Study of the anomalous magnetic behavior of nanostructures by X-ray magnetic circular dichroism

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Overview

1. Tutorial: what is X-ray Magnetic Circular Dichroism
2. Scientific cases:
   A. Anomalous Palladium magnetism in nanostructures
   B. Giant orbital magnetic moment of Co/Au nanostructures
   C. Magnetic domain reconfiguration in MnAs/GaAs films
   D. Fe/MnAs magnetic coupling
   E. Microscopy with magnetic domain sensitivity
4. Conclusion
XMCD reflects the dependence of photon absorption of a material on polarization. X-ray absorption spectroscopy utilizes the energy dependent absorption of x-rays to obtain information about the elemental composition.

X-ray absorption spectra of a wedge sample, revealing the chemical composition.
It also gives information on the chemical environment of the atoms and their magnetic state. Core electrons are excited in the absorption process into empty states above the Fermi energy and thereby probe the electronic and magnetic properties of the empty valence levels.

L-edge x-ray absorption edge spectra of Fe, Co and Ni in the form of the elemental metals and as oxides. They two main structures are called the L3 (lower energy) and L2 absorption edges. The two main peaks in the spectra arise from the spin orbit interaction of the 2p core shell and the total intensity of the peaks is proportional to the number of empty 3d valence states.
The metals are usually ferromagnetic and their magnetic properties are best studied with X-Ray Magnetic Circular Dichroism spectroscopy, while the oxides are usually antiferromagnetic and are studied with X-Ray Magnetic Linear Dichroism.
1. Tutorial: The concept of XMCD – Spin and Orbital Moments

- X-ray absorption process → spin dependent
- Use of right or left circularly polarized photons → transfer angular momentum to the excited photoelectron
- $p_{3/2}$ (L3) and $p_{1/2}$ (L2) levels have opposite spin-orbit coupling → spin polarization opposite at the two edges

Electronic transitions in conventional L-edge x-ray absorption (a), and x-ray magnetic circular x-ray dichroism (b,c), illustrated in a one-electron model. The transitions occur from the spin-orbit split 2p core shell to empty conduction band states. By use of circularly polarized x-rays the spin moment (b) and orbital moment (c) can be determined from linear combinations of the dichroic difference intensities A and B, according to other sum rules.
1. Tutorial: The concept of XMCD – Spin and Orbital Moments

Tune x-ray *energy* for elemental specificity

Tune x-ray *polarization* for magnetic specificity

**Linear Dichroism - Antiferromagnets**

**Circular Dichroism - Ferromagnets**
1. Tutorial: The concept of XMCD – Spin and Orbital Moments

\[ \Delta \mu(E) = \mu^+(E) - \mu^-(E) \]

\( \mu(E) \) - X-ray absorption for different polarizations

\[ \Delta \mu(E) = \text{XMCD signal} \]

Usually one inverts the magnetic field instead of changing polarizations.
1. Tutorial: XMCD – Spin and Orbital Moments sum rules

\( \mu(E) \) - X-ray absorption for different polarizations

\[ \Delta \mu(E) = \mu^+(E) - \mu^-(E) \text{ (XMCD signal)} \]

\[ m_{\text{spin}} = -\frac{6 \int_{L_3} (\mu_+ - \mu_-)dE - 4 \int_{L_3+L_2} (\mu_+ - \mu_-)dE}{\int_{L_3+L_2} (\mu_+ + \mu_-)dE} \times (10 - n_{3d}) \]

\[ m_{\text{orb}} = -\frac{4 \int_{L_3} (\mu_+ - \mu_-)dE}{3 \int_{L_2+L_3} (\mu_+ + \mu_-)dE} \times (10 - n_{3d}) \]
1. Tutorial: XMCD – Spin and Orbital Moments sum rules

\[ m_{spin} = -\frac{6 \int L_3 (\mu_+ - \mu_-)dE - 4 \int L_3 + L_2 (\mu_+ - \mu_-)dE}{\int L_3 + L_2 (\mu_+ + \mu_-)dE} (10 - n_{3d})(1 + \frac{7\langle T_z \rangle}{2\langle S_z \rangle}) \]

\[ m_{orb} = -\frac{4 \int L_3 (\mu_+ - \mu_-)dE}{3 \int L_3 + L_2 (\mu_+ + \mu_-)dE} (10 - n_{3d}) \]

\[ m_{orb}/m_{spin} = \frac{2 \int L_3 + L_2 (\mu_+ - \mu_-)dE}{9 \int L_3 (\mu_+ - \mu_-)dE - 6 \int L_3 + L_2 (\mu_+ - \mu_-)dE} \]
1. Tutorial: XMCD – Spin and Orbital Moments sum rules


Theoretical papers:
1. Tutorial: XMCD – Spin and Orbital Moments sum rules

**TABLE I.** Orbital and spin magnetic moments of bcc Fe and hcp Co in units of $\mu_B$/atom.

<table>
<thead>
<tr>
<th></th>
<th>Fe (bcc)</th>
<th></th>
<th>Co (hcp)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$m_{\text{orb}}/m_{\text{spin}}$</td>
<td>$m_{\text{orb}}$</td>
<td>$m_{\text{spin}}$</td>
</tr>
<tr>
<td>MCD and sum rules</td>
<td>0.043</td>
<td>0.085</td>
<td>1.98</td>
</tr>
<tr>
<td>Gyromagnetic ratio [16]</td>
<td>0.044</td>
<td>0.092</td>
<td>2.08</td>
</tr>
<tr>
<td>OP-LSDA [17]</td>
<td>0.042</td>
<td>0.091</td>
<td>2.19</td>
</tr>
<tr>
<td>OP-LSDA (with OP off) [17]</td>
<td>0.027</td>
<td>0.059</td>
<td>2.19</td>
</tr>
<tr>
<td>SPR-LMTO [10]</td>
<td>0.020</td>
<td>0.043</td>
<td>2.20</td>
</tr>
<tr>
<td>FLAPW [11]</td>
<td>0.023</td>
<td>0.050</td>
<td>2.16</td>
</tr>
<tr>
<td>MCD and sum rules (corrected)</td>
<td>0.043</td>
<td>0.086</td>
<td>1.98</td>
</tr>
</tbody>
</table>
2. Scientific cases: A. Anomalous Palladium magnetism in nanostructures

Surface Ferromagnetism of Pd Fine Particles

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We report clear evidence of the ferromagnetism of gas-evaporated Pd fine particles with a clean surface. The clean Pd particle is found to have a magnetic heterostructure: the surface of the particle is ferromagnetic and the rest is paramagnetic. The size dependence of the magnetic saturation component reveals that the ferromagnetic ordering occurs only on (100) facets of the particle and that the topmost two to five layers from the surface contribute to the ferromagnetism with a magnetic moment of $(0.75 \pm 0.31) \mu_B/\text{atom}$. 

Techniques: DRX, TEM, SQUID

Ferromagnetism on the facets! $(111)$ $(100)$
Techniques:
HRTEM, SQUID

Ferromagnetism due to defects (stacking faults)!
2A. Palladium magnetism: Stoner Criterion for Magnetism of Conduction Electrons

\[ \frac{\Delta E_{\text{kin}}}{2}g(E_F)(\delta E)^2 \]
\[ \Delta E_{\text{pot}} = -\frac{1}{2}U \cdot (g(E_F)\delta E)^2 \]
\[ U = \mu_0\mu_B^2\lambda \]

\[ \Delta E = \Delta E_{\text{kin}} + \Delta E_{\text{pot}} \]
\[ = \frac{1}{2}g(E_F)(\delta E)^2 (1 - U \cdot g(E_F)) \]

\[ \Delta E < 0 \quad \text{Energetically favorable} \]

Stoner Criterion: \[ U \cdot g(E_F) \geq 1 \]
2A. Palladium magnetism: Stoner Criterion for Magnetism of Conduction Electrons

- DOS at the Fermi Energy

- $U \cdot g(E_F) \geq 1$

Almost...
2A. Observation of Ferromagnetism in PdCo nanoparticles encapsulated in Carbon Nanotubes

Técnica de crescimento: Deposição Química na Fase Vapor Assistida por Plasma – PECVD.

- Alto controle;
- Alinhamento vertical.

Distribuição de tamanho: Diâmetro = (70 30)nm
2A. Observation of Ferromagnetism in PdCo em nanoparticles encapsulated in Carbon Nanotubes

Microscopia Eletrônica de Transmissão (TEM)

Homogeneidade da amostra;

Anisotropia de forma das partículas;

Estrutura cristalina: PdCo (fcc) próxima a do Paládio bulk.

Concentração de Pd em relação ao Co ao longo da partícula é aproximadamente constante
2A. Observation of Ferromagnetism in PdCo em nanoparticles encapsulated in Carbon Nanotubes

Magnetometria de amostra vibrante (VSM)
Comportamento magnético global da amostra;

Temperatura ambiente;

Campo de saturação: 1500 Oe

Anisotropia magnética uniaxial:
- eixo duro: H perpendicular;
- eixo fácil: H longitudinal.
2A. A. Observation of Ferromagnetism in PdCo em nanoparticles encapsulated in Carbon Nanotubes

Magnetometria de amostra vibrante (VSM)
Comportamento magnético global da amostra;

Temperatura ambiente;

Campo de saturação: 1500 Oe

Anisotropia magnética uniaxial:
- eixo duro: H perpendicular;
- eixo fácil: H longitudinal.
2A. Observation of Ferromagnetism in PdCo em nanoparticles encapsulated in Carbon Nanotubes

Second derivative:
Removing paramagnetic signal

\[ H_c = 1500 \text{ Oe} \]
2A. Observation of Ferromagnetism in PdCo nanoparticles encapsulated in Carbon Nanotubes

Pd/Co: 4/0.5nm

Hr < 60 Oe
Não apresenta anisotropia

Pd/Co: 4/1nm

Hr < 60 Oe
Não apresenta anisotropia

Pd/Co: 4/4nm

Hr ~ 600 Oe
1000 Oe
Anisotropia evidente
2A. X-ray magnetic circular dichroism of PdCo nanoparticles

XMCD at LNLS

Informação magnética com informação química-estrutural!

Temperatura ambiente;

LNLS, linhas de luz: bordas $L_2$ e $L_3$
Co – PGM (100-1000ev);
Pd – SXS (1000-3000eV);

Campo magnético aplicado:
~10000 Oe (1 T)
<6x o necessário
2A. Observation of Ferromagnetism in PdCo nanoparticles encapsulated in Carbon Nanotubes

**Observation of ferromagnetism in PdCo alloy nanoparticles encapsulated in carbon nanotubes**

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**Dicroísmo Circular Magnético de Raios-X (XMCD)**

- **Cobalto:**
  
  \[ m_{orb}/m_{spin} = (0,12 \pm 0,05) \]

- **Paládio:**
  
  \[ m_{orb}/m_{spin} = (0,07 \pm 0,05) \]

- **Cobalto bulk:** 0,099

2. Scientific cases: B. Room temperature observation of orbital momentum enhancement of Co nanoclusters grown on Au(110)

Low dimensional systems (nanoparticles, clusters, 1d systems) exhibit anomalous magnetic behavior.

Techniques:

- STM (for size determination)
- SQUID (for magnetism)
- XMCD (orbital and spin momentum)

5 Kelvin, 8 Tesla!!!
XMCD at LNLS
New Beamline PGM

EPU-type Undulator beamline
VLS PGM monochromator
Polarized soft-X-rays
Energy = 100-1100eV

Applications:
X-ray magnetic circular dichroism
X-ray photoelectron
Diffraction
X-ray photoelectron spectroscopy
Electron spectroscopy of liquids
Among others...

UFMG
Test experiment: Magnetism of Cobalt nanoparticles grown on Au (110)

Preparation of Au(110) surface (2x1) reconstruction observed by low-energy electron diffraction)
Surface prepared by
1.5 KeV Ar+ sputtering, 400° C annealing, \( P_{\text{base}} = 2 \times 10^{-10} \) mBar

Asymmetric deposition of Cobalt

Cobalt e-beam source

Variable size Co clusters

Au(110)
Preparation experiment at DF-UFMG:

STM and LEED of Au(110) and 4 ml Co/Au(110)
XMCD of Cobalt nanoparticles grown on Au (110)

First measurement of systems of low dimensionality
Room temperature
Applied magnetic field 1.6 Tesla

Beamline PGM -LNLS, Cobalt L₂ e L₃ Edges
PGM (200-1000ev);
X-ray absorption spectroscopy of Cobalt nanoparticles grown on Au (110)
The equivalent of 4 monolayers of Cobalt were deposited. Dichroism is evident.
Determination of orbital moments is possible if magnetization is not saturated.

\[ m_{\text{spin}} = - \frac{6 \int_{L_3} (\mu_+ - \mu_-)dE - 4 \int_{L_3+L_2} (\mu_+ - \mu_-)dE}{\int_{L_3+L_2} (\mu_+ + \mu_-)dE} \times (10 - n_{3d}) \times \frac{1}{Pol \times \cos \theta} = 2.14 \mu_B \]

\[ m_{\text{orb}} = - \frac{4 \int_{L_3} (\mu_+ - \mu_-)dE}{3 \int_{L_2+L_3} (\mu_+ + \mu_-)dE} \times (10 - n_{3d}) \times \frac{1}{Pol \times \cos \theta} \]

Determination of \( \theta \) using \( m_{\text{spin}} = 2.14 \mu_B \)

\[ \theta(\degree) \]

\[ \text{Cobalt coverage (ml)} \]

\[ B_{\text{ext}} = 1.6 \text{Tesla} \quad T = 300 \text{K} \]
Determination of orbital and spin moments is not possible if magnetization is not saturated.
Large orbital momentum of Cobalt nanoparticles

\[ m_L \text{(bulk Co)} \to 0.2 \]

- High coordination
- Number \( m_L \to 0 \)

Cobalt coverage (monolayers)
Large orbital momentum of Cobalt nanoparticles

\[ m_L (\text{bulk Co}) \rightarrow 0.2 \]
2C. Magnetic domain reconfiguration in MnAs/GaAs(001) films

Atomic Force Microscopy (Topography)

Magnetic Force Microscopy (Magnetic Boundaries)

MFM - The magnetic profile changes at about $T = 31^\circ C$: Meanders $\rightarrow$ Line-shaped structures
2C. Magnetic domain reconfiguration in MnAs/GaAs(001) films: Terrace structure

- $q_x$: terraces period;
- $q_z$: terraces height;
- Elastic scattering:
- Rocking scans.

$s = 642 \text{nm}$
$d = 130 \text{nm}$

Terraces Scattering

$\int H$
$q_x$
$q_z$
$q = k_f - k_i$
$\omega$
$2\theta$

Temperature ($^\circ\text{C}$)

Intensity (arb. units)

Near the resonance, charge scattering increases considerably. Magnetic effects are noticeable, as large as 7% at the Mn L$_{\text{III}}$ edge (639 eV).

Depending on the polarization, different magnetization directions are probed.
2C. MnAs/GaAs(001) films: terrace structure and Magnetic Hysteresis measured by resonant magnetic X-ray scattering

Hysteresis and rocking curves were done as function of temperature.
2C. MnAs/GaAs(001) films: Magnetic Hysteresis measured by resonant magnetic X-ray scattering

Shrinking of ferromagnetic terrace → Reconfiguration of magnetic domains
2C. Magnetic force microscopy of MnAs/GaAs(001) film

Shrinking of magnetic terrace $\rightarrow$ Reconfiguration of magnetic domains!

Thermodynamic model of magnetic reconfiguration ($p = 2.6$)
(J. Appl. Phys. 2006)

Calculation of demagnetization energy

$$E_M = -\frac{1}{2} \int \mathbf{M} \cdot \mathbf{H}_{in} \ ' d^3 r$$

$$\mathbf{H}_{in}' = -\gamma_B D \cdot \mathbf{M}.$$
2C. MnAs/GaAs(001) films: Magnetic Hysteresis measured by resonant magnetic X-ray scattering

\[ E(p, \varphi, H) = \left[ \frac{1}{2} M^2 4\pi \left( D_{zz}^{(3)}(p) - D_{xx}^{(1)}(p) \right) \right] \sin^2 \varphi - HM \cos \varphi, \]

Thermodynamic model of magnetic reconfiguration (J. Appl. Physics 2006)
2D. Fe/MnAs films: chemical sensitivity using resonant magnetic X-ray scattering

\[ \text{Mn L}_3\text{ edge} \rightarrow 640\text{eV, Fe L}_3\text{ edge} \rightarrow 707\text{eV} \]
D. Fe/MnAs films: magnetic hysteresis measured by magnetic resonant X-ray scattering. Each scans is performed at two different absorption edges: Fe and Mn!!!
2D. Fe/MnAs films: Magnetic Hysteresis measured by resonant magnetic X-ray scattering: magnetic coupling between MnAs terraces and Fe film.

Can we make a thermodynamic model of magnetic reconfiguration (current research)?
Ferromagnetic domain pattern for a thin Co layer on NiO(100), showing all four spin directions in Co. The spin directions are pinned by the underlying NiO.
4. Conclusions

- X-ray magnetic circular dichroism reveals magnetism with chemical specificity
- Orbital and spin moments can be determined separately
  - Anomalous Palladium magnetism in nanostructures
  - Giant orbital magnetic moment of Co/Au nanostructures
  - Magnetic domain reconfiguration in MnAs/GaAs films
  - Fe/MnAs magnetic coupling
  - Microscopy with magnetic domain sensitivity
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