What have we learned from Nanosciences— Study of FeSe Superconductor as an example

M. K. Wu
National Dong-Hwa University
Institute of Physics, Academia Sinica

Lecture at the Center for Condensed Matter Sciences
NTU, 15 October 2013

奈米科技是21世紀最熱門的研究與產業新驅力，在奈米尺度下，物質會展現出全然不同的物理化學特性，因此所謂的奈米科技，便是能夠掌控這個尺度的物質基本構件特性，所衍生的新概念和新應用遍及能源光電、電腦半導體、機械工具、生物醫學、環境資源、化學工業等領域，不但創造新一波的科學與產業革命，也將全面影響人類的未來生活。

21世紀之始，美國、日本、歐洲等科技先進國家陸續推動奈米科技大型研究計畫；台灣也不落人後，於2003年啟動「奈米國家型科技計畫」，建立跨領域的研究平台，科學家在此相互討論激盪、合作研究，不但產生大量的一流學術研究成果，也與產業界密切商討技術轉移，使這個發展迅速的創新科技領域產生即時的應用，成果極為豐碩。

《奈米科技最前線》這本書訪問將近30位台灣頂尖科學家，請他們暢談科學靈感迸發的一瞬間，在全球獨創的研究主題中開疆闢土的過程與艱辛，在激烈競爭中合縱連橫的跨領域合作，致力透過奈米科技找到未來生活的全新可能性，令人同感熱血沸騰，充滿期待。

而為了替這個尖端科研計畫培養下一代科學家，這批學者同時參與教育紮根工作，培訓中小學種子教師製作教材，將最新的科學主題帶入十二年國民教育體系，成為全球首例，受到許多國家的注目與學習。《奈米科技最前線》也訪問多位計畫主持人和各級中小學老師，為這個史無前例的「奈米科技K12教育計畫」留下精彩而寶貴的紀錄。

台灣的奈米科技研究走在全球最前線！

獨創的螢光奈米鑽石與奈米標靶藥物傳輸之路
白光LED、新世代氧化物電晶體等尖端技術領先全球
首創口服奈米胰島素造福下一代糖尿病患
獨步全球的奈米研究打開基因治療大門

策劃單位｜中央研究院物理研究所，行政院國家科學委員會，奈米國家型科技計畫
總策劃｜吳茂昆　**策劃執行**｜陳淑美，曾焕基，錢嘉才，張民傑
出版發行｜遠流出版事業股份有限公司

採訪撰稿者簡介

李名揚｜清華大學物理系畢業，因為對新聞寫作有興趣，退伍後報考台灣大學新聞研究所，曾於《聯合報》主跑一年社會新聞，七年科技與教育新聞，是《新聞中的科學一，二》主要撰稿者之一，亦曾任《科學人》雜誌採訪部主任。

黃奕瀠｜政治大學新聞系，慈濟大學人類所畢業，曾任雜誌記者，網路書店科學和人文類採訪編輯、NGO工作者，現為中國時報調查採訪室記者，與同事一起出版《台灣的驕傲》、《消失與重生》，《一起走過，消失與重生》和《台灣關鍵字：十二個社會新動力》等書。

王心瑩｜台灣大學化學系、清華大學生科所畢業，曾任職《科學人》雜誌，現為出版社編輯，譯有《克里克：發現遺傳密碼的人》、《迷戀音樂的腦》、《你保重，我愛你：我和我的聰明鸚鵡艾利斯》（合譯）等書，合著有《台灣科技產業驚嘆號》。

design wangzhihong.com

大眾科學館——46

奈米科技最前線

中央研究院物理研究所、行政院國家科學委員會、奈米國家型科技計畫 策劃
李名揚、黃奕瀠、王心瑩 採訪撰稿

遠流

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Institute of Physics, Academia Sinica　National Science Council　National Program of Nanotechnology

the frontiers of nanotechnology in taiwan

材料、光電、生醫、教育四大領域，台灣奈米科技研究新勢力。

大眾科學館 46

N

奈米科技最前線——材料、光電、生醫、教育四大領域，台灣奈米科技研究新勢力。

the frontiers of nanotechnology in taiwan

中央研究院物理研究所、行政院國家科學委員會、奈米國家型科技計畫 策劃
李名揚、黃奕瀠、王心瑩 採訪撰稿

遠流

遠流
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P8046　NT$400

the frontiers of nanotechnology in taiwan

材料、光電、生醫、教育四大領域，台灣奈米科技研究新勢力！

材料儀器——奈米科學的基礎與應用

尖端電子顯微技術與表面科學…………中研院物理所｜張嘉升
推展奈米材料結構最極限…………中研院院士，清華大學校長｜陳力俊
獨創奈米超音波等分子醫學影像利器…………台大光電所暨電機系｜孫啟光
全球首創的螢光奈米鑽石與生醫應用…………中研院原分所｜張煥正
奈米機械量測的第一把交椅…………中正大學副校長｜鄭友仁

能源光電——科技生活的未來可能性

挑戰奈米雷射的白光雷射之父…………交大光電系｜王興宗
研發奈米材料製程的第一把交椅…………清大物理系｜果尚志
能源光電奈米材料推陳出新…………中研院原分所｜陳貴賢
發展出亞洲第一的奈米複合材料…………交大材料工程系｜韋光華
新一代電晶體的先驅帶領產業邁向未來…………交大電子工程系｜冉曉雯
由電鍍廠到iPhone電池的奈米蛻變之旅…………台科大講座教授｜黃炳照

生物醫學——下一世代的醫療遠景

以果蠅腦解讀出全腦神經叢譜…………清大腦科學研究中心｜江安世
研發出領先全球的奈米光譜技術…………台大凝態科學中心｜王俊凱
以奈米光譜超快速檢測紅菌…………陽明大學微免所｜林奇宏
用奈米光譜聆聽紅菌和故宮古畫的「聲音」…………中研院原分所｜王玉麟
全球獨創的「奈米剪刀」與開分子醫學領域…………成大口腔醫學研究所｜謝達斌
化學家研發智慧型抗癌奈米藥材…………成大化學系｜葉晨聖
首創口服胰島素為糖尿病患帶來希望…………清大化工系，生工所所長｜宋信文

K12教育計畫——全球首創的尖端科學國民教育計畫

未來的十多年間，奈米科技研究將會達到最高峰，
而十多年後的碩博士研究人才，現在人在那裡？
答案是正在接受十二年國民教育的中小學生！
因此，培養奈米人才的步伐，要從十二年國教開始打下良好根基……

奈米科技最前線——
材料、光電、生醫、教育四大領域，
台灣奈米科技研究新勢力。

the frontiers of nanotechnology in taiwan

N

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National Science Council
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National Program of Nanotechnology
奈米國家型科技計畫

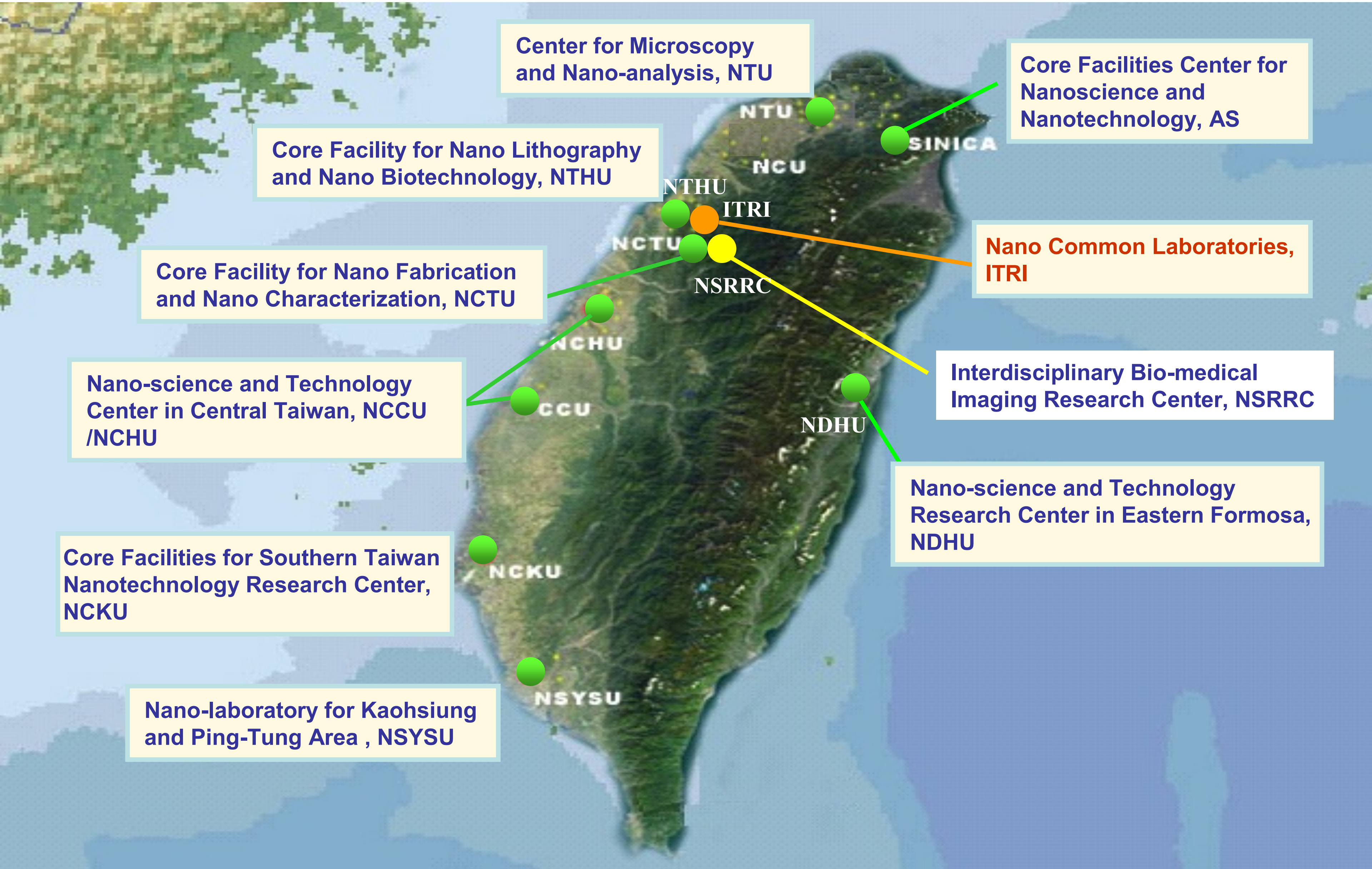
遠流

What we have advanced in Sciences, and how?

Establishment of Core Facilities

- Academic centers are located at the *Academia Sinica*, *National Taiwan University*, *National Tsing Hua University*, *National Chiao Tung University*, *National Chung Cheng University*, *National Cheng Kung University*, *National Sun Yet-Sen University*, and *National Dung Hua University*.
- A *biomedical nano-imaging center* was also set up in 2007.
- These core-facility centers provide professional services that significantly enhance efforts to satisfy needs of academic and industrial R&D.

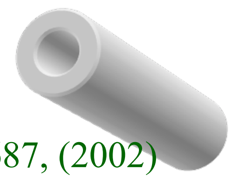
Core Facilities Progrm



1-D Functionalized Integrated Systems

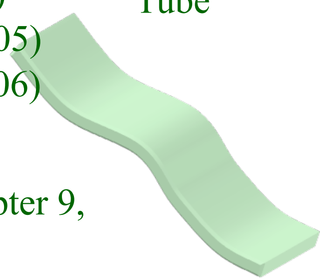
Appl. Phys. Lett. **81**, 22 (2002)
JACS **123**, 2791 (2001)
JACS **127**, 2820 (2005)

Wire/Rod



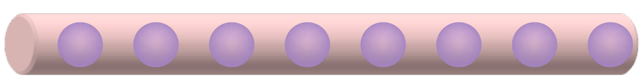
APL .**79**, 3179 (2001)
Adv. Func. Mate. **12**, 687, (2002)
APL **81**, 4189 (2002)
APL **86**, 203119 (2005)
JACS **128**, 8368 (2006)

Tube



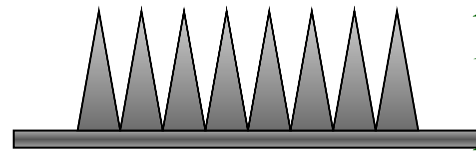
Z.L. Wang Ed., Chapter 9, pp.259-309, Kluwer (2004)
Adv. Fun. Mat. **16**, 537 (2006)

Belt



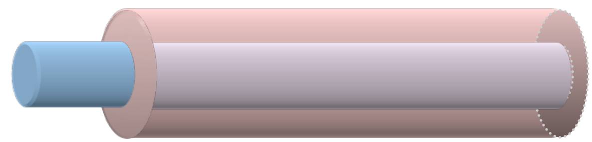
Peapod

Adv. Mater. **14**, 1847 (2002)
Nature Mater. **5,** 102 (2006)



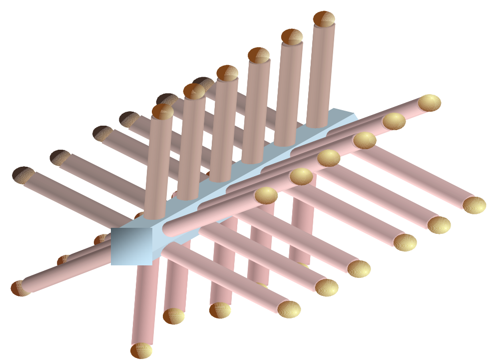
Nanotip

APL. **83**, 1420 (2003)
Nano. Lett. **4**, *471* (2004)
Chem. Mater. **17**, 553 (2005)
Adv. Func. Mat. **15**, 783 (2005
APL **86**, *203119 (2005)*
US Patent 6,960,528,B2
APL (2006)



Core-shell

APL. **81**, 1312 (2002)
Nano. Lett. **3**, *537* (200



Brush

Adv. Func. Mater. **14**, 233 (200

Other Thin Films:
DRM **14**, 1010 (2005)
APL **86**, 21911 (2005)
APL **86**, 83104 (2005)
APL **86**, 161901 (2005)
APL **87**, 261915 (2005)
JVST B **24**, 87 (2006)
APL **88**, 73515 (2006)

The violation of the Stokes–Einstein relation in supercooled water

Sow-Hsin Chen, Francesco Mallamace, **Chung-Yuan Mou**, **Matteo Broccio**, Carmelo Corsaro, Antonio Faraone, and **Li Liu**

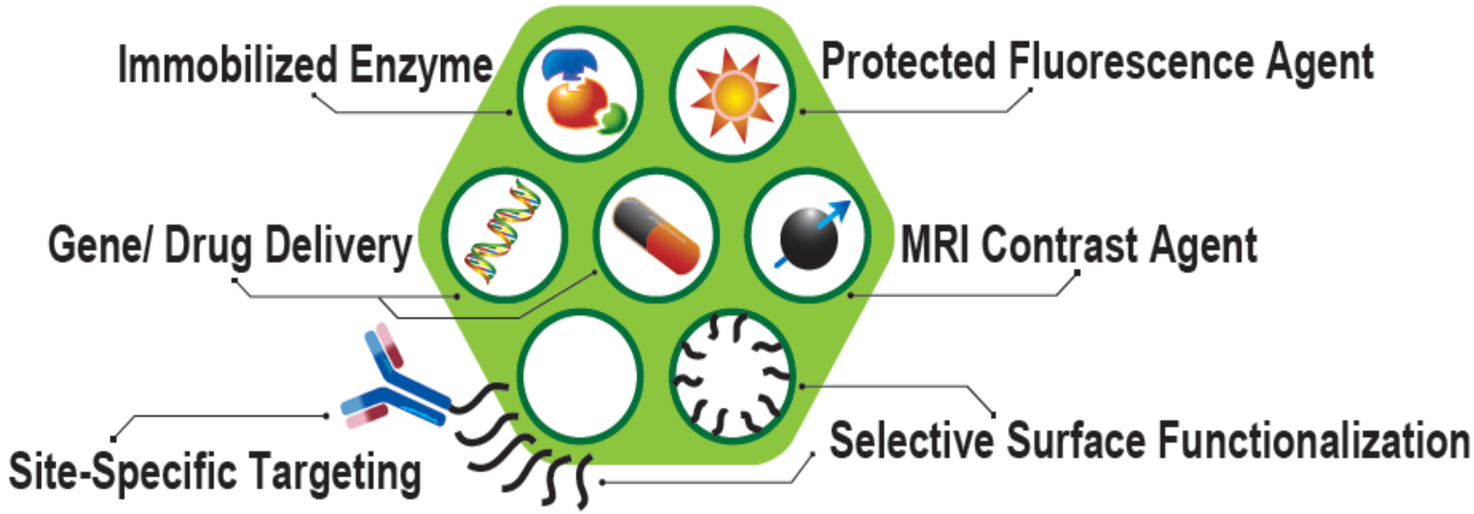
Abstract

By confining water in nanopores, so narrow that the liquid cannot freeze, it is possible to explore its properties well below its homogeneous nucleation temperature T_H 235 K. In particular, the dynamical parameters of water can be measured down to 180 K, approaching the suggested glass transition temperature T_g 165 K. Here we present experimental evidence, obtained from Nuclear Magnetic Resonance and Quasi-Elastic Neutron Scattering spectroscopies, of a well defined decoupling of transport properties (the self-diffusion coefficient and the average translational relaxation time), which implies the breakdown of the Stokes–Einstein relation.

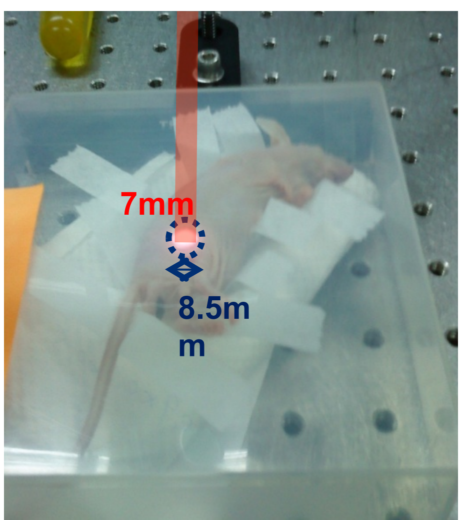
In 2005, PNAS established an annual award that recognizes recently published PNAS papers of outstanding scientific excellence and originality. The lab motto of Nick Cozzarelli, our late Editor-in-Chief, was "Blast ahead," as he encouraged researchers to push the envelope of discovery. This year the award is renamed the Cozzarelli Prize, and the Editorial Board has reorganized the above article, "The violation of the Stokes-Einstein Relation in supercooled water", as an excellent example of these same qualities.

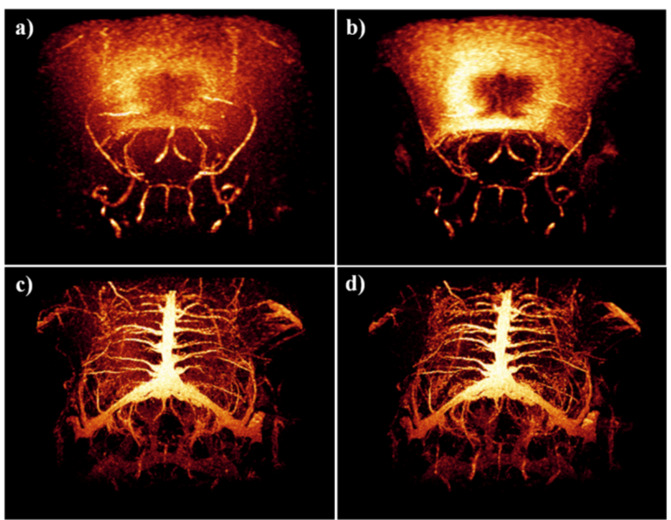
Mesoporous silica as Nanocarriers

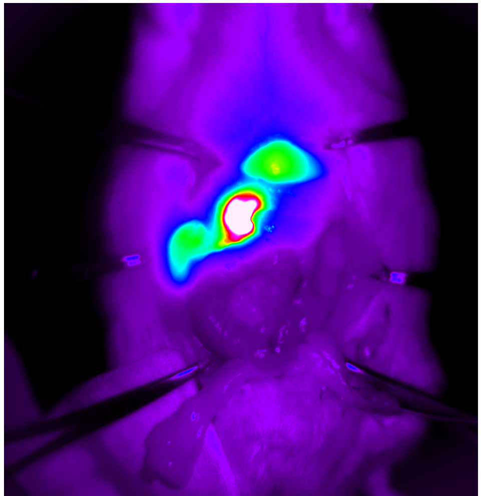
S.H. Wu, Y. Hung, C.Y. Mou, *Chem Comm* (Feature Article, 2011, In Press)



Photodynamic therapy | **Magnetic Resonance Angiography** | **Oral drug delivery**

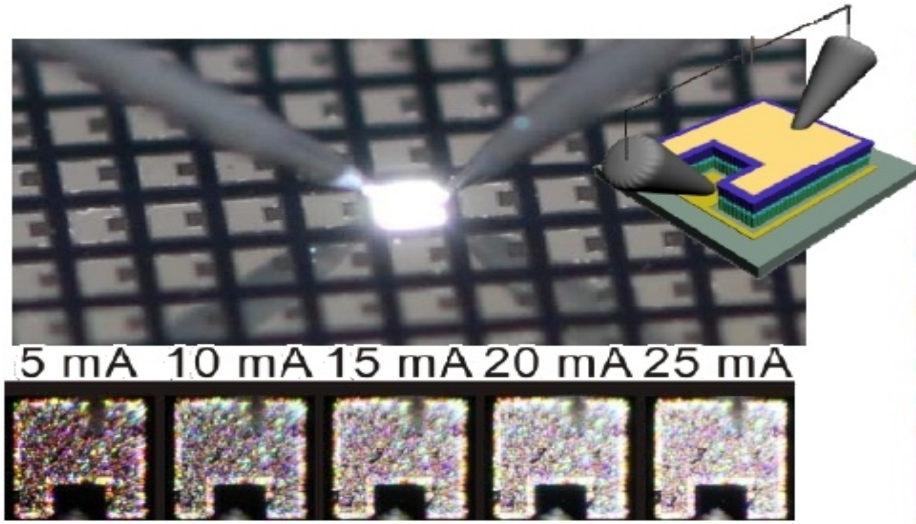


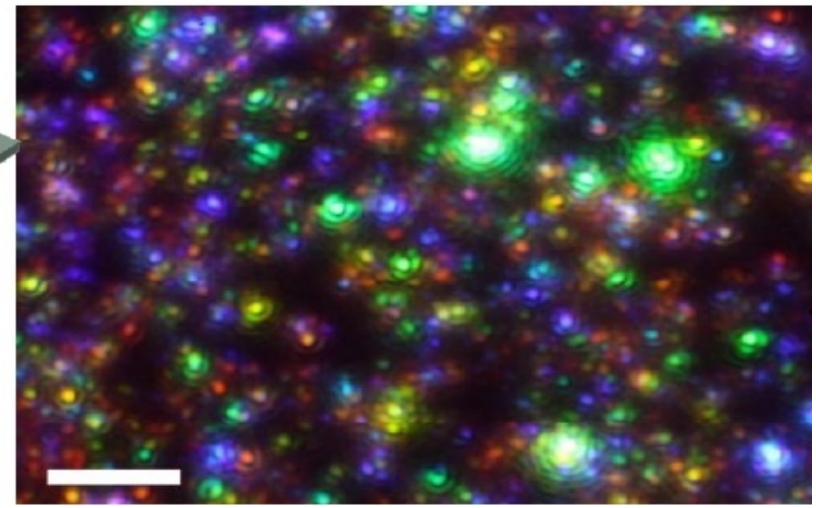




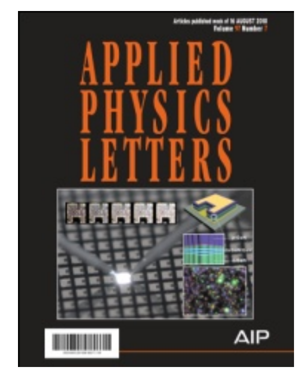
GaN Nanorod Array for White-light LED

Appl. Phys. Lett. **97**, 073101 (2010)

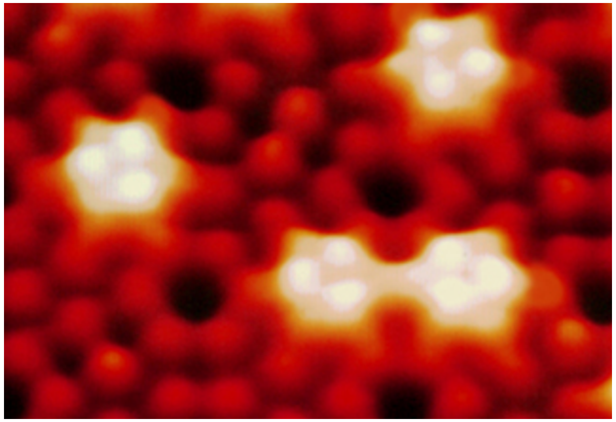
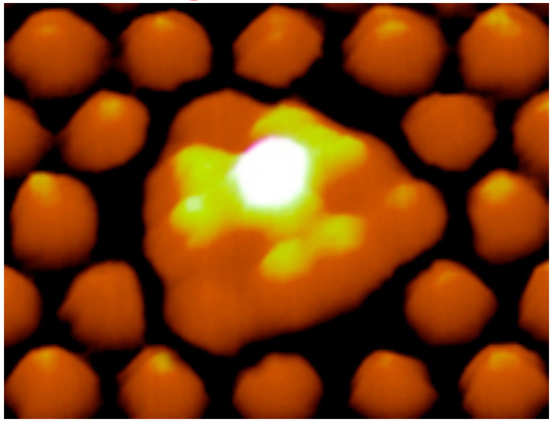
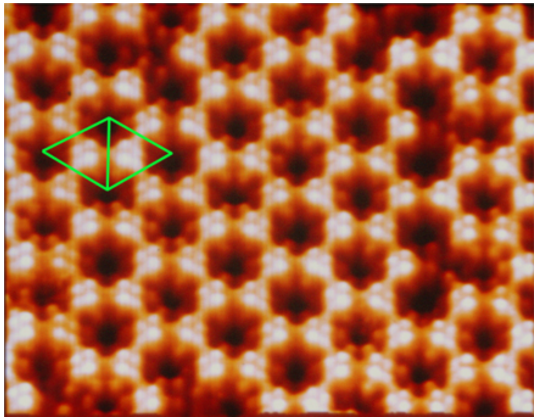
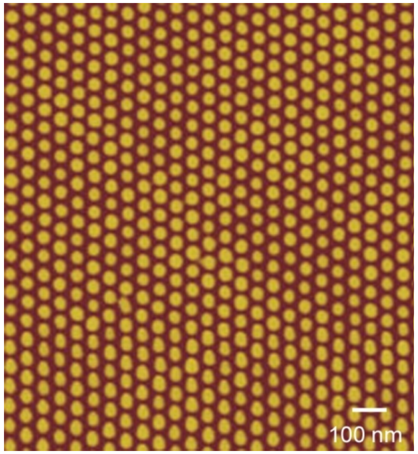


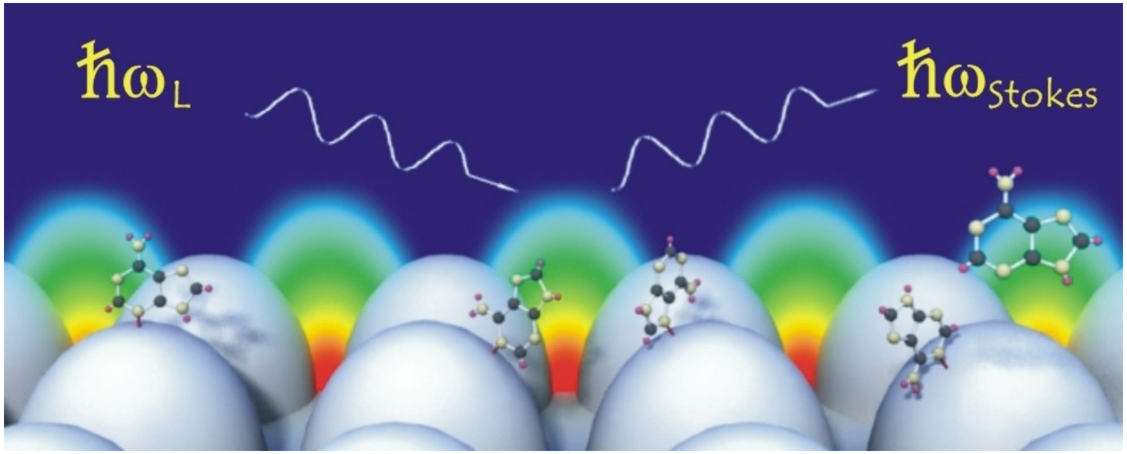


- Good quality of GaN nanorod arrays have been demonstrated.
  – Strain free, defect suppression, low refractive index
- Nanorods-on-Si growth templates can serve as a good system for InGaN-nanodisk-based full-color light-emitting devices.
- A new approach is shown for generating high-quality white light LED with high color rendering capability and high efficiency.



Creating Monodispersed Ordered Arrays of Surface-Magic-Clusters and Anodic Alumia Nanochannels by Constrained Self-organization



Prof. Yuh-Lin Wang 王玉麟
IAMS Academia Sinica, Taiwan

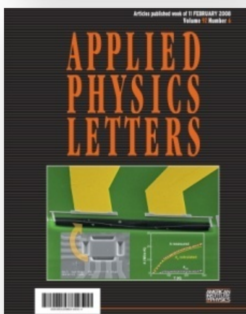
NanoCore Research Highlights

Cover Story

Proteomics ***7***, *3038-3050 (2007)*

Targeted protein quantitation and profiling using PVDF affinity probe and MALDI-TOF MS

Institute of Chemistry, Academia Sinica

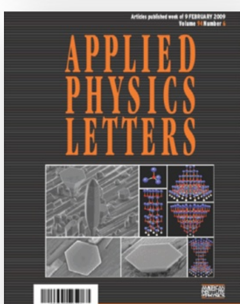


Cover Story

Appl. Phys. Lett., ***92***, *063101 (2008)*

Electrical and thermal transport in single nickel nanowire

Institute of Physics, Academia Sinica



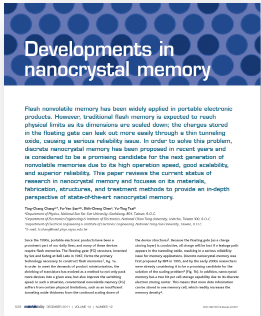
Cover Story

Appl. Phys. Lett., ***94***, *062105 (2009)*

Self-assembled GaN hexagonal micropyramid and microdisk

Department of Physics, National Sun Yat-Sen University

NanoCore Research Highlights (cont'd)

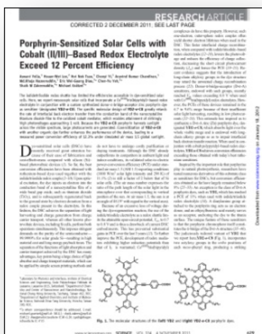

Developments in nanocrystal memory

Invited Review Article

*Materials Today, **14(12)**, 526 (2011)*

Developments in nanocrystal memory

Department of Physics, National Sun Yat-Sen University


RESEARCH ARTICLE

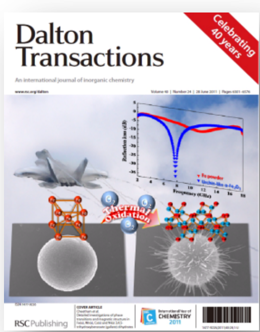
Porphyrin-Sensitized Solar Cells with Cobalt (II/III)–Based Redox Electrolyte Exceed 12 Percent Efficiency

*Science ,**334**, 629 (2011)*

Porphyrin-Sensitized Solar Cells with Cobalt (II/III)–Based Redox Electrolyte Exceed 12 Percent Efficiency

Department of Chemistry and Center of Nanoscience and Nanotechnology, National Chung Hsing University

Department of Applied Chemistry and Institute of Molecular Scinece, National Chiao Tung University



Cover Story

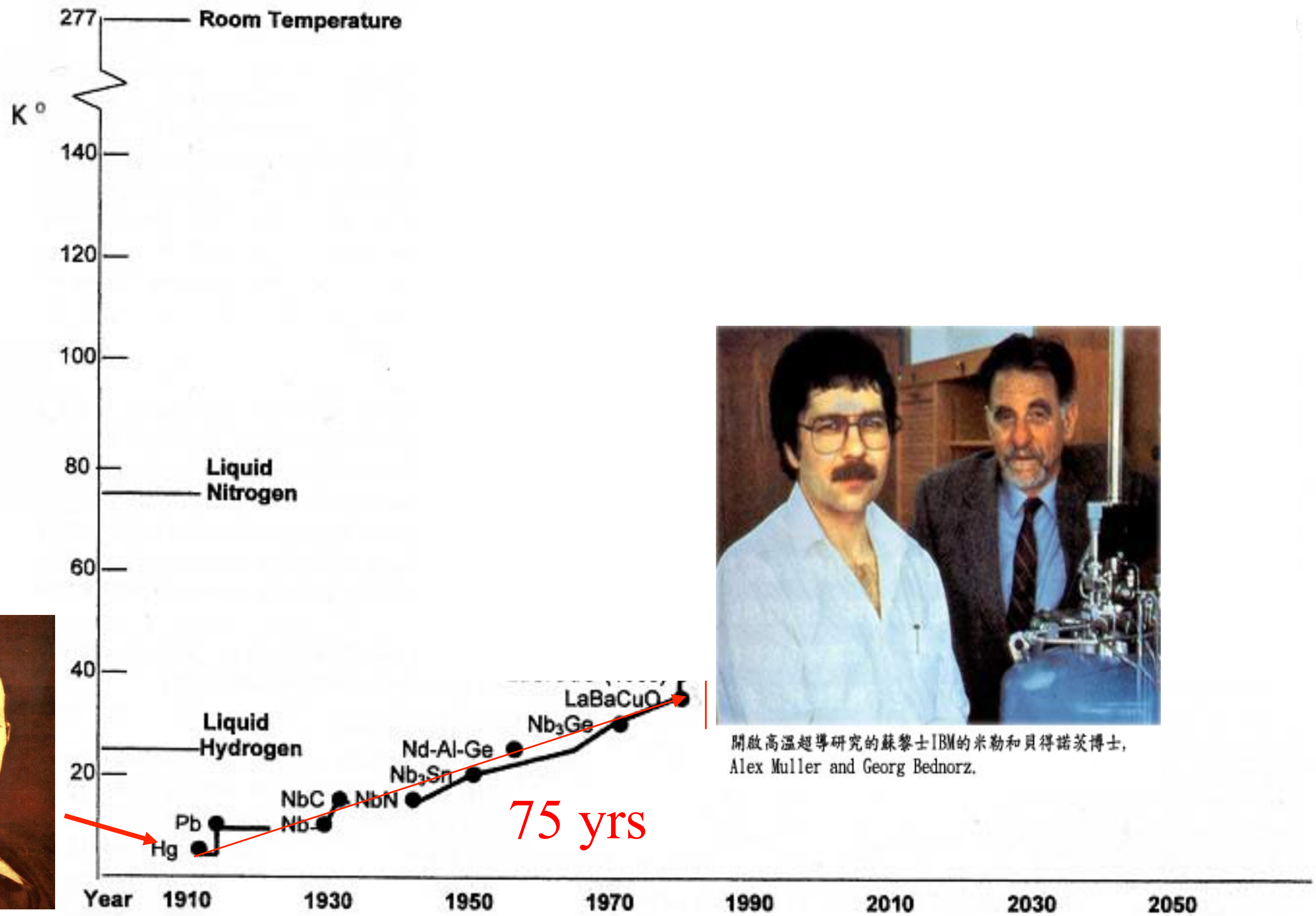
*Dalton Transactions, **41**, 723 (2012)*

A 3D α-Fe_2O_3 nanoflake urchin-like structure for electro-magnetic wave absorption

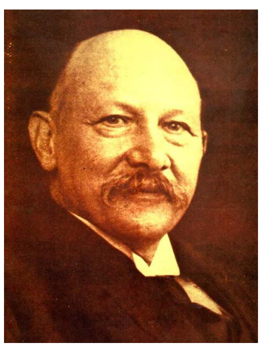
Department of Chemical Engineering, National Chung Cheng University

- What has Nanotechnology done for Sciences and Society ?
  - For Sciences
    - New Insights into: Quantum phenomena; Atomic assembly; Interactions among biology and physical sciences; New tools—Atomic manipulation, bioimaging...
  - For Society
    - New Technology for: Biomedical applications; Daily life applications; Agriculture; Energy; Water; Environment; New industries….

An Example: Development in High Temperature Superconductivity—My Personal Journey



History of Discovery of Superconductors. Incerases in Critical Temperature. Vertical scale in degrees Kelvin.



開啟高溫超導研究的蘇黎士IBM的米勒和貝得諾茲博士,
Alex Muller and Georg Bednorz.

Discovery of Tc > 77K SC

VOLUME 58, NUMBER 9 PHYSICAL REVIEW LETTERS 2 MARCH 1987

Superconductivity at 93 K in a New Mixed-Phase Y-Ba-Cu-O Compound System at Ambient Pressure

M. K. Wu, J. R. Ashburn, and C. J. Torng
Department of Physics, University of Alabama, Huntsville, Alabama 35899

and

P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu[a]
Department of Physics and Space Vacuum Epitaxy Center, University of Houston, Houston, Texas 77004
(Received 6 February 1987; Revised manuscript received 18 February 1987)

A stable and reproducible superconductivity transition between 80 and 93 K has been unambiguously observed both resistively and magnetically in a new Y-Ba-Cu-O compound system at ambient pressure. An estimated upper critical field $H_{c2}(0)$ between 80 and 180 T was obtained.

PACS numbers: 74.70.Ya

VOLUME 58, NUMBER 9 PHYSICAL REVIEW LETTERS 2 MARCH 1987

High-Pressure Study of the New Y-Ba-Cu-O Superconducting Compound System

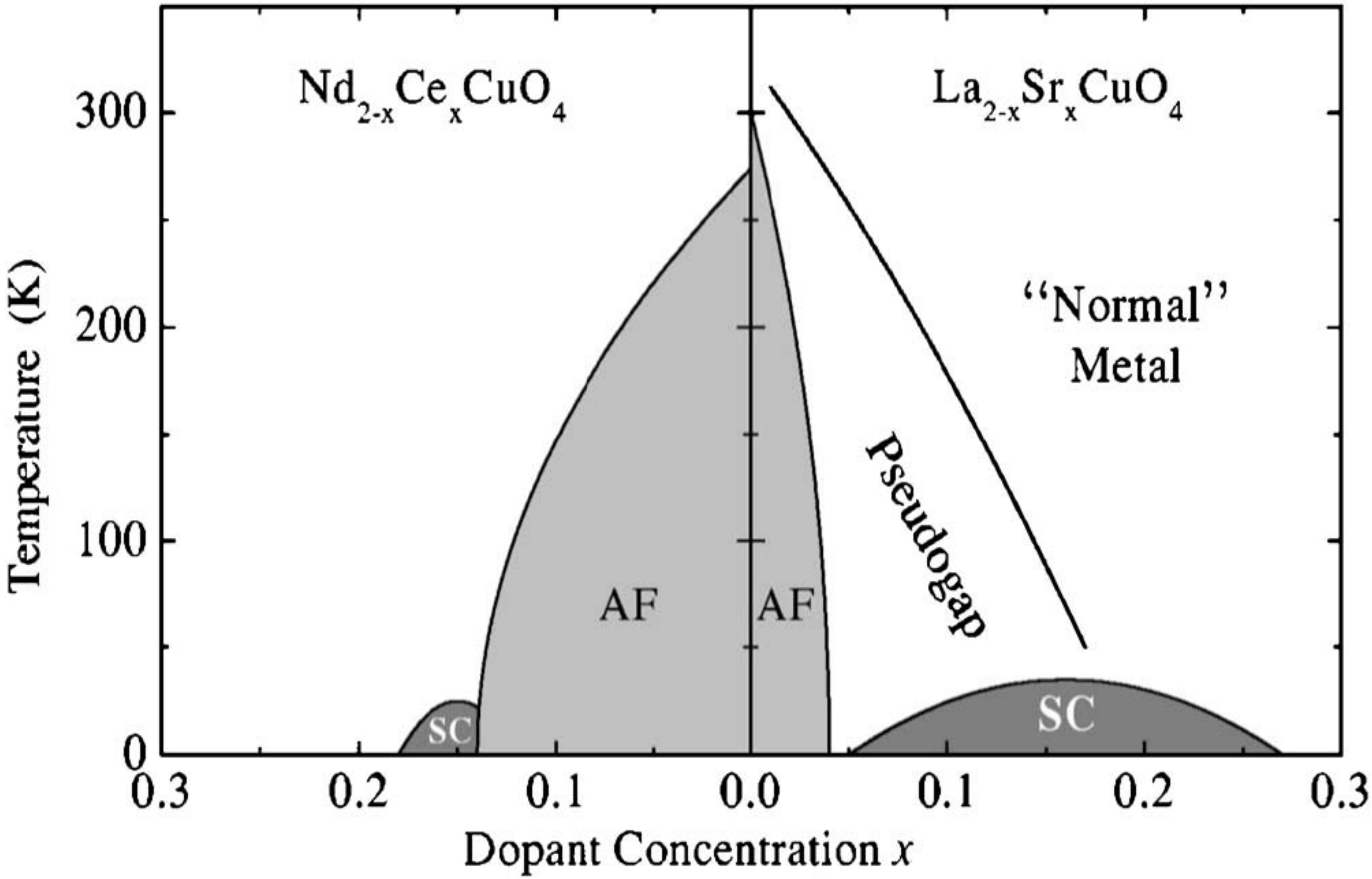
P. H. Hor, L. Gao, R. L. Meng, Z. J. Huang, Y. Q. Wang, K. Forster, J. Vassilious, and C. W. Chu[a]
Department of Physics and Space Vacuum Epitaxy Center, University of Houston, Houston, Texas 77004

and

M. K. Wu, J. R. Ashburn, and C. J. Torng
Department of Physics, University of Alabama, Huntsville, Alabama 35899
(Received 6 February 1987; Revised manuscript received 18 February 1987)

The pressure effect on the superconducting state above 77 K in the new Y-Ba-Cu-O compound system has been determined. In strong contrast to what is observed in the La-Ba-Cu-O and La-Sr-Cu-O systems, pressure has only a slight effect on the superconducting transition temperature.

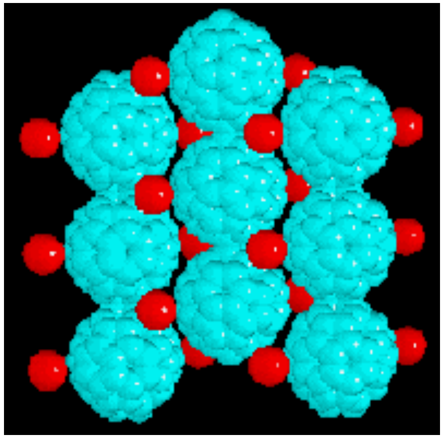
PACS numbers: 74.70.Ya



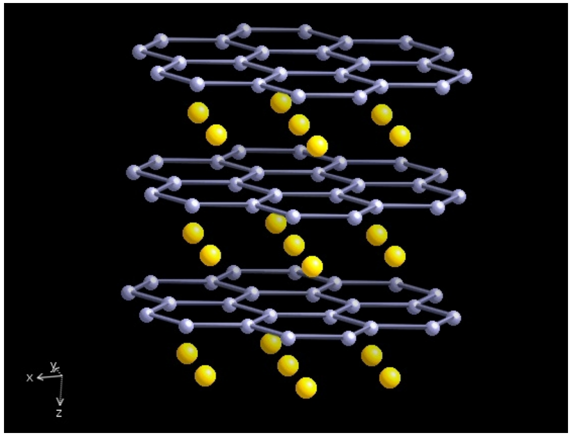
Schematic phase diagram of high-*Tc superconductors* showing hole doping right side and electron doping left side. From Damascelli *et al., 2003.*

The Best Accomplishments

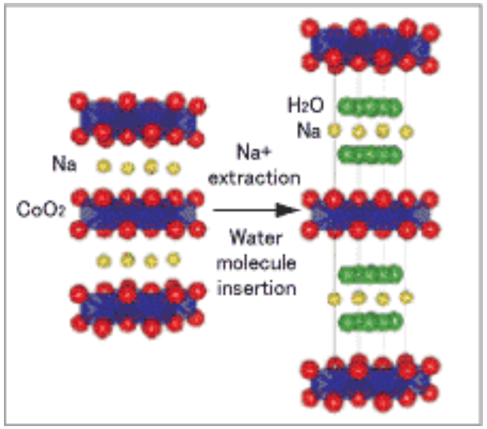
- *Triumph of Physicists, Chemists and Material Scientists*



Rb Dopded C_{60}



MgB_2



$Na_xCoO_2 \cdot yH_2O$

J|A|C|S
COMMUNICATIONS

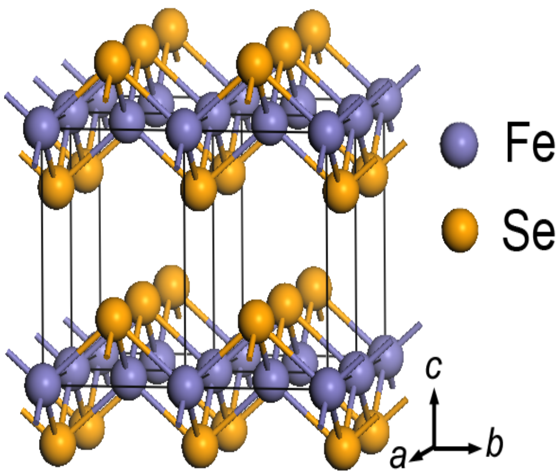
Published on Web 00/00/0000

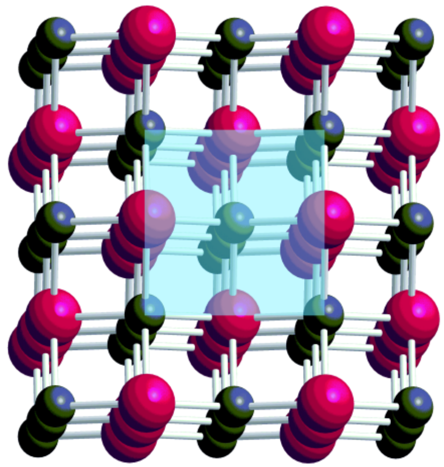
Iron-Based Layered Superconductor $La[O_{1-x}F_x]FeAs$ ($x = 0.05-0.12$) with $T_c = 26$ K

Yoichi Kamihara,*,† Takumi Watanabe,‡ Masahiro Hirano,†,§ and Hideo Hosono†,‡,§

ERATO-SORST, JST, Frontier Research Center, Tokyo Institute of Technology, Mail Box S2-13, Materials and Structures Laboratory, Tokyo Institute of Technology, Mail Box R3-1, and Frontier Research Center, Tokyo Institute of Technology, Mail Box S2-13, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

FeSe system





- Structure type: B10, anti-PbO
- Pearson symbol: tP4
- Space group: P4/nmm, No. 129
- a= 3.783, C= 5.534
- Fe 2a x=0 y=0 z=0
- Se 2c x=0 y=1/2 z=0.26

PNAS

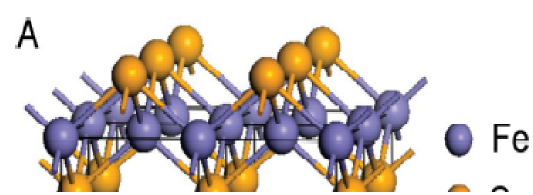
Superconductivity in the PbO-type structure α-FeSe

Fong-Chi Hsu*†, Jiu-Yong Luo*, Kuo-Wei Yeh*, Ta-Kun Chen*, Tzu-Wen Huang*, Phillip M. Wu‡, Yong-Chi Lee*, Yi-Lin Huang*, Yan-Yi Chu*†, Der-Chung Yan*, and Maw-Kuen Wu*§

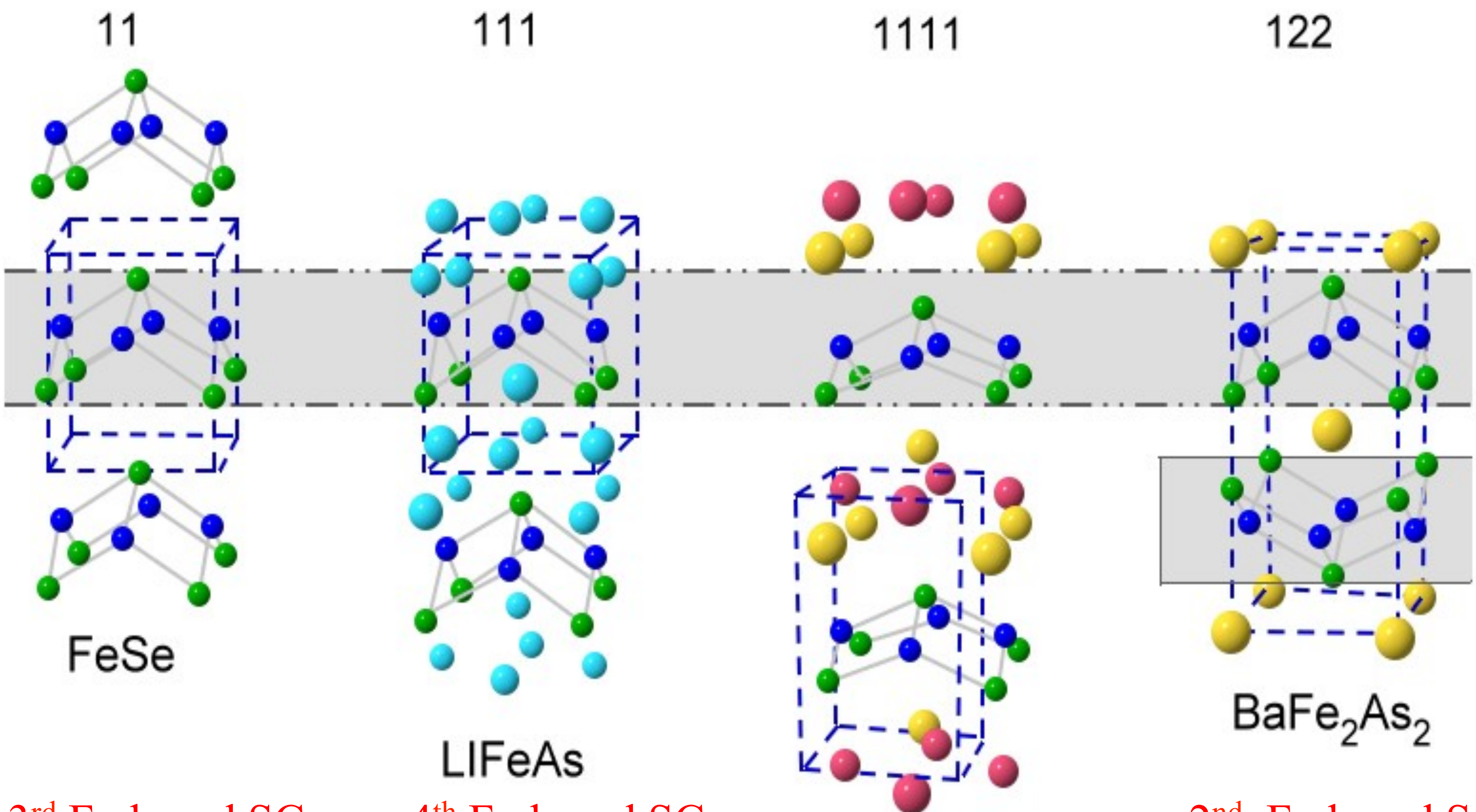
*Institute of Physics, Academia Sinica, Nankang, Taipei 115, Taiwan; †Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan; and ‡Department of Physics, Duke University, Durham, NC 27708

Contributed by Maw-Kuen Wu, July 28, 2008 (sent for review July 26, 2008)

The recent discovery of superconductivity with relatively high transition temperature (Tc) in the layered iron-based quaternary oxypnictides $La[O_{1-x}F_x]$ FeAs by Kamihara *et al.* [Kamihara Y, Watanabe T, Hirano M, Hosono H (2008) Iron-based layered superconductor La[O1-xFx] FeAs (x = 0.05–0.12) with Tc = 26 K. *J Am*



The common Features in Fe-based superconductors



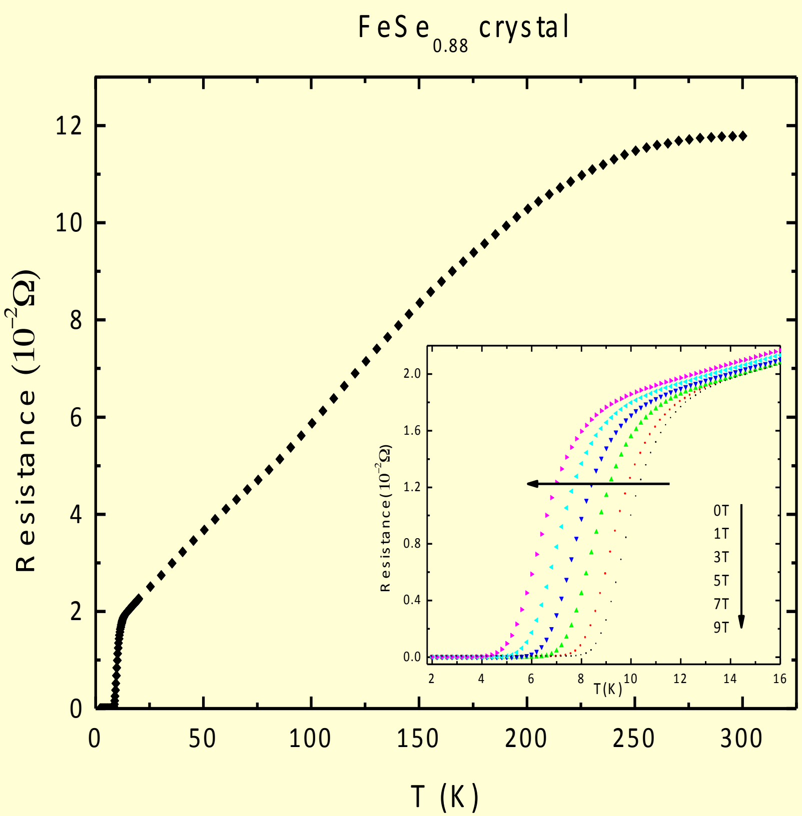
3rd Fe-based SC
Found in
Taiwan

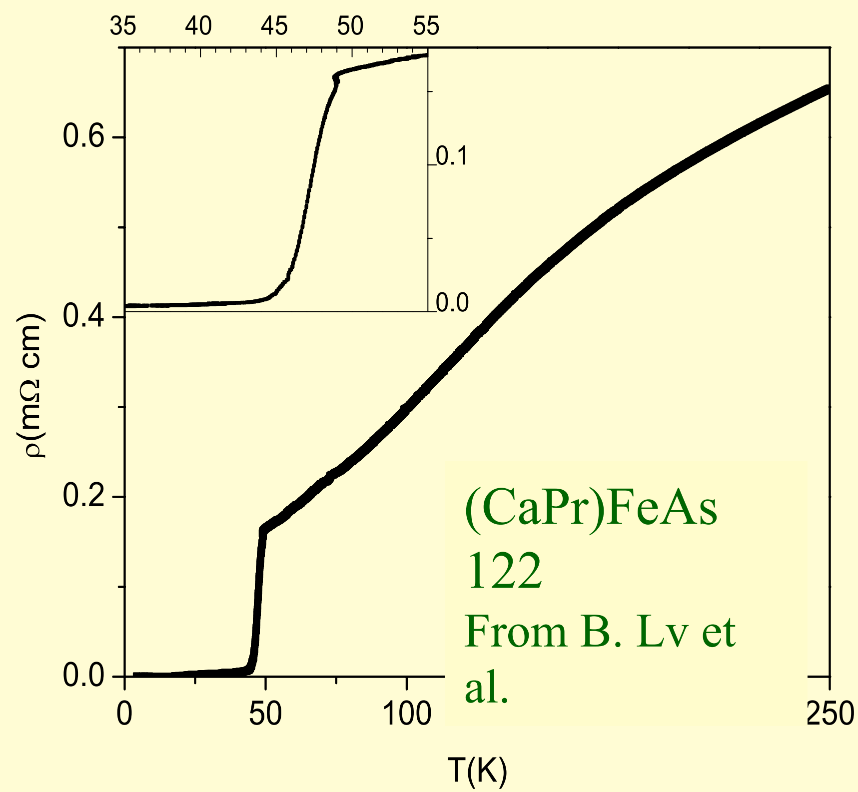
4th Fe-based SC
Found in China

1st Fe-based SC
Found in Japan

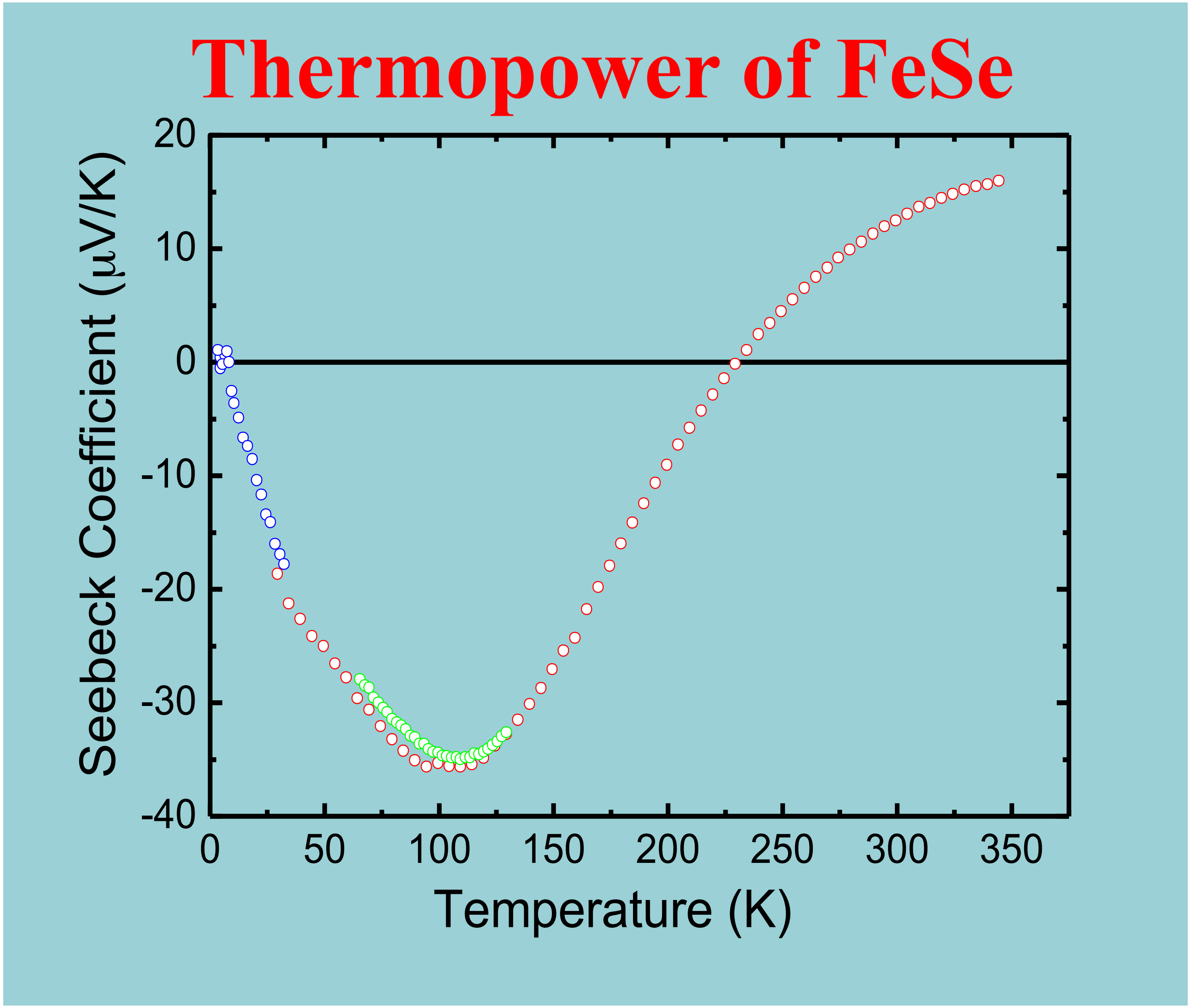
2nd Fe-based SC
Found in
Germany

The common Features in Fe-based superconductors?





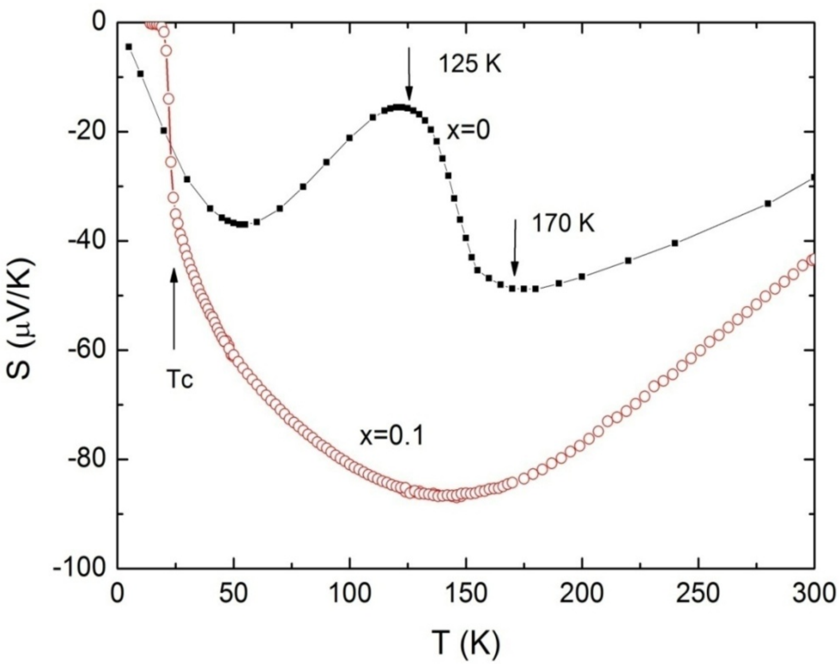
The common Features in Fe-based superconductors

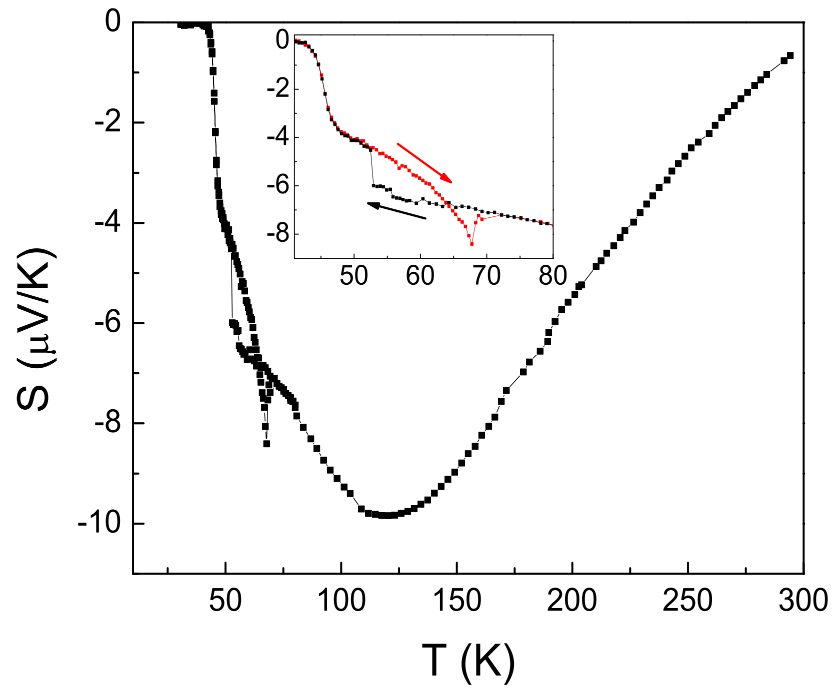


Thermopower of Pnictides

F- doped 1111 , LaFeAsO1-xFx, x=0, 0.1

Electron-Doped CaFe2As2

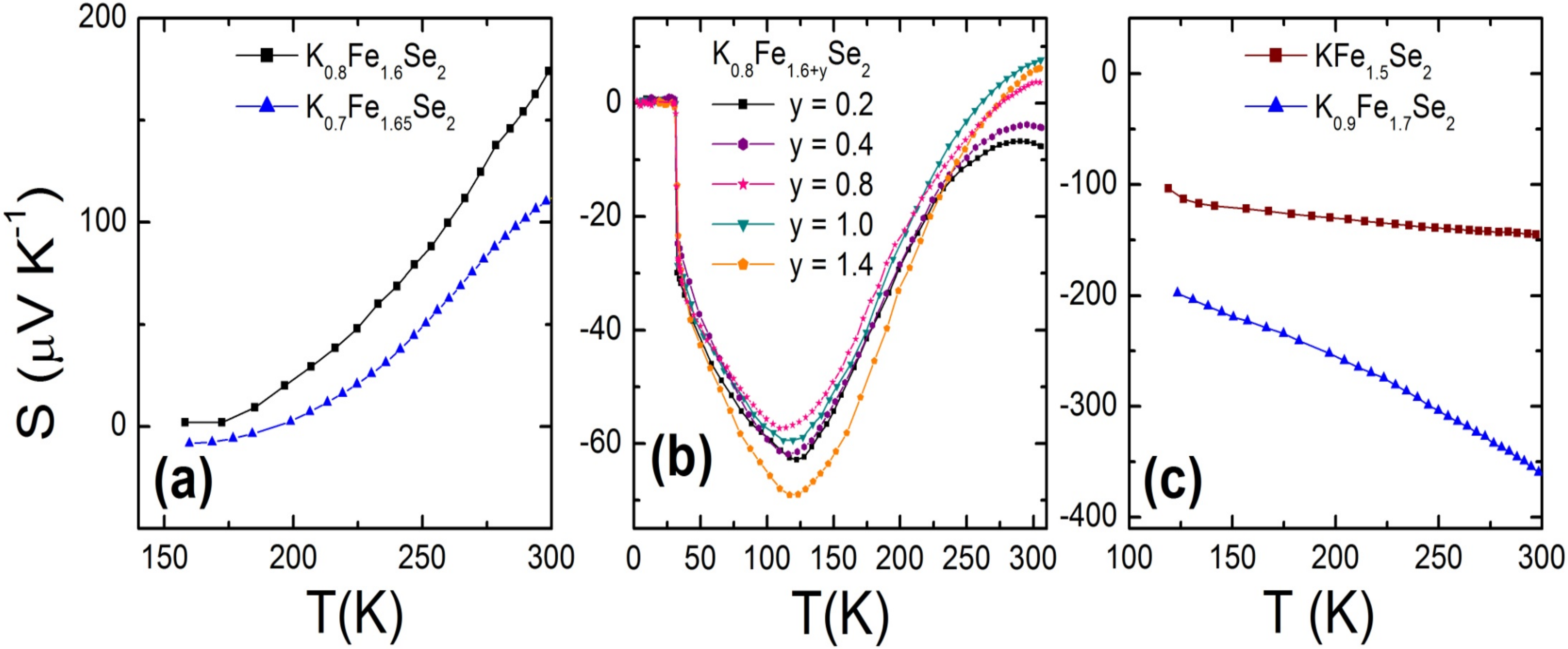




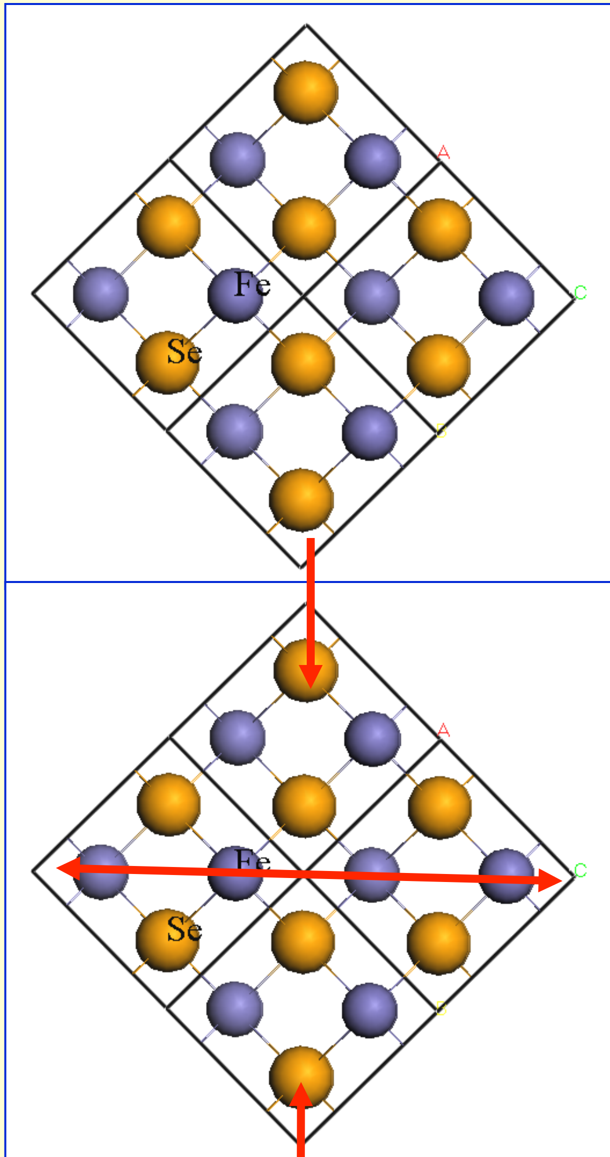
From Prof. Z.A. Xu

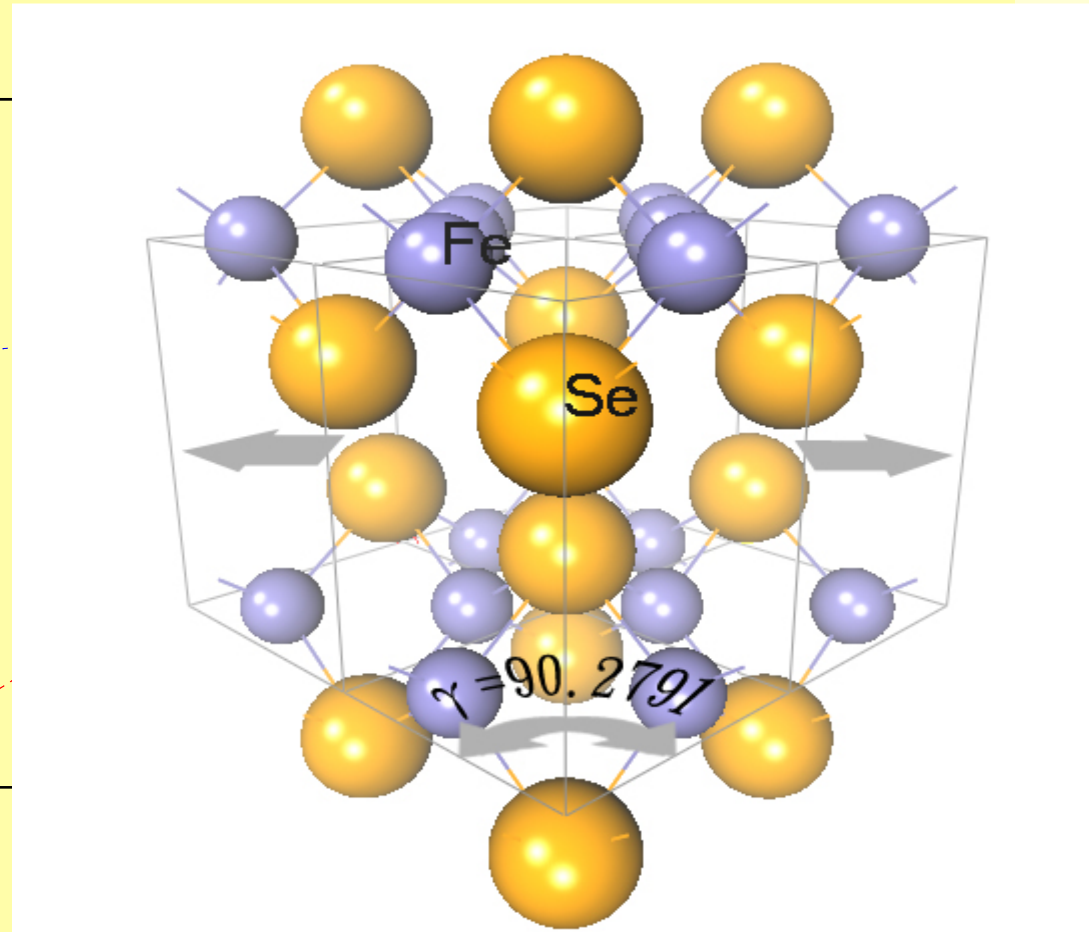
From Prof. C.W. Chu

Thermoepower of $K_{1-x}Fe_{2-y}Se_2$ in three regimes



From Prof. X. H. Chen



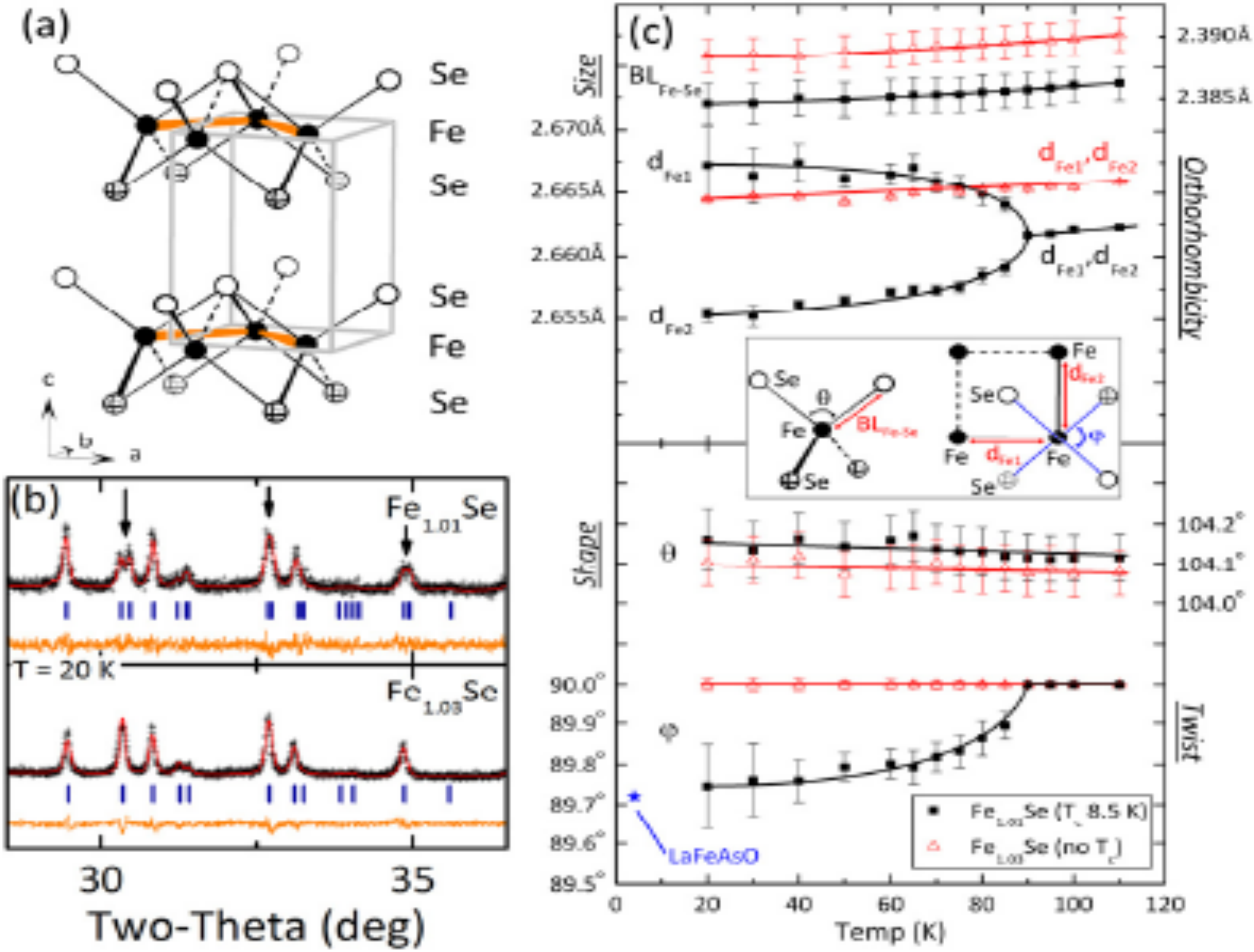


T(K)

Simulation 6K

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

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



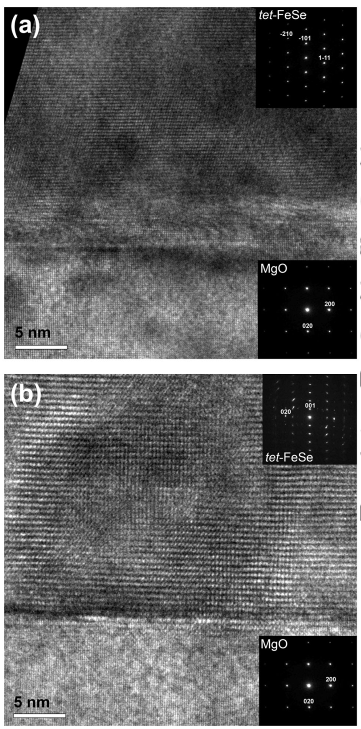
McQueen *et al.*, PRL 2009

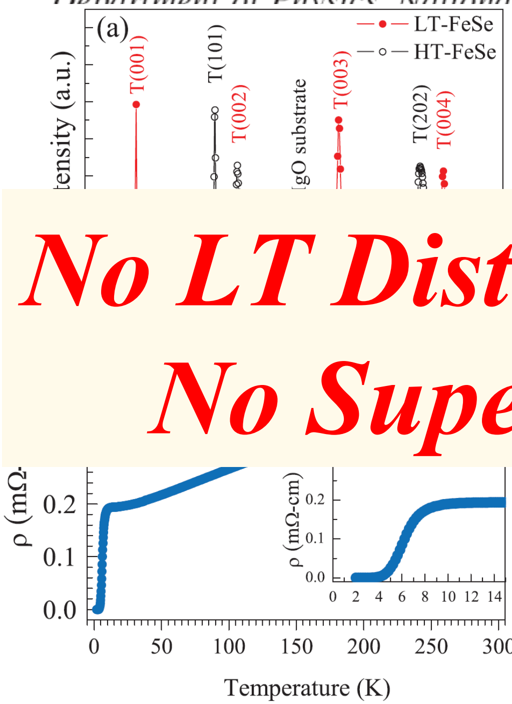
PRL **103,** 117002 (2009) PHYSICAL REVIEW LETTERS week ending 11 SEPTEMBER 2009

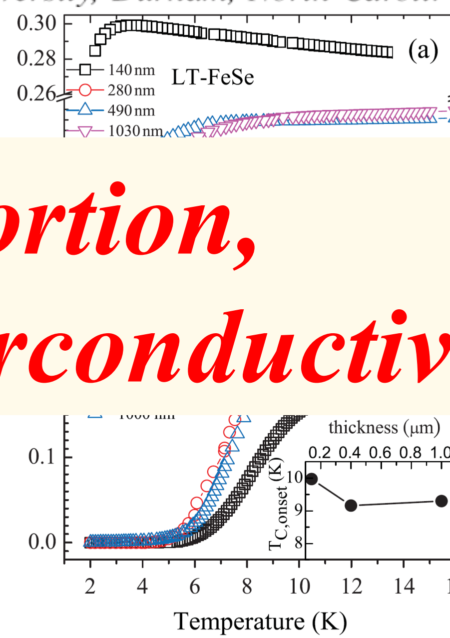
Crystal Orientation and Thickness Dependence of the Superconducting Transition Temperature of Tetragonal $FeSe_{1-x}$ Thin Films

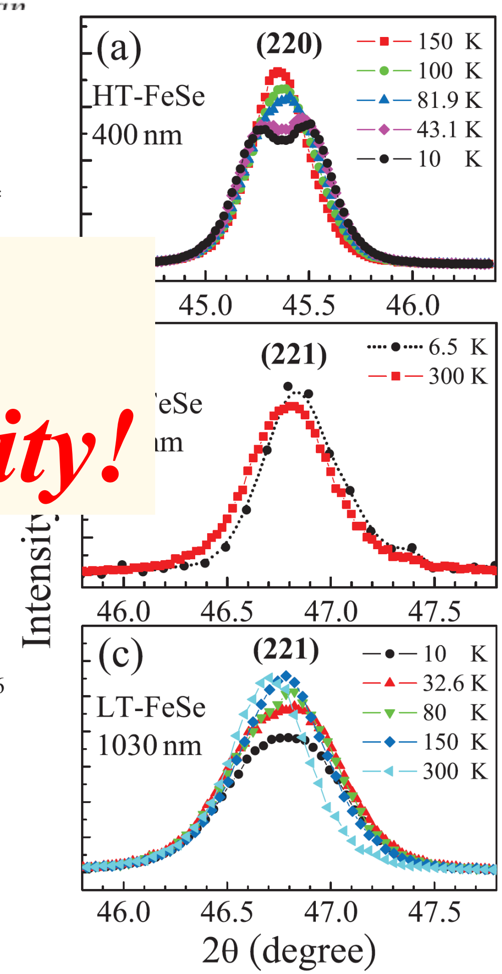
M. J. Wang,[1,*] J. Y. Luo,[2] T. W. Huang,[2] H. H. Chang,[3] T. K. Chen,[2] F. C. Hsu,[1] C. T. Wu,[3] P. M. Wu,[4] A. M. Chang,[4] and M. K. Wu[2,3,†]

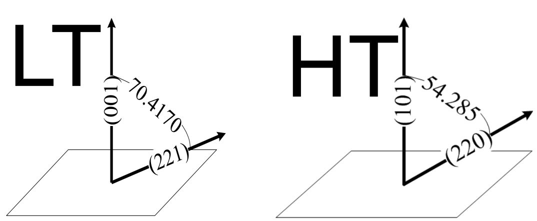
[1]Institute of Astronomy and Astrophysics, Academia Sinica, Taipei, Taiwan
[2]Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan
[3]Department of Physics, National Tsing Hua University, Hsinchu,
...niversity, Durham, North Caroli...





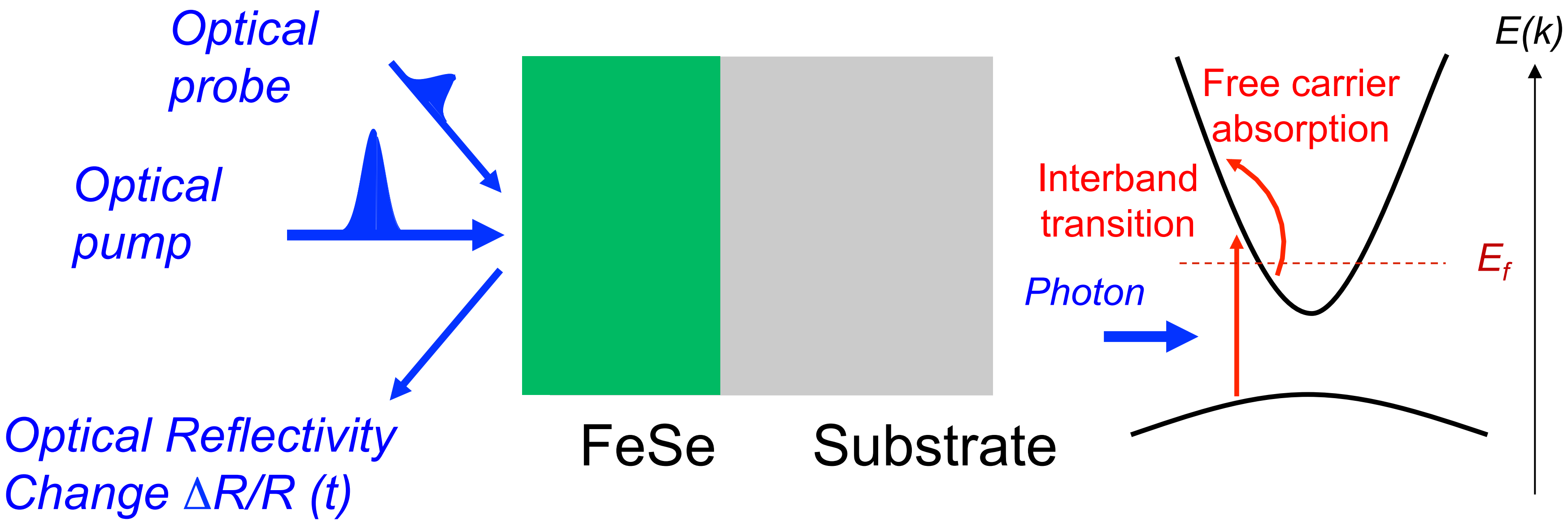






No LT Distortion, No Superconductivity!

Femtosecond optical pump-probe spectroscopy



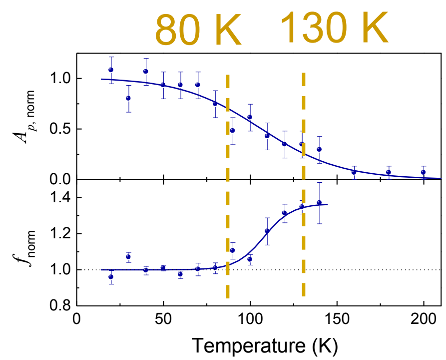
Pump/probe = 400/800 nm
(corresponding to probe of Fe 3-d orbital)

Pump fluence = 5.3 μJ/cm^2
(measurement was done under the perturbation regime)

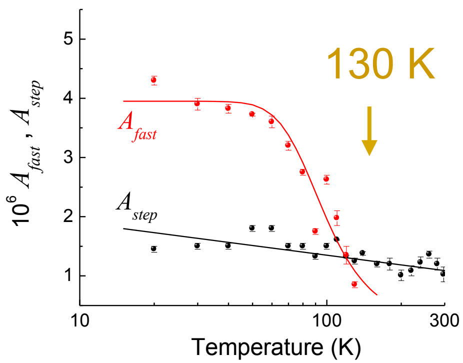
Correlation between different dynamics at T = 80~130 K

Indication of optical absorption

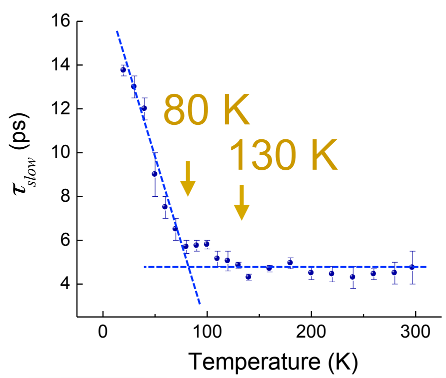
Indication of spin fluctuation

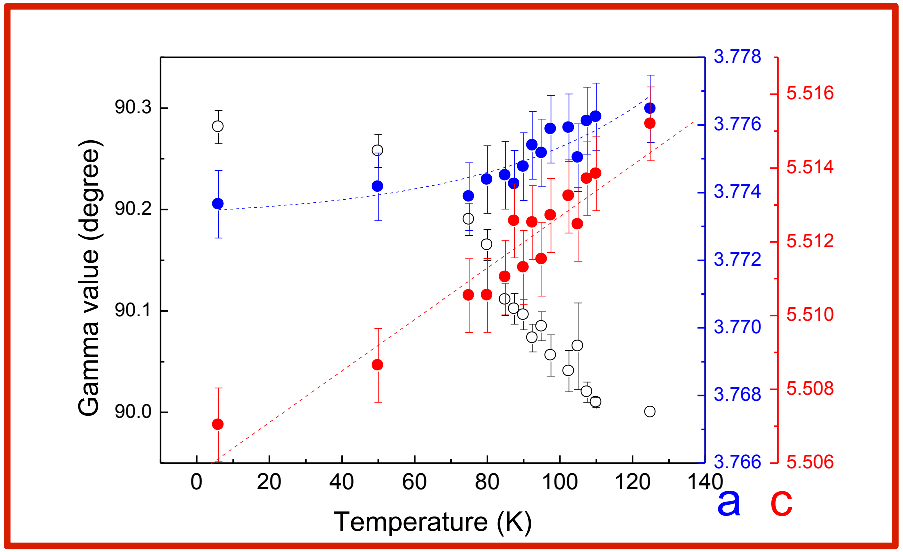


A_{fast}: gap-like feature



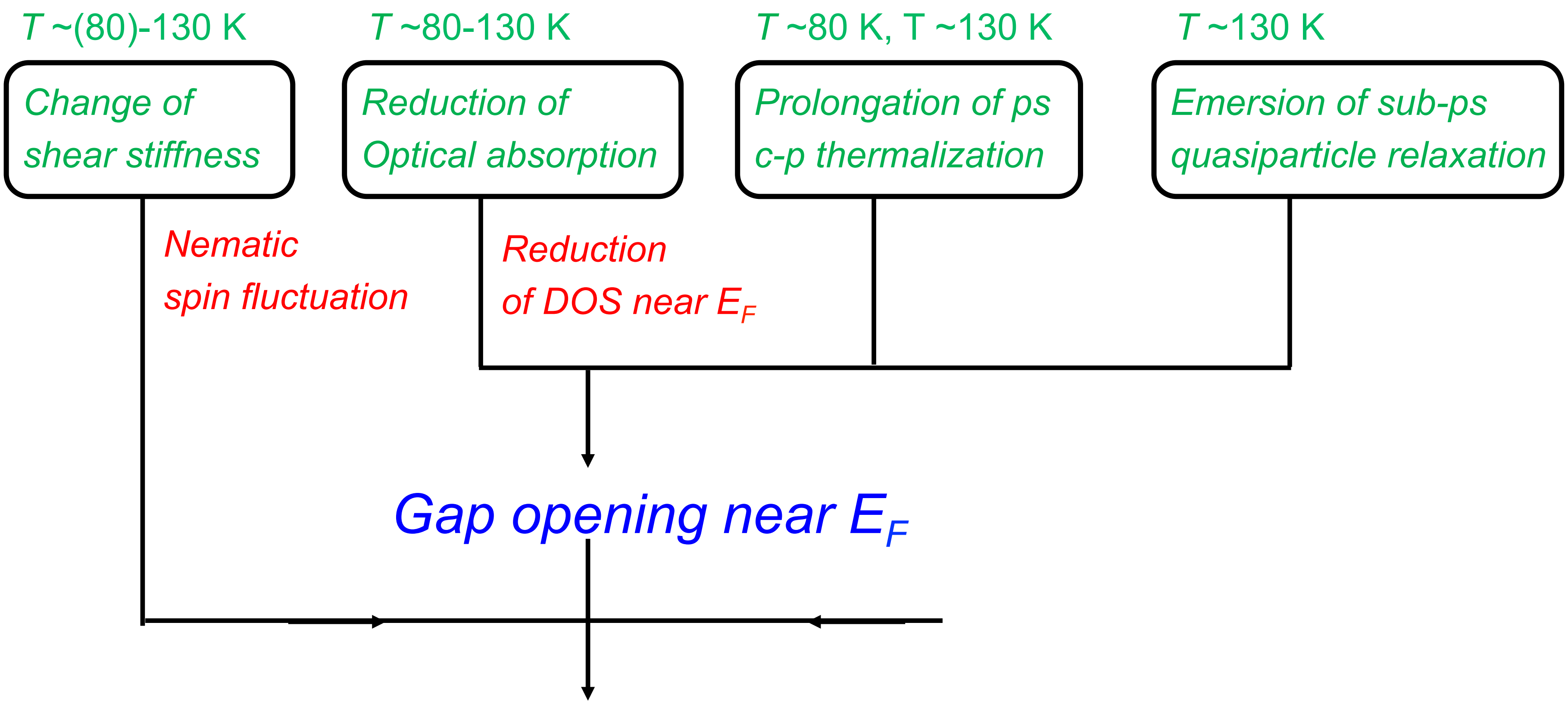
τ_{slow}: carrier-phonon thermalization





Wen, et al., PRL **108**, 267002 (2012)

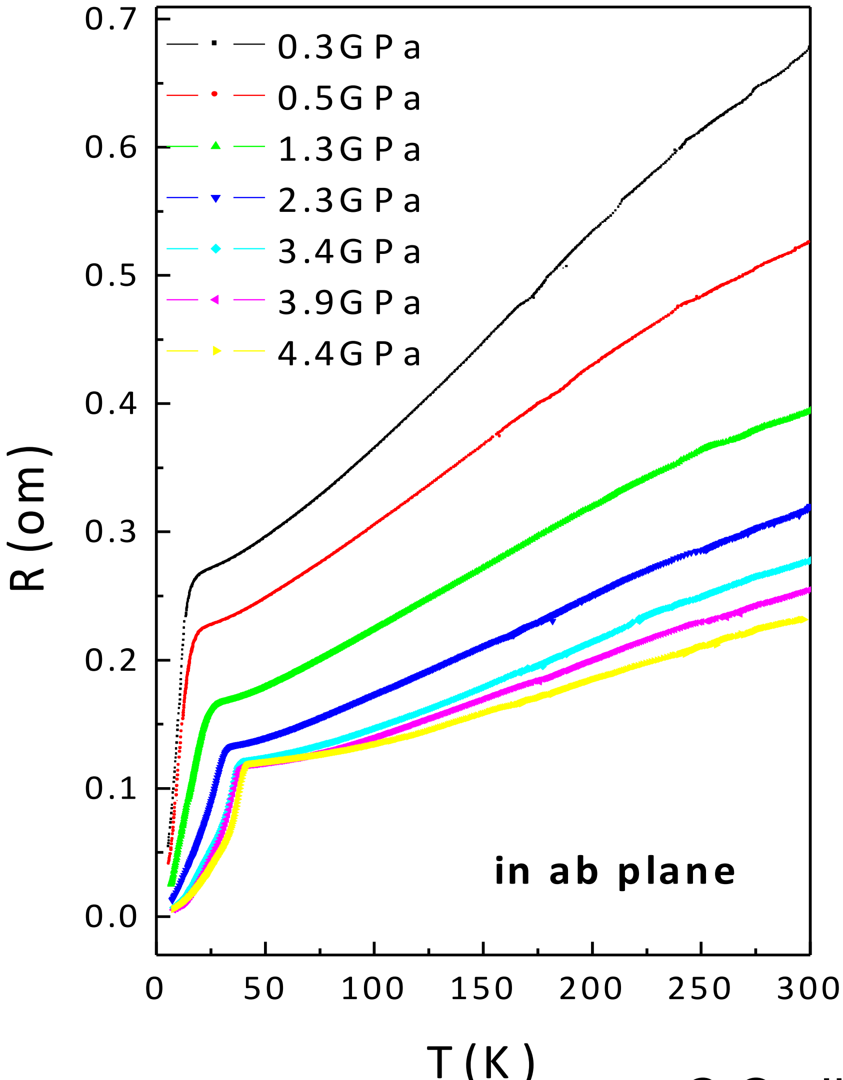
Relation between all clues obtained by optical pump-probe

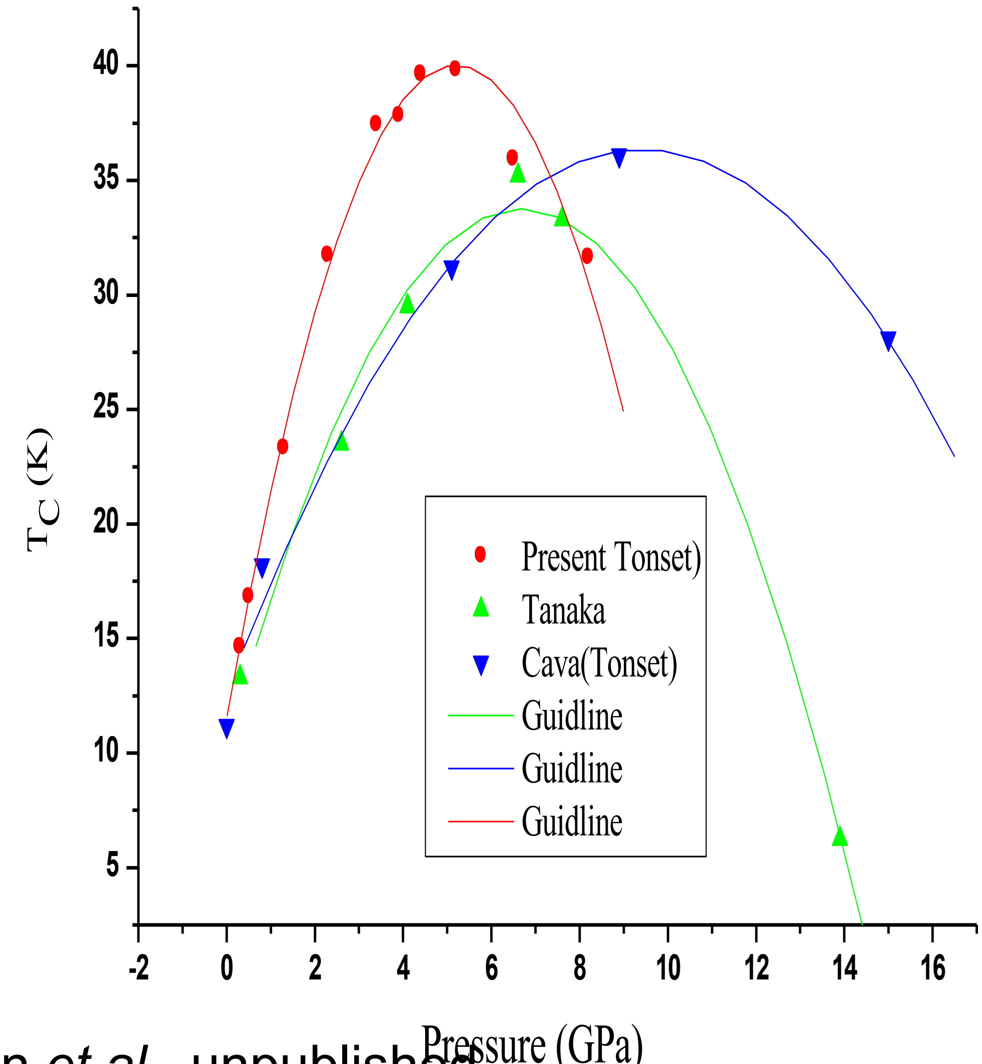


Spin fluctuation and modification of electronic band structure develop at/near the temperature of structural phase transition.

Wen, et al., PRL **108**, 267002 (2012)

Pressure Effect on FeSe

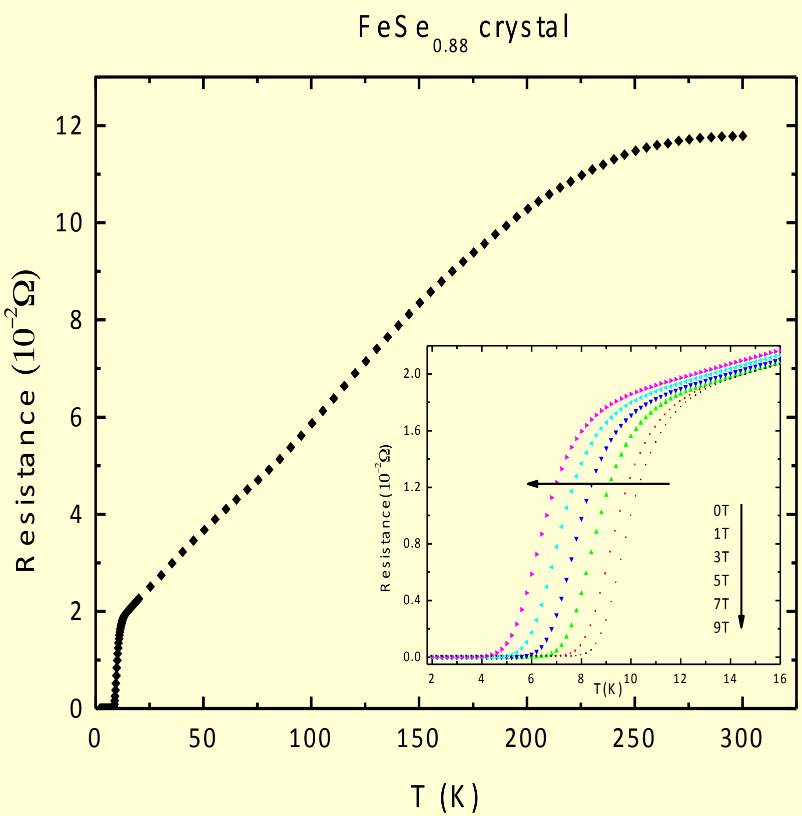


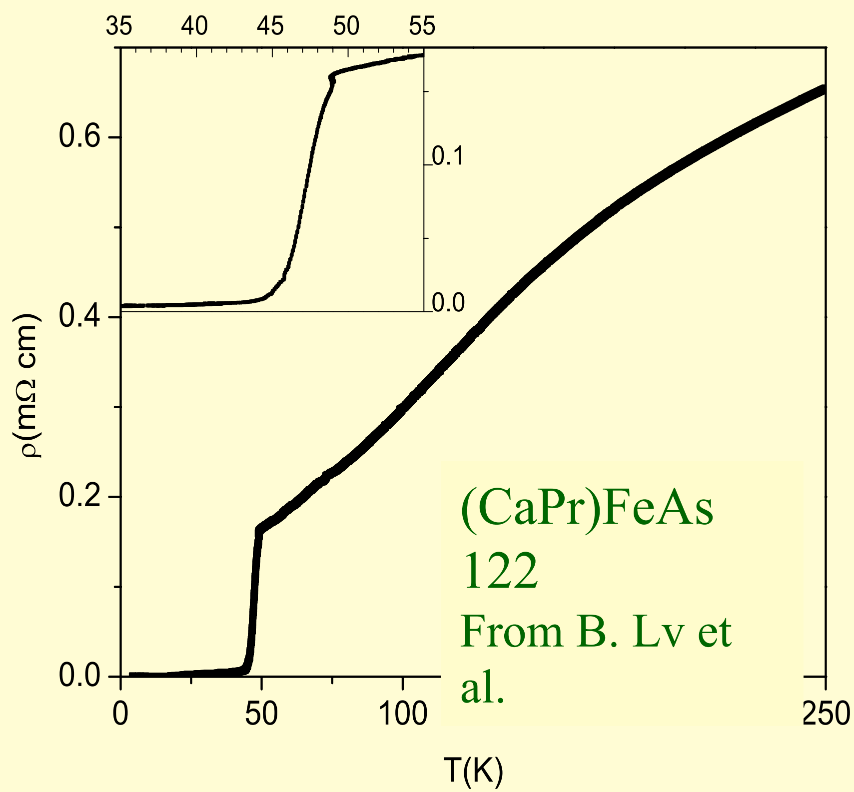


C.Q. Jin *et al.*, unpublished

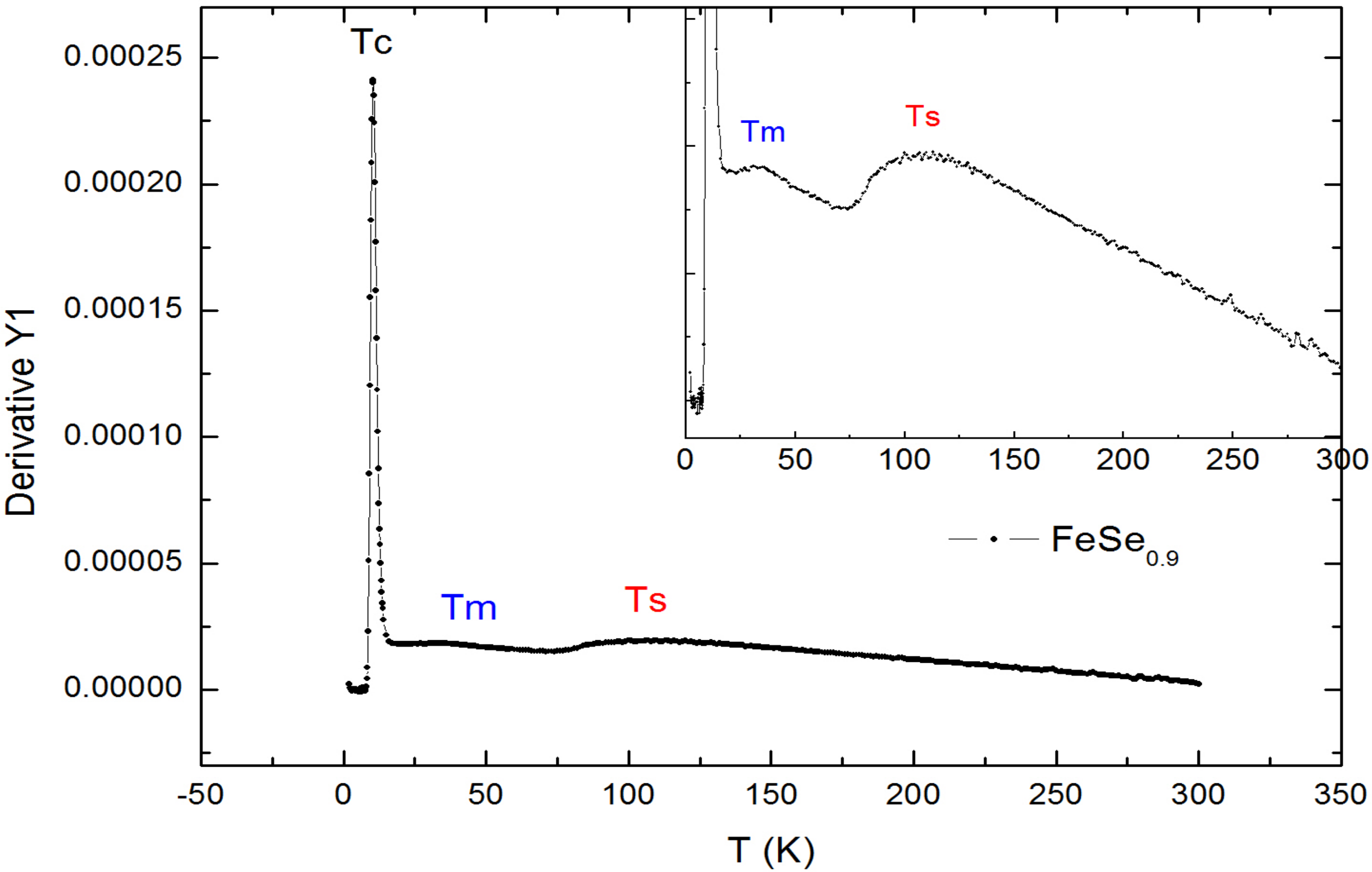
Mizuguchi Y *et al*., APL, 2008; Medvedev, S *et al*., NAT. MATER., 2009

Resistivity of FeSe & (CaPr)FeAs

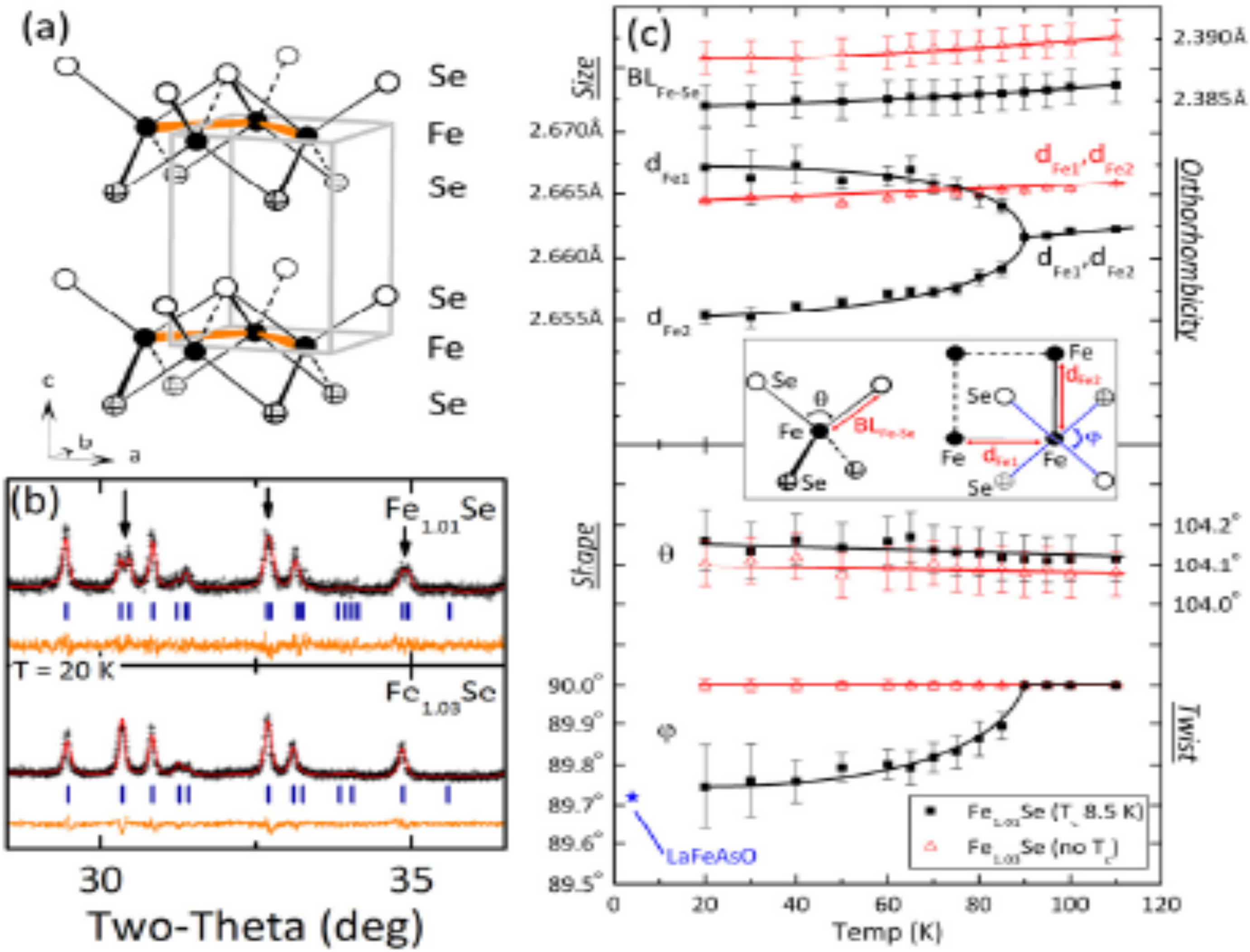




Electrical Resistivity of FeSe—Suggest the existence of higher Tc phase?

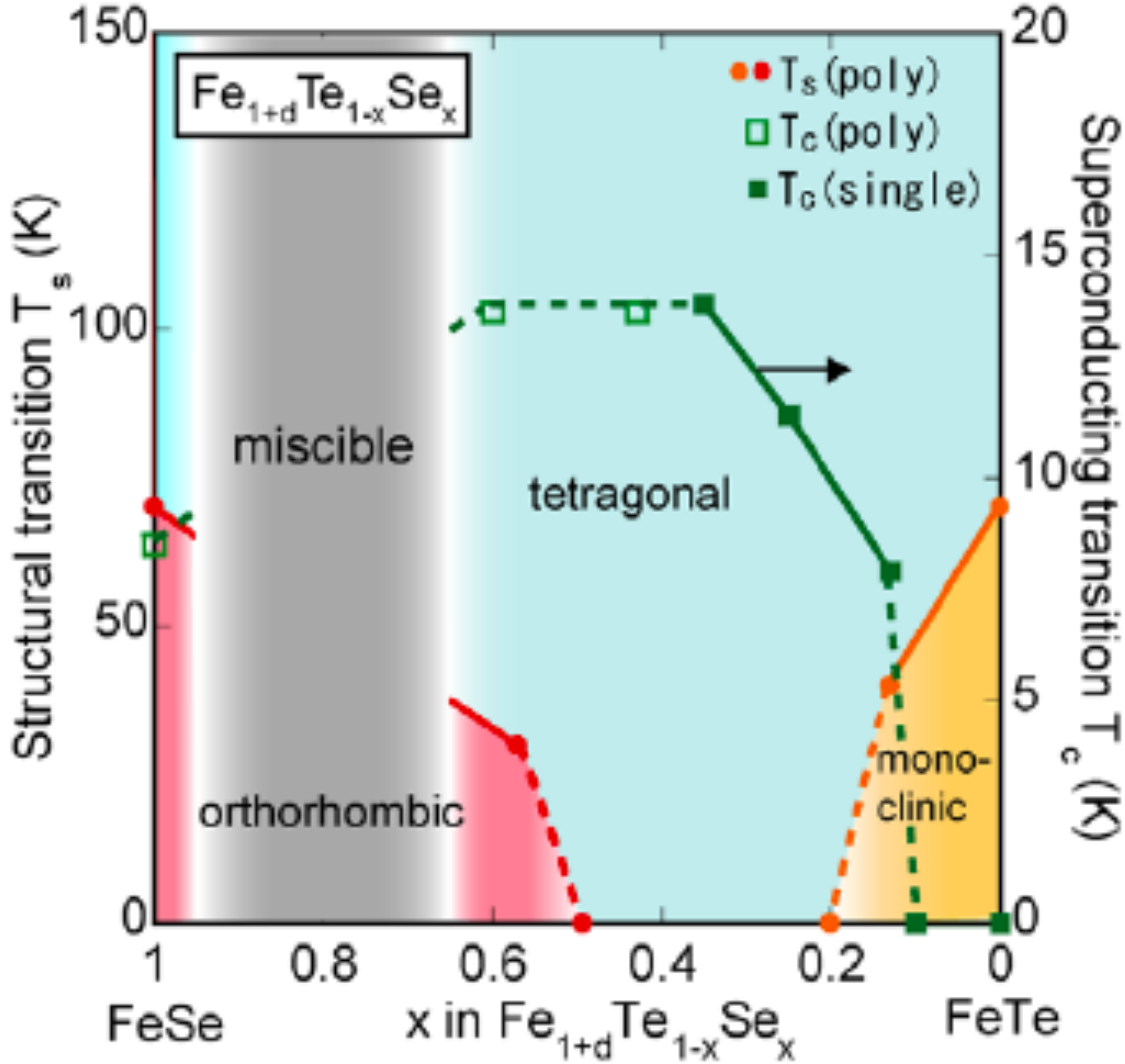


What is the Exact Stoichiometry of $Fe_{1+x}Se$?



McQueen *et al.*, PRL 2009

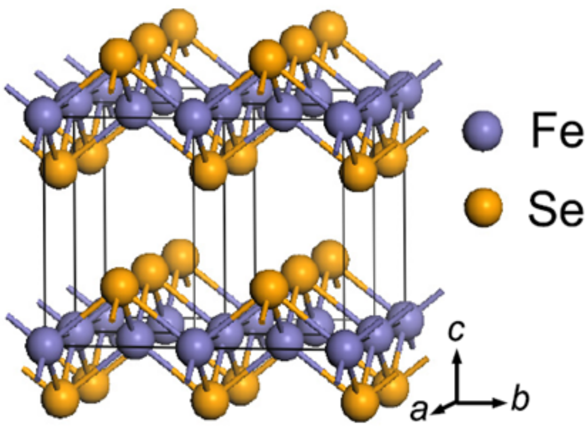
What is the Phase Diagram of $Fe_{1+x}Se$?



Y. Mizuguchi and Y. Takano, A Review, 2013

Three kinds of Fe selenide superconductors

Bulk FeSe (2008)

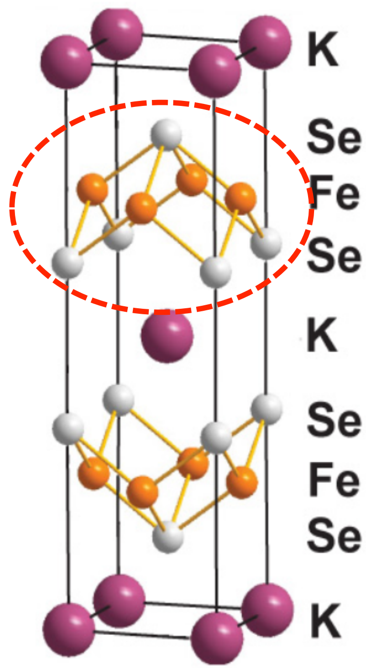


T_c ~ 9K

~ 36.7 K at 8.9GPa

$K_{1-x}Fe_{2-y}Se_2$ (2011)

Alkali intercalated FeSe

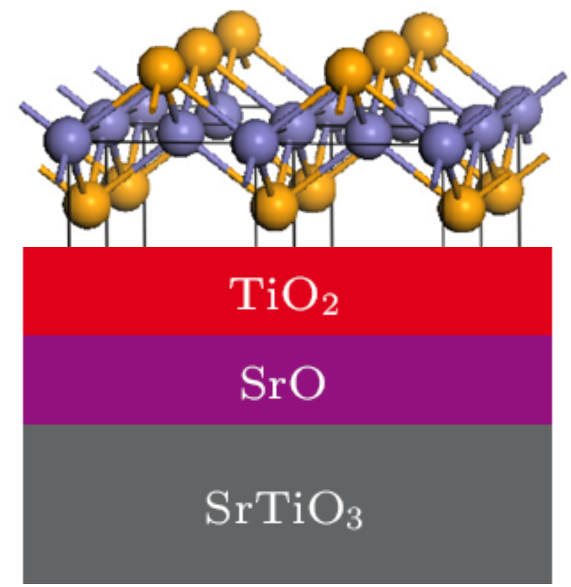


T_c ~ 33K

~ 48 K at 11 GPa

FeSe monolayer (2012)

on $SrTiO_3$ substrate

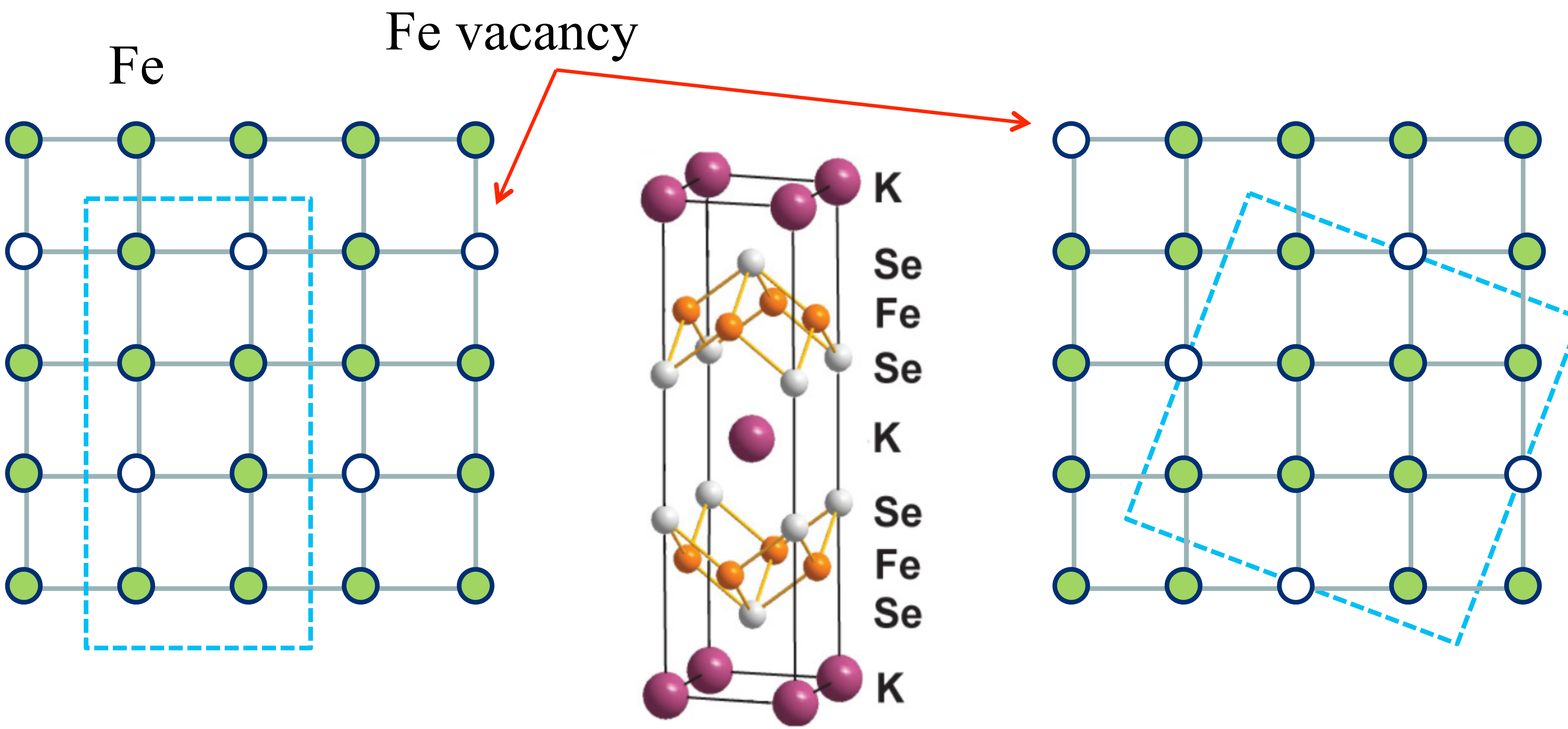


T_c > 30K

~ 65K ?

decreasing dimensionality

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



$KFe_{1.5}Se_2$
rhombus-order

$K_{0.8}Fe_{1.6}Se_2$
$\sqrt{5} \times \sqrt{5}$ order

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

Study of FeSe Nano-Structure

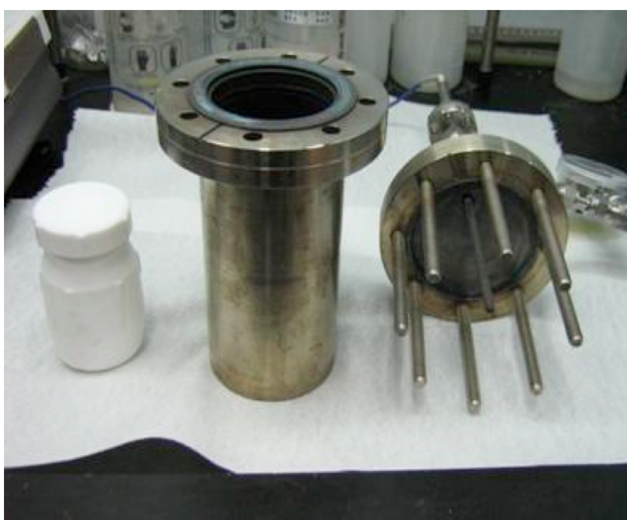
- The unanswered questions led us to speculate that the presence of defects in FeSe is critical to its superconductivity
- Nanostructures provide important insight into the better understanding of defects in materials of interest
- Techniques to fabricate FeSe nanostructure are well-developed and simple

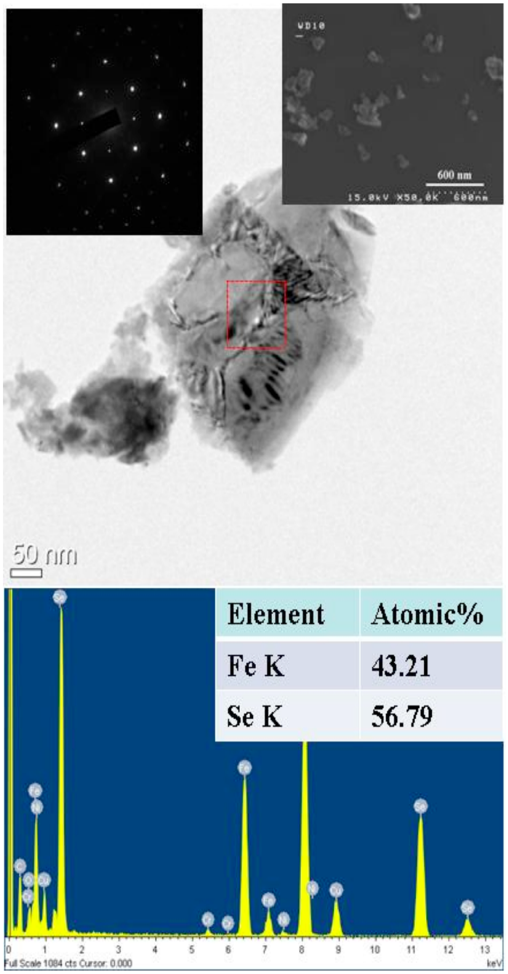
Fe was mixed with Se/(SeTe) powder and introduced into a 2 ml stainless steel Swagelok union reactor at room temperature in a N_2-filled glove box.

The filled reactor was closed tightly with another plug and placed at the center of the tube's furnace.

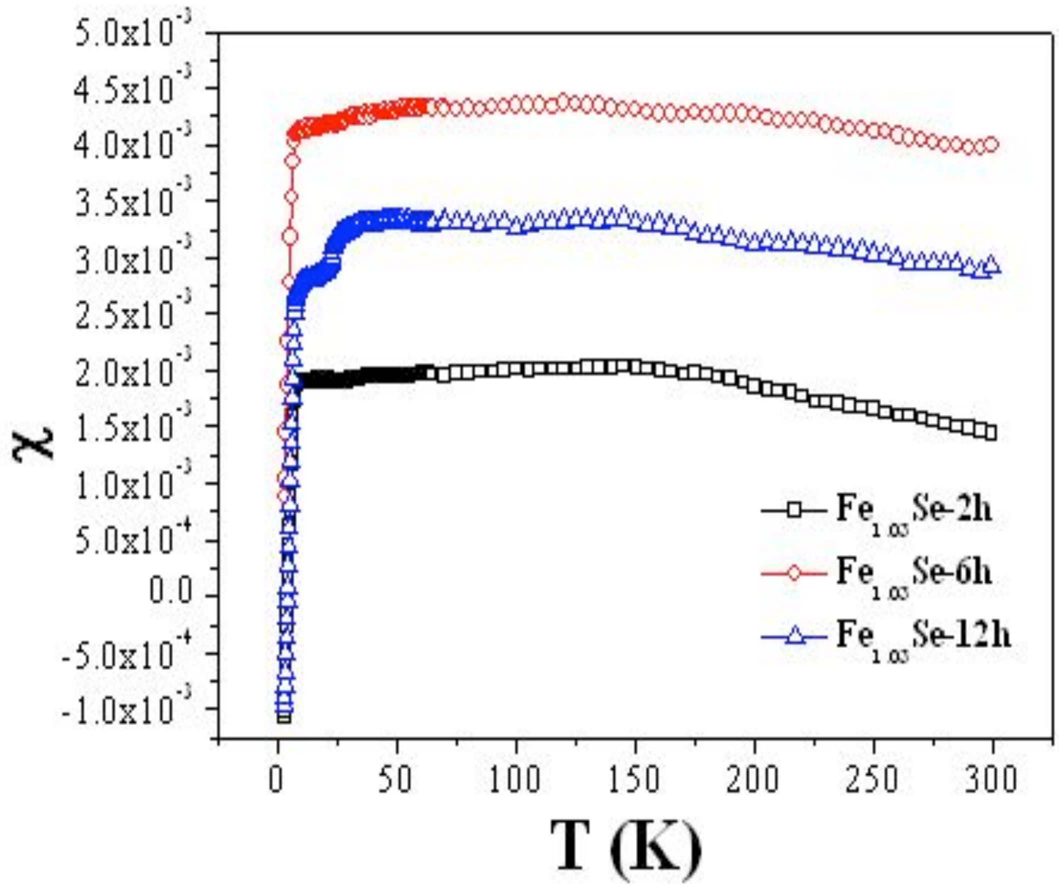
The temperature of the furnace was raised to 700℃ at a rate of 20℃/min, and the temperature was keep at 700 ℃ for 30 min.

The reactor, heated to 700 ℃ , was gradually cooled (5h) to room temperature and open.

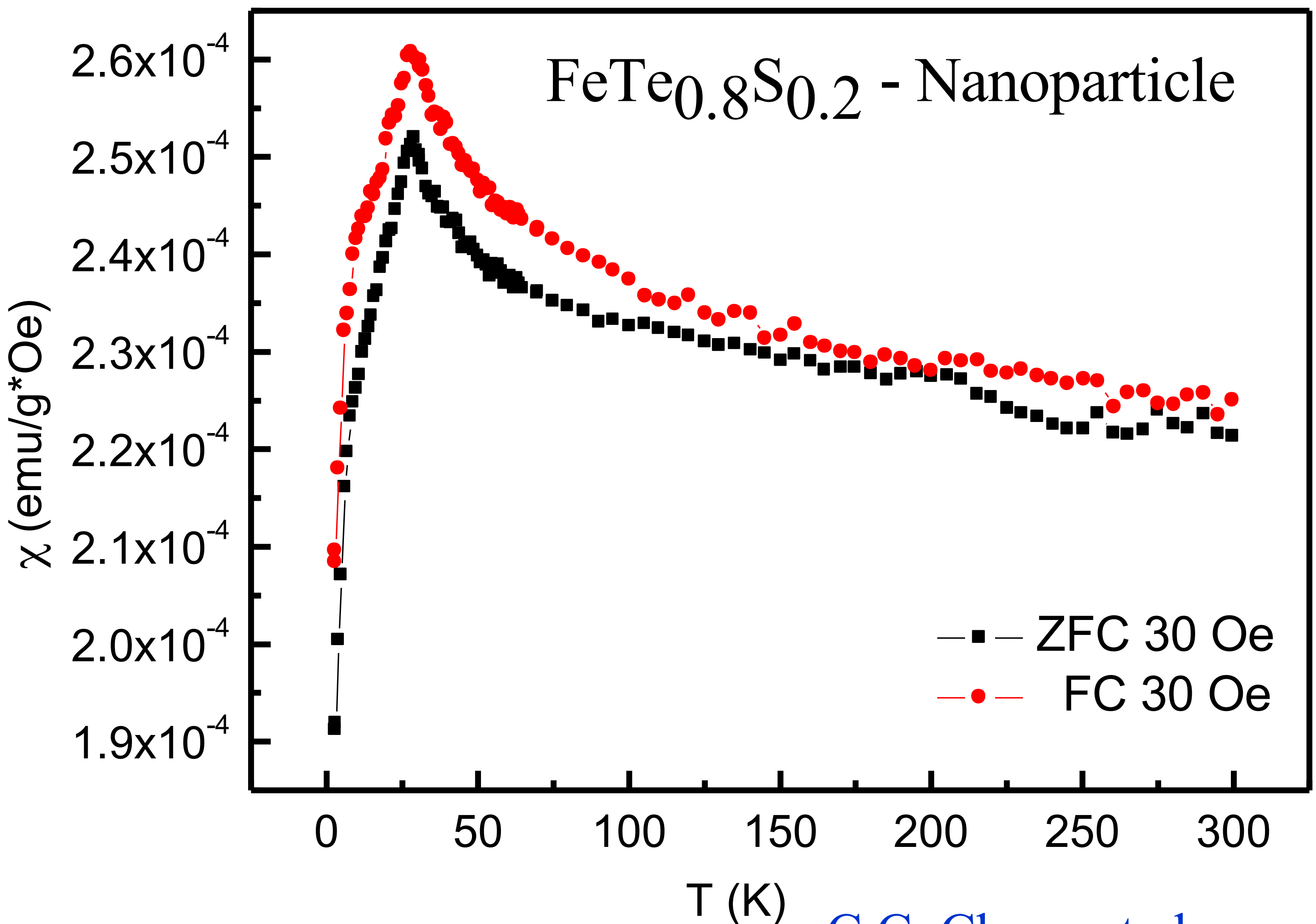


Element	Atomic%
Fe K	43.21
Se K	56.79

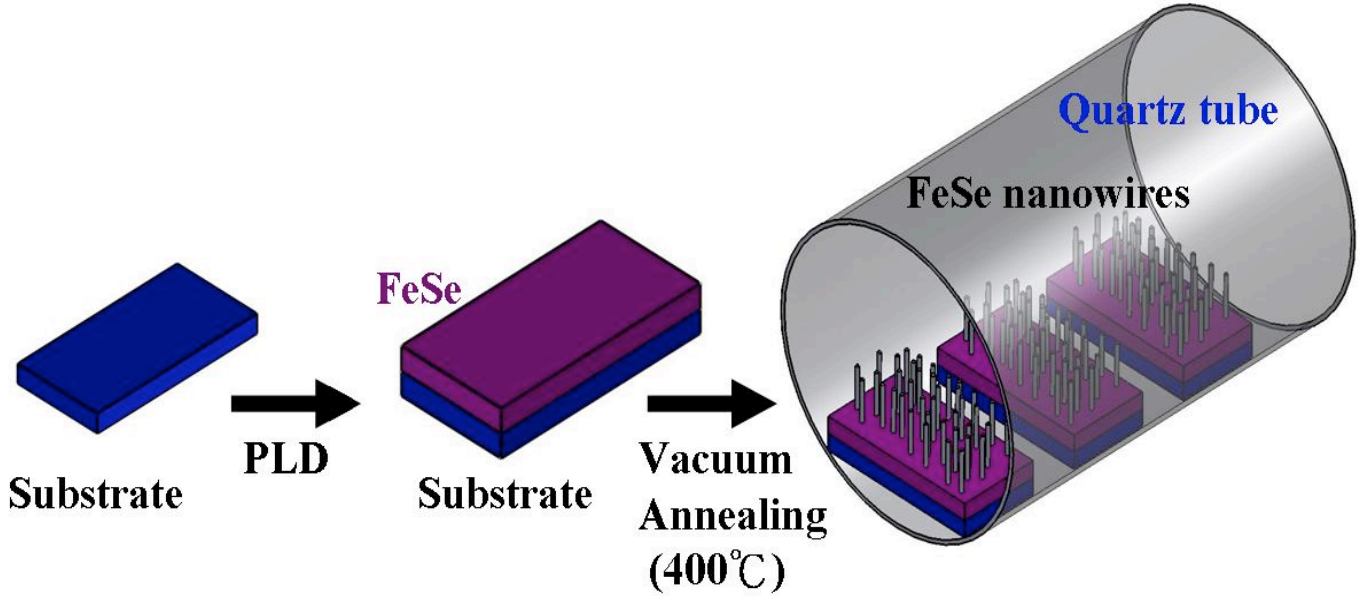


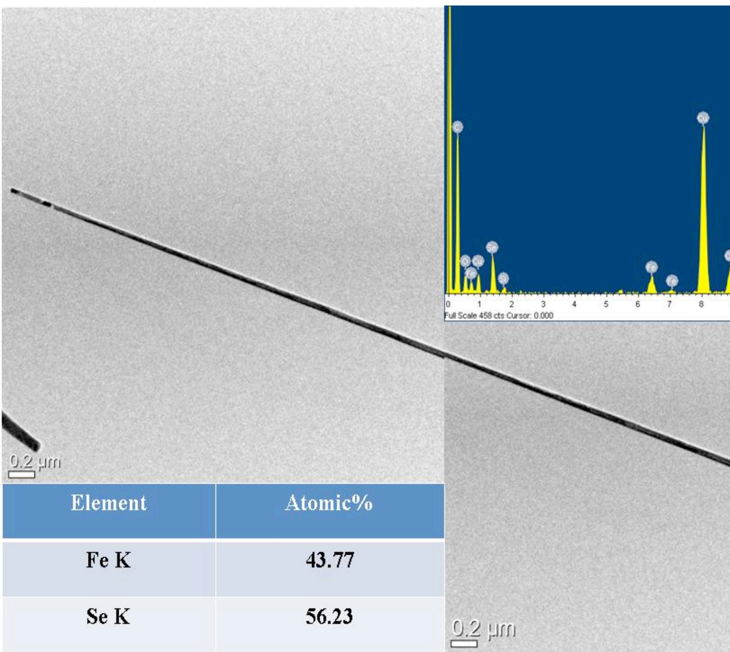
Fe-Te-S Nanoparticle



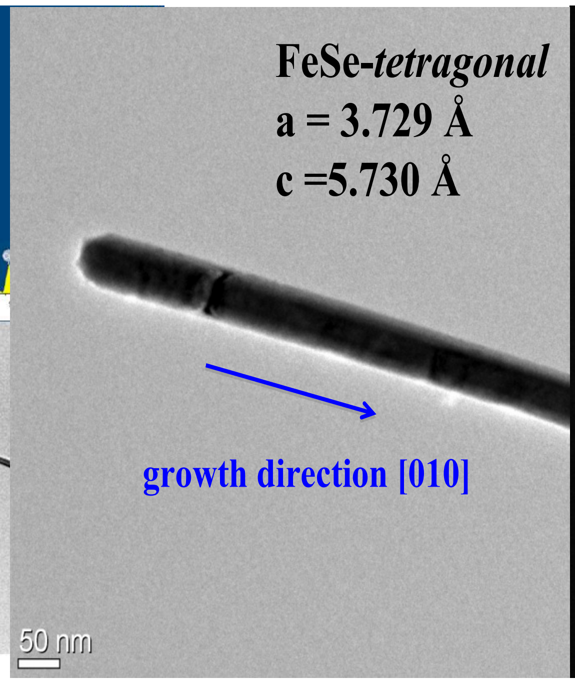
C.C. Chang et al., unpublished

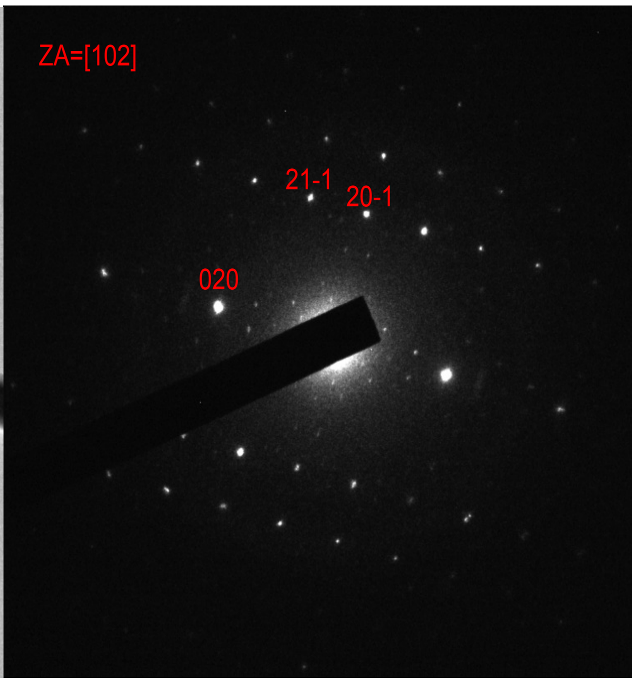
Fe-Se-(Te) (tetragonal) Nanowire



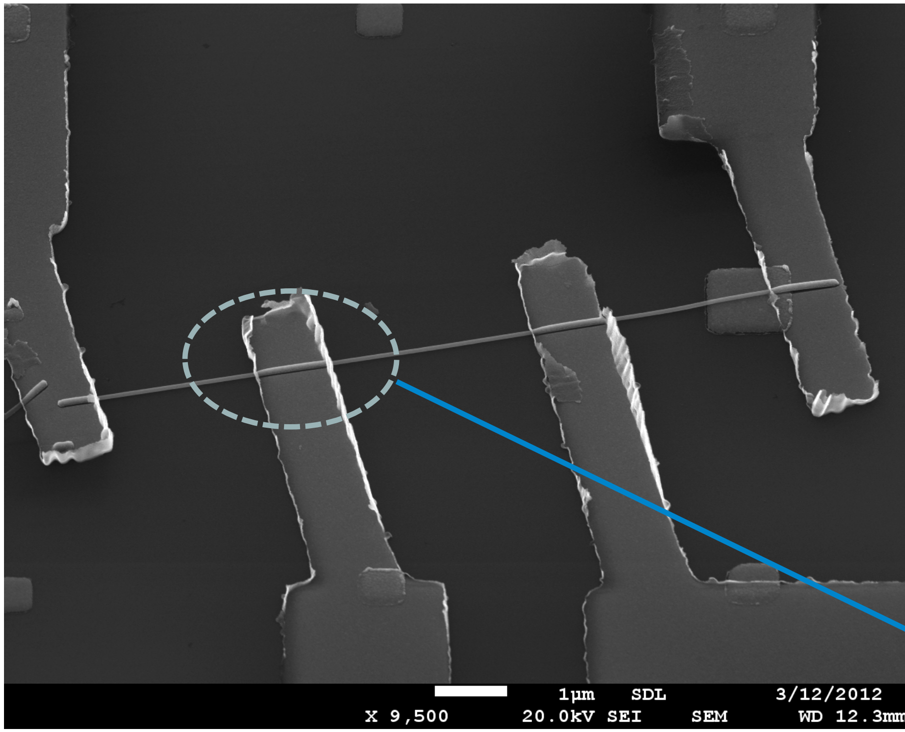


Element	Atomic%
Fe K	43.77
Se K	56.23

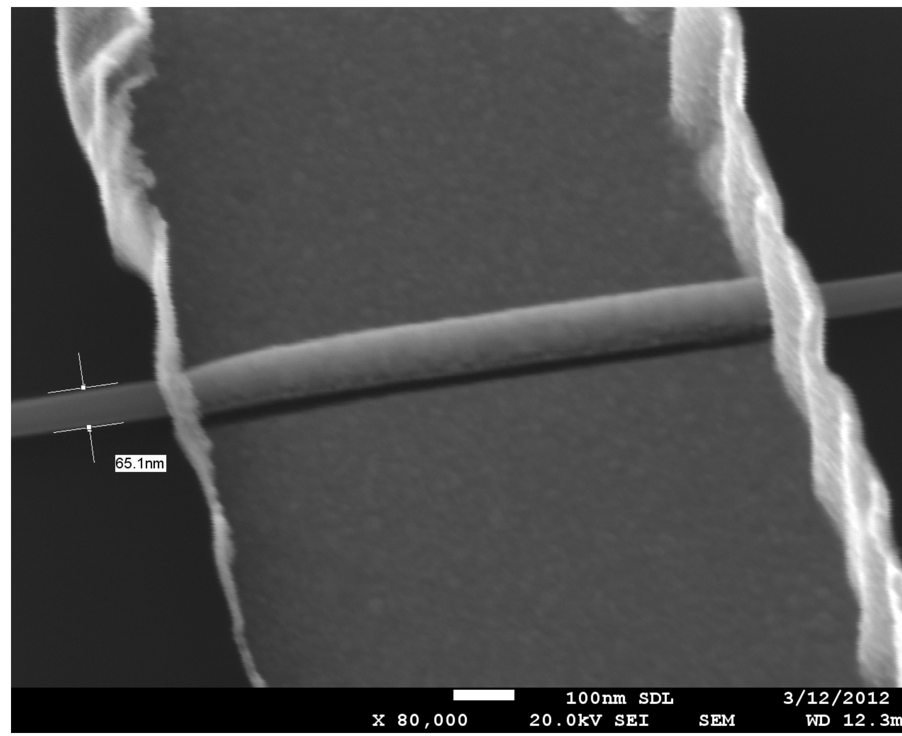




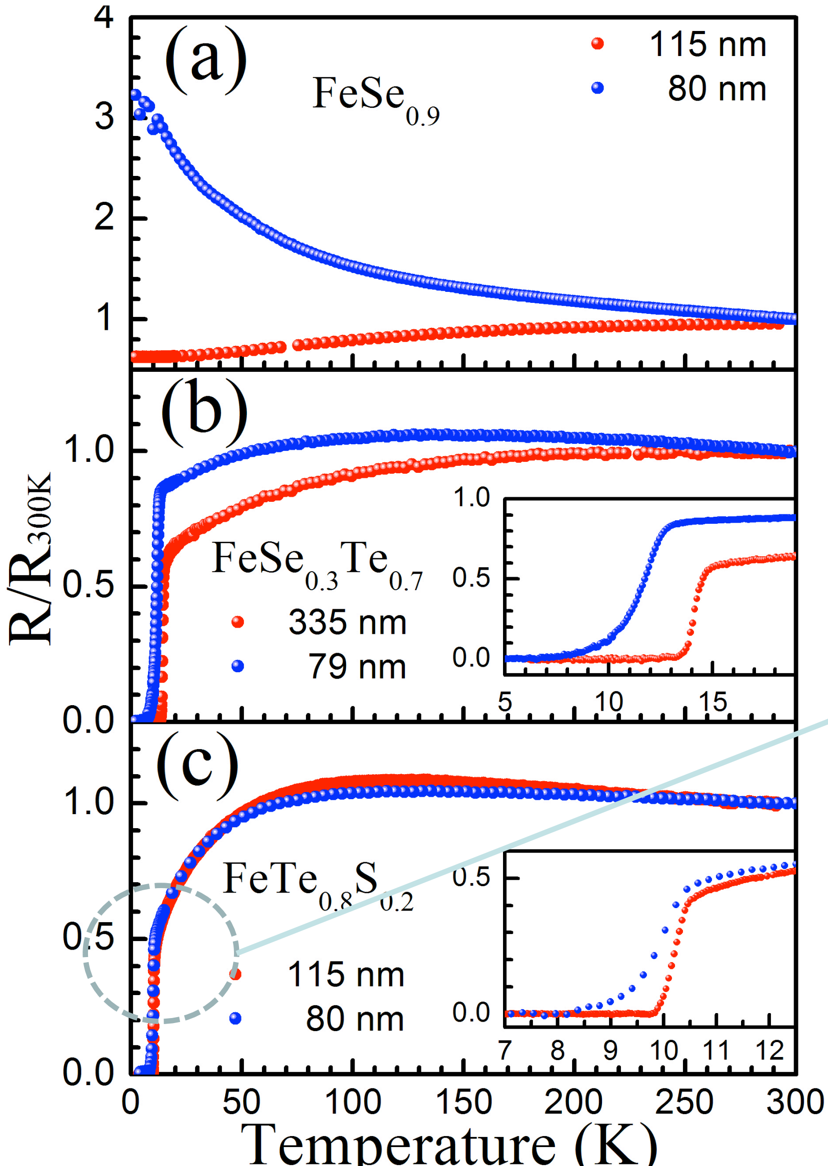
Nanowires, Fe(Te-S/Se)

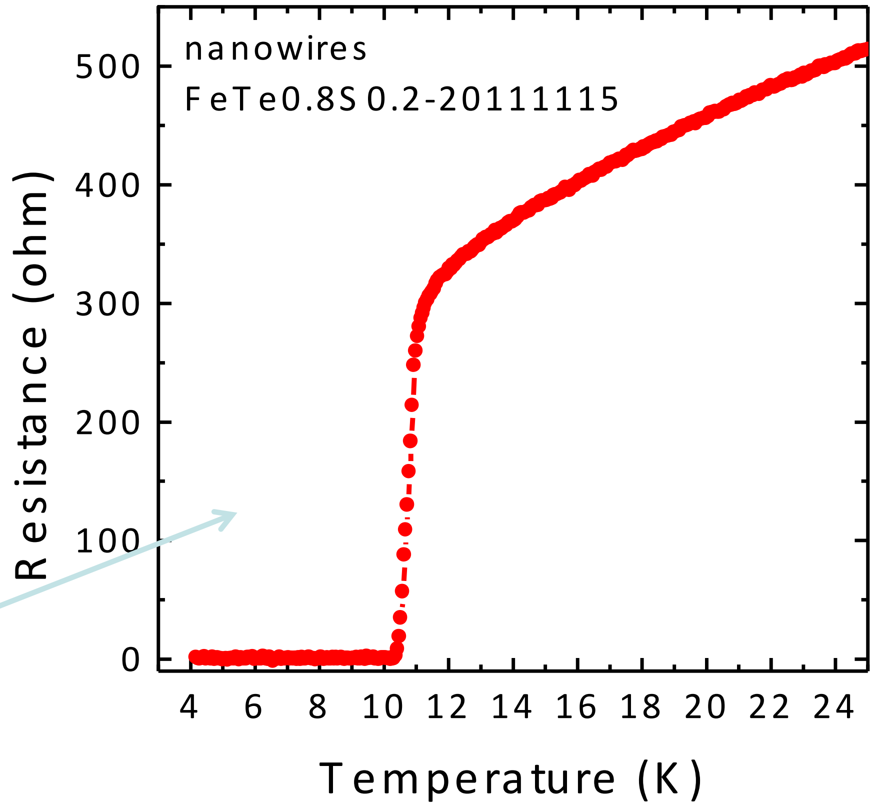


after electrode patterning



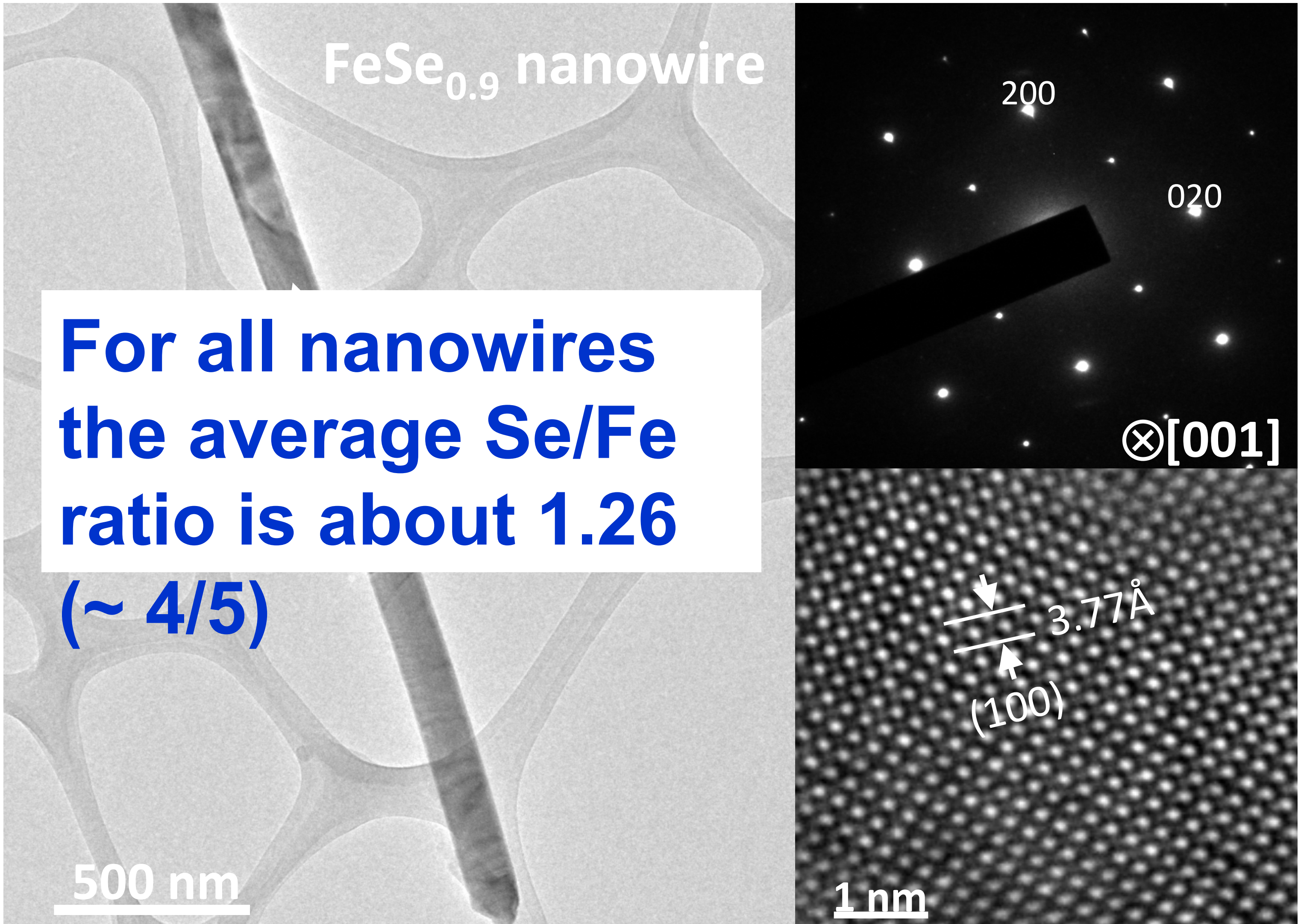
Electrical Resistance of Fe-Se-(Te) Nanowires



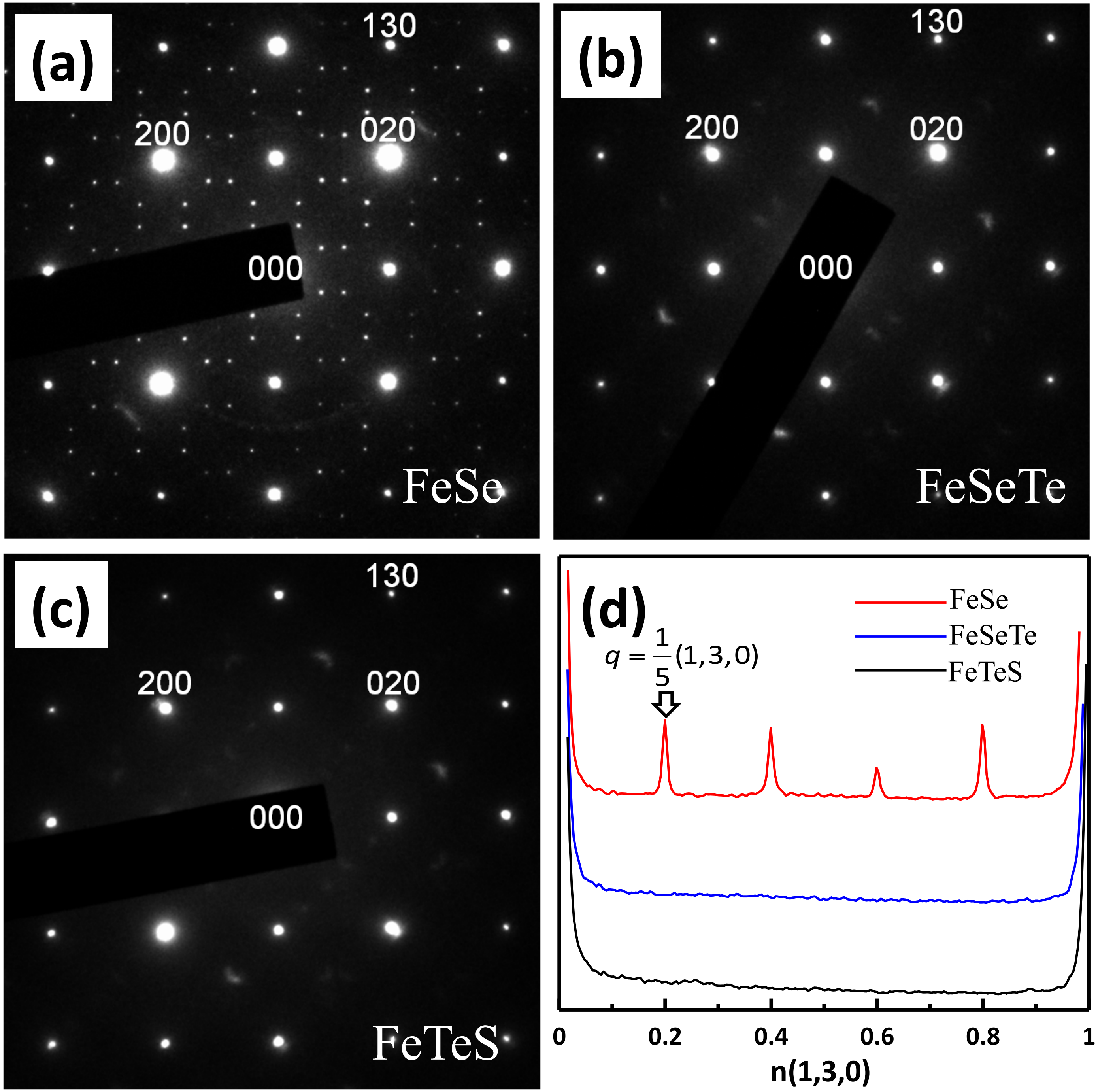


H.H. Chang et al., submitted

$FeSe_{0.9}$ nanowire

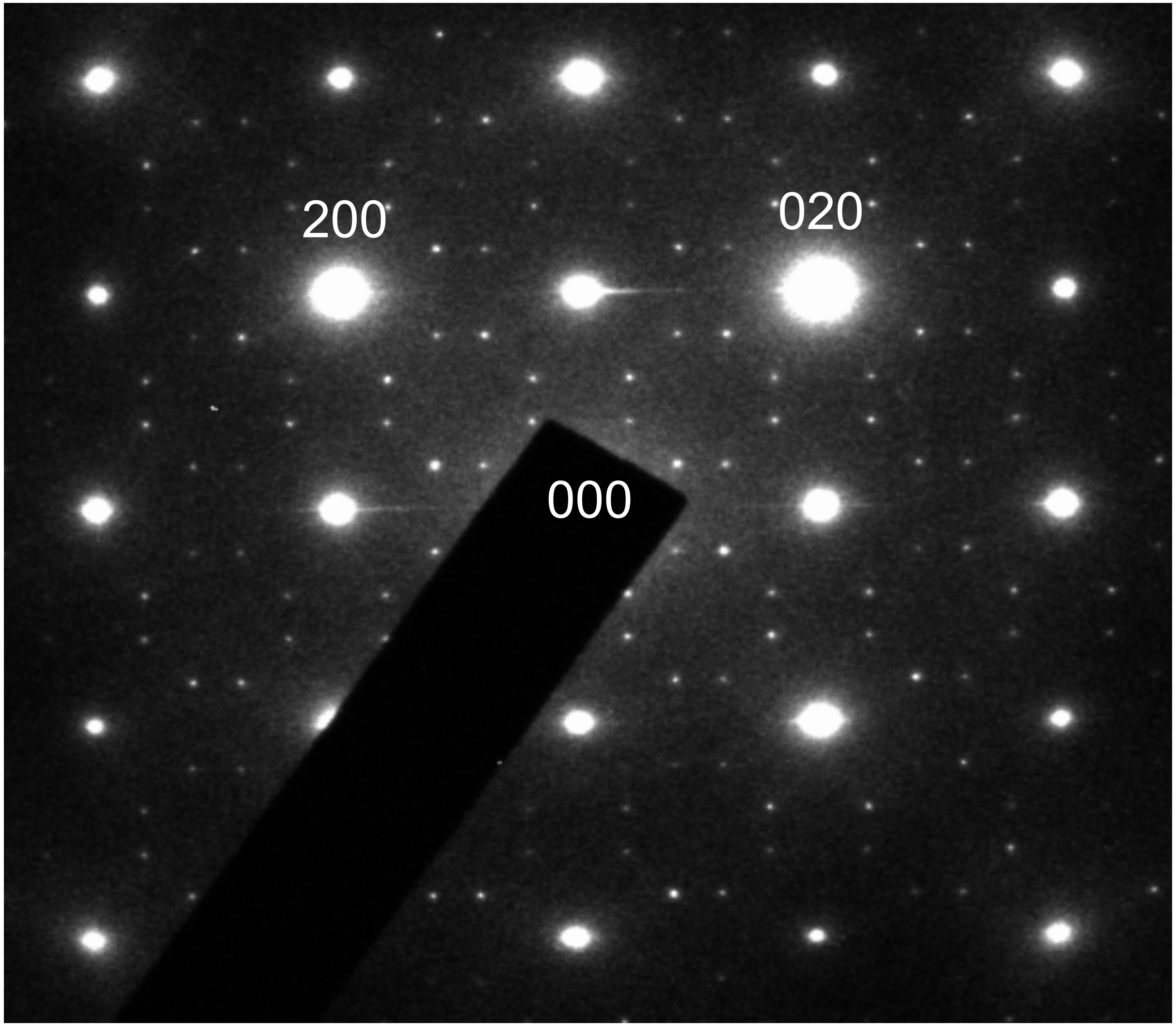


For all nanowires the average Se/Fe ratio is about 1.26 (~ 4/5)

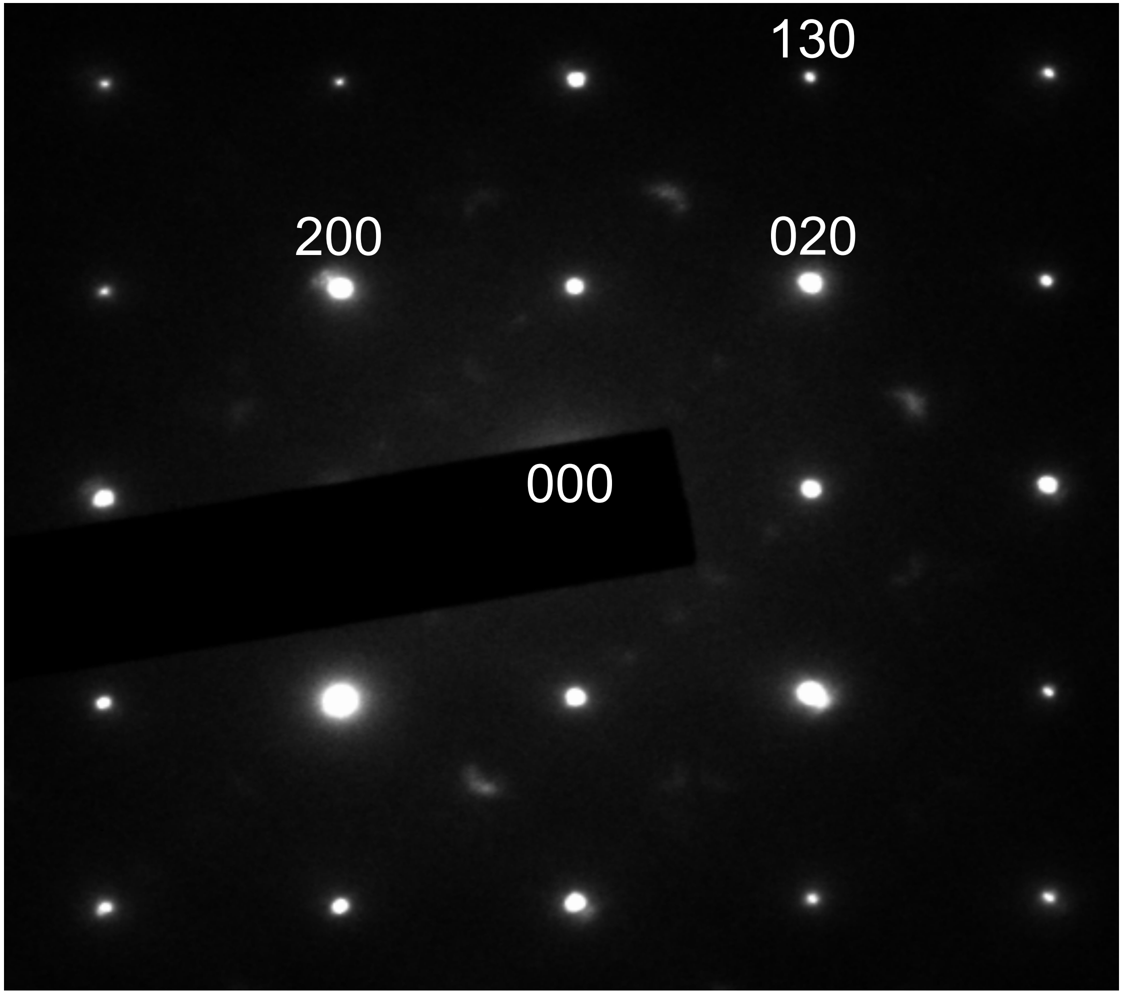


(a)
130
200
020
000
FeSe
(b)
130
200
020
000
FeSeTe
(c)
130
200
020
000
FeTeS
(d)
$q = \frac{1}{5}(1,3,0)$
FeSe
FeSeTe
FeTeS
0
0.2
0.4
0.6
0.8
1
n(1,3,0)

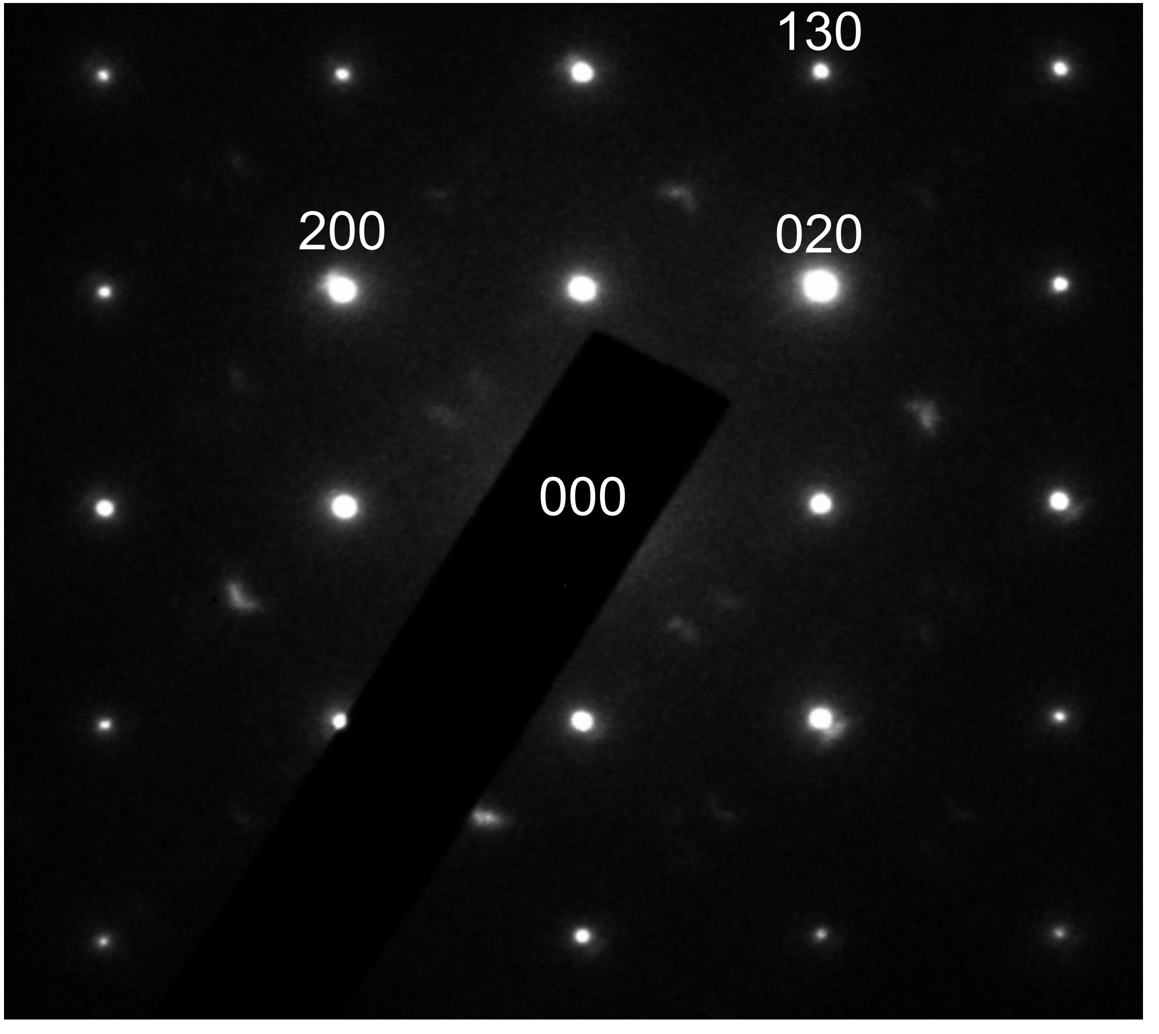
FeSe Nanowire_20120827-8F_no.2



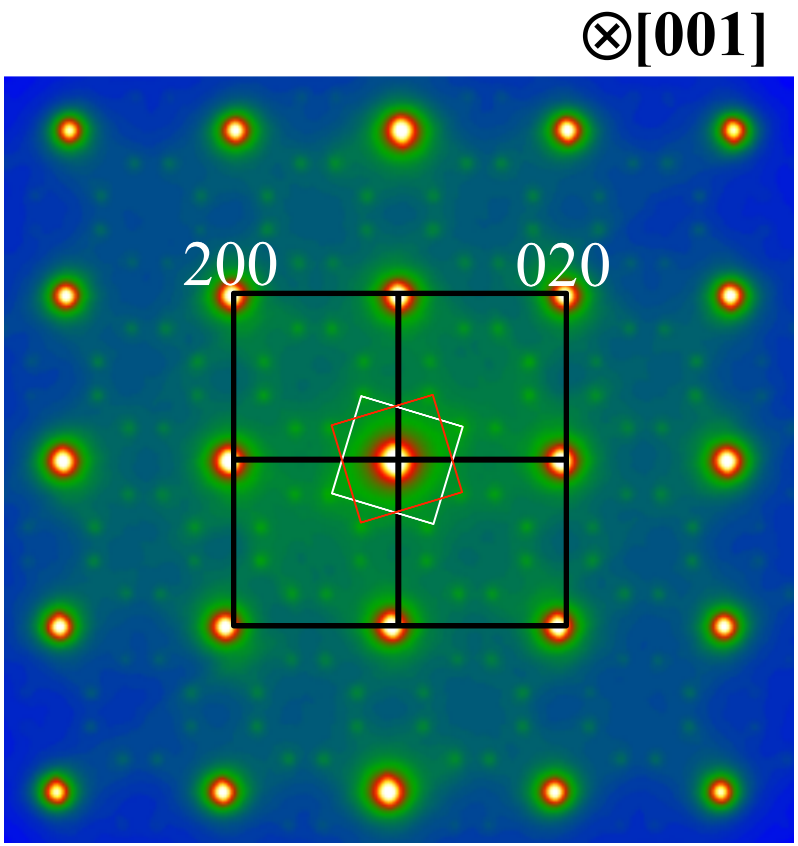
FeTeS Nanowire_20120202_no.3



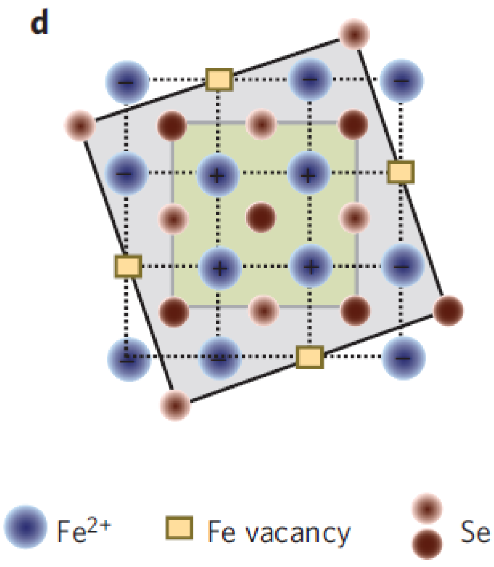
FeSeTe Nanowire_20120207_no.3

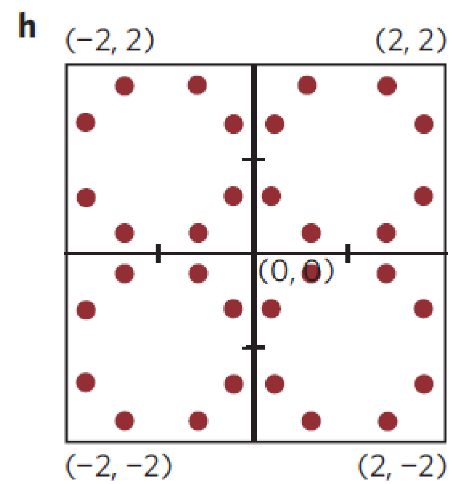


Electron diffraction of FeSe NPS



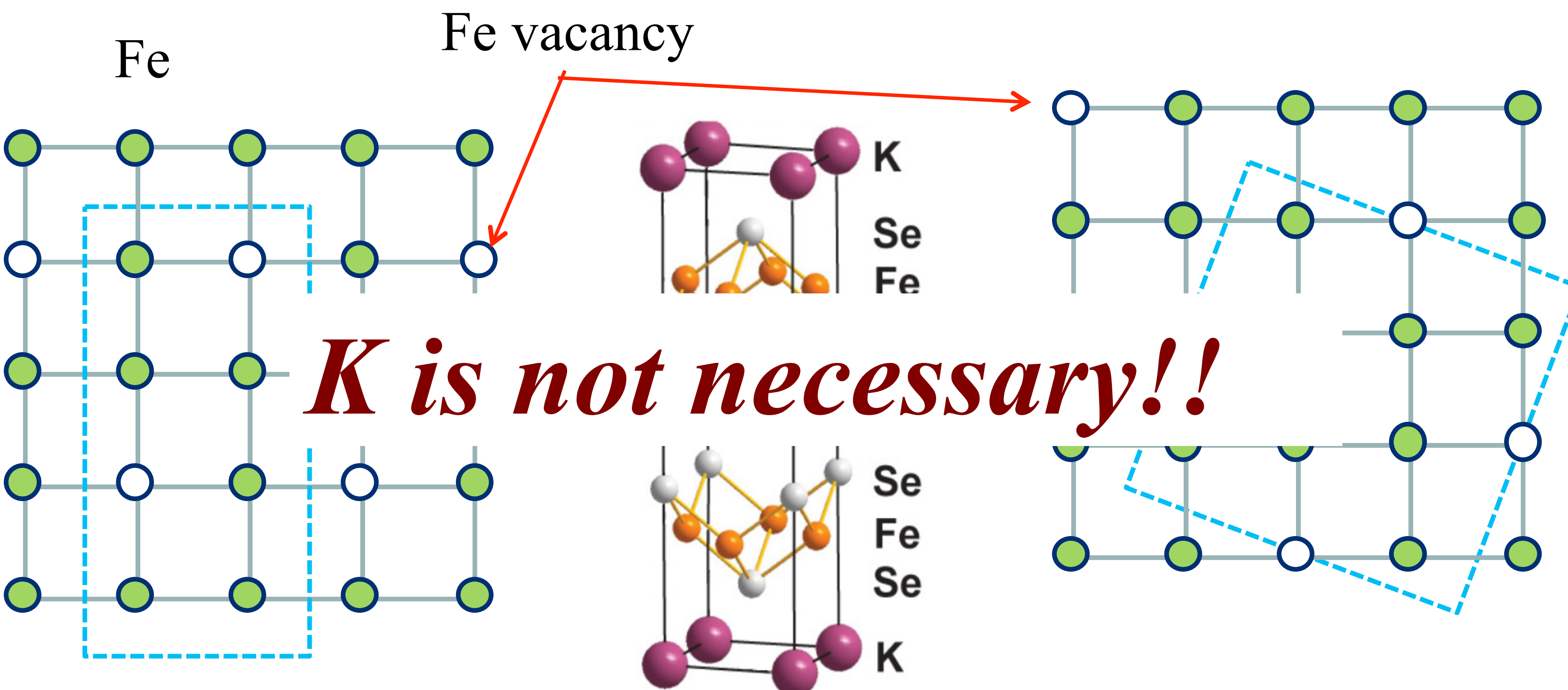
Superlattice structure





Refs: Nature Physics 8(2012)709.

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



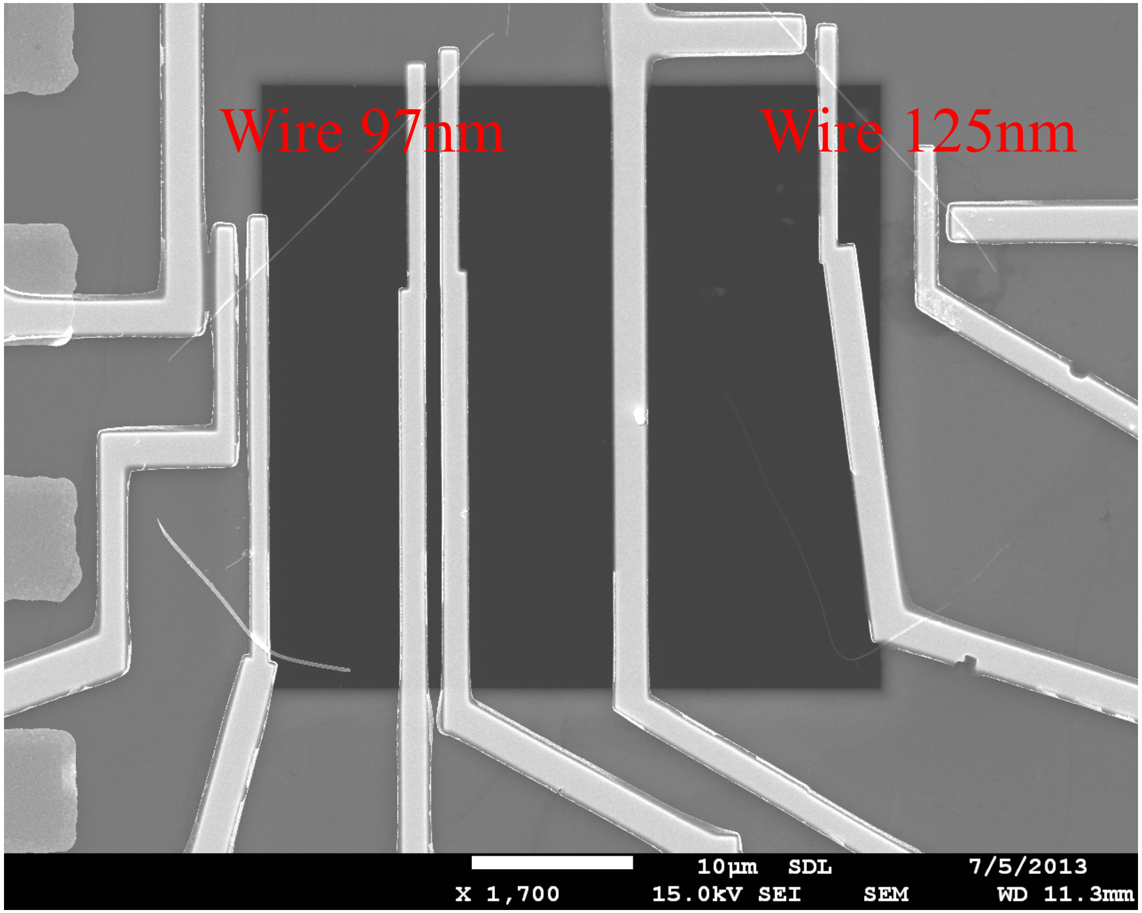
K is not necessary!!

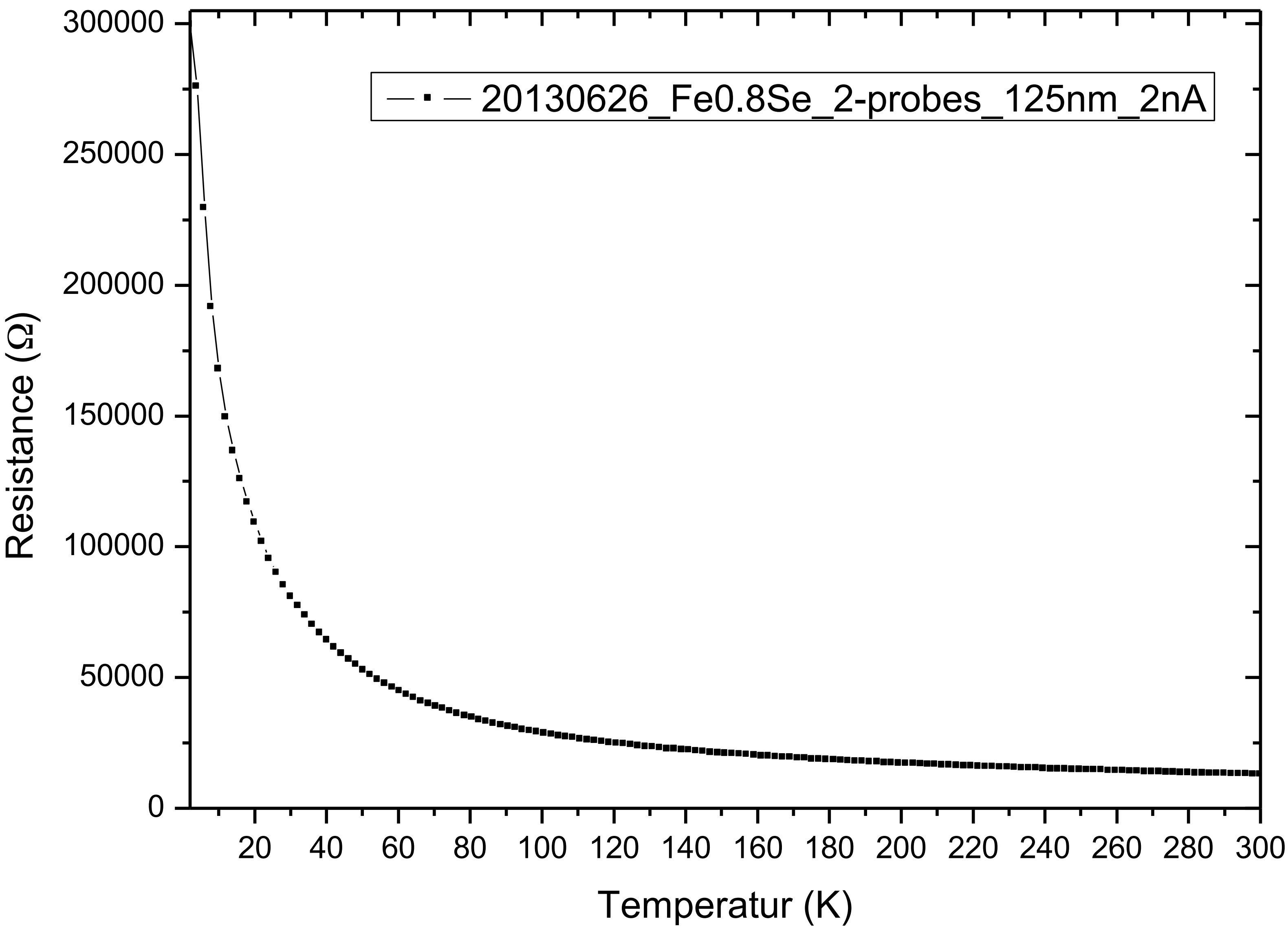
$KFe_{1.5}Se_2$
rhombus-order

$K_{0.8}Fe_{1.6}Se_2$
$\sqrt{5} \times \sqrt{5}$ order

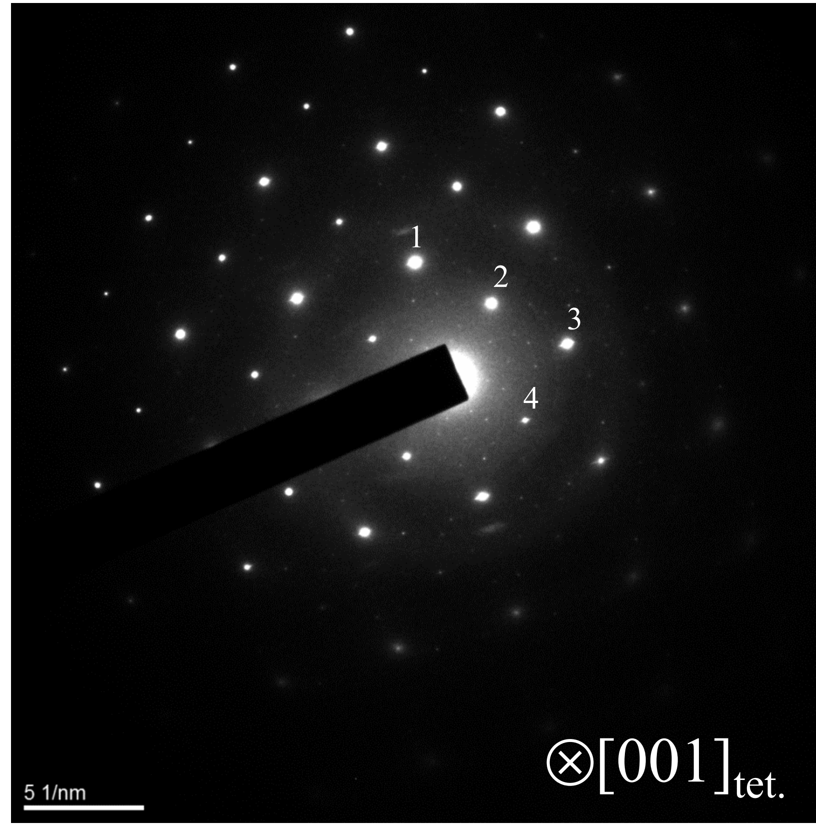
Yan, Gao, Lu, Xiang, PRL **106**, 087005 (2011)

20130626_FeSe_Nanowires





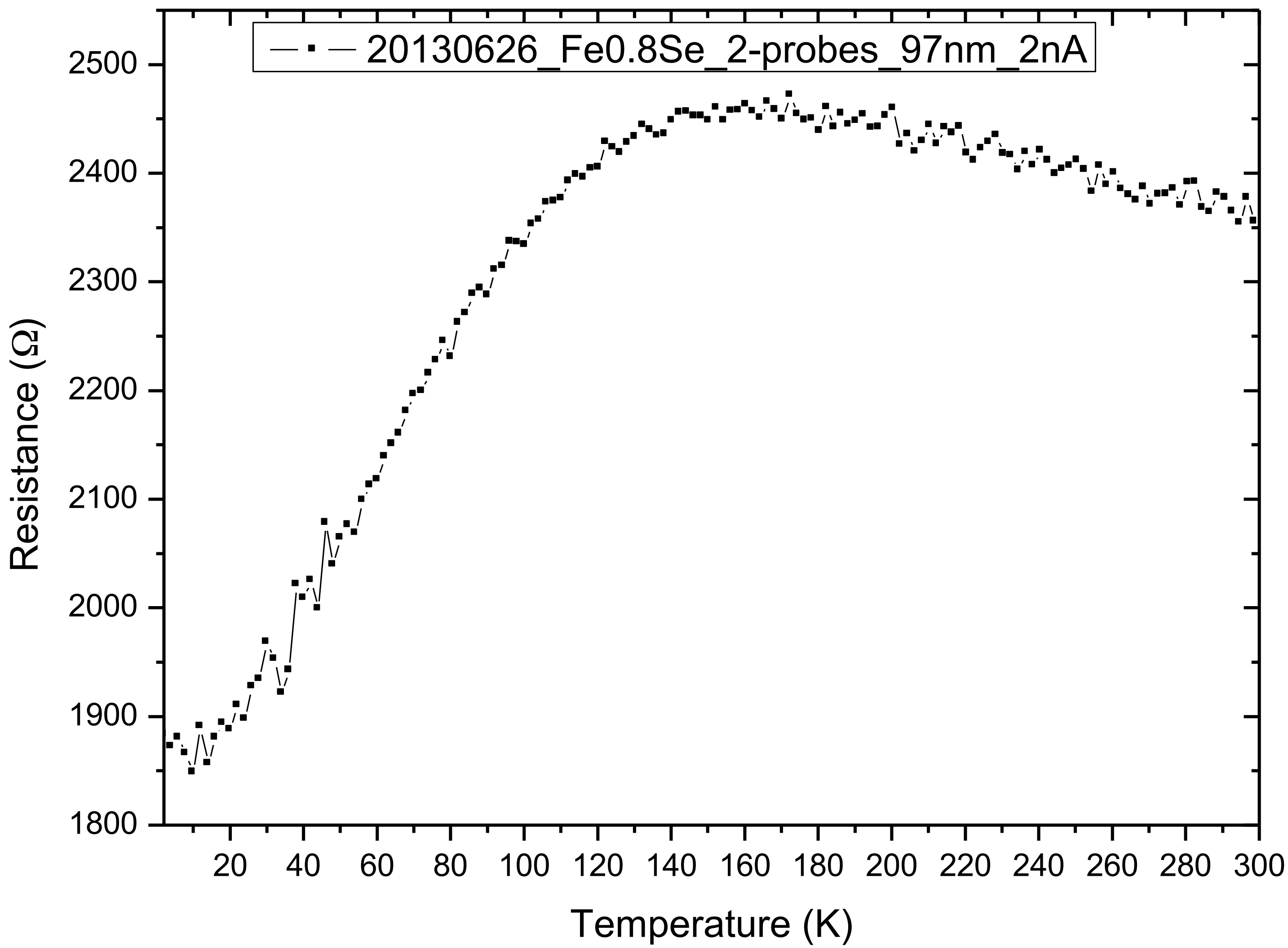
20130626_Fe0.8Se_2-probes_125nm_2nA
Resistance (Ω)
Temperatur (K)
0
50000
100000
150000
200000
250000
300000
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

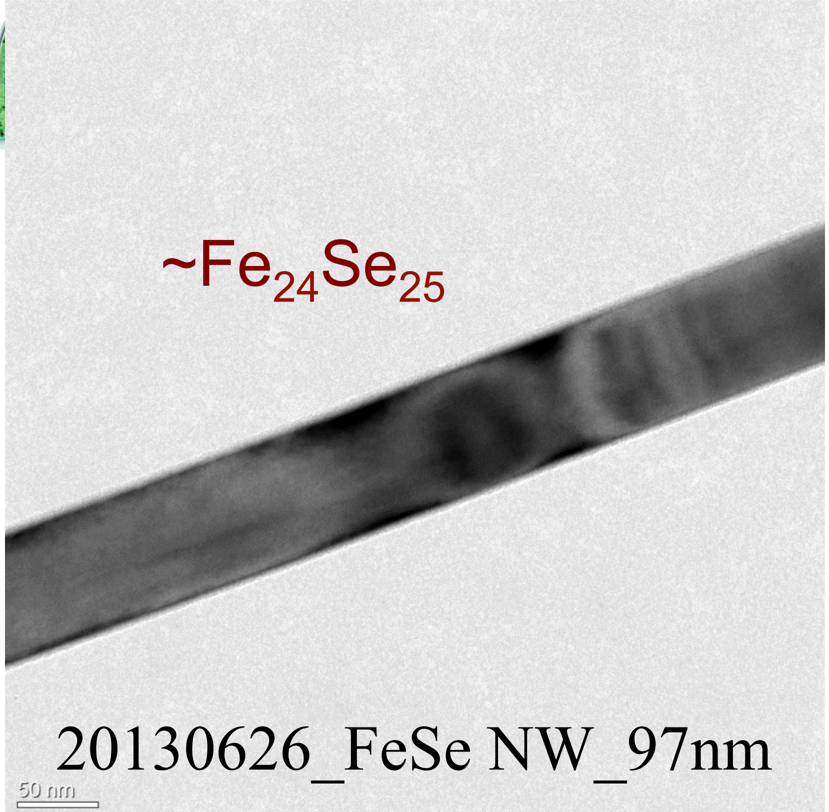


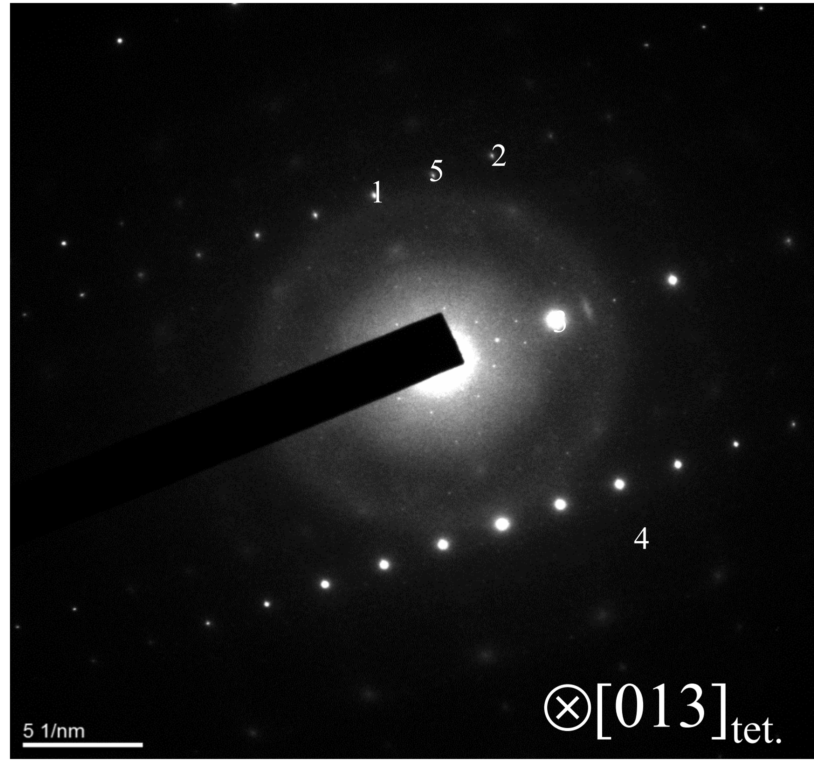
20130626_FeSe NW_125nm

(Ref: J. Phys. Chem. Solids **71**(2010)495)

	d-spacing (Å)	degree to spot#1	(h k l)	d-spacing (Å) Refs.	degree to spot#1 refs.
1	1.988	0.00	(2, 0, 0)	1.885	0
2	2.773	45.43	(1, 1, 0)	2.666	45
3	1.955	89.34	(0, 2, 0)	1.885	90
4	2.791	134.47	(-1, 1, 0)	2.666	135


20130626_Fe0.8Se_2-probes_97nm_2nA
Resistance (Ω)
Temperature (K)
1800
1900
2000
2100
2200
2300
2400
2500
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

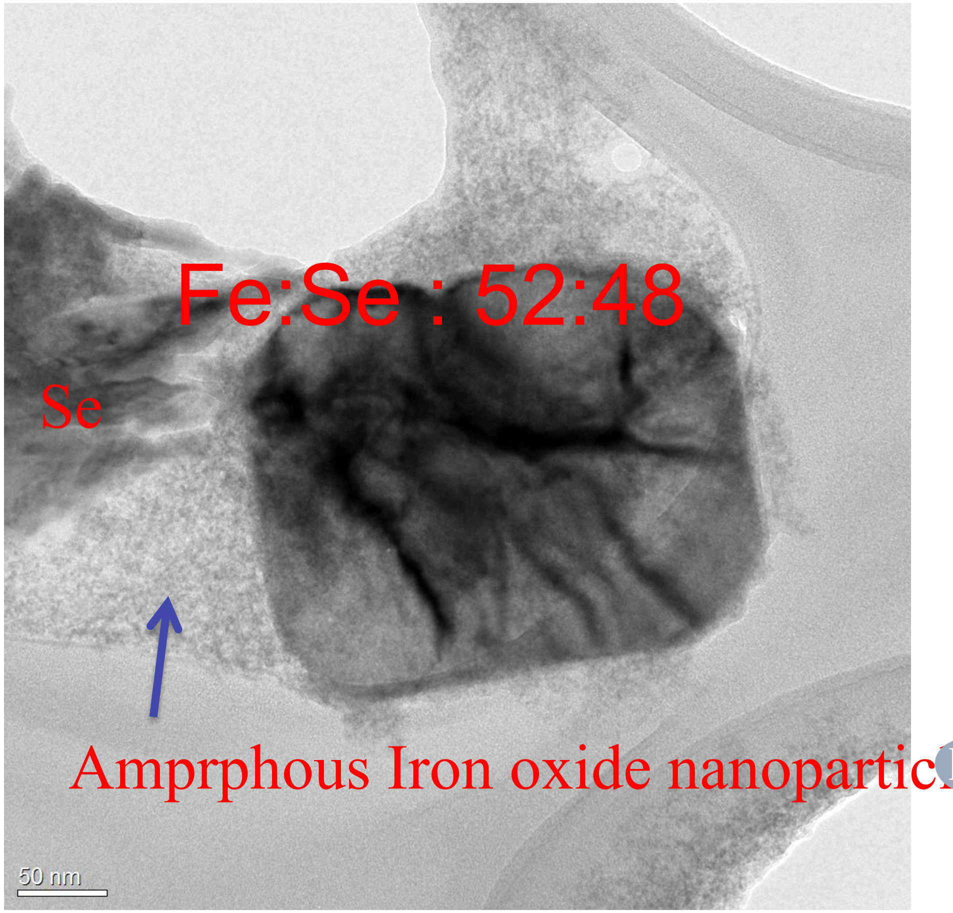


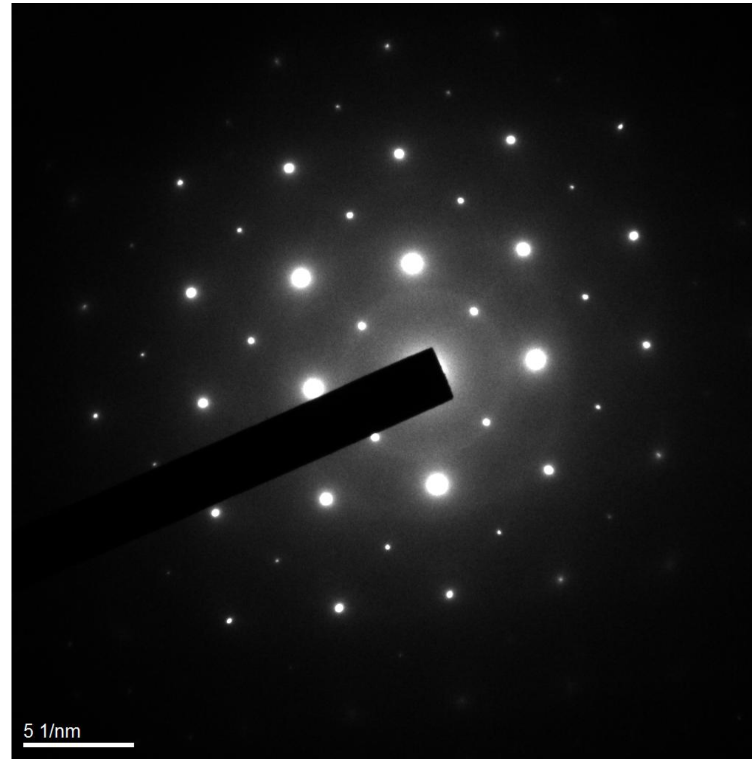


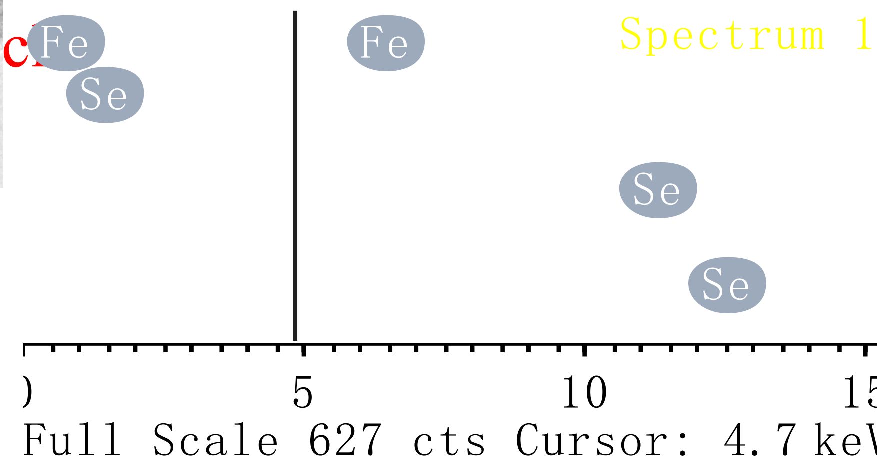
(Ref: *J. Phys. Chem. Solids* **71**(2010)495)

	d-spacing (Å)	degree to spot#1	(h k l)	d-spacing (Å) Refs.	degree to spot#1 refs.
1	1.265	0.00	(0, -3, 1)	1.225	0
2	1.054	33.31	(2, -3, 1)	1.027	33.02
3	1.946	88.83	(2, 0, 0)	1.885	90
4	1.066	146.60	(2, 3, -1)	1.027	146.98
5	1.200	18.12	(1, -3, 1)	1.165	18

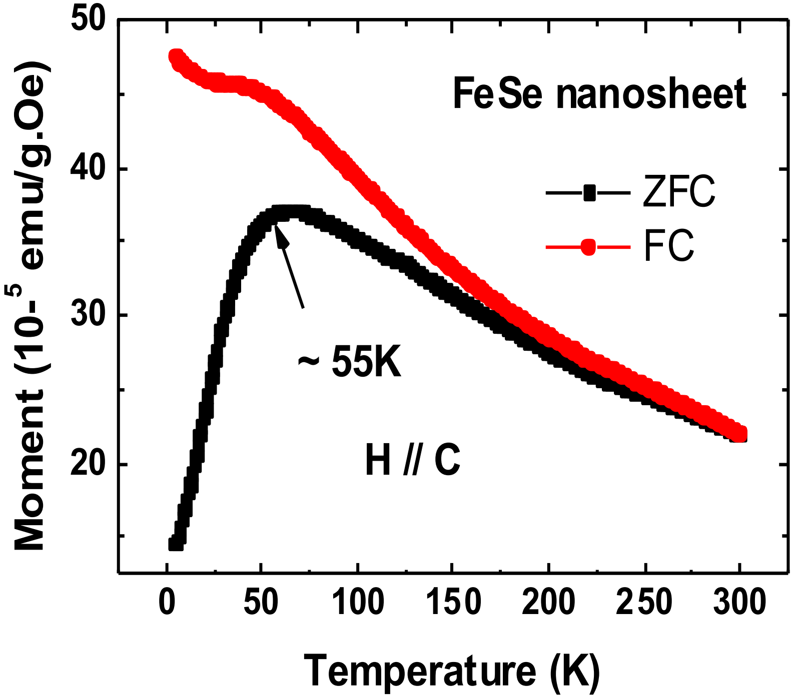
20130321_$Fe_{1.05}Se$_700 ℃-50 h-quenching



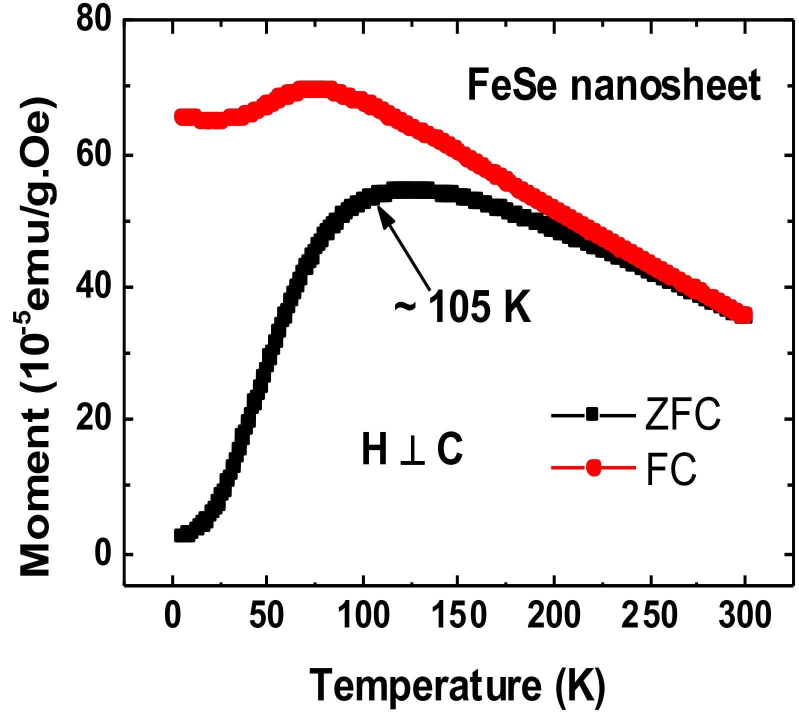




MT of FeSe nano-particle



S1, H along c

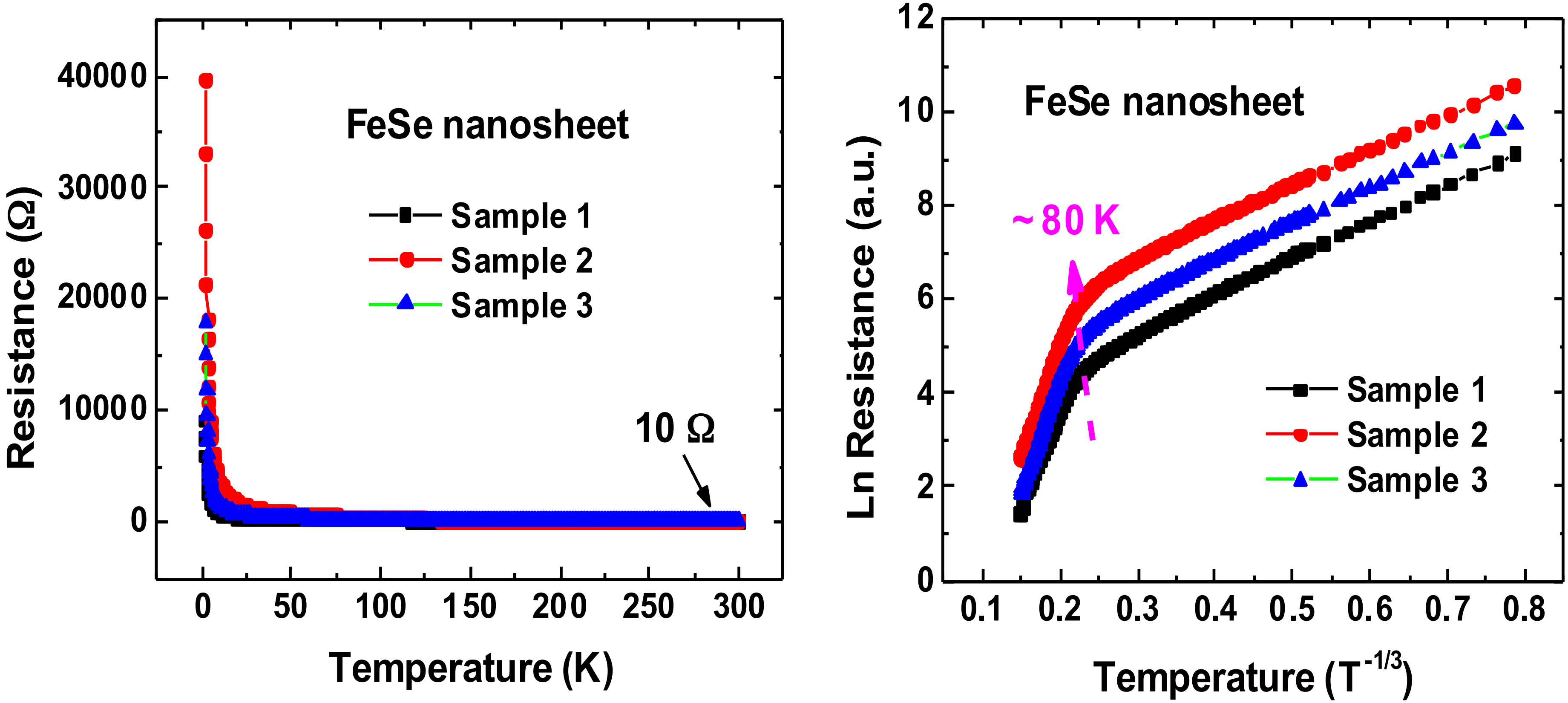


S2, H perpendicular to c

$T_m \sim 50 - 100$ K

The stoichiometry is Fe_4Se_5

Resistivity of FeSe nanosheet



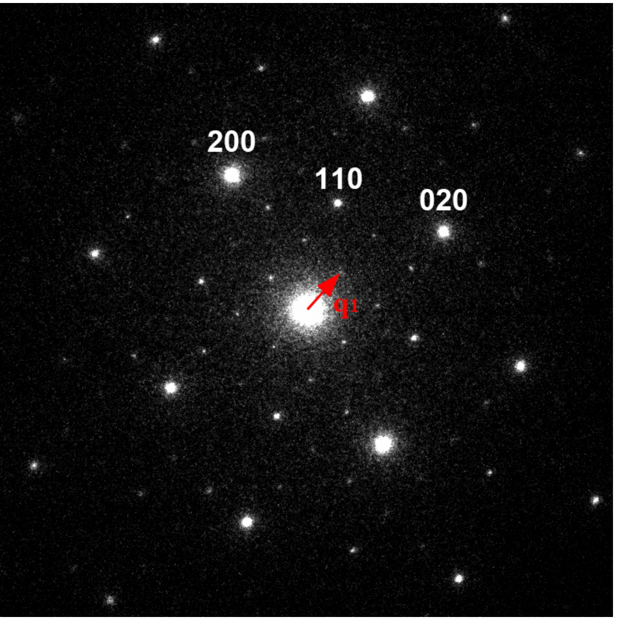
$T_\sigma \sim T_m$!

Structure/magnetic transition around 80 K?

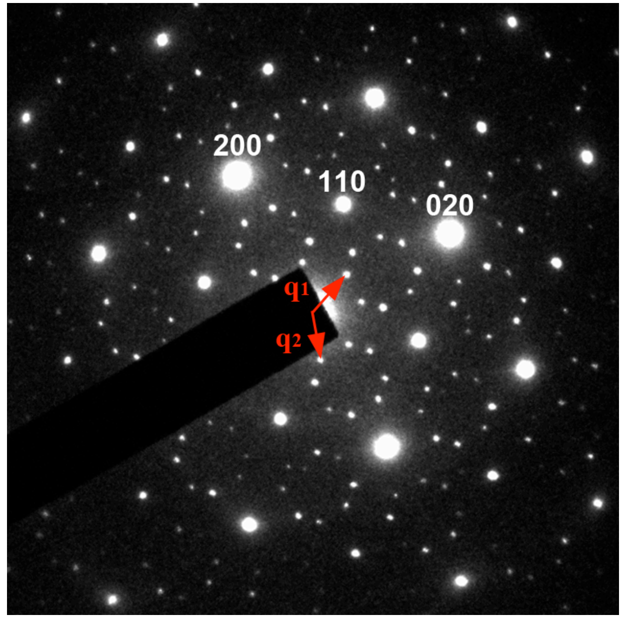
Fe vacancy scattering induced VRH?

β-Fe_4Se_5 → $\sqrt{5}\times\sqrt{5}$

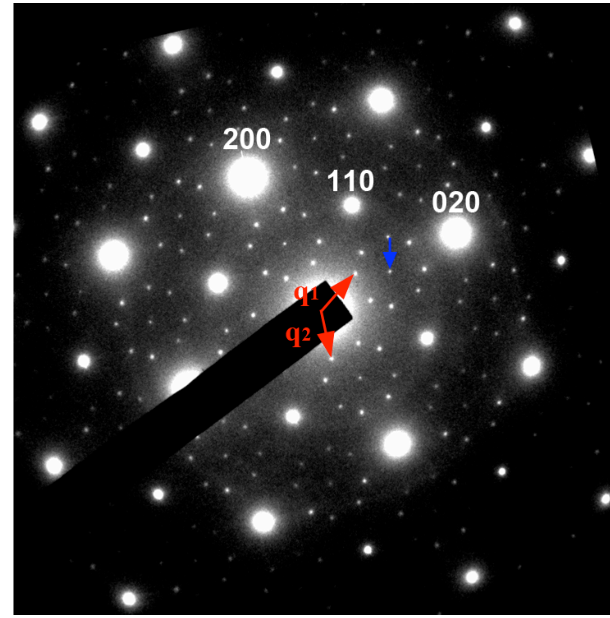
ZA = [001]



ZA = [001]

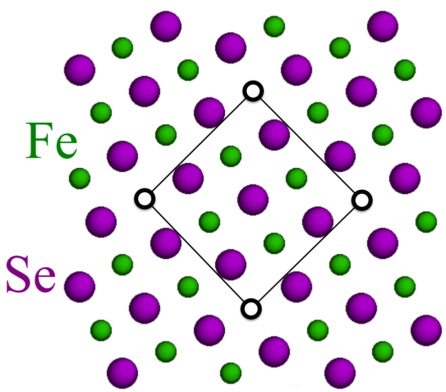


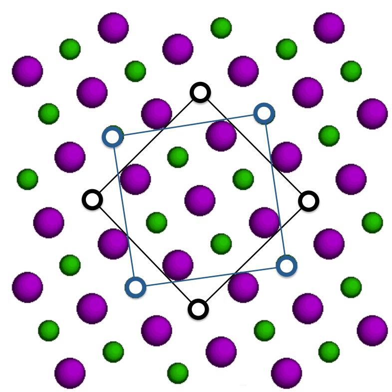
ZA = [001]



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

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





?

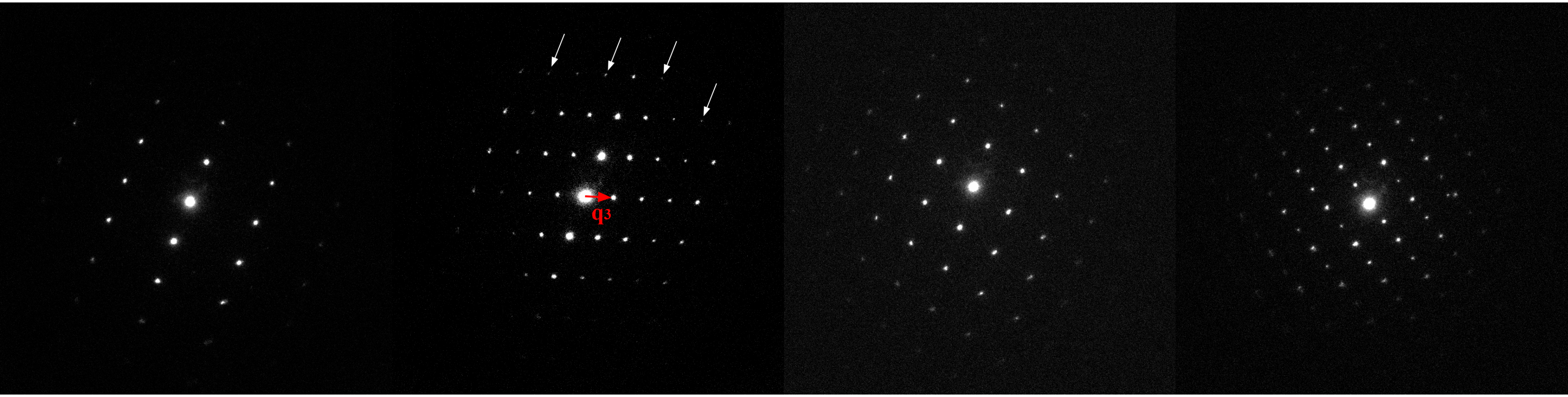
β-Fe_4Se_5(square: $\sqrt{5}\times\sqrt{5}$)

with twinned superstructure

with forbidden reflections at *h*00, 0*k*0, *h* odd, *k* odd.

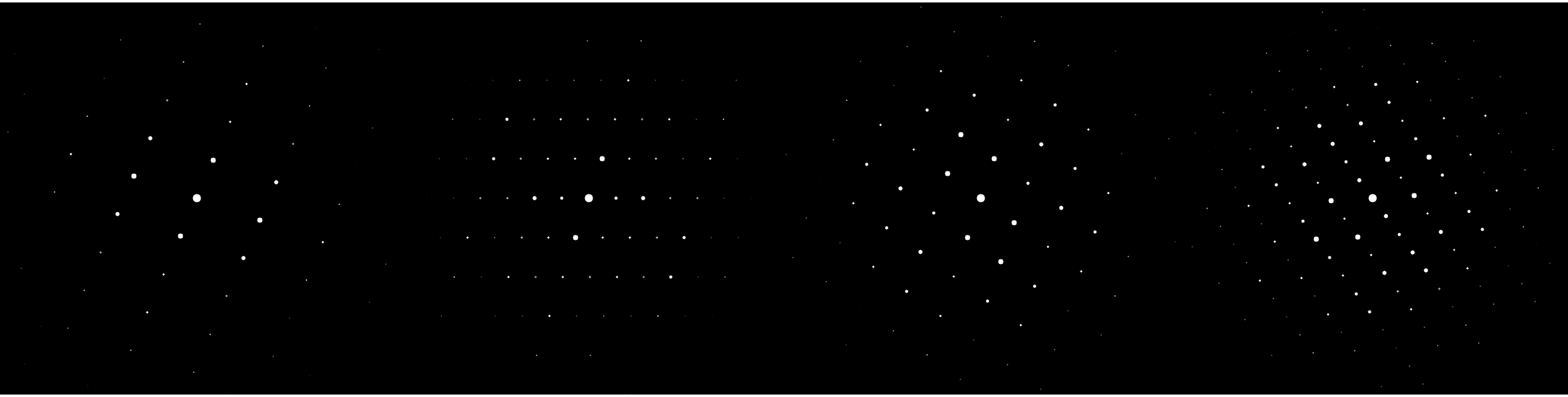
β-Fe_3Se_4 → √2×√2 with d_{100} shift every other plane

ZA = [-131] ZA = [-121] ZA = [-111] ZA = [010]



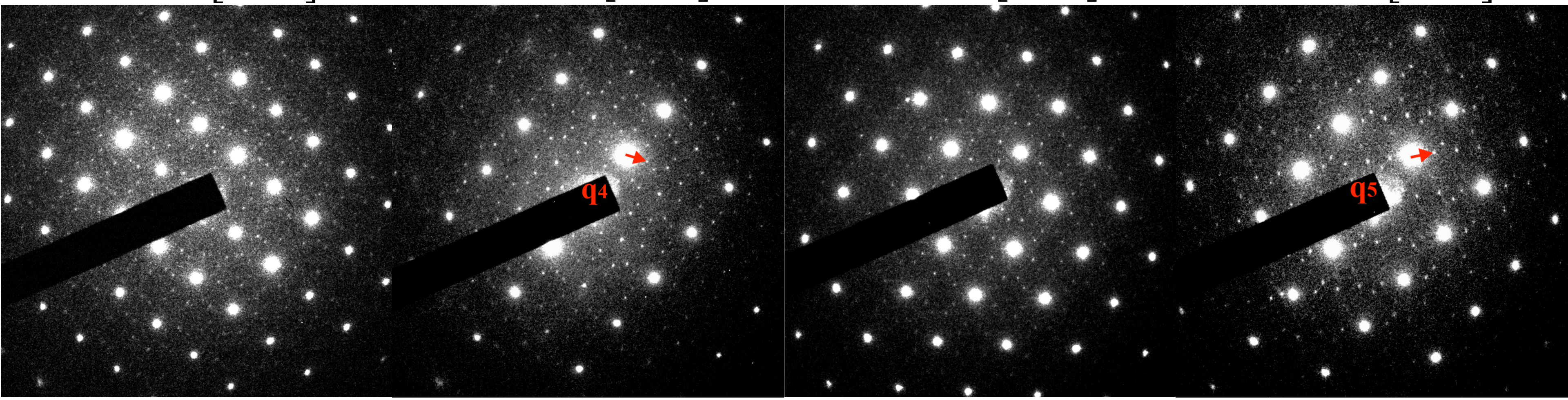
$\mathbf{q}_3$= (1/2, 1/2, 1/2)

simulated kinematical electron diffraction patterns



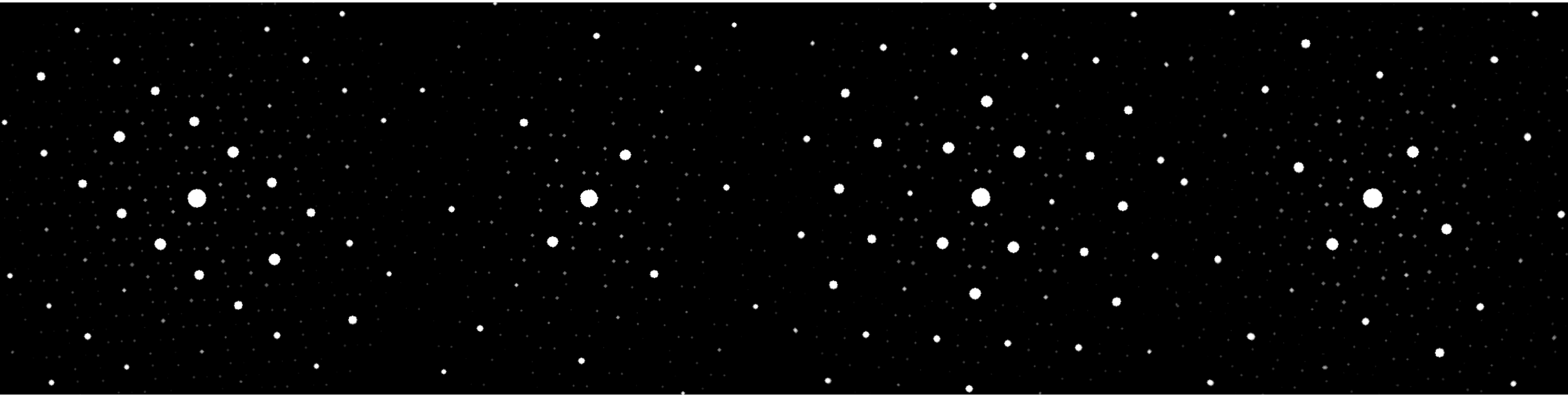
β-Fe_9Se_{10} → √10×√10 with twin and with ½d_{310} shift every other plane

ZA = [-101] ZA = [-212] ZA = [-111] ZA = [-121]

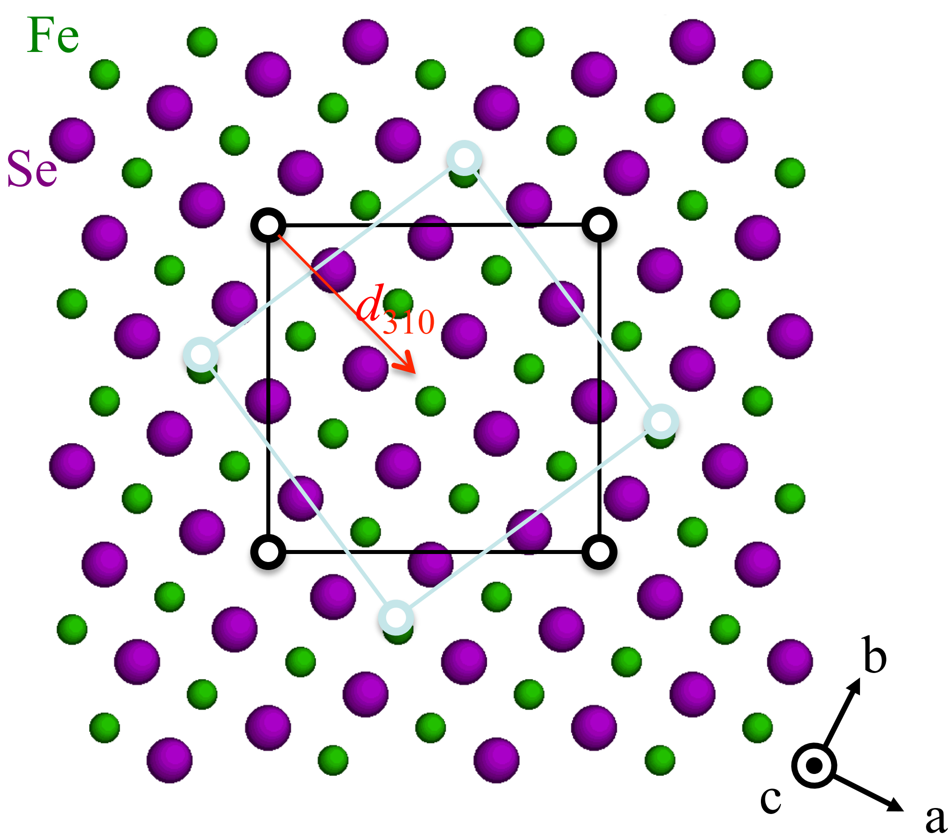


$\mathbf{q}_4$= (2/5, 1/5, 0) $\mathbf{q}_5$= (1/5, 2/5, 0)

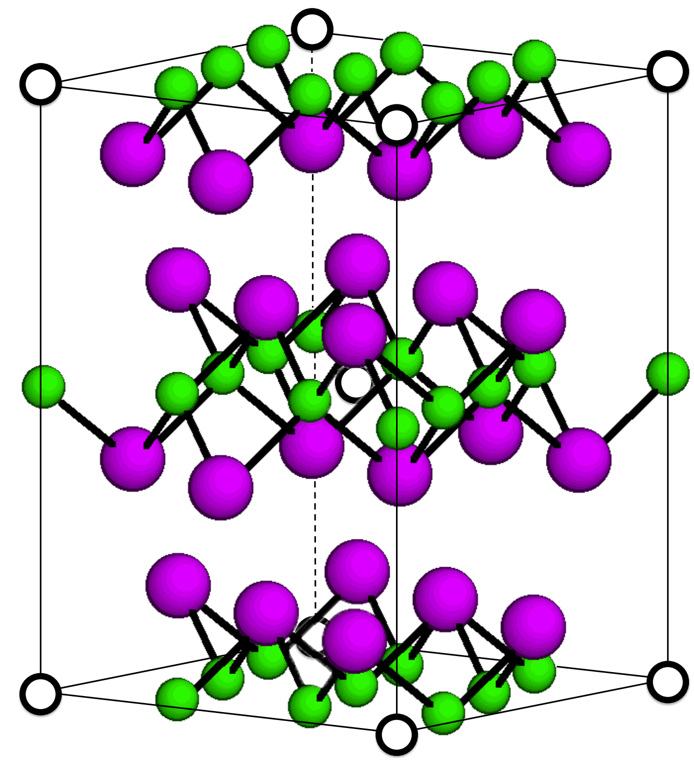
simulated kinematical electron diffraction patterns



β-Fe_9Se_{10} → √10×√10 with twin and with ½d_{310} shift every other plane



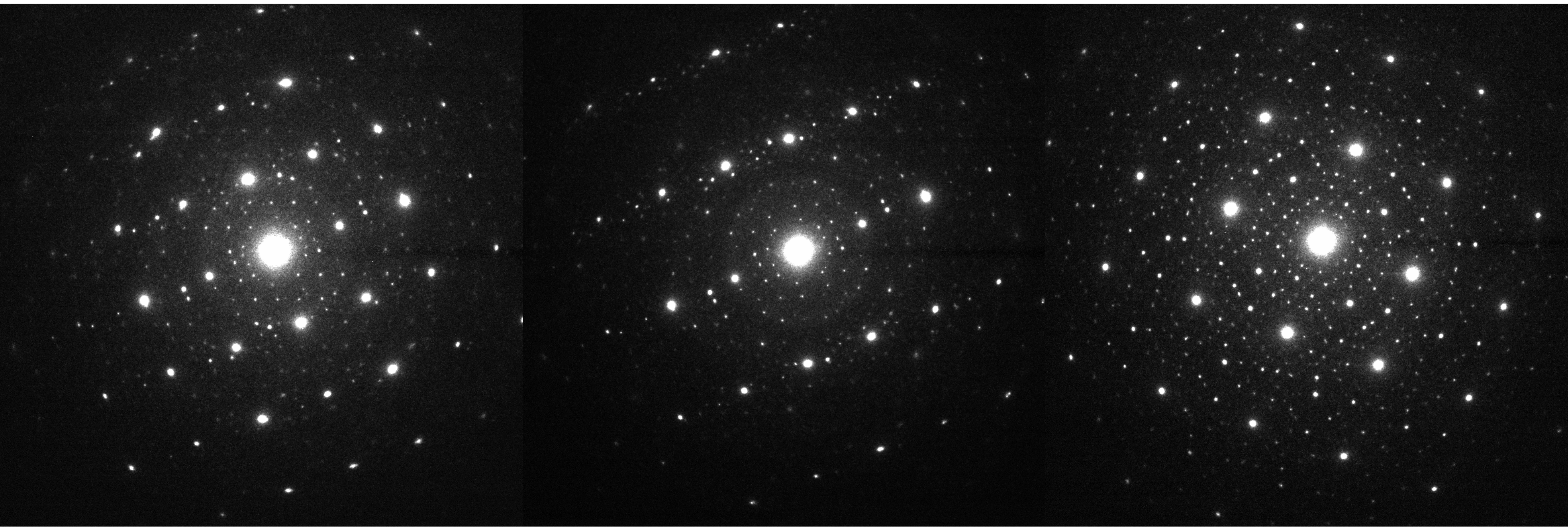
β-Fe_9Se_{10} with twinned superstructure

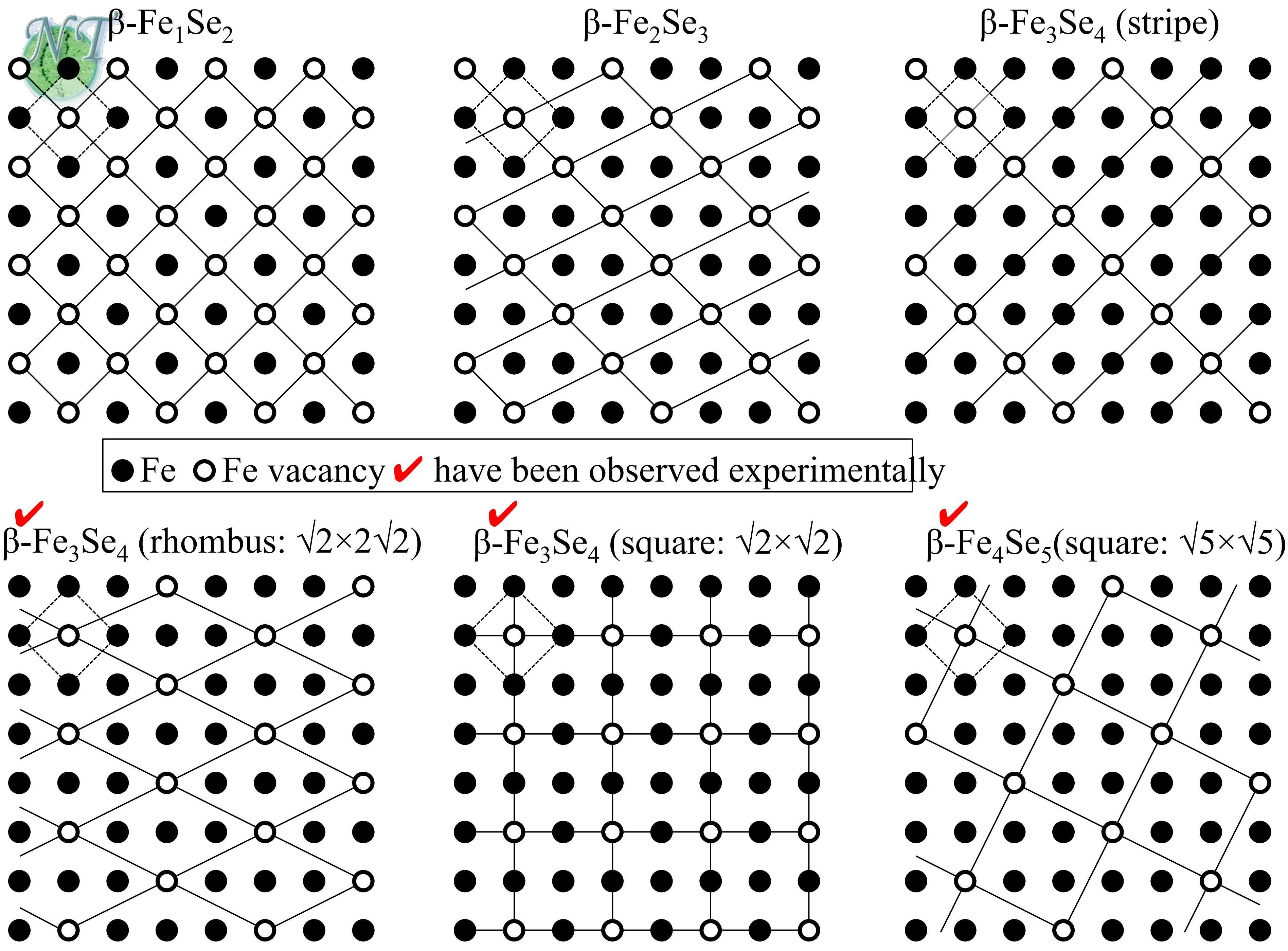


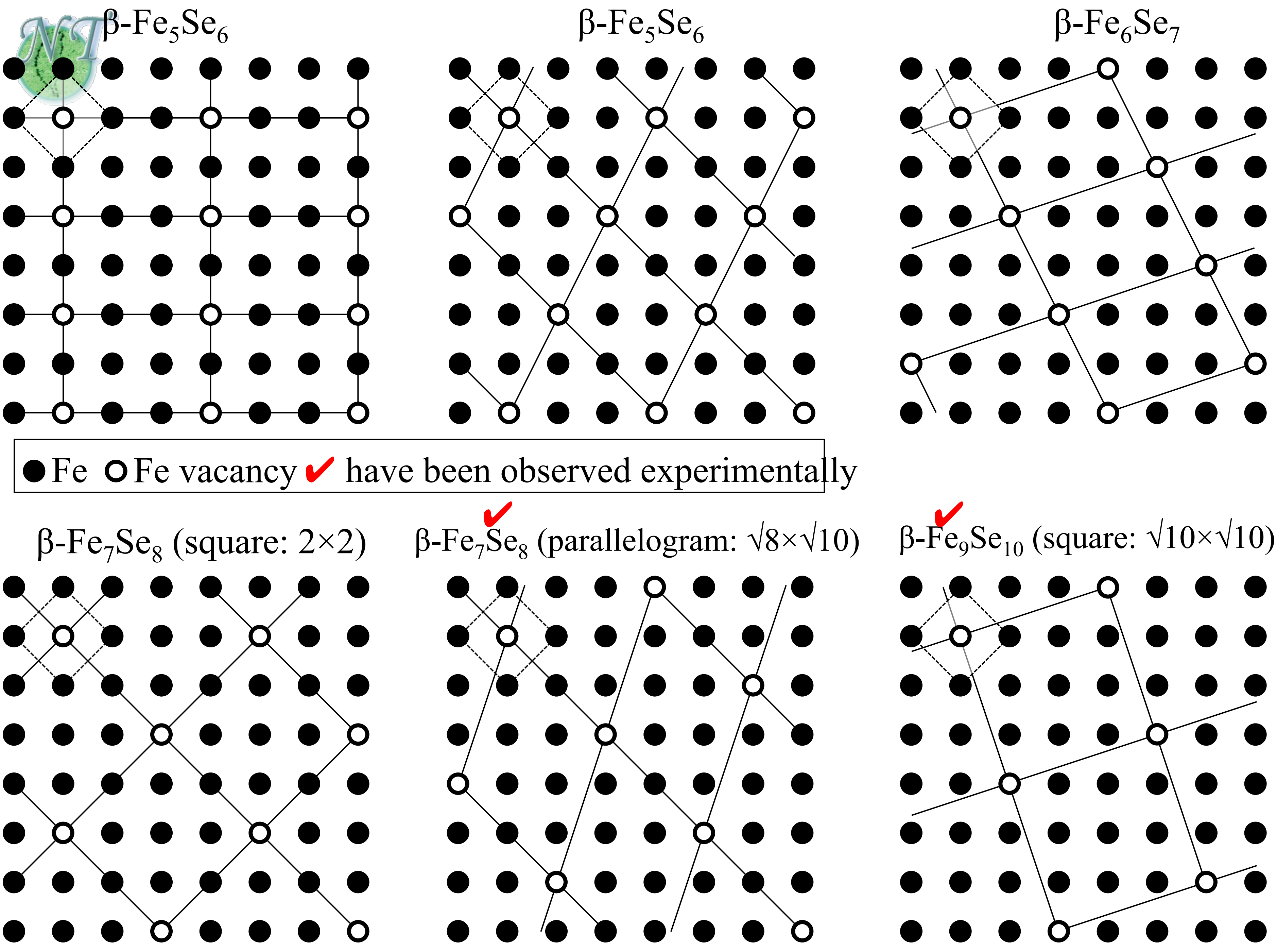
Fe-vacancy I-cell

β-$Fe_{1-x}Se_4$ (x = ?) unknown superstructure

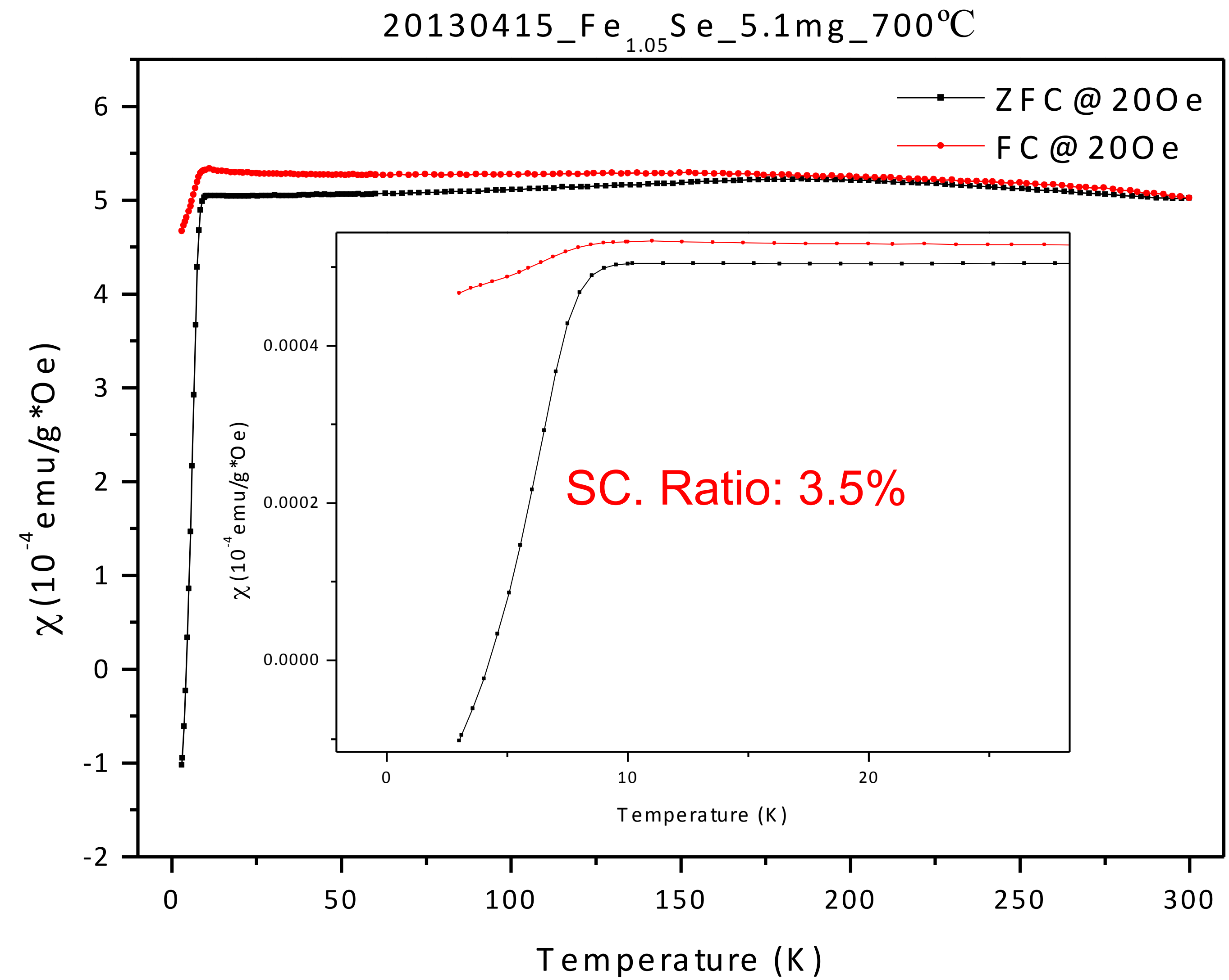
ZA=[1-12] ZA=[1-13] ZA=[001]




β-Fe1Se2
β-Fe2Se3
β-Fe3Se4 (stripe)
Fe
Fe vacancy
✔ have been observed experimentally
✔ β-Fe3Se4 (rhombus: √2×2√2)
✔ β-Fe3Se4 (square: √2×√2)
✔ β-Fe4Se5(square: √5×√5)

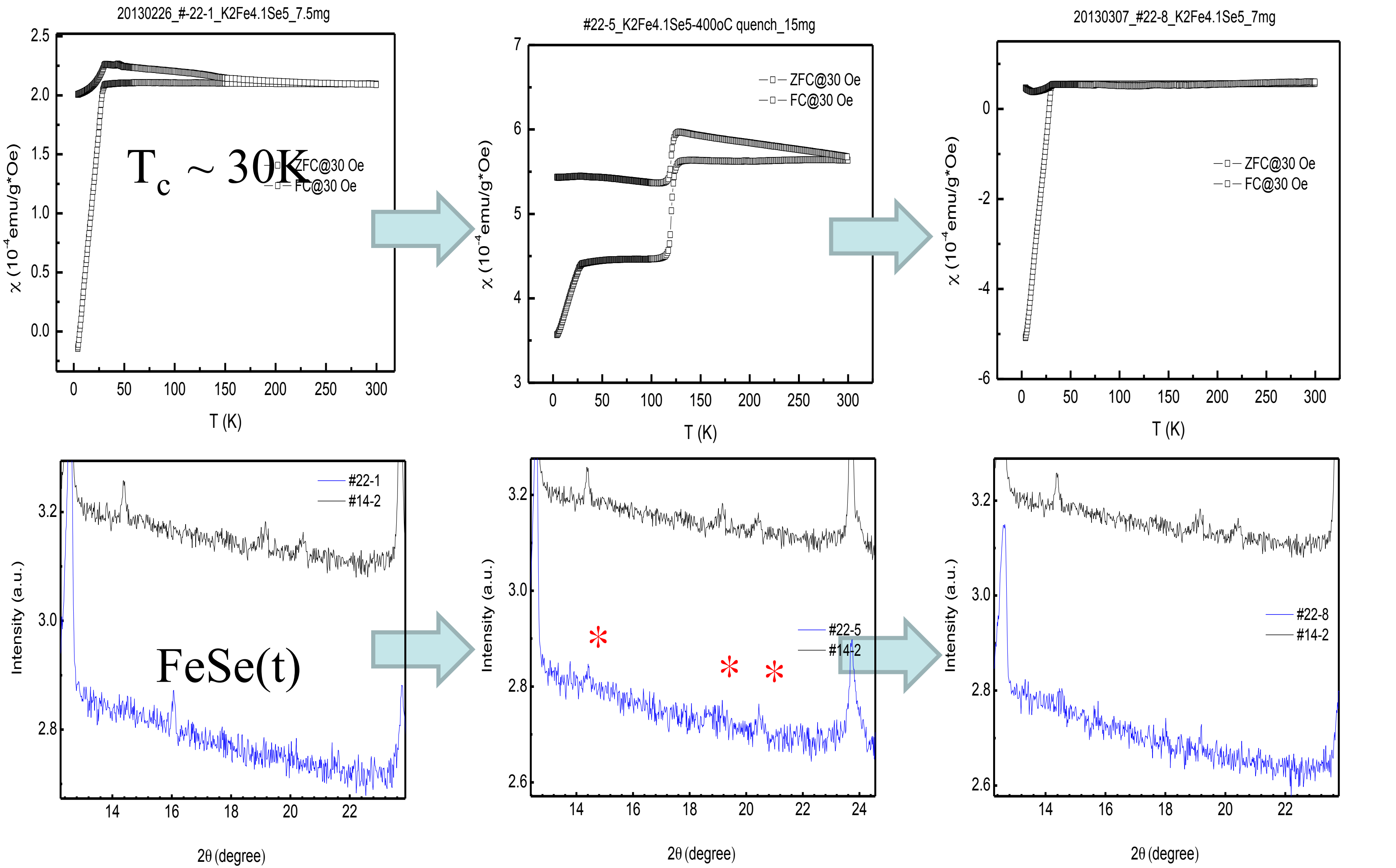

β-Fe_5Se_6
β-Fe_5Se_6
β-Fe_6Se_7
Fe Fe vacancy have been observed experimentally
β-Fe_7Se_8 (square: 2×2)
β-Fe_7Se_8 (parallelogram: √8×√10)
β-Fe_9Se_{10} (square: √10×√10)

700 ℃ -7 h-quenching



K-Fe-Se

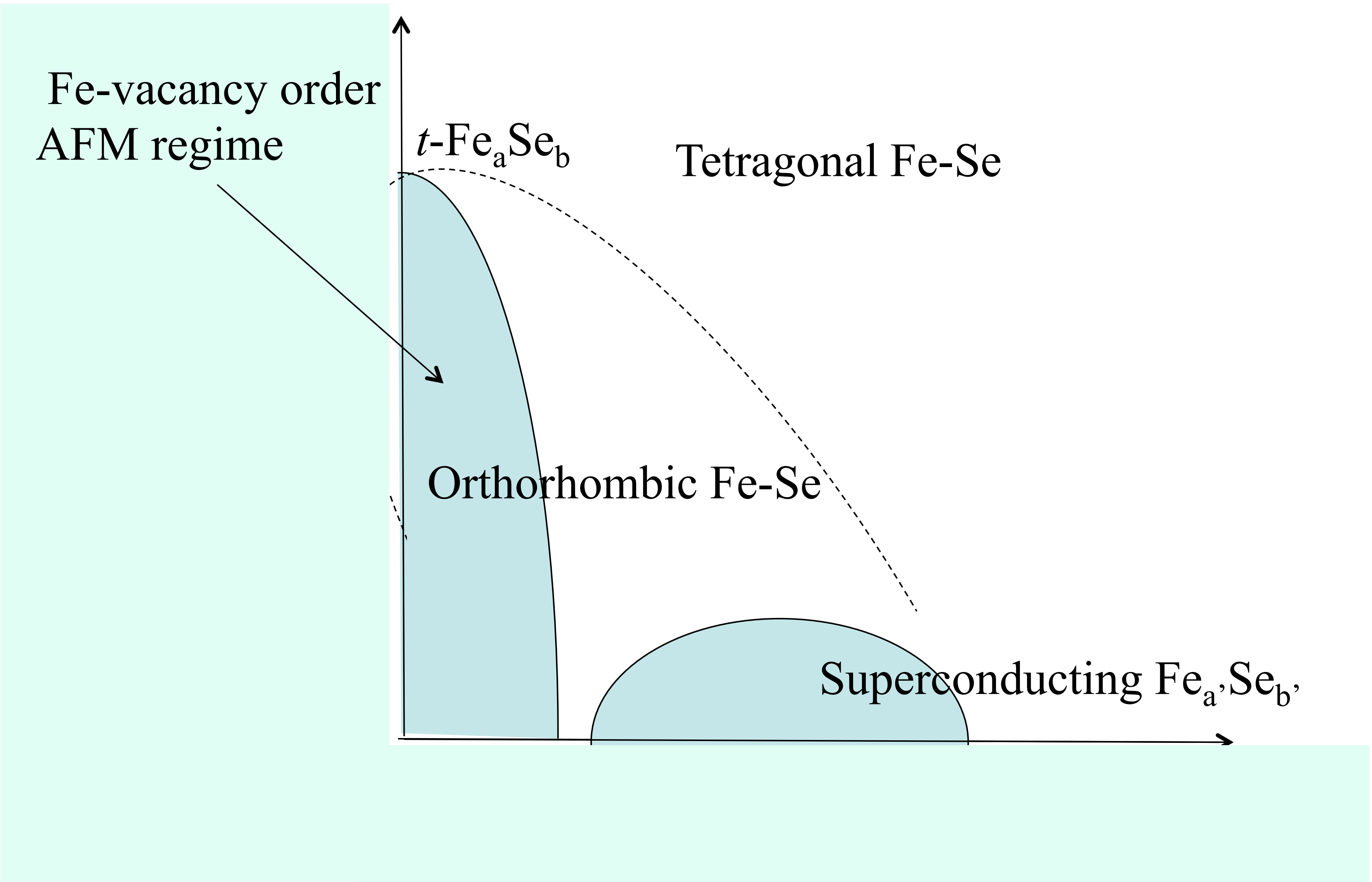
750°C quench | 400°C quench | 750°C quench

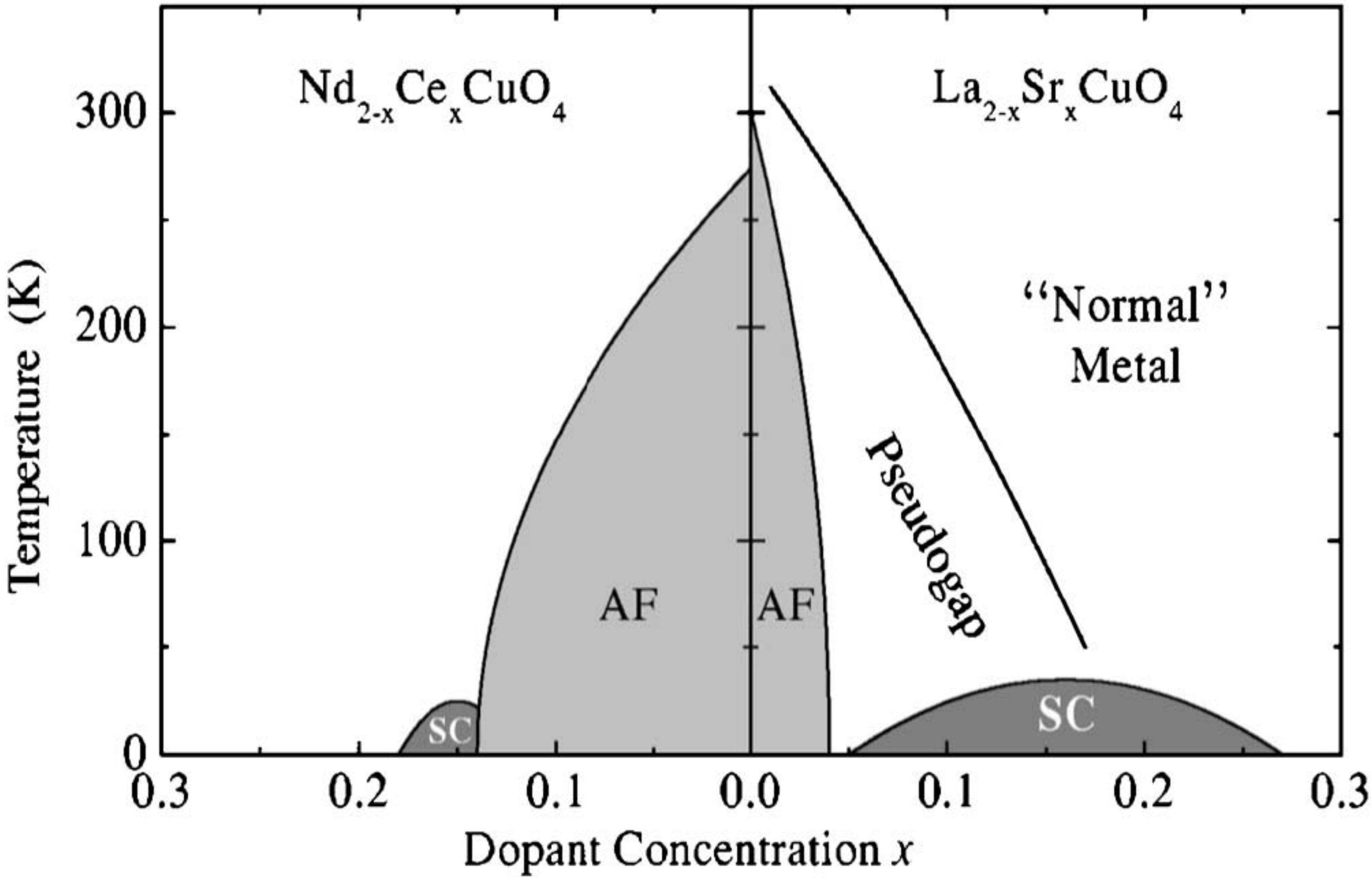


Summary of Fe-vacancy

- Possible types of Fe-vacancy order
- Samples:
  - β-$Fe_{1-x}Se$ from potassium removal of $K_{1-x}Fe_{2-y}Se_2$ bulk/crystal
  - β-$Fe_{1-x}Se$ nanosheets via an aqueous chemical route
  - β-$Fe_{1-x}Se$ small crystal from a high-pressure route
- β-Fe_3Se_4 (x = 0.25) → $\sqrt{2}\times\sqrt{2}$
- β-Fe_4Se_5 (x = 0.2) → $\sqrt{5}\times\sqrt{5}$
- β-Fe_9Se_{10} (x = 0.1) → $\sqrt{10}\times\sqrt{10}$

Proposed Phase Diagram of Fe-Se





Schematic phase diagram of high-*Tc superconductors* showing hole doping right side and electron doping left side. From Damascelli *et al., 2003.*

Summary

- A new phase diagram for Fe-chalcogenides is proposed—Needs further confirmation —detailed studies by annealing nanowires (or nanoparticles) of different compositions
- All observed anomalies from transport, magnetic, and optical measurements can possibly associate with orbital modification and gap opening—needs theoretical support


P1F
配電室