Magnetism as seen with X-Rays

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Magnetic Materials Today

Magnetic materials for energy applications

Magnetic nanoparticles for biomedical and environmental applications

Magnetic thin films for information storage and processing
Magnetic Materials Characterization Wish List

- Sensitivity to ferromagnetic and antiferromagnetic order
- Element specificity = distinguishing Fe, Co, Ni, ...
- Sensitivity to oxidation state = distinguishing Fe$^{2+}$, Fe$^{3+}$, ...
- Sensitivity to site symmetry, e.g. tetrahedral, $T_d$; octahedral, $O_h$
- Nanometer spatial resolution
- Ultra-fast time resolution

Soft X-Ray Spectroscopy and Microscopy
Spectroscopy

Light/Photon Source → Monochromator → Sample

Intensity vs. Wavelength, Photon Energy

Incoming photon is absorbed by the atom

Excited state

Lowest energy level

Electron

Nucleus

Lowest energy level
Soft X-Ray Spectroscopy (ν ≈ 500-1000eV, λ ≈ 1-2nm)
X-Ray Absorption – Detection Modes

Electron yield:
+ Absorbed photons create core holes subsequently filled by Auger electron emission
+ Auger electrons create low-energy secondary electron cascade through inelastic scattering
+ Emitted electrons \( \propto \) probability of Auger electron creation \( \propto \) absorption probability
Soft X-Ray Absorption – Probing Depth

```
I_t = I_o e^{-\mu t}
```

Sample

<table>
<thead>
<tr>
<th>Element</th>
<th>10eV below $L_3$</th>
<th>at $L_3$</th>
<th>40 eV above $L_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1/\mu$ [nm]</td>
<td>$1/\mu$ [nm]</td>
<td>$1/\mu$ [nm]</td>
</tr>
<tr>
<td>Fe</td>
<td>550</td>
<td>17</td>
<td>85</td>
</tr>
<tr>
<td>Co</td>
<td>550</td>
<td>17</td>
<td>85</td>
</tr>
<tr>
<td>Ni</td>
<td>625</td>
<td>24</td>
<td>85</td>
</tr>
</tbody>
</table>

~10-20 nm layer thick films supported by substrates transparent to soft x-rays
X-Ray Absorption – Detection Modes and Probing Depth

Electron sample depth: 2-5 nm in Fe, Co, Ni

⇒ 60% of the electron yield originates from the topmost 2-5 nm
X-Ray Absorption – Fundamentals

Experimental Concept:
Monitor reduction in x-ray flux transmitted through sample as function of 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, ....
‘White Line’ Intensity

Intensity of $L_{3,2}$ resonances is proportional to number of $d$ states above the Fermi level, i.e. number of holes in the $d$ band.
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\[ I_0 \rightarrow I_t = I_0 e^{-\mu t} \]

Sample
X-ray Absorption – Valence State

Influence of the charge state of the absorber

N. Telling et al., Appl. Phys. Lett. 95, 163701 (2009)

X-Ray Absorption – Configuration Model

Configuration model, e.g. L edge absorption:

+ Excited from ground/initial state configuration, $2p^6 3d^8$ to exited/final state configuration, $2p^5 3d^9$
+ 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

Ni$^{2+}$ in NiO: $2p^6 3d^8 \rightarrow 2p^5 3d^9$

http://www.anorg.chem.uu.nl/CTM4XAS/

J. Stöhr, H.C. Siegmann, Magnetism (Springer)
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Sensitivity To Site Symmetry: Ti\(^{4+}\) \(L_{3,2}\)

- Electric dipole transitions: \(d^0 \rightarrow 2p^5 3d^1\)
- Crystal field splitting \(10D_q\) acting on 3d 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)
X-Ray Absorption – Lattice Symmetry

Influence of lattice site symmetry at the absorber

G. Van der Laan
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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

$$|m| \propto \mu_B \left( n_e^{maj} - n_e^{min} \right)$$
Calculate transition probabilities from filled $2p_{3/2}$ and $2p_{1/2}$ states to empty states in $d$-band for circularly polarized x rays using Fermi’s Golden Rule
Origin of X-ray Magnetic Circular Dichroism

$$|f\rangle$$
final state $|f\rangle$
final state energy $\varepsilon_f$

$$|i\rangle$$
initial state $|i\rangle$
initial state energy $\varepsilon_i$

Wave functions describe electronic and photon states
Energies include electronic and photon energies
Origin of X-ray Magnetic Circular Dichroism

Calculate transitions probabilities $T_{if}$ considering photon as time-dependent perturbation, i.e. an electromagnetic (EM) field.
Transition probability per unit time, $T_{if}$, from a state $i$ to a state $f$

$$T_{if} = \frac{2\pi}{\hbar} \left| \langle f | \mathcal{H}_{\text{int}} | i \rangle \right|^2 \delta(\varepsilon_i - \varepsilon_f) \rho(\varepsilon_f)$$

Fermi’s Golden Rule

$T_{if}$ Dimension [time$^{-1}$]

Initial state: wavefunction $|i\rangle$, energy $\varepsilon_i$

Final state: wavefunction $|f\rangle$, energy $\varepsilon_f$

$\rho(\varepsilon_f) = \text{density of final states per unit energy}$

$\mathcal{H}_{\text{int}}$ interaction Hamiltonian,

product of momentum operator $p$ and vector potential $A$

$$\mathcal{H}_{\text{int}} = \frac{e}{m_e} p \cdot A$$
Consider strong ferromagnet with one filled spin band:
- All spin down $d$ states filled
- Spin up $d$ states partially filled

This specific case:
Only spin up electron excited

X-ray absorption of circularly polarized photons with angular momentum $q = \pm 1$ in units of $\hbar$
Origin of X-ray Magnetic Circular Dichroism

\[ q = +1 \quad q = -1 \quad q = 0 \]

\[ m_j = \frac{-5}{2} \quad \frac{-3}{2} \quad \frac{-1}{2} \quad \frac{1}{2} \quad \frac{3}{2} \quad \frac{5}{2} \]

\[ L_3: \text{X rays with } q = +/−1 \text{ excite } 62.5\%/37.5\% \text{ of the spin up electrons} \]

\[ L_2: \text{X rays with } q = +/−1 \text{ excite } 25\%/75\% \text{ of the spin up electrons} \]
Taking into account 2x higher population of $2p_{3/2}$ state as compared to $2p_{1/2}$ state:

$\Rightarrow$ Identical magnitude XMCD at $L_3$ and $L_2$ with opposite sign
X-Ray Magnetic Circular Dichroism (XMCD)

Magnitude of XMCD depends on:
+ expectation value of 3d magnetic moment
+ degree of circular photon polarization, $P_{\text{circ}}$
+ geometry

$|_{\text{XMCD}} = I_{\uparrow\downarrow} - I_{\uparrow\uparrow}$

Photon energy (eV)

$X_{\text{A}}$ (arb. units)

$X_{\text{MCD}}$ (arb. units)
X-Ray Magnetic Circular Dichroism (XMCD)

+ 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

Magnetic Bionanospinels

Fe<sup>2+</sup>,<sub>O</sub><sub>h</sub>

Fe<sup>3+</sup>,<sub>T<sub>d</sub></sub>

Fe<sup>3+</sup>,<sub>O</sub><sub>h</sub>

Co-ferrite-1
6 at% Co

Co-ferrite-2
23 at% Co

V. Cocker et al.,
Magnetic Bionanospinels

+ Geobacter sulfurreducens bacteria form magnetite nanocrystals (15nm) via extracellular reduction of amorphous Fe(III)-bearing minerals
Comparing XMCD spectra with model compounds and/or calculations
⇒ Identifying magnetic phases
The element-specificity makes XMCD measurements an ideal tool to determine induced moments at interfaces between magnetic and non-magnetic elements.

Magnetic Interfaces

- 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

A < 0  B > 0

+ Theoretically derived sum rules correlate XMCD spectra with spin and orbital moment providing unique tool for studying magnetic materials.

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

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

J. Stöhr, H.C. Siegmann, Magnetism (Springer)
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 $\mu_B$

Element-specific Magnetization Reversal

Monitoring field dependence of XMCD

⇒ Element-specific information on magnetization reversal in complex magnetic nanostructures.
XMCD is the difference in x-ray absorption between antiparallel and parallel orientation of magnetic moment and photon spin.

The XMCD magnitude reflects the magnetic moment aligned parallel to the x-ray beam.
+ In fact:
Magnetic moments are not fully aligned with applied fields but precess around them.
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+ Is it possible to measure the precession of magnetic moments making use of the pulsed nature of synchrotron radiation and XMCD?
X-Ray Ferromagnetic Resonance

Pulsed nature of synchrotron radiation
Example: Advanced Light Source

- 256-320 bunches for 500mA beam current
- Bunch spacing: 2 ns
- Pulse length 70ps

Pulse length 70 ps

bunch spacing
Dynamic XMCD measurement, i.e. synchronize x-ray pulses with FMR precession

X-ray pulse repetition signal, ~500 MHz
X-Ray Ferromagnetic Resonance

Static XMCD

Dynamic XMCD

XMCD (arb. units)

Photon energy (eV)

Microwave delay (ps)

FeCo\textsubscript{GaAs} XMCD.opj

XMCD (arb. units)

L\textsubscript{3}

L\textsubscript{2}

Co

x-rays

M(t)

M

M

X\textsubscript{A} (arb. units)
Precession is resonantly excited in the NiFe layer with an 4 GHz RF field.

The resonance field of the CO layer is higher, i.e. no precession is excited in the Co layer.

Precession in Py, Cu$_{75}$Mn$_{25}$, and Co layers are probed by XMCD using left- and right-circularly polarized x-rays at Ni, Mn, and Co edges, respectively.

The Cu$_{75}$Mn$_{25}$ spin precession is a direct indicator of the AC spin current through the structure.
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.
Structural Changes In PbZr$_{0.2}$Ti$_{0.8}$O$_3$

- 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

X-Ray Magnetic Linear Dichroism

Isotropic $d$ electron charge density
⇒ No polarization dependence

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

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

$+ \text{XMLD allows investigating ferri- and ferromagnets as well as antiferromagnets}$

$+ \text{XMLD spectral shape and angular dependence are determined by magnetic order and lattice symmetry}$
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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

Planar Domain Wall

Magnetic Microscopy
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.

Magnetic Coupling At Co/NiO Interface

Taking into account the geometry dependence of the Ni XMLD signal

⇒ Perpendicular coupling of Co and NiO moments at the interface.

Magnetic Vortices

+ 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)
Nanoscale Magnetic Phases

+ BiFeO$_3$ – multiferroic = ferroelectric + antiferromagnetic
+ Compressive strain on rhombohedral phase (R-phase) induced by substrate
  ⇒ tetragonal-like phase (T-phase)
+ Partial relaxation of epitaxial strain
  ⇒ Formation of a nanoscale mixture of T- and R-phases

Q. He et al., Nature Comm. 2, 225 (2011)
Highly distorted R-phase is the source of enhanced magnetic moment in the XMCD image.

Q. He et al., Nature Comm. 2, 225 (2011)
Ultrafast Magnetism

+ Energy reservoirs in a ferromagnetic metal
+ Deposition of energy in one reservoir

⇒ Non-equilibrium distribution and subsequent relation through energy and angular momentum exchange

Electron-phonon relaxation time

Electron-spin relaxation time

Spin-lattice relaxation time

J. Stöhr, H.C. Siegmann, Magnetism (Springer)
Ultrafast Dynamics Of Spin And Orbital Moments

+ 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 120fs x-ray pulses

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

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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

![Graph showing spin and orbital moments](image)

$S_z$ and $L_z$ vs. delay (ps)

$\tau_{th} = 280 \pm 20$ fs

$\tau_{th} = 220 \pm 20$ fs


Electron-phonon relaxation time $\tau_{el-lat}$

Electron-spin relaxation time $\tau_{el-sp}$

Spin-lattice relaxation time $\tau_{lat-sp}$
References And Further Reading

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