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X-ray absorption spectroscopy: from synchrotron radiation to short-range order determination

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[3]*Helmholtz-Zentrum Berlin*

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Outline

Synchrotron radiation
    X-ray absorption spectroscopy

Short-range order and local distortions

Results on $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$
- Theoretical
- Experimental

Conclusions and general remarks

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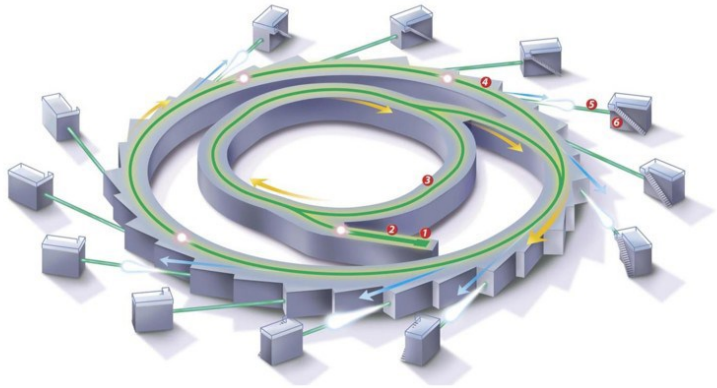
The magic world of synchrotrons



1. Electron Gun
2. Linac
3. Booster Ring
4. Storage Ring
5. Beamline
6. End station

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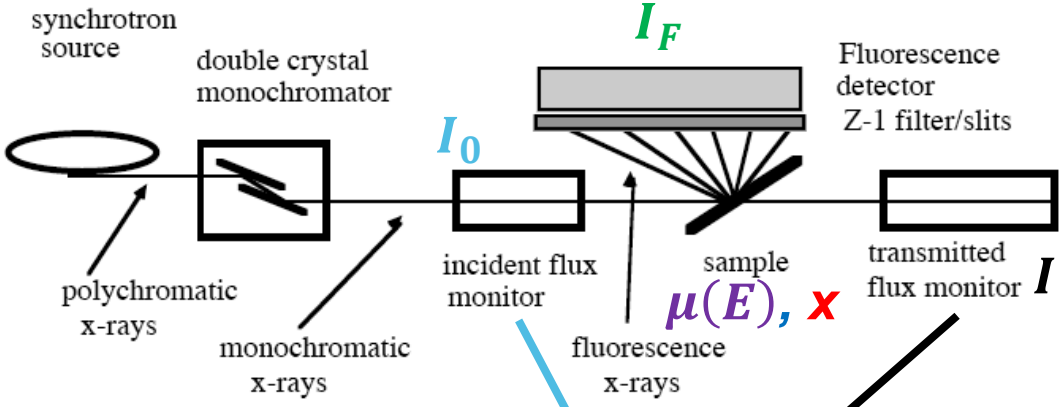
X-ray absorption spectroscopy I: setup



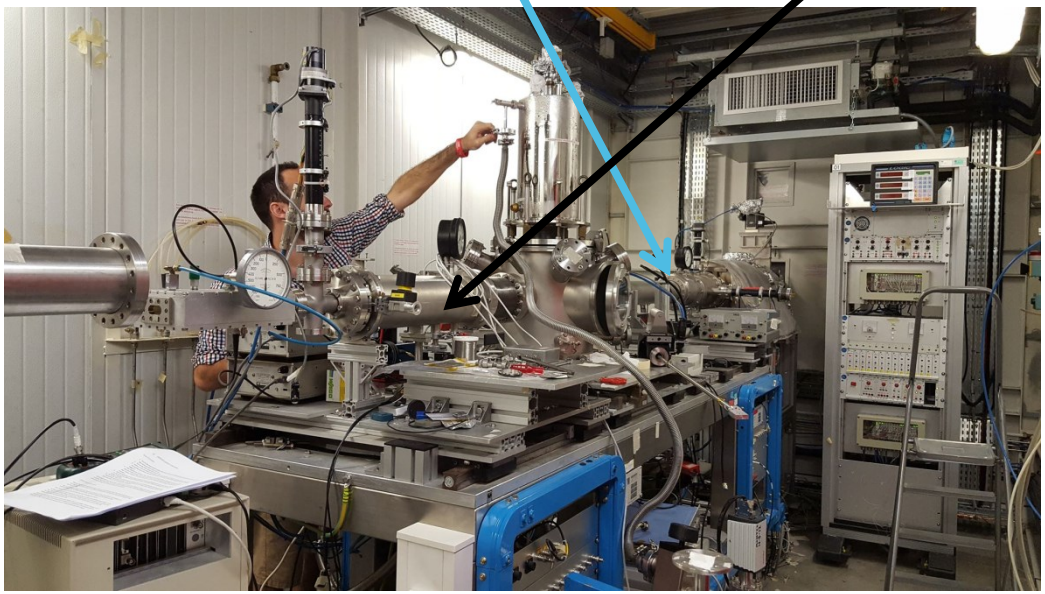
Transmission mode

$$I = I_0 \exp(-\mu(E)x)$$

$$\mu(E)x = ln\,(I_0/I)$$

Fluorescence mode

$$\mu(E) \propto I_F/I_0$$



LISA beamline BM-08

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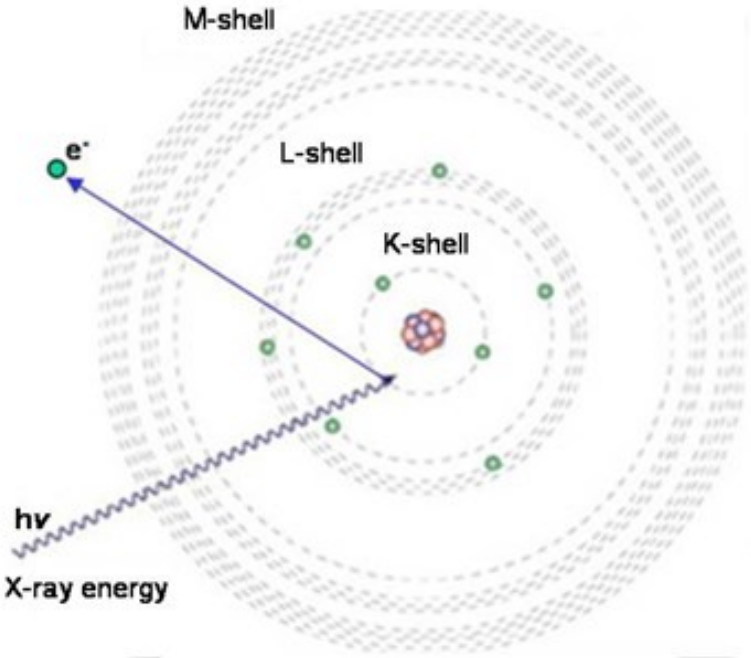
X-ray absorption spectroscopy II: qualitative interpretation



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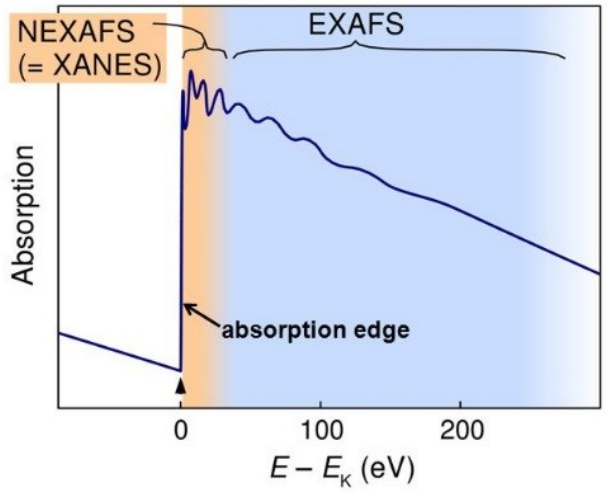
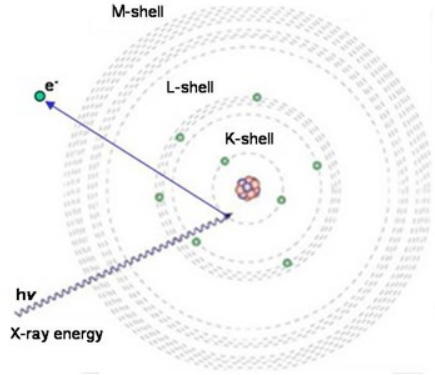
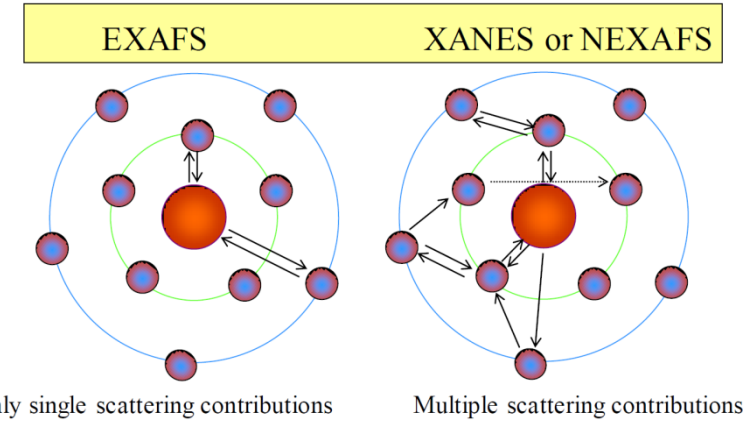
X-ray absorption spectroscopy II: qualitative interpretation



XANES: X-ray Absorption Near-Edge Structure

EXAFS: Extended X-ray Absorption Fine Structure





High energy photoelectrons
50 – 1000 eV from edge
Transition to continuum

Local structure:

Bond distance
Number and type of neighbors
Disorder

Low energy photoelectrons
< 50 eV from edge
Transition to unfilled, nearly bound states, continuum

Local site symmetry
Charge state
Orbital Occupancy

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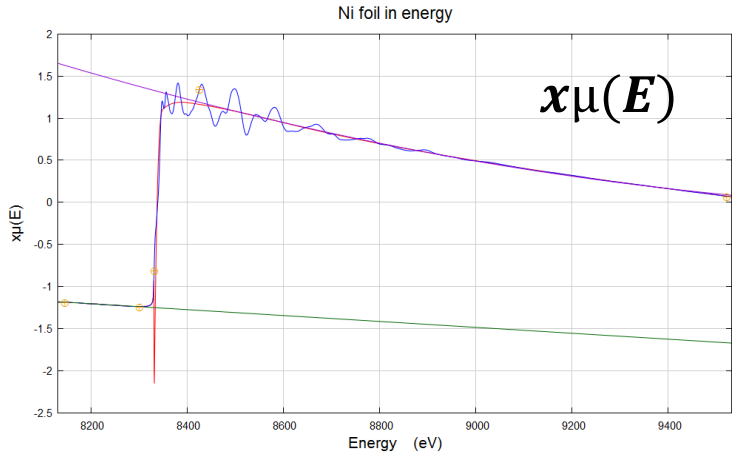
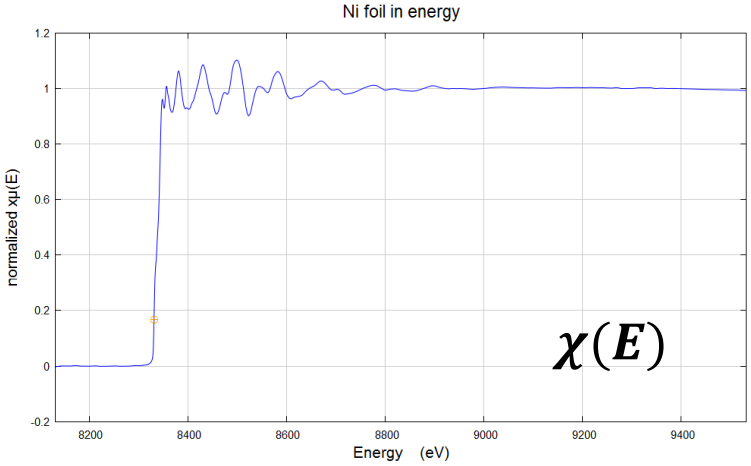
XAS III: experimental spectra

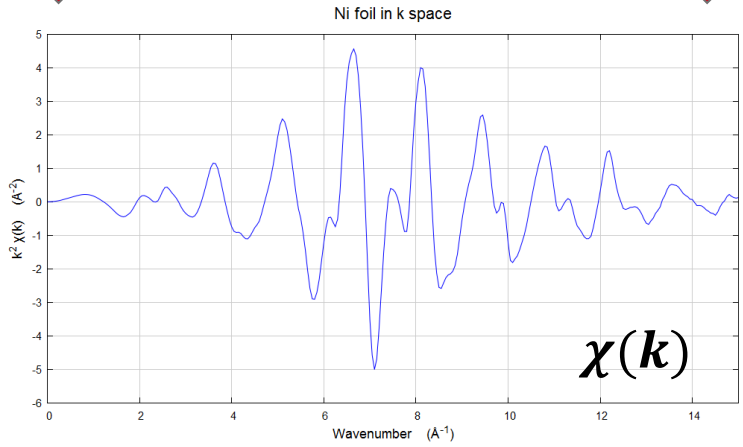


Normalization



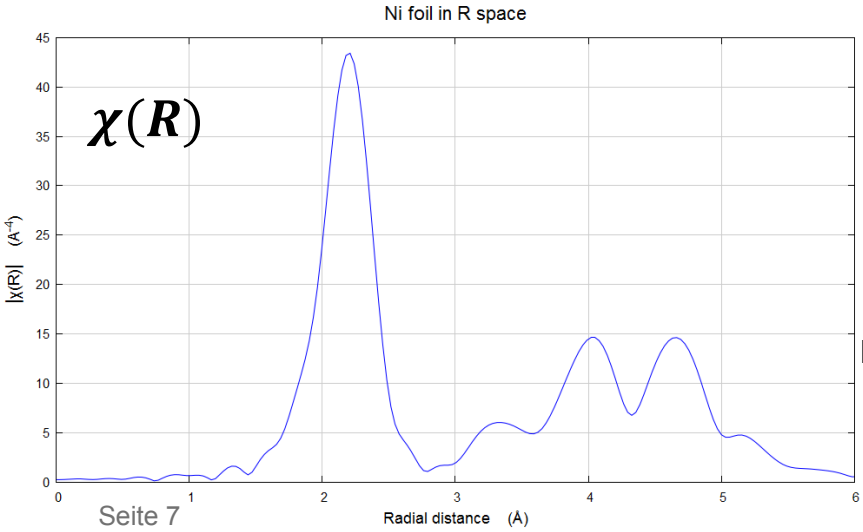
From Energy to k space

$$k = {2\pi}/{\lambda} = \sqrt{{2m_e(E - E_0)}/{\hbar^2}}$$



From k space to R space

Fourier Transform



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XAS IV: theory, EXAFS equation

Interference between outgoing wavefunction and backscattered wavelets:

Outgoing photoelectron wavefunction: damped propagating spherical wave

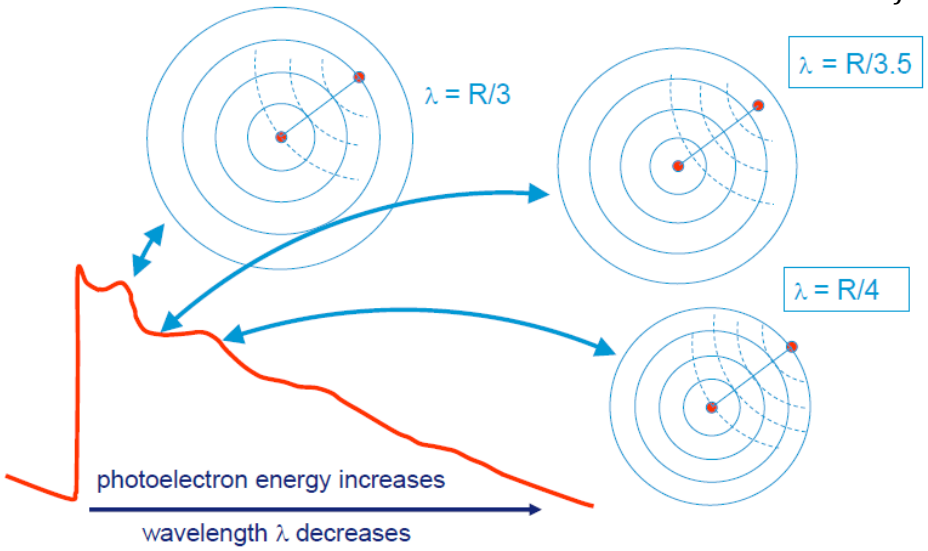
$$Sp(k) = A(k)\frac{e^{ikR}}{kR}e^{-R/\lambda^*(k)}$$

Backscattered wavelets

$$\chi_j(\mathrm{k}) = B_j(k)\sin[\varphi_j(k)]$$

EXAFS equation

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



The probability of absorption oscillates due to constructive and destructive interference

Amplitude:

S_0^2: amplitude reduction factor

N_j: Number of neighbors; the higher, the larger the signal

$f_j(k)$: (back)scattering amplitude; the stronger, the larger the signal

σ_j : static + thermal disorder; amplitude damping at large k

$\lambda^*(k)$: electron mean free path (around 10-20 Å in the EXAFS region)

Phase:

$\delta_j(k)$: phase-shift from photoelectron (back-)scattering

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XAS IV: theory, EXAFS equation

EXAFS equation

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

Amplitude:

S_0^2: amplitude reduction factor (incomplete overlap initial-final state)

N_j: Number of neighbors; the higher, the larger the signal

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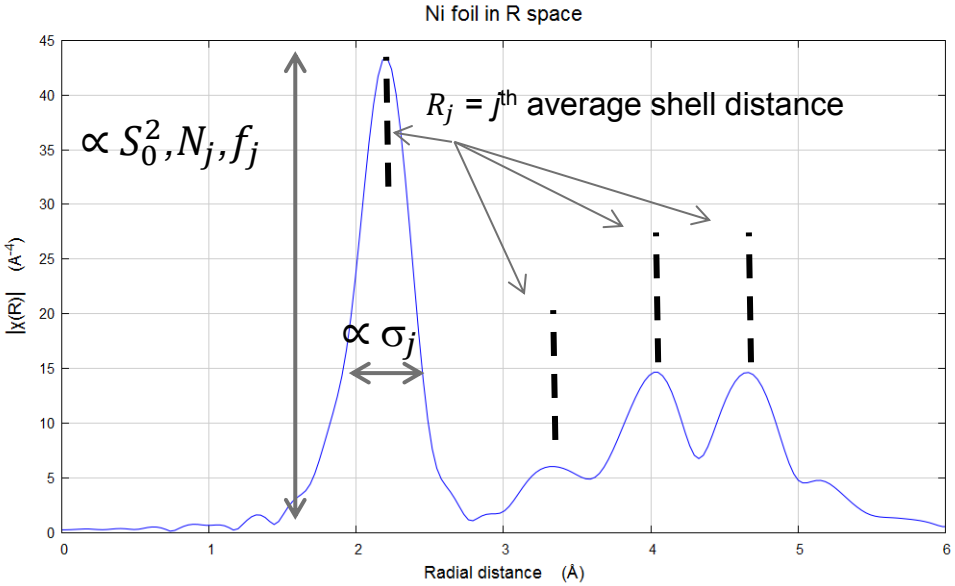

$f_j(k)$, $\delta_j(k)$ depend on atomic number *Z* of the scattering atom: we can determine the species of the neighboring atom (ΔZ ≥ 3).

Known $f_j(k)$, $\delta_j(k)$, we can determine

N coordination number of neighboring atom (< 10 - 20%)

R distance to neighboring atom(s) (< 0.01-0.02 Å)

σ^2 mean square disorder of neighbor distance

XAS IV: theory, EXAFS equation

EXAFS equation $$\chi(\mathrm{k}) = S_0^2 \sum_j \frac{N_j f_j(k)}{kR_j^2} e^{-2R_j/\lambda^*(k)} e^{-k^2\sigma_j^2} \sin[2kR_j + \delta_j(k)]$$

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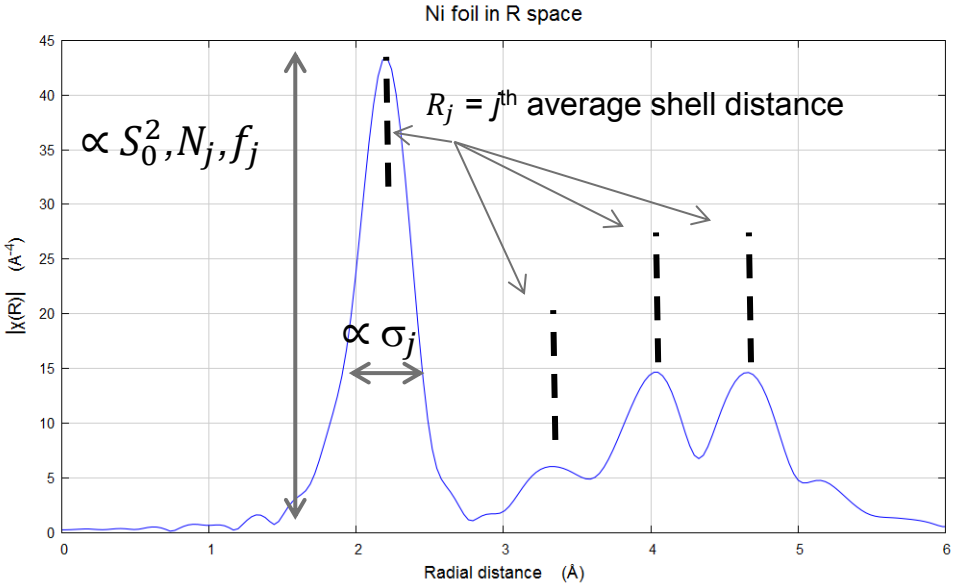

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we can determine **the species of the neighboring atom (ΔZ ≥ 3).**

Known $f_j(k)$, $\delta_j(k)$, we can determine

Short-range order

N **coordination number of neighboring atom (< 10 - 20%)**

R **distance to neighboring atom(s) (< 0.01-0.02 Å)**

σ^2 **mean square disorder of neighbor distance**

Local distortions

Short-range order, local distortions and EXAFS

$$\chi(\mathrm{k}) \sim \mathrm{S}_0^2 \sum_j \frac{N_j f_j(k)}{kR_j^2} e^{-2R_j/\lambda^*(k)} e^{-k^2\sigma_j^2} \sin[2kR_j + \delta_j(k)]$$

Short-range order

- ***neighboring atom species (ΔZ ≥ 3)***
- ***coordination number N of neighboring atom (< 10 - 20%)***

Tricky: depends on the specimen constituents

Local distortions

- ***R distance to neighboring atom(s) (< 0.01-0.02 Å)***
- ***σ^2 mean square disorder of neighbors distance***

Generally easy to determine

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$Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$

Short-range order

- *neighboring atom species (ΔZ ≥ 3)*
- *coordination number N of neighboring atom (< 10 - 20%)*

Tricky: depends on the specimen constituents

Atom	Z	
Al	13	
Cr	24	
Fe	26	
Co	27	
Ni	28	
Cu	29	

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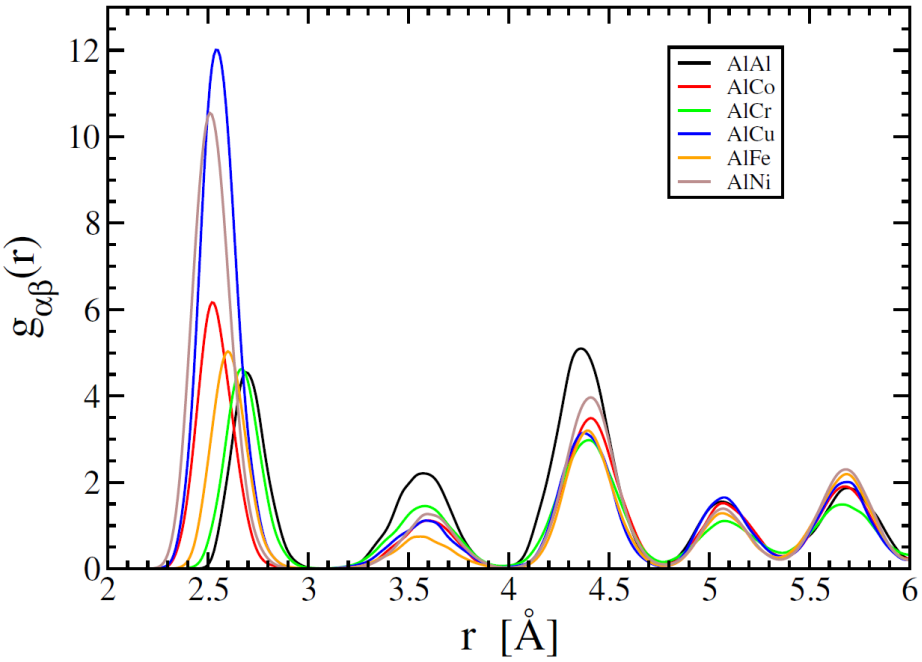
Short-range order in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$

Pair correlation data: simulation



Courtesy of Prof. Michael Widom, Carnegie Mellon University

Does short-range order exist in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$?

Bond	d (Å)	$g_{\alpha\beta}$ (r)
Al-Al	2.69	4.54
Al-Co	2.52	6.16
Al-Cr	2.67	4.62
Al-Cu	2.54	**12.00**
Al-Fe	2.60	5.03
Al-Ni	2.51	**10.54**

From simulation (MonteCarlo + Molecular dynamics):

- Al-Ni and Al-Cu bonds preferred
- Al-Al bond suppressed

Experimentally, Al preferred bonding not yet directly proved

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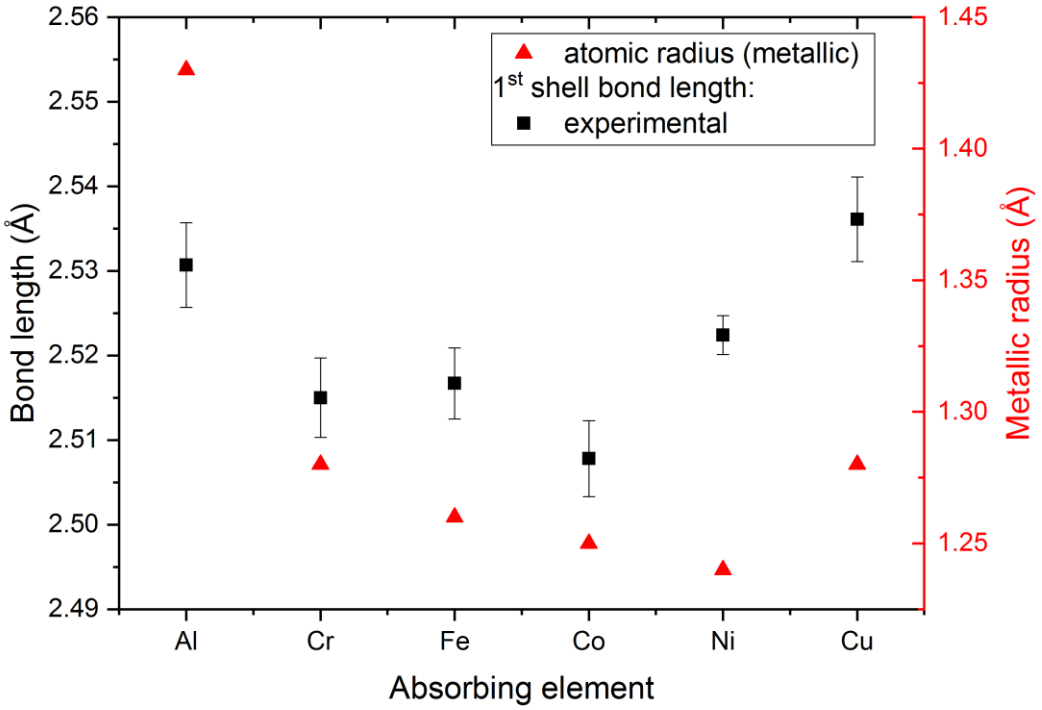
Local distortions in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$

Bond lengths: EXAFS



1st shell bond lengths from EXAFS:

- *V*-shaped trend: minimum at Co
- Atomic sizes: minimum at Ni
- Ni: largest mismatch with atomic size considerations

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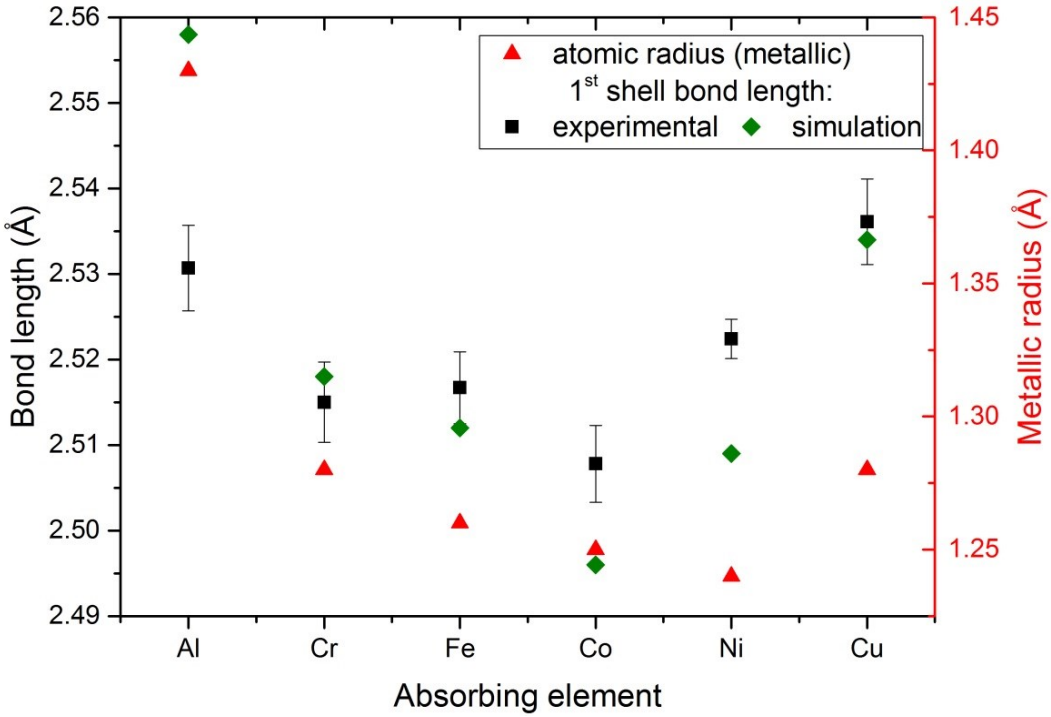
Local distortions in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$

Bond lengths: EXAFS



1st shell bond lengths from EXAFS:

- *V*-shaped trend: minimum at Co
- Atomic sizes: minimum at Ni
- Ni: trend mismatch with atomic size considerations

1st shell bond lengths from simulations:

- *V*-shaped trend: minimum at Co
- Al, Co and Ni: largest mismatches with experimental data

Conclusions and general remarks

Synchrotron techniques to resolve short-range order

- X-ray absorption spectroscopy:
  - especially effective if the system has most of its constituents with $\Delta Z \geq 3$ (e.g. Ti-Zr-Hf based)
  - complementary structural simulations are needed for comparison with XAS results
  - Bond lengths and distortions around specific elements are generally easy to determine
- X-ray / neutron pair distribution function (similar restrictions applies in the case of X-rays)

System $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$

- First simulations support experimental trend 1st shell bond length distances
- AlNi and AlCu preferred ordering to confirm / clarify with experimental data
- First manuscript on EXAFS in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$ close to submission
- More at the poster (BA1170/39-1) session: XANES, Bader charges …

Measurements at the beamlines require generally around-the-clock work every day for up to a week

- Anybody interested to join the experiments / giving a helping hand? If yes, you are welcome!
- Open for collaborations

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Thank you for your attention

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