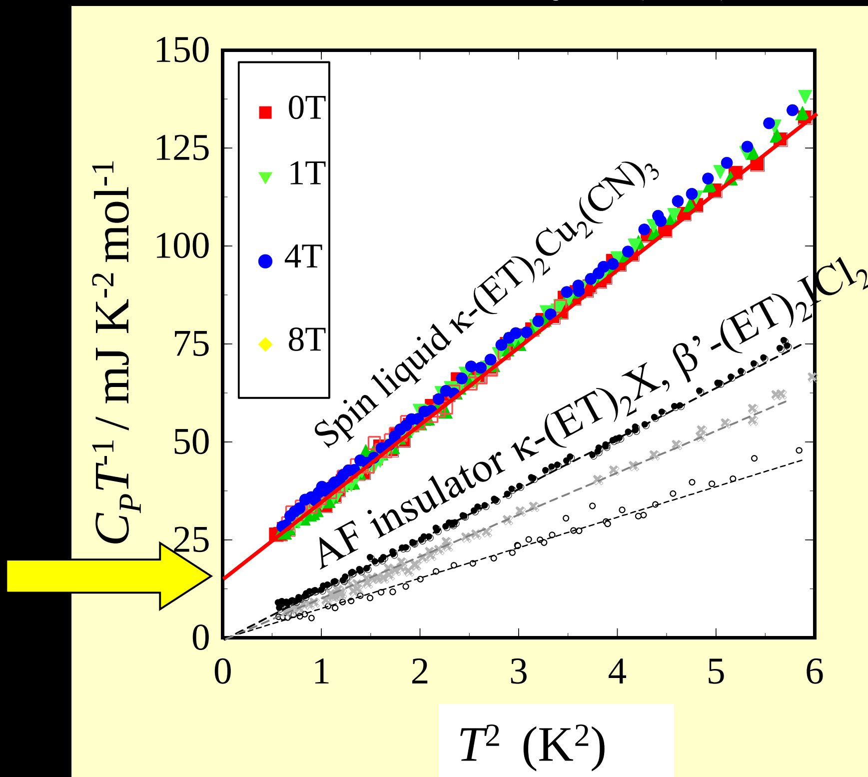
Spin liquid in κ-$(ET)_2Cu_2(CN)_3$; Gapless or gapped

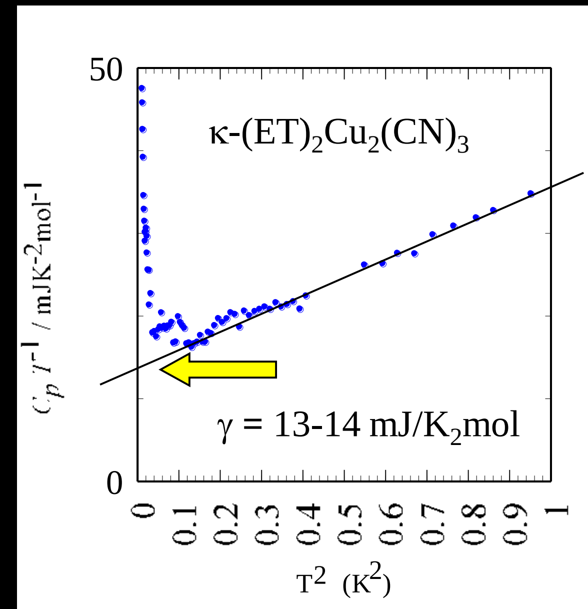
Specific heat → ***gapless*** (γ = 13-14 mJ/K^{2}mol)

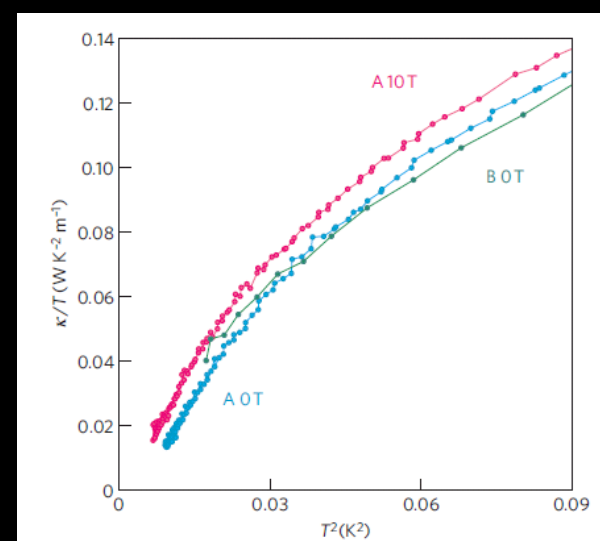
Wilson ratio ~ 1.1

→ *Degenerate chargeless Fermionic objects*

S. Yamashita *et al.*, , Nature Phys. 4 (2008) 459



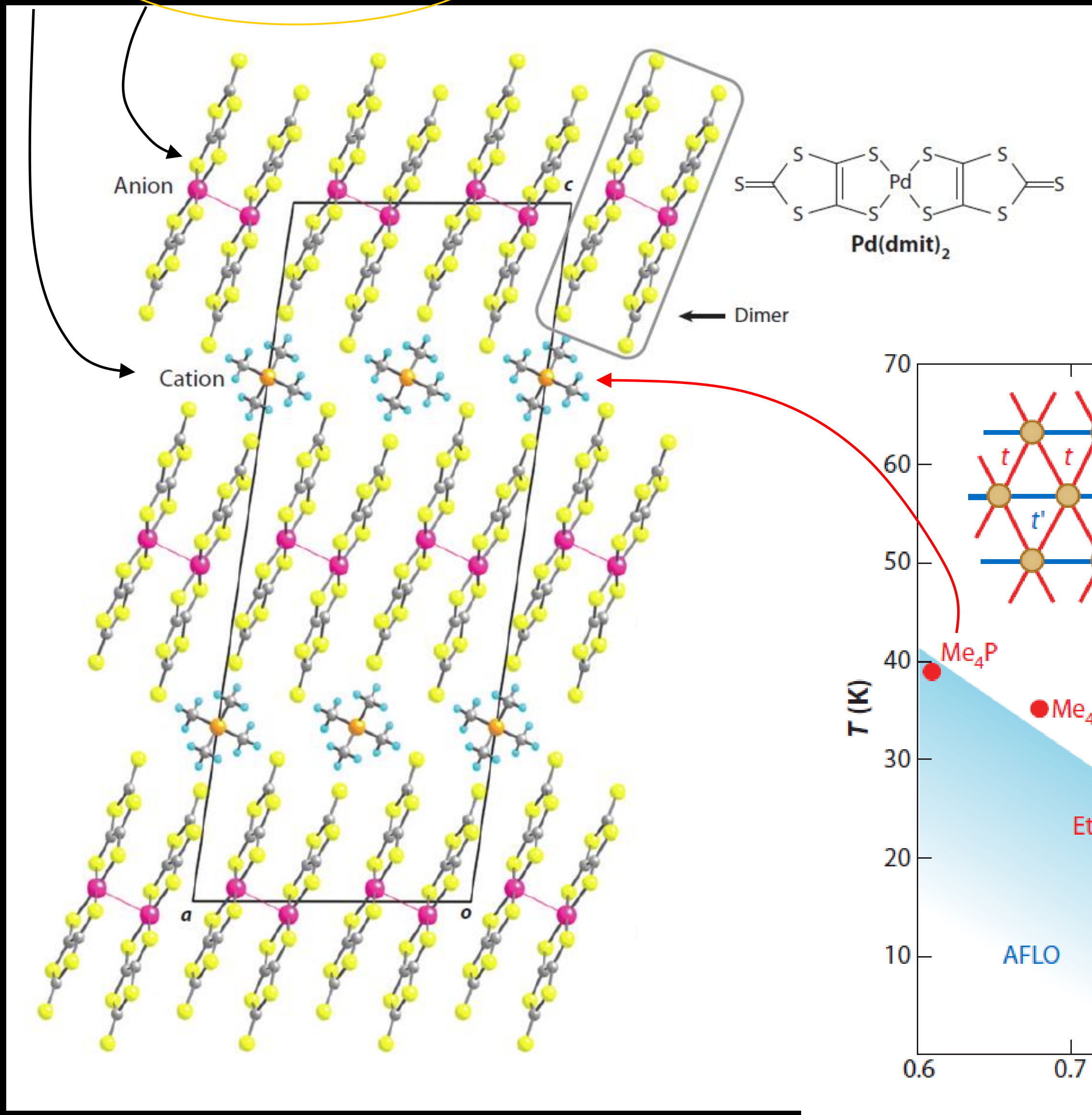


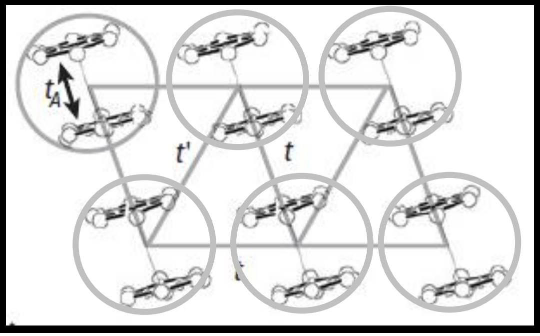


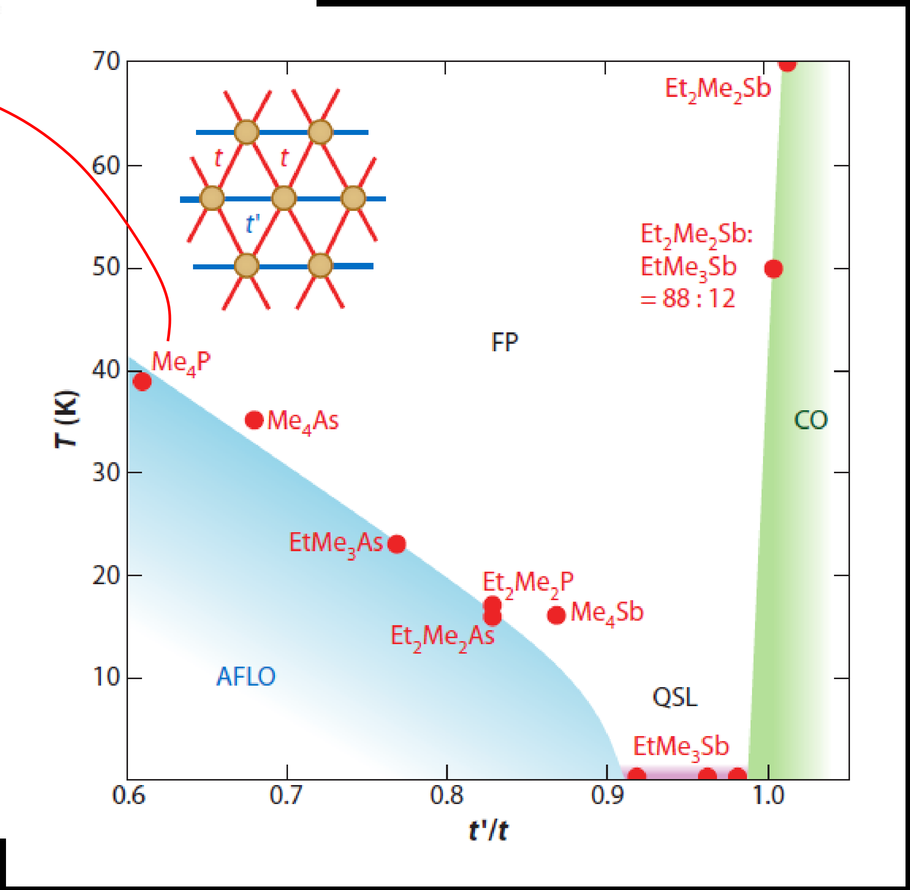
Thermal conductivity → ***gapped***; 0.46 K

M. Yamashita et a., Nature Phys. 5 (2009) 44

$A[Pd(dmit)_2]_2$; quasi-triangular lattice systems



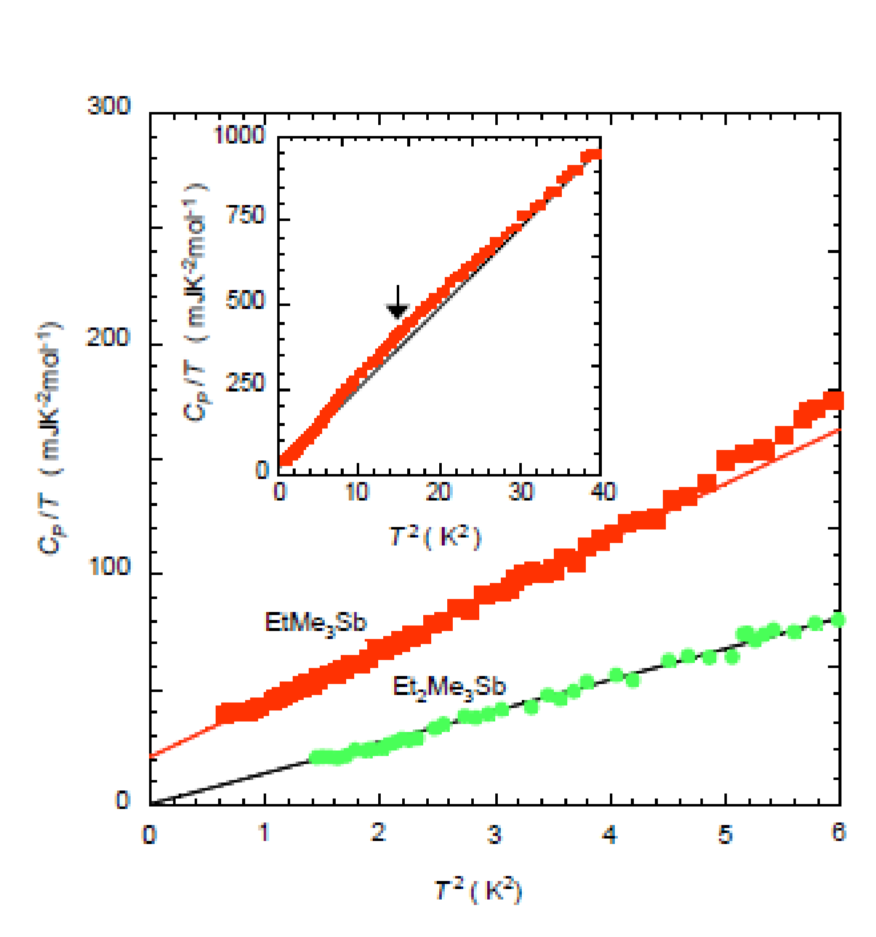




Spin liquid in $EtMe_3Sb[Pd(dmit)_2]_2$

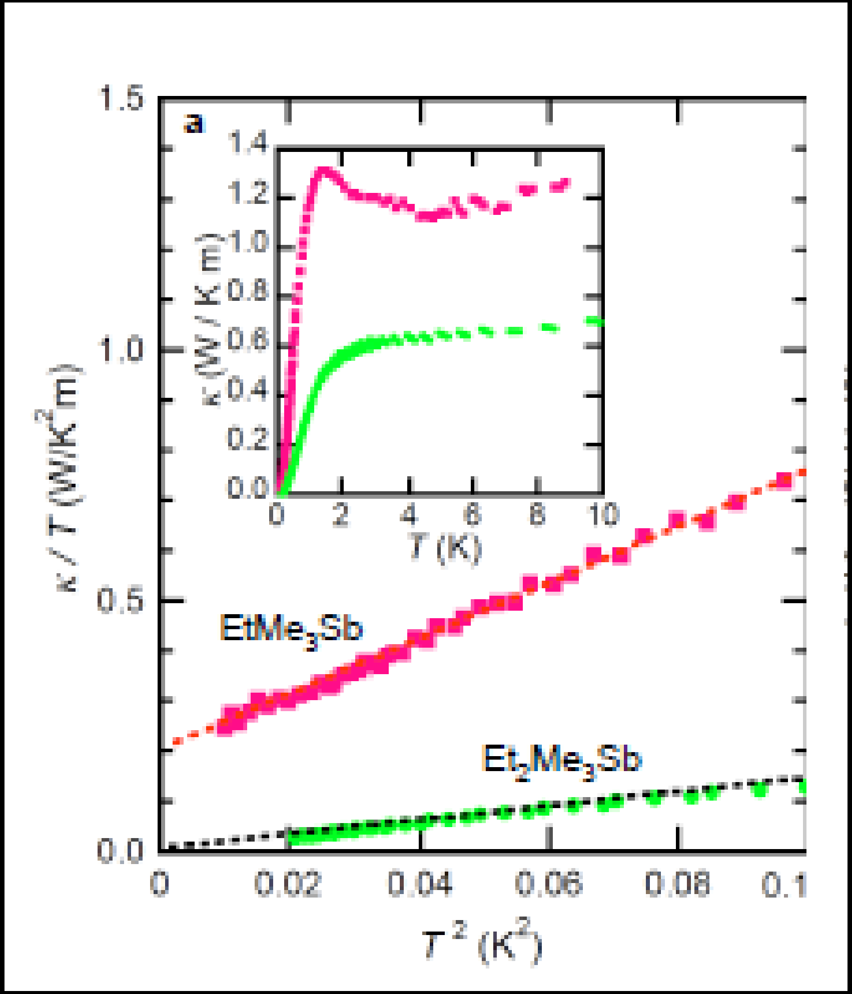
Specific heat

S. Yamashita et al., Nat. Commun. 2, 275 (2011)



Thermal conductivity

M. Yamashita et al, Science 328, 1246 (2010)

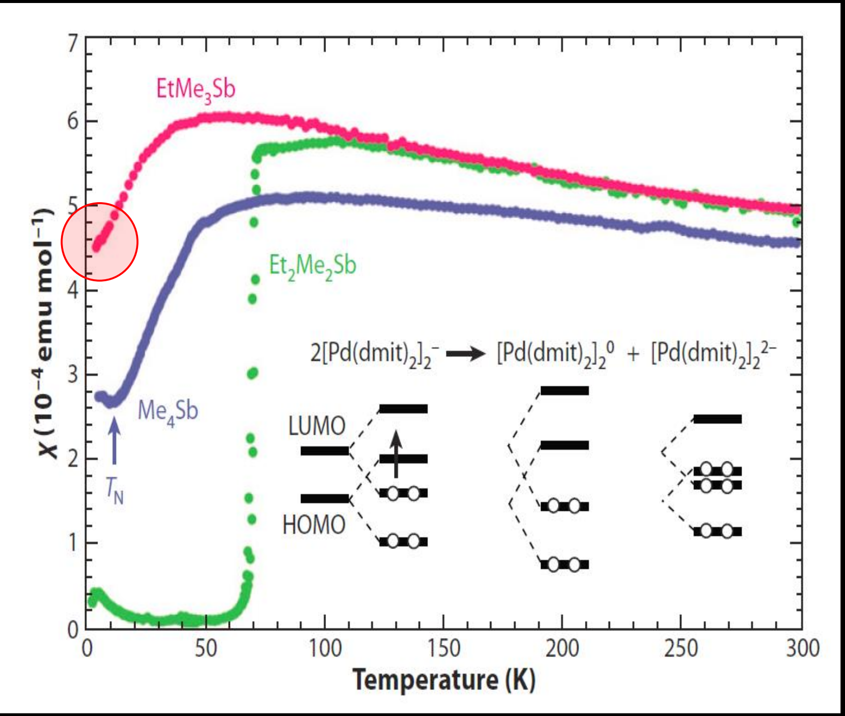


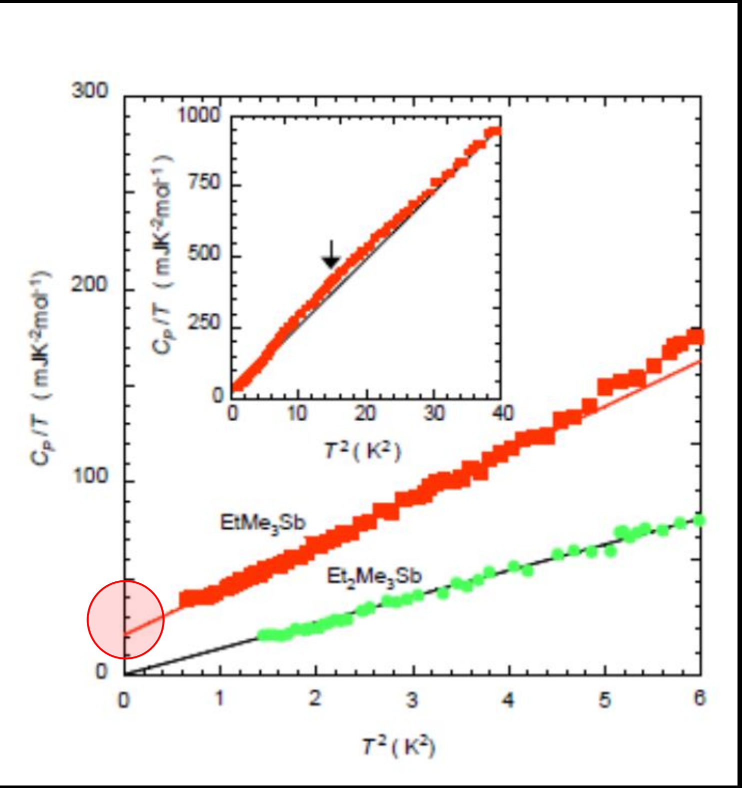
Wilson ratio

R_W=1.6

χ_{spin} =4.5 emu/mol

γ =20 mJ/mol K^2



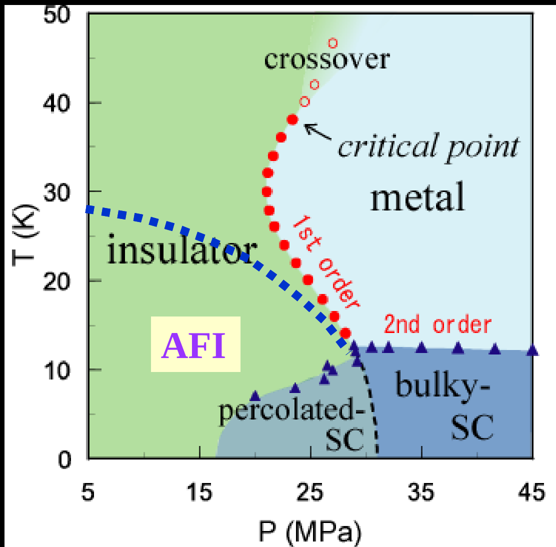


R. Kato, Bull. Chem. Soc. Jpn. 87, 355 (2014)

S. Yamashita et al., Nat. Commun. 2, 275 (2011)

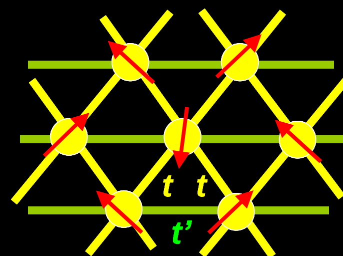
Charge excitation in antiferromagnet and spin liquid

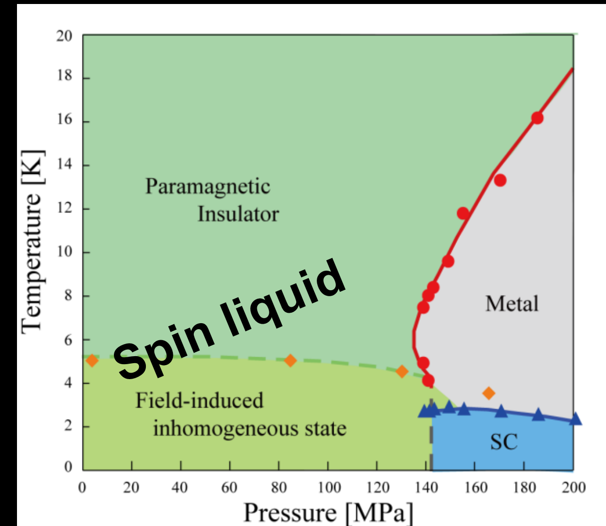
Charge gap is clearly opened on AF ordering, but remains undeveloped in spin liquid.

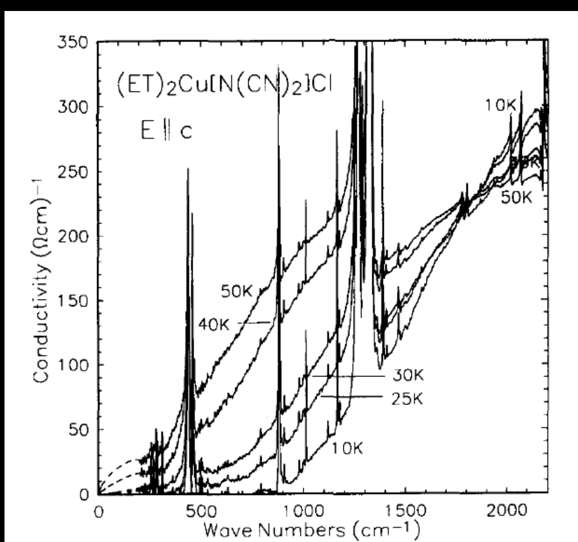


$t'/t = 0.75$

$t'/t = 1.06$



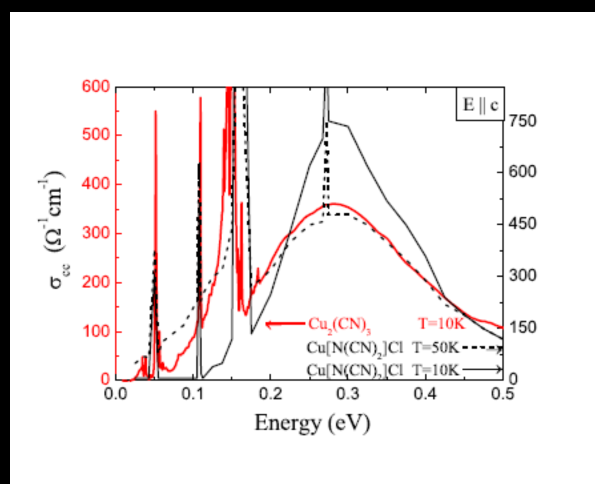


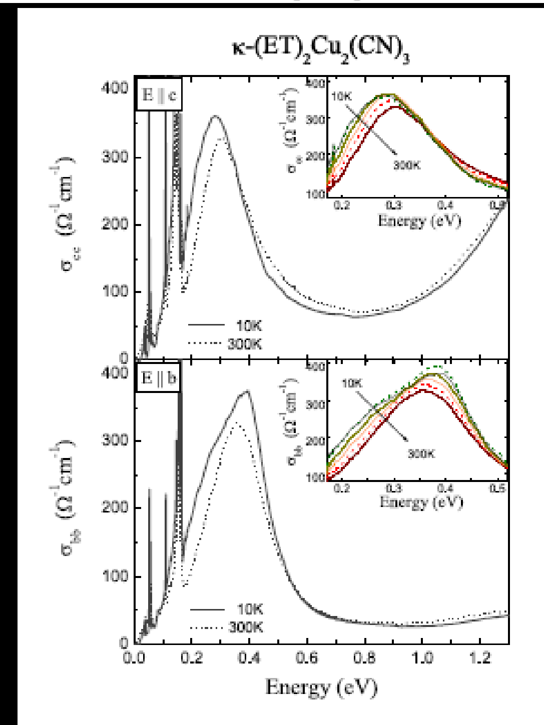


Kornelsen et al., SSC 81 (1992)343

Optical conductivity

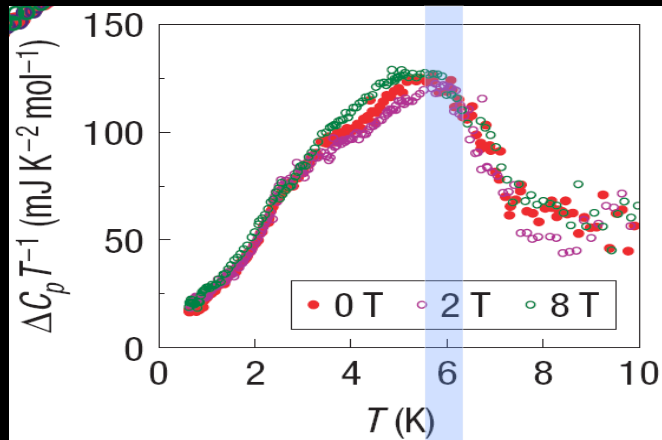
Kezsmarki et al.
PRB 74(2006)201101



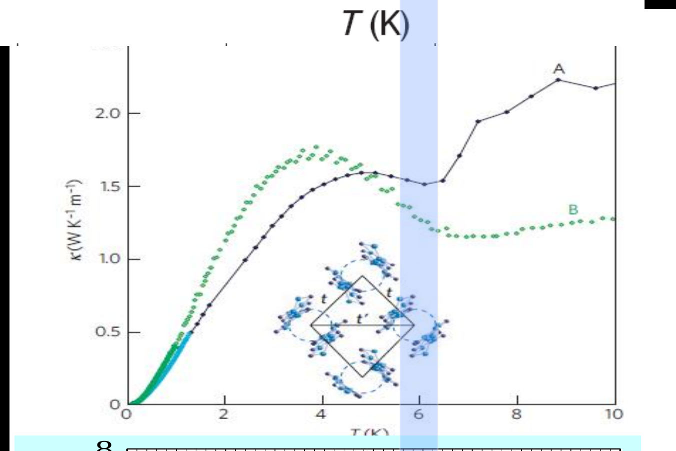


Thermodynamic anomaly at 6K in κ-$(ET)_2Cu_2(CN)_3$

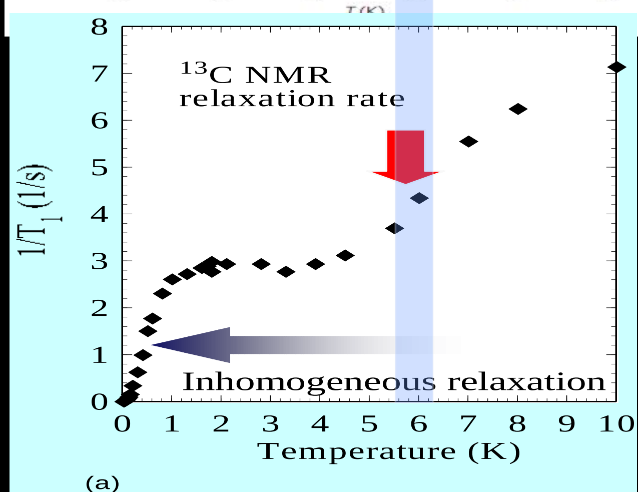
Specific heat
S. Yamashita *et al*., *Nature Phys*. 4 (2008) 459



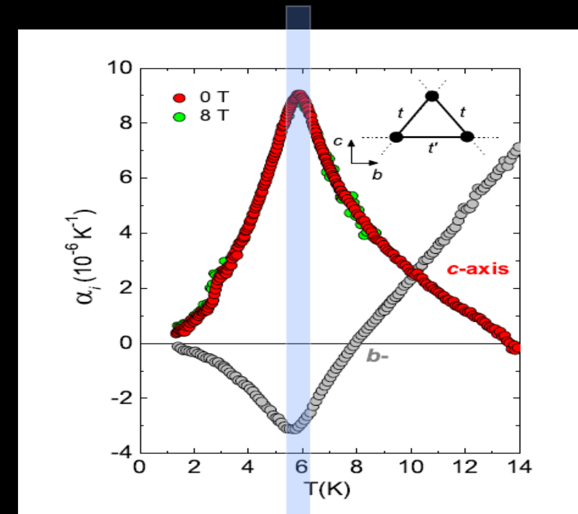
Thermal conductivity
M. Yamashita *et al*., *Nature Phys*. **5** (2009) 44



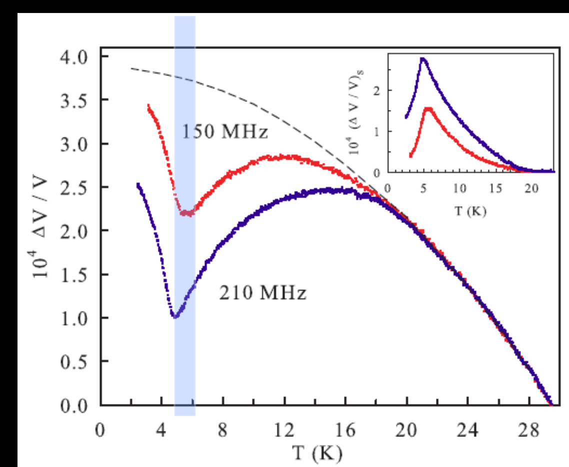
NMR Relaxation rate
Shimizu et al.,
PRB **70** (2006) 060510



Thermal expansion coefficient
Manna et al., *PRL* **104** (2010) 016403



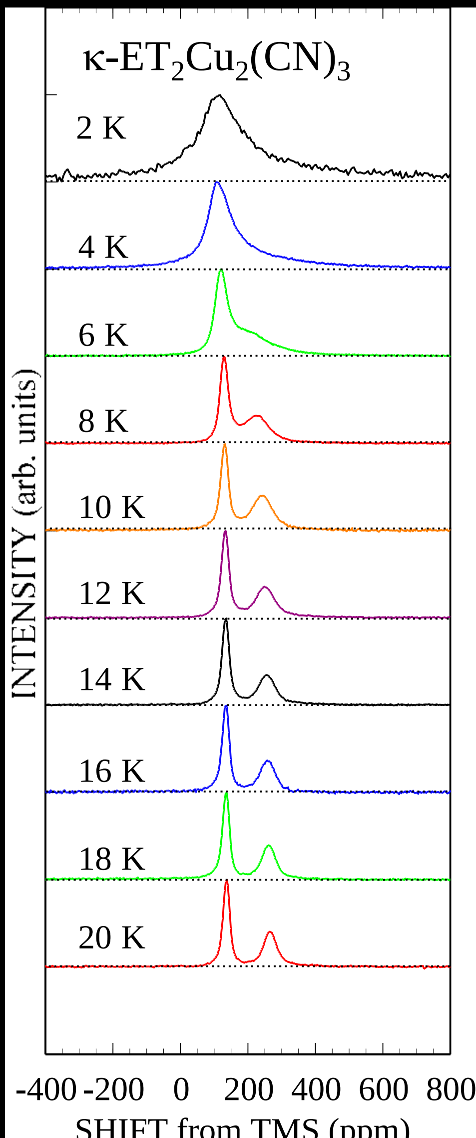
Ultrasound velocity
Poirier et al.,



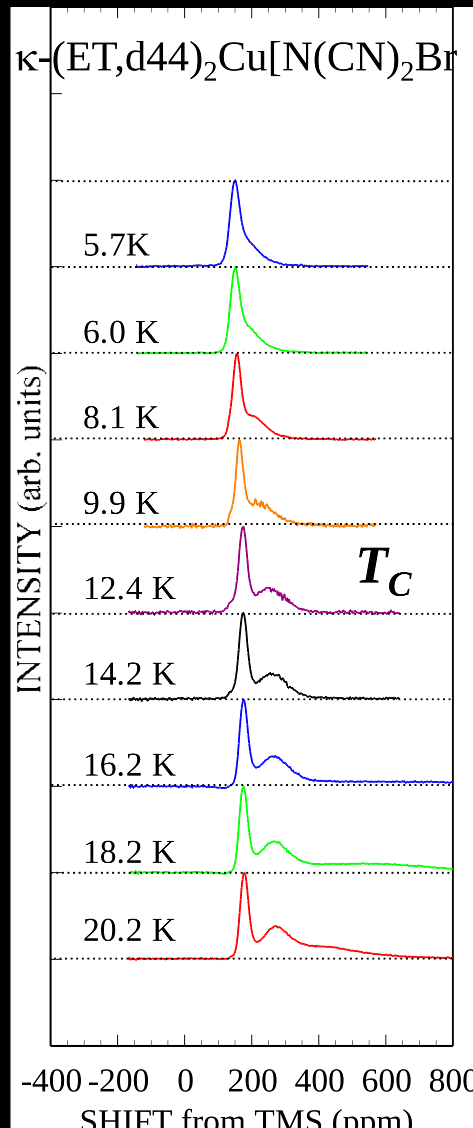
Can you distinguish SL and SC ?

NMR spectra *B* // *a* axis

SL

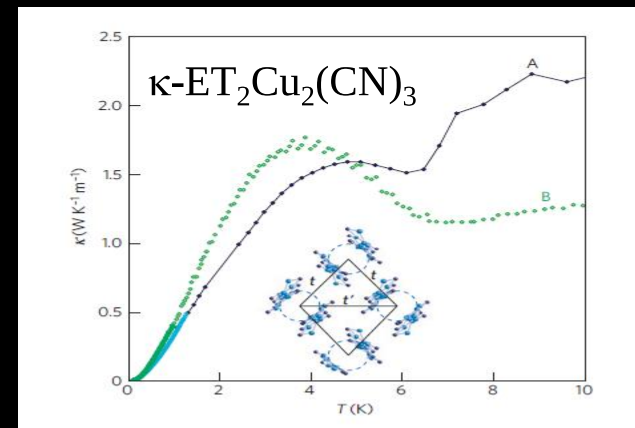


SC



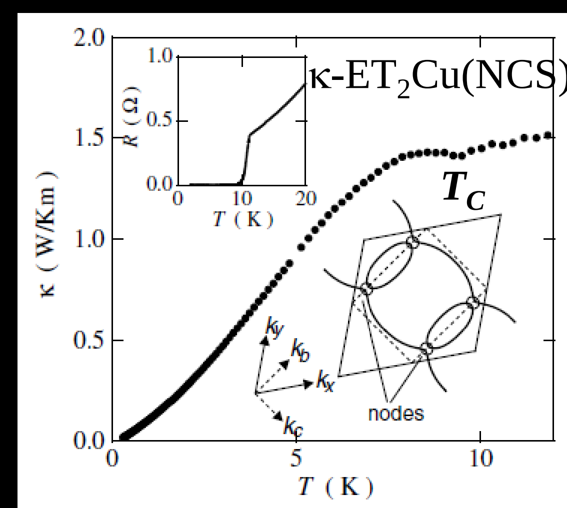
Thermal conductivity

SL



M. Yamashita *et al*., *Nature Phys*. 5 (2009) 44

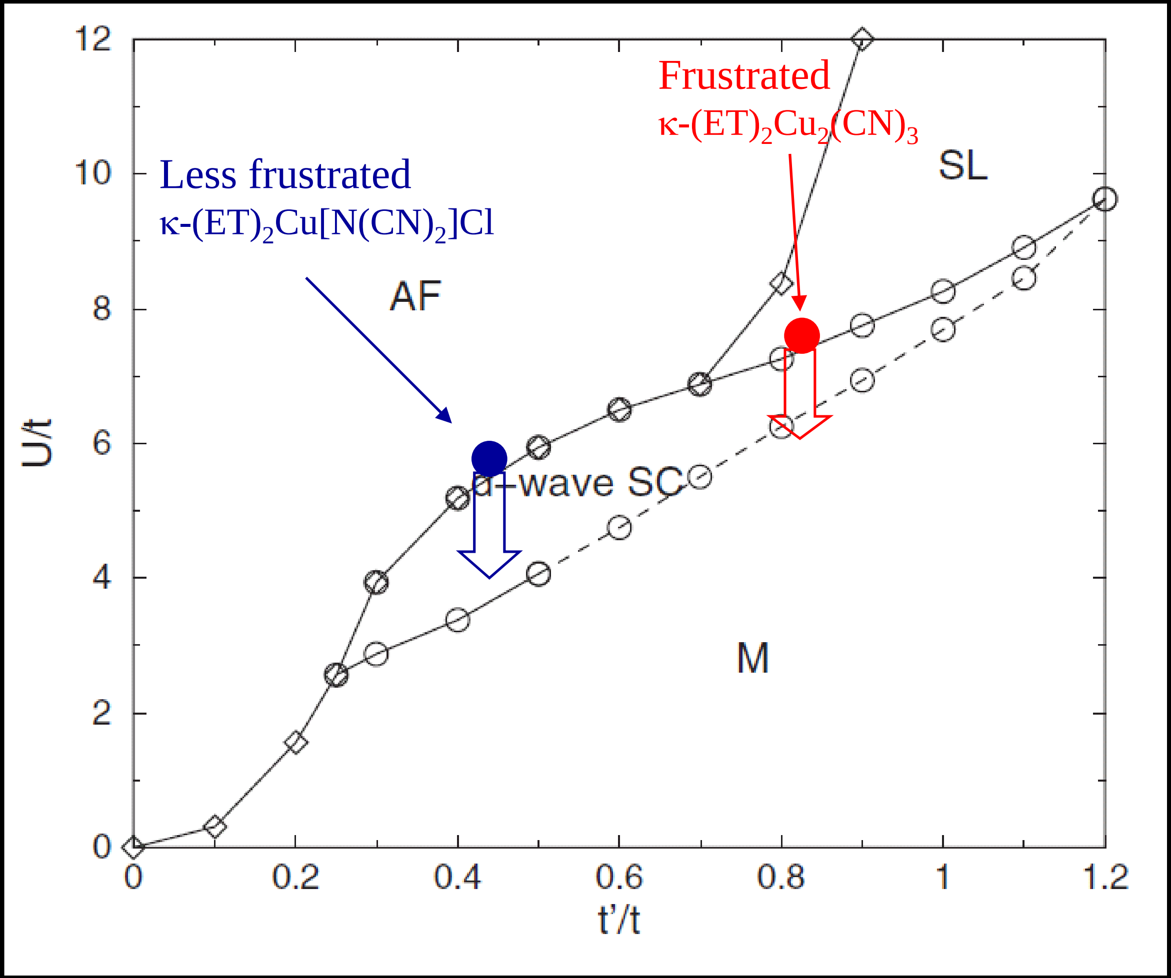
SC

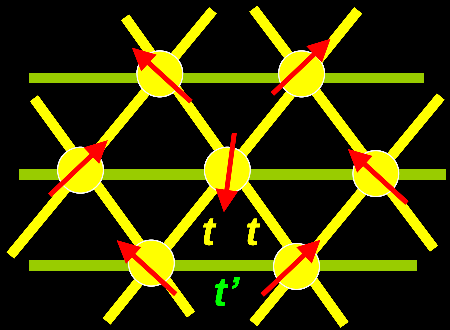


Y. Matsuda *et al*.,
J. Phys: Condens. Matter 5 (2006) R705

Pressurize AFI and spin liquid

½-filled Hubbard model (Cluster DMFT)
Kyung, Tremblay PRL (2006)





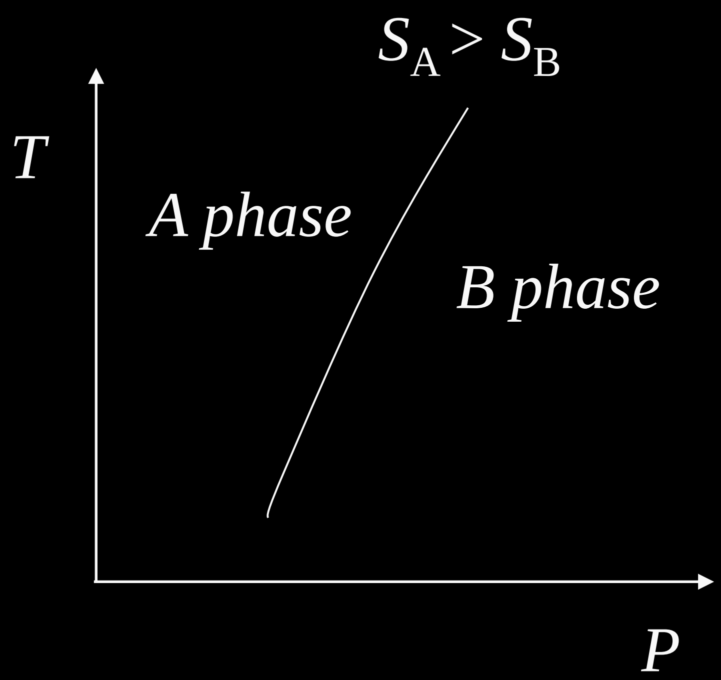
Material parameters

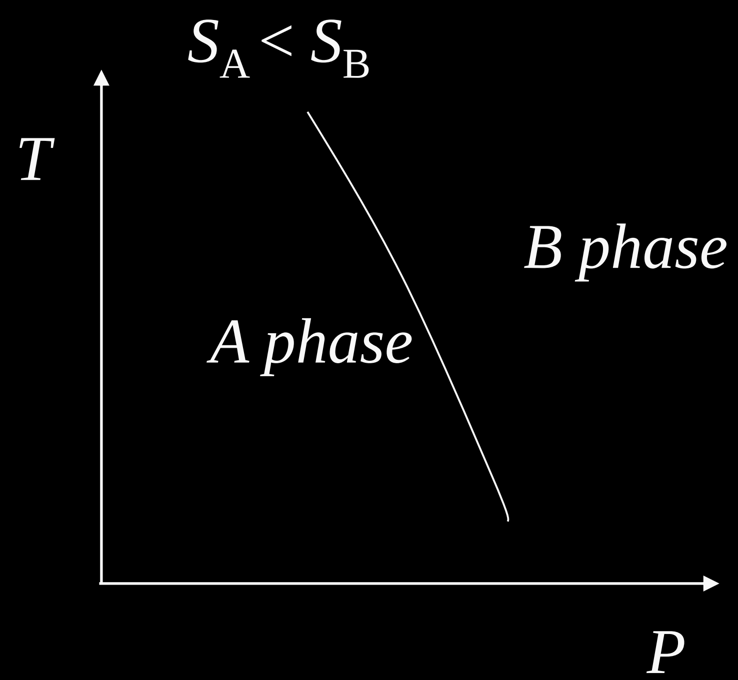
Kandpal et al.
PRL 103 (2009) 067004

Entropy balance known from phase diagram

Clausius Clapeyron $dT/dP = (V_A - V_B)/(S_A - S_B)$

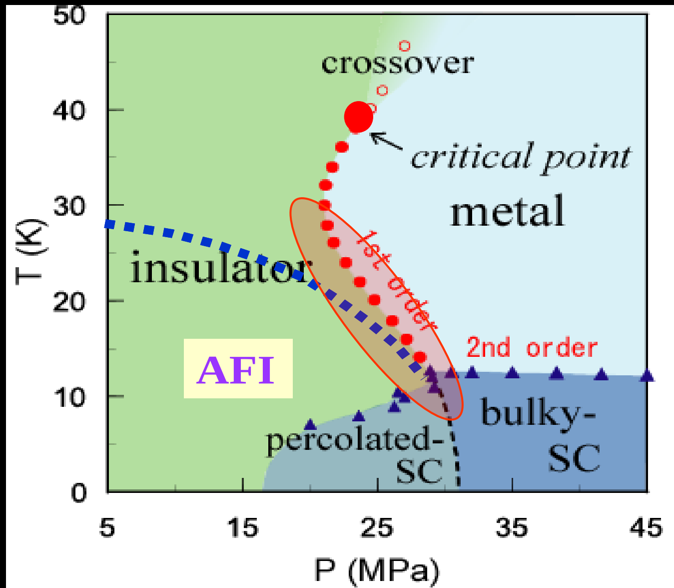
>0





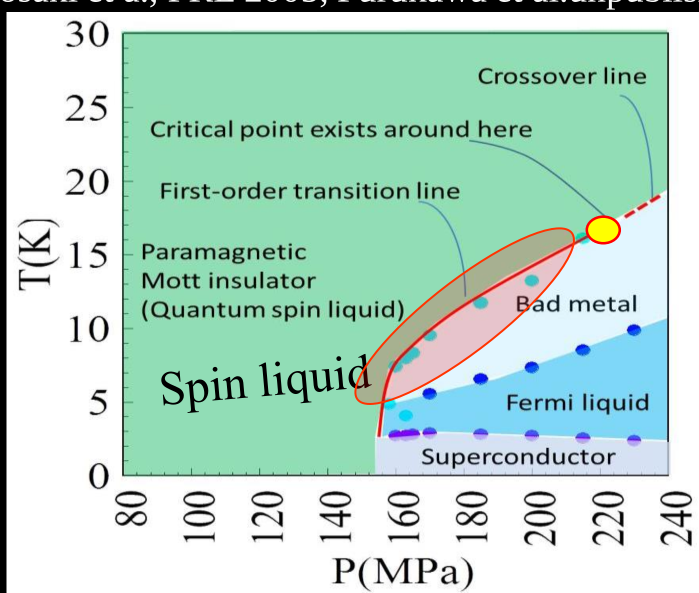
κ-$(ET)_2Cu[N(CN)_2]Cl$ *t'/t* ~ 0.44-0.75

Kagawa *et al*., Nature 2005 , PRL 2004; PRB 2004,



κ-$(ET)_2Cu_2(CN)_3$ *t'/t* ~ 0.80-1.06

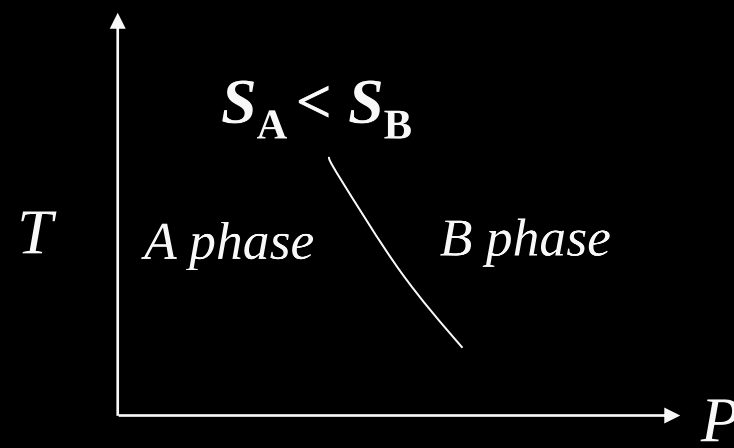
Kurosaki et a., PRL 2005, Furukawa et al.unpublished

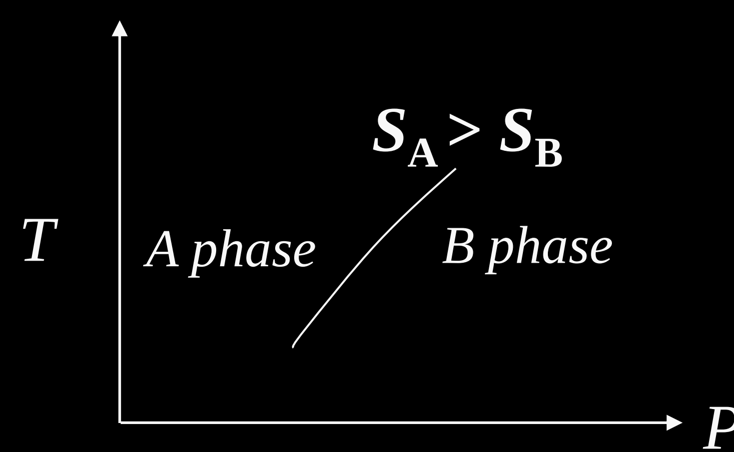


Thermodynamics of Mott transition

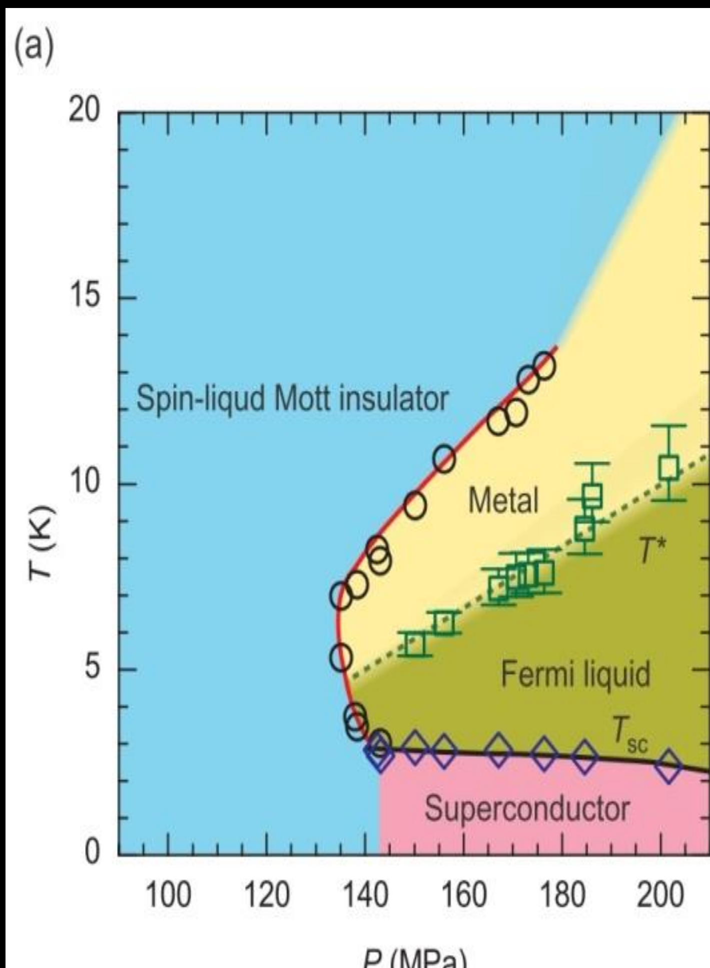
Clausius Clapeyron

$$dT/dP = \Delta V/\Delta S = \underbrace{(V_A - V_B)}_{>0}/(S_A - S_B)$$



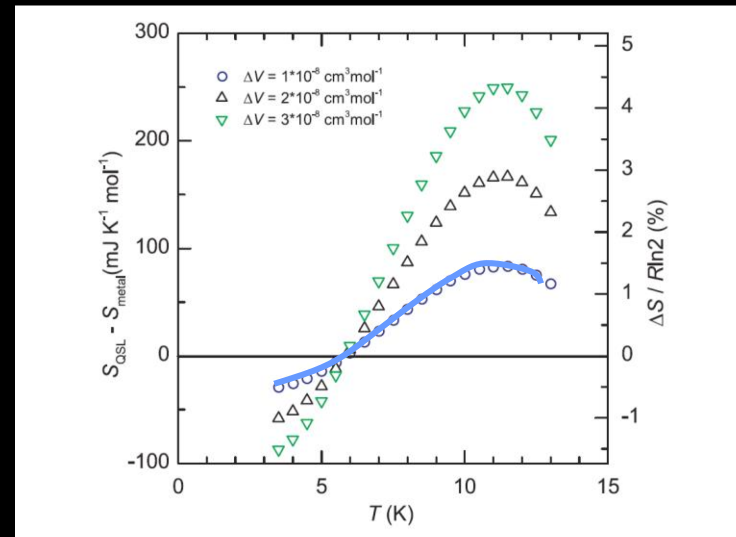


Entropy of spin liquid



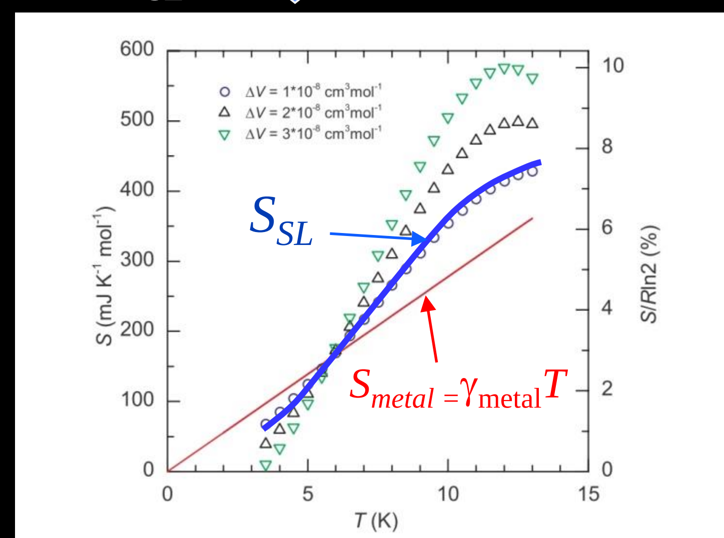
parameter

$\Delta S = S_{SL} - S_{metal} = (dP/dT)\,\Delta V$



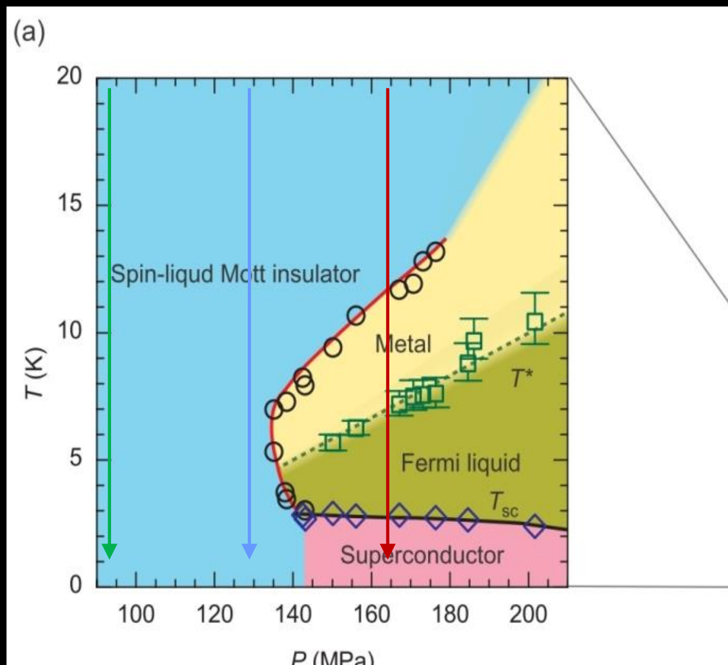
S_{SL}

γ_{metal}=27.5 mJ/mol K^2

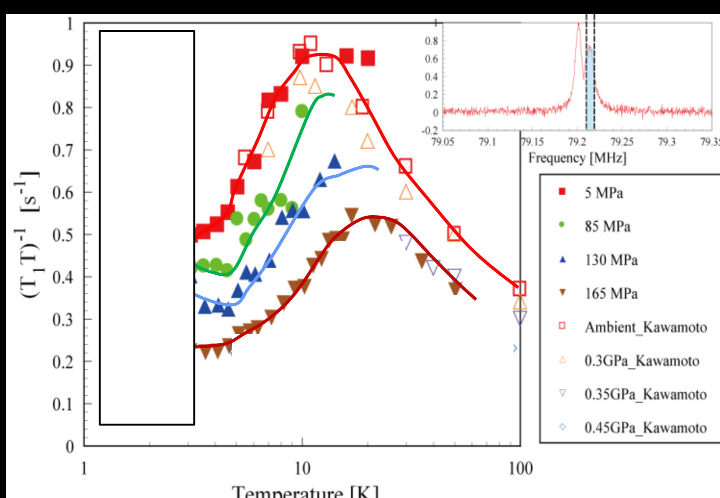


Mott transition of SL; drastic change in charge transport but not in spin

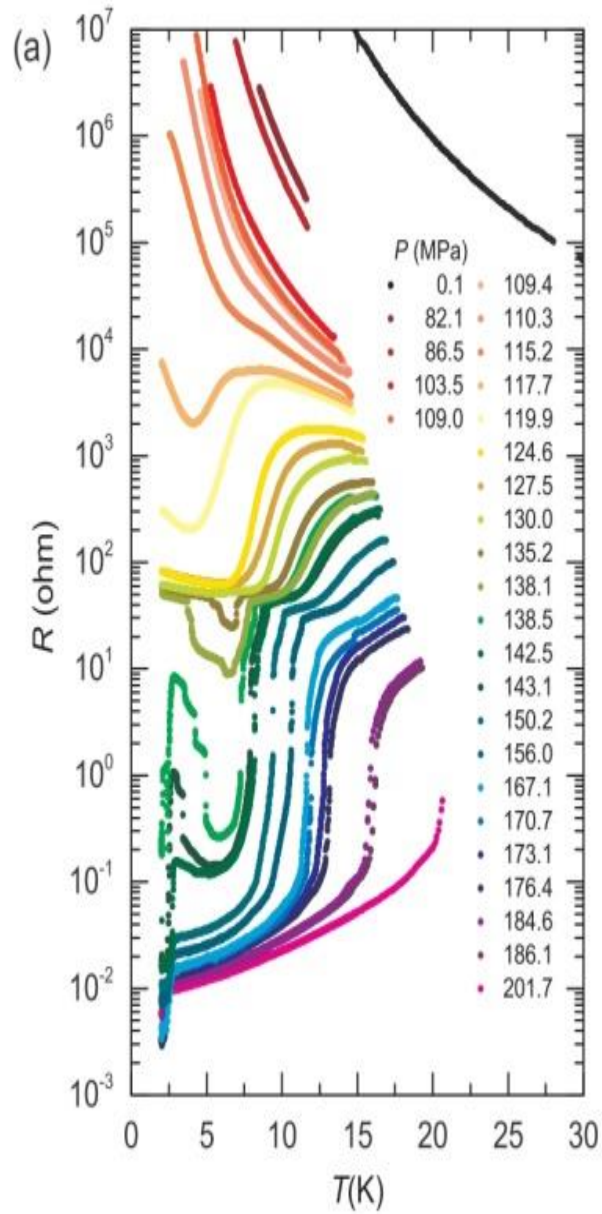
Phase diagram



NMR
$1/T_1$

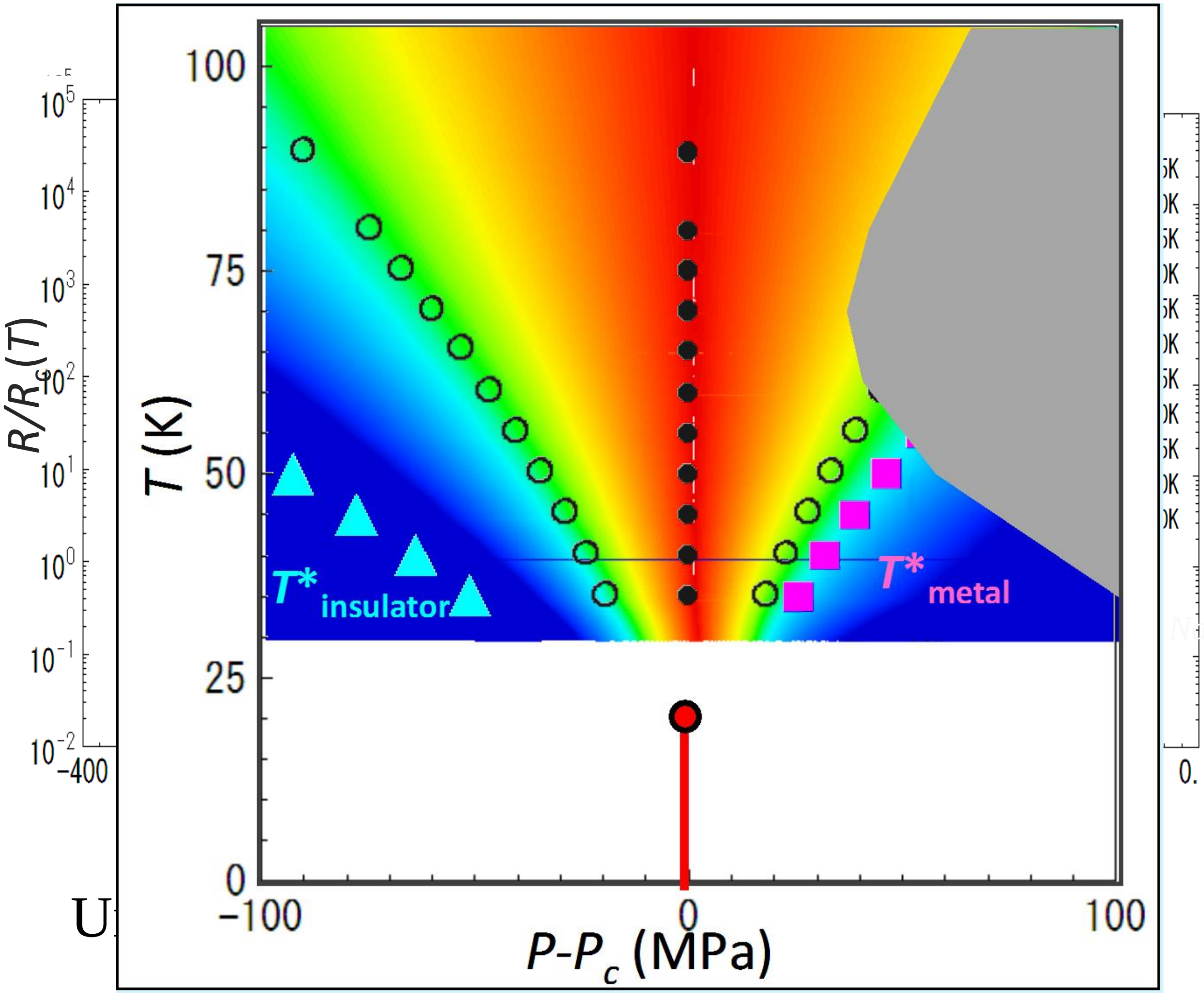


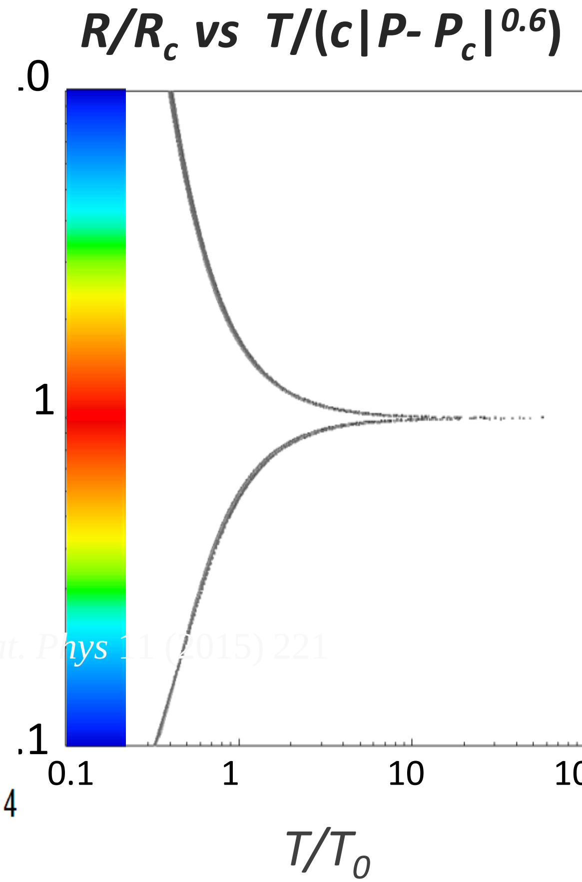
resistivity



Experimental test of scaling

Furukawa et al., *Nat. Phys* 11 (2015) 221

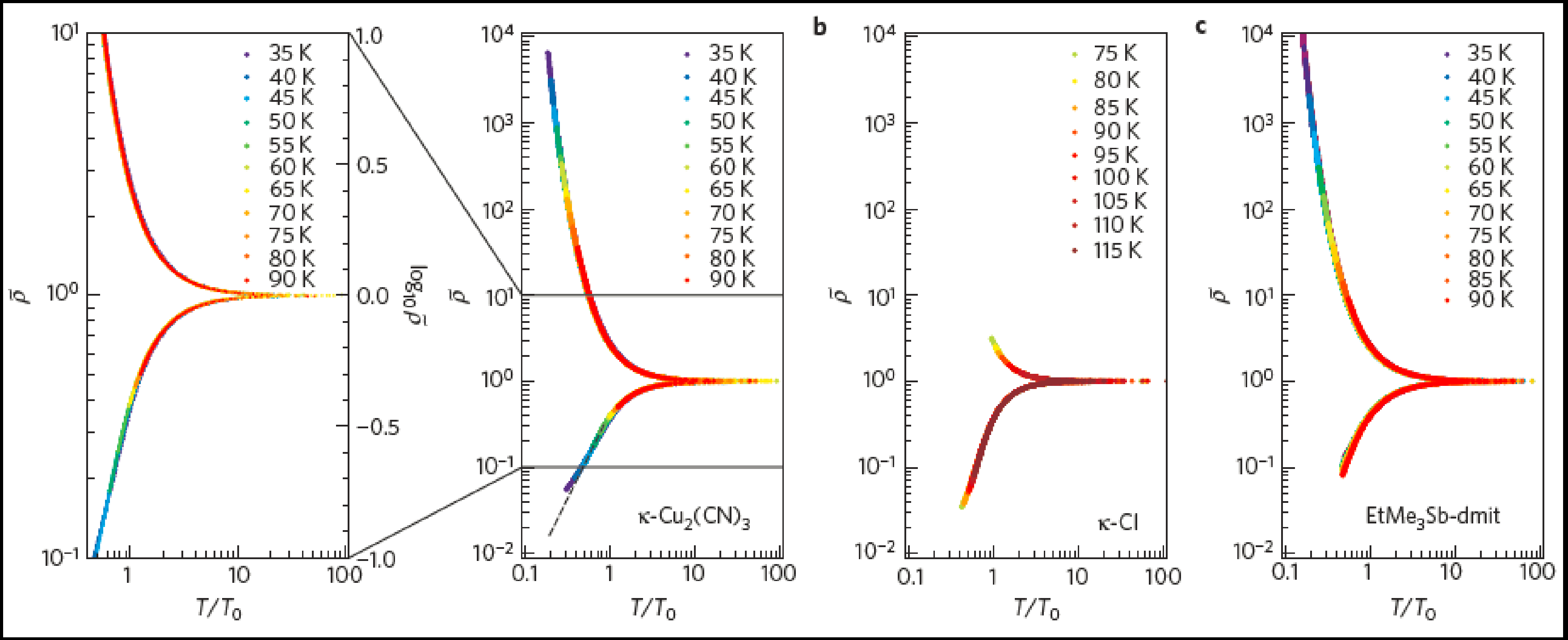




Perfect scaling for $T > 1.5T_c$

QC scaling --- nearly material -independent

Furukawa et al., Nat. Phys 11 (2015) 221



κ-(ET)$_2$Cu$_2$(CN)$_3$

SL/SC

$z\nu$=0.62±0.02

κ-(ET)$_2$Cu[N(CN)$_2$]Cl

AFI/SC

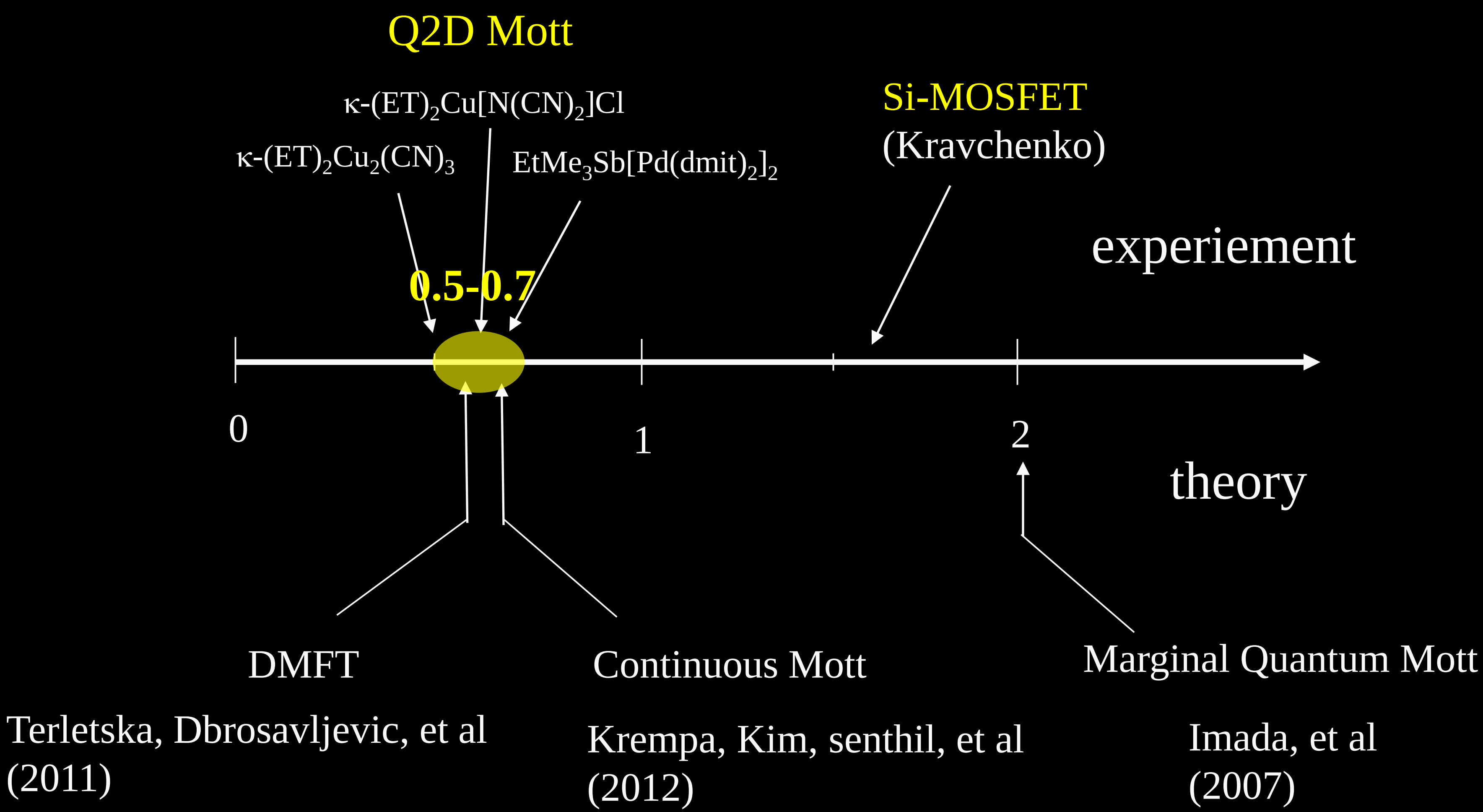
$z\nu$=0.49±0.01

EtMe$_3$Sb[Pd(dmit)$_2$]$_2$

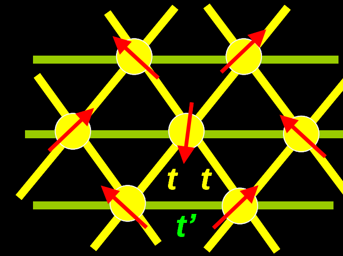
SL/Metal

$z\nu$=0.68±0.04

Critical exponents, zν, in metal-insulator transitions

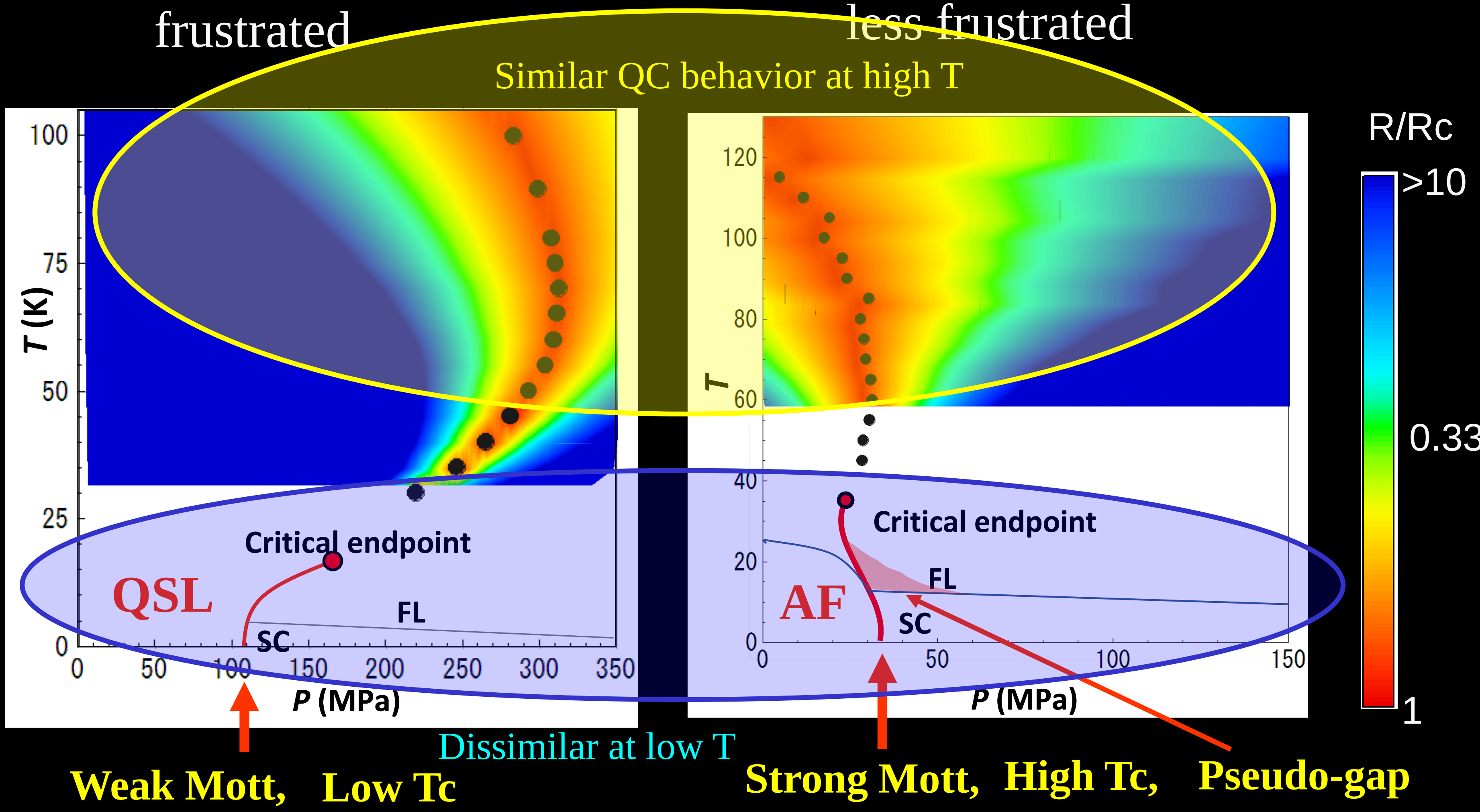


Mott phase diagrams of quasi-triangular lattices



κ-$(ET)_2Cu_2(CN)_3$
t'/t=0.80-1.0
frustrated

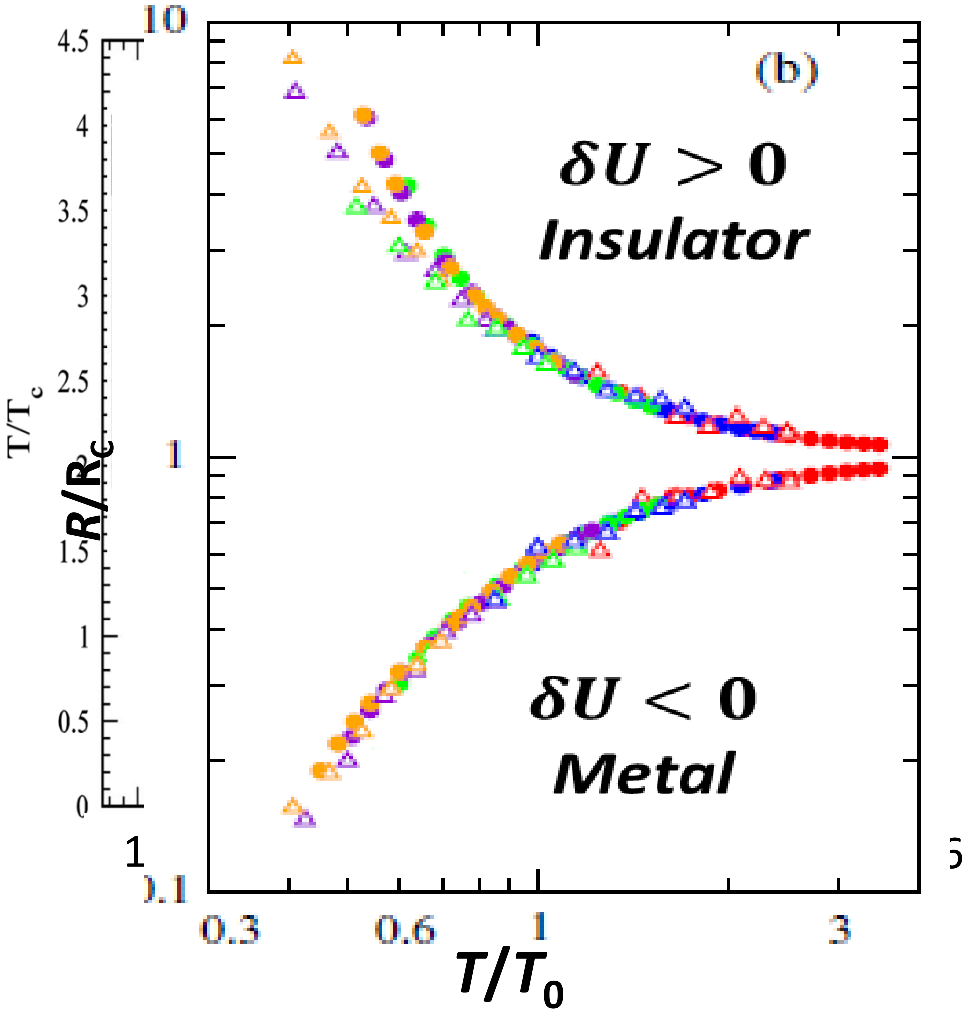
κ-$(ET)_2Cu[N(CN)_2]Cl$
t'/t=0.44-0.75
less frustrated



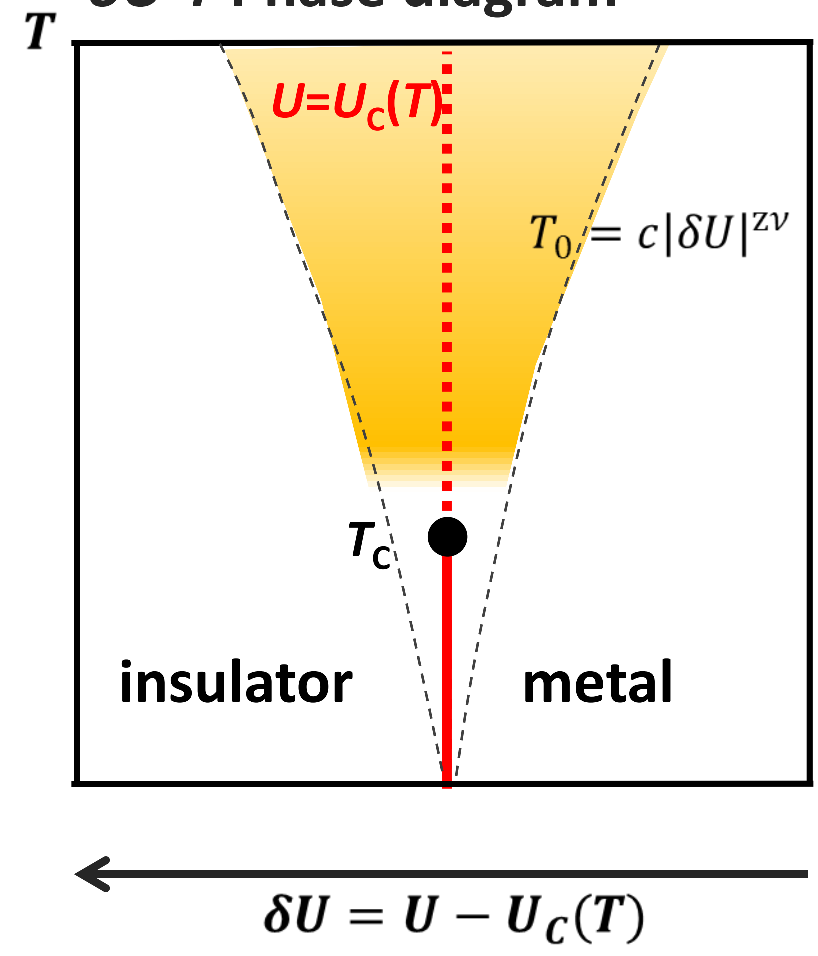
Single-site DMFT of Hubbard model

H.Terletska , V.Dobrosavljevic *et al.,Phys. Rev. Lett* **107**, 026401(2011)

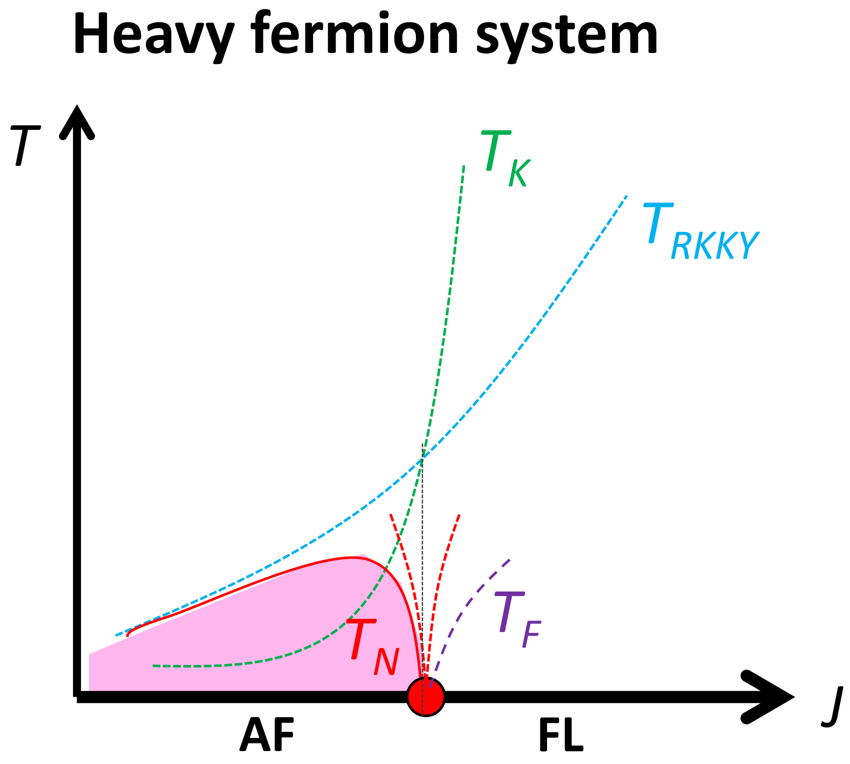
U-T Phase diagram

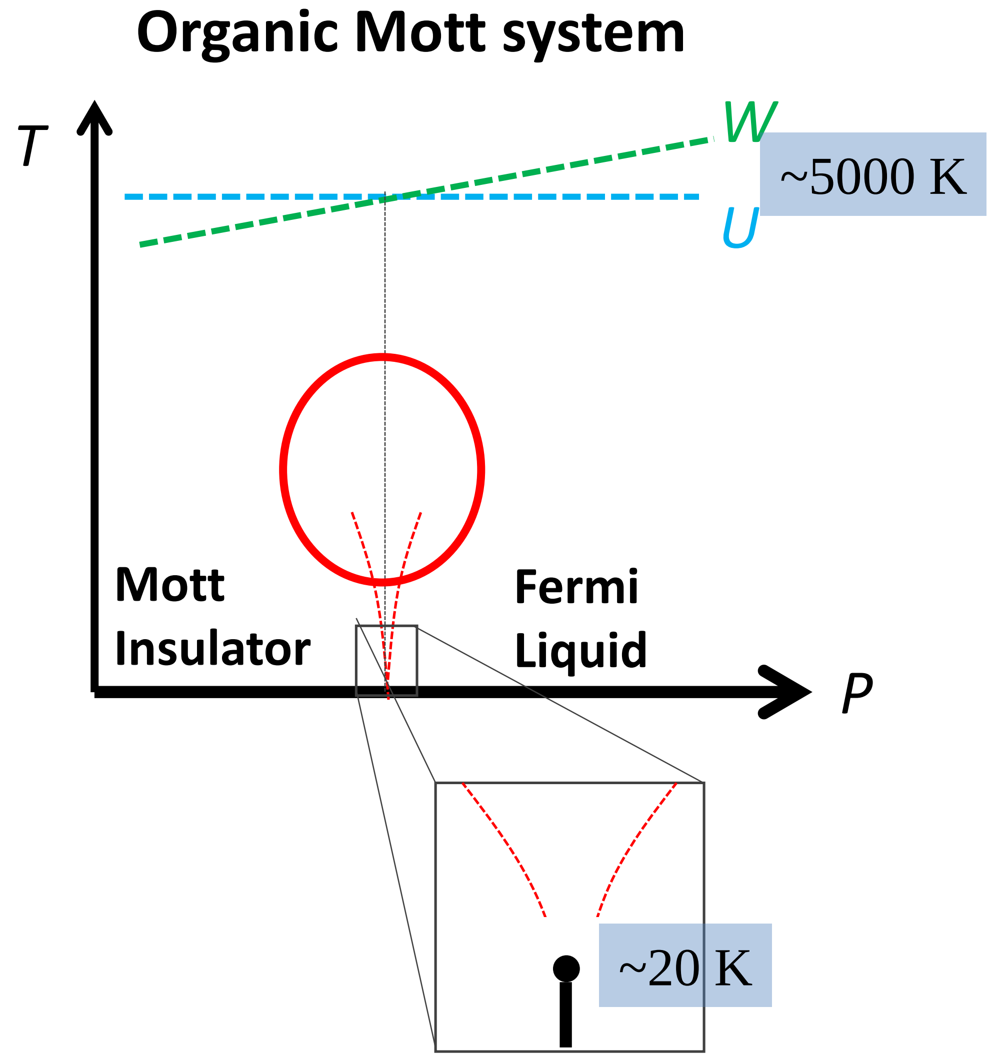


δU-T **Phase diagram**



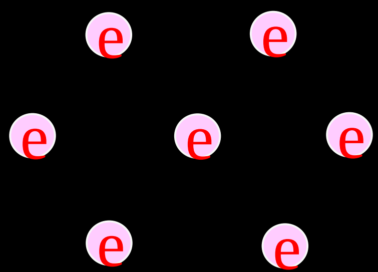
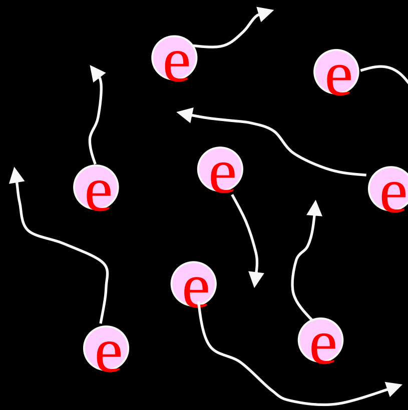
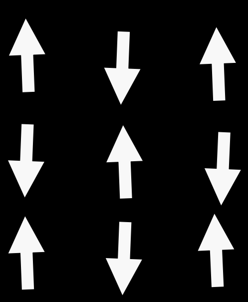
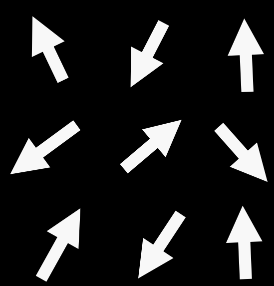
Possible quantum critical behavior in an intermediate energy range





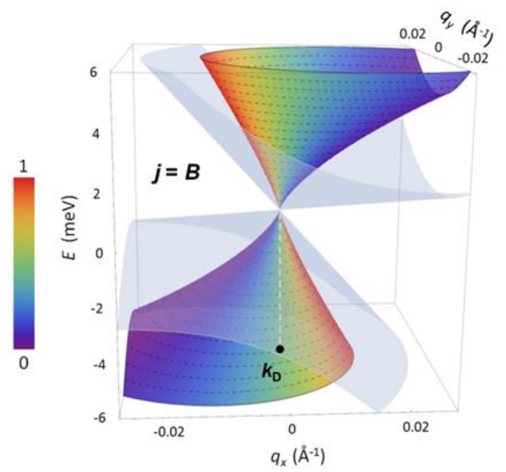
Quantum criticality ($T_c <\ T << t,U$)

Why eager for spin liquid ?

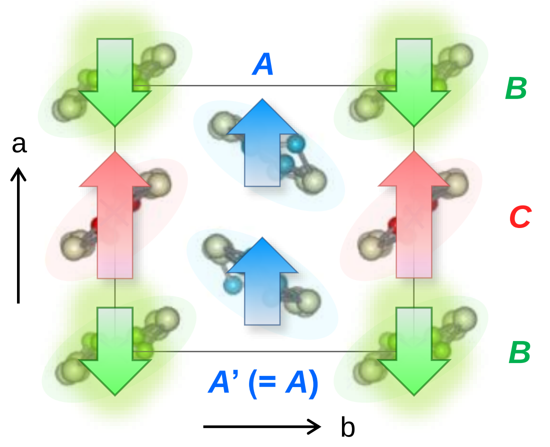
	Classical	**Quantum**	**And more**
electron	 Wigner Xtal	 Fermi liquid	superconductivity electronics …… …..
spin	 Magnet	 Quatum spin liquid	

Electron correlation in massless Dirac fermions

Dirac cone reshaping



Ferrimagnetism



M. Hirata *et al*., Nat. Commun. (2016) in press
D. Liu *et al*., PRL (2016)
K. Miyagawa *et al*., JPSJ (2016)
K. Ishikawa *et al*., PRB (2016)

NMR

Michihiro Hirata

NMR

Kyohei Ishikawa

東京大学
THE UNIVERSITY OF TOKYO

NMR

Kazuya Miyagawa

Sample preparation

Masafumi Tamura

TOKYO UNIVERSITY OF SCIENCE since 1881

NMR

Claude Berthier

LNCMI

cnrs

RG calculation (continuum model)

Denis Basko

LPMMC laboratoire de physique et de modélisation des milieux condensés

Université Joseph Fourier GRENOBLE

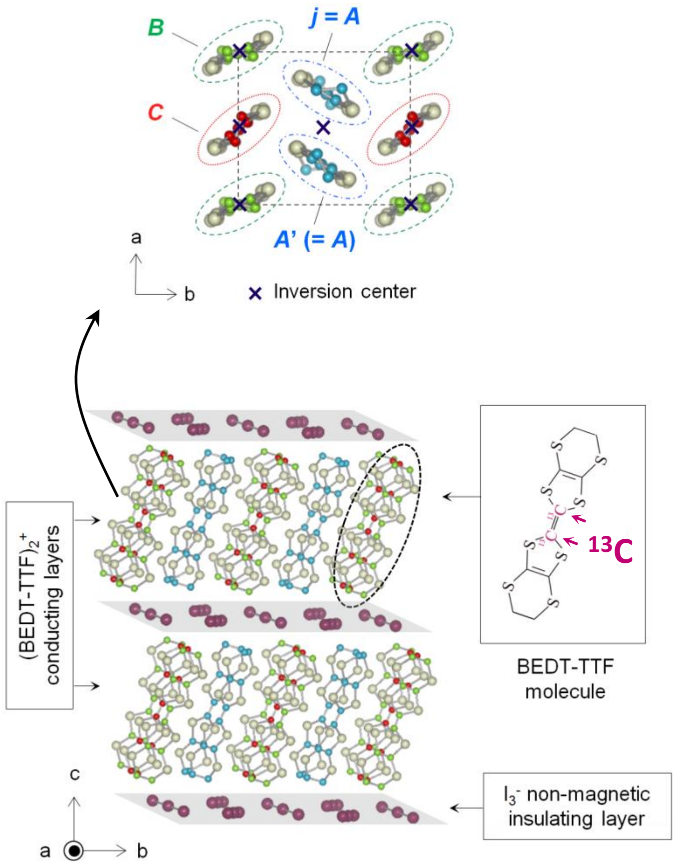
Mean-field calculation (lattice model)

Akito Kobayashi

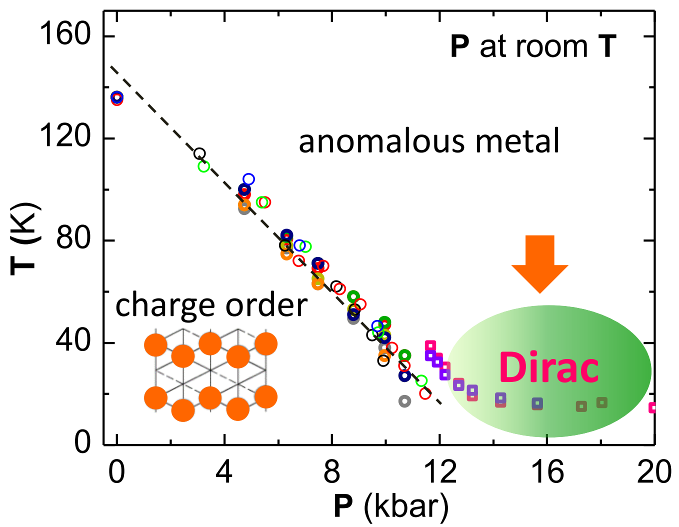
Genki Matsuno

名古屋大学
NAGOYA UNIVERSITY

Organic Conductor α-$(BEDT\text{-}TTF)_2I_3$



Phae diagram

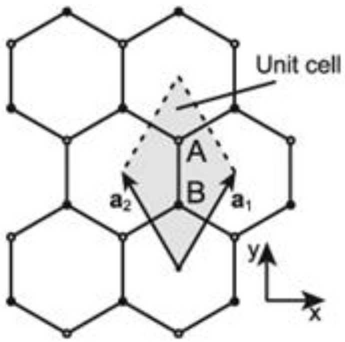


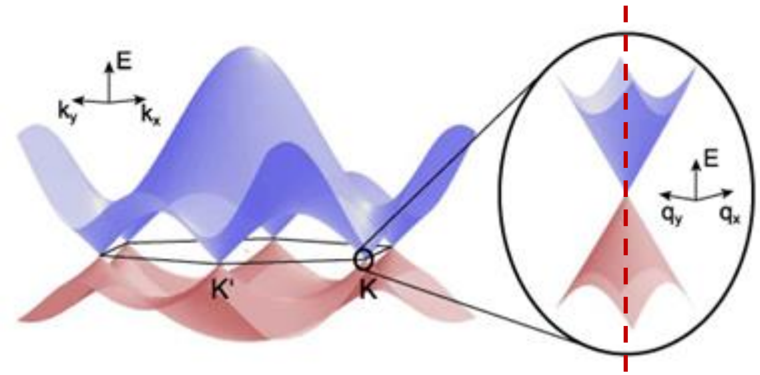
D. Liu *et al.*, PRL, in press
H. Schwenk *et al.*, *Mol. Cryst. Liq. Cryst.* **119** (1985)

Charge order is suppressed by pressure and a Dirac semimetal emerges !

1. Dirac Cones Everywhere

◆ **Vertical cone in Graphene ← Atomic Orbs. (A & B sublat.)**



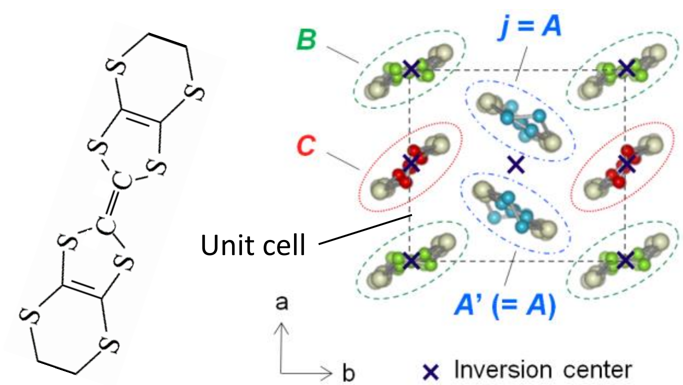


General cones exist in various systems: d-wave SC, ^{3}He, Topological Ins., ***Organic Solids***

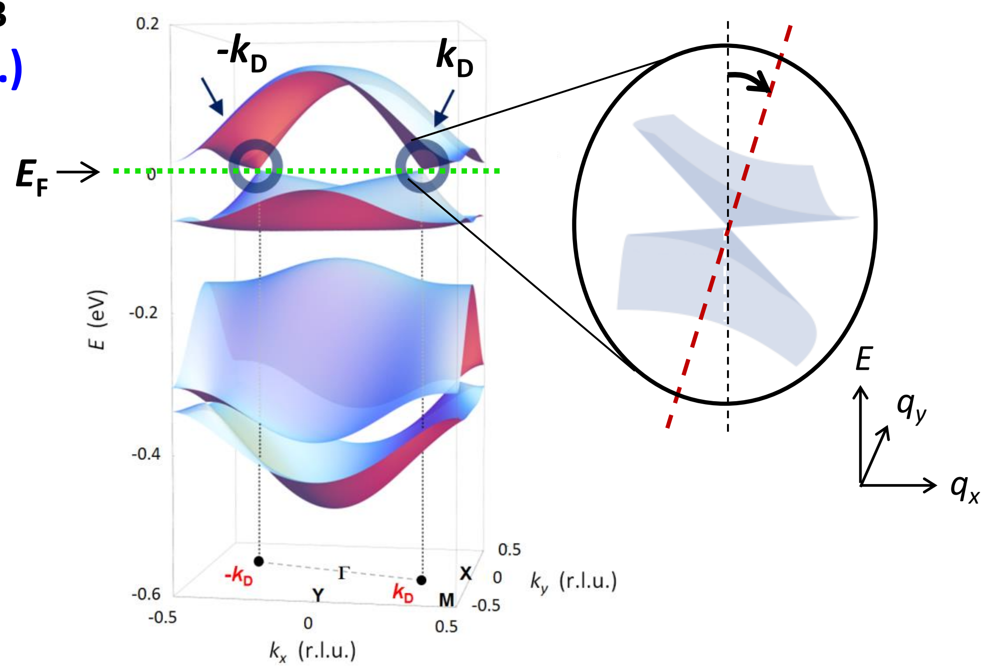
K. Asano et al., *PRB* (2011), T. O. Wehling *et al.*, Adv. Phys. (2014)

◆ ***Titled*** **cone in α-(BEDT-TTF)$_2$I$_3$**

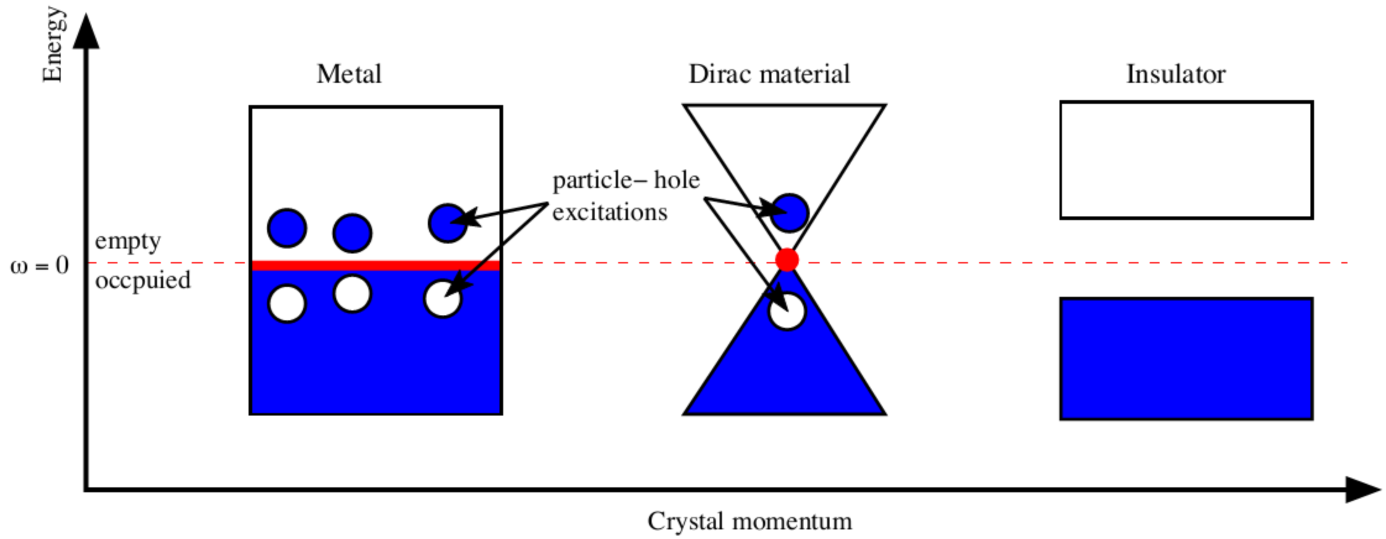
← Molecular Orbs. (A, A', B, C sublat.)



S. Katayama *et al., Eur. Phys. J. B* **67** (2009)
M.O. Goerbig *et al., PRB* **78** (2008)
K. Kajita *et al., JPSJ* **83** (2014)



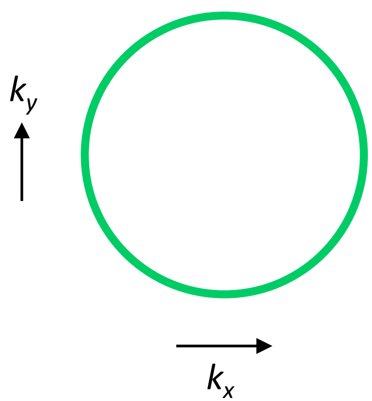
2. Short-ranged or Long-ranged?



Fermi surface

Fermi point

Gapped



Unscreened →

Coulomb interaction is Short-ranged ***Long-ranged***

T. O. Wehling *et al.*, Adv. Phys. **63**, 1-76 (2014)

Unscreened Long-range Coulomb Interaction

SOVIET PHYSICS JETP VOLUME 32, NUMBER 4 APRIL, 1971

POSSIBLE EXISTENCE OF SUBSTANCES INTERMEDIATE BETWEEN METALS AND DIELECTRICS

A. A. ABRIKOSOV and S. D. BENESLAVSKIĬ

L. D. Landau Institute of Theoretical Physics

Submitted April 13, 1970

Zh. Eksp. Teor. Fiz. 59, 1280–1298 (October, 1970)

The question of the possible existence of substances having an electron spectrum without any energy gap and, at the same time, not possessing a Fermi surface is investigated. First of all the question of the possibility of contact of the conduction band and the valence band at a single point is investigated within the framework of the one-electron problem. It is shown that the symmetry conditions for the crystal admit of such a possibility. A complete investigation is carried out for points in reciprocal lattice space with a little group which is equivalent to a point group, and an example of a more complicated little group is considered. It is shown that in the neighborhood of the point of contact the spectrum may be linear as well as quadratic.

The role of the Coulomb interaction is considered for both types of spectra. In the case of a linear dispersion law a slowly varying (logarithmic) factor appears in the spectrum. In the case of a quadratic spectrum the effective interaction becomes strong for small momenta, and the concept of the one-particle spectrum turns out to be inapplicable. The behavior of the Green's functions is determined by similarity laws analogous to those obtained in field theory with strong coupling and in the neighborhood of a phase transition point of the second kind (scaling). Hence follow power laws for the electronic heat capacity and for the momentum distribution of the electrons.

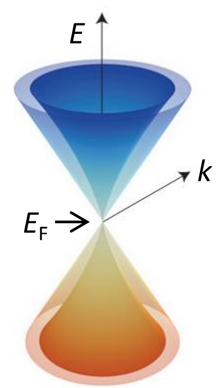
- ✓ Long-range part preserved
- ✓ **Logarithmic *divergence* of v_F**

$$v(k) = v\left(1 + \frac{\alpha}{4}\ln(\Lambda/k)\right), \quad \Lambda/k \gg 1$$

A. A. Abrikosov *et al.*, *JETP* **32** (1971)

A. A. Abrikosov

- Reshaping of *vertical* axes cones in graphene



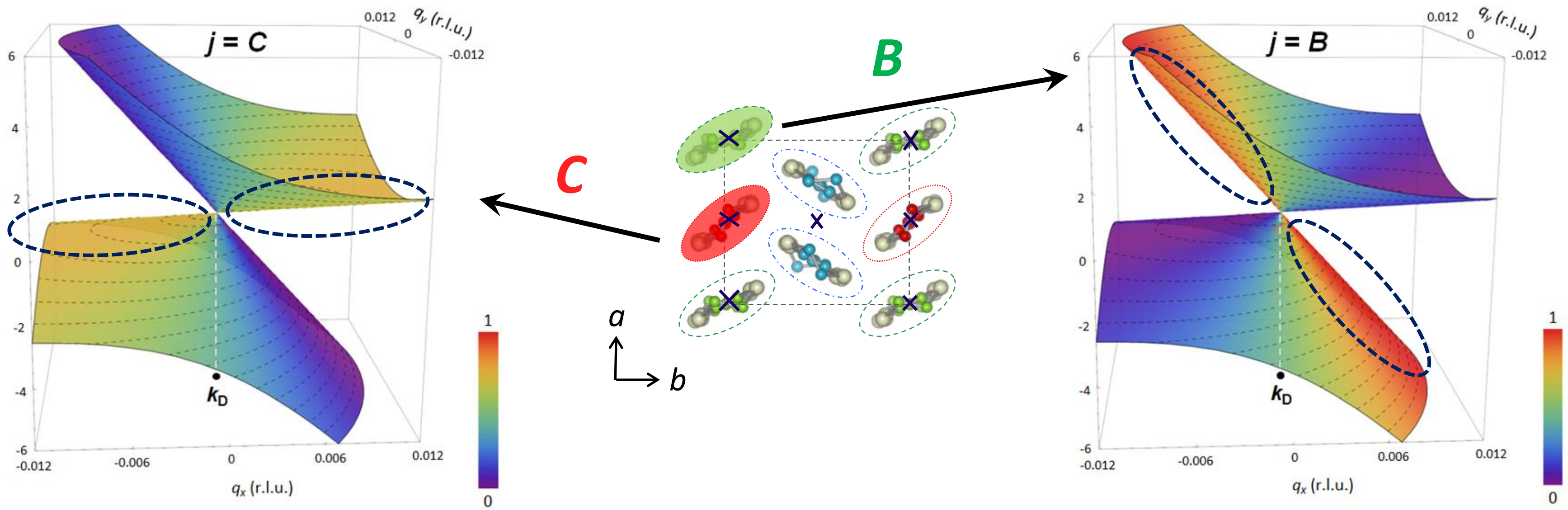
D. C. Elias *et al.*, *Nat. Phys.* **7** (2011)
C. Faugeras *et al.*, *PRL* **114** (2015)
V. N. Kotov *et al.*, *Rev. Mod. Phys.* ***84*** (2012)

Molecular site to *k*-space correspondence

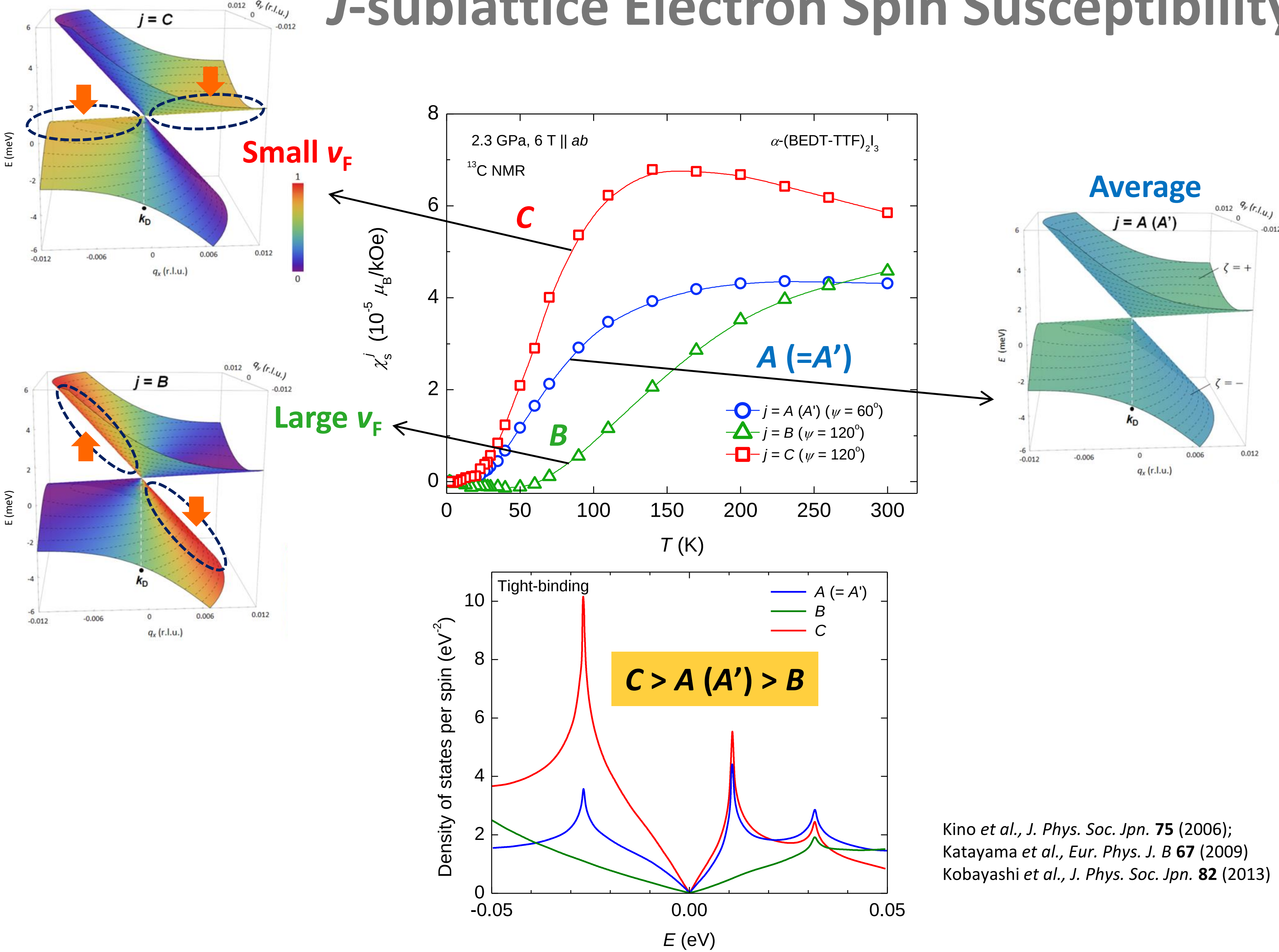
S. Katayama *et al.*, *Eur. Phys. J. B* **67** (2009)

Gentle slope (Small v_F)

Steep slope (Large v_F)

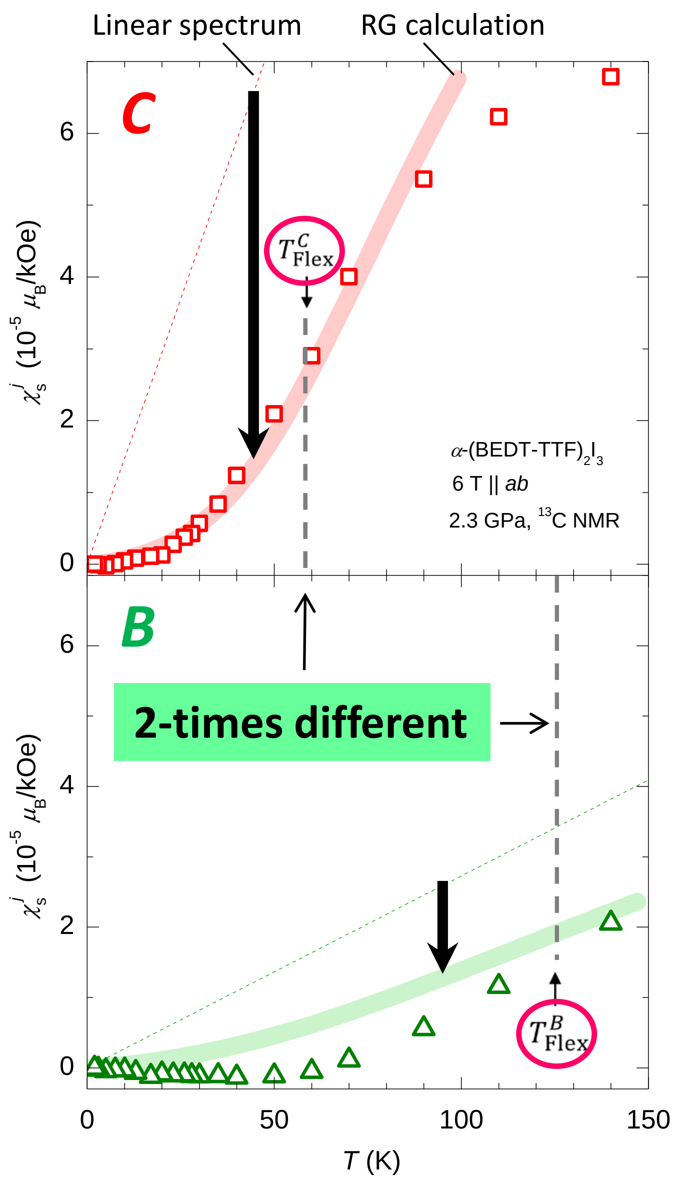


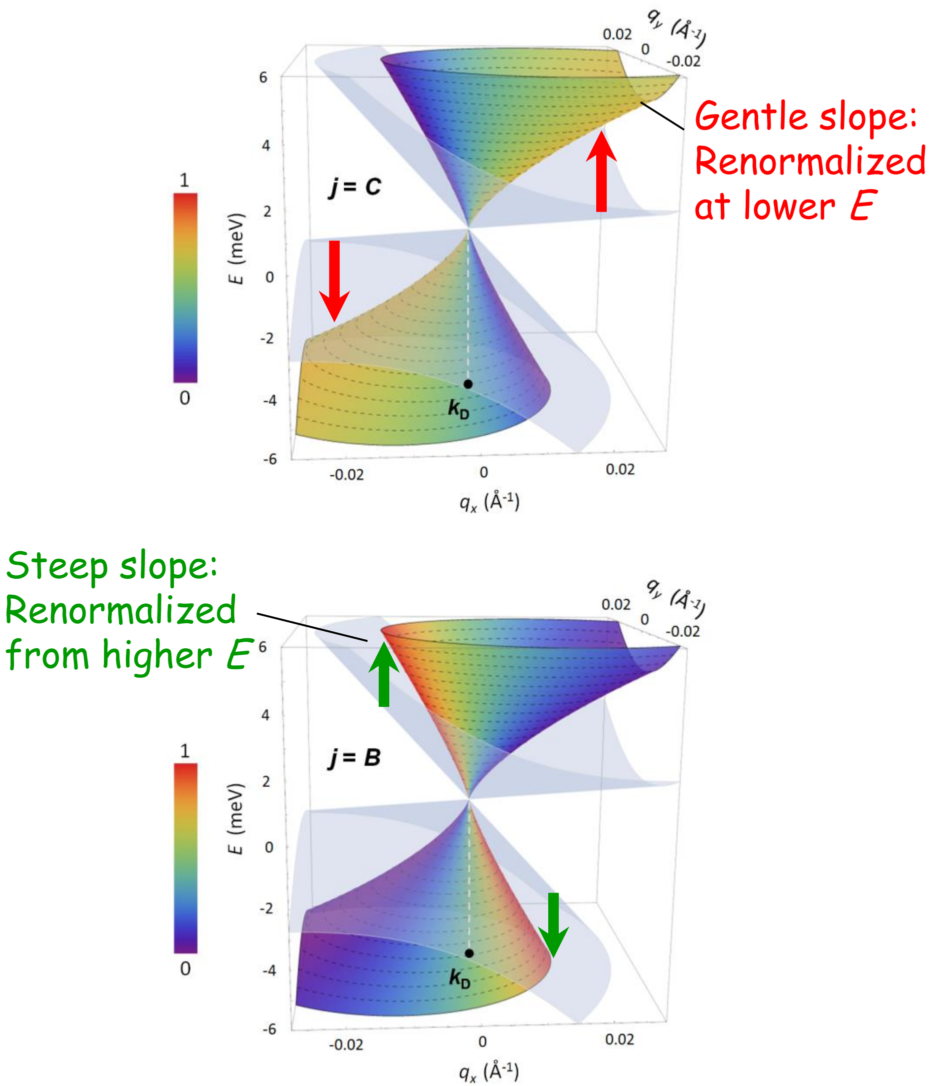
J-sublattice Electron Spin Susceptibility



Kino *et al.*, *J. Phys. Soc. Jpn.* **75** (2006);
Katayama *et al.*, *Eur. Phys. J. B* **67** (2009)
Kobayashi *et al.*, *J. Phys. Soc. Jpn.* **82** (2013)

A Non-uniform v_F Renormalization





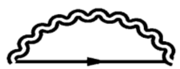
Renormalization Group (RG) Calculation

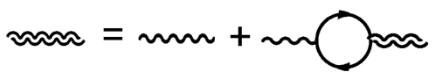
Anisotropic tilted cone

$$E_\zeta(\boldsymbol{q}) = \hbar\left(\boldsymbol{w}_0\cdot\boldsymbol{q} + \zeta\sqrt{v_x{}^2 q_x{}^2 + v_y{}^2 q_y{}^2}\right)$$

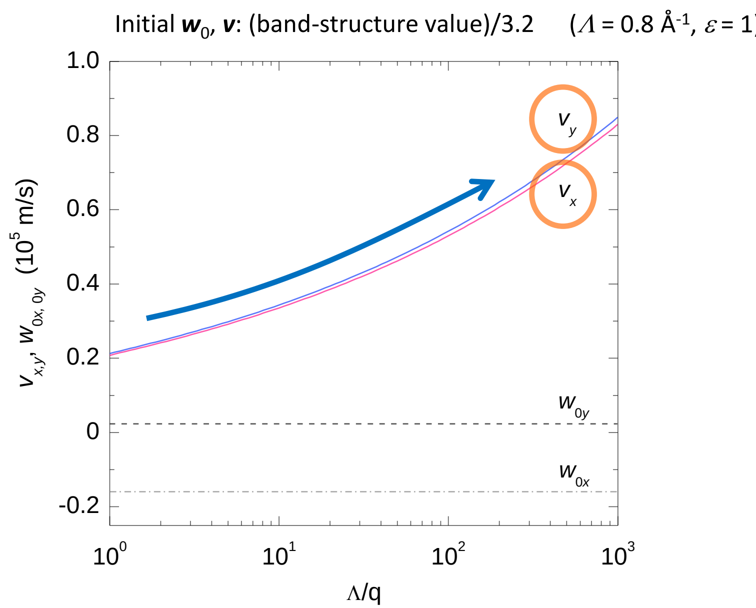
S. Katayama *et al.*, *Eur. Phys. J. B* **67** (2009)

RPA self energy





(cf. H. Isobe *et al.*, *J. Phys. Soc. Jpn.* **81** (2012): using HF exchange term )



RG equations (leading order in 1/*N*; *N* >> 1)

$$\frac{1}{v_x}\frac{dv_x}{dl} = \frac{8}{\pi^2 N}\int_0^{2\pi}\frac{d\varphi}{2\pi}2\cos^2\varphi\, F(g_\varphi)$$

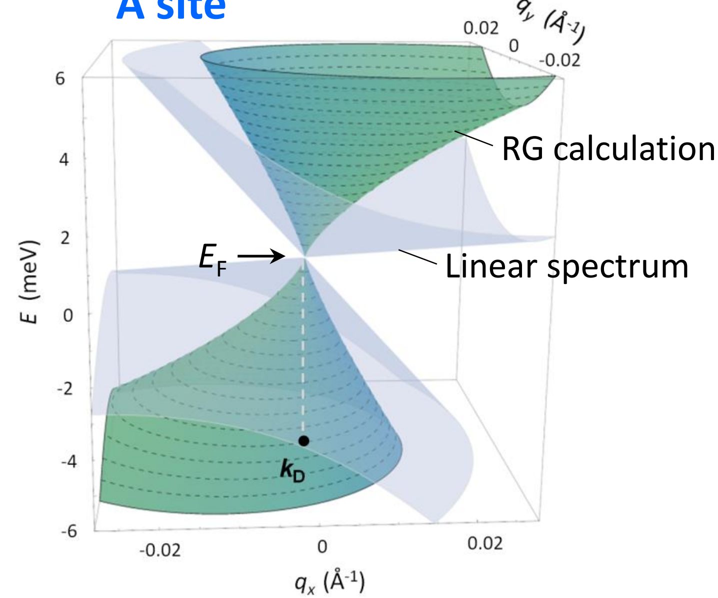
$$\frac{1}{v_y}\frac{dv_y}{dl} = \frac{8}{\pi^2 N}\int_0^{2\pi}\frac{d\varphi}{2\pi}2\sin^2\varphi\, F(g_\varphi)$$

N = 4: fermion flavor, $\boldsymbol{q} = (\boldsymbol{k} - \boldsymbol{k}_D) = q(\cos\varphi, \sin\varphi)$, $l = \ln(\Lambda/q)$

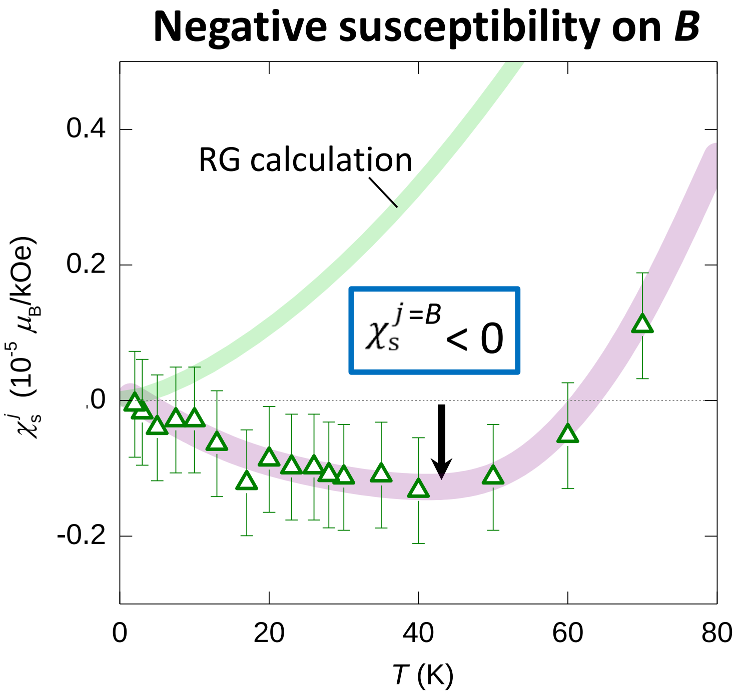
$$F(g_\varphi) = \left(-\pi/2 + g_\varphi + \arccos g_\varphi/\sqrt{1-g_\varphi{}^2}\right)/g_\varphi$$

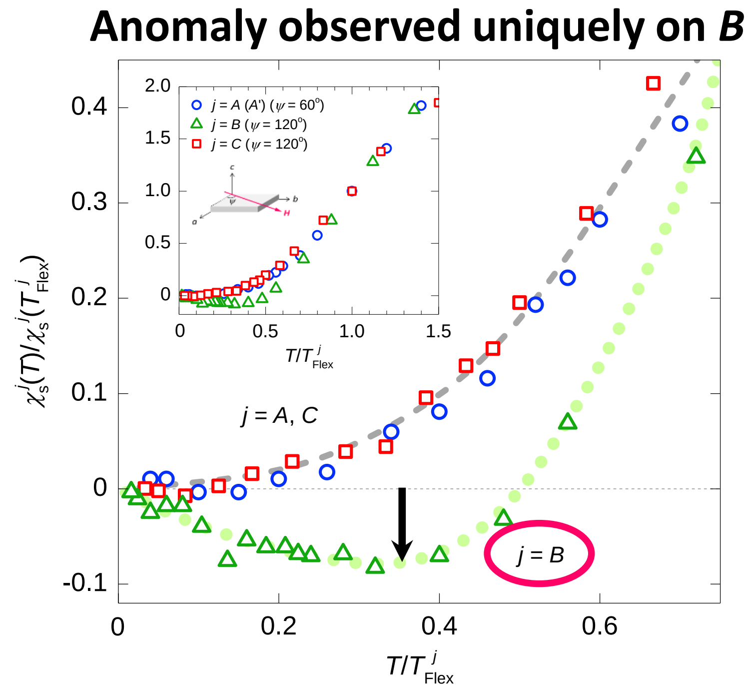
$$g_\varphi = 2\pi e^2 N/16\,\varepsilon\sqrt{v_x{}^2\sin^2\varphi + v_y{}^2\cos^2\varphi}$$

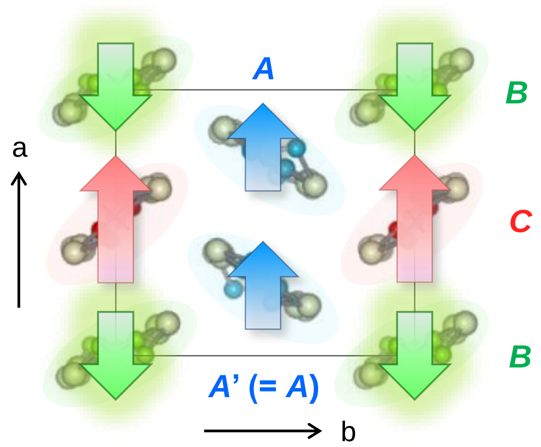
A site



Negative Susceptibility on the *B* Sublattice







Ferrimagnetic spin Polarization exist on top of the v_F renormalization

Hubbard model; Mean-field calculation

A. Kobayashi *et al.*, *J. Phys. Soc. Jpn.* **82** (2013)

Hubbard model (nearest neighbor)

$$H = \sum_{(i\alpha:j\beta),\sigma} \left(t_{i\alpha:j\beta}\, a^{\dagger}_{i\alpha\sigma} a_{j\beta\sigma} + \mathrm{h.c.}\right) + \sum_{j\alpha} U\, a^{\dagger}_{j\alpha\uparrow} a^{\dagger}_{j\alpha\downarrow} a_{j\alpha\downarrow} a_{j\alpha\uparrow}$$

$$\sum_{j=1}^{4} \tilde{\epsilon}_{ij\sigma}(\boldsymbol{k})\, d_{j\eta\sigma}(\boldsymbol{k}) = E_{\eta\sigma}(\boldsymbol{k})\, d_{i\eta\sigma}(\boldsymbol{k}),$$

$$\tilde{\epsilon}_{ij\sigma}(\boldsymbol{k}) = \epsilon_{ij}(\boldsymbol{k}) + U \langle N_{i\sigma}\rangle \delta_{ij},$$

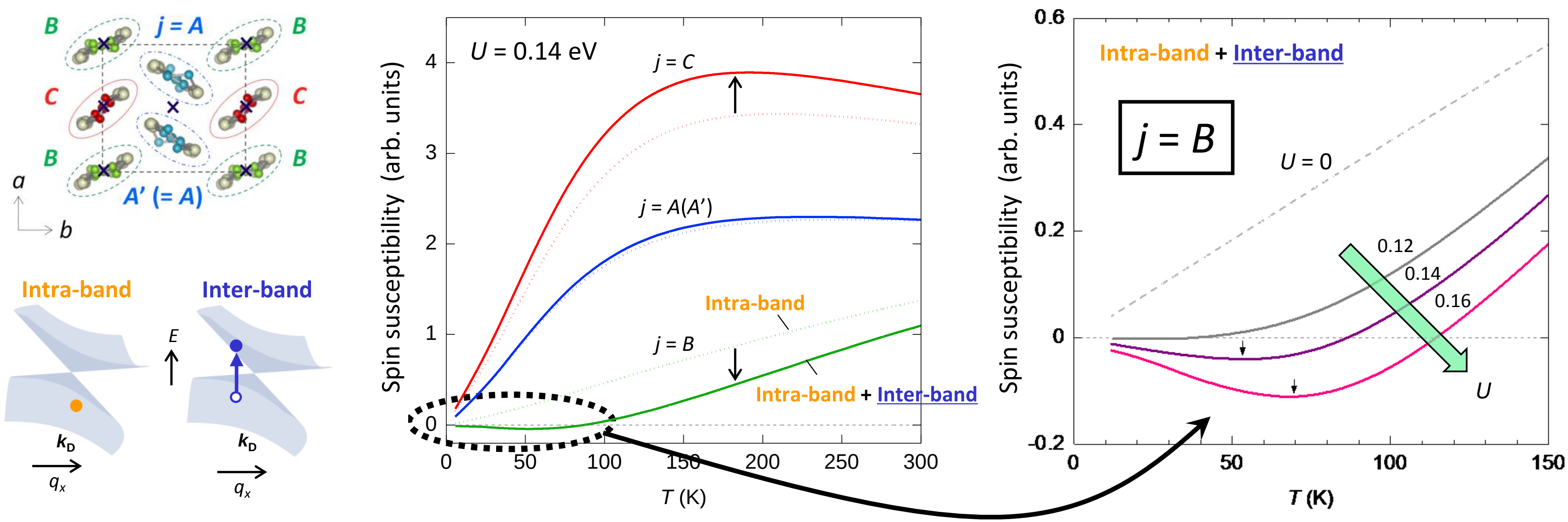
$$\langle N_{j\sigma}\rangle = \frac{1}{N_{\mathrm{u.c.}}} \sum_{\boldsymbol{k}} \sum_{\eta=1}^{4} d^{*}_{j\eta,-\sigma}(\boldsymbol{k})\, d_{j\eta,-\sigma}(\boldsymbol{k})\, f\left(E_{\eta,-\sigma}(\boldsymbol{k}) - \mu\right),$$

RPA spin susceptibility (Q = 0)

$$\chi_{ij,\,\mathrm{RPA}}(\boldsymbol{Q},\omega) = (\hat{\chi}_{\mathrm{RPA}})_{ij}(\boldsymbol{Q},\omega) = \left[\left(\hat{I} - \hat{\chi}^{(0)} U \hat{I}\right)^{-1} \hat{\chi}^{(0)}\right]_{ij} (\boldsymbol{Q},\omega),$$

$$\chi^{j}_{\mathrm{RPA}} = \sum_{i=1}^{4} \chi_{ij,\,\mathrm{RPA}}(\boldsymbol{0}, 0)$$

$$\chi^{(0)}_{ij}(\boldsymbol{Q},\omega) = -\frac{1}{N_{\mathrm{u.c.}}} \sum_{\boldsymbol{k}} \sum_{\eta,\eta'=1}^{4} \mathcal{F}^{\eta\eta'}_{ij}(\boldsymbol{k},\boldsymbol{Q}) \frac{f\left(E_{\eta}(\boldsymbol{k}+\boldsymbol{Q})\right) - f\left(E_{\eta'}(\boldsymbol{k})\right)}{E_{\eta}(\boldsymbol{k}+\boldsymbol{Q}) - E_{\eta'}(\boldsymbol{k}) - \hbar\omega - i\delta},$$



Hubbard model; Mean-field calculation

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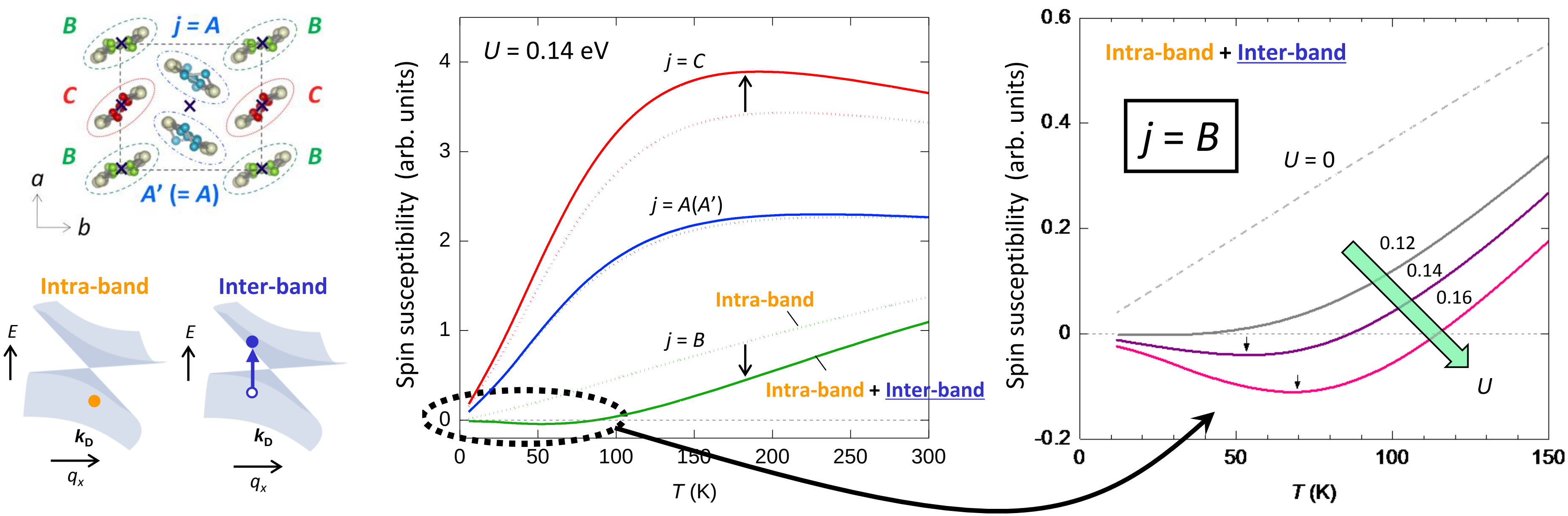
A. Kobayashi *et al.*, *J. Phys. Soc. Jpn.* **82** (2013)

$$\sum_{j=1}^{4} \tilde{\epsilon}_{ij\sigma}(\boldsymbol{k})\, d_{j\eta\sigma}(\boldsymbol{k}) = E_{\eta\sigma}(\boldsymbol{k})\, d_{i\eta\sigma}(\boldsymbol{k}),$$

$$\tilde{\epsilon}_{ij\sigma}(\boldsymbol{k}) = \epsilon_{ij}(\boldsymbol{k}) + U \langle N_{i\sigma}\rangle \delta_{ij},$$

$$\langle N_{j\sigma}\rangle = \frac{1}{N_{\mathrm{u.c.}}} \sum_{\boldsymbol{k}} \sum_{\eta=1}^{4} d^{*}_{j\eta,-\sigma}(\boldsymbol{k})\, d_{j\eta,-\sigma}(\boldsymbol{k})\, f\!\left(E_{\eta,-\sigma}(\boldsymbol{k}) - \mu\right),$$

Ferrimagnetic Polarization due to SR Coulomb Int.

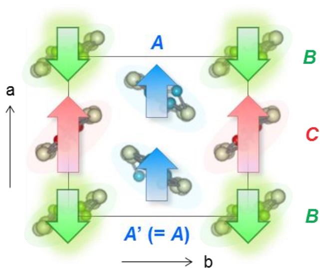


Conclusions

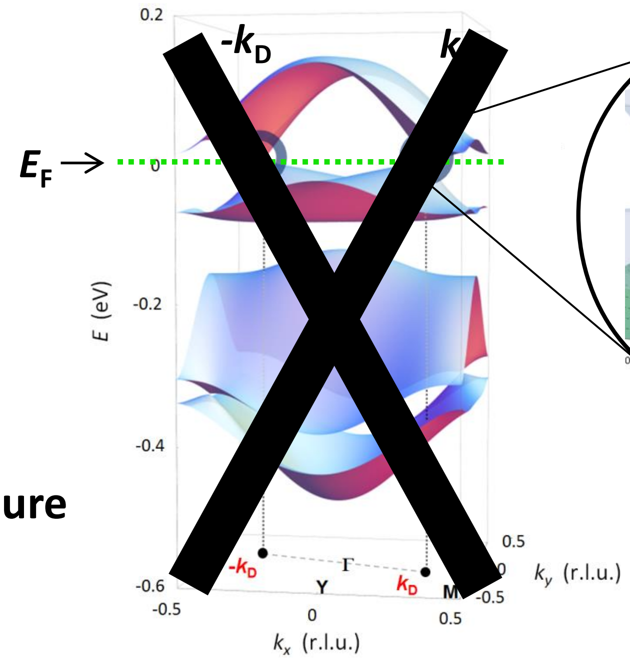
Short-range Coulomb, U, V

Long-range Coulomb, 1/r

Ferrimagnetism



Collapse of band structure into charge order state



Cone reshaping