

Quantum Criticality in Organic Conductors

Electrons at the edge of Classical and Quantum Worlds

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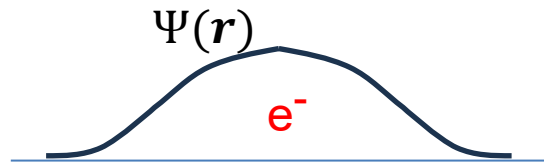
University of Tokyo

Quantum criticality ----- where does it appear ?

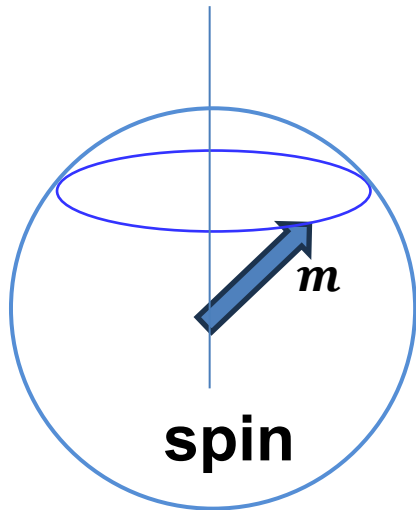
- Mott metal-insulator transition
- Quantum spin liquid (QSL)
- Superconductivity in doped QSL

Quantum particle

Uncertainty in position/direction

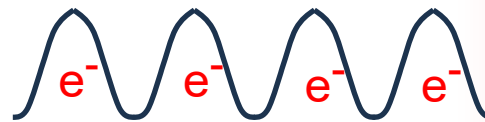


charge

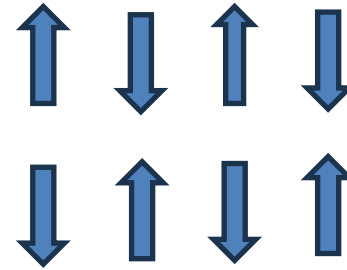


Interacting quantum particles

Renormalized classical

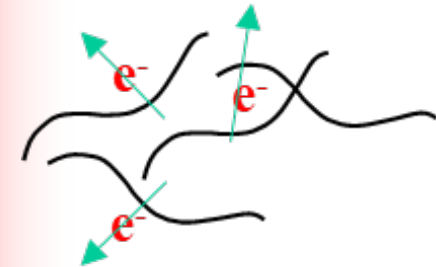


Insulator

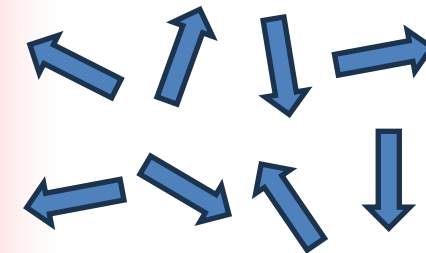


Magnet

Quantum critical



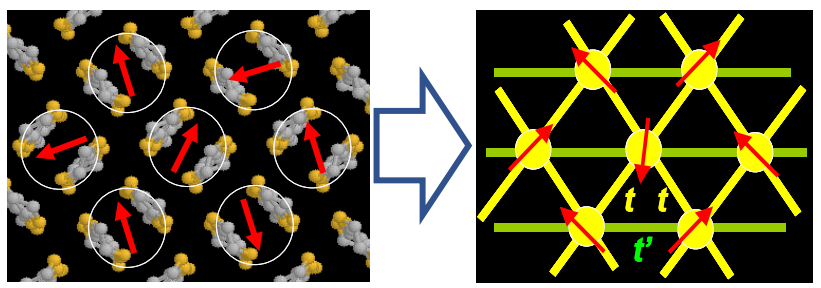
Fermi liquid (FL)



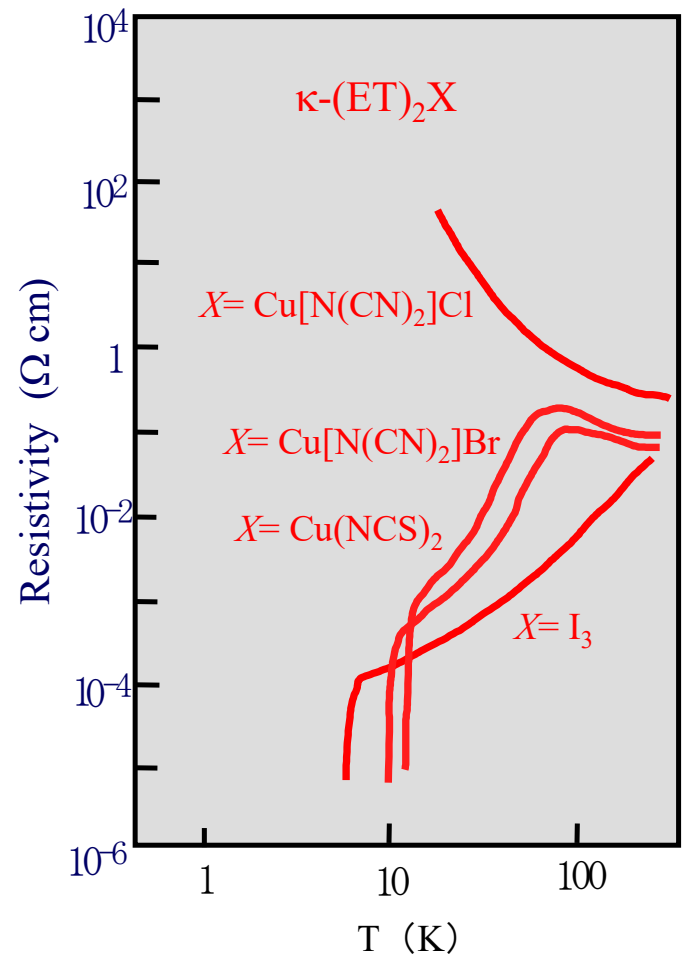
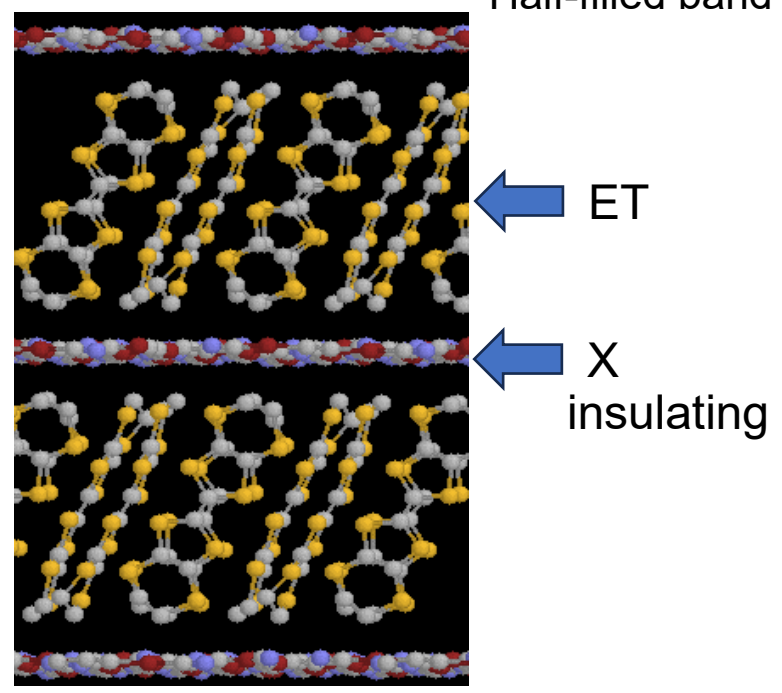
Quantum spin liquid (QSL)

Layered organic systems $\kappa\text{-(ET)}_2\text{X}$ with triangular lattices situated across the Mott transition

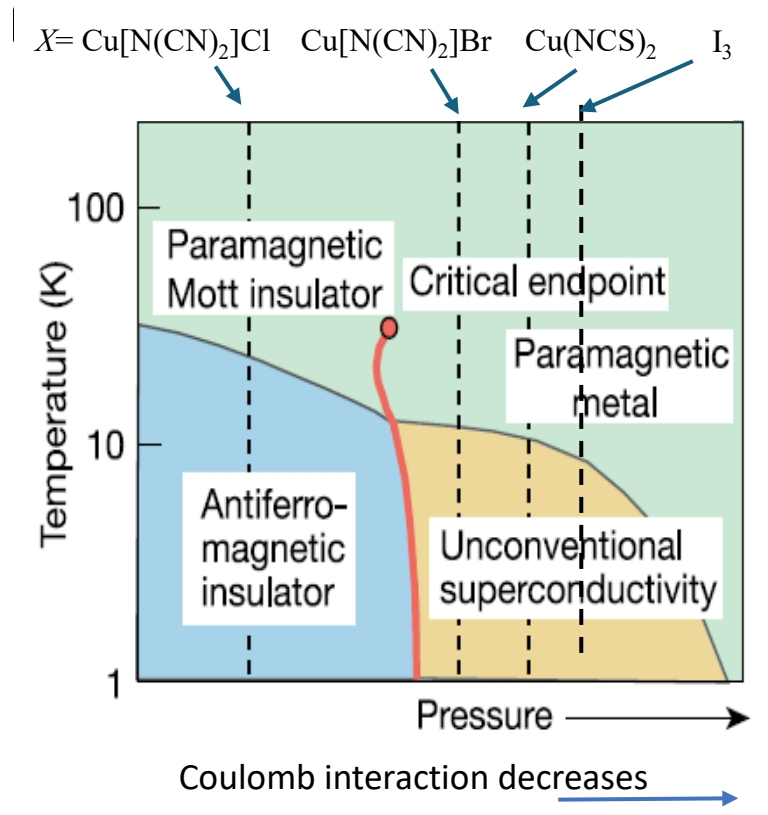
In-plane structure



Half-filled band



A. Kobayashi et al., Chem Lett. 16, 459 (1987).
 H. Urayama-Mori et al., Chem. Lett., 55 (1988).
 A. M. Kini et al, Inorg. Chem. 29, 2555 (1990).

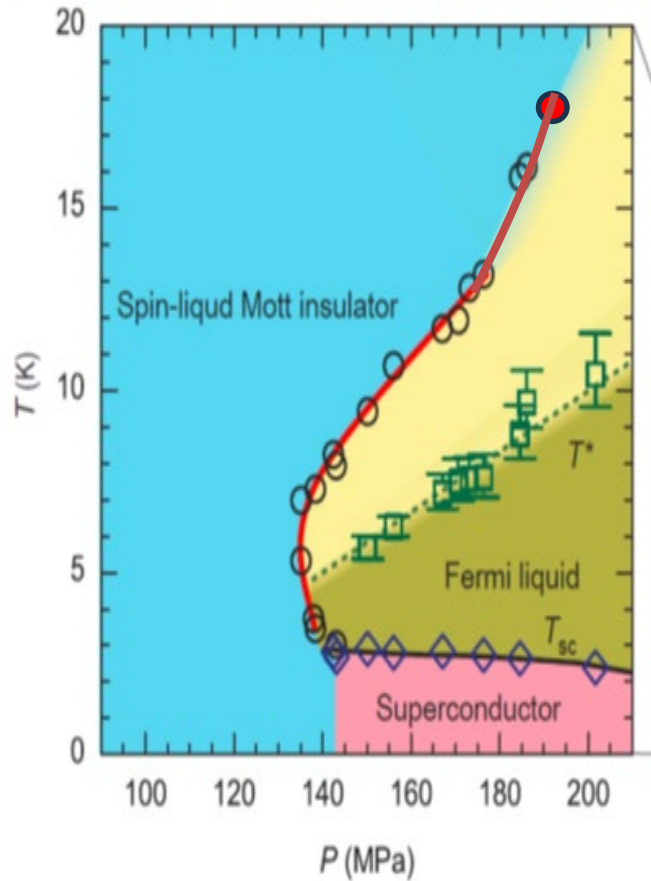


K. K. Solid State Physics (1995)
 Kagawa et al., Nature 436, 534 (2005)

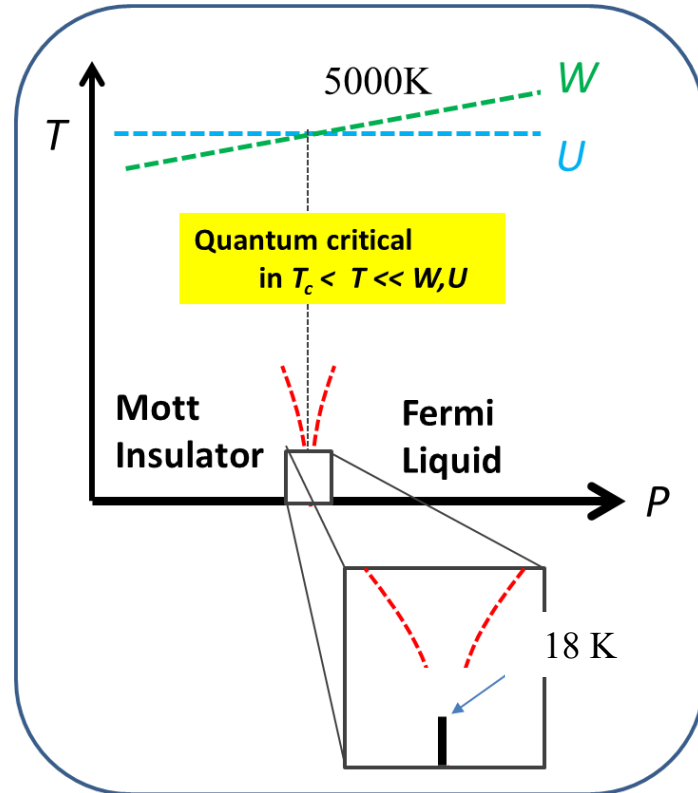
Mott quantum criticality for $T > T_c$?

Theoretical: Terletska et al., PRL107, 026401 (2011)

P-T phase diagram: $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$



Furukawa et al., Nat. Commun. 9, 307 (2018)

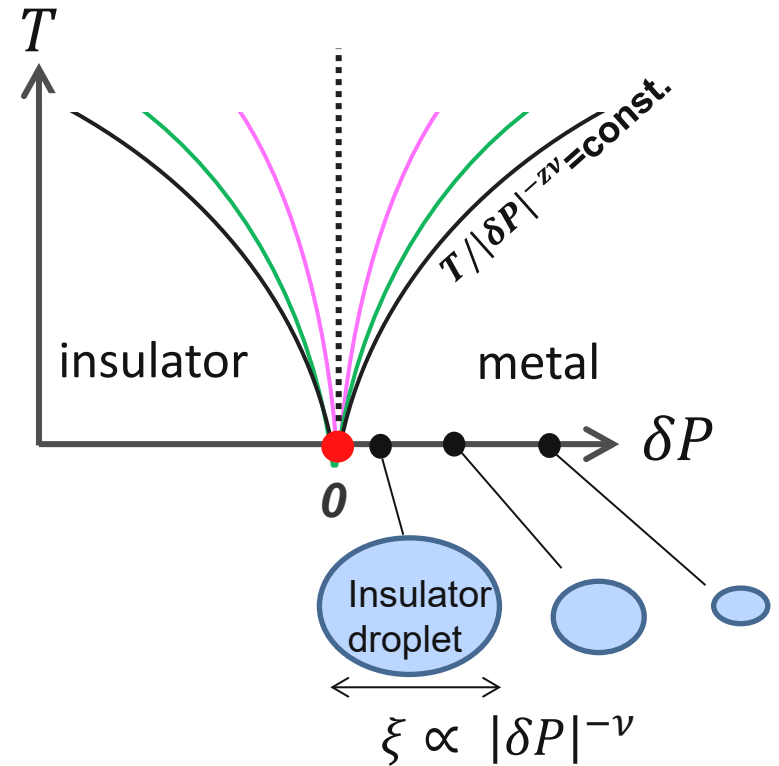


Quantum critical scaling

$$\rho(T, \delta P) / \rho(T, 0) = f(T / |\delta P|^{-z\nu})$$

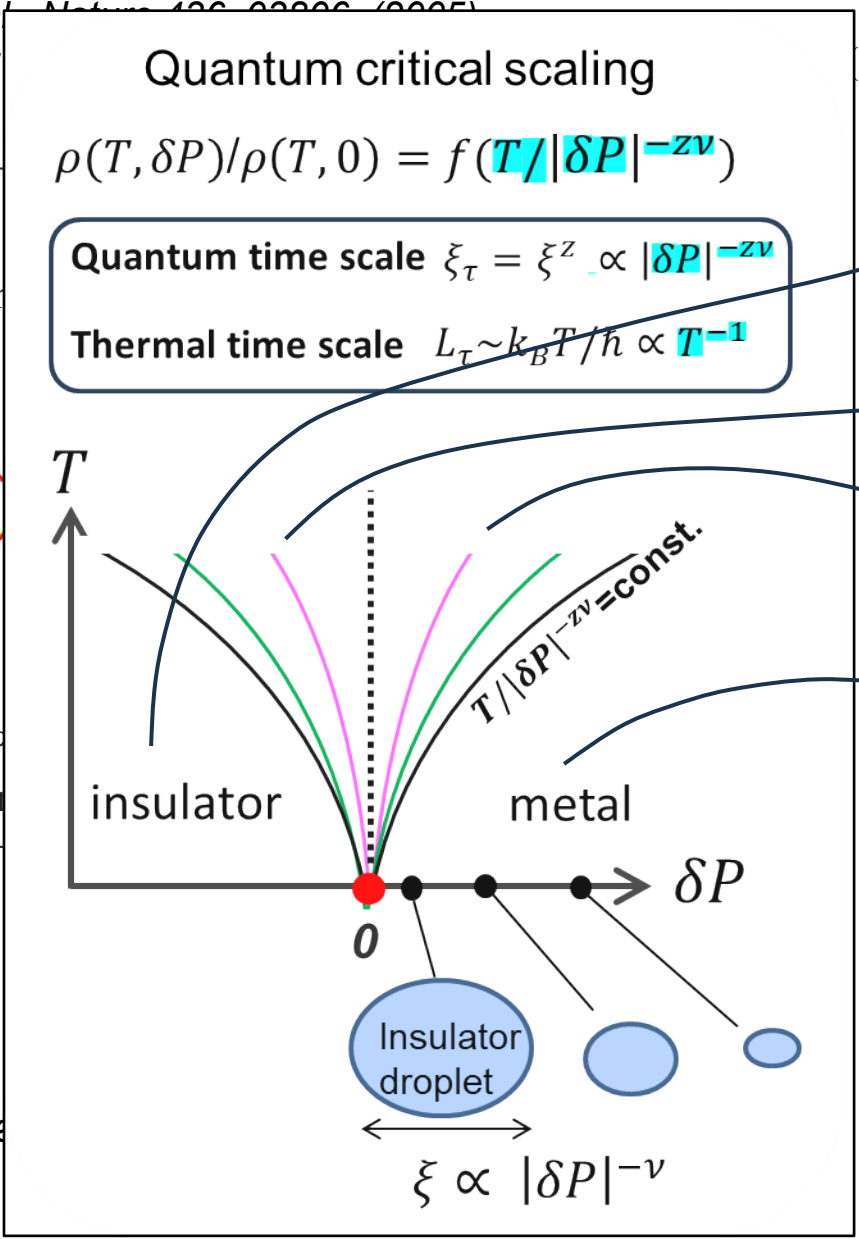
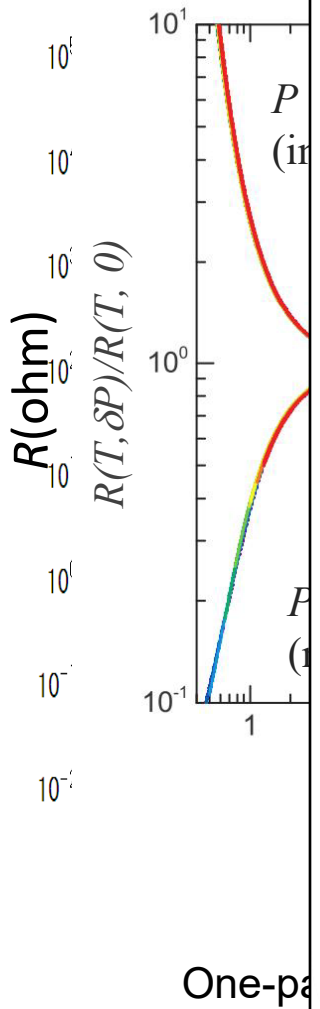
Quantum time scale $\xi_\tau = \xi^z \propto |\delta P|^{-z\nu}$

Thermal time scale $L_\tau \sim k_B T / \hbar \propto T^{-1}$

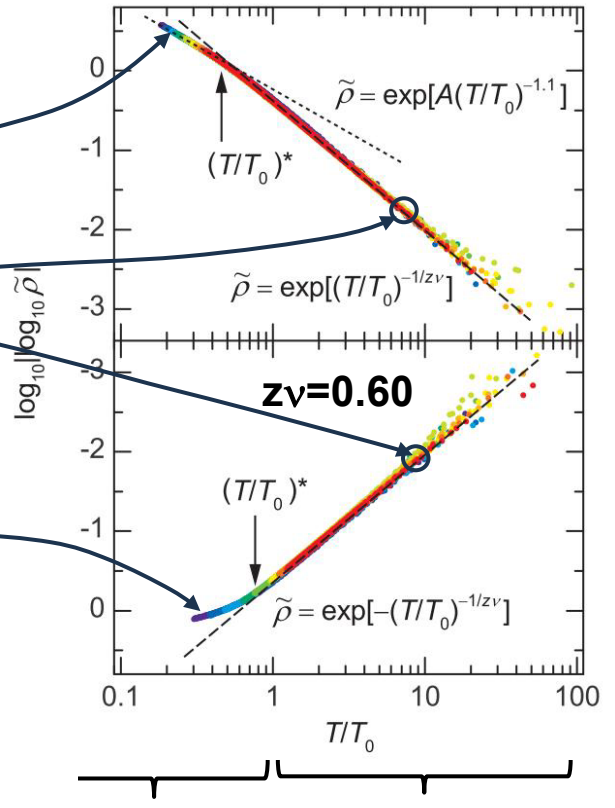


Experimental test of Mott quantum critical transport *with He-gas pressure*

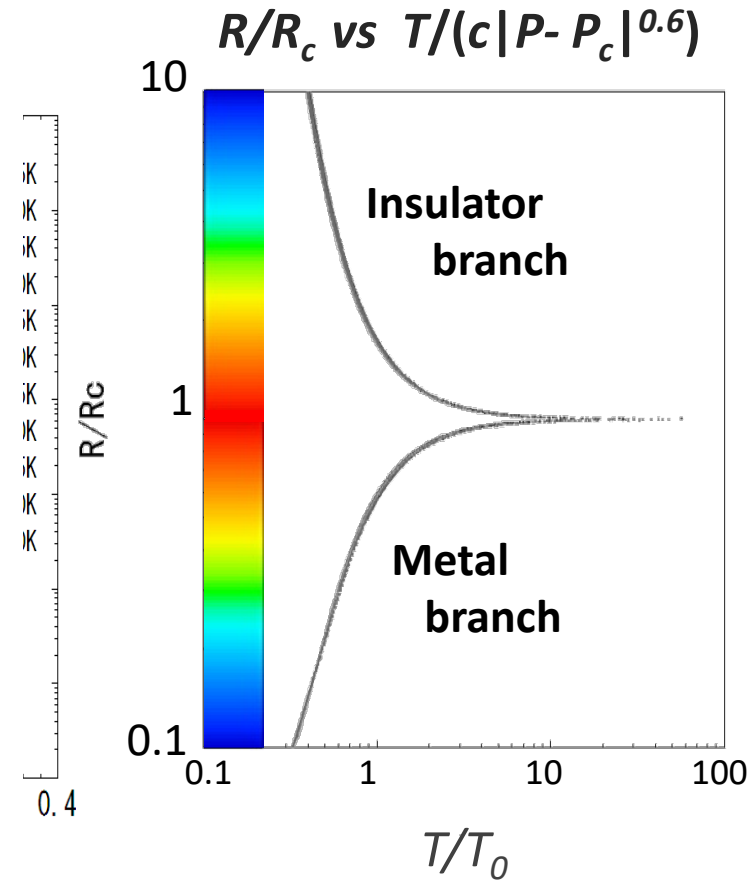
Kagawa et al. *Nature* 426, 668-671 (2003)
 Furukawa et al. *Science* 304, 1488-1491 (2004)



(2018)



Theoretical: Terletska et al., PRL107, 026401 (2011)



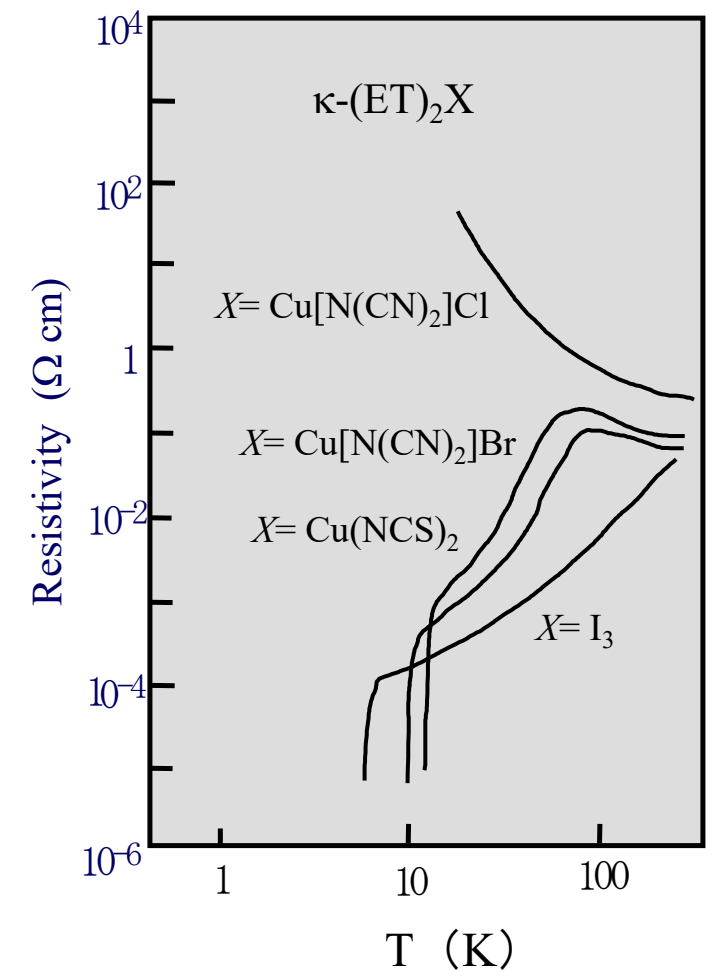
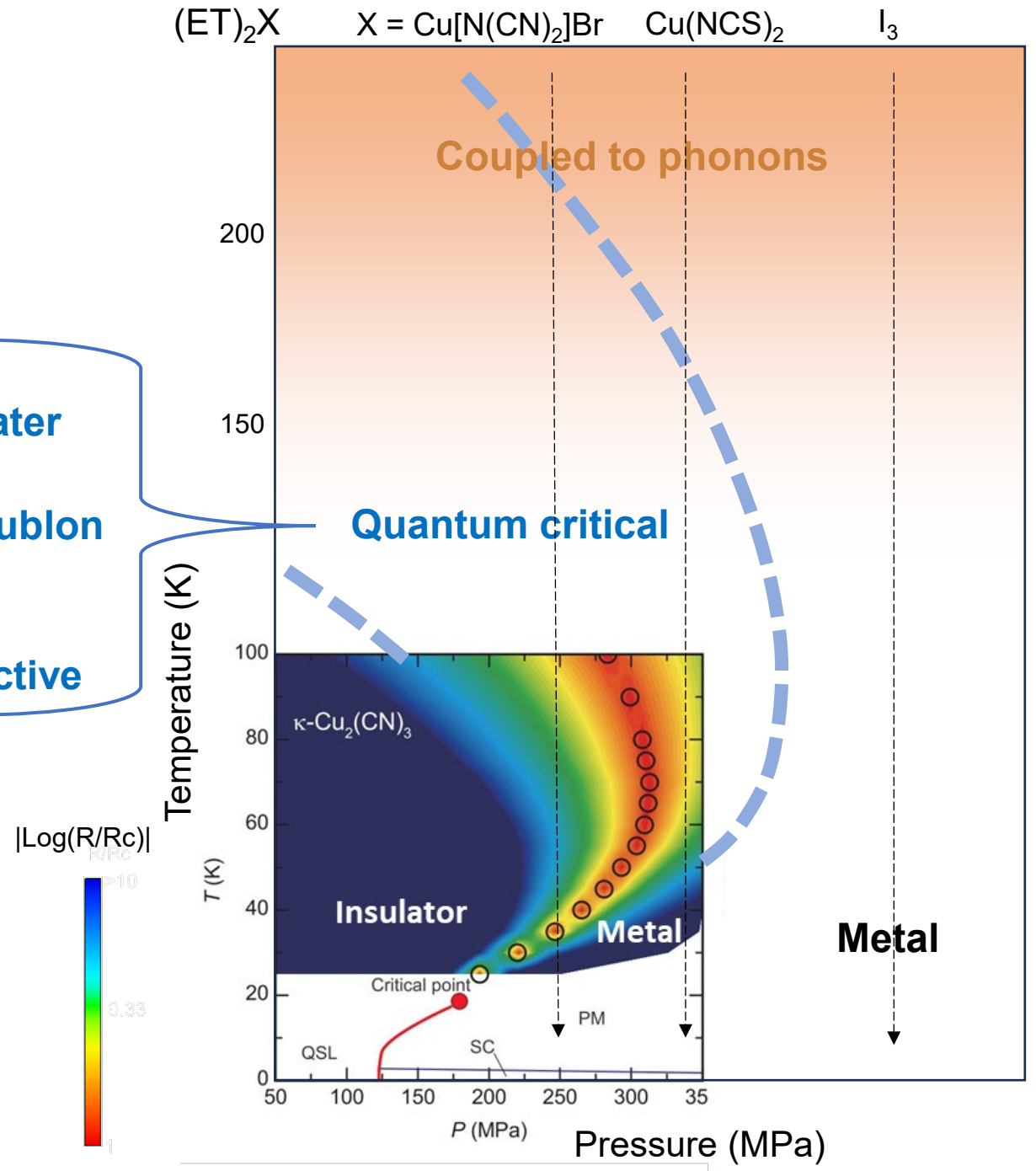
Quasi-particle excitations **Quantum critical**

Conductivity governed by holon/doublon density fluctuations

$$T/T_0 = T / (c|P-P_c(T)|^{z\nu})$$

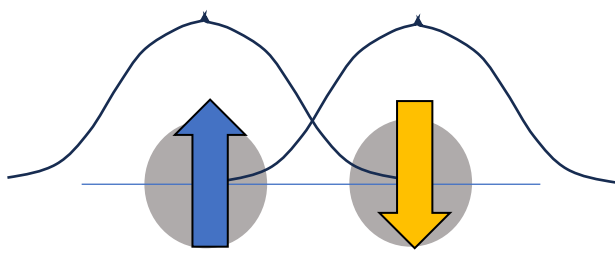
Scaling for $T > 1.5T_c$

- Quantum version of supercritical water
- gigantic holon/doublon fluctuations
- can be highly reactive

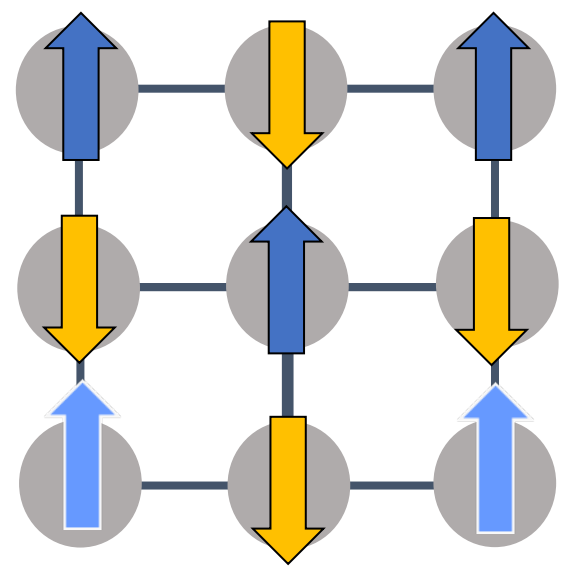


AF-interacting spins

*Pauli exclusion principle
favors antiparallel configuration*

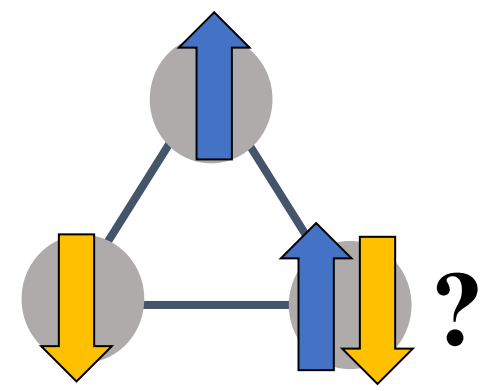


happy 😊
on a square lattice



Neel state

Unhappy 😞
on a triangular lattice



Spin frustration

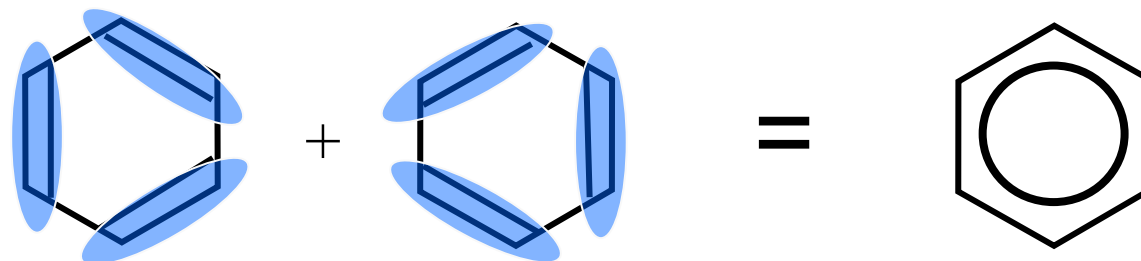
1973 P. W. Anderson
Quantum Spin liquid (QSL) ?

Resonating valence bond (RVB) state as a QSL

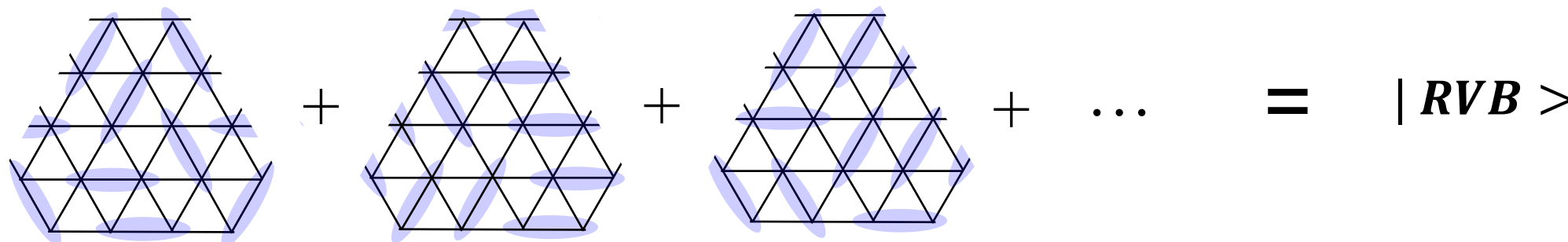


P. W. Anderson

benzene



Triangular
lattice



(RVB-based) QSL

Excited state

Gapped RVB

Nodal RVB

**Gapless spinon
Fermi surface**

Gapped Chiral QSL

gapless

k_y

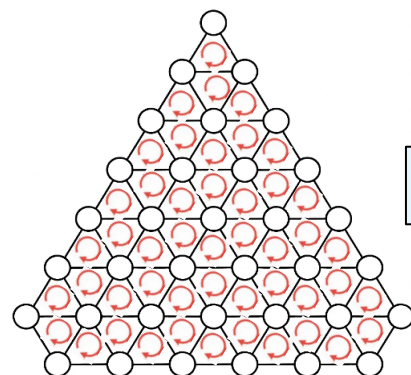
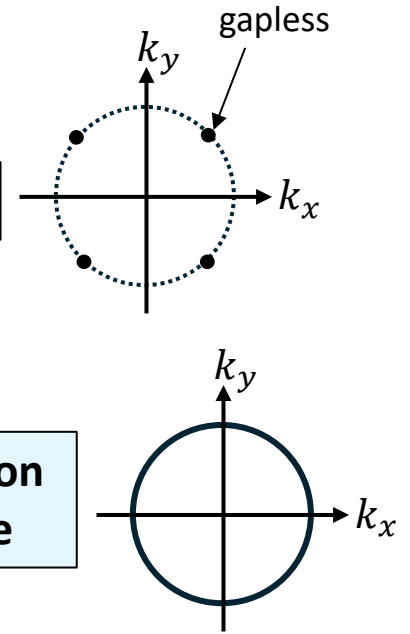
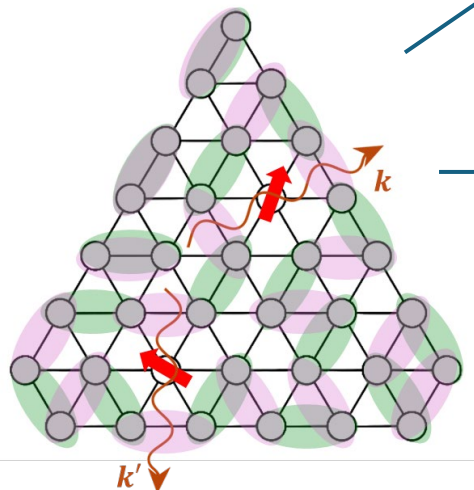
k_x

S_i

S_j

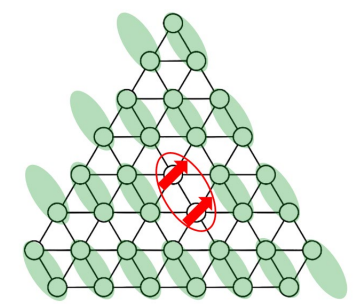
S_k

$$\chi_{ijk} = \bar{S}_i \cdot (\bar{S}_j \times \bar{S}_k)$$

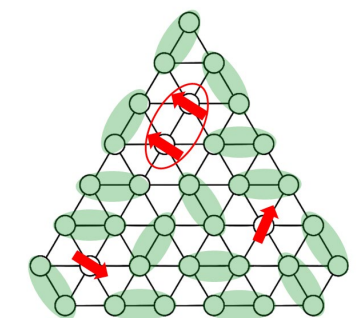


No QSL

Valence Bond Crystal (VBC)



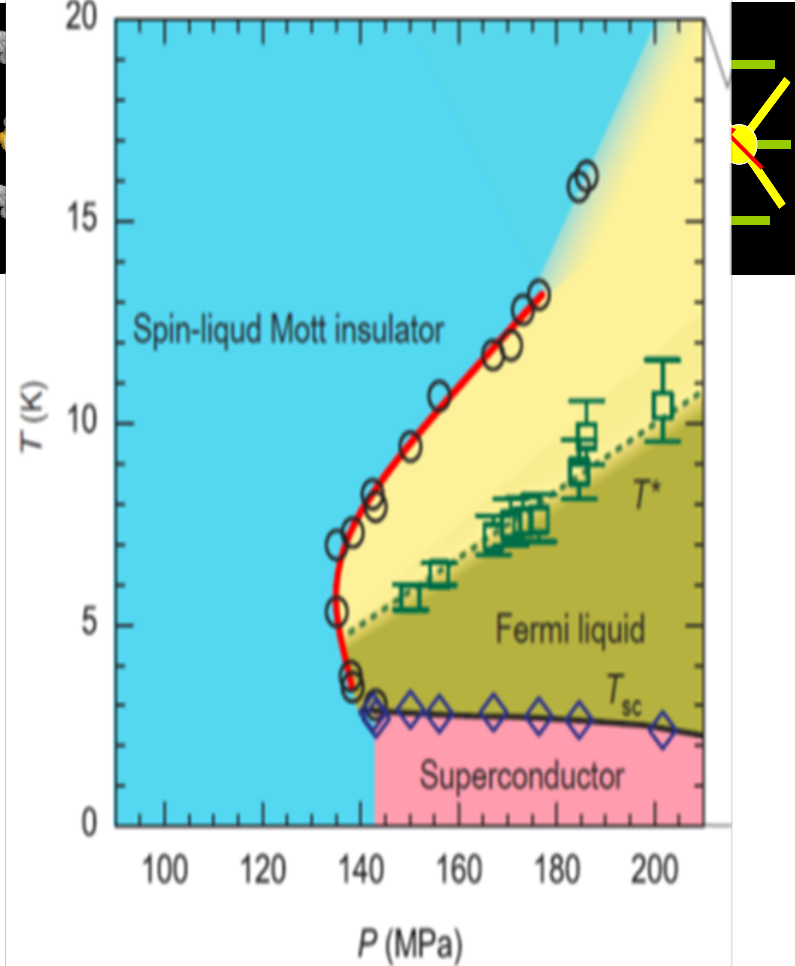
Valence Bond Glass (VBG)



Quantum spin liquid (QSL) candidates with a triangular lattice

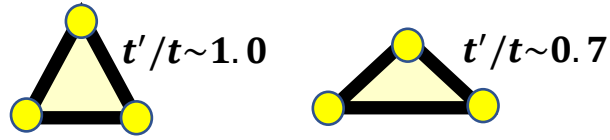
Organic material near Mott transition

P-T phase diagram: $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_3$



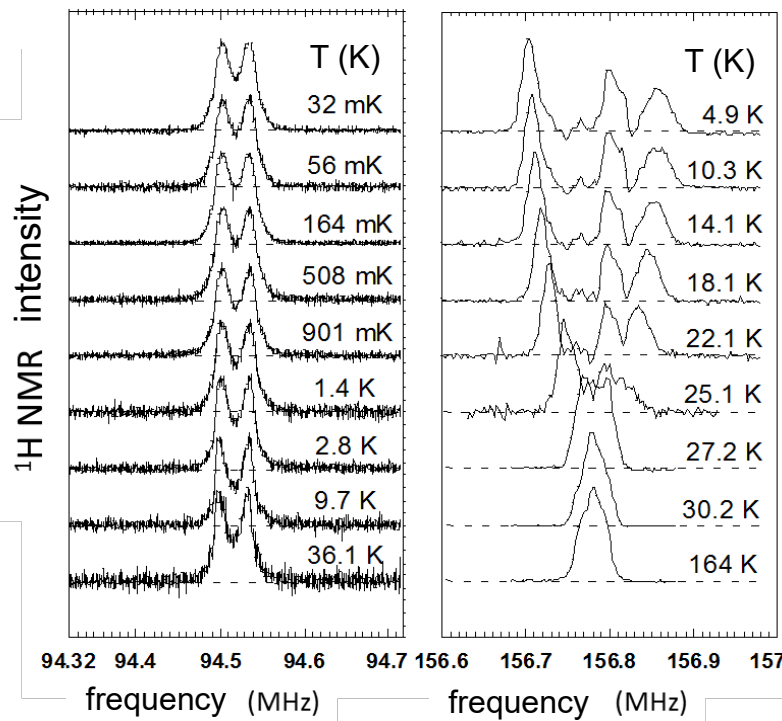
Furukawa et al., Nat. Commun. 9, 307 (2018)

^1H NMR spectra



Triangular lattice Deformed triangular lattice

$\kappa\text{-(BEDT-TTF)}_2\text{Cu}_2(\text{CN})_3$ $\kappa\text{-(BEDT-TTF)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$



No spectral change

Spectral splitting



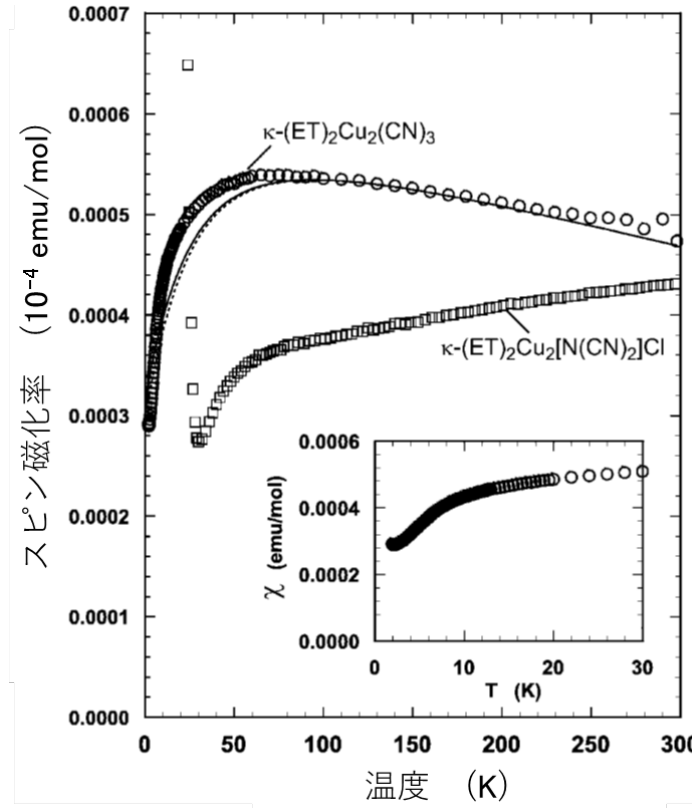
QSL !



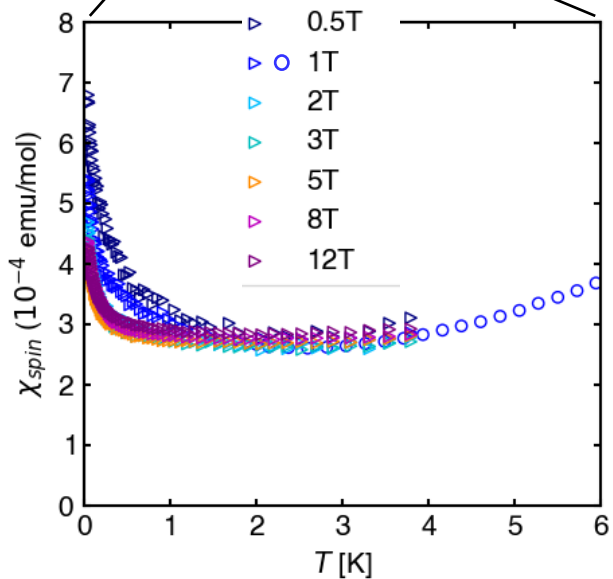
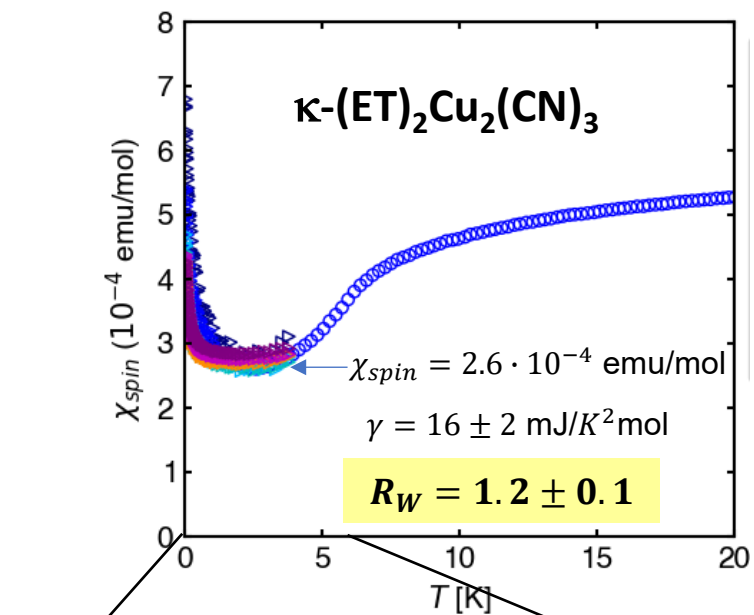
AFM

Shimizu et al., PRL 91, 107001 (2003).

Magnetic susceptibility

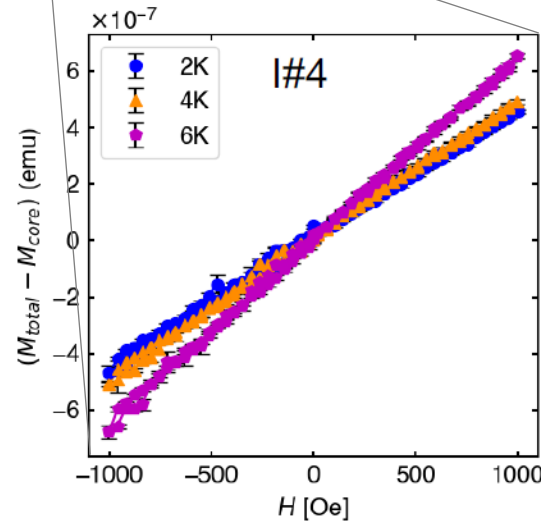
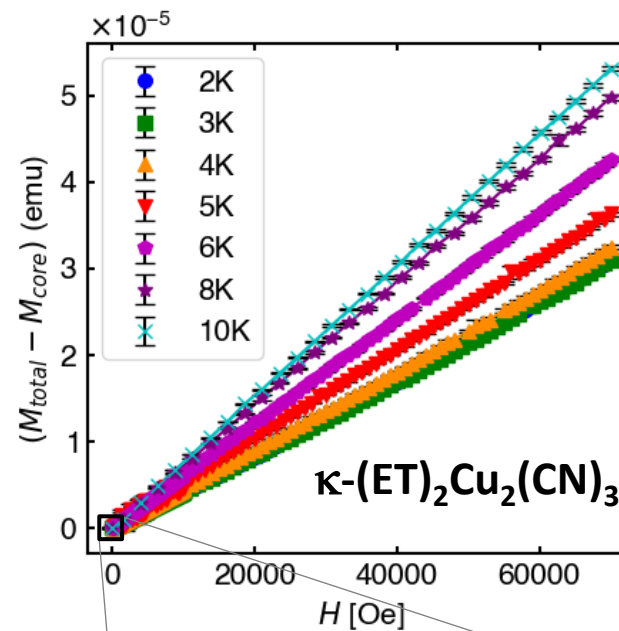


Spin susceptibility down to 50 mK



Pauli-paramagnetic like

Magnetization



- Magnetization is proportional to B

→ Exclude impurity or orphan spins

→ Gapless spin excitation

- $\chi(=M/B)$ is insensitive to T

→ Exclude fully gapped and nodal spin excitation

QSL (RVB)

Excited state

~~Gapped RVB~~

Nodal RVB

**Gapless spinon
Fermi surface**

~~Gapped Chiral QSL~~

gapless

k_y

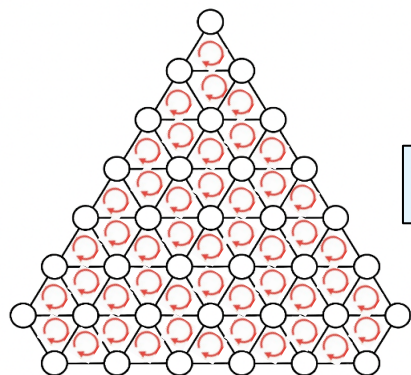
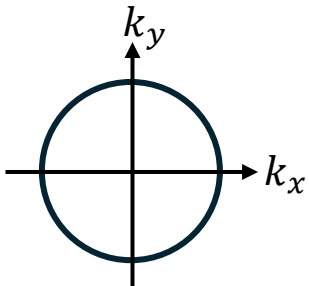
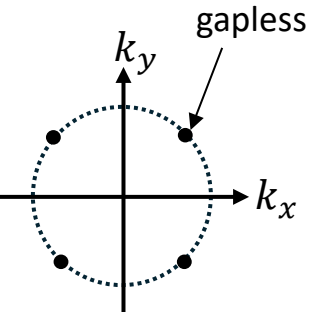
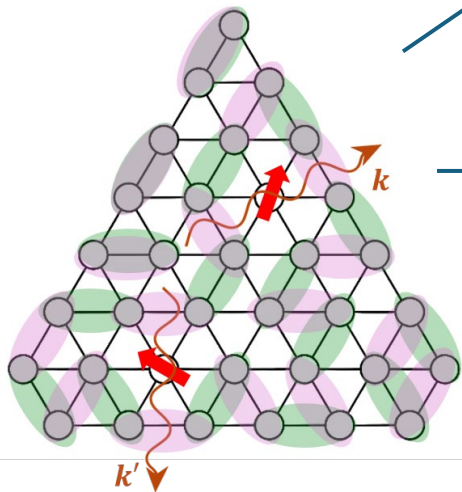
k_x

S_i

S_j

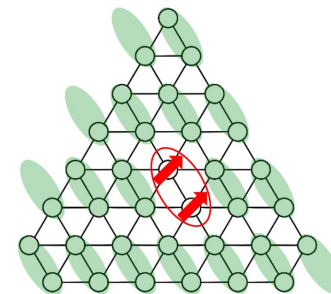
S_k

$$\chi_{ijk} = \bar{S}_i \cdot (\bar{S}_j \times \bar{S}_k)$$

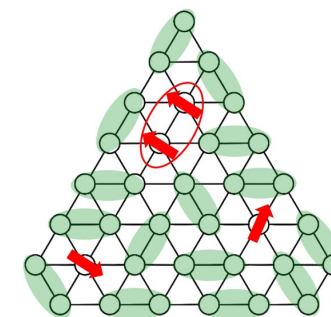


No QSL

~~Valence Bond Crystal
(VBC)~~



**Valence Bond Glass
(VBG)**



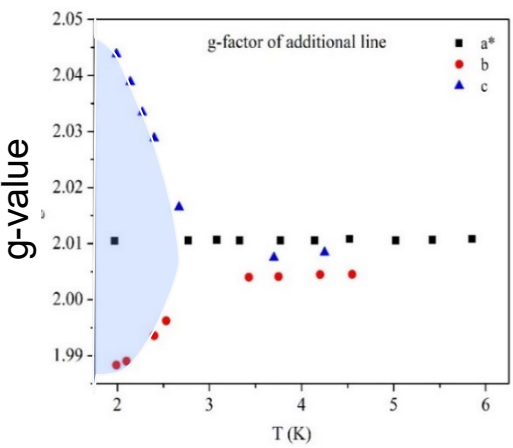
Inhomogeneous moments emerge nonlinearly with magnetic field at low temperatures.



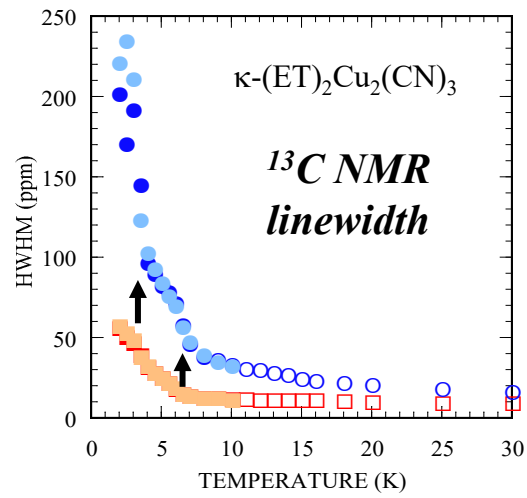
Miyagawa
Urai

Sudip

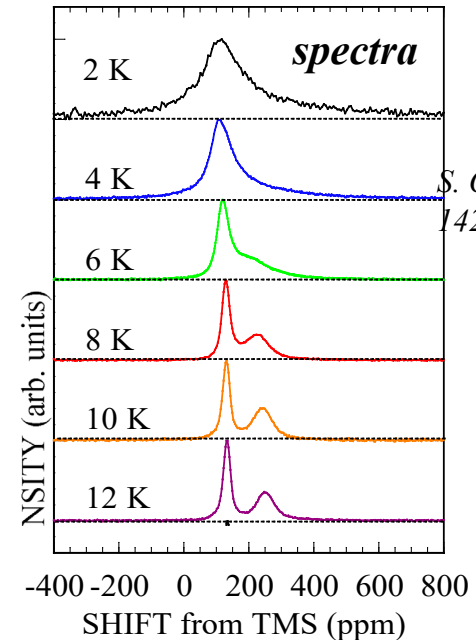
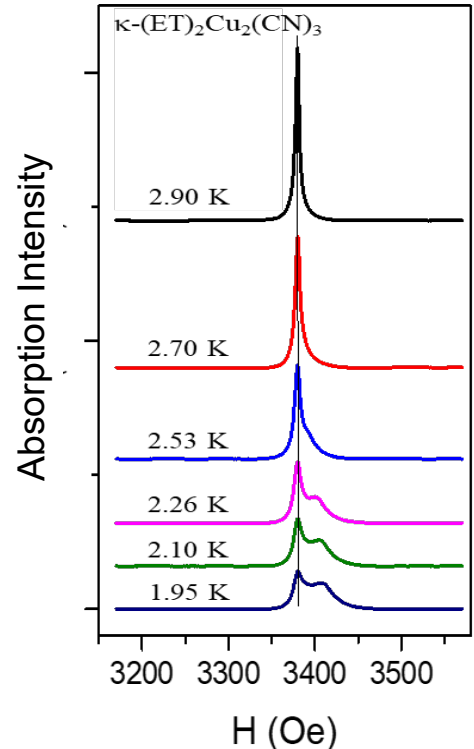
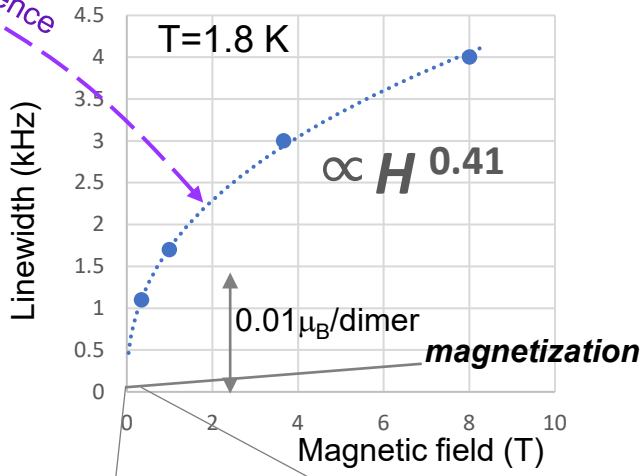
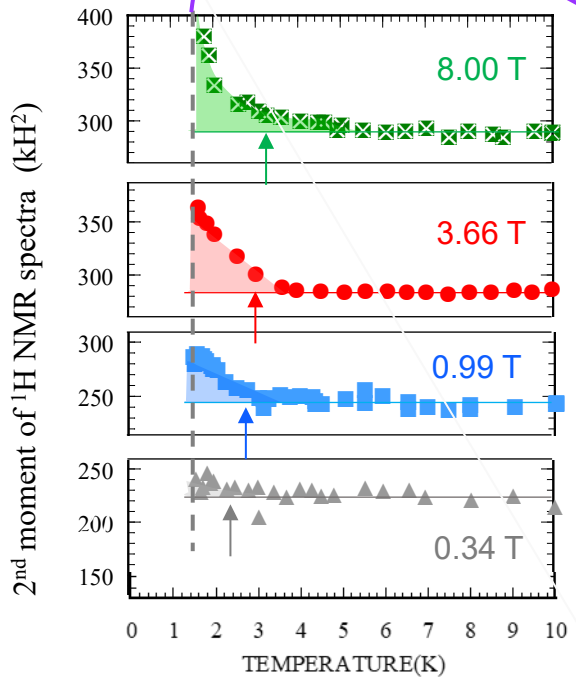
ESR



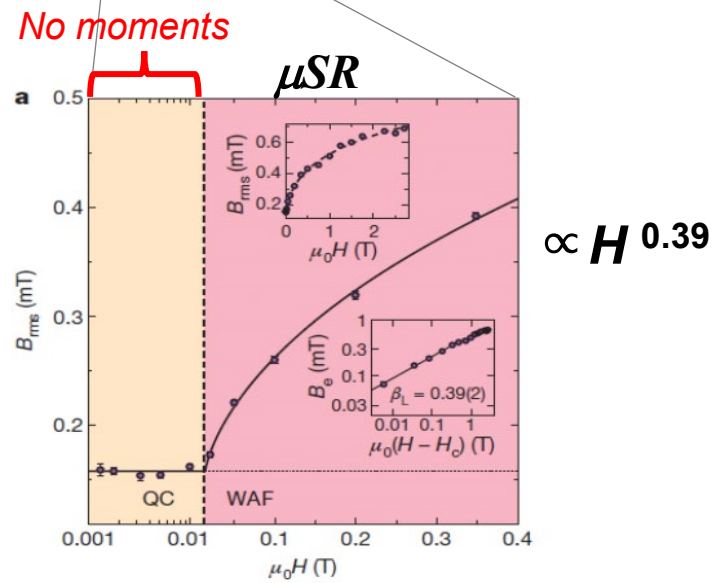
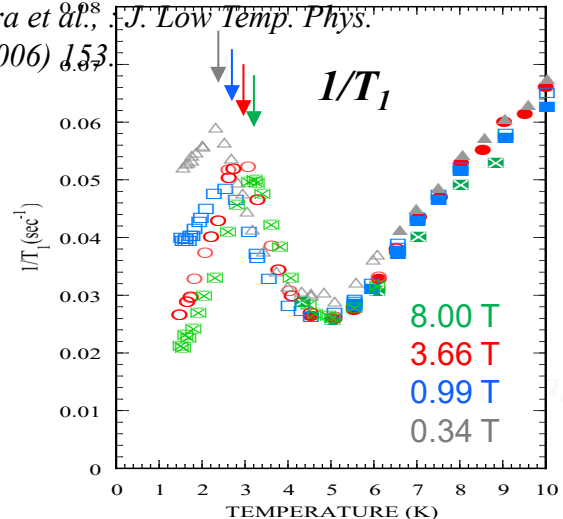
^{13}C NMR



^1H NMR



S. Ohira et al., J. Low Temp. Phys. 142 (2006) 153



Pratt et al. Nature 471 (2011)612

cf. Nakajima, Goto et al., JPSJ 81 063706 (2021)

At $T < 2-3$ K,

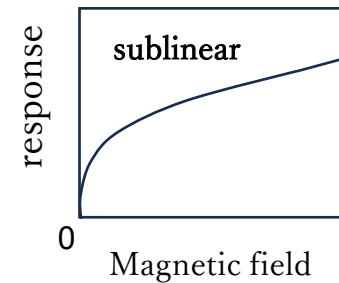
- Quantum-critical moment growth, $\propto B^{0.4}$

- Exclude fully gapped spin excitations
- Exclude fully gapless spin excitations

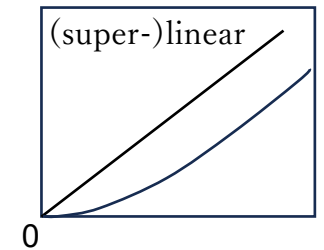
- Transverse moment (perpendicular to B)

- Exclude localized spin excitations

Non-perturbative



Perturbative



QSL (RVB)

Excited state

~~Gapped RVB~~

Nodal RVB

~~Gapless spinon Fermi surface~~

~~Gapped Chiral QSL~~

gapless

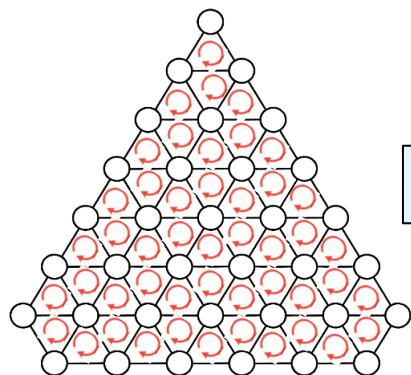
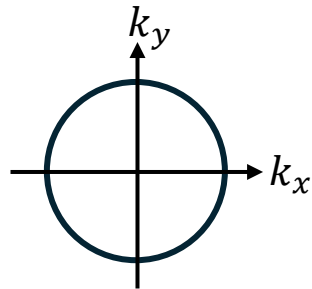
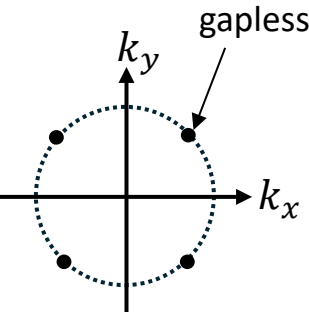
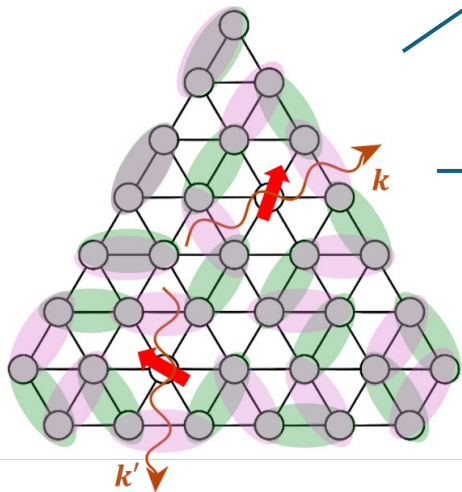
k_y

k_x

S_i

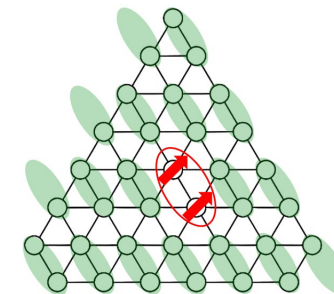
S_j S_k

$$\chi_{ijk} = \bar{S}_i \cdot (\bar{S}_j \times \bar{S}_k)$$

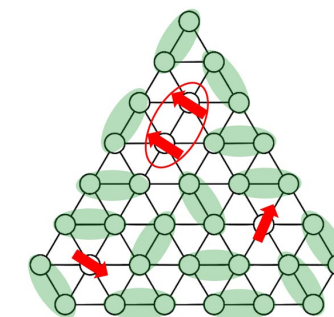


No QSL

~~Valence Bond Crystal (VBC)~~

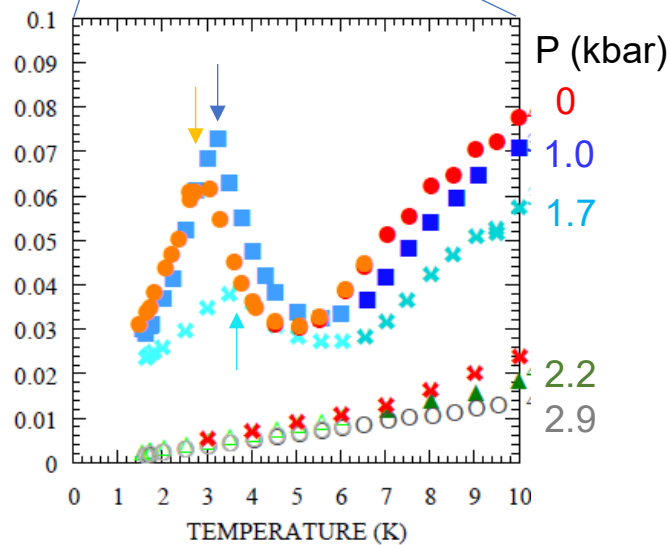
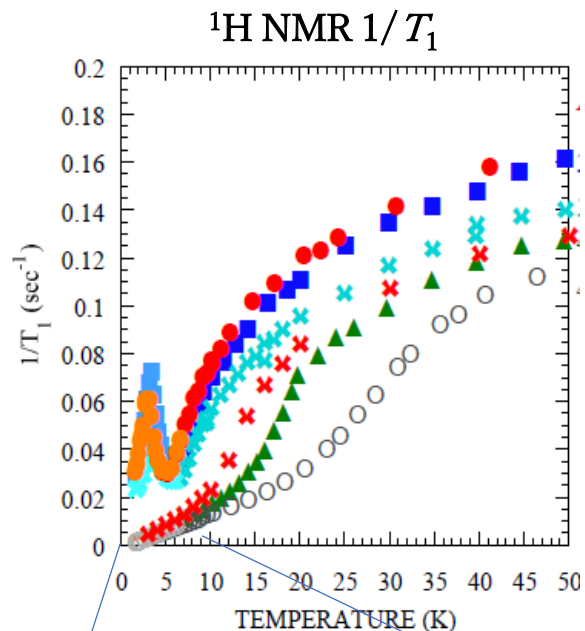
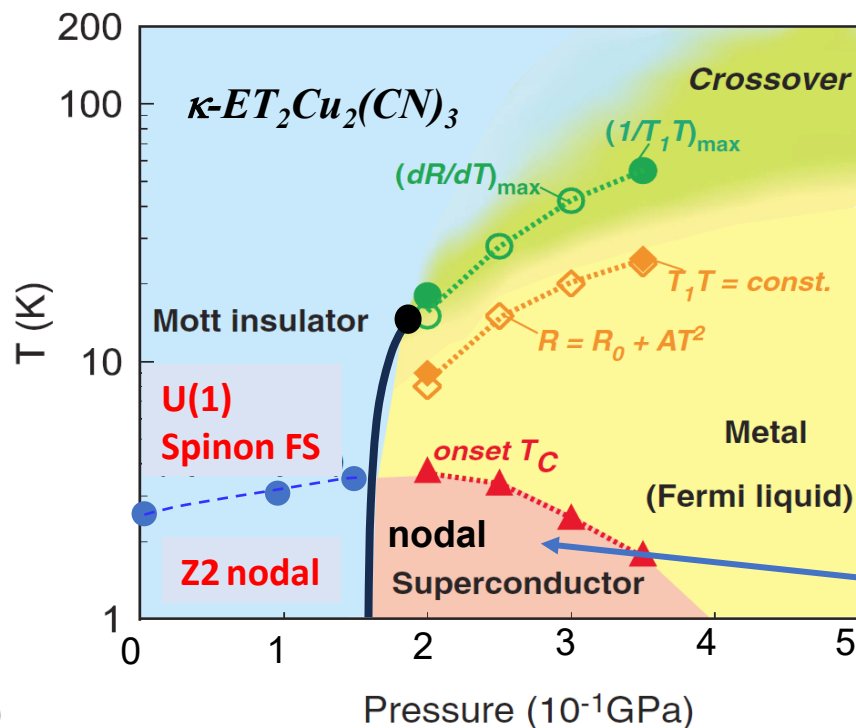


~~Valence Bond Glass (VBG)~~

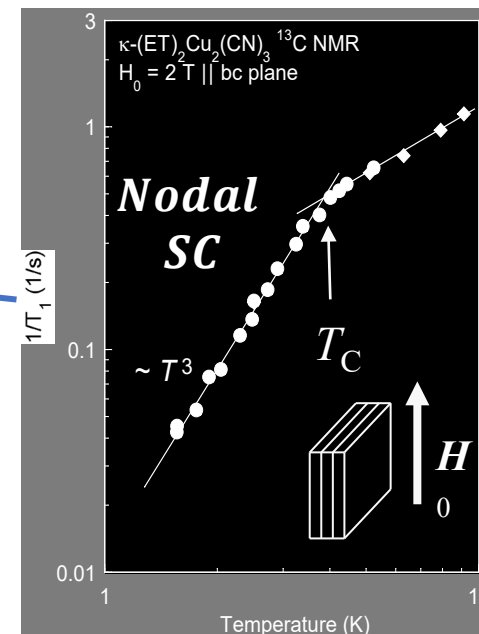


Pressure dependence: quantum critical SL evolves to nodal superconductivity

Pressure-temperature phase diagram



¹³C NMR 1/T₁ in SC under pressure



Shimizu *et al.*, *PRB* **81**, 224508 (2010)

Spin liquid superconductivity

$$|RVB\rangle = P_G |BCS\rangle$$

$$|spinon\ FS\rangle = P_G |BCS; \Delta \rightarrow 0\rangle$$

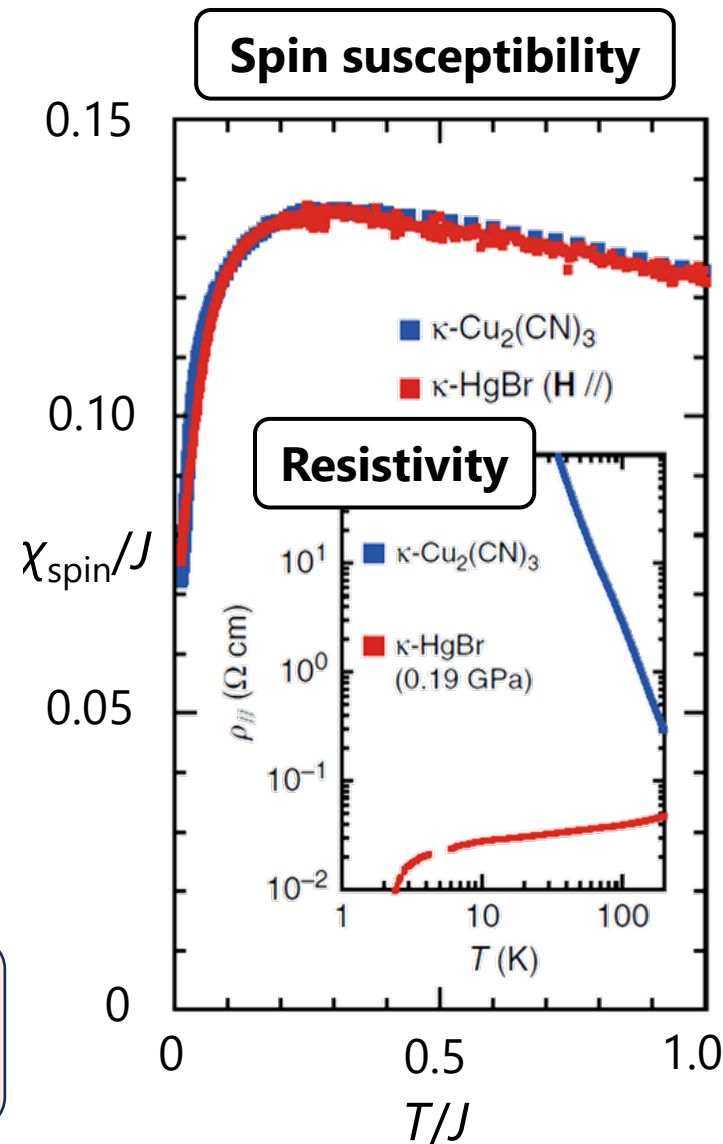
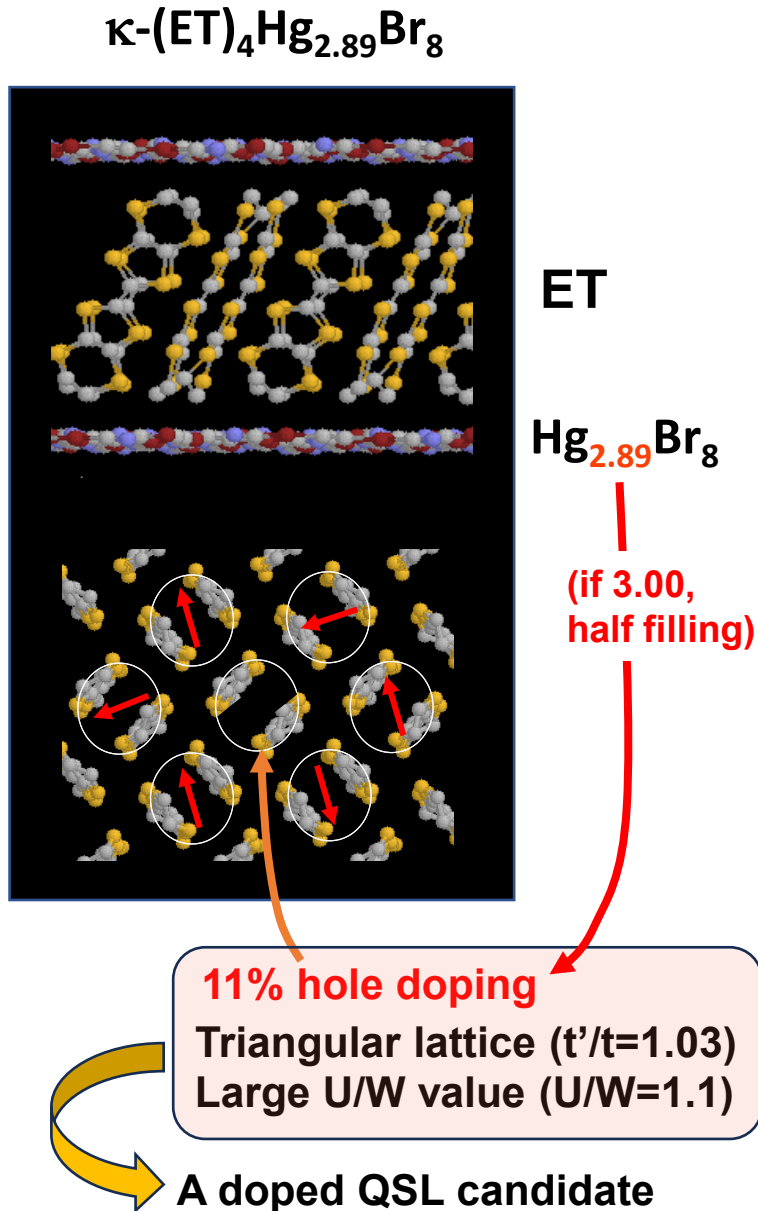
$$|nodal\ QSL\rangle = P_G |nodal\ BCS\rangle$$

$$|Chiral\ QSL\rangle = P_G |chiral\ SC\rangle$$

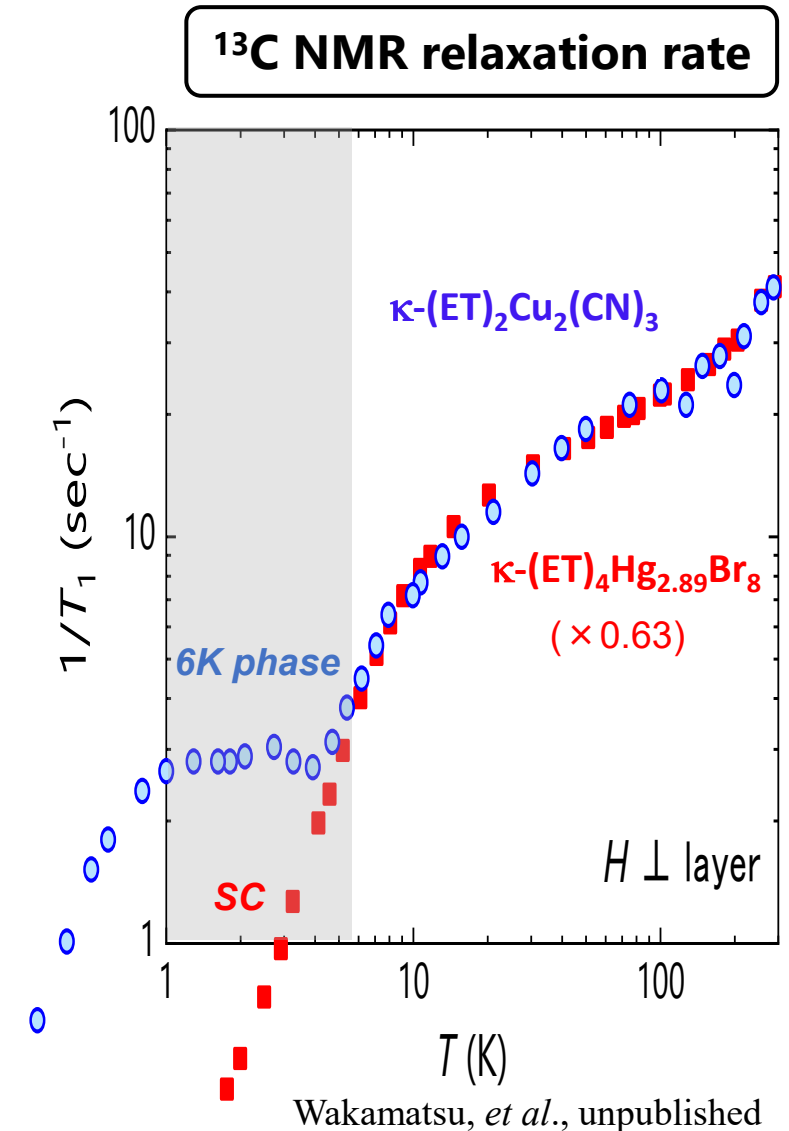
Gutzwiller projection $\sim?$ Mott transition

Doped QSL candidate, Lyubovskaya salt κ -(ET)₄Hg_{2.89}Br₈ (11% hole doped)

Charges get delocalized, but spins remain QSL-like!



Oike, *et al.*, *Nat. Commun.* **8**, 756 (2017).

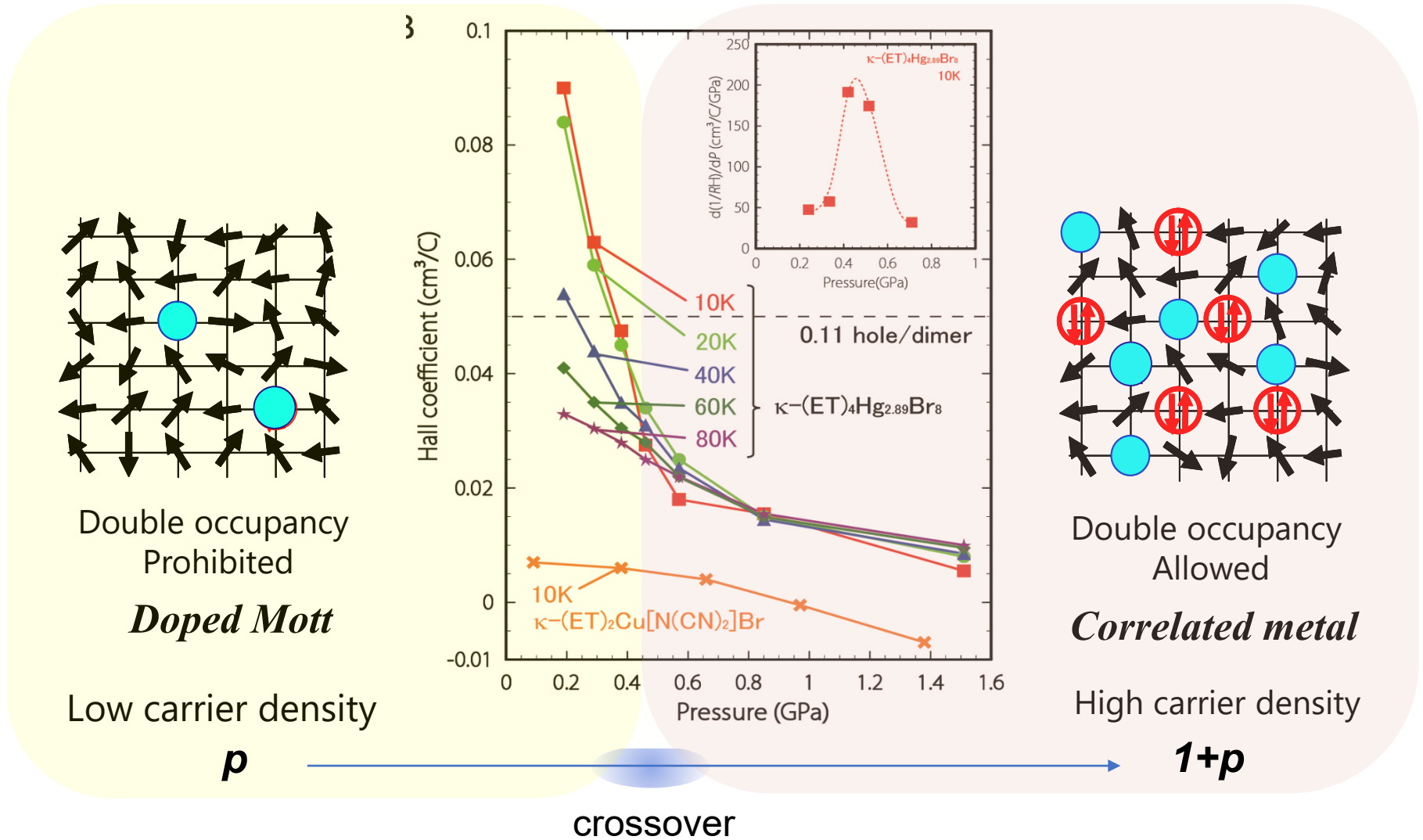
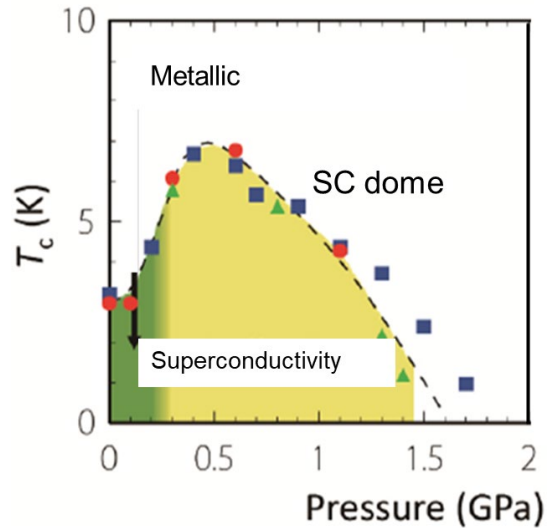


Wakamatsu, *et al.*, unpublished

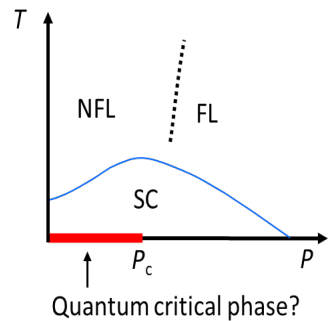
Pressure dependence of Hall coefficient: from doped QSL to correlated metal



Hall coefficient $\sim (\text{carrier number})^{-1}$



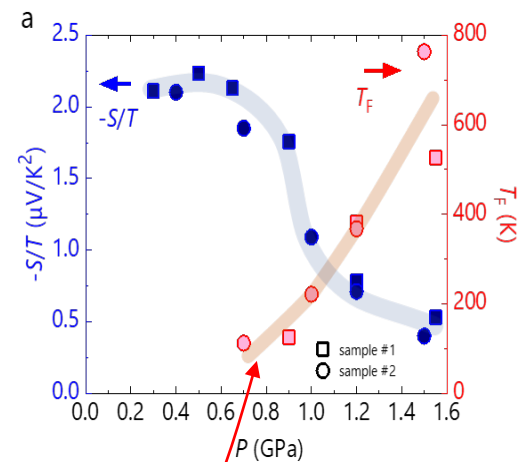
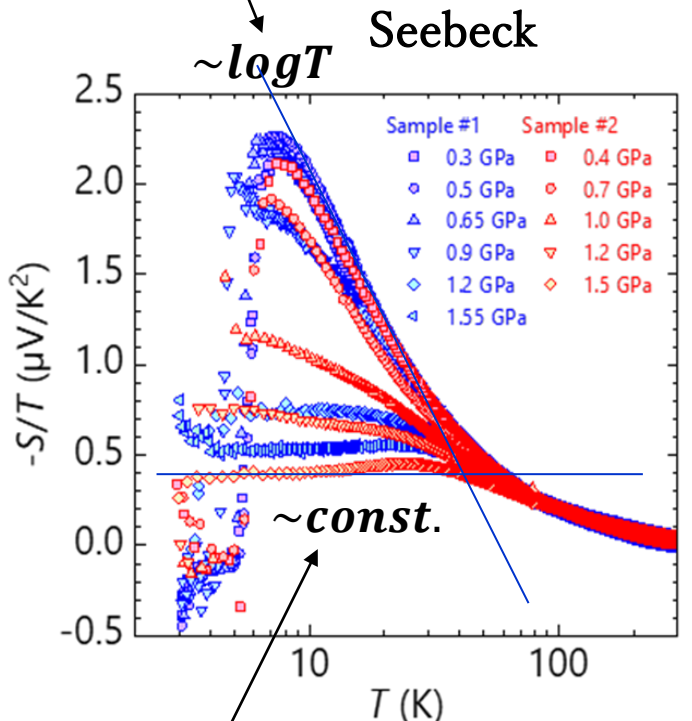
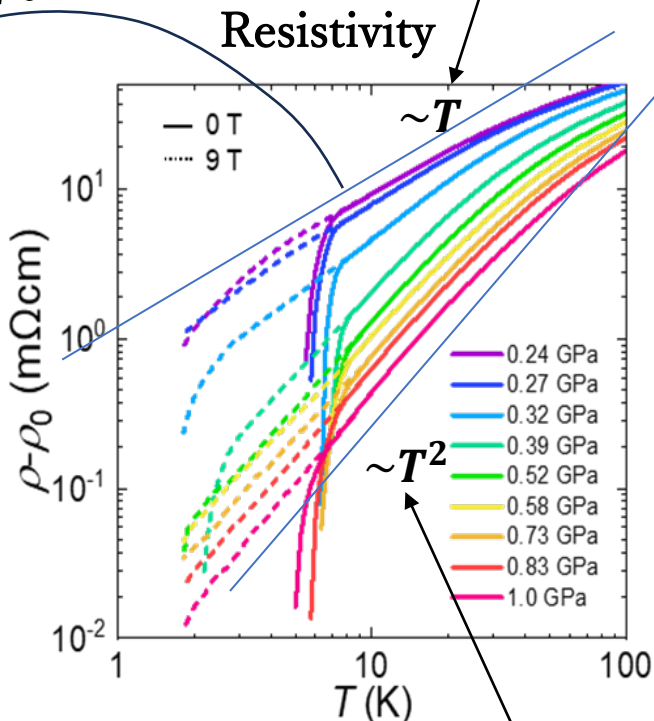
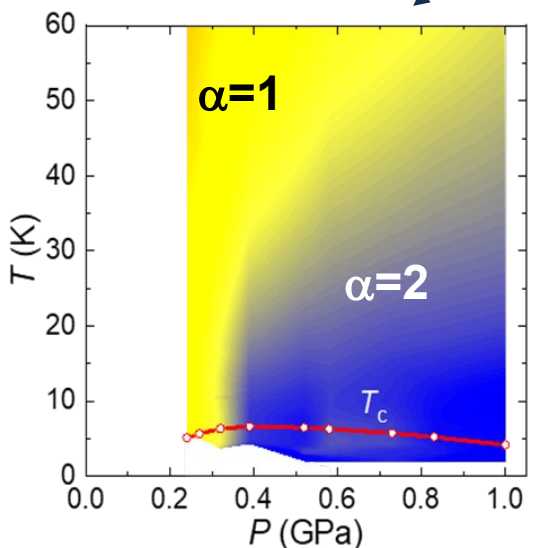
Crossover from a strange metal to a conventional metal to by pressure



$$\rho = \rho_0 + AT^\alpha$$

Low pressures
Non-Fermi liquid & quantum critical

$$\frac{S}{T} = \gamma \ln\left(\frac{T}{T_0}\right) \quad T_0 \sim 50 \text{ K}$$



High pressures
Fermi liquid

$$\frac{S}{T} = \pm \frac{\pi^2}{3} (1 + \lambda) \frac{k_B}{e} \frac{1}{T_F}$$

Oike, et al., *Phys. Rev. Lett* **114**, 067002 (2015).

Theoretical: 1-order transition

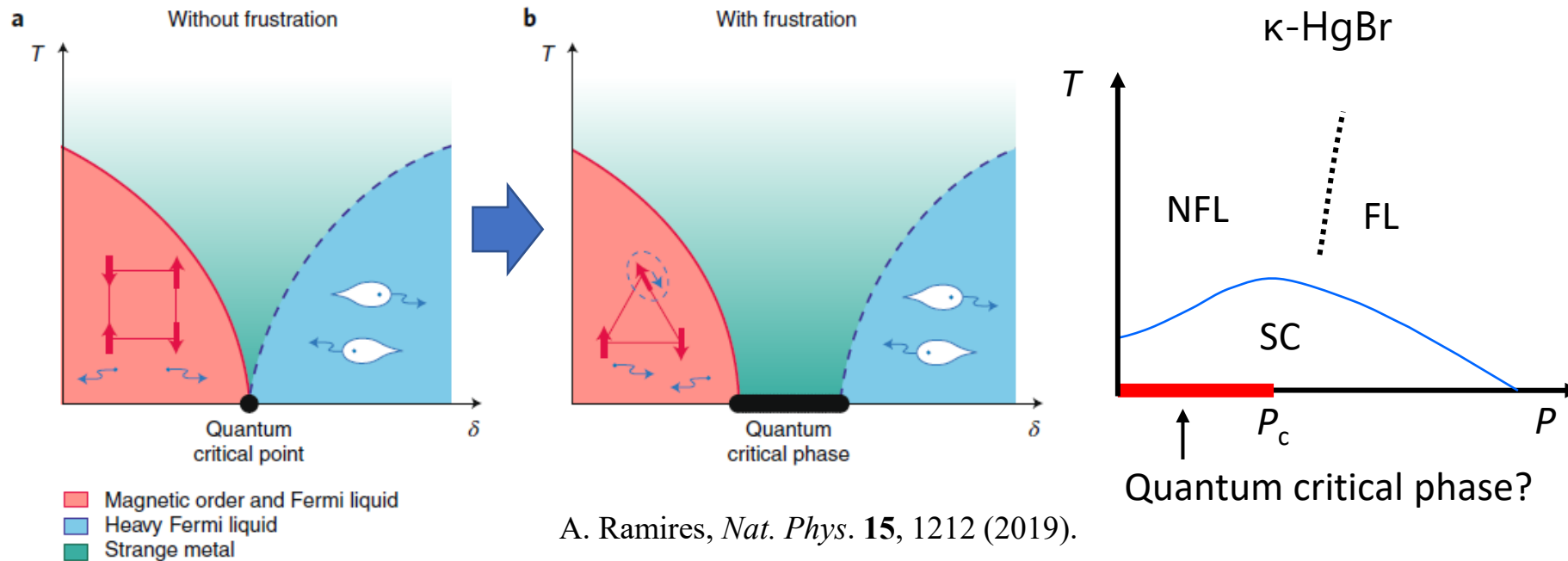
Suzuki et al, *Phys Rev X* **12**_011016 (2022)

Wakamatsu et al., *Nat. Commun.* 14:3679 (2023).

Quantum critical "phase"

CePdAl (Heavy fermion system with Kagome lattice)
→ Emergence of quantum critical *phase*, (not a point)
H. Zhao, *et al.*, *Nat. Phys.* **15**, 1261 (2019).

Frustration makes QC point to QC phase



A. Ramires, *Nat. Phys.* **15**, 1212 (2019).

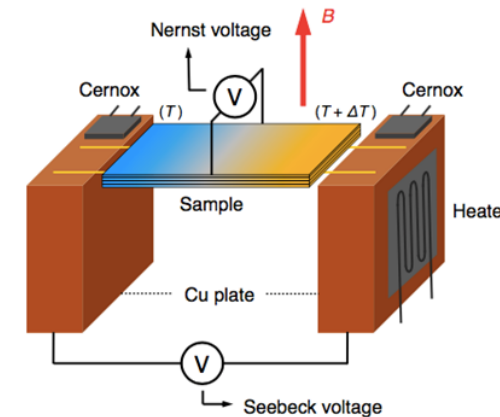
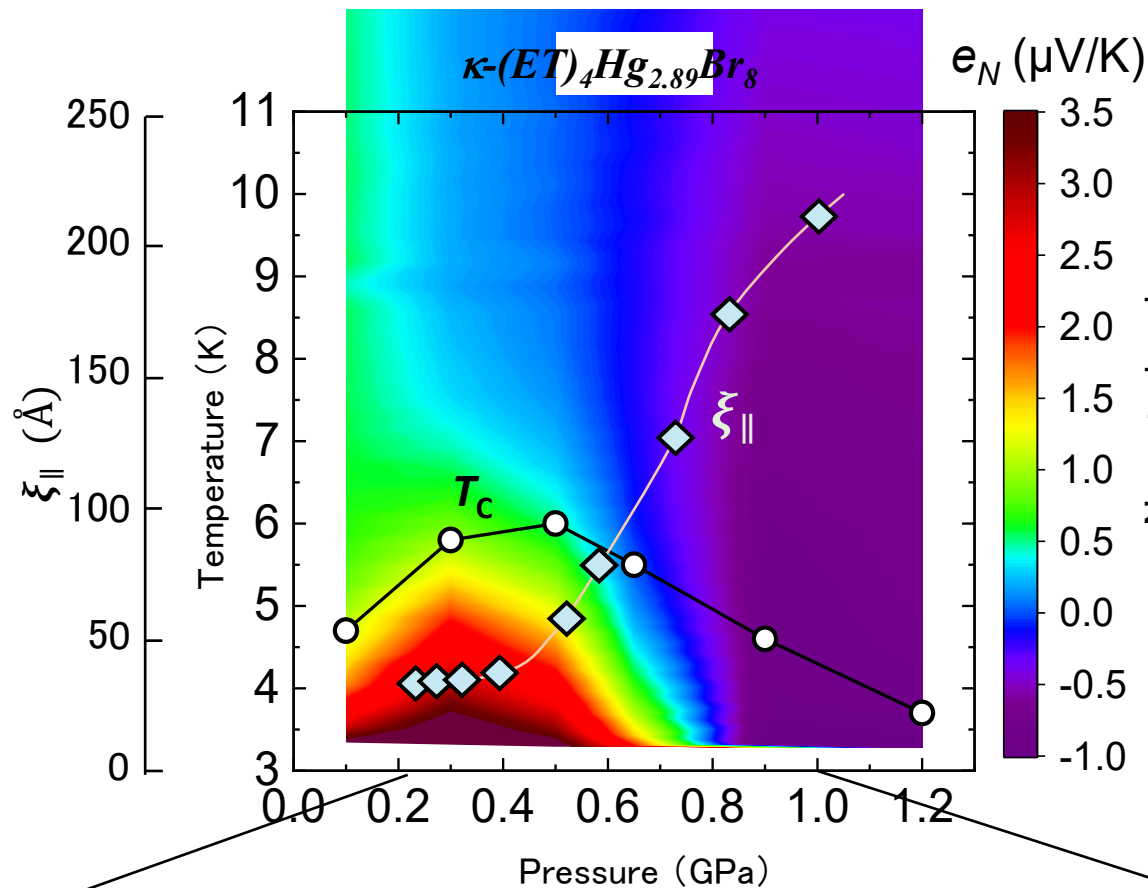
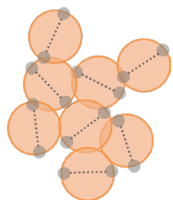
M. Vojta, *Rep. Prog. Phys.* **81**, 064501 (2018)

Large H_{c2} , short coherence length, BEC-like pairing at low pressures

Suzuki *et al.*,
Phys. Rev. X **12**, 011016 (2022).

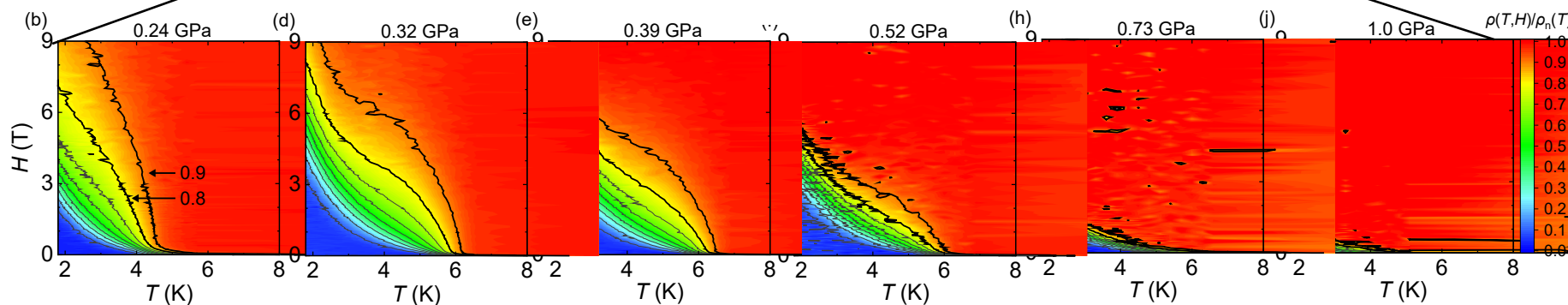
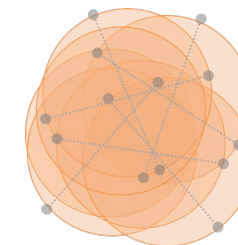
$k_F \xi \sim 2-3$

BEC-like



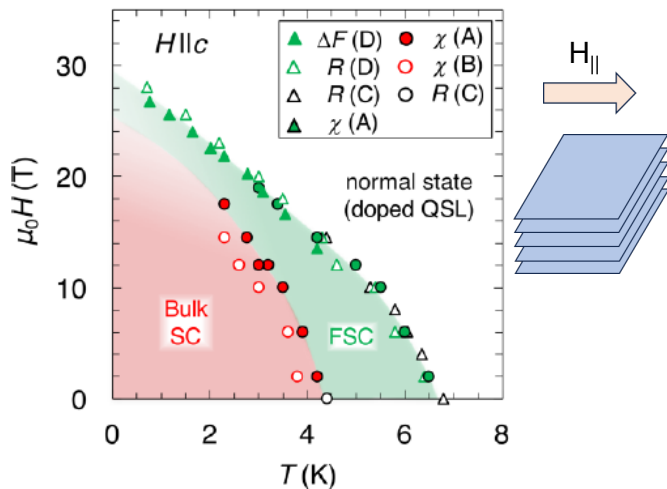
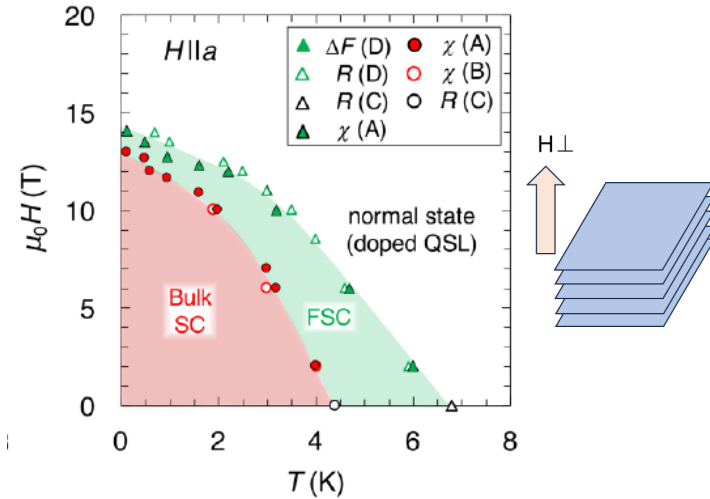
$k_F \xi \sim 50$

BCS-like



Huge Upper critical field

Ambient pressure



Cooper Pair breaking: orbital effect & spin effect

$$H_{C2}^{orb} \ll H_{C2}^{spin} \sim H_P$$

$$\mu_B H_P = \Delta_0 / \sqrt{2} \quad \Delta_0 = 1.76 k_B T_C$$

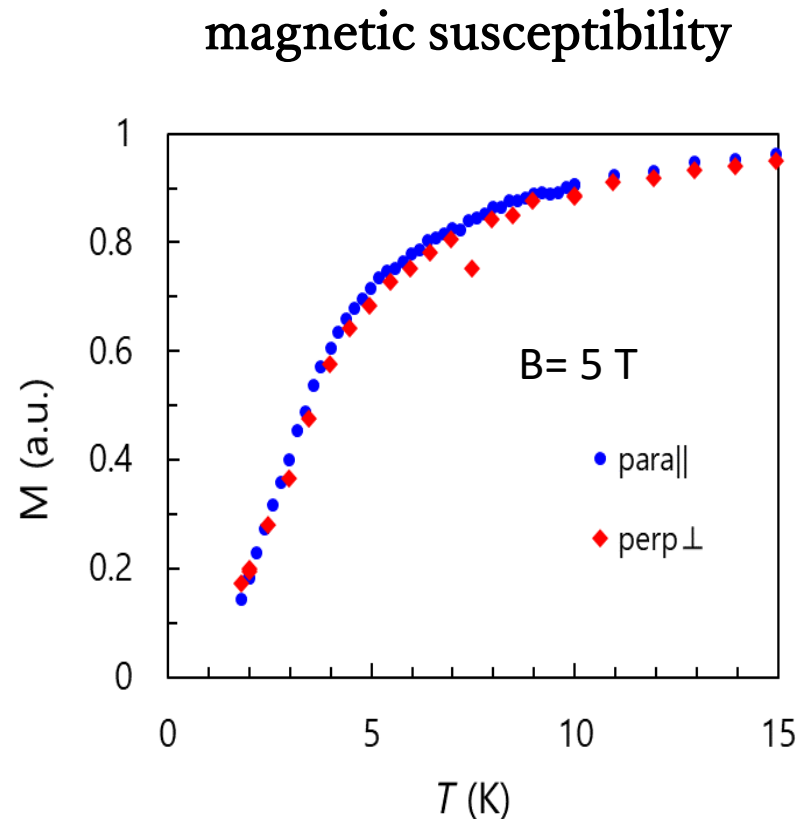
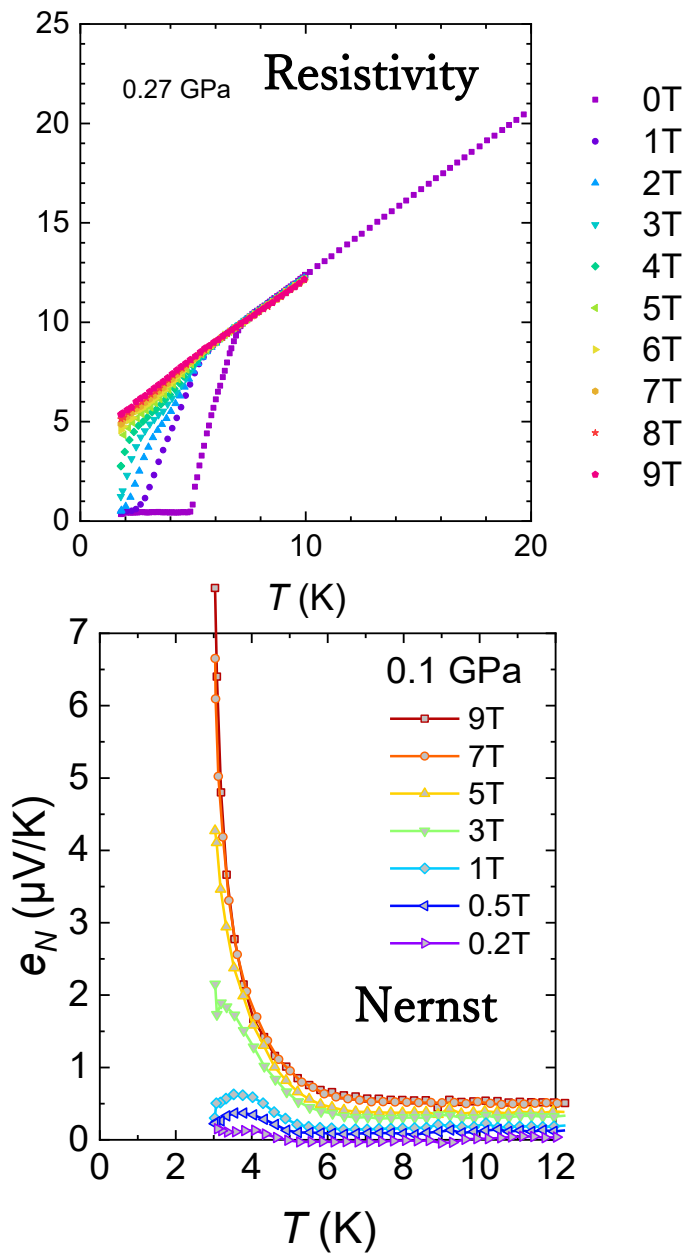
$$H_P^{BCS} = 1.84 T_C$$

	0 GPa	1.0 GPa
T_C (K)	4.0	4.5
H_P^{BCS} (Tesla)	7.4	8.3
$H_{C2\perp}$ (Tesla)	14	1.5 ± 0.5
$H_{C2\parallel}$ (Tesla)	30	

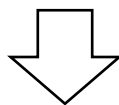
$$\Delta_0^{(d)} \approx 2.14 k_B T_C$$

$$H_P^{(d)} \approx 2.4 T_C$$

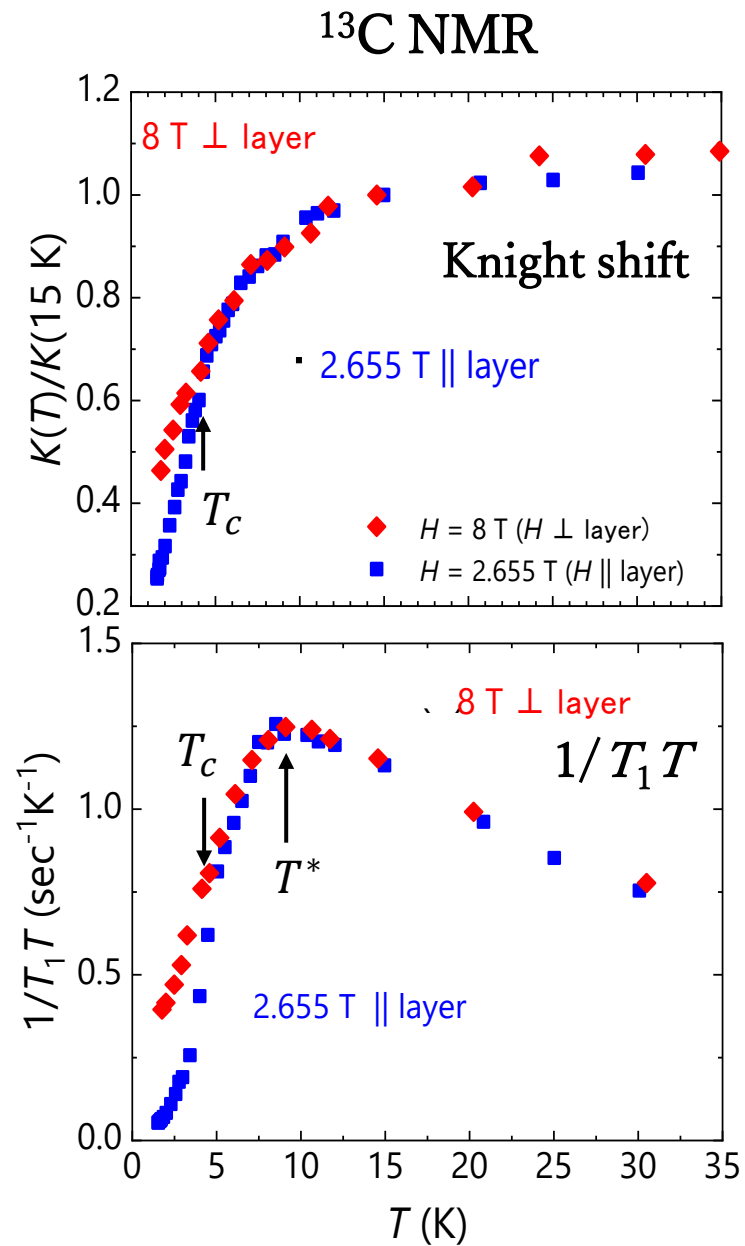
Enhanced Nernst and depressed spin fluctuations above T_c



χ goes to zero without anisotropy.



Not due to SC diamagnetism



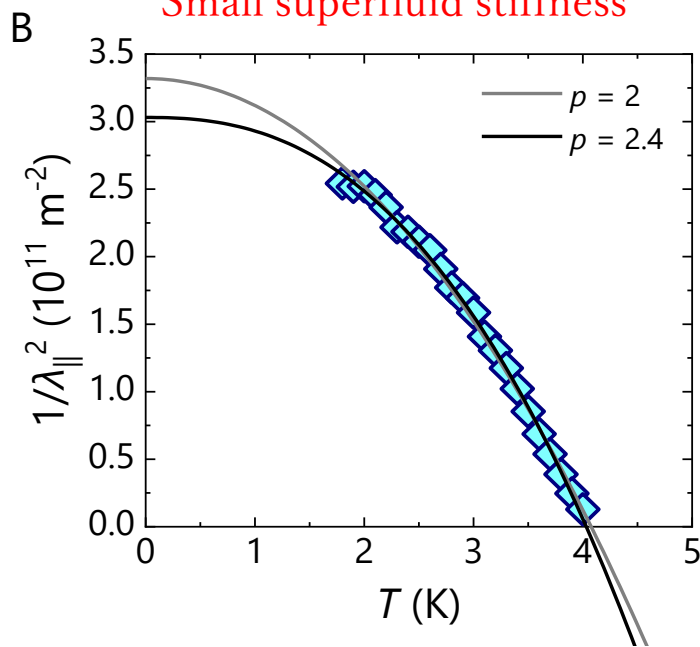
Reduced Superfluid density & large T_c/T_F value

$n_S \sim 15 \pm 5\%$ of total carriers

$$\frac{n_S}{m^*} = \frac{c^2}{4\pi e^2} \frac{1}{\lambda_L^2}$$

$\lambda_{exp}(0) = 1820$ nm

Small superfluid stiffness

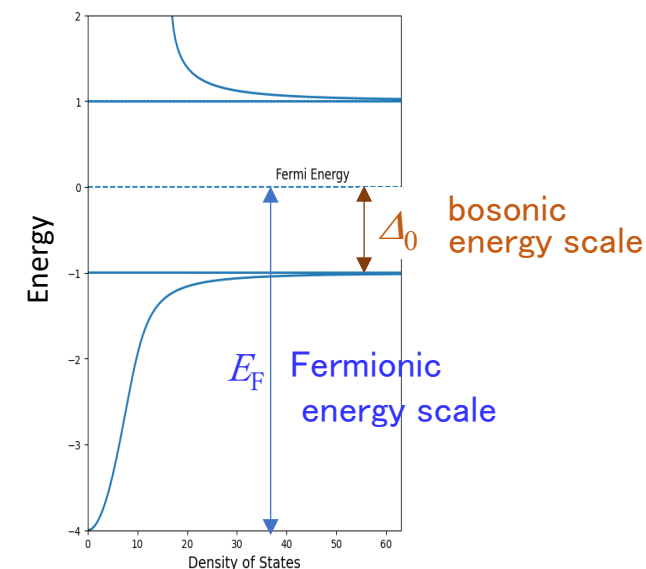
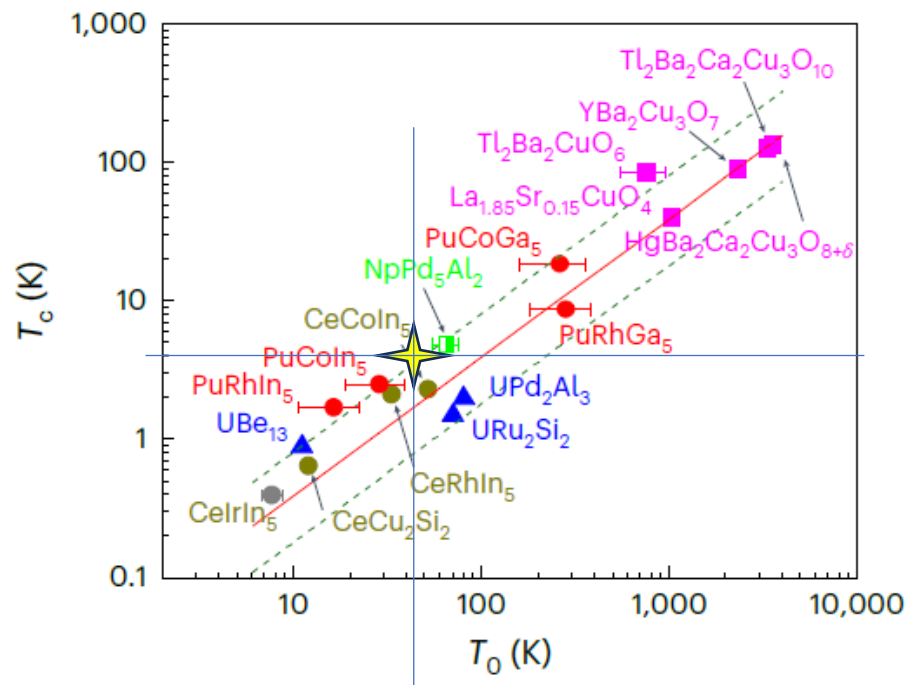


$$\frac{T_c}{T_F} \sim 0.1$$

$T_c \sim 4$ K,
 $T_F \sim 45$ K ($k_B T_F = \pi \hbar^2 d / \mu_0 e^2 \lambda_L^2$)

$$\frac{\Delta_0^{(d)}}{E_F} \gtrsim 0.2$$

$$\Delta_0^{(d)} \gtrsim 2.14 k_B T_c$$



Strange metal/strange superconductivity in the doped QSL, κ -(ET)₄Hg_{2.89}Br₈

Nodal FL* (fractionalized metal)

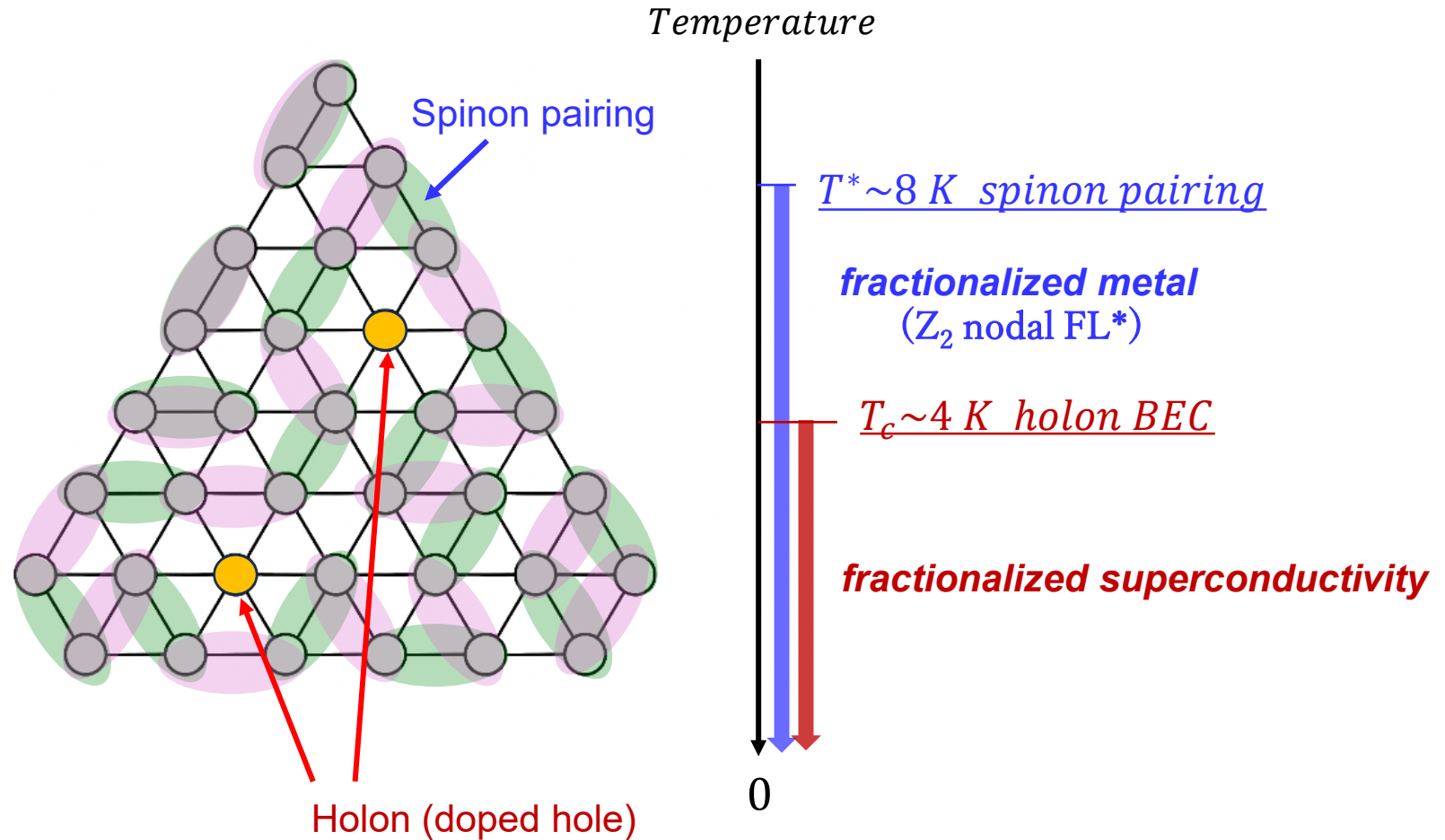
T. Senthil, S. Sachdev, and M. Vojta, Phys. Rev. Lett. **90**, 216403(2003).

$T > T_c$: strange metal

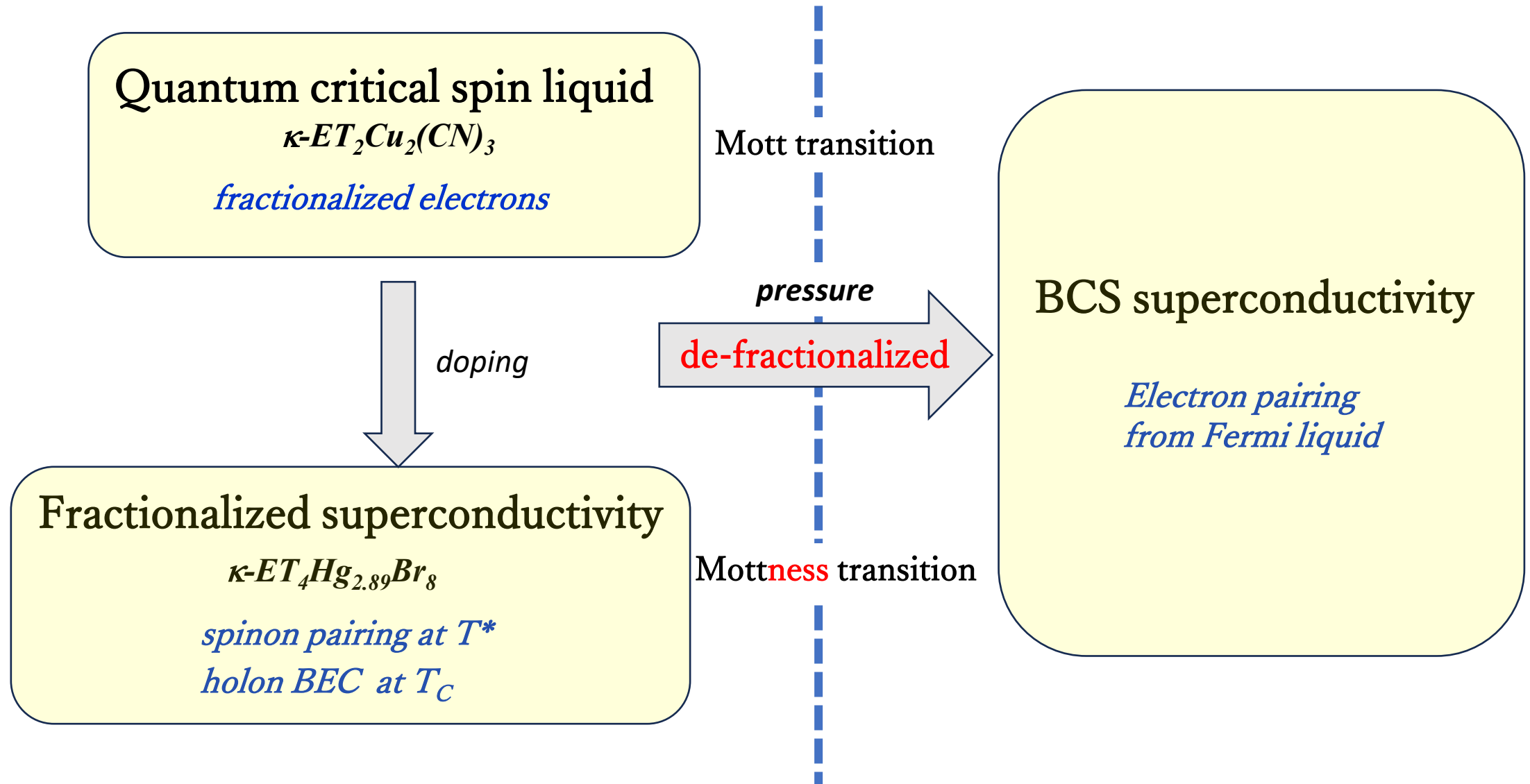
reduced carrier density
non-Fermi liquid
quantum critical
Nernst signal enhanced
 χ_{spin} goes toward zero

$T < T_c$: strange superconductivity

reduced superfluid density
BEC-like feature
Huge H_{c2}
Small T_c/T_F



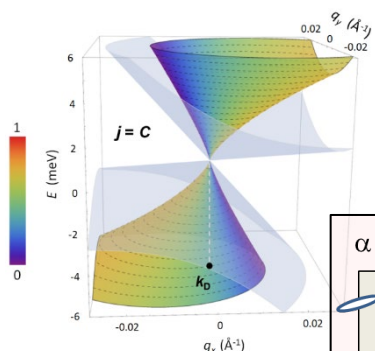
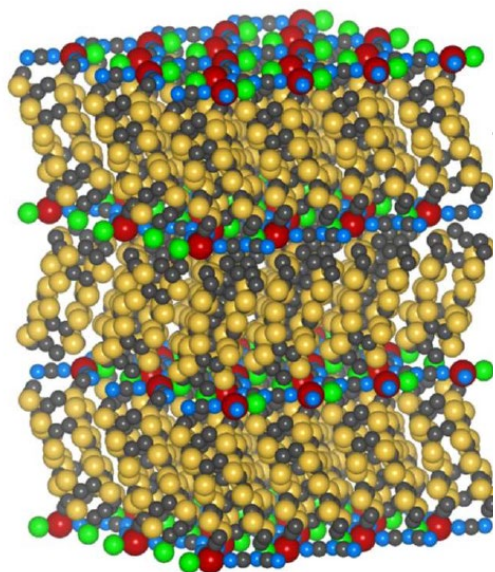
Quantum spin liquid evolves to superconductivity



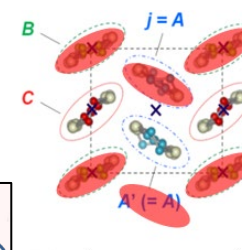
A key to materials science is
how to create unstable states in stable structures



Emeritus Prof. Nakasuji
 中筋一弘 先生



Dirac/Weyl
 Topo. Gap opening
 QHE, AQHE



Wigner Physics

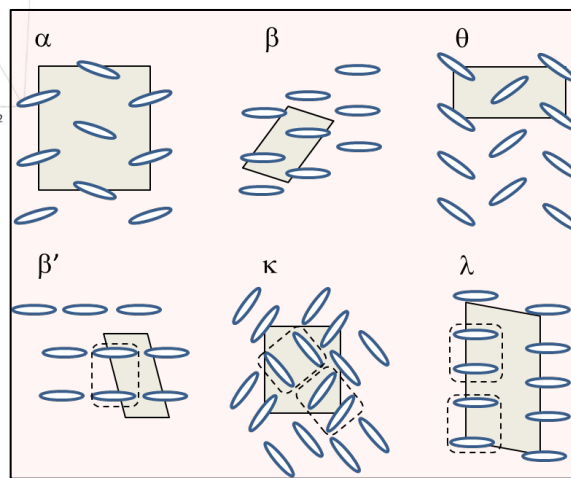
charge order
 charge glass

Dirac physics

In-plane
 structure

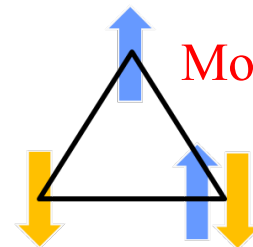
U, V, t

(Kino, Seo, Hotta, Fukuyama)



Mott physics

Quantum critical state



Antiferromagnet
 ? Altermagnet
 Spin liquid
 Unconventional SC

Nonreciprocal
 transport

CISS

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