WINTER SCHOOL OF SYNCHROTRON RADIATION

31.01. – 04.02. 2011 Liptovský Ján, Slovakia

Š. Michalik: X-ray Diffraction and X-ray Absorption Spectroscopy in the Study of Materials with Disordered Structure

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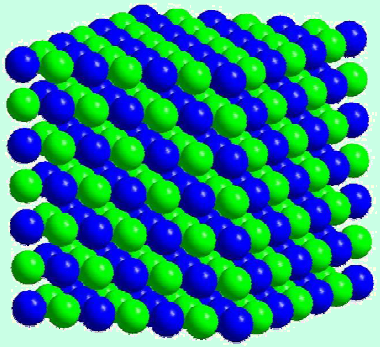
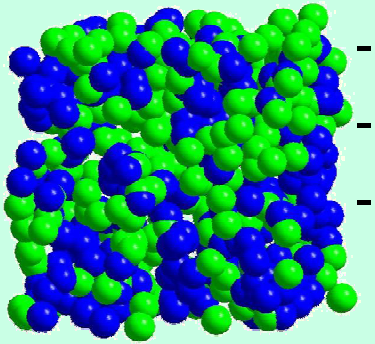
Materials with Disordered Structure

Ordered (crystalline) structure



- periodic structure
- long range order
- symmetry

Disordered (amorphous) structure



- no periodicity
- short range order
- no symmetry

Real life example

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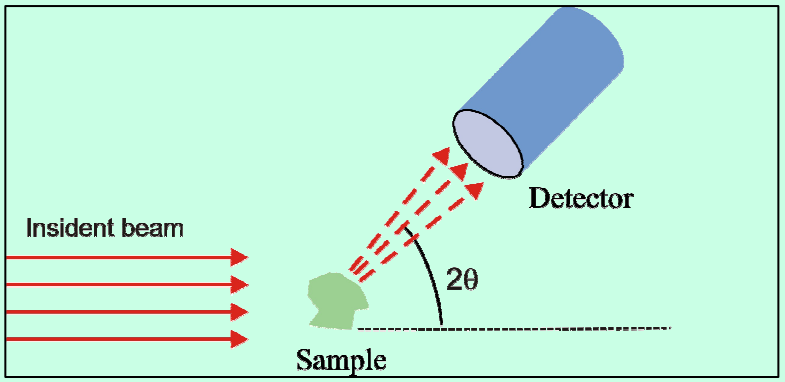
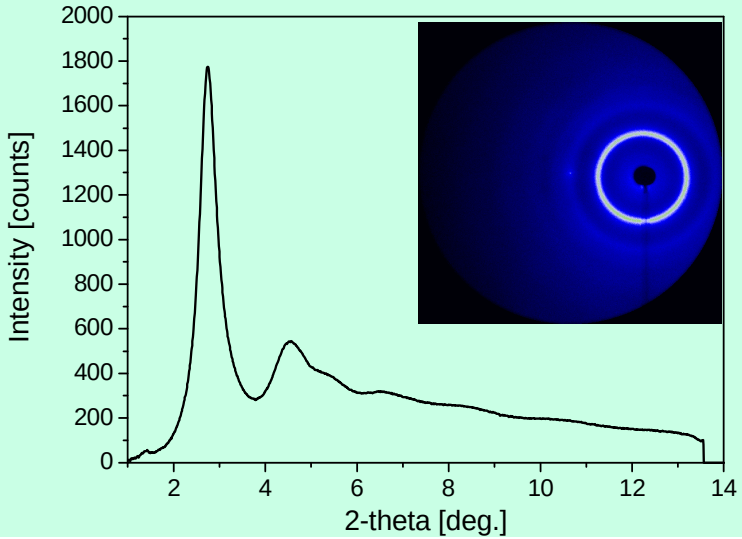
X-ray diffraction experiments



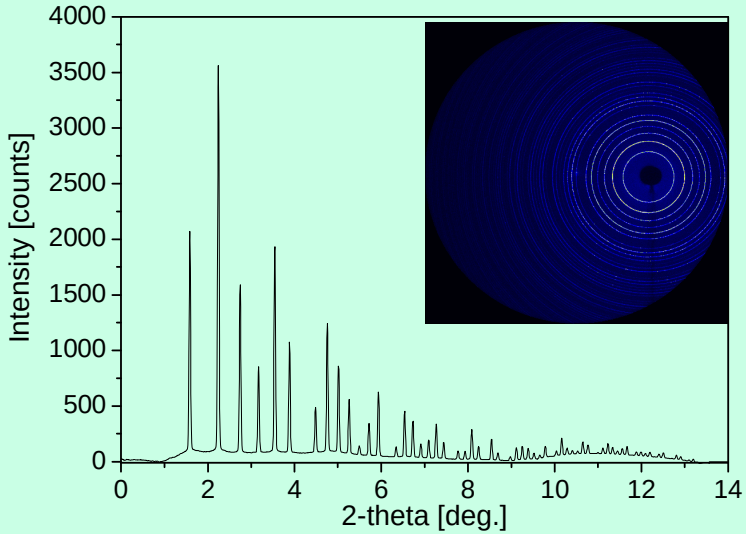
The main idea is to measure the variation in scattered intensity due to interference effects as a function of the (diffracted) angle

$$Q = \frac{4\pi}{\lambda}\sin(\theta)$$ - a ***wave transfer vector***

Amorphous material

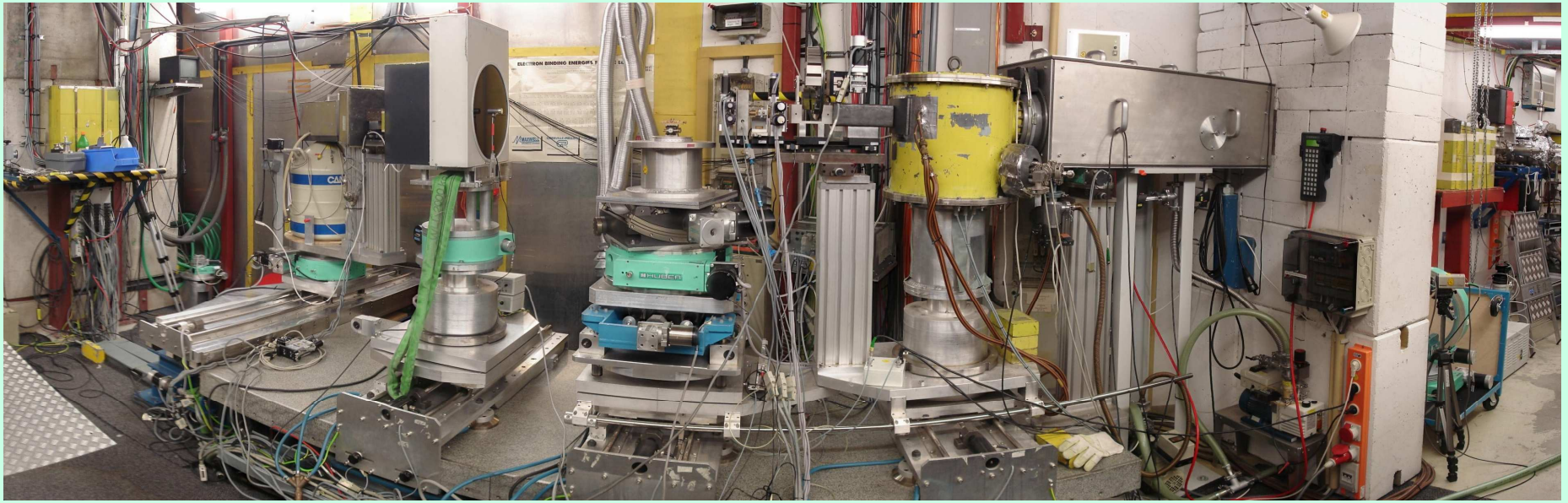


Crystalline material



Experimental station BW5

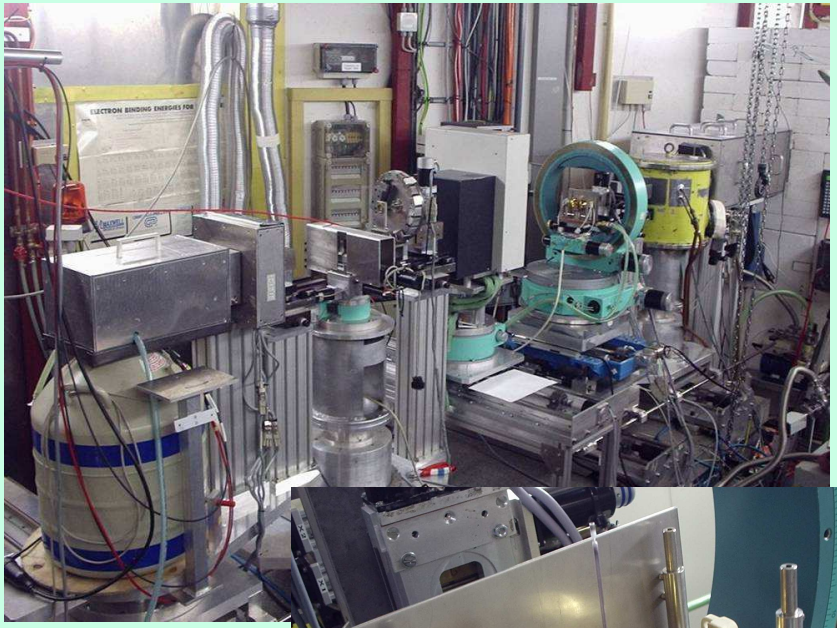
BW5 is dedicated to X-ray scattering experiments at energies between 60 and 150 keV.

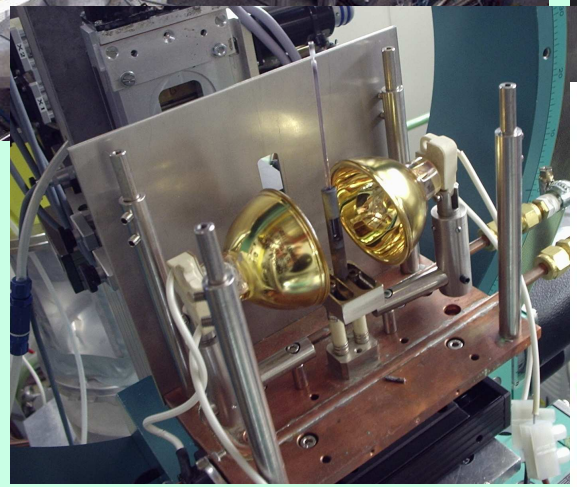


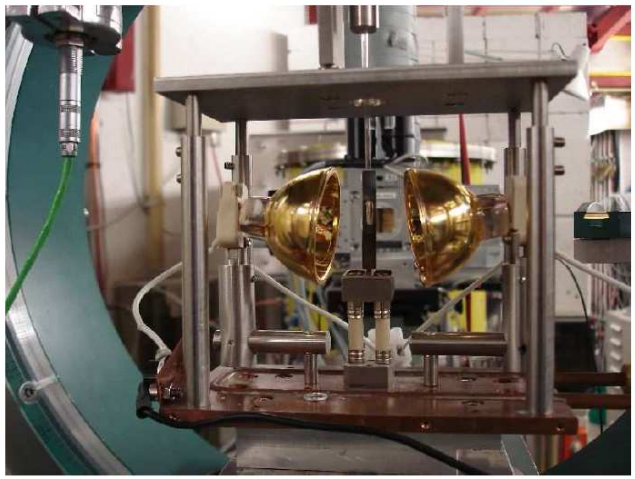
Present applications are:

- charge density studies of single crystals
- structural phase transitions
- *analysis of the pair distribution function of amorphous material and liquids*
- texture analysis of powder materials

Experimental station BW5







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Photon energy, wavelength and penetration depth

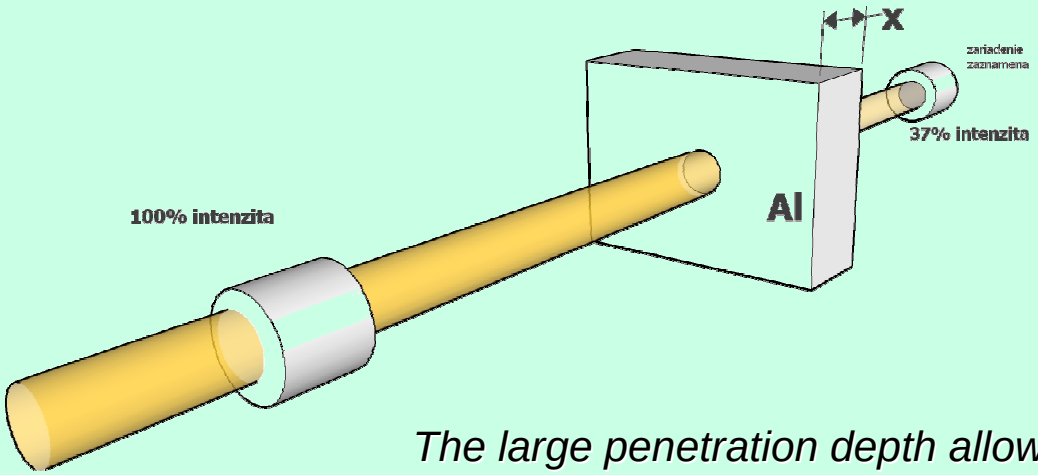
$$\lambda[\mathring{A}] = \frac{hc}{\varepsilon} = \frac{12.398}{\varepsilon[keV]}$$

200 eV = 62 Å *soft x-rays*

8.05 keV = 1.54 Å standard x-ray *Cu lamp*

100 keV = 0.124 Å *hard x-rays*

Å = 10^{-10} m
eV = 1.602×10^{-19} J

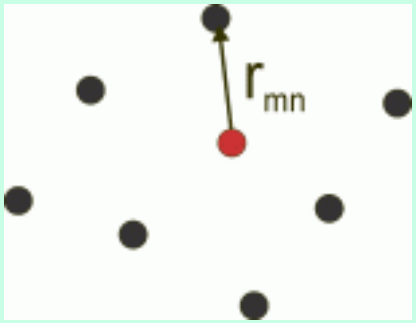


200 eV	x = 0.1 µm
9 keV	x = 0.103 mm
100 keV	x = 2.2 cm !!!

The large penetration depth allows the investigation of bulk materials and complex sample environments.

Theory of diffraction on disordered materials

The scheme of amorphous alloys



$$I(\mathbf{Q}) = \sum_{m}^{N} f_m(\mathbf{Q}) e^{i\mathbf{Q}\cdot\mathbf{r}_m} \sum_{n}^{N} f_n(\mathbf{Q}) e^{-i\mathbf{Q}\cdot\mathbf{r}_n}$$

$$S(Q) \equiv \frac{I(Q)/N - f^2(Q)}{f^2(Q)} = 1 + \int_0^\infty \underbrace{4\pi r[\rho(r) - \rho_0]}_{D(r)} \frac{\sin(Qr)}{Q} dr$$

where $\rho(r)$ and ρ_0 are the local and average atomic number densities. $D(r)$ – the reduced pair distribution function

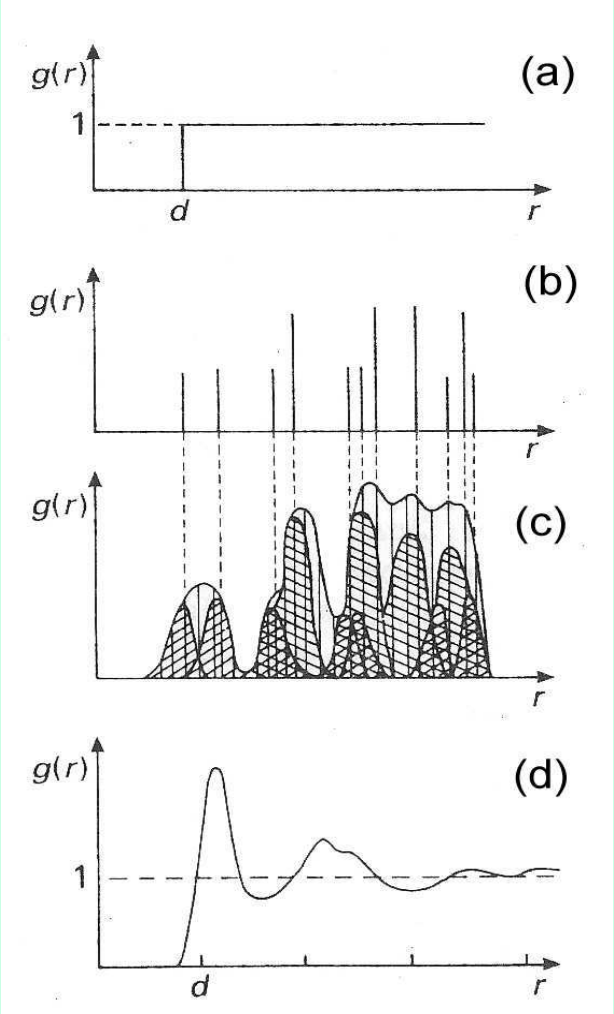
Fourier transformation

$$S(Q) = \int_0^\infty D(r) \frac{\sin(Qr)}{Q} dr$$

$$D(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ$$

*We are able **directly** to perform the real space analysis (in the space of interatomic distances)*

Pair distribution functions



gas

ideal crystal

real crystal

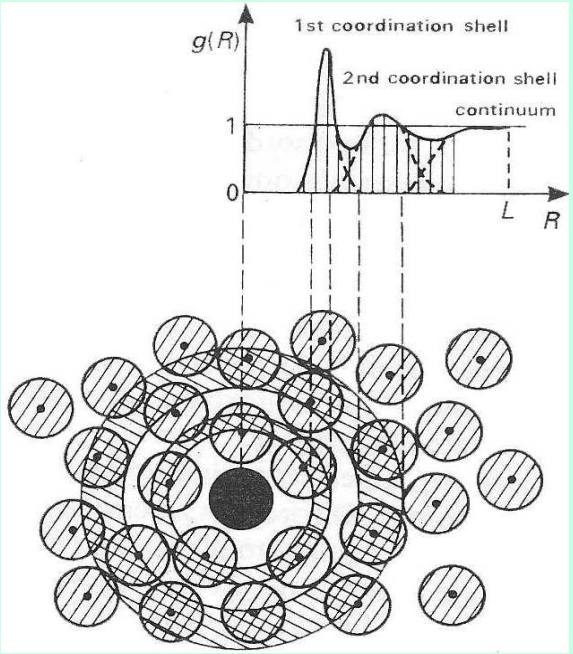
amorphous alloy

The reduced distribution function D(r)

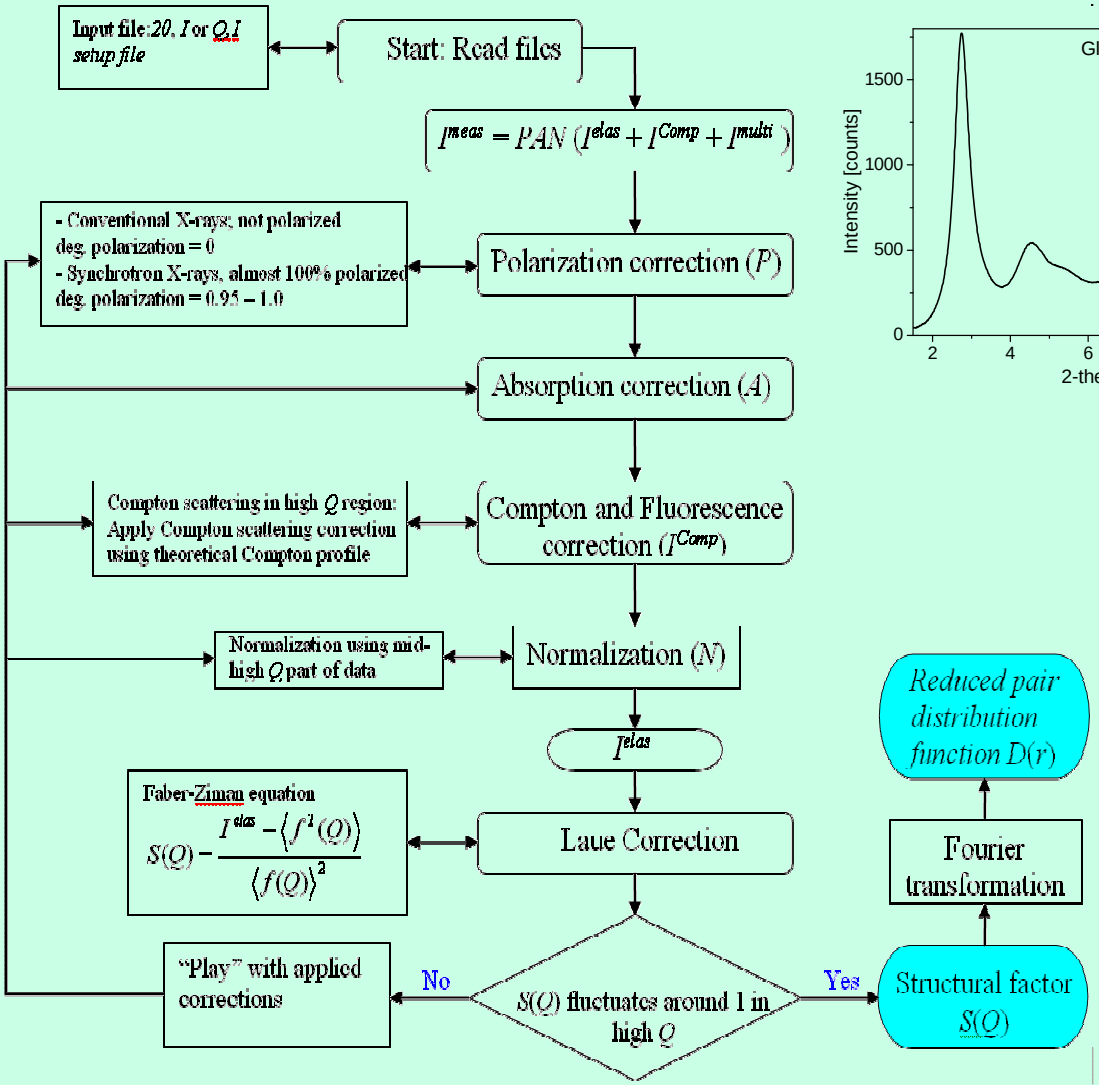
$$D(r) = 4\pi r[\rho(r) - \rho_0]$$

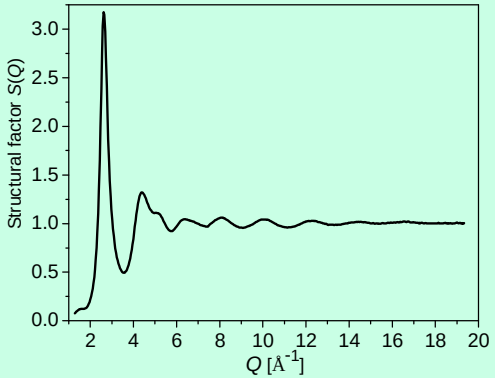
The atomic pair distribution function g(r)

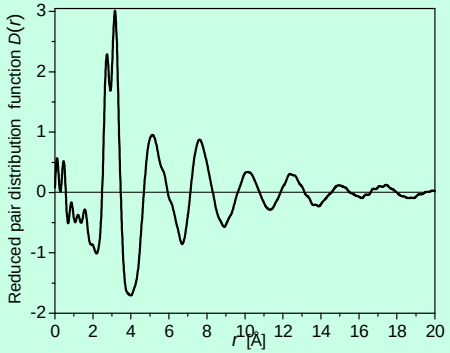
$$g(r) = \rho(r) / \rho_0$$



The structural factor extraction





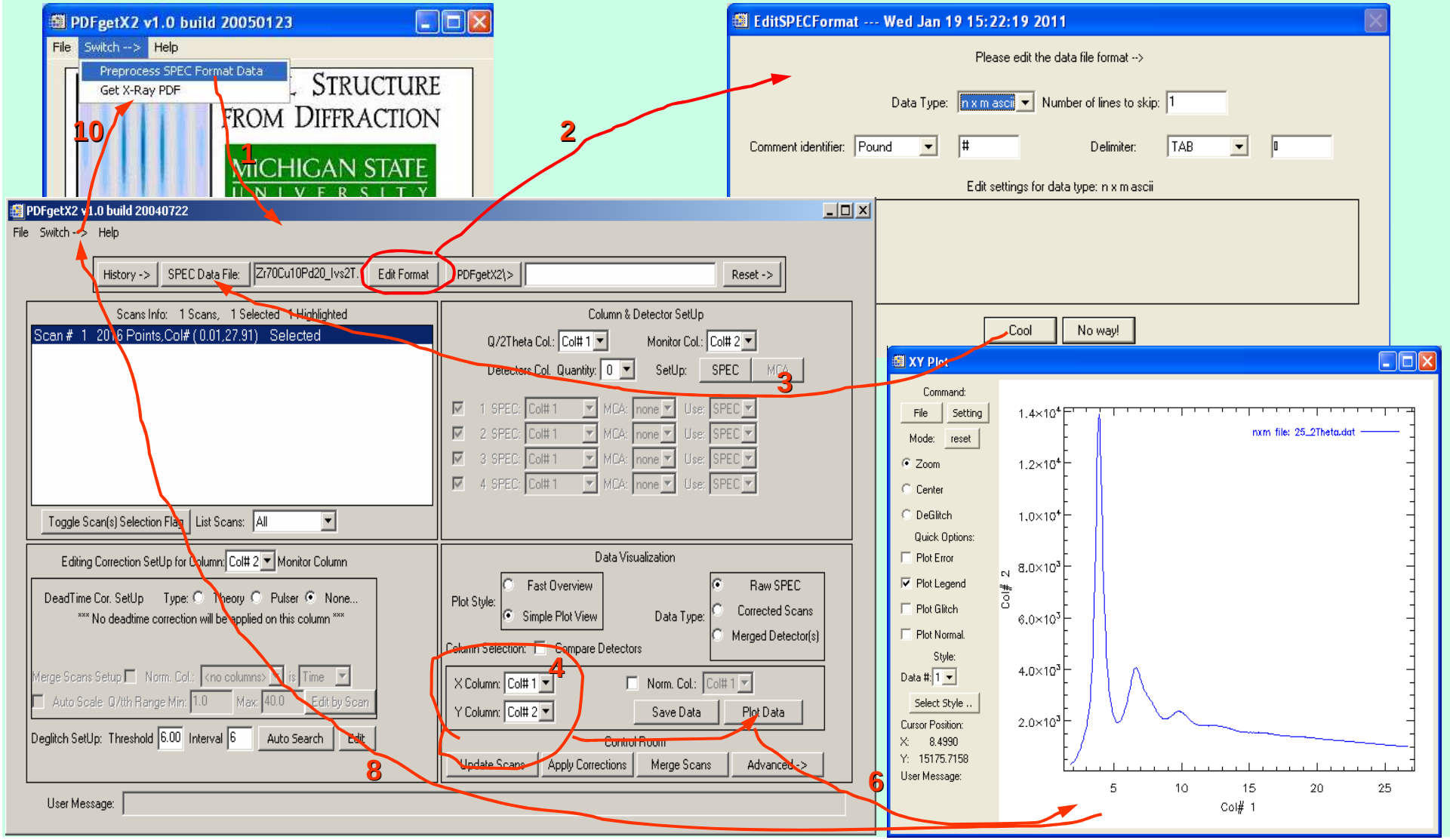


How to do it?

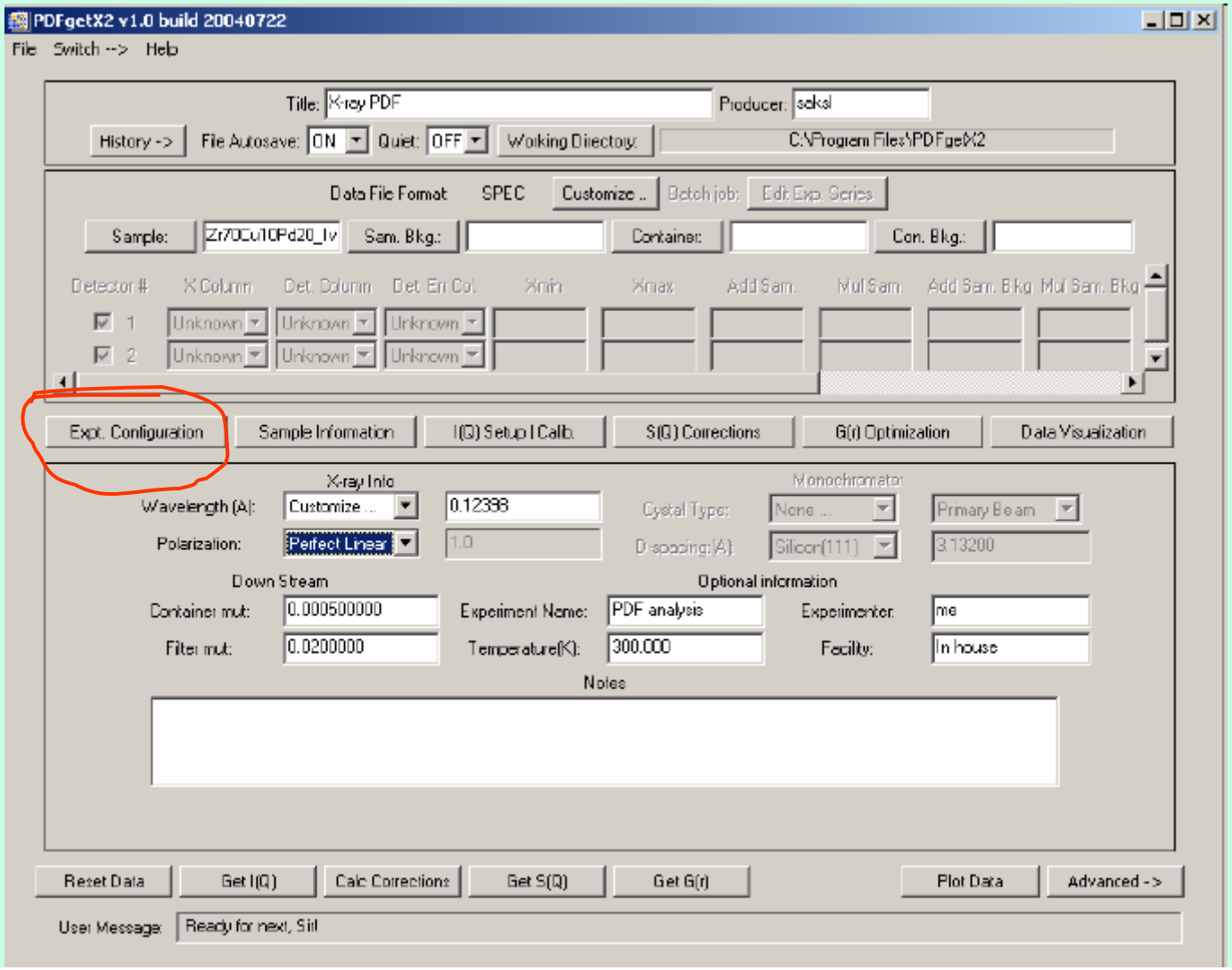
Software PDFGetX2

http://www.pa.msu.edu/cmp/billinge-group/programs/PDFgetX2/

Preprocess a data file



Setup an exp. configuration



Define wavelength and polarization.

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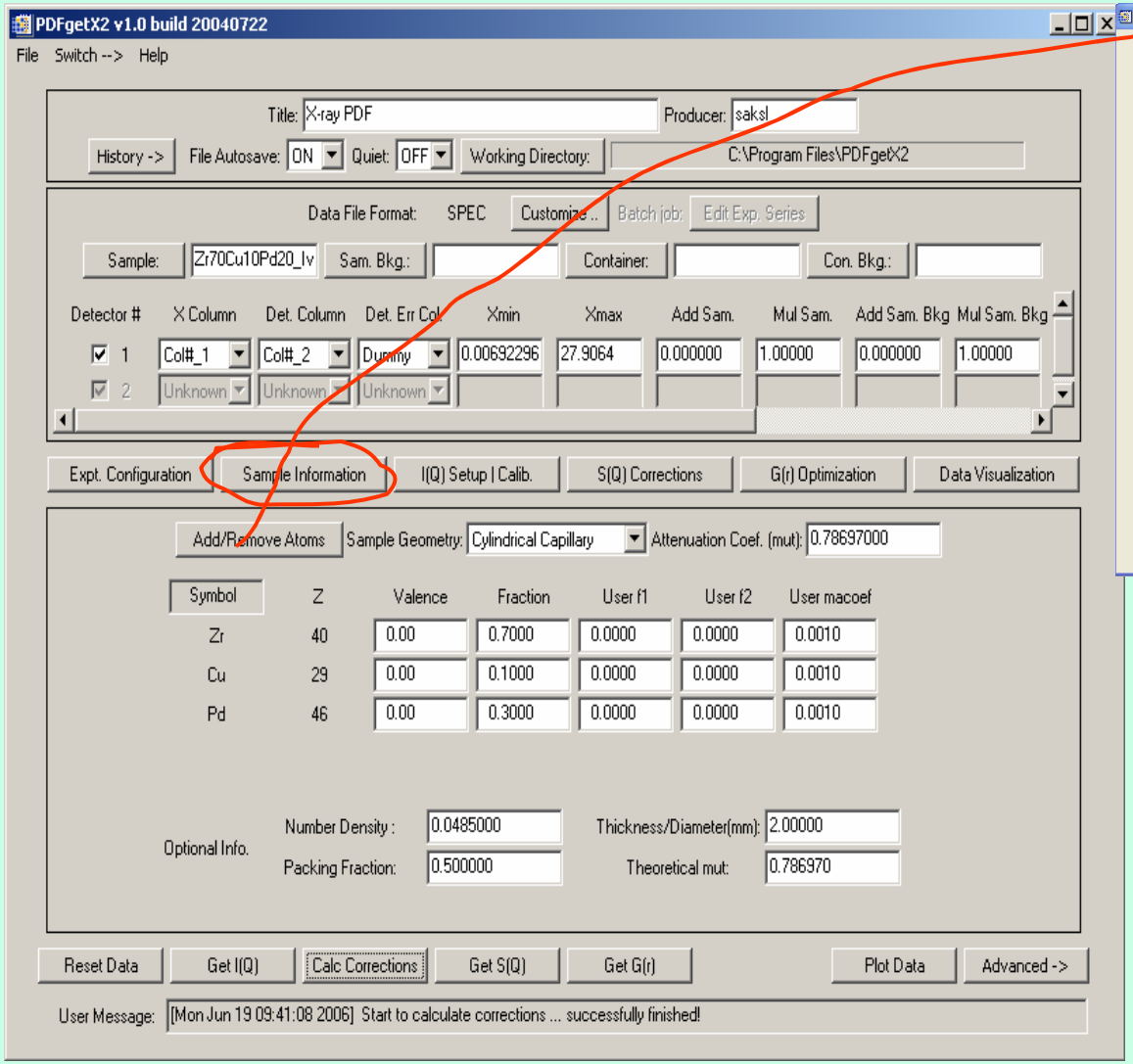
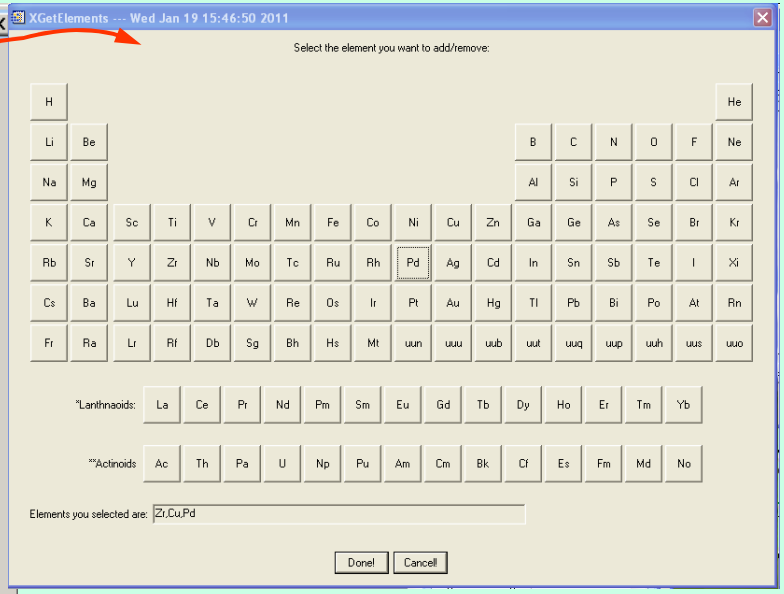
Setup the sample information



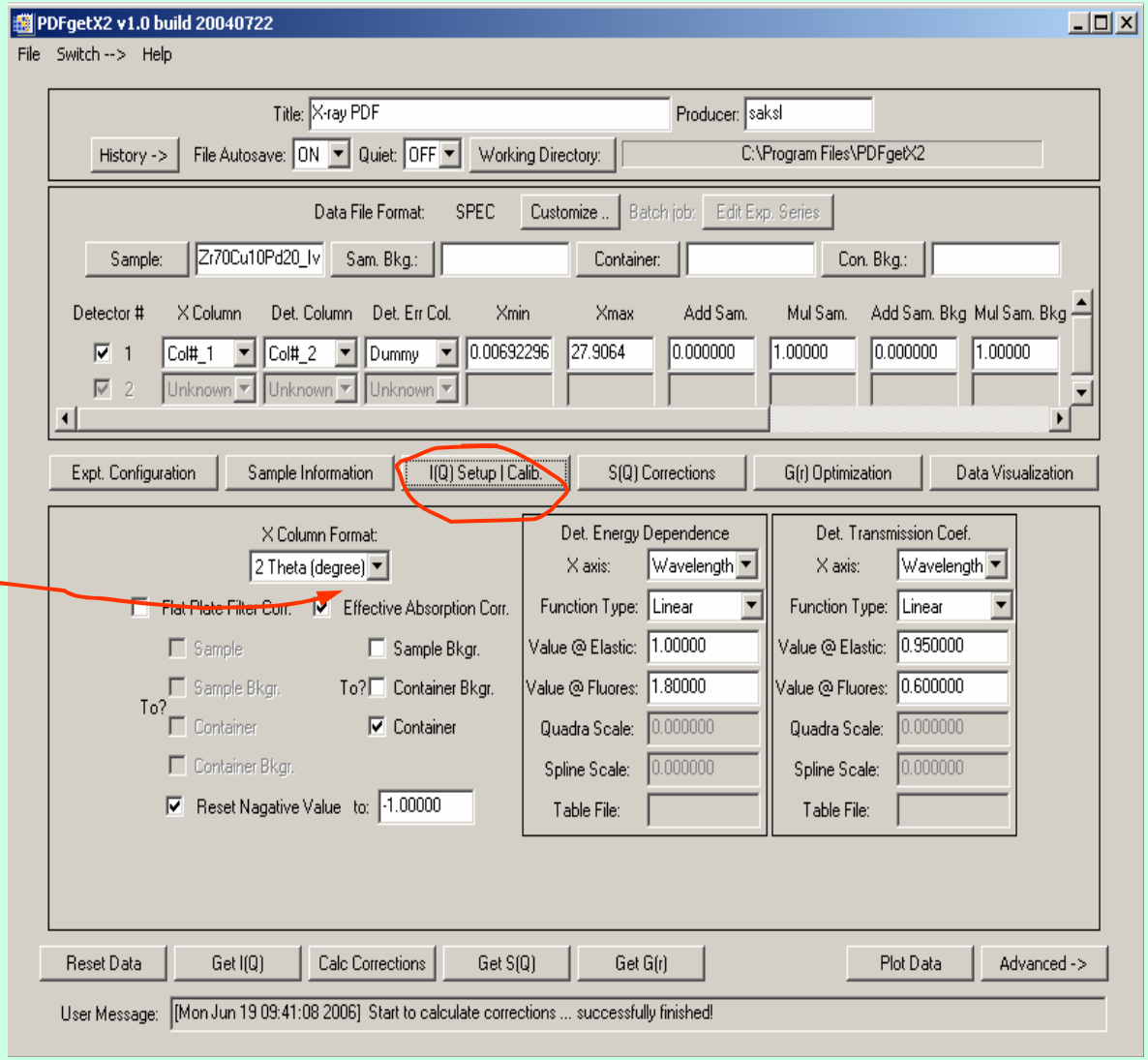


Define the sample chemical composition, the sample geometry, the number density and other parameters.

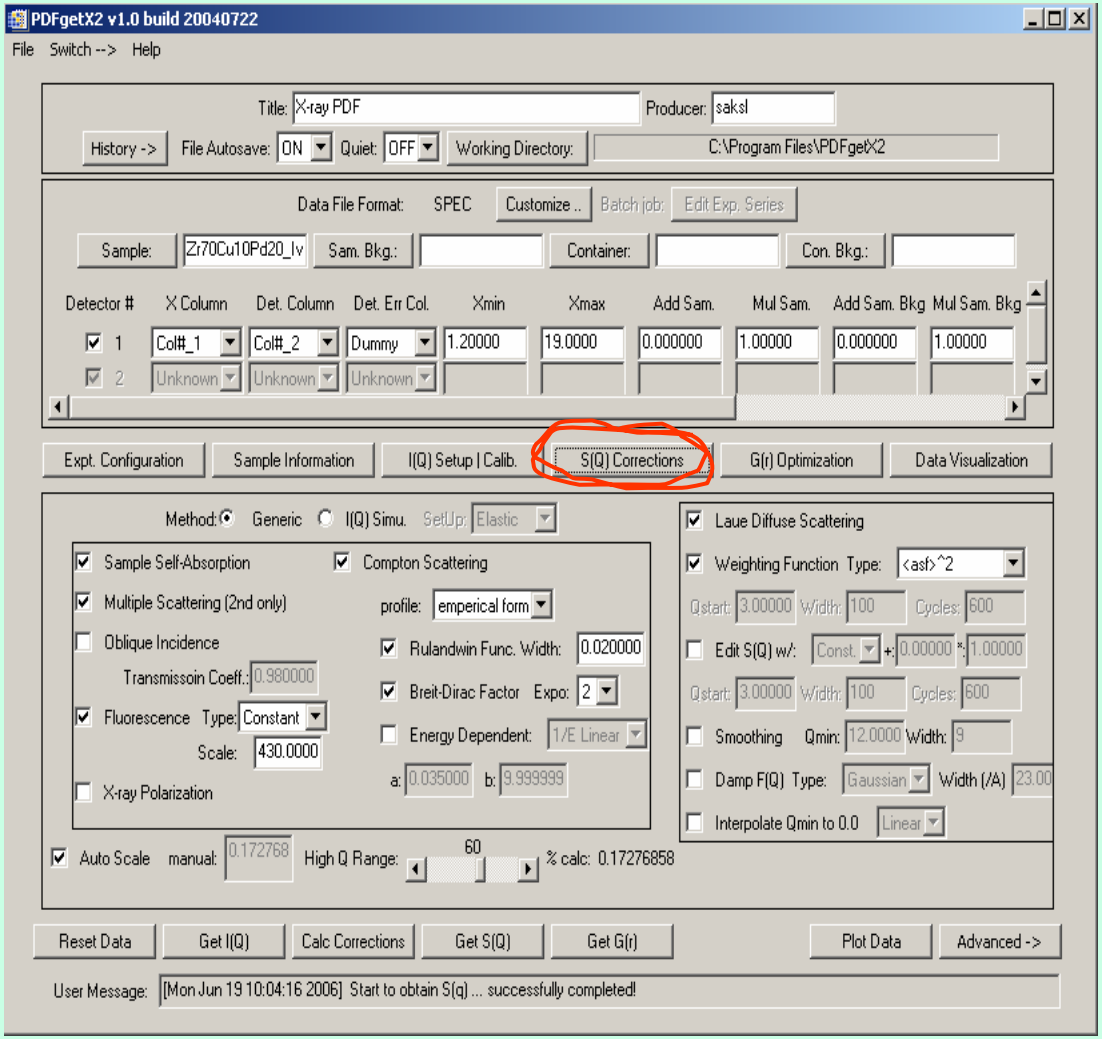
Push “Reset Data”, “Get I(Q)” and then “Calc Correction” and so the “theoretical mut” will be calculated. The calculated value put into “Attenuation Coef. (mut)”.

I(*Q*) setup

Choose a correct a X Coumn Format

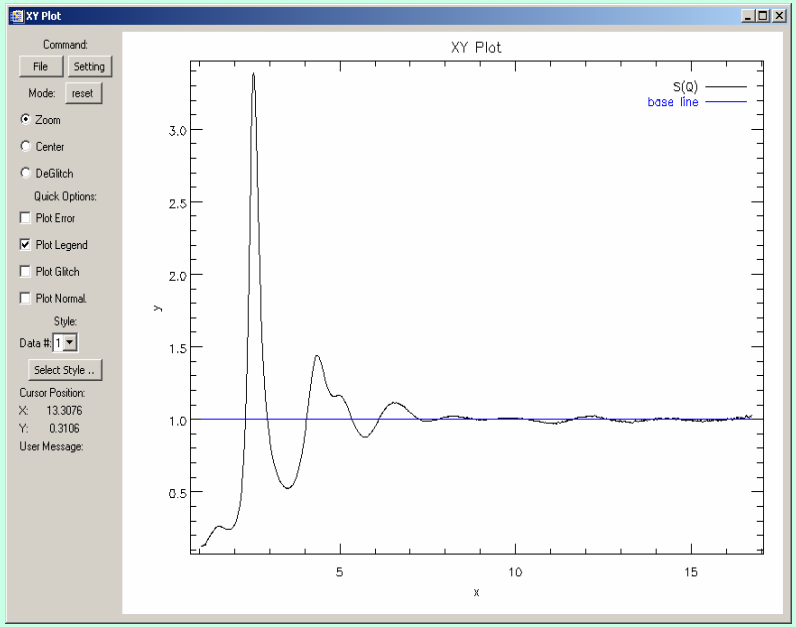


Setup S(Q) corrections



Apply all necessary correction in order that *S(Q) oscillates around 1.*

Push “Get S(Q)”



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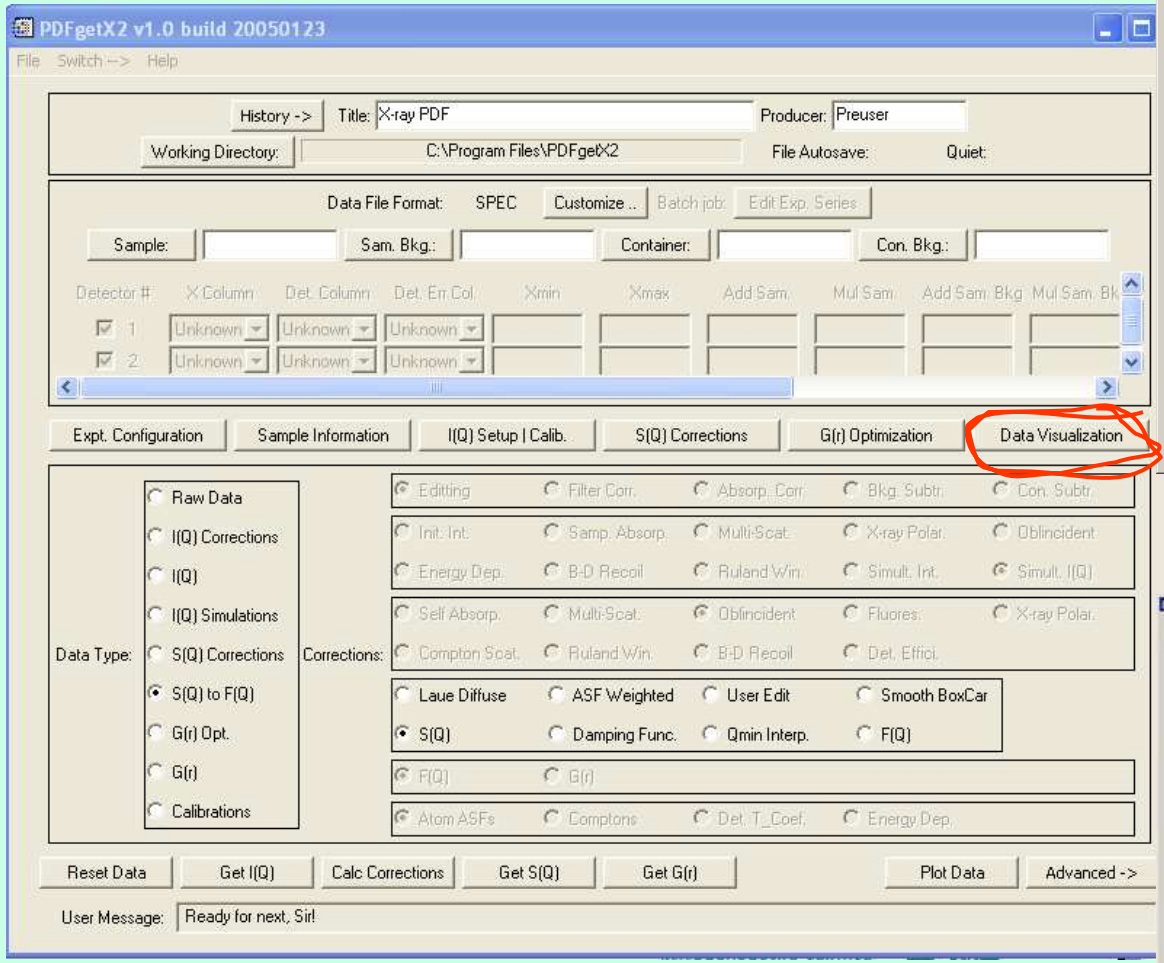
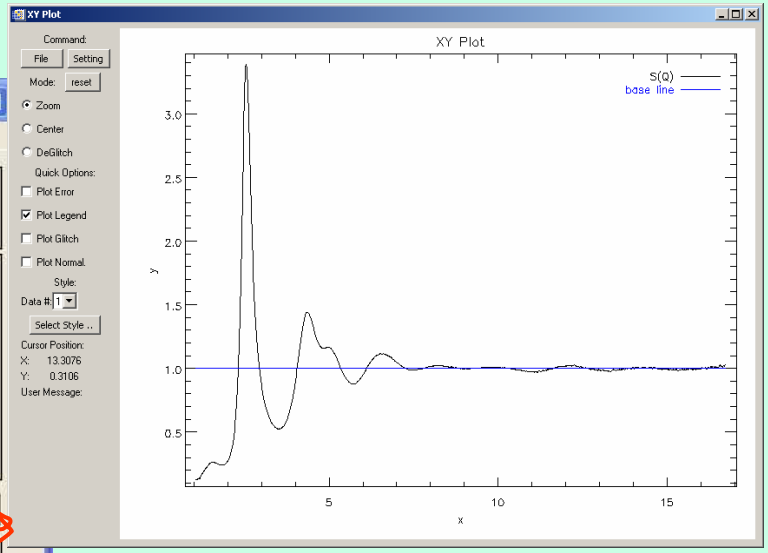
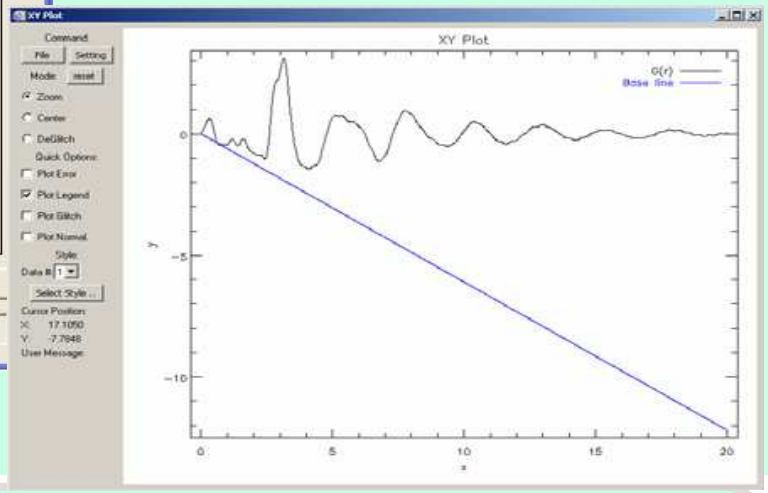
Múdrosť minulosti – poznatky prítomnosti – vzdelanie budúcnosti.

Data visualization





Push “Get G(r)”



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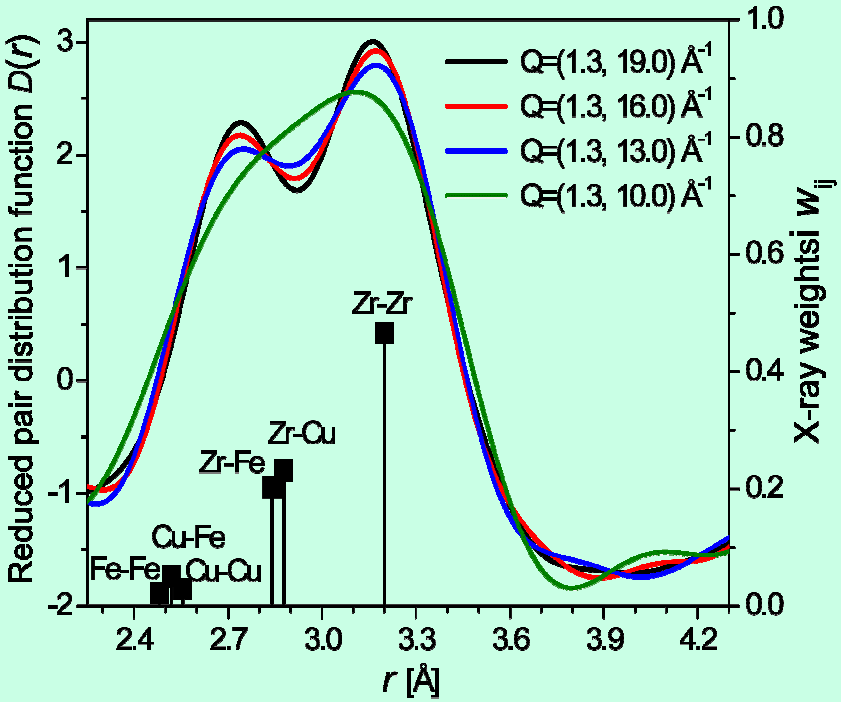
One example – is the high Q needed?

First coordination shell of D(r) of the $Zr_{60}Fe_{20}Cu_{20}$ glassy alloy.



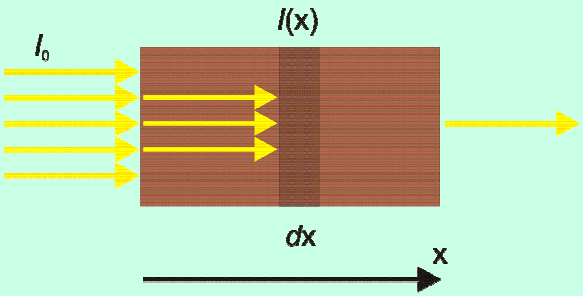
Atomic pairs	Interatomic bond lengths [Å]	X-ray weights w_{ij}
Zr-Zr	3.200	0.4660
Zr-Cu	2.878	0.2313
Zr-Fe	2.841	0.2020
Cu-Fe	2.519	0.0501
Cu-Cu	2.556	0.0287
Fe-Fe	2.482	0.0219

Shortening of interatomic Zr-Fe and Zr-Cu distances about 3.5 % is observed.

We need the *Q vector* as high as possible in order to improve the resolution Δr in the real space.

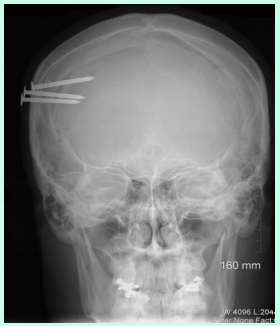
$$\Delta r = (Q_{\max} - Q_{\min}) / \pi$$

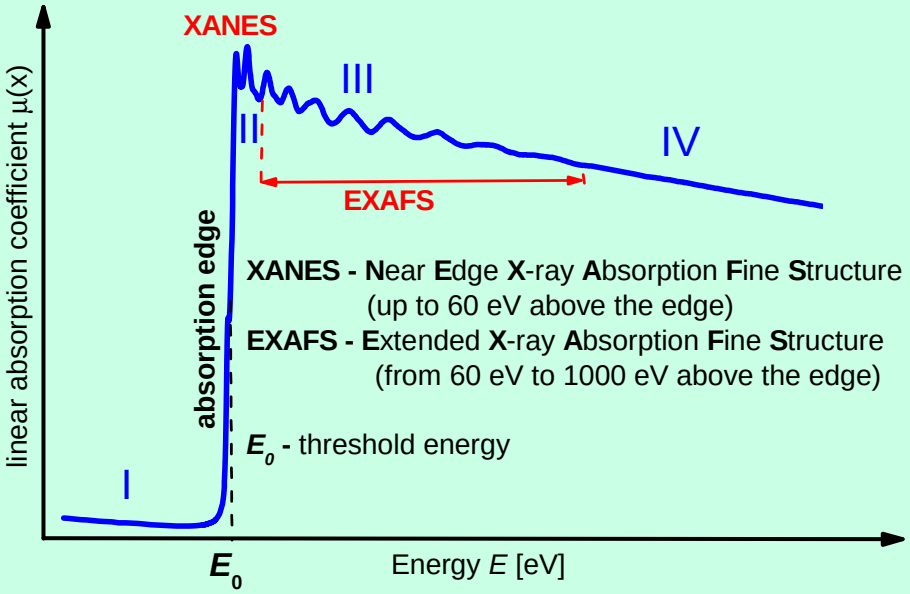
X-ray absorption



$$I = I_0 e^{-\mu(E)x}$$

$$\mu(E) \approx \frac{\rho Z^4}{E^3}$$



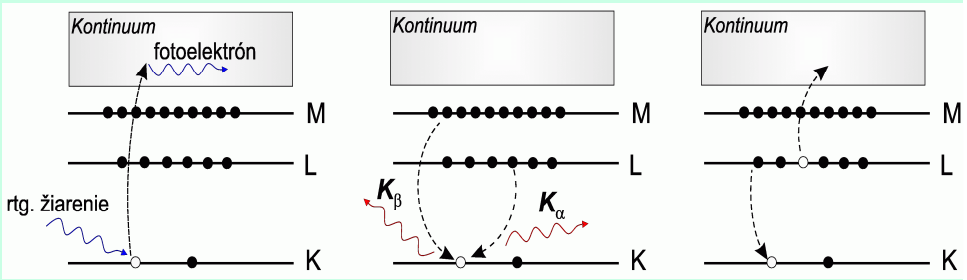


XANES - Near Edge X-ray Absorption Fine Structure
(up to 60 eV above the edge)
EXAFS - Extended X-ray Absorption Fine Structure
(from 60 eV to 1000 eV above the edge)

E_0 - threshold energy

Fermi golden rule

$$\mu(E) \propto \sum_f \left| \left\langle \psi_f \left| \hat{\varepsilon}.\mathbf{r} \right| \psi_i \right\rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$



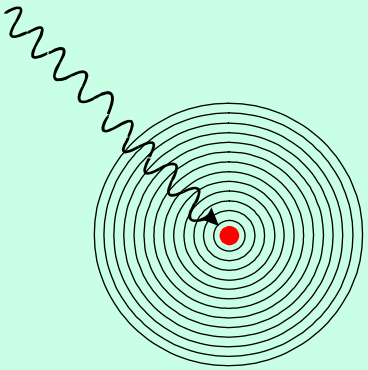
emission of a photoelectron

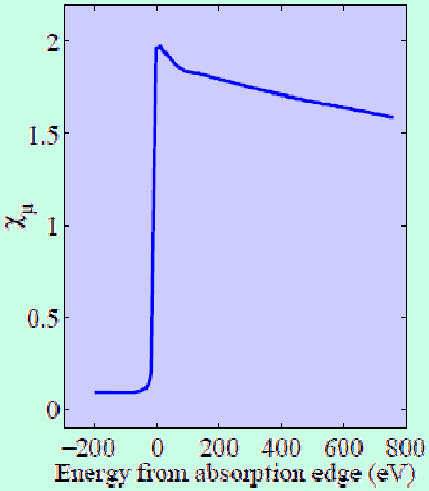
characteristic x-rays are emitted

Auger's electrons are produced

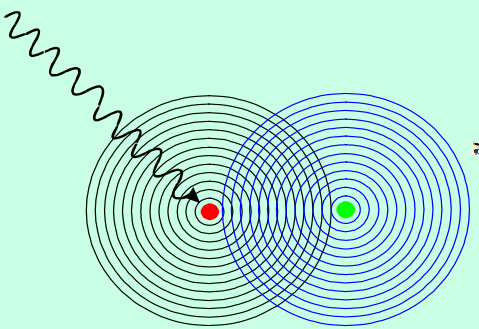
X-ray absorption fine structure signal (XAFS)

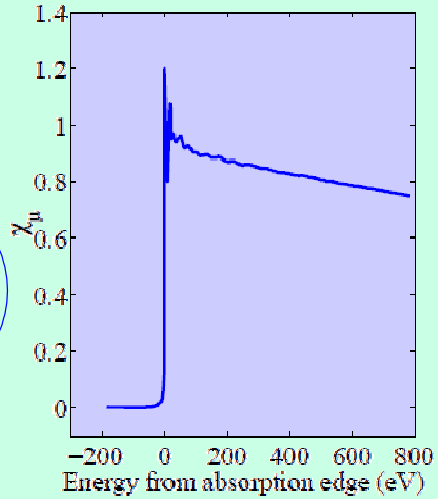
XAFS of one atom (inert gases)



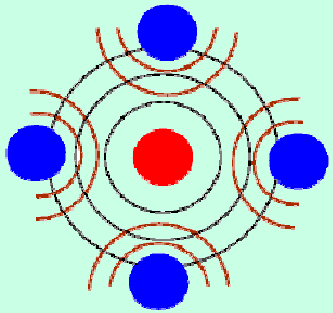


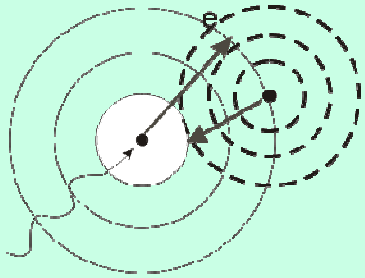
XAFS of two atoms

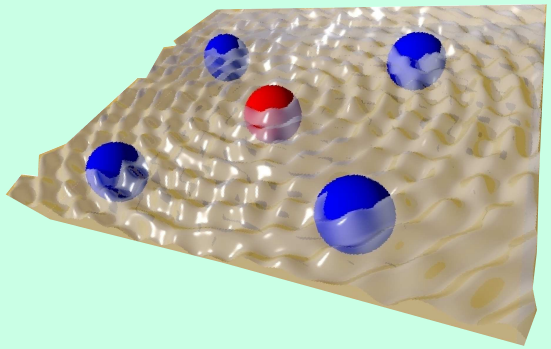




Explanation



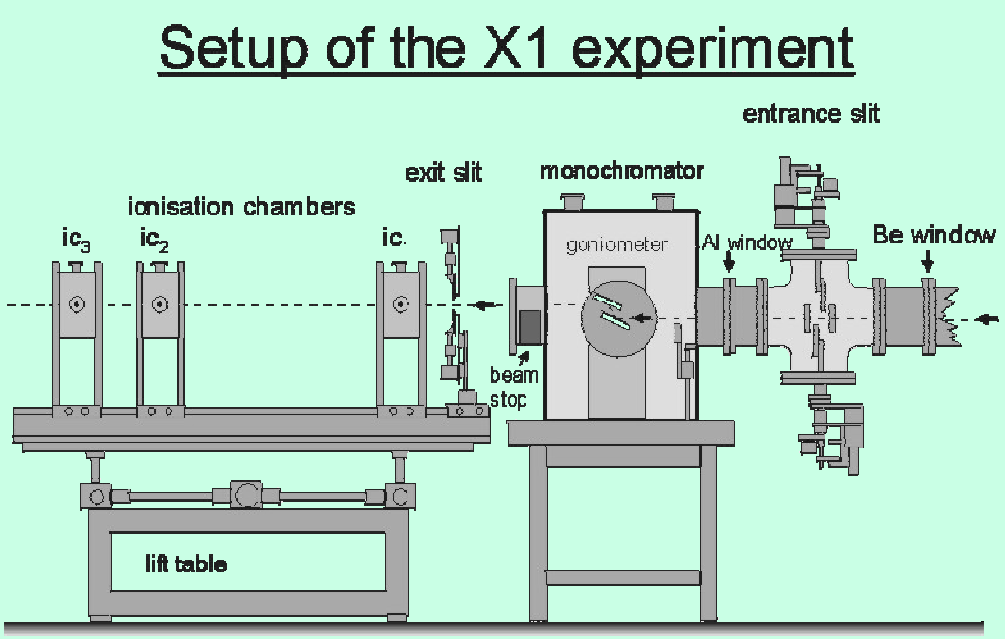


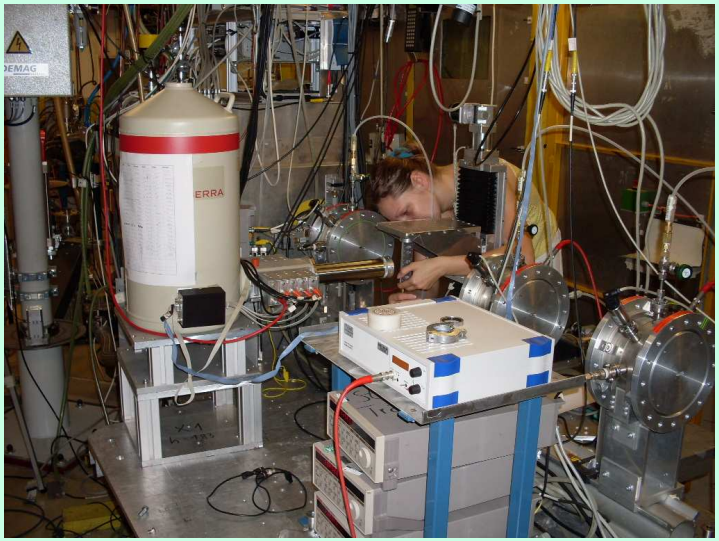


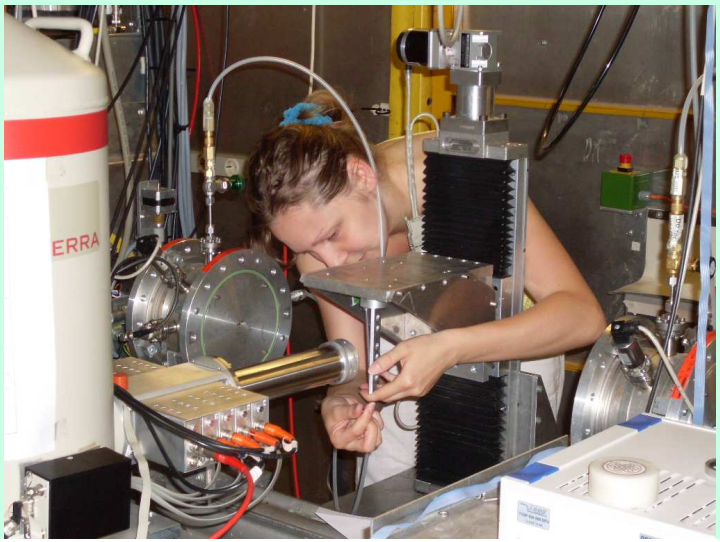
XAFS is the result of interference effects of outgoing and backscattered photo-electrons.

Oscillations of $\mu(E)$ are an unique fingerprint of a local atomic structure around an absor-bing atom.

Experimental realization







Modes of realization

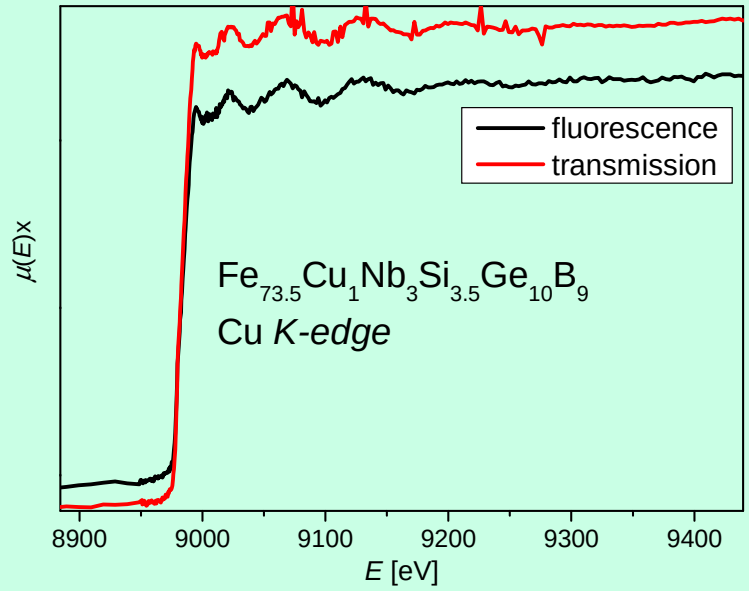
Transmission mode: the most preferable, easiest for realization and data correction

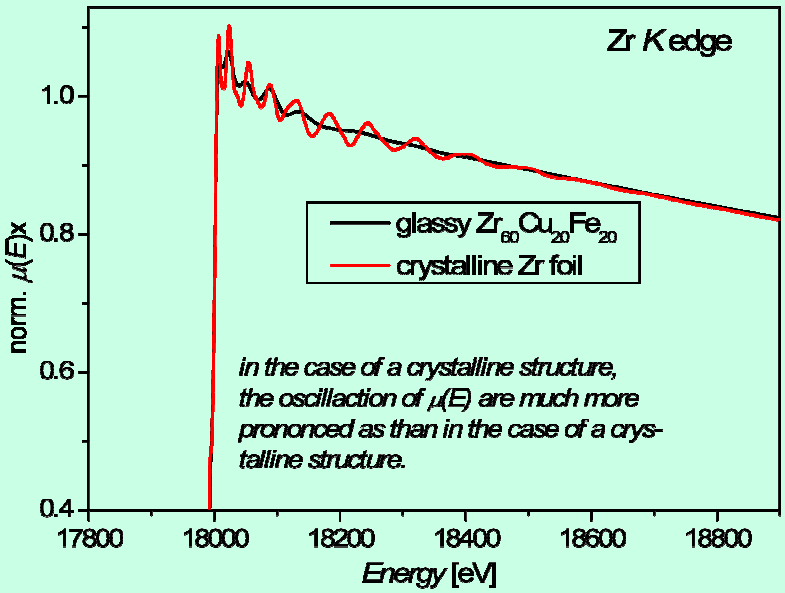
Fluorescence mode: characteristic x-rays are detected

Total electron yield mode: electrons are detected

Experimental realization – practical aspects

Transmission mode – a sample must be homogeneous with constant thickness, absorption $\mu(E)x < 2.6$, not too low concentration of absorbing atoms

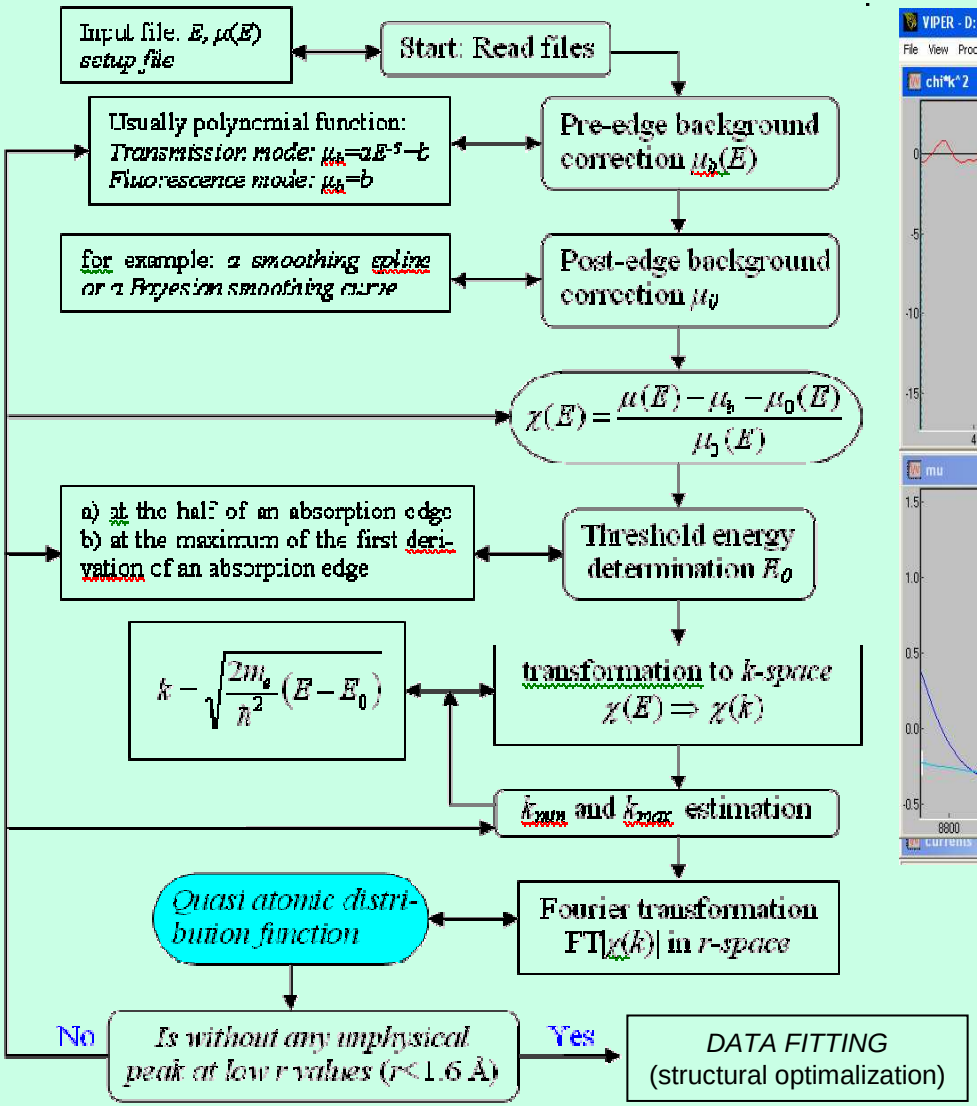


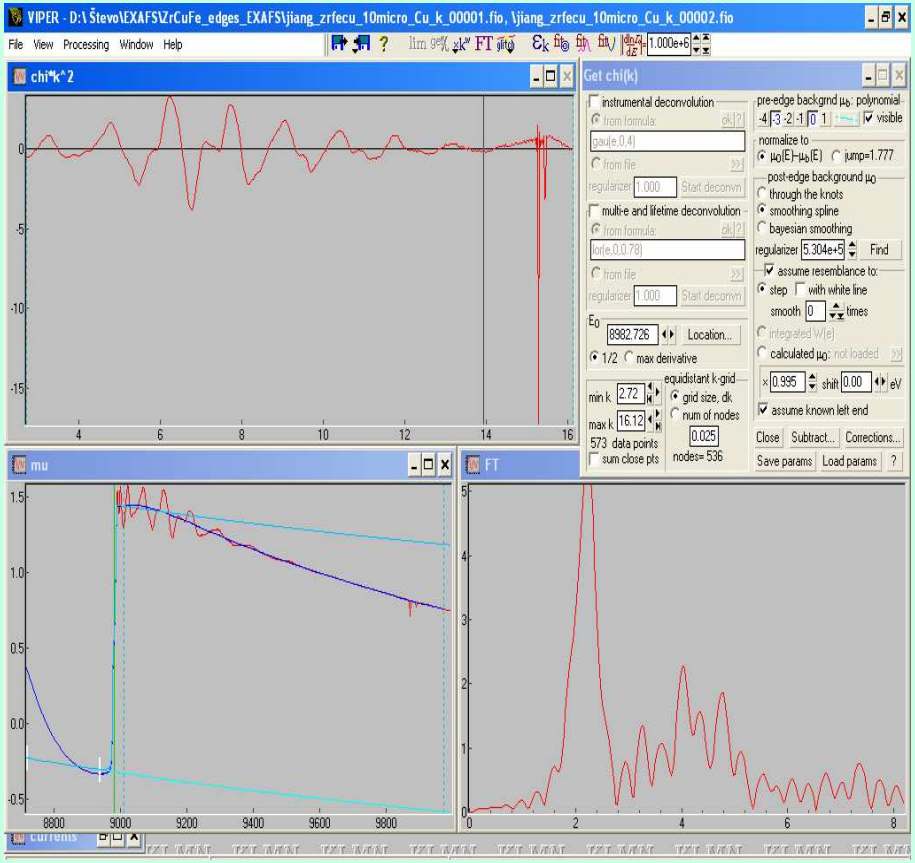


Example for a $Fe_{73.5}Cu_1Nb_3Si_{3.5}Ge_{10}B_9$ ribbon:
absorption μ(E)x =2.0
Fe *K-edge*: x = 8.5 μm Cu *K*-edge: x = 15.2 μm
Nb *K*-edge: x = 85 μm Ge *K*-edge: x = 21.9 μm

low absorbing element concentration results in spikes and strong background tail contribution

Data processing

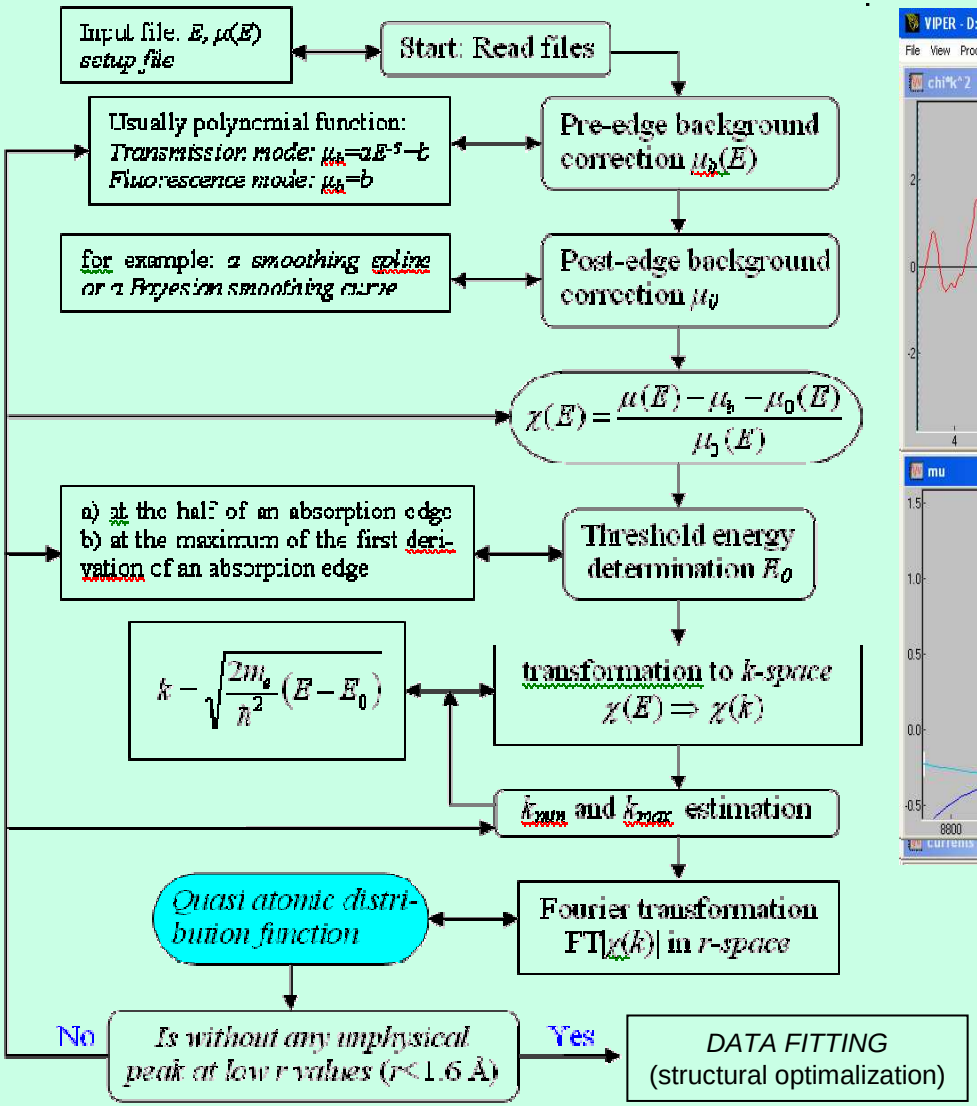


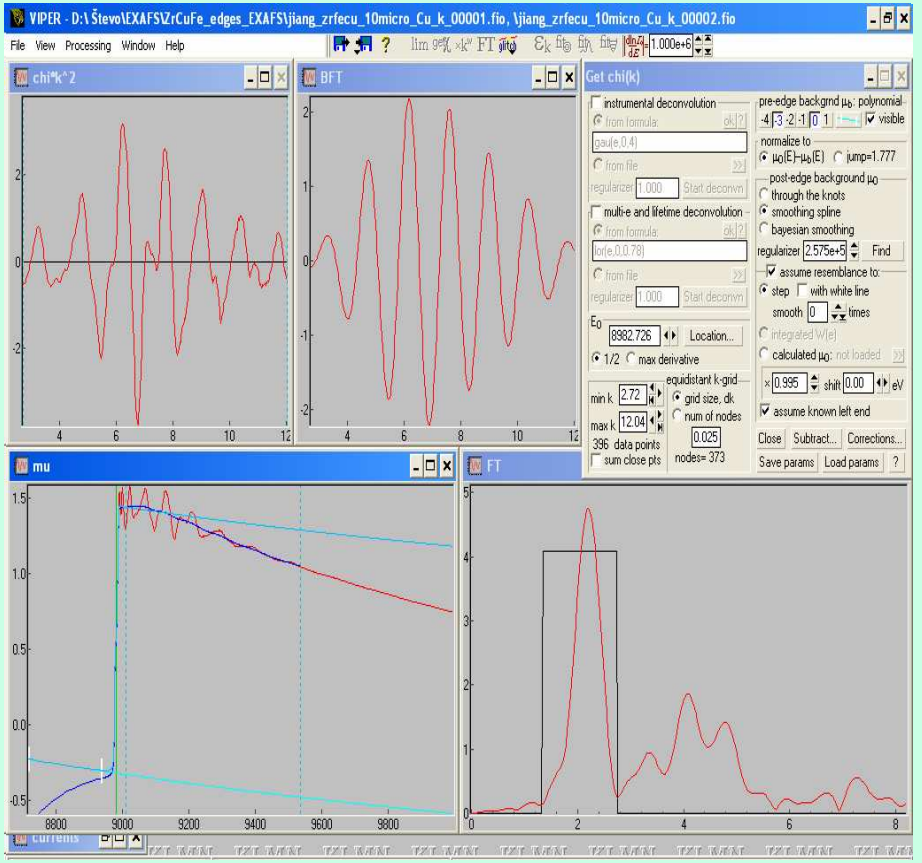


Software VIPER

http://www.cells.es/Beamlines/CLAESS/software/viper.html

Data processing





Data processing

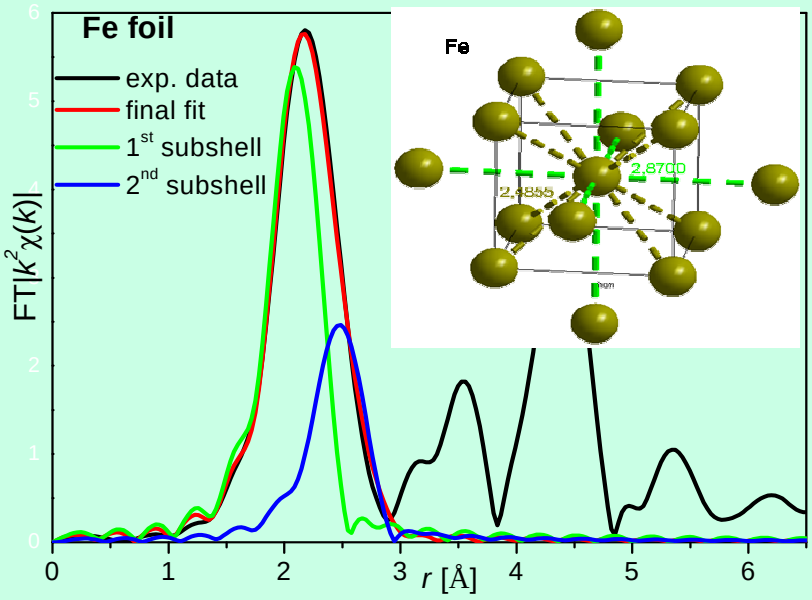
Input model signal
FEFF software

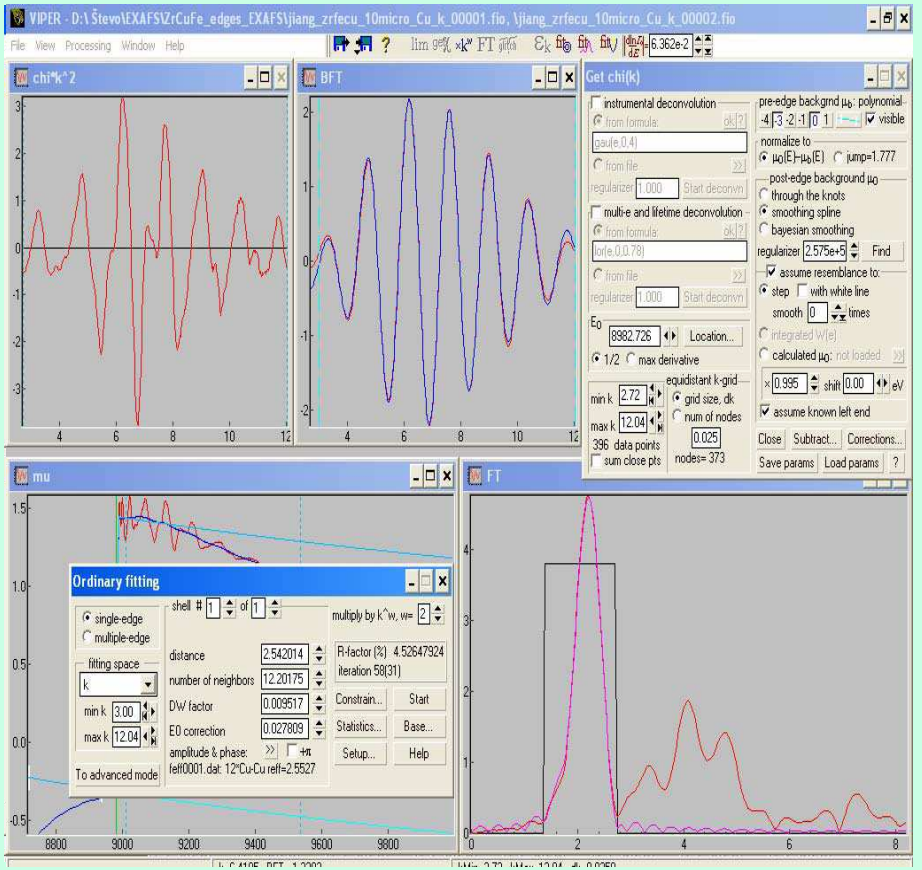
↓

DATA FITTING
(structural optimalization)

↓

Output: N, r, σ, ΔE_0

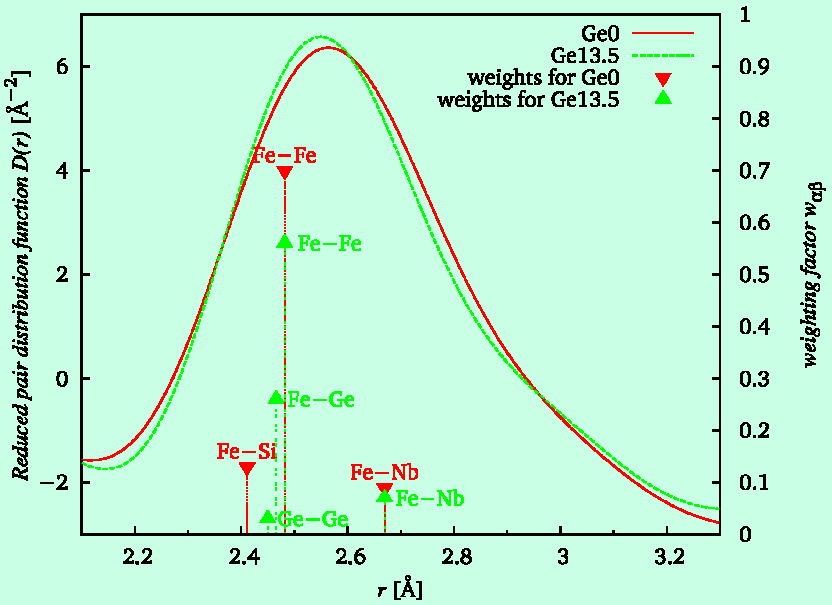




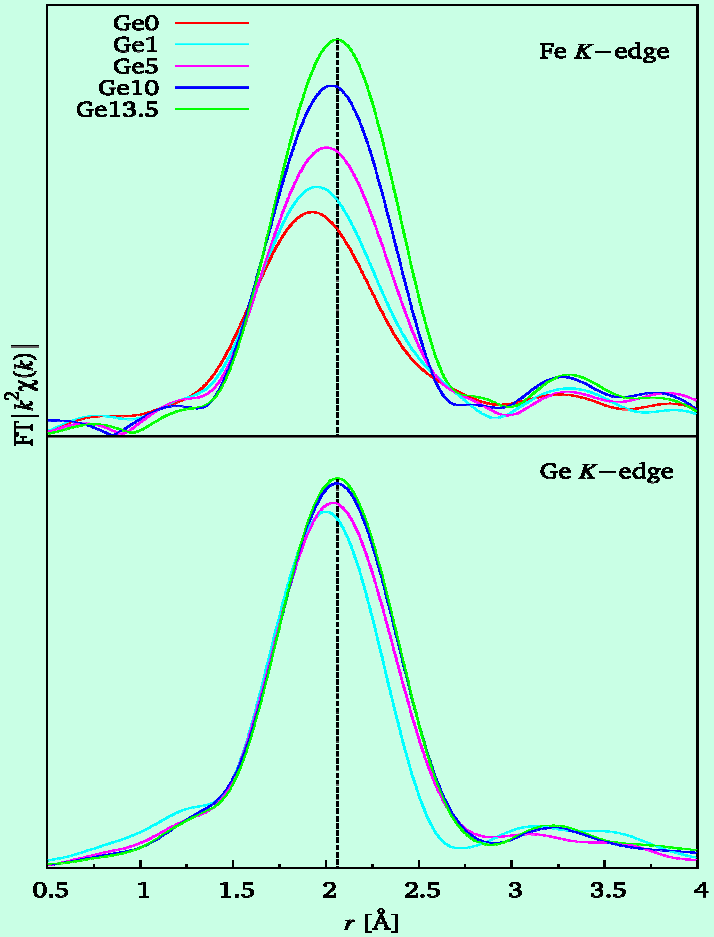
One example

$Fe_{73.5}Cu_1Nb_3Si_{(13.5-x)}Ge_xB_9$

XRD – real space



EXAFS – real space



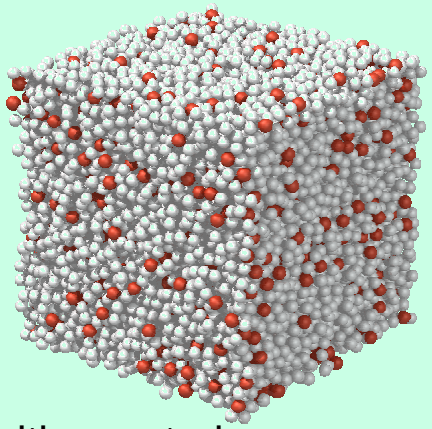
Principle of RMC modeling

The aim is to minimize difference between functions obtained from model and experiment

$$\psi^2 = \frac{1}{\delta}\sum_{i=1}^{m}\left[\zeta^{\exp} - \zeta^{RMC}\right]^2$$

How???

Box of ~ 10 000 atoms



with constrains:
- minimum interatomic distances
- atomic density

1. Move:
One particle is moved randomly taking into account applied constraints.

2. Acceptance of the move:
First the experiment-model difference is calculated
If $\psi^2_{n+1} < \psi^2_n$ the move is always accepted.
If $\psi^2_{n+1} > \psi^2_n$ the move is accepted with the probability $\exp[-(\psi^2_{n+1} - \psi^2_n)/2]$

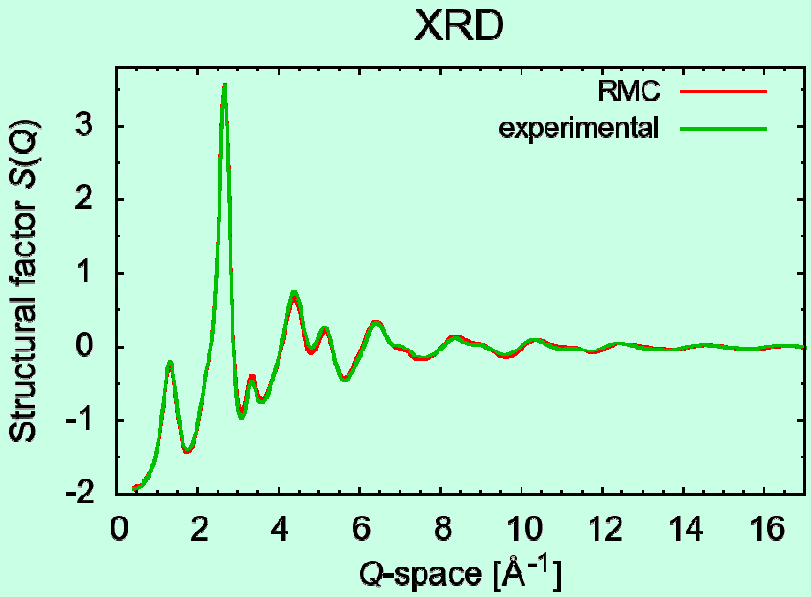
3. Settling:
Everything is repeated until ψ^2 begins to oscillate around a constant value.

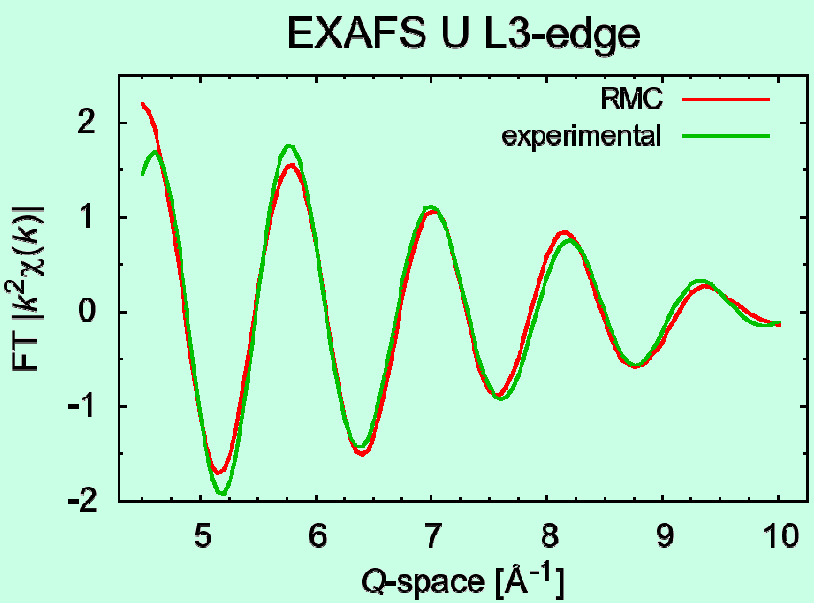
Experimental data:
- ***XRD***, ND, ED
- ***EXAFS***
- SAXS, SANX

Result:

We have an 3D structural model which is consistent with experimental data.

One example: RMC modelling of a binary $Al_{92}U_8$ glassy alloy



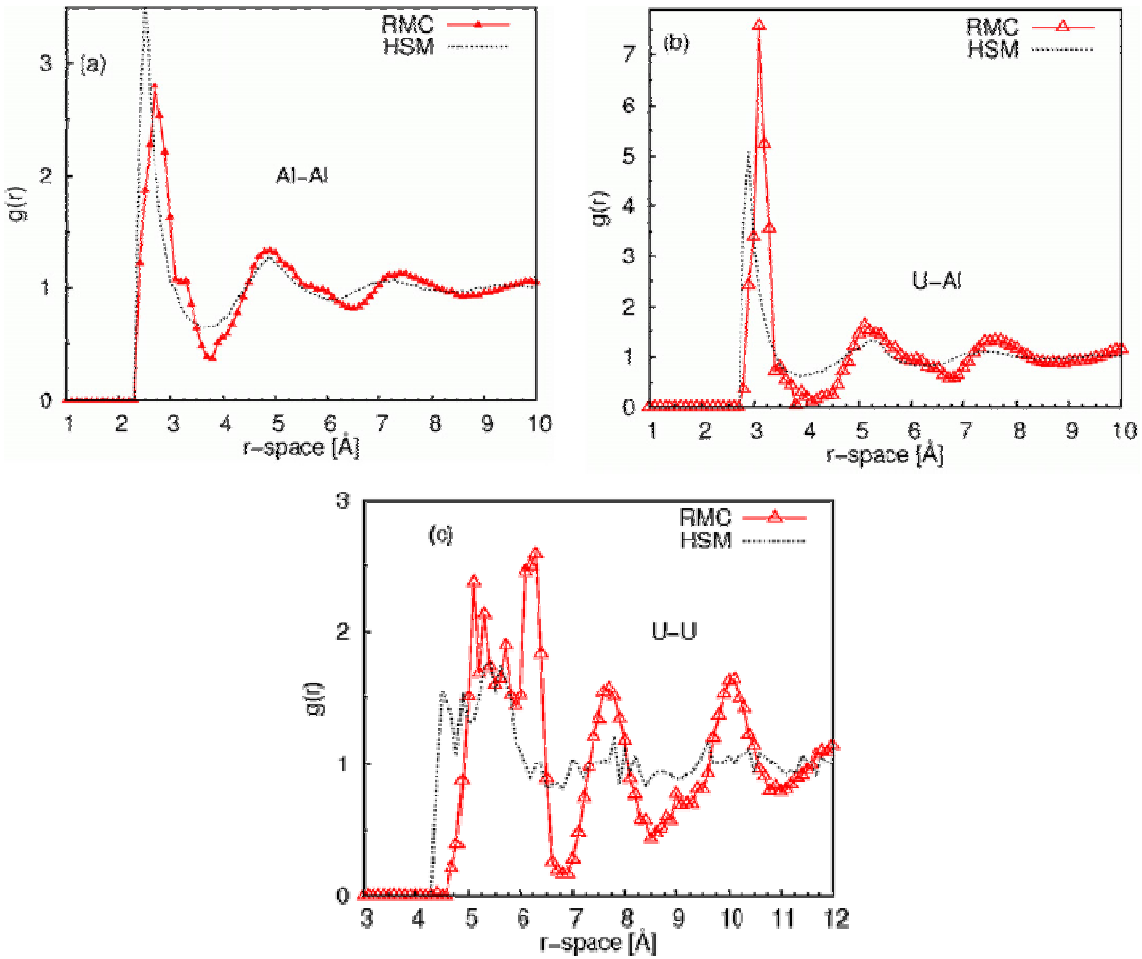


Nice match is obtained between experimental data and model data produced on the base of Reverse Monte Carlo simulation

We can perform analysis of the produced 3D structural model.

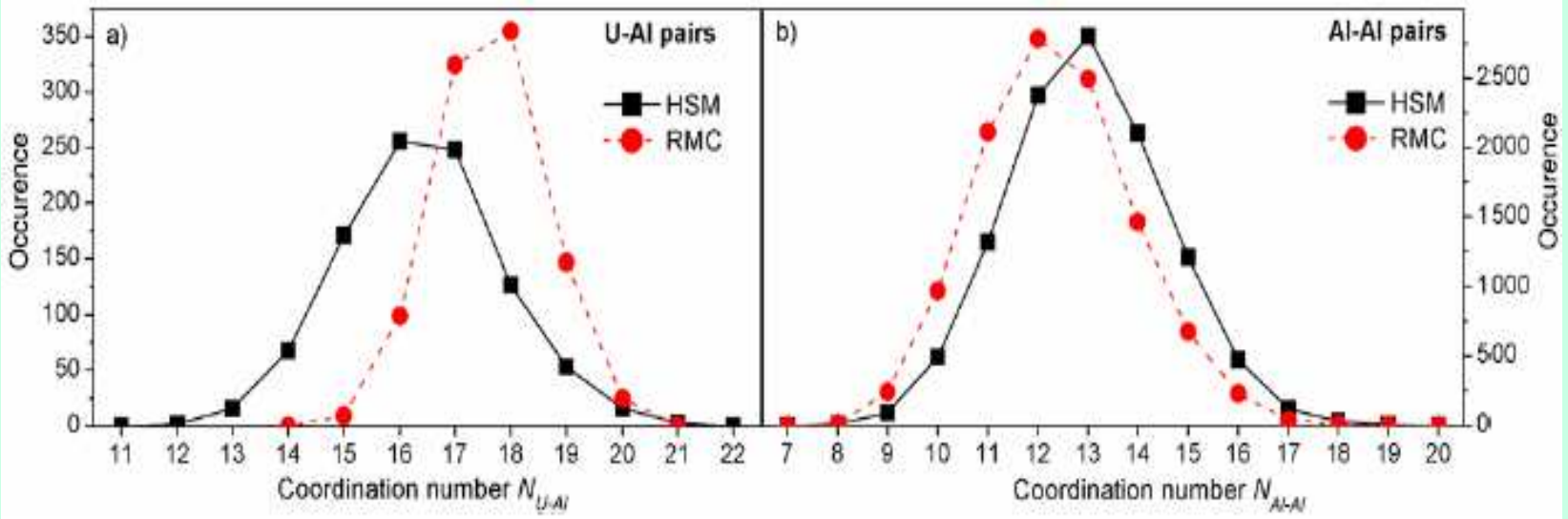
RMC modeling

Partial atomic pair distribution functions can be directly calculated !!!



RMC modeling

Distributions of coordination numbers can be evaluated !!!



Conclusions

- high energy x-ray diffraction: from the structural factor $S(Q)$, the pair distribution function $D(r)$ is calculated → a local atomic arrangement around an average atom is seen and long range correlations are detectable.
- x-ray absorption spectroscopy: an element sensitive method, the nearest neighbouring of a specific type of atoms is observable.
- Combination of XRD and XAFS: compact information about amorphous structure can be obtained.
- Reverse Monte Carlo simulation is a method which can be used for modelling of a 3D disordered structure in a real space.

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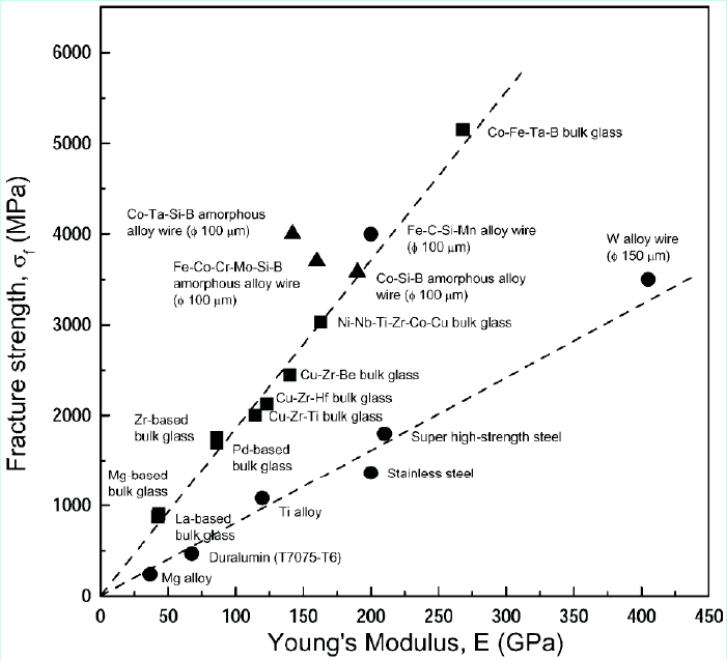
Prečo kovové sklá?

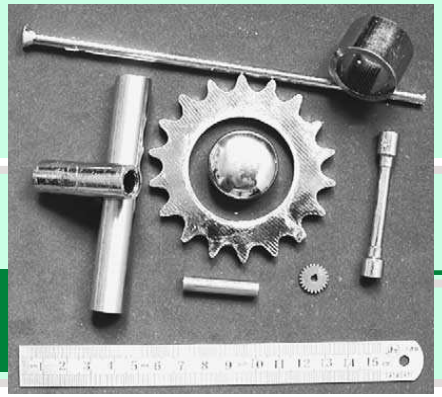
- Výborné mechanické vlastnosti
  vysoké hodnoty medzi pevnosti, lomovej húževnatosť, tvrdosti, výborné elastické vlastnosti...
- Výborné magnetické vlastnosti
  magneticky mäkké materiály
- Výborné antikorózne vlastnosti
- Zaujímavé termodynamické vlastnosti
  existencia teploty sklenia T_g, výrazný pokles viskozity, ľahká tvarovateľnosť materiálu

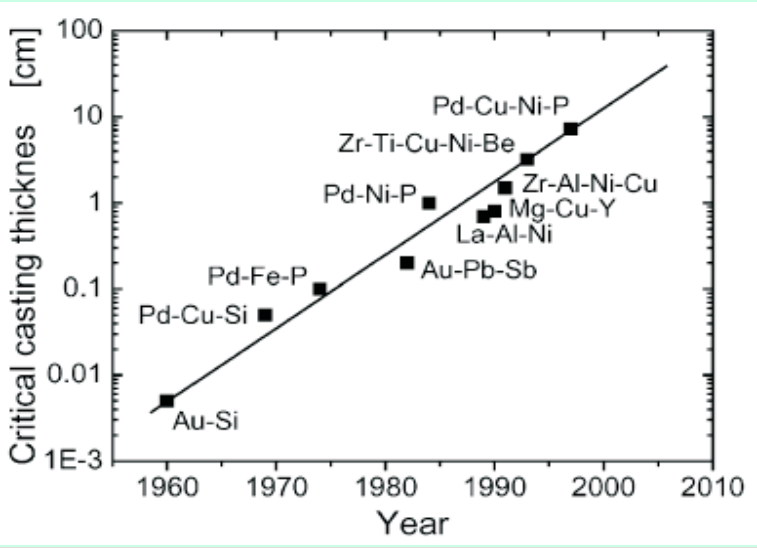


Nevýhody

- obmedzená schopnosť sklenia
- neexistencia oblasti plastickej deformácie

Vitalloy 1
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$

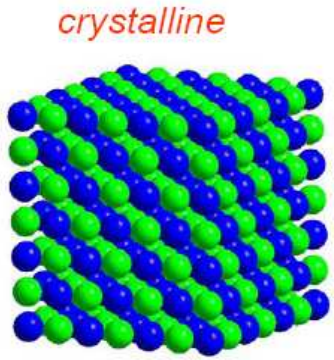


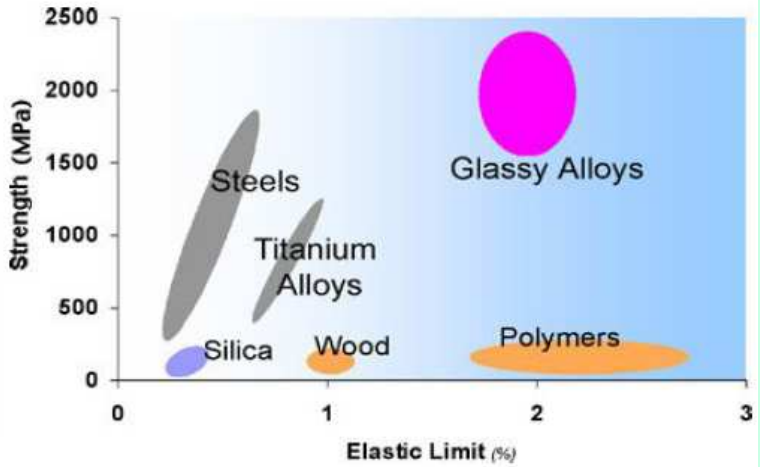


Predmet môjho štúdia

Charakterizácia neusporiadanej štruktúry kovových skiel s využitím vysoko intenzívnych röntgenových zdrojov

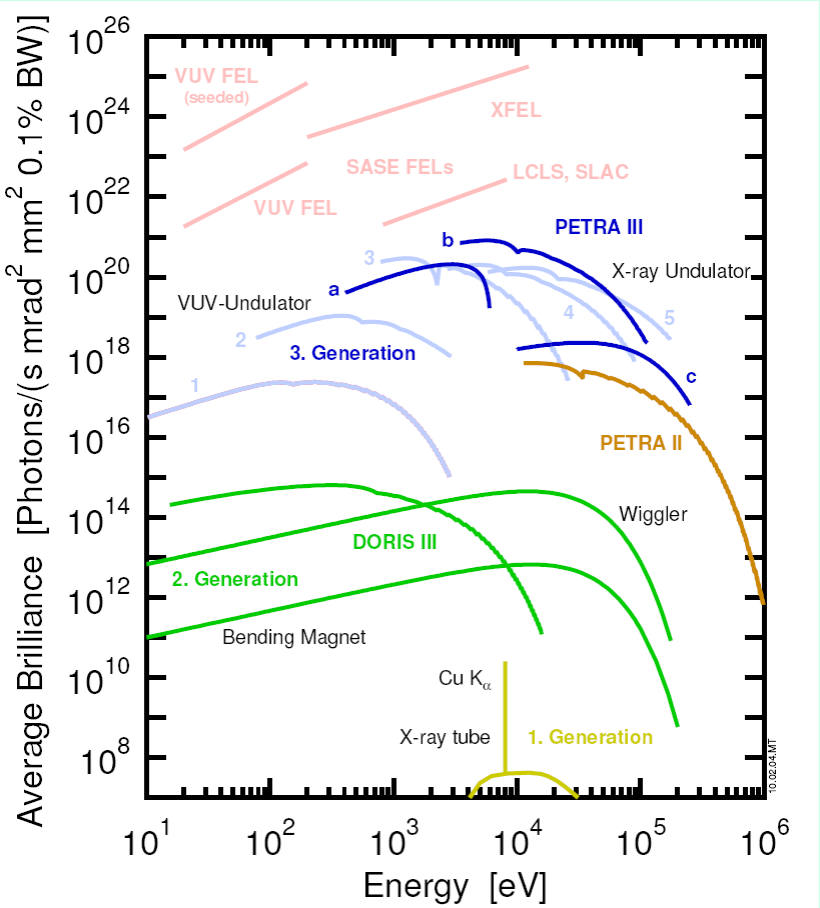
Metallic glasses are a new class of engineering materials having an amorphous structure on atomic level and unlike metals, they can be easily deformed at high temperature.

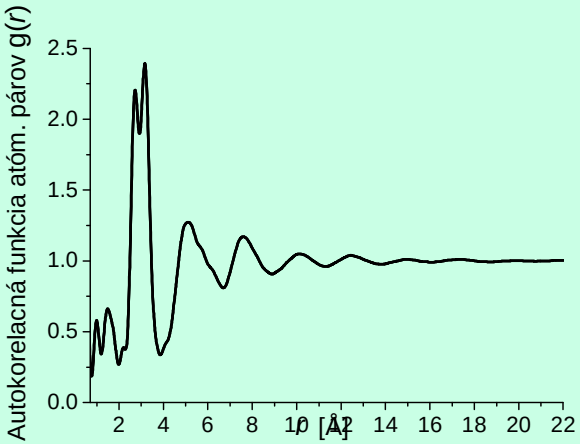




Zhrnutie: vlastnosti SŽ

- vysoká intenzita
- nízka emitancia, SŽ je takmer úplne kolimované
- vysoký stupeň lineárnej alebo eliptickej polarizácie
- široké a spojité energetické spektrum
- pulzný charakter žiarenia na úrovni nanosekúnd





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