Magnetic Scattering

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Introduction to Magnetic Scattering

• Magnetic Scattering with Neutrons
• Essential tool for the study of magnetic materials
• Elastic Scattering (diffraction) – magnetic structure, phase transitions
• Inelastic Scattering (spectroscopy) – magnetic dynamics, excitations, interactions

• Magnetic Scattering with X-rays
• How does it work?
• When is it a good idea?
Suggestions for Further Reading...

• Magnetic Scattering with Neutrons:
  Introduction to the Theory of Thermal Neutron Scattering, G. L. Squires (2012)
  Theory of Neutron Scattering from Condensed Matter (Vol. 2), S. W. Lovesey (1984)

• Magnetic Scattering with X-rays:
  X-ray Scattering and Absorption by Magnetic Materials, S. W. Lovesey & S. P. Collins (1996)

“Magnetic Scattering” by J. W. Lynn and B. Keimer in Handbook of Magnetism (arXiv:1910.01218)
Magnetic Scattering with Neutrons

- One of the “killer applications” of neutron scattering
- Essential tool for investigating magnetic materials
Magnetic Scattering with Neutrons

- Neutrons are spin $\frac{1}{2}$ particles
- They carry no charge, but do carry a magnetic dipole moment:
  \[
  \mu_n = -\gamma \mu_N \sigma
  \]

\( \gamma = 1.913 \)  
(Gyromagnetic ratio)

\( \mu_N = \frac{e\hbar}{2m_n} \)  
(Nuclear magneton)

- \( \mu_n \) can interact with the electrons in a material via magnetic potentials
- Scattering from these potentials can be comparable in strength to nuclear scattering
• **Magnetic moments** arise on atoms which have **unpaired electrons** in partially filled electronic orbitals

• Most common families of magnetic materials tend to be based on elements with partially filled d- or f-shells (e.g. **transition metals** or **rare earth/lanthanides**)

**Transition Metals:**

- Up to 10 d-levels to fill

**Lanthanides/Rare Earths and Actinides:**

- Up to 14 f-levels to fill
Magnetic Materials

- Size of magnetic moments is determined by Hund’s Rules:

\[
\begin{align*}
3z^2 - r^2 & \quad x^2 - y^2 \\
\end{align*}
\]

- e.g. Mn^{2+} (3d^5)

\[
S = \frac{5}{2}
\]
Magnetic Materials

• Size of magnetic moments is determined by Hund’s Rules:

\[ 3z^2 - r^2 \quad x^2 - y^2 \]

\( e_g \) orbitals

\( zr \quad yz \quad xy \)

\( t_{2g} \) orbitals

e.g. Cu\(^{2+}\) (3d\(^9\))

\[ S = 1/2 \]
Magnetic Interactions

- Direct exchange:

- Superexchange:

- RKKY exchange:

Describe interactions by a magnetic Hamiltonian:

\[ H = J \sum_{i,j} S_i \cdot S_j \]

(exchange parameter)
Magnetic Order

Paramagnet
\((T > T_C)\)

Ferromagnet
\((T < T_C)\)

Antiferromagnet
\((T < T_N)\)
Magnetic Structures

- Magnetically ordered structure that develops in a material depends on nature of underlying magnetic interactions

Structures can be relatively simple...

A) ferromagnetic  b) antiferromagnetic  c) ferrimagnetic  d) triangular  e) curled  f) umbrella  

h) sine or cosine  i) circular helix  j) elliptical helix
Geometric Frustration

• We can also try to design magnetic materials which don’t order at all:

• Geometrically frustrated magnets can display exotic quantum ground states at low temperatures, e.g. quantum spin liquids, spin ices, spin glasses...
Scattering from a Magnetically Ordered Crystal

- How can we detect magnetic order in a neutron scattering experiment?

**Paramagnetic State (T > T_N)**

**Antiferromagnetic State (T < T_N)**

- Development of AF order increases size of unit cell → **new magnetic Bragg peaks appear**
First Observation: Magnetic Neutron Scattering from MnO

- Early neutron diffraction experiments at the ORNL X-10 Graphite Reactor:

First direct evidence of antiferromagnetism

*Shull, Strauser, and Wollan, Phys. Rev. 83, 333 (1951)*
First Observation: Magnetic Neutron Scattering from MnO

- Early neutron diffraction experiments at the ORNL X-10 Graphite Reactor:

  Peak intensity $\propto$ staggered magnetization

\[ T_c \text{ (SPECIFIC HEAT)} \]
\[ T_c \text{ (MAGNETIC)} \]

\[ \text{MnO} \]

**Fig. 7.** Temperature dependence of magnetic intensity for MnO. The Curie temperatures suggested by specific heat and magnetic susceptibility data are shown.

**Fig. 5.** Antiferromagnetic structure existing in MnO below its Curie temperature of 110 K. The magnetic unit cell has twice the linear dimensions of the chemical unit cell. Only Mn ions are shown in the diagram.

**Fig. 4.** Neutron diffraction patterns for MnO taken at liquid nitrogen and room temperatures. The patterns have been corrected for the various forms of extraneous, diffuse scattering mentioned in the text. Four extra antiferromagnetic reflections are to be noticed in the low temperature pattern.

First direct evidence of antiferromagnetism

*Shull, Strauser, and Wollan, Phys. Rev. 83, 333 (1951)*
Magnetic Scattering Cross Section

- What fraction of neutrons will scatter off a sample with a particular change in energy and momentum?

- Change in momentum: \( \vec{Q} = \vec{k} - \vec{k}' \)

- Change in energy: \( \Delta E = \hbar \omega = \frac{\hbar^2 k^2}{2m} - \frac{\hbar^2 k'^2}{2m} \)

- Apply Fermi’s Golden Rule (1\(^{st}\) order perturbation theory):

\[
\frac{d^2 \sigma}{d\Omega \, dE'} \big|_{k,\sigma,\lambda \rightarrow k',\sigma',\lambda'} = \left( \frac{m}{2\pi \hbar^2} \right)^2 \left( \frac{k'}{k} \right) |\langle k' \, \sigma' \, \lambda' | V_m | k \, \sigma \, \lambda \rangle|^2 \delta(E_\lambda - E_{\lambda'} + \hbar \omega)
\]

(Kinematics) (Interaction Term) (Energy Conservation)
The Magnetic Potential

In order to evaluate the matrix element in the interaction term, we need to determine the magnetic potential produced by all of the unpaired electrons in the material:

\[ V_m = \vec{\mu}_n \cdot \vec{B} \]

(Magnetic Potential)

(Magnetic Dipole Moment of Neutron)

(Magnetic Field Produced by Unpaired Electrons)

Must consider:

- \( B_l = \) Magnetic field from \textit{orbital motion} of an electron
- \( B_s = \) Magnetic field from \textit{spin} of an electron
Magnetic Scattering Cross Section

• Evaluating the interaction term $|\langle k' \sigma' \lambda' | V_m | k \sigma \lambda \rangle|^2$ can be quite complicated.

• Jumping to the final result:

$$\frac{d^2 \sigma}{d\Omega \, dE'} = \frac{(\gamma r_0)^2}{2 \pi \hbar} \frac{k'}{k} N \left[ \frac{1}{2} gF(Q) \right]^2 \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta)$$

$$\times \sum_l e^{i \tilde{Q} \cdot \tilde{l}} \int \left\langle e^{-i \tilde{Q} \cdot \tilde{u}_0(t)} e^{i \tilde{Q} \cdot \tilde{u}_l(t)} \right\rangle \left\langle S^\alpha_0(0) \ S^\beta_l(t) \right\rangle e^{-i \omega t \, dt}$$

Key features:

1. From constants – magnetic scattering comparable in strength to nuclear scattering ($\sim r_0^2$)
2. Proportional to square of magnetic form factor, $F(\vec{Q})^2$
Magnetic Scattering Cross Section

• Evaluating the interaction term $|\langle k' \sigma' \lambda' | V_m | k \sigma \lambda \rangle|^2$ can be quite complicated.

• Jumping to the final result:

$$
\frac{d^2 \sigma}{d\Omega \, dE'} = \frac{(γr_0)^2}{2\pi \hbar} \left( \frac{k'}{k} \right) N \left[ \frac{1}{2} gF(\vec{Q}) \right]^2 \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta) \\
\times \sum_l e^{i\vec{Q} \cdot \vec{l}} \int \left< e^{-i\vec{Q} \cdot \vec{u}_0(t)} e^{i\vec{Q} \cdot \vec{u}_l(t)} \right> \left< S_0^\alpha(0) S_l^\beta(t) \right> e^{-i\omega t} dt
$$

Key features:

3. **Polarization factor** – describes dependence on spin direction. Term vanishes if components of spin are parallel to scattering vector $\vec{Q} \rightarrow$ only sensitive to $S \perp \vec{Q}$
Magnetic Scattering Cross Section

• Evaluating the interaction term $|\langle k' \sigma' \lambda' | V_m | k \sigma \lambda \rangle|^2$ can be quite complicated.

• Jumping to the final result:

$$\frac{d^2 \sigma}{d\Omega \, dE'} = \frac{(\gamma r_0)^2}{2\pi \hbar} \frac{k'}{k} \frac{N}{k} \left[ \frac{1}{2} g F(\hat{Q}) \right]^2 \sum_{\alpha \beta} \left( \delta_{\alpha \beta} - \hat{Q}_\alpha \hat{Q}_\beta \right)$$

$$\times \sum_l e^{i \hat{Q} \cdot \hat{l}} \int e^{-i \hat{Q} \cdot \hat{u}_0(0)} e^{-i \hat{Q} \cdot \hat{u}_l(t)} \left\{ S_0^\alpha(0) S_l^\beta(t) \right\} e^{-i \omega t \, dt}$$

Key features:

4. **Dynamic spin pair correlation function** – measures correlation between spin $\alpha$ at origin and $t = 0$ and spin $\beta$ at position $l$ and time $t$. The Fourier transform of this term is the **dynamic structure factor**, $S(\hat{Q}, \omega)$
Magnetic Form Factor

• $F(\mathbf{\hat{Q}}) = \text{Fourier transform of the spin distribution in real space}$

\[
F(\mathbf{\hat{Q}}) = \int S(\mathbf{r}) e^{i\mathbf{\hat{Q}} \cdot \mathbf{r}} d^3r
\]

• Analogous to chemical form factor for x-ray scattering
• Typically drops off monotonically as $\mathbf{\hat{Q}}$ increases

Shull, Strauser, and Wollan, Phys. Rev. 83, 333 (1951)

$F(\mathbf{\hat{Q}})$ decreases faster as wavefunctions become more spatially extended.
Elastic Magnetic Scattering

- For elastic scattering (i.e. diffraction), we have: \( \Delta E = \hbar \omega = \frac{\hbar^2 k^2}{2m} - \frac{\hbar^2 k'^2}{2m} = 0 \)

- What we measure is the **time-independent** structure factor, \( S(\vec{Q}) \)

\[
\frac{d\sigma}{d\Omega} = (\gamma r_0)^2 \frac{k'}{k} N \left[ \frac{1}{2} gF(\vec{Q}) \right]^2 e^{-2W} \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta) \times \sum_l e^{i\vec{Q} \cdot \vec{l}} \int \langle S_0^\alpha \rangle \langle S_l^\beta \rangle
\]

Debye-Waller Effect

Polarization Factor:
Only sensitive to \( S \perp \vec{Q} \)

Add up spins with a phase factor of \( e^{i\vec{Q} \cdot \vec{l}} \)
Elastic Magnetic Scattering: Examples

- **Mn$_5$(VO$_4$)$_2$(OH)$_4$ Single Crystal**
- Measured on CORELLI at SNS
- **Rods** of diffuse scattering above $T_N$ – indicative of shorter-range quasi-2D magnetic correlations
- Well-defined **Bragg peaks** below $T_N$ – indicative of 3D long-range magnetic order
- In general:

  \[ I \propto M^2 = M_0^2 \left( 1 - \frac{T}{T_C} \right)^{2\beta} \]

\[ \xi \propto \frac{1}{Q} \] = correlation length

Garlea et al, AIP Advances 8, 101407 (2018)
Inelastic Magnetic Scattering

- For inelastic scattering (i.e. spectroscopy), we have: \( \Delta E = \hbar \omega = \frac{\hbar^2 k^2}{2m} - \frac{\hbar^2 k'^2}{2m} \neq 0 \)
- This implies that \( |\vec{k}| \neq |\vec{k}'| \rightarrow \text{change in both } \vec{Q} \text{ and } \omega \)
- What we measure is the **dynamical structure factor** \( S(\vec{Q}, \omega) \)

**Key points:**

- Study *dynamic* magnetic moments (on time scales of \(10^{-9}\) to \(10^{-12}\) sec)

\[
S(\vec{Q}, \omega) = \frac{1}{1-e^{-\beta \hbar \omega}} \frac{\chi''(\vec{Q},\omega)}{\pi (g\mu_B)^2} = \left[n(\omega)\chi''(\vec{Q},\omega)\right] \text{ (Fluctuation-Dissipation Theorem)}
\]

- Intensity integrated over all \( \vec{Q}, \omega \) is constant: \( \int d\omega \int_{BZ} d\vec{Q} \ S(\vec{Q}, \omega) \sim S(S + 1) \) (Total Moment Sum Rule)
Inelastic Magnetic Scattering: Spin Waves

• When a neutron scatters off a sample it can create or destroy an excitation

• If sample is magnetically ordered (e.g. a FM spin chain), the incident neutron can create a spin “defect” which is distributed over all possible sites

• We call this collective excitation a spin wave or magnon

\[
\mathbf{k}, \omega \rightarrow \mathbf{k}', \omega'
\]

Spins are coupled through magnetic Hamiltonian: 

\[
H = J \sum_{i,j} S_i \cdot S_j
\]
Inelastic Magnetic Scattering: Spin Waves

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Spins are coupled through magnetic Hamiltonian: \( H = J \sum_{i,j} S_i \cdot S_j \)
Inelastic Magnetic Scattering: Examples

- Yb$_2$Ti$_2$O$_7$ (top) and Er$_2$Ti$_2$O$_7$ (bottom) Single Crystals
- Measured on DCS at NIST
- Fit spin wave dispersion to theoretical model and extract detailed exchange parameters ($J_1$, $J_2$, $J_3$, $J_4$)
- Magnetic interactions explain low temperature magnetic ground states

Ross et al, Phys. Rev. X 1, 021002 (2011)
Savary et al, Phys. Rev. Lett. 109, 167201 (2012)
How can we distinguish magnetic scattering?

(1) Temperature dependence:
- Magnetic scattering decreases with increasing $T$ (disappears at $T > T_C$)
- Phonon scattering increases with increasing $T$ ($\propto$ thermal population)

(2) Momentum dependence:
- Magnetic scattering decreases with increasing $|Q|$ ($\propto |F(Q)|^2$)
- Phonon scattering increases with increasing $|Q|$ ($\propto |e \cdot Q|^2$)

(3) Polarization dependence (with polarized beam):
- Magnetic scattering mostly spin flip
- Nuclear scattering mostly non-spin flip

(More on this from Chuck Majkrzak later this morning)
Magnetic Scattering with X-rays

- X-rays carry no magnetic moment
- Primary interaction with matter: **E-field** of x-ray + **charge** of electrons
- Also interacts through: **B-field** of x-ray + **spin** of electrons
- Unlike neutrons:
  1. Magnetic scattering is MUCH weaker than charge scattering

\[
\frac{A(\text{magnetic})}{A(\text{charge})} = \frac{\hbar \omega}{mc^2} \quad \text{(for single electron)}
\]

Amplitude ratio:

- At $E_i \sim 5$ keV:
  - Amplitude ratio $\sim 10^{-2}$
  - Intensity ratio $\sim 10^{-4}$

2. X-ray photon energies ($\sim 0.5$ to 50 keV) are orders of magnitude larger than typical energy scales for magnetic excitations ($\sim 0.5$ to 500 meV)
First Observation: Magnetic X-ray Scattering from NiO

NiO: Antiferromagnet ($T_N \sim 250 \, ^\circ C$)

- NON-RESONANT magnetic x-ray scattering
- Lab-based experiment carried out using x-ray tube source (Cu Kα, $\lambda = 1.54 \, \text{Å}$)
- Hard!
- Counting time: 3 days/scan ($\sim 2 \, \text{cts/min signal on } \sim 18 \, \text{cts/min bkgd}$)

- Compare to magnetic neutron scattering:

*De Bergevin and Brunel, Phys. Lett. 39A, 141 (1972)*

*Shull et al, Phys. Rev. 83, 333 (1951)*
To the Synchrotron: Magnetic X-ray Scattering from Ho

Ho: Incommensurate spiral antiferromagnet ($T_N \sim 131$ K)

- NON-RESONANT magnetic x-ray scattering
- Synchrotron-based experiment (SSRL)
- Higher flux and higher momentum resolution

- Compare to magnetic neutron scattering:
  - X-ray: 25 cts/s on 10 cts/s, $\text{FWHM} = 0.001$ Å$^{-1}$
  - Neutron: 50 cts/s on 0.1 cts/s, $\text{FWHM} = 0.005$ Å$^{-1}$

![Graph showing temperature dependence of Ho(004) magnetic satellite](image)

**FIG. 1.** Temperature dependence of the Ho(004) magnetic satellite taken with synchrotron radiation (lines drawn to guide the eye). Inset: Right, schematic representation of the magnetic structure of Ho (after Koehler9). Left, projections of the magnetic unit cell for different spin-slip structures. For simplicity the doublet has been drawn as two parallel spins.

*D. Gibbs et al, Phys. Rev. Lett. 55, 234 (1985)*
On Resonance: Magnetic X-ray Scattering from Ho

- **RESONANT MAGNETIC X-RAY SCATTERING**
- First predicted by M. Blume (1985)
- Synchrotron-based experiment (NSLS, CHESS)
- Tune incident energy to Ho L\(_3\)-edge (\(E_i = 8.067\) keV, \(\lambda = 1.54\) Å)
- Take advantage of polarized beam and resonant enhancement at absorption edge
- Magnetic peak intensity enhanced by ~50x!

Gibbs et al, Phys. Rev. Lett. 61, 1241 (1988)

More on resonant scattering from Mark Dean in Week 2
Resonant Magnetic X-ray Scattering

\[ F_j(E) = \sigma^{(0)}(E)\varepsilon_i \cdot \varepsilon_0^* + \sigma^{(1)}(E) \varepsilon_i \times \varepsilon_0^* \cdot M_j + \sigma^{(2)}(E) \left[ (\varepsilon_i \cdot M_j)(\varepsilon_0^* \cdot M_j) - \frac{1}{3} \varepsilon_i \cdot \varepsilon_0^* \right] \]

- Scattering tensor for magnetic x-ray scattering:
- Intensity of magnetic Bragg peaks:

Hard x-rays (> 5 keV)
Tender x-rays (1-5 keV)
Soft x-rays (< 1 keV)
Resonant Magnetic X-ray Scattering: Examples

$\alpha$-Li$_2$IrO$_3$ single crystal (Kitaev model candidate)

Sr$_2$IrO$_4$ single crystal (spin-orbital Mott insulator)

Ba$_2$IrO$_4$ thin film (13 nm thickness = 10 ng)

Williams et al, Phys. Rev. B (2016)

Kim et al, Nat. Comm. (2014)

Clancy et al, arXiv: 2203.13102
Magnetic X-ray Scattering

Advantages:

• Element (and even orbital) specificity
• Smaller samples (ideal for thin films, high pressure diamond anvil cell experiments)
• Better resolution in momentum

Disadvantages:

• More complicated theory/modeling
• Magnetic scattering much weaker than charge scattering
• Worse resolution in energy
• Restricted momentum transfer (soft x-ray)

X-ray and neutron scattering are highly complimentary techniques for the study of magnetic materials
Neutron Scattering at McMaster

Home to McMaster Nuclear Reactor – Canada’s most powerful research reactor

- 5 MW open-pool reactor used for **neutron scattering**, medical isotopes, neutron radiography, neutron activation/irradiation studies, positron beams…
- Currently 2 neutron scattering beamlines: **MAD** (triple-axis) and **MacSANS** (more coming soon)
Lecture Feedback

https://forms.office.com/g/5YB3gjtjKs

Any Questions?

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