ICTP
The Abdus Salam
International Centre
for Theoretical Physics

UNESCO
United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

Advanced School on Synchrotron Techniques in Environmental Scientific Projects

Trieste – Italy, 15-26 April 2013

elettra

Antonella Iadecola

XAFS

Tuesday, 16 April: XRF/XAFS (Room:Leonardo da Vinci Building Euler Lecture Hall)

16 April 2013

08:30 - 10:00	**D. Eichert** / *Elettra, Trieste* **X-Ray Fluorescence: Spectrometry, Spectroscopy and Microscopy - Tools for Environmental Science**
10:00 - 10:30	**---** Coffee Break **---**
10:30 - 11:45	**D. Grolimund** **Combining XRF/XAFS/XRD Techniques for Environmental Studies**

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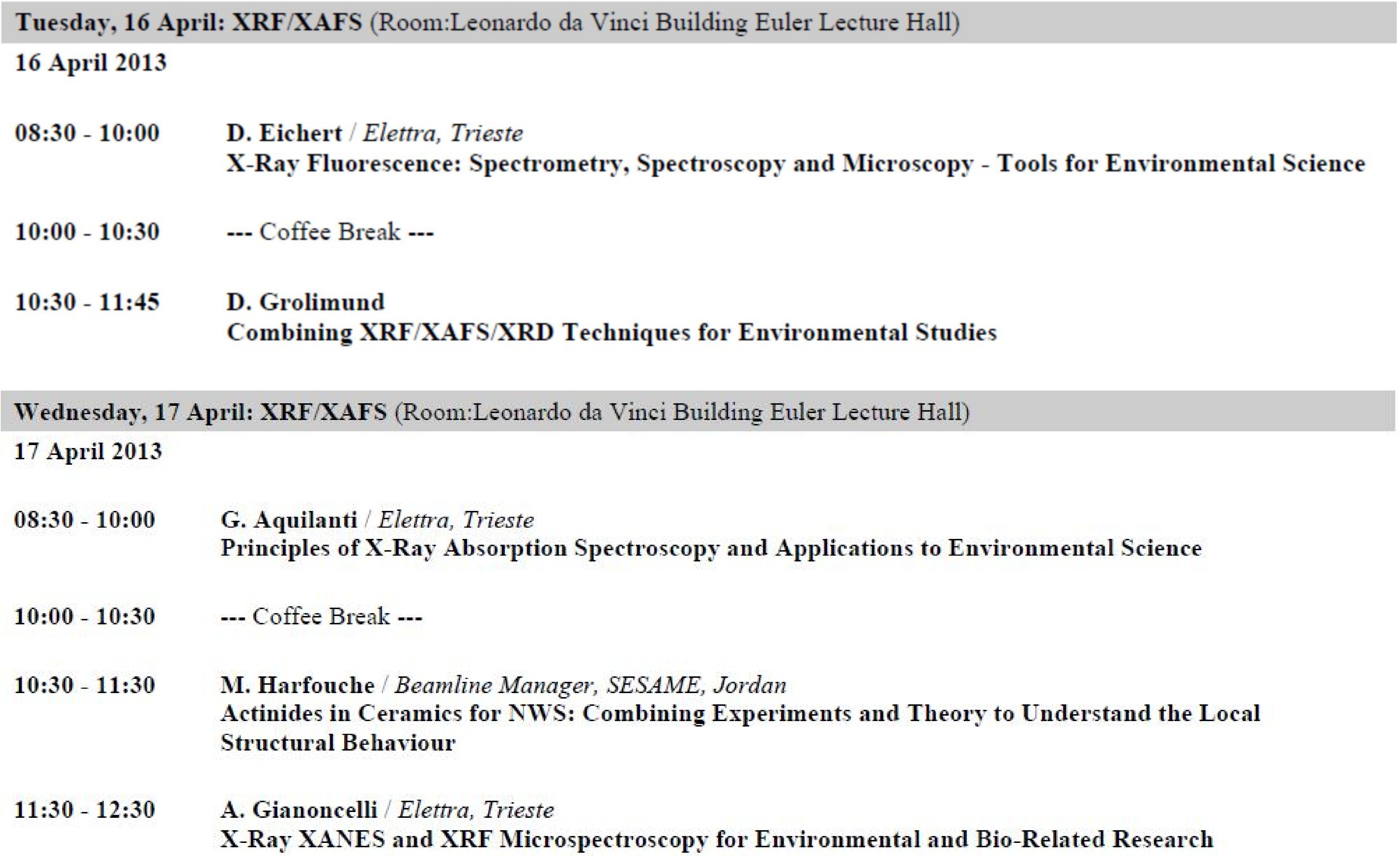
11:30 - 12:30	**A. Gianoncelli** / *Elettra, Trieste* **X-Ray XANES and XRF Microspectroscopy for Environmental and Bio-Related Research**



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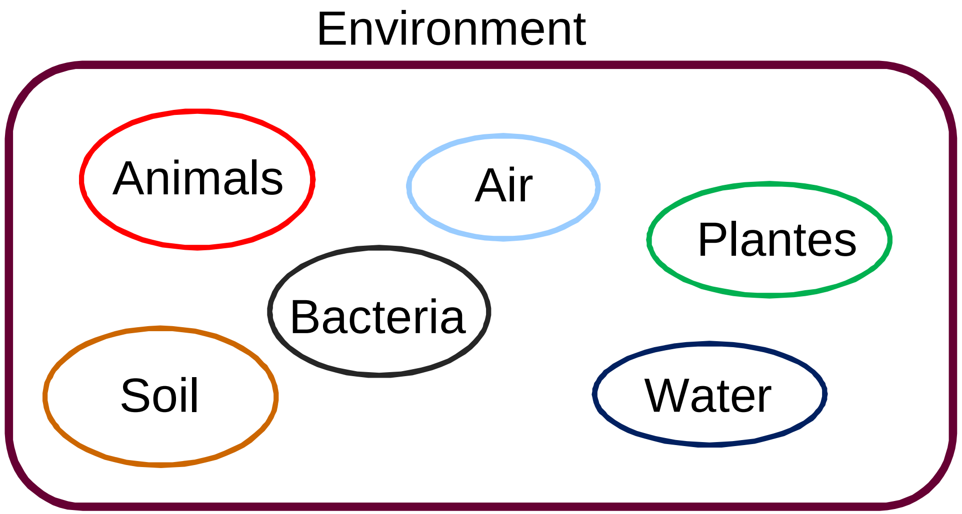
What is the environment? How to control the contamination?



Environment

Animals

Air

Plantes

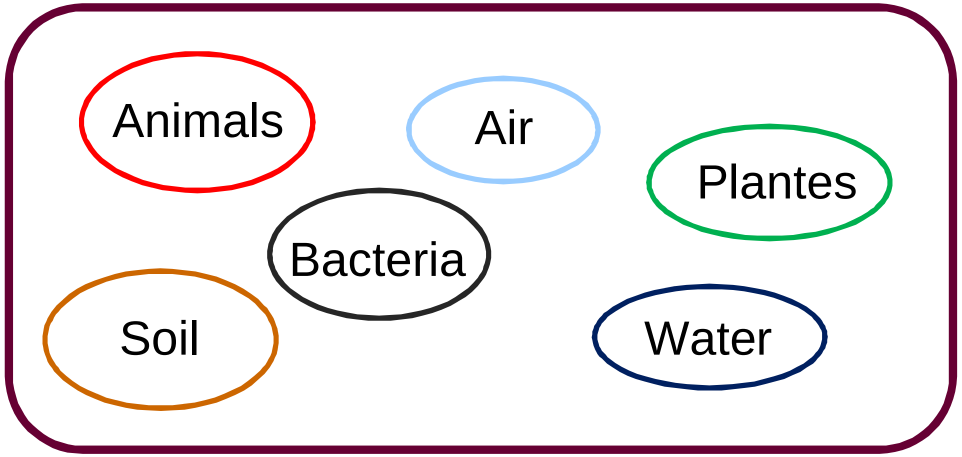
Bacteria

Soil

Water

Interplay between different elements

Environment



Animals

Air

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Bacteria

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Water

+ Contamination = ?

When the environment is contaminated the degree of complexity increases

Interplay between different elements

Study of local structure is essential

to understand how each single element acts on the environment

and to control the contamination

Environment

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Air

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Bacteria

Soil

Water

+ Contamination = ?

When the environment is contaminated the degree of complexity increases

Interplay between different elements

Study of local structure is essential

to understand how each single element acts on the environment

and to control the contamination

X-ray absorption spectroscopy applied to a toy-model

XAFS SPECTROSCOPY APPLIED TO EXOTIC SUPERCONDUCTORS

Antonella Iadecola

Elettra Sincrotrone Trieste

Outline

- Overview on the Fe based-system
- X-ray absorption spectroscopy
- Applications
- Conclusions

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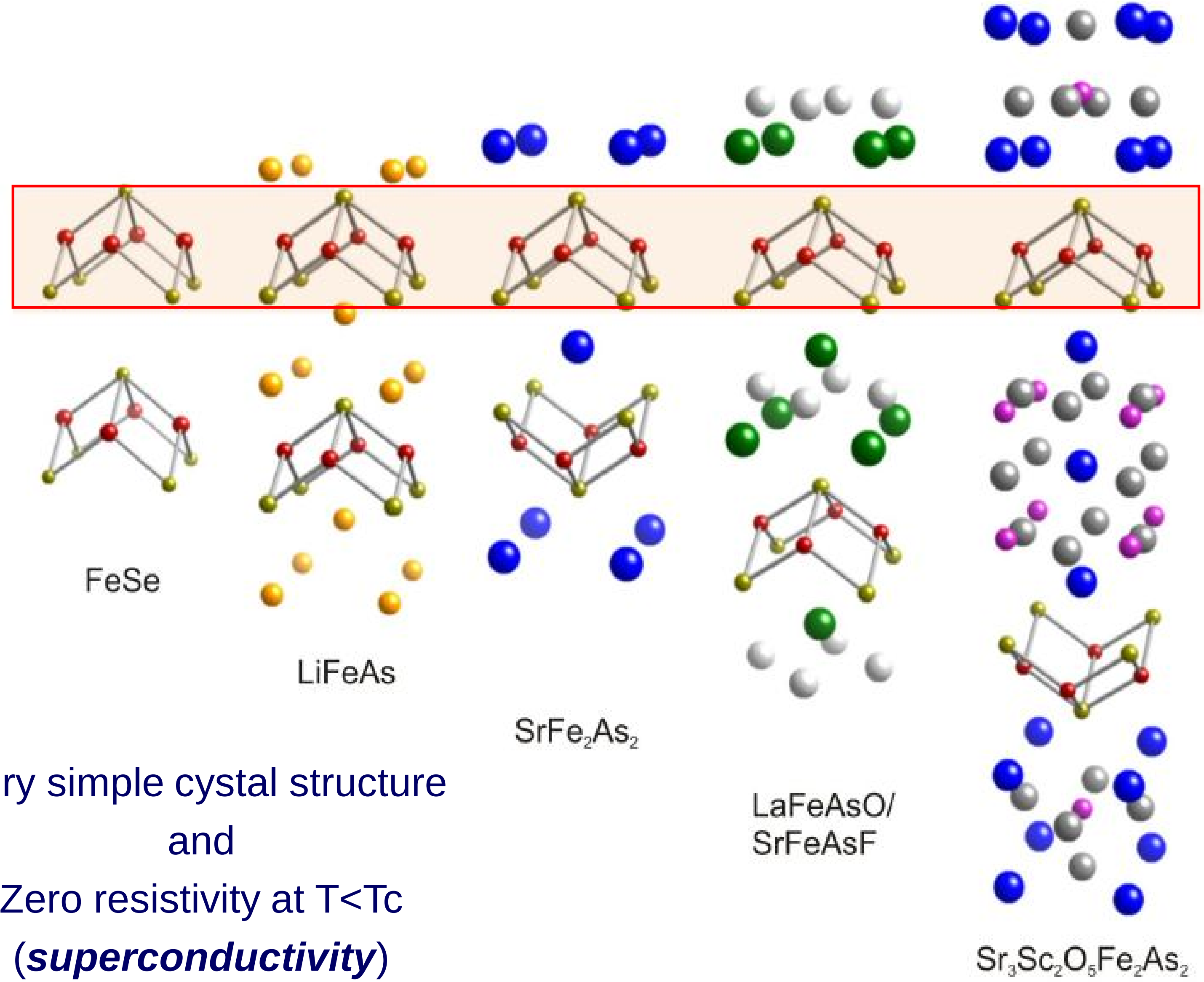
Overview on the Fe based-system



Very simple cystal structure

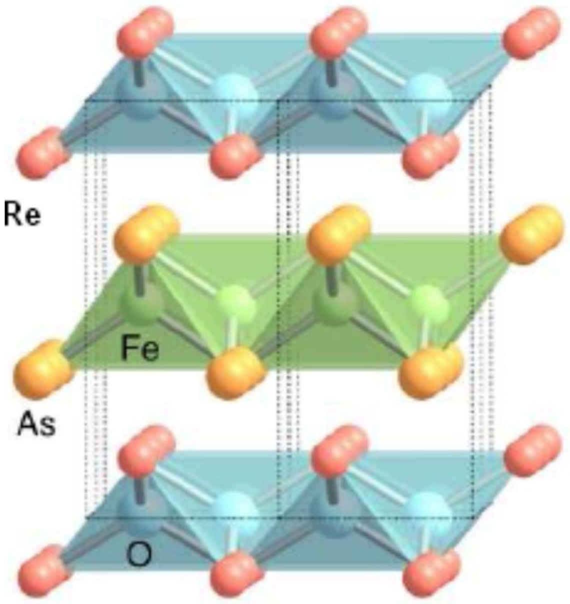
and

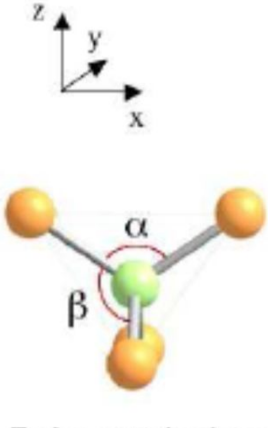
Zero resistivity at T<Tc

(***superconductivity***)

Overwiev on the Fe based-system

Highest T_c (~ 55 K)



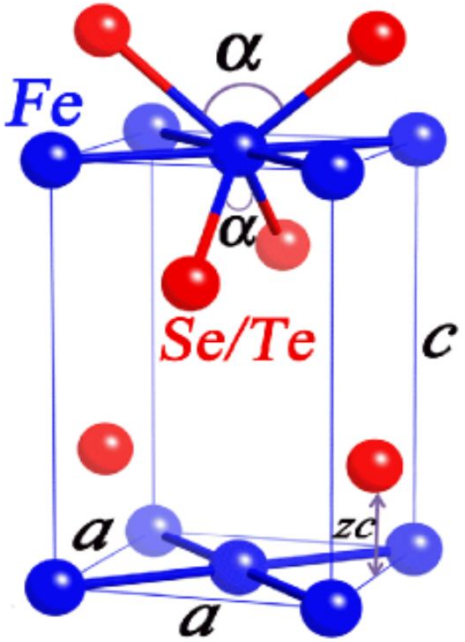


FeAs$_4$-tetrahedron

Tc depends on:

- ✓Rare-earth size
- ✓F-doping
- ✓Oxygen deficency
- ✓Hydrostatic pressure

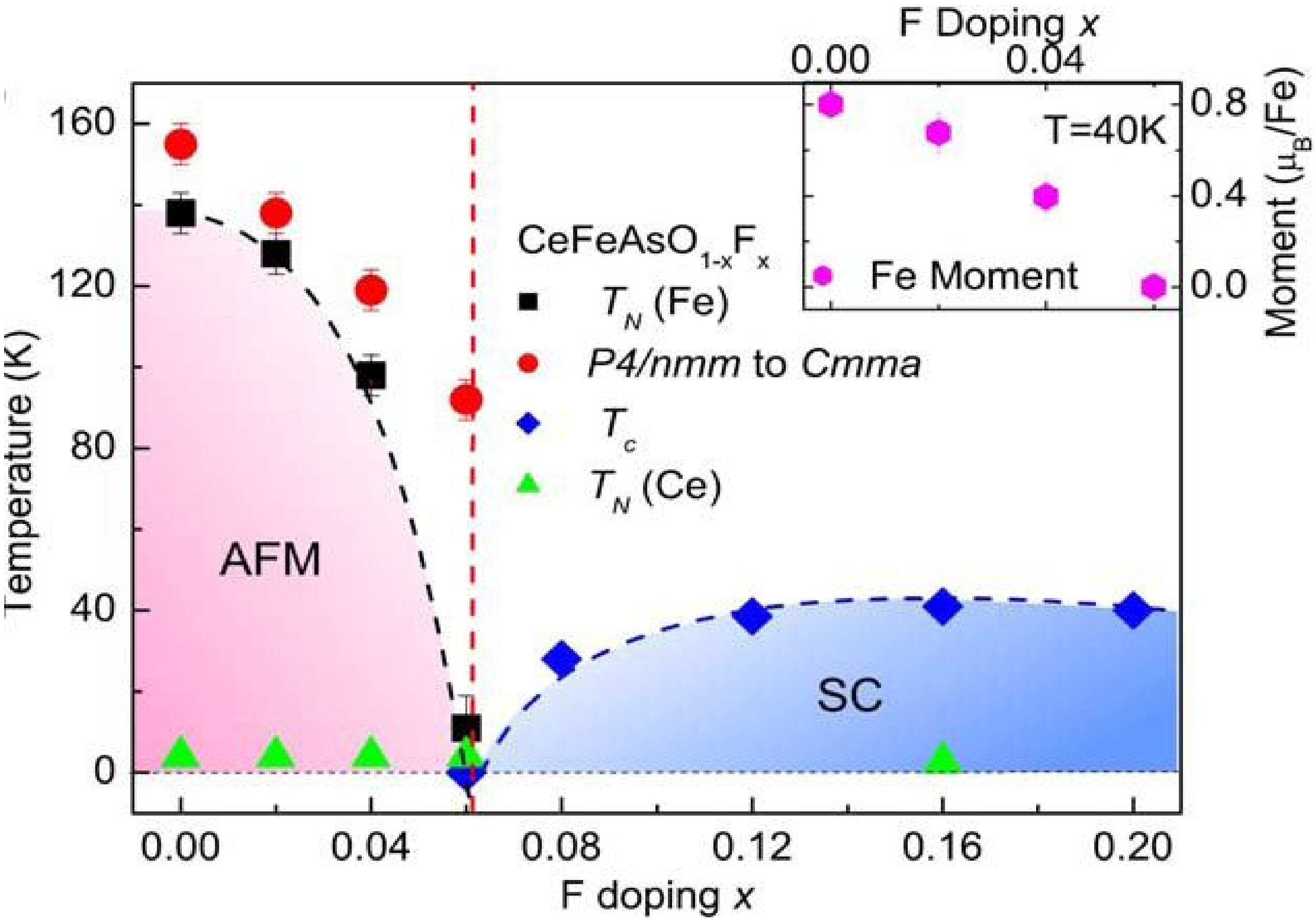
Simplest structure



Tc depends on:

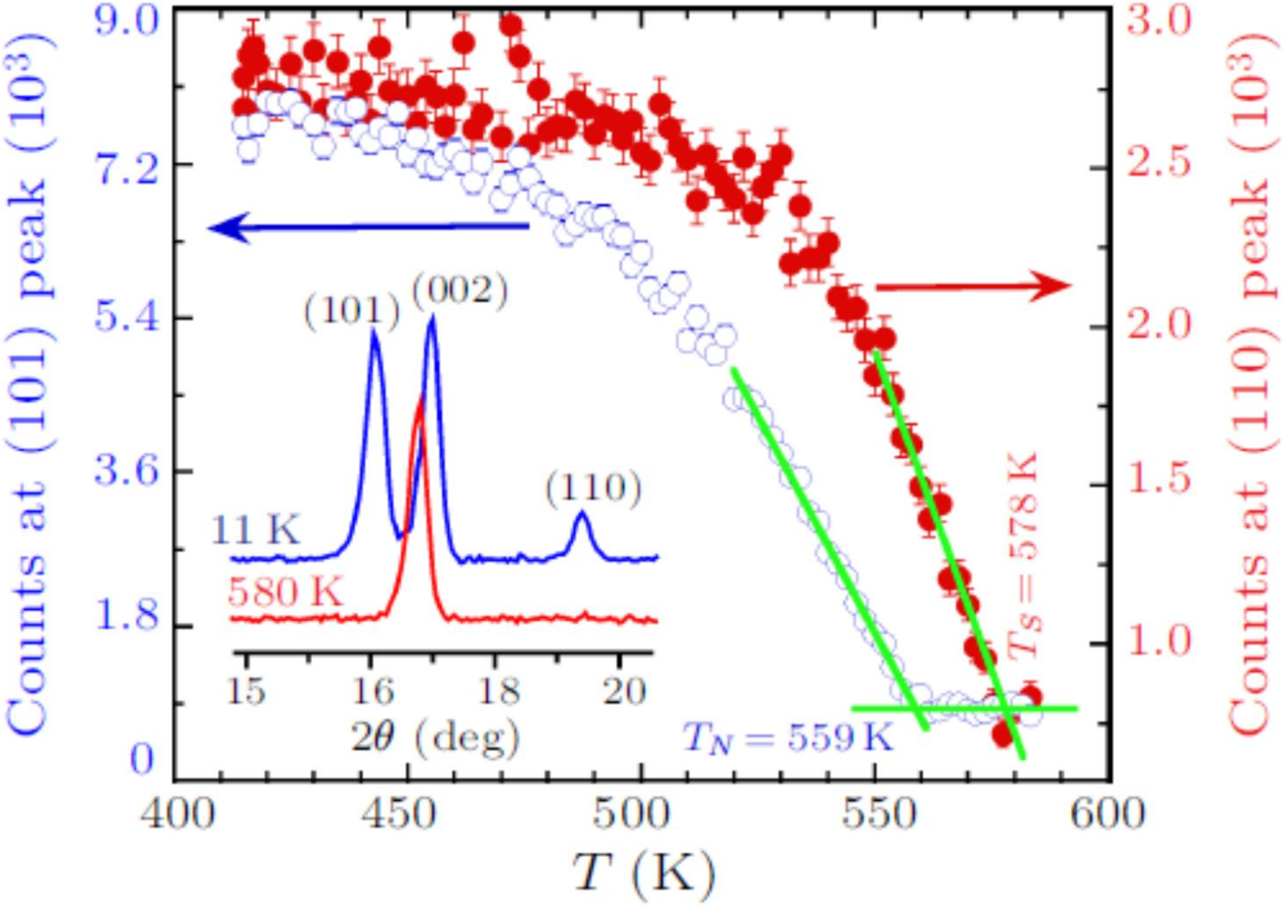
- ✓Te substitution
- ✓Stechiometry
- ✓Hydrostatic pressure
- ✓Tensil strain

Overview on the Fe based-system



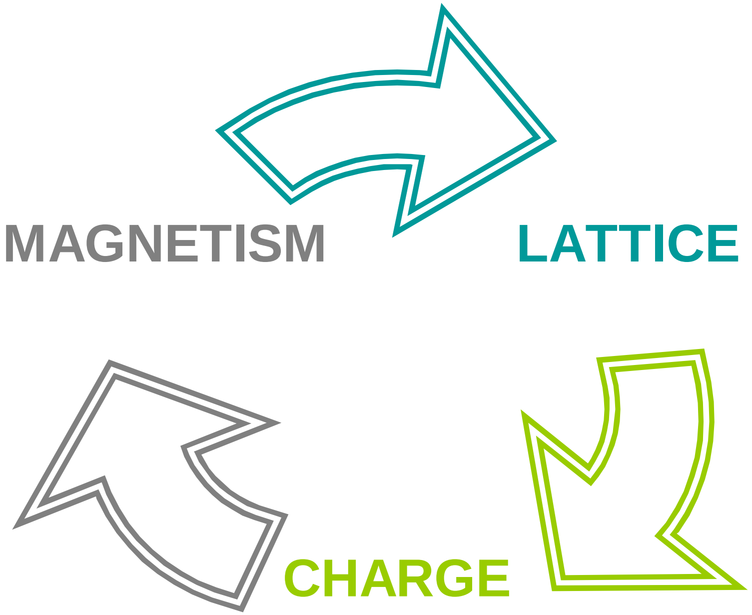
Structural transition combined with zero resistivity (*superconductivity*)

Overview on the Fe based-system



Structural transition combined with magnetic transition (from AFM to PM state)

Overview on the Fe based-system



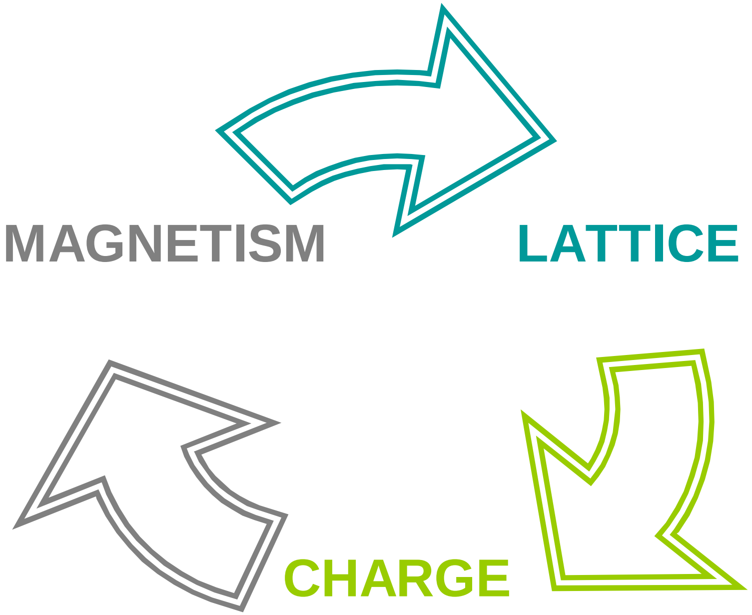
MAGNETISM

LATTICE

CHARGE

The crystallographic structure is not able to explain the properties in these systems

Overview on the Fe based-system



MAGNETISM

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The crystallographic structure is not able to explain the properties in these systems

LOCAL STRUCTURE

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- X-ray absorption spectroscopy
- Applications
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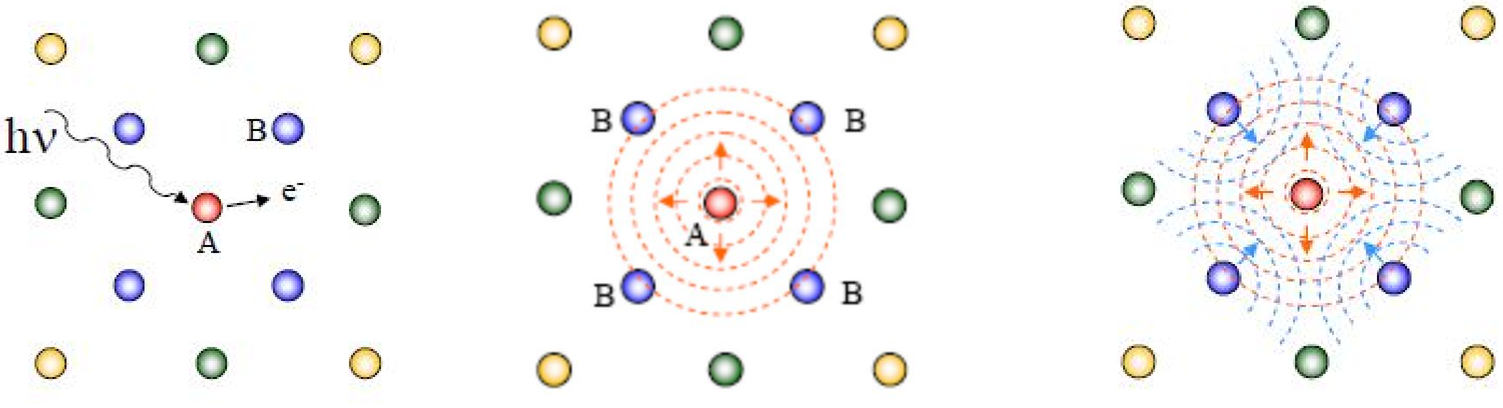
X-ray Absorption Spectroscopy

- **Photoelectric effect**

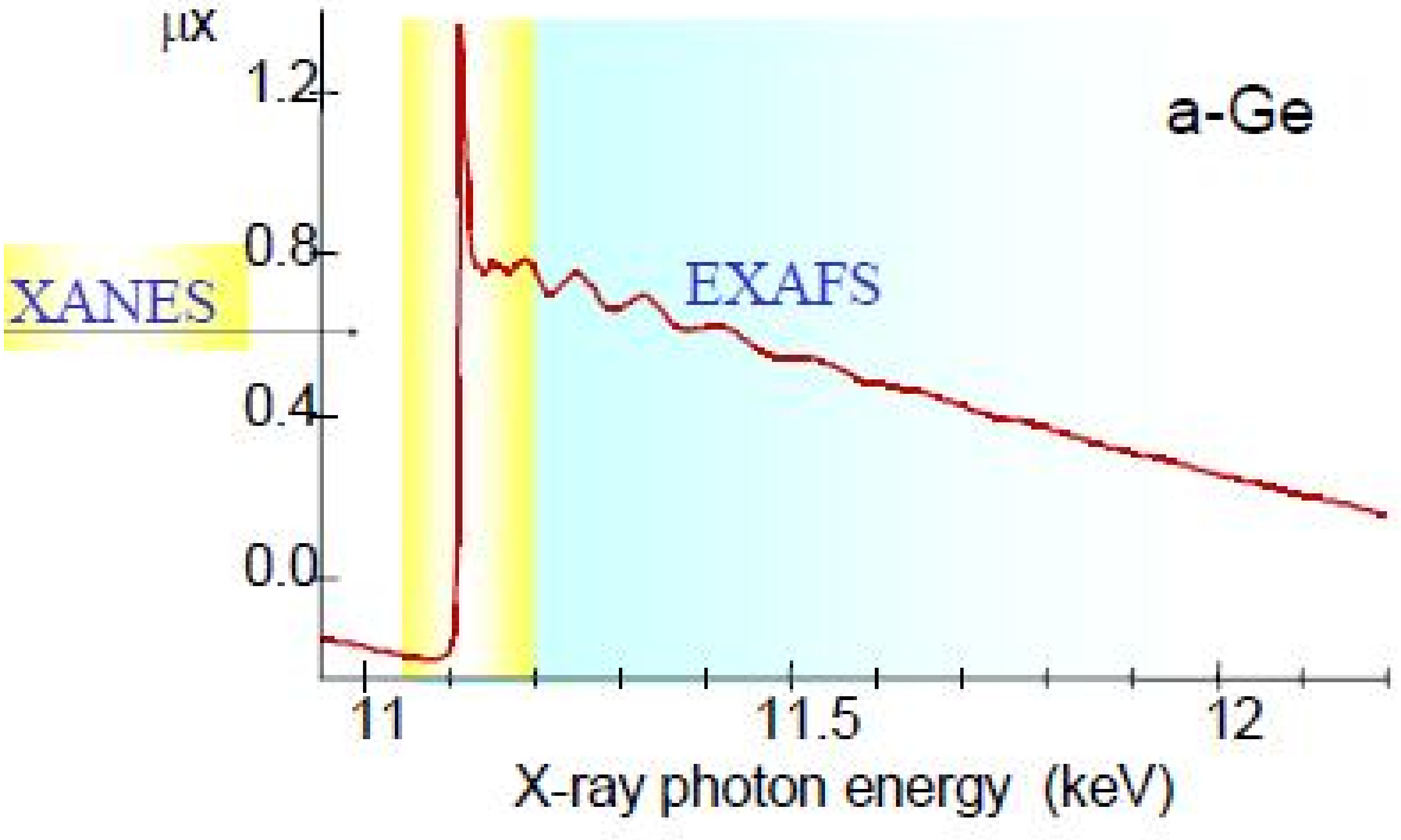


- **Site selective method**

- **Fast technique 10^{-15} s**

- **No need long-range ordering**

X-ray Absorption Spectroscopy



The EXAFS formula

$$\chi(k) = \sum_{j} \frac{N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)}\, e^{-2k^2\sigma_j^2}}{kR_j{}^2} \sin[2kR_j + \delta_j(k)]$$

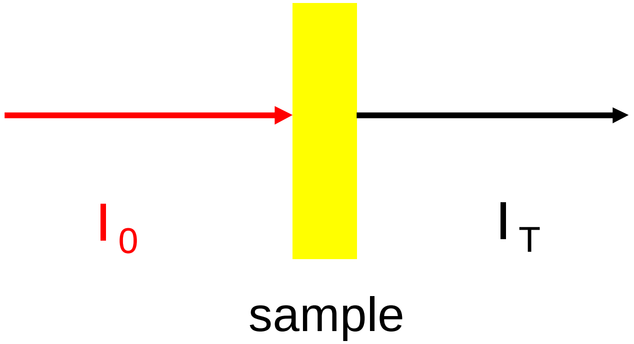
$f_j(k)$	Amplitude scattering
δ_j	Phase shift
R	Distance to the neighbouring atom
N	Coordination number of the neighbouring atom
σ^2	Correlated fluctuations of the bond

$$\boxed{\sigma^2 = \sigma_0^2 + \sigma^2(T) = \sigma_0^2 + \frac{\hbar^2}{2\mu k_B \theta_E}\coth(\frac{\theta_E}{2T})}$$

μ	reduced mass
k_B	Boltzmann constant
$\hbar$	Planck constant/2π
θ_E	Einstein temperature

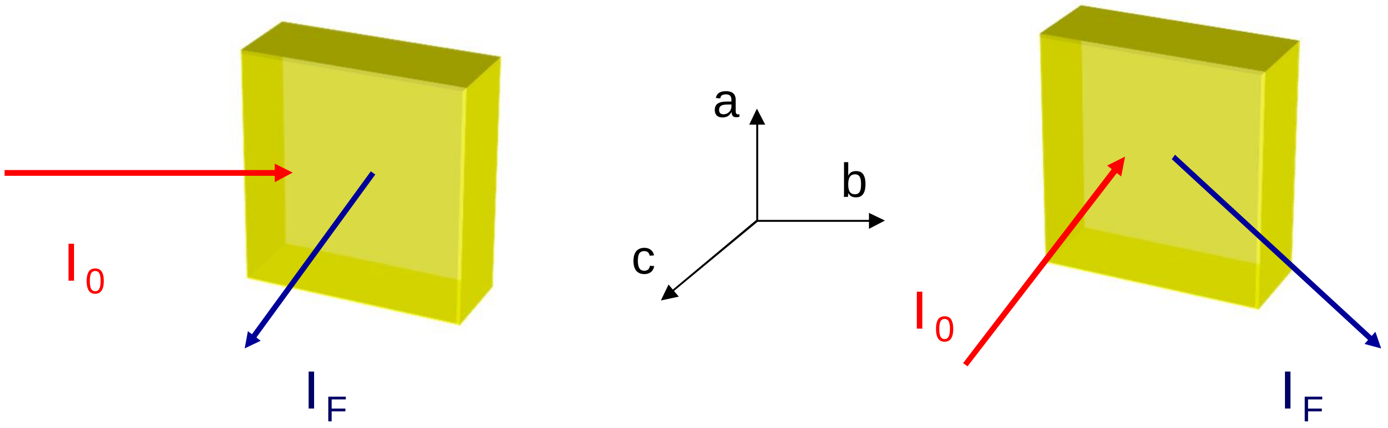
Experimental details

- Unpolarized measurements : transmission mode (powder samples)



$$\mu_T = \ln(\frac{I_0}{I_T})$$

- Polarized measurements : fluorescence mode (single crystals)



$$\mu_F = \frac{I_F}{I_0}$$

Grazing incidence : E||c polarization

Normal incidence : E||ab polarization

The XANES interpretation

XANES can be described *qualitatively* (and nearly *quantitatively*) in terms of

coordination chemistry	regular, distorted octahedral, tetrahedral, . . .
molecular orbitals	p-d orbital hybridization, crystal-field theory, . . .
band-structure	the density of available electronic states
multiple-scattering	multiple bounces of the photoelectron

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A simple equation for XANES does not exist!

XANES calculations are becoming reasonably accurate and simple. These can help explain what *bonding orbitals* and/or *structural characteristics* give rise to certain spectral features.

Quantitative XANES analysis using first-principles calculations are also possible.

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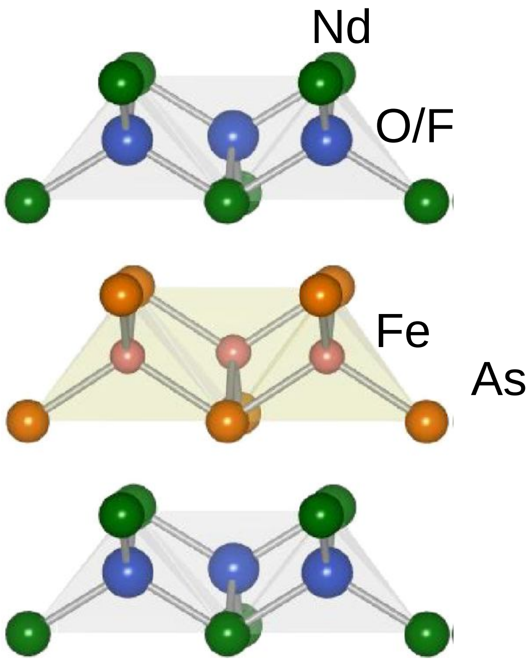
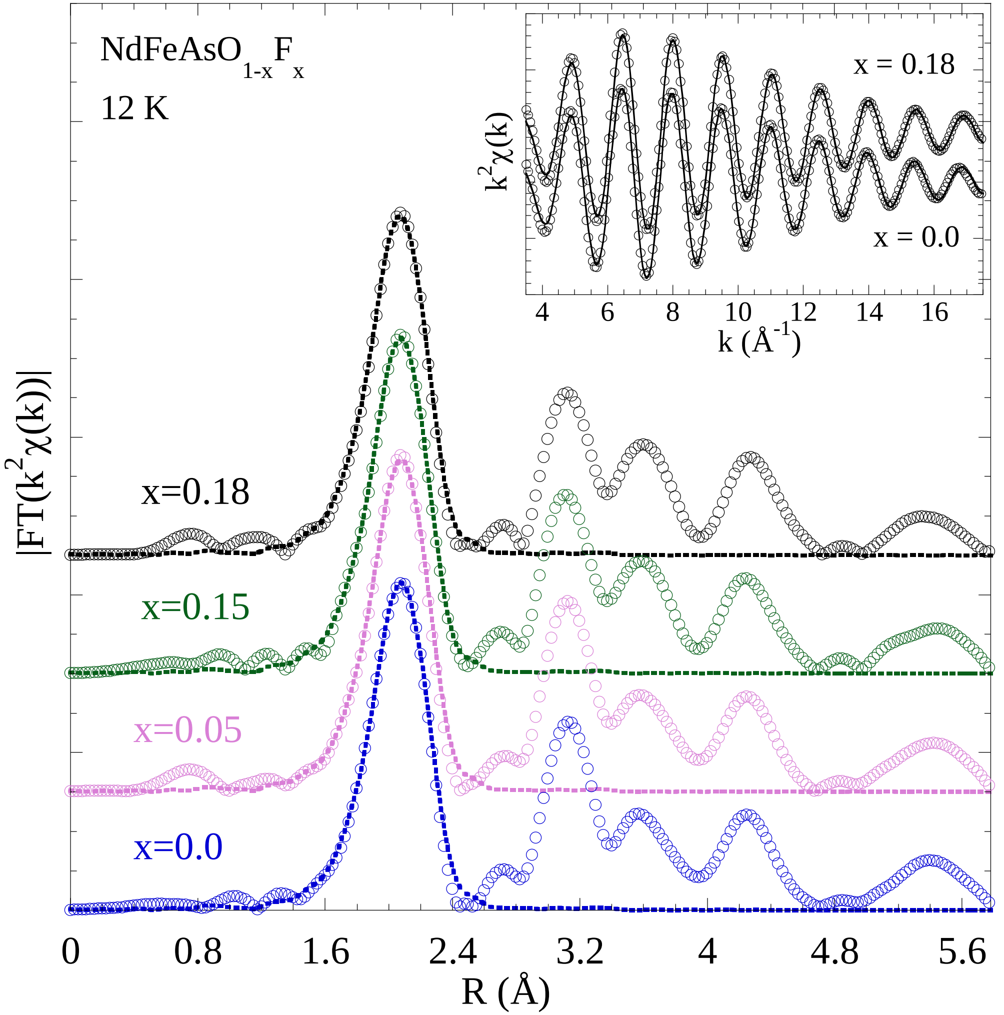
The effect of temperature on $NdFeAsO_{1-x}F_x$

- ✓As K-edge EXAFS





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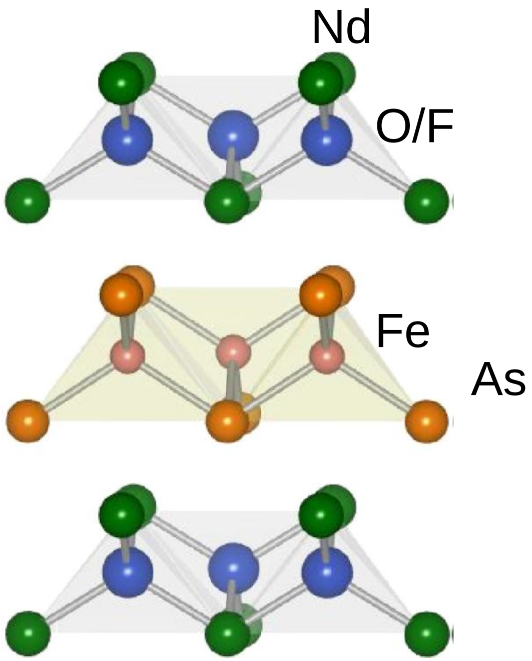
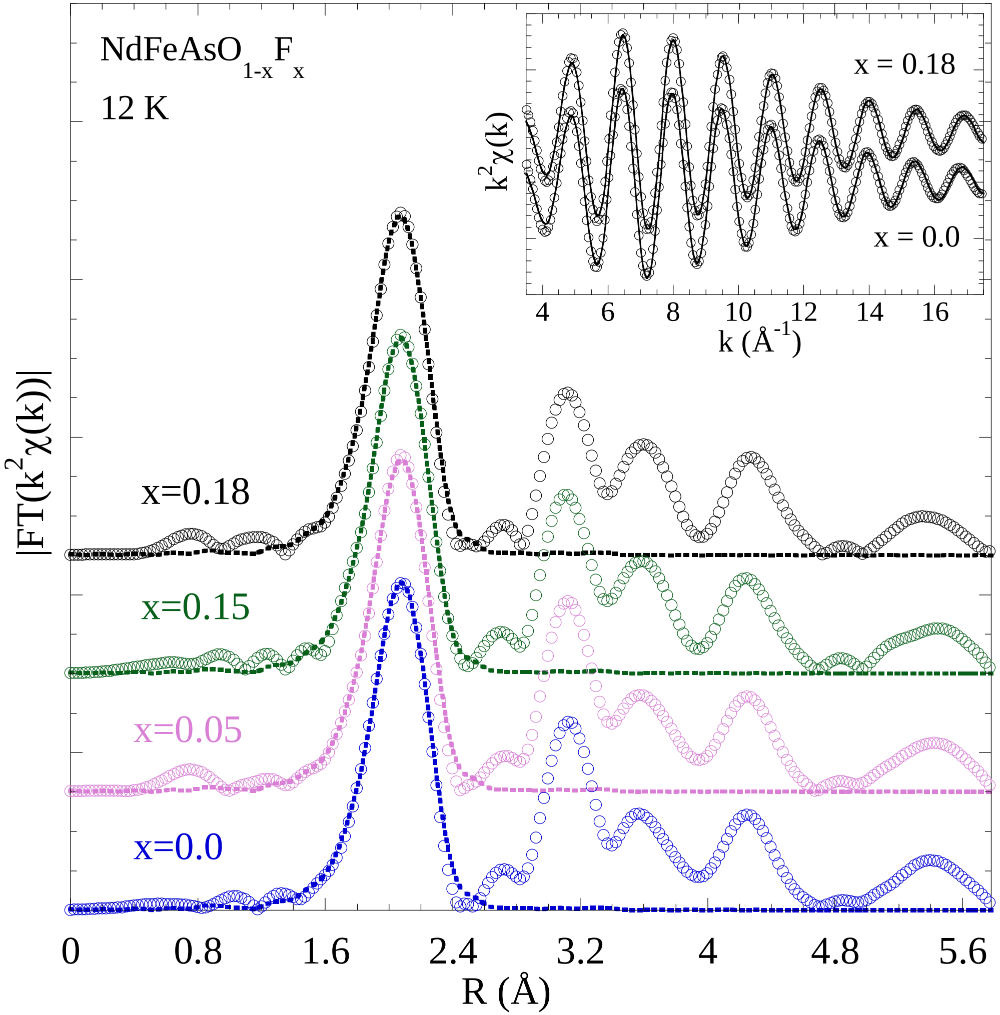
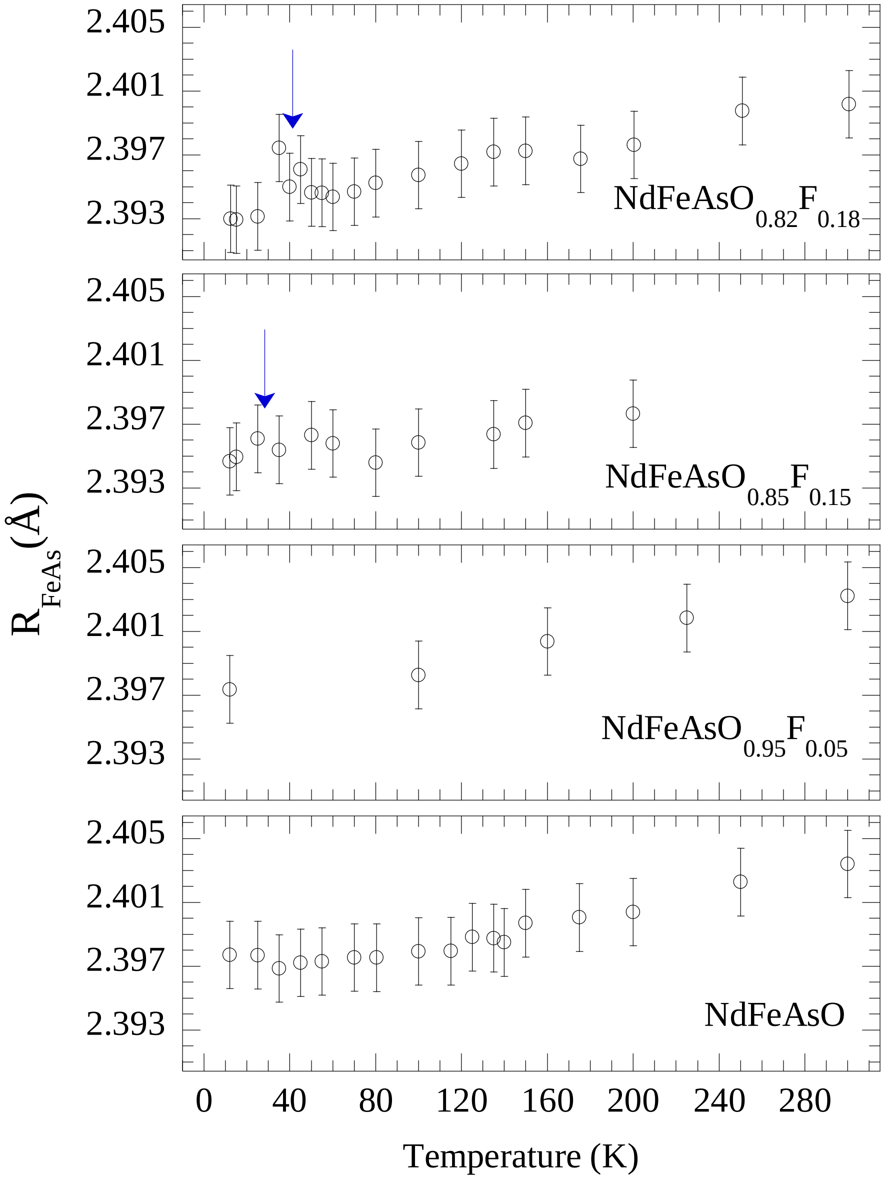




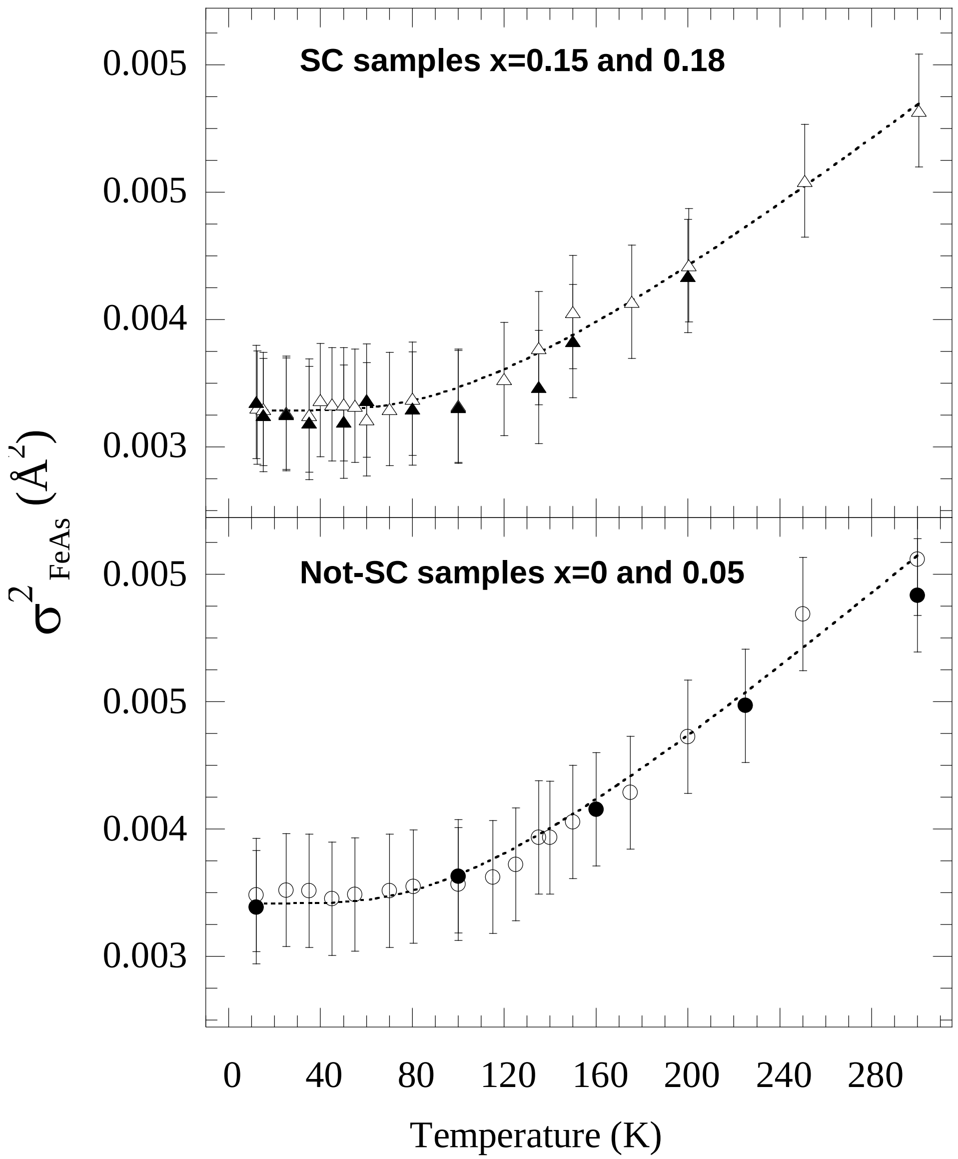
Only Fe-As shell contribute to the main peak of FT

The effect of temperature on the distance



- **Low temperature anomalies observed in x=0.15 and 0.18 samples**
- **As-Fe bond-length not influenced by fluorine doping**

The Debye-Waller Factors



$$\sigma^2_{As-Fe} = \frac{\hbar^2}{2\mu k_B \theta_E}\coth\left(\frac{\theta_E}{2T}\right)$$

Two different Einstent temperature

$$\theta_E = (348 \pm 12)K \quad \text{for SC samples}$$
$$\theta_E = (326 \pm 12)K \quad \text{for not - SC samples}$$

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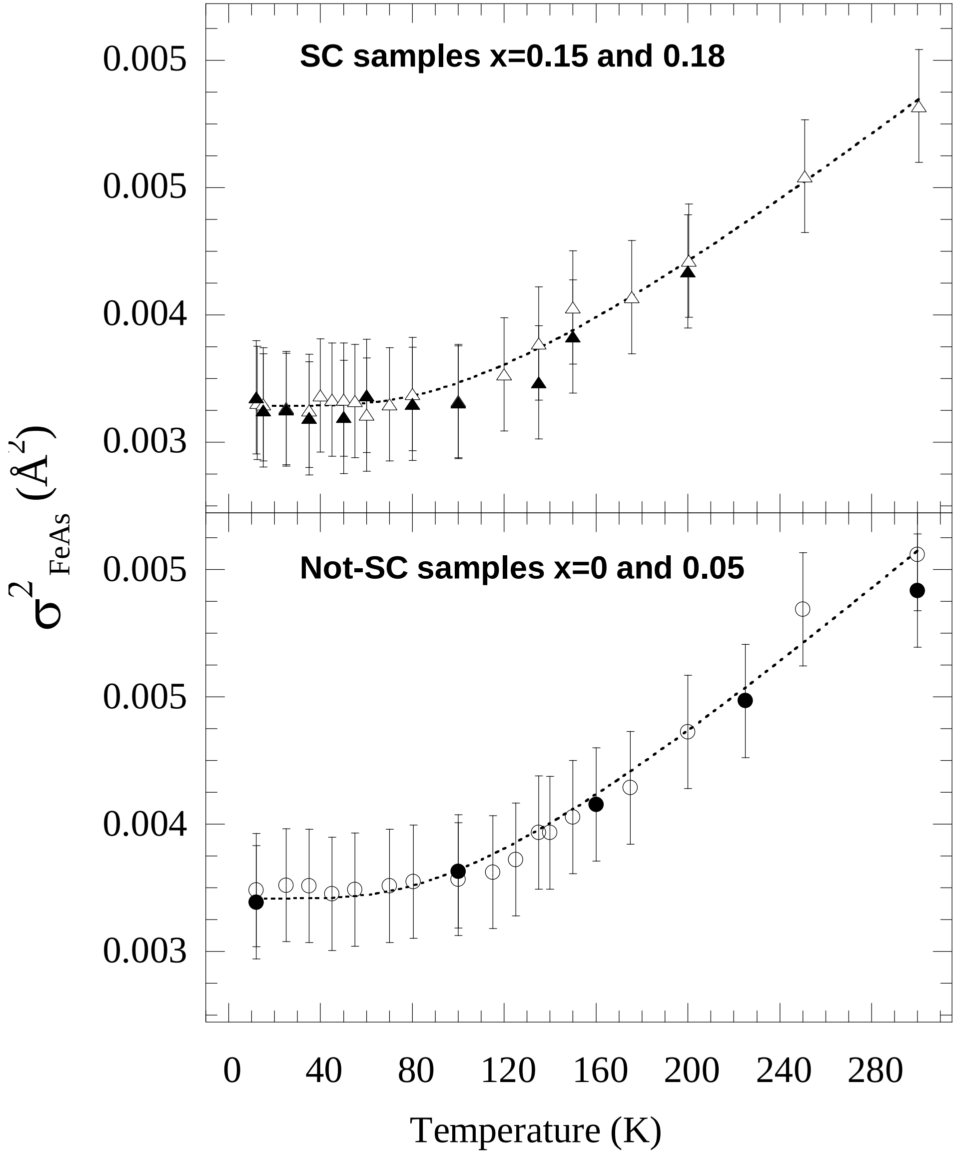

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Because the local force constant is

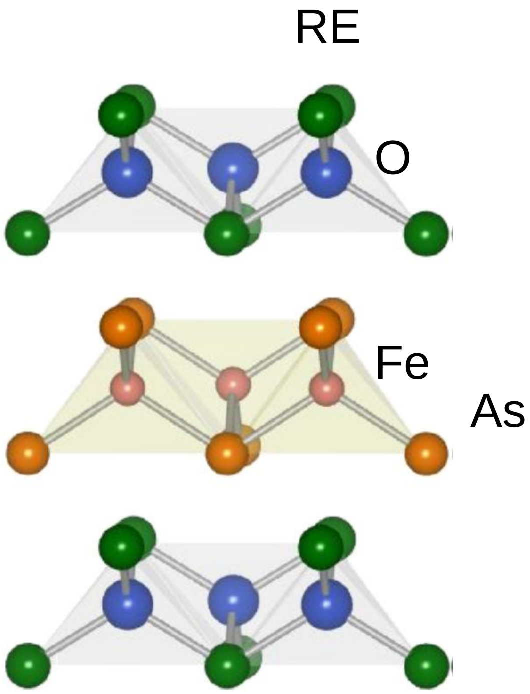
$$\boxed{k \propto \mu\theta_E^2}$$

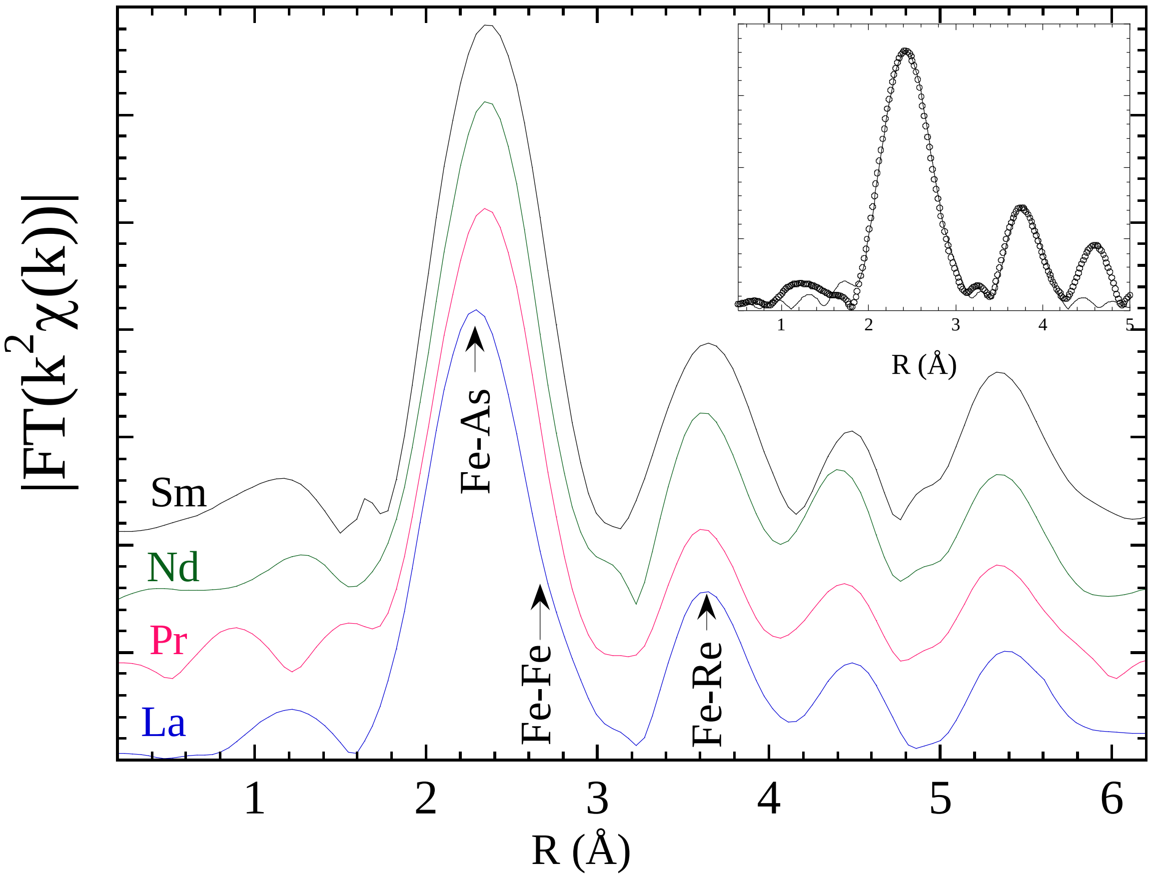
Two different local force constants

$$k = 6.65 eVA^{-2} \quad \text{for SC samples}$$
$$k = 5.85 eVA^{-2} \quad \text{for not - SC samples}$$

The effect of chemical pressure on REFeAsO

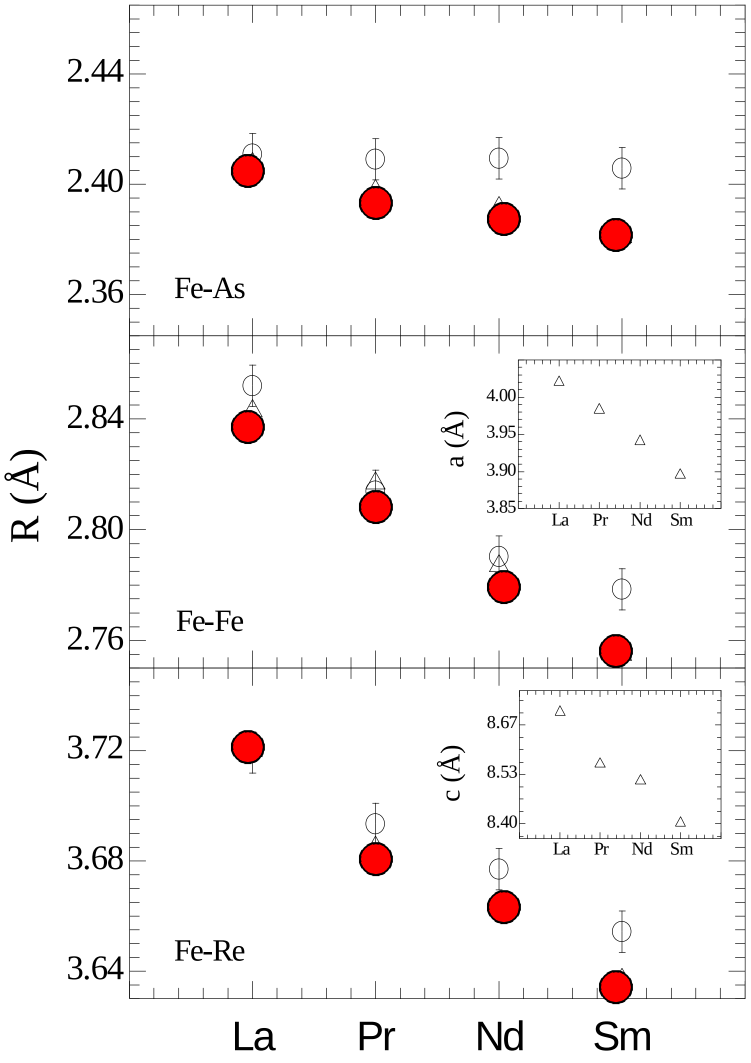
✓Fe K-edge EXAFS





Three shell model (Fe-As, Fe-Fe and Fe-RE)

The effect of chemical pressure on REFeAsO

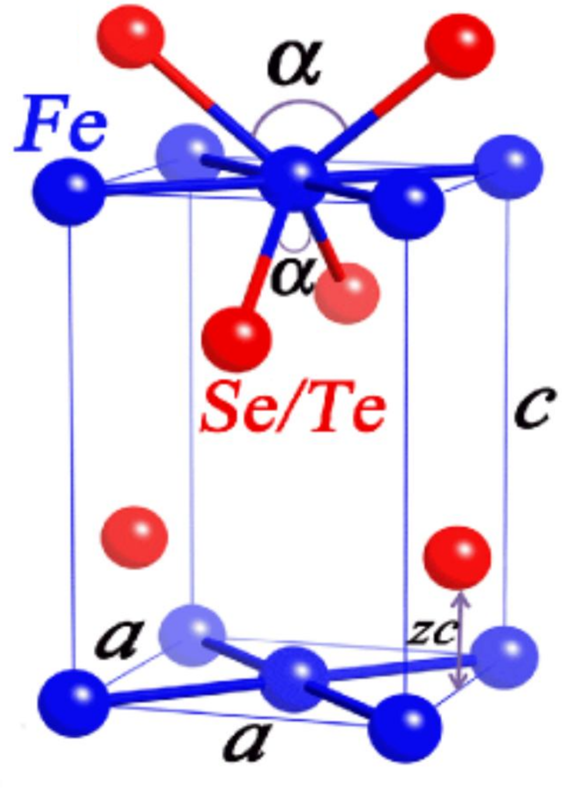


- **Fe-As bond strongly covalent**

- **Unit cell compressed as chemical pressure effect**

- ***Local structure is significantly different from the average structure***

The local structure of $FeSe_{1-x}Te_x$



The distances from x-ray diffraction are

R Fe-Se ≈ 2.39 Å for $FeSe_{0.88}$

R Fe-Se/Te ≈ 2.47 Å for $FeSe_{0.5}Te_{0.5}$

In $FeSe_{0.5}Te_{0.5}$ the Te and Se atoms occupy the same site!!!

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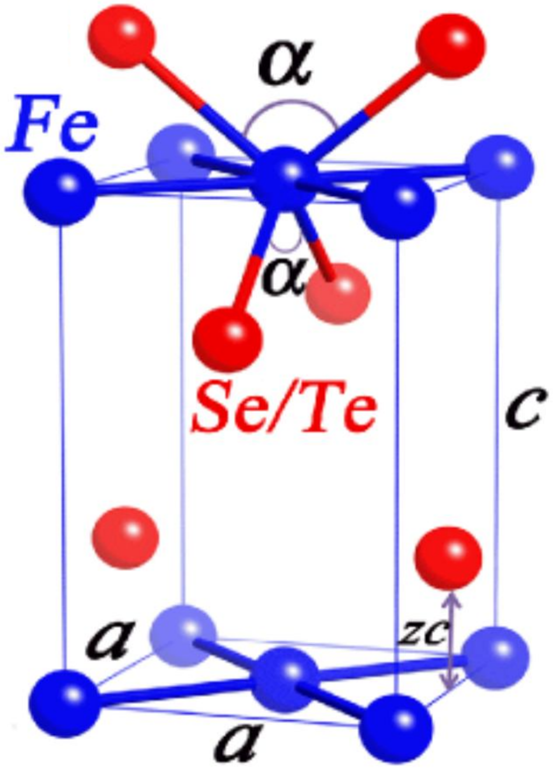

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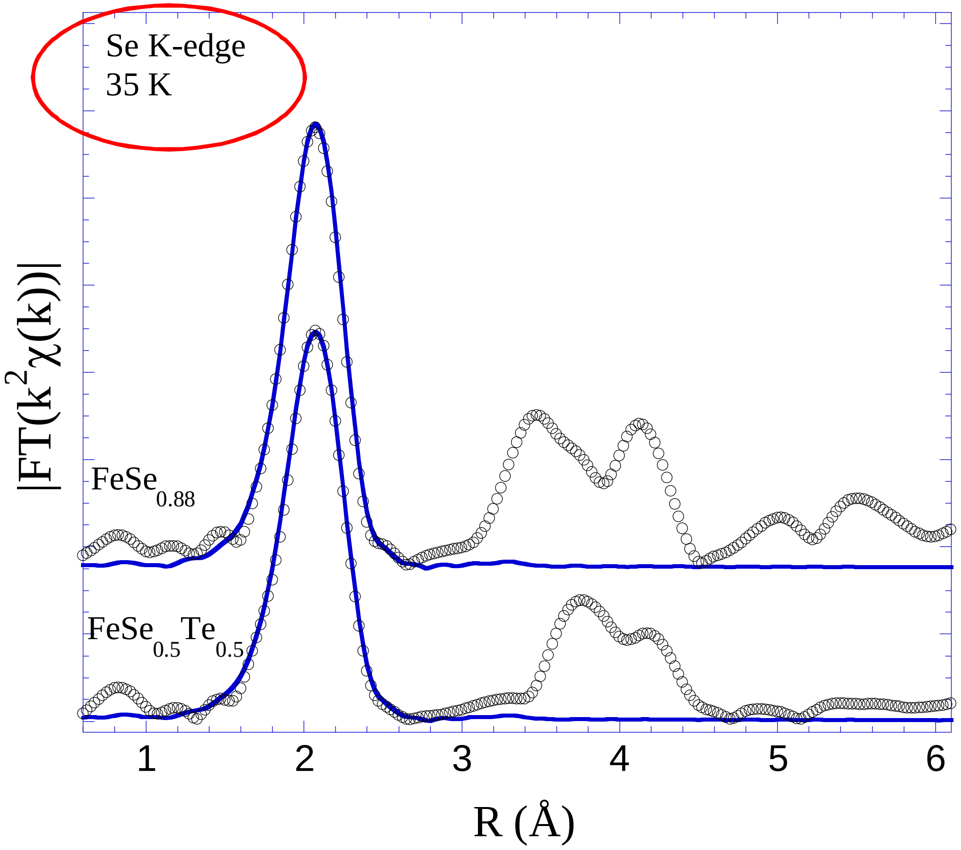
What about the local structure?

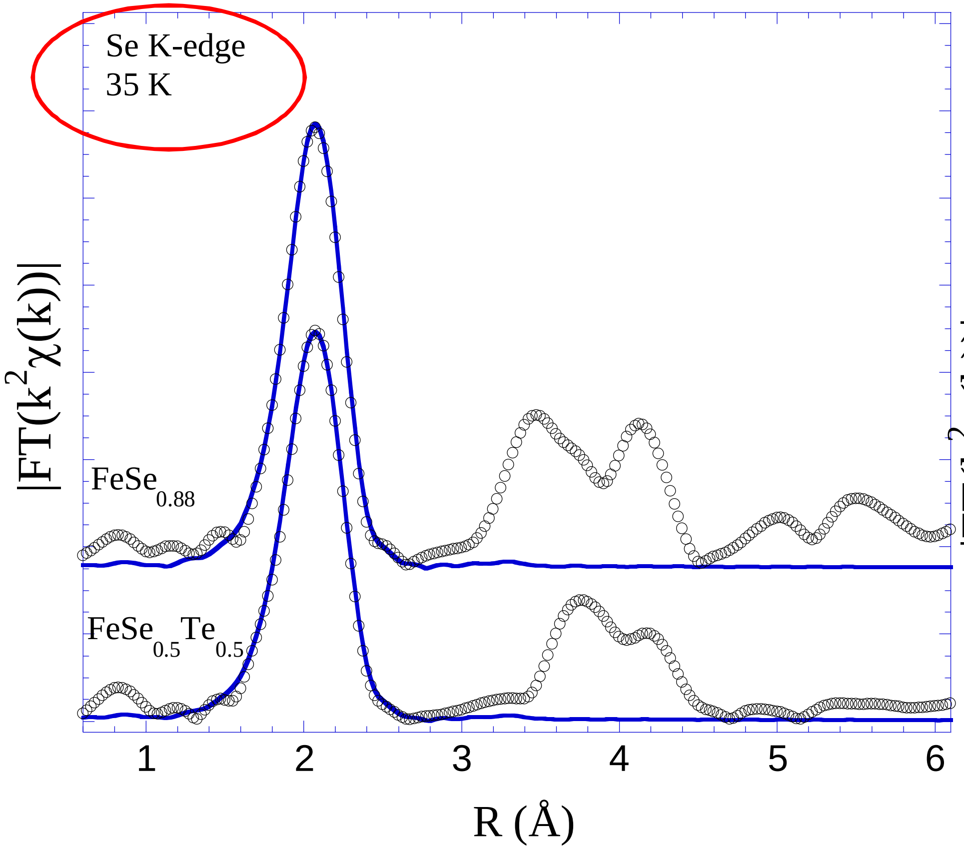
Se and Fe K-edges EXAFS on $FeSe_{1-x}Te_x$

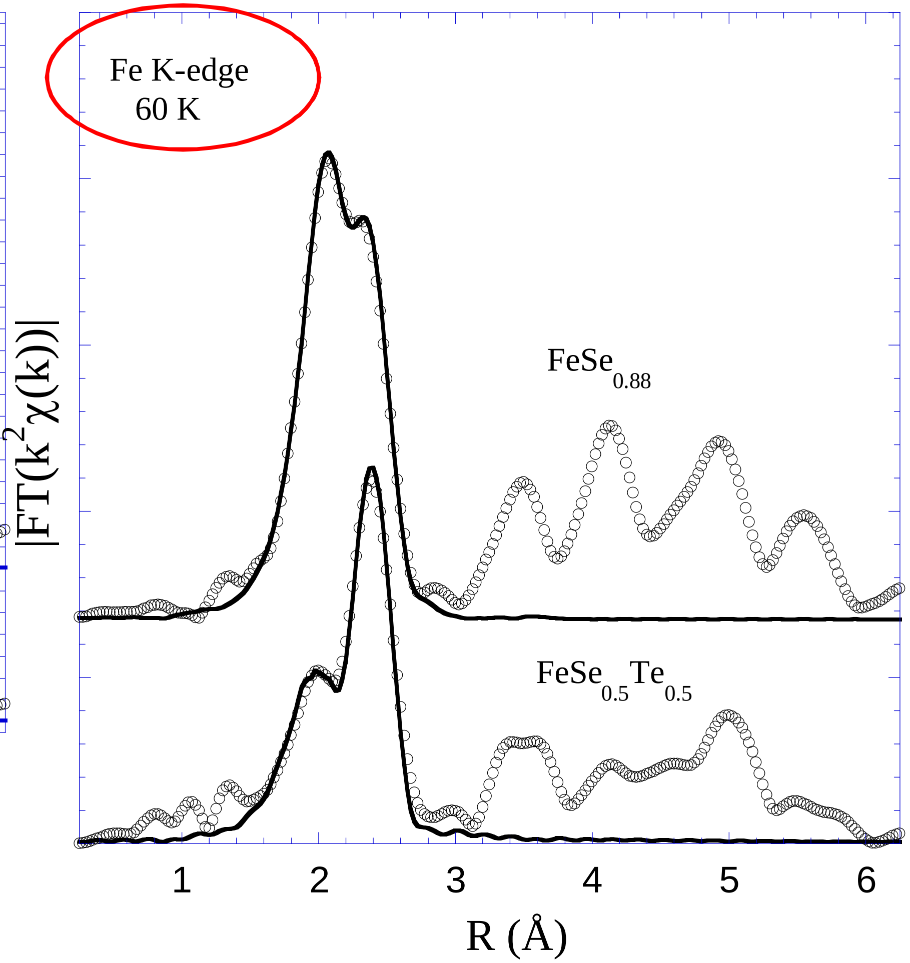


There are four Fe near neighbors
at a distance 2.4 Å main peak at 2 Å.

The next nearest neighbors of Se are eight Se
and four Fe atoms (3.0–4.5 Å)

Se and Fe K-edges EXAFS on $FeSe_{1-x}Te_x$





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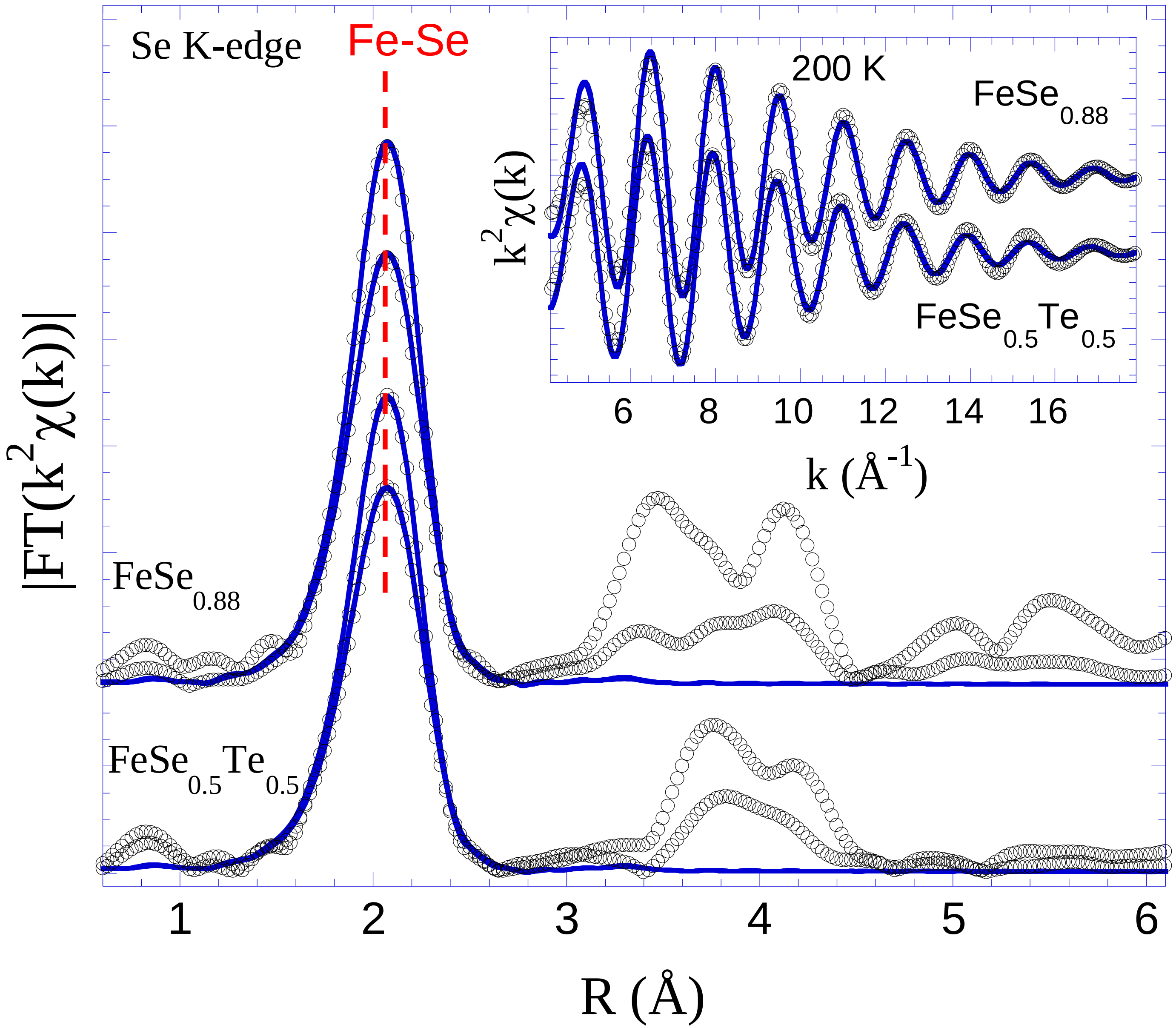
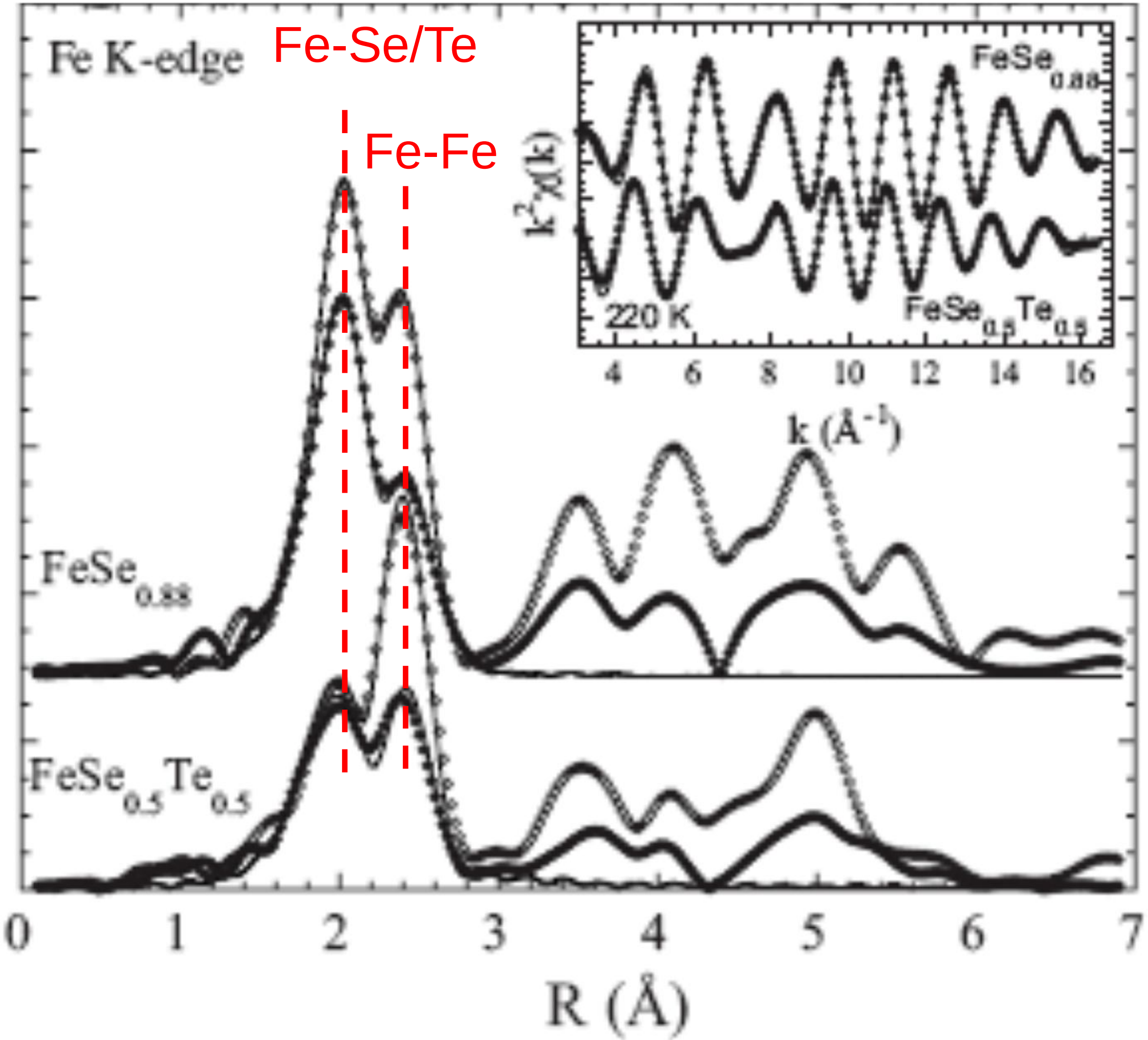
For the Fe site probed by Fe *K* edge the near neighbors are four Se(Te) at a distance 2.4 Å and four Fe atoms at a distance 2.6 Å

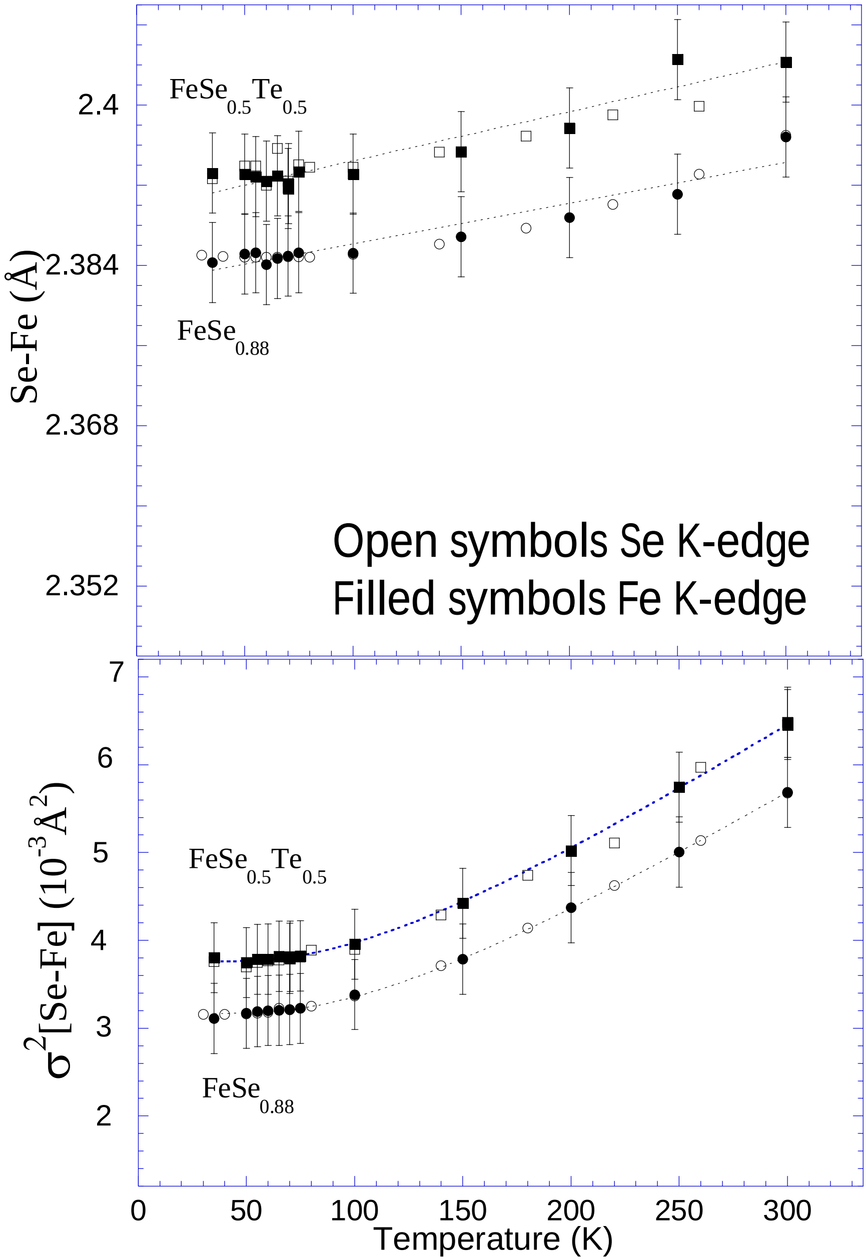
Se K-edge EXAFS as a function of T



Fe K-edge EXAFS as a function of T



Results for the Se-Fe bond on $FeSe_{1-x}Te_x$



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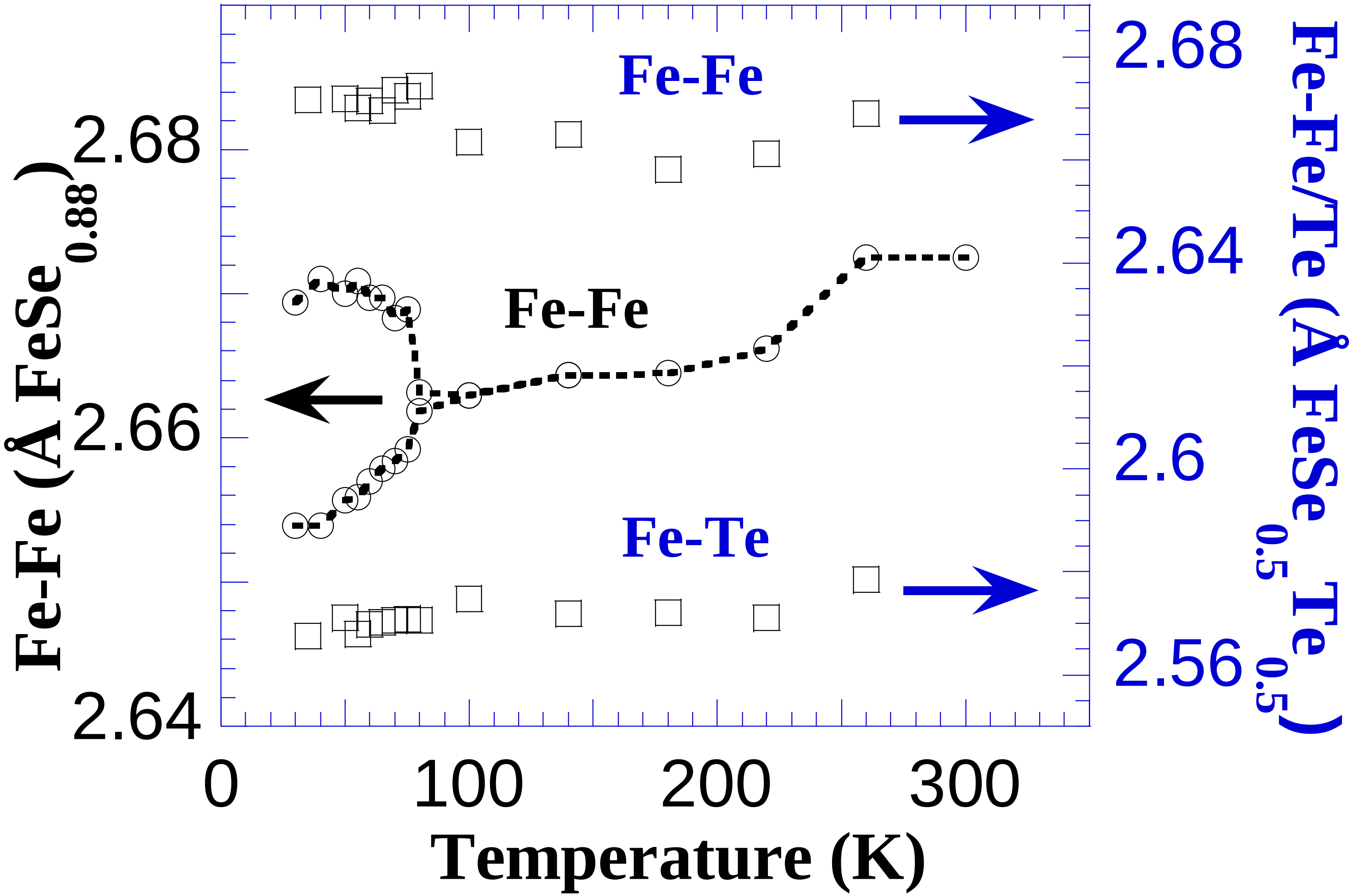
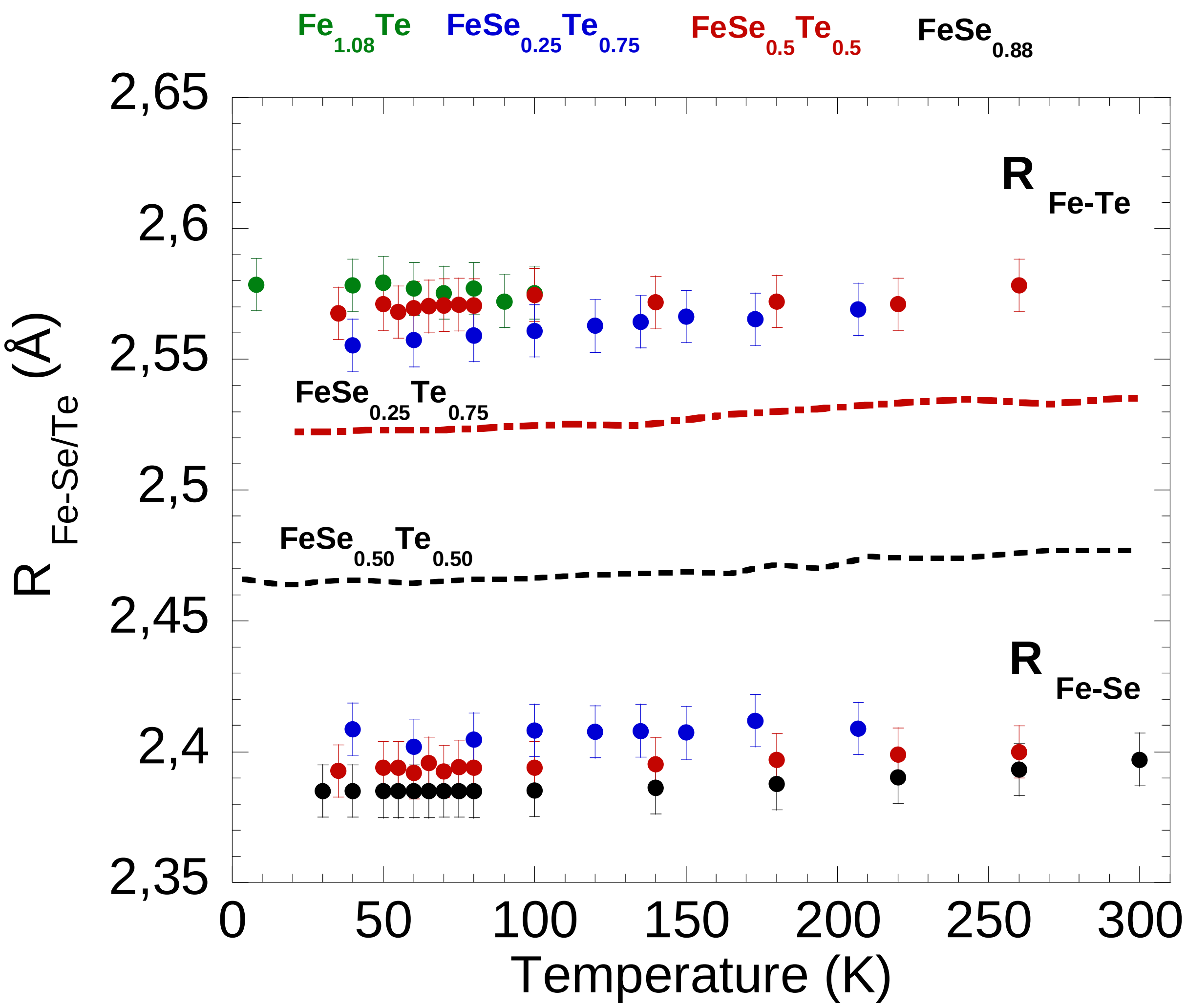


Local structure is different from the average structure!



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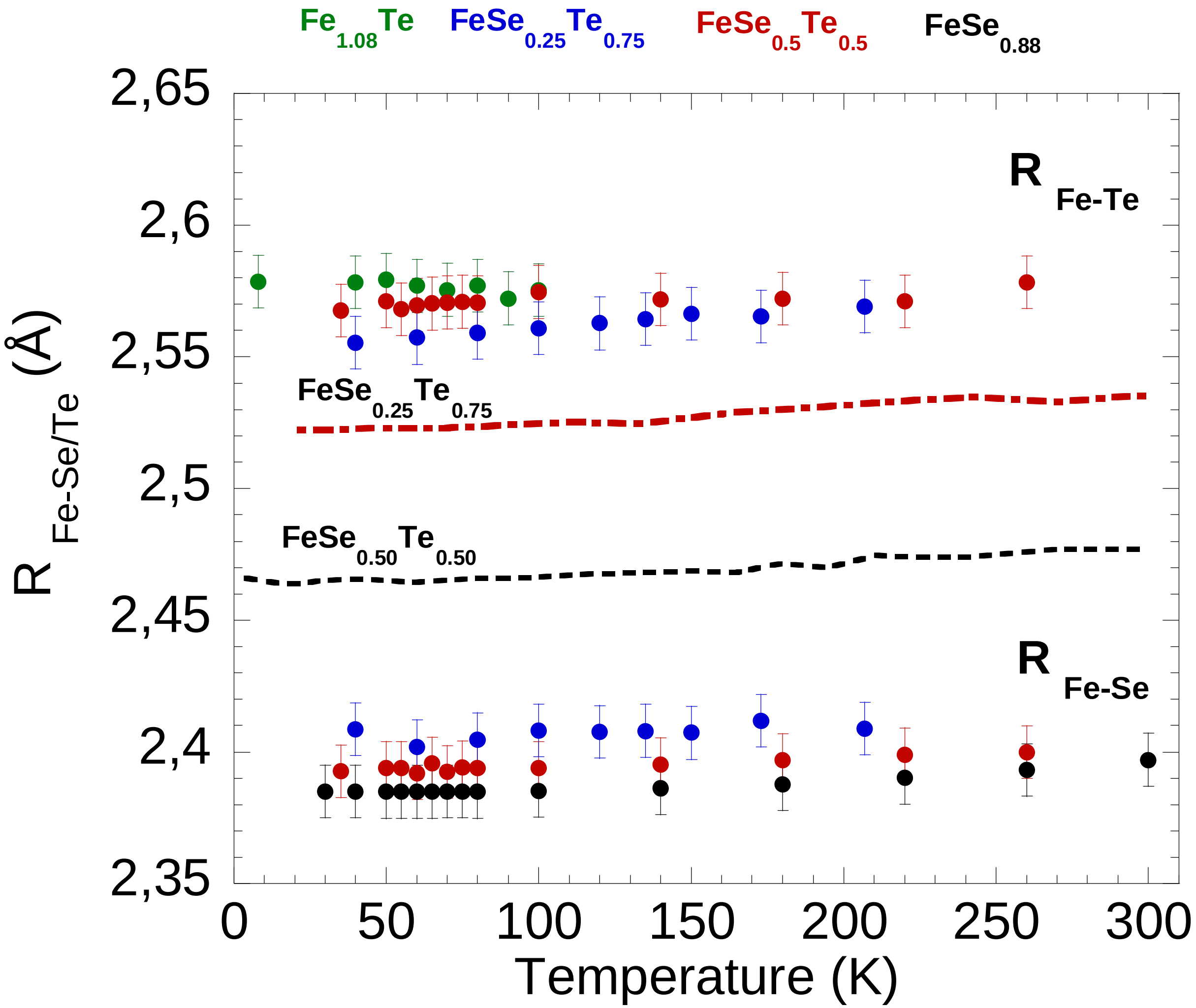

Distinct site occupation by the Se and Te atoms!

Local structure is different from the average structure!

The Fe-Se and Fe-Te bond lengths in the ternary system are found to be very different from the average crystallographic Fe-Se/Te distance, and almost identical to the Fe-Se and Fe-Te distances for the binary FeSe and FeTe systems

distinct site occupation by the Se and Te atoms:

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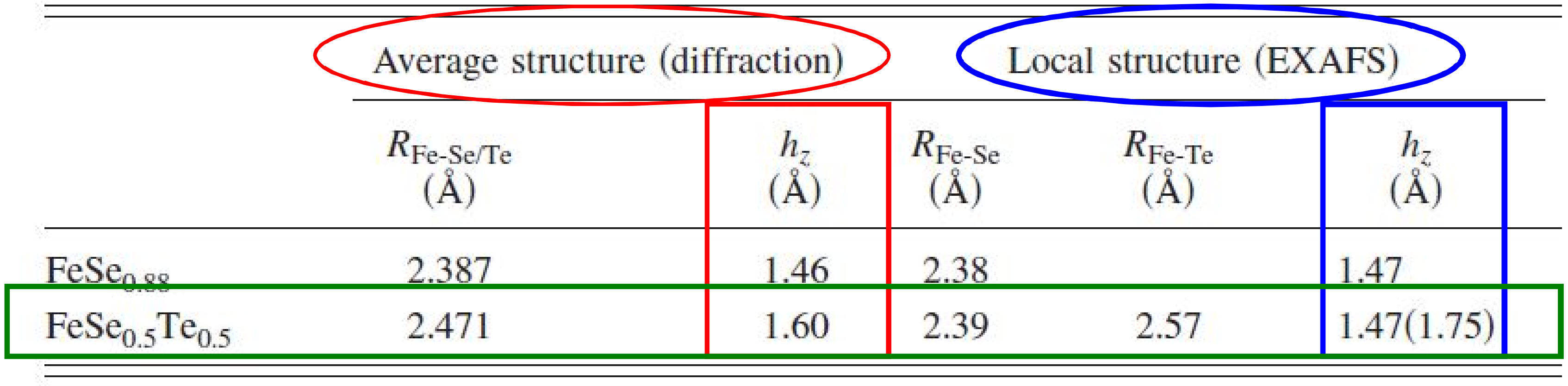

	Average structure (diffraction)		Local structure (EXAFS)		
	$R_{\text{Fe-Se/Te}}$ (Å)	h_z (Å)	$R_{\text{Fe-Se}}$ (Å)	$R_{\text{Fe-Te}}$ (Å)	h_z (Å)
$FeSe_{0.88}$	2.387	1.46	2.38		1.47
$FeSe_{0.5}Te_{0.5}$	2.471	1.60	2.39	2.57	1.47(1.75)

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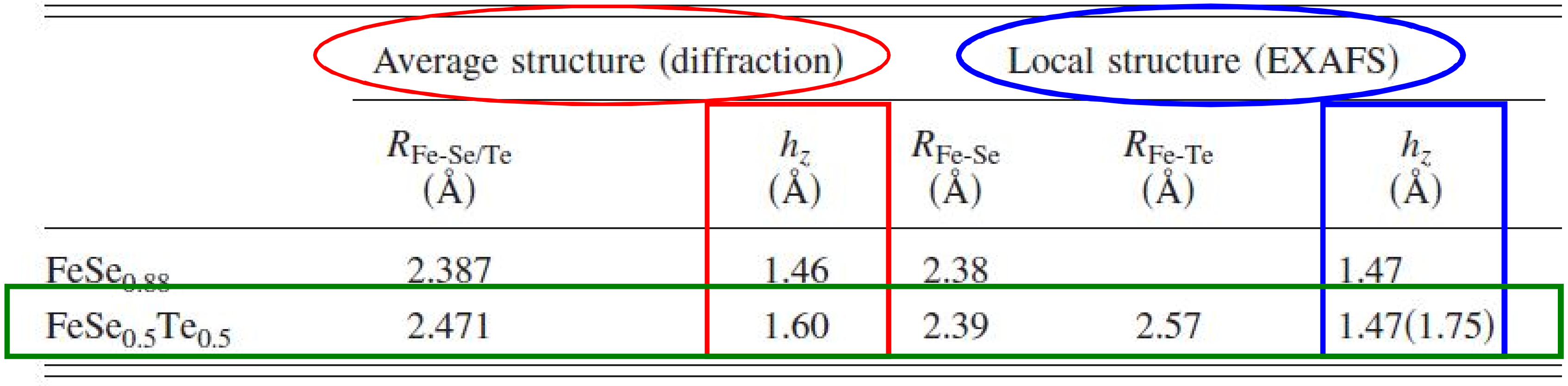

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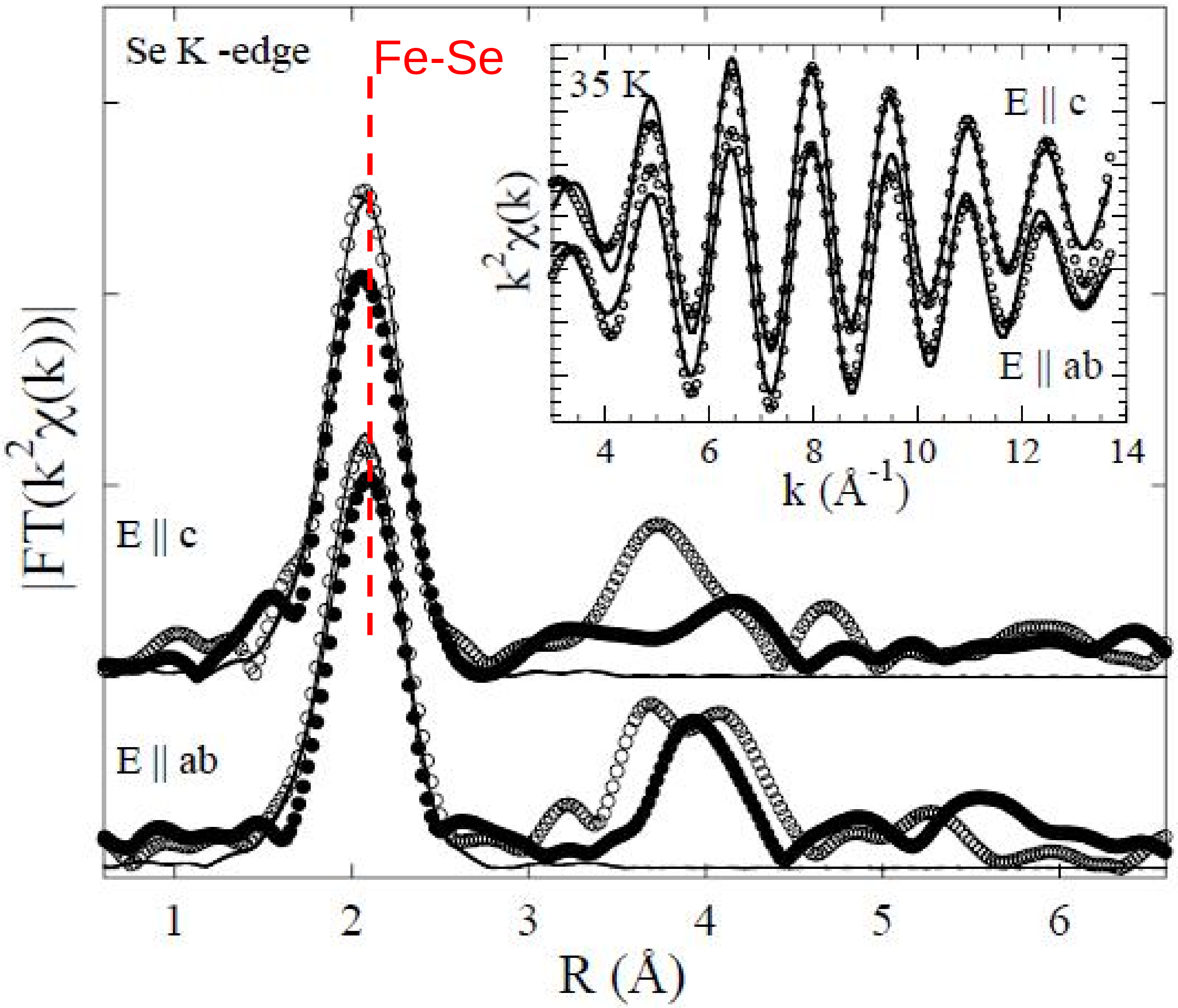
While these differences in the local structure look negligible,

They are very important in the electronic and magnetic properties!!!

Polarized EXAFS on $FeSe_{0.25}Te_{0.75}$ single crystal



The crystallographic Se site in the $FeSe_{0.25}Te_{0.75}$ has 4 nearest-neighbours Fe atoms at ~2.5 Å

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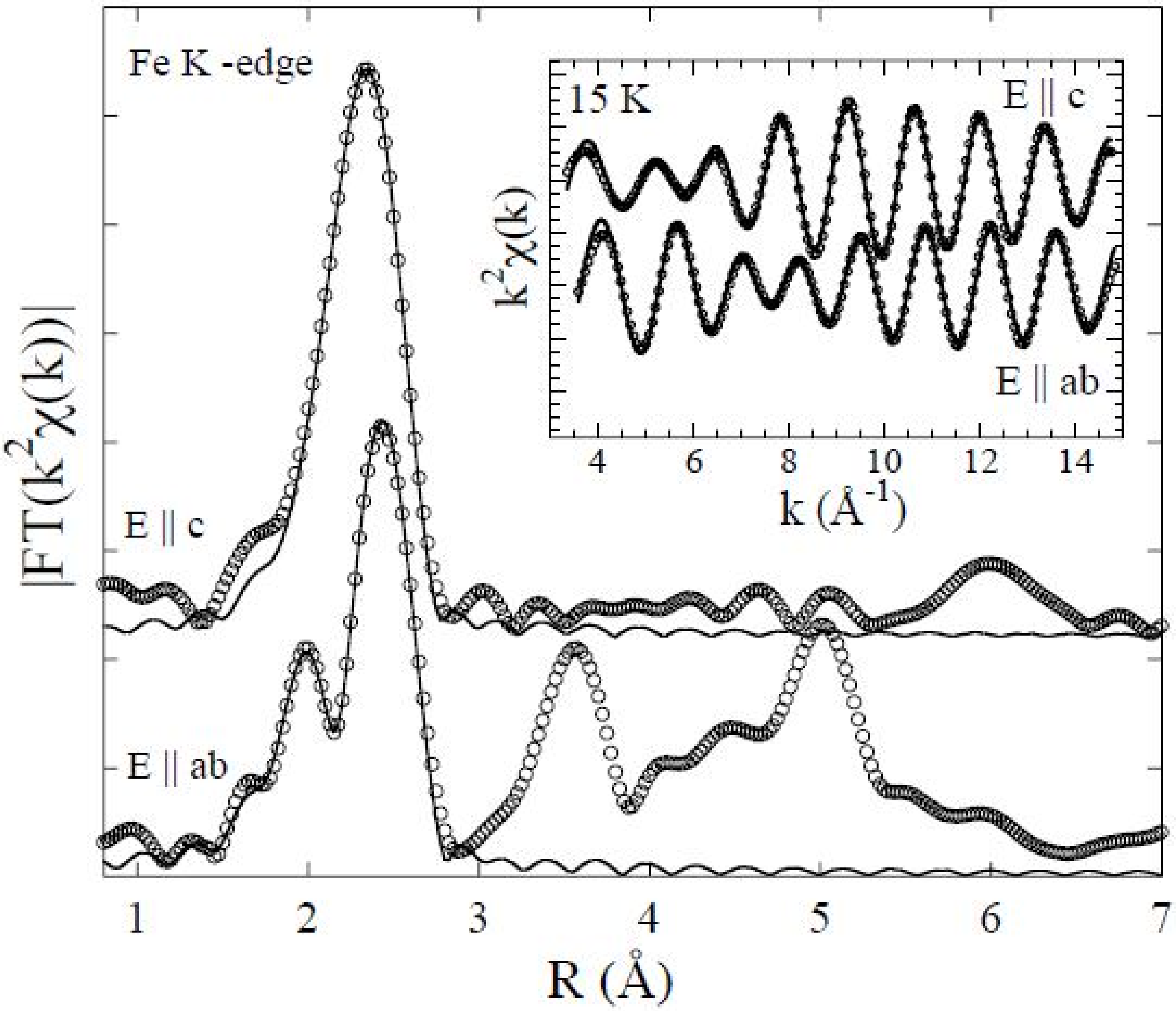
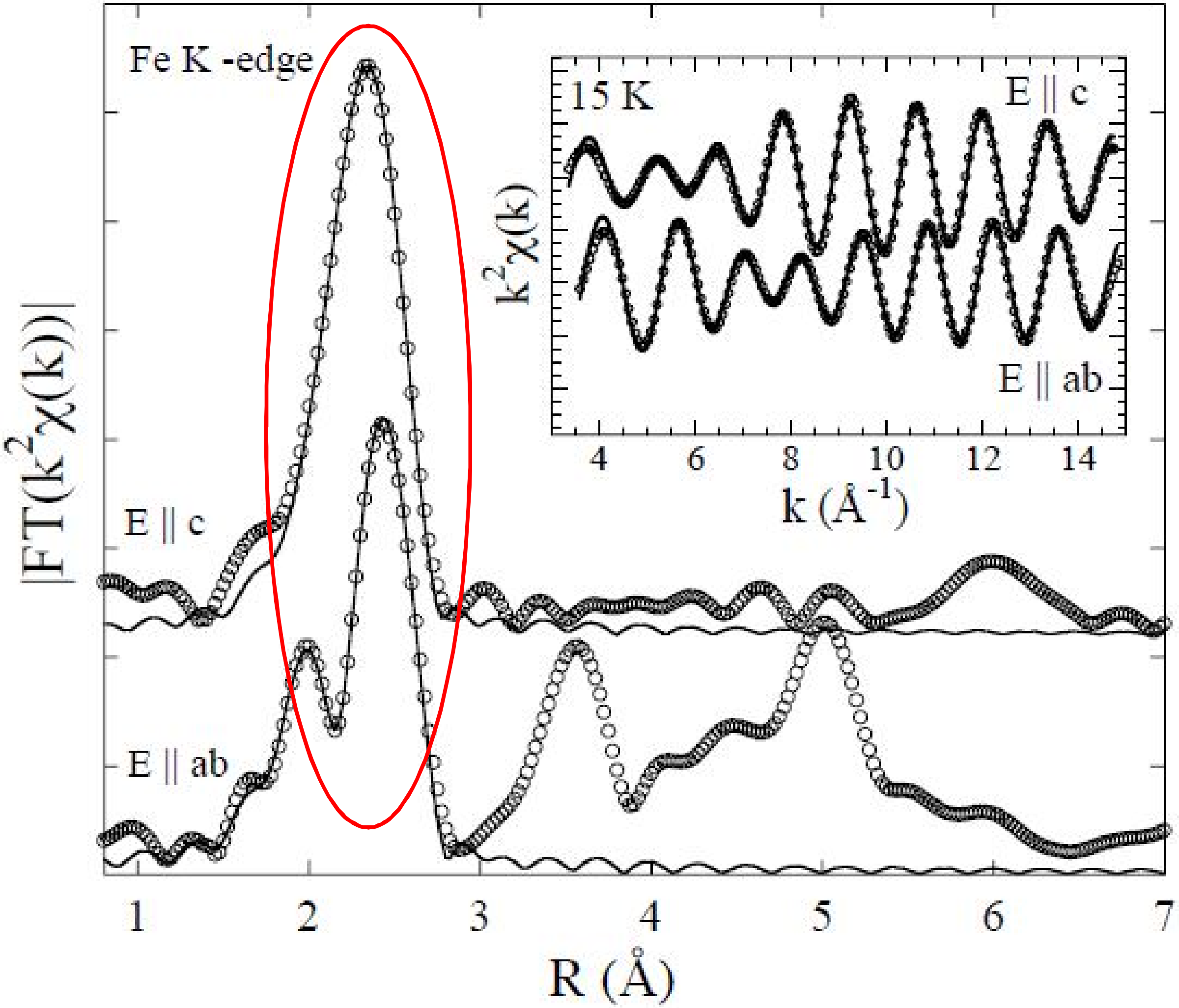


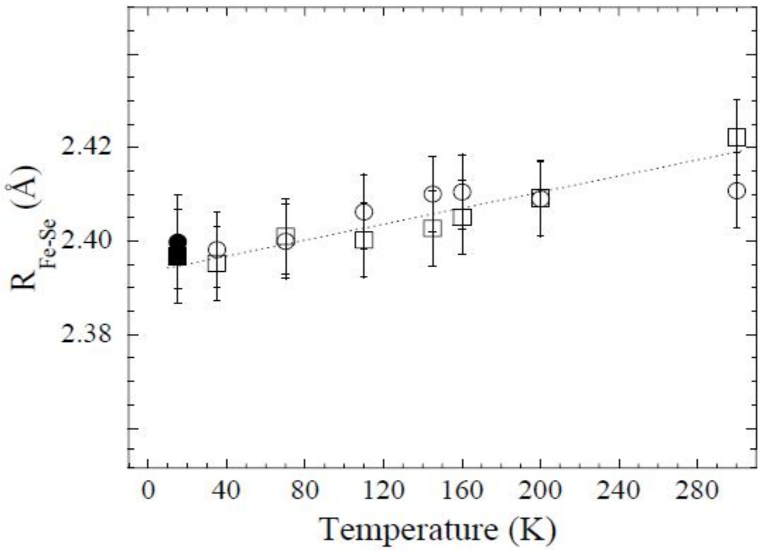
The crystallographic Fe site in the $FeSe_{0.25}Te_{0.75}$ has 4 nearest-neighbours Se/Te atoms at ~2.5 Å and the next 4 Fe atoms at ~2.7 Å in the E||ab polarization

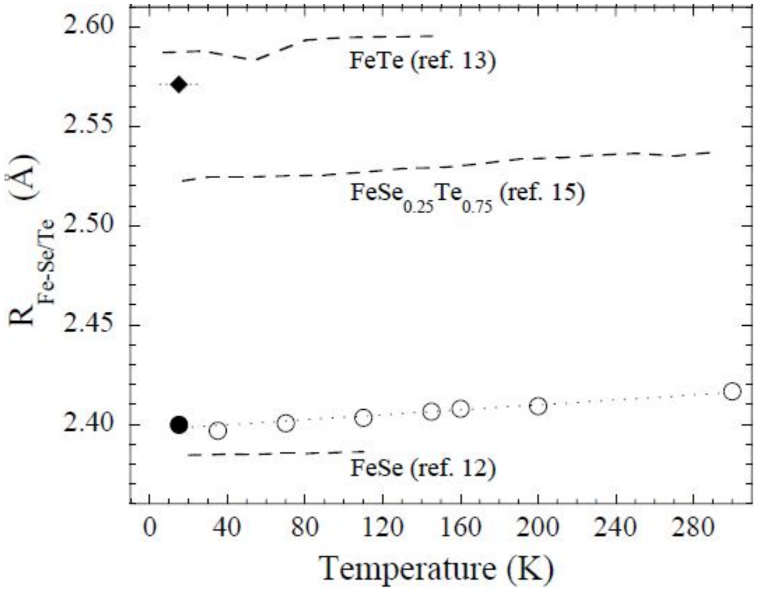
Polarized EXAFS on $FeSe_{0.25}Te_{0.75}$ single crystal



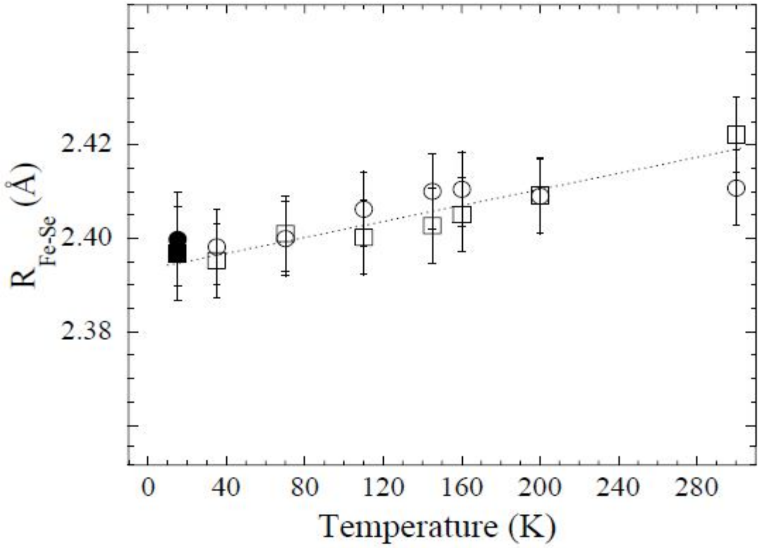
The crystallographic Fe site in the $FeSe_{0.25}Te_{0.75}$ has 4 nearest-neighbours Se/Te atoms at ~2.5 Å and the next 4 Fe atoms at ~2.7 Å in the E||ab polarization with **the Fe-Fe contribution being masked in the E||c geometry**.

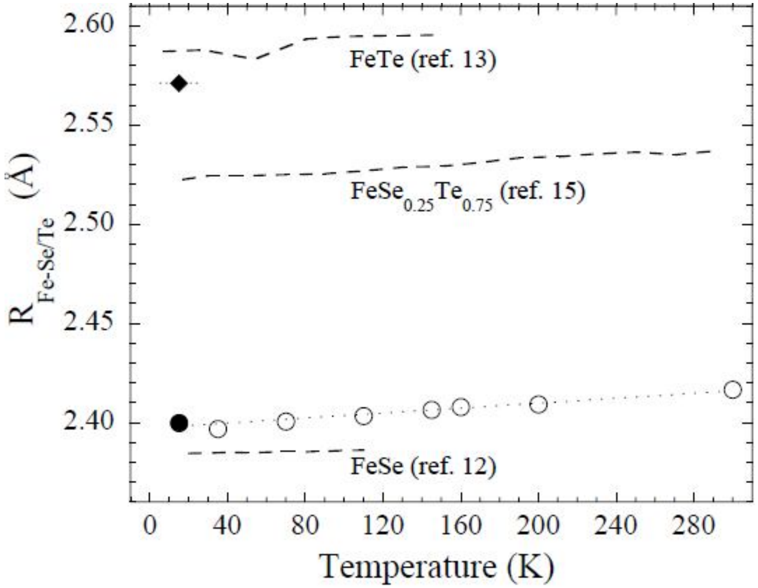
Results from polarized EXAFS on $FeSe_{0.25}Te_{0.75}$ single crystal

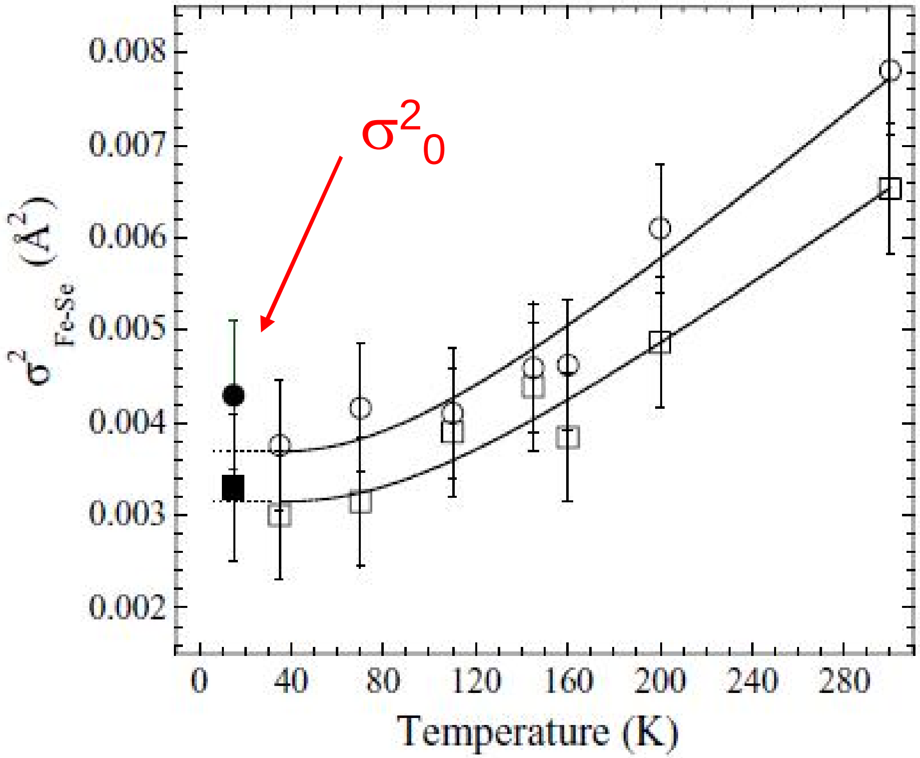




Results from polarized EXAFS on $FeSe_{0.25}Te_{0.75}$ single crystal



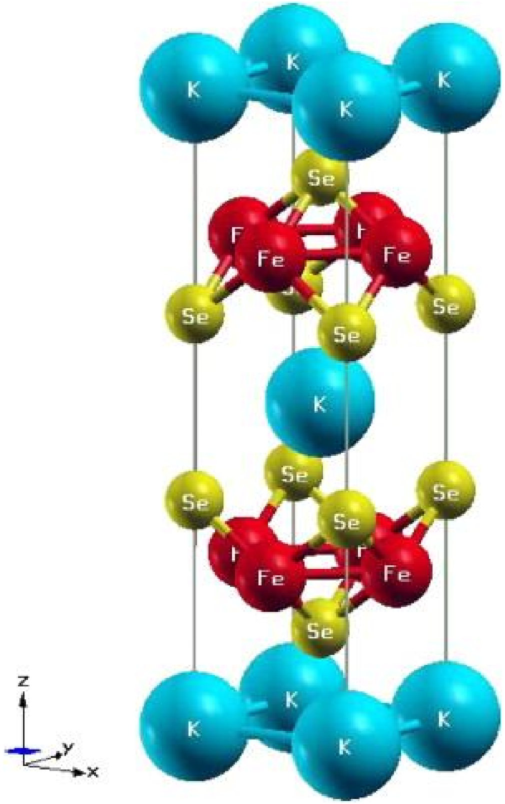




Similar trends of DWFs
but
different static disorder

Polarized EXAFS on $K_{0.8}Fe_{1.6}Se_2$

Crystal structure is very similat to $FeSe_{0.88}$



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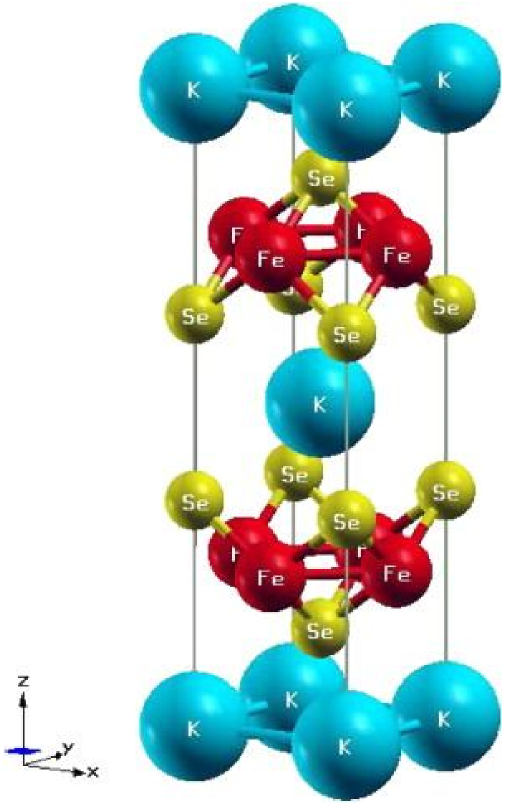

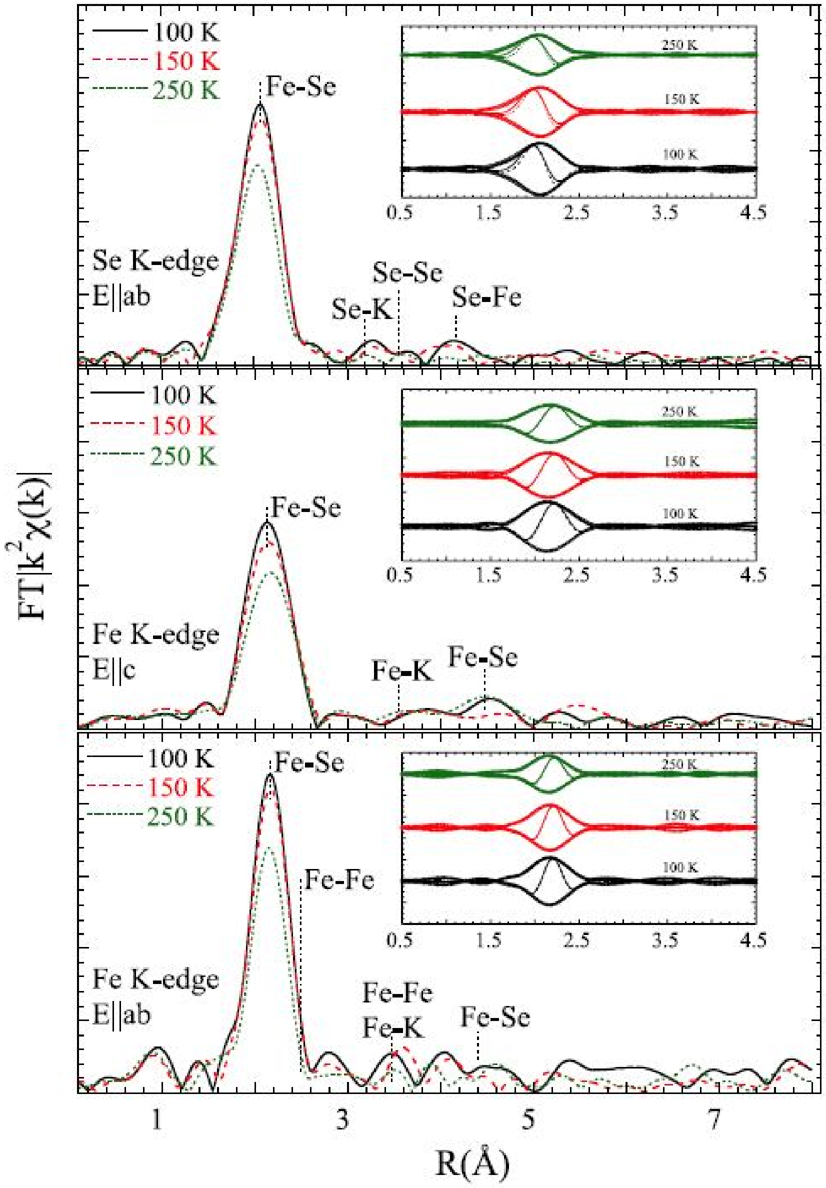

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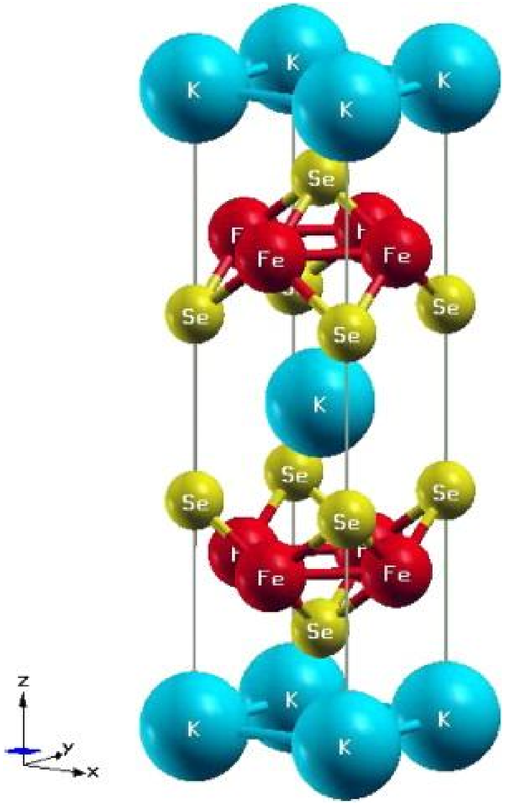
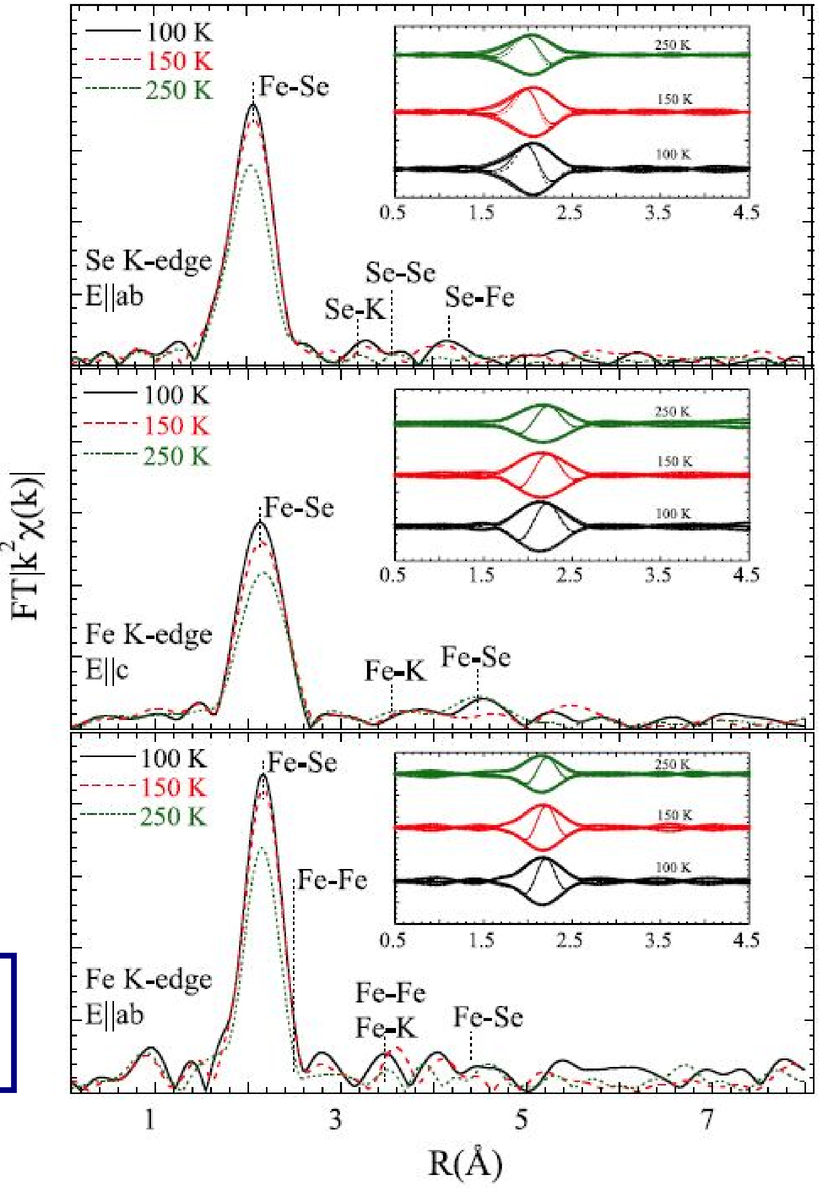
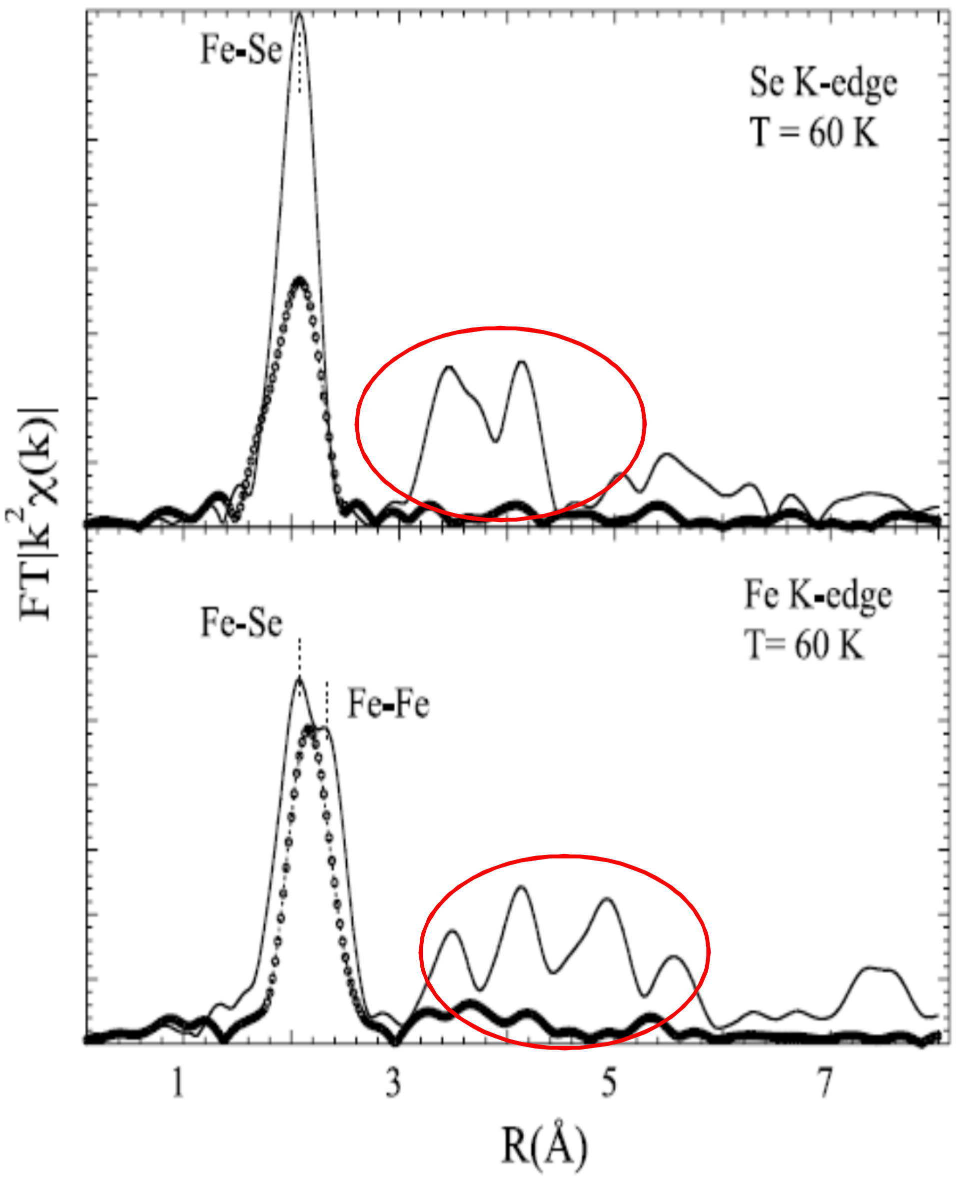




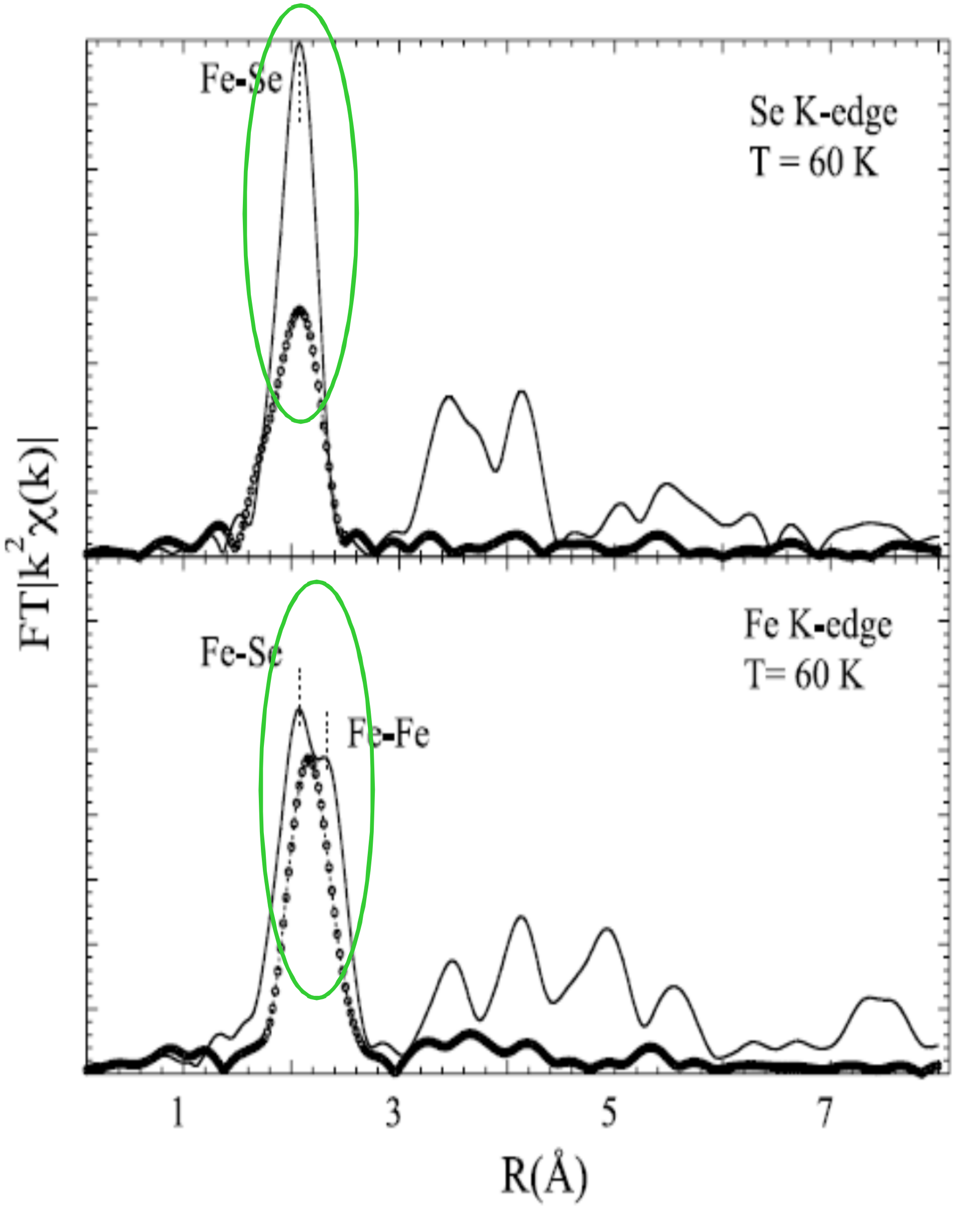
Contribution expected from farther atoms is apparently absent

A comparision with the FeSe system



Longer distance contributions absent

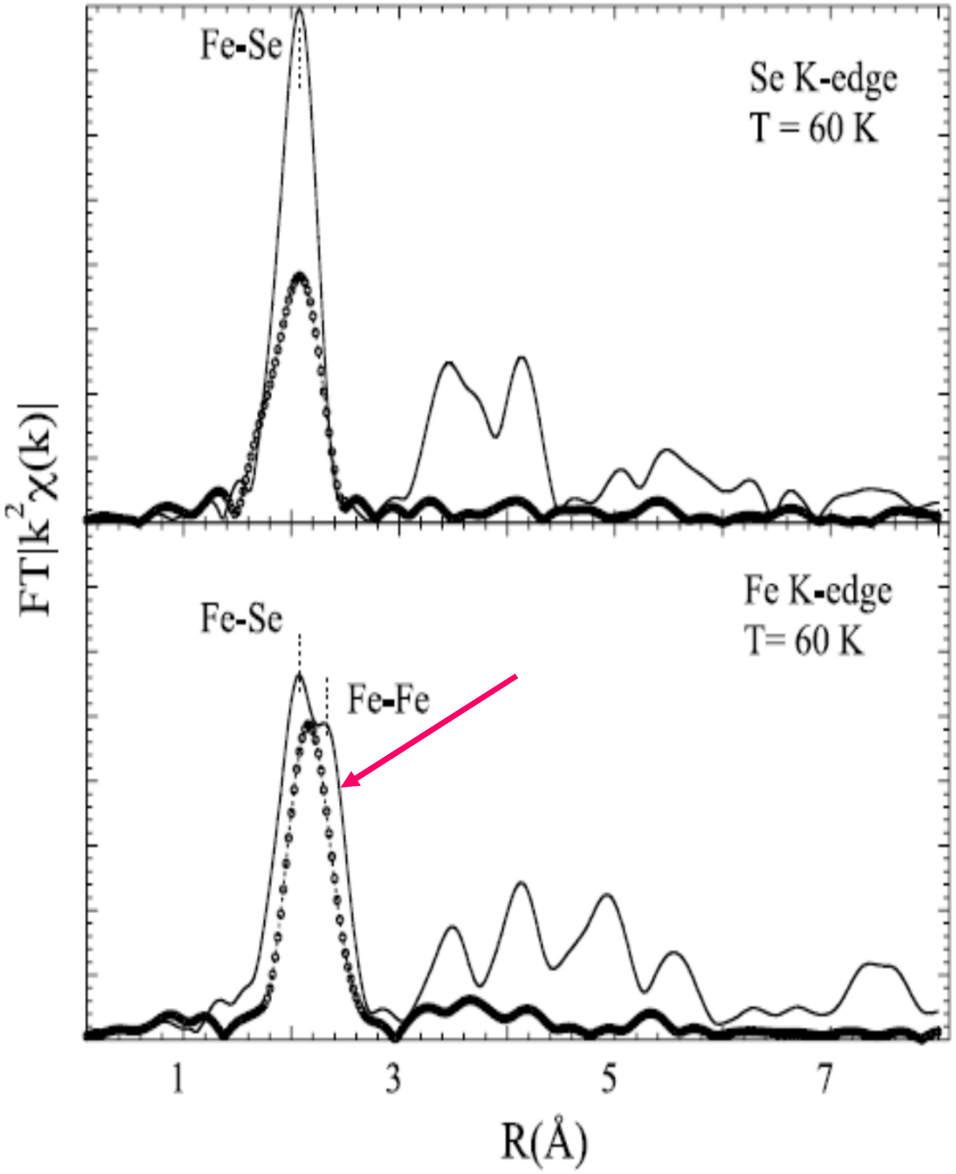
A comparision with the FeSe system



Longer distance contributions absent

FT magnitude damped

A comparision with the FeSe system



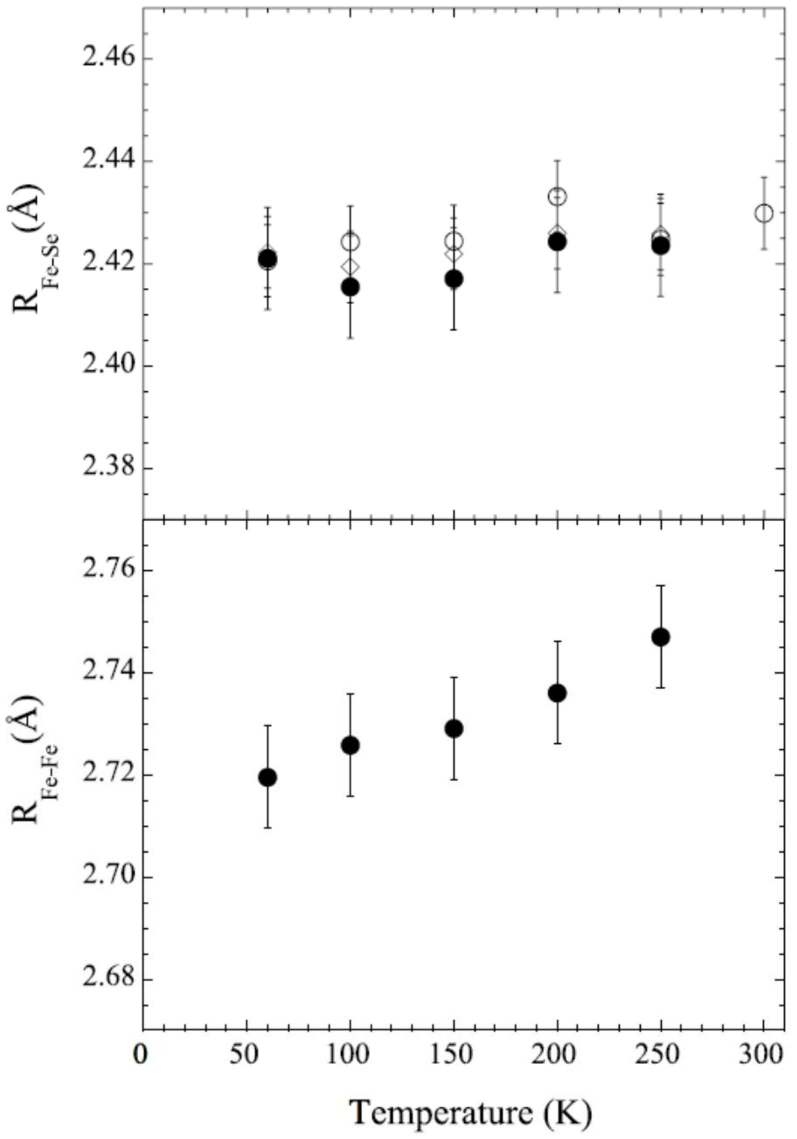
Longer distance contributions absent

FT magnitude damped

Contribution due to Fe-Fe distance damped

Large disorder

Results from polarized EXAFS on $K_{0.8}Fe_{1.6}Se_2$

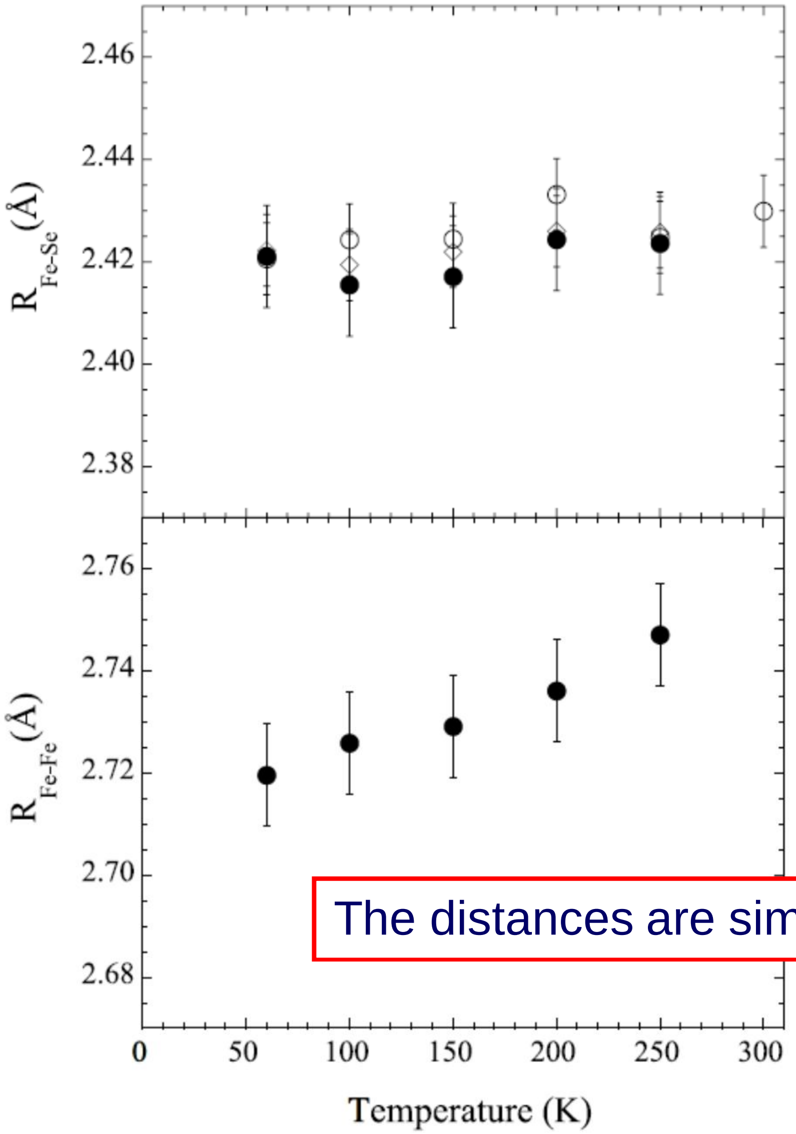


- ✓Distances obtained from EXAFS slightly shorter than the average bondlenghts

- ✓Fe-Se bondlenght not affected by temperature

- ✓Fe-Fe distance varies with temperature.

Results from polarized EXAFS on $K_{0.8}Fe_{1.6}Se_2$



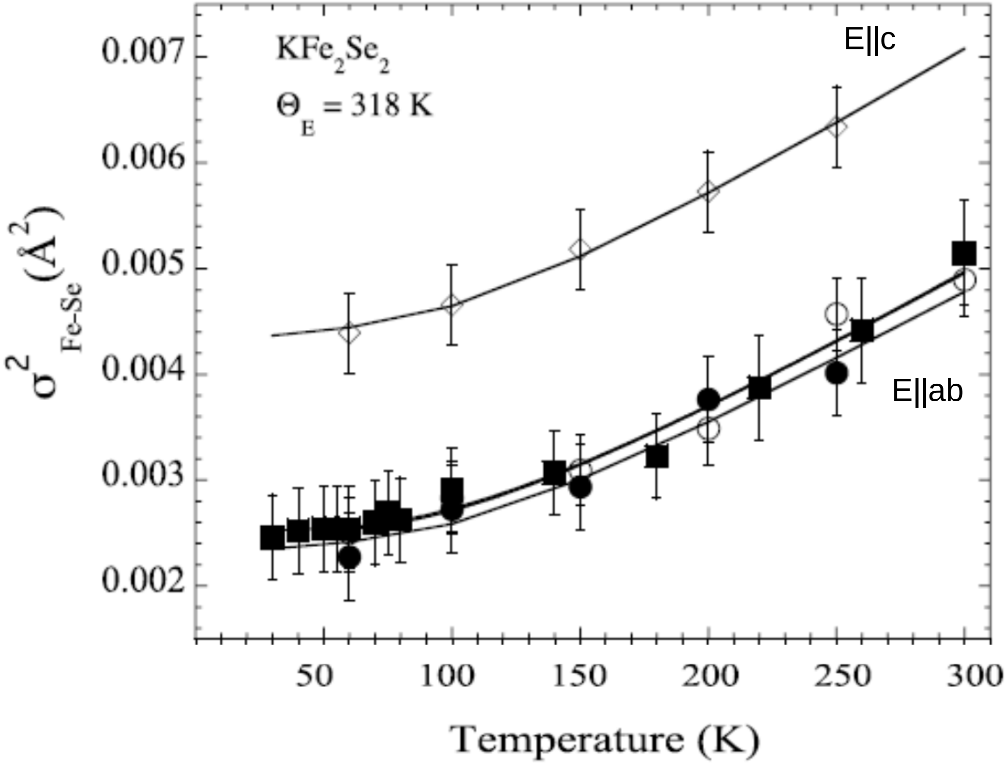
✓Distances obtained from EXAFS slightly shorter than the average bondlenghts

✓Fe-Se bondlenght not affected by temperature

✓Fe-Fe distance varies with temperature.

The distances are similar to that ones obtained on $FeSe_{0.88}$

The Debye-Waller Factors of Fe-Se bond



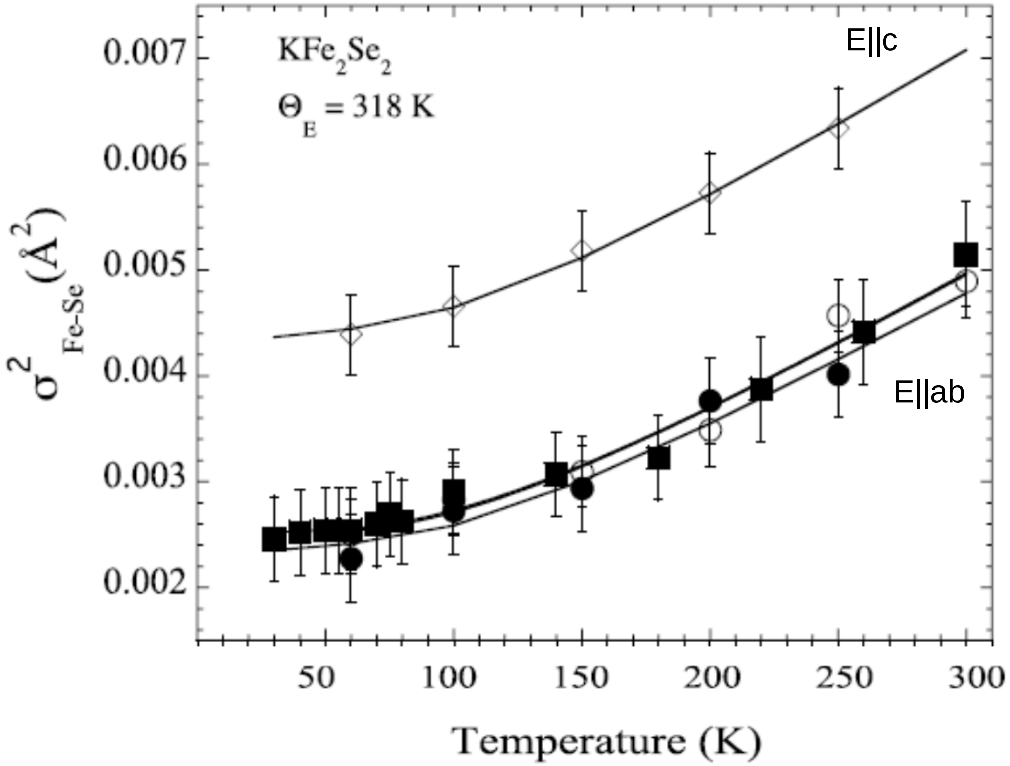
$$\sigma^2 = \sigma_0^2 + \sigma^2(T)$$

$$\sigma_0^2(E \parallel ab) \approx 0.0002$$

$$\sigma_0^2(E \parallel c) \approx 0.002$$

Large disorder along *c* direction due to K-intercalation

The Debye-Waller Factors of Fe-Se bond



$$\sigma^2 = \sigma_0^2 + \sigma^2(T)$$

$$\sigma_0^2(E \parallel ab) \approx 0.0002$$

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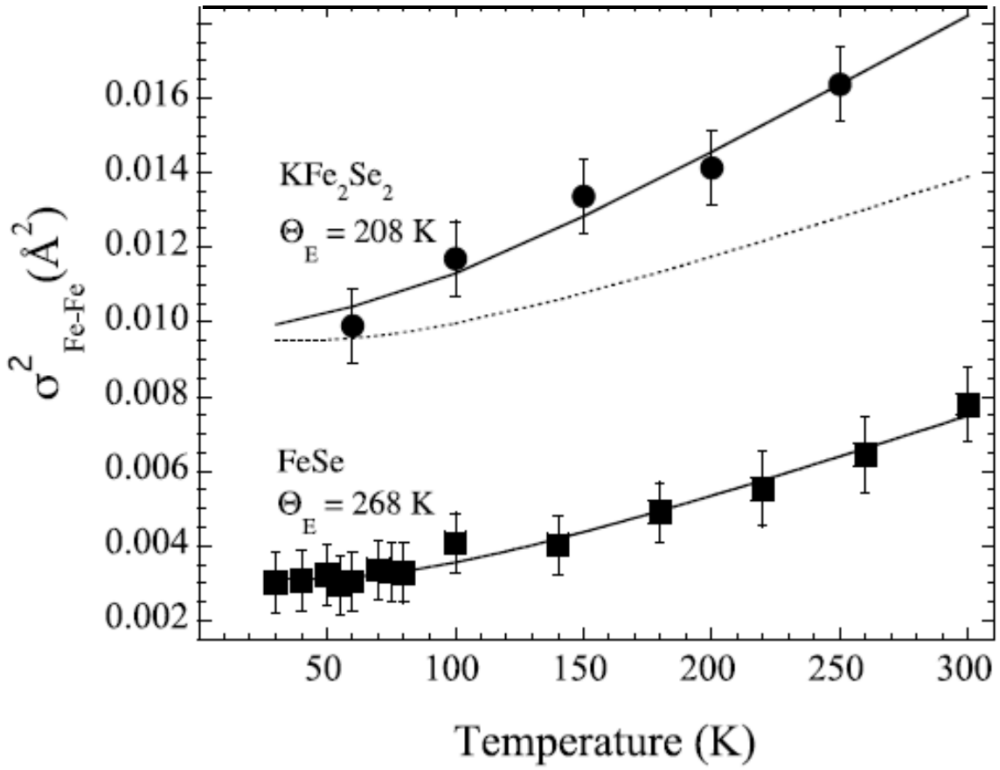
Large disorder along *c* direction due to K-intercalation

Considering the correlated Einstein model

$$\boxed{\sigma^2{}_{Se-Fe} = \frac{\hbar^2}{2\mu k_B \theta_E}\coth(\frac{\theta_E}{2T})} \longrightarrow \begin{array}{l} \theta_E \approx 318K \\ k \approx 5.8\, eVA^{-2} \end{array}$$

The Debye-Waller Factors of Fe-Fe bond



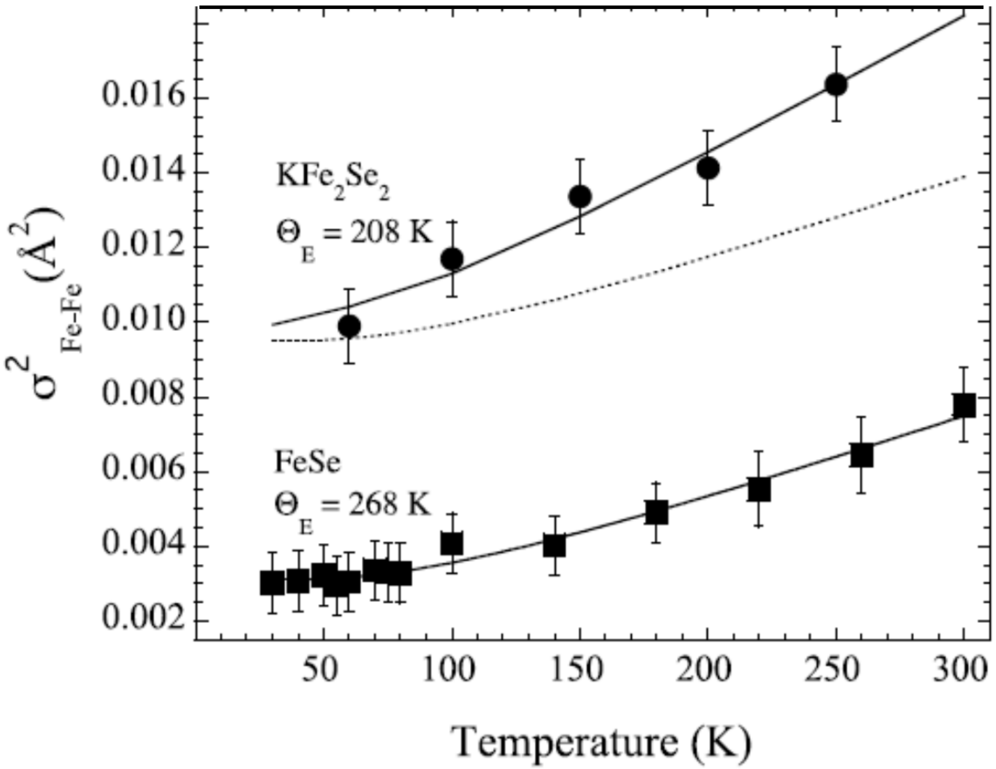
$$\sigma^2 = \sigma_0^2 + \sigma^2(T)$$

$$\sigma_0^2(KFeSe) \approx 0.006$$

$$\sigma_0^2(FeSe) \approx 0.0002$$

Disorder due to Fe vacancies

The Debye-Waller Factors of Fe-Fe bond



$$\sigma^2 = \sigma_0^2 + \sigma^2(T)$$

$$\sigma_0^2(KFeSe) \approx 0.006$$

$$\sigma_0^2(FeSe) \approx 0.0002$$

Disorder due to Fe vacancies

Fe-Fe bond relatively relaxed in KFeSe

$$\theta_E(KFeSe) \approx 208K \qquad k(KFeSe) \approx 2.1\, eVA^{-2}$$

$$\theta_E(FeSe) \approx 268K \qquad k(FeSe) \approx 3.5\, eVA^{-2}$$

Outline

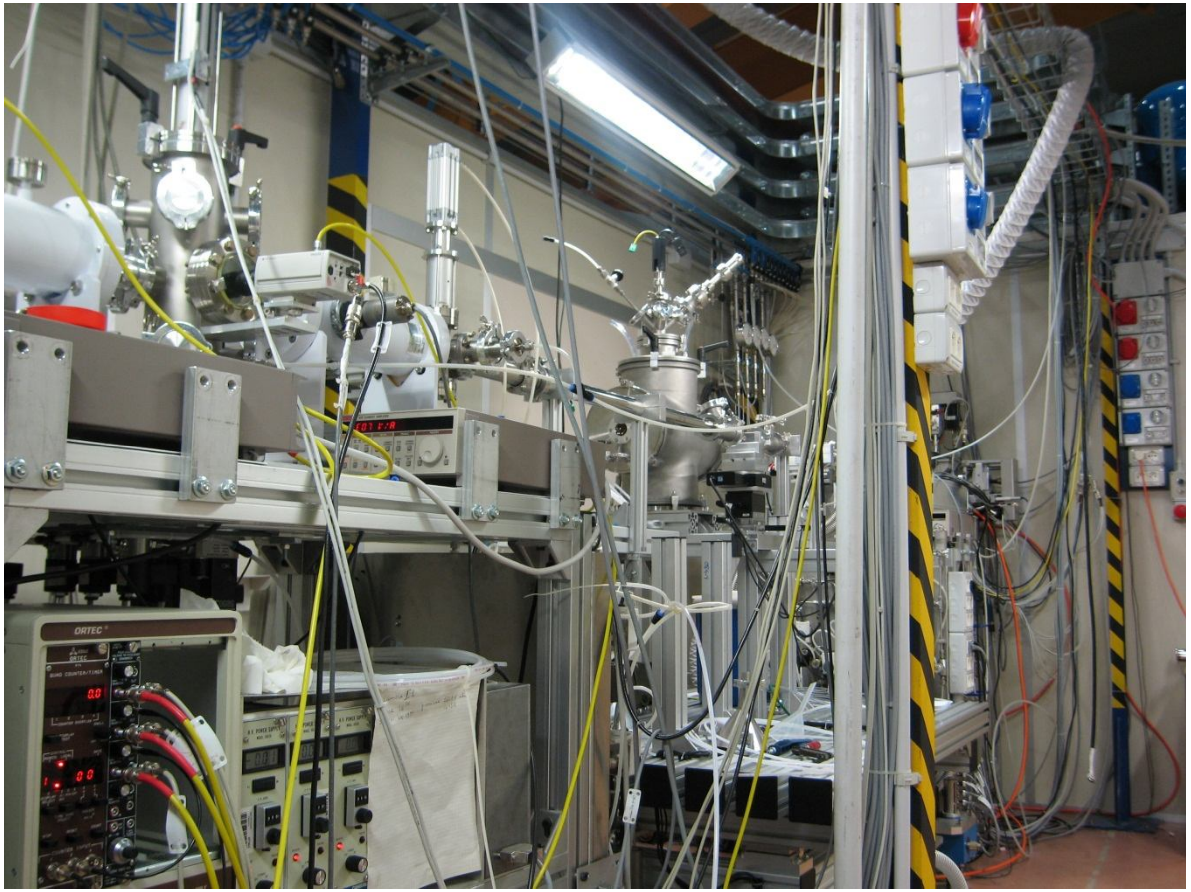
- Overview on the Fe based-system
- X-ray absorption spectroscopy
- Applications
- Conclusions

Conclusions

- Crystallographic structure is not enough to explain the functional properties of some systems

- The EXAFS allows to obtain informations on:
  - Bond distortion (distances)
  - The bond fluctuations (thermal DWF)
  - The intrinsic disorder (σ^2_0)
  - Anisotropy of the system (polarized EXAFS)

Thank you for attention!



See you at the XAFS beamline
from 22th to 24th April