Emergent phenomena in charge instability

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ECRYS to EGLASS in 2D charge-frustrated system θ-$(ET)_2X$

Topological excitations in 1D neutral-ionic transition TTF-CA

EGLASS in charge-frustrated system - θ-$(ET)_2X$ -

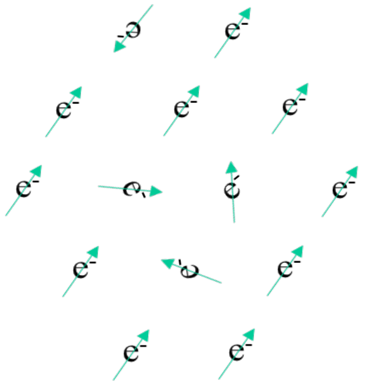
- Classical manifestations; slow dynamics, aging, short-range order
- Anomalously high crystallization speed
- Classical to quantum crossover in E-glass

<u>Collaborators</u>

UTokyo, Appl. Phys.	H. Murase, T. Sato (IMS), T. Baba, S. Arai, T. Hasegawa, F. Kagawa (TIT), H. Oike, K. Miyagawa,
UTokyo, ISSP	H. Mori (ISSP)
Tokyo Sci. Univ.	M. Tamura (Tokyo Sci. Univ.)

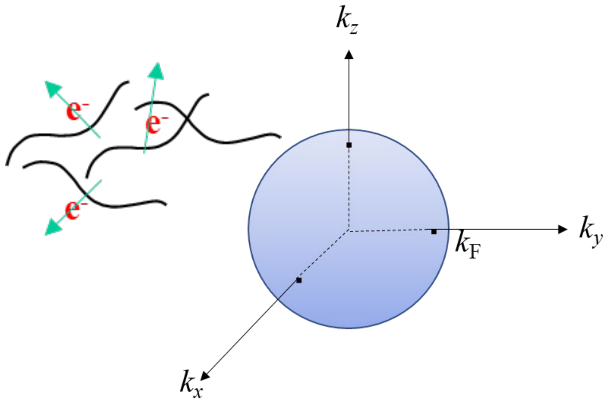
Crystallization of repulsive electrons

Wigner Crystal



$$E = \left(\frac{e^2}{4\pi\epsilon^2}\right)\frac{1}{r} \propto \boldsymbol{n^{1/2}}$$

Fermi-degenerate fluid



Free space

$$E = \frac{\hbar^2 k_F^2}{2m} \propto \boldsymbol{n}$$ in 2D

can be diminished

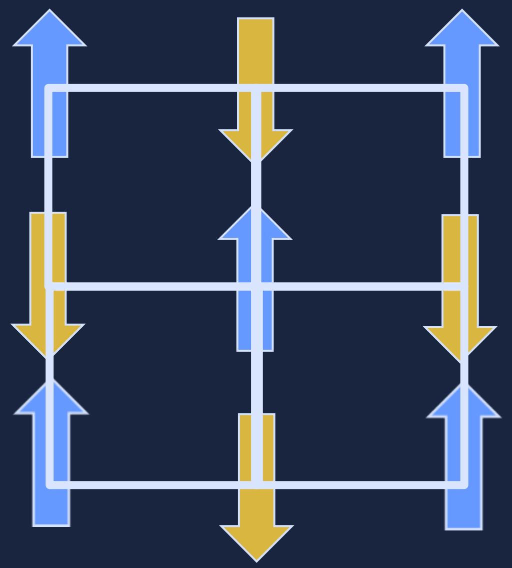
Lattice

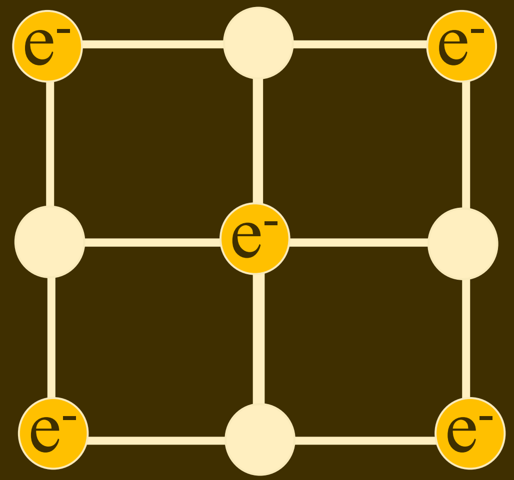
$$E \propto \boldsymbol{t}$$

1/2 filling	**1/4 filling**

All electrons are happy on a square lattice

Spin order



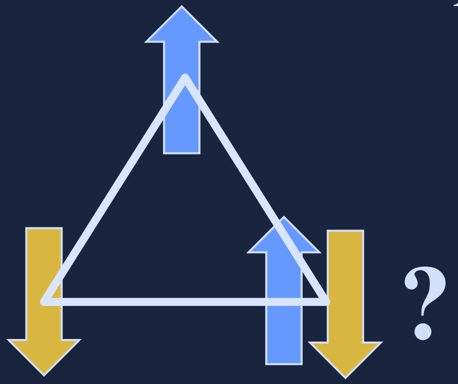


E-crystal

Electrons are unhappy on a triangular lattice

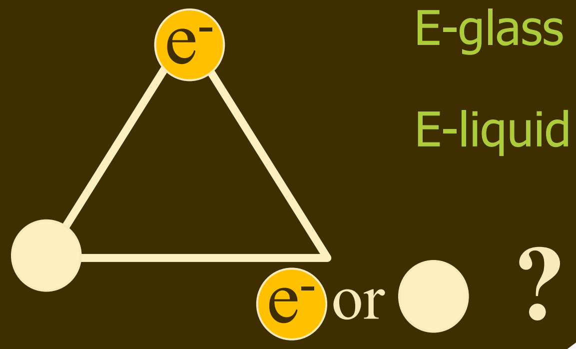
Spin glass

Spin liquid



E-glass ?

E-liquid ?



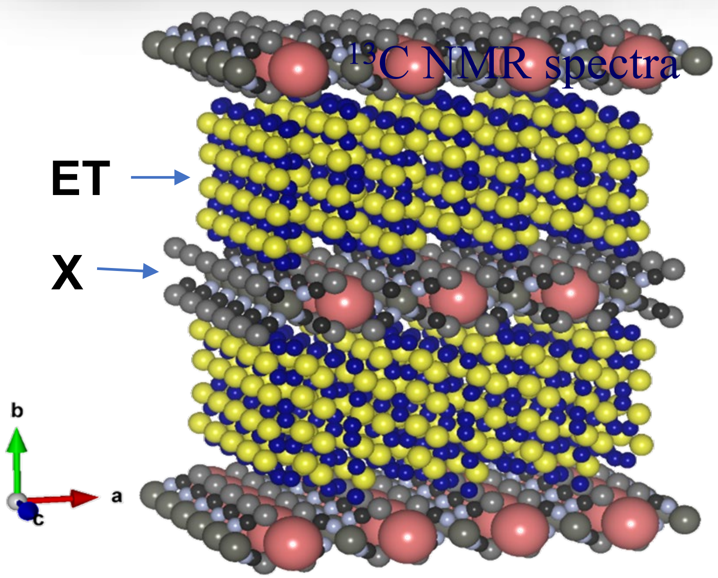
Spin frustration

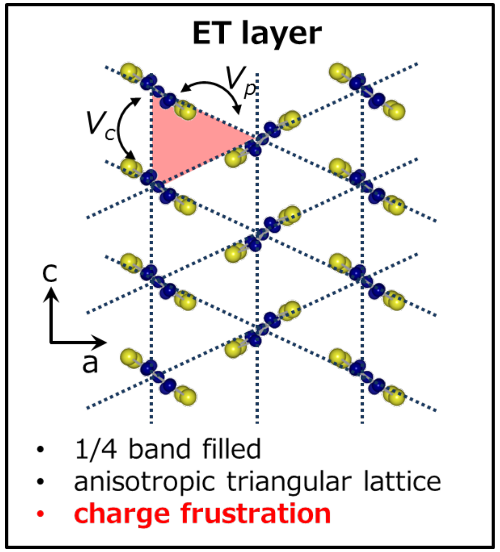
Charge frustration

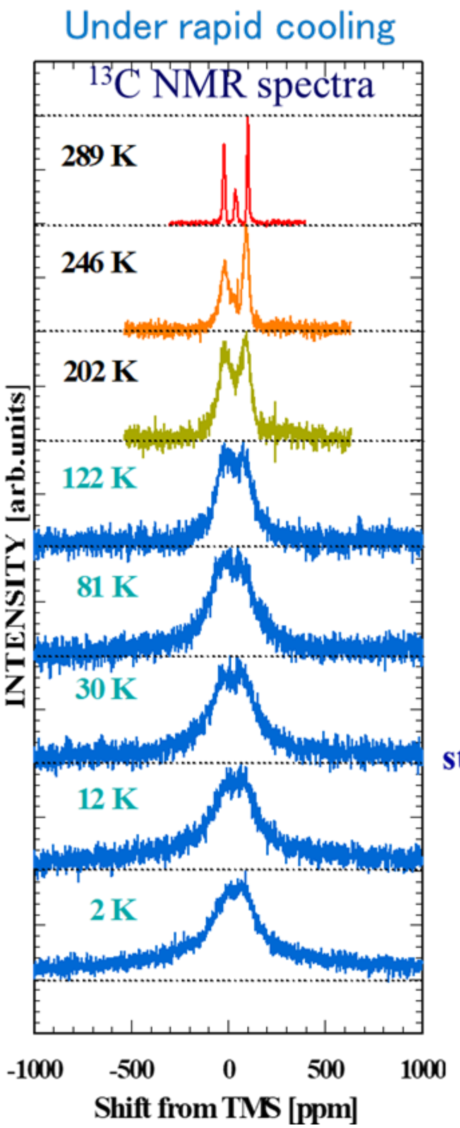
Charge frustrated materials, θ-$(ET)_2X$

Charge order suppressed by rapid cooling

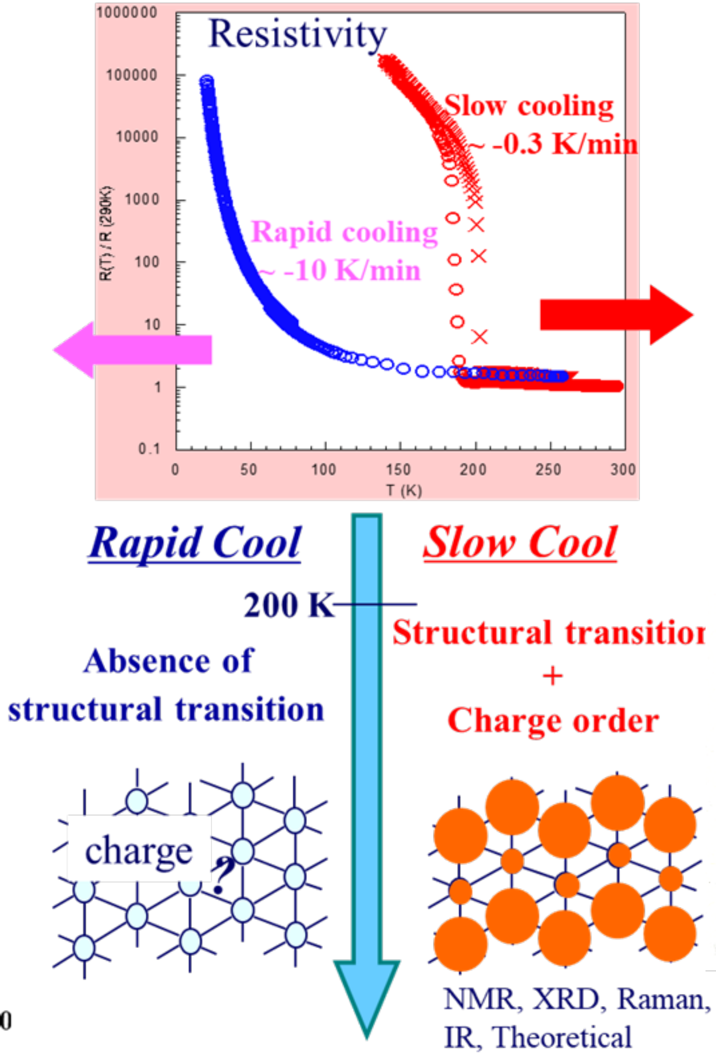
$X=RbZn(SCN)_4$

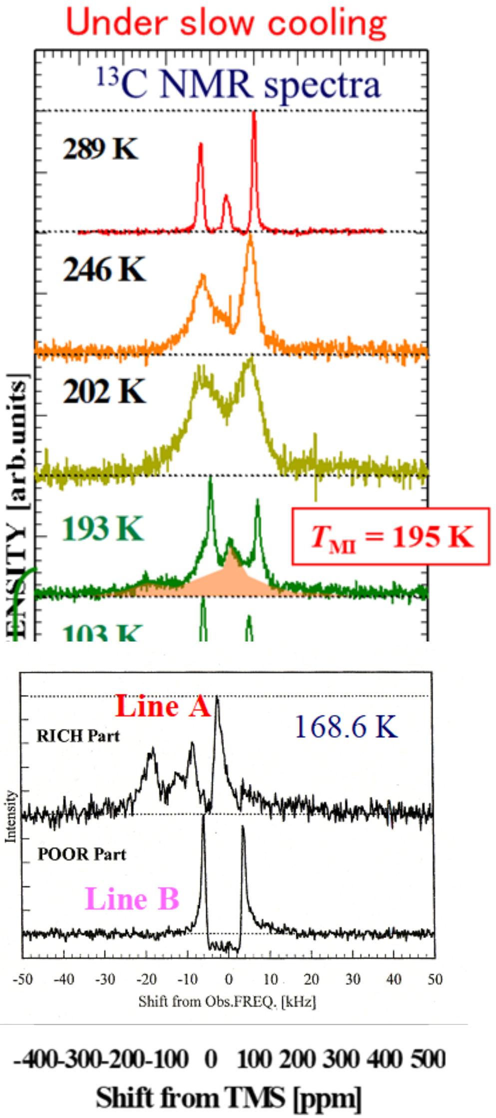






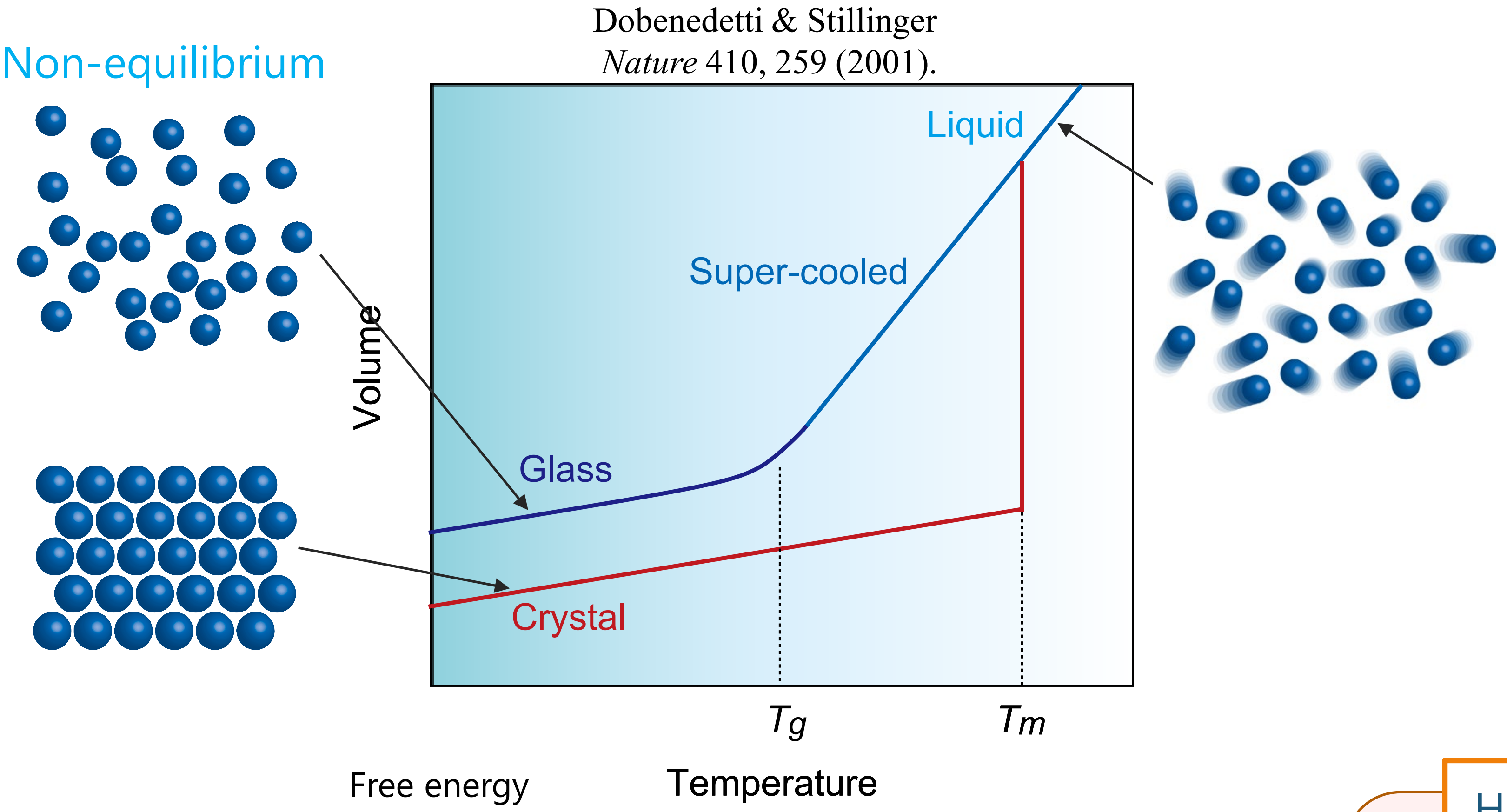
Miyagawa et al., PRB (2000)

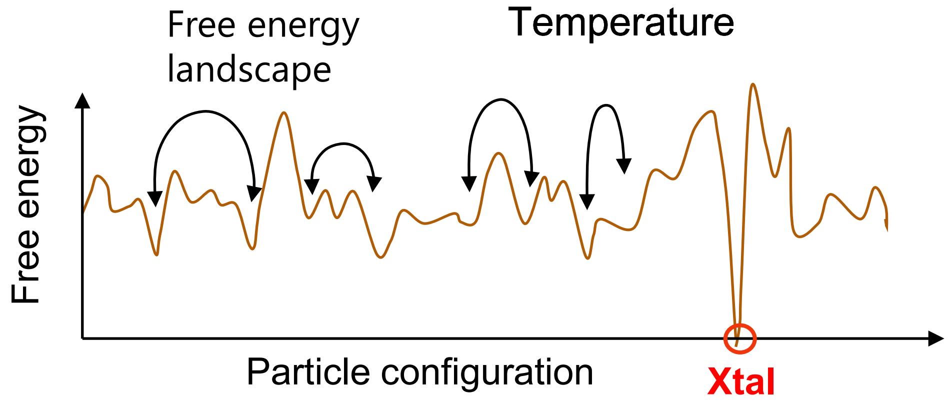




Anisotropy of △ lattice is varied by X

Non-Equilibrium Supercooled Liquid and glass





<u>Classical glass former</u>

Atoms
Molecules
Polymers
Colloids

Electronic glass former ?
(without disorder)

Theoretically, yes
in classical limit
Dobrosavljevic, Fratini, PRL(2015)
in quantum regime
Fratini →talk on Friday

Hallmarks of classical Glass

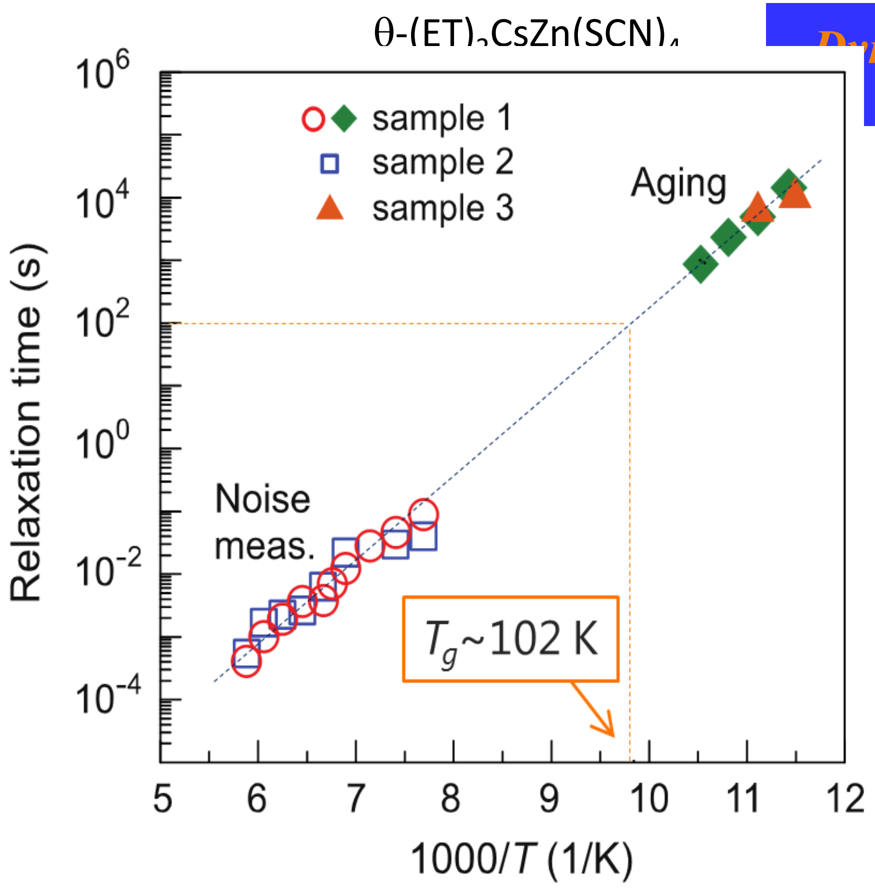
- **slow dynamics**
- **non-equilibrium**
- **short/middle-range correlation**
- **crystallization**

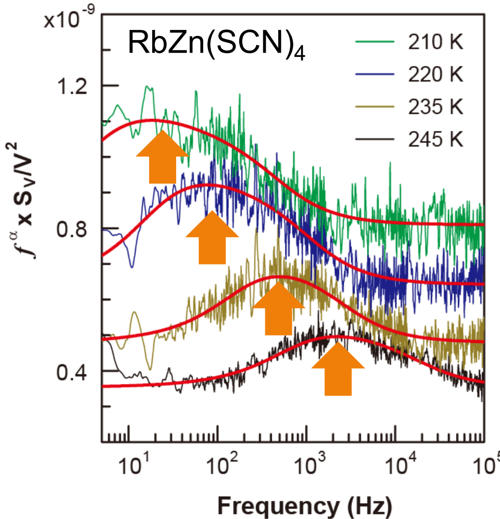
Hallmarks of Glass

Dynamics

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)

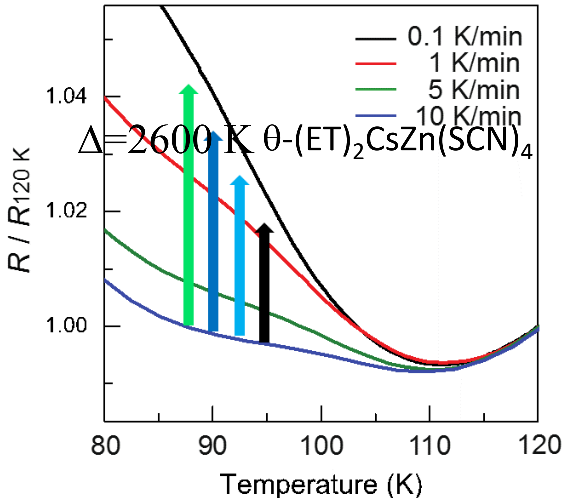
佐藤、賀川



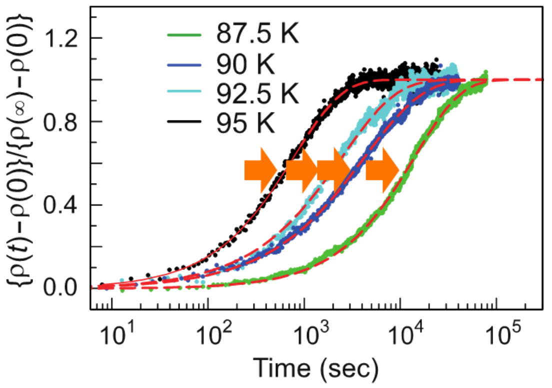


Non-equilibrium nature

ρ depends on cooling rate

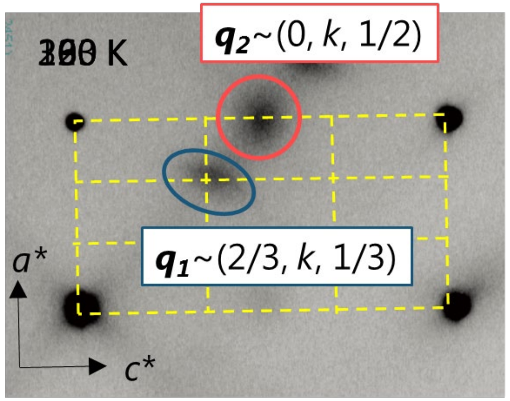


Aging

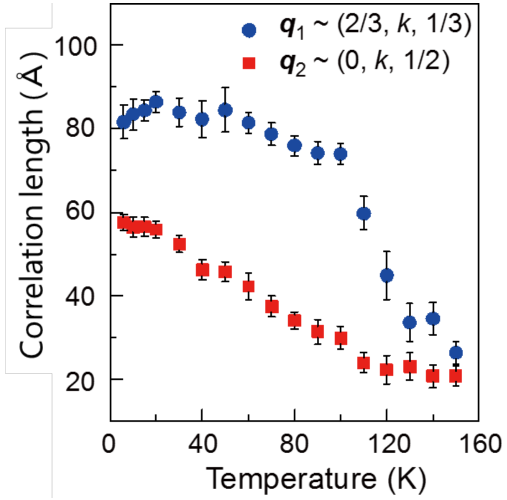


middle-range correlation

X-ray diffuse scattering



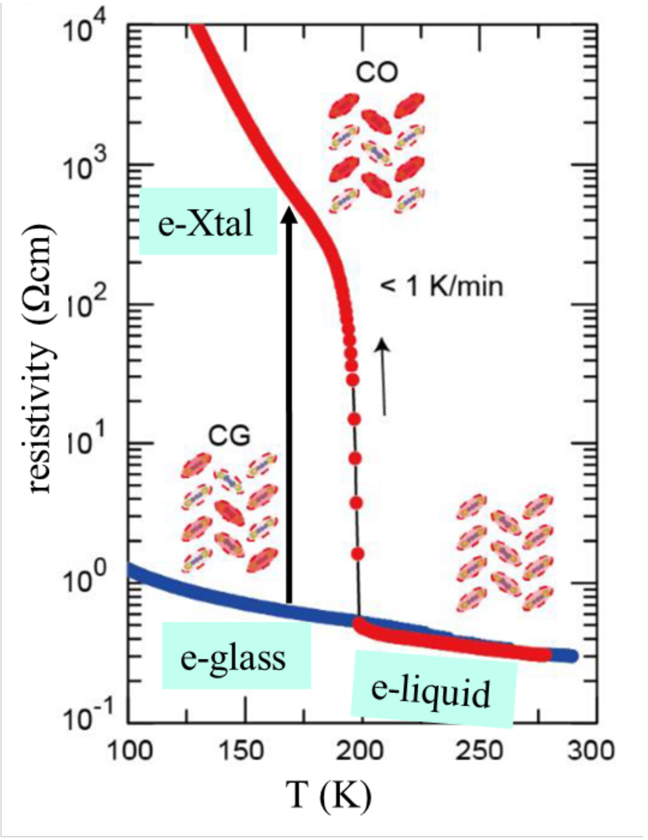
Correlation length levelling off



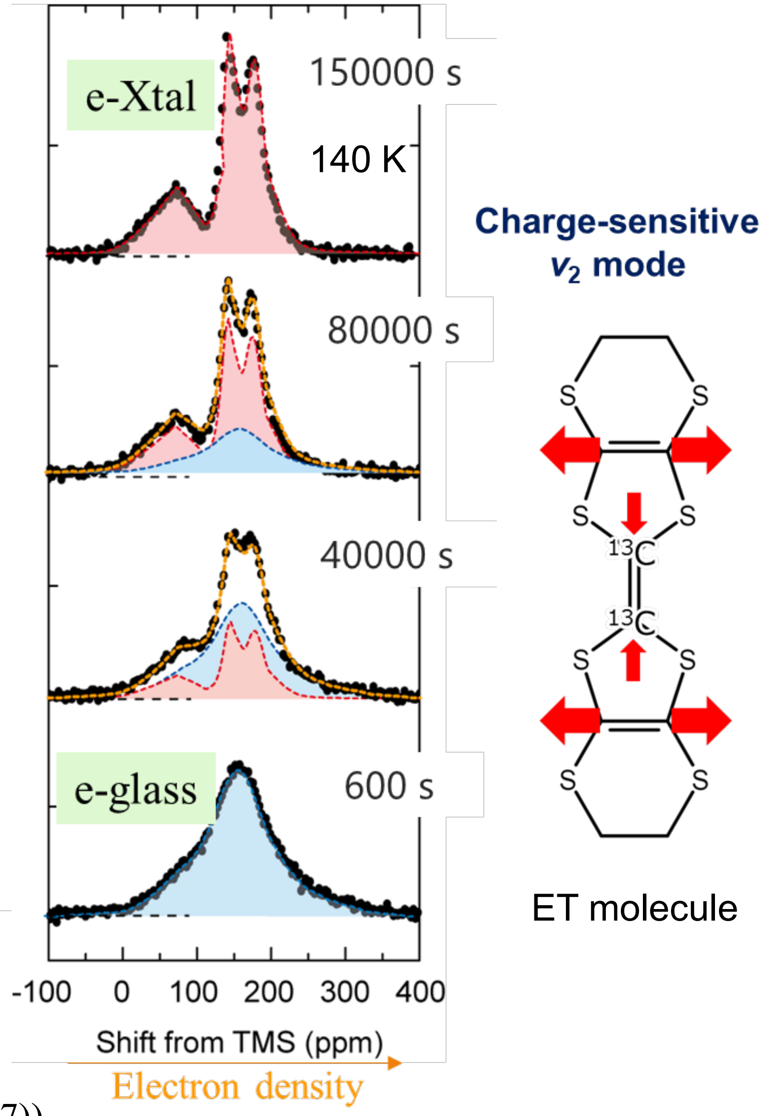
Electronic crystallization: NMR and Raman

θ-$(ET)_2RbZn(SCN)_4$

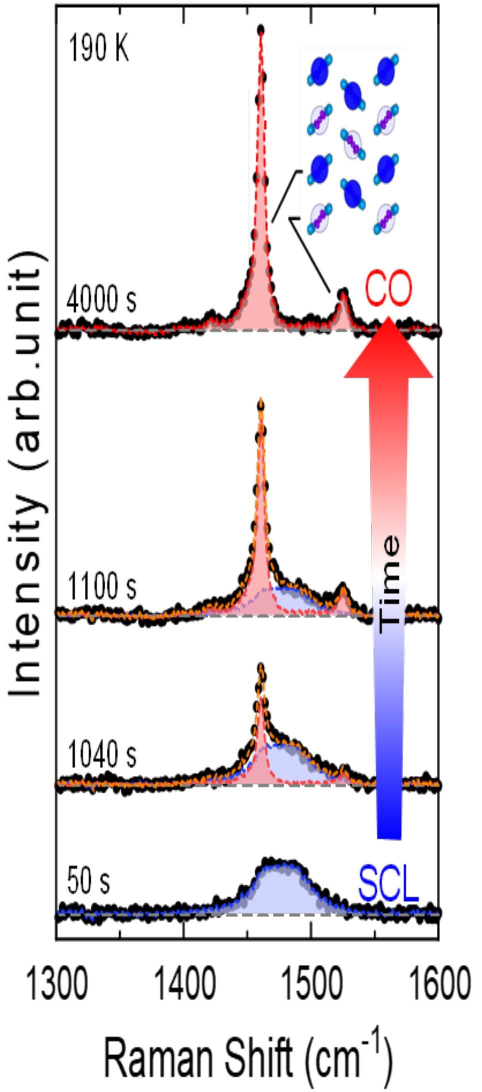
Resistivity



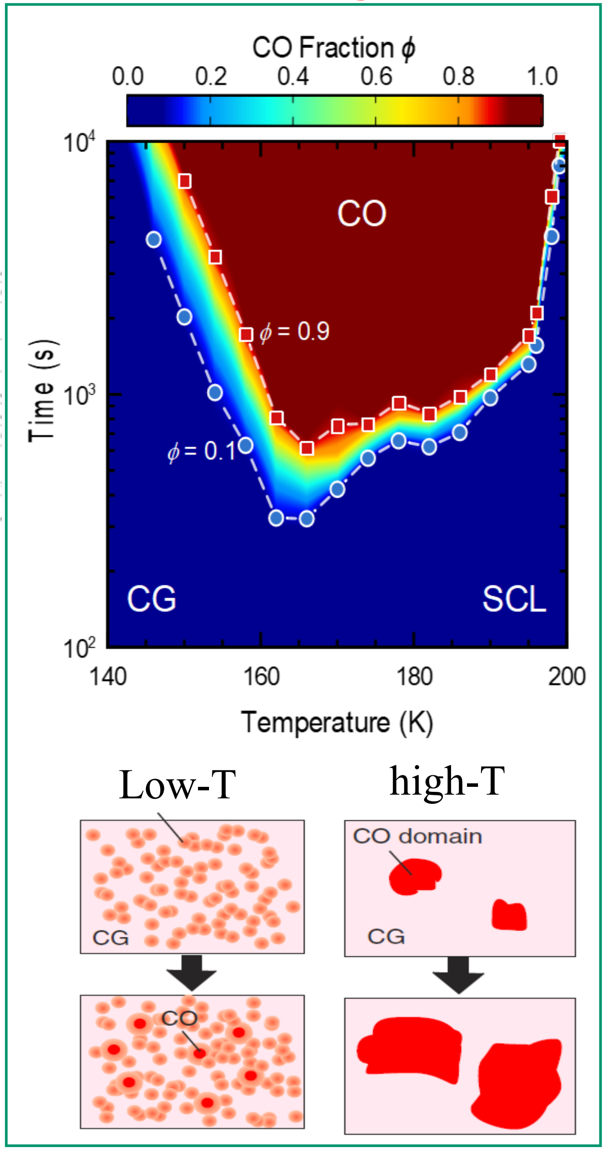
^{13}C NMR spectra



Raman spectra



TTT diagram



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

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

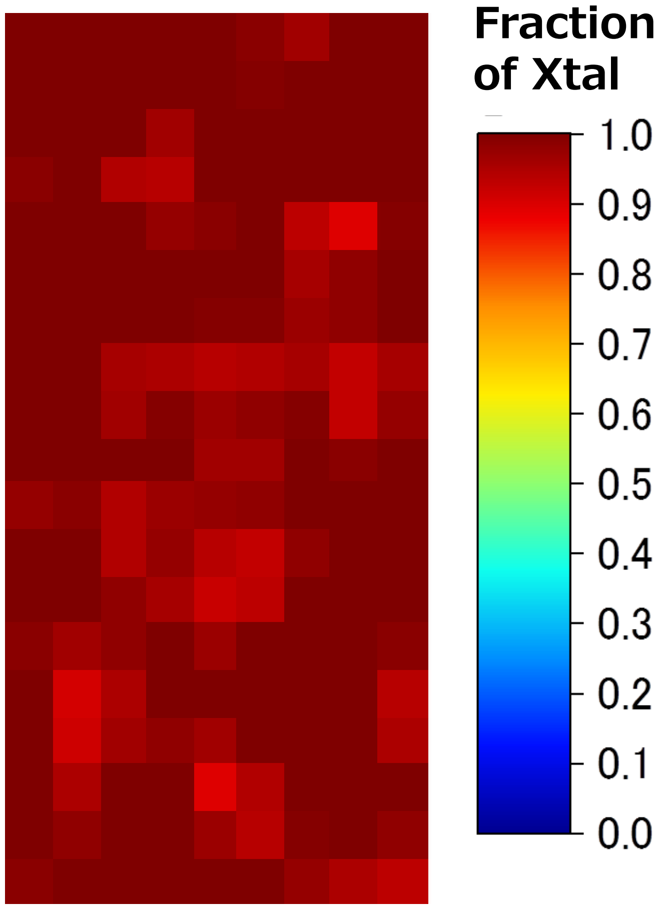
Murase *et al.*, arXix:2201.04855

Raman imaging of E-crystallization at high T

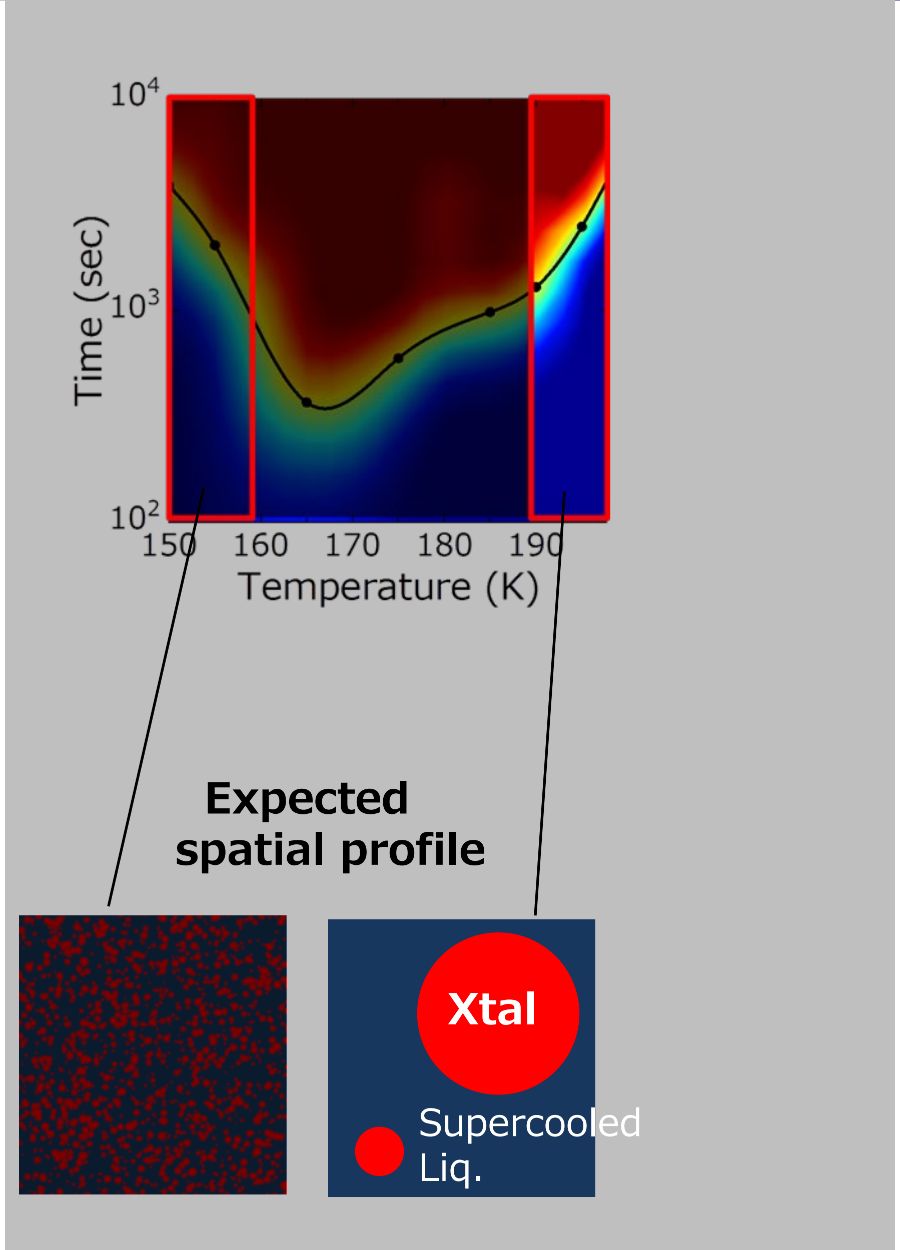
T_q = 195 K

150 s interval
6.5×6.5 μm²/pixel

20 μm



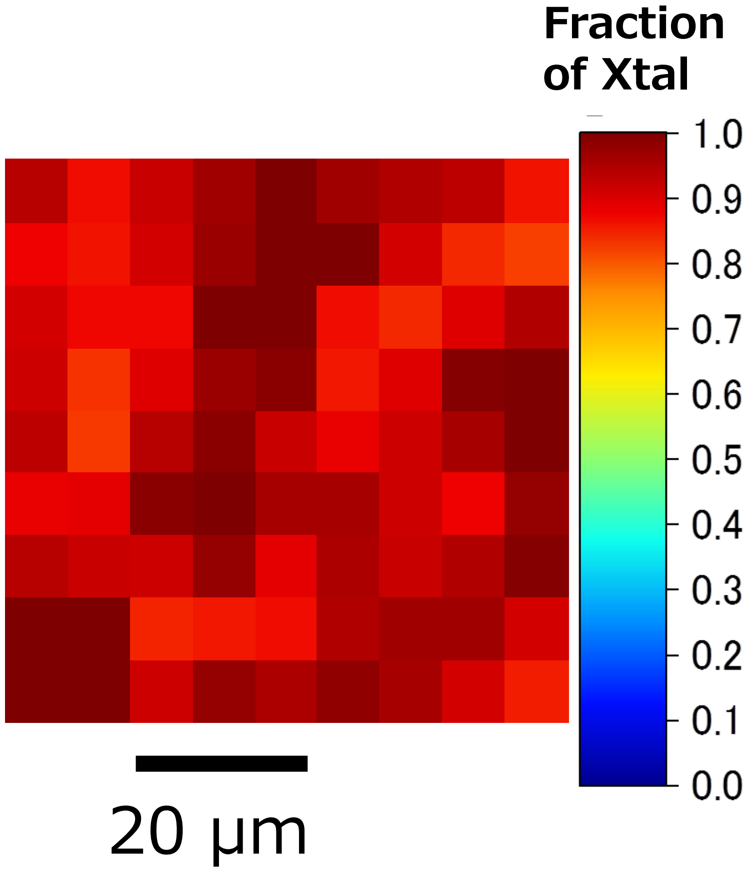
Macroscopically inhomogeneous



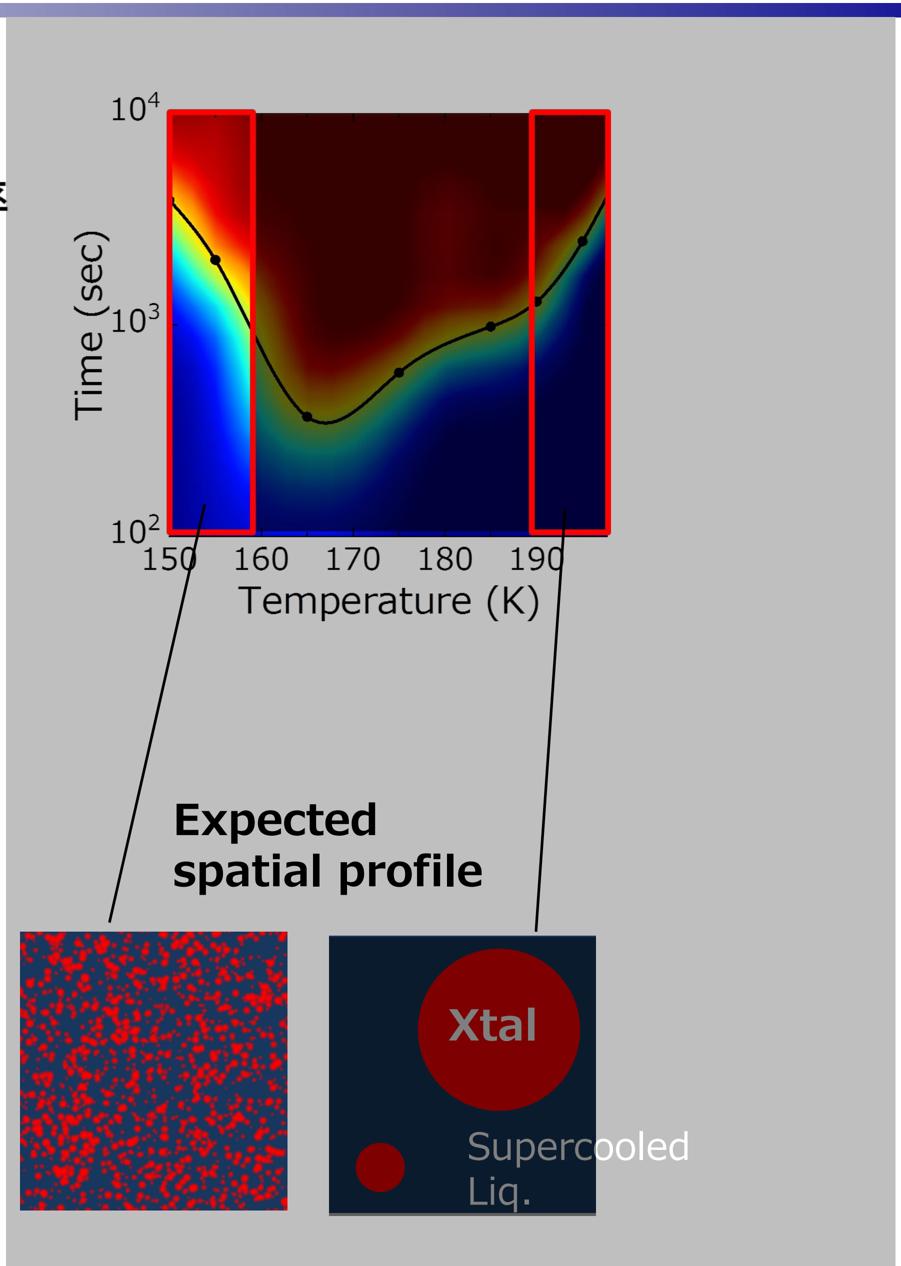
Raman imaging of E-crystallization at low T

T_q = 155 K

60 s interval
6.5×6.5 μm²/pixel

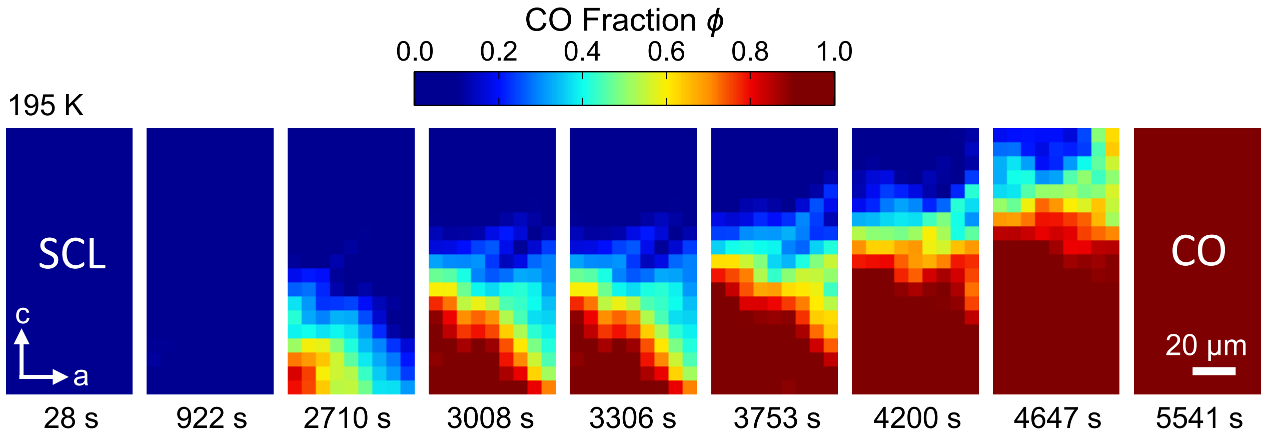


homogeneous



Ultrafast crystal growth ! quantum effect ?

Murase *et al.*, arXiv:2201.04855



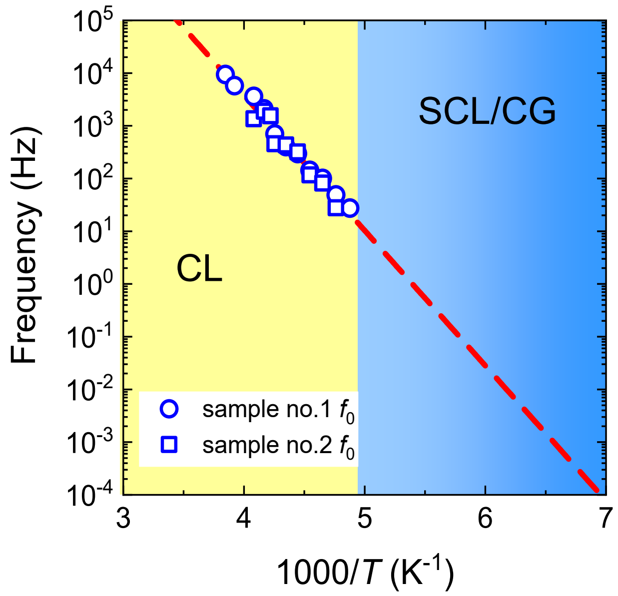
l = lattice constant 0.5 nm

$$\Delta\mu = \frac{\Delta H}{T_{CO}}\Delta T$$

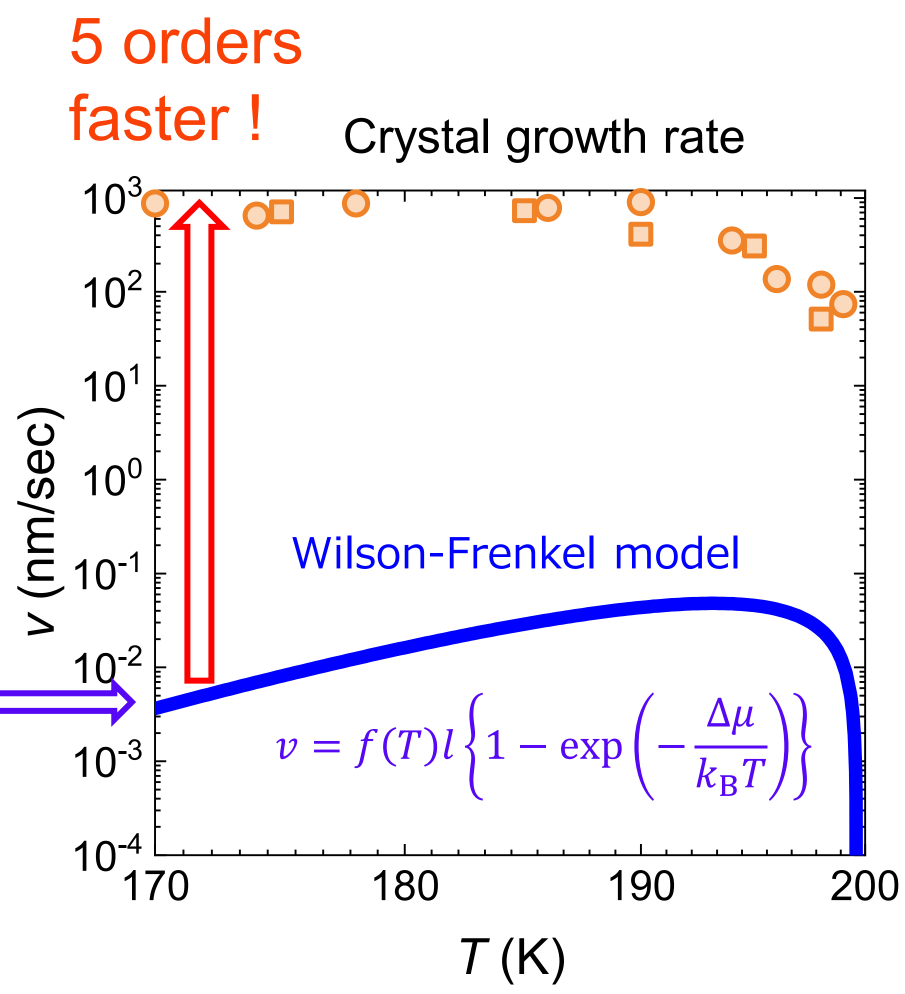
ΔH=160 K

T. Takeno, *et al.*, *J. Phys.: Conf. Series* **150**, 042201 (2009).

***f*(*T*)** from resistance noise



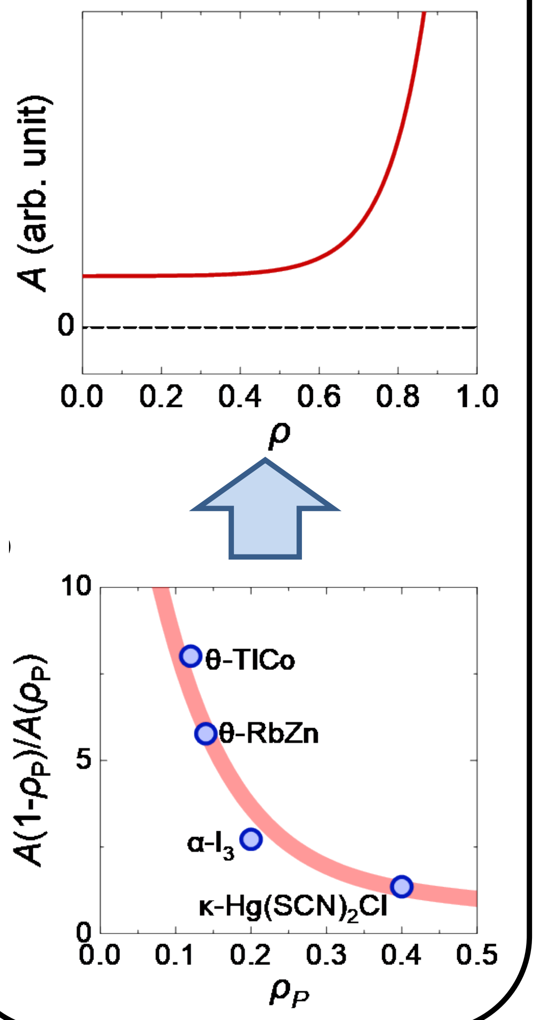
F. Kagawa, *et al.*, *Nat. Phys.* **9**, 419 (2013).



~~Classical Wilson-Frenkel model.~~

Raman spectrum → Charge density distribution

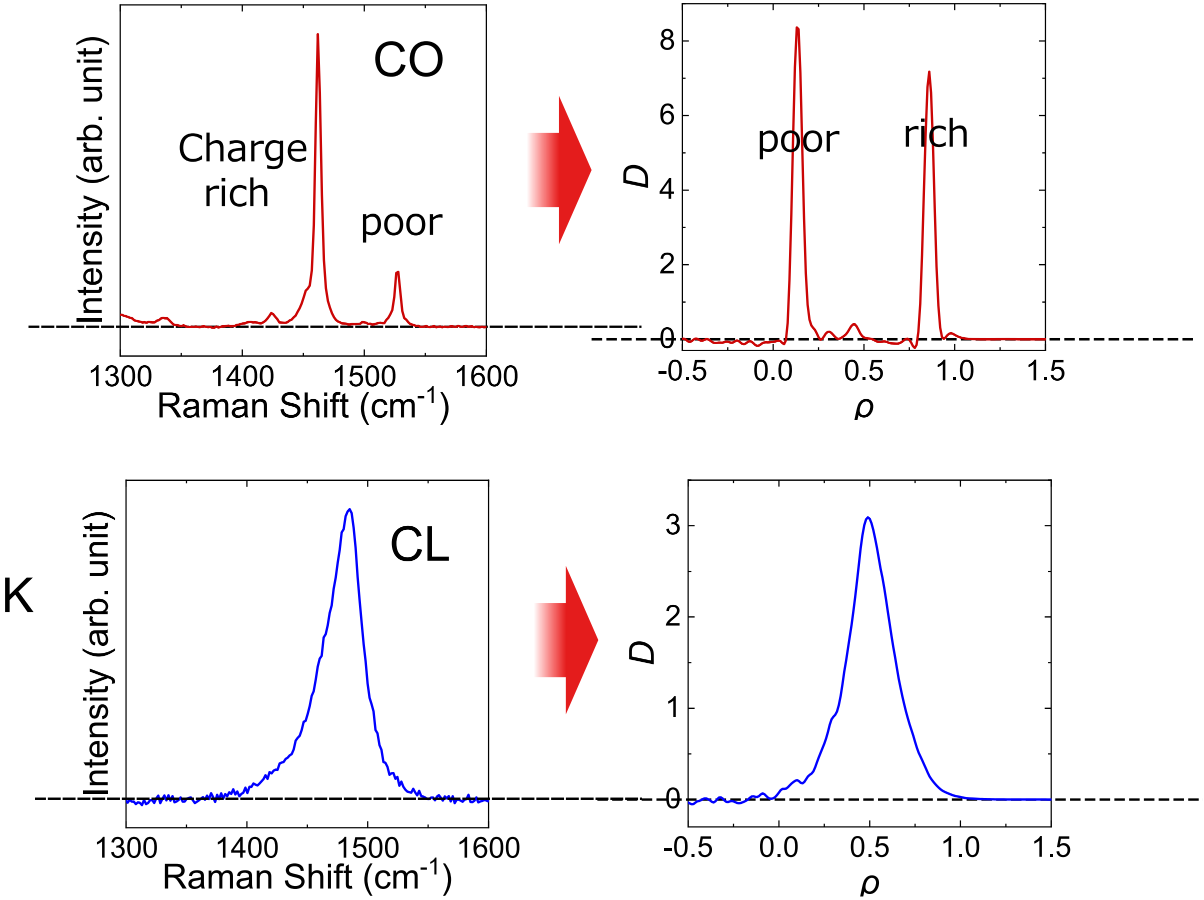
ρ-dependent
Raman tensor



Raman
spectrum

Charge density
distribution

CL
300 K

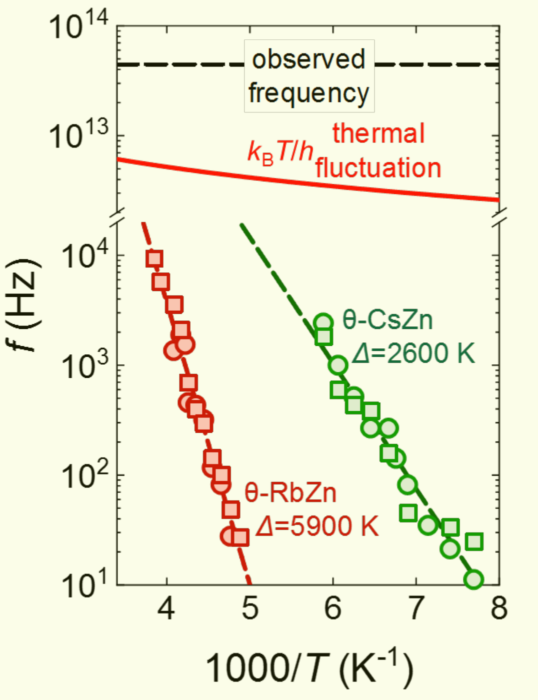


From classical to quantum charge glass

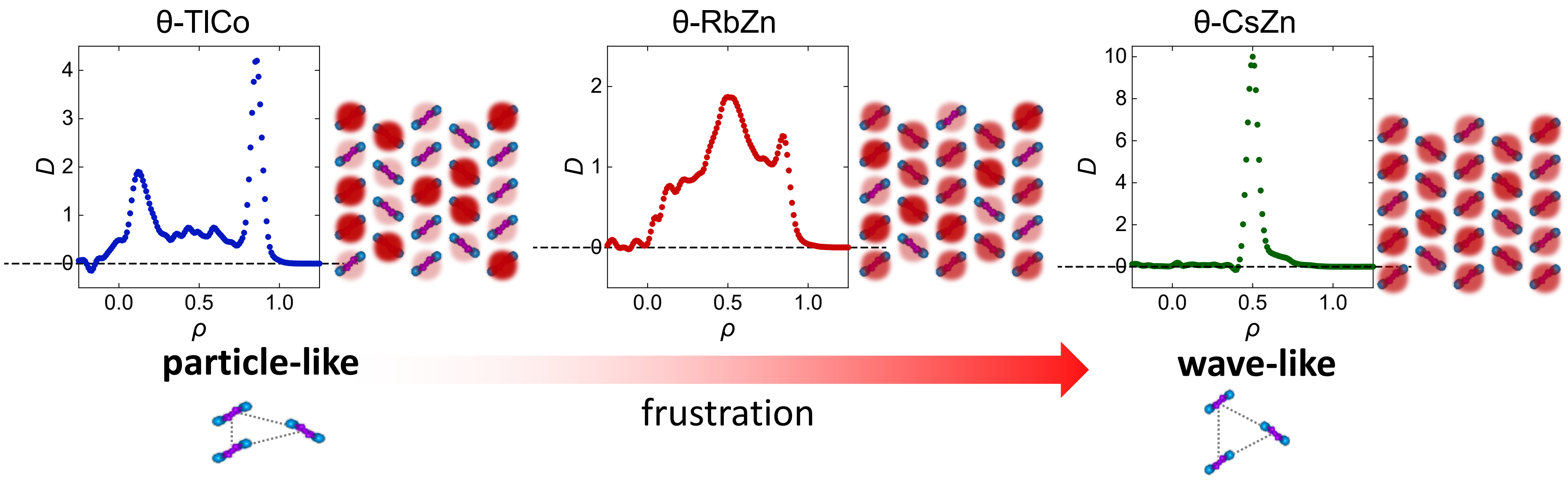
Murase *et al.*, arXiv.2205.10795

Raman time scale

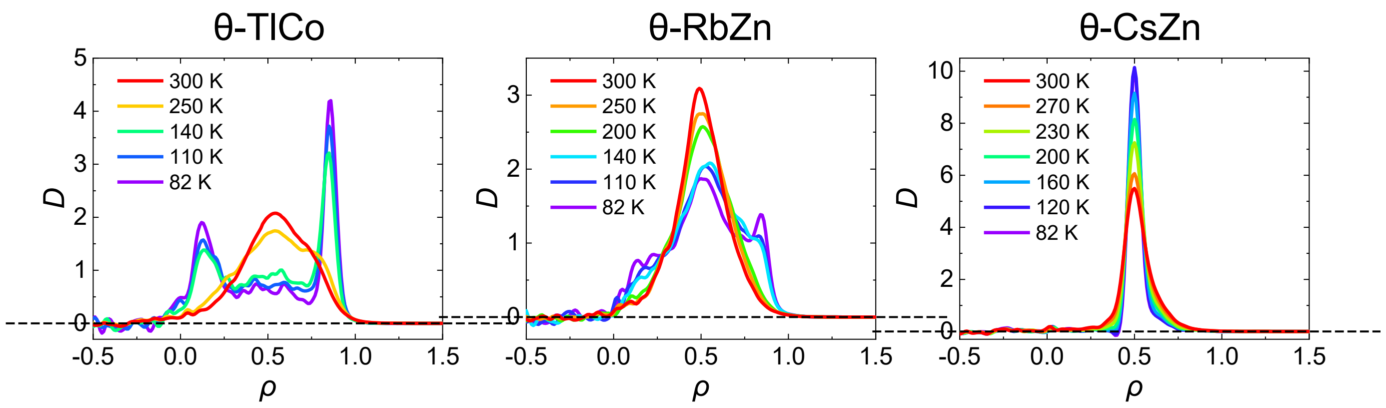
$f_{obs} >> f_{thermal} >>>> f_{glass}$

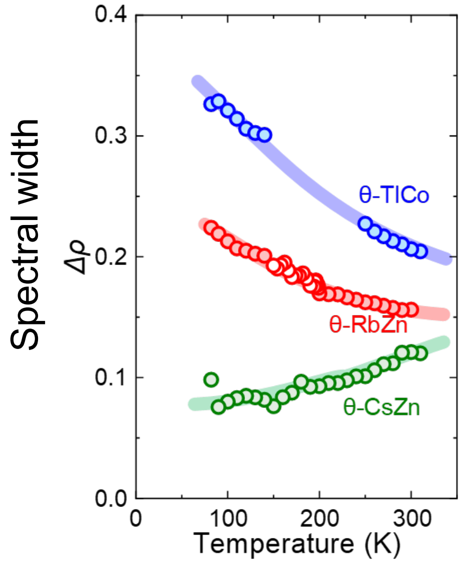


Frustration dependence of charge density in CG at 82 K



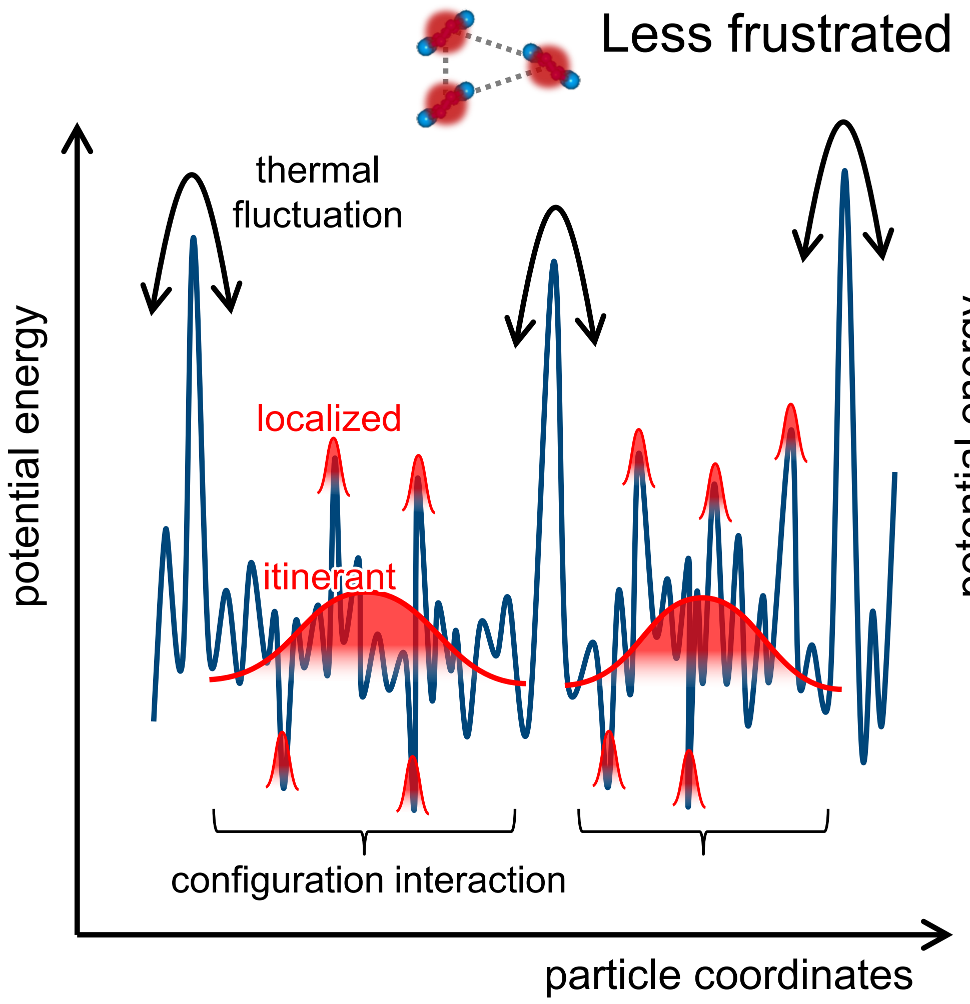
Temperature dependence of charge density



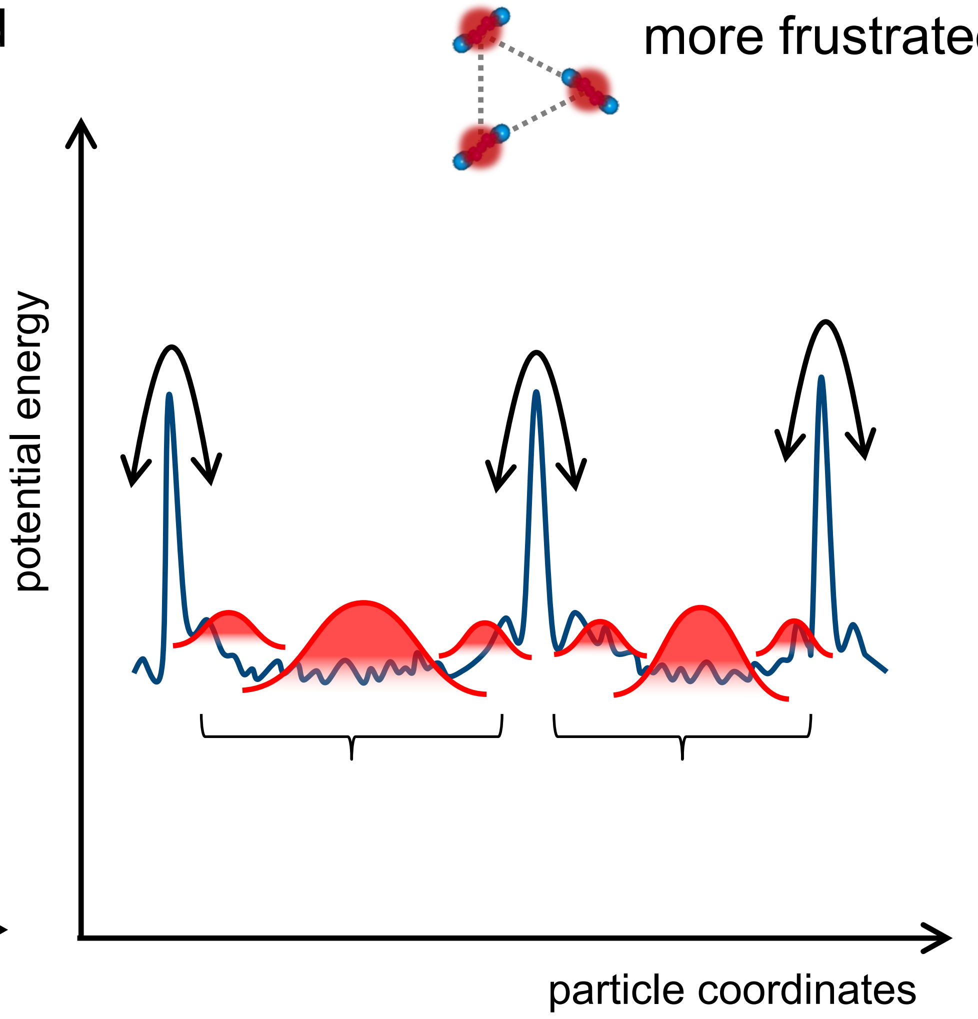


Theoretical: Fratini → talk on Friday

Discussion in terms of energy landscape



Classical glass

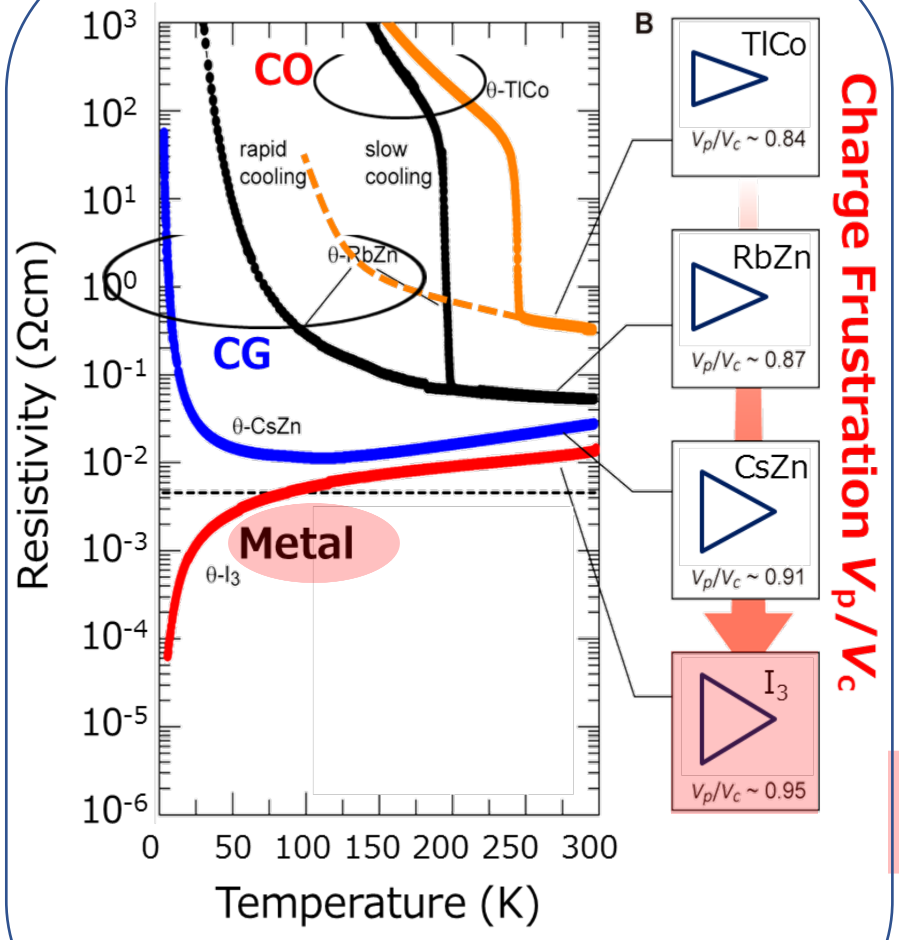


Quantum glass

Murase *et al.*, arXiv.2205.10795

Murase et al, unpublished

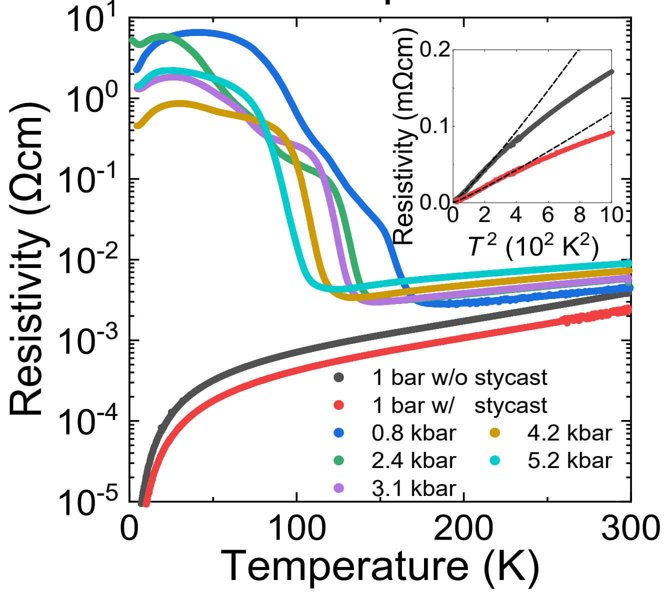
Frustration driven quantum melting of CO/CG

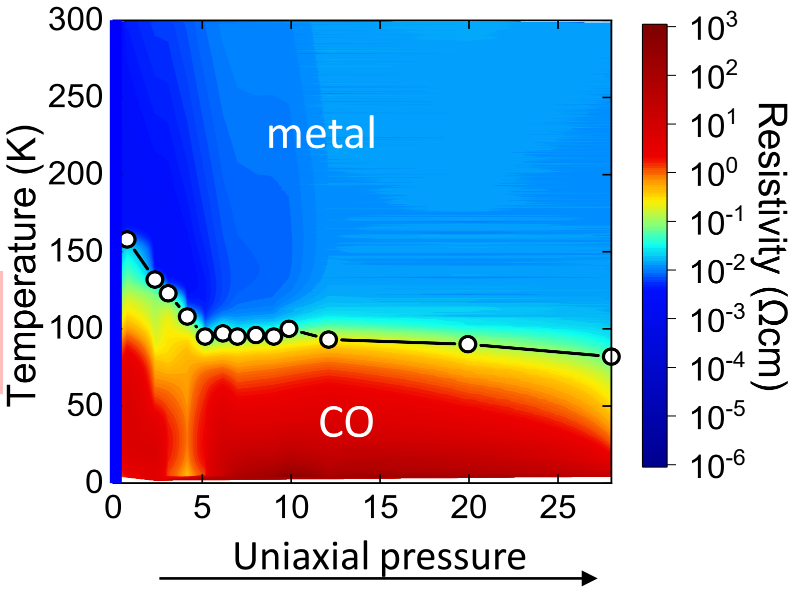


T. Sato, *et al.*, *Nat. Mater.* **11** (2019).

Uniaxial pressure

Uniaxial pressure

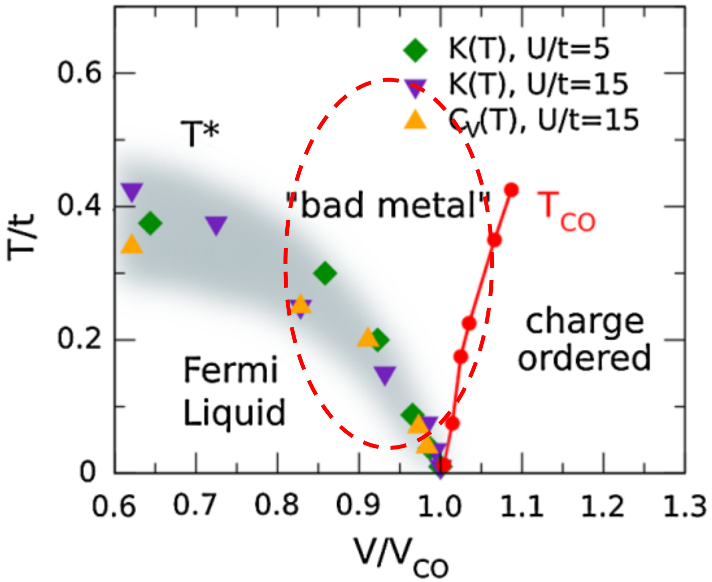




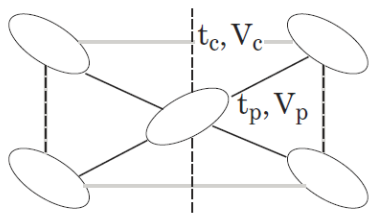
Distortion of triangular lattice

Strange metal arising from frustration-driven charge instability

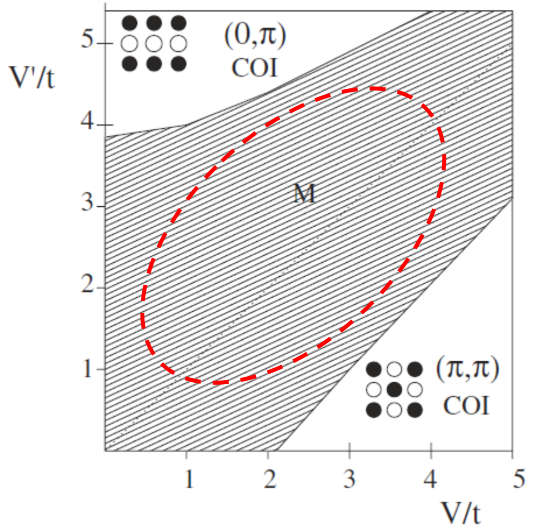
Cano-Cortes, Merino, Fratini et al.,   PRL (2010)



theoretical



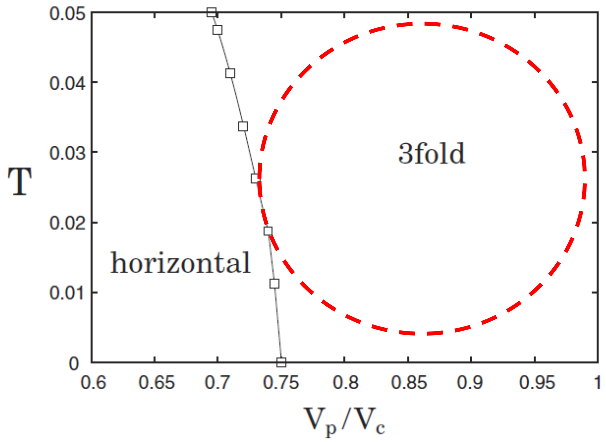
J. Merino et al, PRB(2007)

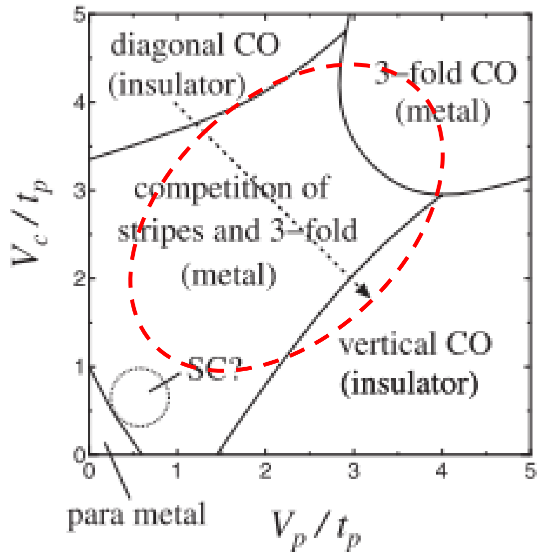


H. Watanabe, et al, JPSJ (2006)

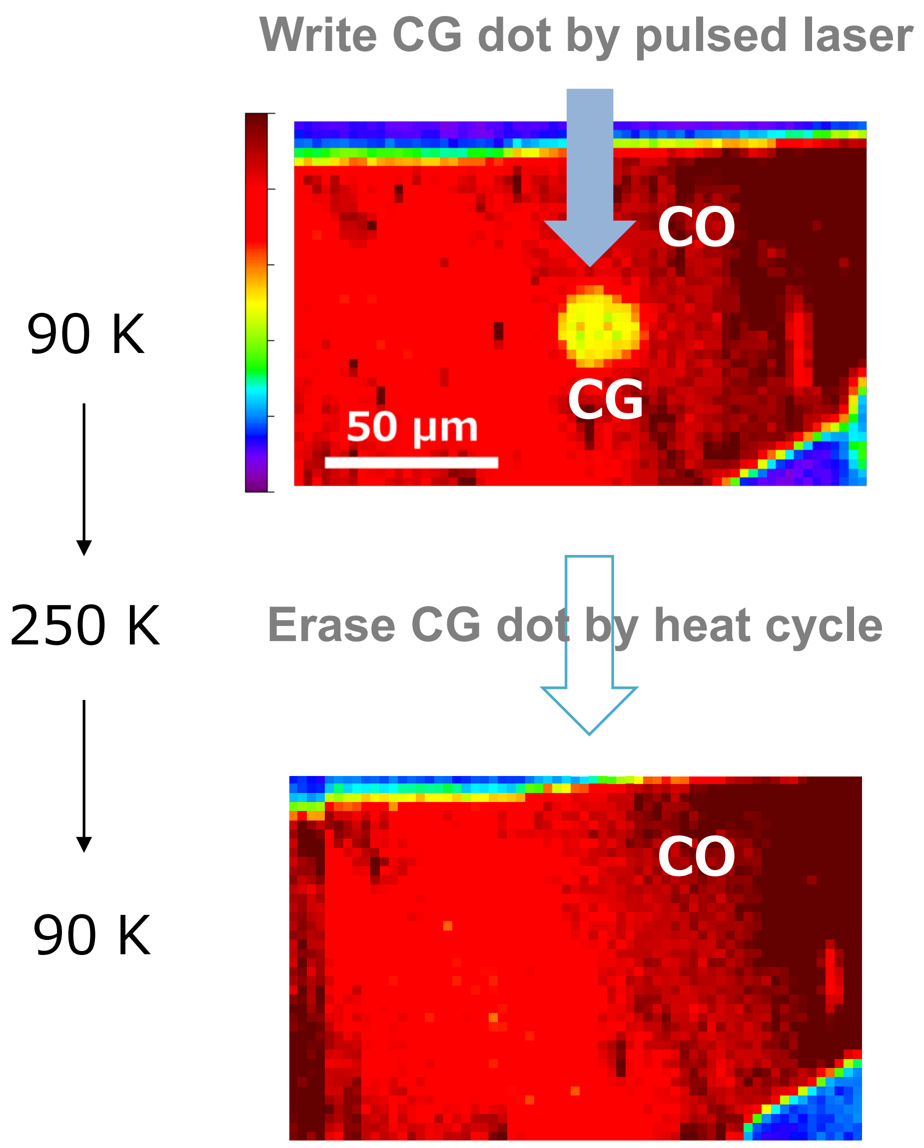
Y. Tanaka & K. Yonemitsu JPSJ (2007)

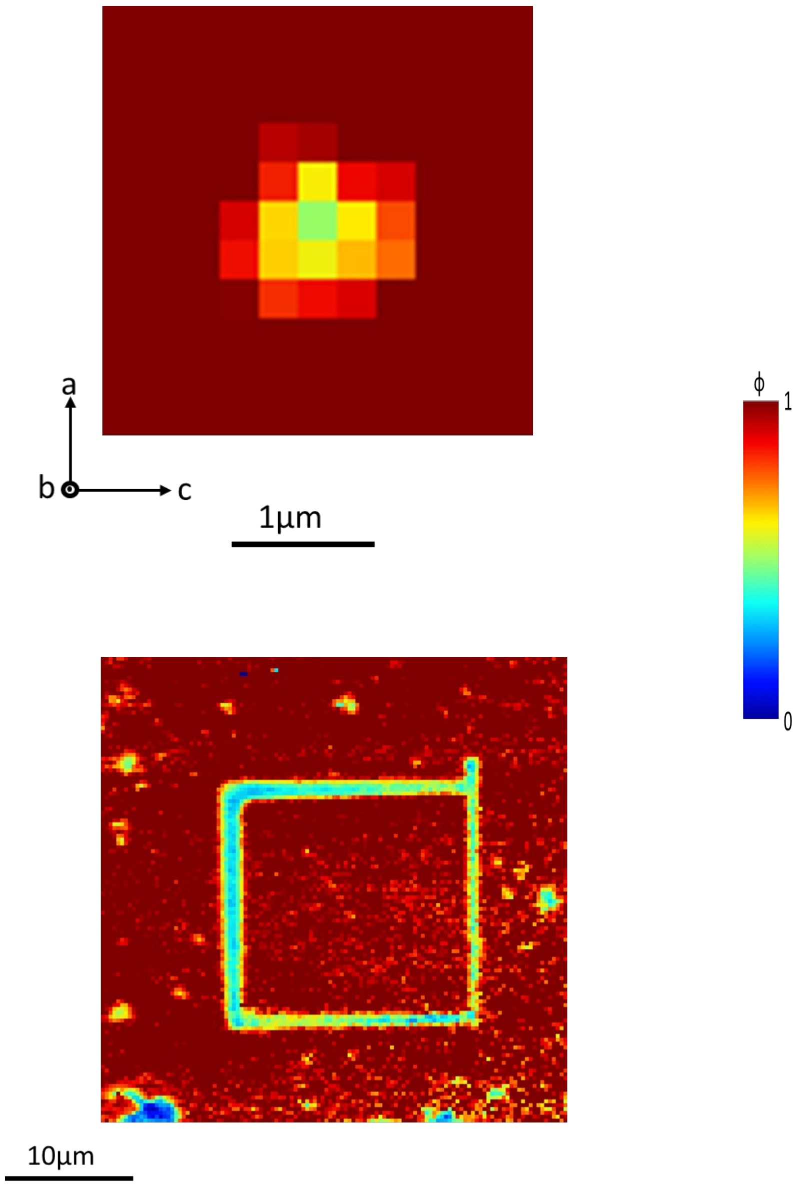
Février, S. Fratini, PRB (2015)





Write/erase E-glass on E-Xtal substrate by laser





Topological excitations in neutral-ionic (NI) transition

- What is NI transition
- Phase diagram of NI transition in TTF-CA
- two types of topological excitations
  - domain wall
  - spin soliton, charge soliton
- Ongoing trials and perspective

UTokyo, Applied Phys. K. Sunami, R. Takehara, F. Iwase,
M. Hosoda, T. Nishikawa, K. Miyagawa

UTokyo, Adv. Mat. Sci. T. Miyamoto, H. Okamoto

RIKEN R. Kato

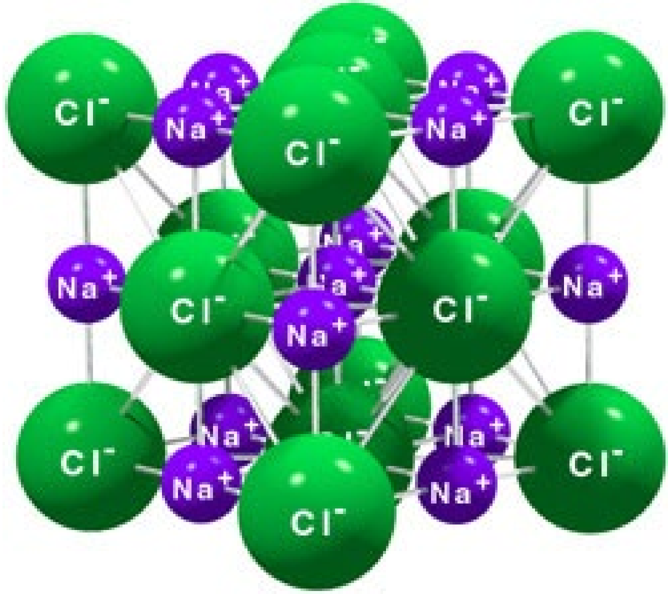
AIST S. Horiuchi

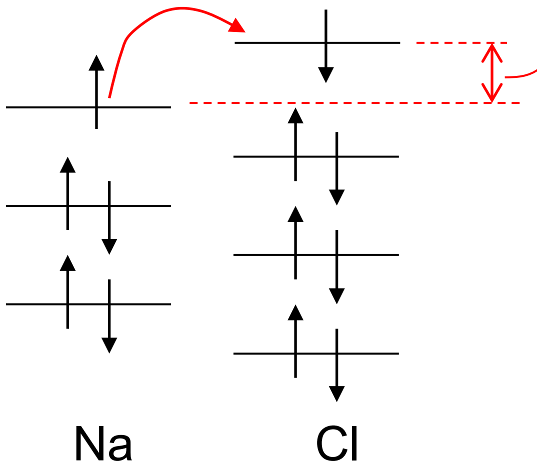
Ionic crystal ⟷ **Neutral crystal**

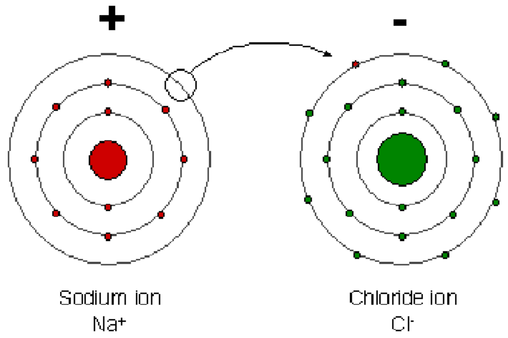
Neutral-ionic transition

Madelung gain αV vs. **Energy cost** $\Delta\varepsilon$

$Na^{+}Cl^{-}$

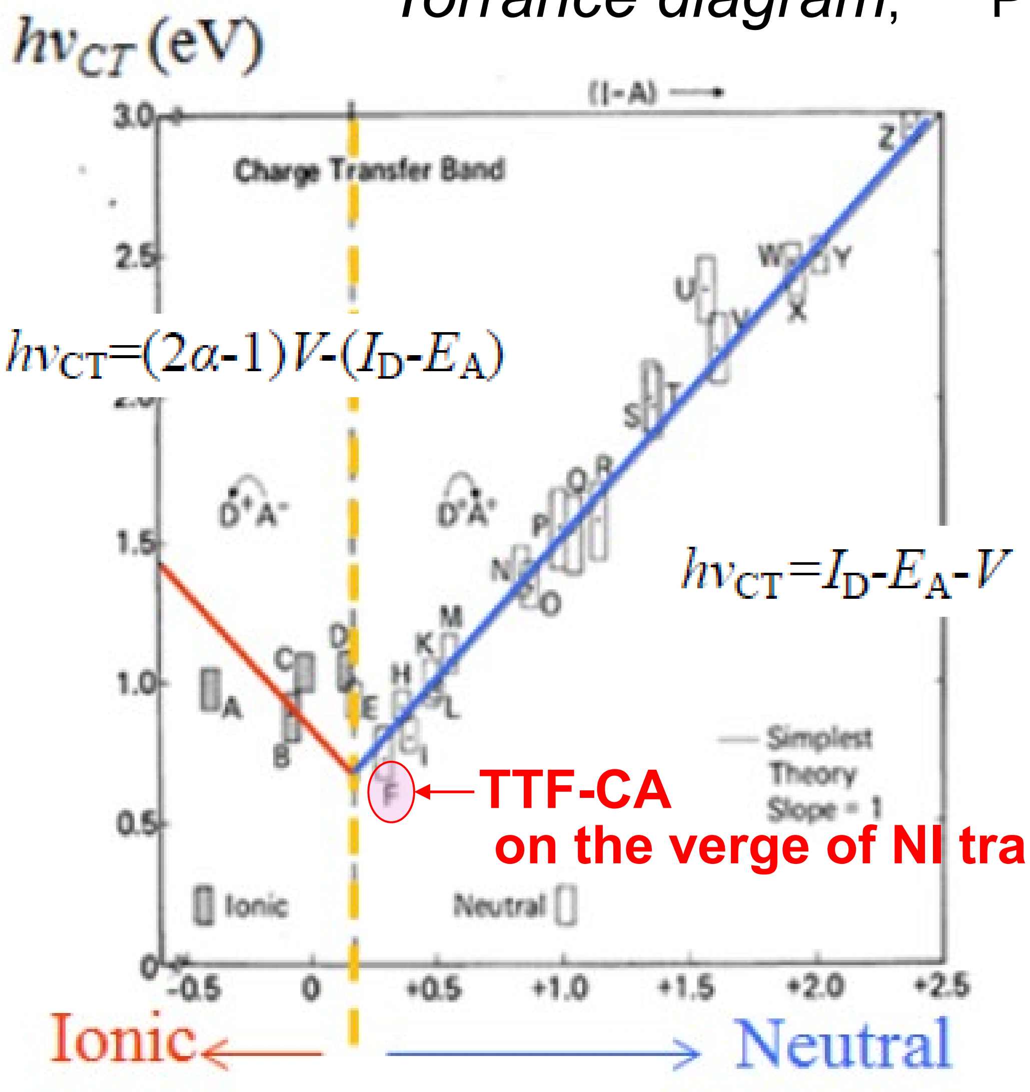






Combinations of donor (D) and acceptor (A)

Torrance diagram, PRL **46**, 253 (1981)



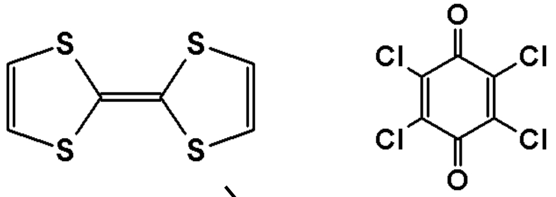
$I_D-E_A=\alpha V$

Symbol	Compound	N/I
A	TMPD-tetrafluoroTCNQ	I
B	dimethylphenazine-TCNQ	I
C	TMPD-TCNQ	I
D	TMPD-chloranil	I
E	TMDAP-TCNQ	N
F	TTF-chloranil	N
G	TTF-fluoranil	N
H	DibenzeneTTF-TCNQ	N
I	DEDMTSeF-diethylTCNQ	N
J	TMDAP-fluoranil	N
K	TTF-dichlorobenzoquinone	N
L	perylene-tetrafluoroTCNQ	N
M	perylene-DDQ	N
N	perylene-TCNE	N
O	perylene-TCNQ	N
P	TTF-dinitrobenzene	N
Q	perylene-chloranil	N
R	pyrene-TCNE	N
S	pyrene-chloranil	N
T	anthracene-chloranil	N
U	hexamethylbenzene-chloranil	N
V	naphthalene-TCNE	N
X	anthracene-PMDA	N
Y	anthracene-tetracyanobenzene	N
Z	phenanthrene-PMDA	N

Neutral-Ionic (NI) transition in TTF-CA

TTF-CA

Donor : TTF　　Acceptor : CA

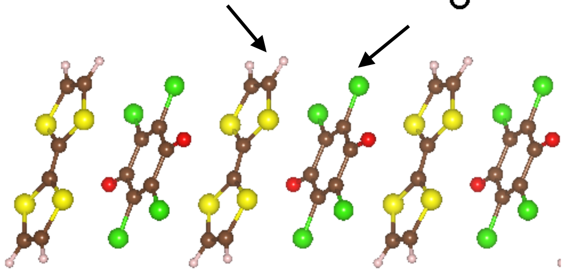


Torrance *et al.*, PRL. (1981)

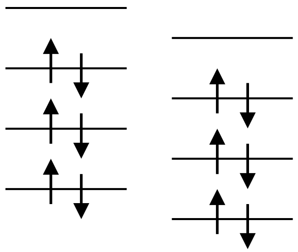
Band insulator

Neutral

dielectric



TTF　CA



Temperature
Pressure

***Charge** transfer*

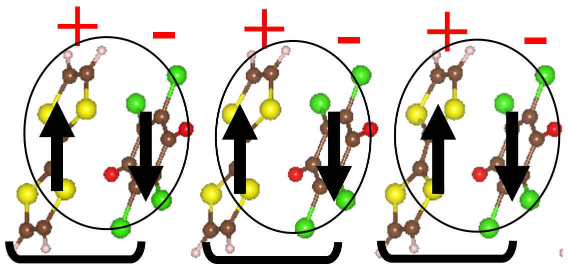
***Spin**-Peierls*

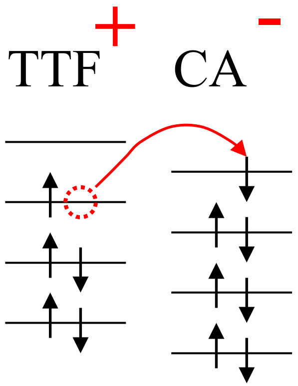
***Lattice** dimerization*

Charge-transferred
Mott insulator

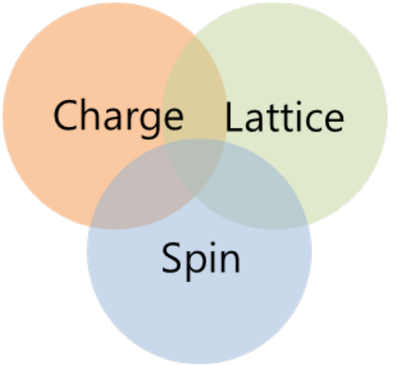
Ionic

ferroelectric



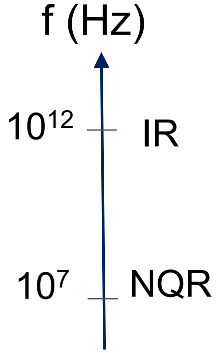


Strongly coupled



Phase diagram of TTF-CA

Time scales of probes



Fluctuating NI domain wall

Fractional change from N to I

Uniform change from N to I

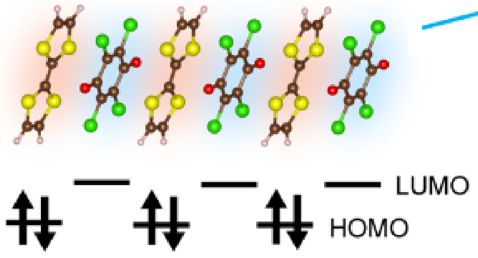
H. Okamoto *et al*., PRB **39**, 10693 (1989)

Dimeric

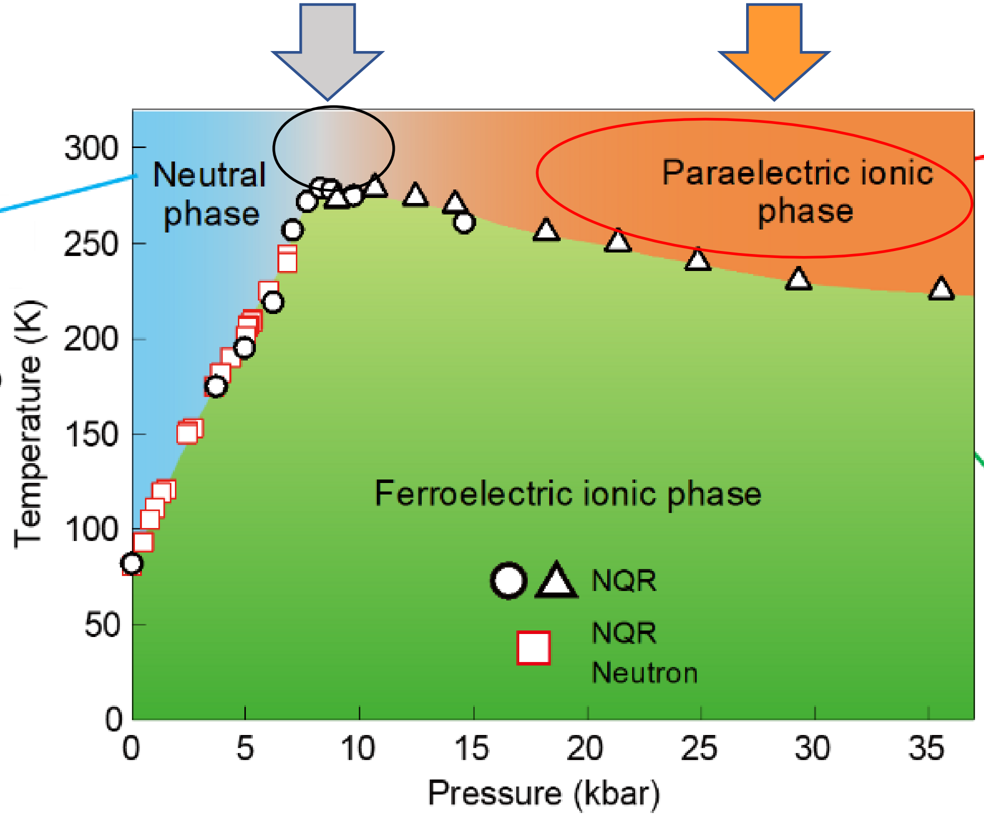
Non-dimeric

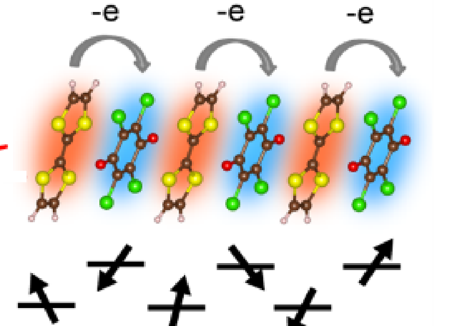
Dimer liquid

R. Takehara, *et al*, PRB, **98** 054103 (2018)

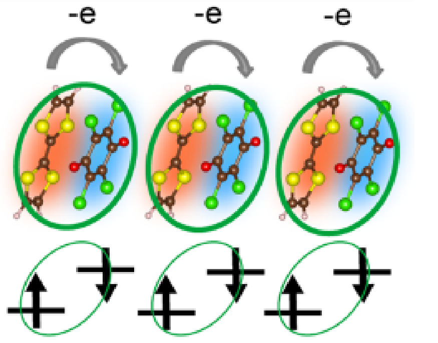


Neutral phase





Paraelectric ionic phase



Ferroelectric ionic phase

R. Takehara, *et al*, PRB, **98** 054103 (2018)

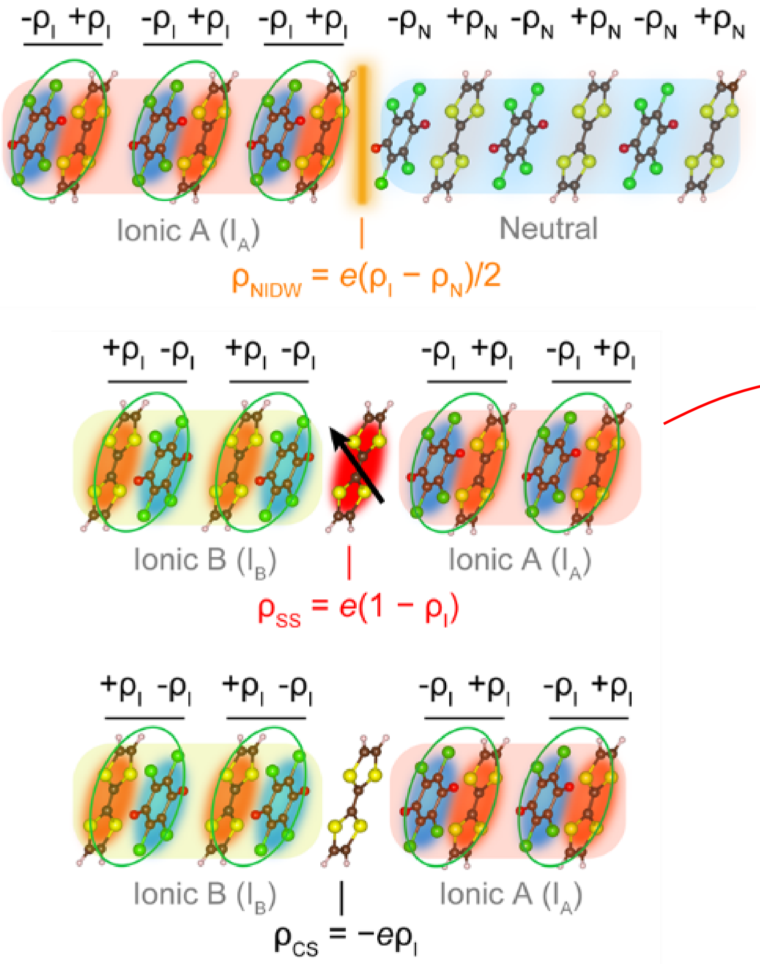
Spin-charge-lattice coupling → emergent topological excitations in 1D

N. Nagaosa, *et al*, J. Phys. Soc. Jpn., **55**, 2745(1986).

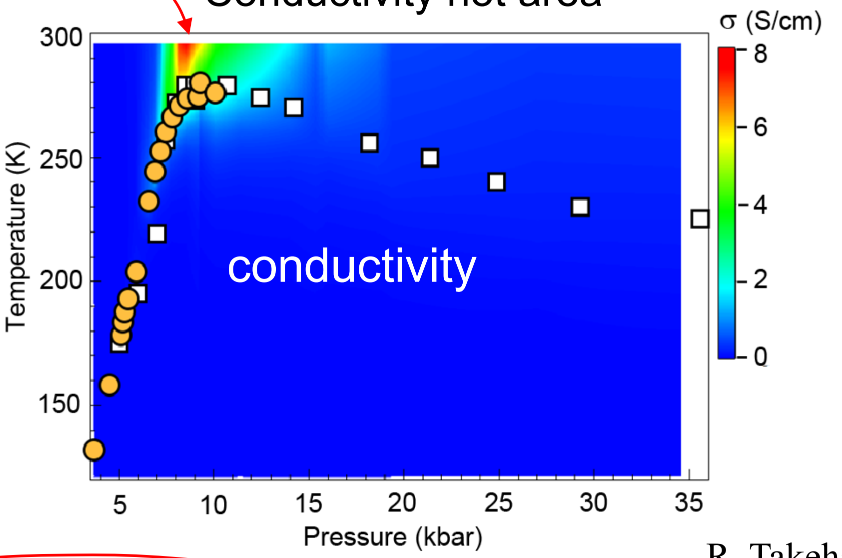
NI domain wall

Spin soliton

Charge soliton

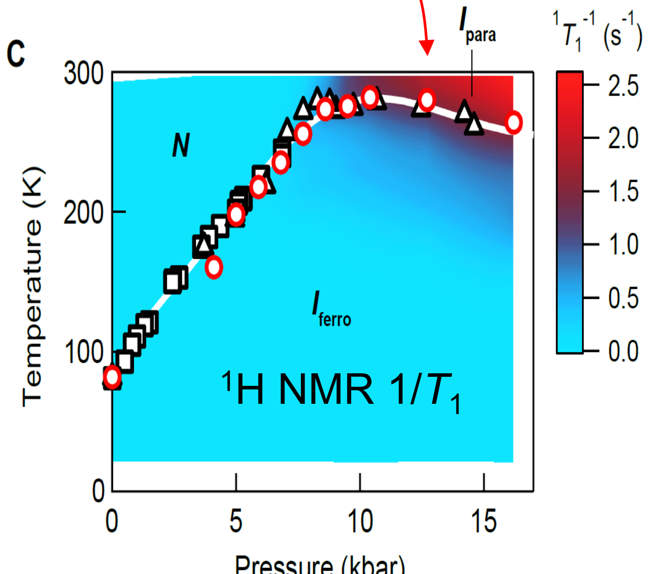


Conductivity hot area



R. Takehara *et al*., *Sci. Adv.* 5, eaax8720 (2019)

Magnetically hot area



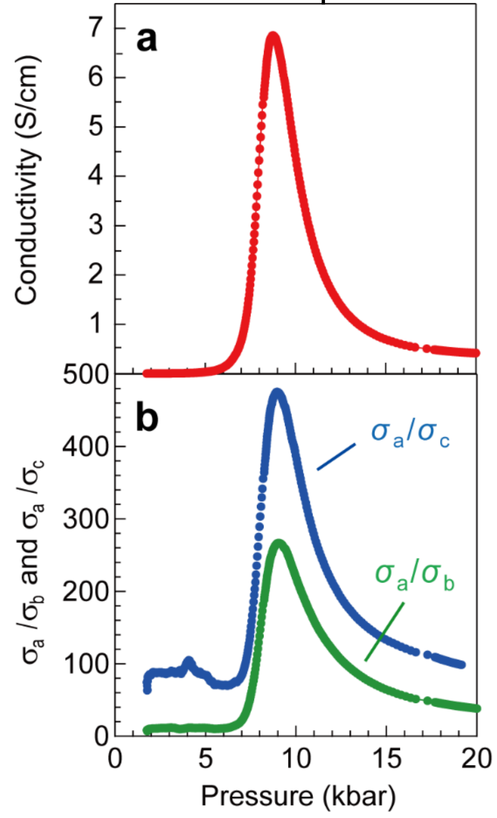
K. Sunami *et al*., *Sci. Adv.* **4,** eaau7725 (2018).

Charge transport gap << charge transfer gap

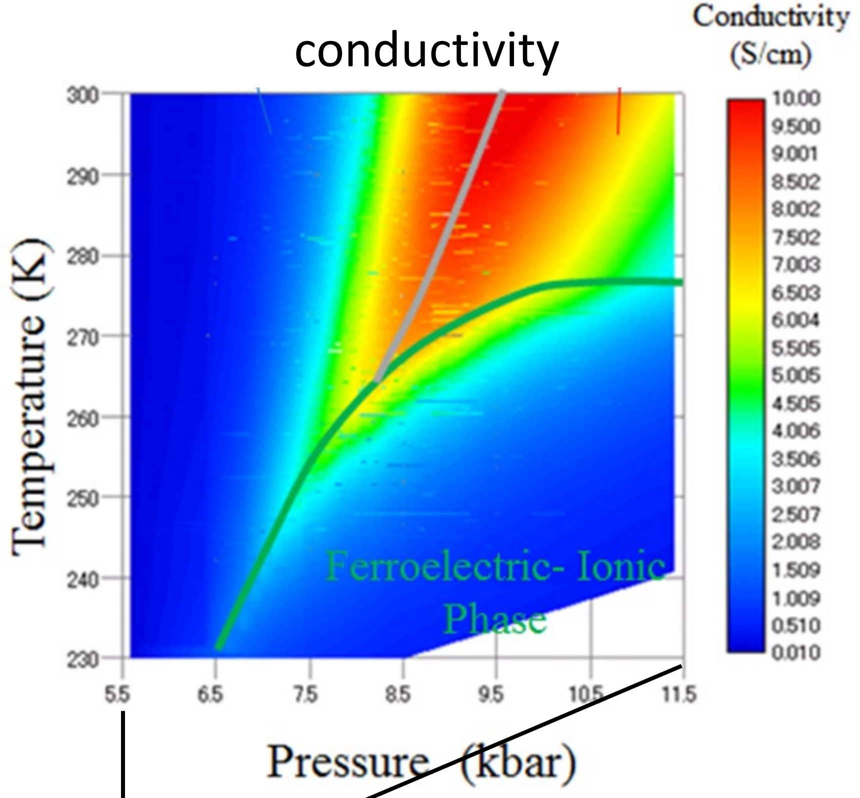
R. Takehara *et al.*, *Sci. Adv.* 5, eaax8720 (2019)

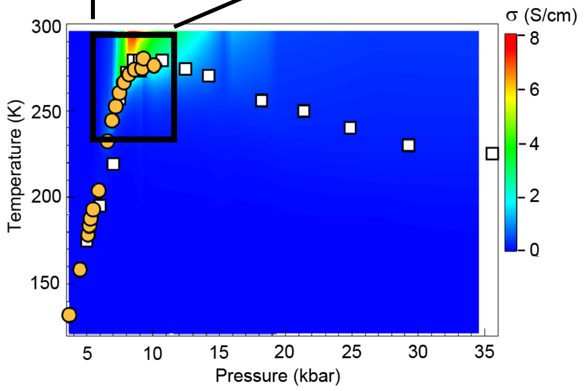
Enhanced conductivity
Enhanced 1d anisotropy

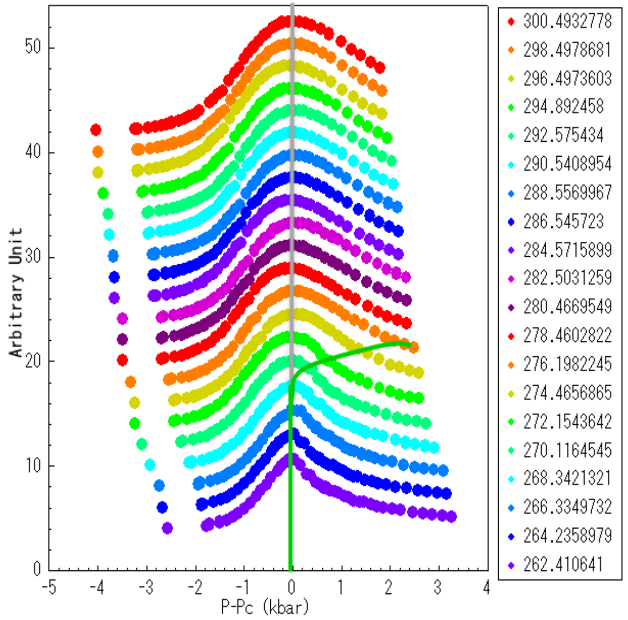
Pressure dependence at room temp.



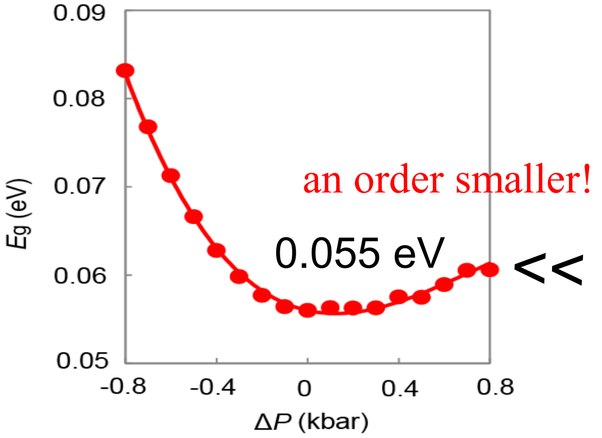
conductivity





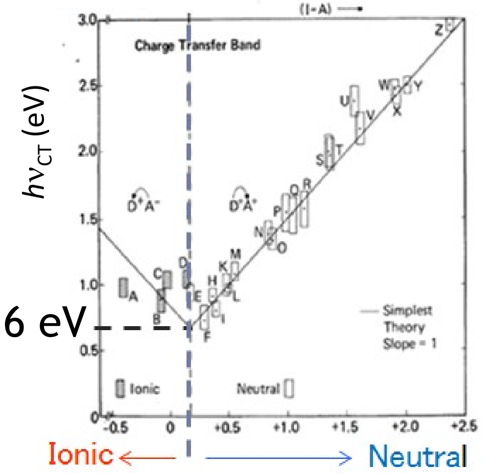


Transport gap



<< 0.6 eV

Charge-transfer gap

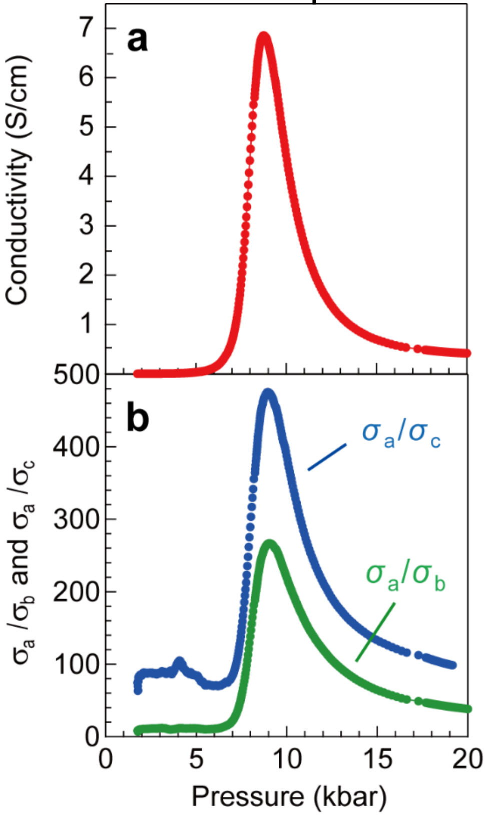


Charge transport gap << charge transfer gap

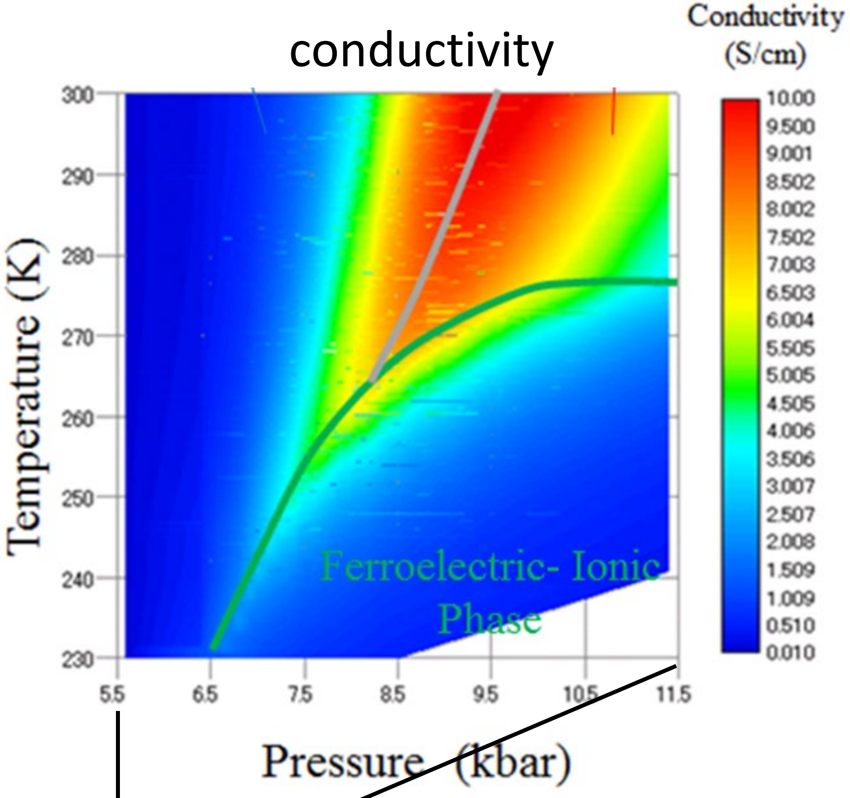
R. Takehara *et al*., *Sci. Adv.* 5, eaax8720 (2019)

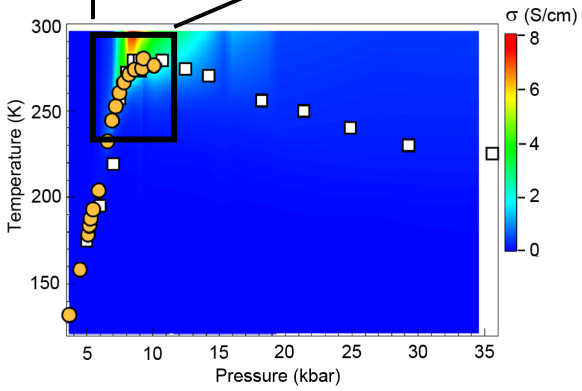
Enhanced conductivity
Enhanced 1d anisotropy

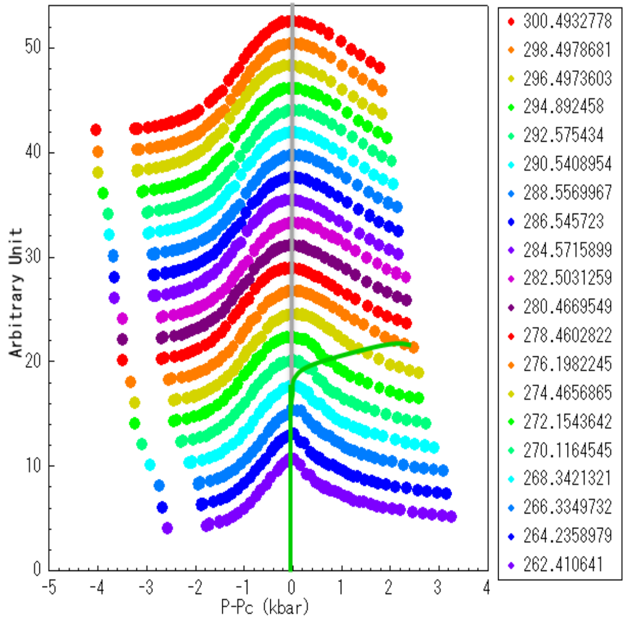
Pressure dependence
at room temp.



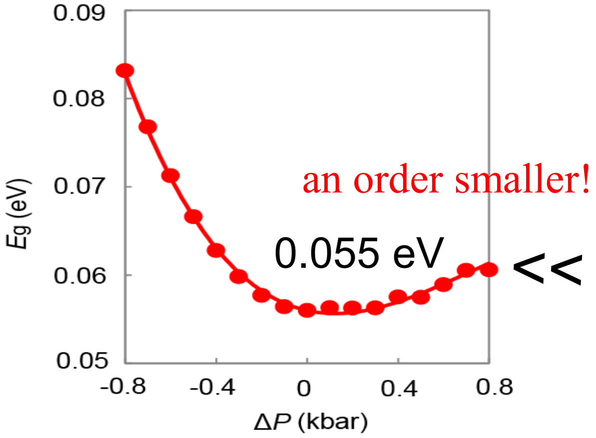
conductivity





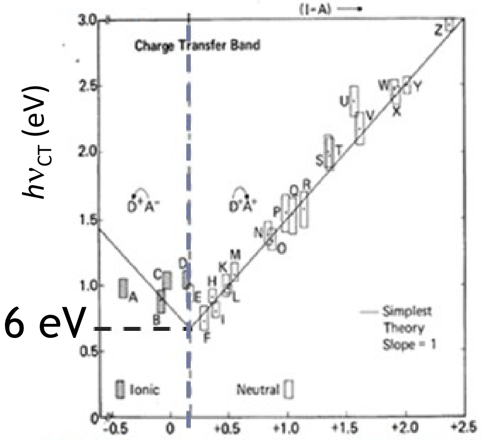


Transport gap



<< 0.6 eV

Charge-transfer gap

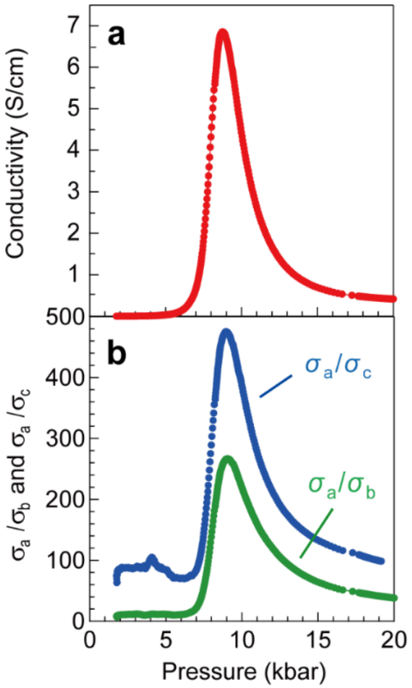


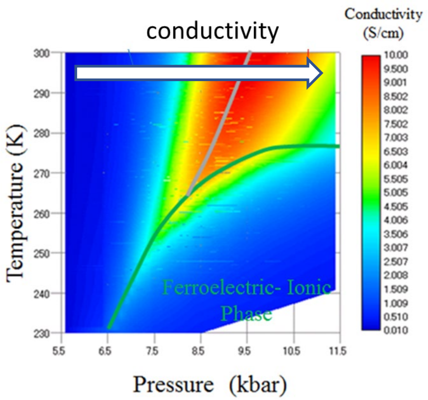
Ionic ← → Neutral

NI domain wall (NIDW) excitations

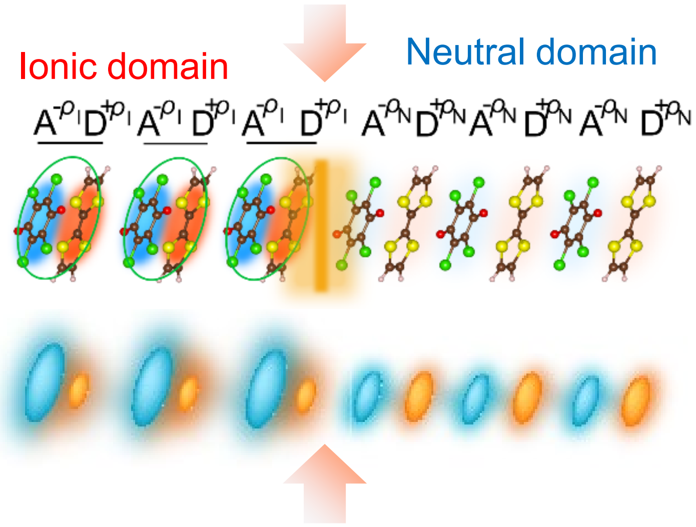
Enhanced conductivity

Enhanced 1d anisotropy





NIDW



Topological charge $\rho_{NIDW} = \frac{e}{2}(\rho_I - \rho_N)$

N. Nagaosa, *et al*, JPSJ, **55**, 2745(1986).
Z. G. Soos *et al*., PRB **75**, 155119 (2007).
M. Tsuchiizu, *et al*, JPSJ., **85**, 104705(2016).

Theoretical

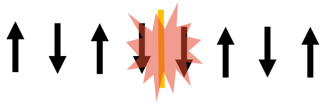
i) Excitation gap (N. Nagaosa, *et al*, JPSJ **55**, 2745(1986))

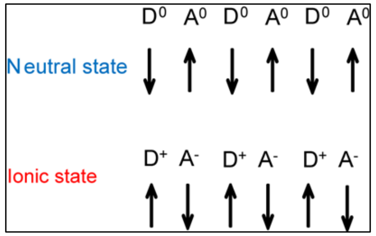
t=0.21～0.25eV、V=0.62～0.72eV ⇨ Δ_{NIDW}=0.030～0.066eV ⟷ Δ_{exp}=0.055 eV

good agreement

ii) Excitation density (R. Bruinsma et al., PRB **27,** 456 (1983))

Mapping NI transition to AF Ising spins ⇨ NI domain wall ≡ spinon



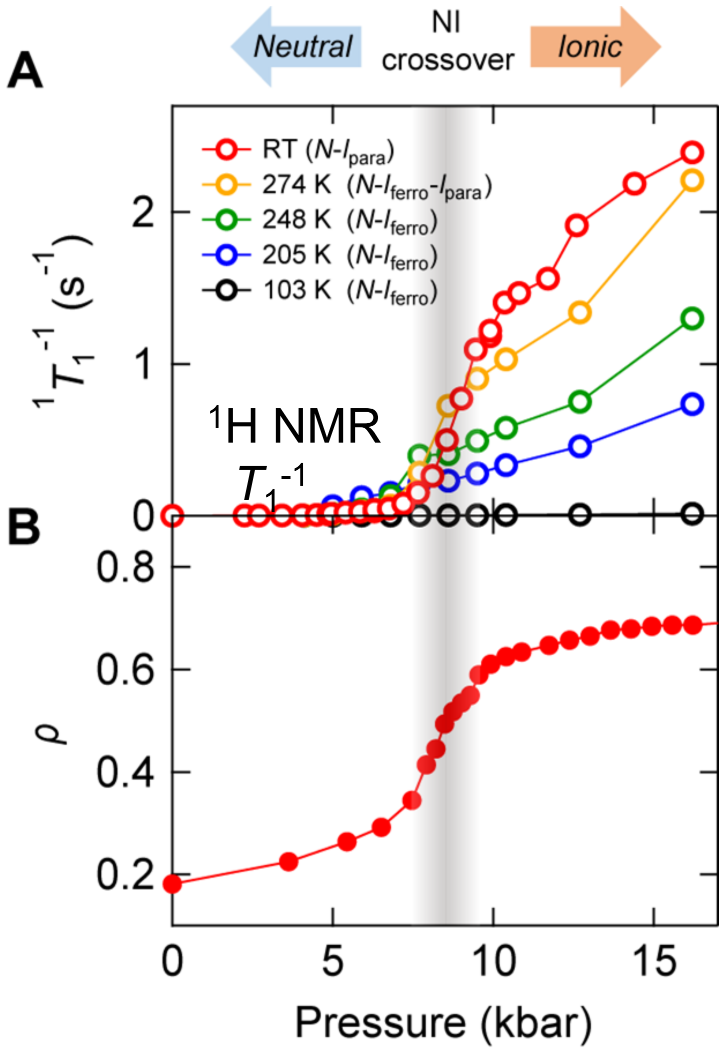


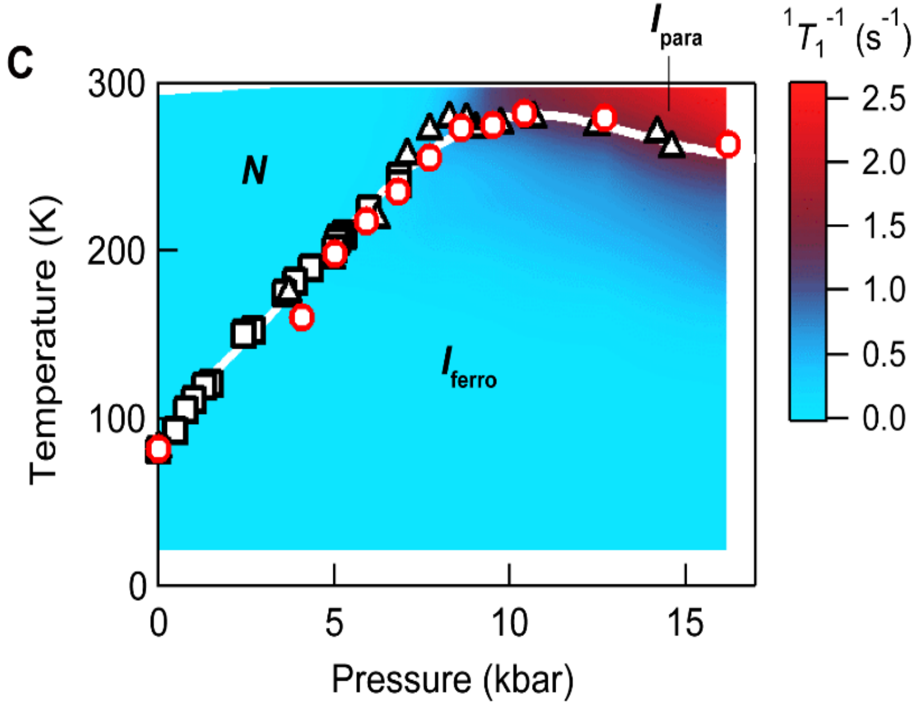
Coherence length $\xi = 1/ln\,(coth\,(E_{DW}/2k_BT))$

⇩

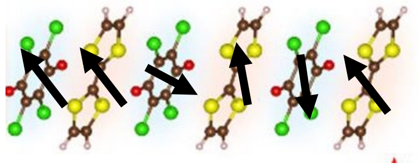
1 NIDW per 5 DA pairs at room temp.

Intense spin excitations in the ionic phase at high T



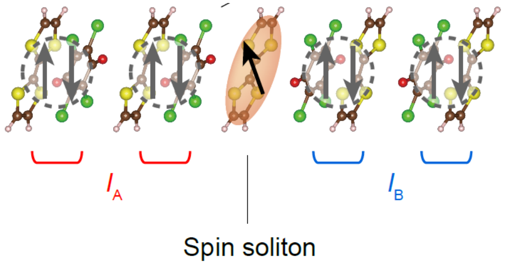


K. Sunami *et al*., *Sci. Adv.* **4,** eaau7725 (2018).



Homogeneous 1D spin chains

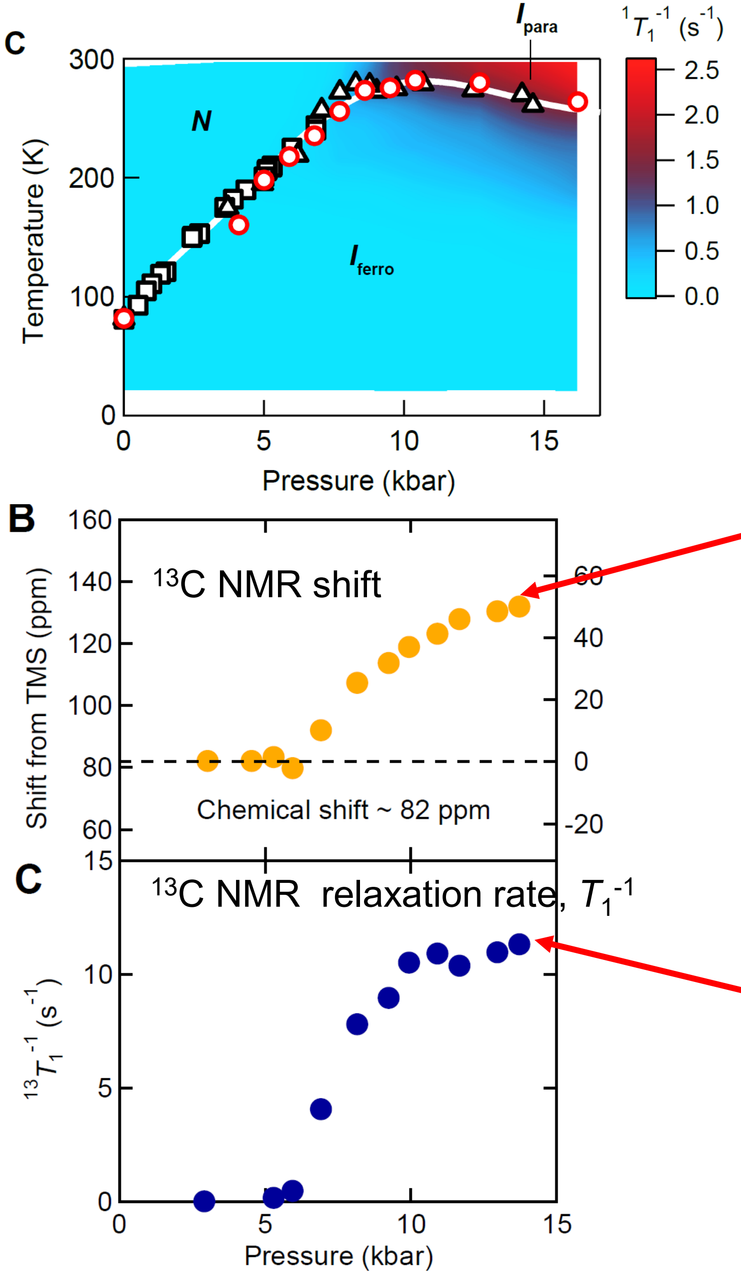
or **?**



Solitonic spins

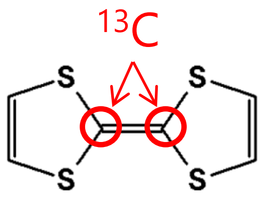
Indication of solitonic spin excitations I

K. Sunami *et al.*, *Sci. Adv.* **4,** eaau7725 (2018).

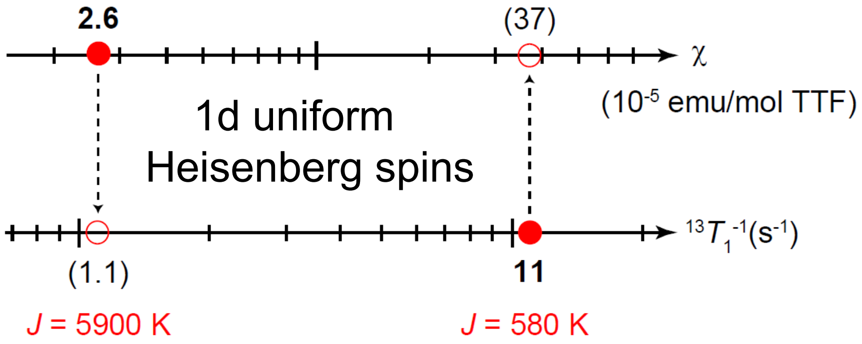


At room temp.

^{13}C NMR



χ ~ 2.6×10^{-5} emu/mol-TTF

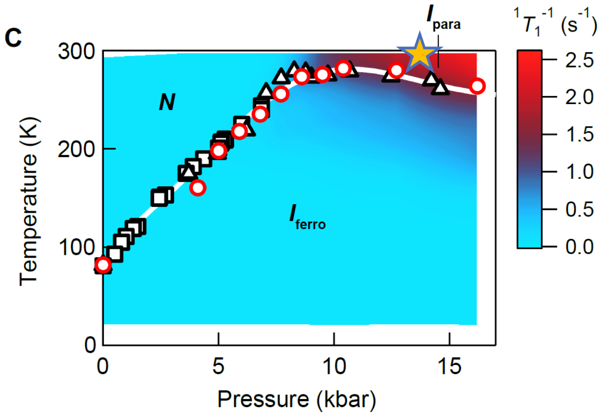


$1/T_1$ ~ 11 s^{-1} @14 kbar

~~Uniform spin model~~

Indication for solitonic spin excitations II

K. Sunami *et al.*, *Sci. Adv.* **4,** eaau7725 (2018).



Spin diffusion model

$$T_1^{-1} = S(\omega) \propto \omega^{-1/2} \quad \text{(1D)}$$

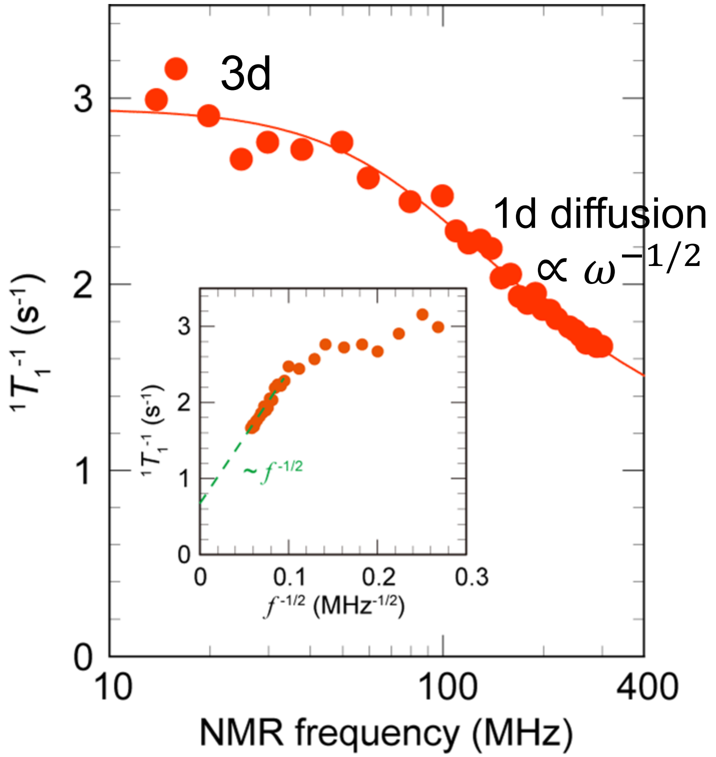
$$\propto const. \quad \text{(3D)}$$

1D-3D crossover spin diffusion model,

$$S(\omega)^{\mathrm{1D-3D}} = \frac{1}{\sqrt{2D_{\parallel}/\tau_{\perp}}}\left(\frac{1+\sqrt{1+(\omega\tau_{\perp})^2}}{1+(\omega\tau_{\perp})^2}\right)^{1/2},$$

fits the data.

Frequency dependence of T_1^{-1}

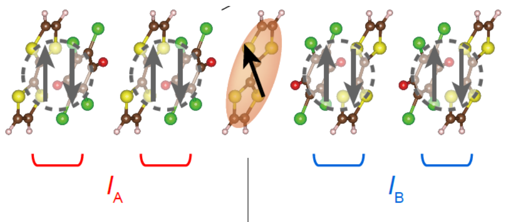


Spin solitons move diffusively along 1D chains with weak inter-chain interactions.

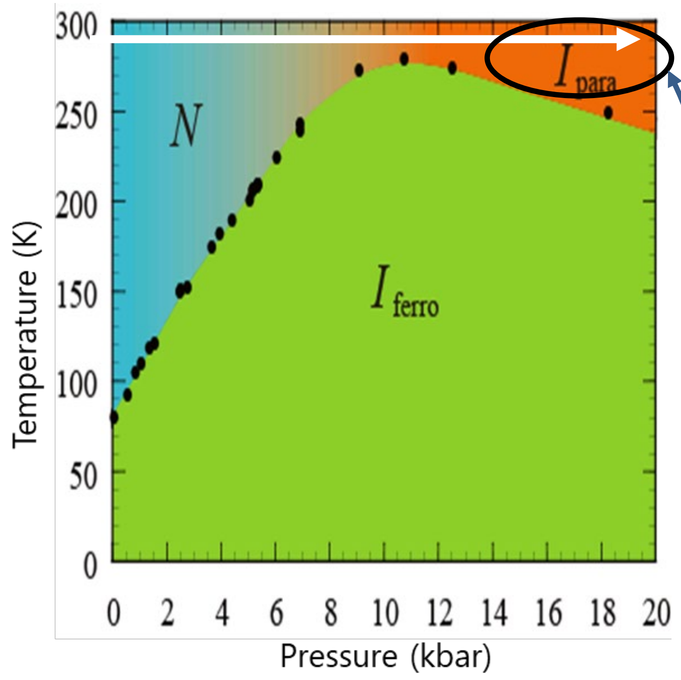
$D_{//}$ (1d diffusion constant)= 5.1×10^{11} sec^{-1}

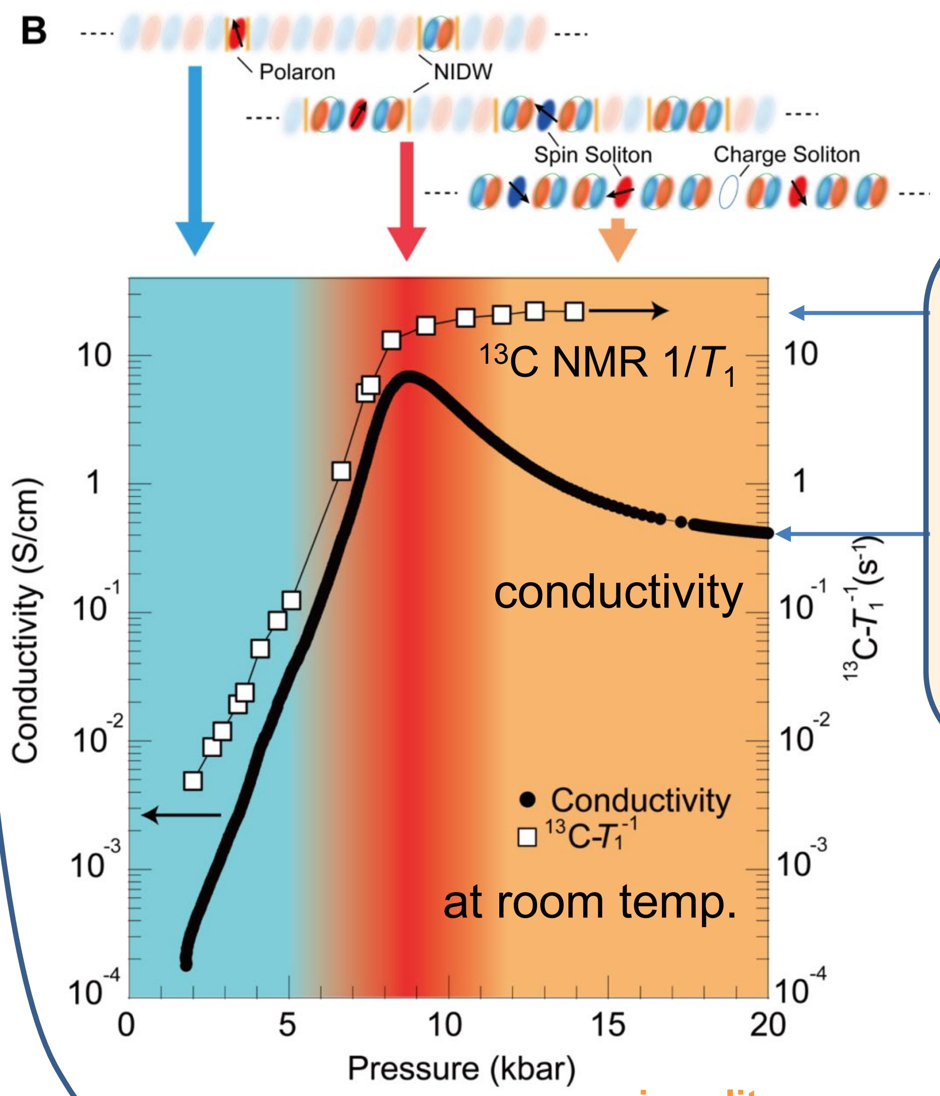
$1/\tau_{\perp}$ (cut-off freq.) $=5.6 \times 10^{10}$ sec^{-1}

1 spin soliton per 10 DA pairs



Spin-soliton charge-soliton composite in the paraelectric ionic phase





polaron

NIDW

spin soliton
charge soliton

1 spin soliton per 10 DA pairs

K. Sunami *et al*., *Sci. Adv.* **4,** eaau7725 (2018).

1 charge soliton per 90 DA pairs

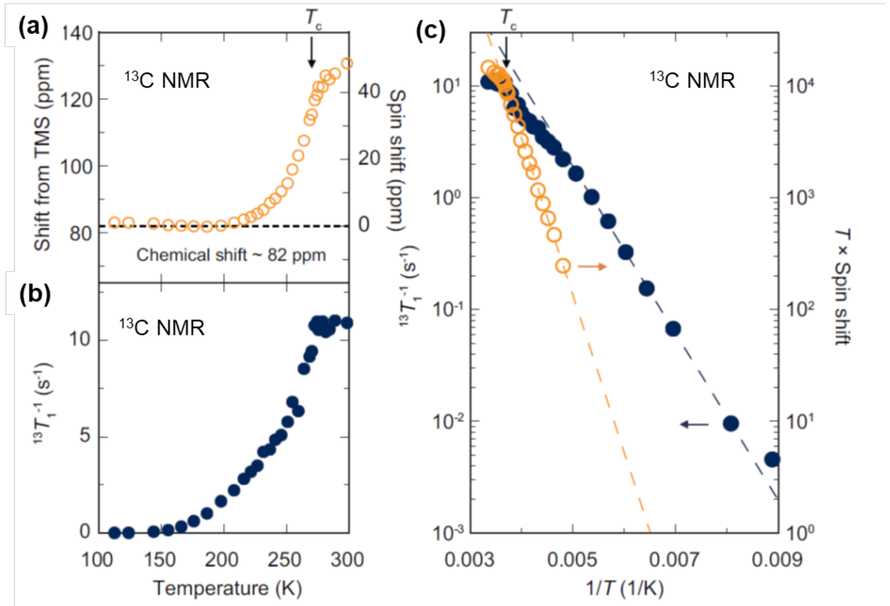
R. Takehara *et al*., *Sci. Adv.* 5, eaax8720 (2019)

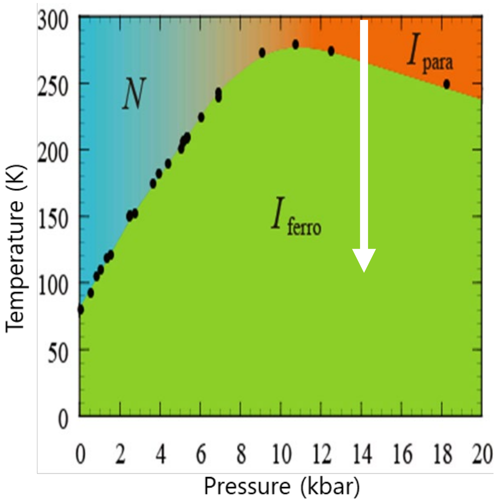
R. Takehara *et al*., *arXiv:* 2201.03889

Spin-rich soliton matter

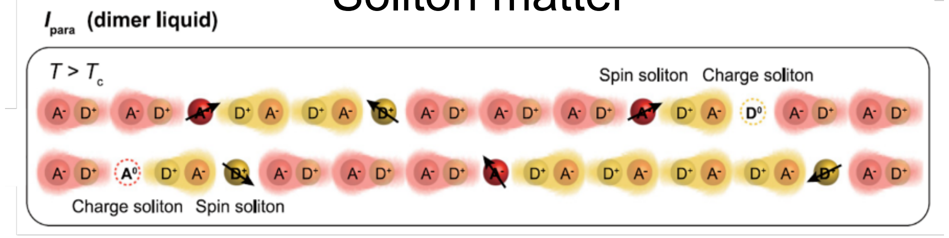
Fate of soliton matter upon ferroelectric transition

^{13}C NMR





K. Sunami et al., PRB 103, 134112 (2021)

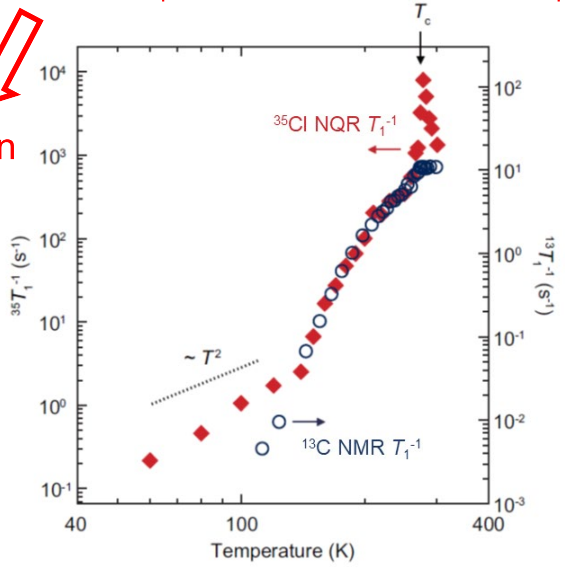


2 channels

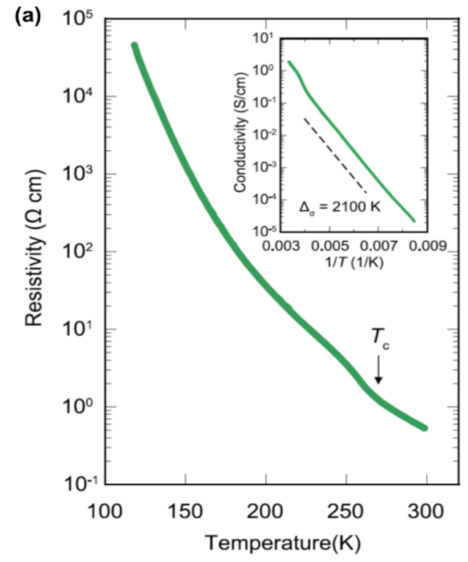
spin-soliton spin soliton binding	spin-soliton charge soliton binding = Polaron
$\Delta_S \sim 3200$ K	$\Delta_n \sim 2010$ K $\Delta_D \sim 240$ K

^{35}C NQR 1/T_1 scales to ^{13}C NMR 1/T_1

polaron

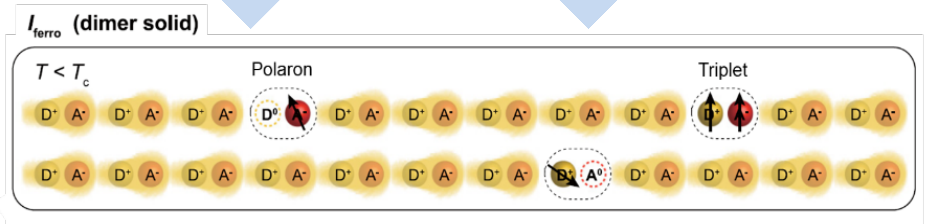


Conductivity σ



$$({}^{13}T_1^{-1})_p \propto n/\sqrt{a}D_{||}$$

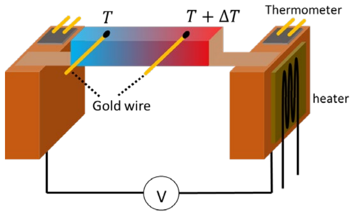
$$\sigma = ne^2 D_{||}/k_B T$$

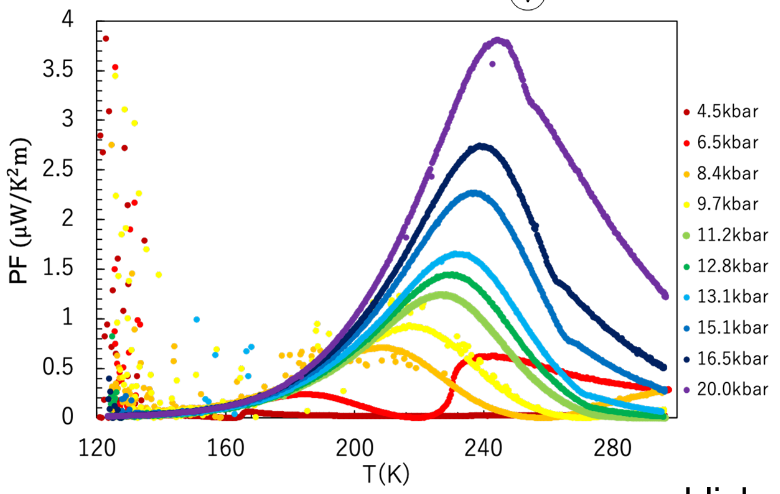


Ferroelectric order

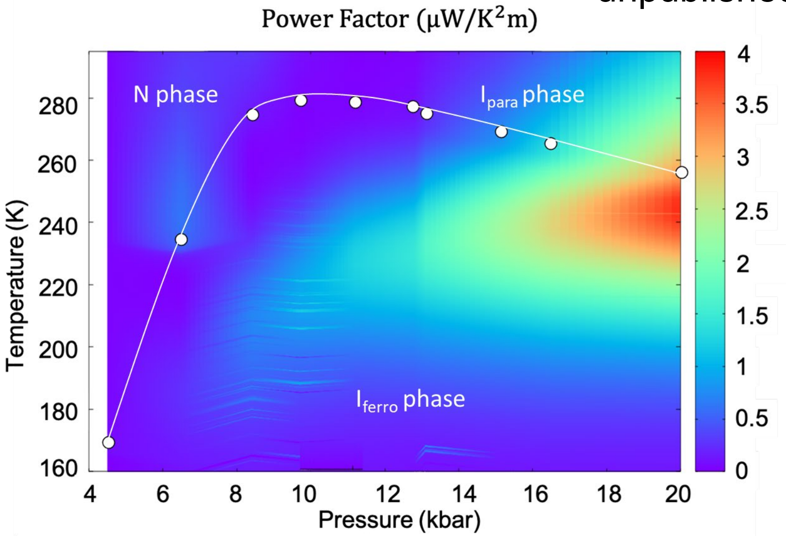
Thermoelectric effect

$$PF = S^2\sigma$$

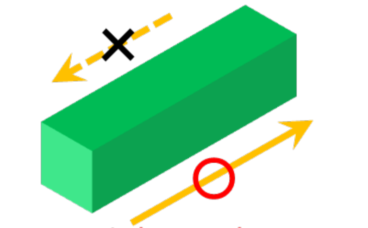




unpublished



Nonreciprocal transport

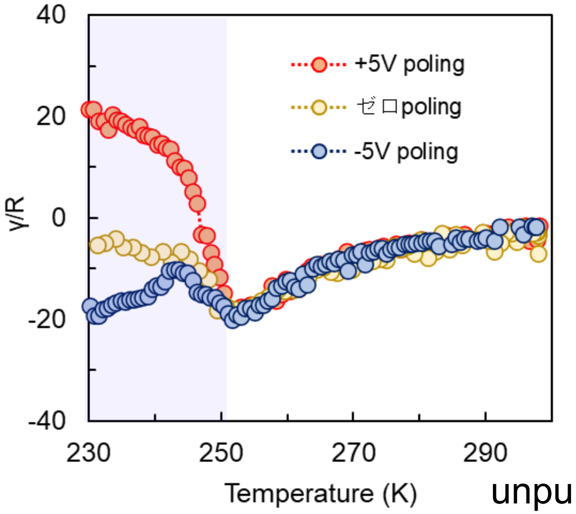


Broken inversion symmetry with correlation

Morimoto & Nagaosa, Sci. Rep. **8**, 2973 (2018).

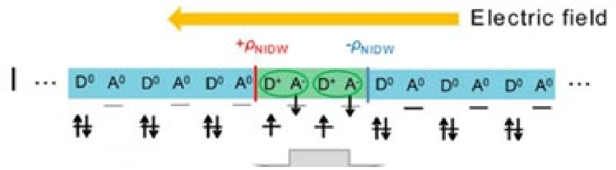
$$R = R_0(1 + \gamma BI)$$
$$V = R_0 I + \gamma R_0 B I^2$$

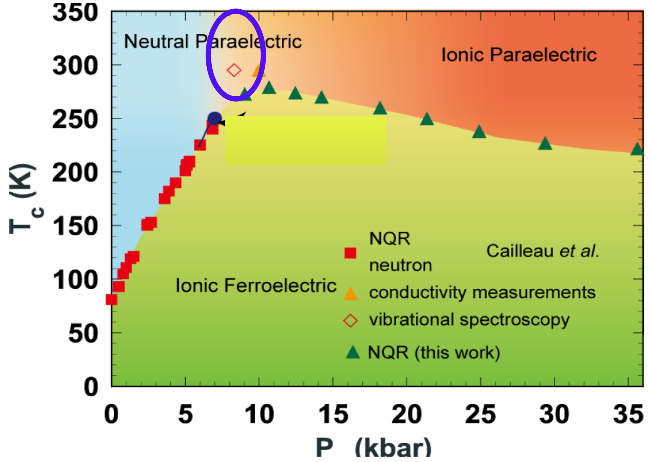
γ : Nonreciprocal parameter

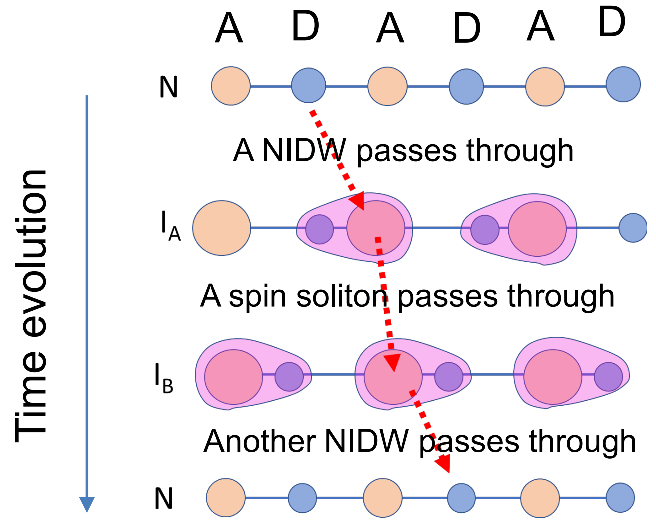


unpublished

Thouless charge pumping







Conclusion & perspective

- Quantum nature of electron glass is being revealed.
- E-glass engineering

- Mobile topological excitations in 1D electronic ferroelectrics
- Functionalize NIDWs and soliton matters

cf. $TMTTF_2X$ by Monceau, Brazovski, Kirova