XAFS:

Study of the local structure around an X-ray absorbing atom

T.Ohta, Univ.Tokyo, Japan

(1) Principle of XAFS

(2) Instrumentation

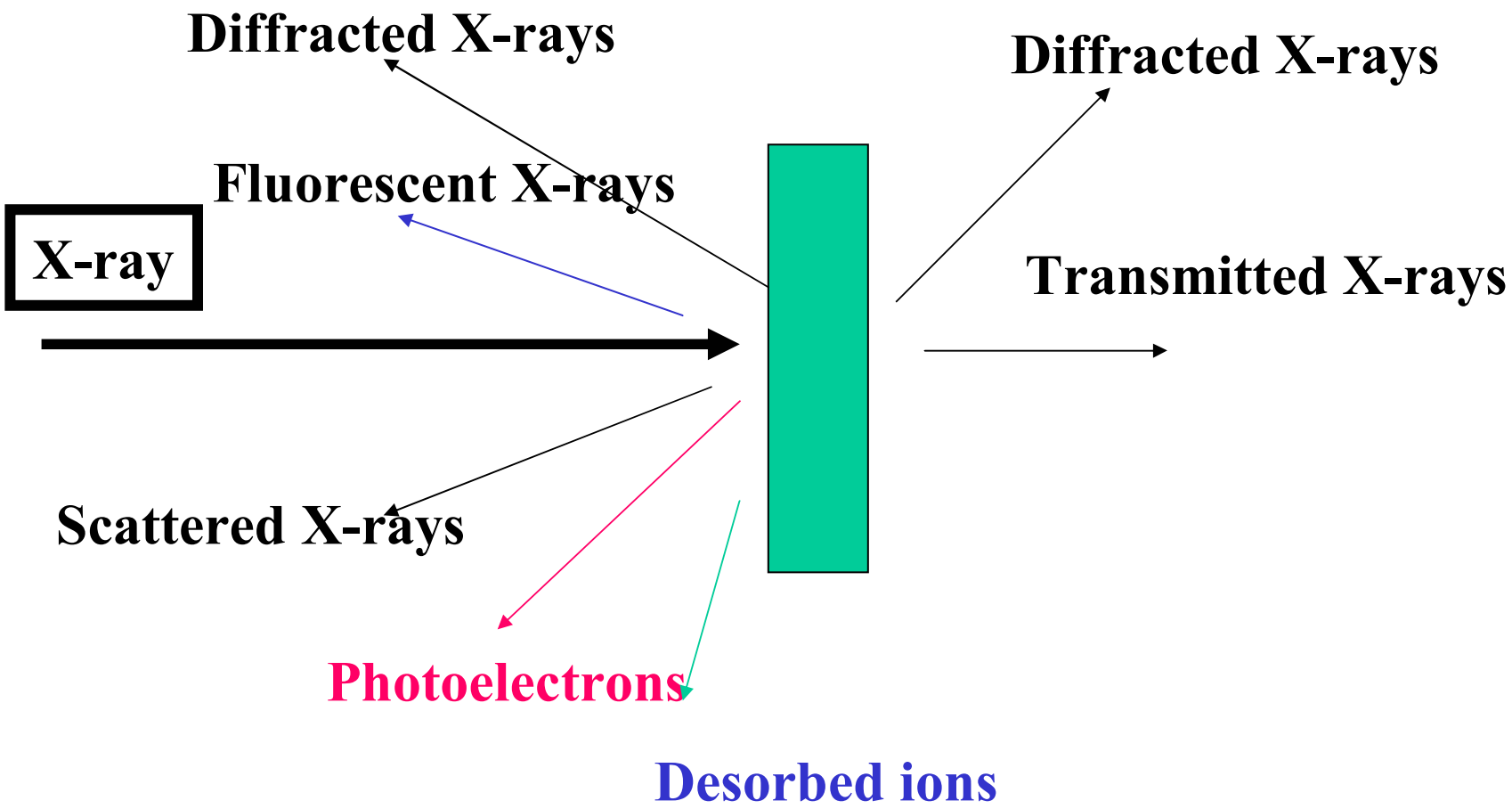
(3) XAFS spectral analysis

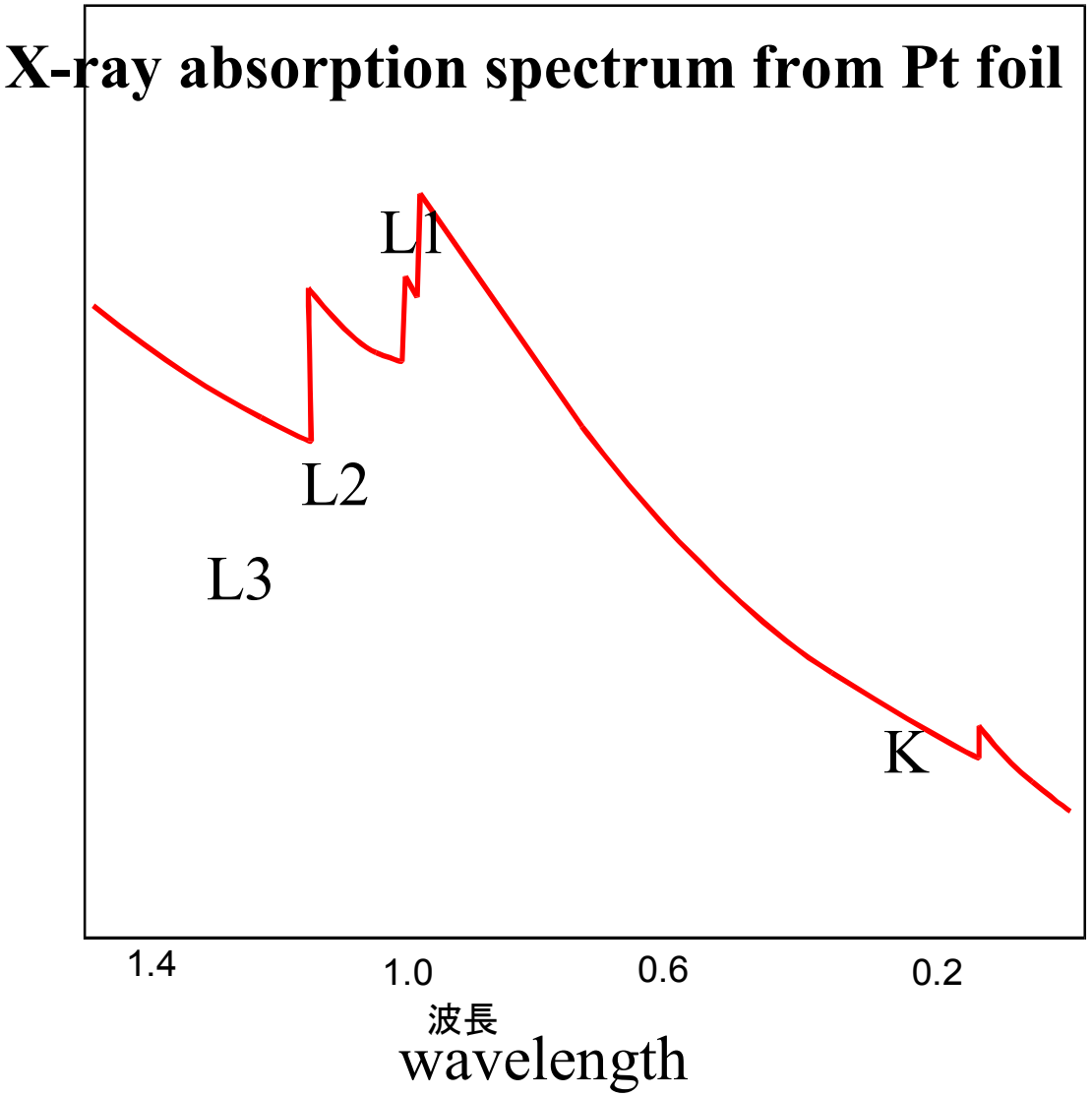
(4) XAFS applications

(5) New directions of XAFS

(1) Principle of XAFS

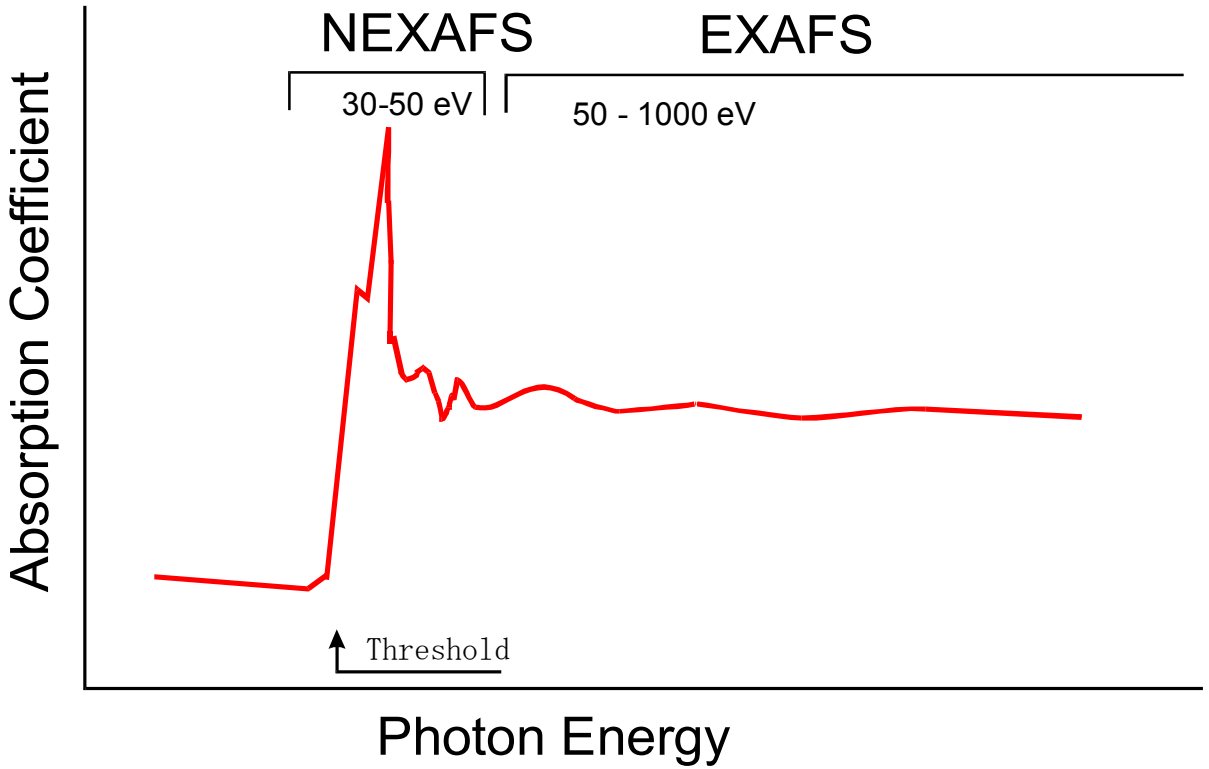
Phenomena caused by X-ray irradiation



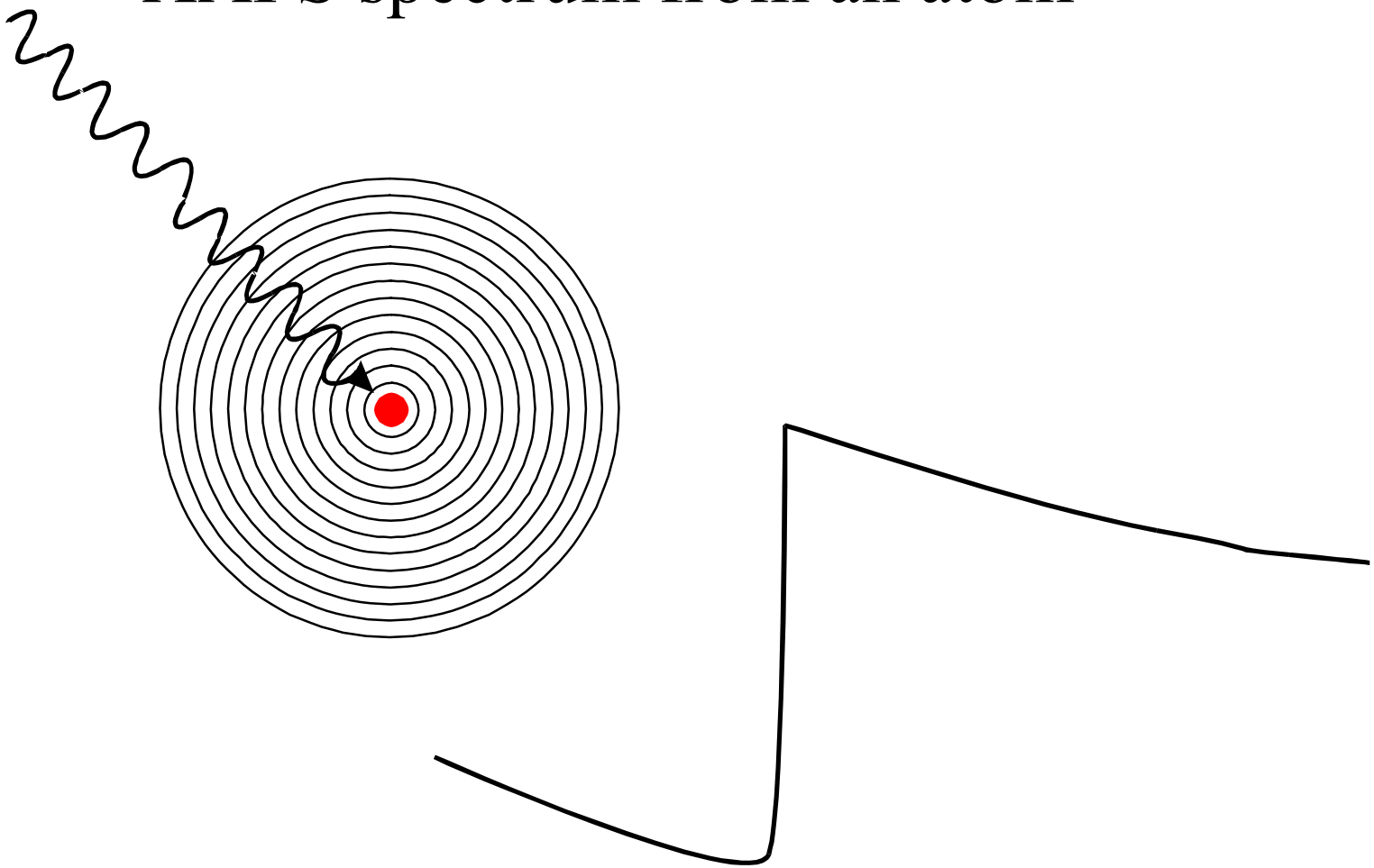

X-ray absorption spectrum from Pt foil
L1
L2
L3
K
1.4
1.0
0.6
0.2
波長
wavelength

XAFS

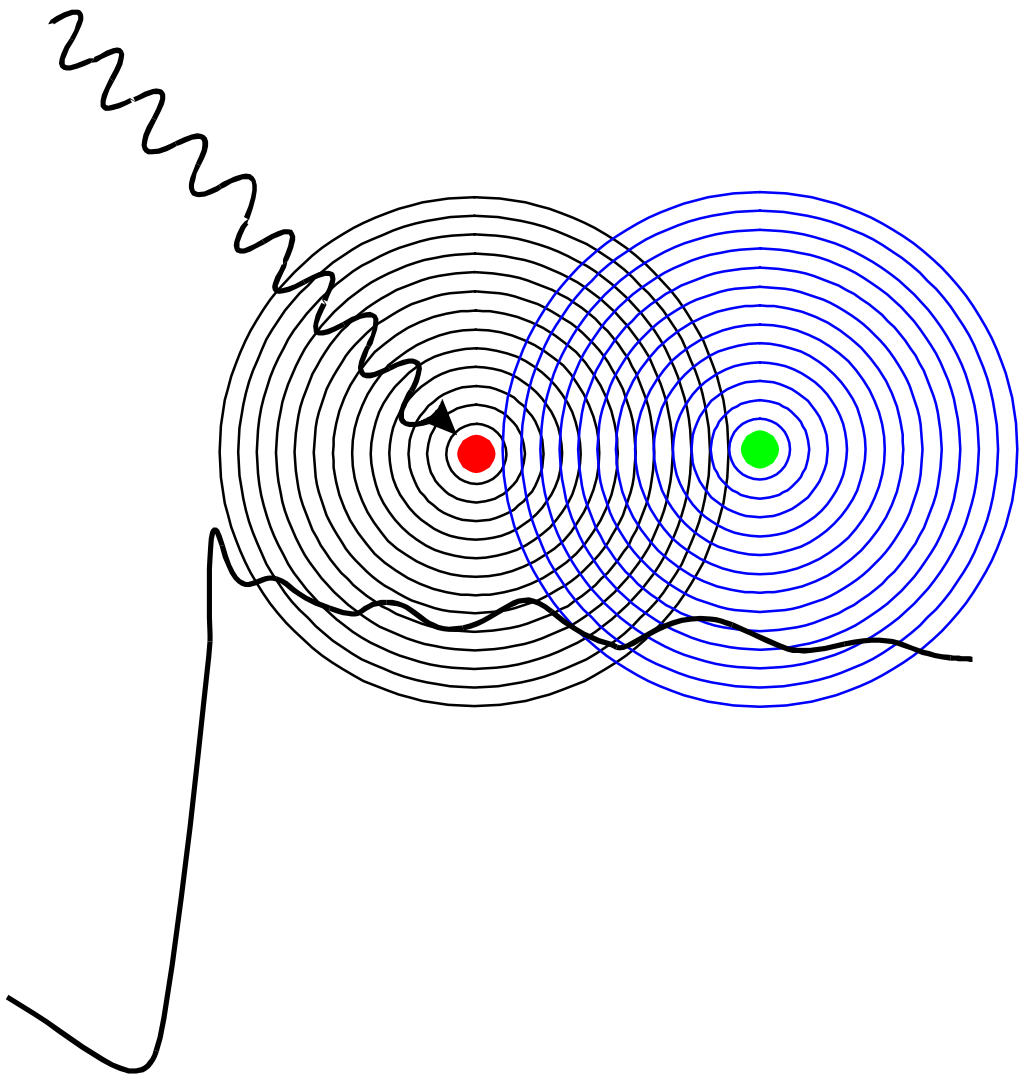
X-ray Absorption Fine Structure :
Local electronic and geometric structures around the x-ray absorbing atom



XAFS spectrum from an atom



XAFS spectrum from a diatomic molecule



X-ray absorption : *Fermi's Golden Rule*

$$\mu = \frac{4\pi^2\omega_e^2}{c} N_a \left|\langle f|e\cdot r|i\rangle\right|^2 \rho(E_f)$$

i: wave function of the initial state→1s

f: wave function of the final state→

superposition of the ejected wave and back-scattered waves

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

Point atom, plane wave, and single scattering approximations

$$\chi(k) = \sum_j A_j(k)\sin\left[2kr_j + 2\delta_j(k)\right]$$

$$A_j(k) = \frac{N_j\left|f(k,\pi)\right|}{kr_j^2}\exp(-2r_j/\lambda)\exp\left(-2\sigma^2k^2\right)$$

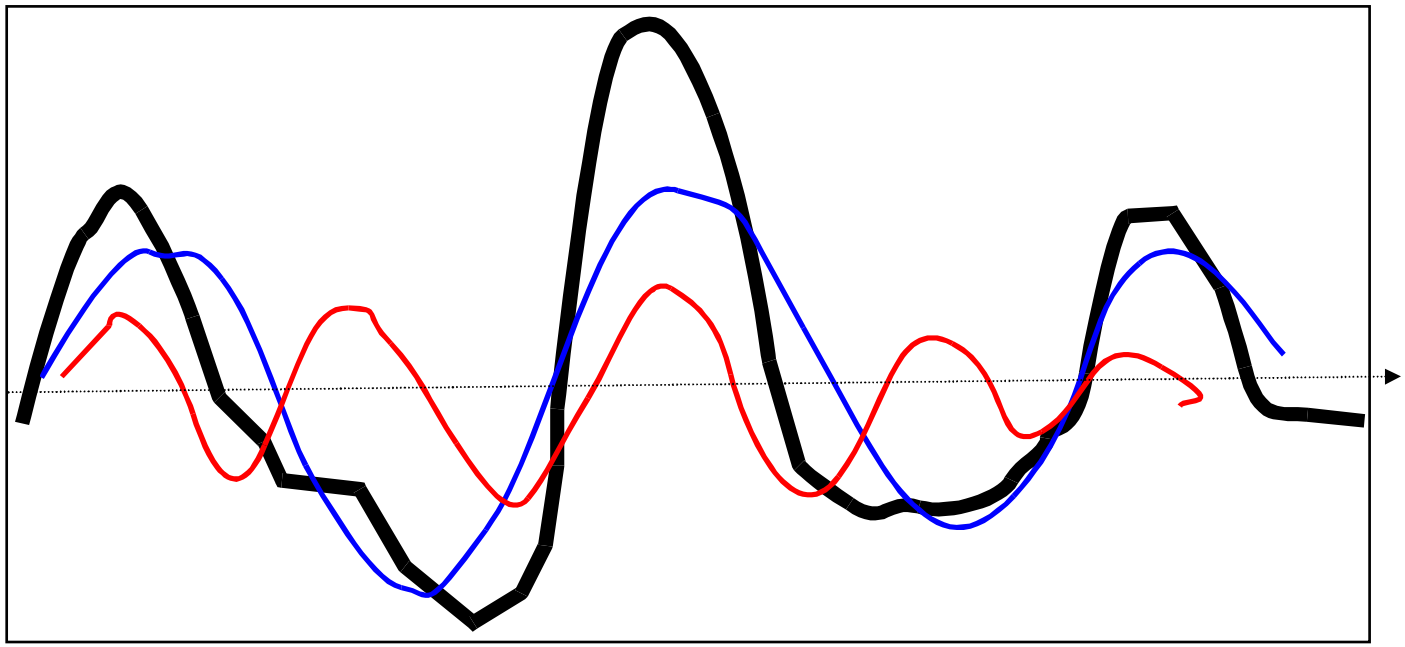
EXAFS oscillation

$$\chi(k) = \sum_i A_i(k)\sin(2kR_i + \phi_i)$$

Ri:bond distance

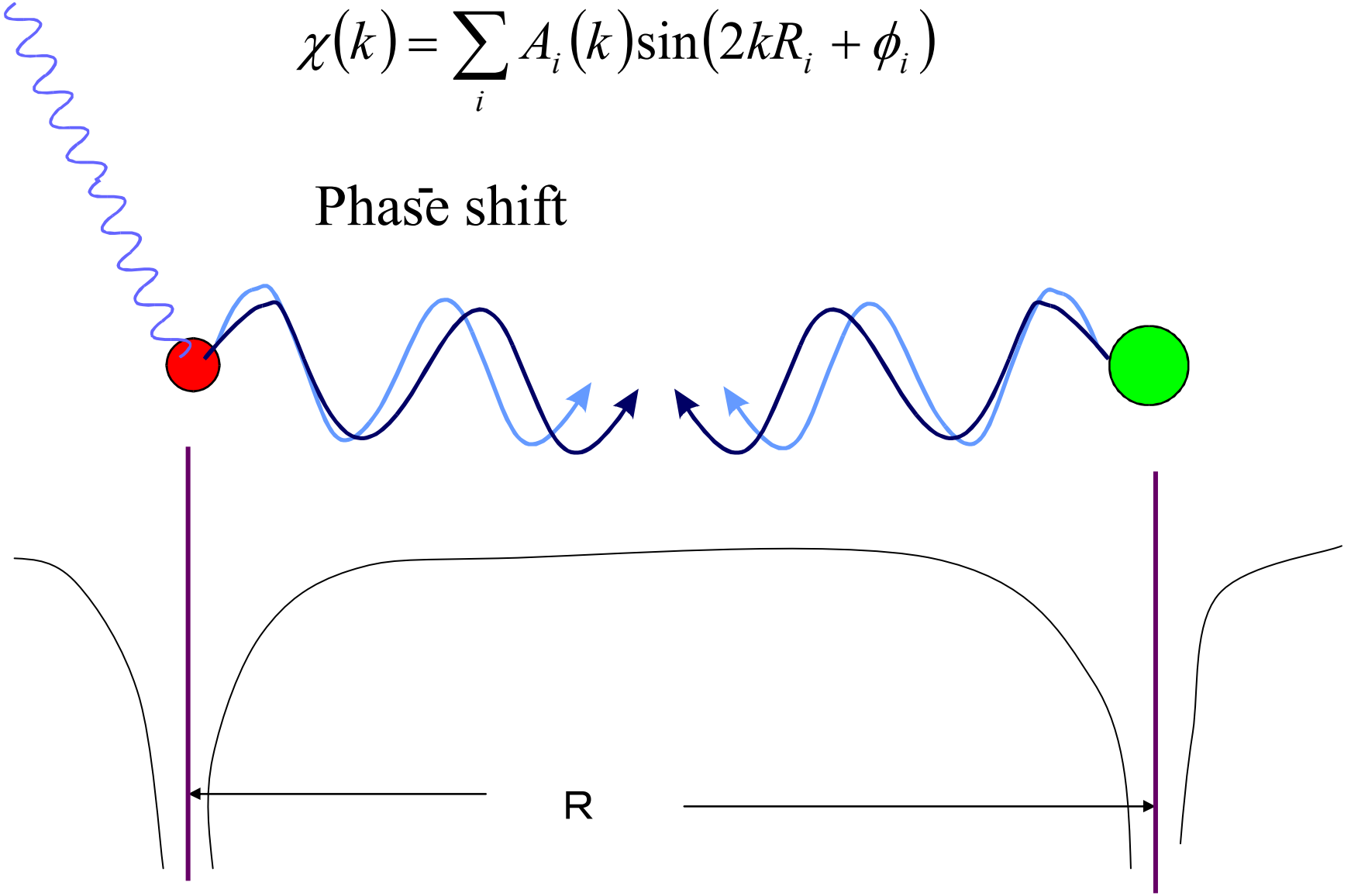
$$k = \frac{p}{\hbar} = \frac{\sqrt{2m(E - E_0)}}{\hbar}$$

ϕ_i Phase shift

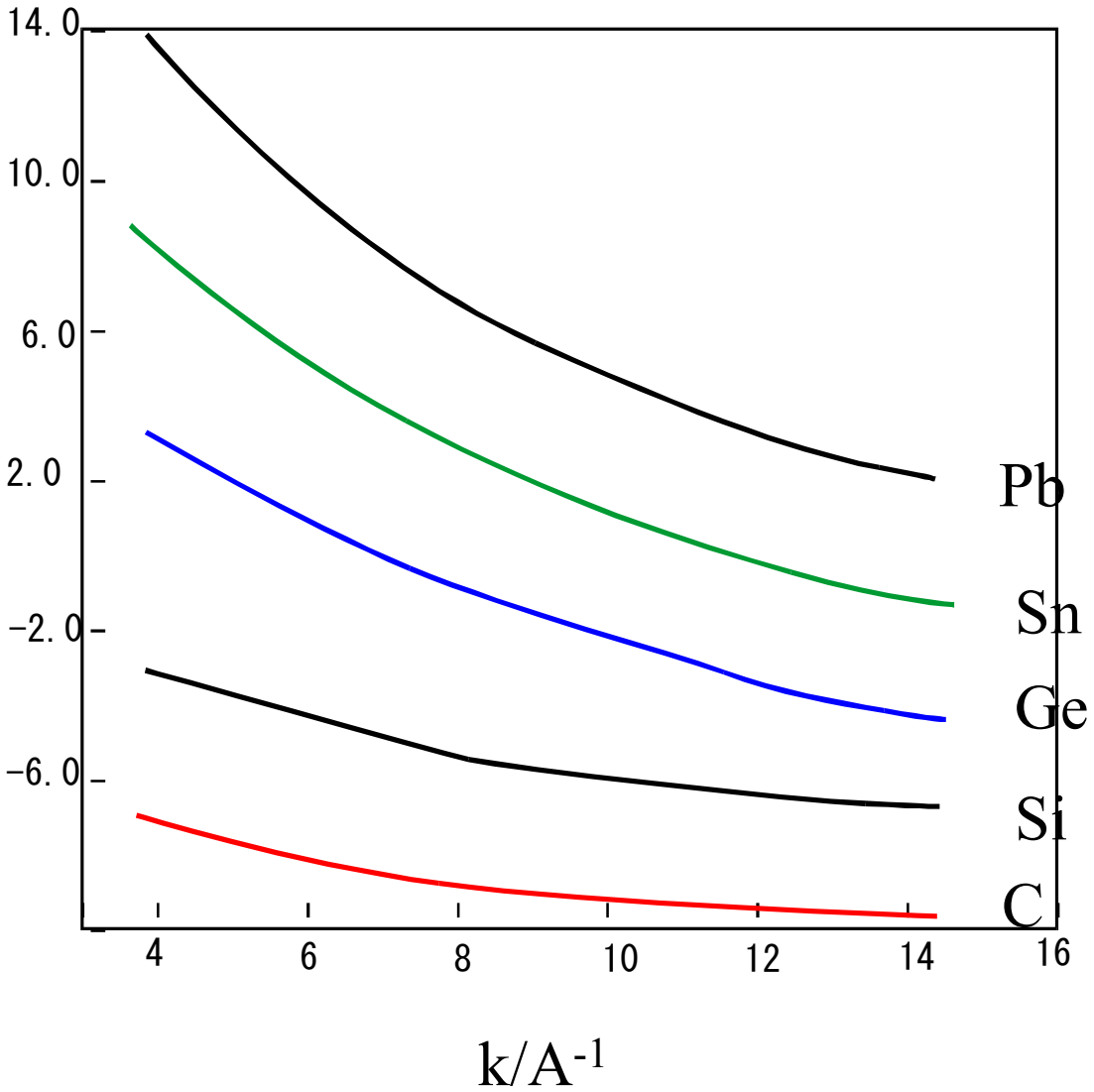


$$\chi(k) = \sum_i A_i(k)\sin(2kR_i + \phi_i)$$

Phase shift



Phase shift of the X-ray absorbing atom



EXAFS amplitude

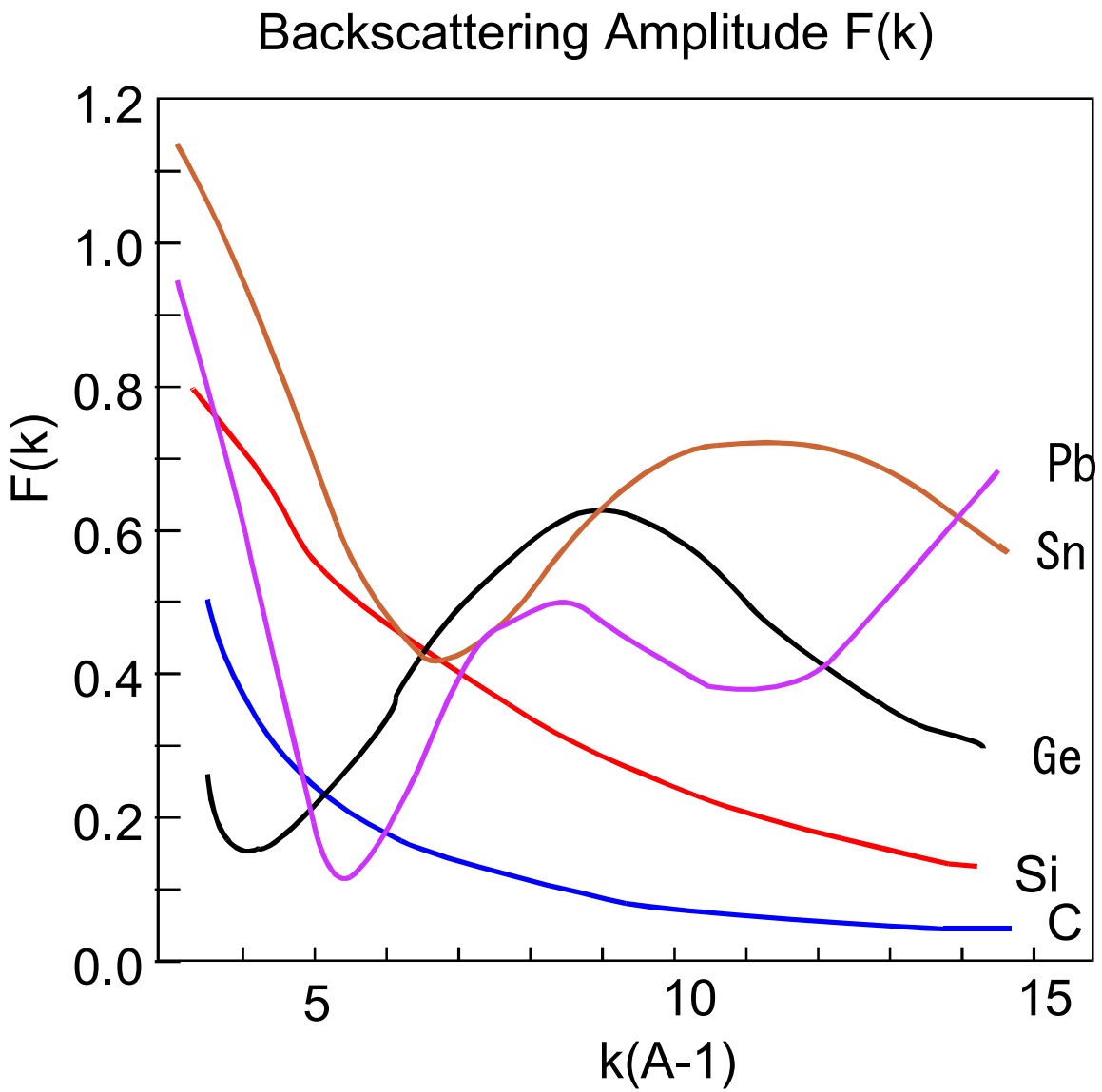
Effective Coordination number

Debye-Waller factor

$$A_i(k) = \frac{N_i^*}{kR_i^2}\left|F_i(k)\right|\exp\left(-2\sigma_i^2 k^2\right)\exp\left(-2\frac{R_i}{\lambda}\right)$$

Back scattering amplitude

Electron mean free path


Backscattering Amplitude F(k)
F(k)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
5
10
15
k(A-1)
Pb
Sn
Ge
Si
C

EXAFS amplitude

High coordination number

Effective Coordi-nation number

Low temperature

Debye-Waller factor

$$A_i(k) = \frac{N_i^*}{kR_i^2}\left|F_i(k)\right|\exp\left(-2\sigma_i^2 k^2\right)\exp\left(-2\frac{R_i}{\lambda}\right)$$

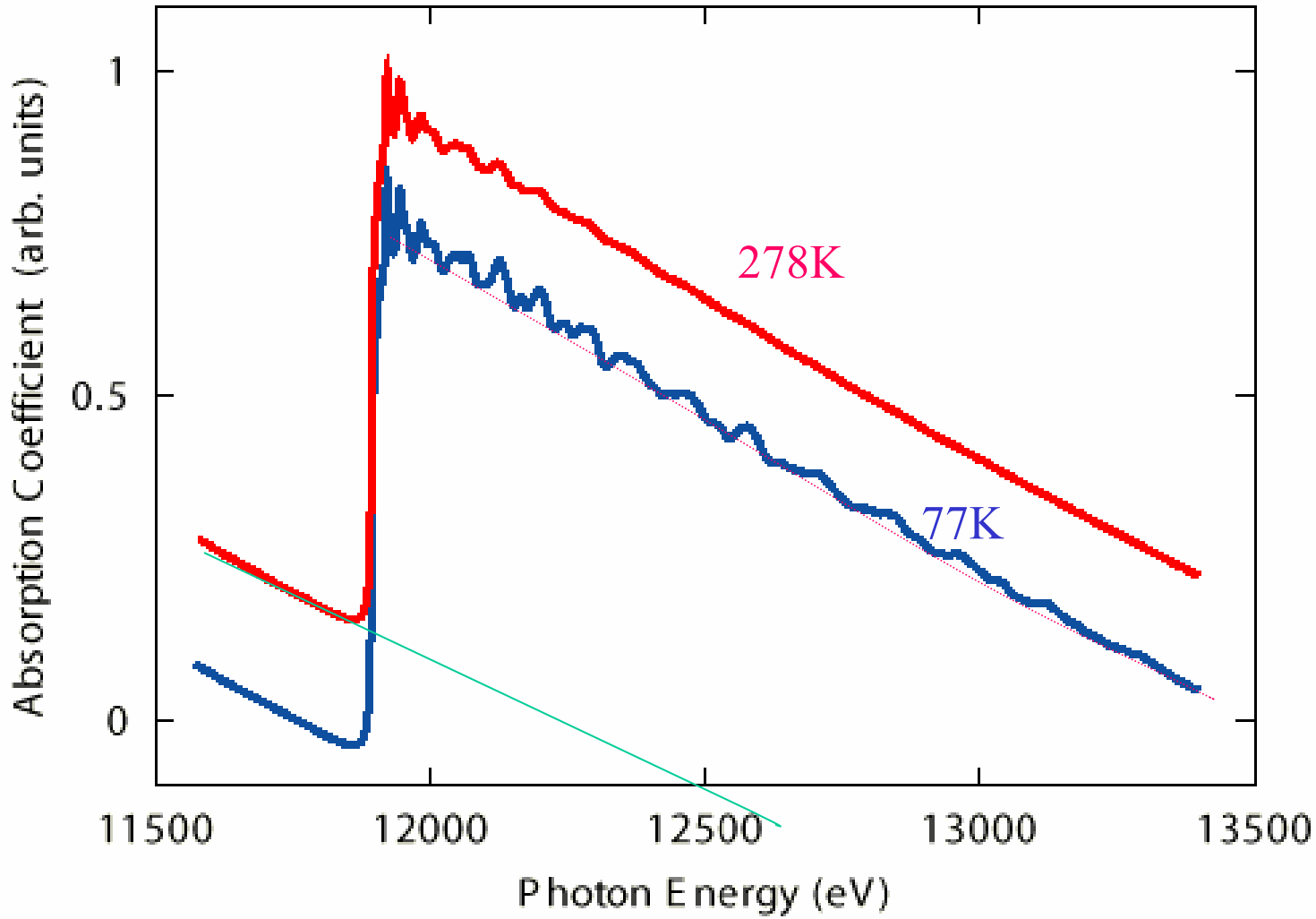
Back scattering amplitude

Electron mean free path

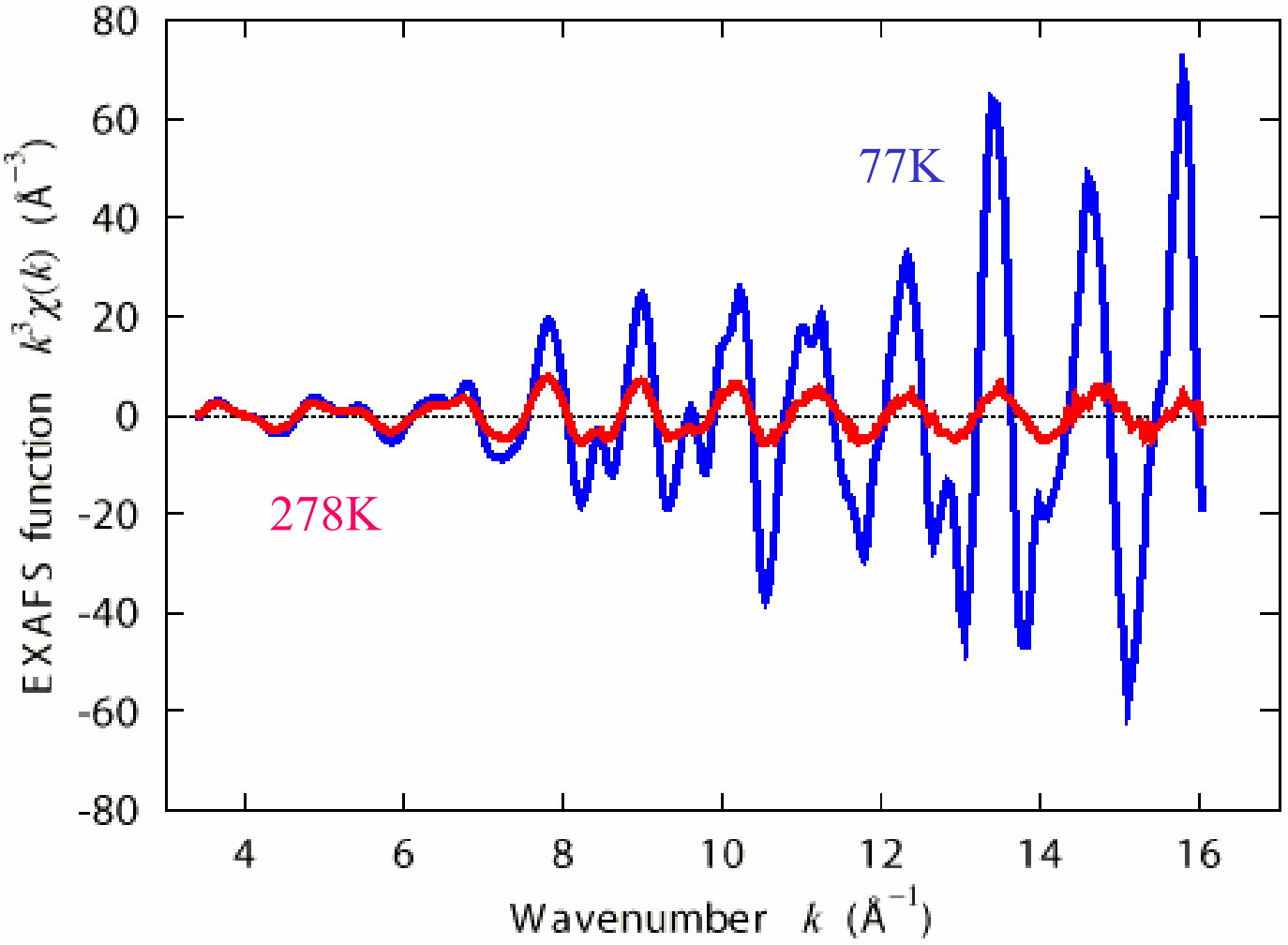
High Z scatterer

Short distance

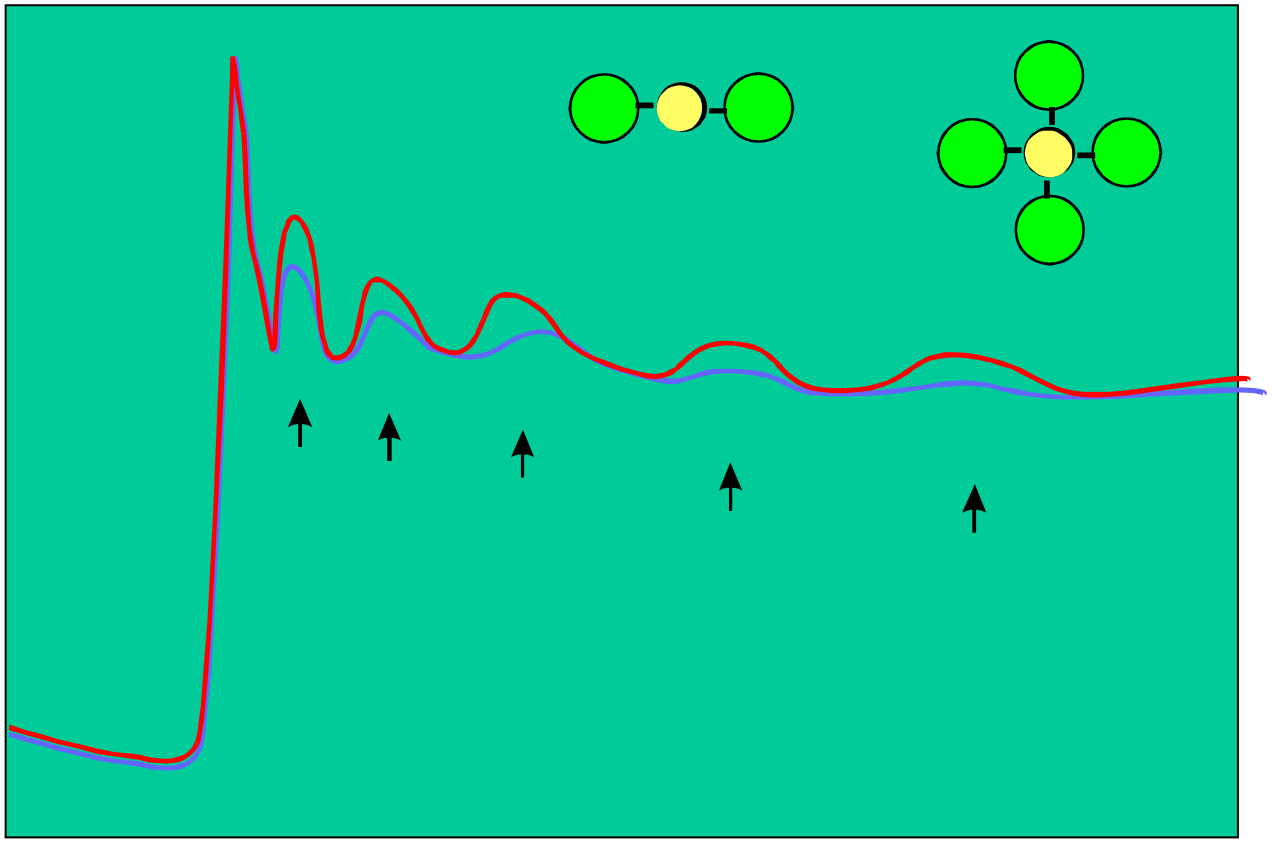
Au K-EXAFS of Au foil



EXAFS oscillation of Au K-edge

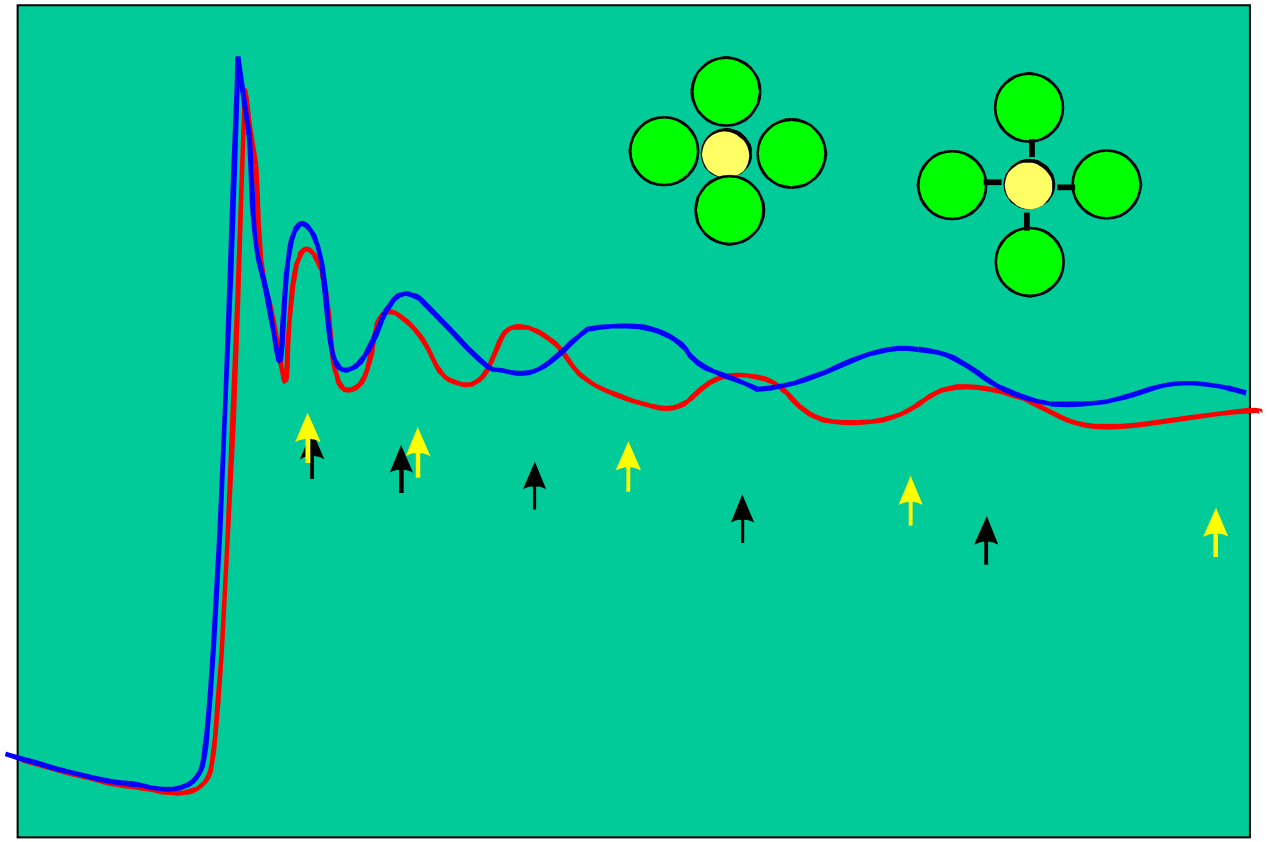


If the coordination number decreases,



Photon Energy

If the bond distance increases,

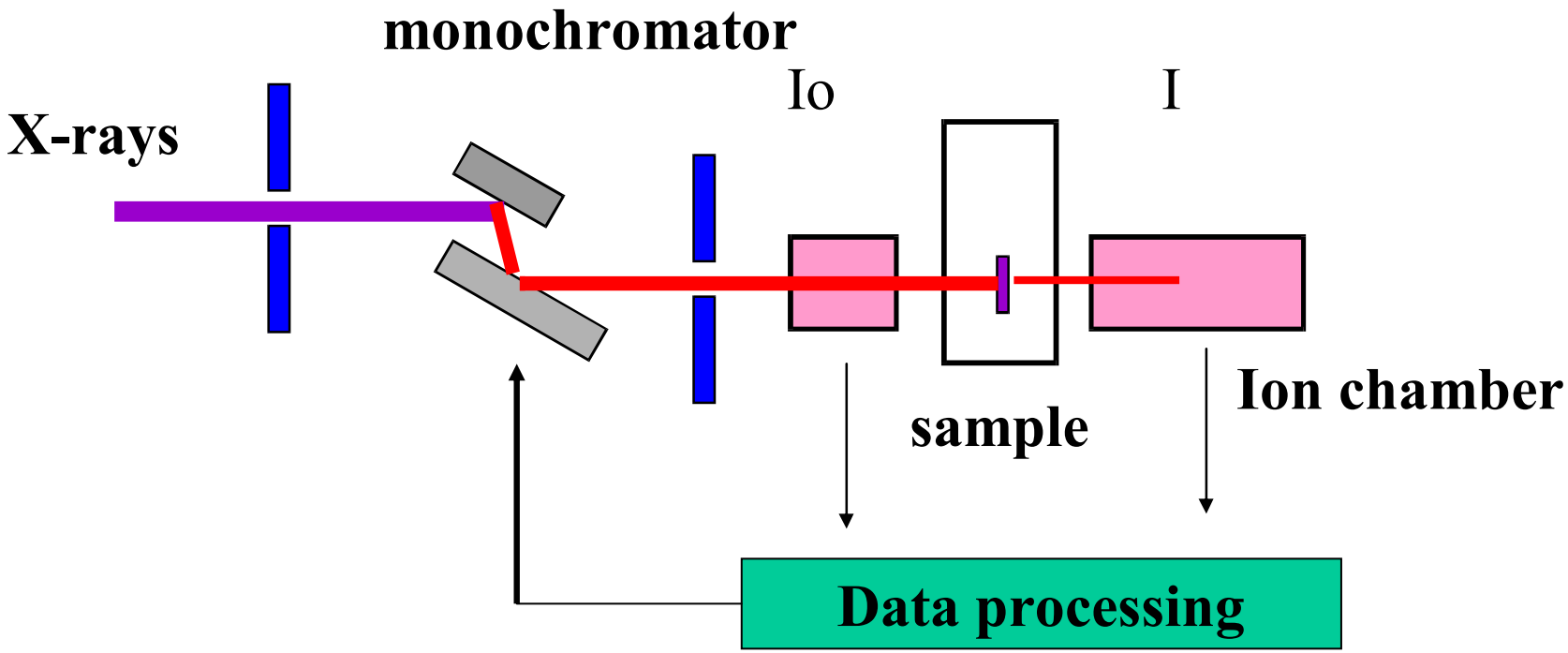


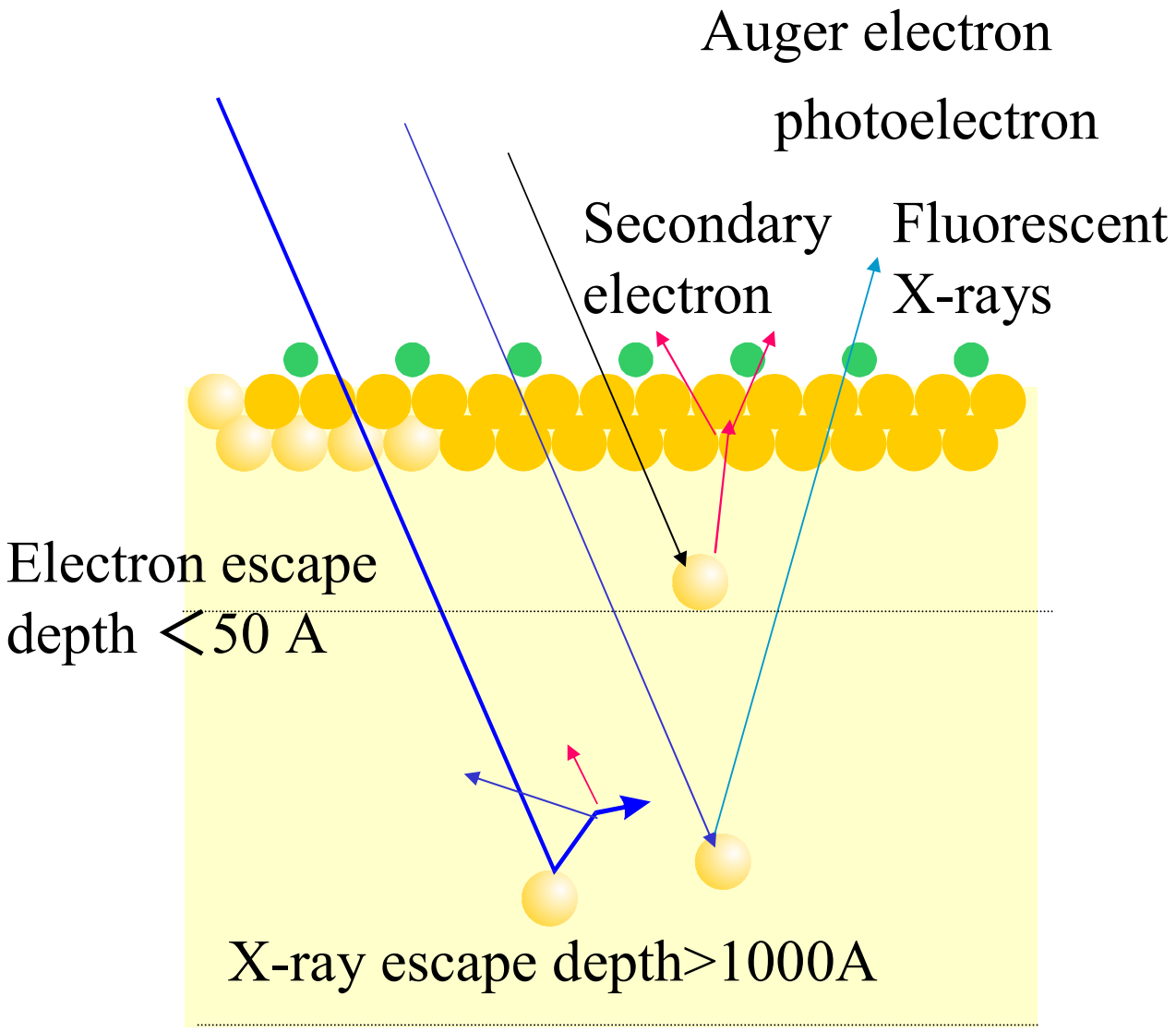
Photon Energy

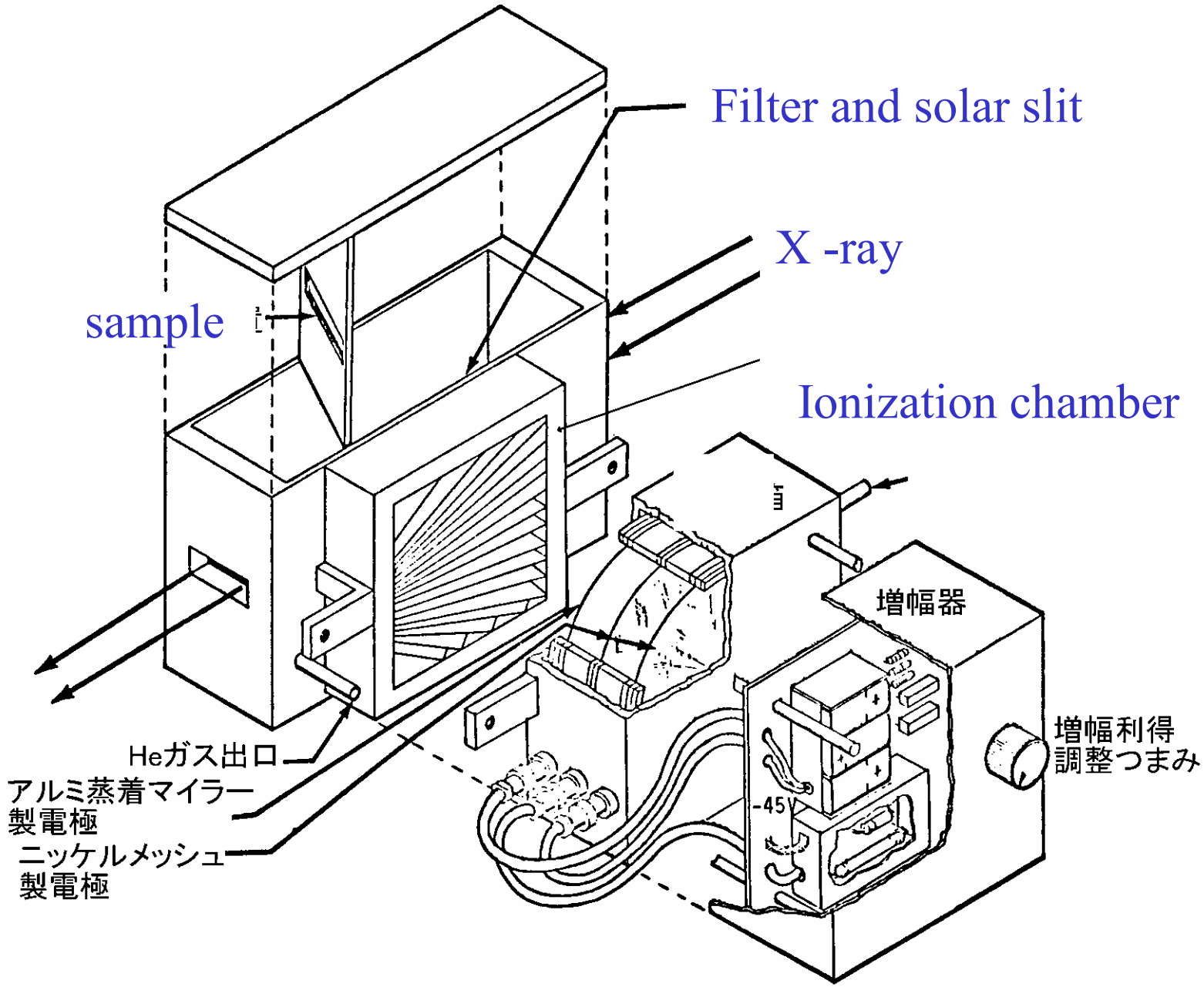
(2) Instrumentation

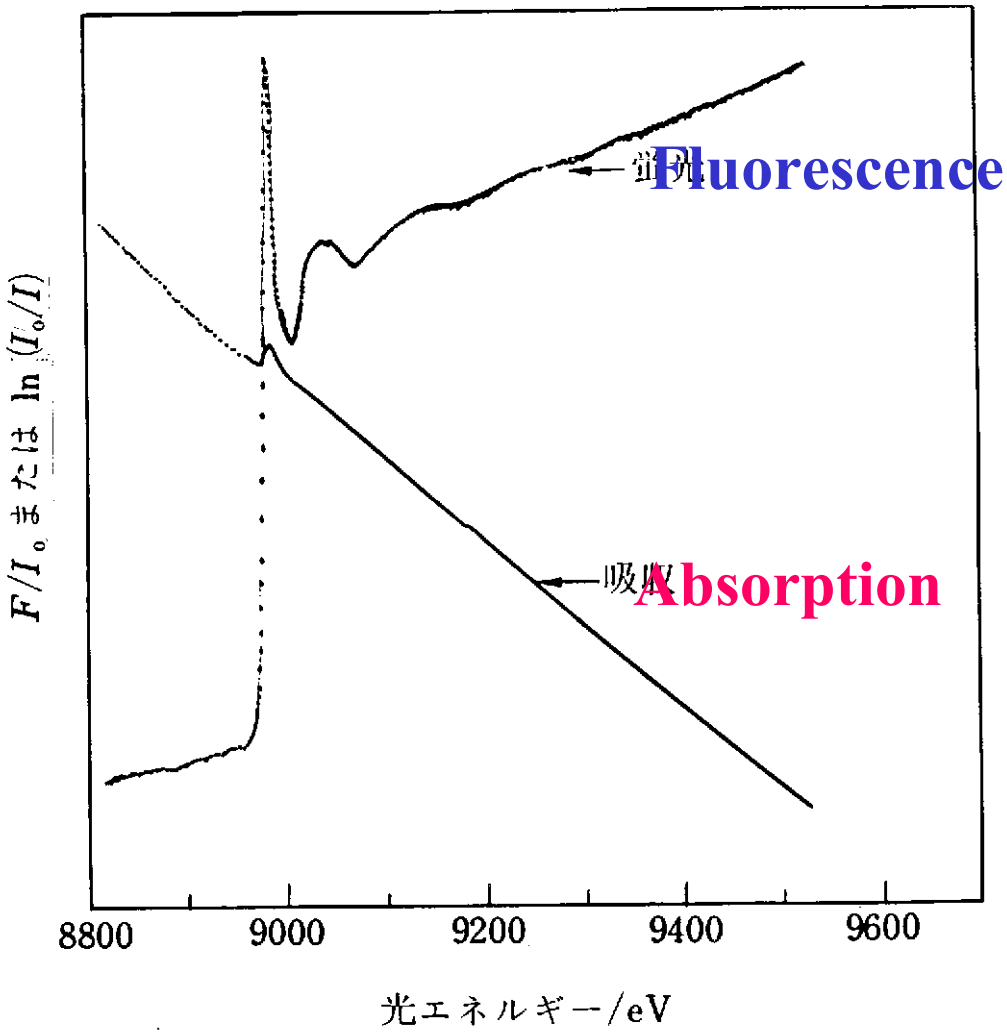
Experimental method of XAFS

《transmission method》




Auger electron
photoelectron
Secondary electron
Fluorescent X-rays
Electron escape depth ＜50 A
X-ray escape depth>1000A

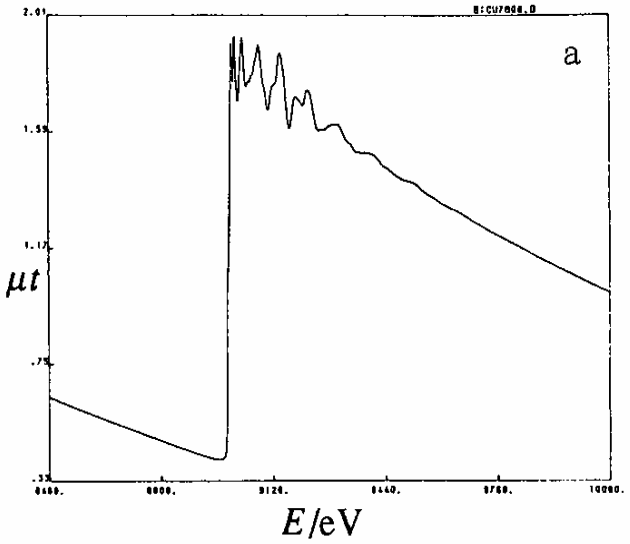

Filter and solar slit
X -ray
sample
Ionization chamber
増幅器
増幅利得
調整つまみ
-45V
Heガス出口
アルミ蒸着マイラー
製電極
ニッケルメッシュ
製電極

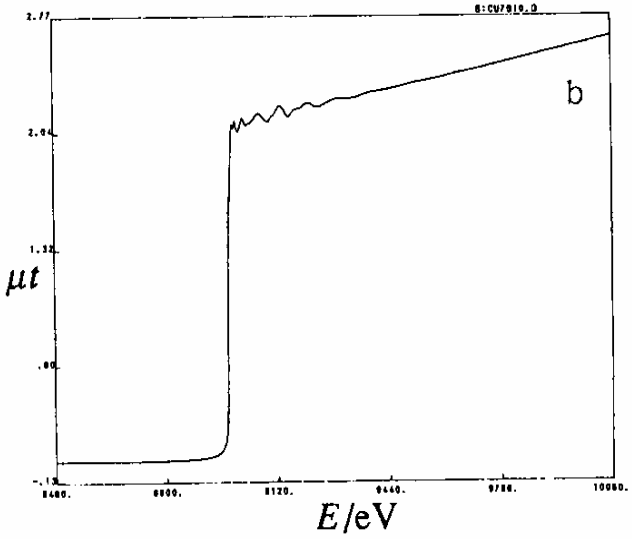


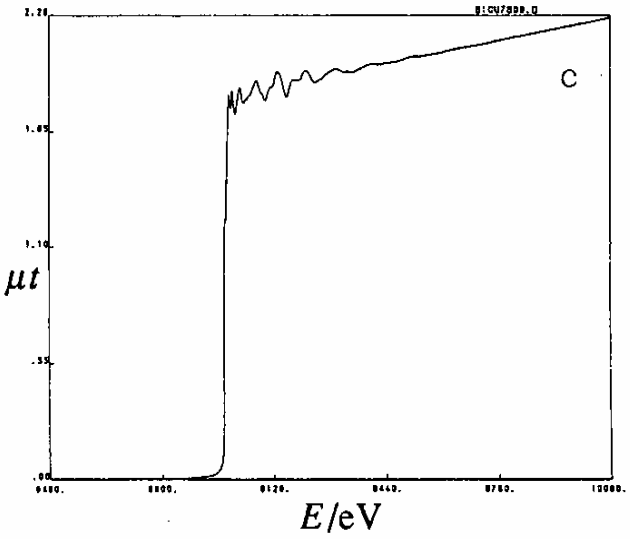
Cu K-XAFS of $CuSO_4$ 10mMol aq. solution

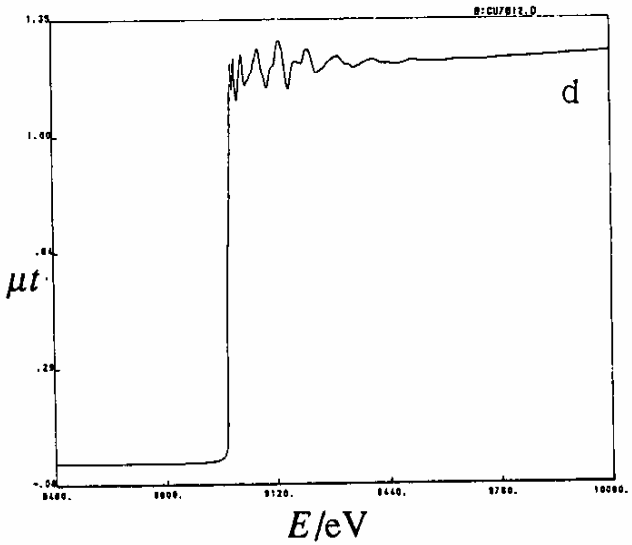
0.5 mm film

6μm film





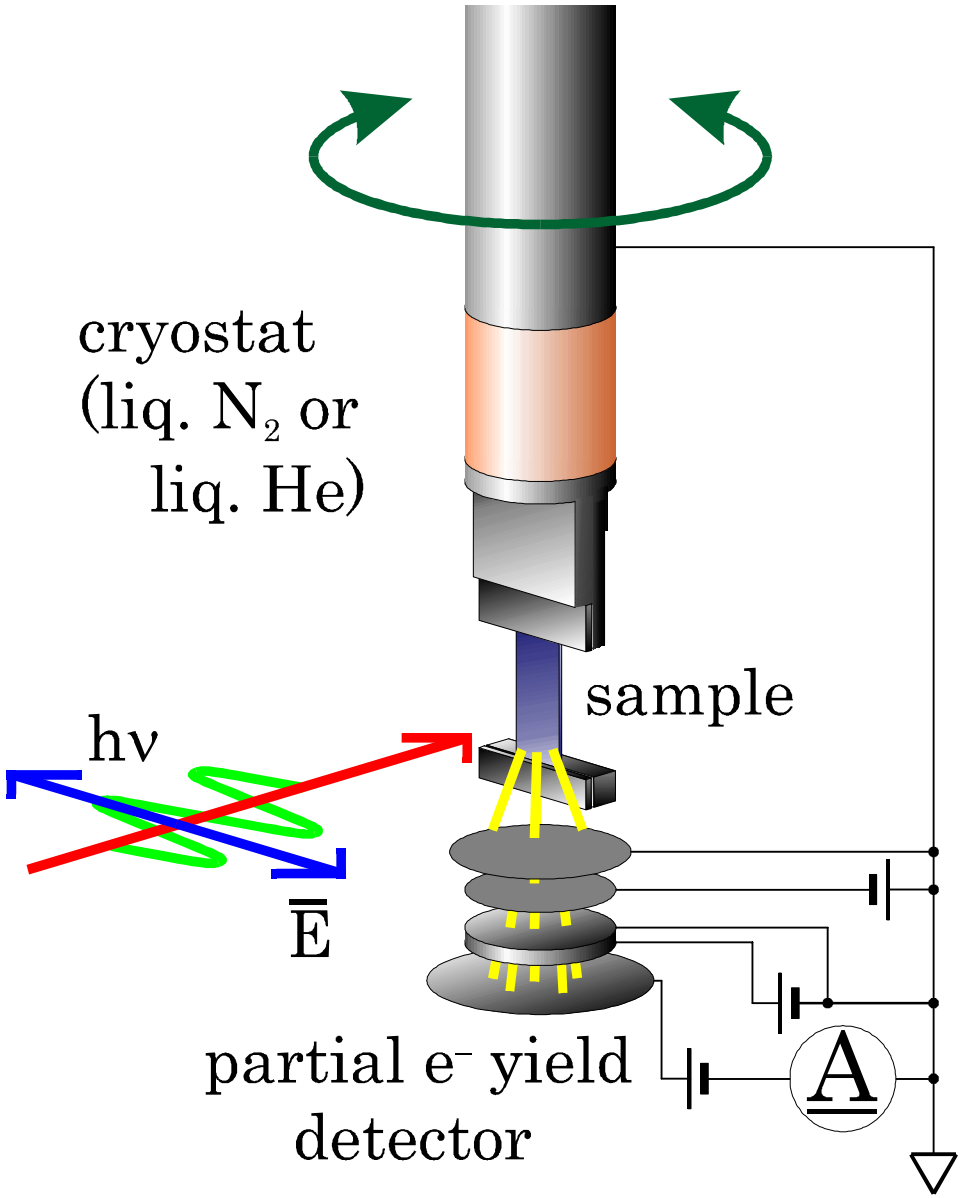


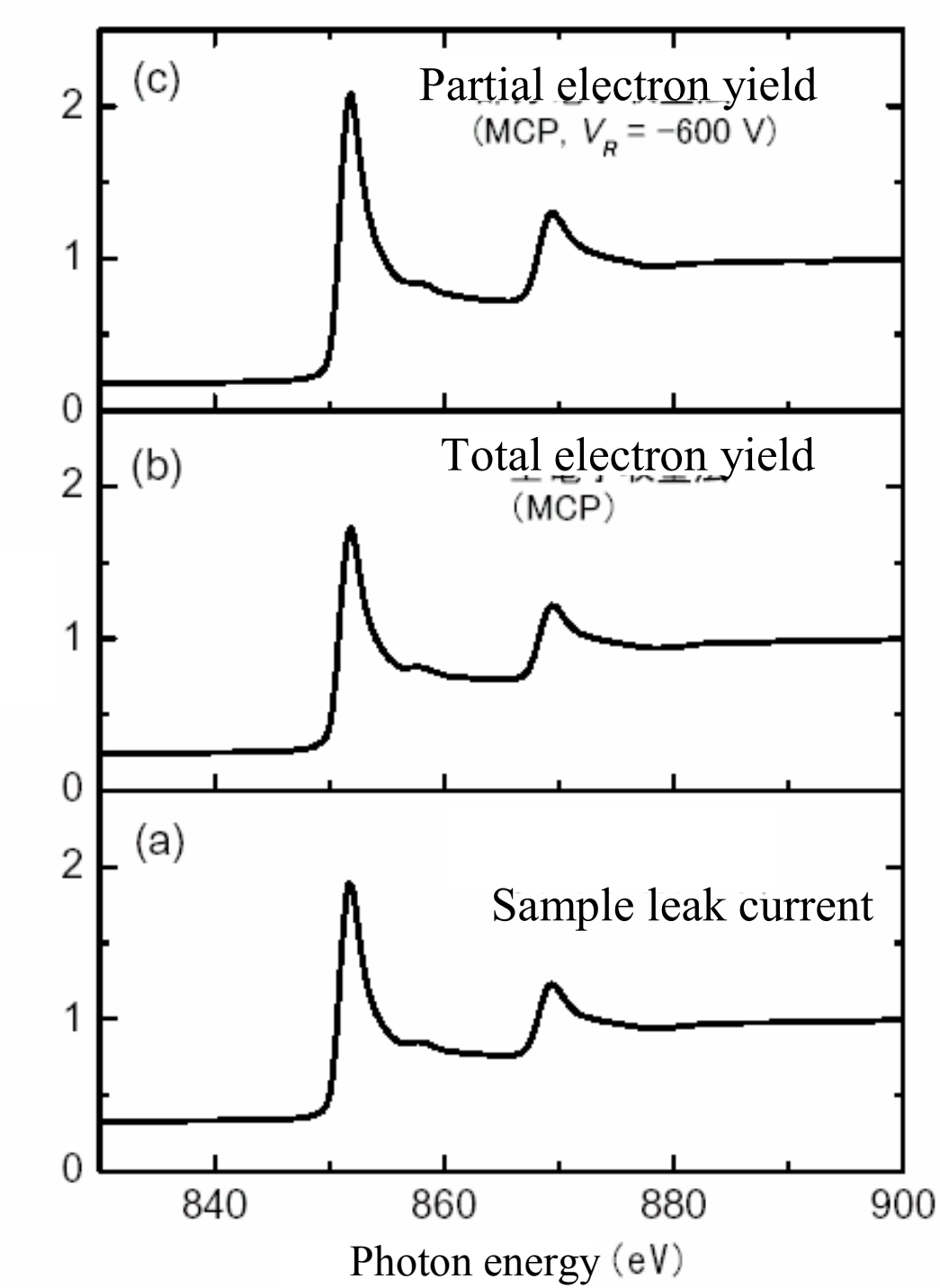


Transmission

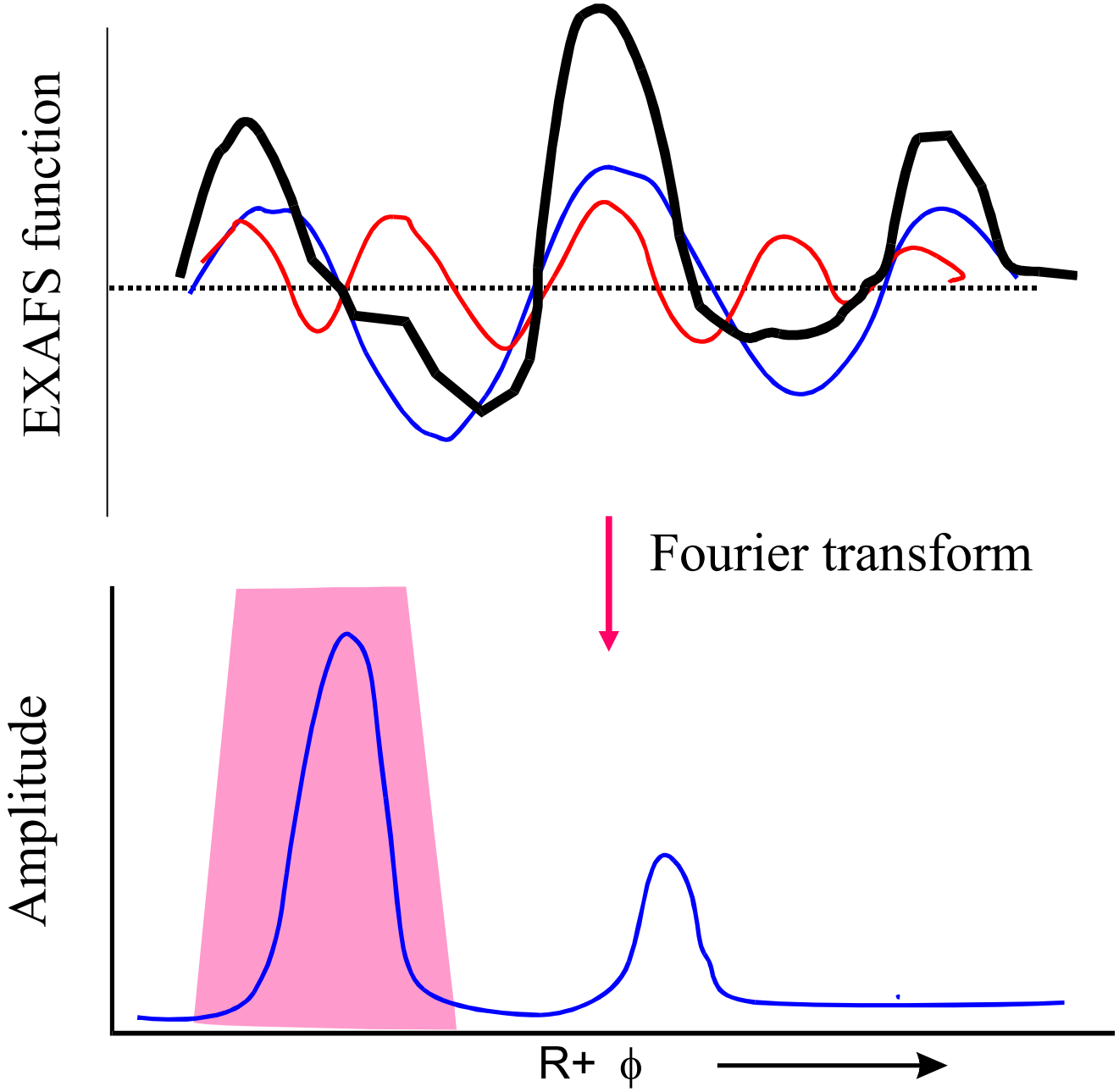
Fluorescence

Partial electron yield → x-ray absorption of surface atoms

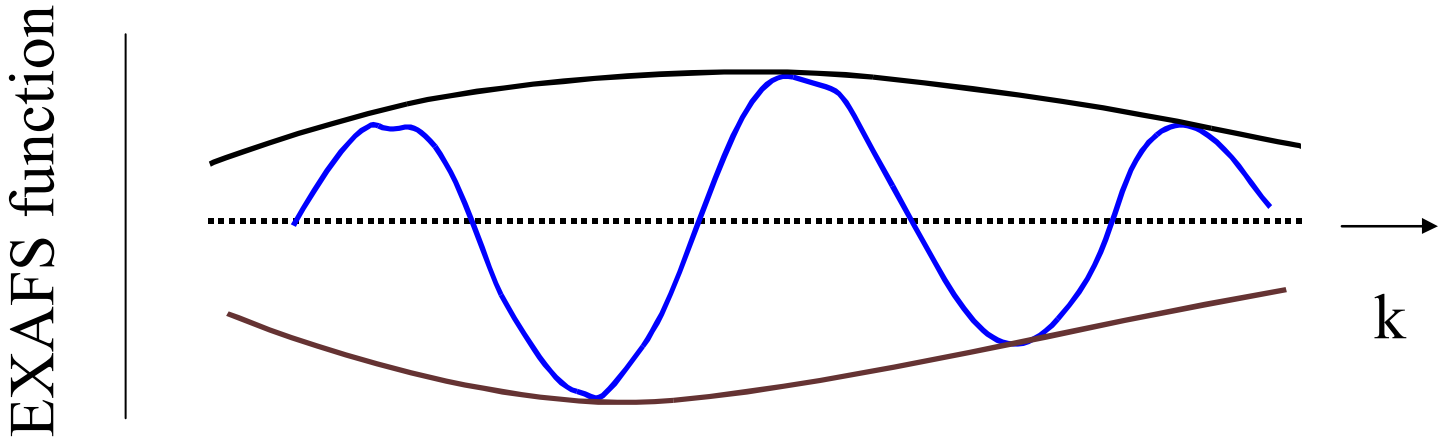



(c)
Partial electron yield
(MCP, V_R = −600 V)
(b)
Total electron yield
(MCP)
(a)
Sample leak current
0
1
2
840
860
880
900
Photon energy (eV)

(3) XAF S spectral analysis


EXAFS function
Fourier transform
Amplitude
R+ ϕ

Back Fourier Transformation



Amplitude

Envelope

Polarization

Temperature

Direction of Bond, Adsorp-Tion site

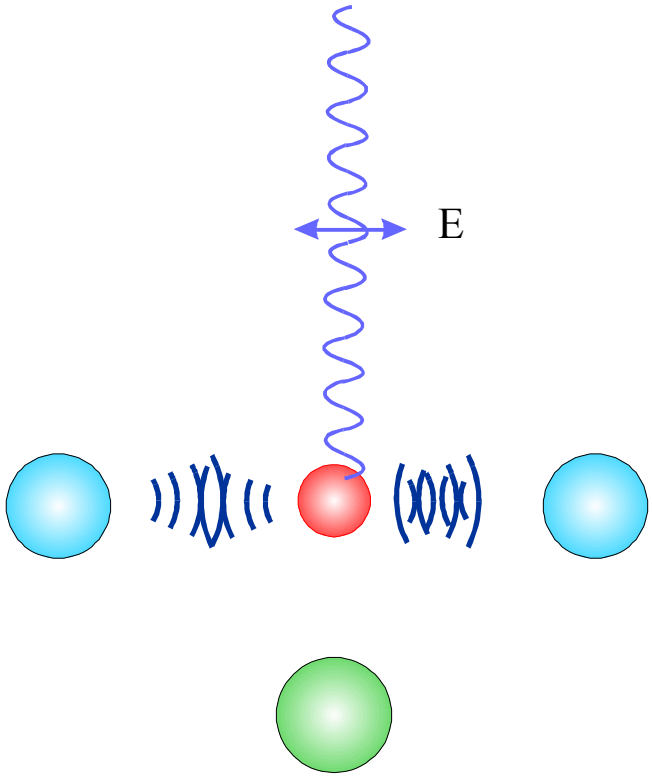
Coordina-tion number

Bond stiffness

Kind of scatterer

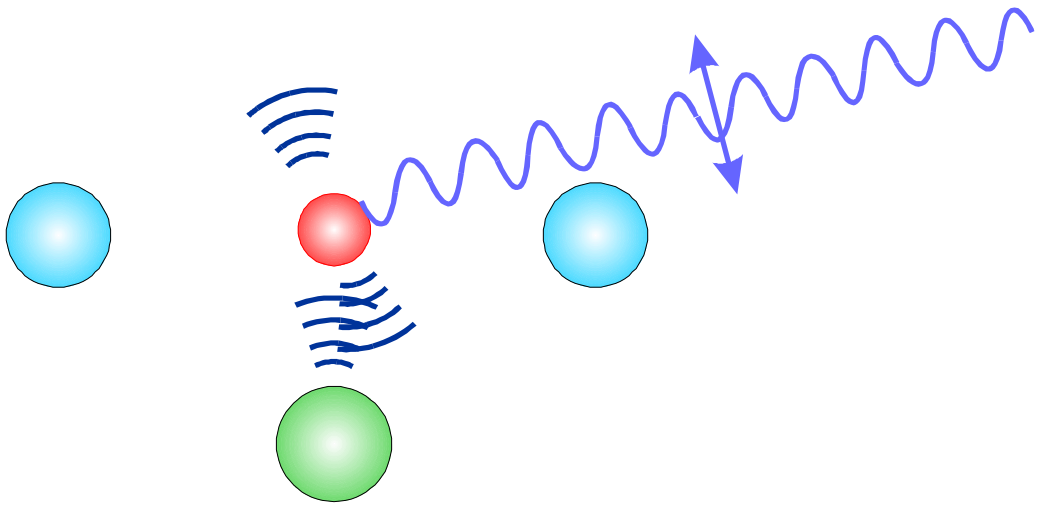
Polarization Dependent EXAFS

K-absorption(1s → p-like continuum)



Polarization Dependent EXAFS

K-absorption(1s → p-like continuum)



Temperature dependence

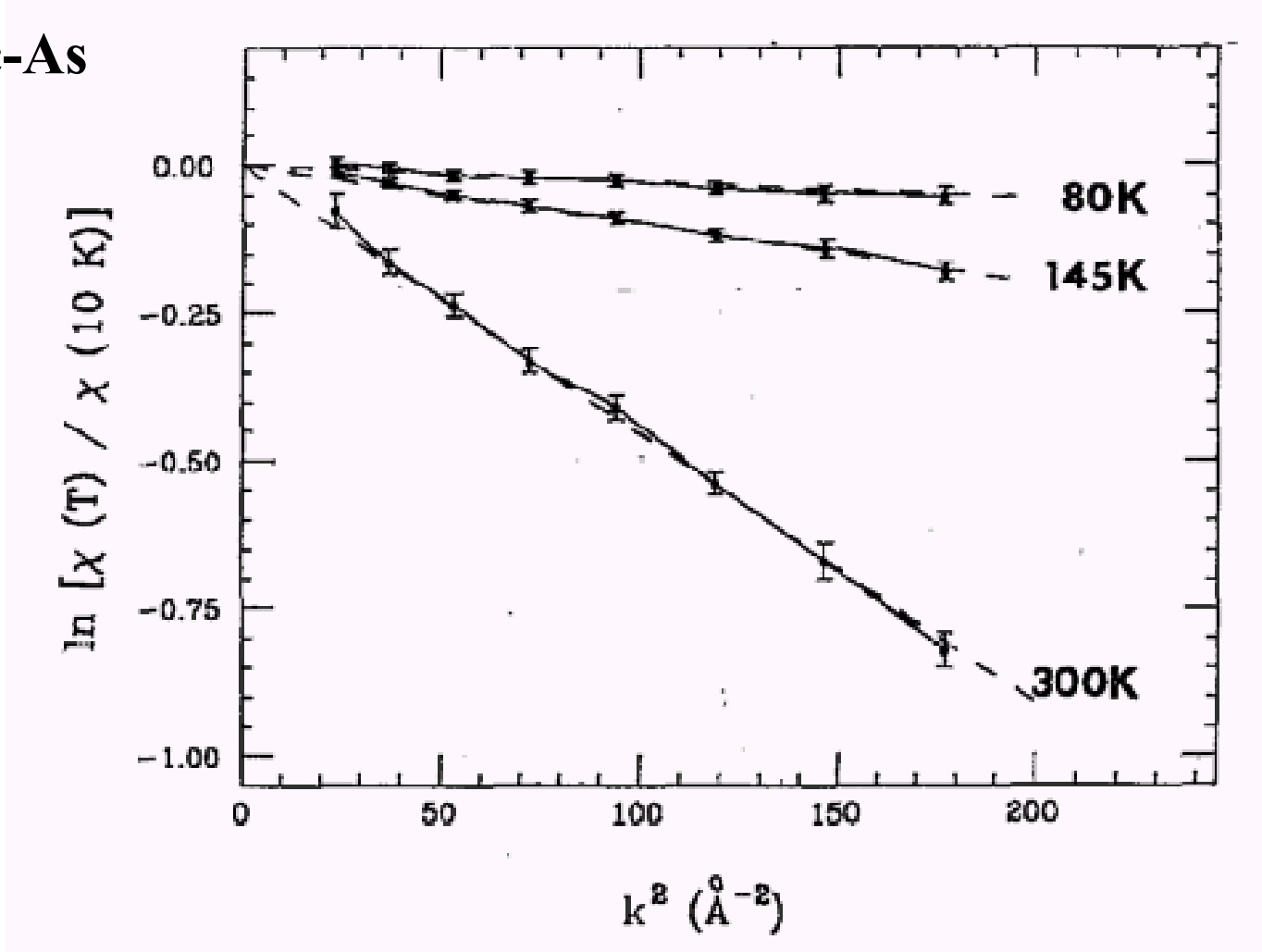
$$\chi(k) = \sum_j A_j(k) \sin\left[2kr_j + 2\delta_j(k)\right]$$

$$A_j(k) = \frac{N_j \left| f(k,\pi) \right|}{kr_j^2} \exp(-2r_j/\lambda) \exp\left(-2\sigma^2 k^2\right)$$

$$\ln \frac{A(k,T_2)}{A(k,T_1)} \cong 2k^2 \left[\sigma^2(T_1) - \sigma^2(T_2)\right]$$

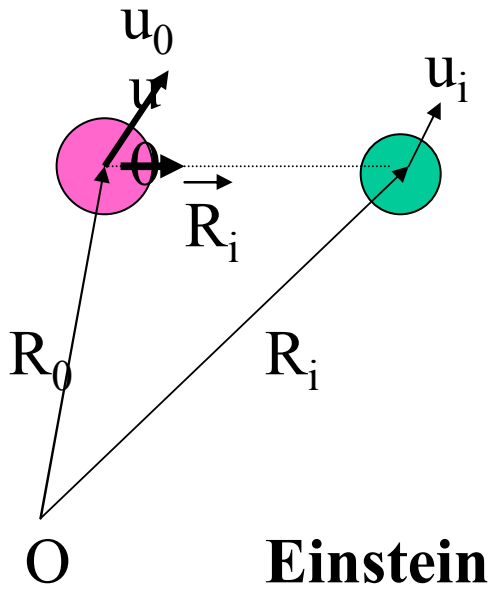
Determination of $\sigma^2(T)$

c-As



$$\ln \frac{A(k,T_2)}{A(k,T_1)} \cong 2k^2\left[\sigma^2(T_1) - \sigma^2(T_2)\right]$$

What can we get from $\sigma^2(T)$



$$\sigma_i^{\,2} = \left\langle \left[(u_i - u_0) \cdot \vec{R}_i \right]^2 \right\rangle$$

$$= \left\langle \left(u_i \cdot \vec{R}_i \right)^2 \right\rangle + \left\langle \left(u_0 \cdot \vec{R}_i \right)^2 \right\rangle + 2 \left\langle \left(u_0 \cdot \vec{R}_i \right) \cdot \left(u_i \cdot \vec{R}_i \right) \right\rangle$$

$$\vec{R}_i = \frac{R_i - R_0}{\left| R_i - R_0 \right|}$$

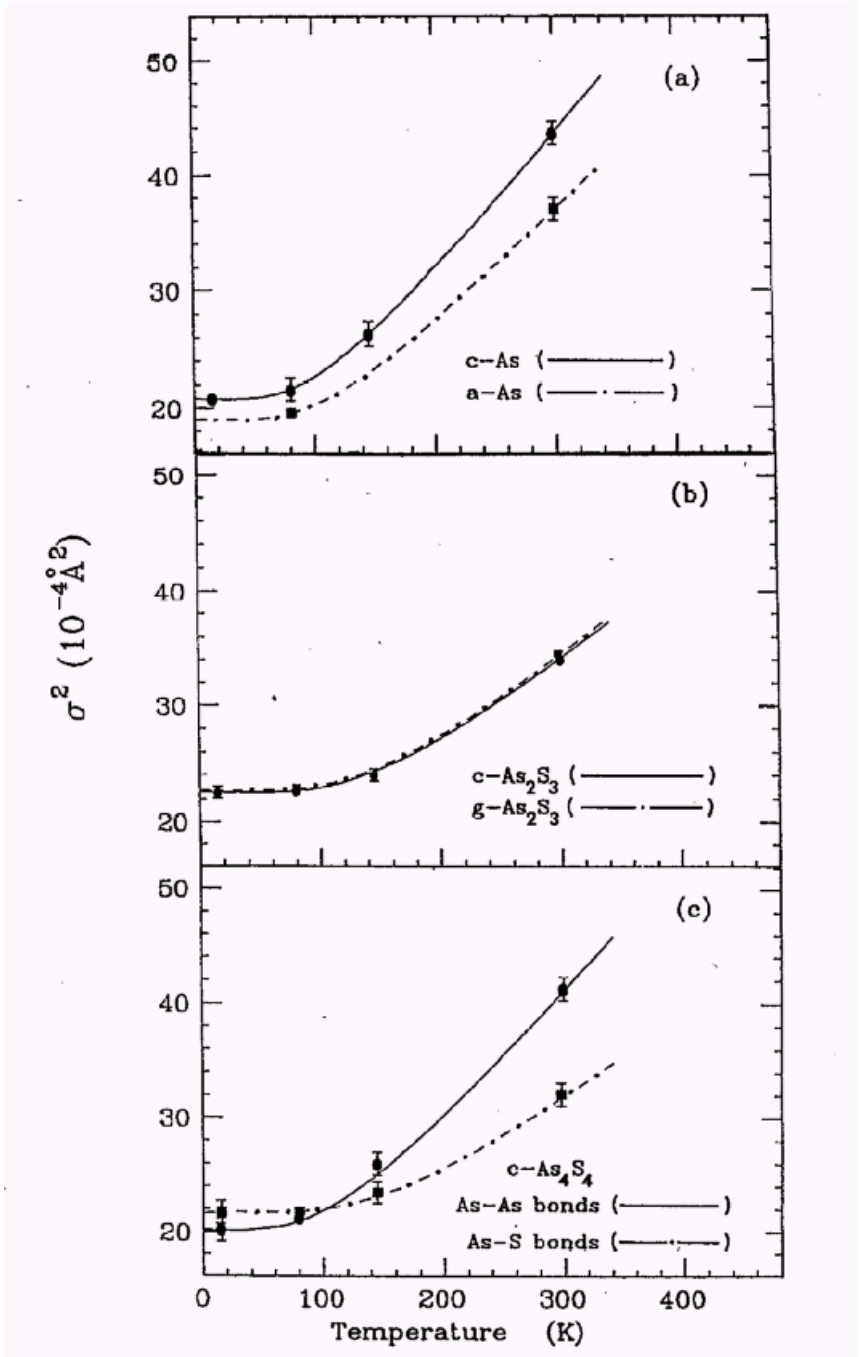
Einstein model

Einstein frequency

$$\sigma_i^2(T) = \frac{\hbar}{2\mu\omega_E} \coth\left[\frac{\hbar\omega}{2kT} \right]$$

$$f_E = c^2 \mu \omega_E^2$$

$$\sigma_i^2 = \frac{\hbar}{2\mu\omega_E} \left[\coth\left(\frac{\hbar\omega}{2kT_2} \right) - \coth\left(\frac{\hbar\omega}{2kT_1} \right) \right]$$



c-As

As-As: 216 cm^{-1}

a-As

As-As: 234 cm^{-1}

c-As_2S_3

As-S: 332 cm^{-1}

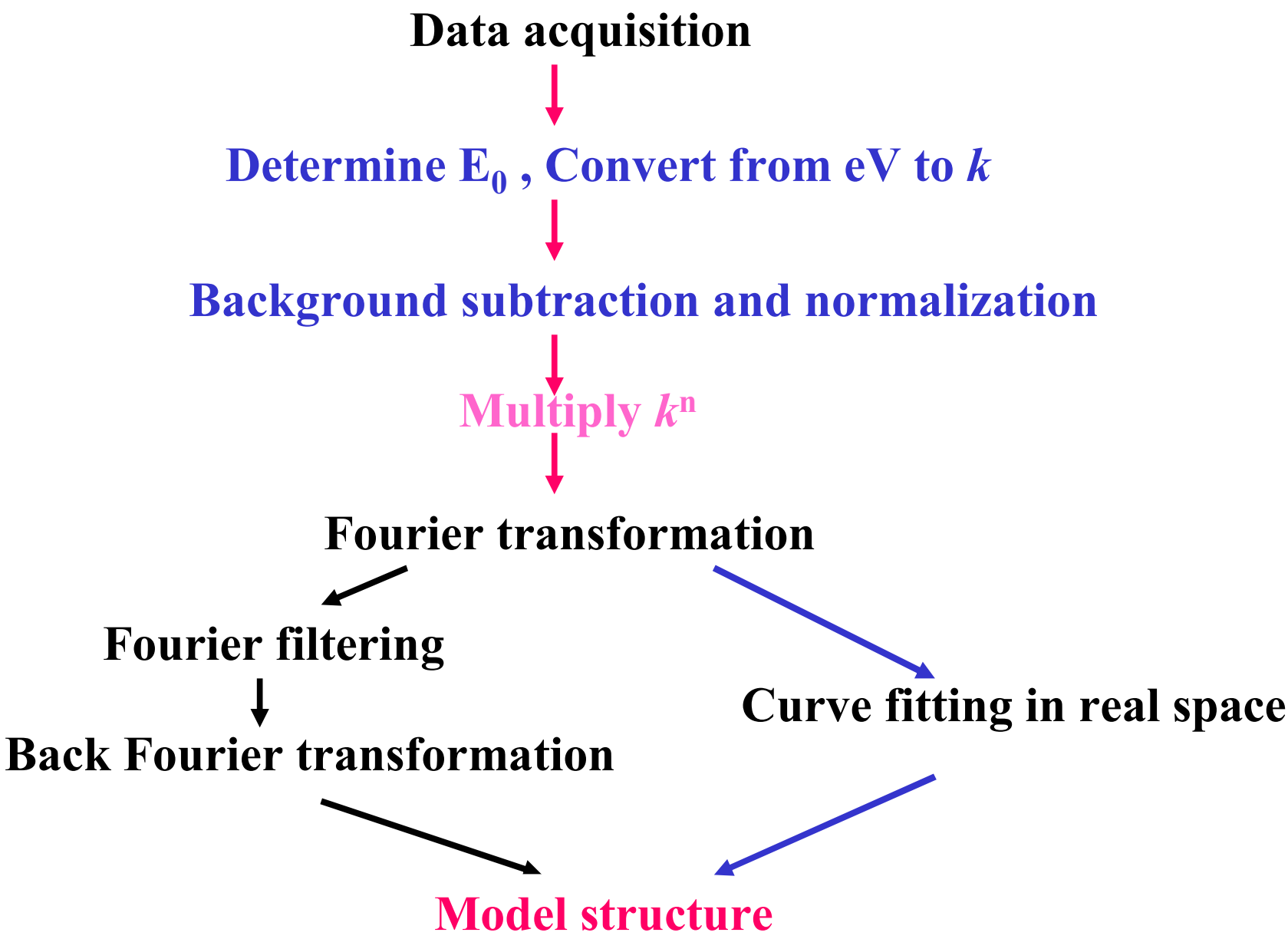
g-As_2S_3

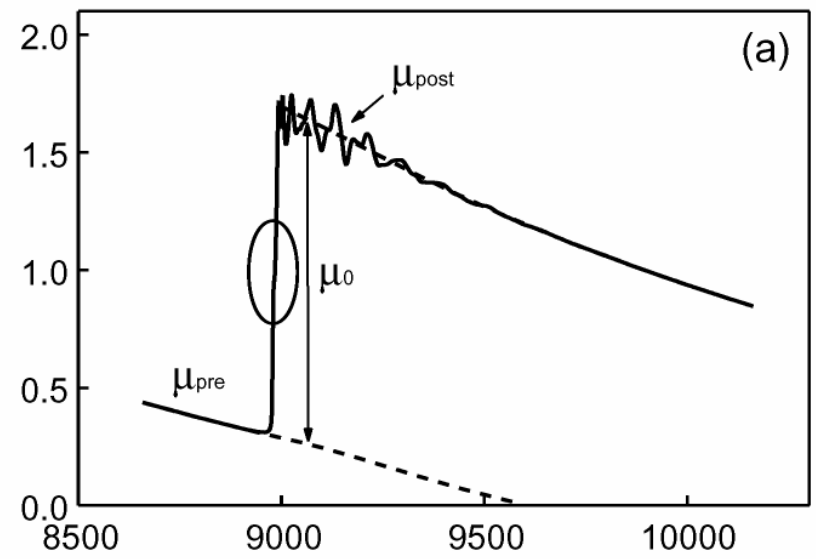
As-S: 330 cm^{-1}

c-As_4S_4

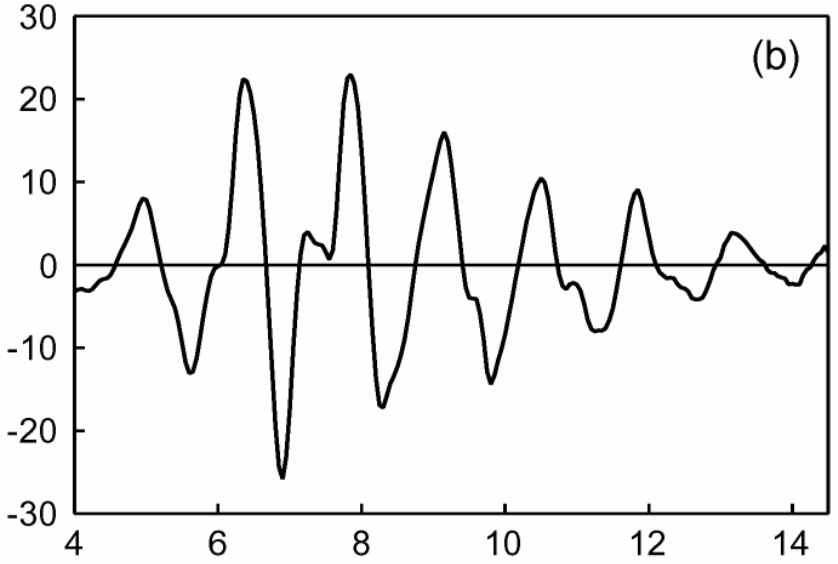
As-As: 222 cm-1

As-S : 342 cm-1

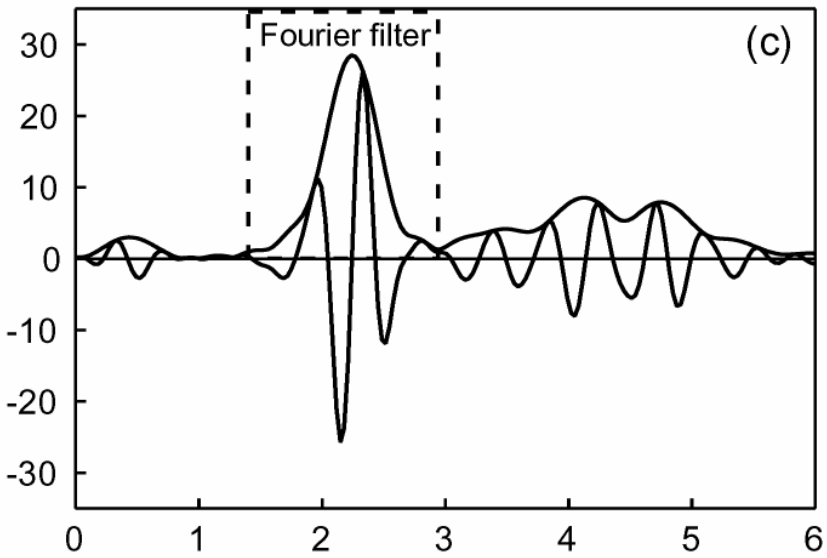

Data acquisition
Determine E_0 , Convert from eV to k
Background subtraction and normalization
Multiply k^n
Fourier transformation
Fourier filtering
Back Fourier transformation
Curve fitting in real space
Model structure



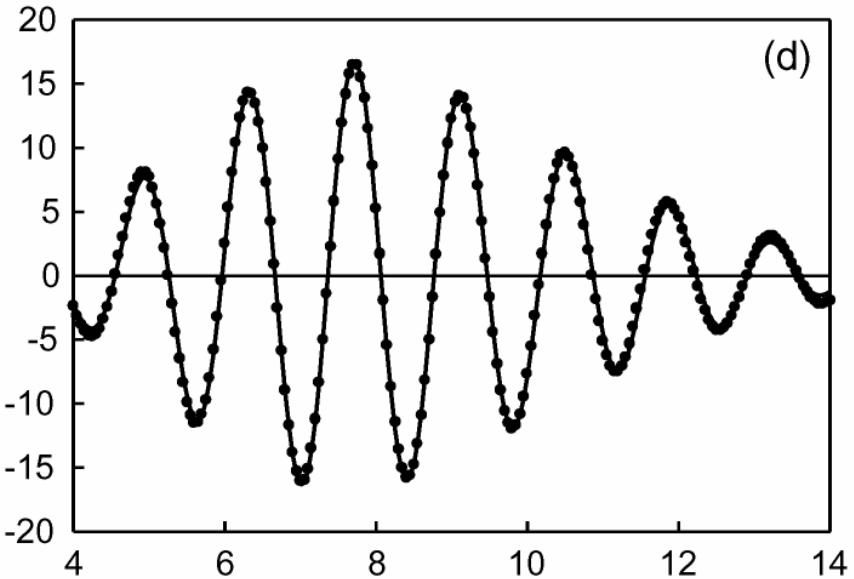
X-ray energy(eV)



EXAFS χ(k)

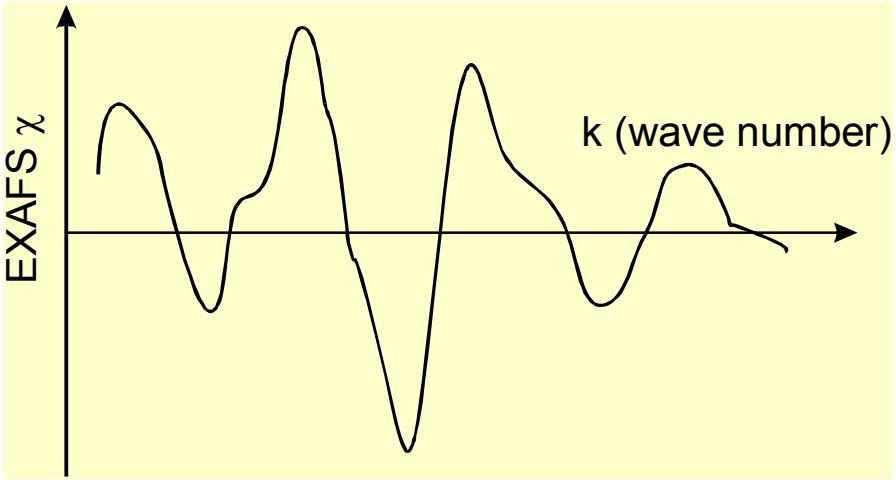


Atomic distance(Å)



EXAFS γ(k)

EXAFS analysis-1



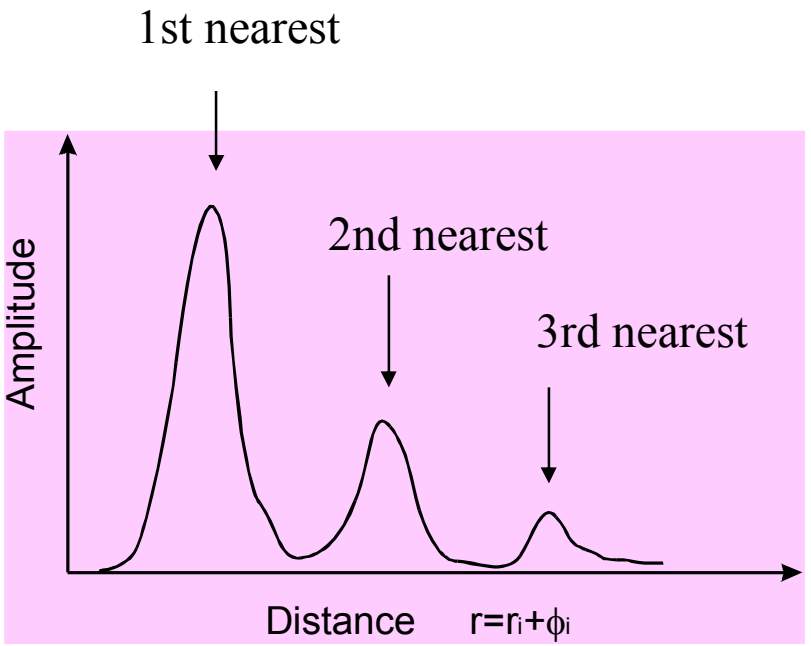
$$\chi(k) = \sum_i A_i(k)\sin(2kr_i + \phi_i)$$

amplitude

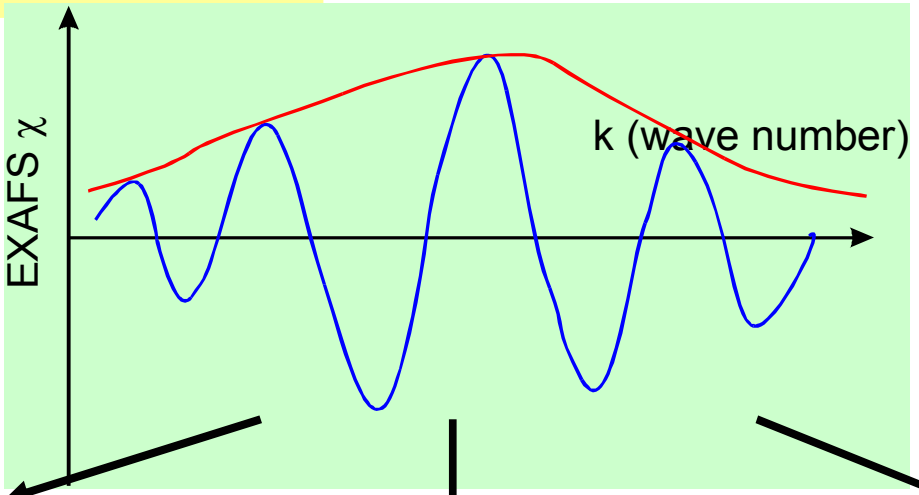
Atomic distance

Phase shift

Fourier transformation



EXAFS analysis-2



Effective Coordination Number

Debye-Waller factor

Back scattering amplitude

Direction of chemical bond

Pair Potential Function

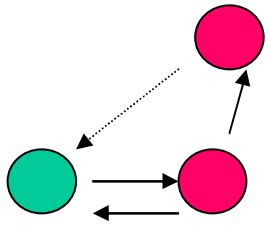
Kind of scattering atom

Limitation and Improvement of XAFS theory

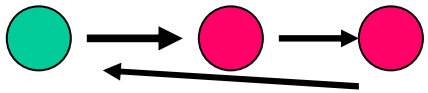
- Multiple scattering effect

  which is enhanced at XANES region and also at longer distance above 3 A.

  →FEFF program developed by J.Rehr can be used for spectral simulation.



negligible



Non-negligible

Shadowing effect

Limitation and Improvement of XAFS theory

- **Vibrational anharmonicity**

  The formula assumes a Gussian distribution.

  →Cumulant expansion method has been developed to take into the anharmonicity,

which gives the information of real bond distance, thermal expansion coefficients, radial distribution curve.

$$\chi(k) = \frac{N}{kR^2}\,\mathrm{Im}\left[f_{eff}(k,kR)\exp\left(2ikR + \sum_{n=2}^{\infty}\frac{(2ik)^n}{n!}C_n \right)\right]$$

$$= \frac{N}{kR^2}F_{eff}(k,kR)\exp\left[-2C_2k^2 + \frac{2}{3}C_4k^4 - \cdots \right]\sin\left[2kR + \phi_{eff}(k,kR) - \frac{4}{3}C_3k^3 + \cdots \right]$$

$$C_2 = <(r-R)^2> \qquad C_3 = <(r-R)^3> \qquad C_4 = <(r-R)^4> - 3C_2^2$$

where $R = <r>$

(4) XAFS applications

- Catalysis
- Amorphous systems
- Material physics(High Tc, CMR,….)
- Magnetic materials ← XMCD
- Thin films and Surface science
- Environmental science
- Biological materials

(5) Challenge of XAFS

- Time-resolved XAFS spectroscopy
- Micro XAFS or Nano XAFS

Summary--Features of XAFS

- Applicable to any phase (amorphous, liquid, gas), surface/interface and biomaterials
- Measurable under various conditions

  → under high pressure, gaseous atmosphere, for real catalysis
- Polarization dependence →direction of the bond
- Temperature dependence→ strength of any specific bond
- Combined with microbeam →local structure of a local area
- Pump-probe experiment →dynamics of local structure