SCHEDULE

	Date		Topic
1.	Wed	28.02.	Lec-1: Introduction
2.	Mon	04.03.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Mon	04.03.	EXERCISE 1
4.	Wed	06.03.	Lec-3: Crystal Chemistry & BVS
5.	Fri	08.03.	Lec-4: Symmetry & Point Groups
6.	Mon	11.03.	EXERCISE 2
7.	Wed	20.03.	Lec-5: Crystallography & Space Groups (Linda)
8.	Fri	22.03.	Lec-6: XRD & Reciprocal lattice (Linda)
9.	Mon	25.03.	EXERCISE 3 (Linda) Ke4
10.	Thu	04.04.	Lec-7: Rietveld (Linda)
11.	Fri	05.04.	EXERCISE 4: Rietveld (Linda)
	Mon	08.04.	EXERCISE 4: Rietveld (Linda)
12.	Thu	11.04.	Lec-8: ND & GI-XRD 12:15-14, Ke3
13.	Fri	12.04.	Lec-9: XRR & Ellipsometry (Topias) 12:15-14, Ke4
14.	Mon	15.04.	EXERCISE 5: XRR (Topias) 14:15-16 Ke3
	Wed	17.04.	EXERCISE 5: XRR (Topias) 14:15-16 Ke3
15.	Mon	22.04.	Lec-10: Synchrotron radiation & XAS & EXAFS
16.	Thu	25.04.	Mössbauer 12:15-14, Ke3
17.	Fri	26.04.	EXERCISE 6
18.	Mon	29.04.	Seminars: IR, Raman, XPS, SEM, EELS (14:00→16:30)
19.	Mon	06.05.	ADDITIONAL DISCUSSION/QUESTION POSSIBILITY
20.	Mon	13.05.	EXAM (13-17; to be confirmed ?)

INSTRUCTIONS for SEMINAR PRESENTATIONS

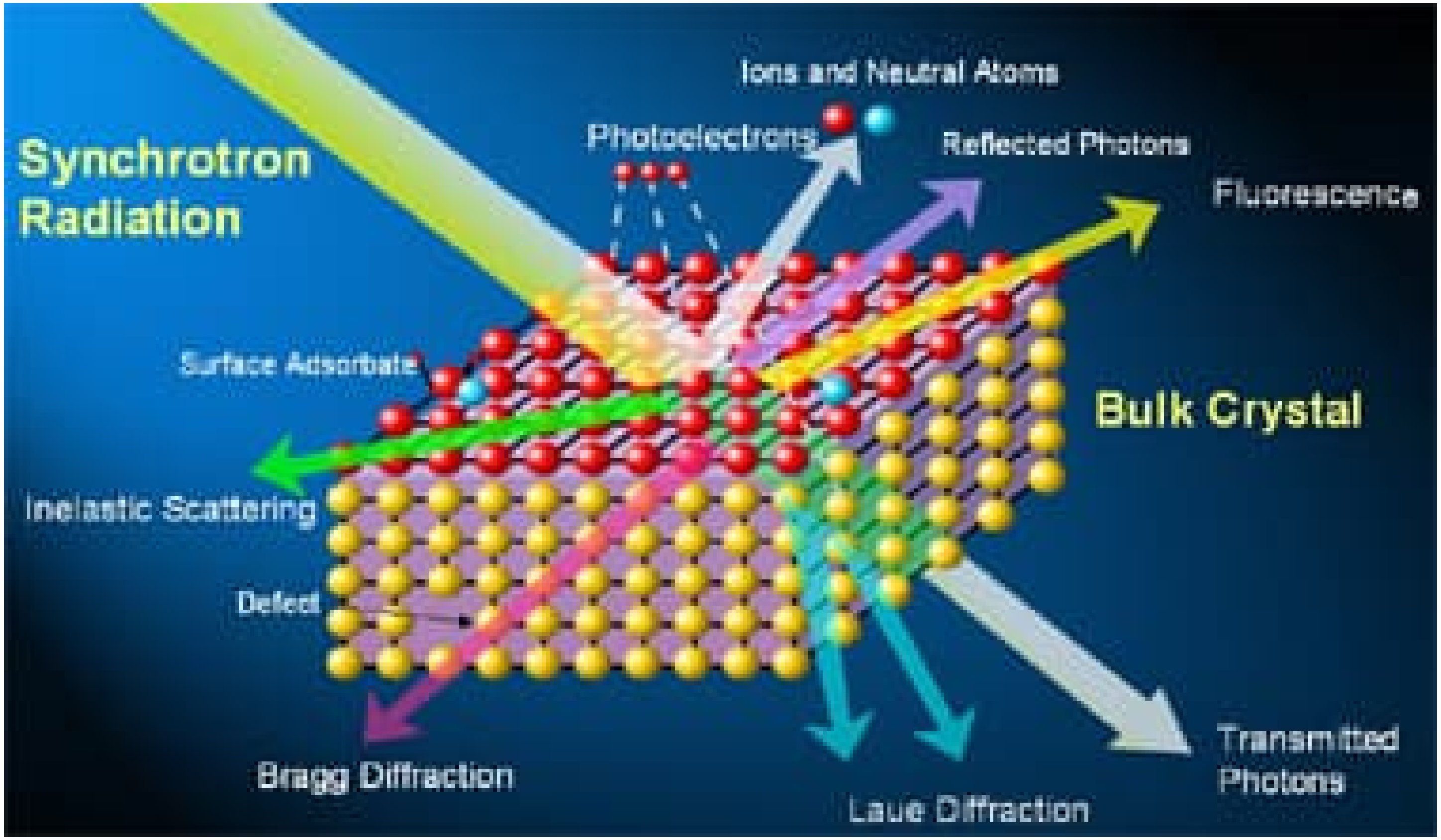
- Topics: **IR, Raman, XPS, SEM, EELS**
- Seminar presentation is mandatory
- Presentation slides will be put up in MyCourses afterwards
- **Seminars are part of the course content and it is likely that there will be questions in the exam related to these seminars**
- Given in a group of two students
- Evaluated in the scale: 10 ~ 20 points
- Presentation: **20+5** minutes
- Rough content of the presentation:
    - principle of the technique
    - type of information gained
    - interpretation of the measured data
    - pros & cons
    - **two to four research examples**
      (you will be given some relevant research papers for an example)

LECTURE 10:
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)

X-RAYS & MATERIAL

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



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

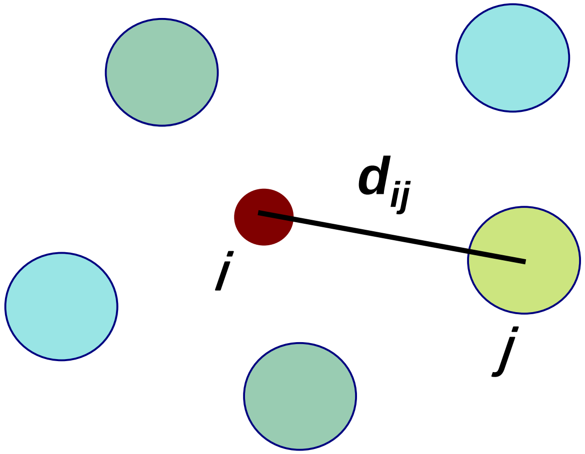
Bond-Valence-Sum (BVS) for Inorganics

- 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:

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

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

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

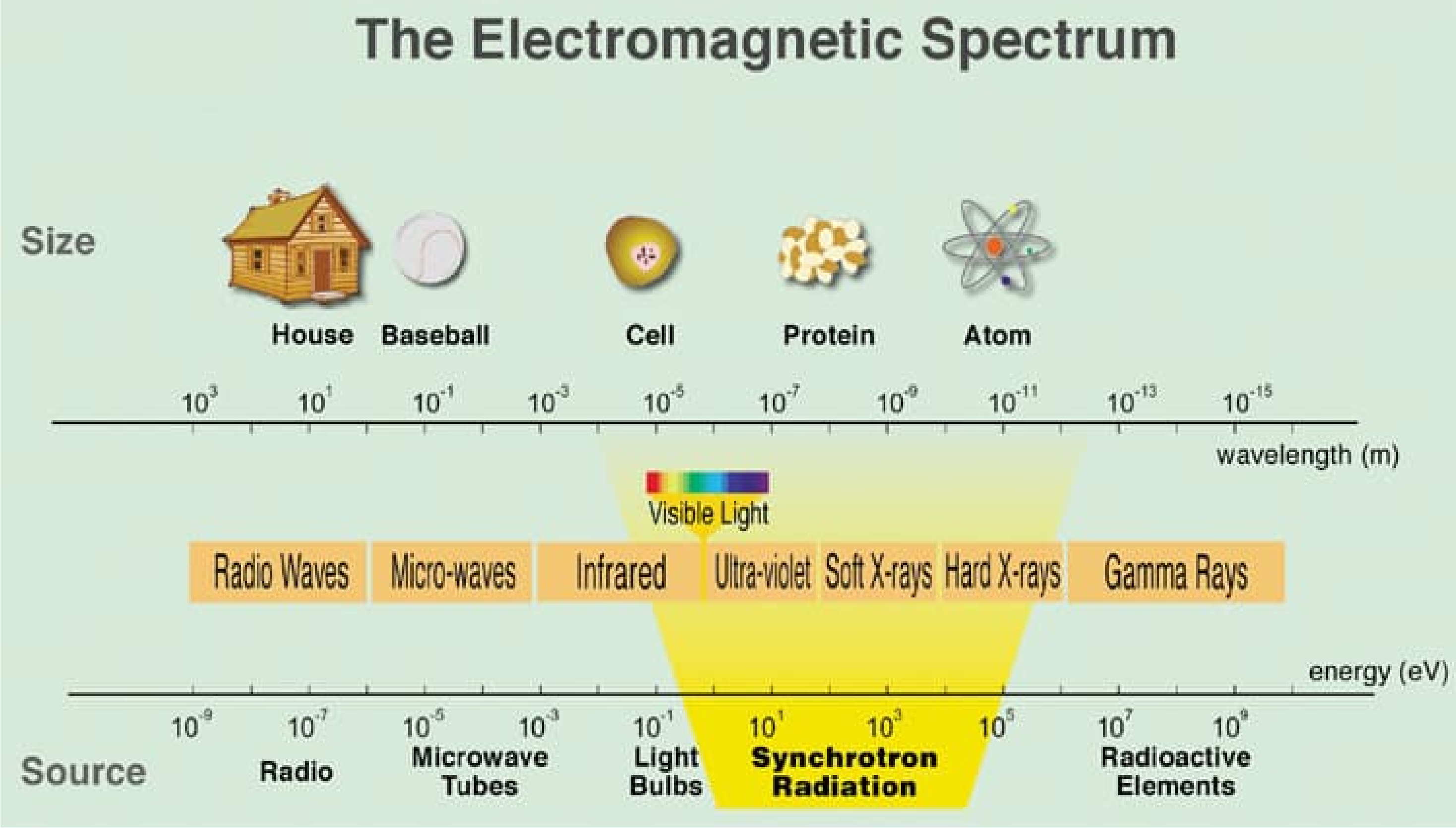


PRODUCTION OF X-RAYS

- Wavelength of X-rays: 0.01 Å ~ 100 Å
- 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 very close to the speed of light
  - kinetic energy of the particles is changed with magnets
  - **very intense continuous spectrum**

SYNCHROTRON RADIATION

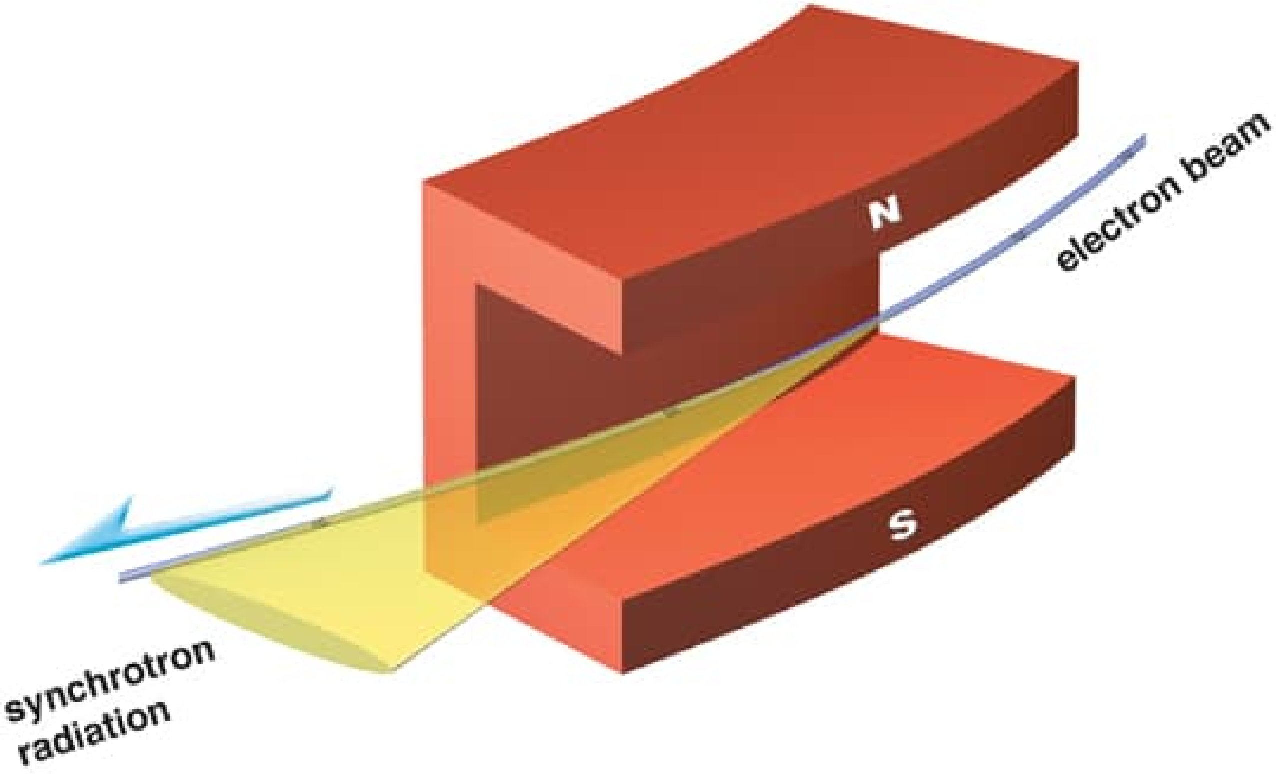
- **Continuous band of electromagnetic spectrum including infrared, visible light, ultraviolet and x-rays**
- **Accidentally discovered in an electron synchrotron of the General Electric Company, USA, in 1947**



http://www.nsrrc.gov.tw

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 have been 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

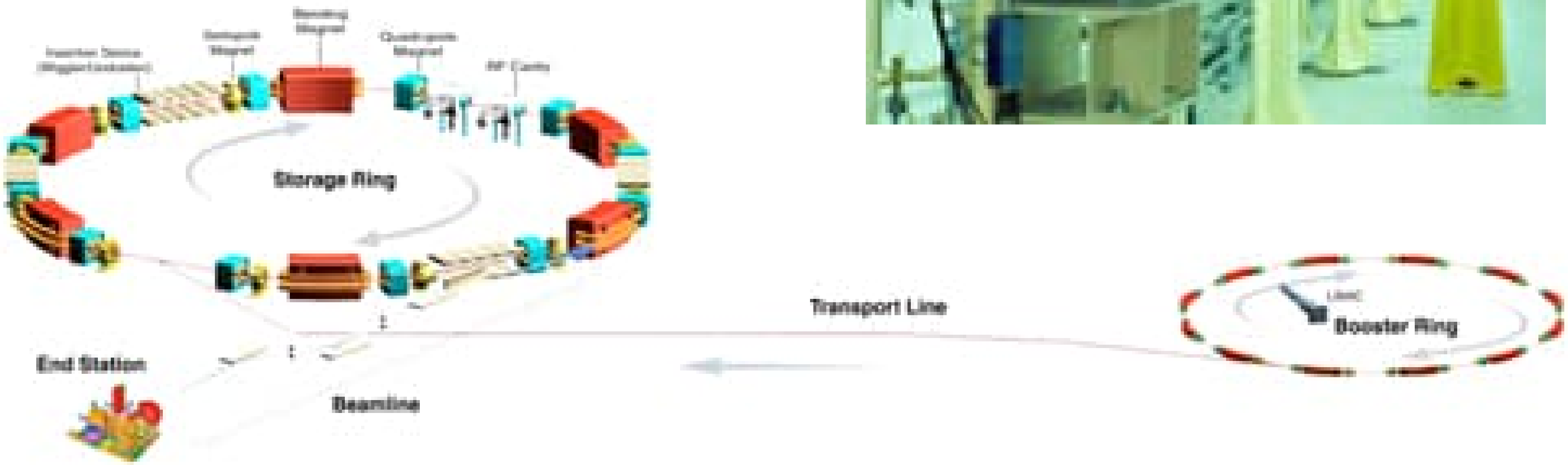
Booster Ring (72 m in circumference):

- Electrons with 99.999995 % of light speed

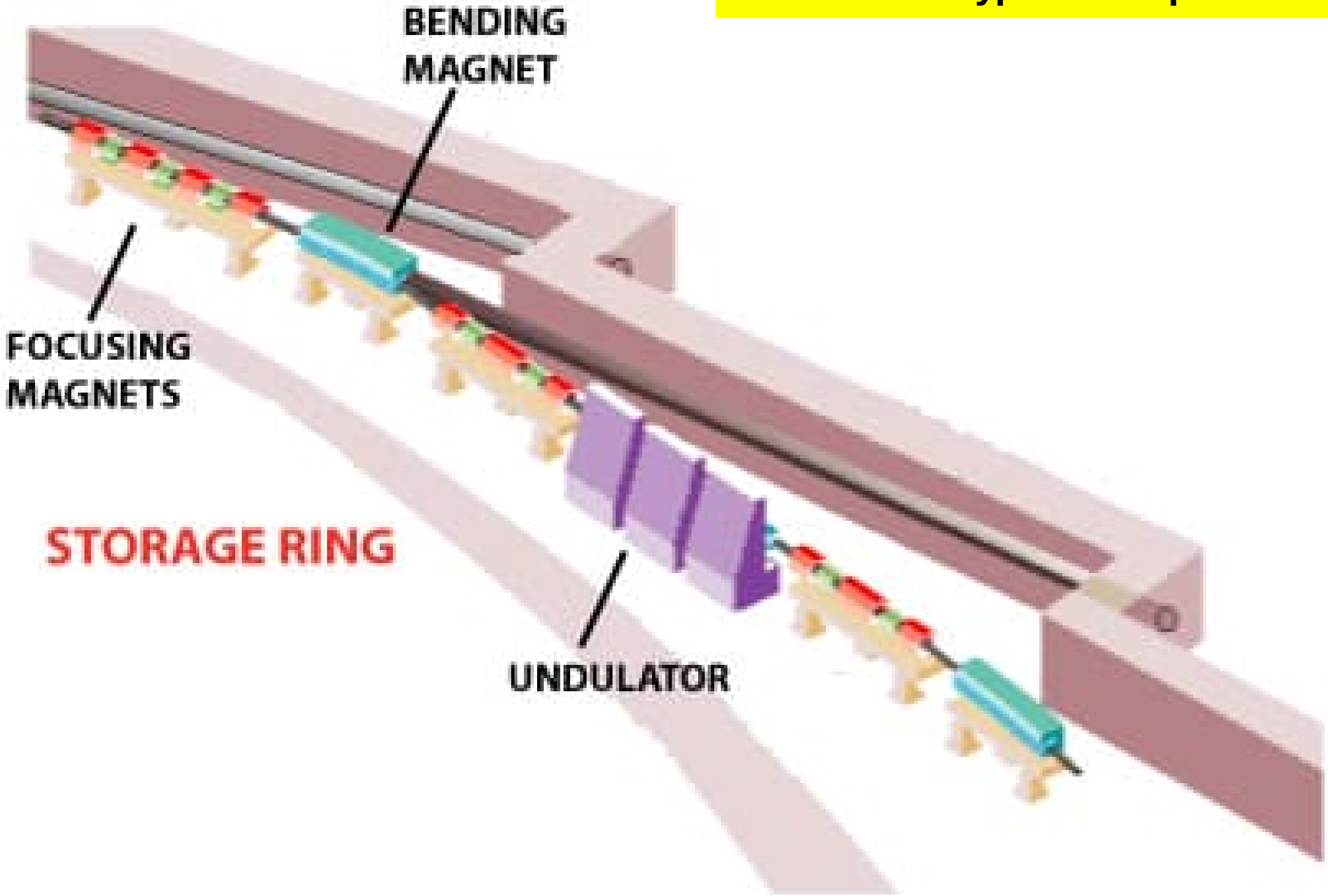
LINAC

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.

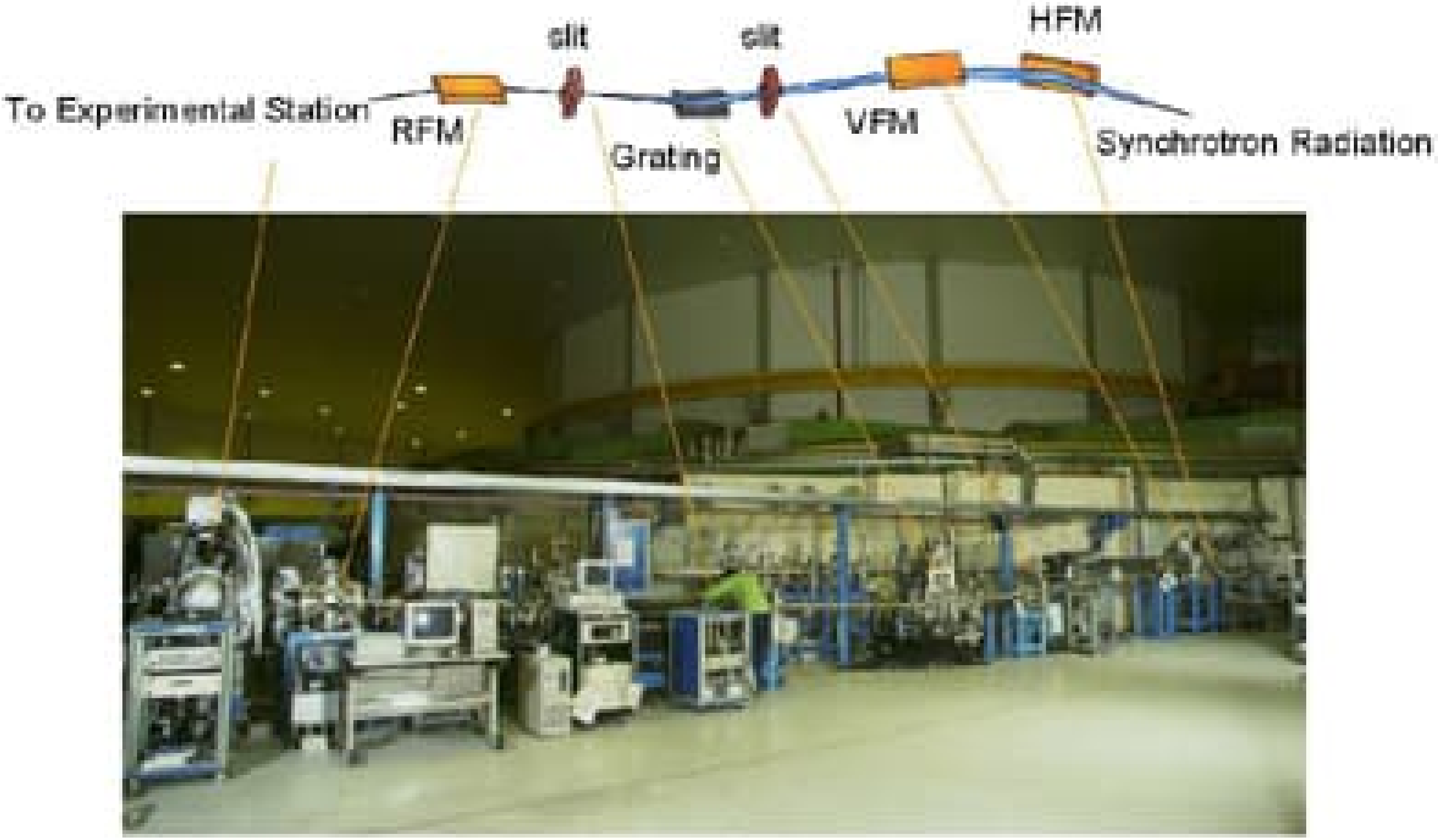
Transport Line



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.

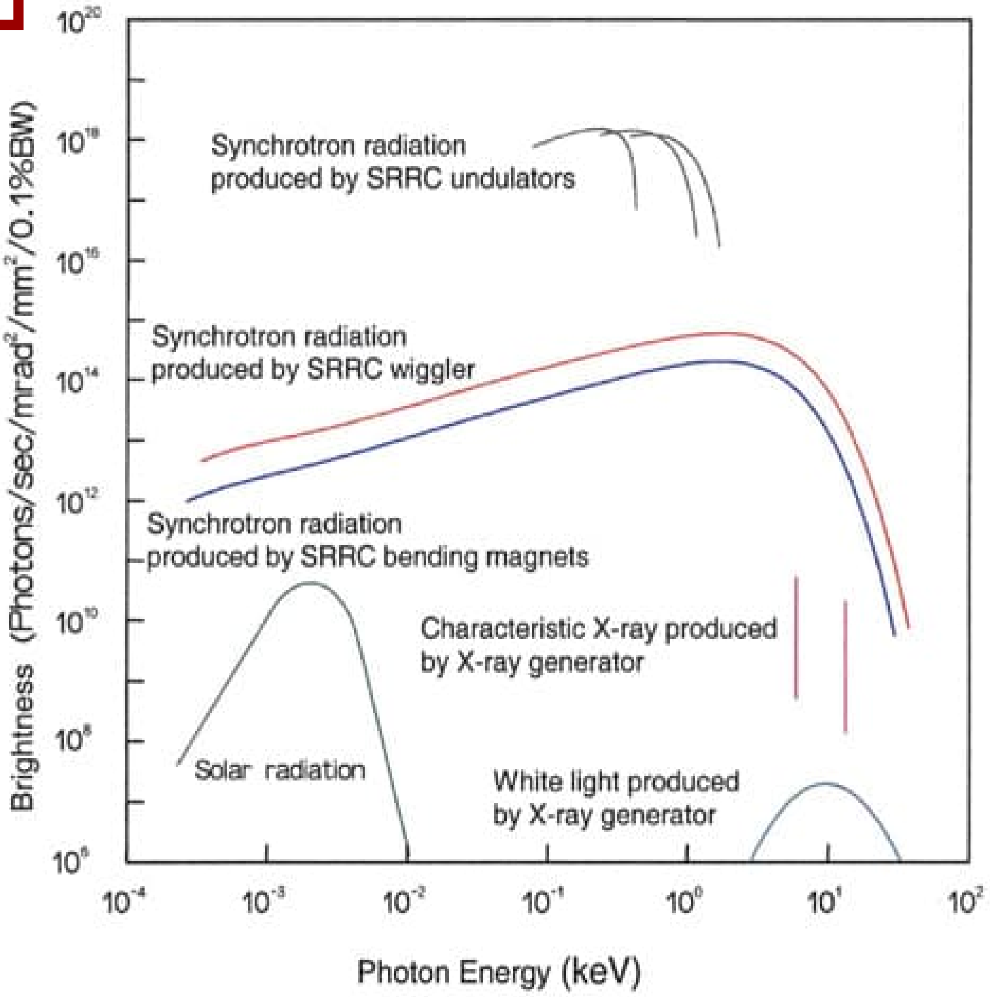


HFM: Horizontal Focussing Mirror
VFM: Vertical Focussing Mirror
RFM: Refocussing Mirror

Synchrotron Radiation

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

http://www.nsrrc.gov.tw



The ESRF* & ILL* With Grenoble & the Beldonne Mountains

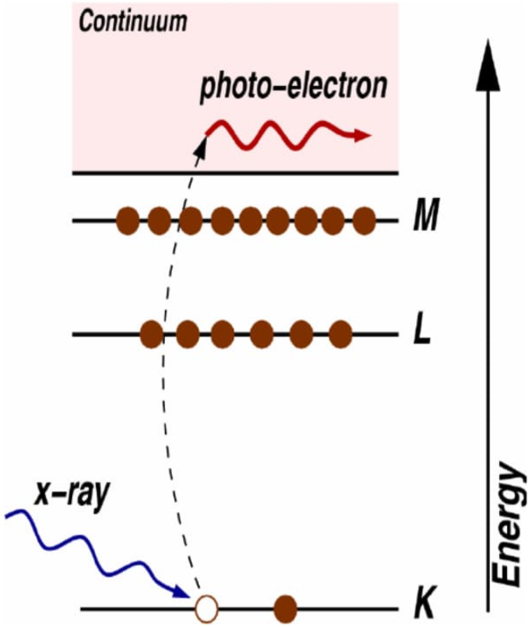
Photo ESRF/Studio de la Revirée

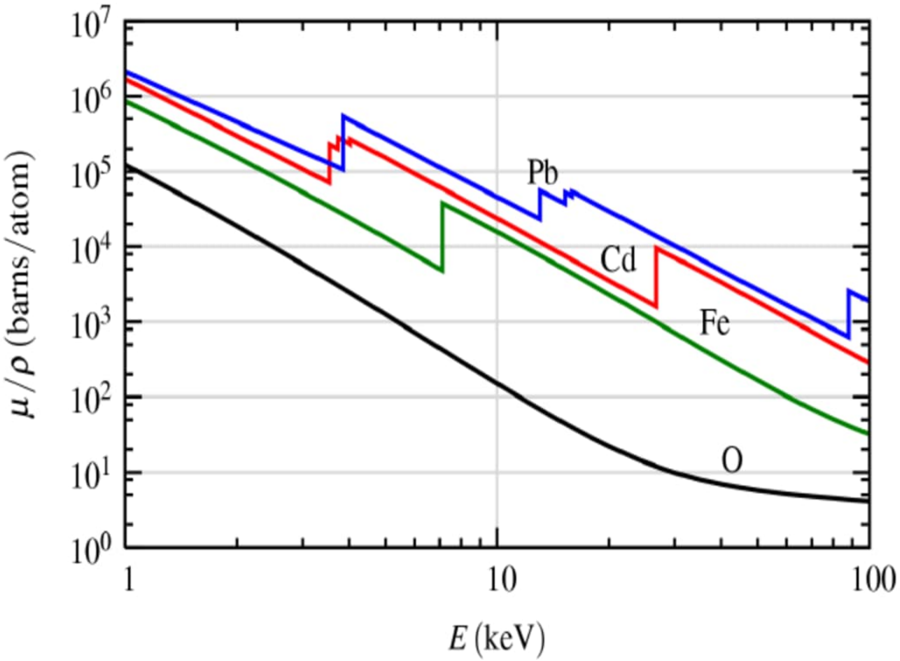
*ESRF = European Synchrotron Radiation Facility; ILL = Institut Laue-Langevin

X-RAY ABSORPTION

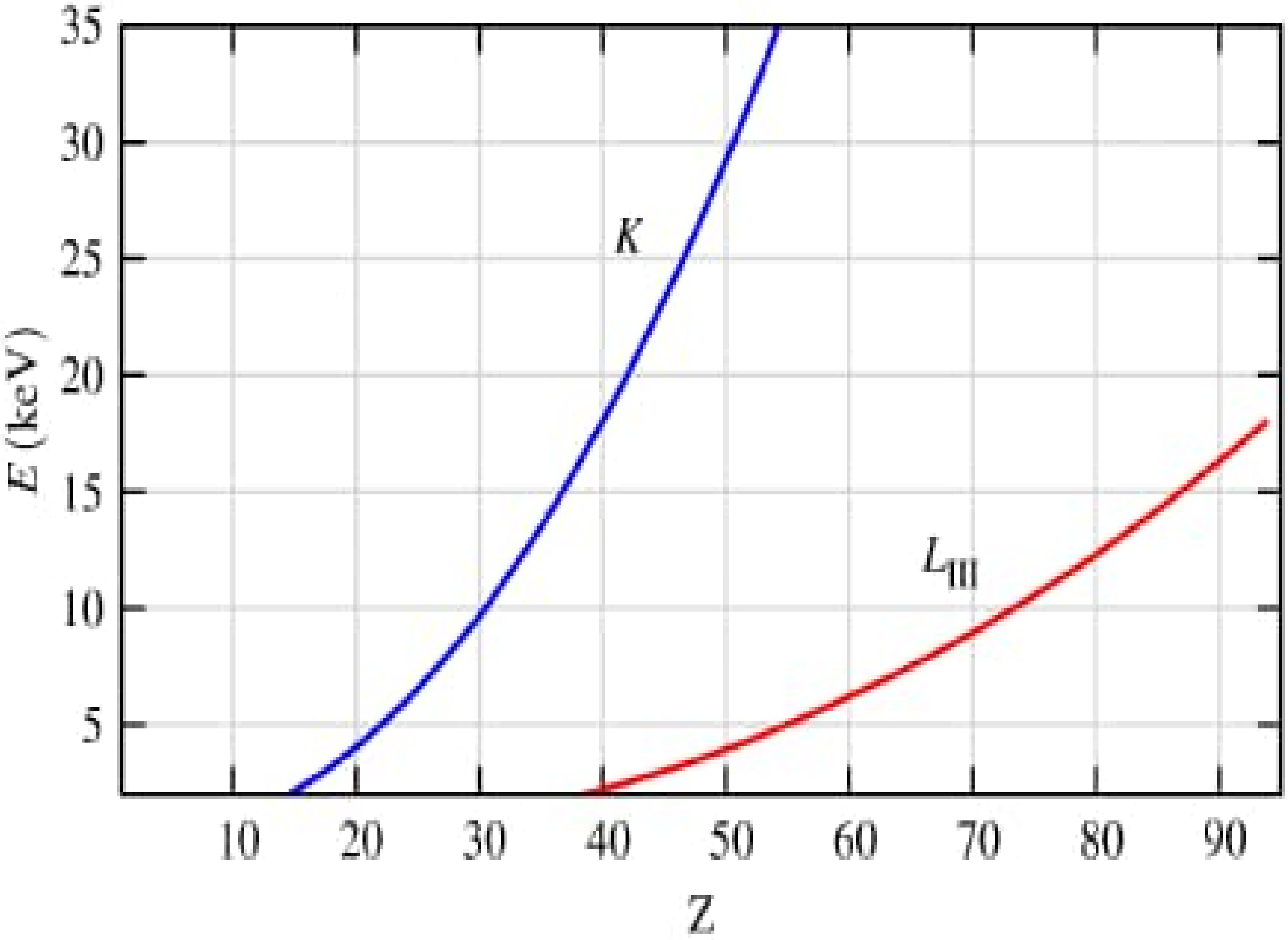
- Wavelength/energy of x-rays corresponds to energies required to remove electrons from inner shells
- Absorption decreases with increasing energy, until at a certain energy it increases abruptly → **ABSORPTION EDGE**
- Absorption edge corresponds to the bonding energy of inner shell electron

  → *K*-edge, *L*-edge ...



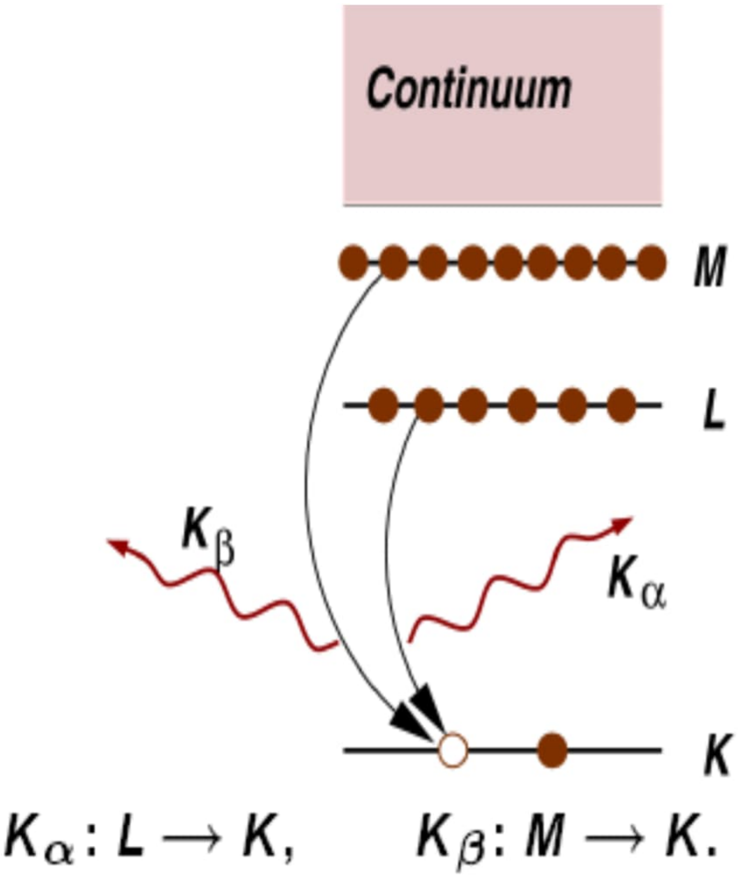


Absorption-edge energy depends on the atomic number (~Z^2)



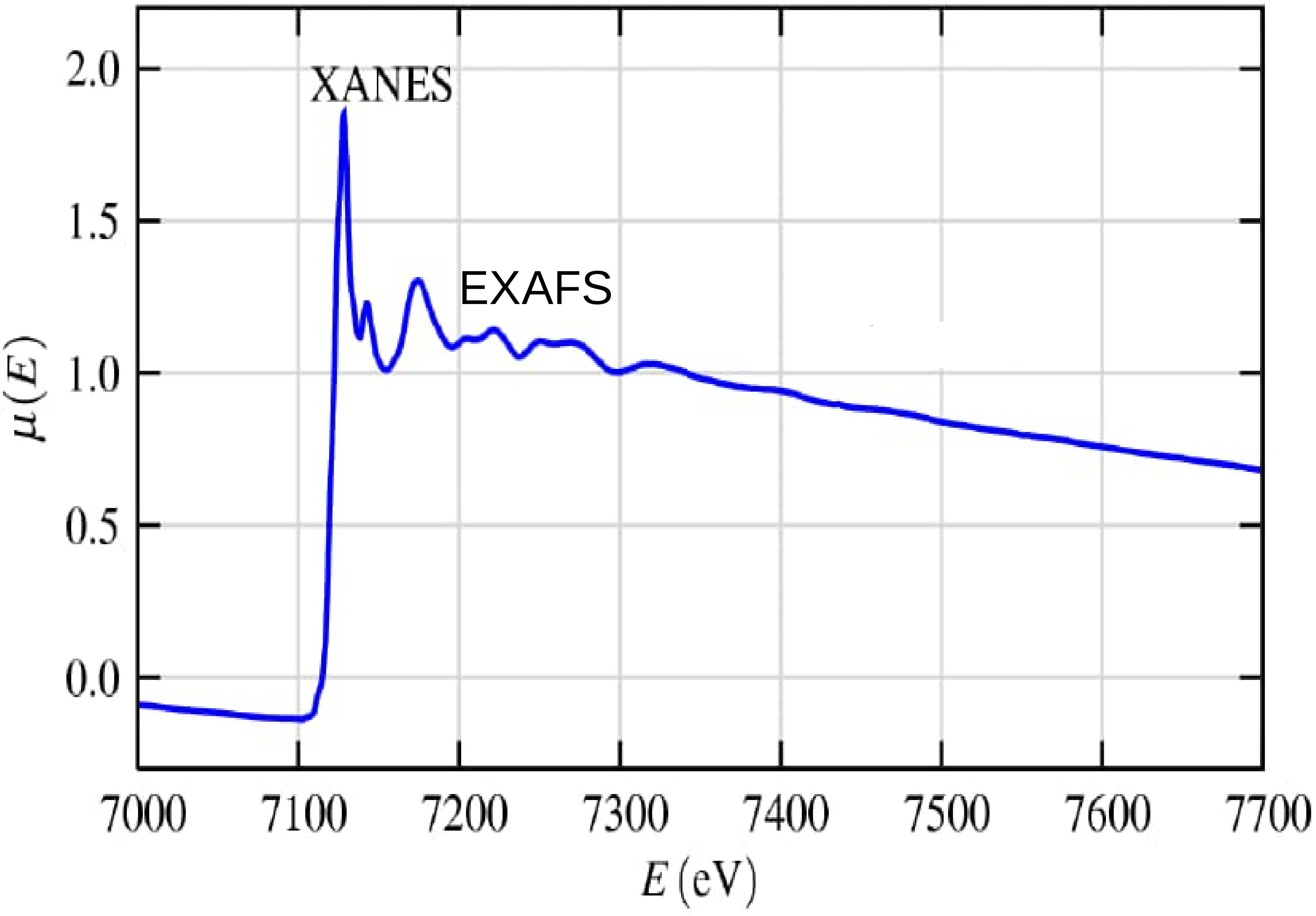
To investigate X-ray absorption, we may measure X-ray intensity of transmitted radiation or fluorescence radiation (both depend on the magnitude of absorption)

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

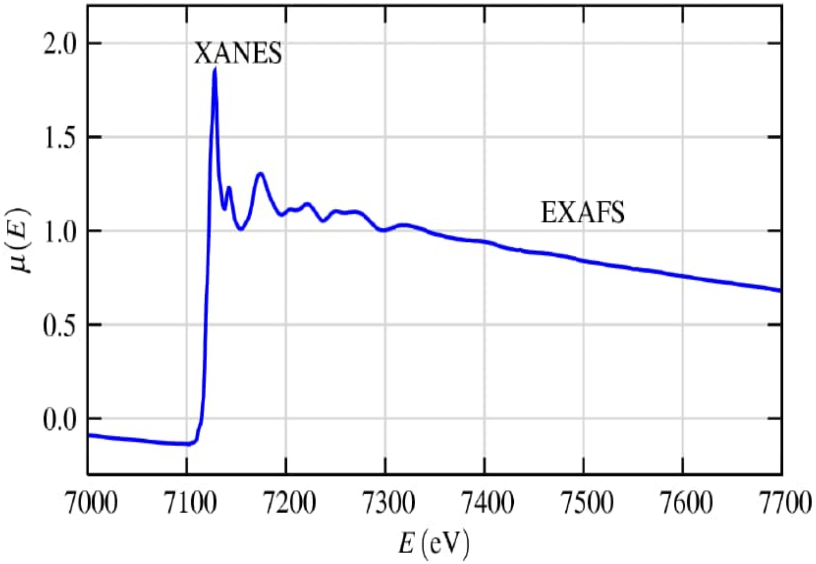


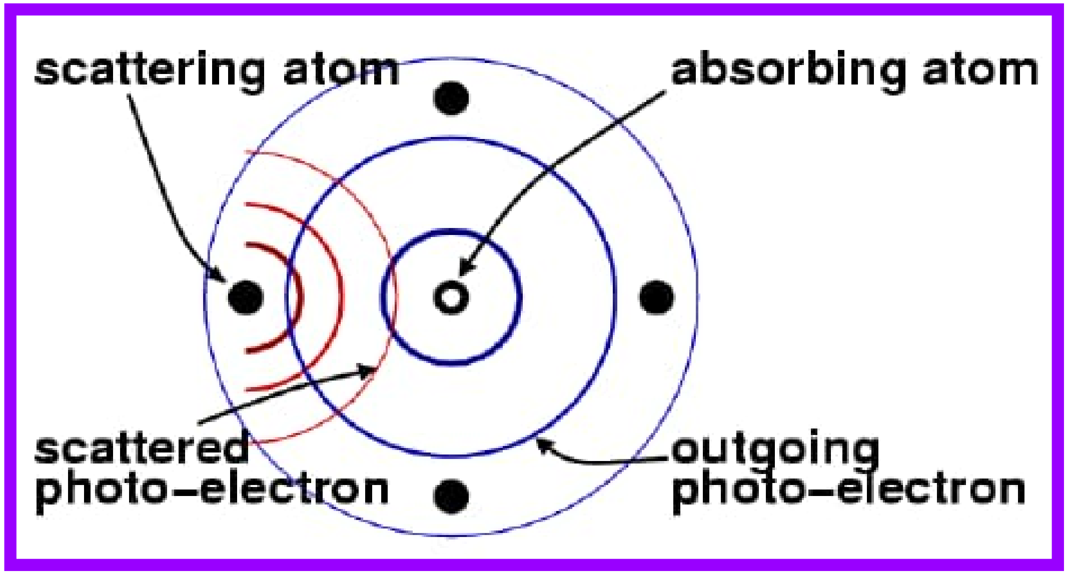
XANES/EXAFS

- 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 may be used
- 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)

- Oscillatios 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-spesific)
- 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)

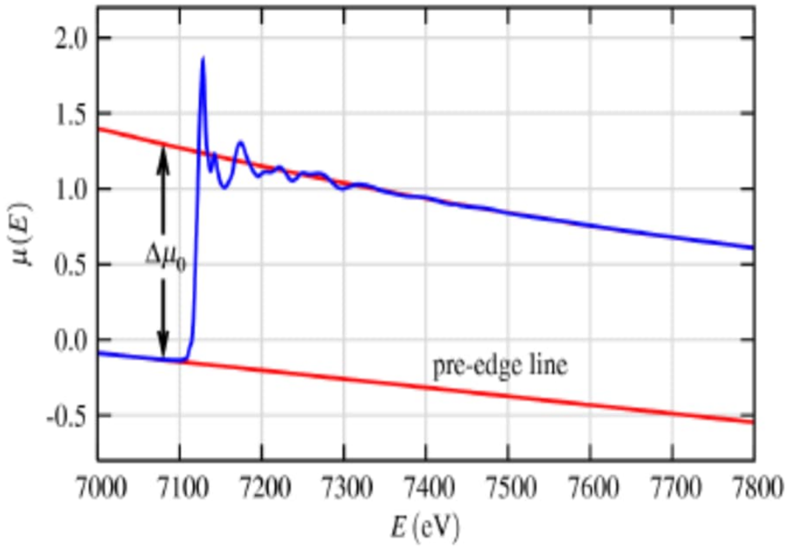
STEPS in EXAFS DATA ANALYSIS

- Conversion of measured intensities to μ(E)
- Pre-edge background subtraction (instrumental errors etc)
- μ(E) normalized to vary from 0 to 1
- Post-edge background removal (smooth curve)
- Conversion from energy to (photoelectron) wave number: E → 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)

$$\boxed{\mathrm{k} = \sqrt{\frac{2\mathrm{m}(\mathrm{E} - \mathrm{E}_0)}{\hbar^2}}}$$

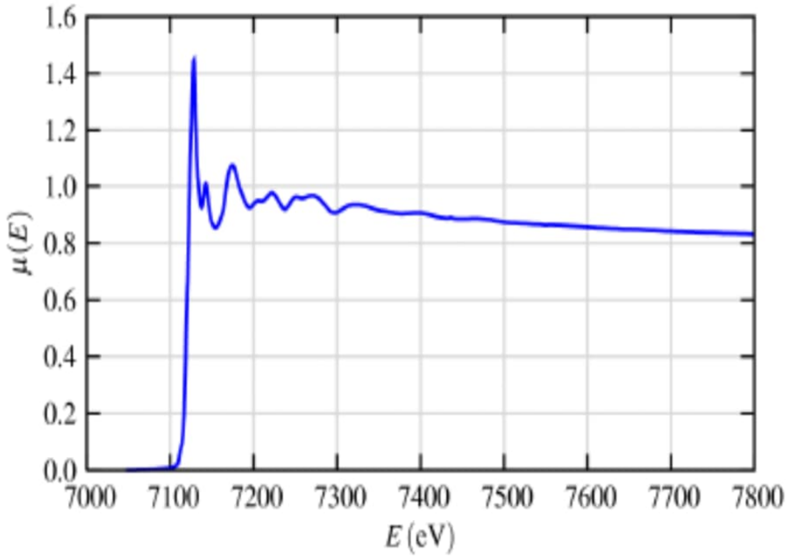
Matt Newville
Consortium for Advanced Radiation Sources
University of Chicago

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



Pre-Edge Subtraction

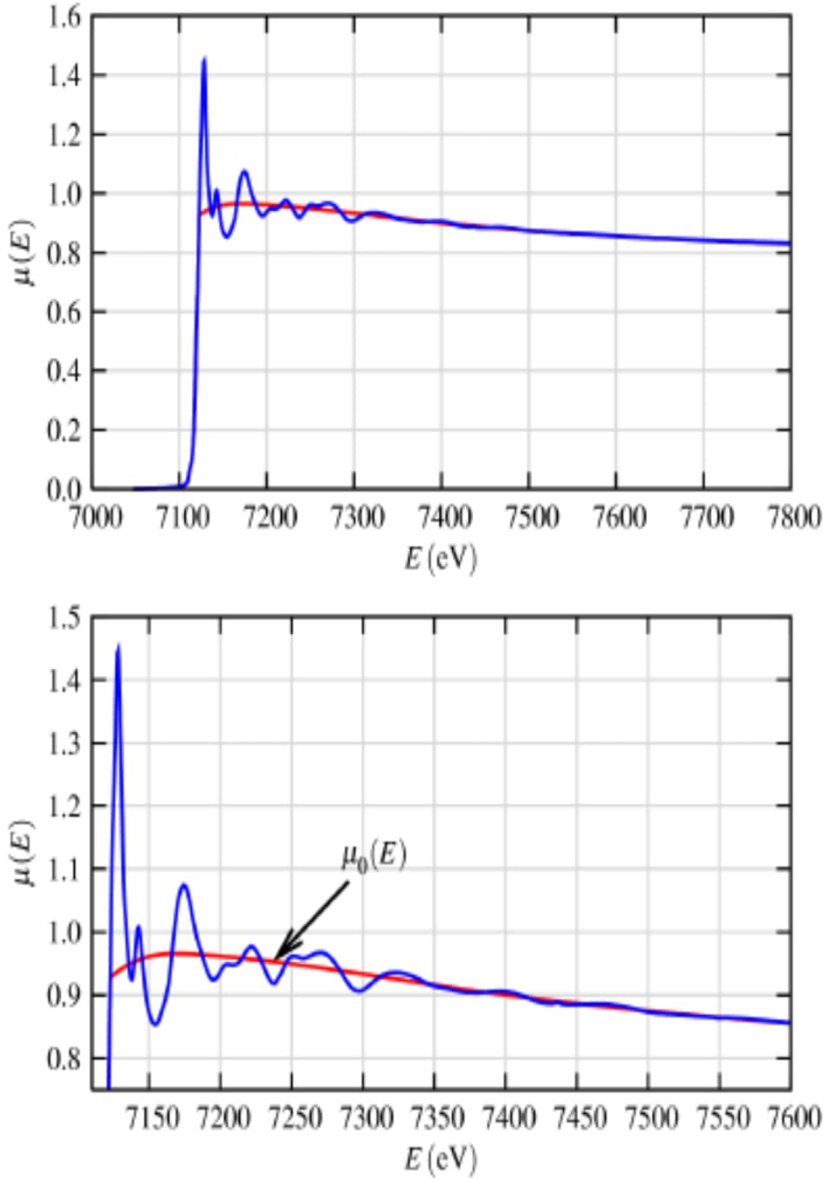
We subtract away the background that fits the *pre-edge* region. This gets rid of the absorption due to other edges (say, the Fe L_{III} edge).



Normalization

We estimate the *edge step*, $\Delta\mu_0(\mathrm{E}_0)$ by extrapolating a simple fit to the above $\mu(\mathrm{E})$ 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 $\mu_0(\mathrm{E})$ (the absorption coefficient without neighboring atoms).

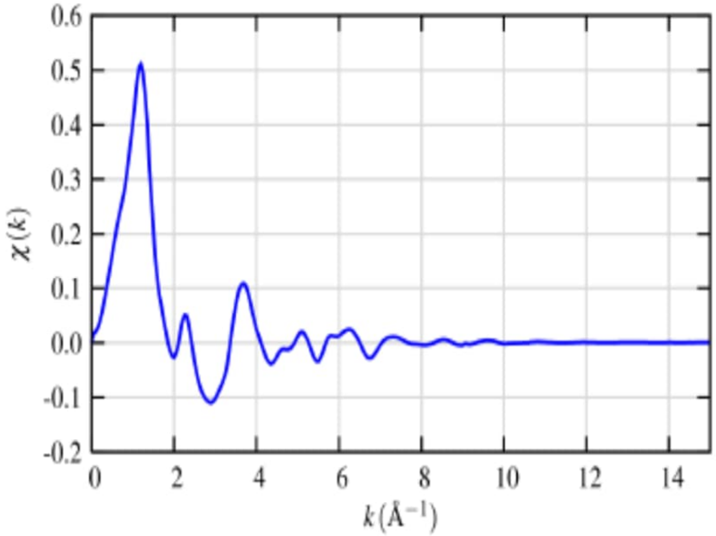
We approximate $\mu_0(\mathrm{E})$ by an adjustable, smooth function: a *spline*.

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

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

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

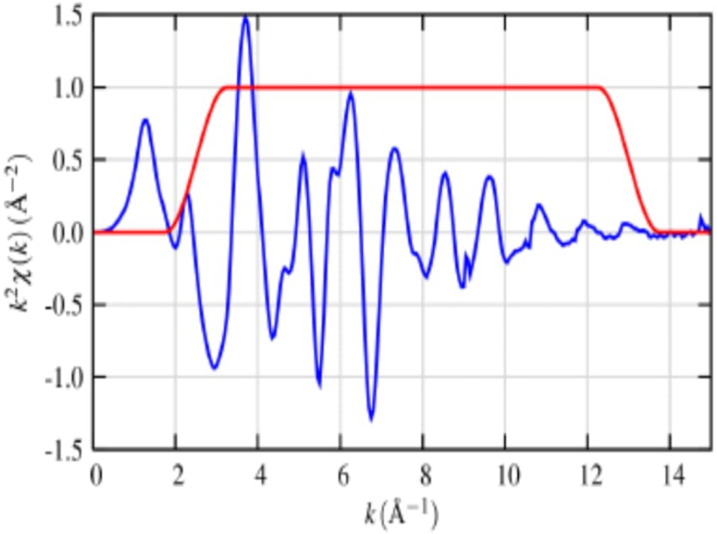
$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$



$\chi(k)$

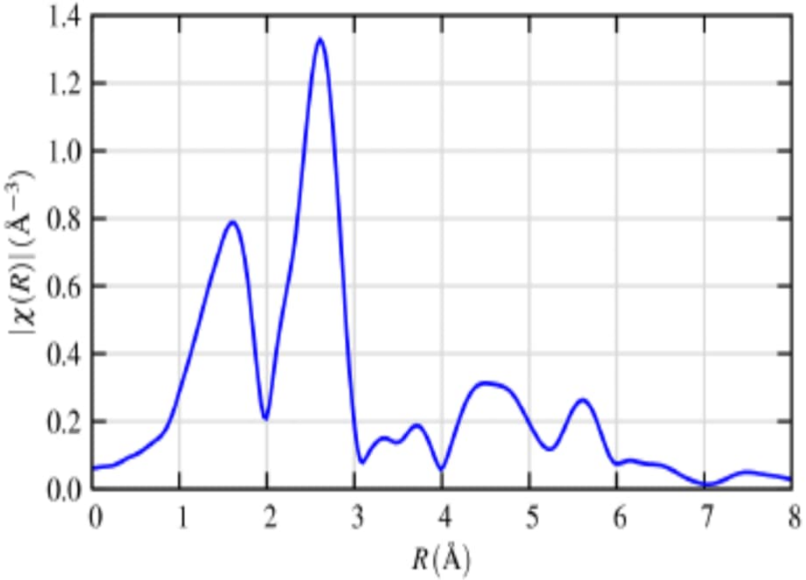
The raw EXAFS $\chi(k)$ usually decays quickly with k, and difficult to assess or interpret by itself.

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



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

- **Fourier transform from k to R (= distance) space**



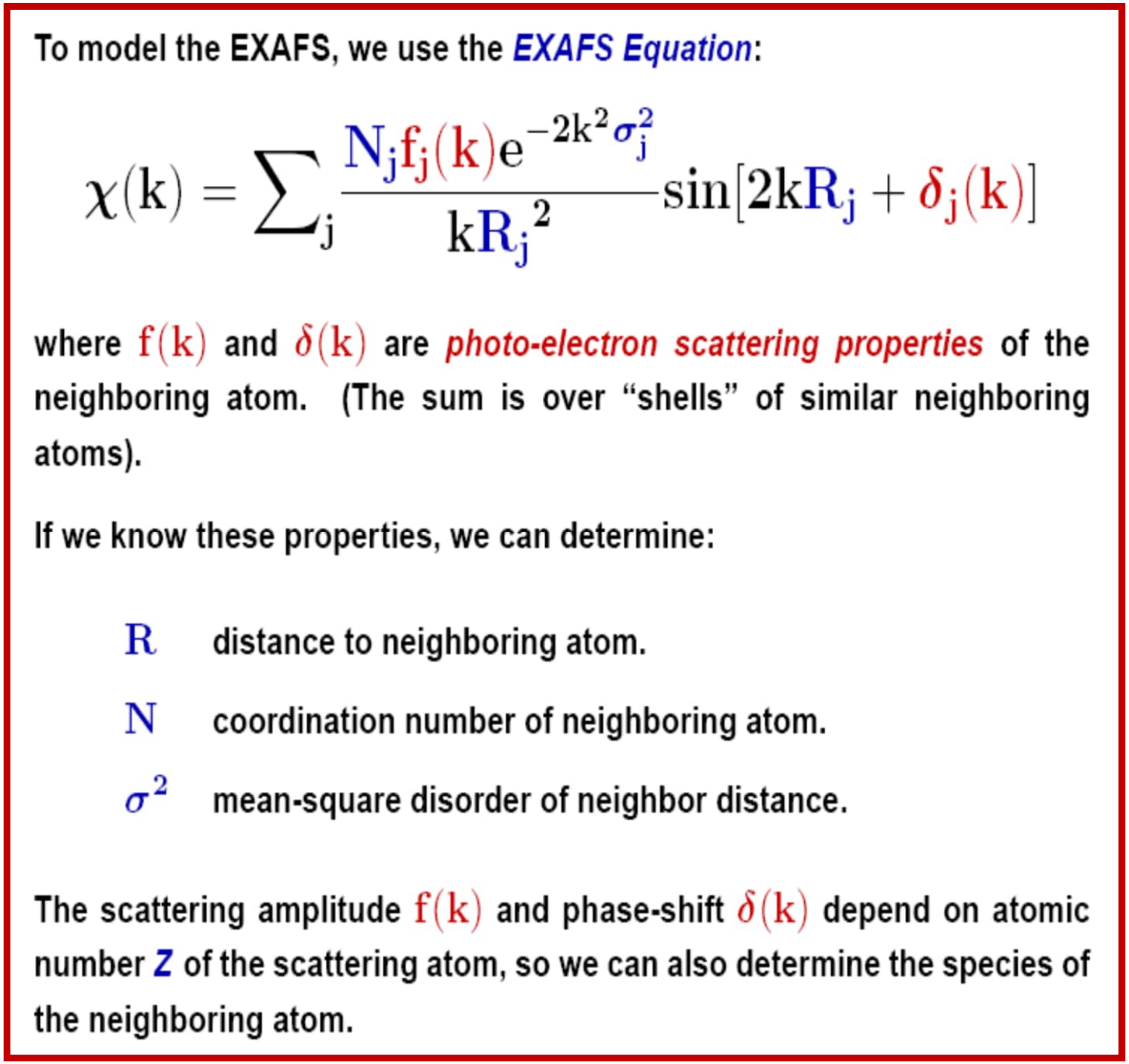
$\chi(\mathrm{R})$

The Fourier Transform of $\mathrm{k}^2\chi(\mathrm{k})$ 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*, $\delta(\mathrm{k})$: $\sin[2\mathrm{kR} + \delta(\mathrm{k})]$.

A shift of -0.5Å is typical.

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



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

$$\chi(\mathrm{k}) = \sum_{\mathrm{j}} \frac{\mathrm{N_j f_j(k)} e^{-2\mathrm{k}^2\sigma_{\mathrm{j}}^2}}{\mathrm{kR_j}^2} \sin[2\mathrm{kR_j} + \delta_{\mathrm{j}}(\mathrm{k})]$$

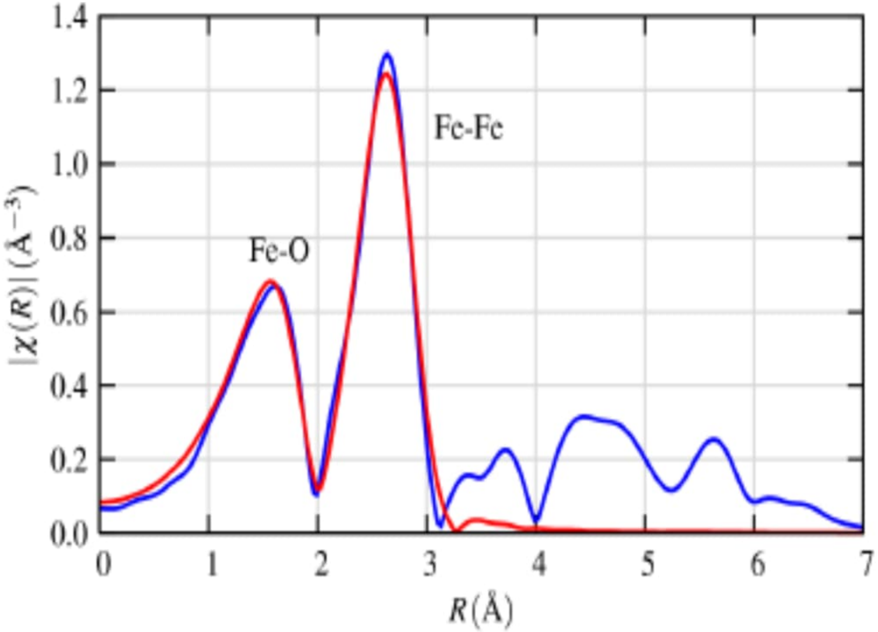
where $f(k)$ and $\delta(k)$ are ***photo-electron scattering properties*** of the neighboring atom. (The sum is over “shells” of similar neighboring atoms).

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



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

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

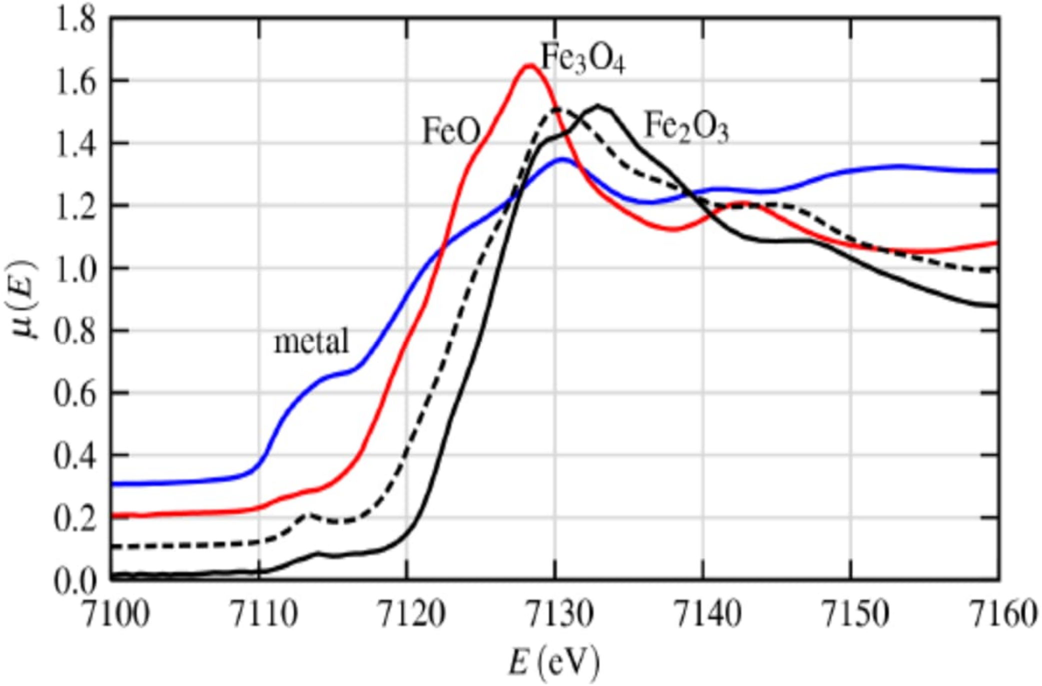
6 O at 2.13Å, 12 Fe at 3.02Å.

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)

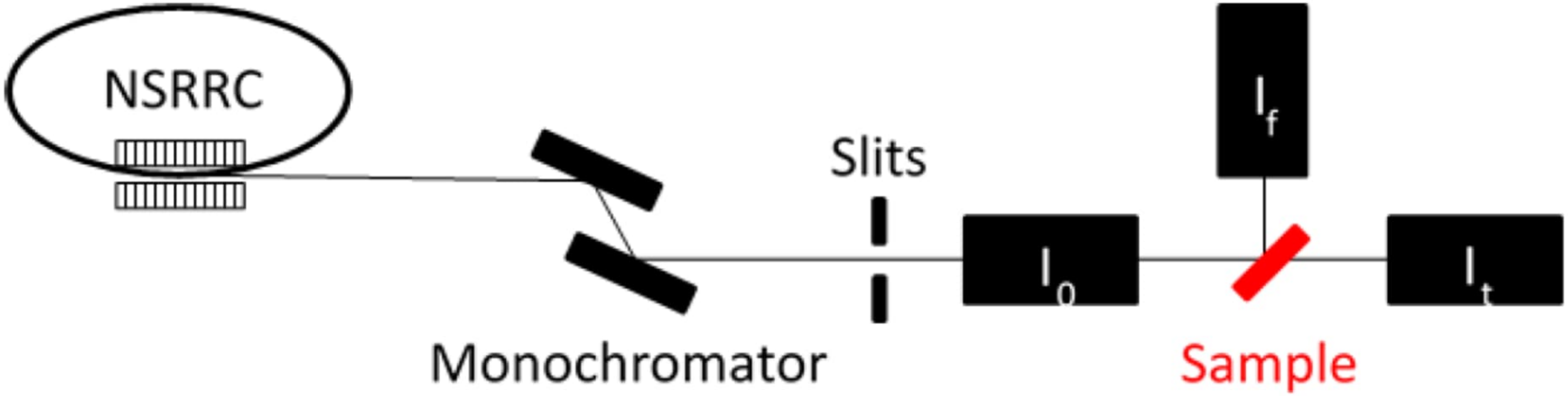
- Inner-shell electrons are excited (not to continuum as in EXAFS but) to the (partially) empty outer orbitals
  → knowledge of the outer orbital energy/electron configuration
  → oxidation state of the absorbing atom
- Excitation of electrons from the inner shells to the outer orbitals requires less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



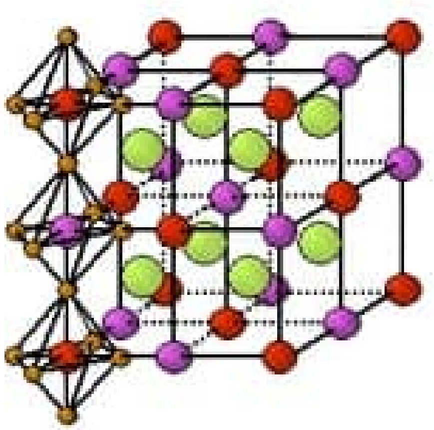
National Synchrotron Radiation Research Center (NSRRC), Hsinchu, TAIWAN

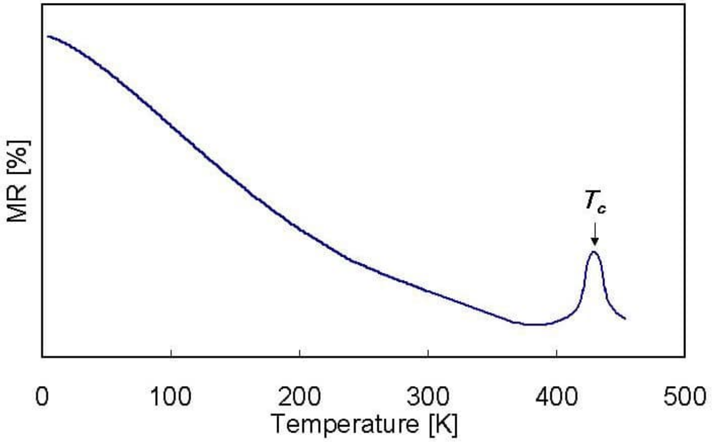
XANES & EXAFS

- 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**



$MR = (\rho_0 - \rho_H)/\rho_0$





Sr_2FeMoO_6

***B*-site ordered**
double perovskite

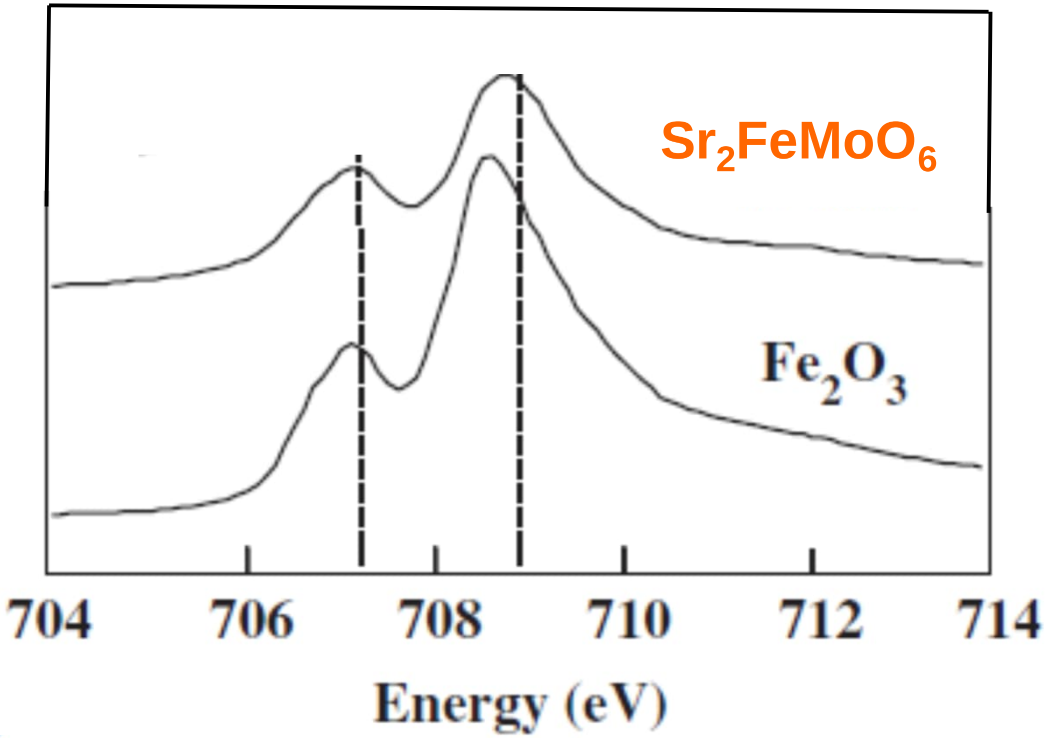
- **Ferrimagnetic conductor (T_c = ~ 420 K): Fe^{III} d^5 (*hs*) & Mo^{V} d^1**
- **Halfmetallic: conduction electrons are spin polarized**
- **Magnetoresistance (MR) effect**

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

Mössbauer spectroscopy: Mixed-valent iron: $Sr_2Fe^{II/III}Mo^{V/VI}O_6$

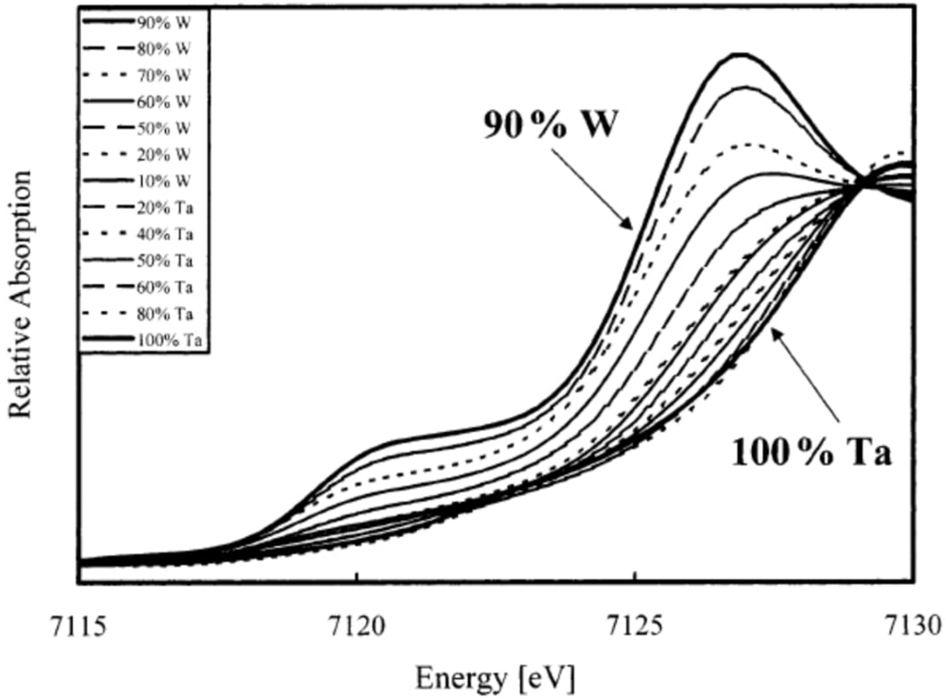
“Evidence for **Valence Fluctuation** of Fe in Sr_2FeMoO_{6-w} Double Perovskite”,
J. Lindén, T. Yamamoto, M. Karppinen, H. Yamauchi and T. Pietari,
Appl. Phys. Lett. 76, 2925 (2000).

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

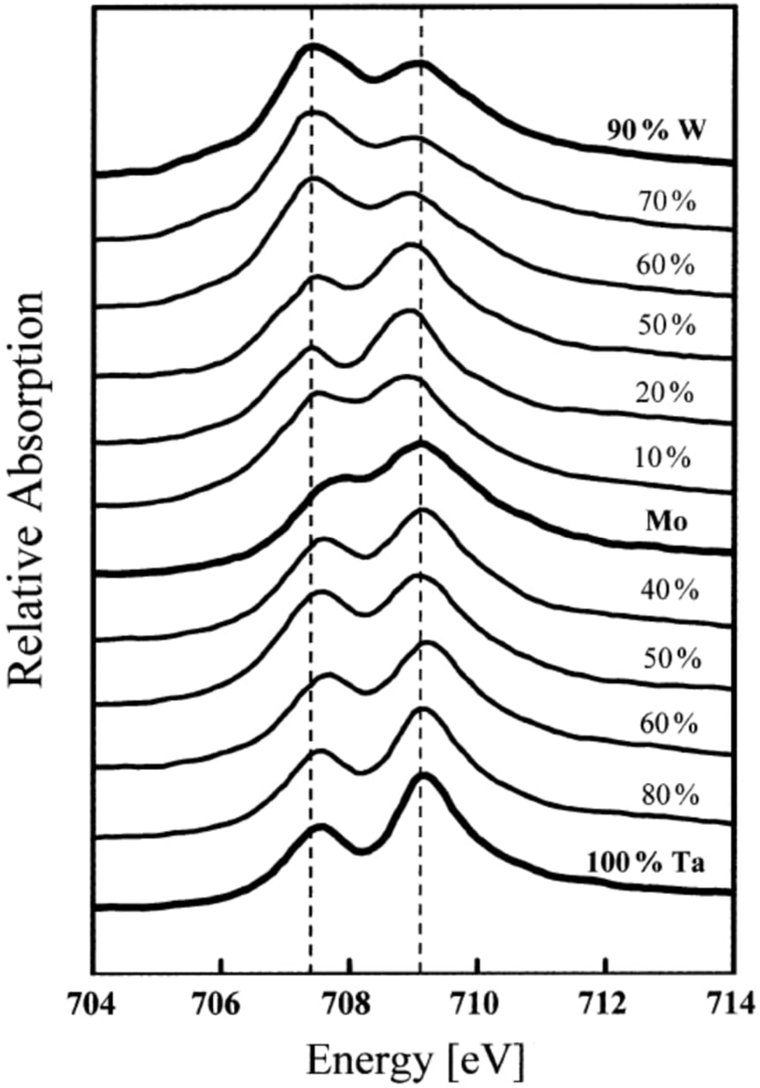


$Sr_2Fe(Mo,W^{VI}/Ta^{V})O_6$

Fe *K* XANES

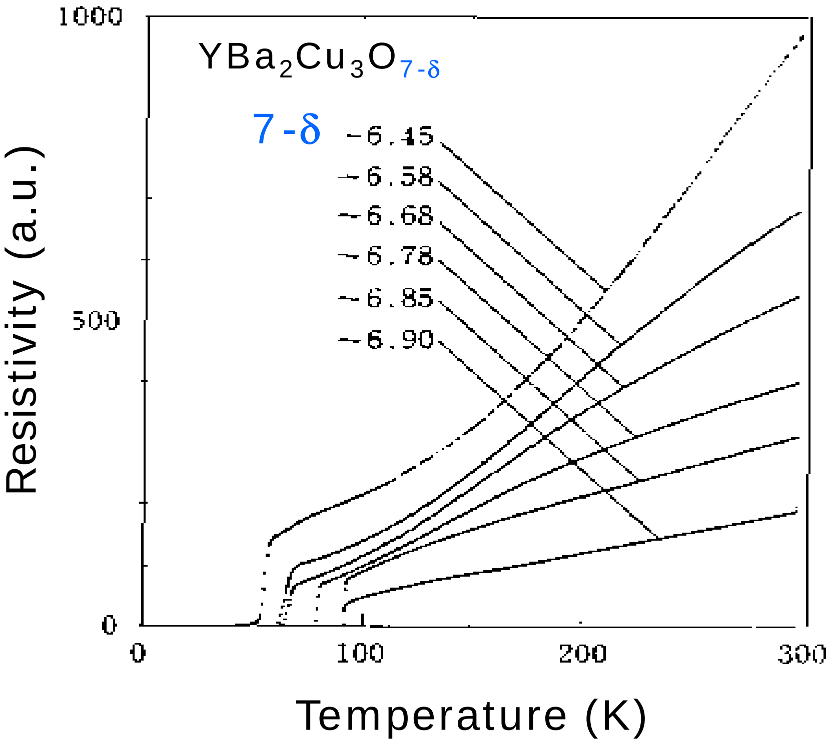


Fe L_3 XANES



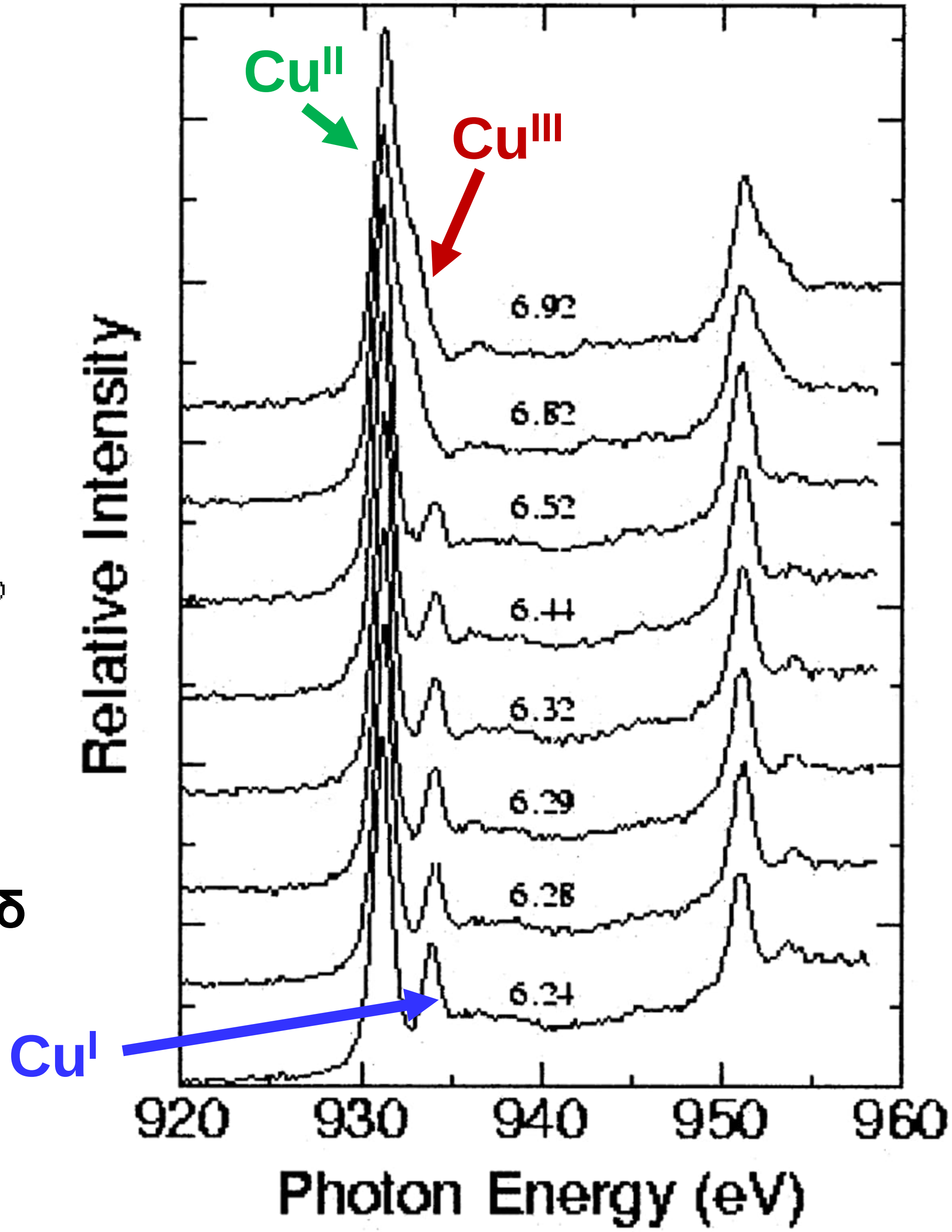
More systematic study shows mixed-valent Fe(II/III) !

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

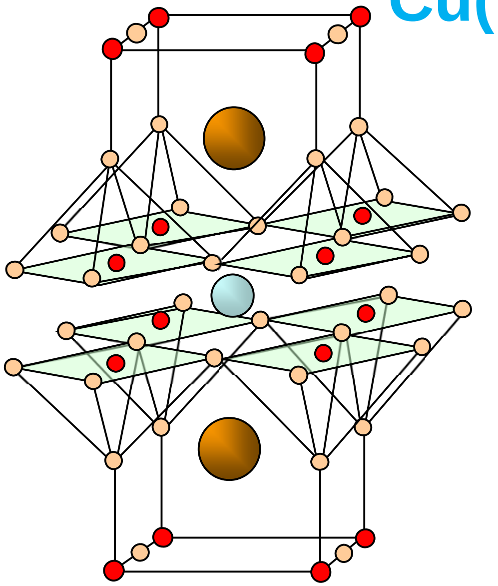


$Cu(1)Ba_2YCu(2)_2O_{7-\delta}$

Cu *L* XANES



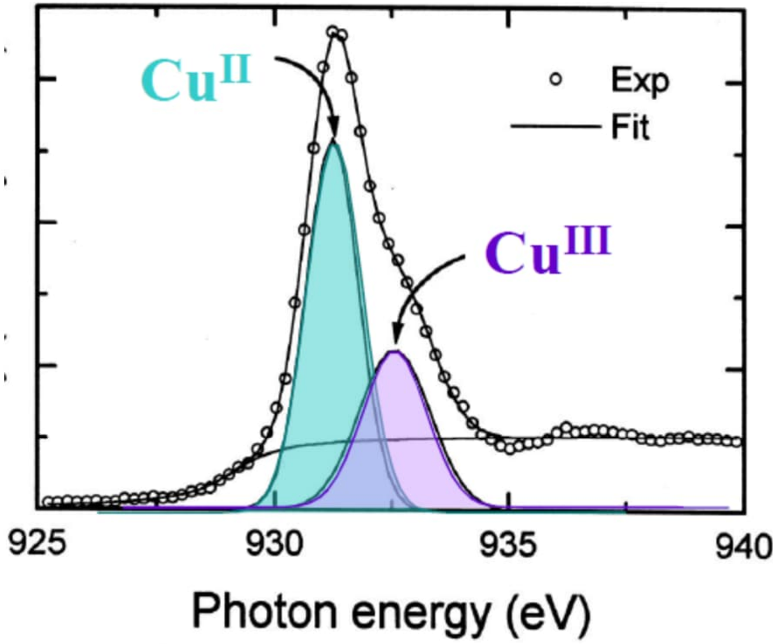
$Cu(1)Ba_2YCu(2)_2O_{7-\delta}$



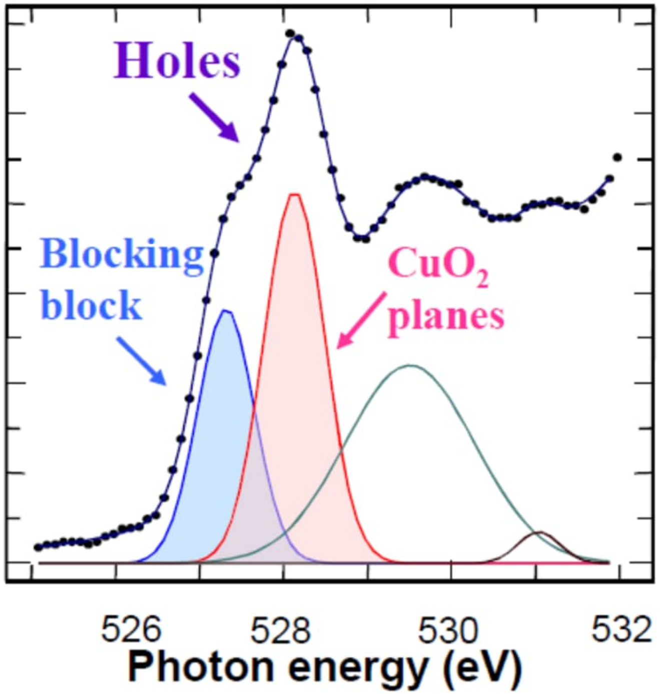
Cu(1)O (blocking block)

$Cu(2)O_2$ plane

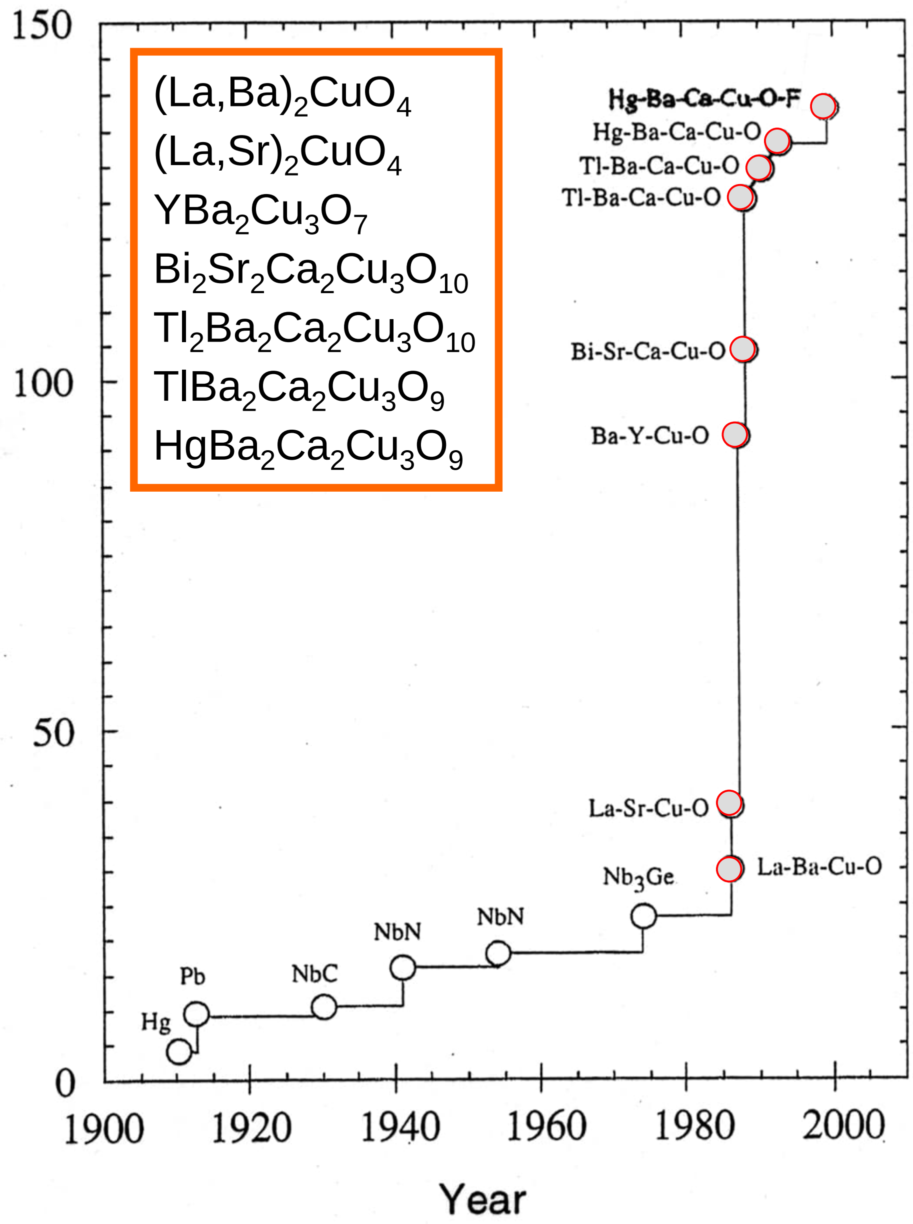
Cu *L* XANES → average V(Cu)



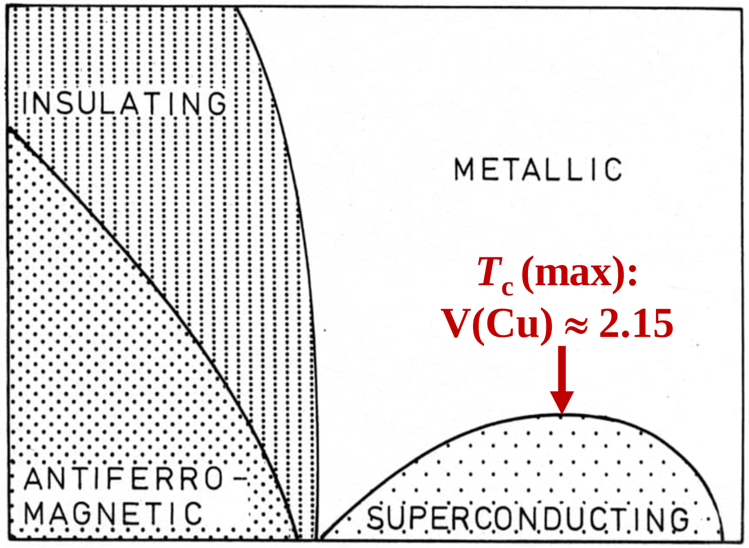
O *K* XANES



High-T_c superconductors



$(La,Ba)_2CuO_4$
$(La,Sr)_2CuO_4$
$YBa_2Cu_3O_7$
$Bi_2Sr_2Ca_2Cu_3O_{10}$
$Tl_2Ba_2Ca_2Cu_3O_{10}$
$TlBa_2Ca_2Cu_3O_9$
$HgBa_2Ca_2Cu_3O_9$

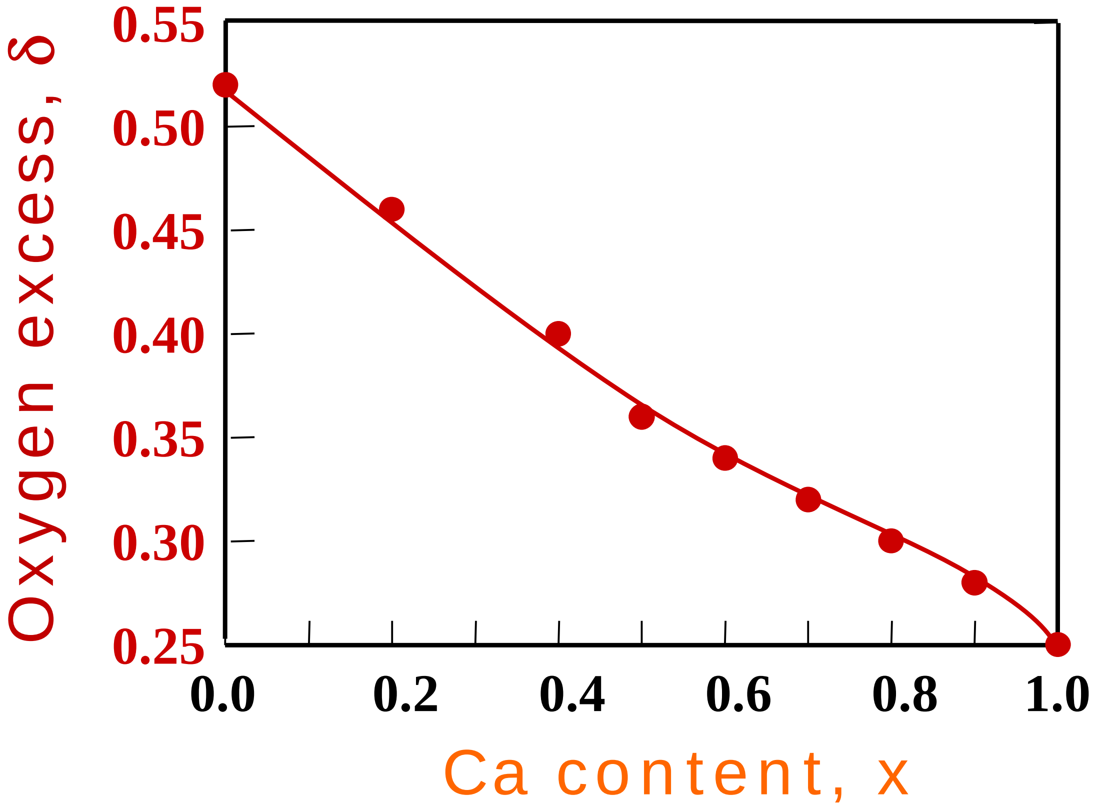


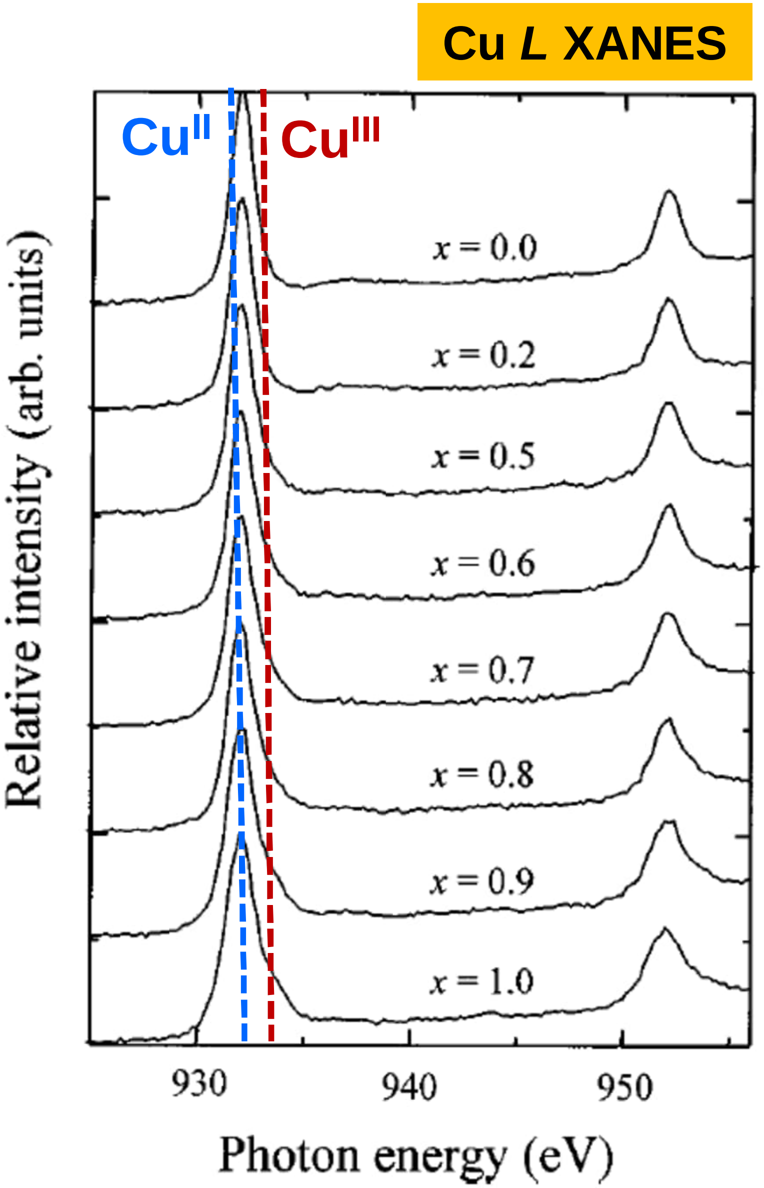
T_c (max):
V(Cu) ≈ 2.15

CuO_2-plane hole concentration: p(CuO_2)
[valence of copper → V(Cu) – 2]

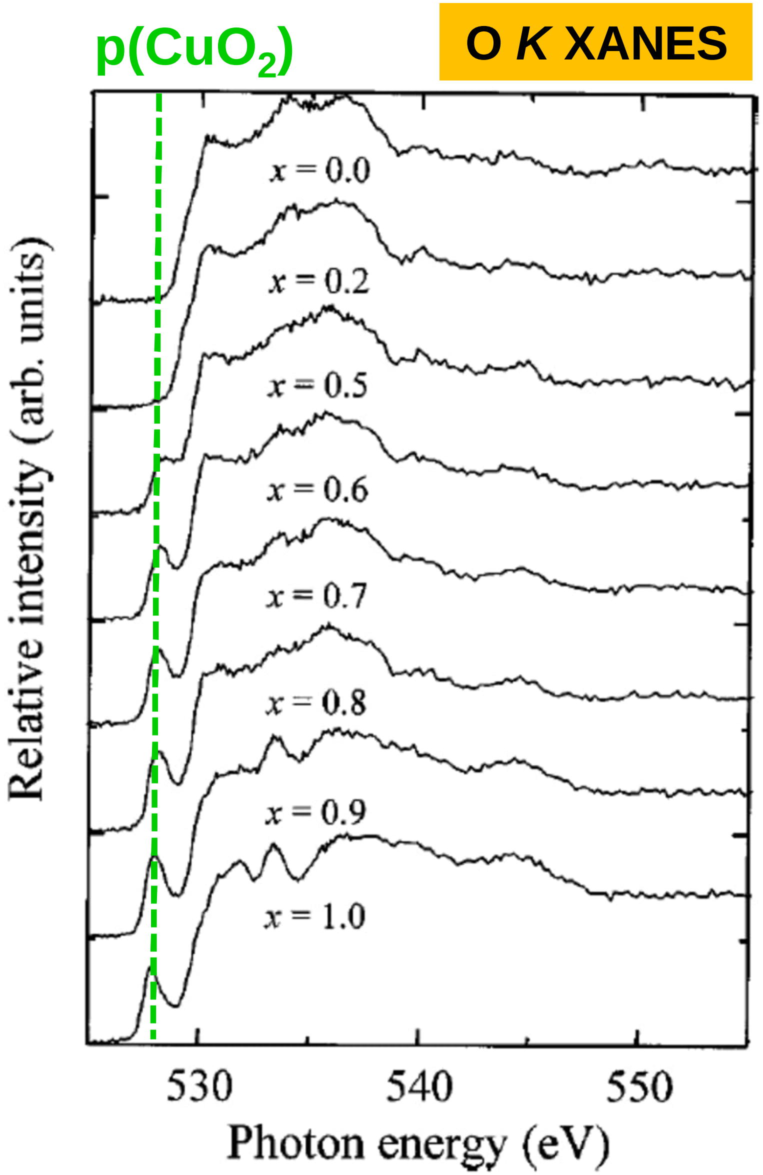
$Bi_2Sr_2(Y_{1-x}Ca_x)Cu_2O_{8+\delta}$

- 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) ?





Cu *L* XANES



O *K* XANES

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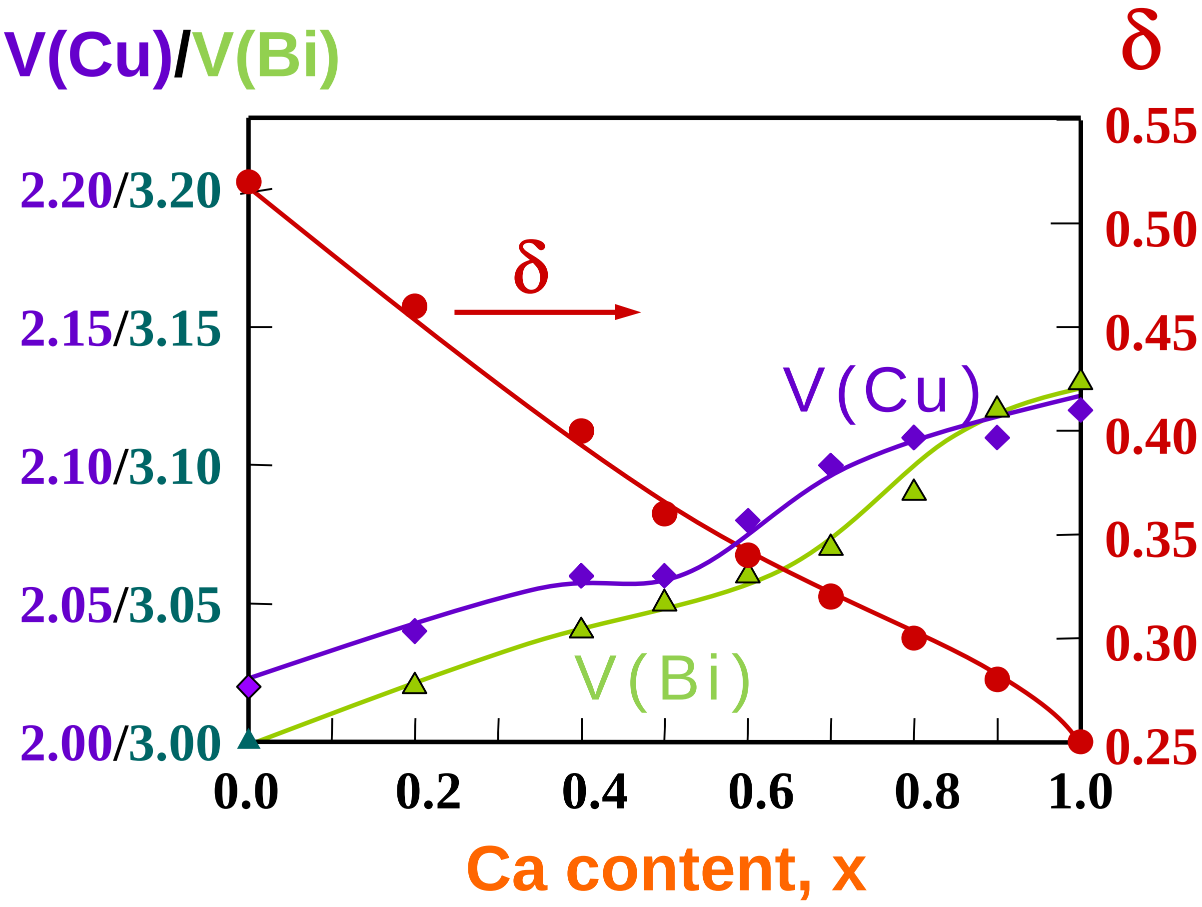
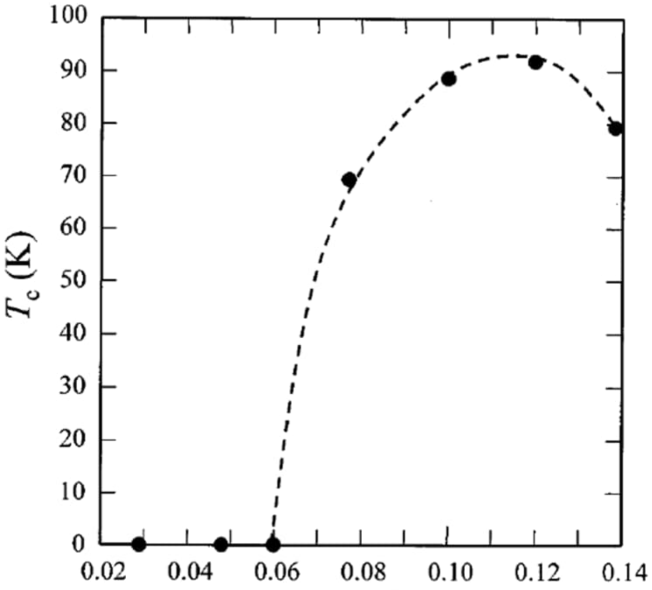
$Bi_2Sr_2(Y_{1-x}Ca_x)Cu_2O_{8+\delta}$





$p(CuO_2) = V(Cu)-2$

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