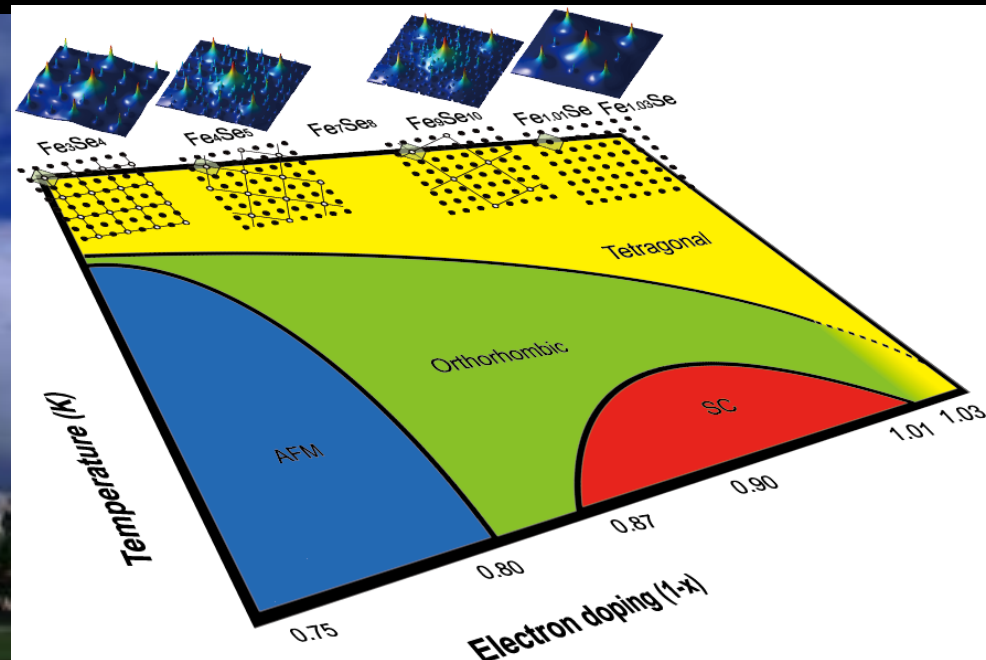


Recent Development in Fe-Chalcogenide Superconductors



M. K. Wu

National Dong-Hwa University
Institute of Physics, Academia Sinica

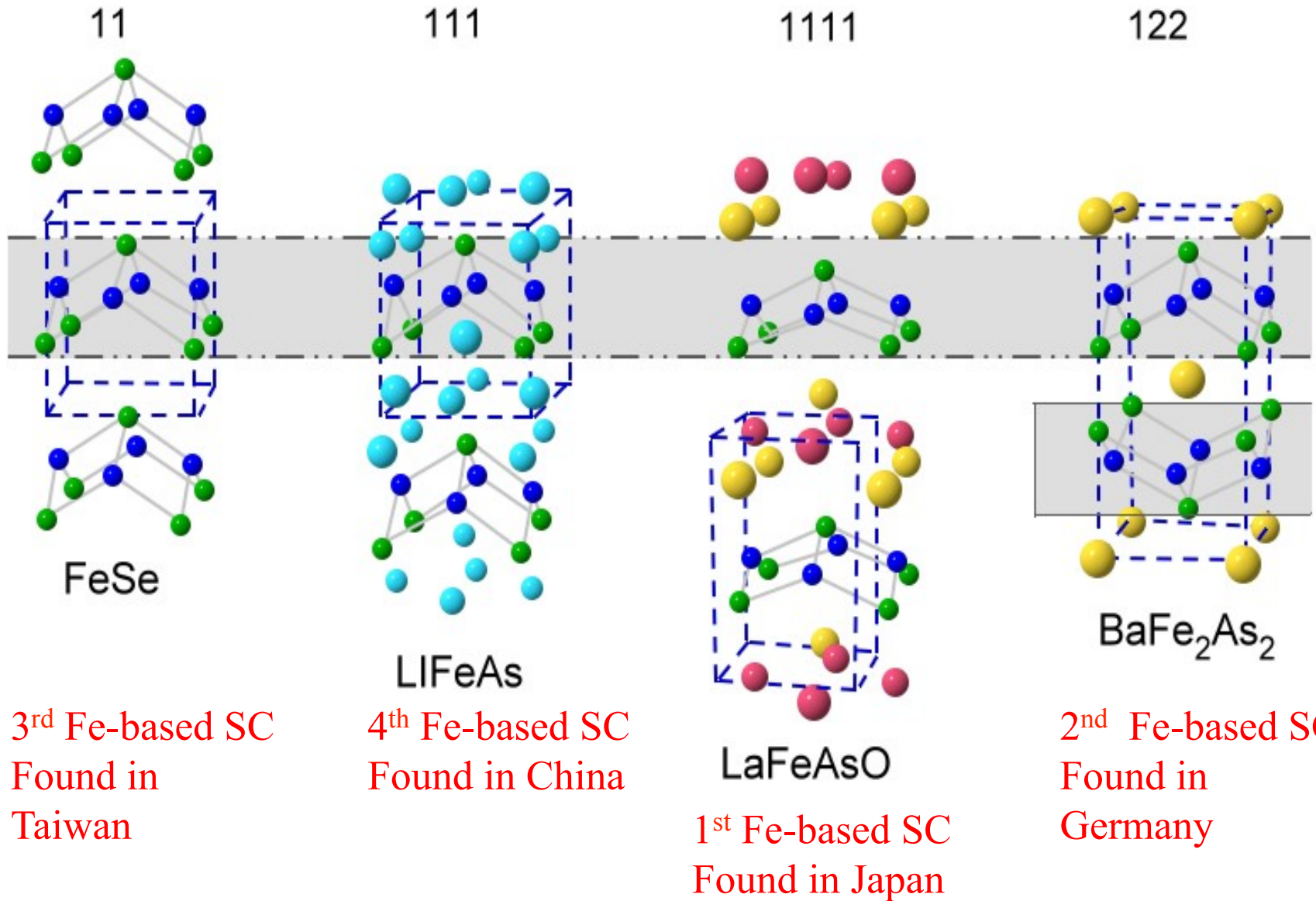
OUTLINE

1. Unresolved questions in FeSe
2. Properties of nano-dimensional FeSe
3. Observations of Fe-vacancy order in FeSe and its implications
4. Phase Diagram for FeSe System
5. Phase III problems?

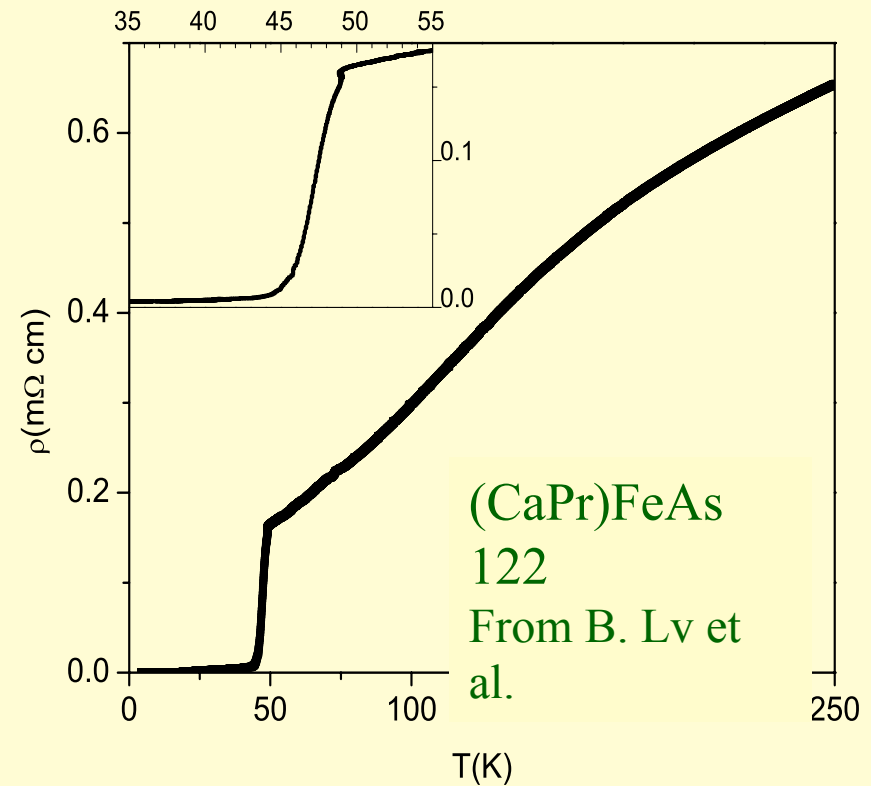
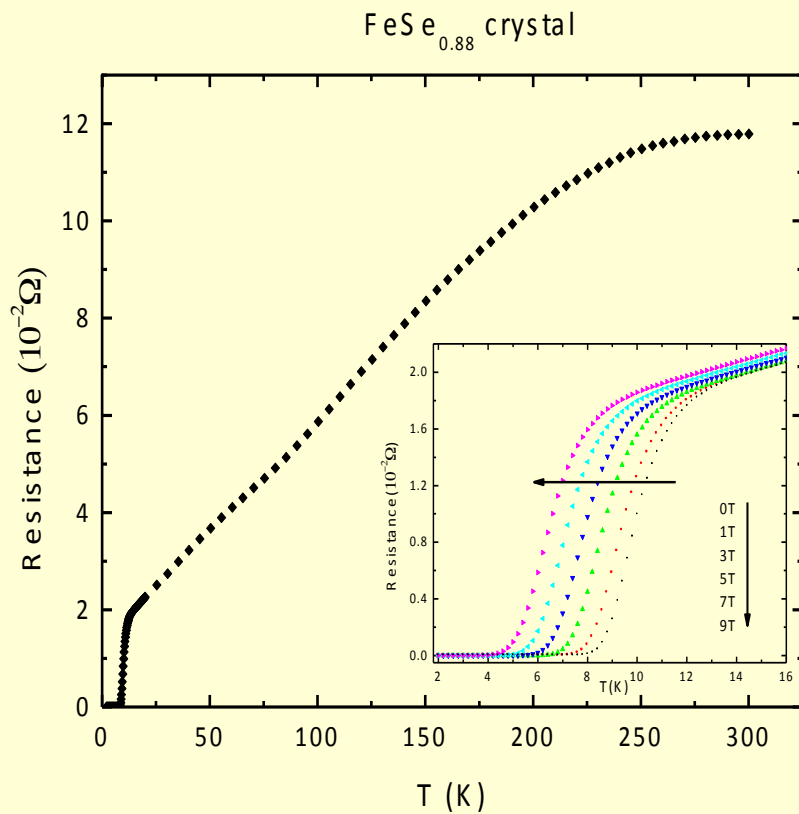
Results appear on PNAS, December 16 online early edition, 2013

We acknowledge the financial supports from Academia Sinica, the National Science Council of Taiwan and the US AFOSR/AOARD

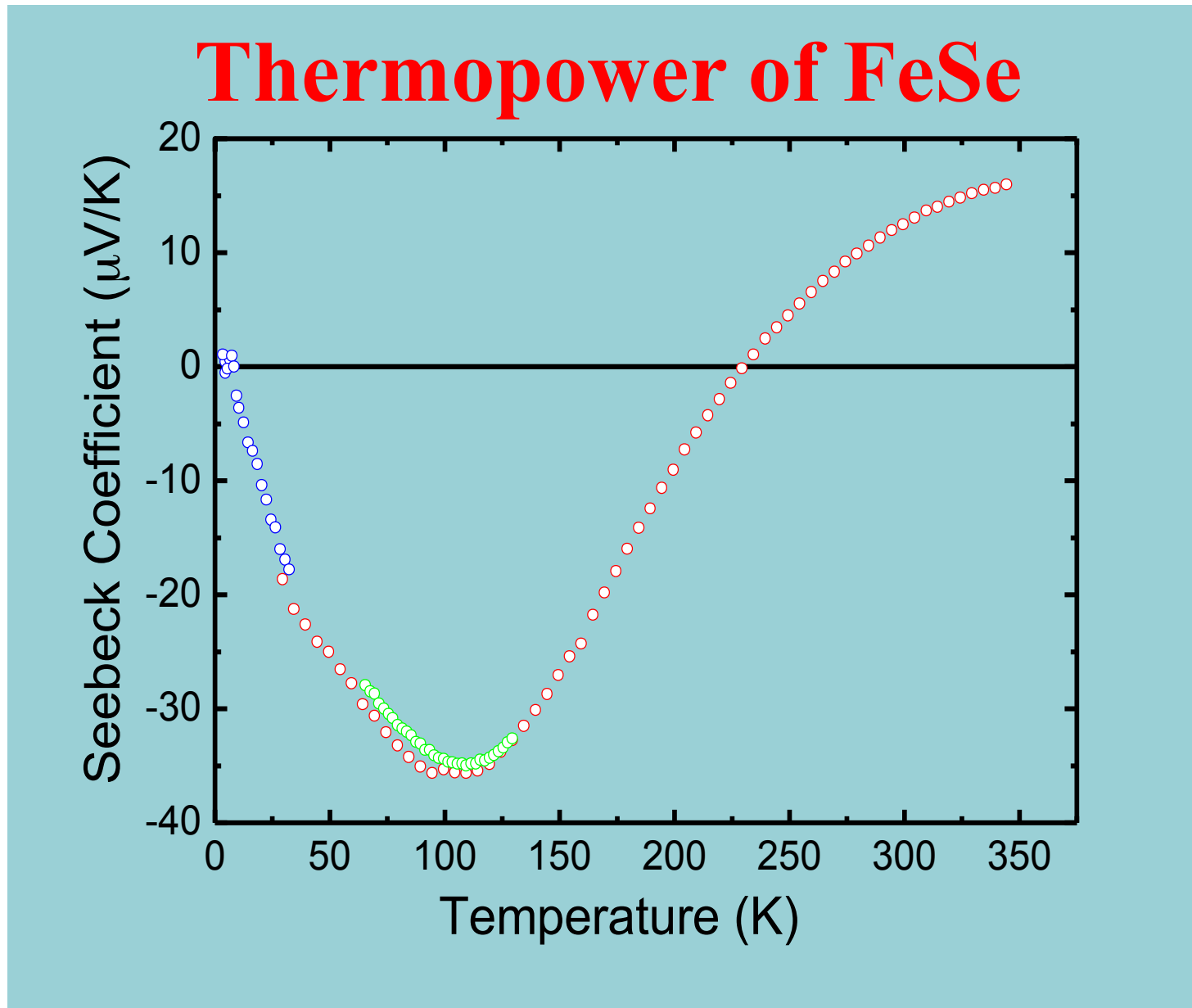
The common Features in Fe-based superconductors



The common Features in Fe-based superconductors?

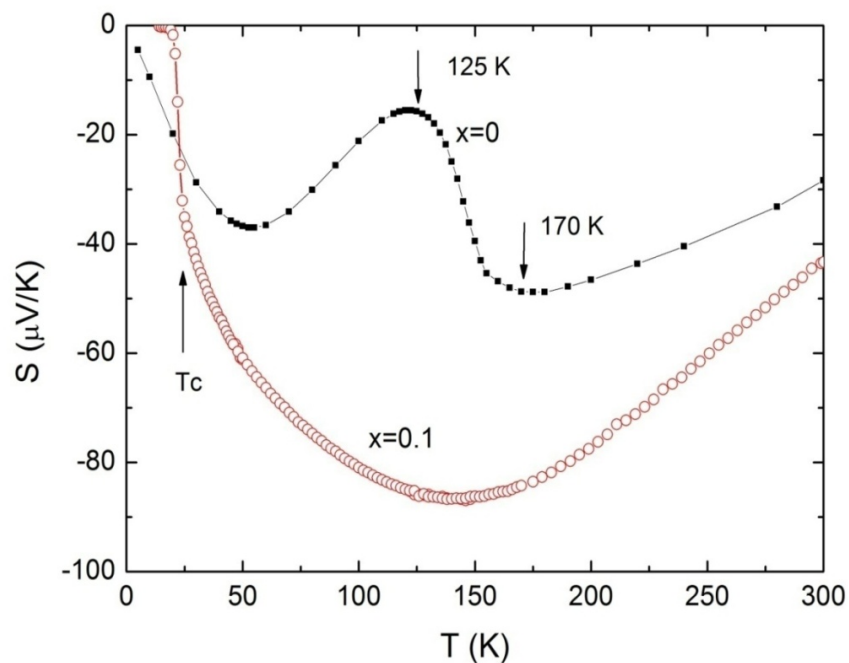


The common Features in Fe-based superconductors



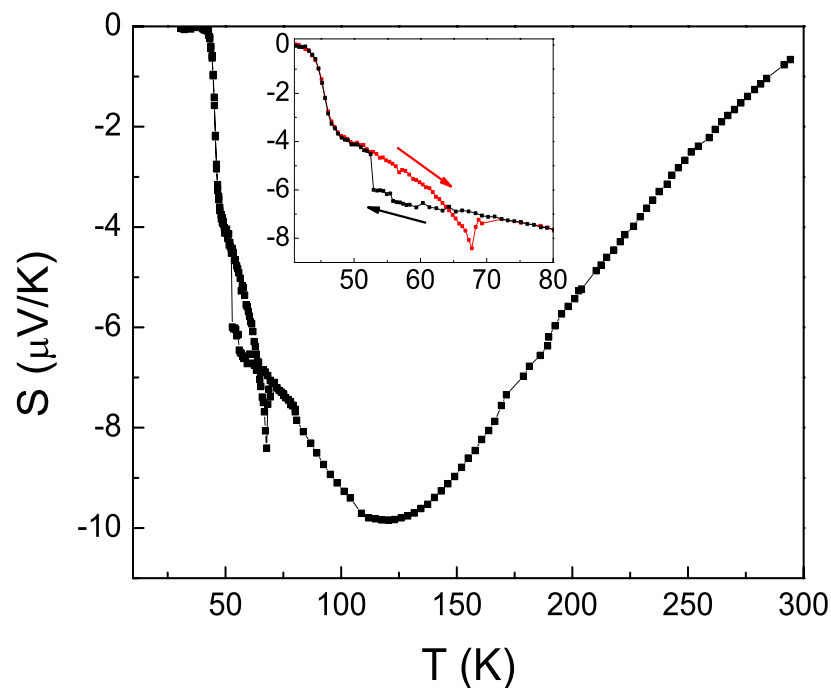
Thermopower of Pnictides

F- doped 1111 , $\text{LaFeAsO}_{1-x}\text{F}_x$, $x=0, 0.1$



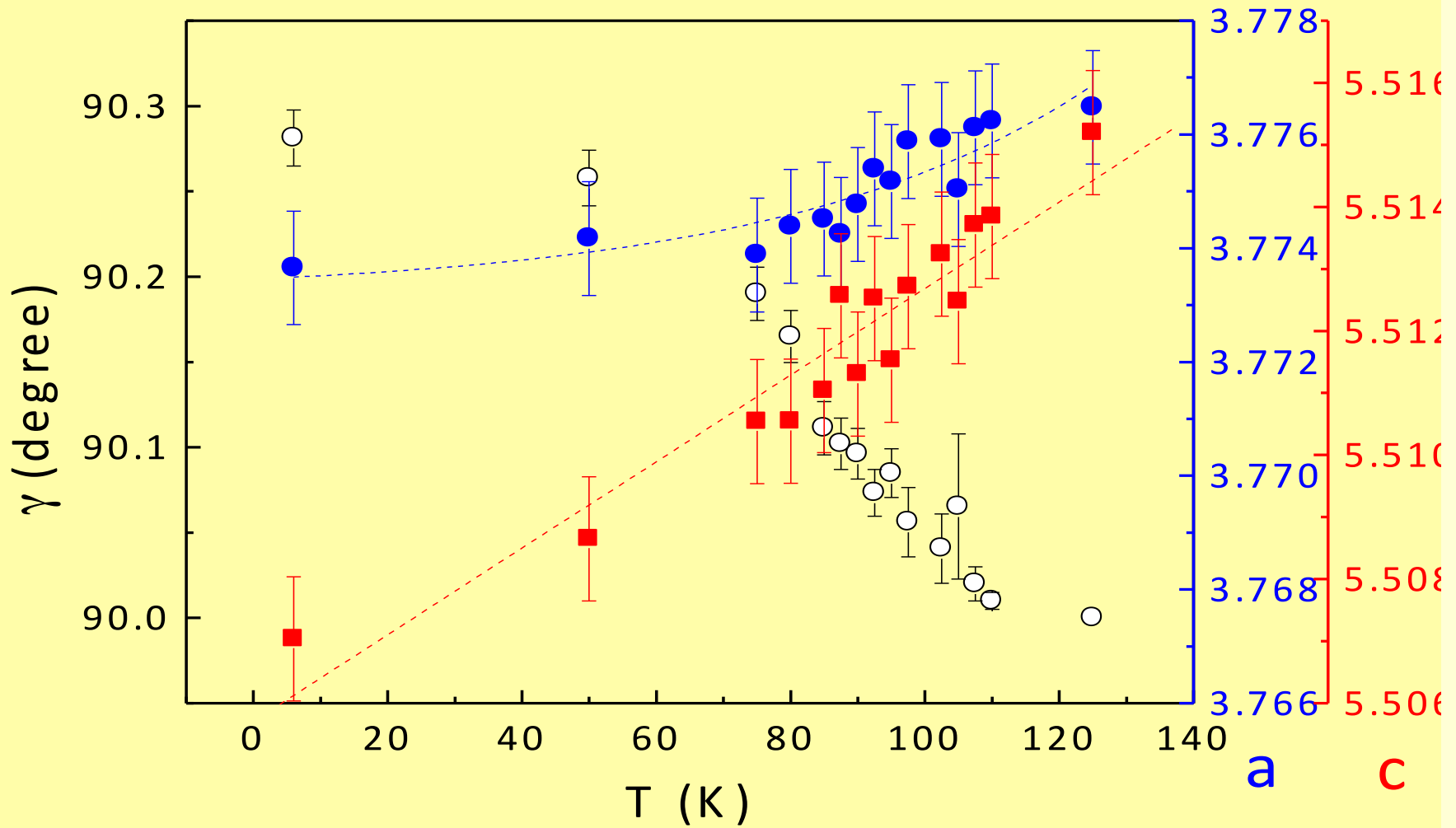
From Prof. Z.A.
Xu

Electron-Doped CaFe_2As_2



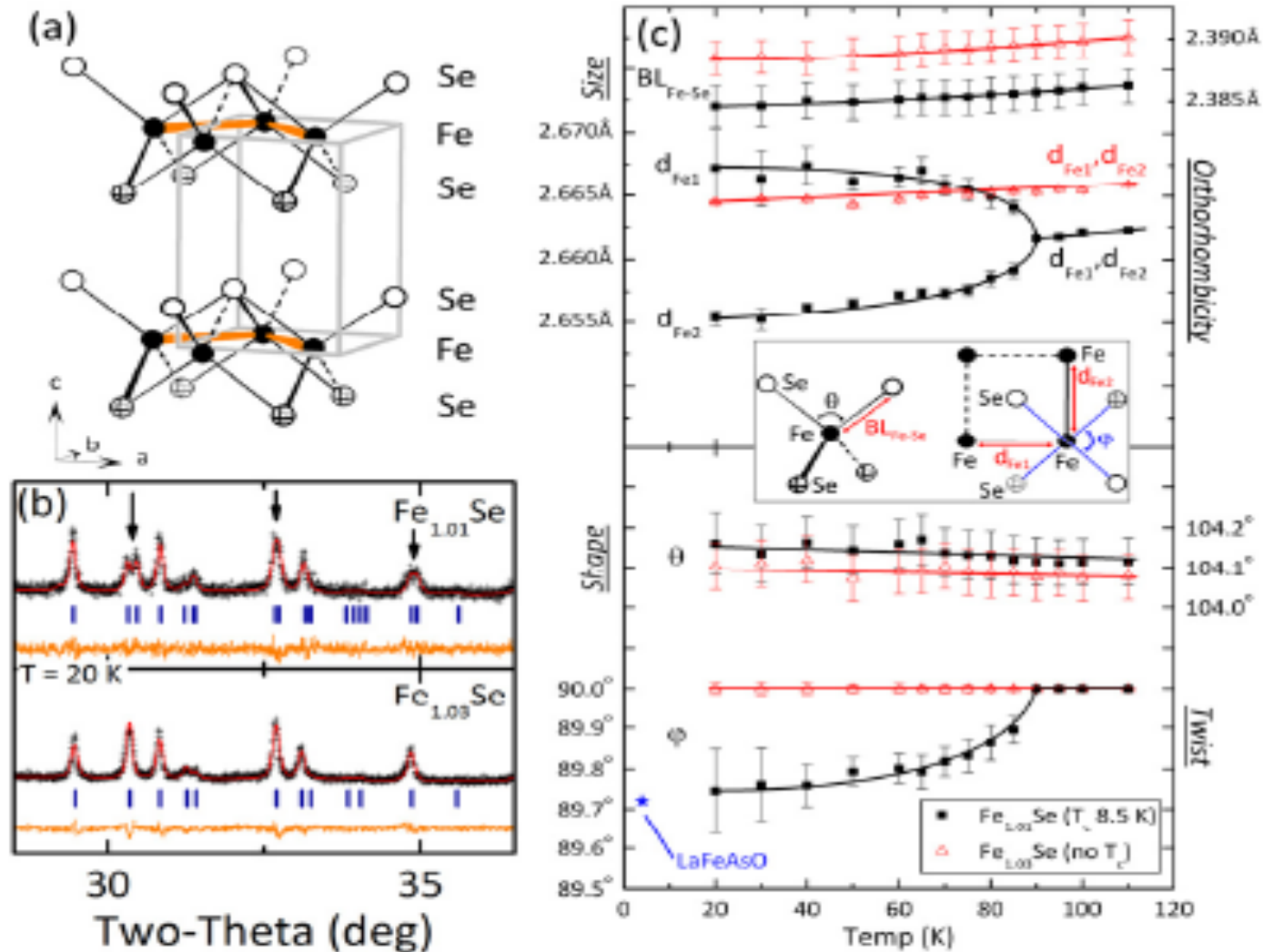
From Prof. C.W. Chu

10



M.K. Wu et al., Physica C., 2009

The Structural Phase Transition in Fe_{1+x}Se



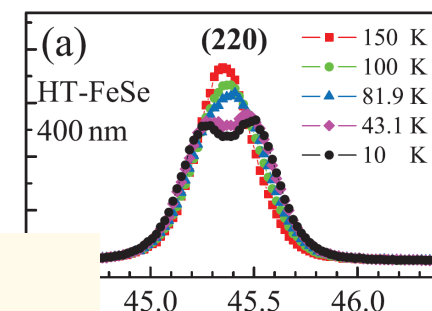
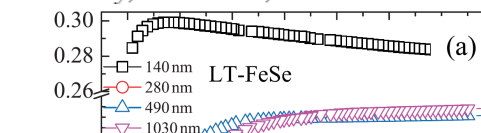
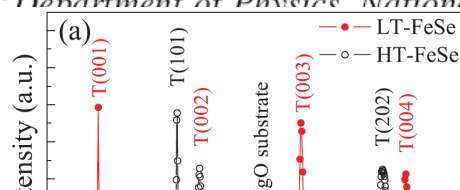
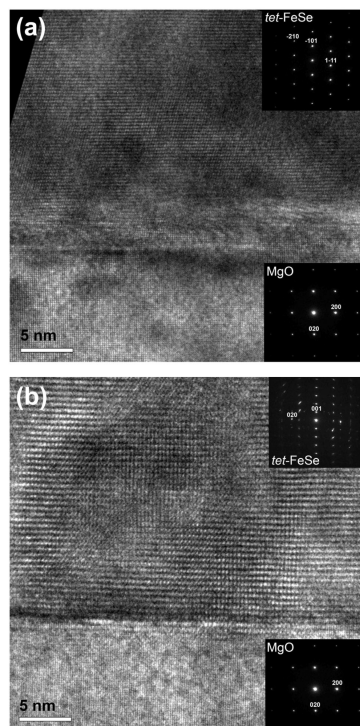
Crystal Orientation and Thickness Dependence of the Superconducting Transition Temperature of Tetragonal FeSe_{1-x} Thin Films

M. J. Wang,^{1,*} J. Y. Luo,² T. W. Huang,² H. H. Chang,³ T. K. Chen,² F. C. Hsu,¹ C. T. Wu,³ P. M. Wu,⁴
A. M. Chang,⁴ and M. K. Wu^{2,3,†}

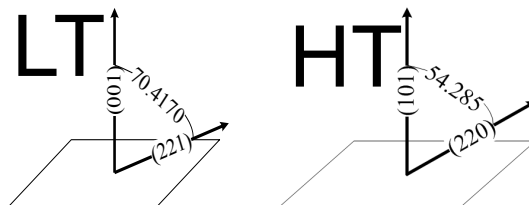
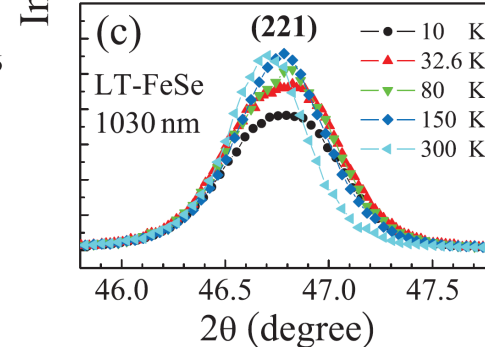
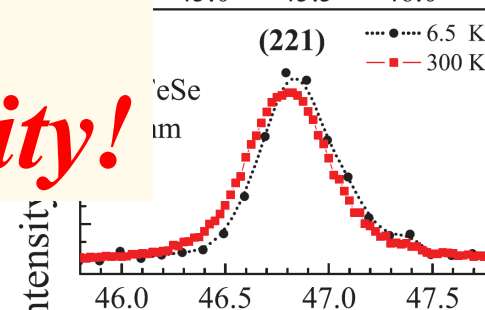
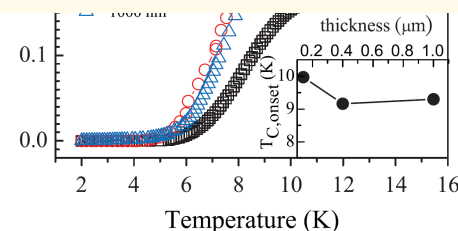
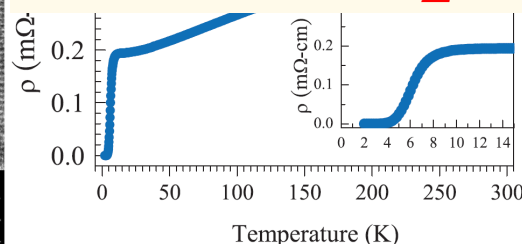
¹*Institute of Astronomy and Astrophysics, Academia Sinica, Taipei, Taiwan*

²*Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan*

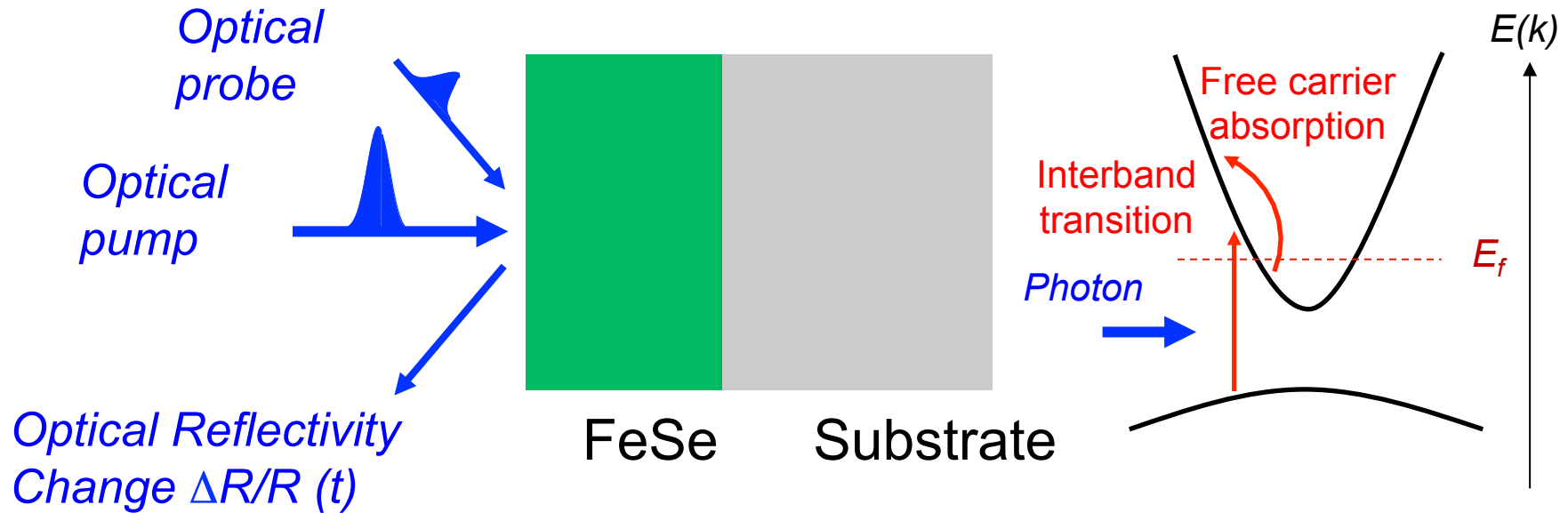
³*Department of Physics, National Tsing Hua University, Hsinchu, Taiwan*
⁴*University, Durham, North Carolina*



***No LT Distortion,
No Superconductivity!***



Femtosecond optical pump-probe spectroscopy



Pump/probe = 400/800 nm
(corresponding to probe of Fe 3-d orbital)

Pump fluence = $5.3 \mu\text{J}/\text{cm}^2$
(measurement was done under the perturbation regime)

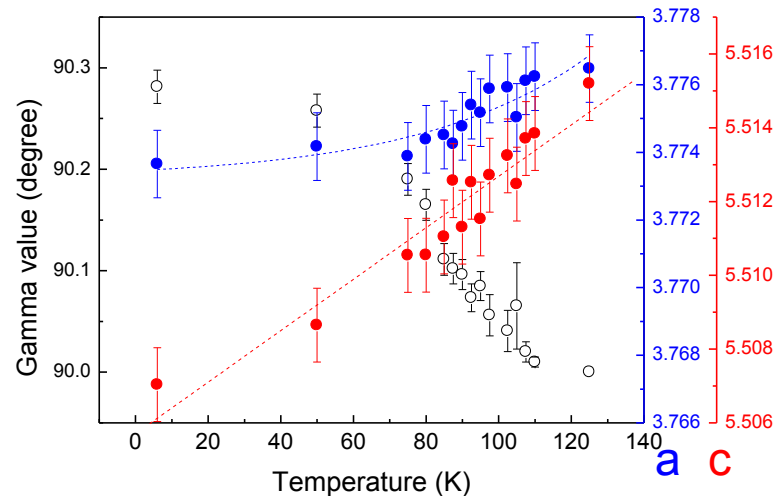
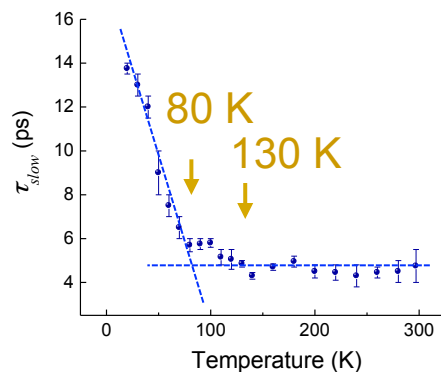
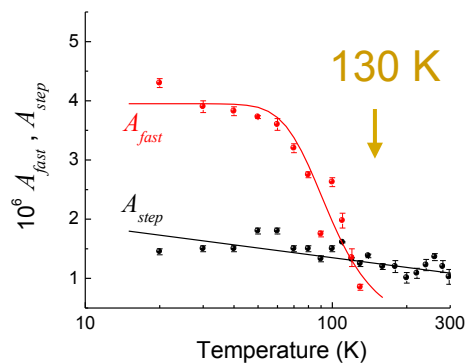
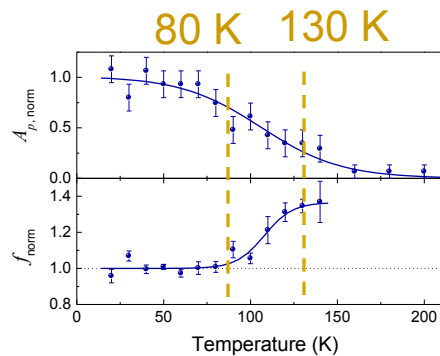
Correlation between different dynamics at $T = 80 \sim 130$ K

Indication of
optical absorption

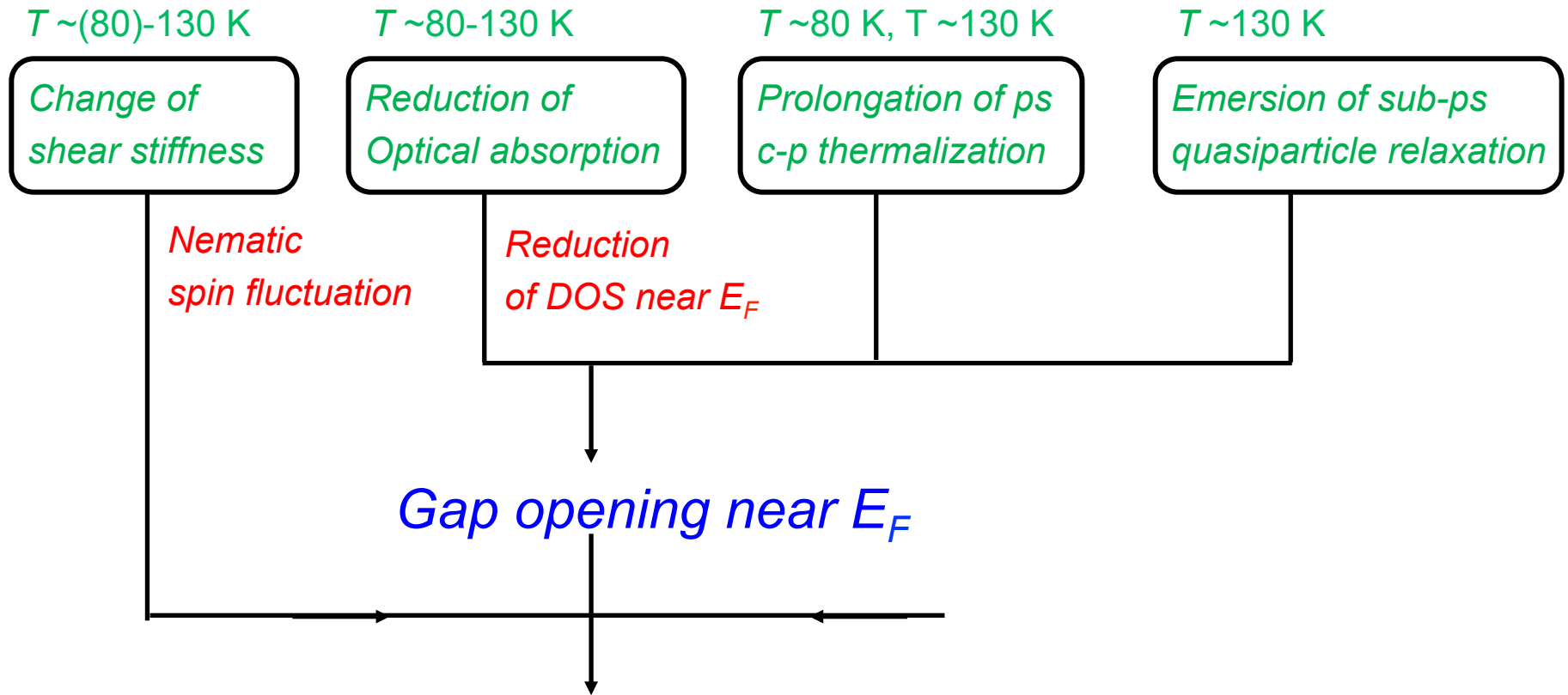
Indication of
spin fluctuation

A_{fast} :
gap-like feature

τ_{slow} :
carrier-phonon
thermalization

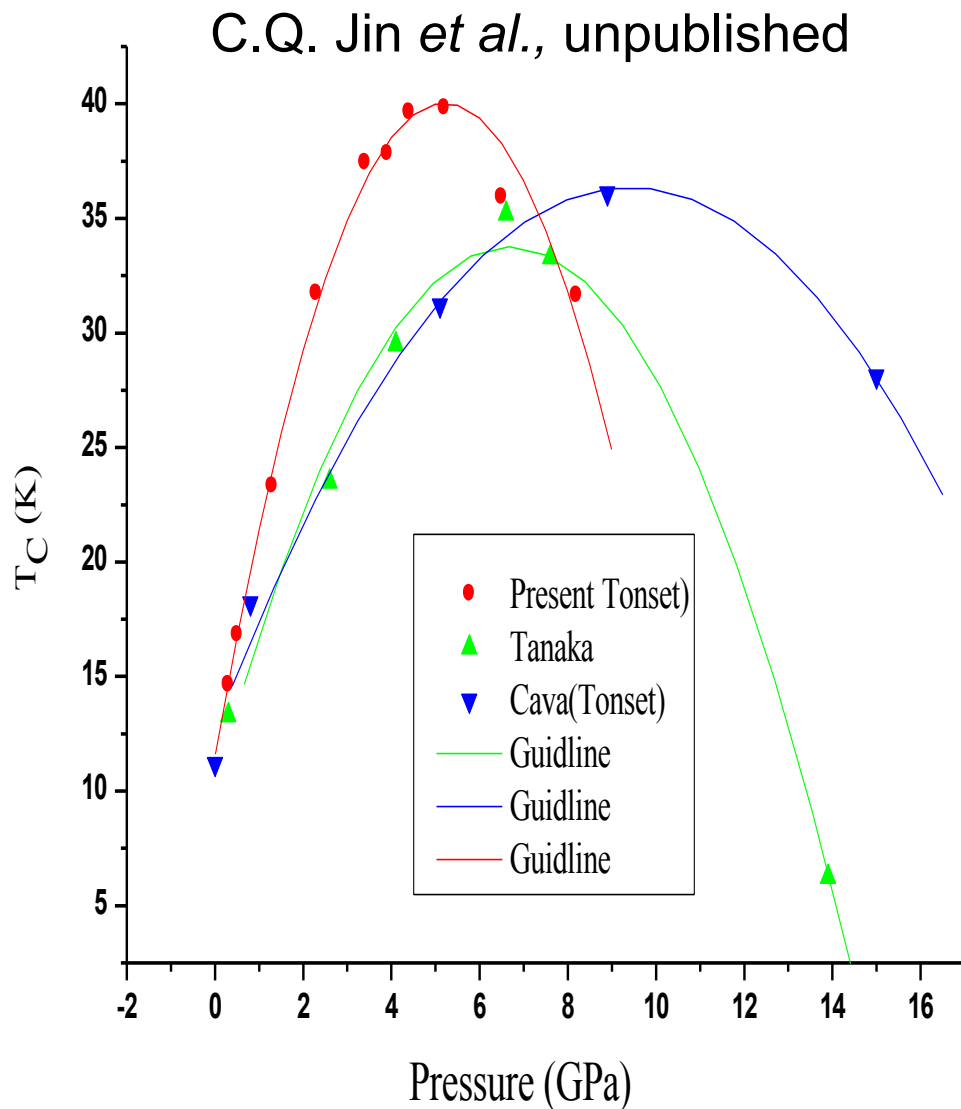
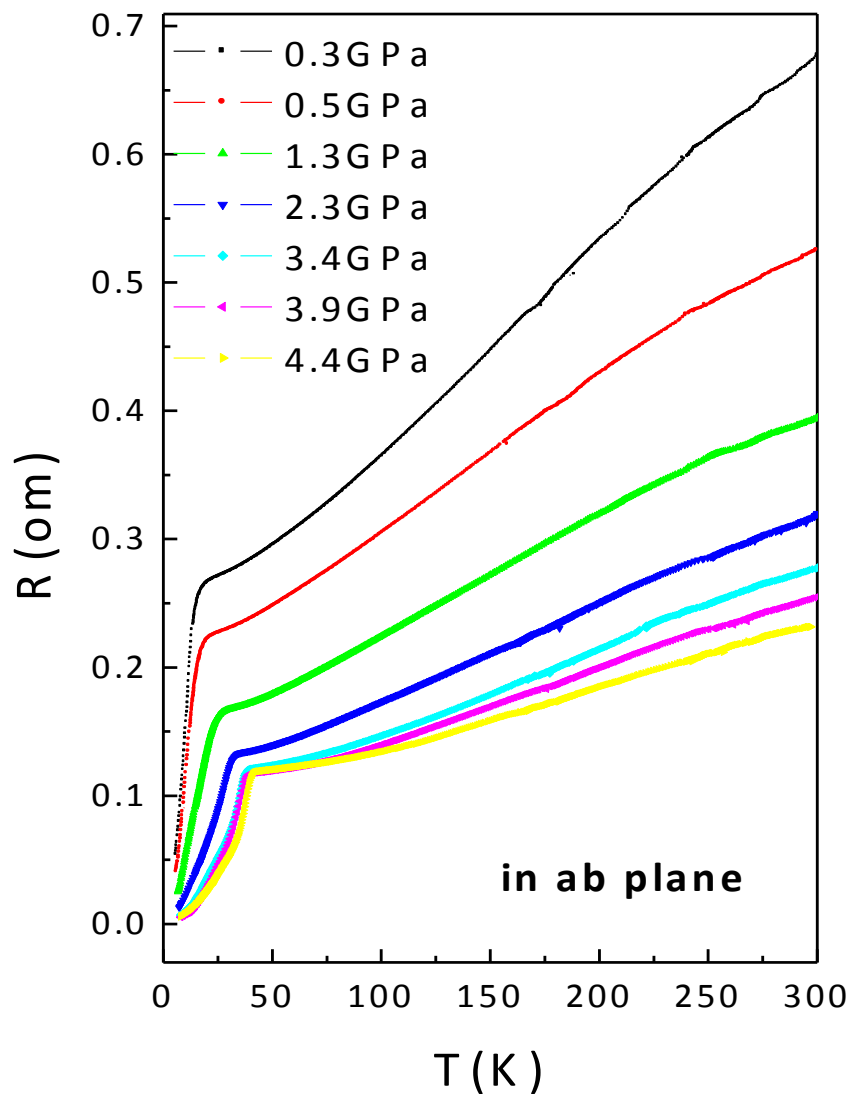


Relation between all clues obtained by optical pump-probe

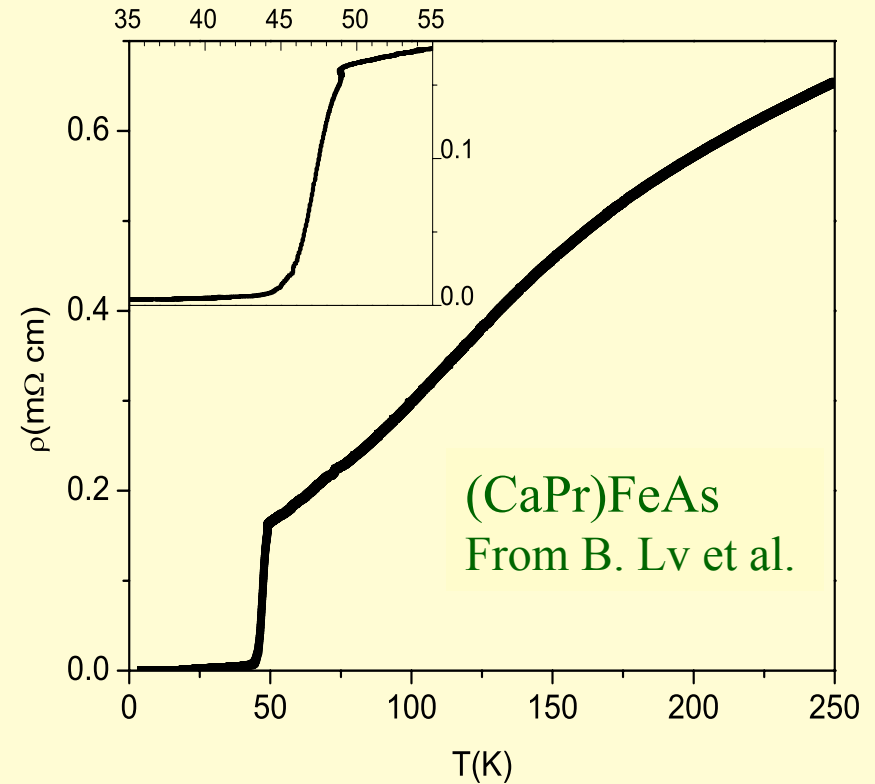
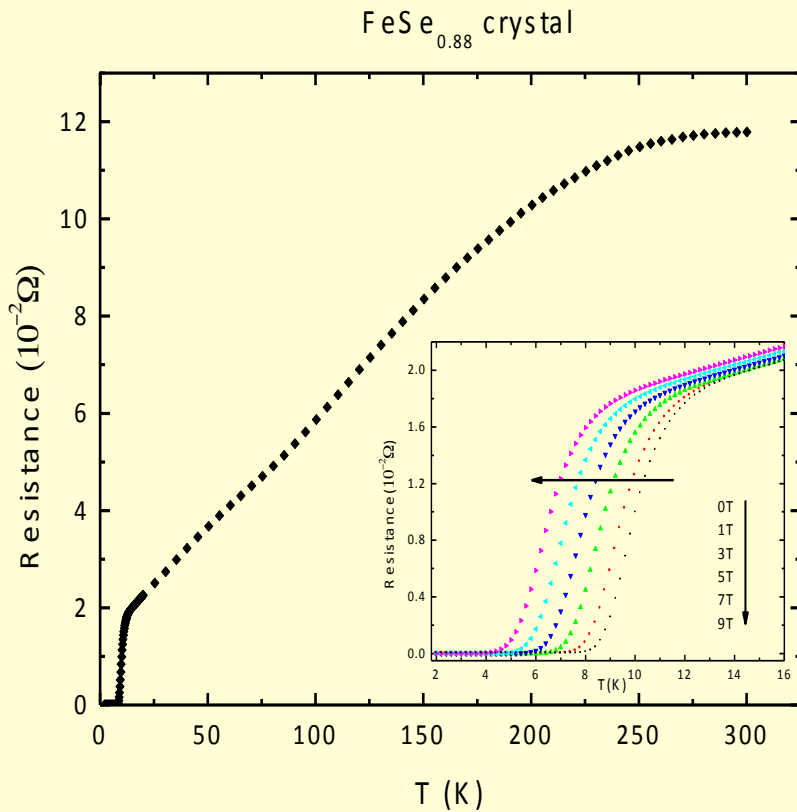


Spin fluctuation and modification of electronic band structure develop at/near the temperature of structural phase transition.

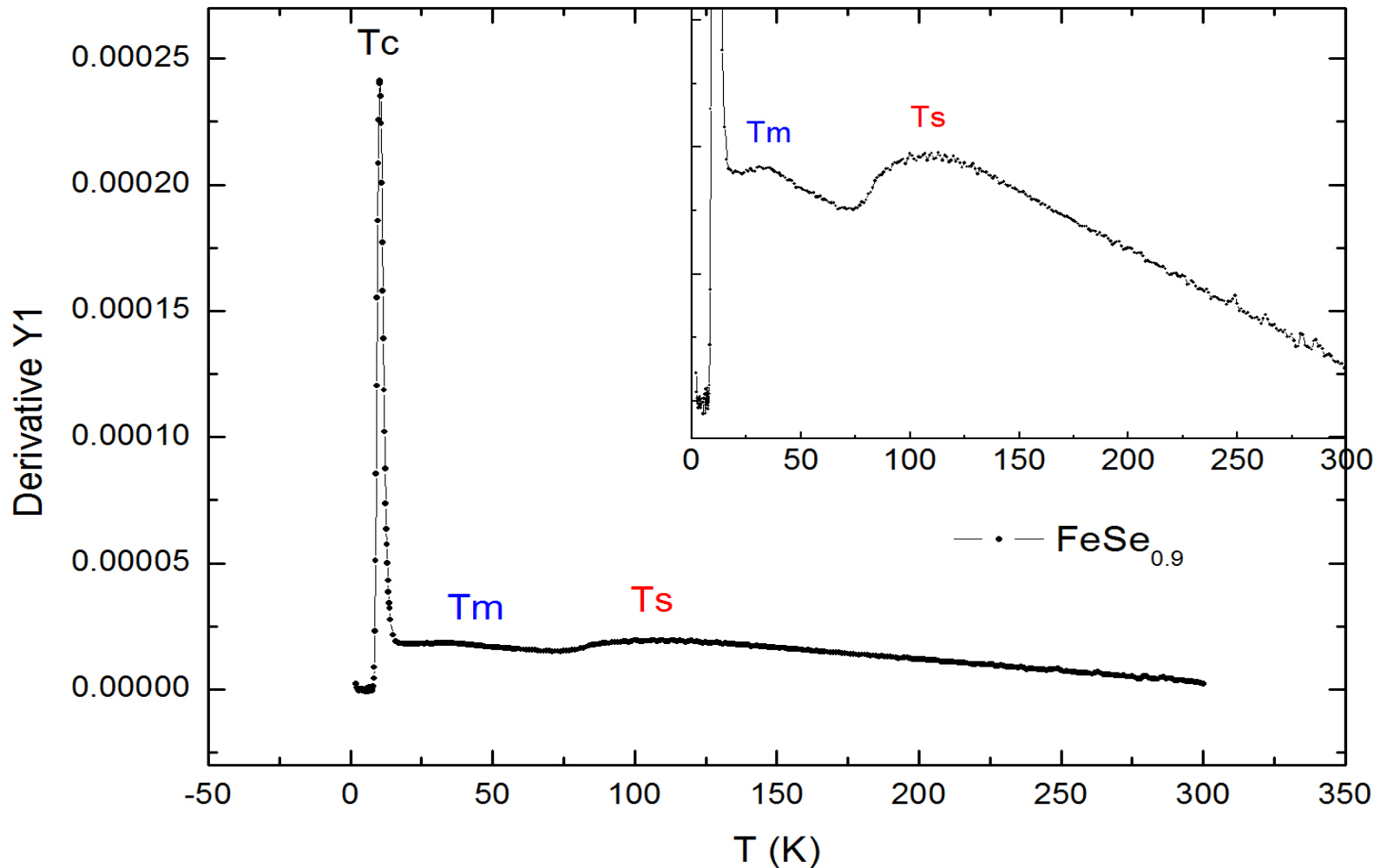
Pressure Effect on FeSe



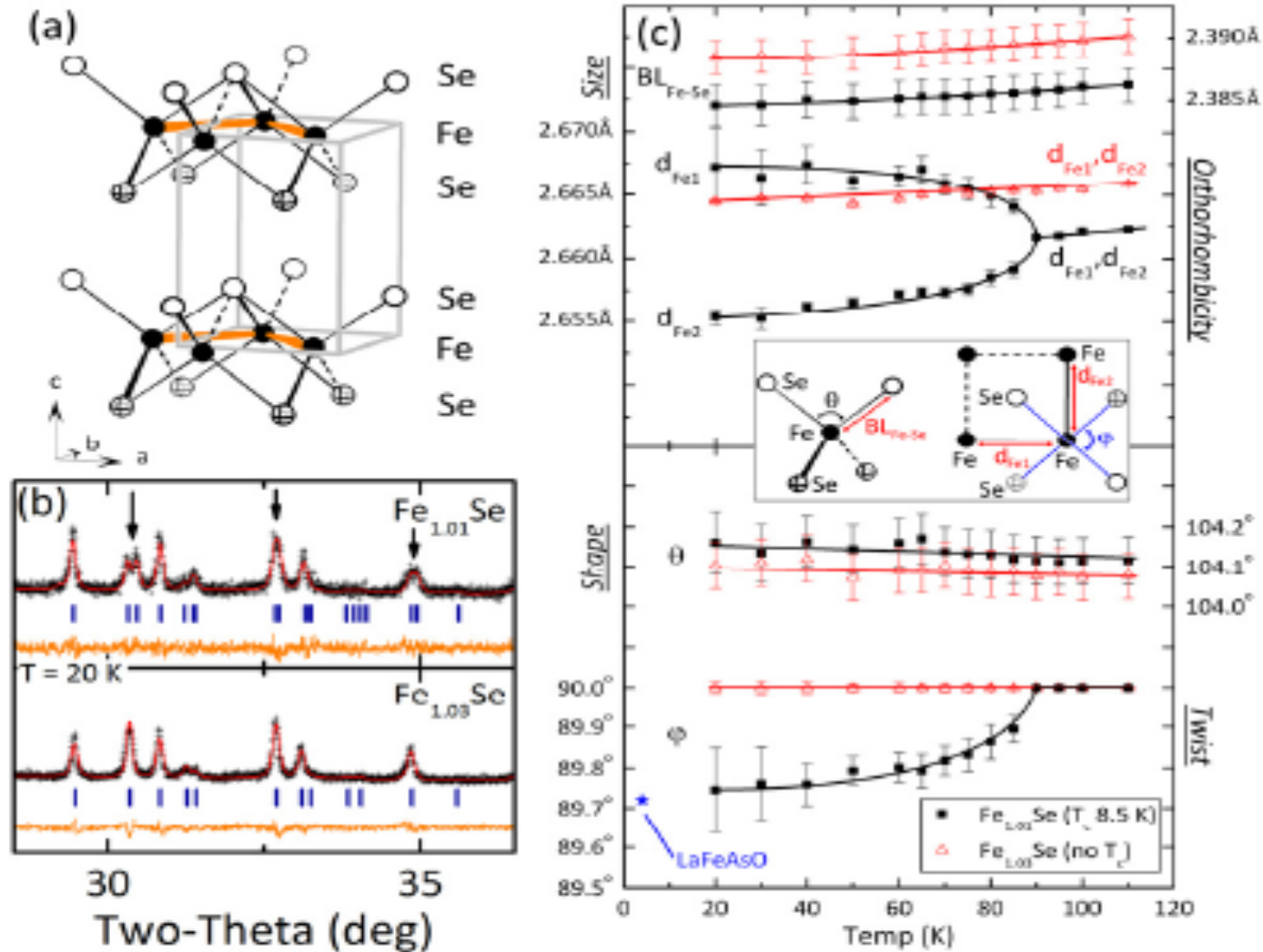
Resistive behavior in Fe-based superconductors?



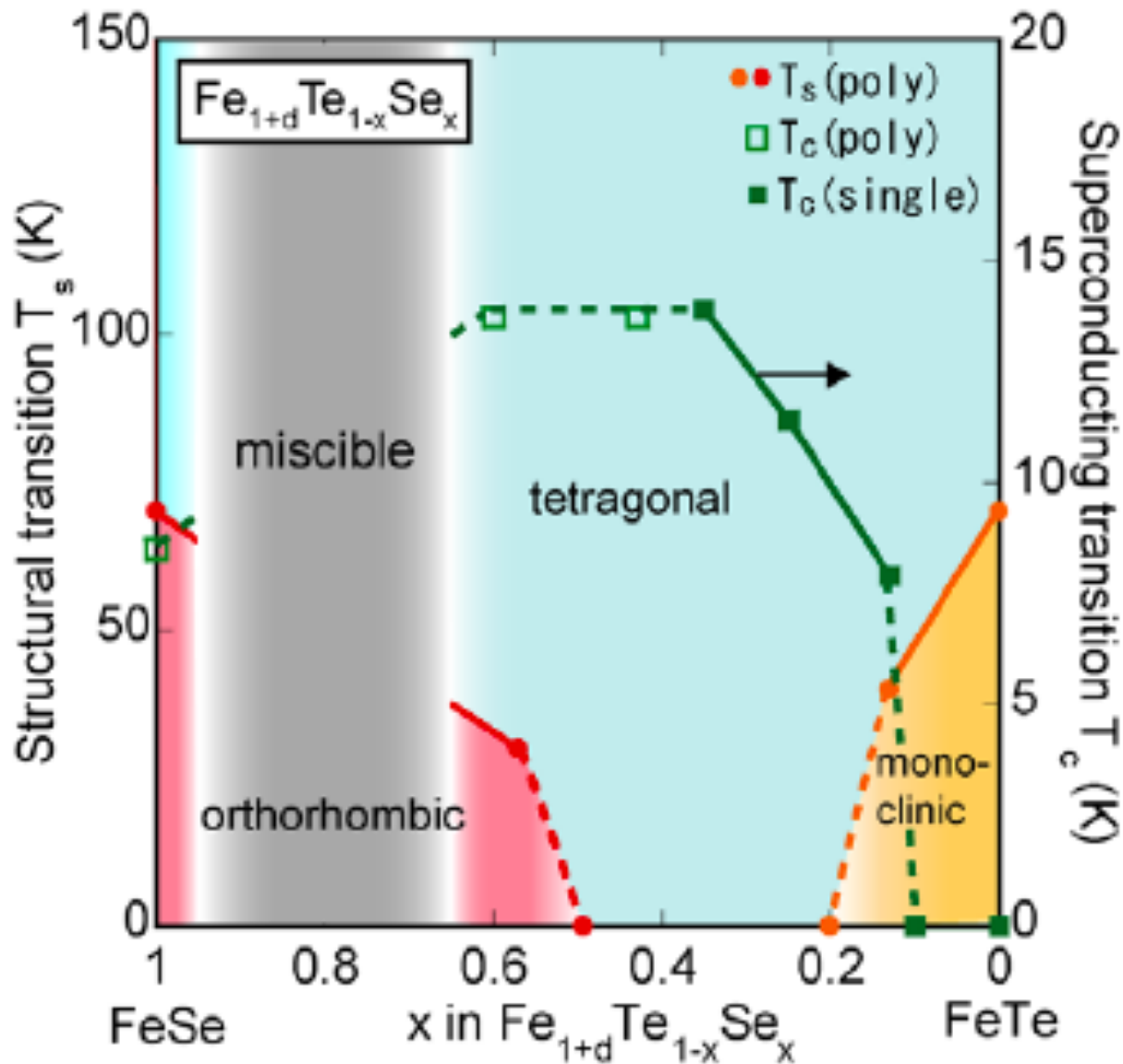
Electrical Resistivity of FeSe—Suggest the existence of higher T_c phase?



What is the Exact Stoichiometry of Fe_{1+x}Se ?

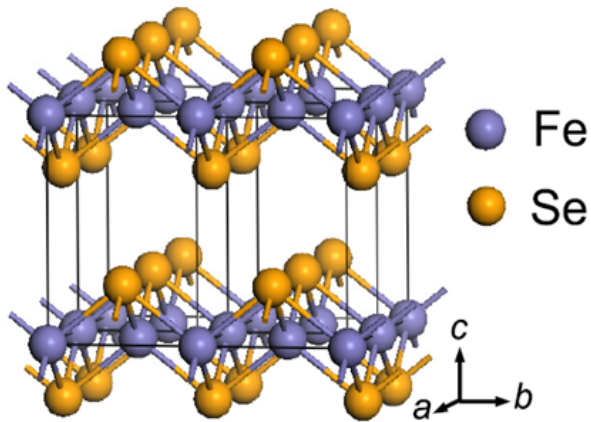


What is the Phase Diagram of Fe_{1+x}Se ?



Three kinds of Fe selenide superconductors

Bulk FeSe (2008)



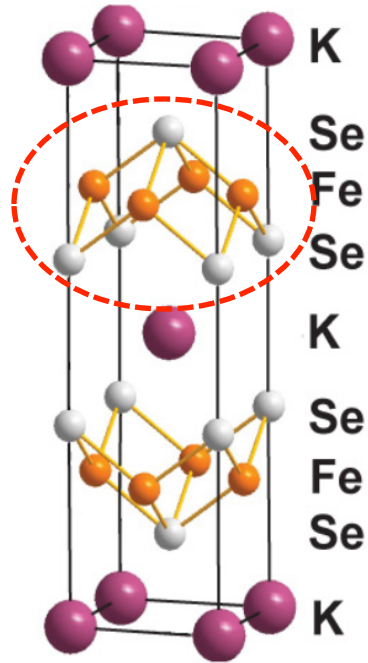
$T_c \sim 9\text{K}$

$\sim 36.7\text{ K at}$

8.9GPa

$\text{K}_{1-x}\text{Fe}_{2-y}\text{Se}_2$ (2011)

Alkali intercalated FeSe

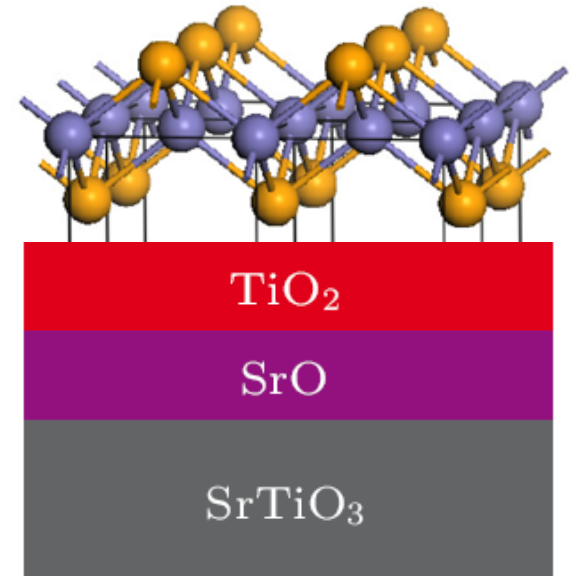


$T_c \sim 33\text{K}$

$\sim 48\text{ K at } 11\text{ GPa}$

FeSe monolayer (2012)

on SrTiO_3 substrate



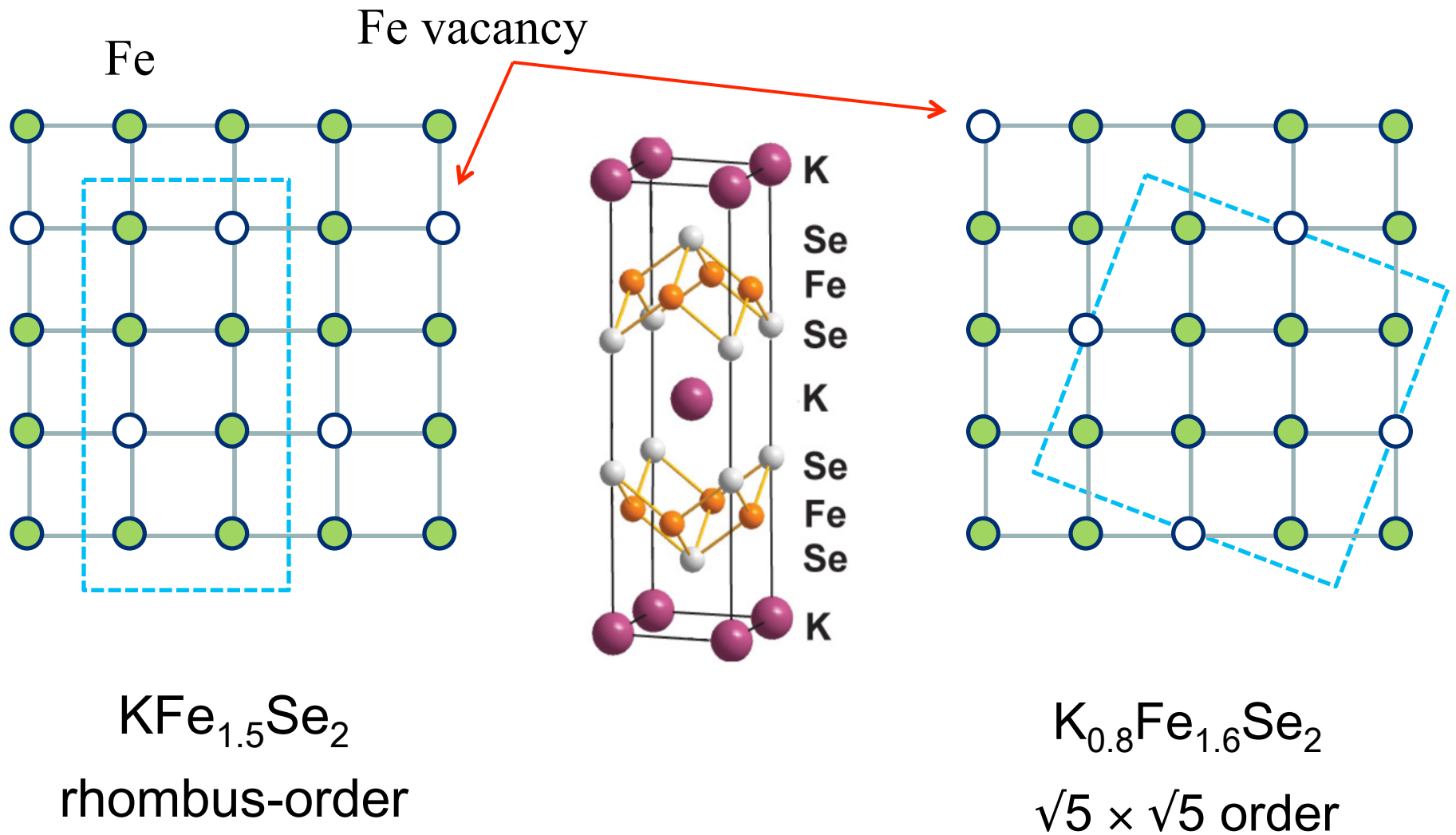
$T_c > 30\text{K}$

$\sim 65\text{K} ?$

decreasing dimensionality



Fe vacancy order in $K_{1-x}Fe_{2-y}Se_2$



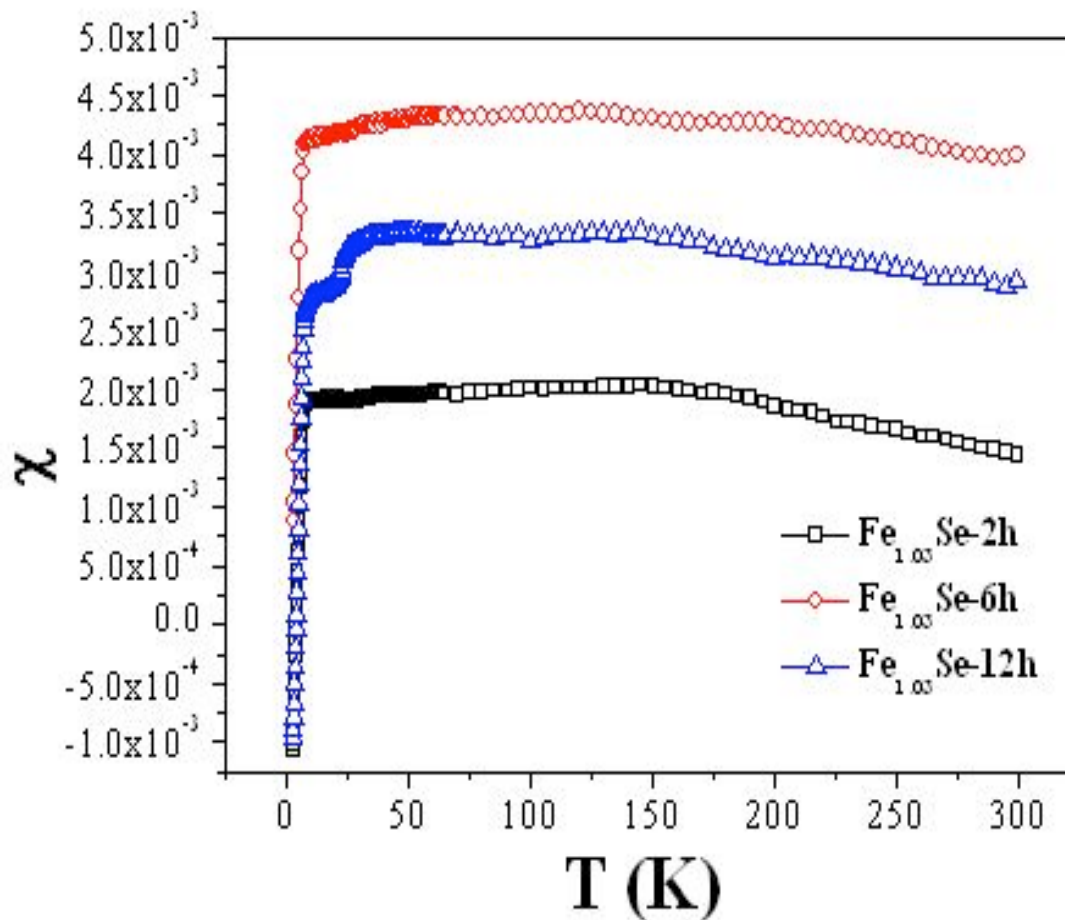
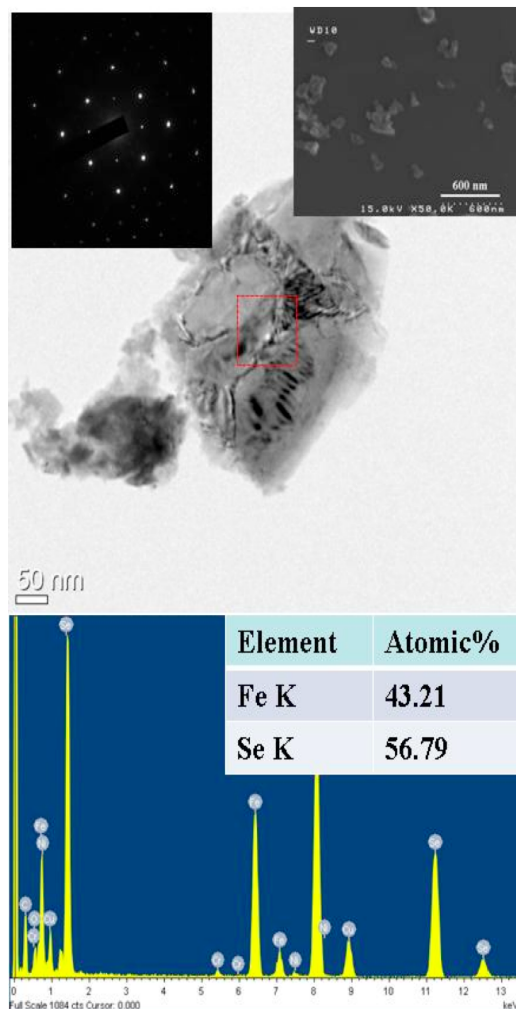
Yan, et al., PRL 106, 087005 (2011)

Study of FeSe Nano-Structure

- The unanswered questions led us to speculate that the presence of defects in FeSe is critical to its superconductivity
- Nanostructures provide important insight into the better understanding of defects in materials of interest
- Techniques to fabricate FeSe nanostructure are well-developed and simple

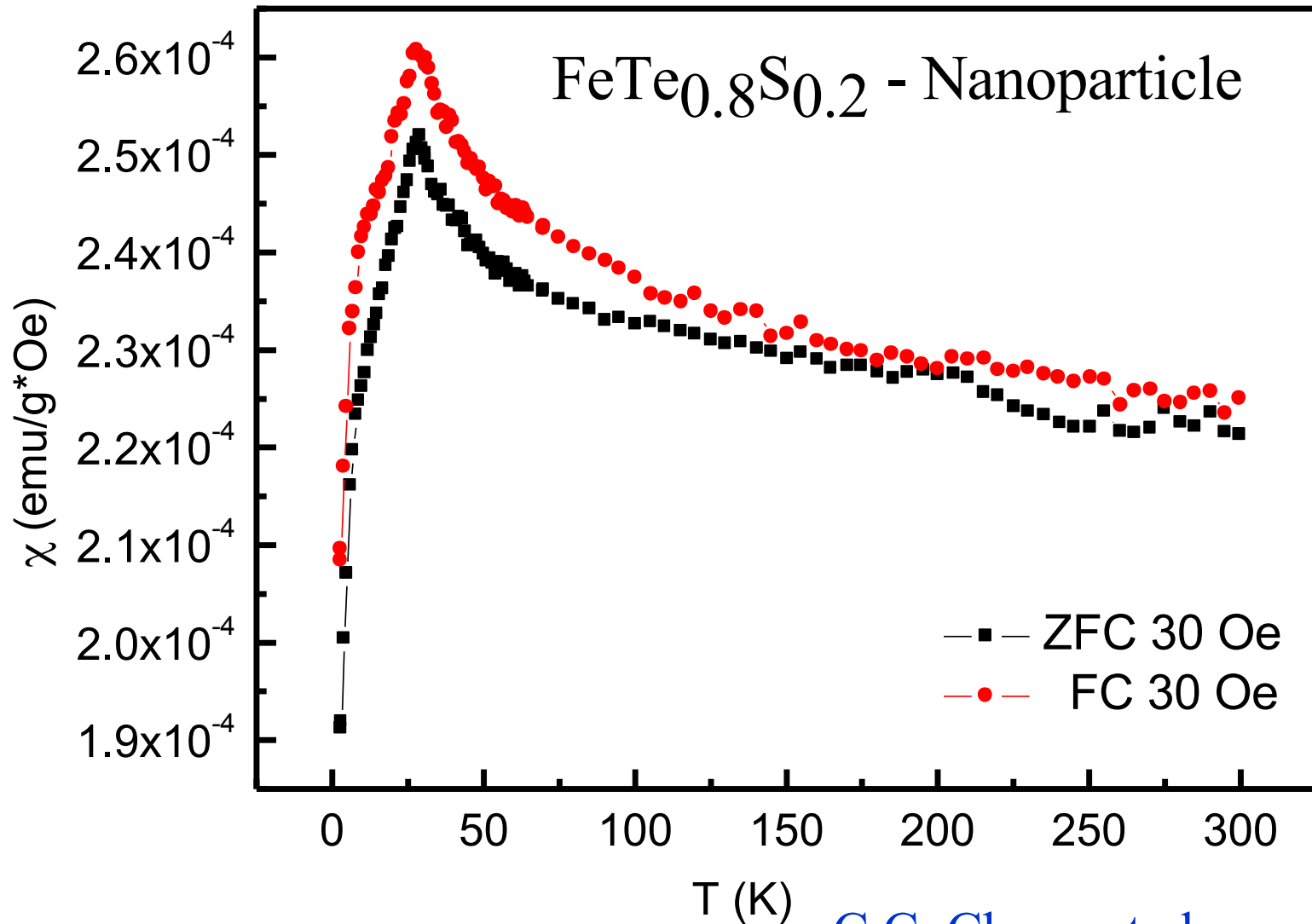
FeSe Nanoparticle

Reaction under Autogenic Pressure at Elevated Temperature (RAPET)



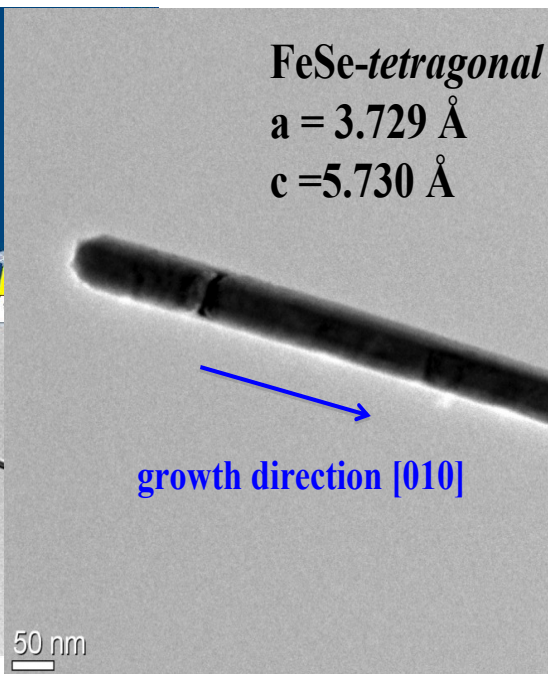
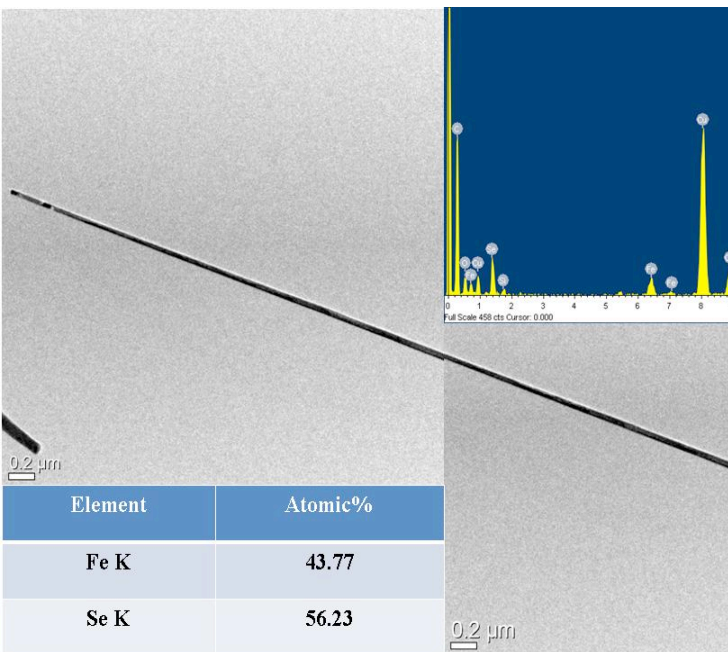
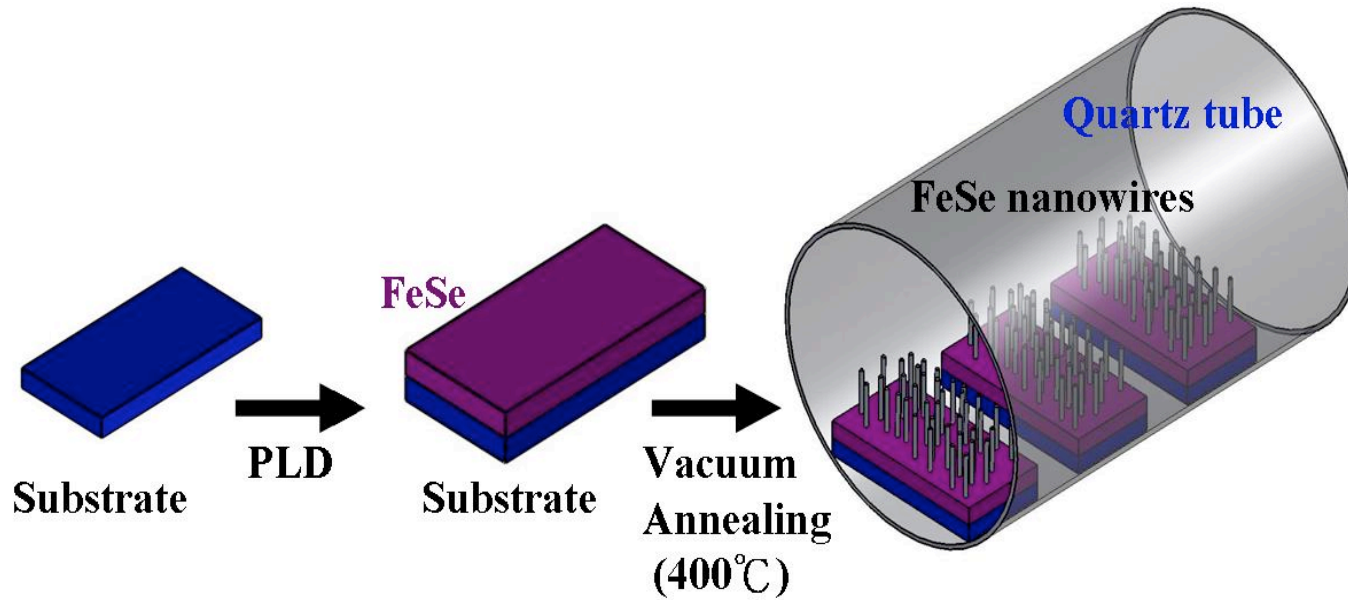
C.C. Chang et al., SSC, 2011

Fe-Te-S Nanoparticle

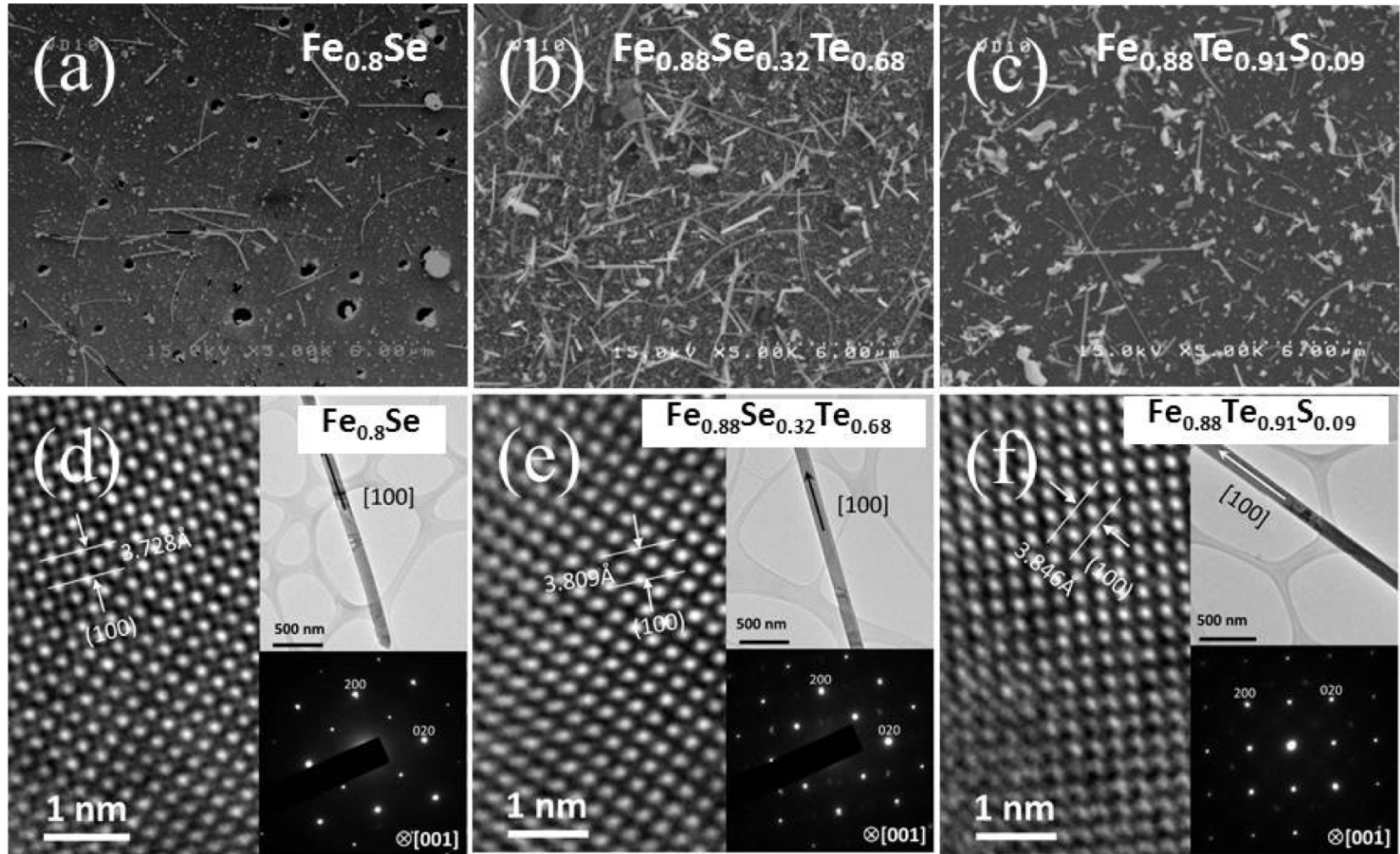


C.C. Chang et al., unpublished

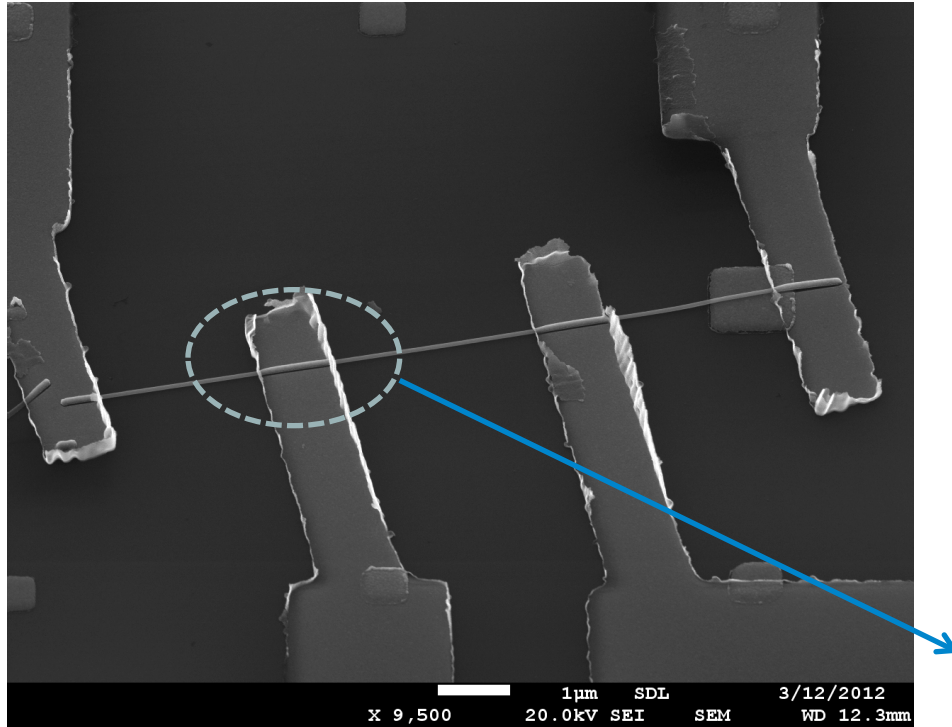
Fe-Se-(Te) (tetragonal) Nanowire



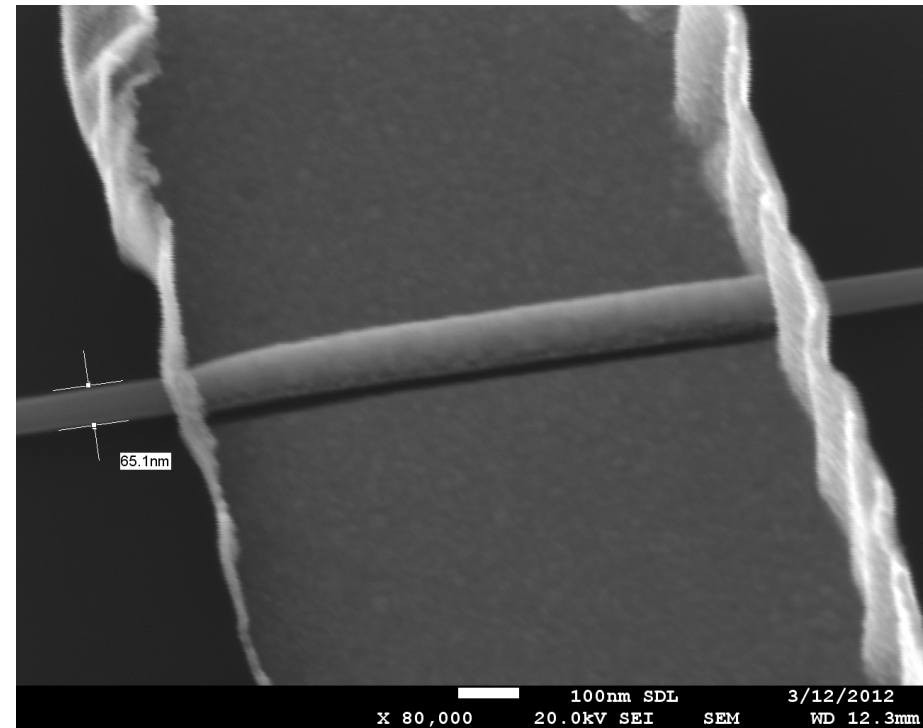
TEM images of Fe-Se-(Te) Nanowire



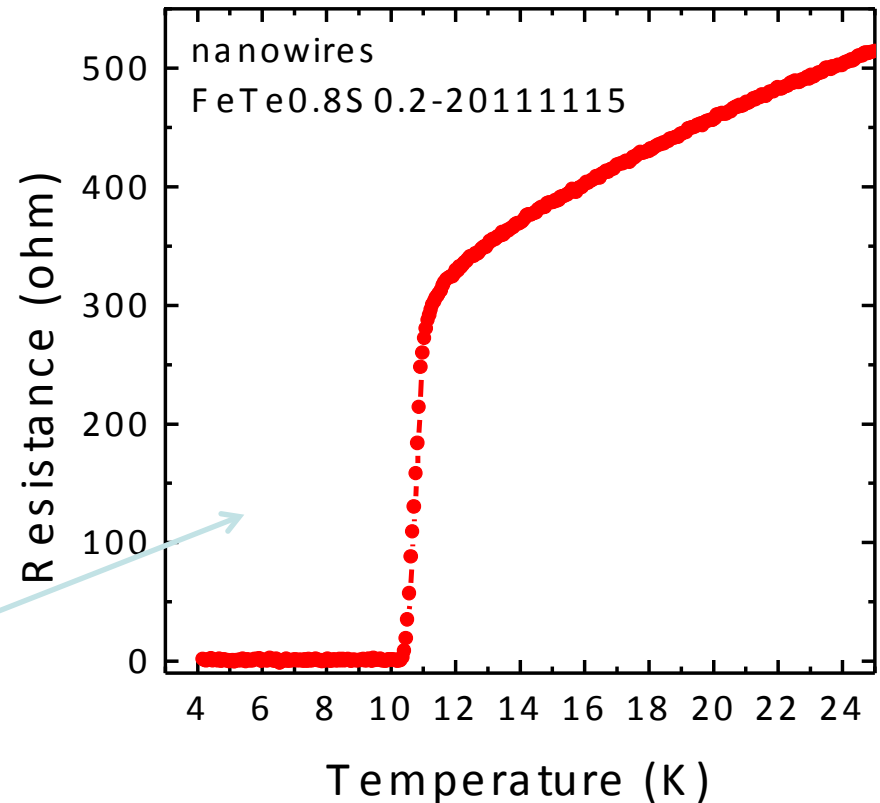
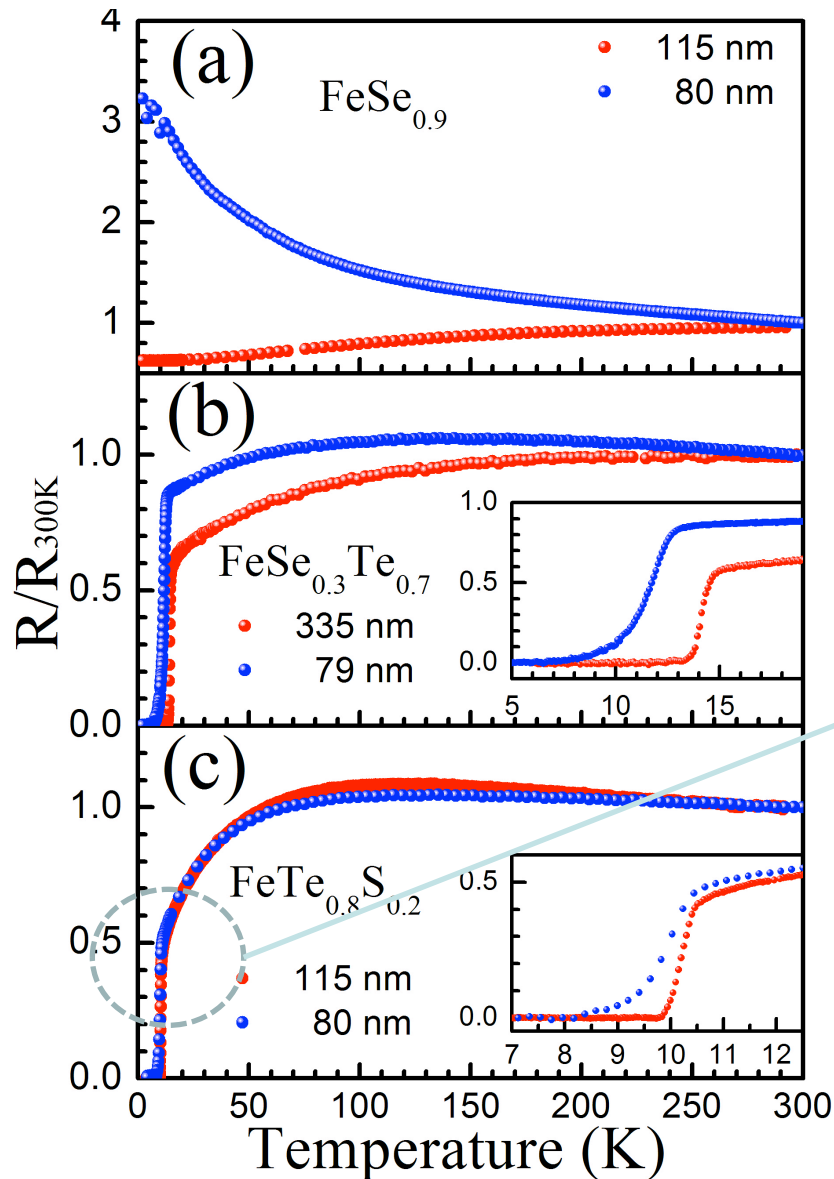
Nanowires, Fe(Te-S/Se)



after electrode patterning

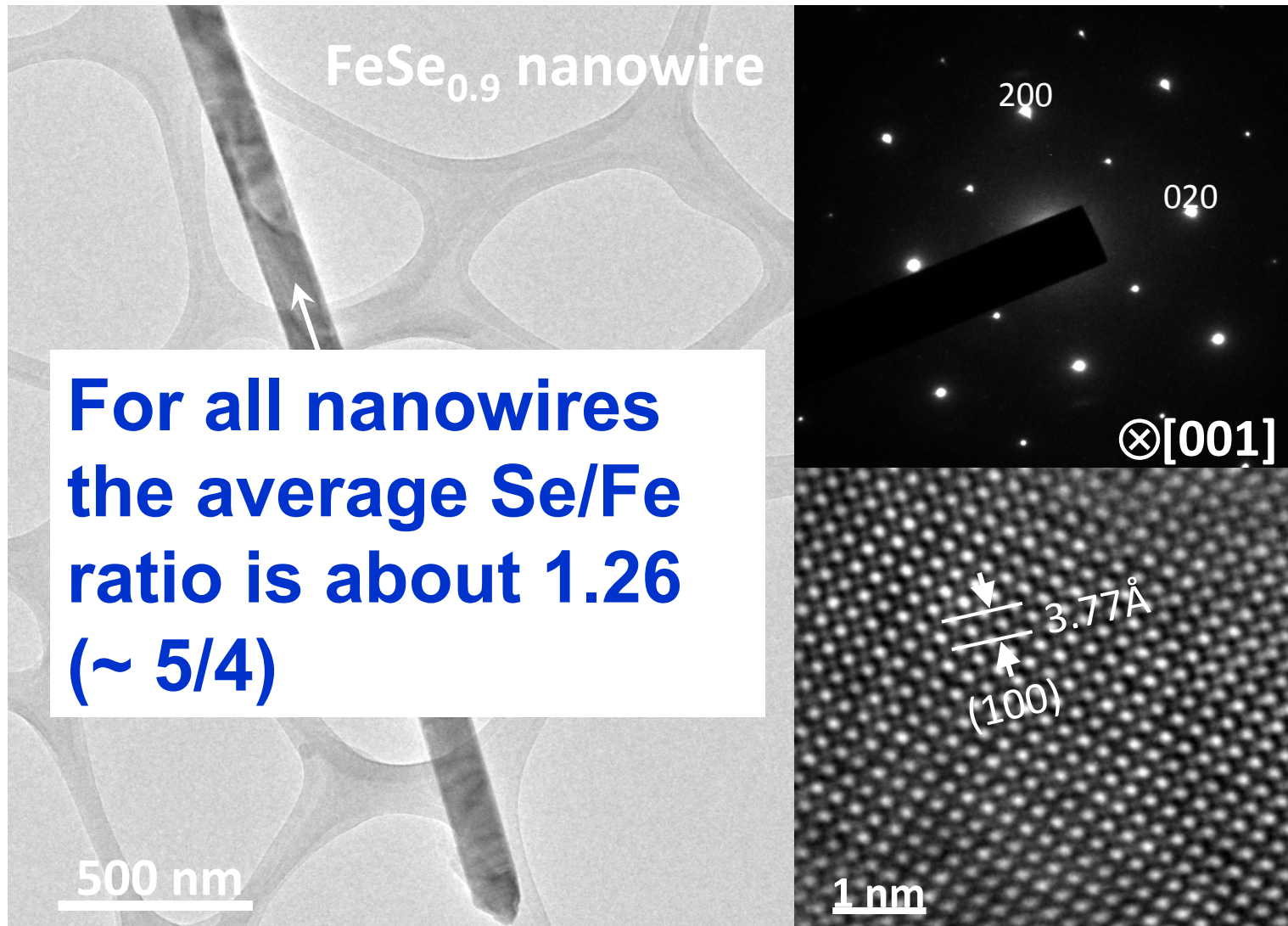


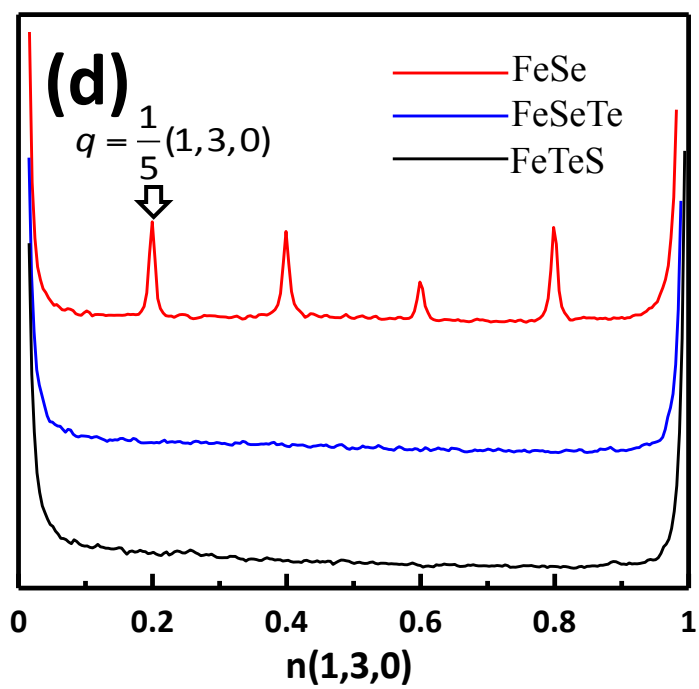
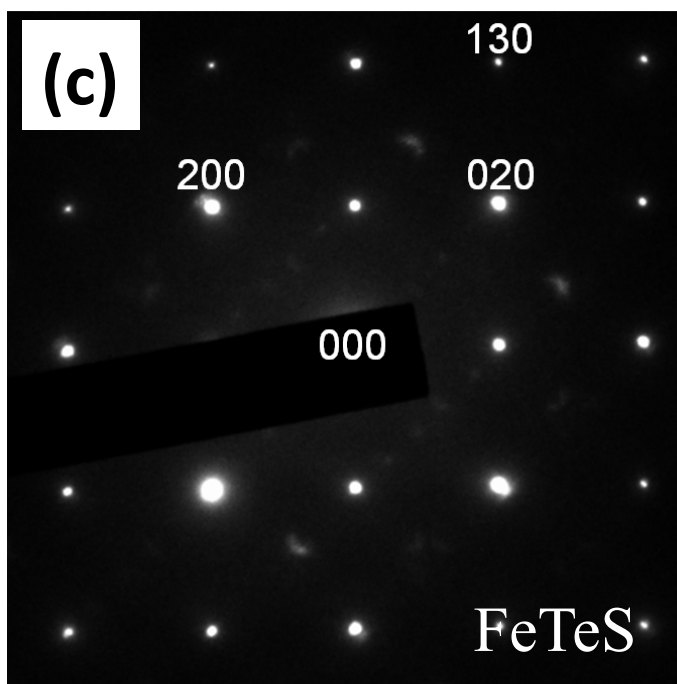
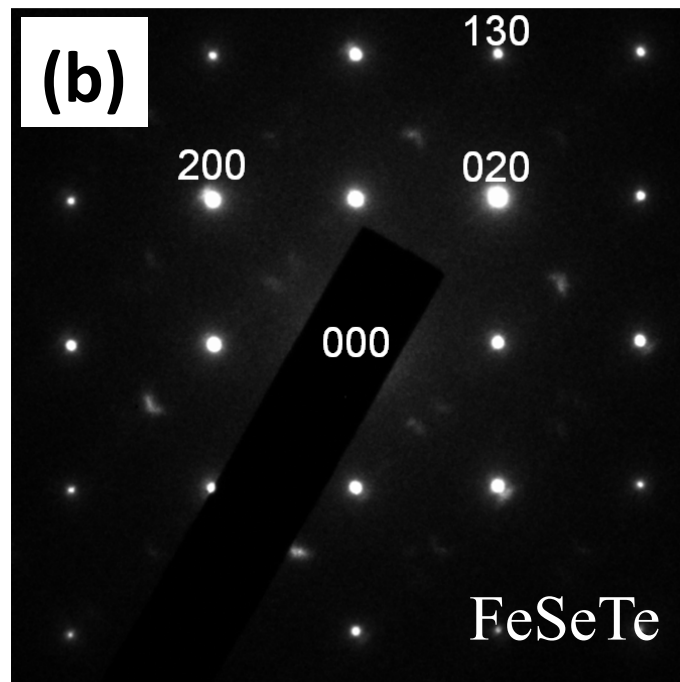
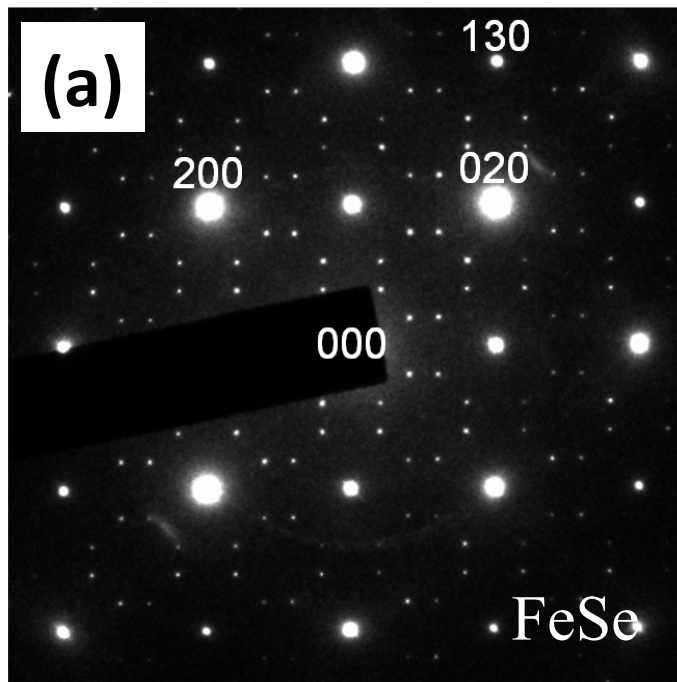
Electrical Resistance of Fe-Se-(Te) Nanowires



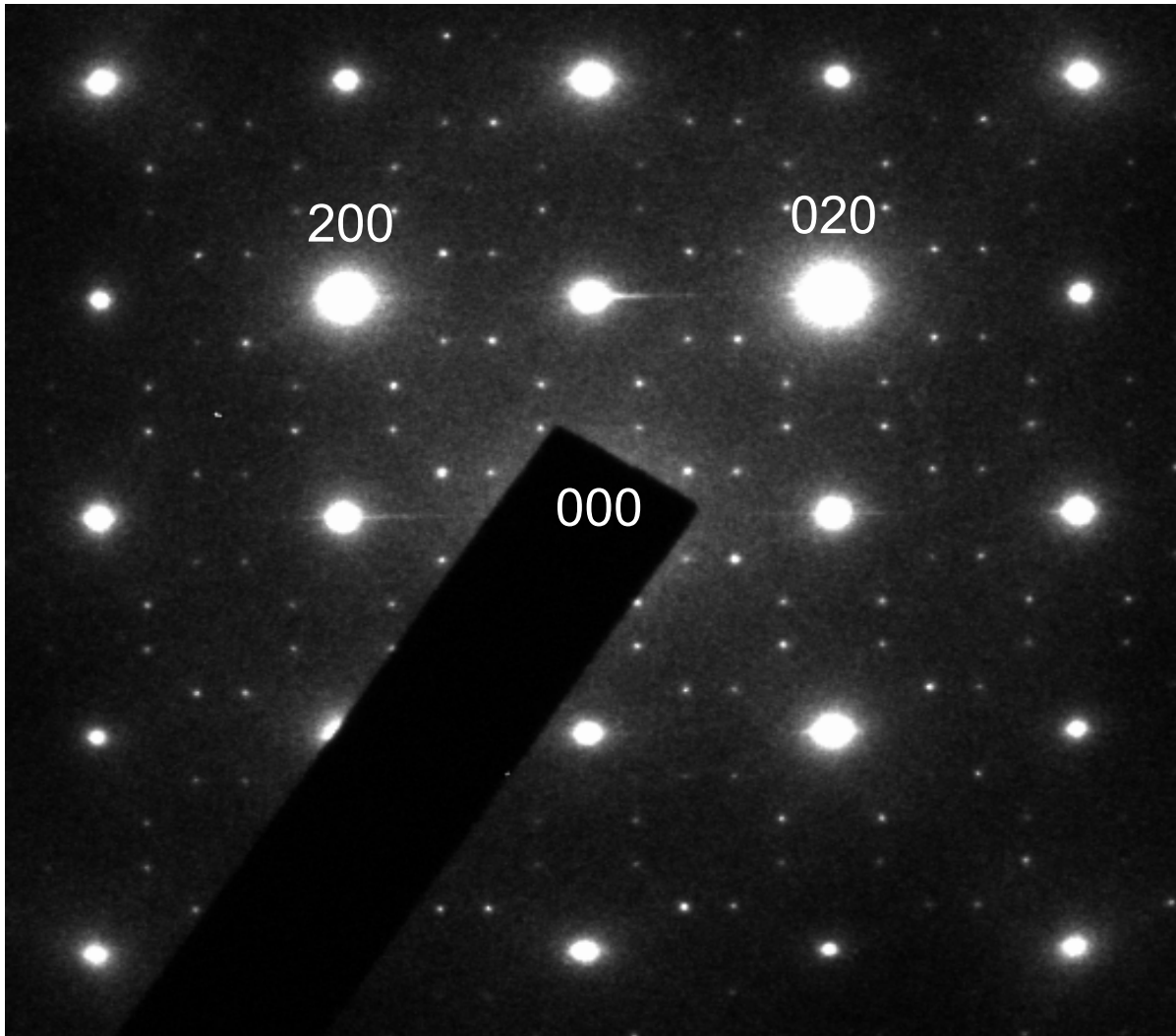
H.H. Chang et al., submitted

$\text{FeSe}_{0.9}$ nanowire

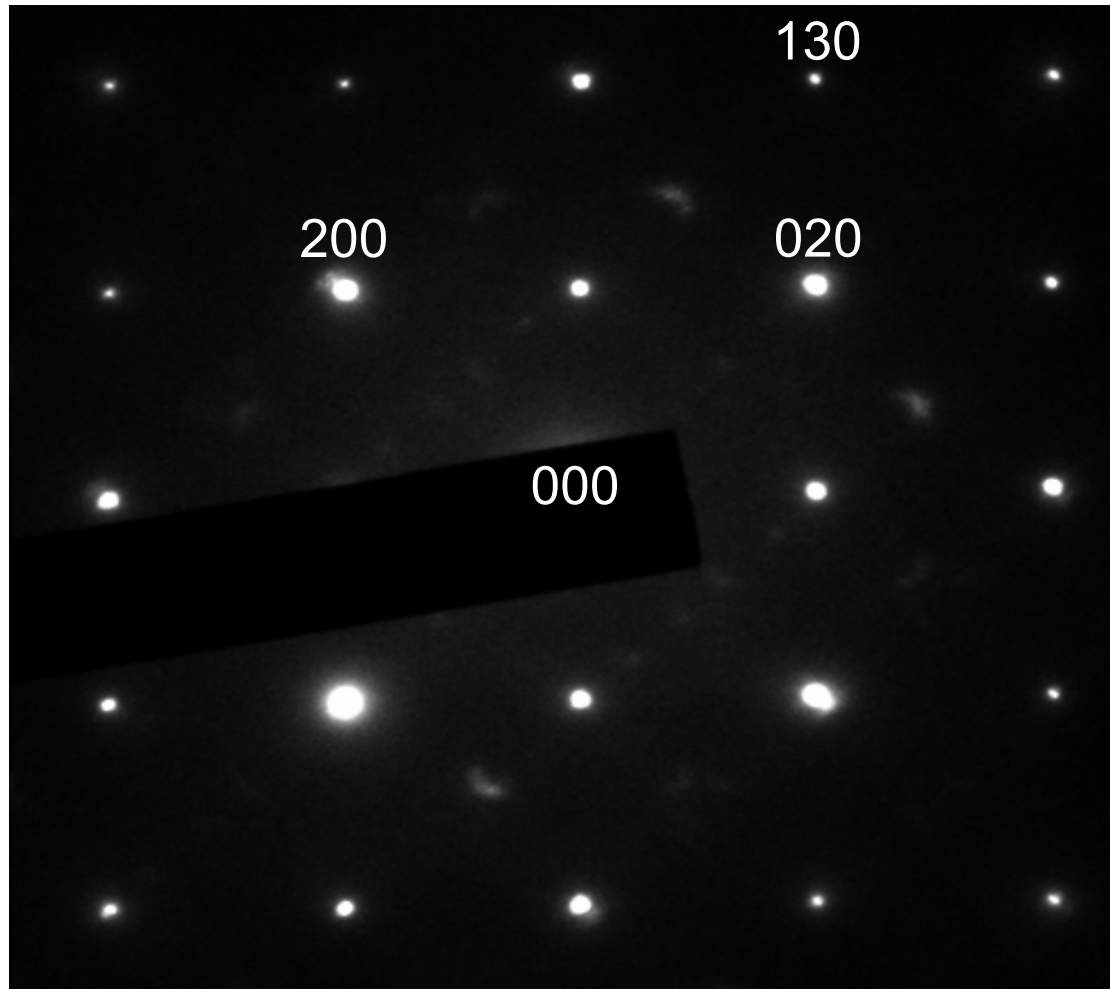




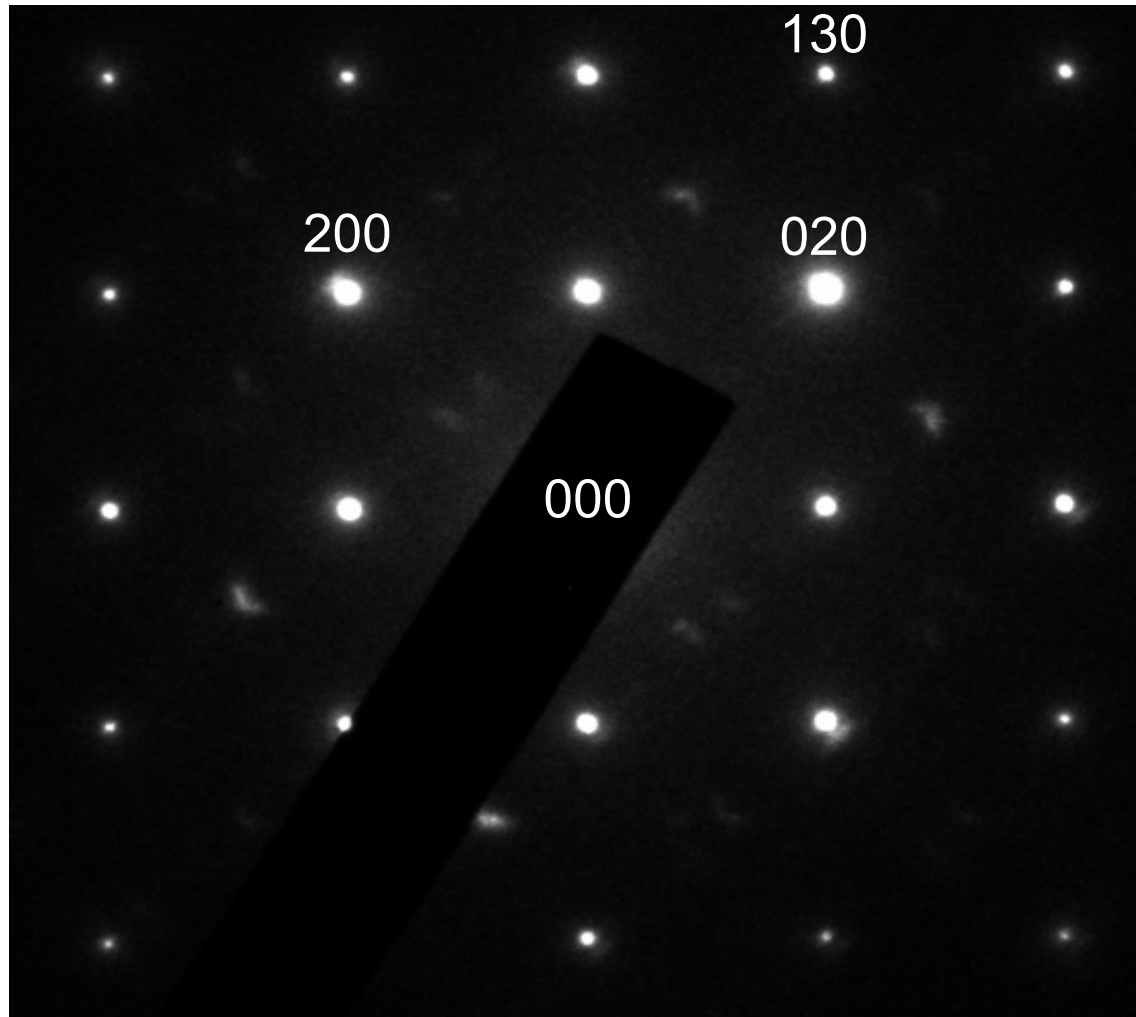
FeSe Nanowire_20120827-8F_no.2



FeTeS Nanowire_20120202_no.3

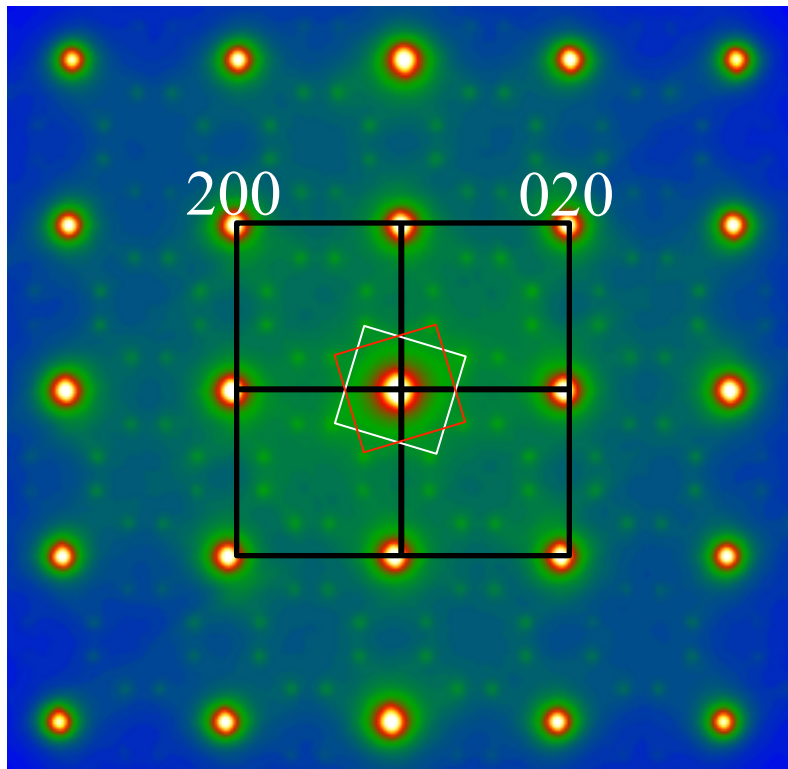


FeSeTe Nanowire_20120207_no.3

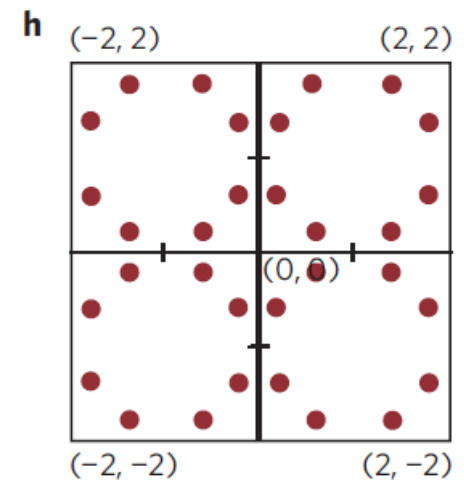
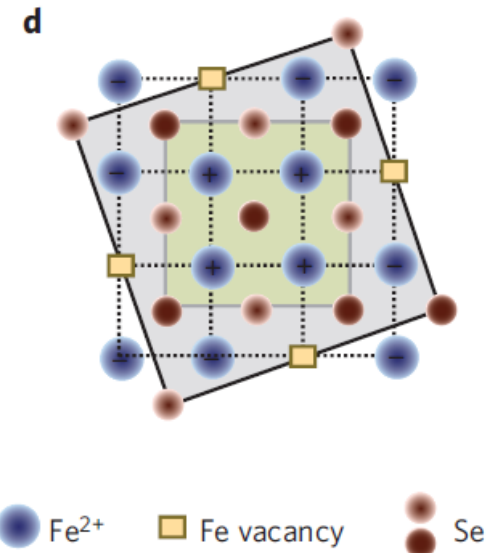


Electron diffraction of FeSe NPS

$\otimes[001]$

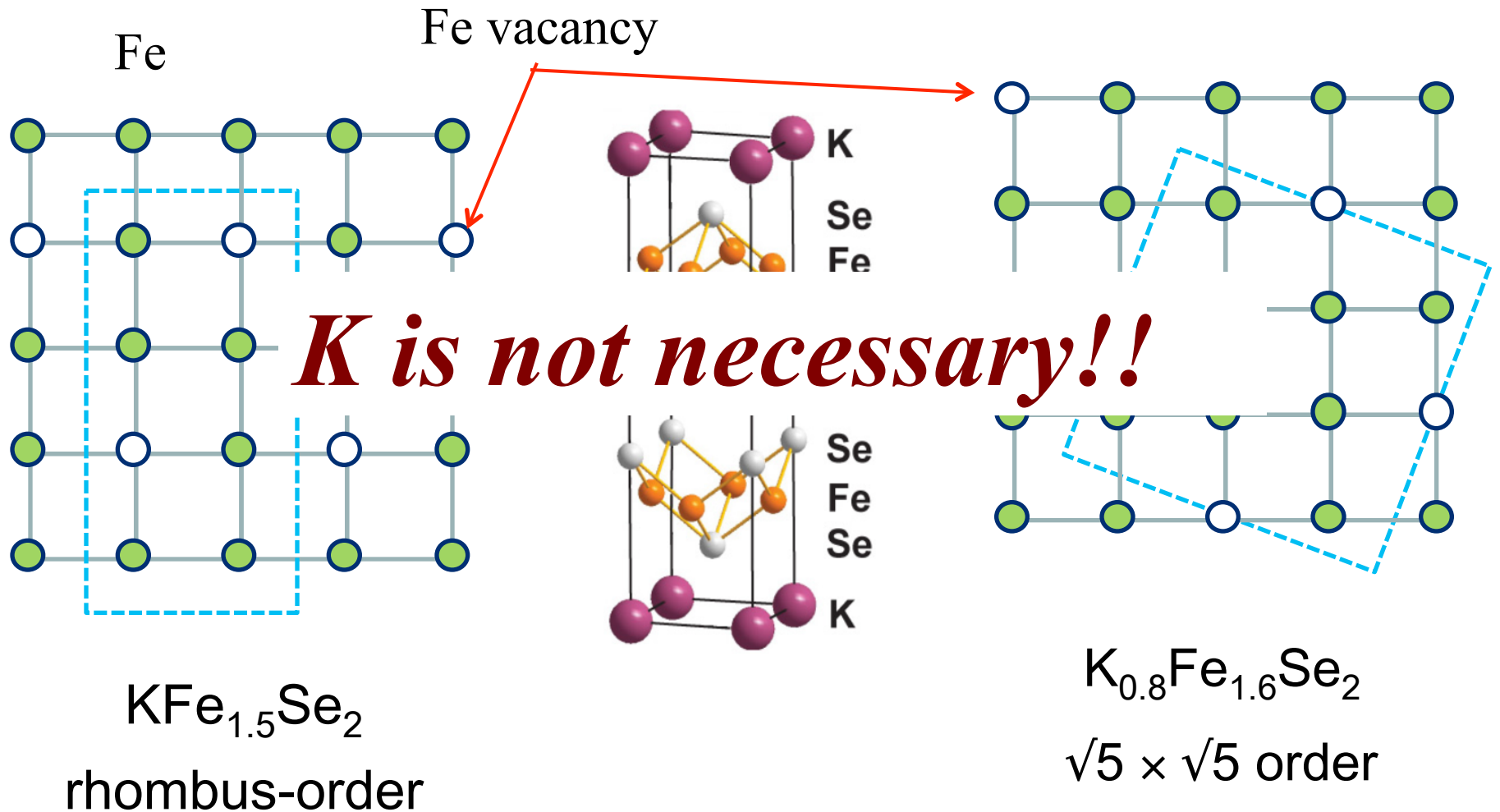


Superlattice structure

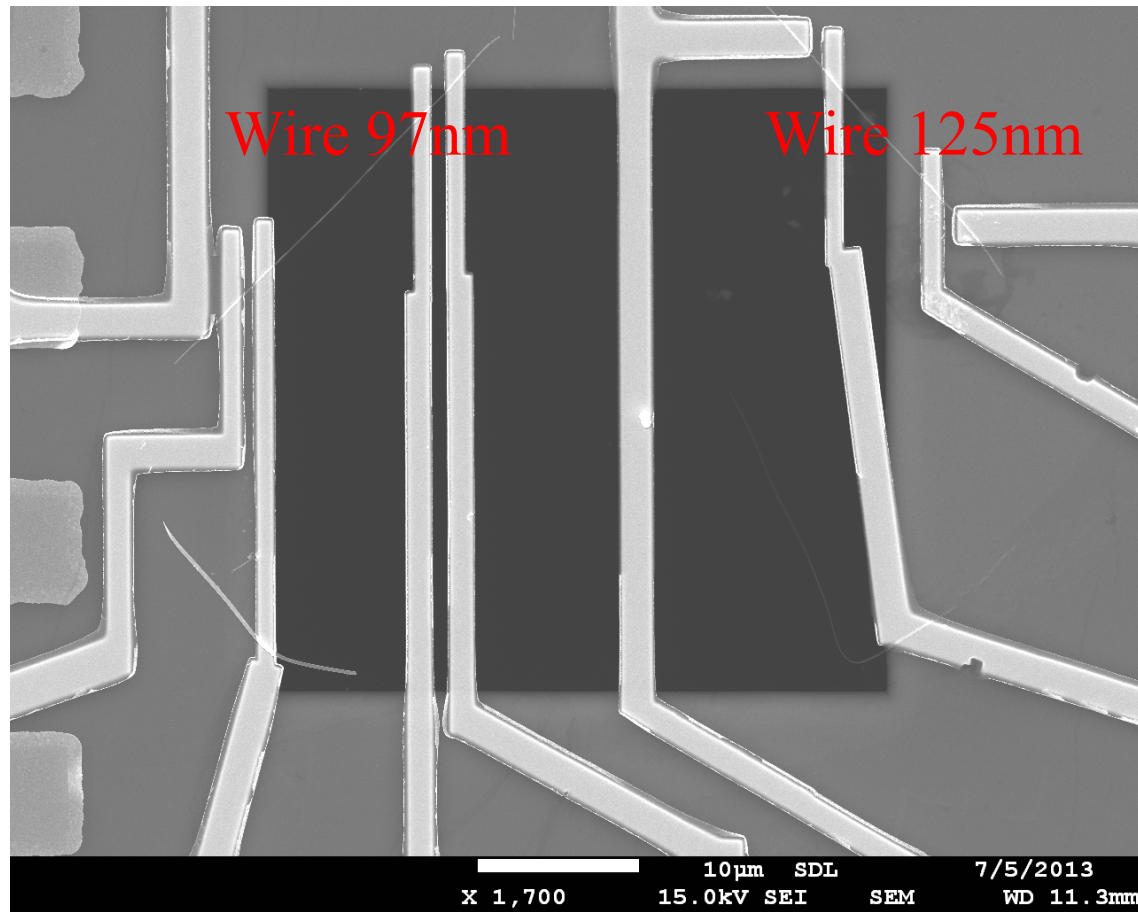


Refs: Nature Physics 8(2012)709.

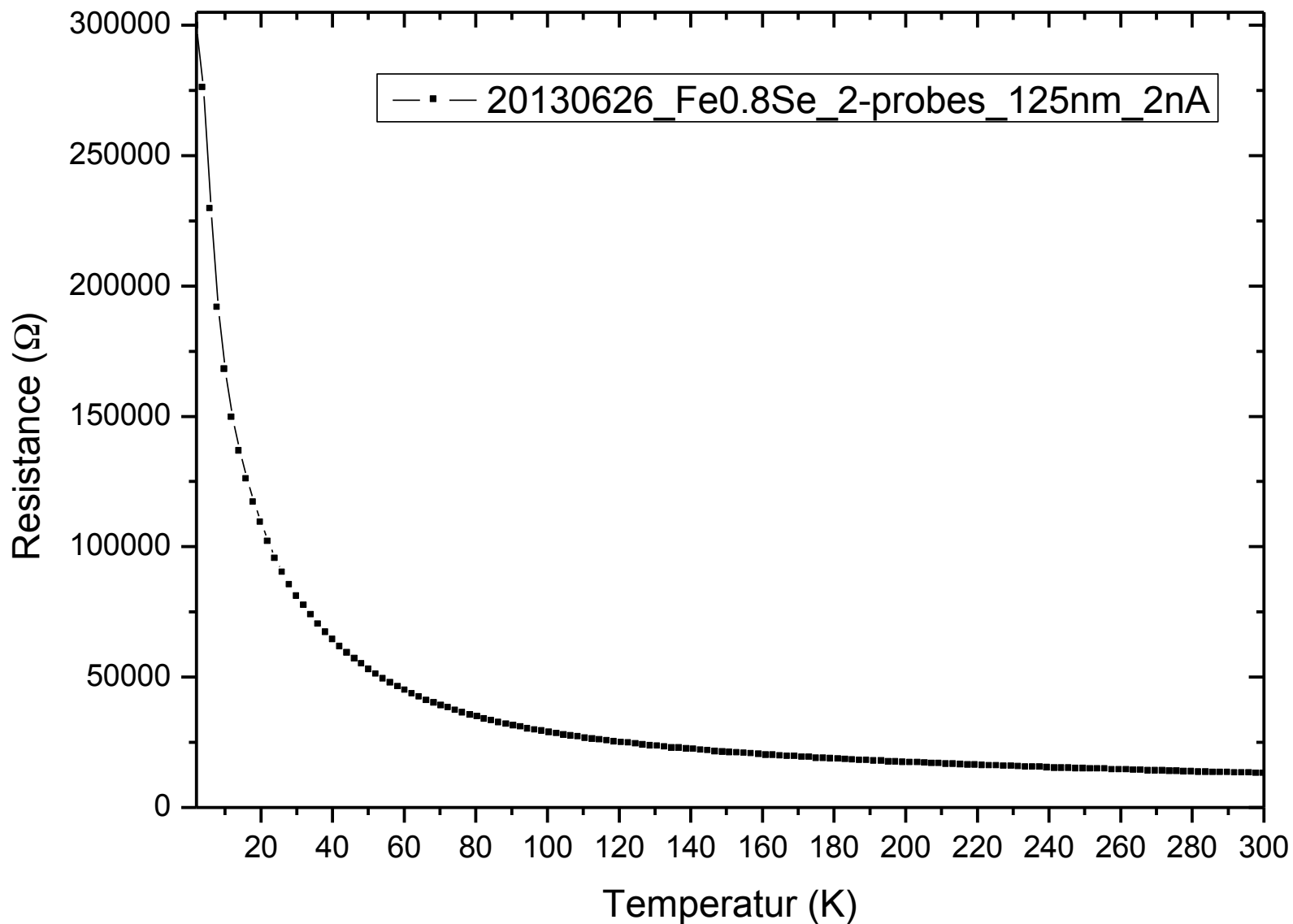
Fe vacancy order in $K_{1-x}Fe_{2-y}Se_2$



20130626_FeSe_Nanowires

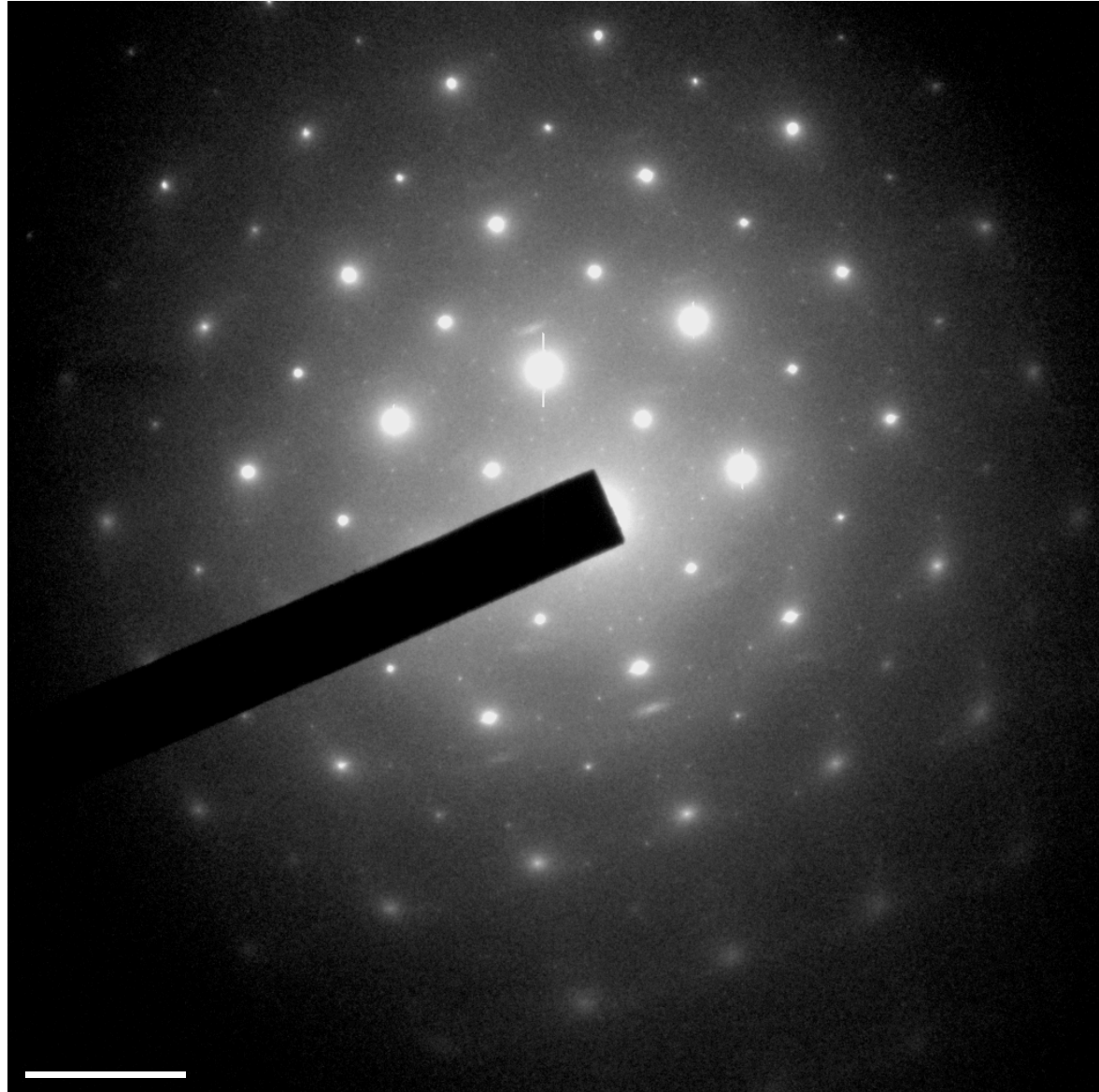


20130605_FeSe_Nanowires_125nm

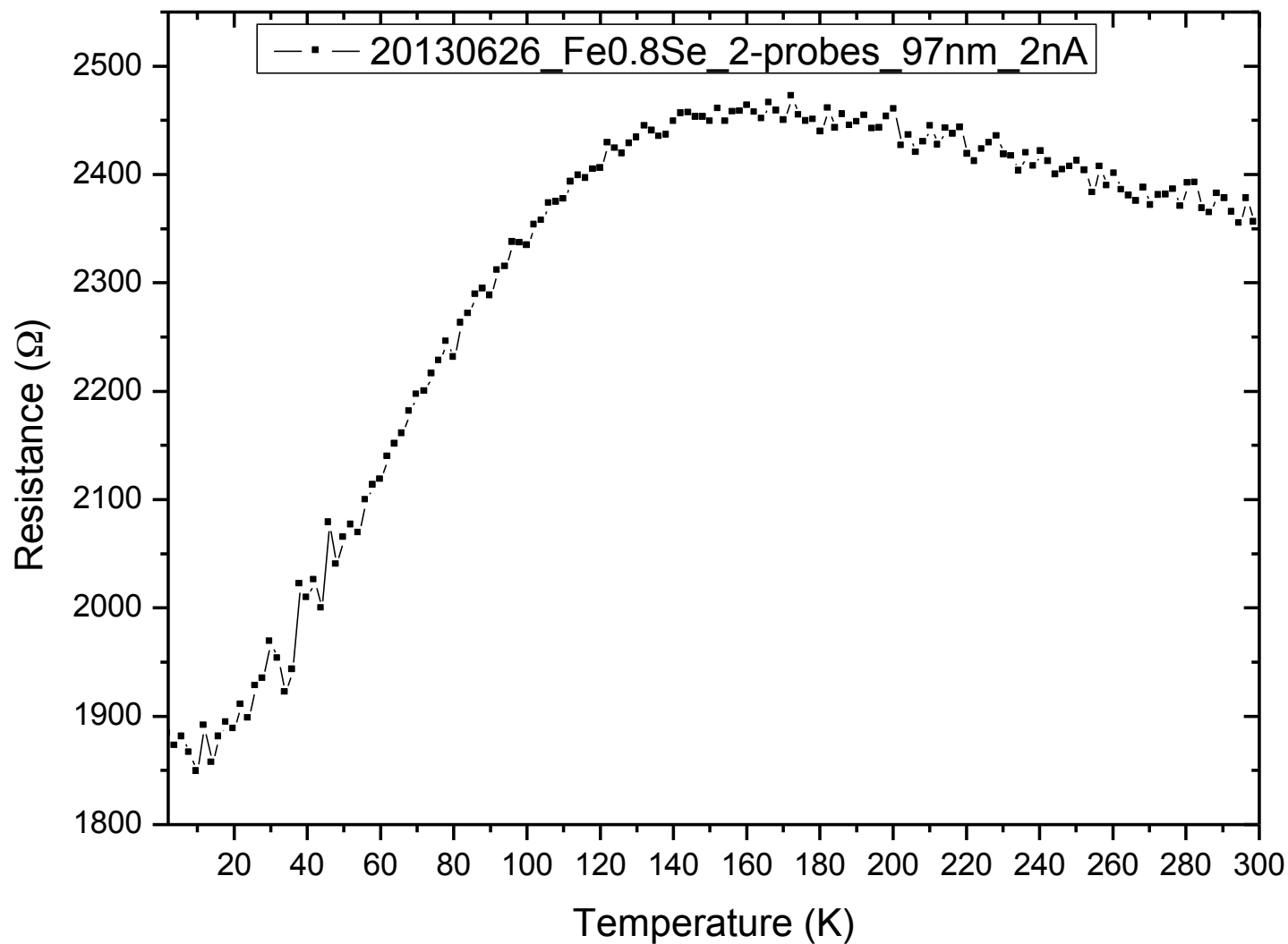


Before EBL

20130605_FeSe_Nanowires_125nm Tetragonal phase

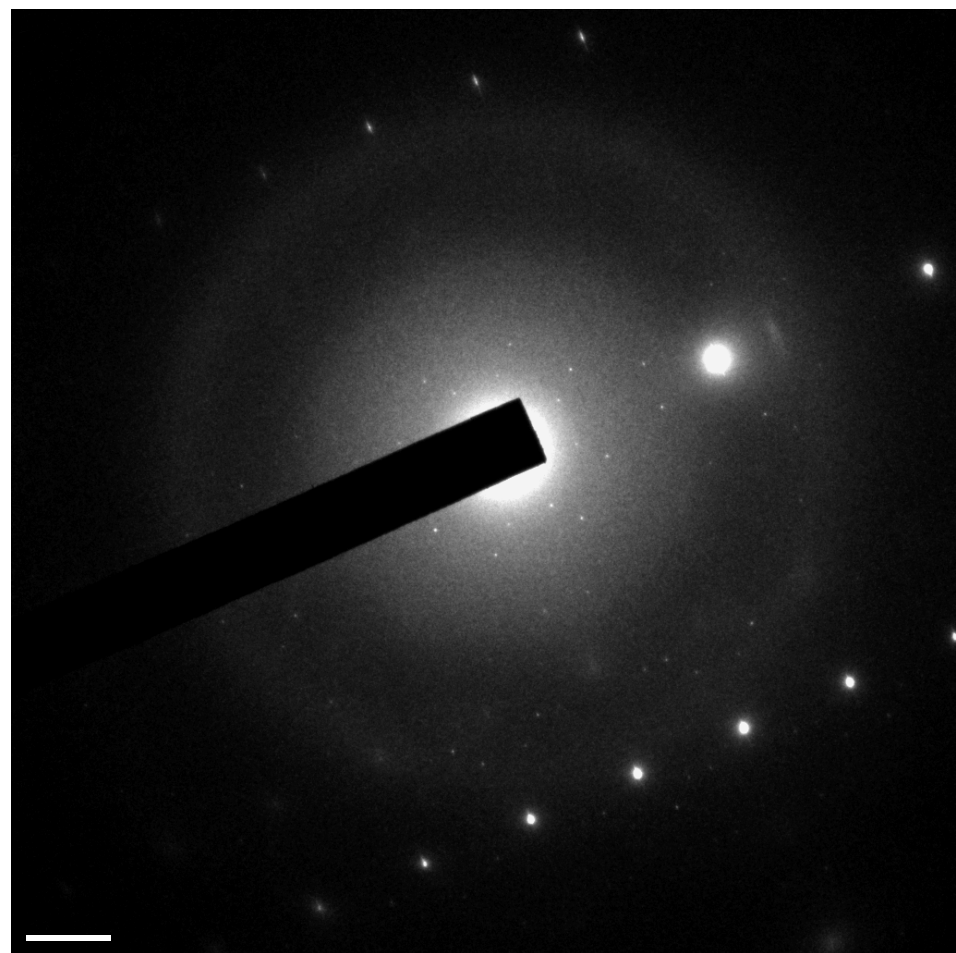
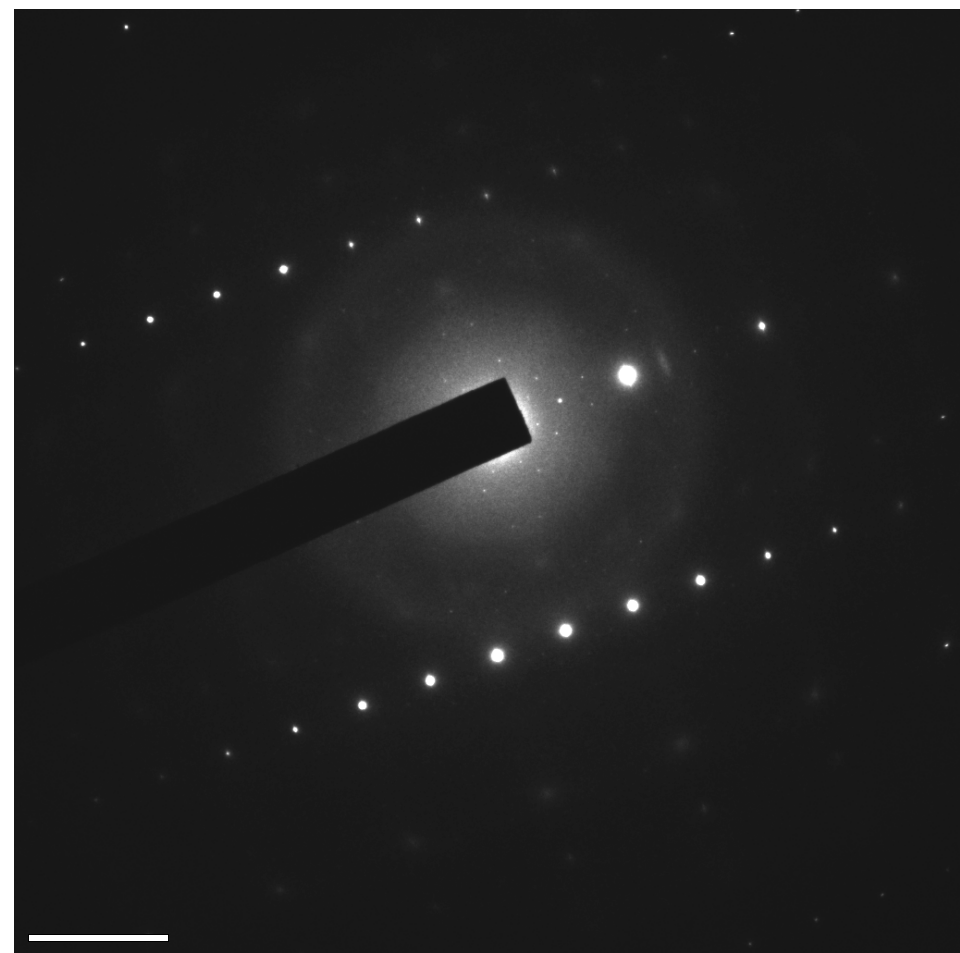


20130605_FeSe_Nanowires_97nm



Before EBL

20130605_FeSe_Nanowires_97nm Tetragonal phase



After EBL

20130605_FeSe_Nanowires_97nm Tetragonal phase

new phase ($\text{Fe}_{24}\text{Se}_{25}$)

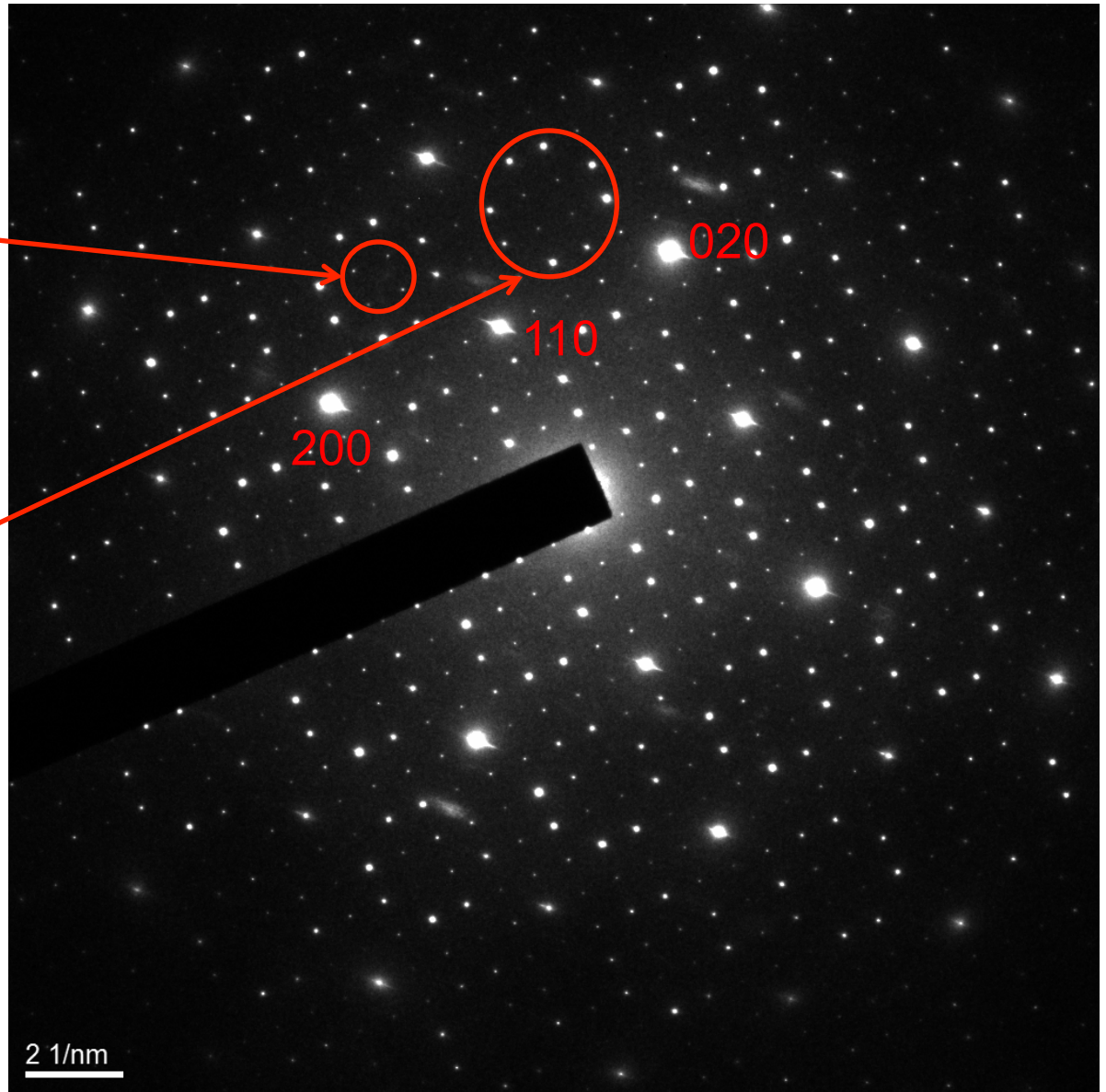
020

110

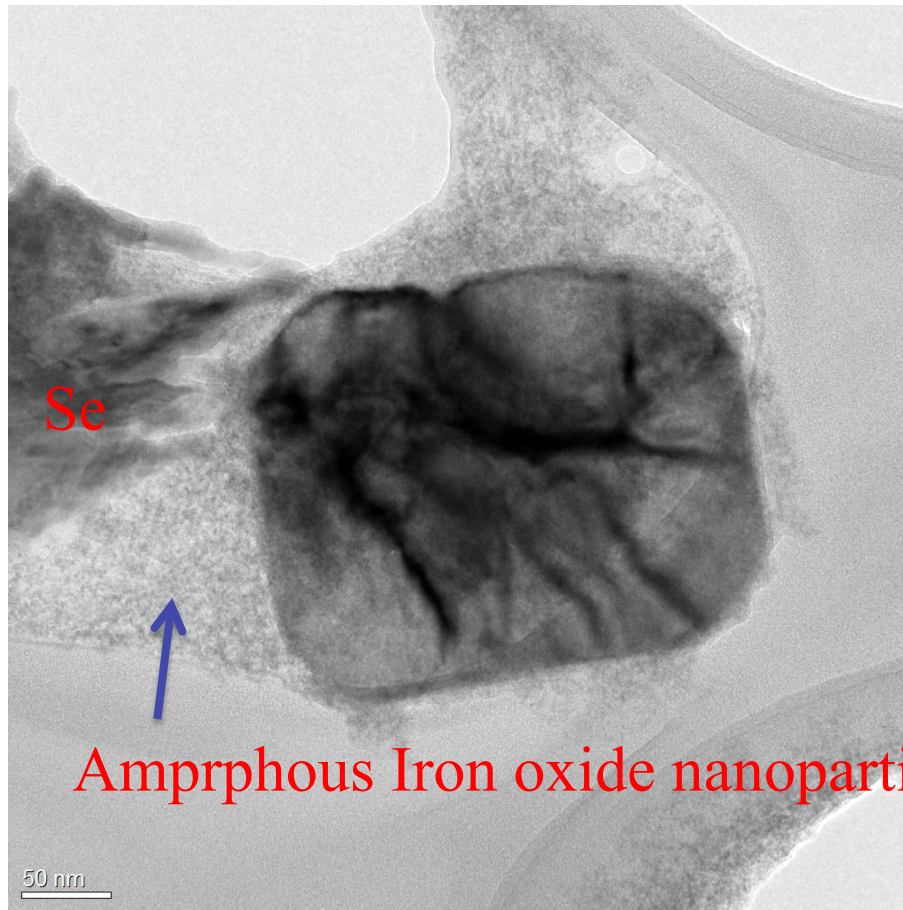
200

Fe_4Se_5 phase

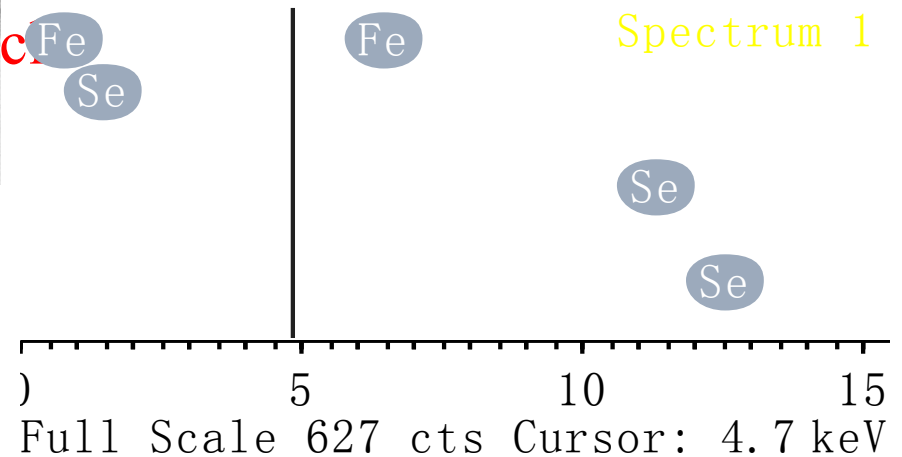
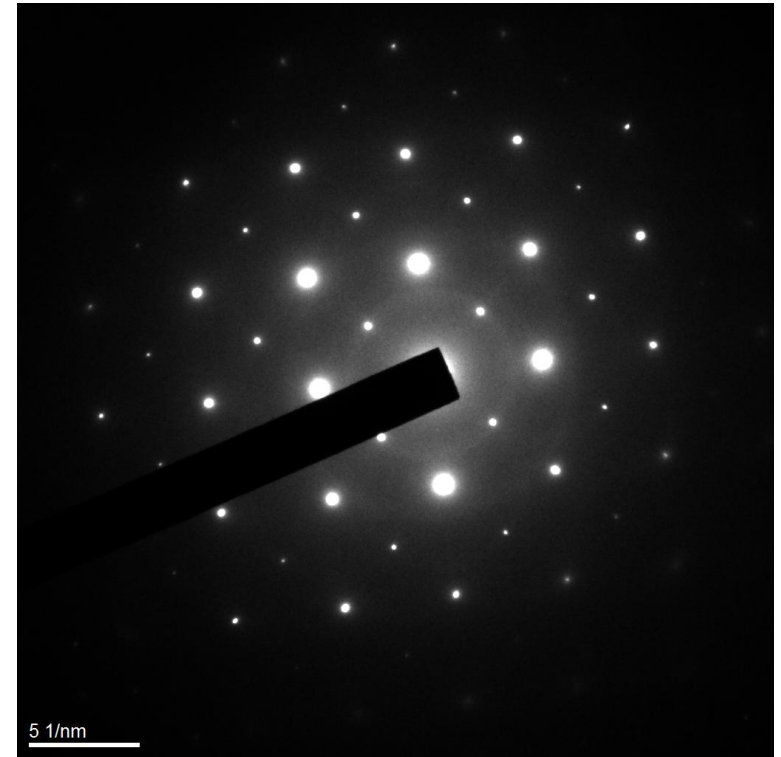
2 1/nm



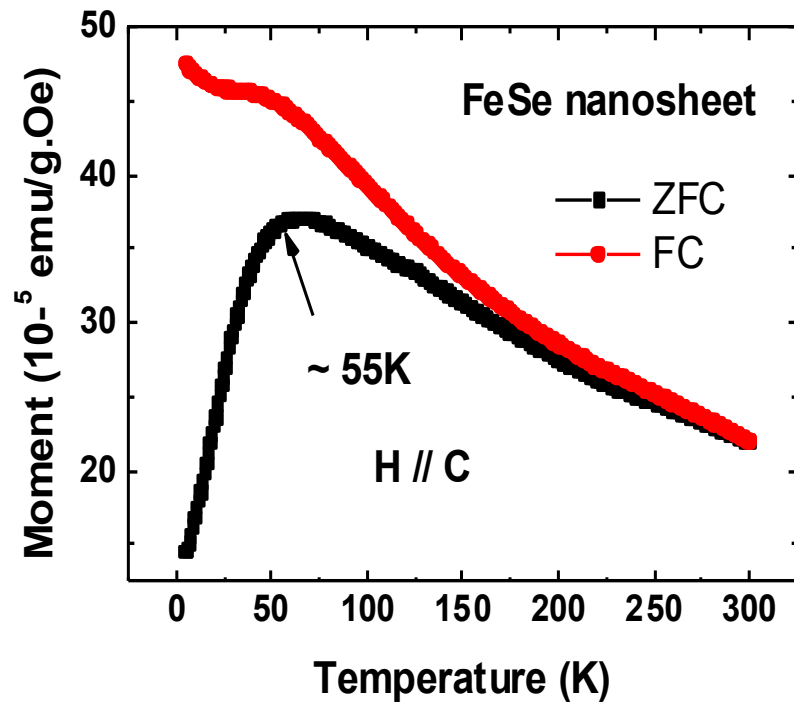
Fe-vacancy order in Fe_4Se_5 Nanosheet



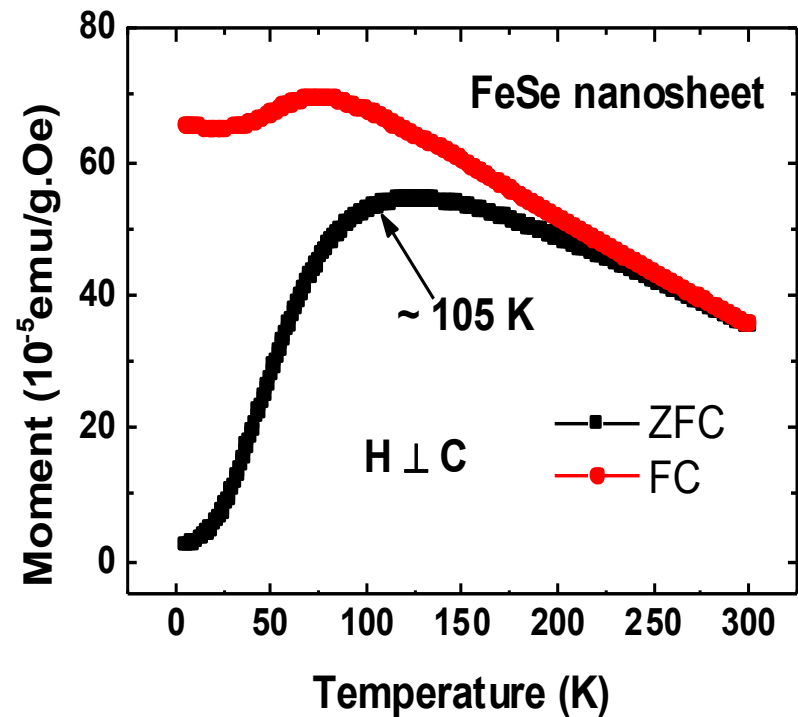
20130321_Fe_{1.05}Se_700 °C -
50 h - quench



MT of FeSe nanosheet



S1, H along c

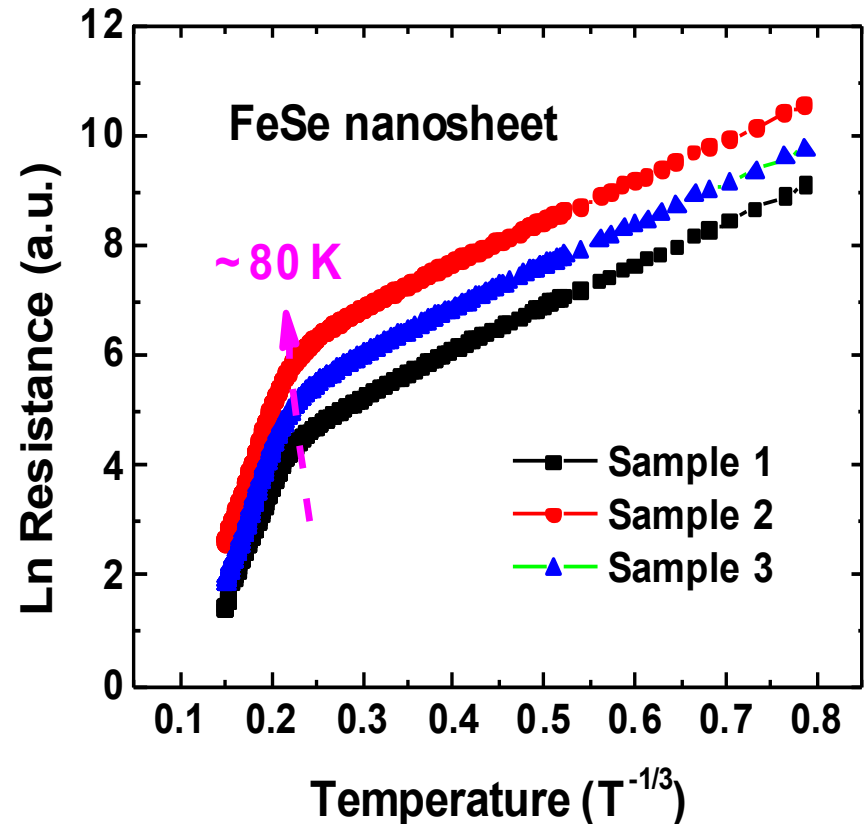
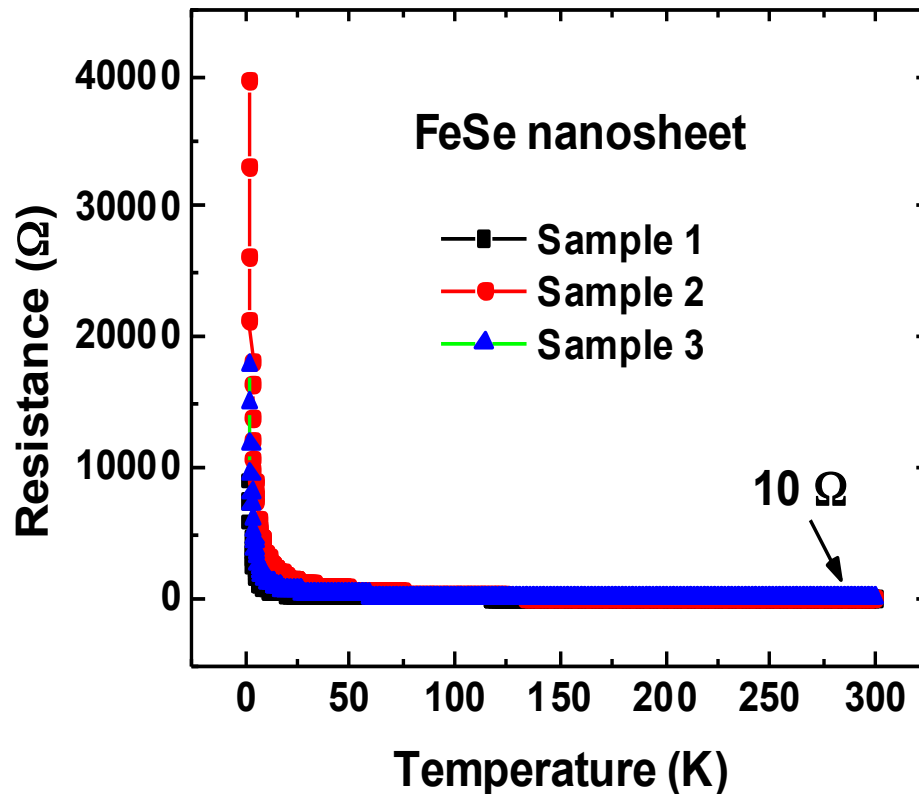


S2, H perpendicular to c

$T_m \sim 50 - 100$ K

The stoichiometry is Fe_4Se_5

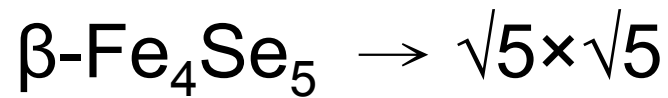
Resistivity of FeSe nanosheet



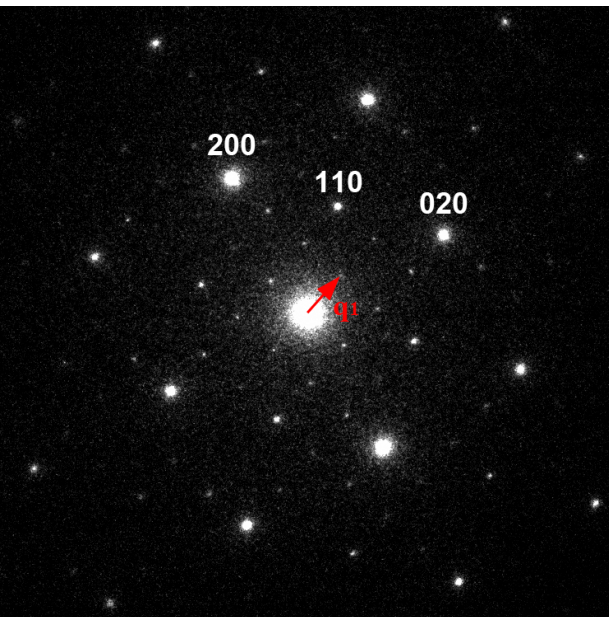
$$T_{\sigma} \sim T_m !$$

Structure/magnetic transition around 80 K?

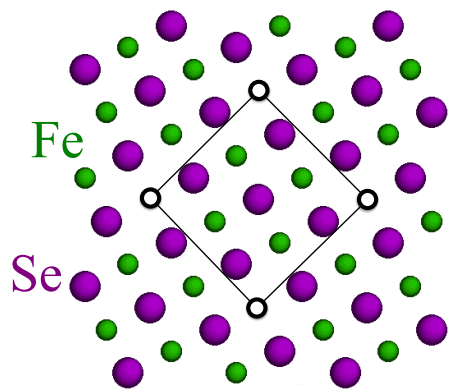
Fe vacancy scattering induced VRH?



ZA = [001]

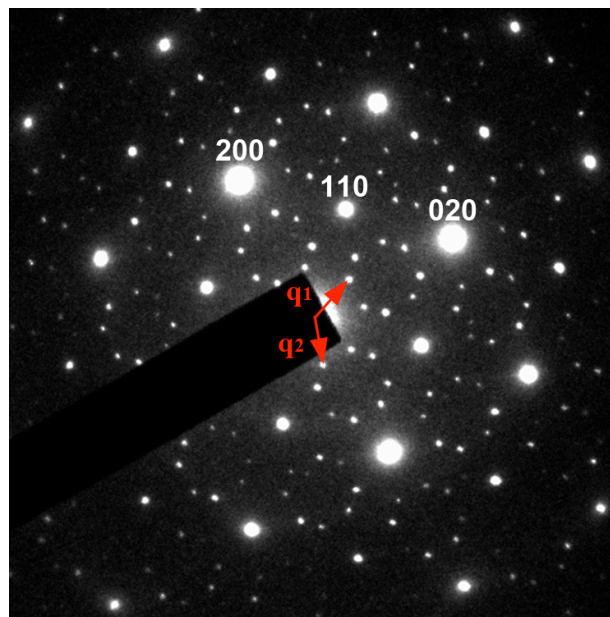


$$\mathbf{q}_1 = (1/5, 3/5, 0)$$

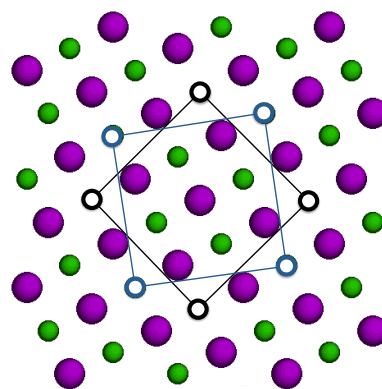


$\beta\text{-Fe}_4\text{Se}_5$ (square: $\sqrt{5} \times \sqrt{5}$)

ZA = [001]

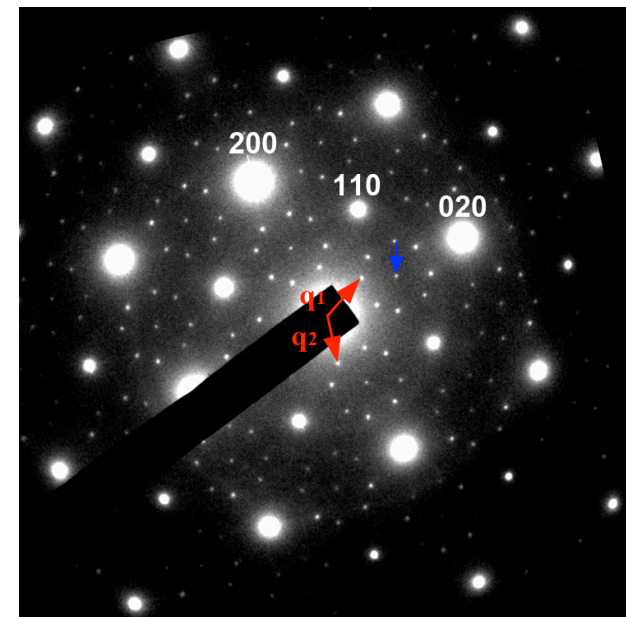


$$\mathbf{q}_2 = (3/5, 1/5, 0)$$



with twinned superstructure

ZA = [001]



?

with forbidden reflections at $h00$, $0k0$, h odd, k odd.

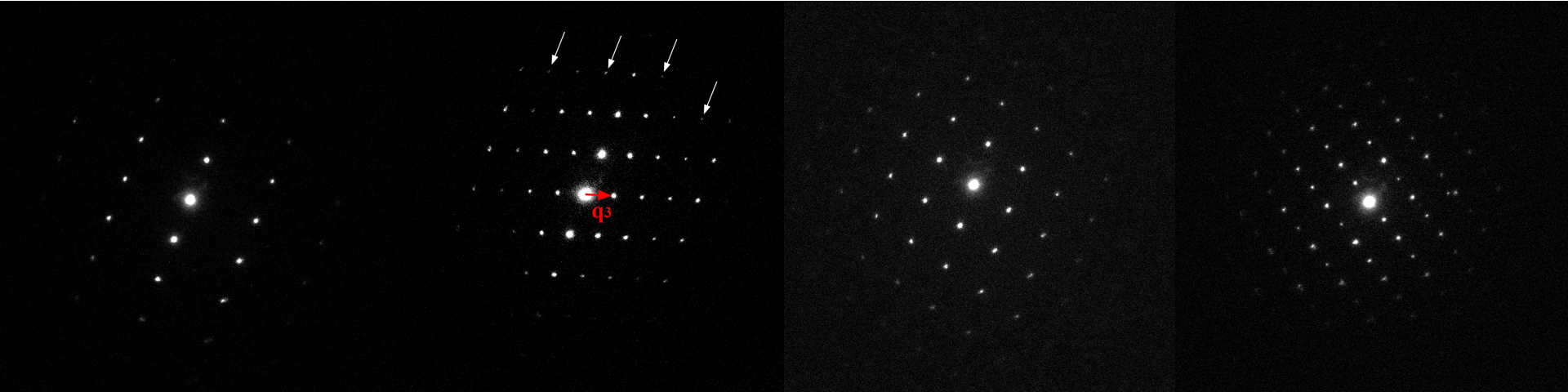
$\beta\text{-Fe}_3\text{Se}_4 \rightarrow 2 \times 2$ with d_{100} shift every other plane

ZA = [-131]

ZA = [-121]

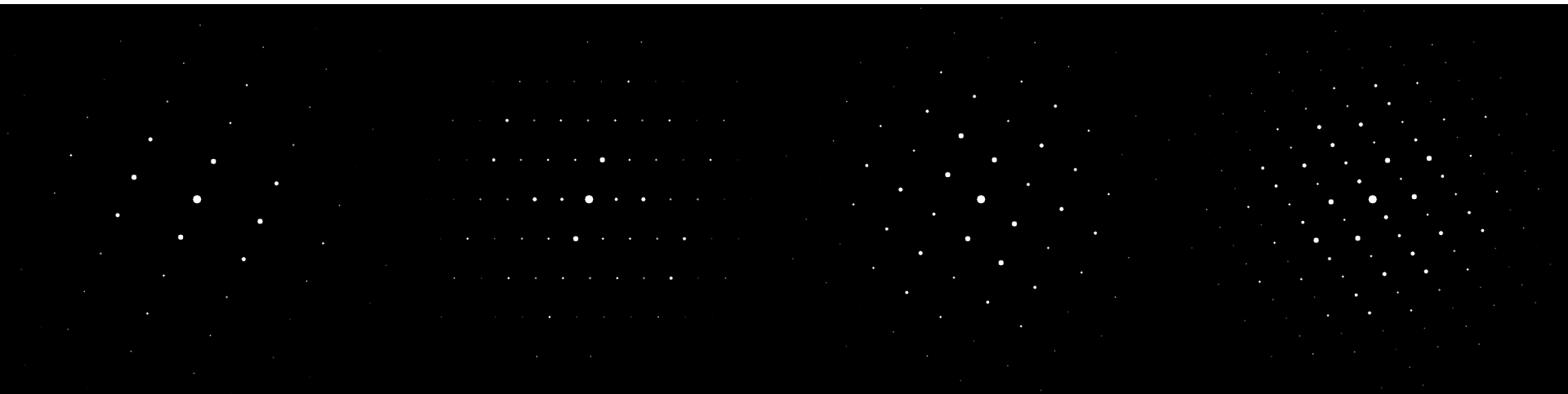
ZA = [-111]

ZA = [010]



$$\mathbf{q}_3 = (1/2, 1/2, 1/2)$$

simulated kinematical electron diffraction patterns



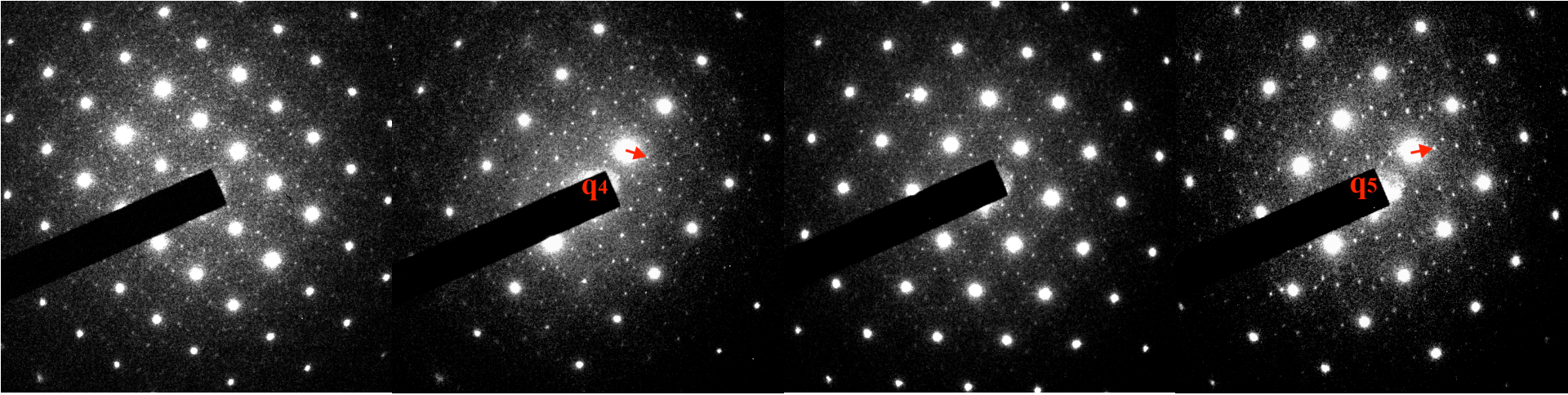
$\beta\text{-Fe}_9\text{Se}_{10} \rightarrow \sqrt{10} \times \sqrt{10}$ with twin and with $\frac{1}{2}d_{310}$ shift every other plane

ZA = [-101]

ZA = [-212]

ZA = [-111]

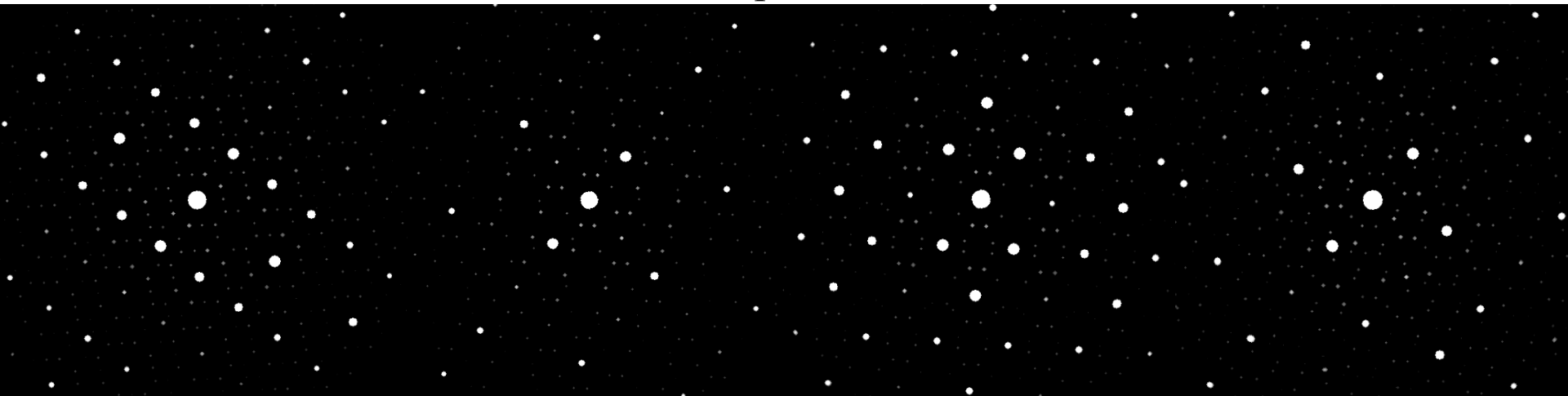
ZA = [-121]



$$\mathbf{q}_4 = (2/5, 1/5, 0)$$

$$\mathbf{q}_5 = (1/5, 2/5, 0)$$

simulated kinematical electron diffraction patterns

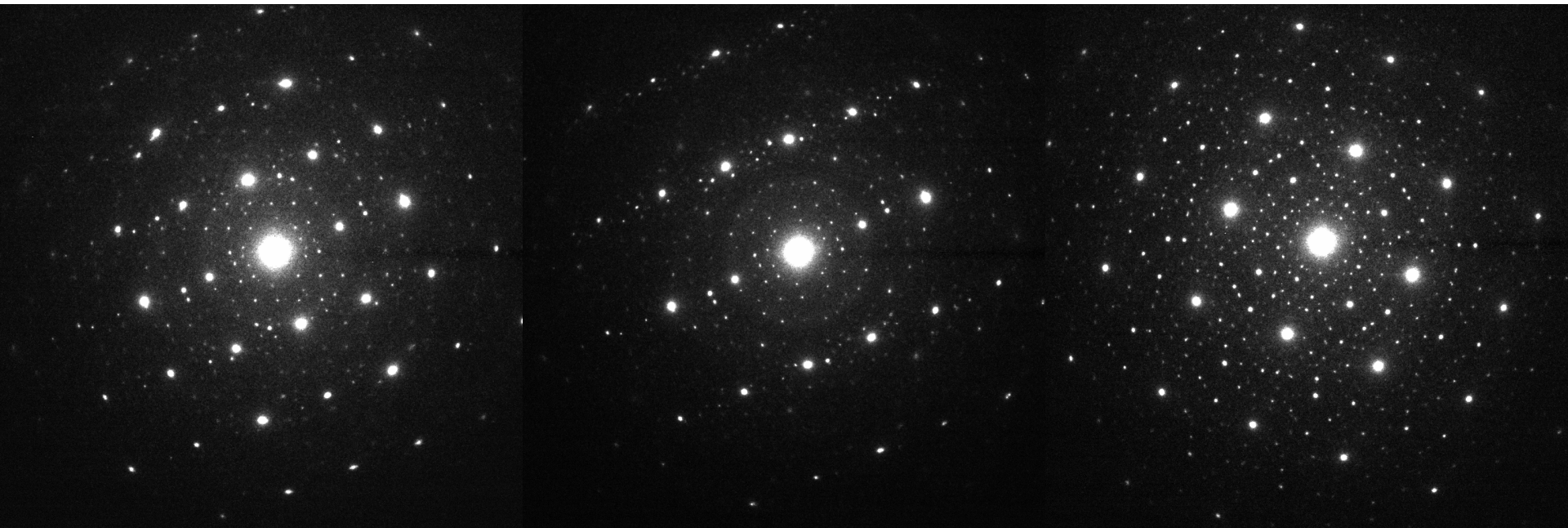


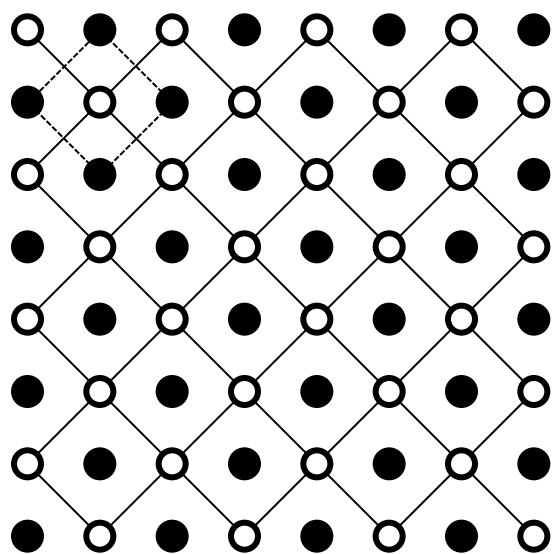
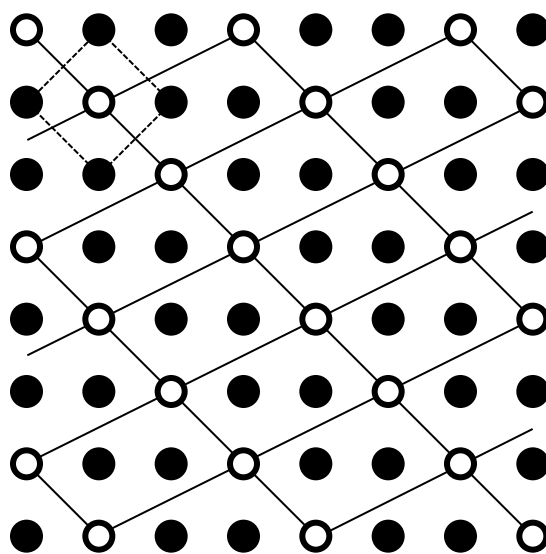
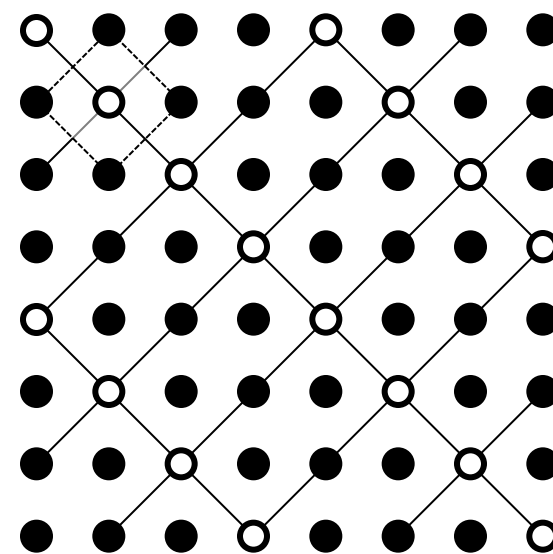
$\beta\text{-Fe}_{1-x}\text{Se}_4$ ($x = ?$) unknown superstructure

ZA=[1-12]

ZA=[1-13]

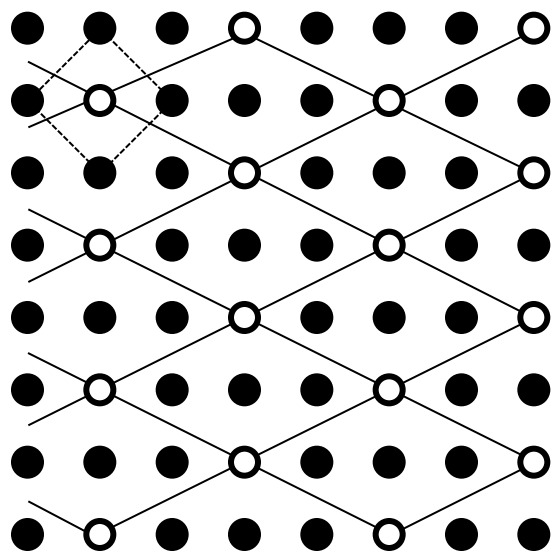
ZA=[001]



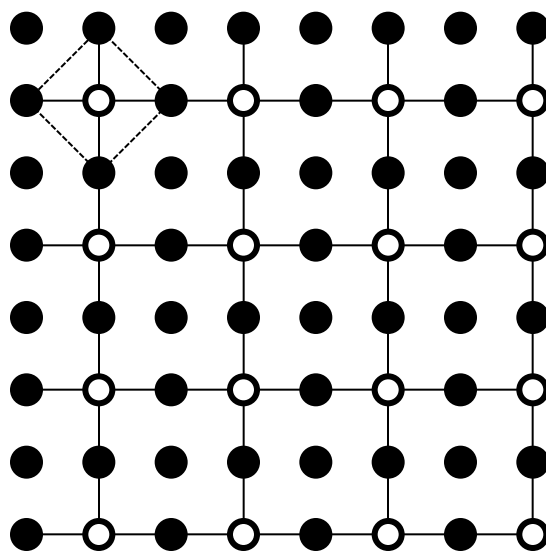
$\beta\text{-Fe}_1\text{Se}_2$  $\beta\text{-Fe}_2\text{Se}_3$  $\beta\text{-Fe}_3\text{Se}_4$ (stripe)

● Fe ○ Fe vacancy ✓ have been observed experimentally

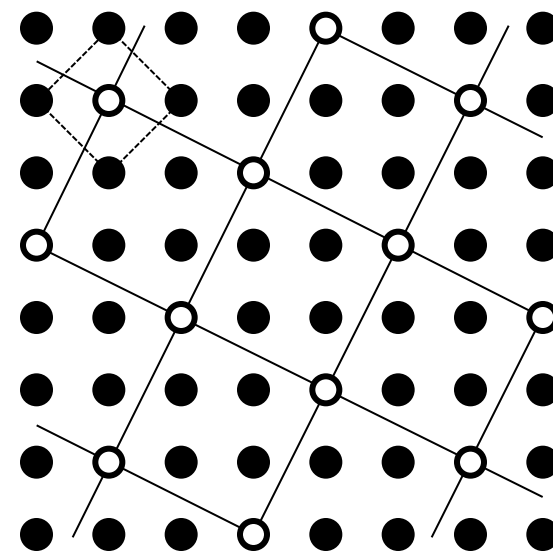
✓ $\beta\text{-Fe}_3\text{Se}_4$ (rhombus: $\sqrt{2} \times 2\sqrt{2}$)

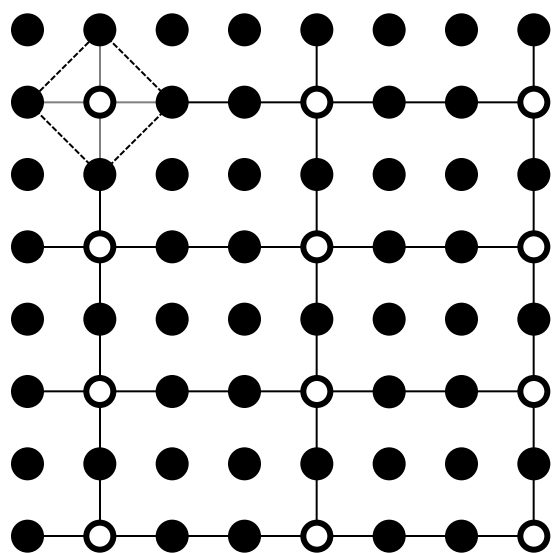
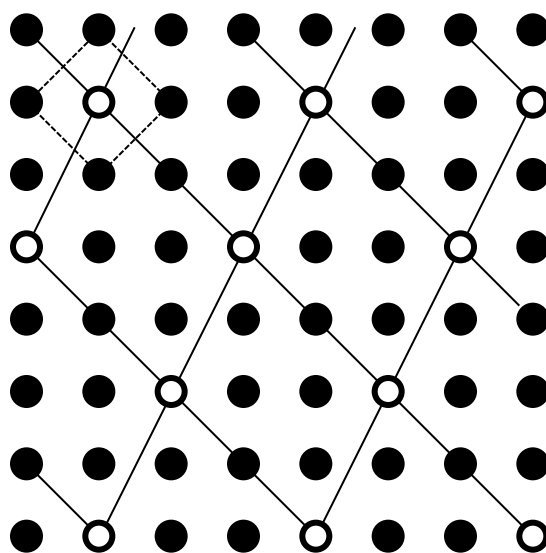
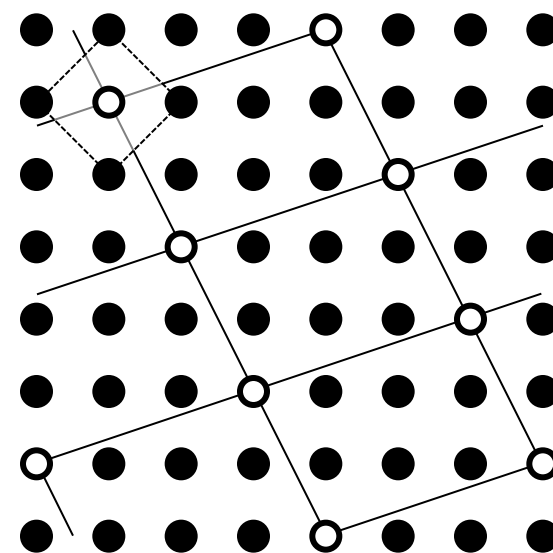


✓ $\beta\text{-Fe}_3\text{Se}_4$ (square: 2×2)

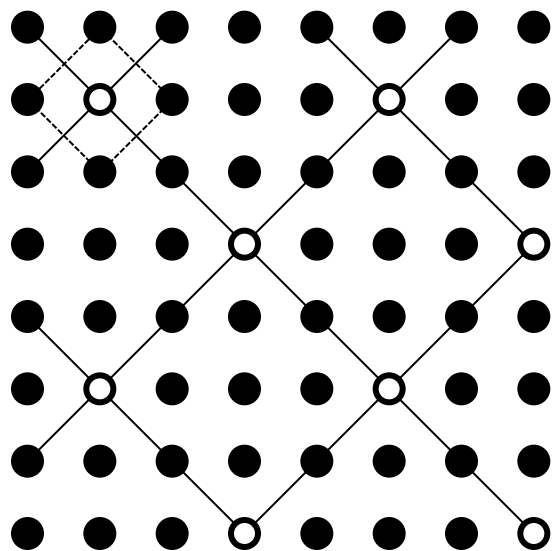
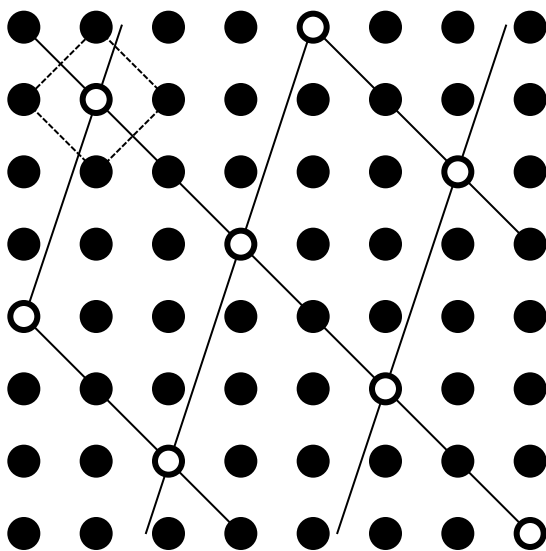
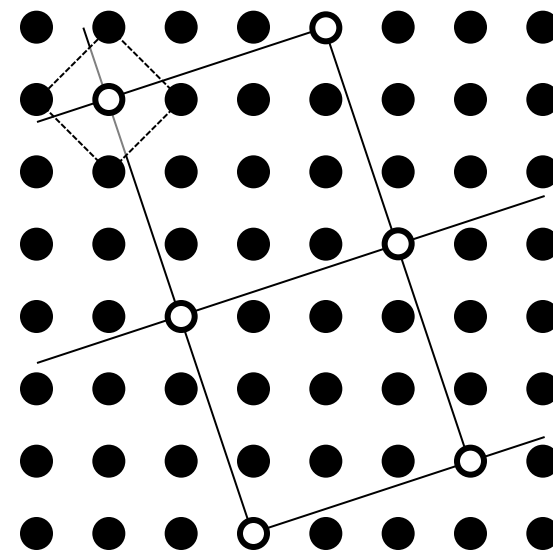


✓ $\beta\text{-Fe}_4\text{Se}_5$ (square: $\sqrt{5} \times \sqrt{5}$)

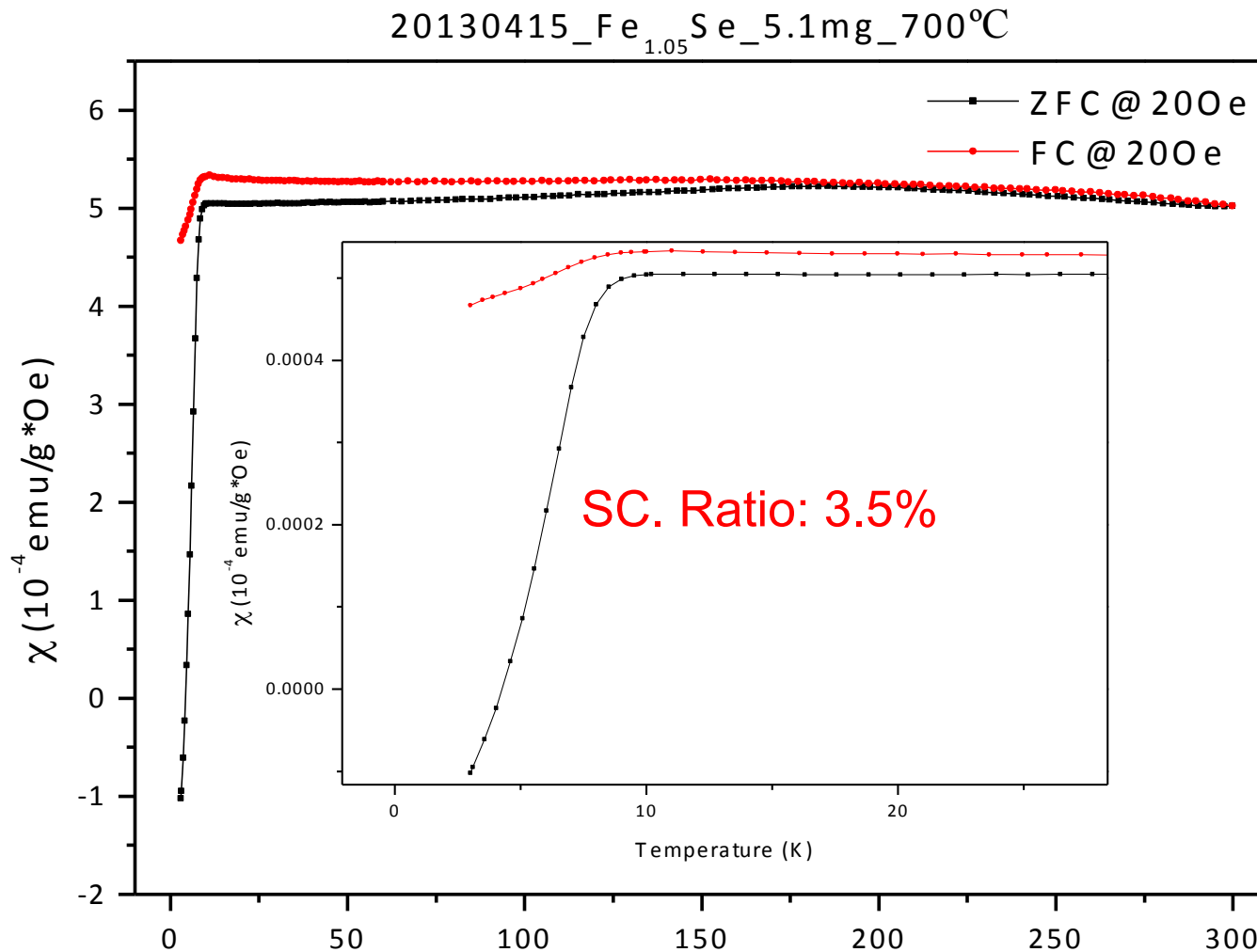


$\beta\text{-Fe}_5\text{Se}_6$  $\beta\text{-Fe}_5\text{Se}_6$  $\beta\text{-Fe}_6\text{Se}_7$ 

● Fe ○ Fe vacancy ✓ have been observed experimentally

 $\beta\text{-Fe}_7\text{Se}_8$ (square: 2×2) $\beta\text{-Fe}_7\text{Se}_8$ (parallelogram: $\sqrt{8}\times\sqrt{10}$) ✓ $\beta\text{-Fe}_9\text{Se}_{10}$ (square: $\sqrt{10}\times\sqrt{10}$) ✓

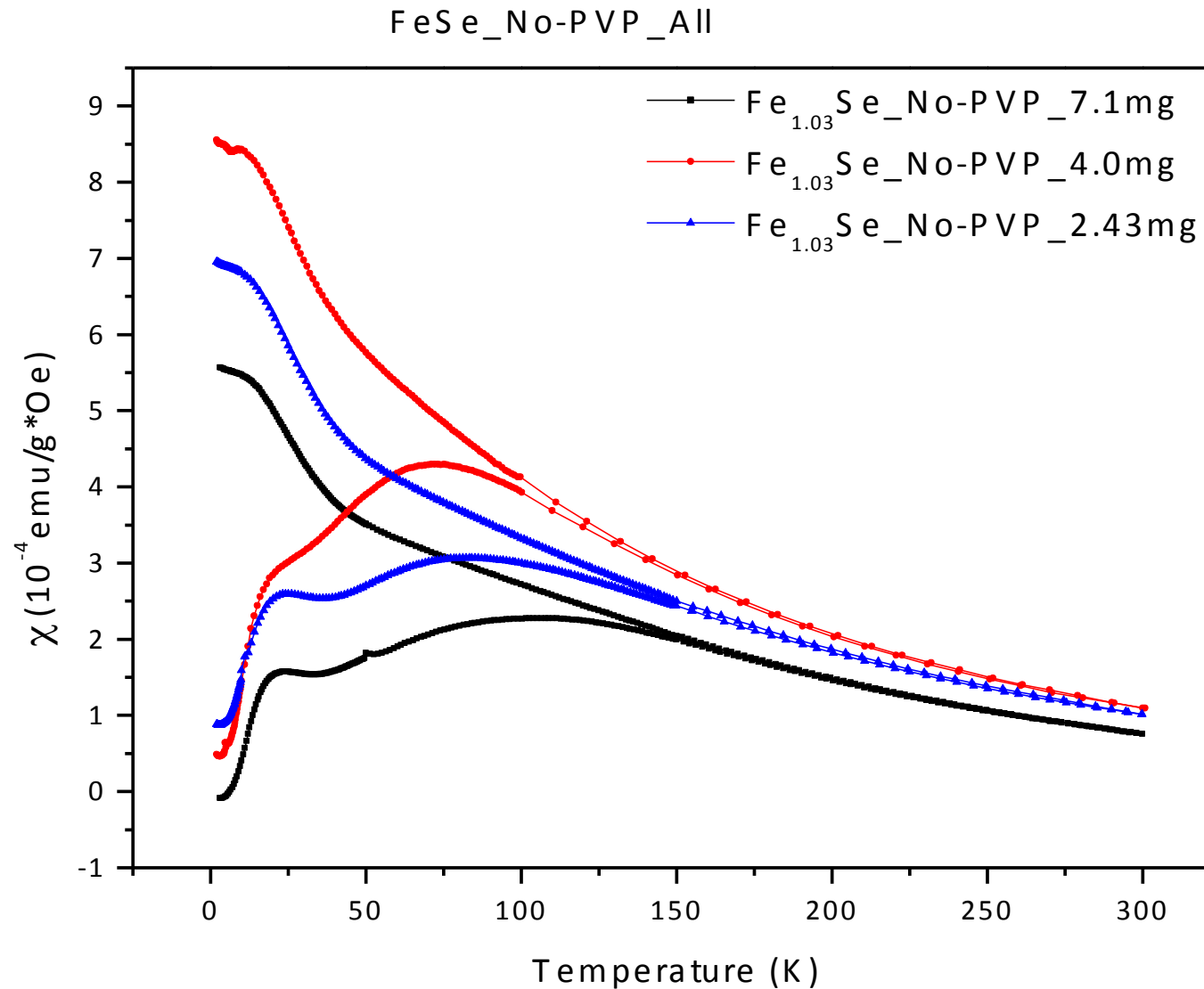
Anneal Fe₄Se₅ nanosheet leads to superconductivity



700 °C -7 h-quenching

Temperature (K)

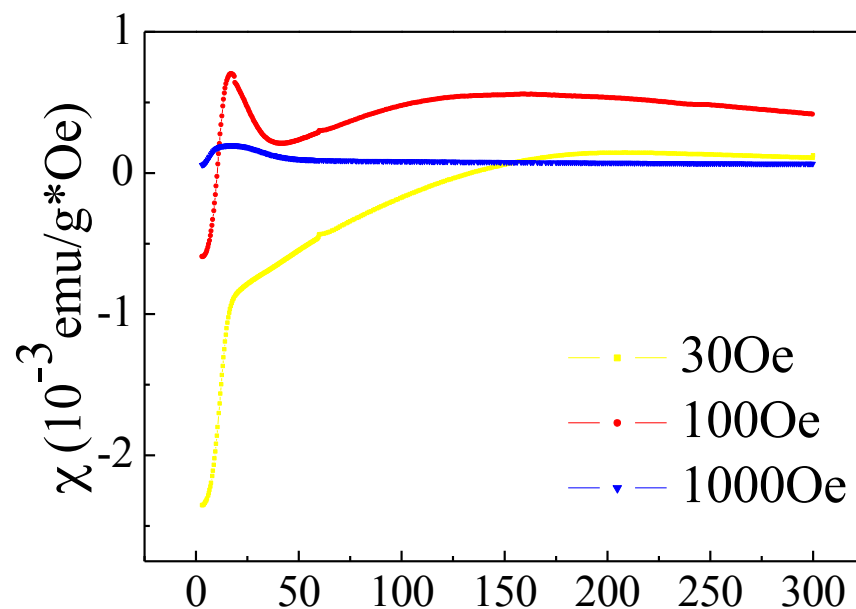
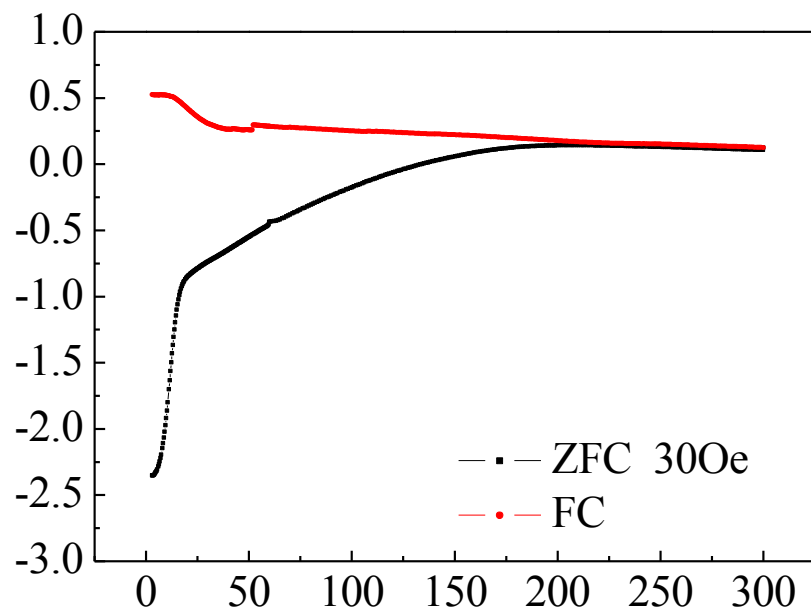
Magnetic Susceptibility of FeSe-nanosheet



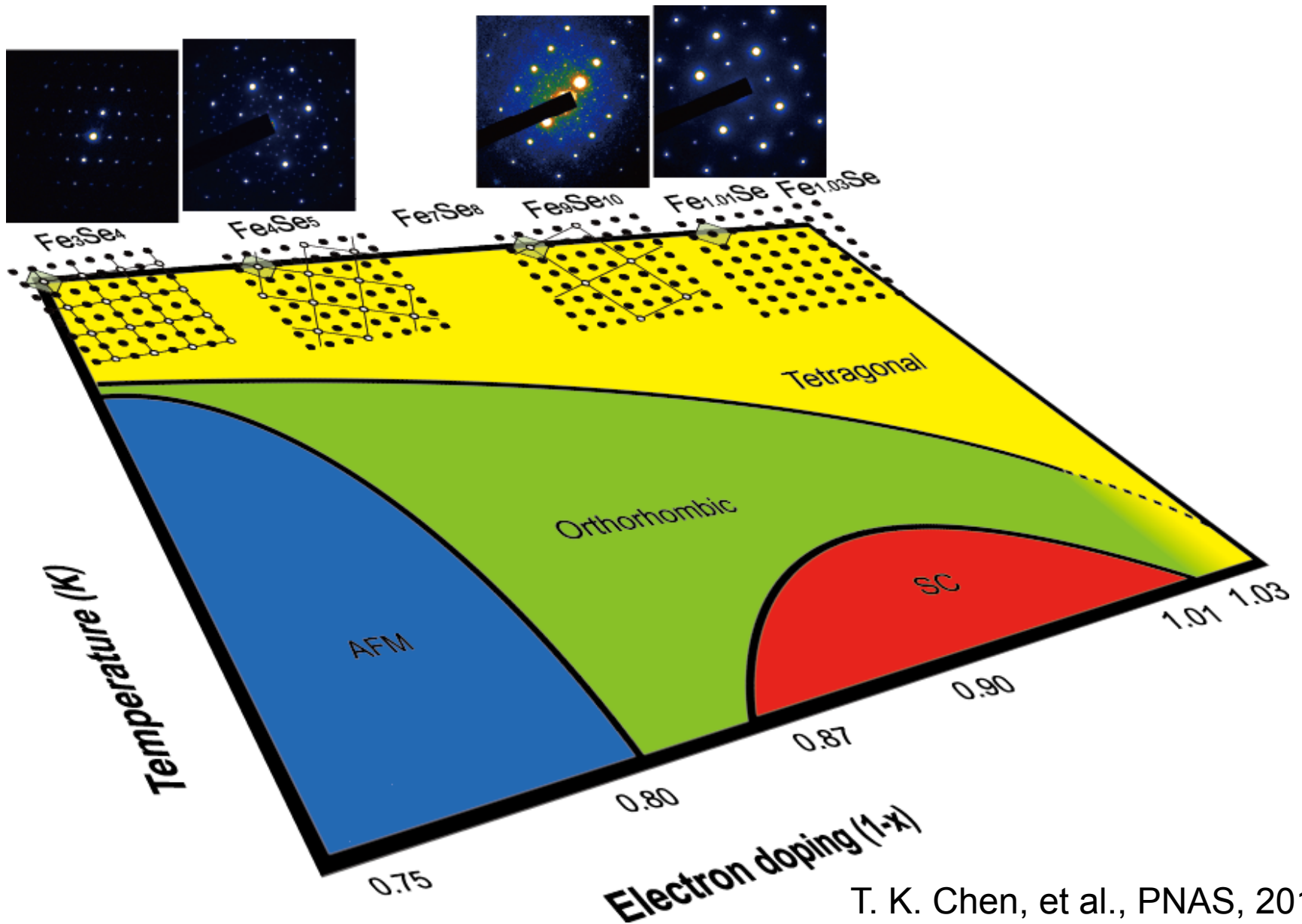
Magnetic Susceptibility of FeSe-nanosheet

Magnetic Field Dependent

indicates $T_c > 20\text{K}$

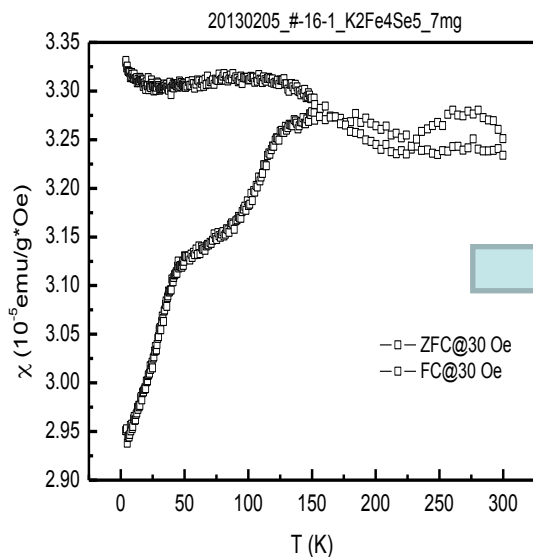


Phase Diagram of Fe-Se

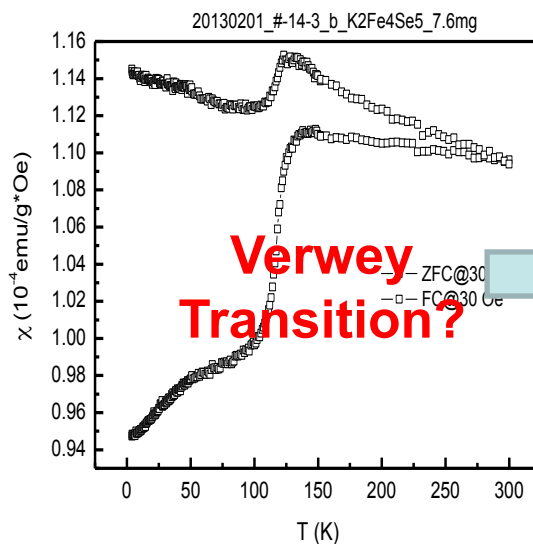


Re-examine $\text{K}_2\text{Fe}_4\text{Se}_5$ —More stable to synthesize

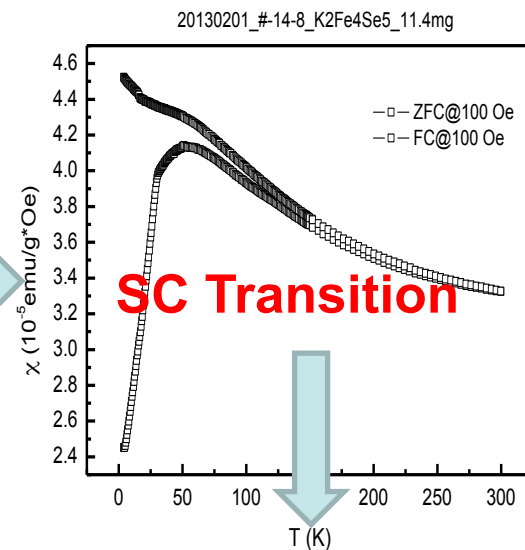
700°C Furnace Cool



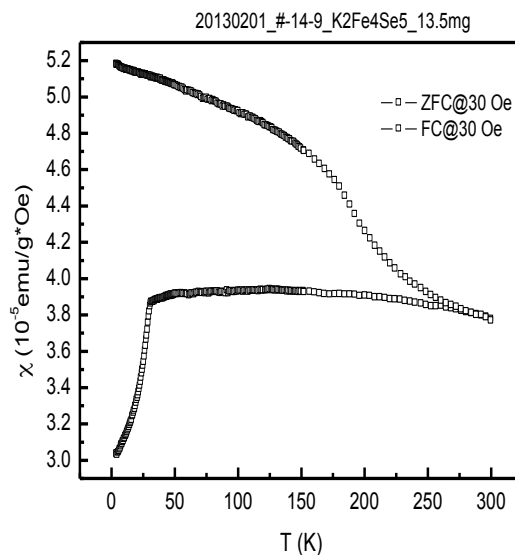
300°C quench



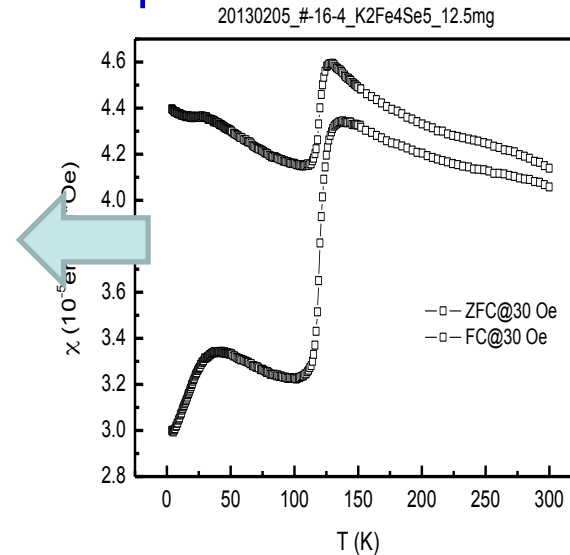
750°C quench



800°C quench

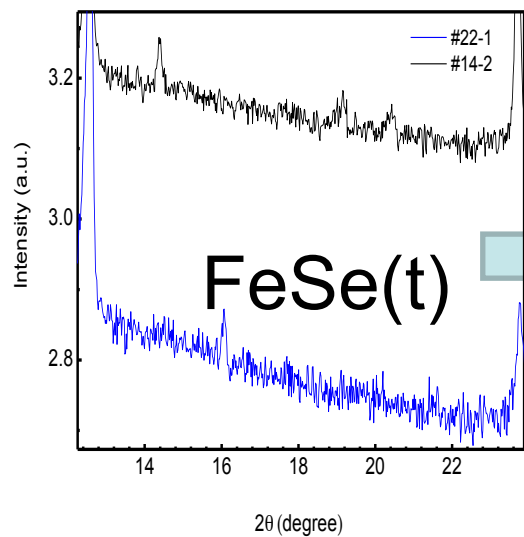
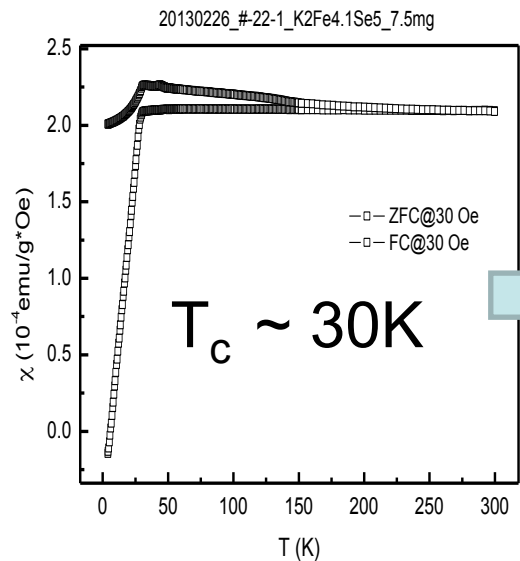


quench+400°C anneal

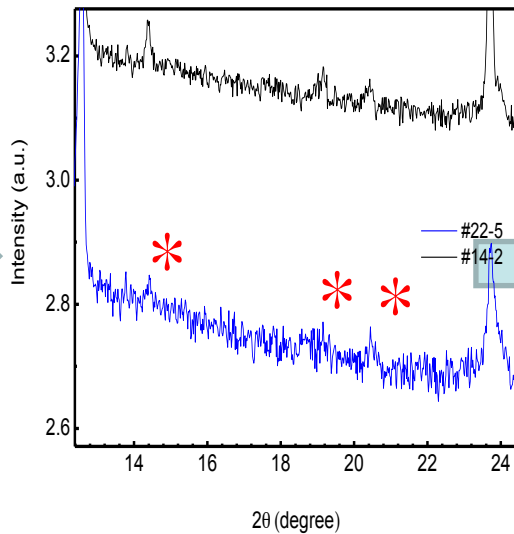
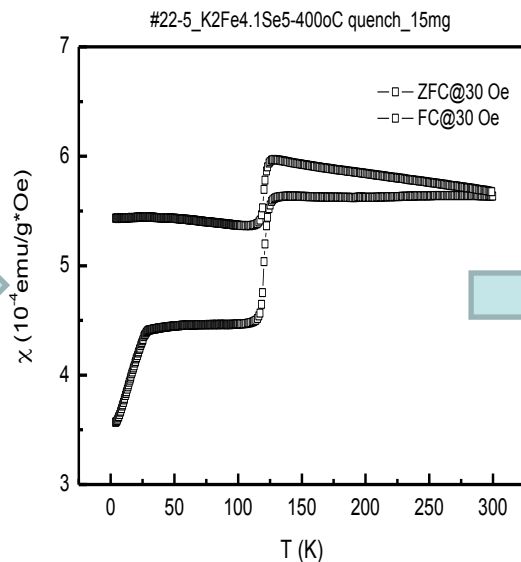




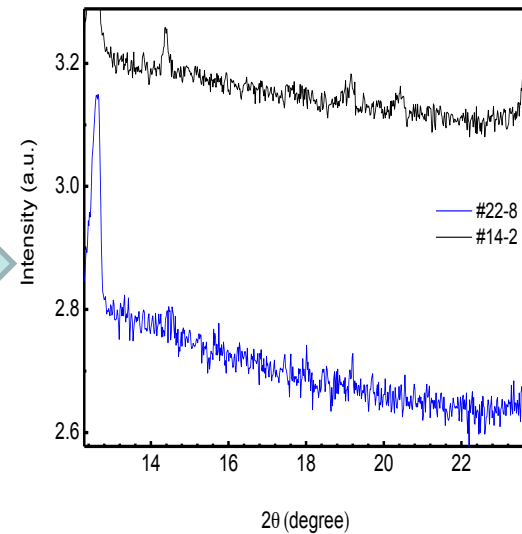
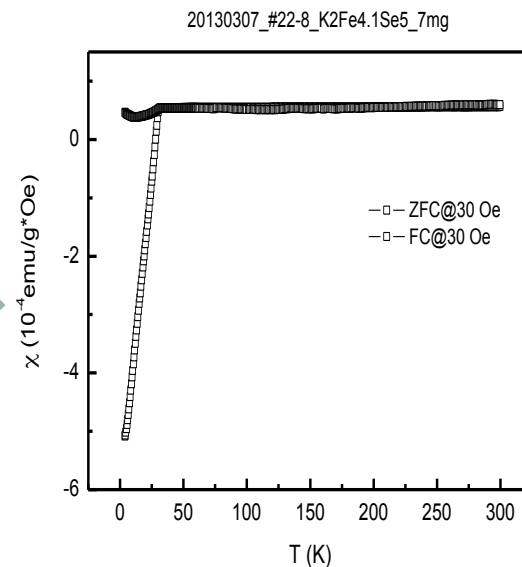
750°C quench

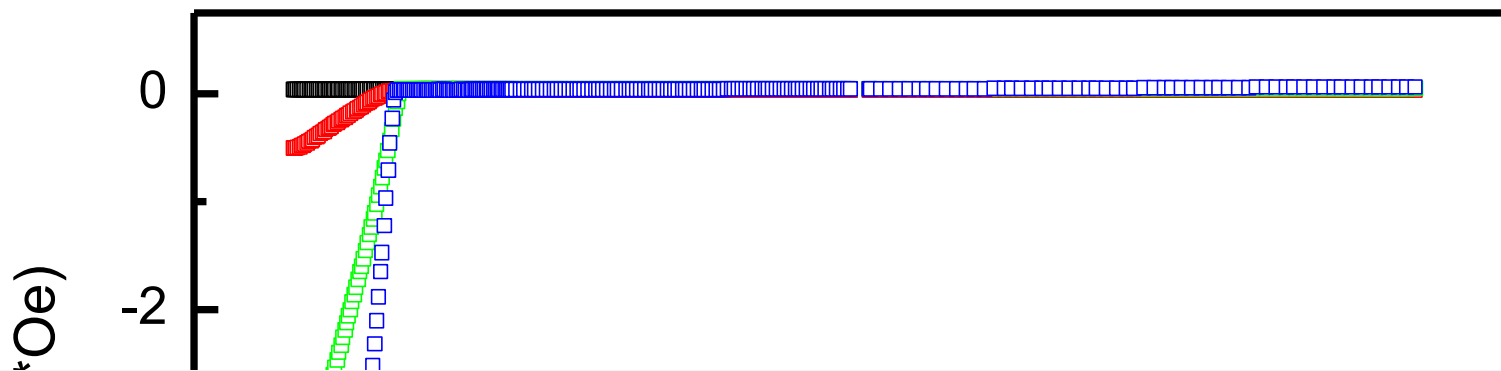


400°C quench

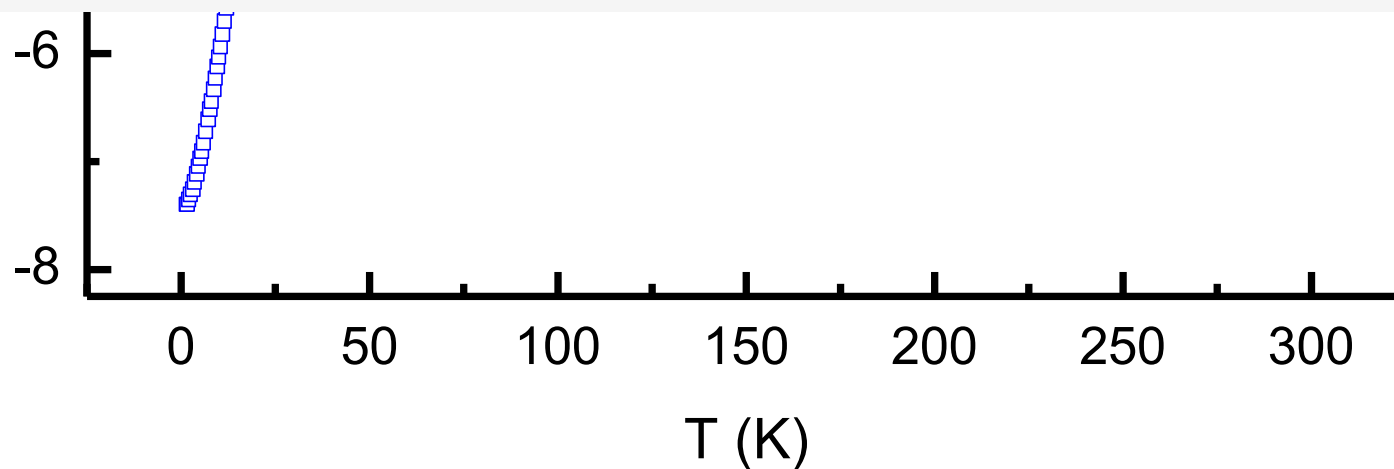


750°C quench

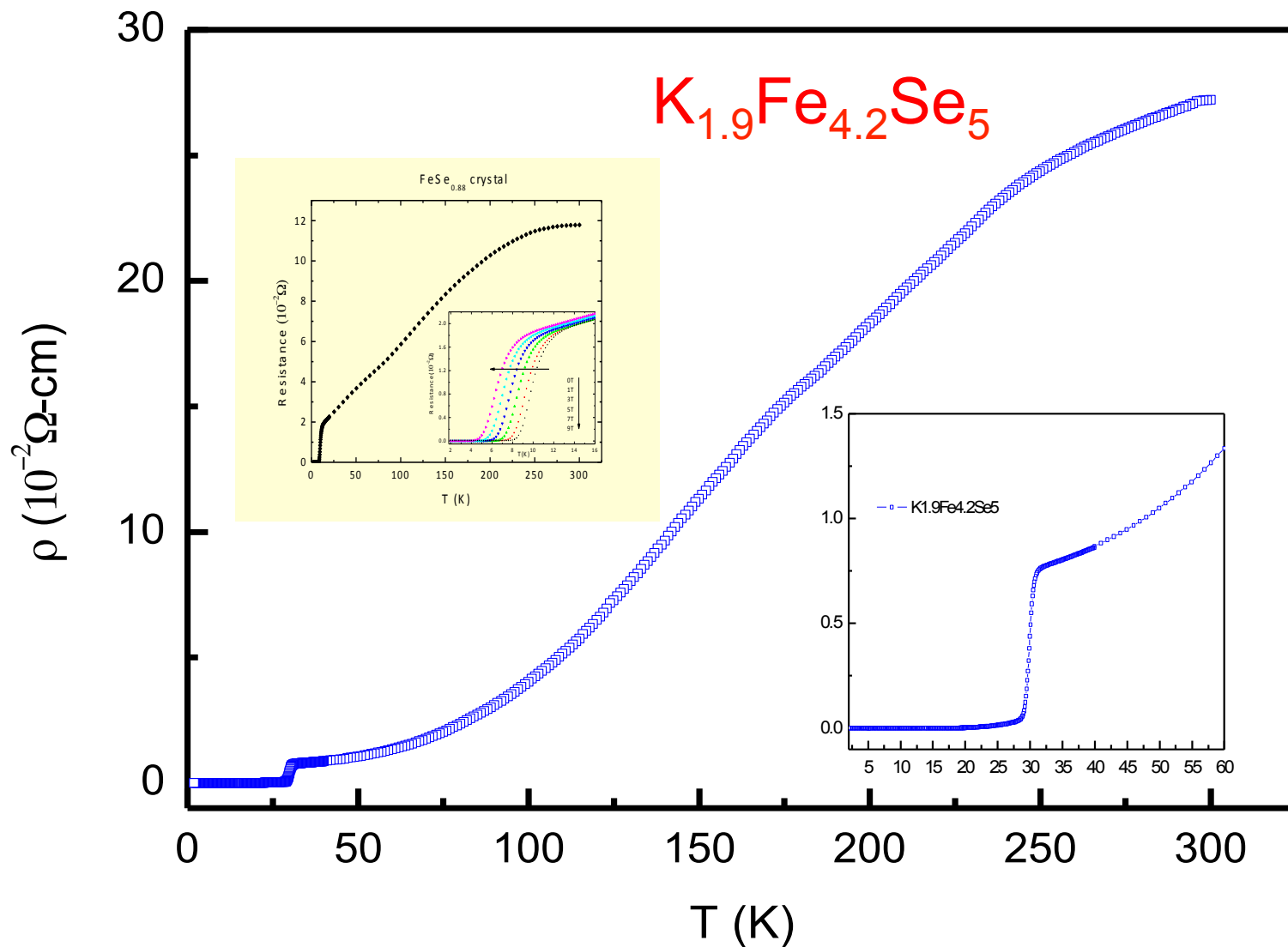




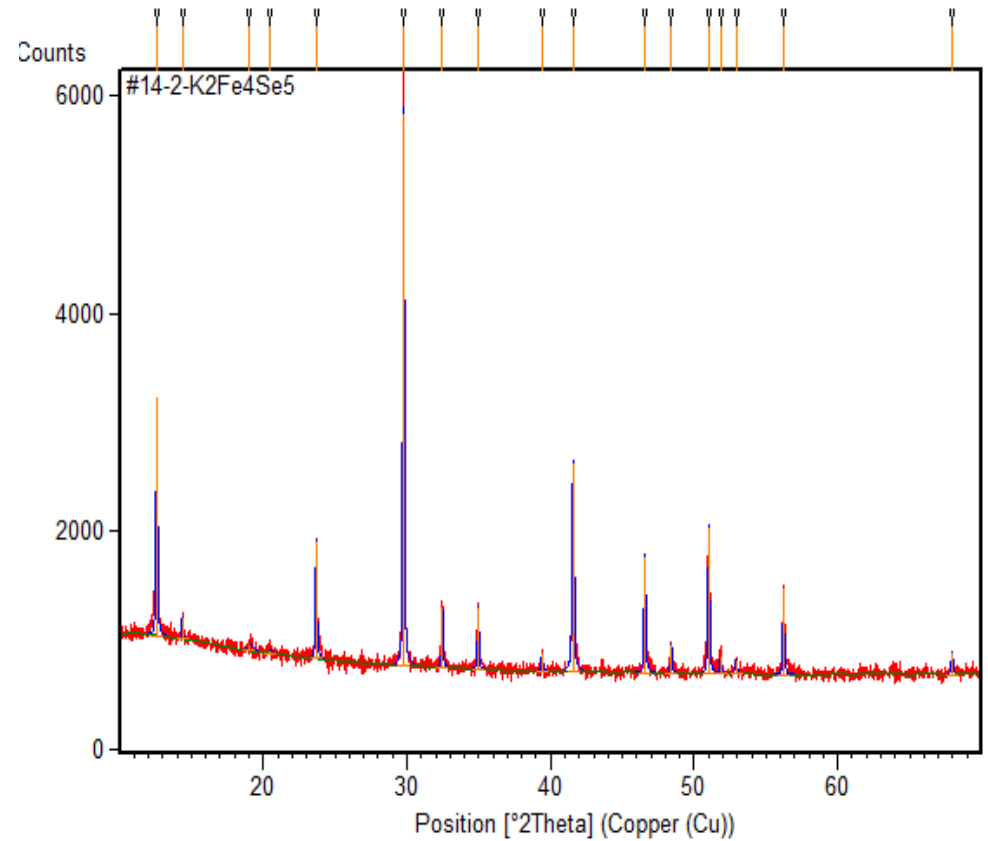
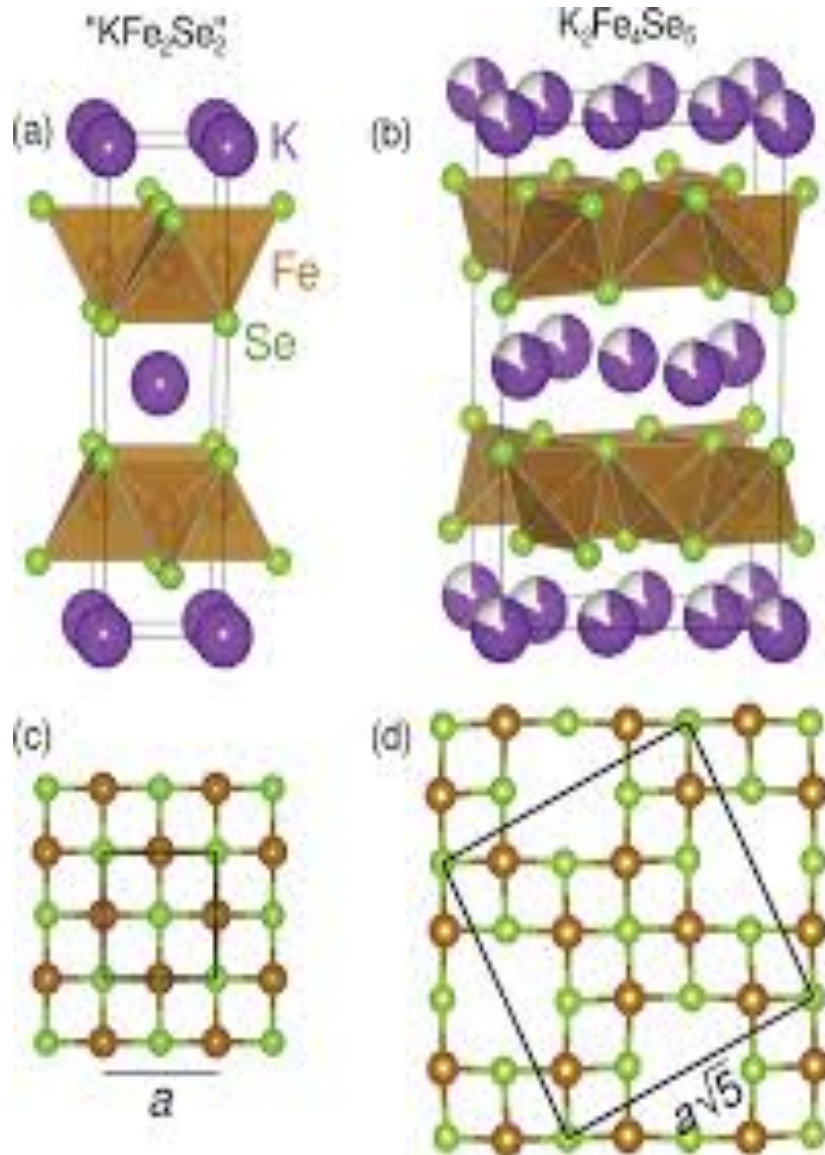
Superconducting Fraction increases with increasing disorder of Fe-vacancy (+ increasing Fe-content) !!

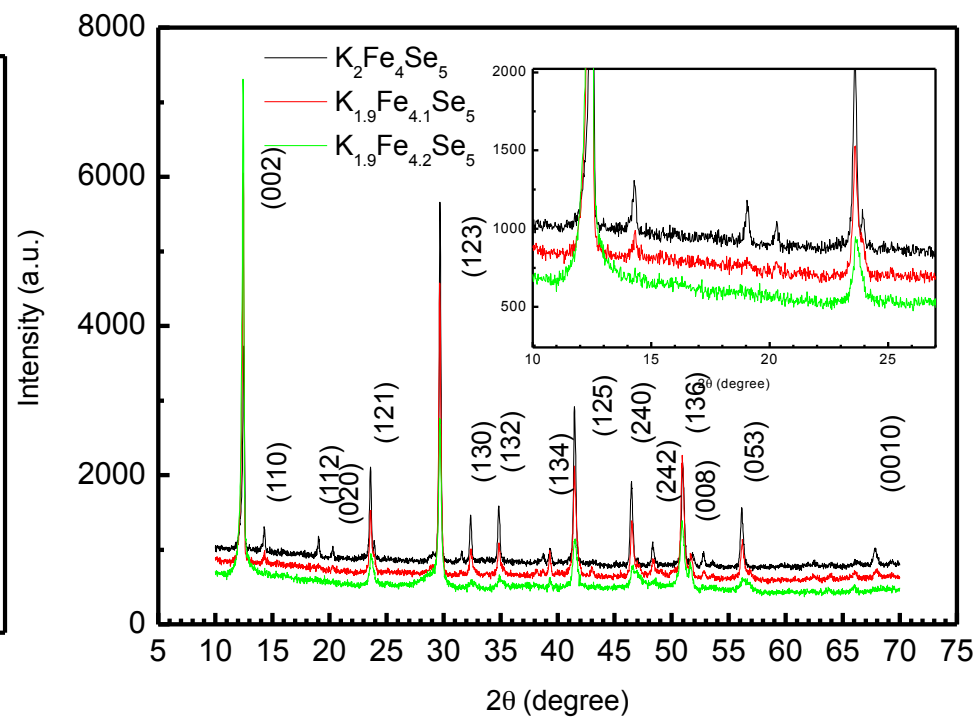
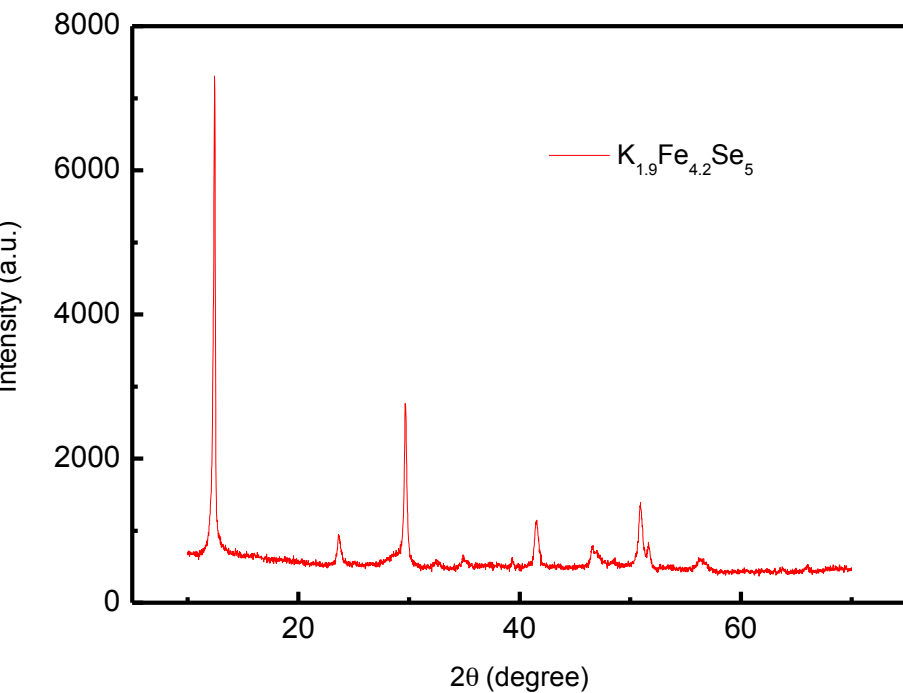
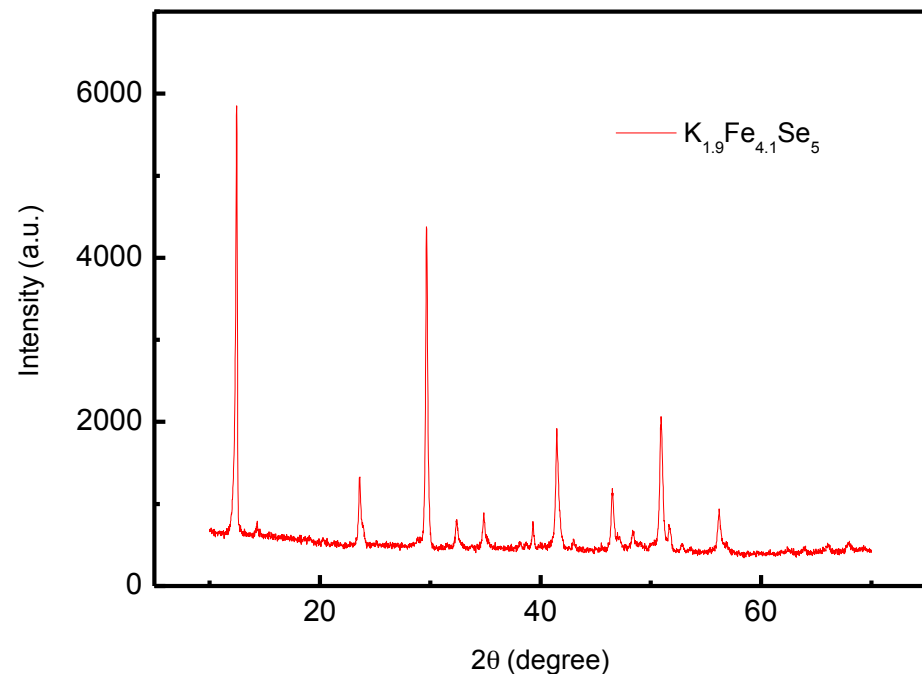
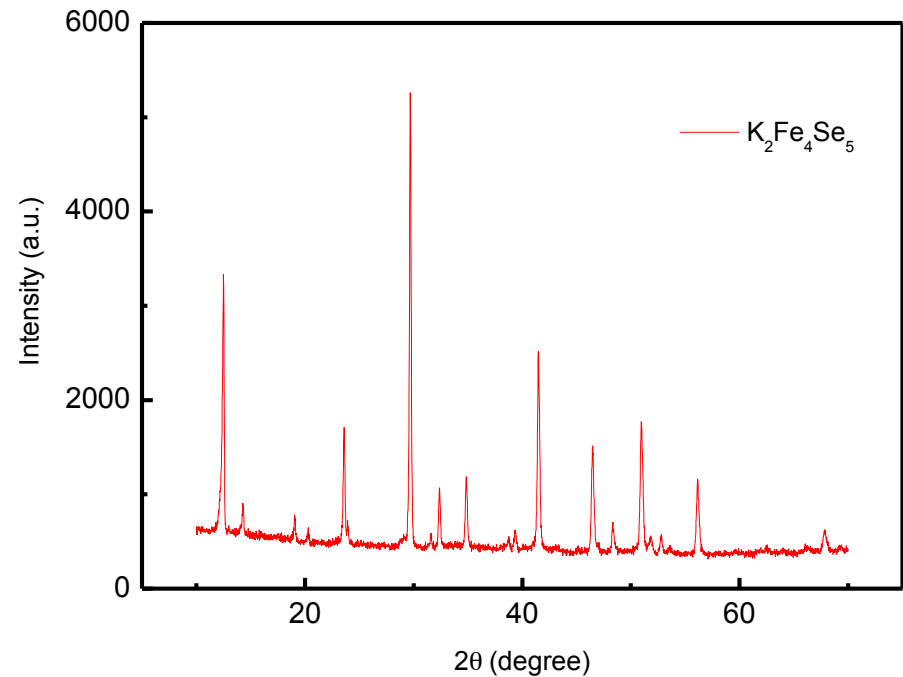


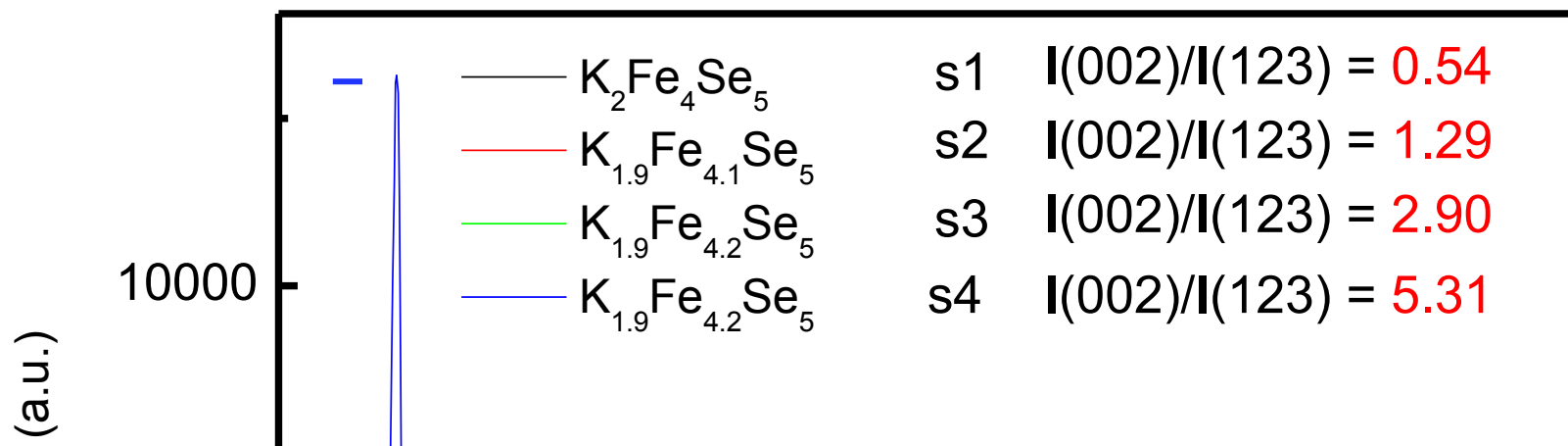
Bulk Resistive Transition



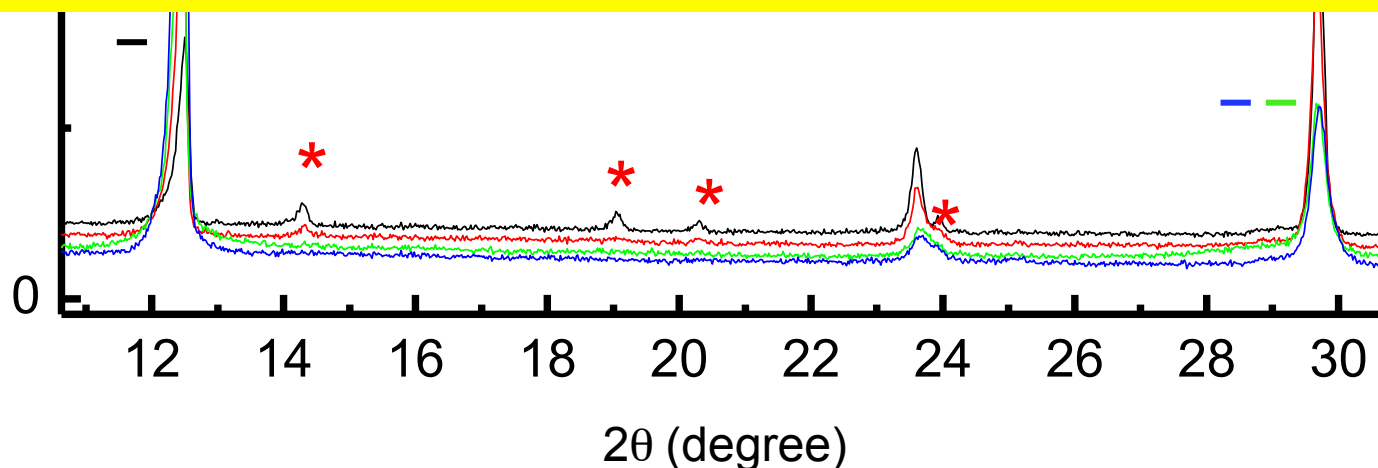
XRD of $K_2Fe_4Se_5$



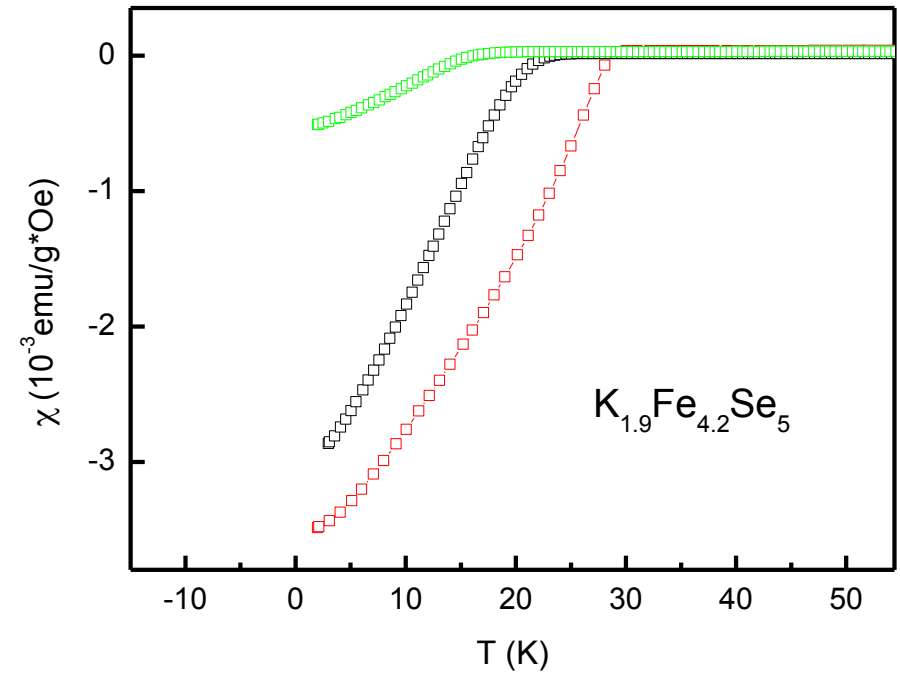
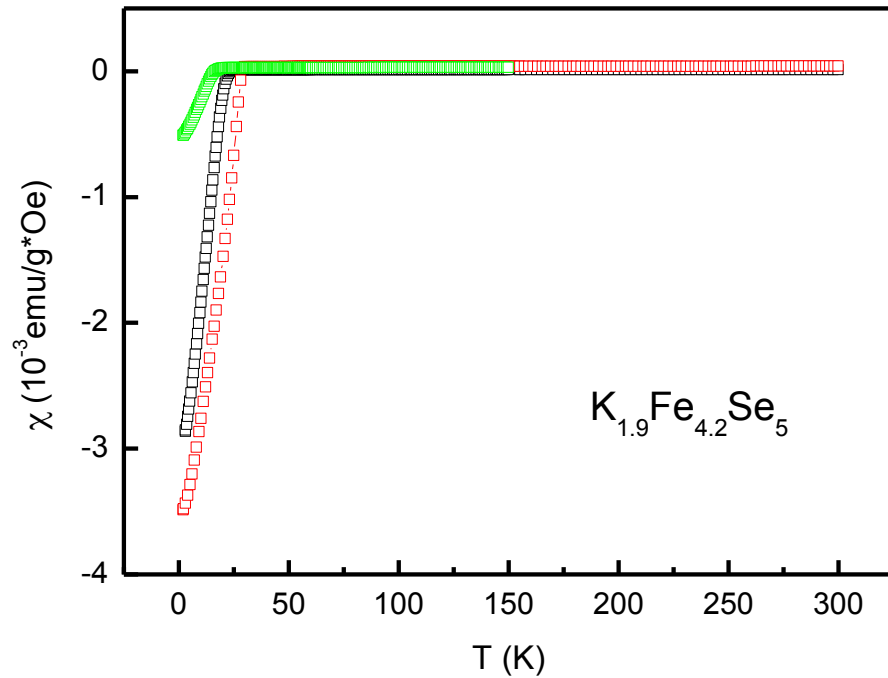




Our results indicate the Fe-vacancy is disordered in superconducting samples



Different T_c can be obtained !!



Summary

- A new phase diagram for Fe-chalcogenide is established
- Fe-vacancy order to disorder transition closely associates with the non-superconducting to superconducting phase transition
- A Verwey-like transition is observed in non-superconducting samples
- More detailed characterizations of these Fe-Se samples with Fe-vacancy are needed

