SPICE-Workshop on "New Spin on Molecular Quantum Materials", Ingelheim, Germany, May 24– 27, 2022

Emergent states of interacting electrons on triangular lattices

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Spin liquid

1. **Quantum spin liquid** - κ-$(ET)_2Cu_2(CN)_3$
   - present status of experiments
2. **Doped quantum spin liquid** - κ-$(ET)_4Hg_{2.89}Hg_8$ -
   - non-FL to FL crossover
   - quantum critical phase — PR X 12_011016 (2022)
   - BEC-BCS crossover — arXiv:2201.10714
   - reduced superfluid density — arXiv:2202.06032
   - preformed pairs & pairing symmetry — arXiv:2205.03682

Charge glass

3. **Quantum charge glass** - θ-$(ET)_2X$ -
   - classical manifestations (slow dynamics, aging, short-range order)
   - anomalously high crystallization speed — arXix:2201.04855
   - classical to quantum crossover — arXiv:2205.10795

Today's talk is based on collaboration with

K. Miyagawa, Kagawa, Shimizu, Kurosaki, Furukawa, H. Oike, M. Urai, Y. Suzuki,
K. Wakamatsu, Y. Ueno, T. Fujii, J. Ibuka, T. Sato, H. Murase (U Tokyo)

G, Saito, M. Maesato (Kyoto U.)

T. Sasaki, S. Iguchi, M. Saito (Tohoku U., IMR)

R. Kato (RIKEN)

H. Taniguchi, M. Itou (Saitama U.)

S. Yamashita, Y. Nakazawa (Osaka)

F. Pratt (Rutherford-Appleton)

Y. Kohama, A. Miyake, T. Nomura (ISSP)

B. Mikche, M. Dressel (Stuttgart U.)

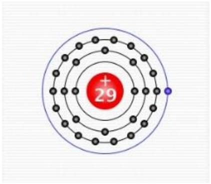
H. Mori (ISSP)

M. Tamura (Tokyo Sci. Univ.)

Organic materials → flexible & controllable lattice geometry

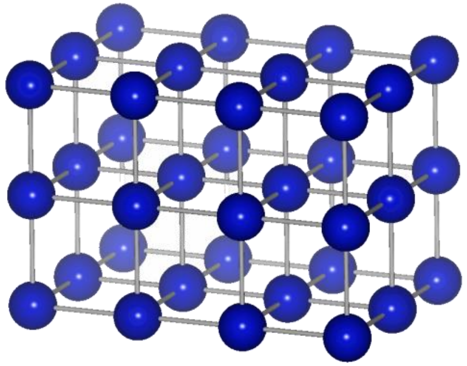
Inorganic materials

atom

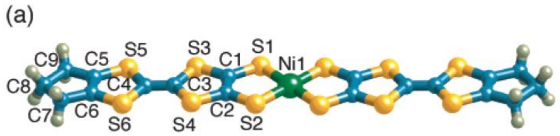


Orbital degeneracy
Spin-orbit coupling
Hunt coupling
……….

lattice



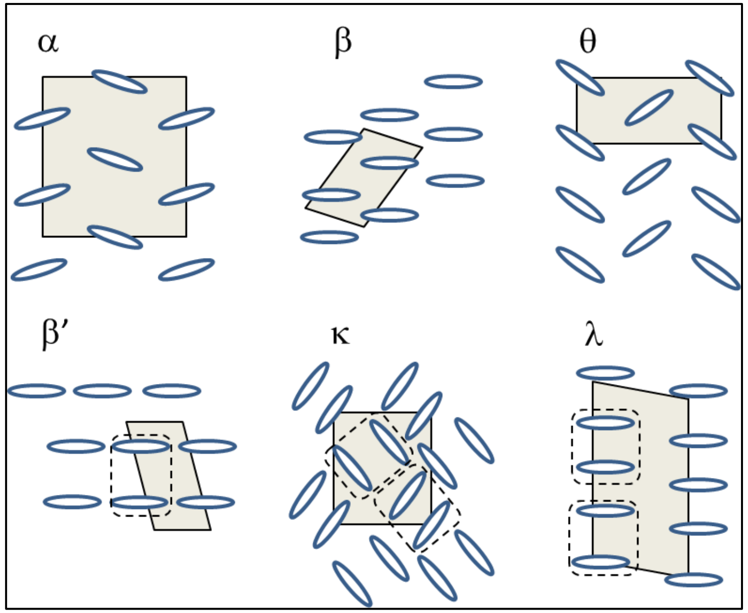
Organic materials



Frontier orbital
(K. Fukui)

lattice

Kino-Fukuyama



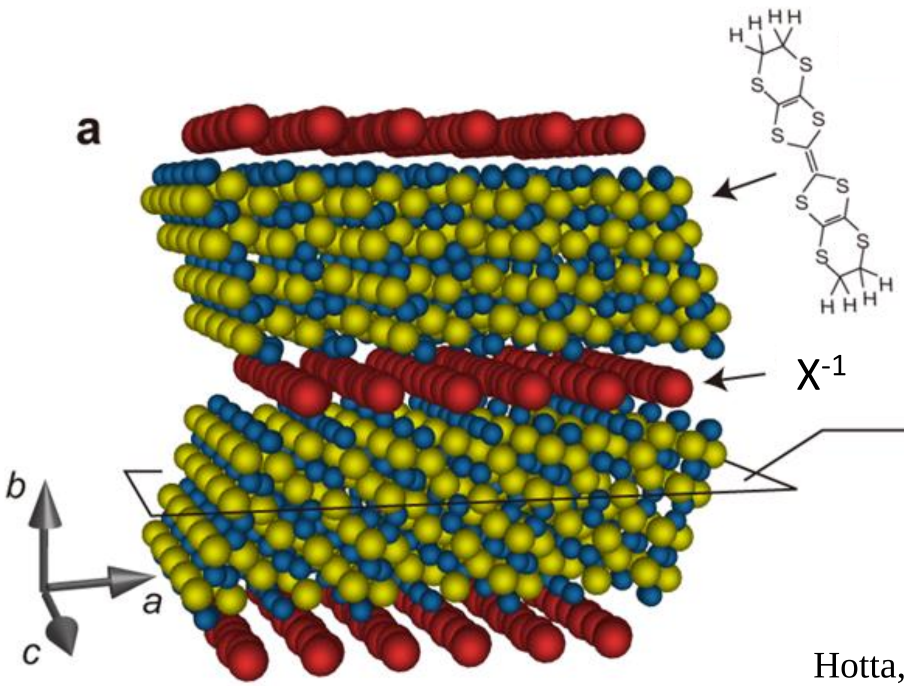
Hotta, Seo, Fukuyama, Chem. Rev., 2004

Organic materials → Physics of interaction and geometry

Various in-plane structures

↓

Diverse correlation phenomena

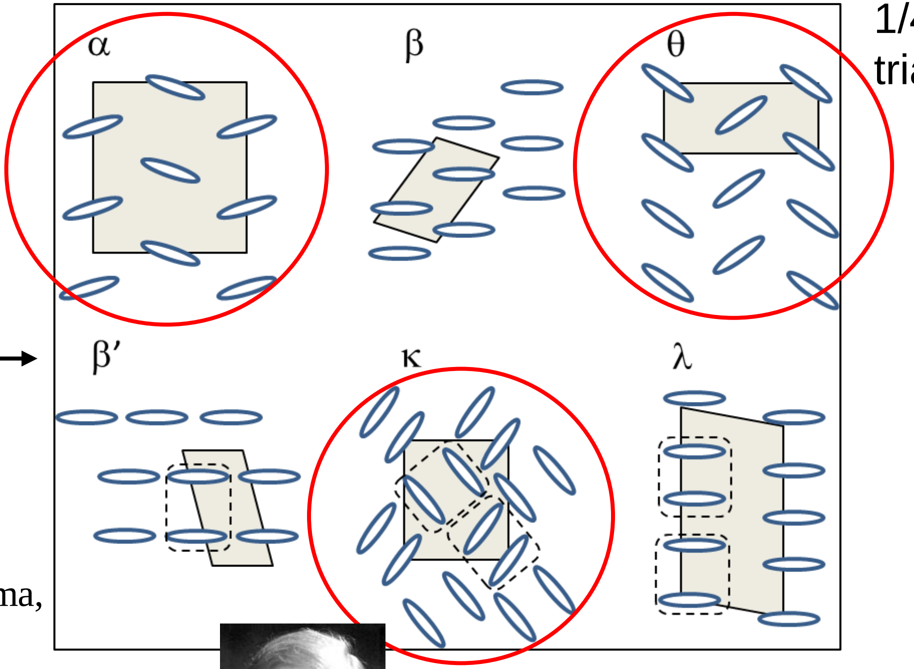


Massless Dirac ele.

Wigner Xtal/glass

1/4-filled band
triangular lattice

+1/2



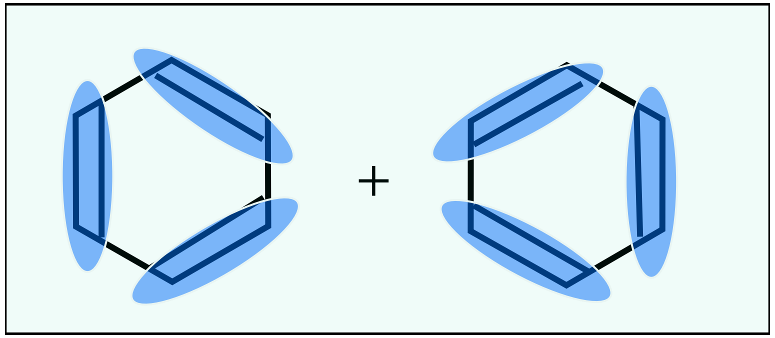
Hotta, Seo, Fukuyama, Chem. Rev., 2004

Mott physics

1/2-filled band
triangular lattice

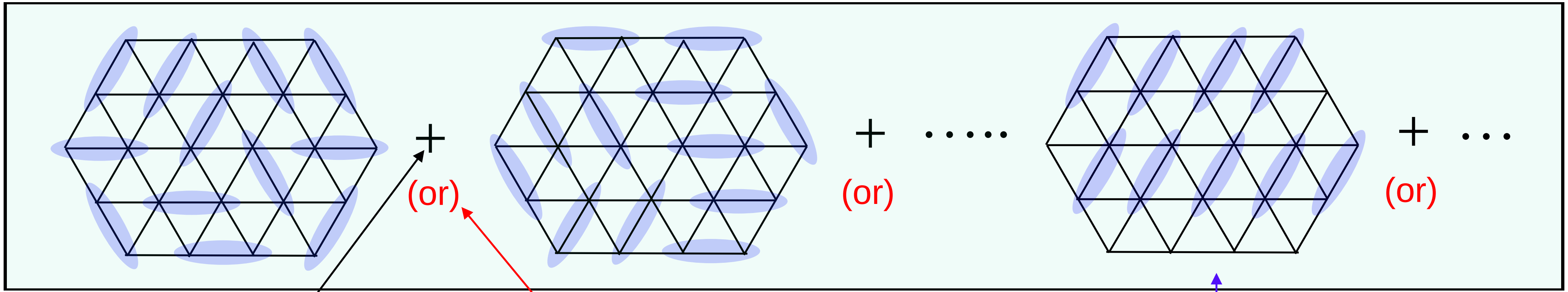
Resonating valence bond (RVB) state as a QSL

benzene



P. W. Anderson

Triangular lattice



RVB

VBG

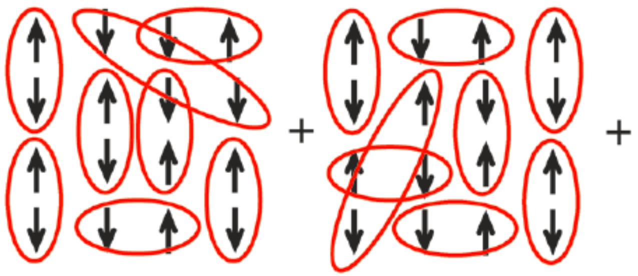
(Valence bond glass)

VBC (or VBS)

(valence bond crystal (or solid))

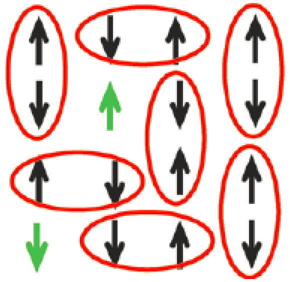
Possible variation of QSLs (according to Ogata)

(P_G: projection operator to remove double occupancies)



$| RVB >= P_G | BCS >$ gapped

$|\text{spinon FS} >= P_G | BCS;\ \Delta \rightarrow 0 >$ gapless



$|\text{spinon Dirac cone} >= P_G | nodal\ BCS >$ gapless (Dirac point)

$|\text{Chiral spin liquid} > = P_G\ |chiral\ SC >$ (?) gapped

Quantum spin liquid (QSL) candidates with a triangular lattice

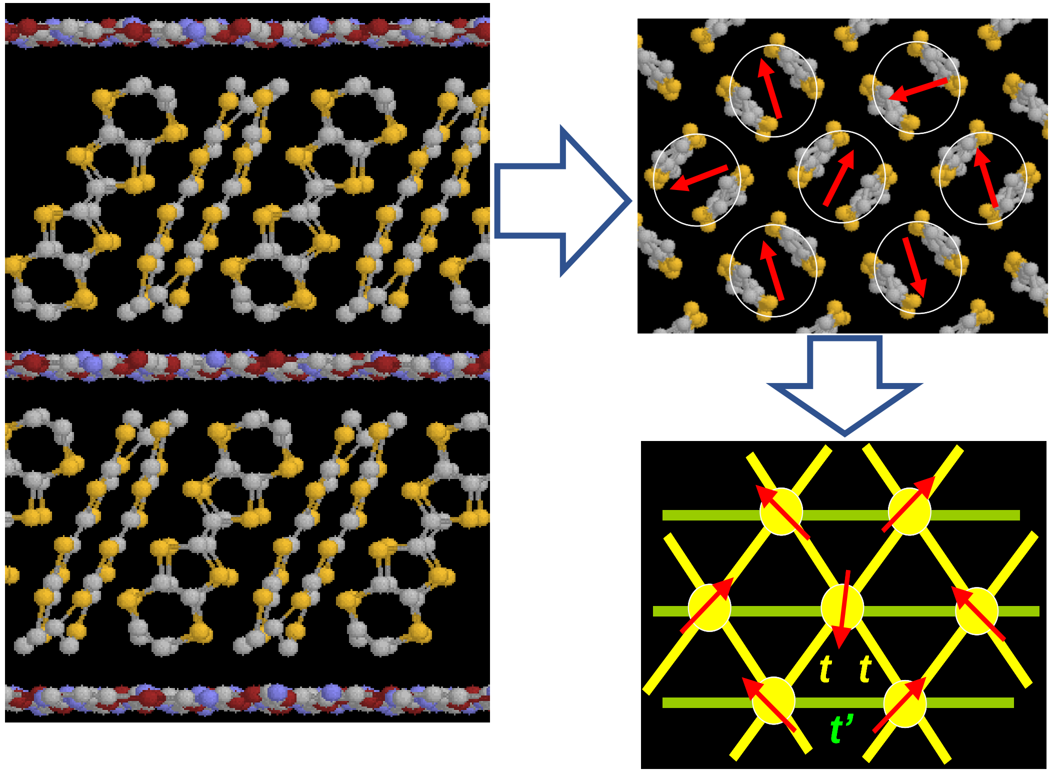
κ-$(ET)_2Cu_2(CN)_3$

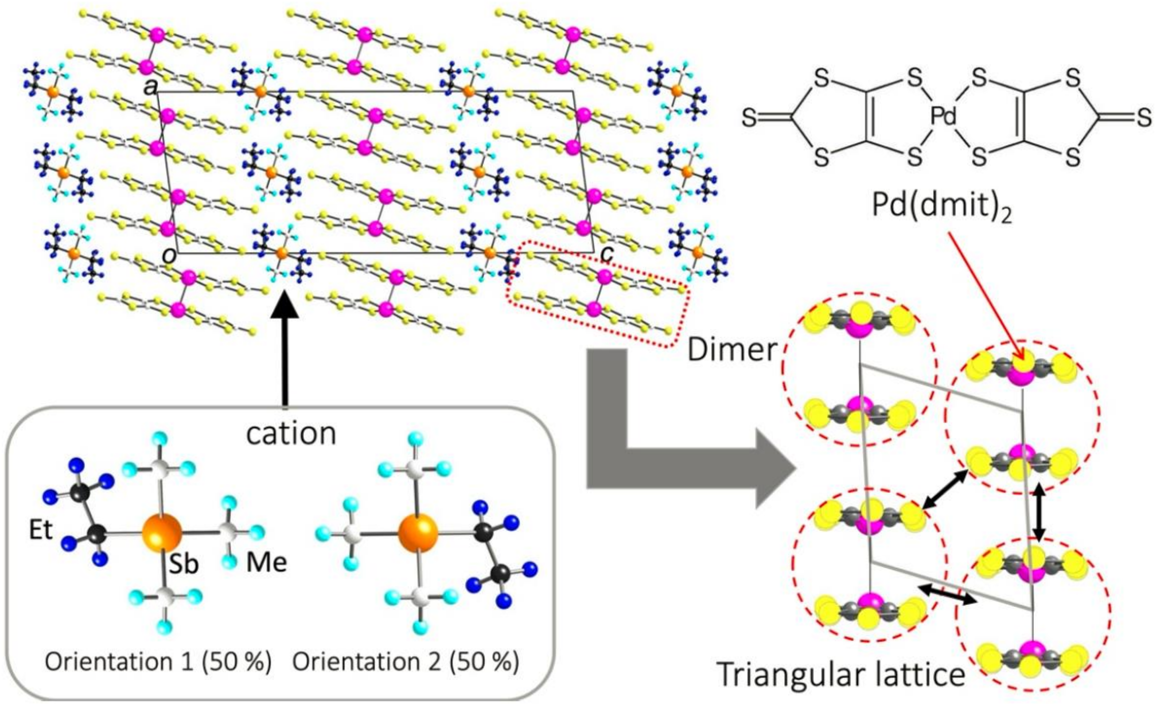
β'-$EtMe_3Sb[Pd(dmit)_2]_2$

Kato, RIKEN

ET

$Cu_2(CN)_3$



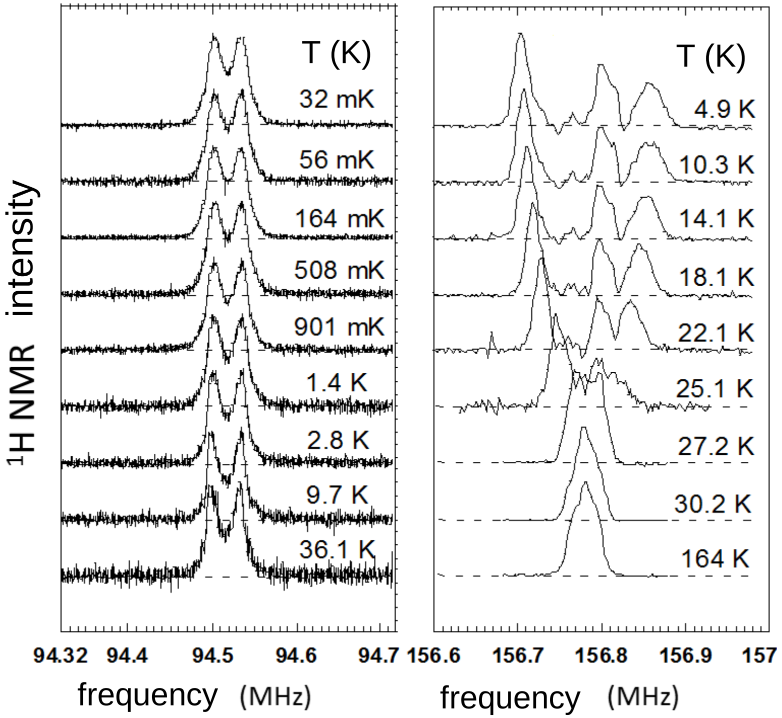


QSL manifestations

^{1}H NMR spectra

Triangular lattice — Deformed triangular lattice

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ — κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl



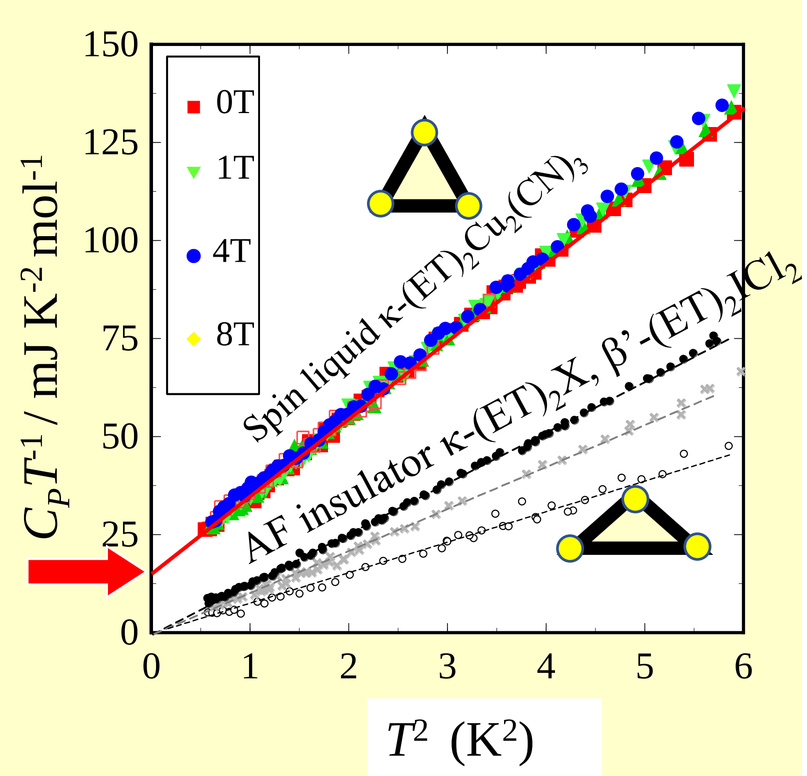
No magnetic order ⇩ **QSL !**

Magnetic order ⇩ AFM

Shimizu et al., Phys. Rev. Lett. (2003)

Specific heat

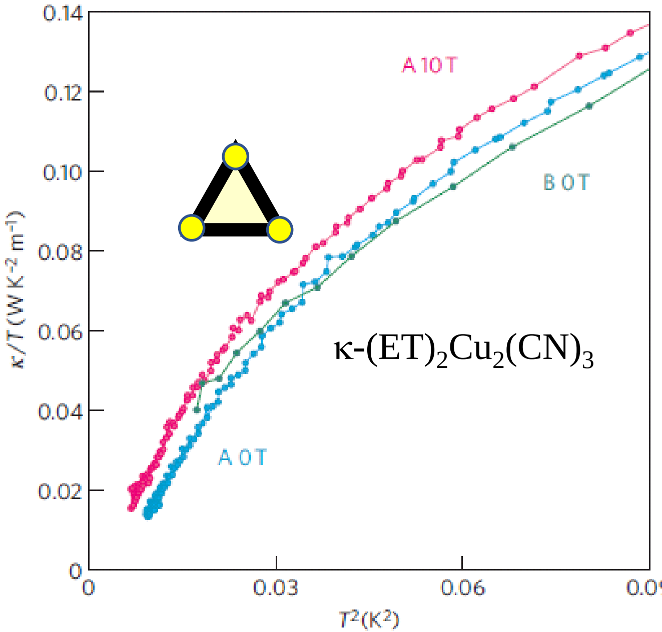
Gapless: γ = 13 mJ/K^{2}mol



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

Thermal conductivity

gapped: Δ=0.46 K



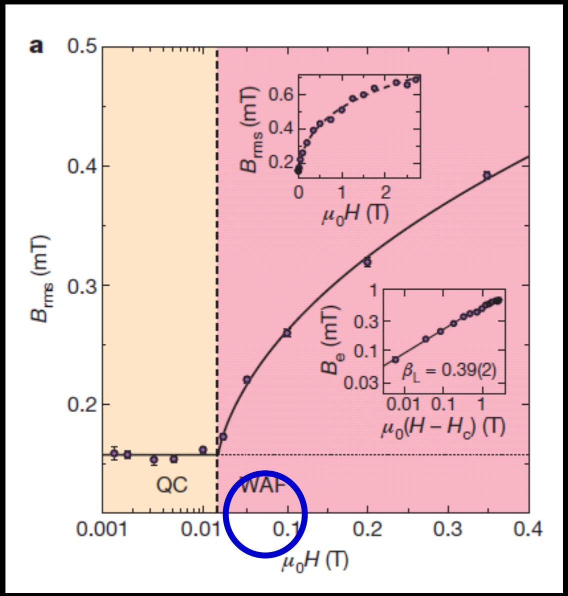
M. Yamashita et al.,
Nat. Phys. 5 (2009) 44

H-T phase diagram determined by μSR

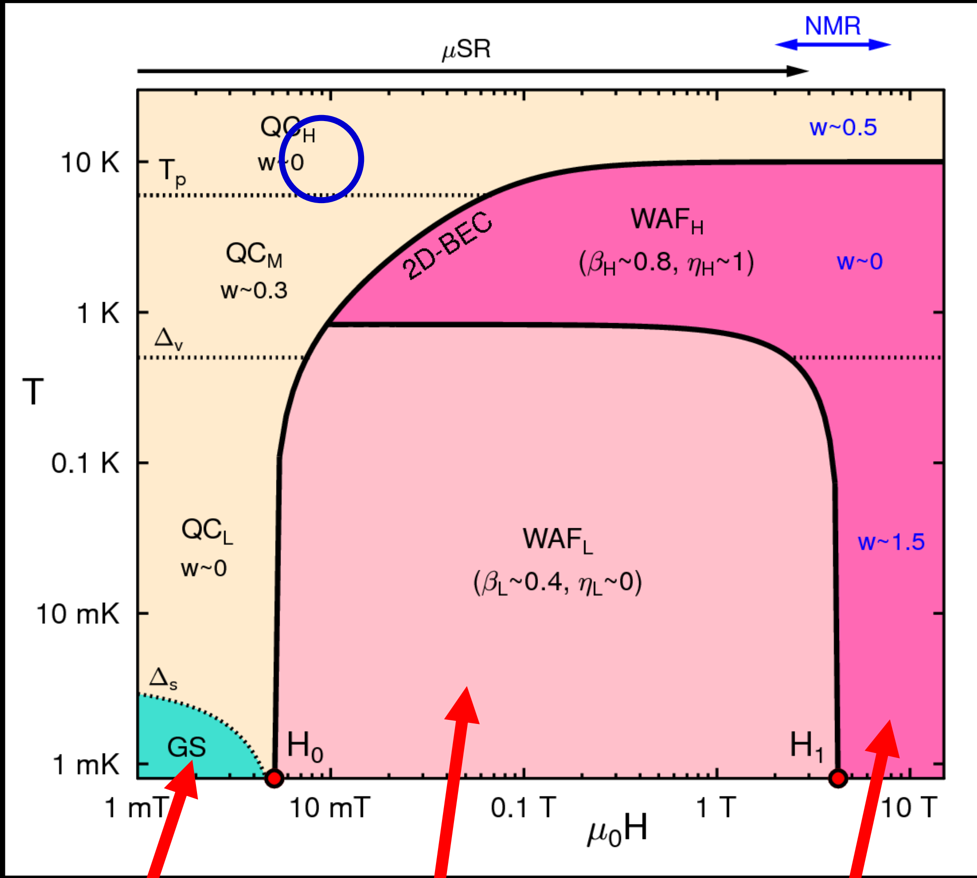
Pratt et al. *Nature* **471** (2011)612

Inhomogeneous internal field induced by external field

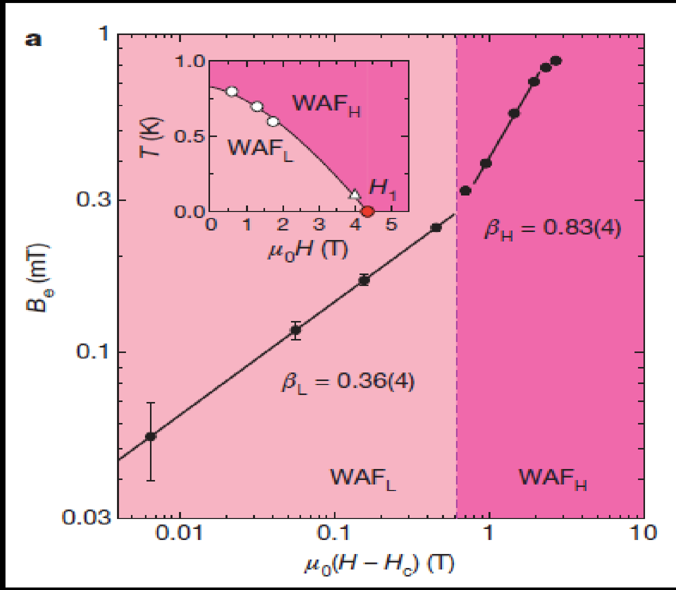
Internal Field



T= 120 mK



Internal Field



Spin gapped (4 mK)

BEC of
Bosonic spinons ?

cf. $BaCuSi_2O_6$

Deconfined
Spinons ?

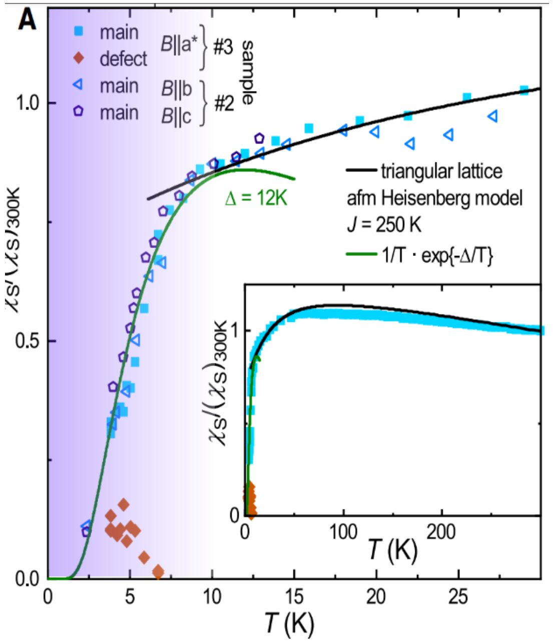
Fermionic ?

Bosonic spinons
Qi, Xu, Sachdev PRL102(2009)176401

Spin gapped or not at low temperatures ?   ESR and NMR

EPR

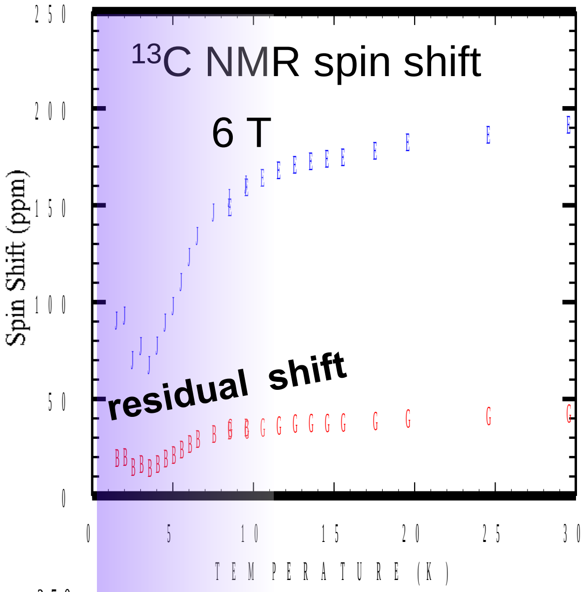
Paramagnetic spins die

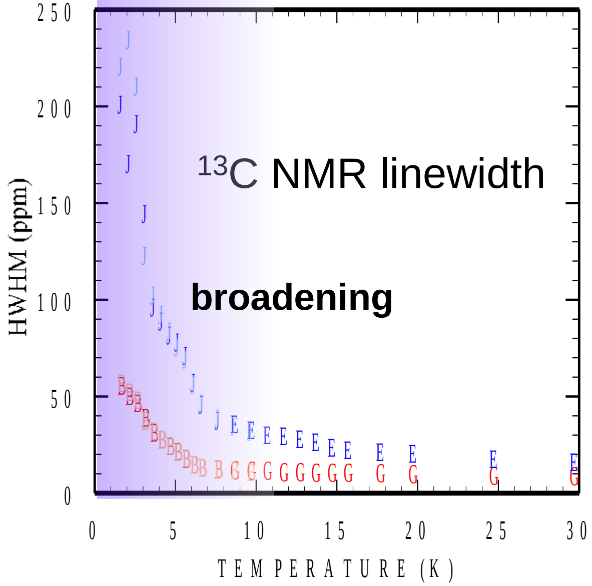


Miksch et al. Science 372, 276 (2021)

$\Delta \sim 10$ K

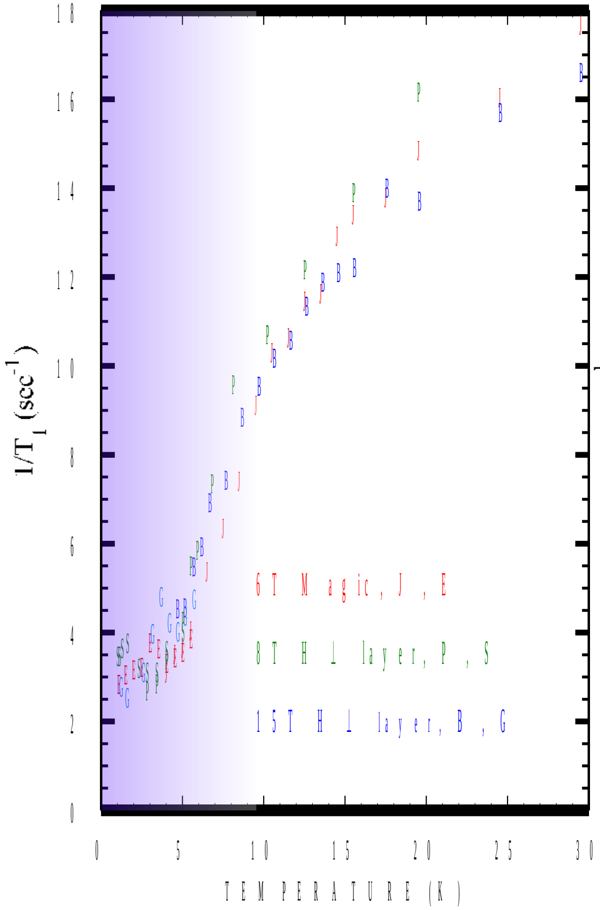
NMR spectra



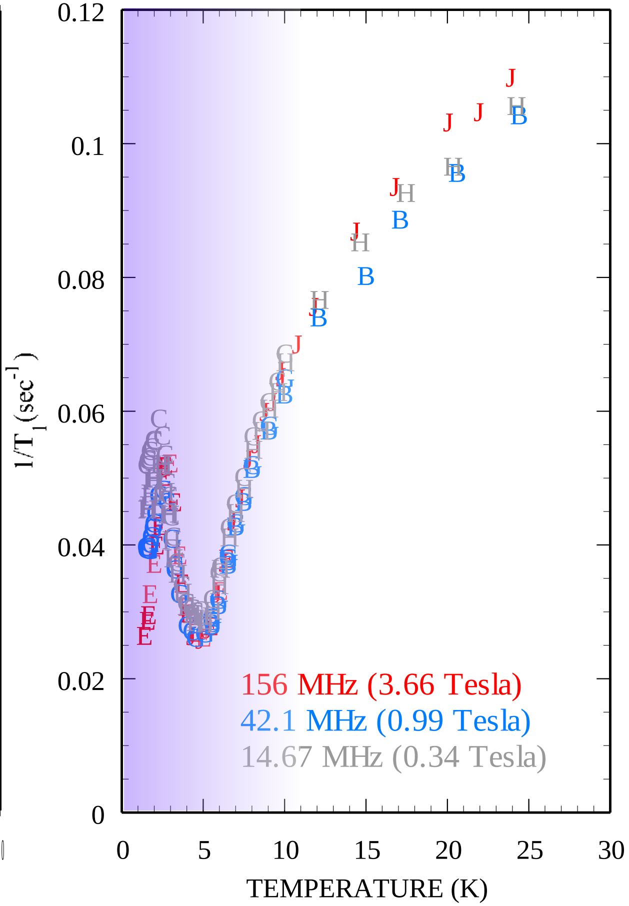


NMR relaxation rate

^{13}C NMR $1/T_1$

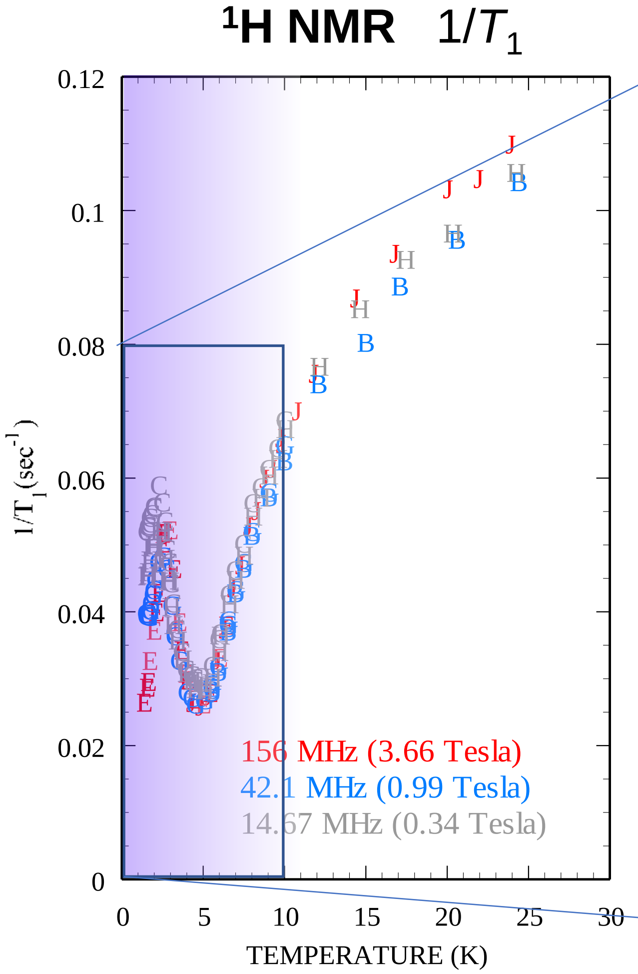


^{1}H NMR $1/T_1$

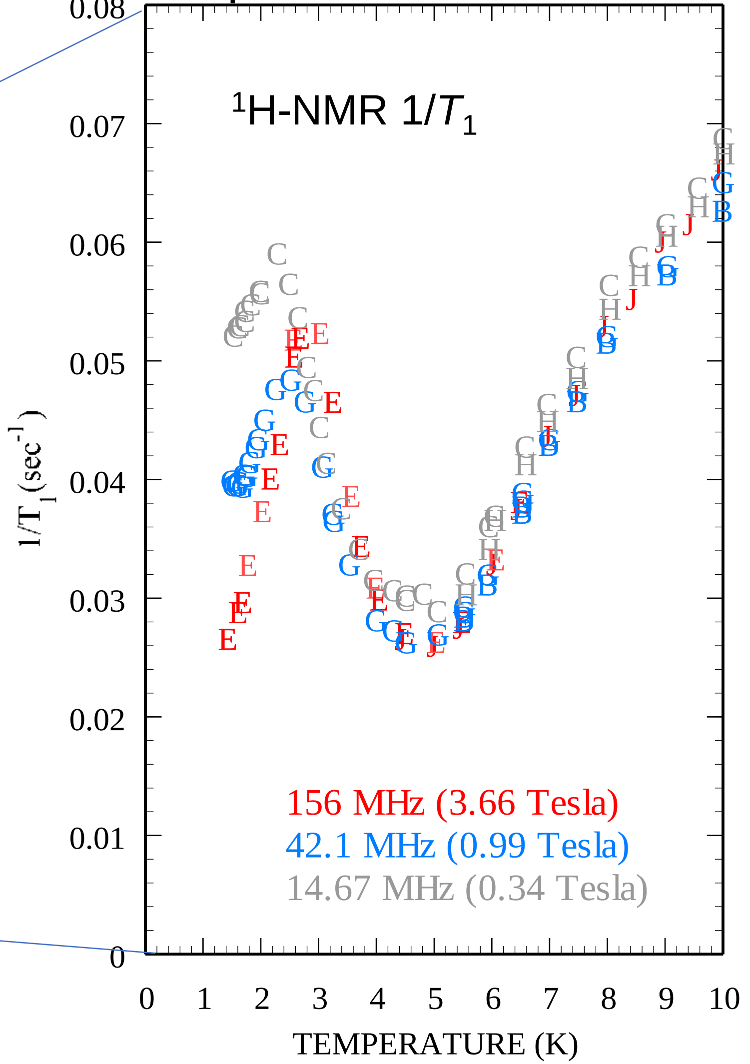


^{1}H NMR relaxation rate

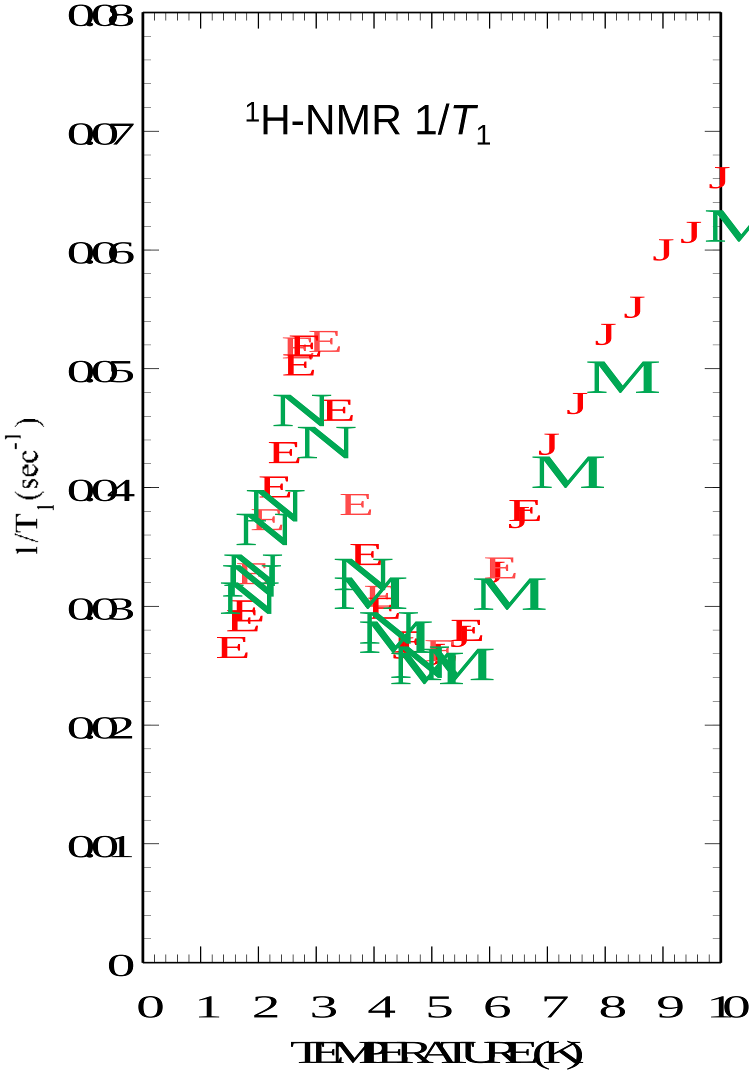
κ-$(ET)_2Cu_2(CN)$



Magnetic field (frequency) dependence



Nearly reproducible in separate samples

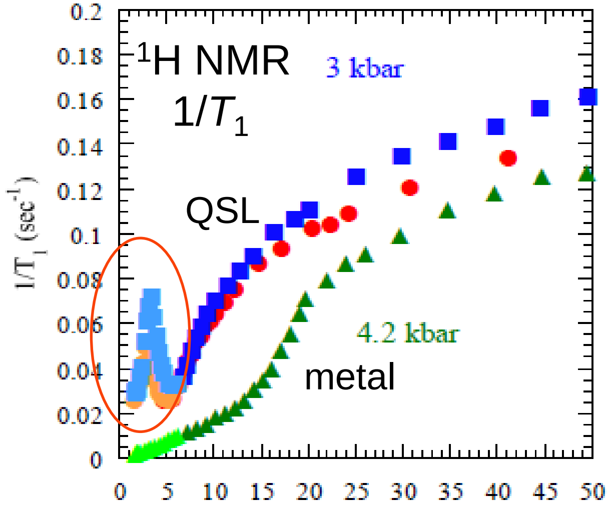


Field-insensitive above 5 K

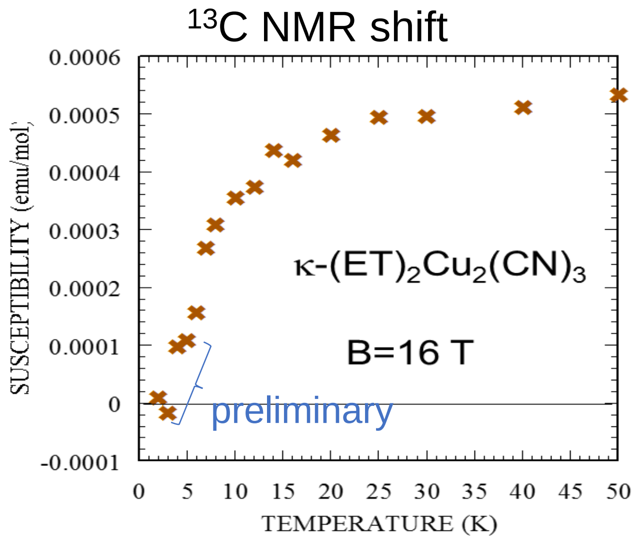
Unconventional spin gapped state: instability of QSL ?

1. Knight shift and $1/T_1$ do not vanish at low-T and line is broadened.

2. $1/T_1$ forms a sharp peak after spin gapped.
   The peak disappears in the metallic phase.



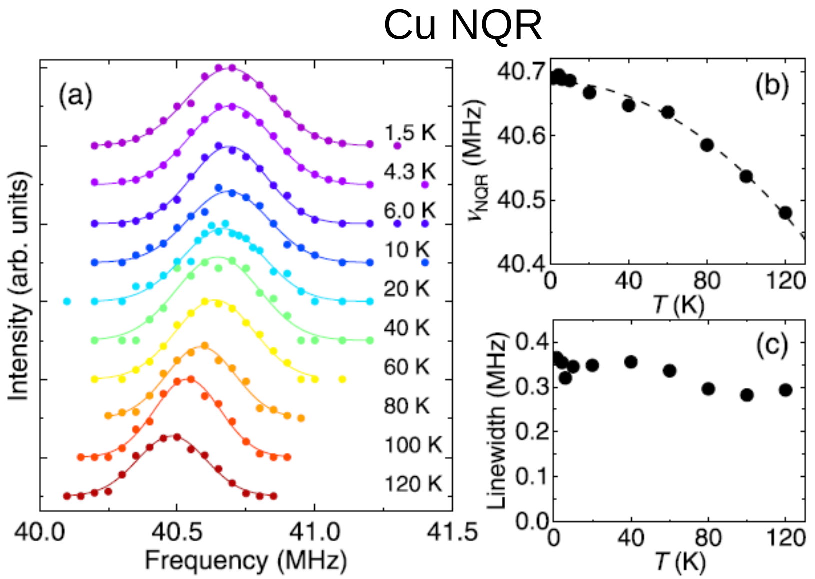
3. The spin-gapped feature is robust even against 16 T.



4. No change in NQR spectra across 6 K.

↓

VBC (VBS) ?

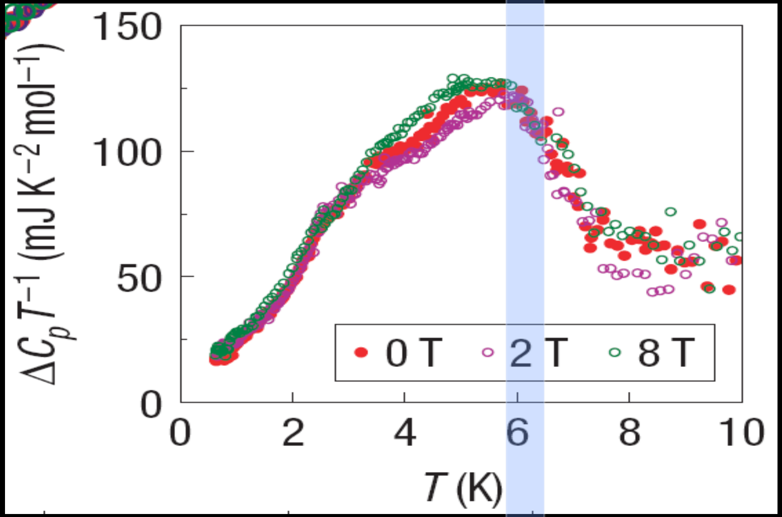


T. Kobayashi et al., PRR **2**, 042023(R) (2020)

6K-anomaly in κ-$(ET)_2Cu_2(CN)_3$

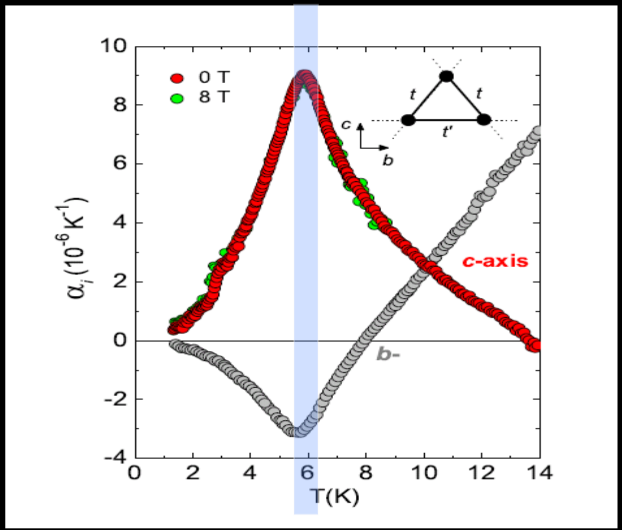
Specific heat

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



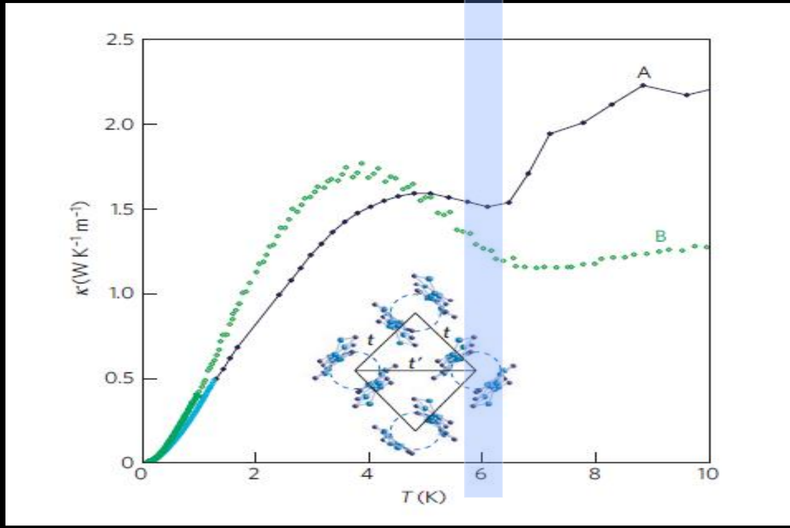
Thermal expansion coefficient

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



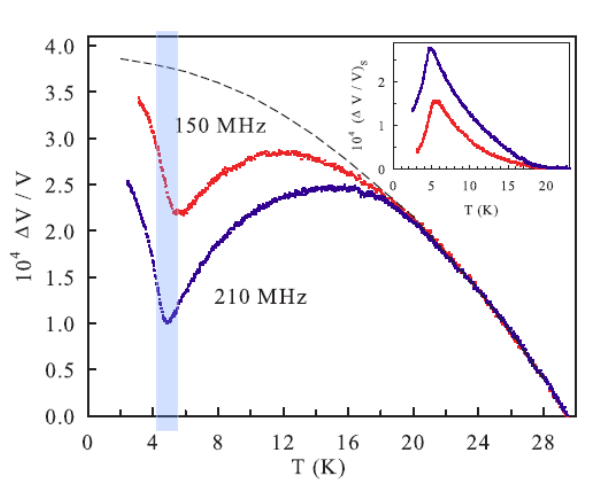
Thermal conductivity

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



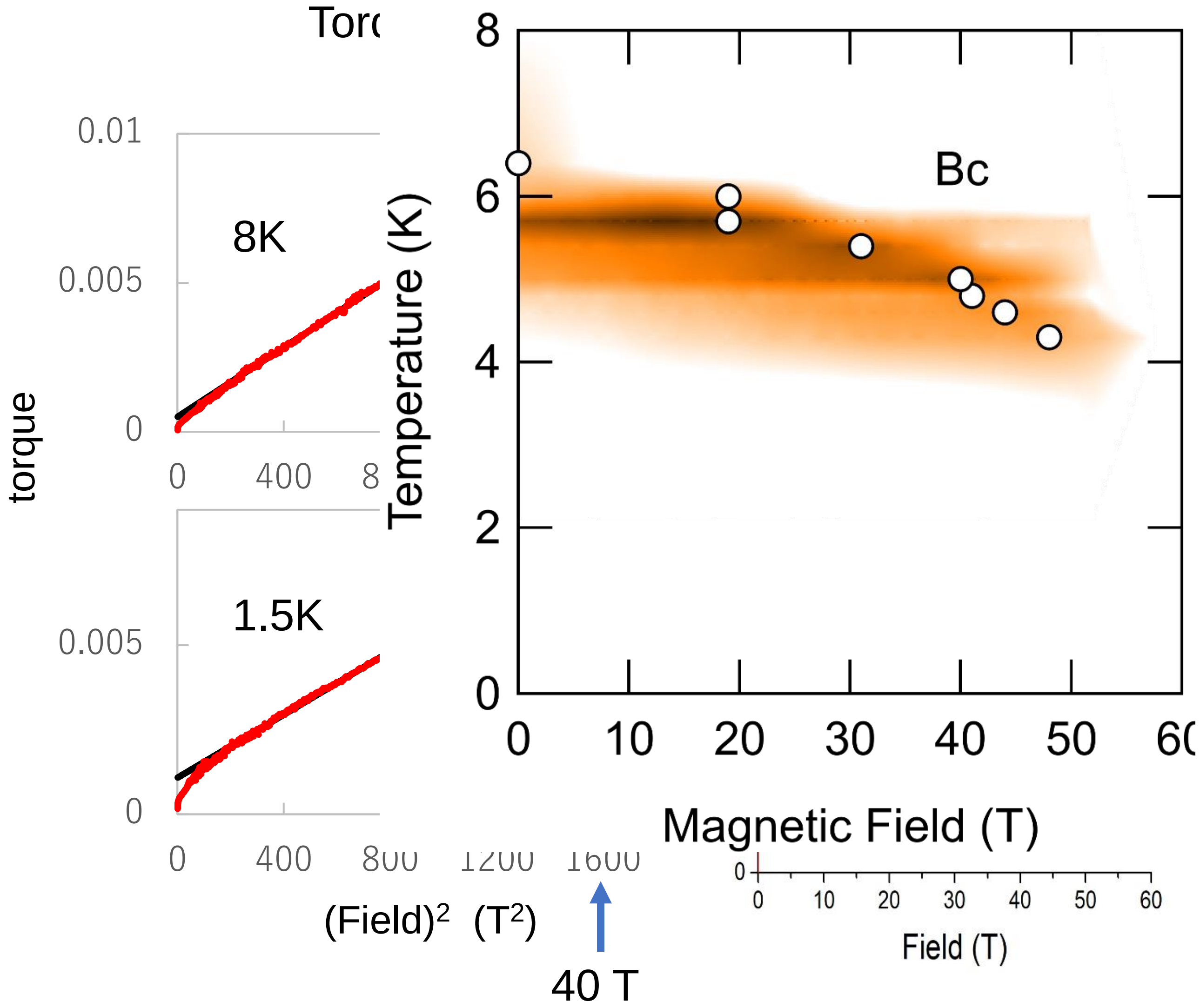
Ultrasound velocity

Poirier et al.,

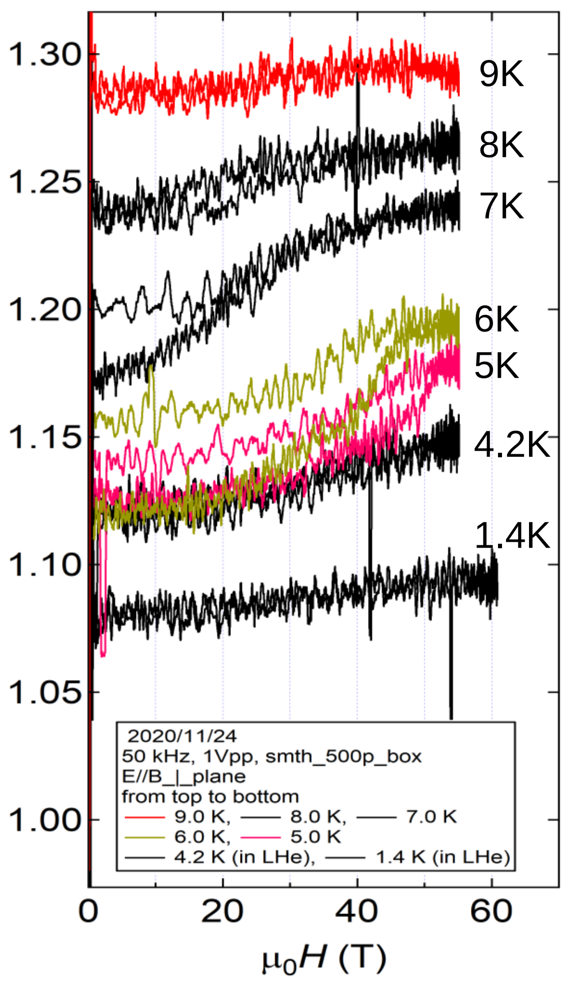


Search for quantum oscillations in κ-$(ET)_2Cu_2(CN)_3$ with magnetic fields up to 60 Tesla at ISSP

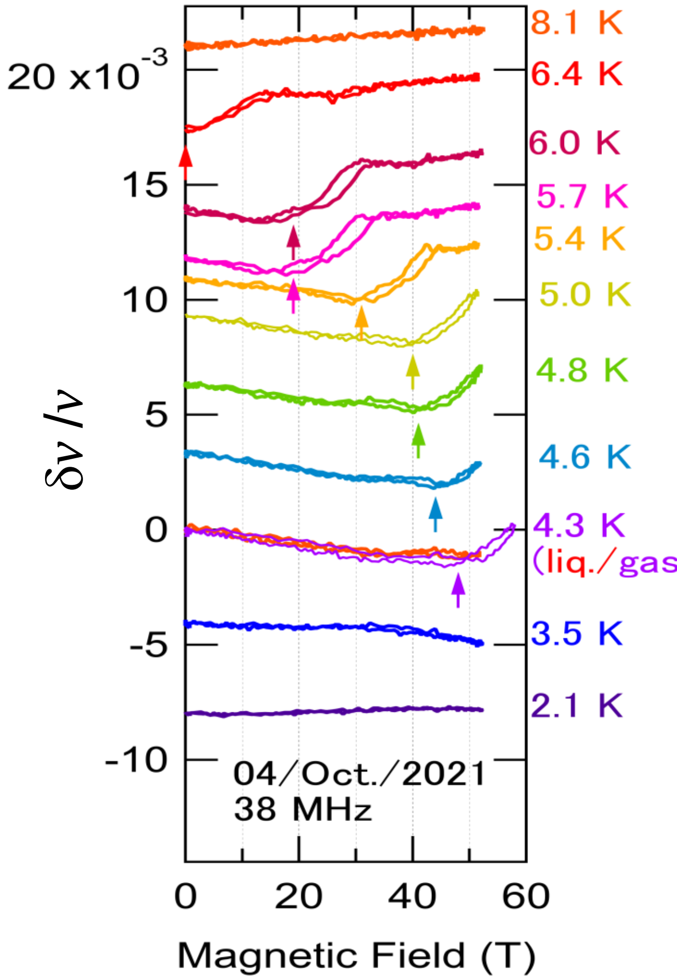
Kohama, Nomura, Miyake, Urai



Dielectric constant



Ultrasonic velocity

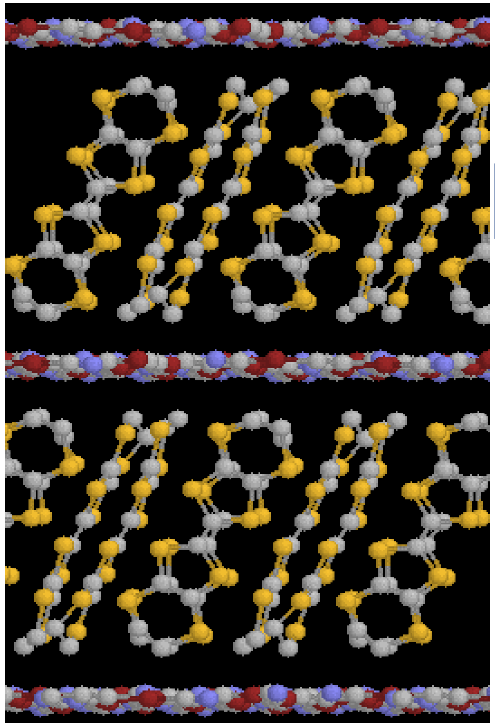


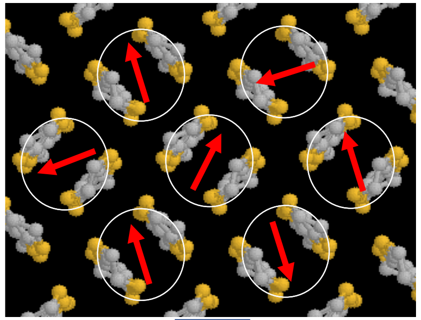
Doped spin liquid candidate κ-$(ET)_4Hg_{2.89}Br_8$ *(11% hole doping)*

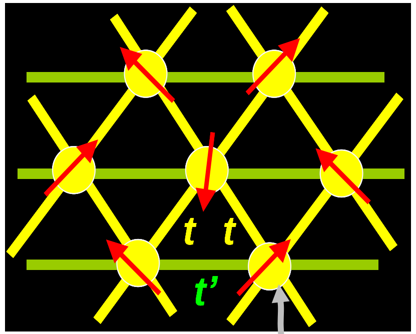
Nonstoichiometric compound κ-$(ET)_4Hg_{2.89}Br_8$

ET

$Hg_{2.89}Br_8$







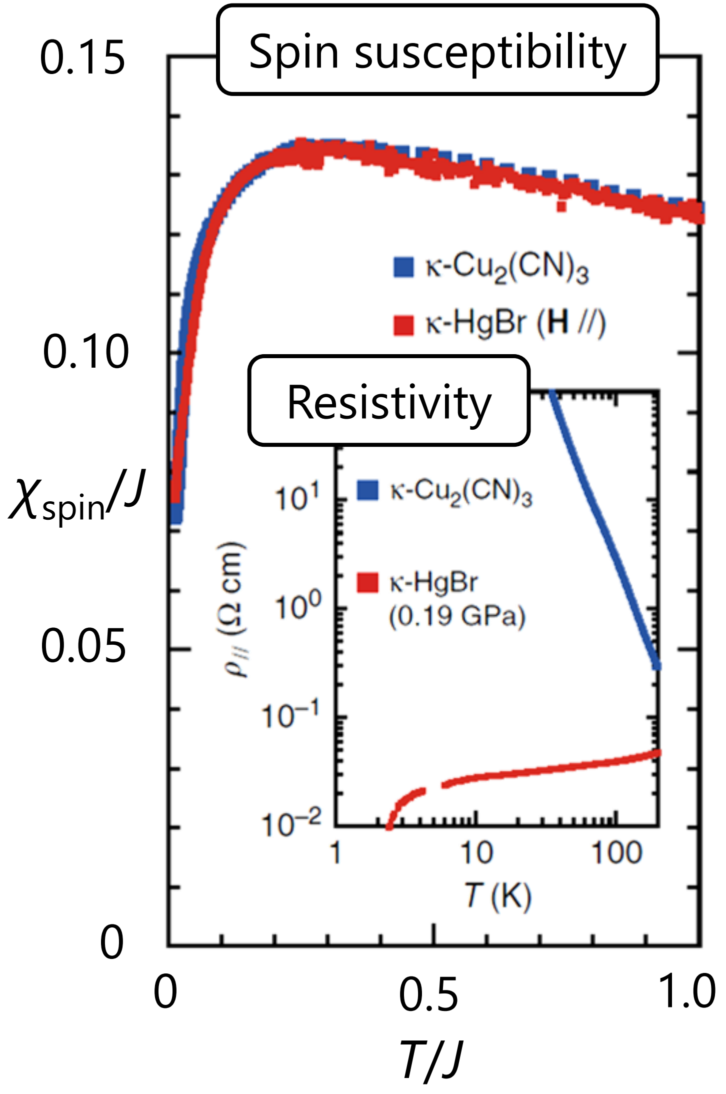
11% vacant !

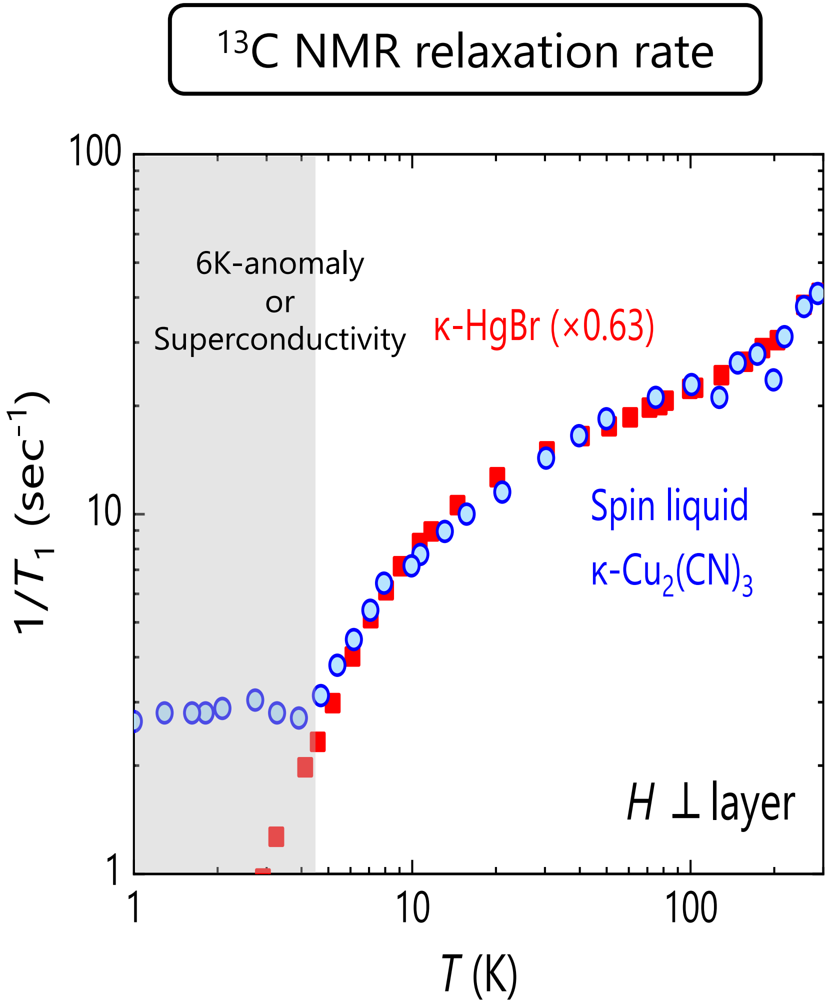
Hg forms an incommensurate sublattice against ET lattice

3.0-2.89=0.11

Non-doped and doped QSL candidates

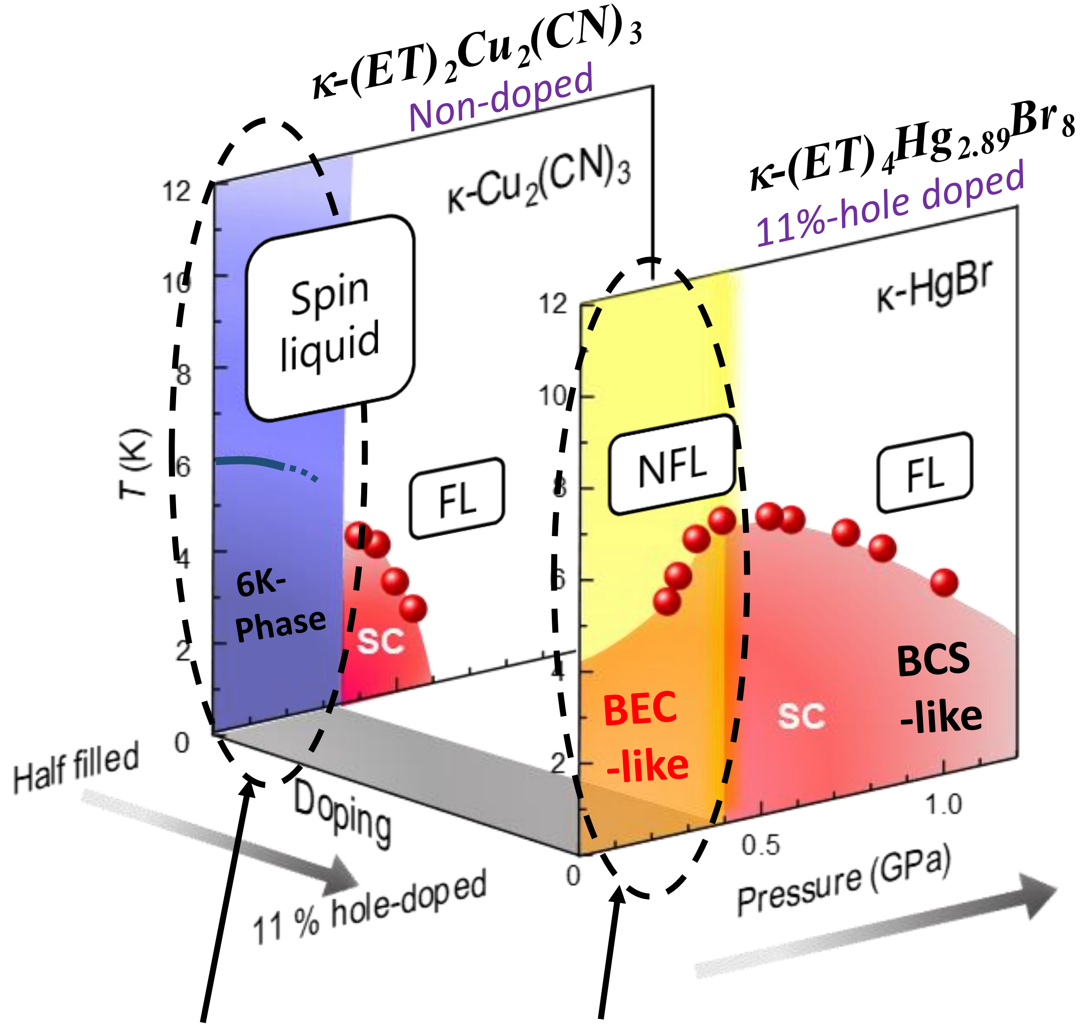
Contrasting conductivity, similar magnetism → Doped QSL





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

Phase diagram : non-doped and doped spin liquid materials



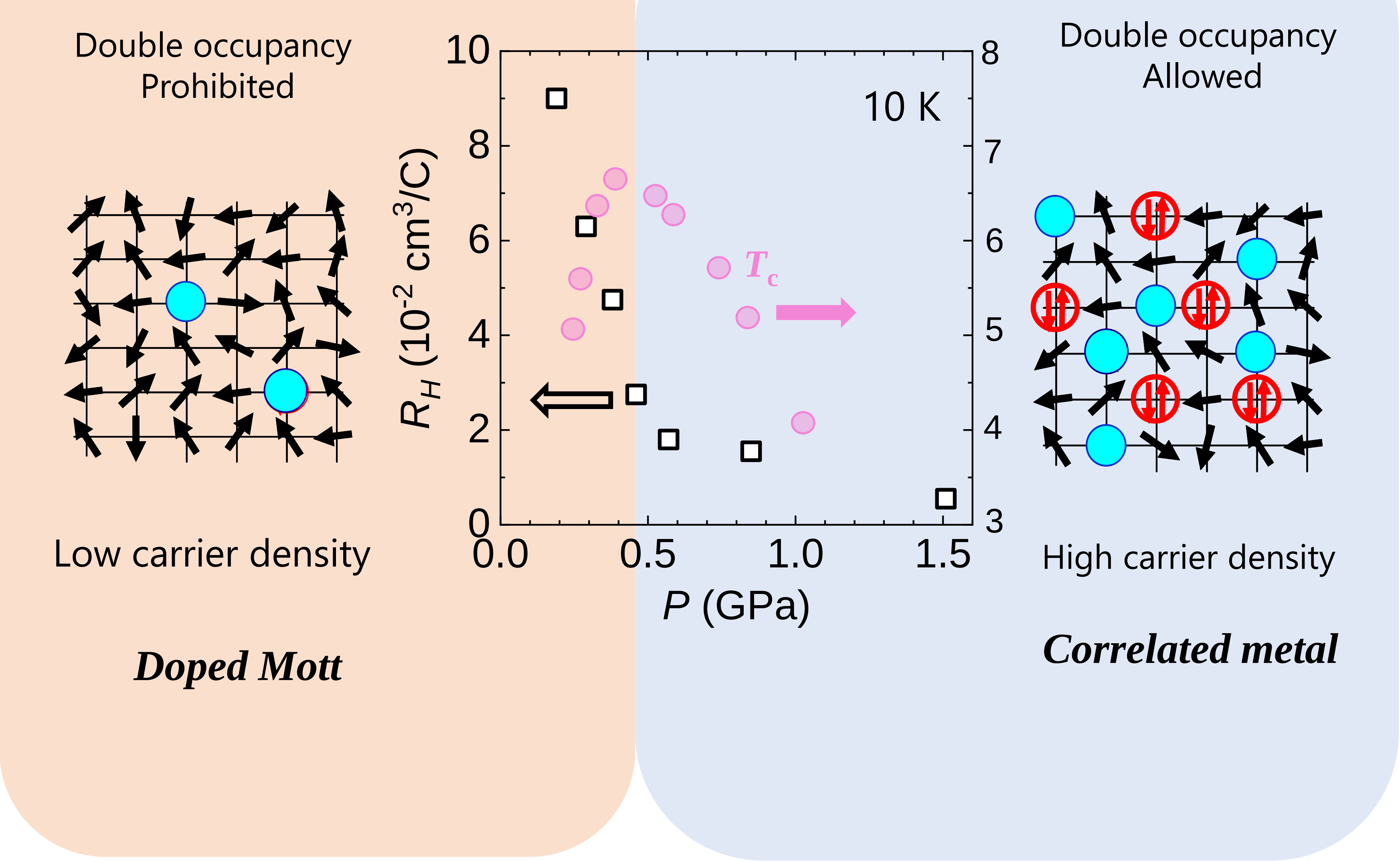
QSL phase → non-Fermi liquid
6-K phase → superconducting phase

Suzuki et al, Phys RevX 12_011016 (2022)

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

***κ*-(ET)$_4$Hg$_{2.89}$Br$_8$**

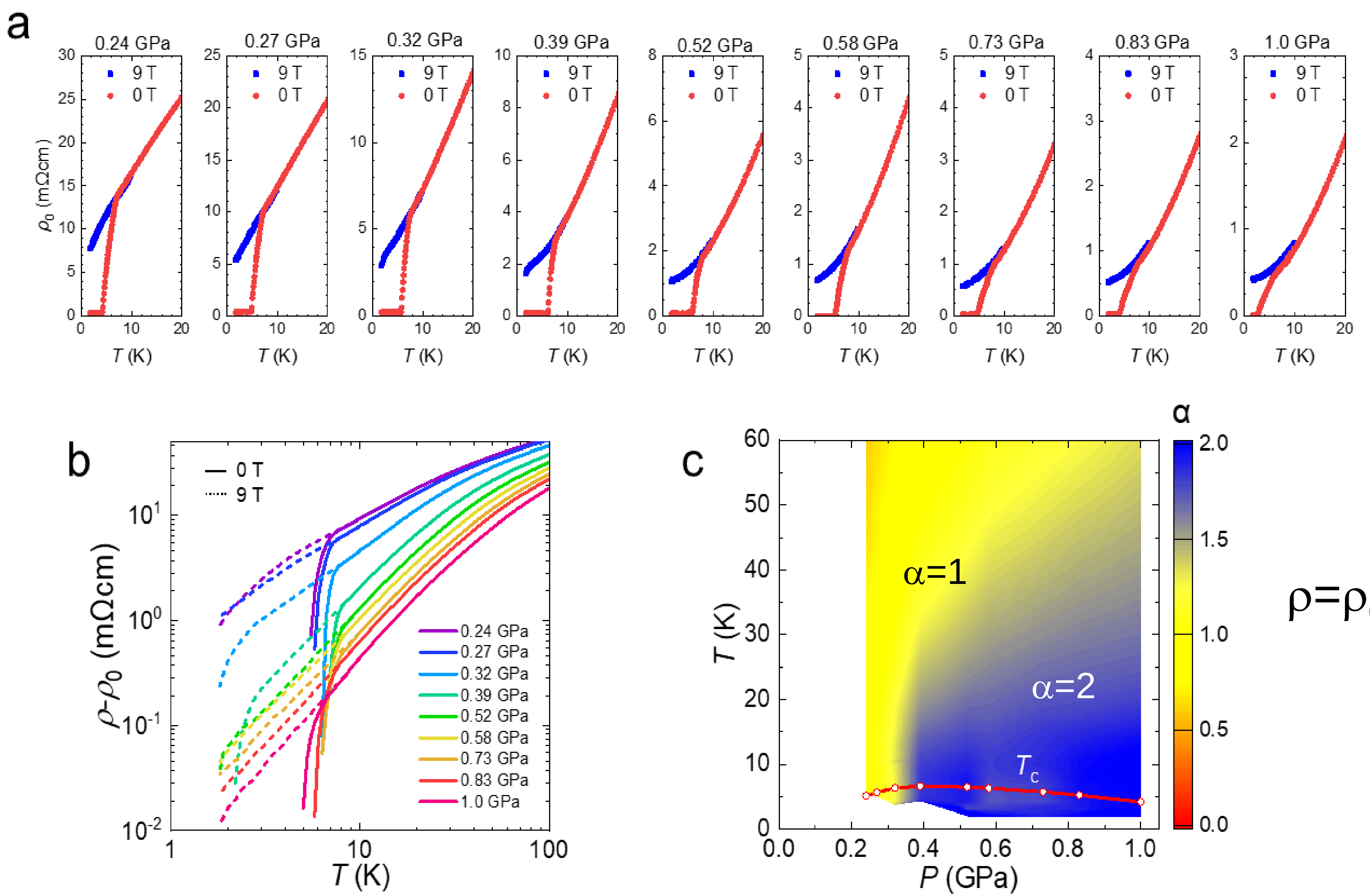
Hall coefficient ~ (***carrier number***)$^{-1}$



H. Oike, *et al.*,
PRL **114**, 067002 (2015).

Non-Fermi liquid to Fermi liquid crossover

κ-(ET)$_4$Hg$_{2.89}$Br$_8$



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

Suzuki et al, Phys RevX 12_011016 (2022)

Quantum criticality

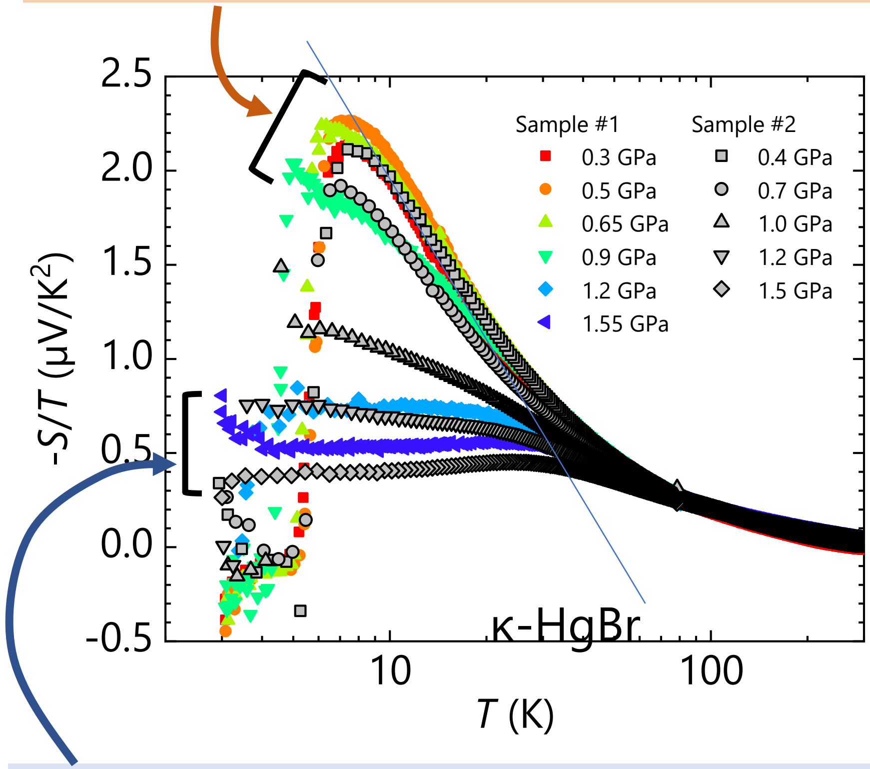
κ-$(ET)_4Hg_{2.89}Br_8$

Wakamatsu et al., arXiv:2201.10714

Seebeck coefficient S (∇T//c-axis)

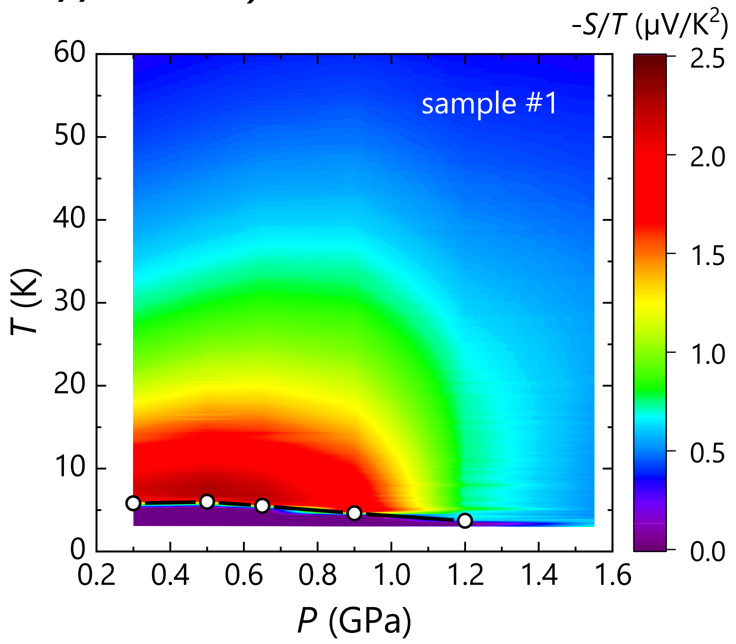
At lower pressures

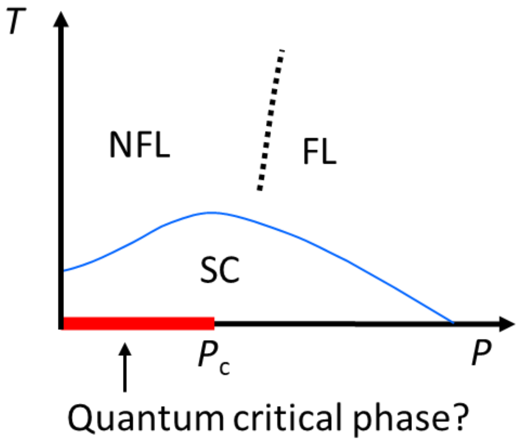
***S/T* ∝ ln *T* → quantum criticality**



At higher pressures

***S/T* = const. → Fermi liquid**



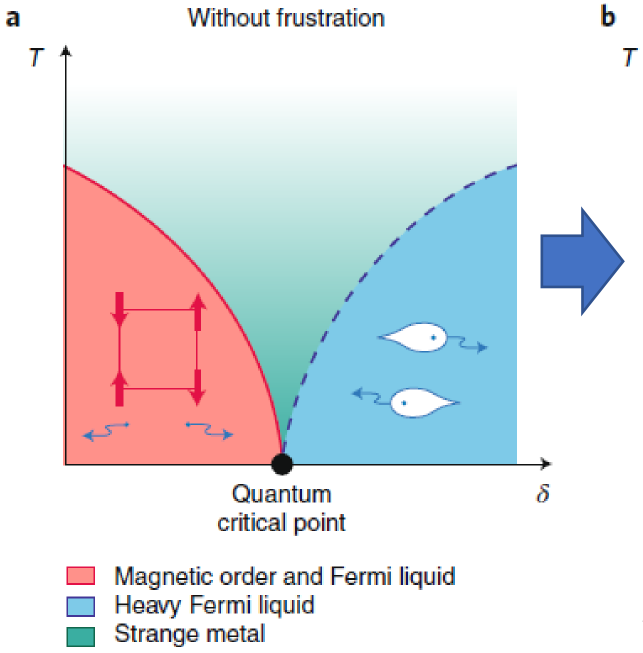


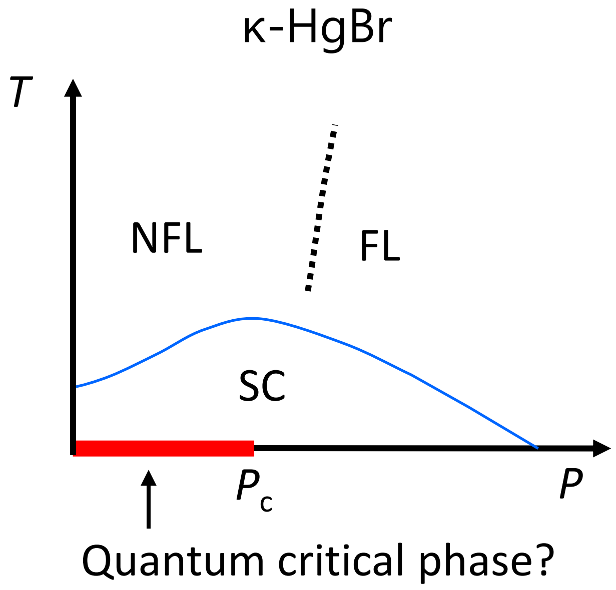
Quantum critical "*phase*"

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





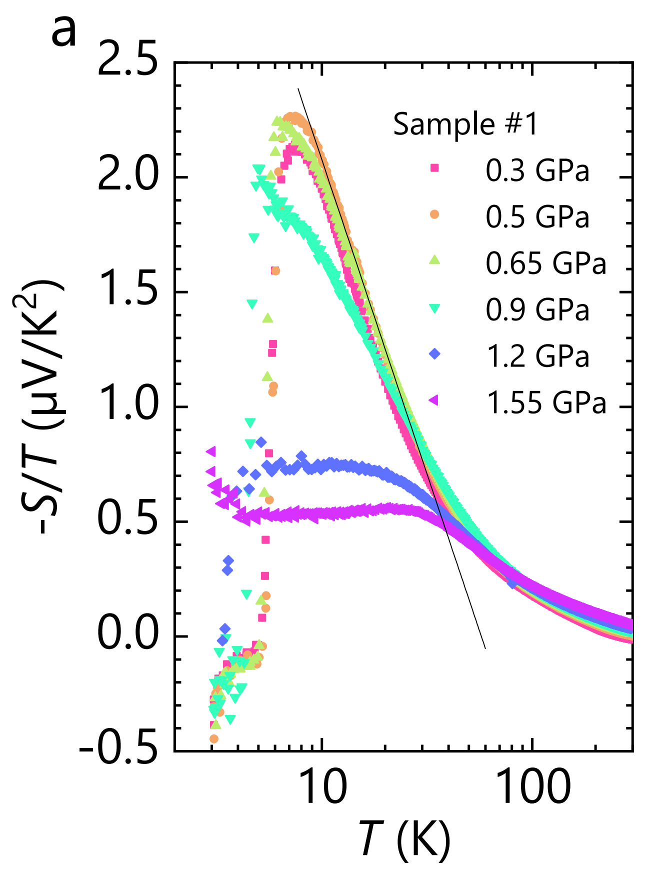
A. Ramires, *Nat. Phys.* **15**, 1212 (2019).

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

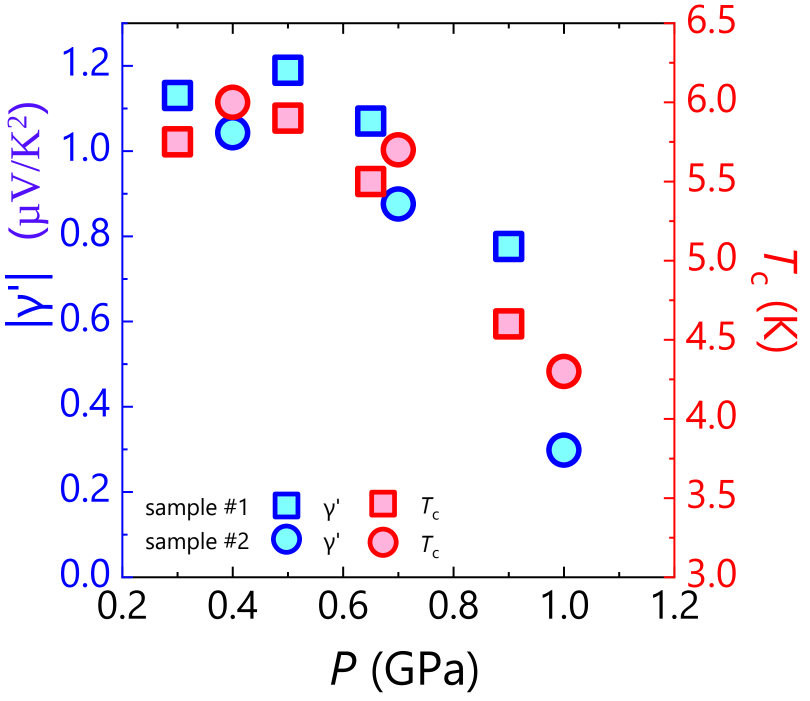
Strength of Quantum criticality

κ-$(ET)_4Hg_{2.89}Br_8$

$$S/T = \gamma' \ln(T/T_0) \quad (10\ \mathrm{K} < T < 30\ \mathrm{K})$$



|γ'| ~ 1



T_c and γ′ are scaled to each other

Table S1 | |γ'| values in the logarithmic part of -*S*/*T*

The |γ'| values in $S/T = \gamma' \ln(T/T_0)$ in the unit of μV/K².

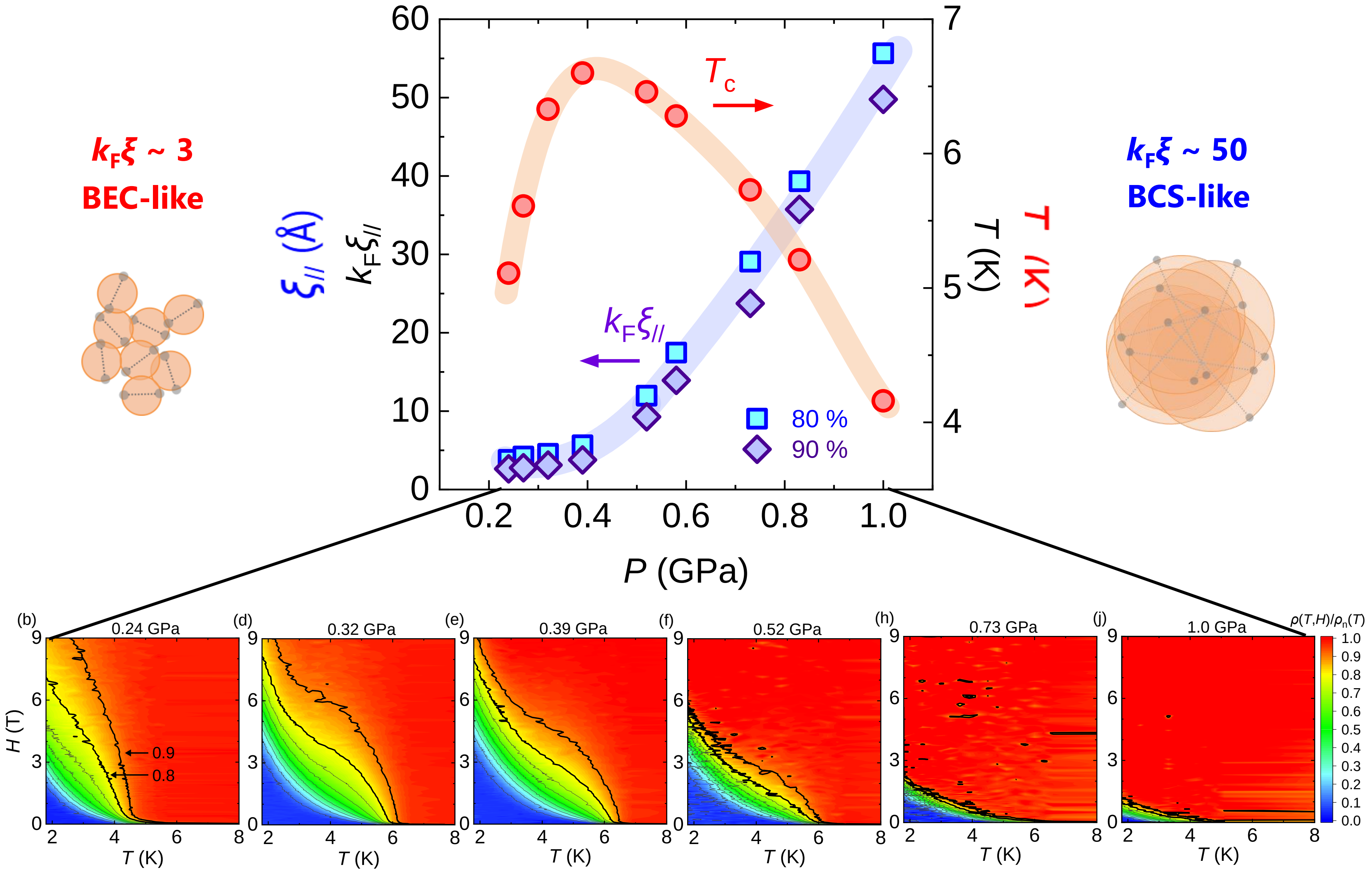
	Material	Slope value (|γ'|)
Cu, Fe SC	Nd-LSCO (p = 0.24) (ref.[6])	0.11
	Eu-LSCO (p = 0.24) (ref.[7])	0.16
	Bi2201 (p = 0.39) (ref.[8])	0.05
	PCCO (x = 0.16-0.19) (ref.[9])	0.012-0.038
	LCCO (x = 0.15-0.17) (ref.[9])	0.0095 – 0.049
	$[BiBa_{0.66}K_{0.36}O_2]CoO_2$ (ref.[10])	0.62
	$Ba(Fe_{1-x}Co_x)_2As_2$ (p=0.022-0.13) (ref.[11])	0.32 - 0.895
	$EuFe_2(As_{1-y}P_y)_2$ (y=0.26, 0.36) (ref.[18])	0.077, 0.16
HF	UCoGe (H=11.1 T) (ref.[12])	2.3
	$YbRh_2Si_2$ (ref.[13])	4.5
	$CeCu_{5.9}Au_{0.1}$ (ref.[14])	6.2
	Ce_2PdIn_8 (ref.[15])	1.6
	YbAgGe (ref.[16])	4.7
	YbPtBi (ref.[17])	0.25

Wakamatsu et al., arXiv:2201.10714

Pressure-induced BEC to BCS

κ-(ET)$_4$Hg$_{2.89}$Br$_8$

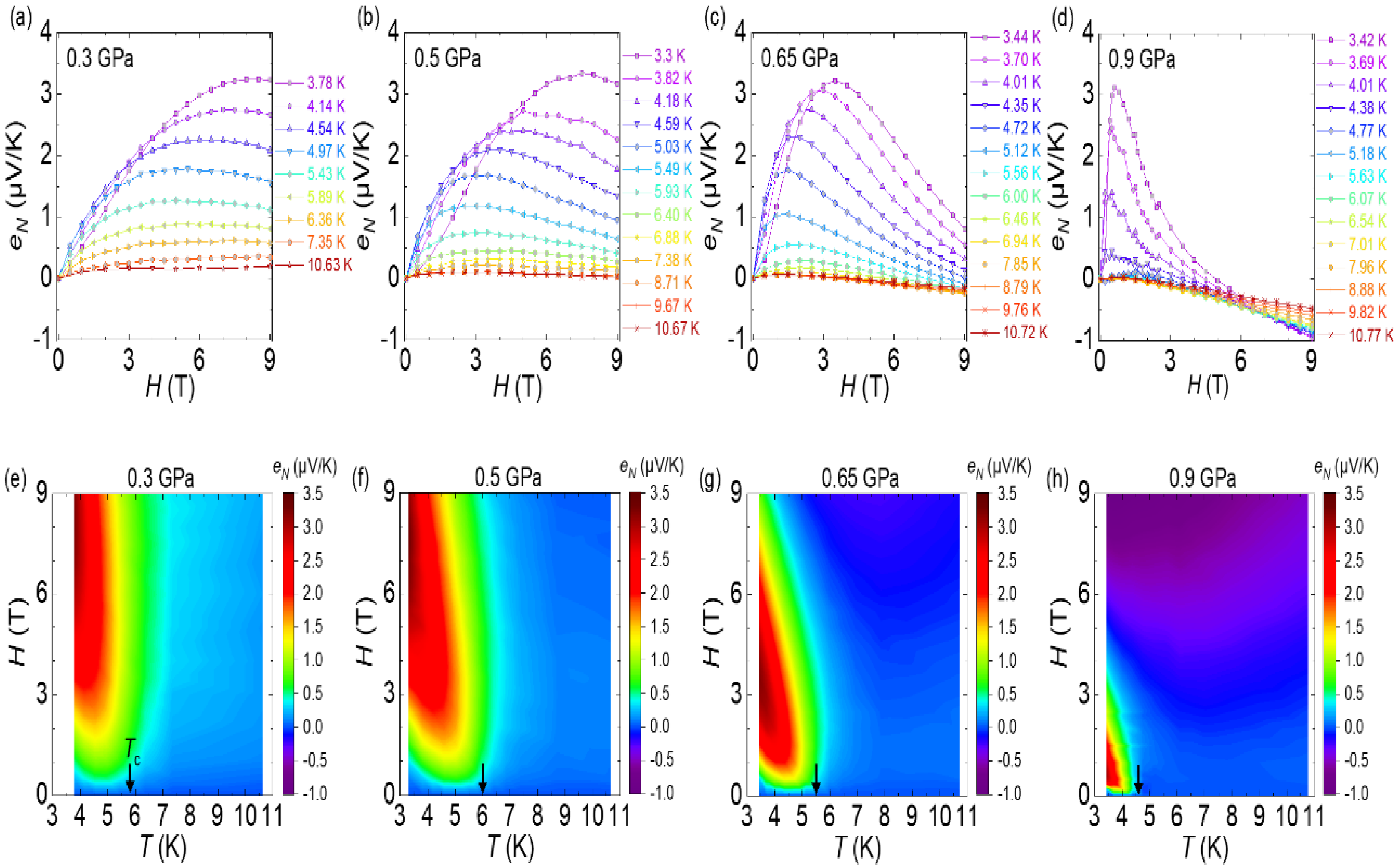
Y. Suzuki *et al.*, Phys. Rev. X **12**, 011016 (2022).

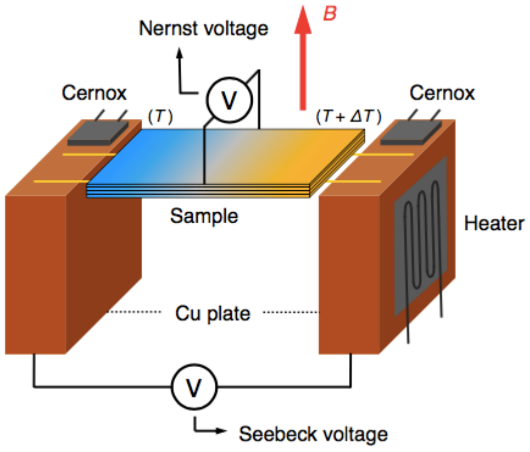


Nernst effect

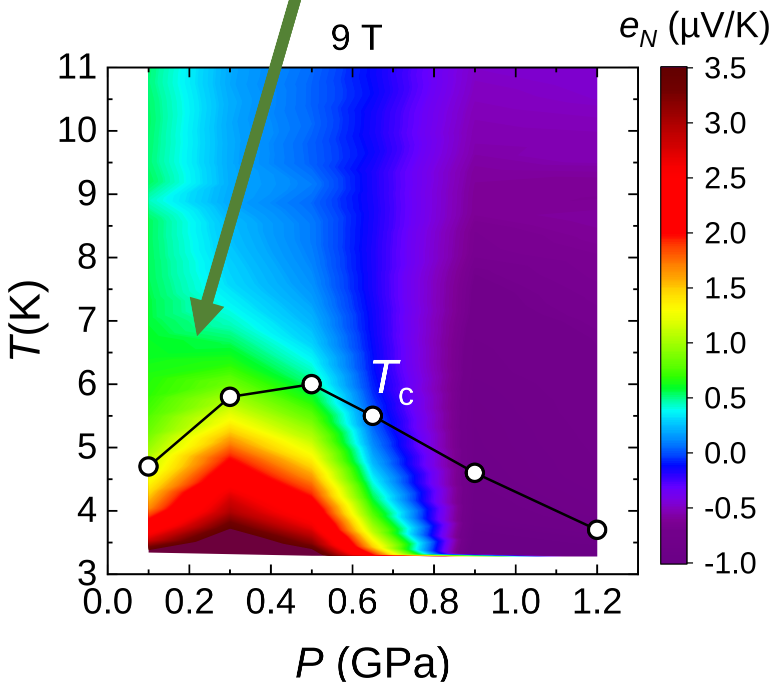
κ-$(ET)_4Hg_{2.89}Br_8$

Field-robust superconductivity





Preformed pairs

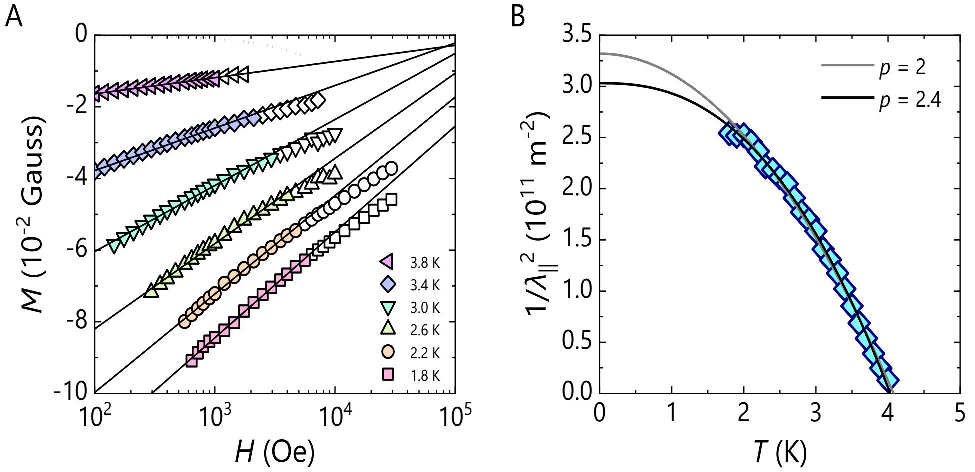


Y. Suzuki *et al.*, Phys. Rev. X **12**, 011016 (2022).

Superfluid density

κ-(ET)$_4$Hg$_{2.89}$Br$_8$

magnetization ⟶ penetration depth

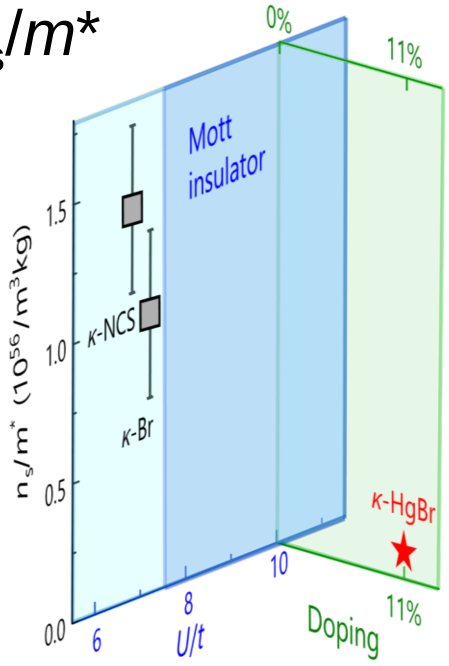


$$-4\pi M = \frac{\varphi_0}{8\pi\lambda^2}\ln\left(\frac{\beta H_{c2}}{H}\right)$$

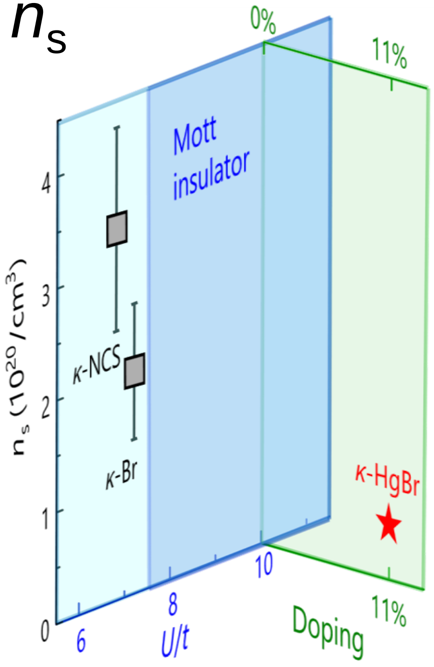
cf. M. Lang et al., *Phys. Rev. B* **46**, 5822-5825 (1992).

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

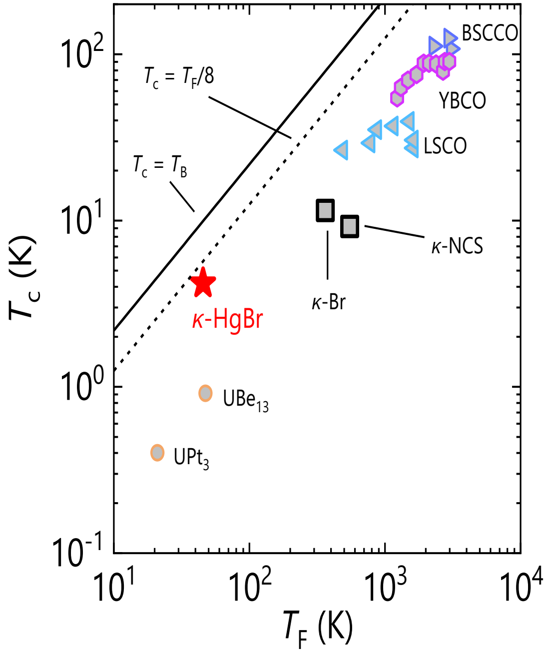
n_s/m^*



n_s



Uemura plot



Reduced superfluid density

n_s ~ 15-25% of total carriers

Large T$_c$/T$_F$ ratio

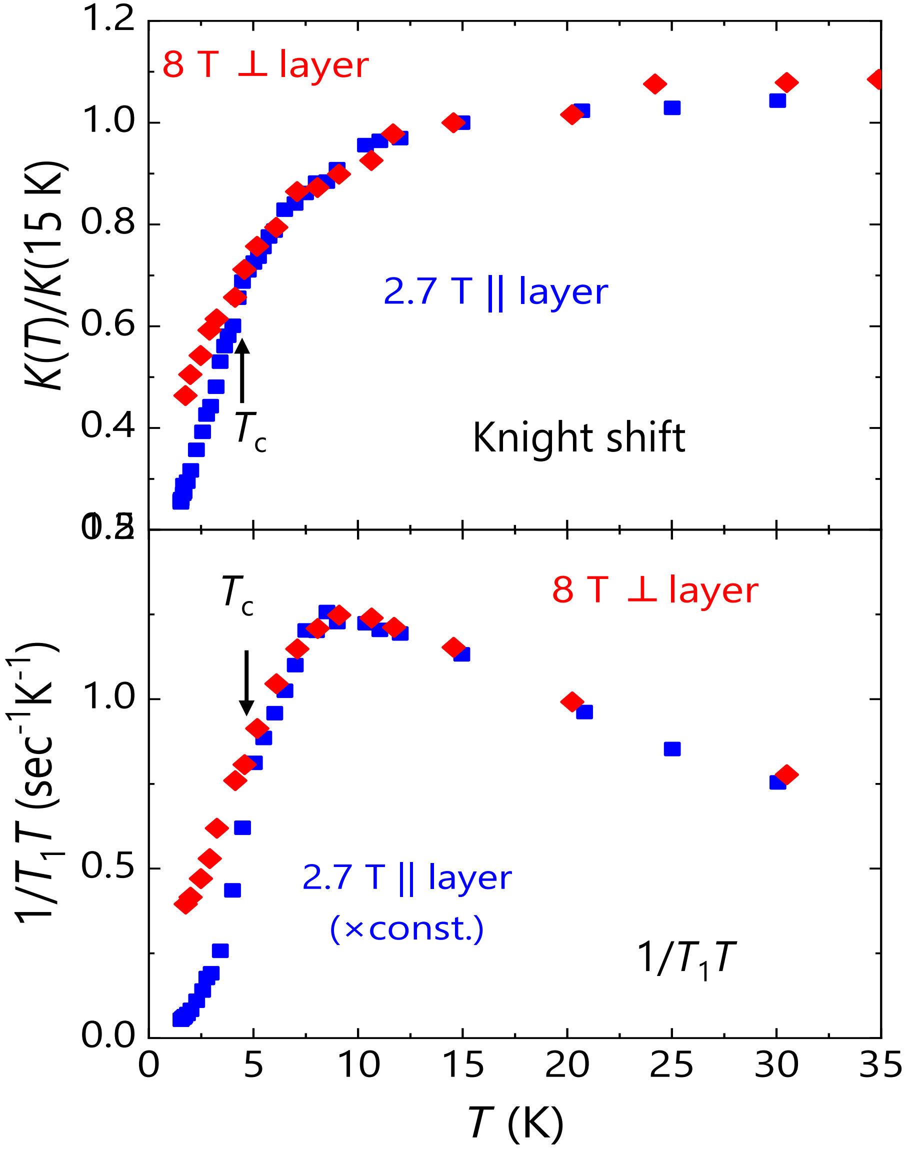
T$_c$/T$_F$ ~ 0.1

Wakamatsu et al., arXiv. 2205.03682

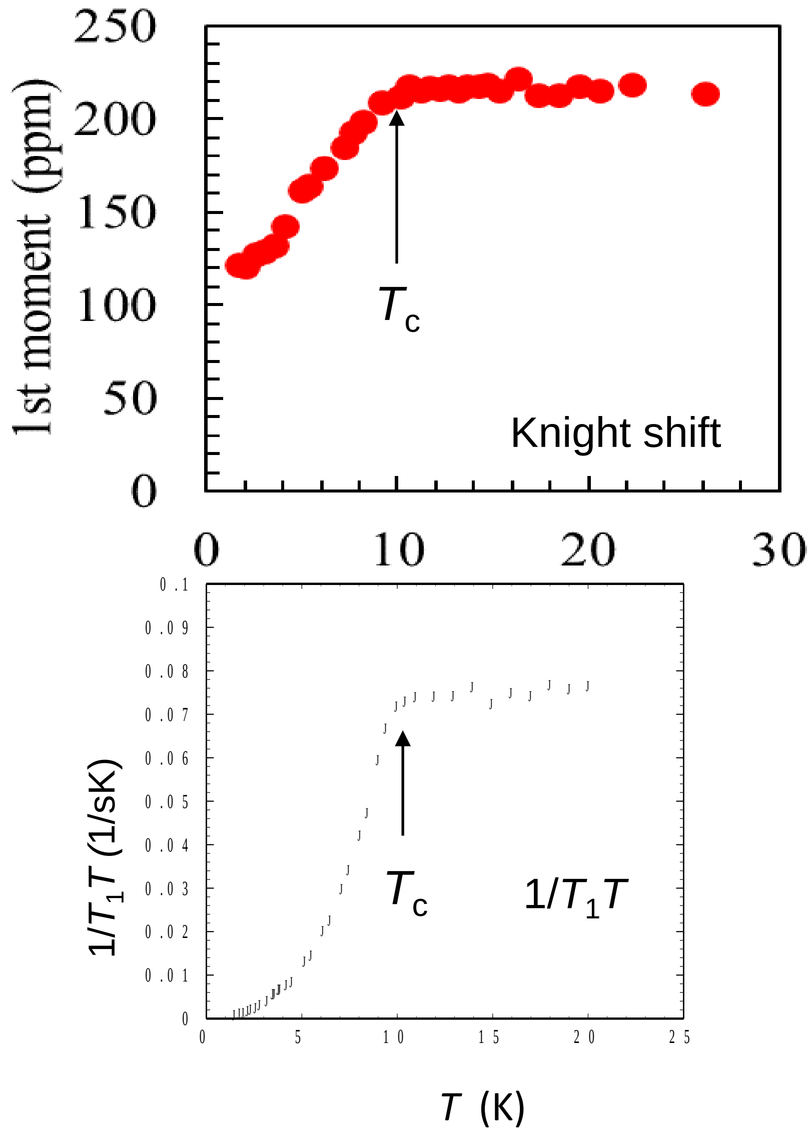
^{13}C NMR Knight shift and relaxation rate $1/T_1$

Preformed pairs (and pseudo-gapped metal)

κ-(ET)$_4$Hg$_{2.89}$Br$_8$ (doped)



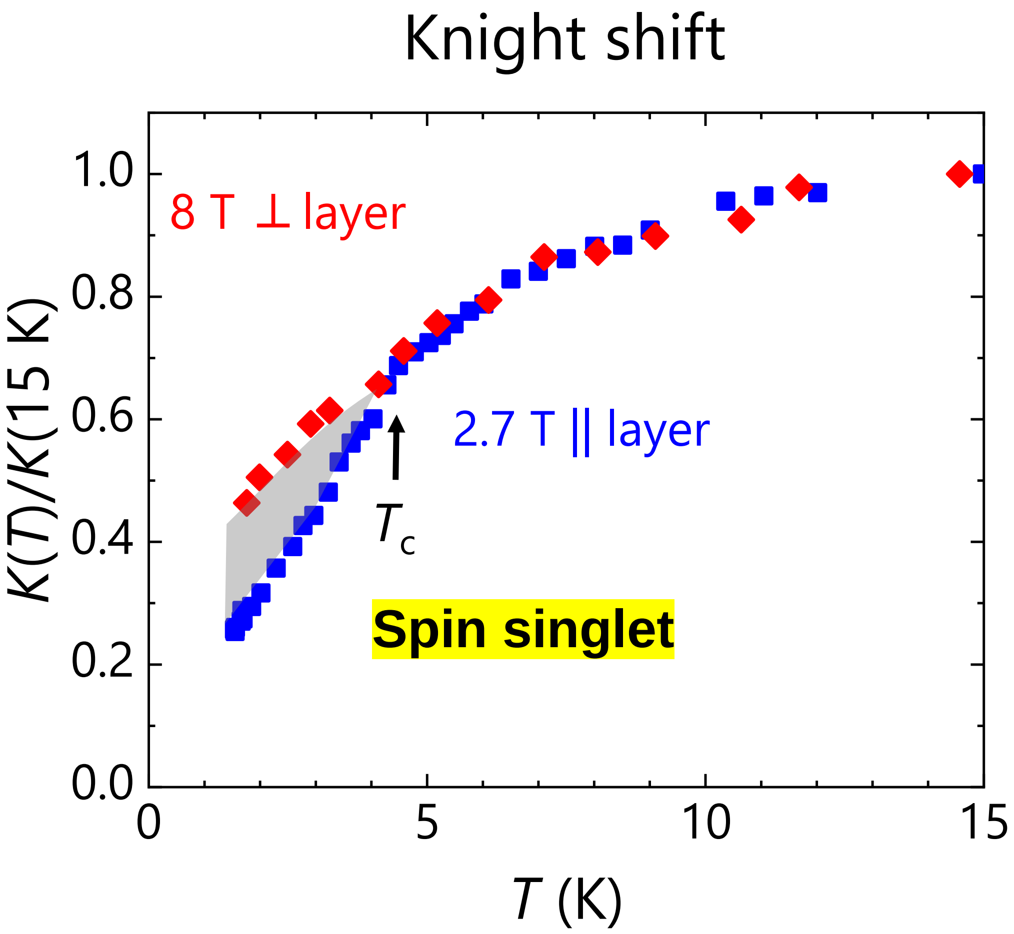
κ-(ET)$_2$Cu(NCS)$_2$ (non-doped)

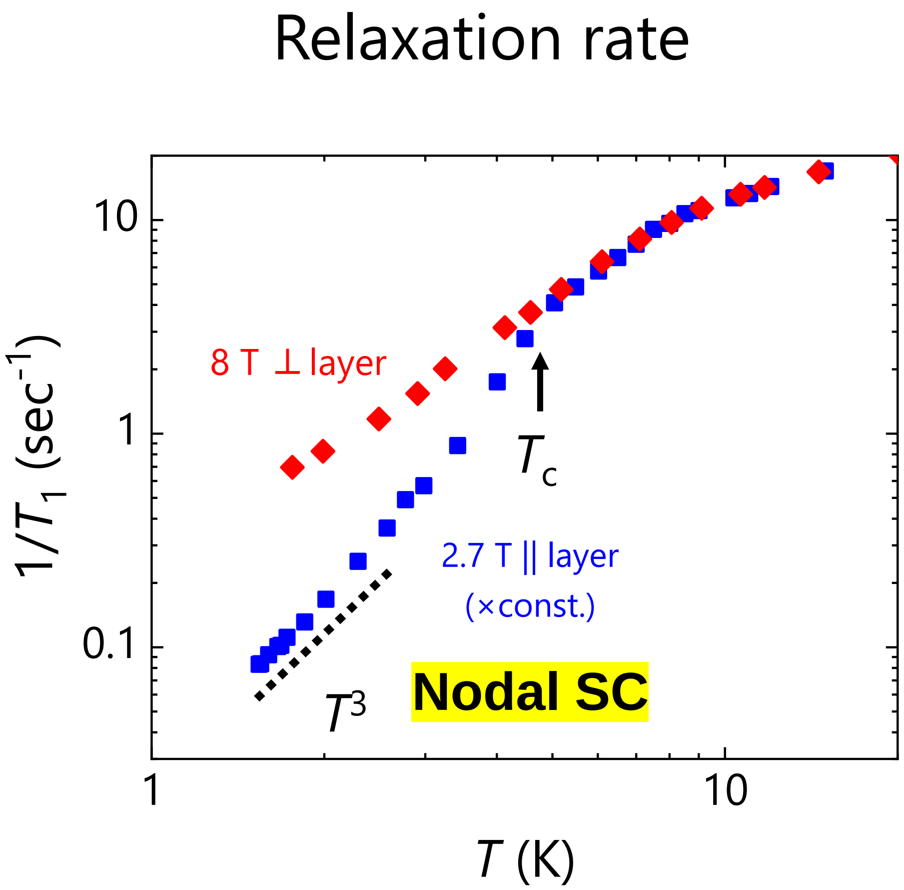


K. Miyagawa *et al.*, Chem. Rev. **104**, 5635 (2004).

Pairing symmetry: ^{13}C NMR

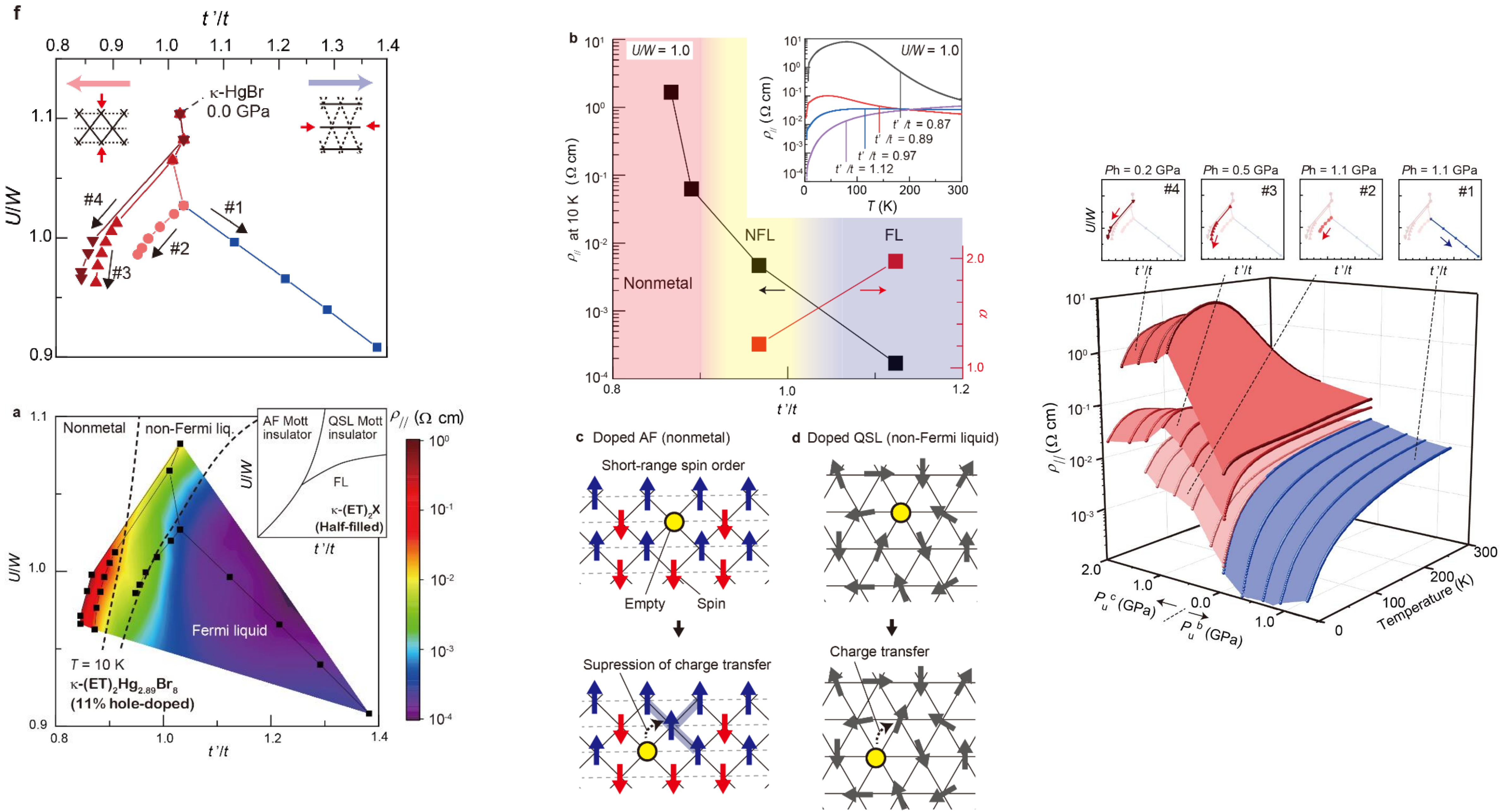
κ-(ET)$_4$Hg$_{2.89}$Br$_8$





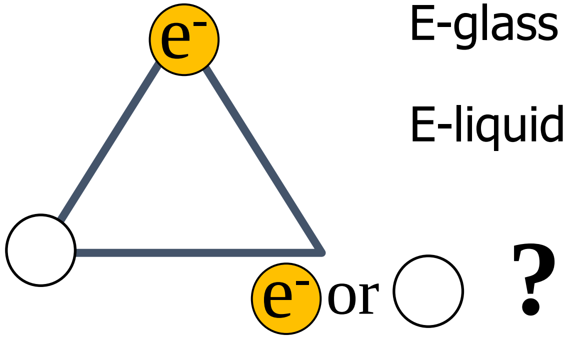
Spin-singlet nodal superconductivity ? ⟺ (?) BEC-like pairing

Combination of hydrostatic and uniaxial pressures: variations of *U*/*t* and *t'*/*t*



Electron (charge) glass

Quarter-filled band electrons
on triangular lattice



E-glass ?

E-liquid ?

Charge frustration

Electronic version of soft matters

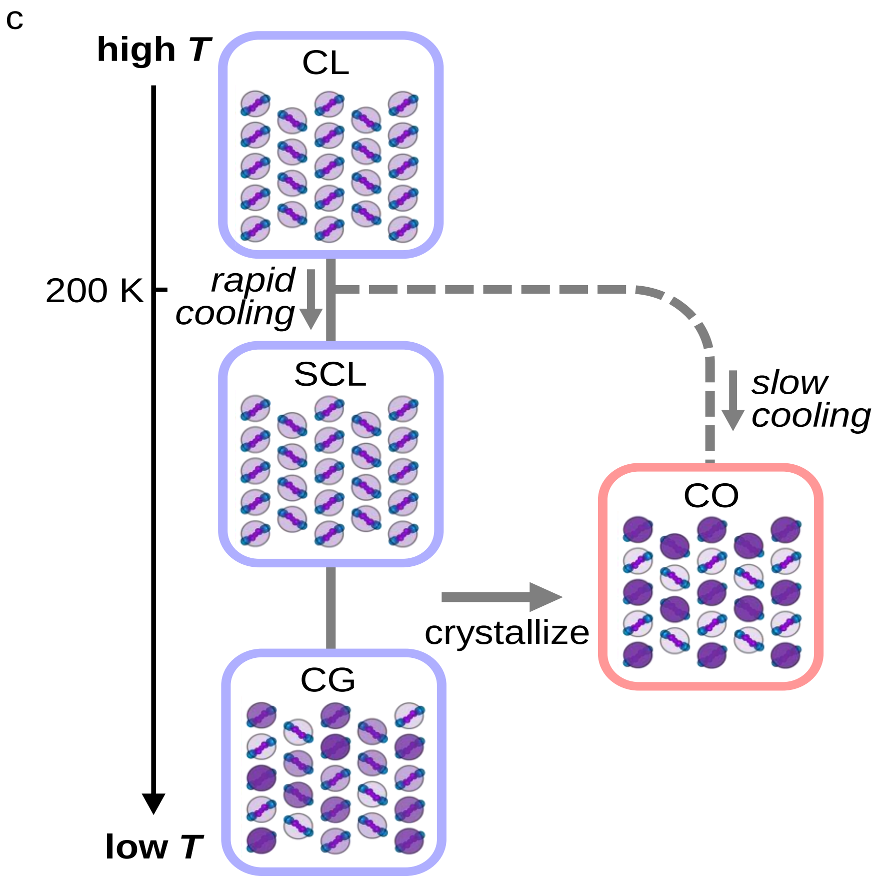
J. Schmalian1 and P. G. Wolynes, PRL 85, 836 (2000)

Self-Generated Randomness

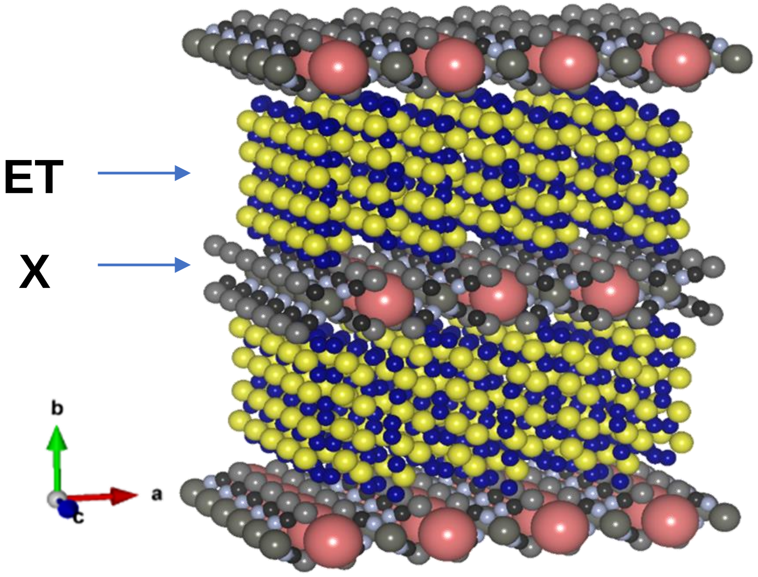
Electronic mayonese

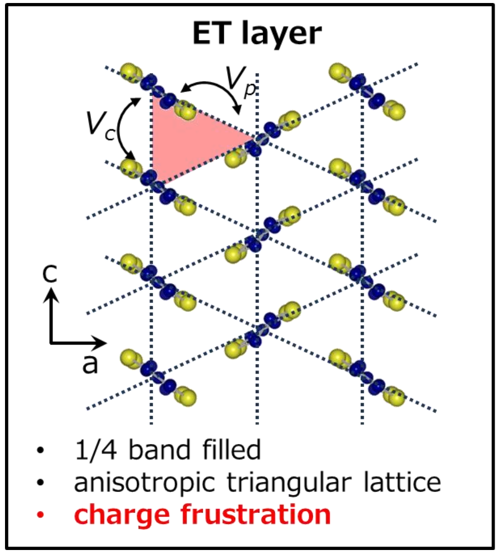
Electron glass

- ✓ **Quantum nature**
- ✓ **Controllable lattice geometry**



Charge frustrated materials, θ-$(ET)_2X$





Non-Equilibrium in Supercooled Liquid

Frustration is a key to holding supercooled liquid and glass

Non-equilibrium

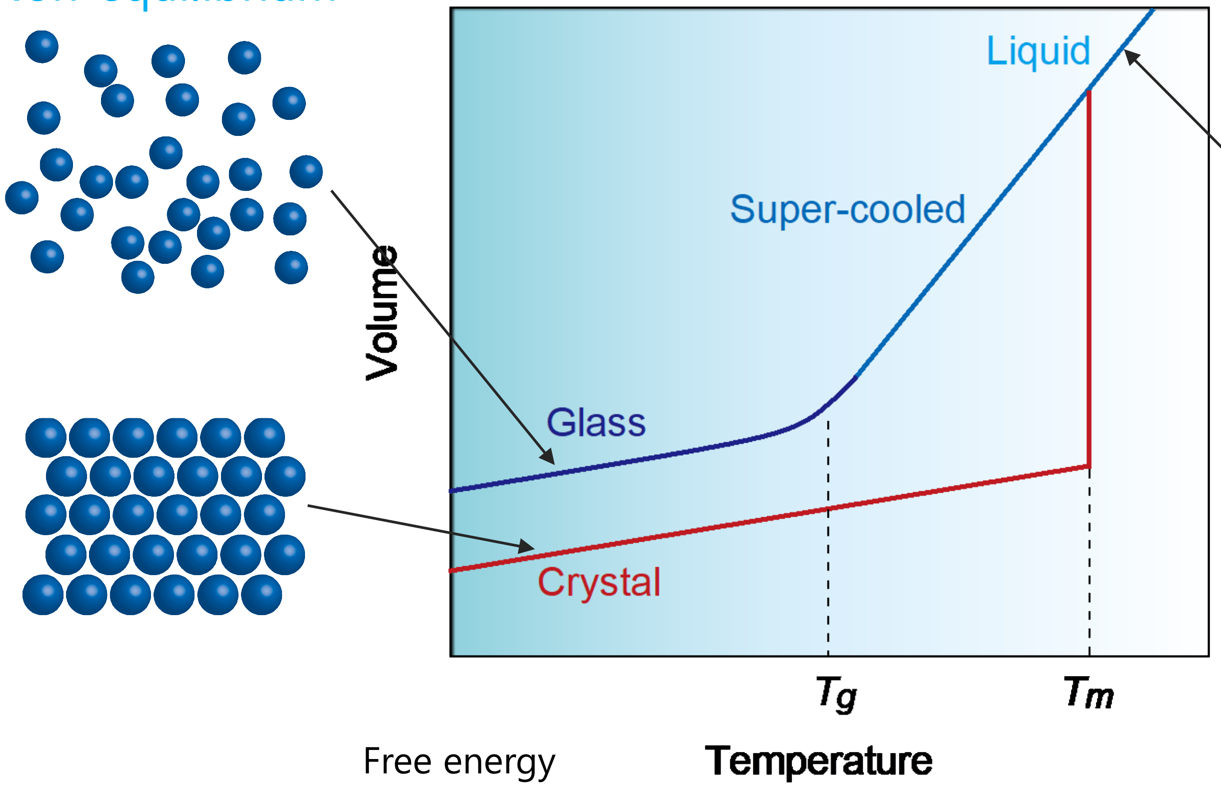
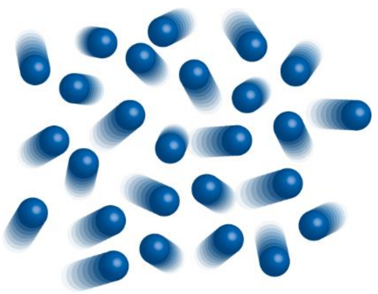
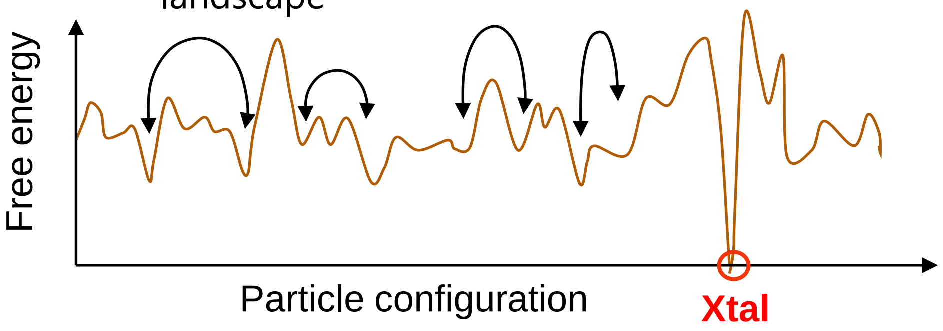


figure from
Dobenedetti & Stillinger
Nature 410, 259 (2001).



Free energy landscape

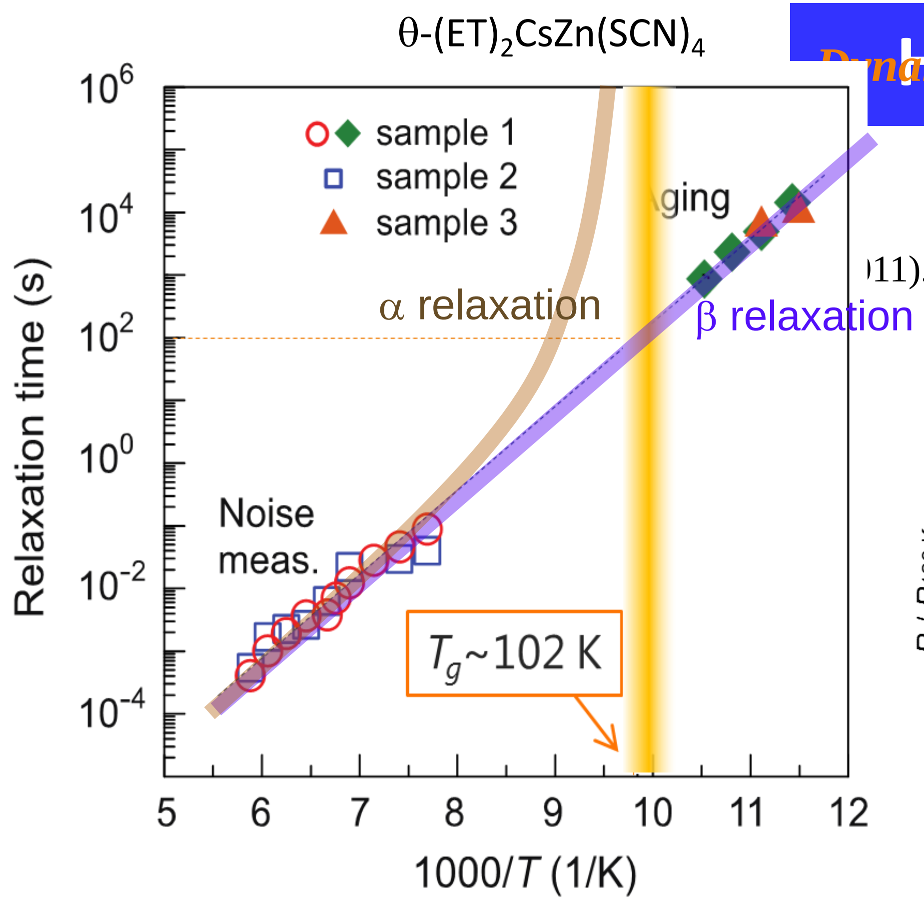


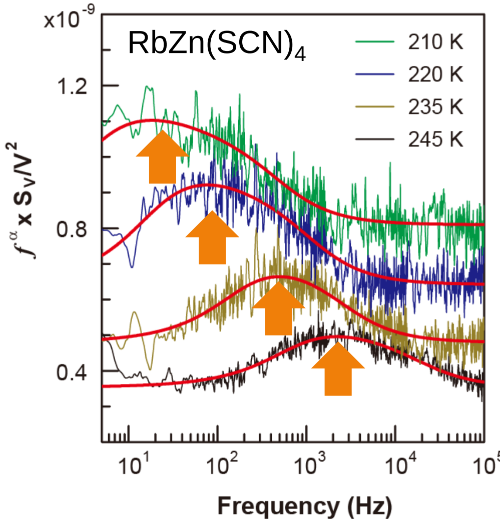
Hallmarks of Glass

- Slow dynamics
- Non-equilibrium
- Short/middle-range correlation

Dynamics Hallmarks of Glass

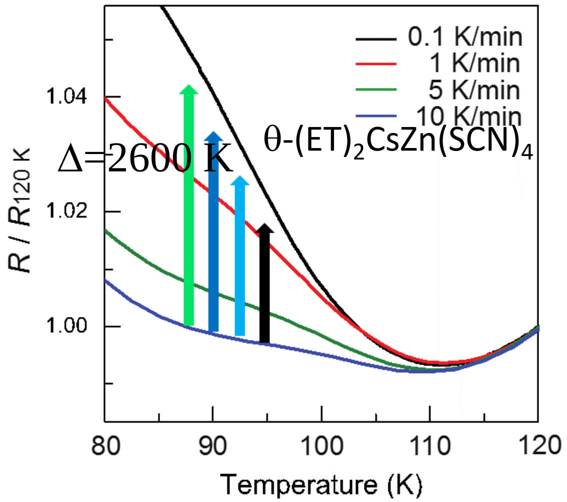
Kagawa *et al.*, *Nat. Phys.* **9**, 419 (2013).
Sato *et al.*, *PRB* **89**, 121102 (2014)
Sato *et al.*, *JPSJ* **83**, 083602 (2014)
Sato *et al.*, *JPSJ* **85**, 123702 (2016)



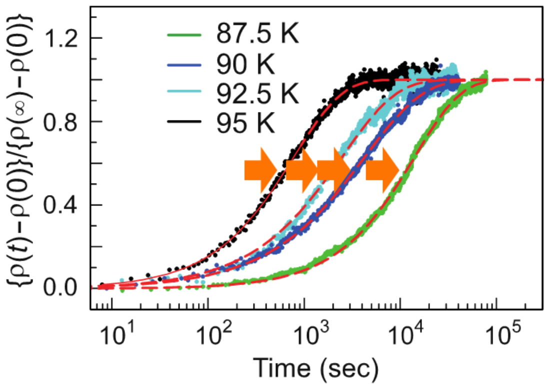


Non-equilibrium nature

***ρ* depends on cooling rate**

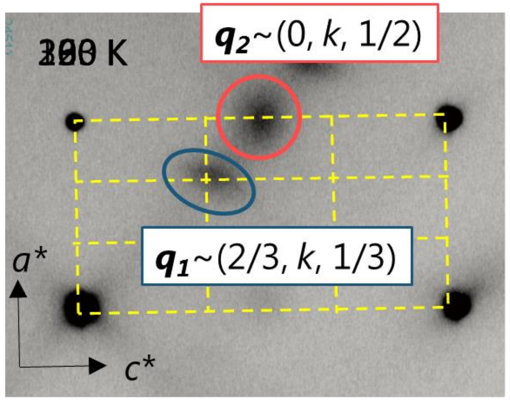


Aging

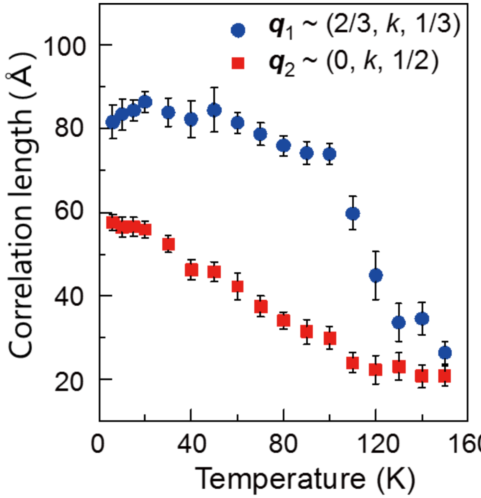


middle-range correlation

X-ray diffuse scattering



Correlation length levelling off

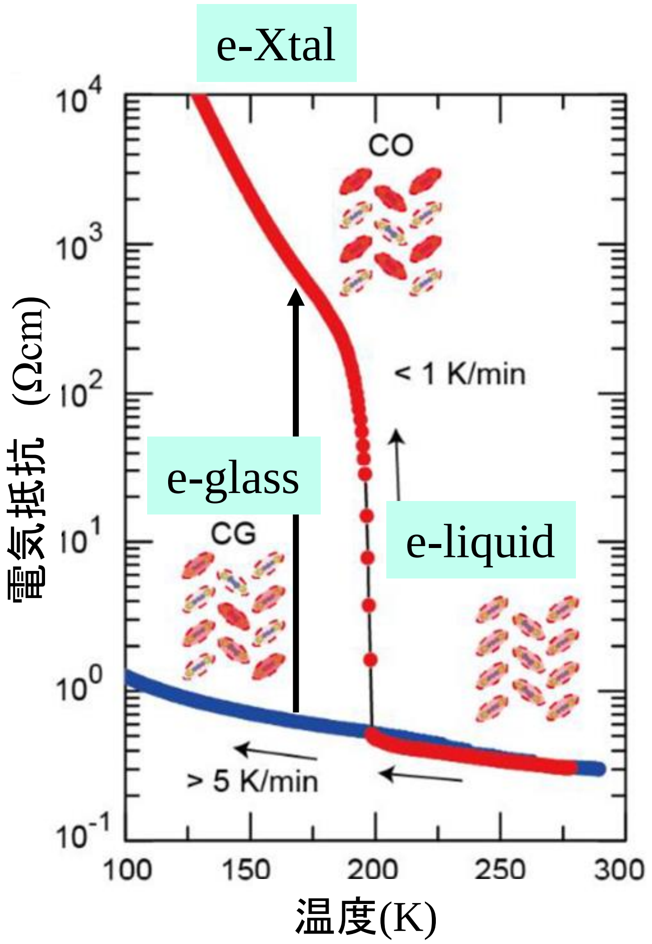


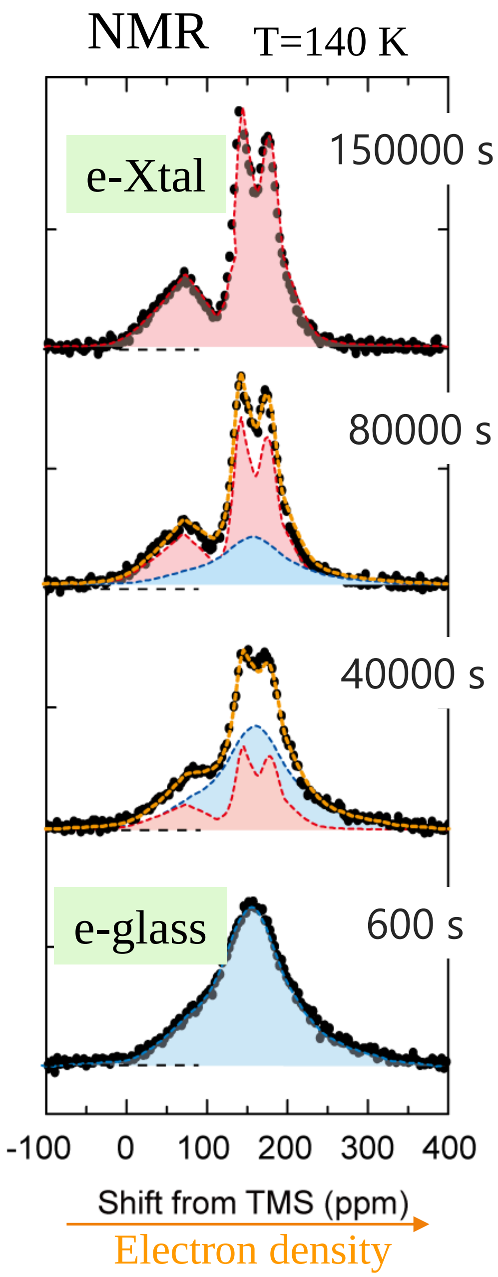
Electronic crystallization: ρ and NMR

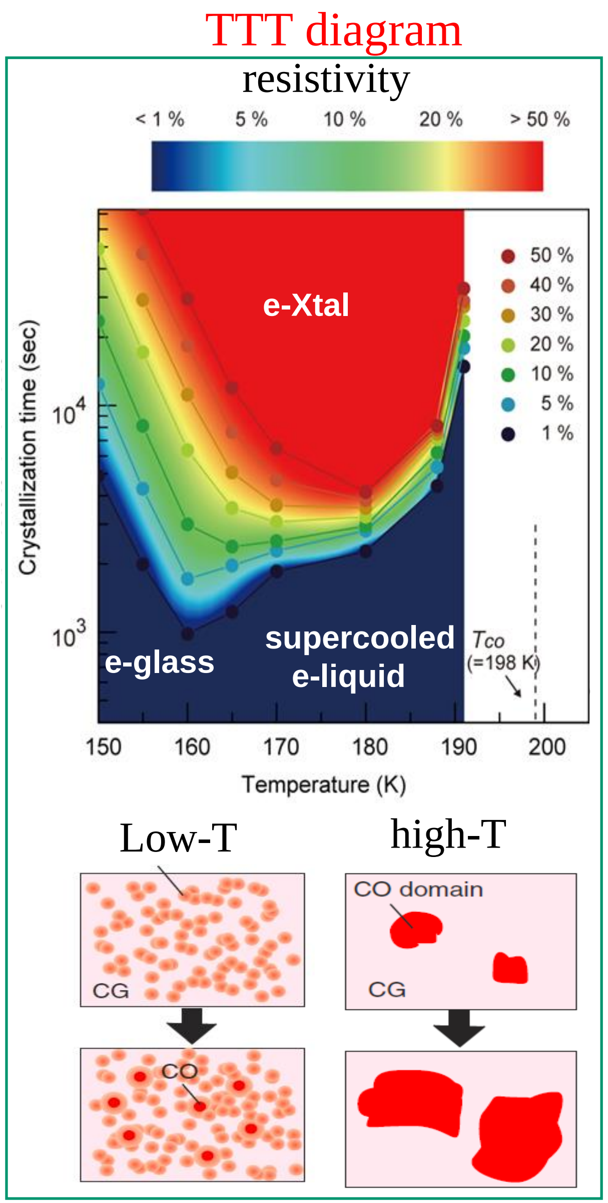
T. Sato et al., Science **357**, 1378 (2017)

(*cf. S. Sasaki et al., Science* **357**, 1381 (2017))

θ-$(ET)_2RbZn(SCN)_4$



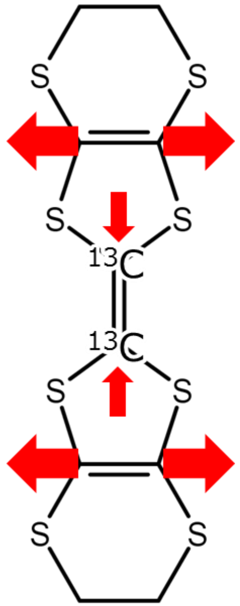




Electronic crystallization: Raman spectroscopy

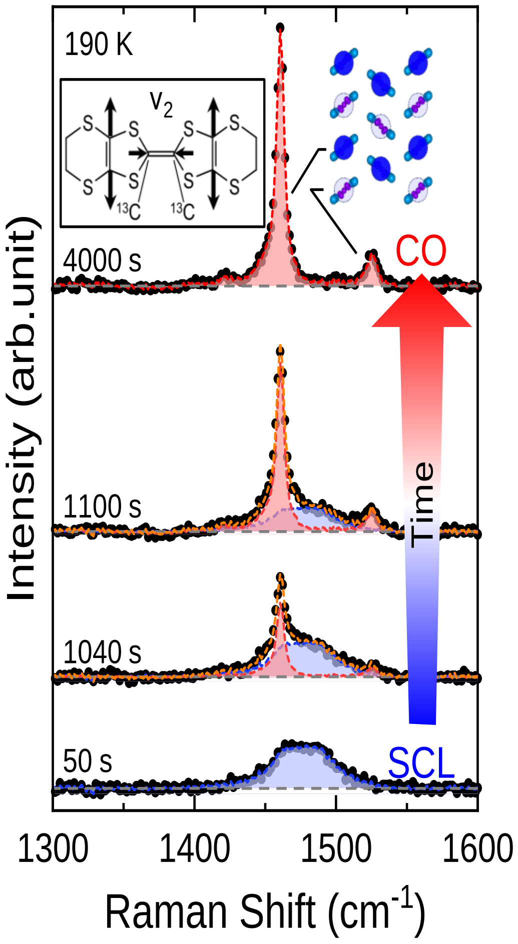
θ-$(ET)_2RbZn(SCN)_4$

Charge-sensitive
***v*$_2$ mode**

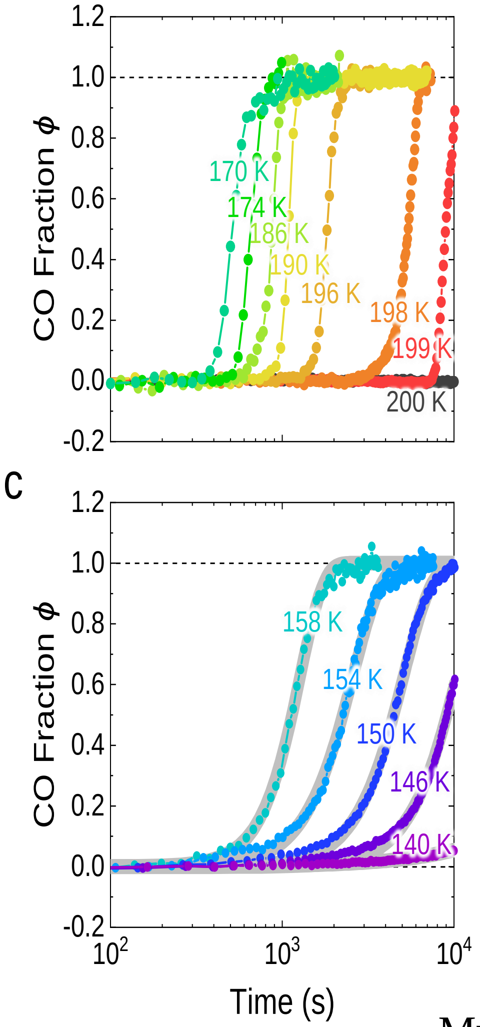


K.Yamamoto, *et al.*,
Phys. *Rev*. B **65**, 085110 (2002).

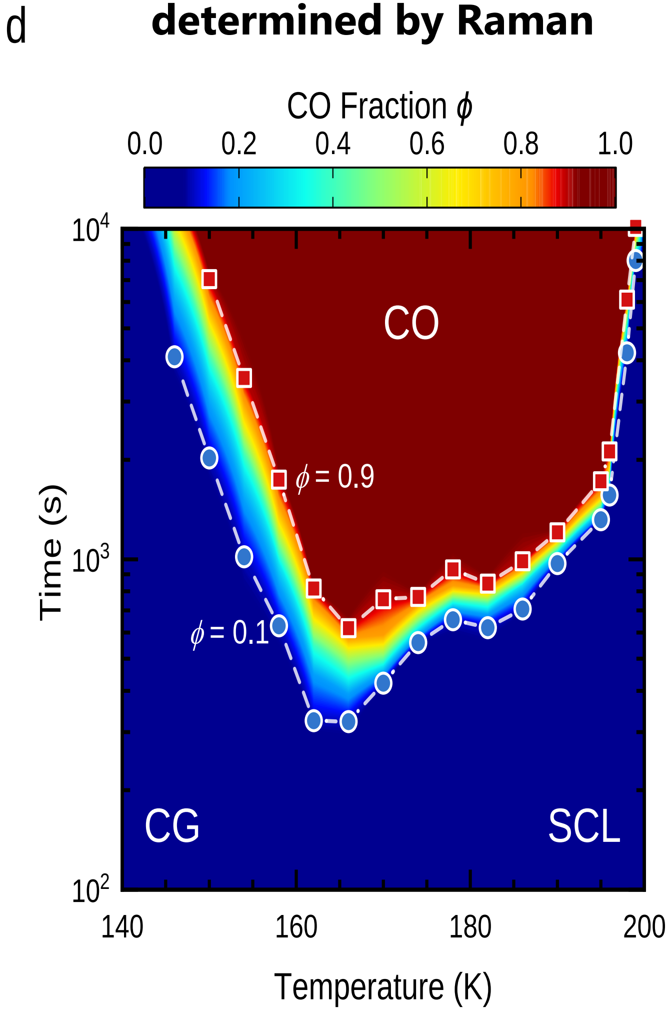
Evolution of Raman spectrum during E-crystallization



Time evolution of E-Xtal fraction



TTT diagram determined by Raman



Murase *et al.*, arXix:2201.04855

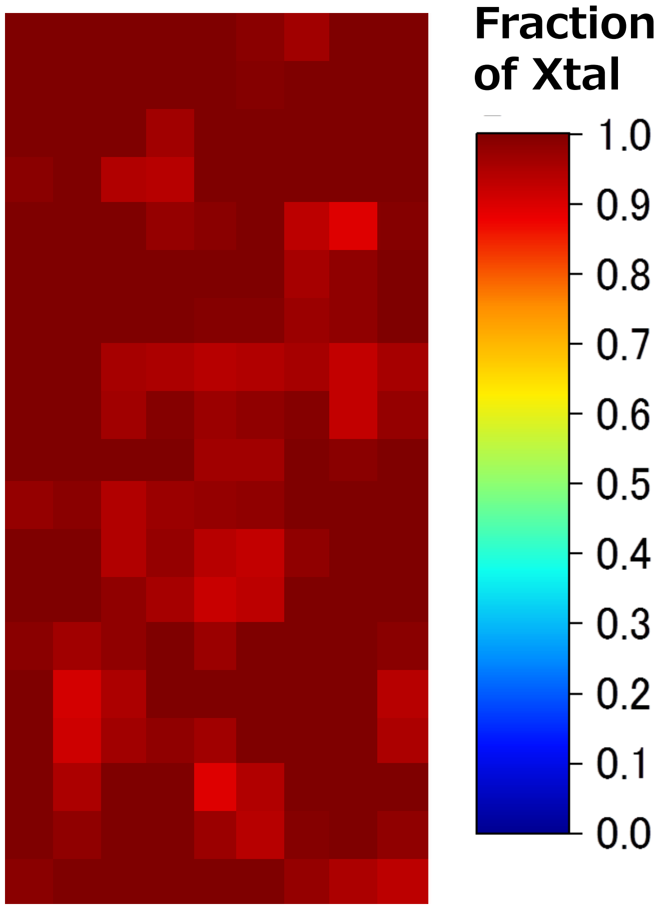
Raman imaging of E-crystallization at high T

村瀬、荒井、平川

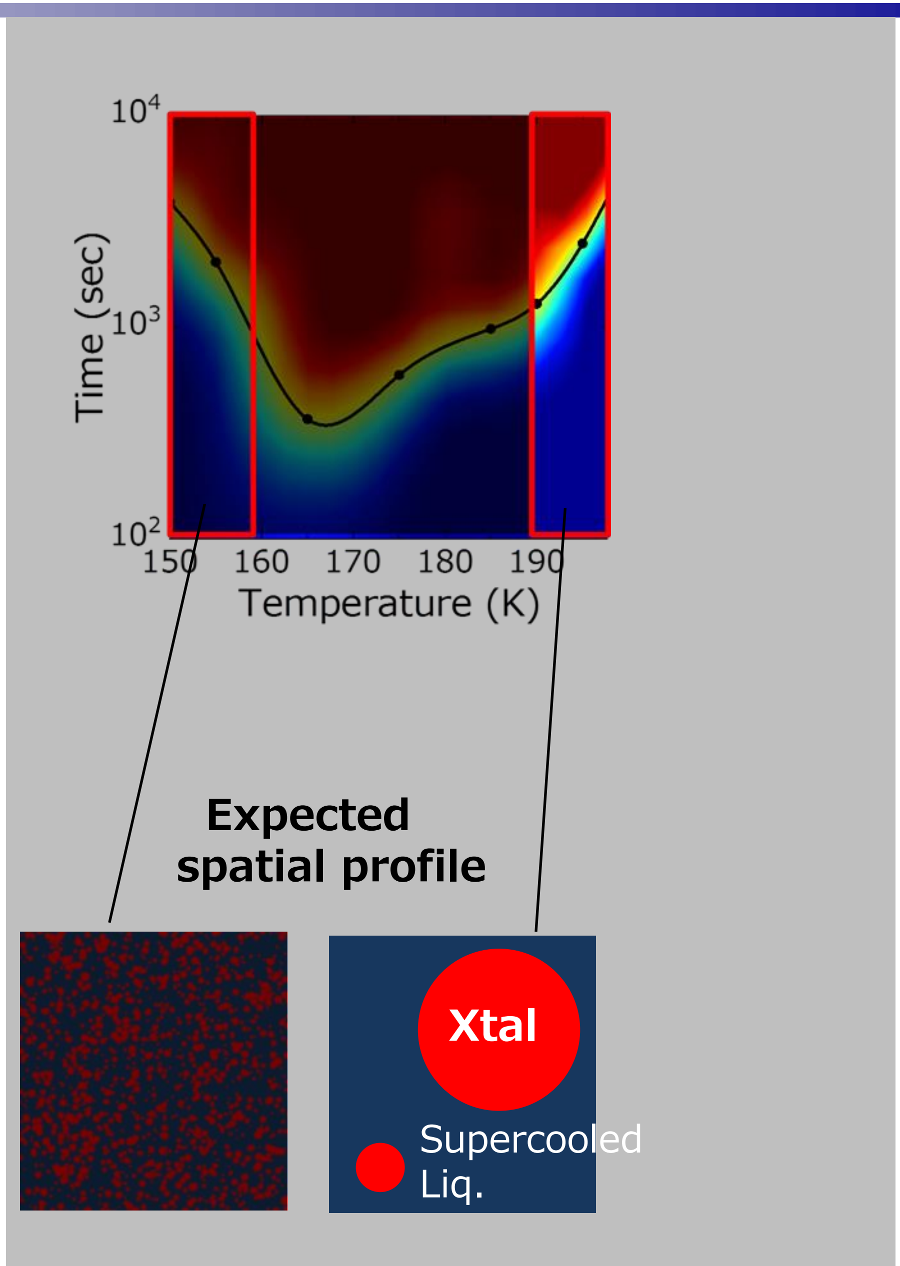
T_q = 195 K

150 s interval
6.5×6.5 μm²/pixel

20 μm



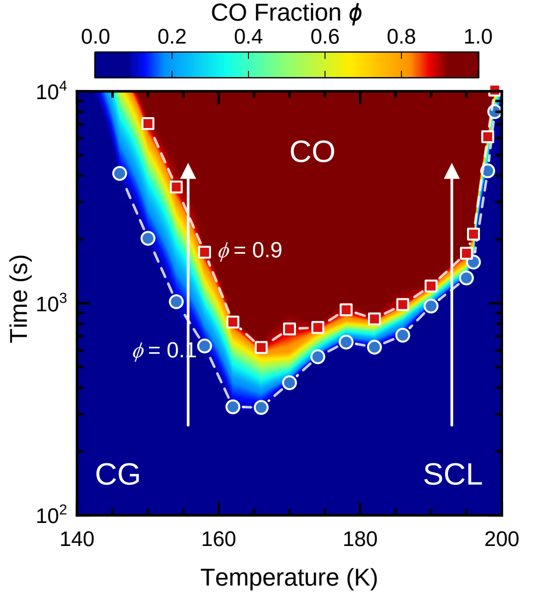
Macroscopically inhomogeneous

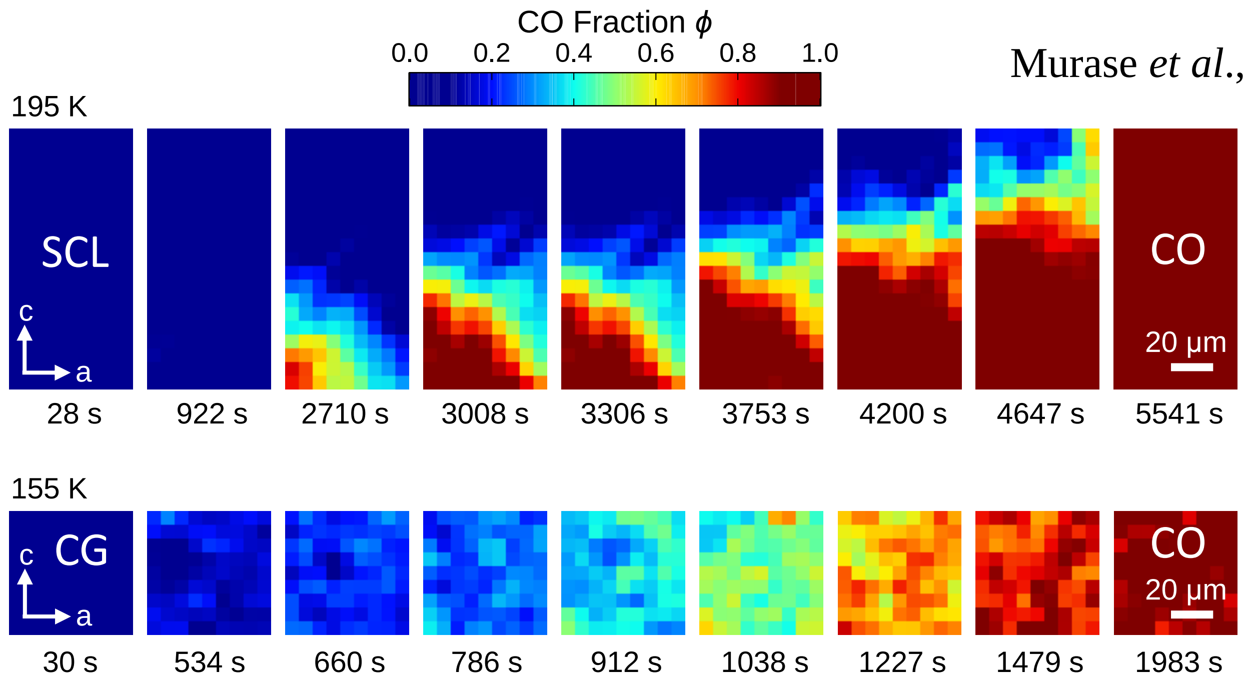


Spaciotemporal observation of electronic crystallization: classical glass

Murase *et al.*, arXix:2201.04855

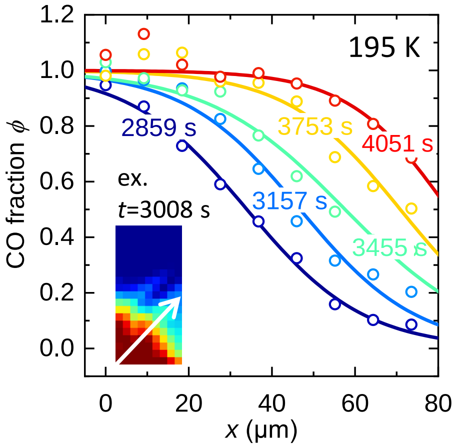
TTT diagram

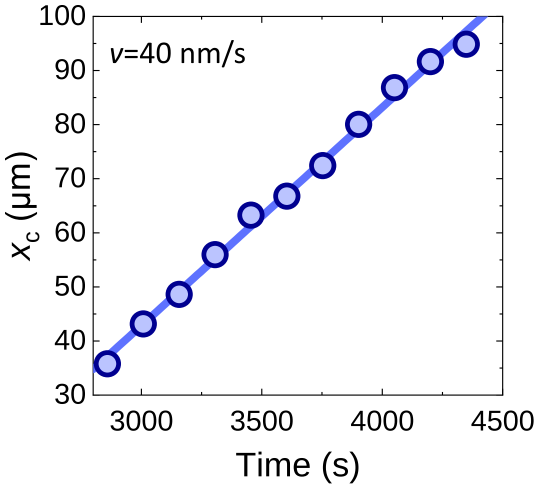


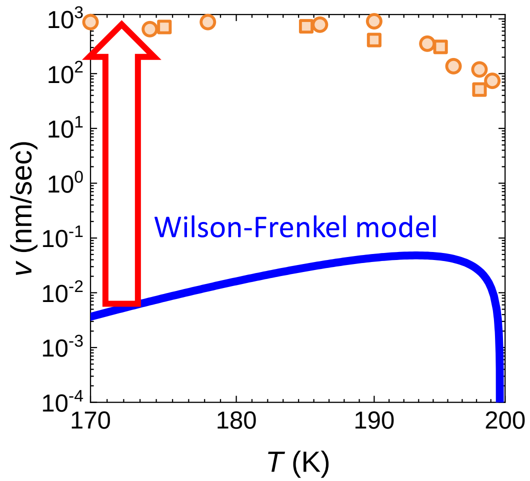


Ultrafast crystal growth: quantum effect ?

five orders of magnitude faster than expected in the classical model !





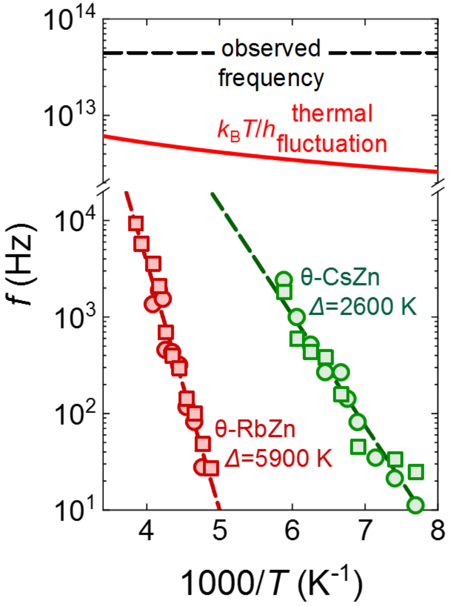


From classical to quantum charge glass

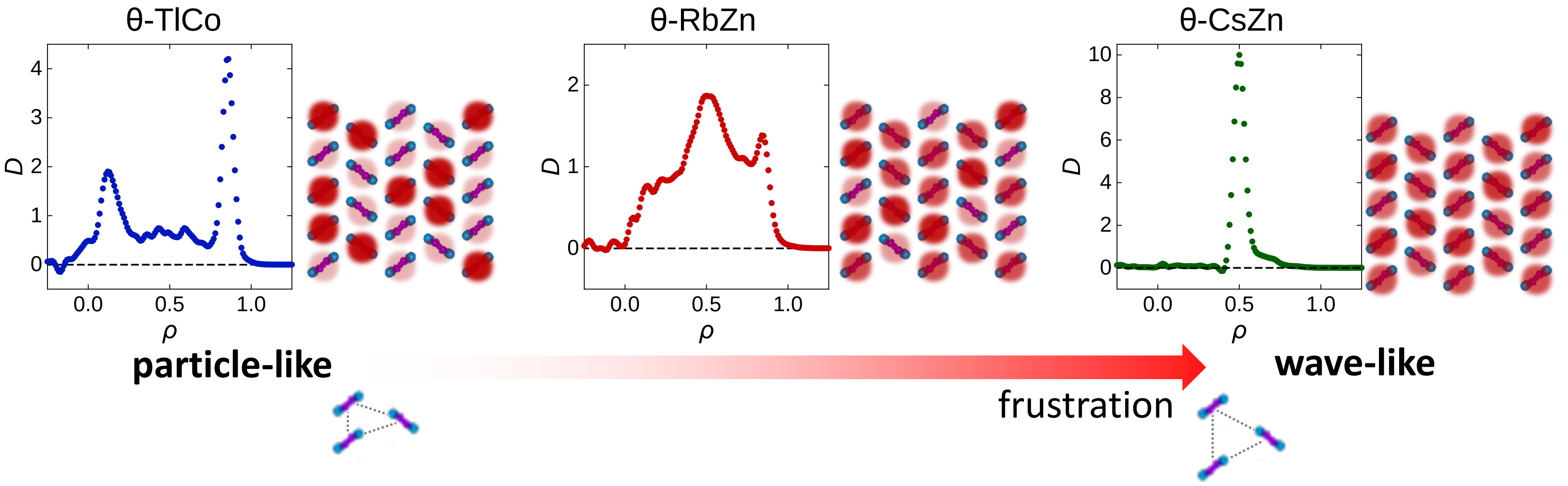
Murase *et al.*, unpublished

Observation time scale

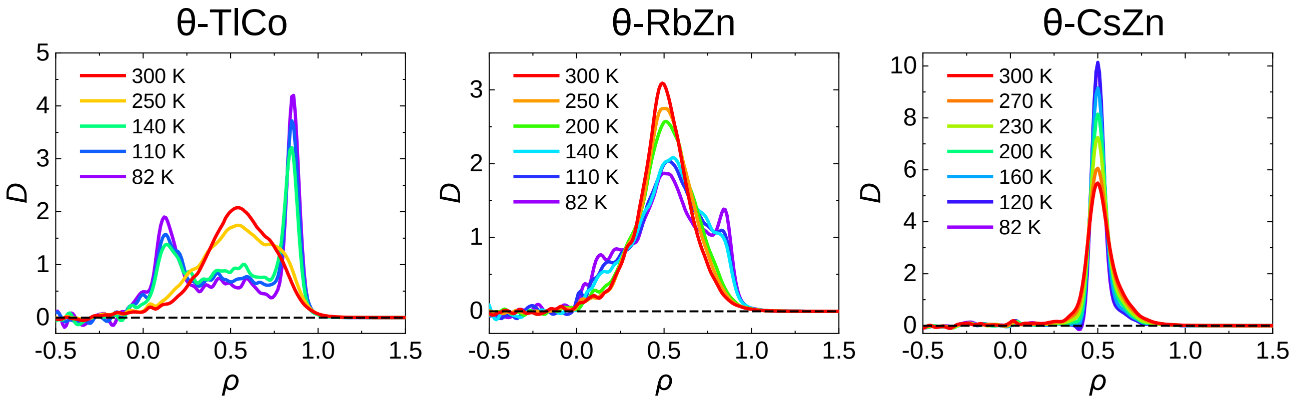
$f_{obs} >> f_{thermal} >>>> f_{glass}$

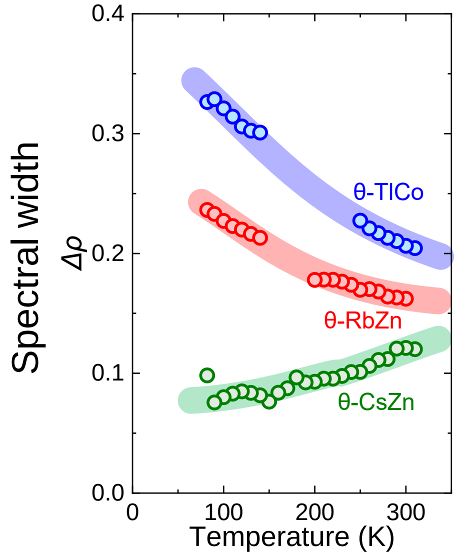


Frustration dependence of charge density in CG at 82 K

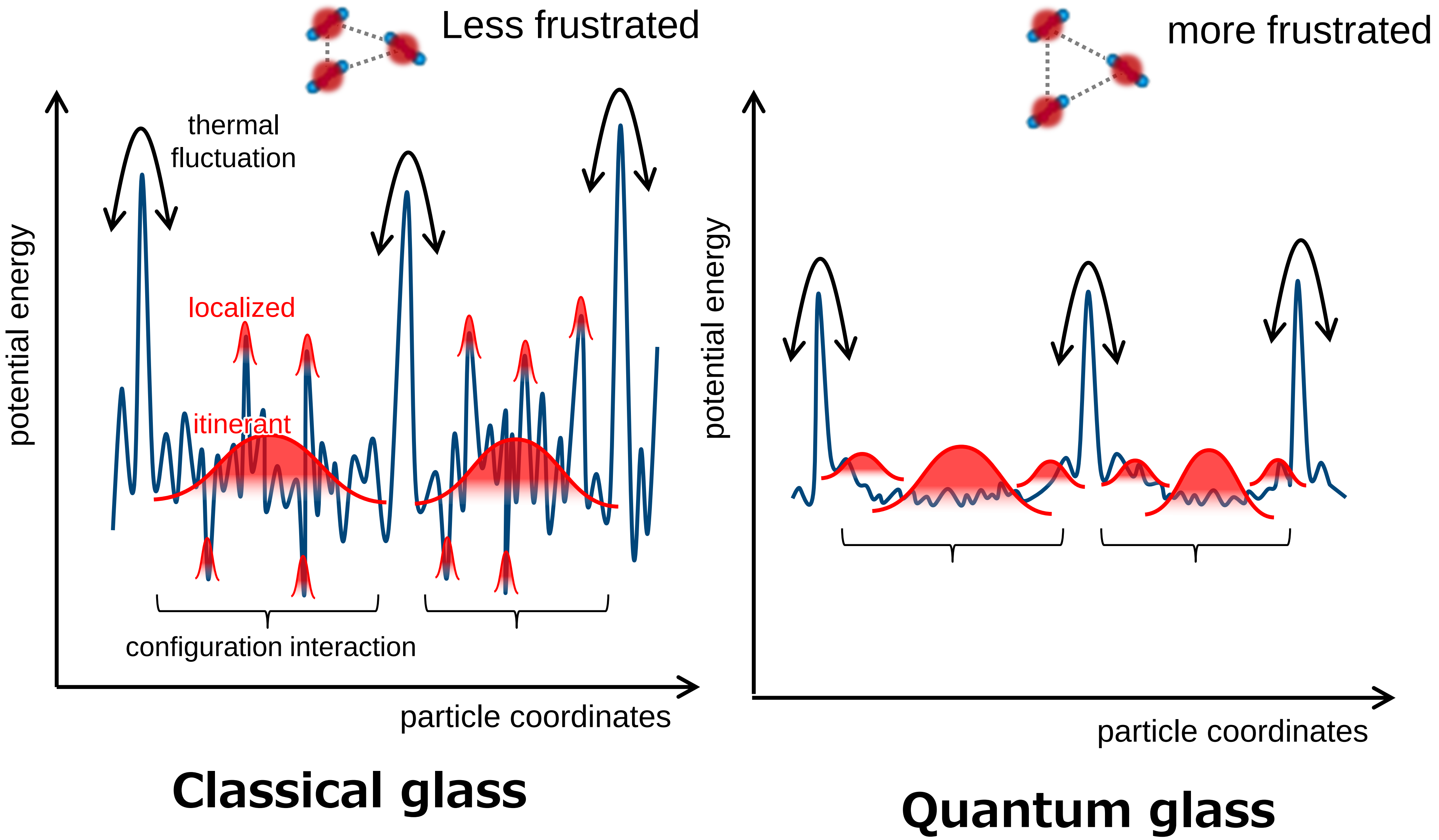


Temperature dependence of charge density

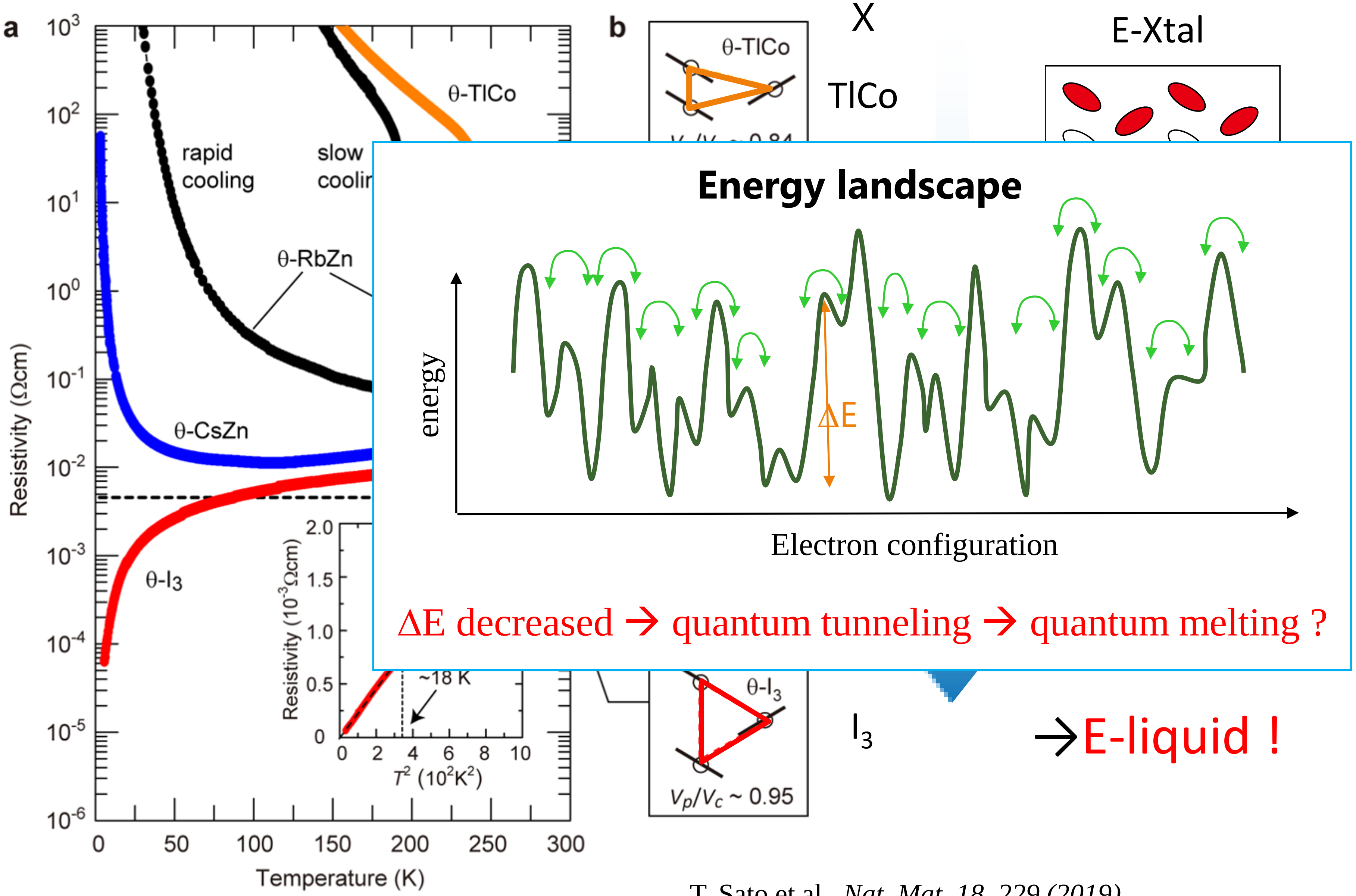




Discussion | Energy landscape



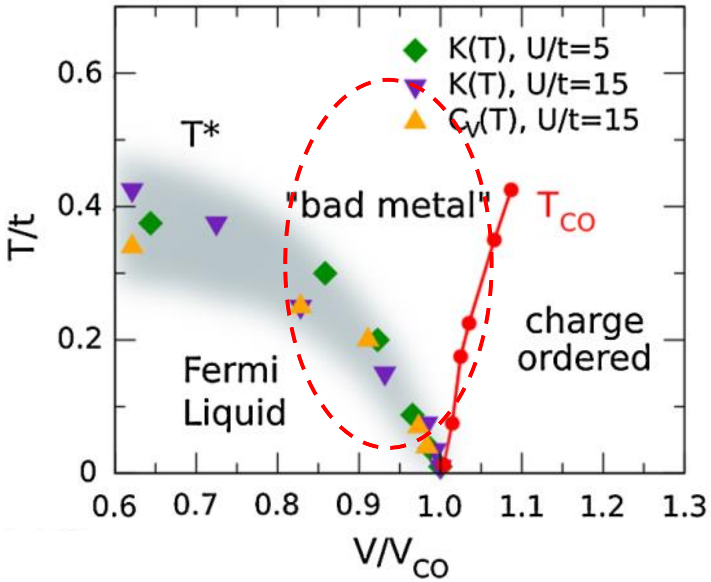
Possible quantum melting of E-glass



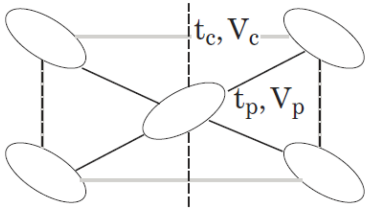
T. Sato et al., *Nat. Mat. 18, 229 (2019)*

Strange metal arising from frustration-driven charge instability

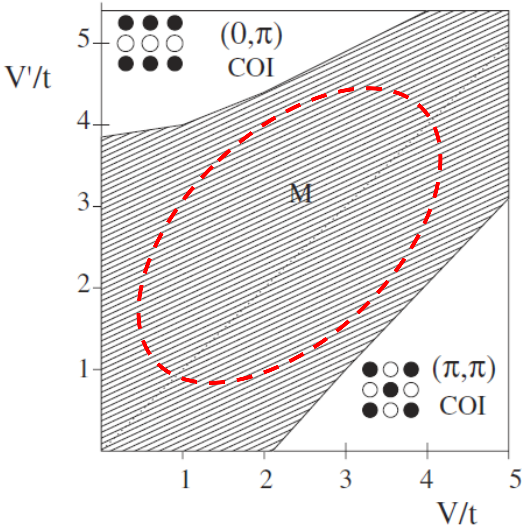
L. Cano-Cortes, et al, PRL **105**, 036405 (2010)
PRB **84**, 155115 (2011)



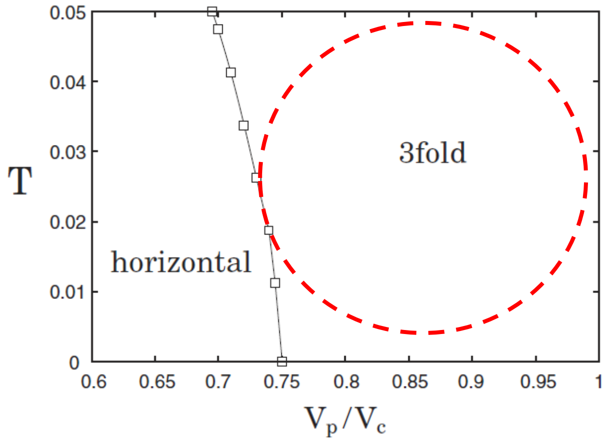
theoretical



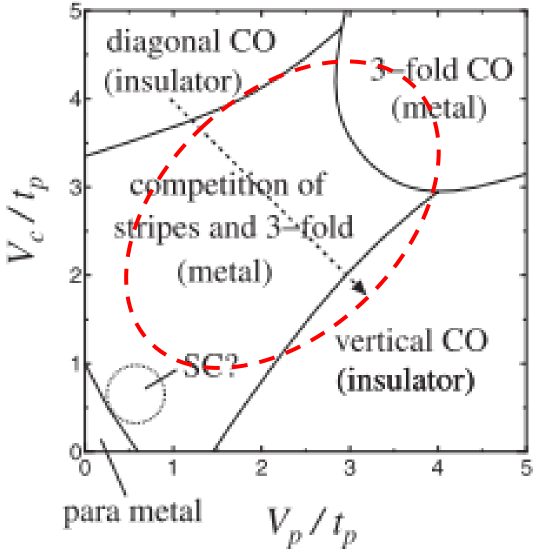
J. Merino et al, *PR B* **71**, 125111 (2005)



Y. Tanaka & K. Yonemitsu JPSJ (2007)



H. Watanabe, et al, JPSJ (2006)



summary

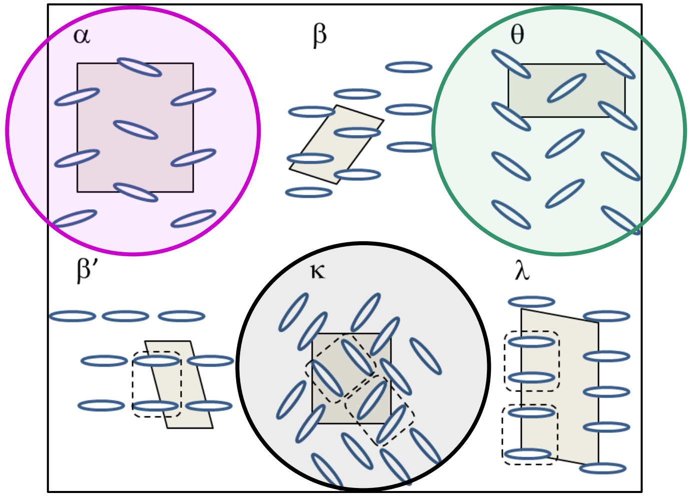
Diverse electronic states spring from a single molecular species, ET, only by changing its arrangement

Massless Dirac electrons

Dirac cone reshaping
Unusual spin correlation
Dynamic mass generation

Electronic Xtal/glass

Non-equilibrium
Slow dynamics
Crystal growth
Quantum glass



Particle physics

Soft matter physics

Mott physics

Quantum Mott criticality
Preformed Cooper pairs
Spin liquid
BEC-BCS crossover