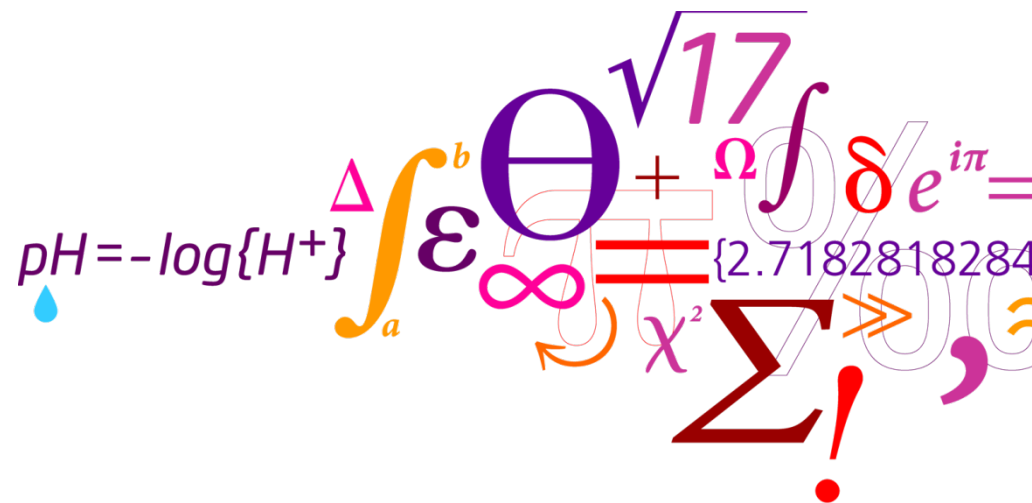


# Introduction to XAFS

Applications of X-ray and neutron scattering in biology, chemistry and physics

*Jonas Andersen, ph.d. student, DTU Chemistry*

*Bastian Brink, ph.d. student, DTU Mechanical Engineering*



# Today's Schedule

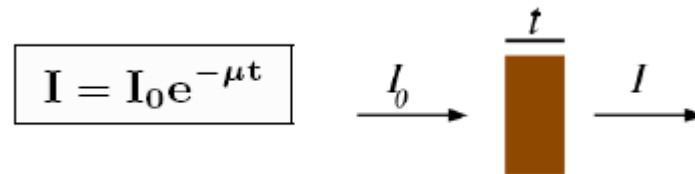
- Introduction to XAFS
  - Theory and Application
- Exercise 1
- 12:00 – 13:00 Lunch Break
- Presentation from Haldor Topsøe
- Exercise 2

# X-ray Absorption Theory

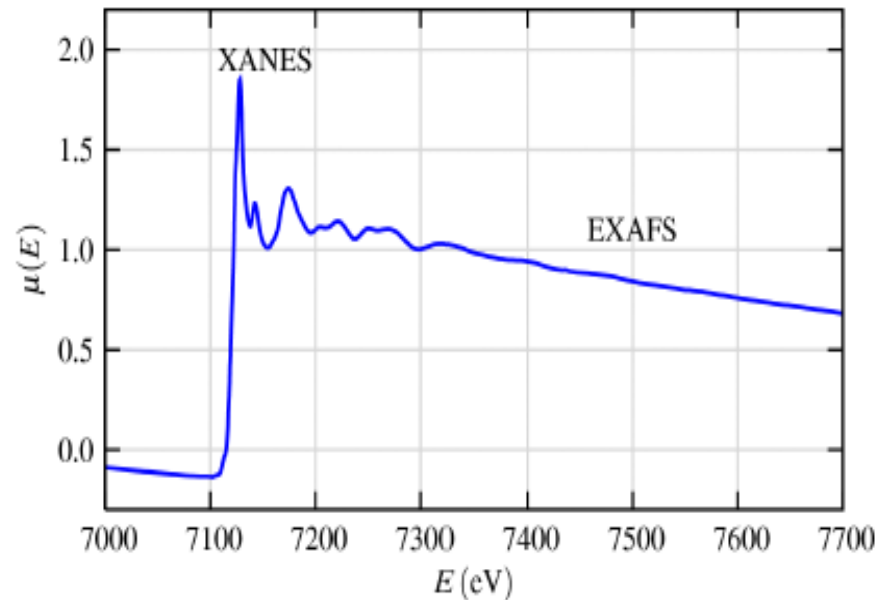
## The absorption coefficient - $\mu$

Transmission of electromagnetic radiation through a material

**Lambert Beers's Law:**

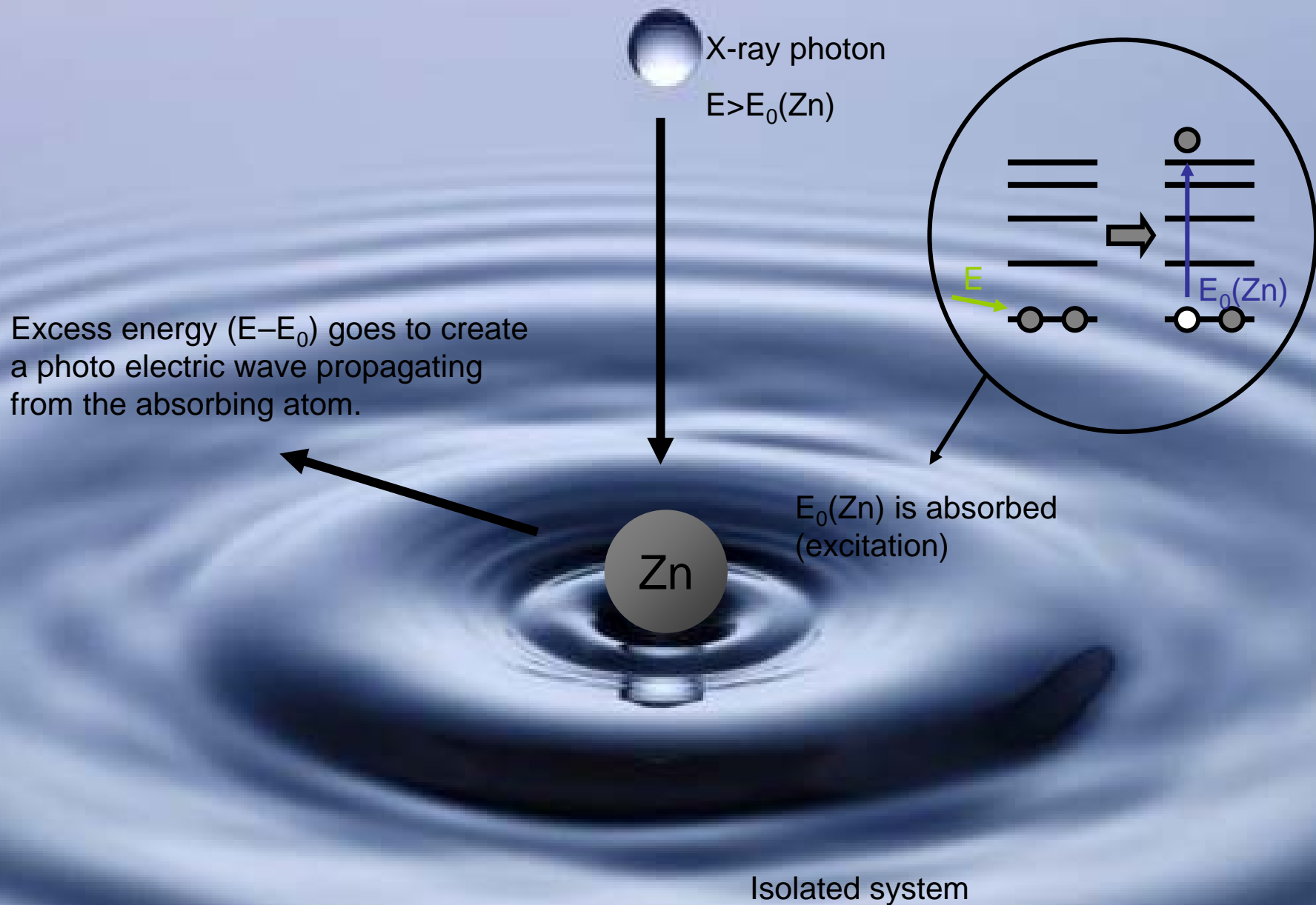


# Introduction to XAFS

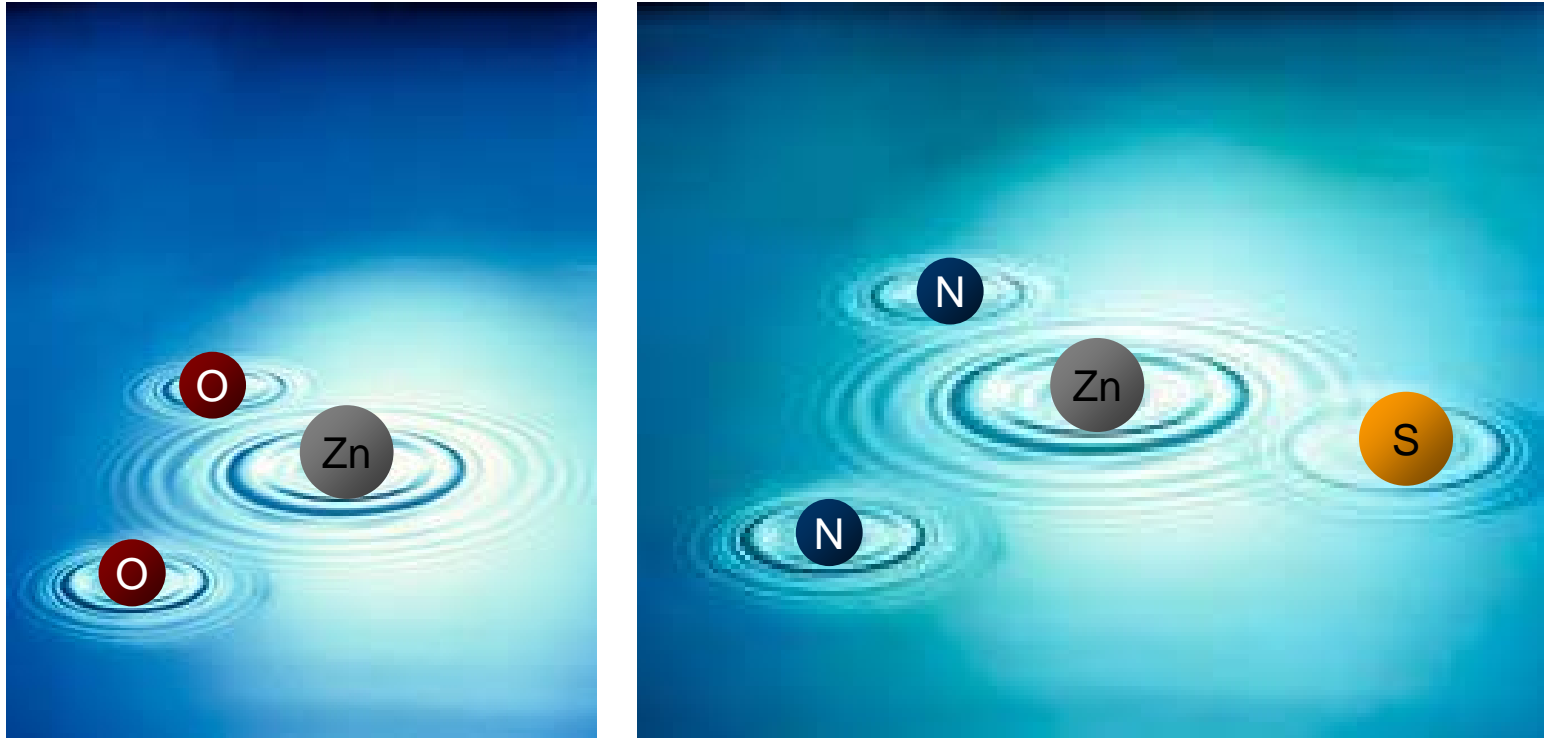


Requirement: High intensity radiation source with variable energy/wavelength - Synchrotron

# Generation of photoelectric wave



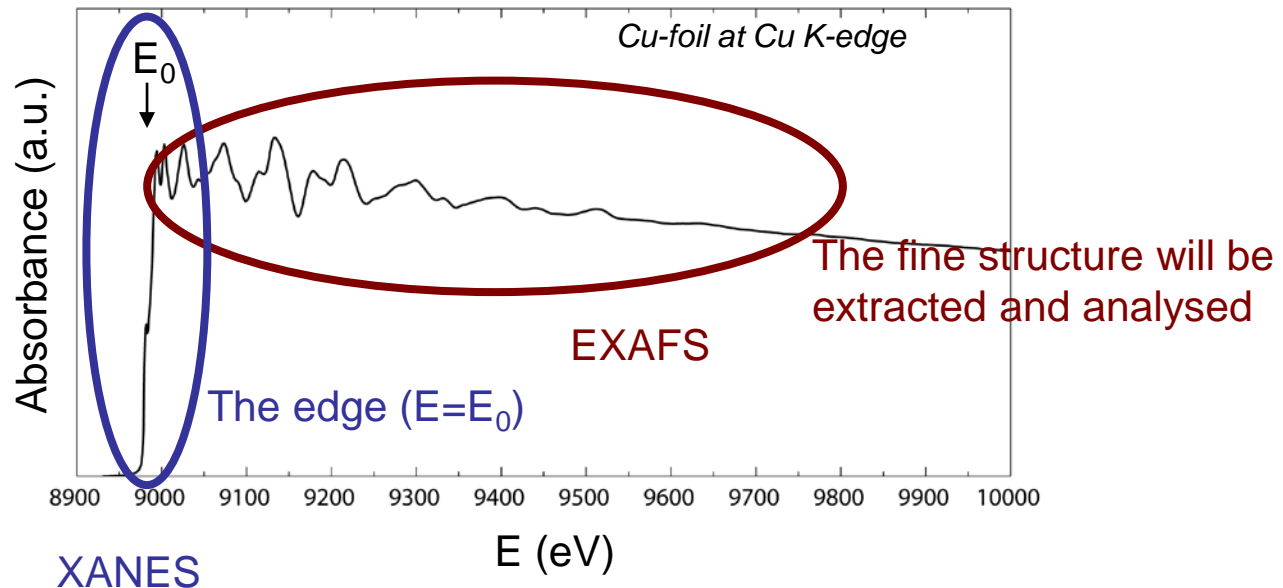
# Backscattering of photoelectric wave



Interference pattern depends on:

- Number of backscatters
- Geometry of backscatters (distance/angles)
- Type of backscatters
- Energy (i.e. wavelength of photoelectric wave)

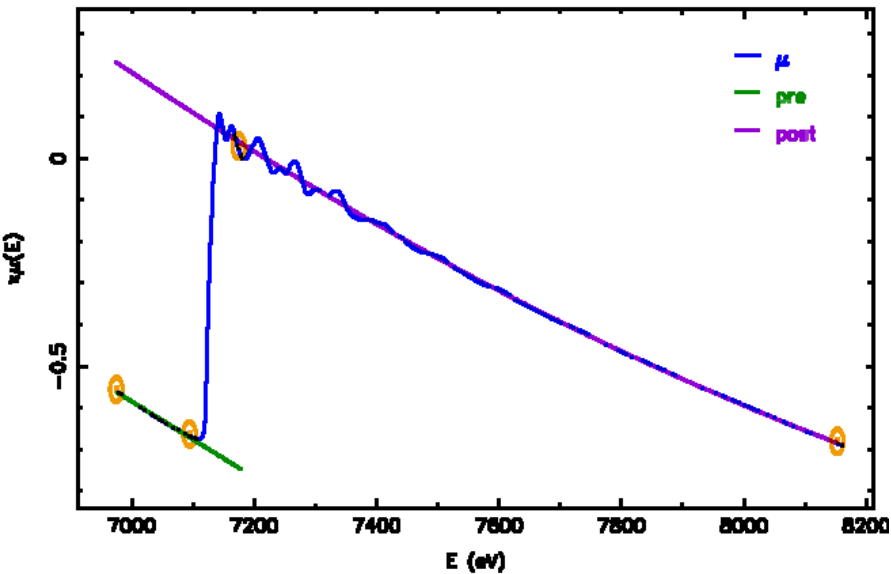
# X-ray absorption spectrum



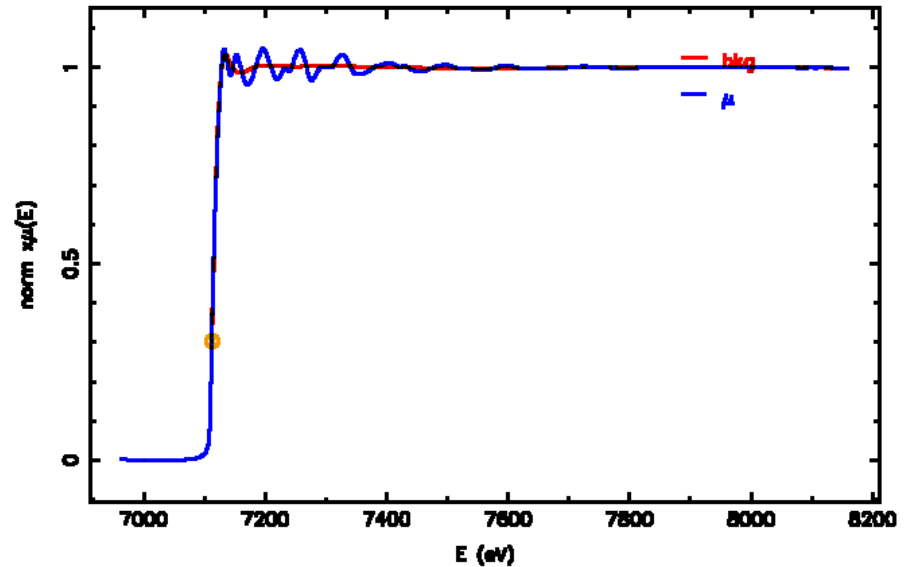
The fine structure is proportional to the 1D projection of the interference pattern and contains information about the coordination geometry.

One spectrum – two techniques: XANES and EXAFS

# Data reduction: Energy space



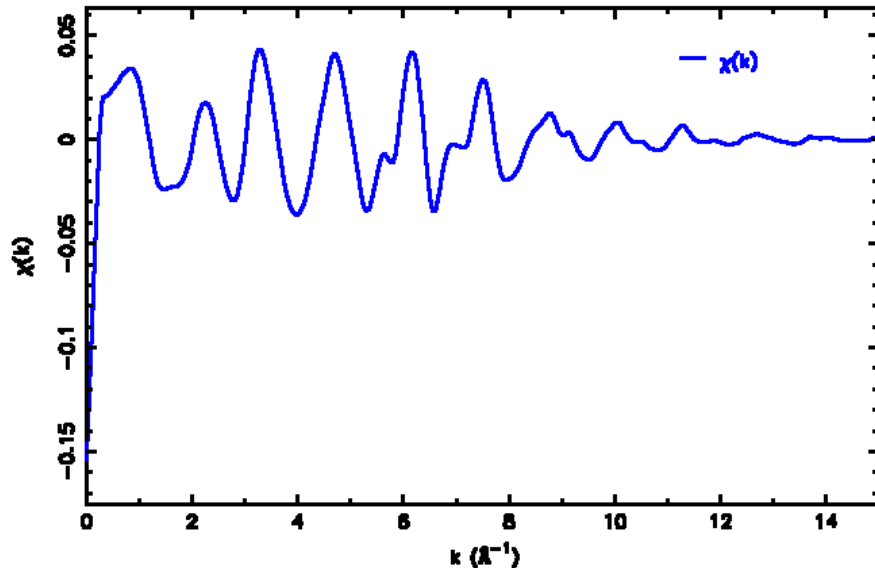
Raw data + pre and post edge lines event



Normalized to one absorption event

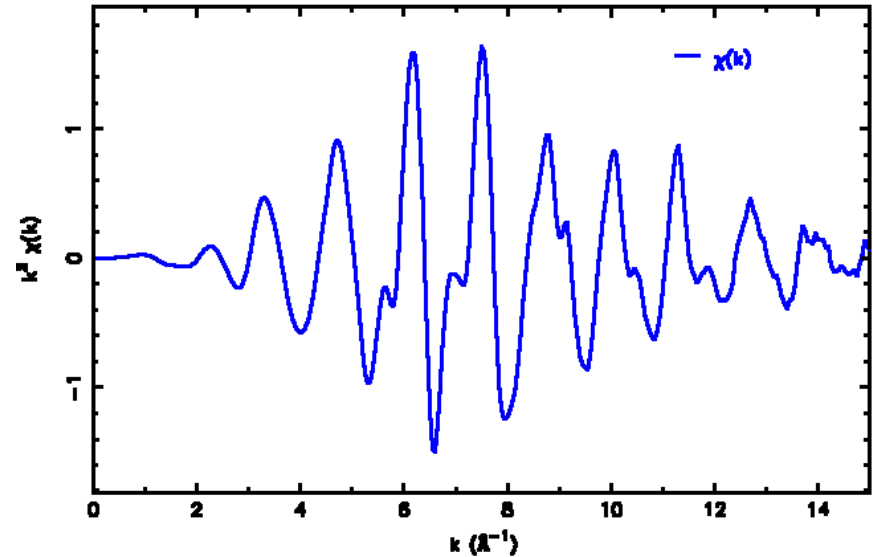


# Data reduction: $k$ -space



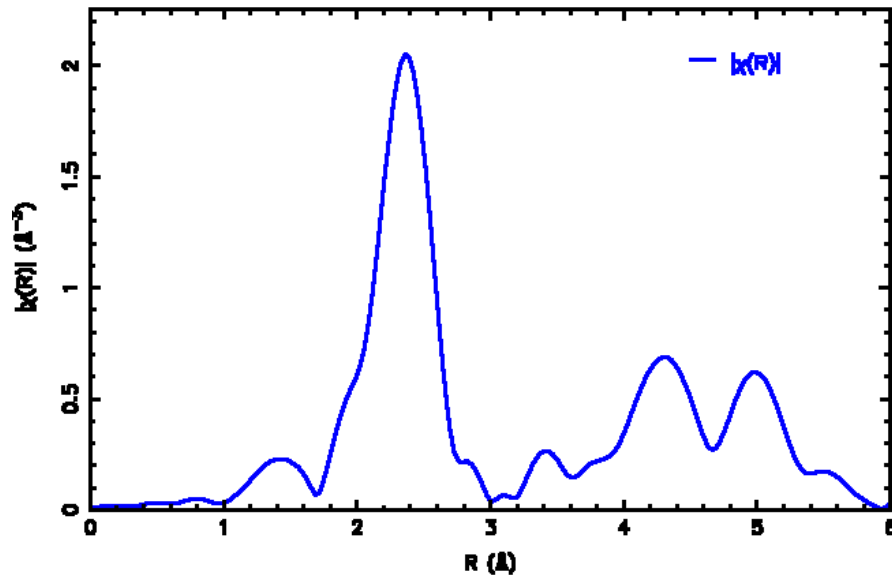
Change scale from X-ray energy to  
Photoelectron wavenumber

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)} \quad k = \sqrt{\frac{2m_e(E-E_0)}{\hbar^2}}$$



$k$ -weighting to enhance features  
at high  $k$  values

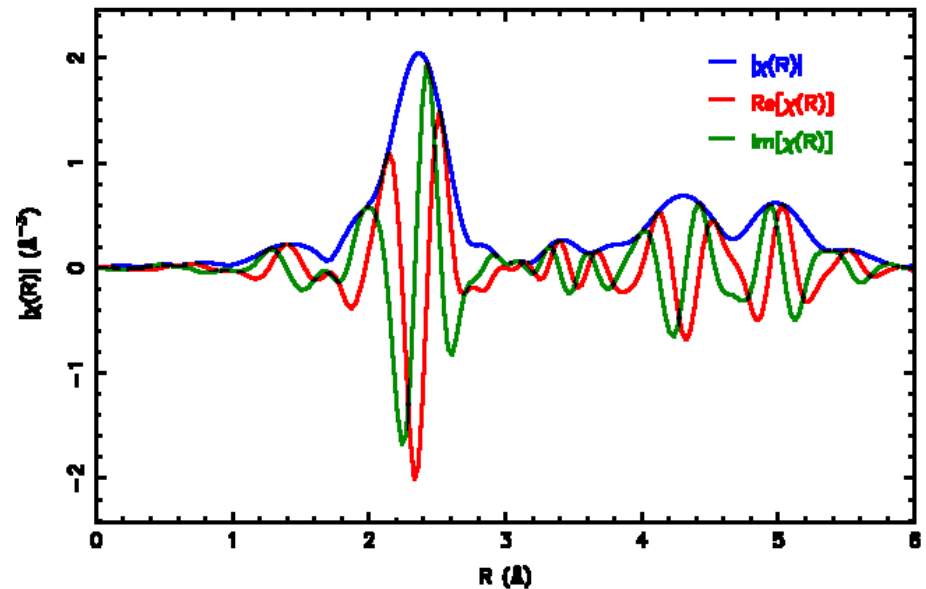
# Data reduction: $R$ -space (Fourier transform)



Frequency filter.

Think radial distribution function but remember that it is not

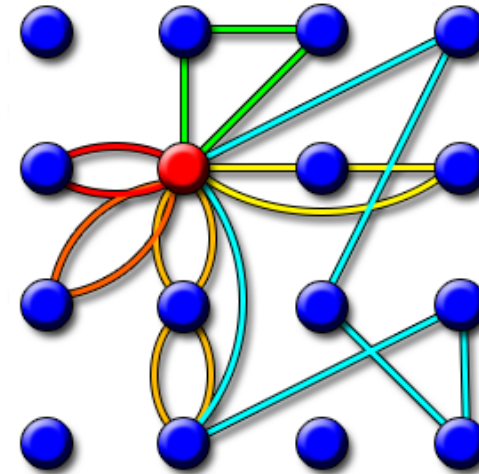
(Depends on e.g. multiple scattering, atom types, scattering factors, phase shift)



Real and imaginary parts

# Interpretation

- Multiple Scattering Theory:



$$\chi(k) = \sum_i \chi_i(k)$$

with each path written as:

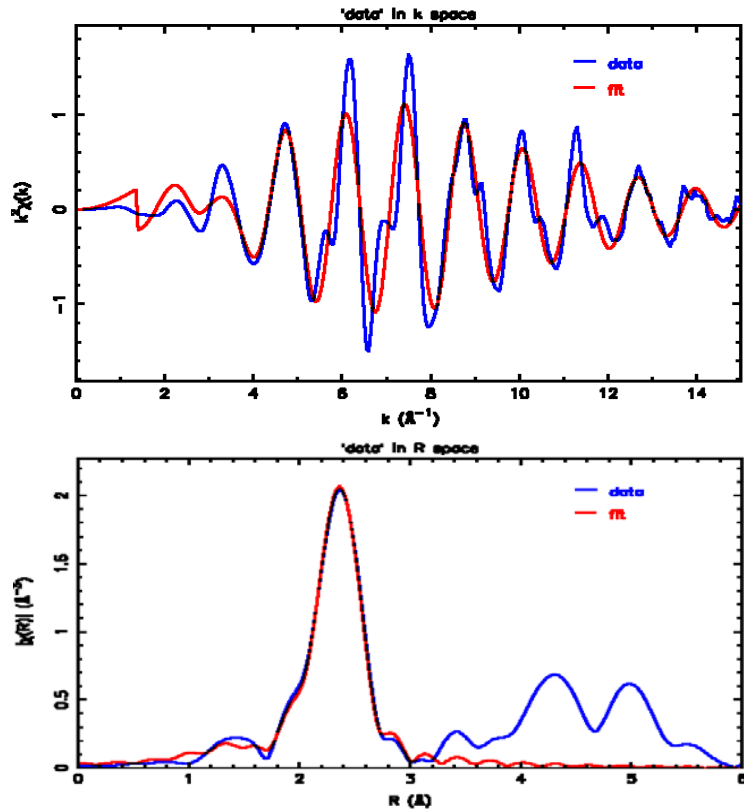
$$\chi_i(k) = \left( \frac{(N_i S_0^2) F_i(k)}{k R_i^2} \sin(2k R_i + \varphi_i(k)) \exp(-2\sigma_i^2 k^2) \exp(-2R_i/\lambda(k)) \right)$$

$$R_i = R_0 + \Delta R$$

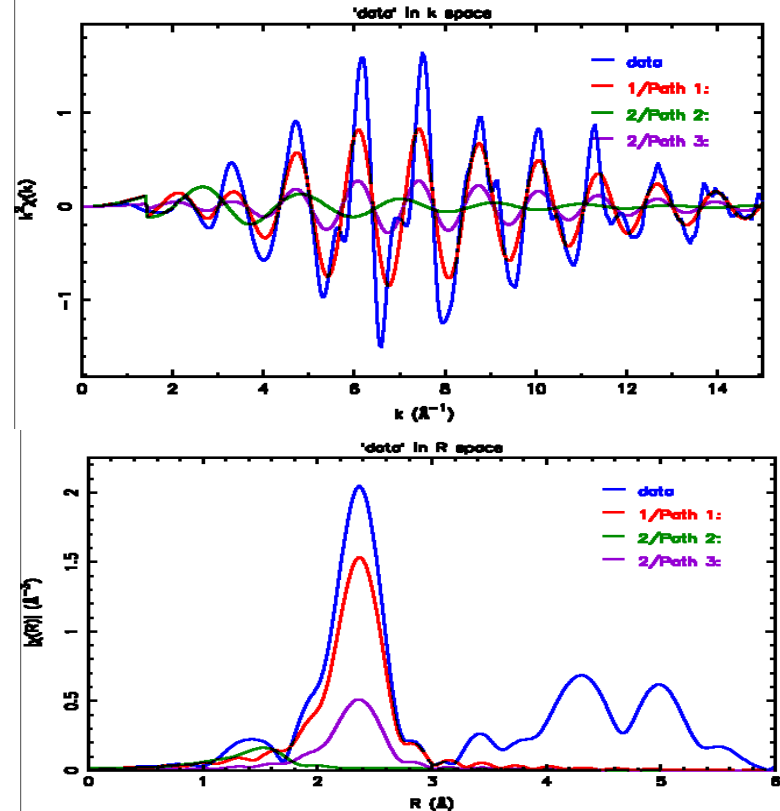
$F_i(k)$  effective scattering amplitude  
 $\varphi_i(k)$  effective scattering phase shift  
 $\lambda(k)$  mean free path  
 $R_0$  initial path length

$N_i$  degeneracy of path  
 $S_0^2$  passive electron reduction factor  
 $E_0$  energy shift  
 $\Delta R$  change in half-path length  
 $\sigma_i^2$  mean squared displacement

# Modelling

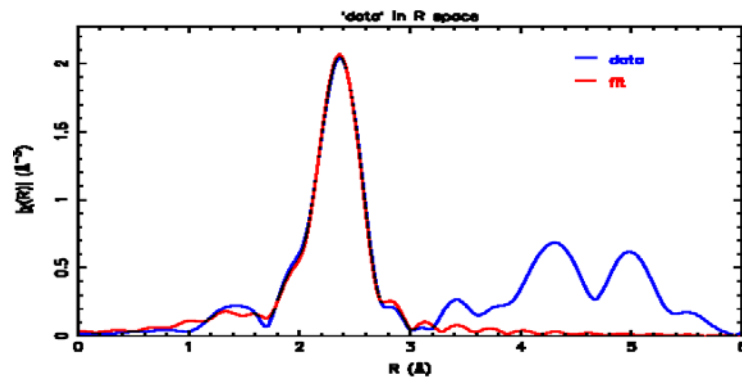
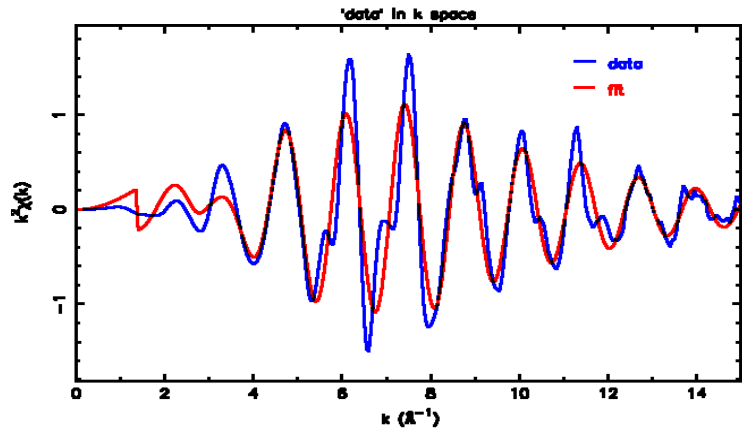


Including only the first short scattering paths

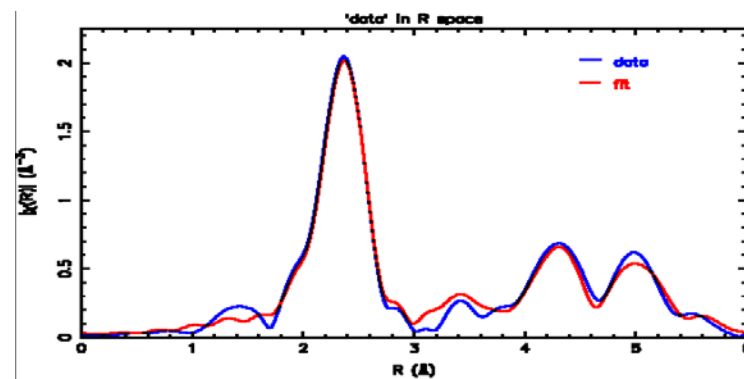
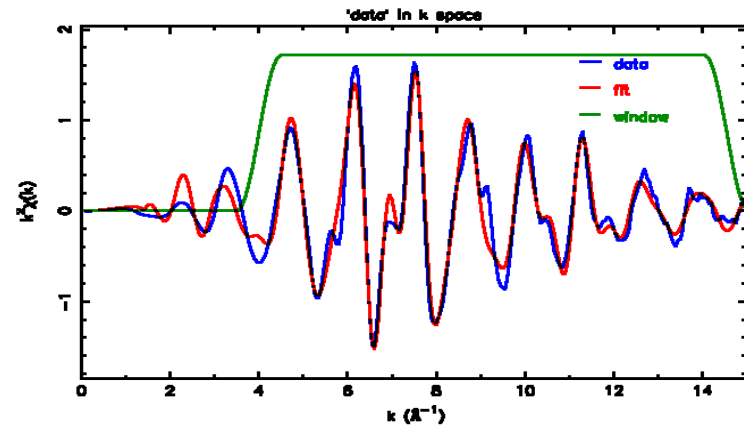


Individual contributions

# Modelling



Including only the first short scattering paths



Adding additional paths

# What can we see with EXAFS?

- EXAFS probes the local environment (within a radius of 5-7Å) around a specific element with very high accuracy.
- Structural information is obtained from a model fitted to the EXAFS data

$$\chi(k) = \sum_j \frac{N_j S_0^2(k)}{k R_j^2} \cdot |f_j^{eff}(k)| \cdot \exp(-2k^2 \sigma_j^2) \cdot \exp\left(\frac{-2R_j}{\Lambda(k)}\right) \cdot \sin(2kR_j - \phi_{ij}(k))$$

$$E_0, R_j = R_j + \Delta R_j$$

- Least squares minimization:

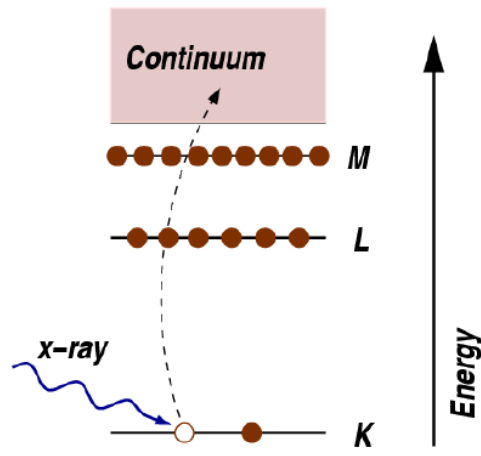
$$\chi^2 = \sum_k [\chi_{Data}(k) - \chi_{Model}(k)]^2$$

$$\chi^2 = \sum_R \left( \sum_k [Re_{Data}(R) - Re_{Model}(R)]^2 + \sum_k [Im_{Data}(R) - Im_{Model}(R)]^2 \right)$$

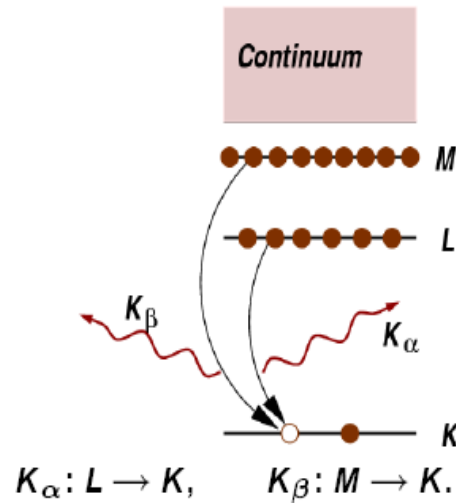
# Which samples can be studied by XAFS?

- The sample requires a presence of an element with an accessible elemental absorption edge
- Concentration of the absorbing element must be high enough
- No need for crystalline samples. The physical state can be of any type (crystals, micro crystals, amorphous solids, liquids, solutions, tissue, cells,...) but must be homogeneous.
- Must be stable in the beam, and radiation damage must be avoided
- Applications within:
  - Biology (metalloproteins, tissue, cells)
  - Catalysis (active sites)
  - Environmental science (trace metals)
  - Pharmaceuticals

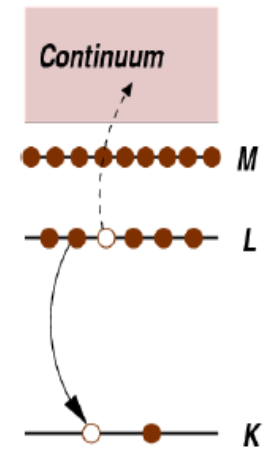
# The absorption of an x-ray photon



Absorption



Fluorescence



Auger effect

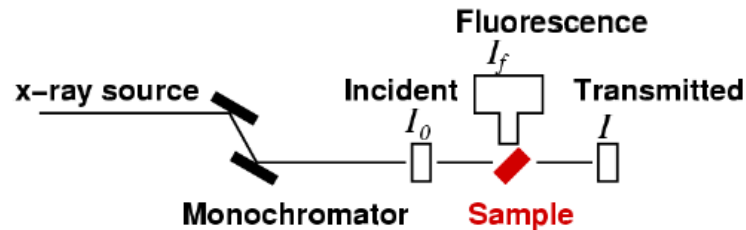


# Data collection mode

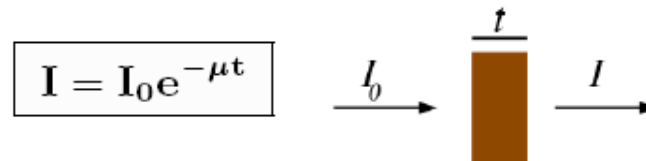
- Transmission:
  - Concentrated samples ( $> 10\%$ )
  - Thickness corresponding to edge step of about 1
    - E.g.  $7\ \mu\text{m}$  for pure Fe. Dilute samples thickness in mm range
- Fluorescence:
  - Dilute samples, down to ppm levels
  - Self-absorption may dampen XAFS oscillations
    - Fluorescent radiation is re-absorbed in the sample and does not reach the detector

# Experimental setup

Typical experiment:



Transmission of intensity through a material:



Absorption (high concentration):  $\mu(E) \propto \log\left(\frac{I_0}{I}\right)$

Fluorescence (low concentration):  $\mu(E) \propto \frac{I_f}{I_0}$

# XAFS at Beamline I811

## Experiment station



1 Hydrogen 1	2 Helium 2	3 Lithium 3	4 Beryllium 4	5 Boron 5	6 Carbon 6	7 Nitrogen 7	8 Oxygen 8	9 Fluorine 9	10 Neon 10	11 Sodium 11	12 Magnesium 12	13 Aluminum 13	14 Silicon 14	15 Phosphorus 15	16 Sulfur 16	17 Chlorine 17	18 Argon 18	
19 Potassium 19	20 Calcium 20	21 Scandium 21	22 Titanium 22	23 Vanadium 23	24 Chromium 24	25 Manganese 25	26 Iron 26	27 Cobalt 27	28 Nickel 28	29 Copper 29	30 Zinc 30	31 Gallium 31	32 Germanium 32	33 Arsenic 33	34 Selenium 34	35 Bromine 35	36 Krypton 36	
37 Rubidium 37	38 Strontium 38	39 Yttrium 39	40 Zirconium 40	41 Niobium 41	42 Molybdenum 42	43 Technetium 43	44 Ruthenium 44	45 Rhodium 45	46 Palladium 46	47 Silver 47	48 Cadmium 48	49 Indium 49	50 Tin 50	51 Antimony 51	52 Tellurium 52	53 Iodine 53	54 Xenon 54	
55 Cesium 55	56 Barium 56	57-70 Lanthanoids	71 Lutetium 71	72 Hafnium 72	73 Tantalum 73	74 Tungsten 74	75 Rhenium 75	76 Osmium 76	77 Iridium 77	78 Platinum 78	79 Gold 79	80 Mercury 80	81 Thallium 81	82 Lead 82	83 Bismuth 83	84 Polonium 84	85 Astatine 85	86 Radon 86
87 Francium 87	88 Radium 88	89-102 Actinoids	103 Lawrencium 103	104 Rutherfordium 104	105 Dubnium 105	106 Seaborgium 106	107 Bohrium 107	108 Hassium 108	109 Meitnerium 109	110 Darmstadtium 110	111 Roentgenium 111	112 Copernicium 112	113 Nihonium 113	114 Flerovium 114	115 Moscovium 115	116 Livermorium 116	117 Tennessine 117	118 Oganesson 118

\*lanthanoids

\*\*actinoids

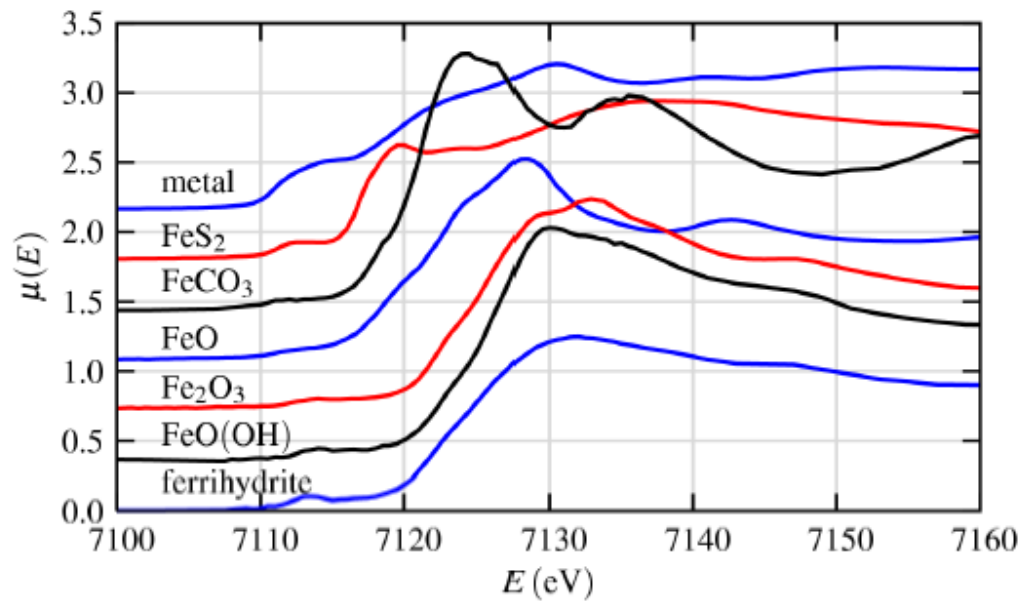
lanthanum 57 138.91	cerium 58 140.12	praseodymium 59 140.91	neodymium 60 144.24	promethium 61 144.91	samarium 62 150.36	europium 63 151.96	gadolinium 64 157.25	terbium 65 158.93	dysprosium 66 162.50	holmium 67 164.93	erbium 68 167.26	thulium 69 168.93	ytterbium 70 173.04
actinium 89 227.03	thorium 90 232.04	protactinium 91 231.04	uranium 92 238.03	neptunium 93 237.05	plutonium 94 244.06	americium 95 243.06	curium 96 247.07	berkelium 97 247.07	californium 98 251.08	einsteinium 99 252.08	fermium 100 257.09	mendelevium 101 258.10	nobelium 102 259.10

**K-edge:** S K-edge to As K-edge  
**L-edge:** Zr L-edge to Au L-edge

**K-edge:** Fe K-edge to Mo K-edge  
**L-edge:** Lu L-edge to Am L-edge

Beam ~ 1 mm wide

# Scientific results – XANES data

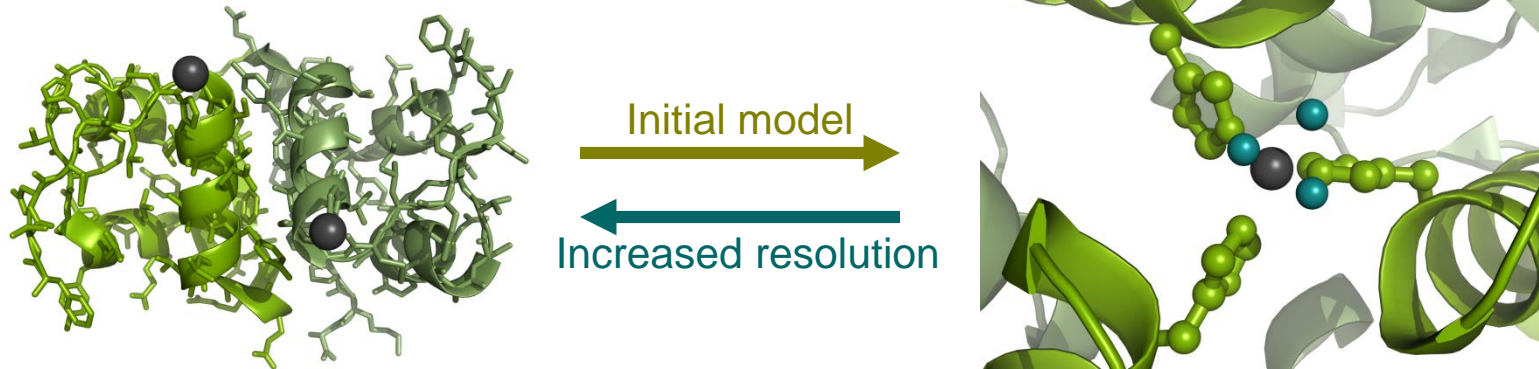


# XRD and XAS studies on insulin

Ph. D. Christian Grundahl Frankær

*" Characterization of Metalloproteins and Biomaterials by X-ray Absorption Spectroscopy and X-ray Diffraction"*

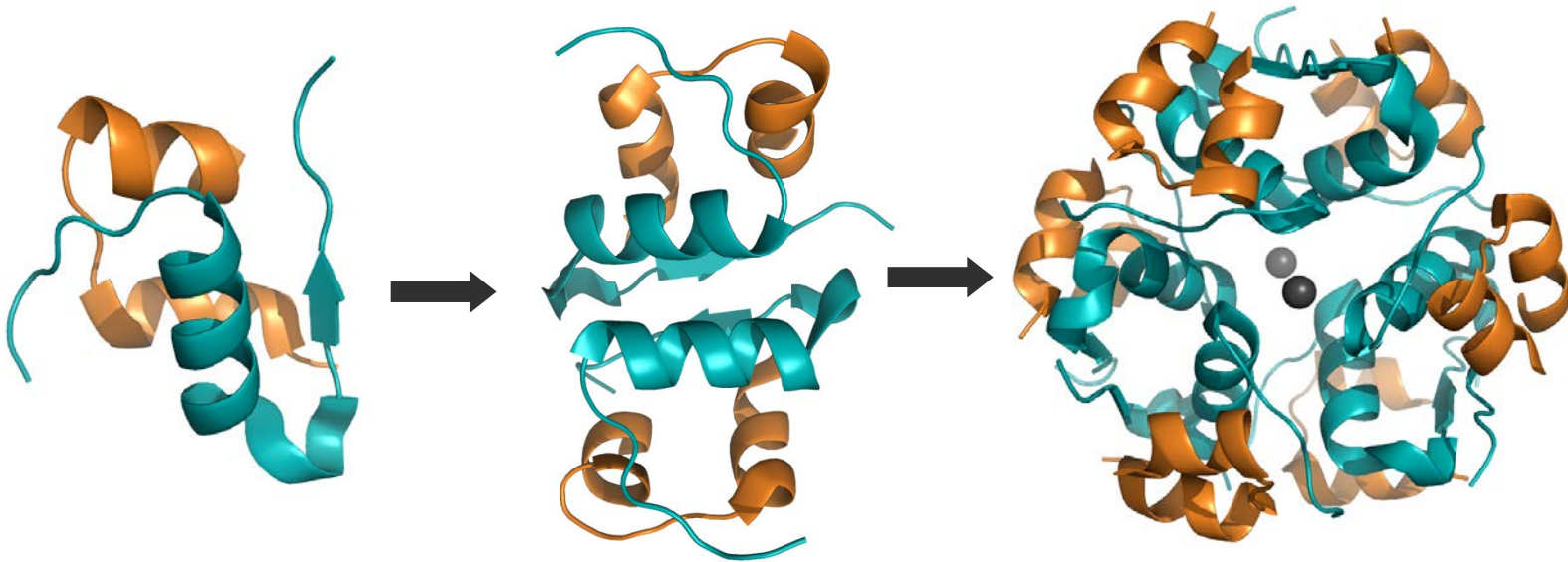
# Complementarity between XRD and XAS



- Single crystal X-ray diffraction
  - Three dimensional structure of the entire protein
  - High level of details, but often not at atomic resolution
  - Requires single crystals of high quality
- X-ray absorption spectroscopy
  - Local structure of the metal cluster (within a radius of 5–7 Å)
  - Ultra high resolution (distances can be determined within accuracies of 0.01 Å)
  - No crystals are required
  - Requires a good starting model

# Insulin

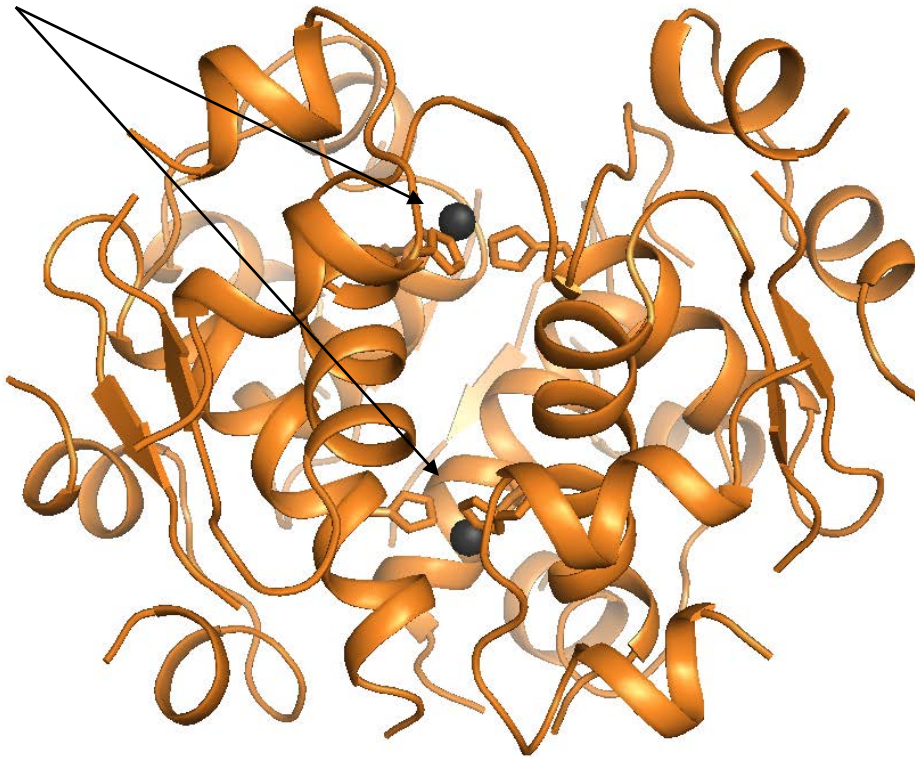
- Monomer (5740 Da) consists of two peptide chains (**A = 21 residues** and **B = 30 residues**) connected by three disulfide bonds
- Monomers assemble to dimers
- Dimers assemble to hexamers in presence of divalent metal ions



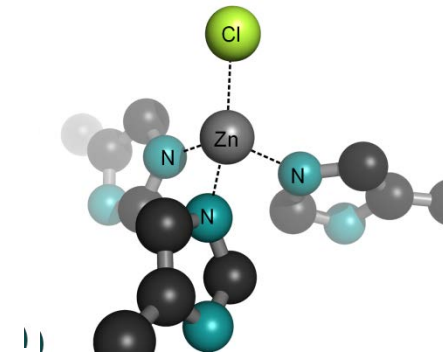
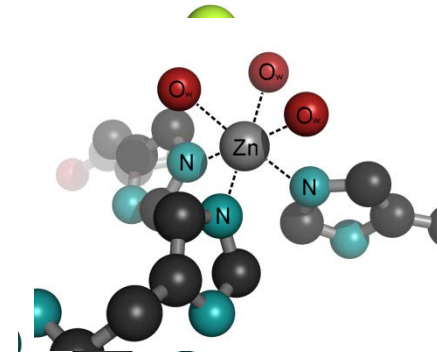


# Insulin hexamer conformations: $M^{2+}$ sites

$M^{2+}$  coordinated to three histidine residues



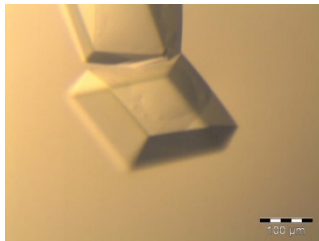
One  $M^{2+}$  octahedral the  
Both  $M^{2+}$  tetrahedral  
Other tetrahedral



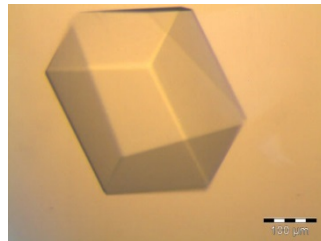


# Single crystal X-ray diffraction

- Crystallization
- Crystal growth



T<sub>6</sub>-insulin



R<sub>6</sub>-insulin

- Data collection
  - MAX-lab, beam-line 911-2

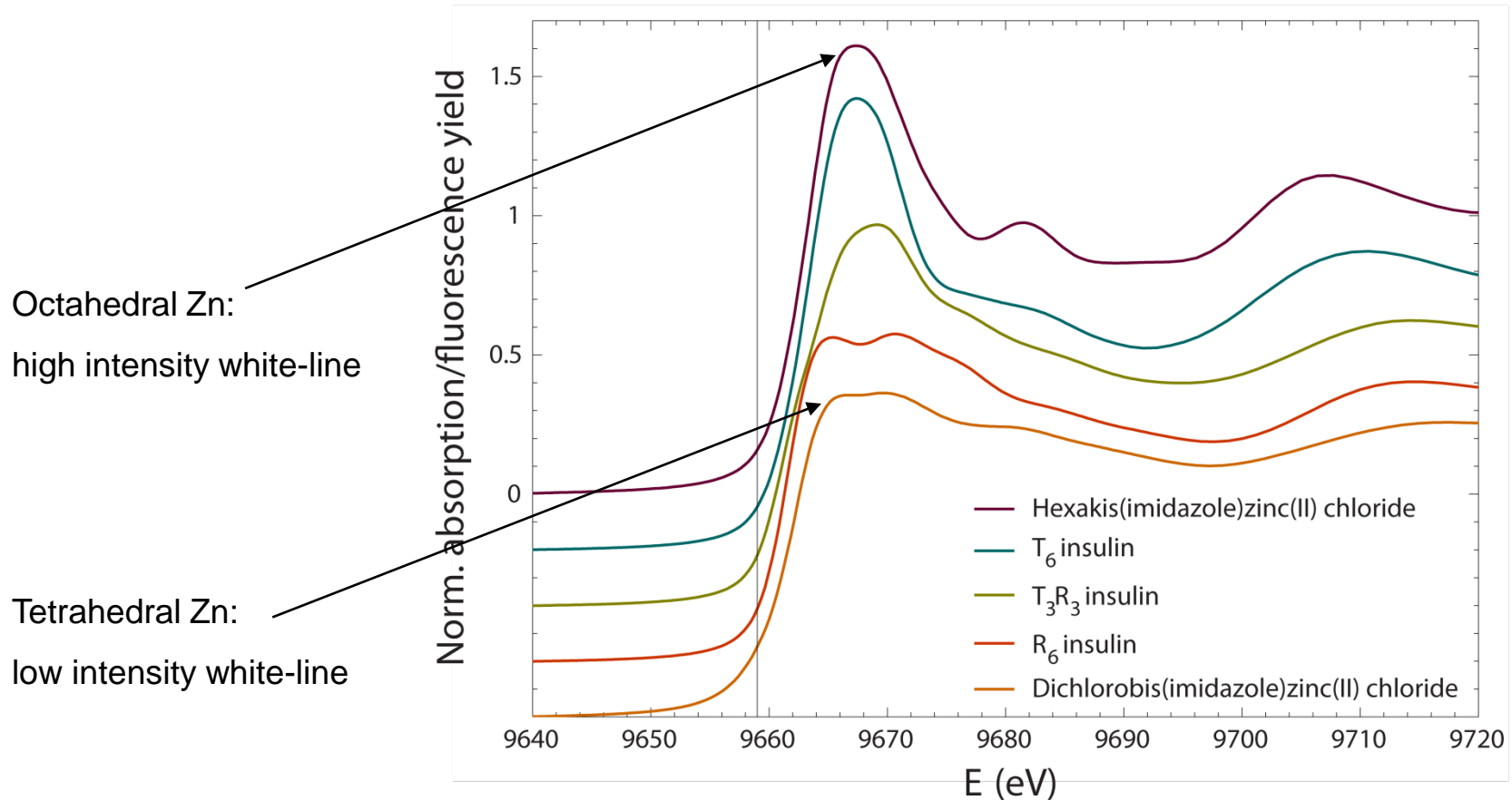
## Crystal structures

	T <sub>6</sub>	T <sub>3</sub> R <sub>3</sub>	R <sub>6</sub>
Space group	<i>R3</i>	<i>R3</i>	<i>R3</i>
<i>a</i>	80.98 Å	79.20 Å	156.24 Å
<i>c</i>	33.49 Å	37.22 Å	78.88 Å
Molecules/as u	2	2	16
Resolution	1.40 Å	1.30 Å	1.80 Å
<i>R</i> <sub>merge</sub>	4.2 %	4.6 %	7.1 %
<i>I</i> / <i>σ</i> ( <i>I</i> )	19.28	14.68	11.65
<i>R</i>	0.1938	0.1439	0.2088
<i>R</i> <sub>free</sub>	0.2285	0.1794	0.2717

Medium resolution  
 → provide good  
 initial EXAFS  
 models

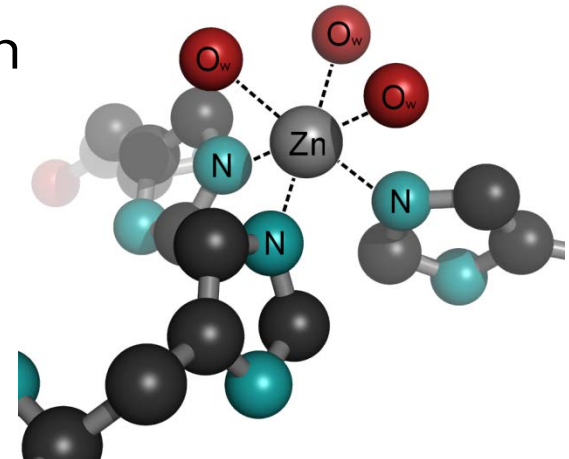
# Qualitative XANES

XANES is a signature of the coordination geometry



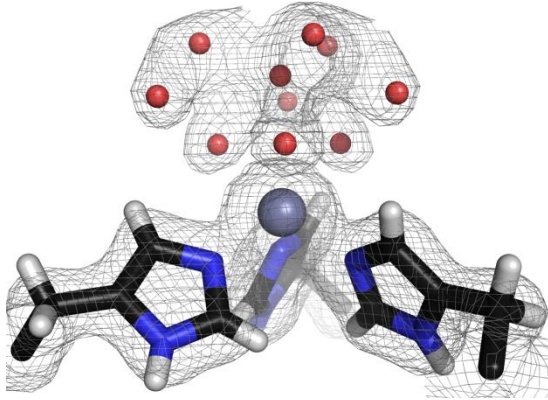
# EXAFS model building

- Coordinates from single crystal XRD structures used as initial model
- Atoms within a 5.6 Å radius from Zn included in the model
- Models were fitted in *EXCURVE*<sup>1</sup>
- Distances and temperature factors refined



<sup>1</sup>Binsted *et al.* (1991) *EXCURV92*. SERC, Daresbury Laboratory, Cheshire, UK

# EXAFS: T<sub>6</sub>-insulin

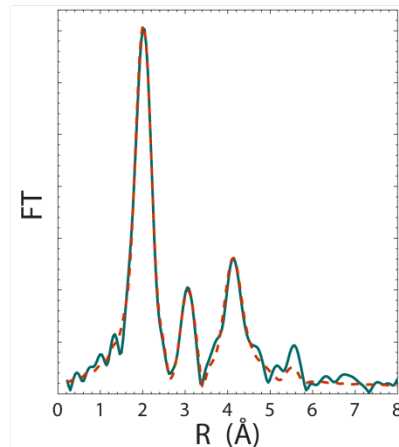
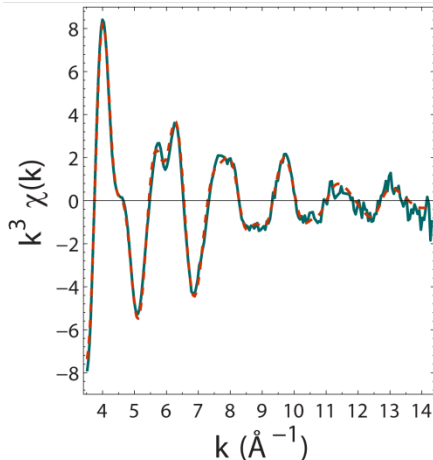


- Restrained refinement
- Octahedral coordination in both Zn sites
- $R = 0.1523$

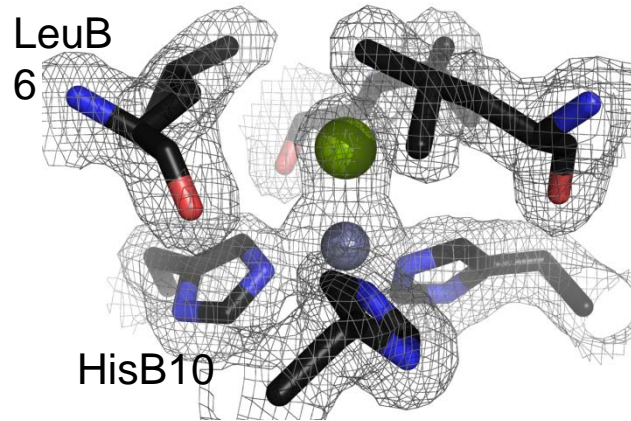
$N_p = 19$	XRD	EXAFS	
	R (Å)	R (Å)	$2\sigma^2$ (Å <sup>2</sup> )
N <sup>ε2</sup> (HisB10)	2.10	2.074(3)	0.012(1)
C <sup>ε1</sup>	3.03	3.07(4)	0.020(3)
C <sup>δ2</sup>	3.13	3.05(3)	0.020(3)
N <sup>δ1</sup>	4.17	4.22(2)	0.017(3)
C <sup>γ</sup>	4.26	4.22(3)	0.017(3)
C <sup>β</sup>	5.69	5.55(5)	0.017(3)
O <sup>w1</sup>	2.29	2.135(11)	0.030(1)
O <sup>w2</sup> (axial)	3.09	2.88(3)	0.021(10)

Extracted EXAFS

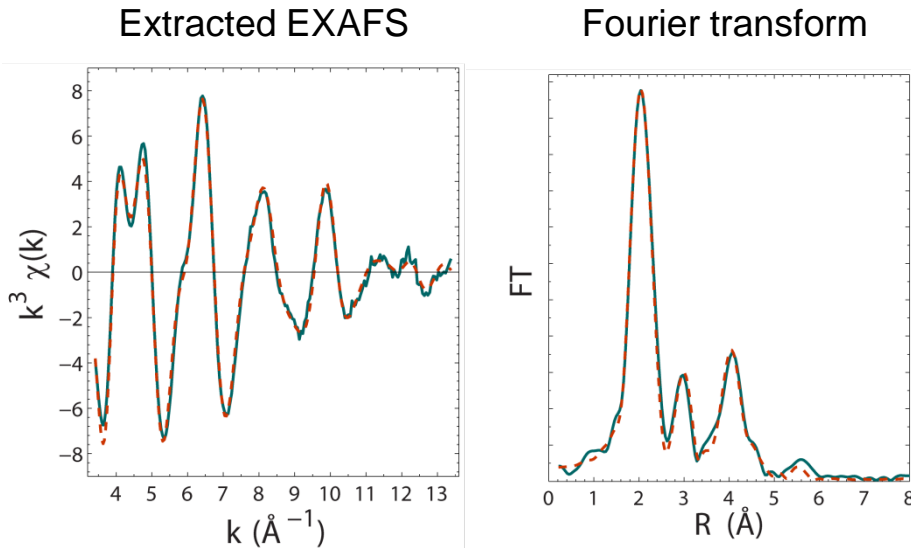
Fourier transform



# EXAFS: R<sub>6</sub>-insulin

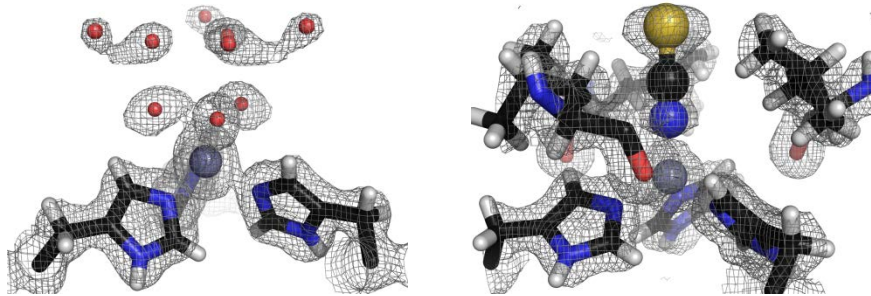


- Restrained refinement
- Tetrahedral coordination in both Zn sites
- $R = 0.1082$
- ~~$N_p = 19$~~



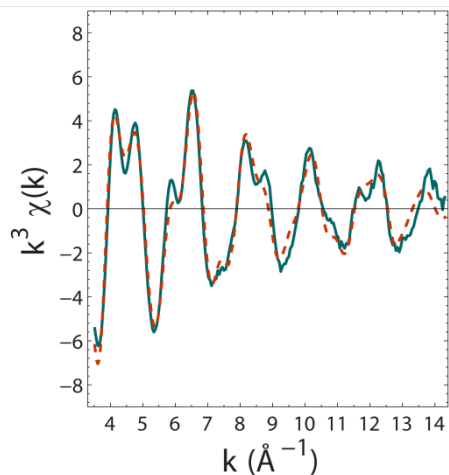
	XRD	EXAFS	
	R (Å)	R (Å)	2σ <sup>2</sup> (Å <sup>2</sup> )
N <sup>ε2</sup> (HisB10)	2.08	2.001(4)	0.007(1)
C <sup>ε1</sup>	3.09	2.98(2)	0.010(3)
C <sup>δ2</sup>	3.04	3.04(2)	0.010(3)
N <sup>δ1</sup>	4.18	4.15(1)	0.012(3)
C <sup>γ</sup>	4.19	4.14(2)	0.012(3)
C <sup>β</sup>	5.60	5.53(3)	0.012(3)
O (LeuB6)	4.87	4.90(5)	0.020(9)
Cl (axial)	2.21	2.218(3)	0.006(1)

# EXAFS: T<sub>3</sub>R<sub>3</sub>-insulin

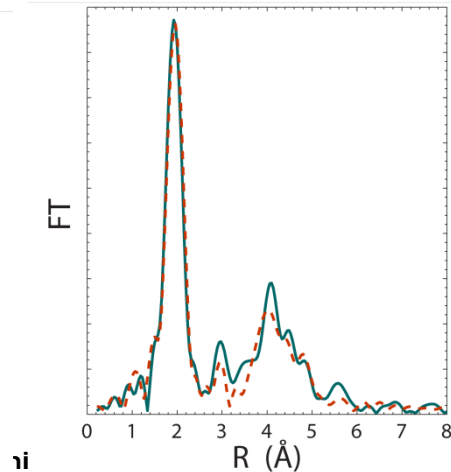


- Constant refinement
- Type II clusters
- Dual coordination with three sulfur coordination

Extracted EXAFS



Fourier transform



	XRD	EXAFS	
	R (Å)	R (Å)	2σ <sup>2</sup> (Å <sup>2</sup> )
N <sup>ε2</sup>	2.07	2.025(11)	0.014(1)
C <sup>ε1</sup>	3.05	2.84	0.018(1)
C <sup>δ2</sup>	3.05	3.16	0.018(1)
N <sup>δ1</sup>	4.16	4.03	0.028(4)
C <sup>γ</sup>	4.20	4.21	0.028(4)
C <sup>β</sup>	5.61	5.66	0.030(3)
O <sup>w1</sup>	2.47	2.289(15)	0.035(5)
N <sup>ε2</sup>	2.02	1.987(11)	0.014(1)
C <sup>ε1</sup>	2.99	2.99	0.018(1)
C <sup>δ2</sup>	3.03	2.96	0.018(1)
N <sup>δ1</sup>	4.10	4.09	0.028(4)
C <sup>γ</sup>	4.16	4.11	0.028(4)
C <sup>β</sup>	5.58	5.52	0.030(3)
N (SCN)	1.83	1.802(9)	0.014(1)
C (SCN)	2.98	2.96	0.018(1)
S (SCN)	4.72	4.69	0.017(3)

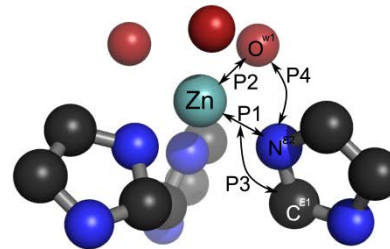
# Quantitative fitting of XANES

- Performed for T<sub>6</sub> and R<sub>6</sub>-insulin
- Calculation of XANES spectra on 4.5 Å clusters (from EXAFS models) using the FDM-methods, *FDMNES*<sup>1</sup>
- Structural parameters (distances and angles) were optimized by a multidimensional interpolation, *FitIt*<sup>2</sup>
- Optimized distances were in agreement with EXAFS results
- Optimized angles differed with up to 10° from the EXAFS results

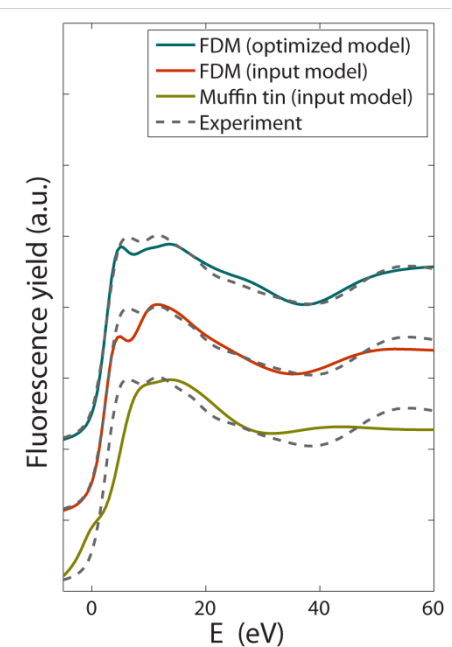
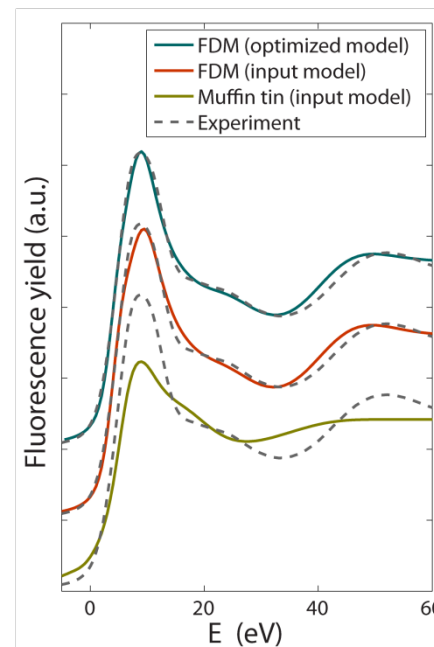
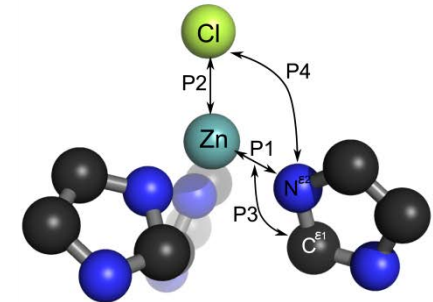
<sup>1</sup>Joly (2001), *Phys. Rev. B* **63**, 125120.

<sup>2</sup>Smolentsev & Soldatov (2007), *Comp. Mat. Sci.* **39**, 569–574.

T<sub>6</sub>-insulin



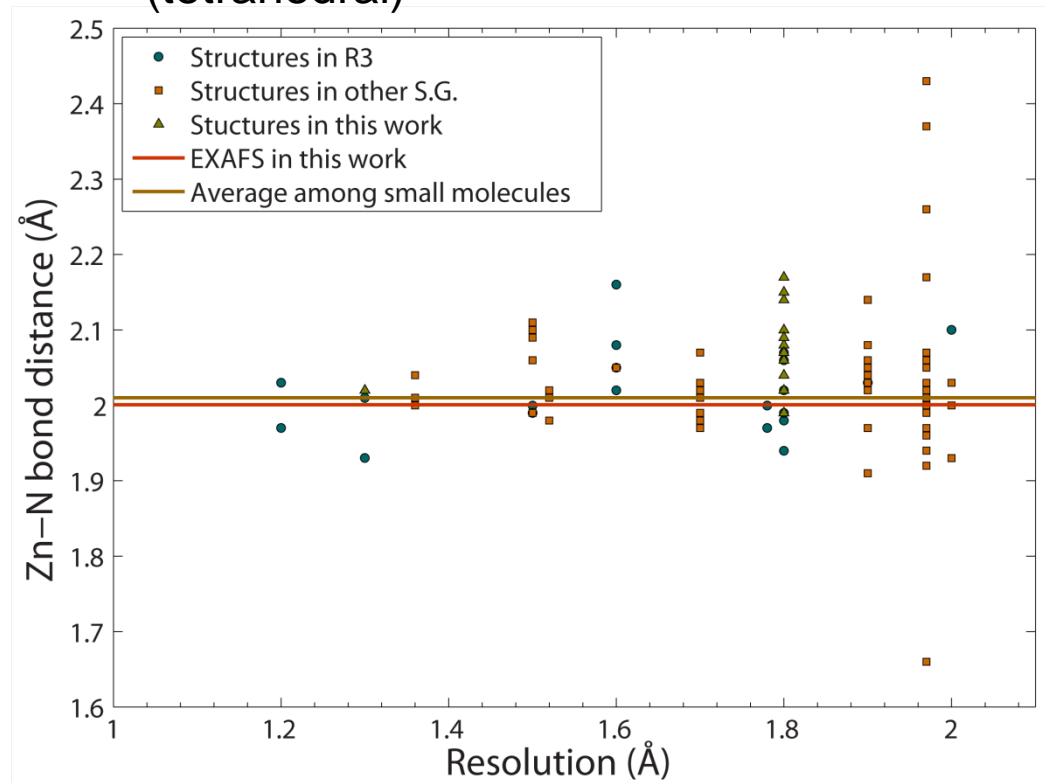
R<sub>6</sub>-insulin



# Comparison of XRD and XAS results with other reported Zn-site geometries

- The accuracy of XRD results depends on resolution of XRD structure
- EXAFS results are closer to the Zn-distances reported in small molecules, i.e. more accurate
- Large discrepancies between XRD and XAS results observed for the Zn–O<sup>w</sup> distance in the 'loose' octahedral T<sub>3</sub>-sites.

Zn–N distances in R<sub>3</sub>-sites (tetrahedral)





# *In-situ* spectroscopic studies of Chromium Catalysts in Ionic Liquids

ATR-FTIR coupled with EXAFS

# Intro

- Glucose isomerization to fructose and following conversion to 5-(hydroxymethyl)furfural (HMF) is catalyzed by a Chromium species in the ionic liquid 1-butyl-3-methyl-imidazolium chloride ([BMIm]Cl).

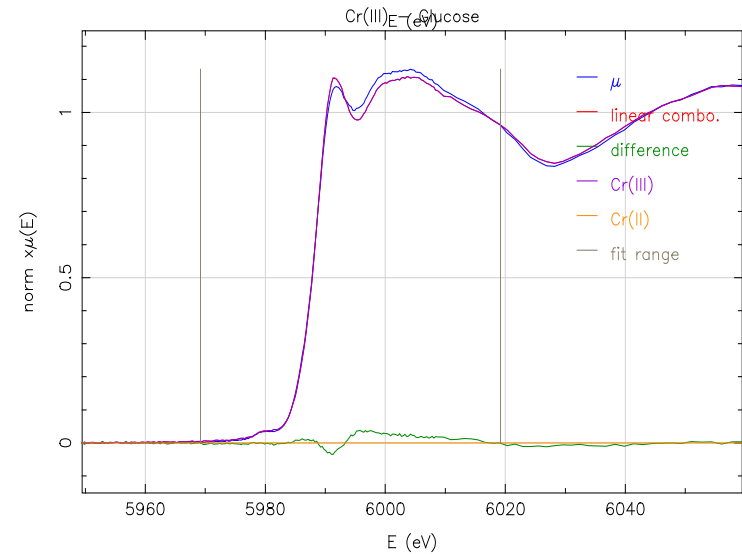
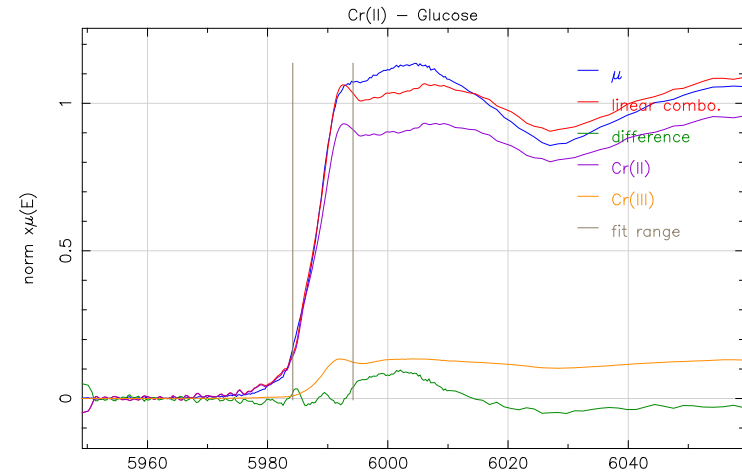


- Controversy regarding coordination sphere and oxidation number.
- EXAFS and XANES can provide information regarding coordination sphere and oxidation state.
- *In-situ* ATR-FTIR can provide information regarding the reaction kinetics.

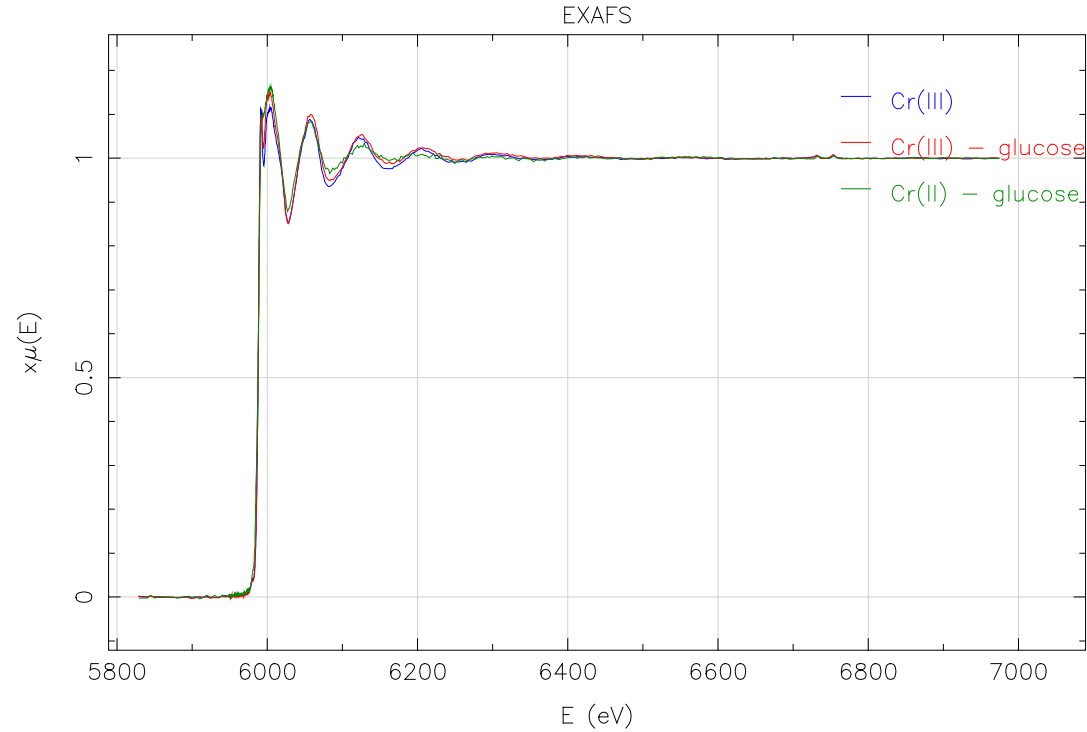
# XANES

- Linear combination fit of Cr(II) and Cr(III) with glucose in [BMIm]Cl

Sample	Cr(II)/[BMIm] Cl/Glucose	Cr(III)/[BMIm] Cl/Glucose
Cr(II) amount	0.879(0.039)	0.000 (0.000)
Cr(III) amount	0.121(0.039)	1.000 (0.000)

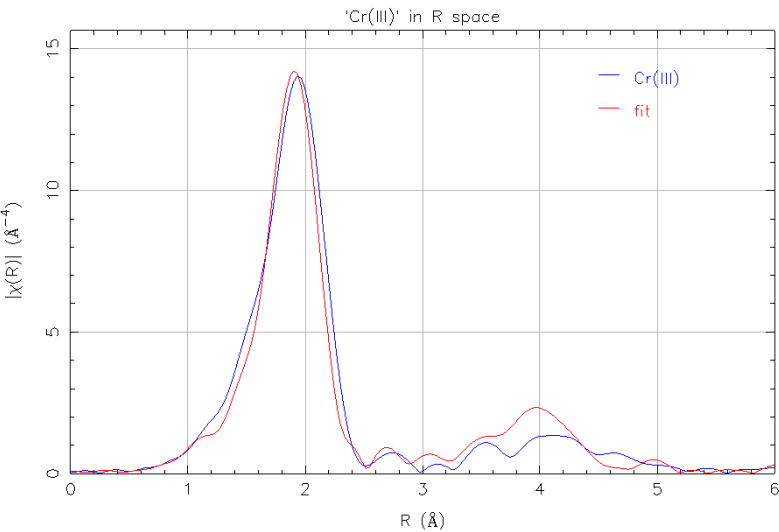


# Background corrected EXAFS data

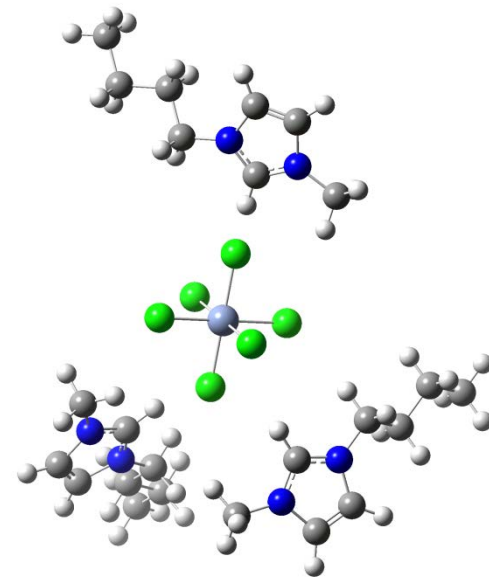


# EXAFS – $[\text{CrCl}_6]^{3-}$ in $[\text{BMI m}]\text{Cl}$

## EXAFS fit



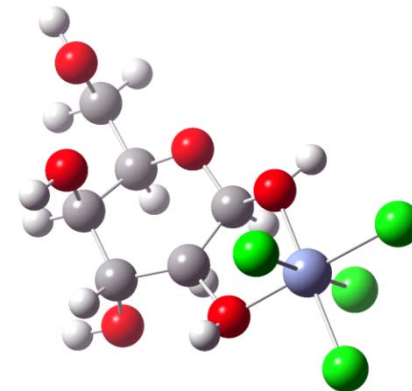
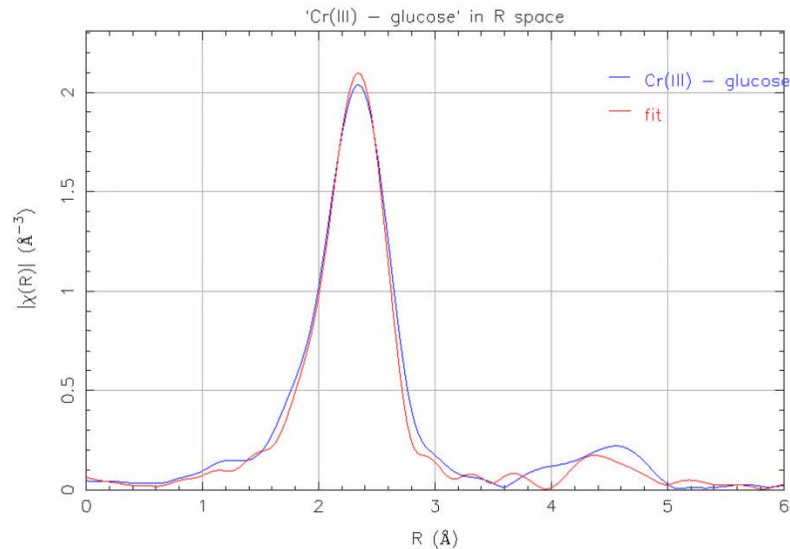
## Schematic drawing



# EXAFS – $[\text{CrCl}_4\text{Glu}]^-$ in $[\text{BmIm}]\text{Cl}$

## Schematic drawing

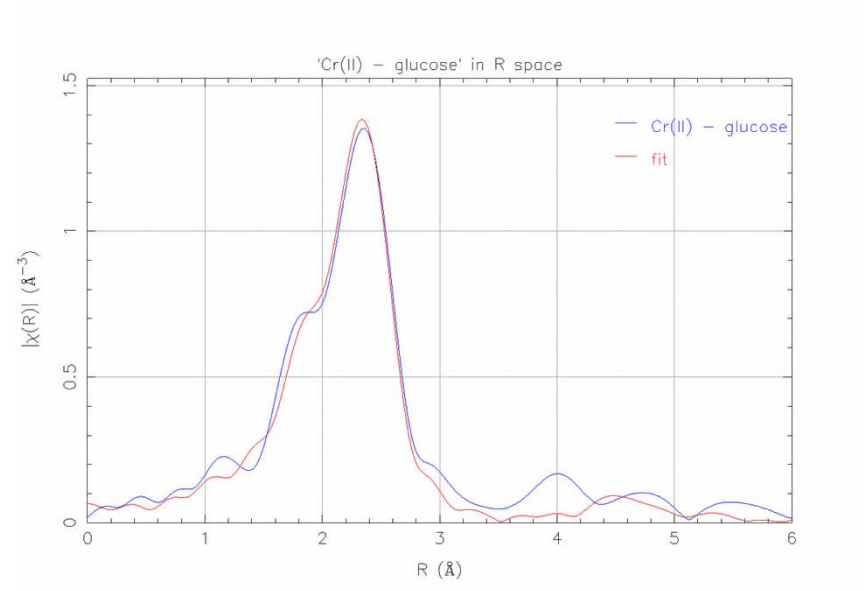
### EXAFS fit



# EXAFS – $[\text{CrCl}_4\text{Glu}]^{2-}$ in $[\text{BMIm}]\text{Cl}$

JT-distorted Cr(II) and Cr(III) (as determined by XANES)

	Bond	Distance (Å)
<b>Tetrachloroglucose chromate(II)</b>	Cr-Cl	2.30
	Cr-Cl <sub>z</sub>	2.40
	Cr-O	1.99
<b>Tetrachloroglucose chromate(III)</b>	Cr-Cl	2.35
	Cr-O	1.93

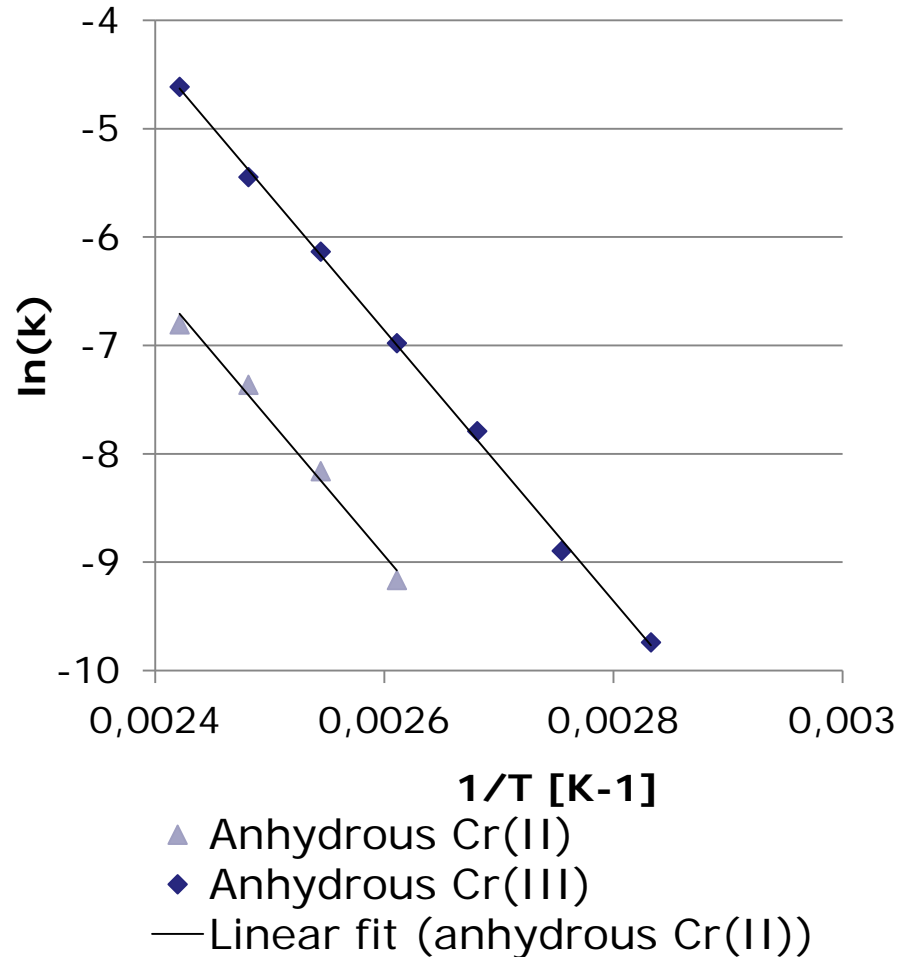


# IR results

Arrhenius plot for the Cr catalyzed reaction.

The Cr(II) reaction is approximate 8 times slower than the Cr(III) reaction. However with exactly same activation energy.

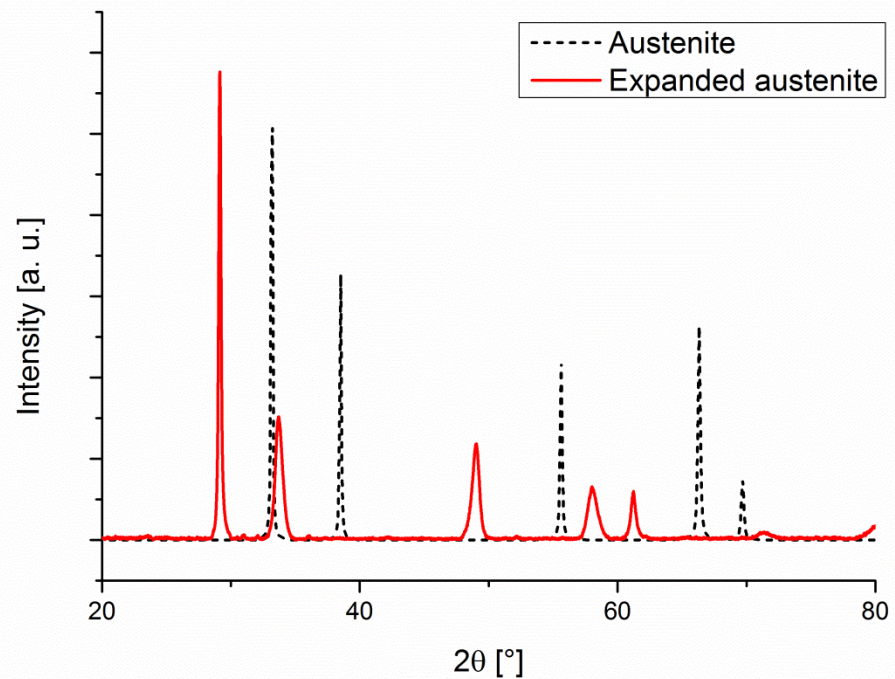
Coupled with XANES results the oxidation state has been determined to be



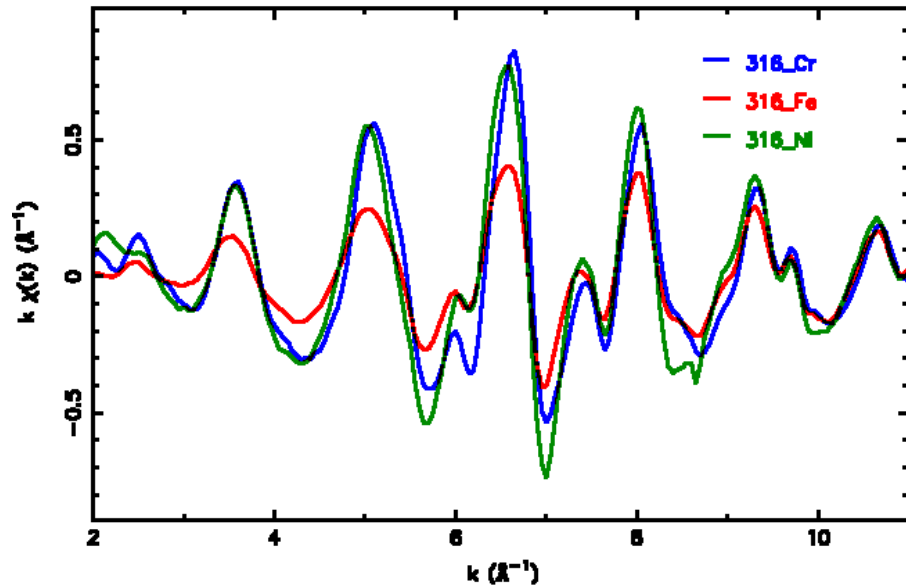


# Nitrogen stabilized expanded austenite

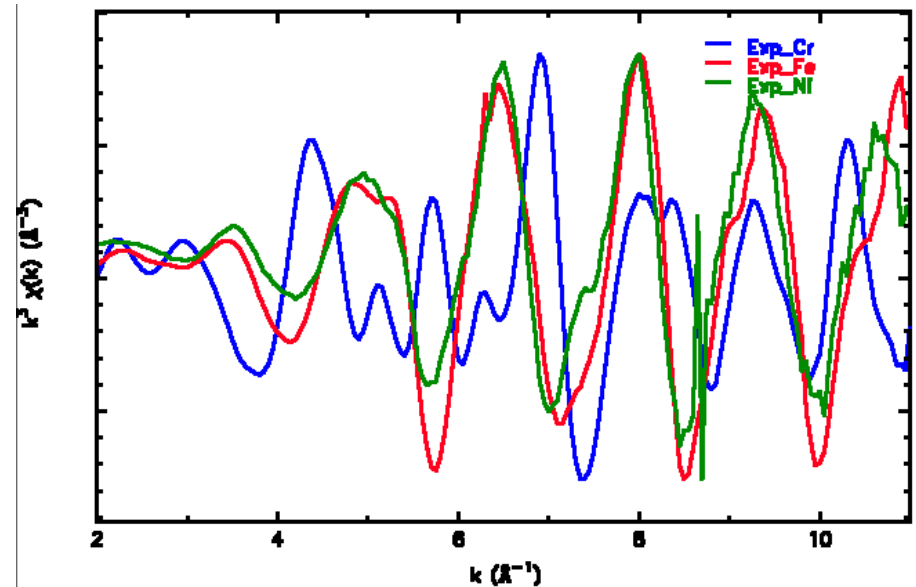
- Austenitic stainless steel
  - *fcc* structure of Fe,Cr,Ni
  - Identical metallic local environments
- Nitriding in  $\text{NH}_3$  atmosphere
  - Solid solution of N
  - Lattice expansion



# Nitrogen stabilized expanded austenite



Untreated steel



Nitrided

Exercise 2 !

## Exercises:

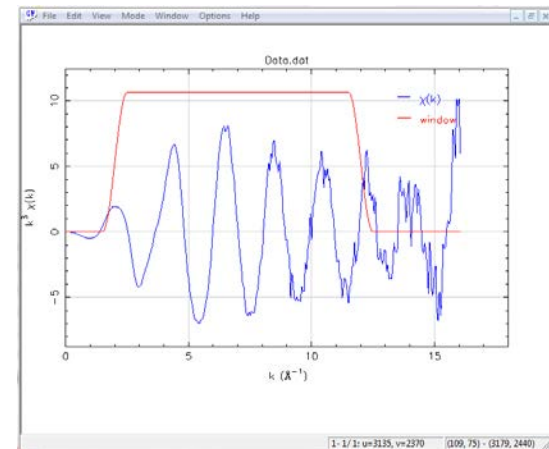
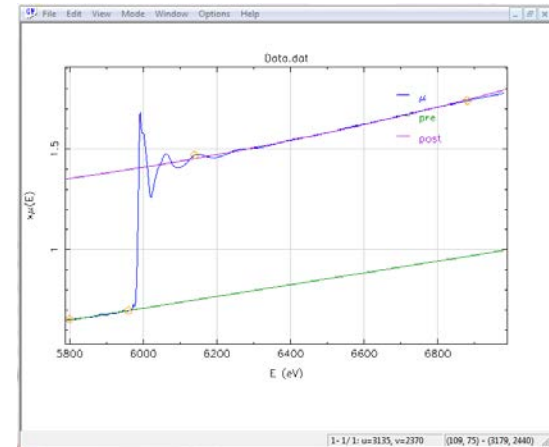
- 1: Fluorescence spectrum of aqueous solution of  $\text{Cr}^{2+}$
- 2: Transmission spectrum: Expanded austenite (Cr and Fe data)
- Raw data -> Normalization, background-removal -> Modelling

# Programs: Athena (Data reduction)

The screenshot shows the Athena software interface with several panels:

- Project:** Current group: Data.dat; File: EXAFS x/EXAFS presentation/[Cr(H2O)6]2+/Cra9\_1\_1.dat; Z: Cr; Edge: K; E shift: -41.9; Importance: 1.
- Background removal:** E0: 5989; Rbkg: 1; k-weight: 2; Edge step: 0.69994; Pre-edge range: -190.067 to -30; Normalization range: 150 to 890.23; Step range: k: 0 to 16; E: 0.000 to 975.356.
- Forward Fourier transform:** k-range: 2 to 13; dk: 1; window type: hanning.
- Backward Fourier transform:** R-range: 1 to 3; dr: 0.0; window type: hanning.
- Plotting parameters:** plot multiplier: 1; y-axis offset: 0.

Two large grey circles highlight the 'Background removal' and 'Forward Fourier transform' sections. A central control panel is also visible, showing buttons for E, k, R, q, kq and a 'Plotting options' section with checkboxes for mu(E), background, pre-edge line, post-edge line, Normalized, and Derivative.



# Programs: Artemis (Modelling)

Artemis

File Edit GDS Data Sum Fits Theory Paths Plot Help

Current project:

Atoms feff.inp Interpretation

Interpretation of the FEFF Calculation

# TITLE ...  
 # Central atom: Chromium (24) K edge energy = 5989 eV  
 # The central atom is denoted by this token. [+]  
 # Cluster size = 20.0 Angstroms, containing 195 atoms.  
 # Curved wave criteria = 2.5.

#	Deg	Reff	amp	fs	Scattering Path
1	6	2.000	100.00		[+] O_1 [+]
2	24	3.414	18.72		[+] O_1 O_1 [+]
3	6	4.000	16.27		[+] O_1 O_1 [+]
4	6	4.000	16.00	1	[+] O_1 [+] O_1 [+]
5	6	4.000	5.37		[+] O_1 [+] O_1 [+]
7	24	4.828	7.64		[+] O_1 O_1 O_1 [+]
8	24	4.828	14.11		[+] O_1 O_1 O_1 [+]
10	48	5.414	3.19		[+] O_1 O_1 O_1 [+]
11	6	6.000	2.83		[+] O_1 O_1 O_1 [+]
13	12	8.000	4.52	1	[+] O_2 O_1 [+]
17	12	10.000	2.95	1	[+] O_2 O_1 [+]
25	24	10.198	4.51		[+] O_3 [+]
26	48	10.222	7.04	1	[+] O_3 O_1 [+]
27	24	10.246	2.88	2	[+] O_1 O_3 O_1 [+]
28	48	10.513	2.72		[+] O_3 O_2 [+]

Document: Feff interpretation

Loaded parameter list from GDS page

Data & Paths

Guess, Def, Set

Craq\_1\_1.chi

- Fit
- fit 1
- FEFF0
- Path 1: [O\_1]:1
- Path 4: [O\_1 [+] O\_1]
- Path 2: [O\_1 O\_1]
- Path 3: [O\_1 O\_1]
- Path 5: [O\_1 [+] O\_1]
- Path 7: [O\_1 O\_1 O\_1]
- Path 8: [O\_1 O\_1 O\_1]
- Path 10: [O\_1 O\_1 O\_1]
- Path 11: [O\_1 O\_1 O\_1]

Fit

Plot selected groups in

k R q

Plotting options

0 0 1 2 3 kw

Main Indic Traces

Plot in R:  Magnitude  Real part  Imaginary part

Plot in q:  Magnitude  Real part  Imaginary part

Window  Background  Residual

kmin: 0 kmax: 15  
 Rmin: 0 Rmax: 6  
 qmin: 0 qmax: 15

Document: Plotting

Current project:

#	Name	Math Expression
1	g: amp	0.7
2	g: enot	0
3	g: delr	0
4	g: ss	0.003
5	g: delr2	0
6	g: ss2	0.003

etc

Edit selected parameter

[ ] = [ ]

Guess  Def  Set  Skip  Restrain  After

Undo edit New Grab Discard Hide

Document: Guess, Def, Set

Path parameter math expressions

label: [ ]

N: 6  S02: amp

delE0: enot

delR: delr

sigma^2: ss

Ei: [ ]

3rd: [ ]

4th: [ ]