

LECTURE 8:

X-RAY ABSORPTION SPECTROSCOPY (XAS)

- Synchrotron radiation
- REMEMBER: Local structure & Valence are very much related
- EXAFS (Extended X-ray Absorption Fine-Structure)
 - Local structure (= number & distance of neighbouring atoms)
- XANES (X-ray Absorption Near-Edge Structure)
 - Valence (= oxidation state)

Crystal structure and redox states (= valences) are highly related, recall e.g. the empirical BVS approach to address the correlation !!!

Bond-Valence-Sum (BVS) for Inorganics

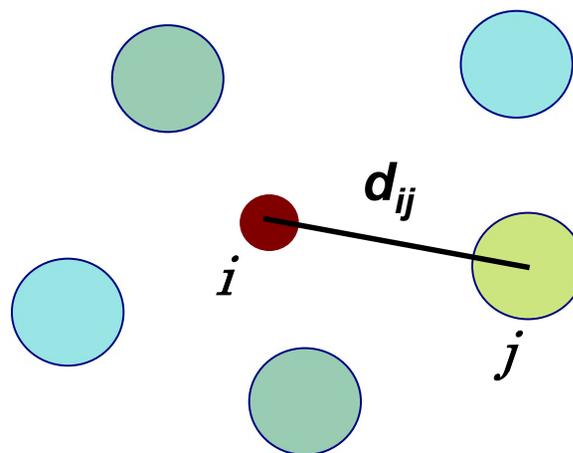
- Quantitative relation between the bond valence and the bond length
- Bond valence can be fractional & Neighbours may be unequivalent
- The shorter the bond, the stronger it is, and the larger the s_{ij} is

- Empirical equation:

$$s_{ij} = \exp[(R_{ij}^0 - d_{ij})/0.37]$$

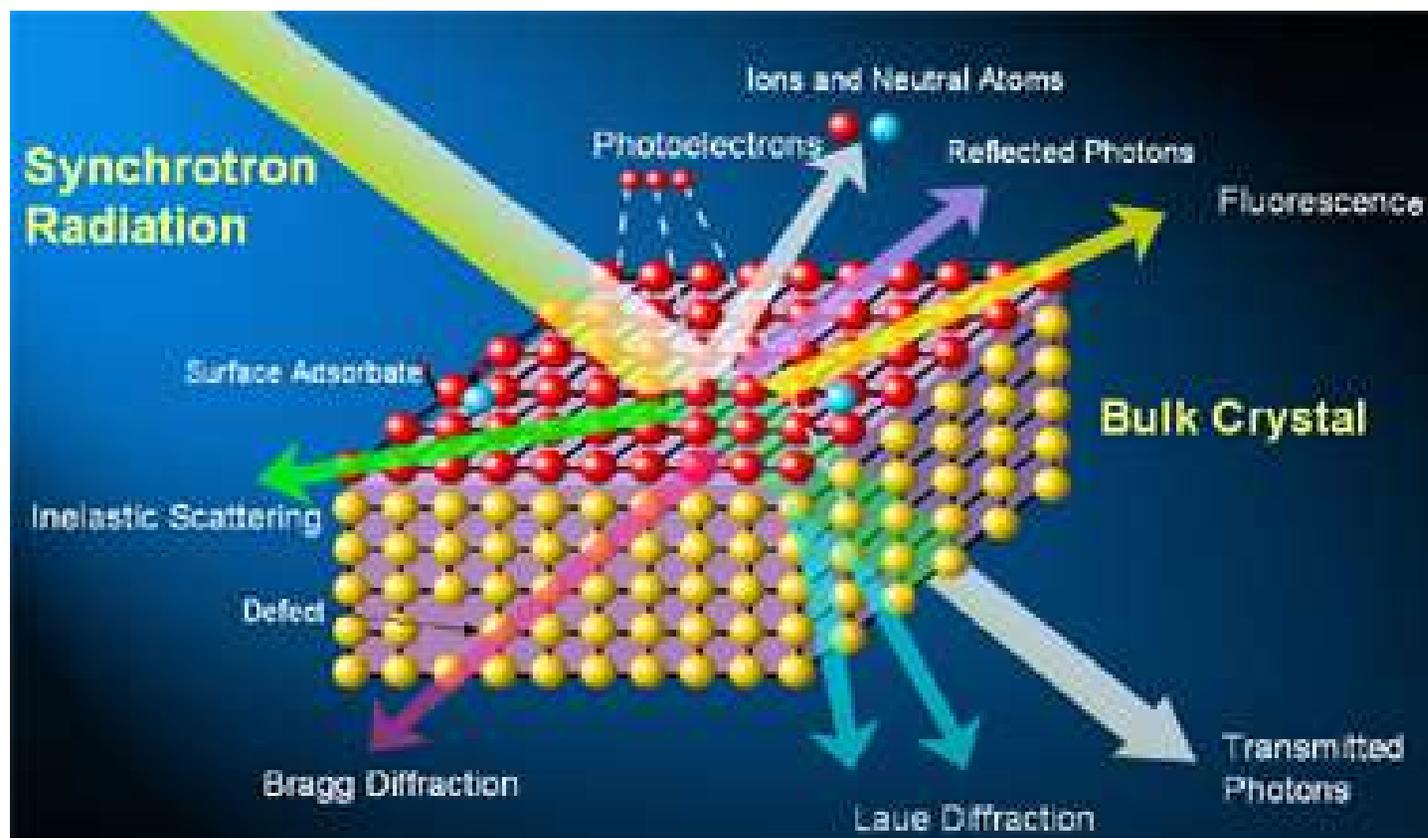
$$V_i = \pm \sum s_{ij}$$

- R_{ij}^0 values tabulated
(for various i-j combinations)



X-RAYS & MATERIAL

- Diffraction of x-rays from regular atom planes → XRD
- Fluorescence radiation created by x-rays → XRF
- Photoelectrons created by x-rays → XPS (ESCA)
- Absorption of x-rays → XANES & EXAFS

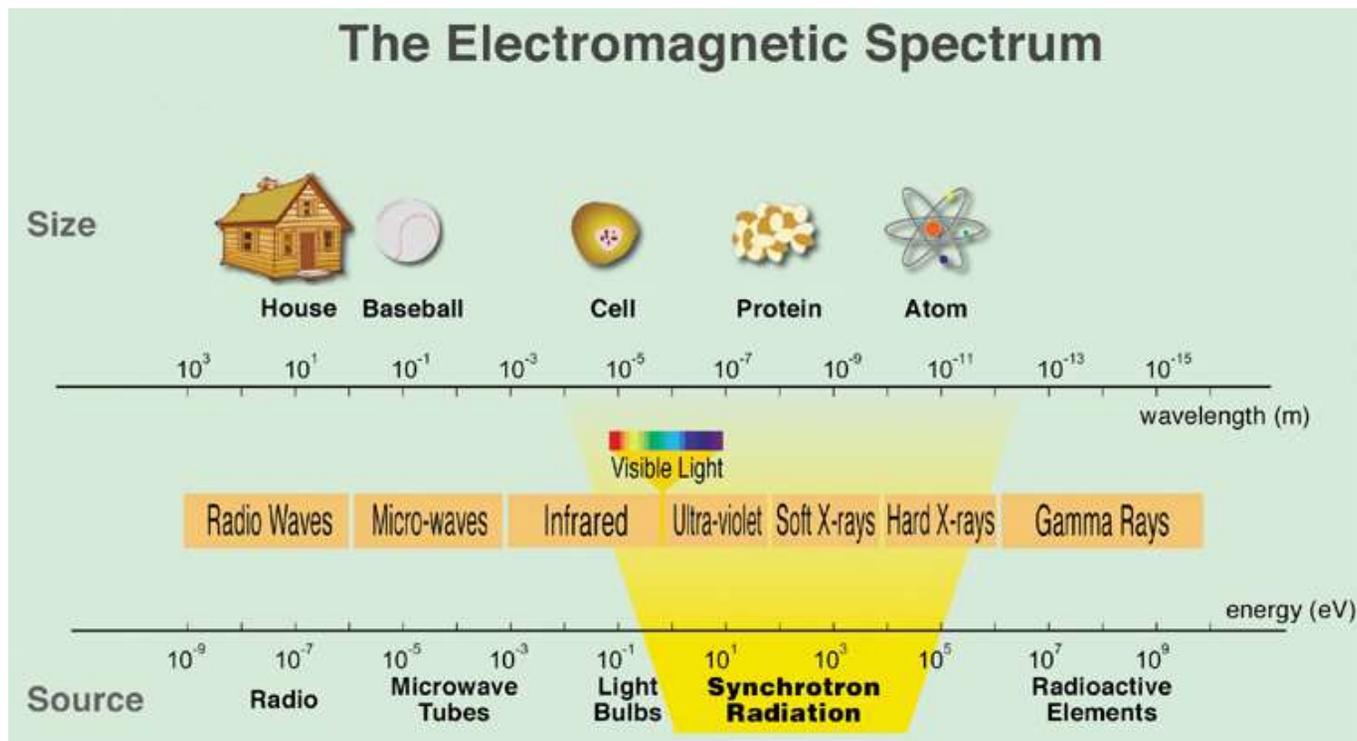


PRODUCTION OF X-RAYS

- Wavelength of X-rays: $0.01 \text{ \AA} \sim 100 \text{ \AA}$
- **Conventional X-ray tube**
 - heated W wire as an electron source
 - acceleration of electrons with external voltage
 - bombarding of the electrons to metal anode (Cu, Mo, etc.)
 - **characteristic line spectrum**
- **Synchrotron**
 - charged particles (e.g. electrons) are accelerated to move with a speed close to the speed of light
 - kinetic energy of the particles is changed with magnets
 - **very intense continuous spectrum**

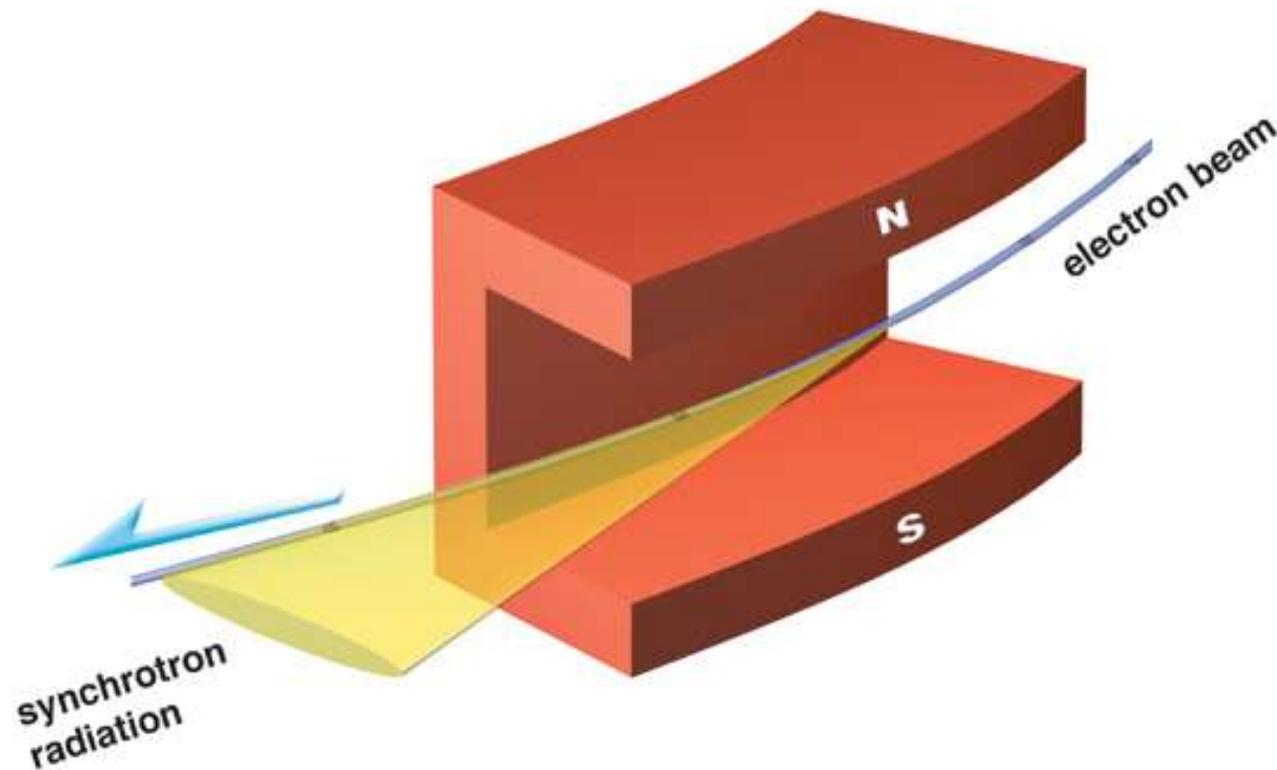
SYNCHROTRON RADIATION

- Continuous band of electromagnetic spectrum including infrared, visible light, ultraviolet and x-rays
- Accidentally discovered in an electron synchrotron of the General Electric Company, USA, in 1947



How is synchrotron radiation produced?

Whenever electrons moving close to the speed of light are deflected by a magnetic field, they radiate a thin beam of radiation tangentially from their path. This beam is called “**synchrotron radiation**”.



Example: NSRRC, Taiwan
National Synchrotron Radiation Research Center

- Relatively small synchrotron
- Particularly suitable for light elements, e.g. oxygen → We are frequent users
- Creation of ACCELERATED ELECTRONS
 - electrons are injected from an **Electron Gun**
 - pre-accelerated to 50 MeV in a linear **LINAC**
 - accelerated to 1.5 GeV in a **Booster Ring**

Electron Gun



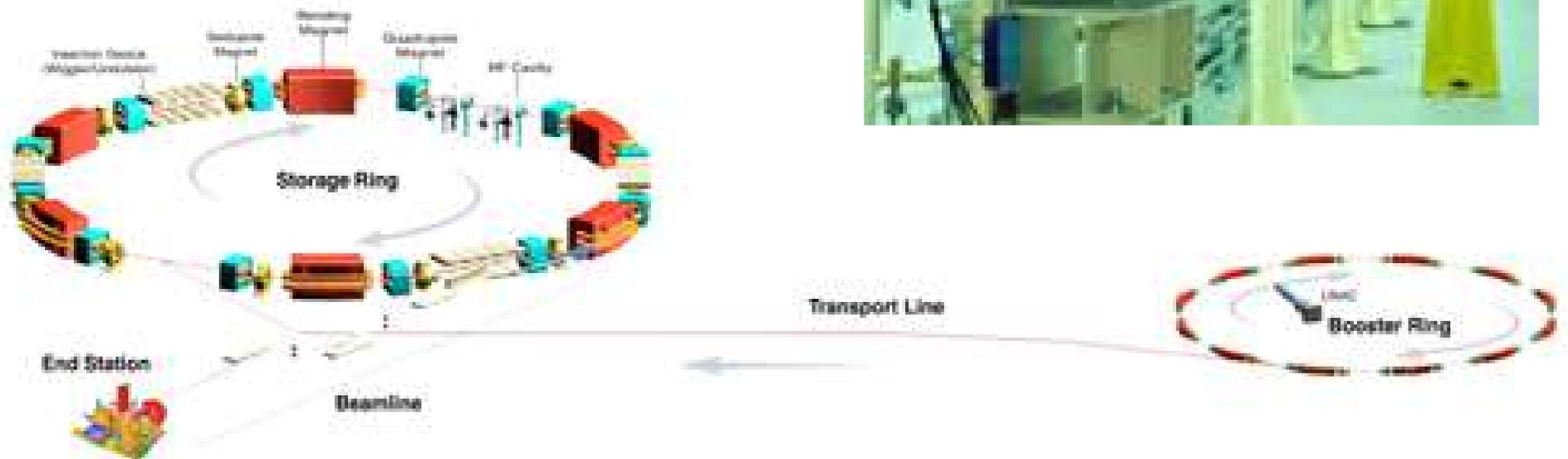
Booster Ring (72 m in circumference):
- Electrons with 99.999995 % of light speed

LINAC

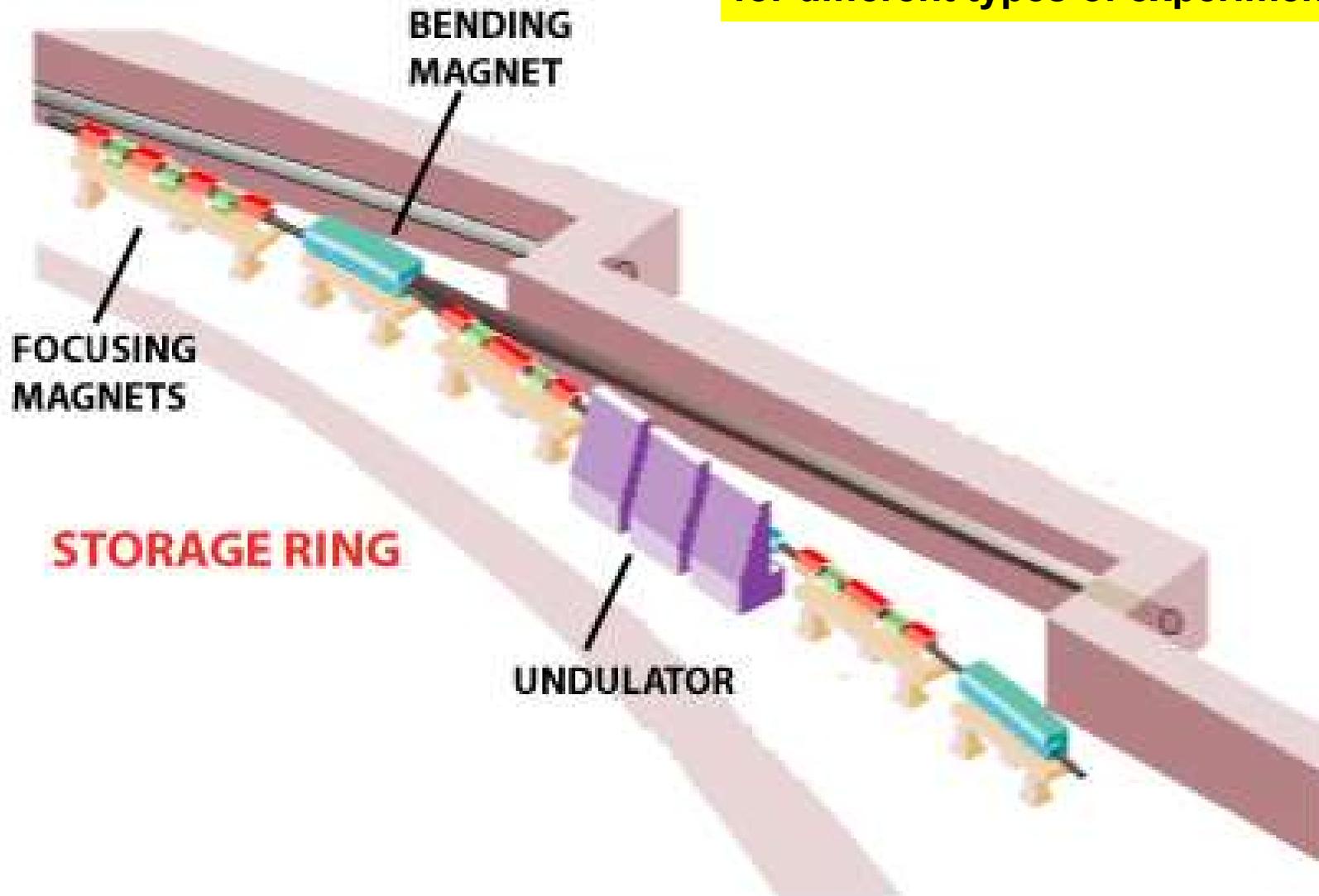


Accelerated electrons are sent through a 70-meter long **Transport Line** into a hexagonal, 120-meter **Storage Ring**, where they circulate with an energy of 1.5 GeV in ultra-high-vacuum pipes for several hours, emitting synchrotron radiation.

Transport Line



There are different types of **magnets** attached to the storage ring to generate X-ray light with different characteristics for different types of experiments



The emitted light is channeled through **Beamlines** to the **Experimental Stations**, where experiments are conducted.

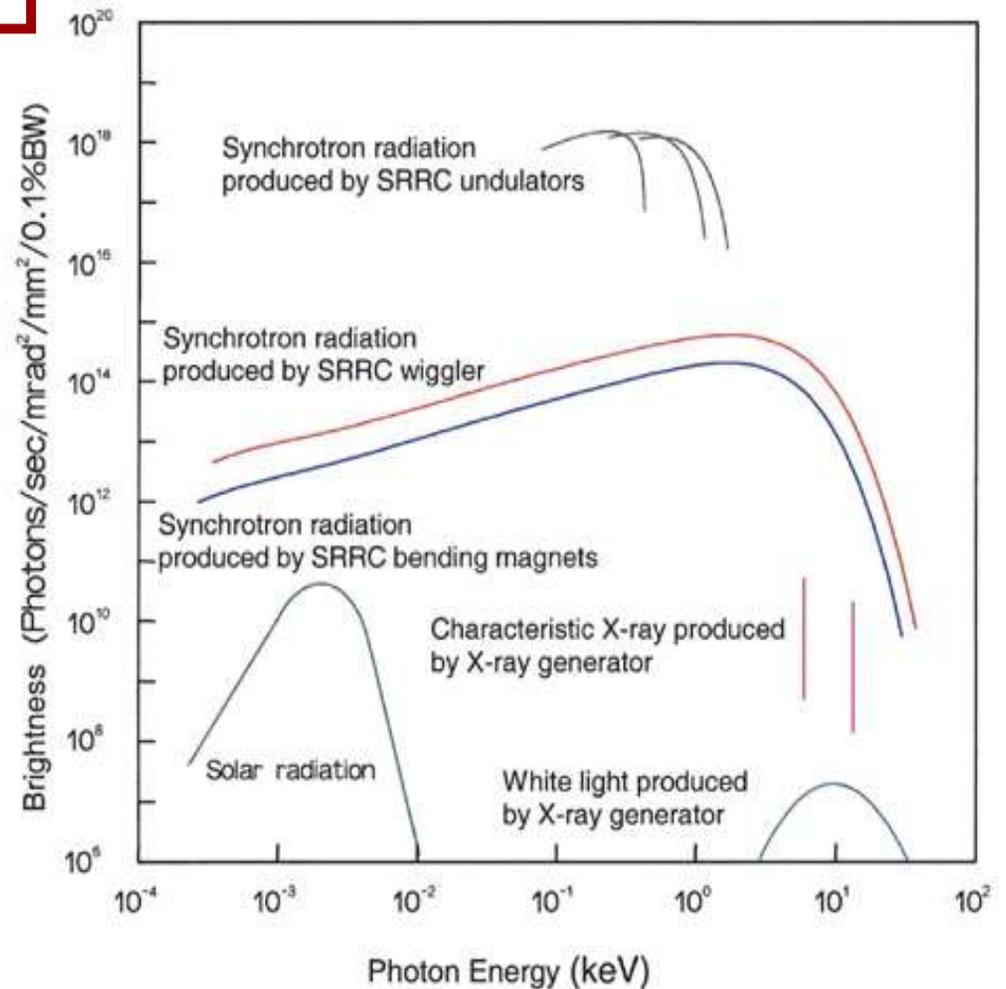


HFM: Horizontal Focussing Mirror
VFM: Vertical Focussing Mirror
RFM: Refocussing Mirror

Synchrotron Radiation

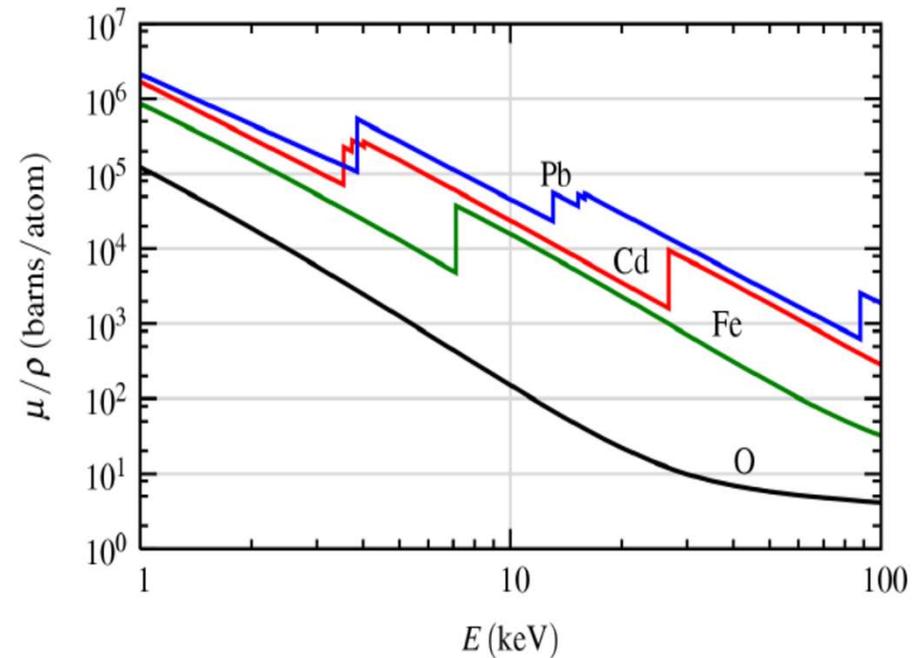
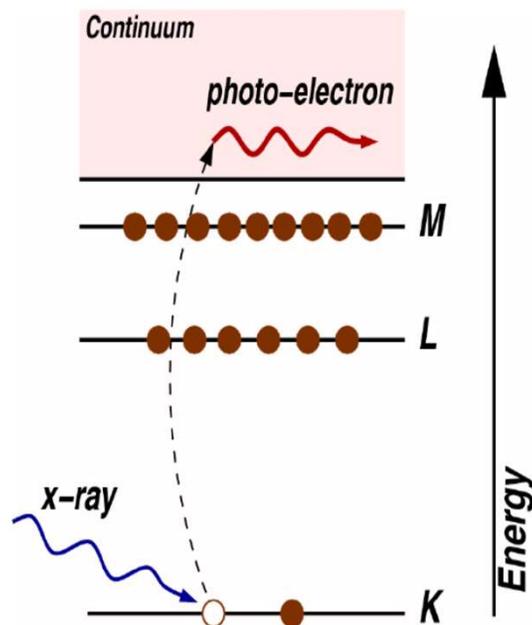
- High intensity
- Continuous spectrum
- Polarized (oscillate to same direction)
- Excellent collimation (X-rays parallel)
- Pulsed-time structure

<http://www.nsrrc.gov.tw>

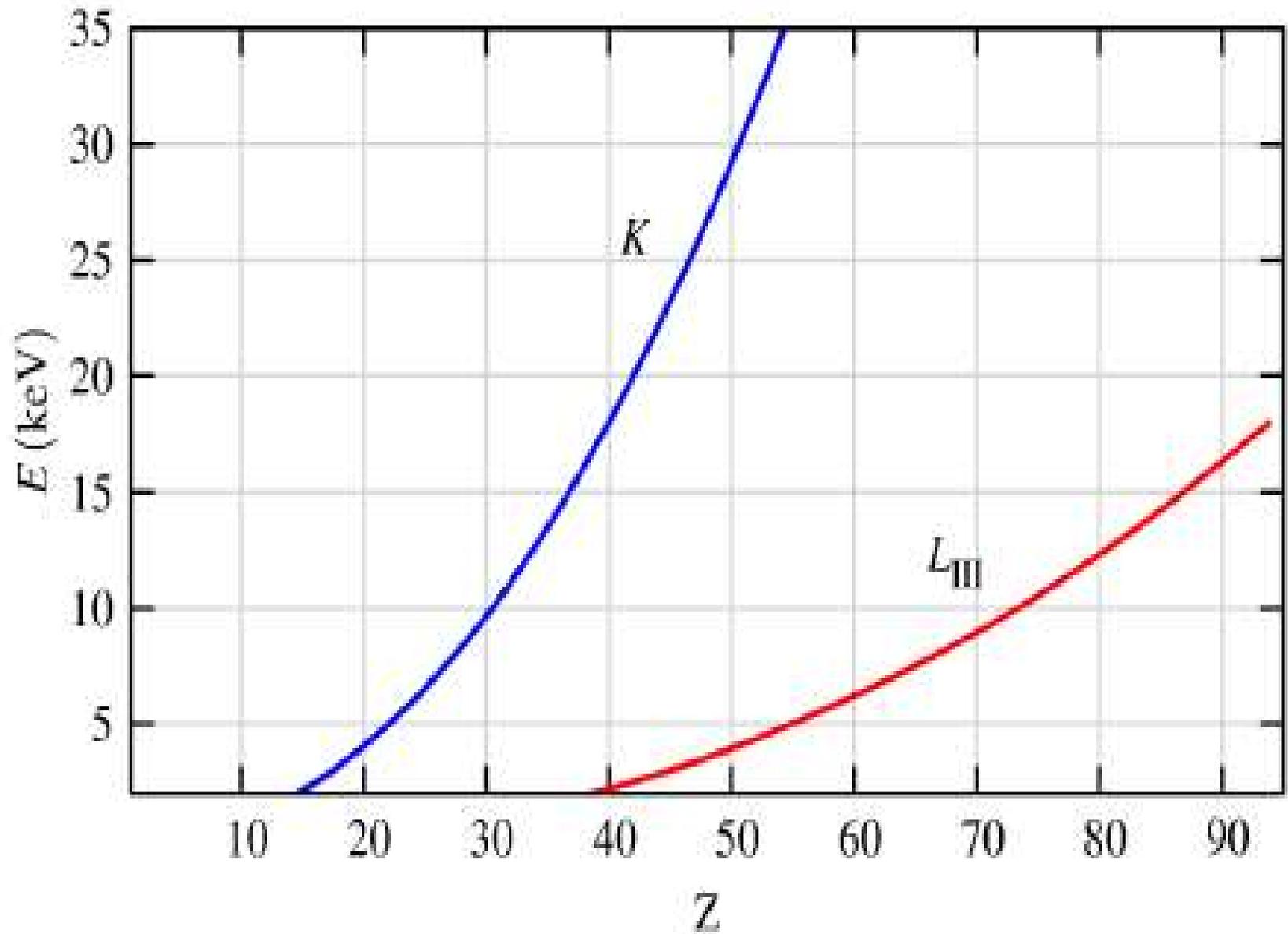


X-RAY ABSORPTION

- Wavelength/energy of x-rays corresponds to energies required to remove electrons from inner shells
- Absorption decreases with increasing energy, until at a certain energy it increases abruptly → **ABSORPTION EDGE**
- Absorption edge corresponds to the bonding energy of inner shell electron → *K*-edge, *L*-edge ...

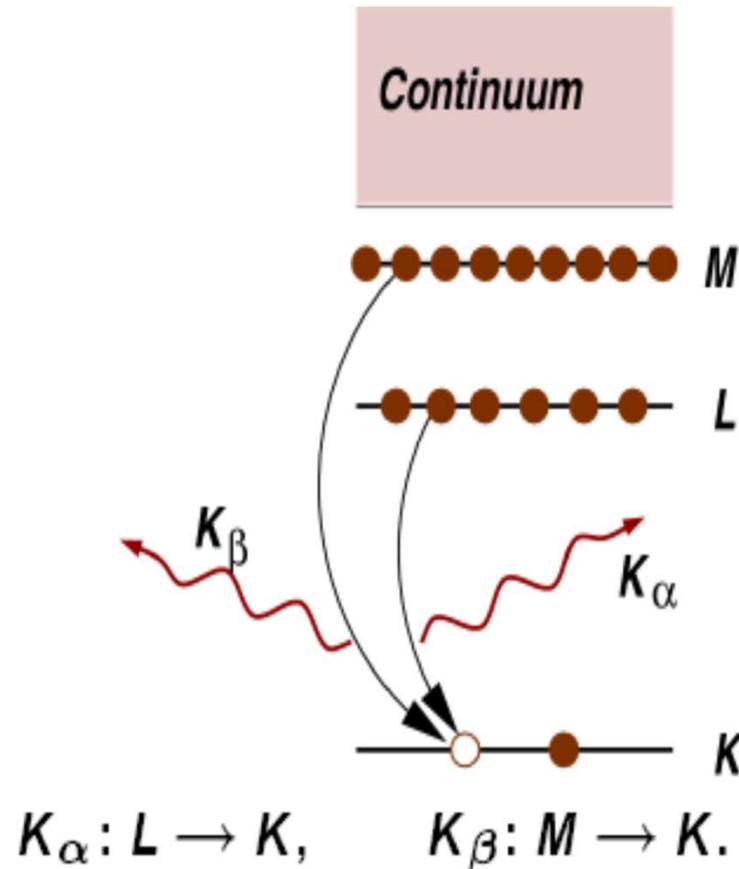


Absorption-edge energy depends on the atomic number ($\sim Z^2$)



To investigate X-ray absorption, we may measure X-ray intensity of transmitted radiation or fluorescence radiation (both depend on the magnitude of absorption)

X-ray fluorescence



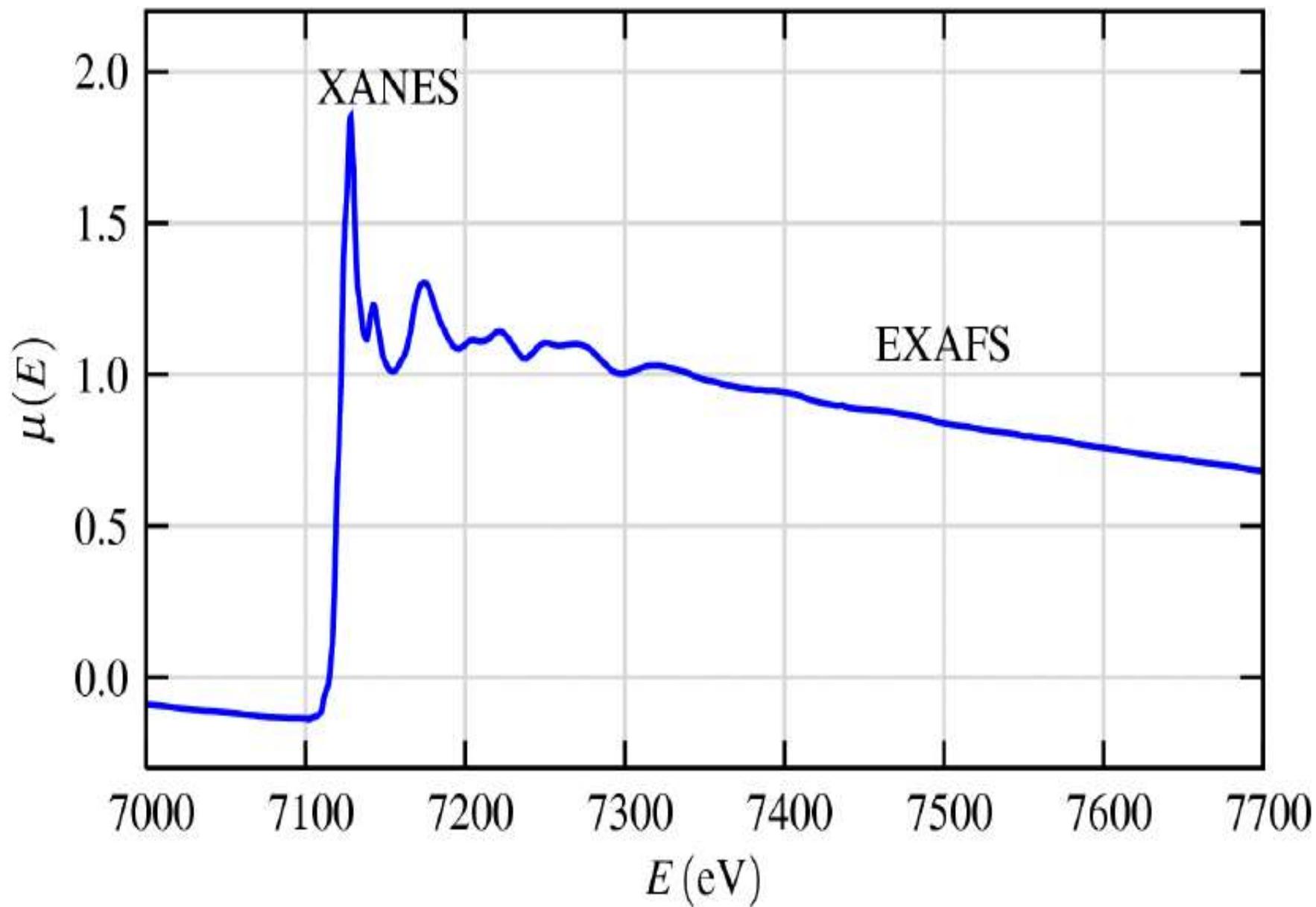
XAS: X-ray Absorption Spectroscopy

XAFS: X-ray Absorption Fine-Structure

EXAFS: Extended X-ray Absorption Fine-Structure

XANES: X-ray Absorption Near-Edge Structure

μ : absorption coefficient

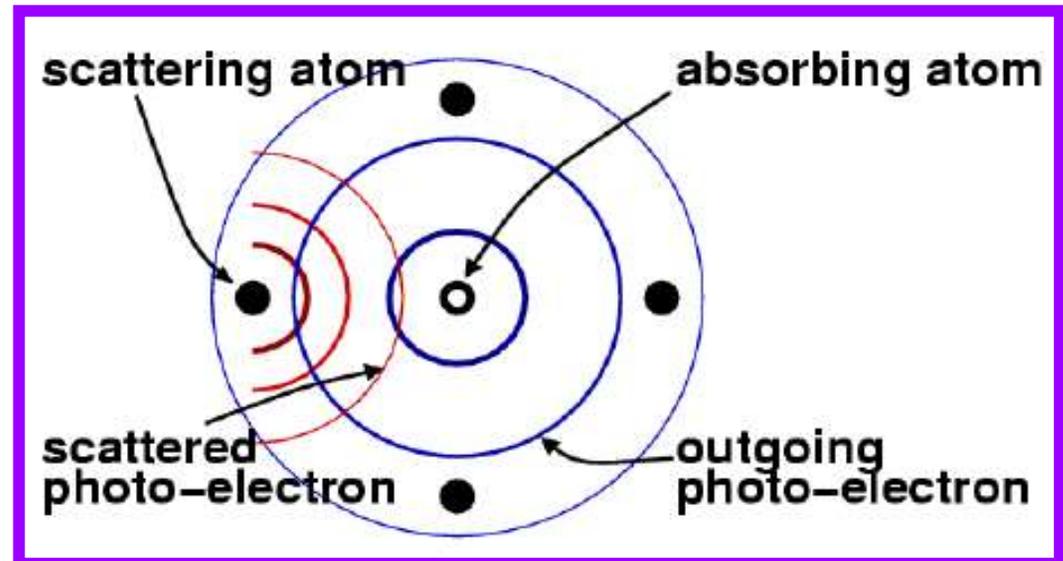
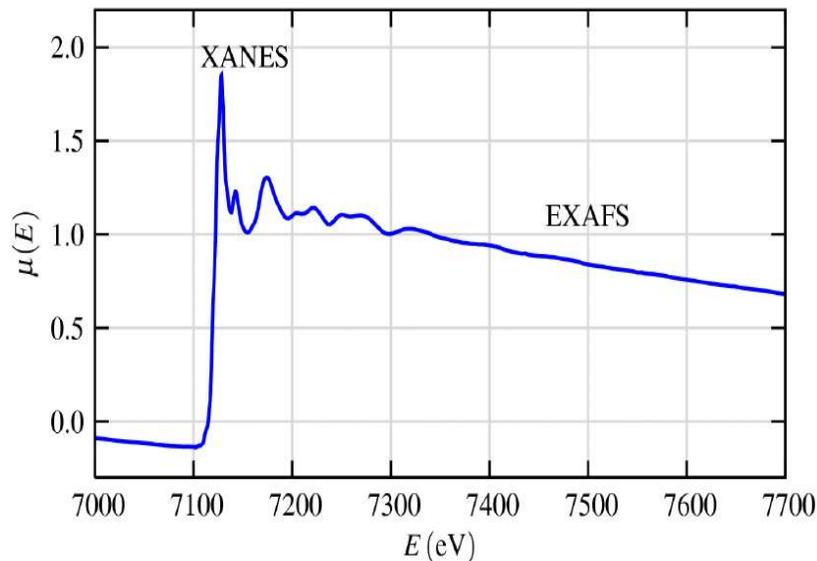


XANES/EXAFS

- In EXAFS/XANES spectroscopy X-ray absorption is measured in the vicinity of absorption edge
- Synchrotron radiation is needed as a source of **intense** and **continuous** X-ray radiation
- Both transmittance and fluorescence measurements
- Absorption edge energy specific to each element
→ EXAFS/XANES spectroscopy is element specific
- Possible for all elements except for the very lightest elements

EXAFS (Extended X-ray Absorption Fine Structure)

- Oscillations in the high-energy side of the absorption edge
- Oscillation phenomenon was known for a longer time but the explanation was given in the 1970s → EXAFS theory
- Simplified explanation: x-ray energy absorbed → photoelectrons removed from inner shell → sphere waves → scatter from the **neighbouring atoms**
- Due to this backscattering → interference effect → **oscillations** → **EXAFS**
- **Oscillations depend on the neighbouring atoms (type, number, distance)**



EXAFS

- element-specific (absorption edge energy is element-specific)
- most of the elements except the very lightest ones are "seen"
- solid materials (crystalline and amorphous), thin films, catalyst surfaces, liquids, ...
- **local structure** (neighbouring atoms, coordination number, bond lengths)

STEPS in EXAFS DATA ANALYSIS

- Conversion of measured intensities to $\mu(E)$
- Pre-edge background subtraction (instrumental errors etc)
- $\mu(E)$ normalized to vary from 0 to 1
- Post-edge background removal (smooth curve)
- Conversion from energy to (photoelectron) wave number: $E \rightarrow k$
- Weighting k values (to give more impact for higher k values)
- Fourier transform from k to R (= distance) space
- Isolation of appropriate "shells" by Fourier filtering
- Modelling to EXAFS equation to get: R and N (= coordination number)

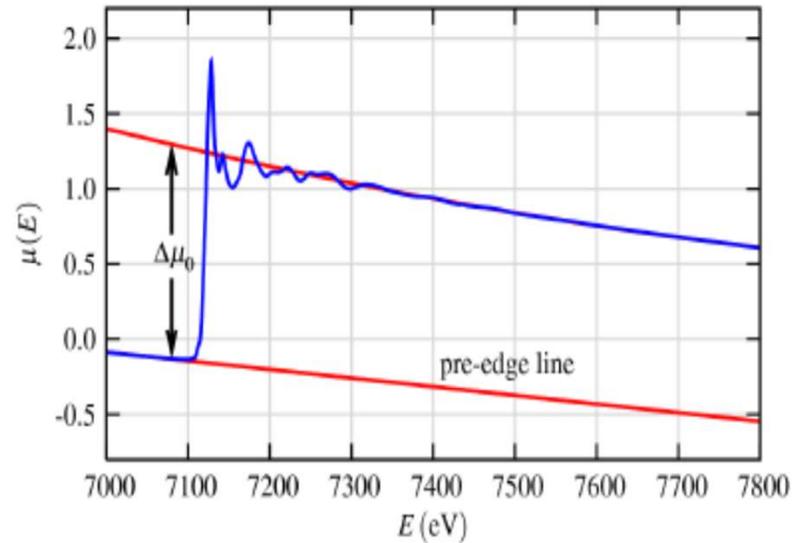
$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$

Matt Newville

Consortium for Advanced Radiation Sources

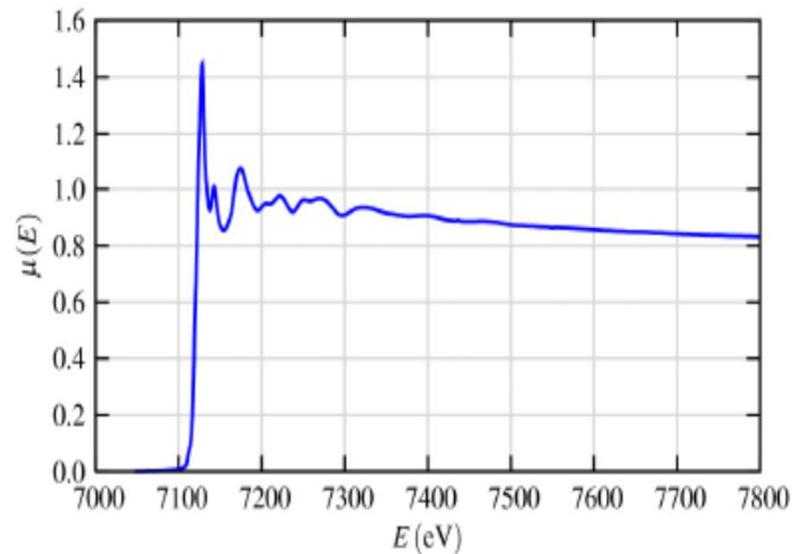
University of Chicago

- Absorption coefficient (μ) versus X-ray energy
- Pre-edge background subtraction
- Normalization



Pre-Edge Subtraction

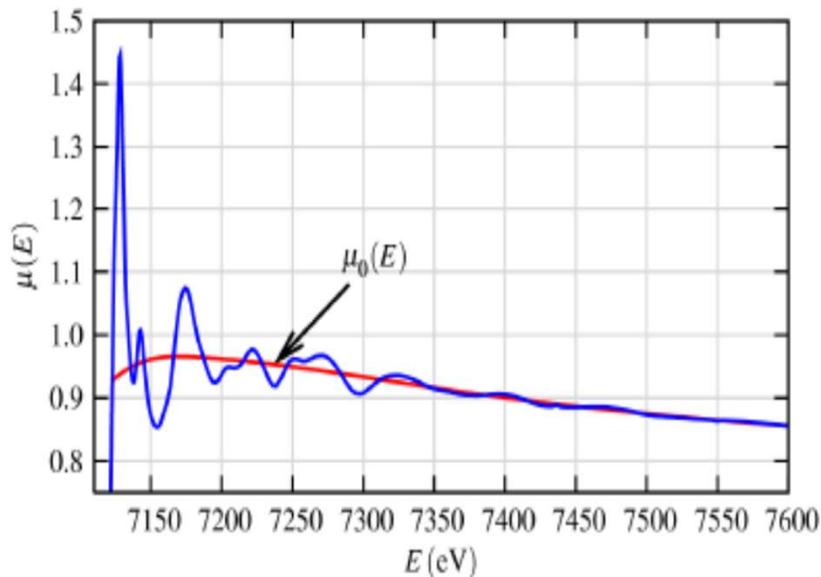
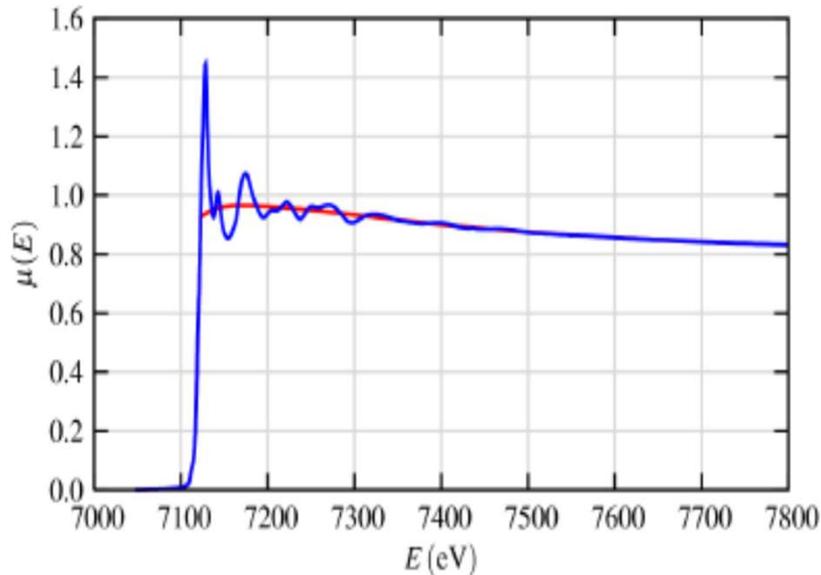
We subtract away the background that fits the *pre-edge* region. This gets rid of the absorption due to other edges (say, the Fe L_{III} edge).



Normalization

We estimate the *edge step*, $\Delta\mu_0(E_0)$ by extrapolating a simple fit to the above $\mu(E)$ to the edge. We normalize by this value to get the absorption from 1 x-ray.

- **Post-edge background subtraction**



Post-Edge Background

We don't have a measurement of $\mu_0(E)$ (the absorption coefficient without neighboring atoms).

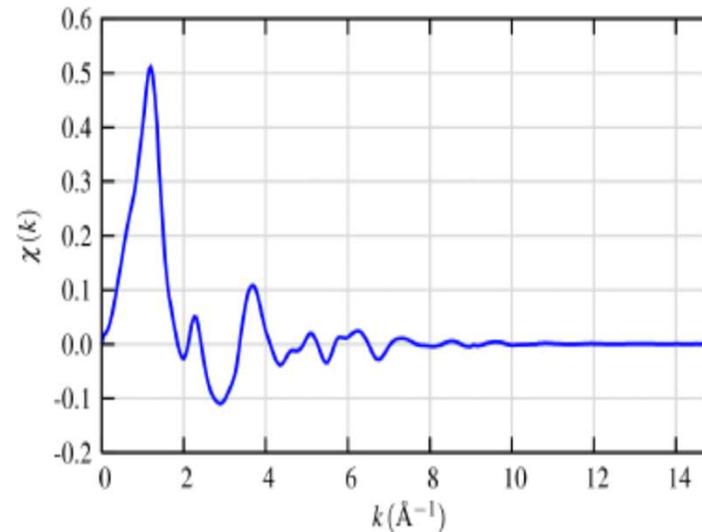
We approximate $\mu_0(E)$ by an adjustable, smooth function: a *spline*.

This can be somewhat dangerous – a flexible enough spline could match the $\mu(E)$ and remove all the EXAFS!

We want a spline that will match the *low frequency* components of $\mu_0(E)$.

- Conversion from energy to (photoelectron) wave number: $E \rightarrow k$
- Weighting k values (to give more impact for higher k values)

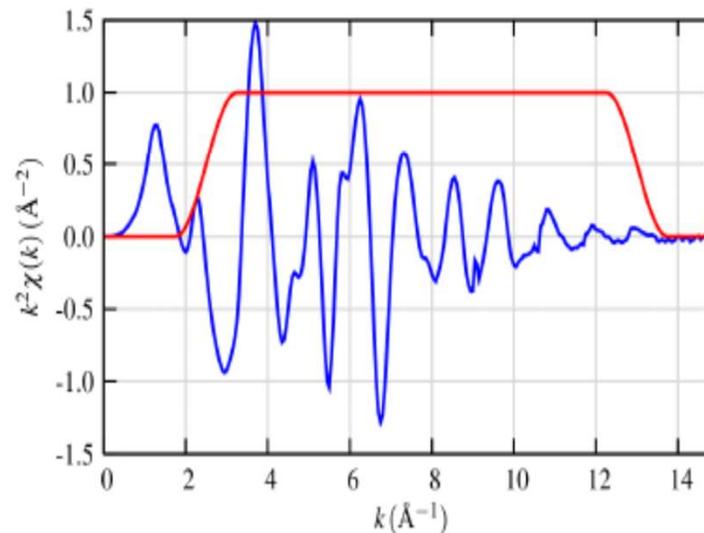
$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$



$\chi(k)$

The raw EXAFS $\chi(k)$ usually decays quickly with k , and difficult to assess or interpret by itself.

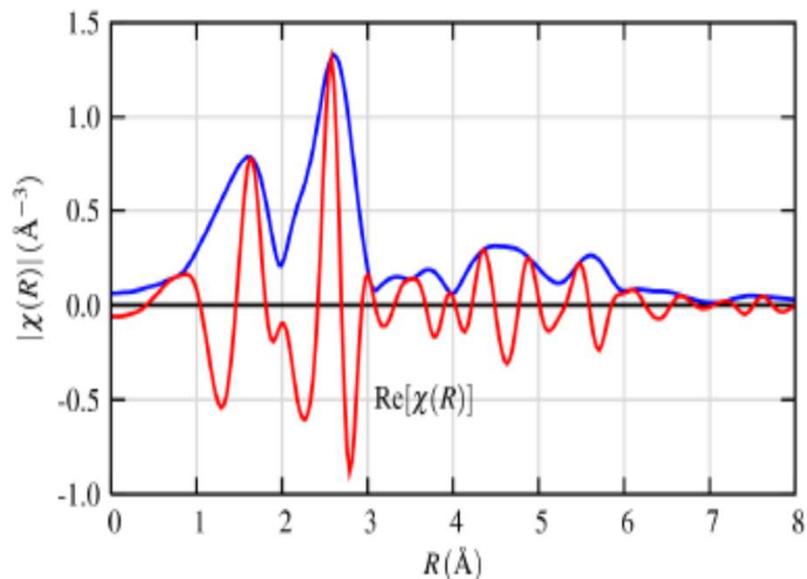
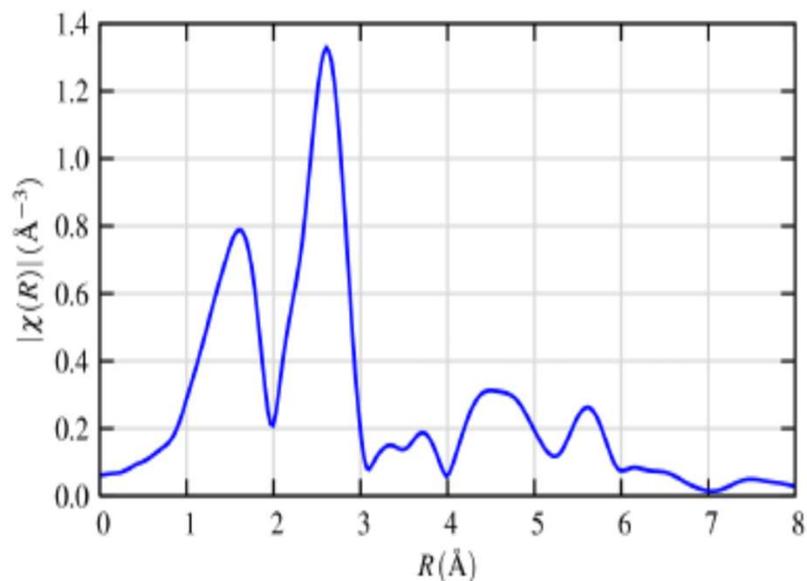
It is customary to weight the higher- k portion of the spectra by multiplying by k^2 or k^3 .



k-weighted $\chi(k)$: $k^2\chi(k)$

$\chi(k)$ is composed of sine waves, so we'll Fourier Transform from k to R -space. To avoid "ringing", we'll multiply by a *window function*.

- Fourier transform from k to R (= distance) space
- Isolation of appropriate "shells" by Fourier filtering



$\chi(R)$

The Fourier Transform of $k^2\chi(k)$ has 2 main peaks, for the first 2 coordination shells: Fe-O and Fe-Fe.

The Fe-O distance in FeO is 2.14Å, but the first peak is at 1.6Å. This shift in the first peak is due to the **phase-shift**, $\delta(k)$: $\sin[2kR + \delta(k)]$.

A shift of -0.5Å is typical.

$\chi(R)$ is complex:

The FT makes $\chi(R)$ complex. Usually only the amplitude is shown, but there are really oscillations in $\chi(R)$.

Both real and imaginary components are used in modeling.

- **Modelling to EXAFS equation to get: R and N (= coordination number)**

To model the EXAFS, we use the *EXAFS Equation*:

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

where $f(k)$ and $\delta(k)$ are *photo-electron scattering properties* of the neighboring atom. (The sum is over “shells” of similar neighboring atoms).

If we know these properties, we can determine:

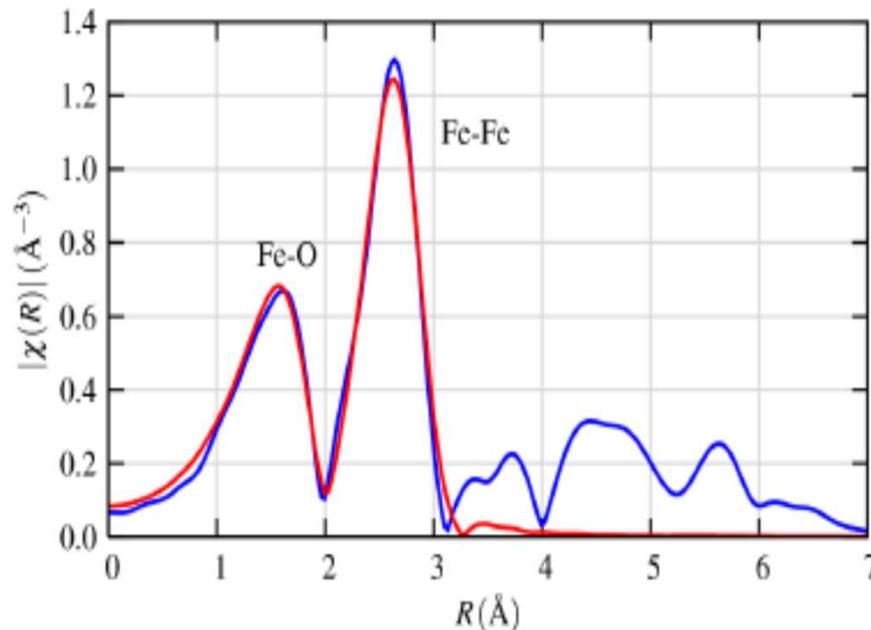
R distance to neighboring atom.

N coordination number of neighboring atom.

σ^2 mean-square disorder of neighbor distance.

The scattering amplitude $f(k)$ and phase-shift $\delta(k)$ depend on atomic number Z of the scattering atom, so we can also determine the species of the neighboring atom.

REMEMBER: phase-shift of ca. 0.5 Å possible



$|\chi(R)|$ data for FeO (blue), and fit of 1st and 2nd shells (red).

The results are fairly consistent with the known values for crystalline FeO:

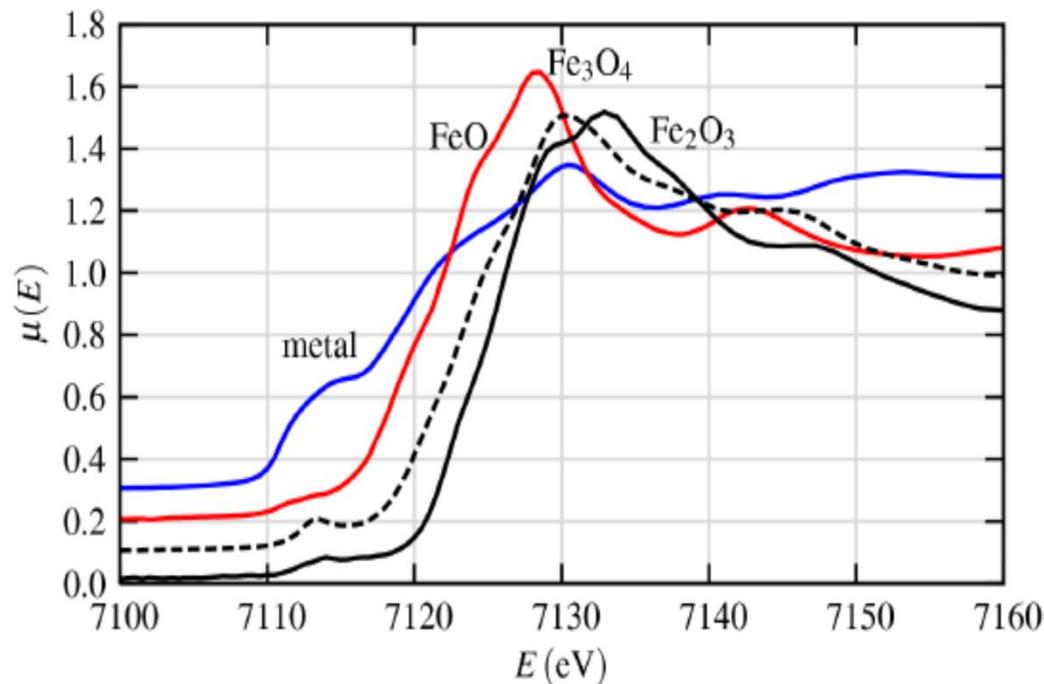
6 O at 2.13Å, 12 Fe at 3.02Å.

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)

XANES (X-ray Absorption Near Edge Structure)

- Inner-shell electrons are excited (not to continuum as in EXAFS but) to the (partially) empty outer orbitals
 - knowledge of the outer orbital energy/electron configuration
 - oxidation state of the absorbing atom
- Excitation of electrons from the inner shells to the outer orbitals requires less energy than removing them totally from the atom
 - absorption peak below the absorption edge → XANES spectroscopy

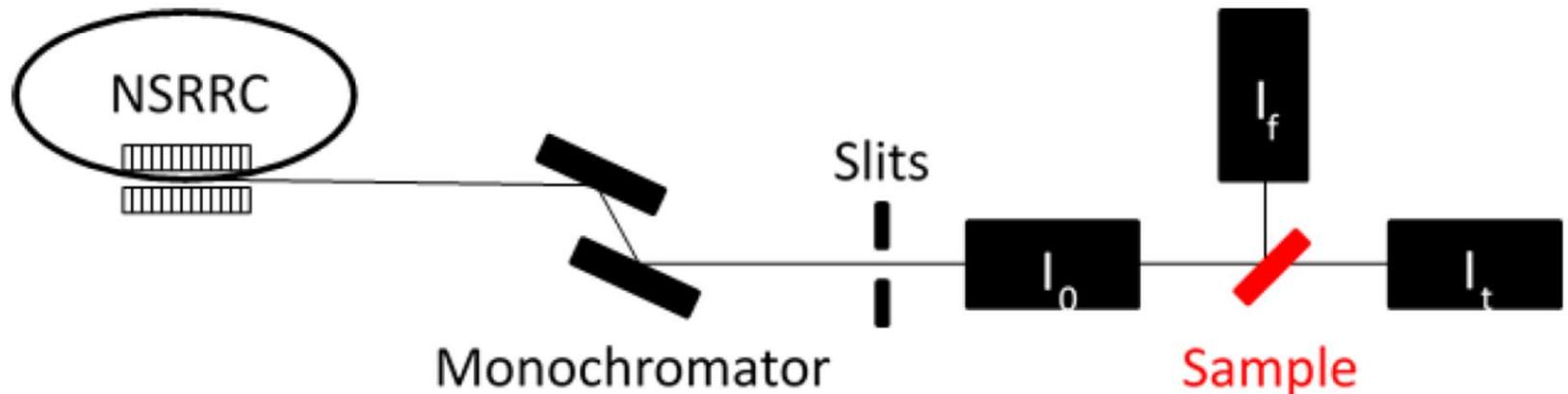


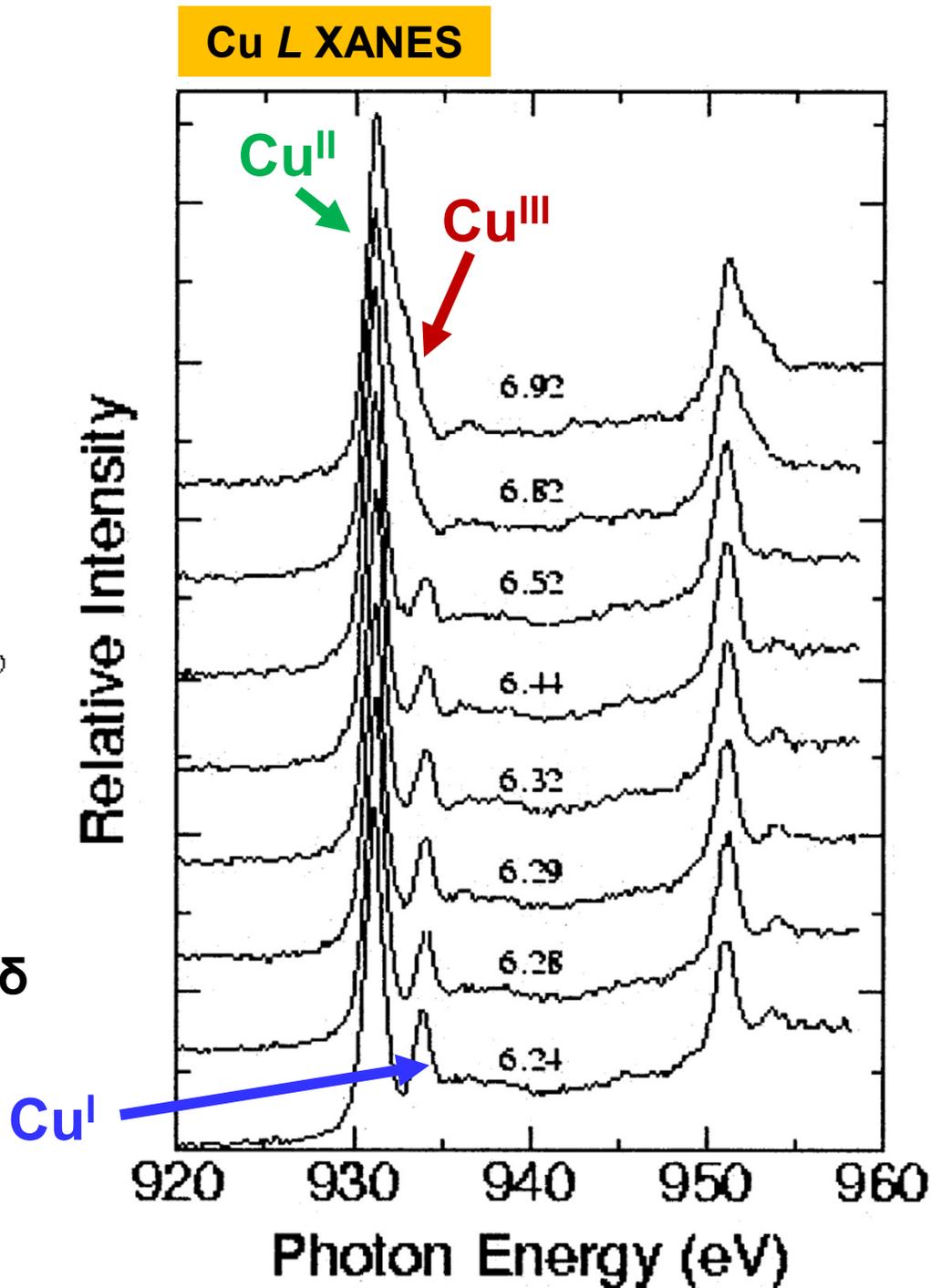
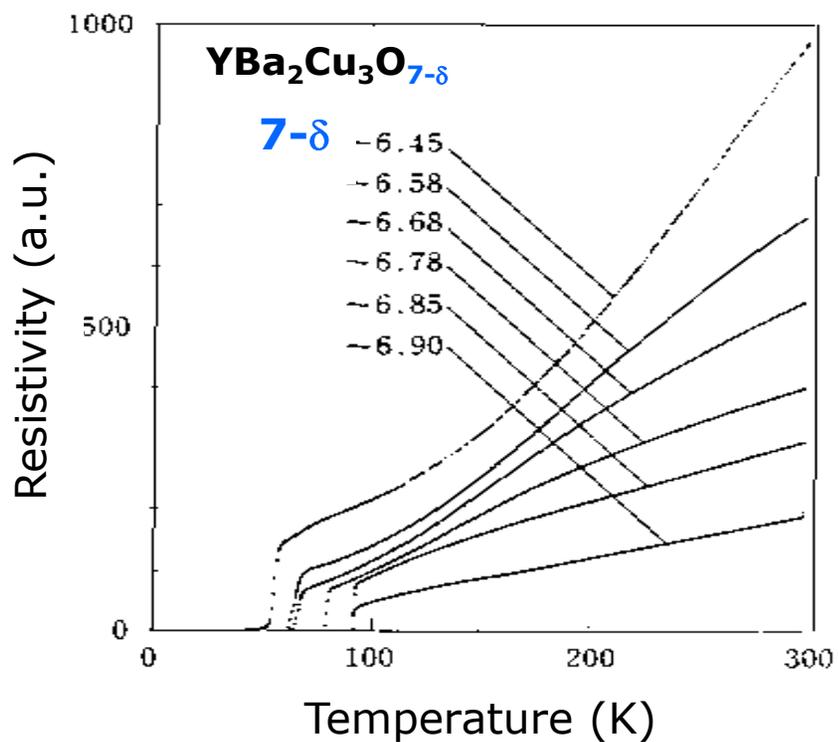
National Synchrotron Radiation Research Center (NSRRC), Hsinchu, TAIWAN

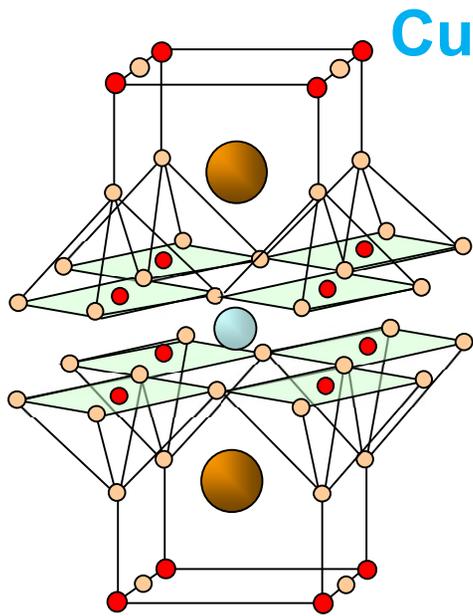


XANES & EXAFS

- Collaboration with Dr. Jin-Ming Chen
→ 38 joint publications since 2001
- Cu-K, Cu-L, Fe-K, Fe-L, Co-L, Ru-L, Nb-L, Ta-L, Mo-L, W-L, Bi-L, Ce-M, Sr-K, Se-K, **O-K**



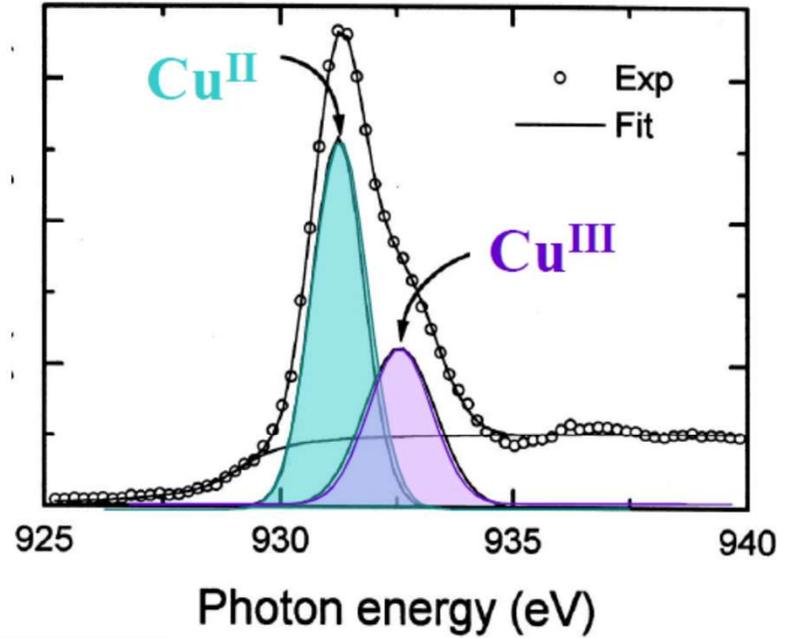




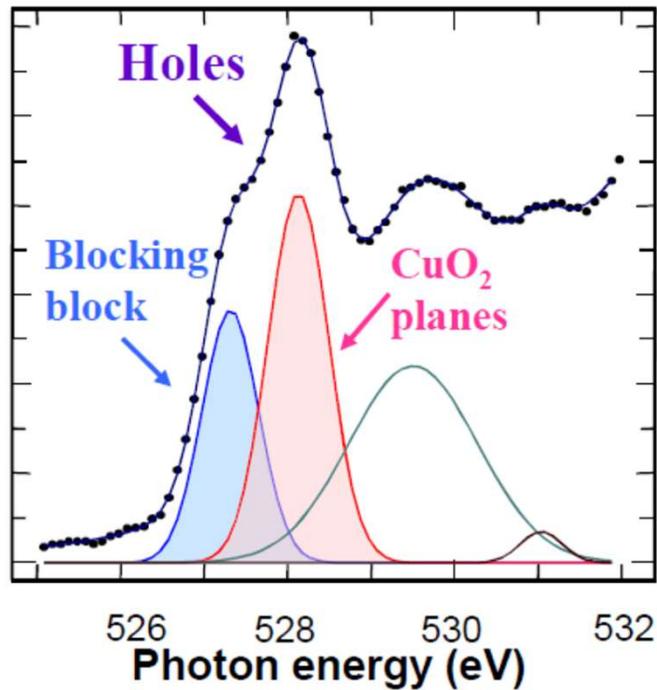
Cu(1)O (blocking block)

Cu(2)O₂ plane

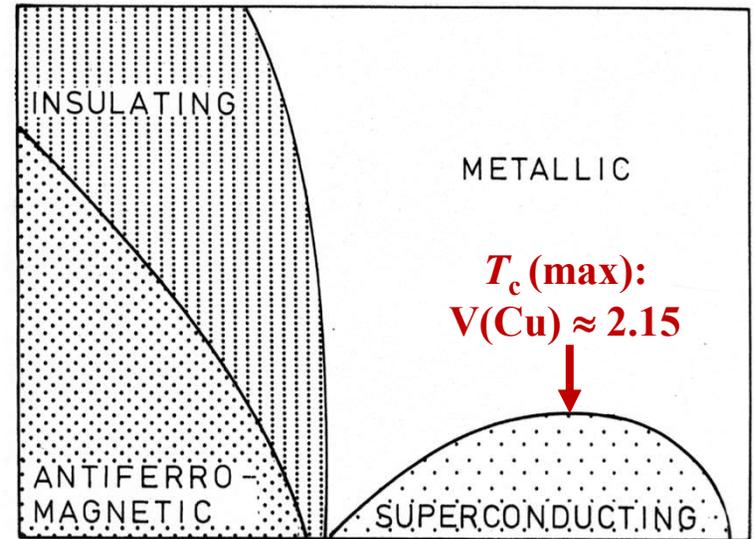
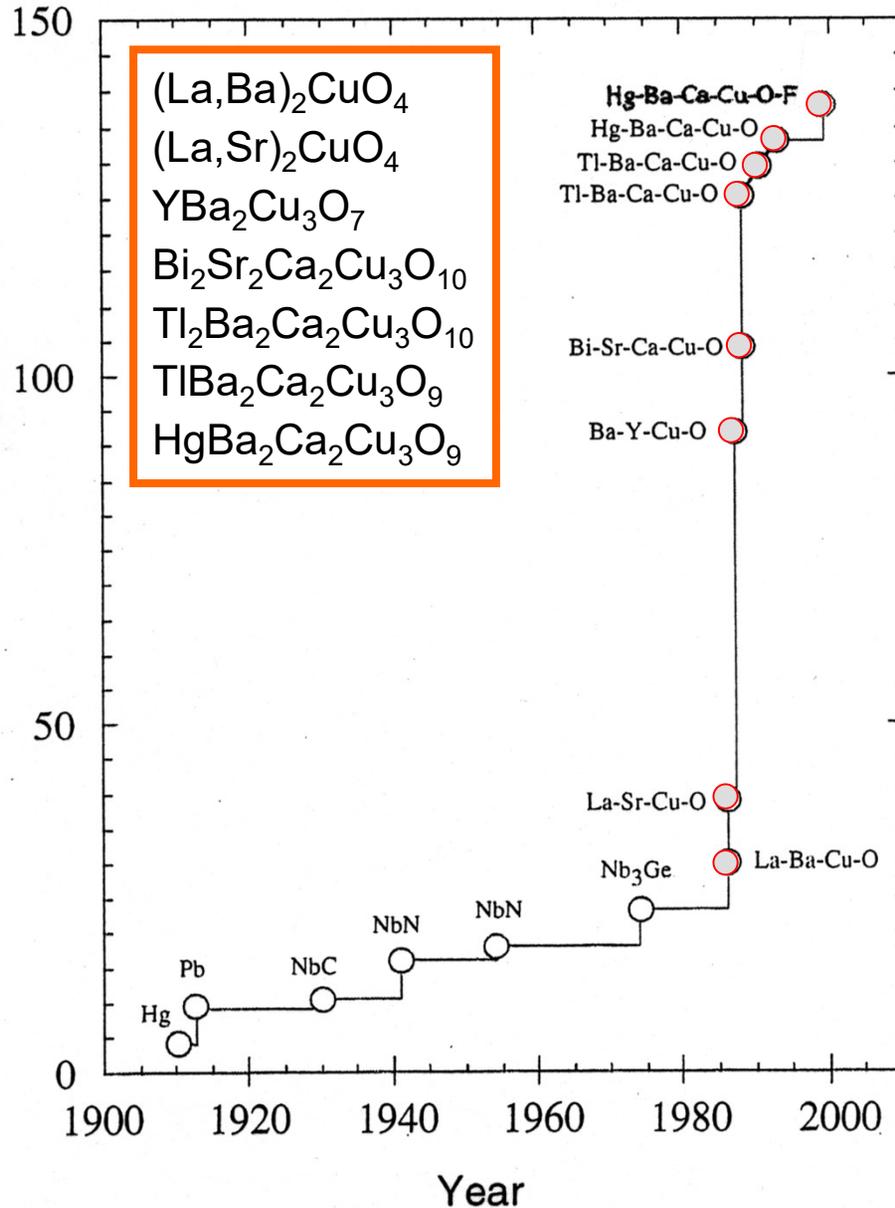
Cu L XANES → average V(Cu)



O K XANES



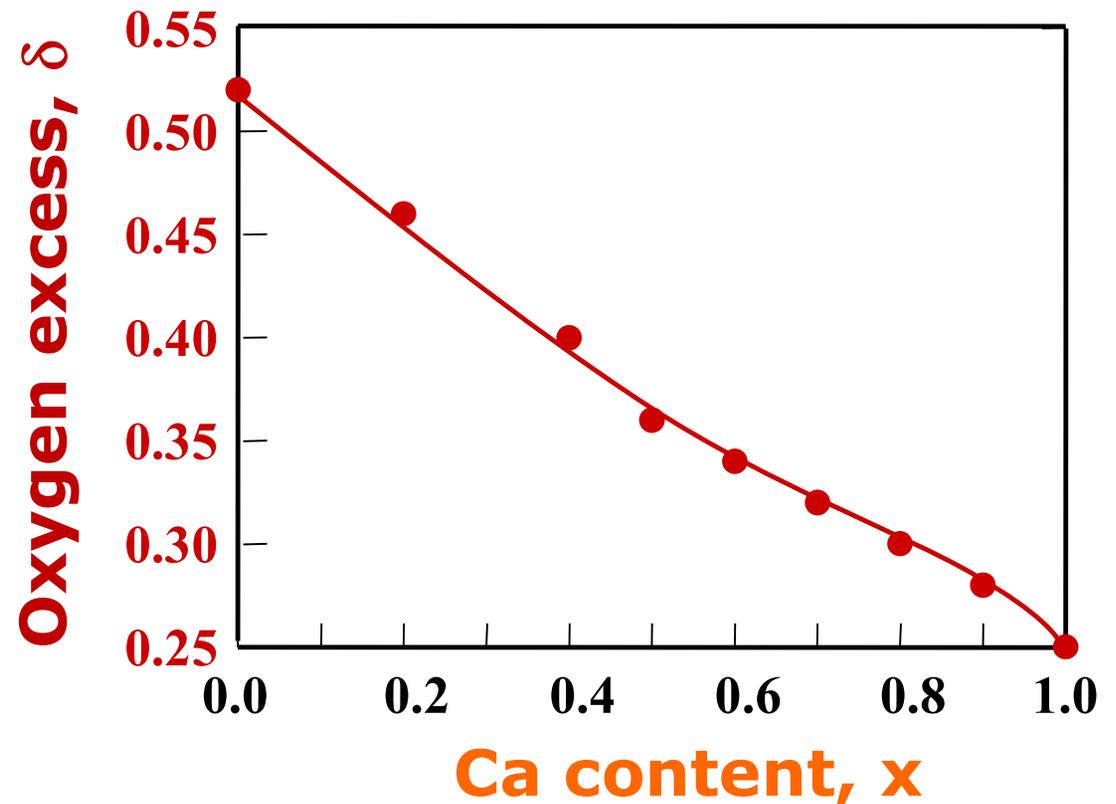
High- T_c superconductors

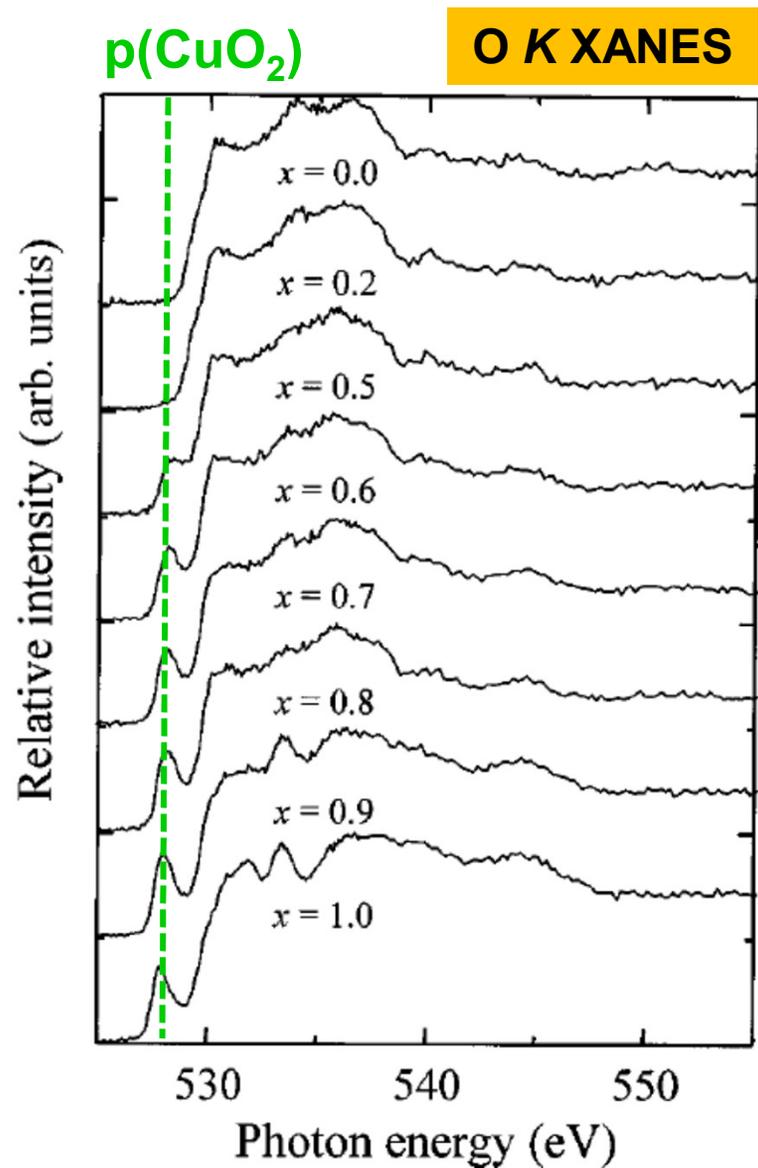
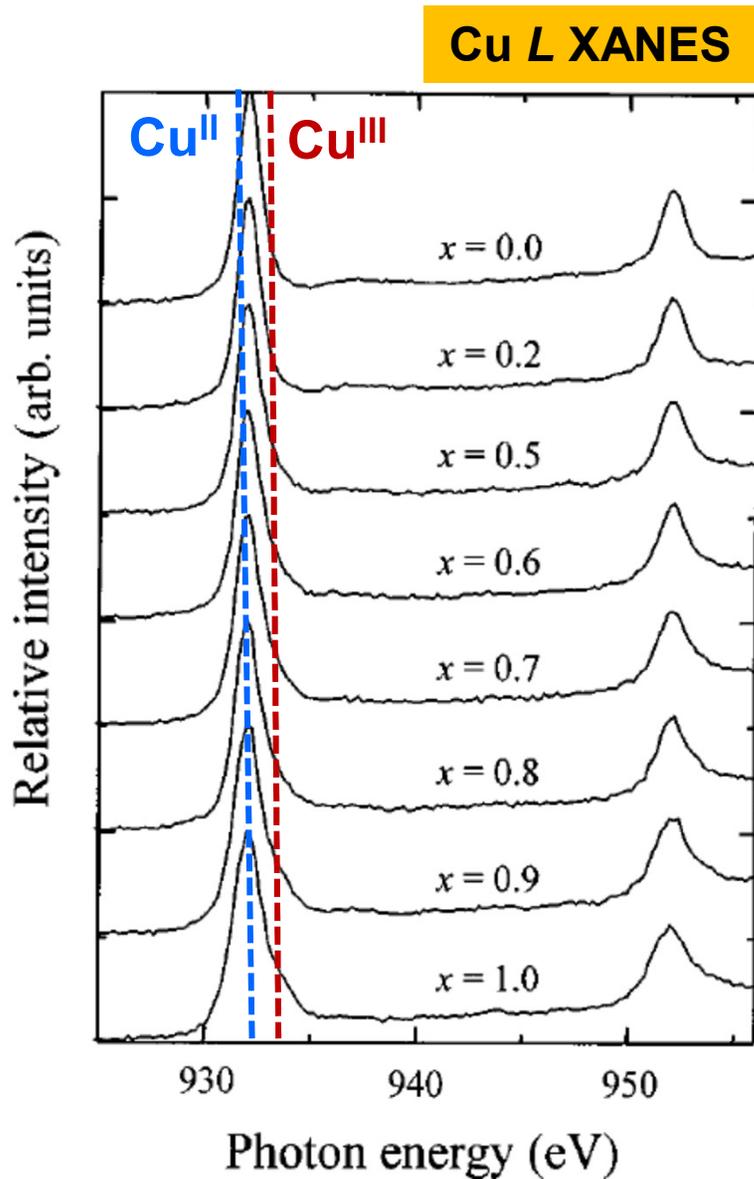


CuO₂-plane hole concentration: $p(CuO_2)$
[valence of copper $\rightarrow V(Cu) - 2$]

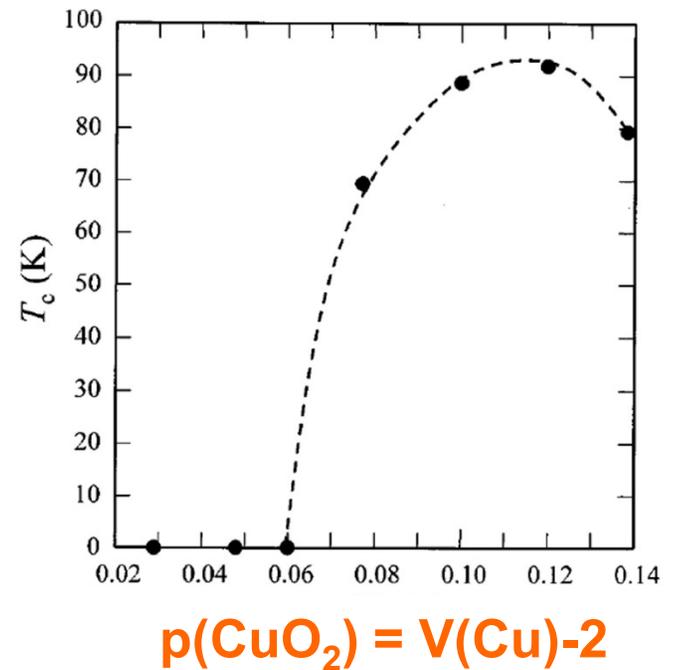
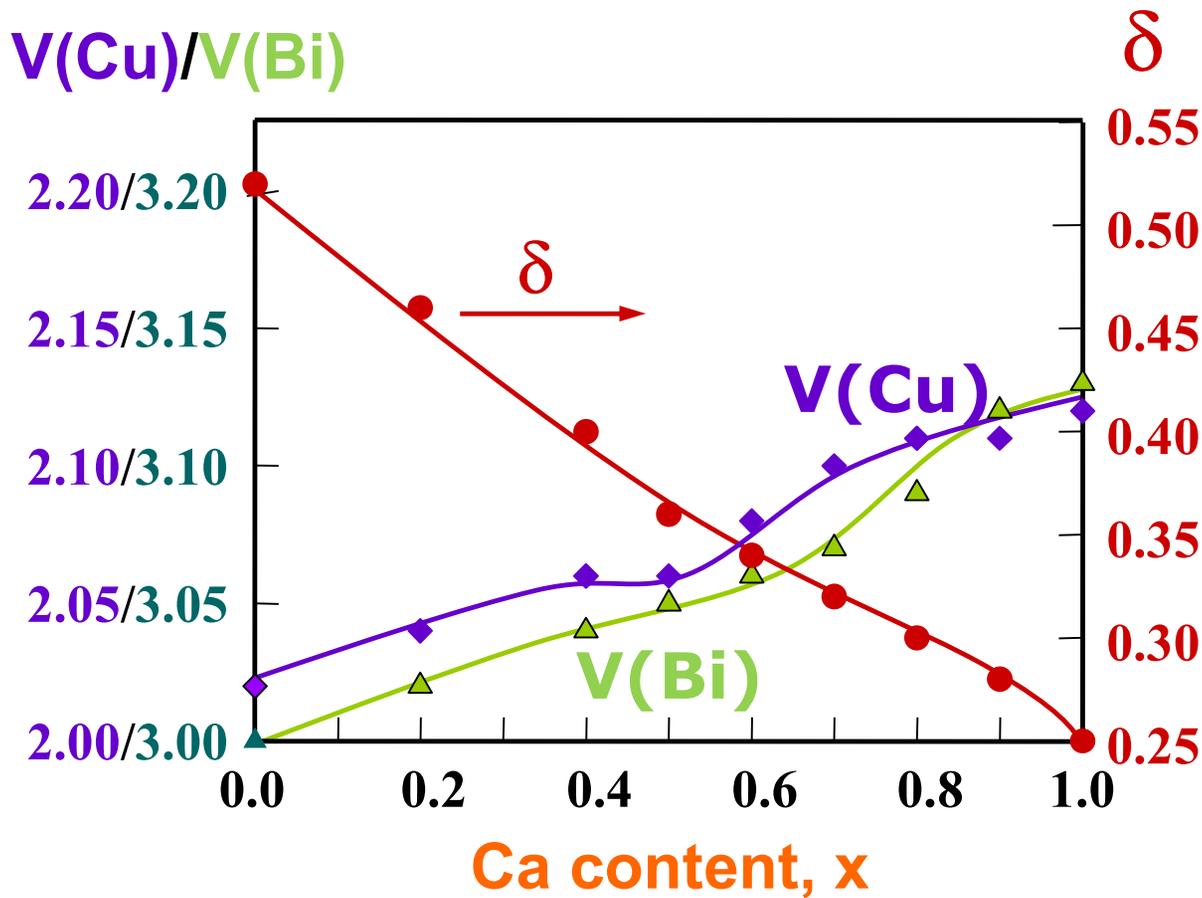


- Ca^{II} -for- Y^{III} substitution increases the T_c
- oxygen content can be determined by chemical redox titration
- with increasing Ca^{II} -for- Y^{III} substitution level oxygen content gradually decreases
- what happens to the hole-doping level (= valence of copper) ?



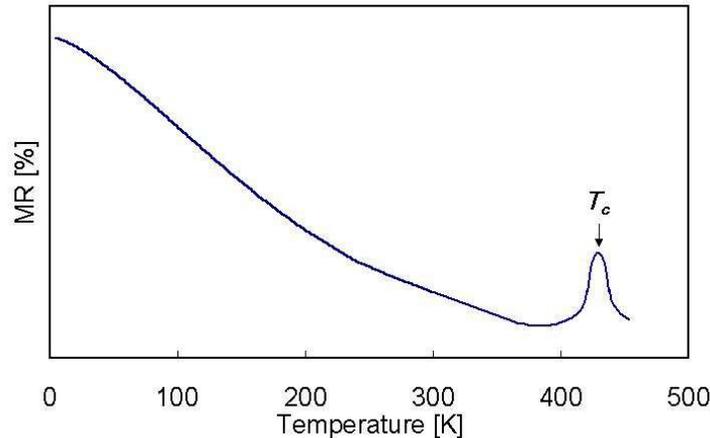
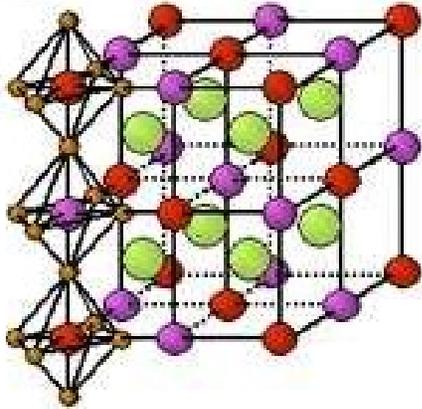


M. Karppinen, K. Kotiranta, T. Nakane, S.C. Chang,
J.M. Chen, R.S. Liu & H. Yamauchi,
Phys. Rev. B **67**, 134522 (2003).



M. Karppinen, K. Kotiranta, T. Nakane, S.C. Chang,
 J.M. Chen, R.S. Liu & H. Yamauchi,
Phys. Rev. B **67**, 134522 (2003).

$$\text{MR} = (\rho_0 - \rho_H) / \rho_0$$



B-site ordered
double perovskite

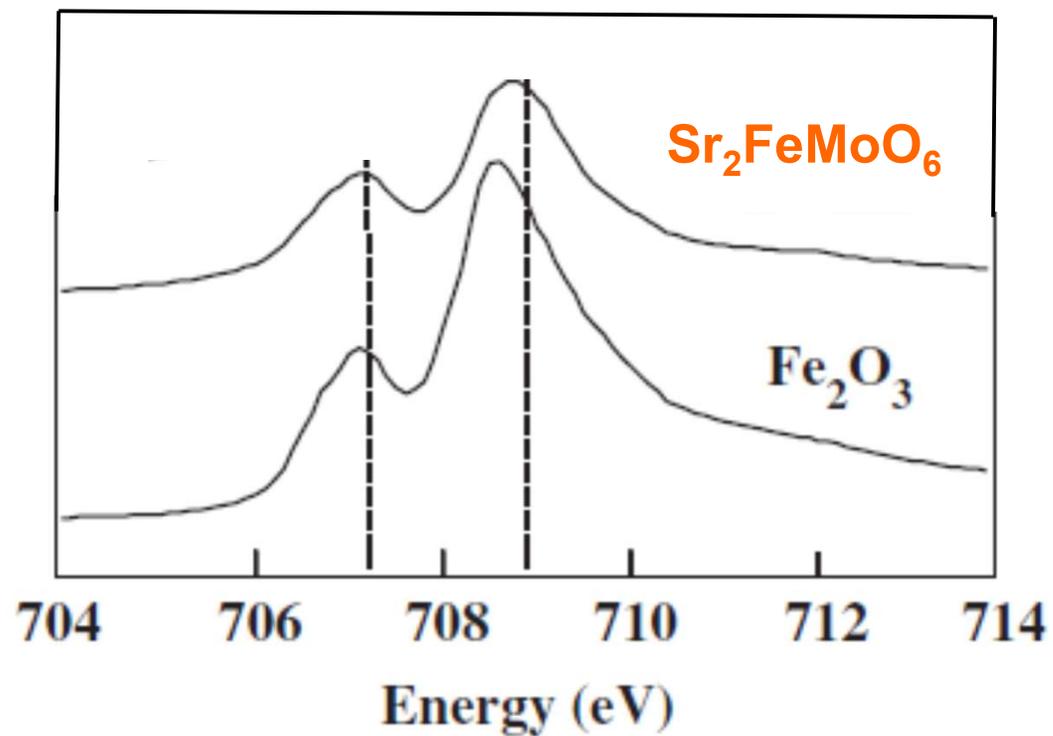
- Ferrimagnetic conductor ($T_c = \sim 420$ K): Fe^{III} d^5 (*hs*) & Mo^{V} d^1
- Halfmetallic: conduction electrons are spin polarized
- Magnetoresistance (MR) effect

K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura and Y. Tokura, *Nature* **395**, 677 (1998).

Mössbauer spectroscopy: Mixed-valent iron: $\text{Sr}_2\text{Fe}^{\text{II/III}}\text{Mo}^{\text{V/VI}}\text{O}_6$

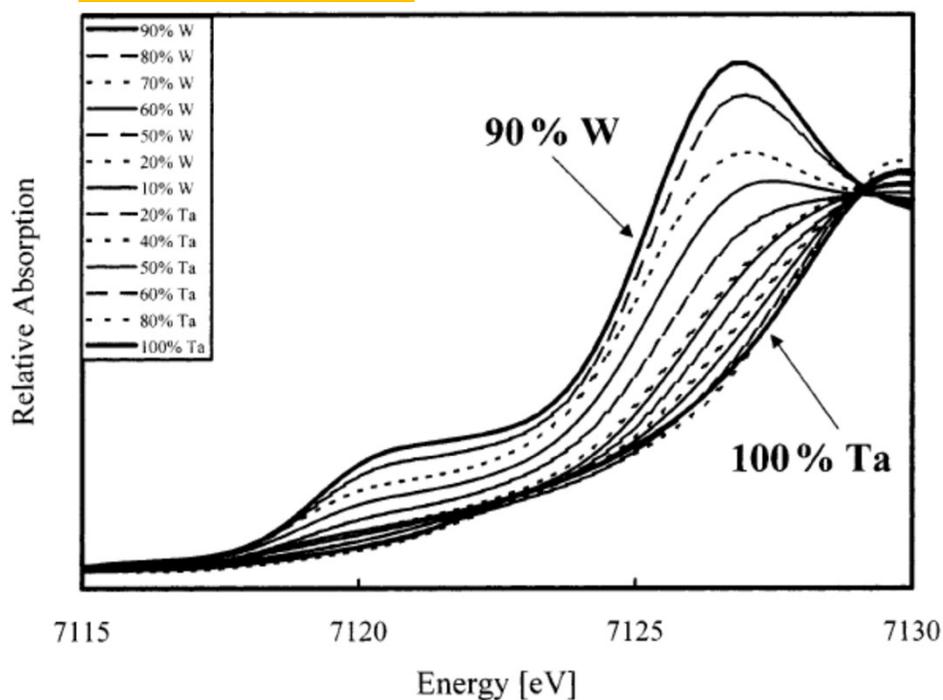
“Evidence for **Valence Fluctuation** of Fe in $\text{Sr}_2\text{FeMoO}_{6-w}$ Double Perovskite”,
J. Lindén, T. Yamamoto, M. Karppinen, H. Yamauchi and T. Pietari,
Appl. Phys. Lett. **76**, 2925 (2000).

How does XANES show the valence state of Fe ?
- From first glance looks similar to Fe_2O_3 !

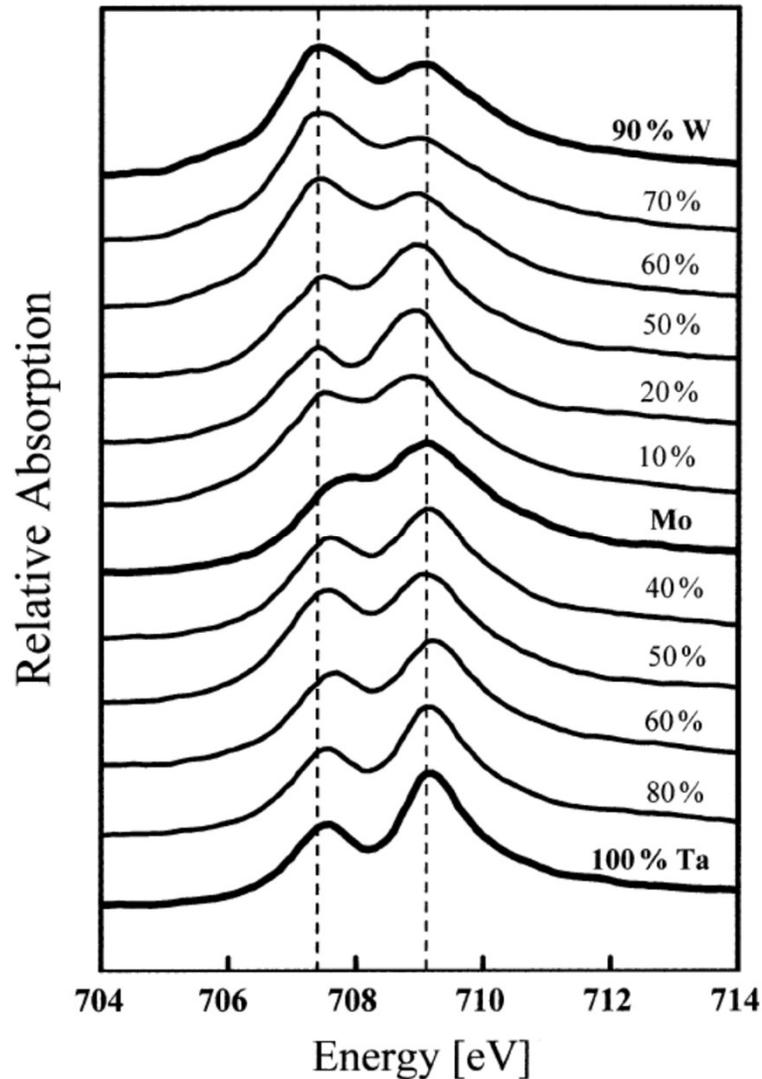




Fe K XANES



Fe L_3 XANES



More systematic study shows mixed-valent Fe(II/III) !

M. Karppinen, H. Yamauchi, Y. Yasukawa, J. Lindén, T.S. Chan, R.S. Liu & J.M. Chen, *Chem. Mater.* **15**, 4118 (2003).