

# Evolution of the charge density wave in Sulfur substituted $1T$ -TiSe<sub>2</sub>

## *A combined ARPES and STM/STS study*

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Growth of Single Crystals :

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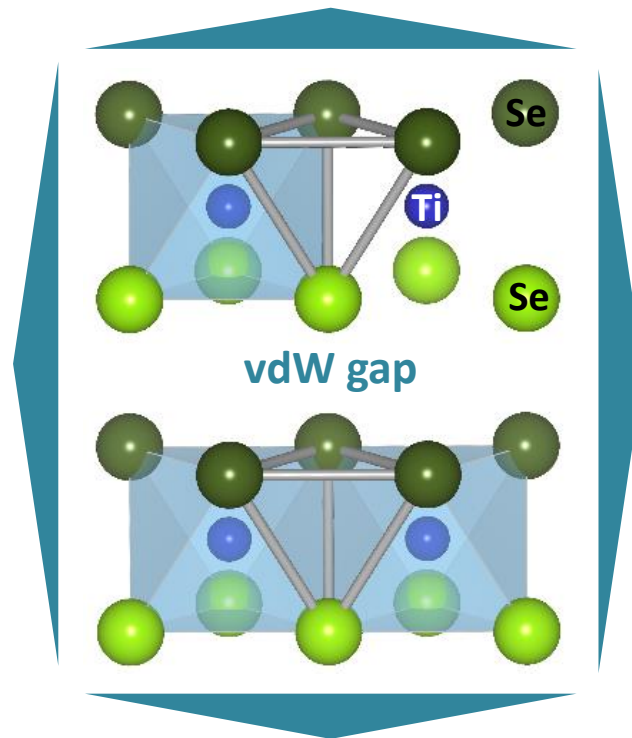
# Motivation

## 1T-TiSe<sub>2</sub> : an intriguing compound

### Charge Density Wave

$T_{\text{CDW}} \sim 200$  K, new 2x2x2 structure

F. Di Salvo, PRB, vol. **14**, 4321 (1976)



### Superconductivity

Cu doped 1T-TiSe<sub>2</sub>

E. Morosan, Nat. Phys. **2**, 544 (2006)

Under pressure

A. F. Kusmartseva, PRL, vol. **103**, 236401 (2009)

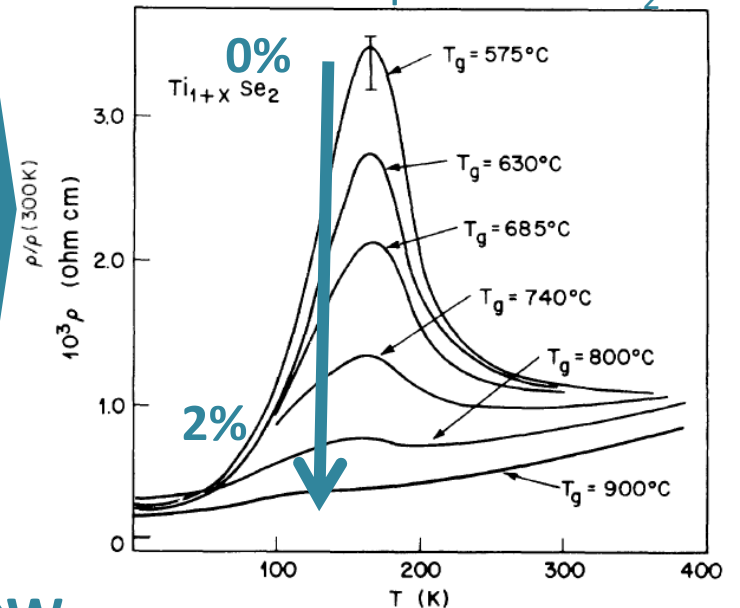
### Local resilience of the CDW

In Ti self-doped 1T-TiSe<sub>2</sub>

B. Hildebrand, PRB, vol. **95**, 081104 (2017)

### Anomalous resistivity

Ti self-doped 1T-TiSe<sub>2</sub>



F. Di Salvo, PRB, vol. **14**, 4321 (1976)

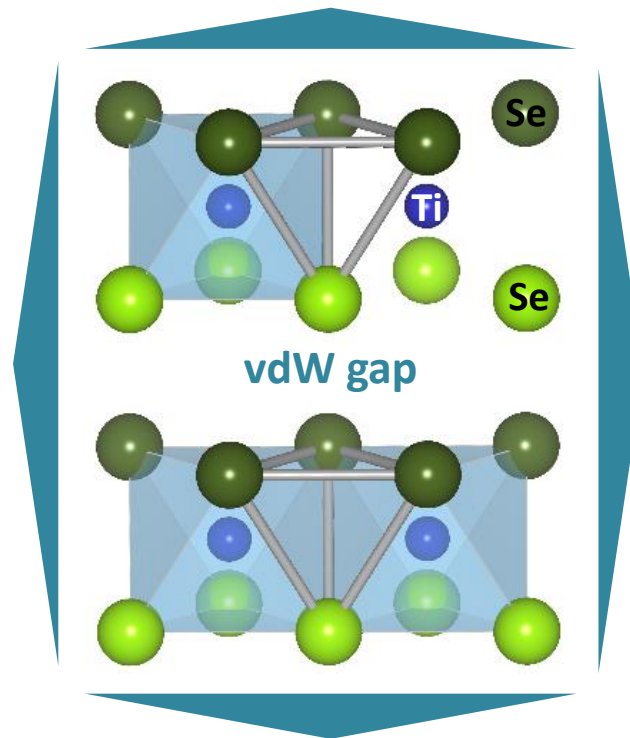
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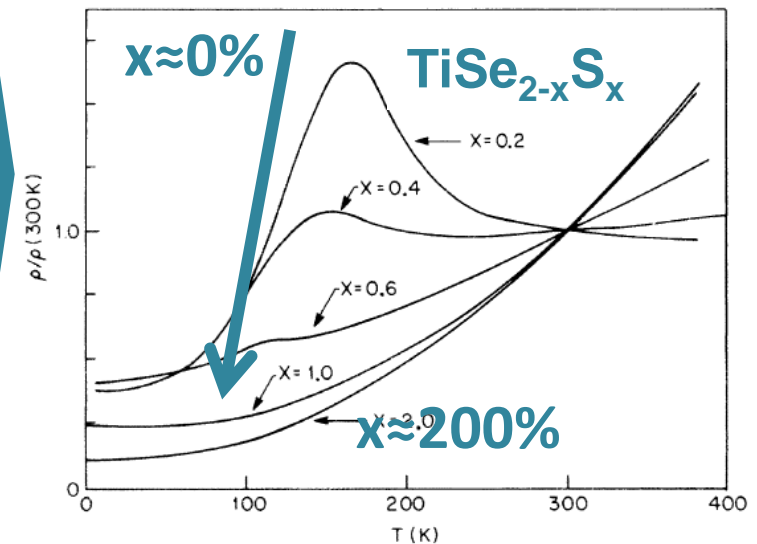
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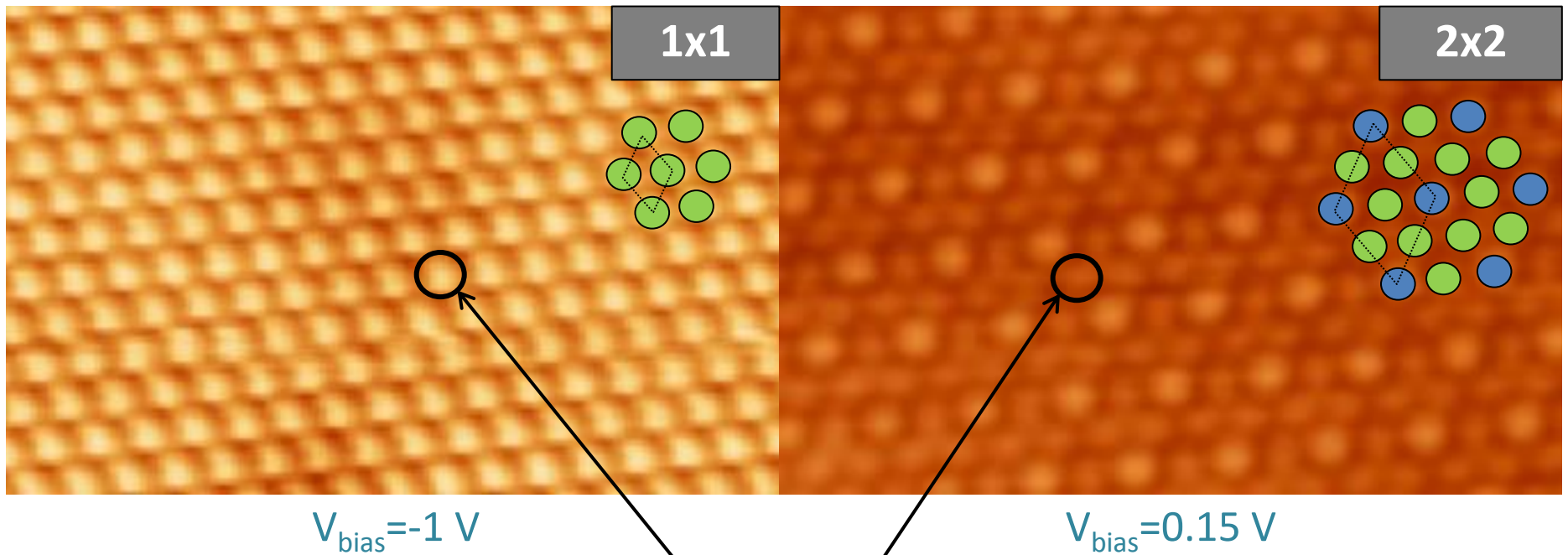


F. Di Salvo, PRB, vol. **14**, 4321 (1976)

Influence of Sulfur on the transition temperature and CDW behavior?

# STM on $1T\text{-TiSe}_{2-x}\text{S}_x$

Real space

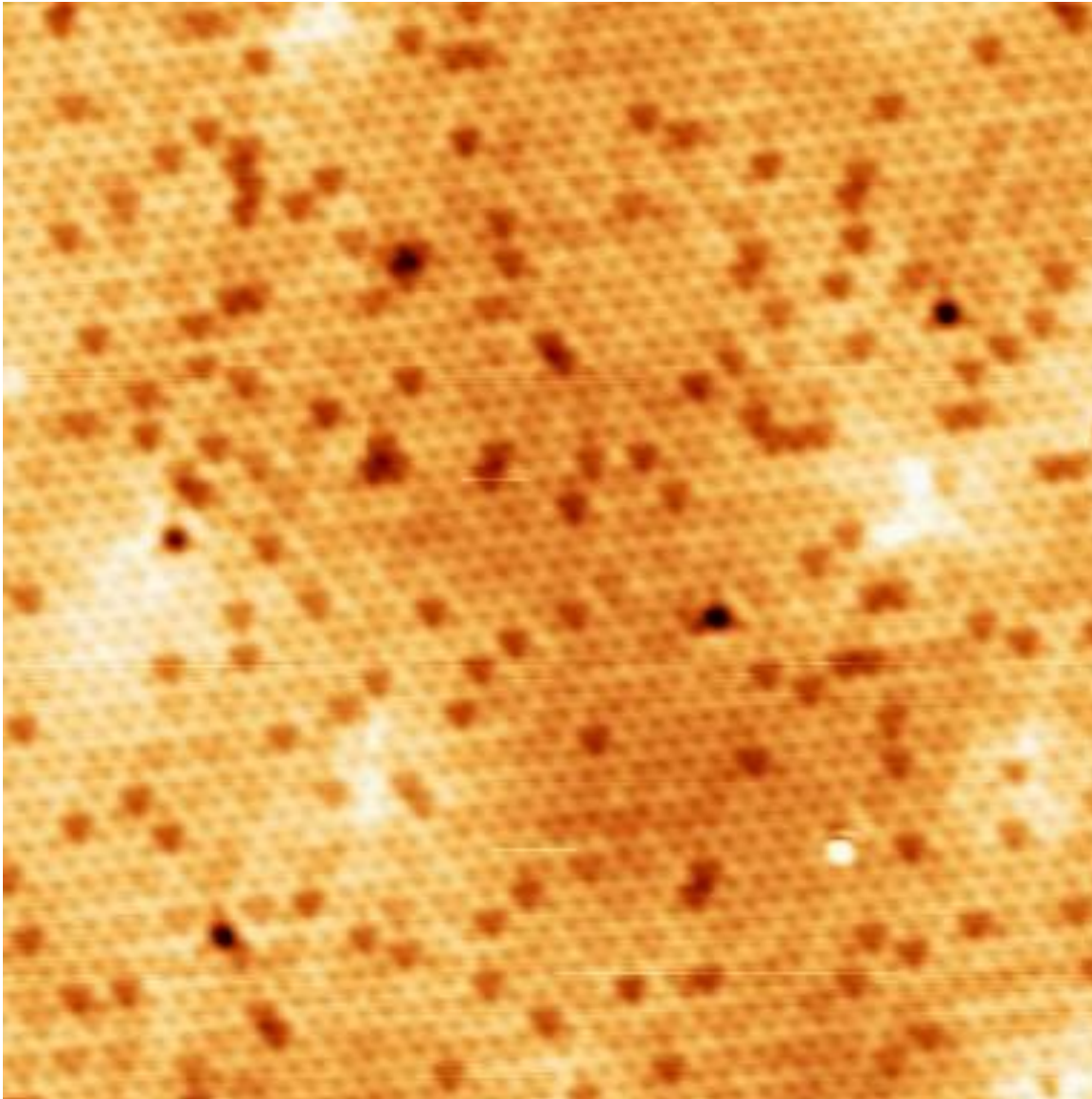


The topmost layer of  $1T\text{-TiSe}_2$  is a Se layer.

# Characterization of samples $1T\text{-TiSe}_{2-x}\text{S}_x$

## Identification of S atoms

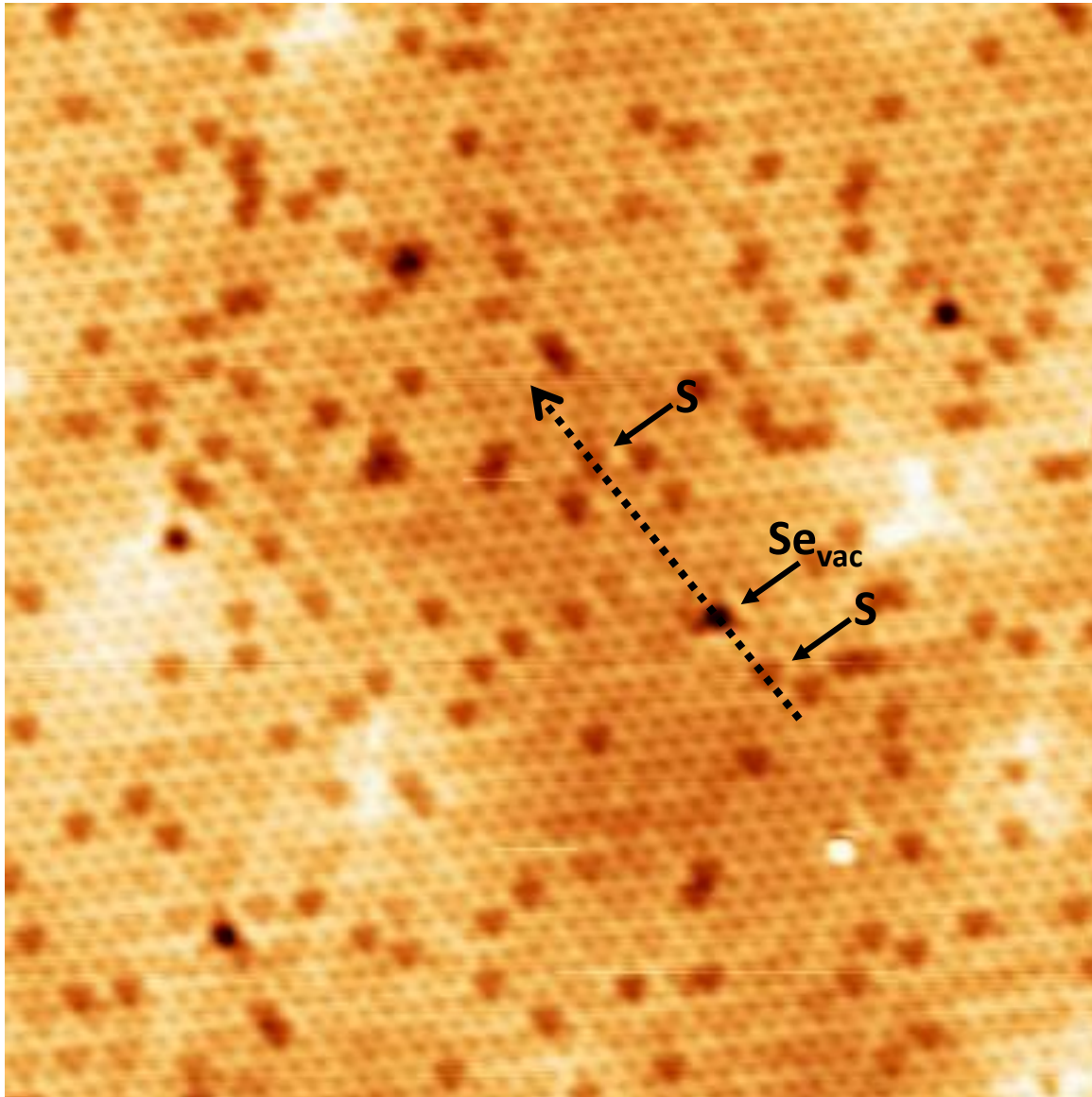
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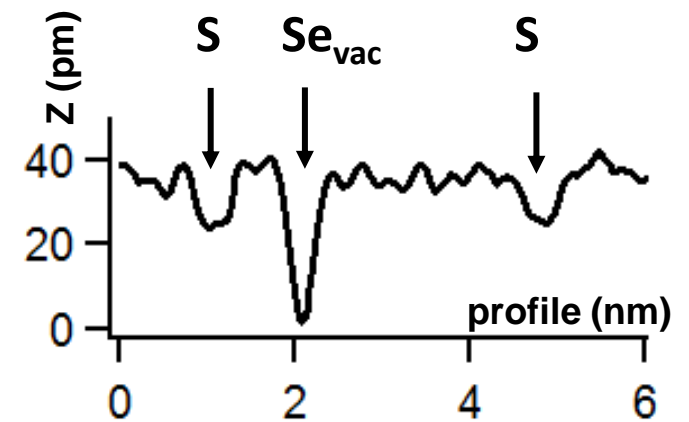
$V_{\text{bias}} +0.6 \text{ V}$ ,  $I_t = 0.15 \text{ nA}$ ,  $15 \times 15 \text{ nm}^2$  at **4.5 K**

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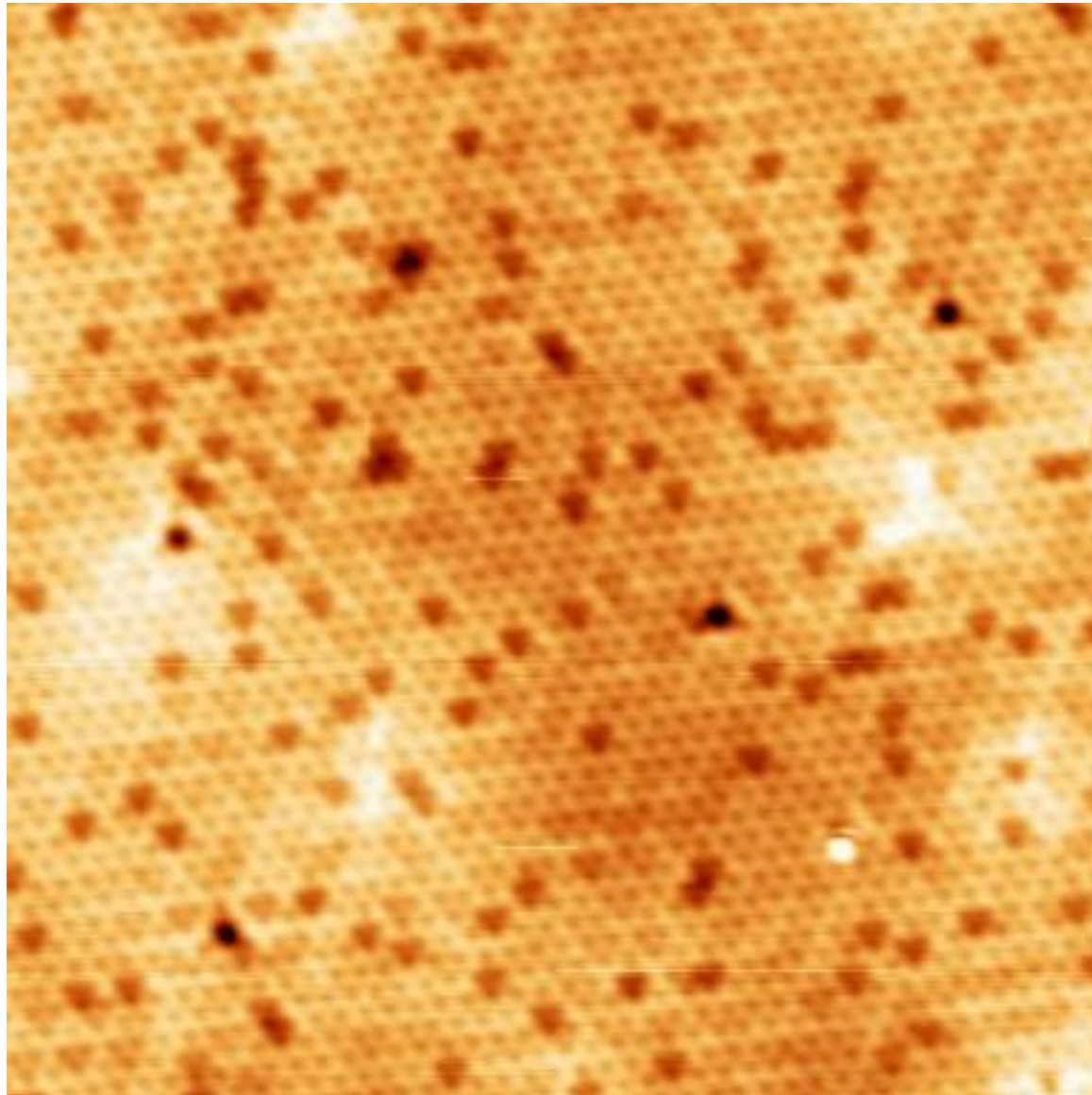
S substitution – Se vacancy distinction



$V_{\text{bias}} + 0.6 \text{ V}$ ,  $I_t = 0.15 \text{ nA}$ ,  $15 \times 15 \text{ nm}^2$  at  $4.5 \text{ K}$

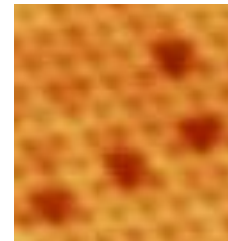
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$V_{\text{bias}} + 0.6 \text{ V}$ ,  $I_t = 0.15 \text{ nA}$ ,  $15 \times 15 \text{ nm}^2$  at  $4.5 \text{ K}$

Sulfur depletion of  $\sim 14 \text{ pm}$



$V_{\text{bias}} + 0.6 \text{ V}$



$V_{\text{bias}} + 0.3 \text{ V}$

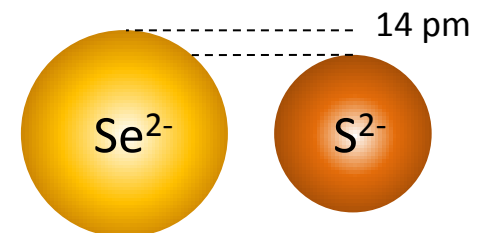


$V_{\text{bias}} - 0.5 \text{ V}$



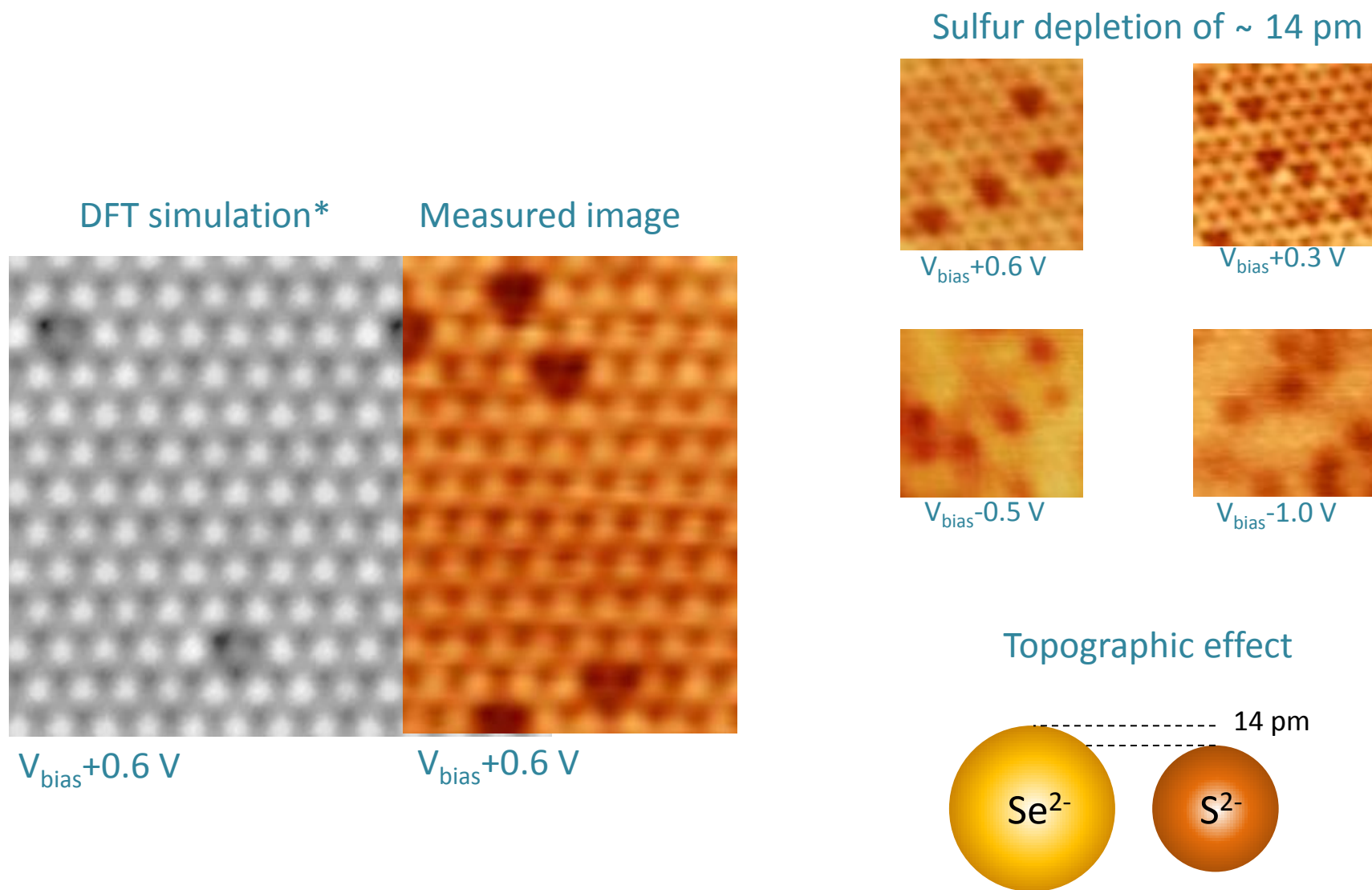
$V_{\text{bias}} - 1.0 \text{ V}$

Topographic effect



# Characterization of samples $1T\text{-TiSe}_{2-x}\text{S}_x$

## Identification of S atoms

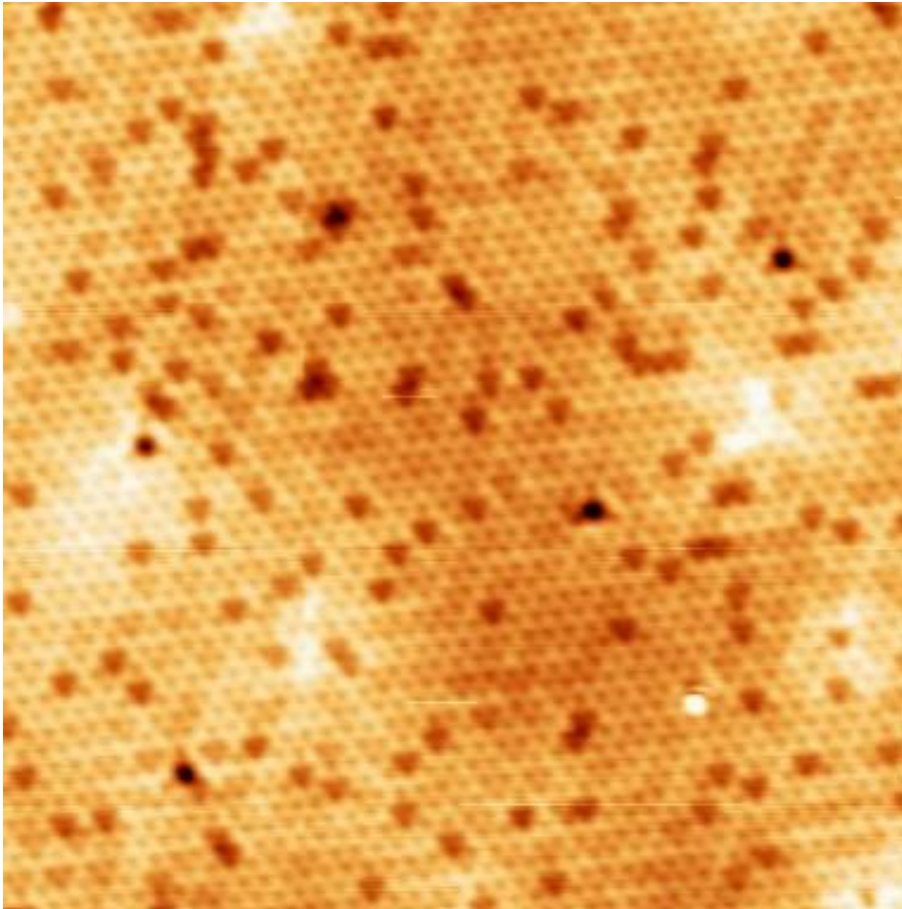




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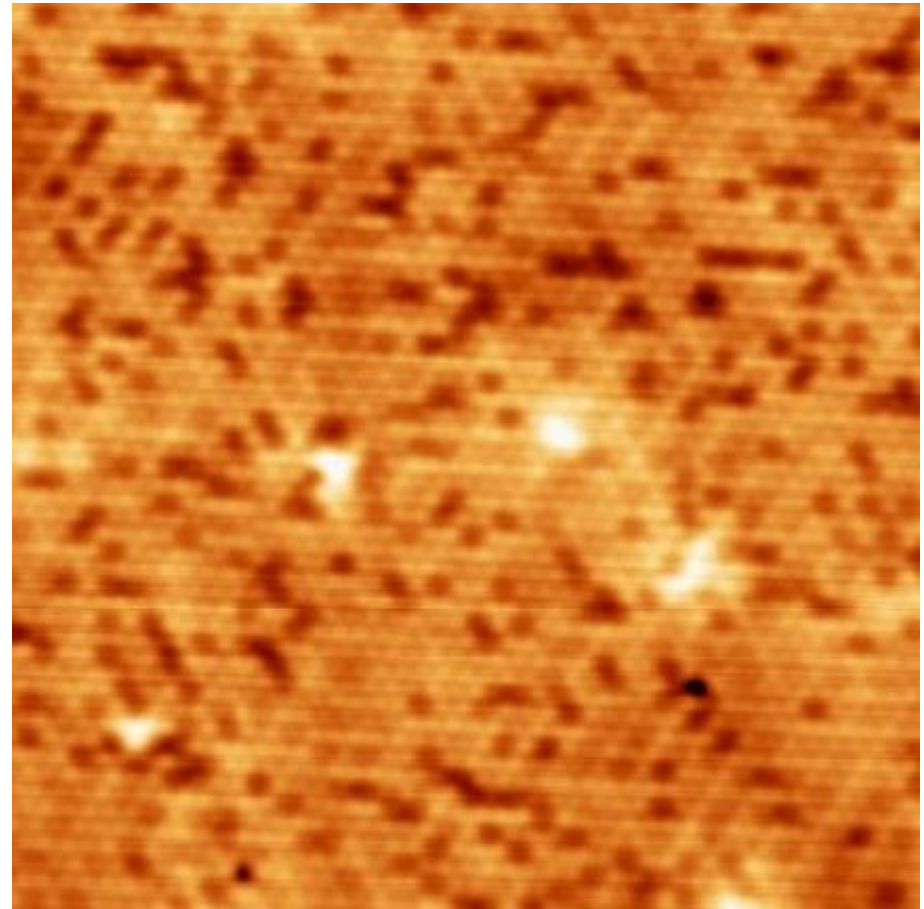
Precise determination of Sulfur concentrations

$x = 0.12$



$V_{\text{bias}} + 0.6 \text{ V}$ ,  $I_t = 0.15 \text{ nA}$ ,  $15 \times 15 \text{ nm}^2$  at  $4.5 \text{ K}$

$x = 0.34$

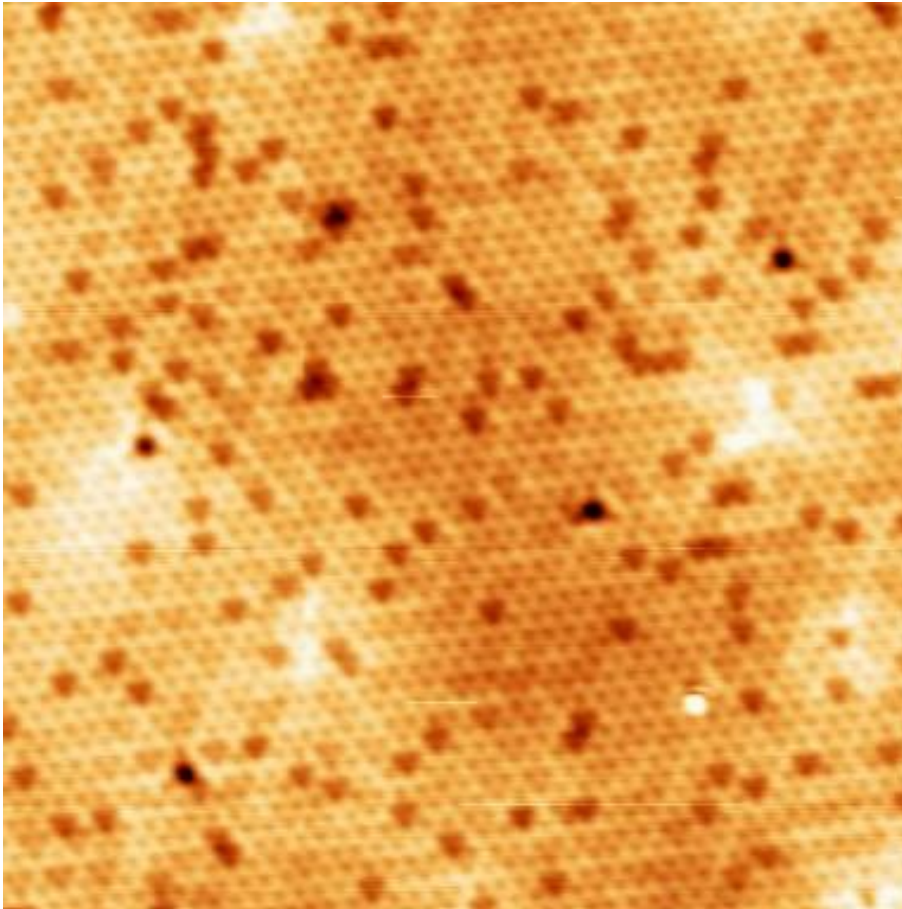


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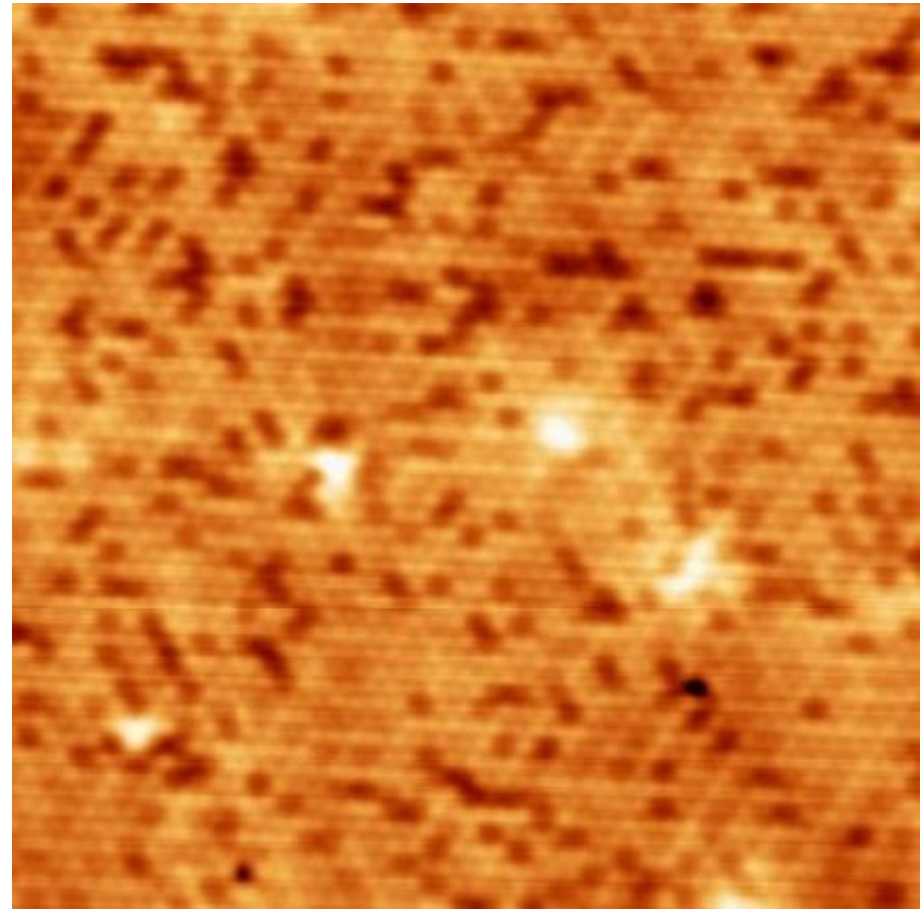
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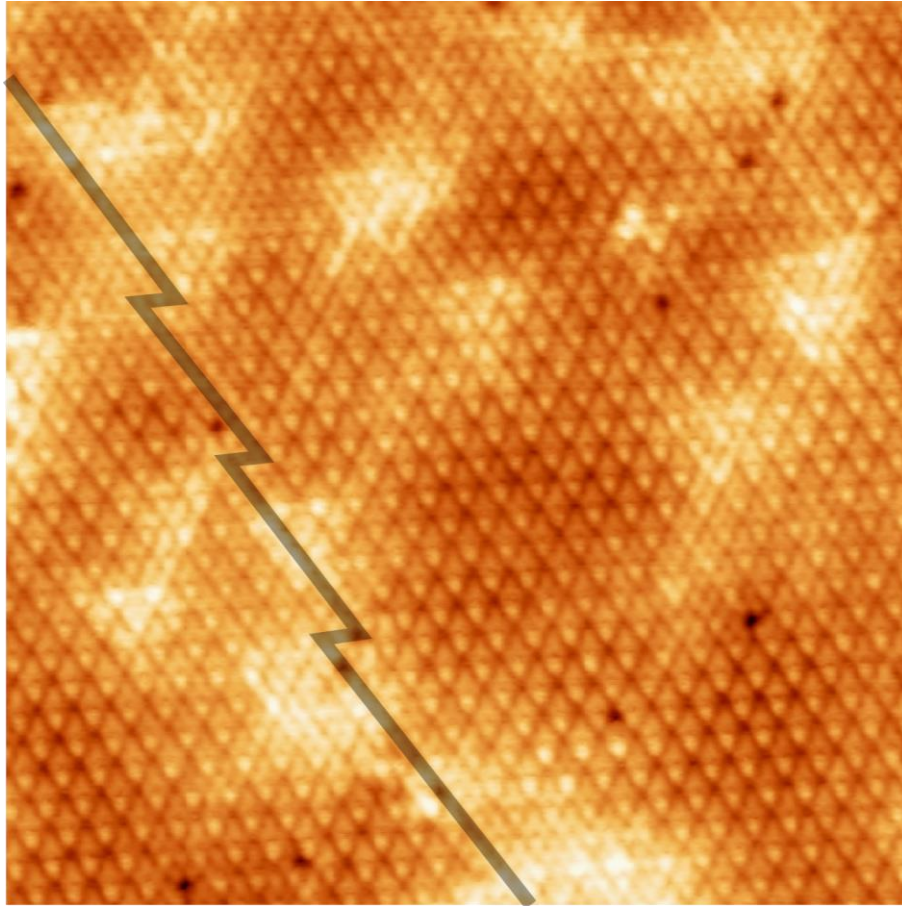


Ensure negligible Intercalated-Ti concentration

# Characterization of samples $1T\text{-TiSe}_{2-x}\text{S}_x$

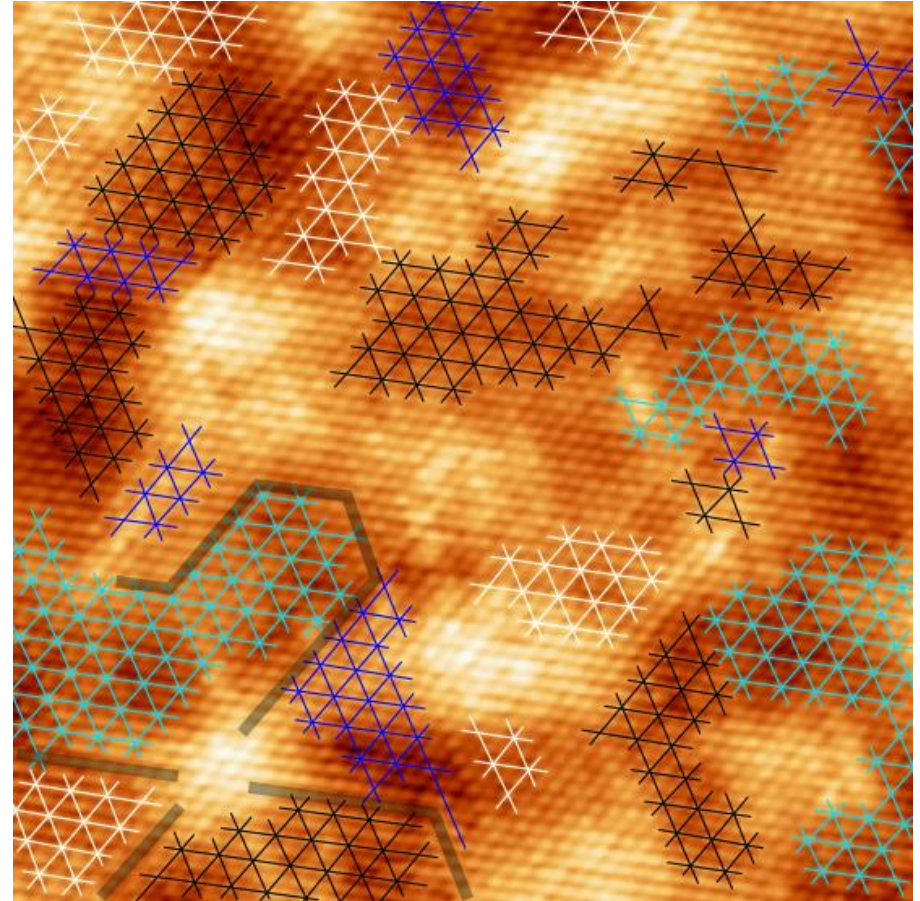
## Effect of intercalated-Ti

~ 1.2 % intercalated-Ti (no sulfur)



$V_{\text{bias}} 0.1 \text{ V}$ ,  $I_t = 0.2 \text{ nA}$ ,  $17 \times 17 \text{ nm}^2$  at **4.5 K**

~ 2.5 % intercalated-Ti (no sulfur)



$V_{\text{bias}} -0.05 \text{ V}$ ,  $I_t = 0.2 \text{ nA}$ ,  $17 \times 17 \text{ nm}^2$  at **4.5 K**

Phase-shifted domains : break of the CDW long-range coherence

B. Hildebrand, PRB, vol. **93**, 125140 (2016)

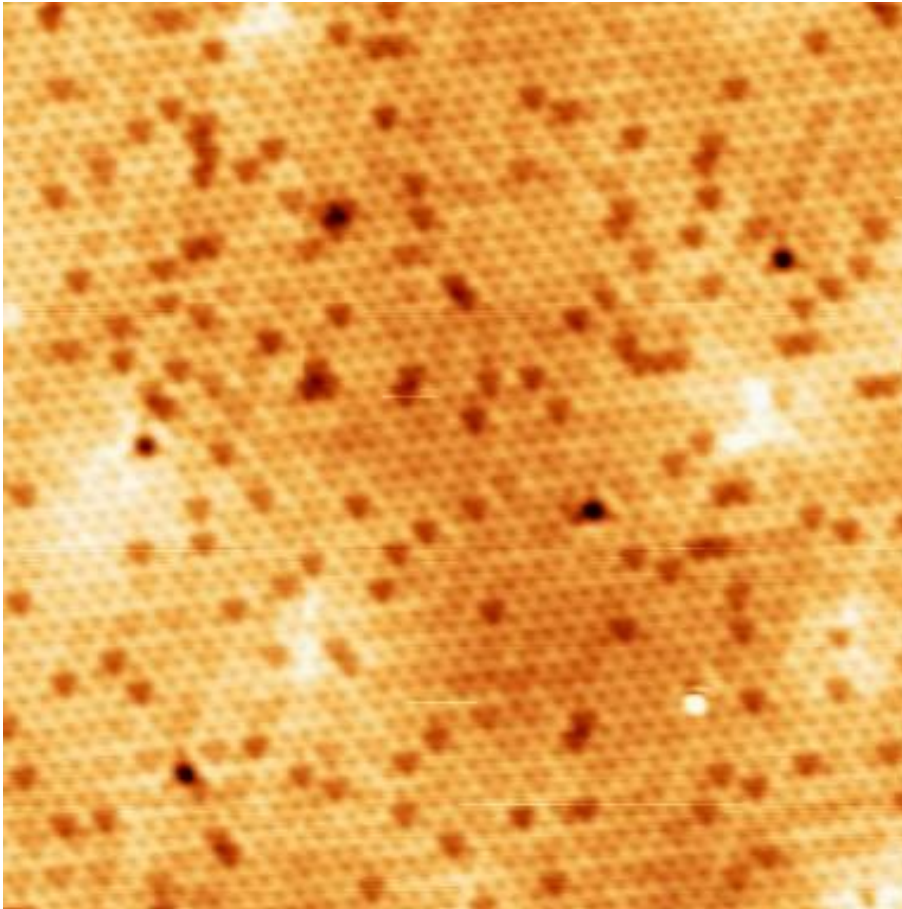


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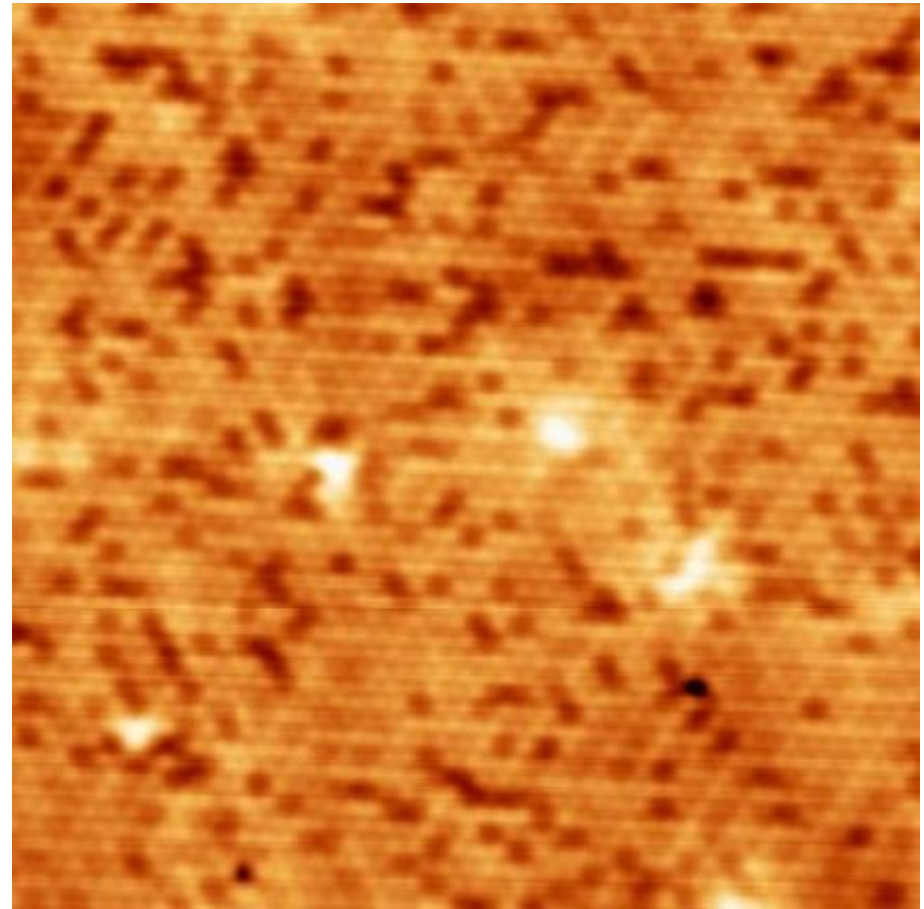
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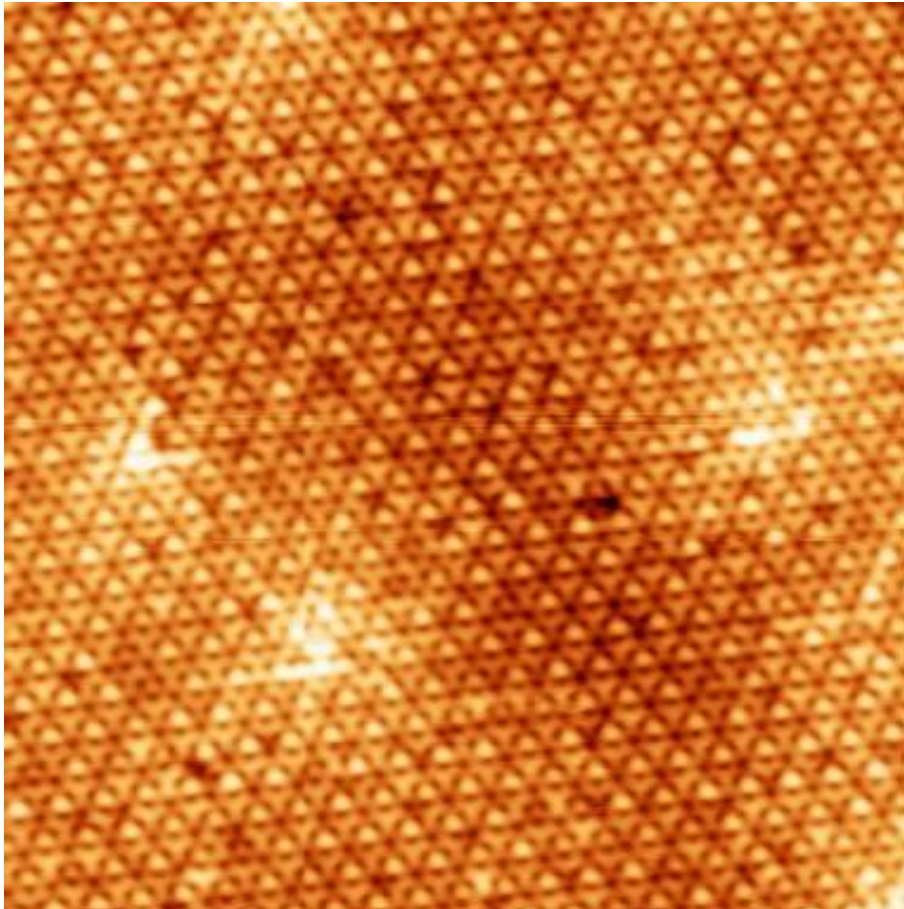
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Less than 0.2% of intercalated-Ti  $\rightarrow$  effects of Sulfur substitution only

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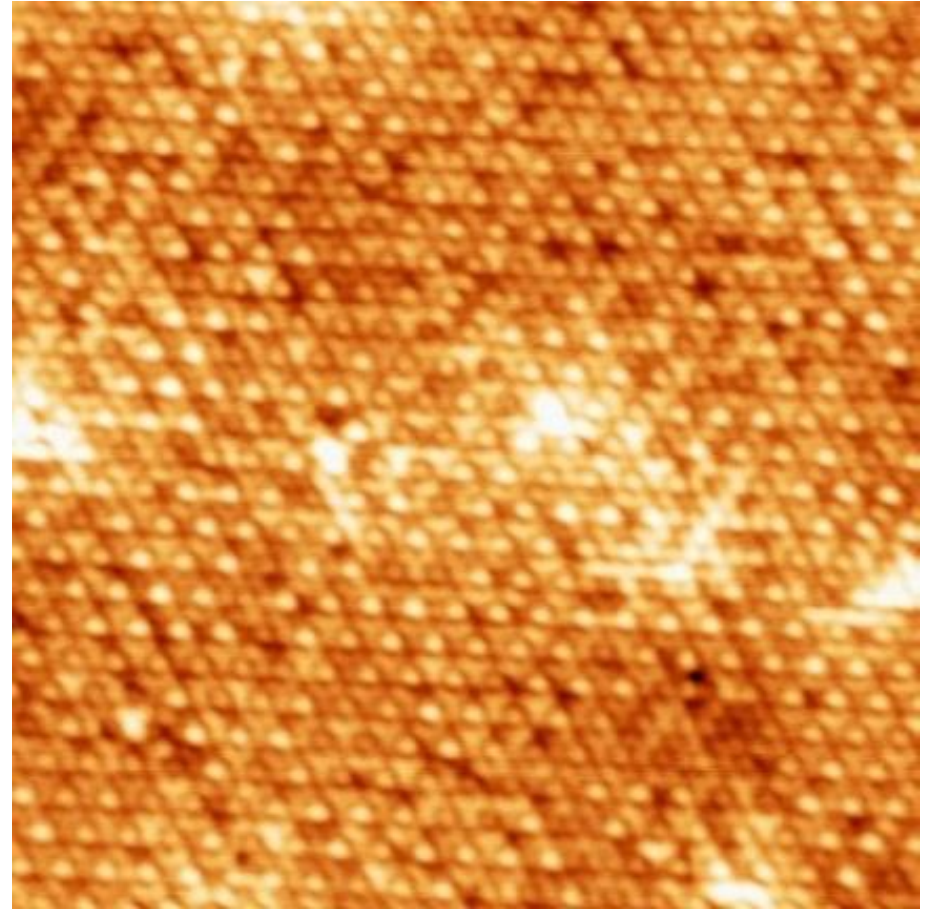
Long-range coherence of the CDW

$x = 0.12$



$V_{\text{bias}} + 0.15 \text{ V}$ ,  $I_t = 0.15 \text{ nA}$ ,  $15 \times 15 \text{ nm}^2$  at  $4.5 \text{ K}$

$x = 0.34$



$V_{\text{bias}} + 0.15 \text{ V}$ ,  $I_t = 0.15 \text{ nA}$ ,  $15 \times 15 \text{ nm}^2$  at  $4.5 \text{ K}$

Inexistence of phase-slip

Long-range coherence of the  $2 \times 2$  in-plane electronic modulation

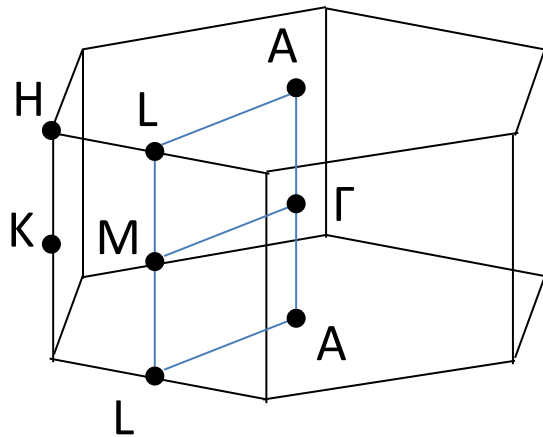
What about ARPES measurements ?

# ARPES on 1T-TiSe<sub>2</sub>

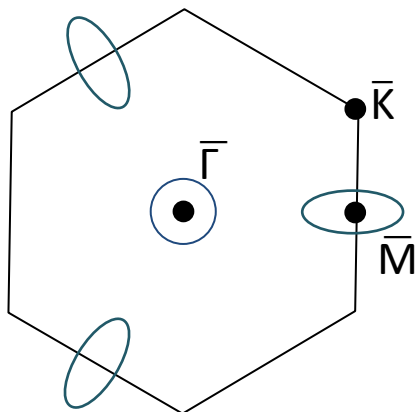
## Reciprocal space

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Brillouin zone of the 1x1x1 structure



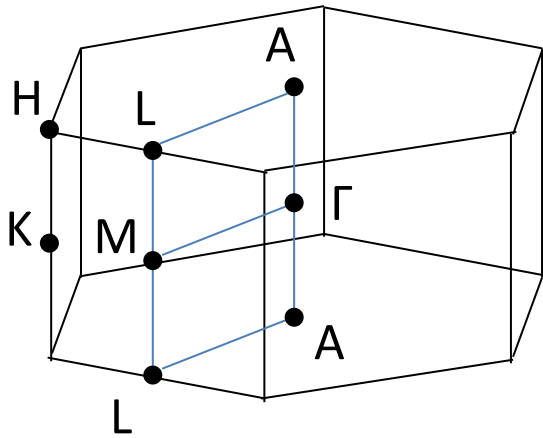
Top view  
near- $E_F$  band structure



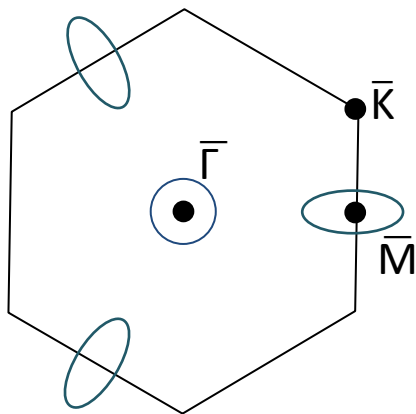
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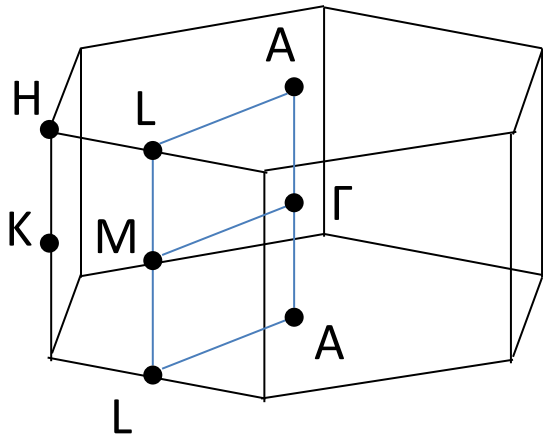
T-dependent ARPES study from  $T_{\text{ROOM}}$  to 10 K

UPS with He I,  $E_{h\nu} = 21.2$  eV (close to **A** and **L** points)

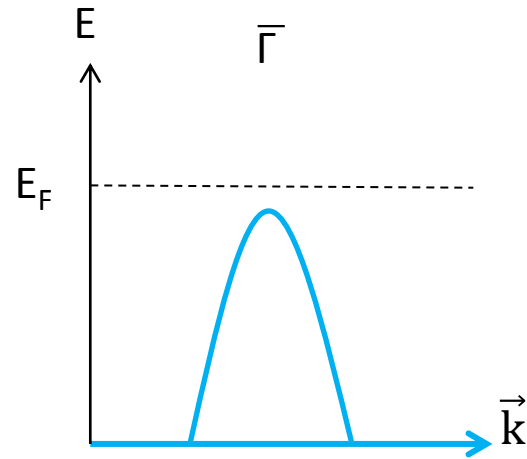
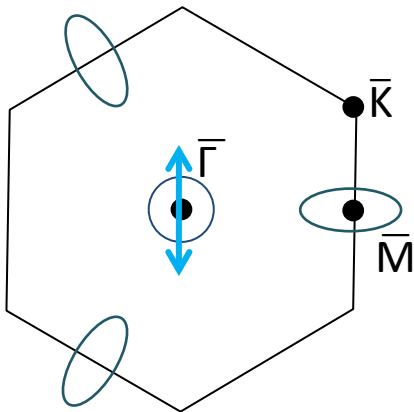
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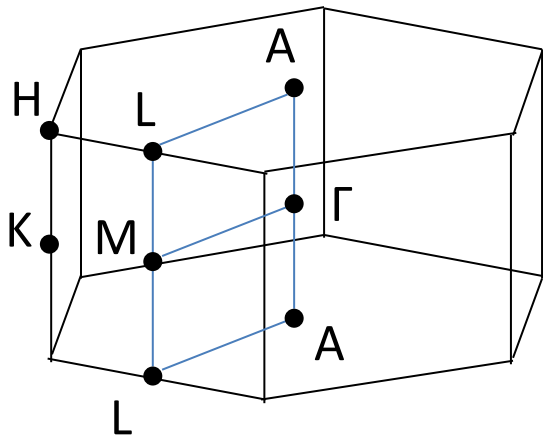
- Se 4p VB at  $\bar{\Gamma}$  (Cut //  $\bar{\Gamma} - \bar{K}$ )



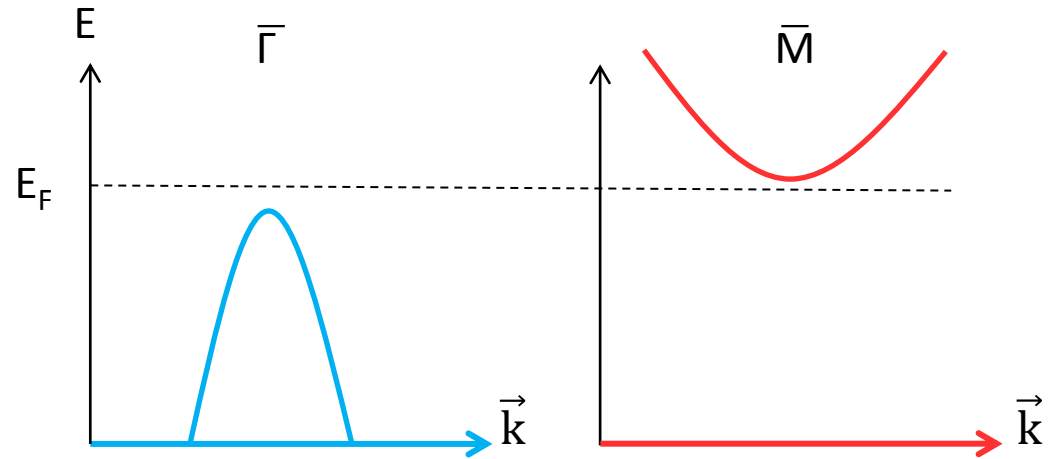
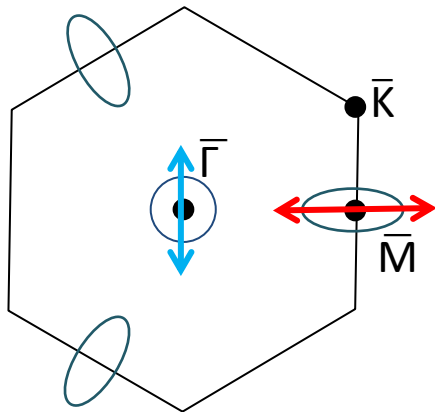
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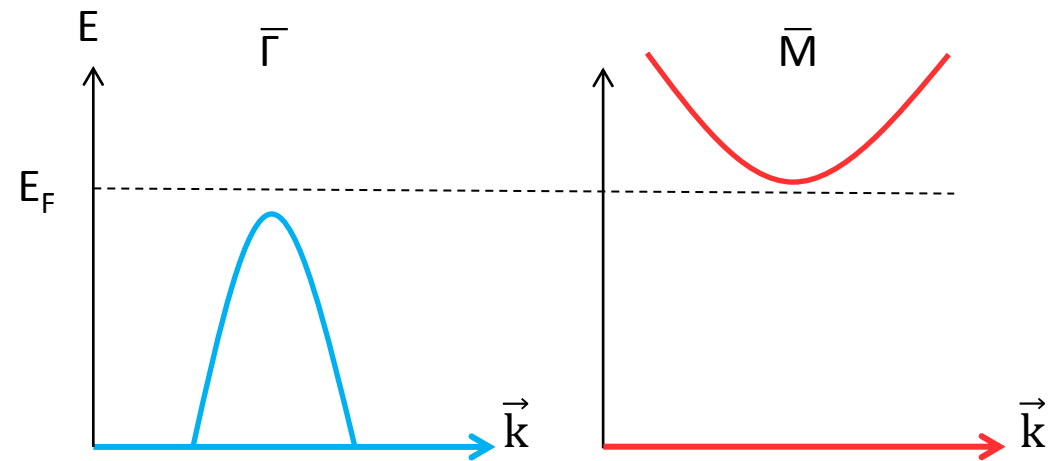
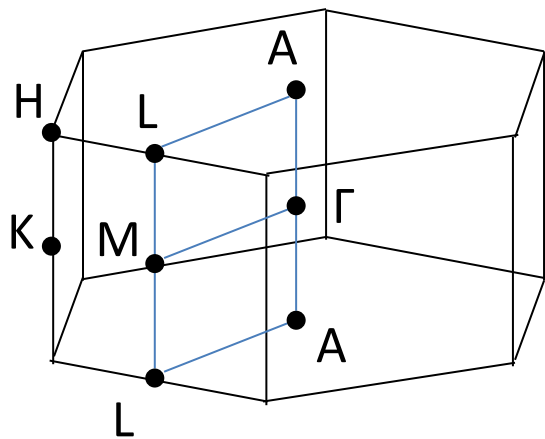
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- Se 4p VB at  $\bar{\Gamma}$  (Cut //  $\bar{\Gamma} - \bar{K}$ )
- Ti 3d CB at  $\bar{M}$  (Cut //  $\bar{\Gamma} - \bar{M}$  (long axis))

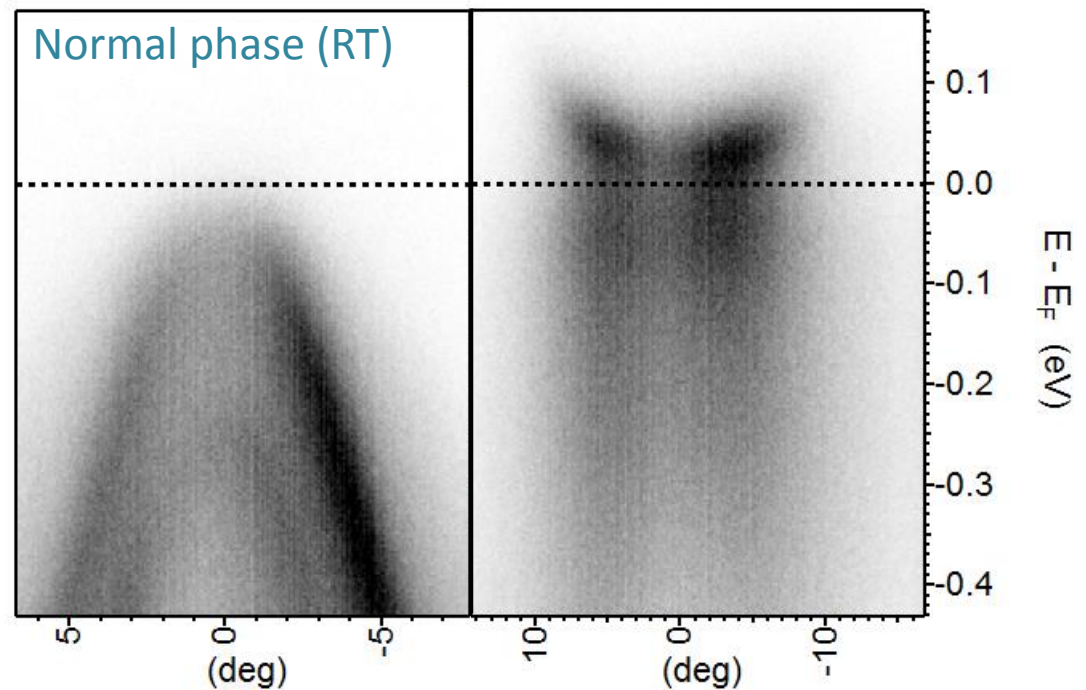
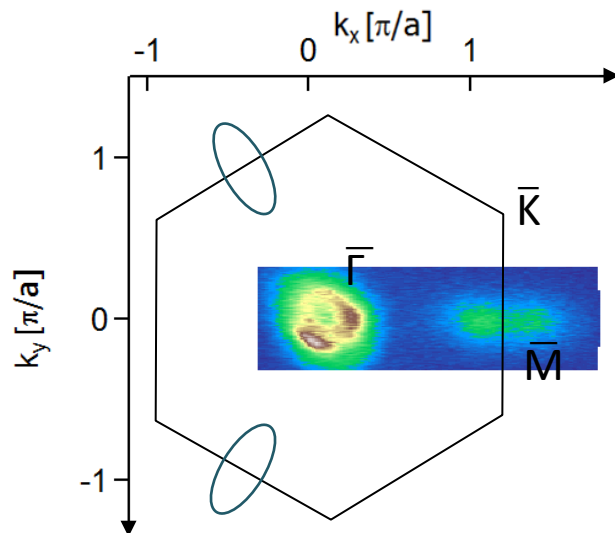
# ARPES on 1T-TiSe<sub>2</sub>

Pristine at RT

Brillouin zone of the 1x1x1 structure



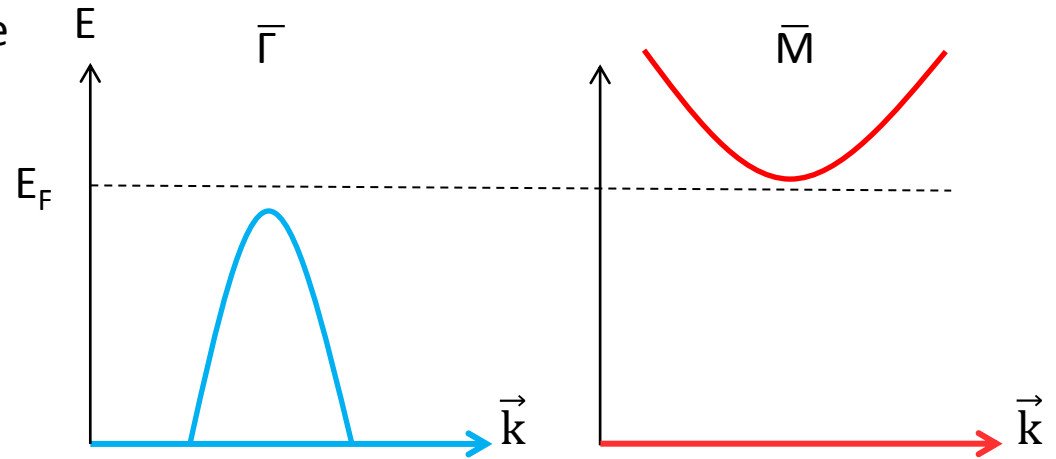
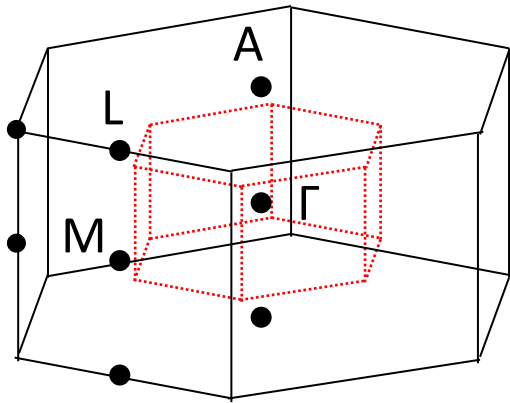
-0.33 eV below E<sub>F</sub>



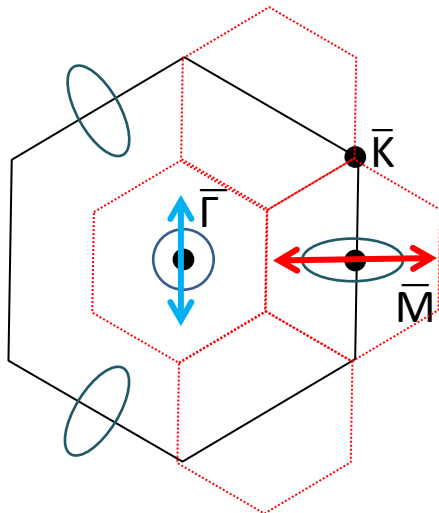
# ARPES on 1T-TiSe<sub>2</sub>

CDW phase

Reduced Brillouin zone of the 2x2x2 structure



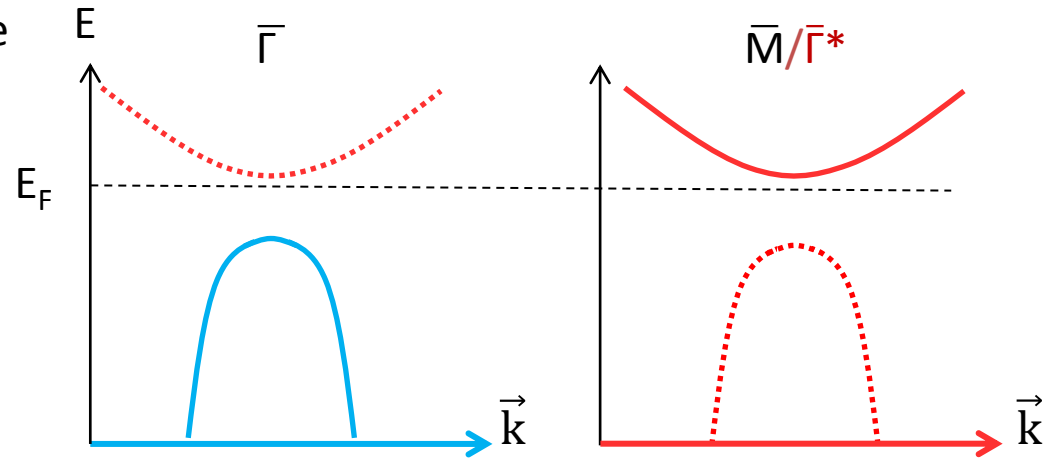
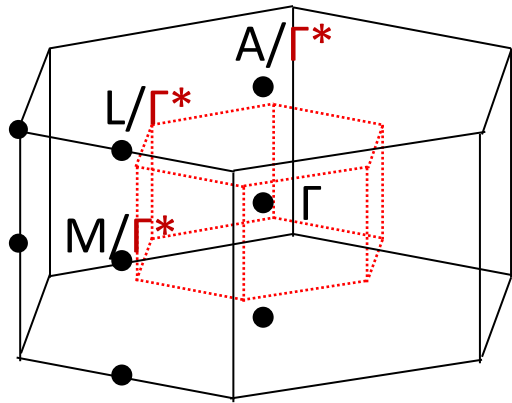
Top view  
near- $E_F$  band structure



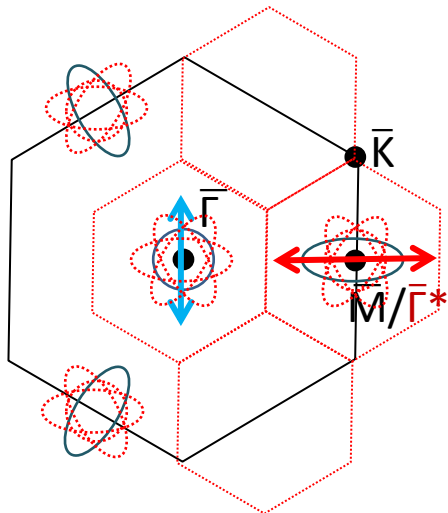
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CDW phase

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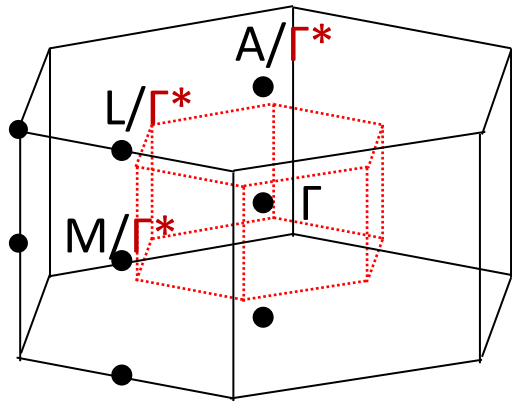
Top view  
near-EF band structure



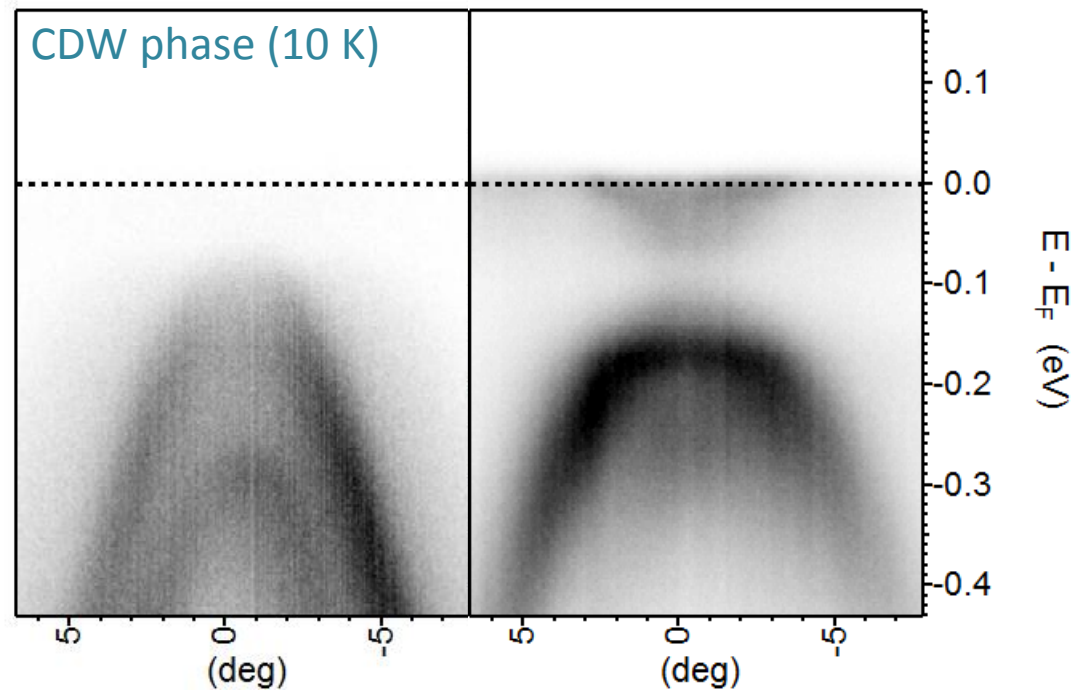
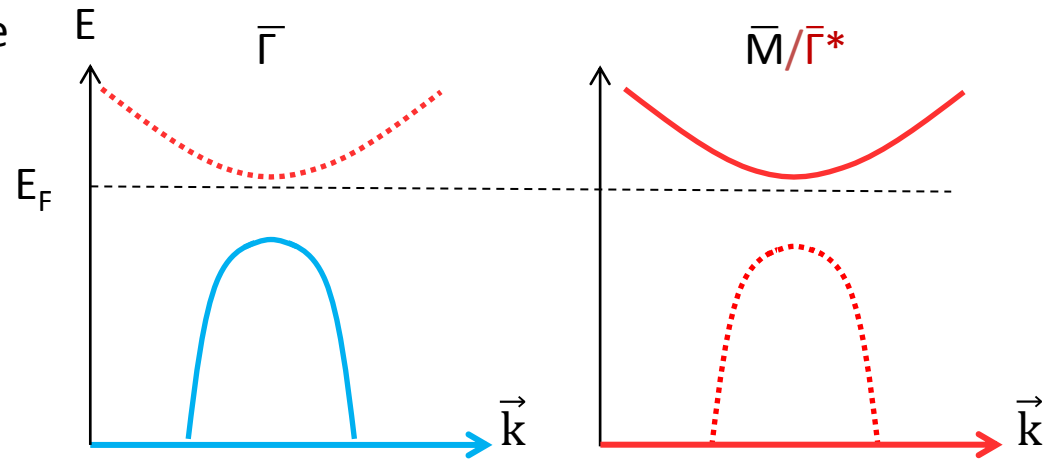
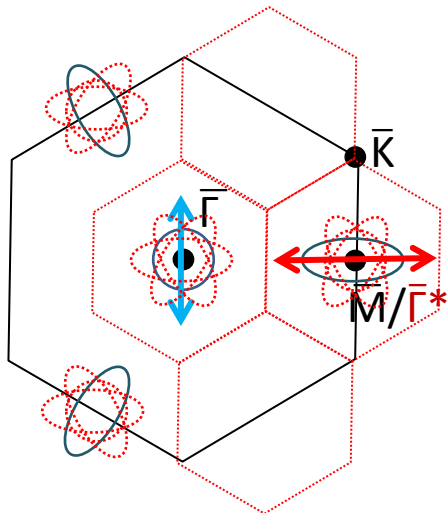
# ARPES on 1T-TiSe<sub>2</sub>

Pristine at 10 K

Reduced Brillouin zone of the 2x2x2 structure



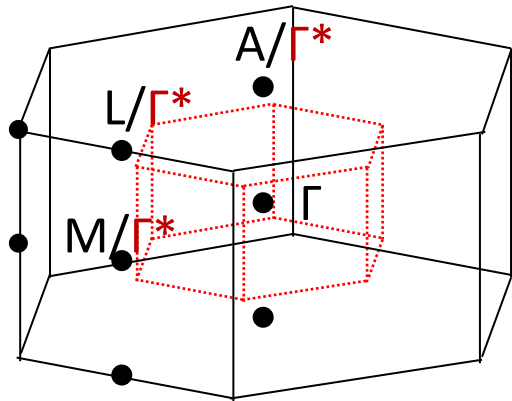
Top view  
near-EF band structure



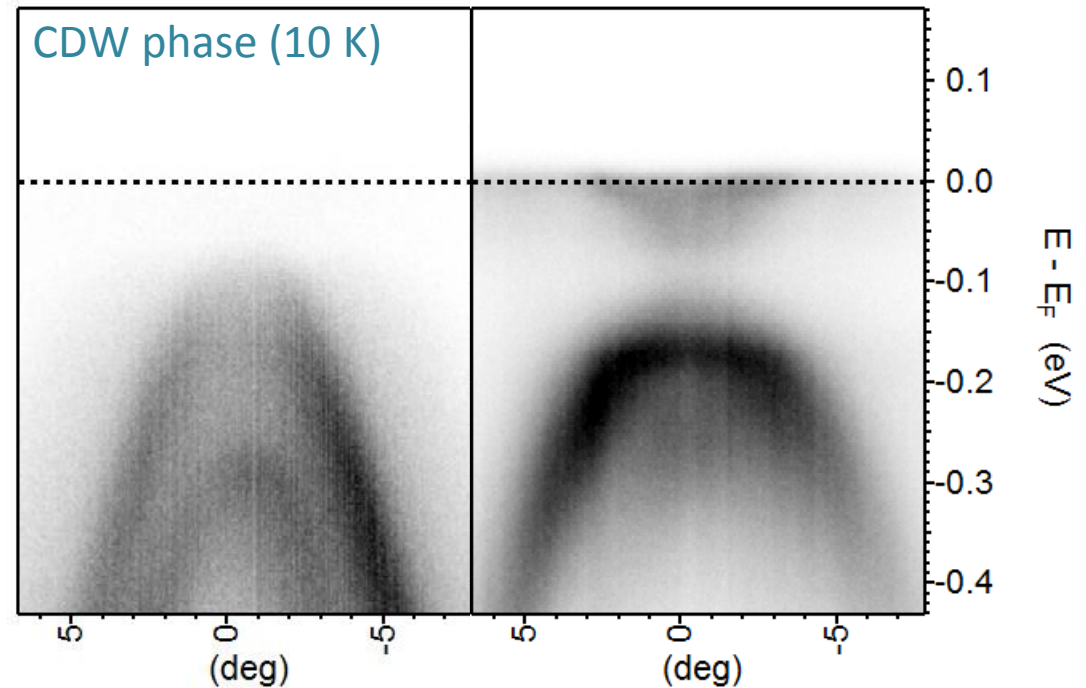
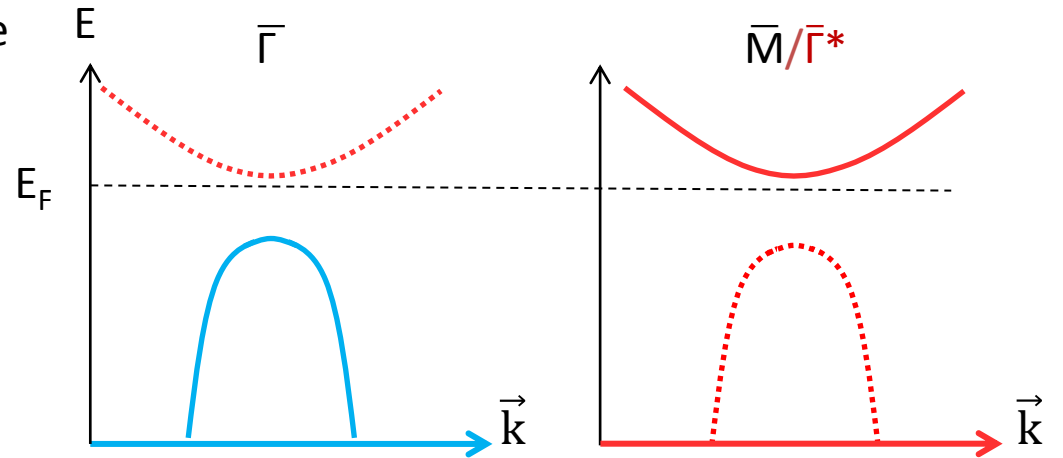
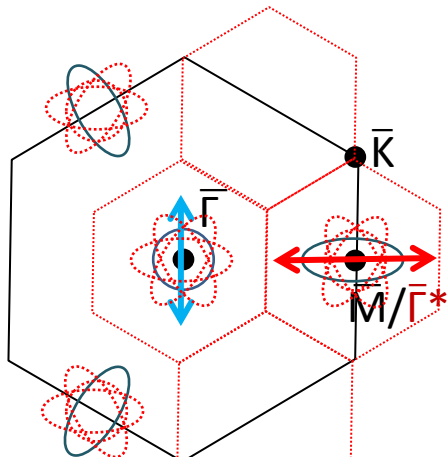
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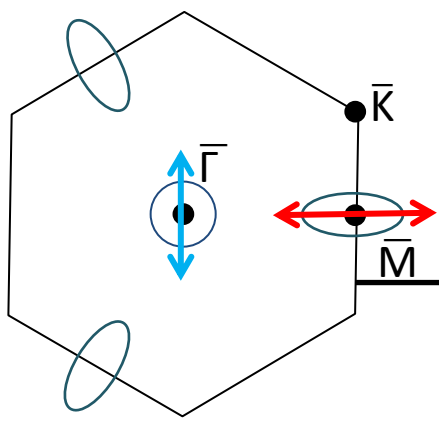
Top view  
near-EF band structure



Semiconductor or semimetal ?

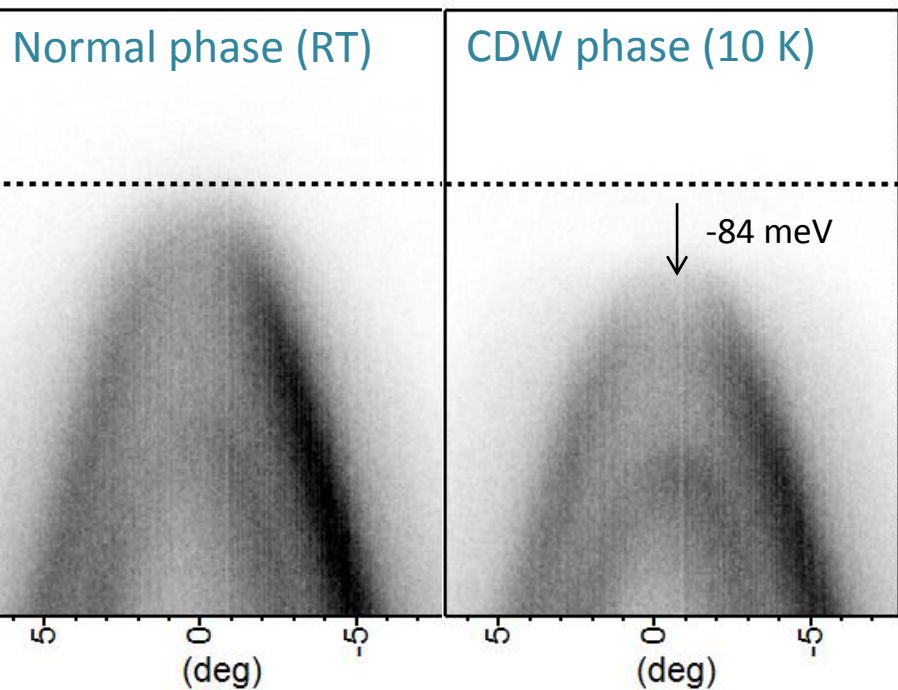
# ARPES on 1T-TiSe<sub>2</sub>

Pristine

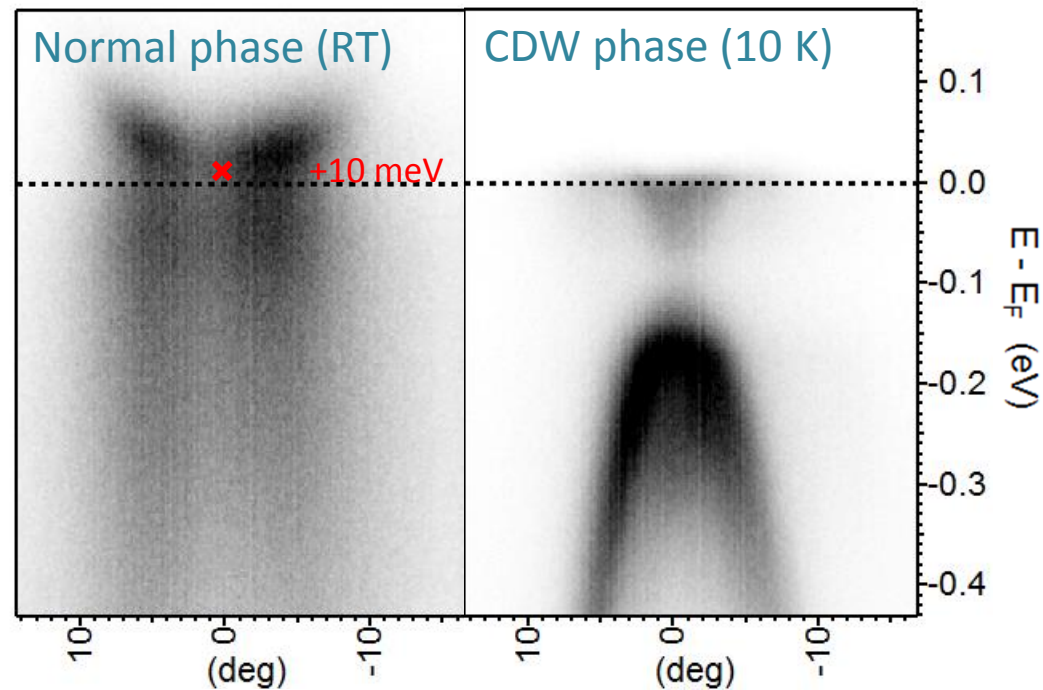


$\bar{\Gamma}$

$\bar{M}$



Se 4p VB slightly below  $E_F$

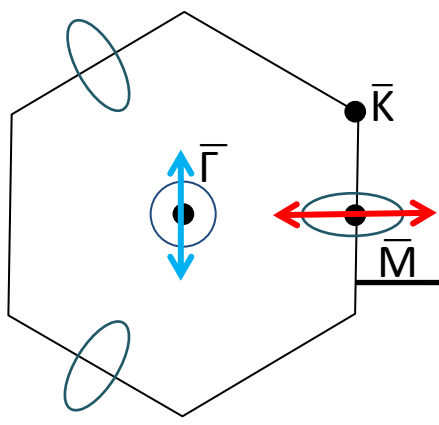


Ti 3d CB above  $E_F$

Semiconductor at  $T_{\text{ROOM}}$

# ARPES on 1T-TiSe<sub>2</sub>

Pristine



$\bar{\Gamma}$

$\bar{M}$

Normal phase (RT)

CDW phase (10 K)

0.1

0.0

-0.1

-0.2

-0.3

-0.4

$E - E_F$  (eV)

5

(deg)

5

(deg)

-84 meV

Se 4p VB slightly below  $E_F$

Normal phase (RT)

CDW phase (10 K)

0.1

0.0

-0.1

-0.2

-0.3

-0.4

$E - E_F$  (eV)

10

(deg)

-10

(deg)

-10

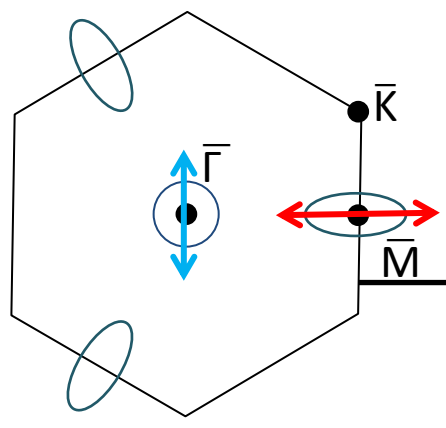
+10 meV

Ti 3d CB above  $E_F$

Semiconductor at  $T_{\text{ROOM}}$

Doped samples?



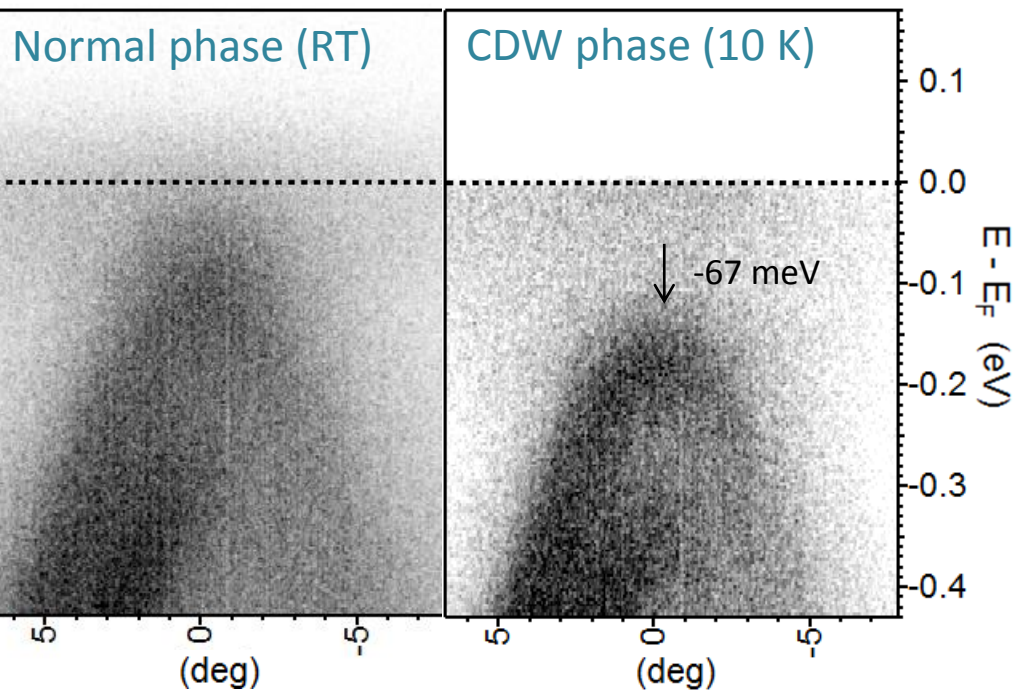


# ARPES on 1T-TiSe<sub>2-x</sub>S<sub>x</sub>

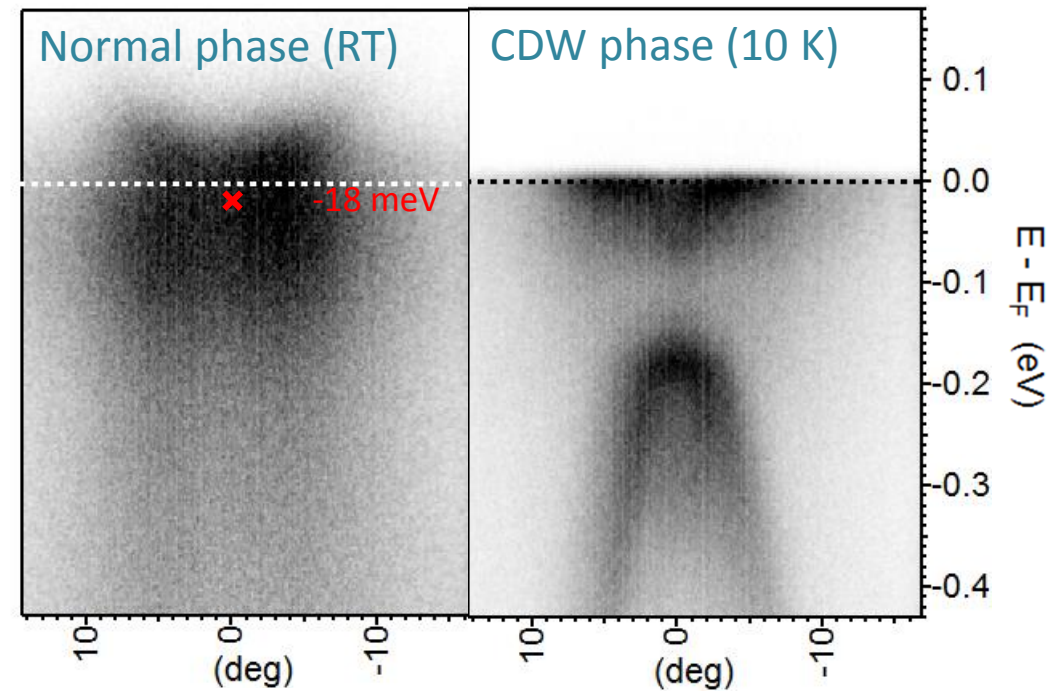
$x = 0.12$

$\bar{\Gamma}$

$\bar{M}$

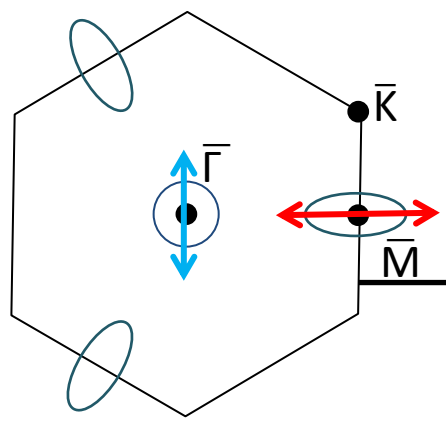


Se 4p VB below  $E_F$



Ti 3d CB below  $E_F$

Semimetal at  $T_{\text{ROOM}}$

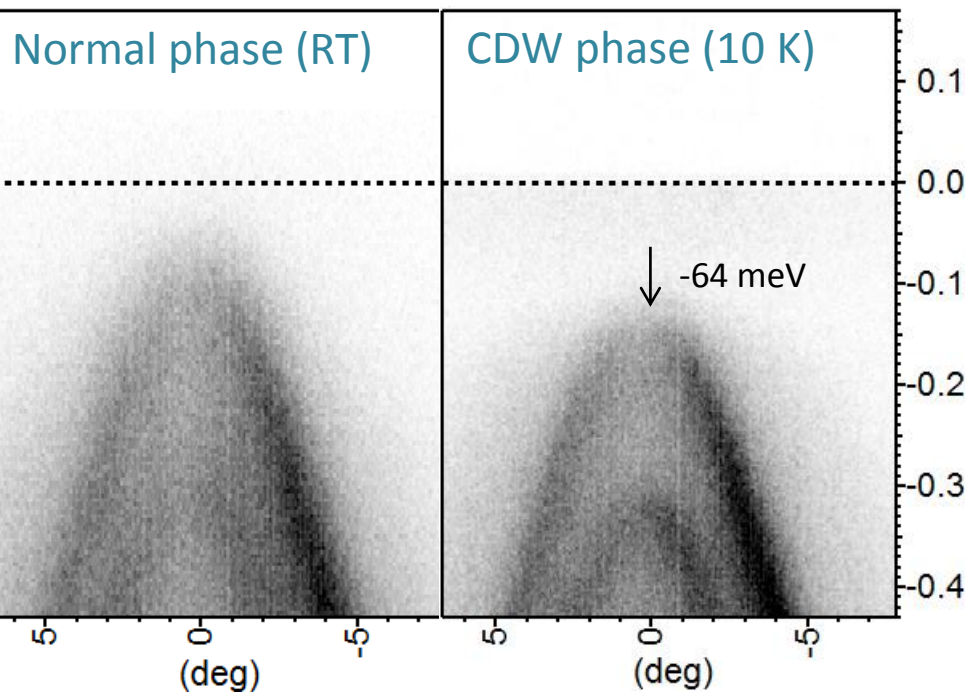


# ARPES on 1T-TiSe<sub>2-x</sub>S<sub>x</sub>

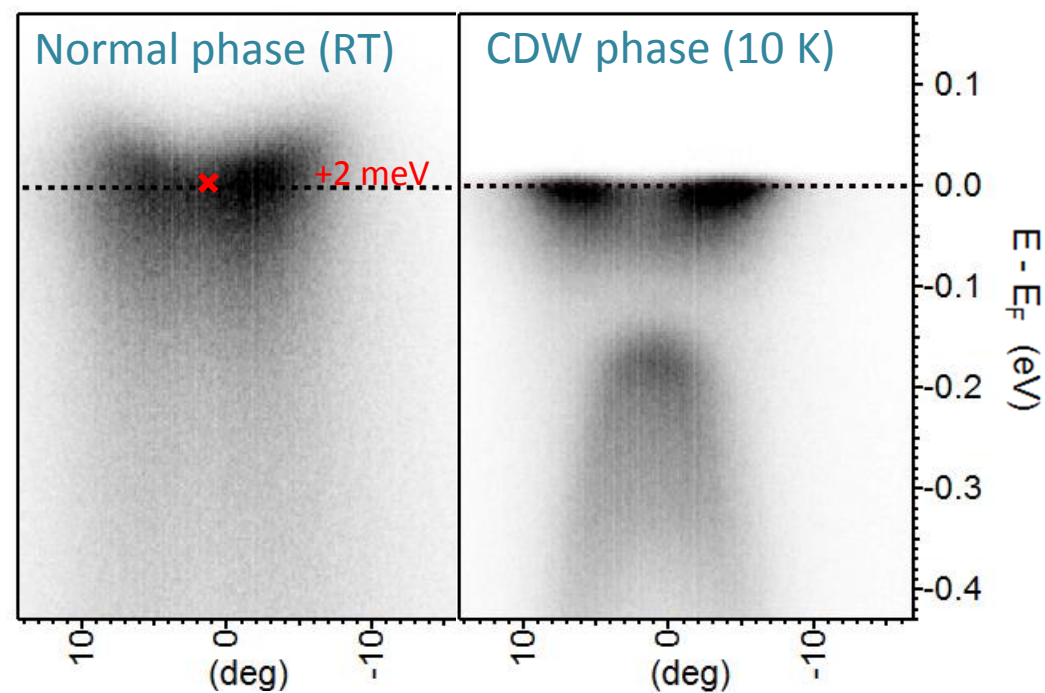
$x = 0.34$

$\bar{\Gamma}$

$\bar{M}$

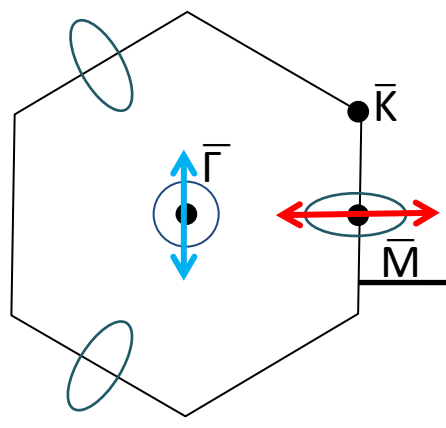


Se 4p VB below  $E_F$



Ti 3d CB slightly above  $E_F$

Semiconductor at  $T_{\text{ROOM}}$

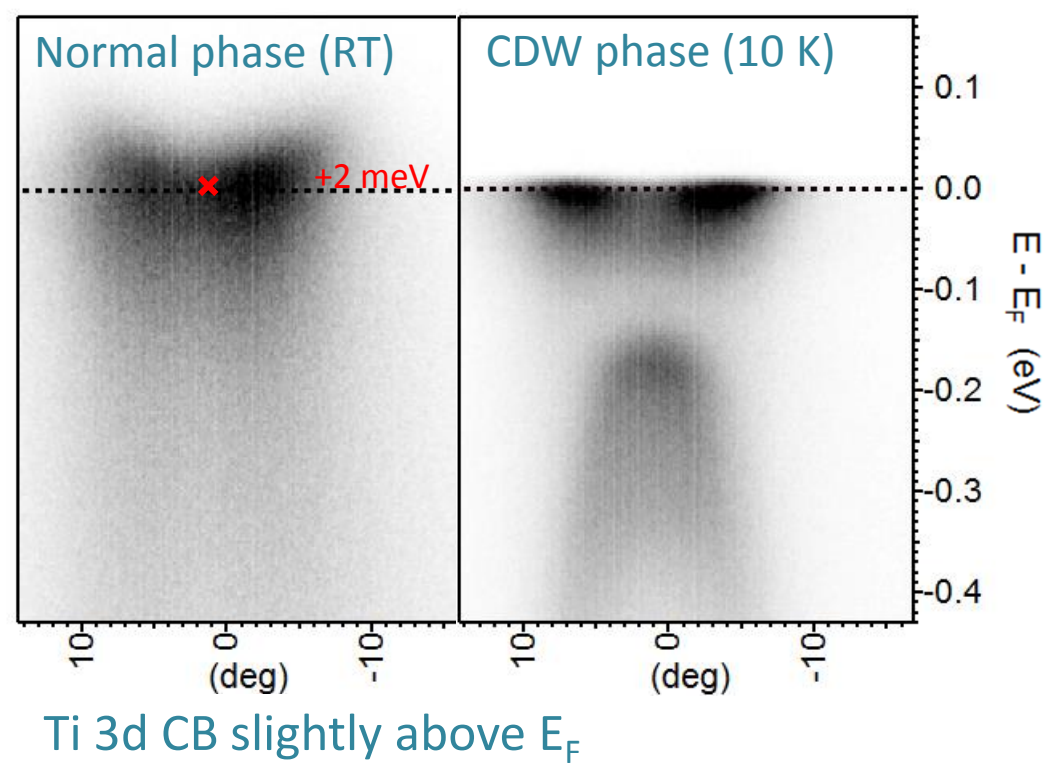
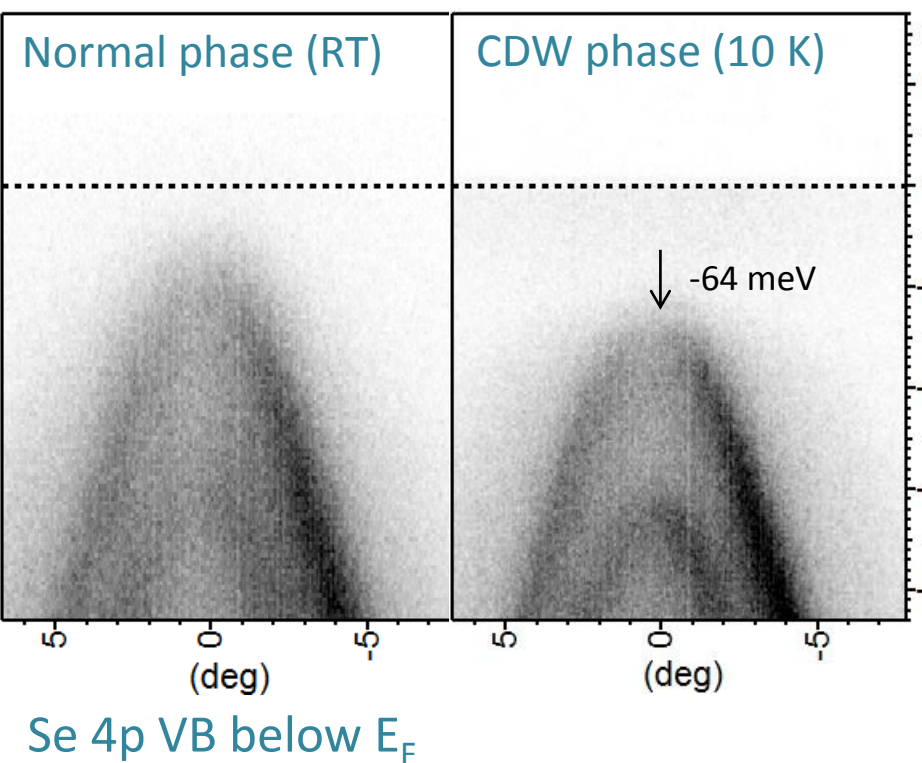


# ARPES on 1T-TiSe<sub>2-x</sub>S<sub>x</sub>

$x = 0.34$

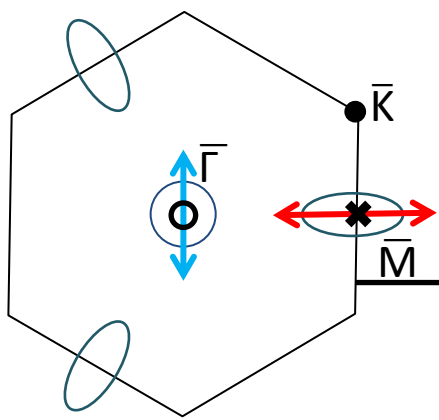
$\bar{\Gamma}$

$\bar{M}$



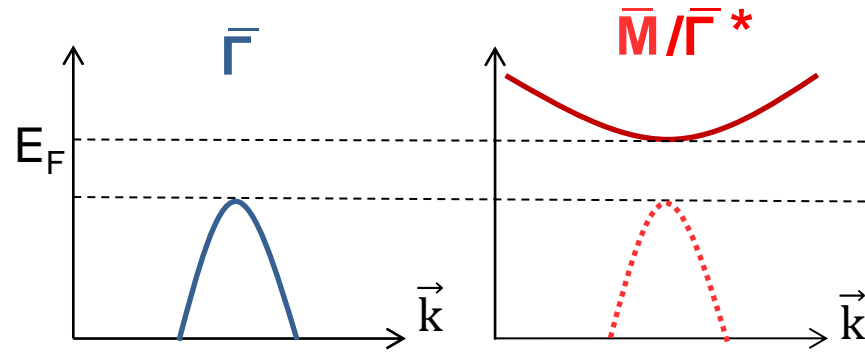
Semiconductor at  $T_{ROOM}$

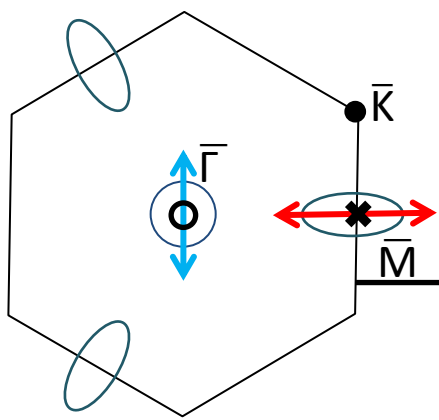
Evolution of the gap size with temperature?



# ARPES on 1T-TiSe<sub>2-x</sub>S<sub>x</sub>

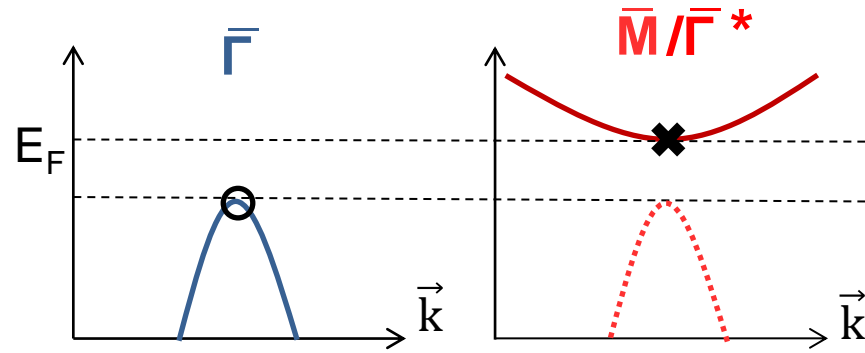
T-dependence Pristine





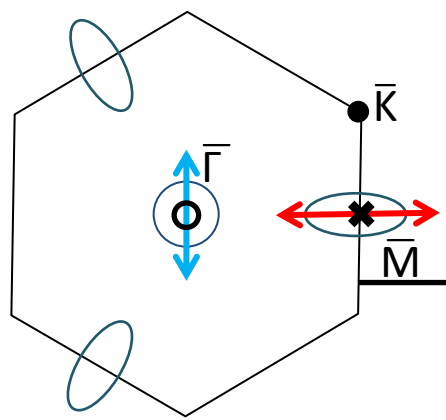
# ARPES on $1T\text{-TiSe}_{2-x}\text{S}_x$

T-dependence Pristine



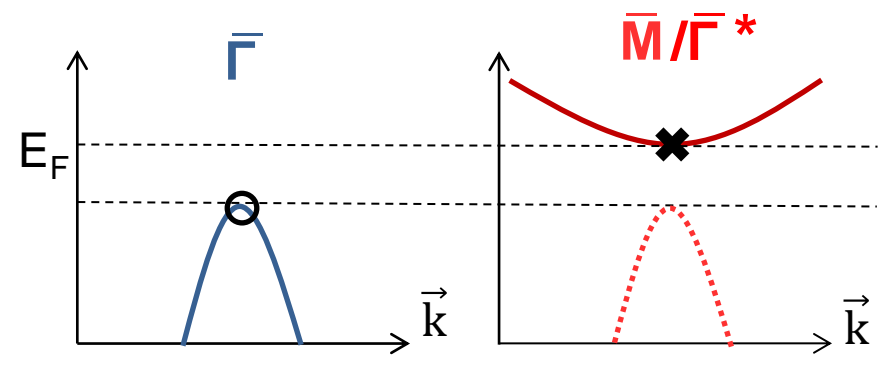
} Indirect band gap squared

$$\bullet = (\times - \circ)^2$$



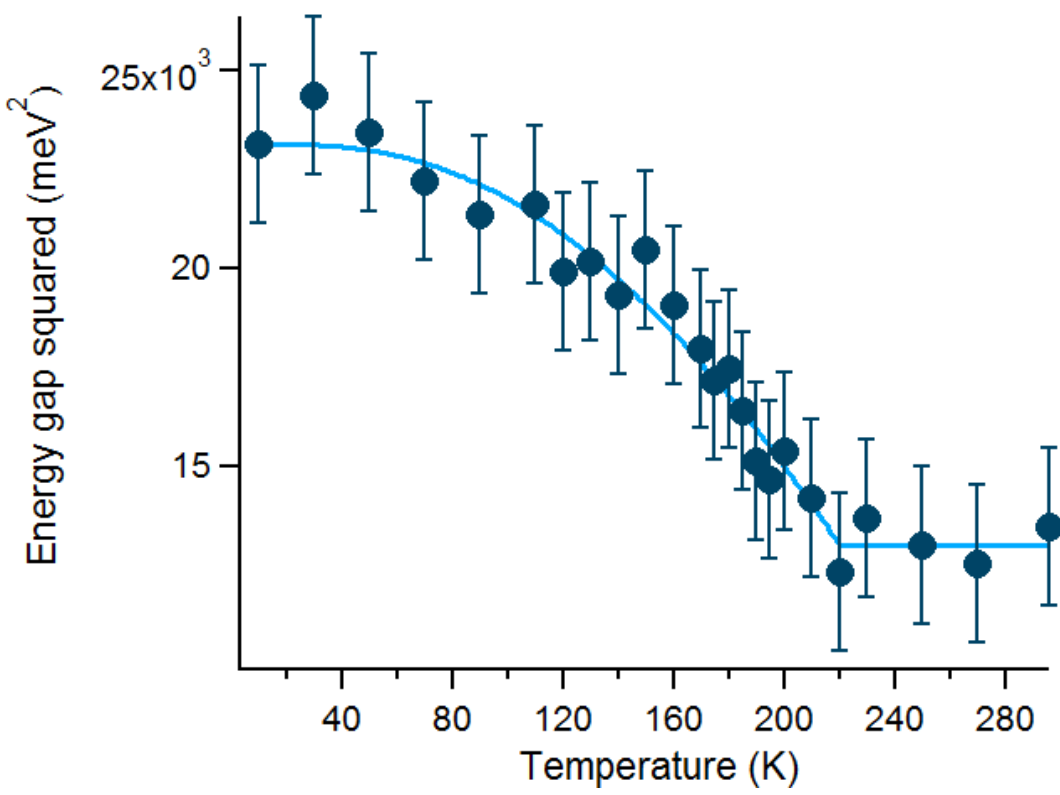
# ARPES on 1T-TiSe<sub>2-x</sub>S<sub>x</sub>

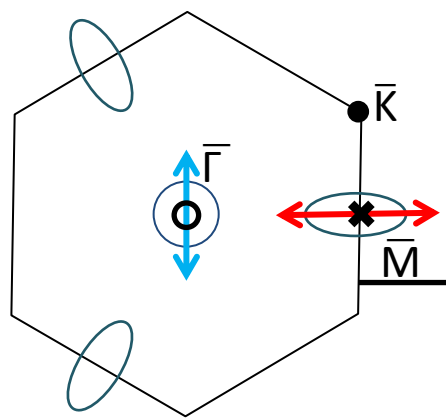
## T-dependence Pristine



} Indirect band gap squared

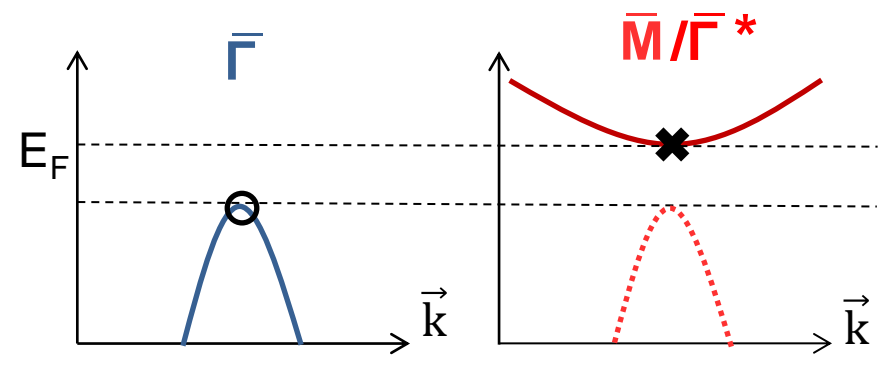
● = ( x - ○ )<sup>2</sup>



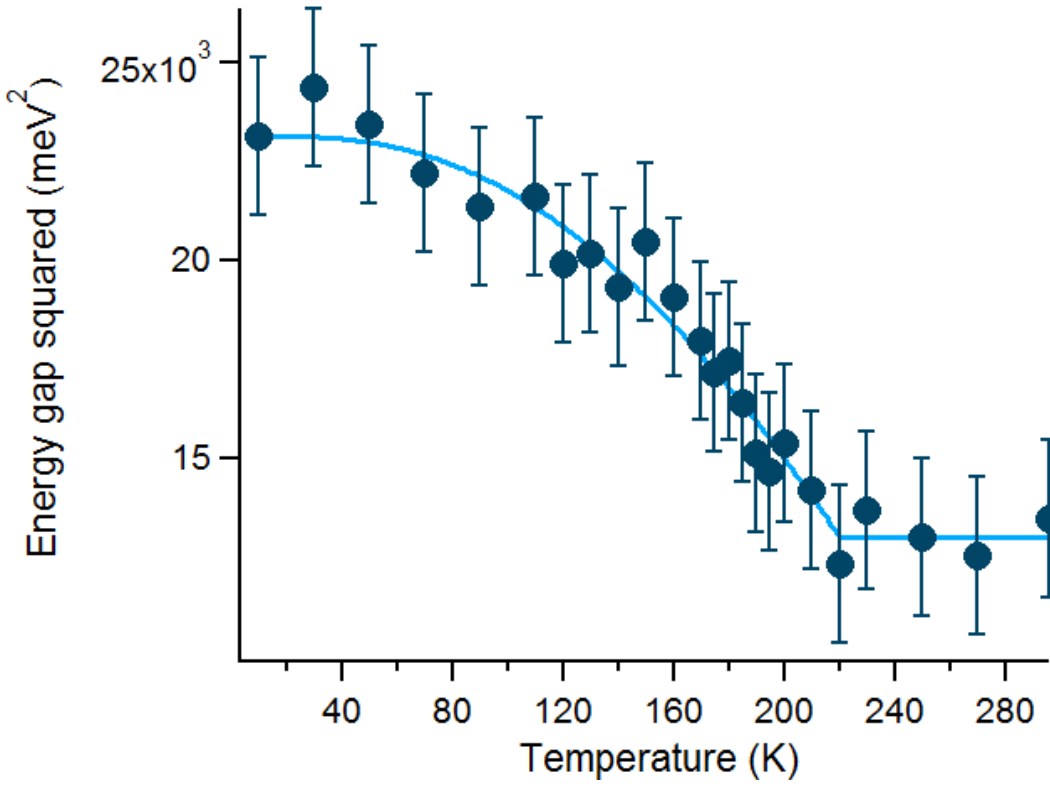


# ARPES on 1T-TiSe<sub>2-x</sub>S<sub>x</sub>

## T-dependence Pristine



} Indirect band gap squared  
 ● = ( ✕ - ○ )<sup>2</sup>

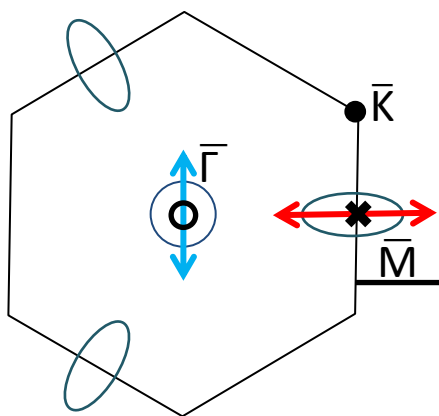


Semi-empirical BCS-type gap equation  
 P. Chen *et al.*, Nat. Comm. 6, 8943 (2015)

$$\Delta^2(T) - \Delta^2(T_C) \propto \tanh^2\left(A \sqrt{\frac{T_C}{T} - 1}\right)$$

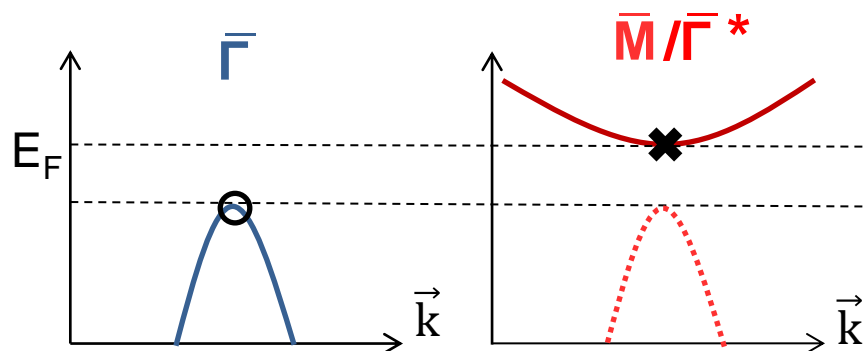
$$T_{CDW} = 220 \text{ K} \pm 5 \text{ K}$$

What about the Sulfur doped samples?



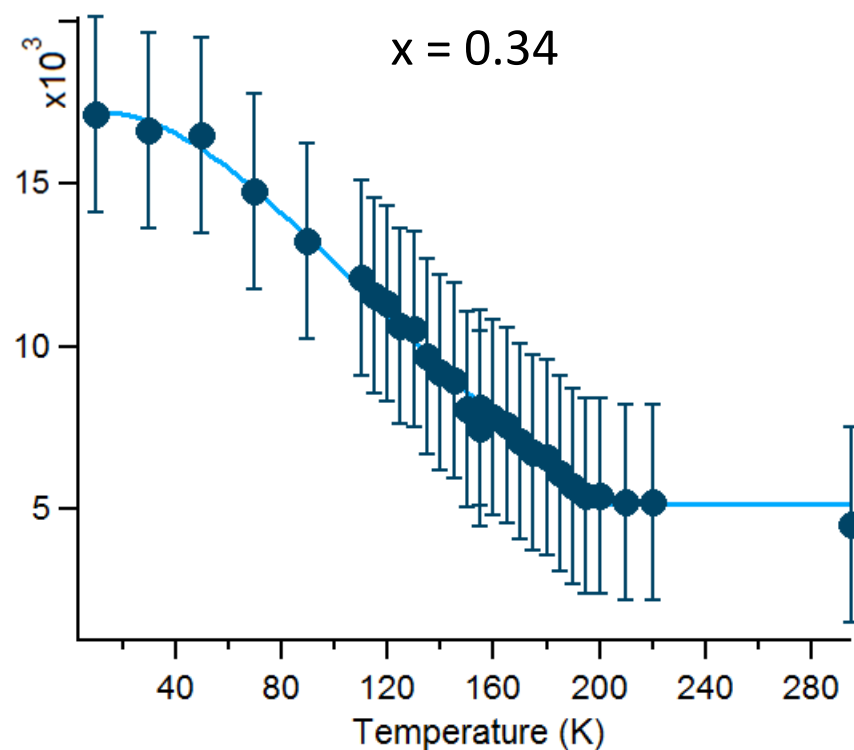
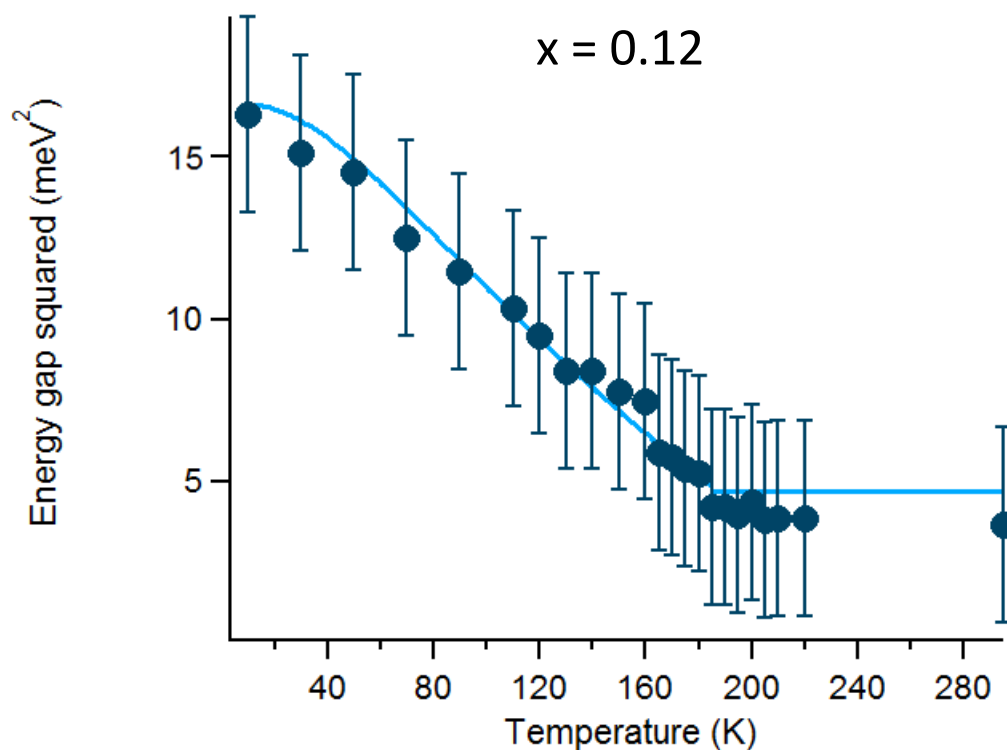
# ARPES on 1T-TiSe<sub>2-x</sub>S<sub>x</sub>

T-dependence S-doped

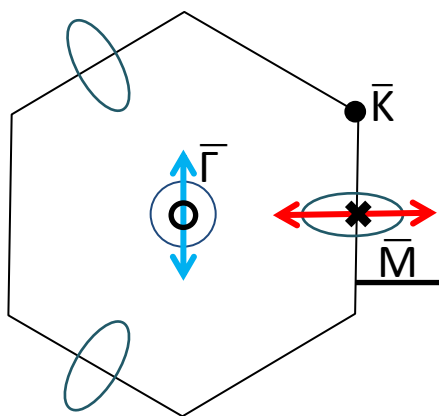


} Indirect band gap squared

$$\bullet = (\times - \circ)^2$$

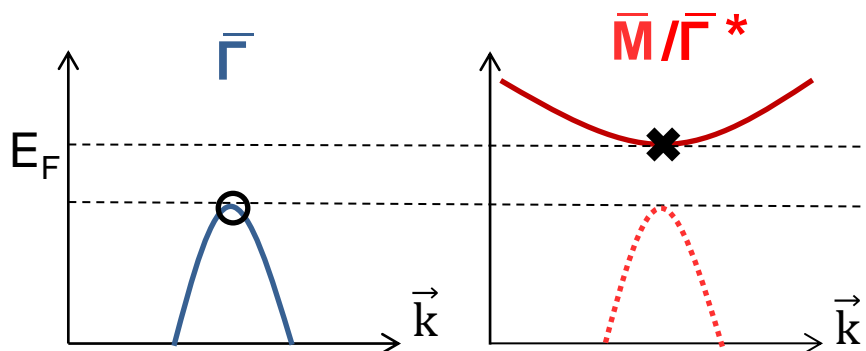






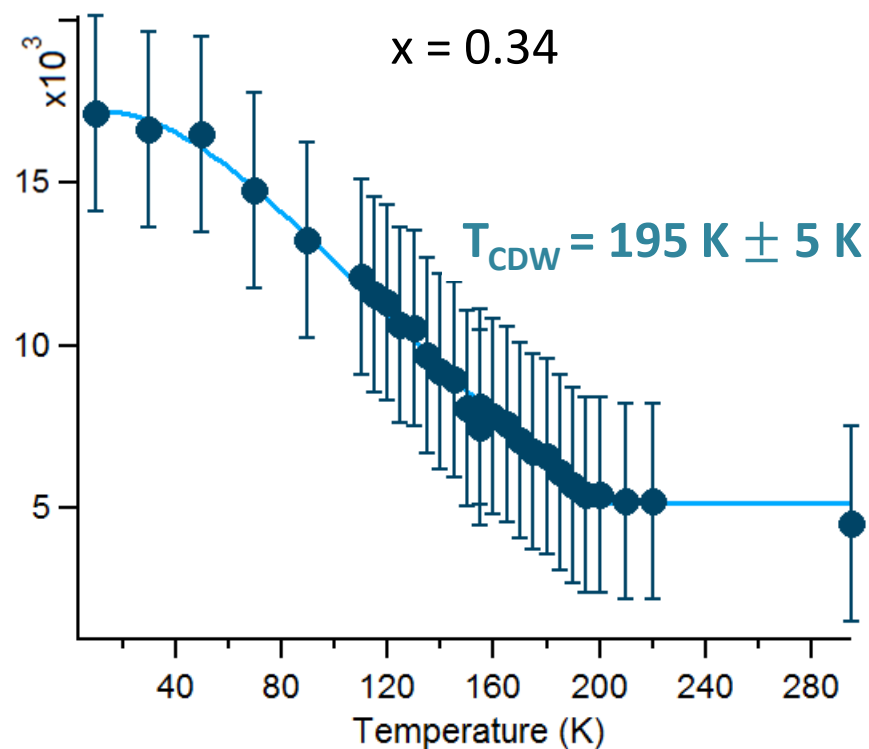
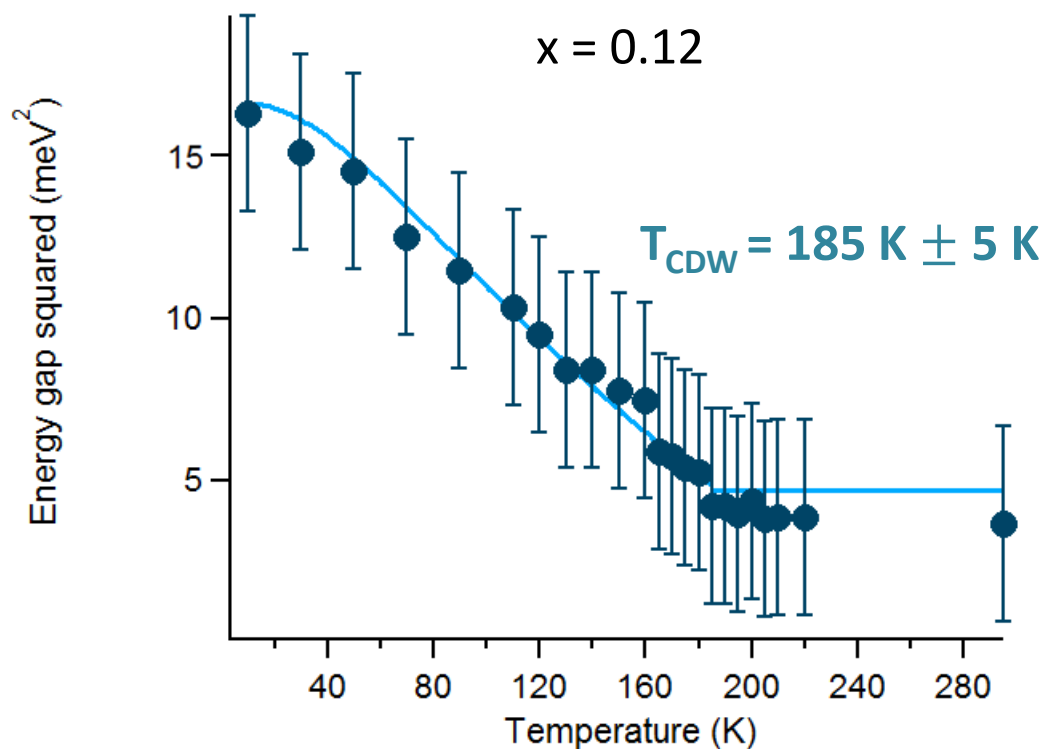
# ARPES on 1T-TiSe<sub>2-x</sub>S<sub>x</sub>

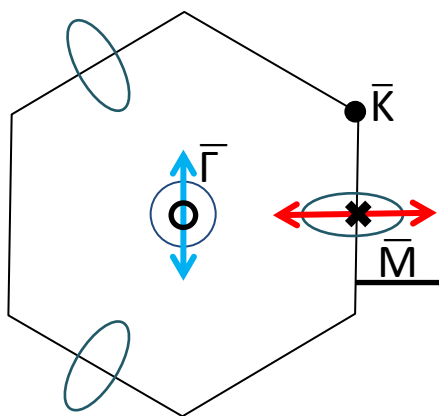
T-dependence S-doped



} Indirect band gap squared

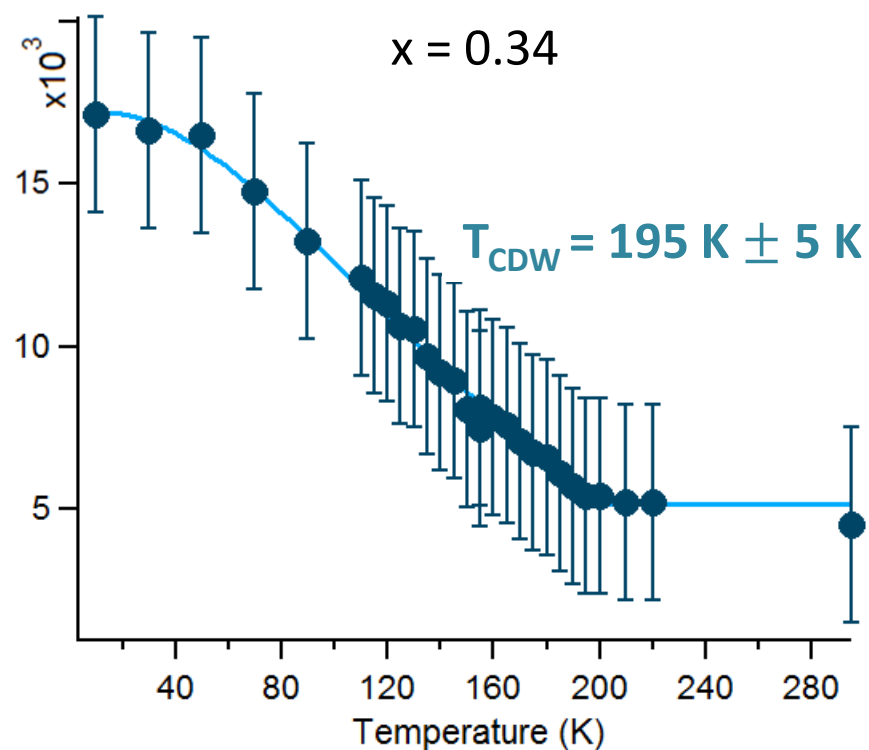
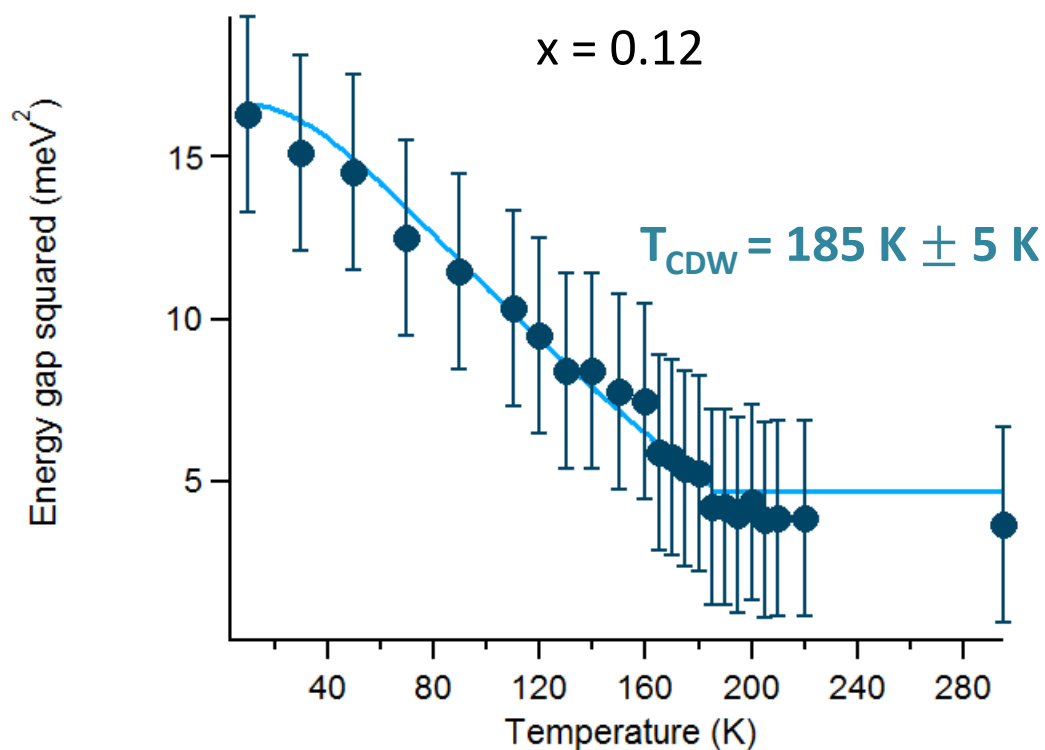
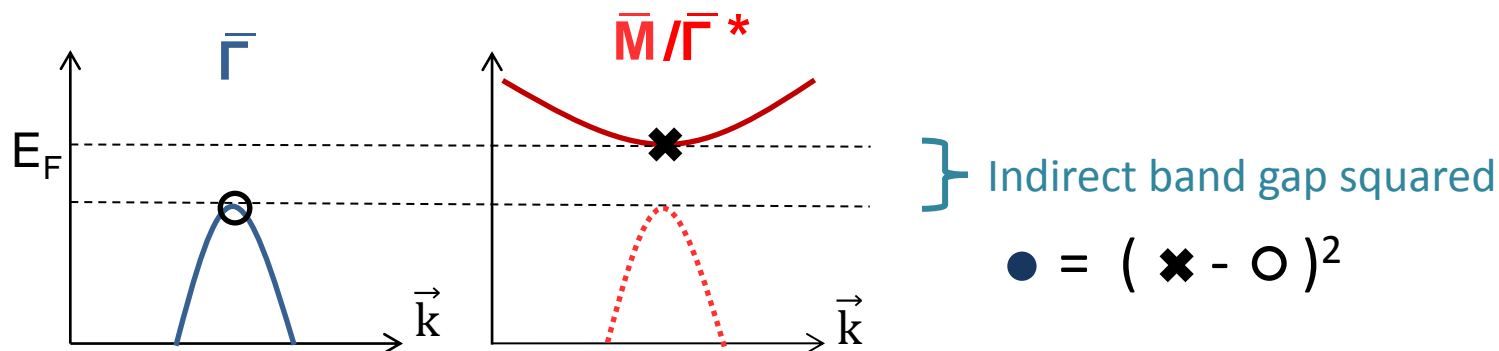
$$\bullet = (\times - \circ)^2$$





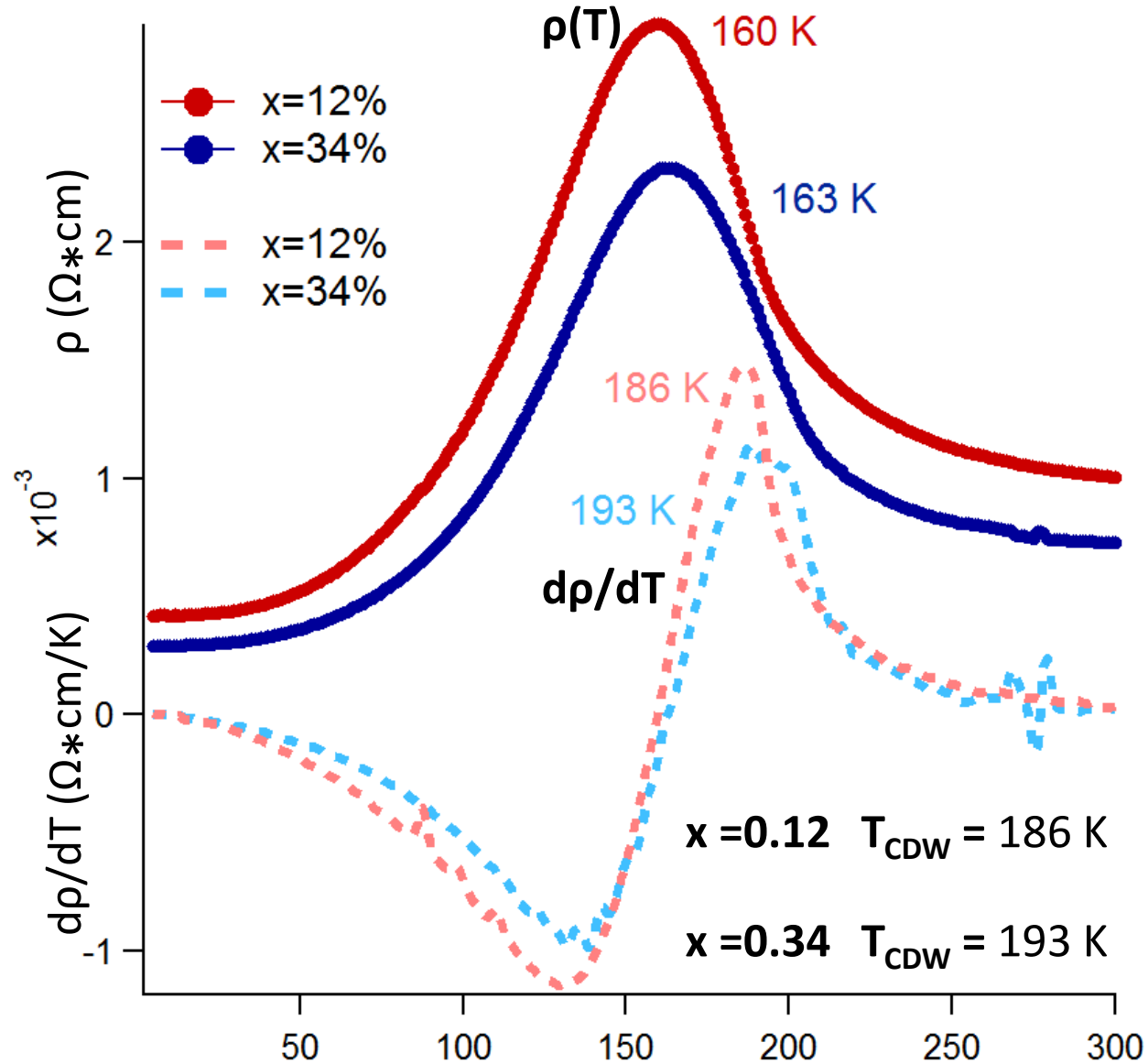
# ARPES on 1T-TiSe<sub>2-x</sub>S<sub>x</sub>

T-dependence S-doped



Consistent with temperature-dependent resistivity measurements?

# Resistivity of $1T\text{-TiSe}_{2-x}\text{S}_x$



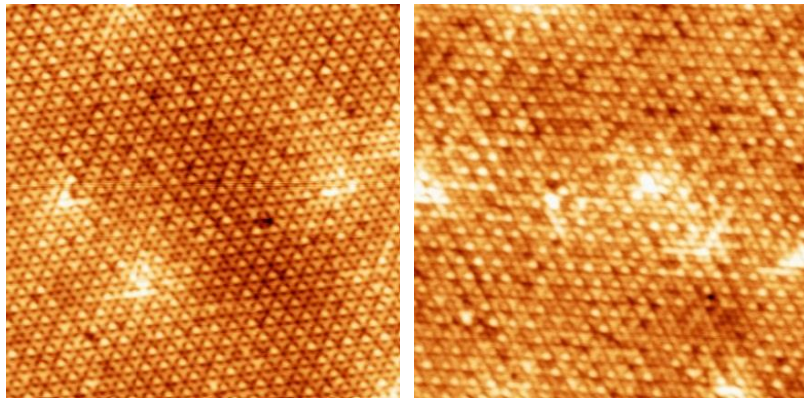
Transition temperatures from resistivity in agreement with ARPES

# Summary

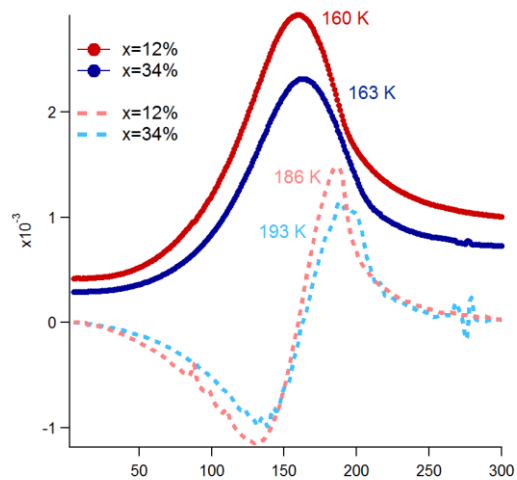
## STM/STS

$x = 0.12$

$x = 0.34$



## $\rho(T)$

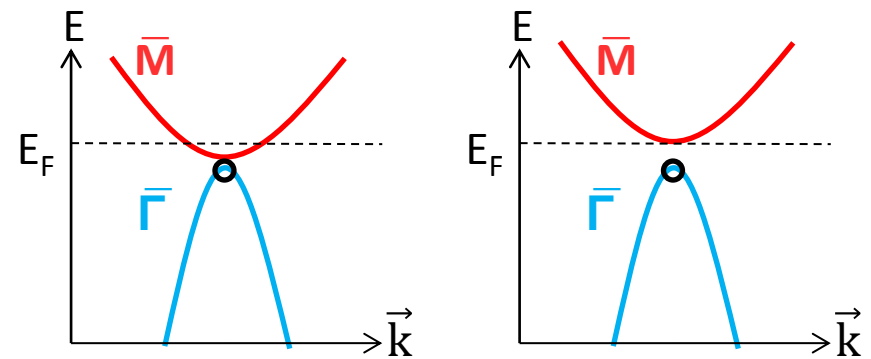


## ARPES

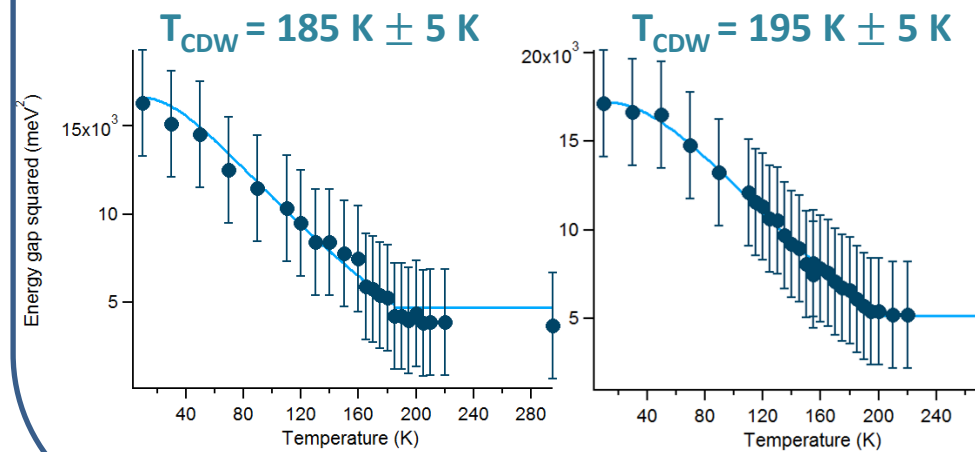
$x = 0.12$

$x = 0.34$

Normal phase

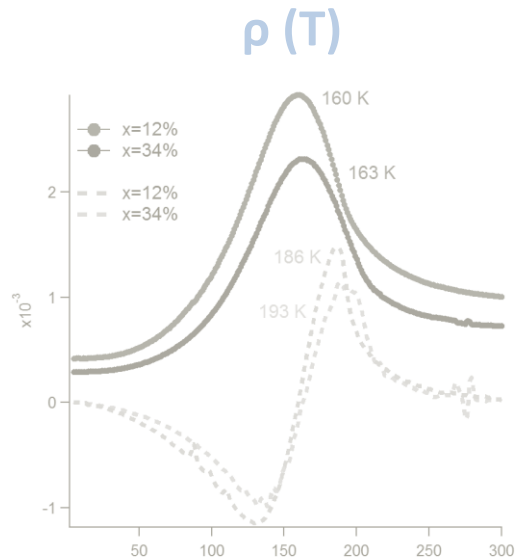
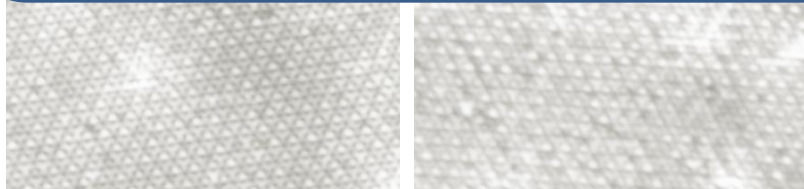


## $f(T)$

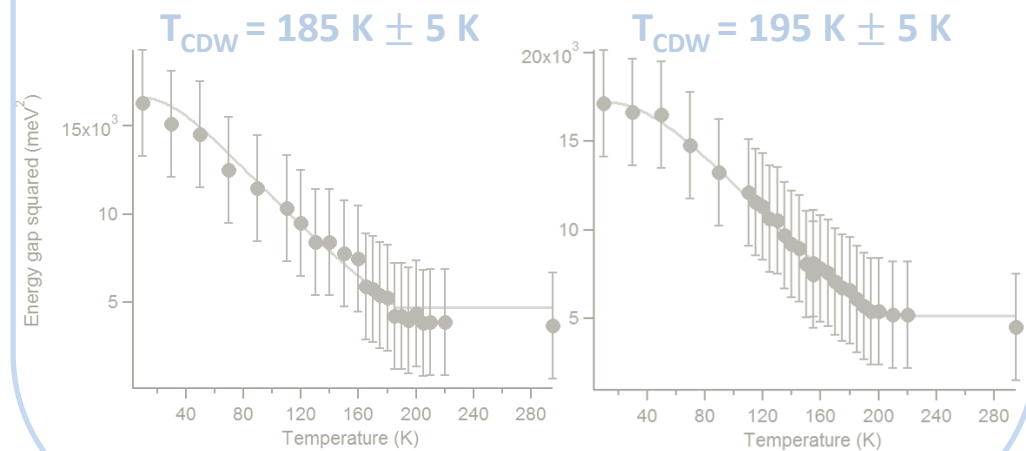
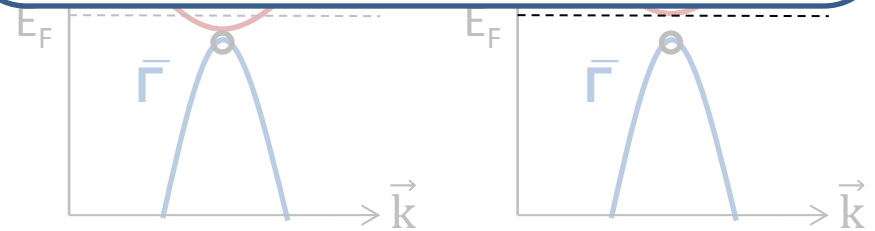


# Outlook

- pristine  $\text{TiSe}_2$  semiconductor
- sulfur lowers  $T_{\text{CDW}}$  nonlinearly
- slight reentrant behavior for low sulfur concentration



- $\text{TiSe}_2$  under pressure becomes semimetallic
- $\text{TiS}_2$  is a semiconductor with no CDW



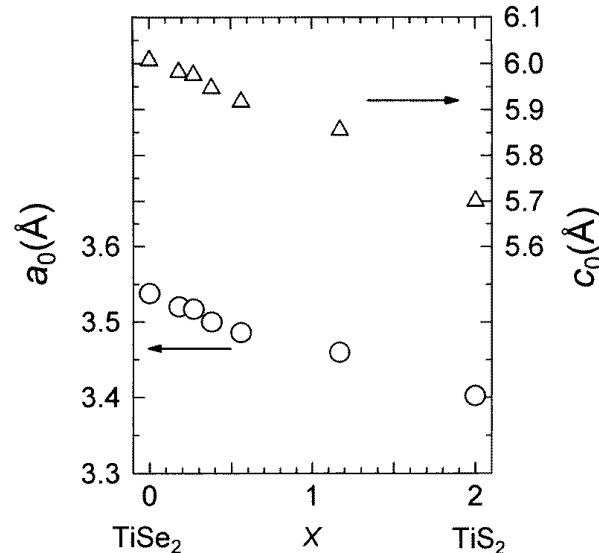
# Outlook

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- $\text{TiS}_2$  is a semiconductor with no CDW



structural effect of isovalent S substitution



Y. Miyahara *et al.*, *J. Phys.: Condens. Matter* **8**, 7453 (1996)

**Competition between a positive chemical pressure effect and band reconstruction**