Diffraction from magnetic materials

Navid Qureshi
Motivation

Impact of magnetic neutron scattering

H. Rietveld presents a least-squares program able to refine crystal and magnetic structures

J. Rodríguez Carvajal presents the FullProf package

correlated with

- availability of computing tools
- relevant topics in new materials
Motivation

Impact of magnetic neutron scattering

correlated with

› availability of computing tools
› relevant topics in new materials
Motivation

Impact of magnetic neutron scattering

correlated with

- availability of computing tools
- relevant topics in new materials

Methods and computing programs
Motivation

Impact of magnetic neutron scattering

correlated with

- availability of computing tools
- relevant topics in new materials

Multiferroics
Motivation

Impact of magnetic neutron scattering

correlated with

- availability of computing tools
- relevant topics in new materials

Superconductors
Motivation

Impact of magnetic neutron scattering

correlated with

› availability of computing tools

› relevant topics in new materials

Nanoparticles
Motivation

Impact of magnetic neutron scattering

correlated with

- availability of computing tools
- relevant topics in new materials

Order phenomena in manganites
Outline

- **Reminder: Nuclear scattering**
  - scattering amplitude, Fourier transform

- **Magnetic scattering**
  - scattering potential, directional dependence

- **Magnetic structures**
  - Ferro, antiferro, cycloids, helices, ...

- **Scattering from a unit cell**
  - Magnetic structure factor, interaction vector

- **Experimental procedure**
Conventions for this lecture

Wave vector and scattering vector

\[ k_i : \text{initial wavevector} \]
\[ k_f : \text{final wavevector} \]
\[ k : \text{momentum transfer, scattering vector} \]
\[ G : \text{reciprocal lattice vector} \]

Elastic scattering: \( |k_i| = |k_f| = k \)
Nuclear scattering

**Scattering cross section**

Number of neutrons $n$ detected in solid angle $\Omega$

$$\frac{dn}{ns^{-1}} = \Phi_{ncm^{-2} s^{-1}} \cdot d\Omega \cdot \sigma(\theta, \varphi)$$

$\sigma$ has the unit of a surface

usually in barns $= 10^{-24}$ cm$^2$
Nuclear scattering

Scattering cross section

The wave function at a spatial position \( r \) = sum of transmitted and scattered spherical wave function.

\[
v_{scat}^k(r) = e^{ikr} + f_k(\theta, \varphi) \frac{e^{ikr}}{r}
\]

Only \( f_k(\theta, \varphi) \) depends on the scattering potential \( V(r) \).
Nuclear scattering

Scattering cross section

- mediated by strong force, short ranged ($\text{fm} = 10^{-15}$ m)

- neutron wavelength much larger ($10^{-10}$ m)
  - cannot probe internal structure
  - scattering is isotropic

- the interaction between the neutron and the atomic nucleus is represented by the Fermi pseudo-potential, a scalar field that is 0 except very close to the nucleus

$$V(r) = \frac{2\pi \hbar^2}{m_n} b \delta^3(r)$$

advantage: neutron senses atomic position and not the electron cloud (bonds)
Nuclear scattering

Scattering cross section

The scattering amplitude is related to the **Fourier transform of the potential function.**

\[ f_k(\theta, \varphi) = -\frac{1}{4\pi} \frac{2\mu}{\hbar^2} \int V(r) e^{-ikr} d^3r \]

With the Fermi pseudo potential for neutron scattering from a nucleus

\[ V(r) = \frac{2\pi \hbar^2}{m_n} b \delta^3(r) \]

\[ |f_k(\theta, \varphi)| = b \]

Neutron scattering from a nucleus is isotropic!

\[ b \text{ is in the order of } 10^{-12} \text{ cm} \]
Nuclear scattering

Comparison to X-rays

The amplitude of the scattered wave (the Fourier transform of the potential function) is called the atomic **form factor** $f$ (X-rays) or **scattering length** $b$ (neutrons).

- **Nucleus $\sim 10^{-15}$ m**
- **Electron shell $\sim 10^{-10}$ m**

**advantage with neutrons:** scattered intensity does not drop with increasing scattering angle
Nuclear scattering

Comparison to X-rays

Scattering lengths (analog to X-ray form factor)

superposition of resonance scattering with slowly increasing potential scattering due to atomic weight

advantages: contrast between neighbouring elements
light elements can be measured easily
isotope effect (\(b_H=-3.7, b_D=6.8\))
Nuclear scattering

Comparison to X-rays

Scattering lengths (analog to X-ray form factor)

Example KCl:

scattering lengths of K and Cl are very different ➔ strong contrast

X-rays would see a primitive cell with half the lattice constant

superposition of resonance scattering with slowly increasing potential scattering due to atomic weight

advantages:
contrast between neighbouring elements
light elements can be measured easily
isotope effect ($b_H=-3.7$, $b_D=6.8$)
Magnetic scattering

Electron magnetic moment

Magnetic dipole moment in classical electrodynamics

\[ \mu = I \cdot A \]

\[ = \frac{-e \cdot v_e}{2\pi r} \cdot \pi r^2 = \frac{-e \cdot v_e}{2} \cdot r = \frac{-e}{2m} \cdot mv_e r = -\frac{e}{2m} L \]

Gyromagnetic ratio \( \gamma \): ratio between magnetic dipole moment and total angular momentum

\[ \gamma = -\frac{e}{2m} = -\frac{\mu_B}{\hbar} \quad \text{with} \quad \mu_B = \frac{e\hbar}{2m_e} \]

This works well for the electron’s orbital momentum, but its intrinsic spin momentum cannot be explained in the classical approach \( \rightarrow \) correction by g-factor

\[ \gamma = -g_e \frac{\mu_B}{\hbar} \quad (g_L = 1, g_S = 2) \]
Magnetic scattering

**Electron magnetic moment**

Angular momenta are quantised in units of $\hbar$ $(L = \ldots, -2\hbar, -\hbar, 0, \hbar, 2\hbar, \ldots)$

$$\gamma = -g_e \frac{\mu_B}{\hbar} \quad (g_L = 1, g_S = 2)$$

The magnetic moment of an electron is quantised in $\mu_B$

$$\mu_L = \gamma L = -\frac{e}{2m_e} L = -\mu_B \frac{L}{\hbar} \quad \text{orbital moment (1}\mu_B\text{ per }\hbar\text{)}$$

Spin momenta are quantised in units of $1/2\hbar$

$$\mu_S = \gamma S = -\frac{e}{m_e} S = -2\mu_B \frac{S}{\hbar} \quad \text{spin moment (1}\mu_B\text{ per electron spin)}$$

Total moment due to LS coupling $\mathbf{J} = \mathbf{L} + \mathbf{S}$:

$$\mu_J = -g_J \mu_B \frac{\mathbf{J}}{\hbar}$$
Magnetic scattering

Neutron magnetic moment

Protons, neutrons and many nuclei carry a nuclear spin.

Gyromagnetic ratios of common spin-1/2 particles:

- Electron: $1.76 \cdot 10^5$ MHz/T
- Proton: $267$ MHz/T
- Neutron: $183$ MHz/T

Neutron moment is around 960 times smaller than the electron moment.

Nuclear magnetons:

- Proton: $\mu_p = 2.793 \mu_N$
- Neutron: $\mu_n = -1.913 \mu_N$

For neutrons: $\mu_n = \gamma \mu_N \sigma$ with $\gamma_n = -1.913$
Magnetic scattering

Magnetic scattering potential

Magnetic scattering: interaction of the neutron spin with the magnetic field of an unpaired electron

neutron spin operator: \( \hat{\mu} = \gamma \mu_N \hat{\sigma} \)

The interaction is described by the potential:

\[-\hat{\mu} \cdot H = -\gamma \mu_N \hat{\sigma} \cdot H\]

Magnetic scattering length proportional to electron radius \( e^2/m_e c^2 \):

\[ \gamma r_0 = \frac{\gamma e^2}{m_e c^2} = -0.54 \cdot 10^{-12} \text{ cm} \]

\[ \gamma = -1.91 \]

\[ \mu_N = \frac{m_e \mu_B}{m_n} \]

\[ \text{nuclear magneton} \]

Pauli spin operator \( \hat{\sigma} \)

\[ \hat{\sigma} \]

\[ \text{comparable to nuclear scattering} \]
Magnetic scattering

**Magnetic scattering potential**

Magnetic field due to a single electron moving with velocity $v_e$:

$$\mathbf{H} = \text{curl} \left( \frac{\mu_e \times \mathbf{R}}{|\mathbf{R}|^3} \right) + \frac{-e}{c} \frac{\mathbf{v}_e \times \mathbf{R}}{|\mathbf{R}|^3}$$

(from S. W. Lovesey, Theory of Neutron Scattering from Condensed Matter, Volume 2)

The scattering cross section between the neutron and the electron becomes (after 2 pages):

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} = r_0^2 \frac{k_f}{k_i} \sum_{\alpha \beta} \left( \delta_{\alpha \beta} - \tilde{k}_\alpha \tilde{k}_\beta \right) \sum_{\lambda \lambda'} p_{\lambda} \langle \lambda | \tilde{k}_\alpha^2 | \lambda' \rangle \langle \lambda | \tilde{k}_\beta^2 | \lambda' \rangle \delta(h\omega + E_\lambda - E_{\lambda'})$$

In comparison to nuclear scattering the magnetic cross section has a directional dependence!
Magnetic scattering

Magnetic scattering potential

Like for nuclear scattering the Born approximation holds and the scattered amplitude is the Fourier transformation of the potential function (atomic magnetisation density), the magnetic form factor.

\[ f(k) = \int \rho(r) \exp(ikr) \, dr \]

which is defined by:

\[ f(k) = \frac{g_s}{g} j_0(k) + \frac{g_L}{g} [j_0(k) + j_2(k)] \]

\( g, g_L, g_s \): g-factors
\( j_n \): spherical Bessel functions
Magnetic scattering

Magnetic scattering potential

Like for nuclear scattering the Born approximation holds and the scattered amplitude is the Fourier transformation of the potential function (atomic magnetisation density), the magnetic form factor.

\[ f(k) = \int \rho(r) \exp(ikr) \, dr \]

which is defined by:

\[ f(k) = \frac{g_S}{g} j_0(k) + \frac{g_L}{g} [j_0(k) + j_2(k)] \]

\( g, g_L, g_S \): g-factors
\( j_n \): spherical Bessel functions

analytical approximation:

\[ j_0(s) = A \exp(-as^2) + B \exp(-bs^2) + C \exp(-cs^2) + D \]

\[ j_2(s) = [A \exp(-as^2) + B \exp(-bs^2) + C \exp(-cs^2) + D] \cdot s^2 \]

coefficients \( a, A, b, B, c, C, D \) tabulated on http://www.ill.eu/sites/ccsl/html/ccsldoc.html

\( s = \frac{\sin \theta}{\lambda} \)
Magnetic structures

Ordered magnetic state

In some crystals, some of the atoms/ions have unpaired electrons (transition metals, rare-earths).

Hund’s rule favors a state with maximum $S$ and $L$. The ions possess a localised magnetic moment.

Exchange interactions (direct, superexchange, double exchange, RKKY, dipolar, ...) often stabilize a long-range magnetic order.

\[
\langle S_i \rangle = 0
\]

\[
E_{ij} = -J_{ij} S_i \cdot S_j
\]

\[
\langle S_i \rangle \neq 0
\]
Magnetic structures

**Propagation vector**

The magnetic structure does not necessarily have the same periodicity and symmetry as the underlying crystal structure. The relation between one and another is expressed by the propagation or wave vector.
Magnetic structures

Propagation vector

The magnetic structure does not necessarily have the same periodicity and symmetry as the underlying crystal structure. The relation between one and another is expressed by the propagation or wave vector.

ferromagnetic
Magnetic structures

Propagation vector

The magnetic structure does not necessarily have the same periodicity and symmetry as the underlying crystal structure. The relation between one and another is expressed by the propagation or wave vector.

\[ \alpha \]

\[ 2\alpha \]
Magnetic structures

Propagation vector

The magnetic structure does not necessarily have the same periodicity and symmetry as the underlying crystal structure. The relation between one and another is expressed by the propagation or wave vector.

commensurate antiferromagnetic

\[ q = \left( \frac{1}{2}, 0, 0 \right) \]

magnetic periodicity = 2 x nuclear periodicity → \( q = (1/2 \ 0 \ 0) \)
Magnetic structures

Propagation vector

The magnetic structure does not necessarily have the same periodicity and symmetry as the underlying crystal structure. The relation between one and another is expressed by the propagation or wave vector.

\[ q = \left( \frac{1}{x} \ 0 \ 0 \right) \]

commensurate antiferromagnetic

The magnetic periodicity = x times nuclear periodicity \[ \rightarrow q = (1/x \ 0 \ 0) \]
Magnetic structures

Propagation vector

Magnetic Bragg reflections can be found at \( k = G \pm q \)

**superposition for** \( q = 0 \)

ferromagnetic

**Magnetic satellites for** \( q \neq 0 \)

commensurate AF \( q = (1/2 \ 0 \ 0) \)
incommensurate AF \( q = (1/2 - \delta \ 0 \ 0) \)
Magnetic structures

Fourier expansion of magnetic moments

One usually describes magnetic structures with Fourier components of the magnetic moments:

\[ \mu(r) = \frac{1}{n_q} \sum_q S_q \cdot e^{-iqr} \]

which for a single propagation vector becomes:

\[ \mu(r) = \frac{1}{2} (S_q \cdot e^{-iqr} + S_{-q} \cdot e^{iqr}) \]

\( S_q \) is a complex vector made of linear combinations of basis vectors according to one or more irreducible representations.

Since \( \mu(r) \) is a real vector, one must impose the condition \( S^*_{-q} = S_q \)
Magnetic structures

**Types of magnetic structures**

\[ \mu(r) = S_q \cdot e^{-i qr} = S_q \]

\[ \mu(r) = \frac{1}{2} (S_q \cdot e^{-i qr} + S_{-q} \cdot e^{i qr}) = S_q \cdot (-1)^{2r_x} \]

**q=0 ferromagnetic**

**q=(100) antiferromagnetic (centered cells)**

*real Fourier components*
Magnetic structures

Types of magnetic structures

antiferromagnetic, \( \mathbf{q} = 1/2 \mathbf{G} \) (at the border of the 1st Brillouin zone)

\[
\mu(r) = \frac{1}{2} (S_q \cdot e^{-i\mathbf{qr}} + S_{-q} \cdot e^{i\mathbf{qr}}) = S_q \cdot (-1)^{r_x}
\]

real Fourier components
Magnetic structures

Types of magnetic structures

amplitude-modulated antiferromagnetic, \( q < 1/2G \) (at the interior of the 1st Brillouin zone)

\[
S_q = \mu \hat{u} e^{-iqr} \quad \mu(r) = \mu \hat{u} \cos[2\pi(qr + \phi_q)]
\]

imaginary Fourier components (real and imaginary parts parallel)
Magnetic structures

Types of magnetic structures

antiferromagnetic spirals, $q < 1/2G$ (at the interior of the 1st Brillouin zone)

$$S_q = (\mu_u \hat{u} + i \mu_v \hat{v}) e^{-iqr}$$

$$\mu(r) = \mu_u \hat{u} \cos[2\pi(qr + \phi_q)] + \mu_v \hat{v} \sin[2\pi(qr + \phi_q)]$$

imaginary Fourier components (real and imaginary parts perpendicular)
Magnetic structures

Types of magnetic structures

multi-\( \mathbf{q} \) structures, e.g. conical (ferromagnetic \( \mathbf{q}=0 \) component + helix)

treatment of every component separately
Scattering from a unit cell

**Reminder: Nuclear structure factor**

Imagine two scattering potentials (atoms), the first at 0, the second at $\mathbf{r}$

The path difference is:

$$\Delta s(\mathbf{r}) = \mathbf{r} \cdot \frac{\mathbf{k}_f}{k_f} - \mathbf{r} \cdot \frac{\mathbf{k}_i}{k_i}$$

Therefore, the phase difference is:

$$\varphi(\mathbf{r}) = 2\pi \frac{\Delta s}{\lambda} = k \cdot \Delta s = (\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{r} = \mathbf{G} \cdot \mathbf{r}$$

Sum up phase differences over atoms in unit cell:

$$F(hkl) = \sum_j b_j \exp(i\mathbf{G}\mathbf{r}_j) = \sum_j b_j \exp[2\pi i(hx_j + ky_j + lz_j)]$$

Structure factor $F(hkl)$ is the Fourier transform of the unit cell scattering potential.
Scattering from a unit cell

**Magnetic structure factor**

The magnetic structure factor is obtained in the same way, but it is also proportional to the magnetic moment of the involved atoms. Directional dependence, $\mathbf{F}_M$ is a vector

\[
\mathbf{F}_M(hkl) = \sum_j \mu_j f_j(\mathbf{k}) \exp(i\mathbf{k}\cdot\mathbf{r}_j) = \sum_j \mu_j f_j(\mathbf{k}) \exp[2\pi i (hx_j + ky_j + lz_j)]
\]

Only the component of $\mathbf{F}_M$ which is perpendicular to $\mathbf{k}$ contributes to magnetic scattering:

\[
\mathbf{Q}_M = \hat{\mathbf{k}} \times (\mathbf{F}_M \times \hat{\mathbf{k}})
\]
Scattering from a unit cell

**Example: Ferromagnetic structure**

\[ F_M(hkl) = \sum_j \mu_j f_j(k) \exp(i k r_j) = \sum_j \mu_j f_j(k) \exp[2\pi i(h x_j + k y_j + l z_j)] \]

\[
\begin{align*}
F_M(100) &= \begin{pmatrix} 0 \\ \mu \\ 0 \end{pmatrix} f(k) \\
Q_M(100) &= F_M(100) \\
F_M(010) &= \begin{pmatrix} 0 \\ \mu \\ 0 \end{pmatrix} f(k) \\
Q_M(010) &= 0 \\
F_M(001) &= \begin{pmatrix} 0 \\ \mu \\ 0 \end{pmatrix} f(k) \\
Q_M(001) &= F_M(001) \\
F_M(110) &= \begin{pmatrix} 0 \\ \mu \\ 0 \end{pmatrix} f(k) \\
Q_M(110) &= F_M(110) \sin \alpha
\end{align*}
\]
Experimental procedure

Basic diffractometer (constant wavelength)
Experimental procedure

Basic diffractometer (constant wavelength)

collimator defines the beam shape and divergence
Soller collimators, slits
Experimental procedure

Basic diffractometer (constant wavelength)

- Monochromator

- (Assembly of) high quality single crystals
- Choice of wavelength and resolution
- Typically Cu, Ge, HOPG, Si
- Diffracts also higher harmonics $\lambda/2, \lambda/3, \ldots$

\[ n\lambda = 2d \sin \theta \]
Experimental procedure

Basic diffractometer (constant wavelength)

- Filter diffracts shorter $\lambda$ out of the beam
  
  $\lambda/2d_{\text{Filter}} > 1$

- Typically PG, Be, no $\lambda/2$ filter needed for Si, Ge
  
  (111) is used, because (222) is forbidden
Experimental procedure

Basic diffractometer (constant wavelength)

sample environment
cryostat, cryomagnet, furnace, pressure cell, CryoPAD
Experimental procedure

Basic diffractometer (constant wavelength)

sample environment
cryostat, cryomagnet, furnace, pressure cell, CryoPAD
Experimental procedure

Basic diffractometer (constant wavelength)

collimator
e.g. radial oscillating collimator reduces background from sample environment or another Soller collimator to increase resolution
Experimental procedure

Basic diffractometer (constant wavelength)

detector
gas cells in which an incoming neutron triggers a nuclear reaction producing a charged particle which then is detected typically $^3$He or B$_3$F
Experimental procedure

Time-of-flight diffractometer (polychromatic)

Chopper defines the wavelength band and avoids frame overlap.
Experimental procedure

Time-of-flight diffractometer (polychromatic)

time of flight of the neutrons is related to their wavelength

\[ t = \frac{m_n}{h} \lambda L \]

diffraction pattern is recorded at constant scattering angle (close to 180° for best resolution, small Δt/t)

\[ \frac{\Delta \lambda}{\lambda} = \Delta \theta_M \cot \theta_M \]
Experimental procedure

Powder diffraction

D20 (high flux)

Sample in a vanadium container. V scatters only incoherently.
Experimental procedure

**Powder diffraction**
Experimental procedure

Powder diffraction

Result: Diffraction pattern

Useful information lies in the

- position
- the intensity
- the shape and width

of the reflections.
Experimental procedure

Powder diffraction

1. Position

Bragg’s law \( n\lambda = 2d\sin \theta \)

\[
d = \left( \frac{h^2}{a^2\sin^2 \beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2\sin^2 \beta} - \frac{2hl \cos \beta}{ac\sin^2 \beta} \right)^{-\frac{1}{2}}
\]

monoclinic

\[
d = \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-\frac{1}{2}}
\]

orthorhombic

\[
d = a\left( h^2 + k^2 + l^2 \right)^{-\frac{1}{2}}
\]

cubic

with \( \theta \) and \( \lambda \) known \( \rightarrow \) able to obtain lattice parameters and propagation vectors

Magnetic Bragg reflections can be found at \( k = G \pm q \) \( \rightarrow \)

\[
d = a \left[ (h + q_x)^2 + (k + q_y)^2 + (l + q_z)^2 \right]^{-\frac{1}{2}}
\]
Experimental procedure

Powder diffraction

2. Intensity $I \sim F^2$

nuclear structure factor
(interaction between neutron and core potential of nuclei)

$$F_N(k) = \sum_j b_j \exp(i k r_j) \exp \left( -B_j \frac{\sin^2 \theta}{\lambda^2} \right)$$

magnetic structure factor
(interaction between neutron and electron’s magnetic field)

$$F_M(k) = \sum_j \mu_j f_j(k) \exp(i k r_j) \exp \left( -B_j \frac{\sin^2 \theta}{\lambda^2} \right)$$
Experimental procedure

Powder diffraction

3. Peak width and shape

source, monochromator, slits, collimators, sample strain, stress, correlation length etc. have an influence on the peak shape and the peak width

Caglioti formula

$$\text{FWHM}^2 = u \tan^2 \theta + v \tan \theta + w$$

resolution function minimum at the take-off angle $2\theta_M$ (focussing effect)
Experimental procedure

Powder diffraction

Thermodiffraction

Experimental procedure

Single crystal diffraction - 4-circle geometry

by adjusting $2\theta$, $\omega$, $\chi$ and $\phi$
the sample is put in reflection position

D10 (ILL)

single crystal on Al pin
Experimental procedure

Single crystal diffraction - Normal beam geometry

cryomagnets, pressure cells, ... cannot be tilted much

→ confined to the scattering plane e.g. only \((hk0)\) reflections

→ lifting counter able to reach \(l=1, 2\)...
Experimental procedure

Single crystal diffraction - Laue method

→ every accessible \( hkl \) plane is in reflection position for a particular wavelength
Experimental procedure

Single crystal diffraction - Laue method

- quickly orient single crystals
- observe phase transitions
- magnetic satellites
- find propagation vectors
- structure analysis also possible
Summary

**Diffraction from magnetic materials**

- Magnetic scattering is comparable in intensity to nuclear scattering
- Only the component of the magnetic moment **perpendicular** to the scattering vector is measurable
- The **magnetic form factor** is the Fourier transform of the atomic magnetisation density
- The magnetic structure factor is the Fourier transform of the unit cell magnetisation density
- We measure $I \sim F^2$ → phase information is lost → models necessary
- How do we get those models? See you tomorrow