CRC TRR288

Slow dynamics in the Charge-Glass Forming Organic Conductors θ-(BEDT-TTF)$_2$*MM'*(SCN)$_4$

T. Thomas, Y. Saito, T. Thyzel, Y. Agarmani, H. Sun, M. Lonsky, M. Lang, J. Müller

Goethe University Frankfurt

K. Hashimoto

University of Tokyo, Chiba

T. Sasaki

Tohoku University, Sendai

H. M. Yamamoto

IMS, Okazaki

SPICE Workshop, May 24th-26th 2022, Ingelheim

Outline

1) Quasi-2D Organic Charge-Transfer Salts

- Charge-glass state in θ-$(ET)_2$*MM′*$(SCN)_4$

2) Fluctuation Spectroscopy

3) Structural Transition in θ-$(ET)_2$Cs*M′*$(SCN)_4$

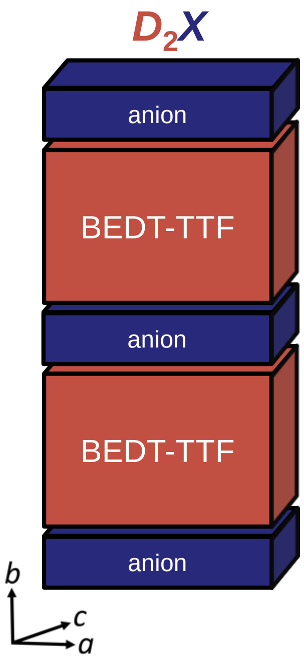
- Resistance
- Thermal expansion
- Resistance noise

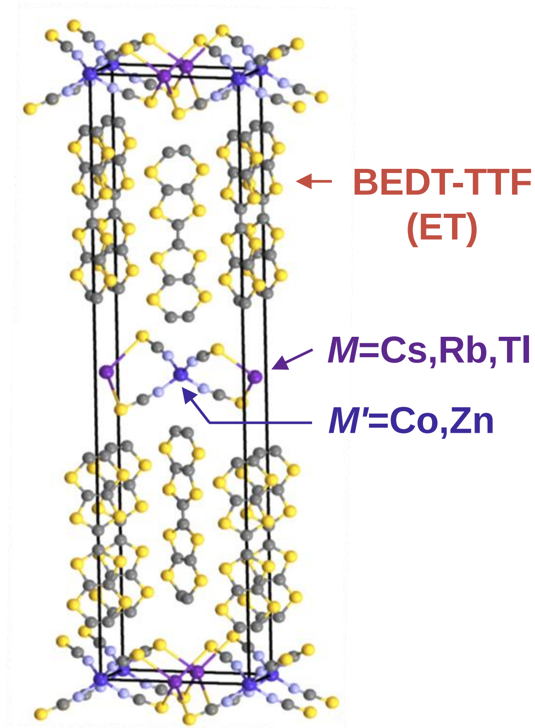
4) Comparison of the Charge-Crystal and Charge-Glass State

- Resistance noise in θ-$(ET)_2RbZn(SCN)_4$
- Resistance noise in θ_m-$(ET)_2TlZn(SCN)_4$

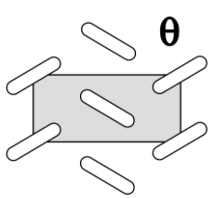
Quasi-2D Organic Charge-Transfer Salts

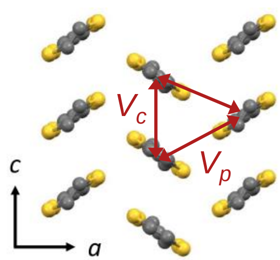
θ-(BEDT-TTF)$_2$*MM'*(SCN)$_4$

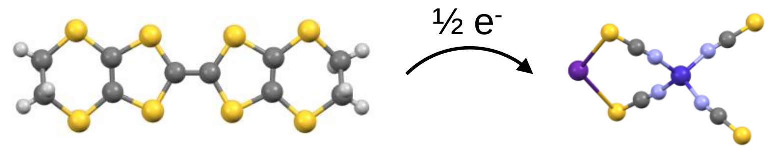




Packing motif:







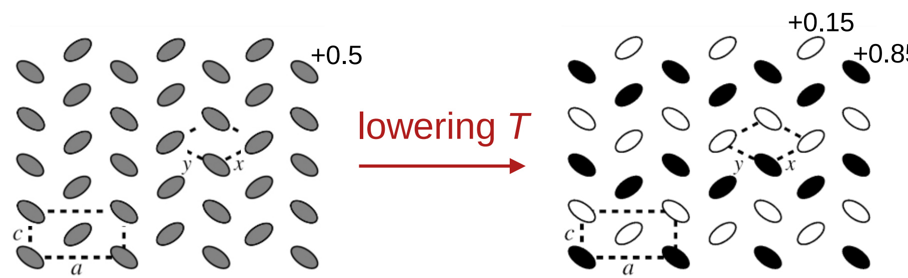
- Charge transfer:

  $[D_2] + [X] \rightarrow [D_2]^{+1} + [X]^{-1}$

  → ¼-filled conduction band

- Strong electronic correlations

  → Charge ordering (CO)



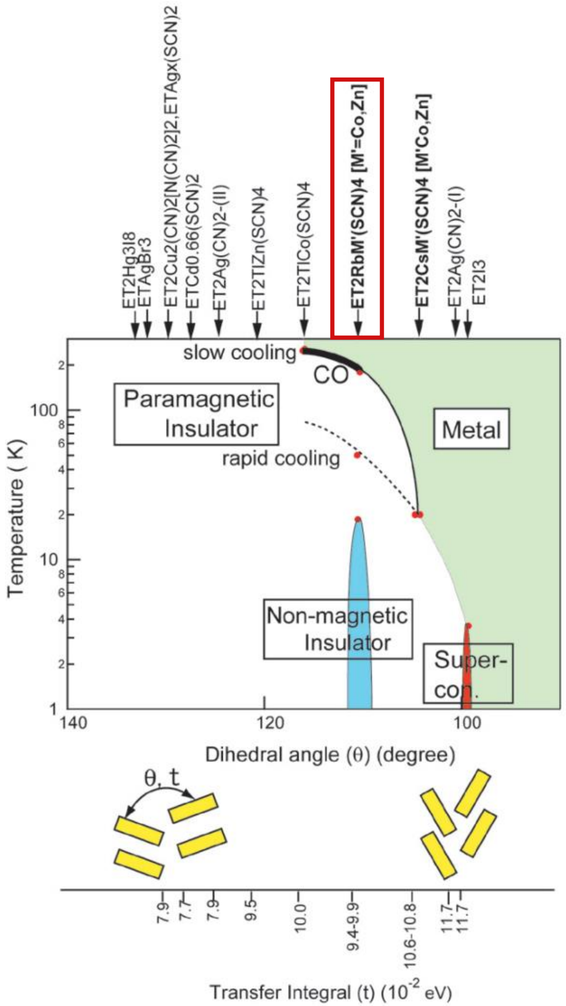
Kuroki, *Sci. Technol. Adv. Mater.* **10,** 024312 (2009)

Extended Hubbard model:

$$\mathcal{H} = \sum_{\langle ij\rangle,\sigma} t_{ij}(c^\dagger_{i\sigma}c_{j\sigma} + c^\dagger_{j\sigma}c_{i\sigma}) + \sum_i U n_{i\uparrow}n_{i\downarrow} + \sum_{\langle ij\rangle} V_{ij}n_i n_j$$

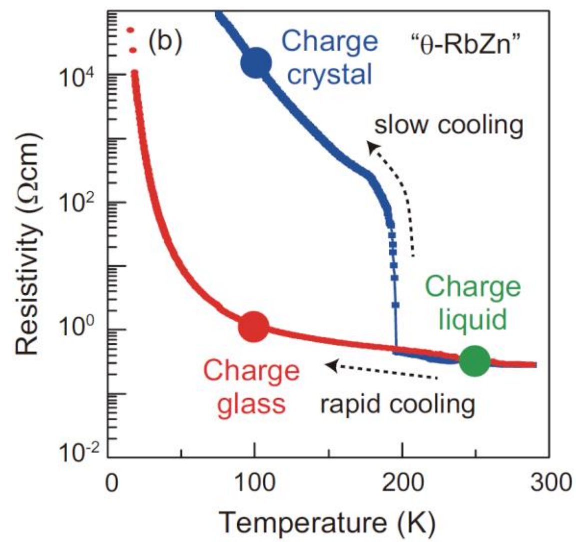
Seo, *JPSJ* **69**, 805 (2000)

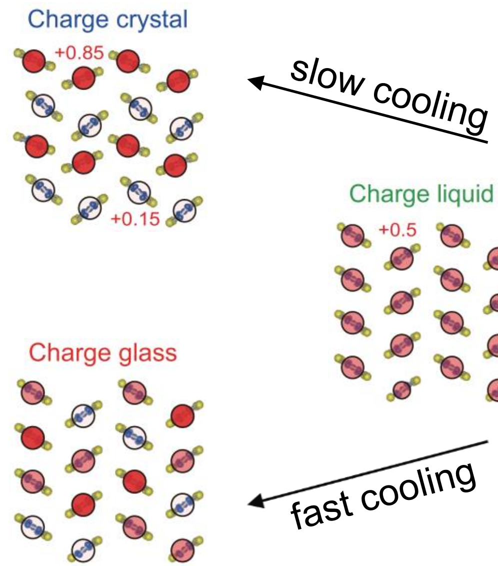
Different Charge States in θ-(BEDT-TTF)$_2X$



Mori et al., *PRB* **57**, 12023 (1998),
Kuroki, *Sci. Technol. Adv. Mater.* **10,** 024312 (2009)

Cooling-rate dependence:

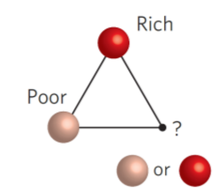




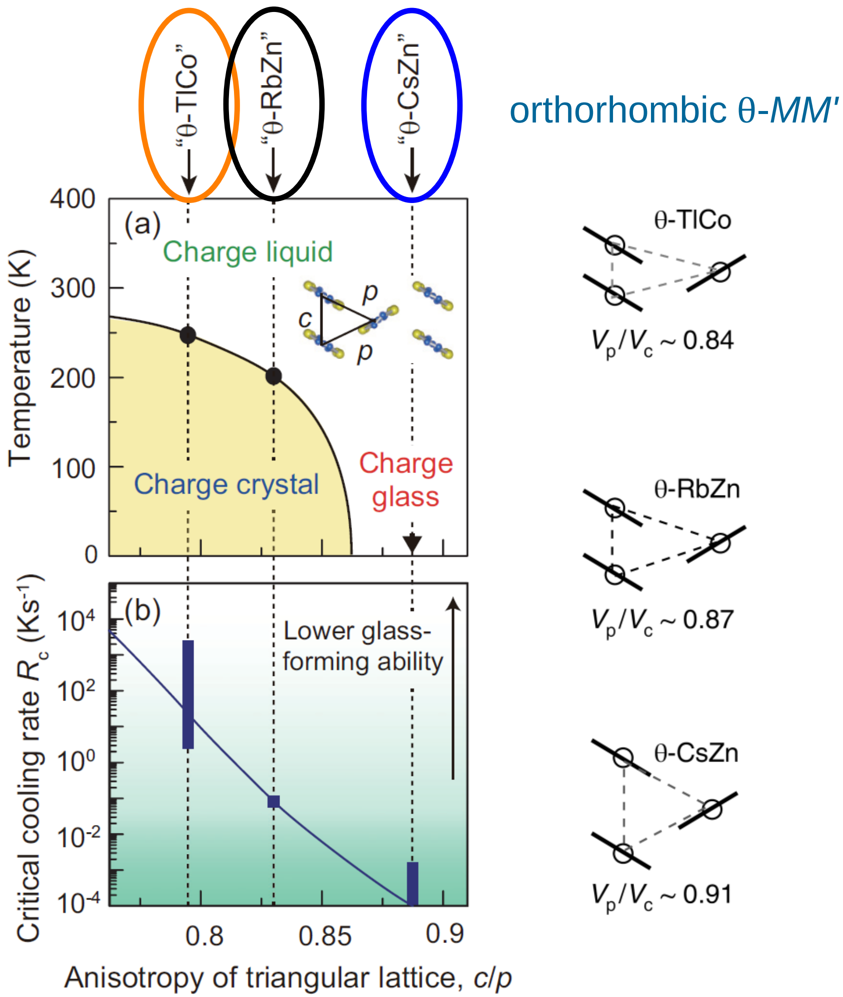
Oike et al., *PRB* **91**, 041101(R) (2015),
Kagawa et al., *Nat. Phys.* **9**, 419 (2013)

- CO transition can be kinetically avoided
  → Charge-glass state

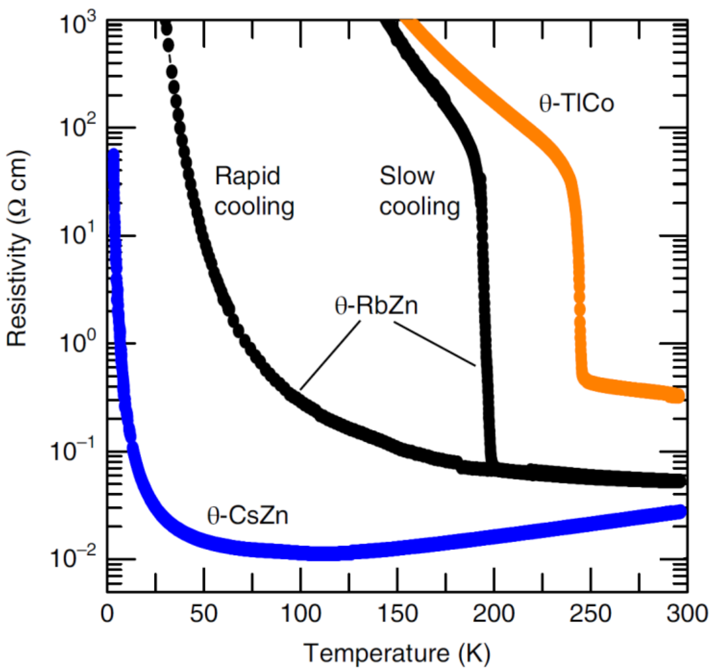
Geometric frustration:



Geometric Frustration



Oike et al., *PRB* **91**, 041101(R) (2015)



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

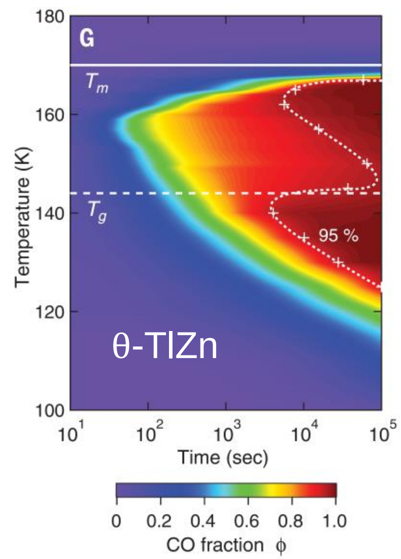
Stronger frustration

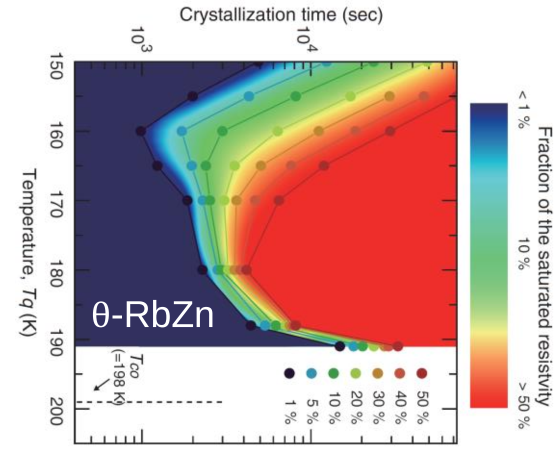
- reduces T_{CO}
- reduces critical cooling rate q_c
- enhances glass-forming ability

Charge-Glass State

- Cooling-rate dependence
- Lack of long-range order
- Non-equilibrium dynamics

Electronic crystallization:





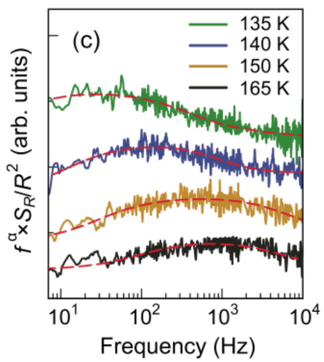
Sasaki et al., *Science* **357**, 1381 (2017),
Sato et al., *Science* **357**, 1378 (2017)

Slow and heterogeneous dynamics

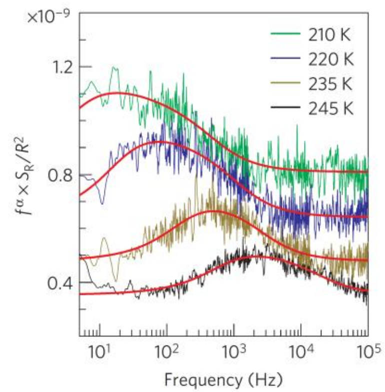
→ **Fluctuation spectroscopy**

Sato et al., *PRB* **89**, 121102(R) (2014),
Kagawa et al., *Nat. Phys.* **9**, 419 (2013),
Sasaki et al., *Science* **357**, 1381 (2017)

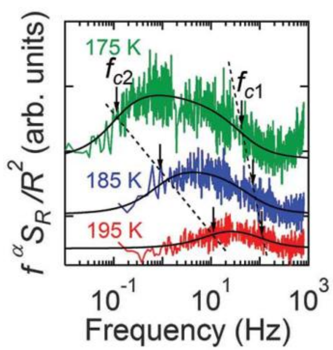
θ-CsZn



θ-RbZn



θ-TlZn



Charge-Glass State

Open questions:

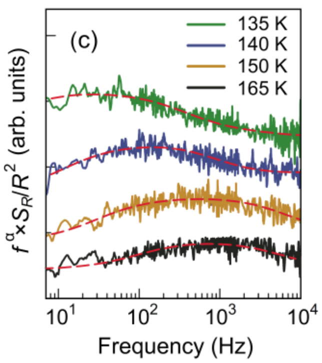
- Charge dynamics in the charge-crystal and charge-glass state?
- Involvement of structural degrees of freedom?

Slow and heterogeneous dynamics

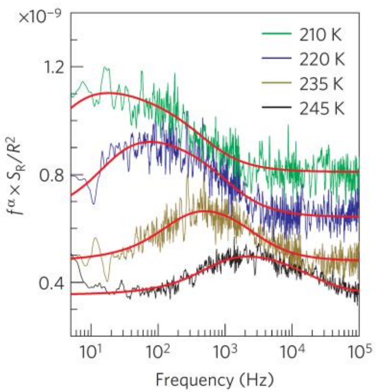
→ **Fluctuation spectroscopy**

Sato et al., *PRB* **89**, 121102(R) (2014),
Kagawa et al., *Nat. Phys.* **9**, 419 (2013),
Sasaki et al., *Science* **357**, 1381 (2017)

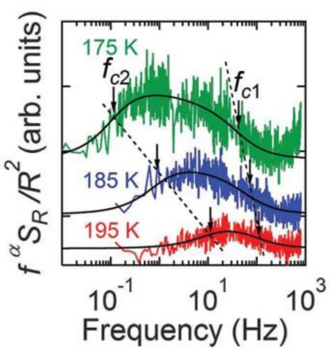
θ-CsZn



θ-RbZn



θ-TlZn



Outline

1) Quasi-2D Organic Charge-Transfer Salts

- Charge-glass state in θ-$(ET)_2$*MM′*$(SCN)_4$

2) Fluctuation Spectroscopy

3) Structural Transition in θ-$(ET)_2$Cs*M′*$(SCN)_4$

- Resistance
- Thermal expansion
- Resistance noise

4) Comparison of the Charge-Crystal and Charge-Glass State

- Resistance noise in θ-$(ET)_2RbZn(SCN)_4$
- Resistance noise in θ_m-$(ET)_2TlZn(SCN)_4$

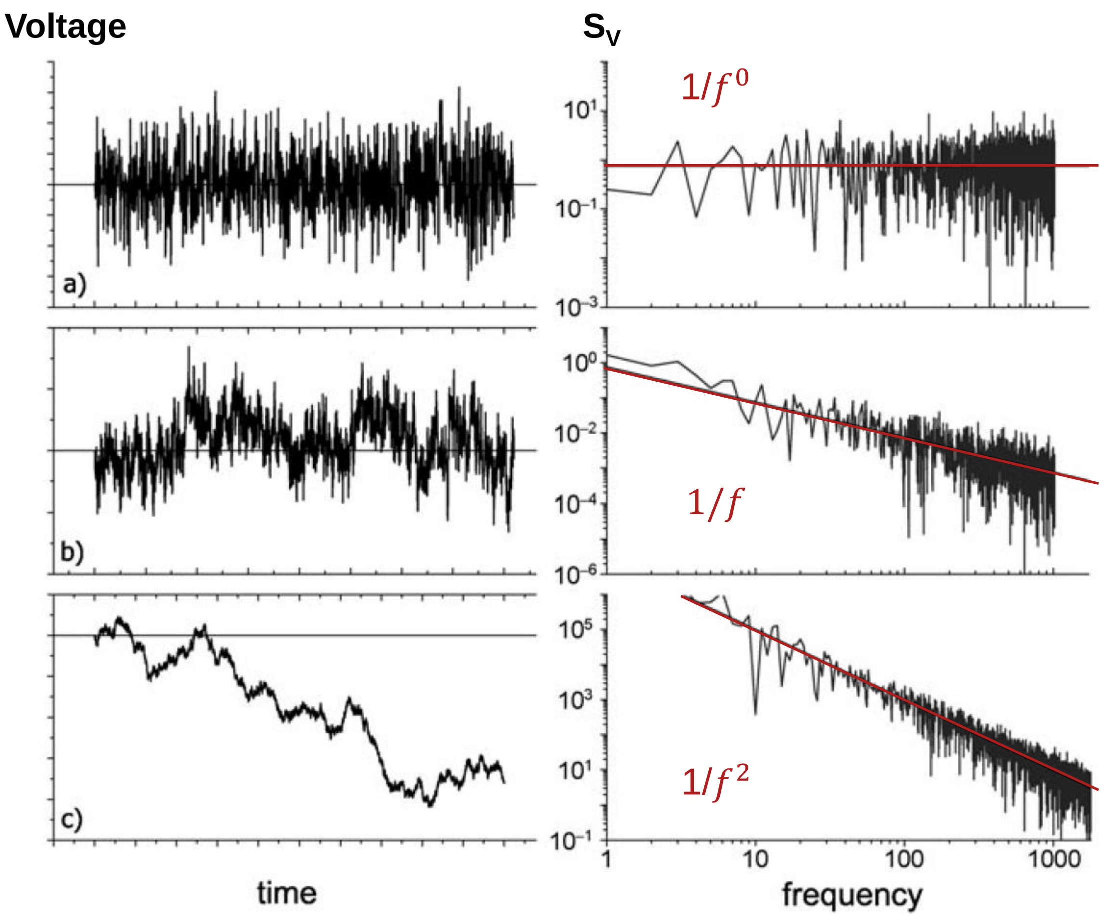
Fluctuation Spectroscopy

Different types of noise:

Müller, *ChemPhysChem* **12**, 1222 (2011)

Power spectral density:

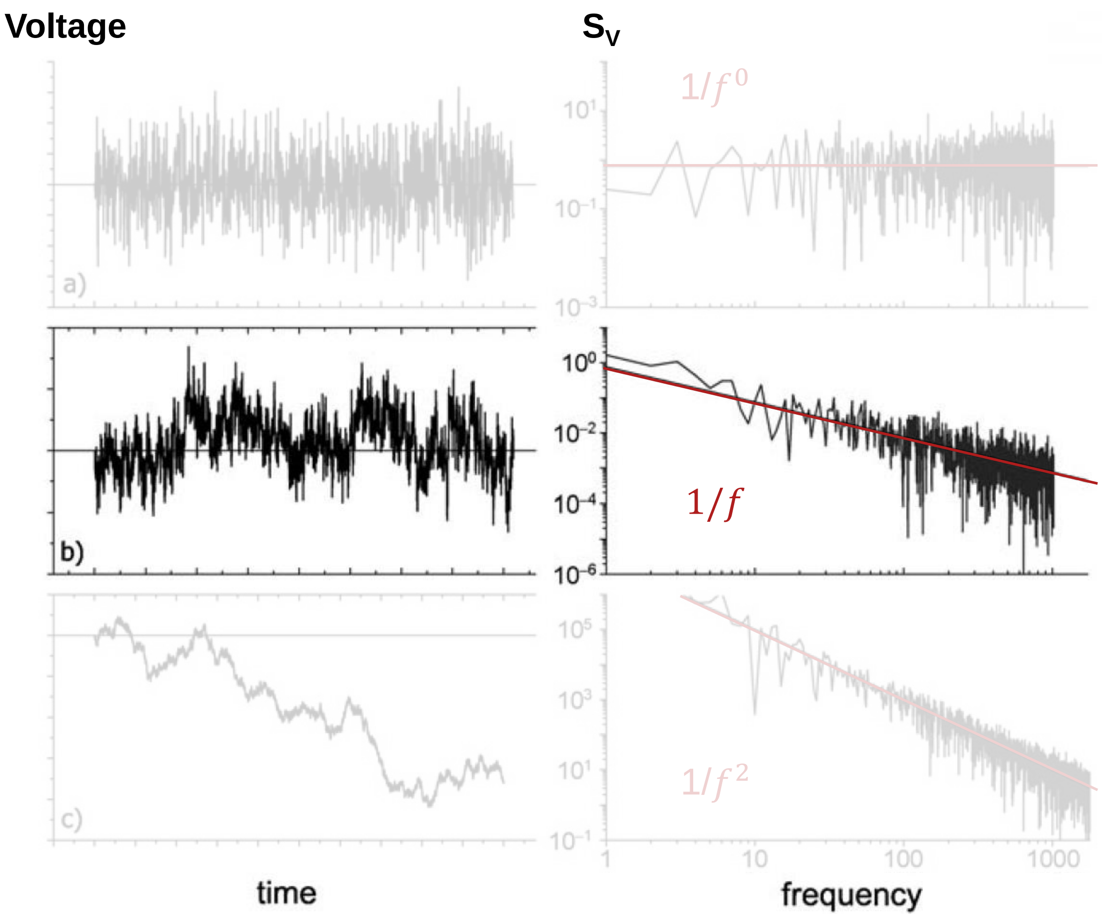
$$S_V(f) = 2 \lim_{T\to\infty} \frac{1}{T} \left| \int_{-T/2}^{T/2} \delta V(t) e^{-i2\pi f t} dt \right|^2$$



Fluctuation Spectroscopy

Different types of noise:

Müller, *ChemPhysChem* **12**, 1222 (2011)



Power spectral density:

$$S_V(f) = 2 \lim_{T\to\infty} \frac{1}{T} \left| \int_{-T/2}^{T/2} \delta V(t) e^{-i2\pi f t} dt \right|^2$$

$1/f$ noise:

$$S_V \propto 1/f^{\alpha}$$

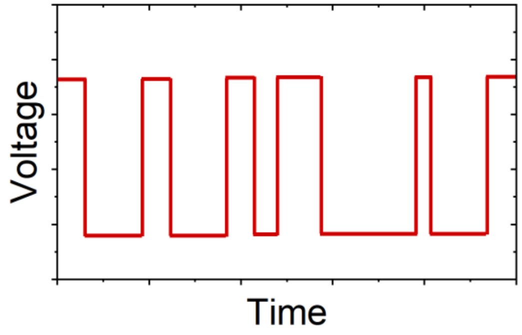
Frequency exponent:

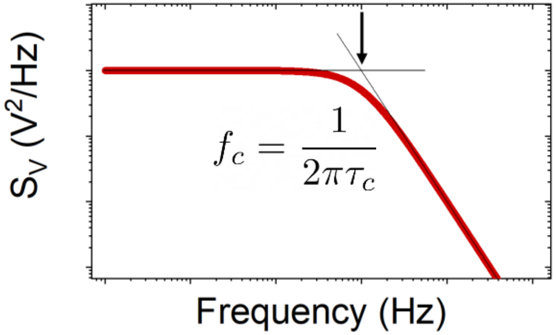
$$\alpha = 0.8 - 1.4$$

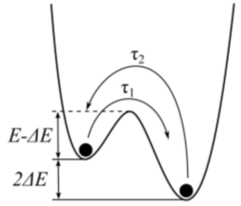
Ubiquitous in nature:
Biology, geology, music,
condensed matter, …

Fluctuation Spectroscopy

Two-level process:







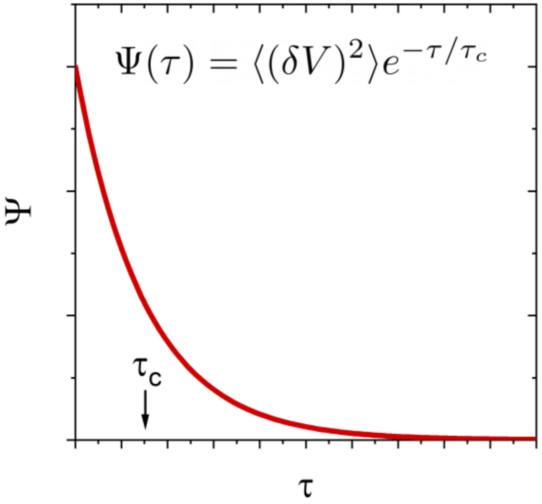
$$\tau_c = \tau_0 \exp\left(\frac{E_A}{k_B T}\right)$$

Wiener-Khinchine theorem:

$$S_V(f) = 4\int_0^\infty \Psi(\tau)\cos(2\pi f\tau)d\tau \quad \propto \frac{\tau_c}{1+4\pi^2 f^2 \tau_c^2}$$

Autocorrelation function: $\Psi(\tau) = \langle \delta V(t)\delta V(t+\tau)\rangle$

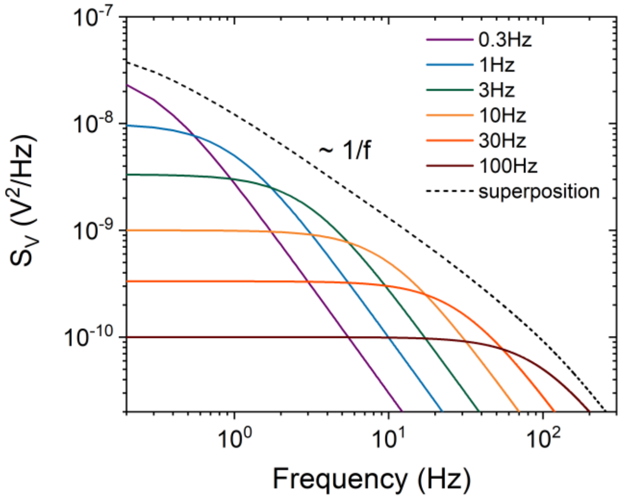
→ Microscopic kinetics of charge carriers



Fluctuation Spectroscopy

Simple model:

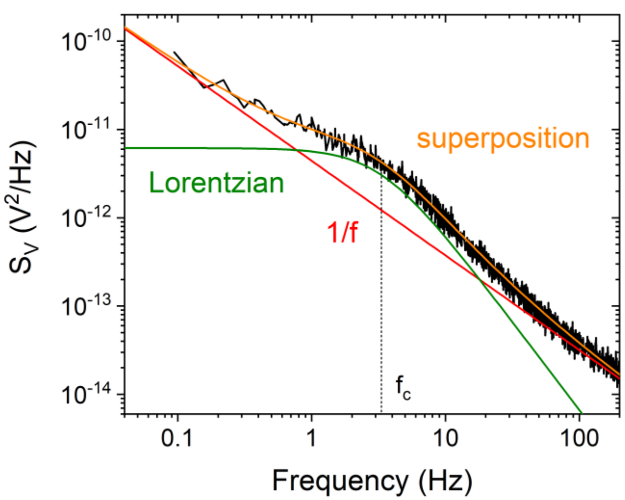
Superposition of many independent fluctuators



Dutta-Dimon-Horn (DDH) model   Dutta et al., *PRL* **43**, 9 (1979)

→ access to energy distribution of fluctuators

Dominating fluctuator:



T-dependence: $f_c = f_0 \exp\left(-\frac{E_A}{k_B T}\right)$

→ access to activation energy of fluctuator

What causes slow dynamics?

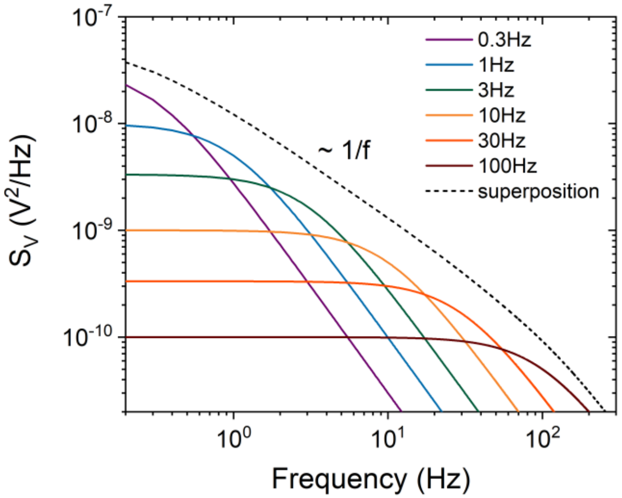
- large activation energy of localized process
- collective effects

Parisi, Physik Journal 10, Nr. 8/9 (2011)

Fluctuation Spectroscopy

Simple model:

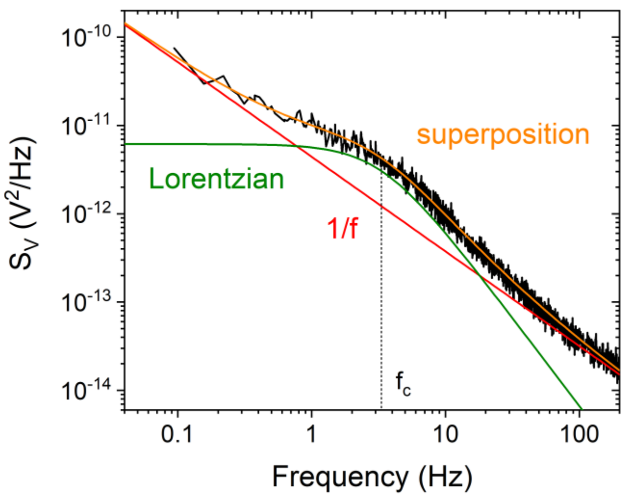
Superposition of many independent fluctuators



Dutta-Dimon-Horn (DDH) model Dutta et al., *PRL* **43**, 9 (1979)

→ access to energy distribution of fluctuators

Dominating fluctuator:



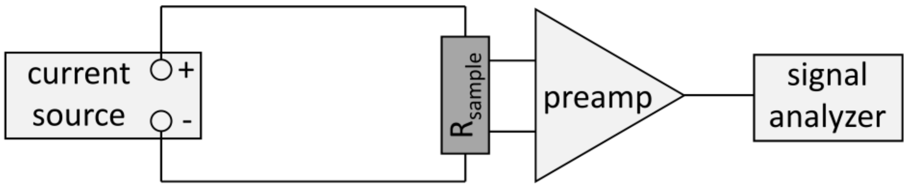
T-dependence: $f_\mathrm{c} = f_0 \exp\left(-\frac{E_\mathrm{A}}{k_\mathrm{B}T}\right)$

→ access to activation energy of fluctuator

Useful for studying

- glassy transitions
- collective effects
- excitation of large clusters
- inhomogeneous current distribution
- percolation
- …

Experiment

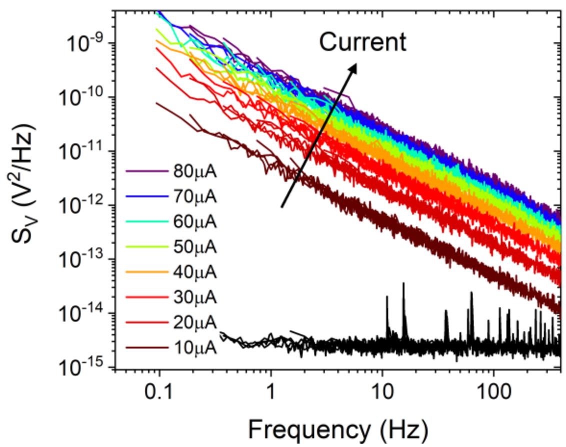


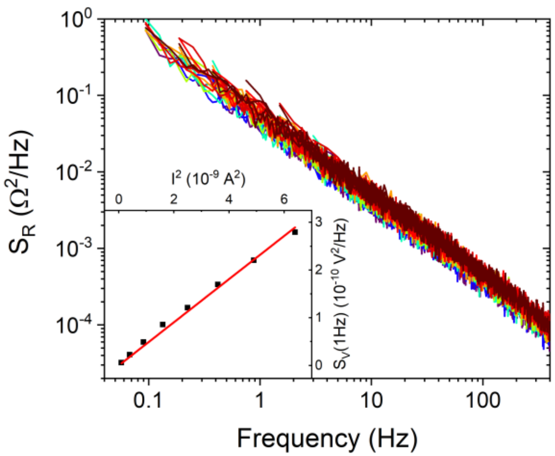
Frequencies: mHz-kHz
Impedances: mΩ-GΩ

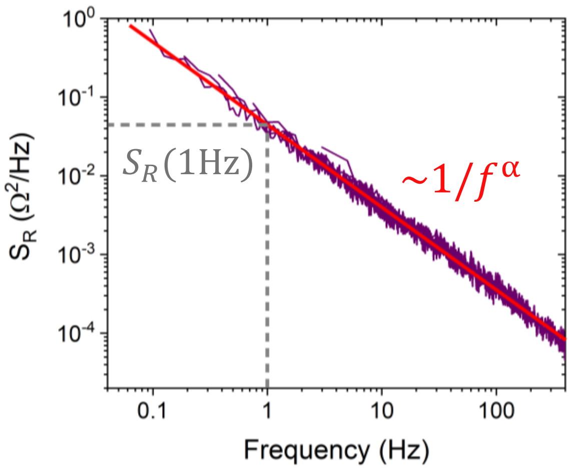
Current/voltage scaling:

$$S_V = \frac{\gamma_H V^2}{n_c \Omega} \frac{1}{f^\alpha} \propto V^2 \propto I^2$$

Hooge, *Phys. Lett. A* **29**, 139 (1969)







- Normalized noise magnitude $S_R(1\text{Hz})/R^2$
- Frequency exponent α

→ in dependence of $T, B, E,$ etc.

Outline

1) Quasi-2D Organic Charge-Transfer Salts

- Charge-glass state in θ-$(ET)_2$*MM′*$(SCN)_4$

2) Fluctuation Spectroscopy

3) Structural Transition in θ-$(ET)_2$Cs*M′*$(SCN)_4$

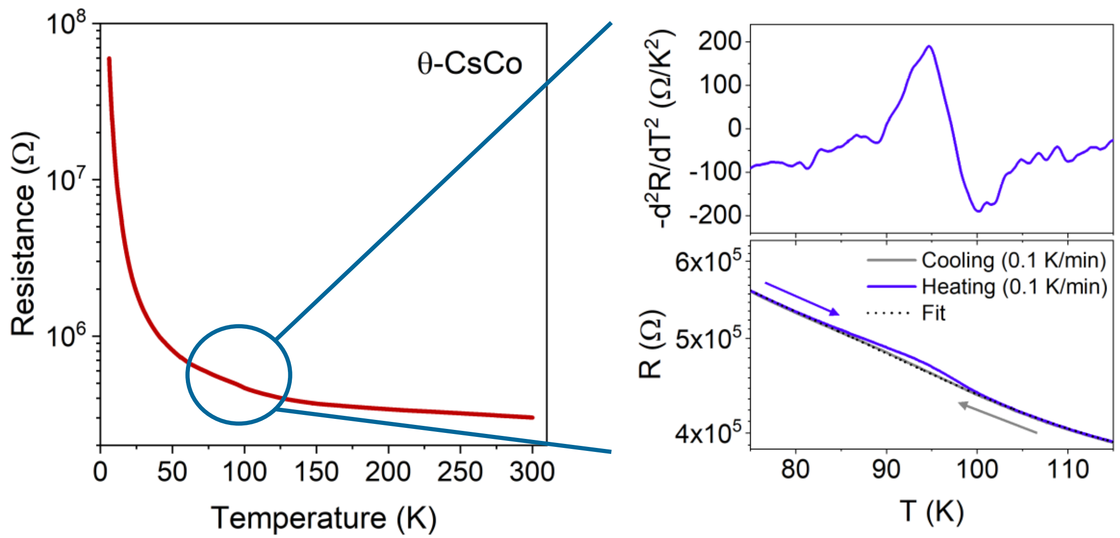
- Resistance
- Thermal expansion
- Resistance noise

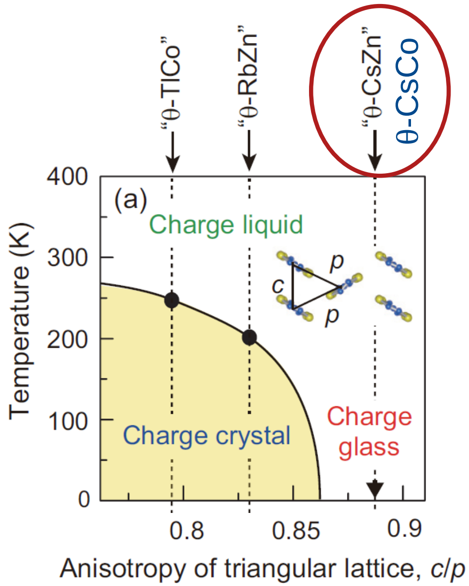
4) Comparison of the Charge-Crystal and Charge-Glass State

- Resistance noise in θ-$(ET)_2RbZn(SCN)_4$
- Resistance noise in $θ_m$-$(ET)_2TlZn(SCN)_4$

Resistance of θ-CsCo

Resistance anomaly at T_g~95K

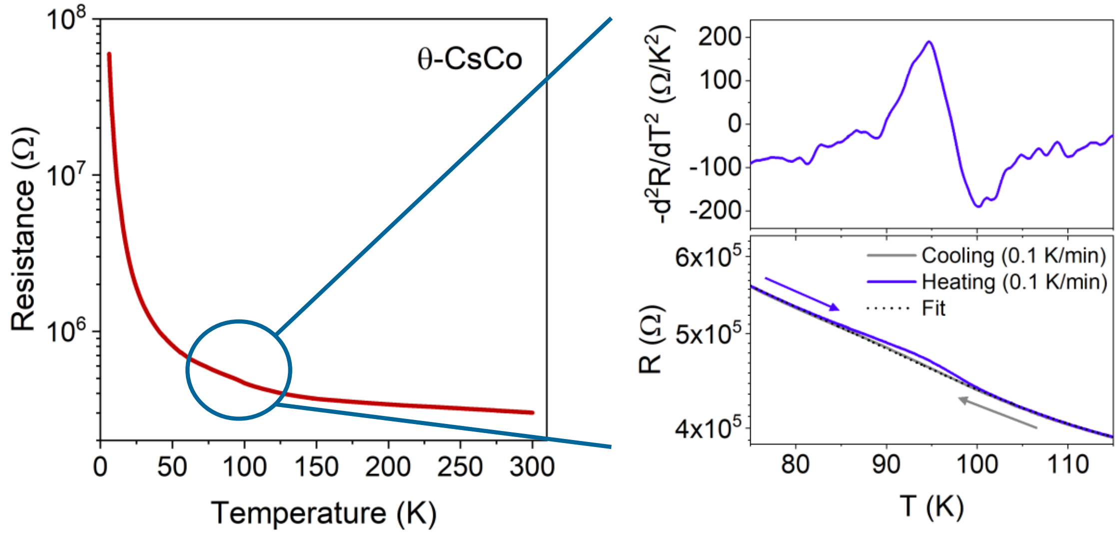


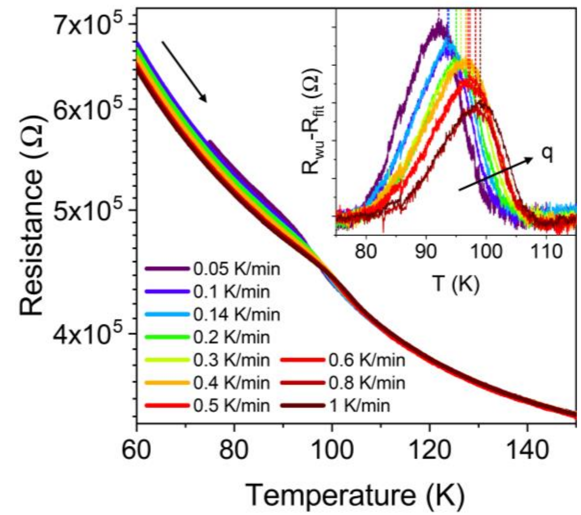


Resistance of θ-CsCo

Resistance anomaly at T_g~95K

Cooling-rate dependence:



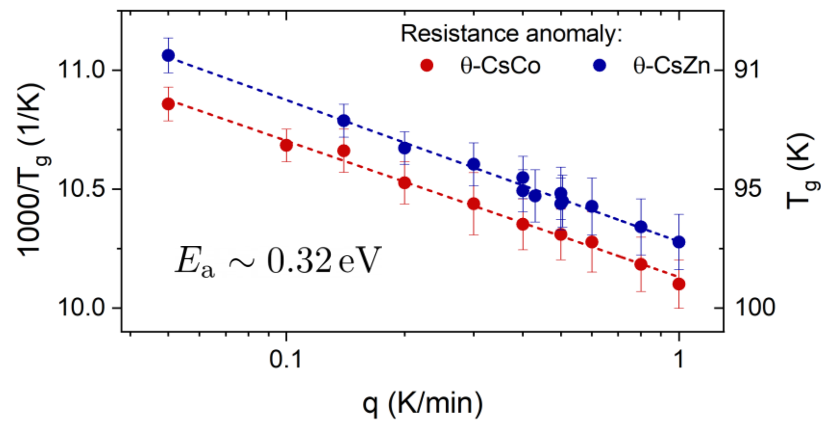


- Hysteresis and q-dependence
- Consistent with measurements on θ-CsZn
- Previously observed Sato et al., *PRB* **89**, 121102(R) (2014)

Criterion for T_g:

$$-|q| \cdot \left.\frac{d\tau}{dT}\right|_{T_\mathrm{g}} \approx 1$$

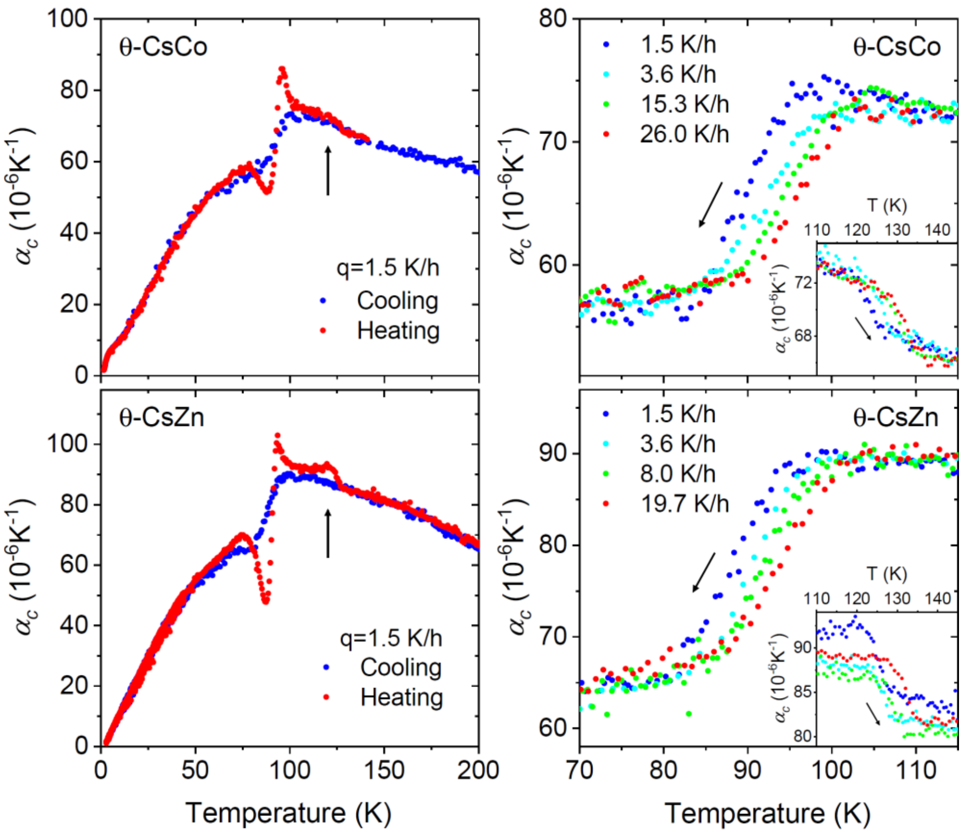
$$\Rightarrow \quad \ln|q| \sim -\frac{E_\mathrm{a}}{k_\mathrm{B}} \cdot T_g^{-1}$$



Thermal Expansion of θ-CsCo

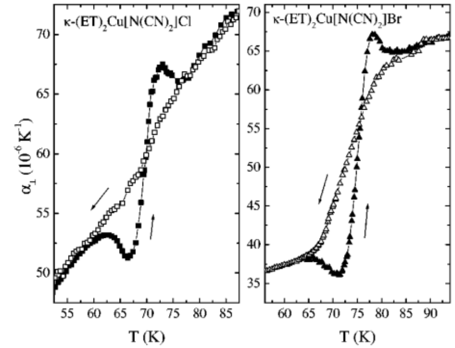
by Dr. Y. Saito, Prof. M. Lang

Cooling-rate dependence:

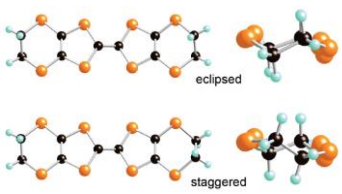


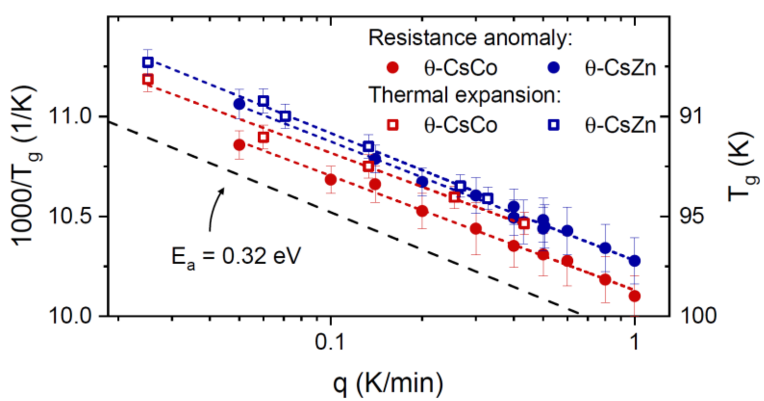
- Structural glass transition at T_g~95K
- Connected to resistance anomaly
- Second glassy transition at $T_g^\dagger$~120K

cf. κ-$(ET)_2X$:

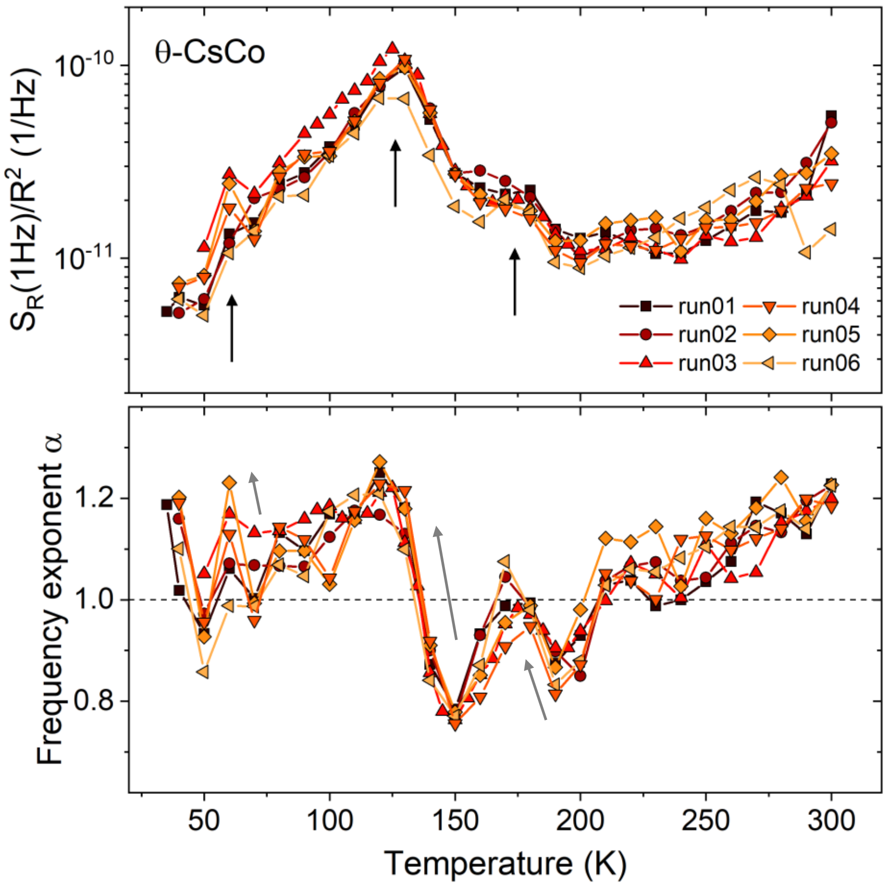


Müller et al., *PRB* **65**, 144521 (2002)
Müller et al., *New J. Phys.* **17**, 083057 (2015)





Resistance Noise in θ-CsCo



- Noise maximum at T~130K
- Spectral weight shifts to lower frequencies

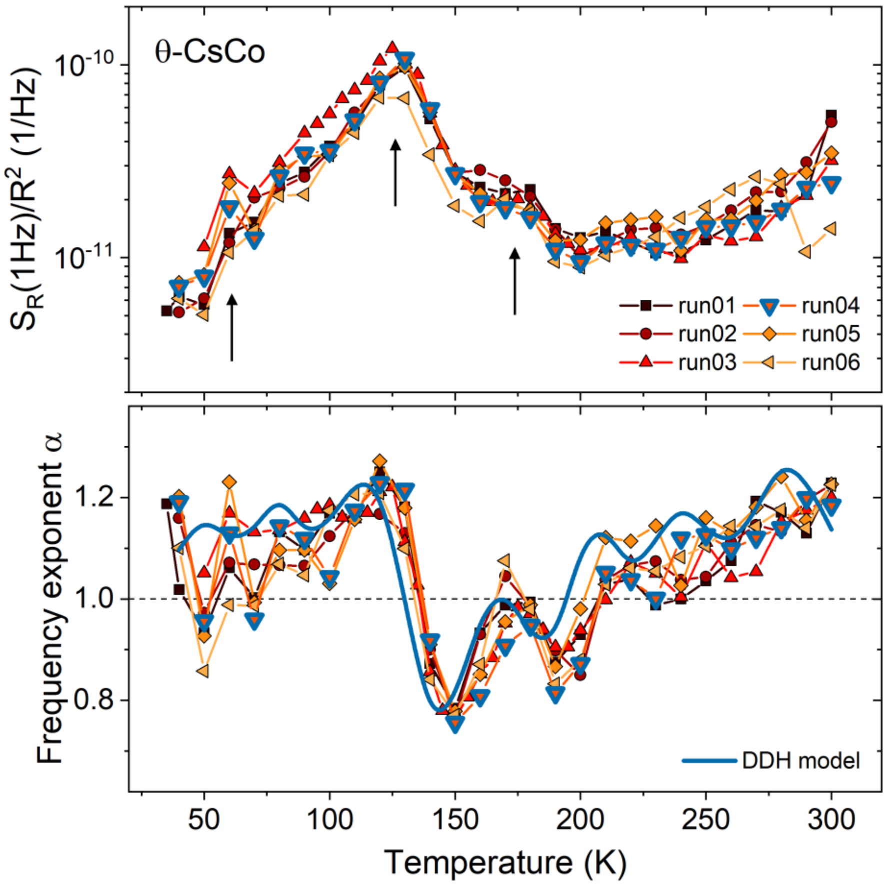
→ Charge dynamics slows down when approaching T_g

- Cf. θ-CsZn

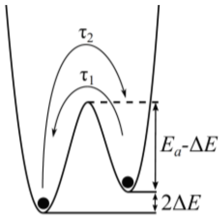
Sato et al., *JPSJ* **85**, 123702 (2016)

- Small features at 175K and 60K

Resistance Noise in θ-CsCo



Dutta-Dimon-Horn model



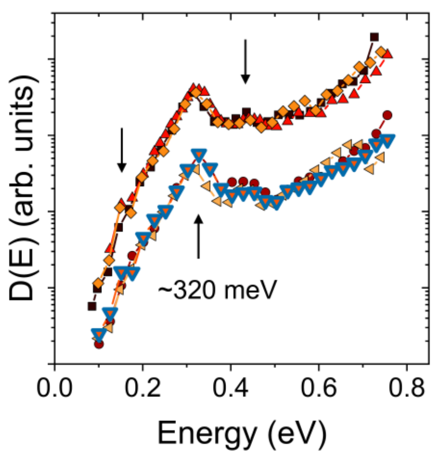
Dutta et al., *PRL* **43**, 9 (1979),
Raquet et al., *PRB* **59**, 12435 (1999)

- Independent fluctuators
- Thermally activated two-level process

$$\tau = \tau_0 \exp\left(\frac{E_A}{k_B T}\right)$$

- Distribution of activation energies

$$\frac{S_R(f)}{R^2}(T) = \frac{1}{\pi f}\int_0^\infty g(T)\frac{D(E)}{\cosh[(E-E_f)/k_B T]}\mathrm{d}E$$



Frequency-Dependent Noise Maximum

- **cf. κ-(ET)$_2$*X***

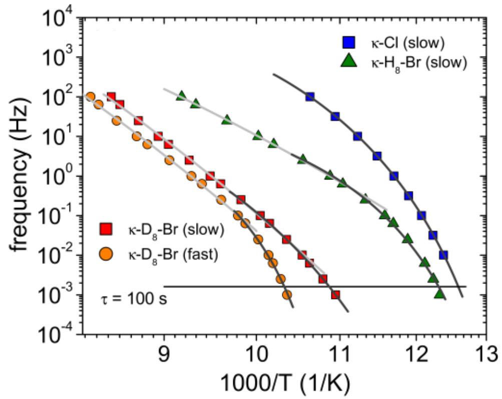
  → similar glassy freezing of EEG in θ-(ET)$_2$*X*

- role of ethylene endgroups for CO:

  → **order-disorder structural transition** of EEG

Alemany *et al., J. Phys.: Condens. Matter* **27**, 465702 (2015)

κ-(ET)$_2$*X*:
fragile glass former



Müller *et al.*, *New J. Phys.* **17**, 083057 (2015)

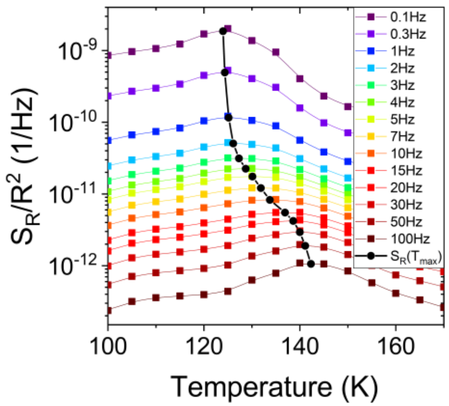
Vogel-Fulcher-Tammann law:

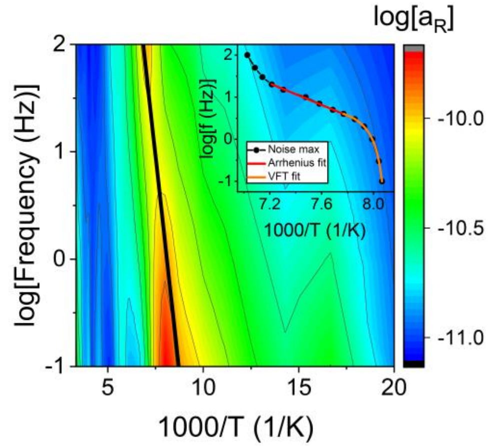
$$f = f_0 \exp\left(\frac{-DT_{\mathrm{VF}}}{T - T_{\mathrm{VF}}}\right)$$

θ-CsCo:

- unusual frequency dependence

→ due to coupling of structural and charge dynamics





Outline

1) Quasi-2D Organic Charge-Transfer Salts

- Charge-glass state in θ-$(ET)_2$*MM′*$(SCN)_4$

2) Fluctuation Spectroscopy

3) Structural Transition in θ-$(ET)_2$Cs*M′*$(SCN)_4$

- Resistance
- Thermal expansion
- Resistance noise

4) Comparison of the Charge-Crystal and Charge-Glass State

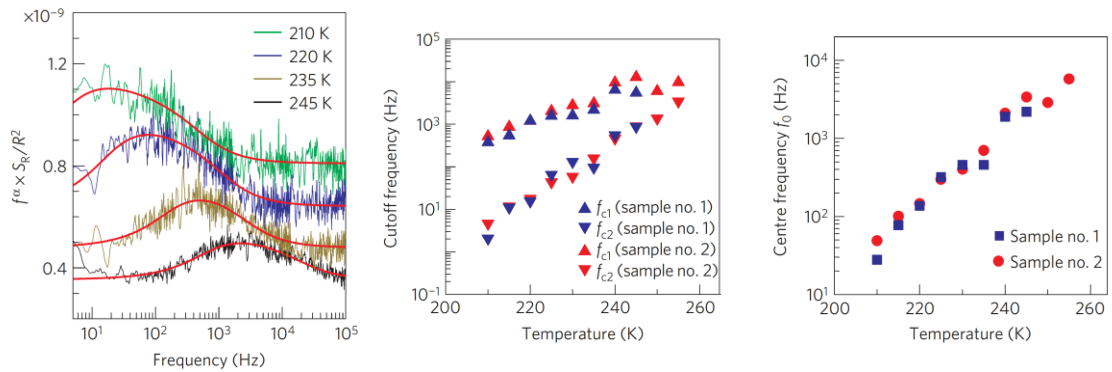
- Resistance noise in θ-$(ET)_2RbZn(SCN)_4$
- Resistance noise in θ_m-$(ET)_2TlZn(SCN)_4$

Previous Results in the CL State

Fluctuation spectroscopy:

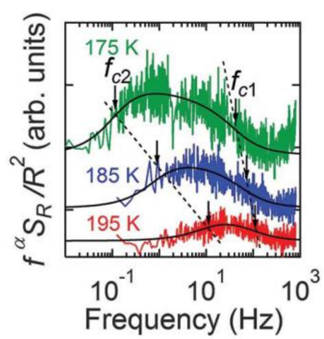
Slow and heterogeneous dynamics above T_{MI}

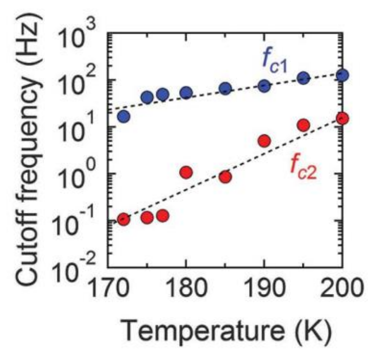
θ-RbZn

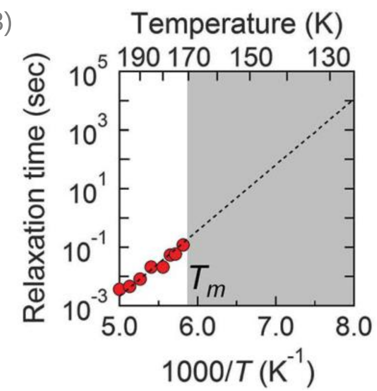


Kagawa et al., *Nat. Phys.* **9**, 419 (2013)

θ-TlZn



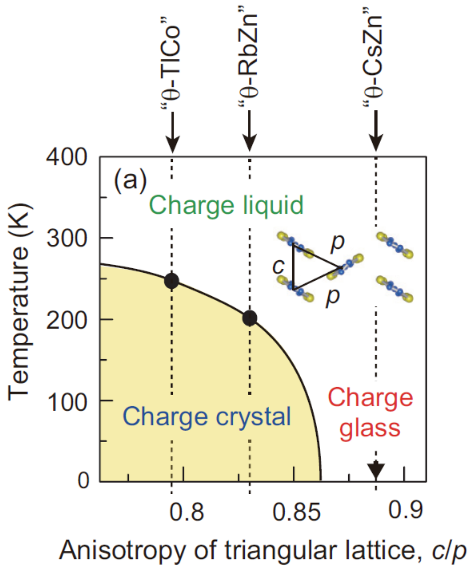




Sasaki et al., *Science* **357**, 1381 (2017)

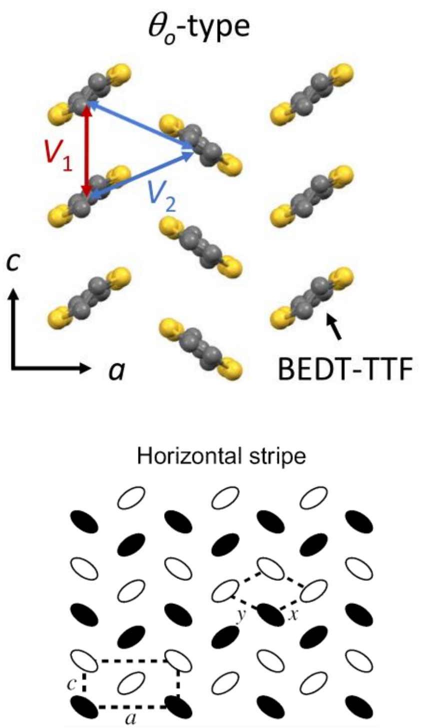
→ extend noise measurements to CC and CG state

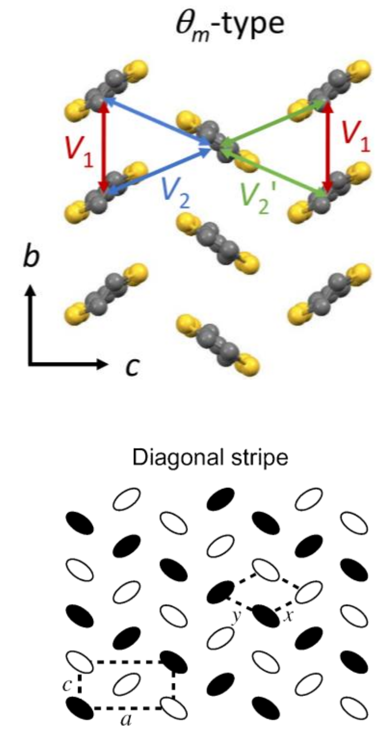
Comparison of the CC and CG State



Orthorhombic θ_o-RbZn

Monoclinic θ_m-TlZn





Varying

- CO pattern
- degree of frustration
- strength of el.-ph. coupling
- critical cooling rates

T_{MI}~200K

q_c~5K/min

T_{MI}~175K

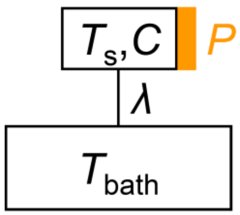
q_c>50K/min

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

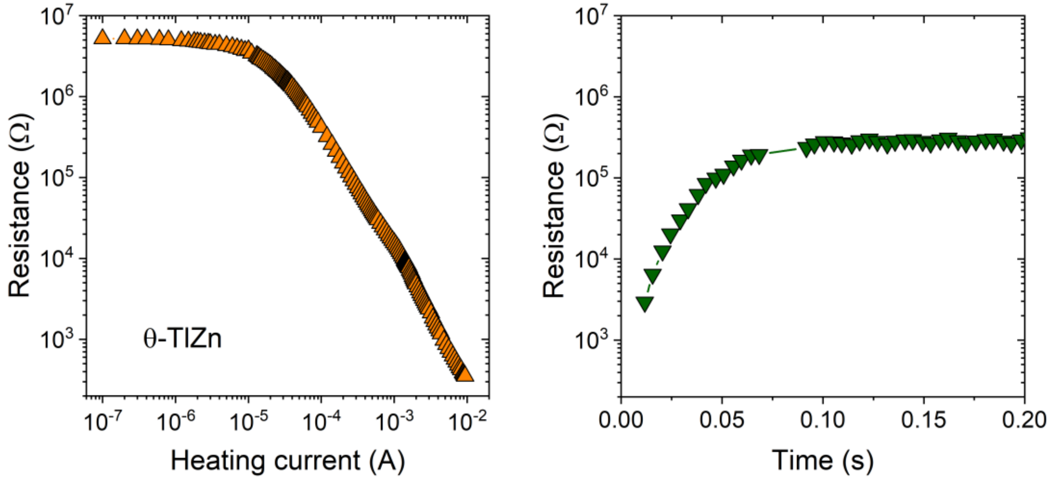
Sasaki et al., *Science* **357**, 1381 (2017)

Comparison of the CC and CG State

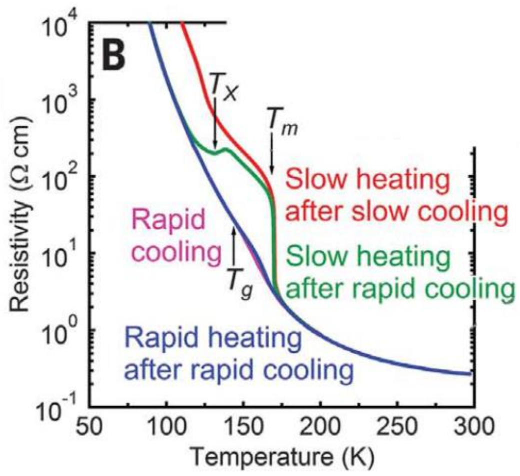
Heat pulse method



Hartmann et. al., *PRB* **90**, 195150 (2014)

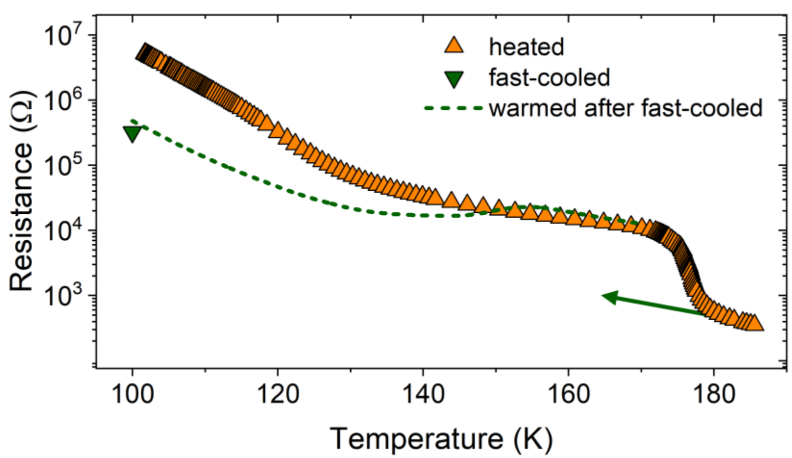


→ Cooling rates of q~700K/s



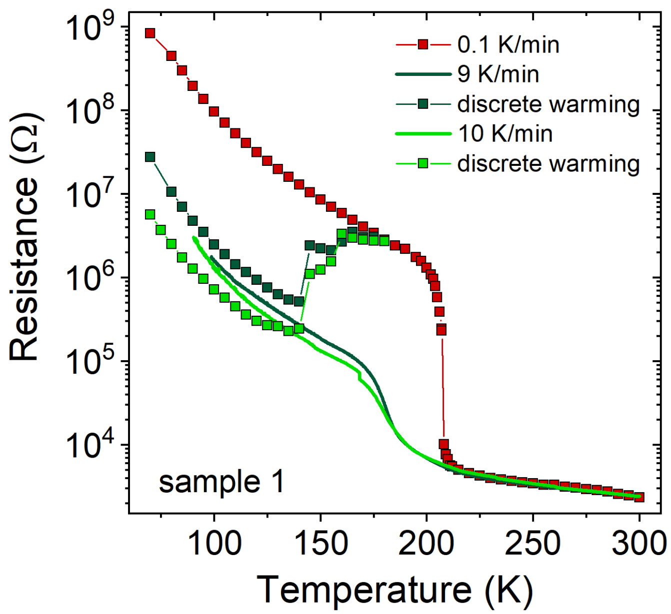
Sasaki et al., *Science* **357**, 1381 (2017)

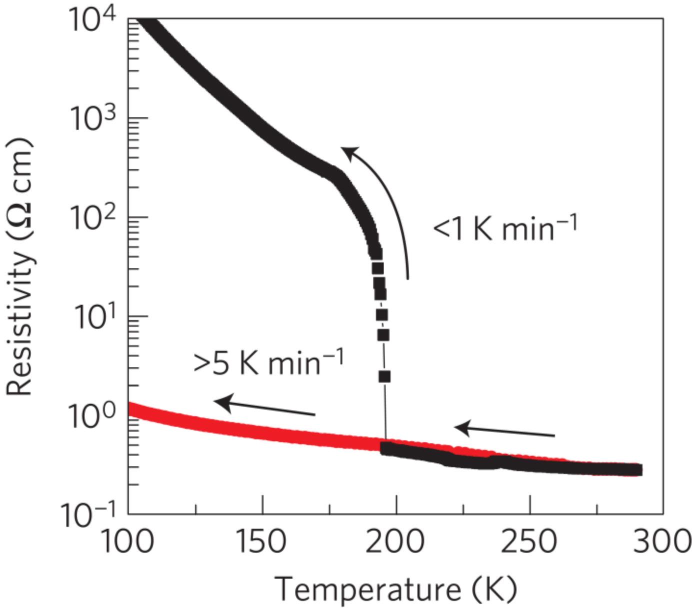
T_{start}=100K



Resistance of θ-RbZn

Cooling-rate dependence





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

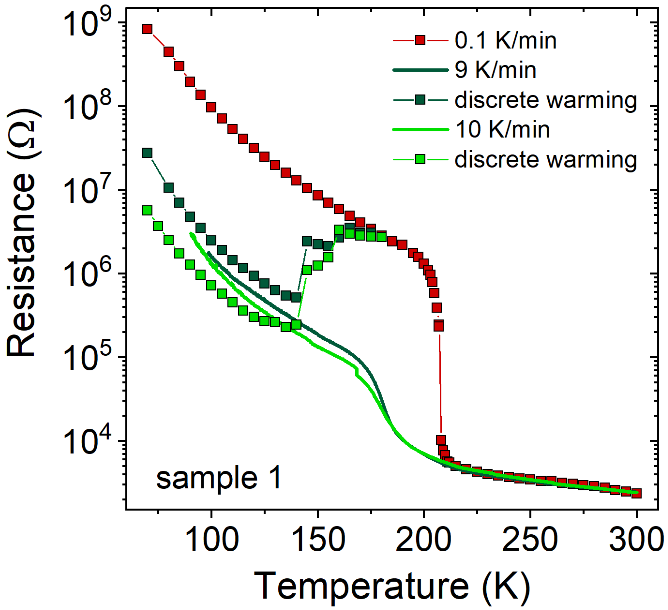
Critical cooling rate q_c~5K/min ?!

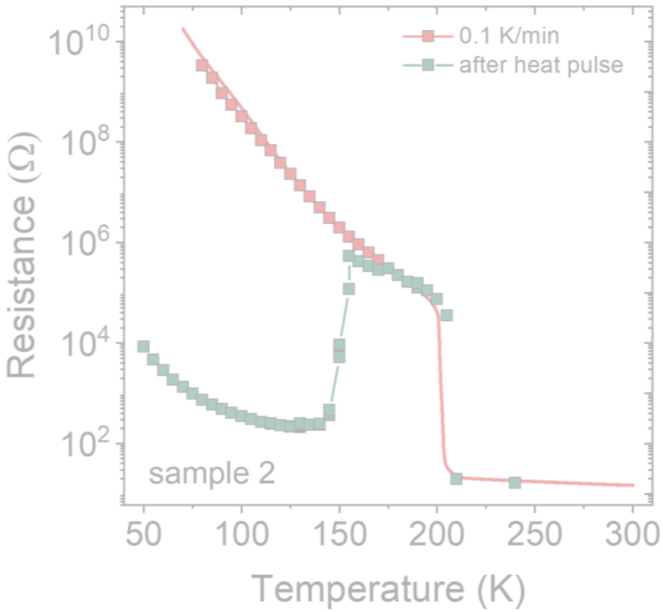
→ dependence on sample quality?

(samples from Prof. H. M. Yamamoto)

Resistance of θ-RbZn

Cooling-rate dependence





Critical cooling rate q_c~5K/min ?!

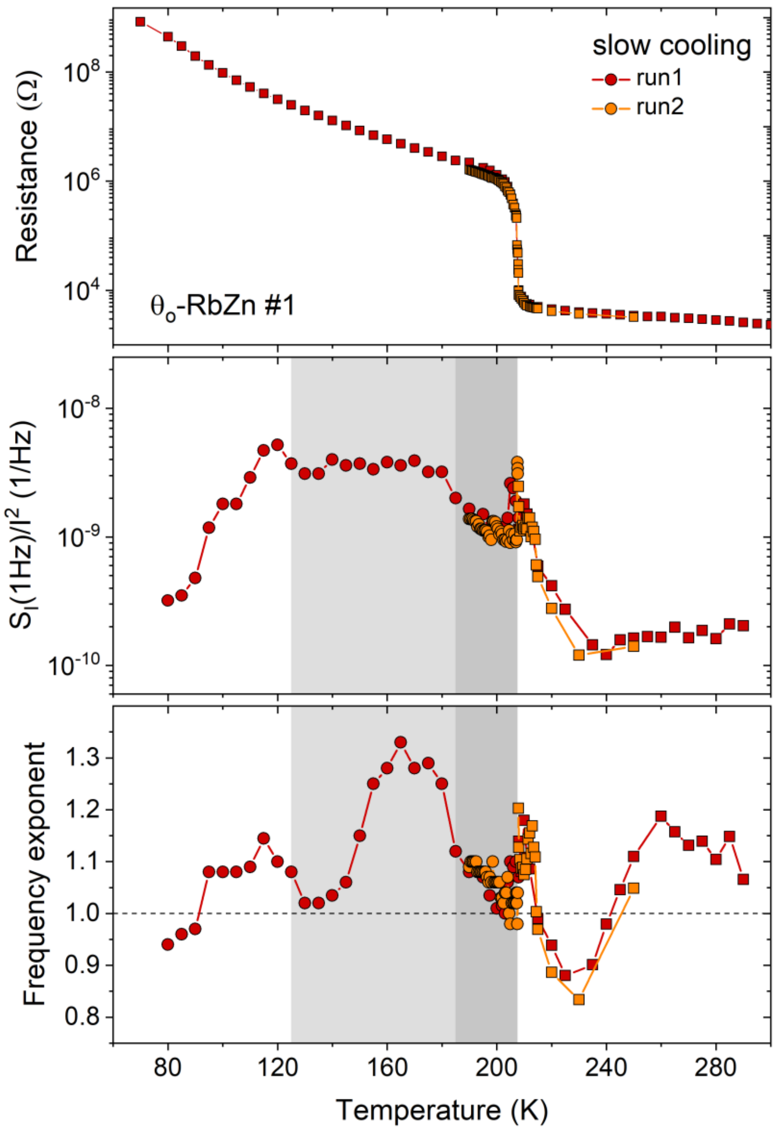
→ dependence on sample quality?

(samples from Prof. H. M. Yamamoto)

Heat pulse method

→ full avoidance of CO transition

θ-RbZn: Charge-Crystal State

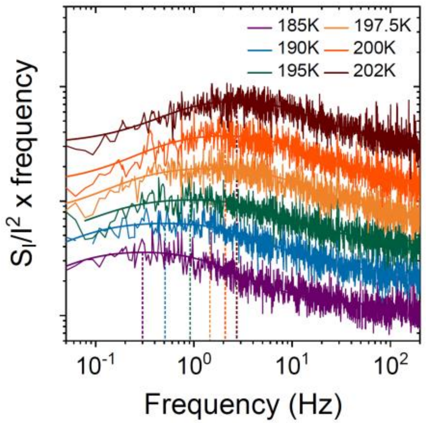


- T_{CO}~200K
- Large peaks at T_{CO}
- Noise increases already above T_{CO}

→ Slowing down of charge cluster and/or structural dynamics

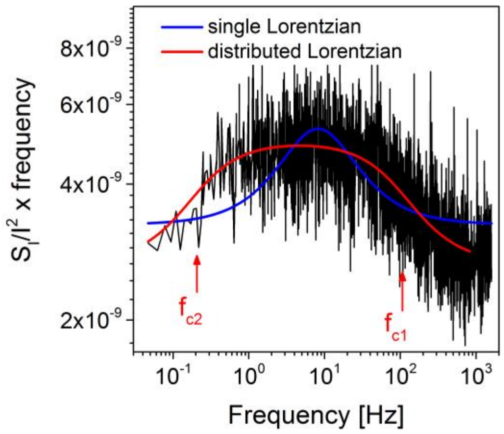
***T*~125-205K:**

- superimposed Lorentzian spectra



θ-RbZn: Charge-Crystal State

Dominating two-level fluctuators (*T*~125-205K)



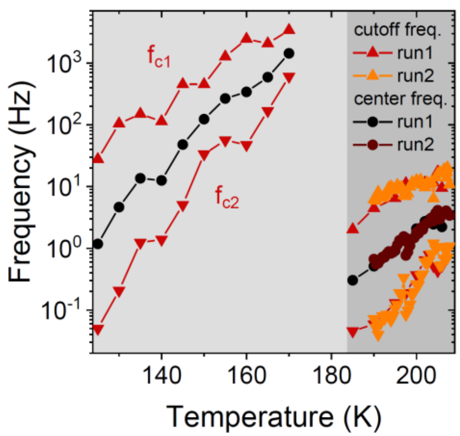
- Distributed Lorentzian model

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

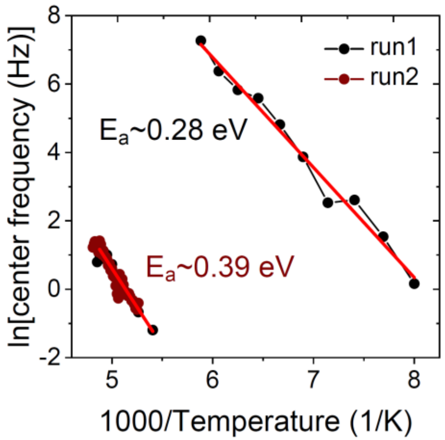
- Characteristic energies

- Slow and heterogeneous dynamics (cf. CL phase)

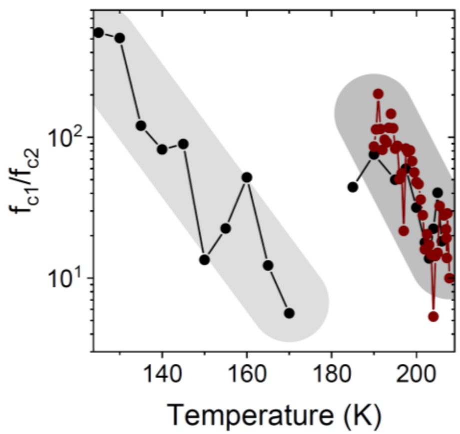
Frequencies:



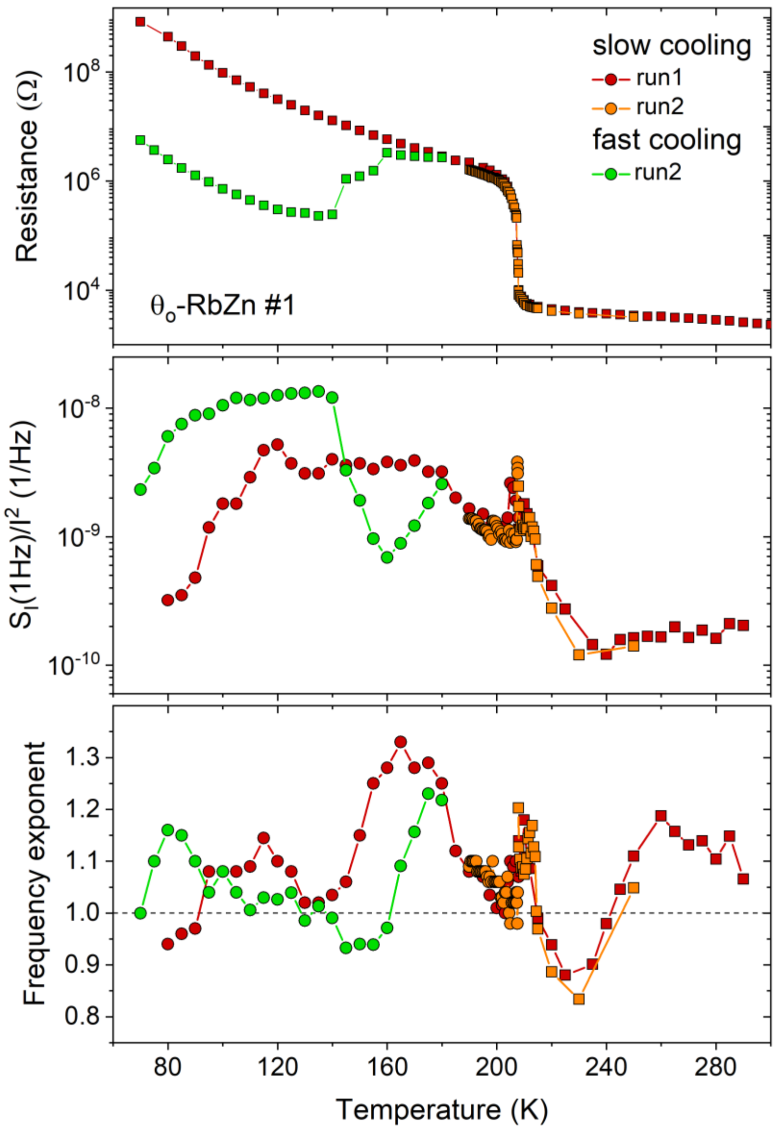
Energies:



Linewidth:



θ-RbZn: Charge-Glass State



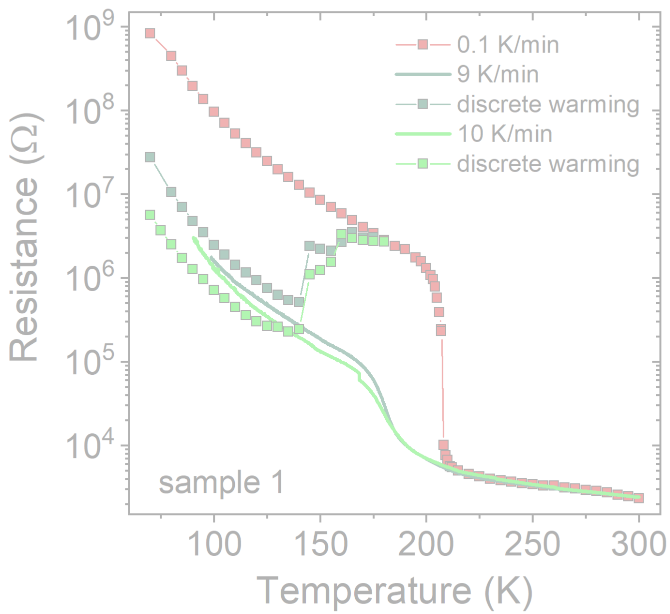
Partly quenched state

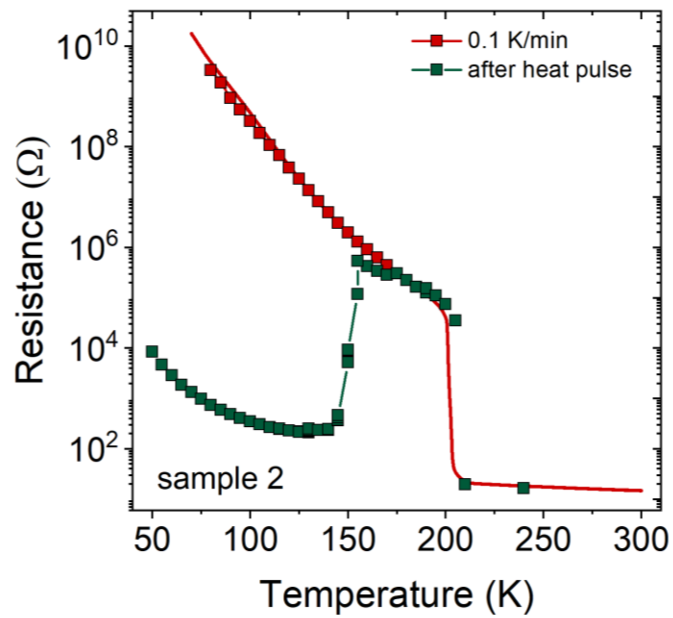
- Relaxation at T~145K
- Complex noise behavior:
  Under-/overshoot of noise magnitude

→ Due to mixed/inhomogeneous state?

θ-RbZn: Charge-Glass State

Fully quenched state





Critical cooling rate q_c~5K/min ?!

→ dependence on sample quality?

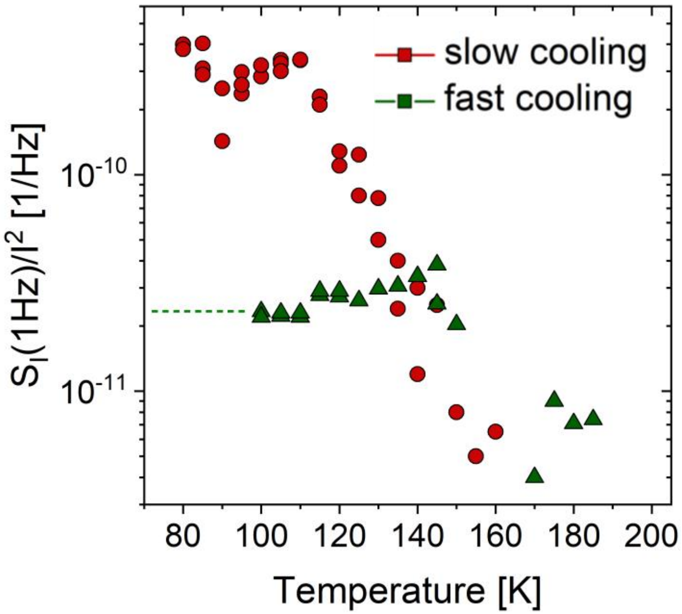
(samples from Prof. H. M. Yamamoto)

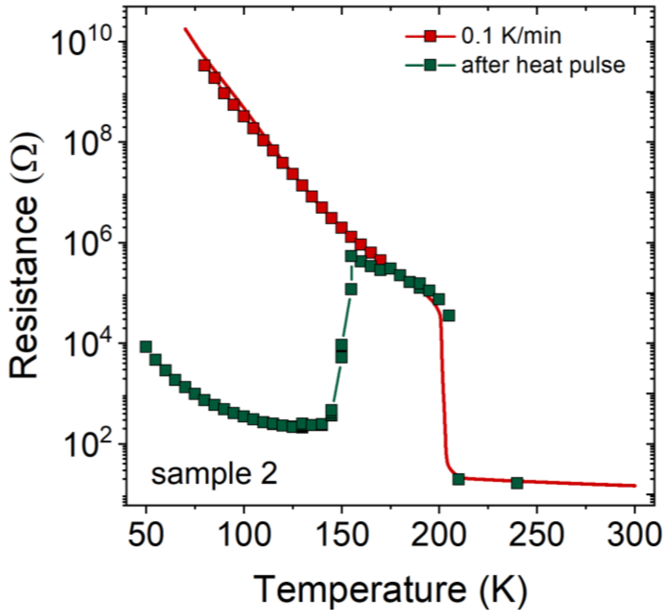
Heat pulse method

→ full avoidance of CO transition

θ-RbZn: Charge-Glass State

Fully quenched state

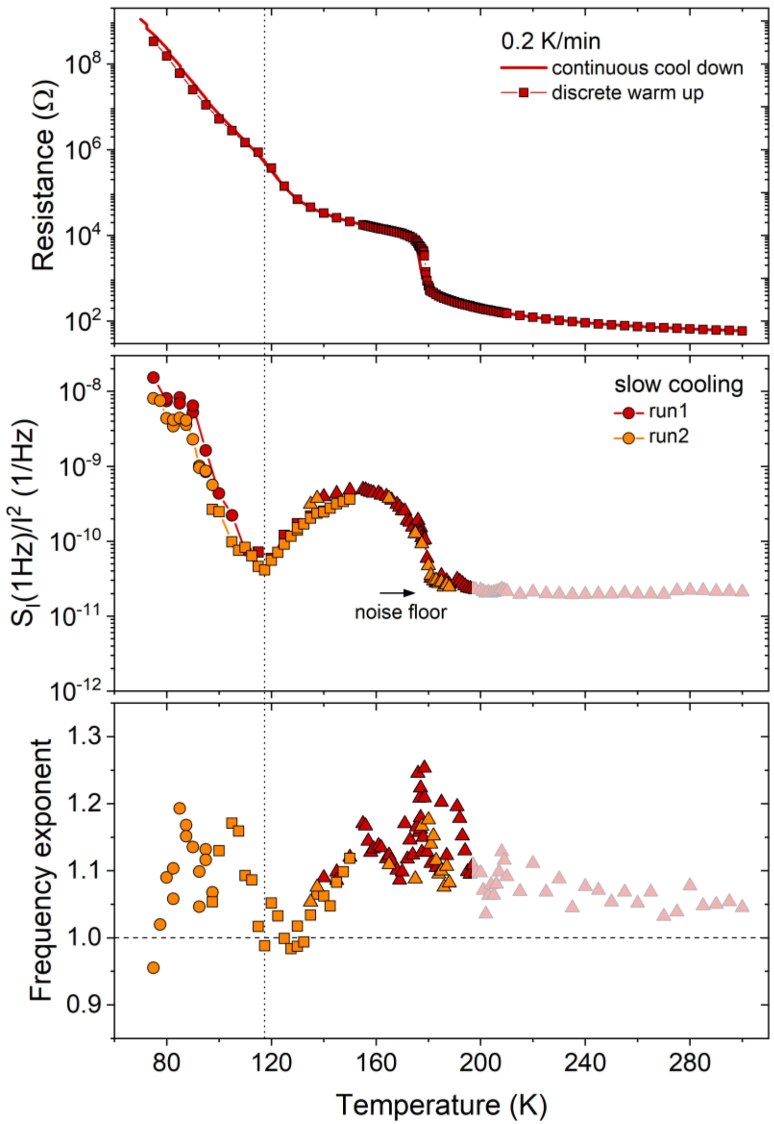




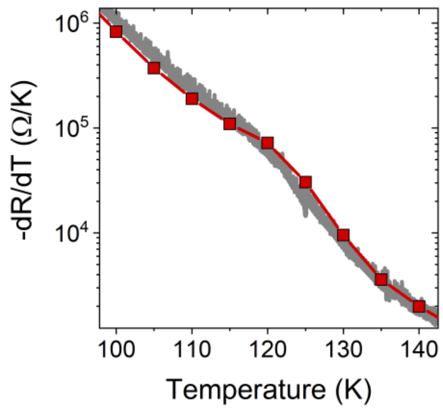
→ Noise in CG state much lower than in CC state

cf. θ_m-TlZn

θ_m-TlZn: Charge-Crystal State

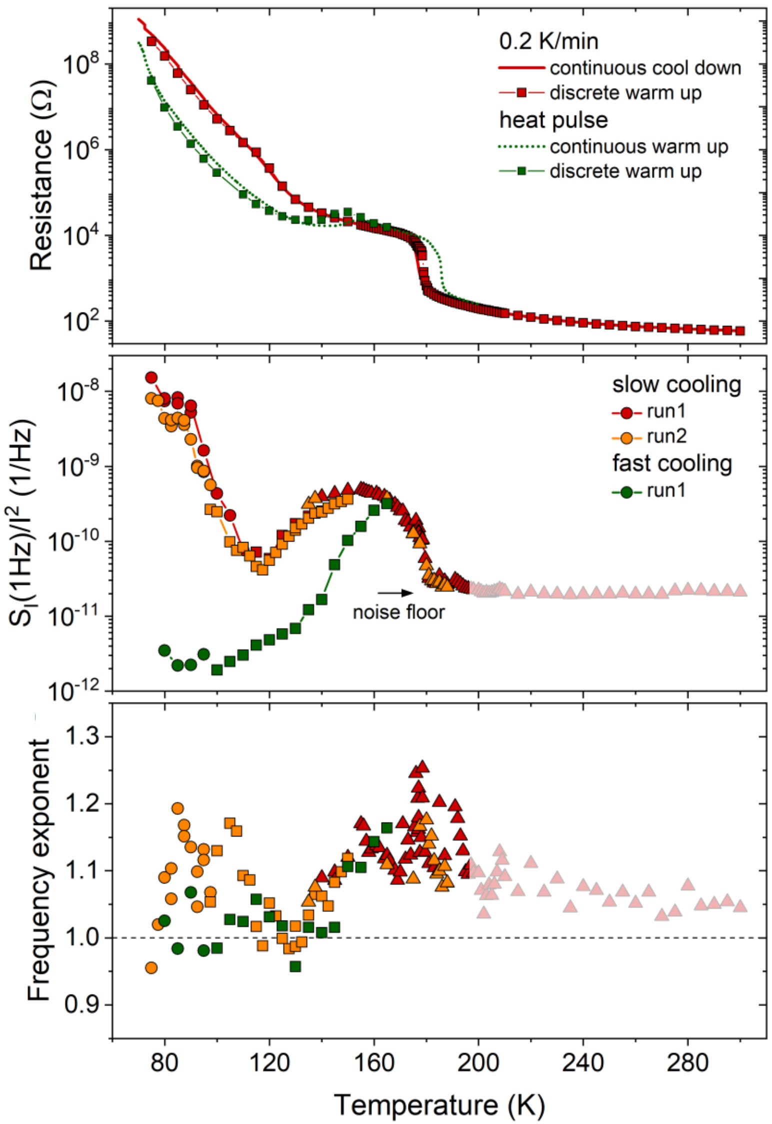


- T_{CO}~175K
- Resistance anomaly at T^*~120K



- Broad noise maximum around T~150K
- Large peaks at transition

θ_m-TlZn: Charge-Glass State



- Heat pulse suppresses CO transition
- Relaxation at T~110K
- Much lower noise magnitude in CG

→ Inhomogeneous current distribution in CC

→ Larger cluster size in CC

→ Lower energy of fluctuators in CG

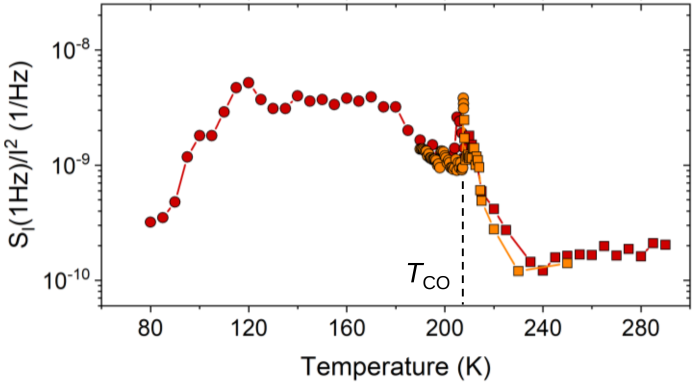
Summary

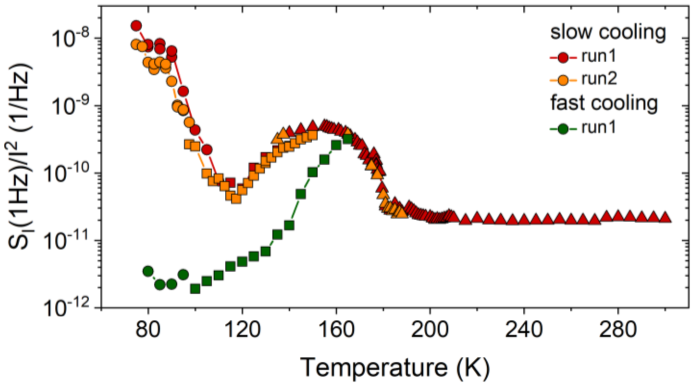
Investigation of the charge dynamics in θ-$(ET)_2$*MM'*$(SCN)_4$ reveals

→ structural glass transition in θ-$(ET)_2$Cs*M'*$(SCN)_4$ Thomas & Saito et al., *PRB* **105**, L041114 (2022)

→ strong fluctuations at phase transition

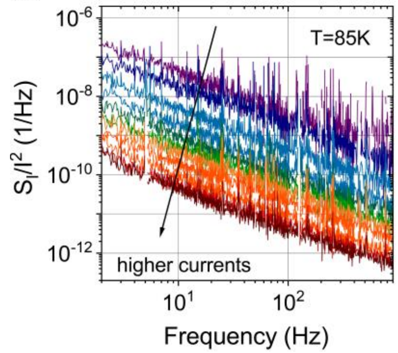
→ large differences in CC and CG state Thomas et al., *PRB* **105**, 205111 (2022)





Open questions:

- Relation between lattice and electron dynamics?
- Influence of disorder by x-ray irradiation?
- Role of ferroelectricity? Current-dependent noise



cf. β'-$(ET)_2ICl_2$, κ-$(ET)_2Cu[N(CN)_2]Cl$, κ-$(ET)_2Hg(SCN)_2Cl$, κ-$(BETS)_2Mn[N(CN)_2]_3$

Müller et al., *PRB* **102**, 100103(R) (2020) Thomas et al., Phys. Status Solidi B, 1800746 (2019)