MAGNETIC SPECTROSCOPY

Elke Arenholz, Advanced Light Source

- X-ray absorption, XA
- X-ray magnetic circular dichroism, XMCD
- X-ray magnetic linear dichroism, XMLD
- X-ray magnetic microscopy
- Magnetization Dynamics

C. Boeglin et al., Nature 465, 458 (2011)

Experimental Concept:
Monitor the reduction in x-ray flux transmitted through sample as function of x-ray photon energy

- **charge state of absorber** Fe$^{2+}$, Fe$^{3+}$
- **symmetry of lattice site** of absorber: O$_h$, T$_d$
- **sensitive to magnetic order**

- **Absorption probability**: x-ray energy, x-ray polarization
- **experimental geometry**

- **core level** ⇒ atomic species of absorber Fe, Co, Ni,
Experimental Concept:
Monitor the reduction in x-ray flux transmitted through sample as function of x-ray photon energy

\[ I_t = I_0 e^{-\mu t} \]

Sample

\[ \hbar \omega \rightarrow e^- \rightarrow \text{core} \]

\[ \text{RuMnIr} \quad \text{CoFe} \quad \text{RuNiFe} \]

\[ \text{MnFe} \quad \text{Ru} \quad \text{CoFe} \quad \text{MnIr} \quad \text{Ru} \]

\[ \frac{I_t}{I_0} \]

\[ 640 \quad 660 \quad 700 \quad 720 \quad 780 \quad 800 \quad 860 \quad 880 \]

photon energy (eV)
+ Change velocity of electrons near the speed of light
→ Emission of wide wavelength range of electromagnetic spectrum (IR, UV, soft x-rays, hard x-rays)
→ Tunable source in the soft x-ray range for x-ray absorption spectroscopy

http://www.ph.surrey.ac.uk/
Change velocity of electrons near the speed of light

⇒ Emission of wide wavelength range of electromagnetic spectrum (IR, UV, soft x-rays, hard x-rays)

⇒ Tunable source in the soft x-ray range for x-ray absorption spectroscopy
Beamlines/Monochromators provide photons with well defined characteristics:
- tunable energy/wavelength
- band width
- fixed polarization: (variable) linear, circular, …
Endstations provide well defined environments for the interaction of samples and photons:
- precisely defined experimental geometries, i.e. angle of x ray beam to sample
- sample temperature
- external magnetic and electric fields
Magnetic fields in arbitrary directions obtained through superposition of fields generated by 4 dipole pairs in octahedral configuration.

Vector magnet at ALS BL4.0.2
Experimental Concept:
Monitor the reduction in x-ray flux transmitted through sample as function of x-ray photon energy
### X-Ray Absorption

#### Equation

\[ I_t = I_o e^{-\mu t} \]

#### Sample

- $I_o$: Initial intensity
- $I_t$: Transmitted intensity
- $\mu$: Linear absorption coefficient

#### Table: Linear Absorption Coefficients

<table>
<thead>
<tr>
<th>Element</th>
<th>$10 \text{ eV below } L_3 \mu \text{ [nm}^{-1}\text{]}$</th>
<th>$at \ L_3 \mu \text{ [nm}^{-1}\text{]}$</th>
<th>$40 \text{ eV above } L_3 \mu \text{ [nm}^{-1}\text{]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>$1.8 \times 10^{-3}$</td>
<td>$6.0 \times 10^{-2}$</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>Co</td>
<td>$1.8 \times 10^{-3}$</td>
<td>$5.8 \times 10^{-2}$</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>Ni</td>
<td>$1.6 \times 10^{-3}$</td>
<td>$4.2 \times 10^{-2}$</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

#### Diagram: X-ray Absorption Spectra

- Photon energy (eV) ranges from 640 to 880 eV.
- Intensity ratio $I_t / I_o$ is plotted.
- Elements: Mn, Fe, Co, Ni, Ru, NiFe, CoFe, MnIr, Ru.
X-RAY ABSORPTION

Element | 10eV below $L_3$ | at $L_3$ | 40 eV above $L_3$
1/μ [nm] | 1/μ [nm⁻¹] | 1/μ [nm⁻¹]
--- | --- | --- | ---
Fe | 550 | 17 | 85
Co | 550 | 17 | 85
Ni | 625 | 24 | 85

~10-20 nm layer thick films supported by substrates transparent to soft x-rays
**Electron yield:**

+ Absorbed photons create core holes filled predominantly by Auger electron emission
+ Auger electrons create low-energy secondary electron cascade through inelastic scattering
+ Emitted electrons $\propto$ probability of Auger electron creating $\propto$ absorption probability

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**transmitted intensity $I_t / I_0$**

**electron yield $I_e / I_0$**
X-RAY ABSORPTION – MEASUREMENTS

![Diagram of X-ray absorption measurements](image-url)
Electron sample depth: 2-5 nm in Fe, Co, Ni

60% of the electron yield originates from the topmost 2-5 nm
Experimental Concept:
Monitor the reduction in x-ray flux transmitted through sample as function of x-ray photon energy

\[ I_0 = I_t = I_0 e^{-\mu t} \]

- \( \mu \) is a constant
- \( t \) is the thickness of the sample

**Core Level**
- \( 2p_{3/2} \) and \( 2p_{1/2} \)
- \( L_2 \) and \( L_3 \)

**Valence States**
- \( k \)
- \( \ell \)

**Absorption Probability**
- x-ray energy
- x-ray polarization

**Charge State**
- \( Fe^{2+}, Fe^{3+} \)

**Symmetry**
- \( O_h, T_d \)

**Sensitive to Magnetic Order**

**Atomic Species**
- Fe, Co, Ni,
The intensity of the $L_{3,2}$ resonances is proportional to the number of $d$ states above the Fermi level, i.e. the number of holes in the $d$ band.
Influence of the charge state of the absorber

Influence of lattice site symmetry at the absorber

N. Telling et al.,
Appl. Phys. Lett. 95, 163701 (2009)
**X-ray absorption:**

+ Electrons excited from core shells to unoccupied valence states through absorption of a photon determined by energy and angular momentum conservation.

**Simplest model: One electron picture**

+ Photon transfers its energy and momentum to core electron
+ Core electron excited into unoccupied electronic state.

+ However: Not directly excited electrons also influenced by electron excitation, i.e. hole in core shell.
**Configuration model, e.g. L edge absorption:**

+ Atom is excited from ground/initial state configuration, \(2p^63d^n\) to exited/final state configuration, \(2p^53d^{n+1}\)

+ Omission of all full subshells (spherical symmetric)

+ Takes into account correlation effects in the ground state as well as in the excited state

+ Leads to multiplet effects/structure

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X-RAY ABSORPTION – MULTIPLET EFFECTS

- Fe\(^{3+}\) in LaFeO\(_3\)
- Co\(^{2+}\) in CoO
- Ni\(^{2+}\) in NiO

J. Stöhr, H.C. Siegmann, Magnetism (Springer)
SENSITIVITY TO SITE SYMMETRY: Ti\(^{4+}\) \(L_{3,2}\)

+ Electric dipole transitions: \(d^{0} \rightarrow 2p^{5}3d^{1}\)

+ Crystal field splitting \(10Dq\) acting on 3\(d\) orbitals:

**Octahedral symmetry:**
- \(e\) orbitals towards ligands → higher energy
- \(t_2\) orbitals between ligands → lower energy

**Tetragonal symmetry:**
- \(e\) orbitals → \(b_2 = d_{xy}, e = d_{yz}, d_{yz}\)
- \(t_2\) orbitals → \(b_1 = d_{x^2-y^2}, a_1 = d_{3z^2-r^2}\)

J. Stöhr, H.C. Siegmann, Magnetism (Springer)
Magnetic moments in Fe, Co, Ni well described by Stoner model: $d$-bands containing up and down spins shifted relative to each other by “exchange splitting”

Spin-up and spin-down bands filled according to Fermi statistics

Magnetic moment $|m|$ determined by difference in number of electrons in majority and minority bands

$$|m| = \mu_B (n_{e\text{maj}} - n_{e\text{min}})$$
Photoelectrons excited from $2p_{3/2}$, $2p_{1/2}$ to $3d$ states

**First step:**
+ Excitation of electron from $2p$ states by absorption of circularly polarized x rays
+ Note: Dipole operator does not affect spin
  $\Rightarrow$ No spin flips during excitation
+ Conservation of angular momentum
  $\Rightarrow$ Transfer of angular momentum ($\pm \hbar$) from photon to electron
+ Spin-orbit coupling: Angular momentum of photon transferred in part to electron spin
  $\Rightarrow$ Excited photoelectrons are spin polarized

**Second step:**
+ Unequal spin-up and spin-down populations determine spin or orbital momentum of possible excitations
TWO-STEP MODEL OF XMCD

Magnitude of dichroism depends on
+ degree of circular photon polarization, $P_{circ}$
+ angle $\theta$ between photon angular momentum, $L_{ph}$ and magnetic moment, $m$
+ expectation value of 3$d$ magnetic moment

$I_{XMCD} \propto P_{circ} \langle m \rangle \cos \theta$

J. Stöhr, H.C. Siegmann, Magnetism (Springer)
2$p_{3/2}$ and 2$p_{1/2}$ have opposite spin orbit coupling (l+s, l−s) ⇒ Spin polarization and XMCD have opposite sign at two edges

+ Spin polarization opposite for x rays with opposite helicity, i.e. photon spin, ±ℏ ⇒ XMCD reverses sign with polarization

+ Reversing x ray polarization is equivalent to reversing magnetization/spin direction

J. Stöhr, H.C. Siegmann, Magnetism (Springer)
XMCD provides magnetic information resolving elements Fe, Co, ...

valence states: Fe$^{2+}$, Fe$^{3+}$, ...

lattice sites: octahedral, O$_h$, tetrahedral, T$_d$, ...
Geobacter sulfurreducens bacteria form magnetite nanocrystals (15nm) via extracellular reduction of amorphous Fe(III)-bearing minerals.

CHARACTERISTICS OF MAGNETIC BIONANOSPINELS

Fe$_3$O$_4$

Co-ferrite-1
6 at% Co

Co-ferrite-2
23 at% Co

V. Cocker et al.,
Comparing XMCD spectra with model compounds and/or calculations

⇒ Identifying magnetic phases
SINTERED CoSm PERMANENT MAGNETS

‘CoSm’

XMCD (arb. units)
XA (arb. units)
photon energy (eV)

Fe Sm Co
700 710 720 730

Co Sm
700 750 800 850 900 950 1000 1050 1100

SINTERED CoSm PERMANENT MAGNETS

+ pol. – pol.
The element-specificity makes XMCD measurements an ideal tool to determine induced moments at interfaces between magnetic and non-magnetic elements.

+ Weak Mn XMCD signal
⇒ Uncompensated Mn at Co/IrMn interface

+ Same sign of XMCD signal for Co and Mn
⇒ Parallel coupling of Co and Mn moments

+ Nominal thickness of uncompensated interface moments: (0.5±0.1)ML for Co/Ir$_{20}$Mn$_{80}$.

Monitoring field dependence of XMCD
⇒ Element-specific information on magnetization reversal in complex magnetic nanostructures.
ELEMENT-SPECIFIC MAGNETIZATION REVERSAL

- Monitoring field dependence of XMCD
- Detailed information on magnetization reversal in complex magnetic heterostructures
Theoretically derived sum rules correlate XMCD spectra with spin and orbital moment providing unique tool for studying magnetic materials.

\[ m_S = \mu_B \langle -A + 2B \rangle / C \]

\[ m_L = -2\mu_B \langle A + B \rangle / 3C \]

\[ N_h = \langle I_{L3} + I_{L2} \rangle / C \]
Strong variation of orbital and spin magnetic moment observable as change in relative $L_3$ and $L_2$ intensity in XMCD spectrum.

Co atoms and nanoparticles on Pt have enhanced orbital moments up to $1.1 \, \mu_B$

X-Ray Linear Dichroism:

+ Difference in x-ray absorption for different linear polarization direction relative to crystalline and/or spin axis.

+ Due to the anisotropic charge distribution about the absorbing atom caused by bonding and/or magnetic order.

+ “Search Light Effect”: X-ray absorption of linear polarized x rays proportional to density of empty valence states in direction of electric field vector E.
+ Spontaneous electric polarization due to off-center shift of Ti\(^{4+}\), Zr\(^{4+}\) associated with tetragonal distortion $\Leftrightarrow$ linear dichroism

+ Reversing ferroelectric polarization changes XA $\Leftrightarrow$ Change in tetragonal distortion

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Isotropic $d$ electron charge density
⇒ No polarization dependence

Magnetically aligned system
⇒ Spin-orbit coupling distorts charge density
⇒ Polarization dependence

$\vec{L} \parallel \vec{S}$

$\text{XMLD} = I_{||} - I_{\perp} \propto \langle m^2 \rangle$, $\langle m^2 \rangle = \text{expectation value of the square of the atomic magnetic moment}$

XMLD allows investigating ferri- and ferromagnets as well as antiferromagnets

XMLD spectral shape and angular dependence are determined by magnetic order and lattice symmetry
PLANAR DOMAIN WALL NEAR Co/NiO INTERFACES

MAGNETIC COUPLING AT INTERFACES

La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) ferromagnet
La$_{0.7}$Sr$_{0.3}$FeO$_3$ (LSFO) antiferromagnet

$\Rightarrow$ Perpendicular coupling at LSMO/LSFO interface

MAGNETIC MICROSCOPY

Nature
- Flea
- Human hair ~30 μm wide
- Red blood cells & white cell ~ 5 μm
- Virus ~ 200 nm
- DNA helix ~3 nm width
- Water molecule
- Atom

Technology
- Head of a pin ~ 1 mm
- DVD track
- 1 μm Electrodes connected with nanotubes
- Carbon nanotube ~ 2 nm diameter
- Atomic corral ~ 14 nm diameter

Magnetism
- AFM & FM domains
- Recorded “bits”
- Spin injection
- Media grains
- Nano-particles

J. Stöhr, H.C. Siegmann, Magnetism (Springer)
MAGNETIC MICROSCOPY

10-50 nm spatial resolution

J. Stöhr, H.C. Siegmann, Magnetism (Springer)
Images taken with left and right circularly polarized x-rays at photon energies with XMCD, i.e. Co $L_3$ edge, provide magnetic contrast and domain images.

Images taken with linearly polarized x-rays at photon energies with XMLD, i.e. Ni $L_2$ edge, provide magnetic contrast and domain images.
Taking into account the geometry dependence of the Ni XMLD signal, \( \Rightarrow \) Perpendicular coupling of Co and NiO moments at the interface.

First direct observation of vortex state in antiferromagnetic CoO and NiO disks in Fe/CoO and Fe/NiO bilayers using XMCD and XMLD.

Two types of AFM vortices:
- conventional curling vortex as in ferromagnets
- divergent vortex, forbidden in ferromagnets
- thickness dependence of magnetic interface coupling

J. Wu et al., Nature Phys. 7, 303 (2011)
Energy reservoirs in a ferromagnetic metal
Deposition of energy in one reservoir
Non-equilibrium distribution and subsequent relation through energy and angular momentum exchange

J. Stöhr, H.C. Siegmann, Magnetism (Springer)
+ 256-320 bunches for 500mA beam current
+ Possibility of one or two 5mA "camshaft" bunches in filling gaps
+ Bunch spacing:
  - multibunch mode: 2 ns
  - two-bunch mode: 328 ns
+ Pulse length 70ps

+ <300 fs x ray pulses though “laser bunch-slicing technique”
Orbital (L) and spin (S) magnetic moments can change with total angular momentum is conserved.

Efficient transfer between L and S through spin–orbit interaction in solids

Transfer between L and S occurs on fs timescales.

Co$_{0.5}$Pt$_{0.5}$ with perpendicular magnetic anisotropy

60 fs optical laser pulses change magnetization

Dynamics probed with XMCD using 120 fs x-ray pulses

Linear relation connects Co $L_3$ and $L_2$ XMCD with $L_z$ and $S_z$ using sum rules

ULTRAFAST DYNAMICS OF SPIN AND ORBITAL MOMENTS

- Thermalization: Faster decrease of orbital moment
- Theory: Orbital magnetic moment strongly correlated with magnetocrystalline anisotropy
- Reduction in orbital moment \( \Leftrightarrow \) Reduction in magnetocrystalline anisotropy
- Typically observed at elevated temperatures in static measurements as well

J. Stöhr, H.C. Siegmann
Magnetism– From Fundamentals to Nanoscale Dynamics
Springer

D. Attwood
Soft X-Rays and Extreme Ultraviolet Radiation: Principles and Applications
MAGNETIC SPECTROSCOPY

Elke Arenholz, Advanced Light Source

+ X-ray absorption, XA
+ X-ray magnetic circular dichroism, XMCD
+ X-ray magnetic linear dichroism, XMLD
+ X-ray magnetic microscopy
+ Magnetization Dynamics


C. Boeglin et al., Nature 465, 458 (2011)