Pressure dependence of structural properties of FeSe

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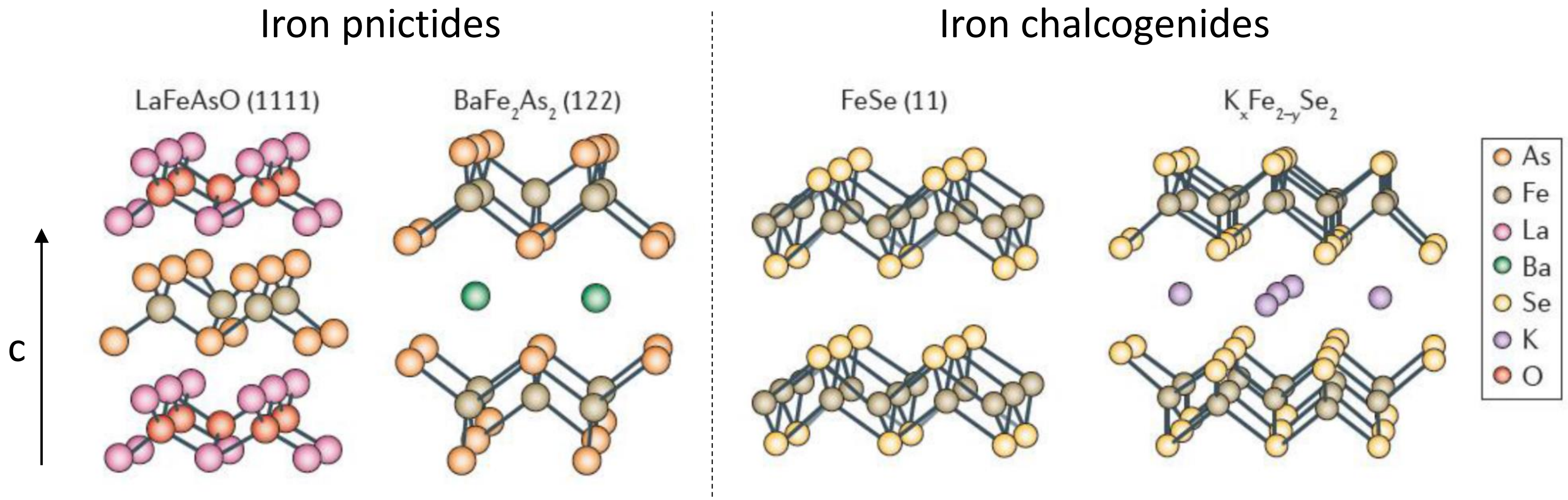
   I. Iron-based superconductors
   II. FeSe
II. Synchrotron XRD
   I. Technique
   II. Samples
   III. Protocol
   IV. Analysis
      I. Single-crystal analysis
      II. Powder-like analysis
III. Conclusion

Introduction

Iron-based superconductors

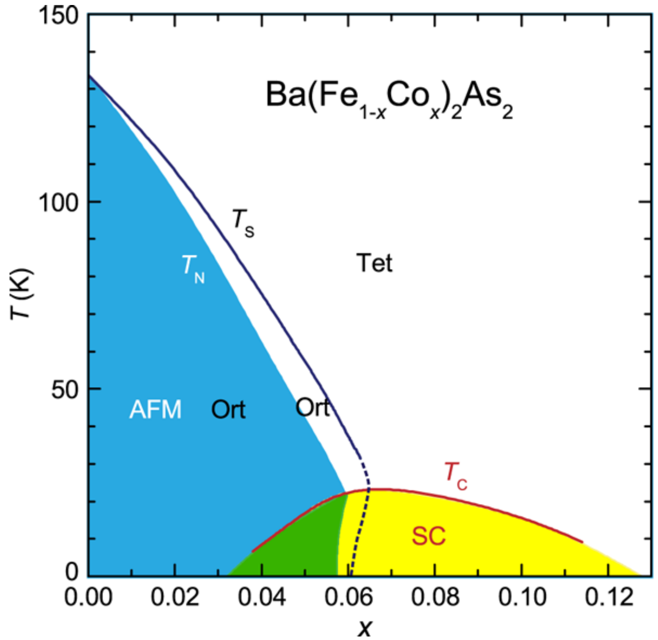
- Superconducting layers of **FeAs** (pnictides) or **FeSe** (chalcogenides) and possibly separated by charge reservoir atom layers (LaO, Ba, K, …).



Q. Si & al; Nature Reviews - Materials, article number 16017 (2016)

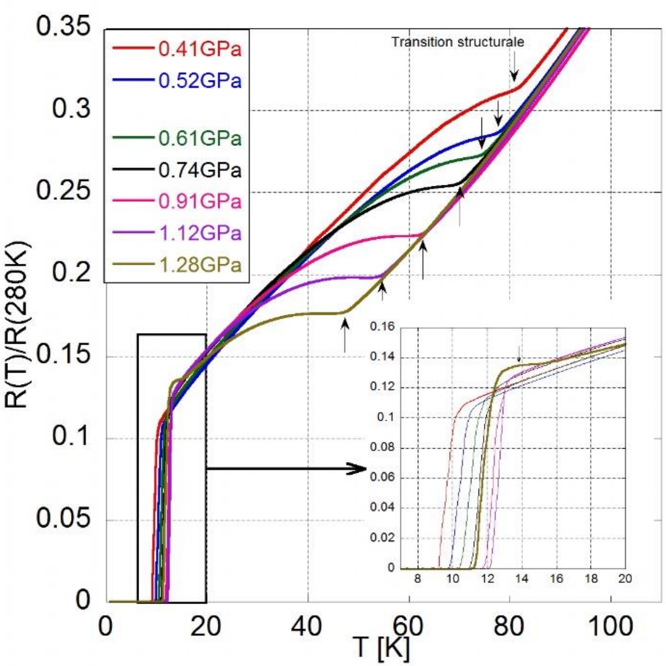
Iron-based superconductors

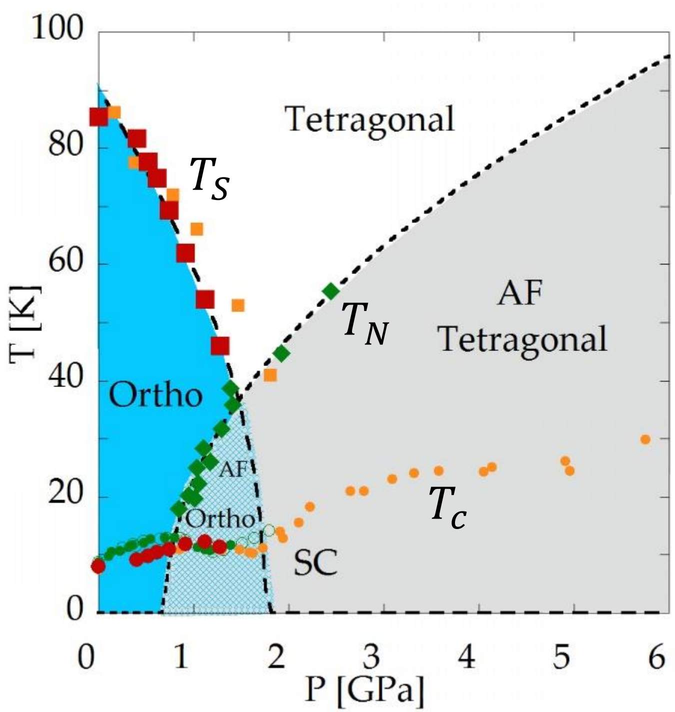
- In pnictides:
  - Lattice distortion T_S + a long range magnetic order T_N (magneto-elastic coupling)
  - Superconductivity enhanced along these transitions (magnetic fluctuations)



FeSe (before 2014)

- $T_c \sim 8\,K$ at $P = 0$, $T_c \sim 38\,K$ at $P \sim 6\,GPa$
- Tetragonal at room temperature
- Structural transition T_S to orthorhombic cell with **no magnetism**
- AFM transition T_N





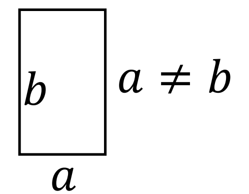
Red: Our work (resistivity measurements)

Green: µ-SR measurements (Bendele et al. (2012))

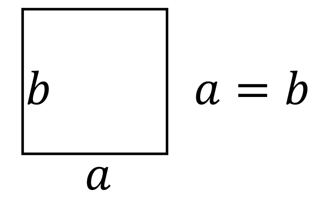
Orange: Resistivity measurements (Miyoshi et al. (2014))

Bendele et al. PRB 85, 064517 (2012)
Miyoshi et al. JPSJ 83, 013702 (2014)

FeSe (before 2014)



Orthorhombic cell
Cmma



Tetragonal cell
P4/nmm

- $T_c \sim 8\ K$ at $P = 0,\ T_c \sim 38\ K$ at $P \sim 6\ GPa$
- Tetragonal at room temperature
- Structural transition T_S to orthorhombic cell with **no magnetism**
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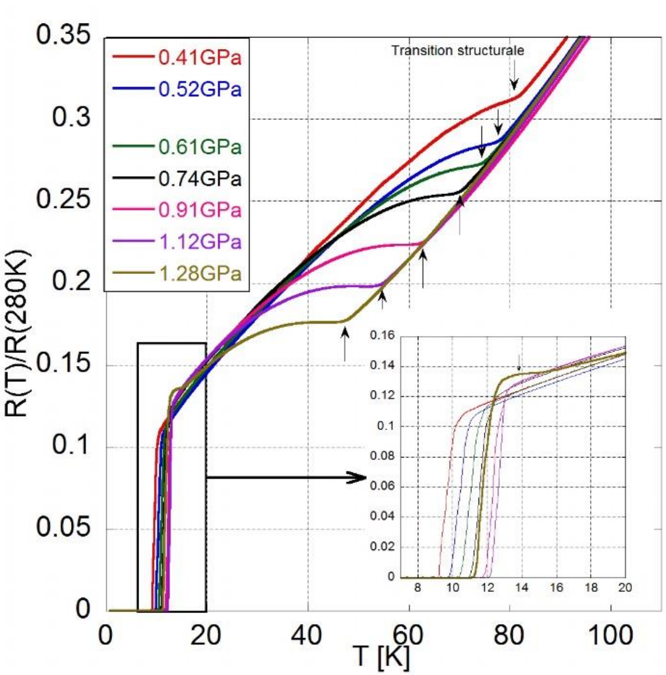

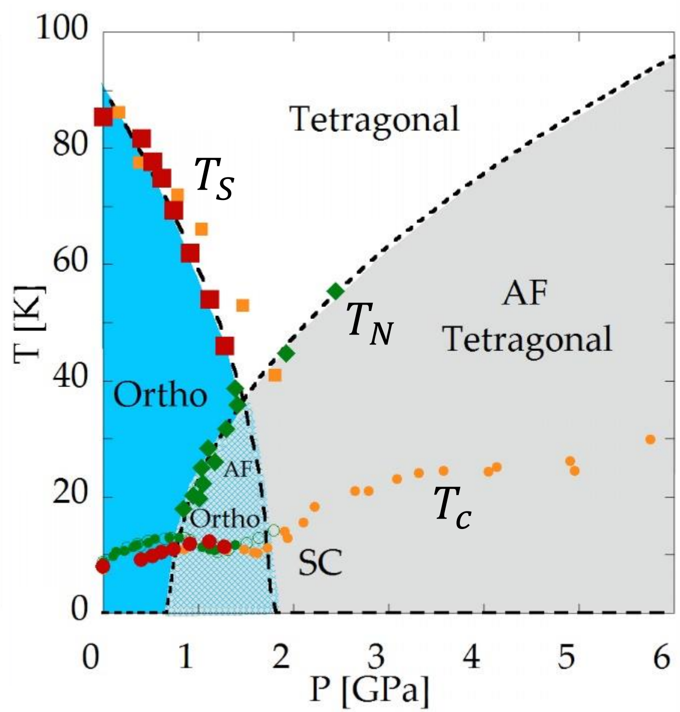

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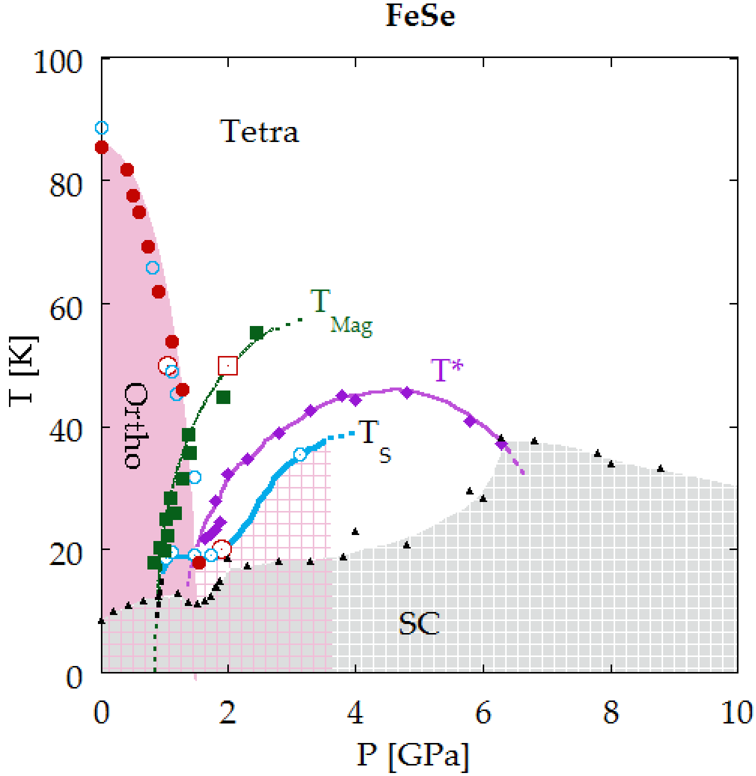
FeSe (now)

- 3 possible structural transitions :
  - Orthorhombic-Tetragonal at 20K, 1.9 GPa
  - Orthorhombic-Tetragonal at 50K, 1 GPa
  - Tetragonal-Monoclinic at 50K, 2 GPa



● Resistivity measurements (OR-T)
■ μ-SR measurements (Bendele et al. (2012))
◆ Resistivity measurements (Sun et al. (2015))
⊙ Synchrotron XRD (Kothapalli et al. (2016))
▲ Superconducting transition (Sun et al. (2015))

⊙ Structural transition (our ESRF measurements)
⊡ Structural transition (our ESRF measurements) (tetragonal <-> monoclinic)

Bendele et al. PRB 85, 064517 (2012)
Sun et al., arXiv:1512.06951v1 (2015)
Kothapalli et al., arXiv:1603.04135v1 (2016)

Motivations and questions

- Get a better understanding of the mechanism of superconductivity
  - Magnetic fluctuations
  - T_c variations

- Is there a magneto-elastic coupling?

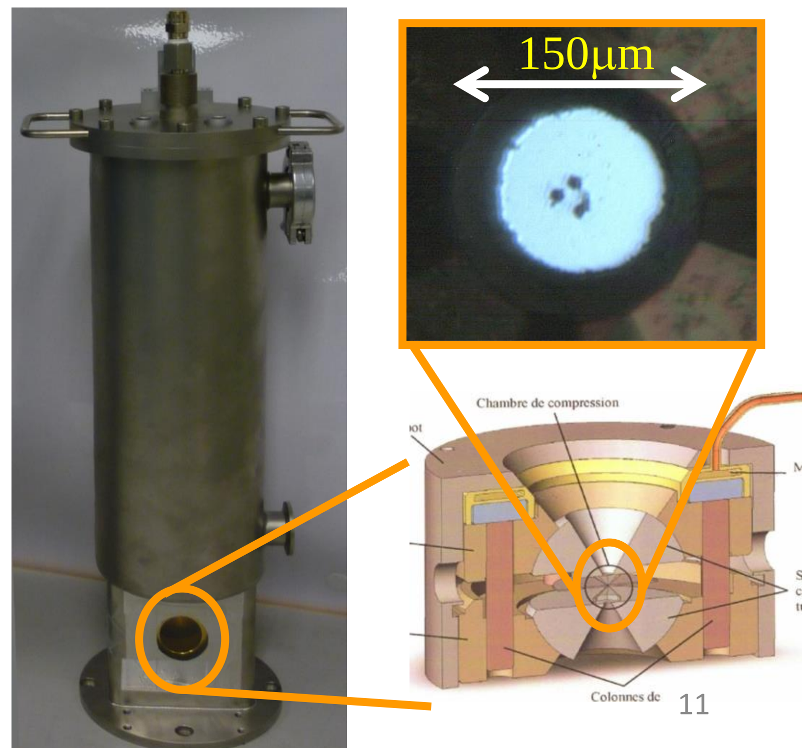
↳ Know the crystallographic structure

Complete PT-phase diagram of FeSe

Synchrotron XRD

Technique

- ESRF (Grenoble) on ID27
- Diffraction on single crystals
- Diamond anvil cell and cryostat:
    - @ 20 and 50 K
    - From 0 to 10 GPa
    - Pressure-transmitting medium: Helium

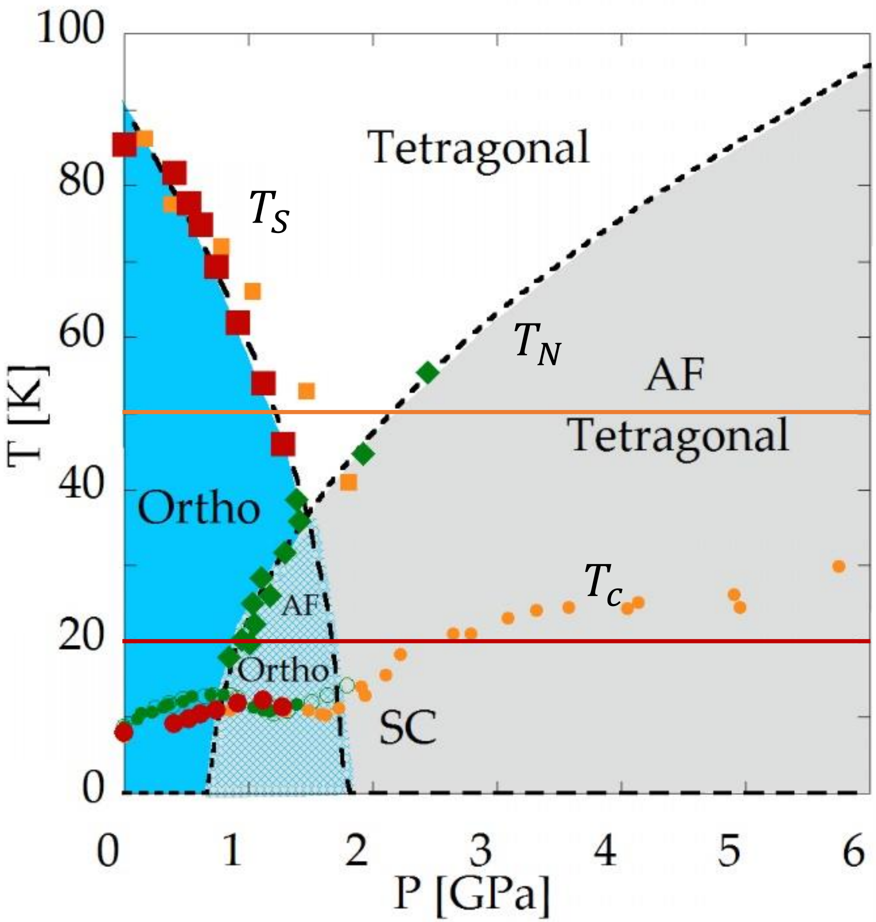


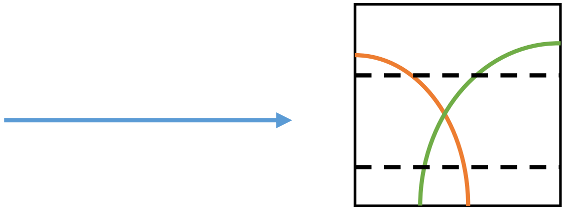
Samples

- Single-crystals of FeSe (Pierre Toulemonde, Néel Institute)
- Chemical Vapor Transport technics
- High quality crystals:
    - Quantum oscillation measurements

Protocol

Pressure dependences at 20 and 50 K



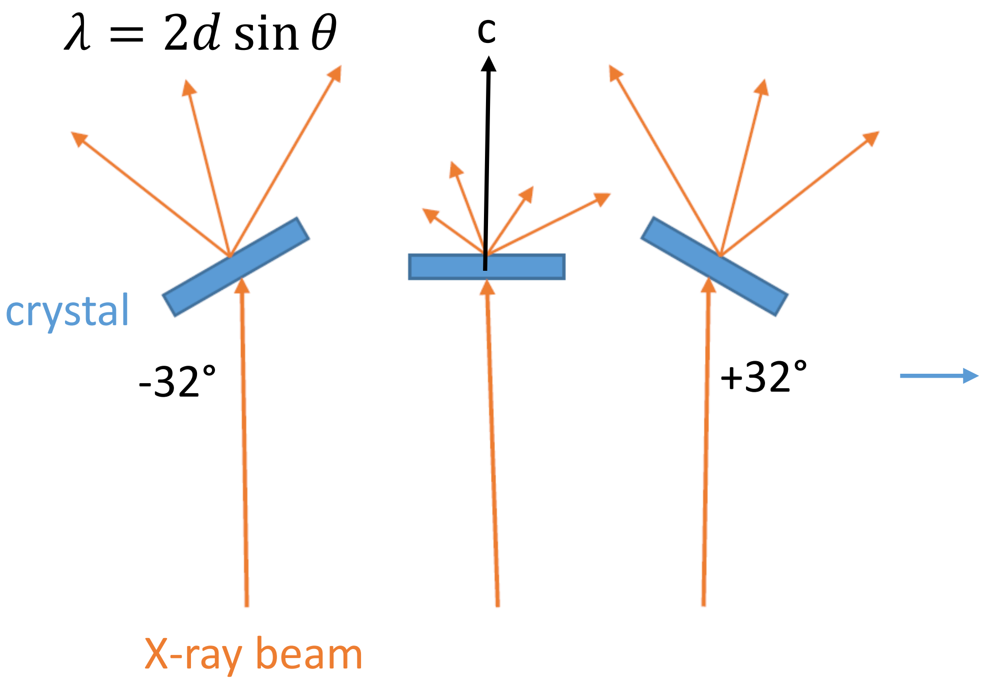


Analysis

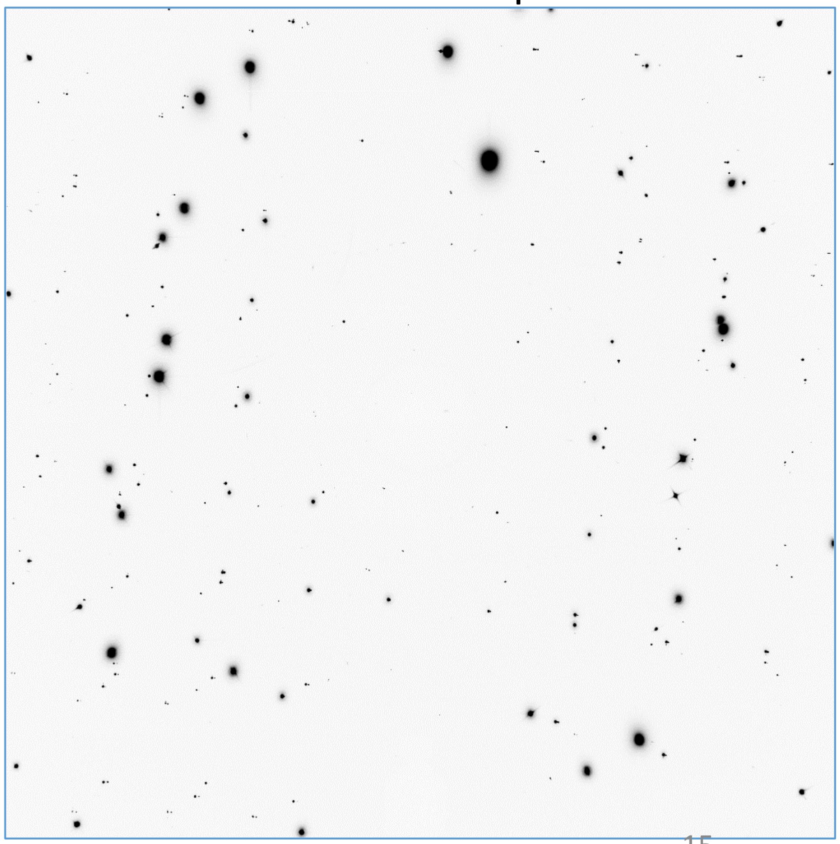
- XRD on single crystals
  - Analysis of single crystal data (Crysalis Pro)
  - Analysis of powder data:
    - Integration of single crystal data to obtain powder diagrams
    - Specific Bragg peak studies

Single-crystal analysis (T=20K)

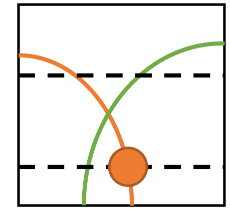
From -32° to 32° (0° = c-axis)



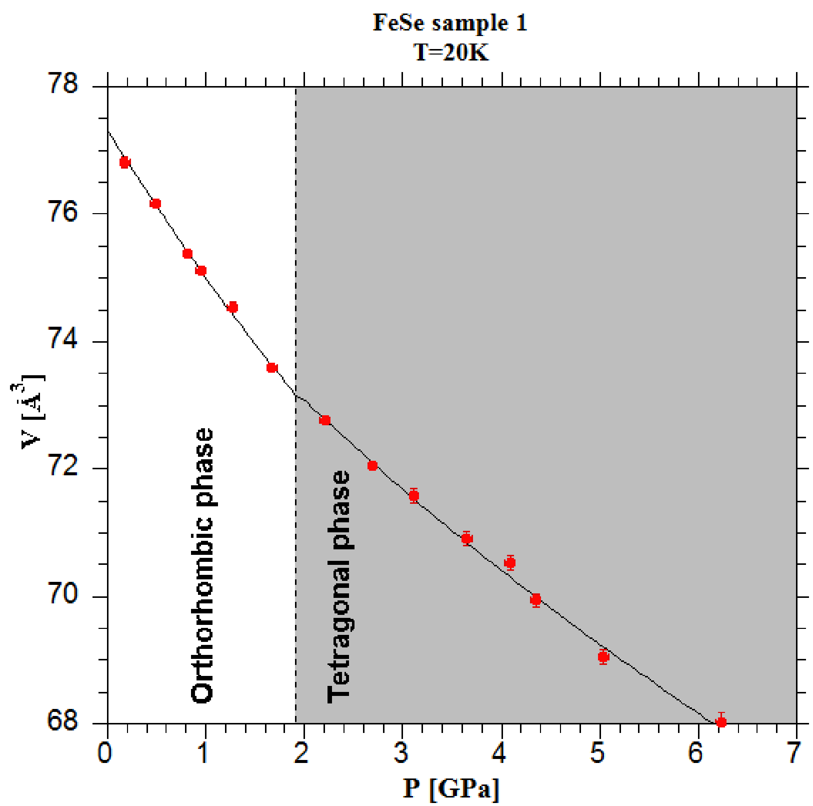
On the detector: reciprocal lattice

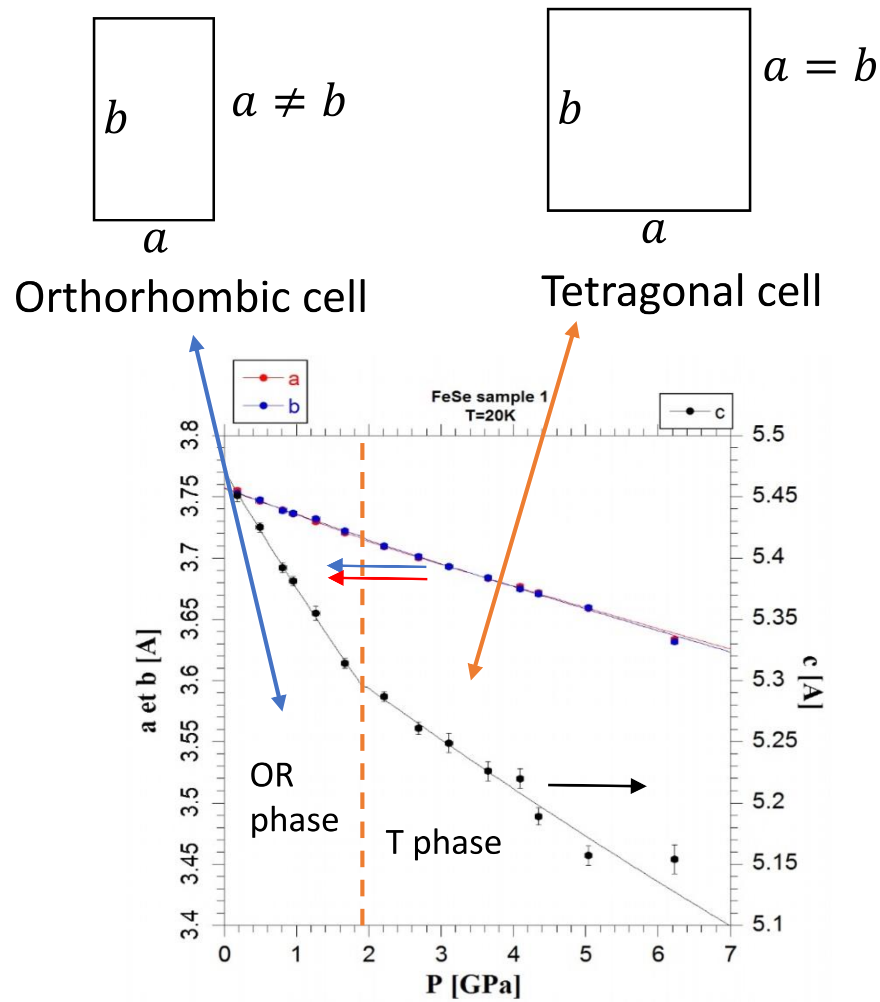


Single-crystal analysis (T=20K)



Deduction of pressure dependence of the cell parameters:





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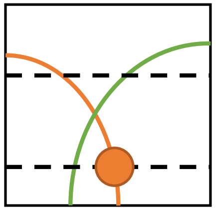


Deduction of the bulk modulus (resistance to compression):

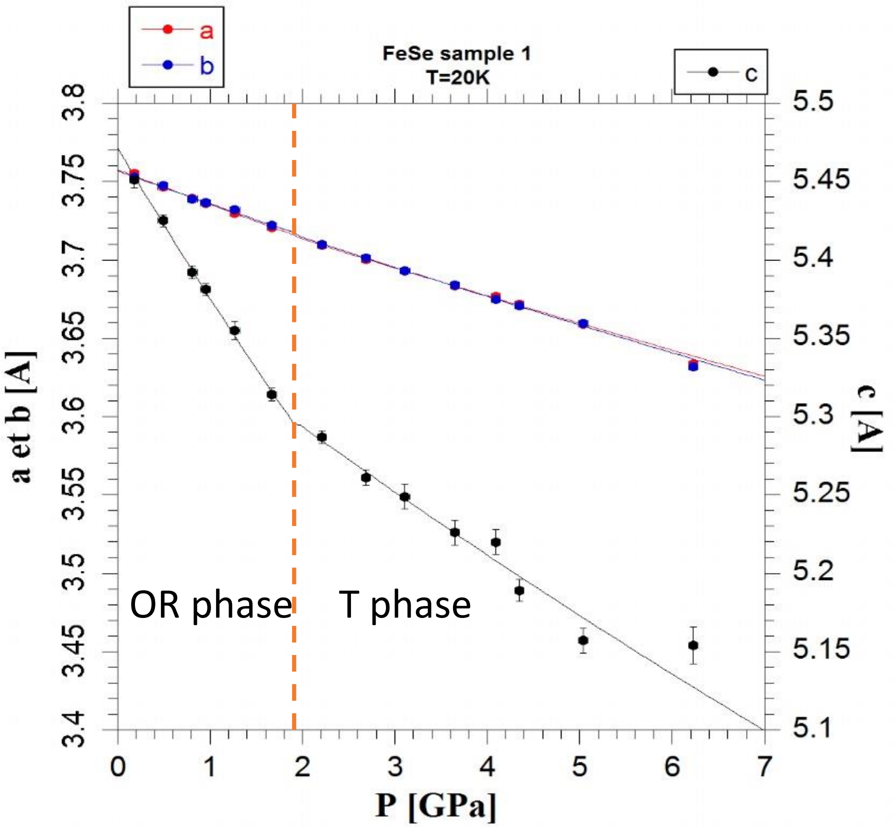


Fig. a-, b- and c-axis pressure dependence

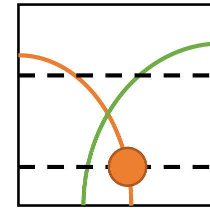
Murnaghan state equation:

$$x(P) = x_0\left(1 + P\left(\frac{4}{K_{0_x}}\right)\right)^{-\frac{1}{4}}$$

$x = a, b, c, V$

K_0: bulk modulus at $P = 0$

Single-crystal analysis (T=20K)



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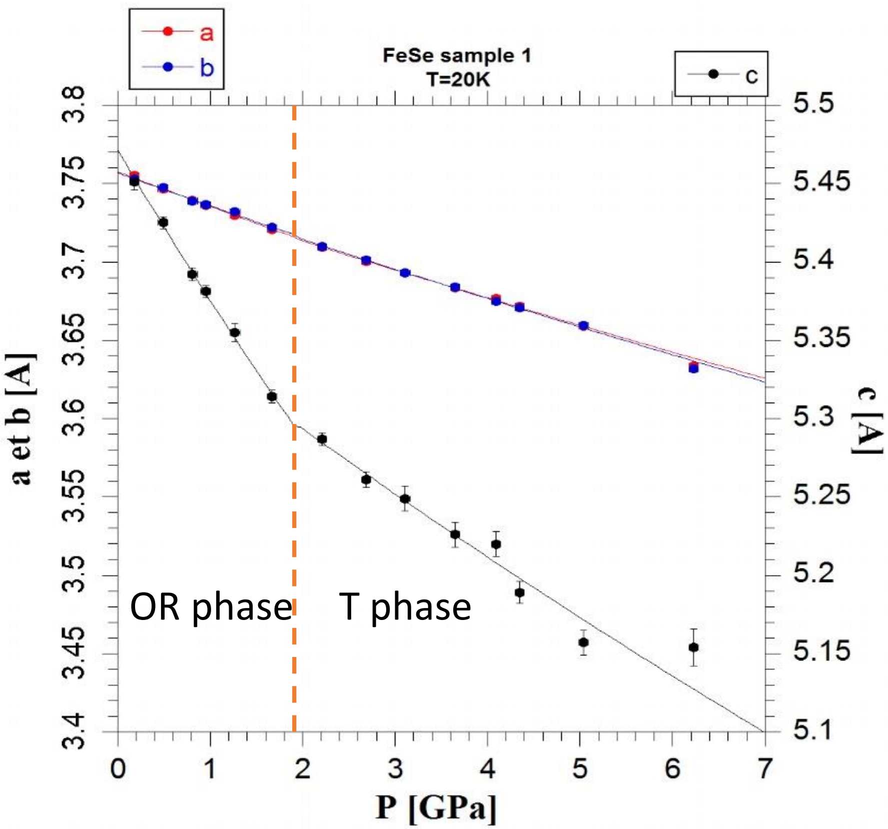

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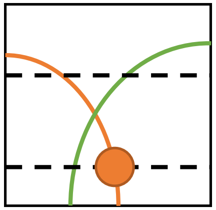
K_0: bulk modulus at $P = 0$

	Orthorhombic phase	Tetragonal phase
K_{0_a}	167 ± 4 GPa	192 ± 2 GPa
K_{0_b}	177 ± 5 GPa	184 ± 2 GPa
K_{0_c}	$54,6 \pm 2,4$ GPa	116 ± 7 GPa
K_0	$30,8 \pm 1,9$ GPa	$41,9 \pm 1,6$ GPa
K_0 (Millican et al.)	31 GPa	...

Millican et al., doi:10.1016/j.ssc.2009.02.011

Single-crystal analysis (T=20K)

- Conclusion:
  - @ 20 K:
    - Structural transition at 1.9 GPa
    - Bulk modulus jump
    - Biggest phenomena: along the c-axis



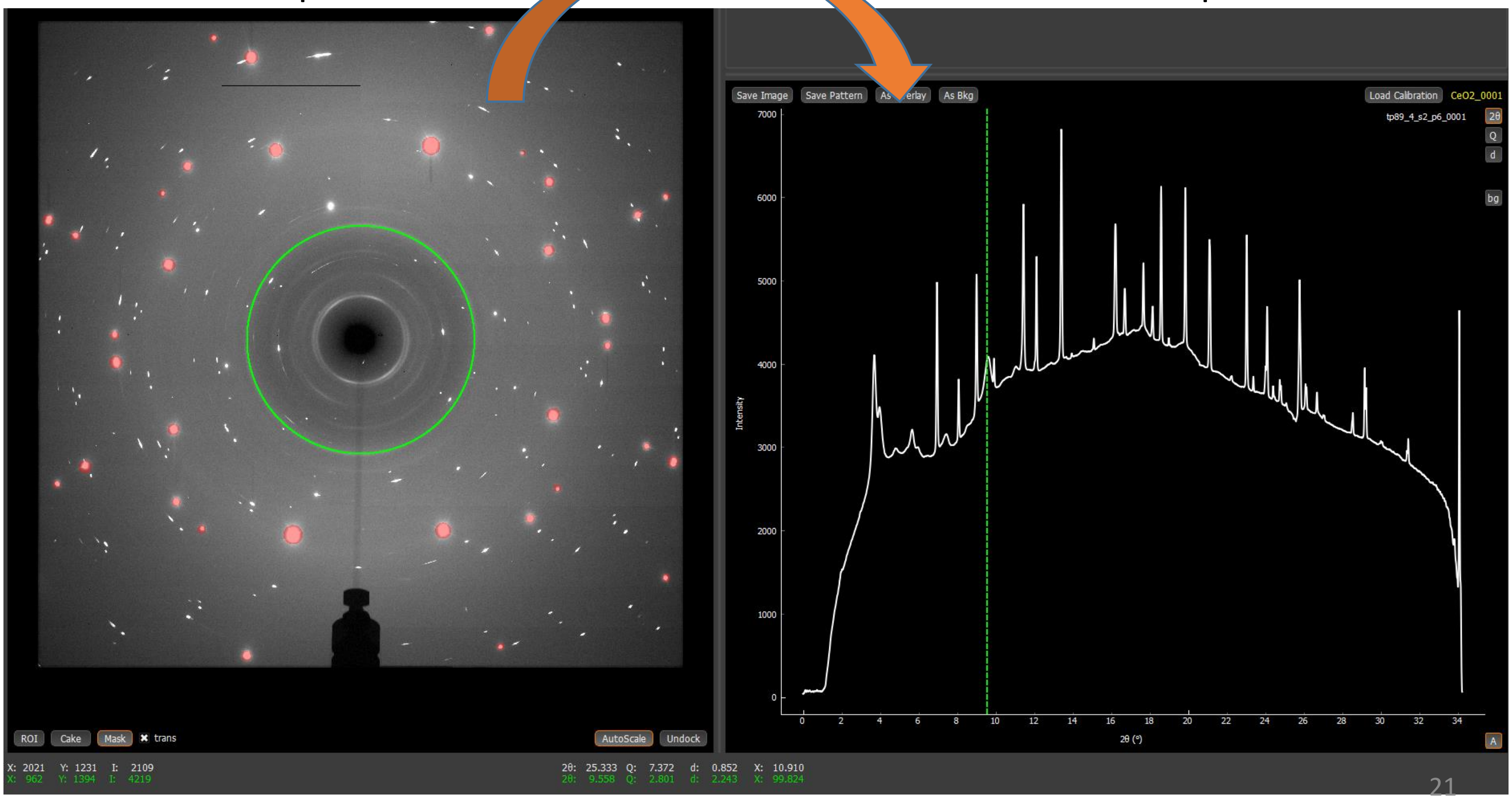
Analysis

- XRD on single crystals
  - Analysis of single crystal data (Crysalis Pro)
  - Analysis of powder-like data:
    - Integration of single crystal data to obtain powder-like pattern
    - Specific Bragg peak studies

Powder-like analysis (T=50K)

2D-pattern

Powder-like pattern

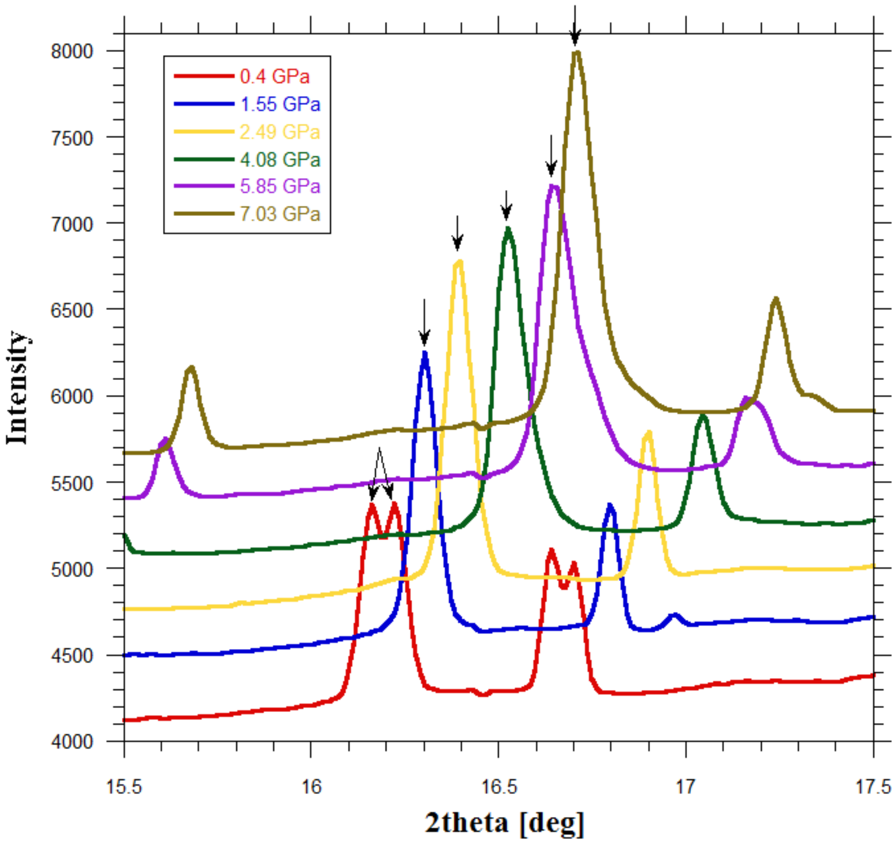


Powder-like analysis (T=50K)

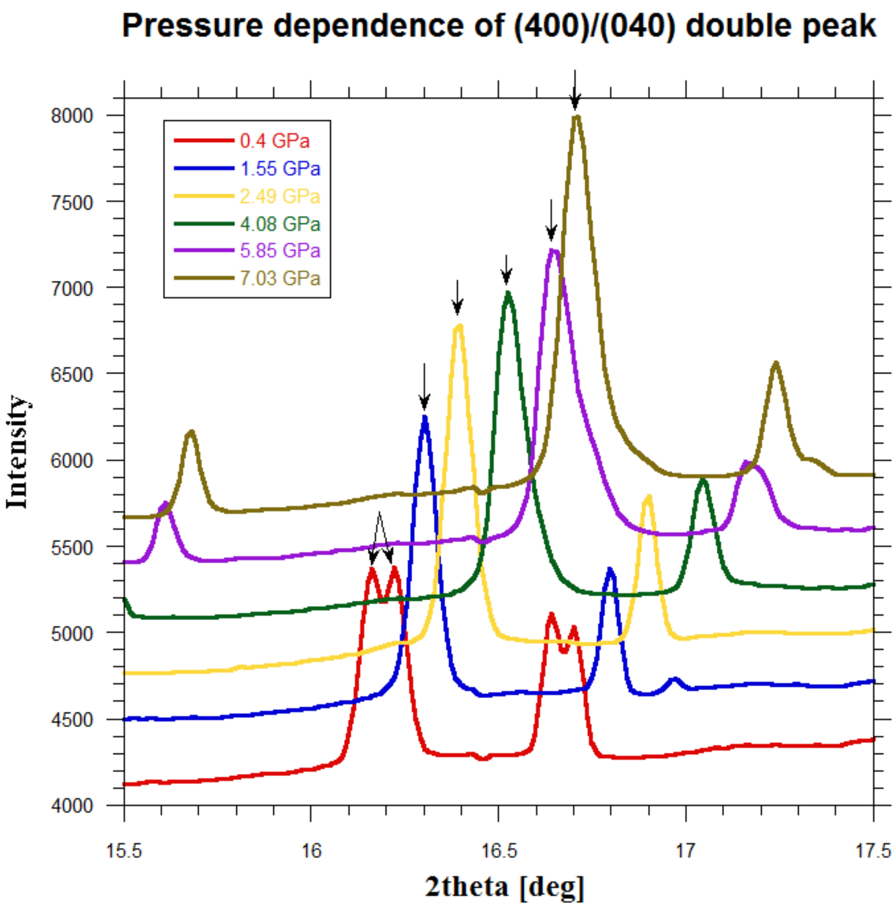
- Studying of the (400)/(040) peaks
  - Deduce cell parameters a and b

Powder-like analysis (T=50K)

Pressure dependence of (400)/(040) double peak



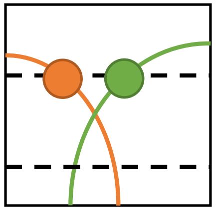
Powder-like analysis (T=50K)

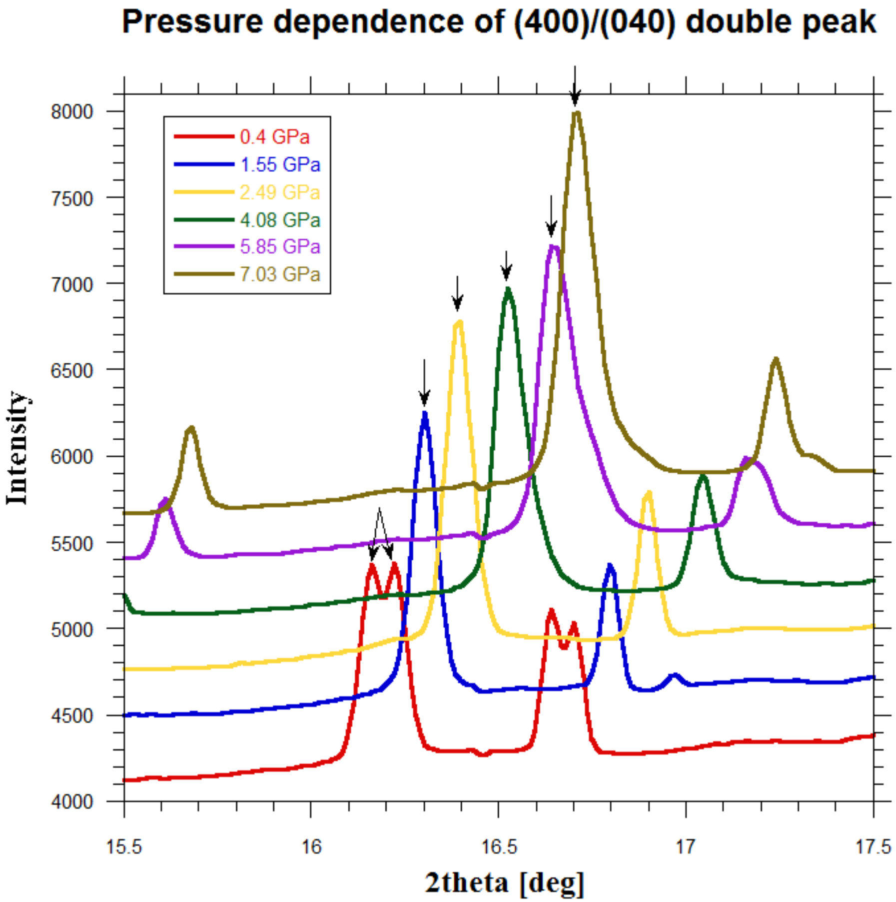


Fit peak with equation:

$$I = I_0\left[(1-\alpha)\exp\left(-\left(2\theta - \frac{(2\theta_0-\epsilon)}{\sigma}\right)^2\right) + \alpha\exp\left(-\left(2\theta - \frac{(2\theta_0+\epsilon)}{\sigma}\right)^2\right)\right]$$

Powder-like analysis (T=50K)





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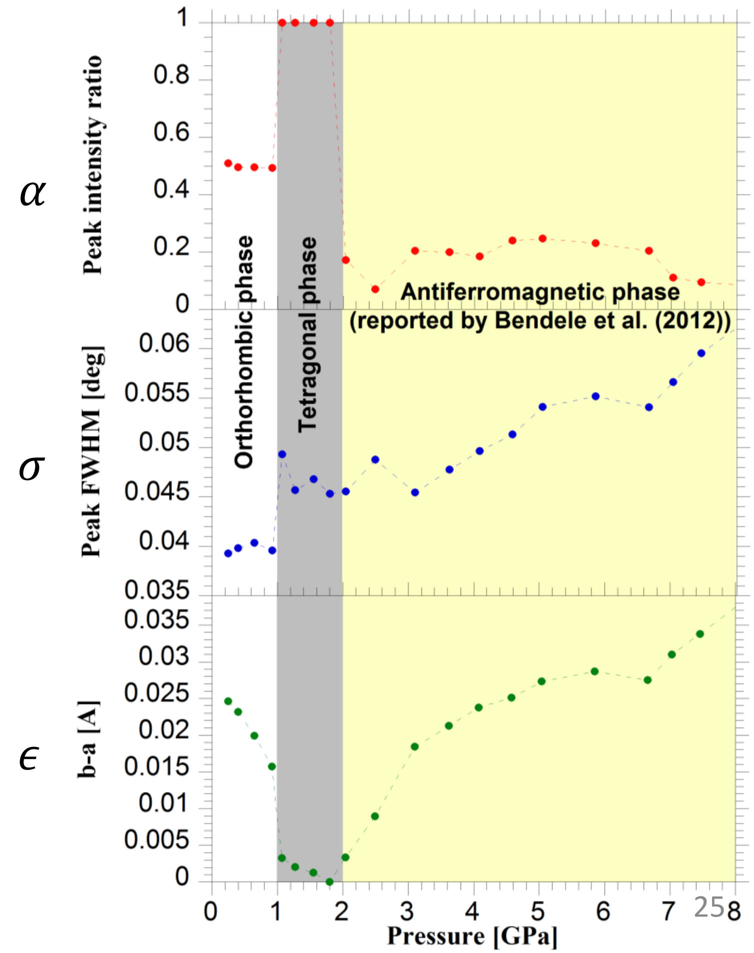
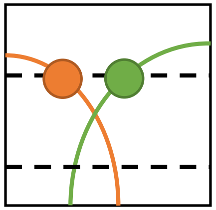
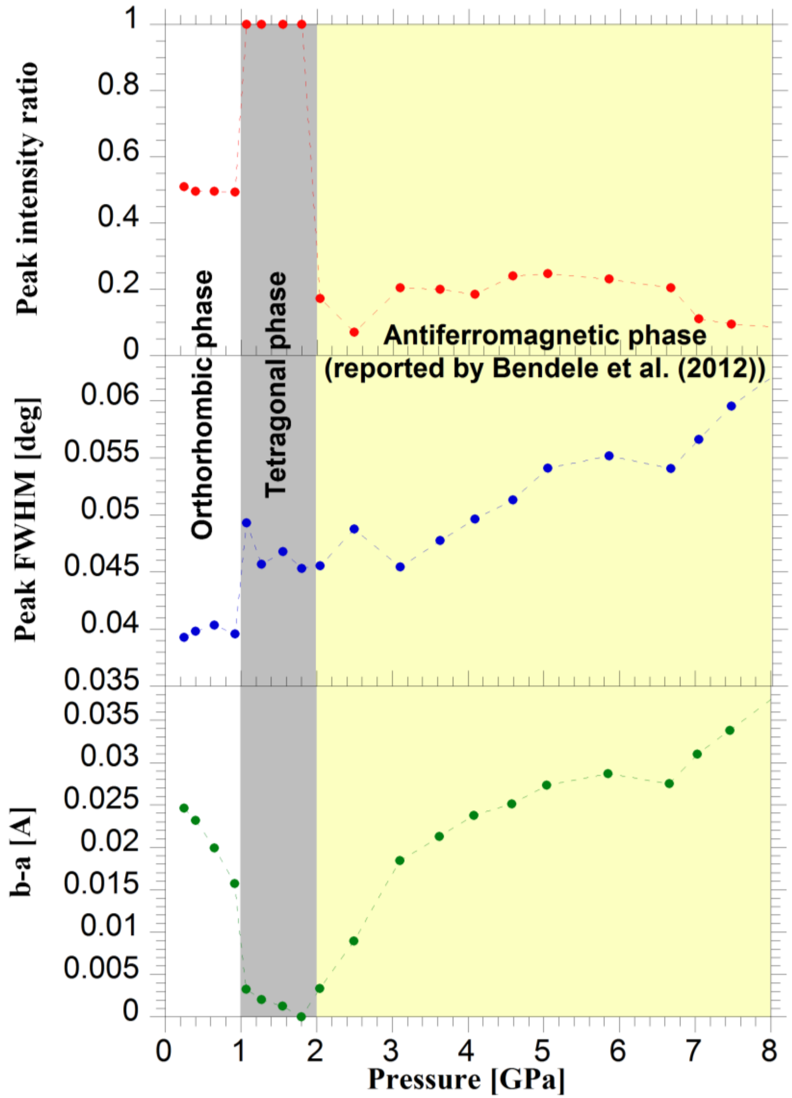
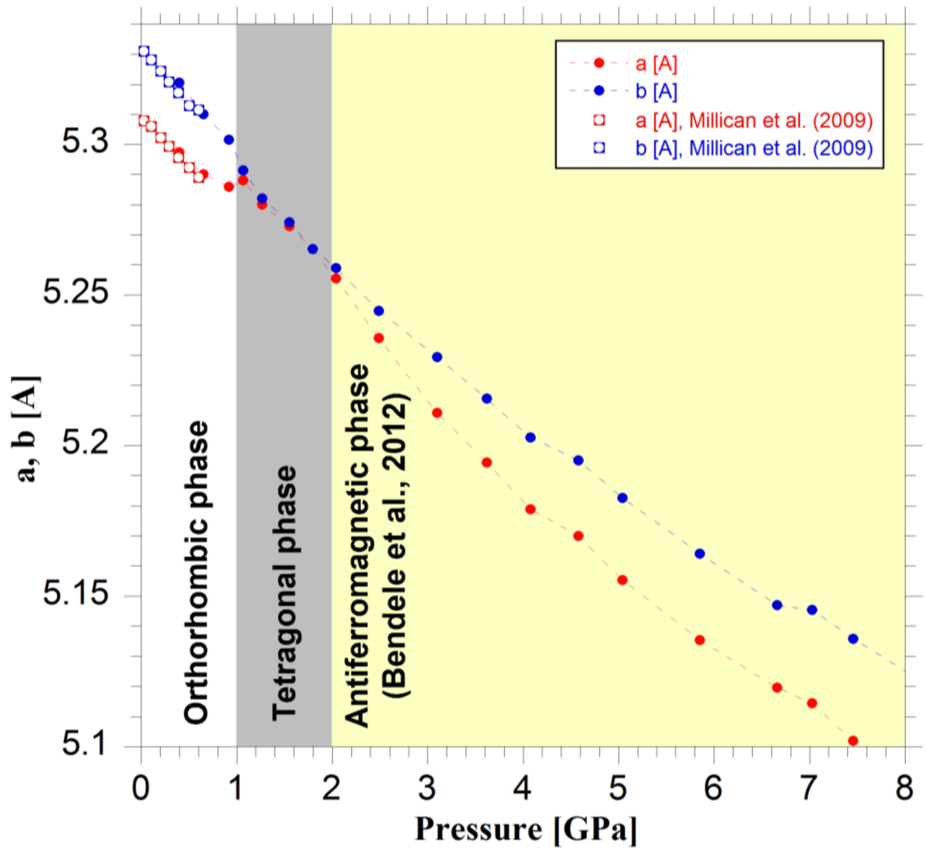


Powder-like analysis (T=50K)





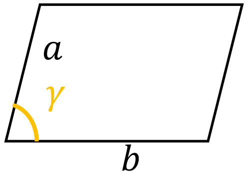


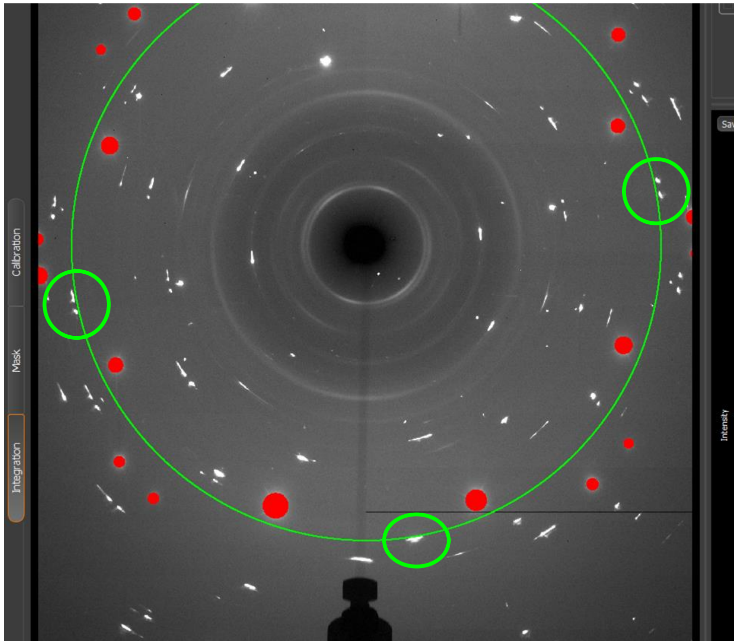
New split between a and b beyond 2 GPa!!!
New orthorhombic phase?

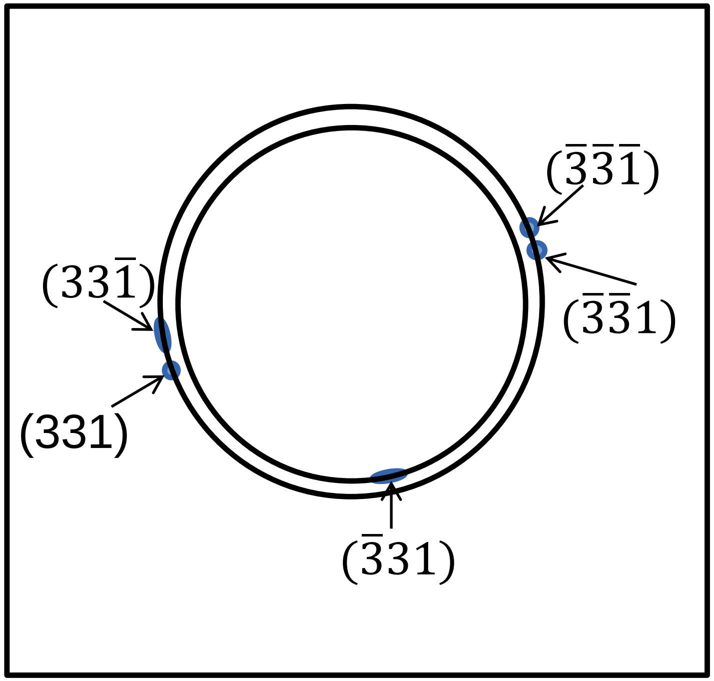
Millican et al., doi:10.1016/j.ssc.2009.02.011

Powder-like analysis (T=50K)

- Studying of the $(331)/(\bar{3}31)$ peaks
  - Looking at the γ angle







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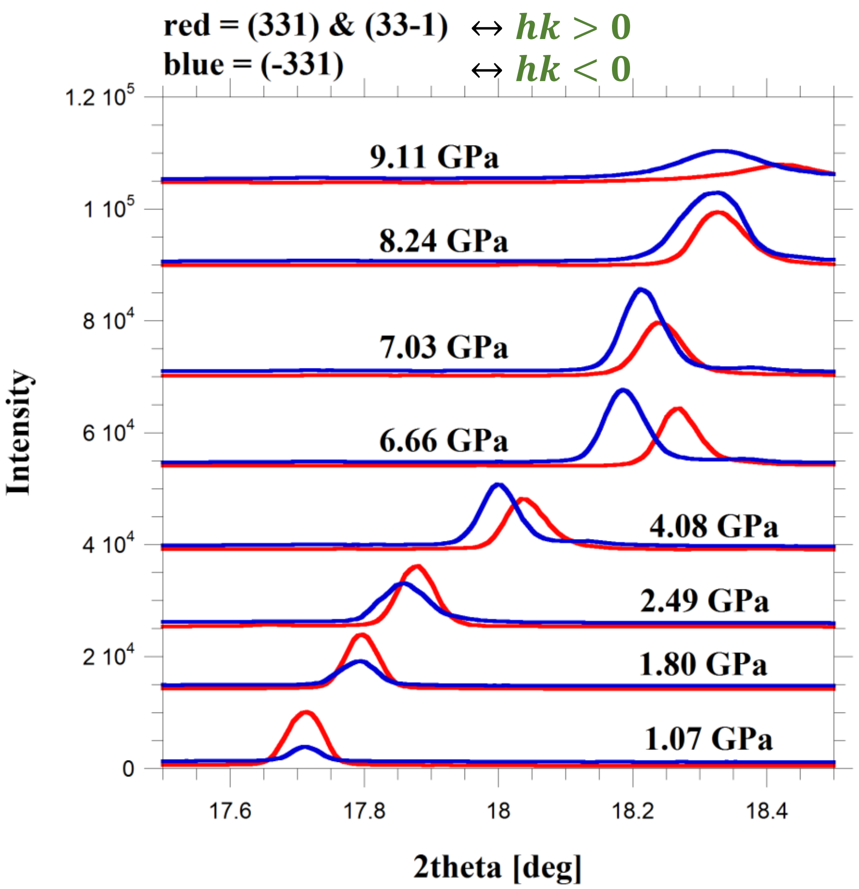
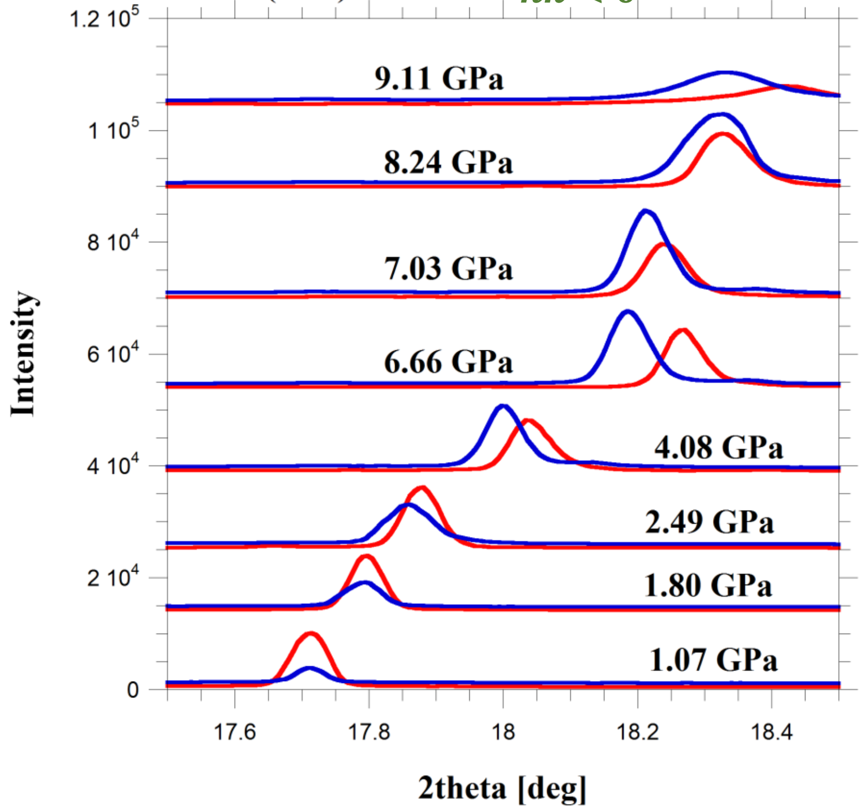


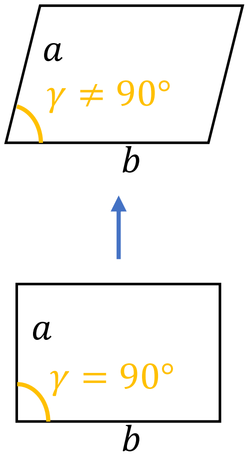
Powder-like analysis (T=50K)

$$\lambda = 2d \sin\theta$$

$$d_{mono} = \frac{\sin^2\gamma}{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\sin^2\gamma - \frac{2hk}{ab}\cos\gamma}$$

red = (331) & (33-1) ↔ $hk > 0$
blue = (-331) ↔ $hk < 0$





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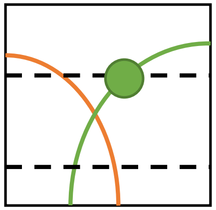

$$\lambda = 2\color{red}{d}\sin\theta$$

$$\downarrow$$

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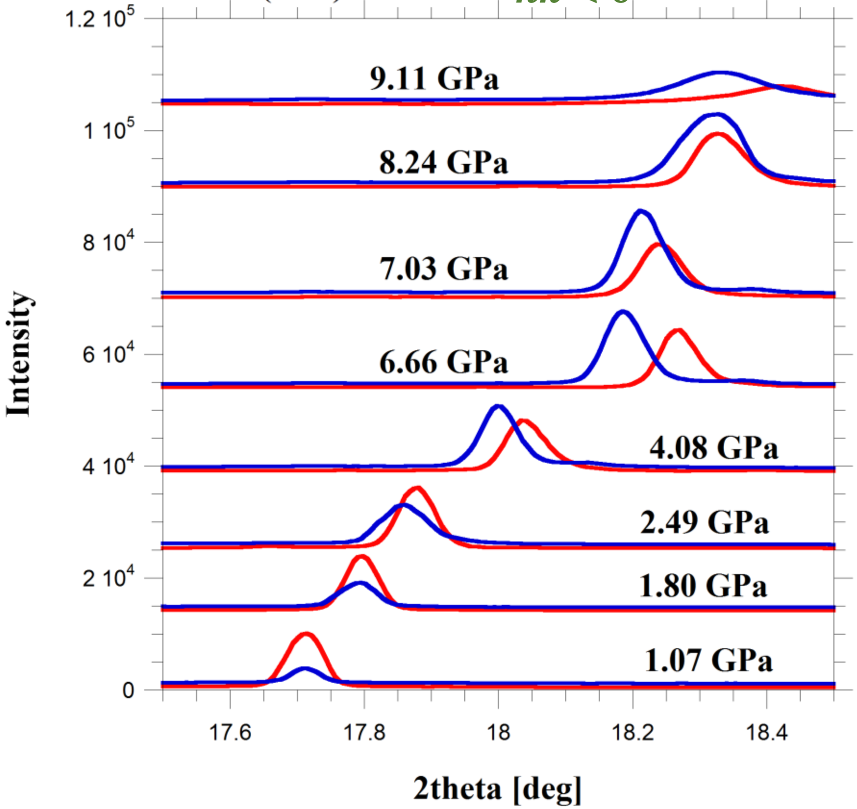
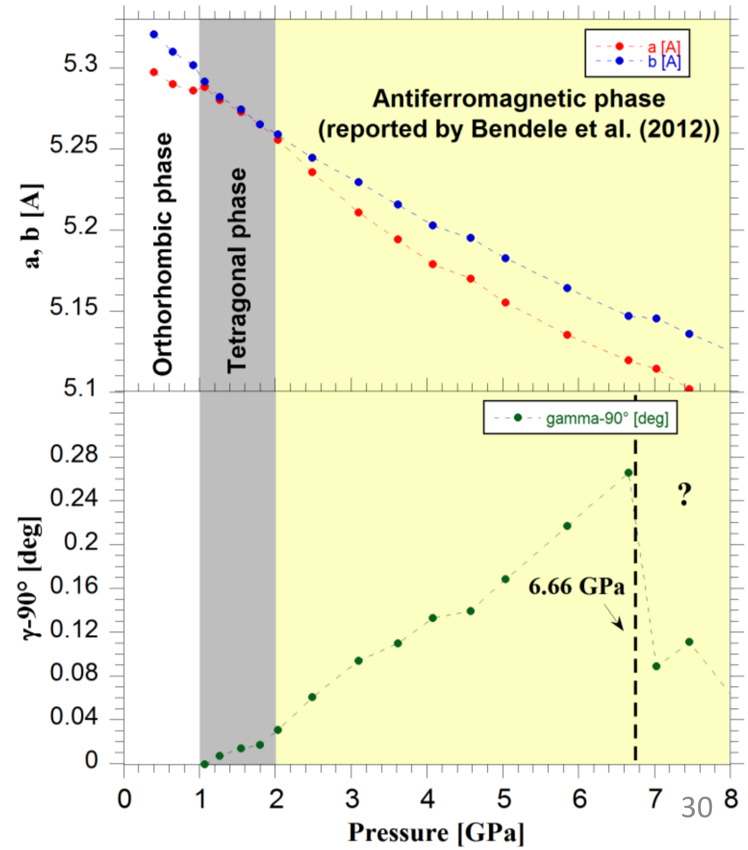
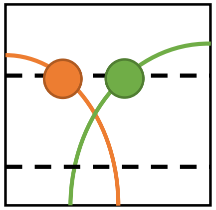




Powder-like analysis (T=50K)

- Conclusion:
  - @ 50 K:
    - At low pressure, orthorhombic phase
    - Between 1 and 2 GPa, tetragonal phase
    - Beyond 2 GPa (magnetic phase reported by Bendele et al. (2012)):
      - **splits between a and b**
      - Possible monoclinic cell



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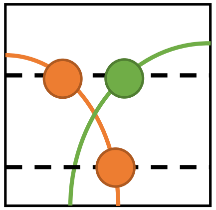
Conclusion

- FeSe PT-phase diagram is still controversial
- At 20 K:
  - Structural transition (OR-T) at 1.9 GPa
- At 50 K:
  - Structural transition (OR-T) at 1 GPa
  - Possible structural transition at 2 GPa
    - Split between a and b
    - γ angle not equal to 90°



Acknowledgement

- Institut Néel:
  - Pierre Rodière
  - Pierre Toulemonde
- ESRF:
  - Volodymyr Svitlyk

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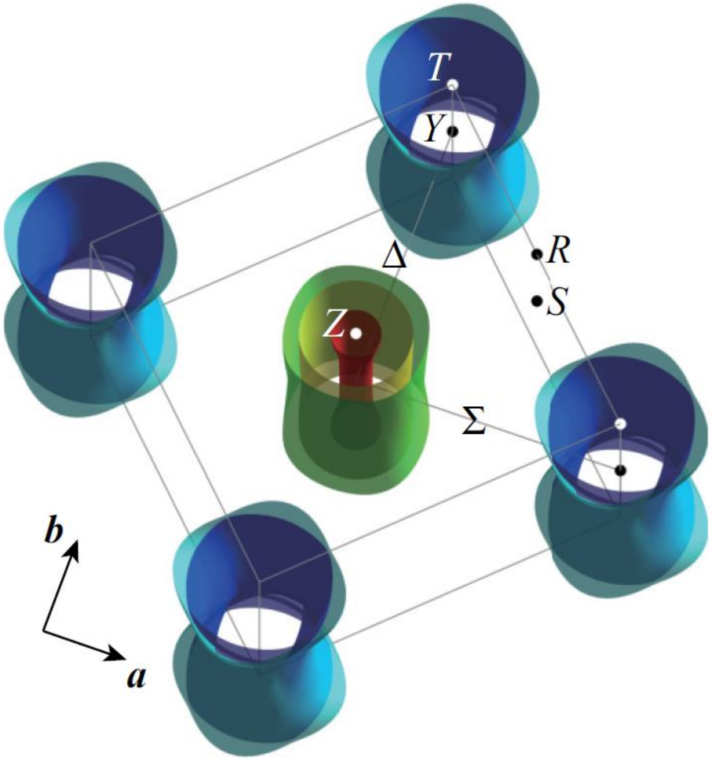
Iron-based superconductors

- Typical Fermi Surface (FS):
  - Holes near the Γ point
  - Electrons near the Y points



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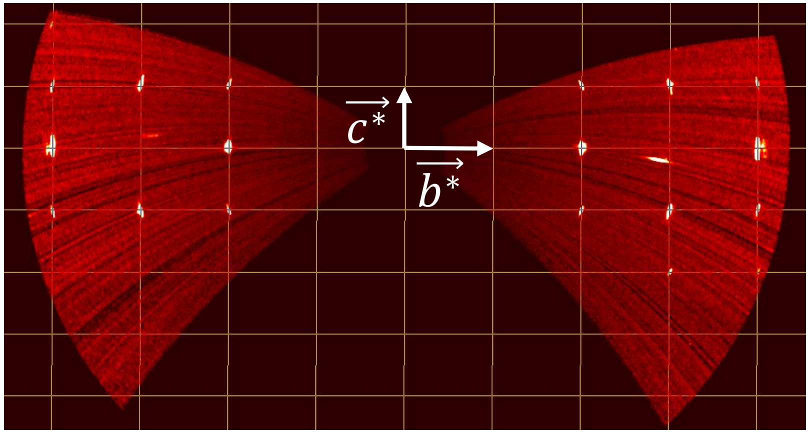
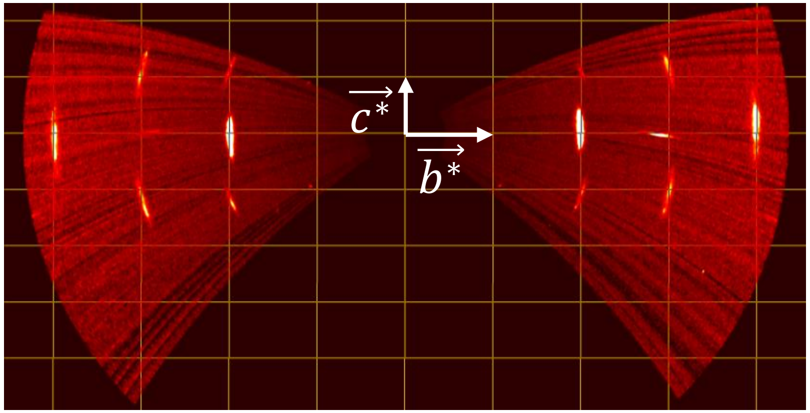
Single-crystal analysis (T=20K)

High crystal degradation beyond 6GPa



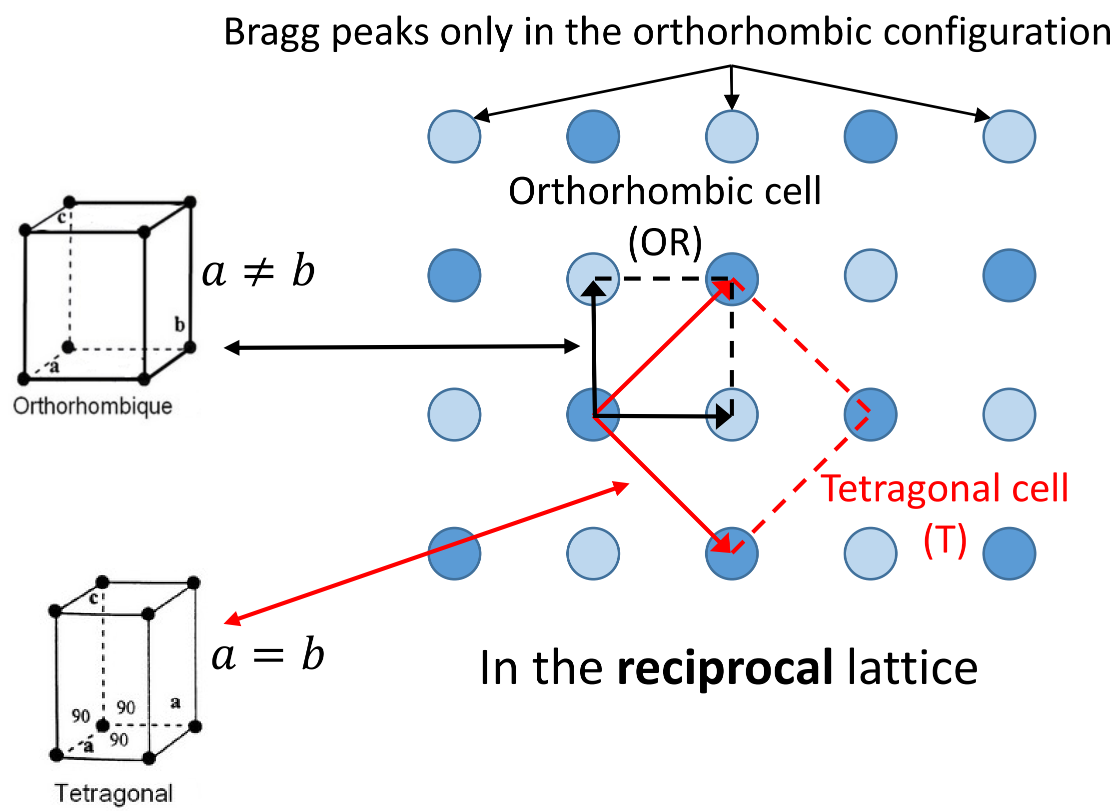
6.23GPa, 0kl plan



6.9GPa, 0kl plan

Single-crystal analysis

Two possible working cells: orthorhombic or tetragonal cell.



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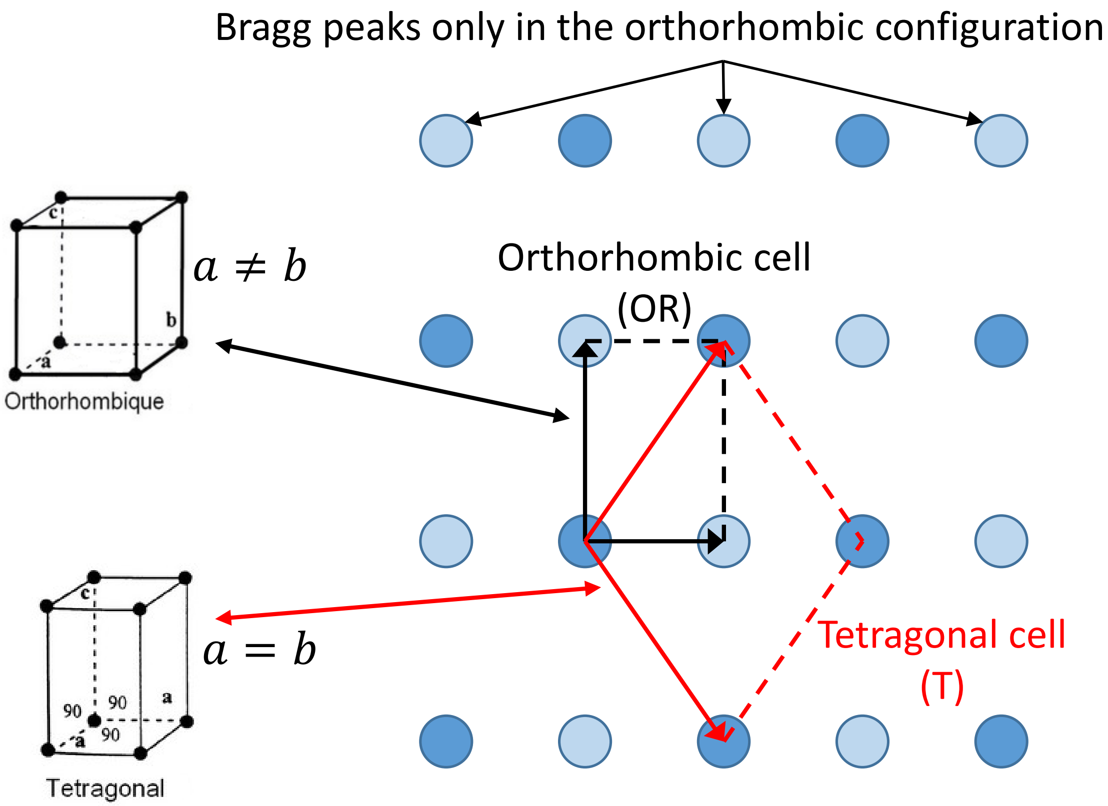
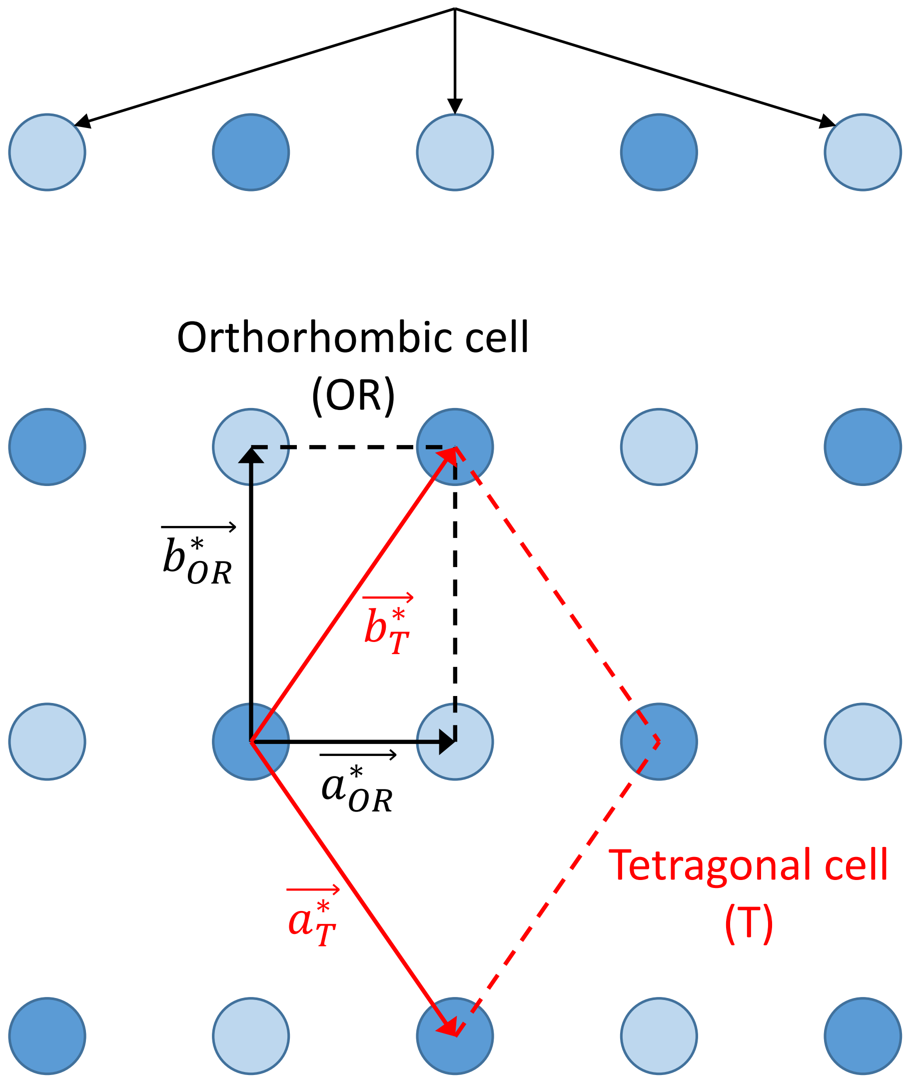


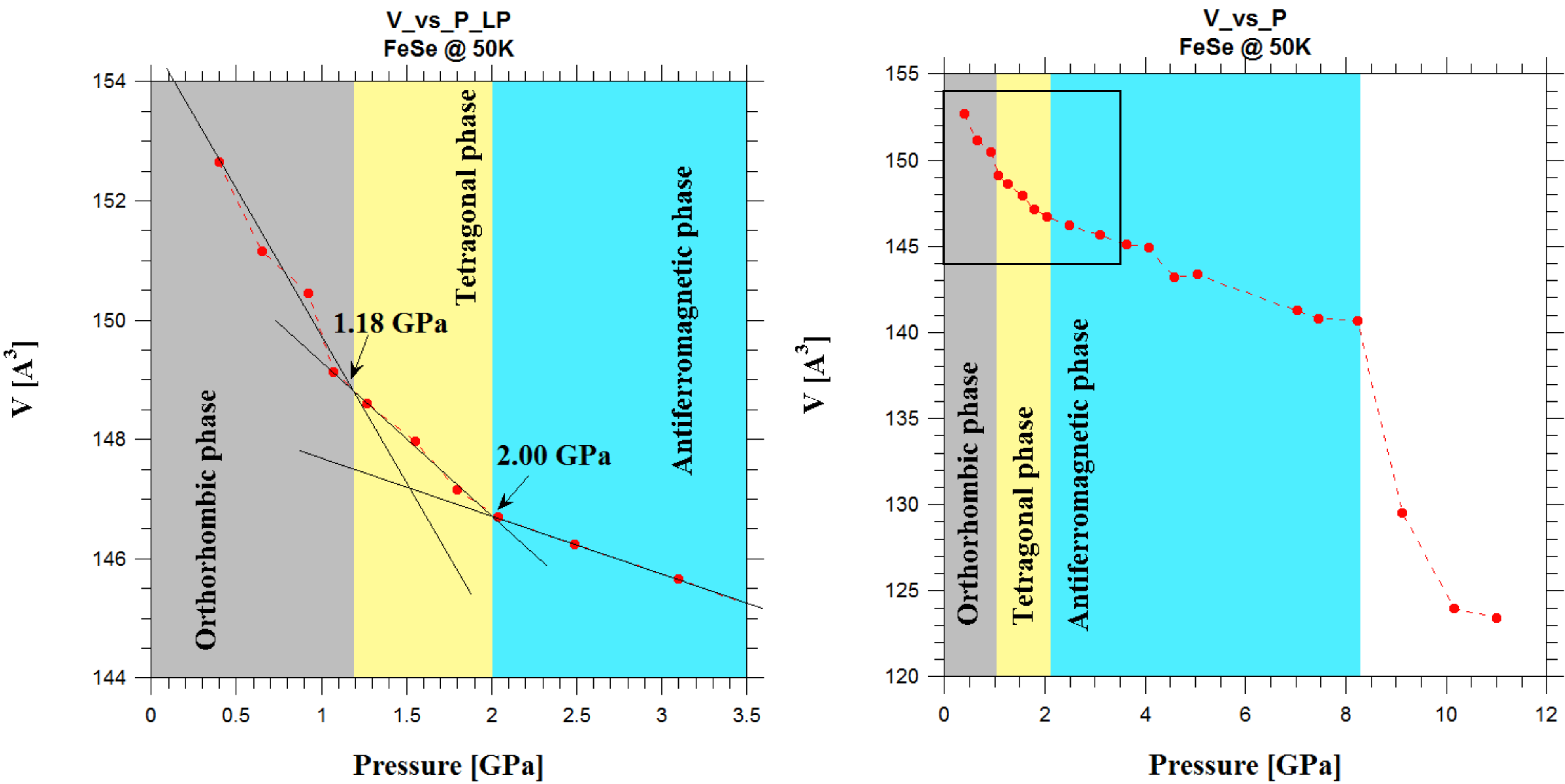
In the **reciprocal** lattice

Bragg peaks only in the orthorhombic configuration



In the **reciprocal** lattice

Powder like analysis



Something happens at 2 GPa (AFM transition reported by Bendele et al., 2012)

Single-crystal analysis

At high pressure ($> 8GPa$), coexistence of two crystallographic phases

Volodymyr Svitlyk, ID27, ESRF, Grenoble