SPIN PHENOMENA INTERDISCIPLINARY CENTER

New Spin on Molecular Quantum Materials

Wasem in Mainz
May 24-26th, 2022

Randomness effect on charge glass formation in θ-type BEDT-TTF compounds

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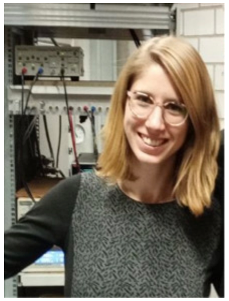
Department of Advanced Materials Science, University of Tokyo, Japan

Collaborators & Acknowledgements

Germany



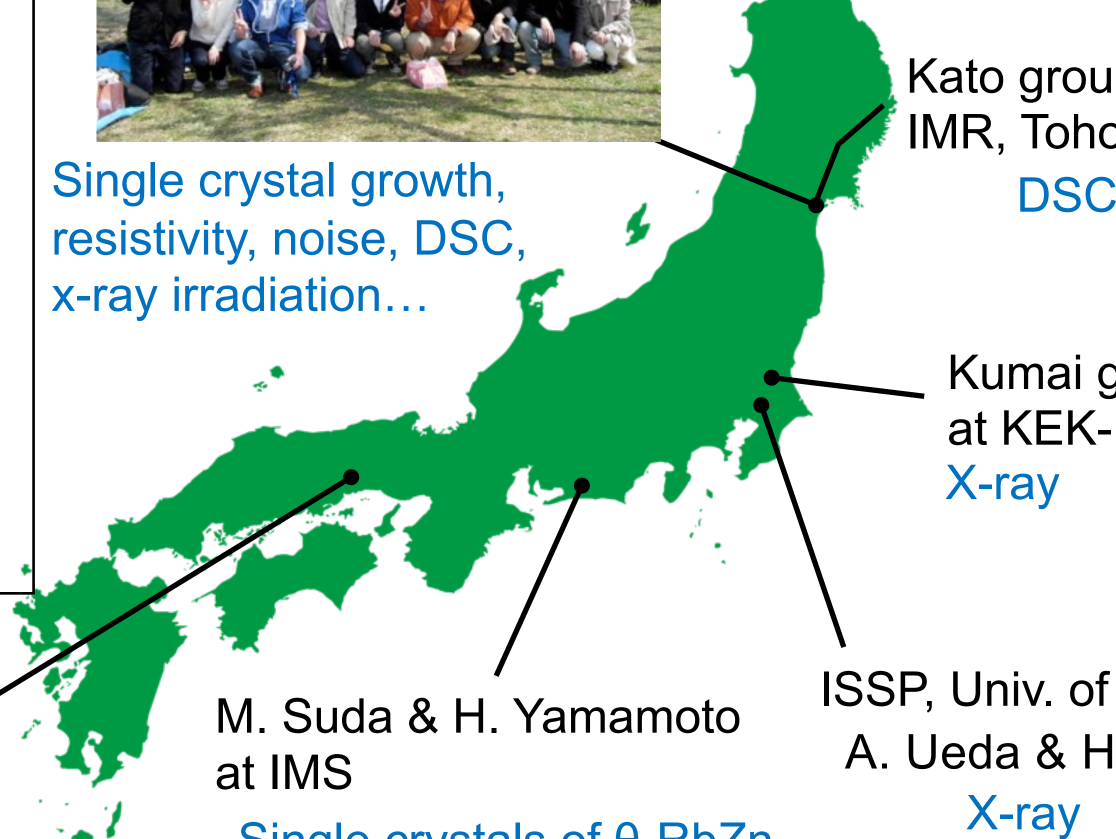
Noise & Thermal expansion

J. Müller & M. Lang
Groups in Frankfurt Univ.

Japan

Sasaki group at IMR, Tohoku Univ.

Single crystal growth, resistivity, noise, DSC, x-ray irradiation…



Kato group at IMR, Tohoku Univ.
DSC

Kumai group at KEK-PF
X-ray

ISSP, Univ. of Tokyo
A. Ueda & H. Mori
X-ray

M. Suda & H. Yamamoto at IMS
Single crystals of θ-RbZn

FT-IR
Y. Ikemoto & T. Moriwaki
at SPring-8 (BL43IR)

Outline

1. Introduction

- Brief introduction of glass formation phenomena and charge liquid/crystal/glass states in θ-BEDT-TTF compounds

2. Comparison of CC and CG states in three different θ-type salts

- Resistivity and optical conductivity spectra in the orthorhombic and monoclinic systems

3. Charge crystallization process probed by thermodynamic quantity

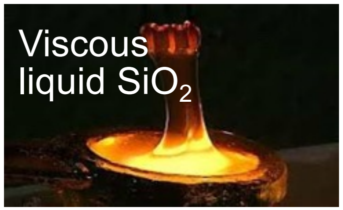
- TTT diagram constructed by DSC measurements

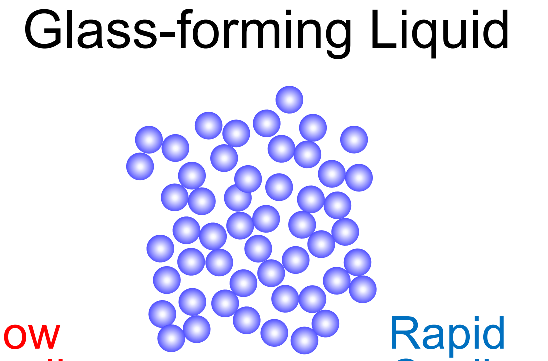
4. Randomness effects on charge crystallization and vitrification

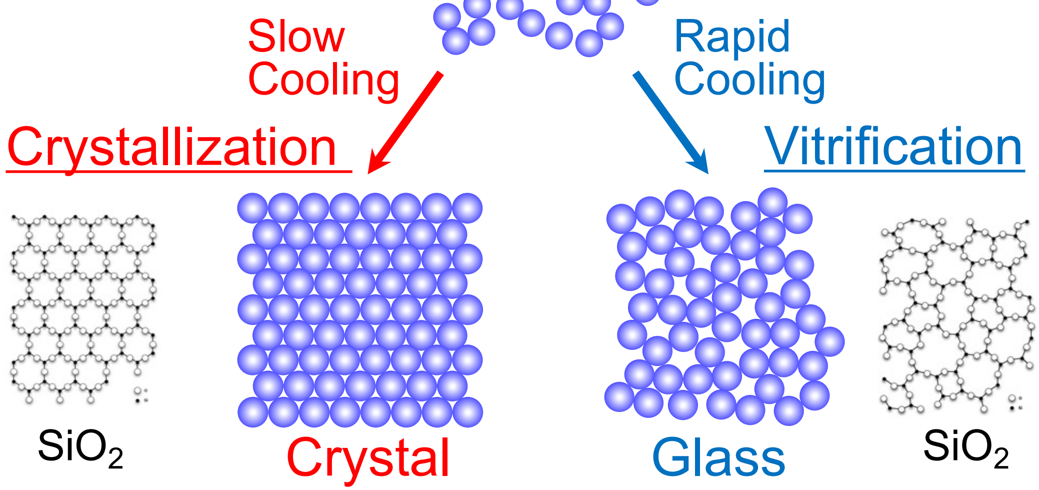
- Reflectivity and DSC measurements for x-ray irradiated samples

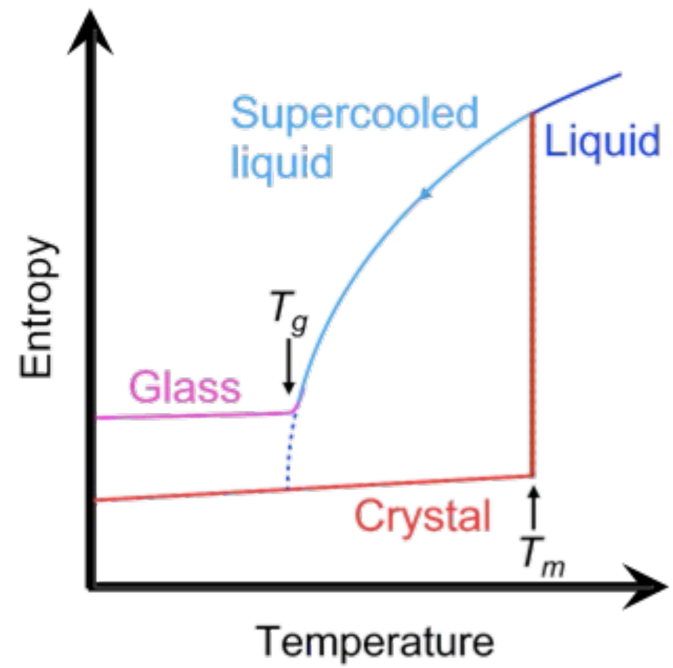
5. Summary

Crystallization vs Vitrification







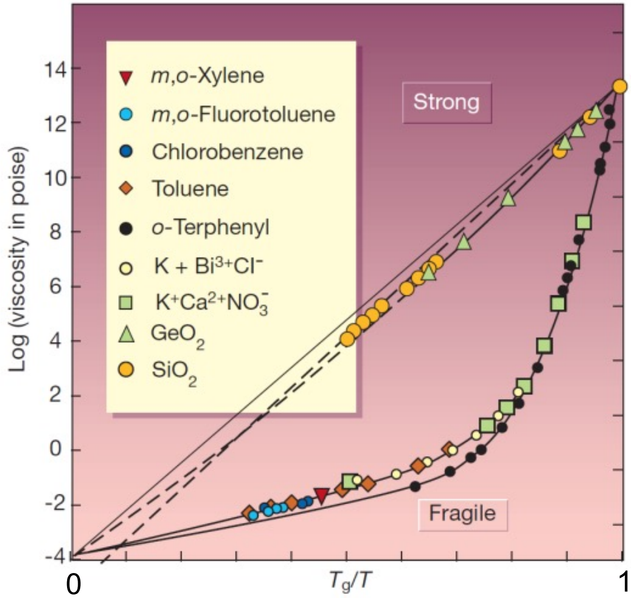


What is the mechanism of glass formation?

- Science 125 Questions: *What is the nature of the glassy state?*
125th Anniversary Issue of Science (2005)
- The 70 Wonders of Physics: *Is Glass a solid or liquid?*
75th Anniversary Issue of JPSJ (2017)

✓ Slowing down of dynamics

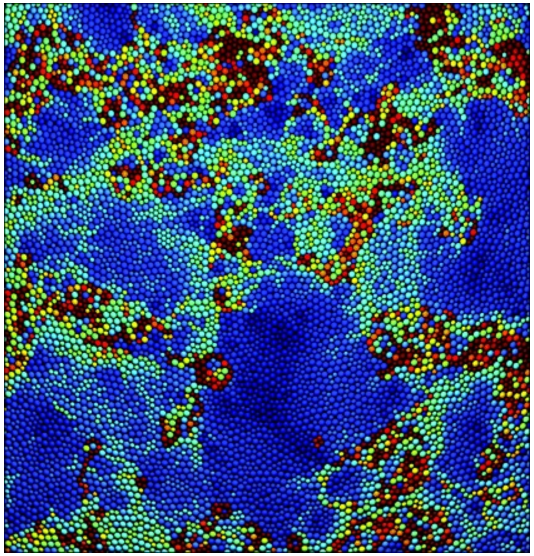
Divergence of viscosity



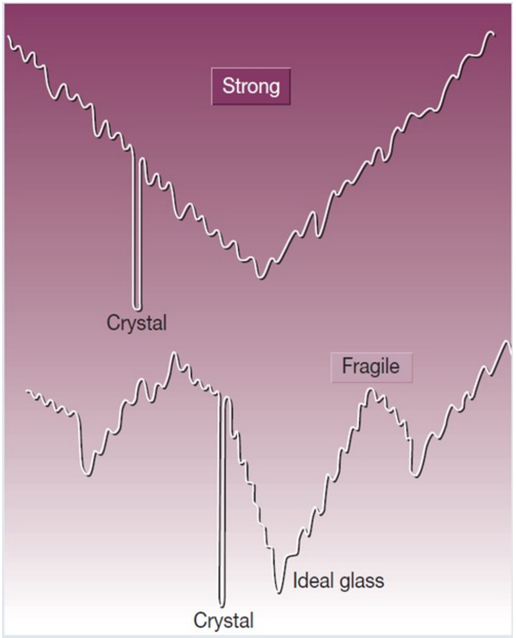
P. G. Debenedetti *et al.*, Nature **410**, 259 (2001).

✓ Dynamical heterogeneity

Heterogeneity in space and time



From the cover of PNAS, Sep. 8th, 2009



Energy landscape

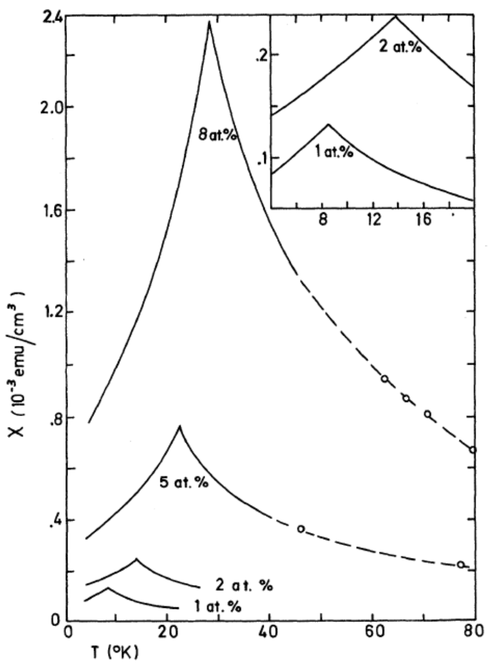
✓ Energy landscape with multiple local minima

Glass formation phenomena in SCES

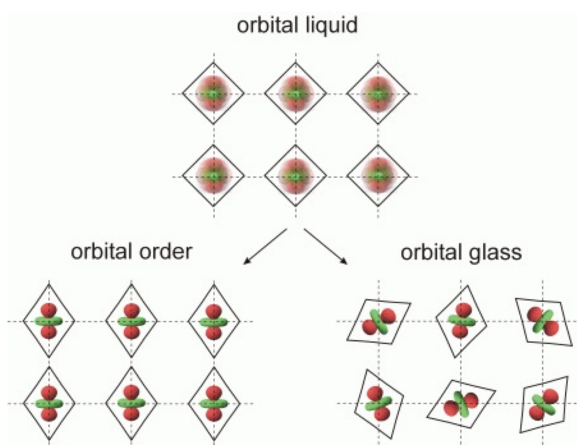
Glass formation phenomena have been reported in various degrees of freedom of electrons in strongly correlated electron systems:

spins, charges, orbitals, and superconducting vortices…

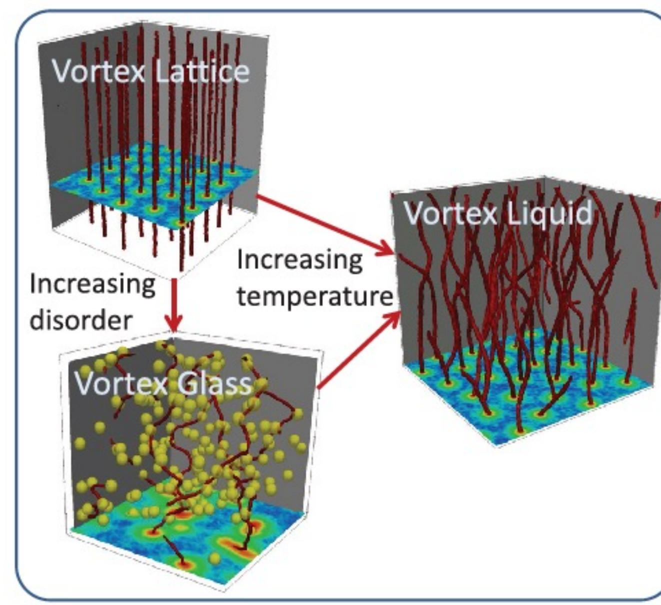
Spin glass



Orbital glass



Superconducting vortex glass



However, the fundamental understanding of the glass formation mechanism is still an open question.

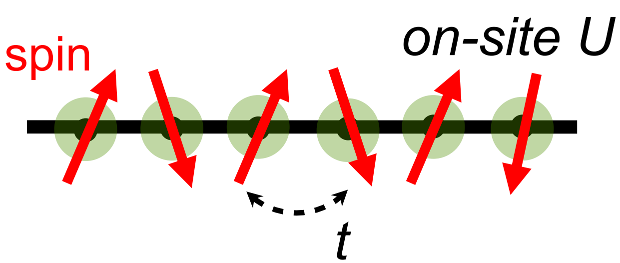
Two representative insulating states in SCES

Extended Hubbard model

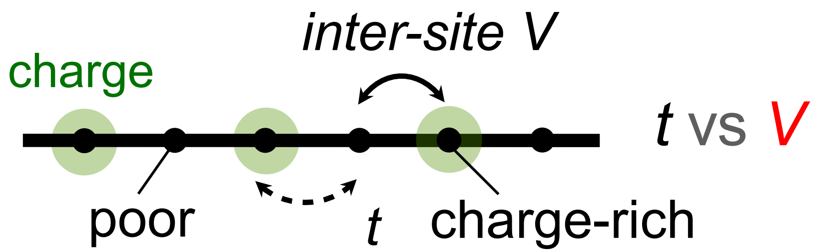
$$H = t \sum_{\langle i,j \rangle \sigma} (c^{\dagger}_{i\sigma} c_{j\sigma} + \mathrm{h.c.}) + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle i,j \rangle} n_i n_j$$

On-site (U), *Inter-site* (V)

1/2-filled → Mott transition

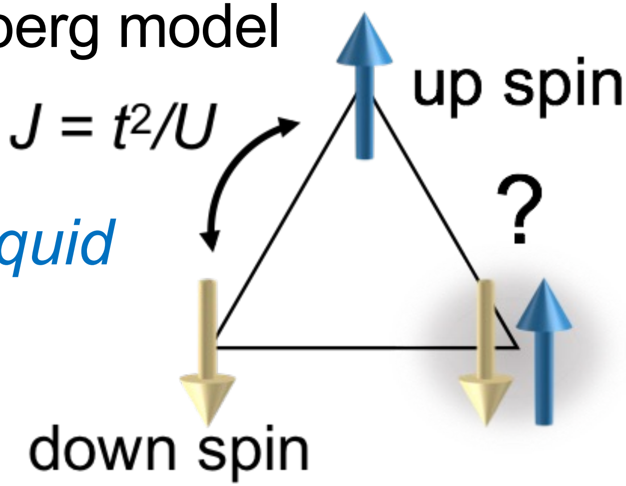


1/4-filled → Charge order (CO)



Spin frustration system

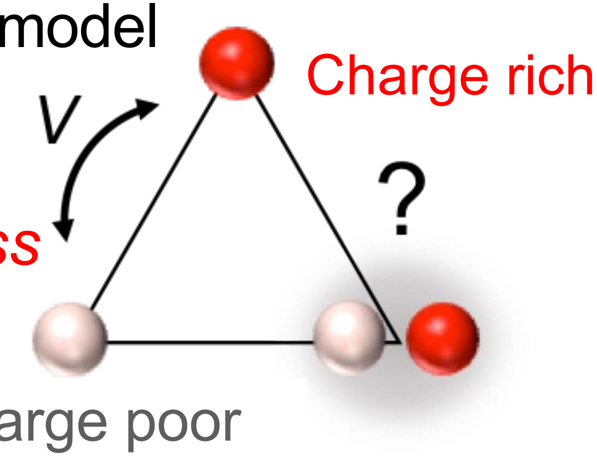
Heisenberg model



Spin liquid

Charge frustration system

Ising model



Charge glass

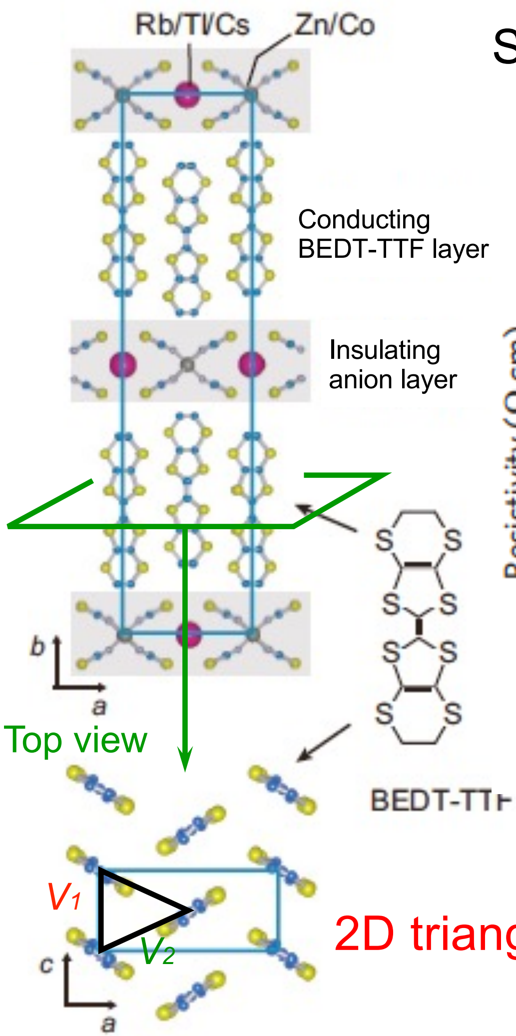
Charge liquid/crystal/glass states in θ-(BEDT-TTF)$_2X$

θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ (abbreviated as θ-RbZn)

+0.5 -1

H. Mori *et al.*, PRB **91**, 041101 (1998).

¼ filled hole band system with a 2D triangular lattice

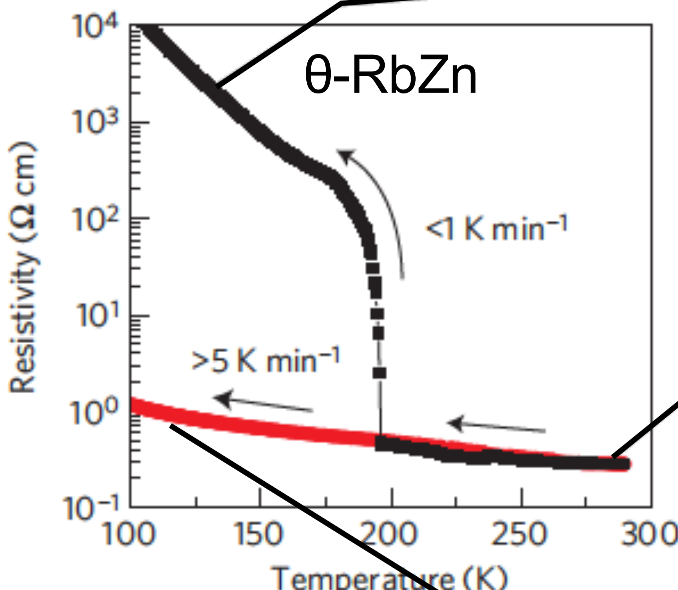


2D triangular lattice

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

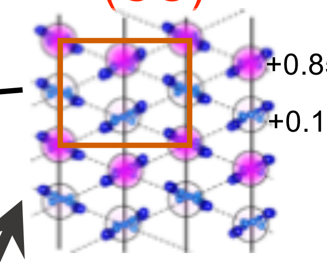
Strong inter-site Coulomb repulsion V

→ Charge ordering (CO)



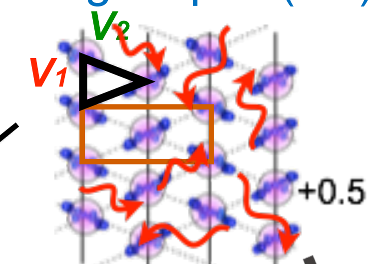
F. Kagawa *et al.*, Nature Phys. **9**, 419 (2013).

Charge crystal (CC)

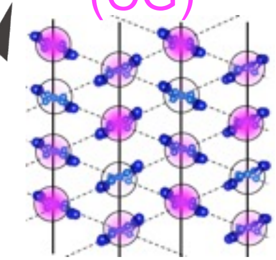


Slow cool

Charge liquid (CL)

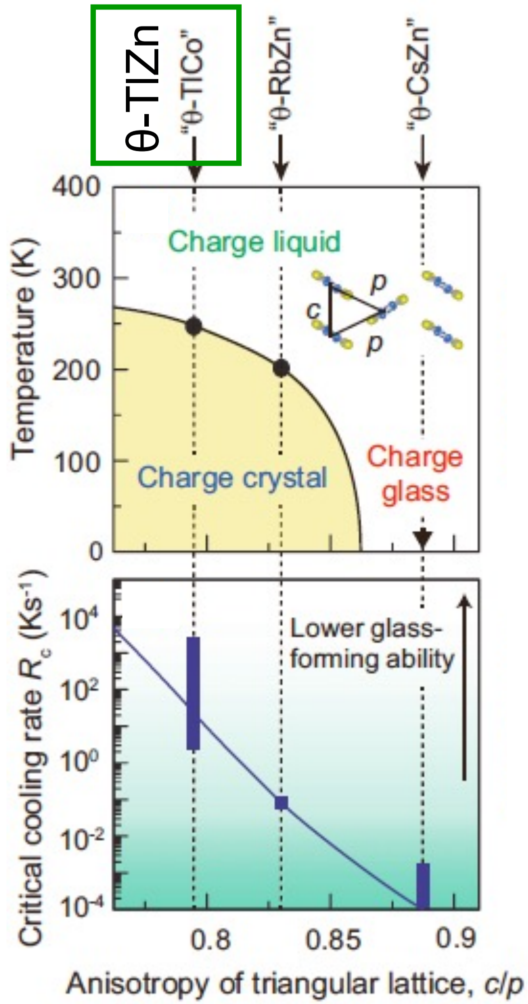


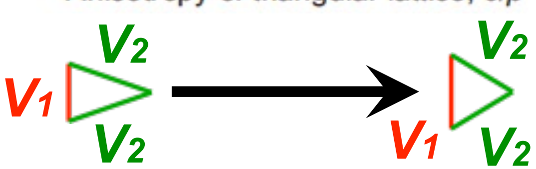
Charge glass (CG)



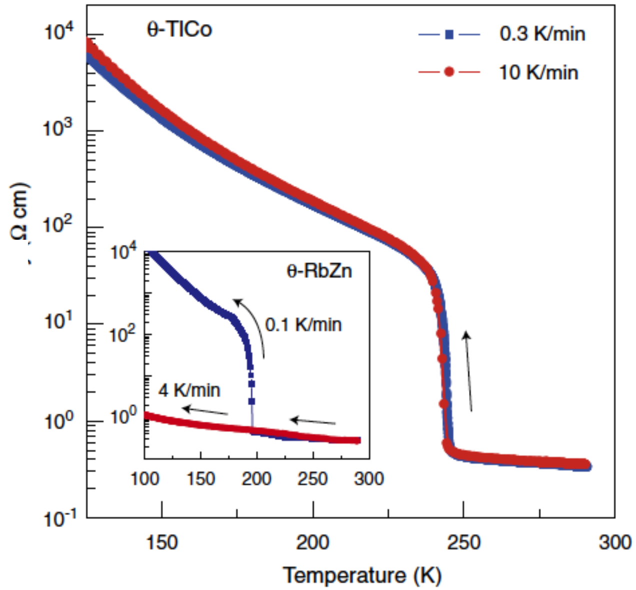
Randomly distributed

θ-(BEDT-TTF)$_2$*MM'*(SCN)$_4$ (abbreviated as θ-*MM'*)

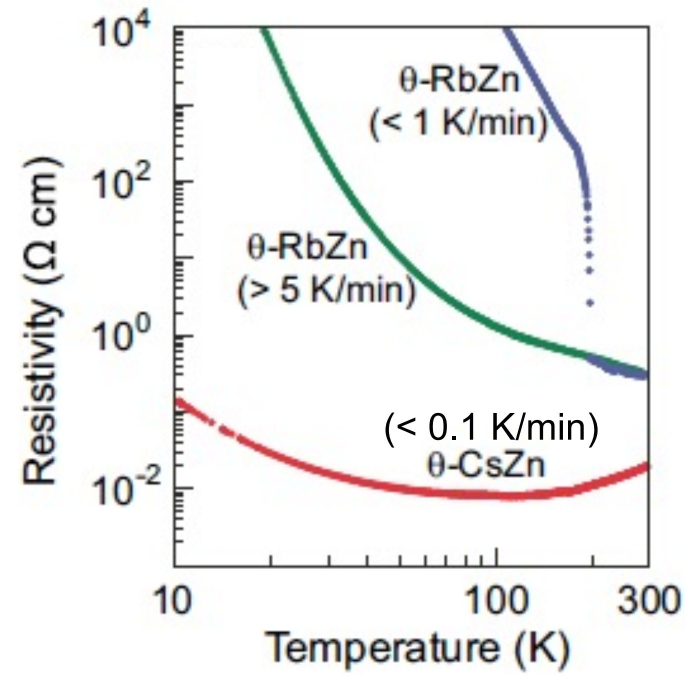




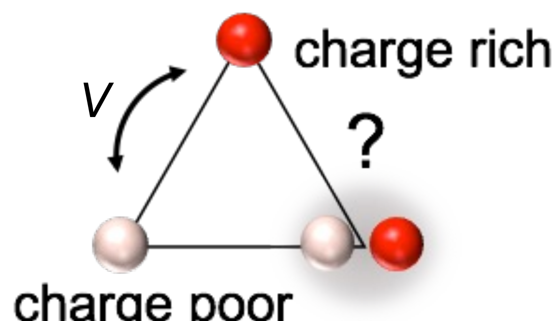
H. Oike *et al.*, PRB **91**, 041101(R) (2015).



T. Sato *et al.*, JPSJ (2014).



T. Sato *et al.*, PRB (2014).



Geometrical frustration between V_1 and V_2

→ *Charge glass formation*

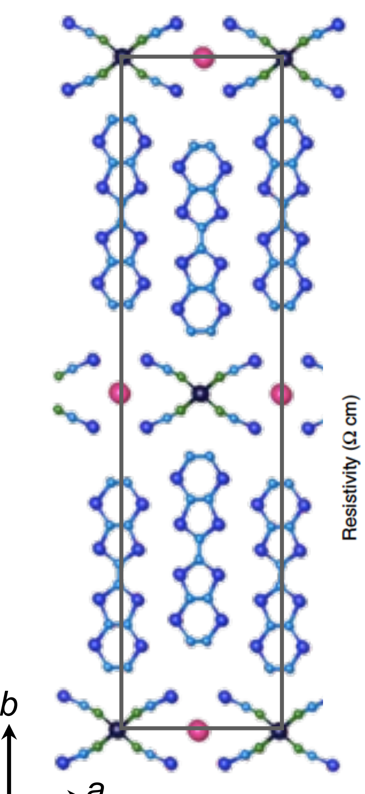
Two different crystal forms in θ-TlZn/TlCo

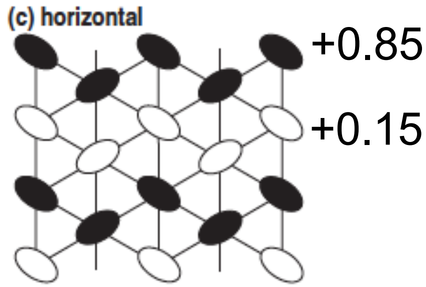
S. Sasaki, KH *et al.*, Science **357**, 1381 (2017).

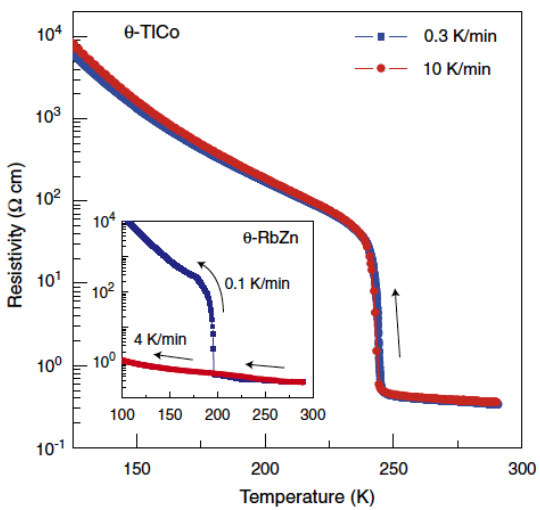
Orthorhombic

θ_o-(BEDT-TTF)$_2$TlCo(SCN)$_4$

- Horizontal CO
- T_m = 240 K
- V_2/V_1 = 0.835





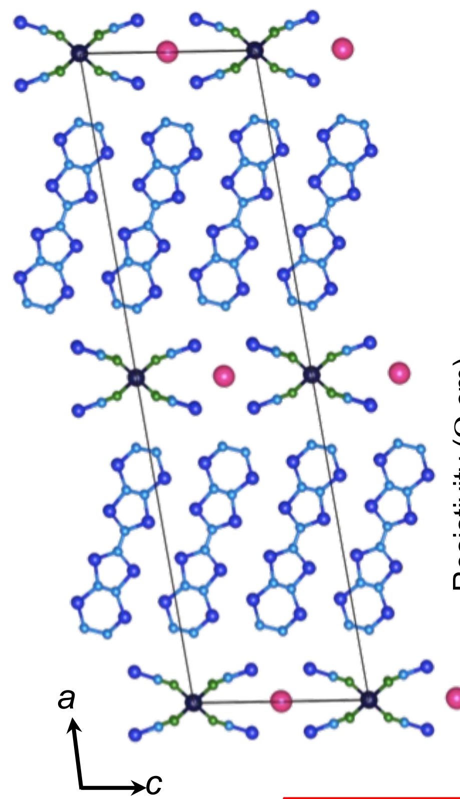


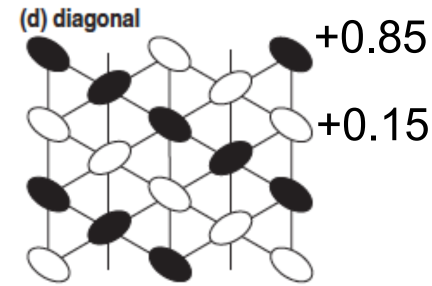
H. Mori *et al.*, Bull. Chem. Soc. Jpn. **71**, 797 (1998).

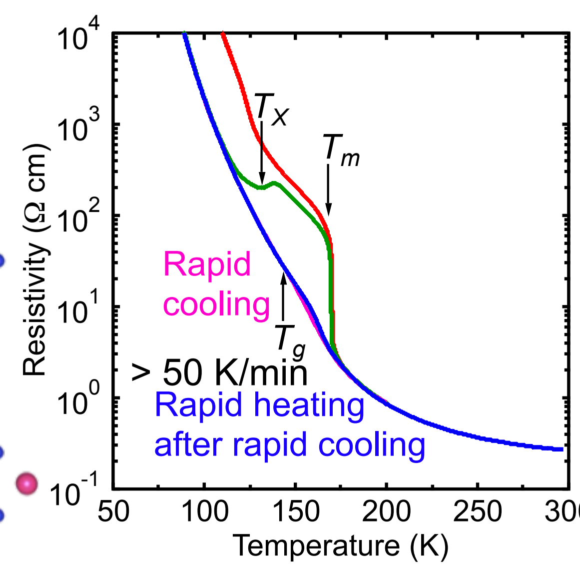
Monoclinic

θ_m-(BEDT-TTF)$_2$TlZn(SCN)$_4$

- Diagonal CO
- T_m = 170 K
- V_2/V_1 = 0.816



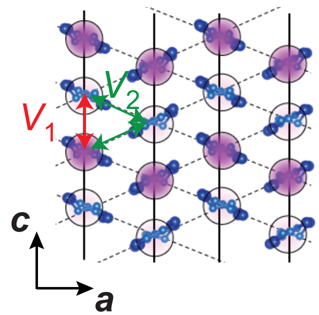




More anisotropic

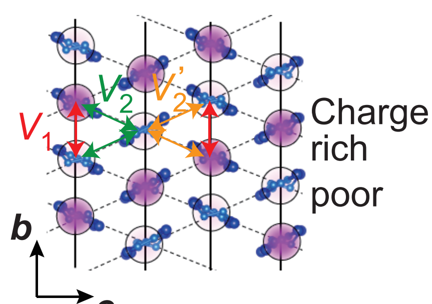
Critical cooling rate for CG formation

θo-type

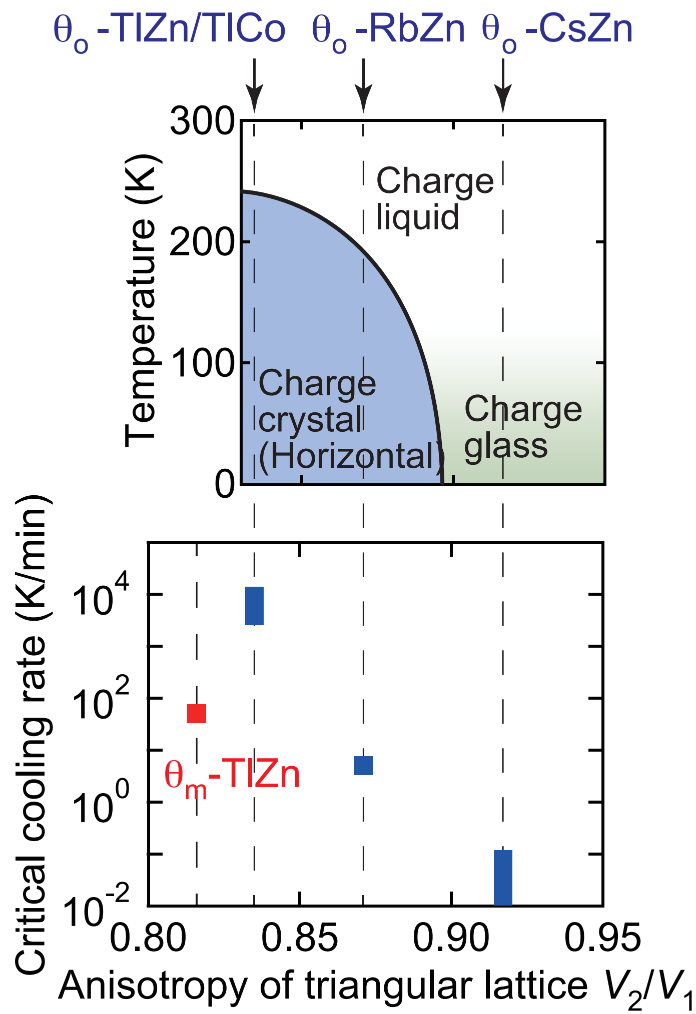


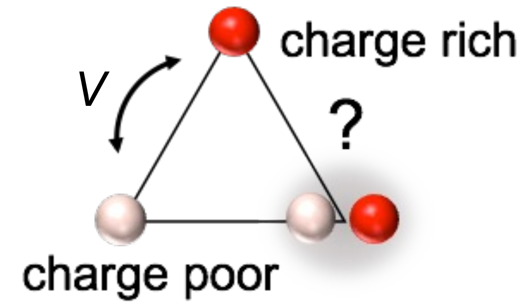
Horizontal CO

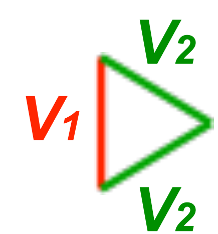
θm-type



Diagonal CO







V_1 vs V_2

Geometrical frustration of equilateral triangular lattice

The critical cooling rate of θ_m-TlZn is slower than that of θ_o-TlCo, suggesting different charge-glass formation mechanisms between these two systems.

1. Introduction

- Brief introduction of glass formation phenomena and charge liquid/crystal/glass states in θ-BEDT-TTF compounds

2. Comparison of CC and CG states in three different θ-type salts

- Resistivity and optical conductivity spectra in the orthorhombic and monoclinic systems

3. Charge crystallization process probed by thermodynamic quantity

- TTT diagram constructed by DSC measurements

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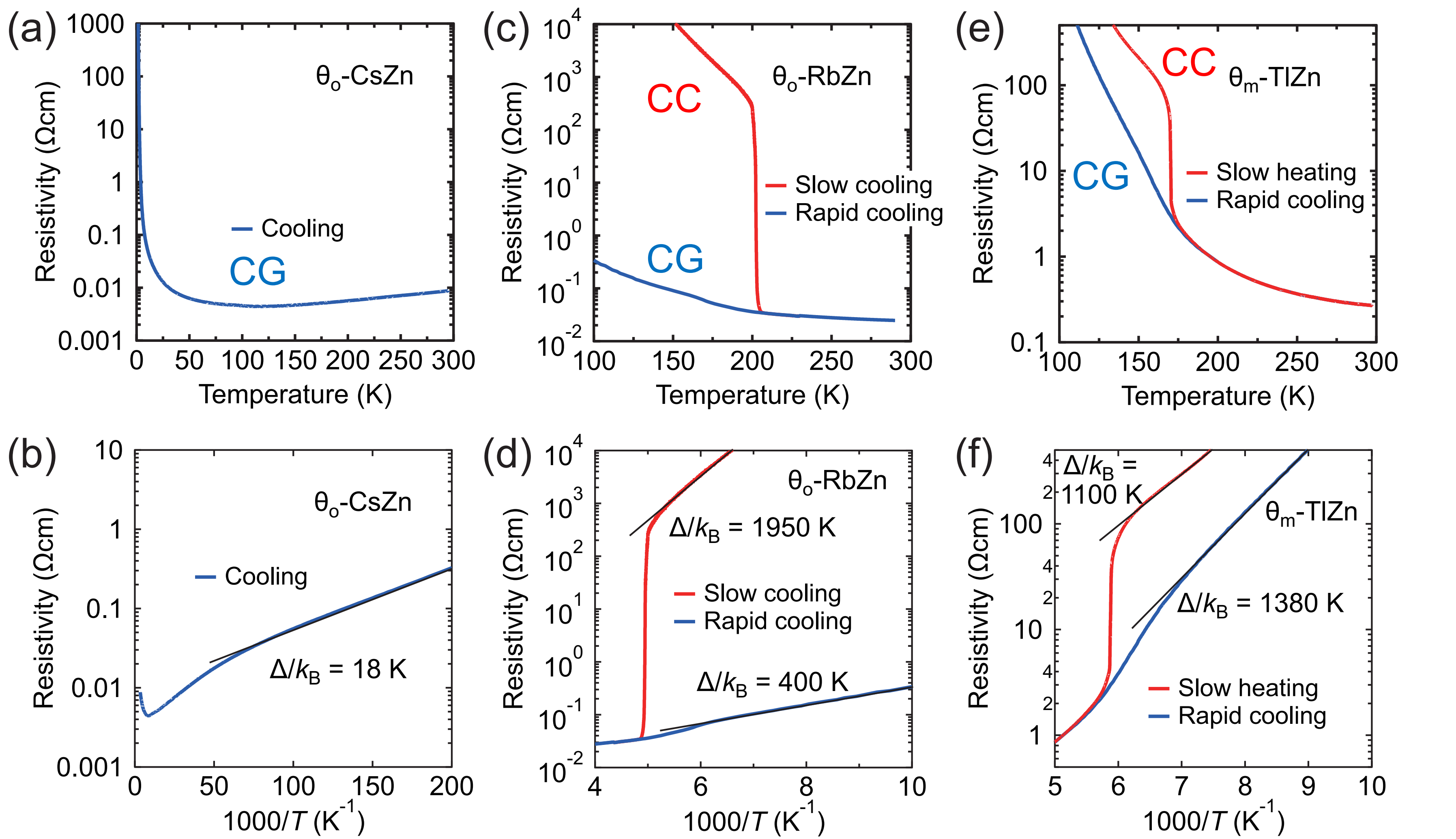
5. Summary

Resistivity curves in CC and CG states

KH *et al.*, submitted.

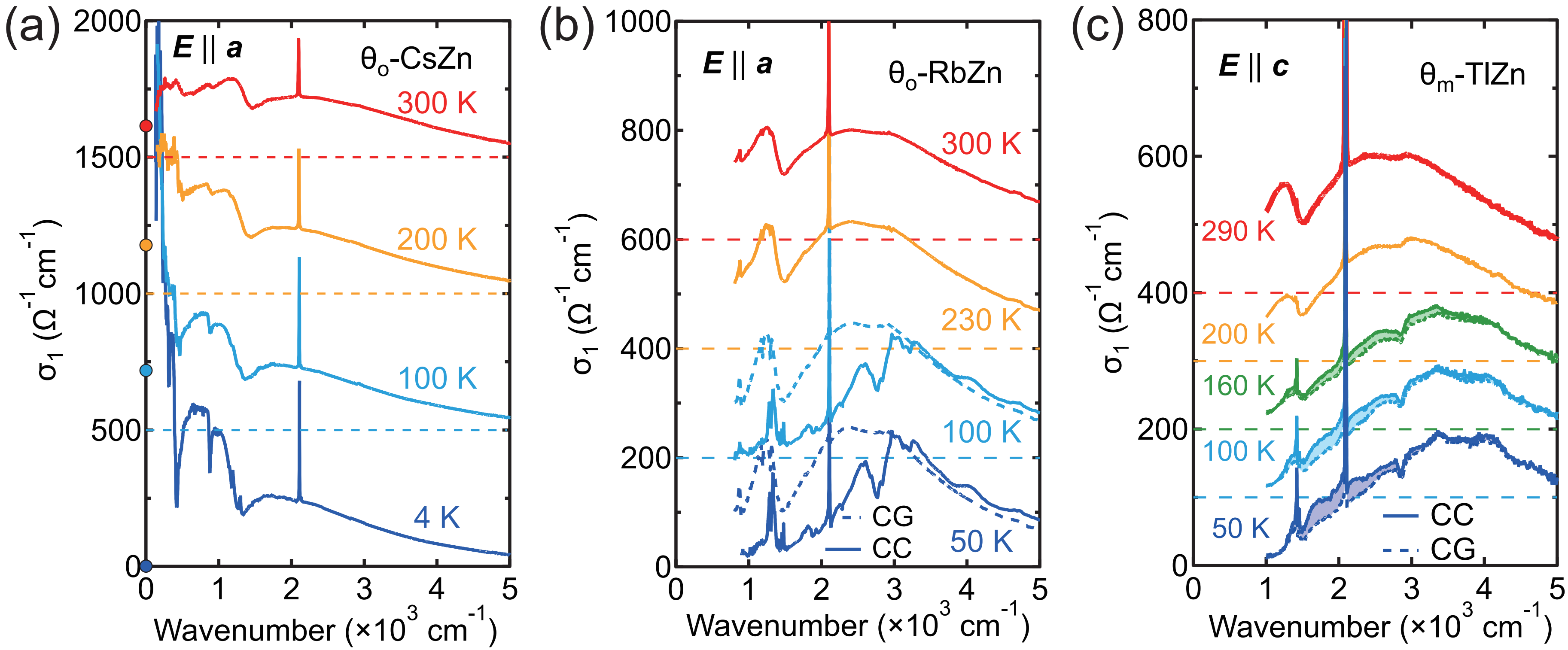


<u>θo-type</u>: large difference between CC and CG states

<u>θm-type</u>: small difference between CC and CG states

Optical conductivity spectra in θ-type compounds

KH *et al.*, submitted.

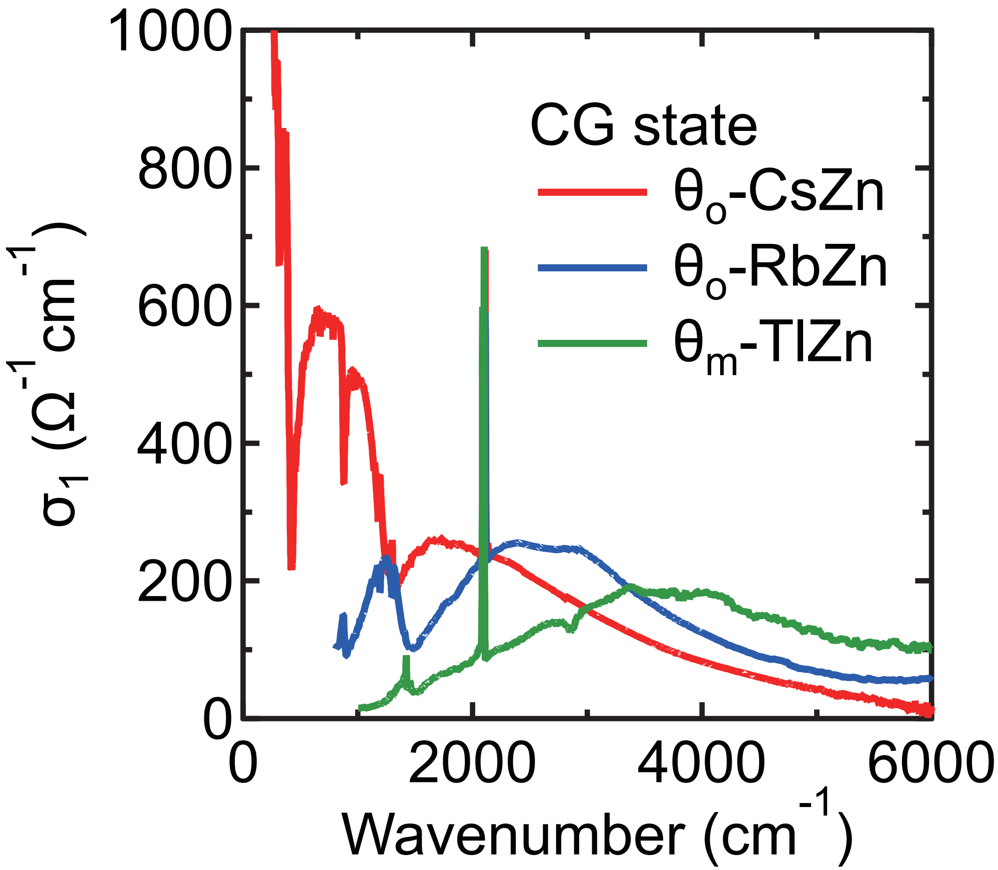


θ_o-type

The CG state exhibits larger low-energy excitations than the CC state and becomes more metallic with increasing V_1/V_2.

θ_m-type

The optical gaps in the CG and CC states are almost identical.



KH *et al*., submitted.

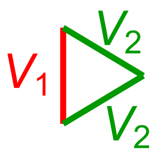
As the anisotropy of the triangular lattice increases, the spectral weight in the low-energy region shifts to a higher-energy region.

Geometrical frustration on equilateral and isosceles triangle lattices

Extended Hubbard model (EHM)

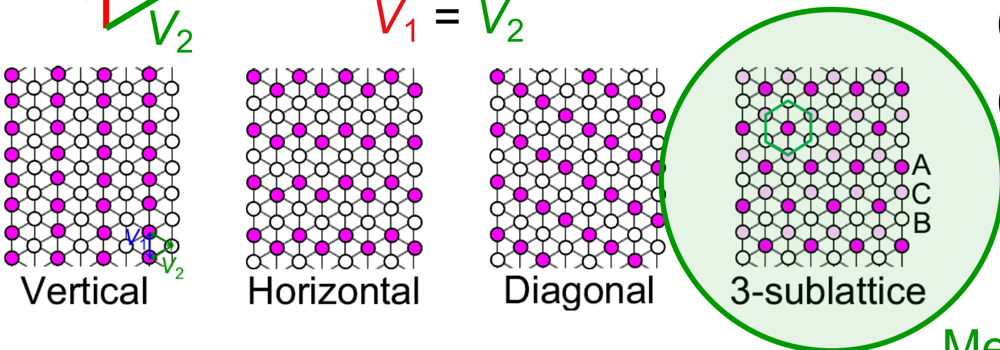
$$H = t \sum_{\langle i,j\rangle\sigma} (c^{\dagger}_{i\sigma} c_{j\sigma} + \mathrm{h.c.}) + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle i,j\rangle} n_i n_j$$

θ_o-type: equilateral triangular lattice



Frustration between V_1 and V_2

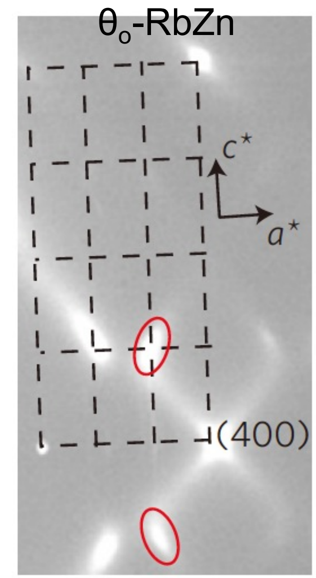
$V_1 = V_2$



Short-range 3-fold COs

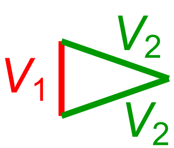
θ_o-CsZn: q_d = (2/3 1/3)

θ_o-RbZn: q_d = (1/4 1/3)



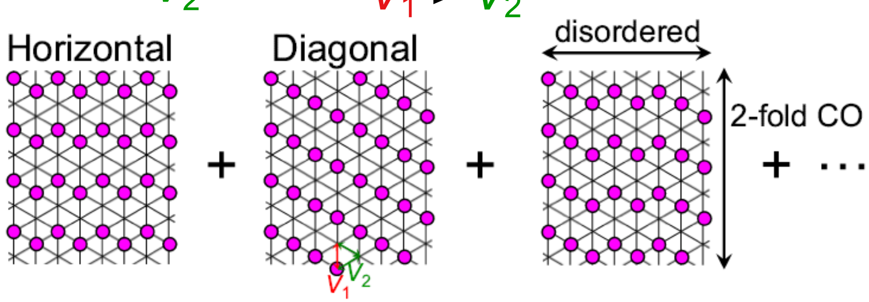
F. Kagawa *et al.*,
Nature Phys. **9**, 419 (2013).

θ_m-type: isosceles triangle lattice



Frustration between two V_2

$V_1 > V_2$

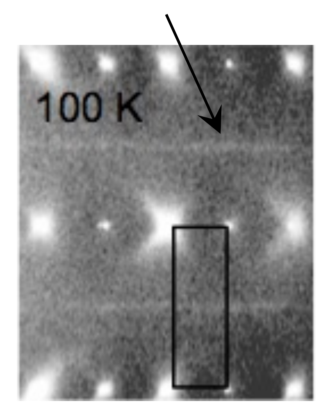


Chain-striped COs along the V_1 direction

Superpositions of insulating 2-fold stripe COs

θ_m-TlZn: q_d = (1/2 l)

Diffuse lines



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

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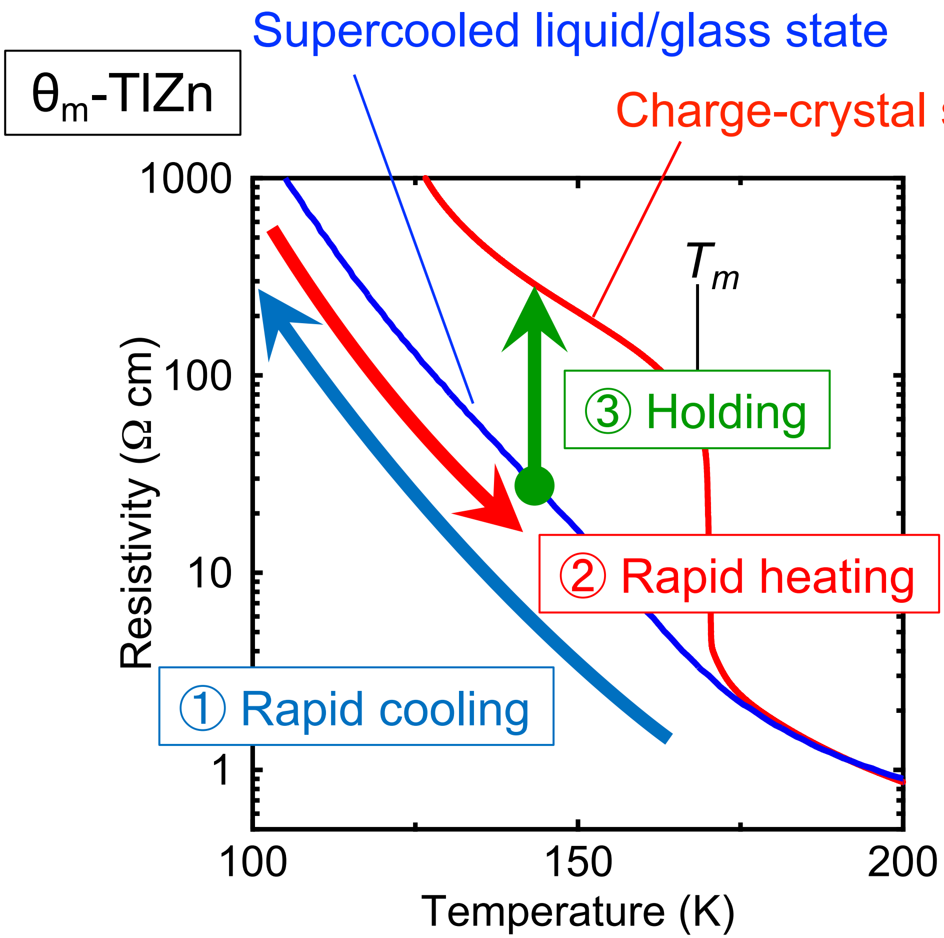
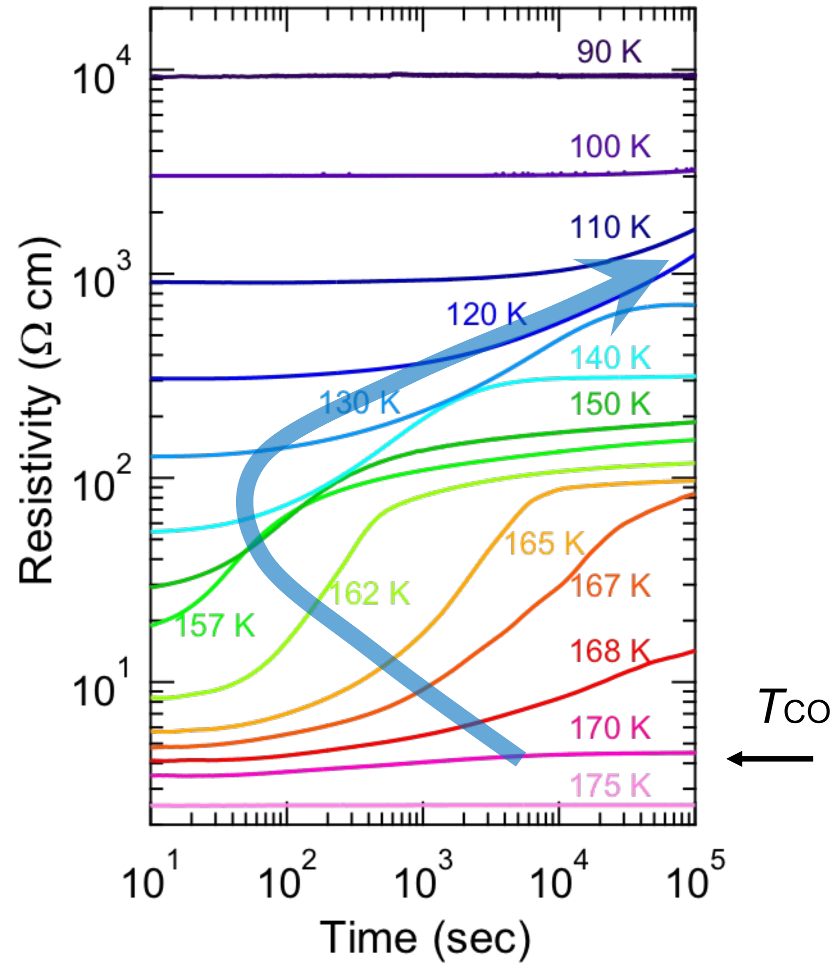


S. Sasaki, KH *et al.*, Science **357**, 1381 (2017).



① Rapid cooling (> 50 K/min)

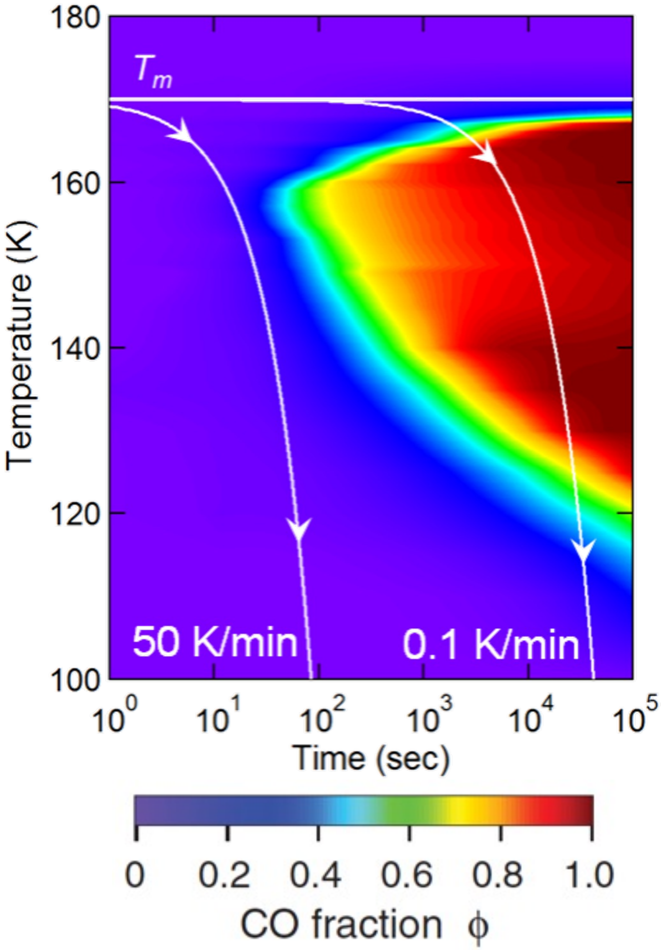
② Rapid heating (> 50 K/min)

③ Holding

The crystallization time becomes faster with decreasing temperature, and then, it becomes slower below ~ 160 K.

Time-Temperature-Transformation (TTT) diagram

θm-TlZn **Dome-shaped**



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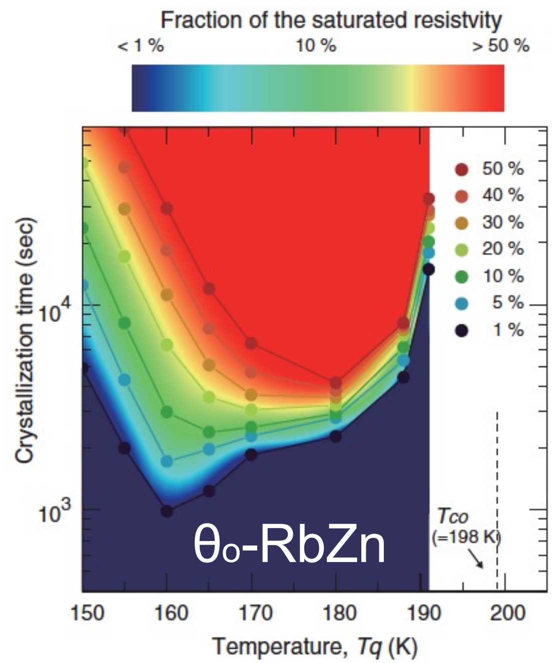
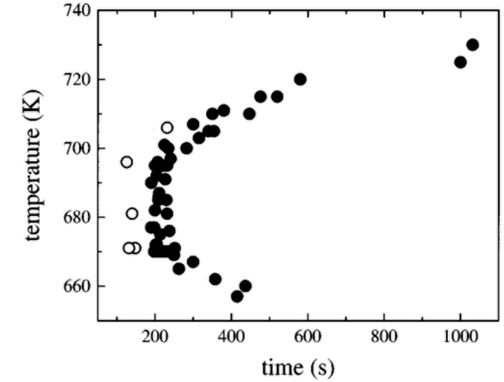


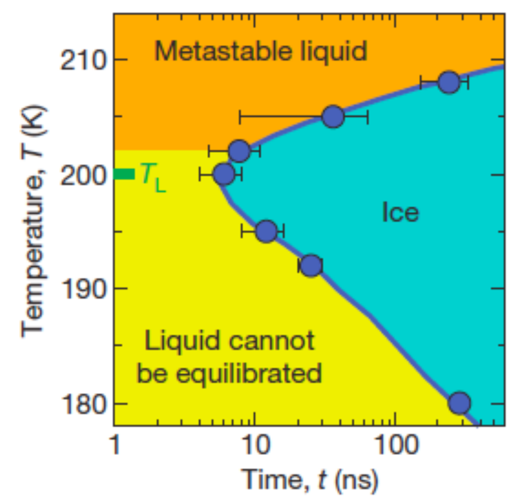
T. Sato *et al.*,
Science **357**, 1378 (2017).

Metallic glass



J. Schroers, *et al.*, APL **77**, 1158 (2000).

H_2O(simulation)



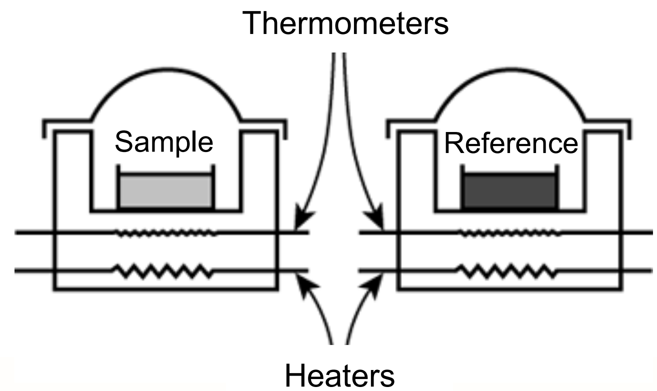
E. B. Moore, *et al.*, Nature **479**, 506 (2011).

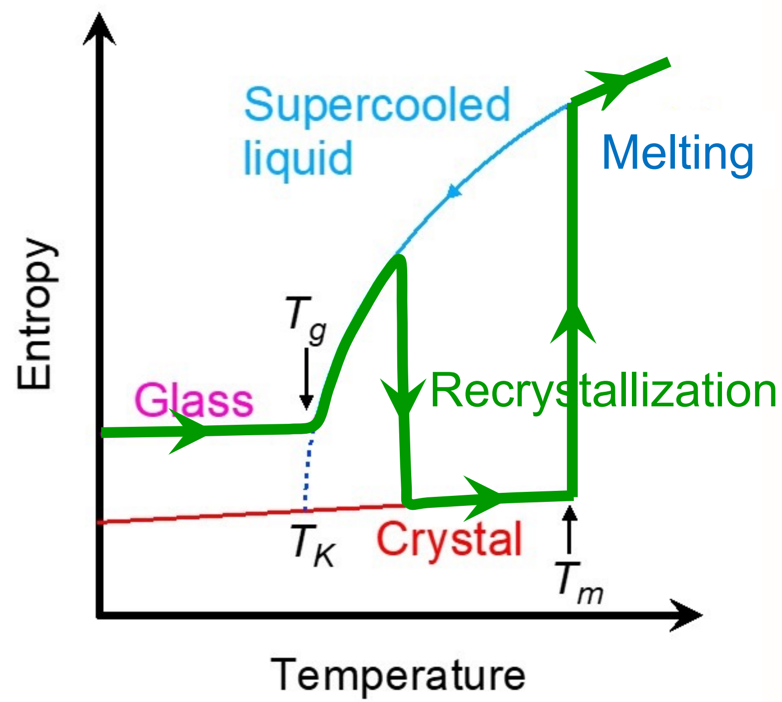
The dome-shaped TTT diagram is universally observed in other glass-forming liquids such as metallic glasses and water as well as θ_o-RbZn.

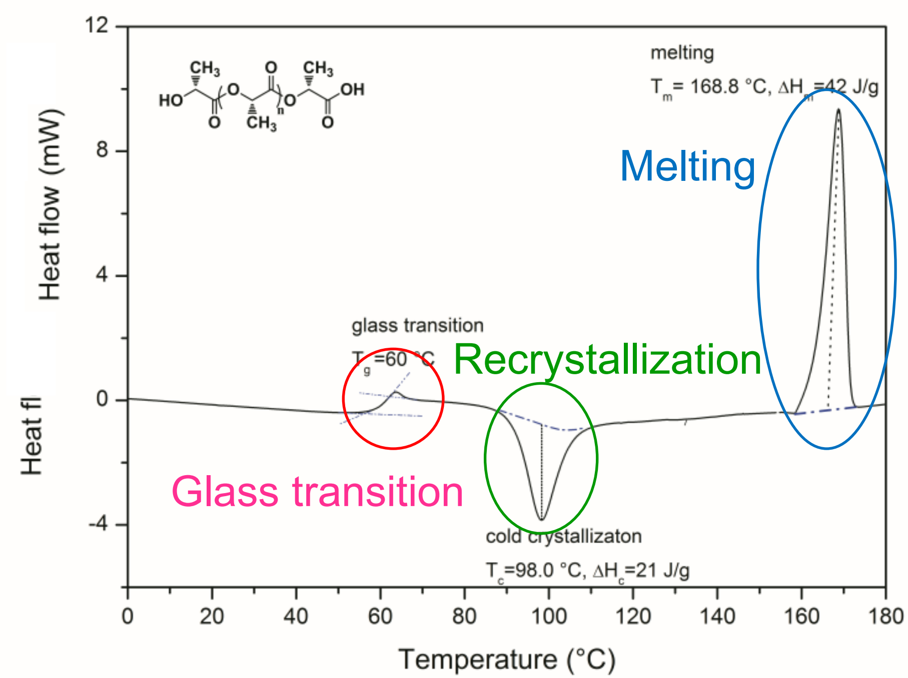
DSC is a very powerful probe to observe crystallization, melting, and glass transitions.

$$\Delta S(T) = \left(\int \underline{\Delta \dot{q}(T) dt} \right) / T$$

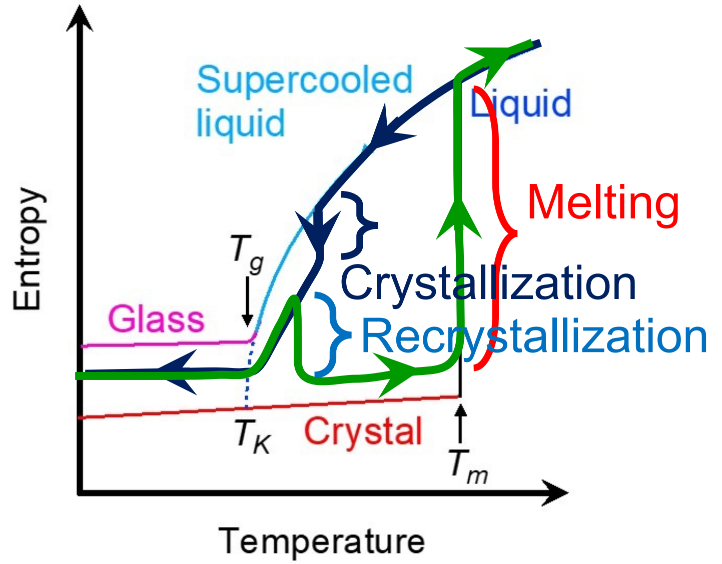
Heat flow







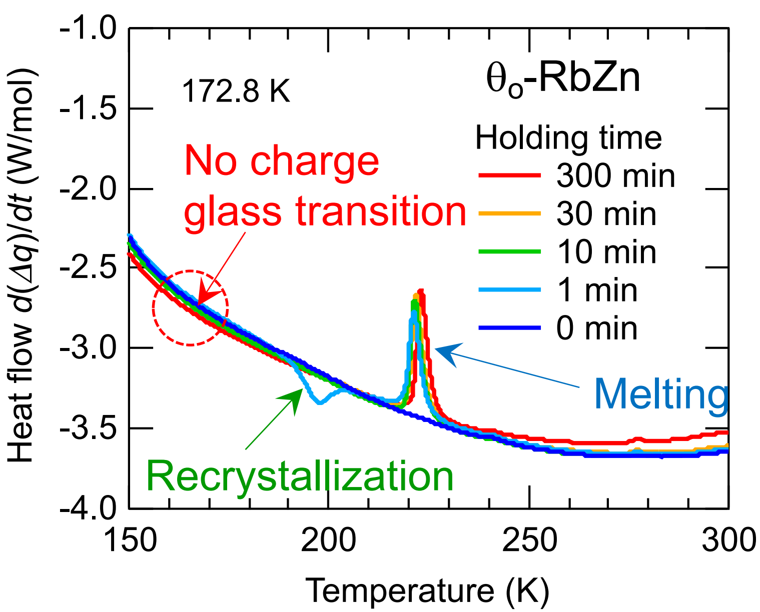
Results of DSC measurements



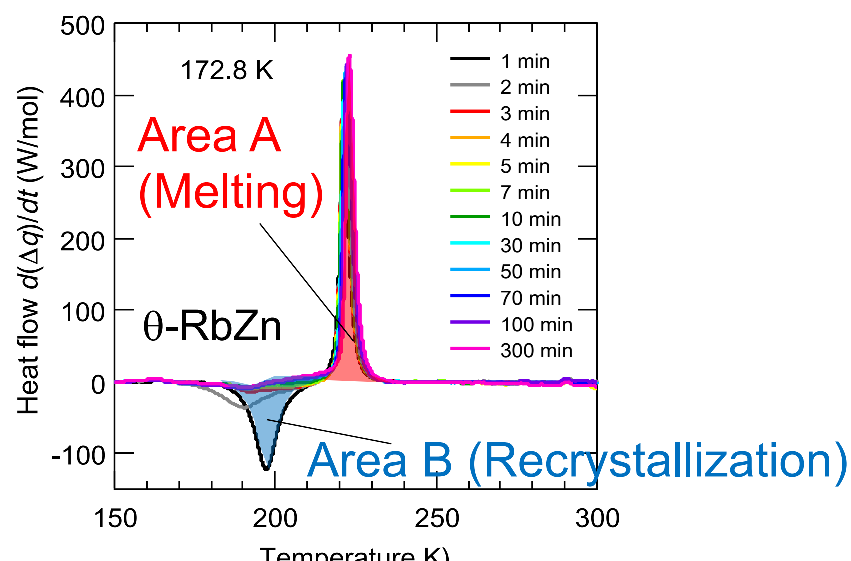
DSC-8500 (Perkin Elmer Corp.) at IMR, Tohoku Univ.
- N_2 liquid (Lowest temperature: 135 K)
- He gas atmosphere
- Cooling/heating rate: 100 K/min

$$\Delta H(T) = \int \Delta\dot{q}(T)dt$$

$$\Delta S = \Delta H/T$$



Entropy change Crystallization = Area A Melting – Area B Recrystallization



- No clear charge glass transition
- Clear charge recrystallization and melting

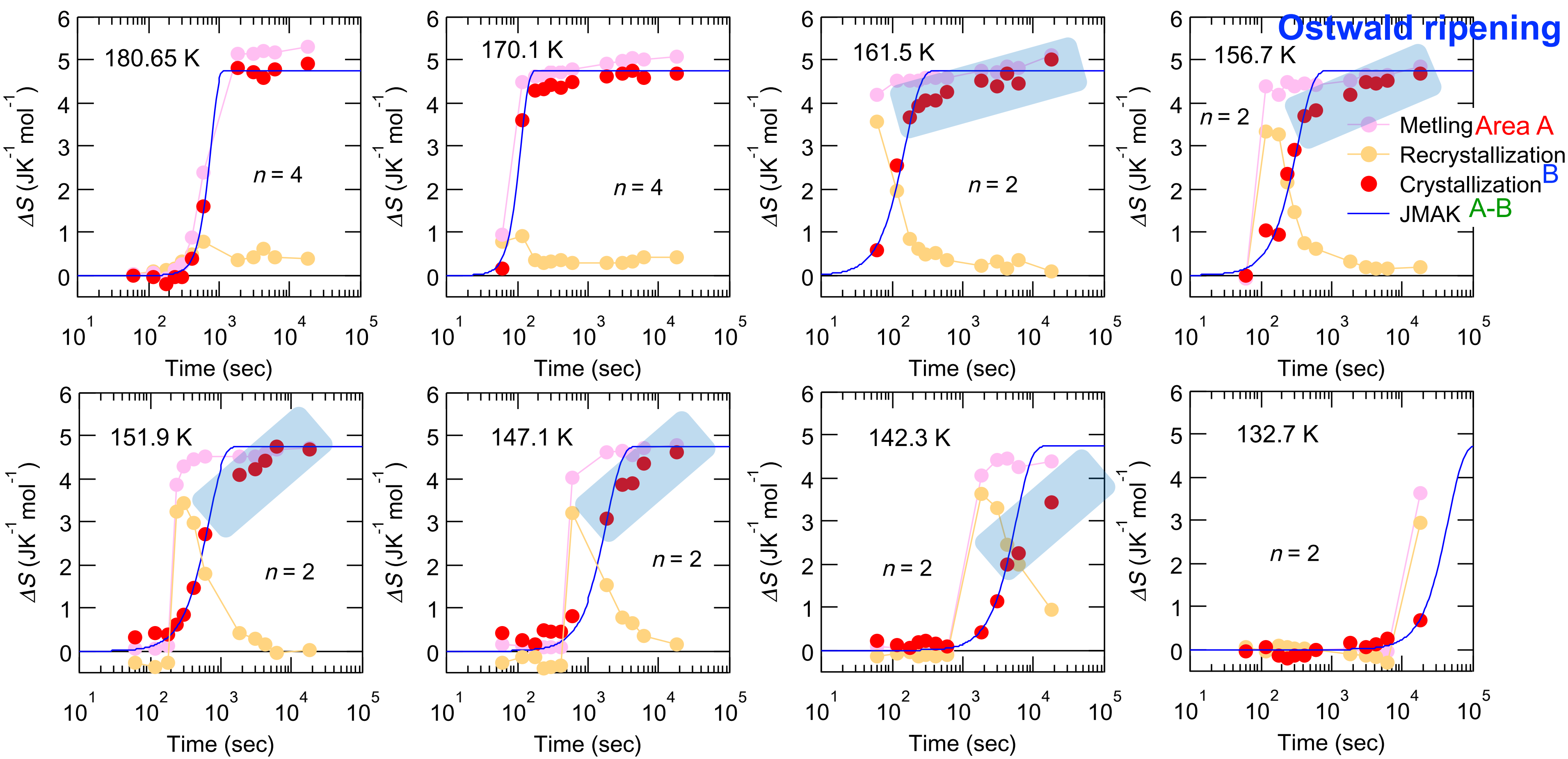
Time evolution of charge crystal growth

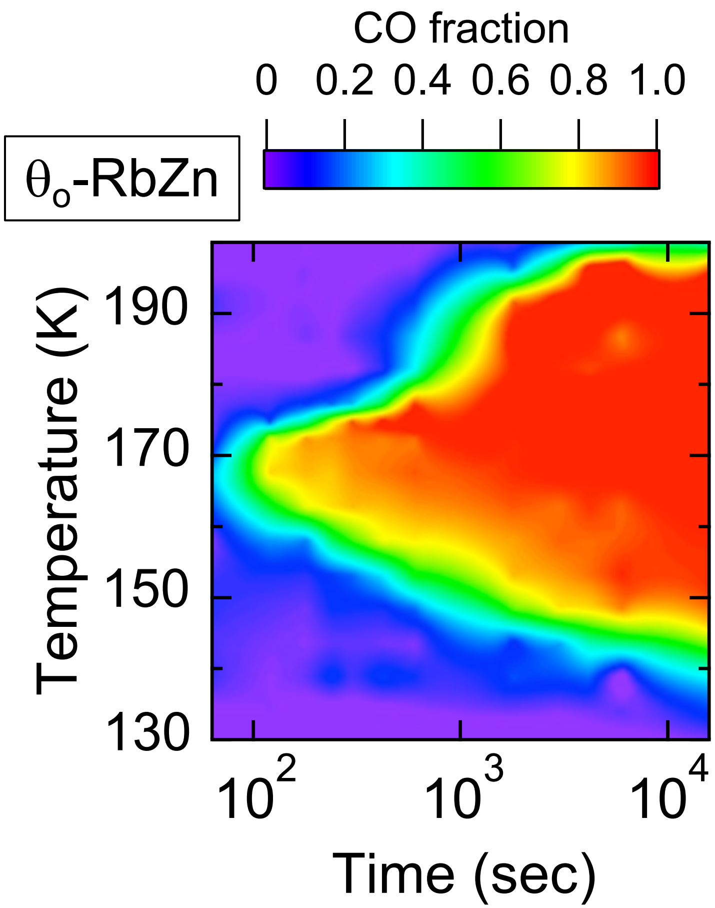
Johnson–Mehl–Avrami–Kolmogorov (JMAK) model

$\phi(t) = 1 - \exp(-bt^n)$ 3D: n = 3-4, 2D: n = 2-3, 1D: n = 1-2

- At high T, 3D crystal growth (n = 4)
- At low T, 1-2D crystal growth (n = 2)
  → Ostwald ripening

Consistent with the results of NMR T. Sato *et al.*, Science **357**, 1378 (2017).





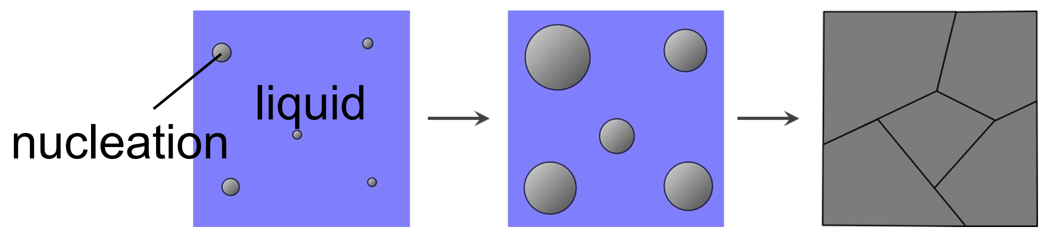
KH *et al.*, *in preparation*

JMAK model

$$\phi(t) = 1 - \exp(-bt^n)$$

3D: n = 3-4
2D: n = 2-3
1D: n = 1-2

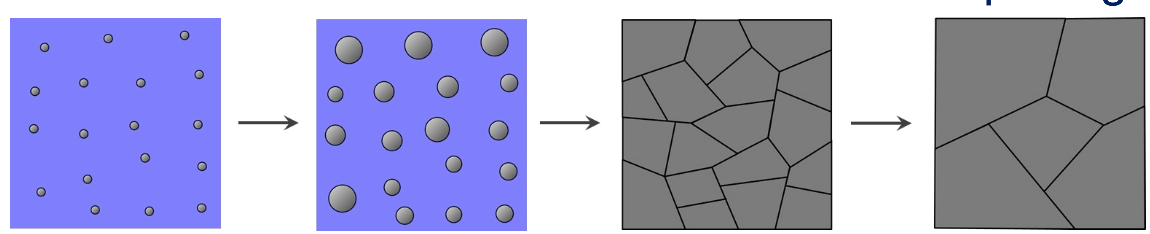
High T: Nucleus growth is dominant



n = 4   3D growth

Low T: Nucleation is dominant

Ostwald ripening



n = 2

1 or 2D growth + Ostwald ripening

Dome shaped TTT diagram constructed by thermodynamic quantity

1. Introduction

➢ Brief introduction of glass formation phenomena and charge liquid/crystal/glass states in θ-BEDT-TTF compounds

2. Comparison of CC and CG states in three different θ-type salts

➢ Resistivity and optical conductivity spectra in the orthorhombic and monoclinic systems

3. Charge crystallization process probed by thermodynamic quantity

➢ TTT diagram constructed by DSC measurements

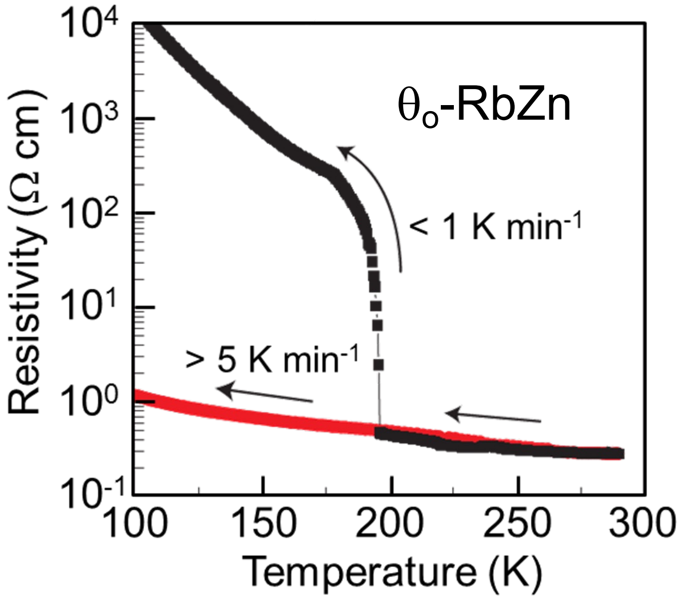
4. Randomness effects on charge crystallization and vitrification

➢ Reflectivity and DSC measurements for x-ray irradiated samples

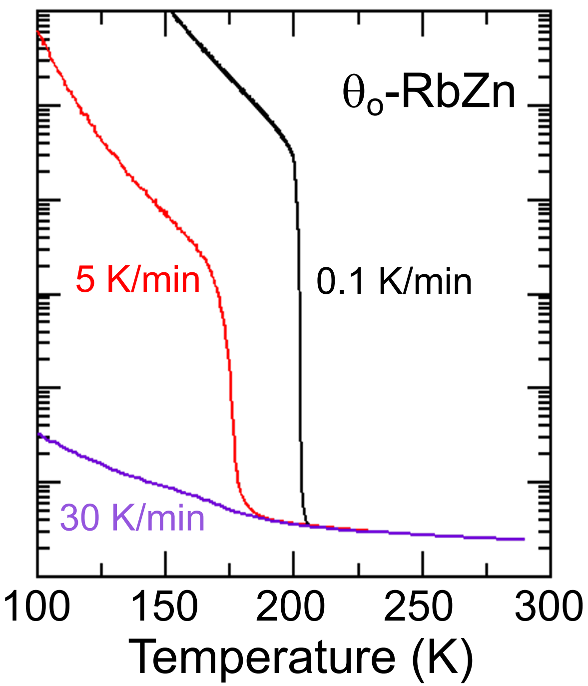
5. Summary

Large sample dependence in the charge glass forming ability

F. Kagawa *et al.*,
Nature Physics **9**, 2642 (2013)



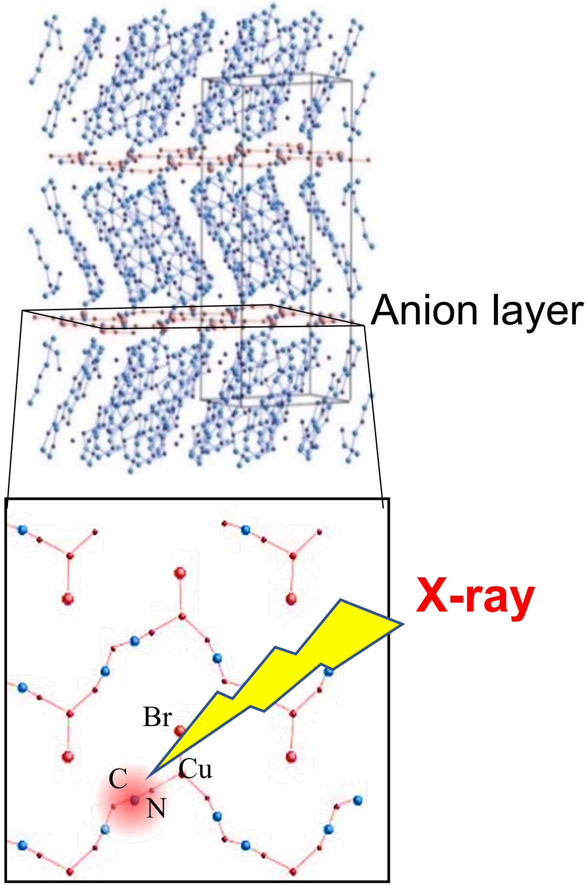
Our crystals (from Yamamoto Group
in the Institute for Molecular Science)



We examined how the randomness effect affects the charge-glass forming ability by using molecular defects introduced by x-ray irradiation.

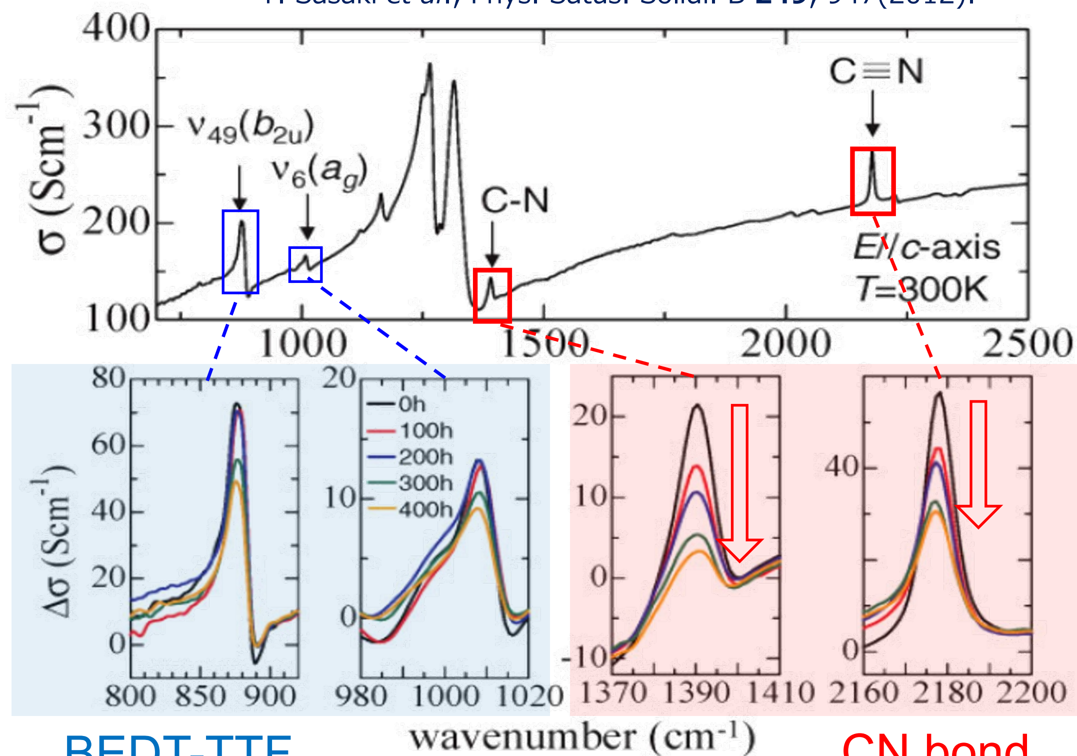
X-ray irradiation effect on κ-type compounds

κ-$(ET)_2Cu[N(CN)_2]Br$



Infrared molecular vibrations in κ-$(ET)_2Cu[N(CN)_2]Br$

T. Sasaki *et al.*, Phys. Satus. Solidi. B **249**, 947(2012).



BEDT-TTF
Small suppressions

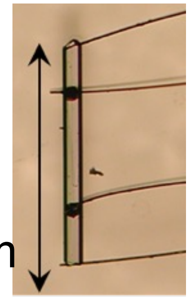
CN bond
Large suppressions

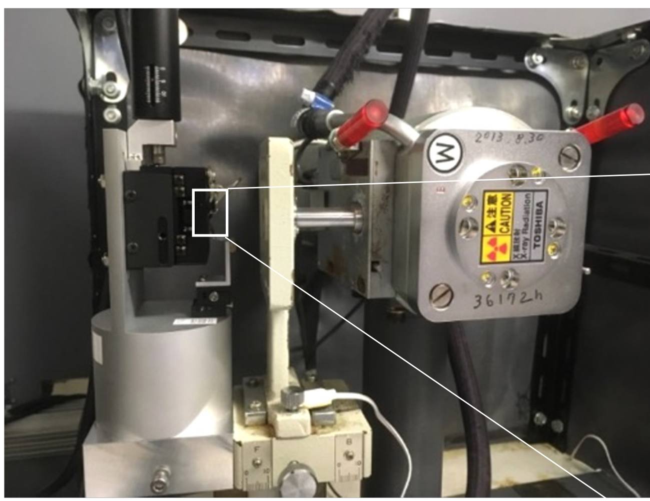
Defects are mainly introduced within the anion layers (CN bonds).

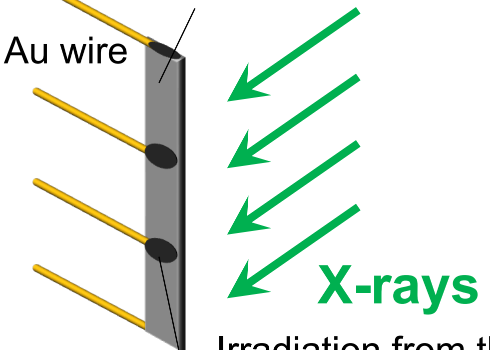
➡ X-ray irradiation does not largely affect the physical properties of π electrons such as charge carriers.

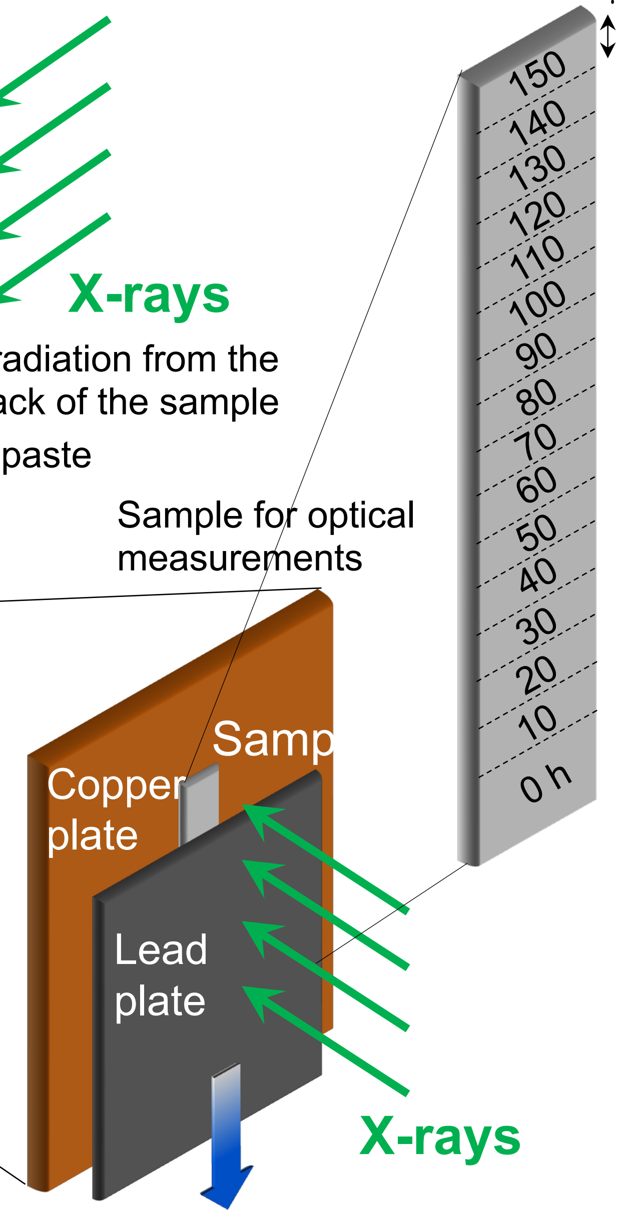
Experimental setup

- θ-$(ET)_2RbZn(SCN)_4$ single crystals
  - Electrochemical redox method
  - Provided by S. Suda and H. Yamamoto
- X-ray irradiation
  - Room temperature
  - Tungsten tube (non-filtered, 40 kV, 20 mA)
  - White x-rays





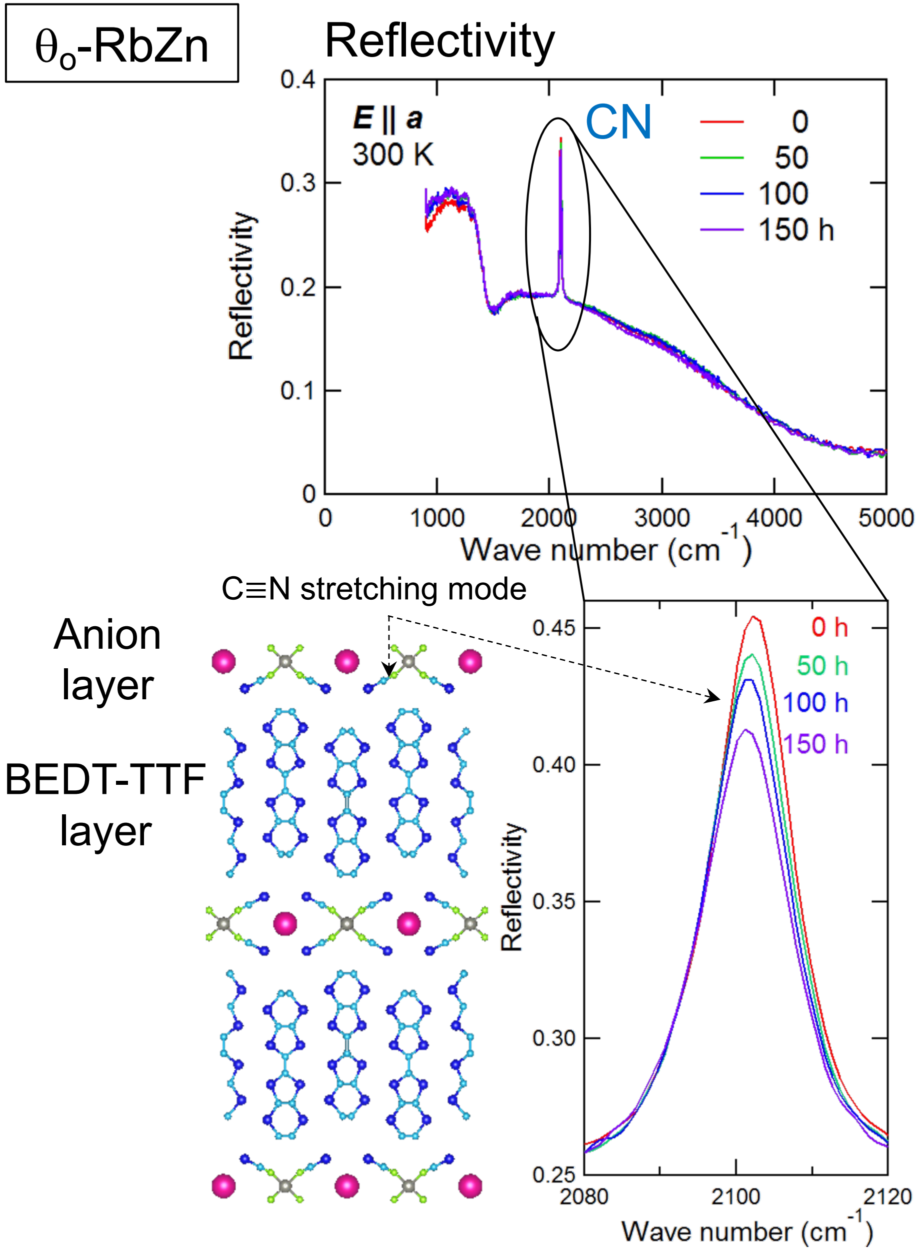


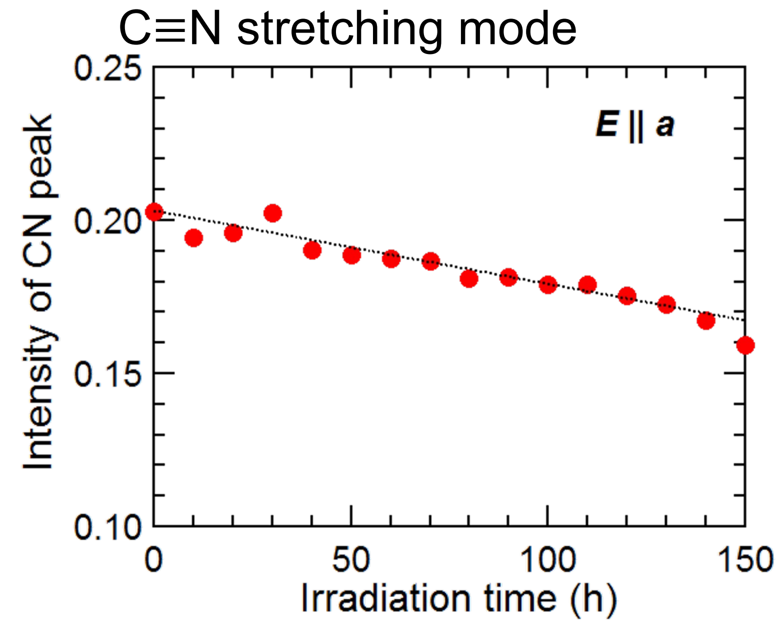


- Experiments
  - Resistivity
  - Optical conductivity
  - Differential scanning calorimetry (DSC)

Molecular defect by x-ray irradiation in θ_o-RbZn

θ_o-RbZn





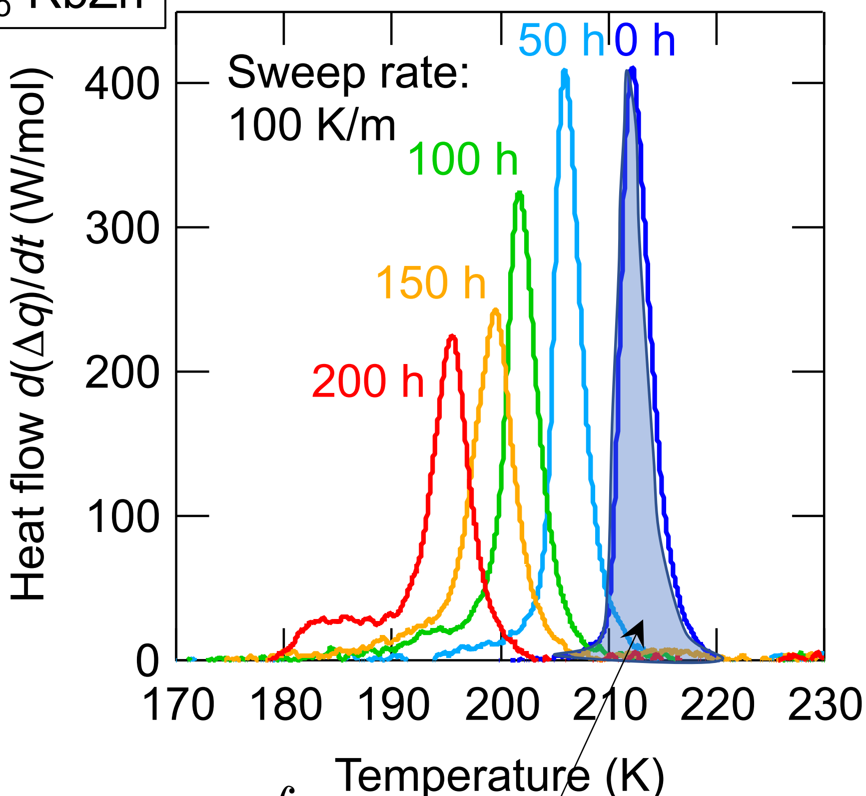
Reduction by 15% after 150 h irradiation

Defects are mainly introduced within the anion layers (CN bonds).

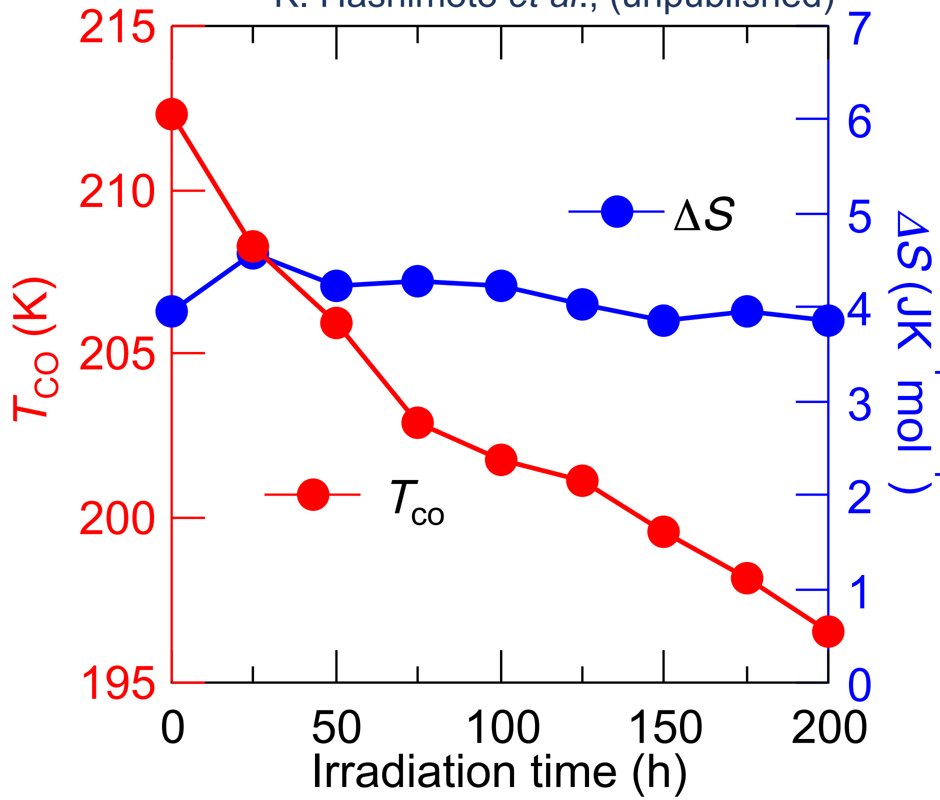
X-ray irradiation effects on T_{CO} and entropy change

- T_{CO} is systematically suppressed by x-ray irradiation.
- Almost no change in the total entropy at the CO transition

θ_o-RbZn



K. Hashimoto *et al.*, (unpublished)



$$\Delta H(T) = \int \Delta\dot{q}(T)dt$$

$$\Delta S = \Delta H / T$$

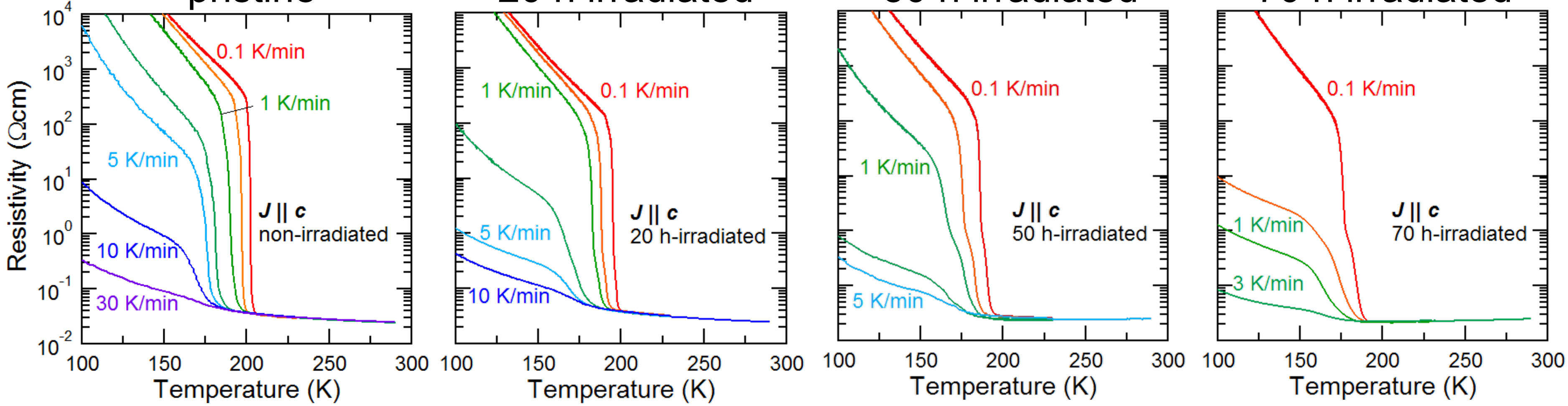
The entropy change at CO is obtained by integrating the heat flow over time and divided by T_{CO}.

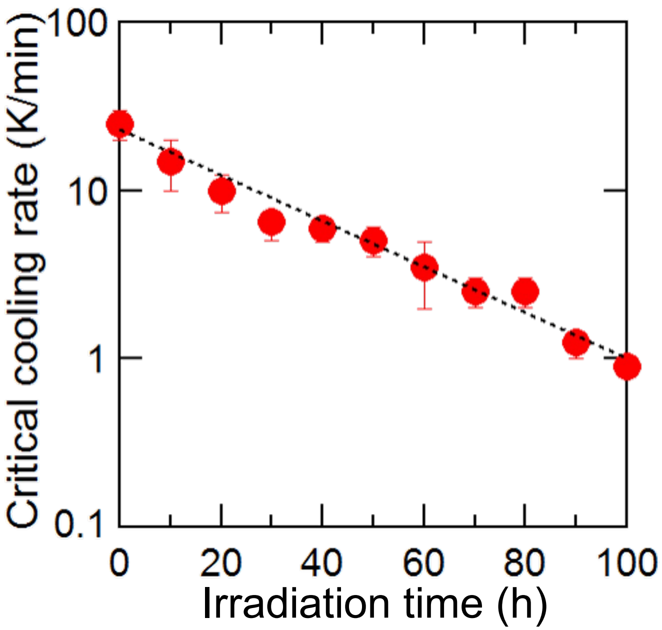
The molecular defects introduced by x-ray irradiation act as impurities.

X-ray irradiation effect on the critical cooling rate

Cooling-rate dependence of the resistivity curve

pristine | 20 h irradiated | 50 h irradiated | 70 h irradiated

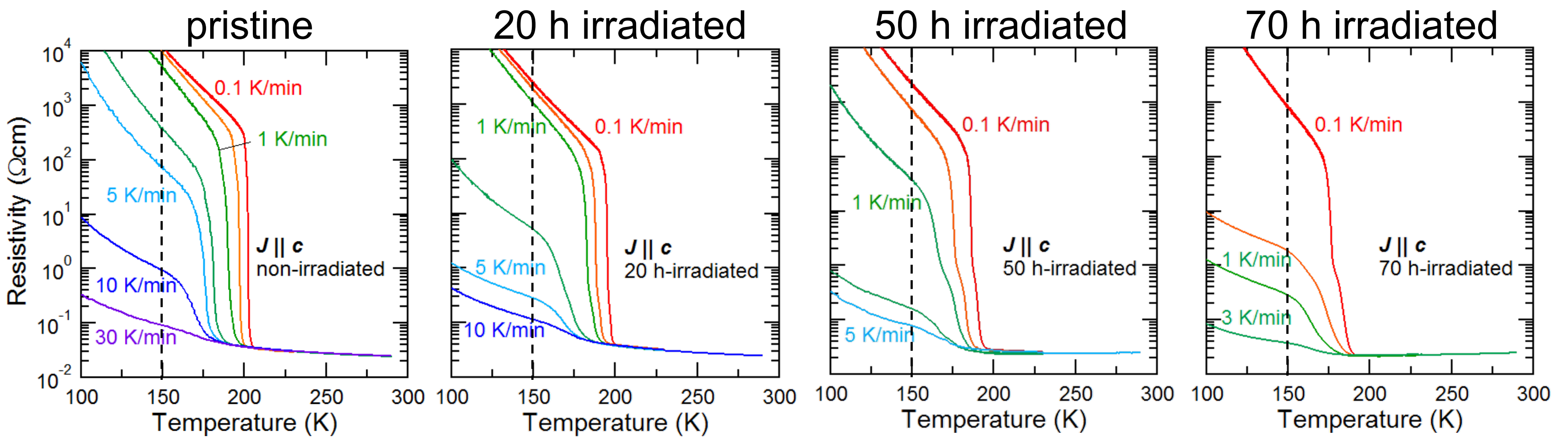


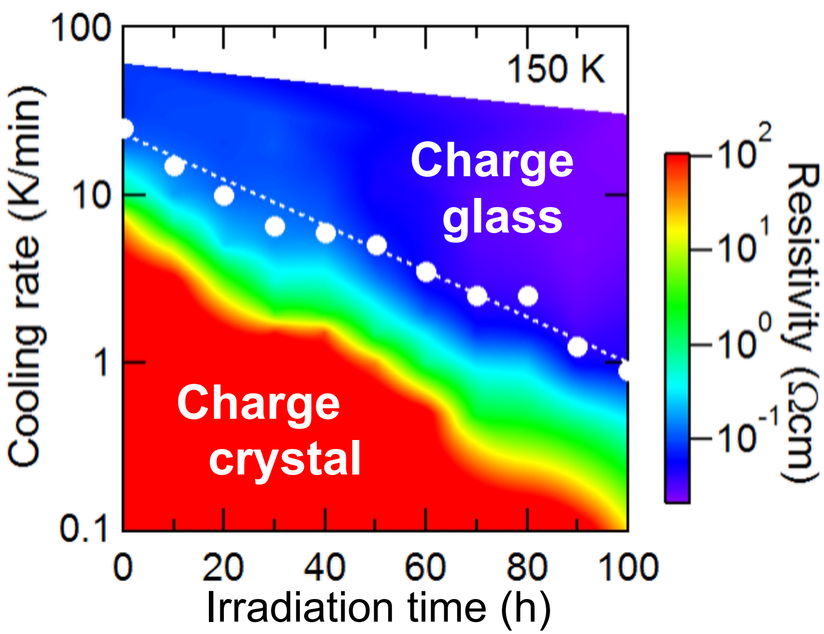


The critical cooling rate for the charge glass formation becomes slower with increasing x-ray irradiation time.

X-ray irradiation effect on the critical cooling rate

Cooling-rate dependence of the resistivity curve



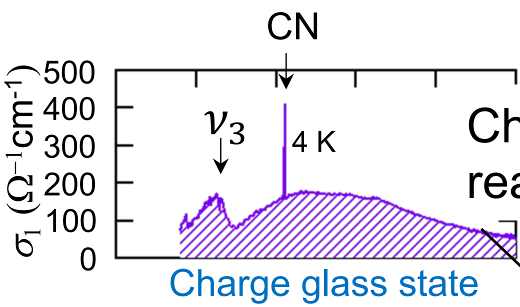


The critical cooling rate for the charge glass formation becomes slower with increasing x-ray irradiation time.

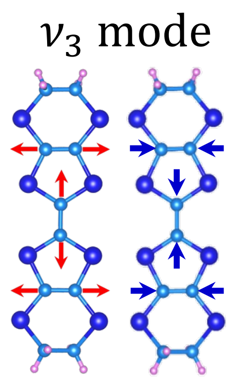
↓

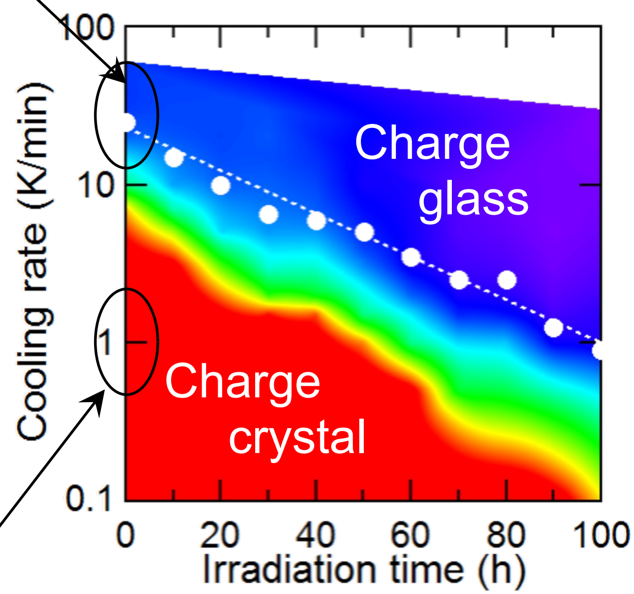
The charge crystal regime is significantly suppressed by randomness introduced by x-rays

X-ray irradiation effect on optical conductivity spectra

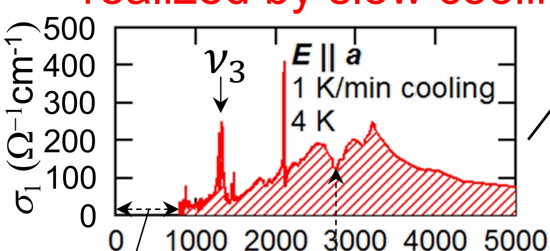


Charge glass state
realized by rapid cooling





Charge crystal state
realized by slow cooling



Optical gap

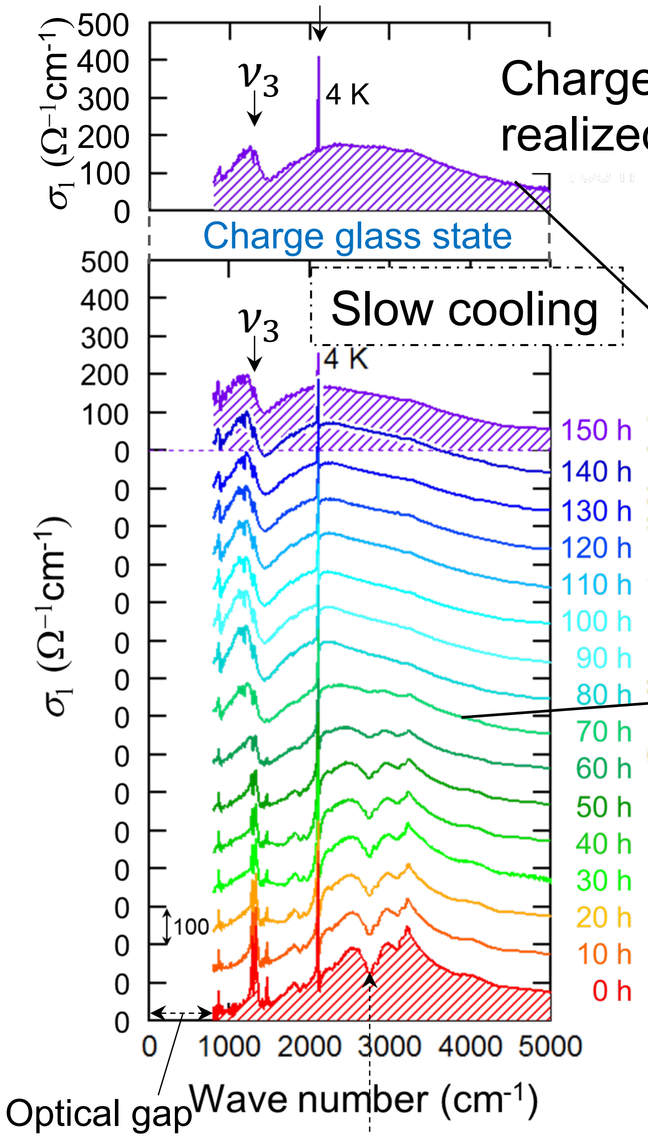
Overtone of ν_3 mode (2ω)

Features of CO state

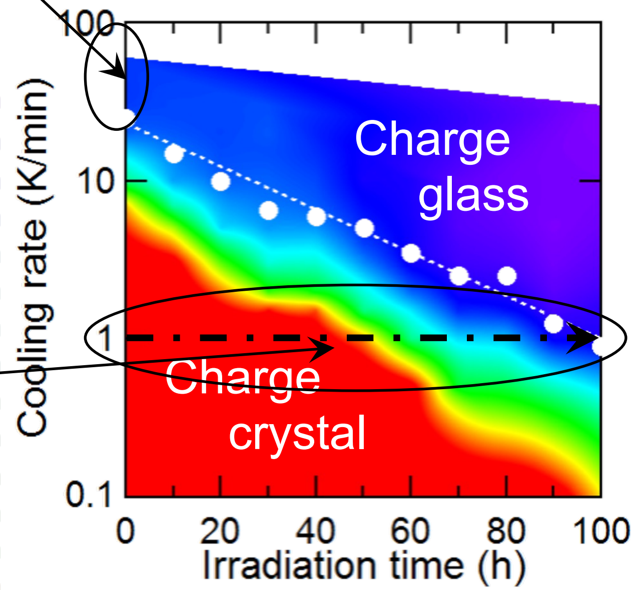
- Clear optical gap
- Sharpening of ν_3 mode
- Overtone of ν_3 mode

K. Yamamoto *et al.*, PRB **84**, 064306 (2011).

X-ray irradiation effect on optical conductivity spectra



Charge glass state realized by rapid cooling



Overtone of ν_3 mode (2ω)

Features of CO state

- Clear optical gap
- Sharpening of ν_3 mode
- Overtone of ν_3 mode

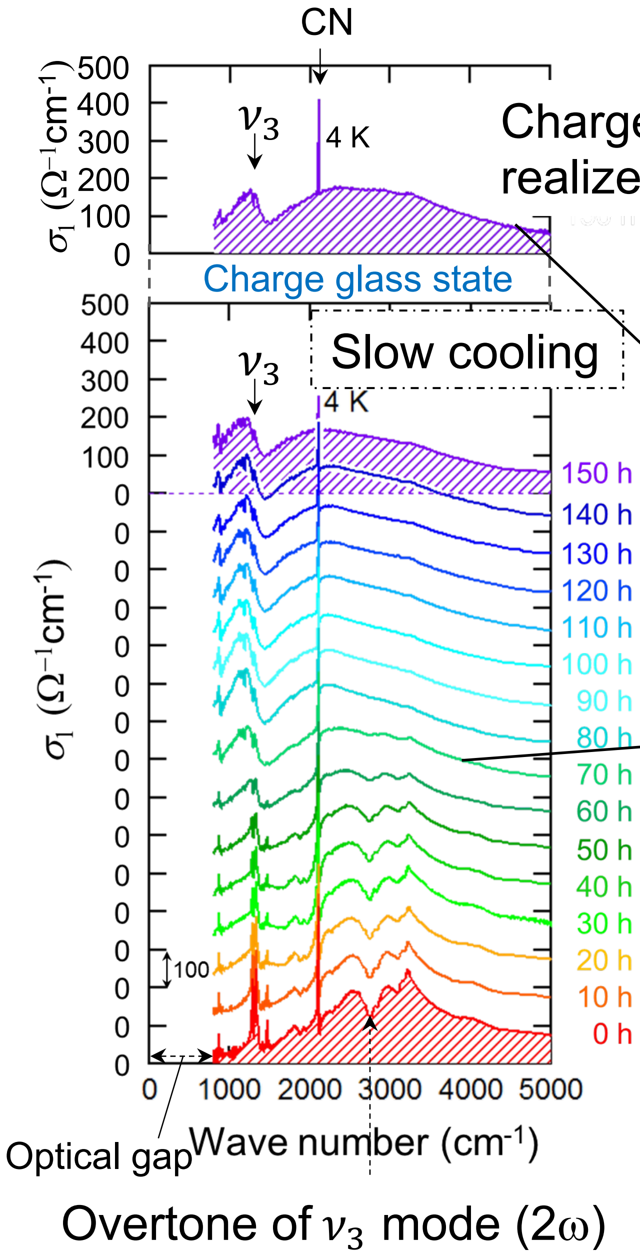
K. Yamamoto *et al.*, PRB **84**, 064306 (2011).

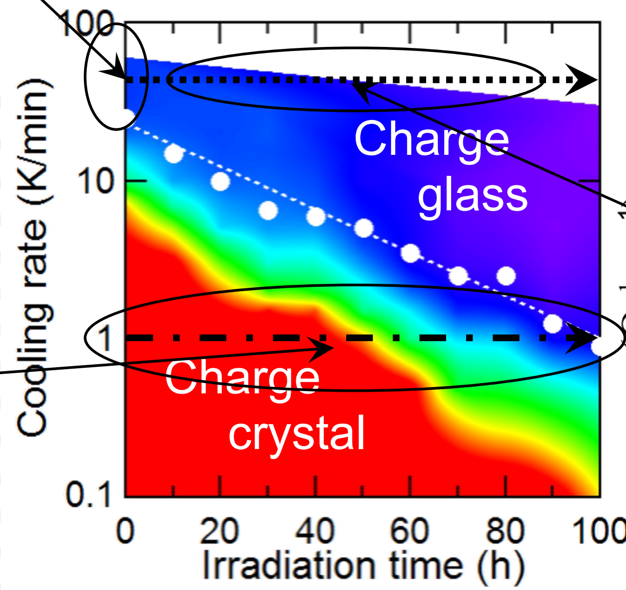
X-ray irradiation effect on the optical conductivity spectra

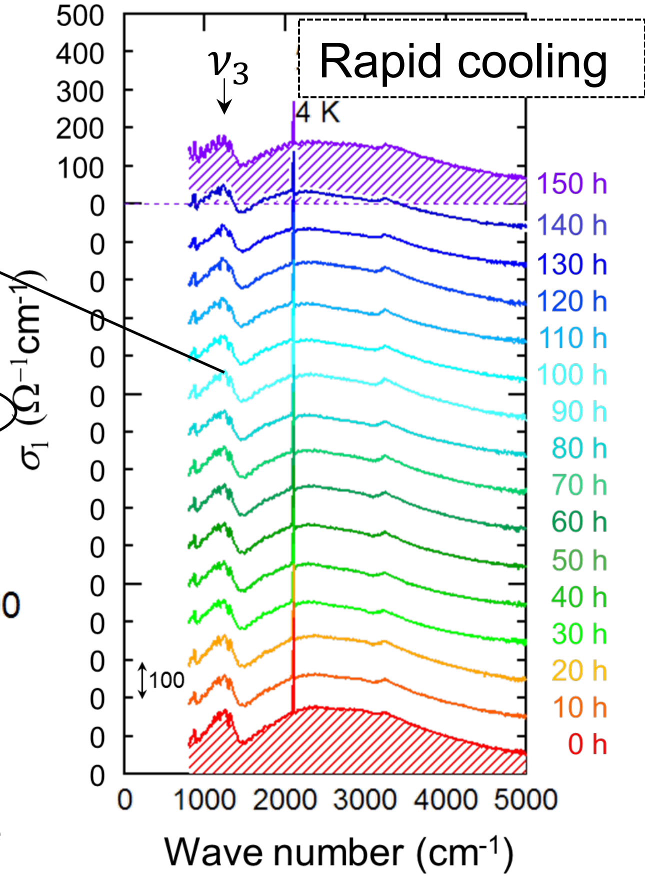
Charge glass state realized by rapid cooling

Very similar

Charge glass state realized by x-rays







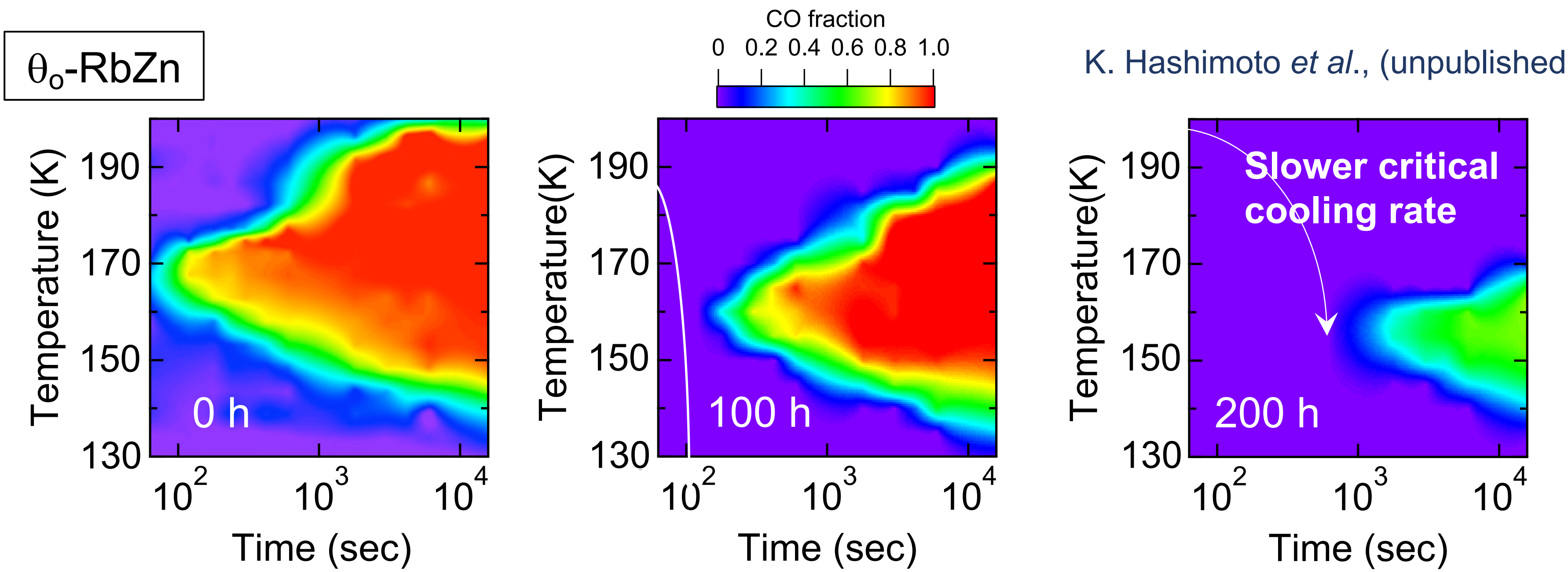
Features of CO state

- Clear optical gap
- Sharpening of ν_3 mode
- Overtone of ν_3 mode

K. Yamamoto *et al.*, PRB **84**, 064306 (2011).

X-ray irradiation effect on TTT diagrams

TTT diagram conducted by DSC measurements



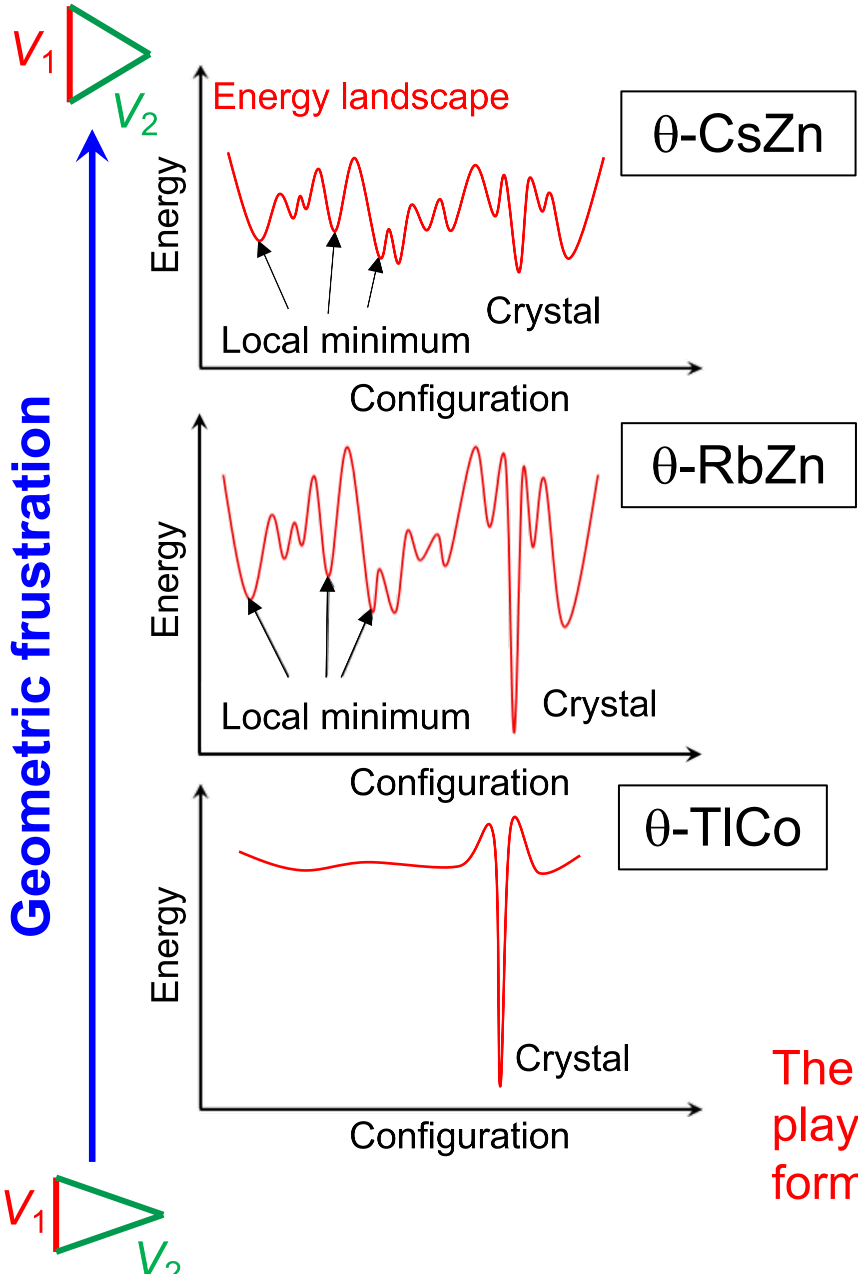
- The charge crystallization regime shifts to a longer-time region.
- The nose temperature decreases.

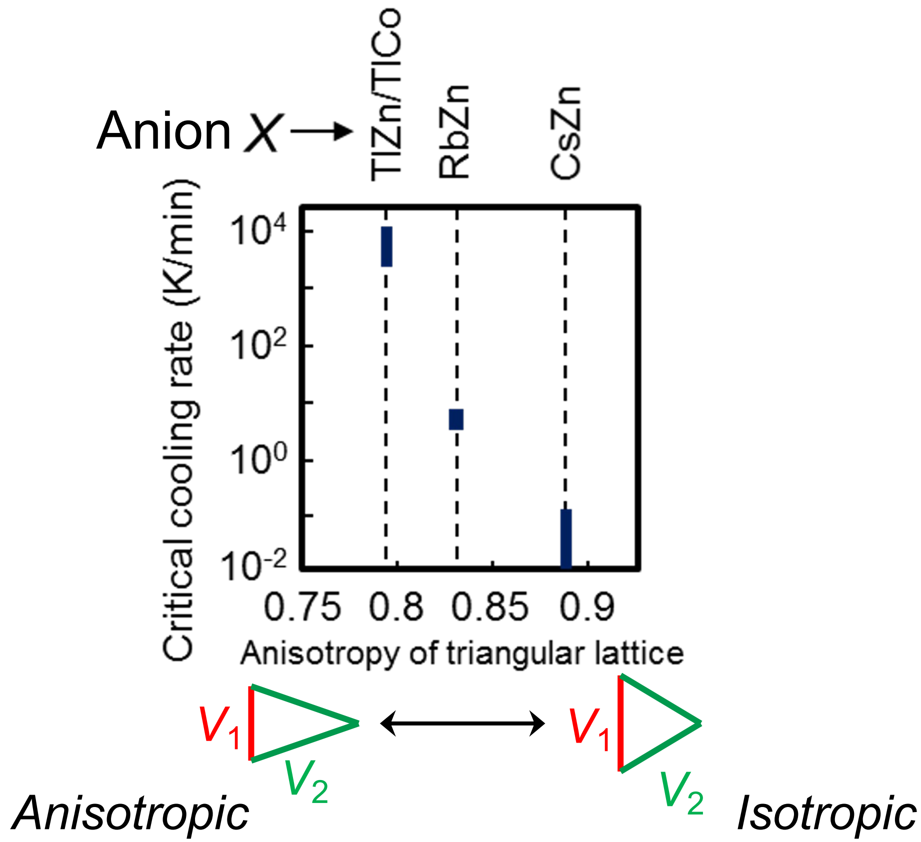
Charge crystallization is significantly suppressed by x-ray irradiation, which leads to a slower critical cooling rate compared to that of the pristine sample.

➢ Even in θ_o-RbZn, one can make a charge glass state in a very slow cooling rate.

Energy landscape

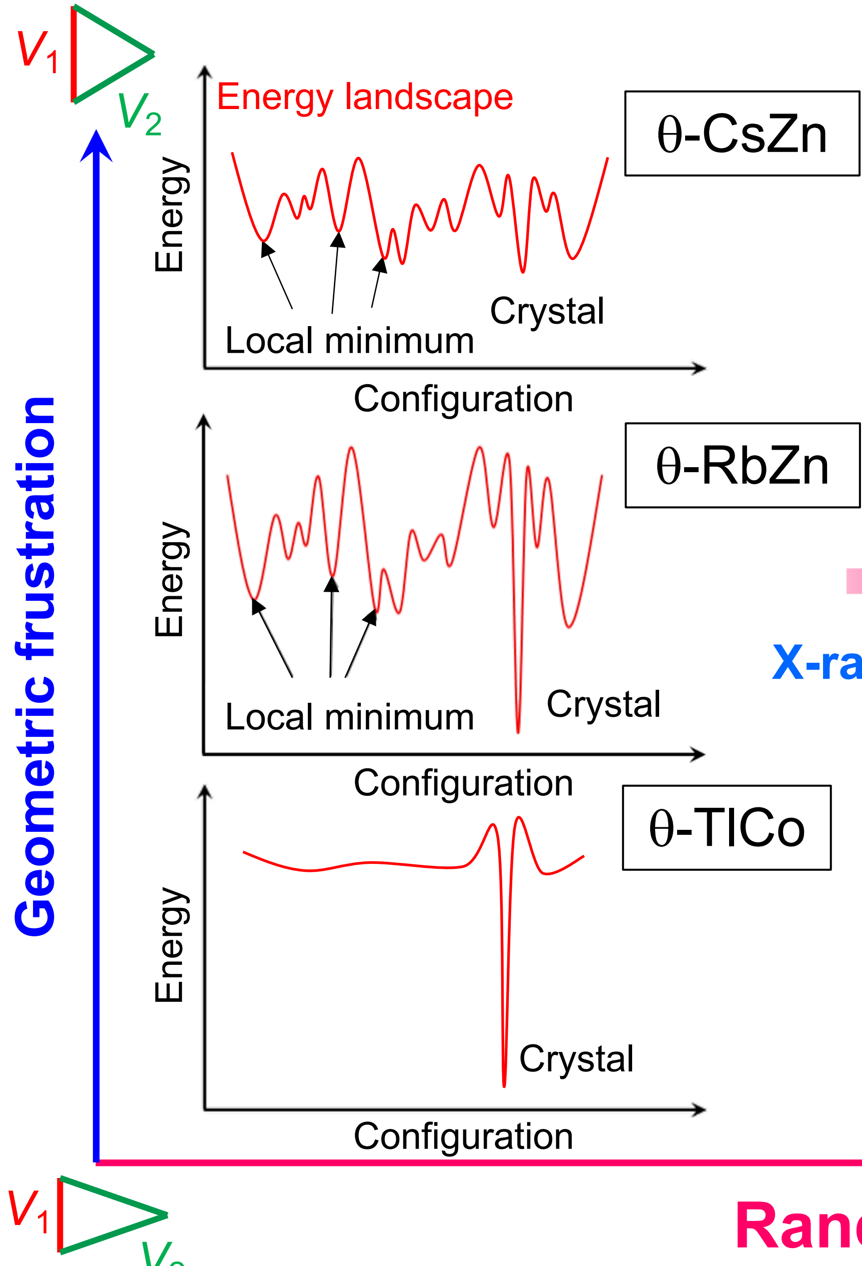
T. Sato *et al*., JPSJ **83**, 083602 (2014).
H. Oike *et al*., PRB **91**, 041101 (2015).





The geometrical frustration of the triangular lattice plays an important role for the charge glass formation in this system.

Energy landscape

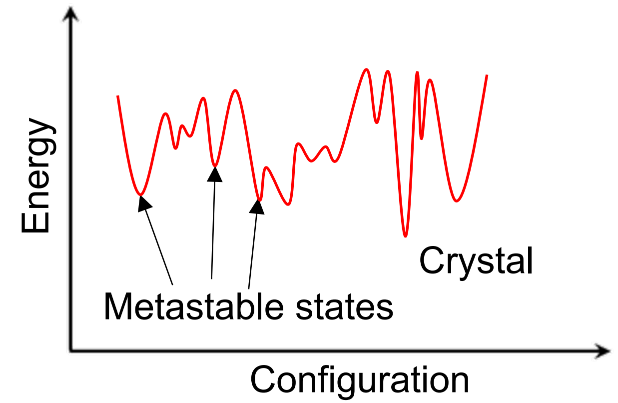


X-rays promotes charge glass formation.

The energy difference between the crystalline state and the metastable states may be reduced.

X-ray irradiated θ-RbZn

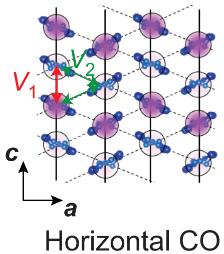
X-ray irradiation



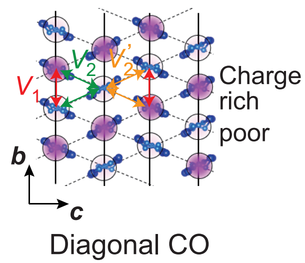
In addition to the geometric frustration, randomness is also an important factor for the charge glass formation.

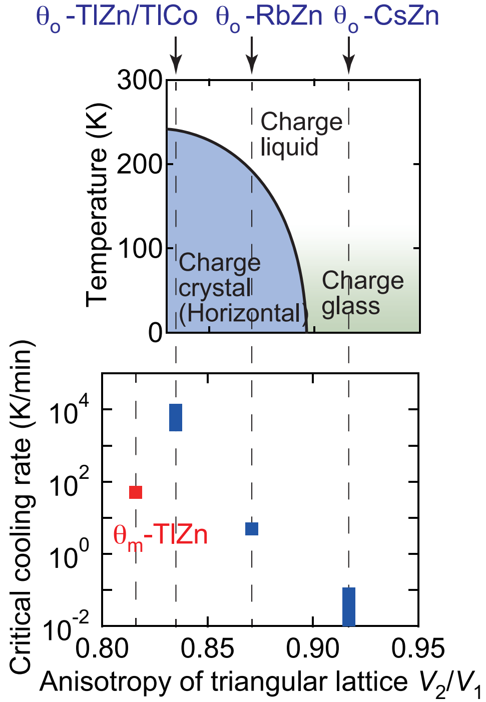
Summary

θo-type



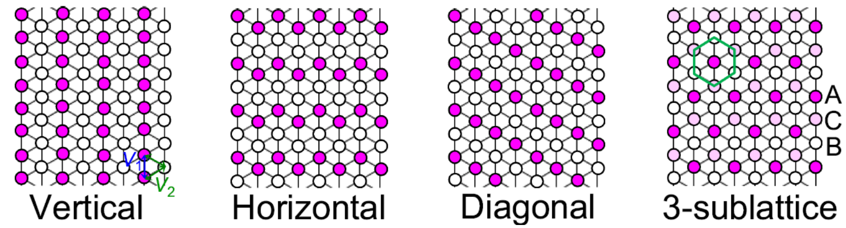
θm-type





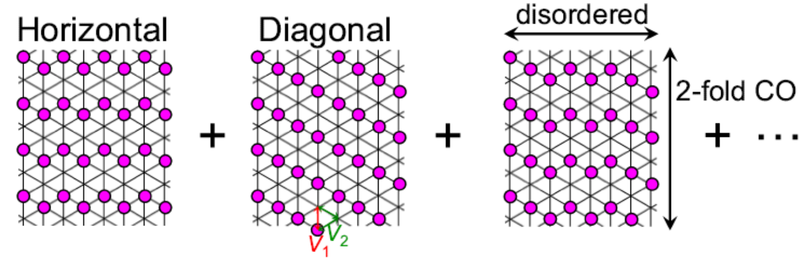
θo-type

Metallic 3-fold COs



θm-type

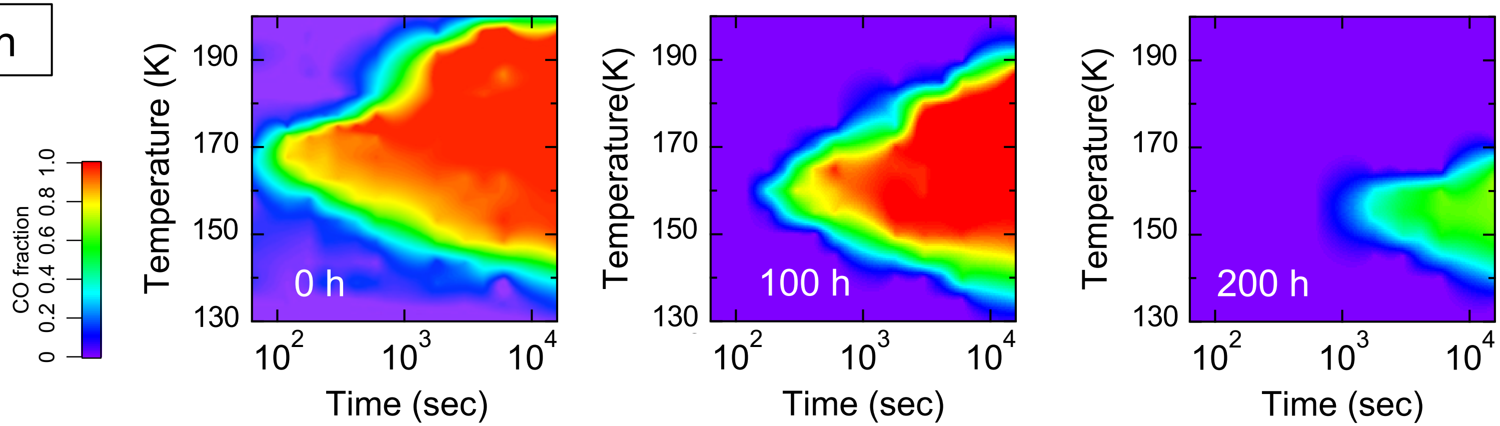
Insulating 2-fold COs



Different charge-glass formation mechanisms in the orthorhombic and monoclinic systems.

TTT diagram conducted by DSC

θ_o-RbZn



Randomness effect is also an important factor for the charge glass formation.