EXAFS data analysis

- <u>Extraction of EXAFS signal</u>

Experimental EXAFS spectrum

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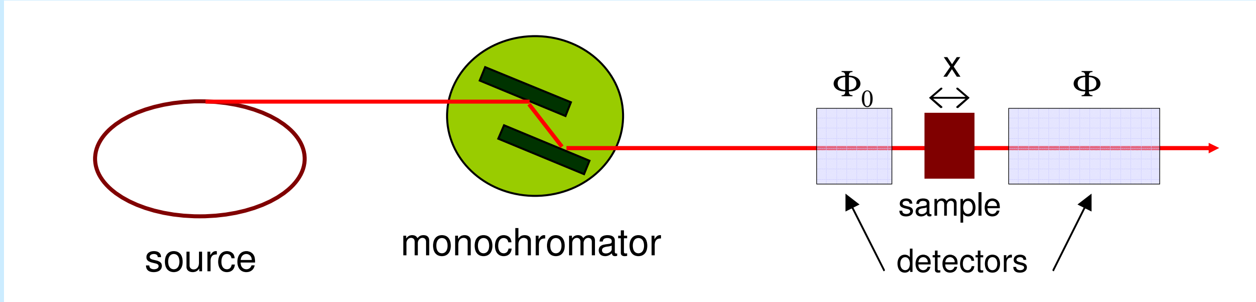

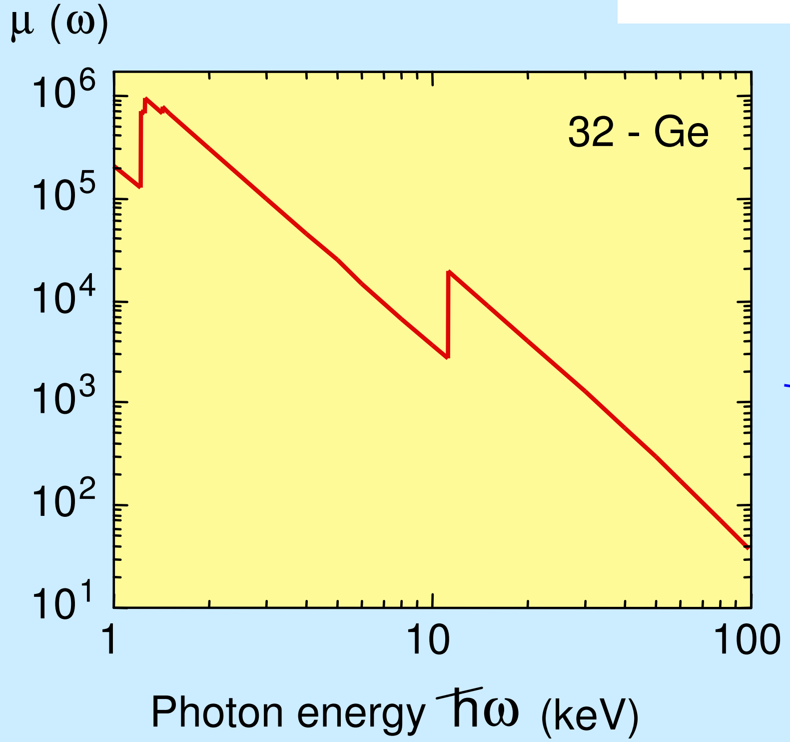

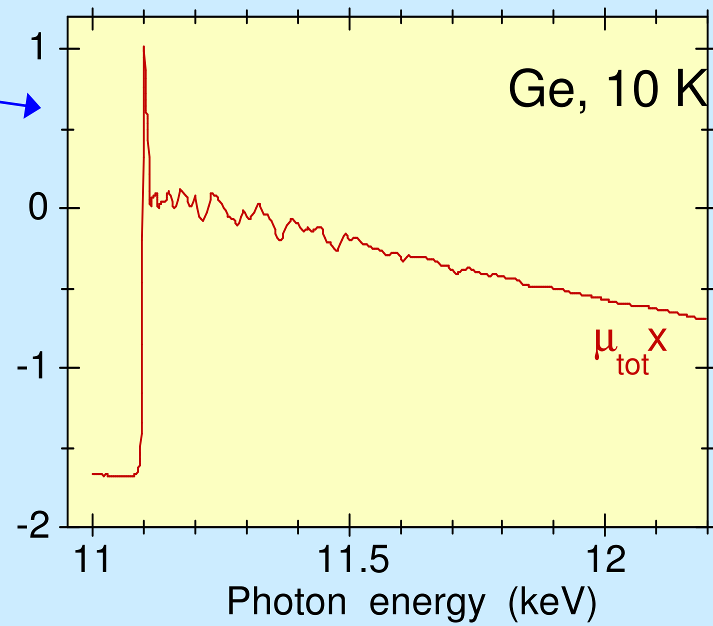

Data analysis - Absorption coefficient

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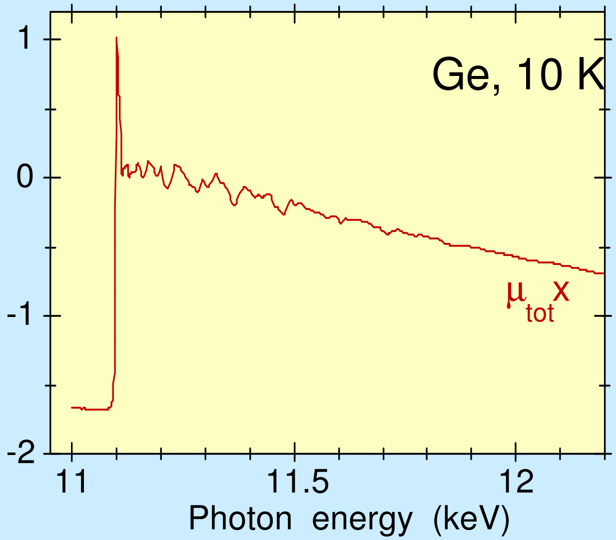
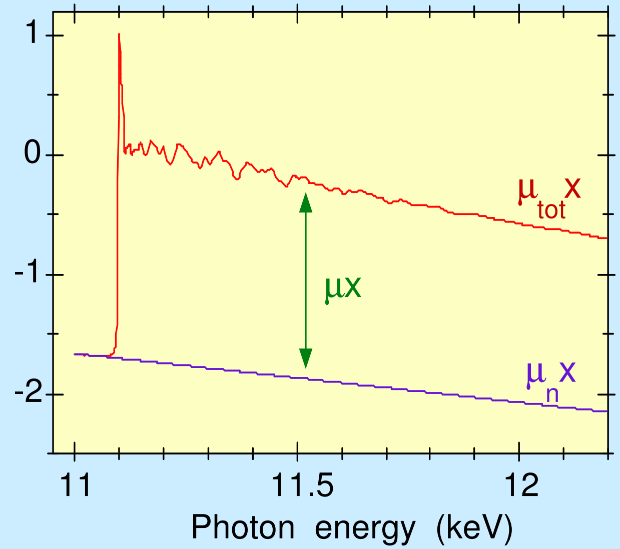
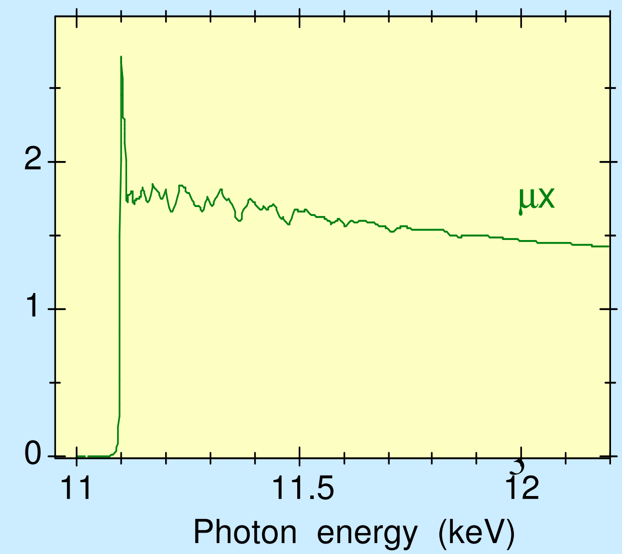
Experimental signal



Extrapolation of pre-edge behaviour



Specific absorption coefficient



Data analysis - The EXAFS signal

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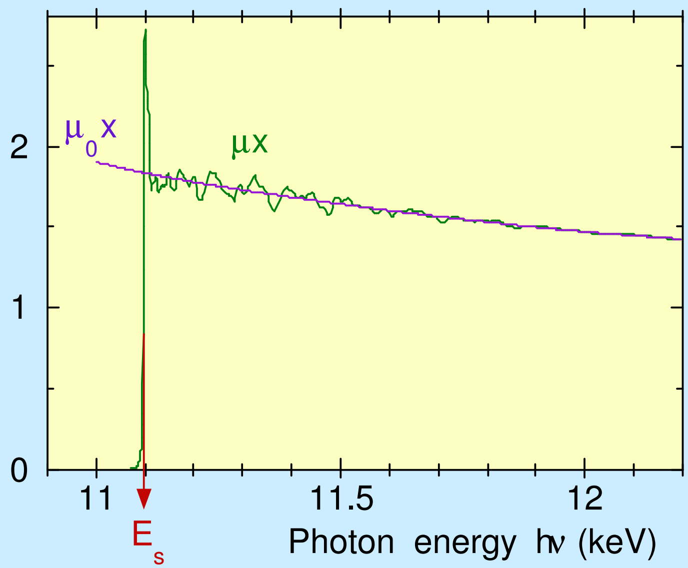
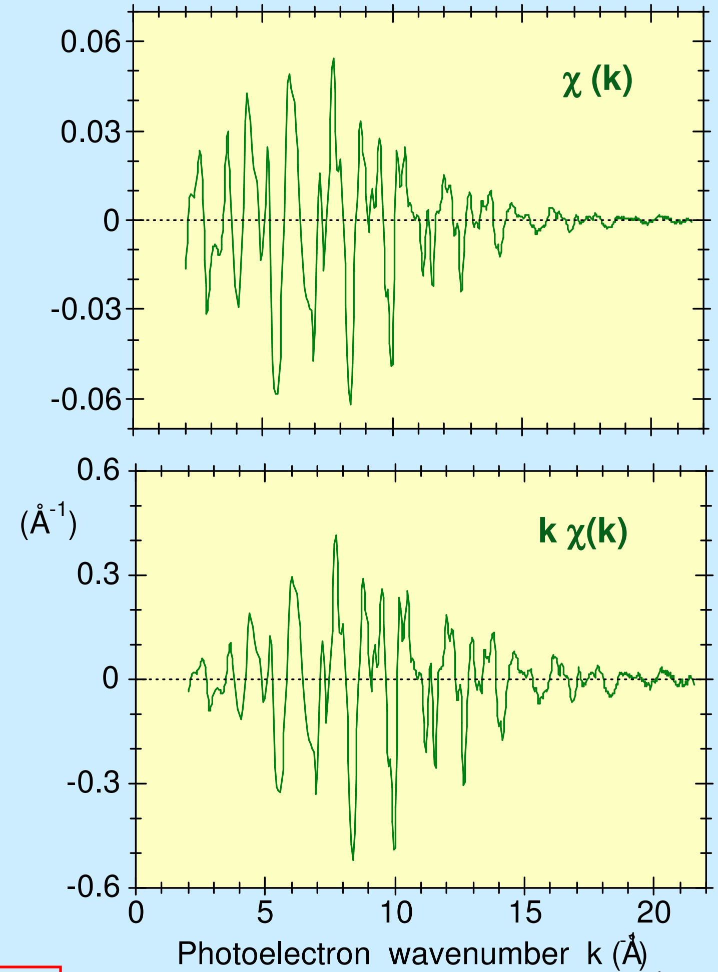
Atomic absorption coefficient



EXAFS signal



$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$

Edge energy

$$k = \sqrt{\frac{2m}{\hbar^2}\,(h\nu - E_s)}$$

Photoelectron wavenumber

Two distances seen by EXAFS

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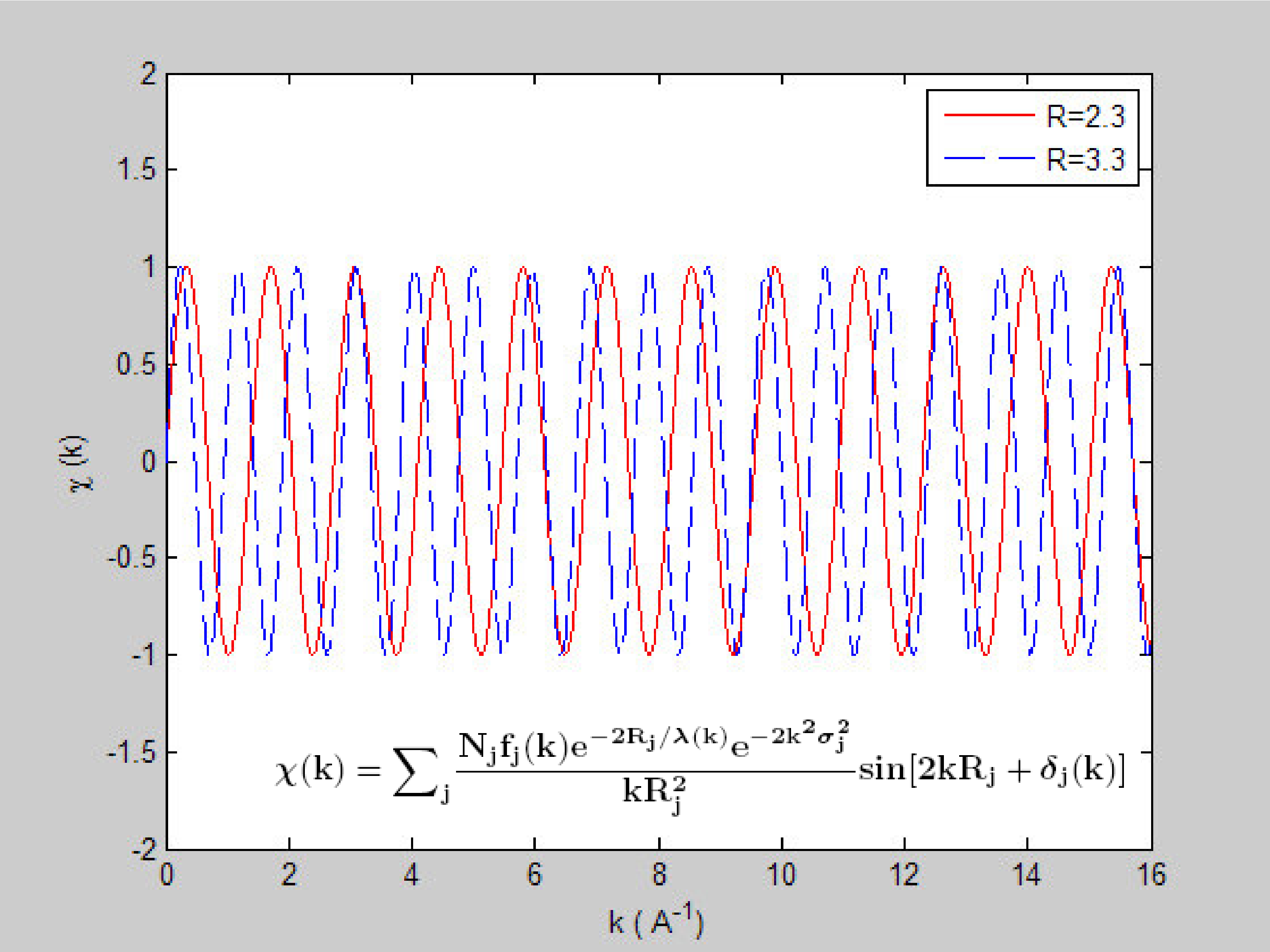

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

The phase's effect

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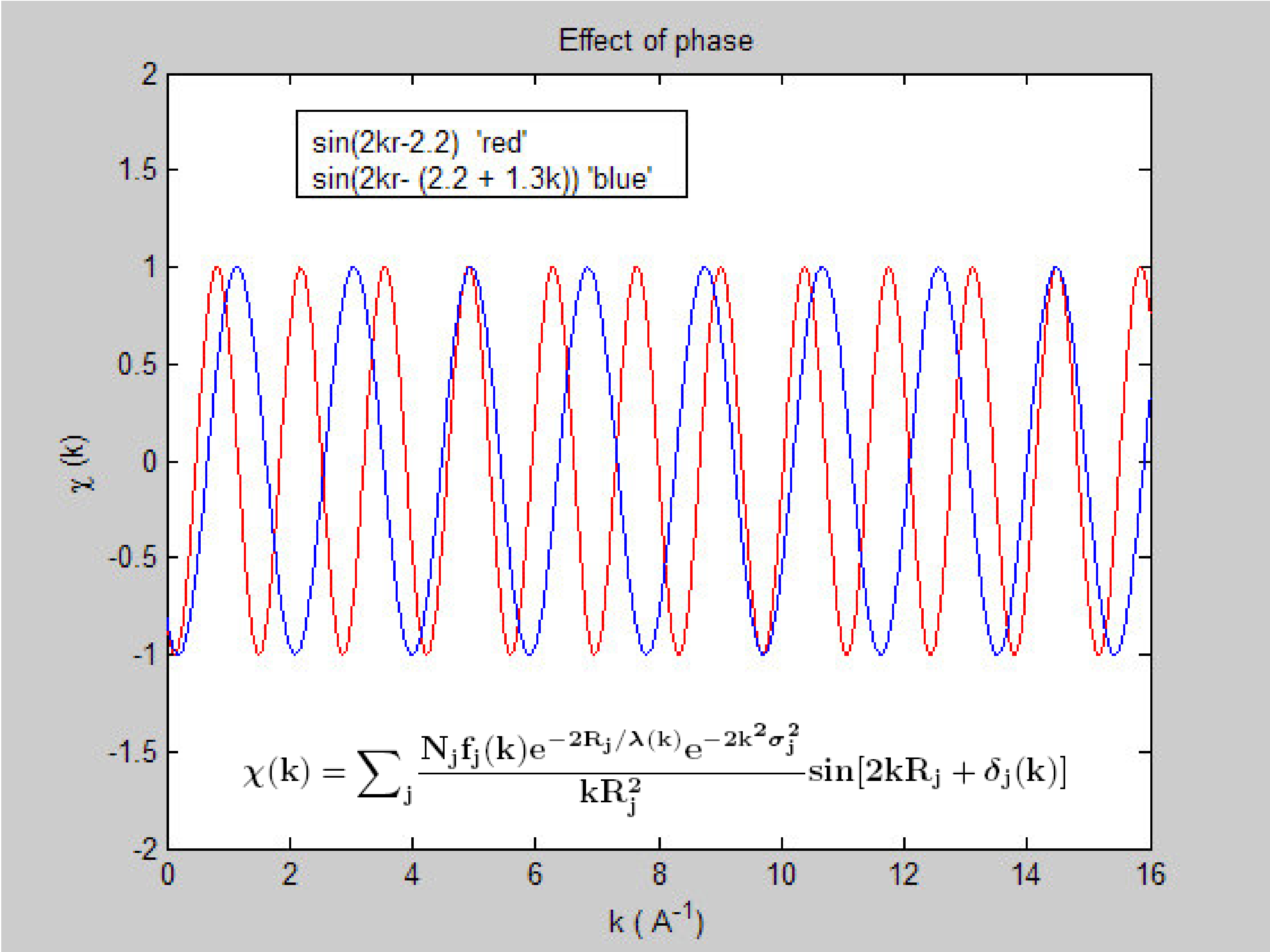

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

The back-scattering function

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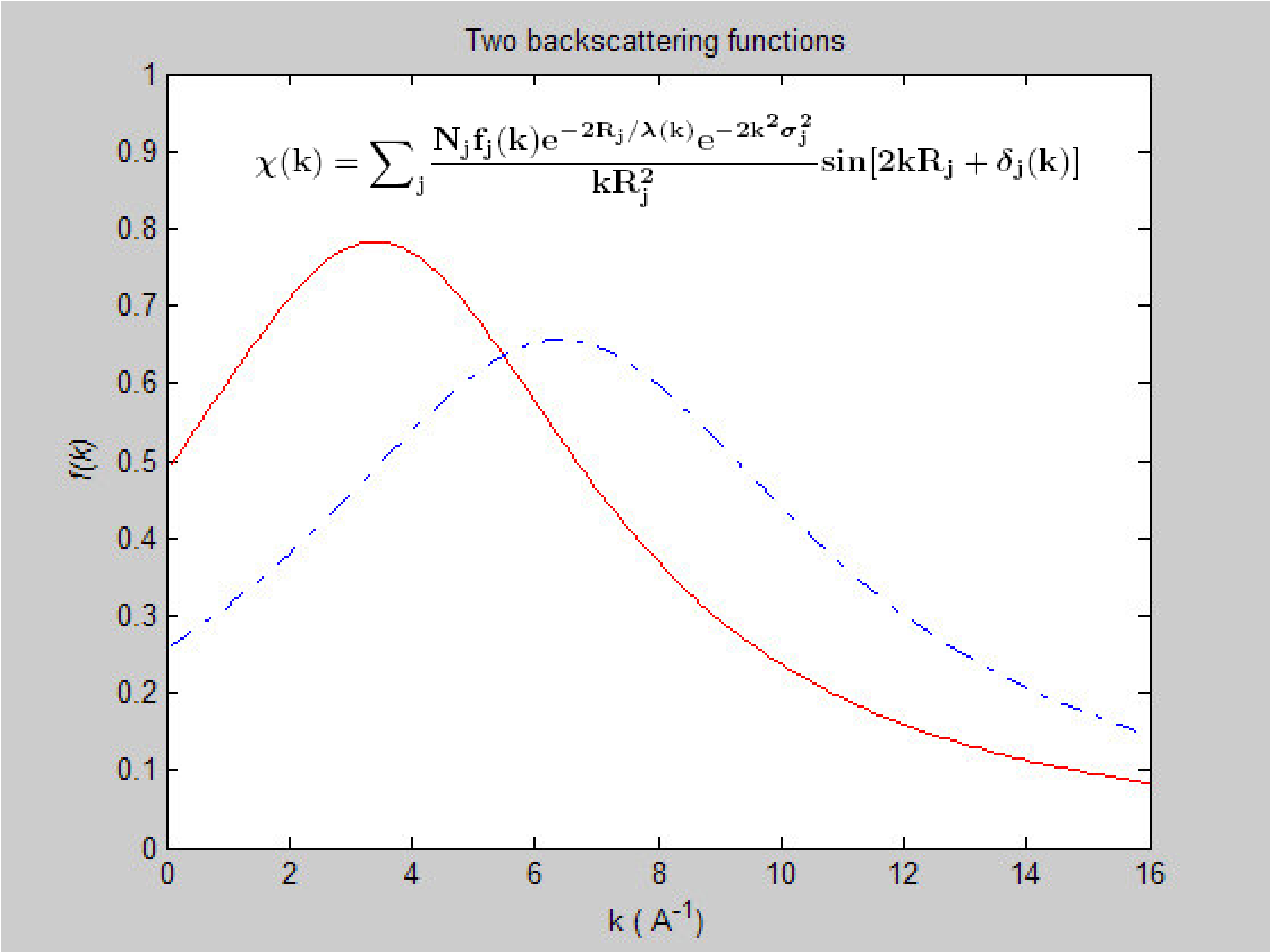

Their effect on EXAFS signal

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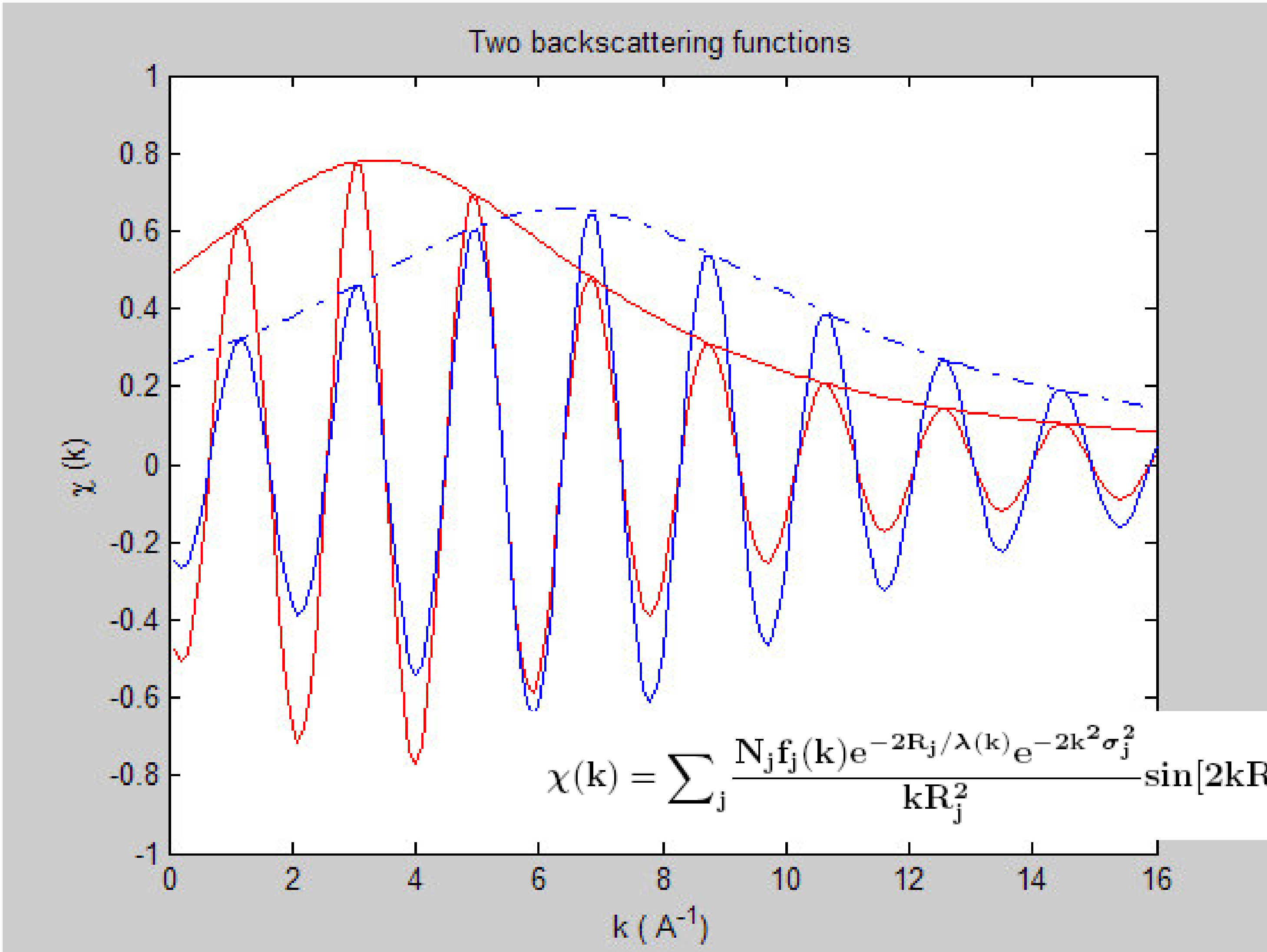

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

The Debye-Waller damping effect

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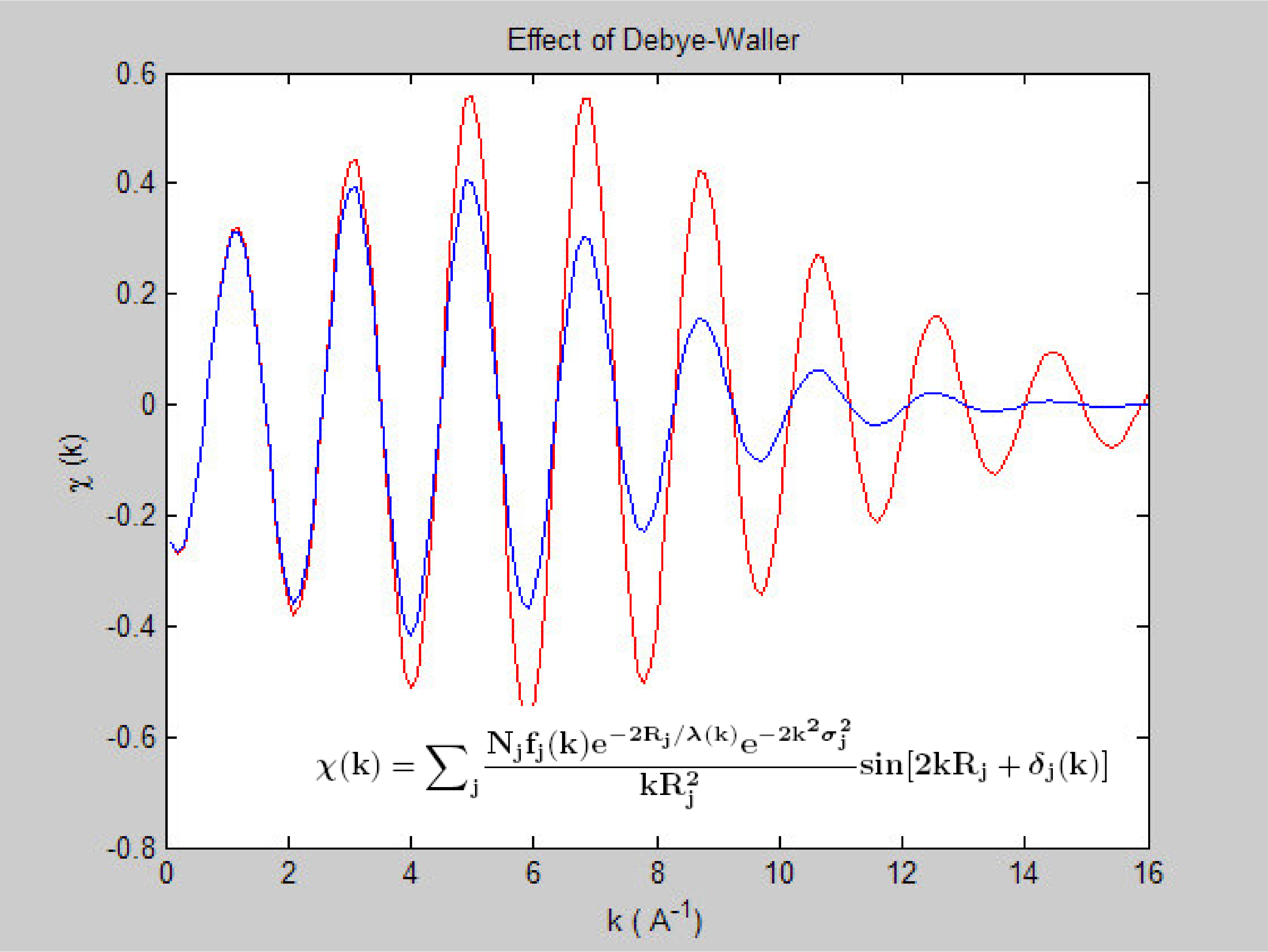
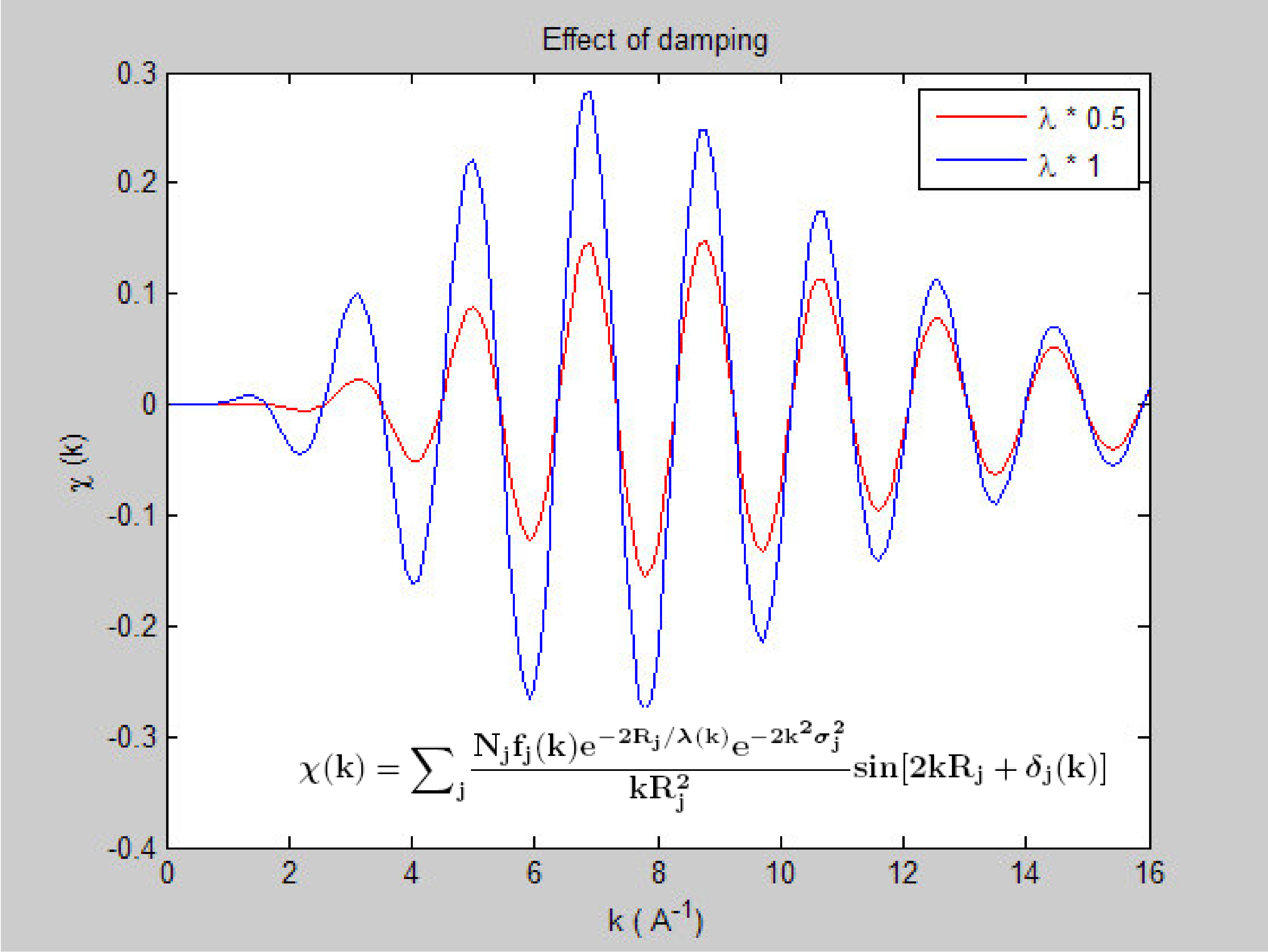


The m.f.p. damping effect



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

Weighting the EXAFS signal

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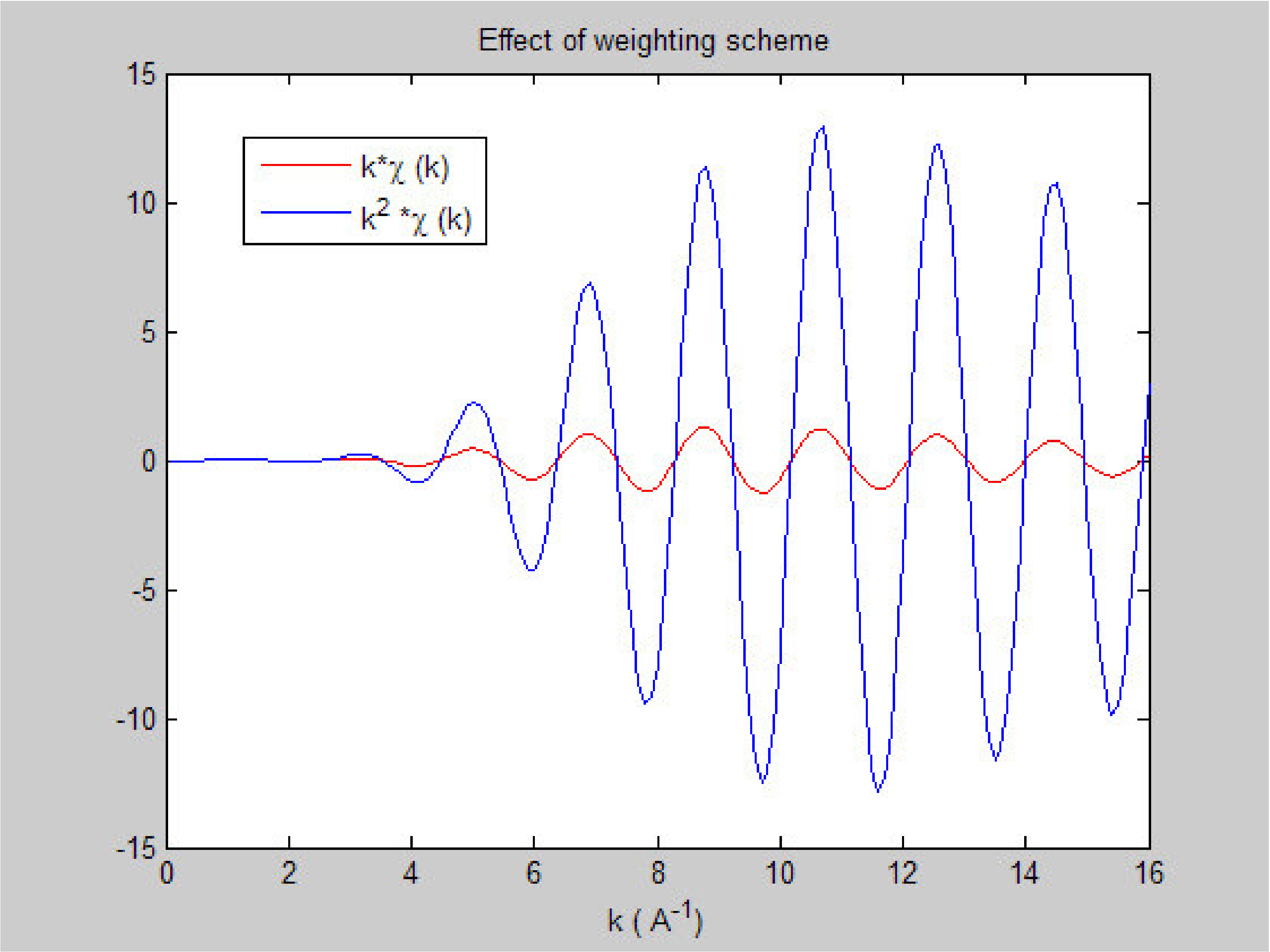

EXAFS signals: examples

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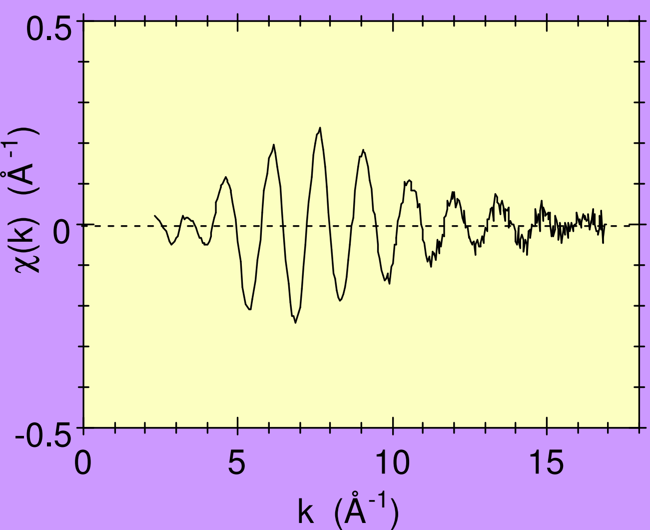
Amorphous Germanium

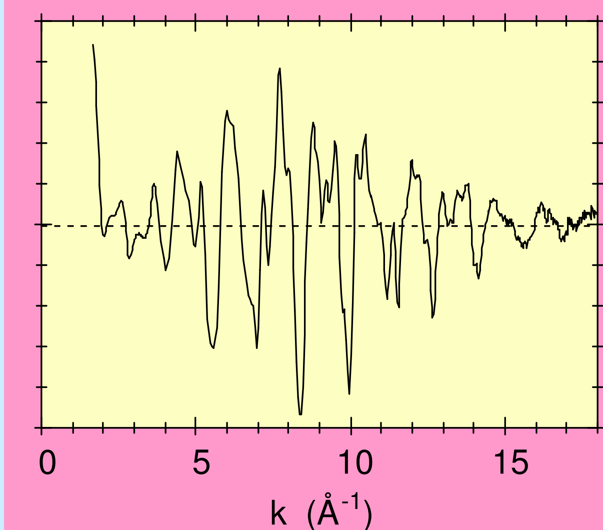
T = 77 K



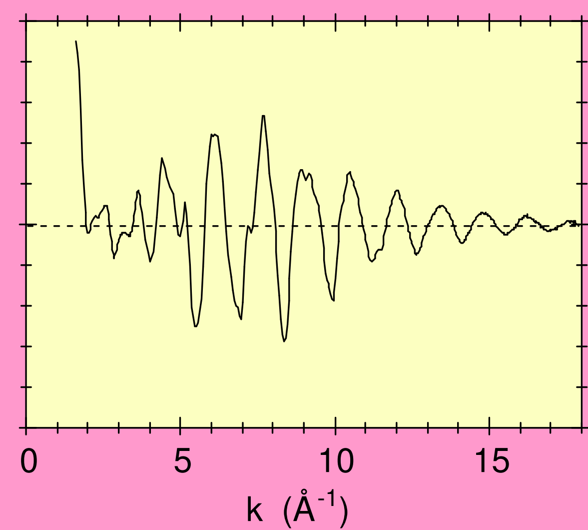
1 coord. shell

Crystalline Germanium

T = 77 K



T = 300 K



Several coord. shells

Temperature effect

Quantitative analysis

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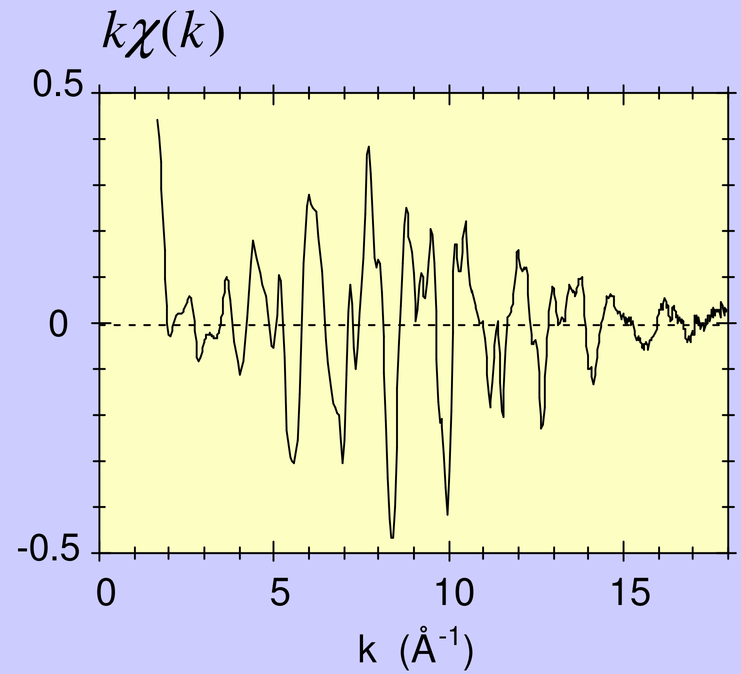
$$\chi(k) = \sum_i A_i(k) \sin \Phi_i(k)$$

Sum over:
- S.S. paths (coord. shells)
- M.S. paths



Input for each path:
- backscattering amplitude
- phaseshifts
- inelastic terms

Different analysis procedures

EXAFS data analysis

- ♠ Fourier transform

Data analysis - Fourier Transform k→r

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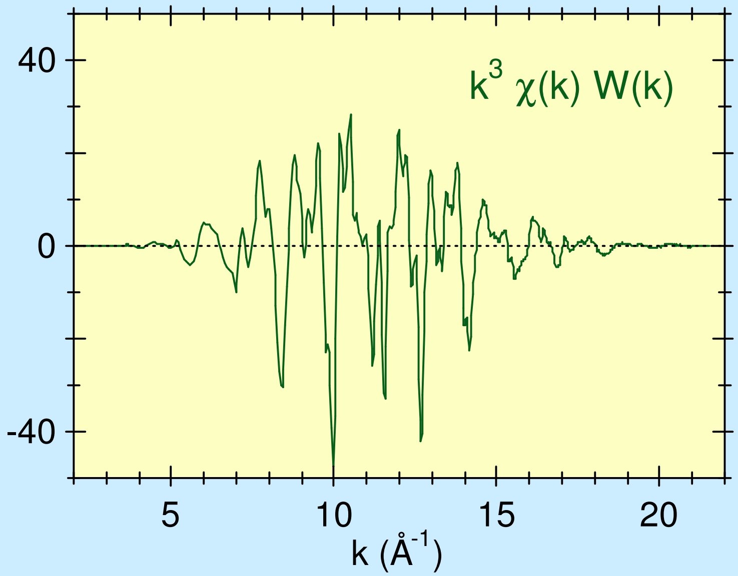
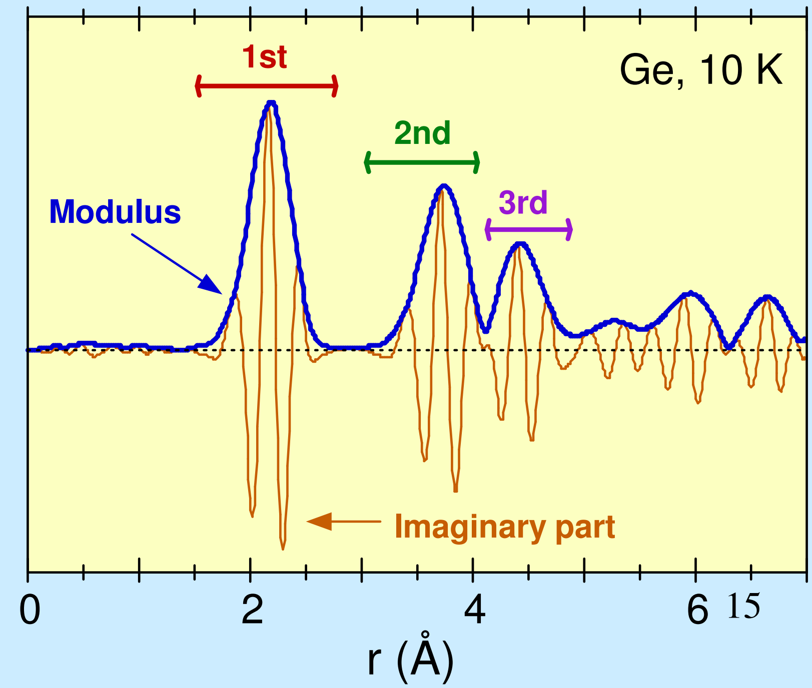


weight window

$$F(r) = \int_{k_{min}}^{k_{max}} \chi(k)\, k^n\, W(k)\, e^{2ikr}\, dk$$



Peak's position and shape influenced by:

- total phaseshifts
- disorder
- Fourier transform window

Fourier Transform and distribution

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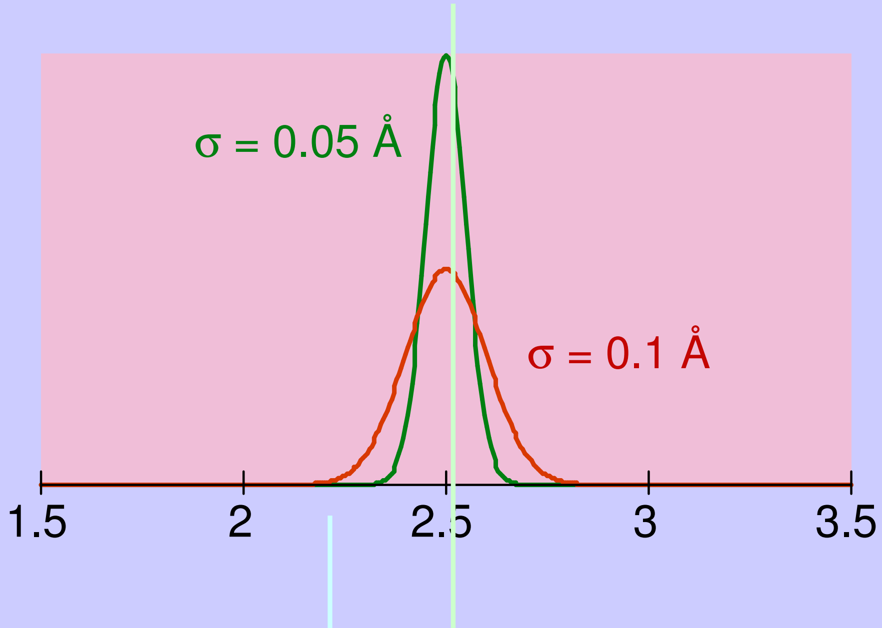
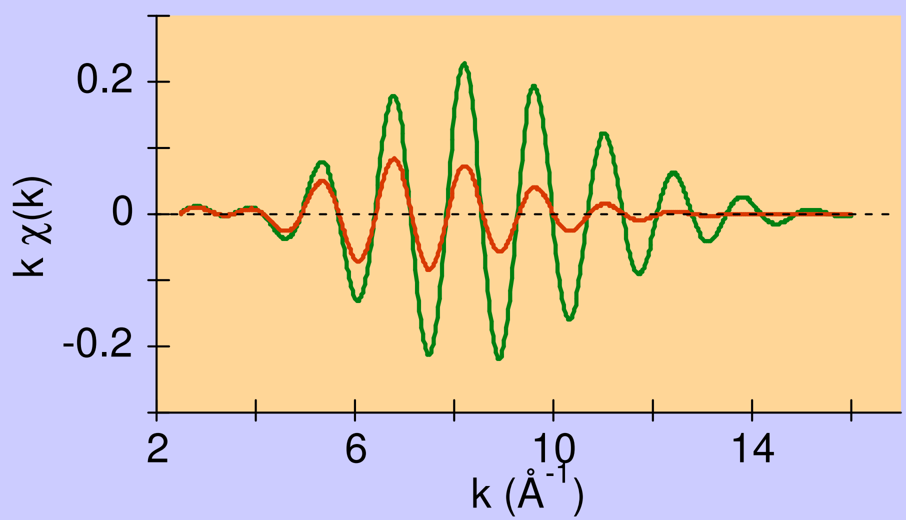
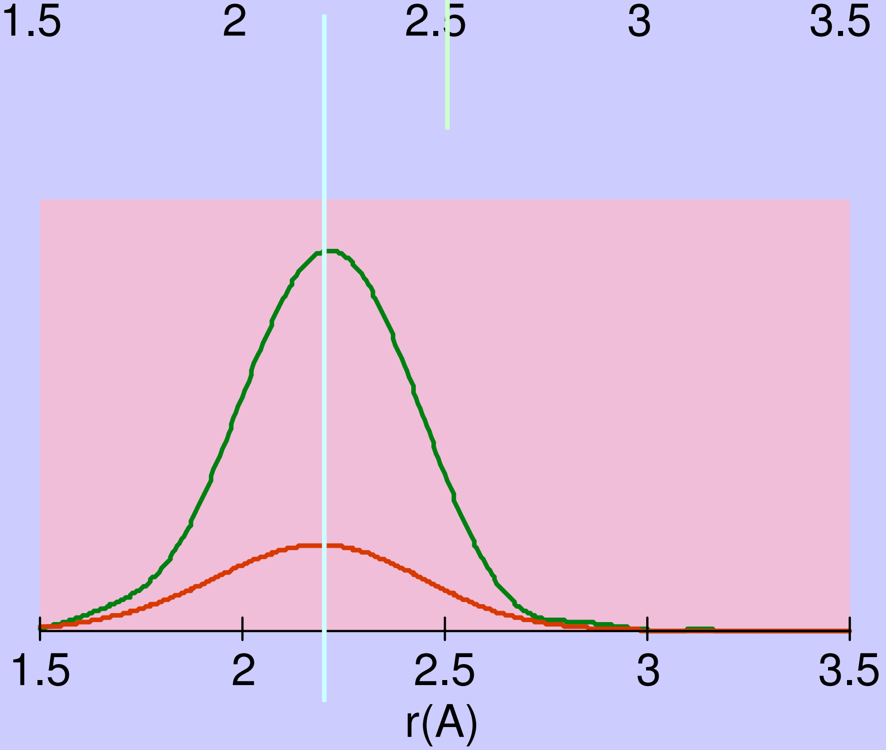


EXAFS simulation
(Ge phases and amplit.)





F.T.: k=2.5-16
K^3, square w.

26 - Iron: bcc structure

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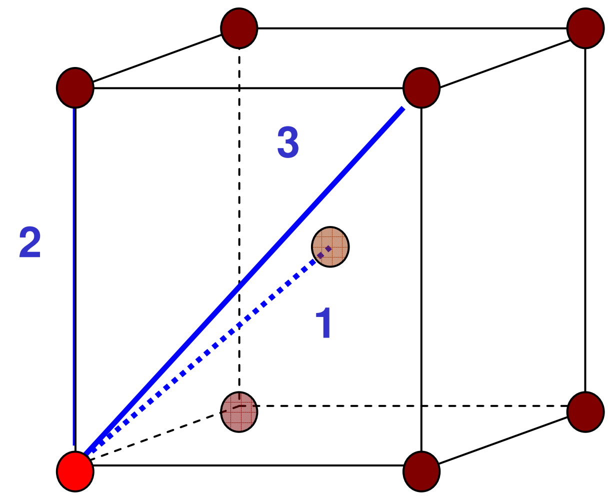
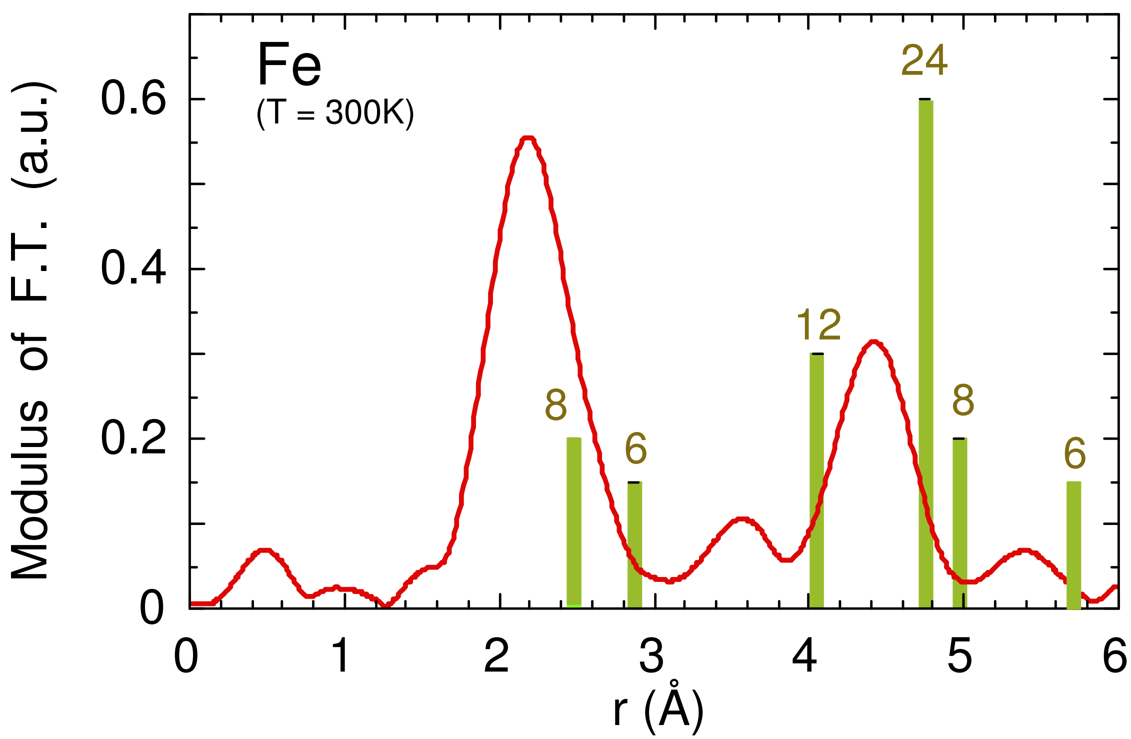
i	N_i	R_i (Å)
1	8	2.48
2	6	2.86
3	12	4.05
4	24	4.75
5	8	4.96
6	6	5.73





a = 2.86 Å

- Peak shift
- Superposition of shells

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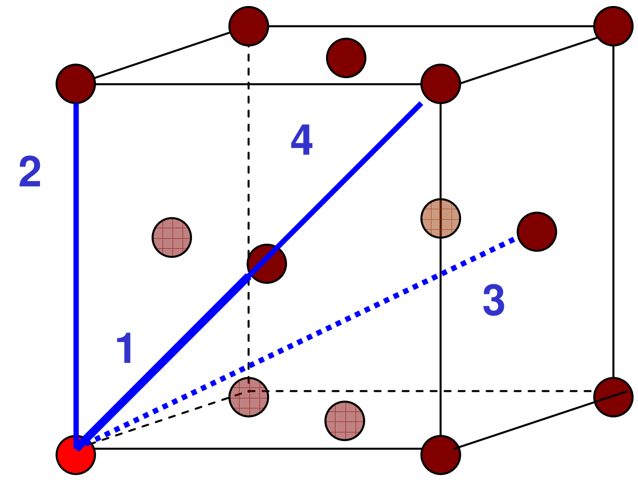
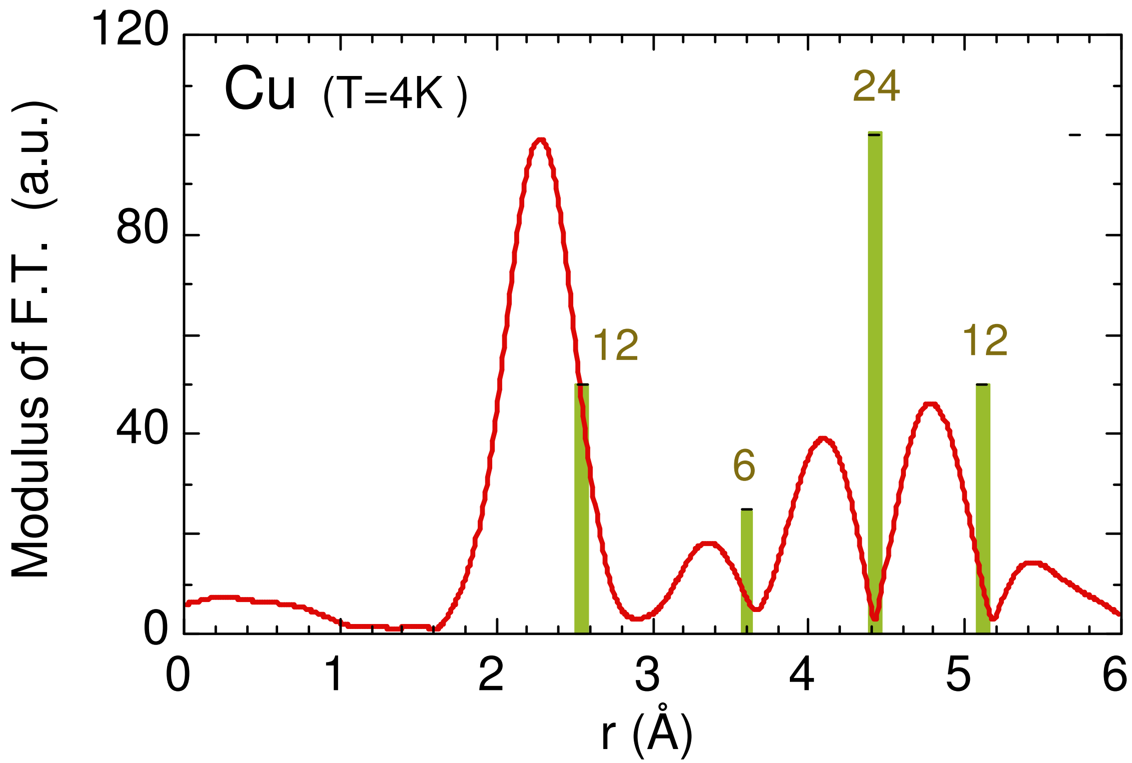
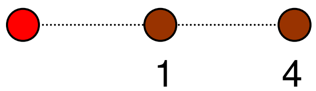
i	N_i	R_i (Å)
1	12	2.55
2	6	3.61
3	24	4.42
4	12	5.10
5	24	5.70
6	8	6.25





a = 3.61 Å

- Peak shift
- Focussing effect



32 - Germanium: diamond structure

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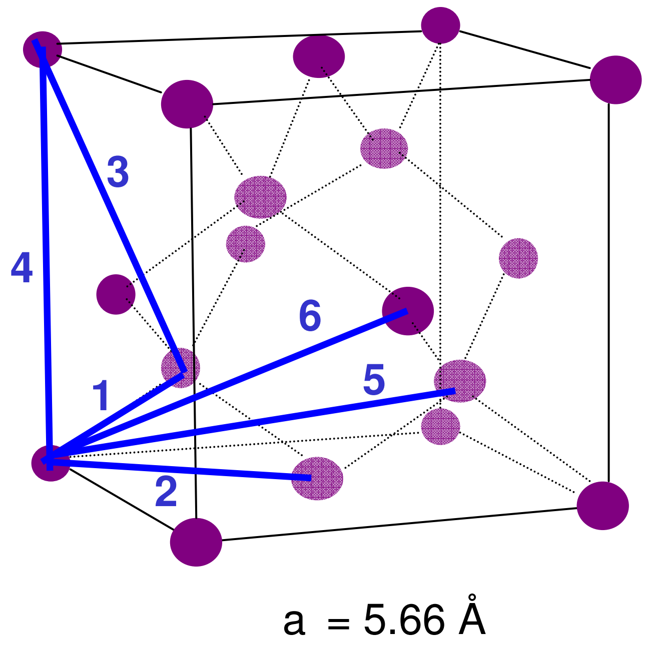
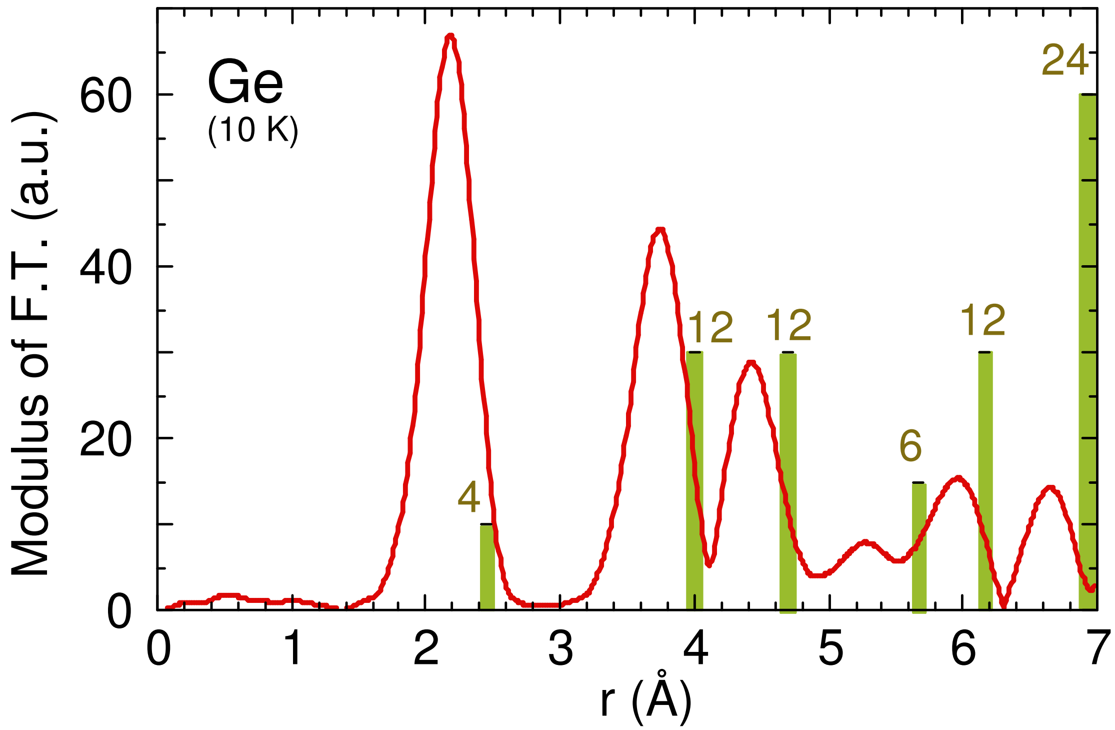
University of Trento (Italy)

i	N_i		R_i (Å)
1	4	a(√3)/4	2.45
2	12	a/√2	4.00
3	12	a(√11)/4	4.69
4	6	a	5.66
5	12	a(√19)/4	6.16
6	24	a(√6)/2	6.93





32-Ge: crystalline and amorphous

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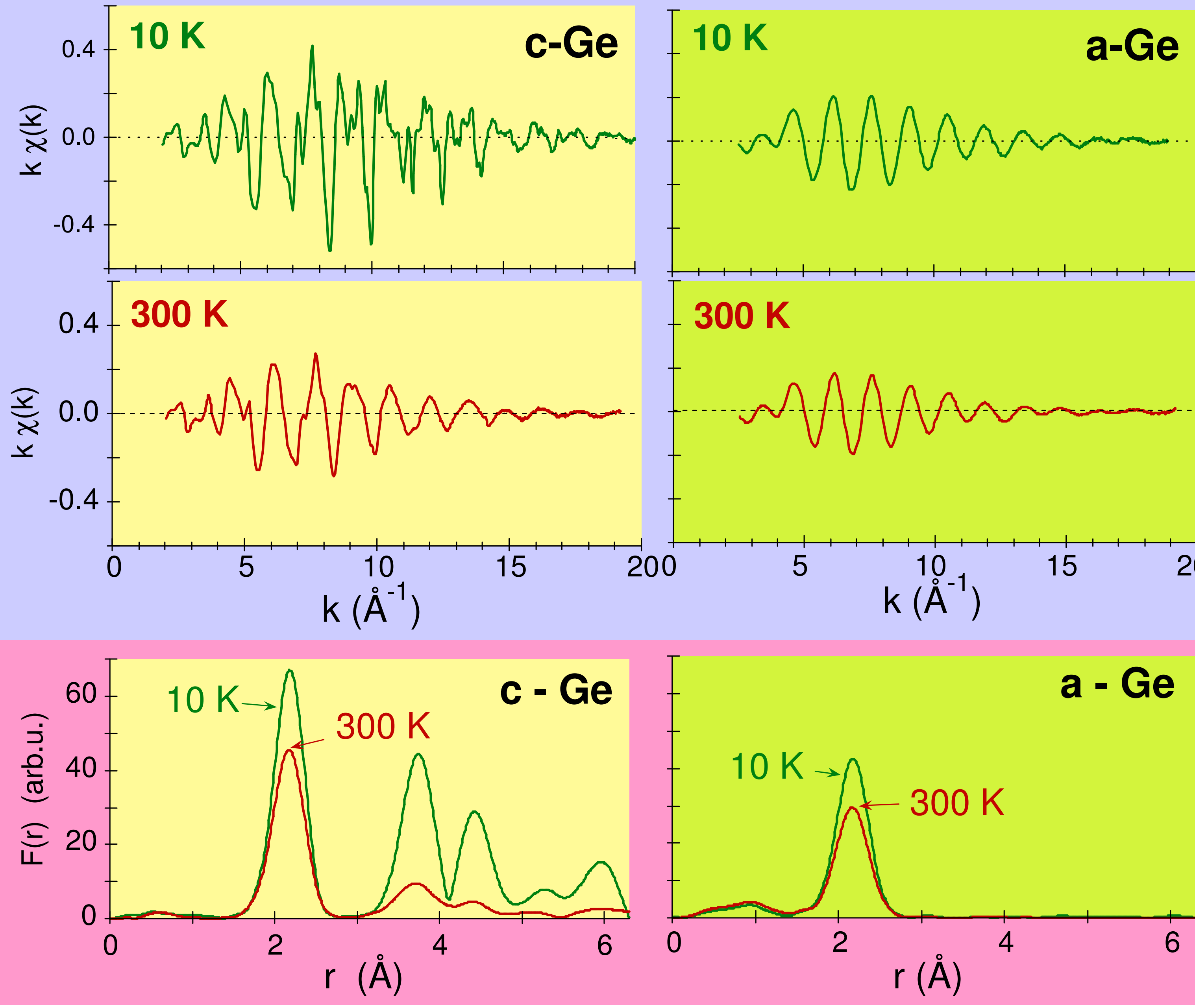
EXAFS signals

Fourier transforms



EXAFS data analysis

♠ Fourier back-transform

Data analysis - Fourier Back-transform r→k

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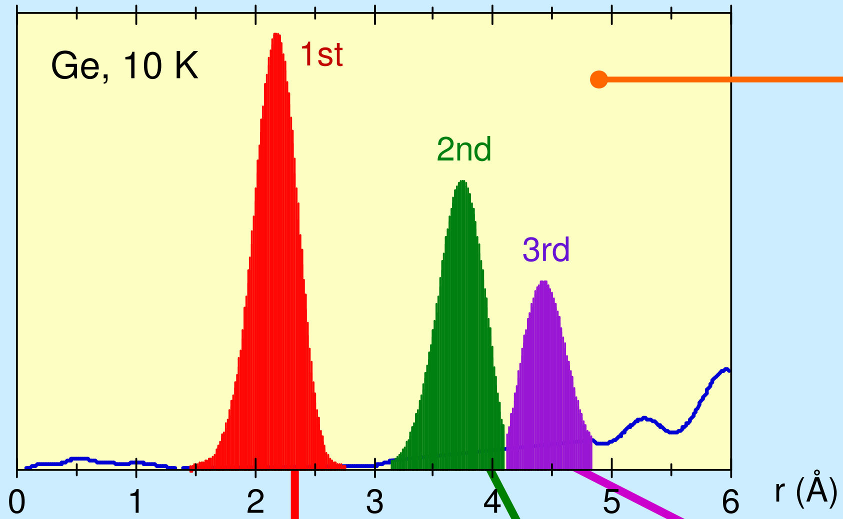
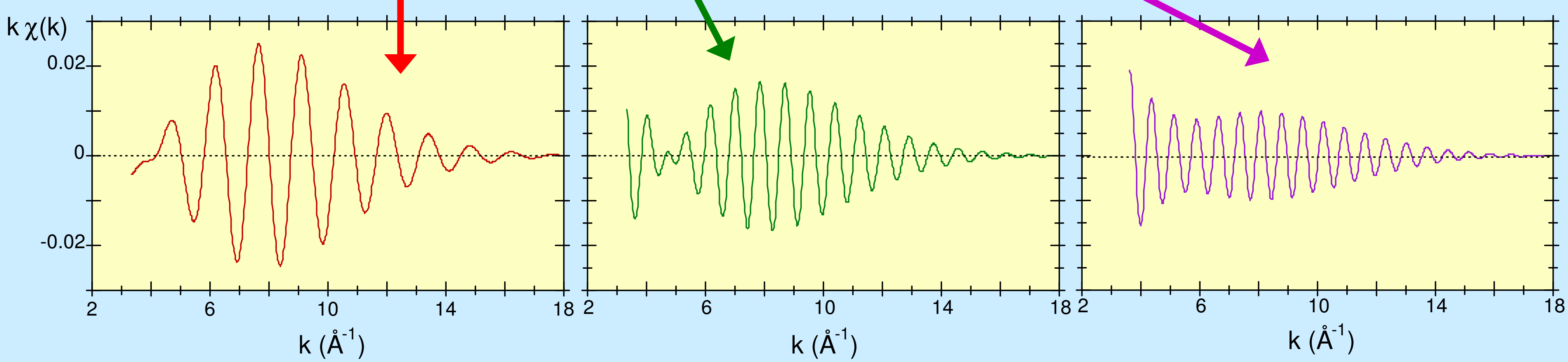


- Peak superposition
- Multiple scattering
- F.T. artifacts

$$\chi'(k) = (2/\pi)\int_{r_{min}}^{r_{max}} F(r)\, W'(r)\, e^{-2ikr}\, dr$$



The cumulants

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Cumulant expansion of EXAFS

$$\ln \int_0^\infty P(r,\lambda_0)\exp(2ikr)\,dr = \sum_{n=0}^{\infty} \frac{(2ik)^n}{n!} C_n$$

Amplitude: even C_n

$$\chi(k) = \frac{S_0^2 e^{-2C_1/\lambda}}{kC_1^2}\left|f(k)\right| N \exp\left[-2k^2C_2 + \tfrac{2}{3}k^4C_4 + \ldots\right]$$
$$\times \sin\left[2kC_1 - \tfrac{4}{3}k^3C_3 + \ldots + \phi(k)\right]$$

Degrees of disorder

Phase: odd C_n

$$\exp(C_0) \approx \frac{\exp(-2C_1/\lambda)}{C_1^2}$$

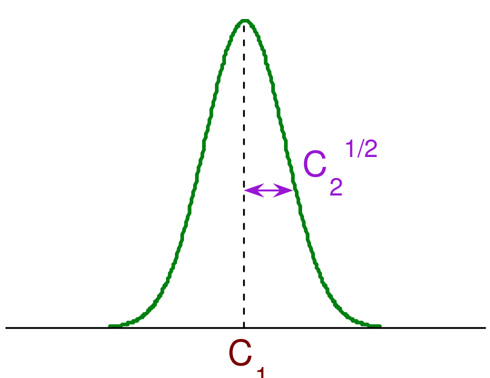
Normalisation

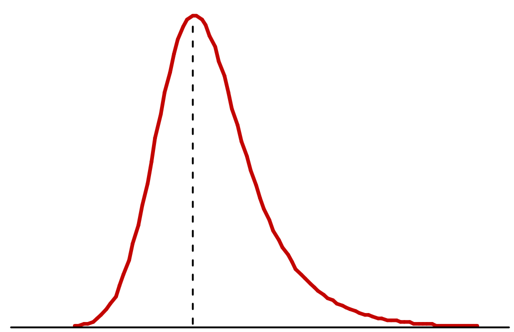
C_1 = mean value — **Position**

C_2 = variance — **width**

$C_3 \Rightarrow$ asymmetry — **shape**

$C_4 \Rightarrow$ flatness





Degrees of disorder

$$\chi(k) = N \left|f(k,\pi)\right| \frac{S_0^2 \, e^{-2C_1/\lambda}}{k \; C_1^2} \exp\left(2k^2 C_2\right) \exp\left(\frac{2}{3}k^4 C_4 + ...\right) \sin\left[2kC_1 - \frac{4}{3}k^3 C_3 + ... + \phi(k)\right]$$

Disorder

Harmonic approx. ⇒ Standard formula

$C_3 = C_4 = ... = 0$

$\exp\left(-2k^2 C_2\right) \equiv \exp\left(-2k^2 \sigma^2\right)$ (EXAFS Debye-Waller factor)

Low-order anharmonic terms

$\Rightarrow C_3, \; C_4, \{C_5, C_6\}$

Cumulant series fastly convergent

High-order anharmonic terms

Cumulant series: slowly convergent
....
not convergent

EXAFS for one shell

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Approx.: Single Scattering Plane waves

- **Theory** (interaction potentials + scattering theory)
- **Experiment** (reference samples)

Inelastic terms | Back-scattering amplitude | Total phase-shift

$$\chi(k) = \frac{S_0^2 e^{-2C_1/\lambda}}{kC_1^2} |f(k,\pi)| N \exp\left[-2k^2C_2 + \frac{2}{4}k^4C_4 + \ldots\right] \sin\left[2kC_1 - \frac{4}{3}k^3C_3 + \ldots + \phi(k)\right]$$

Coordination number ... ***N***

Even cumulants ... C_2, C_4

Odd cumulants ... C_1, C_3 } $P(r,\lambda)$

Data analysis - Independent parameters

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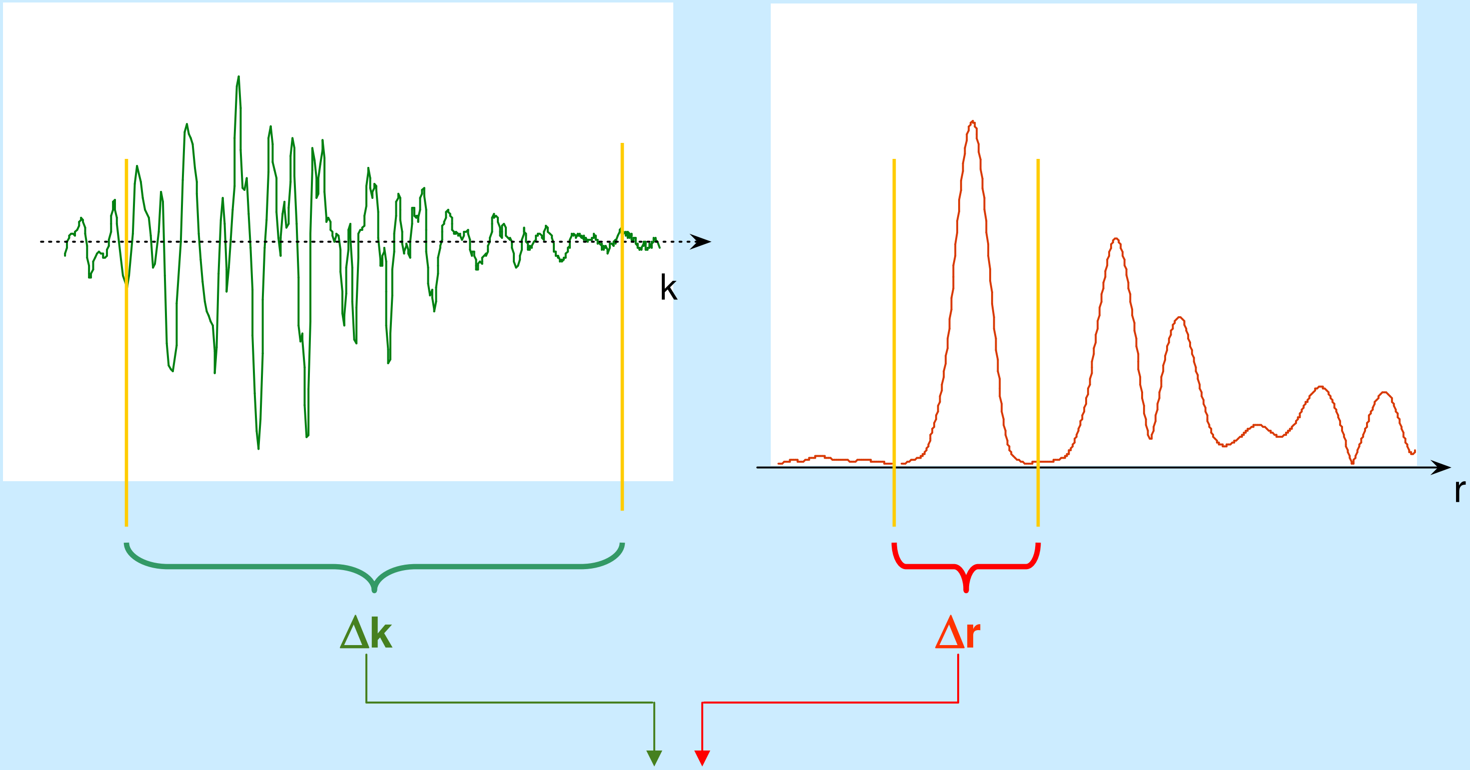

$$N_{\text{ind}} = \frac{2\,\Delta k\,\Delta r}{\pi} + 1$$

Maximum number
of independent parameters

Correlation of parameters

EXAFS data analysis

- ♠ Phase and amplitude analysis

Phase and amplitude

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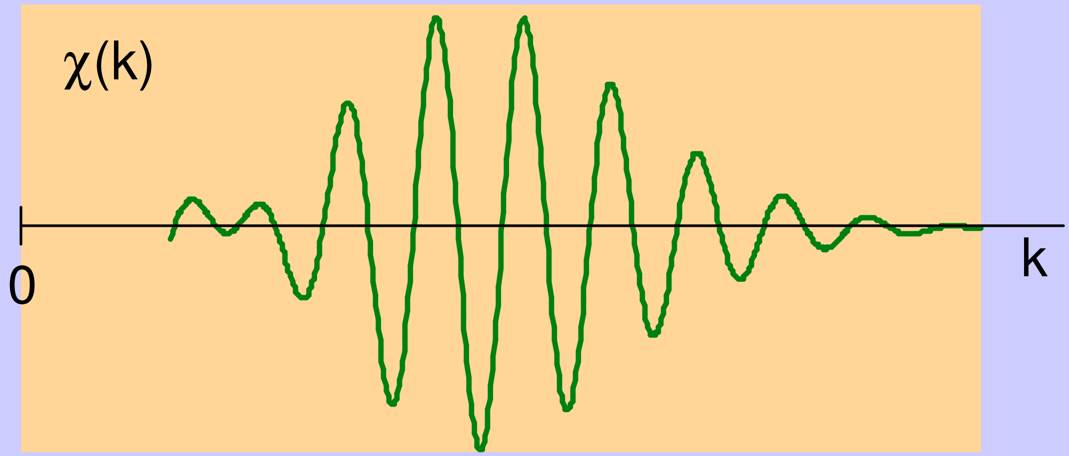

$$\chi(k) = A(k)\sin\Phi(k) = -\frac{1}{2i}A(k)\,\mathrm{e}^{-i\Phi(k)} + \frac{1}{2i}A(k)\,\mathrm{e}^{+i\Phi(k)}$$

$$A(k) = \frac{S_0^2 e^{-2C_1/\lambda}}{kC_1^2}\left|f(k,\pi)\right| N \exp\left[-2k^2C_2 + \frac{2}{4}k^4C_4 + \ldots\right]$$

$$\Phi(k) = 2kC_1 - (4/3)k^3C_3 + \ldots + \phi(k)$$

$$\approx\ 2kC_1 + \vartheta(k)$$

Direct Fourier transform

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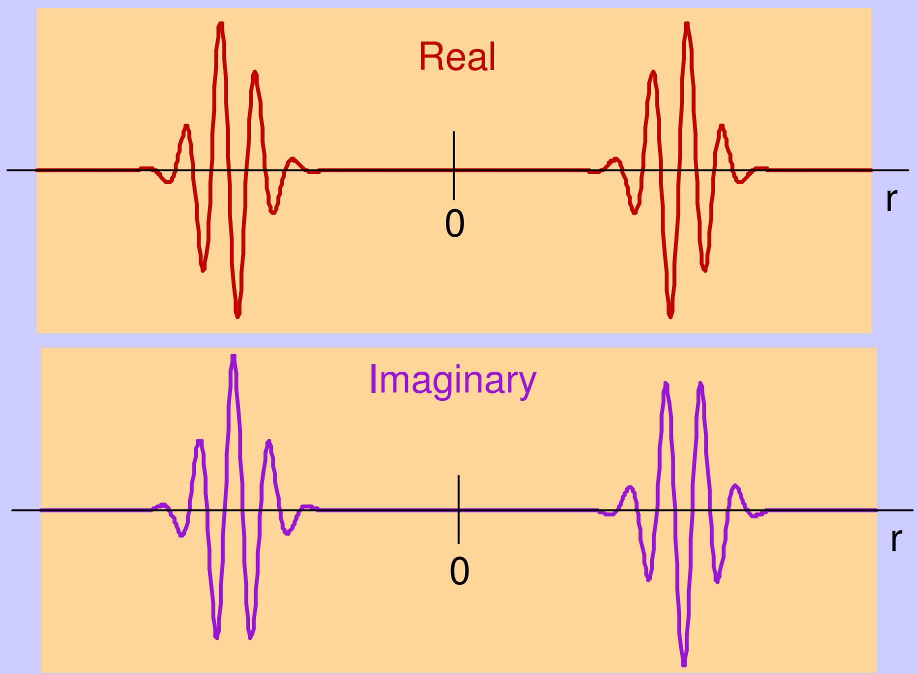
$$F(r) = \int_{k_{\min}}^{k_{\max}} \frac{A(k)}{2i} \left[e^{i\Phi(k)} - e^{-i\Phi(k)} \right] e^{2ikr} dk$$

$$= \int_{k_{\min}}^{k_{\max}} \frac{A(k)}{2i} \left[e^{2ik(C_1+r)+i\theta(k)} - e^{-2ik(C_1-r)+i\theta(k)} \right] dk$$

< 0   > 0

$$F(r) \neq 0 \quad \text{for} \quad \begin{cases} r \approx -C_1 \\ r \approx C_1 \end{cases}$$



(symmetric)

(antisymmetric)

Inverse Fourier transform

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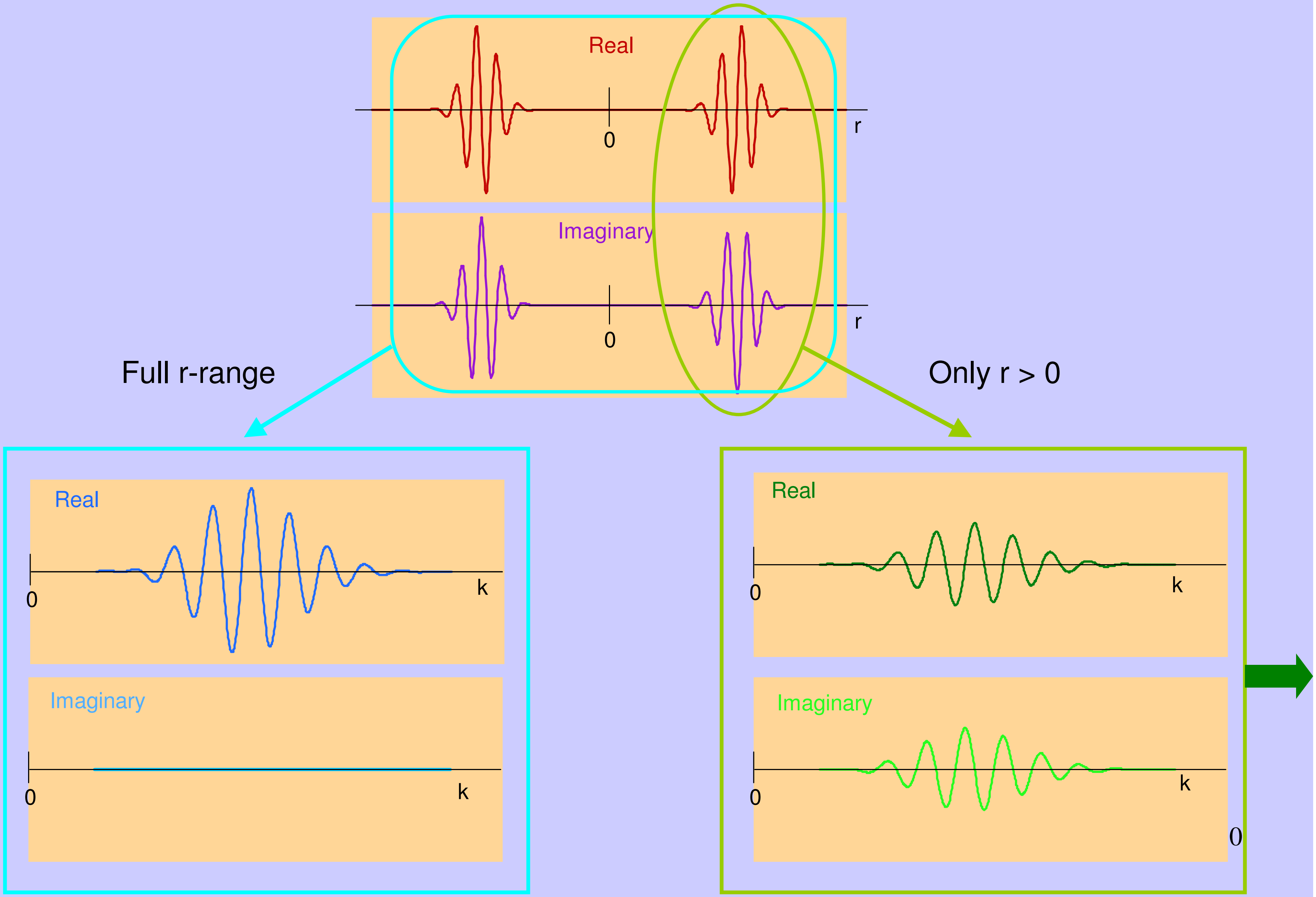
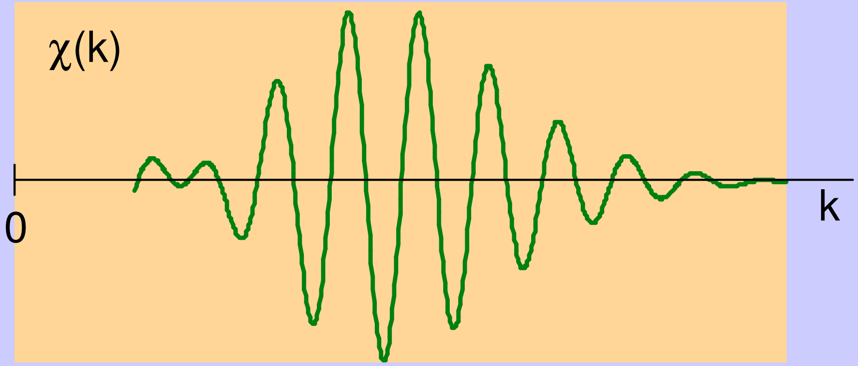


Real and imaginary part

Real original signal

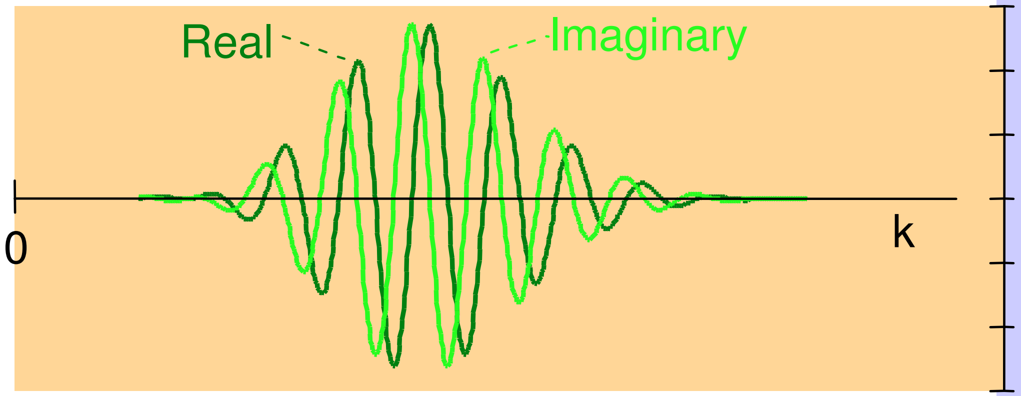


Complex Fourier transform

F.T. artifacts

$$\hat{\chi}(k) = -\frac{\hat{A}(k)}{2i} \exp\left[-i\hat{\Phi}(k)\right]$$

$$= \frac{1}{2} \hat{A}(k) \left[\sin\hat{\Phi}(k) + i\cos\hat{\Phi}(k)\right]$$



Complex filtered signal

Calculation of phase and amplitude

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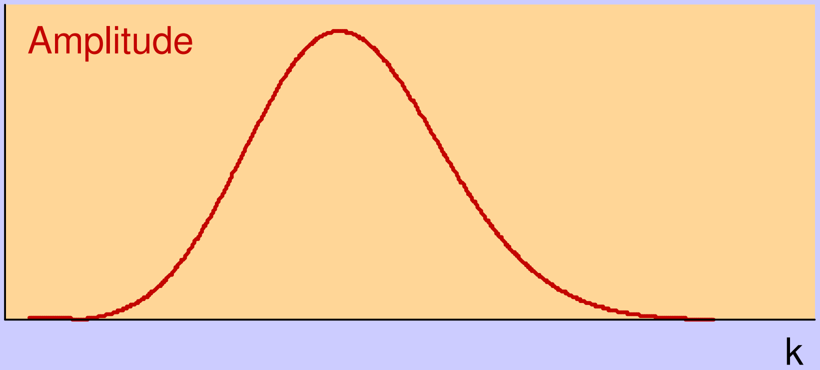
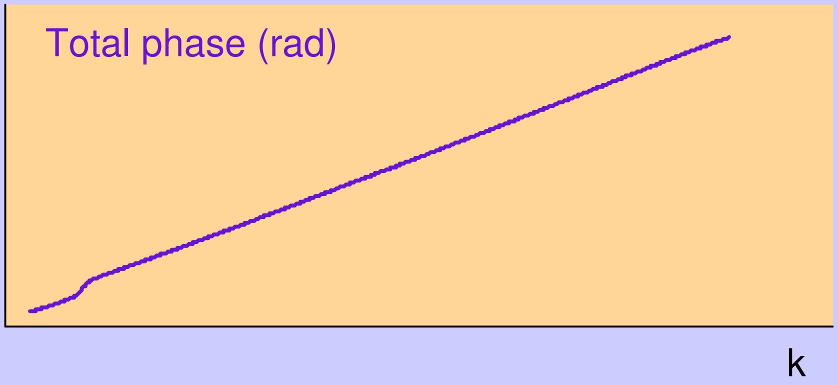
Amplitude

$$\hat{A}(k) = 2\sqrt{[\mathrm{Re}\,\hat{\chi}(k)]^2 + [\mathrm{Im}\,\hat{\chi}(k)]^2}$$

Total phase

$$\hat{\Phi}(k) = \tan^{-1}\left[\frac{\mathrm{Re}\,\hat{\chi}(k)}{\mathrm{Im}\,\hat{\chi}(k)}\right]$$





$$A(k) = \frac{S_0^2\, e^{-2C_1/\lambda}}{C_1^2}\left|f(k,\pi)\right| N \exp\left[-2k^2 C_2 + \frac{2}{4}k^4 C_4 + \ldots\right]$$

?

$$\Phi(k) = 2kC_1 - \frac{4}{3}k^3 C_3 + \ldots + \phi(k)$$

?

“Ratio method” - phases

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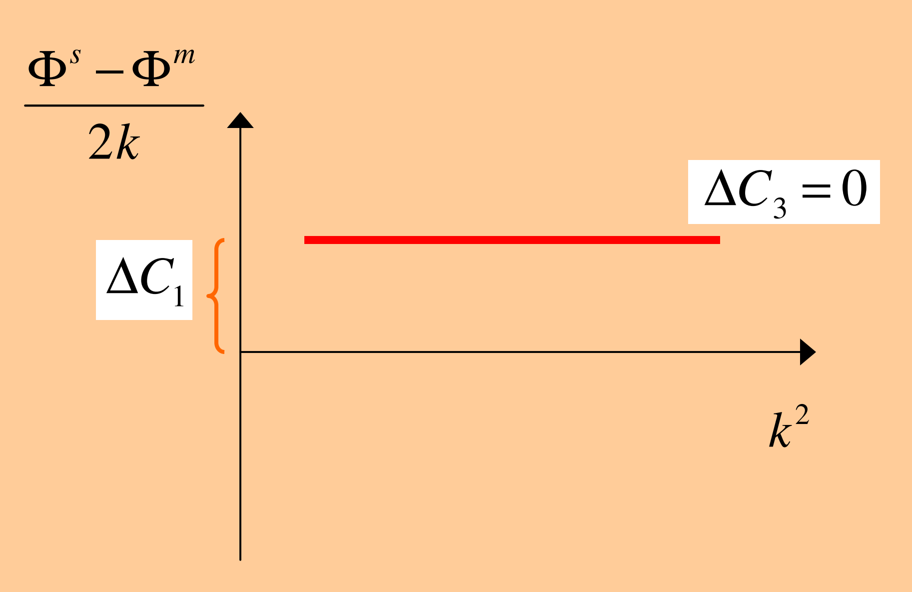
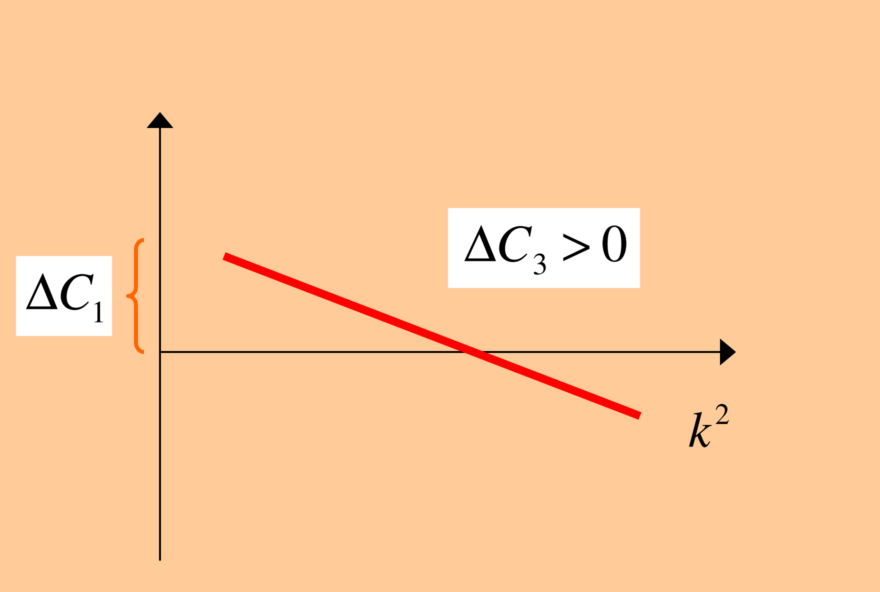
If suitable model compound available …

s = sample
m = model

$$\Phi^s - \Phi^m = 2k\left(C_1^s - C_1^m\right) - \frac{4}{3}k^3\left(C_3^s - C_3^m\right)$$

$$\frac{\Phi^s - \Phi^m}{2k} = \left(C_1^s - C_1^m\right) - \frac{4}{3}k^2\left(C_3^s - C_3^m\right)$$





"Ratio method" - amplitudes

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University of Trento (Italy)

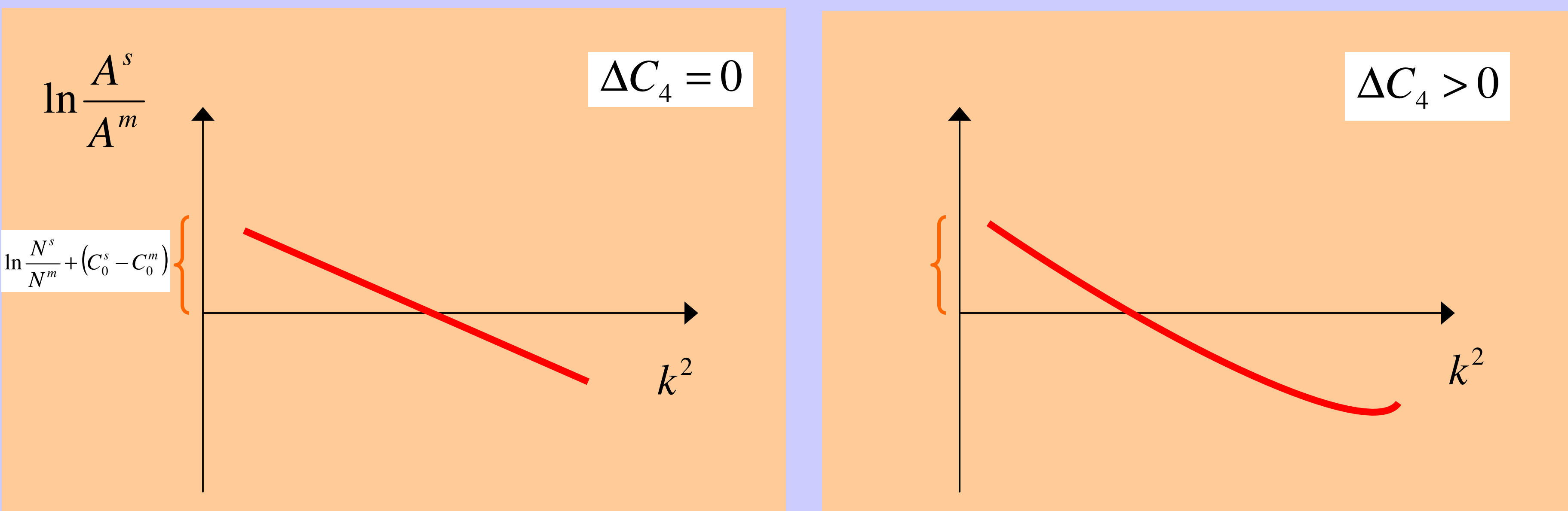
If suitable model compound available …

s = sample
m = model

$$\ln\frac{A^s}{A^m} = \ln\frac{N^s}{N^m} + \left(C_0^s - C_0^m\right) - 2k^2\left(C_2^s - C_2^m\right) + \frac{2}{3}k^4\left(C_4^s - C_4^m\right)$$

intercept

Linear slope



"Ratio method" - results

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Ratio of coordination numbers

$$\frac{N^s}{N^m}$$

$$C_0^s - C_0^m = -2\frac{C_1^s - C_1^m}{\lambda} - 2\left[\ln C_1^s - \ln C_1^m\right]$$

Relative values of cumulants

$$\delta C_i = C_i^s - C_i^m$$

- δC_1 → Thermal expansion
- δC_2 Width
- δC_3 Asymmetry
- ……

- Absolute values ?
- Physical meaning ?

“Ratio method” - OK when …

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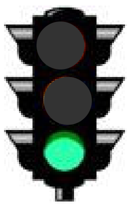
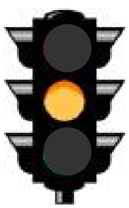
- *Only Single Scattering*
- *Only one distance*
- *Suitable reference model available*

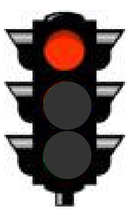
$$\chi(k) \;=\; A(k)\sin\Phi(k)$$



- First coordination shell, one distance
- Same sample-model chemical environment
  - T or p-dep. Studies
  - Amorphous .vs. crystalline samples



- 1st shell, different sample-model chemical environment
- Separated outer shells, weak M.S.



- 1st shell in bcc structure (2 distances)
- Superposed outer shells
- M.S. contributions

Depending on sought accuracy

Copper 1st shell - ratio method

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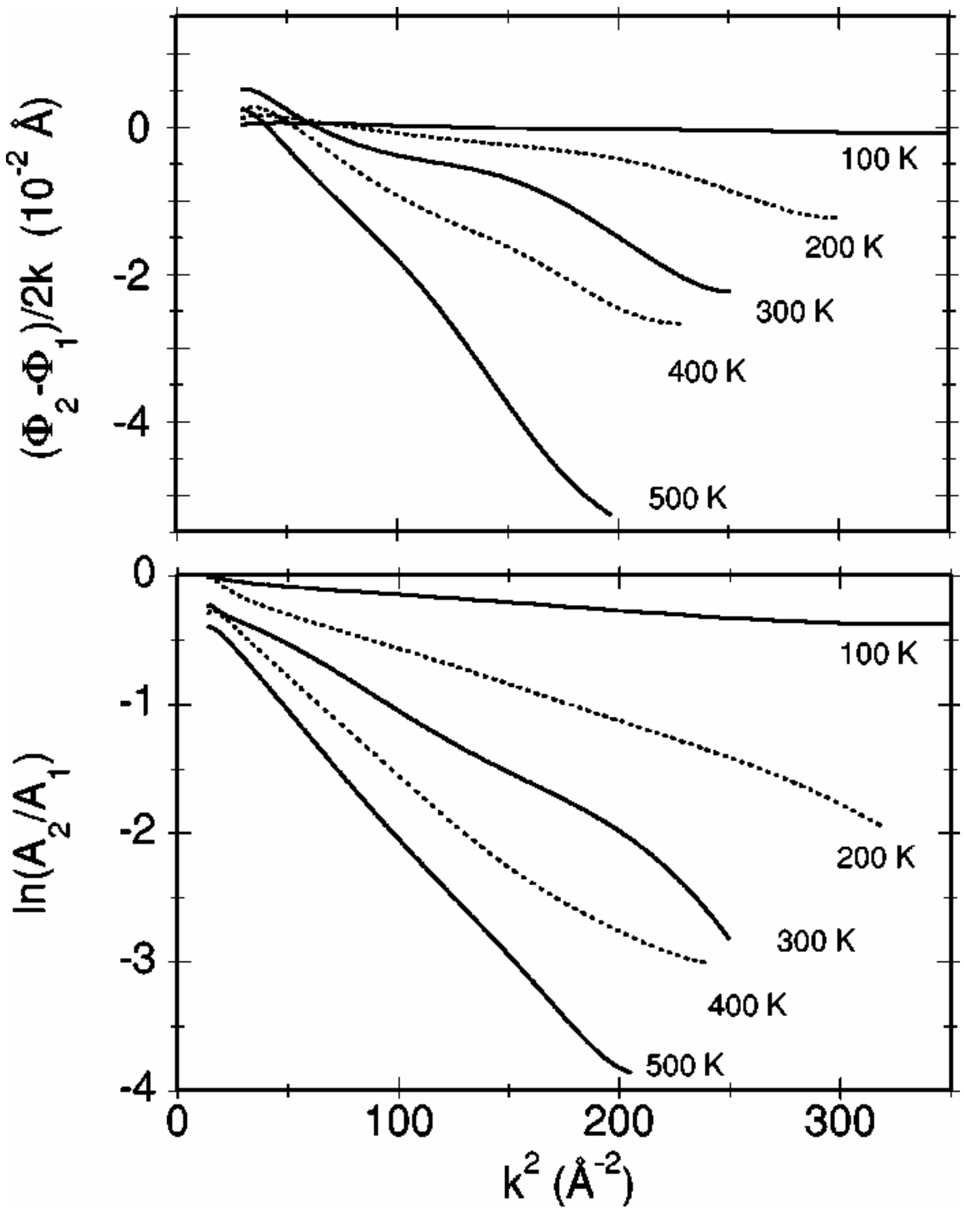


Phases

Amplitudes

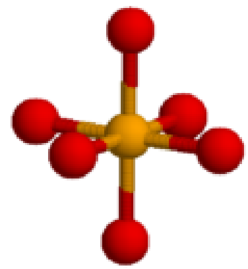
EXAFS data analysis

♠ Fitting with a theoretical model

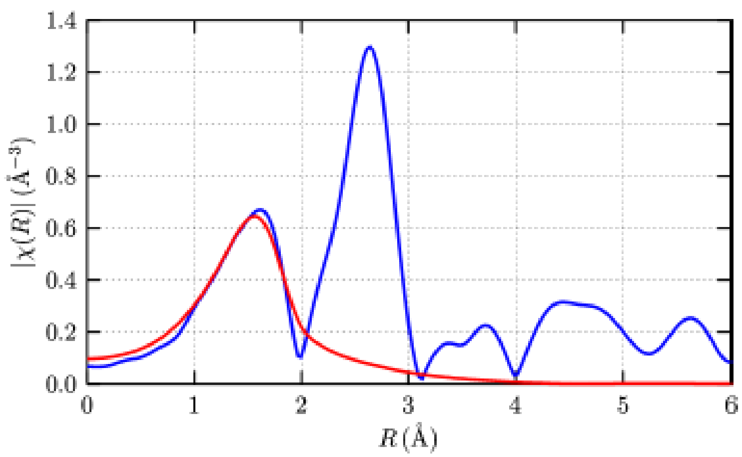
EXAFS Analysis: Modeling the 1st Shell of FeO

FeO has a rock-salt structure.

To model the FeO EXAFS, we calculate the scattering amplitude $f(k)$ and phase-shift $\delta(k)$, based on a guess of the structure, with Fe-O distance $R = 2.14$ Å (a regular octahedral coordination).



We'll use these functions to *refine* the values R, N, σ^2, and E_0 so our model EXAFS function matches our data.

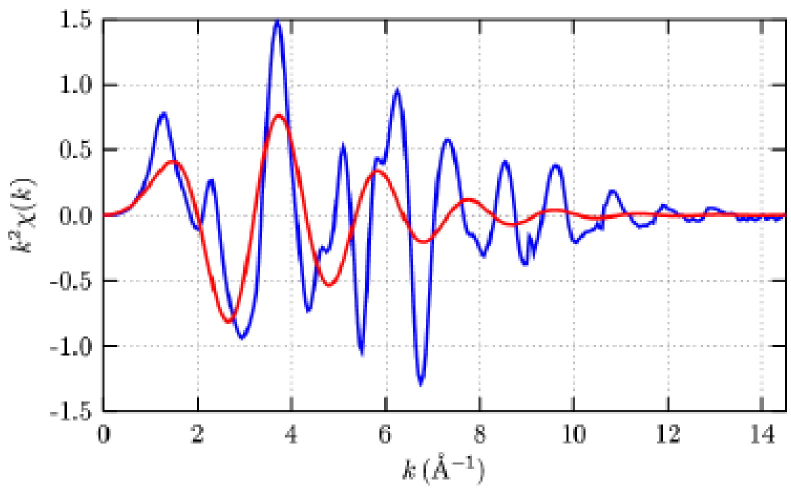


$|\chi(R)|$ for FeO (blue), and a 1st shell fit (red).

Fit results:

N	= 5.8 $\pm$ 1.8
R	= 2.10 $\pm$ 0.02Å
ΔE_0	= -3.1 $\pm$ 2.5 eV
σ^2	= 0.015 $\pm$ 0.005 Å^2.

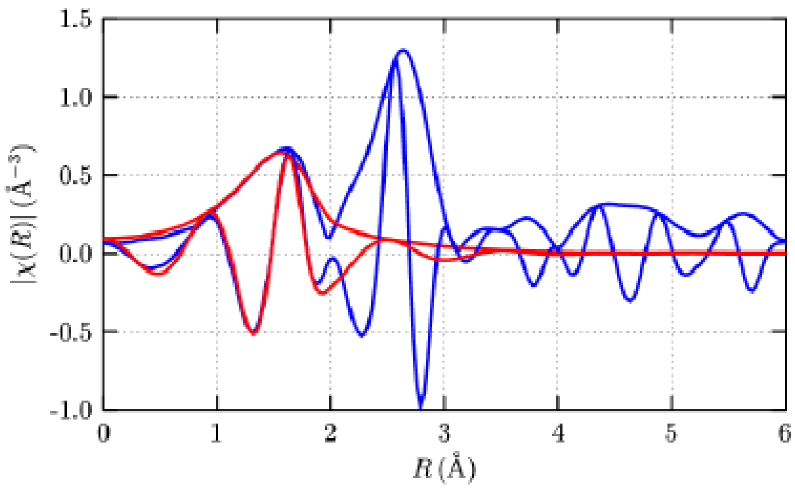
EXAFS Analysis: 1st Shell of FeO



1^{st} shell fit in k space.

The 1^{st} shell fit to FeO in k space.

There is clearly another component in the XAFS!



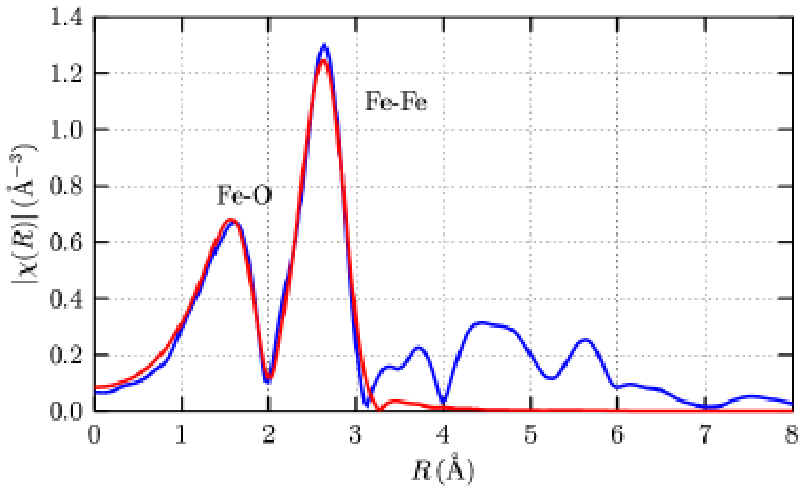
1^{st} shell fit in R space.

$|\chi(R)|$ and Re$[\chi(R)]$ for FeO (blue), and a 1st shell fit (red).

Though the fit to the magnitude didn't look great, the fit to Re$[\chi(R)]$ looks very good.

EXAFS Analysis: Second Shell of FeO

To adding the second shell Fe to the model, we use calculation for $f(k)$ and $\delta(k)$ based on a guess of the Fe-Fe distance, and refine the values R, N, σ^2.
Such a fit gives a result like this:



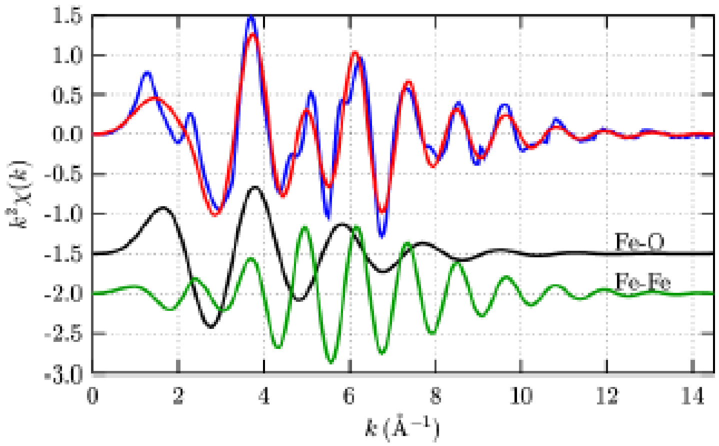
$|\chi(R)|$ data for FeO (blue), and fit of 1st and 2nd shells (red).
The results are fairly consistent with the known values for crystalline FeO:
6 O at 2.13Å, 12 Fe at 3.02Å.

Fit results (uncertainties in parentheses):

Shell	N	R (Å)	σ^2 (Å^2)	ΔE_0 (eV)
Fe-O	6.0(1.0)	2.10(.02)	0.015(.003)	-2.1(0.8)
Fe-Fe	11.7(1.3)	3.05(.02)	0.014(.002)	-2.1(0.8)

EXAFS Analysis: Second Shell of FeO

Other views of the data and two-shell fit:

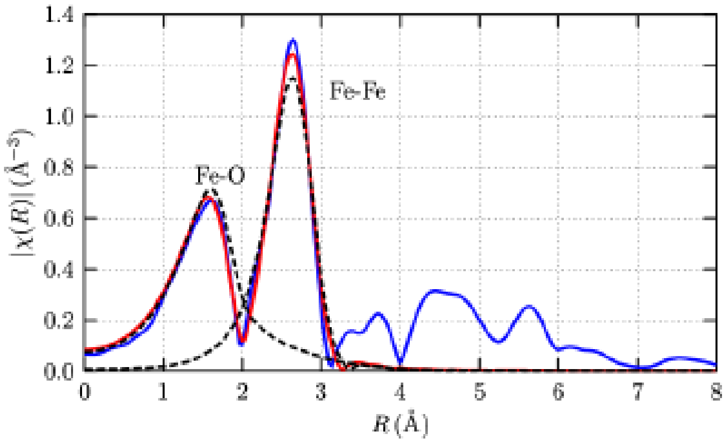


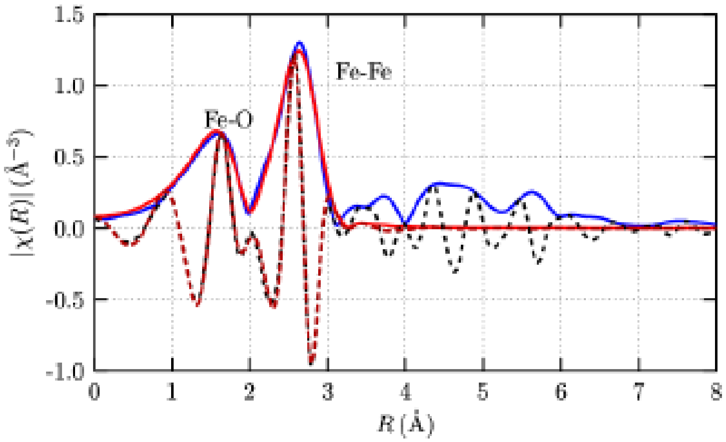
The Fe-Fe EXAFS extends to higher-k than the Fe-O EXAFS.

Even in this simple system, there is some *overlap* of shells in R-space.

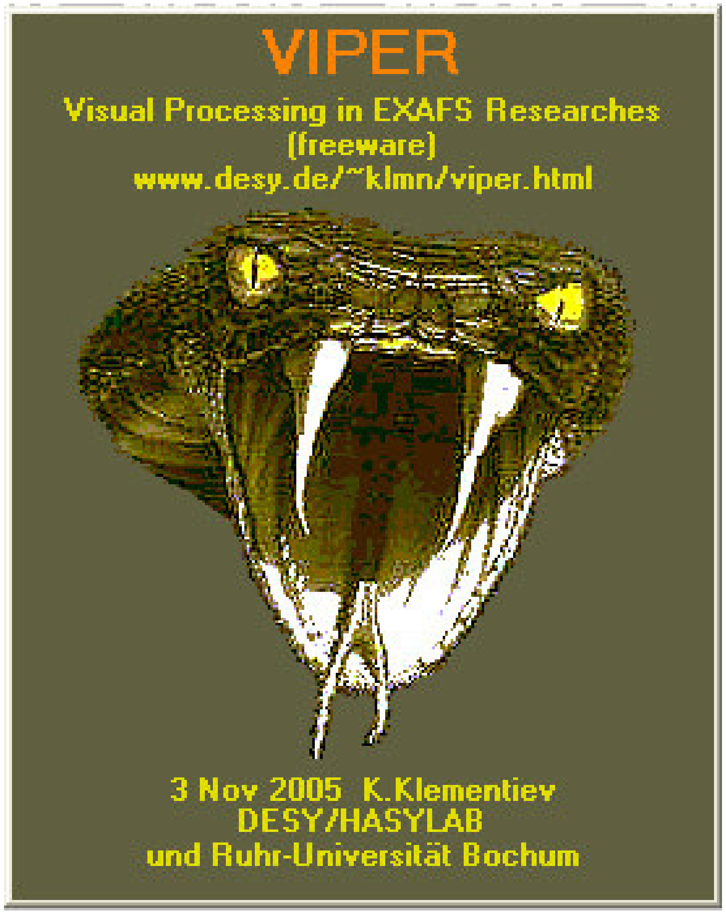
The agreement in Re$[\chi(R)]$ look especially good – this is how the fits are done.

Of course, the modeling can get more complicated than this!





A free program for EXAFS data analysis



Loading data

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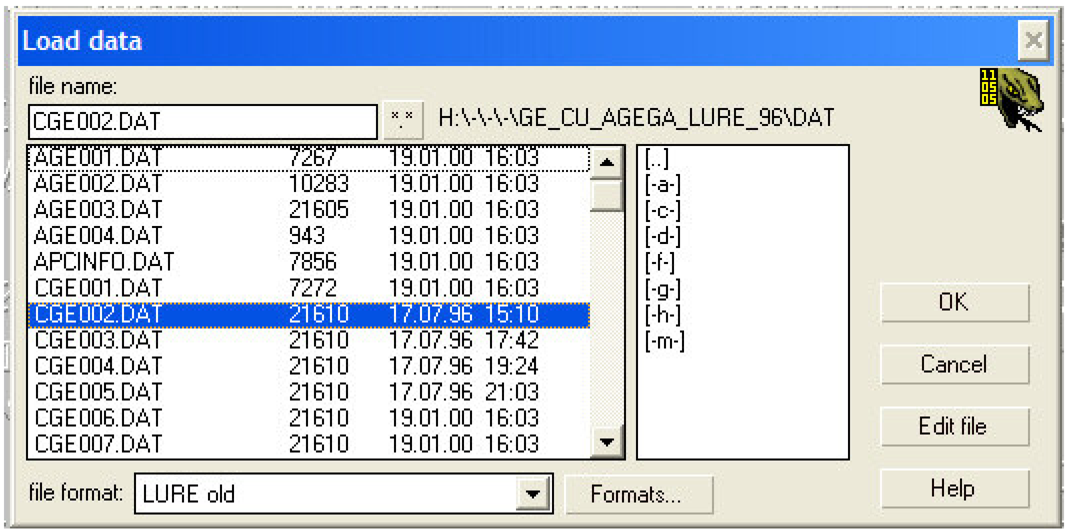

Reading raw data

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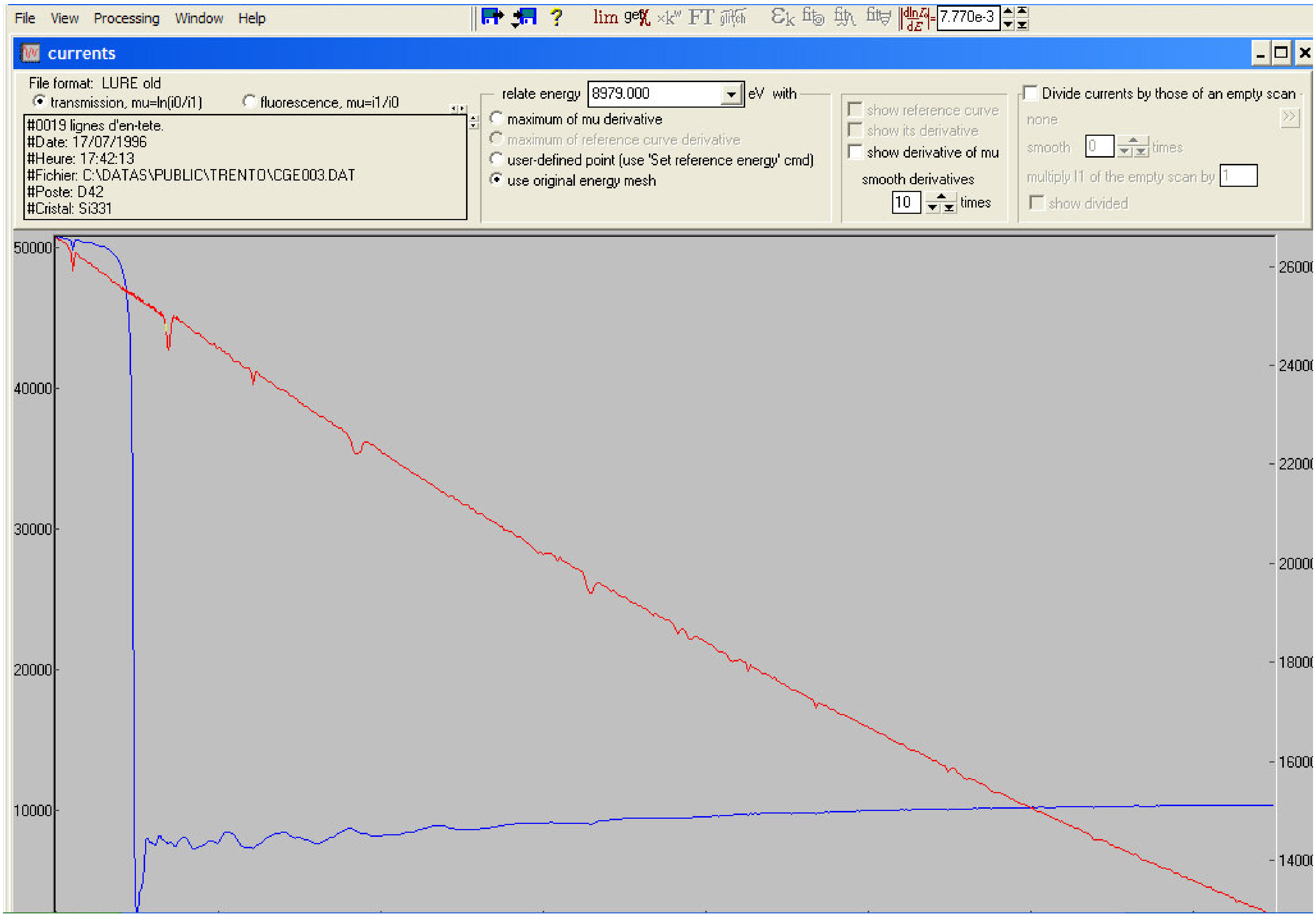

B.G subtraction and FT

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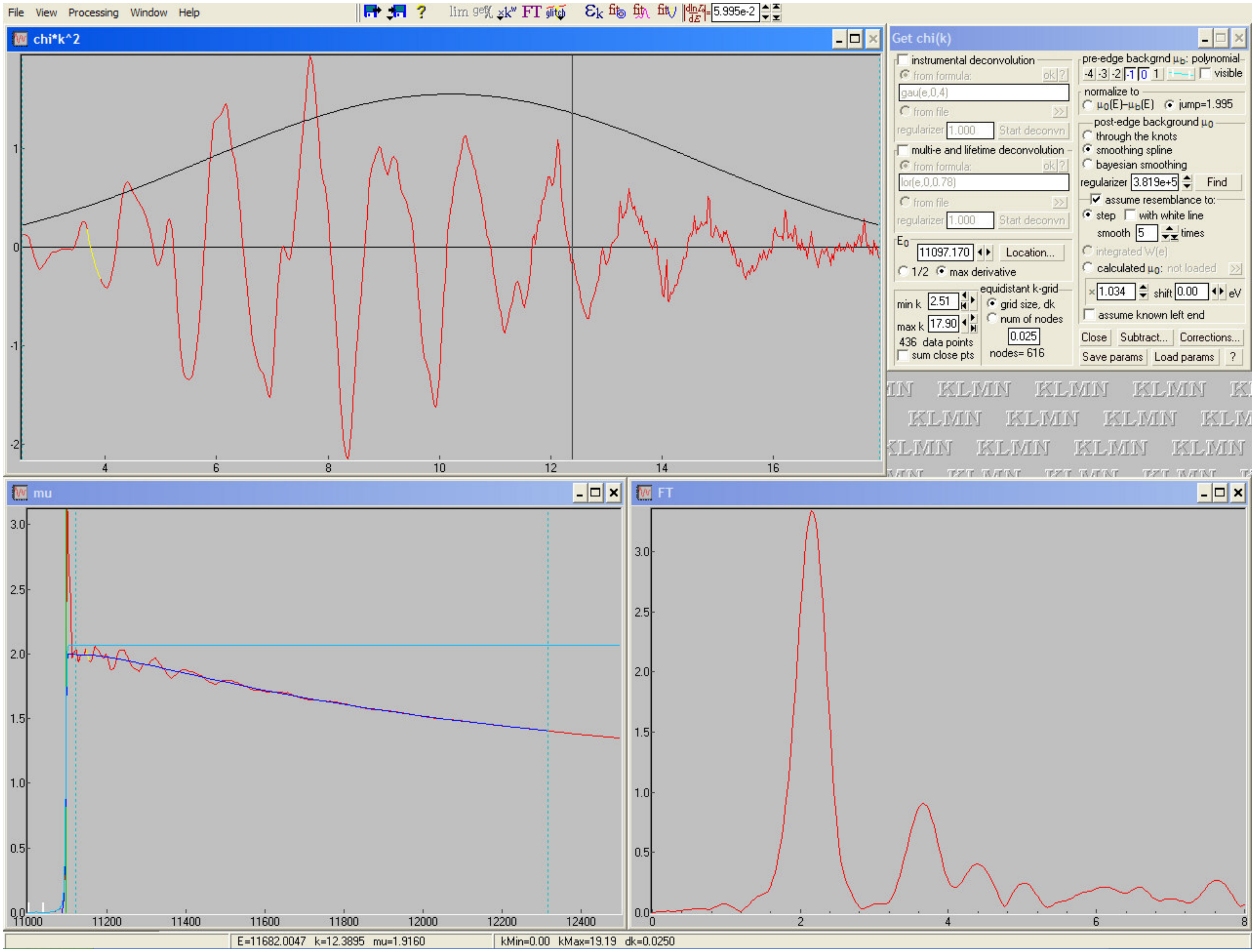

Enlarged view of the edge region

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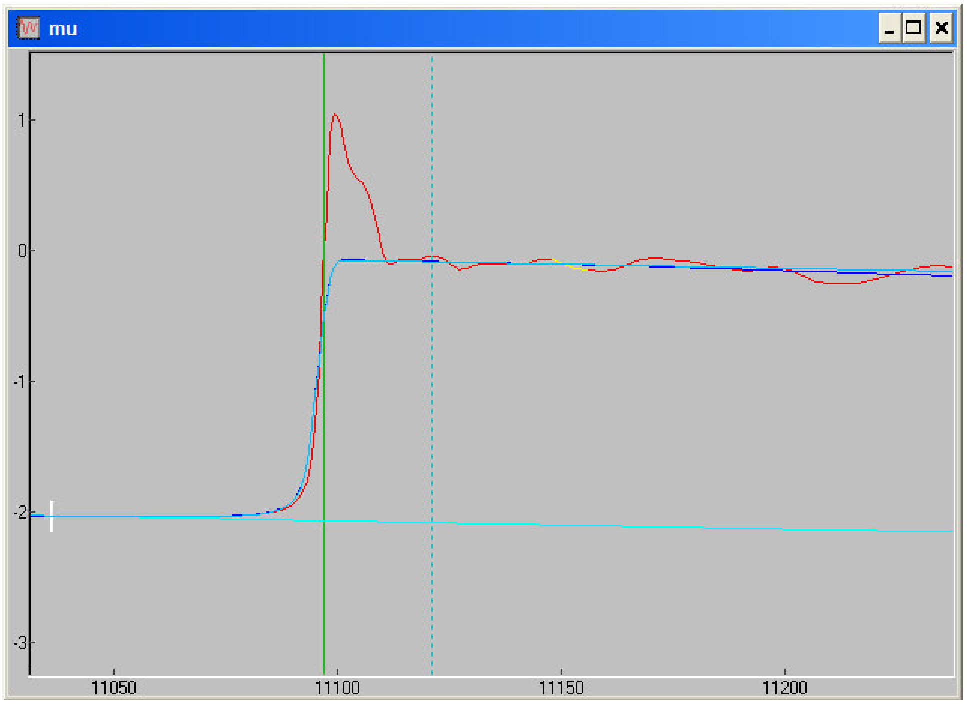

Legend

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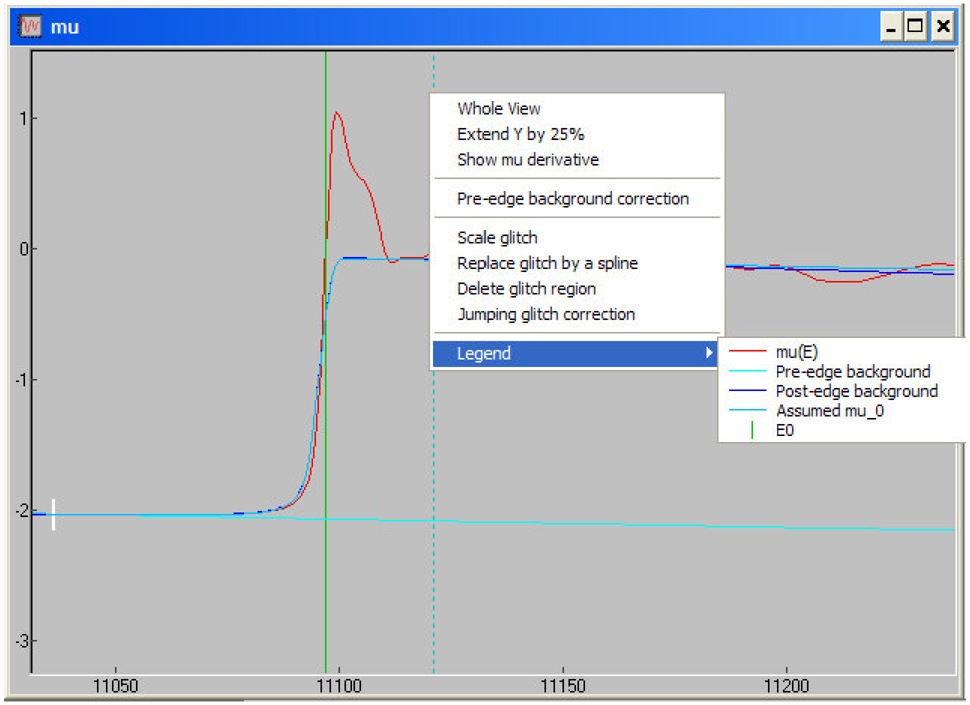

Details about the FT

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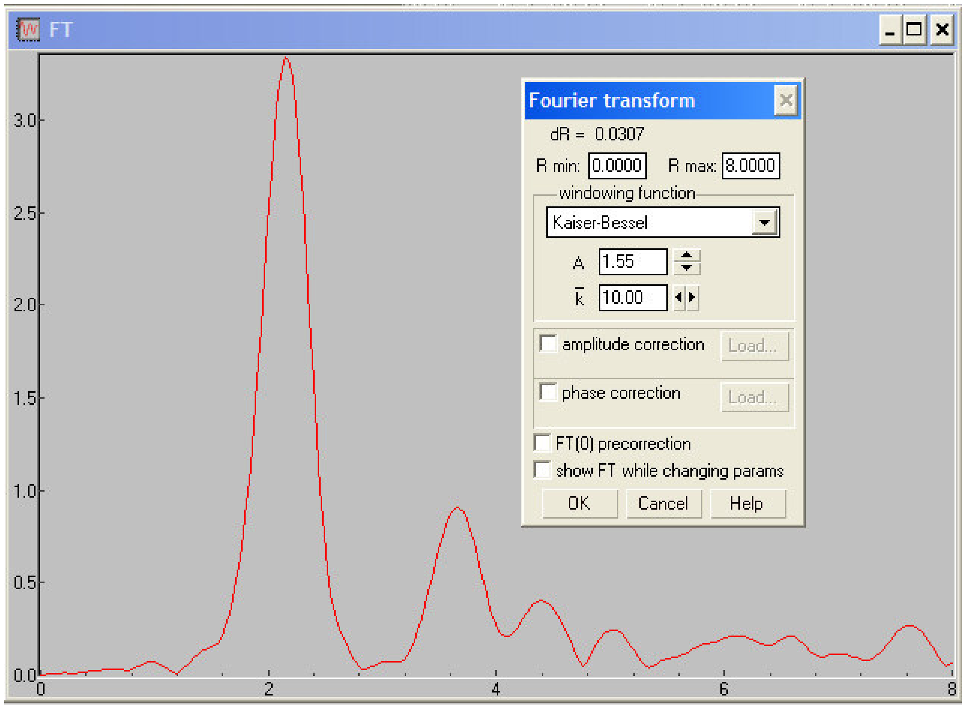
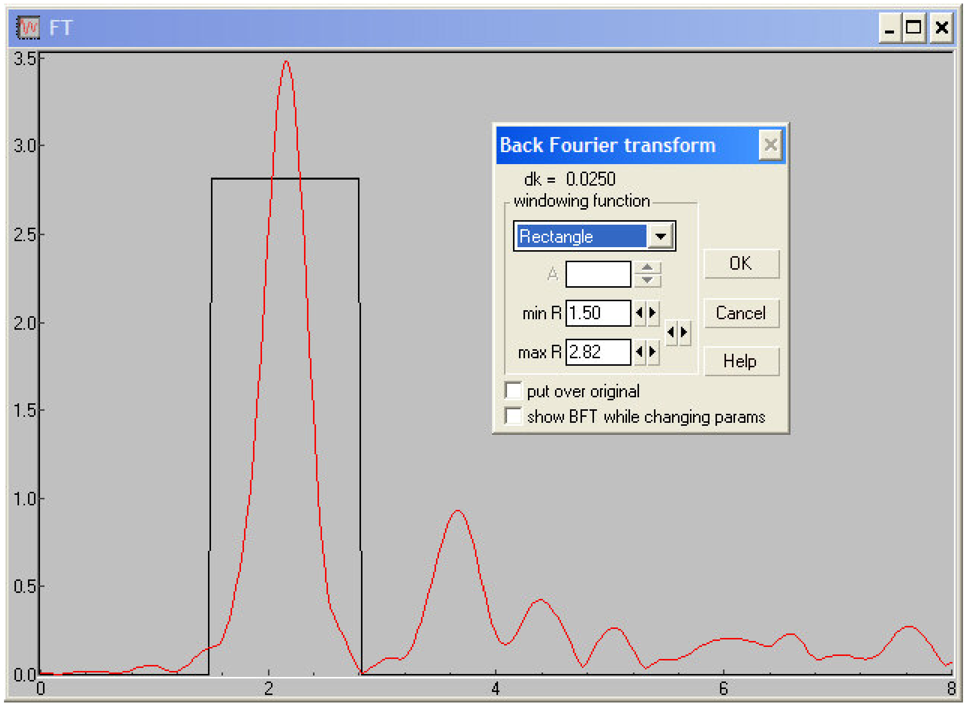


Isolation of the first shell



First shell BFT

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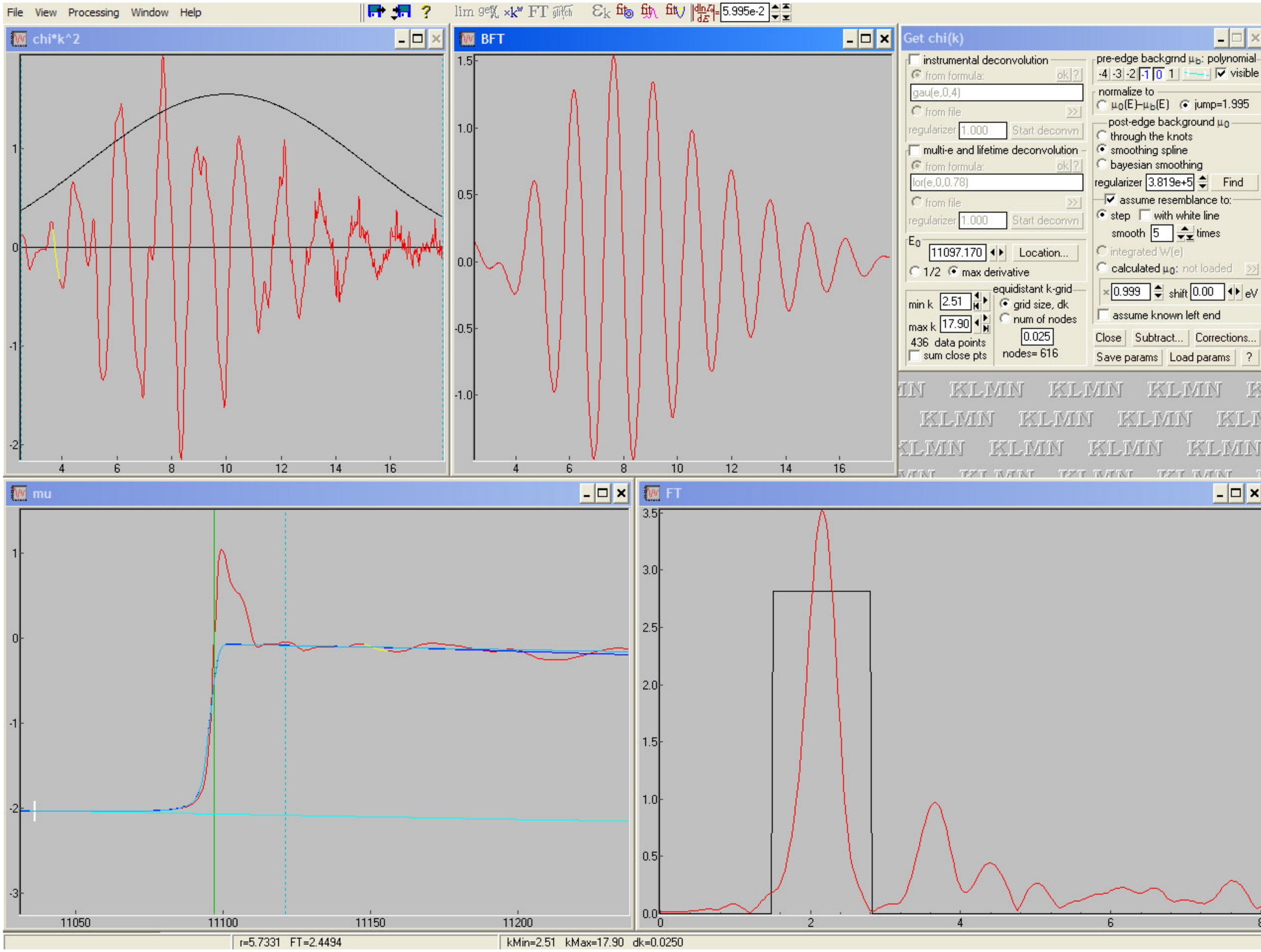

Amplitude and phase calculation

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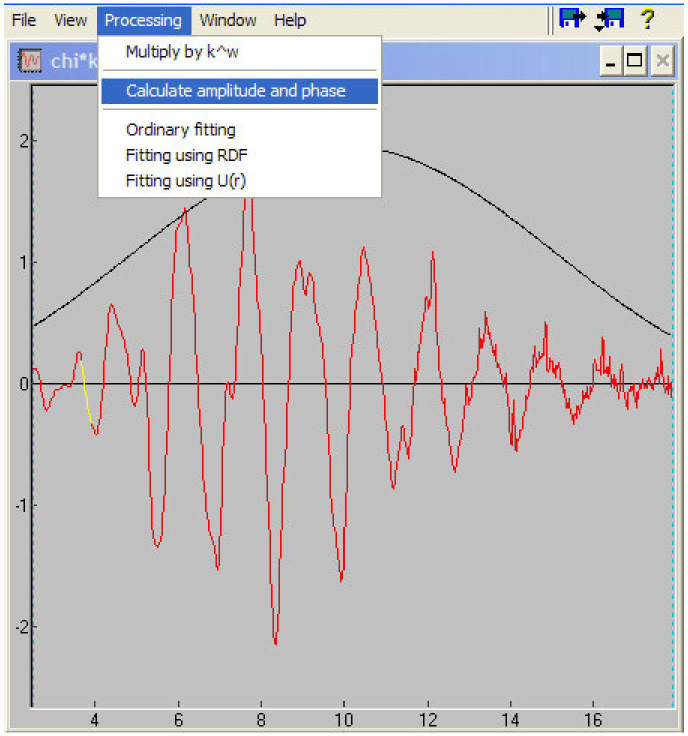

BFT details with calculated amplitude and phase

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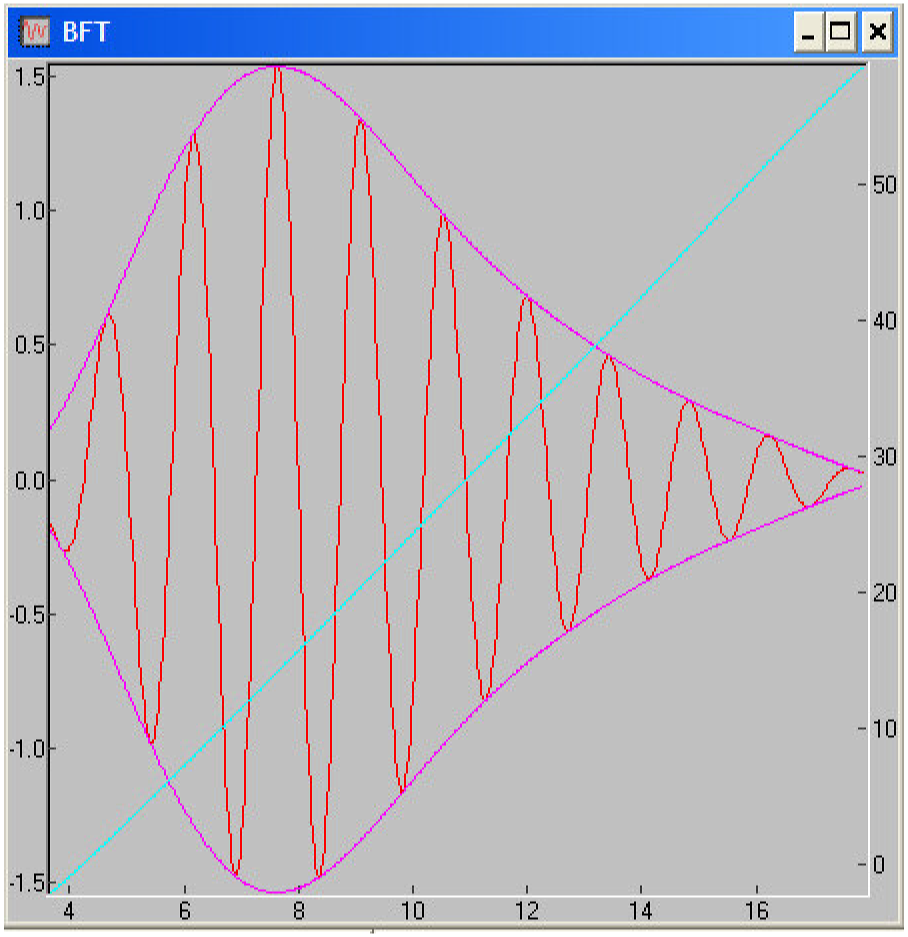

Athena: another (free) program for EXAFS

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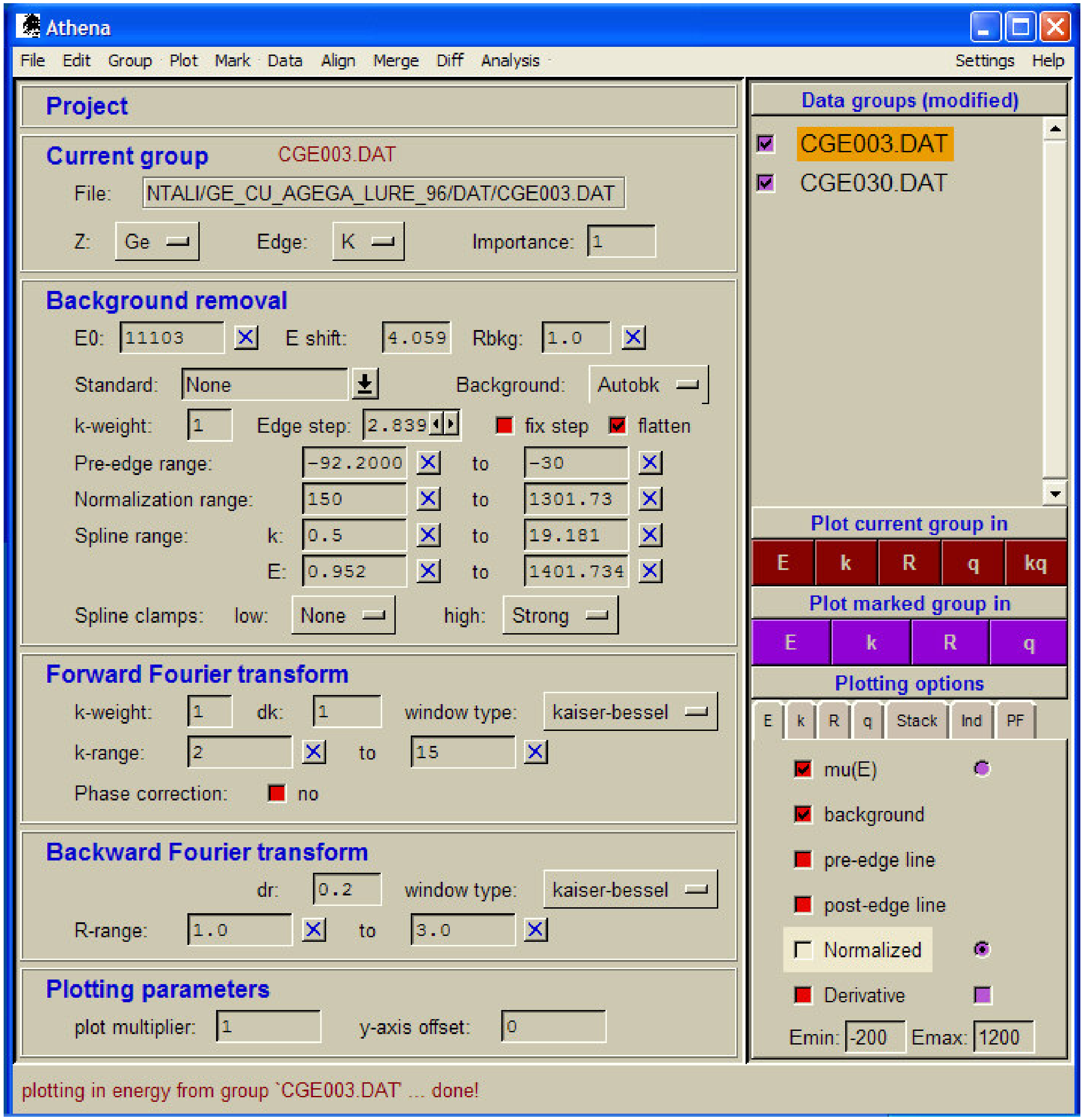

BG removal

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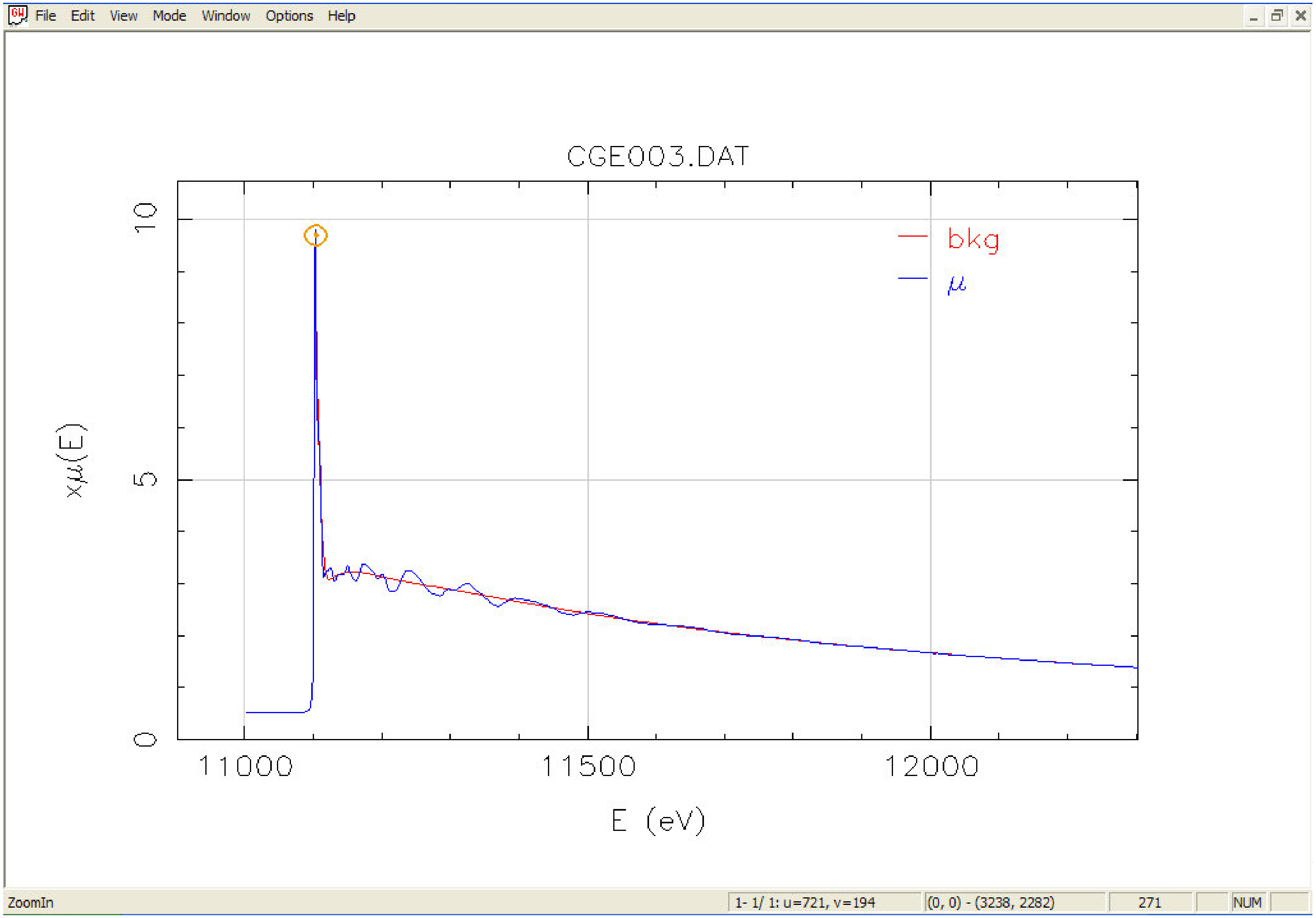

FT of the two samples

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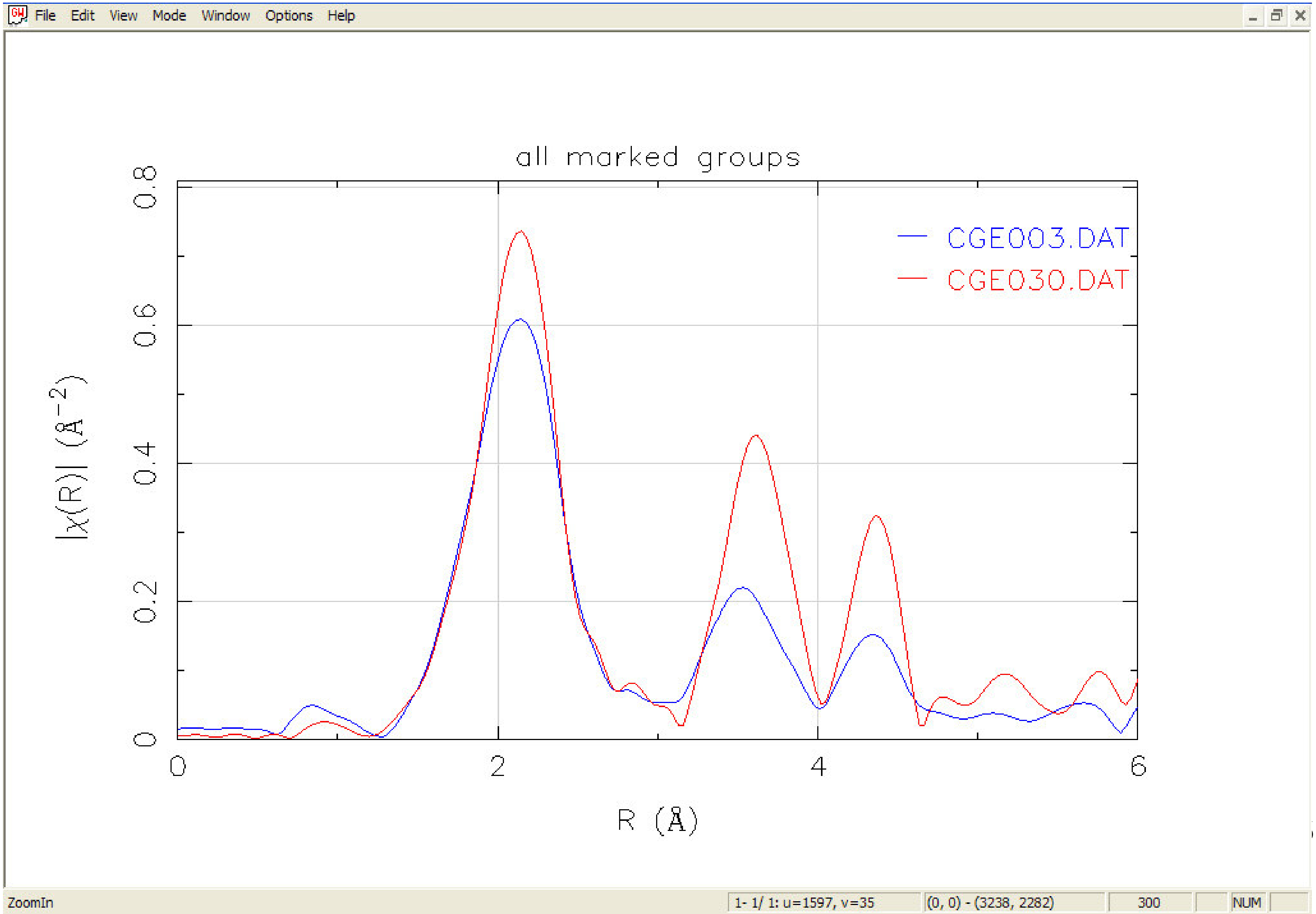

Back FT of the first shell

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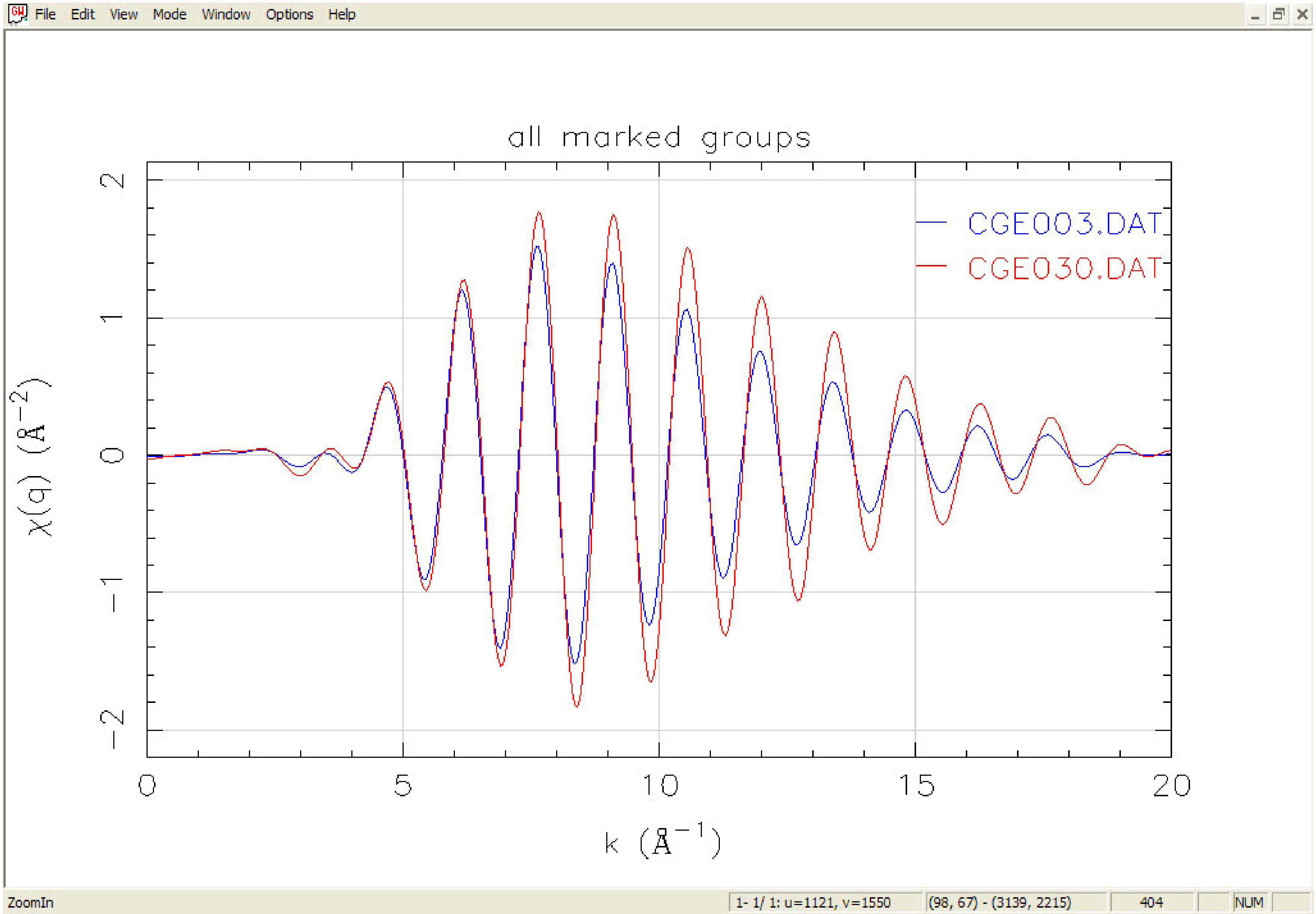
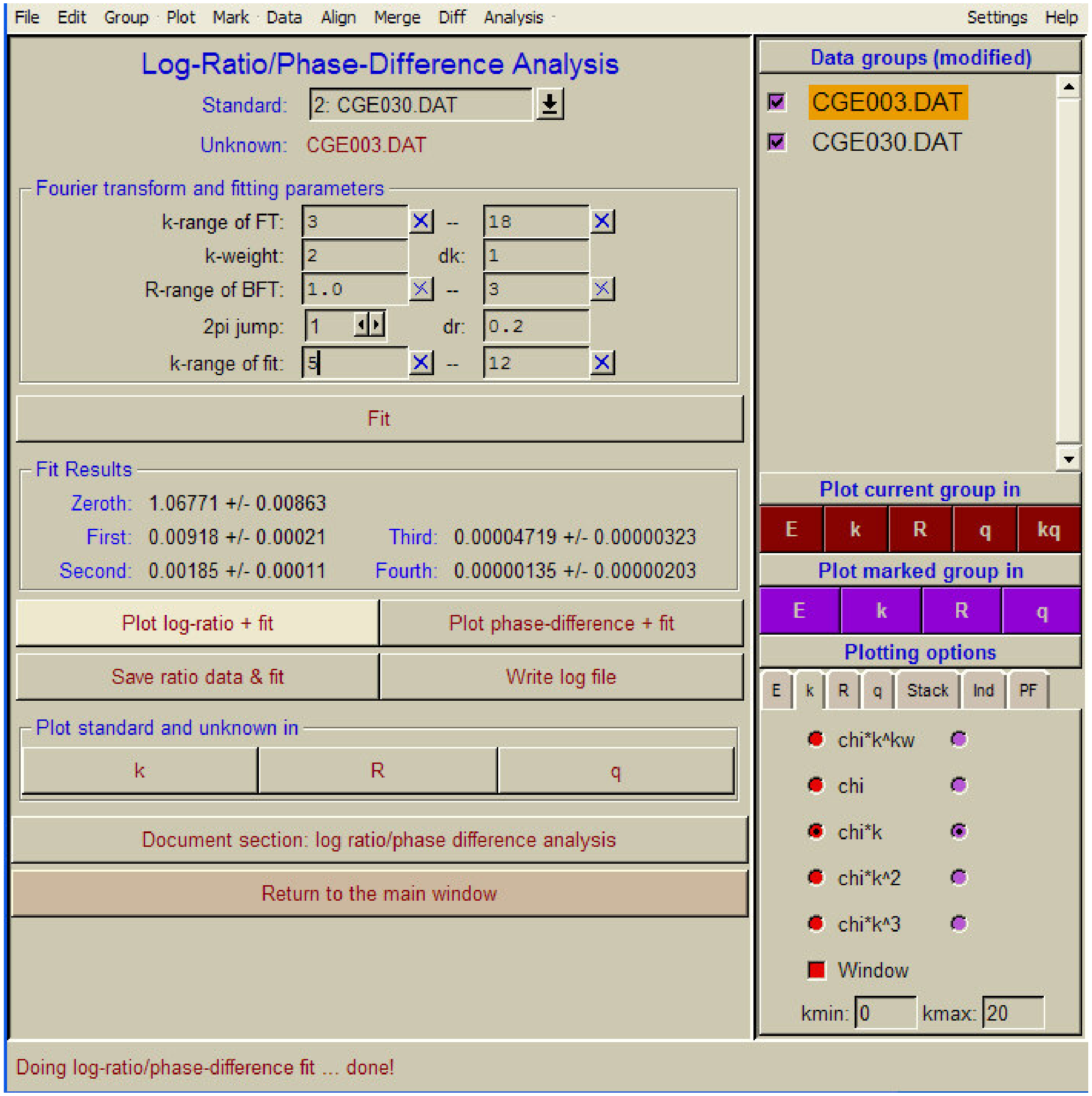


Amplitude-Phase analysis



Amplitude analysis: $\ln(N_s / N_m)$

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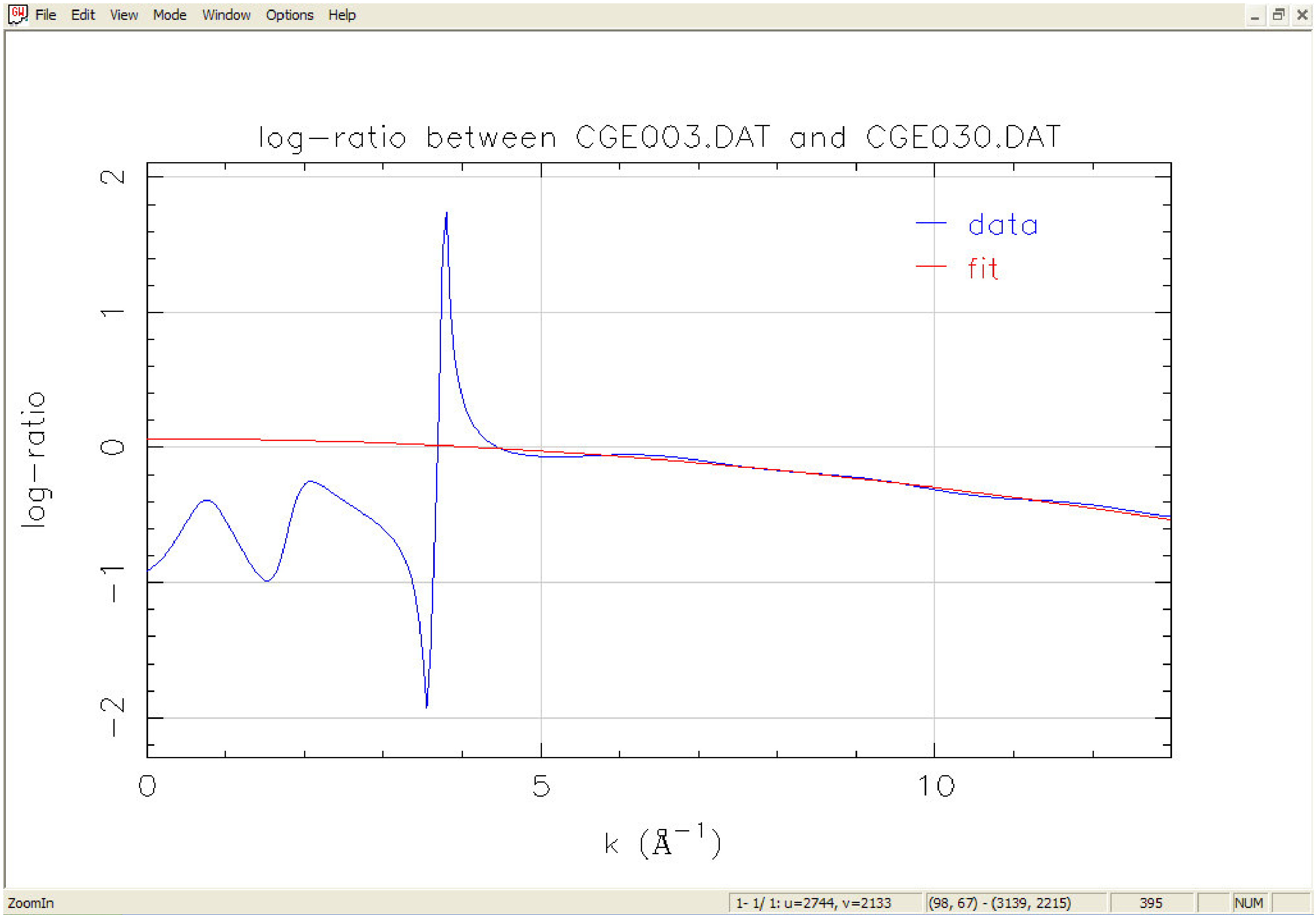

Phase analysis : $\Phi_s - \Phi_m$

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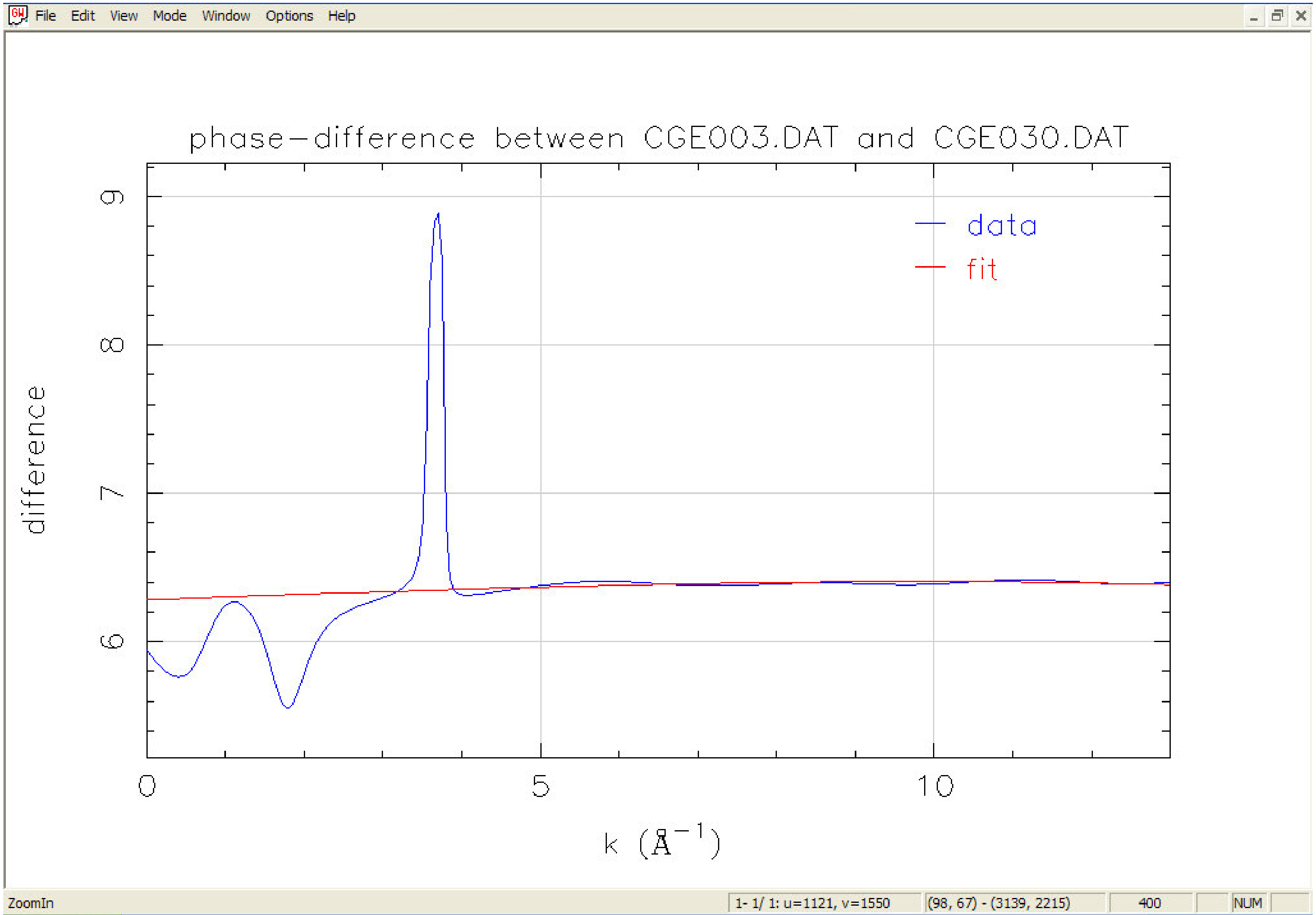

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Thank you for your attention