Recent Development in High Temperature Superconductivity

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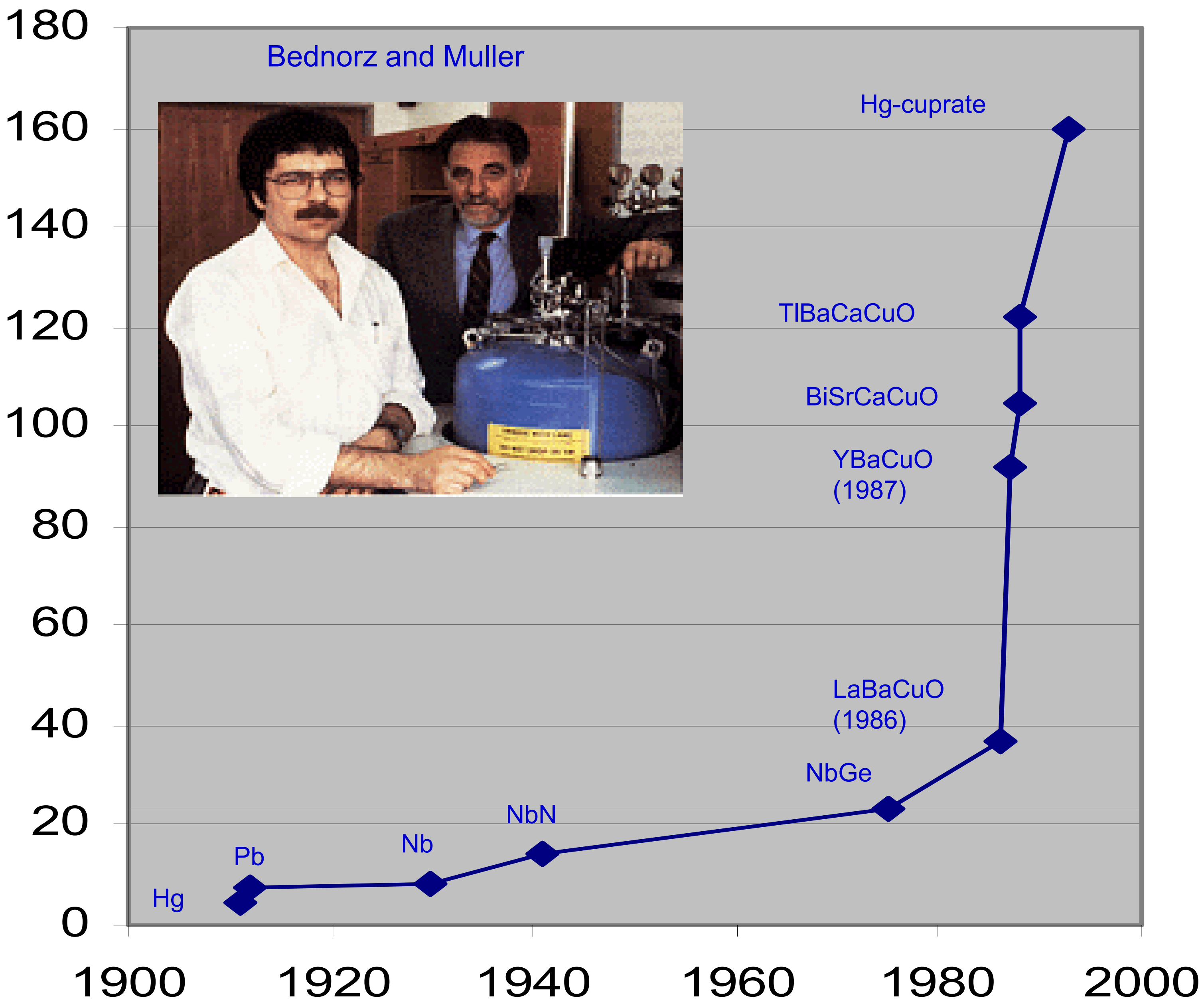
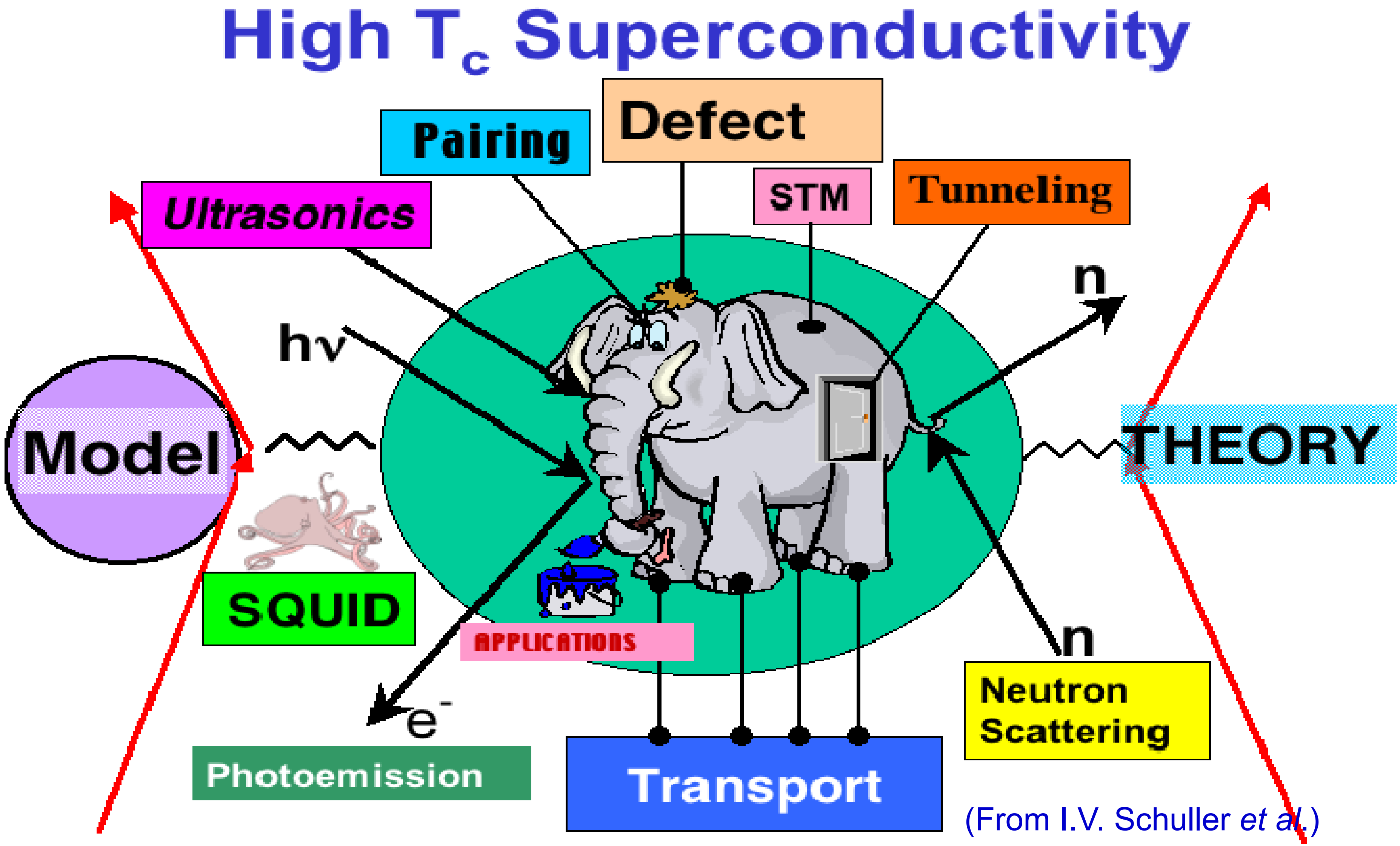
Present at Department of Physics
National Tsing Hua University
Hsinchu, June 3, 2009

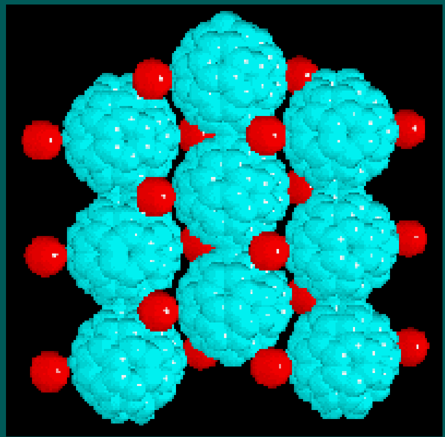

180
160
140
120
100
80
60
40
20
0
1900
1920
1940
1960
1980
2000
Bednorz and Muller
Hg-cuprate
TlBaCaCuO
BiSrCaCuO
YBaCuO
(1987)
LaBaCuO
(1986)
NbGe
NbN
Nb
Pb
Hg

Status of High Temperature Superconductivity

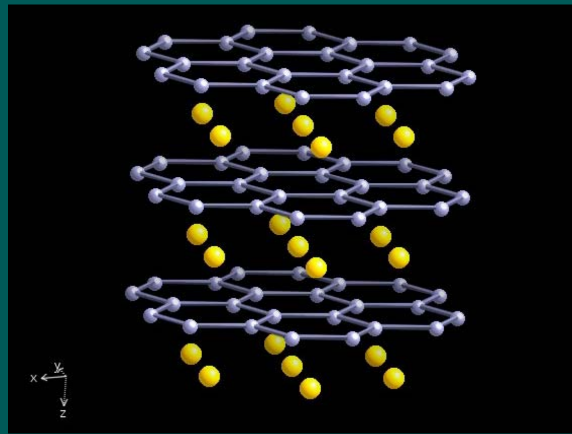


What are the Community best Achieved?

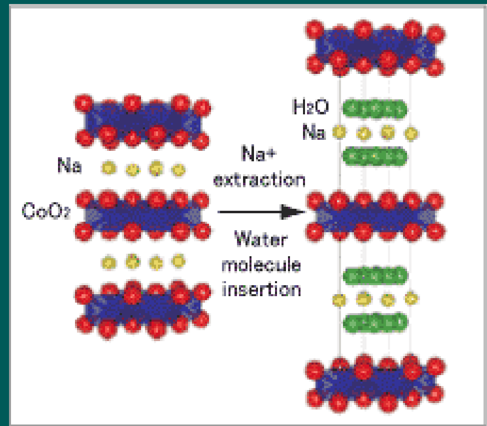
- *A triumph of Chemists, Physicists and Material Scientists*



Rb Dopded C_{60}



MgB_2



$Na_xCO_2 \cdot yH_2O$

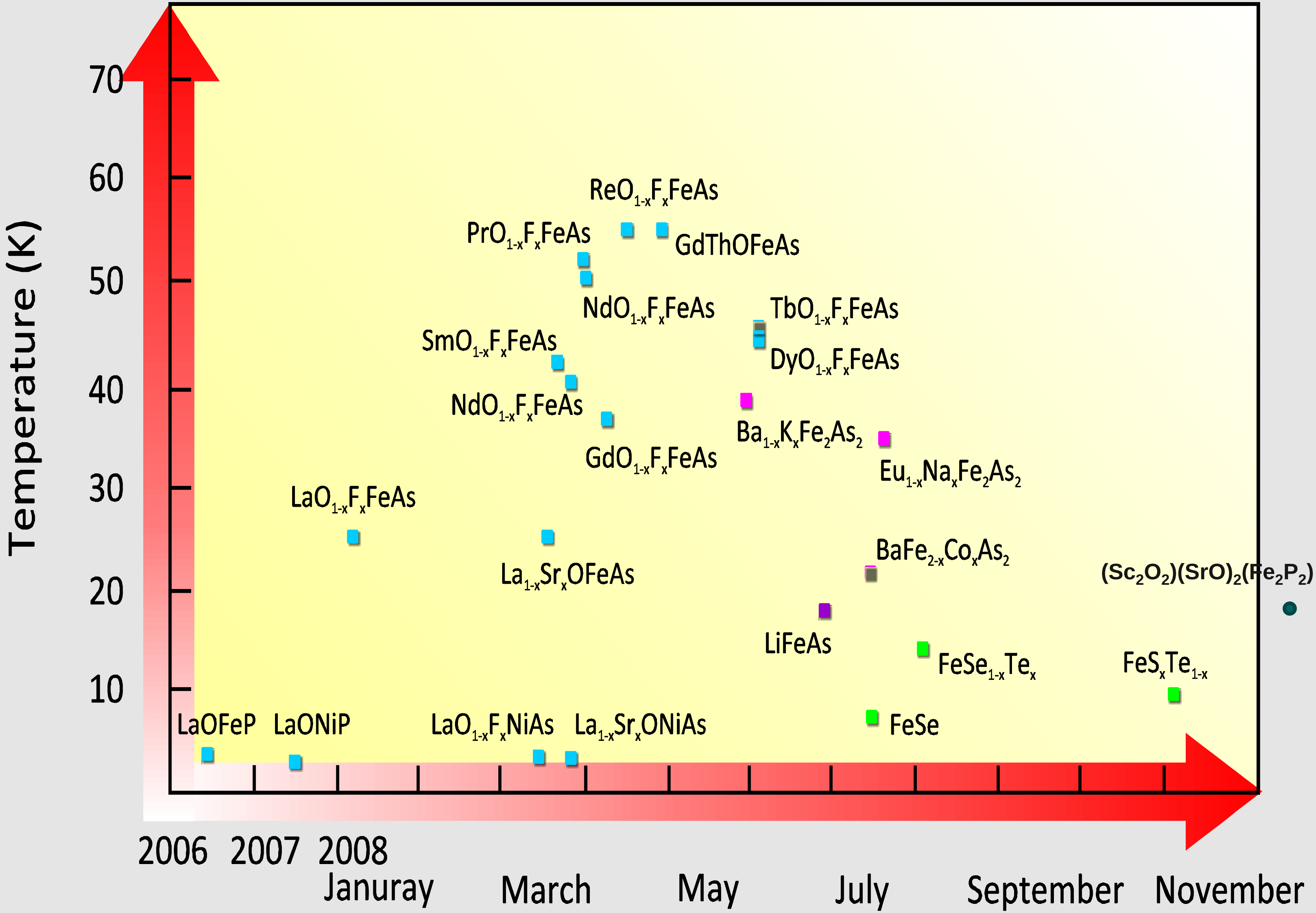
J|A|C|S
COMMUNICATIONS

Published on Web 00/00/0000

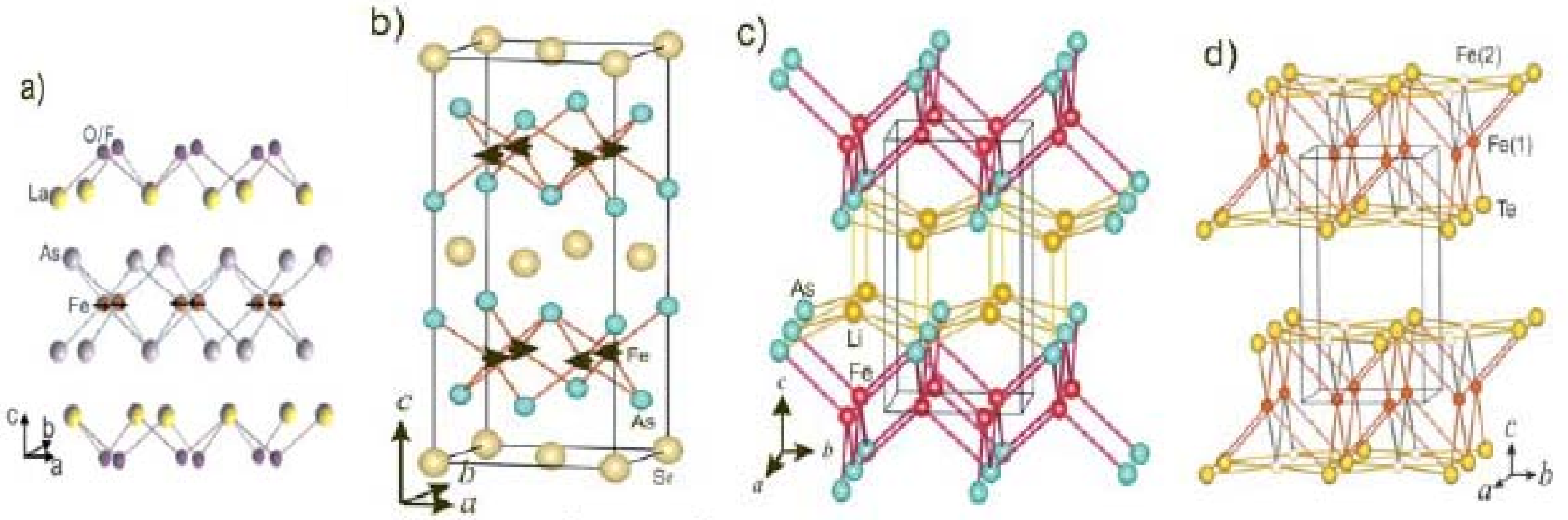
Iron-Based Layered Superconductor $La[O_{1-x}F_x]FeAs$ ($x = 0.05-0.12$) with $T_c = 26$ K

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

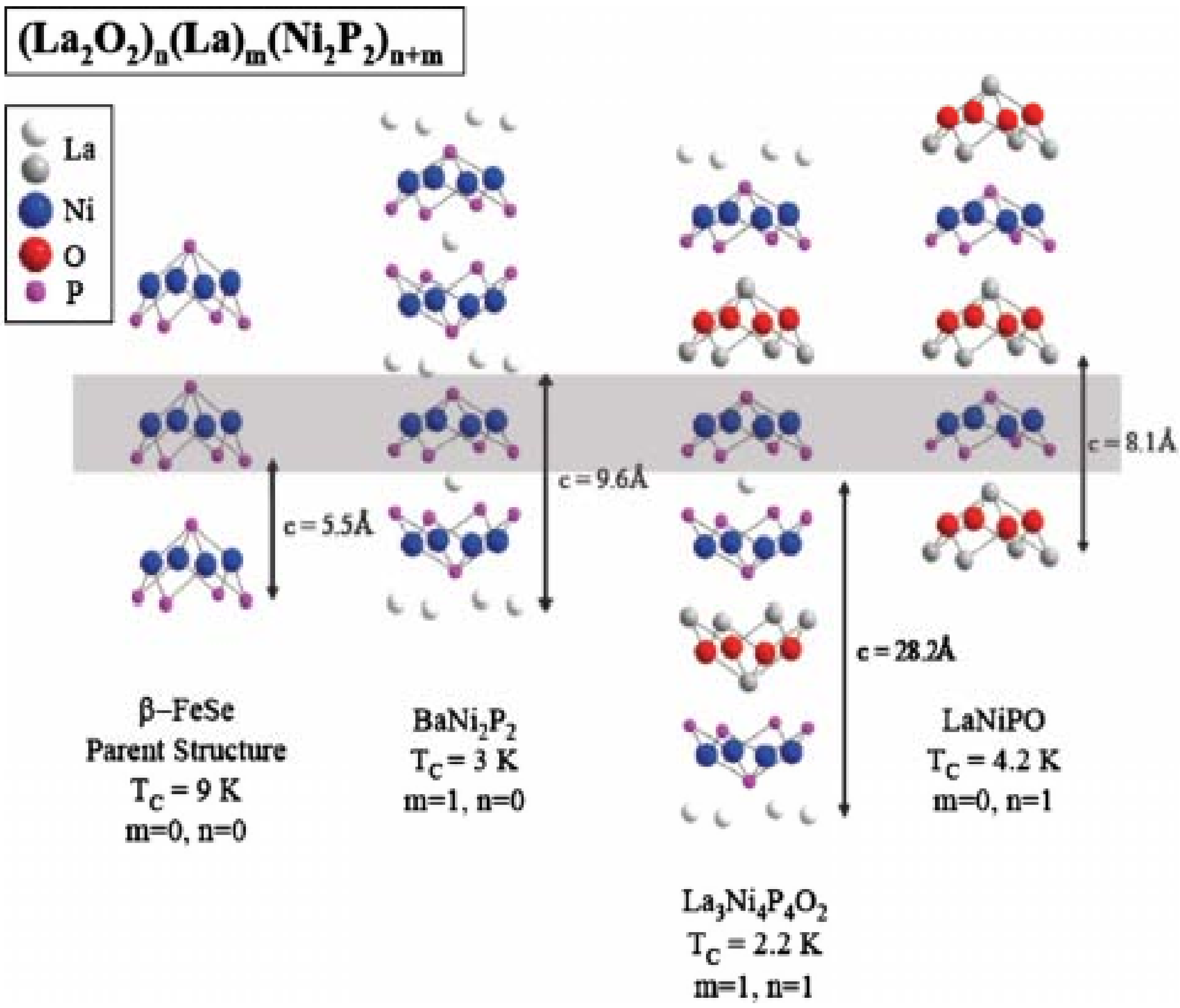
ERATO-SORST, JST, Frontier Research Center, Tokyo Institute of Technology, Mail Box S2-13, Materials and Structures Laboratory, Tokyo Institute of Technology, Mail Box R3-1, and Frontier Research Center, Tokyo Institute of Technology, Mail Box S2-13, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

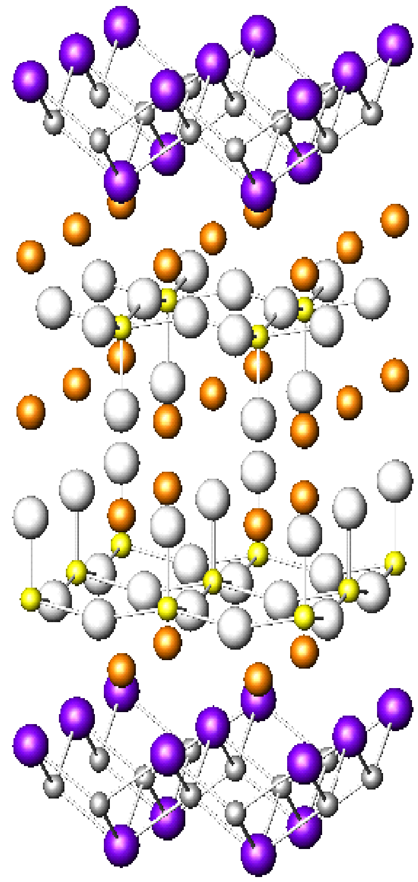


Temperature (K)
70
60
50
40
30
20
10
ReO1-xFxFeAs
PrO1-xFxFeAs
GdThOFeAs
NdO1-xFxFeAs
TbO1-xFxFeAs
SmO1-xFxFeAs
DyO1-xFxFeAs
NdO1-xFxFeAs
Ba1-xKxFe2As2
GdO1-xFxFeAs
Eu1-xNaxFe2As2
LaO1-xFxFeAs
BaFe2-xCoxAs2
La1-xSrxOFeAs
(Sc2O2)(SrO)2(Fe2P2)
LiFeAs
FeSe1-xTex
FeSxTe1-x
LaOFeP
LaONiP
LaO1-xFxNiAs
La1-xSrxONiAs
FeSe
2006
2007
2008
Januray
March
May
July
September
November



	Fe-Fe distance (A)	M-Fe-M angle (o)	Layer distance (A)	Tc (K)
1111(Sm, Pr, Gd..)	2.84	107.4	8.3	~56
122	2.77	108.9	6.5	~38
111	2.67	112.7	6.3	~18
11	2.65	112.18	5.5	~10





$(Sc_2O_2)(SrO)_2(Fe_2P_2)$

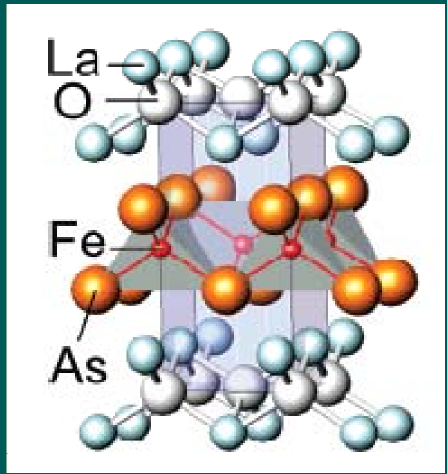
Tc = 17 K

Klimczuk et al. Phys. Rev. B79, 012505 (2009)

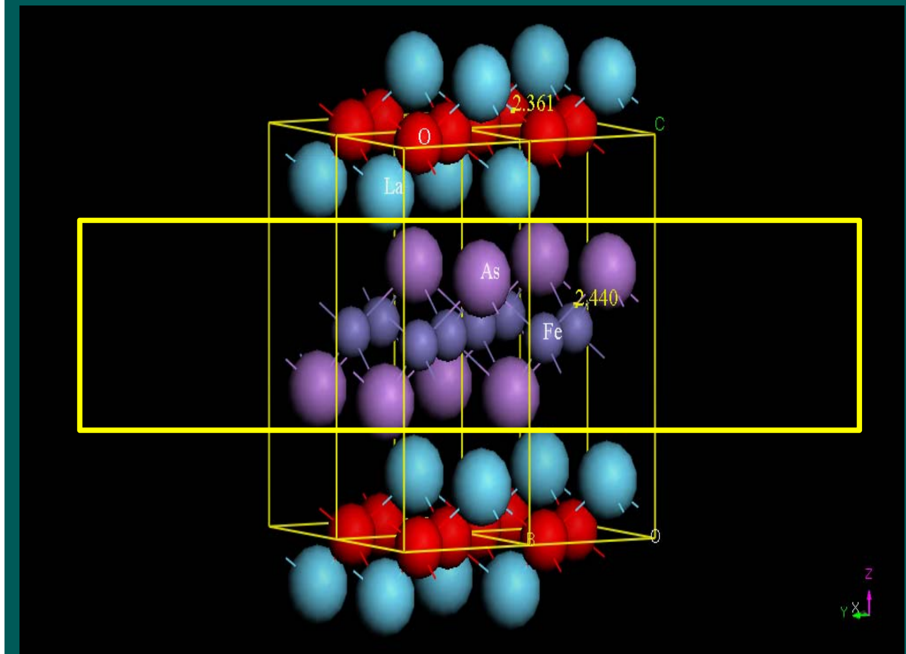
H. Ogino et al.

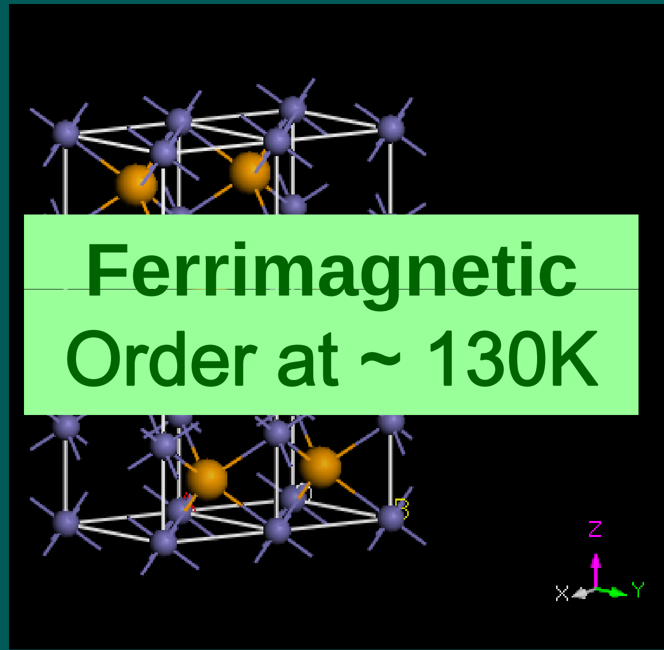
[LaO]$^+$

[FeAs]$^{-}$



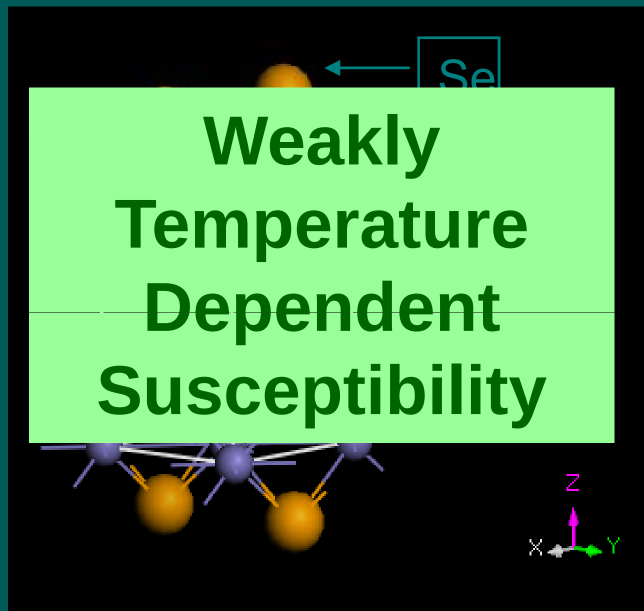
Oxypnictide





Ferrimagnetic Order at ~ 130K

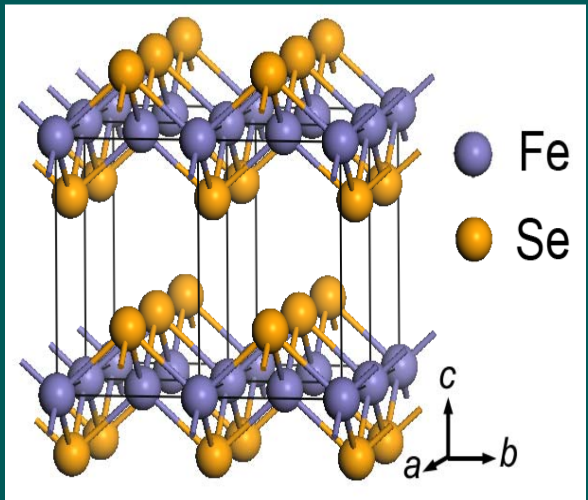
δ-FeSe
hexagonal
a = 3.618,
c = 5.927

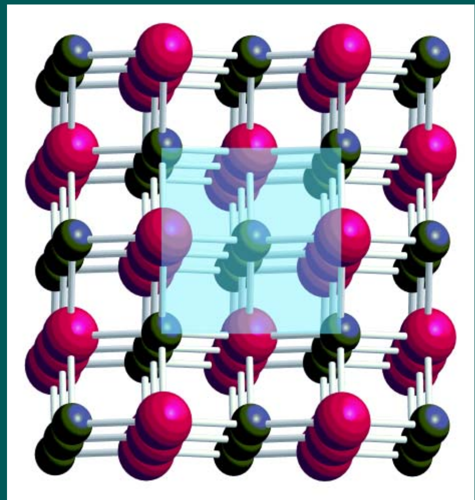


Weakly Temperature Dependent Susceptibility

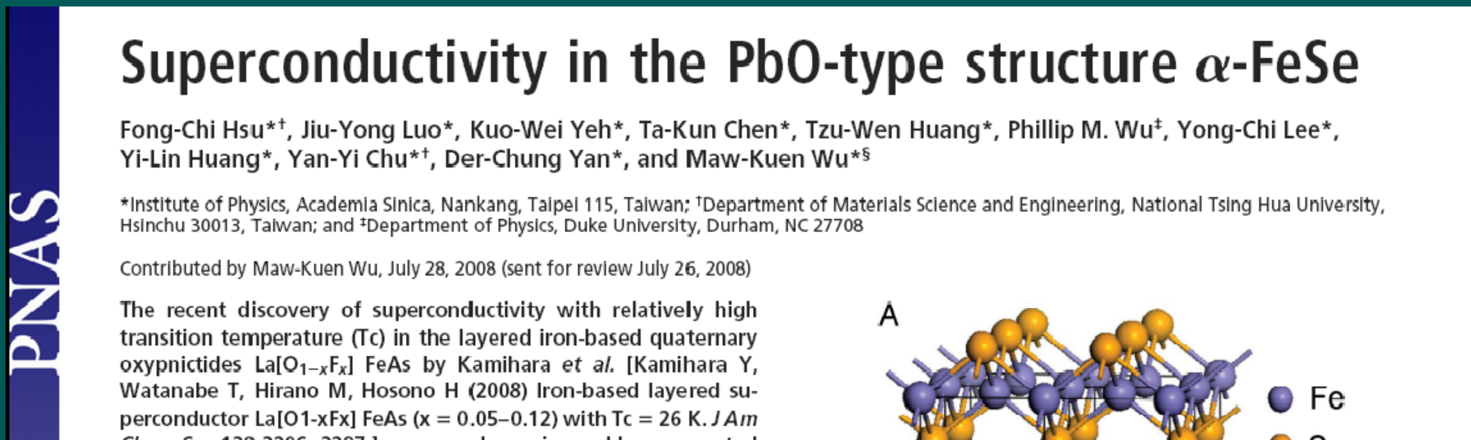
β-FeSe
tetragonal
a = 3.765,
c = 5.518

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*§

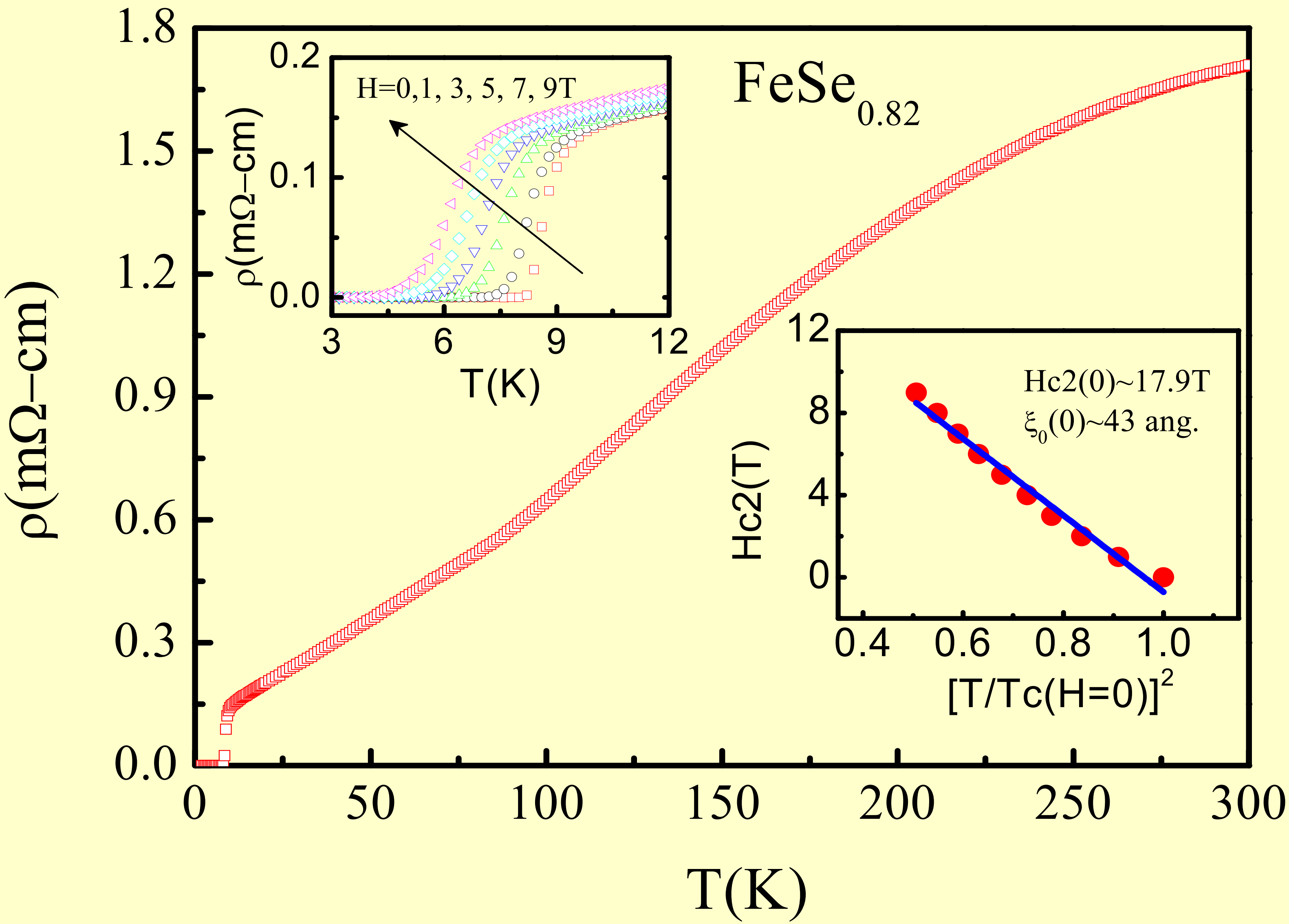
*Institute of Physics, Academia Sinica, Nankang, Taipei 115, Taiwan; †Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan; and ‡Department of Physics, Duke University, Durham, NC 27708

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*

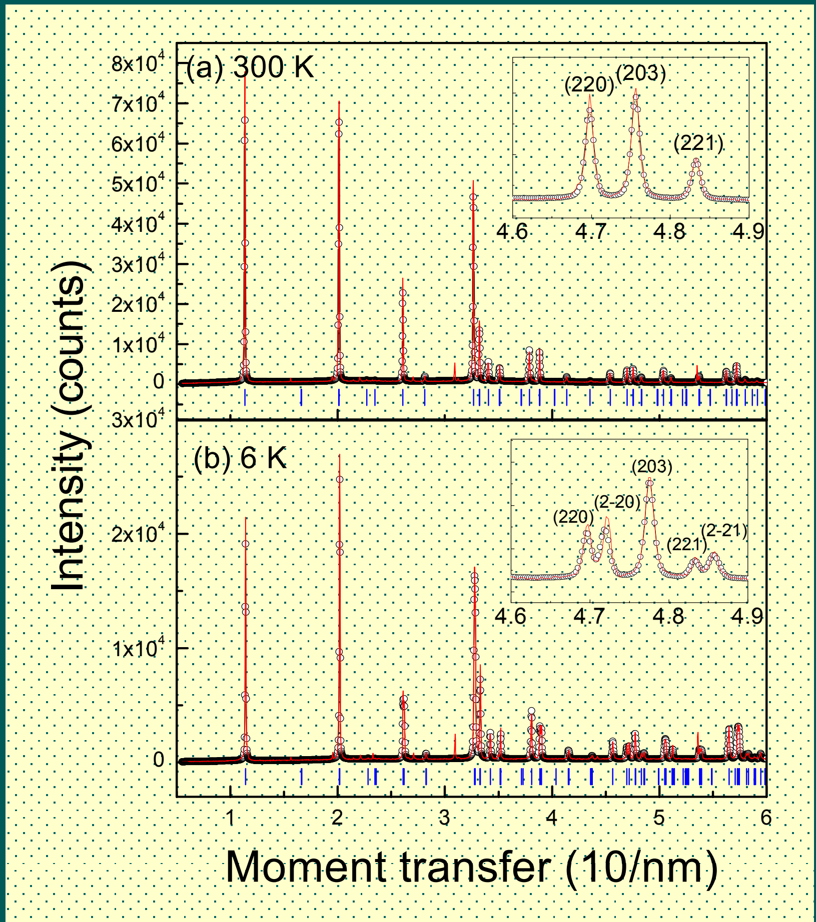
A

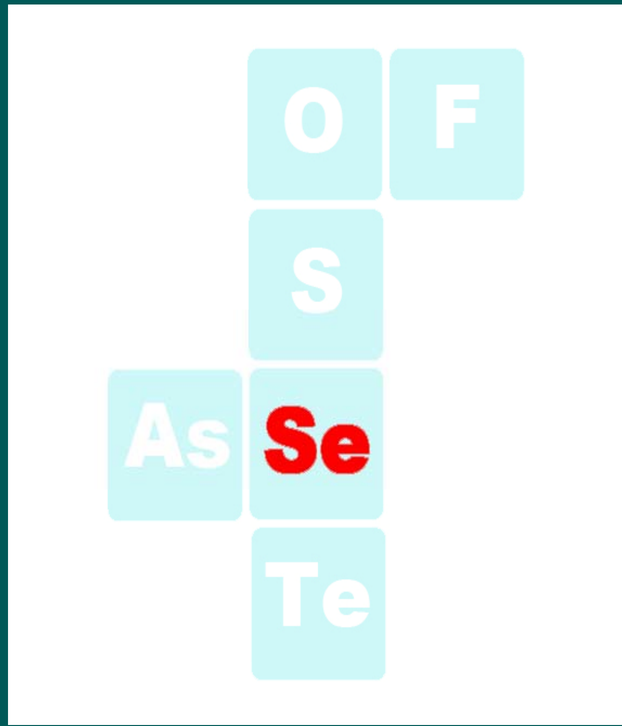
Fe



FeSe0.82
ρ(mΩ–cm)
T(K)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
50
100
150
200
250
300
H=0,1, 3, 5, 7, 9T
0.2
0.1
0.0
3
6
9
12
Hc2(0)~17.9T
ξ0(0)~43 ang.
Hc2(T)
12
8
4
0
0.4
0.6
0.8
1.0
[T/Tc(H=0)]2

$FeSe_{0.82}$

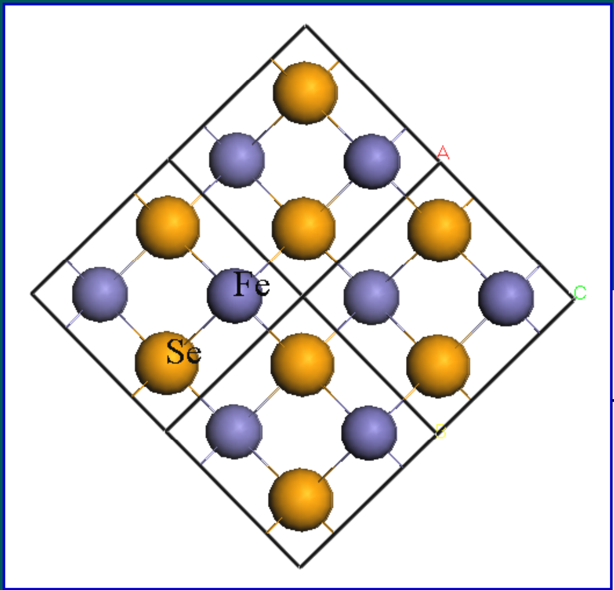




	a (Å)	b (Å)	c (Å)	α	β	γ
300K	3.783	3.783	5.534	90	90	90
6K	3.775	3.775	5.503	90	90	90.279

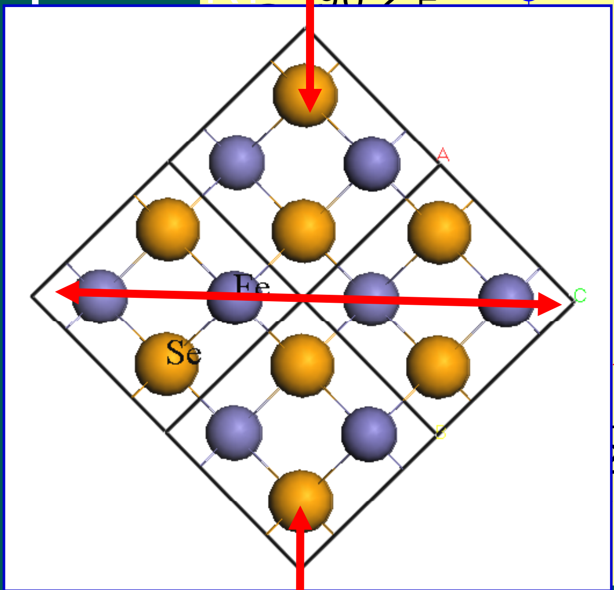
Temperature dependence of the X-ray powder diffractions for FeSe by synchrotron source at BL12b2 in SPring 8 with incident beam wavelength of 0.995 Å. Observed (open black circle) and calculated (red solid line) powder diffraction intensities of FeSe at (a) 300K using space group P4/nmm and (b) 6K using space group P-1. The inset shows a single peak of the (2, 2, 0) , (2, 0, 3) , (2, 2, 1) reflection at room temperature and splitting two peaks of (2, 2, 0), (2, 2, 1) at 6K. Blue vertical lines show the Bragg peak positions.

structure parameter (Fe-Se)

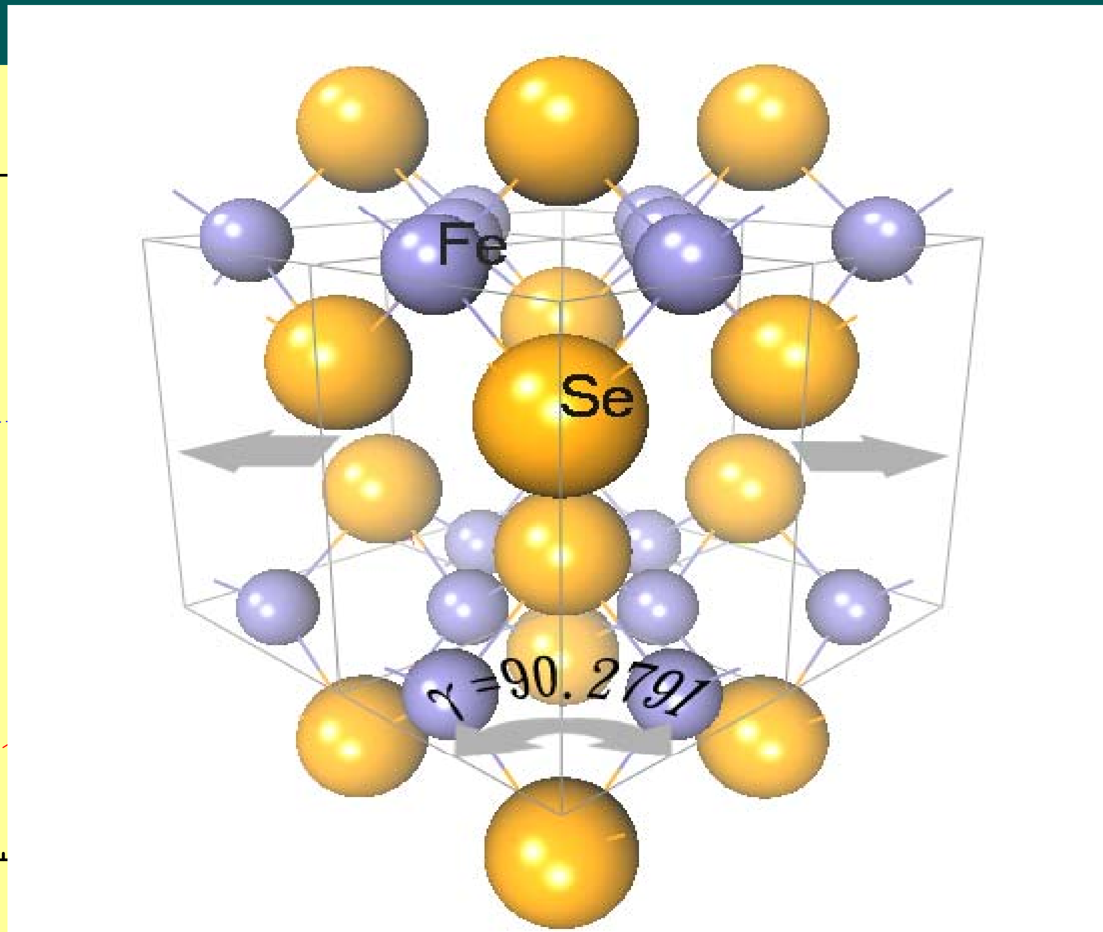


300K

RT 90.2



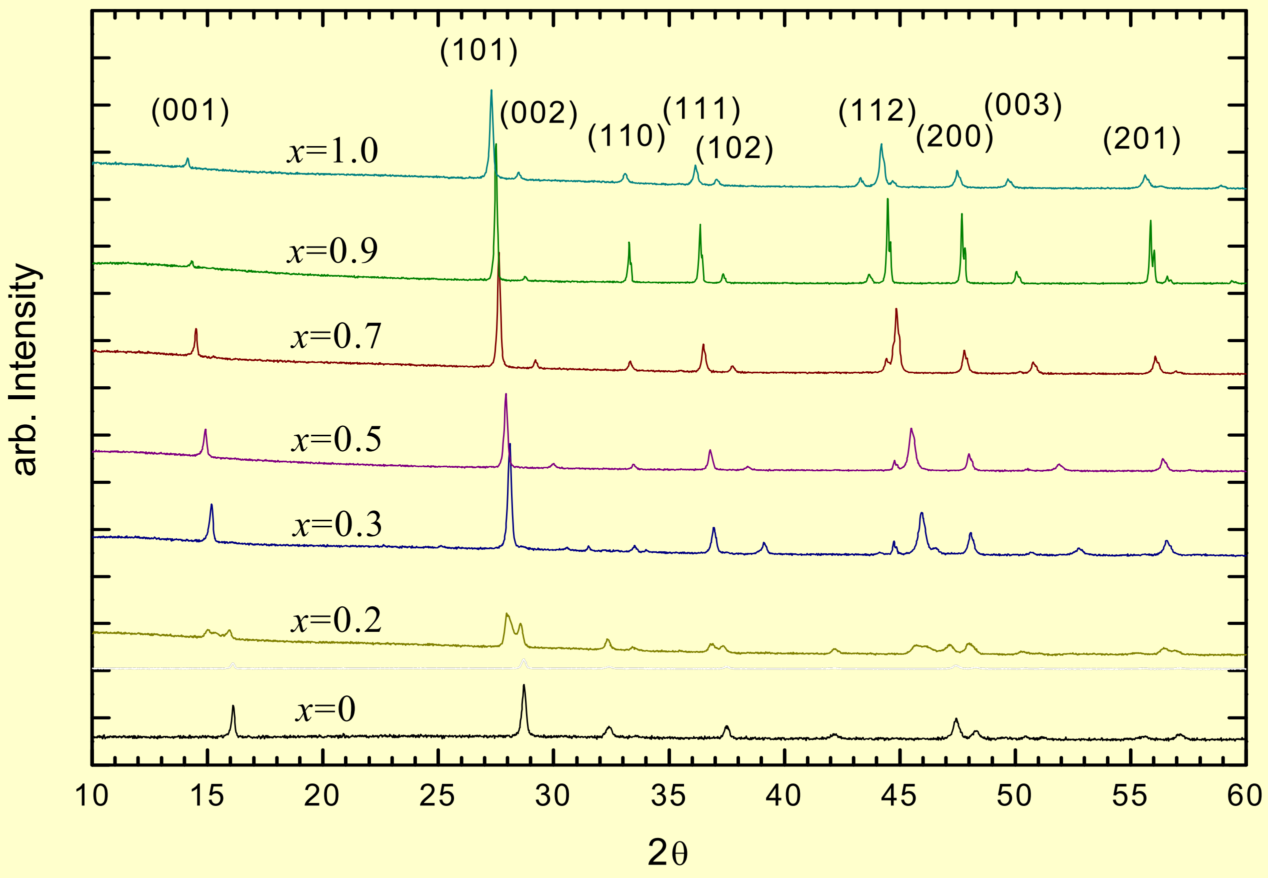
Simulation 6K



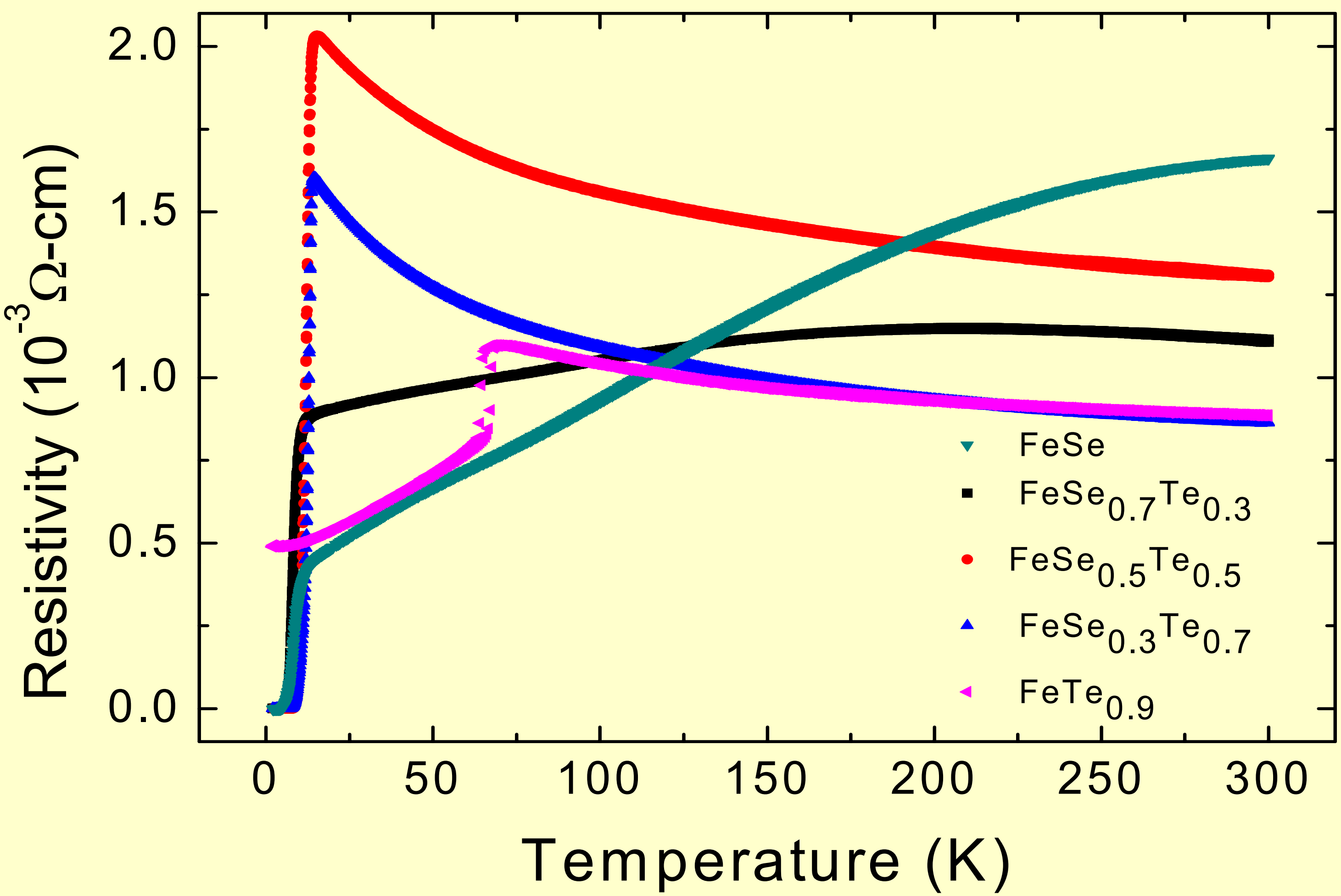
20

T (K)

Te-doping ($FeSe_{1-x}Te_x$)

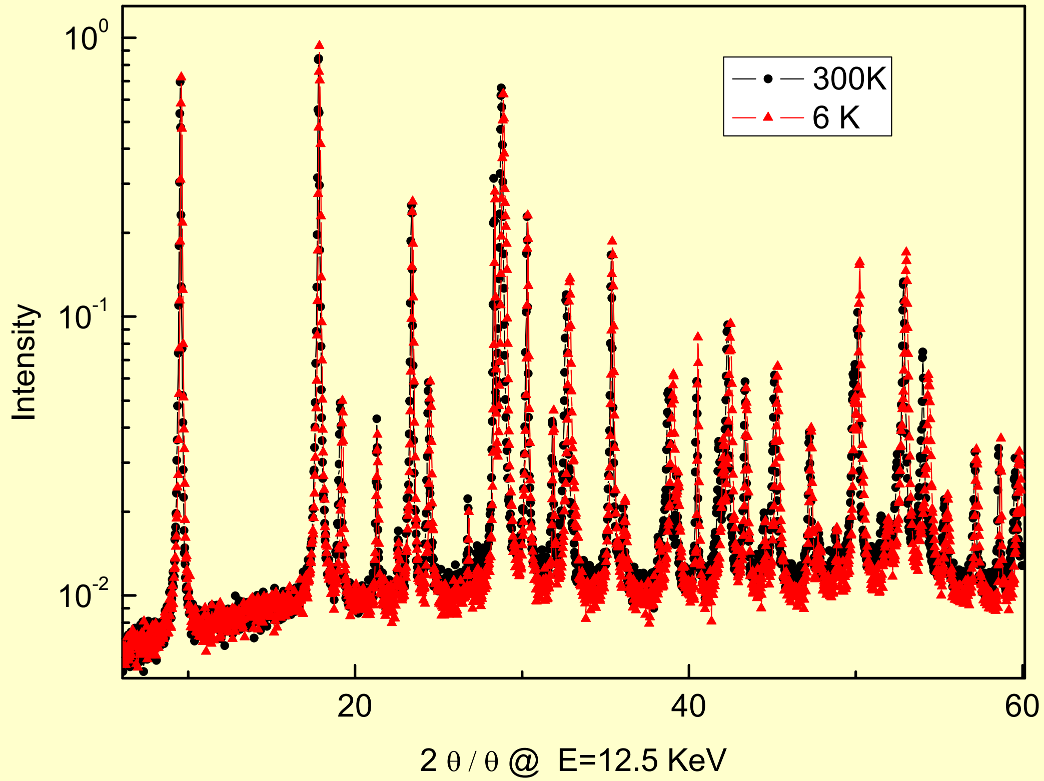


K.W. Yeh, et al., EPL, **84**, 37002 (2008)

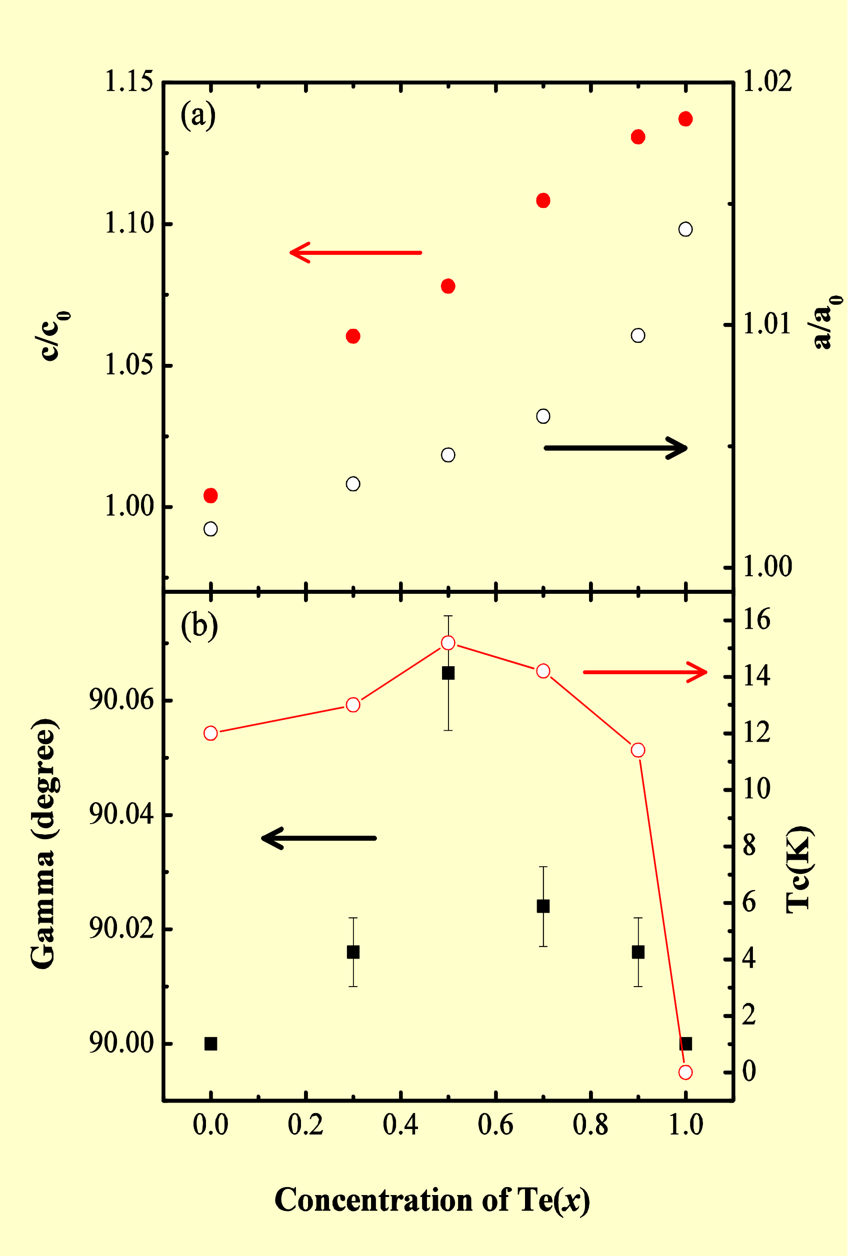


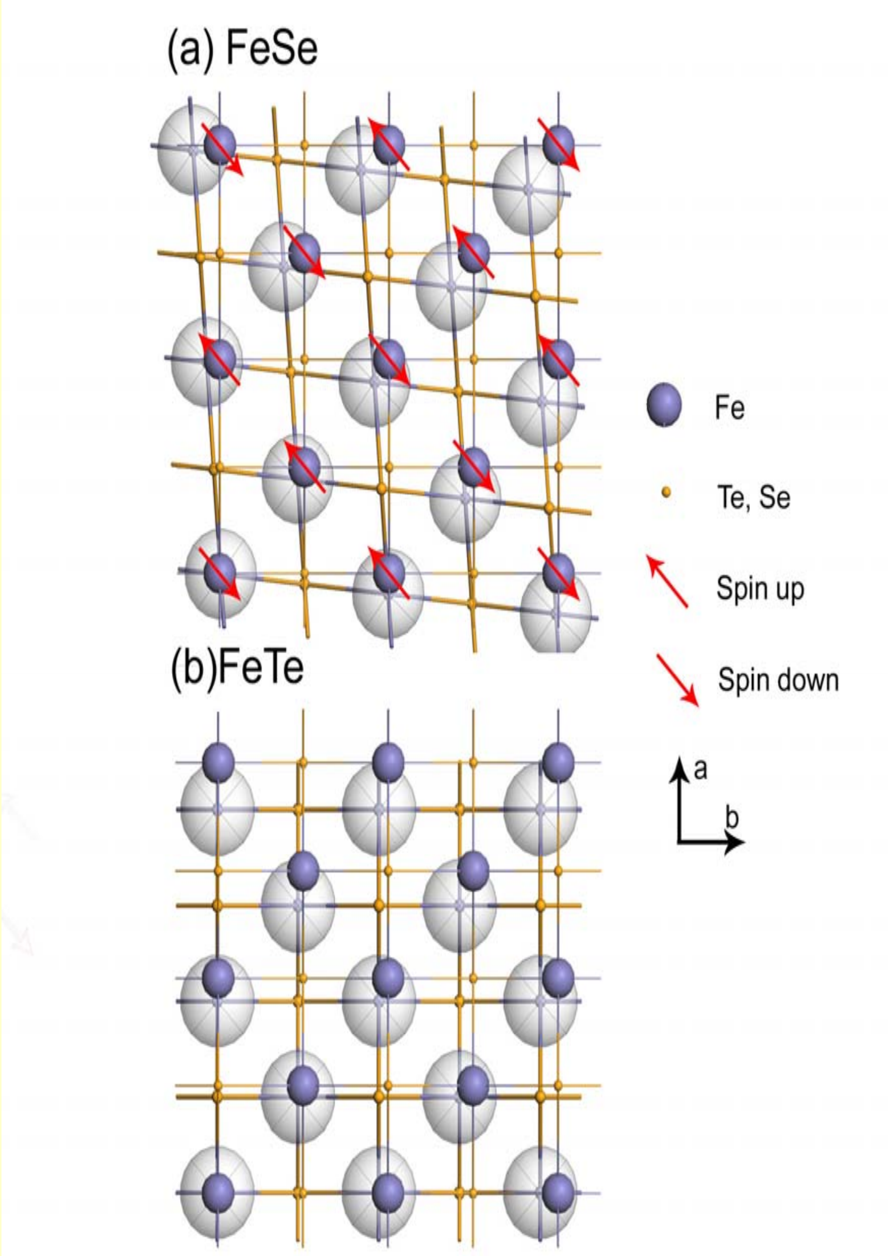
K.W. Yeh, et al., EPL, **84**, 37002 (2008)

$Fe_{0.5}Se_{0.25}Te_{0.25}$ diffraction at low temperature.



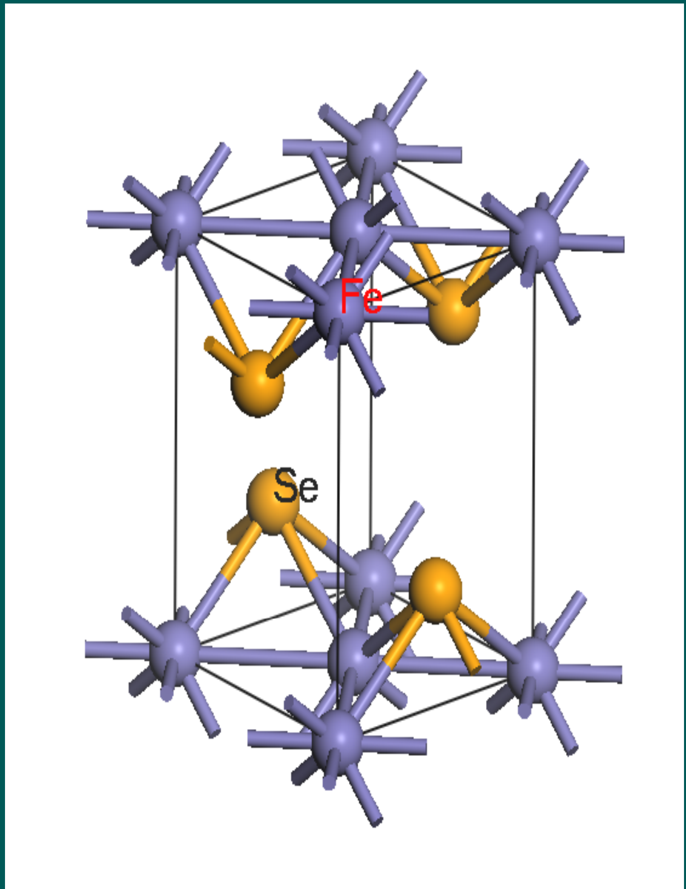
1. Pure phase.
2. Only 211 diffraction which belong the tetragonal phase, started to suffer split into two.

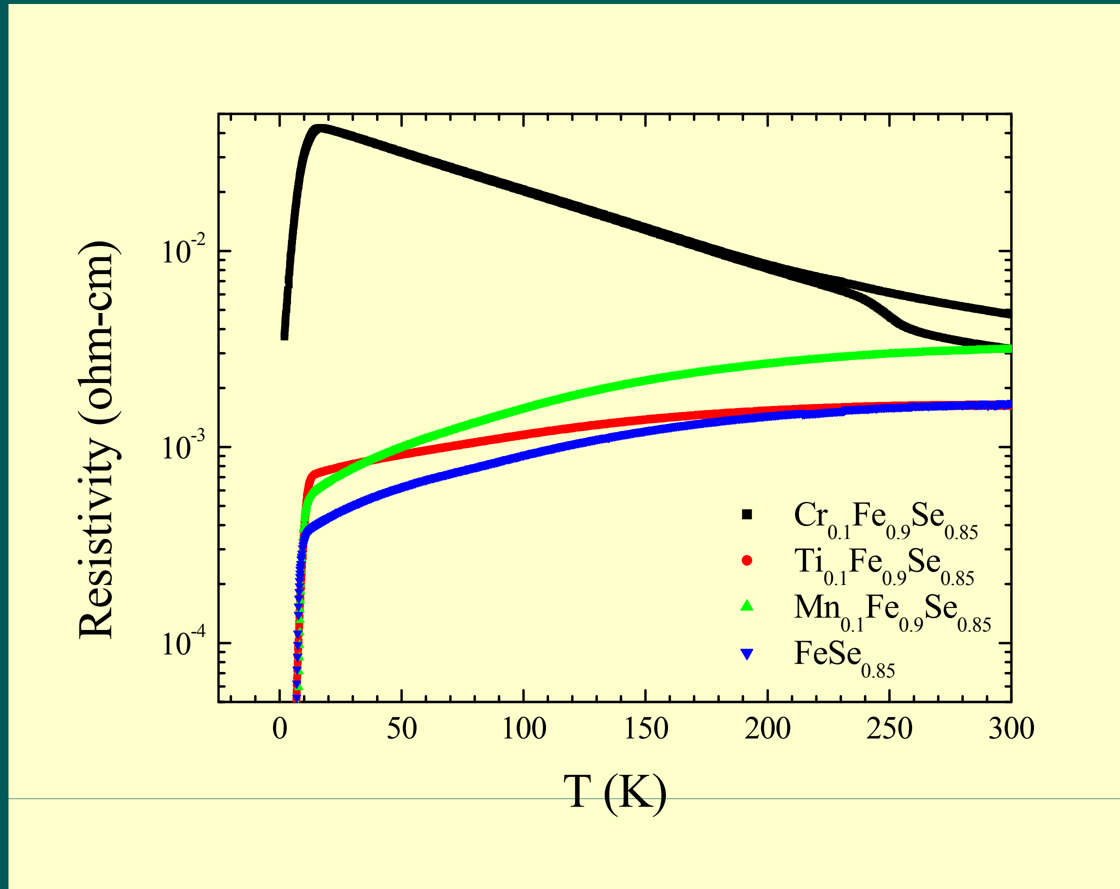


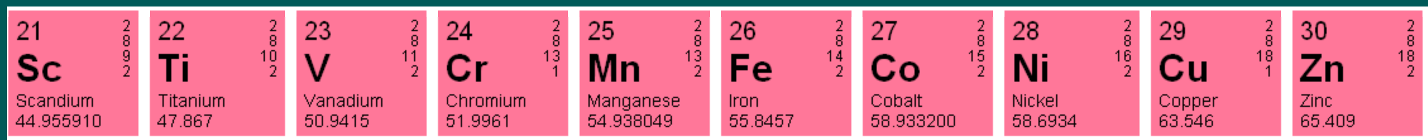


K.W. Yeh, et al., EPL, **84**, 37002 (2008)

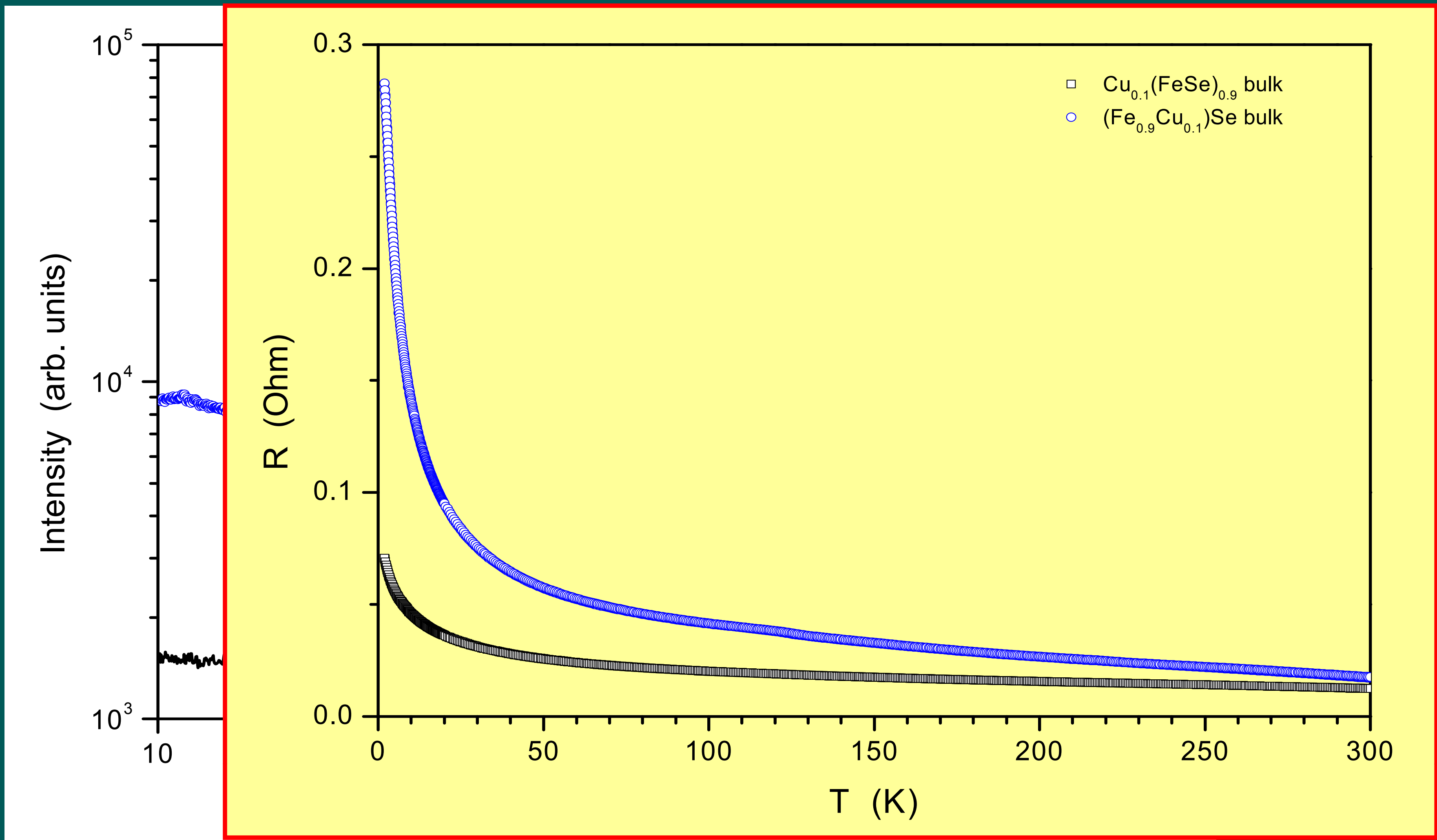
Transition-metal Doping ($Fe_{1-x}Tm_xSe$)



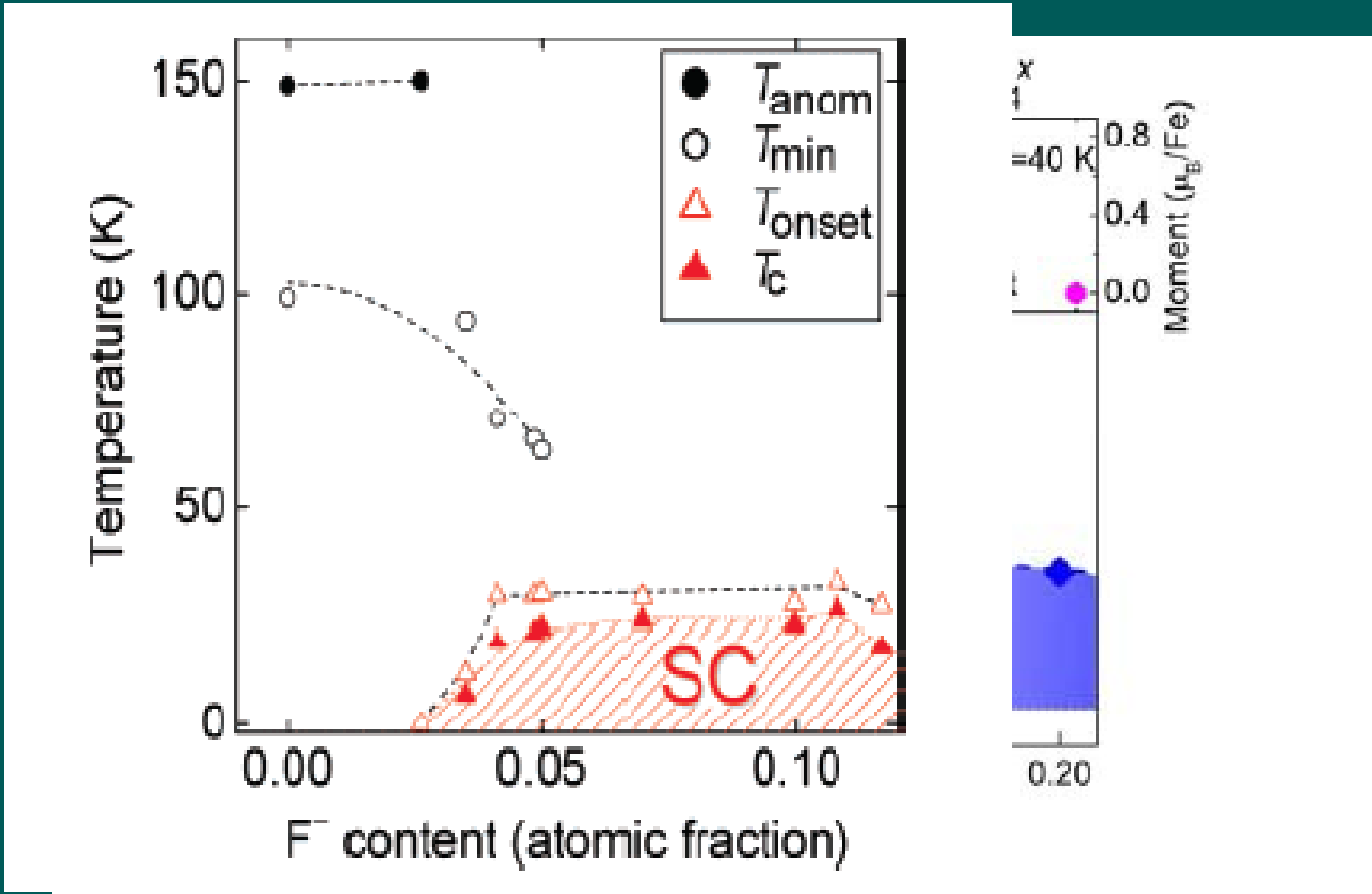




$Cu_{0.1}(FeSe)_{0.9}$ bulk XRD & RT



Phase Diagram



Kamihara et al., JACS, 2008

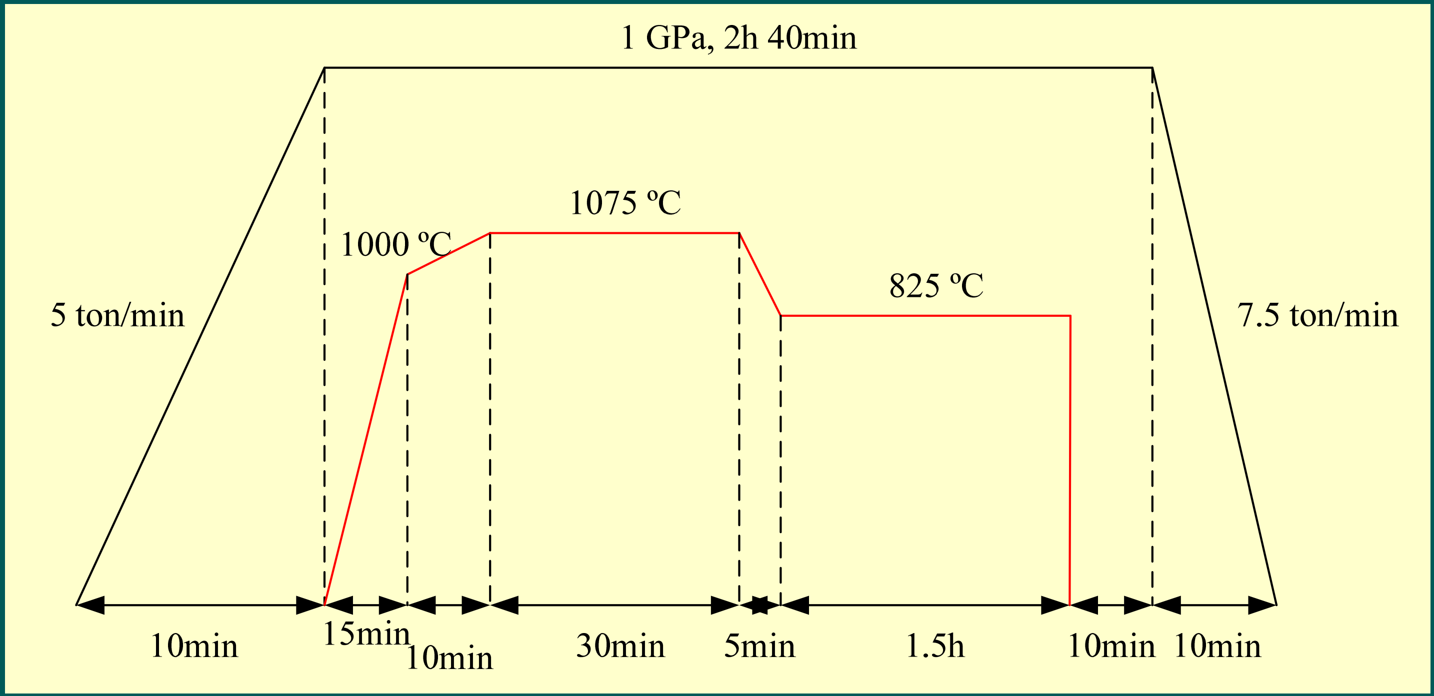
J. Lynn and P.C. Dai, Physica C, 2009

Single Crystal Growth

1. Stoichiometriy weights of Fe and Se powders were mixed with KCl to give a FeSe$_x$ (x=0-0.15) to KCl ratio of 1.5:

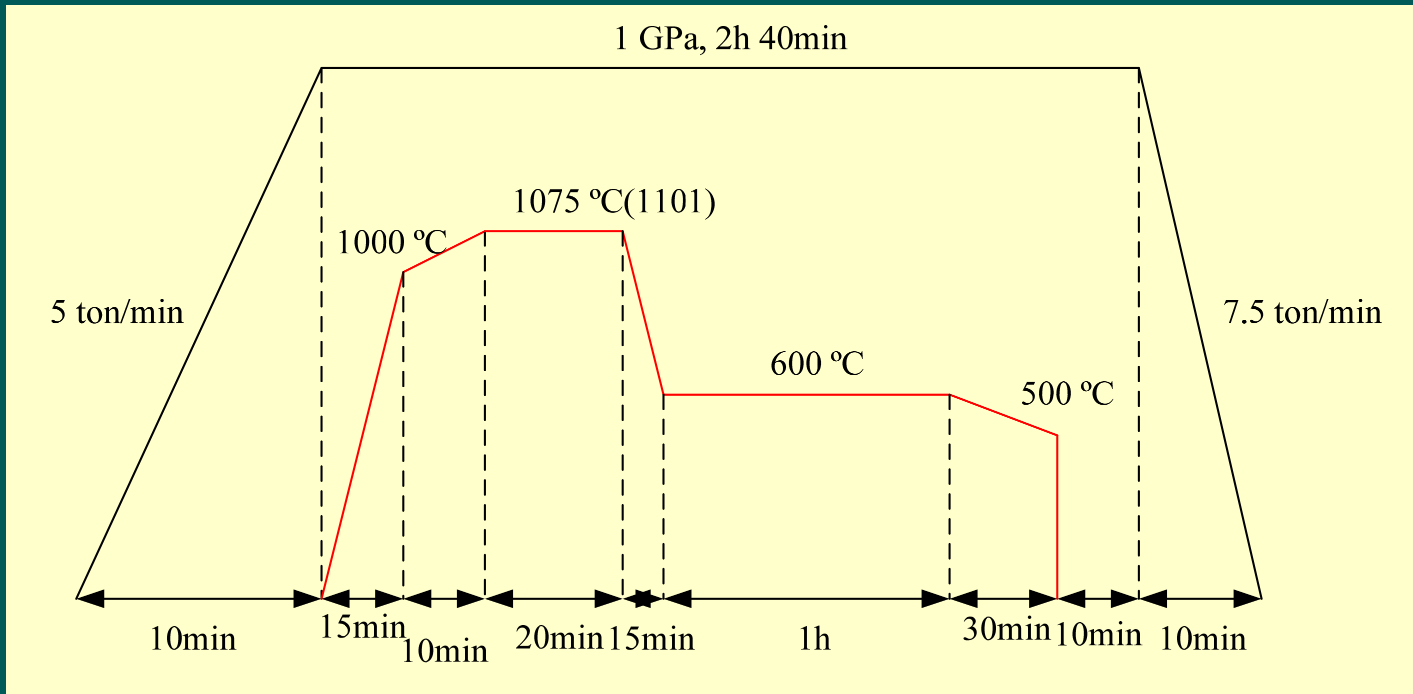
2. These … and the crucibl… ed.
3. The cr… d there for 25-
4. Then it … C. During … cting at the top of the solution and grow in size with time.
5. Later the crucible was cooled to room temperature while annealing at 400 ^{o}C for 20-25 hours before cooling to room temperature.

FeSe crystal growth (High Pressure)

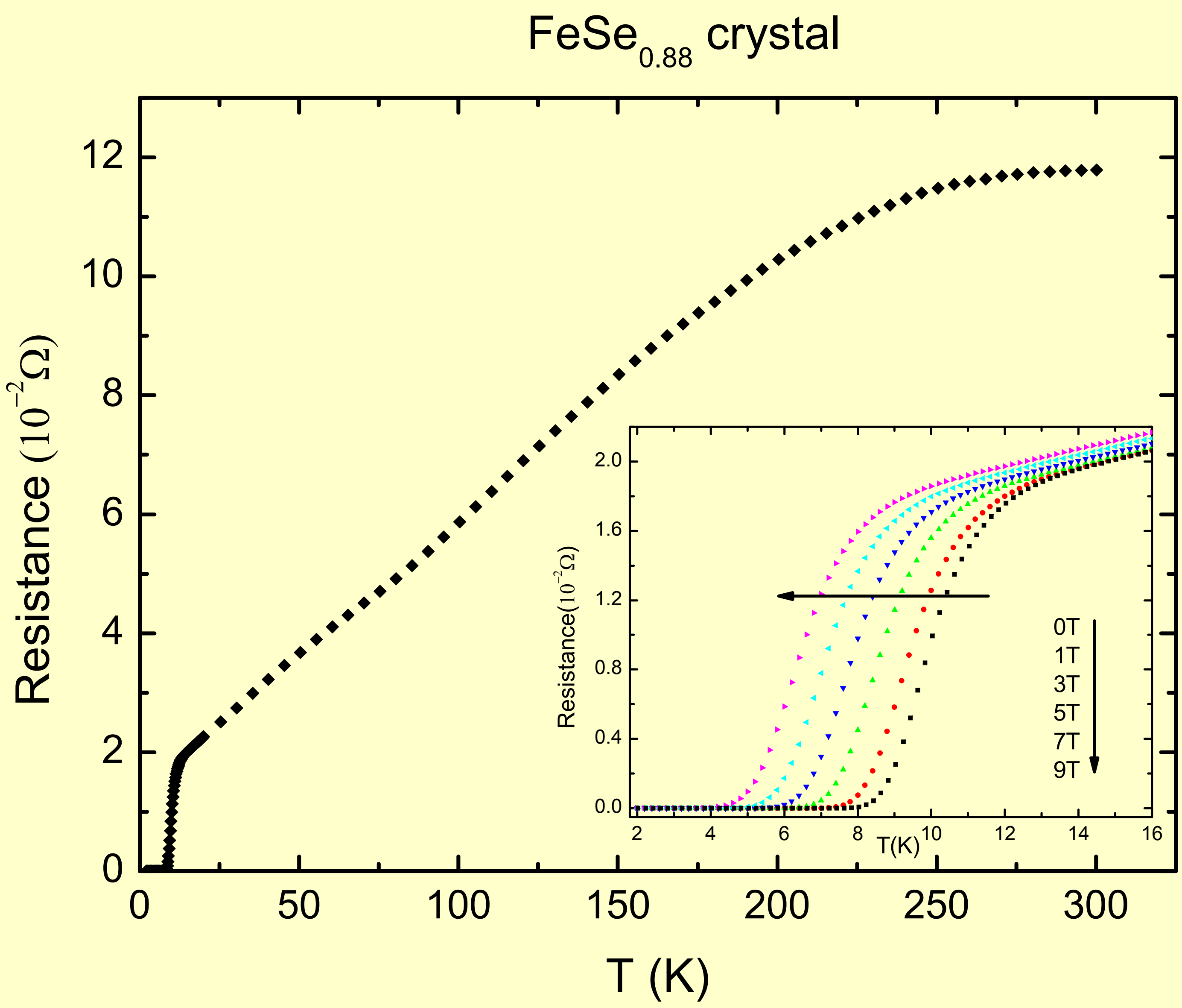


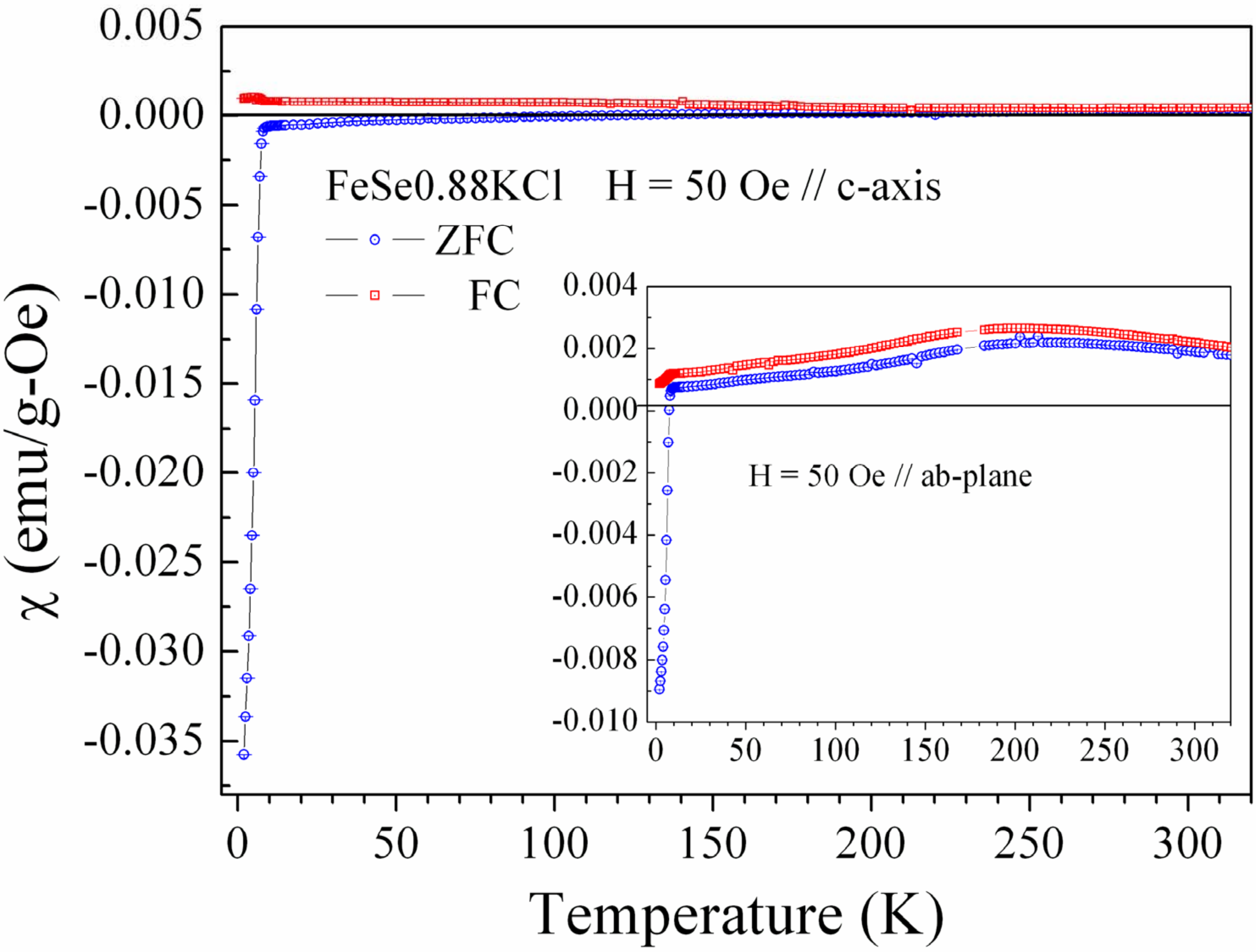
- Sample weight: FeSe powders ~0.32 g.
- Total time: 3h.

Cu(or Mn)$_{0.1}$Fe$_{0.9}$Se crystal (High Pressure)

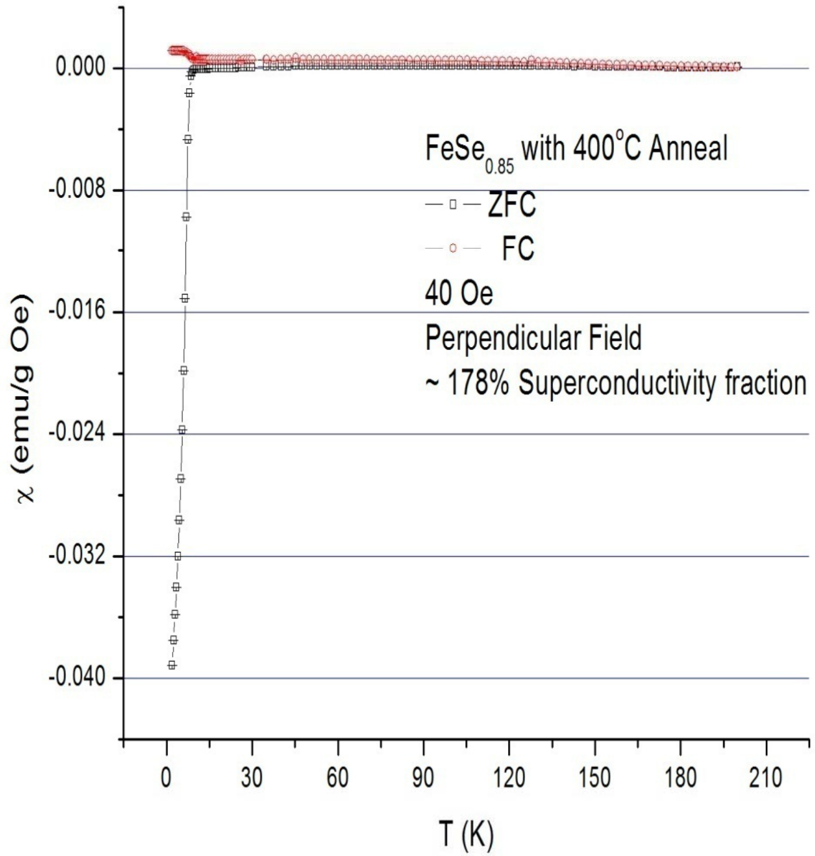


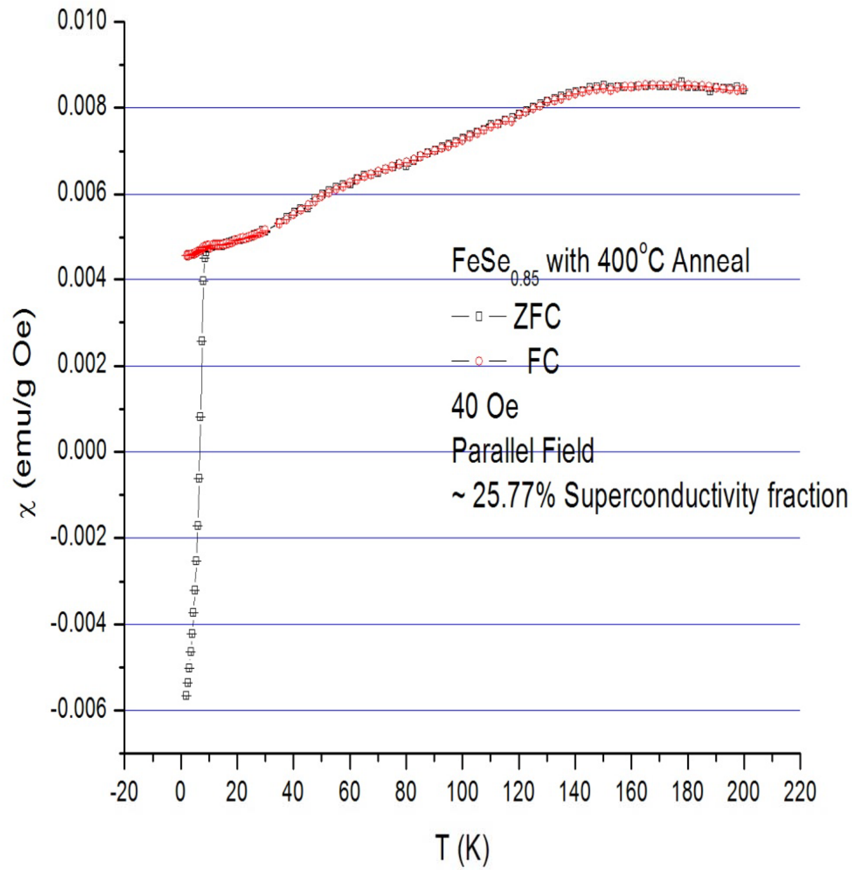
- Cu (or Mn) metal + FeSe powders
- Sample weight: ~0.32 g.
- Total time: 3h.


FeSe0.88 crystal
Resistance (10^-2 Ω)
T (K)
0
2
4
6
8
10
12
0
50
100
150
200
250
300
Resistance(10^-2 Ω)
T(K)
0.0
0.4
0.8
1.2
1.6
2.0
2
4
6
8
10
12
14
16
0T
1T
3T
5T
7T
9T

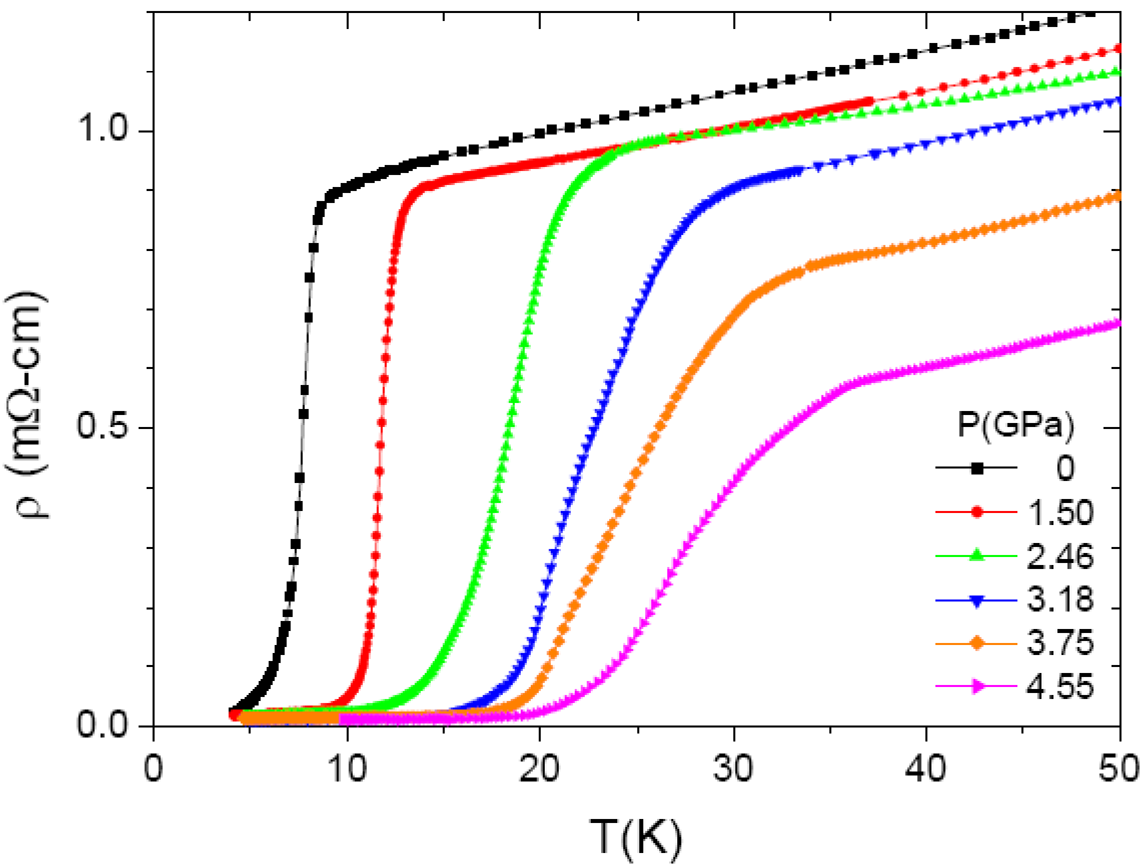


0.005
0.000
-0.005
-0.010
-0.015
-0.020
-0.025
-0.030
-0.035
χ (emu/g-Oe)
0
50
100
150
200
250
300
Temperature (K)
FeSe0.88KCl H = 50 Oe // c-axis
ZFC
FC
0.004
0.002
0.000
-0.002
-0.004
-0.006
-0.008
-0.010
H = 50 Oe // ab-plane

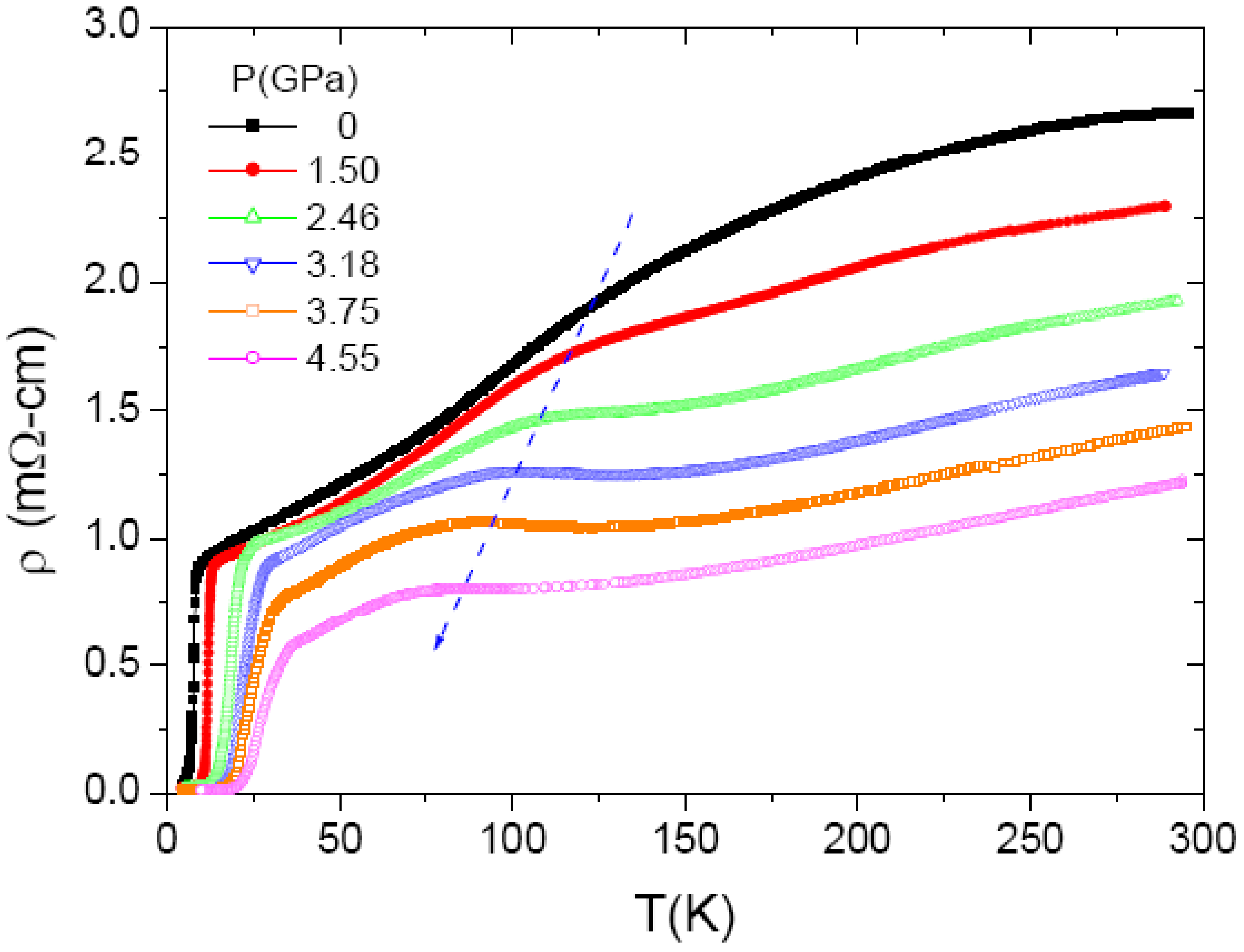




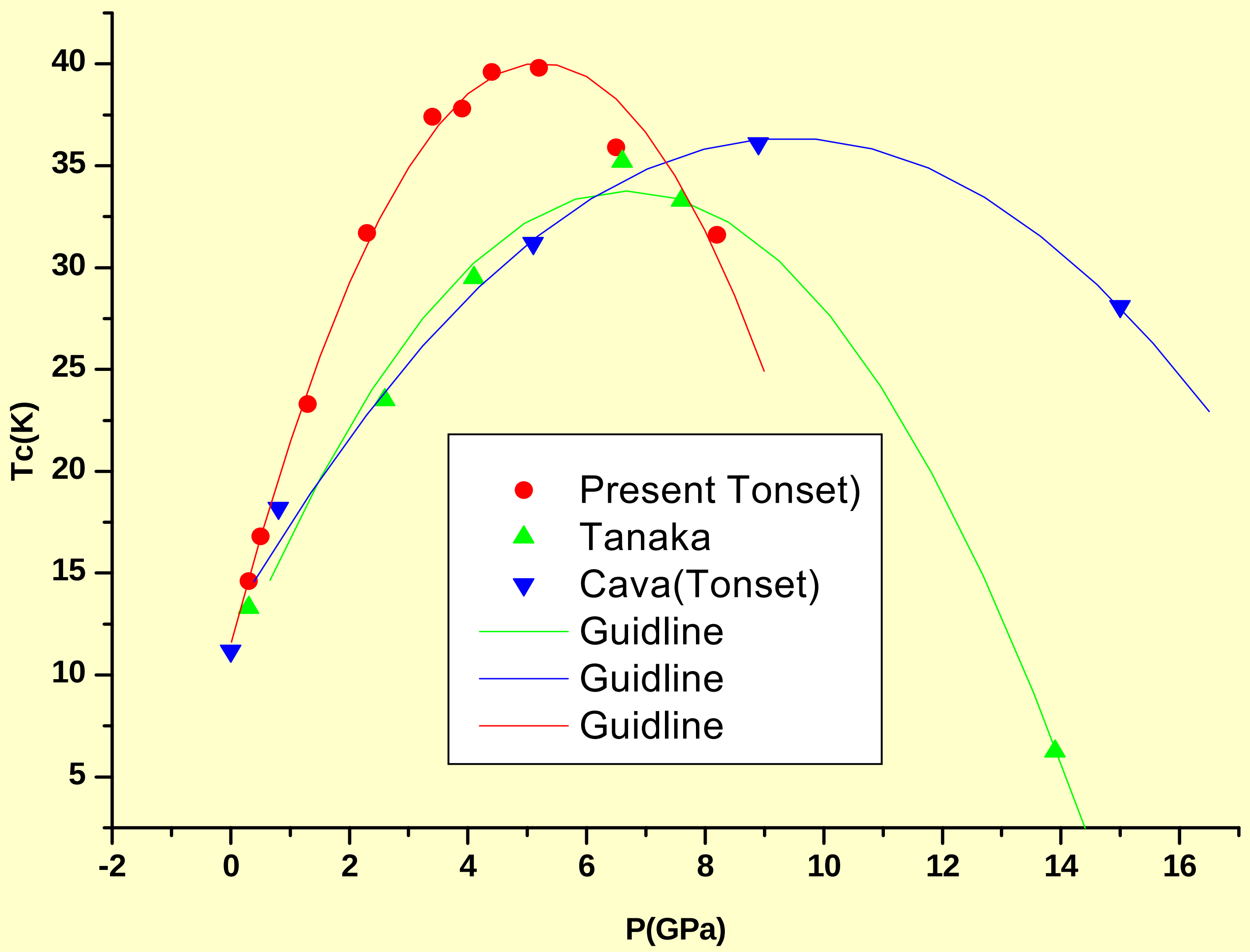
Wilson ratio $$R_W = \frac{\pi^2 k_B^2}{3\mu_B^2}\left(\frac{\chi_{ab}(0)}{\gamma}\right) >> 1$$



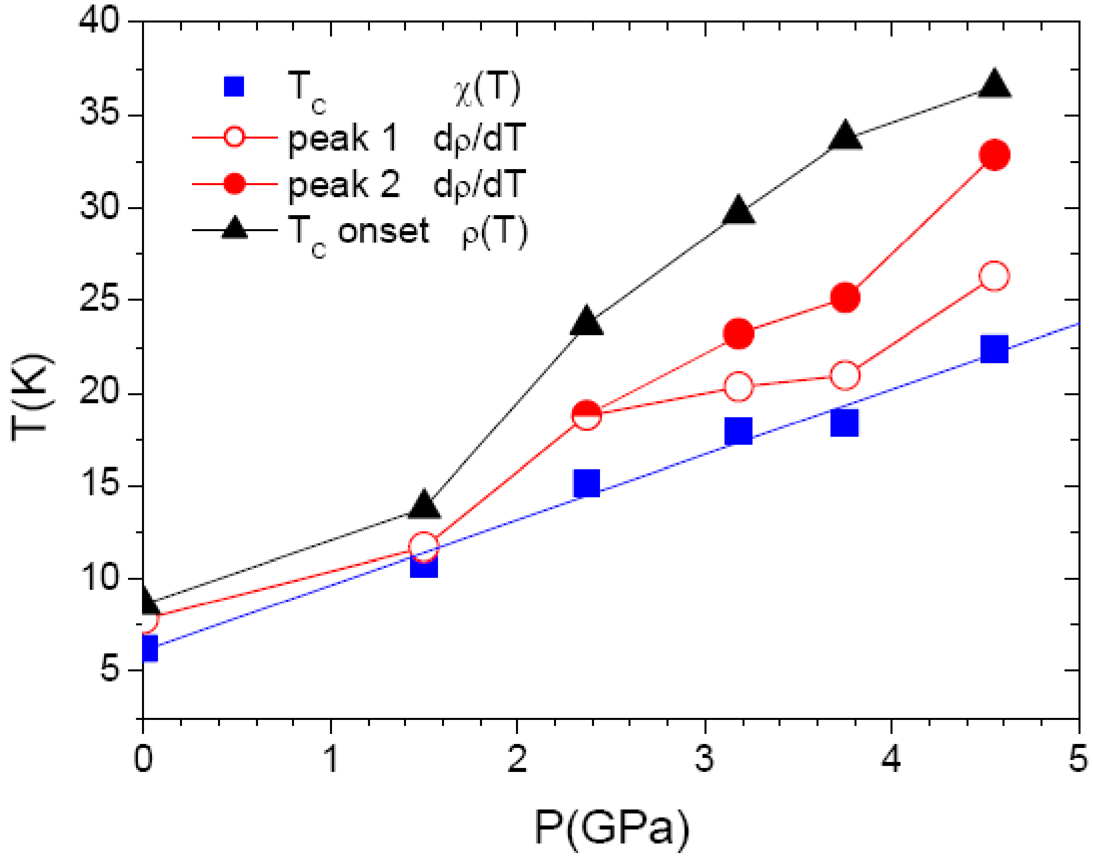
ρ (mΩ-cm)
1.0
0.5
0.0
0
10
20
30
40
50
T(K)
P(GPa)
0
1.50
2.46
3.18
3.75
4.55



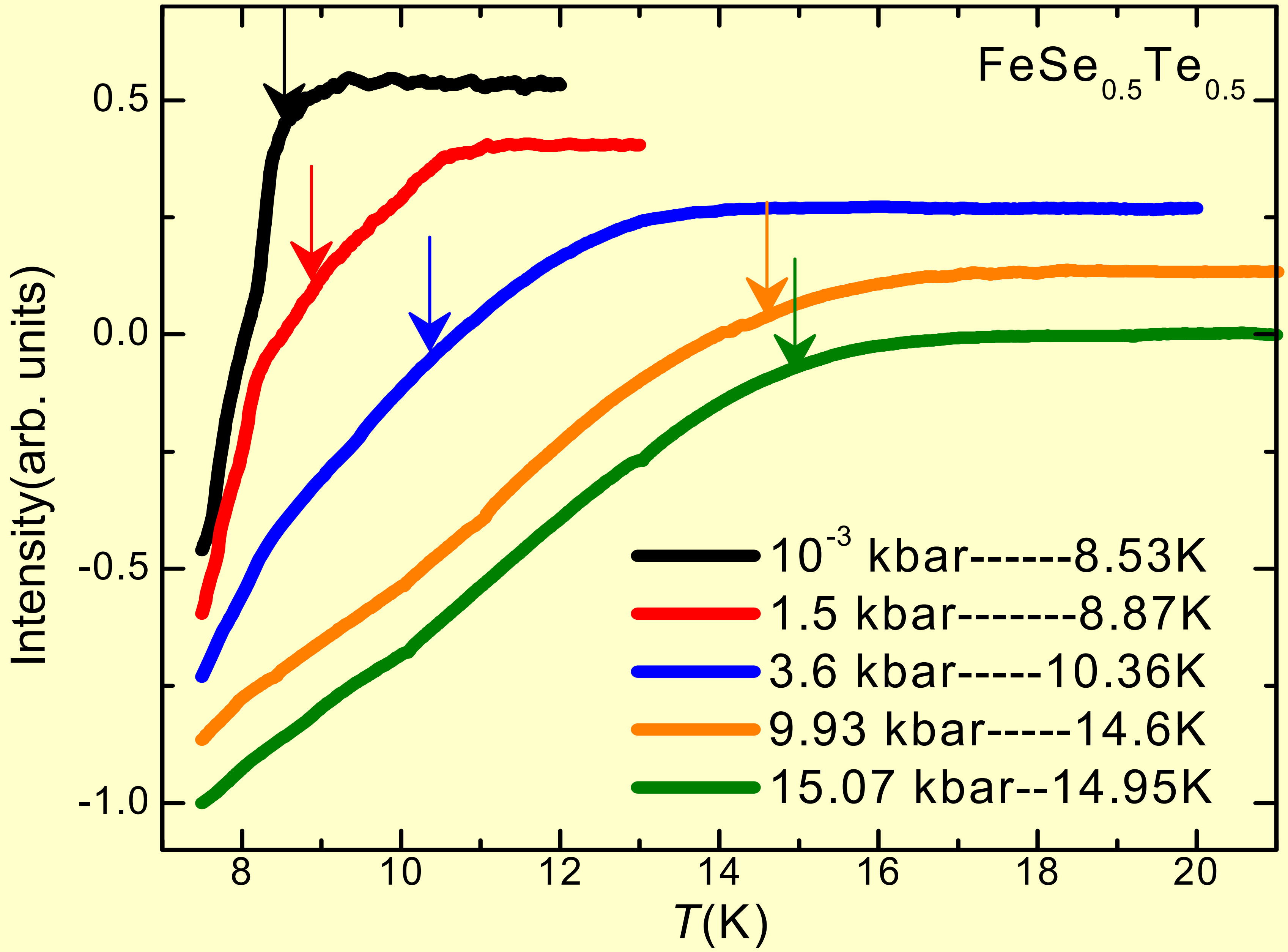
P(GPa)
0
1.50
2.46
3.18
3.75
4.55
ρ (mΩ-cm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
50
100
150
200
250
300
T(K)



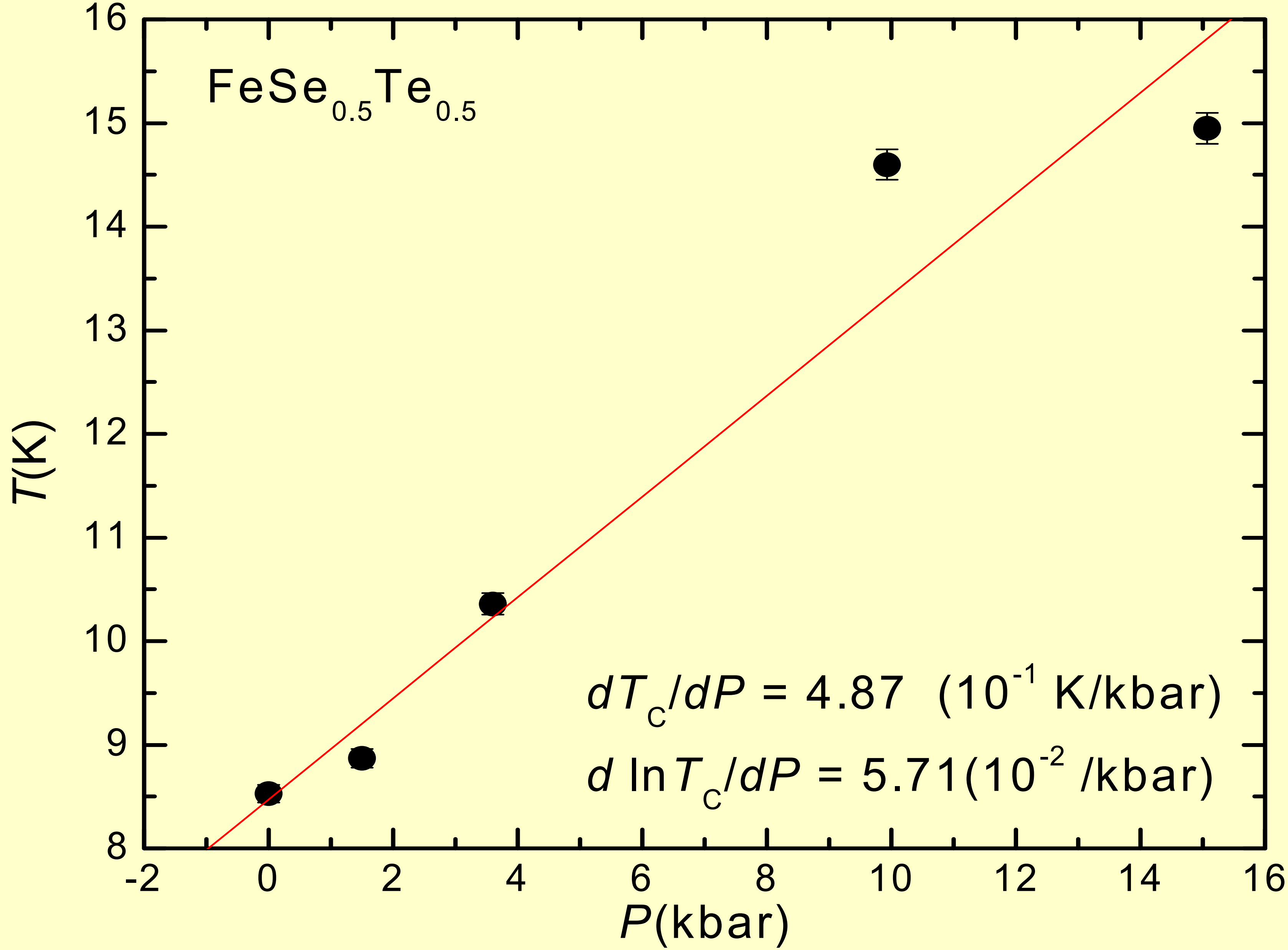
C.Q. Jin et al., unpublished



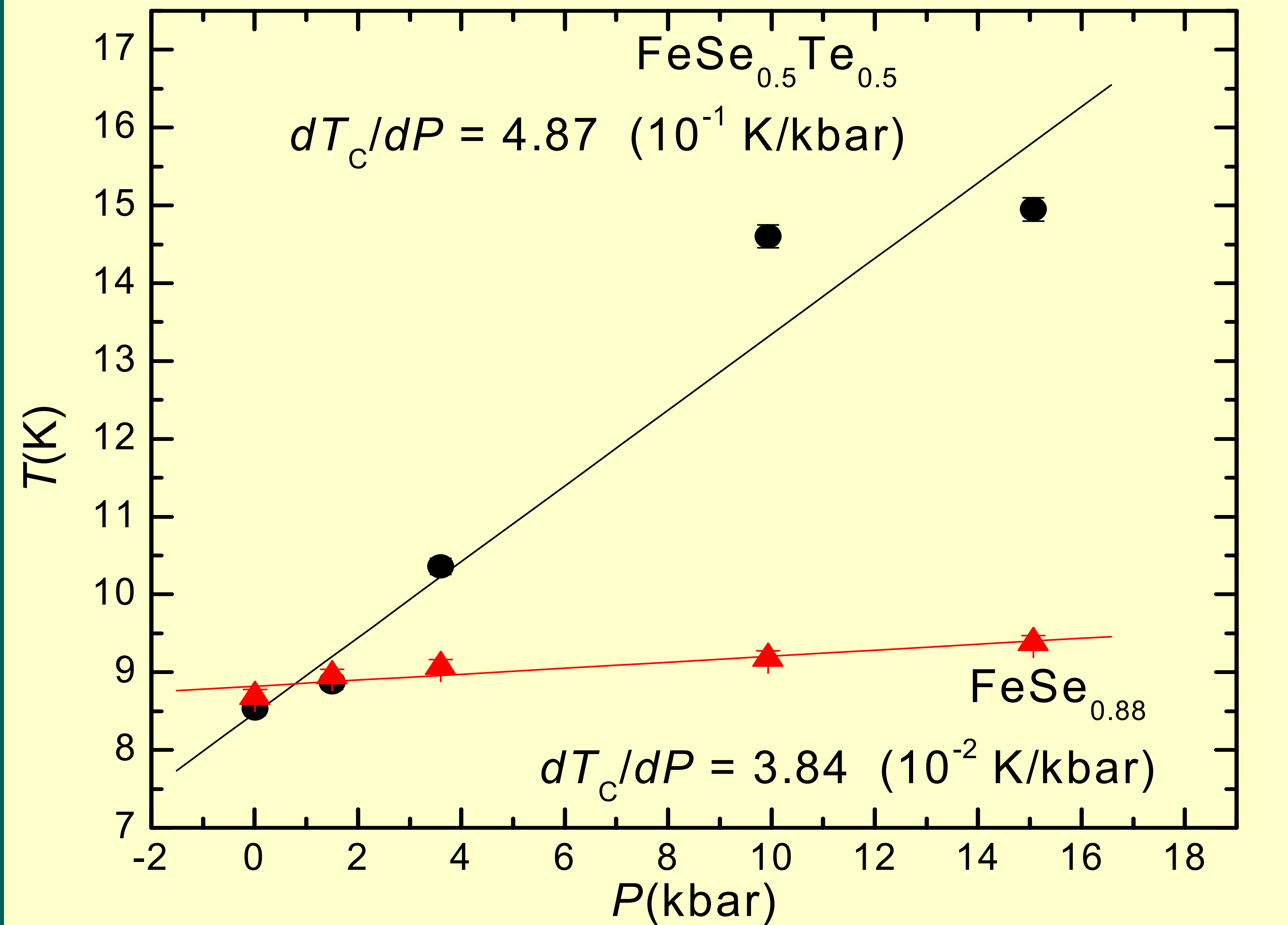
T(K)
P(GPa)
T_c χ(T)
peak 1 dρ/dT
peak 2 dρ/dT
T_c onset ρ(T)
0
1
2
3
4
5
5
10
15
20
25
30
35
40



FeSe0.5Te0.5
Intensity(arb. units)
T(K)
0.5
0.0
-0.5
-1.0
8
10
12
14
16
18
20
10-3 kbar------8.53K
1.5 kbar-------8.87K
3.6 kbar-----10.36K
9.93 kbar-----14.6K
15.07 kbar--14.95K



FeSe0.5Te0.5
dTC/dP = 4.87 (10-1 K/kbar)
d lnTC/dP = 5.71(10-2 /kbar)
T(K)
P(kbar)
16
15
14
13
12
11
10
9
8
-2
0
2
4
6
8
10
12
14
16

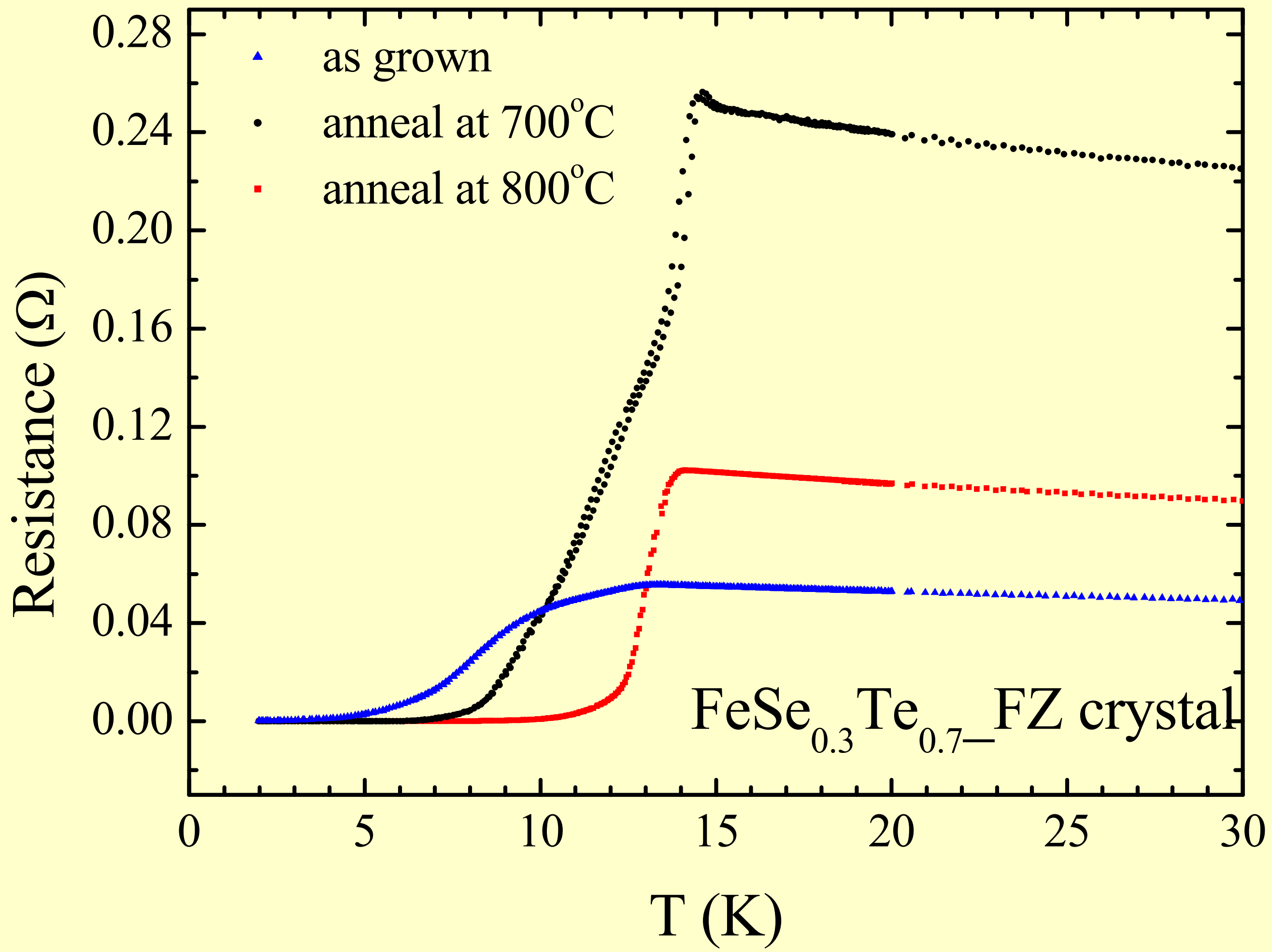


FeSe0.5Te0.5
dTC/dP = 4.87 (10-1 K/kbar)
FeSe0.88
dTC/dP = 3.84 (10-2 K/kbar)
T(K)
P(kbar)

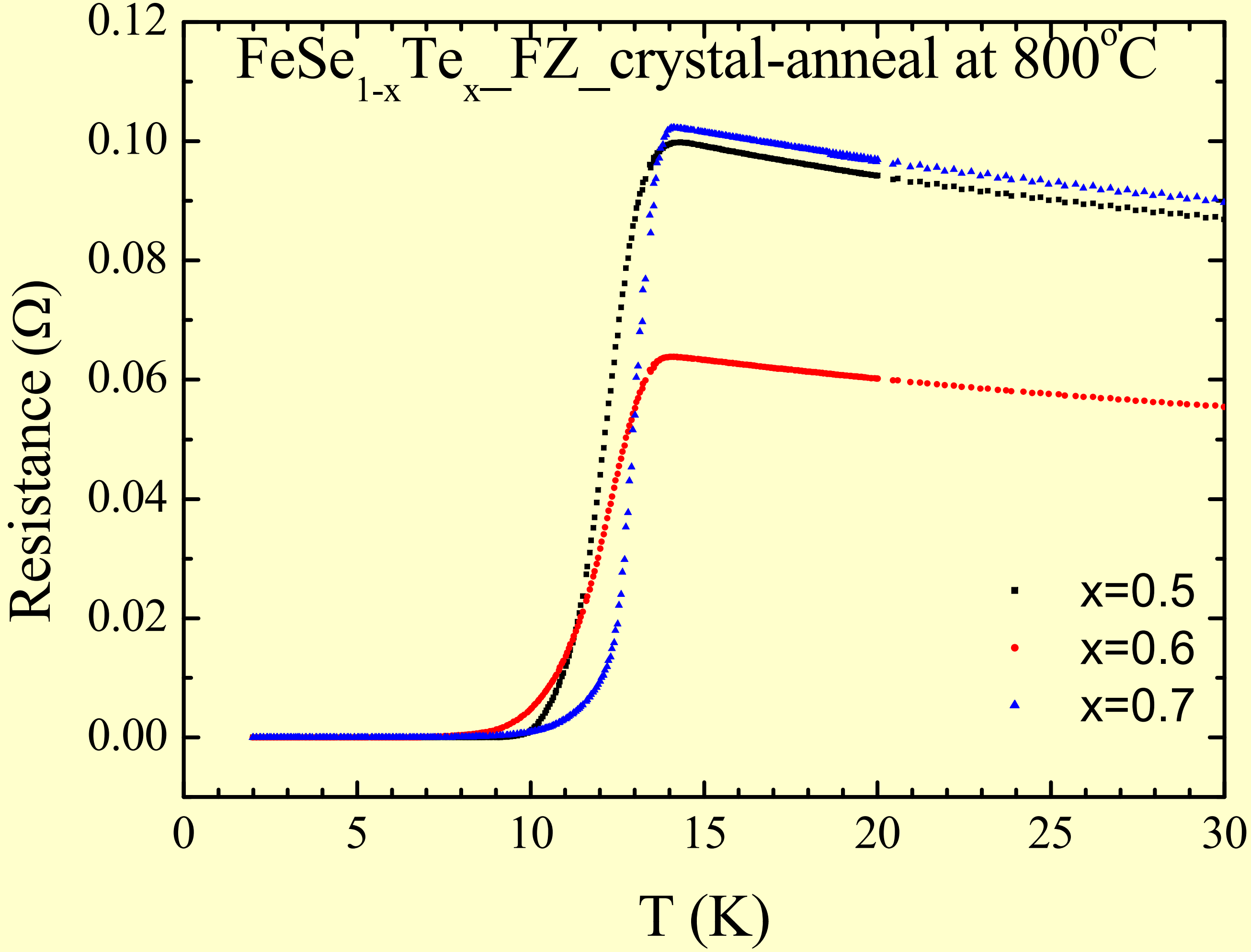
Floating Zone Melt-growth of $FeSe_xTe_{1-x}$ Crystal

- All the crystals are grew in (001) direction and they show very well crystallization.
- Crystals are platelet, easy to peer off
- The properties of the crystal are similar to those of the bulk.
- High temperature post-annealing makes the crystals more homogeneous

Effects of High Temperature Annealing on Crystals



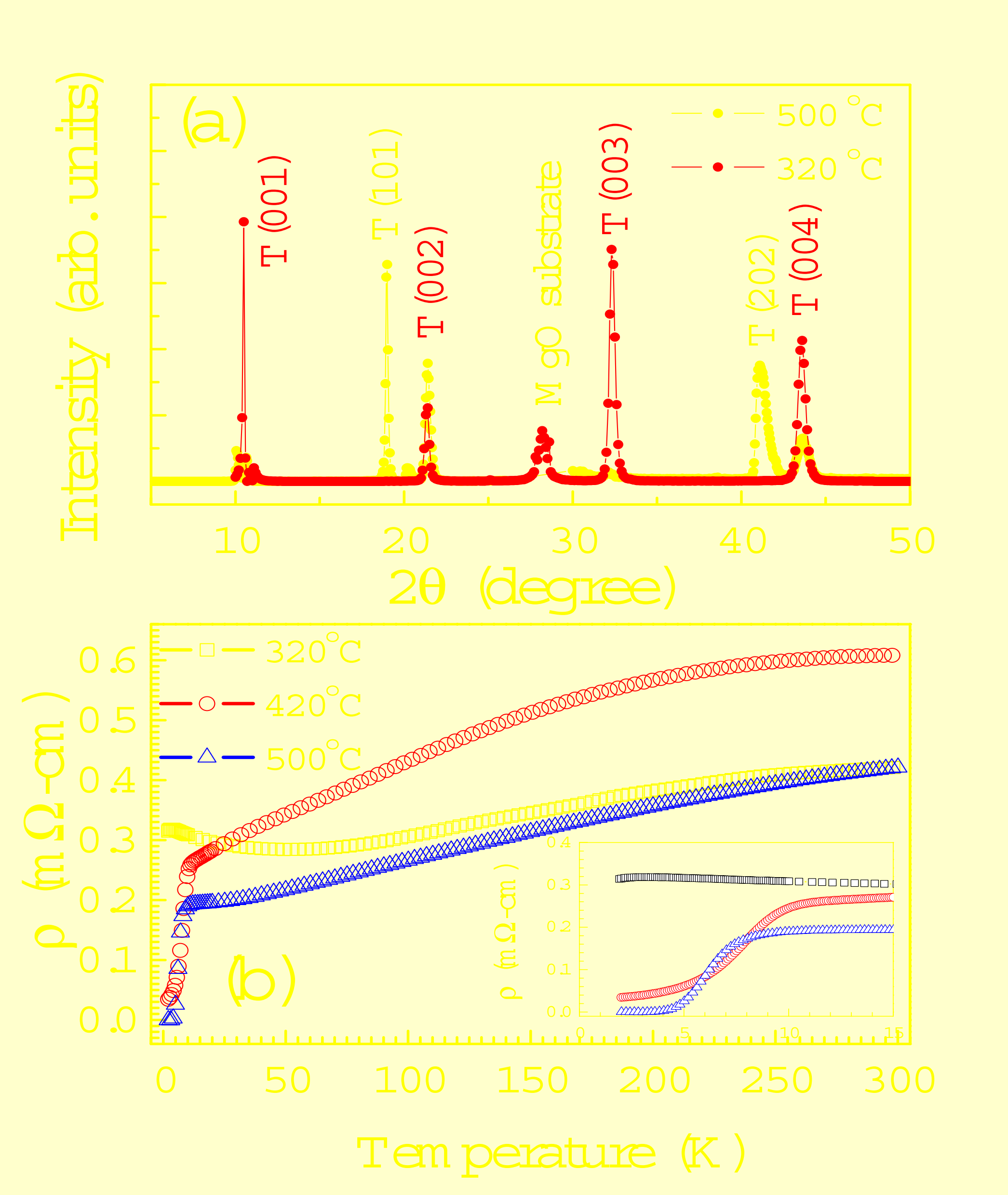
Crystal annealed at 800^oC

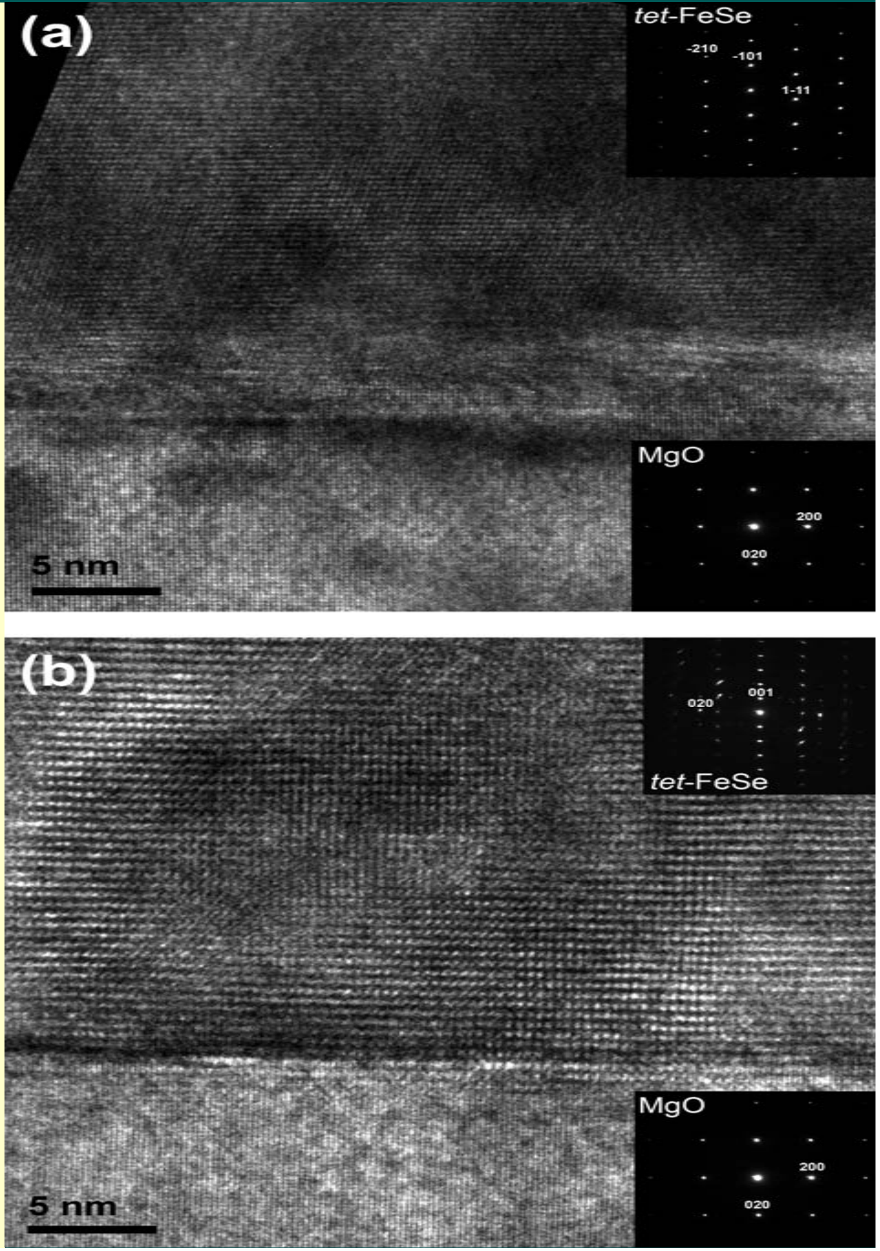


Thin Film by PLD

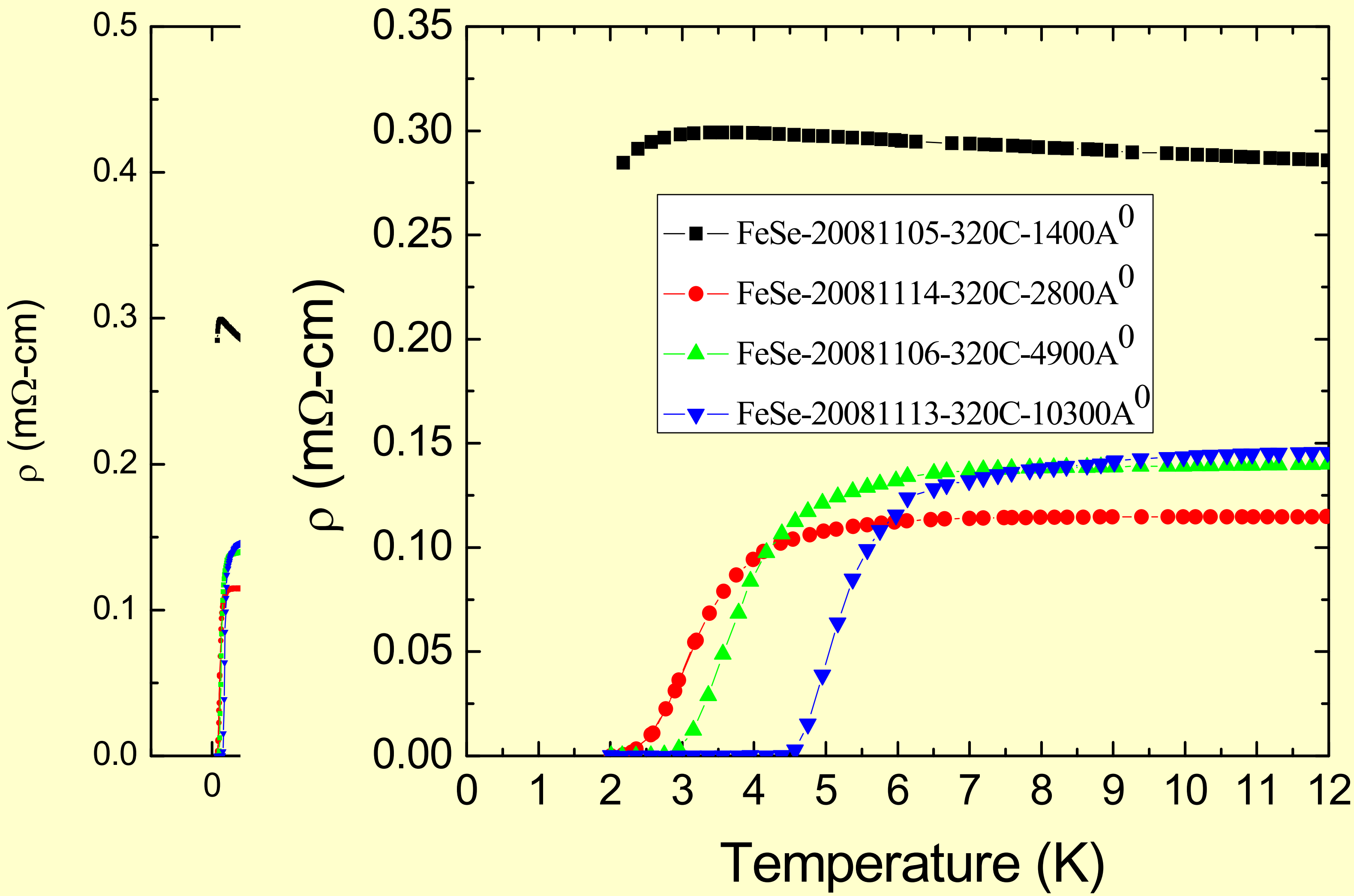
1. Use targets of roughly 1”×8mm
2. Thin films were deposited in a vacuum chamber ($\sim 10^{-5}$ Torr) using a KrF (λ = 248 nm) excimer laser
3. The power density of focused laser on the target is 5~6 J/cm^2, and the repetition rate is 2 Hz.
4. The target-substrate distance is near 50 mm.
5. The substrate temperature of deposition is varied from 250 °C to 500 °C.
6. The deposition rate of thin film is about 0.5Å/shot.
7. In addition, the surfaces of targets were polished before each deposition to improve reproducibility.

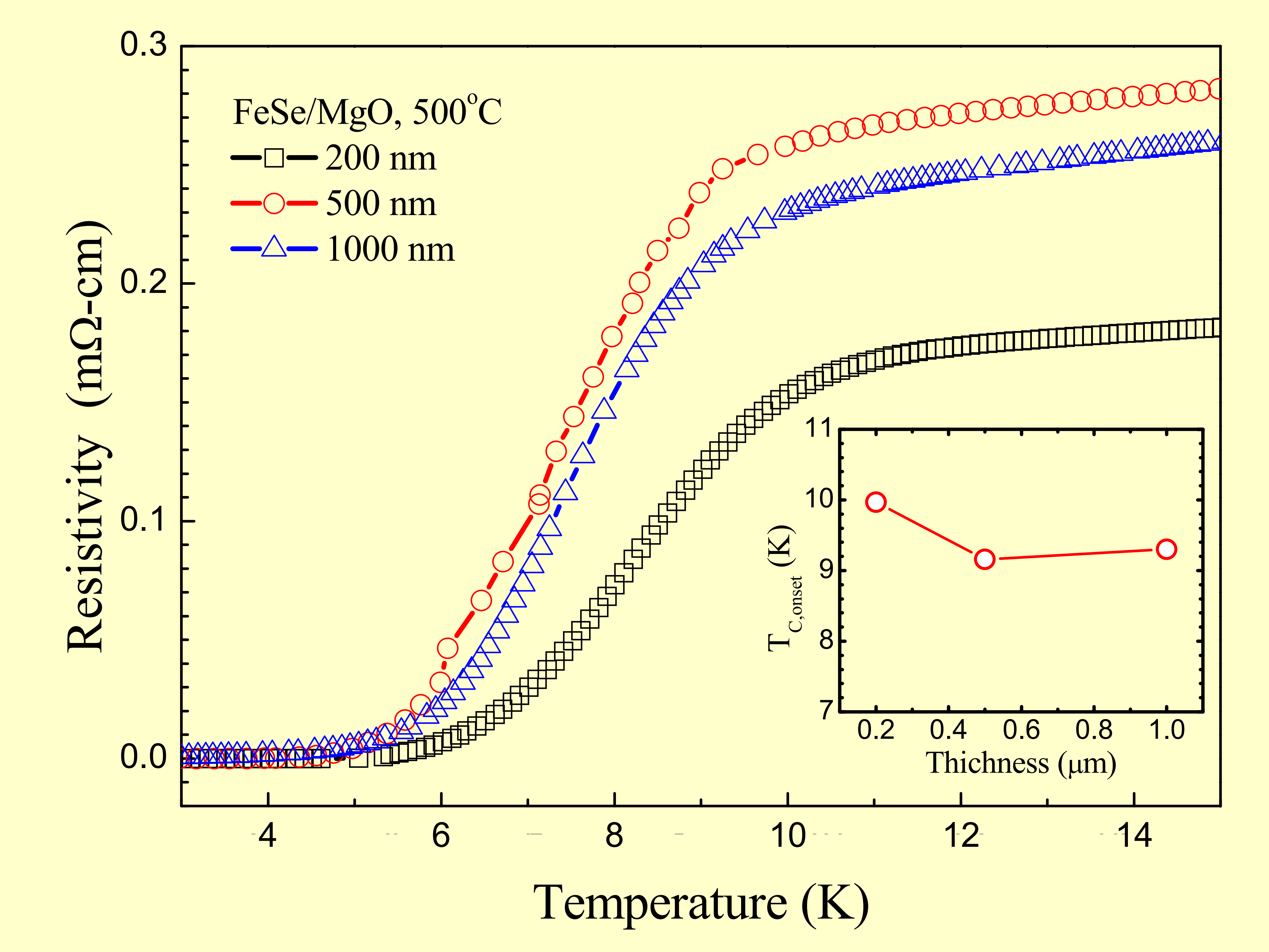
FeSe Thin Film

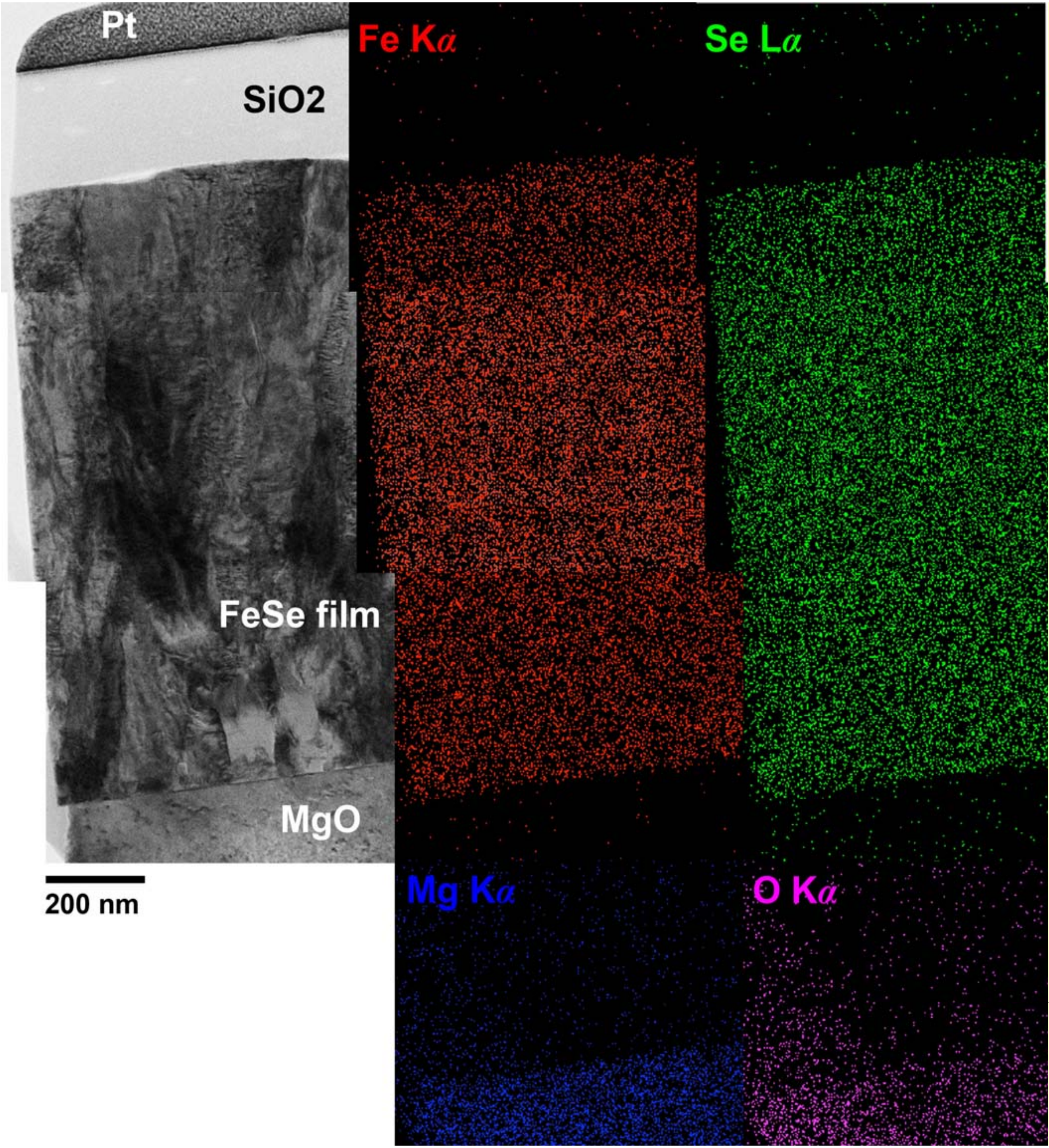




FeSe (Low Temperature Deposition)




FeSe/MgO, 500°C
200 nm
500 nm
1000 nm
Resistivity (mΩ-cm)
Temperature (K)
0.3
0.2
0.1
0.0
4
6
8
10
12
14
$T_{C,onset}$ (K)
Thichness (μm)
11
10
9
8
7
0.2
0.4
0.6
0.8
1.0

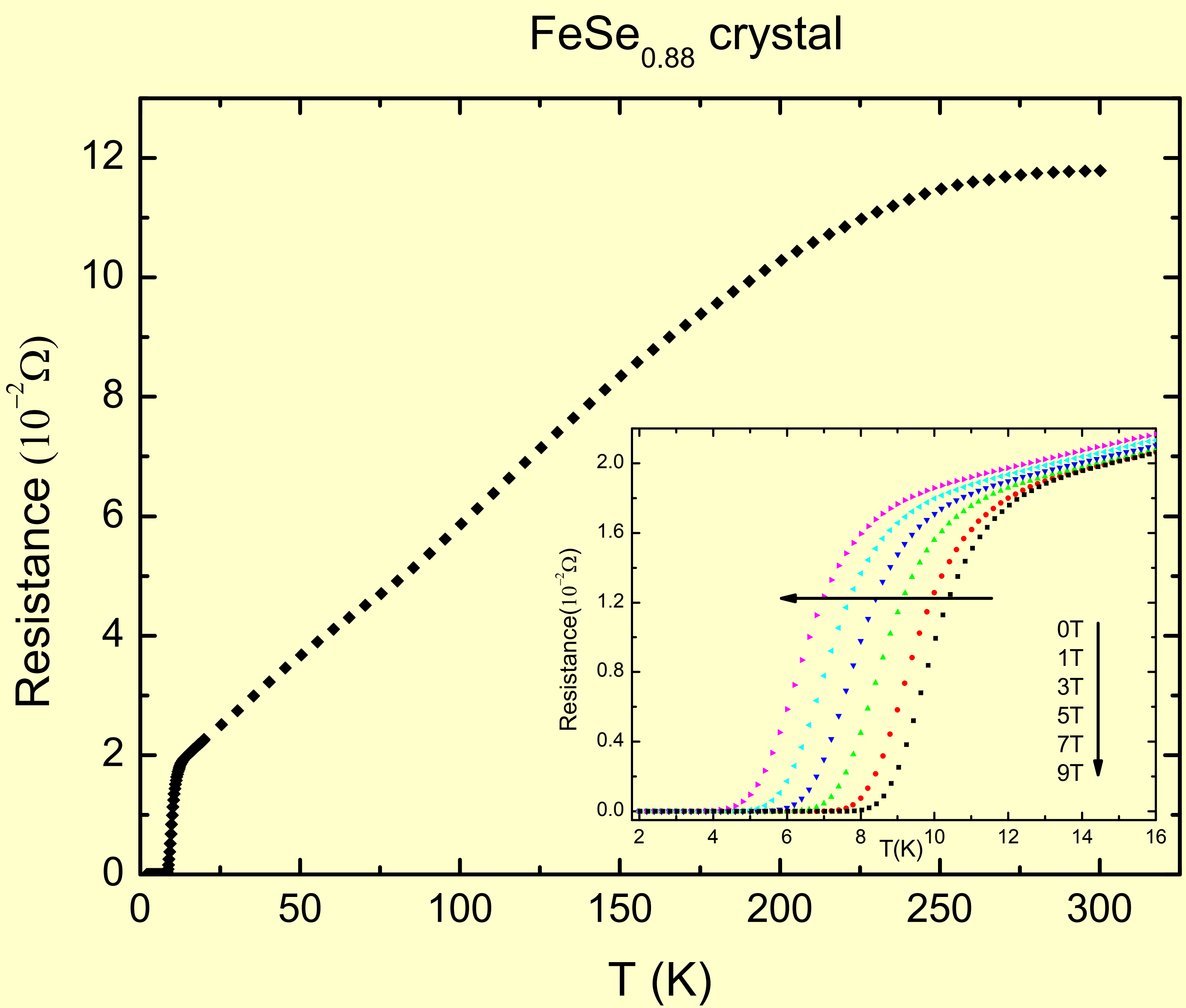


The STEM/EDX mapping of 1 μm (LT-) FeSe thin film grown at 320 °C. The Fe and Se concentrations were found uniformly distributed along the growth direction. This indicates that the sample is relatively homogeneous, and rules out Se gradient as the reason to suppress superconductivity in the low temperature growth films.

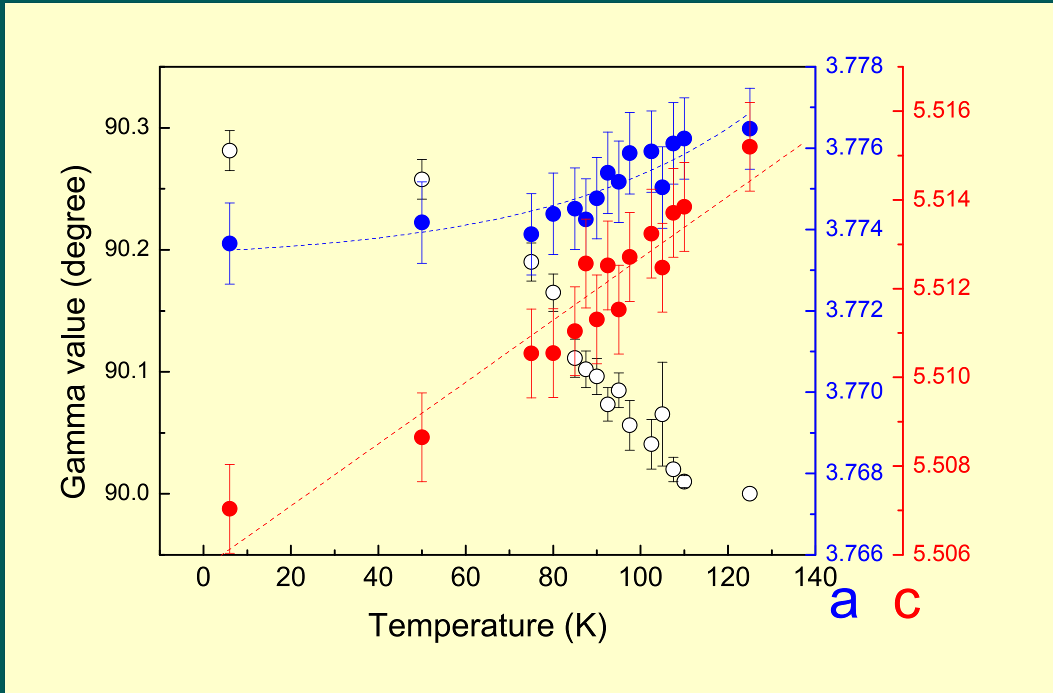
Questions

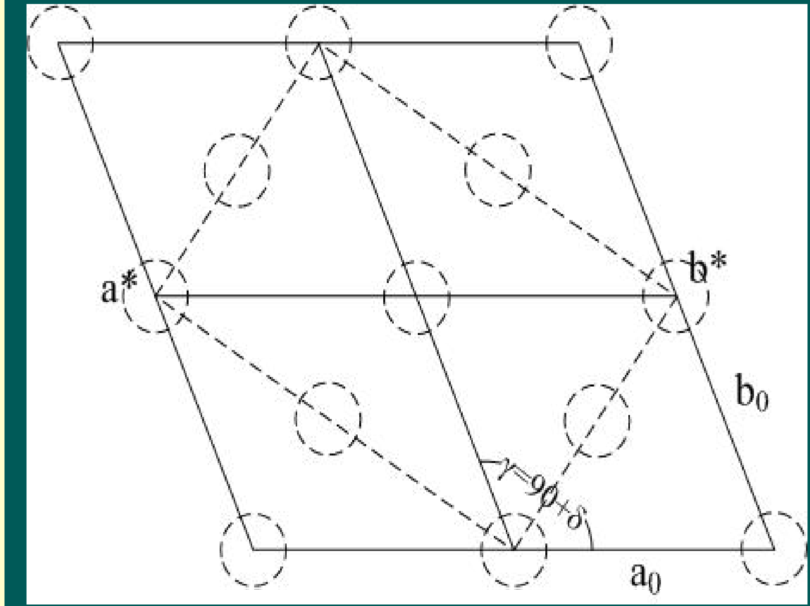
- Why Cu-doping destroys superconductivtiy but not Mn-doping?
- Why FeSe thin films deposit at relatively low temperature (with *00l* preferred orientation on MgO substrate) show strong thickness dependence, but not in those high temperature deposited films (*l0l* orientation)?

Strongly Correlated with the Structural Distortion at low temperature!!



FeSe0.88 crystal
Resistance (10^-2 Ω)
T (K)
0
2
4
6
8
10
12
0
50
100
150
200
250
300
Resistance(10^-2 Ω)
T(K)
0.0
0.4
0.8
1.2
1.6
2.0
2
4
6
8
10
12
14
16
0T
1T
3T
5T
7T
9T

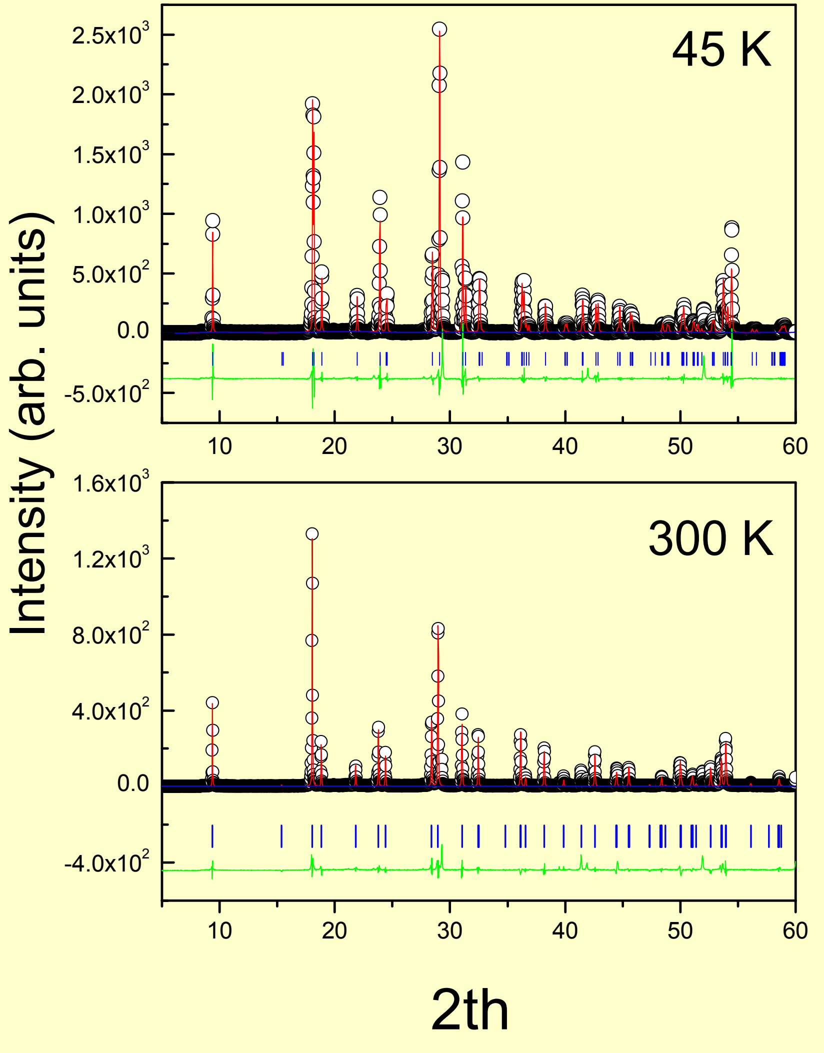


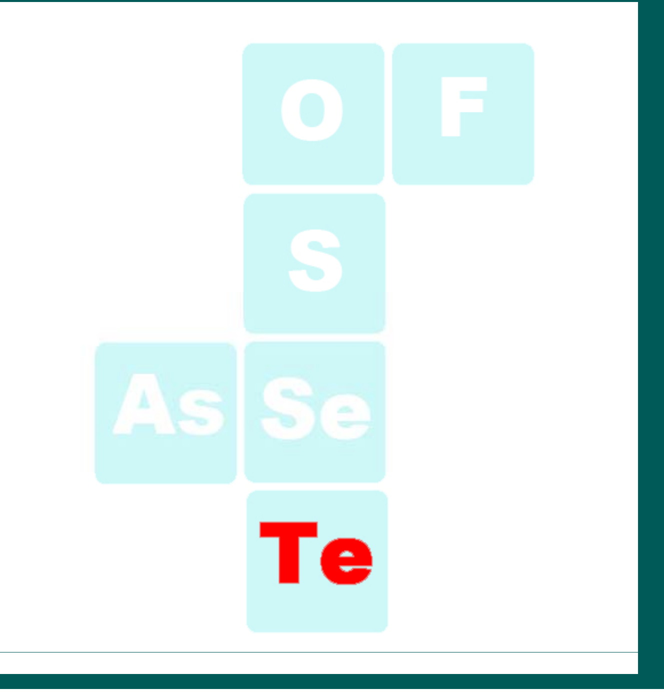


The temperature dependence of gamma value (open black circle), a (blue solid circle) and c (red solid circle) obtained from detailed X-ray refinement by P-1 space group.

The c is shirking as temperature decreasing with a gradient equals to 6.97X10^{-5} A/K. Oppositely, the shirking of a axis is obviously retarding as the phase transition occurring at 105 K.

FeTe



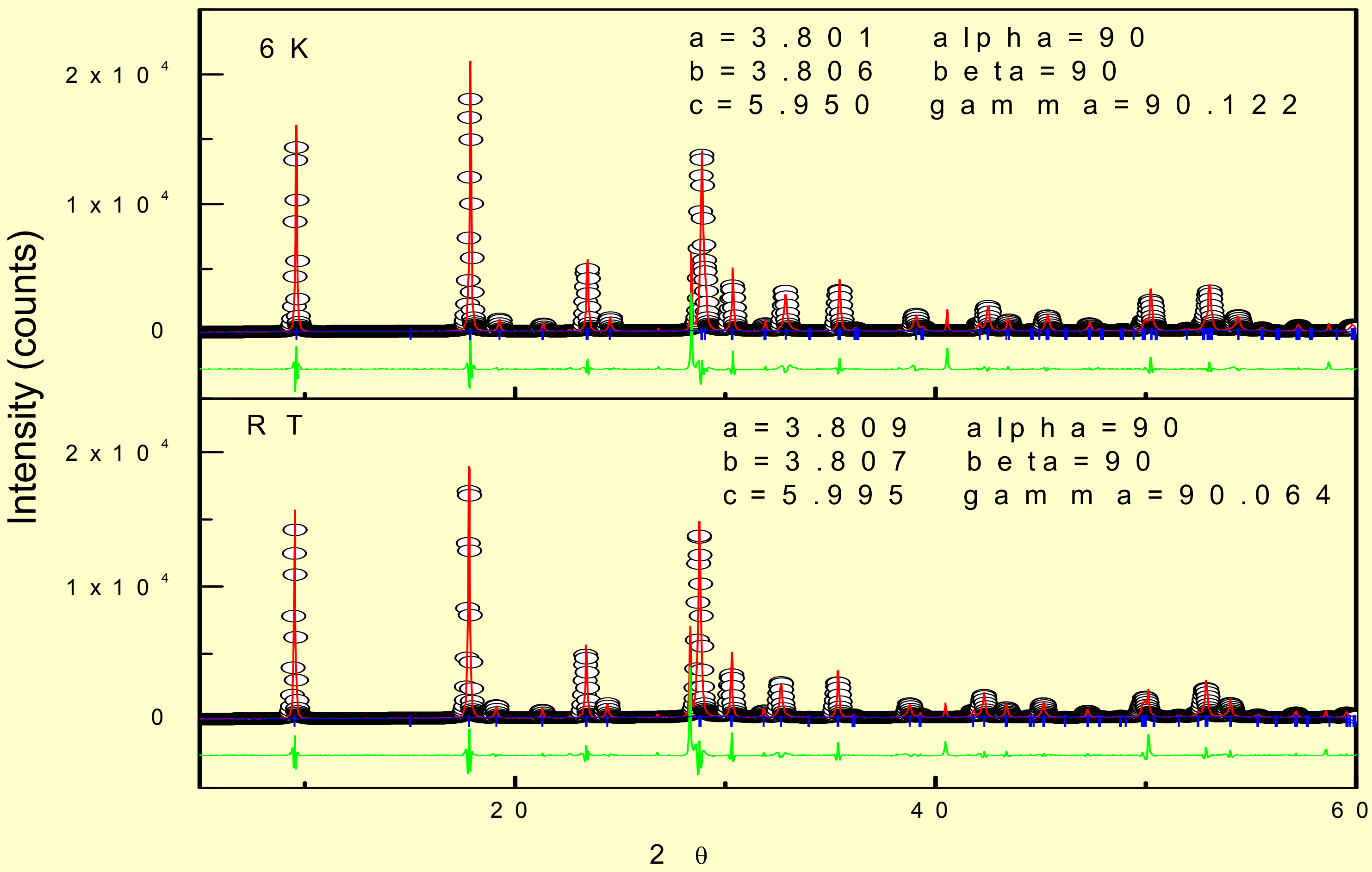


	a (Å)	b (Å)	c (Å)	γ
45K	3.824	3.854	6.303	90
300K	3.861	3.861	6.319	90

Temperature dependence of X-ray diffraction for FeTe using λ=1.0333 A.

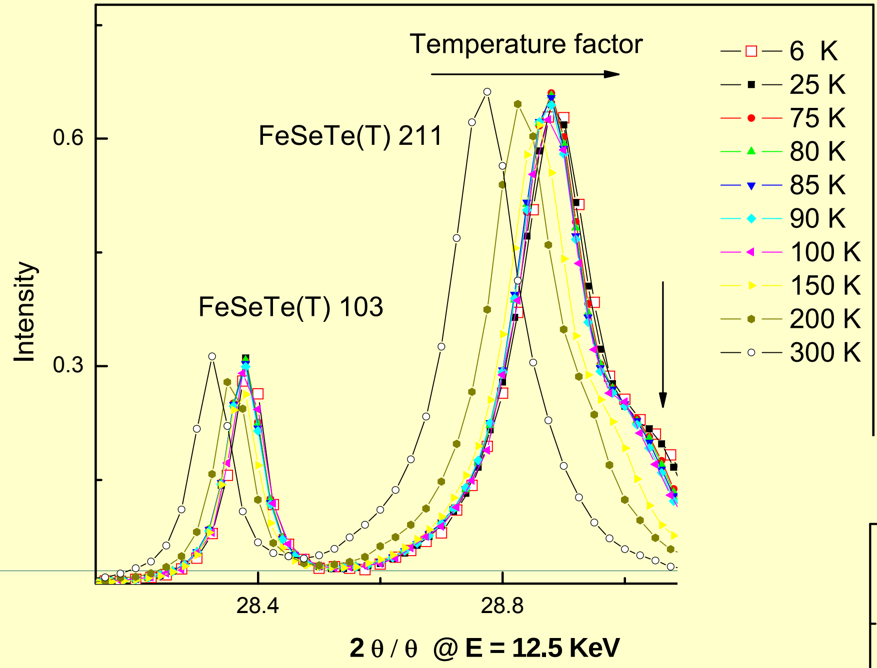
The fitting results shows the different shrinking behavior between FeTe and FeSe. The FeTe compounds become a triclinic crystal which a≠b ≠ c and γ =90. This results might cause from the occupancy of Te is 80% and the larger atom size.

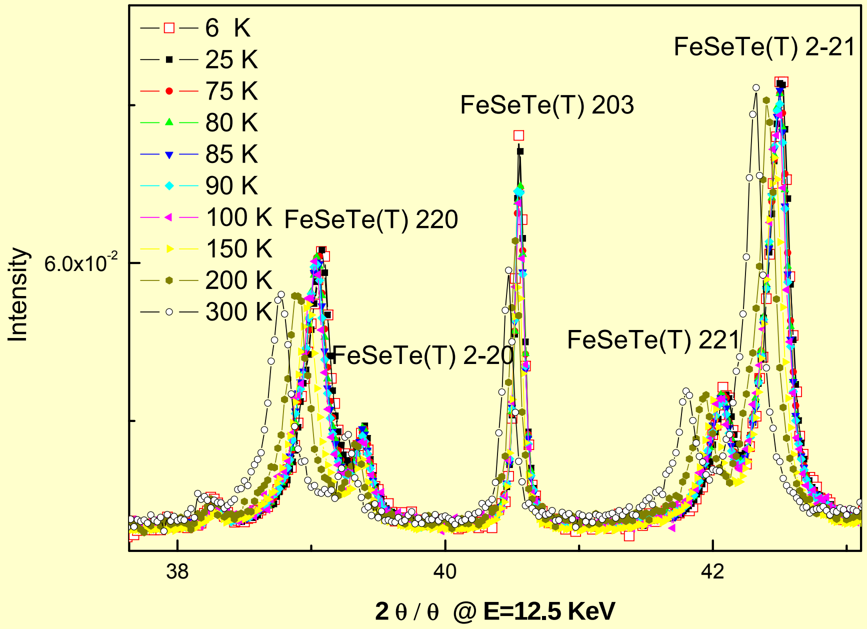
$FeSe_{0.5}Te_{0.5}$



6 K
a = 3.801 alpha = 90
b = 3.806 beta = 90
c = 5.950 gamma = 90.122
R T
a = 3.809 alpha = 90
b = 3.807 beta = 90
c = 5.995 gamma = 90.064
2 x 10^4
1 x 10^4
0
Intensity (counts)
20
40
60
2 θ

$FeSe_{0.5}Te_{0.5}$

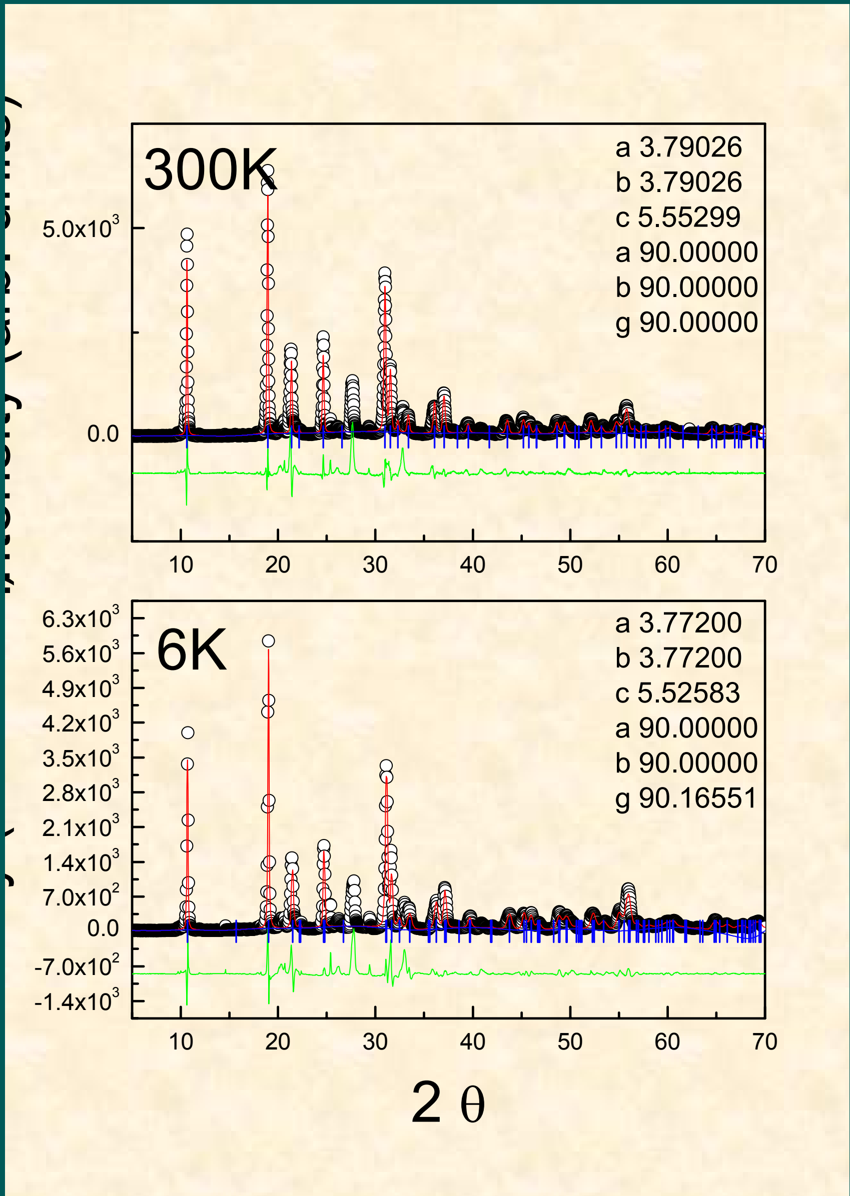




1. Distorted already at room temperature while adding 50% Te.

2. Further distorted at low temperature.

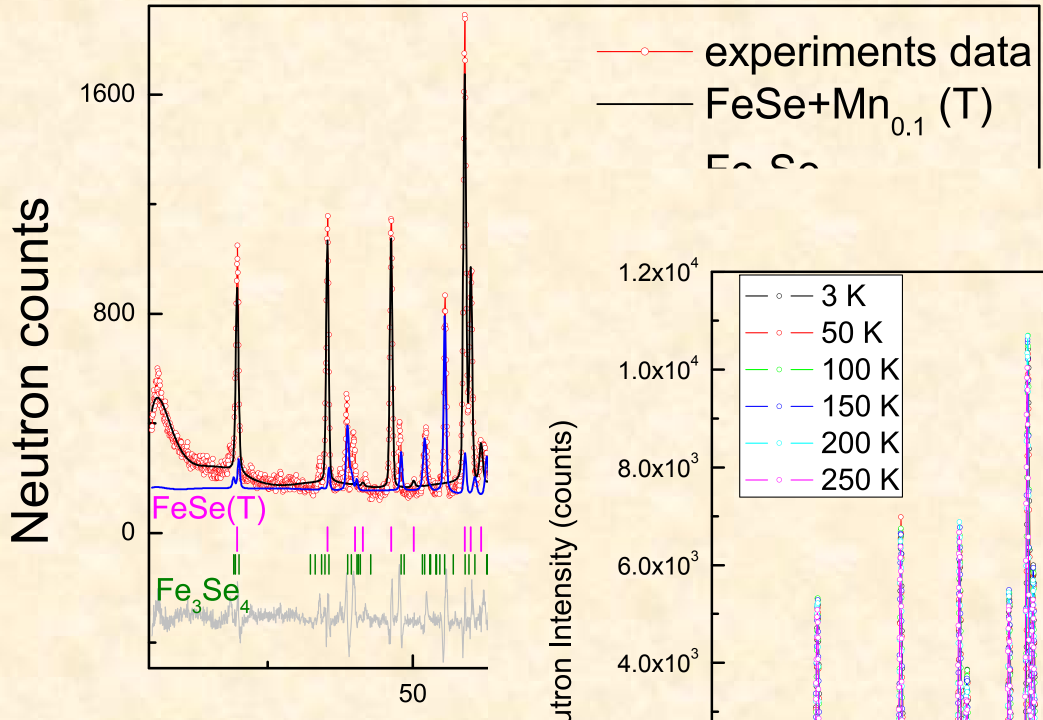
$(Fe_{0.9}Mn_{0.1})Se_{0.85}$

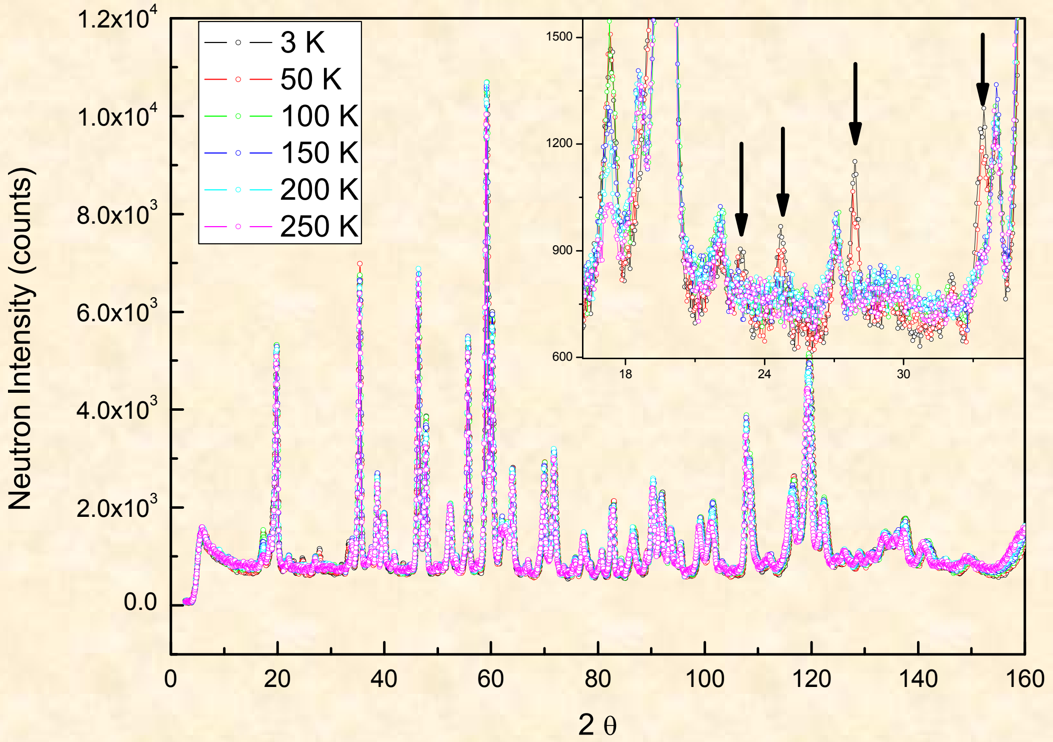


FeSe+Mn0.1

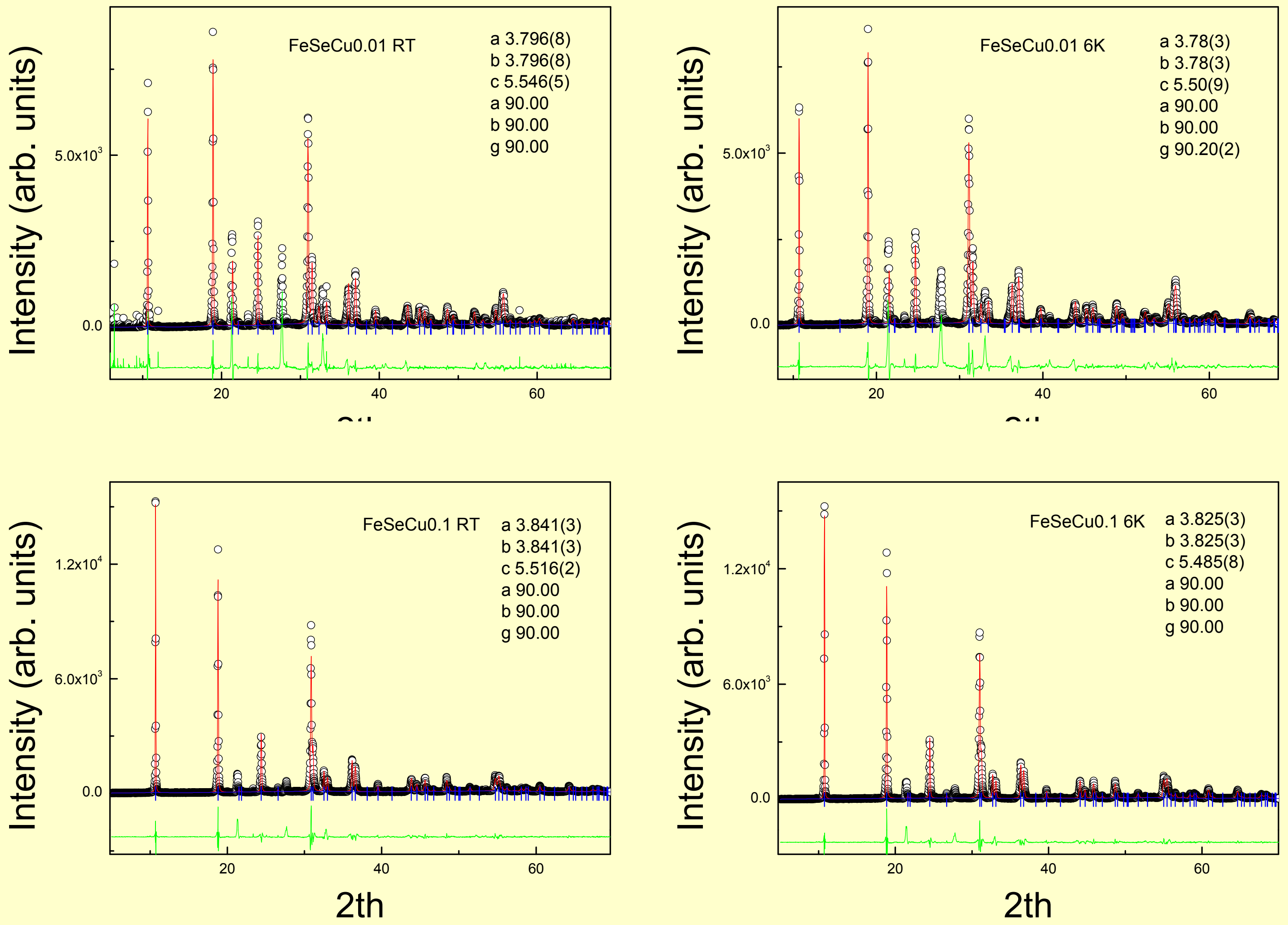
	a (Å)	b (Å)	c (Å)	γ
6K	3.772	3.772	5.526	90.166
300K	3.790	3.790	5.552	90

Neutron diffraction for $Fe_{0.9}Mn_{0.1}Se$

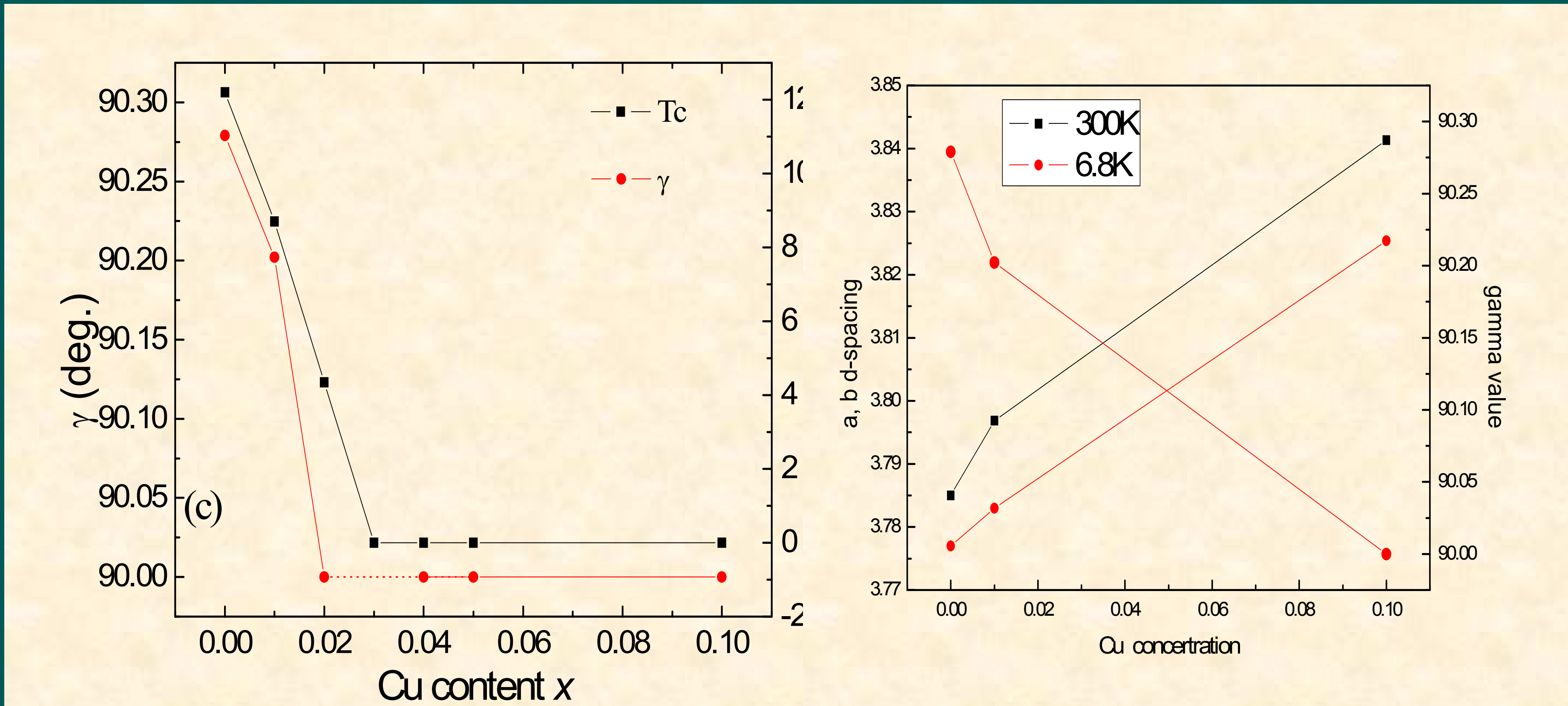




$Fe_{1-x}Cu_xSe$


FeSeCu0.01 RT
a 3.796(8)
b 3.796(8)
c 5.546(5)
a 90.00
b 90.00
g 90.00
FeSeCu0.01 6K
a 3.78(3)
b 3.78(3)
c 5.50(9)
a 90.00
b 90.00
g 90.20(2)
FeSeCu0.1 RT
a 3.841(3)
b 3.841(3)
c 5.516(2)
a 90.00
b 90.00
g 90.00
FeSeCu0.1 6K
a 3.825(3)
b 3.825(3)
c 5.485(8)
a 90.00
b 90.00
g 90.00
Intensity (arb. units)
2th

$Fe_{1-x}SeCu_x$



Tc
γ
(c)
γ (deg.)
Cu content x
300K
6.8K
a, b d-spacing
gamma value
Cu concertration

Neutron diffraction for $Fe_{0.9}Cu_{0.1}Se$

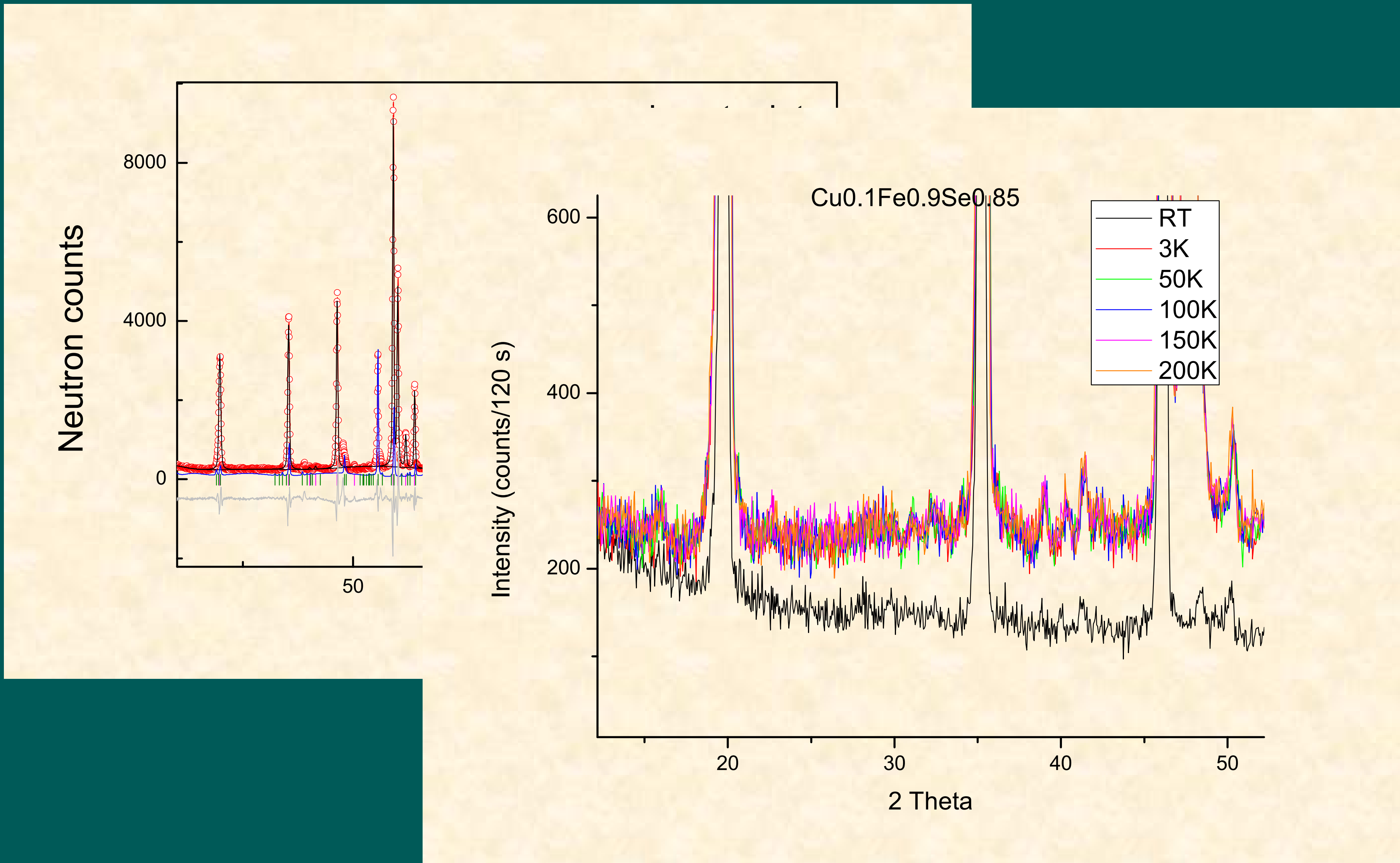
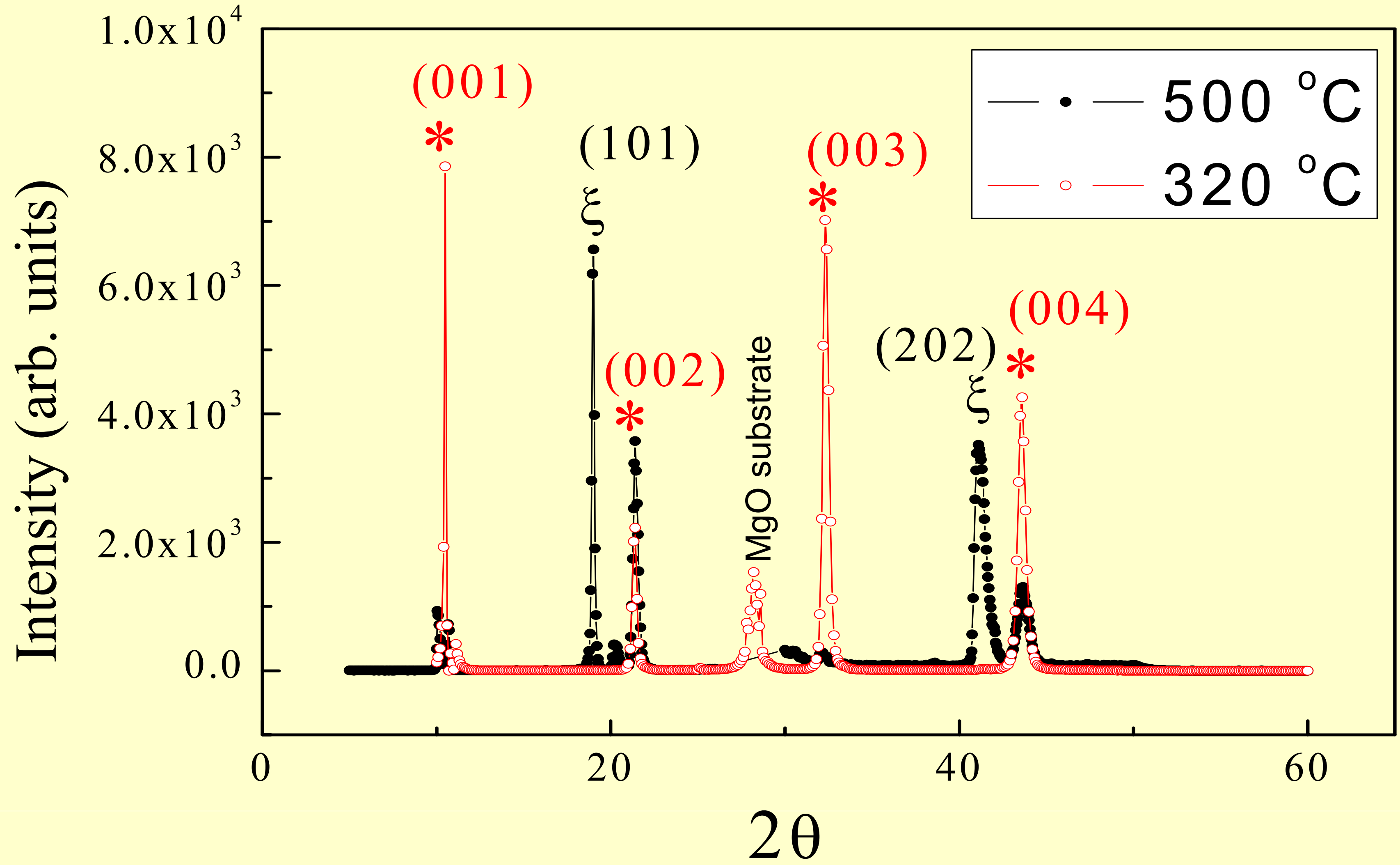
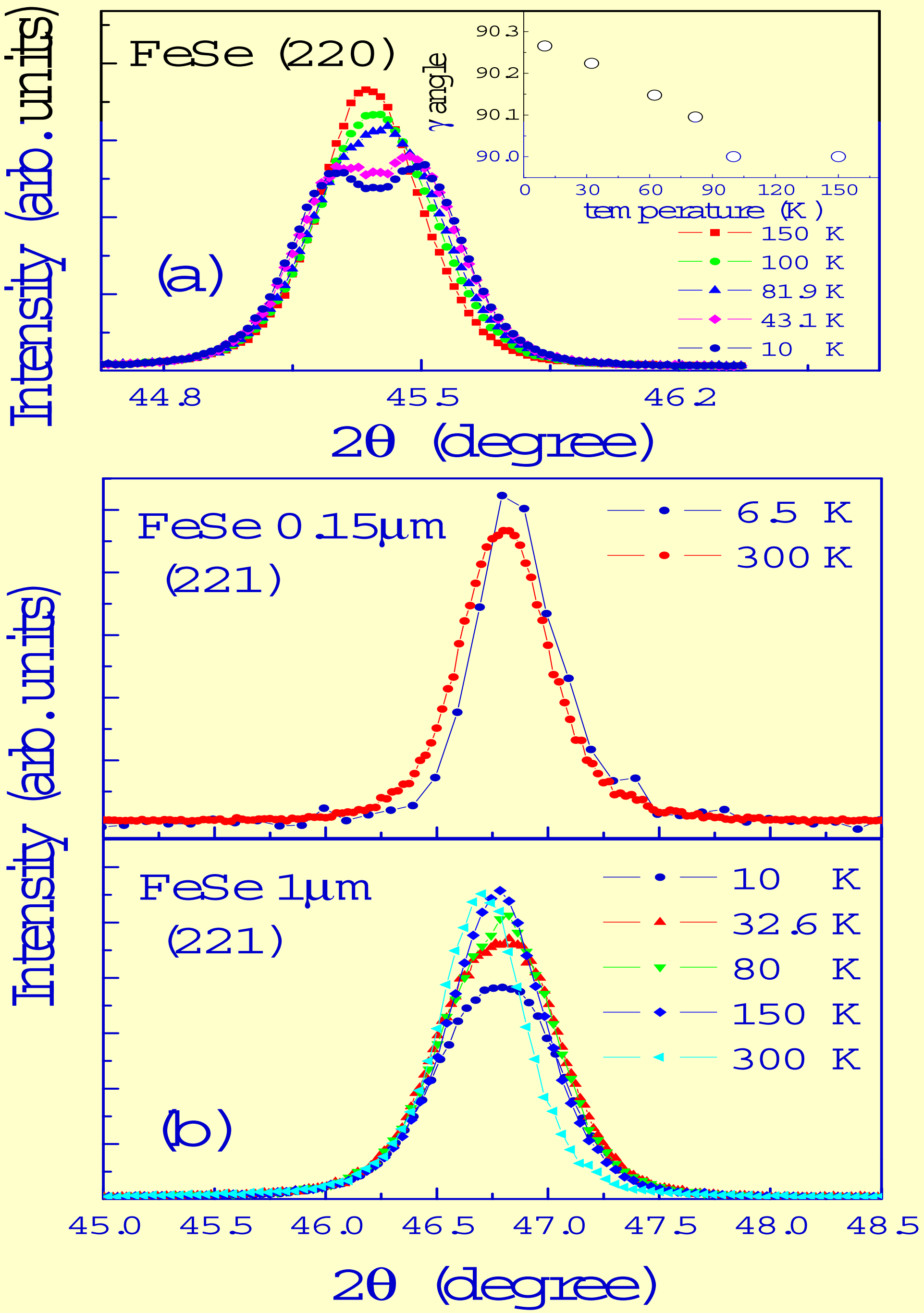


Table X. The critical temperature of superconducting, phase transition temperature and gamma angle for iron selenide

``	Tc	Phase transition temperature	**Gamma angle (o) at 6 K
$FeSe_{0.88}$	8.? K	~105K	90.279
FeTe	none	~80K *	90
$Fe(Se_{0.5}Te_{0.5})$	15.2 K	~100K	90.122
$(FeMn_{0.1})Se$	11.2 K	~85K	90.166
$(FeCu_{0.1})Se$	none	none	90

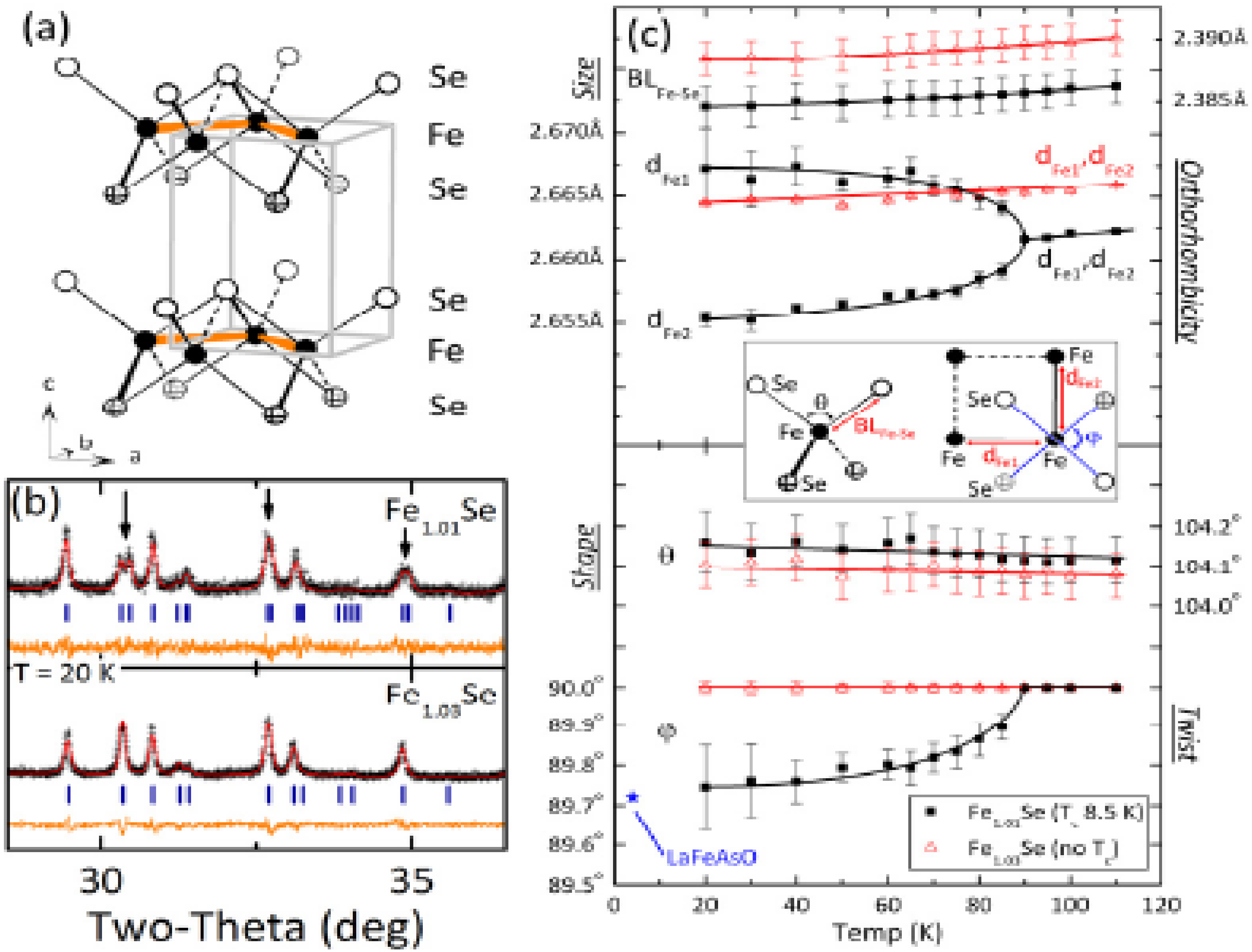


The X-ray diffraction results along the out-of-plane for FeSe thin films which grew at 320 degree (open red circle) and 500 degree (soild black circle). The results show's the orientation at out-of-plane had change from (00a) (red ∗)to (b0b) plane (black ξ).



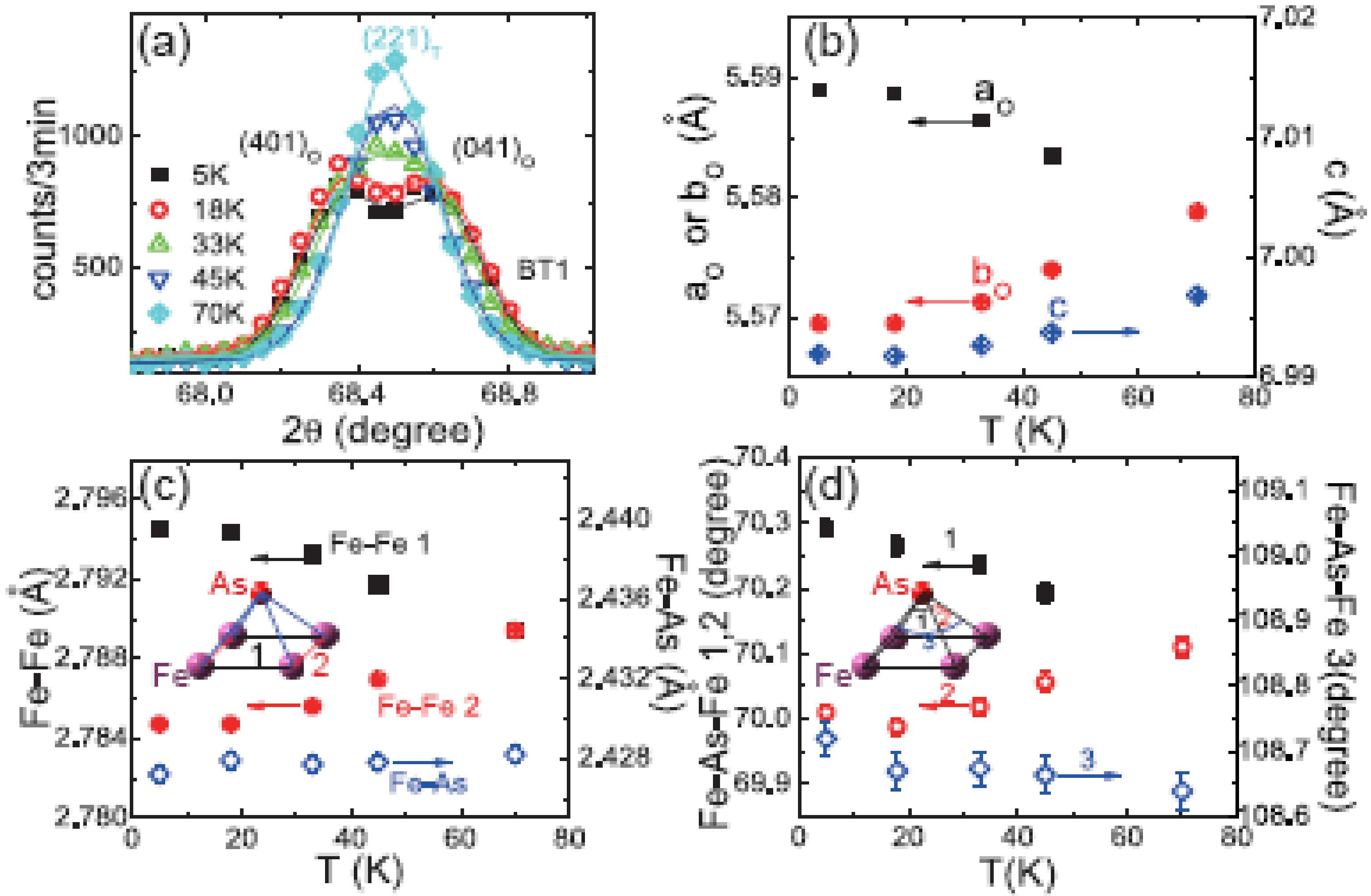
The X-ray diffraction (220) peaks of HT-FeSe film at different temperatures. The results show the splitting of the Bragg peak indicating a structural distortion occurs at around 82K. The inset shows the change of the γ angle with temperature. (b) The X-ray diffraction pattern of LT-FeSe films for (top) 0.15μm and (bottom) 1μm film at different temperatures. The data show that for 0.15μm film the (221) Bragg peak does not change with temperature; for 1μm film the (221) peak becomes broadened at low temperature.

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

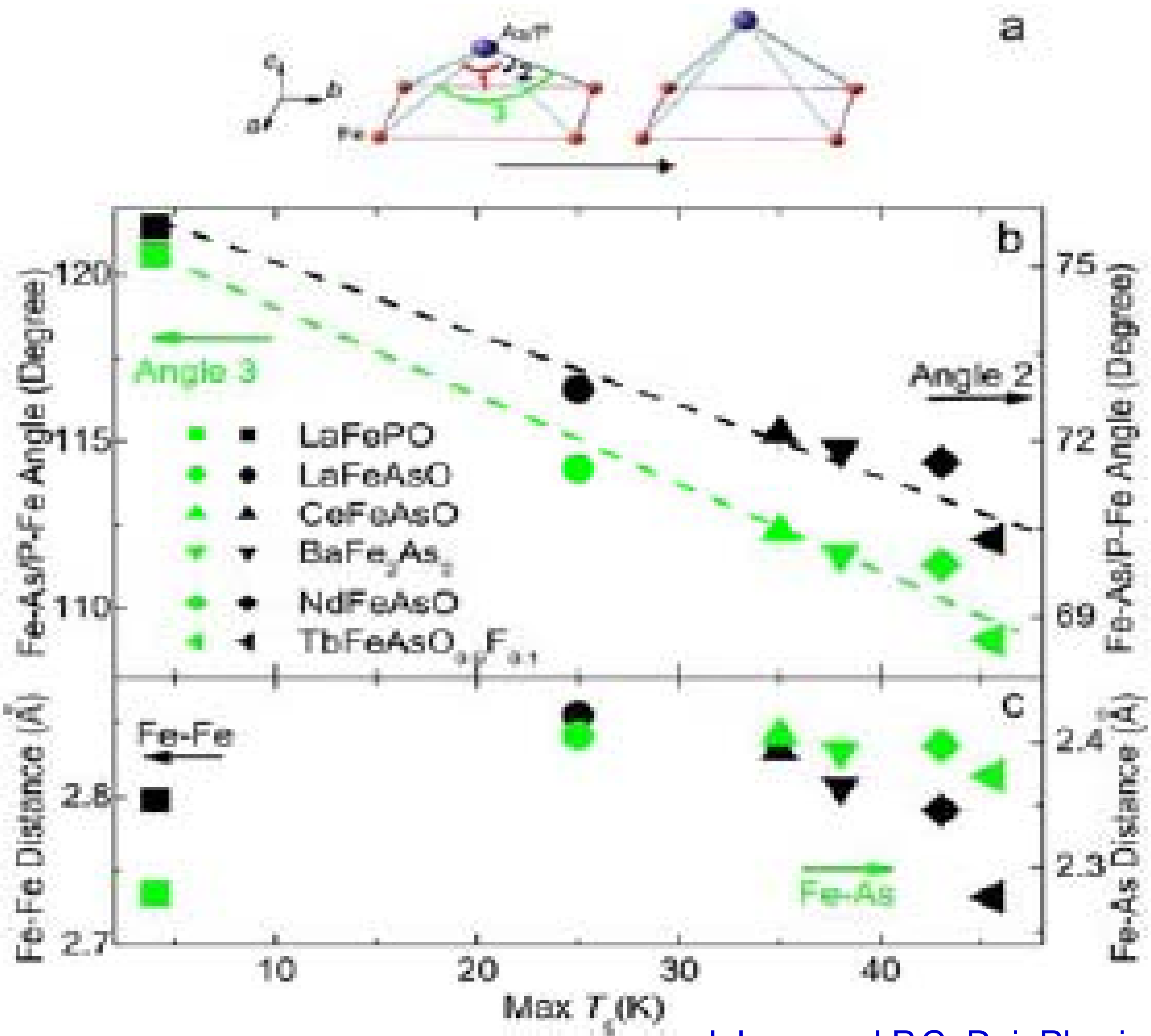


T. M. McQueen et al., arXiv0905.1065

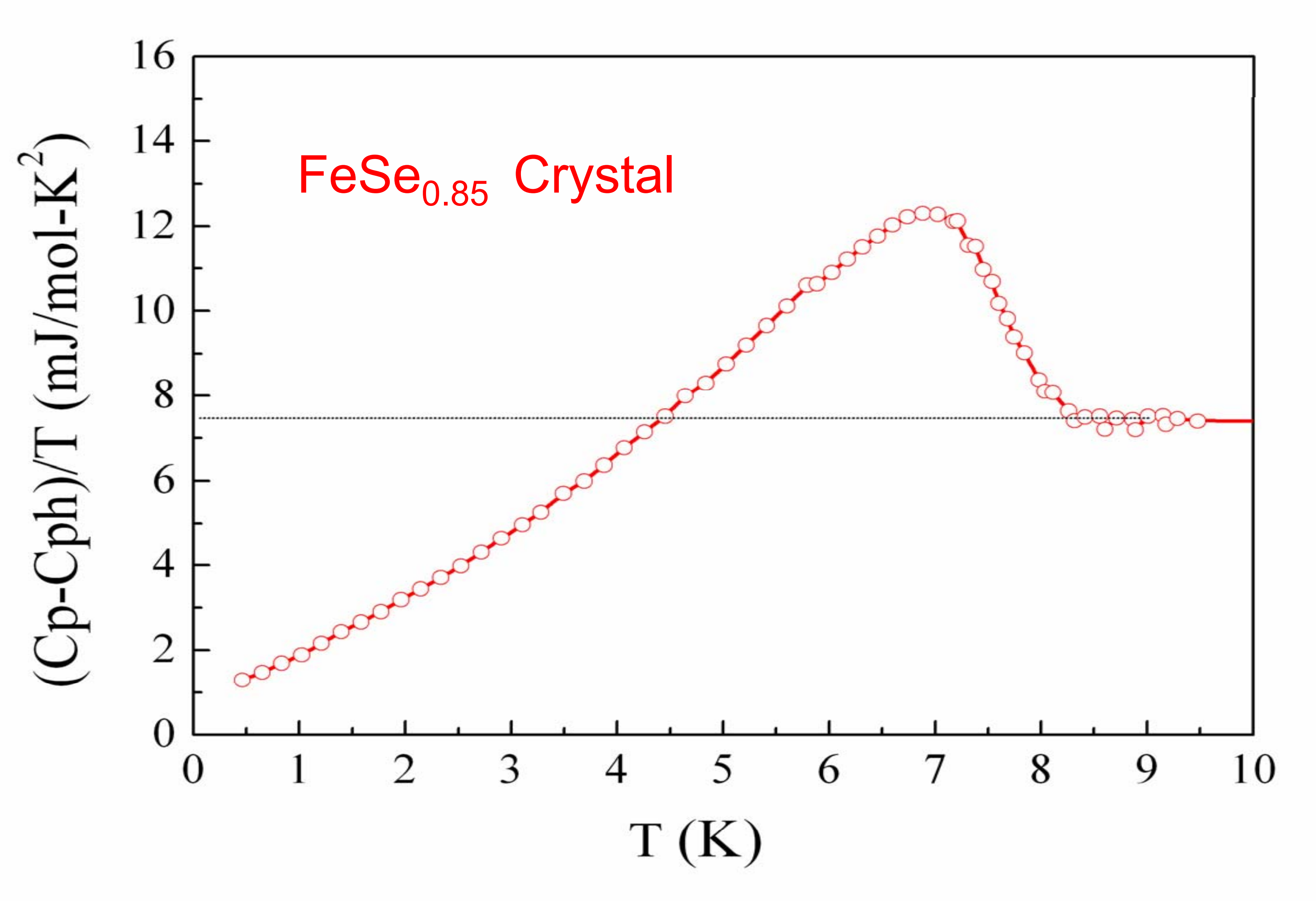
Structural and magnetic phase transitions in Na $_{1-x}$FeAs



Shiliang Li, et al., arXiv0905.0525

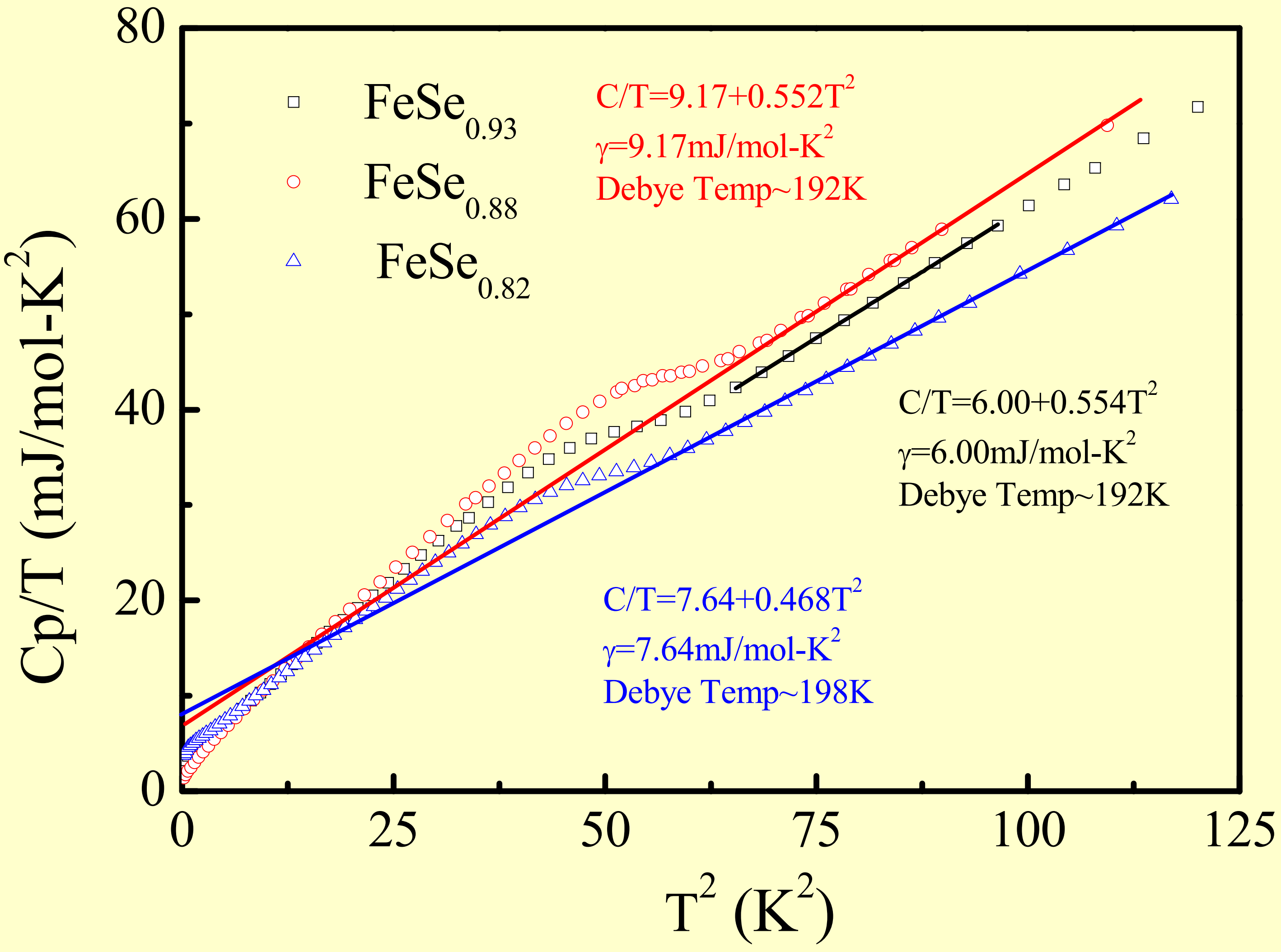


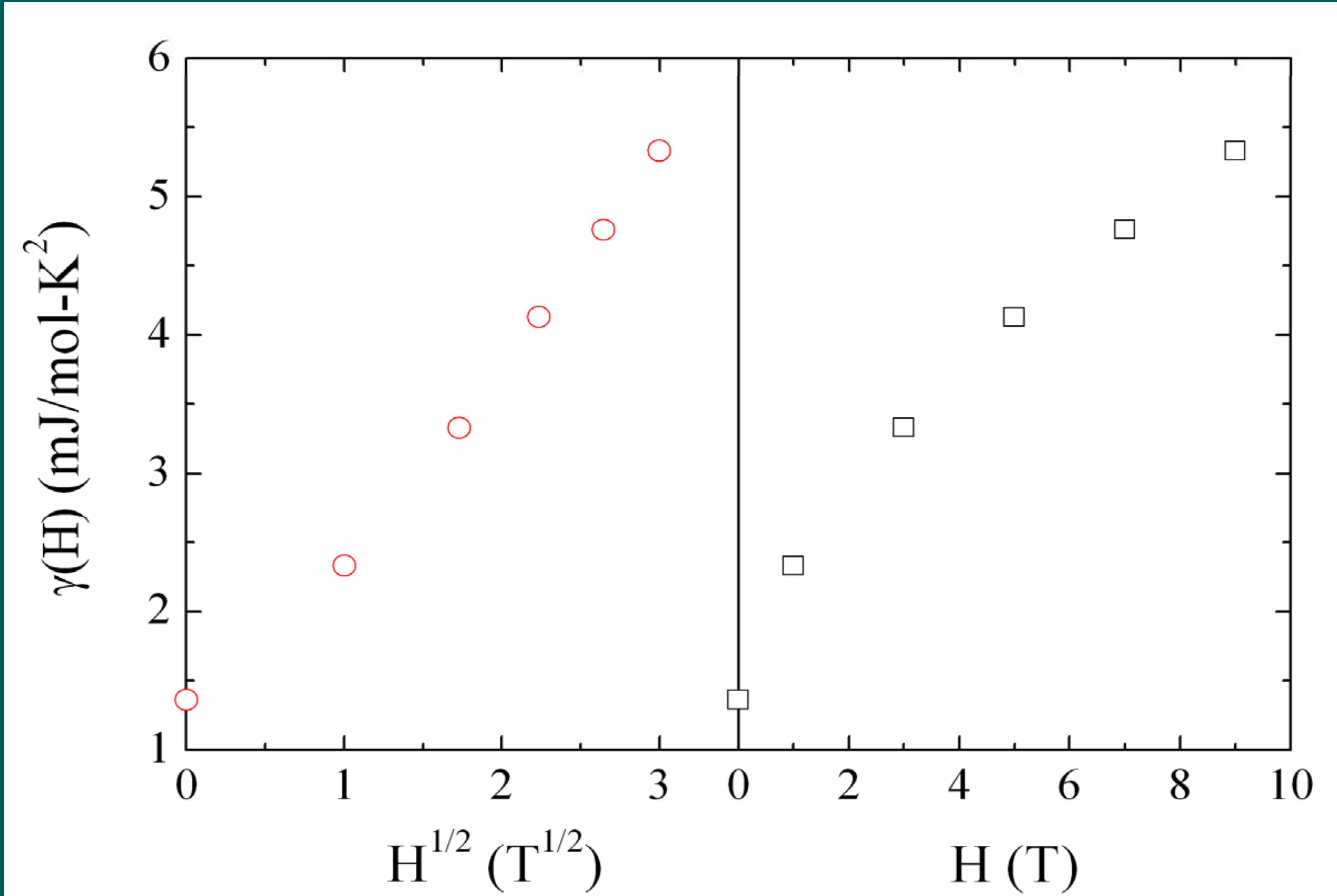
J. Lynn and P.C. Dai, Physica C, 2009



Temperature dependence of (Cp-Cph)/T in a magnetic field of 0 G. The phonon contribution Cph is $0.586T^3$-$1.39E\text{-}4T^5$. A dotted line represents constant electronic specific heat 7.45 $mJ/mol\text{-}K^2$ for comparison.

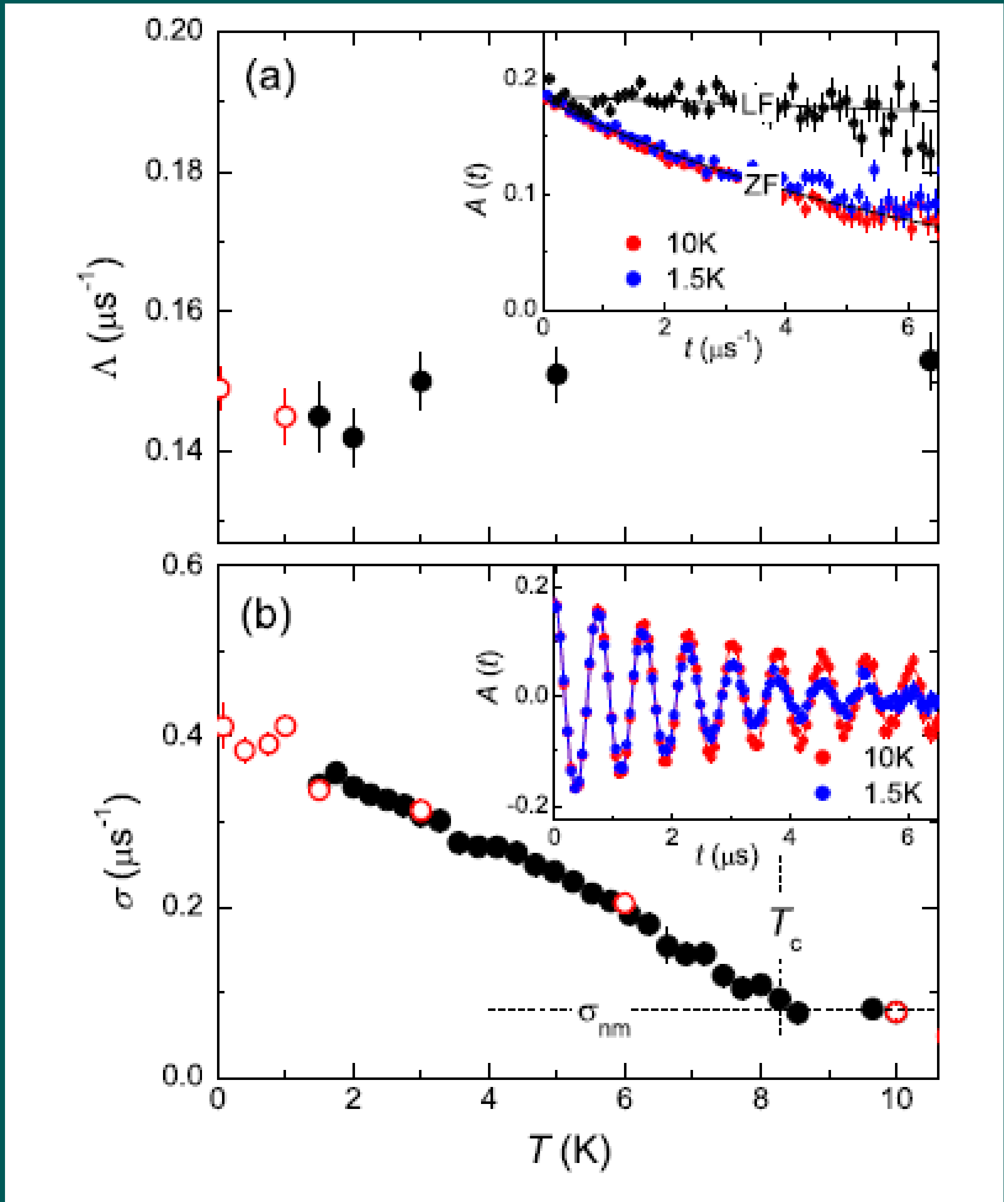
According to the extrapolation fitting curve, the Debye temperature 192~198K seems similar to each other, but there is no systematic change in electronic specific heat in these three samples.





The magnetic field dependence of electronic specific heat of the $FeSe_{0.88}$ sample. The left figure shows the plot of $\gamma(H)$-$H^{1/2}$ and the right one shows the plot of $\gamma(H)$-H.

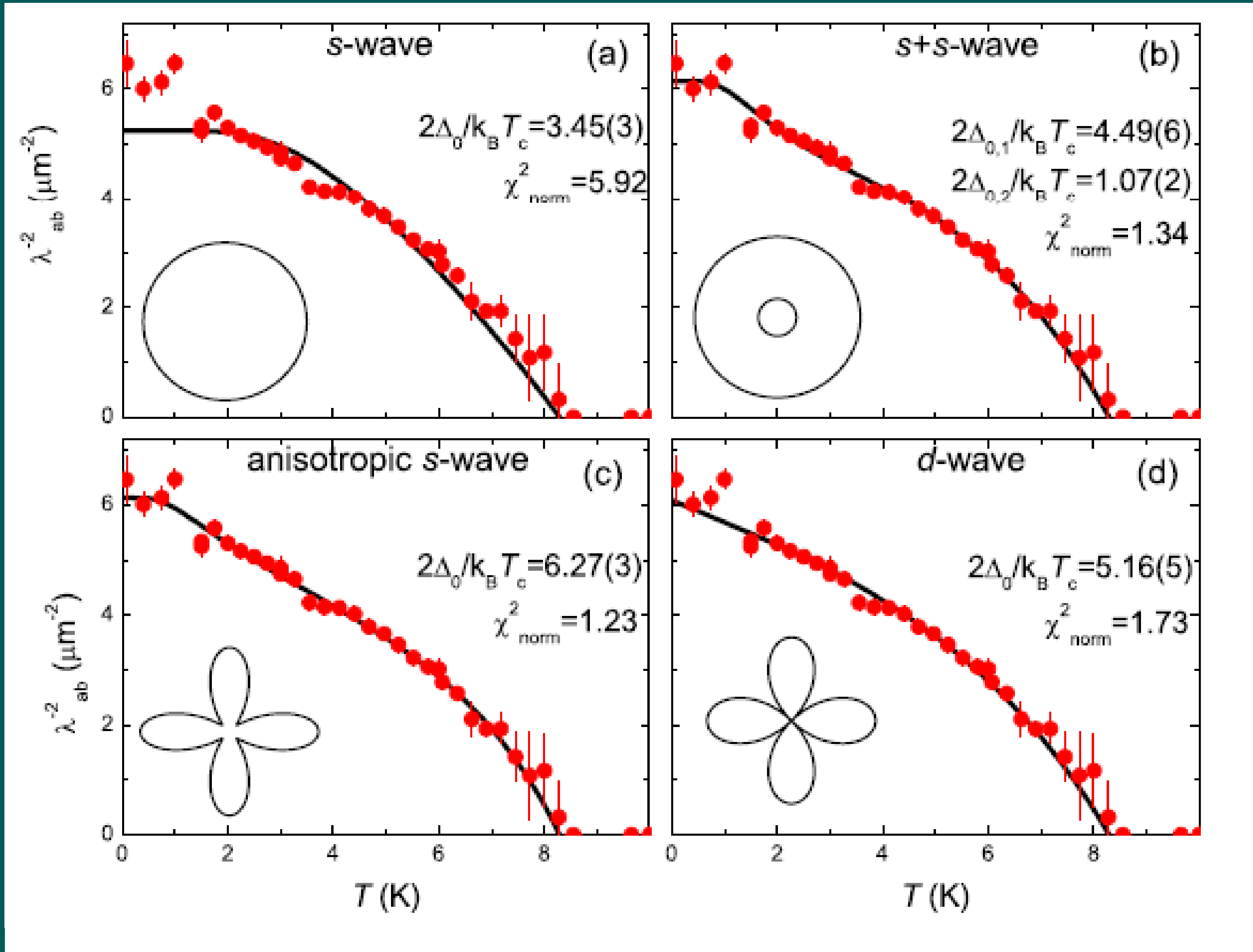
Muon-spin-rotation study



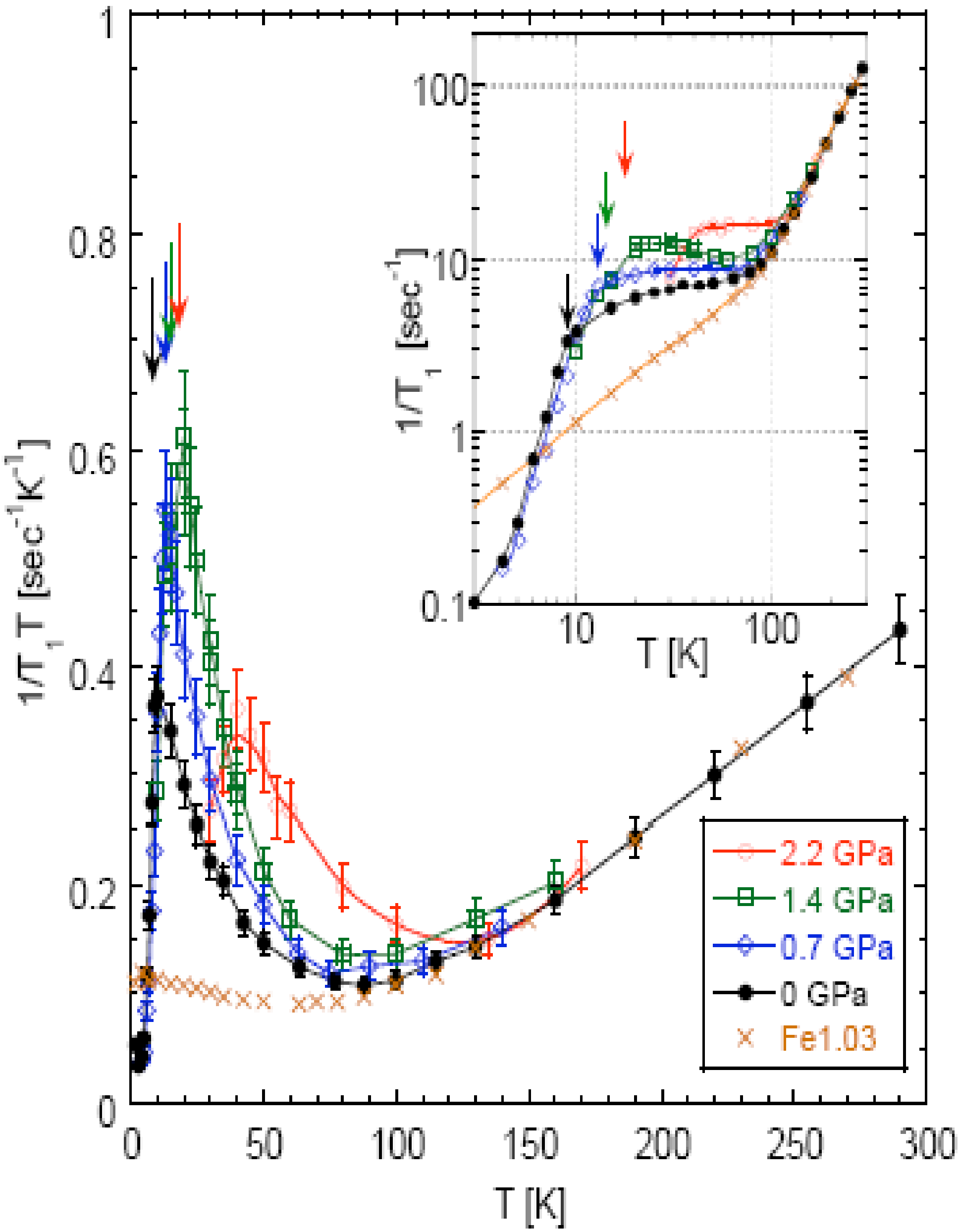
(a) Temperature dependence of the ZF muon depolarization rate of FeSe0.85. The inset shows ZF (T =1.5 and 10 K) and LF (*T=10 K and* $\mu_0 H=0.01$ *T) μSR time* spectra of $FeSe_{0.85}$.

(b) Temperature dependence of the Gaussian depolarization rate obtained in TF μSR experiment at $\mu_0 H=0.01$. The inset shows the TF muon-time spectra above T =10 K and below *T=1.5 K; the transition temperature Tc=8.26 K.*

Khasanov *et al*., PRB **78, 220510R 2008**



Khasanov *et al.*, PRB **78, 220510R 2008**



Imai et al., arXiv:0902.3832v

1. FeSe show no evidence for canonical Fermi liquid above Tc, i.e. the Korringa relation 1/T1TK2 = const. is not satisfied.
2. Large enhancement of 1/T1T below 100K indicates that antiferromagnetic spin fluctuations are strongly enhanced toward Tc .
3. Application of pressure further enhances both spin fluctuations and Tc, pointing toward a link between antiferromagnetic spin fluctuations and the superconducting mechanism.

Summary

- Single crystal and oriented thin films can be prepared, but quality still need further improvement
- Anisotropic magnetic susceptibility in normal state is observed
- A low temperature distortion from tetragonal (P4/mmm) to monoclinic (or orthorhombic) is essential for superconductivity
  - FeSe –γ-angle increases from 90^o to about 90.3^o at ~ 105K; Tc correlates well with inverse of c-lattice parameter (1/c)
  - Te-doping has highest Tc with largest γ; Te-doping enhances H_{c2} and Tc due to more 2D characteristics; pressures effect on Tc of Te-doped sample is much larger than that of Fe-Se
  - 3d-metal doping only Mn sustains superconductivity; the other dopings either suppress low-T structural distortion (Cu-doping) or do not form alpha-phase …..
- Thin film and works from other groups further support the importance of LT structural distortion to superconductivity

Issues

- What is the role of the low temperature phase transition to superconductivity ?
- Does magnetic order coexists with superconductivity at low temperature?
- Is this low temperature distortion “universal” to all high Tc systems?
- Further clarification of the order parameter symmetry !!
- Can we intercalate something between layers to make it more 2-D and raise Tc?

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4. Maxim Avdeev, Andrew Studer; (Bragg Institute, Australian Nuclear Science and Technology Organization)
5. C. Q. Jin (and students) (IoP, CAS)
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