Soft X-ray Absorption and Resonant Scattering

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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)

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1. Basics of x-ray scattering and absorption
2. Soft X-ray Absorption
   - Experimental Setup
   - Applications
     - Chemical analysis
     - Orbital polarization
     - Magnetic Circular Dichroism
3. Resonant Soft X-ray Scattering
   - Basics
   - Examples
     - Verwey transition of Fe₃O₄
     - Charge-Orbital ordering and Quasi-2D magnetic ordering of La₀.₅Sr₁.₅MnO₄
X-ray absorption

absorption coefficient \( \mu \)

\[
-dI(z) = \mu I(z) \, dz
\]

\[
\frac{dI(z)}{dz} = -\mu I(z) \quad I(z) = I_0 e^{-\mu z}
\]

\# of absorption events \( W = I(z) \rho dz \sigma_a = I(z) \mu dz \)

\# of atoms/area \( n \equiv 1 - \delta + i\beta \quad (\alpha \text{ and } \beta \text{ are real numbers}) \)

The wave propagating in the medium is

\[
E_0 e^{i(n_k z)} = E_0 e^{i(1-\delta)kz} e^{-\beta z} \quad \mu = 2\beta
\]

EM waves scattering by an electron

\[ E_{in} = E_0 e^{-i\omega t}, \quad E_0 \parallel \hat{\mathbf{x}} \]

\[ m a = -e(E_{in} + \mathbf{v} \times \mathbf{B}_{in}) \]

The retarded vector potential \( A(r,t) = \frac{1}{4\pi e^2} \int_{V'} \frac{J(r',t')}{|r-r'|} dV' \quad r' = t - |r-r'|/c \)

Far away from the electron: \( |r-r'| \approx r \) \( A(r,t) \approx \frac{1}{4\pi e^2} \int_{V'} J(r',t-r/c) dV' \)

\[ E = -\nabla \Phi - \frac{\partial \mathbf{A}}{\partial t} \]

\[ E(t) = \frac{-r_0 e^{ikr} \cos \psi}{r} \]

The scattering involves a phase shift of \( \pi \)

Thomson scattering length \( r_0 = \frac{e^2}{4\pi e^2 m c^2} = 2.82 \times 10^{-15} \) Å

\[ d\sigma \over d\Omega = r_0^2 \cos^2 \psi \]

\[ \sigma_T = r_0^2 \int \cos^2 \psi d\Omega = \frac{8\pi}{3} r_0^2 \]
X-rays scattered by an atom

Momentum transfer (in units of $\hbar$)

$$q \equiv k' - k$$

$$k' - k = k$$

$$|q|^2 = |k' - k|^2 = k^2 - 2k k' \cos 2\theta + k^2 = 2k^2(1 - \cos 2\theta) = 4k^2 \sin^2 \theta$$

$$q = 2k \sin \theta$$

A volume element $d^3 r$ at $r$ will contribute an amount $-r_0 \rho(r) d^3 r$ to the scattered field with a phase factor $e^{i q \cdot r}$.

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X-rays scattering

Scattering amplitude:

$$-r_0 \int \rho(\bar{r}) e^{i q \cdot \bar{r}} d\bar{r} = -r_0 f^0(\bar{q})$$

Atomic scattering factor

$$f^0(\bar{q}) \equiv \int \rho(\bar{r}) e^{i q \cdot \bar{r}} d\bar{r}$$

$$q \to 0, \quad f^0(\bar{q}) = Z \quad \text{(the number of electrons in the atom)}$$

All of the different volume elements scatter in phase; each electron contributes $-r_0$ to the scattered field.

$f^0$ is independent on photon energy $\hbar \omega$; it is the scattering amplitude in units of $-r_0$.

$f^0$ is the Fourier transform of the charge distribution.

Optical theorem

absorption cross-section

$$\sigma = \frac{-4\pi r_0}{k} f'' = \frac{-4\pi}{k} \text{Im}(f)$$
How does the scattering amplitude $f$ change if the photon energy approaches an absorption edge?

The forced charge oscillator: a classical model of an electron bound in an atom.

\[ m\ddot{x} = -eE - \kappa x - \Gamma' \dot{x} \quad \text{damping force} \]

\[ \ddot{x} + \Gamma \dot{x} + \omega_s^2 x = -\frac{eE_0}{m} e^{-i\omega t} \quad \omega_s = \sqrt{\kappa/m}, \quad \Gamma \equiv \Gamma'/m \]

\[ x = x_0 e^{-i\omega t}, \quad x_0 = -\frac{eE_0}{m} \frac{1}{(\omega_s^2 - \omega^2 - i\omega\Gamma)} \]

\[ E_{\text{wa}}(r,t) = -r_0 \frac{\omega^2}{(\omega^2 - \omega_s^2 + i\omega\Gamma)} \frac{e^{i\omega r}}{r} E_{\text{in}} \]

Resonant scattering amplitude in units of $-r_0$:

\[ f_s = \frac{\omega^2}{(\omega^2 - \omega_s^2 + i\omega\Gamma)} \]

Resonant scattering

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

\[ f_s(q,\hbar\omega) = f^0(q) + f'(h\omega) + i f''(h\omega) \]

\[ f = f'+i f'' \]

\[ f' = \frac{\omega_s^2(\omega^2 - \omega_s^2)}{(\omega^2 - \omega_s^2)^2 + (\omega\Gamma)^2} \]

\[ f'' = -\frac{\omega_s^2\omega\Gamma}{(\omega^2 - \omega_s^2)^2 + (\omega\Gamma)^2} \]

Absorption

\[ \sigma = -\frac{4\pi}{\kappa} \text{Im}(f) \]
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![Diagram](image)
Photo-absorption \[ \frac{d\sigma}{d\Omega} \propto \sum \left| \langle \Psi_f | A \cdot P | \Psi_i \rangle \right|^2 \cdot \delta \left( E_f - E_i - \hbar \omega \right) \]

If \( k \cdot r \ll 1 \), **Dipole approximation:** \( e^{ik \cdot r} \approx 1 + i k \cdot r \approx 1 \)

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

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

\[ \langle f | \varepsilon \cdot P | i \rangle = \frac{\hbar}{i m} \langle f | k \cdot r | i \rangle = \frac{\hbar}{i m} (E_f - E_i) \cdot \varepsilon \langle f | \varepsilon \cdot r | i \rangle \]

\[ |\langle f|\varepsilon\cdot r|i\rangle| = \frac{\hbar P}{i m} \quad \text{if } |\langle f|\varepsilon\cdot r|i\rangle| = 0 \]

\( 1s \rightarrow np \) **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.

**Dipole transition**

Absorption probability: \( W = \frac{2\pi}{\hbar} |M_{ij}|^2 \delta(h\omega - E_f + E_i) \quad M_{ij} \propto \langle f | \varepsilon \cdot \hat{r} | i \rangle \)

\[ \varepsilon \cdot \hat{r} = e_z \sin \theta \cos \phi + e_y \sin \theta \sin \phi + e_z \cos \theta \]

\[ \hat{r} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \]

\[ \cos \theta = \frac{e_{z+} + e_{x+} i e_y}{\sqrt{2}} Y_{1,0}(\theta, \phi) \quad \sin \theta \cdot e^{i\phi} = \frac{e_{z+} + e_{x+} i e_y}{\sqrt{2}} Y_{1,0}(\theta, \phi) \]

\[ \varepsilon \cdot \hat{r} = \sqrt{\frac{4\pi}{3}} \left( -\frac{e_{z+} + e_{x+} i e_y}{\sqrt{2}} Y_{1,1} + \frac{e_{r+} + e_{r+} i e_y}{\sqrt{2}} Y_{1,-1} + e_z Y_{1,0} \right) \]

Selection rule: \( (\Delta m_f \equiv m_f - m_i) \quad \Delta m_i = 0 \)

\( \Delta l = l_f - l_i = \pm 1 \)

L. circularly polarized \( Y_{1,1}; \Delta m_i = +1 \) R. circularly polarized \( Y_{1,-1}; \Delta m_i = -1 \)

For \( 2p \rightarrow 3d \): \( M_{ij} \propto \left\langle 2p^5 3d^{m+1} | \varepsilon \cdot r | 2p^6 3d^{m} \right\rangle \)
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.
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Measurement of Soft X-ray absorption

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

Photoelectric absorption

Photoelectrons or Auger electrons

Fluorescent x-ray emission

Auger electron emission

Intensity (log)

Kinetic energy
Measurement of Soft X-ray absorption

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In transition-metal oxides

soft x-ray absorption & scattering

$\text{TM: } 2p \rightarrow 3d$

$\text{O: } 1s \rightarrow 2p$

direct, element-specific probing of electronic structure of TMO

L-edge XAS provides information on the chemical state, orbital symmetry, and spin state of materials.
L-edge XAS provides information on the chemical state, orbital symmetry, and spin state of materials.
High Temperature Superconducting Cu oxides

La$_2$CuO$_4$  
(Cu$^{2+}$ : 3d$^9$)

Sr doping: La$_2$CuO$_4$ $\rightarrow$ La$_{2-x}$Sr$_x$CuO$_4$

Tetragonal

hole doping: 3d$^9$ $\rightarrow$ 3d$^9$ + O 2p hole

Orbital Characters of Doped Holes in La$_{2-x}$Sr$_x$CuO$_4$

\[ \sigma_{E \perp \hat{c}} \gg \sigma_{E \parallel \hat{c}} \]

3d

3z$^2$-r$^2$

d$_{xy}$, d$_{xz}$, d$_{zx}$

\[ x^2-y^2 \]

L$_2$

L$_3$

X-Ray Abs. Intensity (a.u.)

Photon Energy (eV)

La$_{1.85}$Sr$_{0.15}$CuO$_4$

Chen et al. PRL 68, 2543 (1992)
**O 1s X-Ray Absorption on TMO**

*In a cluster approach*

\[
\text{O 1s XAS} \quad |\Phi\rangle = \alpha^1 |d^{n+1}\rangle + \cdots + \beta^1 |d^n\rangle \\
(\text{neglecting 1s core hole})
\]

**Spectral weight transfer:**

*a fingerprint of strong electron correlations*

A: \( d^9 \rightarrow d^9 \)  
spectral weight arising from doped holes  
(\( \alpha^2 < \beta^2 \))

B: \( d^9 \rightarrow d^{10} \)  
upper Hubbard band

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Magnetic materials:
In some solids, individual ions have non-vanishing average vector moments below a critical temperature. Such solids are called magnetically ordered.

If a solid exhibits a spontaneous magnetization, its ordered state is described as ferromagnetic or ferrimagnetic. A solid with magnetic ordering has no spontaneous called antiferromagnetic.
Polarization of Synchrotron Radiation

Right-handed circularly polarized

Linearly polarized

Left-handed circularly polarized

Soft X-Ray Magnetic Circular Dichroism in Absorption

For $2p_{3/2} \rightarrow 3d$

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 circularly polarized light.

MCD $\equiv \sigma_+ - \sigma_-$
MCD sum rules

\[
m_{\text{orb}} = - \frac{4}{5} \int \frac{(\mu_+ - \mu_-) d\omega}{L_2} \times (10 - n_{3d}) \\
\]

\[
m_{\text{spin}} = - \frac{6}{5} \int \frac{(\mu_+ - \mu_-) d\omega - 4 \int L_2}{L_2} \times (10 - n_{3d}) \times \left[1 + \frac{7}{2} \left(\frac{\mu_+}{\mu_-}\right)^{1/2}\right] \\
\]

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Experimental confirmation:
Chen et al., PRL 75, 152 (1995)

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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.
MCD in K-edge or L₁-edge XAS is not sensitive to spin magnetic moments. Instead, the MCD measures orbital moments. (H. W.)

MCD in L-edge XAS measures both spin and orbital magnetic moments because of the spin-orbit interaction in the core levels.

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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 Curve

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Fe: 2.1 μ_B/atom

Co: 1.2 μ_B/atom
Ferromagnetism in one-dimensional monatomic metal chains

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 orientation of the magnetization, 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 substrate that support the low-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 ordered 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.

![Image of STM topography of the Pd(100) surface.](image)

**Figure 1** STM topography of the Pd(100) surface. a. Periodic step structure (each white line represents a single step). The surface has a 44° misorientation relative to the [110] direction; repeated step interactions result in a narrow terrace with distribution centred at 20 ± 2 Å with 2.6 Å standard deviation. b. Co monatomic chains decorating the Pt step when the vertical dimension is increased for better contrast. The monatomic chains are obtained by evaporating 0.15 monolayers of Co onto the substrate held at $T = 200$ K and previously cleaned by ion sputtering and annealing cycles in ultrahigh vacuum. The chains are linearly aligned and have a spacing equal to the terrace width.

![Image of X-ray absorption spectra.](image)

**Figure 2** Co X-ray absorption spectra for parallel ($\mu_\parallel$) and antiparallel ($\mu_\perp$) direction of light polarization and field-induced magnetization. The dichroic signal ($\mu_\parallel - \mu_\perp$) is obtained by subtraction of the absorption spectra for parallel and antiparallel to the $L_2$ peak. a. Monatomic chains; b. 1 monolayer; c. Bulk (0.2 nm film on Pd(100)). The sample was mounted on a UHV variable-temperature insert that could be rotated with 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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Correlated-Electron Materials

- Variety of fascinating macroscopic phenomena
- Tunable electronic and magnetic properties

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<th>HTSC</th>
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<th>CMR</th>
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<th>High Temperature Superconductivity</th>
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<td>B = 0</td>
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Charge-orbital ordering in correlated electron systems

**Charge ordering:** spatial localization of the charge carriers on certain sites

2+ ● ● ●
3+ ● ● ●

**Spin ordering:** long range ordering of local magnetic moments

**Orbital ordering:** periodic arrangement of specific electron orbitals

Small valence disproportionation!

Δq/ q_{total} << 1

La_{0.5}Sr_{1.5}MnO_{4}
Moritomo et al. (1995)

La_{1/3}Ca_{2/3}MnO_{3}
C. H. Chen et al. (1998)

La_{1.6-x}Nd_{0.4}Sr_{x}CuO_{4}
J. Tranquada et al. (1995)
• With $\hbar \omega = E_{3d} - E_{2p}$, $f_{res}$ enhanced dramatically and ordering of $\Psi_{3d}$ focused.
X-ray magnetic scattering

\[ H_{\text{int}} = \frac{e^2}{2mc^2} \sum_j A(r_j)^2 + \frac{e^2}{mc^2} \sum_j A \cdot P_j - \frac{e^2}{4mc^2} \sum_j s_j \cdot \nabla \times A - \frac{e^2}{2mc^2} \sum_j s_j \cdot \left( \frac{\partial A}{\partial t} \times A \right) \]

Non-resonant

\[ \sigma = \frac{2\pi}{h} |\langle f | H_{\text{int}} | i \rangle|^2 \]

Resonant

\[ \sigma = \frac{2\pi}{h} \sum_n \frac{\langle f | H_{\text{int}} | n \rangle \langle n | H_{\text{int}} | i \rangle}{E_j + \hbar \omega - E_n} \delta(E_i - E_f) \]

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

for \( \hbar \omega \sim 600 \text{ eV} \)

Resonant X-ray magnetic scattering

electric dipole transitions

Hannon et al., PRL(1988)

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

\[ \Delta m_i = \pm 1 \]

\[ \Delta m_i = 1 \]

\[ \Delta m_i = -1 \]

As a result of spin-orbit and exchange interactions, magnetic ordering manifests itself in resonant scattering.
Resonant Soft X-ray Scattering

Charge-orbital ordering in manganite and magnetite
• Wilkins et al., PRL (2003)
• Thomas et al., PRL (2004)
• Dhesi et al., PRL (2004)
• Huang et al., PRL (2006)

CDW or charge stripes in cuprate and nickelate
• Abbamonte et al., Nature Physics (2005)
• Schüßler-Langeheine et al., PRL (2005)

Antiferromagnetic ordering of manganite
• Wilkins et al., PRL (2003)
• Okamoto et al., PRL (2007)

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The Verwey transition of magnetite ($\text{Fe}_3\text{O}_4$)

- Inverted spinel structure (cubic)
  1/3: tetrahedral (A-site) $\text{Fe}^{3+}$
  2/3: octahedral (B-site) $\text{Fe}^{3+}$, $\text{Fe}^{2+}$

- Verwey model:
  charge order-disorder transition of B-site $\text{Fe}^{3+}$ & $\text{Fe}^{2+}$ with $T_V \sim 120 \text{ K}$

$\text{Fe}_3\text{O}_4$ is believed to be a classic example of charge ordering.

Refinement of x-ray and neutron diffraction

- Charge ordering deduced from the Fe-O distance.
- Valence of B-site Fe: 2.4 & 2.6 (rather than 2 & 3)
- (0 0 1)$_c$ and (0 0 1/2)$_c$
  charge modulation along the c-axis

Wright, Attfield, and Radaelli,
LDA+U calculations: charge-orbital ordering

Jeng, Guo, and Huang, PRL (2004)

Leonov et al., PRL (2004)

Breakdown of Anderson's criterion can be explained by the existence of orbital ordering.

(0 0 \(1/2\))\(_c\) resonant scattering at O K-edge of Fe\(_3\)O\(_4\)

\[ R \text{ is the factor accounting for the enhancement of the form factor due to the O K-edge resonance.} \]

Correlation length \( \xi \equiv 1/\Gamma = 900 \text{ Å} \)
(0 0 ½) $c$ resonant scattering at O K-edge of Fe$_3$O$_4$

$\xi \sim 900 \, \text{Å}$

Evidence for the ordering of electronic states associated with the Verwey transition.

Huang et al., PRL (2004)

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Low-dimensional quantum magnetism

Mermin-Wagner (1966): Pure 2D magnetic order only exists at $T=0$.

2D quantum Heisenberg antiferromagnet on a square lattice with $S = \frac{1}{2}$

Spin correlation
\[ \zeta(T) \propto e^{\frac{2\pi \rho S}{k_B T}} \]

Chakravarty et al., PRL 60, 1057 (1988)

\[ \frac{J_\perp}{J} \ll 1 \quad \text{ordered} \]

\[ T_{\text{disordered}} \]

\[ T_{\text{critical}} \]

\[ T = 0 \]

\[ \xi \sim \left| \frac{T}{T_c} - 1 \right|^v \]

Renormalized classical

Quantum critical

Quasi 2D

Non-thermal parameter $g$ ($P$, $B$, doping, …)

Sr$_2$CuO$_2$Cl$_2$

(1/2, 1/2, L/2)

Cu$^{2+}$, $S=1/2$, $T_N=256$ K

\[ \zeta(T) \propto e^{\frac{2\pi \rho S}{k_B T}} \]

Greven et al., PRL(1994)

\[ \frac{J_\perp}{J} \sim 10^{-4} \]
Half-doped single-layered manganite
doping Sr

LaSrMnO$_4$ $\rightarrow$ La$_{0.5}$Sr$_{1.5}$MnO$_4$

Mn$^{3+}$ (d$^4$)

$T_N \sim 110$ K

C.O.
(1/4, 1/4, 0)
$T_{CO} \sim 220$ K

Resonant soft x-ray scattering on La$_{0.5}$Sr$_{1.5}$MnO$_4$

Mn L-edge (2p$\rightarrow$3d)

$\phi = 0$

$(1/4, 1/4, 1/2)$
AFM ordering

$(1/4, 1/4, 0)$
orbital ordering
$I \propto \cos^2 \phi$
\[ \zeta \propto \left( \frac{T}{T_N} - 1 \right)^{-\nu}, \quad \nu = 0.75 \pm 0.04 \]

La\textsubscript{0.5}Sr\textsubscript{1.5}MnO\textsubscript{4}

113 K \(\{1/4, 1/4, 1/2\}\)

semi-classical

\[ \zeta(T) \propto e^{2\pi\eta S/k_BT} \]
Appendix: Basic of Magnetic Circular Dichroism in X-ray Absorption

Considering L-edge $2p_{3/2} \rightarrow 3d$ absorption, and ignoring the spin-orbit interaction in the 3d bands,

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

For left-handed circular light

$$\sigma_+ \propto R(r)^2 \left| \left\langle Y_{lm} \frac{\epsilon_x + i \epsilon_y}{\sqrt{2}} Y_{lm} \right| j, m_j \rangle \right|^2$$

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

For light-handed circular light

$$\sigma_- \propto R(r)^2 \left| \left\langle Y_{lm} \frac{\epsilon_x - i \epsilon_y}{\sqrt{2}} Y_{lm} \right| j, m_j \rangle \right|^2$$

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

Clebsch-Gordan coefficients

$$Y_{lm} = \sum_{m_{l_1} m_{l_2}} (l_1 m_{l_1} m_{l_2} | l, m) Y_{l_1 m_1} Y_{l_2 m_2}$$

$$Y_{l_1 m_1} Y_{l_2 m_2} = \sum_{m_{l_1} m_{l_2}} (l m_{l_1} m_{l_2} | l, m) Y_{lm}$$

$$Y_{l_1 m_1} Y_{l_2 m_2} = Y_{l_1, l_2} Y_{l_2, l_1} = \sqrt{\frac{4l_1 + 1}{l_1}} \delta_{l_1, l_2} \delta_{m_1, m_2}$$
\[
\sigma \propto \left| \langle l, m_l | \mathbf{e} \cdot \mathbf{E} | j, m_j \rangle \right|^2
\]
\[
\mathbf{e} \cdot \mathbf{E} = \sqrt{2} \left( e^{-i\theta} Y_{1,1} + e^{i\theta} Y_{1,-1} + \mathcal{C} \right)
\]
\[
\sigma_x \propto R(r)^2 \left| \langle Y_{l_m, j} | e_x \pm i e_y Y_{l_m, j} | j, m_j \rangle \right|^2
\]
\[
\sigma_y \propto \left| \langle Y_{l_m, j} | e_x - i e_y Y_{l_m, j} | j, m_j = \frac{3}{2}, m_j = \frac{-3}{2} \rangle \right|^2 = \frac{1}{3}
\]
\[
\vdots
\]
\[
\sigma_z \propto \left| \langle Y_{l_m, j} | e_x - i e_y Y_{l_m, j} | j, m_j = \frac{3}{2}, m_j = \frac{3}{2} \rangle \right|^2 = \frac{1}{3}
\]
\[
\vdots
\]
\[
\text{Clesbsch-Gordan coefficients}
\]
\[
Y_{l_m, j} = \sum_{m_l = -l}^{l} (l_m l_2 m_2 | l, m) W_{l_m, l_2, m_2} Y_{l_2, m_2}
\]
\[
Y_{l_m, j} Y_{l_m, j} = \sum_{m_l = -l}^{l} (l_m l_2 m_2 | l, m) Y_{l_m, l_2, m_2}
\]