

X-Ray Absorption Spectroscopy

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Stanford Synchrotron Radiation Laboratory

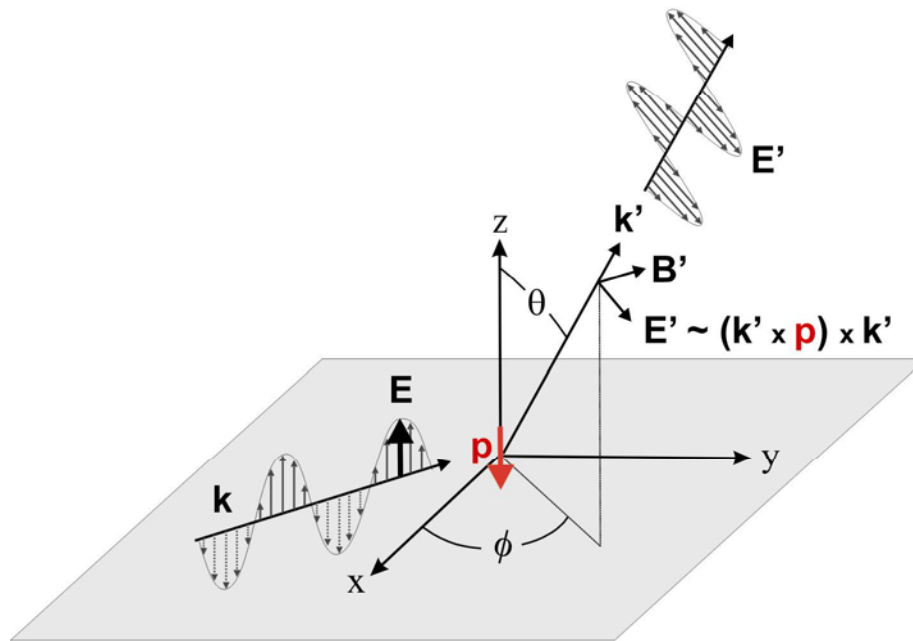
<http://www-ssrl.slac.stanford.edu/stohr/index.htm>

<http://www-ssrl.slac.stanford.edu/stohrgroup/>

Classical Picture of X-Ray Interactions with Matter:

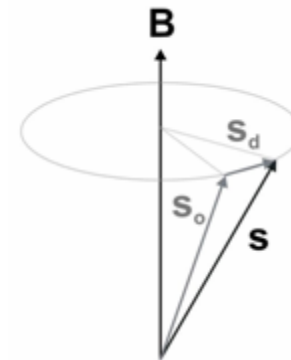
Non Resonant X-Ray Scattering

Electric Dipole Scattering

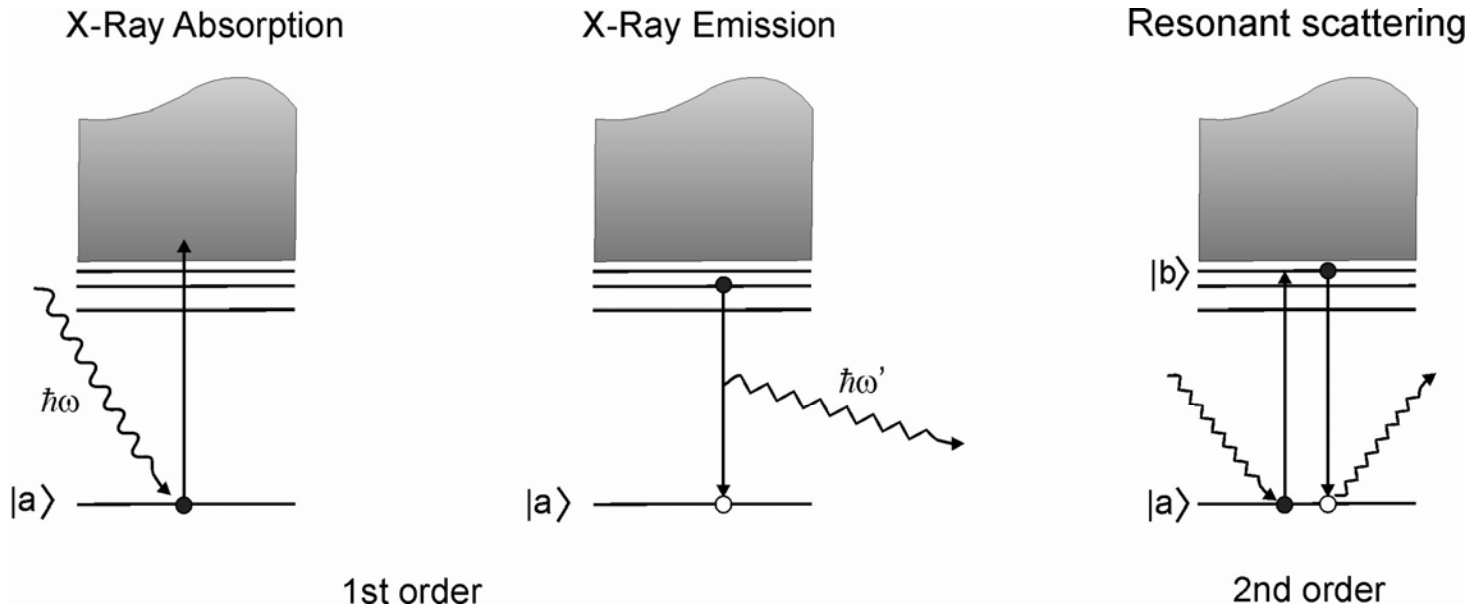


Relative Intensity: **1**

Magnetic Dipole Scattering



Quantum Theoretical X-Ray Interactions with Matter: The Basic Processes



$$\mathcal{H}_{int} = \frac{e}{m_e} \mathbf{p} \cdot \mathbf{A} \qquad E = -\partial A / \partial t$$

The transition probability per unit time, T_{if} , from a state i to a state f is given up to second order by,

$$T_{if} = \frac{2\pi}{\hbar} \left| \langle f | \mathcal{H}_{int} | i \rangle + \sum_j \frac{\langle f | \mathcal{H}_{int} | j \rangle \langle j | \mathcal{H}_{int} | i \rangle}{\epsilon_i - \epsilon_j} \right|^2 \delta(\epsilon_i - \epsilon_f) \rho(\epsilon_f) \quad (109)$$

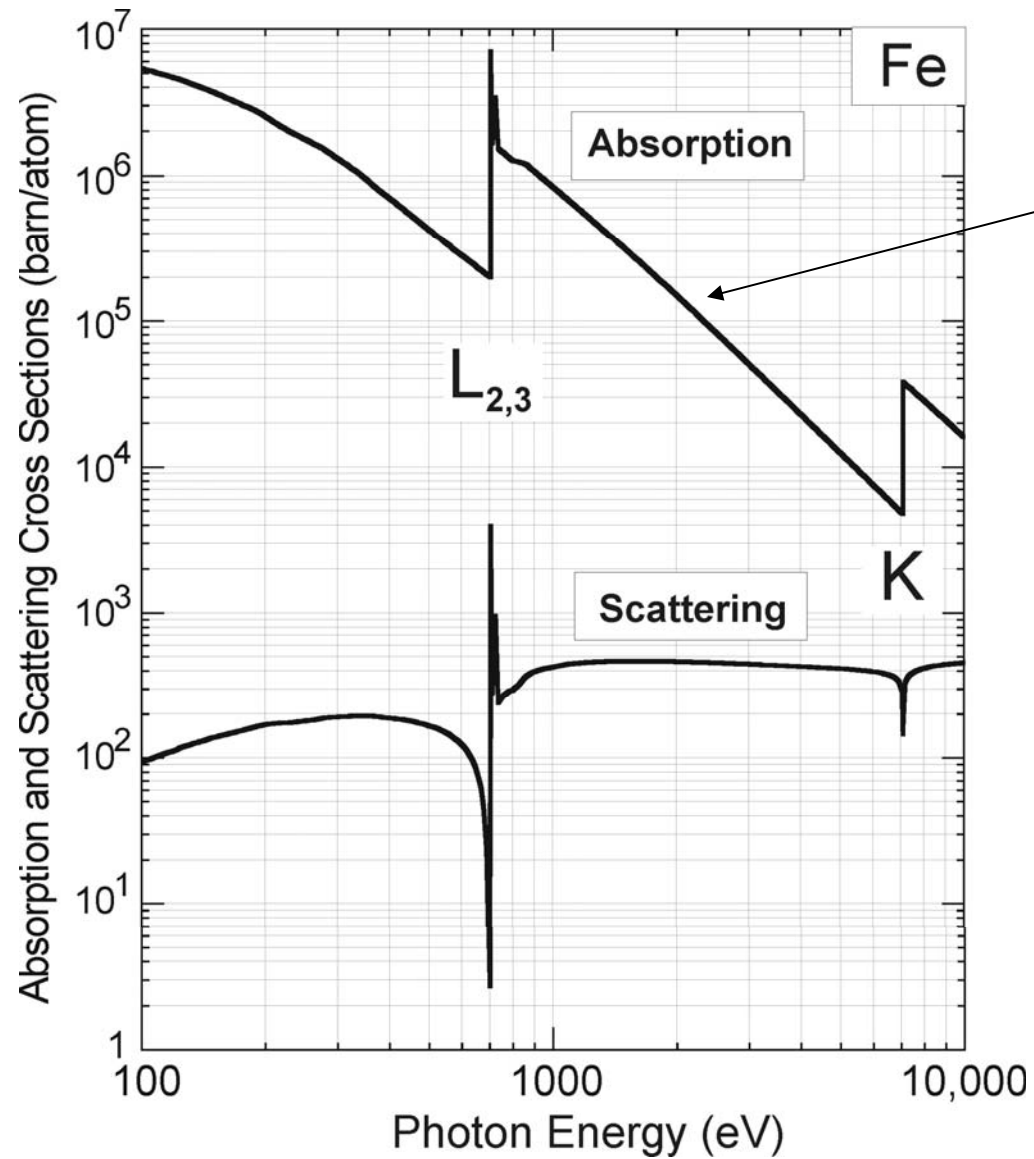
Fermi's Golden rule

The sum is over all possible states of energy ϵ_j . The dimension of T_{if} is [1/time].

Kramers-Heisenberg relation

X-Ray Interactions with Matter

Cross Sections

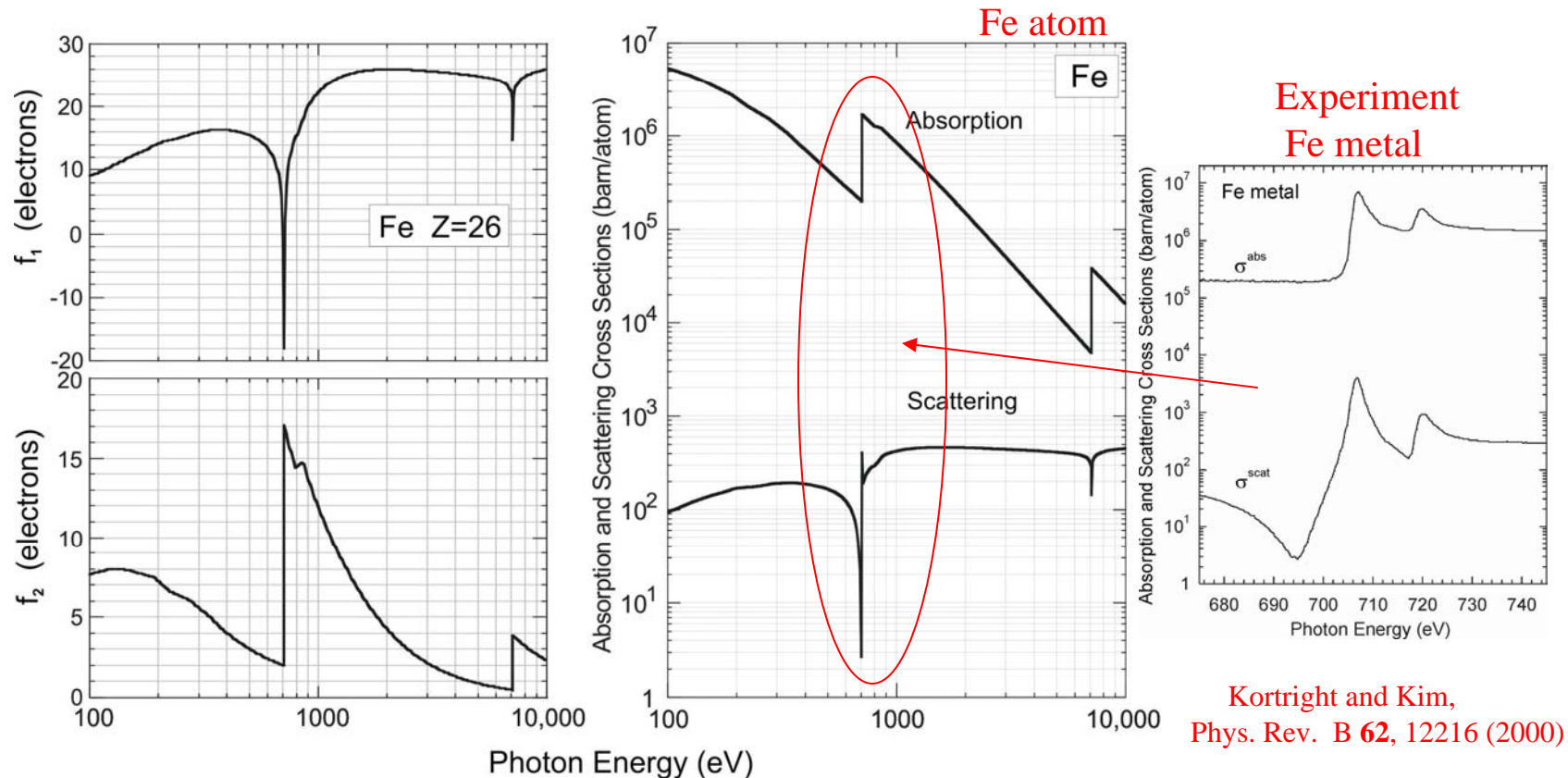


X-Ray Absorption and Scattering Cross Sections per Atom

Scattering: $\sigma^{scat}(E) = \sigma_e \left([f_1(E)]^2 + [f_2(E)]^2 \right)$

Absorption: $\sigma^{abs}(E) = \frac{C^*}{E} f_2(E)$

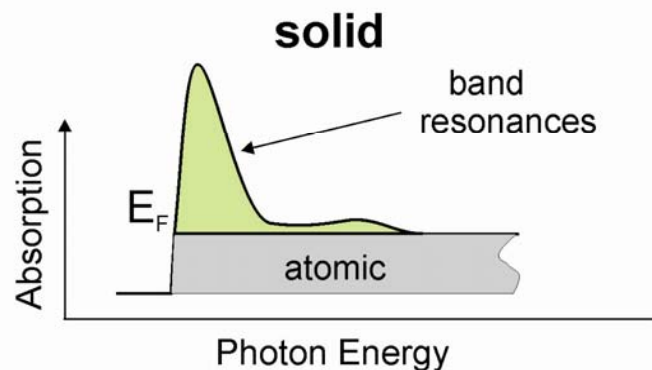
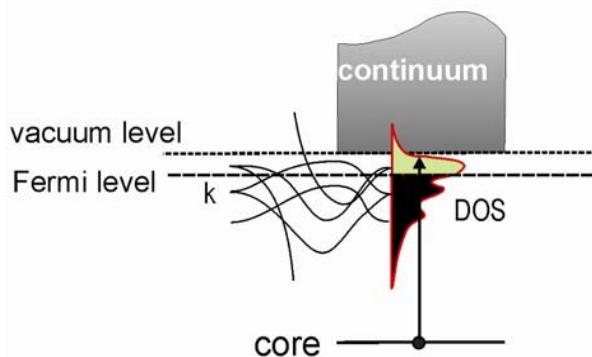
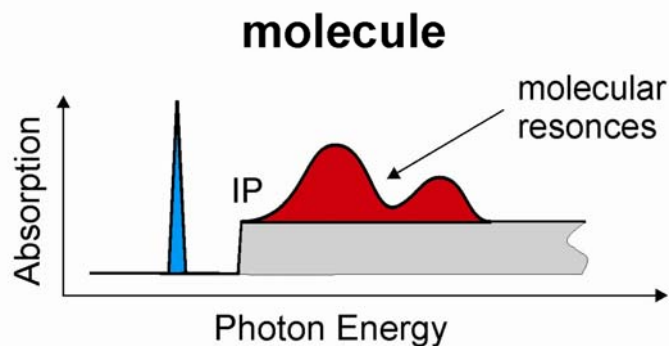
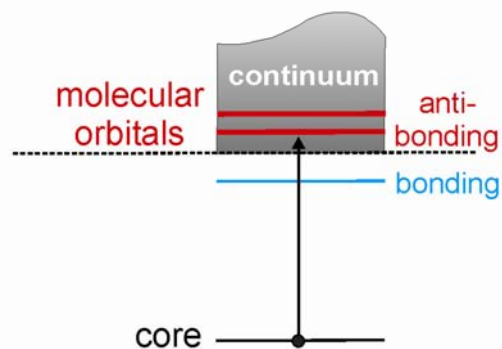
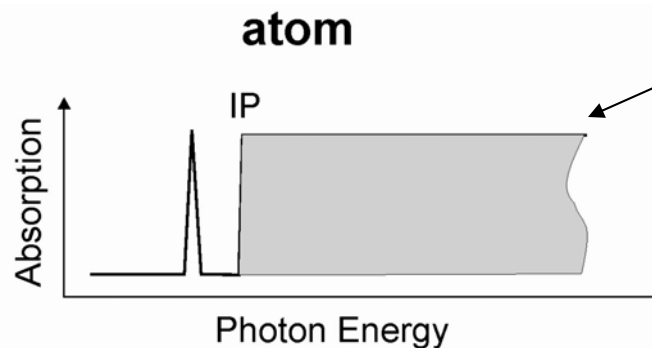
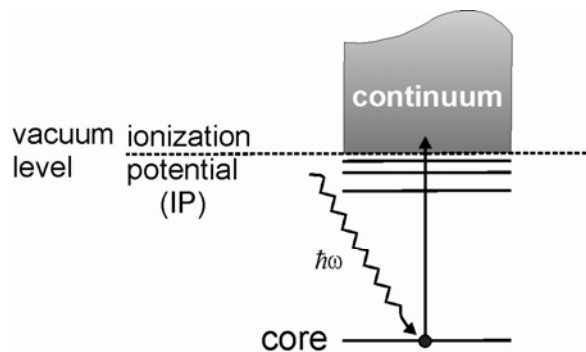
Thomson Cross section
 $C^* = 2hc r_0 = 0.70 \times 10^8 \text{ barn eV}$



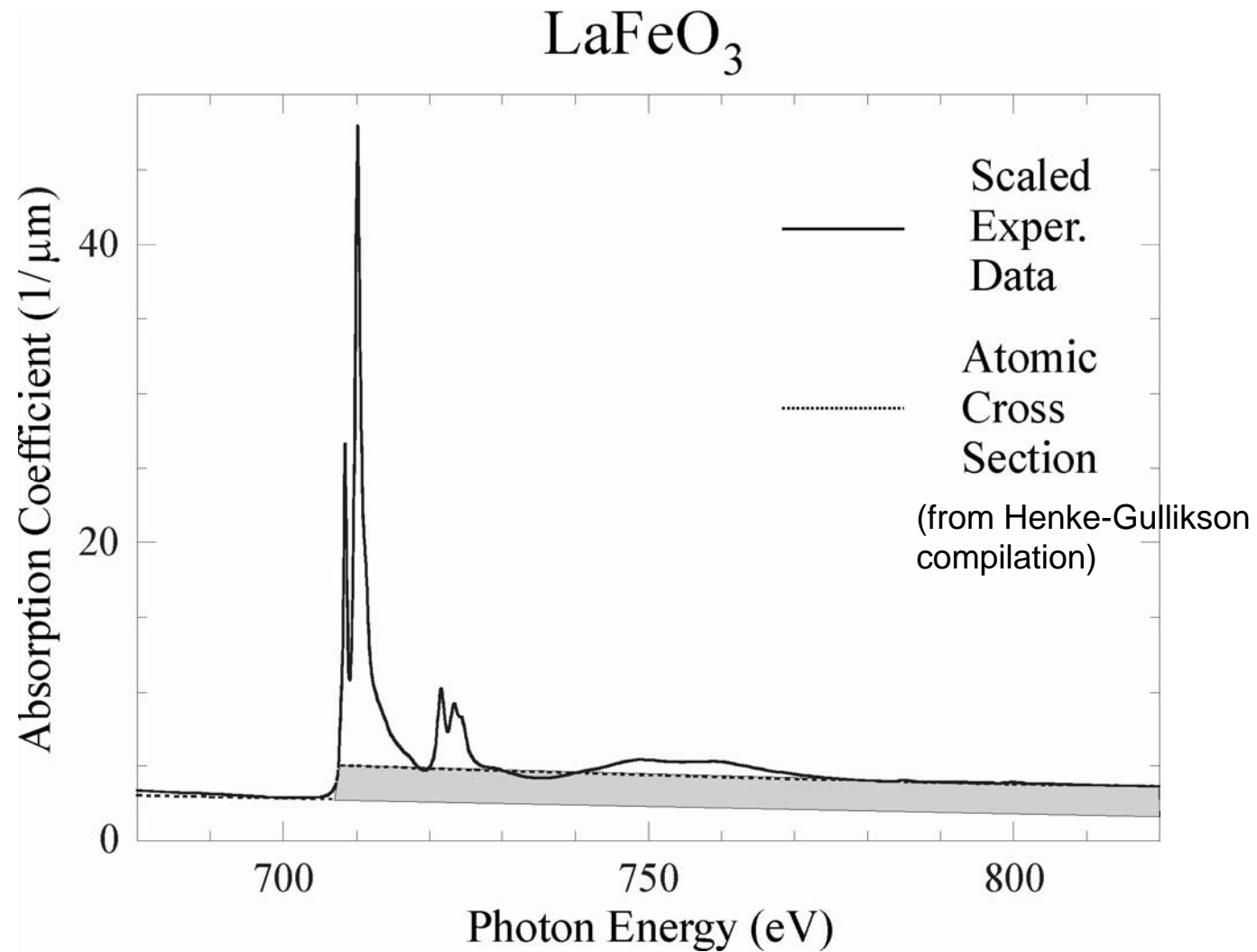
Kortright and Kim,
 Phys. Rev. B **62**, 12216 (2000)

f_1 and f_2 tabulated Henke-Gullikson factors
<http://www-cxro.lbl.gov/index.php?content=/tools.html>

X-ray Absorption Spectra in a Nutshell

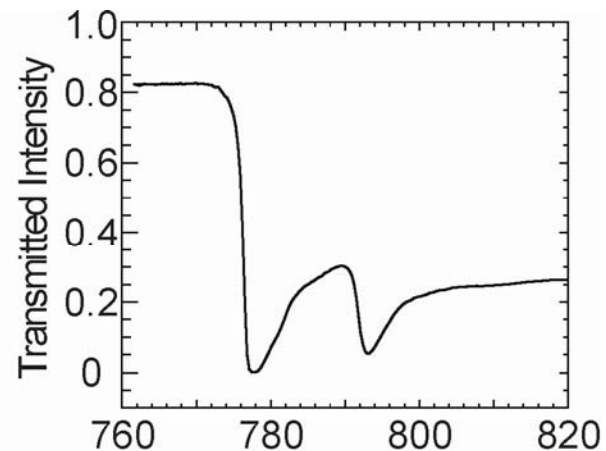
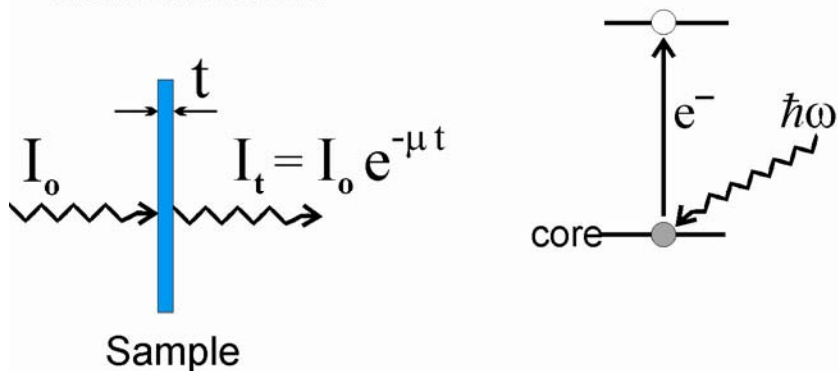


Absolute absorption coefficients from experimental spectra

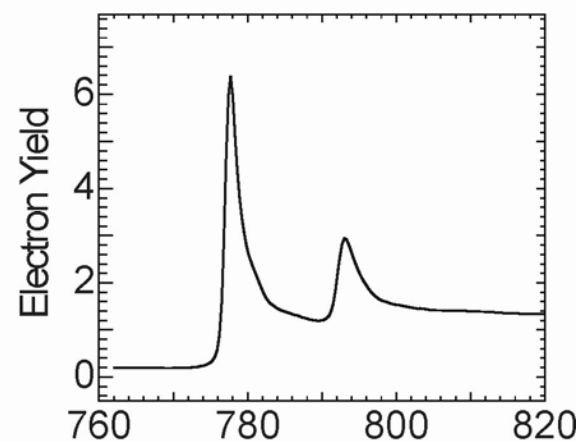
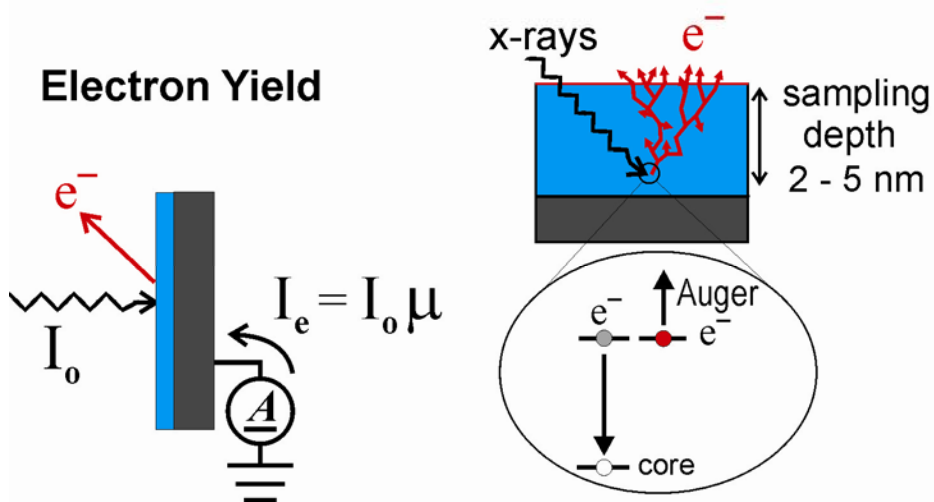


Experimental X-Ray Absorption Techniques

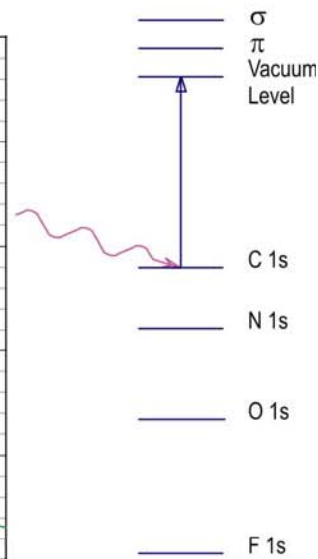
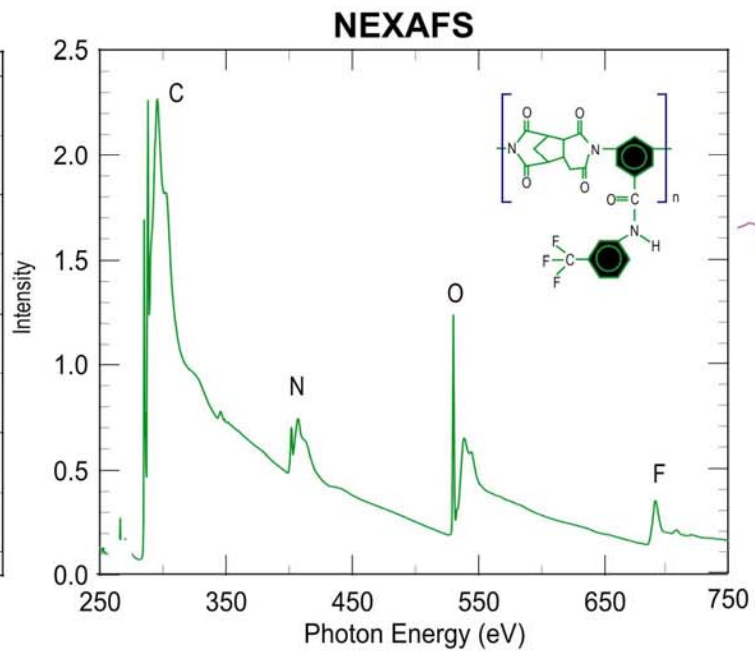
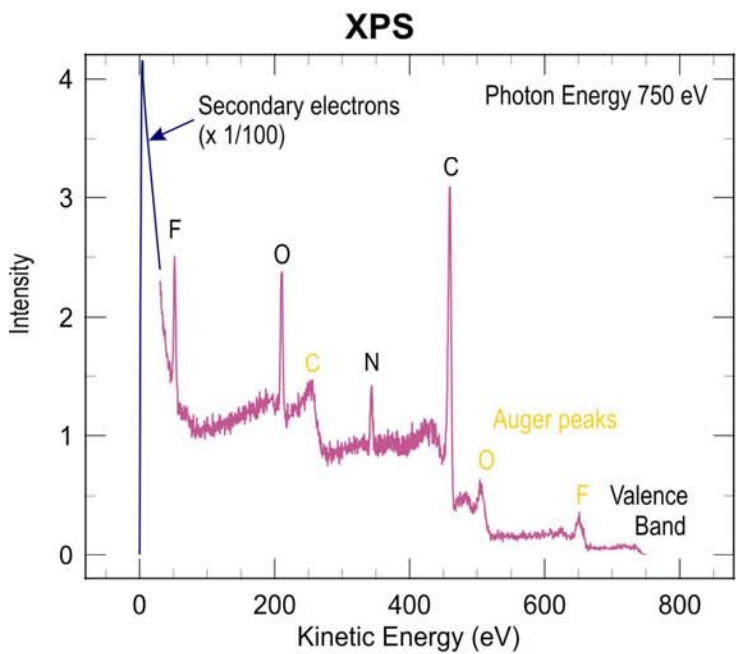
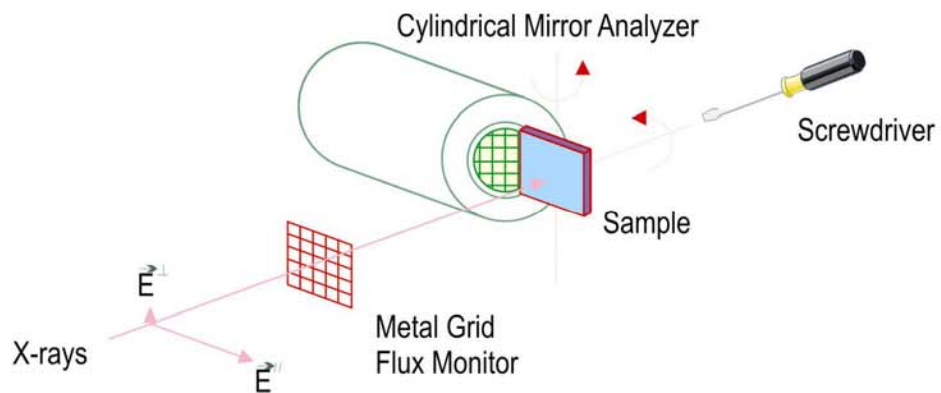
Transmission



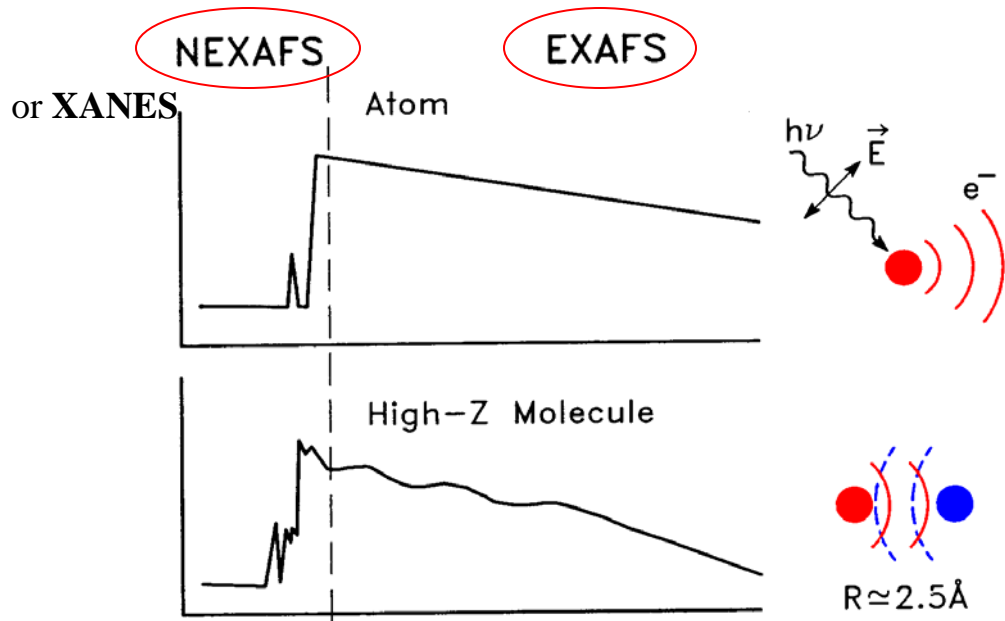
Electron Yield



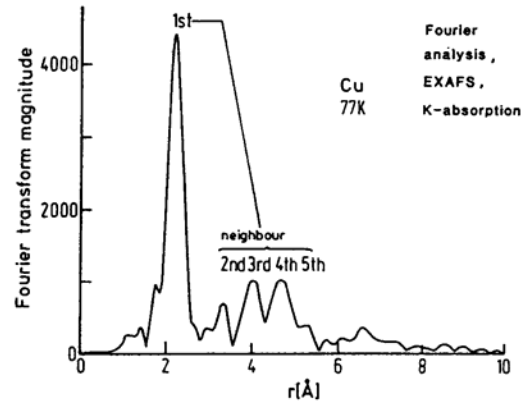
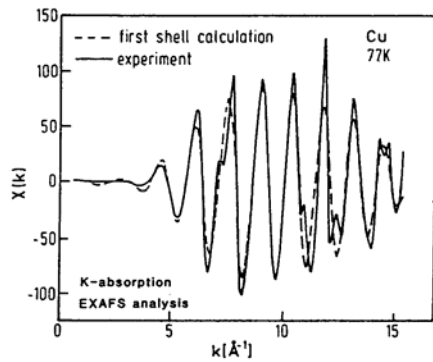
Experimental Set-Up



Names: XAFS – NEXAFS – XANES - EXAFS



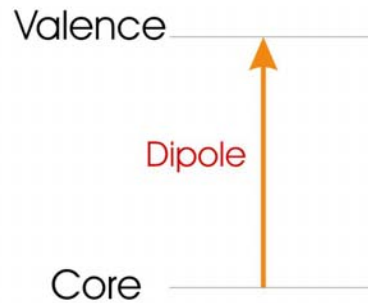
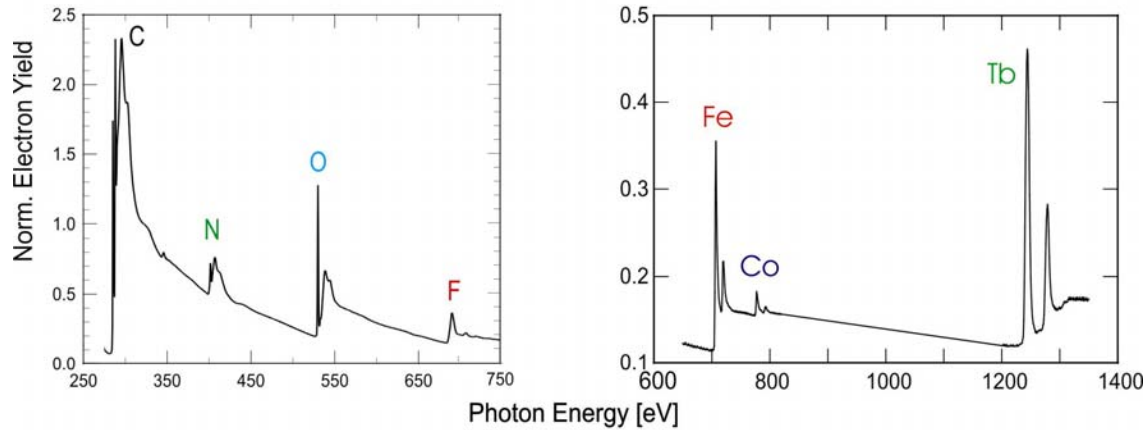
Interference of outgoing photoelectron and scattered waves



Nearest neighbor distances

Number of neighbors

Valence Shell Properties and X-Ray Absorption

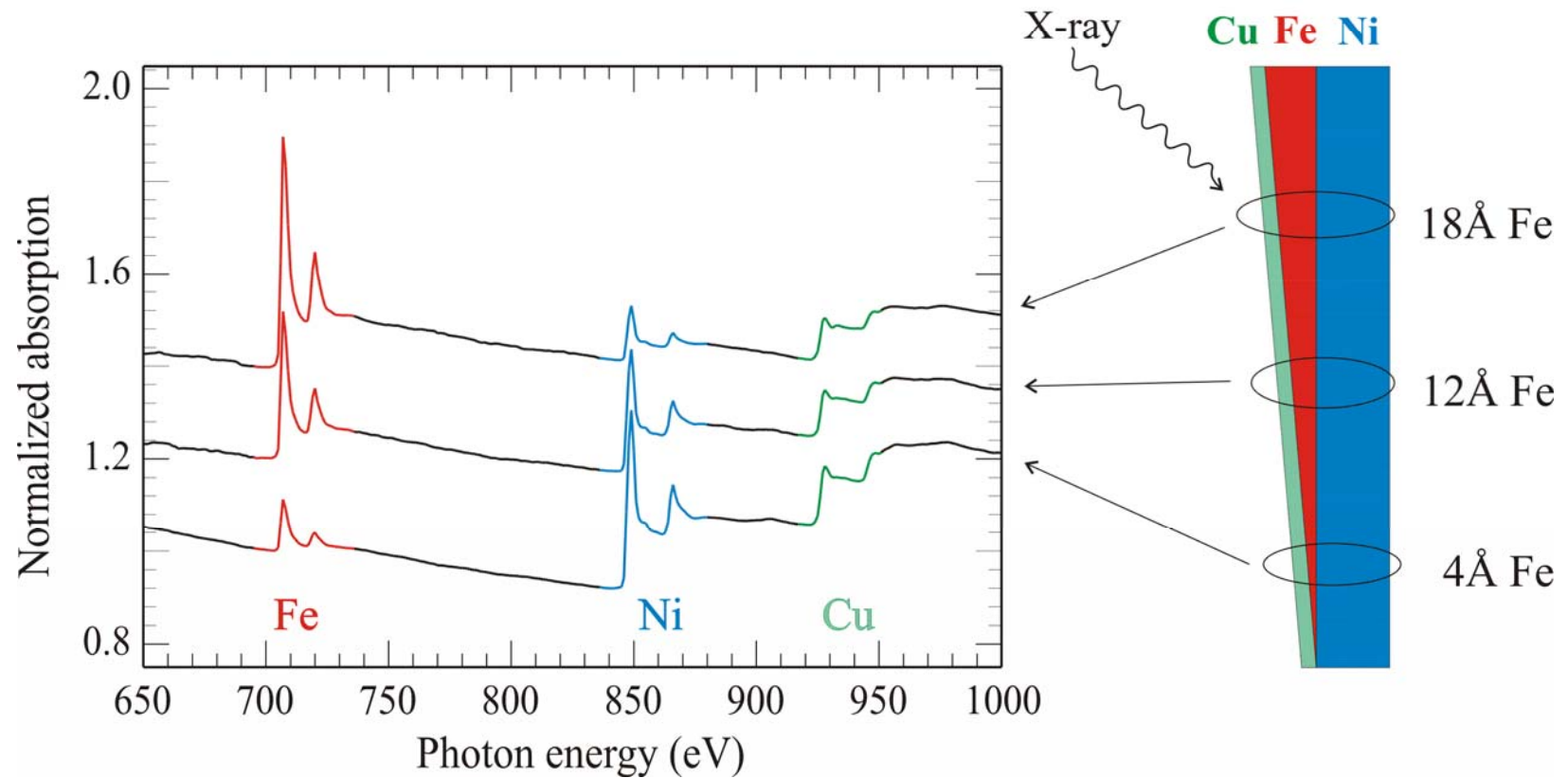


Polymers: p-orbitals
 Trans. Met.: d-orbitals
 Rare Earths: f-orbitals

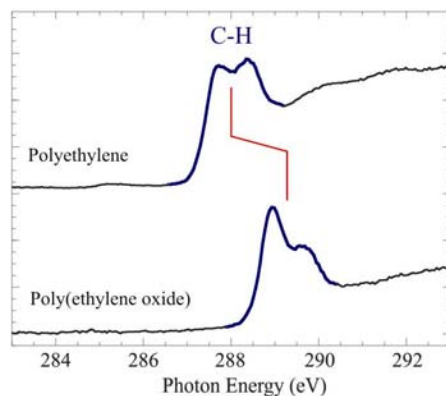
1s K-edge
 2p L edge
 3d M edge

X-rays can pick samples apart :
 elemental sensitivity

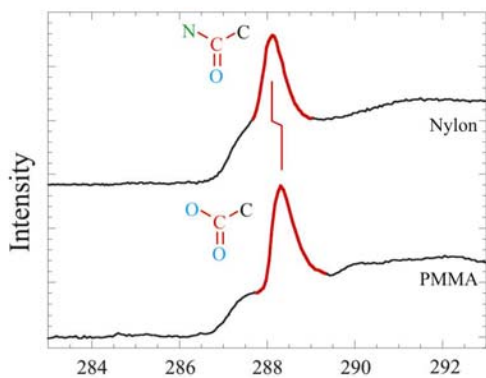
X-rays can pick materials apart: layer-by-layer



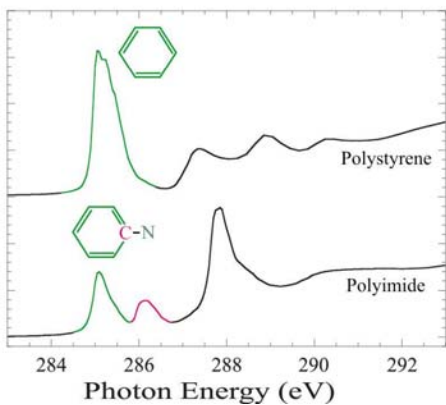
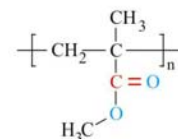
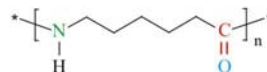
NEXAFS spectra of polymers: building block picture



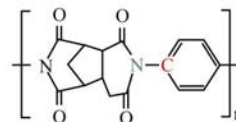
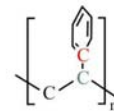
Carbon-Hydrogen Bonds



Unsaturated Bonds

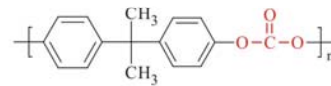
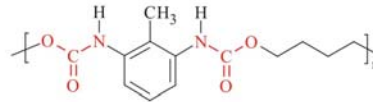
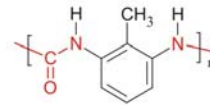
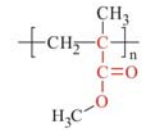
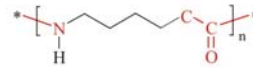
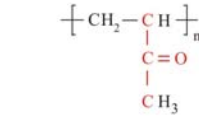
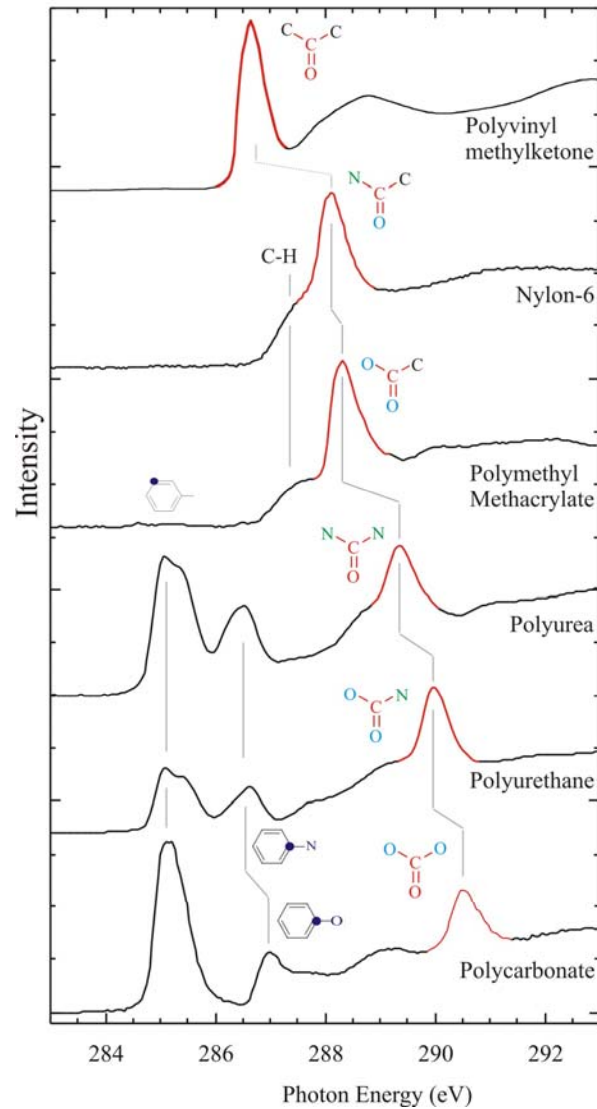


Aromatic Rings



Chemical Sensitivity

Chemical Shift of C=O π Resonance



Core level shifts

and

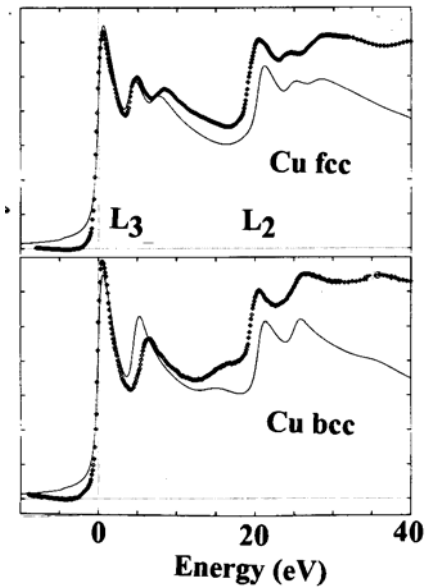
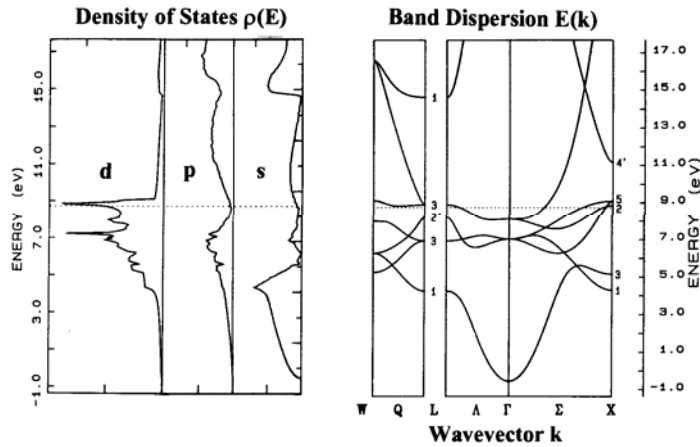
Molecular orbital shifts

XAFS of Transition Metals

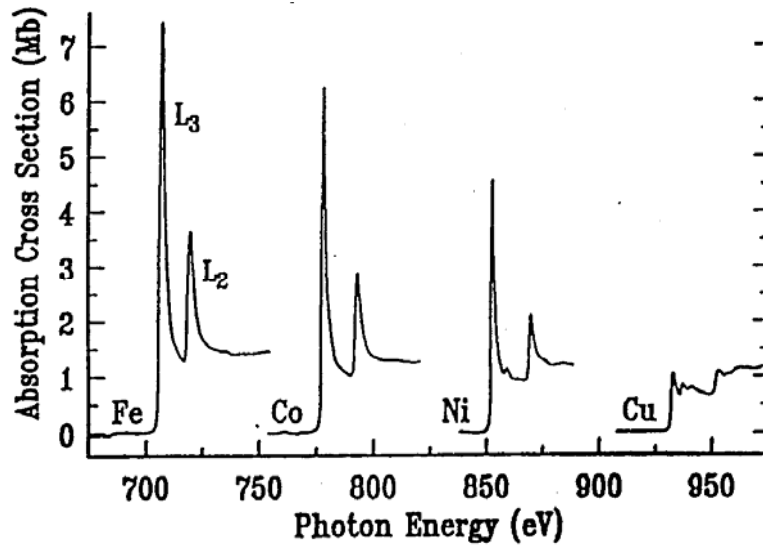
Dipole selection rule $\Delta l = \pm 1$

$2p \rightarrow 3d$

$2p \rightarrow 4s$

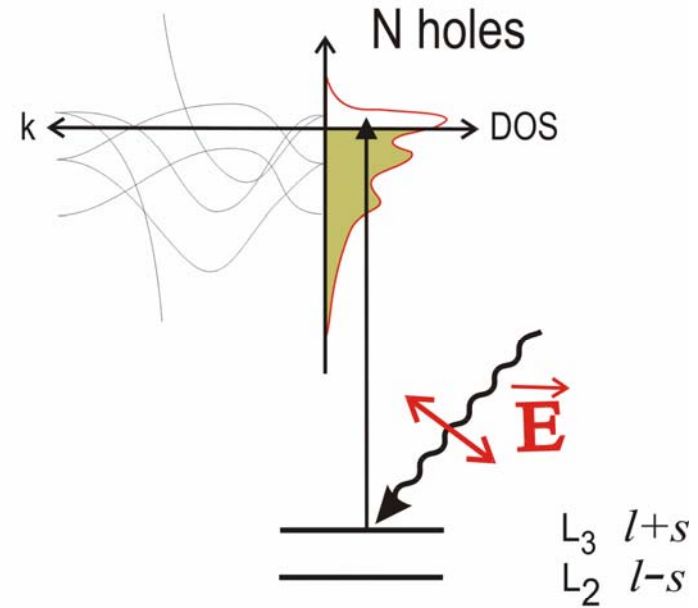
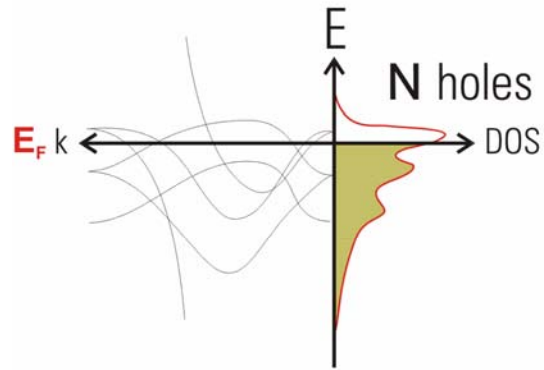


Ebert et. al. Phys. Rev. B 53, 16067 (1996).

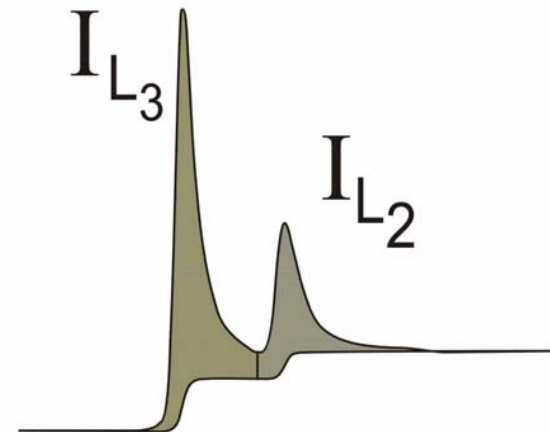


Total intensity reflect number of empty holes

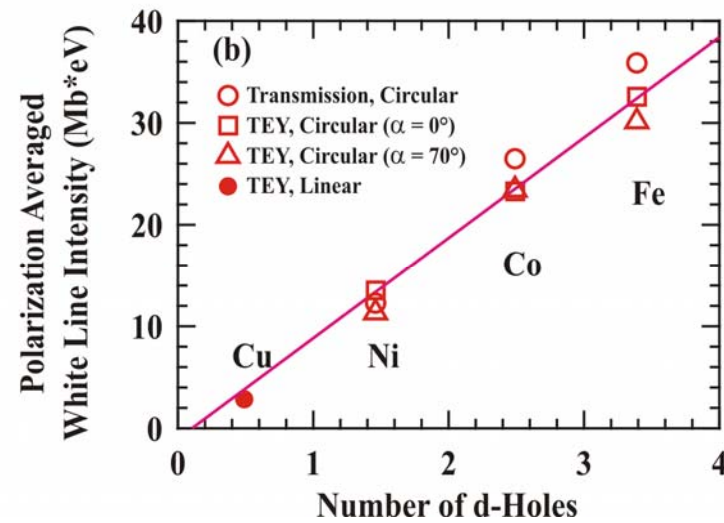
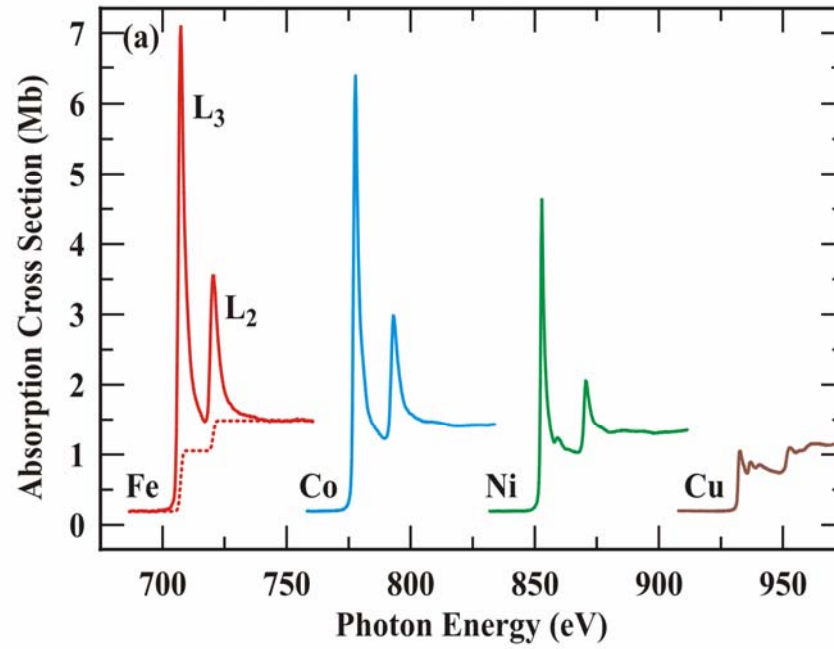
Properties of 3d Transition Metals



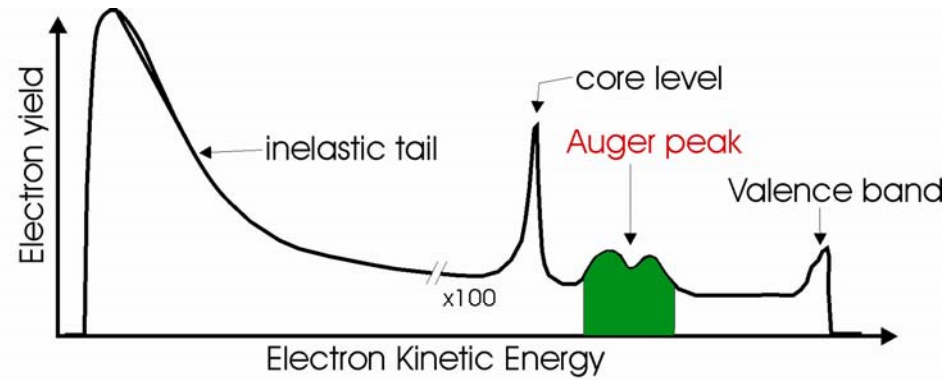
	holes
Fe	3.4
Co	2.5
Ni	1.5



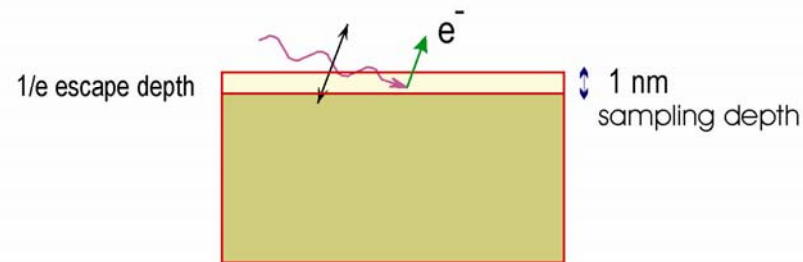
White Line Intensity in 3d Metals



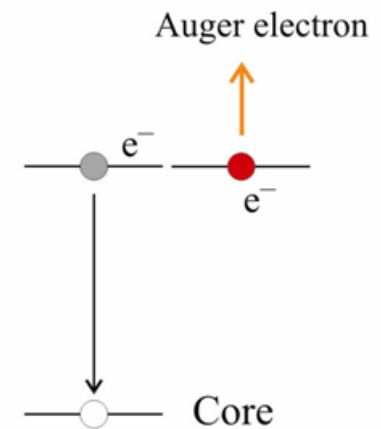
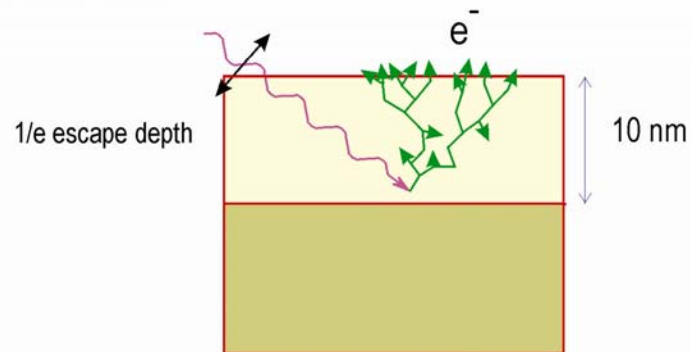
Electron Yield Sampling Depth



Auger Electron Yield

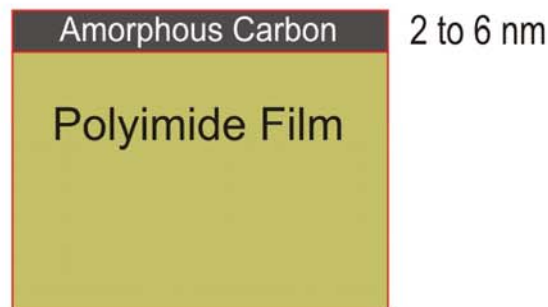
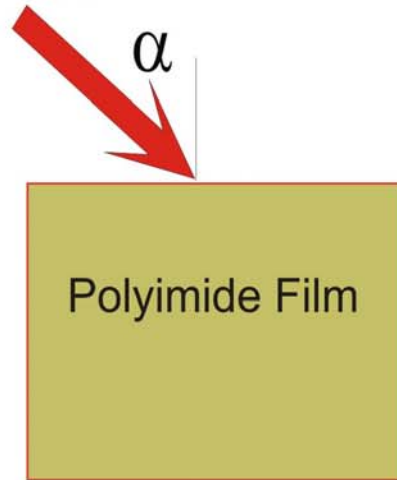


Total Electron Yield

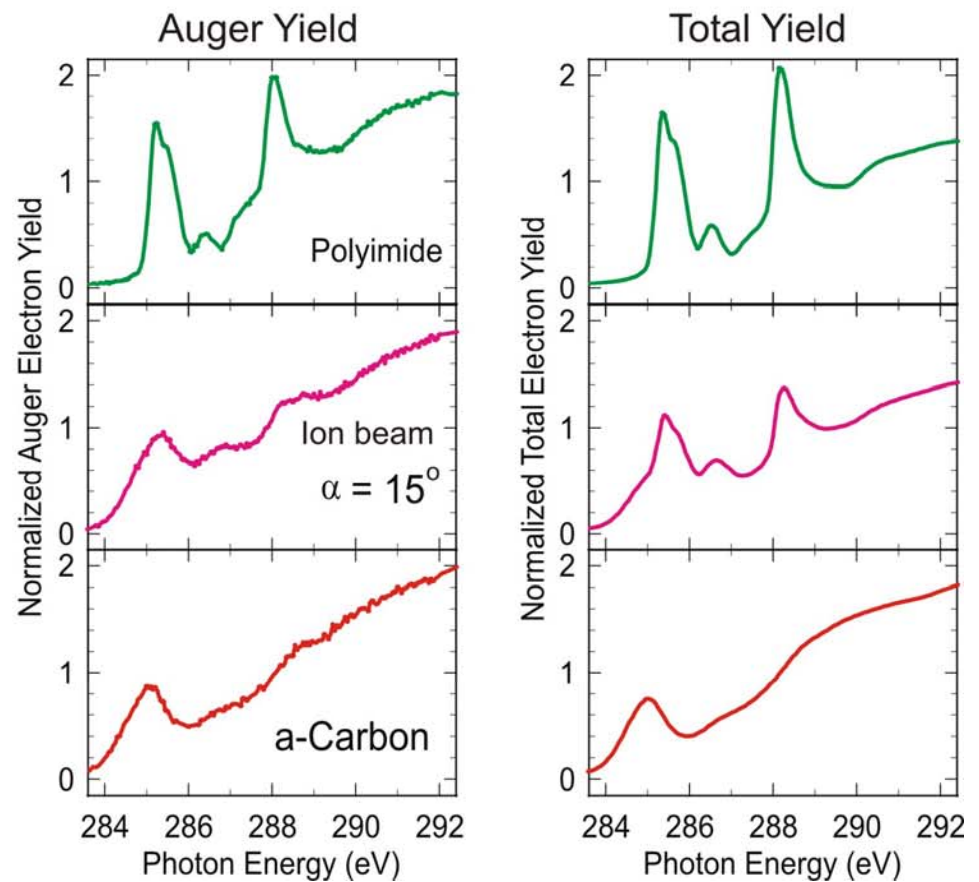


Surface sensitivity of total and Auger yield

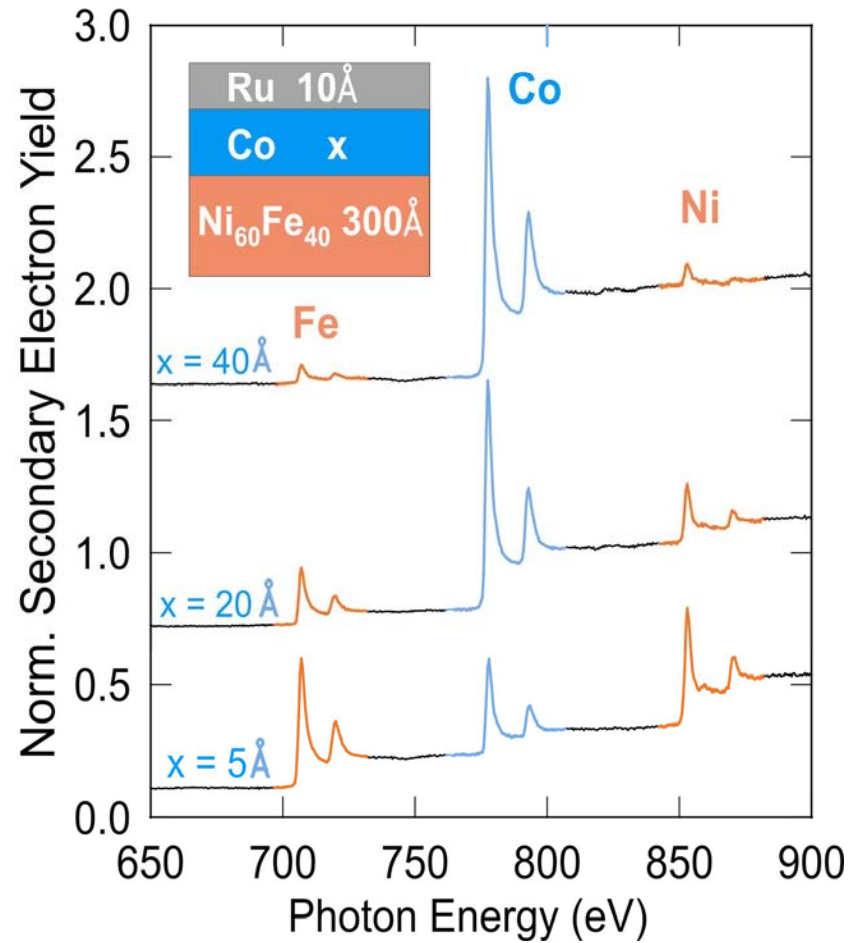
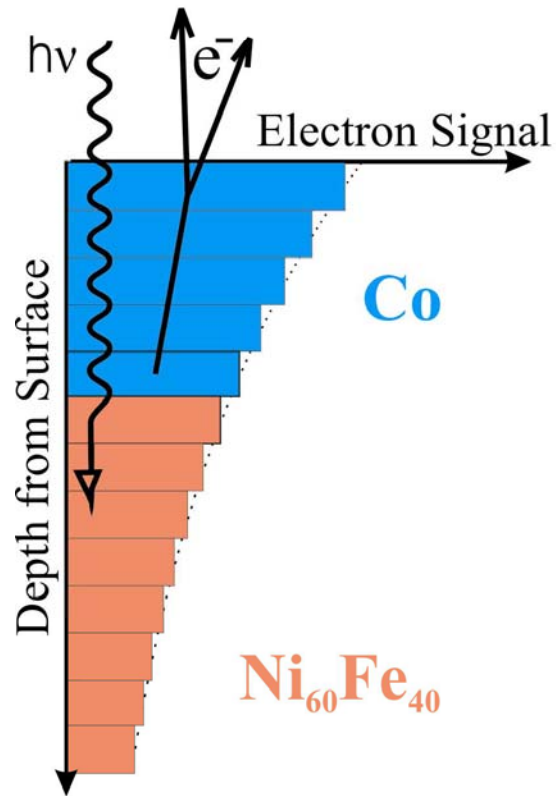
Ion Beam



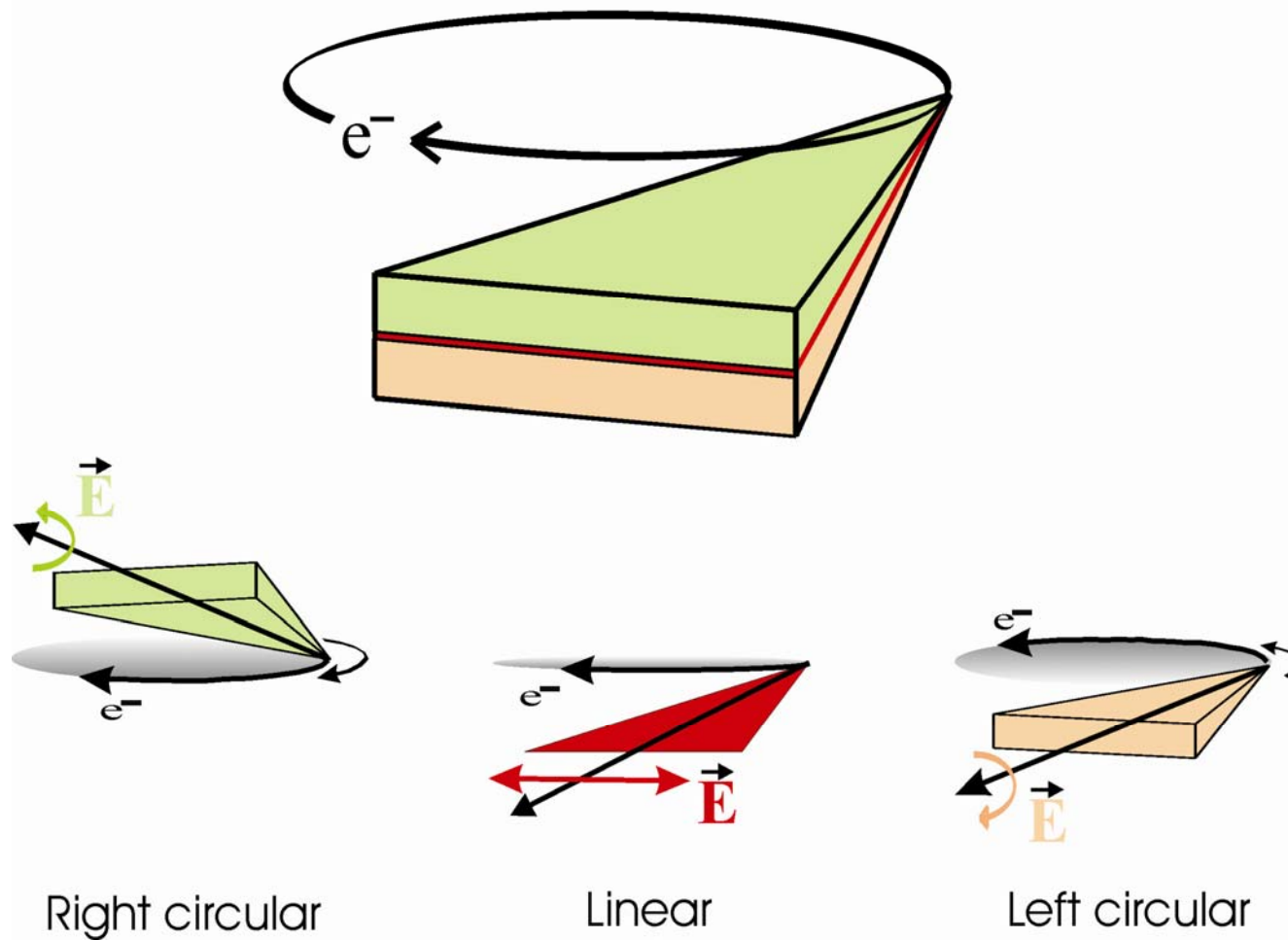
Ion Beam Conversion of Polyimide



Effective Electron Sampling Depth total yield

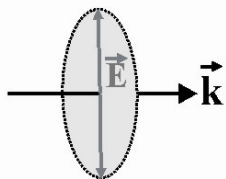
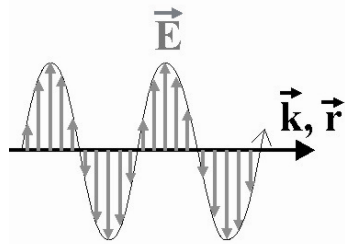


Polarization of Synchrotron X-Rays



Polarization definitions

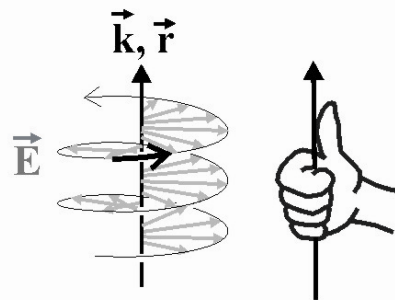
Linear polarization



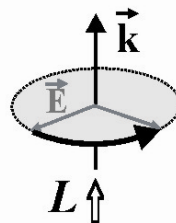
defines
axis

Right circular polarization

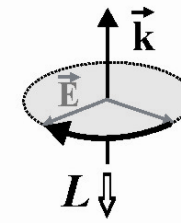
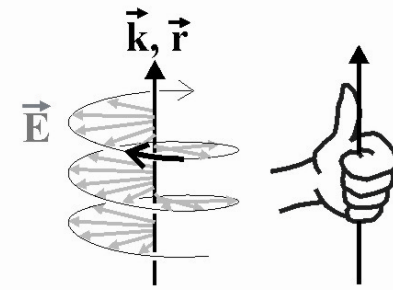
space



time



Left circular polarization



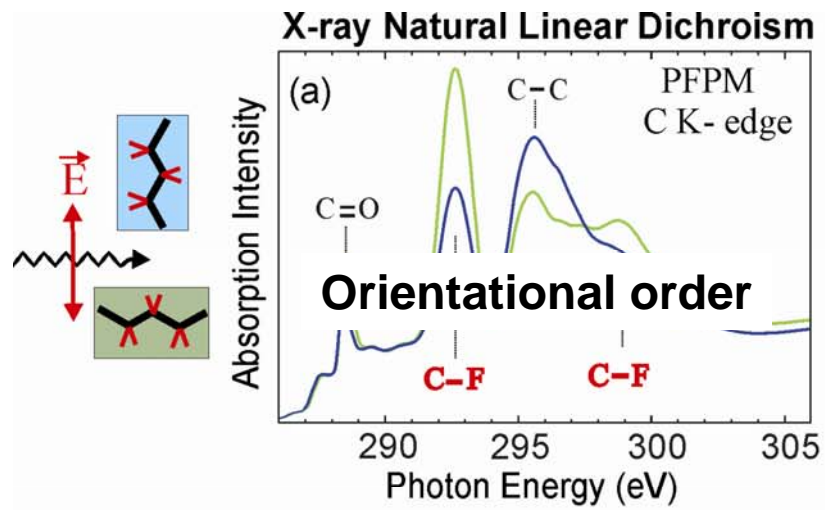
defines

handedness (chirality)

or

direction (photon angular momentum)

Polarized x-rays offer orientation sensitivity



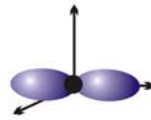
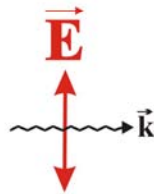
Stöhr *et al.*, Phys. Rev. Lett. **47**, 381 (1981)

X-Ray Natural Linear Dichroism

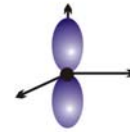
The Search Light Effect

K-edge

probe empty **p** orbitals



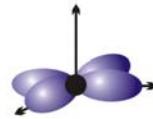
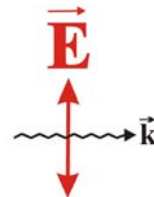
no
absorption



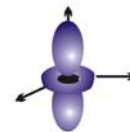
large
absorption

L-edge

probe empty **d** orbitals



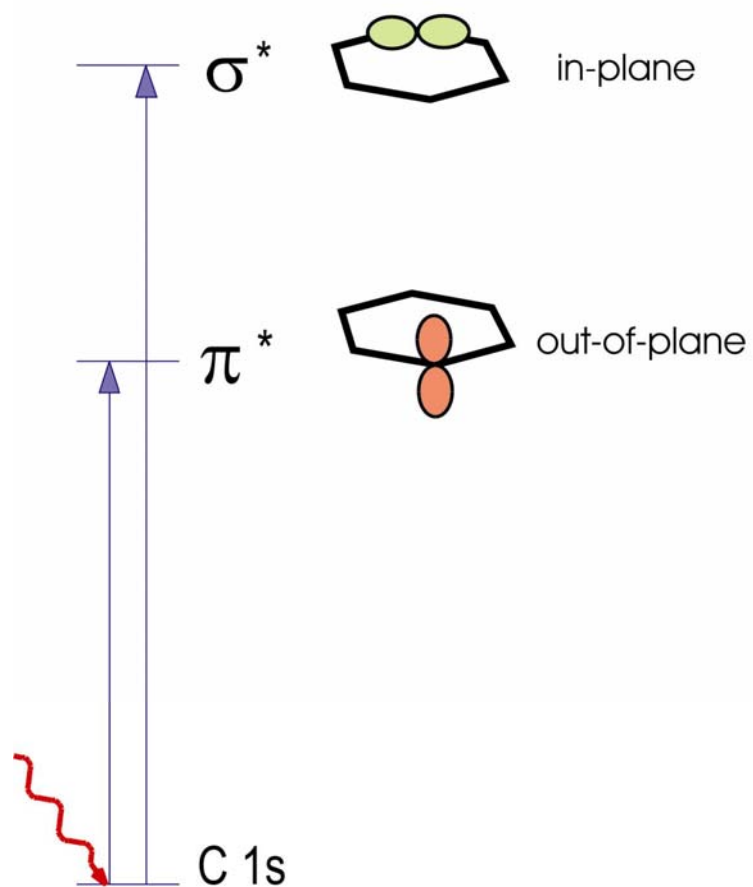
no
absorption



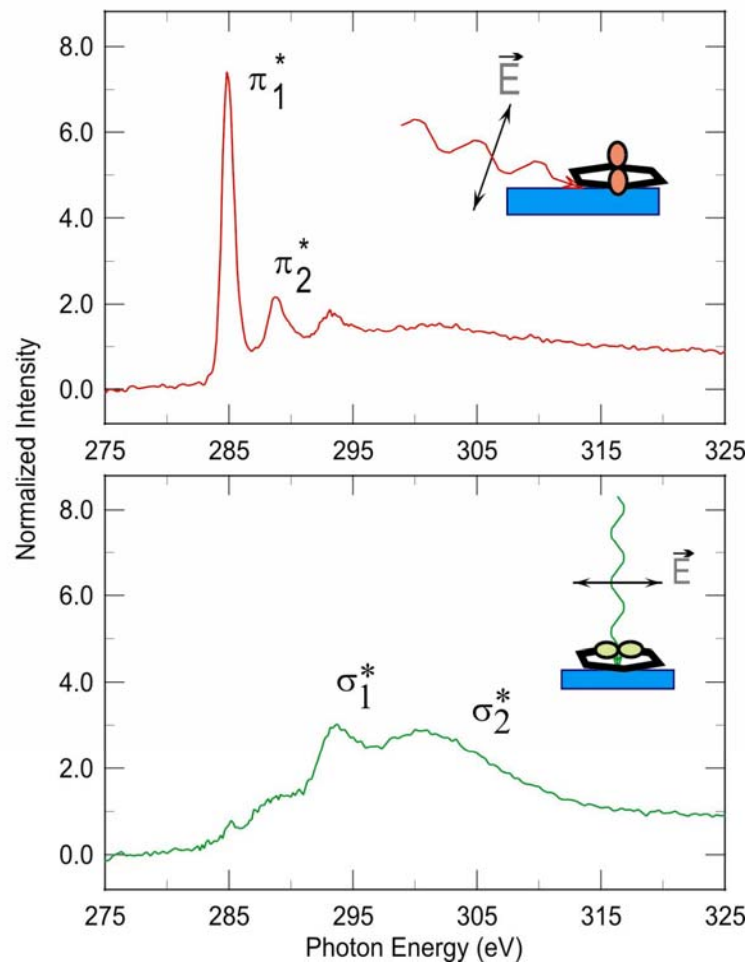
large
absorption

The "Search Light Effect"

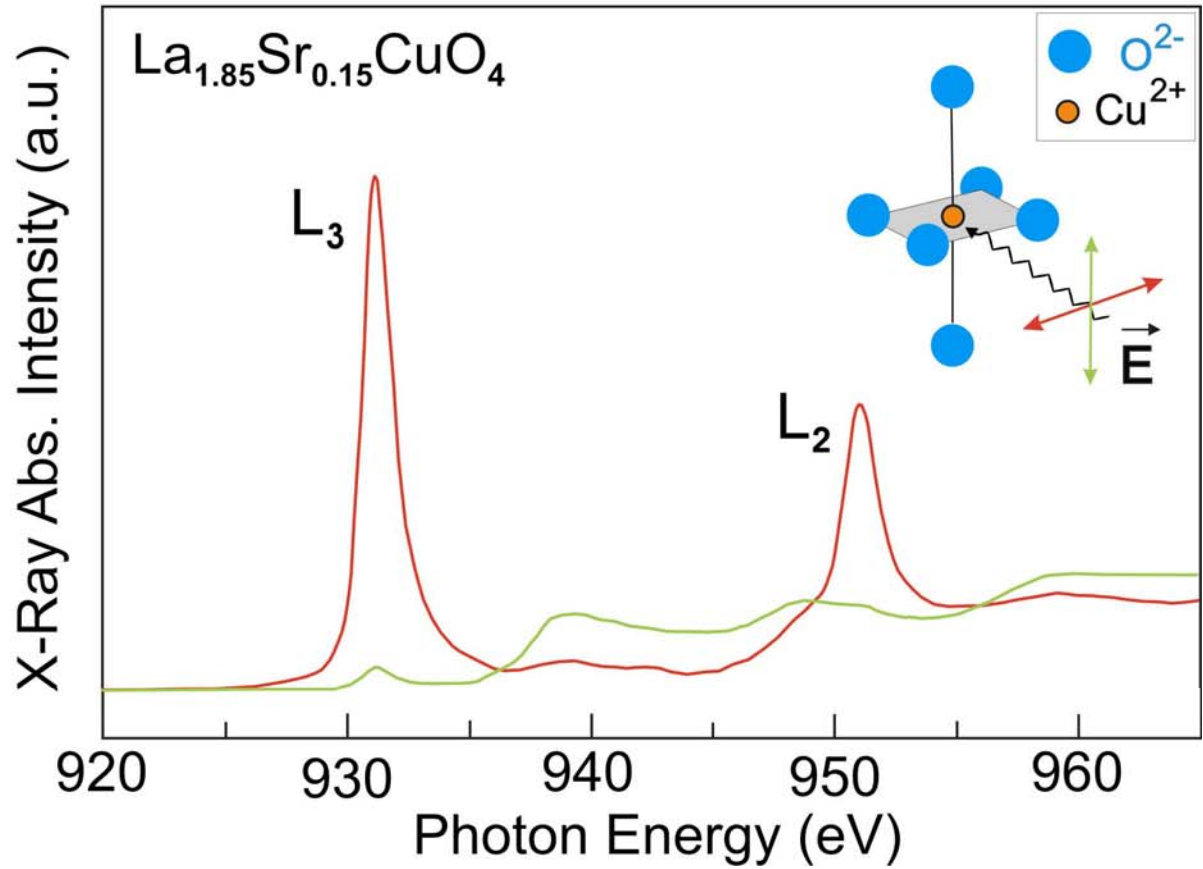
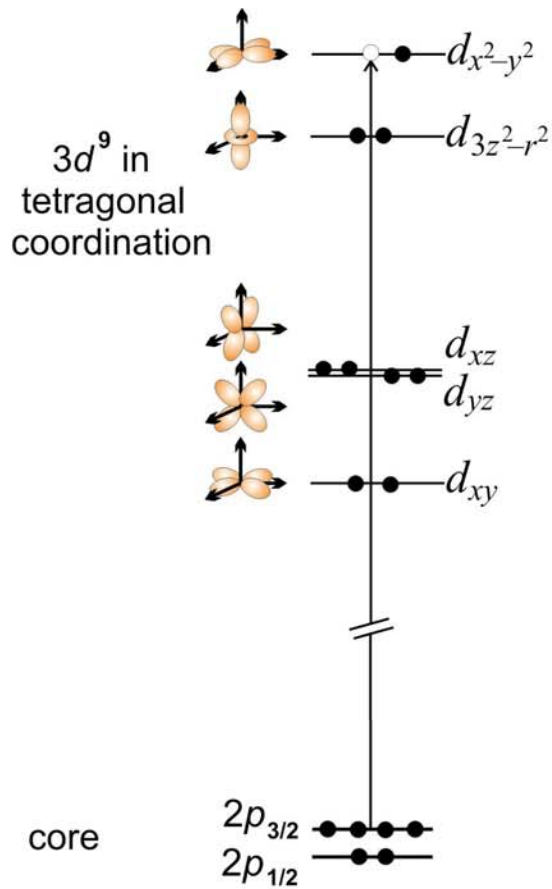
Benzene Molecular Orbitals



Lying-down benzene on Ag (110)

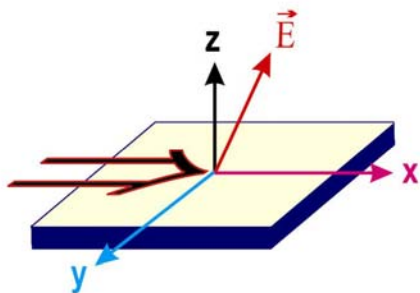


Linear Charge Dichroism in a d-electron system

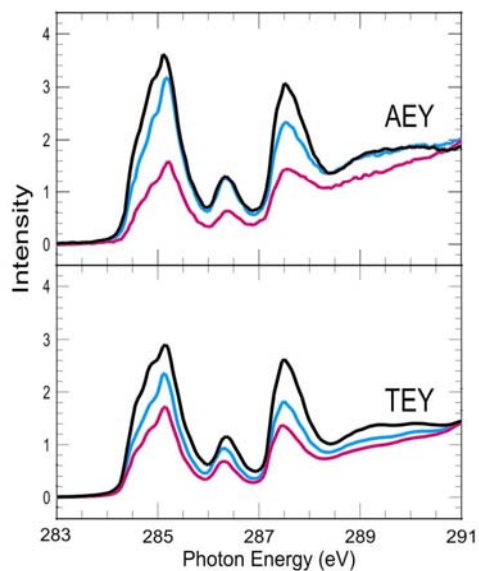


C. T. Chen *et al.* PRL **68**, 2543 (1992)

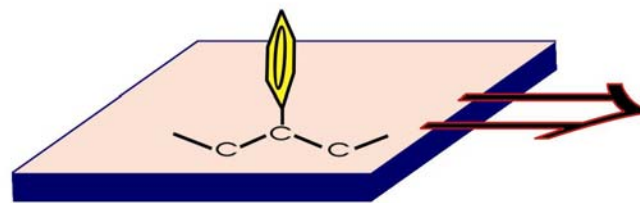
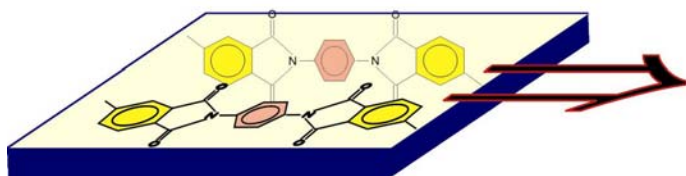
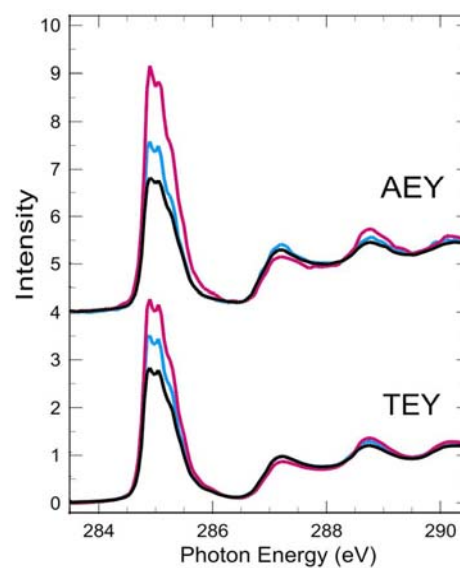
Polarization Dependent NEXAFS Probes Bond Anisotropy at Surface



Polyimide

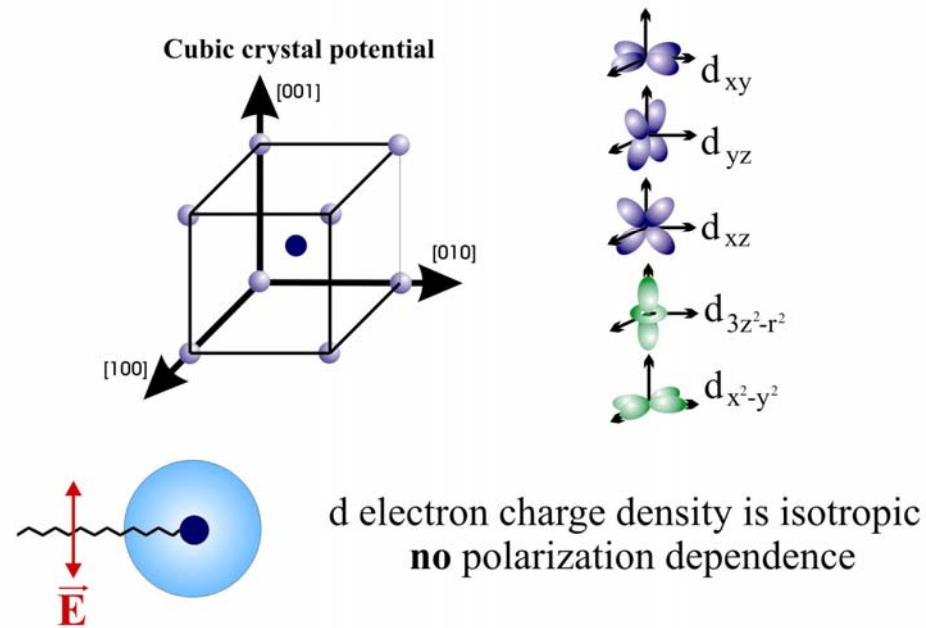


Polystyrene

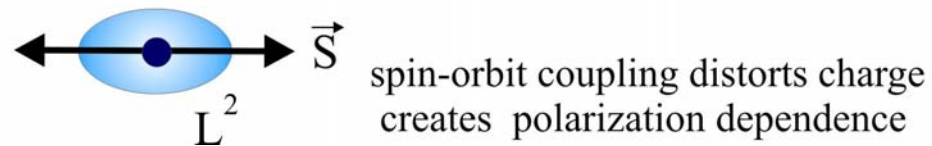


X-Ray **Magnetic Linear** Dichroism

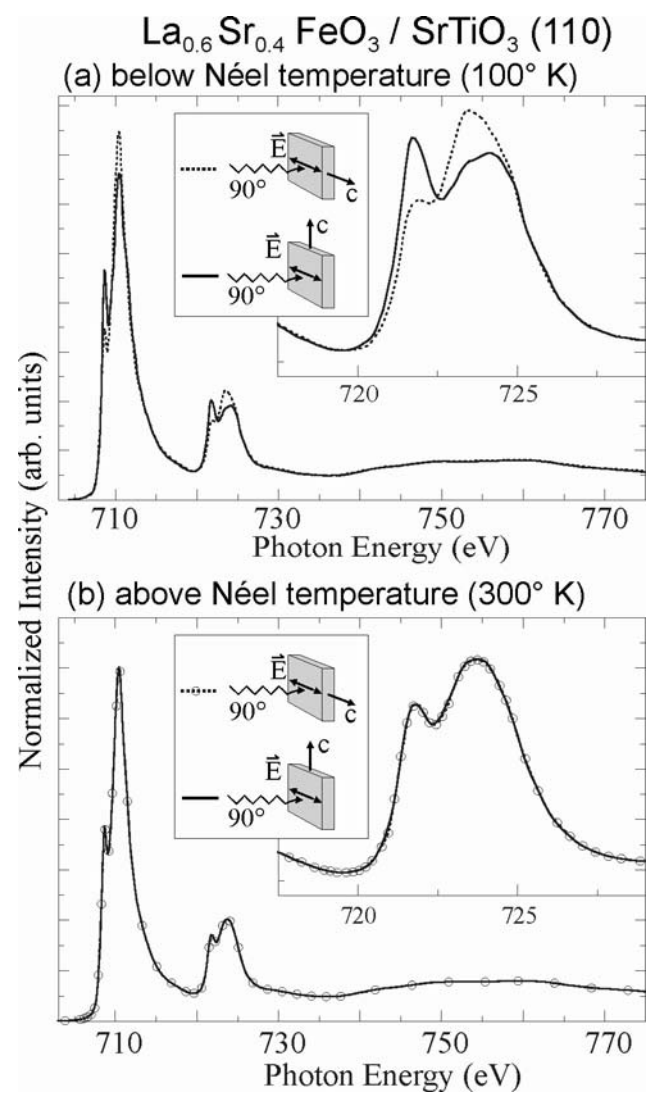
Non-magnetic state



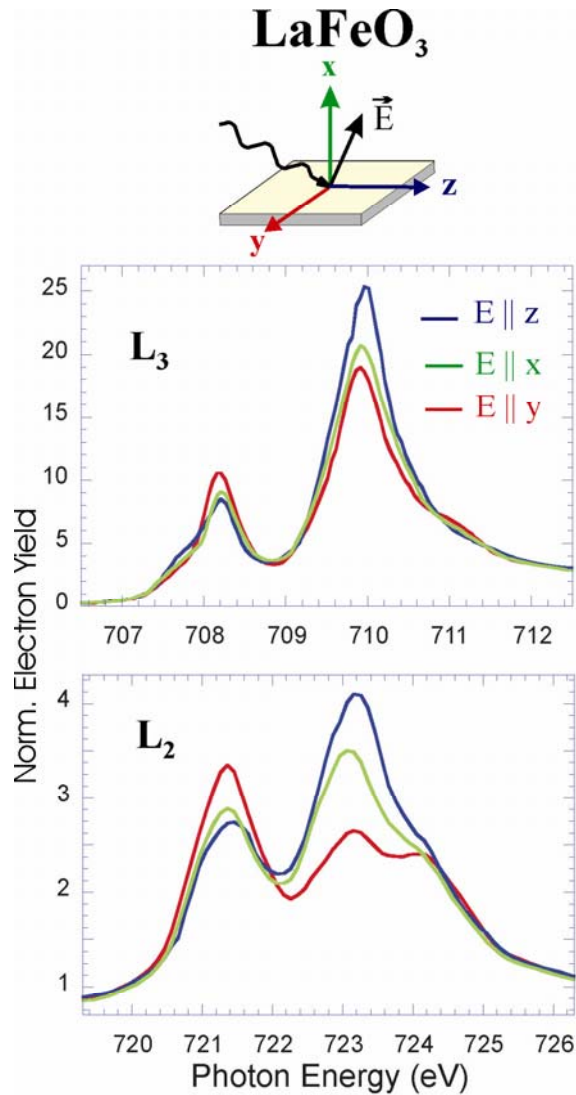
Magnetic state - preferred spin axis



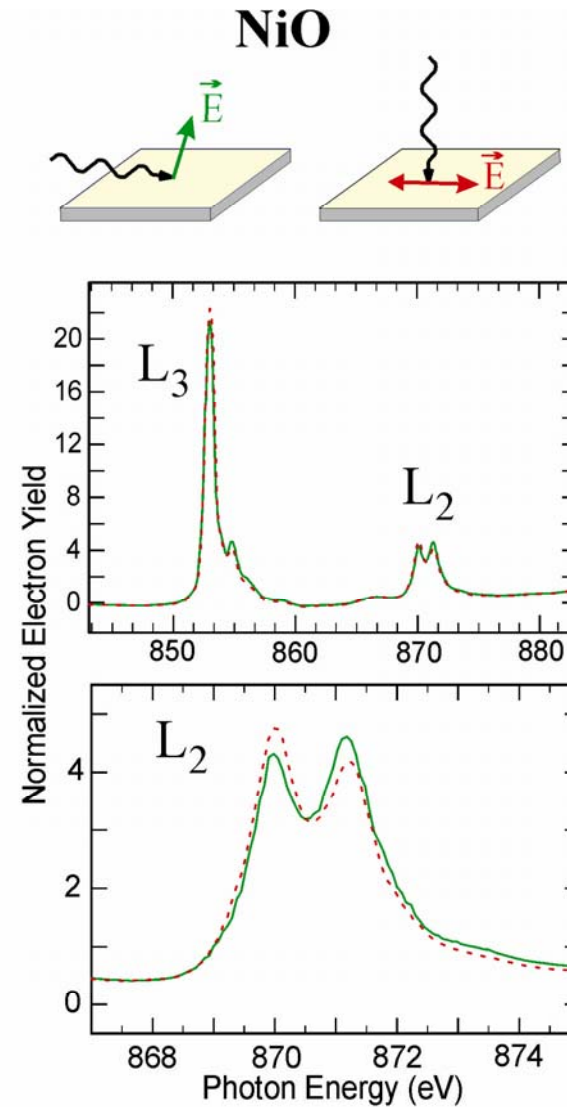
XMLD – spectra below and above T_N



XMLD spectra of two oxides

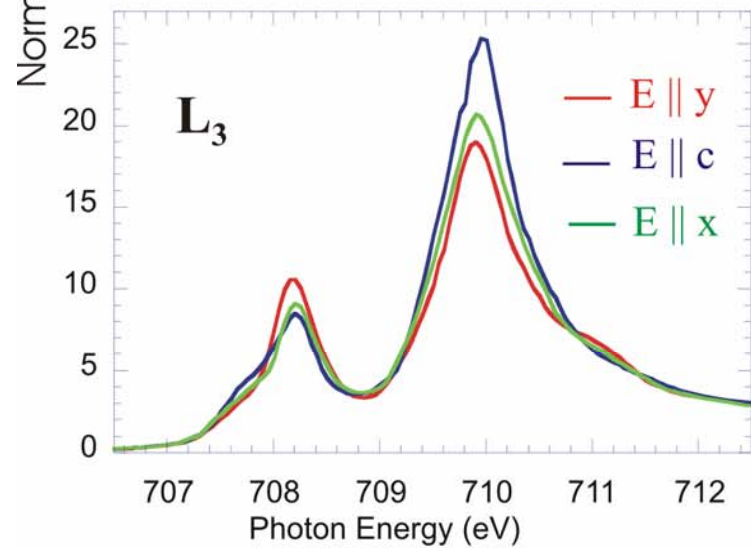
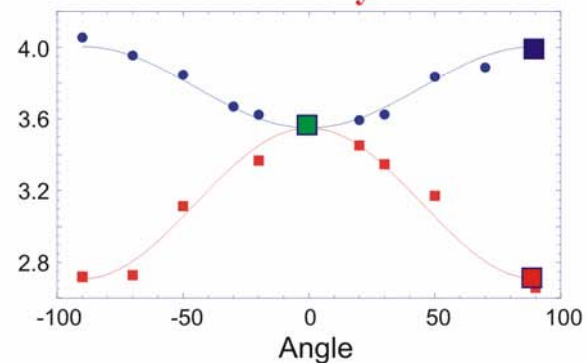
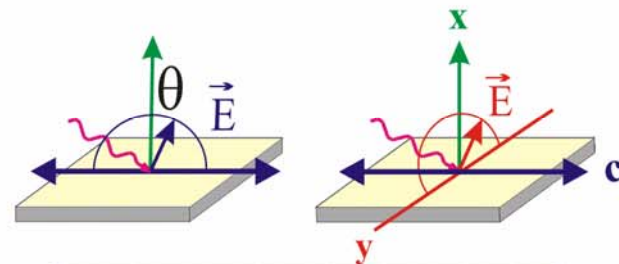
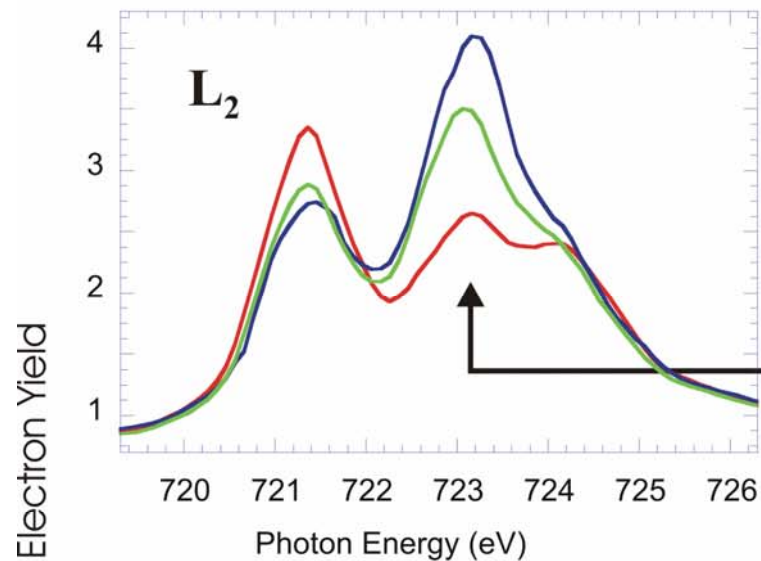


Kuiper *et al.*, Phys. Rev. Lett. **70**, 1549 (1993)
Lüning *et al.* Phys. Rev. B **67**, 214433 (2003)

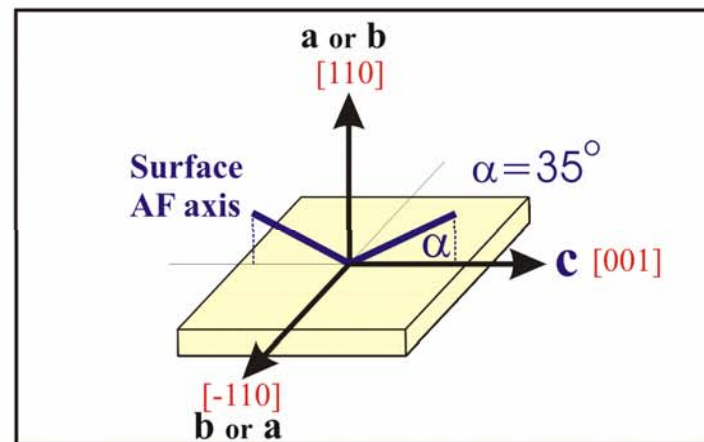


Alders *et al.*, Phys. Rev. B **57**, 11623 (1998)

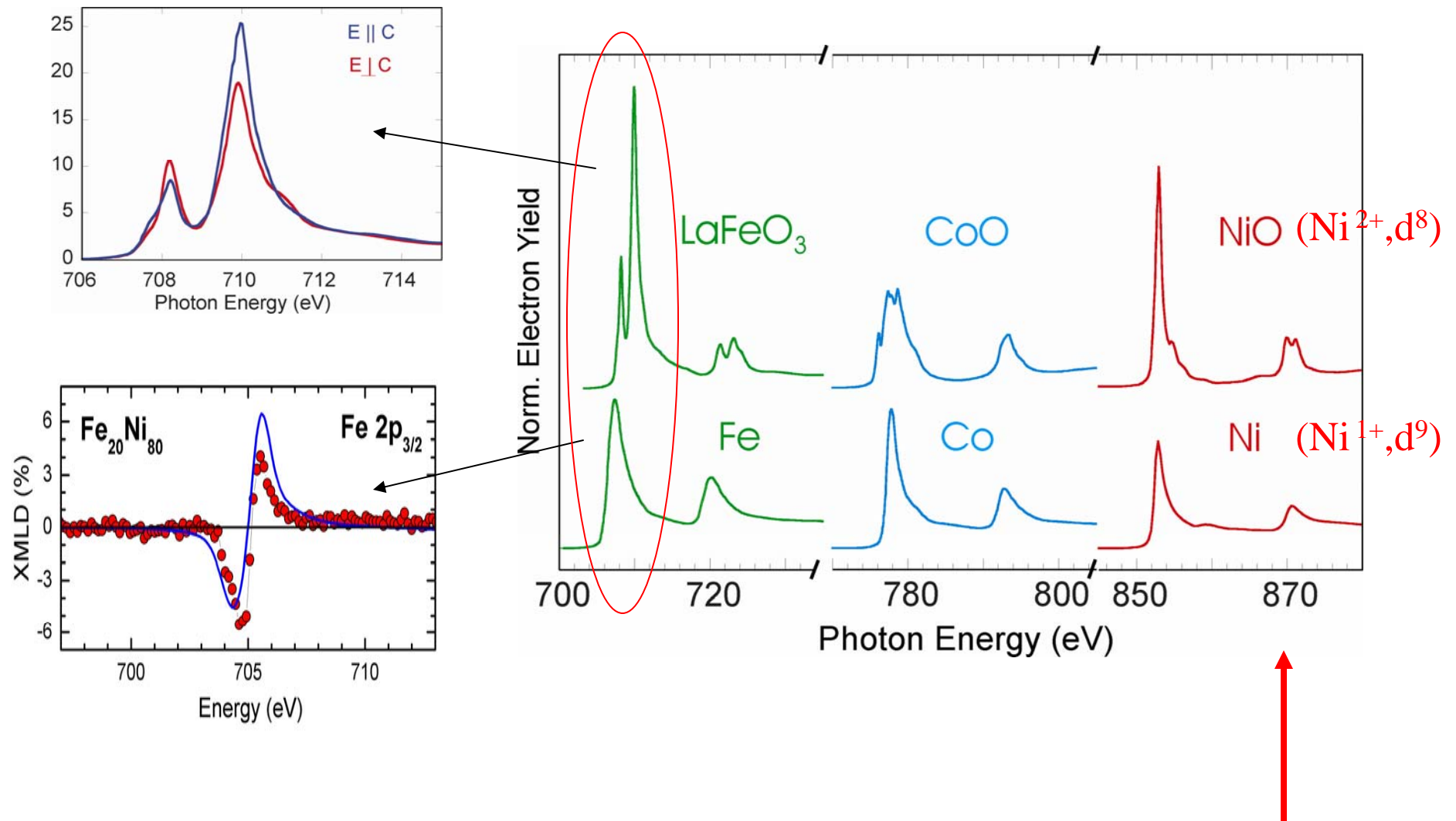
XAFS Spectra and Orientation of AF Axis in LaFeO_3 on $\text{SrTiO}_3(110)$



AF axis is rotated from bulk

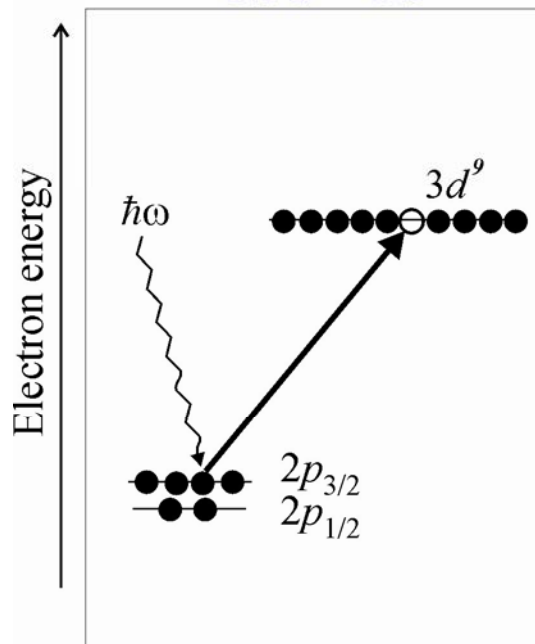
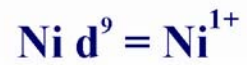
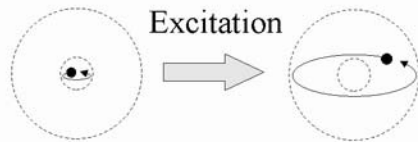


XMLD effects especially strong in multiplet peaks

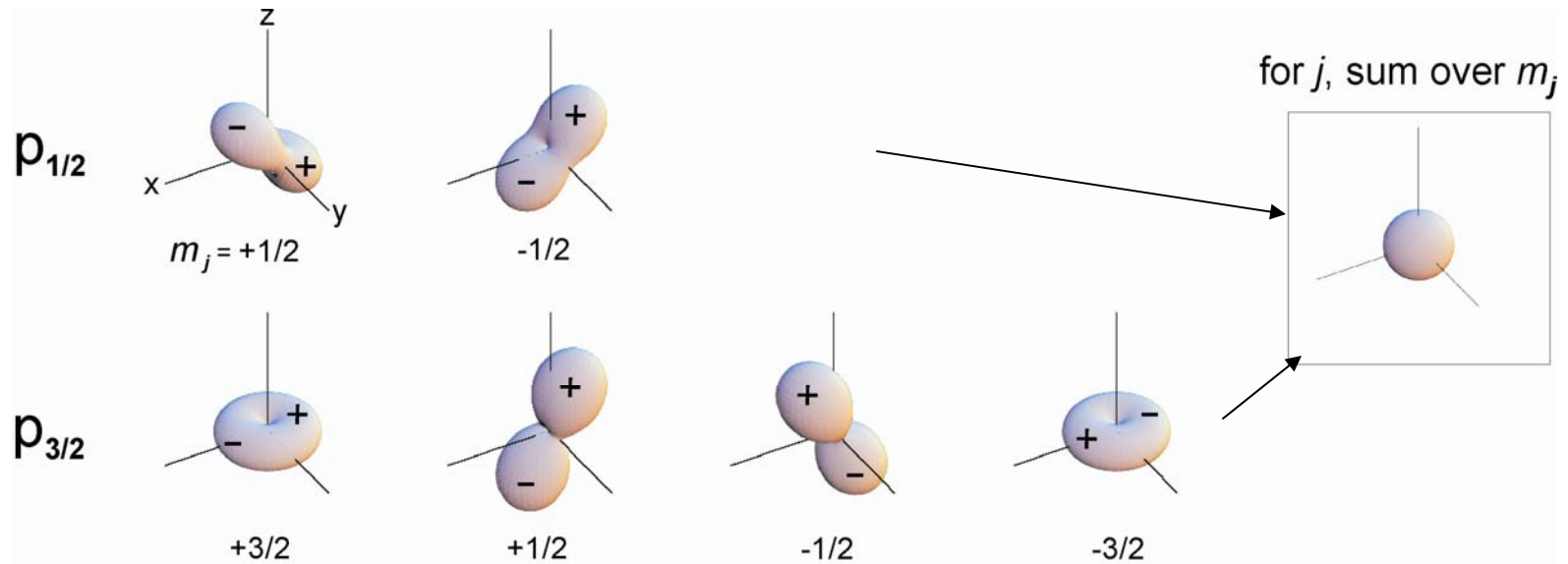


Description of the X-Ray Absorption Process

One-electron model



Detailed origin of x-ray **magnetic linear** dichroism



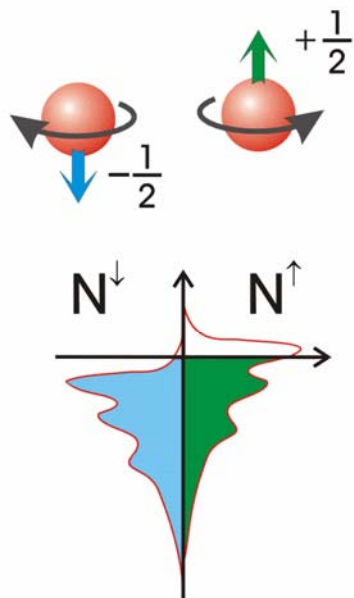
Each spin orbit state ℓ_j is spherically symmetric

Each multiplet $^{2S+1}L_J$ is spherically symmetric

Linear magnetic dichroism

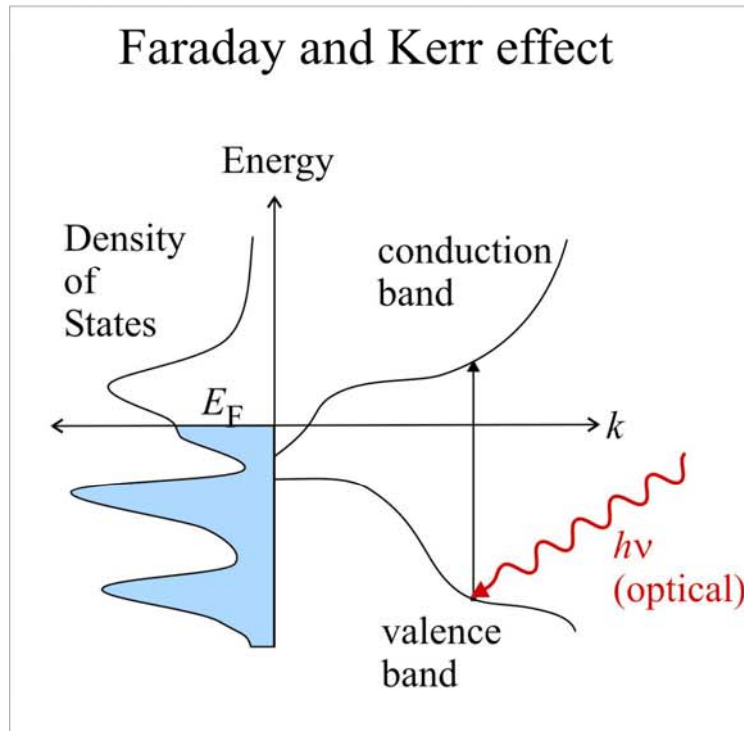
arises from unequal contributions of states m_j (M_J)

X-ray Magnetic Circular Dichroism

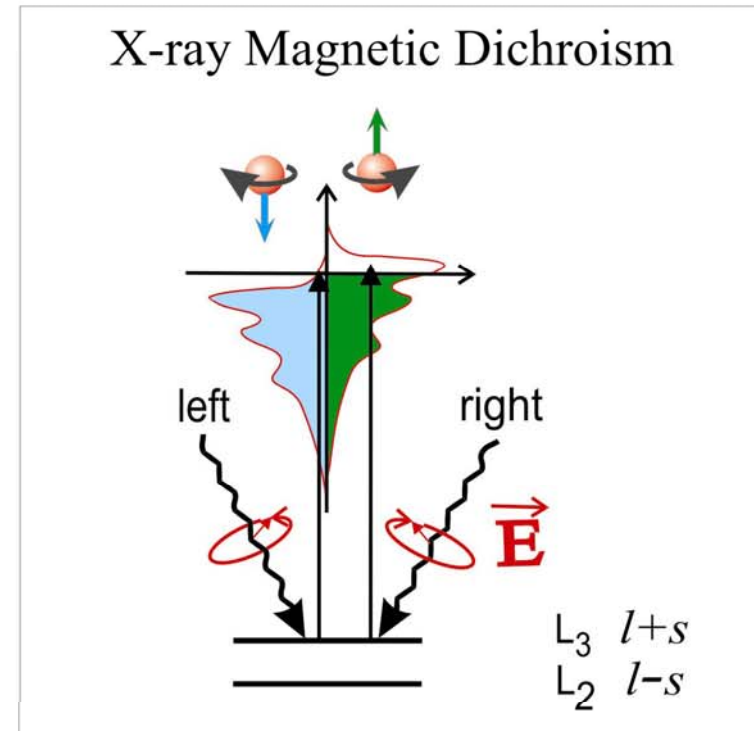


$m_{\text{spin}}^{\text{tot}}$	$m_{\text{spin}}^{\text{d}}$	$m_{\text{spin}}^{\text{sp}}$
2.19	2.26	-0.07
1.57	1.64	-0.07
0.62	0.64	-0.02

Magnetic Circular Dichroism

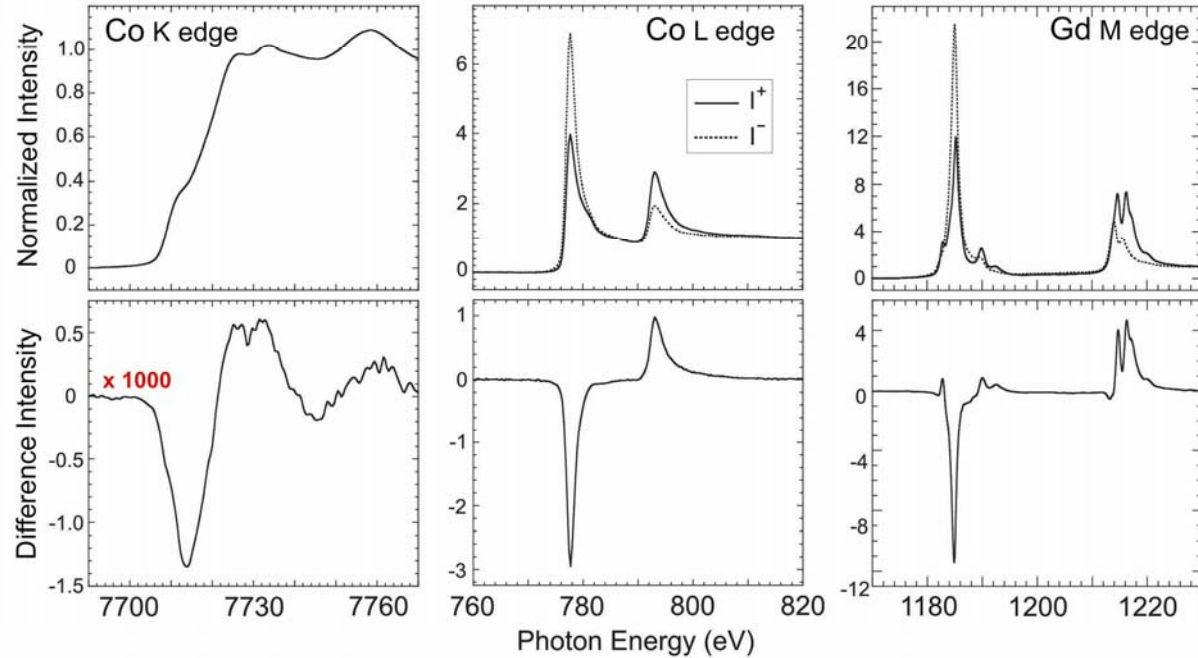
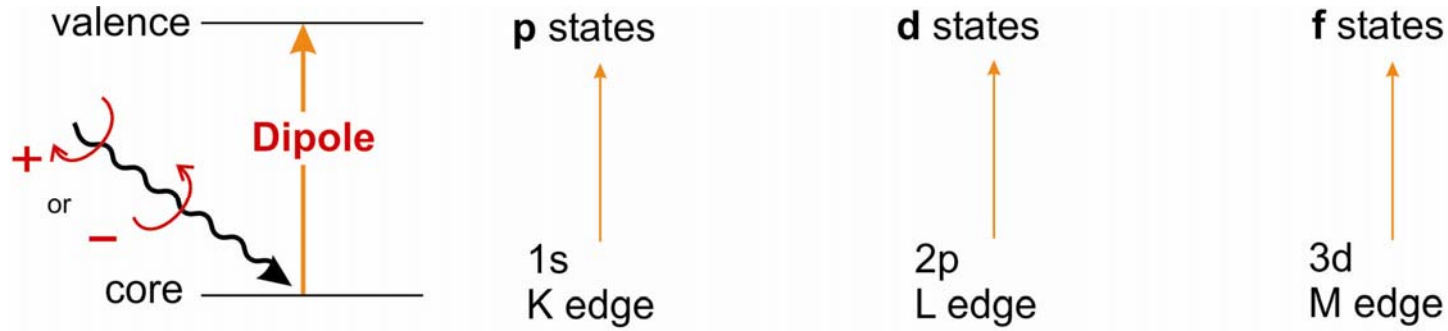


Magneto-optical response:
weak, k -dependent



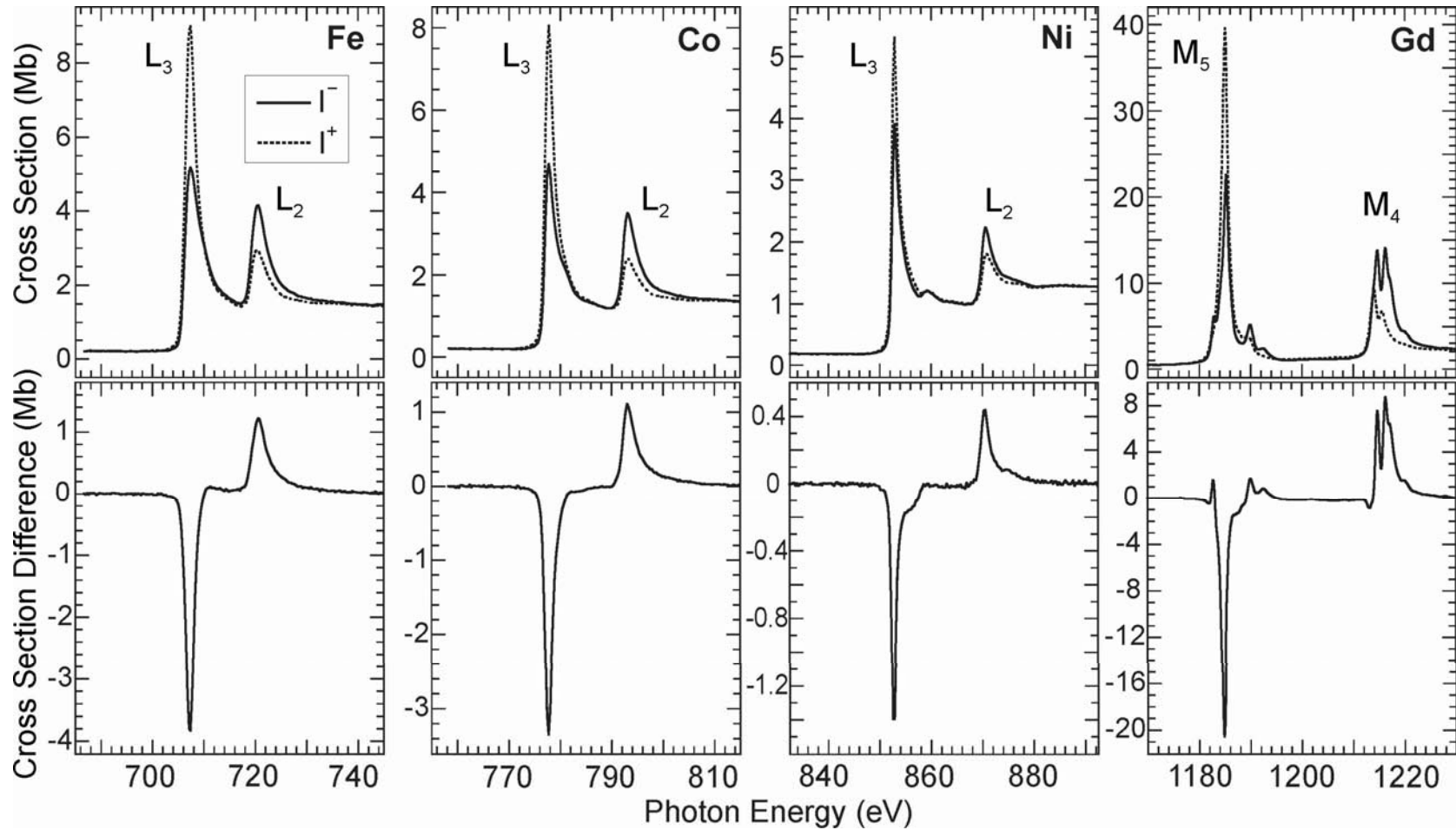
X-ray response:
strong, k -integrated quantities
number of holes, spin moment, orbital moment

Soft x-rays are best for magnetism

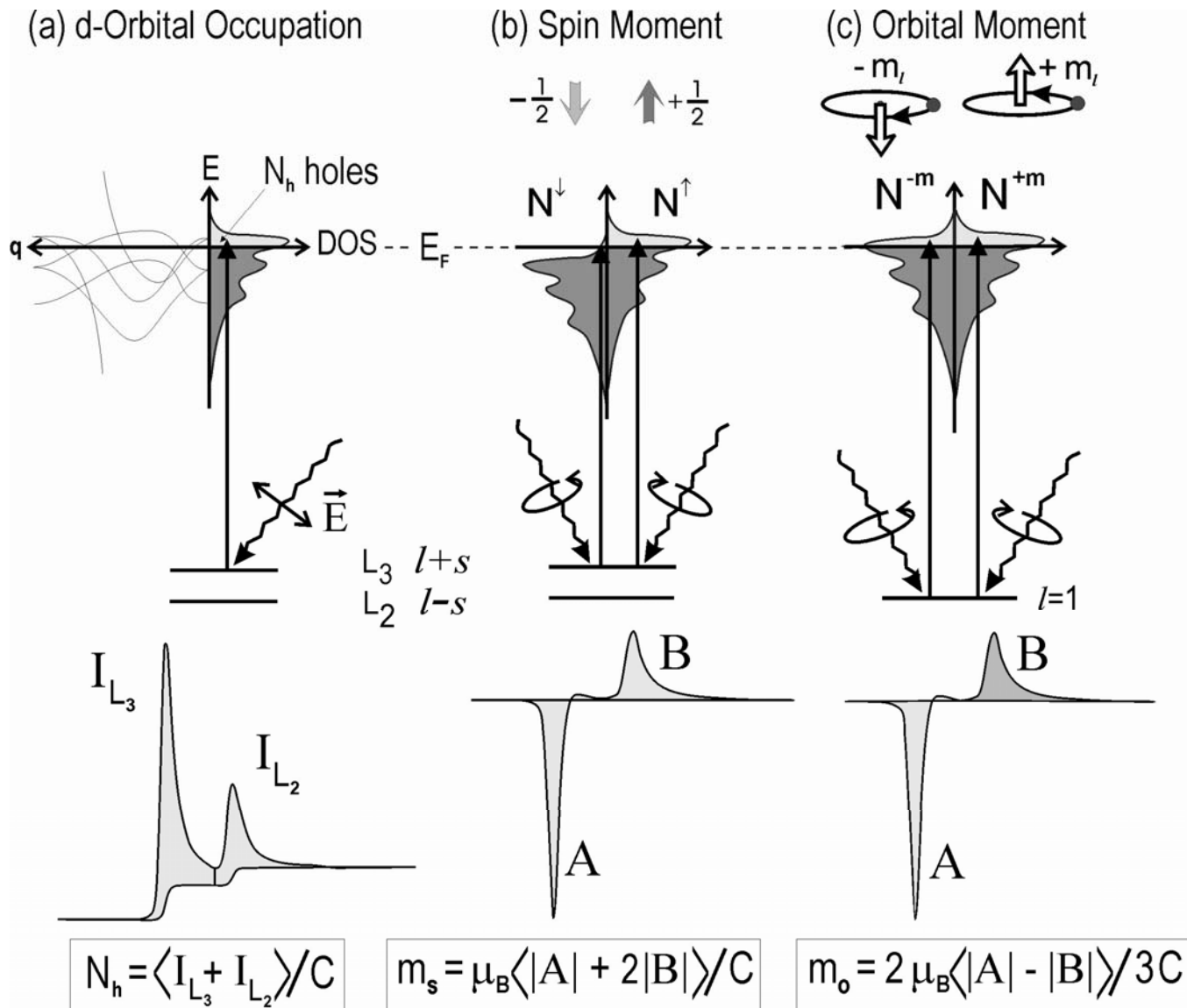


Sum Rules: XMCD intensity \longleftrightarrow spin and orbital moments of electronic ground state

XMCD spectra of the pure ferromagnetic metals

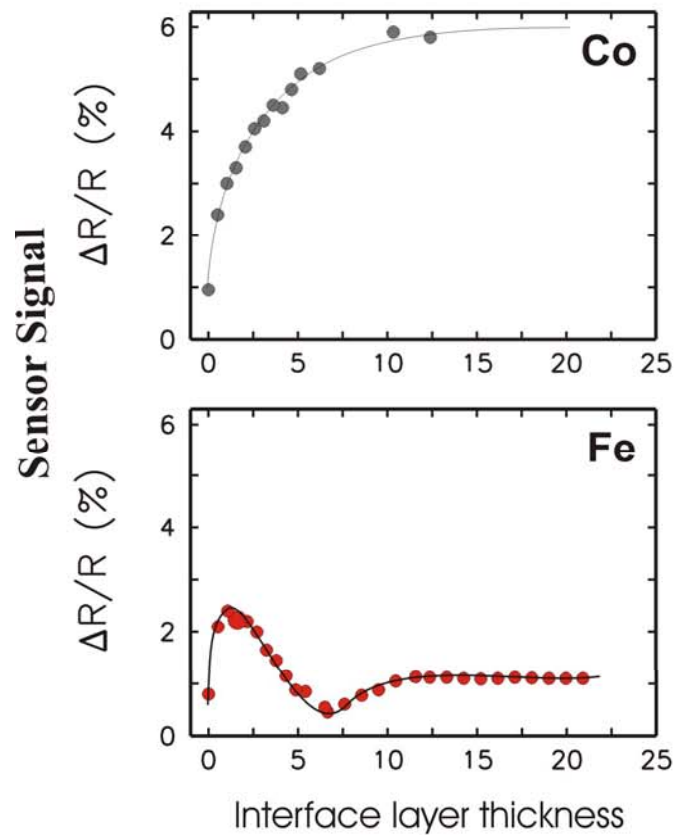


The sum rules

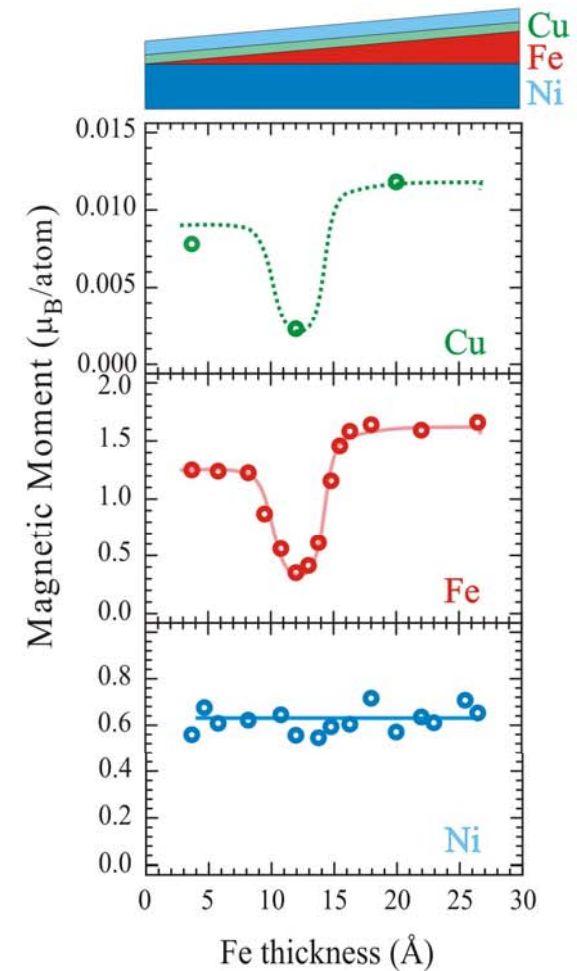


Thickness Dependence of Magneto-Resistance for **Co** and **Fe** nano-layers

Device Performance



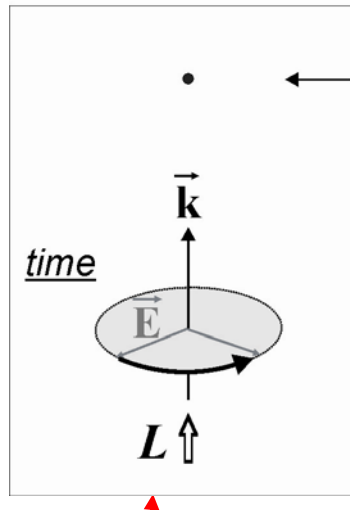
X-Rays tell why Fe does not work



X-ray Natural Circular Dichroism

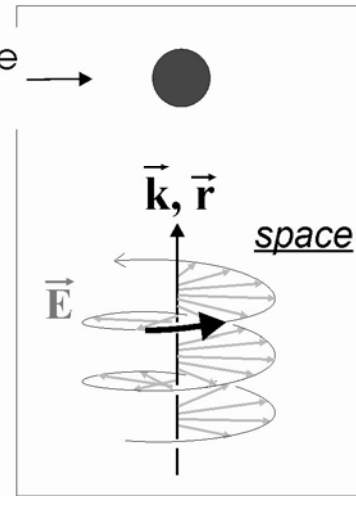
X-Ray Circular Dichroism

The electric dipole approximation



Wavevector dependent contributions

relative size of atom



Pasteur's and Faraday's experiments

