National Synchrotron Radiation Research Center

Soft X-ray Absorption Spectroscopy

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Soft X-ray Absorption Spectroscopy

Basic

Experimental Setup

Unique Features of Soft X-ray absorption

- Chemical analysis
- Orbital polarization
- Magnetic Circular Dichroism

Applications

- Magnetic materials
- Energy materials

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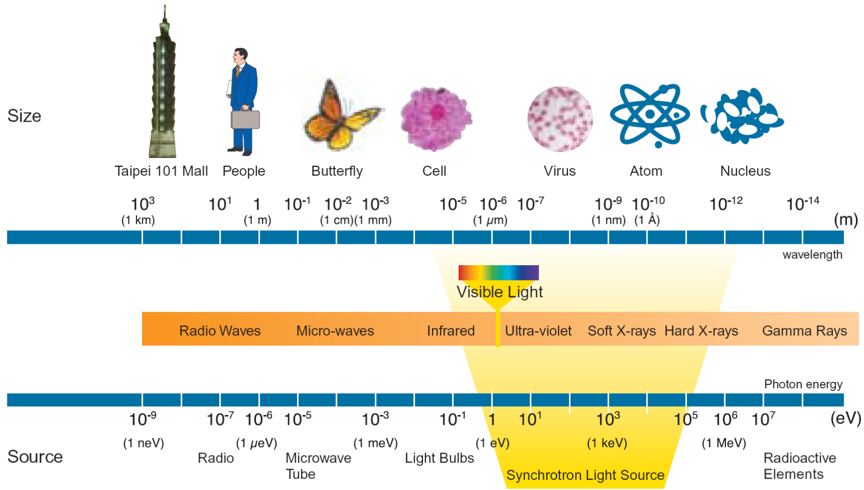
Electromagnetic Spectrum



Soft x-ray: 250 eV ~ a few keV

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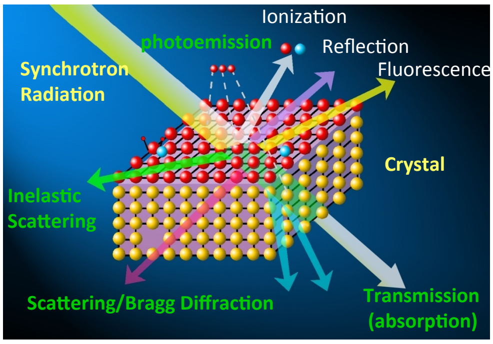
Interaction of photons with matter:



Photoelectric effect

Photoabsorption

Scattering/diffraction

- **lattice structure: arrangement of atoms**
- **electronic states**
- **magnetic order**
- **excitations (electronic states or phonons)**

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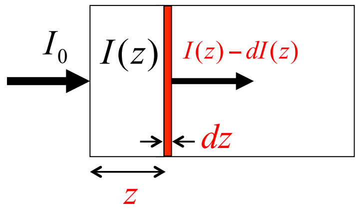
Basics of X-ray absorption



Intensity decrease due to absorption by dz

$$-dI(z) = I(z)\underbrace{\rho dz}_{\text{\# of atoms/area}} A = I(z)\mu dz$$

A: area

absorption coefficient: $\mu = \rho\sigma_a$ σ_a: absorption cross section

$$-dI(z) = \mu\, I(z)\ dz \qquad \frac{dI(z)}{dz} = -\mu\, I(z) \qquad I(z) = I_0 e^{-\mu z}$$

The wave propagating in the medium is

$$E_0 e^{i(nkz)} = E_0 e^{i(1-\delta)kz} e^{-\beta kz}$$

index of refraction

$$n \equiv 1 - \delta + i\beta$$

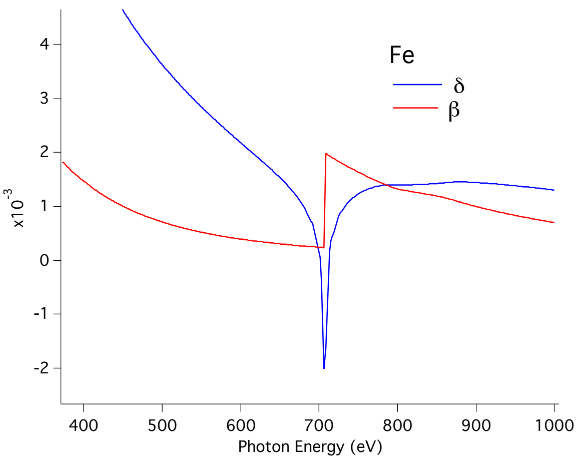
(δ and β are real numbers)

$$\mu = 2\beta k \qquad \because\ I \propto |E|^2$$

$$\delta, \beta << 1$$

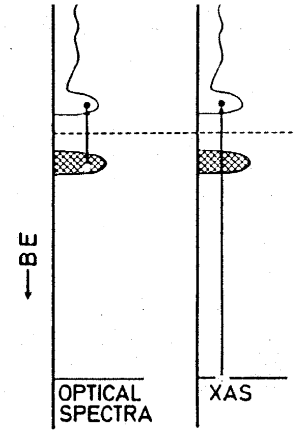
Refractive Index

$$n = 1 - \delta + i\beta = 1 - \frac{n_a r_e \lambda^2}{2\pi}(f_1^0 - i f_2^0)$$



X-ray Absorption spectroscopy

An x-ray absorption (XAS) process excites one core electron to the unoccupied state and a core hole is created.



The interaction Hamiltonian $H_I = \frac{e\mathbf{A}\cdot\mathbf{p}}{m}$

$\vec{A} = \hat{\varepsilon} e^{i(\mathrm{k}\cdot\mathrm{r}-\omega t)}$ ε polarization of x-ray

Absorption probability

$$W = \frac{2\pi}{\hbar}\left|M_{ij}\right|^2 \delta(\hbar\omega - E_f + E_i)$$

$$M_{ij} = \left\langle f \left| \tfrac{e}{m}\mathbf{A}\cdot\tfrac{\hbar}{i}\nabla \right| i \right\rangle$$

Dipole approximation $\mathrm{k}\cdot\mathrm{r} << 1,$

$e^{i\mathrm{k}\cdot\mathrm{r}} \approx 1$ $\quad \vec{A} \approx \hat{\varepsilon} e^{-i\omega t}$ $\quad M_{ij} \propto \langle f | \boldsymbol{\varepsilon}\cdot\mathbf{r} | i \rangle$

For 2p → 3d: $M_{ij} \propto \langle 2p^5 3d^{n+1} | \boldsymbol{\varepsilon}\cdot\mathbf{r} | 2p^6 3d^n \rangle$

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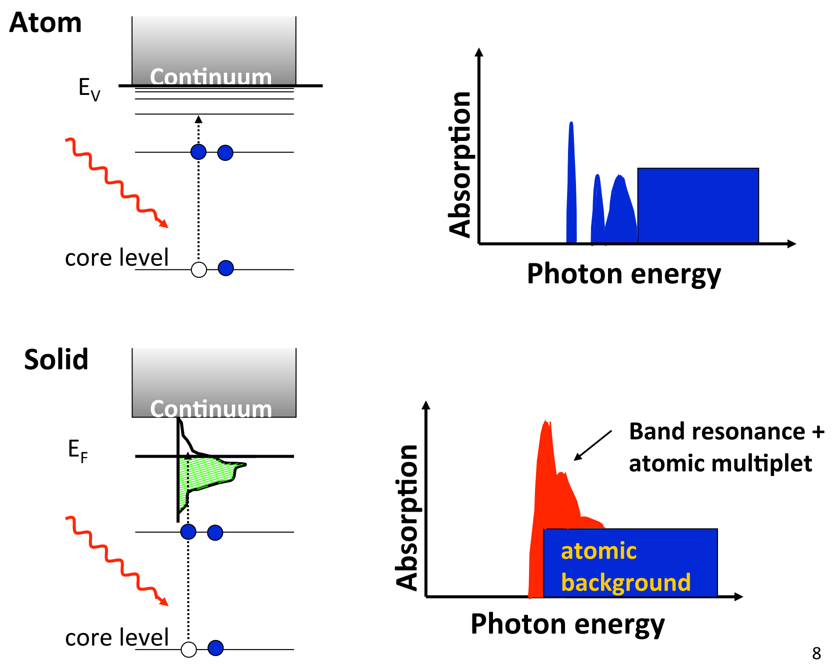

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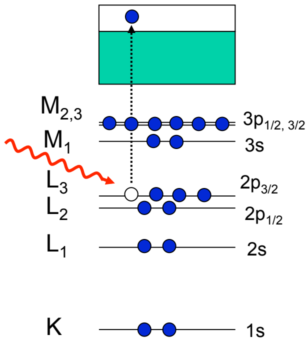
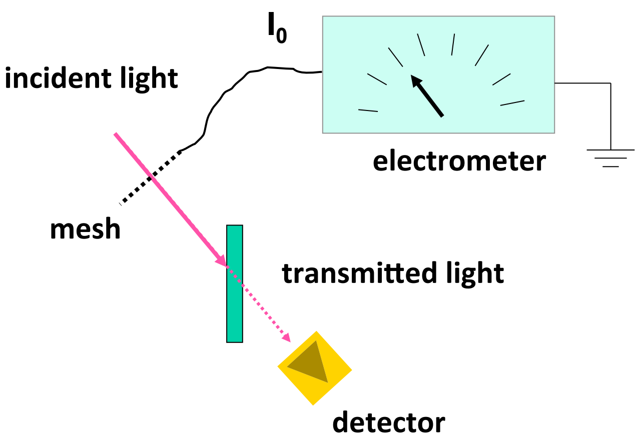
Dipole allowed transitions : $\Delta l = \pm 1,\ \Delta m_l = \pm 1, 0; \quad \Delta s = 0$

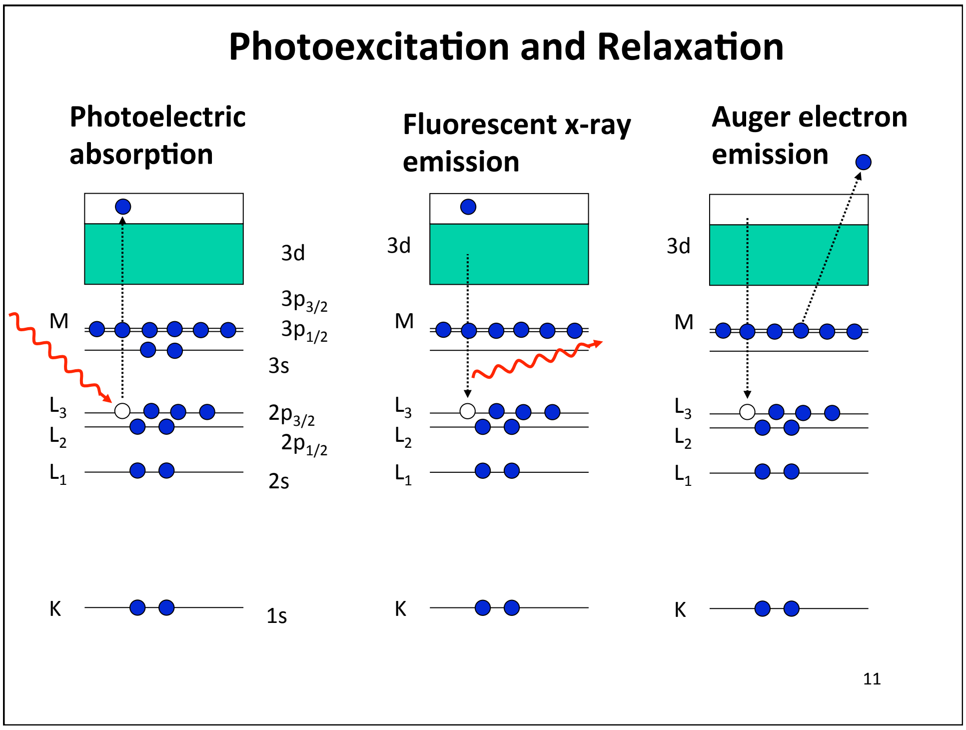
$1s \rightarrow np$ **K-edge** **XAS can be accurately described with single-particle methods.**

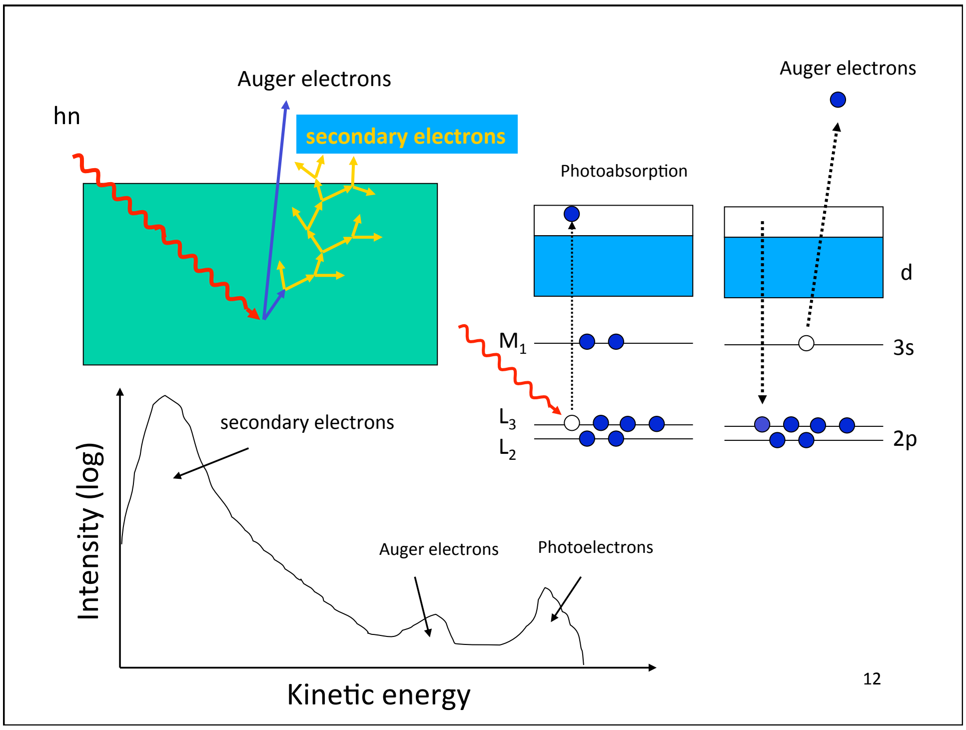
$2p \rightarrow 3d$ **L-edge** **XAS: the single-particle approximation breaks down and the pre-edge structure is affected by the core hole wave function.** **The multiplet effect exists.**



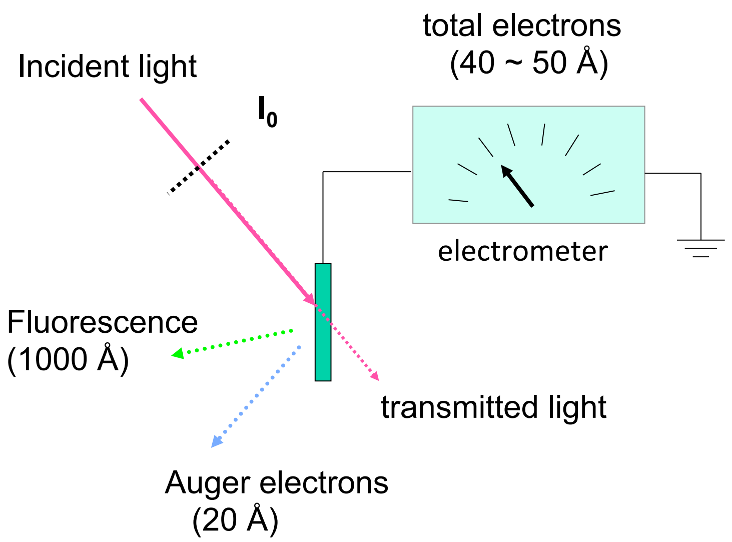
Measurement of Soft X-ray Absorption




Photoexcitation and Relaxation
Photoelectric absorption
Fluorescent x-ray emission
Auger electron emission
3d
3p3/2
3p1/2
3s
2p3/2
2p1/2
2s
1s
M
L3
L2
L1
K
11


hn
Auger electrons
secondary electrons
Photoabsorption
Auger electrons
d
M1
3s
L3
L2
2p
Intensity (log)
secondary electrons
Auger electrons
Photoelectrons
Kinetic energy
12

Measurement of Soft X-ray Absorption



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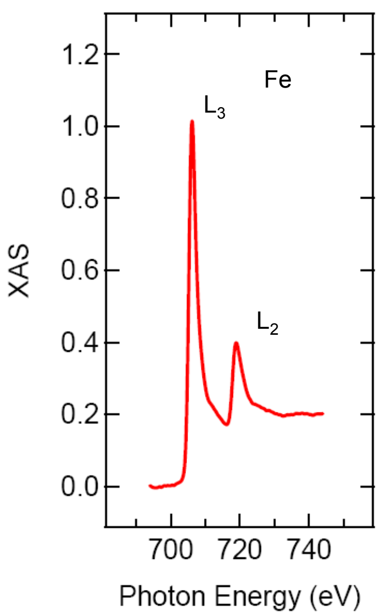
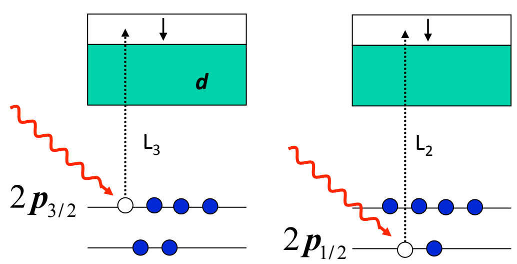


- Two absorption "peaks" from $2p \rightarrow 3d$:



- **Absorption cross section is proportional to numbers of d holes and density of states in the core level.**
- **L-edge XAS provides information on the chemical state, orbital symmetry, and spin state of materials.**

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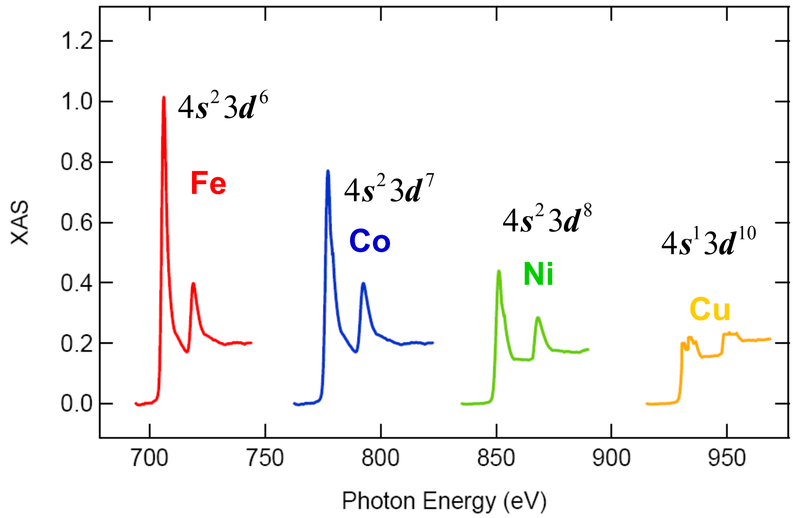

Each element has specific absorption energies.
"finger print" → element specific spectroscopy

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L-edge XAS provides information on the chemical state, orbital symmetry, and spin state of materials.

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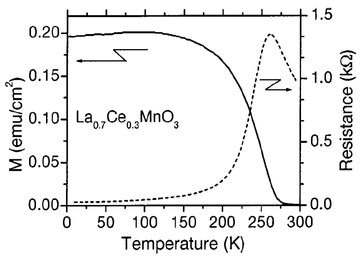
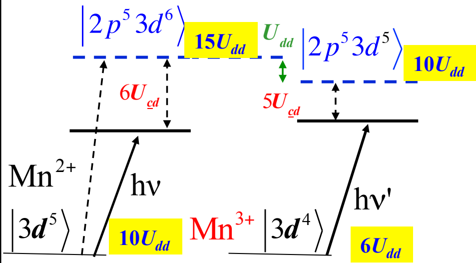
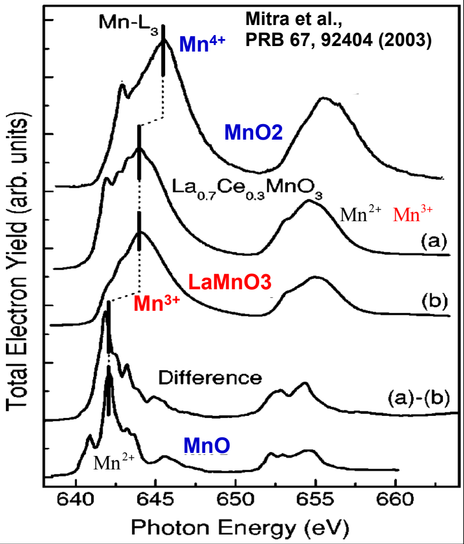


hole doping: $Mn^{3+} \rightarrow Mn^{4+}$ La^{3+}

$LaMnO_3$ → $La_{1-x}Sr_xMnO_3$ Sr^{2+}

$La_{0.7}Ce_{0.3}MnO_3$ ***electron doping?*** $Mn^{3+} \rightarrow Mn^{2+}$



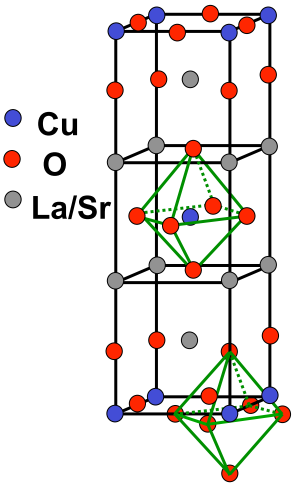


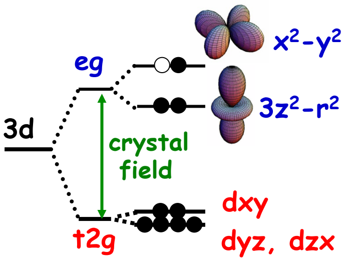
- **Coulomb interactions of 3*d* + core-hole valence interaction**

$$h\nu' - h\nu = U_{cd} - U_{dd}$$

High-Temperature Superconducting Cu oxides

La2CuO4
(Cu^{2+} : $3d^9$)





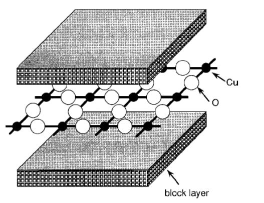
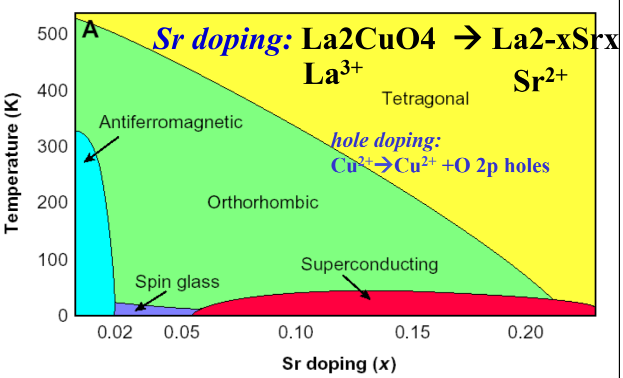
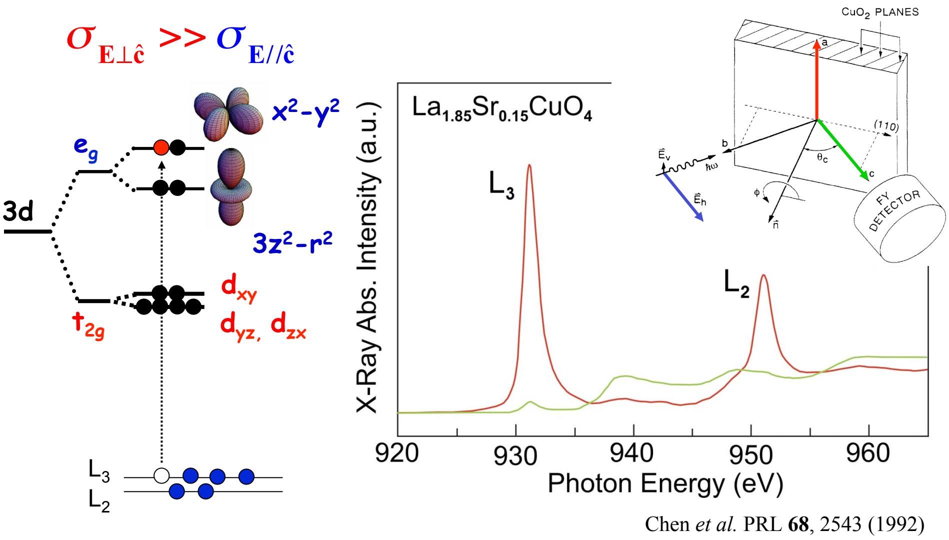


FIG. 117. Conceptual illustration of stacking of CuO_2 layers sandwiched by block layers.



Orbital Characters of Doped Holes in La2-xSrxCuO4

$\sigma_{E\perp\hat{c}} >> \sigma_{E//\hat{c}}$



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

L-edge XAS provides information on the chemical state, orbital symmetry, and spin state of materials.

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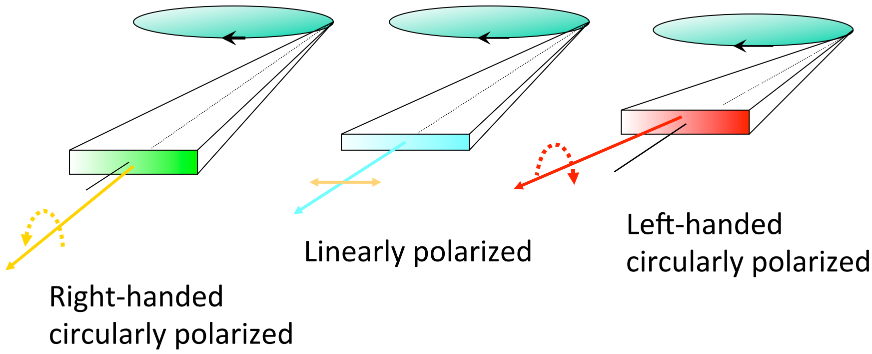
Polarization of Synchrotron Radiation



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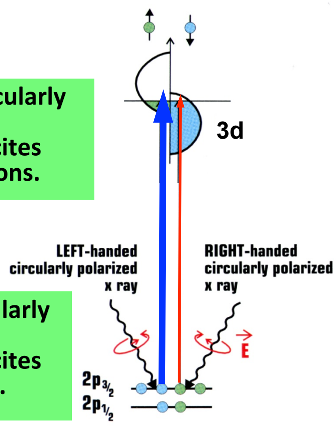
Soft X-Ray Magnetic Circular Dichroism in Absorption

For $2p_{3/2}$→3d

Right-handed circularly polarized light preferentially excites spin-down electrons.

Left-handed circularly polarized light preferentially excites spin-up electrons.



L_3 →3d

For spin up,

$$\frac{\text{left-handed}}{\text{right-handed}} = 5/3$$

For spin down

$$\frac{\text{left-handed}}{\text{right-handed}} = 3/5$$

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Soft X-Ray Magnetic Circular Dichroism in Absorption

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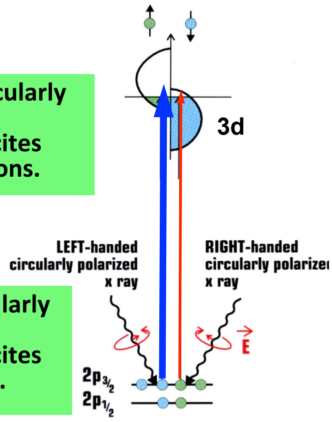
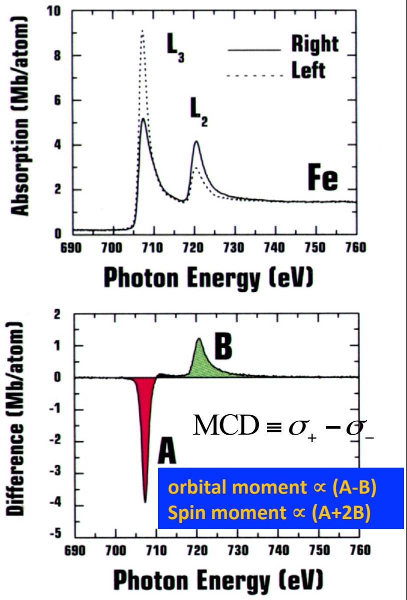
Right-handed circularly polarized light preferentially excites spin-down electrons.

Left-handed circularly polarized light preferentially excites spin-up electrons.





MCD is defined as the difference in absorption intensity of magnetic systems excited by left- and right-handed circularly polarized light.

Soft X-Ray Magnetic Circular Dichroism in Absorption

Soft X-ray MCD in absorption provides a unique means to probe:

element-specific magnetic hysteresis
orbital and spin moments
magnetic coupling.

There are two ways to obtain a MCD spectrum:

1) **Fixing M, measure XAS with left and right circular lights.**
2) **Fixing the helicity of light, measure XAS with two opposite directions of M.**

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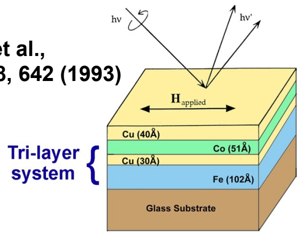
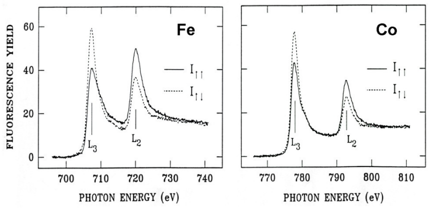
Element-Specific Magnetic Hysteresis Measurements

A New Technique for Studying Interlayer Magnetic Coupling

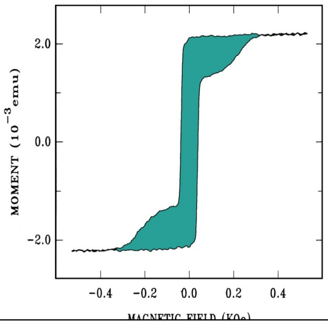
Chen et al.,
PRB 48, 642 (1993)

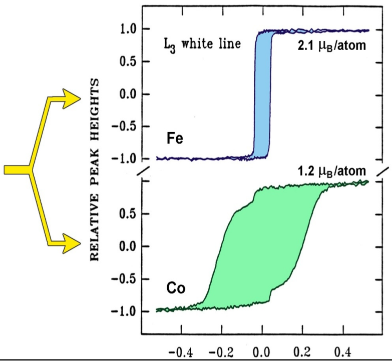


SXMCD Hysteresis Curves



Conventional Hysteresis C





Ferromagnetism in one-dimensional monatomic metal chains

P. Gambardella*, A. Dallmeyer†, K. Maiti†, M. C. Malagoli†,
W. Eberhardt†‡, K. Kern*§ & C. Carbone†||

Nature 416, 301 (2001)

Two-dimensional systems, such as ultrathin epitaxial films and superlattices, display magnetic properties distinct from bulk materials[1]. A challenging aim of current research in magnetism is to explore structures of still lower dimensionality[2–6]. As the dimensionality of a physical system is reduced, magnetic ordering tends to decrease as fluctuations become relatively more important[7]. Spin lattice models predict that an infinite one-dimensional linear chain with short-range magnetic interactions spontaneously breaks up into segments with different orientation of the magnetization, thereby prohibiting long-range ferromagnetic order at a finite temperature[7–9]. These models, however, do not take into account kinetic barriers to reaching equilibrium or interactions with the substrates that support the one-dimensional nanostructures. Here we demonstrate the existence of both short- and long-range ferromagnetic order for one-dimensional monatomic chains of Co constructed on a Pt substrate. We find evidence that the monatomic chains consist of thermally fluctuating segments of ferromagnetically coupled atoms which, below a threshold temperature, evolve into a ferromagnetic long-range-ordered state owing to the presence of anisotropy barriers. The Co chains are characterized by large localized orbital moments and correspondingly large magnetic anisotropy energies compared to two-dimensional films and bulk Co.

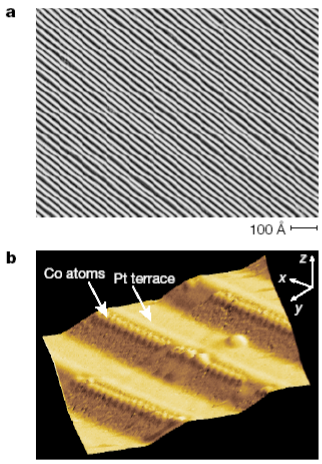


Figure 1 STM topographs of the Pt(997) surface. **a**, Periodic step structure (each white line represents a single step). The surface has a 6.45° miscut angle relative to the (111) direction; repulsive step interactions result in a narrow terrace width distribution centred at 20.2 Å with 2.9 Å standard deviation. **b**, Co monatomic chains decorating the Pt step edges (the vertical dimension is enhanced for better contrast). The monatomic chains are obtained by evaporating 0.13 monolayers of Co onto the substrate held at $T = 260$ K and previously cleaned by ion sputtering and annealing cycles in ultrahigh vacuum (UHV). The chains are linearly aligned and have a spacing equal to the terrace width.

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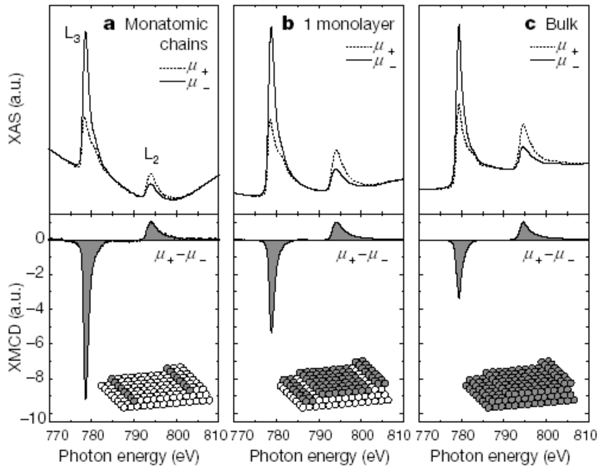

Figure 2 Co X-ray absorption spectra for parallel (μ_+) and antiparallel (μ_-) direction of light polarization and field-induced magnetization. The dichroism signal ($\mu_+ - \mu_-$) is obtained by subtraction of the absorption spectra in each panel and normalization to the L_2 peak. **a**, Monatomic chains; **b**, one monolayer; **c**, thick Co film on Pt(997). The sample was mounted onto a UHV variable-temperature insert that could be rotated with the respect to the direction of the external magnetic field applied parallel to the incident photon beam. Spectra were recorded in the electron-yield mode at $T = 10$ K and

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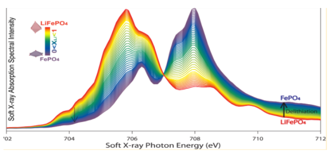
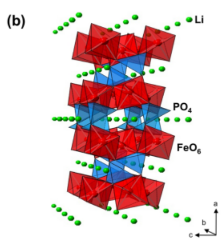
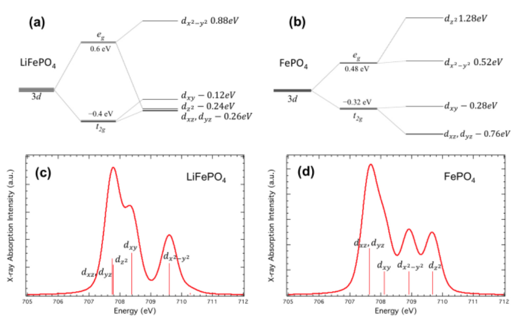
Phase Transformation and Lithiation Effect on Electronic Structure of Li_xFePO_4: An In-Depth Study by Soft X-ray and Simulations

Xiaosong Liu,[†] Jun Liu,[‡] Ruimin Qiao,[†,∥] Yan Yu,[¶] Hong Li,[#] Liumin Suo,[#] Yong-sheng Hu,[#] Yi-De Chuang,[†] Guojiun Shu,[⊥] Fangcheng Chou,[⊥] Tsu-Chien Weng,[△] Dennis Nordlund,[△] Dimosthenis Sokaras,[△] Yung Jui Wang,[×] Hsin Lin,[×] Bernardo Barbiellini,[×] Arun Bansil,[×] Xiangyun Song,[‡] Zhi Liu,[†] Shishen Yan,[∥] Gao Liu,[‡] Shan Qiao,[⊗] Thomas J. Richardson,[‡] David Prendergast,[§] Zahid Hussain,[†] Frank M. F. de Groot,[∇] and Wanli Yang[*,†]







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Jens Als-Nielsen and Des McMorrow, “Elements of Modern X-ray Physics” (Wiley & Sons)

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Thank you!

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