General introduction to XAS

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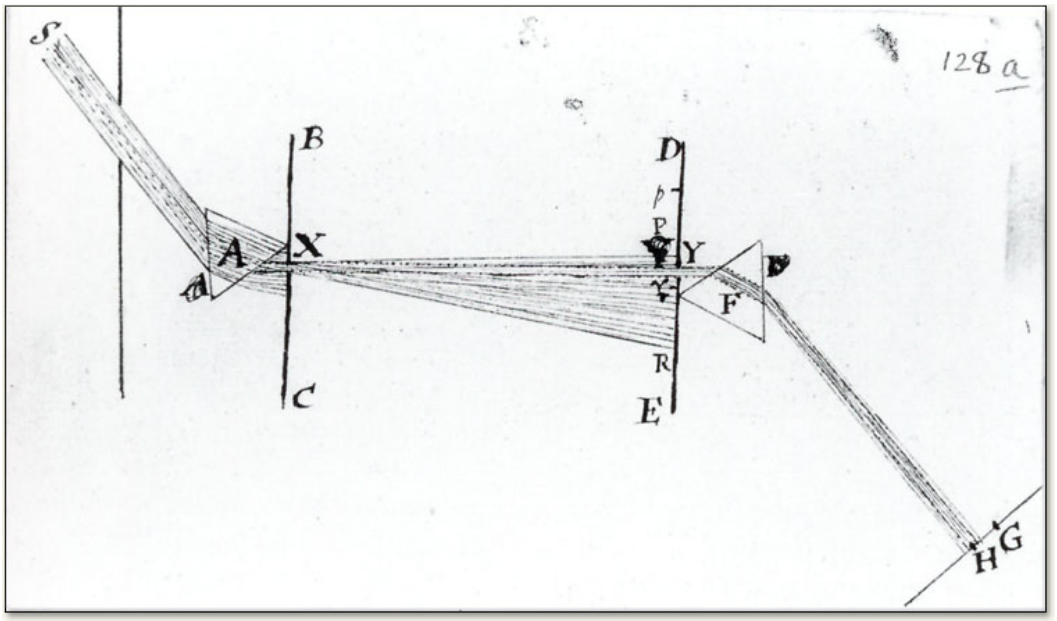
5^{th} School on X-ray Spectroscopy Methods - 22-23/Aug/2016

Spectroscopy??

- It seems that was Sir Isaac Newton (him again...) that called spectra the dispersion of white light by a prism.



http://www.webexhibits.org/colorart/bh.html

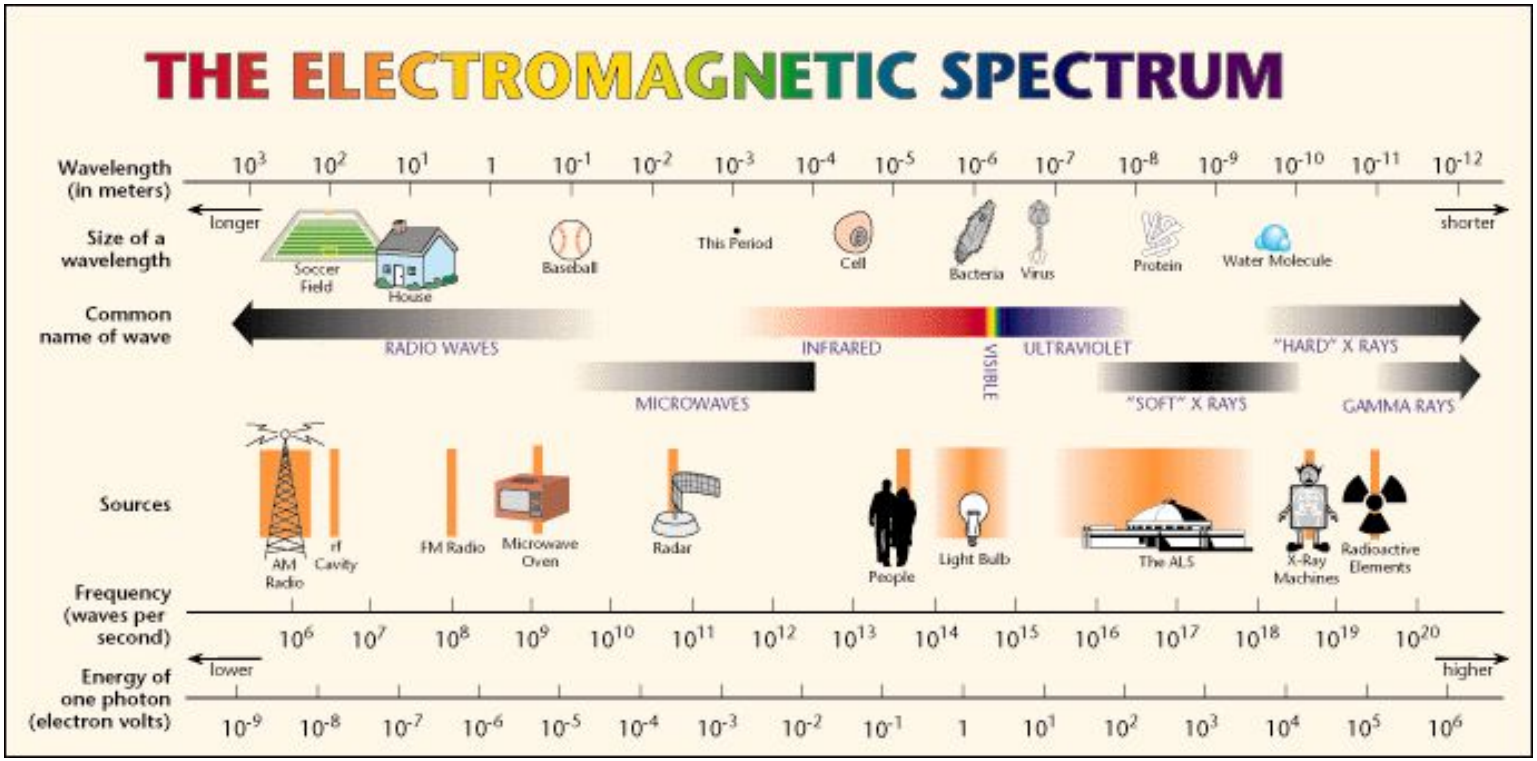
Yes! Spectroscopy!!

- Distorted definition: spectroscopy is how a physical property depends on the energy (wave length or number, frequency) of a test probe (radiation, electrons, neutrons, ions, etc);
- Normally the variations (spectra) can be indirectly correlated with useful information by means of models;
- Do you like acronyms? Pick yours...: XAS, XANES, EXAFS, XMCD, XMLD, RIXS, XES, XRF, XPS, UPS, ARPES, ARUPS, EELS, FTIR, AES, UVS, PDMS, TOFMS, NMR, EPR, FMR, ESCA, μSR, INS, LIBS, CRIMS, IRMS, MIMS, ZECSY, ESR, TOCSY, SEFT, QMS, ...

X-ray absorption

physical property absorption of electromagnetic radiation by matter

energy/frequency check the electromagnetic spectrum...

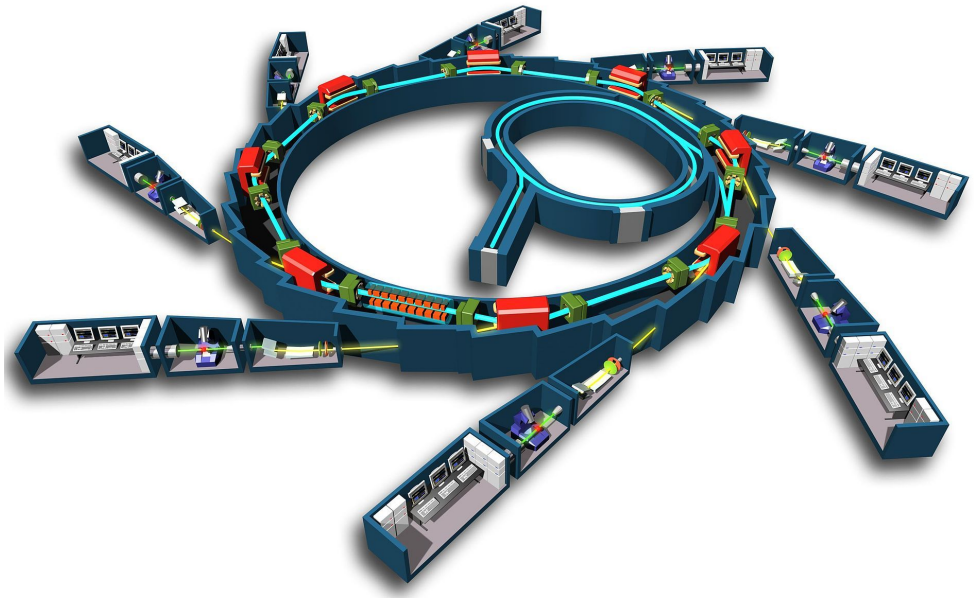


www2.lbl.gov/MicroWorlds/ALSTool/EMSpec/EMSpec2.html

Outline

Outline

Synchrotrons



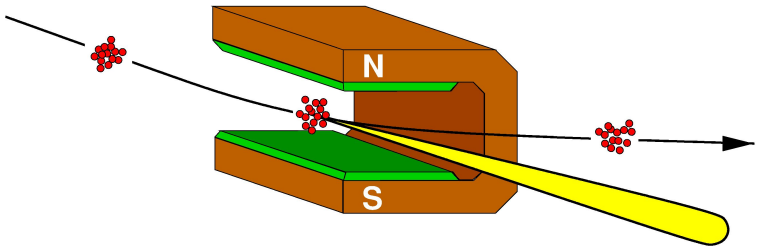
en.wikipedia.org/wiki/synchrotron_light_source

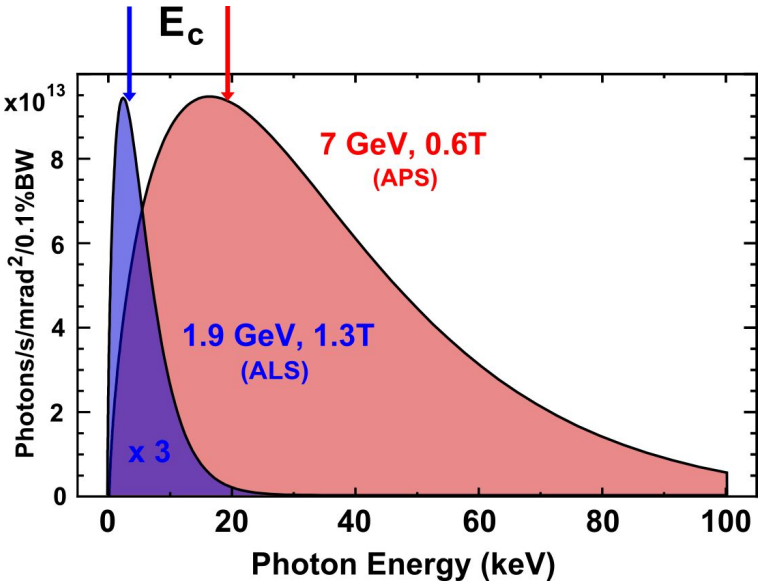
- particle accelerator: e^-
- continuous radiation energy spectra: μwaves to γ-rays
- 1^{st}, 2^{nd} or 3^{rd} generation

Synchrotron radiation

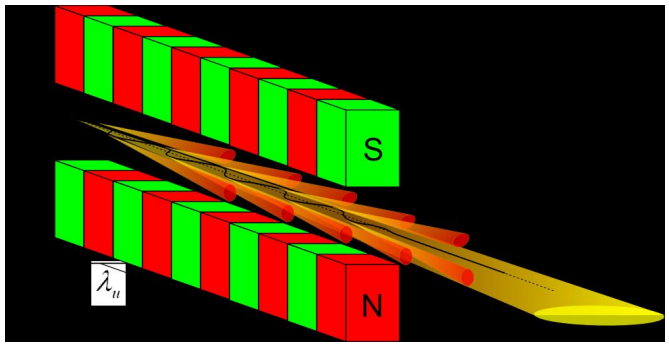
http://photon-science.desy.de/research/studentsteaching/primers/synchrotron_radiation/index_eng.html

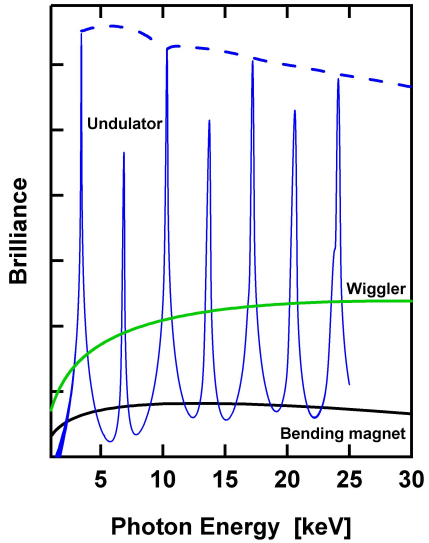
- bend magnets





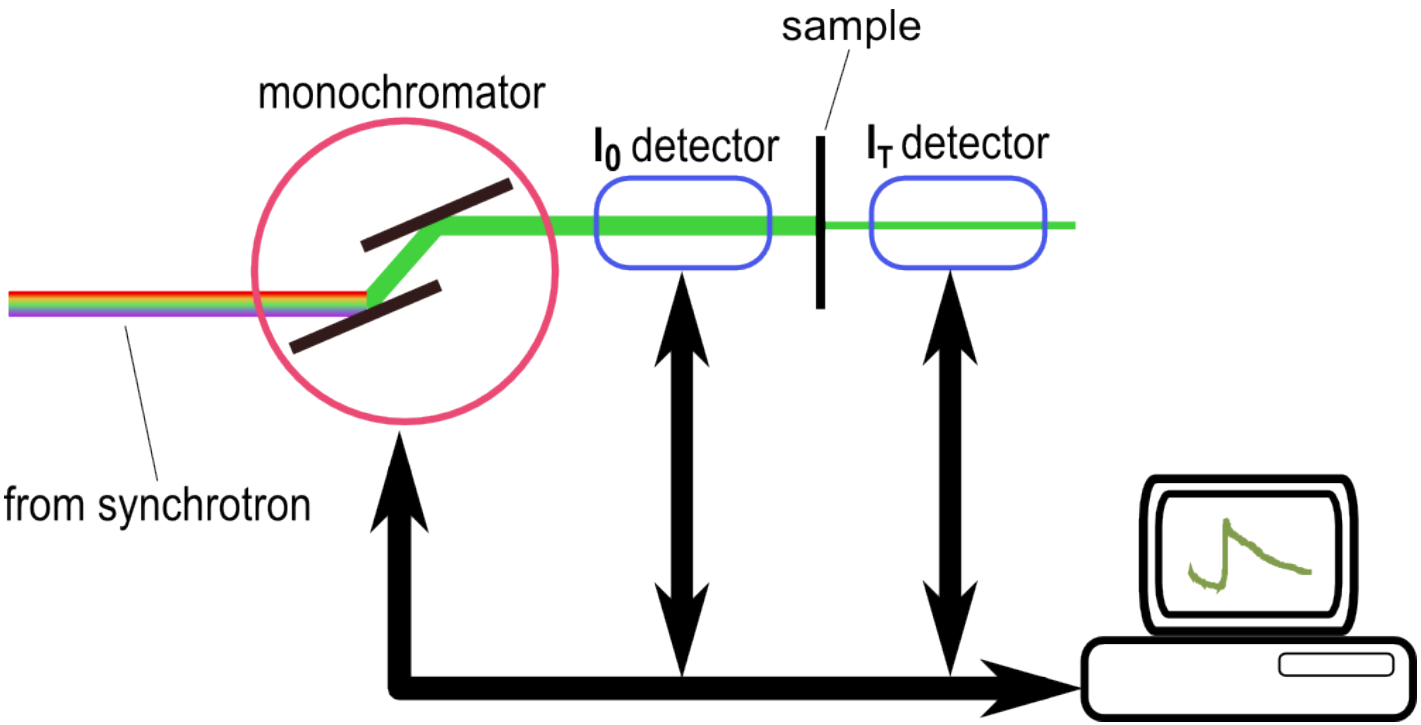
- insertion devices





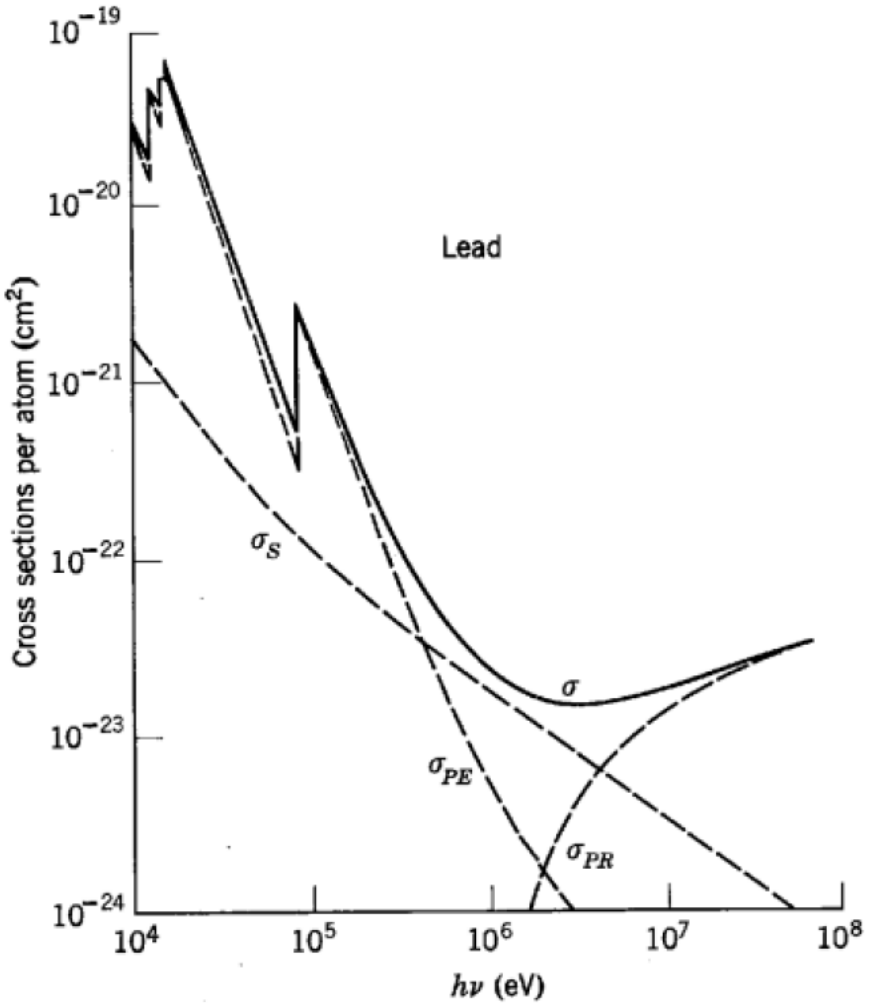
Outline

The classic X-ray absorption experiment



$I_T = I_0 e^{-\mu t}$ μ:linear absorption coefficient

How radiation interacts with matter

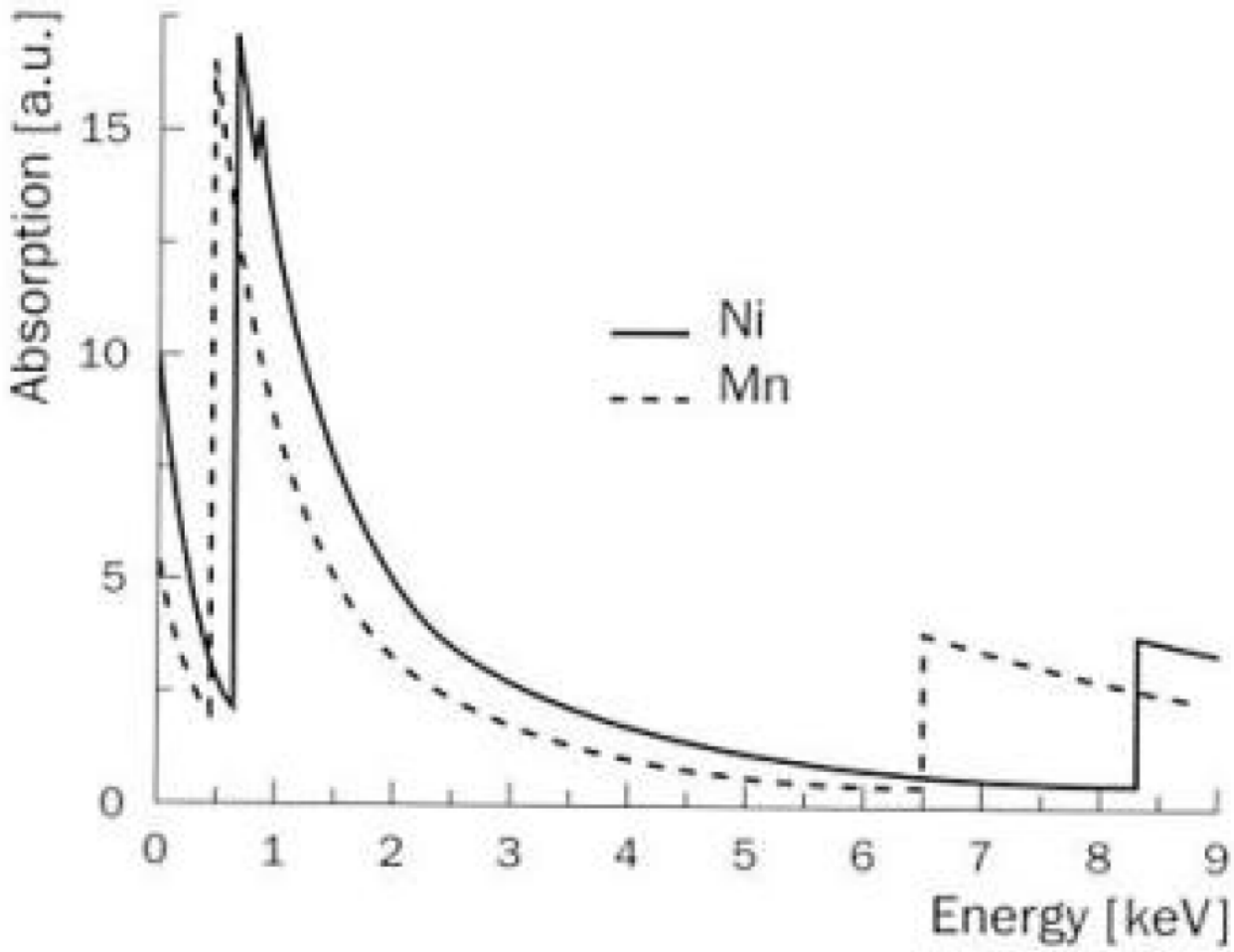


Radiation-matter interaction has several components:

- photoelectric effect
- Compton scattering
- pair creation

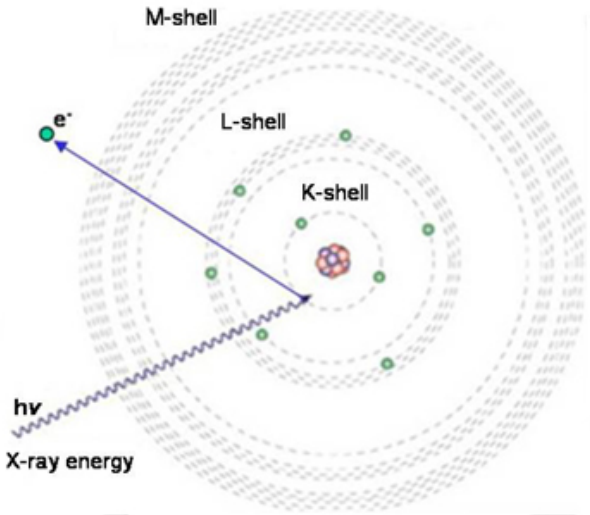
Fig 2-17 Eisberg & Resnick

XAS: ABSORPTION EDGES

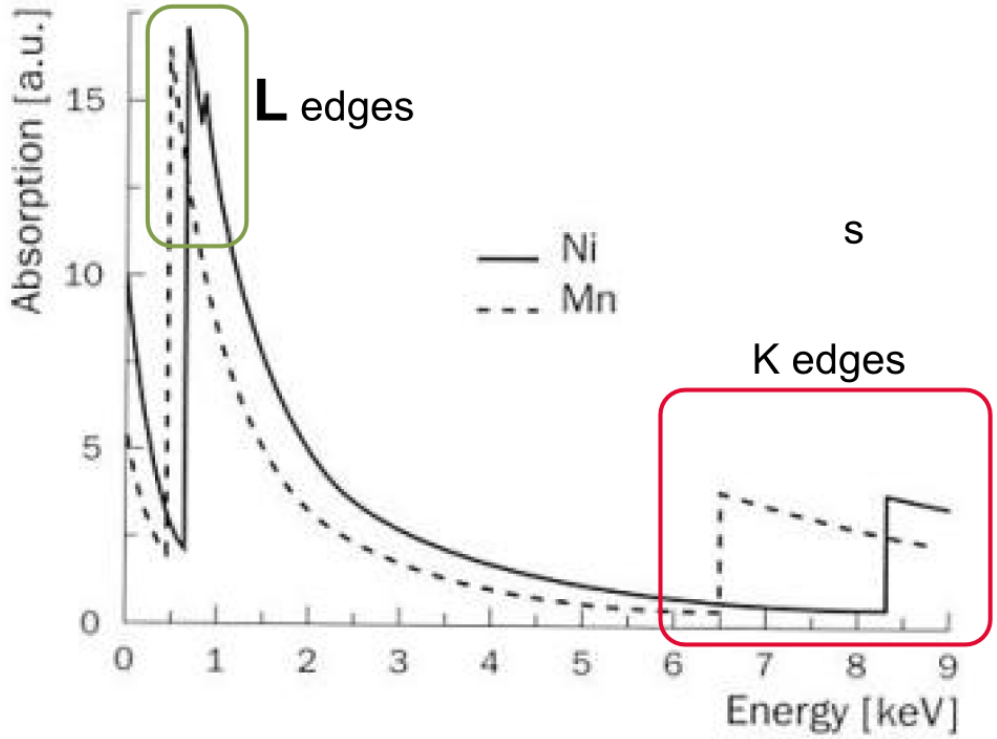


from Neutron and X-ray Spectroscopy, E. Lelièvre et al, Springer

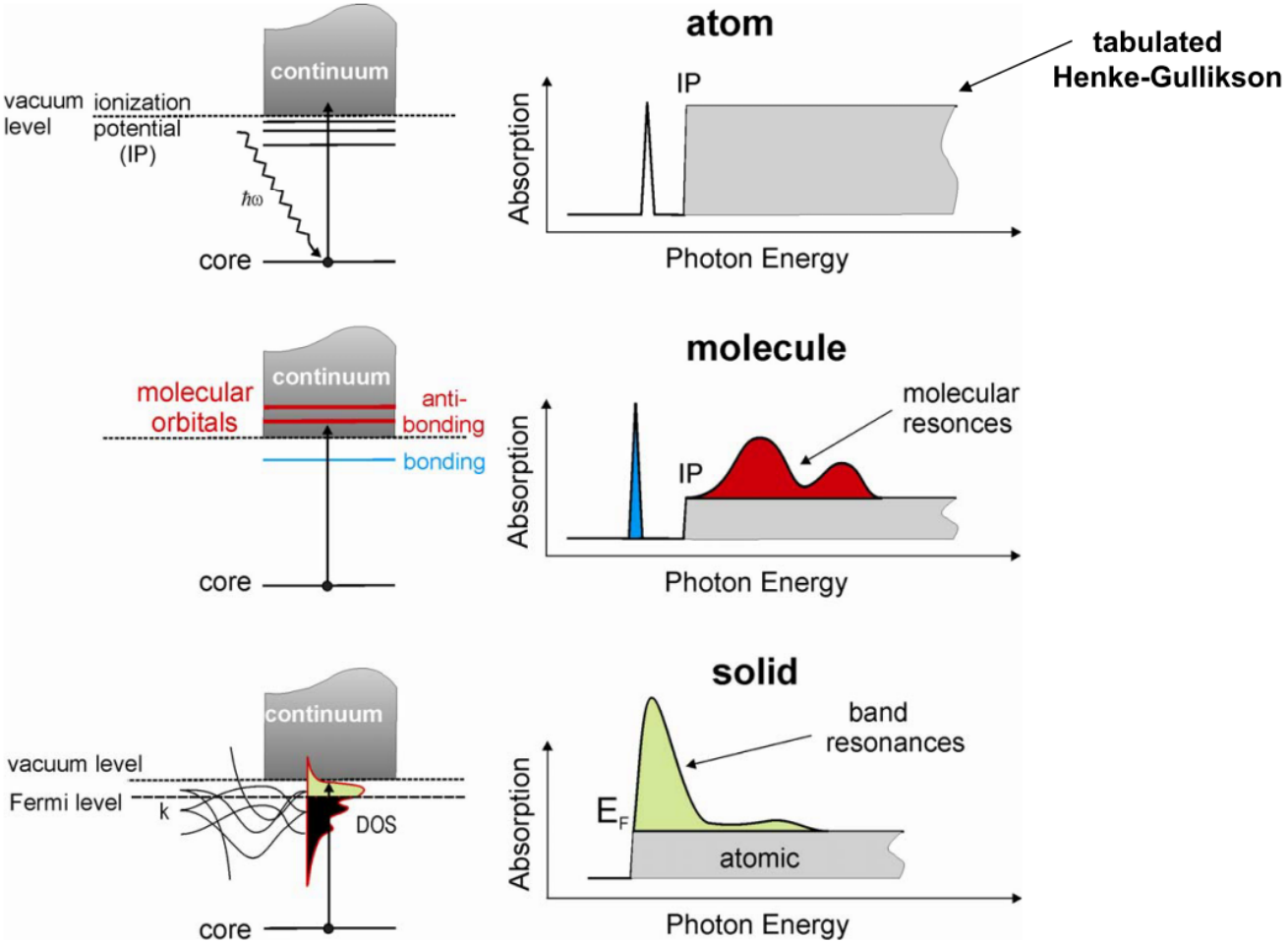
XAS: ABSORPTION EDGES



http://ssrl.slac.stanford.edu/nilssongroup/corelev

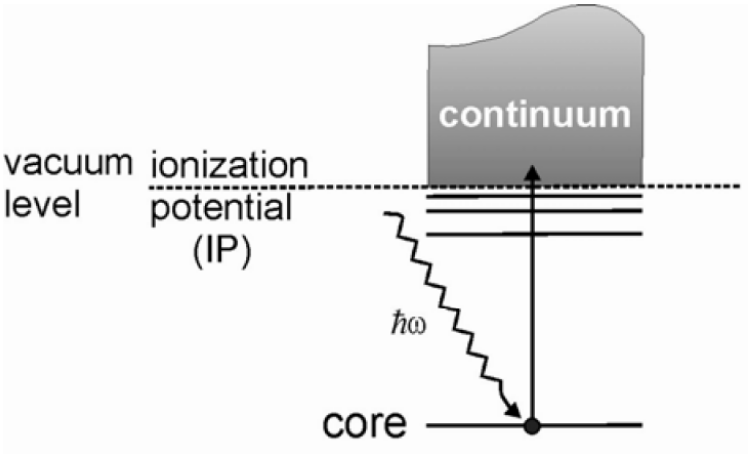


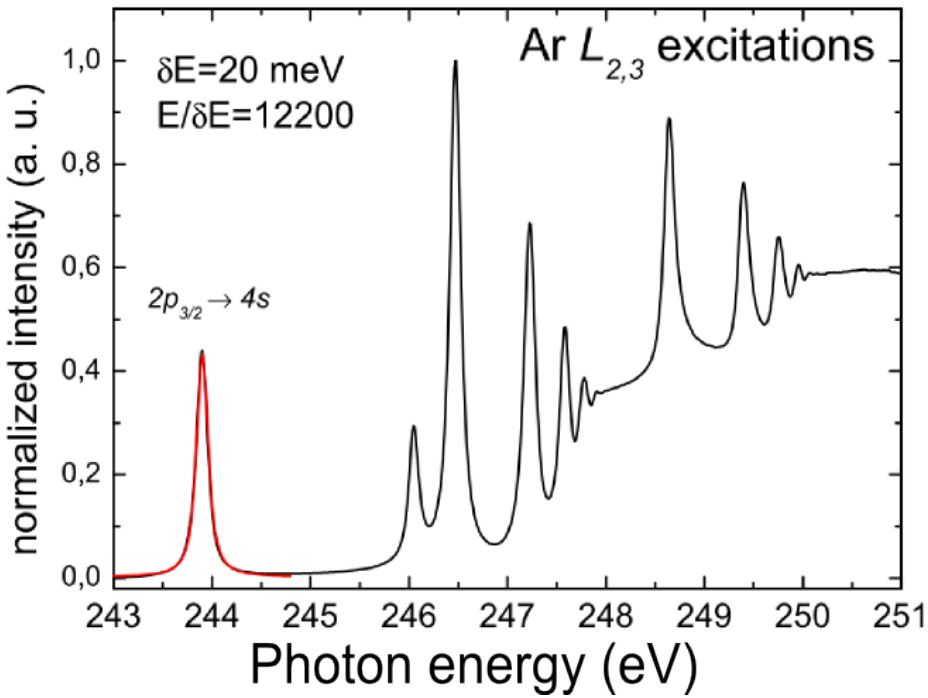
XAS: ELECTRON TRANSITION



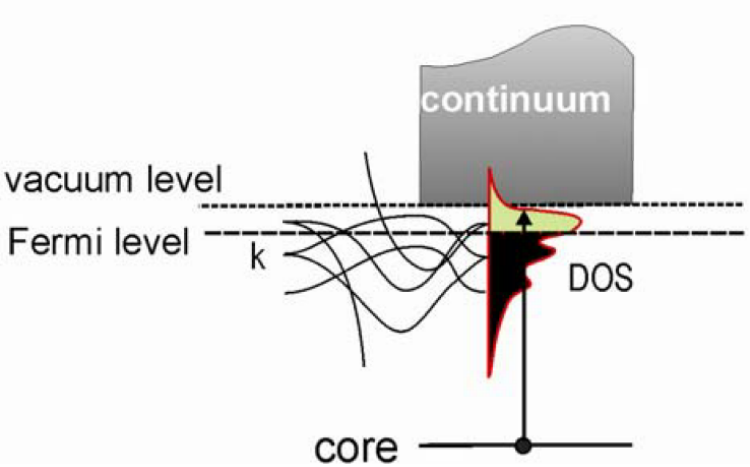
from J. Stohr presentation found at http://ast.coe.berkeley.edu/srms/

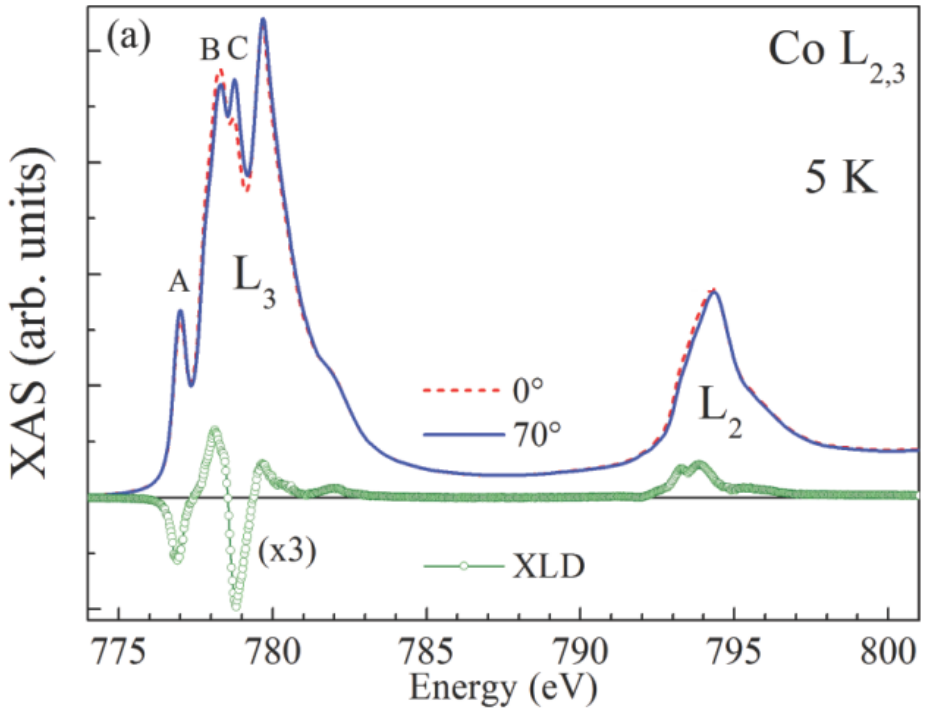
XAS in atoms: Argon





XAS in solids: Cobalt oxide

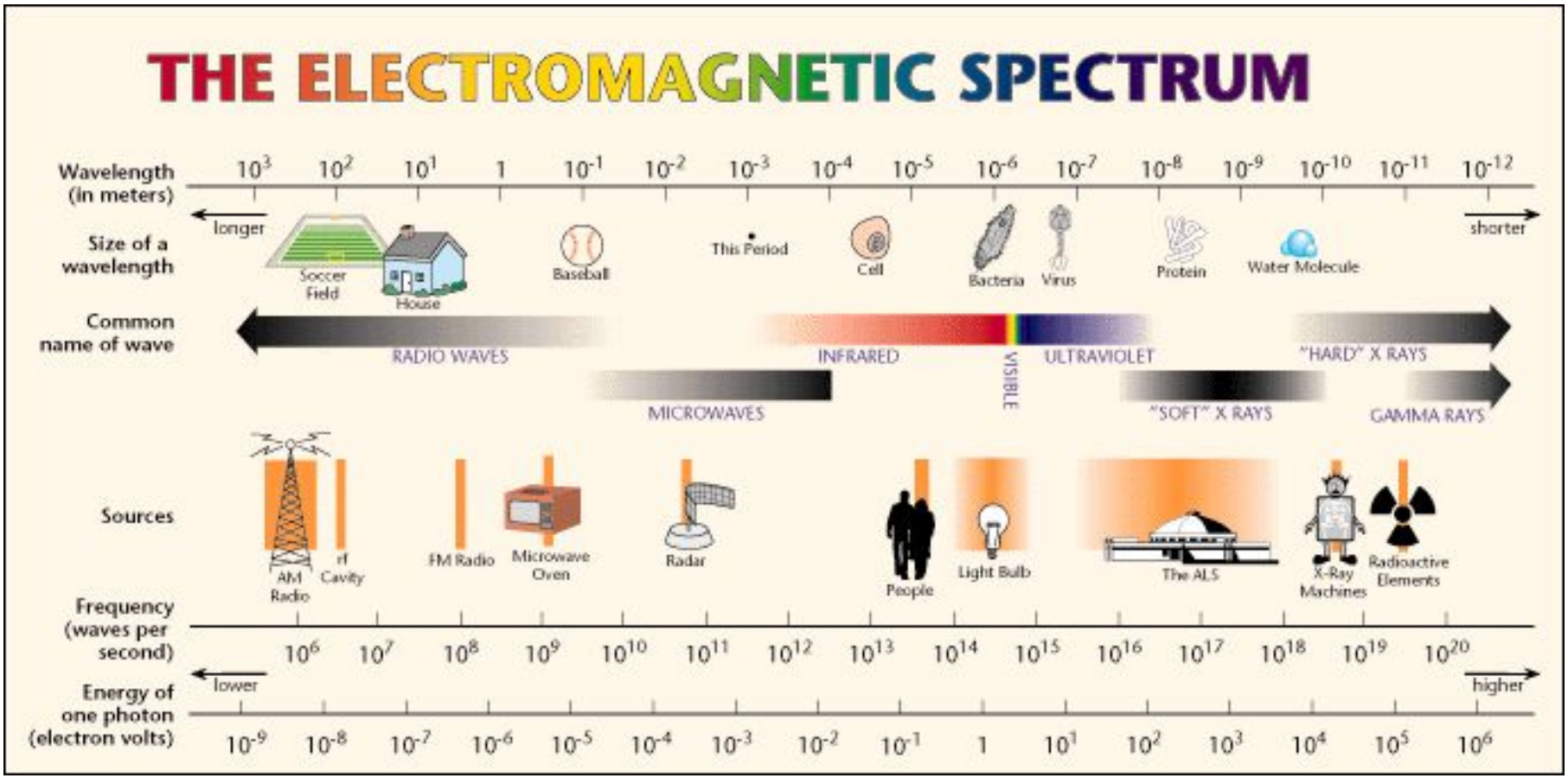




Lamirand et al., PRB 88 (2013) 140401

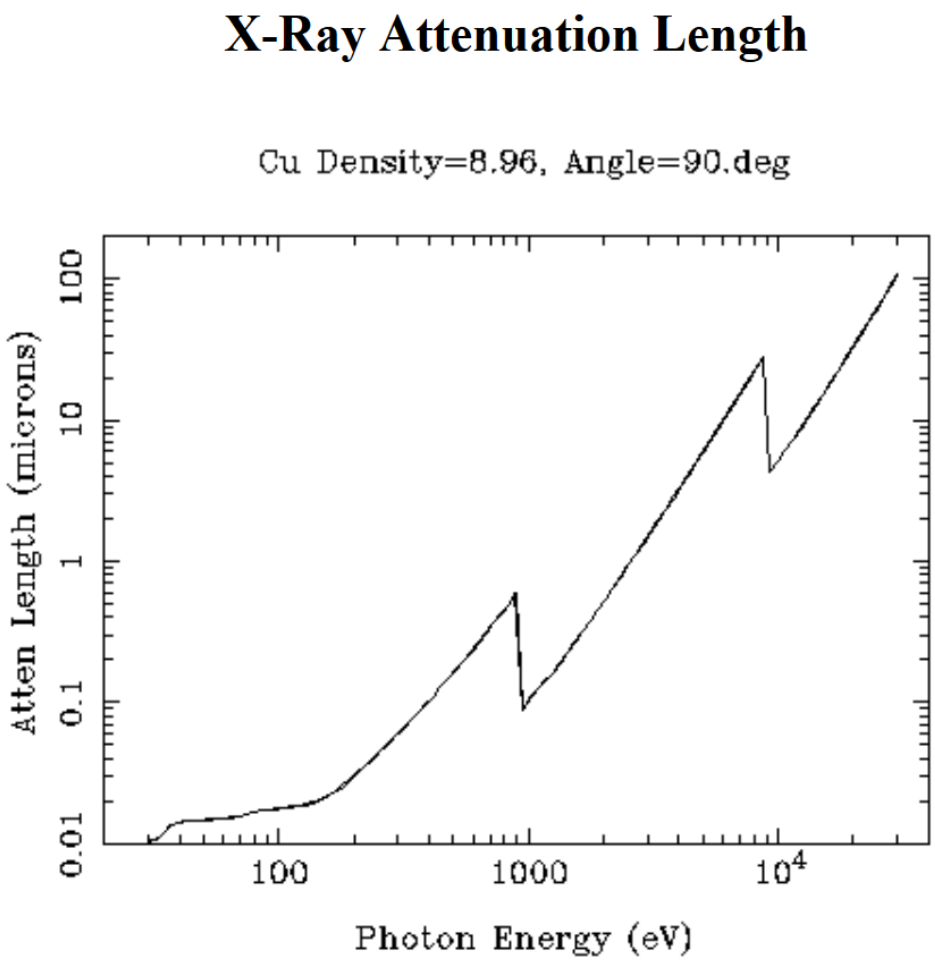
Outline

Tender, hard, soft: X-rays for all tastes...



www2.lbl.gov/MicroWorlds/ALSTool/EMSpec/EMSpec2.html

Attenuation length



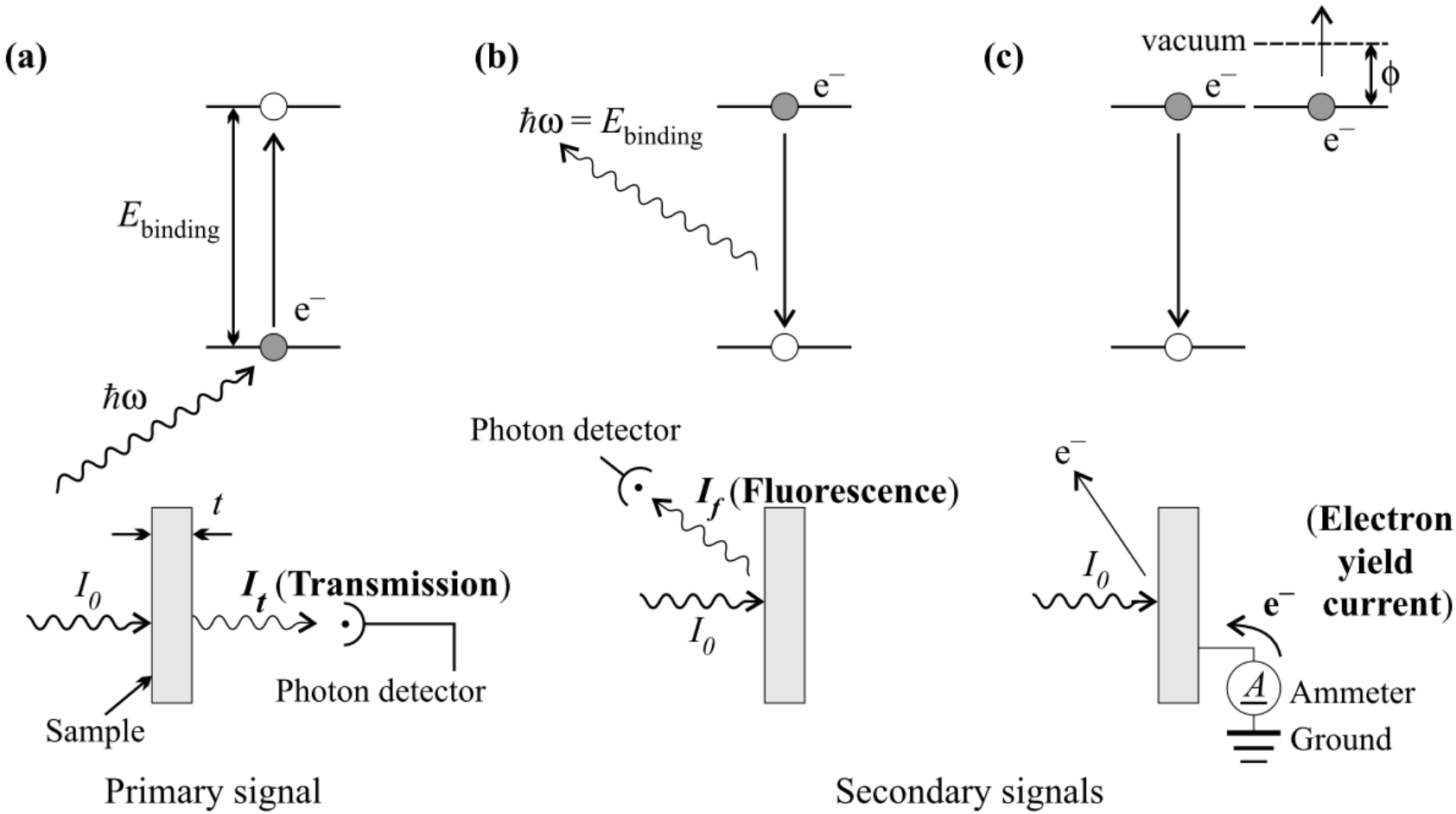
http://henke.lbl.gov/optical_constants

Attenuation length is the reciprocal of linear absorption coefficient. It is tabulated.

Optimun signal/noise thickness is when edge jump is equal to 1.

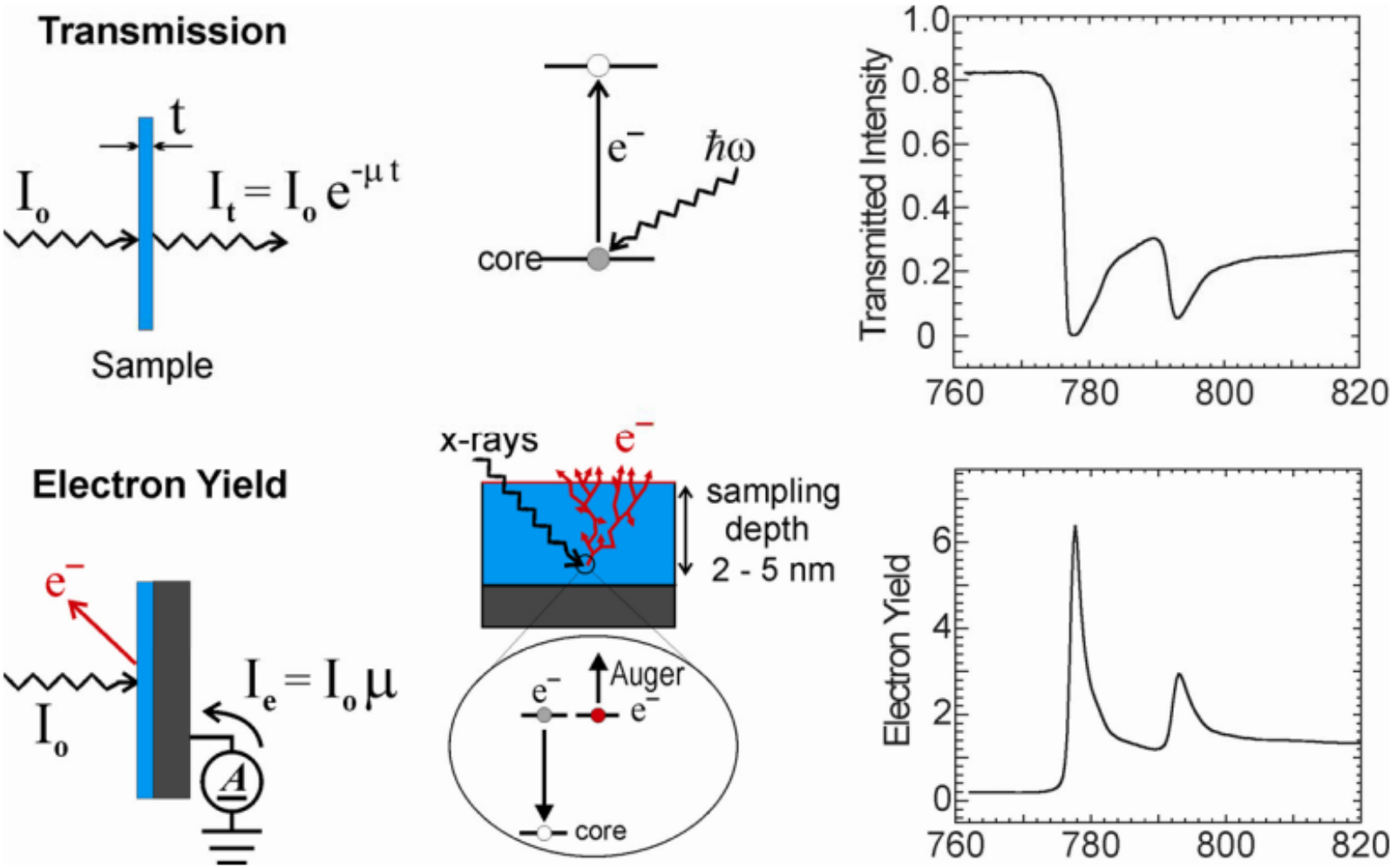
- Cu K edge: 6 μm
- Cu L edge: 120 nm

XAS: DETECTION MODES



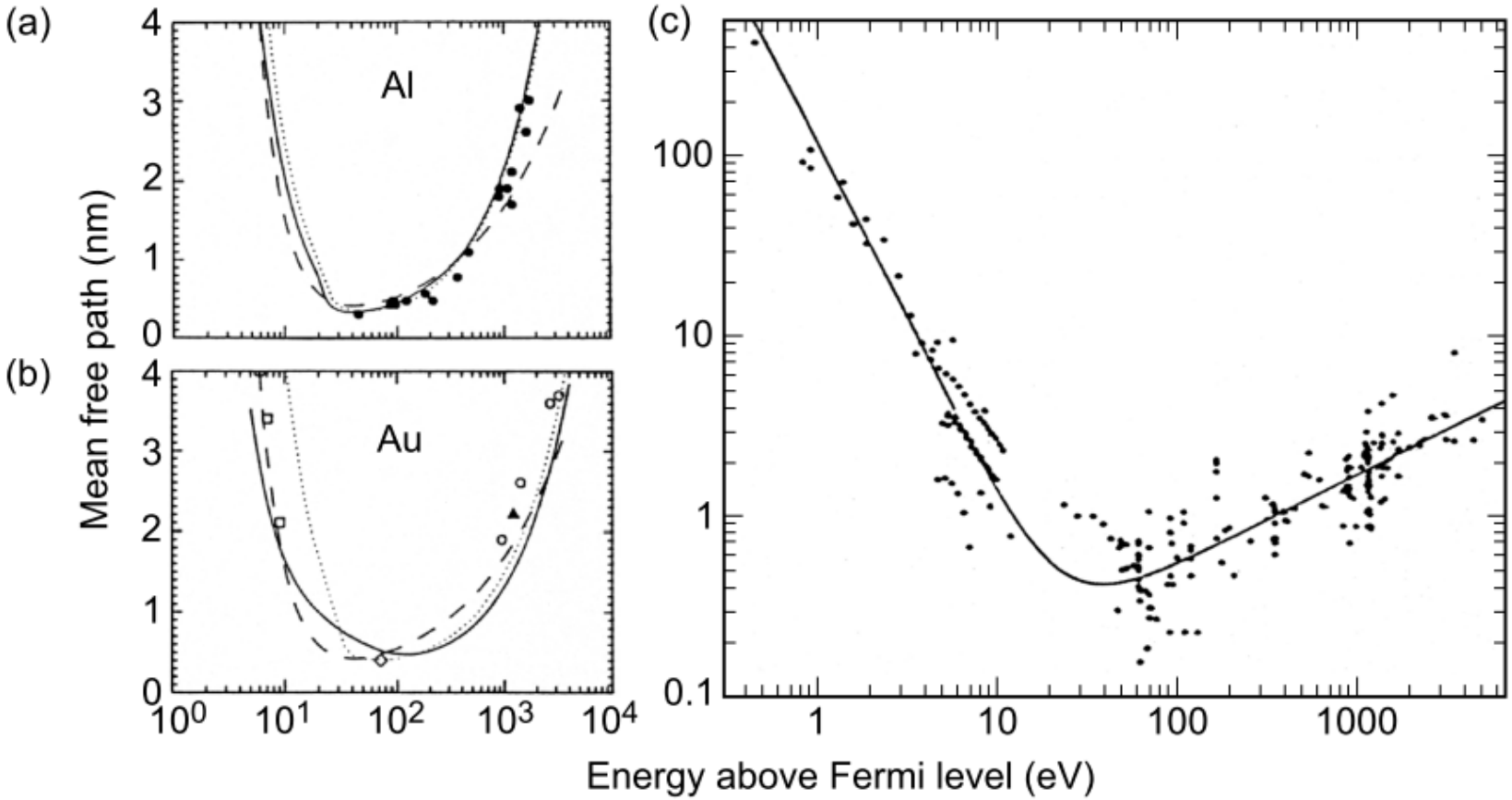
from Reiko Nakajima, PhD thesis (1998)

XAS: DETECTION MODES



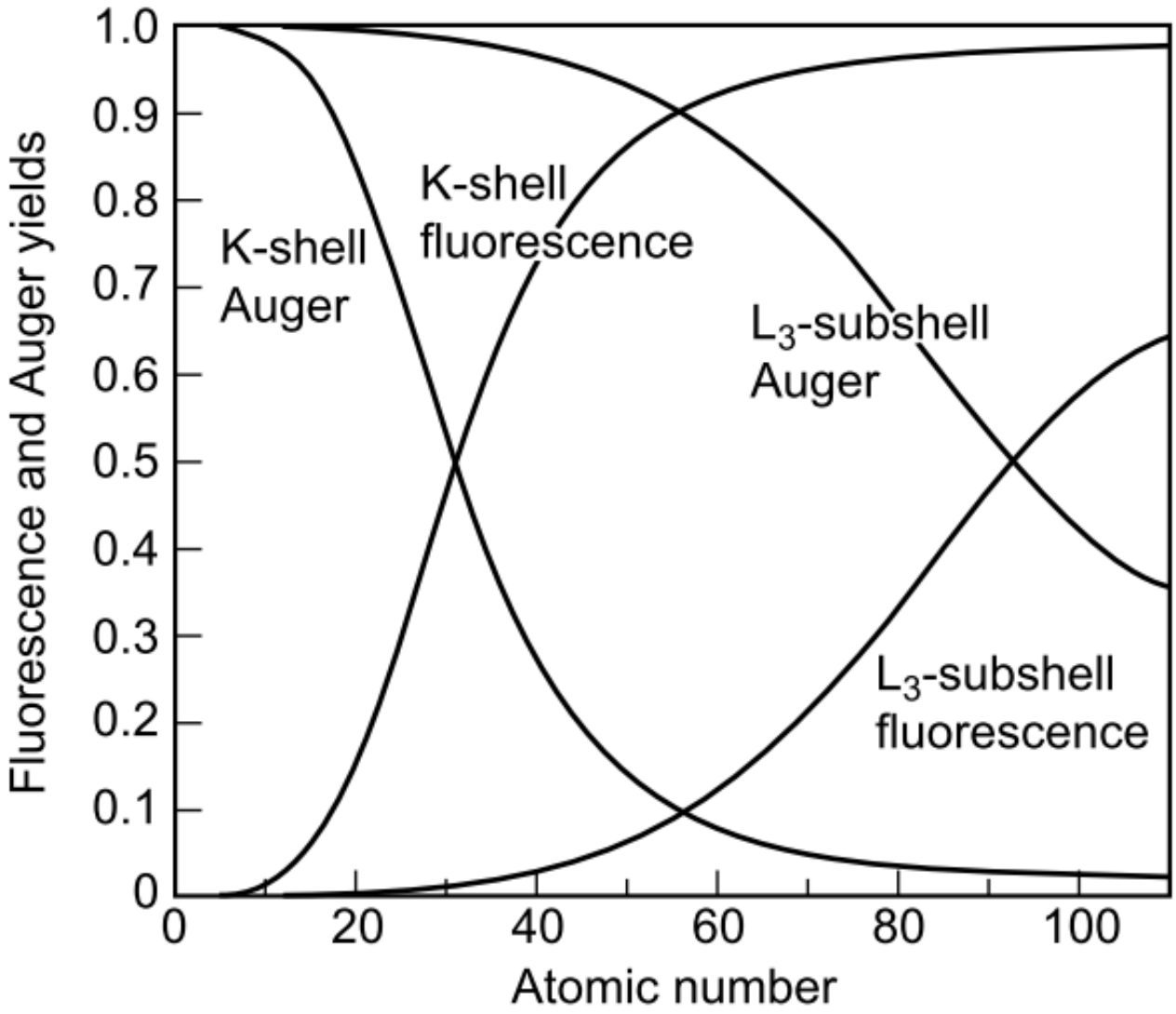
from J. Stohr presentation found at http://ast.coe.berkeley.edu/srms/

The electron mean free path



https://people.eecs.berkeley.edu/ attwood/srms/2007/Lec02.pdf

Fluorescence vs electron yield



https://people.eecs.berkeley.edu/ attwood/srms/2007/Lec02.pdf

Take in consideration

Hard X-rays

1. Are bulk sensitive
2. Can be used in transmission
3. Fluorescence: very effective
4. Don't need ultra high vacuum

Soft X-rays

1. Are very, very surface sensitive
2. Normally use electron yield
3. Fluorescence: weak
4. Need ultra high vacuum

Outline

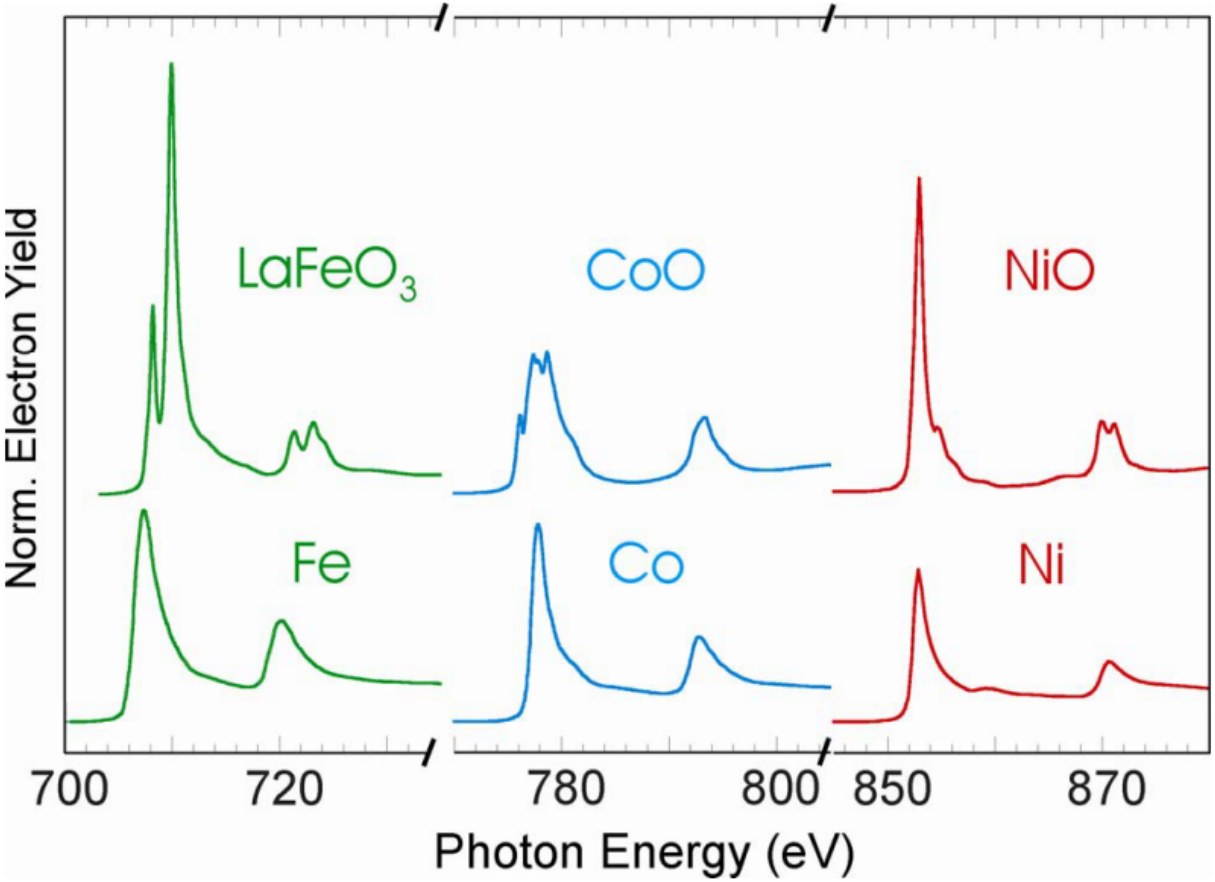
Let's start: X-ray absorption spectroscopy

5th School on X-ray Spectroscopy Methods			
Program			
Time	**August, 22nd**	**Title**	**Speaker**
9h-10:30h	Plenary Lecture 1 *Auditório Anel*	General Introduction to XAFS	Julio Cezar
10:30h-11h	Coffee break		
11h-12:30	Plenary Lecture 2 *Auditório Anel*	XANES: Information content, high resolution and simulations	Frederico Lima
12:30-14h	Lunch		
14h-18h	Parallel Session A *Auditório LNNano*	Athena	Santiago Figueroa and Flávio Vicentin
	Parallel Session B *Sala 211 Dir. LNLS*	Sum Rules XMCD	Julio Cezar
	Parallel Session C *Auditório LNLS*	XRF Microscopy and Micro-Spectroscopy	Carlos Peréz, Dalton Abdala and Hudson Wallace
18h-19h	Visit to LNLS Beamlines		Douglas Galante
19h-20h	Poster Session and Cocktail		
Time	**August, 23rd**	**Title**	**Speaker**
9h-10:30h	Plenary Lecture 3 *Auditório Anel*	High-Resolution Resonant Inelastic Soft X-ray Scattering	Jan-Erik Rubensson
10:30h-11h	Coffee break		
11h-12:30h	Plenary Lecture 4 *Auditório Anel*	EXAFS	Santiago Figueroa
12:30h-14h	Lunch		
14h-18h	Parallel Session A *Auditório LNNano*	Artemis	Santiago Figueroa and Dalton Abdala
	Parallel Session D *Sala 11 dir. LNLS*	XEOL	Verônica Teixeira and Mário Valerio
	Parallel Session E *Auditório LNLS*	XANES Simulations	Frederico Lima

We should, but we're not going to discuss about...

EXAFS	Extended X-ray absorption fine structure
XRF	X-ray fluorescence
RIXS	Resonant inelastic X-ray scattering
XES	X-ray emission spectroscopy
XEOL	X-ray excited optical luminescence
DAFS	Diffraction anomalous fine structure
PEEM	Photoelectron emission microscopy
STIF	Some technique that I forgot...

Soft X-rays absorption spectroscopy



from J. Stohr presentation found at http://ast.coe.berkeley.edu/srms/

X-ray Absorption Spectroscopy (XAS)

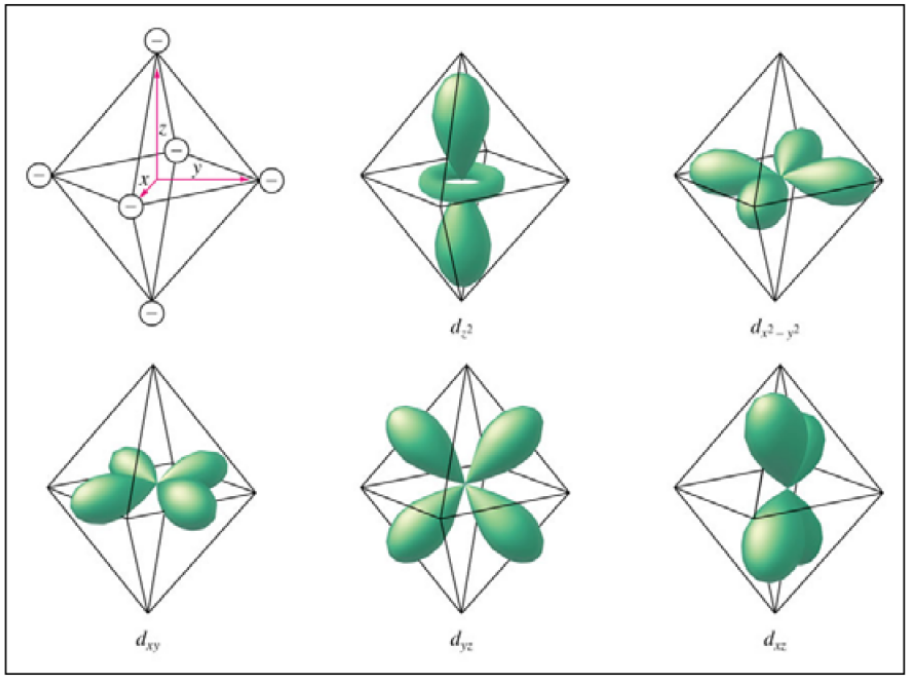
X-ray Absorption Near Edge Spectroscopy (XANES)

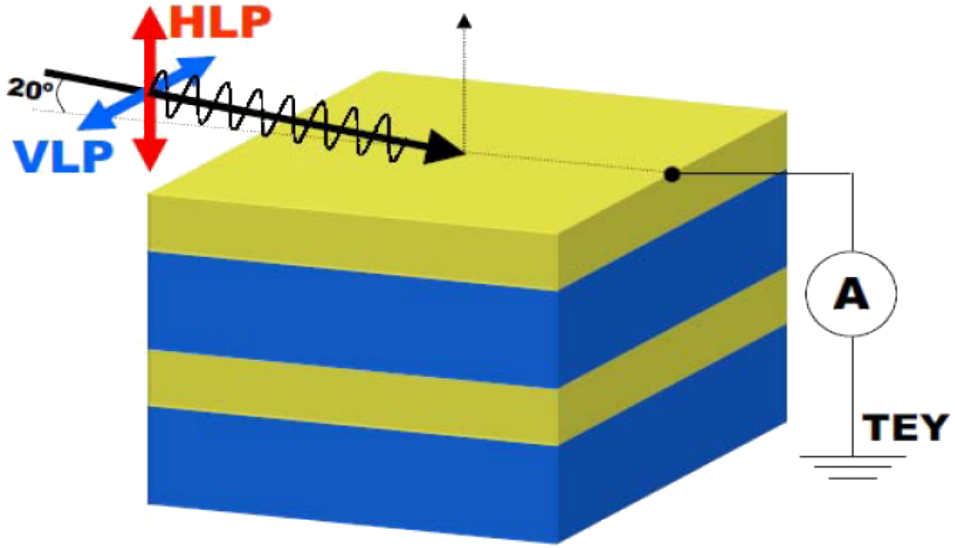
Breaking the symmetry 1: structural anisotropy

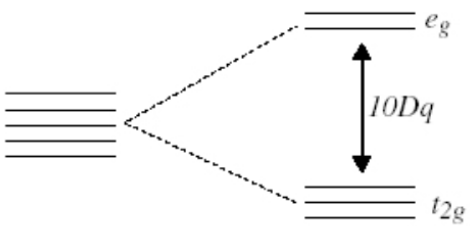
- Radiation interacts strongly with electrons;
- The strongest term in the interaction is between the photon electric field and electrons;
- Near edge features require empty states in the atom;
- Fermi Golden Rule in the dipolar approximation:

$$T_{if} \propto |\langle f|\hat{e} \cdot \hat{r}|i\rangle|\delta(E_i - E_f)\rho(E_f) \quad (1)$$

Exploring structural anisotropies: perovskites

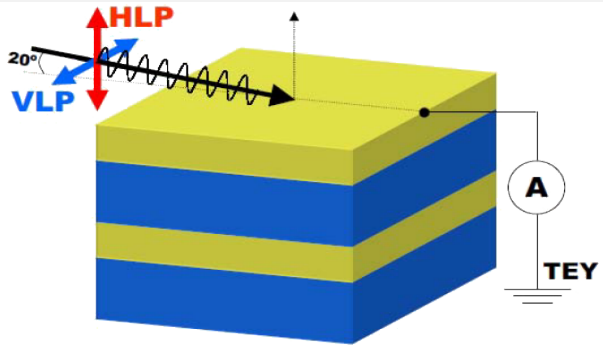


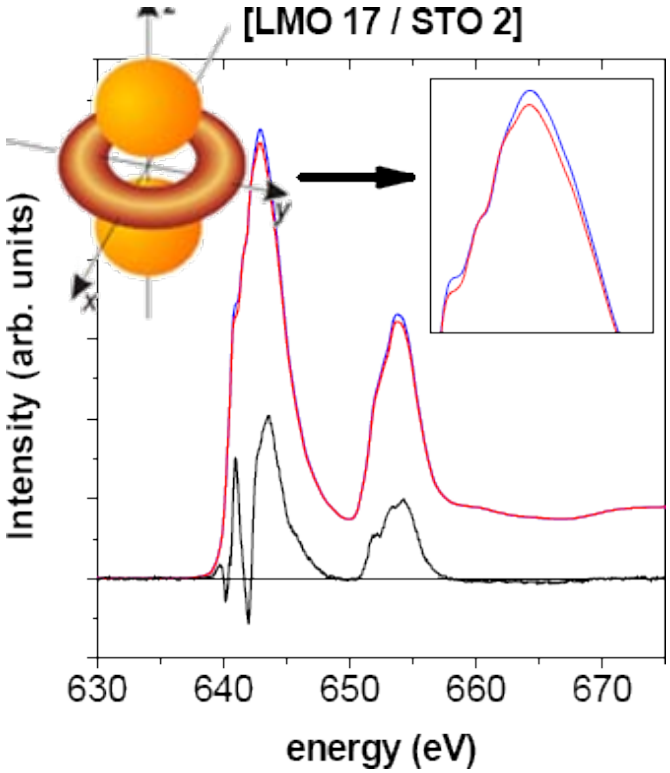


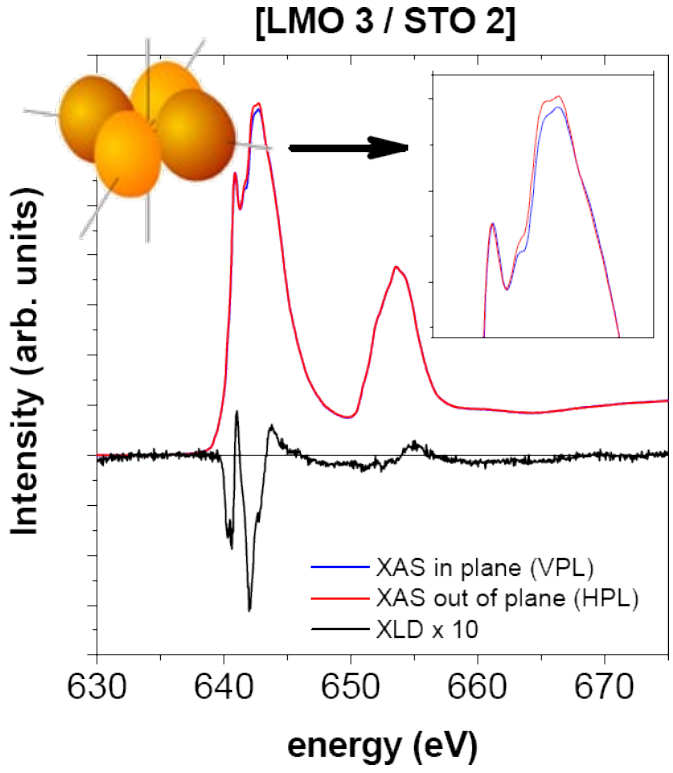


Natural linear dichroism in $LaMnO_3/SrTiO_3$

- X-ray Linear Natural Dichroism (XLD ou XLND)
- Grazing incidence to probe in and out of plane directions;

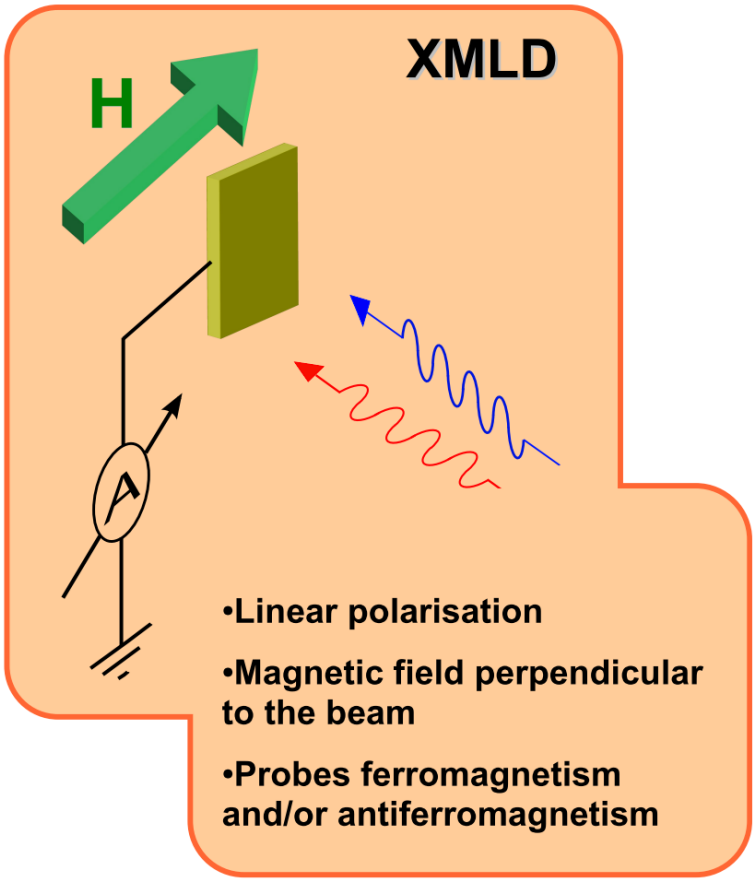






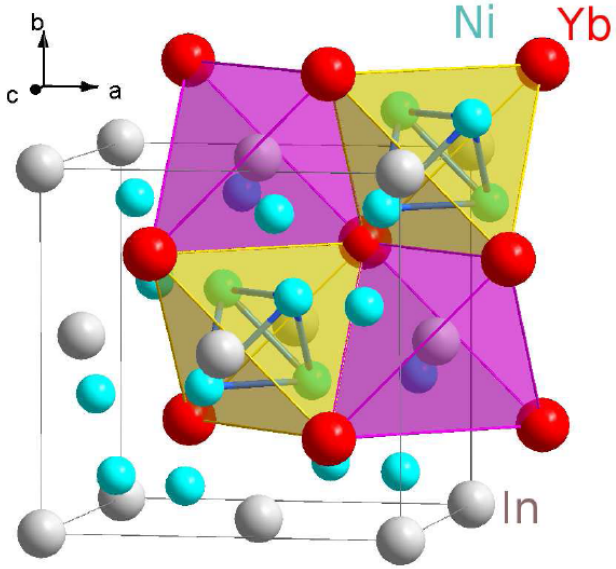
Garcia-Barriocanal et al., Nature Communications 1 (2010) doi:10.1038/ncomms1080

Magnetic Linear Dichroism



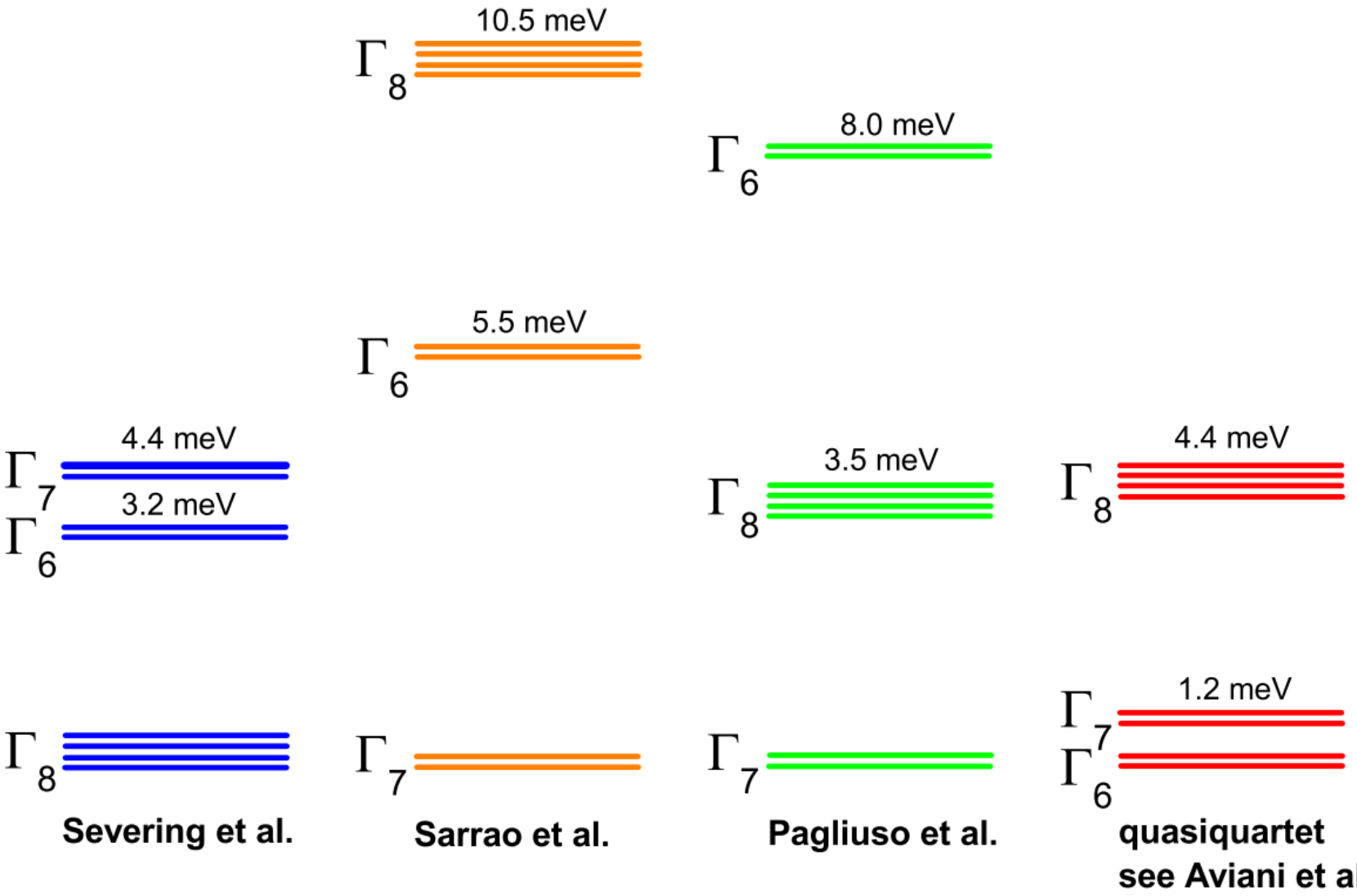
- X-ray Linear Magnetic Dichroism (XMLD)
- Anisotropy "induced" by magnetization;
- Adds up to natural dichroism!!
- Attention to the geometry: magnetic field perpendicular the X-ray beam propagation.

$YbInNi_4$

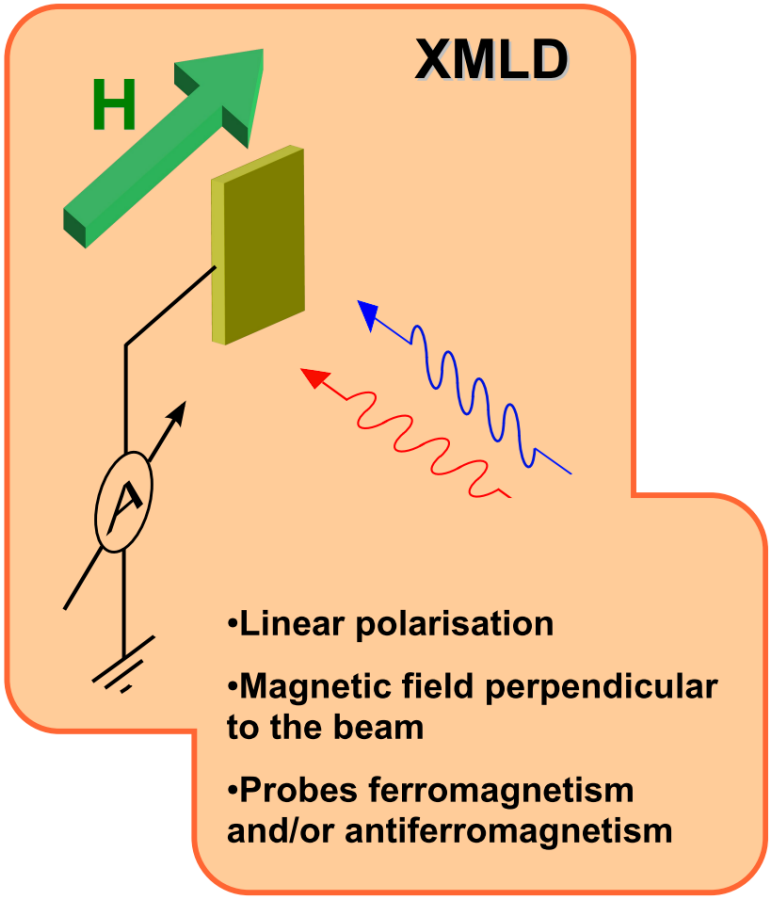


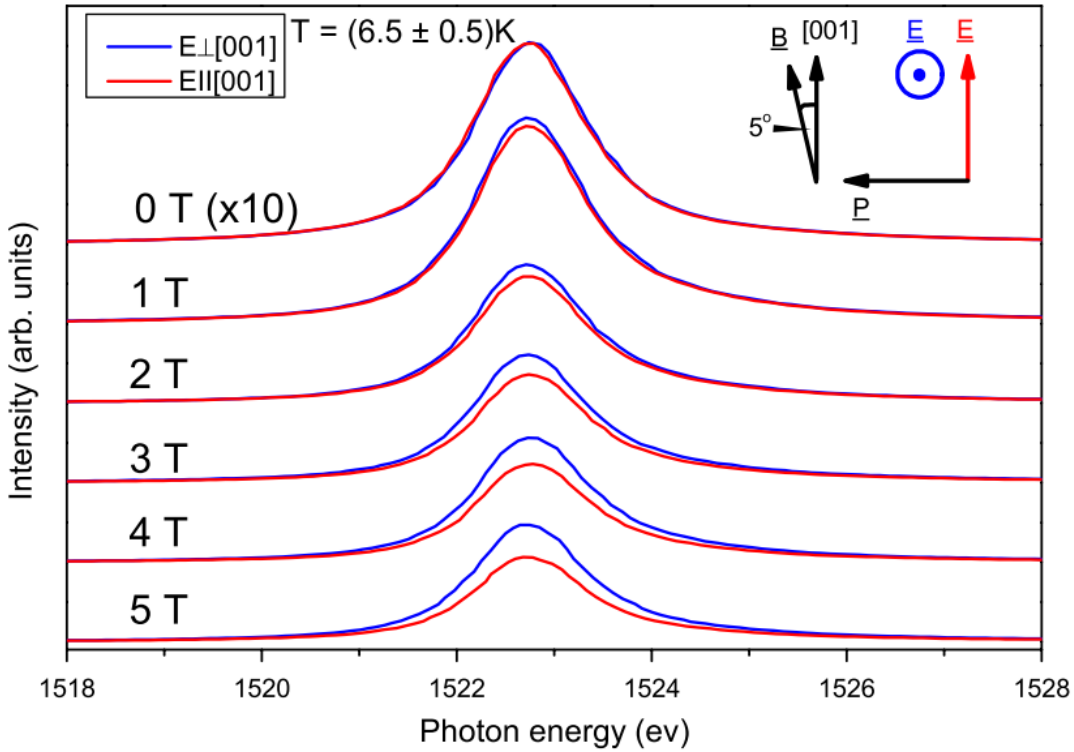
- cubice crystal lattice;
- Yb and In offset FFC lattices by 1/4, 1/4, 1/4;
- Ni tetrahedra around Yb e In;
- magnetic order below 3 K;
- Yb valence fixed 3+ .

$YbInNi_4$: debatable ground state

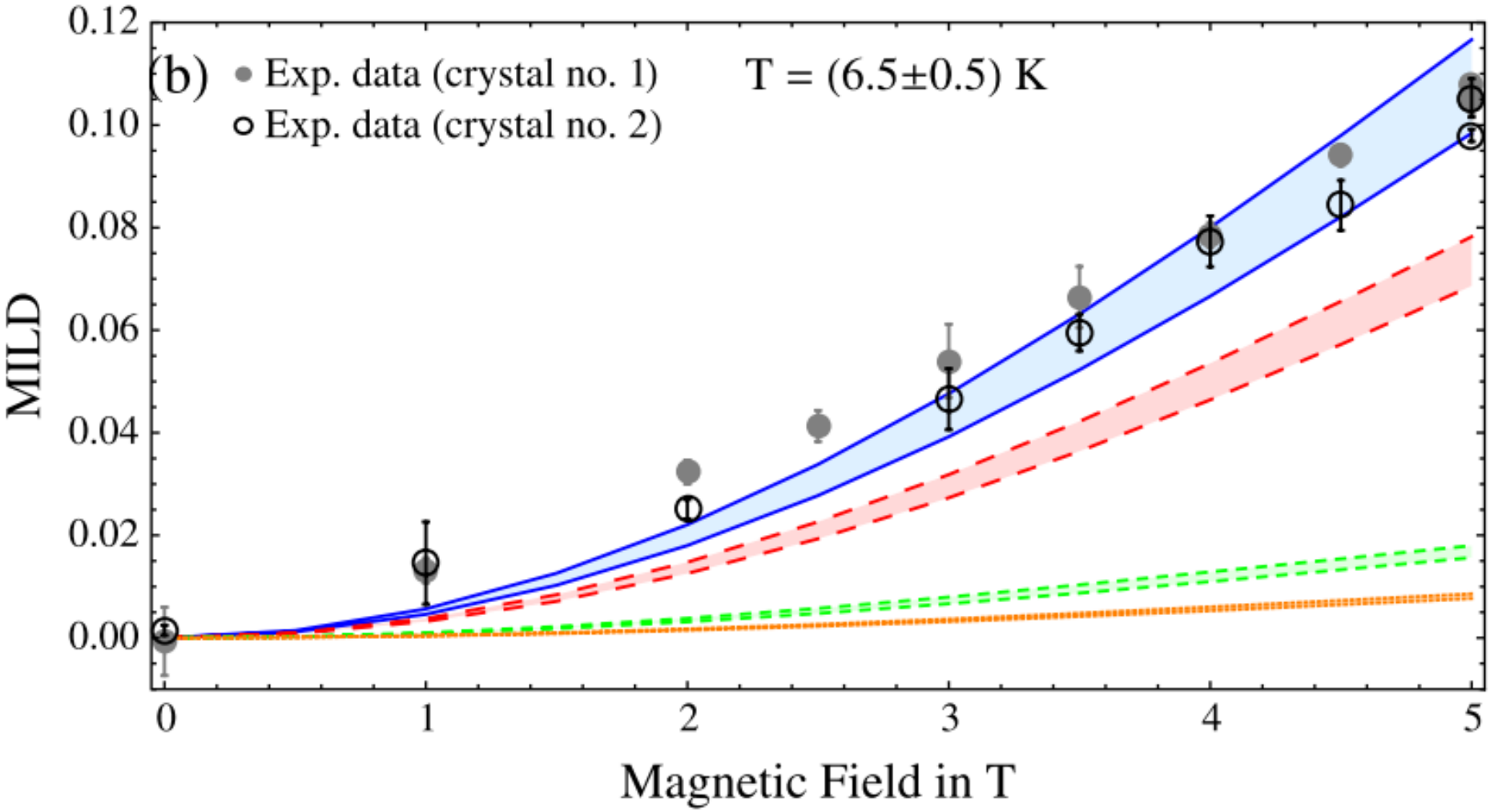


XMLD: $YbInNI_4$



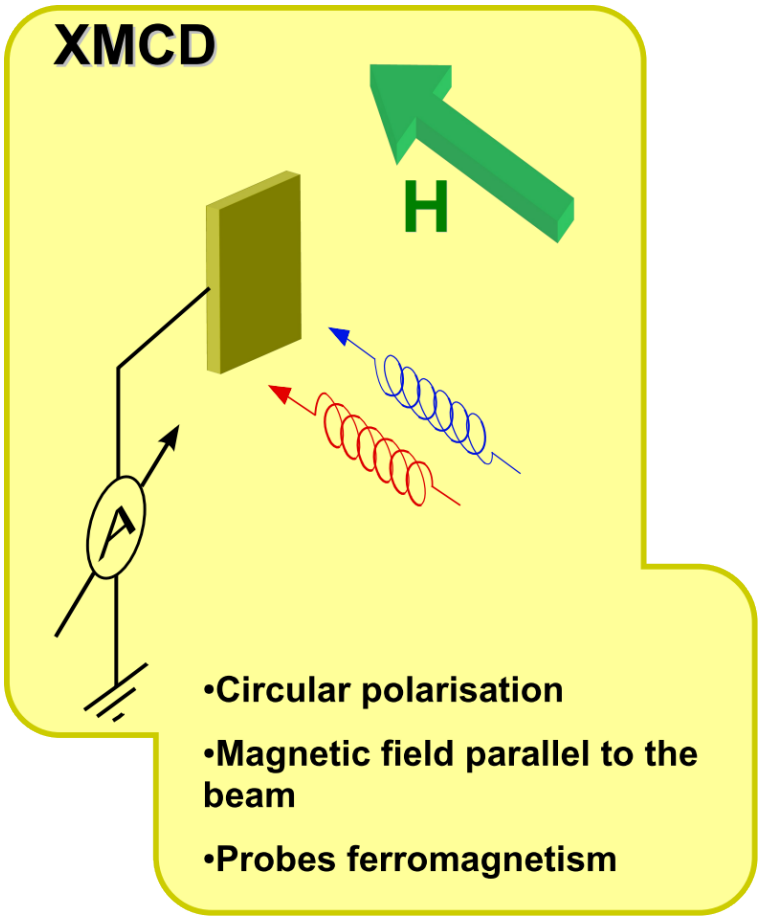


XMLD at the Yb M_5 edge



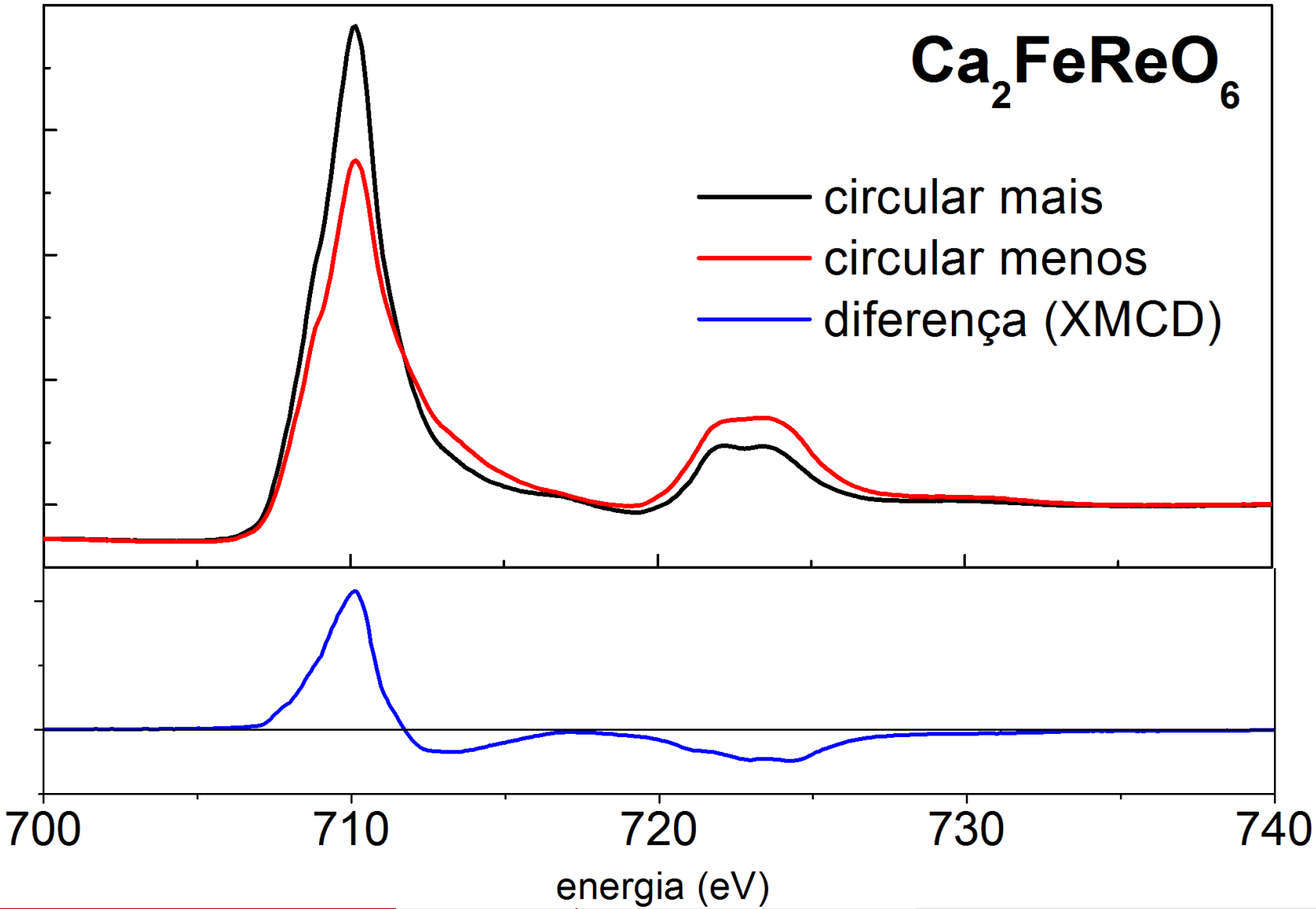
Willers et al., PRL 107, 236402 (2011)

Magnetic circular dichroism

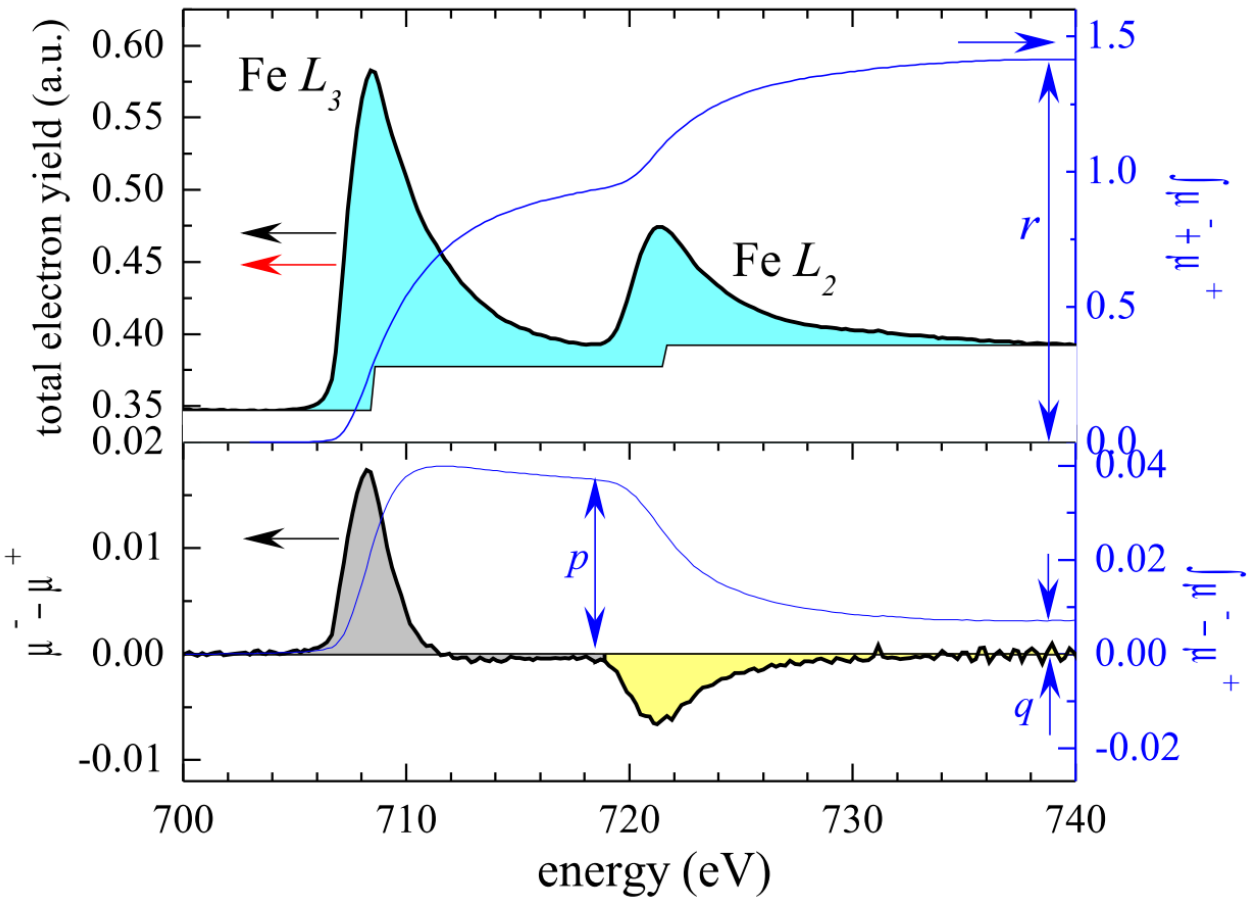


- X-ray Circular Magnetic Dichroism (XMCD)
- Anisotropy once more "induced" by magnetization;
- Effect does not add up with linear dichroism (natural or magnetic)
- Attention to the geometry: magnetic field parallel to the X-ray beam propagation direction

Fe XMCD on Ca_2FeReO_6



XMCD: SUM RULES INTEGRALS



$$m_{orb} = \langle L_Z \rangle = -n_h \frac{4q}{3r} \qquad m_{spin} = 2\langle S_Z \rangle + 7\langle T_Z \rangle = -n_h \frac{6p - 4q}{r}$$

XMCD is really cool!!

- XMCD is one of the most powerful tools to study magnetic materials :
  - magnetic information for each element in the sample;
  - for the same element, magnetic information for different orbitals;
  - element sensitive hysteresis curves;
  - element sensitive magnetic anisotropy;
  - very sensitive: soft X-rays can detect hundreths of monolayer ;
- ... but requires very good experimental data;
- ... sum rules are not universal. To avoid troubles: spectra simulation (ab initio, multiplets,...)!
- ... requires a good week of night shifts in the beam line.

Outline

XAS: TAKE AWAY MESSAGES

- XAS: intrisically element sensitive;
- XAS: needs a synchrotron;
- Can use hard or soft X-rays;
- Different detection modes:
  - transmission: well suited for hard X-rays; bulk sensitive;
  - fluorescence: works better with hard X-rays; bulk sensitive;
  - total electron yield: soft X-rays; surface sensitive;
- Absorption spectroscopy requires empty levels at the absorbing atom.