Soft X-ray Absorption and Resonant Scattering

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Chairon 2008, SPring8, Japan  
Oct. 3

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1. Soft X-ray Absorption
   - Basic
   - Experimental Setup
   - Applications
     - Chemical analysis
     - Orbital polarization
     - Magnetic Circular Dichroism

2. Resonant Soft X-ray Scattering
   - Introduction
   - Basic of resonant X-ray scattering
   - Examples:
     - Magnetic Transition of a Quantum Multiferroic LiCu2O2
Soft x-ray: 250 eV ~ a few keV

Interaction of photons with matter:

- **Photoelectric effect**
- **Photoabsorption**
- **Scattering/diffraction**

- **lattice structure**: arrangement of atoms
- **electronic states**
- **magnetic order**
- **excitations (electronic states or phonons)**
Photo-absorption\[
\frac{d\sigma}{d\Omega} \propto \sum \left| \left\langle \Psi_f \left| A \cdot P \right| \Psi_i \right\rangle \right|^2 \cdot \delta \left( E_f - E_i - \hbar \nu \right)
\]

If \( \mathbf{k} \cdot \mathbf{r} < < 1 \), Dipole approximation: \( e^{i\mathbf{k} \cdot \mathbf{r}} \approx 1 + i \mathbf{k} \cdot \mathbf{r} \approx 1 \)

\[ \mathbf{A} = \varepsilon e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} = \varepsilon e^{-i\omega t} \]

\( \varepsilon \) polarization of x-ray

\[ \frac{d\sigma}{d\Omega} \propto \sum \left| \left\langle f \left| \mathbf{e} \cdot \mathbf{P} \right| i \right\rangle \right|^2 \cdot \delta \left( E_f - E_i - \hbar \nu \right) \propto \sum \left| \left\langle f \left| \mathbf{e} \cdot \mathbf{r} \right| i \right\rangle \right|^2 \cdot \delta \left( E_f - E_i - \hbar \nu \right) \]

\[ \therefore \left\langle f \left| \mathbf{e} \cdot \mathbf{P} \right| i \right\rangle = \frac{i m}{\hbar} \cdot \left\langle f \left| \mathbf{H} \right| i \right\rangle = \frac{i m}{\hbar} (E_f - E_i) \cdot \left\langle f \left| \mathbf{r} \right| i \right\rangle = i m \omega \left\langle f \left| \mathbf{e} \cdot \mathbf{r} \right| i \right\rangle \]

\[ \left[ \mathbf{H}, \mathbf{r} \right] = \frac{\hbar}{i m}, \text{ if } \left[ \mathbf{H}(r), \mathbf{r} \right] = 0 \]

1s → np K-edge XAS can be accurately described with single-particle methods.

2p → 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.
Dipole transition

Absorption probability: \[ W = \frac{2\pi}{\hbar} |M_{ij}|^2 \delta(\hbar \omega - E_f + E_i) \]
\[ M_{ij} \propto \left( f \cdot \hat{r} \right)_i \]
\[ \mathbf{\varepsilon} \cdot \hat{r} = e_z \sin \theta \cos \phi + e_y \sin \theta \sin \phi + e_x \cos \theta \]
\[ \hat{r} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \]
\[ \cos \theta = \sqrt{\frac{e_x}{e_x + e_y}} Y_{1,0}(\theta, \phi) \]
\[ \sin \theta \cdot e^{i\phi} = \frac{e_x + i e_y}{\sqrt{2}} Y_{1,1}(\theta, \phi) \]
\[ \mathbf{\varepsilon} \cdot \hat{r} = \sqrt{\frac{4\pi}{3}} \left( \frac{-e_x + i e_y}{\sqrt{2}} Y_{1,1} + \frac{e_x + i e_y}{\sqrt{2}} Y_{1,-1} + \mathbf{\varepsilon}_r Y_{1,0} \right) \]

Selection rule: \[ (\Delta m_i \equiv m_f - m_i) \]
\[ \Delta m_i = 0 \]
\[ \Delta l \equiv l_f - l_i = \pm 1 \]

L, circularly polarized
\[ Y_{1,1}: \Delta m_i = +1 \]
R, circularly polarized
\[ Y_{1,-1}: \Delta m_i = -1 \]

For 2p \( \rightarrow \) 3d:
\[ M_{ij} \propto \left\{ 2p^5 3d^{n+1} \mathbf{\varepsilon} \cdot \mathbf{r} \right| 2p^6 3d^n \} \]

• 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.
Each element has specific absorption energies. “finger print” → element specific spectroscopy

In transition-metal oxides

**soft x-ray absorption & scattering**

*TM: 2p → 3d*

*O: 1s → 2p*

**direct, element-specific probing of electronic structure of TMO**
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Measurement of Soft X-ray absorption

- Incident light
- mesh
- transmitted light
- detector
- $I_0$
- electrometer
Photoexcitation and Relaxation

Photoelectric absorption

Fluorescent x-ray emission

Auger electron emission

Auger electrons

Photoabsorption

Intensity (log)

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

Polarization of Synchrotron Radiation

Right-handed circularly polarized

Linearly polarized

Left-handed circularly polarized
Soft X-Ray Magnetic Circular Dichroism in Absorption

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

\[ \text{MCD} \equiv \sigma_+ - \sigma_- \]

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

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

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.

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

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

Soft X-Ray Magnetic Circular Dichroism in Absorption
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 Curve

Two-dimensional systems, such as ultrathin epitaxial films and superlattices, display magnetic properties distinct from bulk materials. A challenging aim of current research in magnetism is to explore structures of still lower dimensionality. As the dimensionality of a physical system is reduced, magnetic ordering tends to decrease as fluctuations become relatively more important. Spin lattice models predict that an infinite one-dimensional linear chain with short-range magnetic interactions spontaneously breaks up into segments with different orientations of the magnetizations, thereby prohibiting long-range ferromagnetic order at a finite temperature. 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 metal 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 topographies 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; repetitive step interactions result in a narrow terrace width distribution centered at 20.2 Å with 2.6 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 320 Å.
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Spin, Charge, and orbital ordering in correlated electron systems

La$_{0.5}$Sr$_{1.5}$MnO$_4$ by Moritomo et al. (1995)

La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_4$ by J. Tranquada et al. (1995)

La$_{1/3}$Ca$_{2/3}$MnO$_3$ by C. H. Chen et al. (1998)

Small valence disproportionation!

$\Delta Q / Q_{\text{total}} \ll 1$

Elastic x-ray scattering

$\mathbf{k} = \frac{2\pi}{\lambda}$

modulation vector

$|\mathbf{k}| = |\mathbf{k}'|$

A volume element $d^3\mathbf{r}$ at $\mathbf{r}$ will contribute an amount to the scattering field with a phase factor $e^{i\mathbf{q} \cdot \mathbf{r}}$. The scattering form factor is

$f_q \equiv \sum_{j} \rho(\mathbf{r}_j) e^{i\mathbf{q} \cdot \mathbf{r}_j}$

Fourier transform of charge distribution.

$\frac{d\sigma}{d\Omega} \propto |f_q|^2$
Resonant scattering

As the photon energy $\hbar \omega$ approaches the binding energy of one of the core-level electrons,

$$f_s(q, \hbar \omega) = f^0(q) + f'(\hbar \omega) + i f''(\hbar \omega)$$

dispersion corrections

Absorption

$$\sigma = -\frac{4\pi}{k} \text{Im}(f)$$

Advantage of Resonant Soft X-ray Scattering

$$f_{res} \sim \sum_{3d} \langle \Psi_{2p} | \bar{e} \cdot \bar{r} e^{i\bar{k} \cdot \bar{r}} | \Psi_{3d} \rangle \langle \Psi_{3d} | \bar{e} \cdot \bar{r} e^{i\bar{k}' \cdot \bar{r}} | \Psi_{2p} \rangle \hbar \omega - (E_{3d} - E_{2p} - i\Gamma)$$

momentum transfer

$\bar{q} \equiv \bar{k}' - \bar{k}$$

$\Psi_{3d}$

$\Psi_{2p}$

$\tilde{k}$

$\tilde{k}'$

$\tilde{e}$

$E_{3d}$

$E_{2p}$

$E_p$

Unoccupied Valence-band

Occupied Valence-band

Narrow core-levels (long lifetimes)

$\hbar \omega = E_{3d} - E_{2p}$, $f_{res}$ enhanced dramatically and ordering of $\Psi_{3d}$ focused.
Setup of Soft X-ray Scattering

1.5 GeV
NSRRC, Taiwan

UHV two-circle
diffractometer

X-ray magnetic scattering

\[
H_{int} = \frac{e^2}{2mc^2} \sum_j A(r_j)^2 + \frac{e}{mc} \sum_j A \cdot \mathbf{P}_j - \frac{e}{2mc} \sum_j \mathbf{s}_j \cdot \nabla \times A - \frac{e^2}{2(mc^2)} \sum_j \mathbf{s}_j \cdot \left( \frac{\partial A}{\partial t} \times A \right)
\]

Non-resonant

\[
\sigma \sim \frac{2\pi}{\hbar} \left| \langle f | H_{int} | i \rangle \right|^2
\]

Resonant


\[
\frac{f_{mag}}{f_{charge}} \sim \frac{\hbar \omega}{mc^2} \sim 10^{-3} \quad \frac{\sigma_{mag}}{\sigma_e} \sim 10^{-6}
\]

for \( \hbar \omega \sim 600 \text{ eV} \)
Resonant X-ray magnetic scattering

**electric dipole transitions**

\[
\Delta m_i = \pm 1
\]

\[
f_{\text{mag}}^{\text{res}} = -i \frac{3\lambda}{8\pi} (\varepsilon^* \times \varepsilon_0) \cdot \hat{z} (F_{1,1} - F_{1,-1})
\]

\[
\Delta m_i = 1 \quad \Delta m_i = -1
\]

As a result of spin-orbit and exchange interactions, magnetic ordering manifests itself in resonant scattering.

**Resonant soft x-ray magnetic scattering:**

- Cross section comparable to that of neutron scattering.
- Good \(k\) resolution (\(\Delta k < 0.0005 \ \text{Å}^{-1}\))
- Spectroscopic information.
- Limited to a small \(k\) space, less bulk sensitive.
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Magnetism: ordering of spins

Ferroelectricity: polar arrangement of charges

Magnetization can be induced by H field

Electric polarization can be induced by E field
**Magnetolectric effect**

Induction of magnetization by an electric field; induction of polarization by a magnetic field.

- first presumed to exist by Pierre Curie in 1894 on the basis of symmetry considerations

Multiferroics: materials exhibiting ME coupling

Cr$_2$O$_3$
BiMnO$_3$
BiFeO$_3$

However, the effects are typically too small to be useful in applications!

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**Two contrasting order parameters**

Magnetization: time-reversal symmetry broken

\[ t \Rightarrow -t: \quad \vec{M} \Rightarrow -\vec{M} \]
\[ \vec{P} \Rightarrow \vec{P} \]

Polarization: inversion symmetry broken

\[ \vec{r} \Rightarrow -\vec{r}: \quad \vec{P} \Rightarrow -\vec{P}, \quad \vec{M} \Rightarrow \vec{M} \]
\[ \vec{P} = q\vec{r} \]
Recently discovery in the coexistence and gigantic coupling of antiferromagnetism and ferroelectricity in frustrated spin systems such RMnO$_3$ and RMn$_2$O$_5$ (R=Tb, Ho, …) revived interest in “multiferroicity.”

- $T_C < T_N$
- Frustrated magnetic systems.
LiCu$_2$O$_2$

orthorhombic, $Pnma$

$a=5.734$ Å, $b=2.856$ Å, $c=12.415$ Å

Qausi-1D spin ½ chain:

- Characterization of the ground state?
- Multiferroicity

(Park et al. PRL98, 057601; Seki et al., cond-mat 0810.2533)

Two transitions?

Masuda et al., PRL (2004)

Seki et al., PRL (2008)
Masuda et al., PRL (2004)

\[ \mathbf{P} \propto \hat{e} \times (\mathbf{S}_n \times \mathbf{S}_{n+1}) \]
along the \( a \) axis

\[ q = (1/2, \zeta, 0) \]
in units of \( (\frac{2\pi}{a}, \frac{2\pi}{b}, \frac{2\pi}{c}) \)

\[ \zeta = \frac{1}{HWHM} \]

\( T = 10 \text{ K}: \quad \zeta_a = 690 \text{ Å} \quad \zeta_b = 2100 \text{ Å} \quad \text{Cu}^{2+} \quad 2p_{3/2} \)

LiCu\(_2\)O\(_2\) (100) single crystal
Resonant soft x-ray magnetic scattering

5 mm

930 eV
non-zero scattering intensity above $T_N$

Masuda et al.,  PRL (2004)

onset of the long-range spin ordering and induced P

transition temperature of the precursor phase

SW Huang et al., PRL (2008)
There is an in-plane short-range AFM ordering above $T_N$. The extension of the zero-temperature AFM ordering is essential for inducing $P$. 

$\vec{q} = (q_{a,b}, 1)$

- There is an in-plane short-range AFM ordering above $T_N$
- Extension of the zero-temperature AFM ordering
- Spin coupling along the $c$ axis is essential for inducing $P$. 
The ground state of LiCu$_2$O$_2$ exhibits a long range AFM ordering.

The spin coupling along the c axis is essential for inducing P.

Above $T_N$, in-plane correlation

$\xi(T) \propto e^{2J_S/\kappa B T}$

renormalized classical behavior

average

$J \sim 4.25$ meV
**Appendix:** Basic of Magnetic Circular Dichroism in X-ray Absorption

Considering L-edge 2p\(_{3/2}\) → 3d absorption, and ignoring the spin-orbit interaction in the 3d bands,

\[
\sigma \propto \left| \langle l, m_j | \mathbf{e} \cdot \hat{r} | j, m_j \rangle \right|^2
\]

For left-handed circular light

\[\sigma_+ \propto R(r)^2 \cdot \left| \langle Y_\text{in} | e^{-i \theta} \frac{e_y + i e_x}{\sqrt{2}} Y_{l-1} | j, m_j \rangle \right|^2\]

Clesbch-Gordan coefficients

\[Y_{\text{in}} = \sum_{m_{l,m_j}} \left| l, m_j \right\rangle Y_{l,m} Y_{l,m_j}\]

\[Y_{l,m} = \sum_{l',m_{l',m_j}} \left| l', m_{l',m_j} \right\rangle Y_{l,m} Y_{l',m_j}\]

\[Y_{l,m} Y_{l,m_j} = \sum_{l',m_{l',m_j}} \left| l', m_{l',m_j} \right\rangle Y_{l,m} Y_{l',m_j}\]

\[Y_{l,m} Y_{l,m_j} = Y_{2,2} \quad Y_{l,m} Y_{l+1, m+1} = \sqrt{\frac{1}{18}} Y_{40,0} \]

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

Right-handed circularly polarized light preferentially excites spin-down electrons.
\[ \sigma \propto | \langle l, m \mid \mathbf{e} \cdot \hat{r} \mid j, m_j \rangle |^2 \]

\[ \mathbf{e} \cdot \hat{r} = \sqrt{\frac{\hbar}{2 \beta}} e^{i \phi} Y_{l, m} + e^{-i \phi} Y_{l,-m} \]

\[ \sigma_+ \propto R(r)^2 \left| \left\langle l, m \mid \frac{e^{-i \phi}}{\sqrt{2}} Y_{l, m} \mid j, m_j \right\rangle \right|^2 \]

\[ \sigma_- \propto \left| \left\langle Y_{2, l} \mid \frac{e^{-i \phi}}{\sqrt{2}} Y_{l, m} \mid j, m_j = \frac{1}{2}, m_l = \frac{1}{2} \right\rangle \right|^2 \]

\[ Y_{l, m} Y_{j, m_j} = \sqrt{\frac{1}{2}} Y_{2, l} + \ldots \]

\[ \sigma_+ \propto \left| \left\langle Y_{2, l} \mid \frac{e^{-i \phi}}{\sqrt{2}} Y_{l, m} \mid j, m_j = \frac{1}{2}, m_l = \frac{1}{2} \right\rangle \right|^2 \]

\[ Y_{l, m} Y_{j, m_j} = \sqrt{\frac{1}{2}} Y_{2, l} + \ldots \]

**Clebsch-Gordan coefficients**

\[ Y_{lm} = \sum_{m_{l,m}} \left( l, m \mid l, m \right) Y_{lm} Y_{l,m} \]

\[ Y_{l,m} Y_{l,m} = \sum_{m_{l,m}} \left( l, m \mid l, m \right) Y_{lm} Y_{l,m} \]