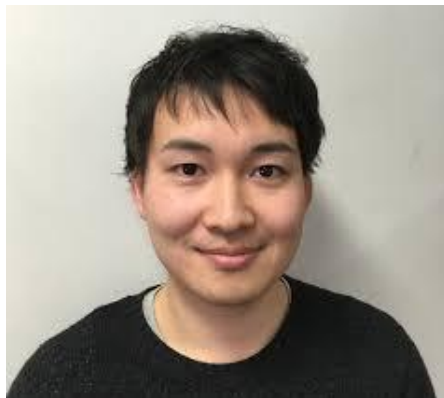


Study of the structural and electronic property of excitonic insulators Ta_2NiSe_5 and TiSe_2

Hiroshi Sawa
Nagoya Univ., Japan



Akihito Nakano
Faculty of Science

Shunsuke Kitou
D3 in our Lab.



Collaborators

Nagoya Univ.

Akihito Nakano,
Shunsuke Kitou,
Naoyuki Katayama

Physical properties under pressure

Univ. of Electro-Communications
ISSP

Kazuyuki Matsubayashi
Taku Okada, Yoshiya Uwatoko

Synchrotron X-ray experiments

CROSS
Photon Factory, IMSS, KEK
JASRI (SPring-8)
SRRC, QST

Kouji Munakata, Akiko Nakano
Hajime Sagayama, Reiji Kumai
Kunihisa Sugimoto, Satoshi Tsutsui
Naoyuki Maejima, Akihiko Machida,
Tetsu Watanuki

DFT calculation

Hiroshima Univ.

Takumi Hasegawa

Theoretical discussions

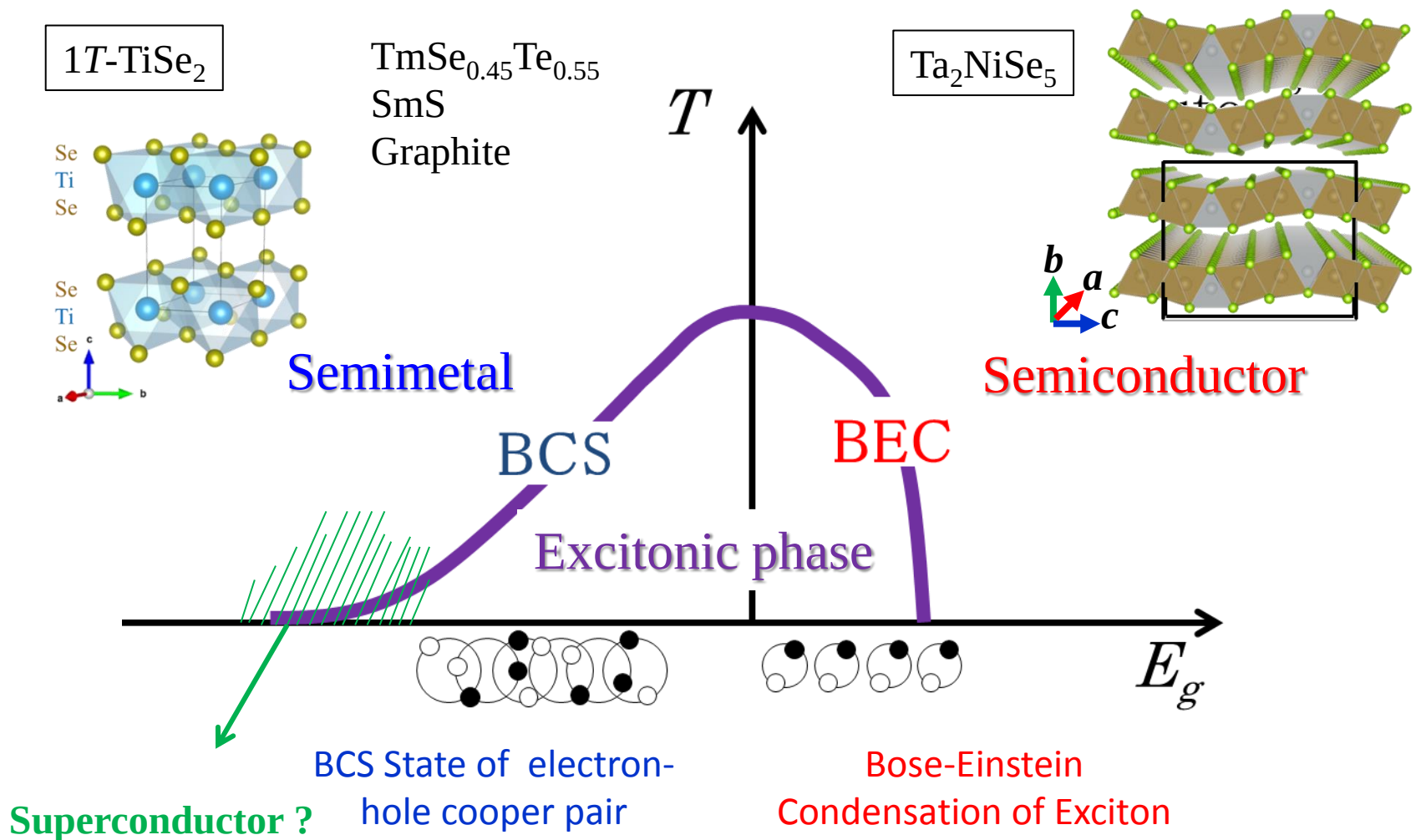
Chiba Univ.
Columbia Univ.

Yukinori Ohta
Tatsuya Kaneko

Outline

- Phase Diagram of Excitonic Insulator
- Structure transition of TiSe_2
 - Charge Density Wave $\sim$ band filling control
- Structural study of Ta_2NiSe_5
- Universality?

BCS-BEC crossover



W. Kohn, *Phys. Rev. Lett.* **19**, 439 (1967).

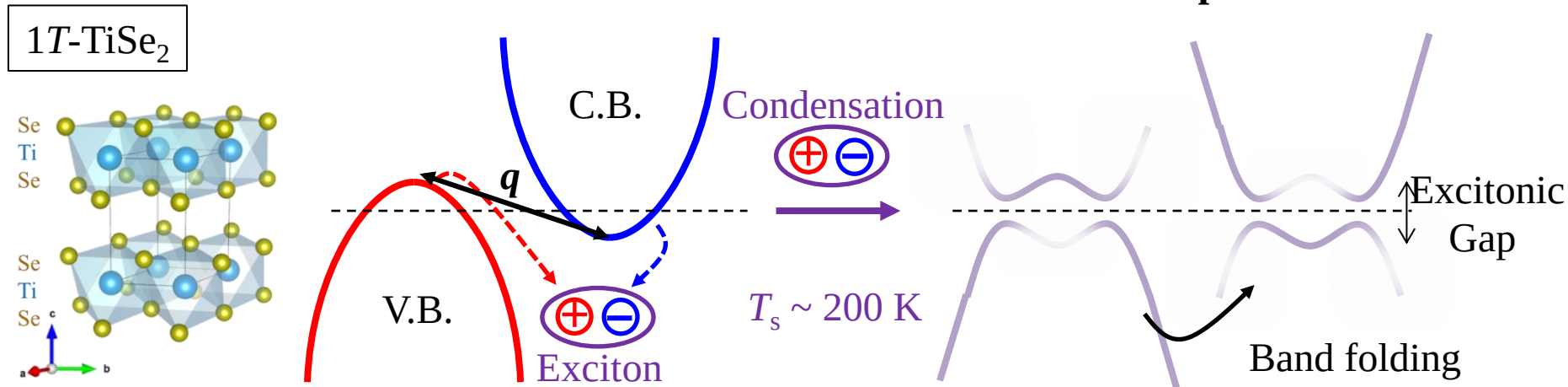
P. Bhattacharyya and S. S. Jha, *J. Phys. C: Solid State Phys.* **11**, 805 (1978).

V. Phan, et al., *Phys. Rev.* **B 81**, 205117 (2010).

Candidate compound of Excitonic insulator

Candidate compound... $\text{TmSe}_{0.45}\text{Te}_{0.55}$, SmS (under high pressure)
graphite (under strong magnetic field)

1T-TiSe_2 ... Excitonic CDW at 200 K ?



Th. Pillo, et al., *Phys. Rev. B* **61**, 16213 (2000).

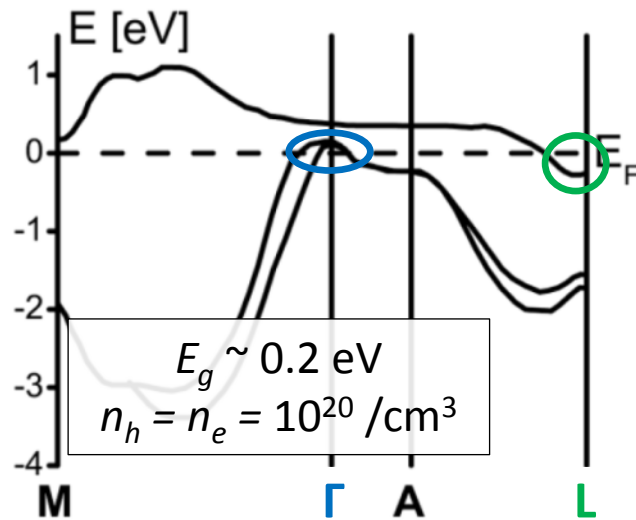
Other “phononic” mechanisms have been proposed...
(CDW^[1], band – type Jahn Teller^[2])

[1] H. P. Hughes, *J. Phys. C: Solid State Phys.* 10, L319 (1977).

[2] R. M. White *et al.*, *Il Nuovo Cimento B* 38, 280 (1977).

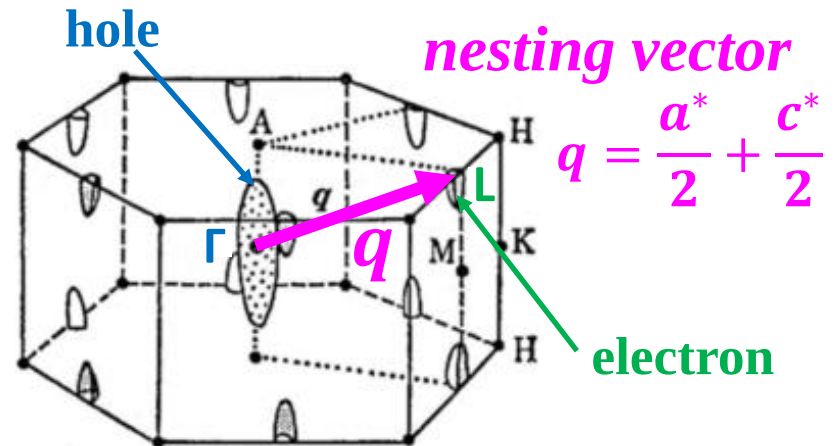
Electronic structure of 1T-TiSe₂

Semimetallic Band Structure



Julia C. E. Rasch *et al.*, PRL **101**, 237602 (2008).

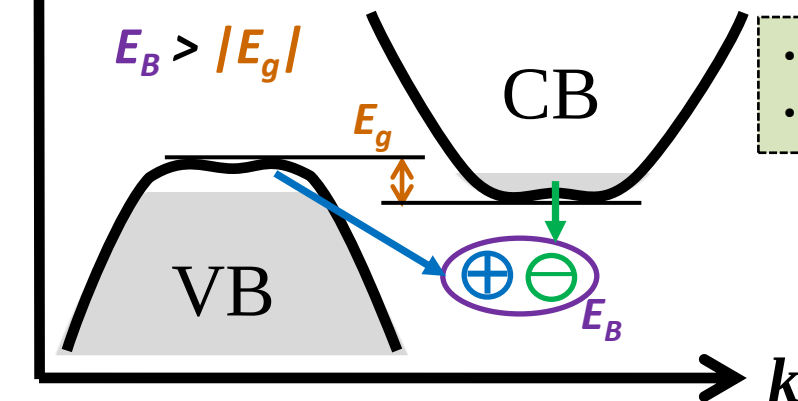
Brillouin Zone Layout



A. Zunger, A.J. Freeman, PRB **17**, 1839 (1978).

- ✓ 3D FS
- ✓ electron FS size $\neq$ hole FS size
- Unlikely CDW induced by nesting

- Excitonic Interaction -



- small carrier density
- small screening effect

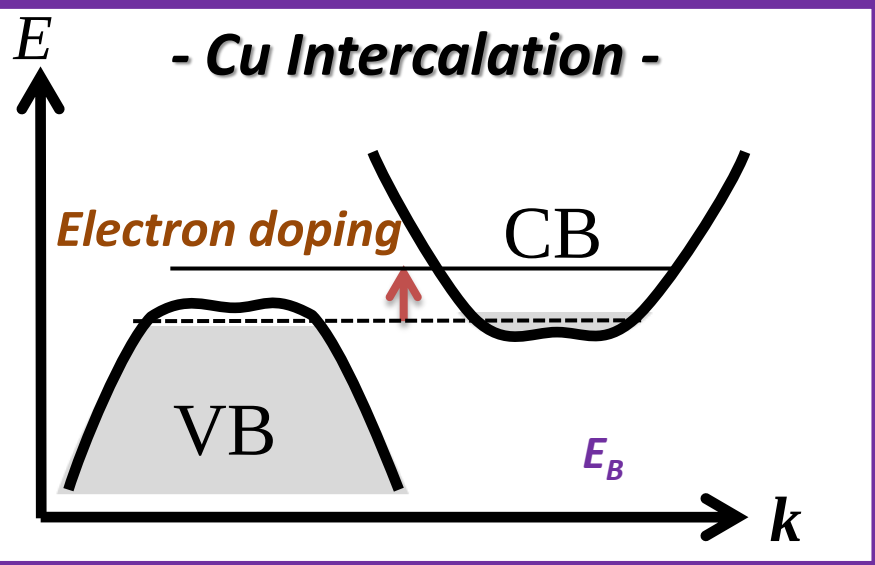
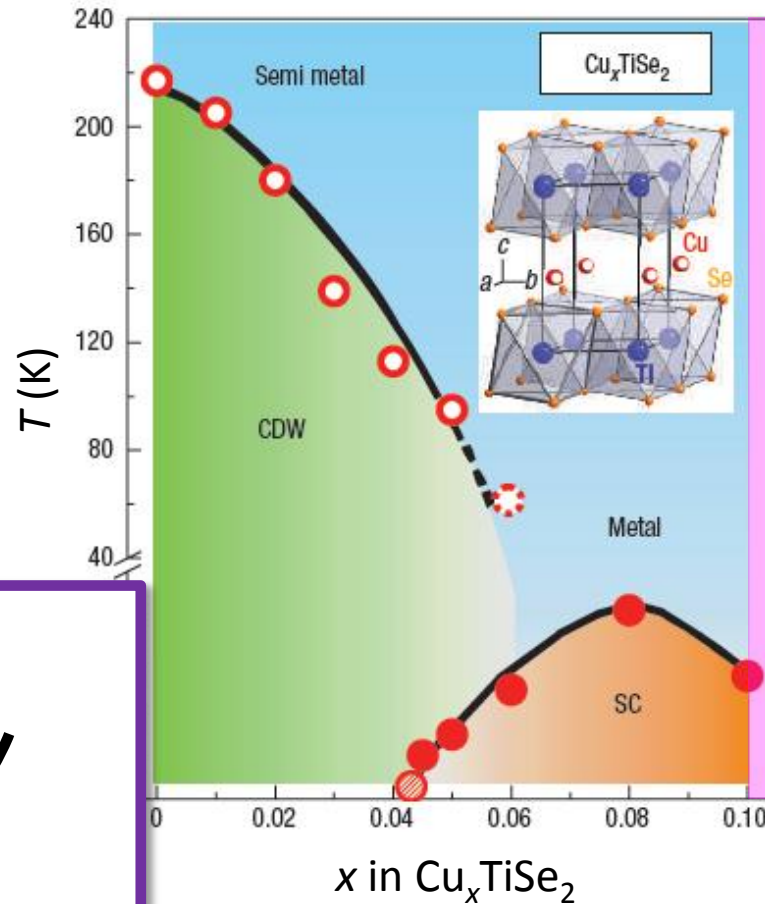
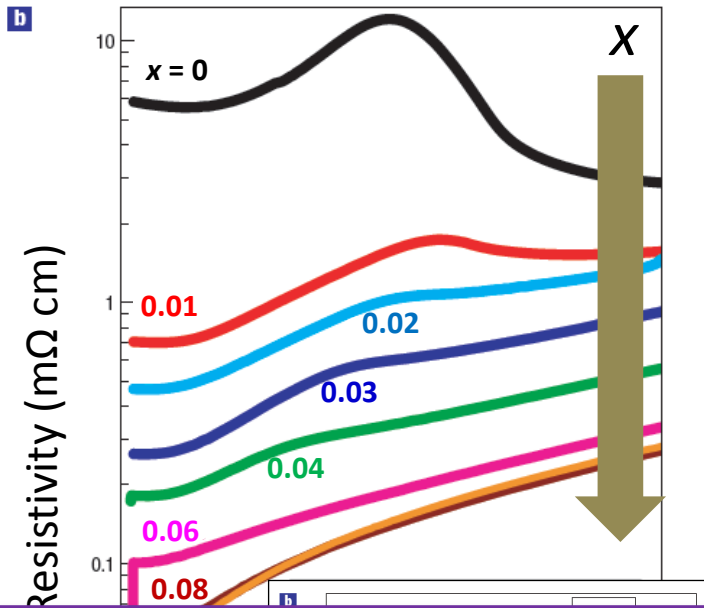
“Electron-Phonon Coupling”

and/or

“Electron-Hole (Excitonic) Interaction”
 are important!

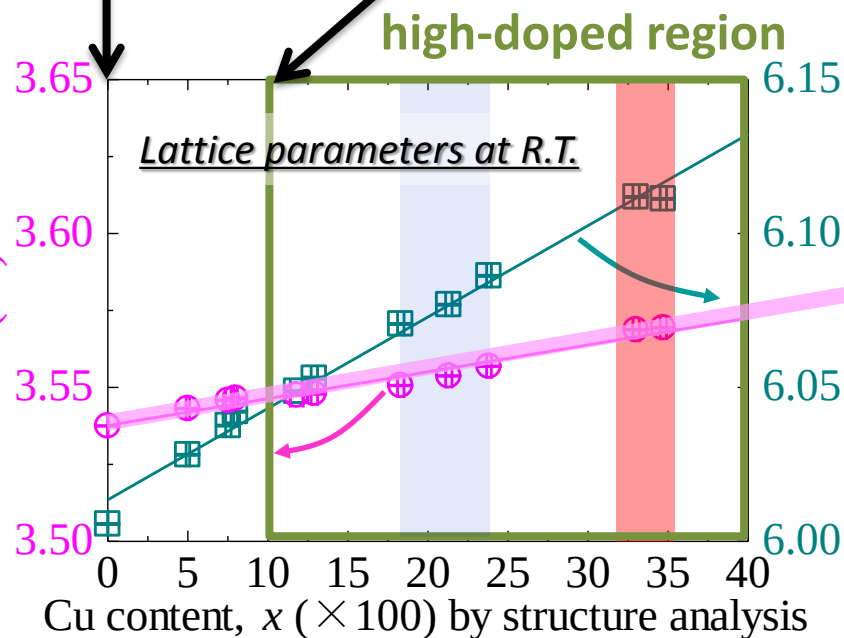
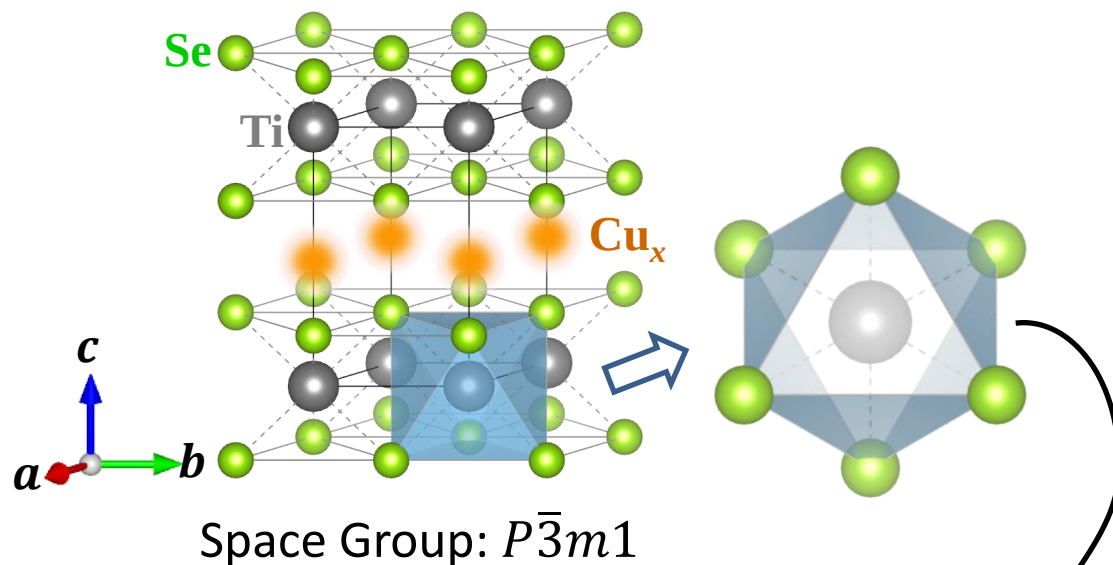
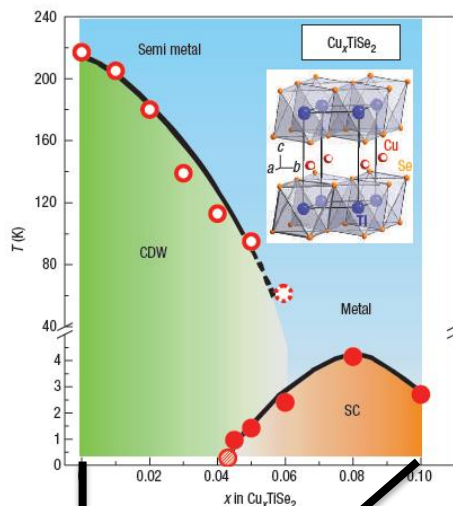
W. Khon, PRL **19**, 439 (1967). D. Jerome, PR **158**, 462 (1967).

Superconductivity in Cu^+ intercalated 1T-TiSe_2

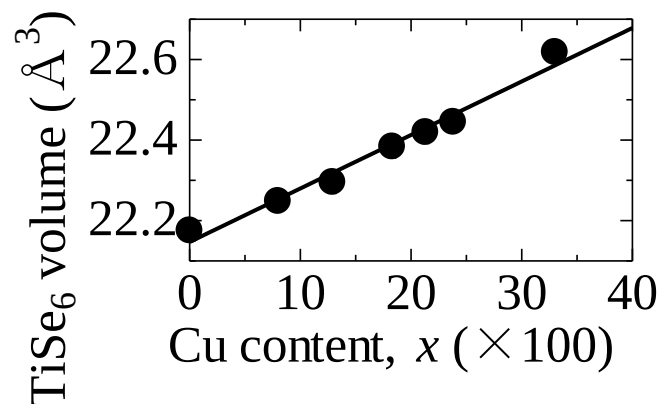


✓ SC in $0.04 \leq x \leq 0.10$

Successful synthesis of Cu high-doped TiSe_2



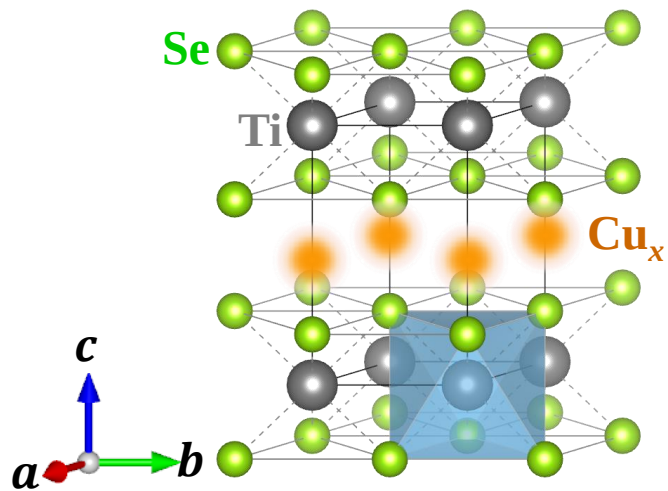
TiSe_6 octahedron



✓ Electron doping from Cu^+ to TiSe_2 layers

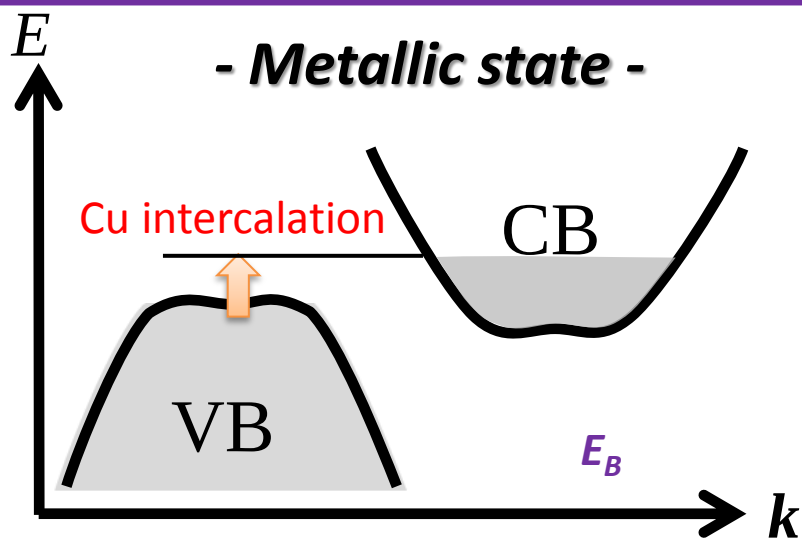
S. Kitou et al., PRB **99**, 081111(R) (2019).

New phases in Cu_xTiSe_2 ($x \sim 1/3$)



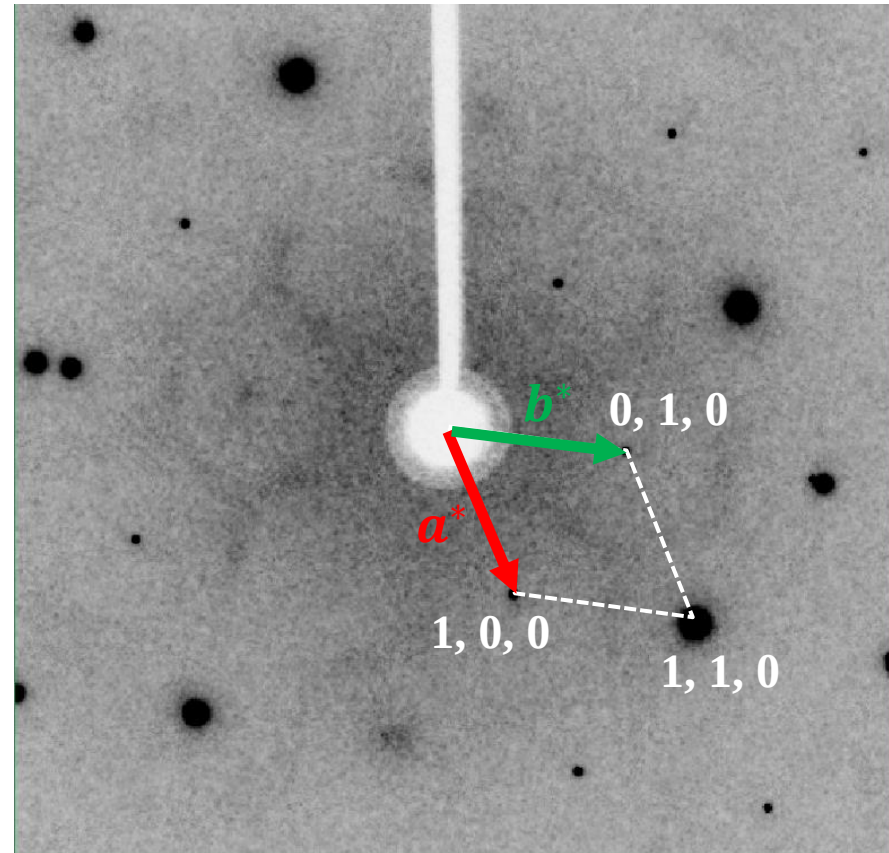
Space Group: $P\bar{3}m1$

- **Metallic state** -



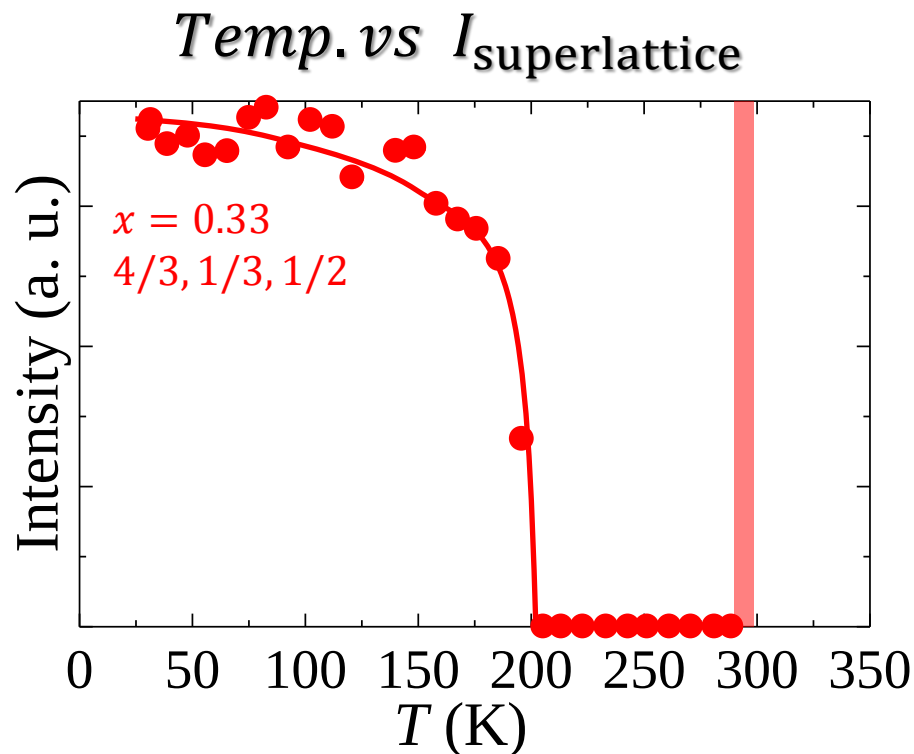
$\text{Cu}_{0.33}\text{TiSe}_2$

R.T.



HT phase

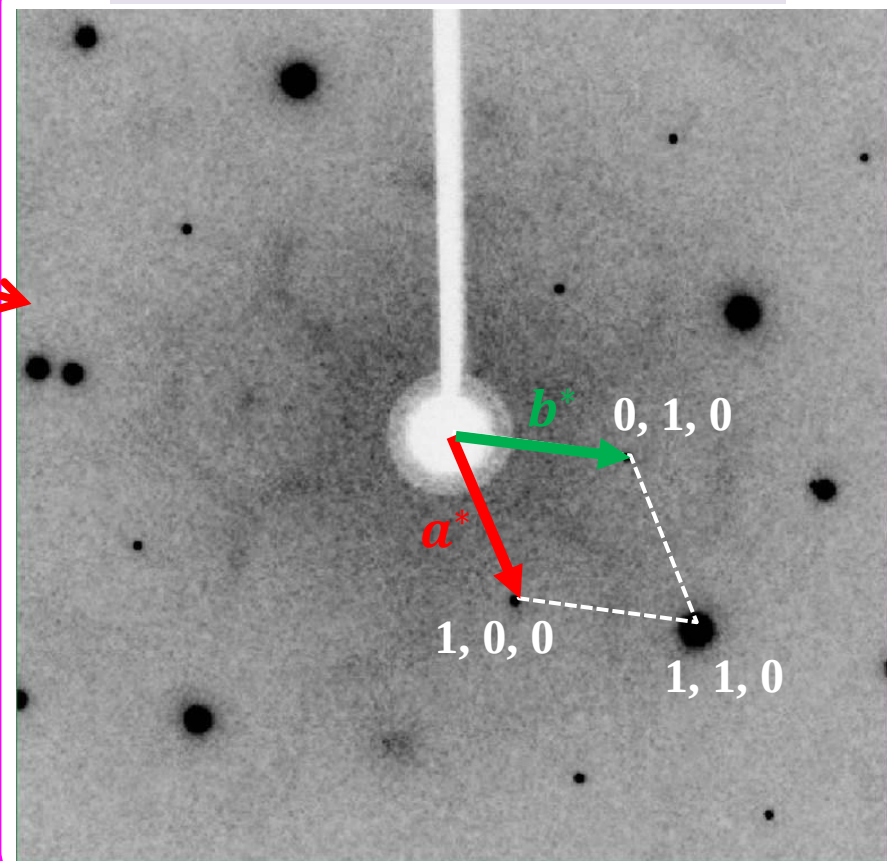
New phases in Cu_xTiSe_2 ($x \sim 1/3$)



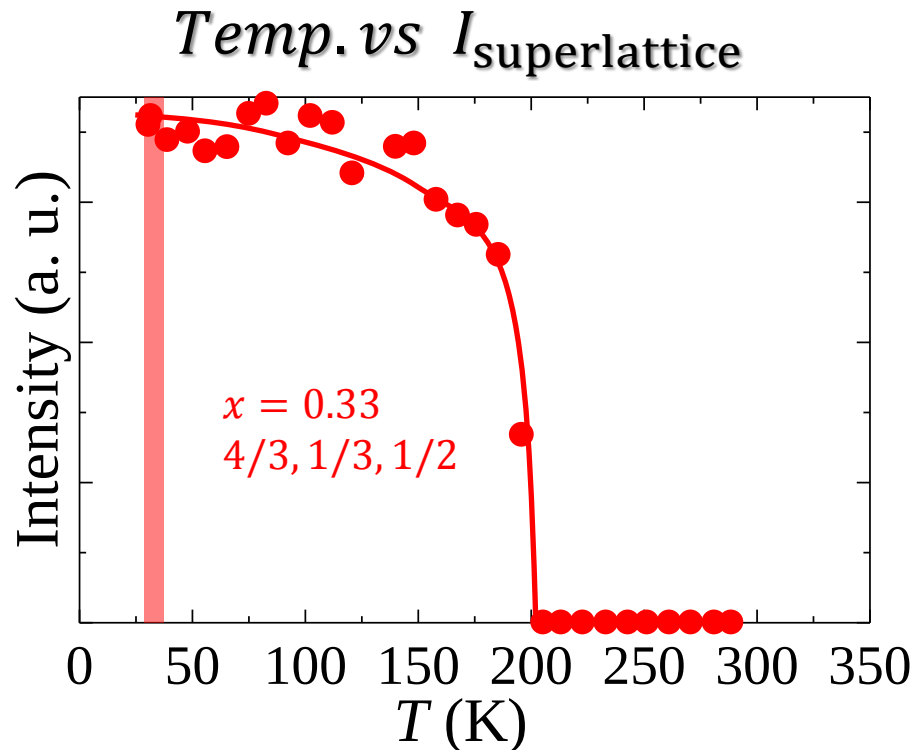
$T_{\gamma 2} \sim 200$ K

$\text{Cu}_{0.33}\text{TiSe}_2$

Decreasing temperature



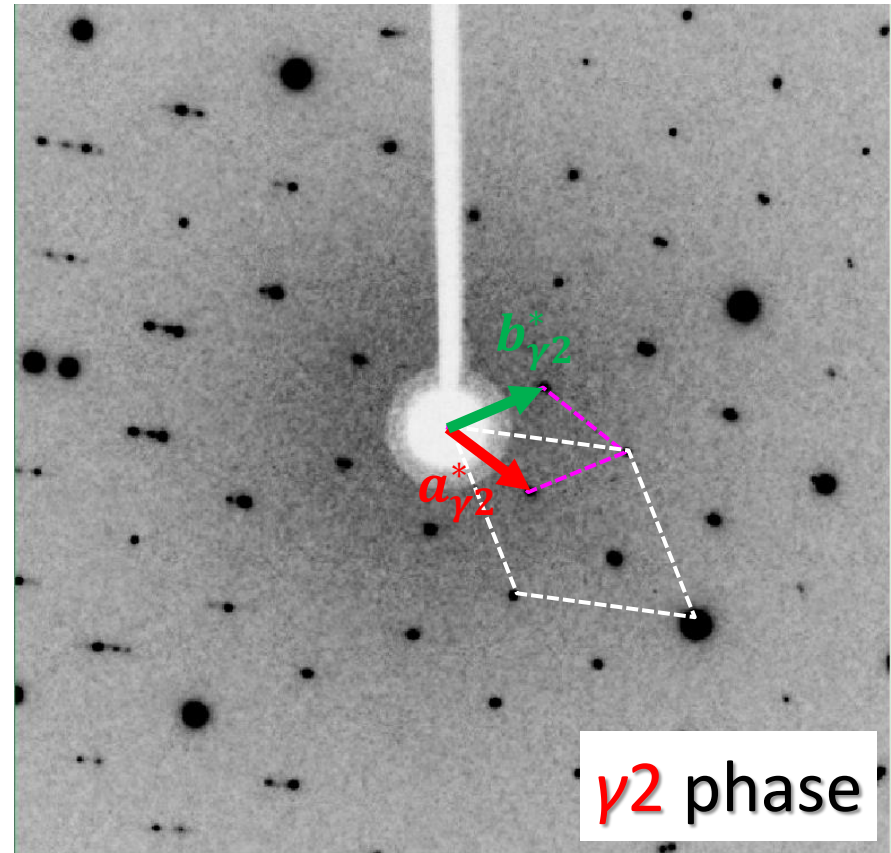
New phases in Cu_xTiSe_2 ($x \sim 1/3$)



$$T_{\gamma 2} \sim 200 \text{ K}$$

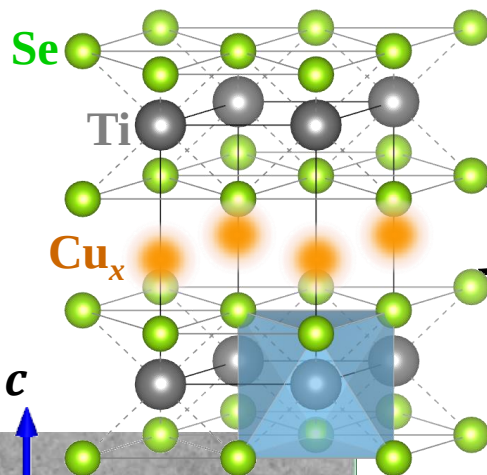
$\text{Cu}_{0.33}\text{TiSe}_2$

31 K $\sqrt{3}a \times \sqrt{3}b \times 2c; P\bar{3}1c$

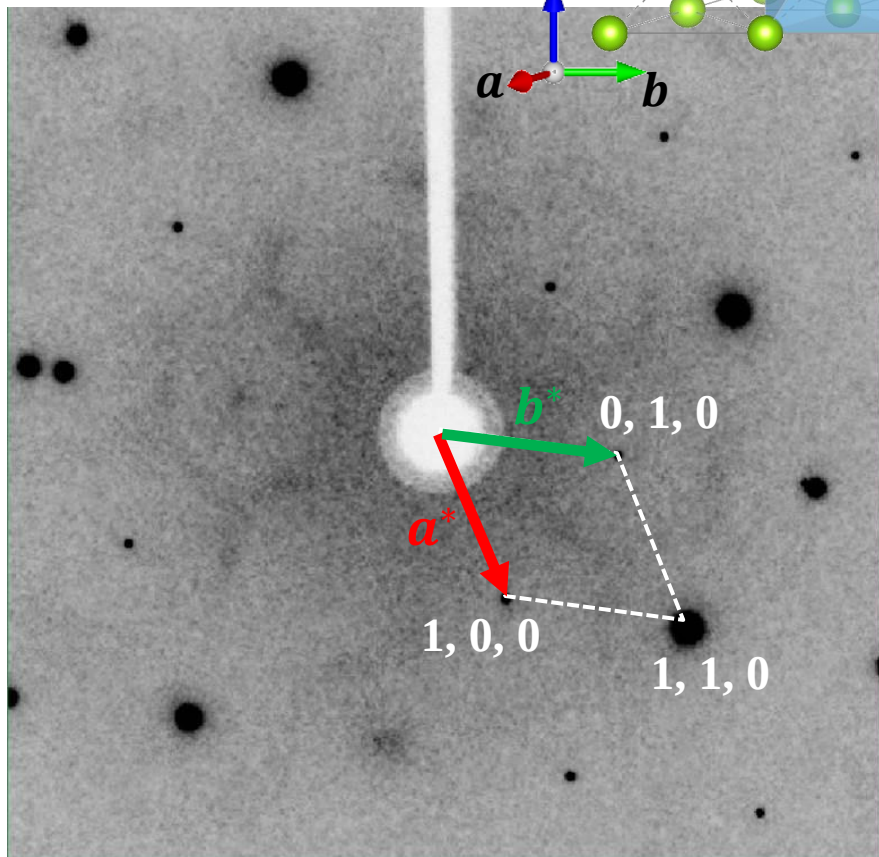
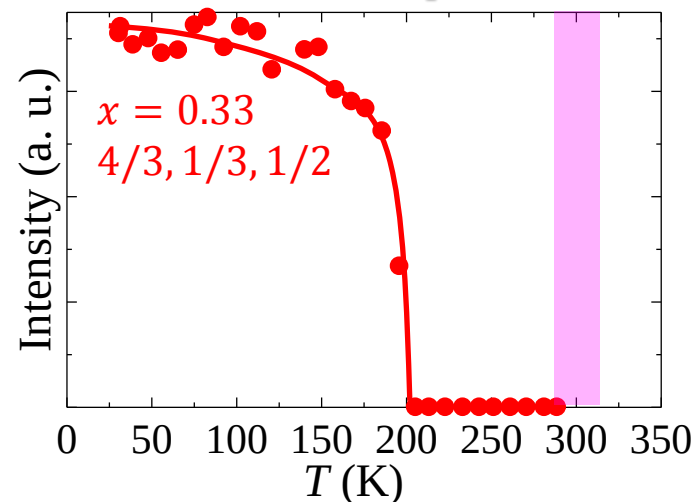


Averaged structure of Cu_xTiSe_2 Cu-disordering state

LT phase



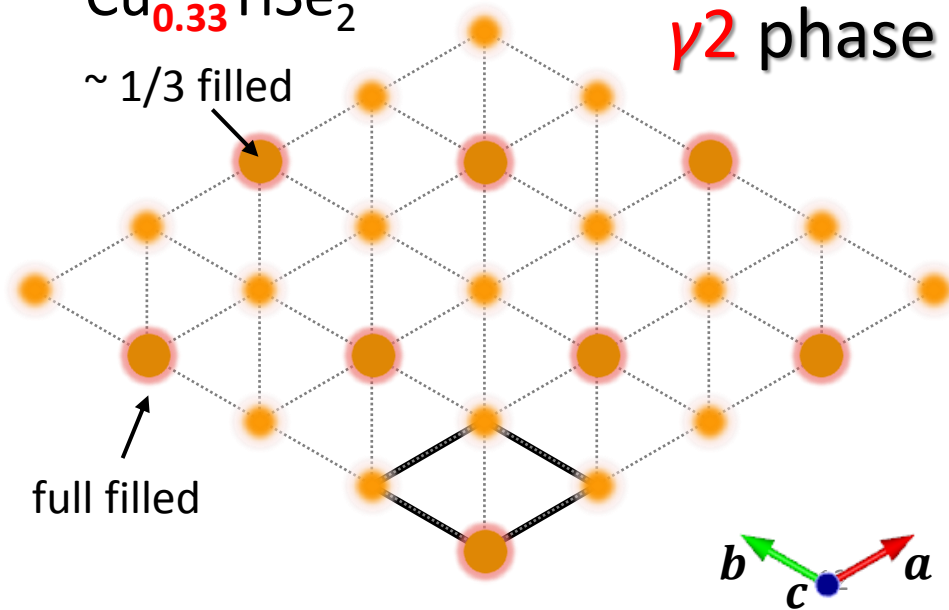
Temp. vs $I_{\text{superlattice}}$



$\text{Cu}_{0.33}\text{TiSe}_2$

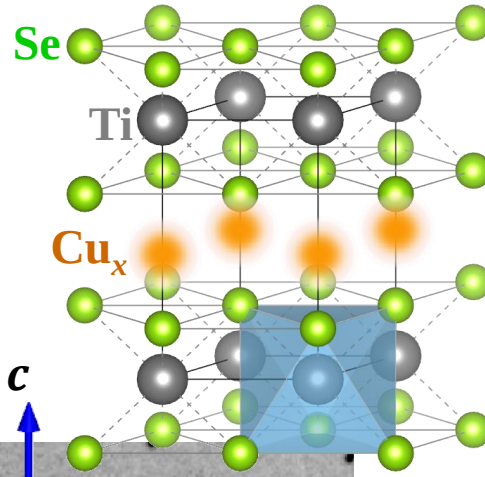
$\sim 1/3$ filled

γ_2 phase

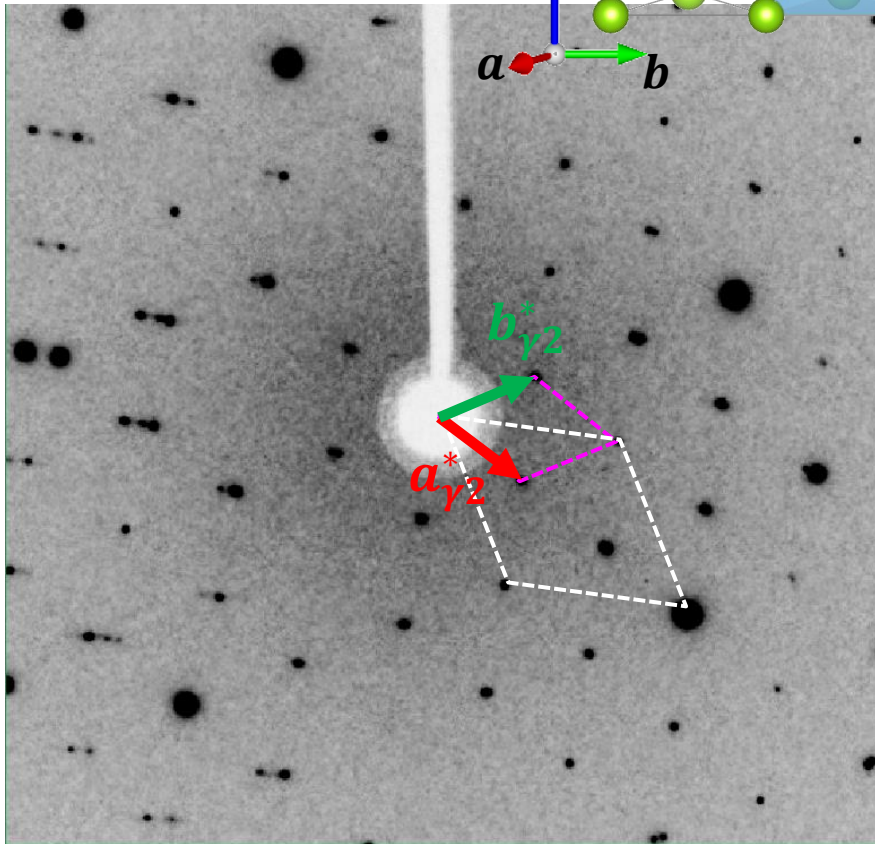
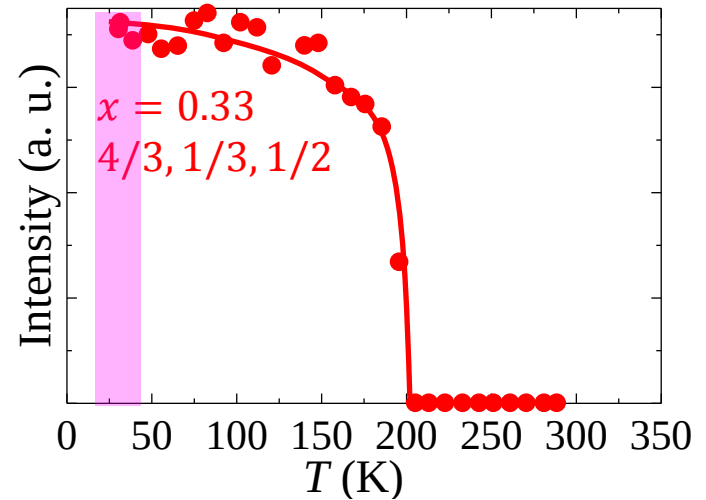


Averaged structure of Cu_xTiSe_2 Cu-disordering state

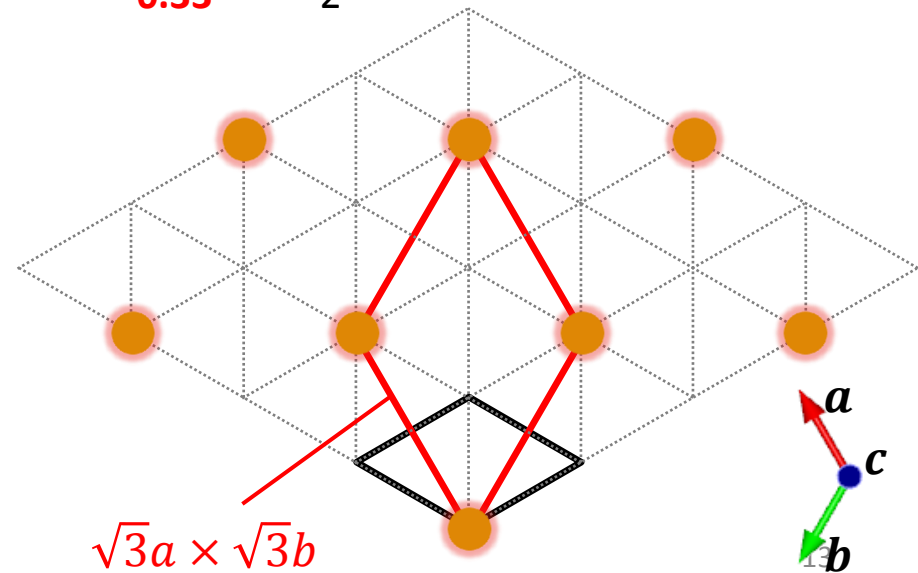
LT phase



Temp. vs $I_{\text{superlattice}}$

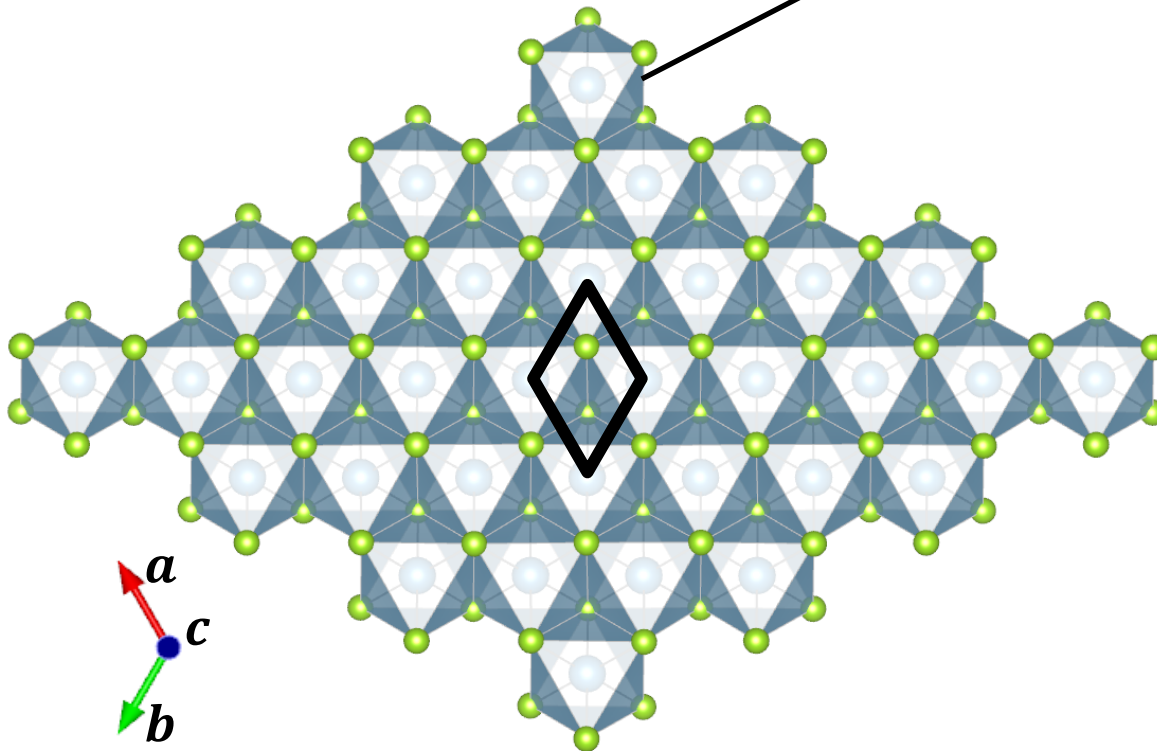
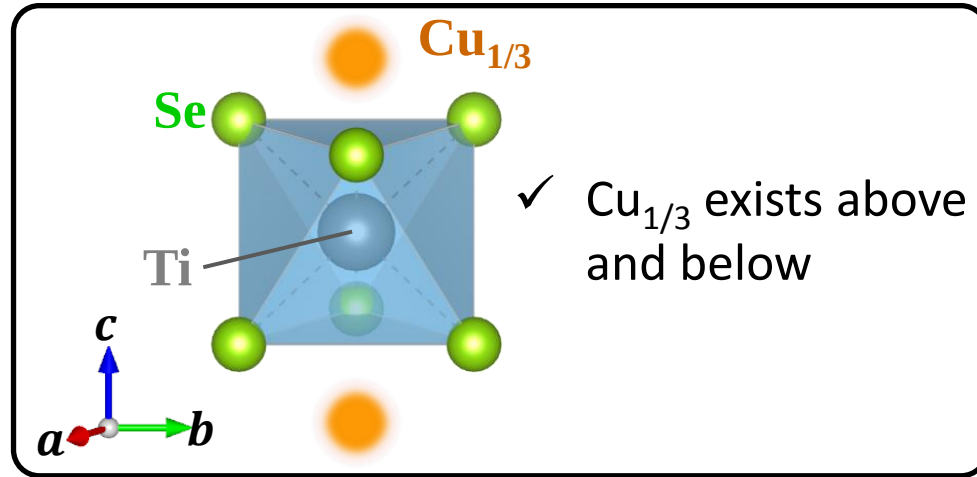


$\text{Cu}_{0.33}\text{TiSe}_2$

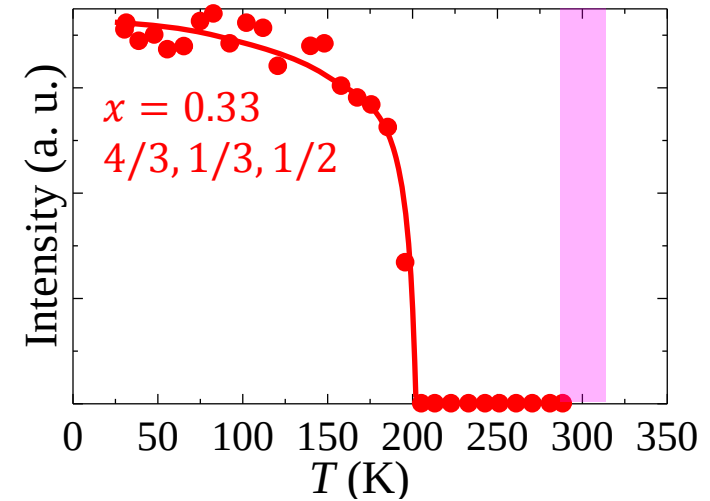


Structural change of TiSe_2 layers in $\text{Cu}_{0.33}\text{TiSe}_2$

HT phase



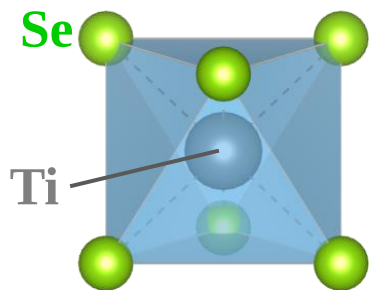
Temp. vs $I_{\text{superlattice}}$



Structural change of TiSe_2 layers in $\text{Cu}_{0.33}\text{TiSe}_2$

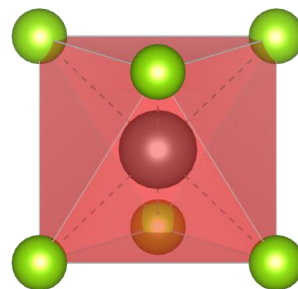
LT phase

Small (electron-poor)

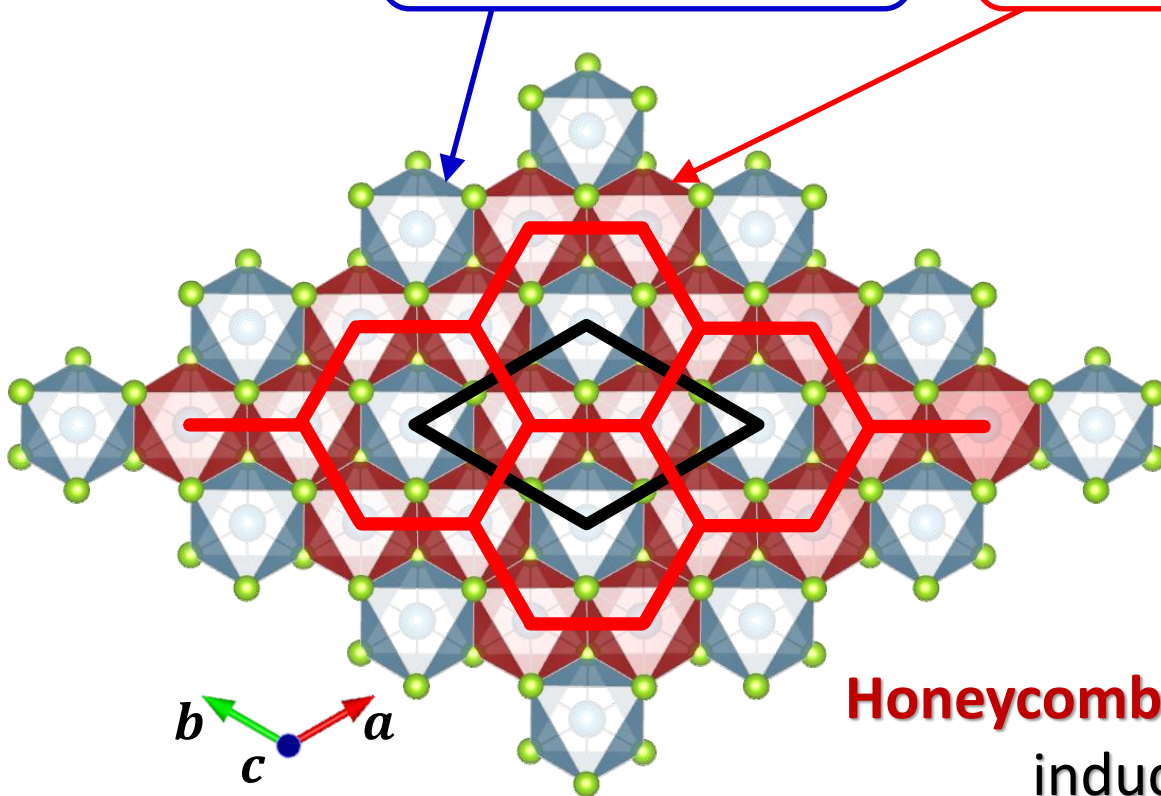


$$V_1 = 22.318 \text{ \AA}^3$$

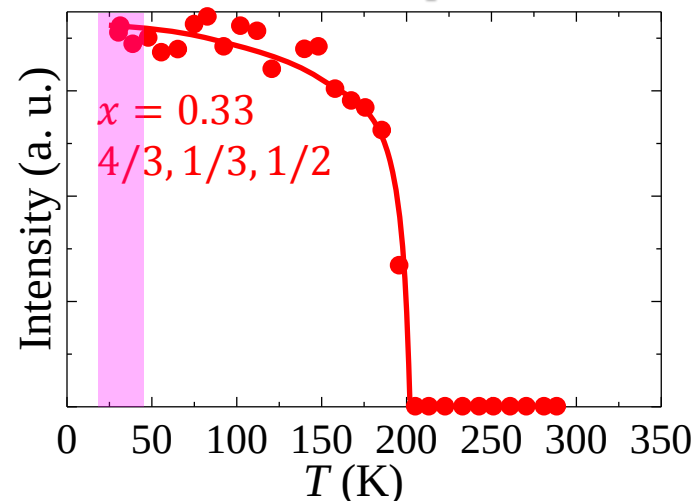
Large (electron-rich)



$$V_2 = 22.572 \text{ \AA}^3$$



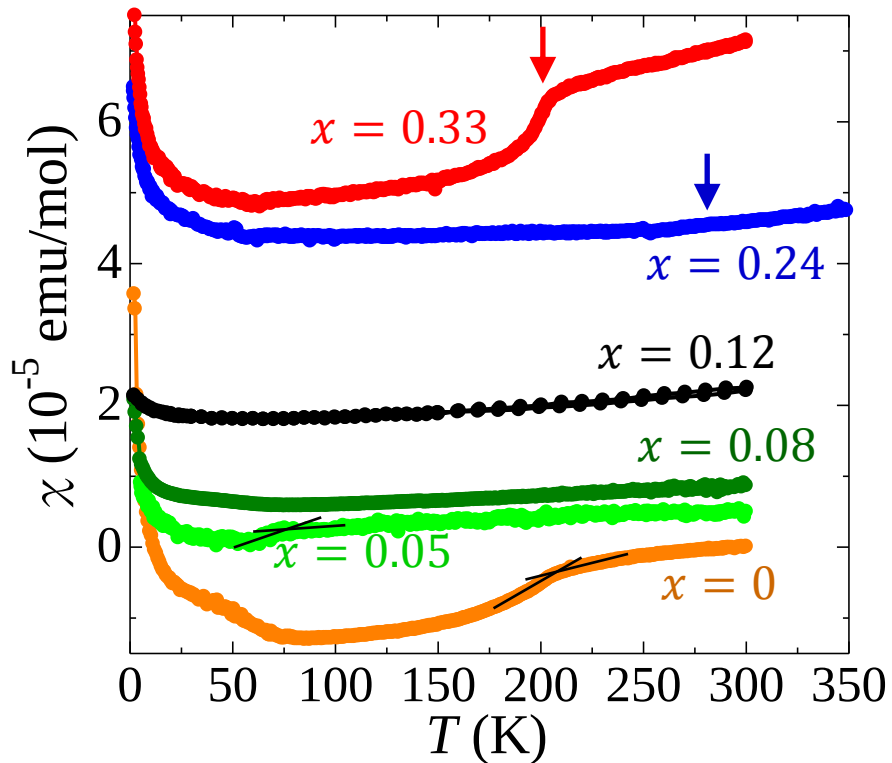
Temp. vs $I_{\text{superlattice}}$



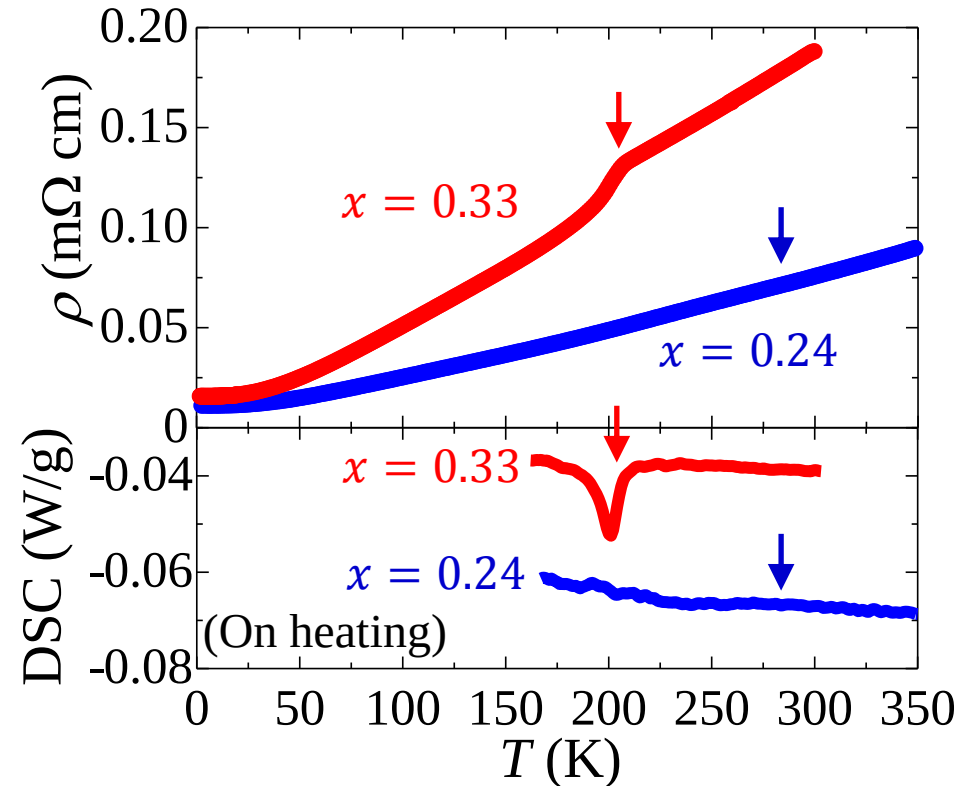
Honeycomb lattice type CDW in TiSe_2
induced by Cu-ordering

Why are there differences in physical properties?

Magnetic susceptibility



Electric resistivity & DSC

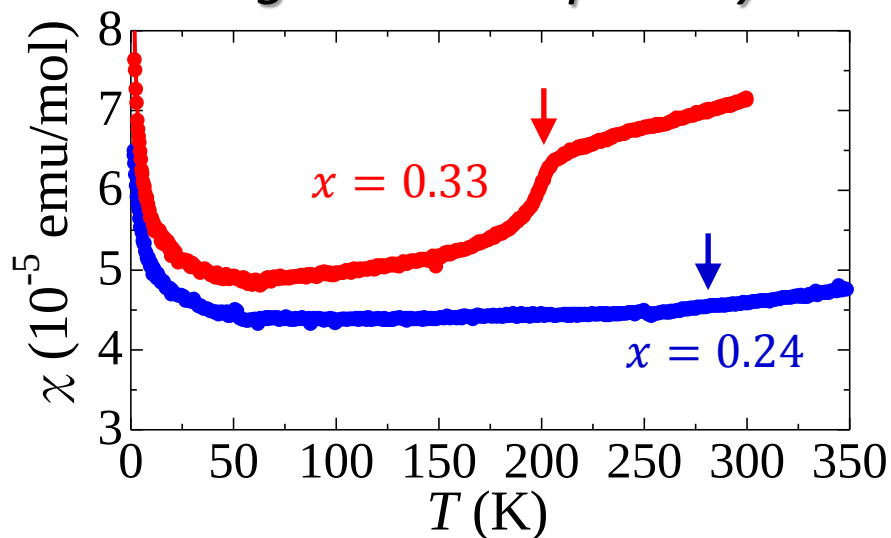


cf. DSC: Differential Scanning Calorimetry

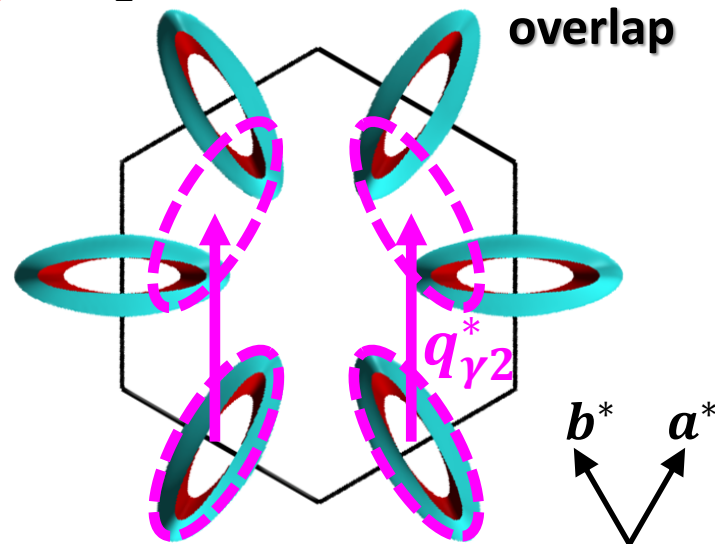
- ✓ $\Delta S = 0.96 \text{ J mol}^{-1} \text{ K}^{-1}$ in $x = 0.33$ (no hysteresis loop)
- ✓ No SC down to 120 mK in $x \geq 0.13$

“nesting condition” with Cu-ordering

Magnetic susceptibility

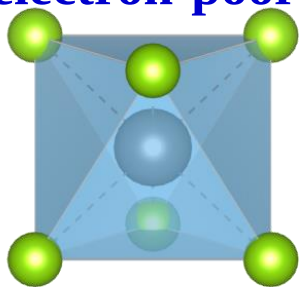


Partly ($\sim 1/6$) overlap

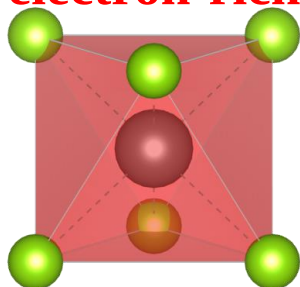


Commensurate connection between
“**Cu-ordering**” and “**Nesting of FSs**”
→ Charge Density Wave?

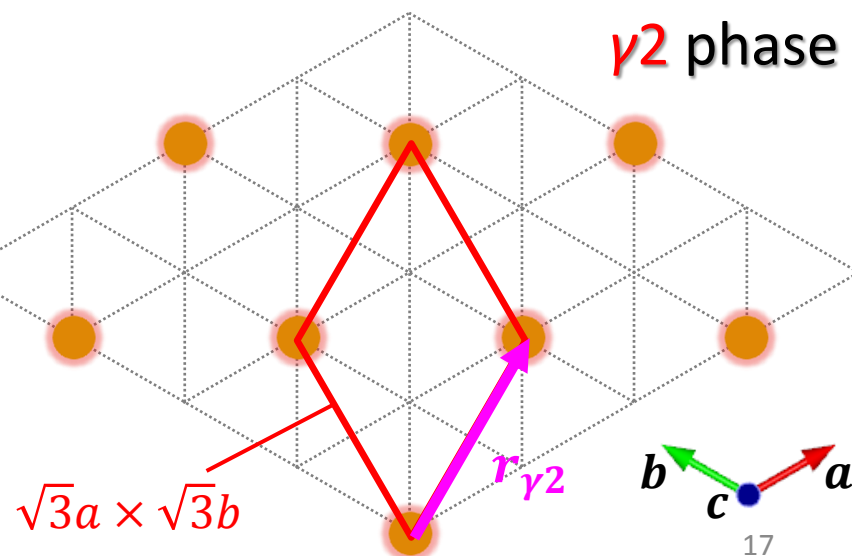
electron-poor



electron-rich



$\gamma 2$ phase

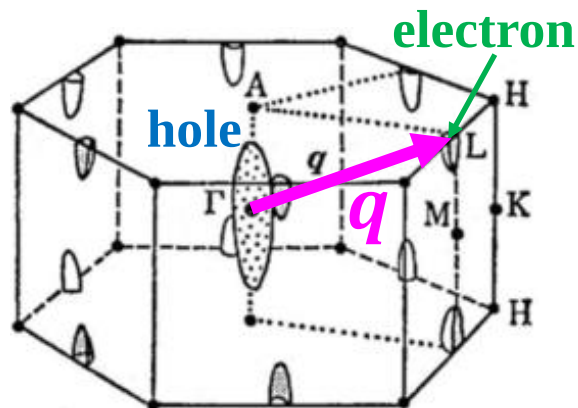


CDW in “non-doped TiSe₂”

CDW in “Cu_{0.33}TiSe₂”

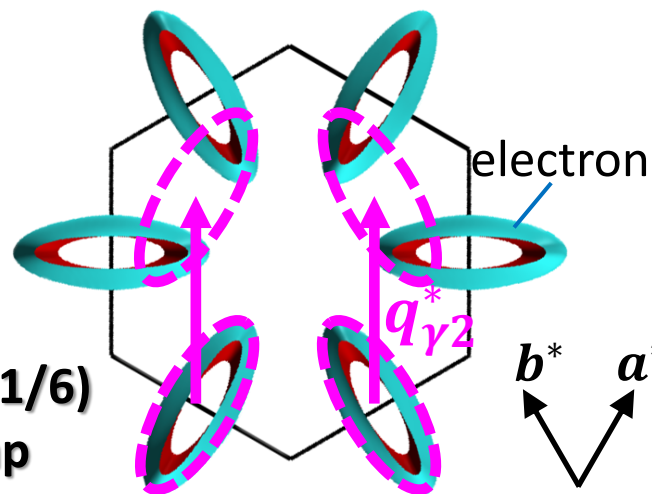
excitonic interaction

nesting condition

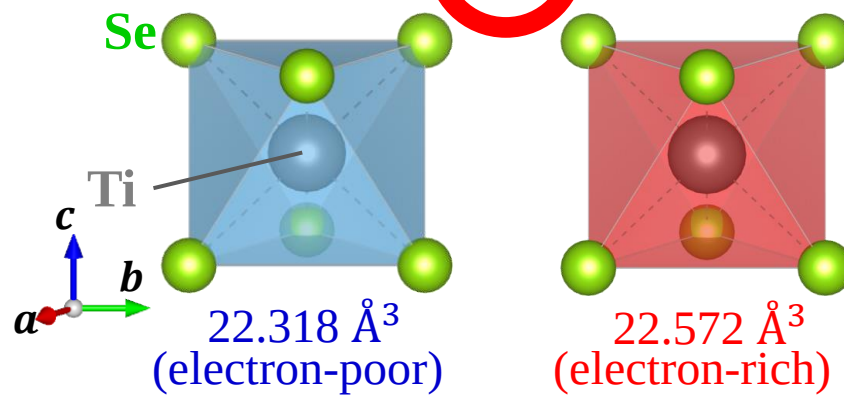


A. Zunger, A.J. Freeman, PRB **17**, 1839 (1978).

Partly (~ 1/6)
overlap

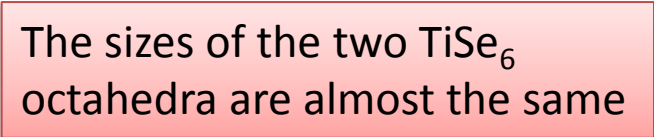


charge disproportionation

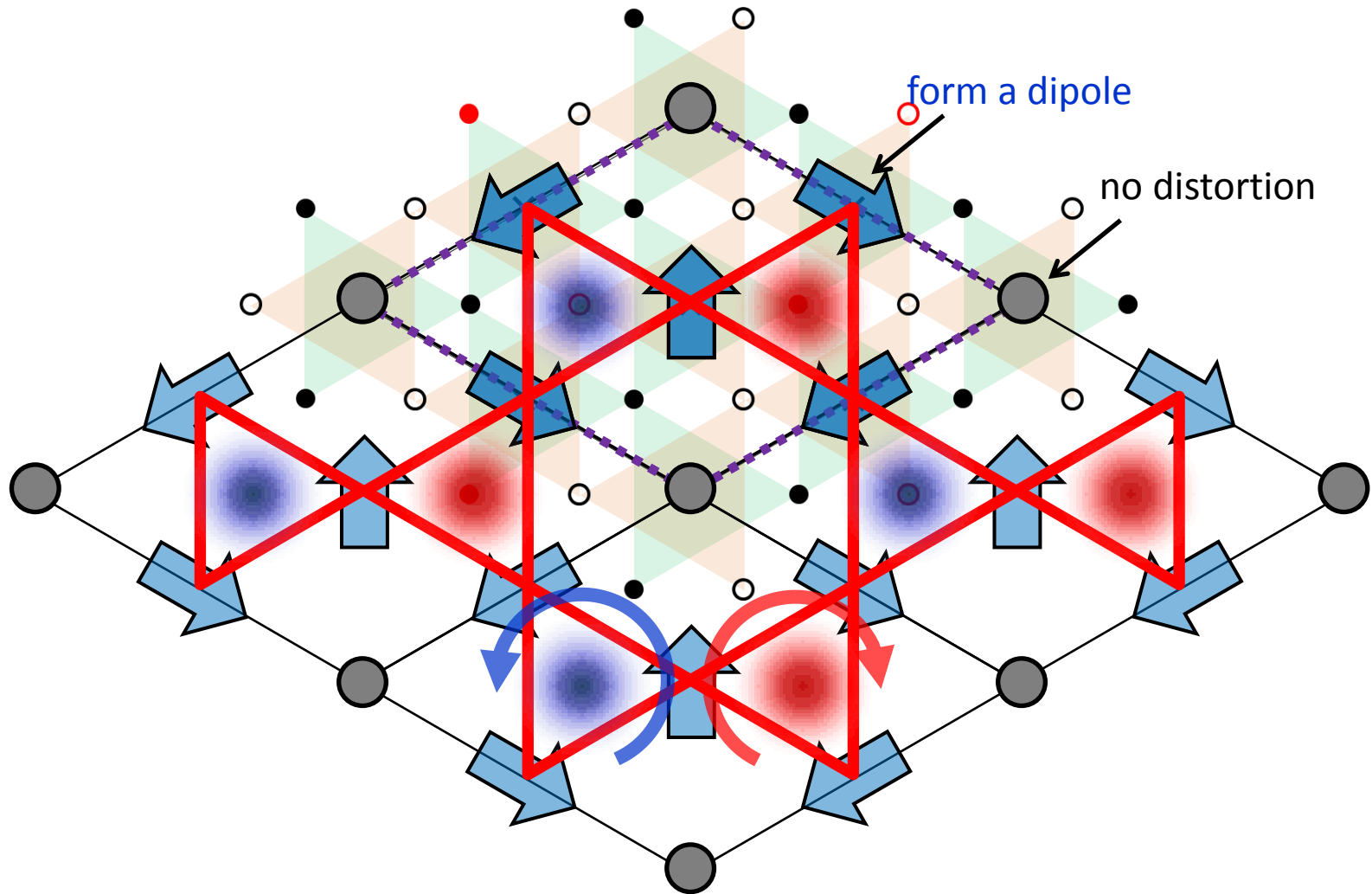


S. Kitou *et al.*, PRB **99**, 081111(R) (2019).¹⁸

4



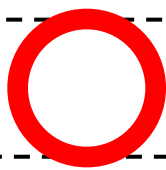
Electric dipoles form a kagome lattice



Electric dipoles form kagome lattices by coexistence with undistorted TiSe_6 octahedra

CDW in “non-doped TiSe₂”

CDW in “Cu_{0.33}TiSe₂”



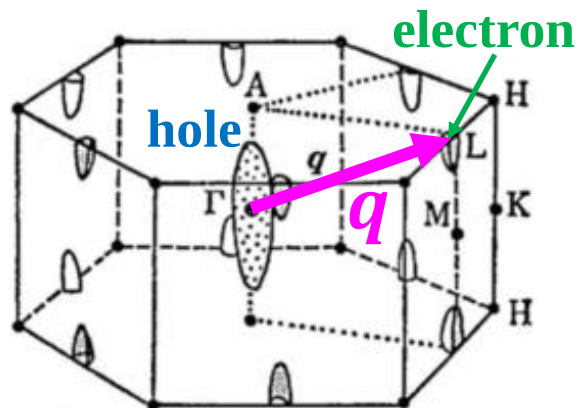
excitonic interaction



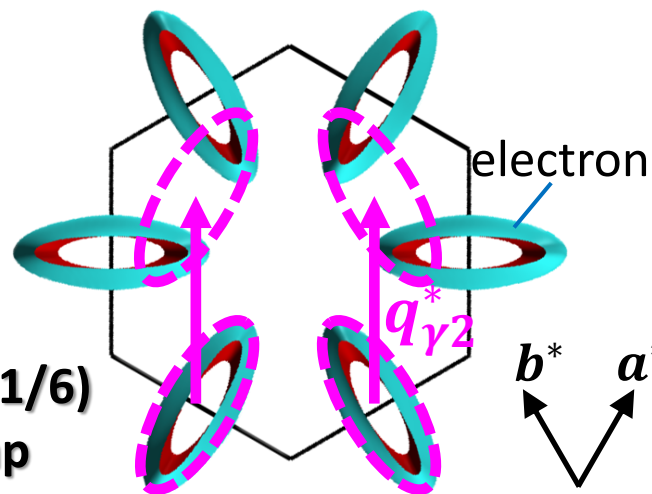
nesting condition



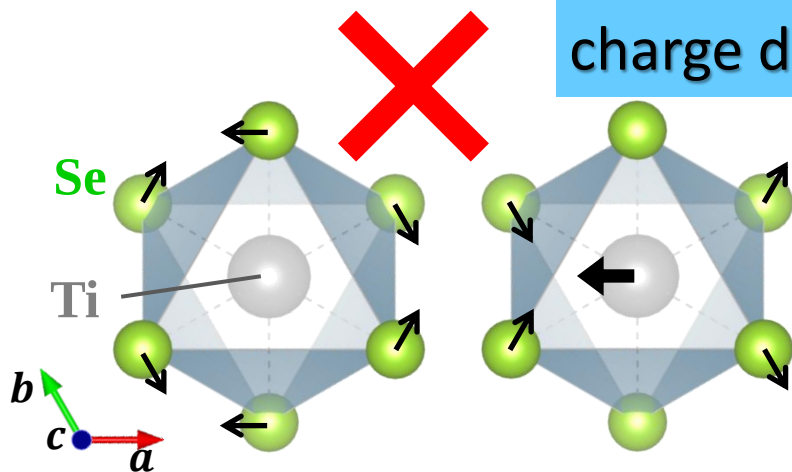
Partly (~ 1/6)
overlap



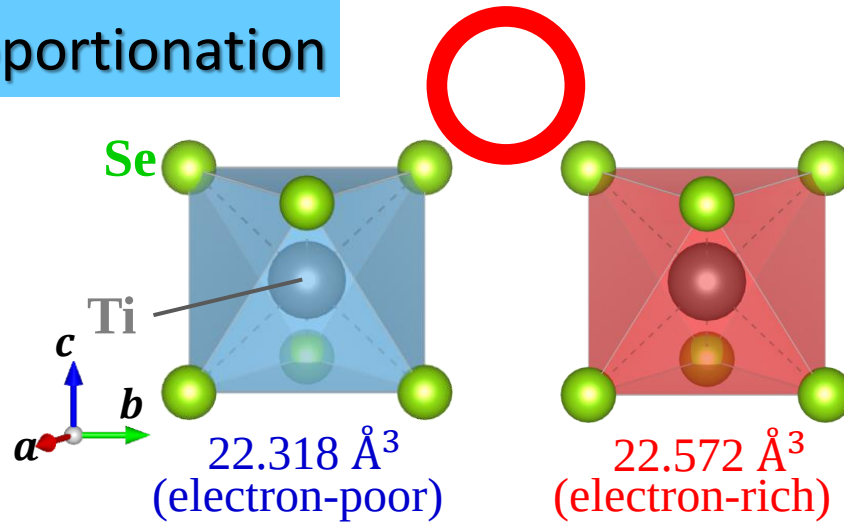
A. Zunger, A.J. Freeman, PRB **17**, 1839 (1978).



charge disproportionation



S. Kitou *et al.*, PRB **99**, 104109(2019)



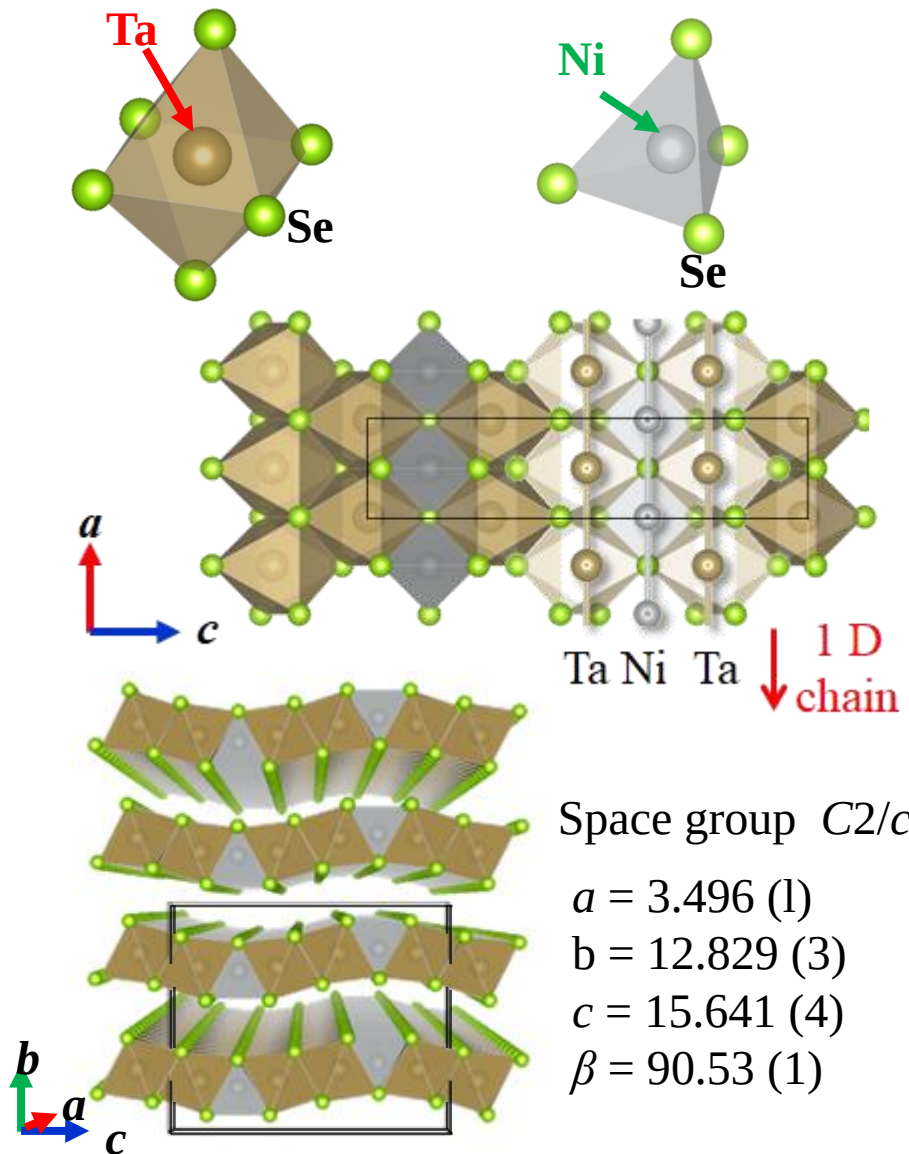
S. Kitou *et al.*, PRB **99**, 081111(R) (2019)²¹

Outline

- Phase Diagram of Excitonic Insulator
- Structure transition of TiSe_2
 - Charge Density Wave $\sim$ band filling control
- Structural study of Ta_2NiSe_5
- Universality?

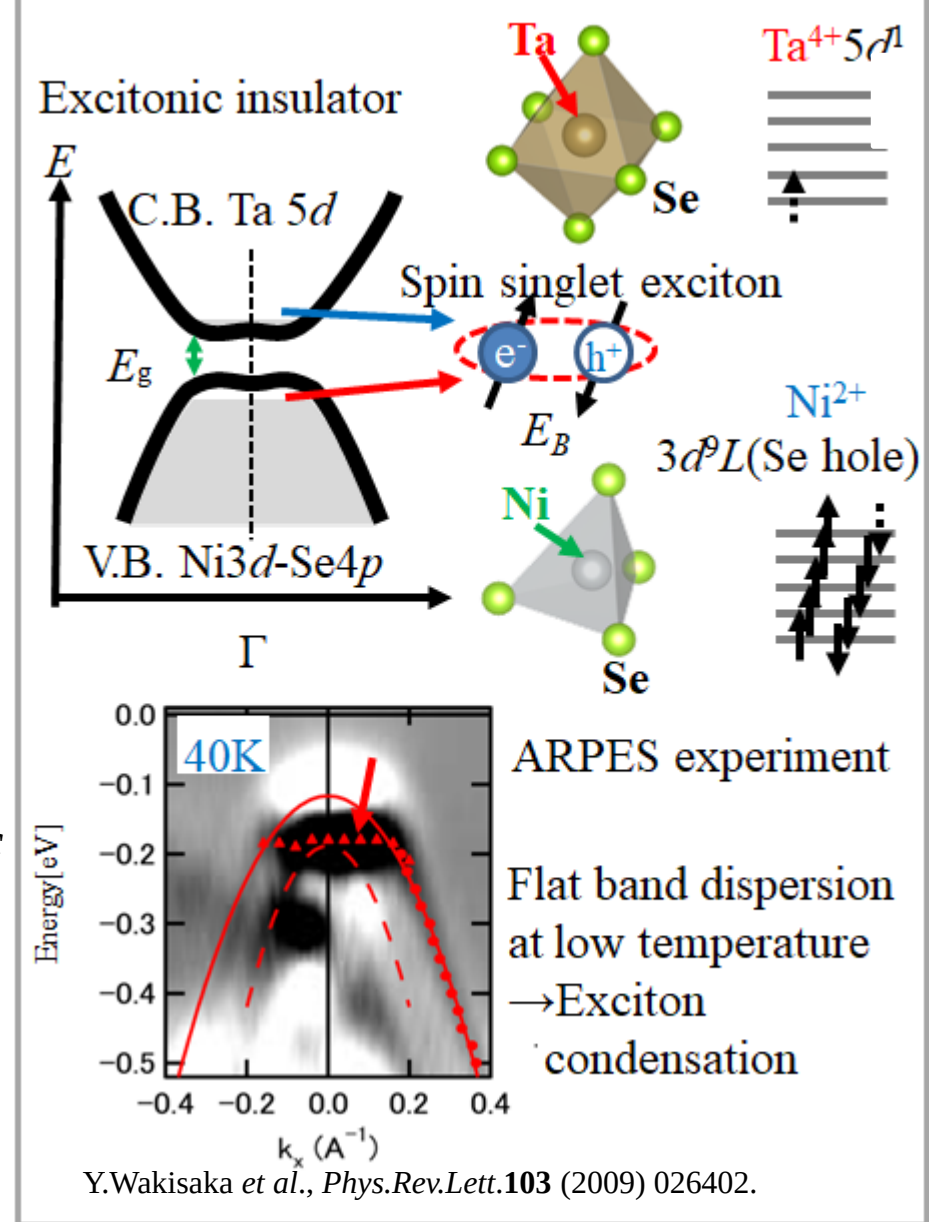
Structure and physical properties of Ta_2NiSe_5

Crystal structure

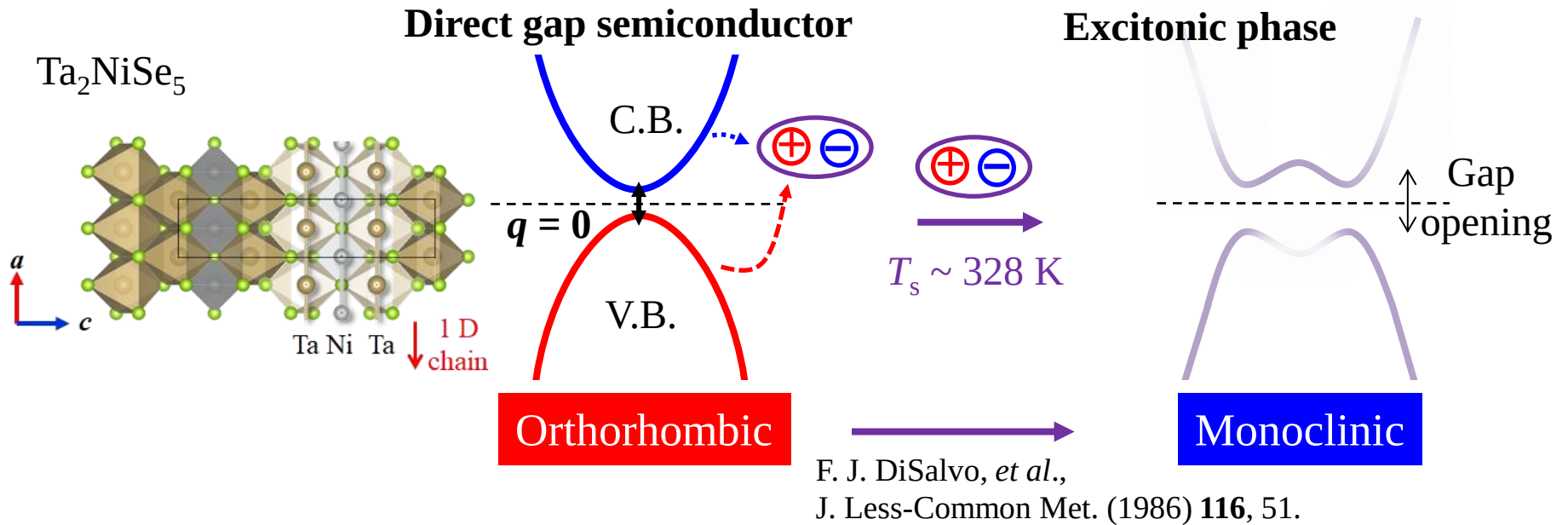


STEVEN A. SUNSHINE *et al.*, Inorg.Chem.(1985)

Candidate of Excitonic insulator

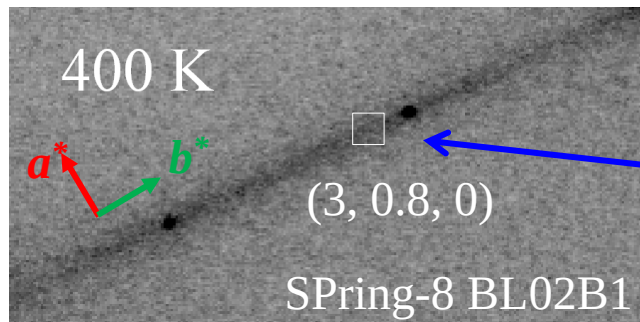


Ferroelastic “like” transition accompanying EI in Ta₂NiSe₅



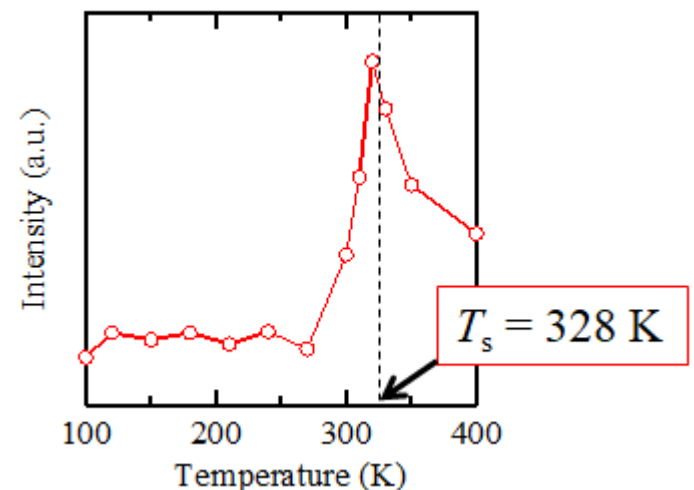
Single crystal XRD (our study)

Ferroelastic “like” transition occurs !



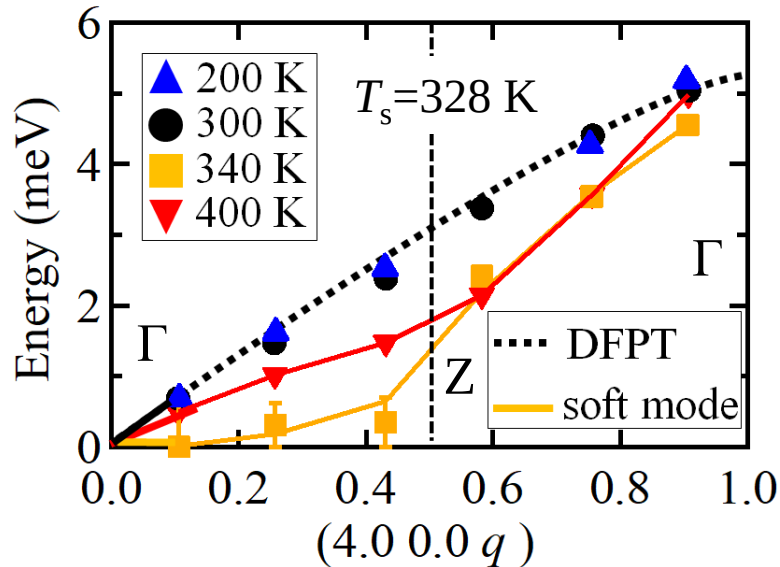
- Strong diffuse scattering
- No superlattice peak

Temp. dependence of intensity of diffuse scattering at (3, 0.8, 0)

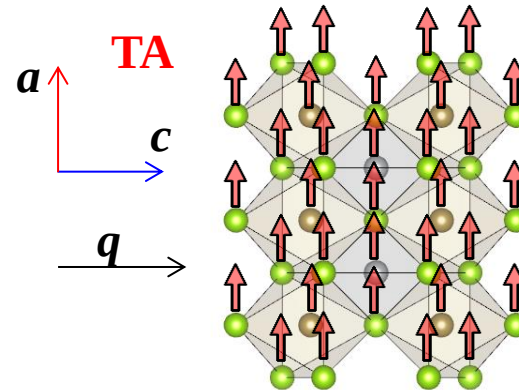
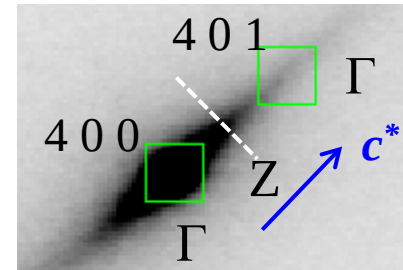


Anomalous softening of transverse acoustic (TA) phonon mode

TA phonon dispersion (expanded B.Z.)

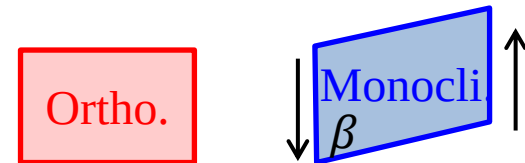


Diffuse scattering at 320 K



- Energy of TA mode decreases to zero in the 80 % of B.Z.

- Anomalous TA mode softening just above $T_s=328$ K



- Softening of elastic constant C_{55} ?

→ Diffuse scattering and TA mode softening are not observed along Γ -X direction.

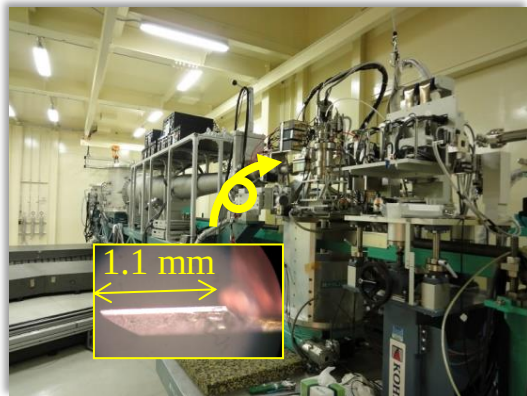
NOT a proper ferroelastic transition

Revealing phonon dynamics by inelastic X-ray scattering

Object : Revealing the electron-phonon coupling mode in Ta_2NiSe_5

Experiment

Inelastic X-ray scattering at BL35XU, SPring-8

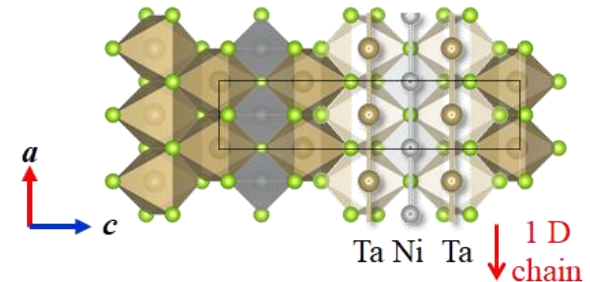
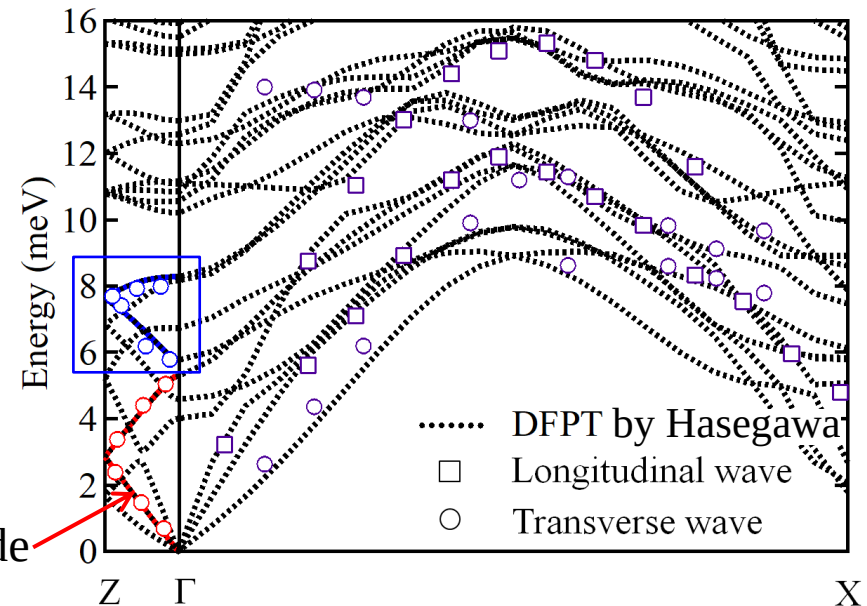


- Energy resolution: 1.5 meV
- q - resolution: $0.11 \text{ \AA}^{-1}$
- Measured Q :
(4, 0, 0), (4, 0, 2)
(0, 0, 14) etc.

Identification

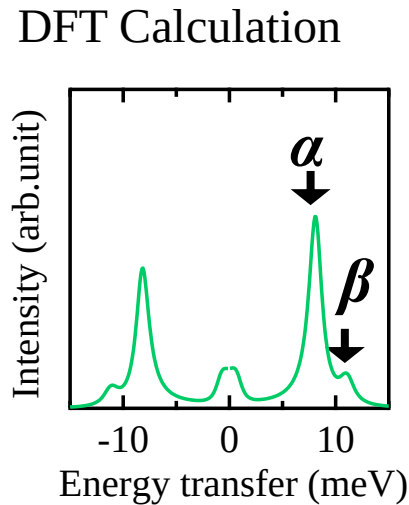
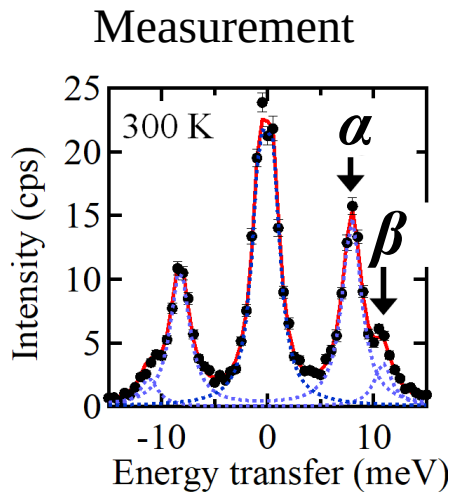
- Phonon calculation by DFPT (ABINIT package)
- Single crystal XRD revealing “frozen” phonon modes

Phonon dispersion at 300 K



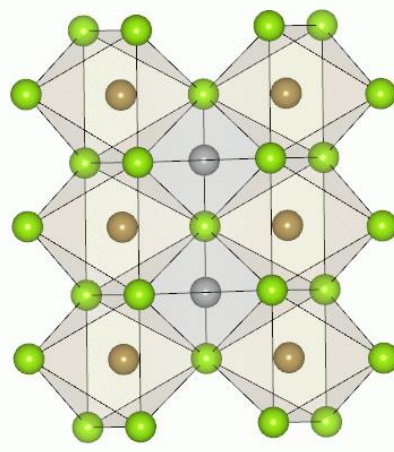
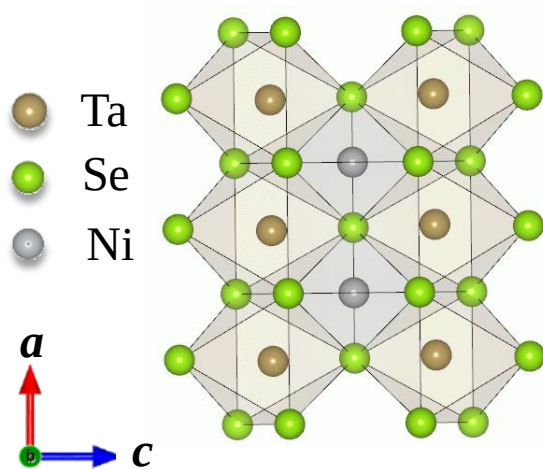
Identification of the electron-phonon coupling mode

TO phonon in DFT calculation



α : mainly Ta

β : mainly Se



Result of the structural analysis

Orthorhombic

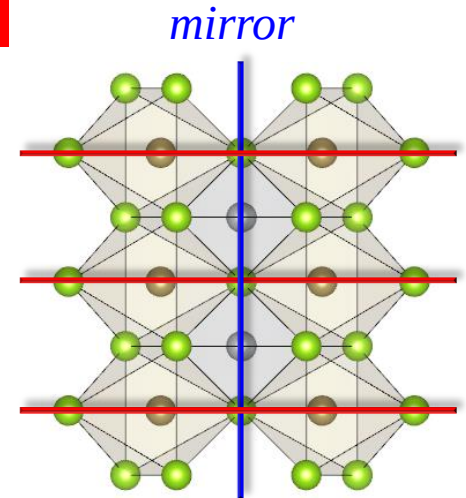
Space group

$Cmcm$

Point group

$m\bar{m}m$

mirror



Monoclinic

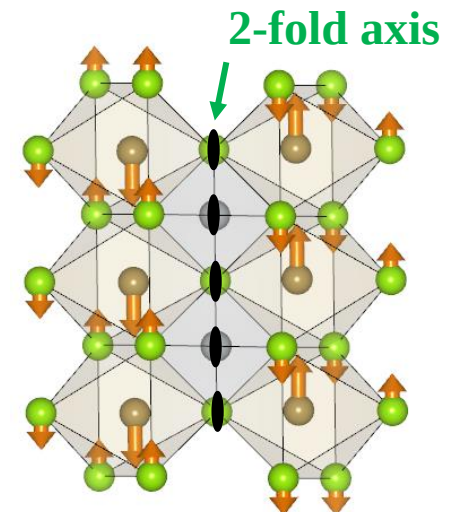
Space group

$C2/c$

Point group

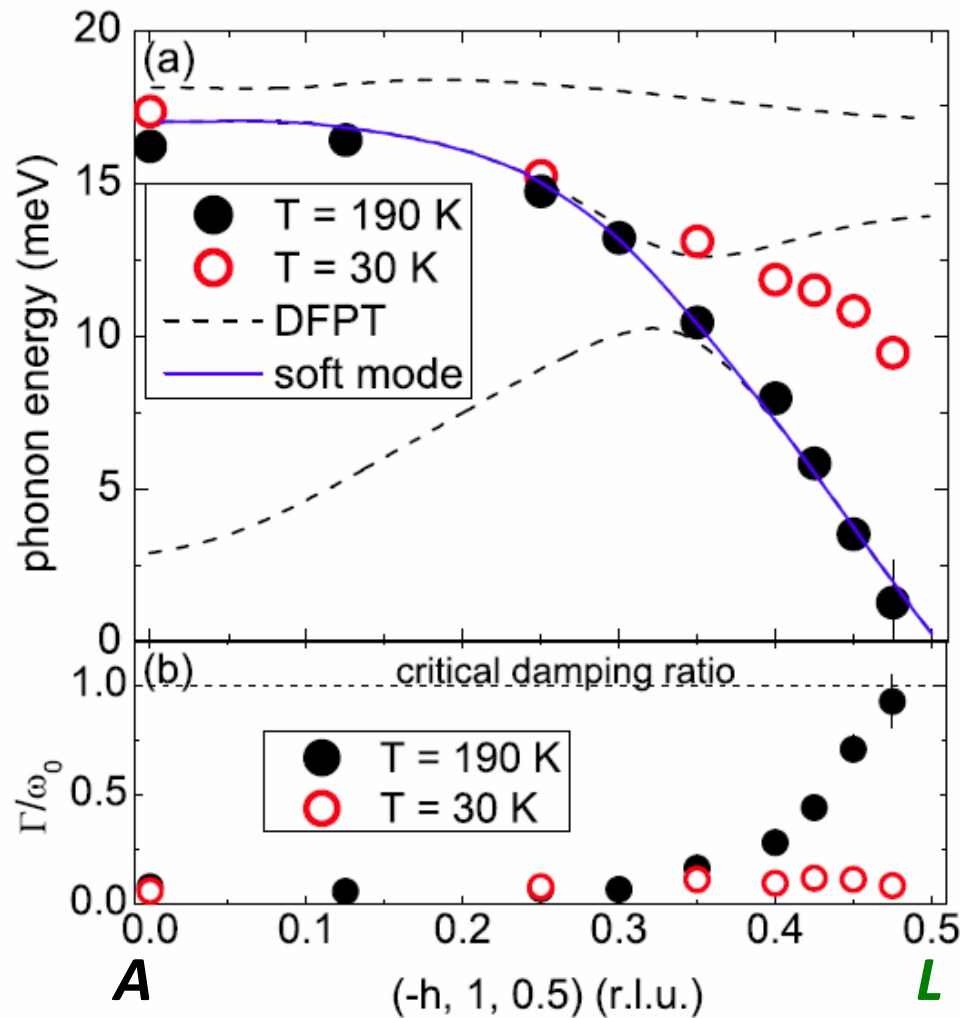
$2/m$

Freezing

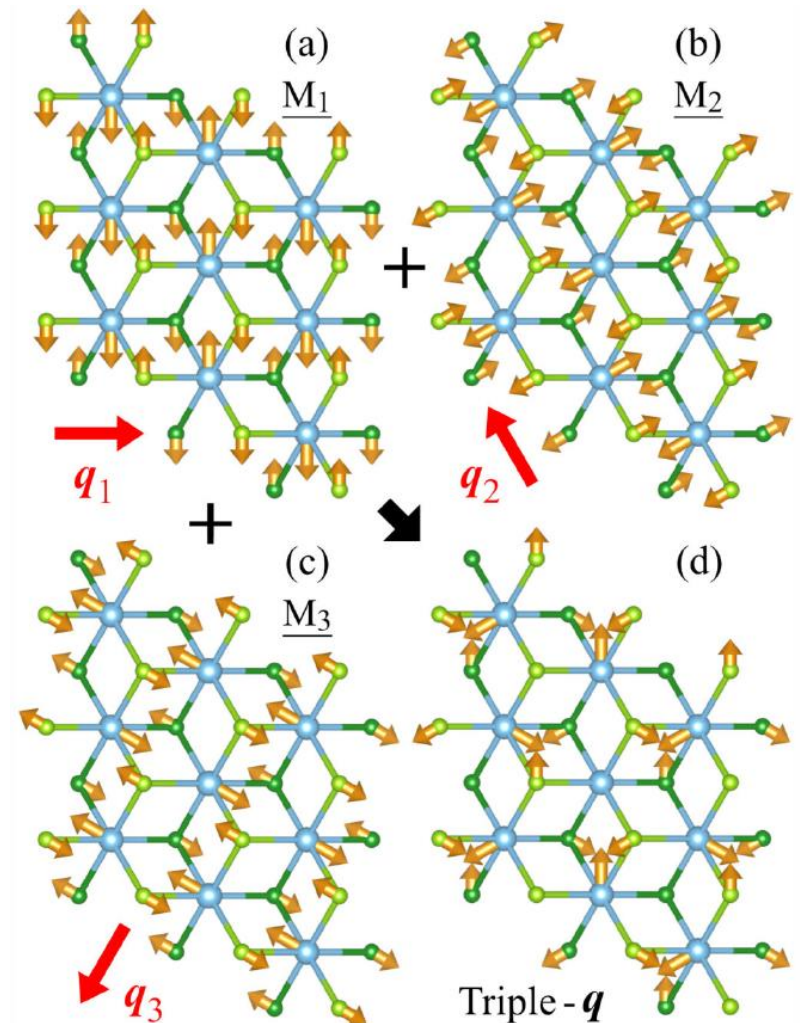


Softening of TO phonon mode in 1T-TiSe₂

Inelastic X-ray scattering



“Triple-q” mode



(-0.5, 1, 0.5)

F. Weber *et al.*, PRL **107**, 266401 (2011).

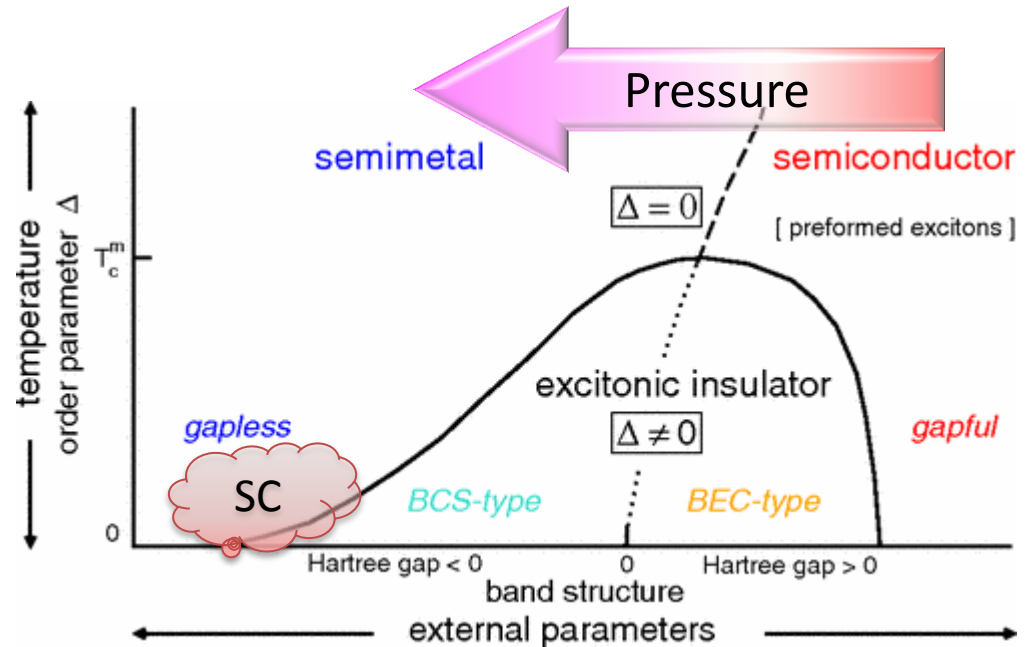
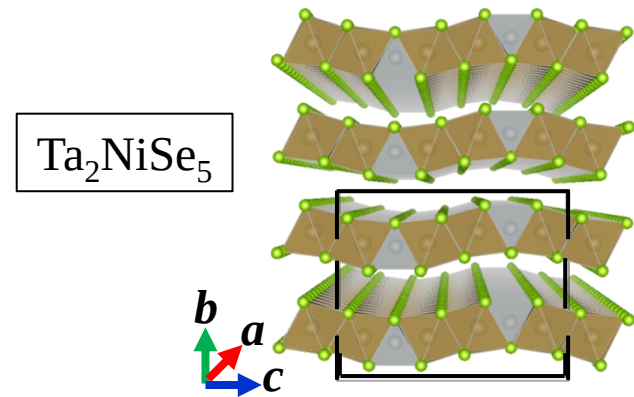
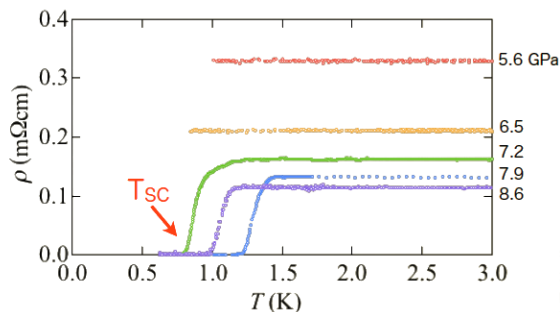
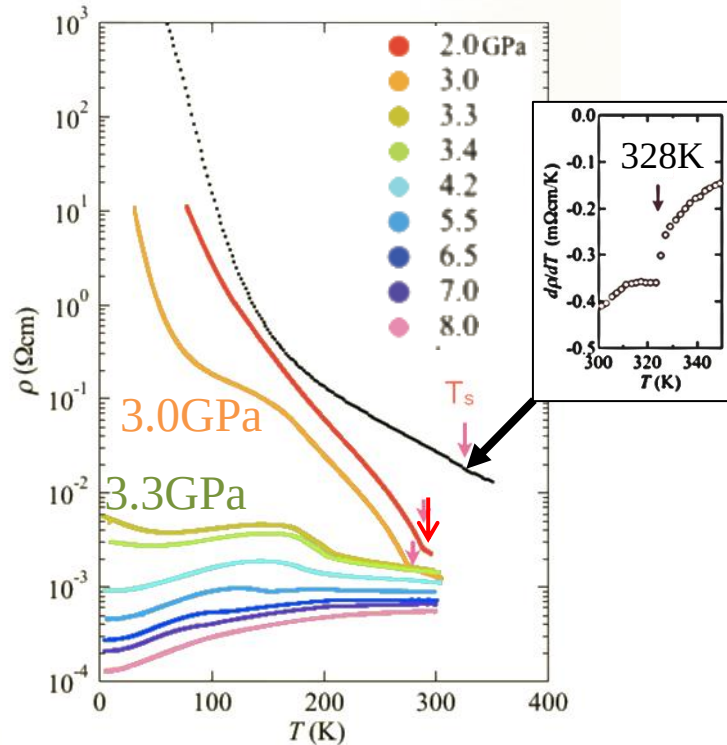
N. Suzuki *et al.*, JPSJ **54**, 4668 (1980).

B. Bianco *et al.*, PRB **92**, 094107 (2015).

T. Kaneko *et al.*, PRB **97**, 155131 (2018).

Various electronic phase under pressures in Ta₂NiSe₅

K. Matusbayashi (2018) submitted unpublished

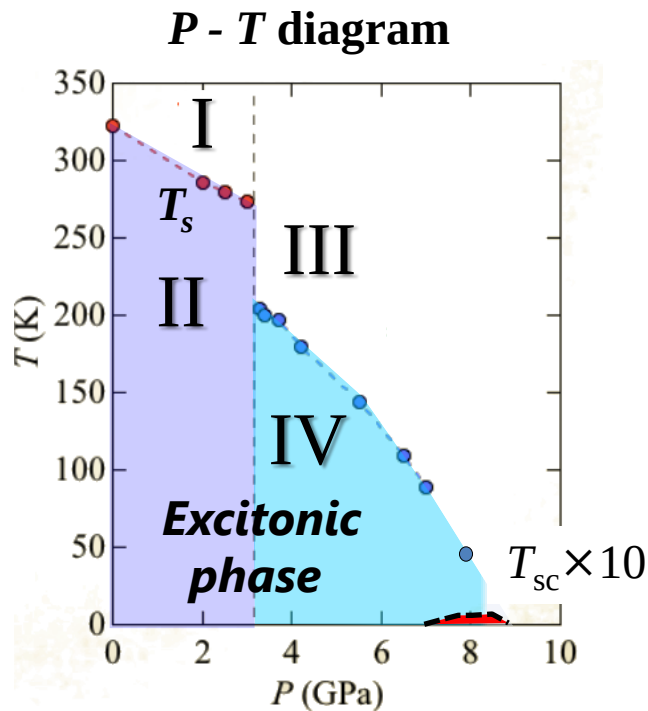


V. Phan, et al., *Phys. Rev. B* **81**, 205117 (2010).

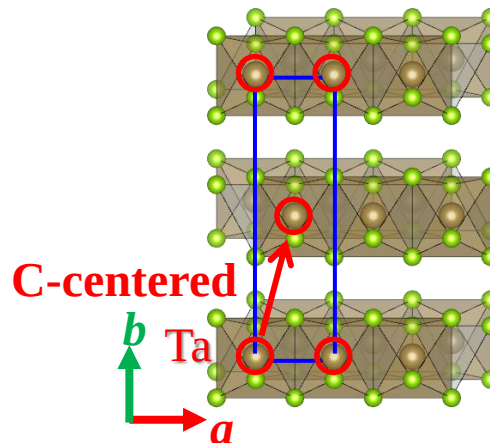
P - T phase diagram of Ta_2NiSe_5

Against Pressure

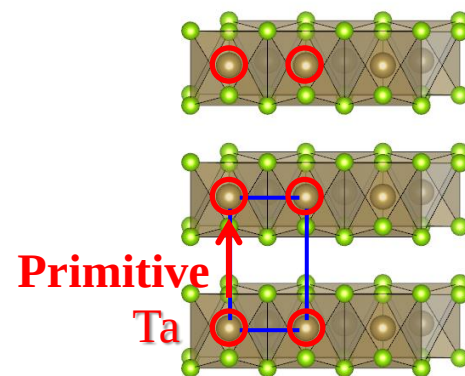
[A. Nakano et al., IUCrJ \(2018\). 5, 158-165](#)



$P < 3$ GPa



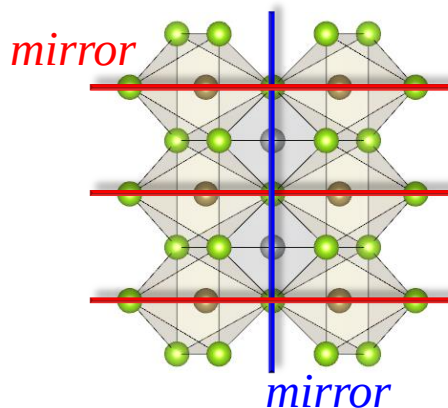
$P > 3$ GPa



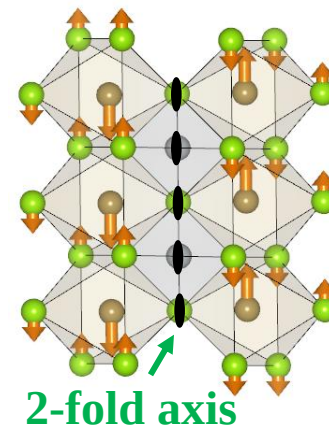
Against Temperature

[A. Nakano et al., PRB \(2018\). 98, 045139](#)

$T > T_s$: Orthorhombic



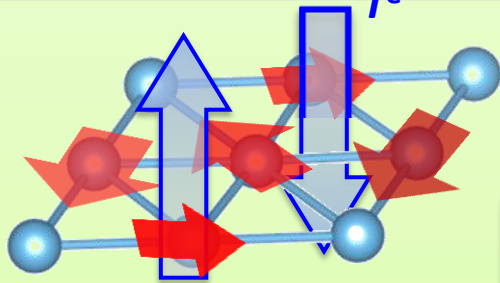
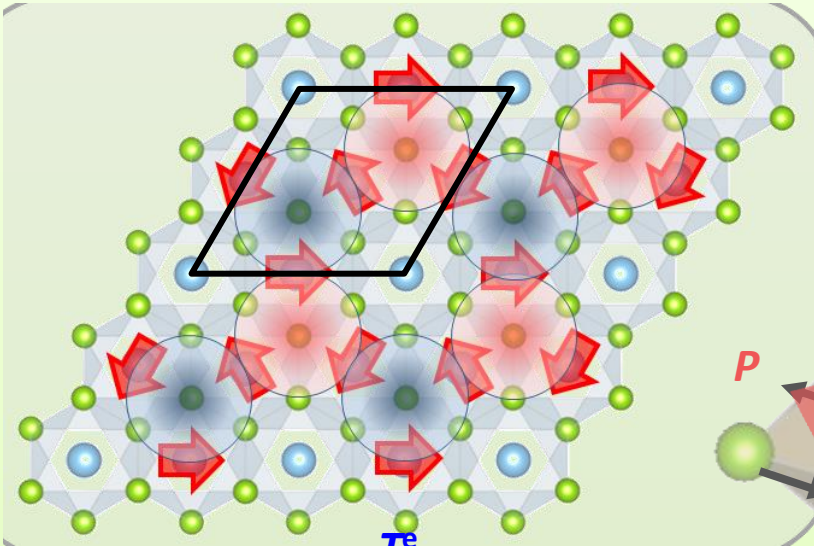
$T < T_s$: Monoclinic



**Excitonic phase continues
until high pressure region
including SC dome !**

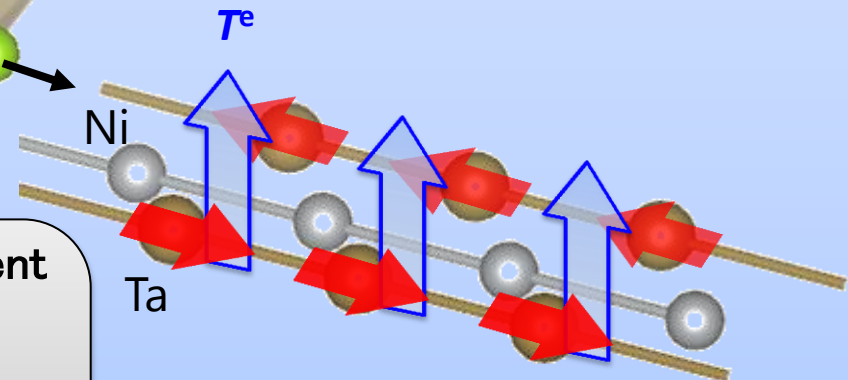
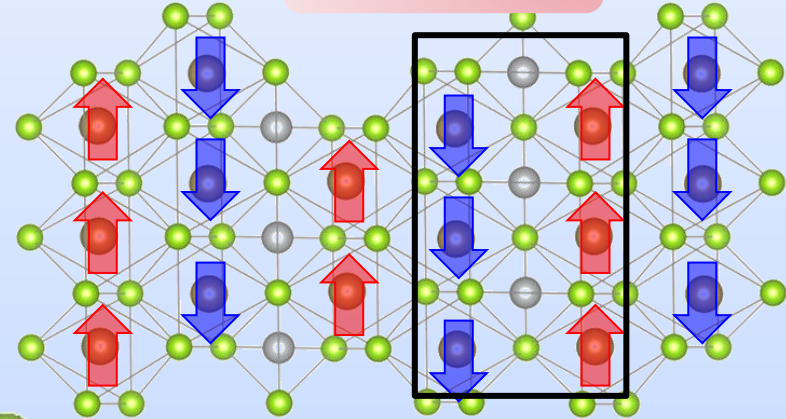
Electric Toroidal Moment in excitonic phase

1T-TiSe₂



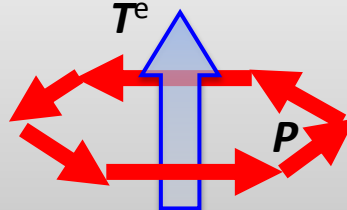
Antiferrotoroidic

Ta₂NiSe₅



Ferrotoroidic

Electric toroidal moment



τ^e : Electric Toroidal Moment

P : Electronic dipole

Thank you for your attention !!

If you need help for structural analysis or precise analysis,
please contact us !

