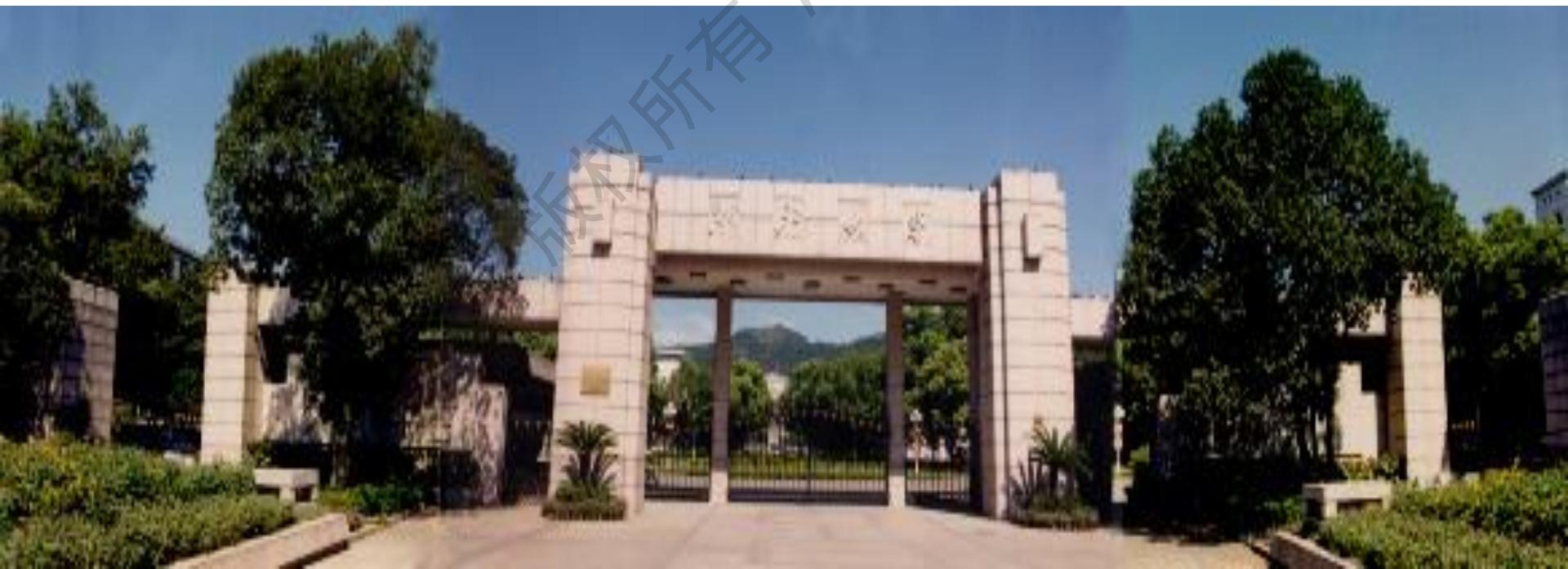


# Exploration of New (Fe,Ni)-Chalcogenide SCs Fe-vacancy order, new AFM states and SC

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# Thanks to my Collaborators

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Xiao-Jia Chen (**High Pressure**)
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K. Yoshimura (**NMR**)
- Discussion in theory  
Jianhui Dai (**HNU, China**),  
Chao Cao (**HNU, China**)  
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Qimiao Si (**Rice Univ. USA**)  
Fuchun Zhang (**ZJU China**)

感谢国家自然科学基金和973项目资助

# Online

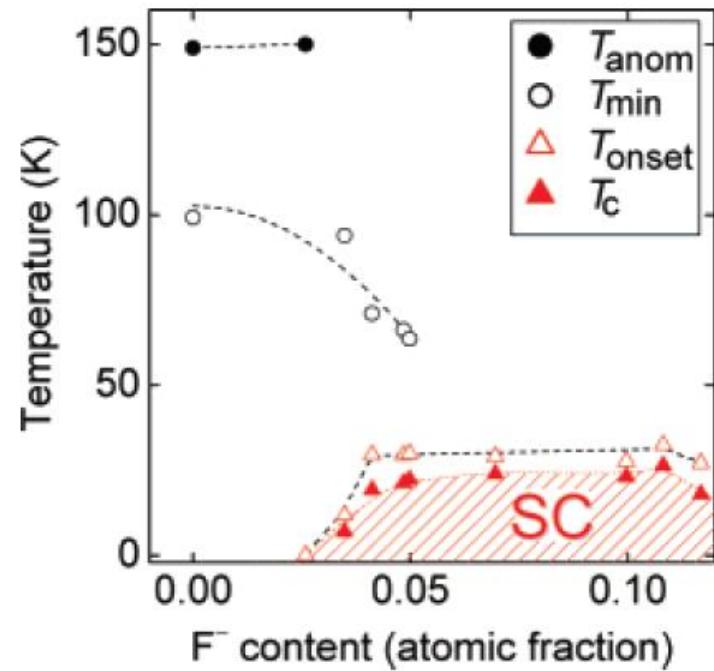
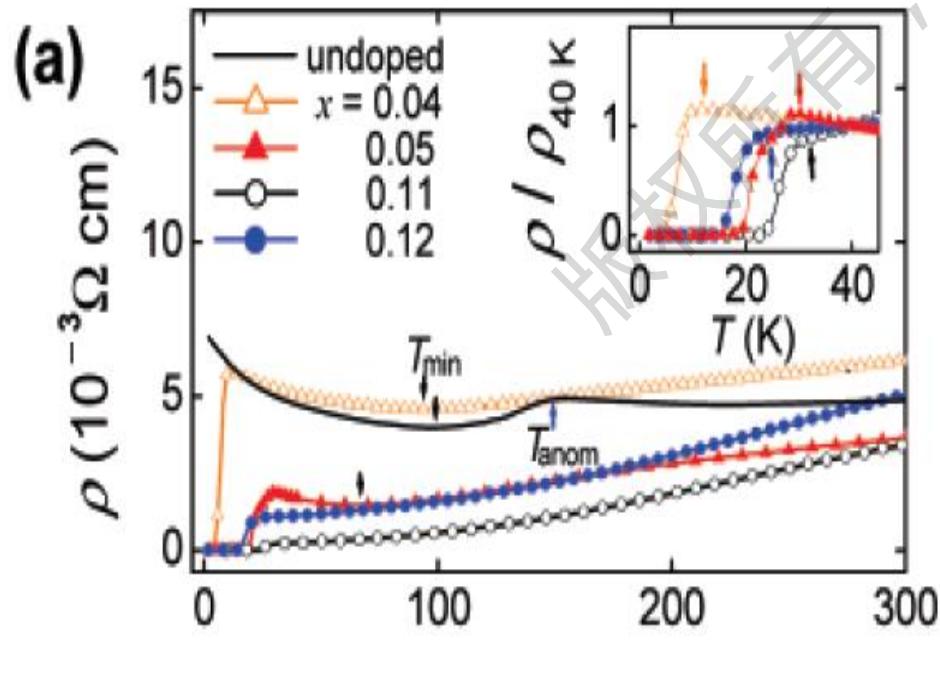
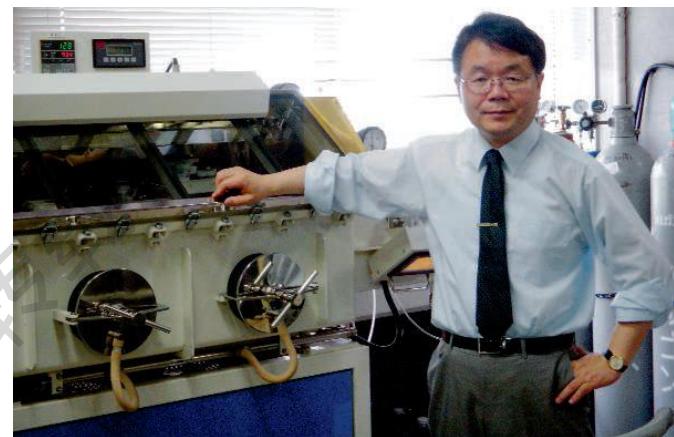
- Review for Fe-Based Superconductors (in short).
- Superconductivity and Bi-collinear AFM in  $\text{FeTe}_{1-x}\text{Se}_x$ .
- Fe-vacancy super-lattice, new AFM states and SC in  $(\text{Tl, K, Rb})\text{Fe}_x\text{Se}_2$ .
- Superconductivity and Heavy Fermion behavior in  $\text{TINi}_2\text{Se}_2$ ,  $\text{TINi}_2\text{S}_2$  crystals.
- Phase Diagram of  $\text{TlCo}_{2-x}\text{Ni}_x\text{Se}_2$  System.

# I. Review for Fe-Based Superconductors

# Discovery of SC in $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ in Feb. 2008

- SC was first discovered in the F doping  $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$  with  $T_c=26\text{K}$ .

Hosono's group J. Am. Chem. Soc, 130, 3296 2008



# Main Fe-based Superconductors

- 1111 Series:

$\text{CeO}_{1-x}\text{F}_x\text{FeAs}$ : **41K**     $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ : **55K**

$\text{PrO}_{0.89}\text{F}_{0.11}\text{FeAs}$ : **52K**     $\text{SmFeAsO}_{1-x}$     **55K**

$\text{CaFFeAs}$ : **36K**,  $\text{La}_{1-x}\text{Sr}_x\text{OFeAs}$  (**Hole doping**)

- 122 Series: (both Hole and Electron Doping)

$\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ,  $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$  **38K**

- 111 Series:  $\text{LiFeAs}$  **16K**

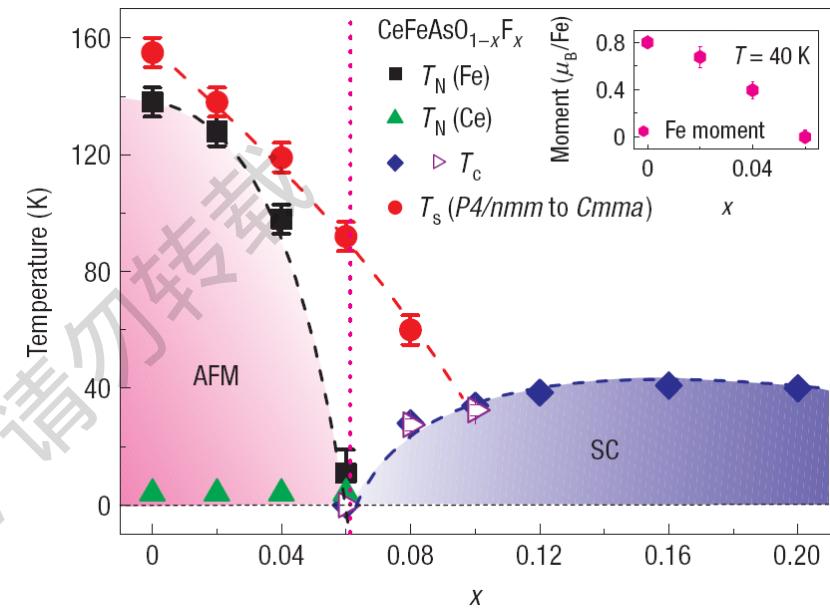
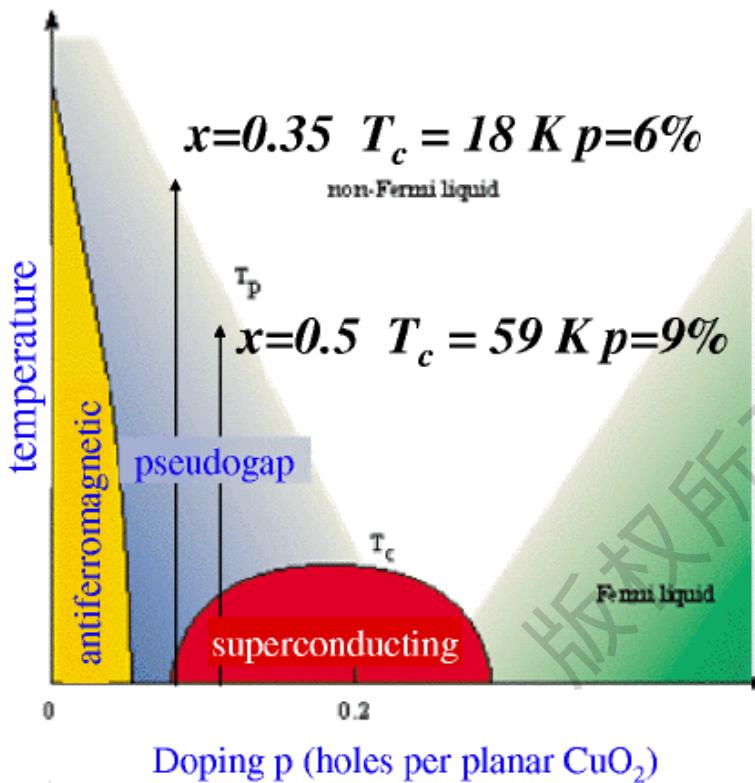
- 11 Series:  $\text{Fe}_{1+\delta}\text{Se}$ , **8–37K**,  $\text{Fe}_{1+\delta}(\text{Te},\text{Se})$  **14K**

- New 122 or 245 series

( $\text{Tl},\text{K},\text{Rb},\text{Cs}\text{Fe}_x\text{Se}_2$  (**32K, 2010.11-12**))

# Similarity in Phase Diagram in both Fe-based compounds and Cuprates

## Cuprate Phase Diagram:



Jun Zhao et al, Nature Mat. 7, 953-959 (2008).

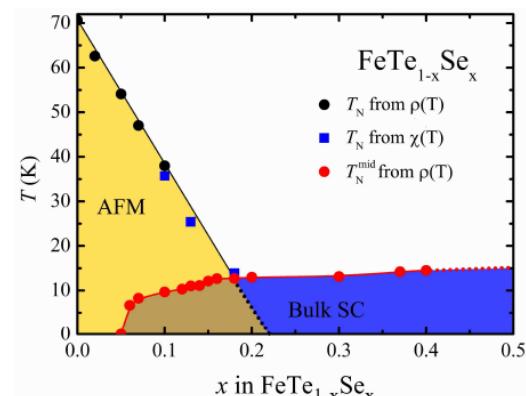


FIG. 2: (Color online) Phase diagram showing the AFM transition temperature,  $T_N$  and the superconducting temperature  $T_C$  as function of  $x$  for FeTe<sub>1-x</sub>Se<sub>x</sub> system.

Chiheng Dong, Minghu Fang et al, PRB 84, 224506(2011)

# The main difference in Parent compounds: insulator (Cuprates) to bad metal (Fe-based)

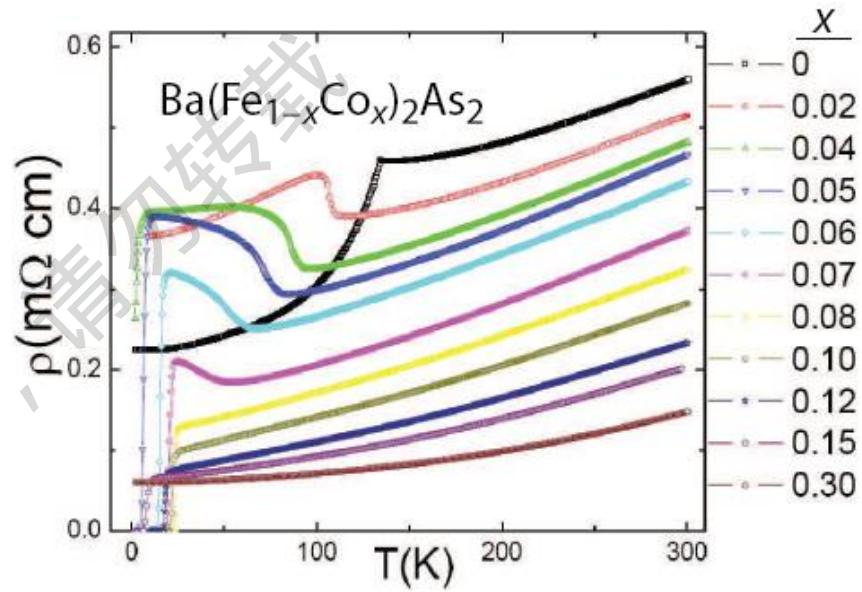
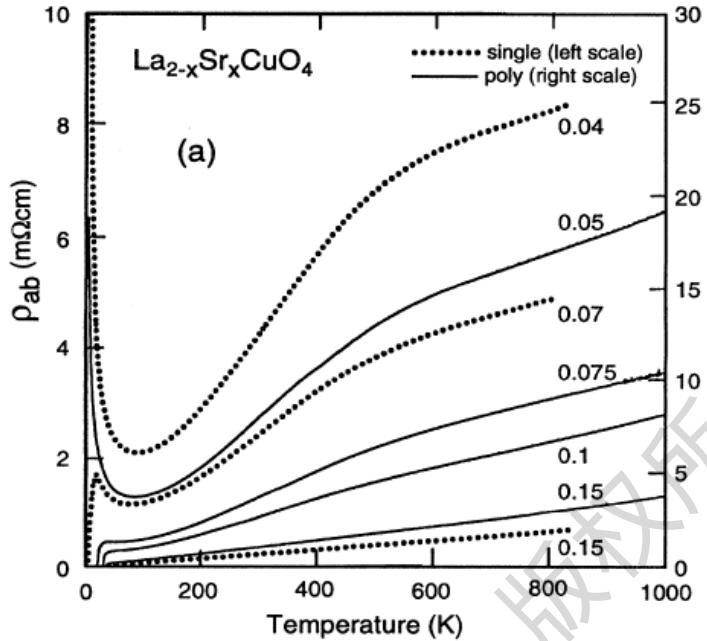


FIG. 44: (Color online) In-plane resistivity  $\rho$  versus temperature  $T$  of  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  crystals for various values of  $x$  as indicated on the right edge of the figure. Reprinted with permission from Ref. 285. Copyright (2009) by the American Physical Society.

Elbio Dagotto, Rev. Mod. Phys. 66, 763 (1994)

L. Fang et al. PRB 80, 140508(R) (2009)

Mott Physics: Strong correlation electron system.

Strong correlation electron system?

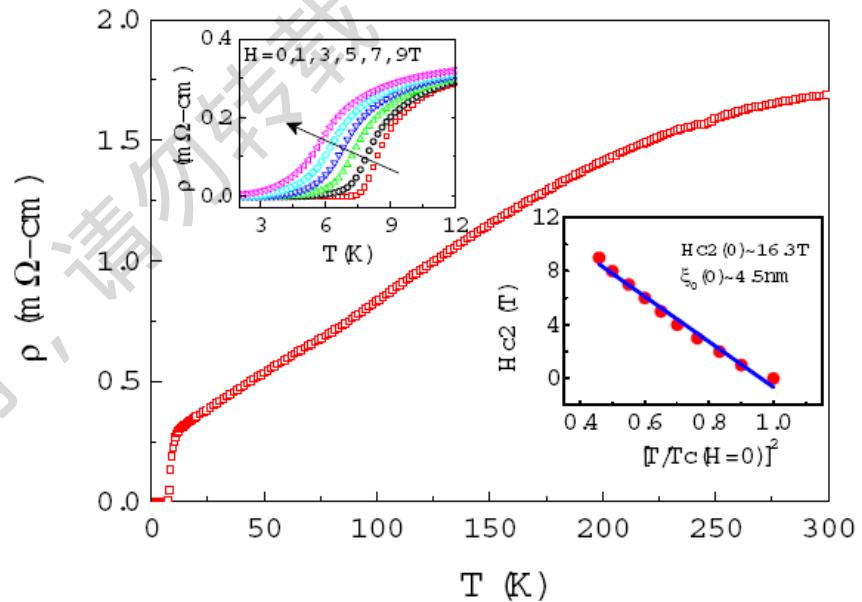
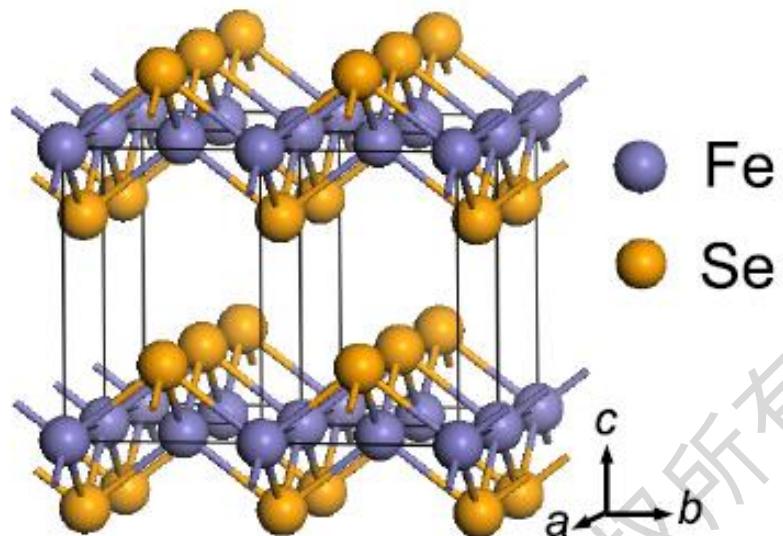
# Motivation

- Is there an unified picture for the Fe- and Cu-based HTSCs? How to develop a unified picture for both? (**in theory**).
- Are there the possibilities to tune the Fe-based compound into an insulator? (**in experiment**).
- Are there some new magnetic long-range order states in the Fe-based compound?

## II. Superconductivity and bi-collinear AFM order in Fe(Te, Se) system

# Lattice Structure of FeSe<sub>1-x</sub> (x=0.03-0.18)

F.C. Hsu et al PNAS, 105, 16262 (2008), arXiv 0807-2369



- In the July, 2008, M.K. Wu's group in Taiwan discovered superconductivity with  $T_c=8\text{K}$  in FeSe compound.
- Single FeSe layer, the simplest structure in Fe-based SCs.

From 2005, our group prepared many  $\text{NiSe}_2$  and  $\text{CoSe}_2$  compounds in order to search for new superconductors. At that time, SC was just discovered in  $\text{Na}_x\text{CoO}_2+y\text{H}_2\text{O}$ , with a triangular lattice.

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1000-3290/2008/57(04)/2409-06

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## $\text{NiS}_{2-x}\text{Se}_x$ 在 $x = 1.00$ 附近的反铁磁量子相变 \*

杨金虎 王杭栋 杜建华 张瞩目 方明虎

(浙江大学物理系, 杭州 310027)

(2007 年 8 月 1 日收到; 2007 年 9 月 6 日收到修改稿)

IA		II A		Periodic Table of the Elements																		0	
1	H 1.00794																					He 4.0026	
2	Li 6.941	Be 9.01219																					
3	Na 22.990	Mg 24.305																					
4	K 39.098	Ca 40.078	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Zn 31	Ga 32	Ge 33	As 34	P 35	S 36	Cl 37	Ar 38			
5	Rb 85.467	Sr 84.790	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54					
6	Cs 132.91	Ba 137.34	* La 138.91	Hf 140.91	Ta 141.91	W 142.01	Re 143.91	Os 144.91	Ir 145.91	Pt 146.91	Au 147.91	Hg 148.91	Hg 149.91	Tl 150.91	Pb 151.91	Bi 152.91	Po 153.91	At 154.91	Rn 155.91				
7	Fr 190.91	Ra 196.91	+ Ac 194.91	Rf 195.91	Ha 196.91	106	107	108	109	110	110												

第 58 卷 第 2 期 2009 年 2 月  
1000-3290/2009/58(02)/1195-05

物理 学 报  
ACTA PHYSICA SINICA

Vol. 58, No. 2, February, 2009  
©2009 Chin. Phys. Soc.

## $\text{Co}(\text{S}_{1-x}\text{Se}_x)_2$ 系统中的铁磁量子相变 \*

杨金虎 王杭栋 杜建华 张瞩目 方明虎†

(浙江大学物理系, 杭州 310027)

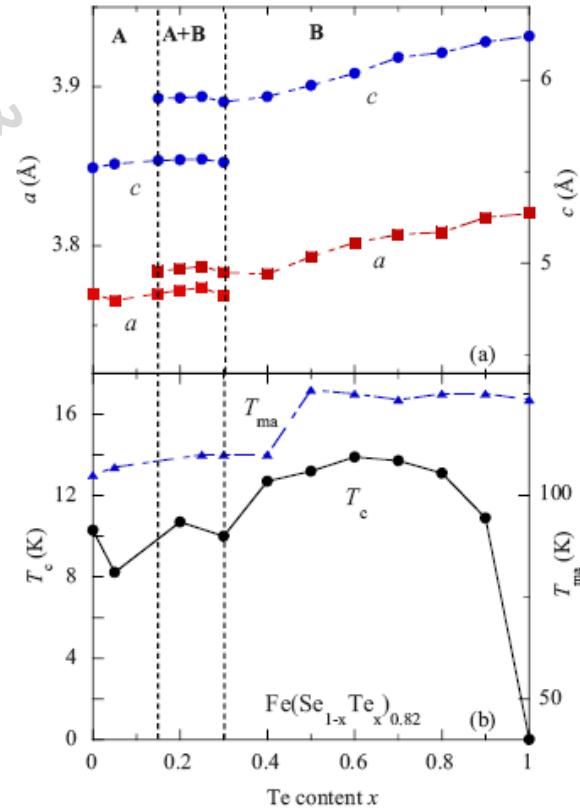
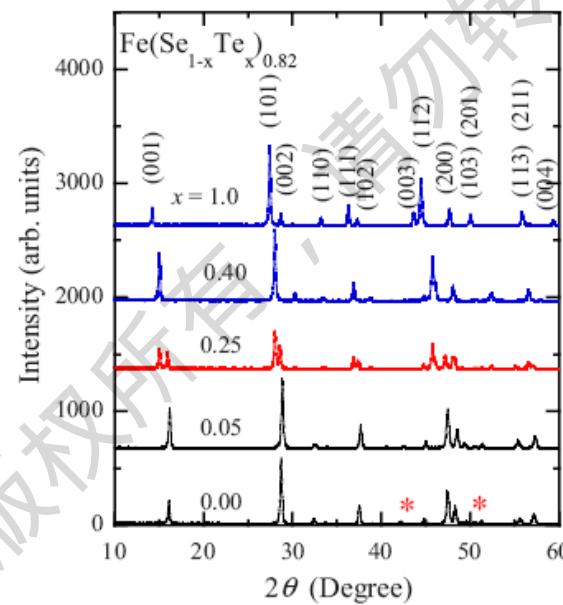
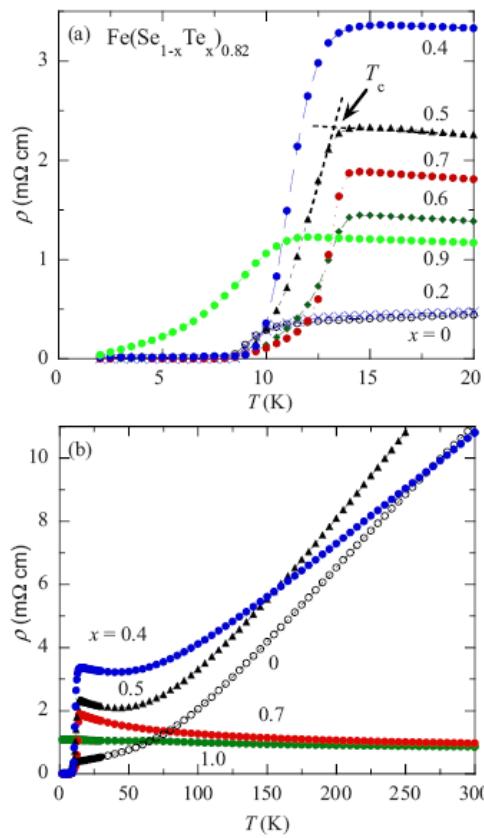
(2008 年 7 月 16 日收到; 2008 年 8 月 16 日收到修改稿)

• Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
* Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

But we are not so luck, did not try to prepare FeSe.

# Superconductivity in $\text{Fe}(\text{Se}_{1-x}\text{Te}_x)_{0.82}$

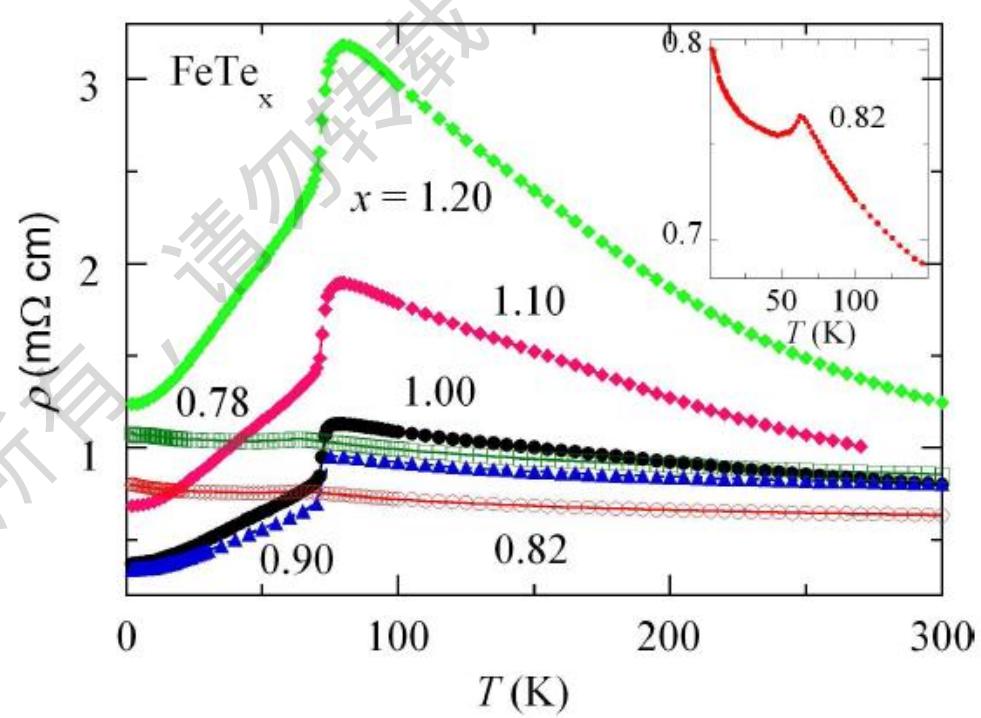
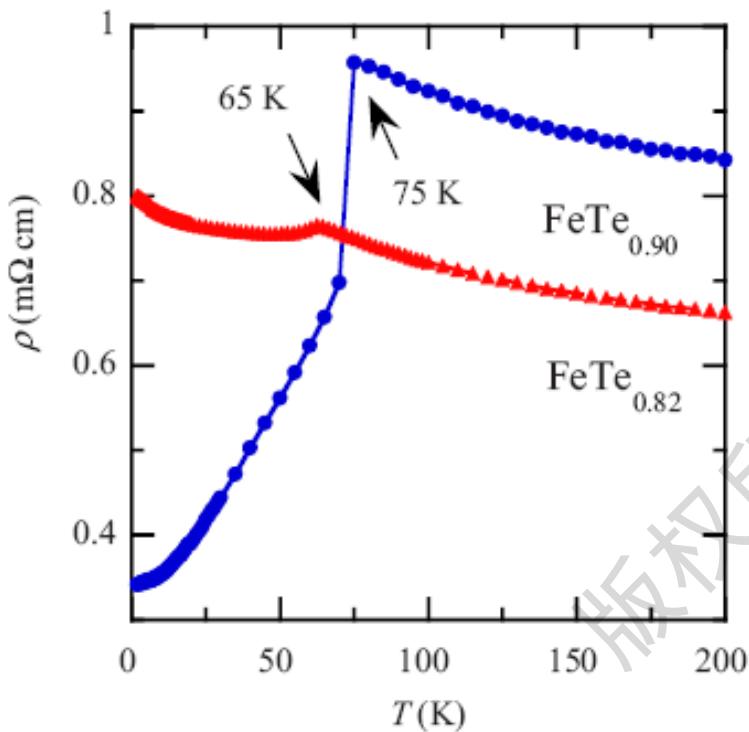
M.H. Fang, Z.Q. Mao et al arXiv0807.4775; PRB, 78, 224503(2008);  
SC in FeSe, F.C. Hsu et al arXiv 0807.2369



In one week after the discovery of SC in  $\text{FeSe}_{1-x}$ , we first reported the superconductivity with  $T_c^{\text{zero}}=14\text{K}$  in  $\text{Fe}(\text{Se}_{1-x}\text{Te}_x)_{0.82}$  system.

# The $\rho(T)$ for the parent compound $\text{FeTe}_x$

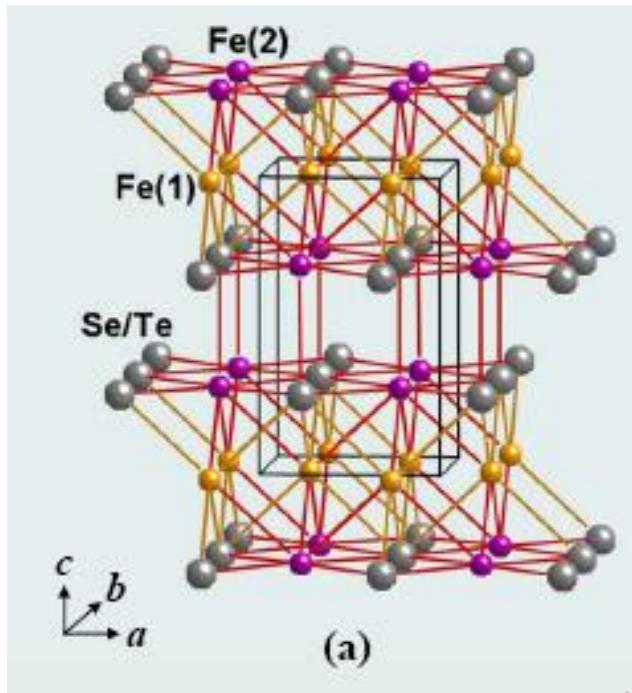
M.H. Fang, ZQ Mao et al *PRB*, 78, 224503(2008), arxiv0807.4775; about 300 citations.  
Wei Bao, Minghu Fang, ZQ Mao et al, arXiv0809.2058, *PRL* 102, 247001 (2009), 360 citations



- Above  $T_N$ , all samples with different composition of  $\text{FeTe}_x$ , their  $\rho(T)$  show semiconducting behavior.
- Below  $T_N$ , their  $\rho(T)$  depend on the excess Fe content.

# Simultaneous Magnetic and Structural transition in $\text{Fe}_{1+\delta}\text{Te}$

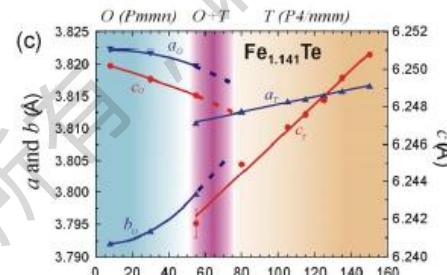
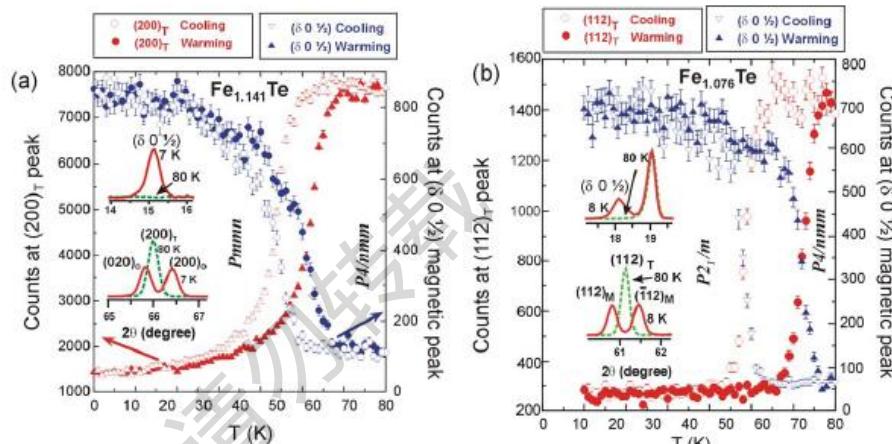
Wei Bao, Minghu Fang, Z.Q. Mao et al, *PRL* 102, 247001 (2009) citation 360



Nominal composition

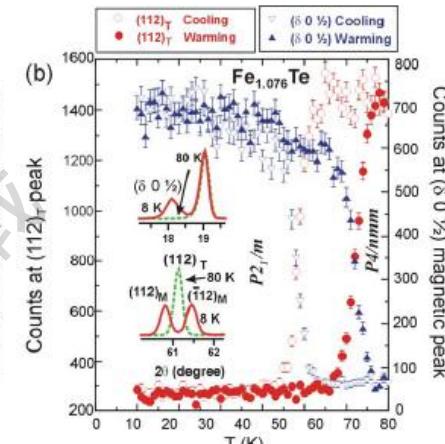
Exact composition

Simultaneous magnetic and structural the first-order transition

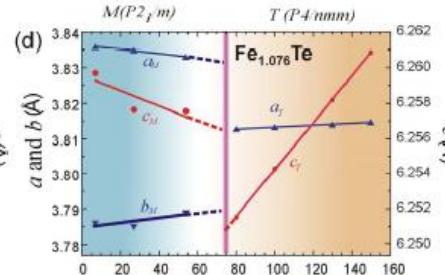


$\text{FeTe}_{0.82}$

$\text{Fe}_{1.141}\text{Te}, T_s \approx 75\text{K}$



$\text{FeTe}_{0.90}$



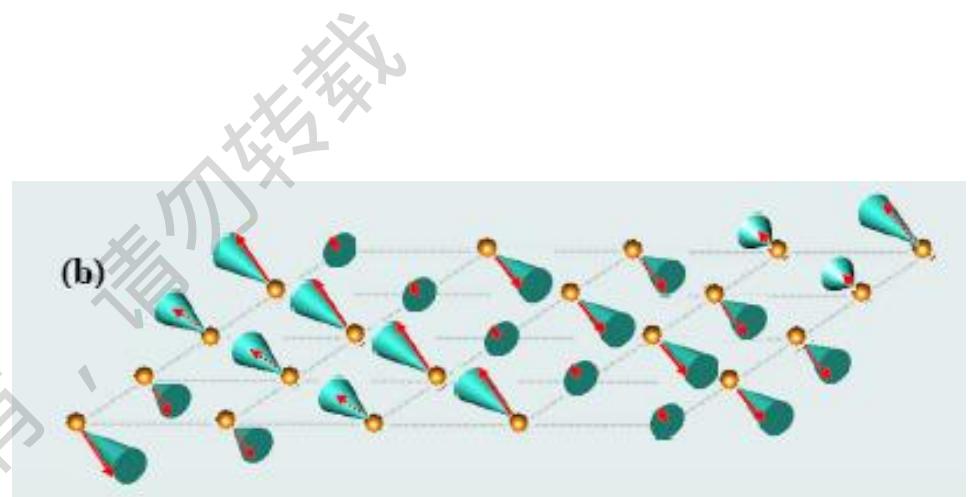
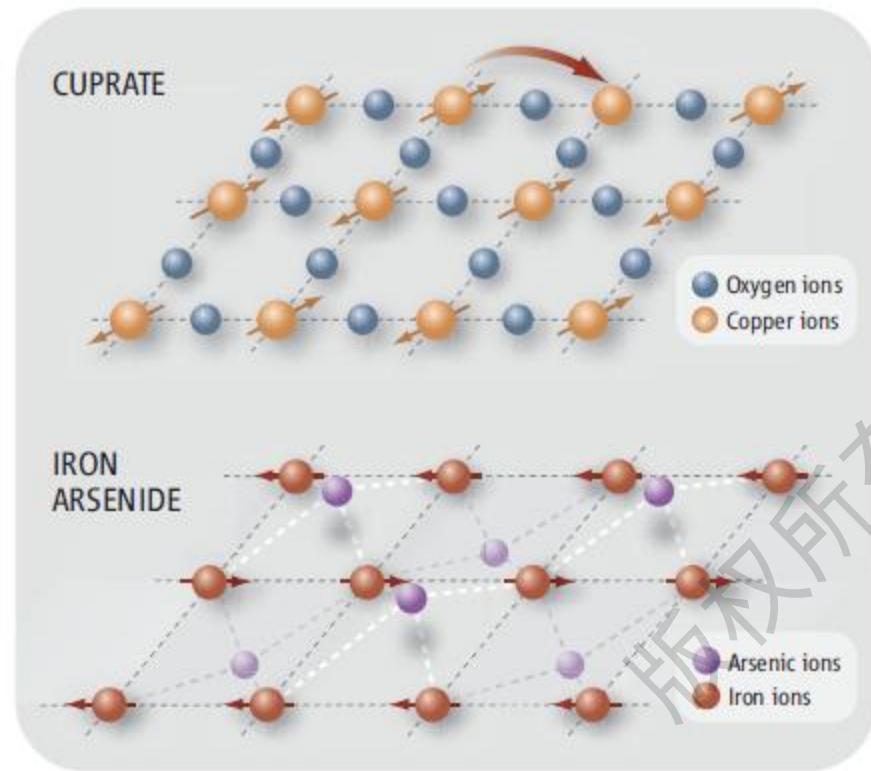
$\text{Fe}_{1.076}\text{Te}; T_s \approx 63\text{K}$

Low Tem. O( $\text{Pmmn}$ )  
→ High Tem. T( $\text{P}4\text{nmm}$ )

Low Tem. ( $\text{P}2_1/\text{m}$ )  
→ High Tem. T( $\text{P}4\text{nmm}$ )

# Bi-collinear AFM Order in the Parent Compound $\text{Fe}_{1.14}\text{Te}$

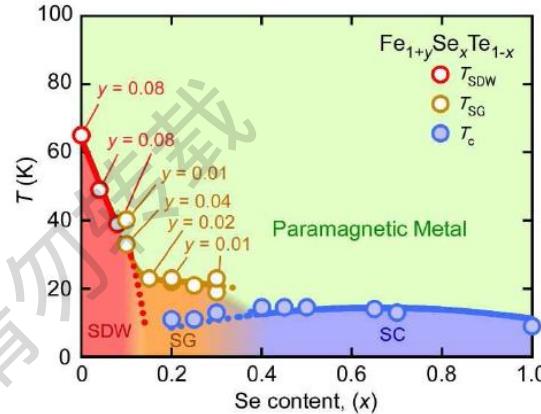
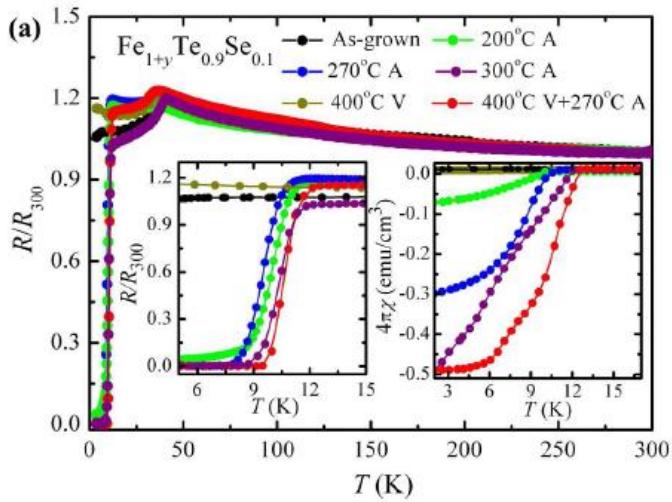
Wei Bao, Minghu Fang, Z.Q. Mao et al, *PRL* 102, 247001 (2009)



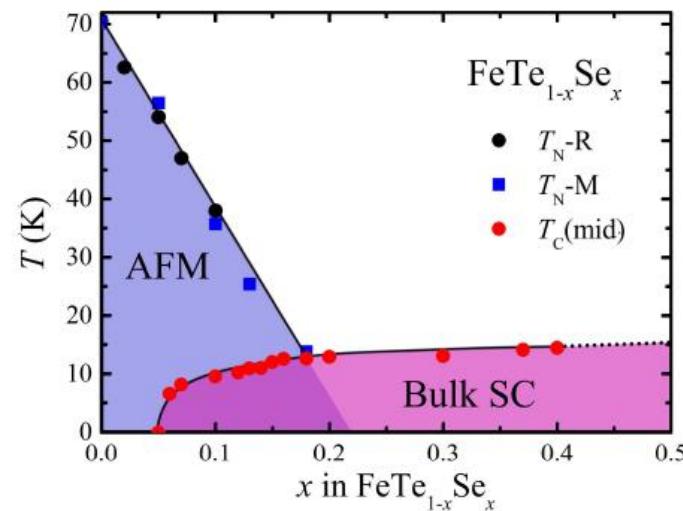
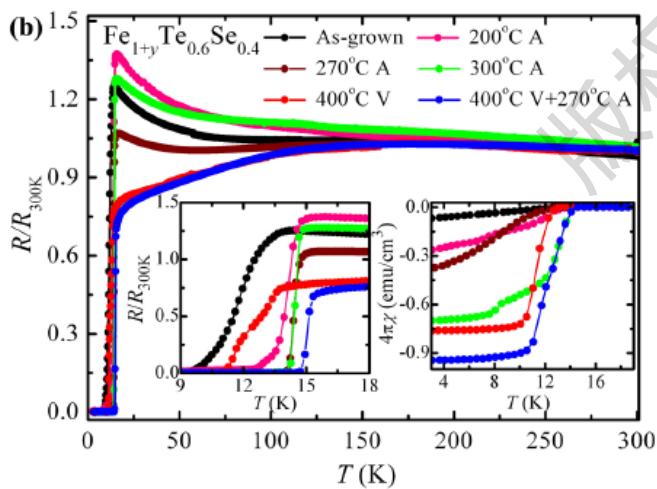
In the parent compound  $\text{LaOFeAs}$ , and  $\text{BaFe}_2\text{As}_2$ , collinear AFM order exists.  
The bi-collinear AFM in  $\text{Fe}_{1.14}\text{Te}$  compound is different from them.

# Intrinsic Phase Diagram for $\text{FeTe}_{1-x}\text{Se}_x$ system with less excess Fe atoms

Chiheng Dong, Minghu Fang et al, *PRB* 84, 224506(2011)



Natayawa et al. arXiv1003.4525, JPSJ79, 113702(2010)

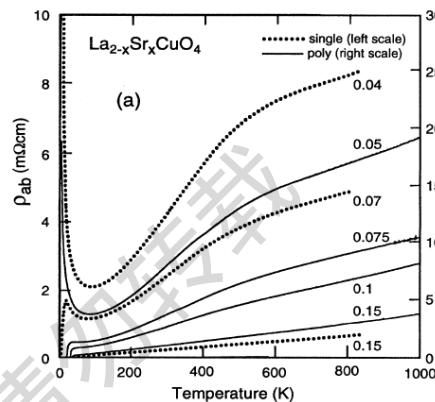
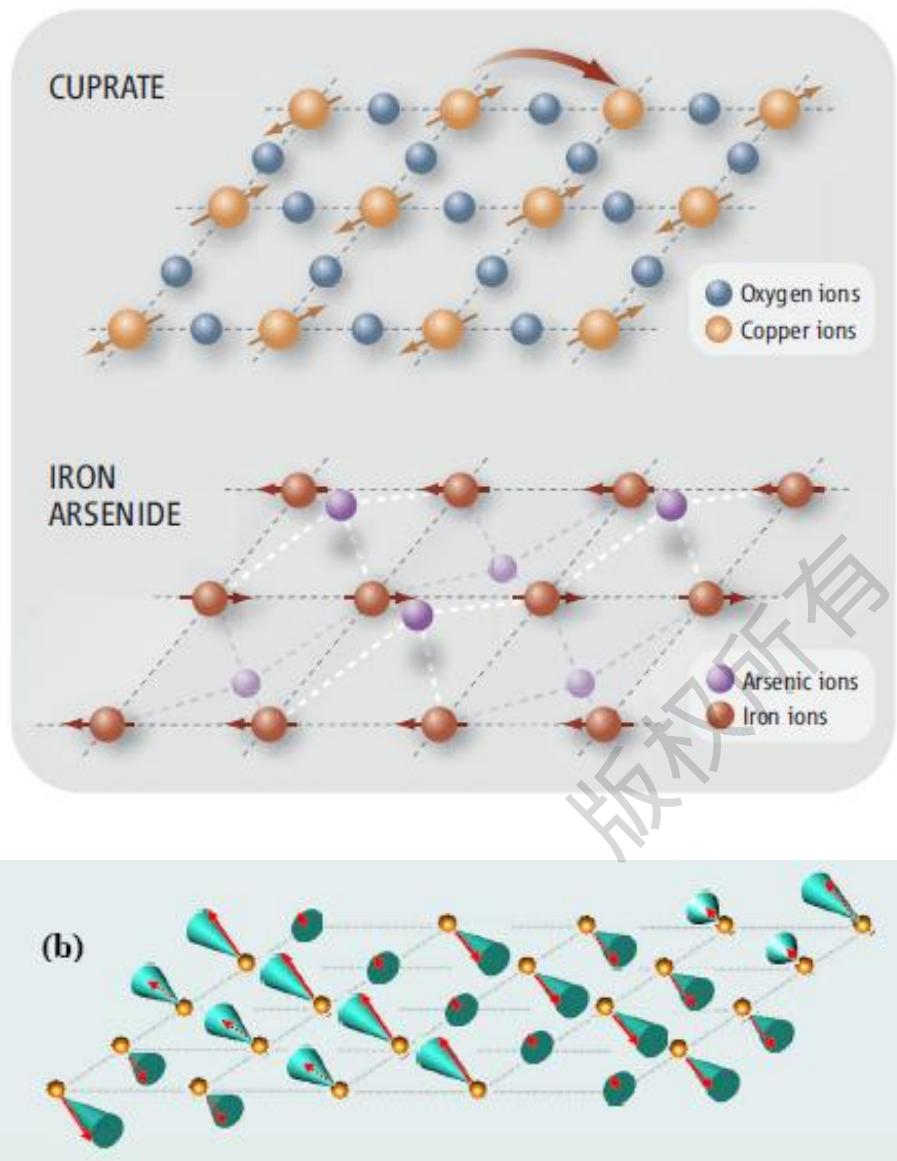


# Conclusions for $\text{FeTe}_{1-x}\text{Se}_x$ system

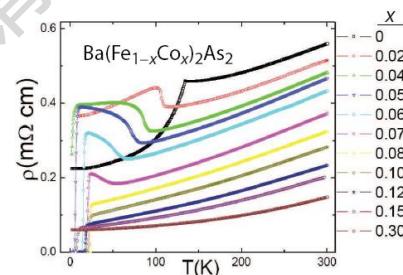
- First report SC with 14K in 11 system.
- To determine the bi-collinear AFM in FeTe.
- It was found that the excess Fe atoms on the Se layer suppress SC.
- To obtain the intrinsic Phase Diagram of  $\text{FeTe}_{1-x}\text{Se}_x$  with less excess Fe atoms. Coexistence of AFM and SC occurs in this system.

### III. Fe-vacancy order, new AFM state and SC in $(\text{Tl},\text{K},\text{Rb})\text{Fe}_x\text{Se}_2$

# Three types AFM ground state with HTSC

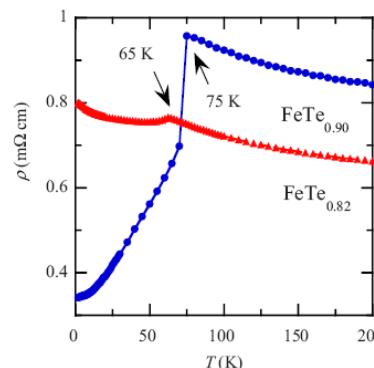


Mott Insulator:



Bad metal?

FIG. 44: (Color online) In-plane resistivity  $\rho$  versus temperature  $T$  of  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  crystals for various values of  $x$  as indicated on the right edge of the figure. Reprinted with permission from Ref. 285. Copyright (2009) by the American Physical Society.

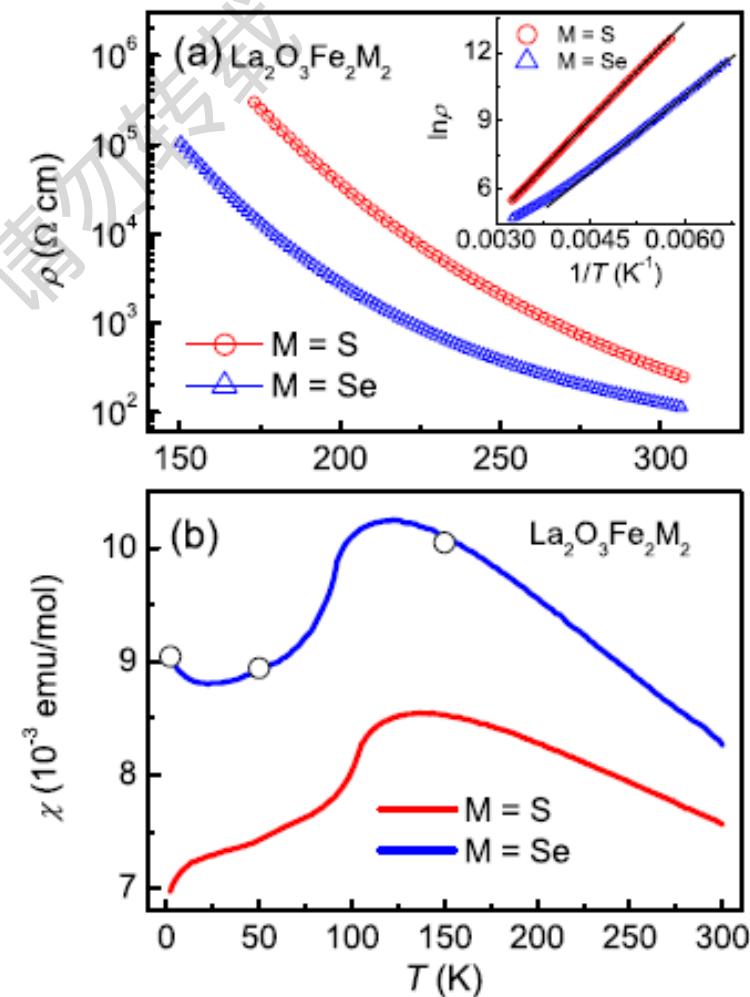
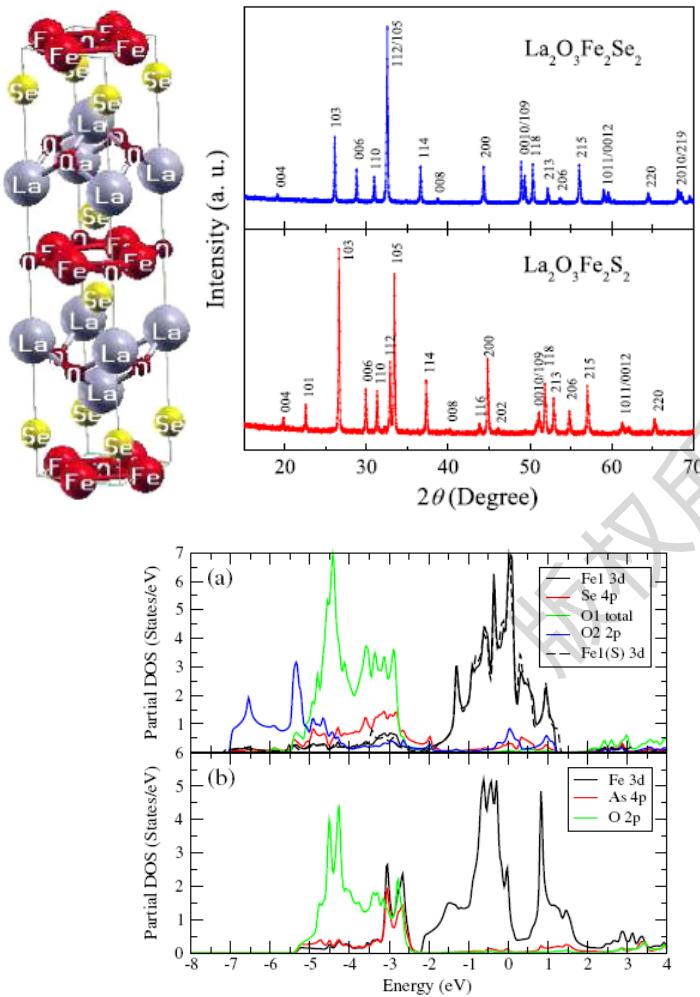


Is there a way to tune to an insulator?

# The First Effort: $\text{La}_2\text{O}_3\text{Fe}_2(\text{Se},\text{S})_2$

## Mott Localization in Iron Oxychalcogenides

Jian-Xin Zhu, Minghu Fang, and Qimiao Si et al. *PRL* 104, 216405 (2010)



The second effort:

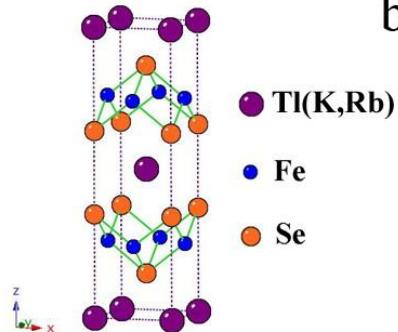
# Super-lattice of Fe-vacancy in $\text{Ti}^{1+}\text{Fe}^{2+}_x\text{Se}^{2-}_2$

Minghu Fang et al, arXiv. 1012.5236, EPL94, (2011) 27009

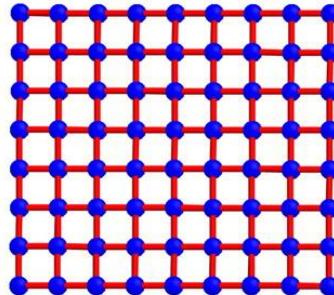
K. Klepp et al. *Monatsh. Chem.*, 109 (1978) 18;

M. Zabel et al, *Rev. Chim. Miner.* 21 (1984) 139;

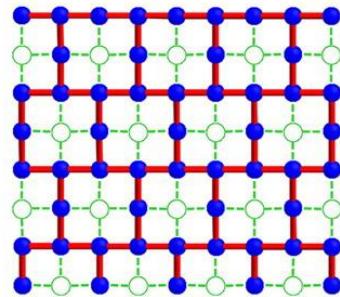
a



b

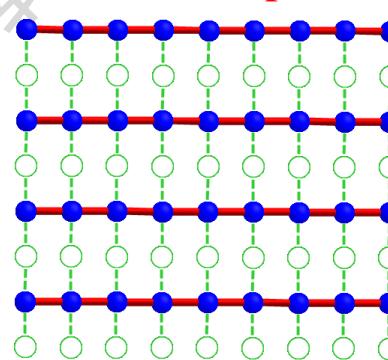


c

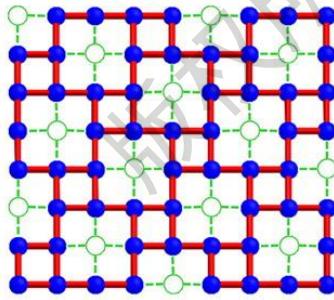


$x = 2.00$

$x = 1.00$ , 112 phase



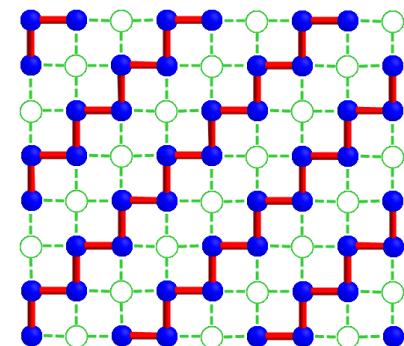
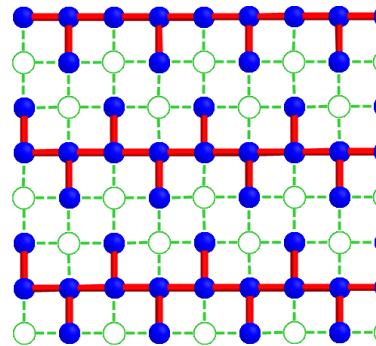
d



$x = 1.50$ ,  $\sqrt{2} \times \sqrt{2}$

$x = 1.60$ ,  $\sqrt{5} \times \sqrt{5}$

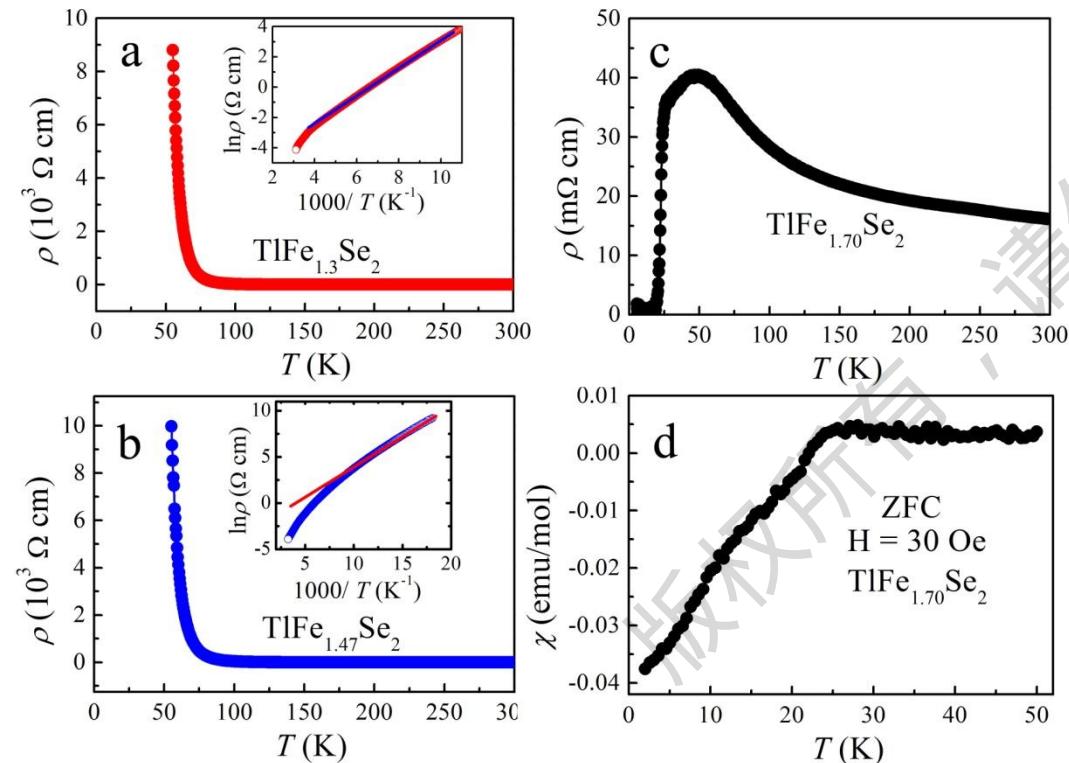
$x = 1.33$ , two possibilities



They should be an AFM insulator or semiconductor.

# Evolution from an AFM Insulating to SC in $\text{TiFe}_x\text{Se}_2$ ( $1.30 \leq x \leq 1.70$ ) crystals

Minghu Fang et al arXiv. 1012.5236, EPL94, (2011) 27009



Composition determined by EDXS.

- The starting materials:  
 $\text{Ti}_{\textcolor{red}{z}}\text{Fe}_2\text{Se}_2$  ( $0.4 \leq z \leq 1.0$ )  
 $\text{TiFe}_{\textcolor{red}{z}}\text{Se}_2$  ( $1.5 \leq z \leq 3.0$ )

A series of crystals obtained:  
 $\text{TiFe}_x\text{Se}_2$  ( $1.3 \leq x \leq 1.70$ ).

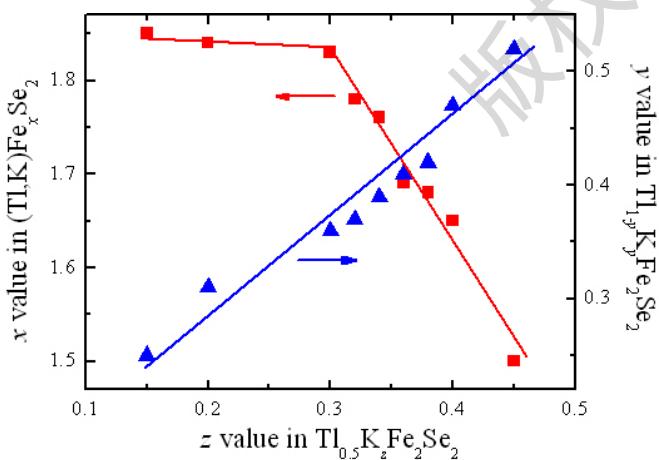
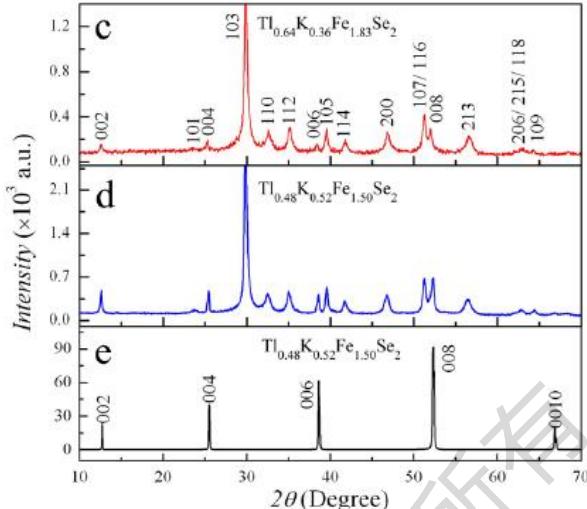
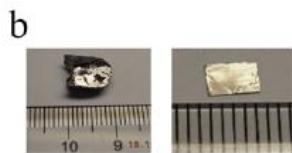
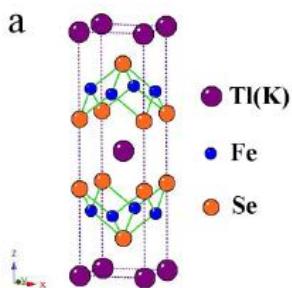
We found that:

- It is difficult that  $x > 1.70$ .
- $x = 1.30, 1.47$ , an insulator. The  $\rho(T)$  exhibits a thermal activated behavior. The activated energy  $E_a = 80.2, 57.7 \text{ meV}$ .
- $x = 1.70$  crystal, SC with  $T_c^{\text{mid}} = 22.4 \text{ K}$ ,  $T_c^{\text{zero}} = 20 \text{ K}$ , but SC volume fraction is very small (<1%).

To get bulk SC, it is necessary to increase Fe content,

## (Tl,K)Fe<sub>x</sub>Se<sub>2</sub> (1.50≤x≤1.88)

Minghu Fang et al arXiv. 1012.5236, EPL94, (2011) 27009



- We add K to the starting materials.

Tl<sub>0.5</sub>K<sub>z</sub>Fe<sub>2</sub>Se<sub>2</sub> (0.15≤z≤0.45)

Tl<sub>0.4</sub>K<sub>z</sub>Fe<sub>2</sub>Se<sub>2</sub> (0.2≤z≤0.5)

Tl<sub>0.8-z</sub>K<sub>z</sub>Fe<sub>2</sub>Se<sub>2</sub> (0.1≤z≤0.4).

- A series of crystal obtained:

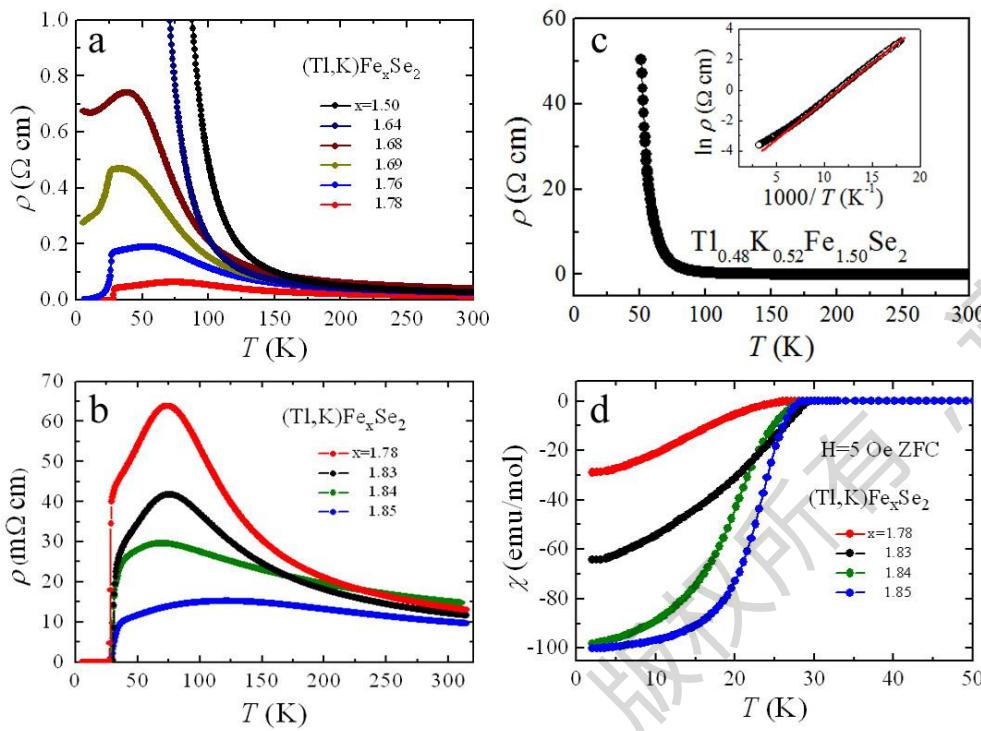
(Tl,K)Fe<sub>x</sub>Se<sub>2</sub> (1.50≤x≤1.88)

- We found that: x value can reach to 1.88, after adding K in the starting materials.

Composition determined by EDXS.

# Evolution from an insulator to SC in (Tl,K)Fe<sub>x</sub>Se<sub>2</sub> (1.50≤x≤1.88) crystals

Minghu Fang et al arXiv. 1012.5236, *EPL*94, (2011) 27009



- (1).  $x=1.50, 1.64$ , an insulator.  
 $\rho(T)$ : thermal activated behavior  
 $E_a=36, 24$ meV for them, respectively.
- (2).  $1.64 < x \leq 1.76$ , insulator phase and SC phase coexists, zero  $\rho$  did not observed above 2K.
- (3).  $x \geq 1.78$ , bulk SC with  $T_c \sim 30$ K, and SC volume fraction increases with Fe-content.
- (4). There is a hump in  $\rho(T)$  at the normal state for all SC crystals.
- (5). Evolution from an insulator to SC occurs in this system.

Guo et al. *PRB* 82, 180520(2010),

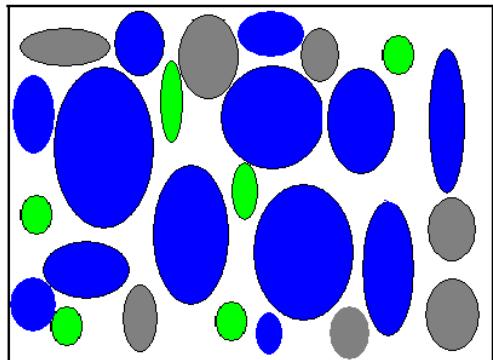
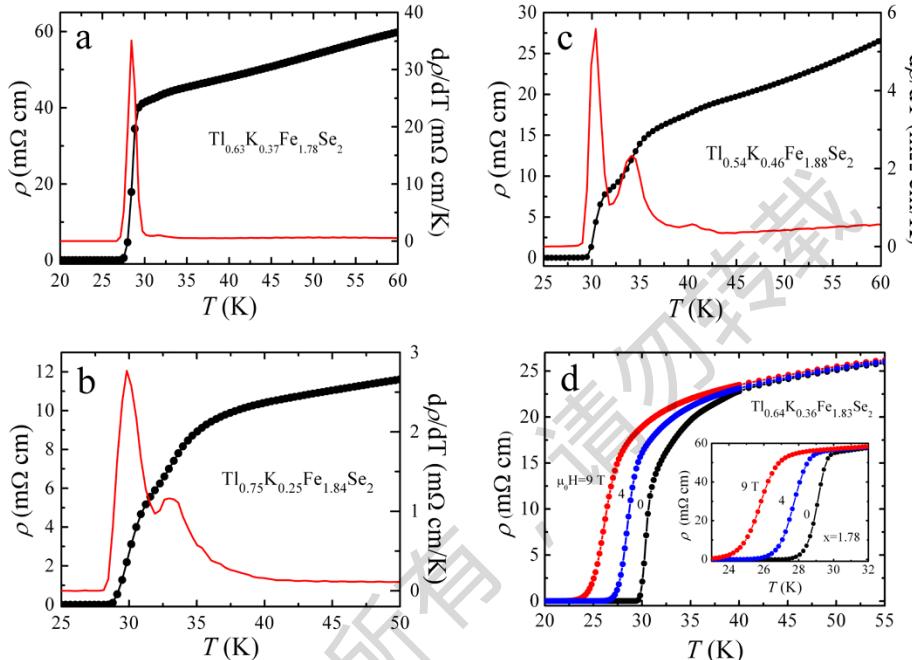
$K_{0.8}Fe_2Se_2$ ,  $T_c=30$ K SC

Krzton-Maziopa et al. *J. Phys. Cond. Matter* 23, 052203(2011)

$Cs_{0.8}Fe_2Se_2$ ,  $T_c=27.4$ K

# 40K SC phase in (Tl,K)Fe<sub>x</sub>Se<sub>2</sub> system

Minghu Fang et al arXiv. 1012.5236, EPL 94, (2011) 27009



$x \approx 1.78 \quad T_c \approx 30\text{K}$

$x \approx 1.80 \quad T_c \approx 35\text{K}$

$x \approx 1.90 \quad T_c \approx 40\text{K}$

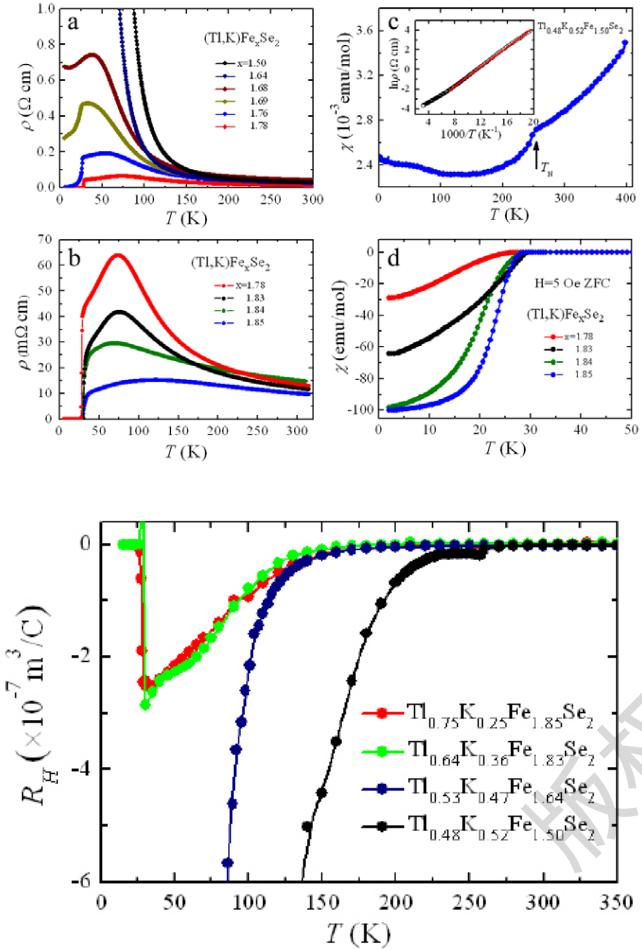
(1).  $x=1.78$ ,  $T_c=28.4\text{K}$ , one SC transition.

(2).  $x=1.84$ ,  $T_c=29.3\text{K}, 33\text{K}$  two SC transitions.

(3).  $x=1.88$ ,  $T_c=30.4\text{K}, 34.1\text{K}$  and  $40.4\text{K}$  three transitions.

Phase separation in Fe-layers for the disorder phase.

# Hall coefficient, $R_H(T)$ , for $(\text{Ti},\text{K})\text{Fe}_x\text{Se}_2$ crystals



We choose four crystals to measure  $R_H(T)$ .  
Two insulators, Two superconductors.

- (1) The negative value of  $R_H$  indicates that the carriers is dominated by electrons, which is consistent with the recent ARPES results, no hole pocket.
- (2)  $|R_H|$  value increases sharply at  $T_N=250$ ,  $123\text{K}$  for both insulators, indicating electron localization occurs.
- (3)  $|R_H|$  value decreases with increasing Fe-content, its value is almost the same for both SC crystals.

Fig. 5: (Color online) Temperature dependence of Hall coefficient for  $(\text{Ti},\text{K})\text{Fe}_x\text{Se}_2$  ( $x = 1.50, 1.64, 1.83$  and  $1.85$ ) crystals. For both  $x = 1.50$  and  $1.64$  crystals, the  $|R_H|$  value increases sharply at  $T_N = 250$  and  $123$  K, respectively. The increase of the Fe-content results in the enhancement of the carrier concentration (  $|R_H|$  value decrease). The  $|R_H|$  value seems to be independent of the K content in the crystals.

# Phase diagram in $(\text{Ti},\text{K})\text{Fe}_x\text{Se}_2$ ( $1.30 \leq x \leq 2.0$ )

Minghu Fang et al arXiv. 1012.5236, *EPL* 94, (2011) 27009

There are three composition regions:

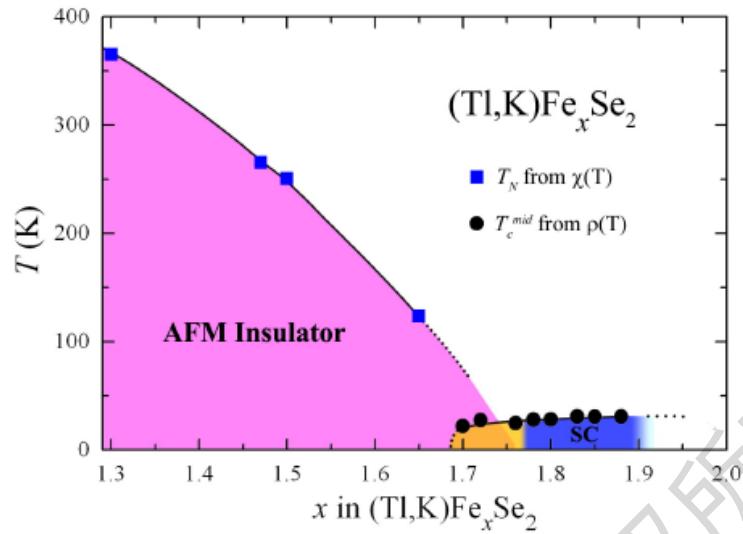
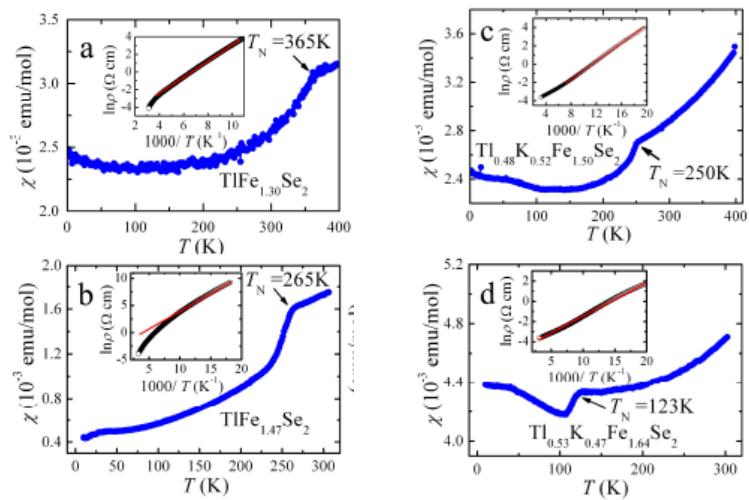


Fig. 6: (Color online) Phase diagram of the magnetism and superconductivity for  $(\text{Ti},\text{K})\text{Fe}_x\text{Se}_2$  ( $1.30 \leq x \leq 2.0$ ). The Néel temperature,  $T_N$ , of the AFM phase, is determined by the onset temperature of the transition in  $\chi(T)$ . The SC transition temperature,  $T_c^{mid}$ , is determined by the middle transition point in  $\rho(T)$ . Note that the crystals with  $x > 1.88$  is difficult to grow in this system due to some chemical reasons.

(1)  $1.30 \leq x < 1.70$ , the compound is an insulator.

(2)  $1.70 \leq x < 1.78$ , SC+Insulator, SC volume fraction is less than 1%.

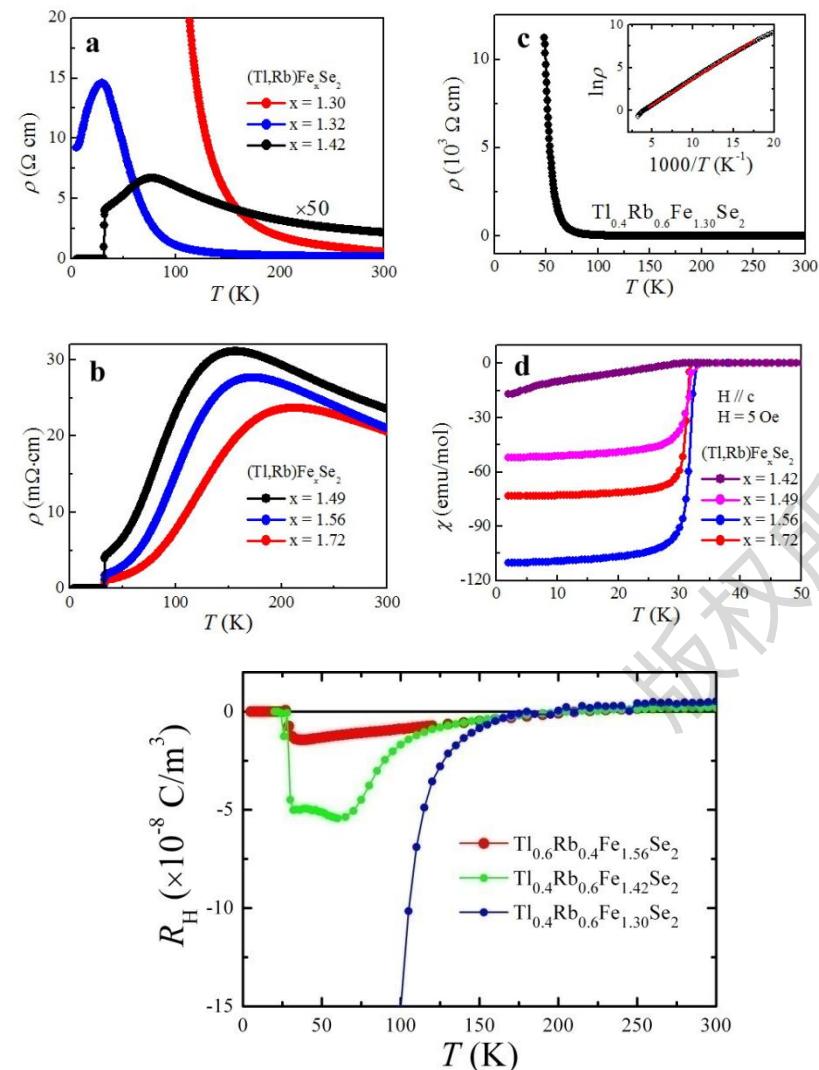
(3)  $1.78 \leq x \leq 1.88$ , bulk SC with  $T_c = 31\text{K}$  emerges.



SC with 31K in  $(\text{Ti},\text{K})\text{Fe}_x\text{Se}_2$  system is at the verge of an AFM insulator.

# Evolution from an insulator to SC in $(\text{Ti},\text{Rb})\text{Fe}_x\text{Se}_2$ ( $1.30 \leq x \leq 1.75$ ) crystals

Hangdong Wang, Minghu Fang et al. *EPL* 93, 47004 (2011)

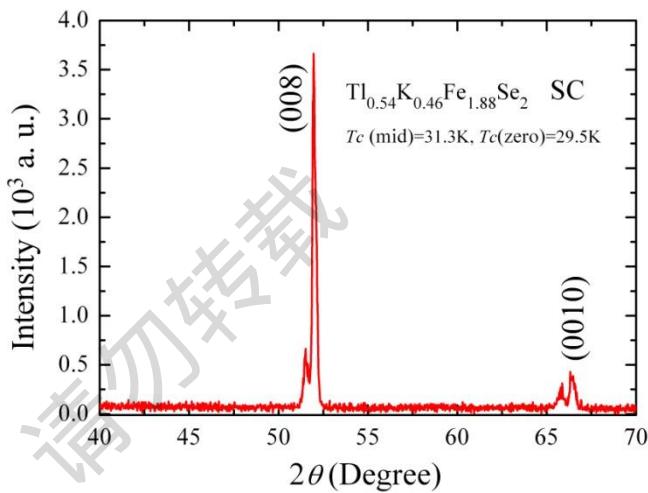
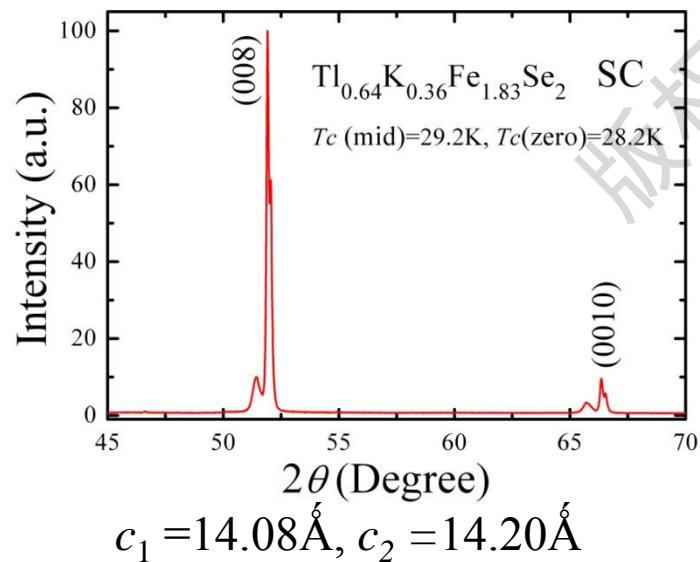
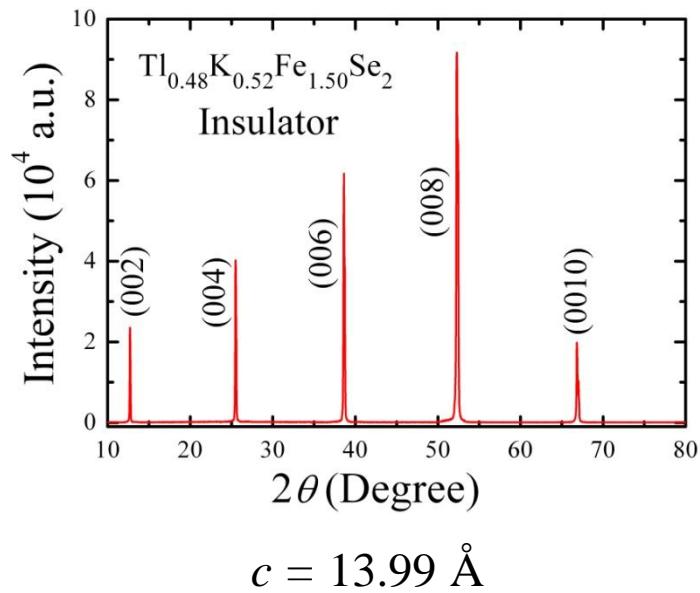


For the superconductors:

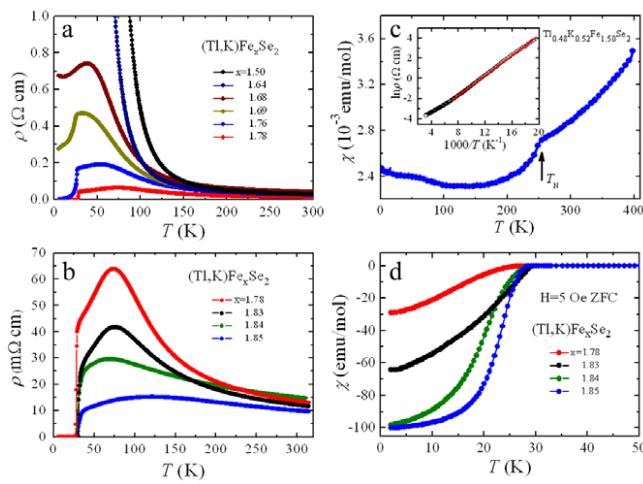
- (1) With Fe-content increase, crystals become SC.
- (2) The SC volume fraction increases with Fe-content.
- (3) Carrier concentration increases with Fe-content.
- (4) Neutron diffraction:  $T_N = 500\text{K}$ , Block AFM coexists with SC phase.

# How to understand the coexistence of Block AFM and SC. Phase separation?

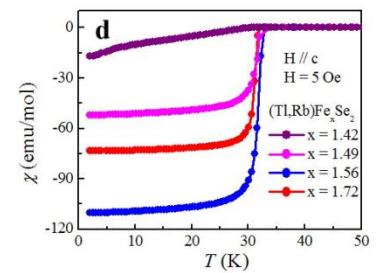
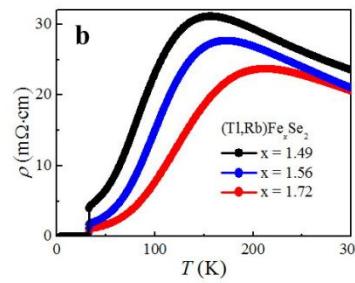
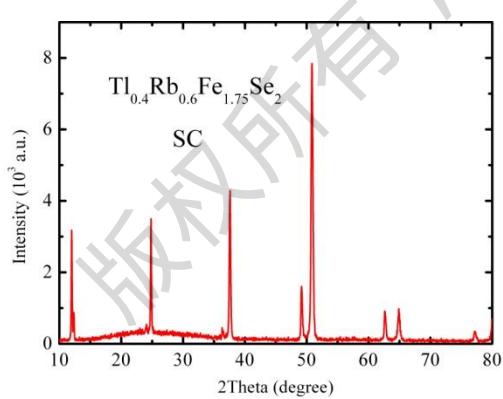
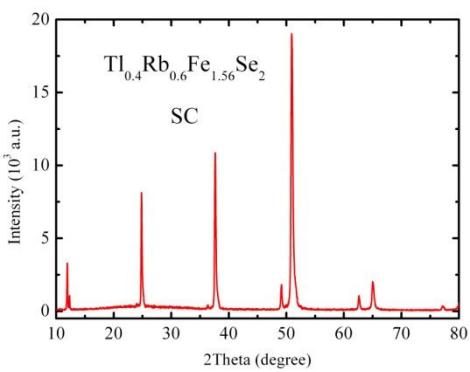
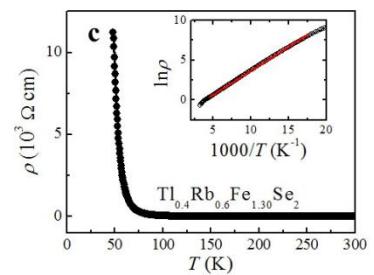
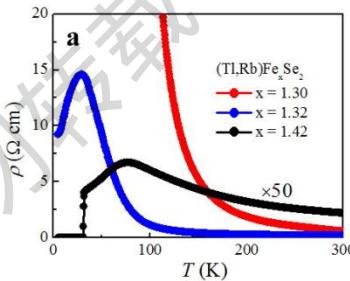
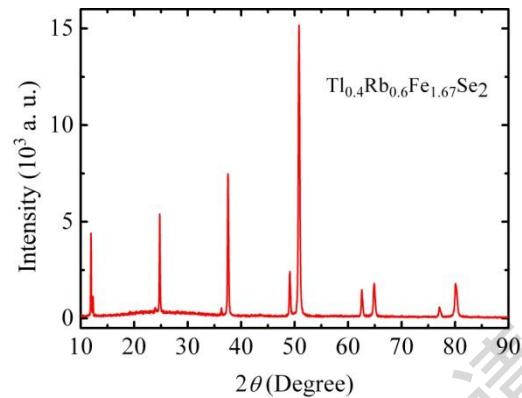
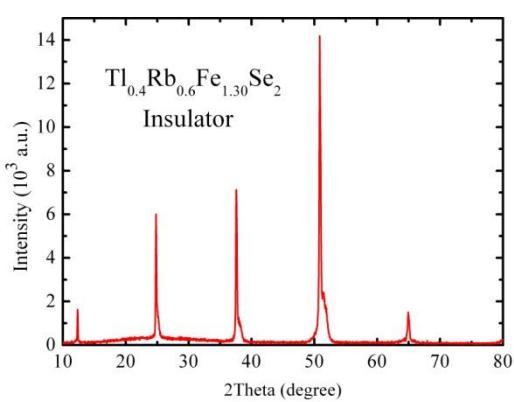
# Evidence 1 -Super-lattice in *c* axis in SC (Tl,K)Fe<sub>x</sub>Se<sub>2</sub>



$$c_1 = 14.07 \text{ \AA}, c_2 = 14.20 \text{ \AA}$$



# Super-lattice in *c* axis in SC $(\text{Ti},\text{Rb})\text{Fe}_x\text{Se}_2$



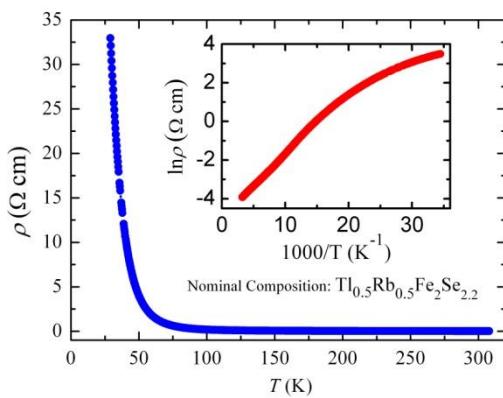
$\text{Ti}_{0.58}\text{Rb}_{0.42}\text{Fe}_{1.72}\text{Se}_2$   
 $c_1 = 14.30 \text{ \AA}$ ,  $c_2 = 14.81 \text{ \AA}$

# Direct evidence 2 for phase separation:

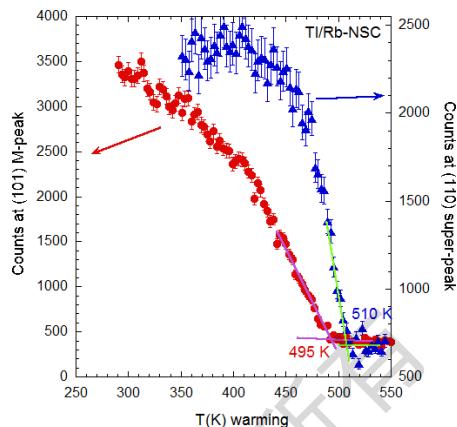
## Neutron Diffraction for $(\text{Ti},\text{Rb})\text{Fe}_x\text{Se}_2$

Q.Z. Huang (Private Comm., unpublished)

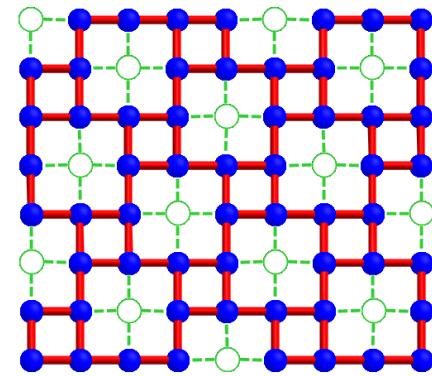
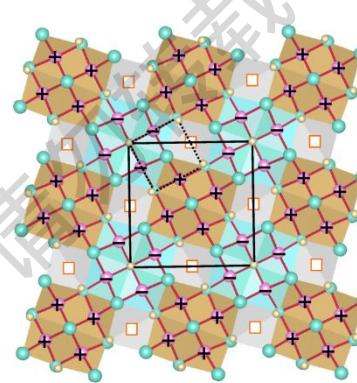
- For Non-SC, AFM insulator (or semiconductor)



$\Delta=400\text{-}500\text{K}$



The Results of ND.

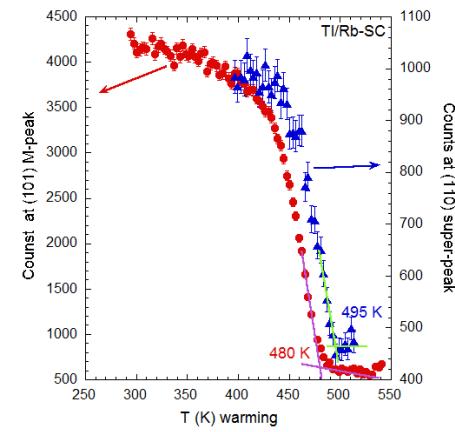
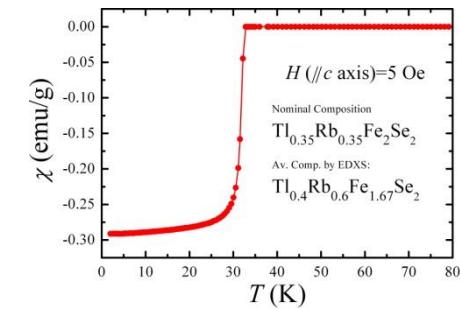
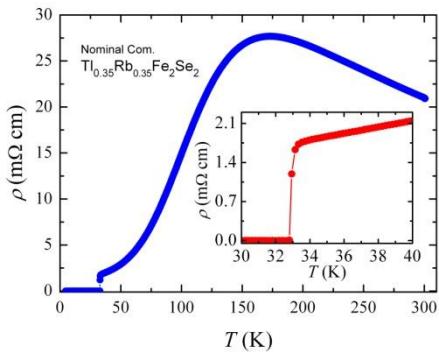


Wei Bao et al.  
arXiv. 1102.3674,  
CPL28, 086104(2011),

Minghu Fang et al.  
arXiv. 1012.5236,  
EPL94, (2011)27009

- Nom. Comp.:  $\text{Ti}_{0.50}\text{Rb}_{0.50}\text{Fe}_2\text{Se}_{2.2}$
- Aver. Comp. by EDS:  $\text{Ti}_{0.46}\text{Rb}_{0.54}\text{Fe}_{1.33}\text{Se}_2$
- Fitting Comp. by ND at 550K:  
 $\text{Ti}_{0.452}\text{Rb}_{0.452}\text{Fe}_{1.578}\text{Se}_2$
- HT (>510K), pure 122 structure,  
 $I4/mmm$ ,  $(\text{Ti},\text{Rb})_{0.904}\text{Fe}_{1.578}\text{Se}_2$
- LT (<500K), pure 245 block phase.  
 $I4/m$ ,  $(\text{Ti},\text{Rb})_{0.904}\text{Fe}_{1.578}\text{Se}_2$

# For SC $\text{Ti}_{0.5}\text{Rb}_{0.5}\text{Fe}_{1.67}\text{Se}_2$ crystals

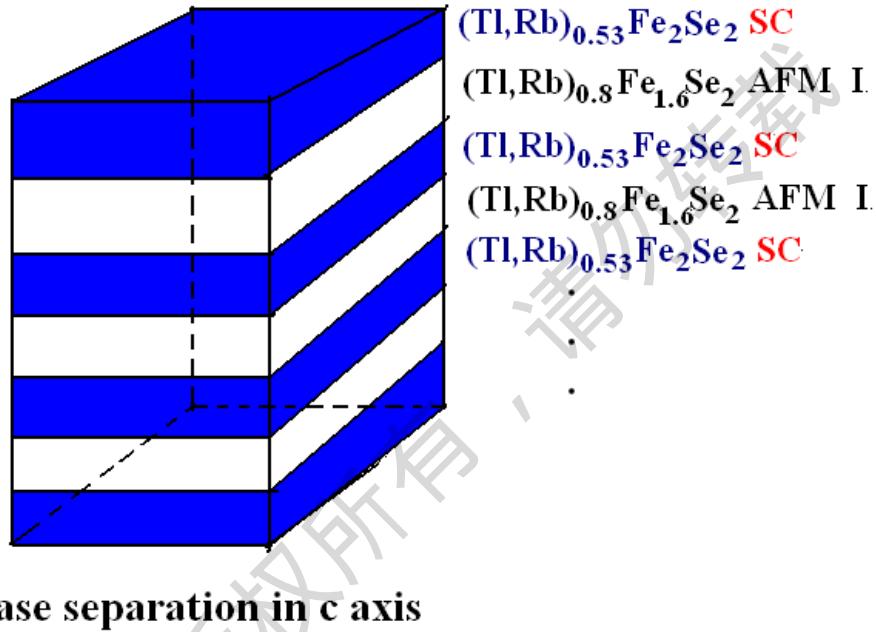


- Nom. Comp.:  $\text{Ti}_{0.35}\text{Rb}_{0.35}\text{Fe}_2\text{Se}_2$
- Aver. Comp. by EDS:  $\text{Ti}_{0.4}\text{Rb}_{0.6}\text{Fe}_{1.67}\text{Se}_2$
- Fitting Comp. by ND at 550K:  $\text{Ti}_{0.374}\text{Rb}_{0.374}\text{Fe}_{1.764}\text{Se}_2$
- Only 122 phase above 510K.
- Two phase exist below 495K.

RT:  $(\text{Ti},\text{Rb})_{0.826}\text{Fe}_{1.563}\text{Se}_2$  (I4/m, AFM 70.9%)  
+  $(\text{Ti},\text{Rb})_{0.532}\text{Fe}_2\text{Se}_2$  (I4/mmm, Non-mag 21.5%)

	30K	RT	400K
I4/m- 245 phase (AFM)	70.8% $a=8.668\text{\AA}$ , $c=14.235\text{\AA}$	70.9% $a=8.707\text{\AA}$ , $c=14.335\text{\AA}$	70.0% $a=8.730\text{\AA}$ , $c=14.355\text{\AA}$
I4/mmm-122 phase (Non-mag.)	20.8% $a=3.826\text{\AA}$ , $c=14.589\text{\AA}$	21.5% $a=3.842\text{\AA}$ , $c=14.820\text{\AA}$	21.8% $a=3.855\text{\AA}$ , $c=14.894\text{\AA}$

# Different Fe-content in various Fe-layer: Phase separation along *c* axis



Fei Han, H.H. Wen et al *Phil. Mag.* 92(2012), 2553-2562 (Disorder)

Z. Wang, J.Q. Li et al. *PRB* 83, 140505(2011); *EPL* 95, 37007(2011) (TEM)

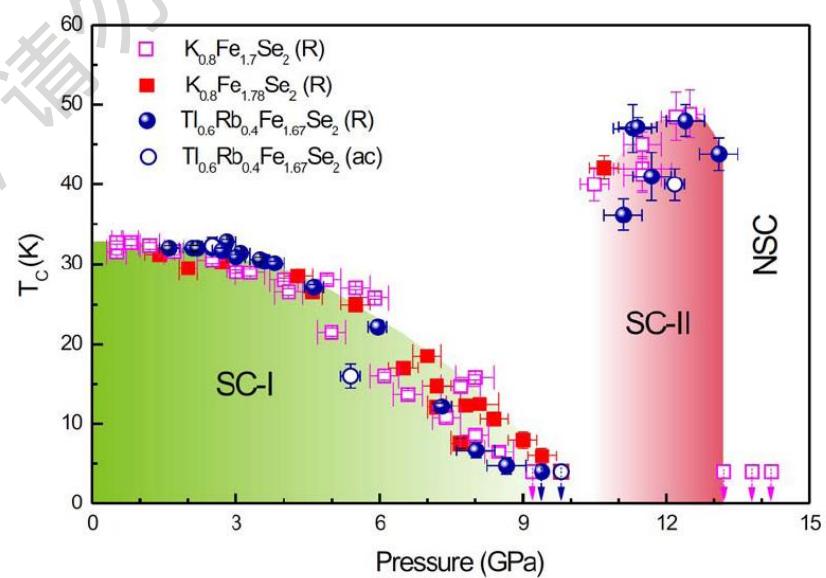
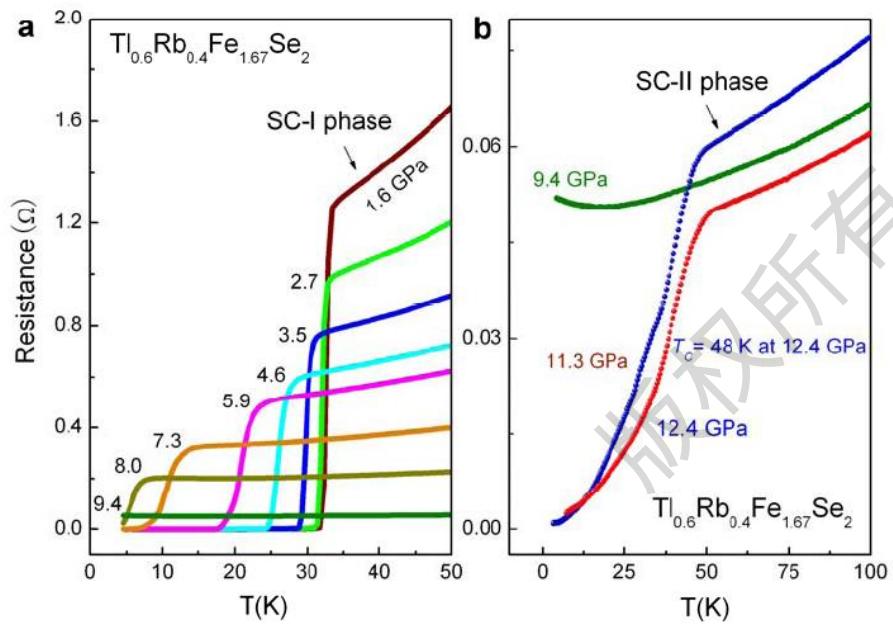
Ricci et al. *PRB* 84, 060511(2011); V. Ksenofontov et al. *PRB* 84, 180508(2011)

R.H. Yuan, N.L. Wang et al. *Sci. Rep.* 2, 221(2012);

W. Li, X. Chen et al. *Nature Phys.* 2155(2011); A. Charnukha et al. *PRL* 109, 017003(2012)

# 48K SC under high pressure

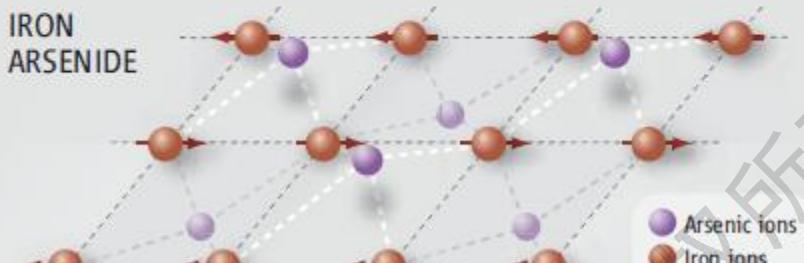
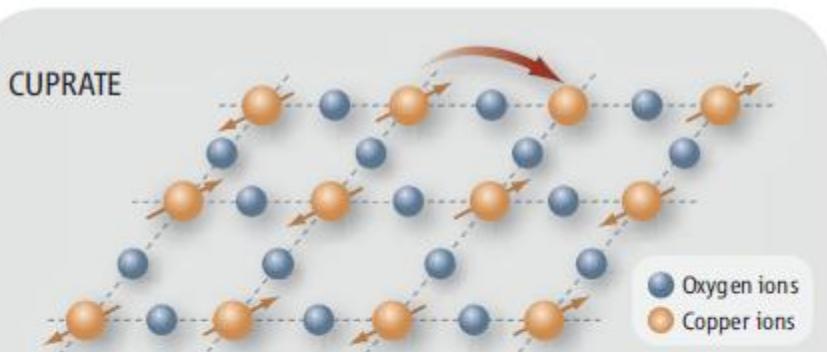
Liling Sun, *Minghu Fang*, Zhongxian Zhao *et al.* *Nature* 483, 67(2012)



## IV. AFM orders in $(\text{Tl}, \text{K}, \text{Rb})\text{Fe}_x\text{Se}_2$

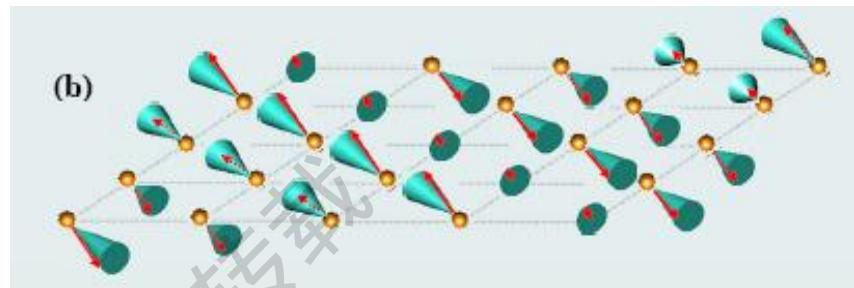
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# Three types AFM Order in the Fe-based Compounds



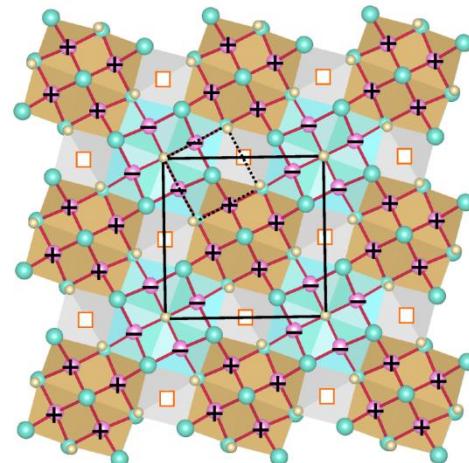
In LaOFeAs, and BaFe<sub>2</sub>As<sub>2</sub>,  
Collinear AFM order.

C. de la Cruz, Pengcheng Dai et al,  
*Nature* 453, 899 (2008)



In FeTe, Bi-collinear AFM order.

W. Bao, Minghu Fang, Z.Q. Mao et al, *PRL*102, 247001(2009)  
M.H. Fang, Z. Q. Mao et al. *PRB*, 78, 224503(2008)

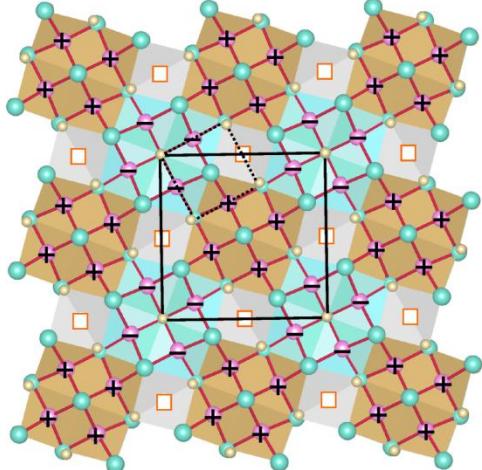
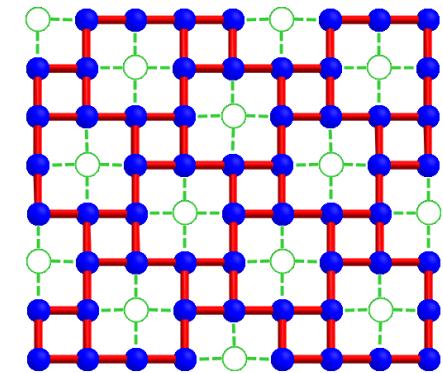


In (Tl,K,Rb,Cs)Fe<sub>x</sub>Se<sub>2</sub>, Block AFM order.

W. Bao et al *CPL*28, 086104(2011),  
W. Bao, X.H. Chen, Minghu Fang et al. *arXiv*1102.2882, *PRL*. 107, 137003 (2011)

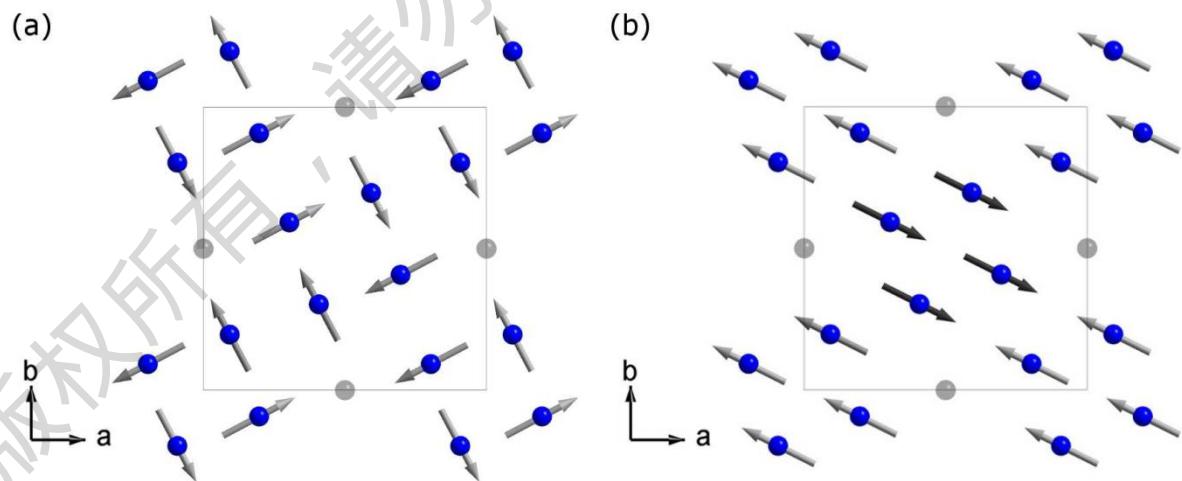
# ND Experiment: Spin reorientation in $\text{TiFe}_{1.6}\text{Se}_2$

A. F. May *et al.* arXiv. 1207.1318, PRL 109, 077003(2012)



Along c axis Block-AFM, Above 100K

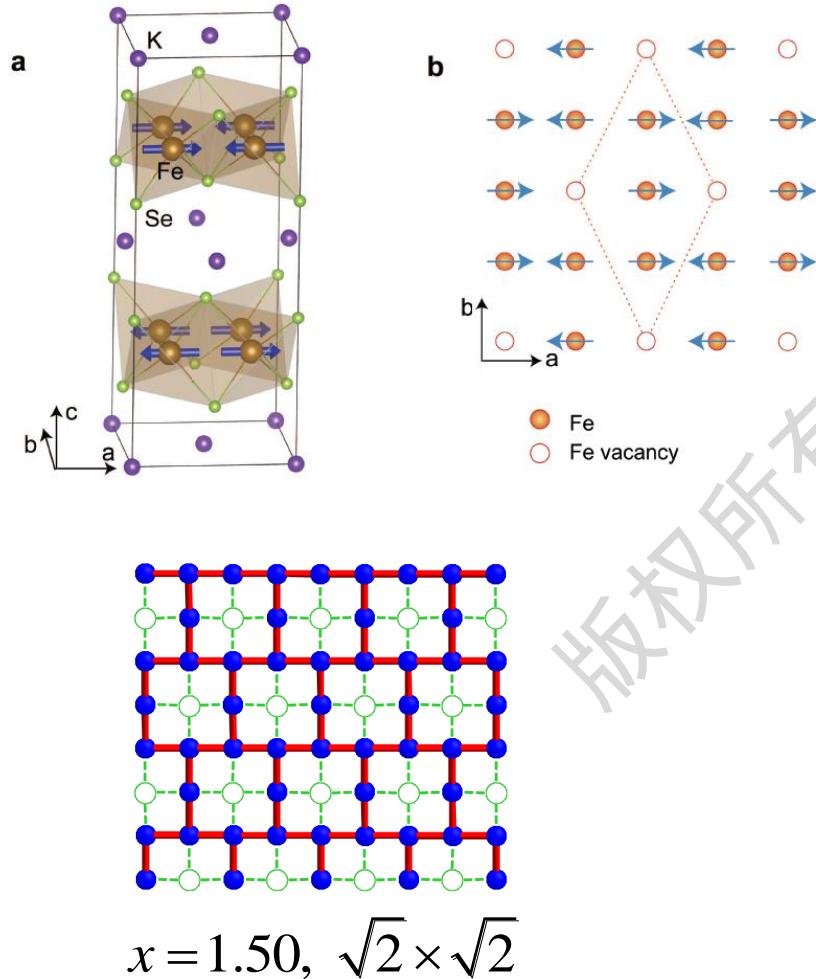
No change in Fe-vacancy super-lattice



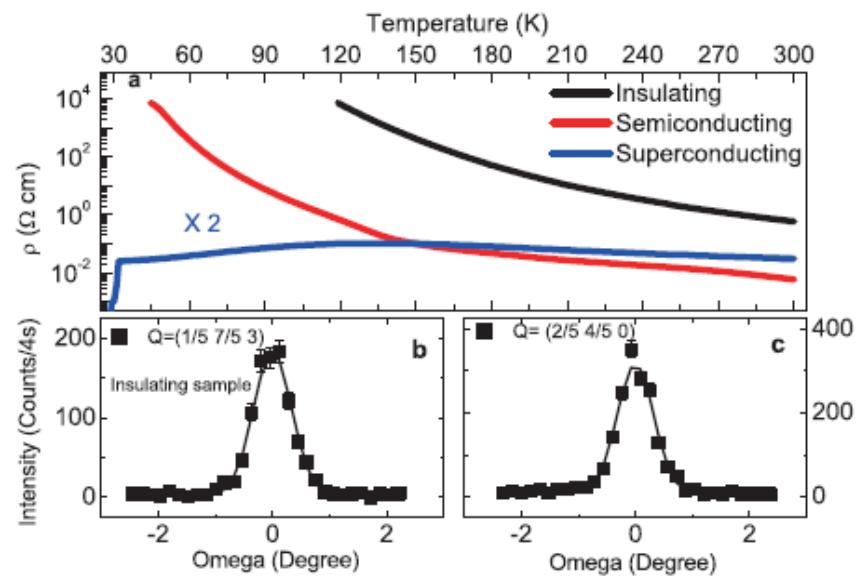
New AFM order, Below 100K  
Non-collinear,  
In-plane Block-checker AFM

# ND Experiment: In addition to the Block-AFM, there is another AFM order in $K_xFe_{2-y}Se_2$

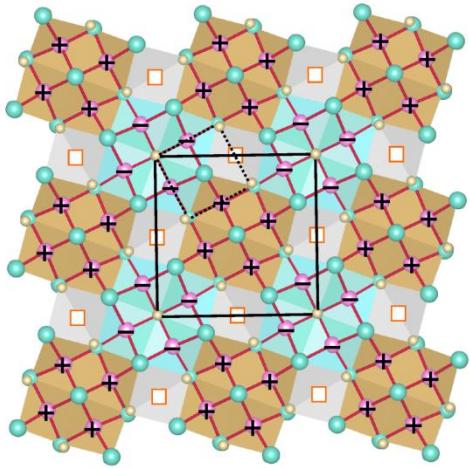
Jun Zhao et al. arXiv. 1205.5992; PRL109, 267003(2012)



In the semiconducting crystals, there is another AFM order. Which is the same as that in pnictides.

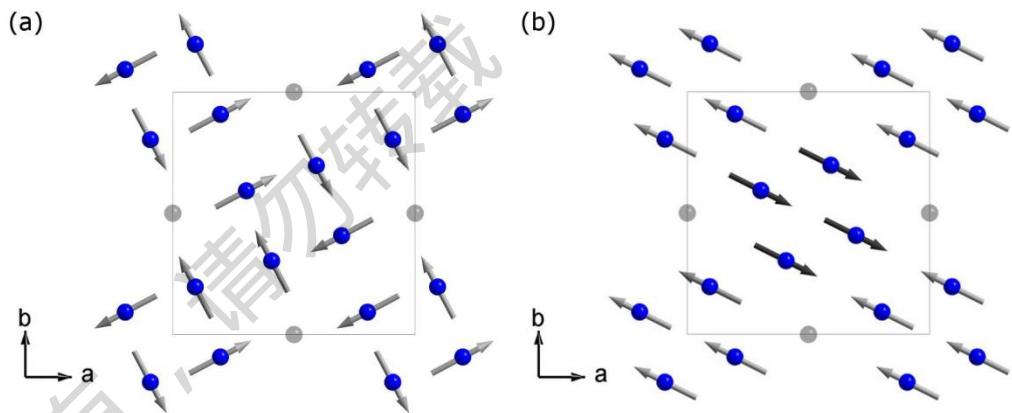


# Which is the parent AFM order of $(\text{Ti},\text{K},\text{Rb})\text{Fe}_x\text{Se}_2$ ?

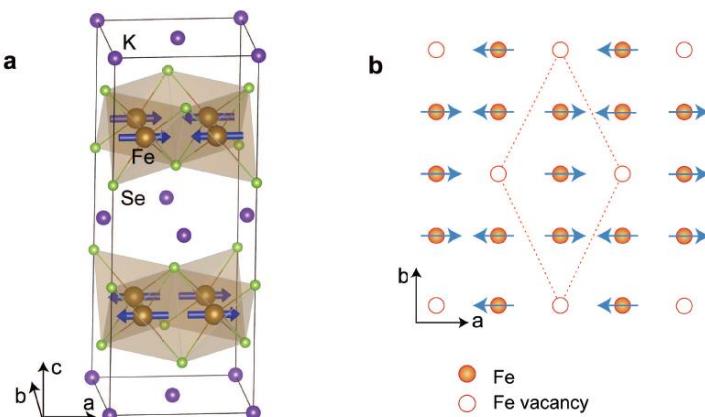


W. Bao et al *CPL*28, 086104(2011),  
W. Bao, et al. *PRL* 107, 137003 (2011)

Jun Zhao et al. *arXiv*. 1205.5992



A. F. May *et al.* *arXiv*. 1207.1318



# Conclusions for $(\text{Ti},\text{K},\text{Rb})\text{Fe}_x\text{Se}_2$ system

- To suggest the existence of **Fe-vacancy super-lattice** in Fe-based SC.
- To discover the **evolution from an insulator to SC** in  $(\text{Ti},\text{K},\text{Rb})\text{Fe}_x\text{Se}_2$  system with increasing Fe content.
- **Phase separation** occurs in the new 122 compound.
- Which is a “**parent AFM**” of  $(\text{Ti},\text{K},\text{Rb})\text{Fe}_x\text{Se}_2$  system?

# RESEARCH FRONTS 2013

100 Top-Ranked Specialties in the Sciences and Social Sciences

PHYSICS

RANK	RESEARCH FRONTS	CORE PAPERS	CITATIONS	MEAN YEAR OF CORE PAPERS
1	Alkali-doped iron selenide superconductors	49	2,000	2011.2
2	Spin-orbit coupled Bose-Einstein condensates	48	1,752	2011.1
3	Dark matter direct detection experiments	48	3,285	2010.6
4	Evidence of majorana fermions	44	2,887	2010.6
5	Top quark forward-backward asymmetry	48	2,213	2010.6
6	Quantum simulations with trapped ions	36	2,017	2010.5
7	Nodal gap structure in Iron-based superconductors	36	1,863	2010.4
8	Holographic Fermi surfaces and entanglement entropy	37	2,643	2010.1
9	Interpreting quantum discord	41	3,650	2010.0
10	Topological Insulators	45	8,957	2009.9

Source: Thomson Reuters Essential Science Indicators

RANK	NATION	%	INSTITUTIONS	%	SCIENTISTS	%
1	China (30)	61.2	Chinese Academy of Sciences (15)	30.6	Gen-Fu Chen, Renmin University (9)	18.4
2	USA (15)	30.6	Renmin University of China (13)	26.5	Xian-Hui Chen, USTC (8)	16.3
3	Germany (7)	14.3	University of Science and Technology of China (8)	16.3	Jun-Bao He, Renmin Univ (7); Du-Ming Wang, Renmin Univ (7); Jian-Jun Ying, USTC (7)	14.3
4	Japan (5) Moldova (5) Switzerland (5)	10.2	Zhejiang University (7)	14.3	Xiang-Feng Wang, USTC (6)	12.2
5	France (4)	8.2	University of Augsberg (6)	12.2	Chi-Heng Dong, Zhejiang Univ (5); Ming-Hu Fang, Zhejiang Univ (5); Jiang-Ping Hu, CAS (5); Ai-Feng Wang, USTC (5); Hang-Dong Wang, Zhejiang Univ (5); Meng Zhang, USTC (5)	10.2

Source: Thomson Reuters Essential Science Indicators

Christopher King  
David A. Pendlebury

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THOMSON REUTERS™

CHINESE SCIENTISTS AT THE FOREFRONT

Thomson Reuters analysts are frequently asked: "When will China have its first home-grown Nobel laureate in the sciences?" It is a question impossible to answer because no one knows what remarkable discoveries will be made in the future or how the Nobel committees decide on their specific honorees for research published in the past. Nonetheless, the rise of China in the internationally influential journal literature indexed by Thomson Reuters—in terms of share of world output—is the most significant event in the structure of scientific research in the past 30 years. In 1983, China produced just .6 percent of articles surveyed by Thomson Reuters in the Science Citation Index (Web of Science). Now, China produces some 13 percent of the literature,

second only to the United States at 29 percent. Output, or world share, does not necessarily align with research impact as measured by citations, but there is typically some correspondence between capacity and quality, eventually.

The research front ranked first in the table on page 18 focuses on a new class of superconducting materials. The analysis below of the national and institutional affiliations of the authors on the front's 49 highly cited core papers reveals China's dominant position in this cutting-edge area of condensed matter physics. Also listed are the researchers with the greatest number of core papers in the front – and all are affiliated with Chinese institutions.

## V. Superconductivity in $\text{TlNi}_2\text{Se}_2$ and $\text{TlNi}_2\text{S}_2$

<b>IA</b>	<b>IIA</b>
<b>1 H</b> 1.00794	<b>4 Be</b> 9.01218
<b>3 Li</b> 6.941	
<b>11 Na</b> 22.9998	<b>12 Mg</b> 24.306
<b>19 K</b> 39.102	<b>20 Ca</b> 40.078
<b>37 Rb</b> 84.75	<b>38 Sr</b> 87.62
<b>55 Cs</b> 132.91	<b>56 Ba</b> 137.34
<b>87 Fr</b> 190.23	<b>88 Ra</b> 196.97

# Periodic Table of the Elements

<b>III A</b>	<b>IV A</b>	<b>V A</b>	<b>VI A</b>	<b>0</b>
<b>5 B</b> 10.811	<b>6 C</b> 12.011	<b>7 N</b> 14.0067	<b>8 O</b> 16.00	<b>9 F</b> 18.9984
<b>13 Al</b> 27.99	<b>14 Si</b> 28.086	<b>15 P</b> 30.974	<b>16 S</b> 32.086	<b>10 Ne</b> 20.1797
<b>31 Ga</b> 69.72	<b>32 Ge</b> 72.61	<b>33 As</b> 74.94	<b>34 Se</b> 78.96	<b>18 Ar</b> 39.948
<b>49 Cd</b> 114.78	<b>50 In</b> 114.87	<b>51 Sb</b> 121.76	<b>52 Te</b> 127.60	<b>53 I</b> 131.90
<b>80 Hg</b> 200.59	<b>81 Tl</b> 204.38	<b>82 Pb</b> 207.2	<b>83 Bi</b> 208.98	<b>86 At</b> 214.00
<b>100 Fm</b> 257.85	<b>101 Md</b> 259.85	<b>102 No</b> 261.90	<b>103 Lr</b> 262.90	

\* Lanthanide Series

<b>58 Ce</b>	<b>59 Pr</b>	<b>60 Nd</b>	<b>61 Pm</b>	<b>62 Sm</b>	<b>63 Eu</b>	<b>64 Gd</b>	<b>65 Tb</b>	<b>66 Dy</b>	<b>67 Ho</b>	<b>68 Er</b>	<b>69 Tm</b>	<b>70 Yb</b>	<b>71 Lu</b>
<b>90 Th</b>	<b>91 Pa</b>	<b>92 U</b>	<b>93 Np</b>	<b>94 Pu</b>	<b>95 Am</b>	<b>96 Cm</b>	<b>97 Bk</b>	<b>98 Cf</b>	<b>99 Es</b>	<b>100 Fm</b>	<b>101 Md</b>	<b>102 No</b>	<b>103 Lr</b>

+ Actinide Series

Nowadays, SC emerging in some Cr, Mn, Cu, Fe, Co compounds with **3d** electrons is close to some **AFM** or **FM** order, such as **Cuprates**, **Fe-based compounds**,  $\text{NaCoO}_2+y\text{H}_2\text{O}$ , especial for the recently discovery **CrAs**, **K<sub>2</sub>Cr<sub>3</sub>As<sub>3</sub>** and **MnP**.

Only in **Ni-based compounds**, SC is not close to any magnetic order, seems to be a conventional SC?

# Ni-Based Superconductors

## Ni-pnictides:

LaONiAs (**2.75 K**), Z. Li *et al* **PRB** 78, 060504(2008), ( $\gamma_N = 7.3 \text{ mJ/mol K}^2$ )  
BaNi<sub>2</sub>As<sub>2</sub> (**0.7 K**), N. Kurita *et al* **PRL** 102, 147004(2009), ( $\gamma_N = 12.3 \text{ mJ/mol K}^2$ )  
SrNi<sub>2</sub>P<sub>2</sub> (**1.4 K**), F. Ronning *et al.* **PRB** 79, 134507(2009), ( $\gamma_N = 15 \text{ mJ/mol K}^2$ )  
BaNi<sub>2</sub>P<sub>2</sub> (**2.4K**), Y. Tomioka *et al.* **PRB** 79, 132506(2009), ( $\gamma_N = 14 \text{ mJ/mol K}^2$ )

Low  $T_C$ , Paramagnetism, Structure Transition, a conventional SC?

## Ni-Chalcogenides:

KNi<sub>2</sub>Se<sub>2</sub> (**0.8 K**), J. R. Neilson *et al* **PRB** 86, 054512(2012), ( $\gamma_N = 44 \text{ mJ/mol K}^2$ )  
KNi<sub>2</sub>S<sub>2</sub> (**0.47K**), J. R. Neilson *et al* **PRB** 87, 045124(2013), ( $\gamma_N = 40 \text{ mJ/mol K}^2$ )

The authors suggested that SC is close to a dynamical CDW order in both systems.

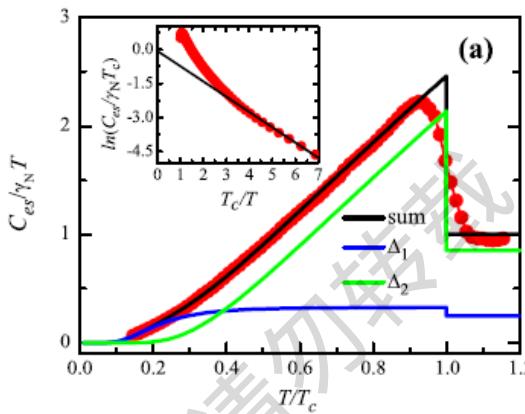
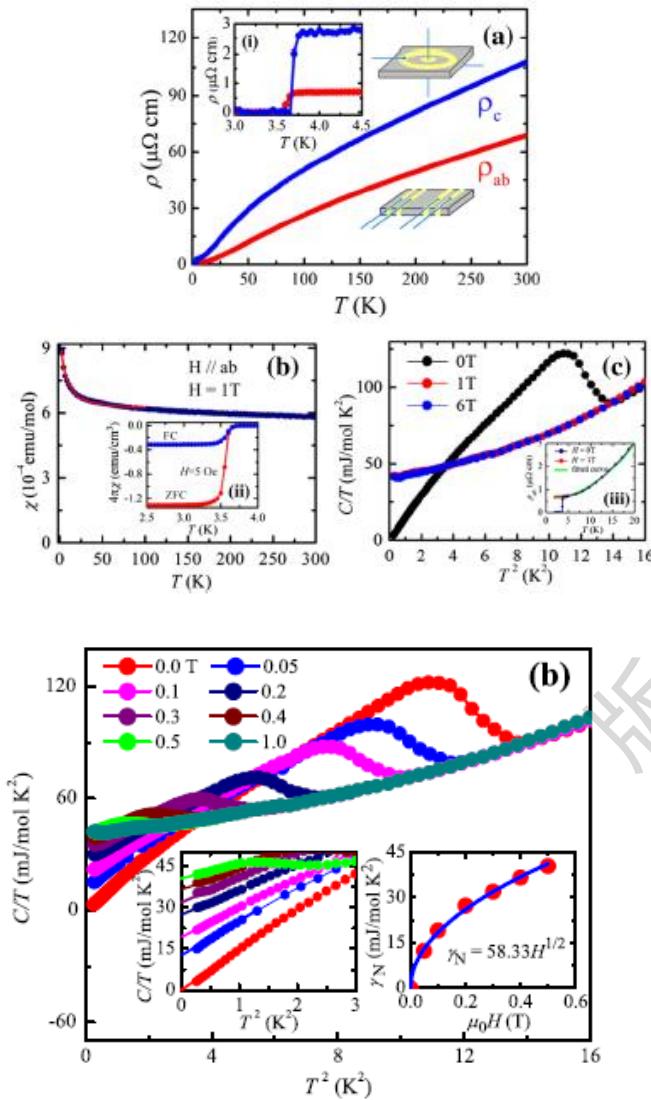
## Our group discovered:

TINi<sub>2</sub>Se<sub>2</sub> (**3.7 K**), M.H. Fang *et al.* **PRL** 111, 207001(2013) ( $\gamma_N = 40 \text{ mJ/mol K}^2$ )  
TINi<sub>2</sub>S<sub>2</sub> (**2.3K**), M.H. Fang *et al* **arXiv:1305.1033**, appearing in **JOP** ( $\gamma_N = 31 \text{ mJ/mol K}^2$ )  
CsNi<sub>2</sub>Se<sub>2</sub> (**2.7K**), M.H. Fang *et al* **arXiv:1508.05167**, ( $\gamma_N = 77.9 \text{ mJ/mol K}^2$ )

Although low  $T_C$ , I shall tell you that their SC is also close to a AFM.  
an Unconventional SC?

# Multi-gap SC in $\text{TlNi}_2\text{Se}_2$

Hangdong Wang, Minghu Fang et al, PRL111, 207001 (2013)

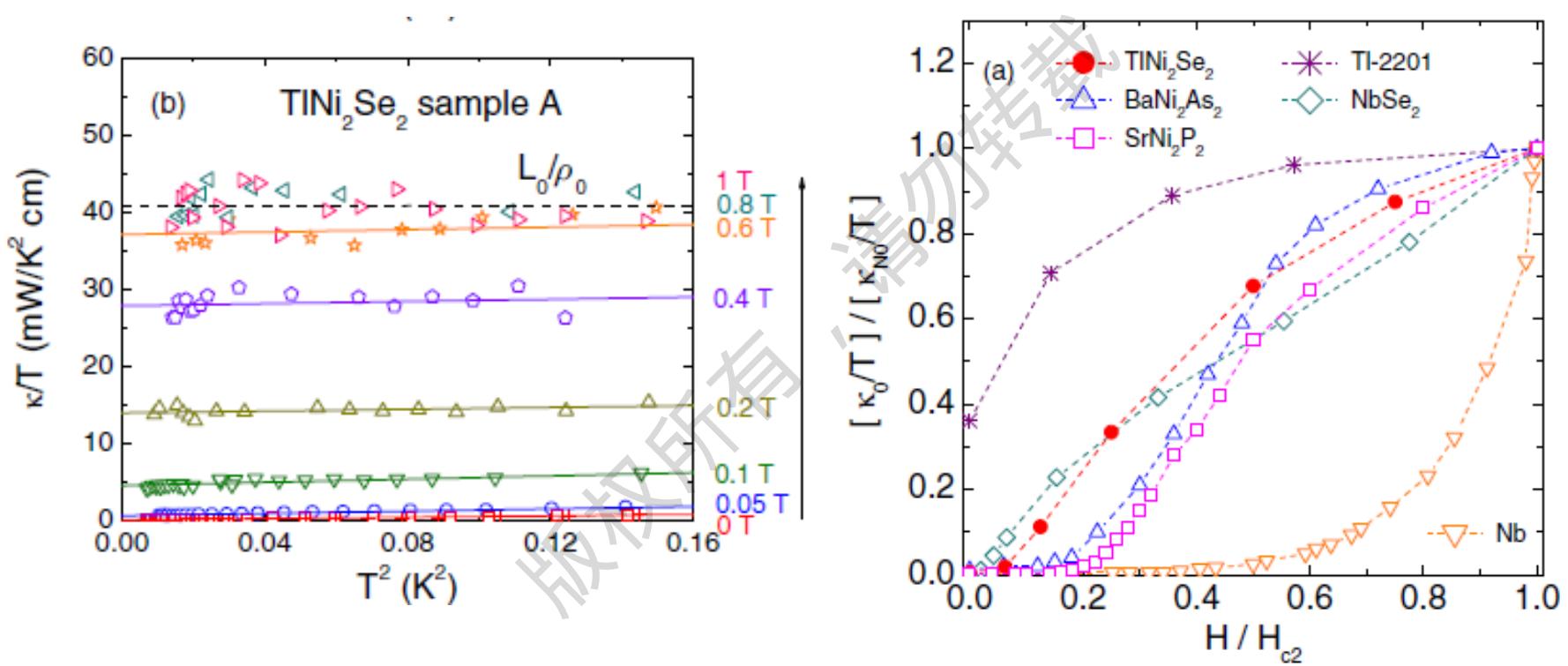


1. SC with  $T_C=3.7\text{K}$
2. In the normal state:  
 $RRR=\rho(300\text{K})/\rho(2\text{K})=103$ , high quality crystals.
3. Small anisotropic.  
 $\rho_c(300\text{K})/\rho_{ab}(300\text{K})=1.57$ , even a layer structure
4. Feimi liquid behavior at LT  
 $\rho_{ab}(T)=\rho_0+AT^2$ ,  $A=4.94\times 10^{-3}\mu\Omega \text{ cm}$
5. Kadowaki-Woods ratio:  $A/\gamma^2=0.308\times 10^{-5}$   
similar to Conventional HF
6.  $\gamma_0=40 \text{ mJ/mol}\cdot\text{K}^2$ ,  $m^*/m_b=14$ , middle correlation?
7.  $\gamma_0(H)\sim H^{0.5}$ , a common feature of  $d$ -wave SC.

Two gaps fitting  
 $\Delta_1=0.84k_B T_C$ , 25%  
 $\Delta_2=2.01k_B T_C$ , 75%

# Thermal Conductivity of $\text{TiNi}_2\text{Se}_2$

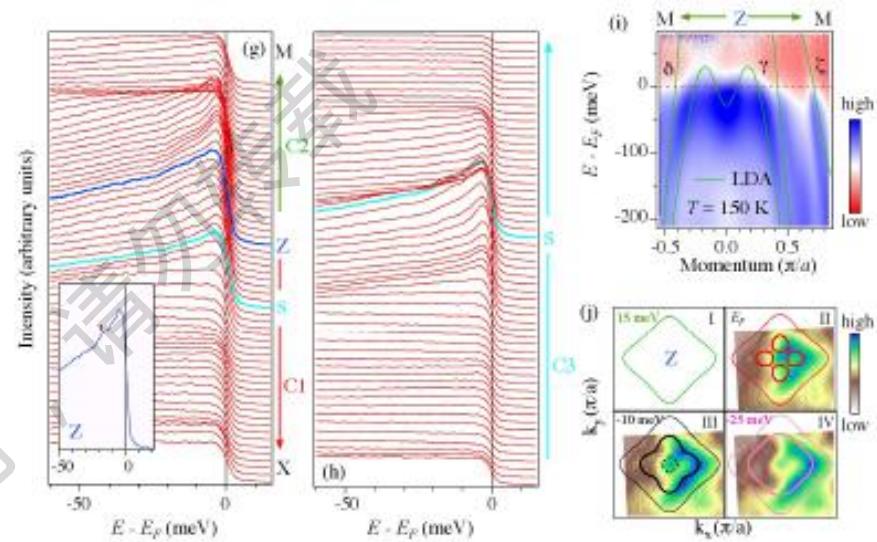
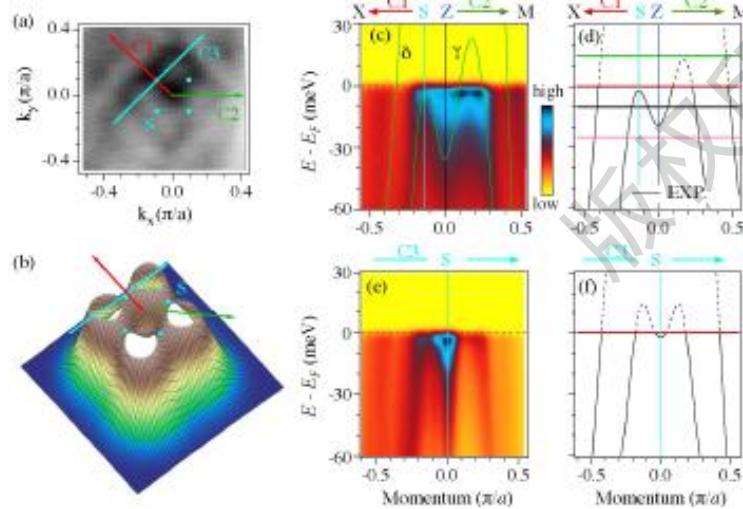
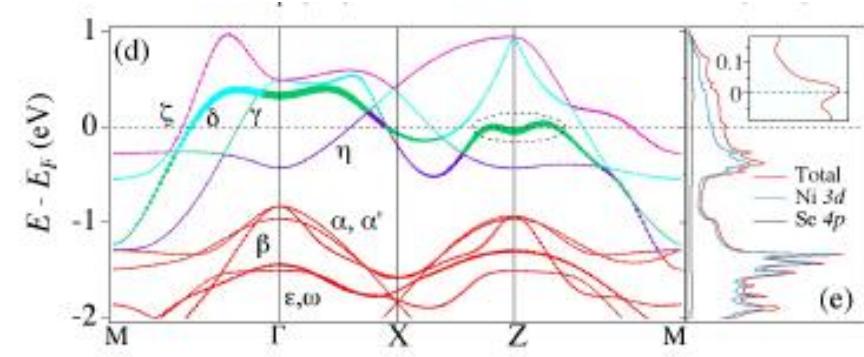
X. C. Hong, Minghu Fang S. Y. Li *et al.* *PRB*90, 060504(R) (2014)



Multi-gap superconductivity, but nodeless!  
Conventional *s*-wave SC?

# Electronic Structure of $\text{TiNi}_2\text{Se}_2$

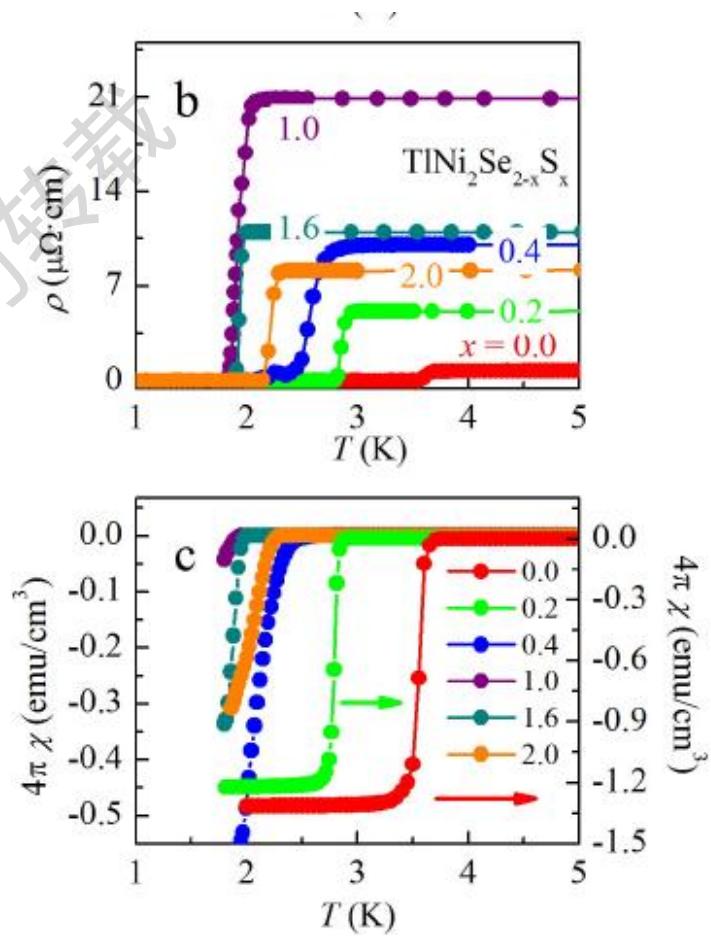
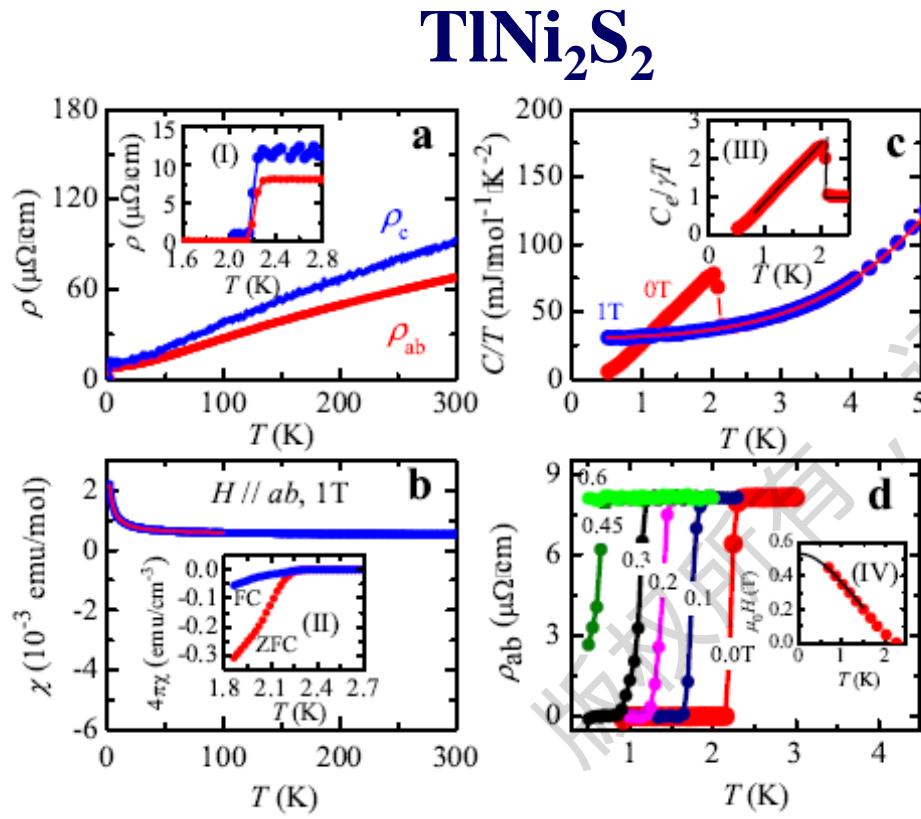
N. Xu, Minghu Fang, H. Ding, and M. Shi *et al.* arXiv. 1412.7016, *PRB* 92, 081116(R) (2015)



1. Near  $E_F$ , Ni 3d - Multiband.
2. Weak electronic correlations, bandwidth renormalization 1.4.
3. Camelback-shaped band lies in the mediate vicinity of Fermi level. A pronounced van Hove singularity results in Heavy band mass.

# SC in $\text{TiNi}_2\text{Se}_{2-x}\text{S}_x$ ( $0 \leq x \leq 2.0$ )

Hangdong Wang, Minghu Fang *et al.* arXiv. 1305.1033, *JOP* in press

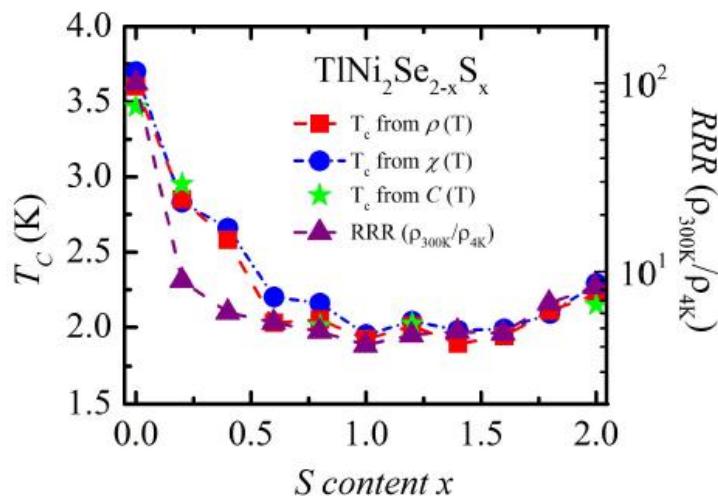
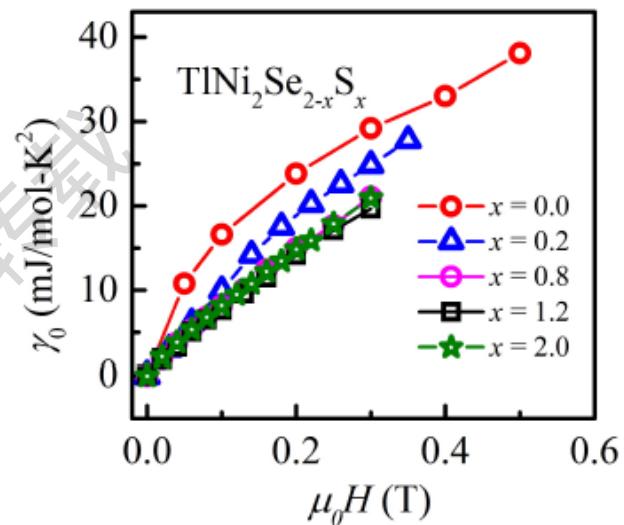
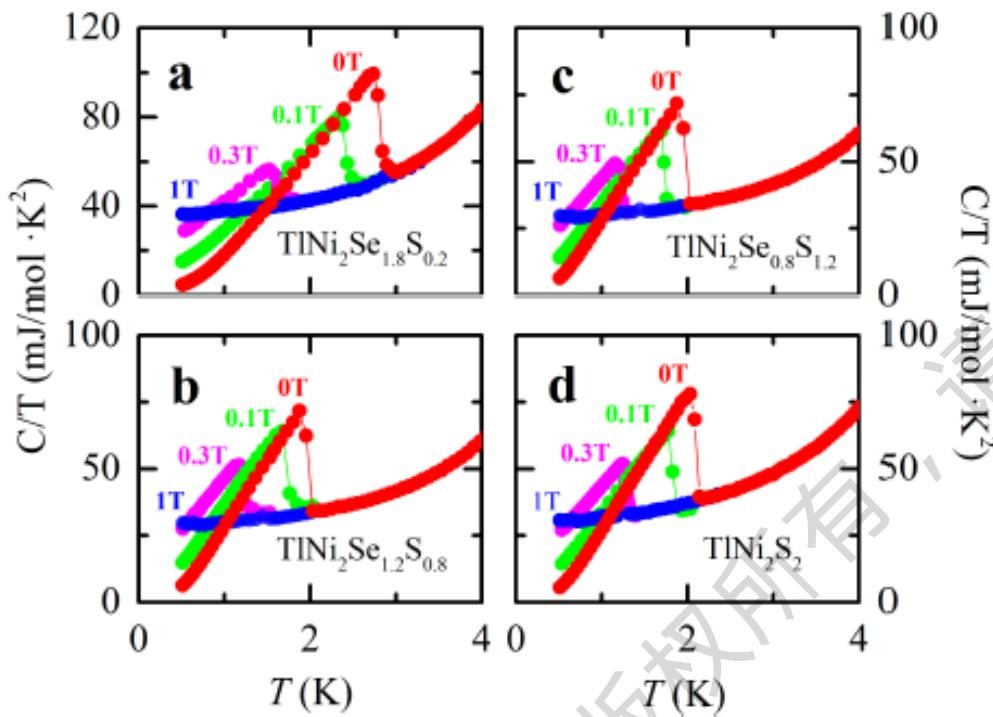


All the  $\text{TiNi}_2\text{Se}_{2-x}\text{S}_x$  ( $0 \leq x \leq 2.0$ ) crystals are SC.

Identical-valance substitution of S for Se may induce:  
Chemical Pressure and Disorder, but no charge carriers.

# SC in $TlNi_2Se_{2-x}S_x$ - continued

Hangdong Wang, Minghu Fang *et al.* arXiv. 1305.1033, *JOP* in press



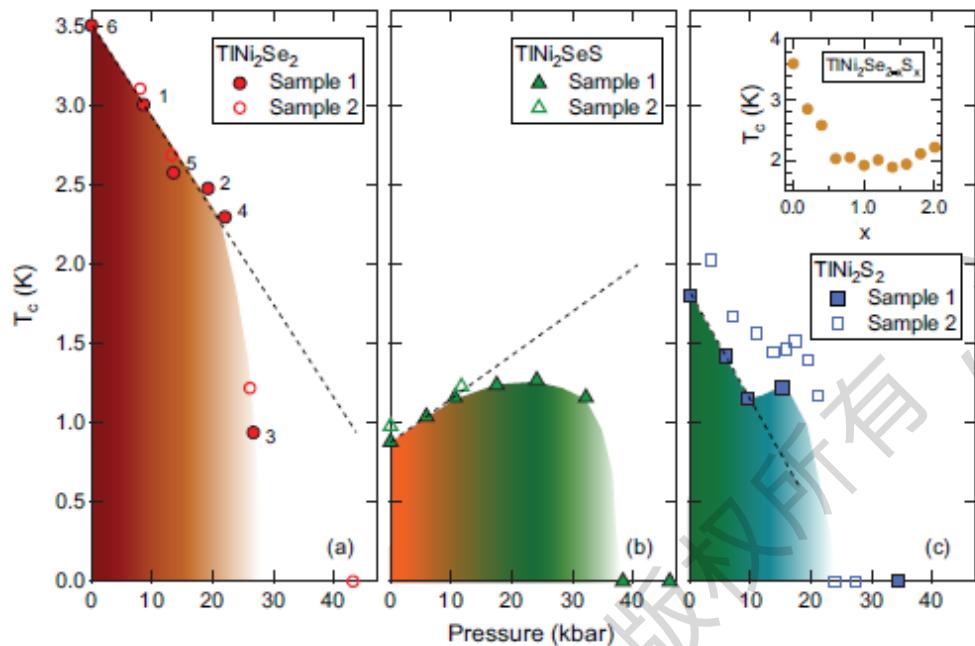
The substitution of S for Se:

1.  $\gamma_0$  decreases.
2.  $\gamma_0(H)$ , From  $H^{0.5}$  to a linear  $H^1$  with S content
3. The relationship between  $T_c$  and disorder.

Provides a platform to study the effect of disorder on the multi-band SC.

# The Pressure Dependence of SC for $\text{TiNi}_2\text{Se}_2$ , $\text{TiNi}_2\text{SeS}$ and $\text{TiNi}_2\text{S}_2$

Swee K. Goh, Hangdong Wang, Minghu Fang *et al.* *PRB*90, 201105(R) (2014)



- (a) At a moderate pressure for all three compositions, SC disappears.
- (b) A dome-shaped pressure dependence of  $T_c$  for  $\text{TiNi}_2\text{SeS}$ .
- (c) Double dome-shaped pressure dependence of  $T_c$  for  $\text{TiNi}_2\text{S}_2$ .

The multi-dome emerges in  $\text{TiNi}_2\text{Se}_{2-x}\text{S}_x$  system. Similar to FeSe: K. Miyoshi *et al.* *JPSJ* 78, 093703(2009),  
M. Bendele *et al.* *PRL* 104, 087003 (2010).  
 $\text{LaFeAsO}_{1-x}\text{H}_x$ , S. Iimura *et al.* *Nat. Commun* 3, 943(2012),  
M. Hiraishi *et al.* *Nat. Phys.* 10, 300(2014)

# Summary for SC in $\text{TiNi}_2\text{Se}_{2-x}\text{S}_x$

- $T_C$  is low, which may relate to a weak correlation.
- A large  $\gamma_N$  may origin from the van Hove singularity.
- Multi-gap nodeless SC, two gaps exist in the SC state.
- $\gamma_N(H) \sim H^{0.5}$  or  $H$ , dependent on S content.
- Dome shape in the pressure dependence of SC.
- $T_C$  relates to the disorder.

Some behaviors is similar to Fe-based SC,  
whether SC in this system is also close to  
magnetic order?

We choose  $\text{Co(3d}^7\text{4s}^2)$  to replace  $\text{Ni(3d}^8\text{4s}^2)$ , what happens?

**Thank you for your attention!**