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Cinthia Piamonteze:: Paul Scherrer Institute

X-Ray Absorption Spectroscopy

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On A New Kind Of Rays
W.C. Röntgen, 1895

ON A NEW KIND OF RAYS.[1]

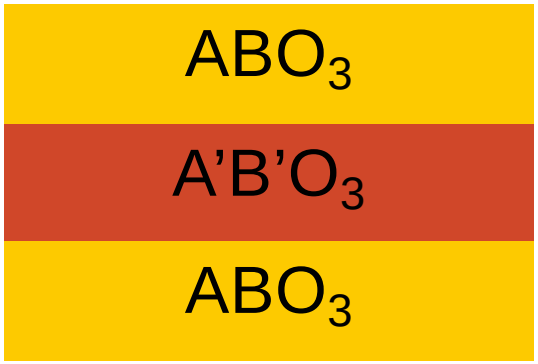
(1) A DISCHARGE from a large induction coil is passed through a Hittorf's vacuum tube, or through a well-exhausted Crookes' or Lenard's tube. The tube is surrounded by a fairly close-fitting shield of black paper; it is then possible to see, in a completely darkened room, that paper covered on one side with barium platinocyanide lights up with brilliant fluorescence when brought into the neighbourhood of the tube, whether the painted side or the other be turned towards the tube. The fluorescence is still visible at two metres distance. It is easy to show that the origin of the fluorescence lies within the vacuum tube.

(2) It is seen, therefore, that some agent is capable of penetrating black cardboard which is quite opaque to ultra-violet light, sunlight, or arc-light. It is therefore of interest to investigate how far other bodies can be penetrated by the same agent. It is readily shown that all bodies possess this same transparency, but in very varying degrees. For example, paper is very transparent; the fluorescent screen will light up when placed behind a book of a thousand pages; printer's ink offers no marked resistance. Similarly the fluorescence shows behind two packs of cards; a single card does not visibly diminish the brilliancy of the light. So, again, a single thickness of tinfoil hardly casts a shadow on the screen; several have to be superposed to produce a marked effect. Thick blocks of wood are still transparent. Boards of pine two or three centimetres thick absorb only very little. A piece of sheet aluminium, 15 mm. thick, still allowed the X-rays (as I will call the rays, for the sake of brevity) to pass, but greatly reduced the fluorescence. Glass plates of similar thickness behave similarly; lead glass is, however, much more opaque than glass free from lead. Ebonite several centimetres thick is transparent. If the hand be held before the fluorescent screen, the shadow shows the bones darkly, with only faint outlines of the surrounding tissues.

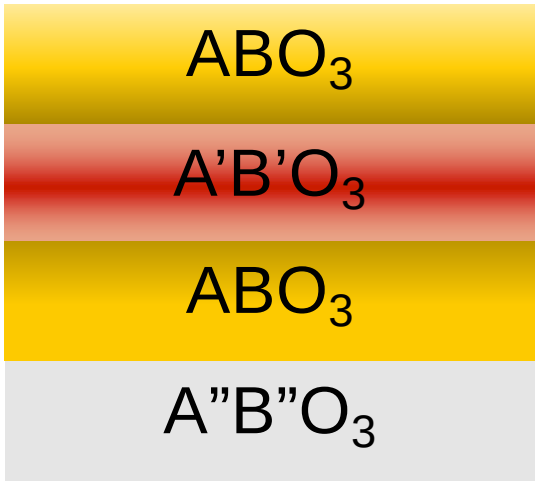
[1] By W. C. Röntgen. Translated by Arthur Stanton from the *Sitzungsberichte der Würzburger Physik-medic. Gesellschaft*, 1895.

A. Stanton, Nature **53**, 274 (1896).

Typical questions for X-ray absorption



Typical questions for X-ray absorption



What is the valence state?

What is the orbital occupation?

What is the magnetic coupling?

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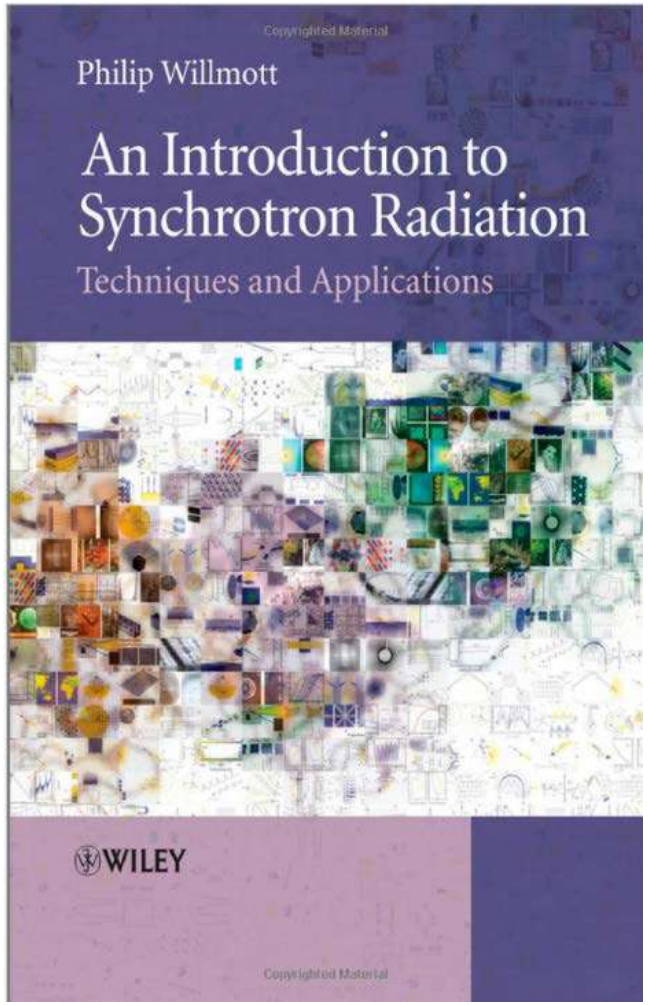
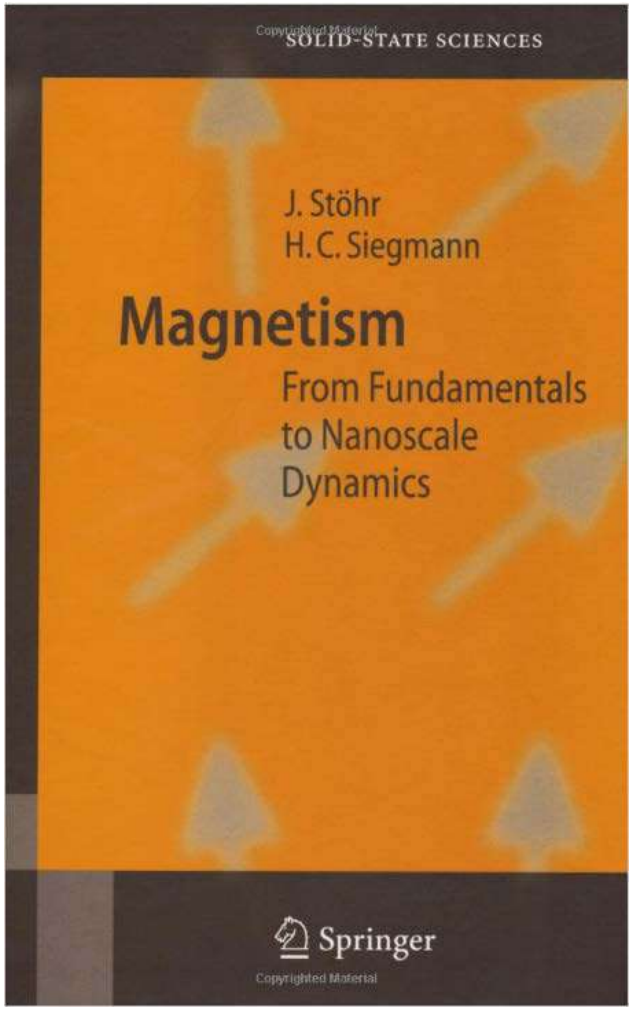
References





Outline of two lectures

- Lecture I:
  - X-ray absorption
- Lecture II:
  - Polarized x-rays: (circular / linear) dichroism

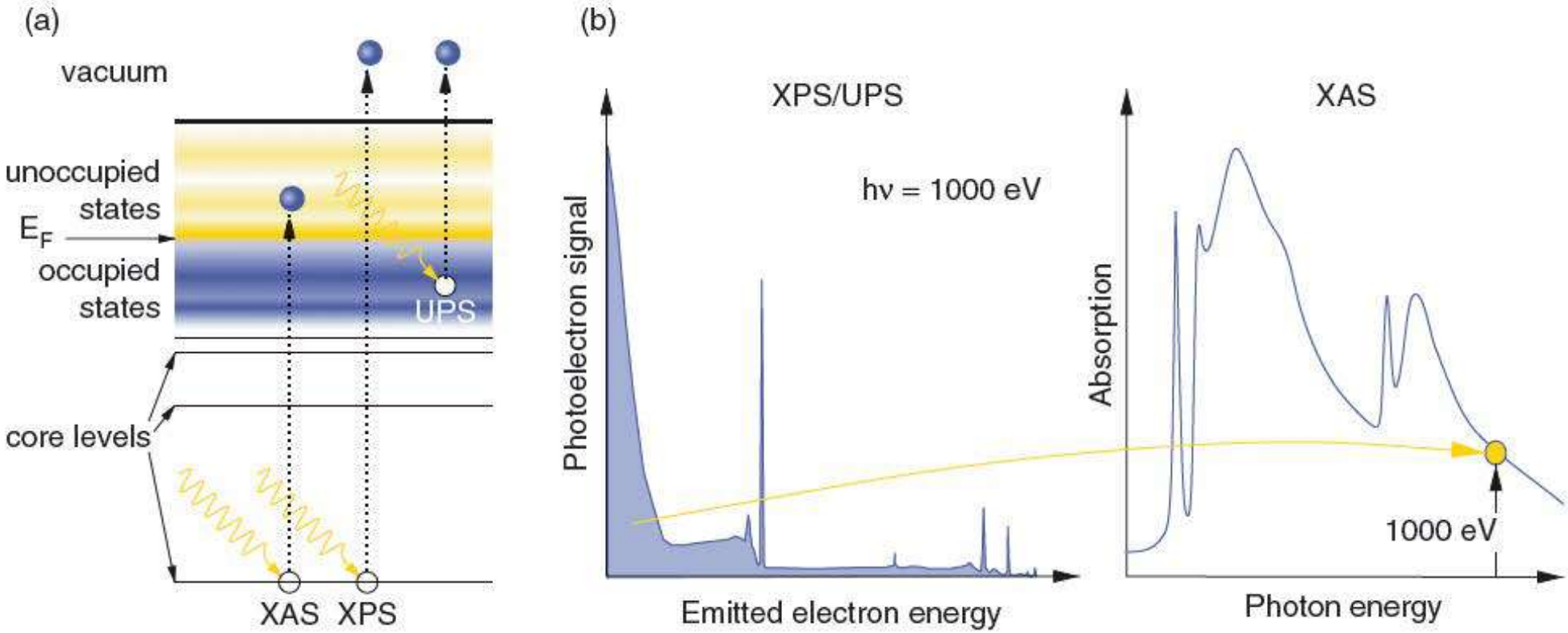
Outline

- General characteristics of synchrotron radiation
- Description of x-ray absorption in general
- Extended x-ray absorption fine structure (EXAFS)
  - Examples
- X-ray absorption at L-edges of transition metals
- Experimental setup
- Detection methods
  - Examples

XPS vs XAS

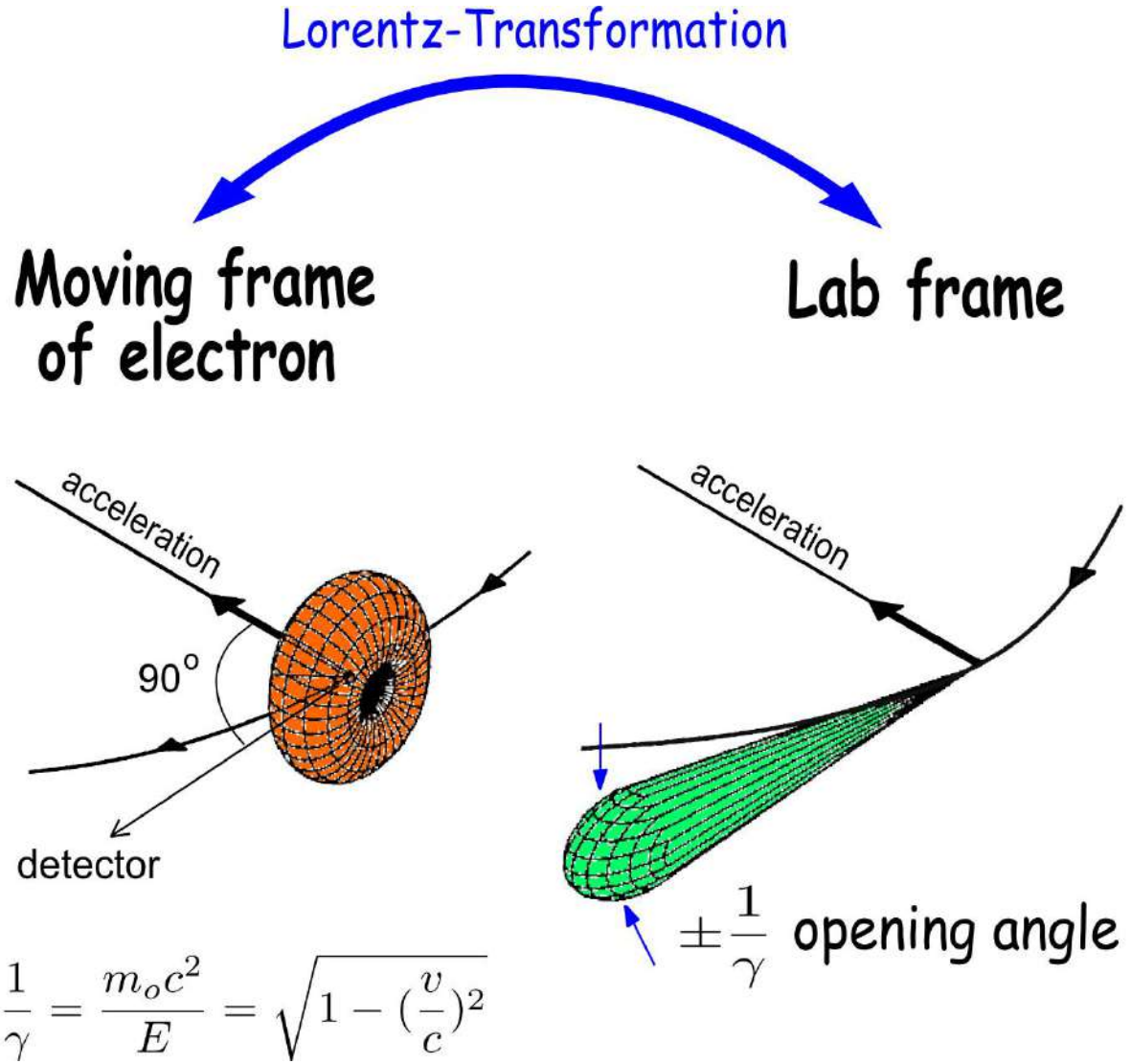
X-ray absorption requires a tunable and intense x-ray source:

=> synchrotron sources: source of intense and <u>polarized</u> x-rays



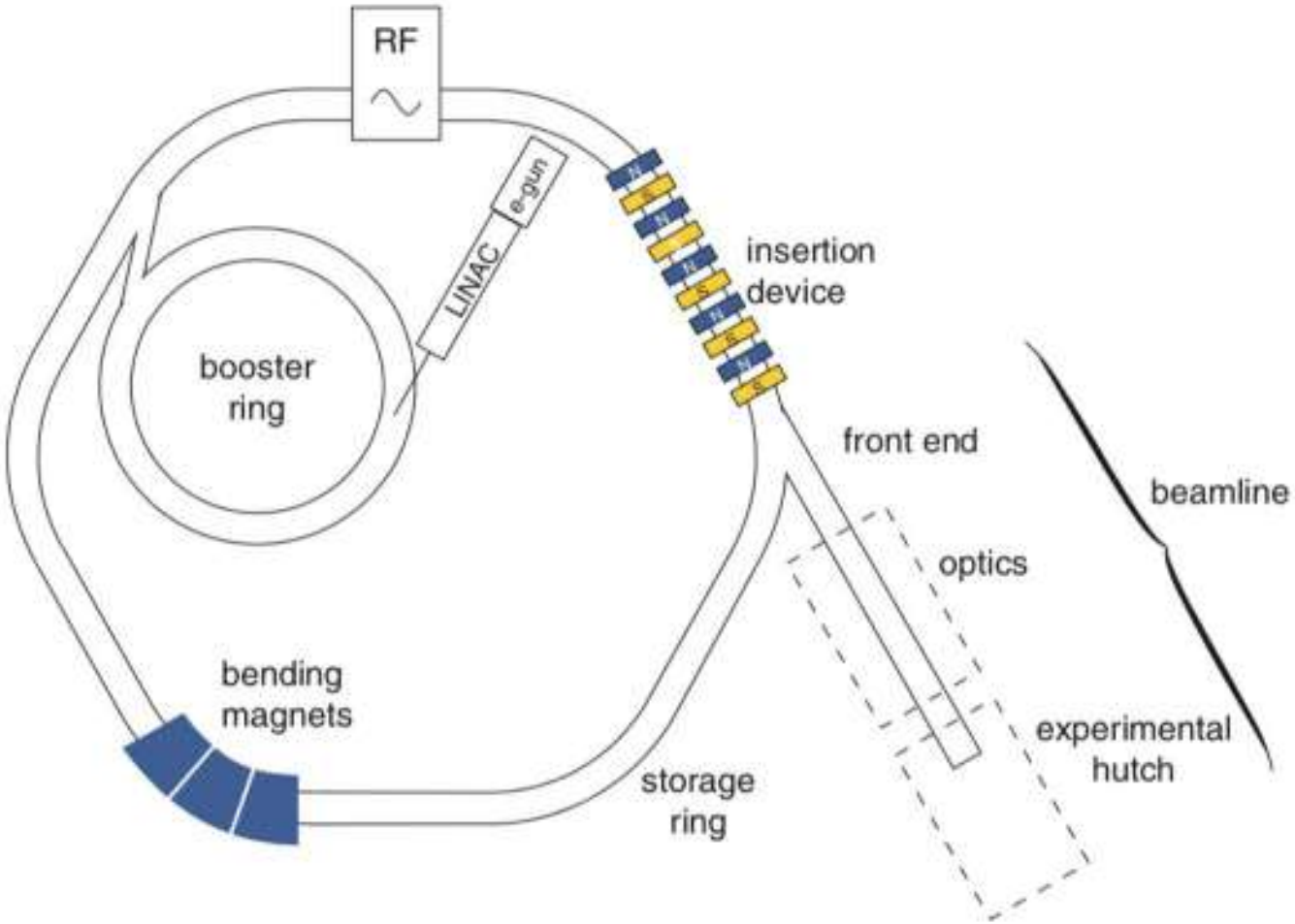
P. Willmott, *An Introduction to Synchrotron Radiation*.

Synchrotron radiation - divergence



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

Source – Synchrotron



P. Willmott, *An Introduction to Synchrotron Radiation*.

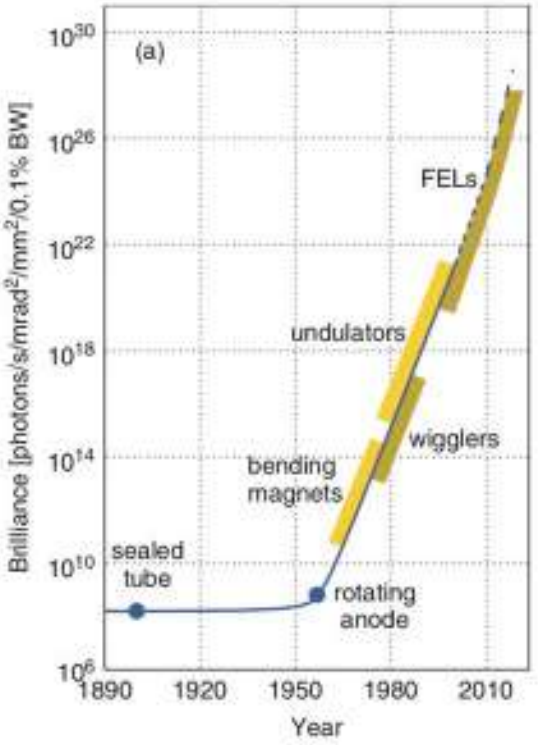
Source - Synchrotron

SLS storage ring – 330 magnets

Synchrotron radiation

Characteristics relevant to x-ray absorption

- High photon flux
- Small divergence => high brilliance
- Continuous in energy



Synchrotron Sources: Free Access

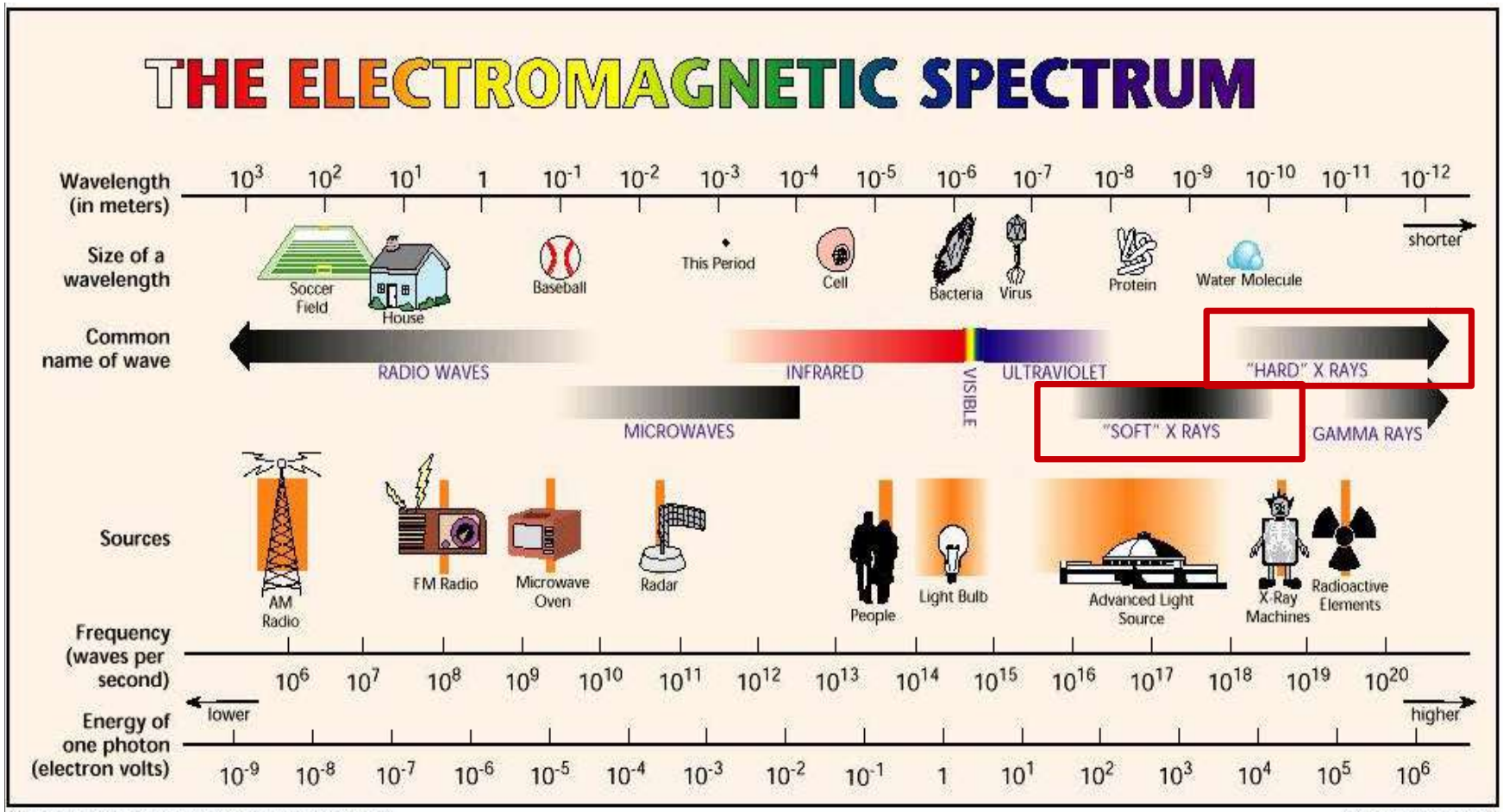
- Access by scientific merit through proposal submission
- Proposal submission deadlines for SLS: Sept. 15th ; March 15th
- Duo.PSI.ch

Synchrotron sources in the world

Source: lightsources.org

Synchrotron sources in Europe

Source: lightsources.org

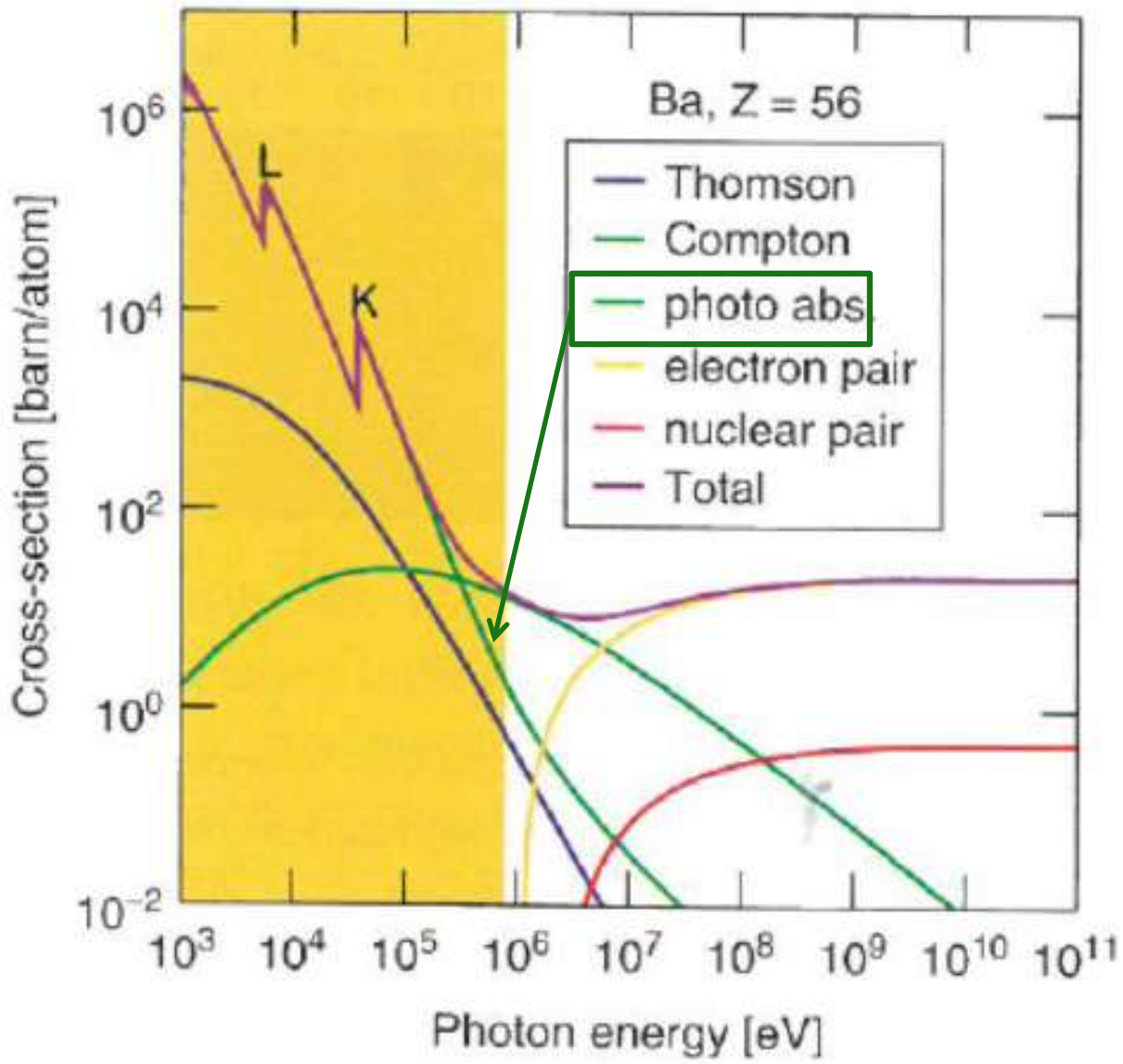


Courtesy of the Advanced Light Source, Berkeley Lab

XBD 9510-06262.ILR

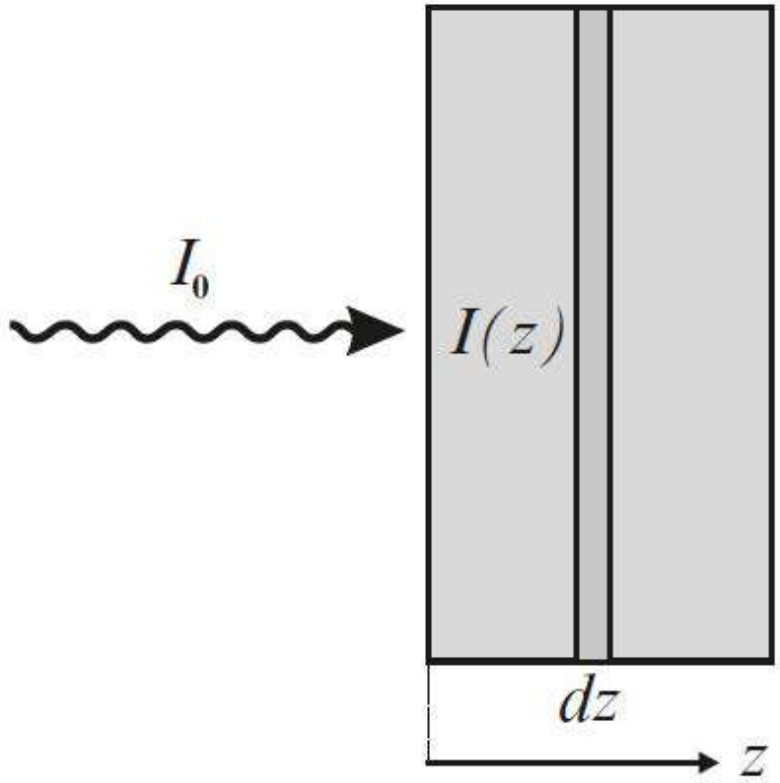
$$E = h\nu = hc/\lambda, \qquad \lambda\,[\text{Å}] = \frac{12.3984}{E\,[\text{keV}]}.$$

Cross sections of photon interaction



P. Willmott, *An Introduction to Synchrotron Radiation*.

Linear x-ray absorption coefficient

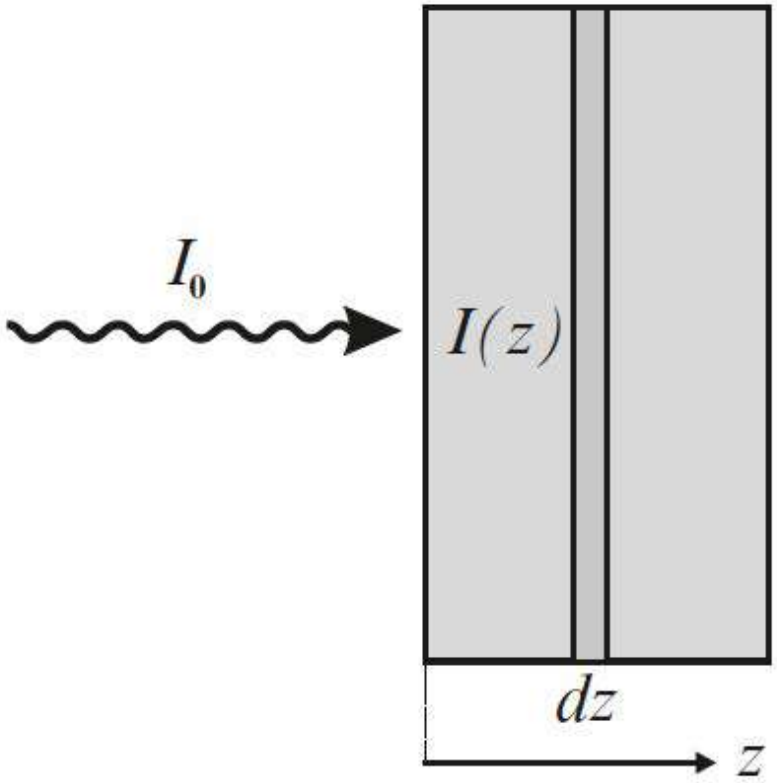


The beam is attenuated by $\mu_x dz$ due to a sheet of thickness dz:

$$-\mathrm{d}I(z) = I(z)\,\mu_x\,\mathrm{d}z$$

J. Stöhr and H. C. Siegmann, *Magnetism: From Fundamentals to Nanoscale Dynamics*

Linear x-ray absorption coefficient



The beam is attenuated by $\mu_x dz$ due to a sheet of thickness dz:

$$-\mathrm{d}I(z) = I(z)\,\mu_x\,\mathrm{d}z$$

$$I(z) = I_0\,\mathrm{e}^{-\mu_x z}$$

μ_x is the linear x-ray absorption coefficient

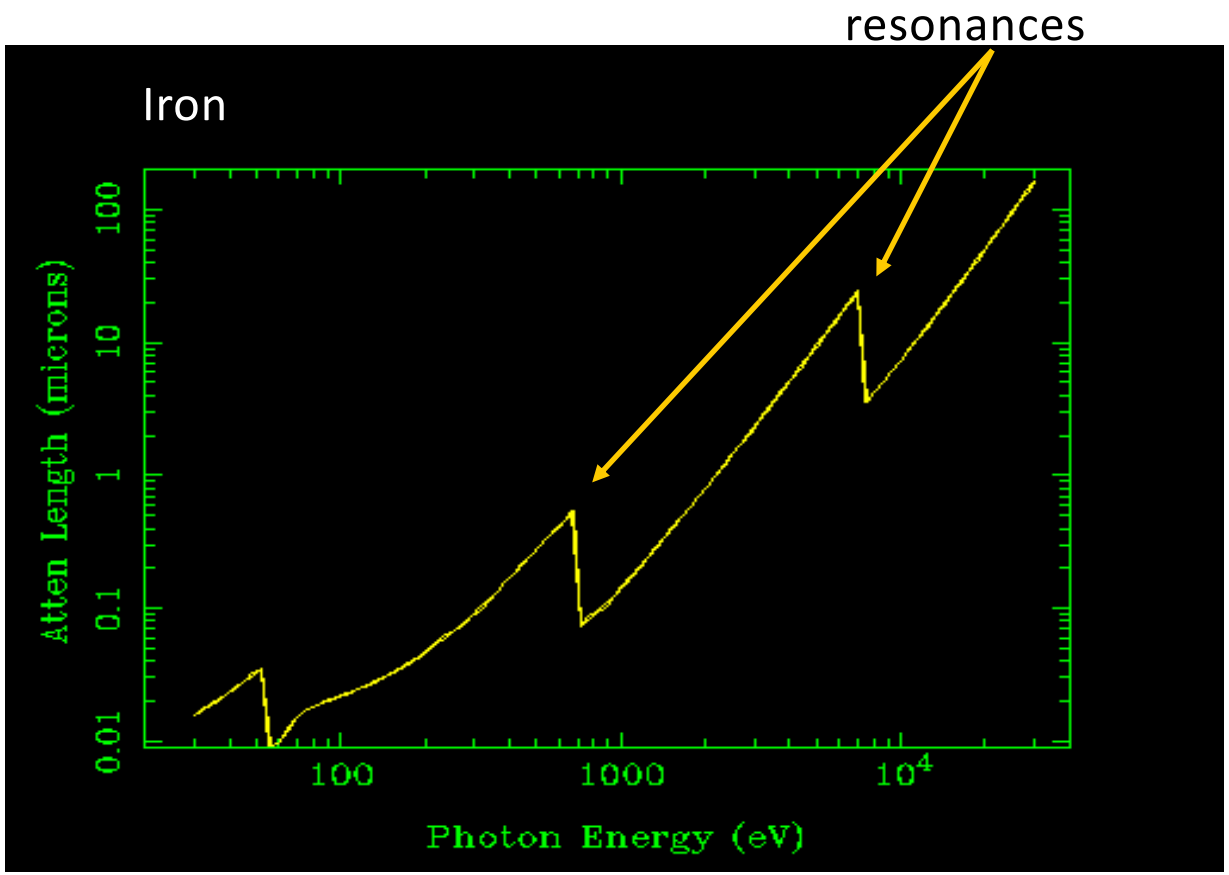
Unit: [1/distance]

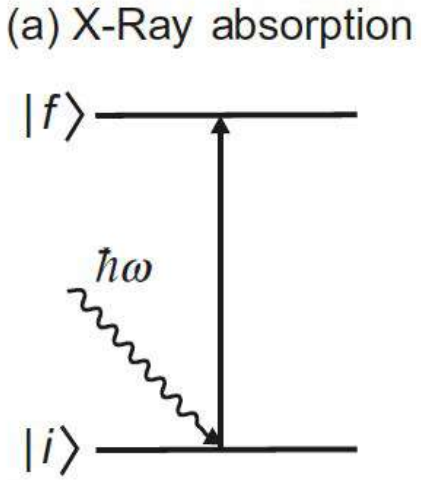
J. Stöhr and H. C. Siegmann, *Magnetism: From Fundamentals to Nanoscale Dynamics*

Attenuations length (λ_x)

$$I(z) = I_0\, e^{-\mu_x z}$$

$\lambda_x = 1/\mu_x$





data from: http://henke.lbl.gov/optical_constants/

Refractive index, linear absorption coefficient, absorption cross section

$$\beta = \frac{\mu_x}{2k} = \frac{\rho_{\mathrm{a}}}{2k}\sigma^{\mathrm{abs}}$$

β: imaginary part of refractive index (dimensionless)

μ_x: linear absorption coefficient ([1/length])

$\lambda_x = 1/\mu_x$ is the x-ray attenuation length:

k: $2\pi/\lambda$, where λ is the x-ray wavelength

ρ_a: atomic number density ([atoms/volume])

σ^{abs}: x-ray absorption cross section ([length^2/atom])

J. Stöhr and H. C. Siegmann, *Magnetism: From Fundamentals to Nanoscale Dynamics*

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Refractive index, linear absorption coefficient, absorption cross section

$$\beta = \frac{\mu_x}{2k} = \frac{\rho_\mathrm{a}}{2k}\,\sigma^\mathrm{abs}$$

$$\sigma = \frac{T_{if}}{\Phi_0}\ .$$

T_{if}: transition probability per unit time

Φ_0: incident photon flux

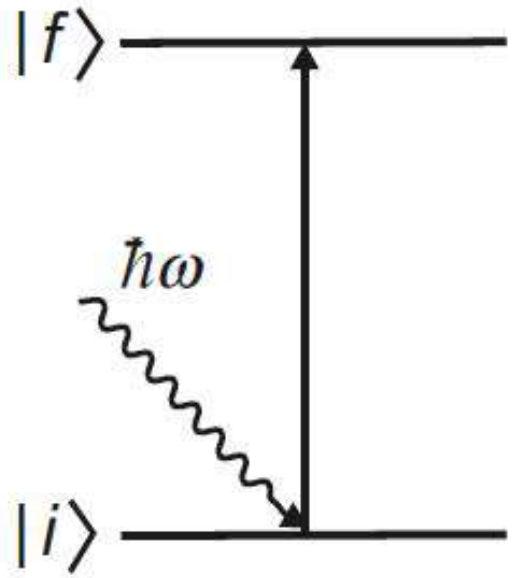
Transition probability per unit time

$$T_{if} = \frac{2\pi}{\hbar} |\langle f | \mathcal{H}_{int} | i \rangle|^2 \delta(\hbar\omega + \mathcal{E}_i - \mathcal{E}_f) \rho(\mathcal{E}_f)$$

energy conservation

density of final unoccupied states

(a) X-Ray absorption



$$\mathcal{H}_{\mathrm{e}}^{\mathrm{int}} = \frac{e}{m_{\mathrm{e}}} \boldsymbol{p} \cdot \boldsymbol{A}$$

electron momentum operator

electric field from electromagnetic wave

Matrix element

$$T_{if} = \frac{2\pi}{\hbar} |\langle f | \mathcal{H}_{int} | i \rangle|^2 \delta(\hbar\omega + \mathcal{E}_i - \mathcal{E}_f) \rho(\mathcal{E}_f)$$

$$\mathcal{M} = \langle b | \boldsymbol{p} \cdot \boldsymbol{\epsilon}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} | a \rangle$$

$$\mathcal{M} = \langle b | \boldsymbol{p} \cdot \boldsymbol{\epsilon}\, (1 + \mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r} + \ldots) | a \rangle$$

$$\boldsymbol{k} \cdot \boldsymbol{r} = \frac{2\pi}{\lambda} \boldsymbol{\epsilon} \cdot \boldsymbol{r}$$

for soft x-rays λ~1nm

2p core shell r~0.01nm

$$\boldsymbol{k} \cdot \boldsymbol{r} \ll 1$$

Matrix element

$$T_{if} = \frac{2\pi}{\hbar} |\langle f | \mathcal{H}_{int} | i \rangle|^2 \delta(\hbar\omega + \mathcal{E}_i - \mathcal{E}_f) \rho(\mathcal{E}_f)$$

$$\mathcal{M} = \langle b | \boldsymbol{p} \cdot \boldsymbol{\epsilon}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} | a \rangle$$

$$\mathcal{M} = \langle b | \boldsymbol{p} \cdot \boldsymbol{\epsilon}\, (1 + \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r} + \ldots) | a \rangle \simeq \langle b | \boldsymbol{p} \cdot \boldsymbol{\epsilon} | a \rangle = \mathrm{i} m_\mathrm{e} \omega \langle b | \boldsymbol{r} \cdot \boldsymbol{\epsilon} | a \rangle$$

dipolar approximation

$$\boldsymbol{k} \cdot \boldsymbol{r} \ll 1$$

Dipolar approximation

dipolar approximation $k \cdot r \ll 1 \Longrightarrow r \ll \frac{1}{k} = \frac{\lambda}{2\pi}$

assumes that the size of the absorbing atomic shell is small relative to x-ray wavelength

$$\mathcal{M} = \langle b| \boldsymbol{p} \cdot \boldsymbol{\epsilon} \, (1 + \mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r} + ...)|a\rangle \simeq \langle b| \boldsymbol{p} \cdot \boldsymbol{\epsilon}|a\rangle = \mathrm{i}m_{\mathrm{e}}\omega \langle b| \boldsymbol{r} \cdot \boldsymbol{\epsilon}|a\rangle$$

for soft x-rays λ~1nm

2p core shell r~0.01nm

Dipole selection rules

$$\mathcal{M} = \langle b|\, \boldsymbol{p}\cdot\boldsymbol{\epsilon}\,(1+\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}+\ldots)|a\rangle \simeq \langle b|\, \boldsymbol{p}\cdot\boldsymbol{\epsilon}|a\rangle = \mathrm{i}m_{\mathrm{e}}\omega\langle b|\, \boldsymbol{r}\cdot\boldsymbol{\epsilon}|a\rangle$$

r: electric dipole operator

allows transition between orbitals such that:

$$\Delta l = \pm 1;\ \Delta s = 0$$

dipole selection rules

The dipole selection rules can be interpreted as follows:

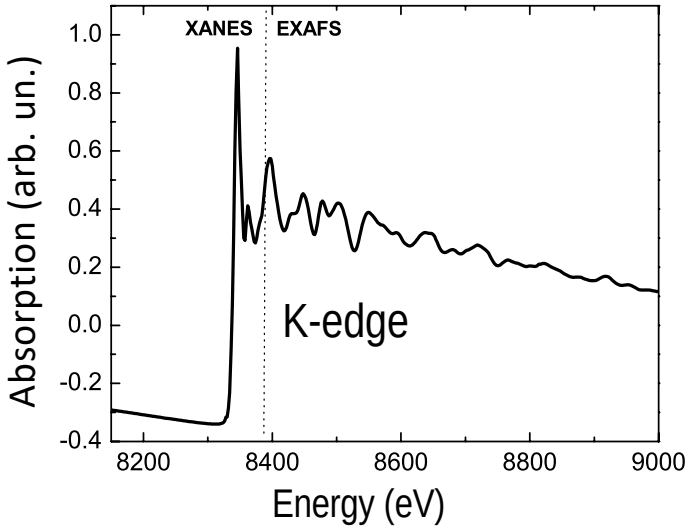
- The x-ray has an angular momentum and therefore allows transition between states that change the angular momentum (l) by 1
- The x-ray has no spin moment and therefore it allows transition between state where the spin moment (s) does not change

Dipole selection rules

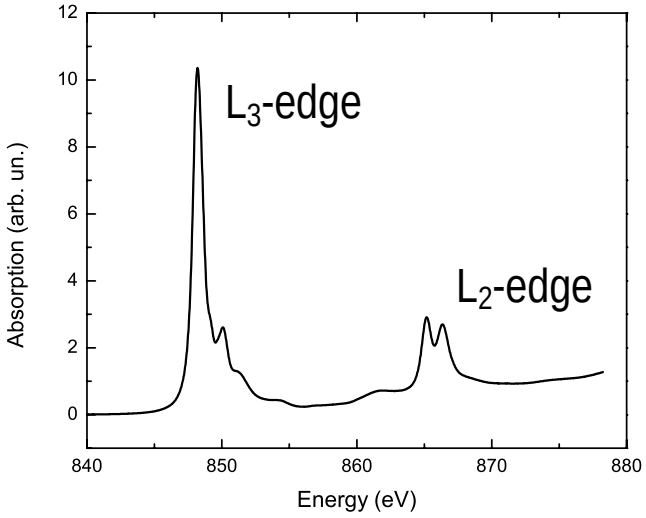
$$\Delta l = \pm 1;\ \Delta s = 0$$

1s core state transition

Ni absorption edges in NiO



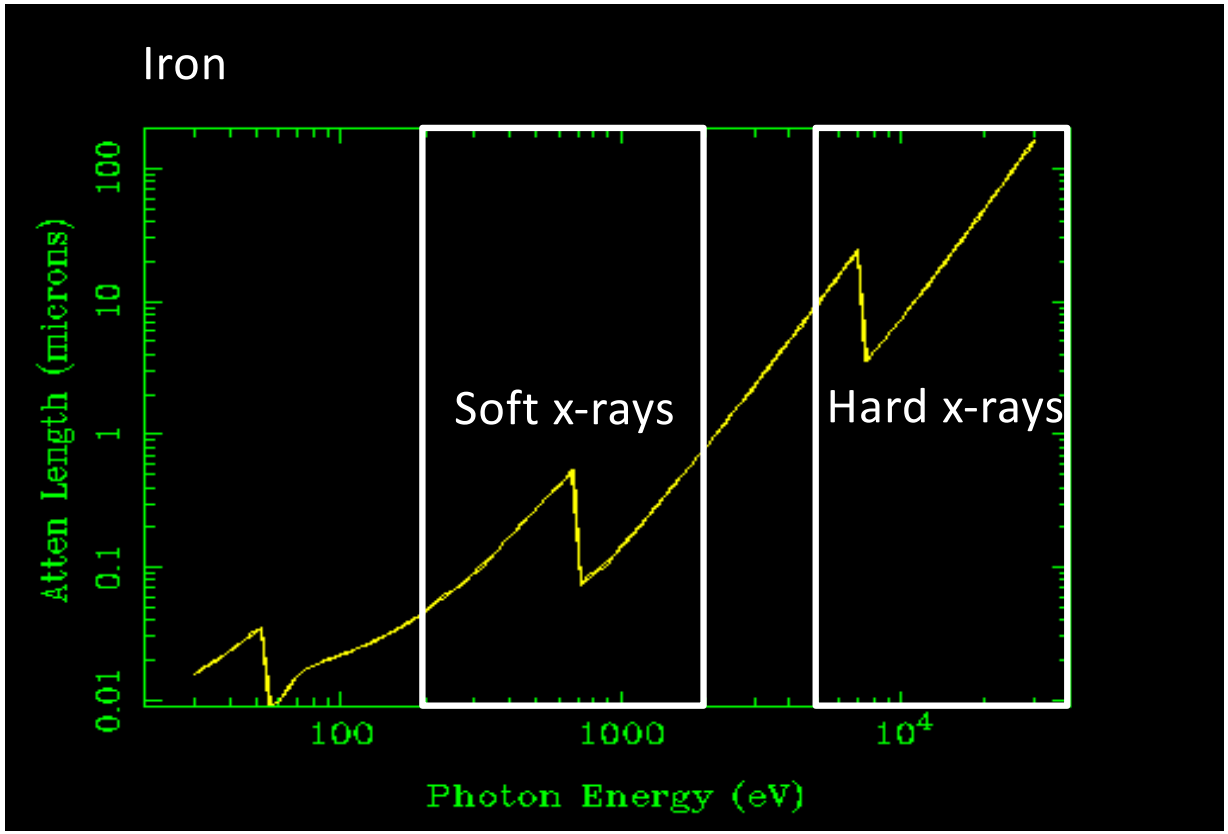
2p core state transition



Tabulated attenuation lengths (λ_x)

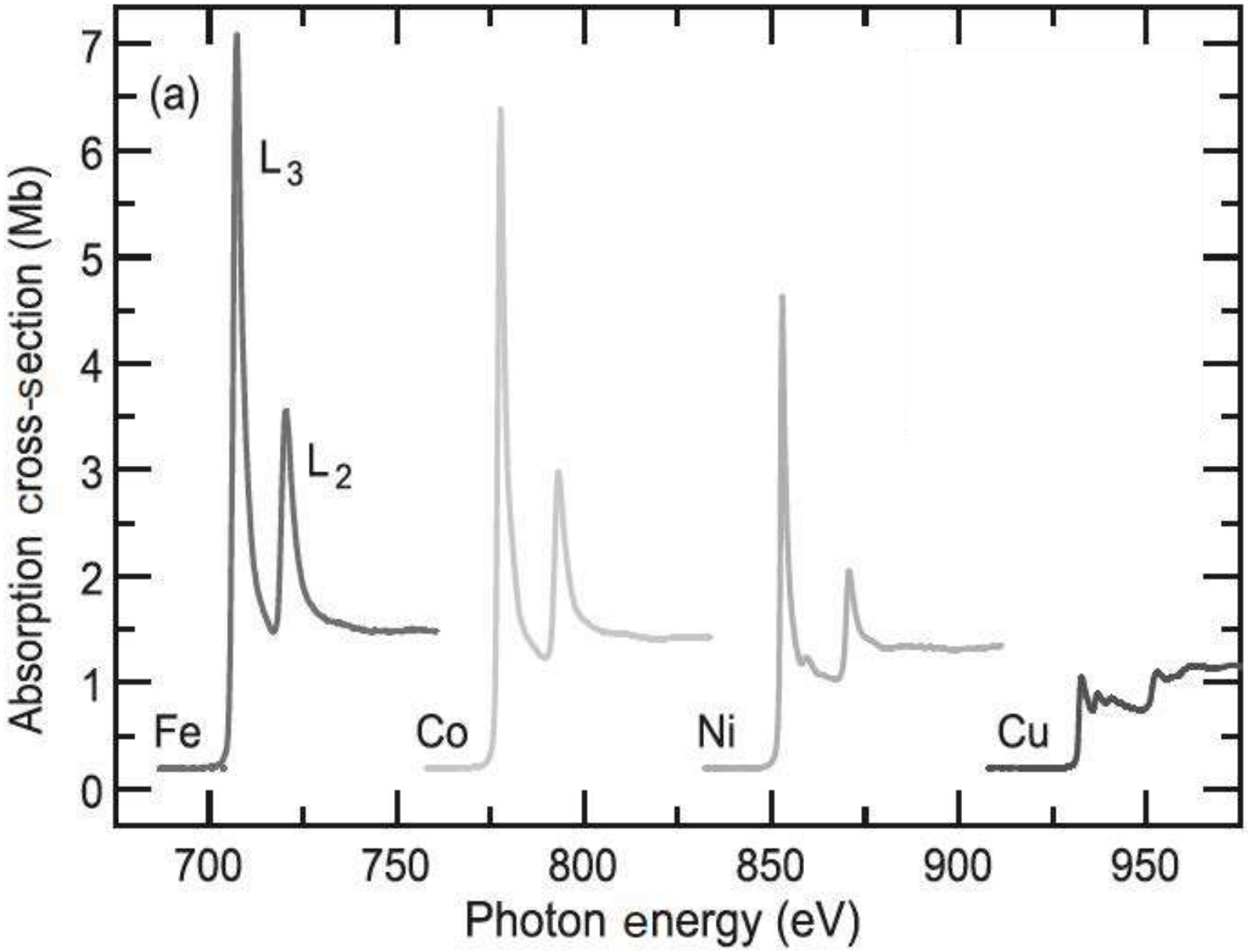
$$I(z) = I_0 \, e^{-\mu_x z}$$

$\lambda_x = 1/\mu_x$



data from: http://henke.lbl.gov/optical_constants/

Element specific



J. Stöhr and H. C. Siegmann, *Magnetism: From Fundamentals to Nanoscale Dynamics*

Summary XAS I

- X-ray absorption probes the density of unoccupied states
- XAS is element specific
- The strongest transition is through electric dipole
  - dipole selection rules:

$$\Delta l = \pm 1;\ \Delta s = 0$$

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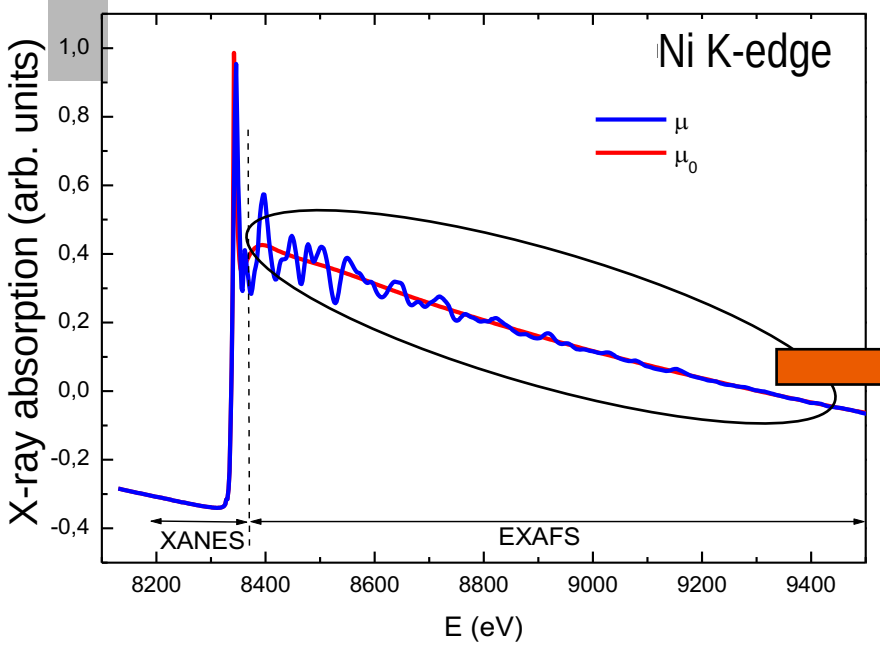
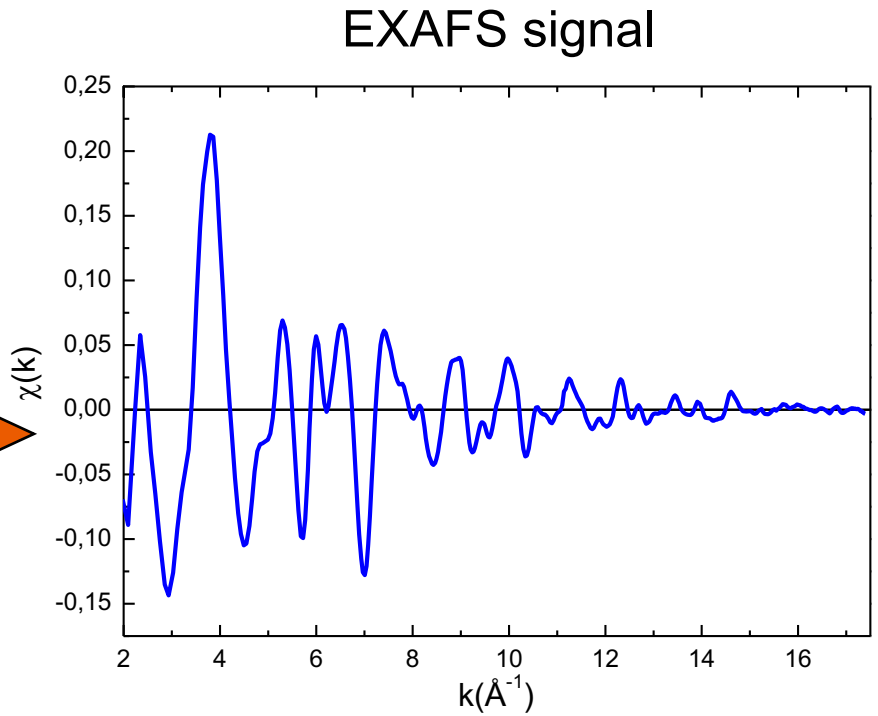
EXAFS

EXAFS signal

Extended X-ray Absorption Fine Structure





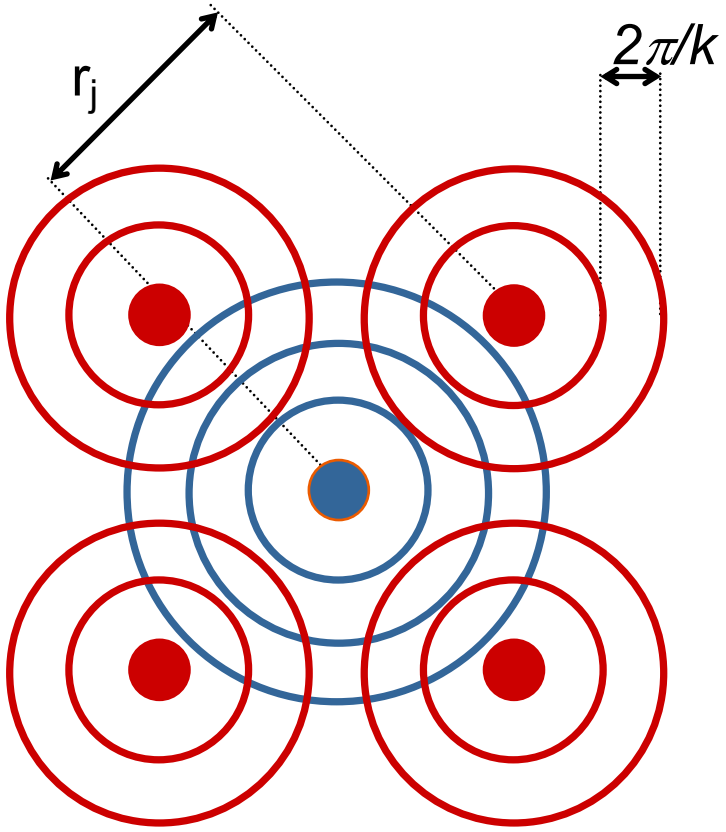
$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$

μ_0: atomic absorption

$$k = \sqrt{2m(E - E_0)}/\hbar \quad \text{[1/distance]}$$

EXAFS equation

$$\chi(\mathrm{k}) = \sum_j \frac{N_j}{kr_j^2} F_j(k,\pi)\sin[2kr_j + \psi_j(k)]e^{-2\sigma_j^2 k^2} e^{-2r_j/\lambda_j(k)}$$



r_j: interatomic distance

N_j: number of neighbors

σ_j: Debye-Waller factor

Fj: back-scattering amplitude

ψj: phase shift

λj: electron mean free path

Absorbing atom

Scatterer

EXAFS Analysis – Fourier Transform

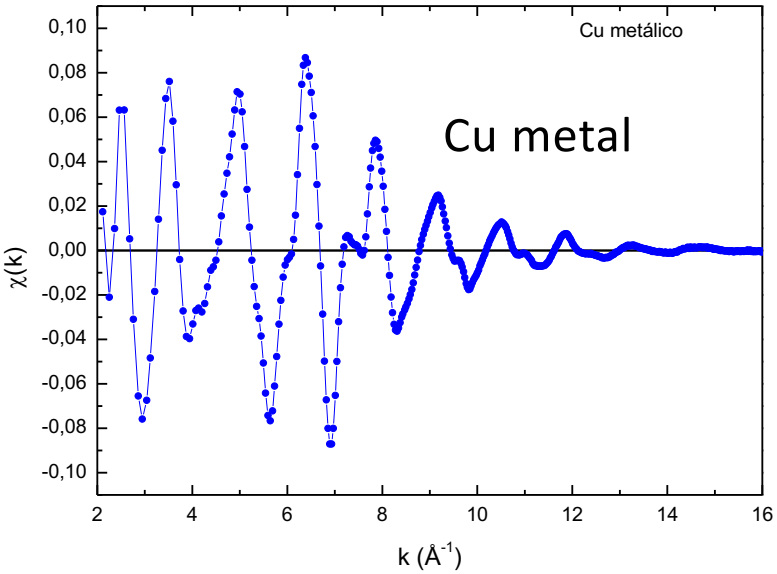
VOLUME 27, NUMBER 18 PHYSICAL REVIEW LETTERS 1 NOVEMBER 1971

New Technique for Investigating Noncrystalline Structures: Fourier Analysis of the Extended X-Ray–Absorption Fine Structure*

Dale E. Sayers† and Edward A. Stern†‡
Department of Physics, University of Washington, Seattle, Washington 98105

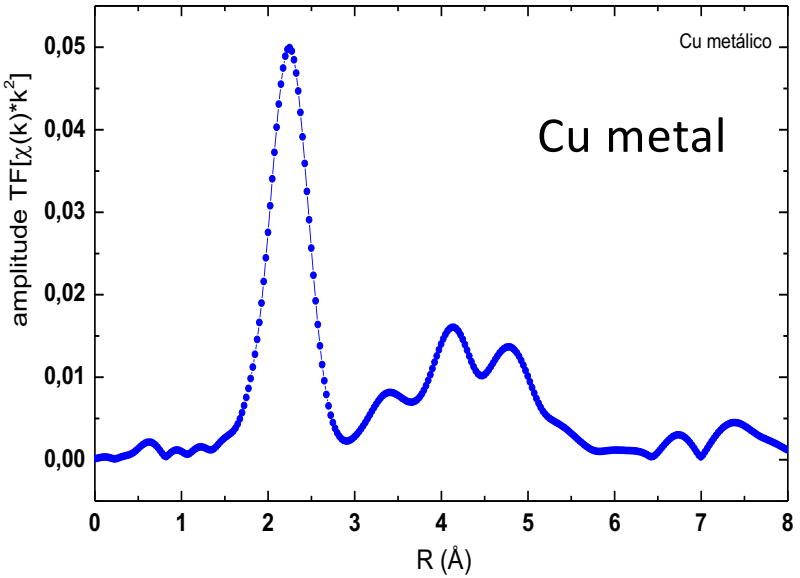
and

Farrel W. Lytle
Boeing Scientific Research Laboratories, Seattle, Washington 98124
(Received 16 July 1971)



Fourier

Transformation



Pseudo radial distribution function

EXAFS –Extended X-ray Absorption Fine Structure

- Can be used to obtain structural parameters around the absorbing atom, as:
  - Number of neighbors
  - Interatomic distances
  - Debye-Waller factor

- It give the structural parameters locally around the absorbing atom
  - Does not require long range order

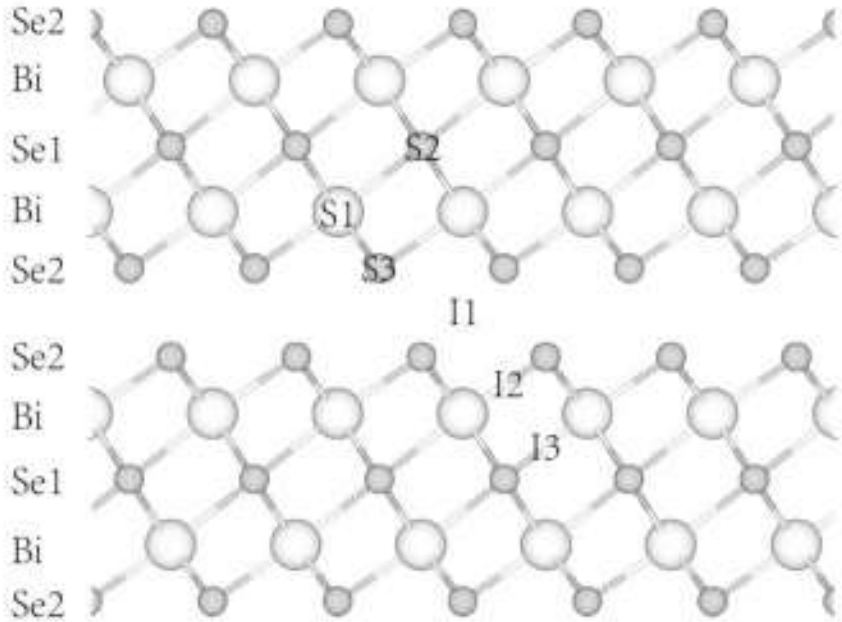
- It's often applied to:
  - Non-crystalline systems
  - Crystalline systems where some structural modifications are not long range ordered
  - Dopants

Example: EXAFS of Cr dopant on Bi_2Se_3

PHYSICAL REVIEW B **90**, 094107 (2014)

Local structures around 3*d* metal dopants in topological insulator Bi_2Se_3 studied by EXAFS measurements

Zhen Liu,[1] Xinyuan Wei,[1] Jiajia Wang,[1] Hong Pan,[1] Fuhao Ji,[1] Fuchun Xi,[1] Jing Zhang,[2] Tiandou Hu,[2] Shuo Zhang,[3] Zheng Jiang,[3] Wen Wen,[3] Yuying Huang,[3] Mao Ye,[4] Zhongqin Yang,[1,*] and Shan Qiao[4,5,1]



Z. Liu, *et al*, PRB **90**, 85 (2014).

Example: EXAFS of Cr dopant on Bi_2Se_3

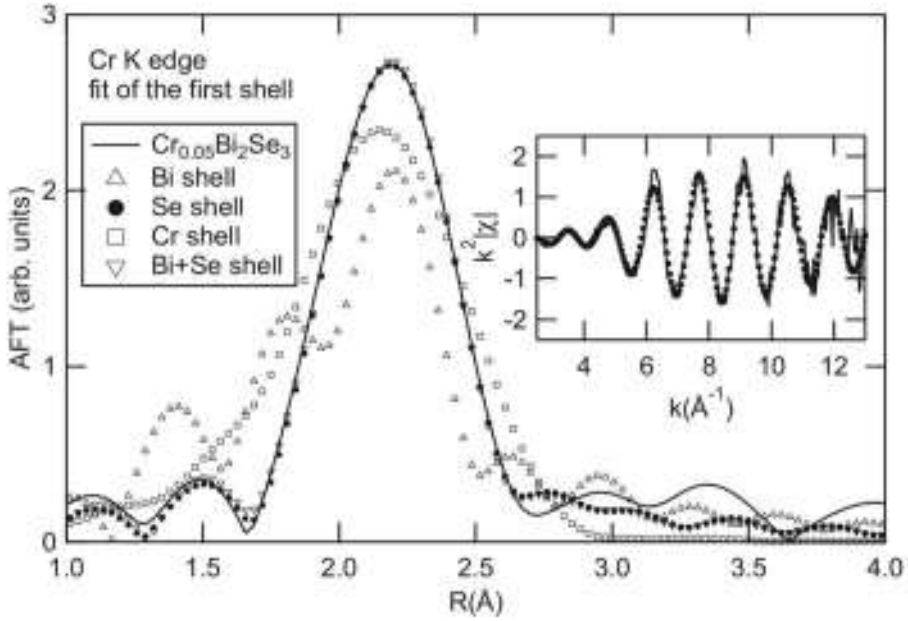


TABLE III. The structural parameters from the first shell fittings with the models.

Model	Pair	R (Å)	N	S_0^2	$\triangle E$ (eV)	σ^2 (Å^2)	R factor
Bi shell	Cr-Bi	2.21 ± 0.01	3 ± 2	0.66	-4 ± 4	0.000 ± 0.003	7%
Cr shell	Cr-Cr	2.54 ± 0.04	8	0.66	-16 ± 7	0.006 ± 0.002	6%
	Cr-Cr	2.93 ± 0.04	6	0.66	-16 ± 7	0.006 ± 0.002	
Se shell	Cr-Se	2.50 ± 0.01	6	0.66	-1 ± 1	0.0033 ± 0.0002	0.2%
Bi+Se shell	Cr-Bi	2.50 ± 0.01	6 ± 1	0.66	-25 ± 10	0.06 ± 0.04	0.2%
	Cr-Se	2.50 ± 0.01	6 ± 1	0.66	-1 ± 1	0.0036 ± 0.0007	

Z. Liu, *et al*, PRB **90**, 85 (2014).

PHYSICAL REVIEW B **71**, 012104 (2005)

Short-range charge order in RNiO$_3$ perovskites (R=Pr, Nd, Eu, Y) probed by x-ray-absorption spectroscopy

Cínthia Piamonteze,[1,2] Hélio C. N. Tolentino,[1] Aline Y. Ramos,[1,3] Nestor E. Massa,[4] Jose A. Alonso,[5] Maria J. Martínez-Lope,[5] and Maria T. Casais[5]

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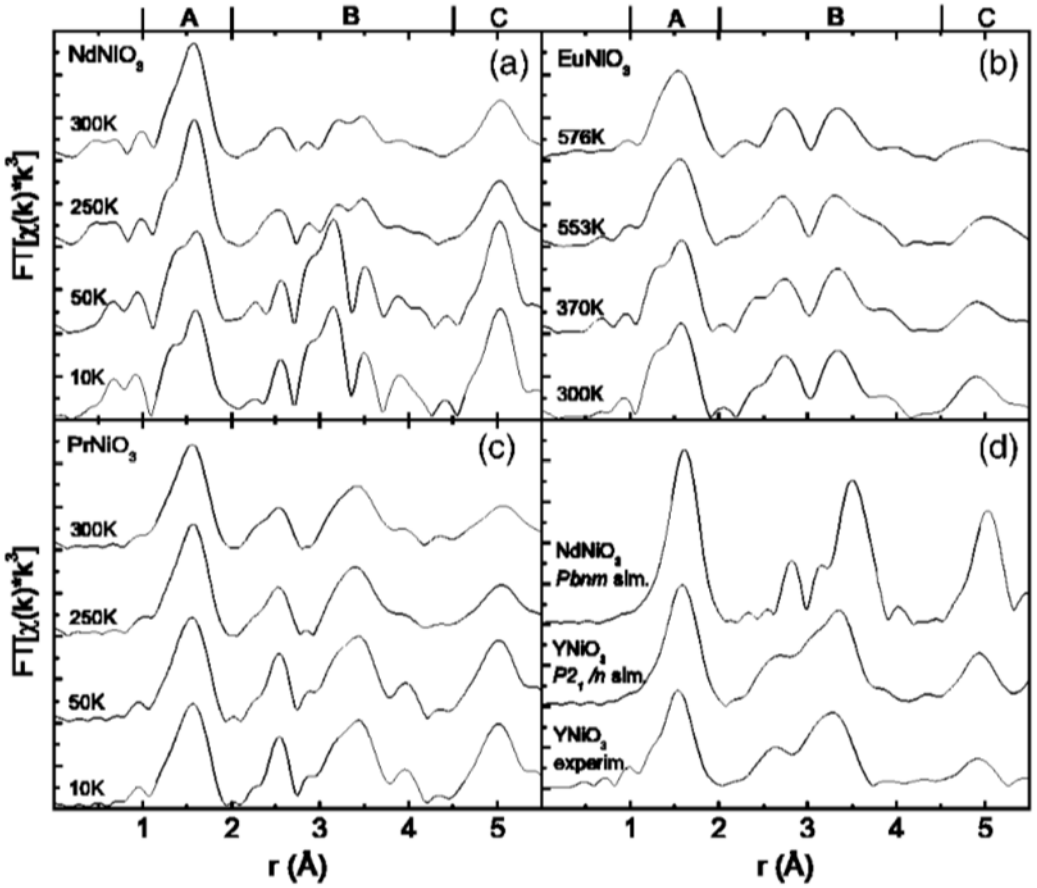
(Received 10 August 2004; published 25 January 2005)



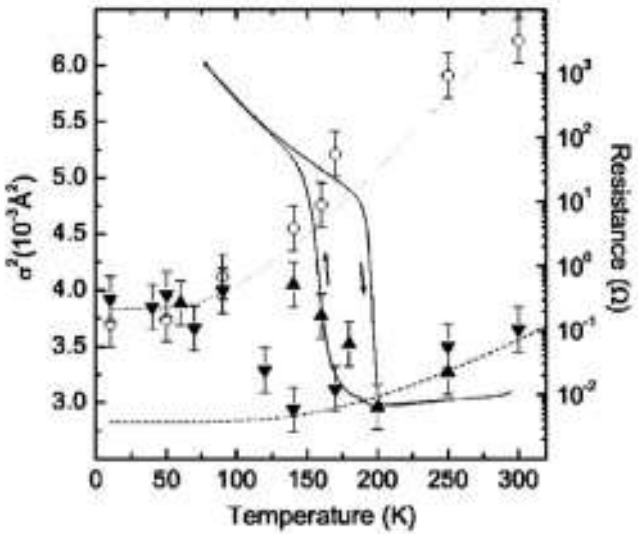


FIG. 3. Total disorder for the $NdNiO_3$ coordination shell while decreasing (▼) and increasing (▲) the temperature, and for Ni shell at 5 Å (○). Thermal behavior for the coordination shell (---) and Ni shell (···), and resistance (—).

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Transition Metal L-edges

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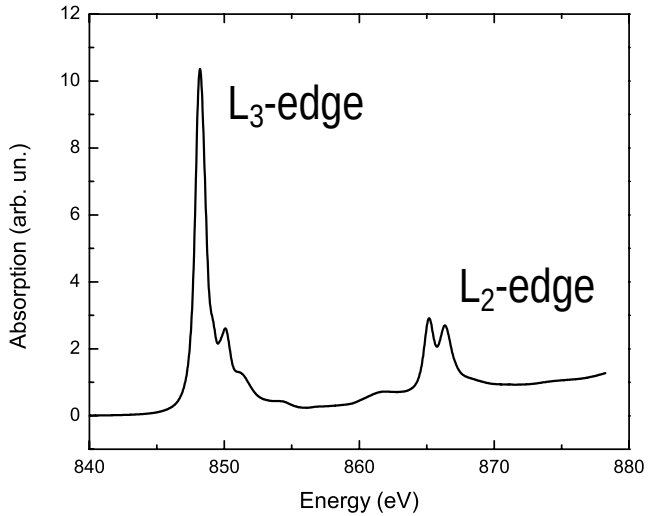
Why should one study the transition metal L-edges?

$L_{2,3}$ edges:
2p core state
transition 2p -> 3d

Ni absorption edges in NiO



Why should one study the transition metal L-edges?

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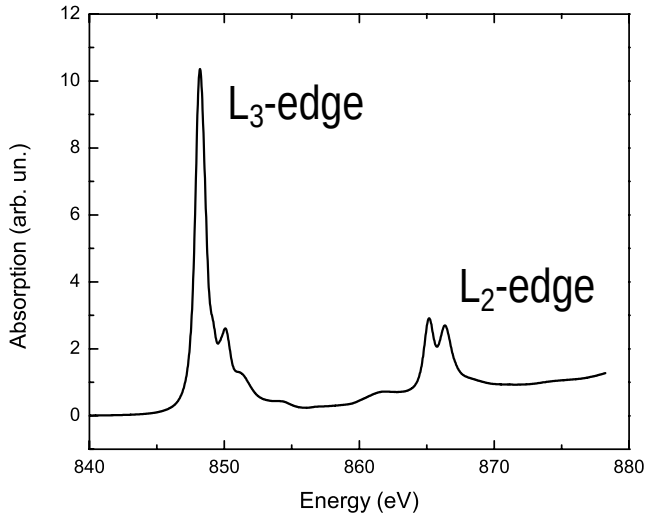
Why should one study the transition metal L-edges?

$L_{2,3}$ edges:
2p core state
transition 2p -> 3d

Ni absorption edges in NiO

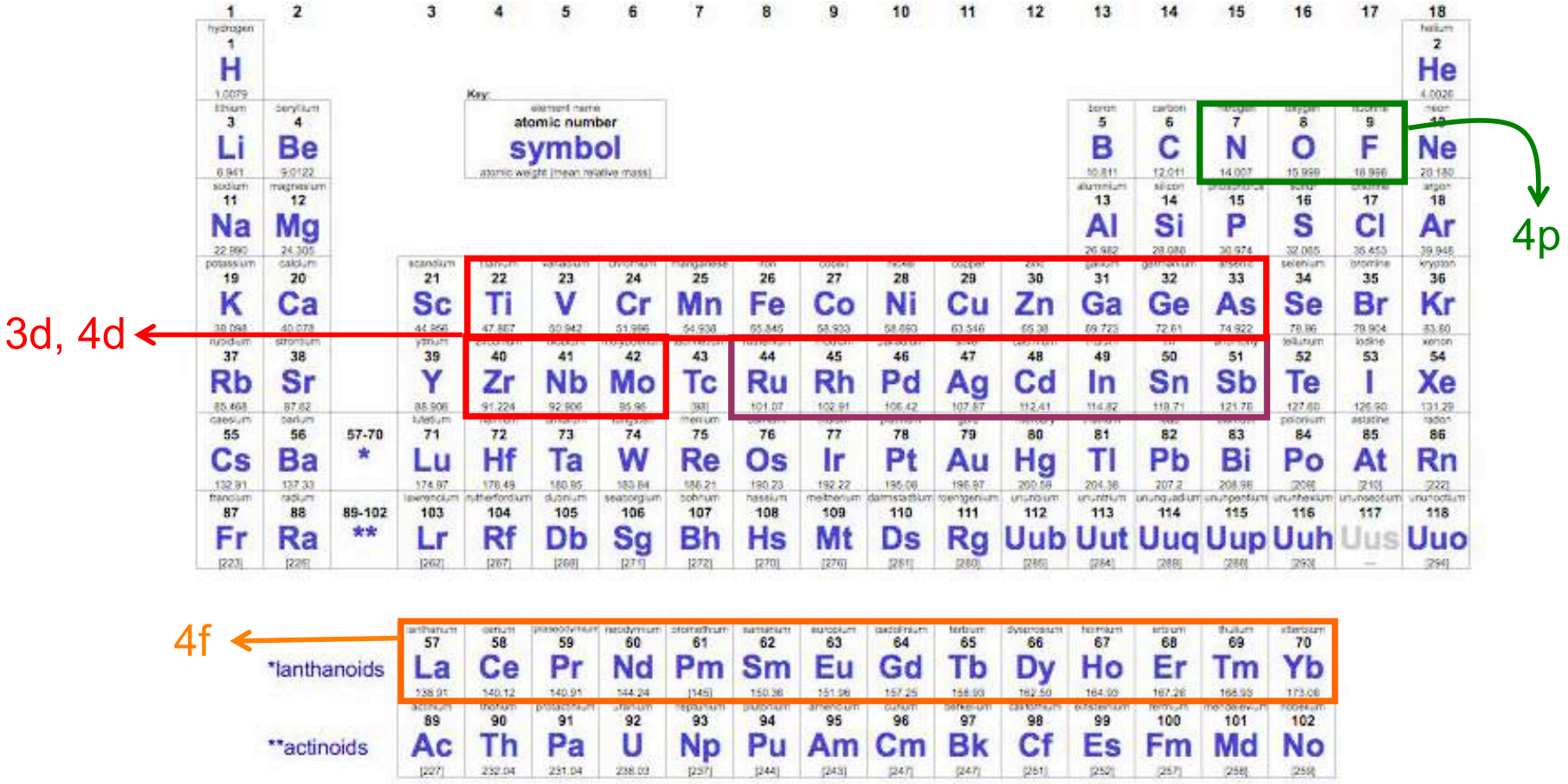


Why should one study the transition metal L-edges?

3d band
- the valence band => valence state
- outer most band => ligand field
- Partially field => magnetism

Soft X-ray range (400eV-2000eV)

- K-edges: 1s $\rightarrow$*4***p**
- $L_{2,3}$-edges: 2p $\rightarrow$*3***d**
- $M_{2,3}$-edges: 3p $\rightarrow$*4***d**
- $M_{4,5}$-edges: 3d $\rightarrow$ *4***f**



K-edge quadrupolar transition

Fe K-edge in different compounds

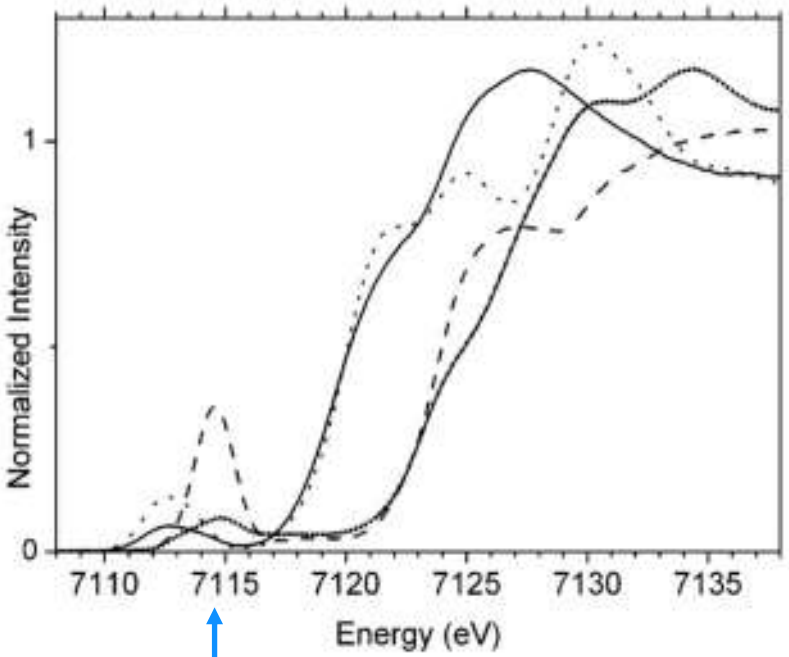


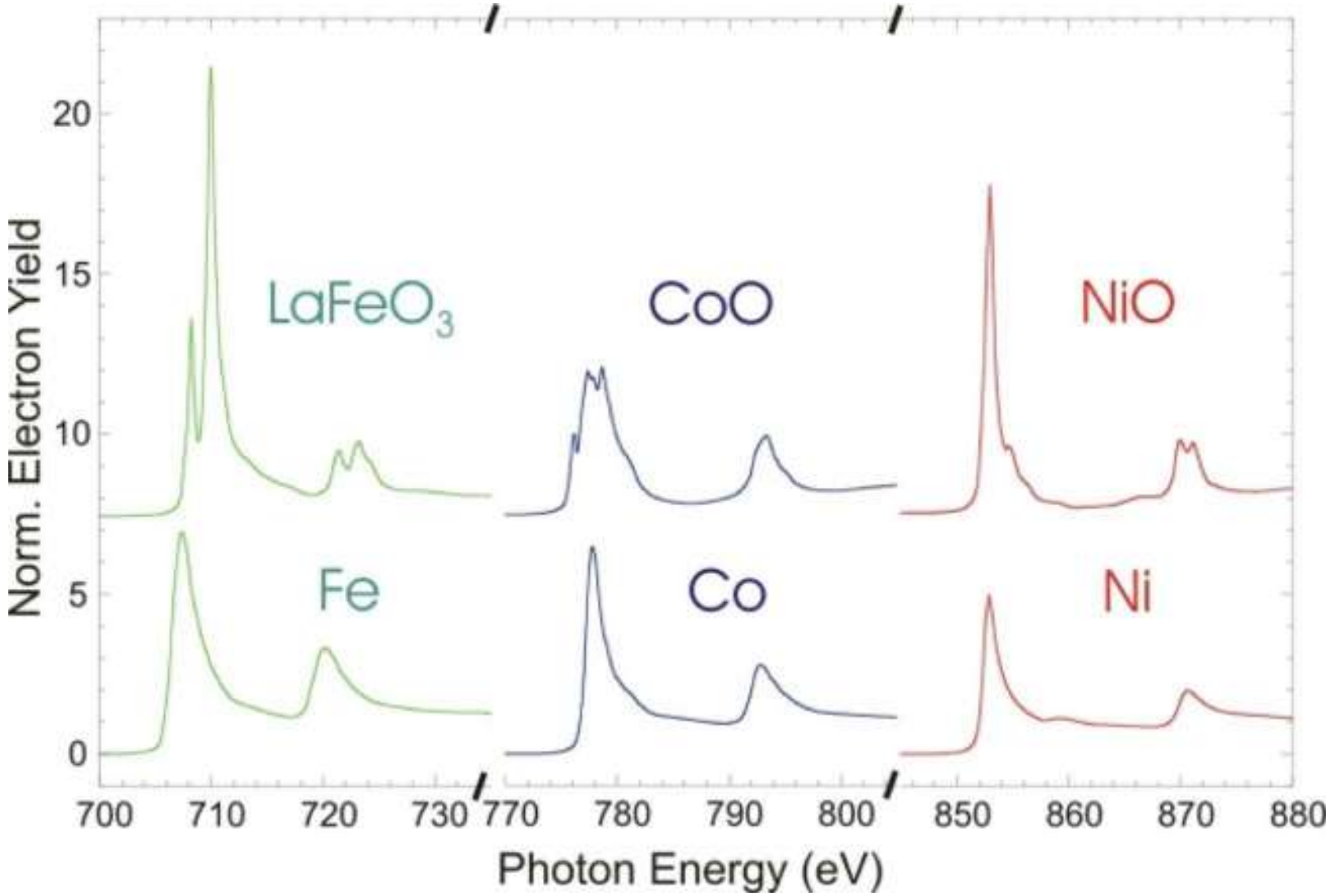
Figure 5. Experimental Fe 1s X-ray absorption spectra of (a) $FeAl_2O_4$ (dotted), (b) Fe_2SiO_4 (solid), (c) Fe_2O_3 (solid with points), and (d) $FePO_4$ (dashed).

Quadrupolar transition 1s -> 3d

F. M. F. de Groot,*et al,* J. Phys. Chem. B **109**, 20751 (2005).

XAS Spectra: oxides x metals

Where does the fine structure from oxides come from?



http://ssrl.slac.stanford.edu/stohr/xmcd.htm

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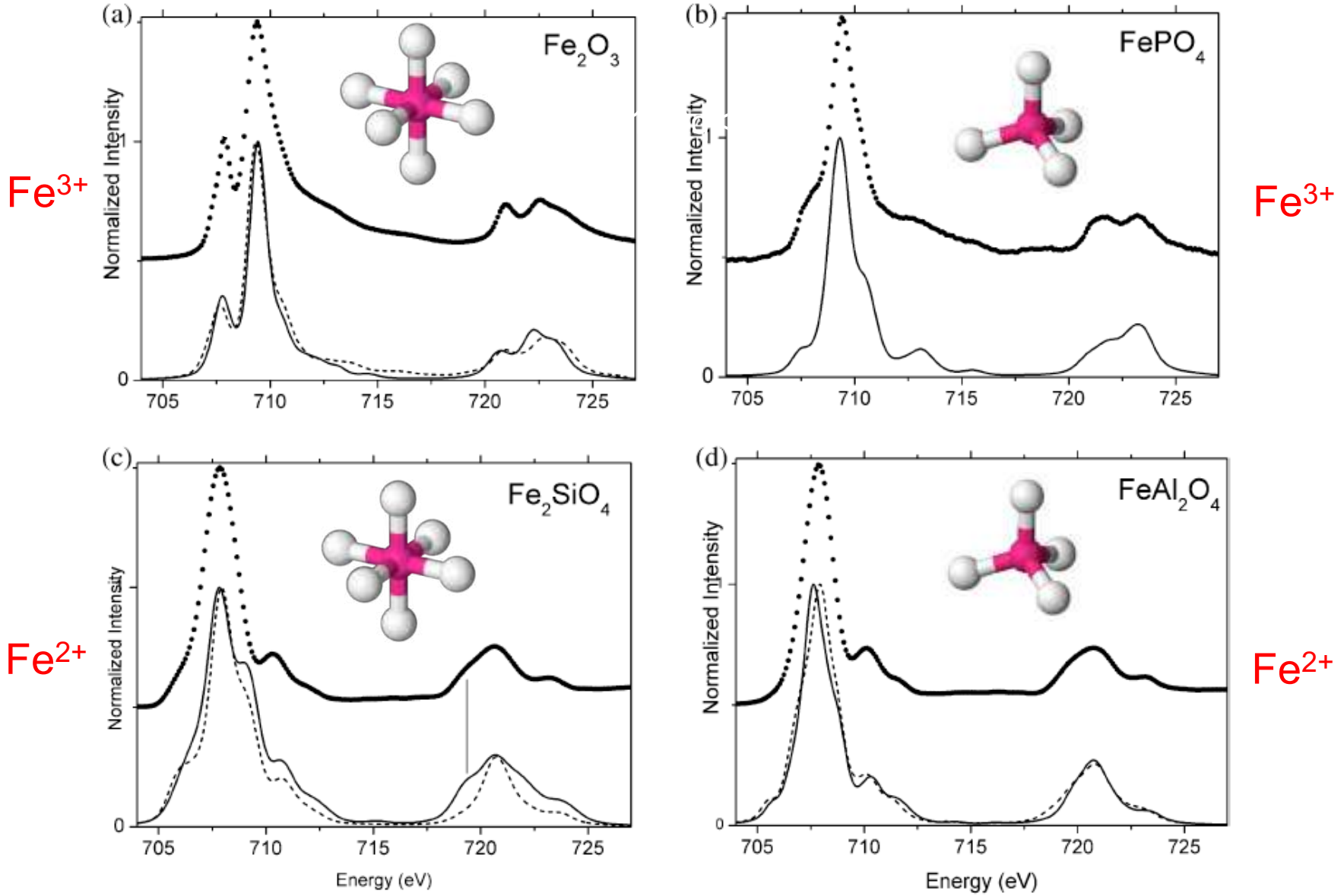
Information contained in the XA Spectra



Fe^{3+}

Fe^{3+}

Fe^{2+}

Fe^{2+}

F. M. F. de Groot *et al.* J. Phys. Chem. B **109** 20751 (2005)

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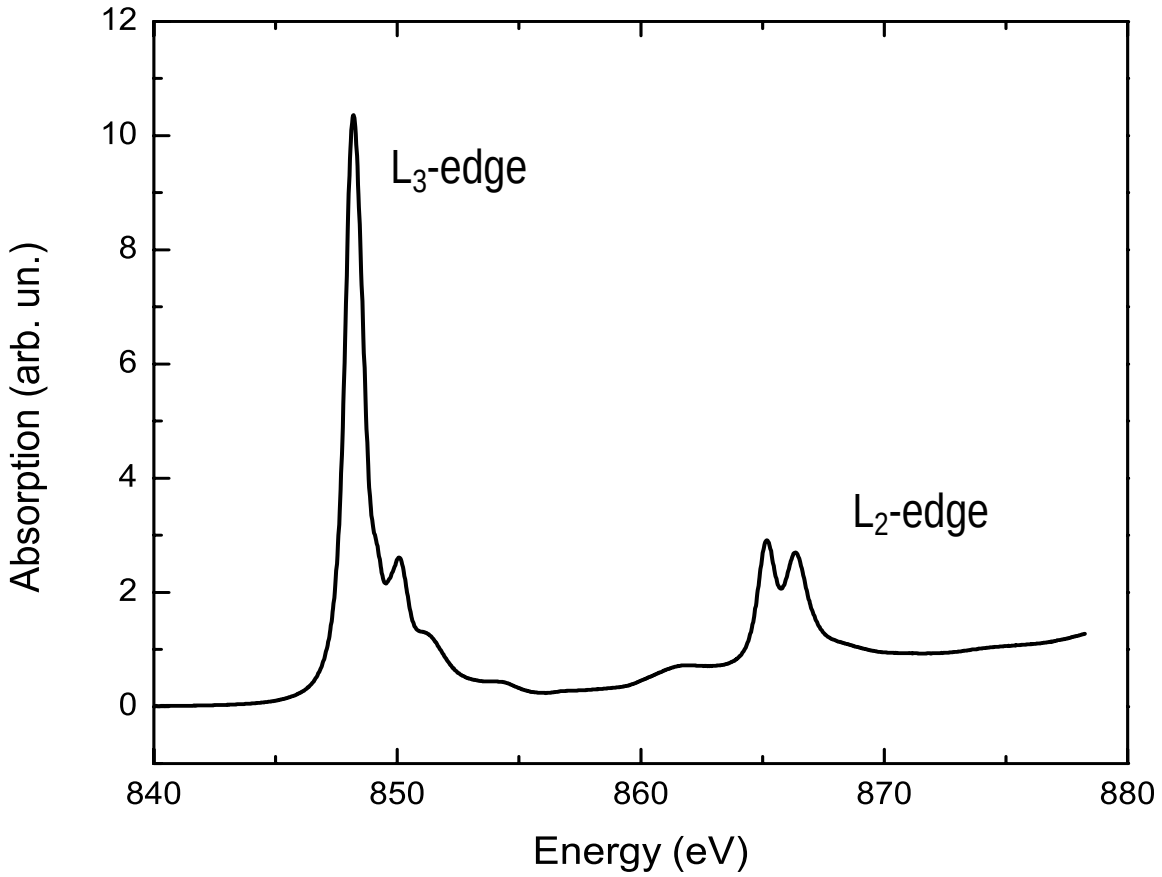
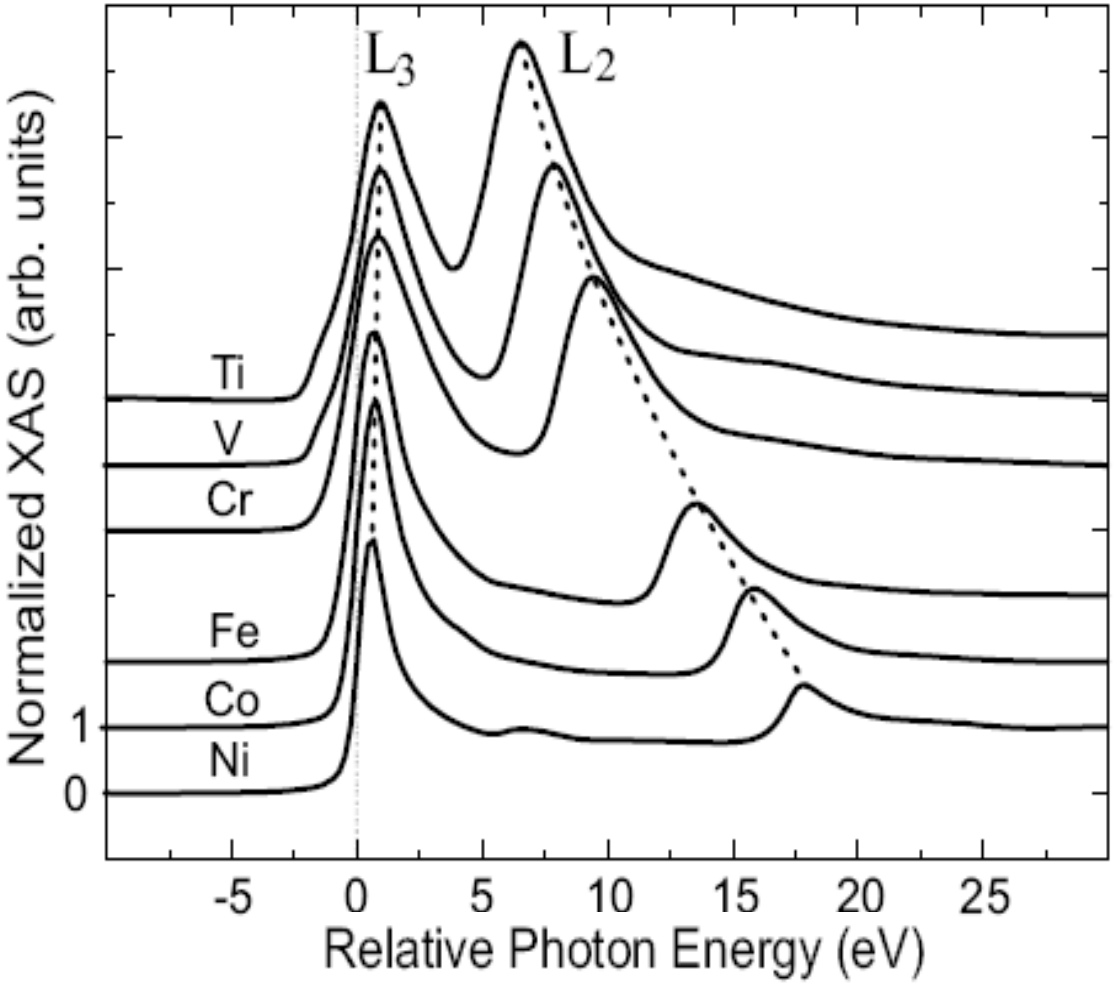
Why are there two edges?



2p spin-orbit

Element	ζ_{2p} (eV)
Mn	6.8
Fe	8.2
Co	9.8
Ni	11.5
Cu	13.5



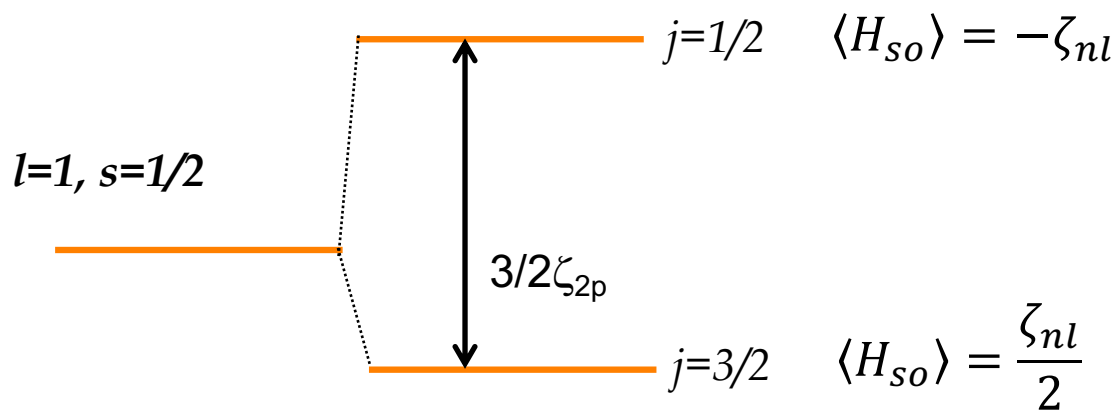
For comparison, 3d spin-orbit ~100meV

L_3 and L_2 edges: Spin-Orbit Coupling

- $L_{2,3}$ edges:
  – transition 2p -> 3d

- Spin-orbit coupling for a 2p hole:
  – l=1
  – s=1/2
  – j=l+s … l-s = **3/2, 1/2**

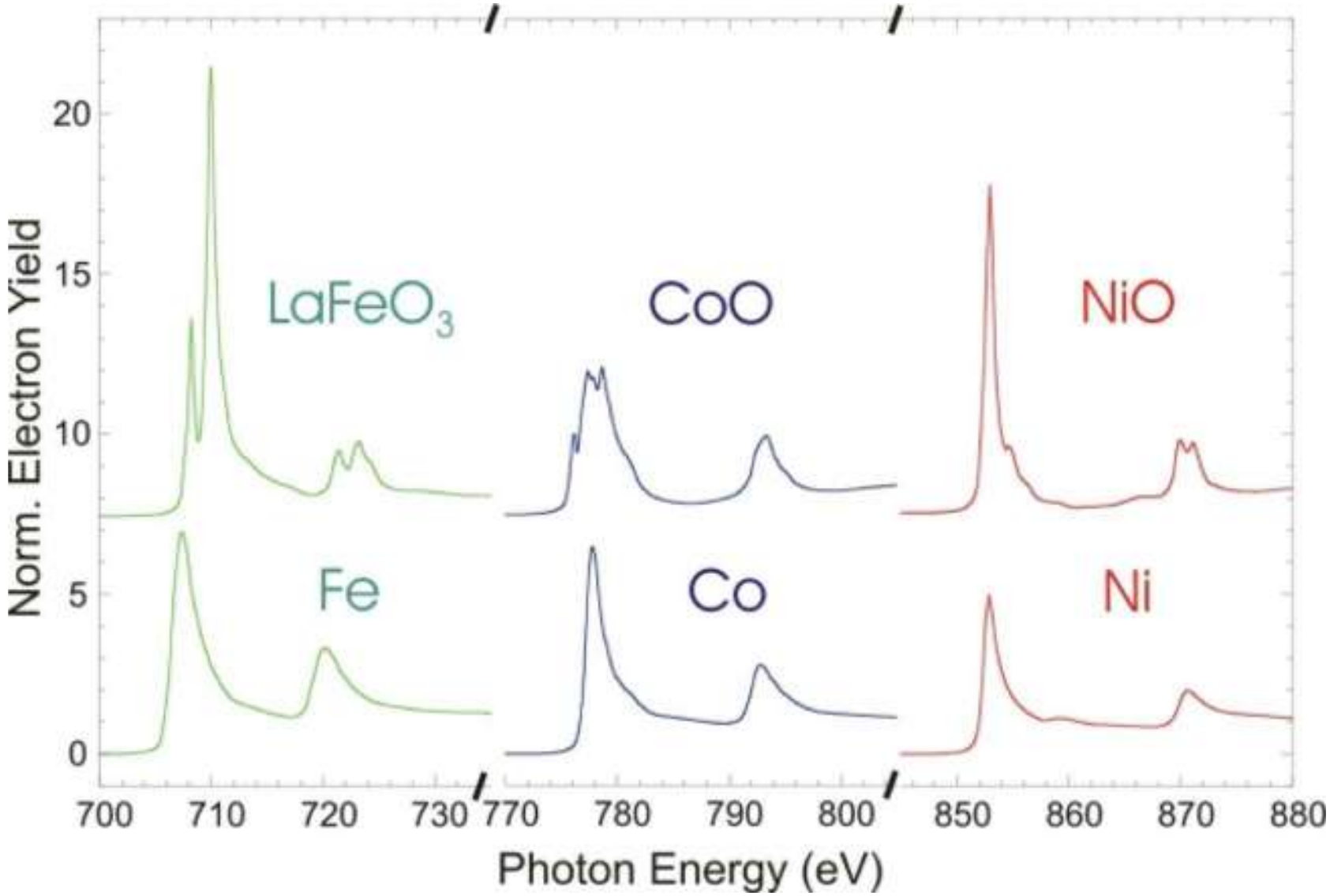
$$\langle H_{so} \rangle = \frac{\zeta_{nl}}{2}[j(j+1) - l(l+1) - s(s+1)]$$



$\zeta_{nl} < 0, for\ more\ than\ half\ filled\ shell$

XAS Spectra: oxides x metals

Where does the fine structure from oxides come from?



http://ssrl.slac.stanford.edu/stohr/xmcd.htm

Ground state of partially filled shells
Hund's rule

- How to define the ground state of a partially filled shell?
- For example: Co^{2+} has 7 electrons in the d-shell.

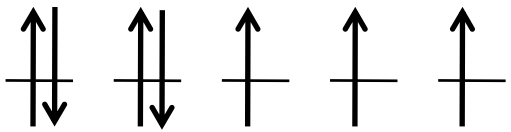
- Hund's rules:
  - 1st: Lowest electronic state has largest total spin **S**

    Pauli's exclusion principle => minimizes Coulomb interaction

  - 2nd: Lowest electronic state has largest total orbital moment **L**

    Electrons circulating in the same direction (parallel angular momentum) => minimizes Coulomb interaction
  - 3rd: Lowest electronic state has largest total angular momentum **J**, if shell is more than half full or smallest total angular momentum **J**, if the shell is less than half full

Co^{2+} d^7



l_z= 2 1 0 -1 -2

S=3/2

L=3

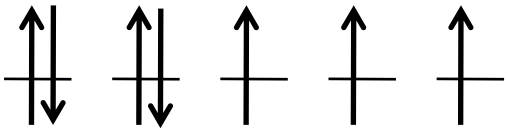
J=9/2

Term Symbol

$^{2S+1}L_J$ $^4F_{9/2}$

XAS: how does the final state looks like?

Co^{2+} d^7



l_z= 2 1 0 -1 -2

S=3/2

L=3

J=9/2

Term Symbol

$^{2S+1}L_J$ $^4F_{9/2}$

Final state XAS at Co $L_{2,3}$-edges in Co^{2+}

$2p^5 3d^8$

Example: XAS of Ti^{4+}

- Initial state $2p^6 3d^0$
  - $^1S_0$
- Final state: $2p^5 3d^1$, same as 2p3d
  - $S_1=1/2$, $S_2=1/2$, $S_{total}=0,1$
  - $L_1=1$, $L_2=2$, $L_{total}=1,2,3$
  - J=L-S … L+S

Term Symbol:
$^{2S+1}L_{2J+1}$

L/S	0	1
1	$^1P_1$	$^3P_0, ^3P_1, ^3P_2$
2	$^1D_2$	$^3D_1 ^3D_2, ^3D_3$
3	$^1F_3$	$^3F_2, ^3F_3, ^3F_4$

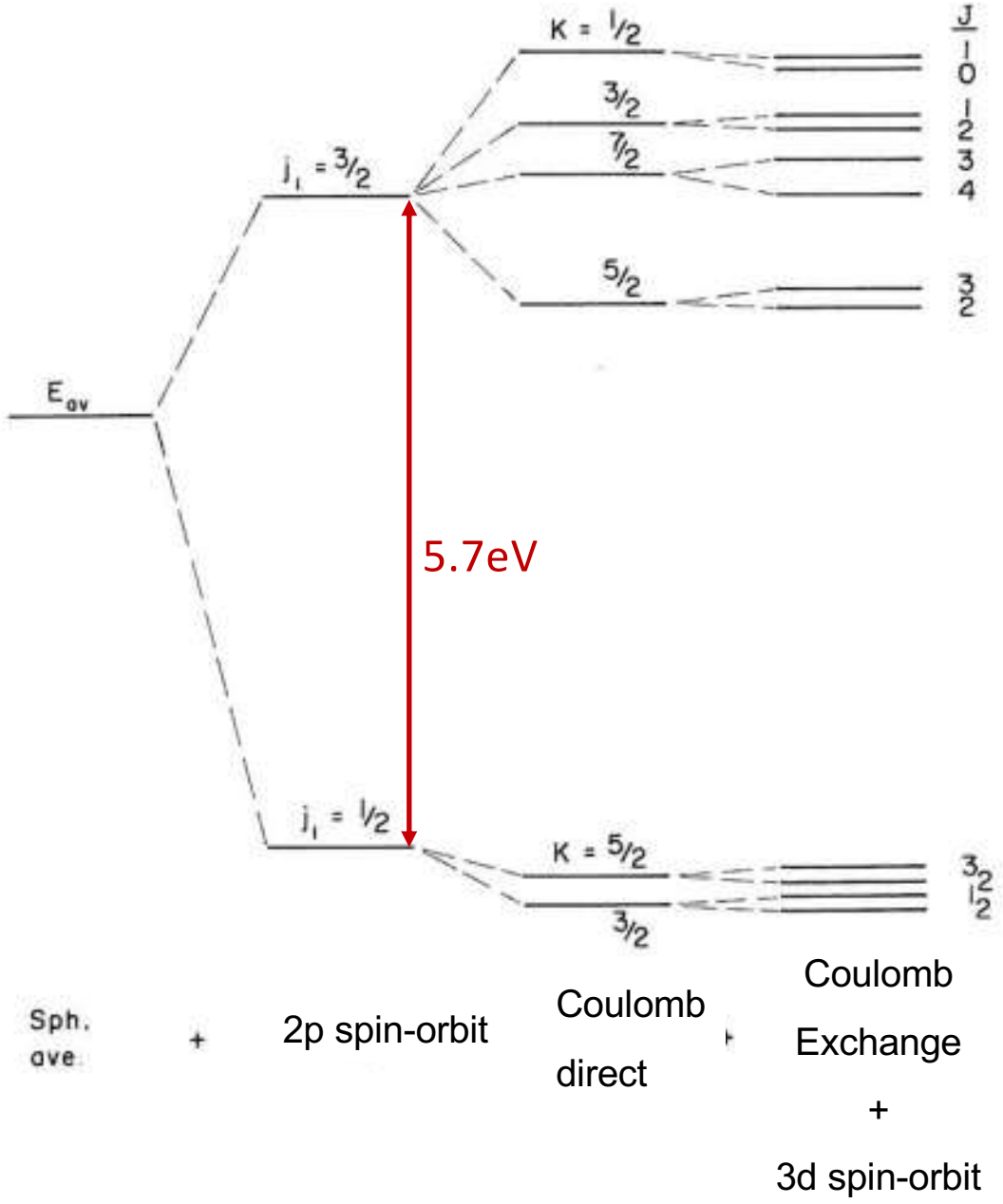
There are 12 different configurations for pd!

pd states

Ti^{4+}: d^0

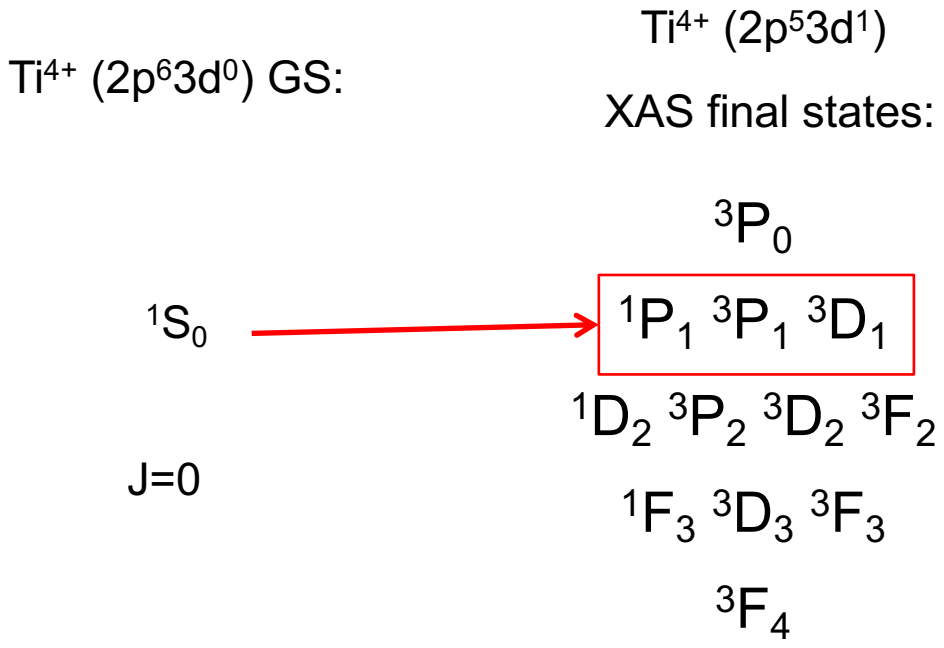
XAS final state:

$2p^5 3d^1$



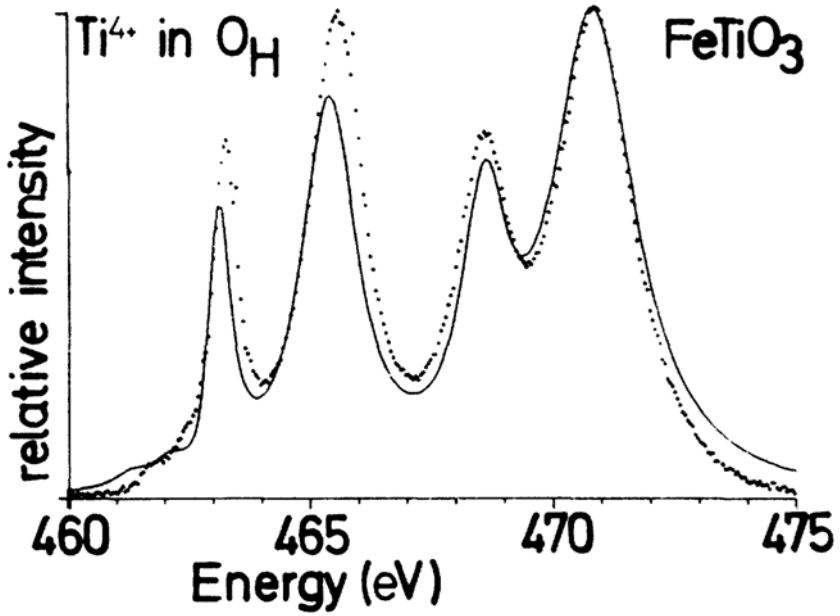
Dipole Selection rules

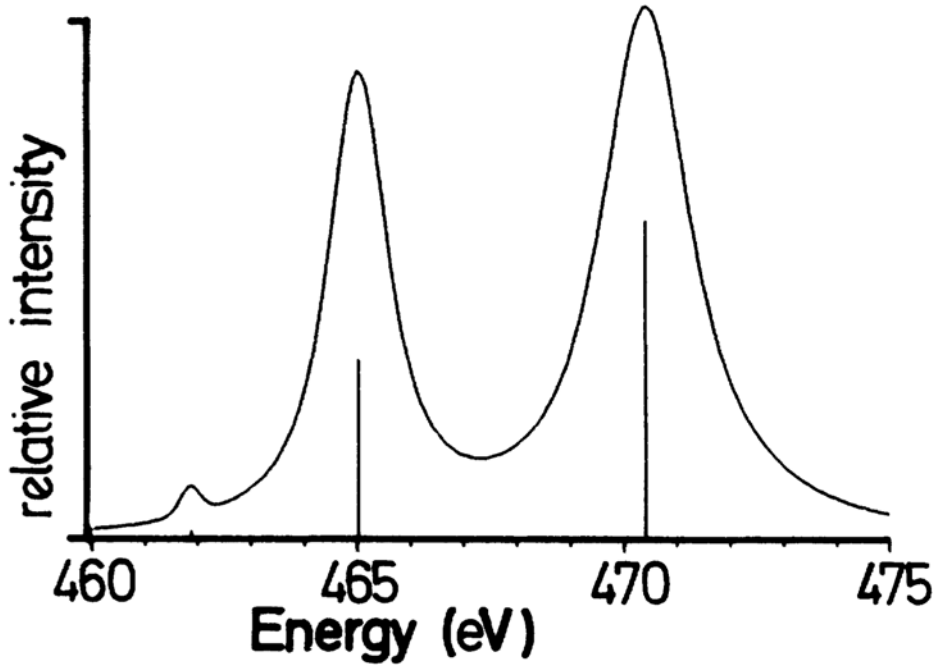
- Dipole Selection Rules:
  - $\Delta J = \pm 1, 0$ (except for J=0)



Ti^{4+} XAS

What is missing?



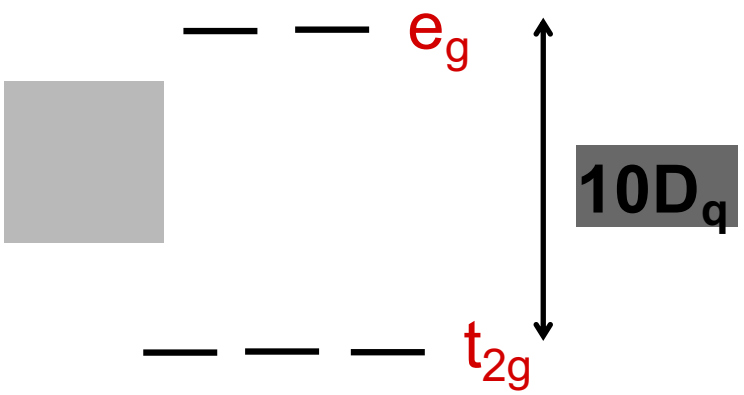


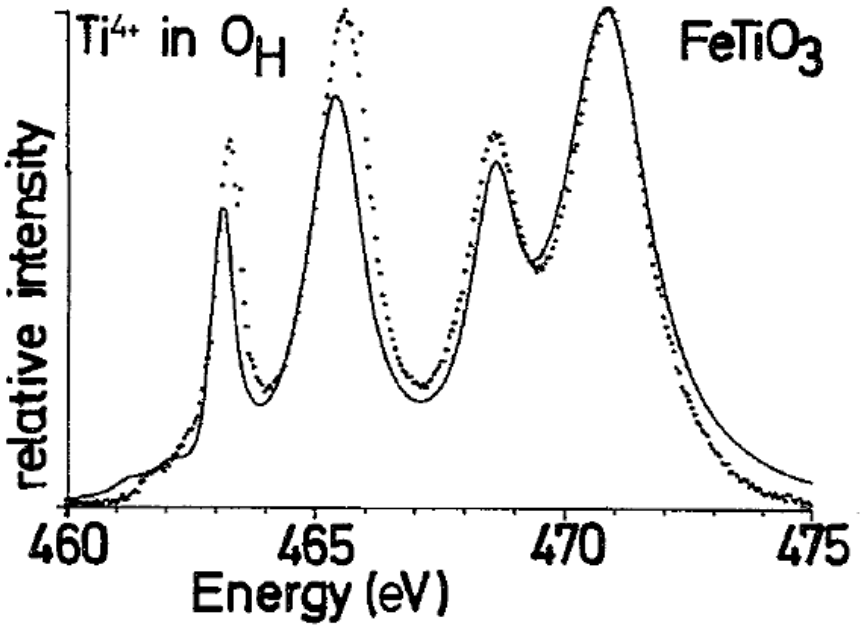
F. M. F. de Groot *et al.* PRB **41**, 928 (1990).

Measured Ti^{4+} XAS

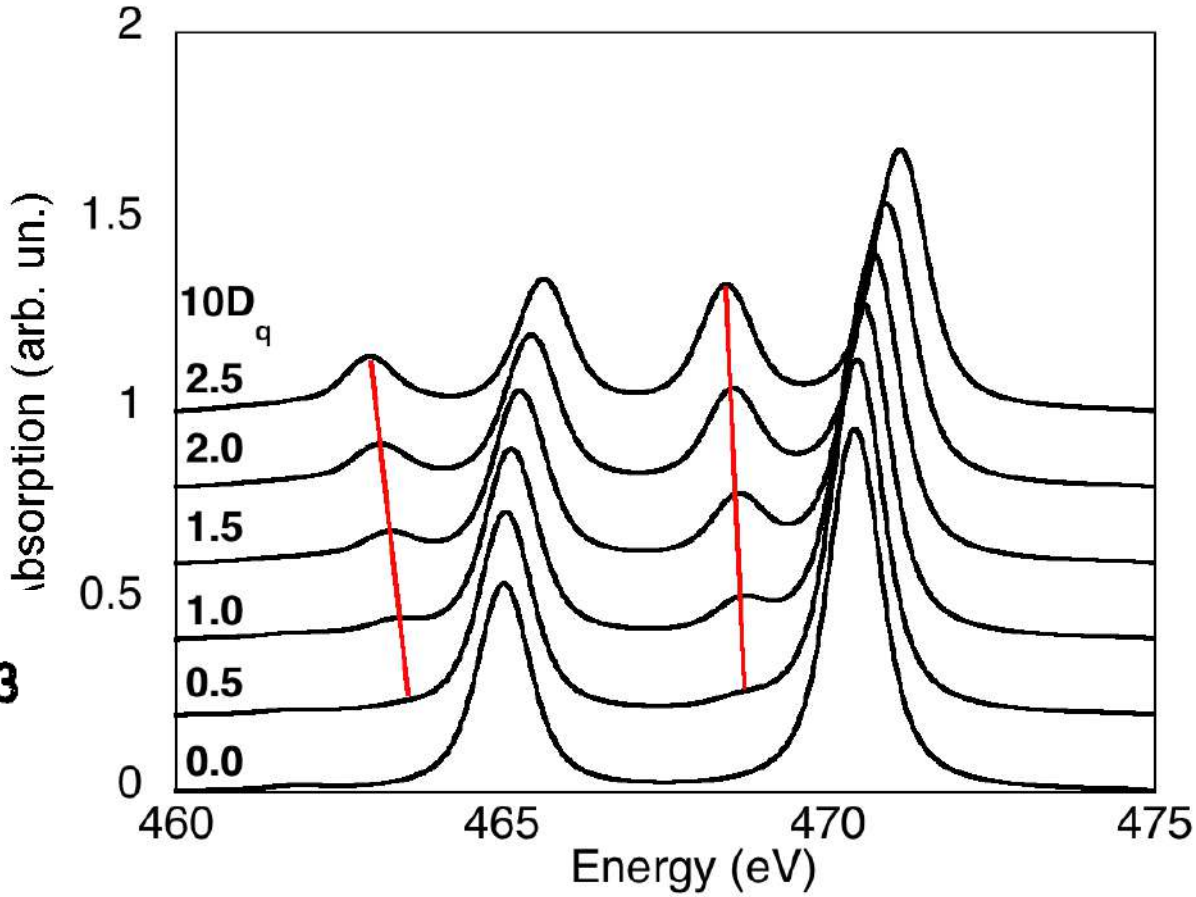
Simulation of Ti^{4+} XAS

Ti^{4+}: Inclusion of Crystal Field Splitting





F. de Groot *et al* PRB **41** (1990) 928



(Some) x-ray absorption simulation codes suitable when multiplet structure is important

- CTM4XAS (http://www.anorg.chem.uu.nl/CTM4XAS/)
  - User friendly. Input: crystal field parameters and charge transfer parameters when necessary
- Quanty (http://www.quanty.org/)
  - More advanced. Possible to include DFT calculations output as input for the multiplet code
- MultiX (http://multiplets.web.psi.ch/)
  - Input parameter is the crystal structure. No inclusion of charge transfer
- **Multiplet structure is typically important for:**
  - **$L_{2,3}$-edges of transition metal oxides. Metallic system often show no multiplet structure**
  - **$M_{4,5}$ edges of lanthanides**

Summary XAS II

- K edge probes p states
- $L_{2,3}$ edges probe d states
- The $L_{2,3}$ edges are split in two due to 2p spin-orbit coupling
- Since the 3d states are partially localized electronic correlations are important to describe the spectrum
- The L-edge spectrum is sensitive to the ligand field around the absorbing atom

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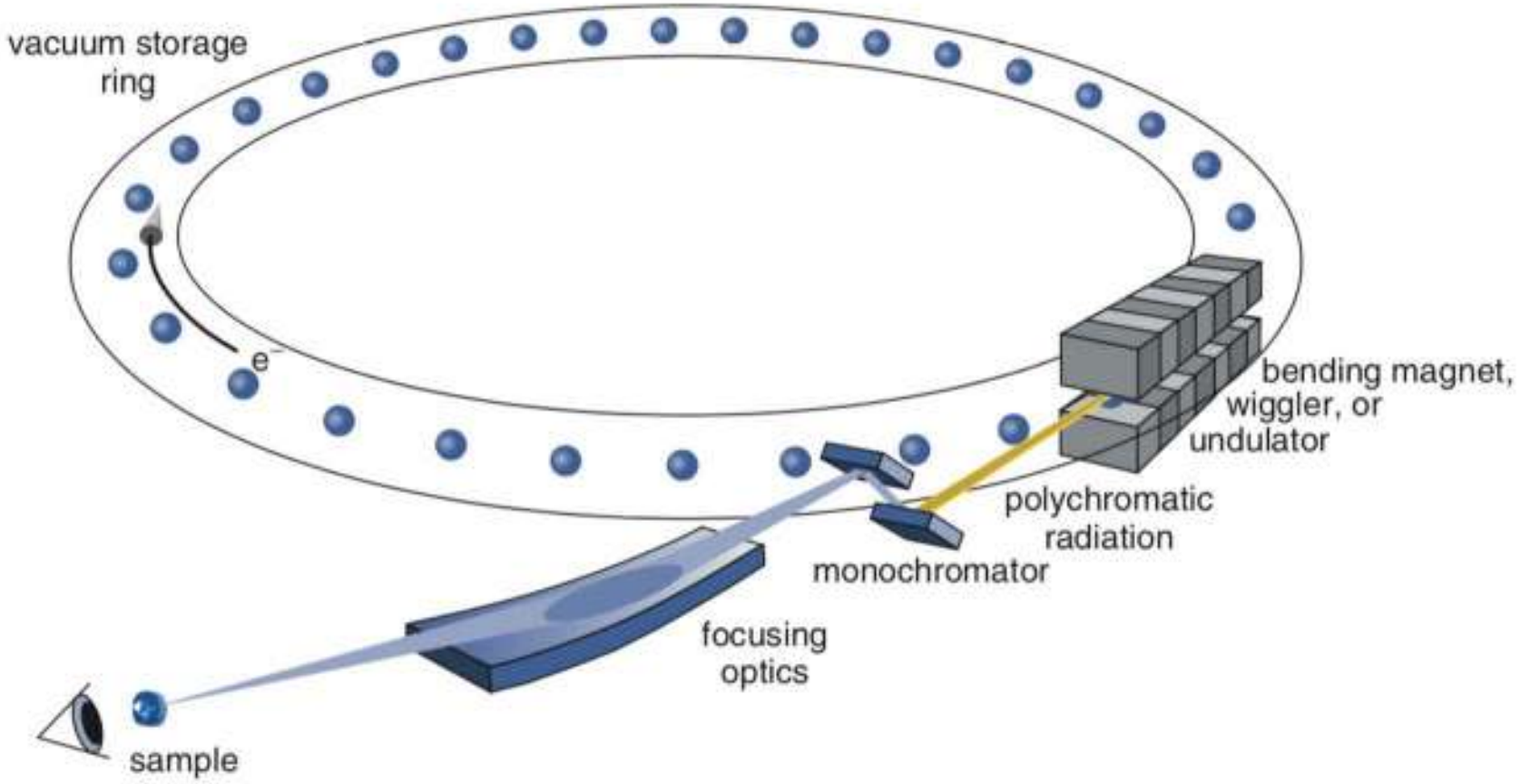
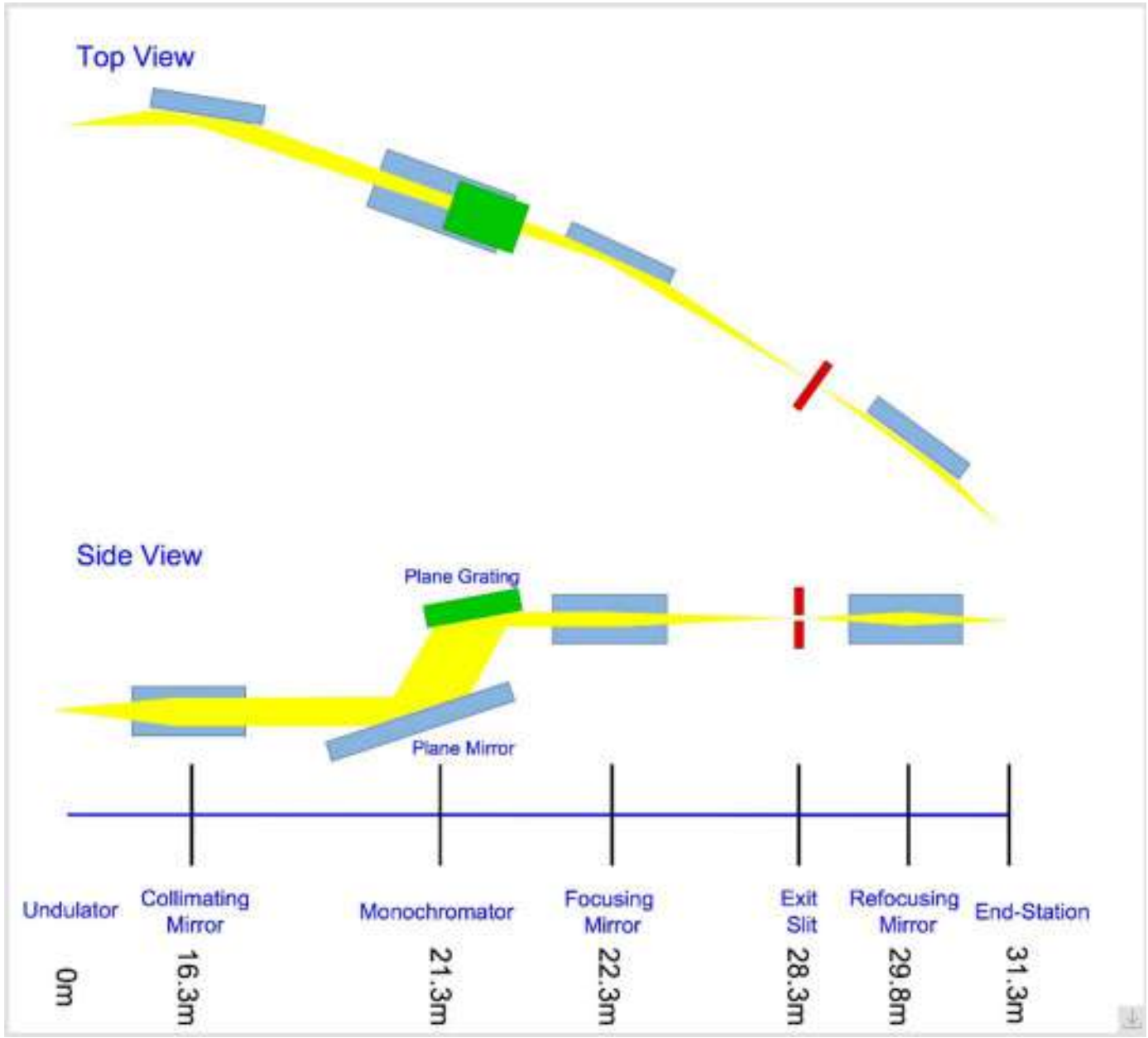
How to measure

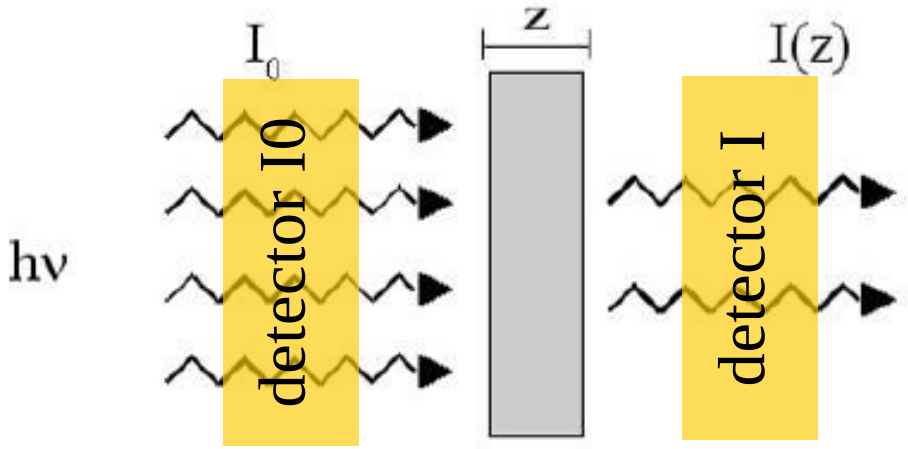
Synchrotron + beamline



Beamline Optics



X-ray absorption detection

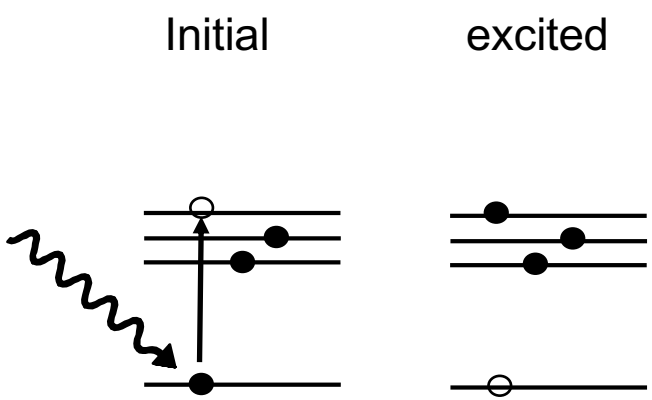


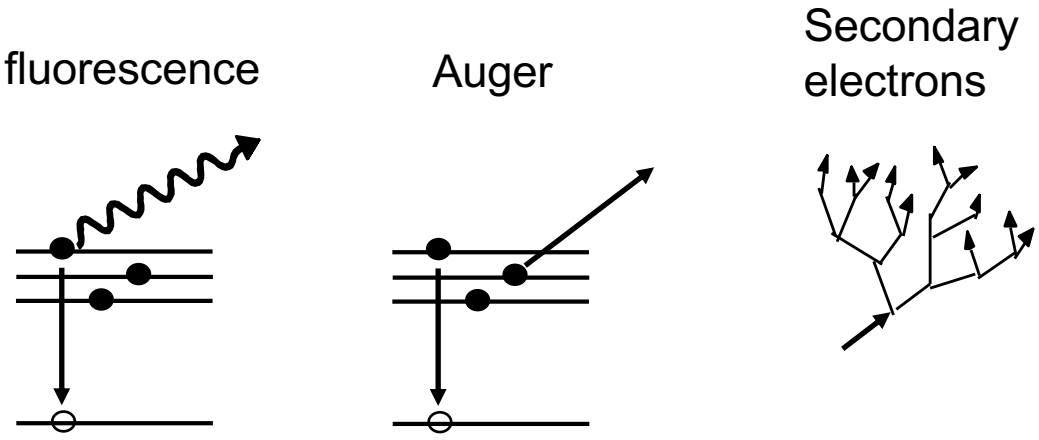
transmission is the most direct

... but not always possible:

- Limitation on sample thickness
- Low contrast in very dilute systems

Decay channels





Soft X-ray range: ~ 5% fluorescence

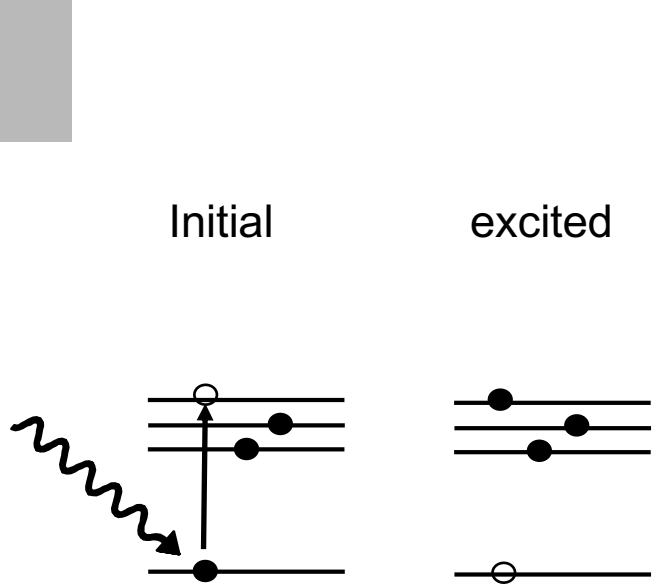
~ 95% Auger

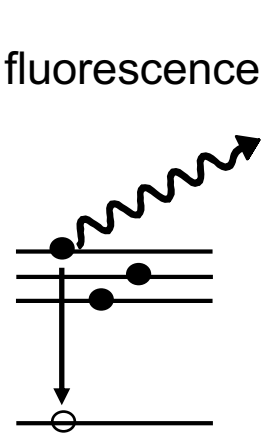
Probing depth in soft X-rays:

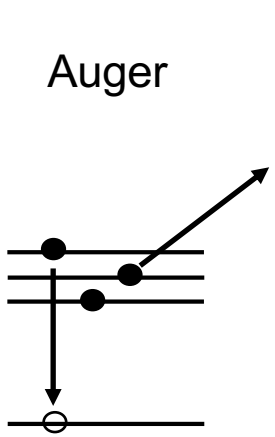
Fluorescence:

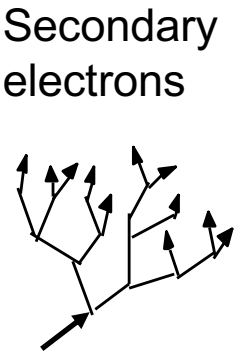
TEY:

Decay channels







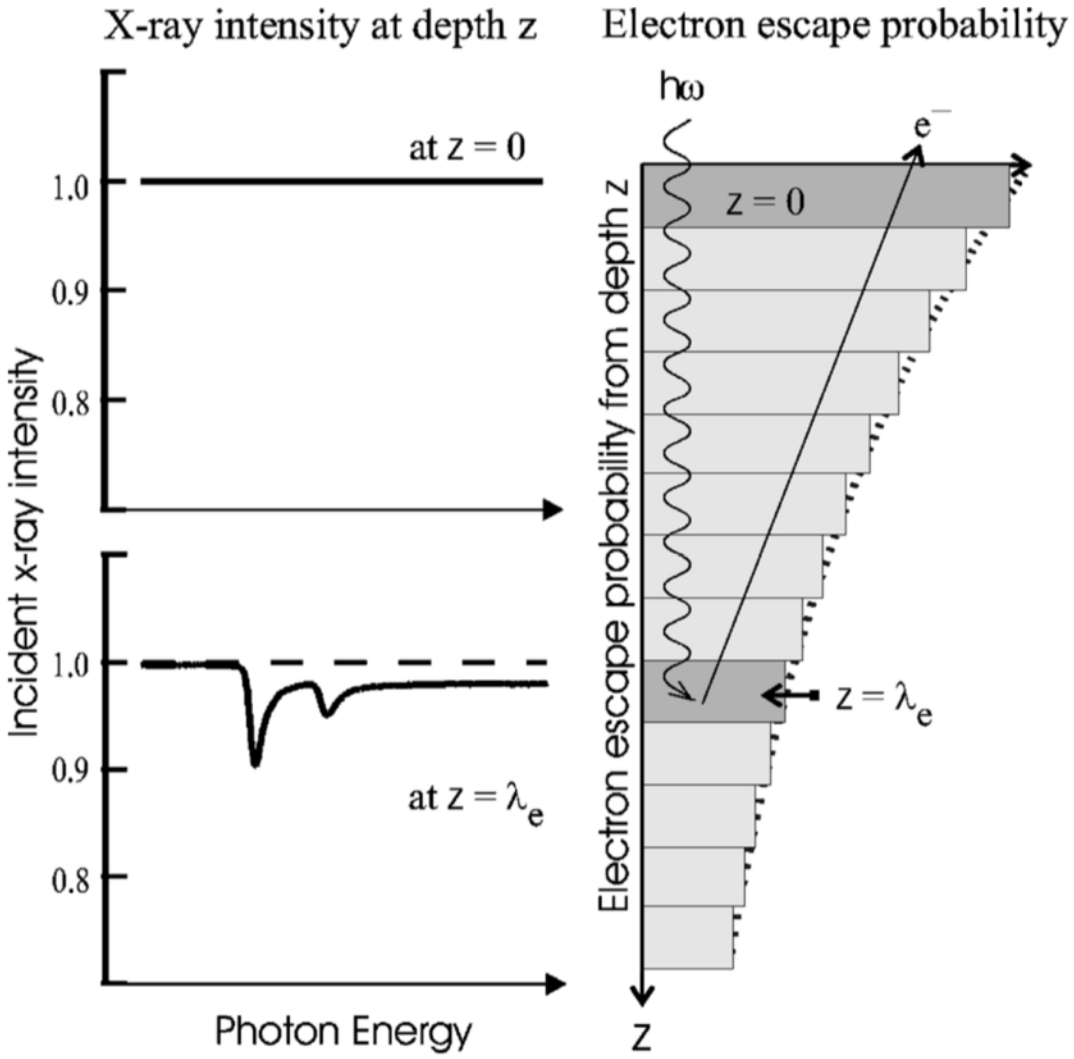


Probing depth in soft X-rays:

Fluorescence: λ_x~100nm

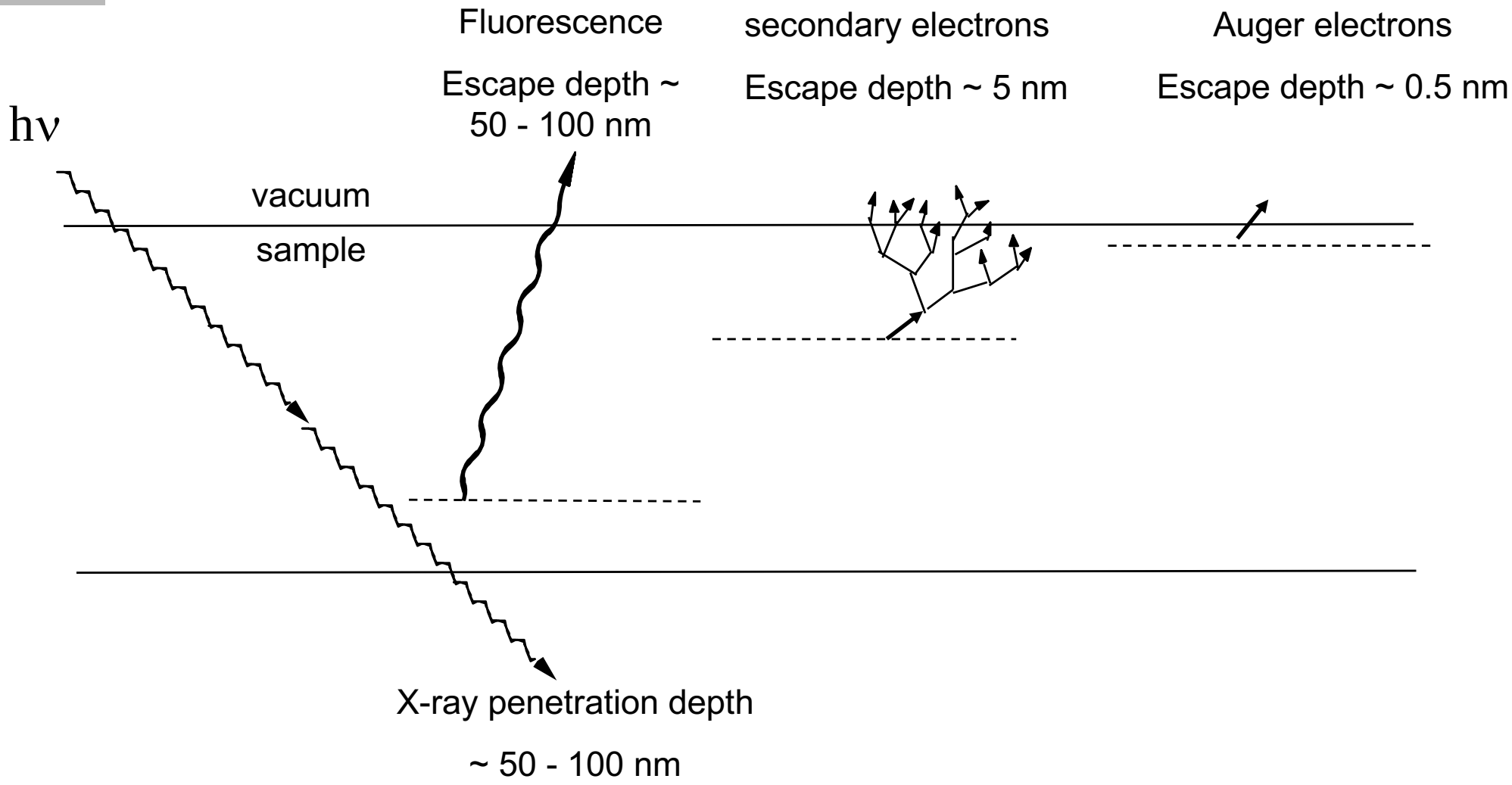
TEY: λ_e~2- 5nm

Meaning of p robing depth

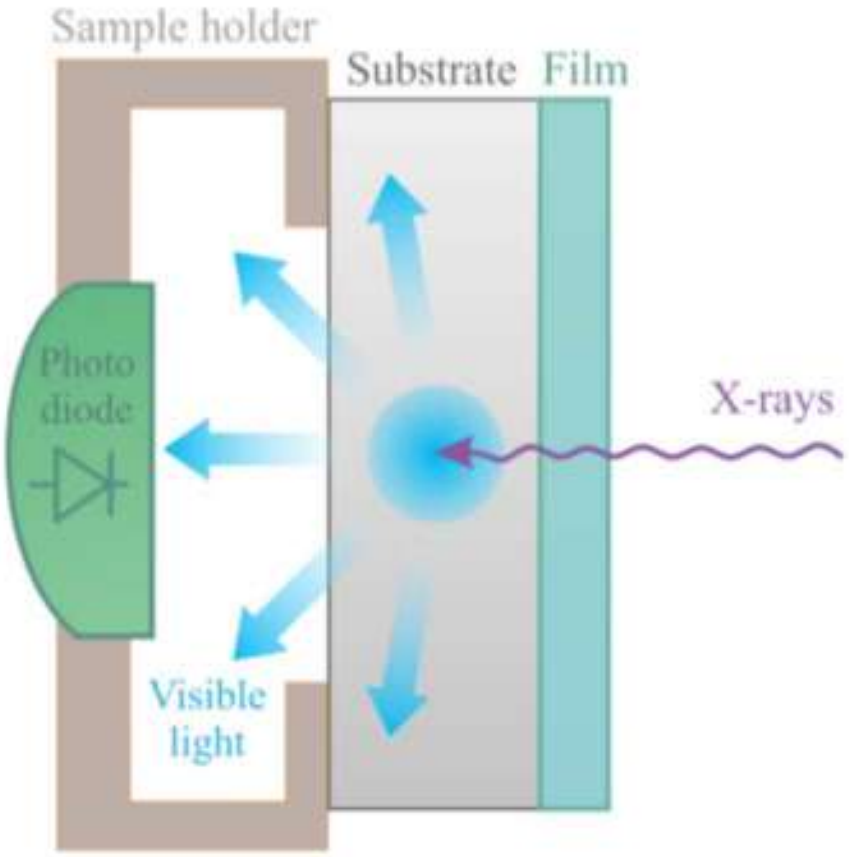


R. Nakajima, J. Stöhr, and Y. U. Idzerda, PRB **59**, 6421 (1999).

Detection methods
Sampling depth



X-ray excited optical luminescence



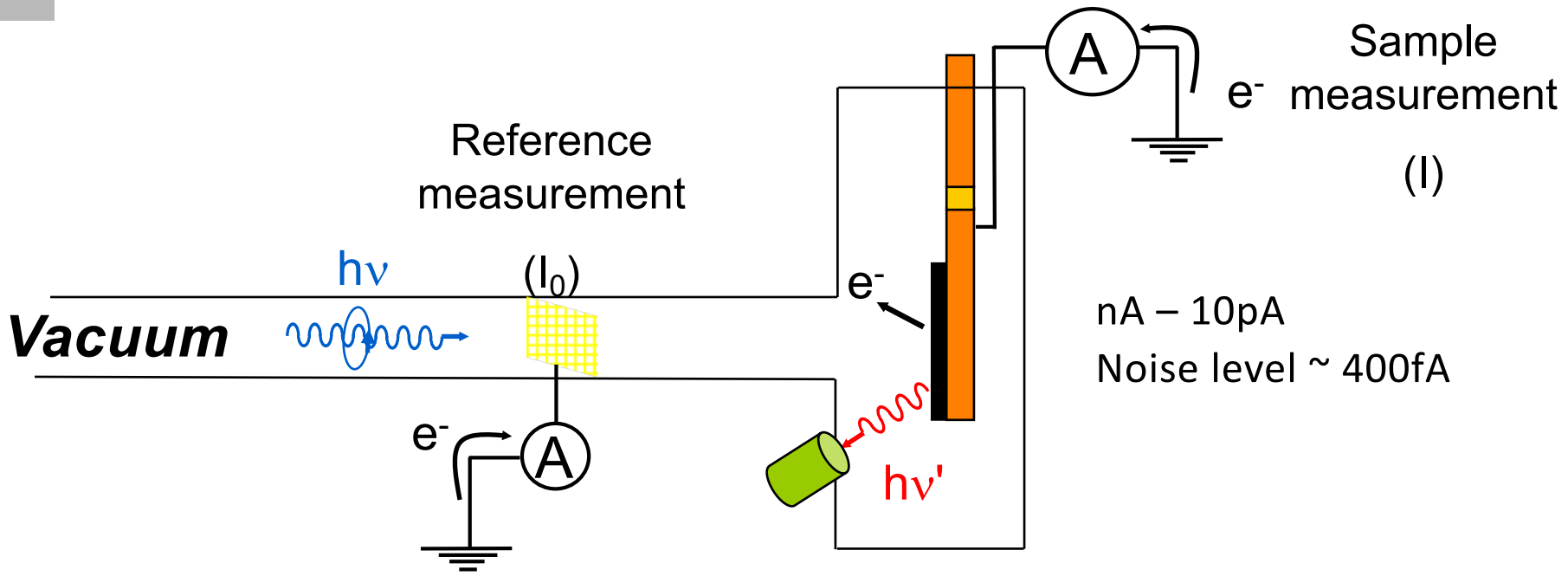
Y. W. Windsor *et al*, PRB **95**, 357 (2017).

Allows transmission like measurements of X-rays in thin films

X-ray penetration depth

~ 100 nm

Scheme of a Experimental Setup



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Examples

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Example: A Living-Dead magnetic layer

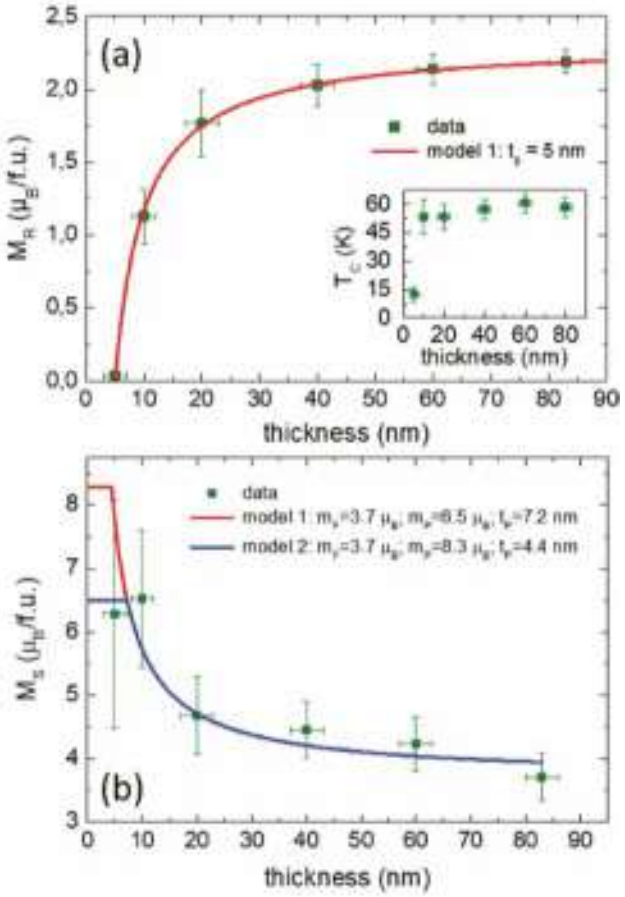
COMMUNICATION
Magnetic Thin Films
ADVANCED MATERIALS
www.advmat.de

A Living-Dead Magnetic Layer at the Surface of Ferrimagnetic $DyTiO_3$ Thin Films

*Raphaël Aeschlimann, Daniele Preziosi, Philipp Scheiderer, Michael Sing, Sergio Valencia, Jacobo Santamaria, Chen Luo, Hanjo Ryll, Florin Radu, Ralph Claessen, Cinthia Piamonteze, and Manuel Bibes**

DTO

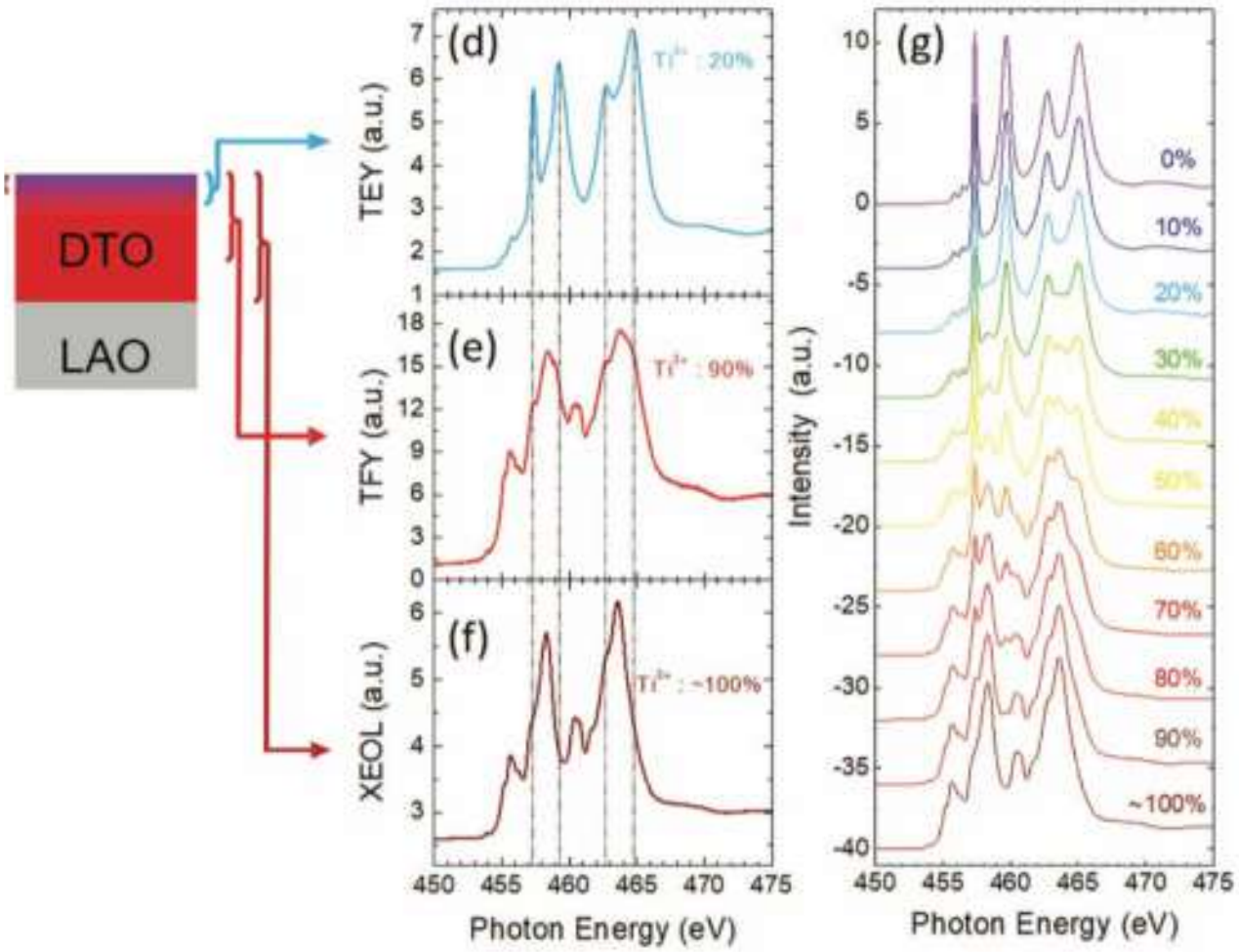
LAO



R. Aeschlimann, *et al*, Adv. Mater. **30**, 1707489 (2018).

Example: A Living-Dead magnetic layer

A Living-Dead Magnetic Layer at the Surface of Ferrimagnetic $DyTiO_3$ Thin Films

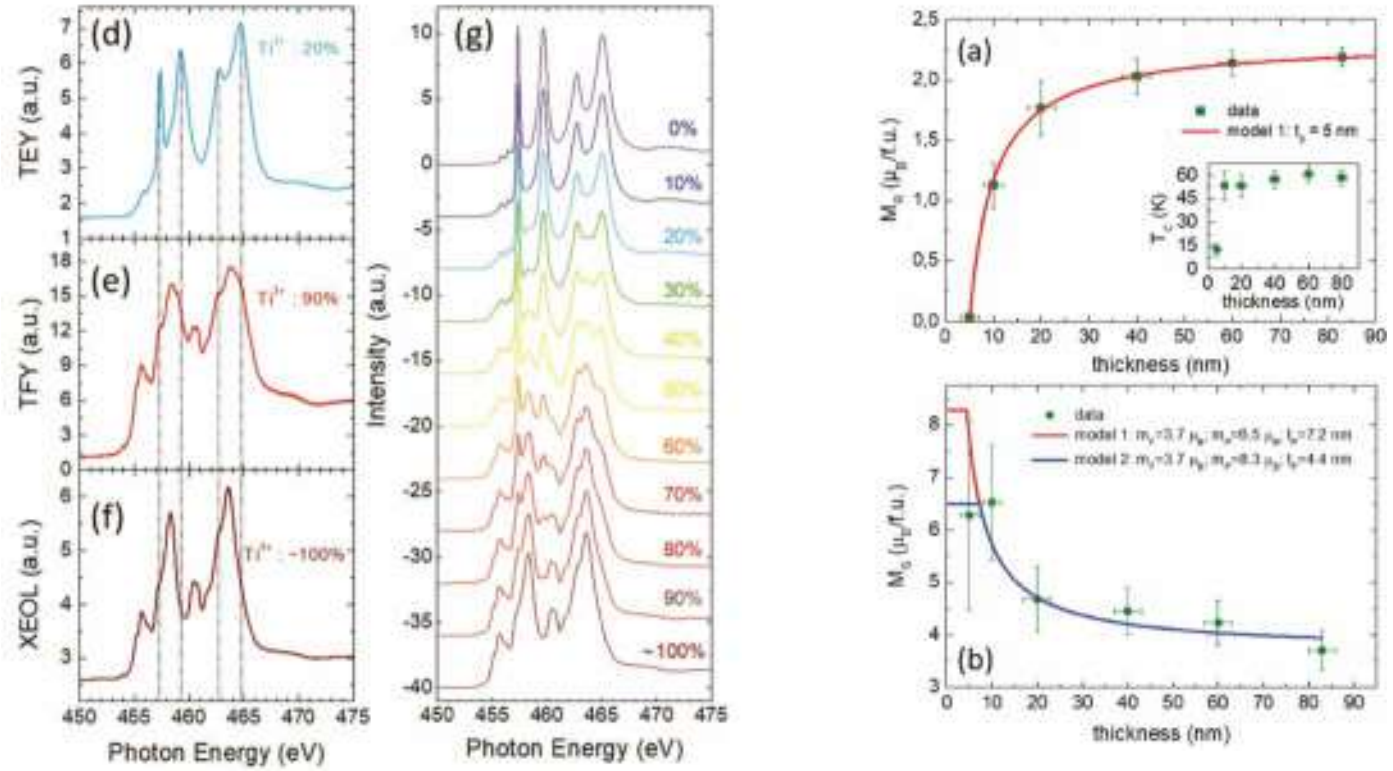


R. Aeschlimann, *et al*, Adv. Mater. **30**, 1707489 (2018).

Example: A Living-Dead magnetic layer

A Living-Dead Magnetic Layer at the Surface of Ferrimagnetic $DyTiO_3$ Thin Films

$$M_{\text{total}} = m_{\text{total}} \cdot t = m_{\text{P}} \cdot t_{\text{P}} + m_{\text{F}} \cdot t_{\text{F}}$$



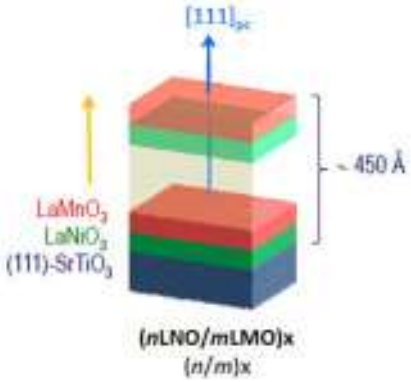
R. Aeschlimann, *et al*, Adv. Mater. **30**, 1707489 (2018).

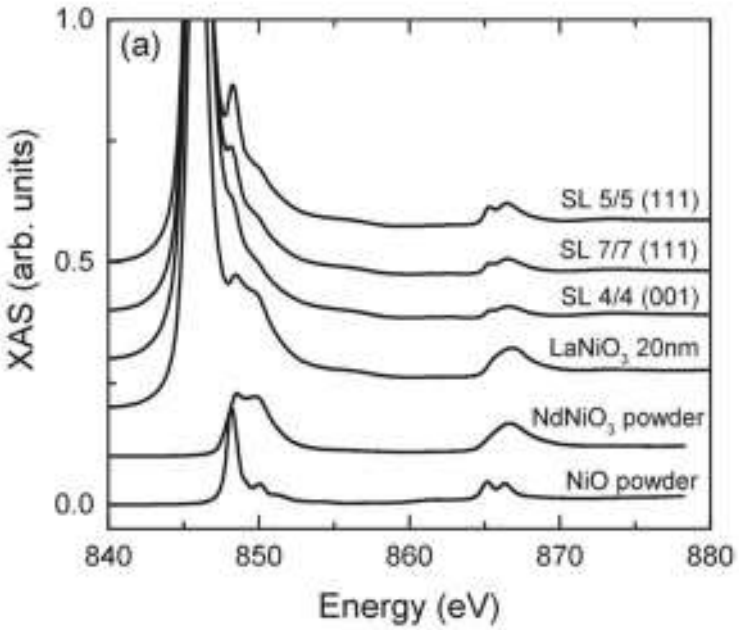
Example: charge transfer at LaMnO3/LaNiO3 superlattices

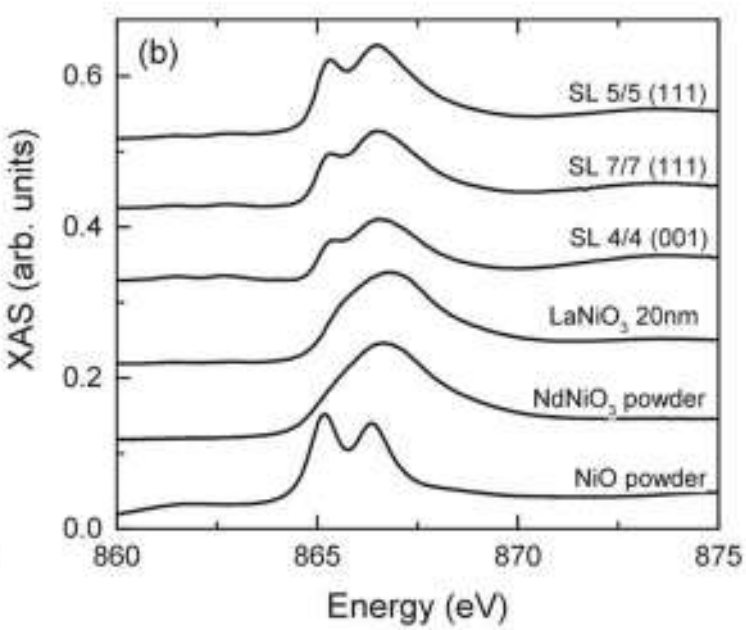
PHYSICAL REVIEW B **92**, 014426 (2015)

Interfacial properties of $LaMnO_3/LaNiO_3$ superlattices grown along (001) and (111) orientations

C. Piamonteze,[1] M. Gibert,[2] J. Heidler,[1] J. Dreiser,[1] S. Rusponi,[3] H. Brune,[3] J.-M. Triscone,[2] F. Nolting,[1] and U. Staub[1]

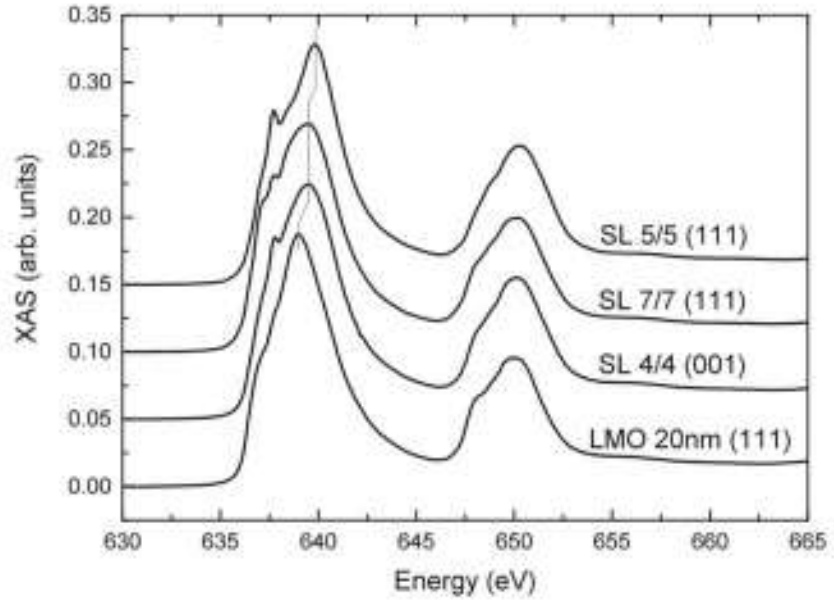


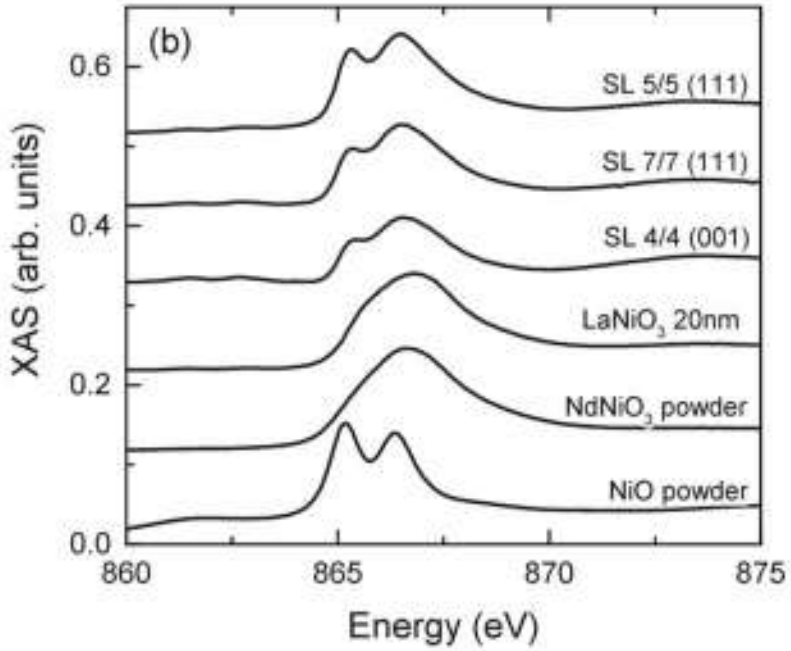




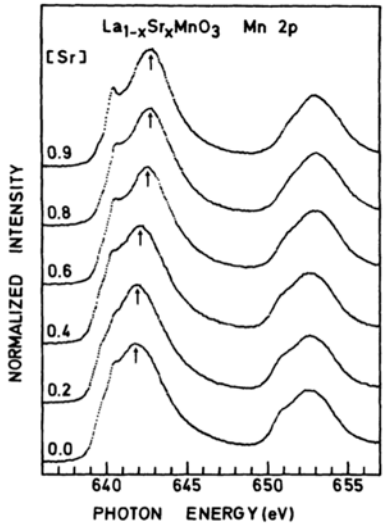
C. Piamonteze, *et al.*, PRB **92**, 014426 (2015).

Example: charge transfer at LaMnO3/LaNiO3 superlattices



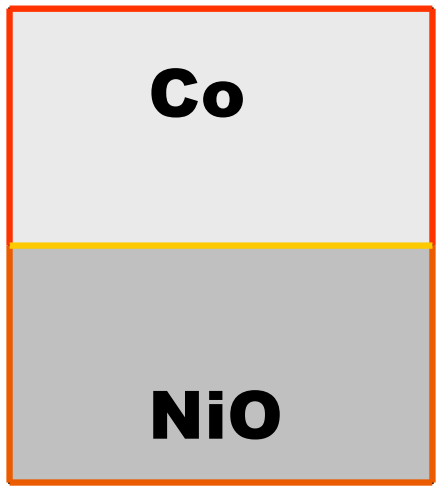


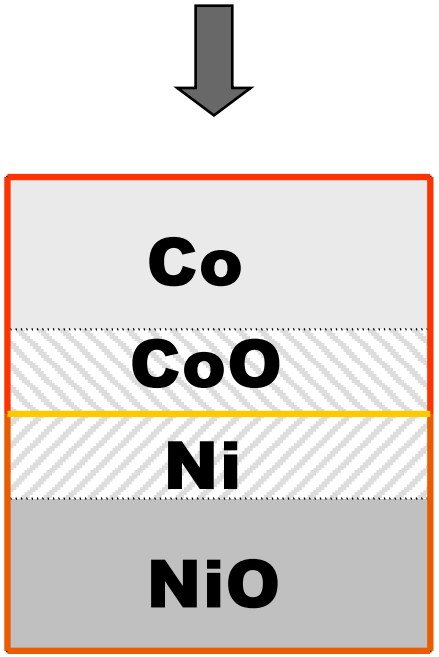
C. Piamonteze, *et al.*, PRB **92**, 014426 (2015).

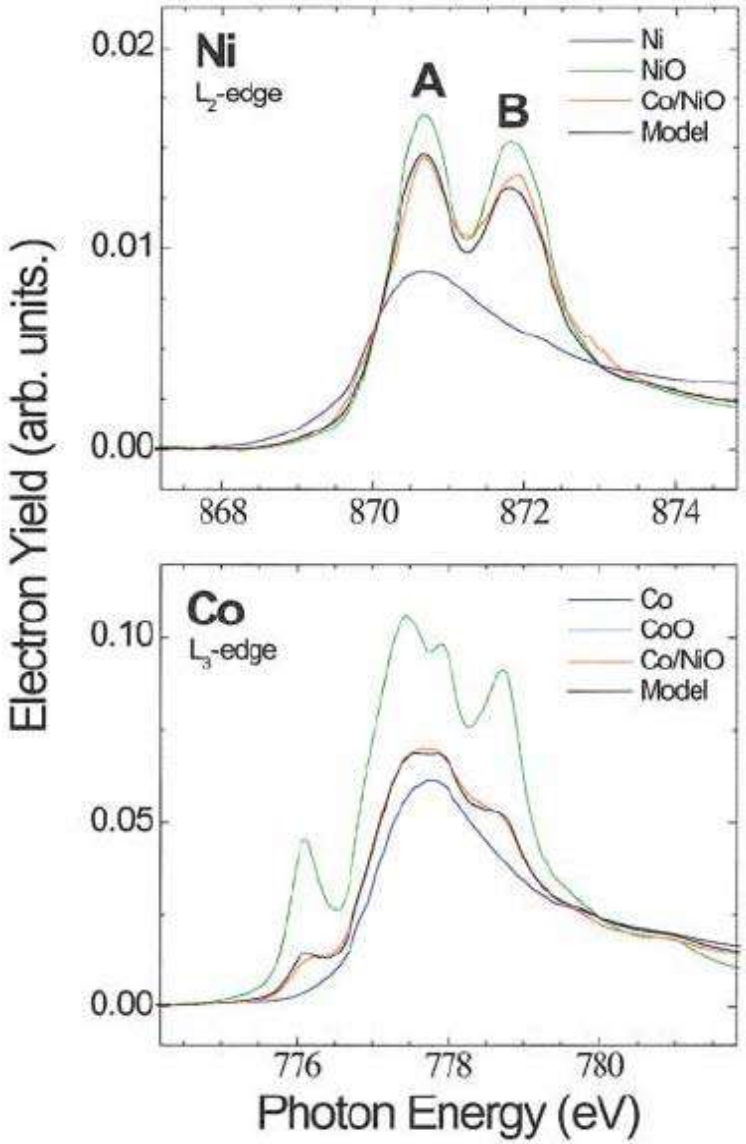


M. Abbate*, et al,* PRB **46**, 4511 (1992).

Example: Metal/oxide interface







Oxidation/reduction at the interface

T. Regan et al, Phys. Rev. B 64, 214422 (2001)

Example: Metal/oxide interface TEY modeling

$$dN_{e,\mathrm{Ni}} = I_0\, e^{-z\mu_{\mathrm{Ni}}(E)}\mu_{\mathrm{Ni}}(E)G_{\mathrm{Ni}}(E)e^{-z/\lambda_{\mathrm{Ni}}}\,dz. \quad \text{(A1)}$$

$$N_{e,\mathrm{Ni}} + N_{e,\mathrm{NiO}} = I_0\left(\frac{G_{\mathrm{Ni}}(E)}{1+\dfrac{1}{\mu_{\mathrm{Ni}}(E)\,\lambda_{\mathrm{Ni}}}}\left(1-e^{-t_{\mathrm{Ni}}[\mu_{\mathrm{Ni}}(E)+1/\lambda_{\mathrm{Ni}}]}\right)\right.$$
$$+\, e^{-t_{\mathrm{Ni}}[\mu_{\mathrm{Ni}}(E)+1/\lambda_{\mathrm{Ni}}]}\frac{G_{\mathrm{NiO}}(E)}{1+\dfrac{1}{\mu_{\mathrm{NiO}}(E)\,\lambda_{\mathrm{NiO}}}}$$
$$\left.\times\left(1-e^{-t_{\mathrm{NiO}}[\mu_{\mathrm{NiO}}(E)+1/\lambda_{\mathrm{NiO}}]}\right)\right). \quad \text{(A2)}$$

T. Regan, *et al* PRB **64**, 214422 (2001).