Magnetic X-ray Scattering

Introduction
What does theory tell us?

Experimental problems

Non-resonant scattering experiments

Resonant scattering experiments

Summary
coupling between magnetism and photons was predicted long ago

parallel developments

technology/theory

F.E. Low, Phys. Rev. 96, 1428 (1954)
M. Blume, J. Appl. Phys. 57, 3615 (1985)
X-ray beam interacting with a single electron

- Thomson scattering
- Spin-only scattering
- Momentum-only scattering
- Relativistic effects:
  - Rather weak effects:
  - No effect at $Q = 0$

$$\frac{mc}{h} = 2.59 \text{ A}^{-1}$$

$$\frac{hQ}{mc} \approx 10^{-3}$$

F. de Bergevin M. Brunel Acta Cryst. 1981
introduction

X-ray beam interacting with bound electrons

discrete electronic levels
possible transitions to excited states:
  core hole + electron in valence band
magnetic sensitivity

photon in - photon out

selectivity:
  chemical species,
electronic shells
introduction

what can be observed and measured?

non-resonant scattering:
- weak but simple scattering amplitude
- spin/orbital momentum

resonant scattering:
- large scattered intensities
- chemical and electronic selectivity
- x-ray spectroscopy
- imaging

importance of x-ray polarisation effects
- links with magneto-optics (optical index, polarisation of light)
x-ray scattering

back to interactions photons-electrons

• write Hamiltonian to describe charges (electrons+nuclei) and photons
• exploit Fermi’s Golden rule to calculate scattering cross-section
• distinguish different regimes (resonant and non resonant)

\[
\text{kinetic energy} \quad \sum_j \frac{1}{2m} \left( \mathbf{p}_j - \frac{e}{c} \mathbf{A}(r_j) \right)^2
\]

\[
\text{potential energy} \quad + \sum_{ij} V(r_{ij}) - \frac{e\hbar}{2mc} \sum_j s_j \cdot \nabla \times \mathbf{A}(r_j)
\]

\[
\text{spin-orbit} \quad - \frac{e\hbar}{2(mc)^2} \sum_j s_j \cdot \mathbf{E}(r_j) \times \left( \mathbf{p}_j - \frac{e}{c} \mathbf{A}(r_j) \right)
\]

\[
\text{radiation field} \quad + \sum_{k\lambda} \hbar \omega_k \left( c^+(k\lambda) C(k\lambda) + \frac{1}{2} \right).
\]


x-ray scattering

radiation field  \[ \mathbf{E}, \mathbf{B} \quad \text{scalar and vector potential } \Phi \text{ and } \mathbf{A} \]

\[
\begin{align*}
\mathbf{B} &= \nabla \times \mathbf{A} \\
\mathbf{E} &= -\nabla \Phi - (1/c) \frac{\partial \mathbf{A}}{\partial t},
\end{align*}
\]

\[
\mathbf{A}(r, t) = \sum_{k, \lambda} \left( \frac{\hbar c^2}{\Omega \omega_k} \right)^{1/2} \times
\]
\[
\times \left[ e^{i(k \cdot r - \omega_k t)} + e^{i(k \cdot r - \omega_k t)} \right]
\]

approximations

perturbation theory:
- first order: linear in Hint
- second order: quadratic in Hint

scattering expts: conservation of number of photons
- first order: quadratic terms in \( \mathbf{A}(r, t) \)
- second order: linear terms in \( \mathbf{A}(r, t) \)
Hamiltonian for interacting electrons and photons

\[ H = H_{el} + H_{rad} + H_{int}, \]
\[ H_{el} = \sum_{i=1}^{N} \left[ \frac{p_i^2}{2m} + V(r_i) + (\frac{\hbar}{2m^2c^2}) s_i \cdot (\nabla V(r_i) \times p_i) \right], \]
\[ H_{rad} = \sum_{k,\lambda} \hbar \omega_k \left( a^\dagger(k,\lambda) a(k,\lambda) + 1/2 \right), \]
\[ H_{int} = \sum_{i=1}^{N} \left[ (\frac{e^2}{2mc^2}) A^2(r_i) - (e/mc) A(r_i) \cdot p_i + \right. \]
\[ \left. - (\frac{e\hbar}{mc}) s_i \cdot (\nabla \times A(r_i)) + \right. \]
\[ \left. + (\frac{e\hbar}{2mc^2}) s_i \cdot \left[ (\partial A(r_i)/\partial t) \times (p_i - (e/c) A(r_i)) \right] \right] \]
\[ = H_1' + H_2' + H_3' + H_4'. \]

approximations

expansion of \(-\frac{e\hbar}{2(mc)^2} \sum_j s_j \cdot E(r_j) \times \left( P_j - \frac{e}{c} A(r_j) \right)\)

contains terms of:

- degree 0,2 in A(r,t) // perturbation 1st order
- degree 1 in A(r,t) // perturbation 2nd order
x-ray scattering

\[ H'_1 = \sum_{i=1}^{N} \left[ \frac{e^2}{2mc^2} A^2(r_i) \right] \quad \text{quadratic in A} \]

\[ H'_2 = \sum_{i=1}^{N} -\left( \frac{e}{mc} A(r_i) \cdot p_i \right) \quad \text{linear in A} \]

\[ H'_3 = \sum_{i=1}^{N} -\left( \frac{e\hbar}{mc} s_i \cdot (\nabla \times A(r_i)) \right) \quad \text{linear in A} \]

\[ H'_4 = \sum_{i=1}^{N} \left( \frac{e\hbar}{2m^2c^3} s_i \cdot \left[ (\partial A(r_i)/\partial t) \times (p_i - (e/c) A(r_i)) \right] \right) \quad \text{linear term in A reduced by } 1/c^2 \text{ w.r.t. } H'_2 \text{ and } H'_3 \text{ - to be neglected} \]

\[ H'_4 = \sum_{i=1}^{N} -\left( \frac{e\hbar}{2m^2c^3} s_i \cdot \left[ (\partial A(r_i)/\partial t) \times (e/c) A(r_i) \right] \right) \quad \text{quadratic in A} \]
x-ray scattering

eigenstate states defined by $H_{el}$ and $H_{rad}$ -

transitions induced by $H_{int}$

Fermi’s Golden Rule

$$\omega = \frac{2\pi}{\hbar} \left| \langle f | H'_1 + H'_4 | i \rangle + \sum_{n} \frac{\langle f | H'_2 + H'_3 | n \rangle \langle n | H'_2 + H'_3 | i \rangle}{E_0 - E_n + \hbar \omega_k} \right|^2 \times \delta(\hbar(\omega_k - \omega_k'))$$

intermediate states $|n>$$$

calculations rather tedious - follow review articles

M. Blume J. Appl. Phys. 57, 3615 (1985)

M. Altarelli, Lectures 2004

M. Blume, in Resonant Anomalous X-ray Scattering Elsevier (1994) p. 496

Eds: G. Materlik, C.J. Sparks and K. Fischer
x-ray scattering

how to relate transition probabilities to scattering?

\[ \frac{d^2 \sigma}{dE dO'} = \frac{\omega \rho(E)}{c/\Omega} \]

\[ \rho(E) dE dO' = \frac{\Omega}{(2\pi)^3 \hbar^3 c^3} E^2 dE dO' \]

two different contributions

terms with no denominator: valid over all photon energies

terms with denominators: resonance/non-resonance

\[ H_1' \]

\[ \langle f | H_1' | i \rangle = \frac{\hbar c^2}{\Omega \omega_k mc^2} \frac{e^2}{\Omega \omega_k mc^2} \times \]

\[ \sum_i \langle 0; (e'_\lambda, k') | (e''_\lambda \cdot e_\lambda) a^\dagger(k', \lambda) a(k, \lambda) e^{i(k-k') \cdot r_i} | 0; (e_\lambda, k) \rangle = \]

\[ = \frac{\hbar c^2}{\Omega \omega_k mc^2} \frac{e^2}{\Omega \omega_k mc^2} \sum_i \langle 0 | e^{i(k-k') \cdot r_i} | 0 \rangle, \]

units: \[ r_0 \equiv \frac{e^2}{mc^2} \quad r_0 = 2.818 \times 10^{-13} \text{cm} \]

polarisation dependence
x-ray scattering

\[ H'_4 \]

\[
\langle f | H'_4 | i \rangle = -i \left( \frac{e^2}{mc^2} \right) \left( \frac{\hbar \omega_k}{mc^2} \right) \left( \frac{\hbar c^2}{\Omega \omega_k} \right) \times \\
\sum_i \langle 0 | e^{i(k-k').r_i} \cdot s_i \cdot (e_{\lambda'}(k') \times e_{\lambda}(k)) | 0 \rangle.
\]

real magnetic term!

electron spin-dependent term with different polarisation dependence

same units \( (r_0) \) but reduced by \( \left( \frac{\hbar \omega_k}{mc^2} \right) \) and phase lag

are there other magnetic terms in a non-resonant regime?

\[
\sum_n \frac{\langle f | H'_2 + H'_3 | n \rangle \langle n | H'_2 + H'_3 | i \rangle}{E_0 - E_n + \Omega \omega_k + \hbar \omega_k}
\]

da, yes!
x-ray scattering

second order terms:

ground state with 1 photon

intermediate states

a - with either 0 photon

\[ |n\rangle = |\Psi_n; 0, 0\rangle; E_n = E(\Psi_n) \]

b - or 2 photons

\[ |n\rangle = |\Psi_n; (e_\lambda', k'), (e'_\lambda', k')\rangle; E_n = E(\Psi_n) + 2\hbar \omega_k \]

tricks with denominators:

case a: \( E_0 - E_n + \hbar \omega_k = 0 \) possible resonance - damping

case b: \( E_0 - E(\Psi_n) - \hbar \omega_k < 0 \) no divergence

\[
\frac{1}{E_0 - E(\Psi_n) + \hbar \omega_k + i\Gamma_n/2} = \frac{1}{\hbar \omega_k} + \frac{1}{E_0 - E(\Psi_n) - \hbar \omega_k} \\
\times \frac{E(\Psi_n) - E_0 - i\Gamma_n/2}{\hbar \omega_k} \\
\times \frac{1}{E_0 - E(\Psi_n) + \hbar \omega_k + i\Gamma_n/2} \\
= -\frac{1}{\hbar \omega_k} + \frac{1}{E_0 - E(\Psi_n)} \\
\times \frac{1}{E_0 - E(\Psi_n) + \hbar \omega_k} \\
\times \frac{1}{E_0 - E(\Psi_n) + \hbar \omega_k},
\]
non-resonant scattering

away from resonance (edge) \( \hbar \omega_{k} \gg E(\Psi_{n}) - E_{0} \)

denominators are simplified

\[
\langle f|H'_{2} + H'_{3}|n\rangle \langle n|H'_{2} + H'_{3}|i\rangle =
\]
\[
= \left( \frac{\hbar c^{2}}{\Omega \omega_{k}} \right) \left( \frac{e}{mc} \right)^{2} \sum_{j=1}^{N} [ e^{i\lambda}_{\lambda'} \cdot p_{j} - i\hbar (k' \times e^{i\lambda}_{\lambda'}) \cdot s_{j} ] e^{-i k' \cdot r_{j}} \langle n \rangle \times
\]
\[
\times \langle n | \sum_{j'=1}^{N} [ e_{\lambda} \cdot p_{j'} + i\hbar (k \times e_{\lambda}) \cdot s_{j'} ] e^{i k' \cdot r_{j'}} | 0 \rangle
\]

case a

finally

\[
\sum_{n} \frac{\langle f|H'_{2} + H'_{3}|n\rangle \langle n|H'_{2} + H'_{3}|i\rangle}{E_{0} - E_{n} + \hbar \omega_{k}} \approx \left( \frac{\hbar c^{2}}{\Omega \omega_{k}} \right) \left( \frac{e}{mc} \right)^{2} \langle 0 | [ C', C ] | 0 \rangle,
\]
with

\[
C' = [ e^{i\lambda}_{\lambda'} \cdot p_{j} - i\hbar (k' \times e^{i\lambda}_{\lambda'}) \cdot s_{j} ] e^{-i k' \cdot r_{j}}
\]
\[
C' = [ e_{\lambda} \cdot p_{j} + i\hbar (k \times e_{\lambda}) \cdot s_{j} ] e^{i k \cdot r_{j}}.
\]
more algebra ! but at the end :

\[
\sum_n \frac{\langle f | H'_2 + H'_3 | n \rangle \langle n | H'_2 + H'_3 | i \rangle}{E_0 - E_n + \hbar \omega_k} = -i \frac{\hbar c^2}{\Omega \omega_k} \left( \frac{e^2}{mc^2} \right) \frac{\hbar \omega_k}{mc^2} \times \\
\times \left[ \langle 0 | \sum_j e^{i \mathbf{q} \cdot \mathbf{r}_j} \frac{i \mathbf{q} \times \mathbf{p}_j}{\hbar k^2} | 0 \rangle (e_{\chi'}^{e^*} \times \mathbf{e}_\lambda) + \langle 0 | \sum_j e^{i \mathbf{q} \cdot \mathbf{r}_j} s_j | 0 \rangle \times \\
\times [(k' \times e_{\chi'}^{e^*})(k' \cdot \mathbf{e}_\lambda) - (k \times \mathbf{e}_\lambda)(k \cdot e_{\chi'}^{e^*}) - (k' \times e_{\chi'}^{e^*}) \times (k \times \mathbf{e}_\lambda)] \right]
\]

same units (\(r_0\)) and reduced by \(\frac{\hbar \omega_k}{mc^2}\) and phase lag

electron spin AND momentum appear in matrix elements
non-resonant scattering

working out the x-ray cross-section in the non-resonant regime

\[ \frac{d\sigma}{dO'} = r_0^2 \left| \sum_j \langle 0 | e^{i\mathbf{q} \cdot \mathbf{r}_j} | 0 \rangle (e_{\lambda'}^* \cdot e_\lambda) + \right. \]

\[ - \frac{i}{m c^2} \frac{\hbar \omega_k}{\hbar_k^2} \left[ \langle 0 | \sum_j e^{i\mathbf{q} \cdot \mathbf{r}_j} \cdot \frac{\mathbf{p}_j}{\hbar k^2} | 0 \rangle \cdot \mathbf{P}_L + \langle 0 | \sum_j e^{i\mathbf{q} \cdot \mathbf{r}_j} \cdot \mathbf{s}_j | 0 \rangle \cdot \mathbf{P}_S \right] \]

\[ (k - k') \equiv q \]

\[ \mathbf{P}_L = (e_{\lambda'}^* \times e_\lambda) \]

\[ \mathbf{P}_S = [(k' \times e_{\lambda'}^*)(k' \cdot e_\lambda) + (k \times e_\lambda)(k \cdot e_{\lambda'}^*) - (k \times e_\lambda)(k' \cdot e_{\lambda'}^*) \times (k \times e_\lambda)]. \]
non-resonant scattering

operator

\[ \sum_j e^{i \mathbf{q} \cdot \mathbf{r}_j} \frac{i \mathbf{q} \times \mathbf{p}_j}{\hbar k^2} \]

relates to orbital momentum (see neutron case)

density of orbital magnetisation

\[ \sum_j e^{i \mathbf{q} \cdot \mathbf{r}_j} \frac{i \mathbf{q} \times \mathbf{p}_j}{\hbar k^2} = \frac{mc}{e \hbar q^2} \mathbf{q} \times [\mathbf{M}_L(q) \times \mathbf{q}] \]

Bohr magneton \( e\hbar/2mc \)

\[ = \frac{1}{2} \frac{q^2}{q^2} \mathbf{q} \times [\mathbf{L}(q) \times \mathbf{q}] \]
non-resonant scattering cross-section for x-rays:

\[
\frac{d\sigma}{dO'} = r_0^2 \left| \sum_j \langle 0 | e^{i\mathbf{q} \cdot \mathbf{r}_j} | 0 \rangle \langle e^{i\mathbf{k}'}_L, e_\lambda \rangle + \frac{-i\hbar\omega_k}{mc^2} \left[ \frac{mc}{\hbar} \langle 0 | \mathbf{q} \times [\mathbf{M}_L(\mathbf{q}) \times \mathbf{q}] | 0 \rangle \cdot \mathbf{P}_L + \frac{mc}{\hbar} \langle 0 | \mathbf{M}_S(\mathbf{q}) | 0 \rangle \cdot \mathbf{P}_S \right] \right|^2
\]

- orbital magnetization
- spin magnetization

\[
\begin{align*}
\mathbf{P}_L & = (e_{k'}^* \times e_\lambda) 4\sin^2 \theta_B \\
\mathbf{P}_S & = [(\mathbf{k}' \times e_{k'}^*) (\mathbf{k}' \cdot e_\lambda) + (\mathbf{k} \times e_\lambda) (\mathbf{k} \cdot e_{k'}^*)] \\
& - (\mathbf{k} \times e_\lambda) (\mathbf{k} \cdot e_{k'}^*) \times (\mathbf{k} \times e_\lambda).
\end{align*}
\]

differentiation through polarisation dependence
non-resonant scattering

use linear polarisation vectors as basis for matrix representation

use scattering amplitudes

\[
\frac{d\sigma}{d\Omega} = r_0^2 \quad tr(\rho') \quad \rho' = M \rho M^+ \quad M = M_c - i \frac{\hbar \omega}{mc^2} M_m
\]

\[
f_n^{\text{charge}} (Q) = - \rho_n (Q) \hat{\varepsilon} \cdot \hat{\varepsilon}' = - \rho_n (Q) \begin{pmatrix} 1 & 0 \\ 0 & \cos 2\theta \end{pmatrix}
\]

\[
f_n^{\text{non-res}} = - i \frac{\hbar \omega_k}{mc^2} \langle M_m \rangle = - i \frac{\hbar \omega_k}{mc^2} \begin{bmatrix} \langle M_{\sigma \rightarrow \sigma} \rangle & \langle M_{\pi \rightarrow \sigma} \rangle \\ \langle M_{\sigma \rightarrow \pi} \rangle & \langle M_{\pi \rightarrow \pi} \rangle \end{bmatrix} = - i \frac{\hbar \omega_k}{mc^2} \\
\begin{bmatrix}
S_2 \sin 2\theta & -2 \sin^2 \theta ((\cos \theta) (L_1 + S_1) - S_3 \sin \theta) \\
2 \sin^2 \theta [\cos \theta (L_1 + S_1) - S_3 \sin \theta] & \sin 2\theta \left[2L_2 \sin^2 \theta + S_2\right]
\end{bmatrix}
\]
non-resonant scattering

non-resonant amplitude depends on $Q$!

$$f_{n}^{\text{non-res}}(Q, k, k') = -i \frac{hQ}{mc} 2S \times$$

$$\left( \begin{array}{c}
\cos \theta \hat{S}_2(Q) \\
\sin \theta \left[ \cos \theta (\hat{S}_1(Q) + \frac{L_1(Q)}{S}) + \sin \theta \hat{S}_3(Q) \right] \\
\sin \theta \left[ \cos \theta (\hat{S}_1(Q)) + \frac{L_1(Q)}{S} \right] + \sin \theta \hat{S}_3(Q)
\end{array} \right)$$

no effect at $Q=0$ - no effect on absorption - no dichroism!

possibility to separate $L(Q)$ and $S(Q)$ polarisation effects

high energy photons : spin-only magnetic scattering

scaling factor : $\frac{hQ}{mc} \approx 10^{-3}$ difficult to observe w/o synchrotron!
non-resonant scattering

first experiments NiO
Magnetic Bragg peak
sealed x-ray tube


experiments NiO
ESRF with same crystal


below and above Tn
non-resonant scattering experiments

experimental details

- clean x-ray beams
- use of polarised x-rays - linear polarisation
- tunability (polarisation and energy - resonance)

applications

- determination of magnetic structures?
- details of magnetic structures?
- magnetism at surfaces?
- L(Q)/S(Q) determination?
experimental details

magnetic scattering amplitude very weak

spurious peaks arising from impurities defects

harmonics in the beam ($\lambda/2$, $\lambda/3$, ….)

clean beams and clean samples
experimental details

experimental set-up

ID beamline ESRF
experimental details

x-ray polarisation

production of polarised x-rays:

insertion devices: linear, circular, elliptical

crystal optics - phase plate crystals
experimental details

x-ray polarisation analysis

linear polarisation: use charge scattering by analyser crystal

circular polarisation: phase plates but difficult!
experimental details

linear polarisation: charge scattering!
### Experimental Details

#### Analyzer Crystals Examples

<table>
<thead>
<tr>
<th>Element</th>
<th>Edge</th>
<th>E (keV)</th>
<th>Analyzer Crystal</th>
<th>d-spacing</th>
<th>θ</th>
<th>Cos²(θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy</td>
<td>L3</td>
<td>7.790</td>
<td>quartz(3 1 -4 3)</td>
<td>1.1802</td>
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<td>Al (2 2 2)</td>
<td>1.16913</td>
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<td>0.00538</td>
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<td></td>
<td></td>
<td>Graphite (0 0 6)</td>
<td>1.11931</td>
<td>90.63</td>
<td>0.00012</td>
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<td></td>
<td></td>
<td>quartz(3 0 -3 3)</td>
<td>1.11467</td>
<td>91.11</td>
<td>0.00038</td>
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<td>quartz(2 0 -2 0)</td>
<td>1.0615</td>
<td>97.13</td>
<td>0.01540</td>
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<tr>
<td>Nd</td>
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<td>6.208</td>
<td>Al (2 2 0)</td>
<td>1.43189</td>
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<td></td>
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<td>LiF (2 2 0)</td>
<td>1.42376</td>
<td>89.08</td>
<td>0.00026</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>quartz(2 0 -2 3)</td>
<td>1.3745</td>
<td>93.19</td>
<td>0.00310</td>
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<tr>
<td></td>
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<td>Al₂O₃ (0 3 0)</td>
<td>1.374</td>
<td>93.23</td>
<td>0.00318</td>
</tr>
</tbody>
</table>

- Select crystal for reflectivity
- Go for large mosaic
- Beware of resolution effects: width of analyzer/divergences
basic experimental problems

- **sample**
  - quality mosaic spread similar to beam divergence to reduce spread in Q of scattered intensity
  - typical values around 0.05-0.01 deg.

- **absorption**
  - x-rays do not propagate deep in bulk samples except at high energy but high quality crystals required
  - no resonance
  - at resonance strong effects due to varying absorption surface orientation and preparation
basic experimental problems

sample environment

- again absorption by windows
- cryostats
- vibrations
- heat load (mW range)

- cryomagnets
- limitations: angular access
- stray fields

- high pressure: high energy only (>8-10 keV)
experiments: non-resonant scattering

non resonant scattering experiments
essentially antiferromagnets: NiO Ho UAs Cr
L/S and interfacial/surface magnetism

only a few ferromagnets
more difficult to observe (flipping ratio)
non resonant scattering NiO

- NiO simple antiferromagnet
  crystal structure NaCl fcc
  Ni$^{2+}$ ions $3d^8$ configuration 2 holes in $3d$ band
  Hund's rules maximise $S$ and then $m_L$
  crystalline electrical field cubic symmetry $t_{2g}$ full (6)
  orbital singlet $e_g$ (2) half full
  $L=0$

  however spin-orbit exists, $g=2.2$ in paramagnetic phase
  magnetic anisotropy in AF phase $T_N=523$ K
  neutron data unable to measure $<L>$
  x-rays can help
non resonant scattering NiO

- pioneering experiment by de Bergevin and Brunel
  search for antiferromagnetic peaks with x-rays
  AF structure known from neutron data: type-II
  ferromagnetic [111] planes are piled up antiferromagnetically
  propagation vector (1/2,1/2,1/2) moments along [11-2] directions
  magnetic domains 4 propagation directions and 3 moment directions
  for each

important details
  unpolarised beam
  sealed x-ray tube
  low power to high energy flux
  not from x-ray lines

signal/noise ratio
non resonant scattering NiO

experiments at ESRF
samples: flat [111] face
azimuthal scans : easy for specular reflections (hhh)
explored 1 T-domain (1/2,1/2,1/2) but 3 S-domains
• experimental conditions
linear undulator
Si(111) optics and mirrors: beam size 0.3x0.2 mm² incident power

sample at room temperature. mounted on 4-circle diffractometer
polarisation analysis PG(006) peak reflectivity 12%
measure in direct beam and reflected beam incident polarisation σ
(P1=0.995±0.005 P2=0.0±0.005 Punp or P3<0.01±0.01)

non resonant scattering NiO

sample quality     rocking curve
no polarisation analysis
how to put intensities on absolute scale?
integrate charge peak intensities

\[
I(Q) = I_0 \frac{\lambda^2 r_0^2 |F(Q)|^2}{2\mu v_a^2 \sin 2\theta} \quad I(Q) = I_0 \frac{8 \lambda^2 r_0 |F(Q)|}{3\pi v_a \sin 2\theta}
\]

mosaic crystal    perfect crystal

to be compared with known structure factors

<table>
<thead>
<tr>
<th></th>
<th>E=7.84 keV</th>
<th></th>
<th>E=17.41 keV</th>
</tr>
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<tbody>
<tr>
<td>peak</td>
<td>Structure reflecting factor calc</td>
<td>Structure reflecting factor obs</td>
<td></td>
</tr>
<tr>
<td>(111)</td>
<td>14.2</td>
<td>(2.7±0.2)×10^{-4}</td>
<td>9.8</td>
</tr>
<tr>
<td>(222)</td>
<td>14.8</td>
<td>(9.5±0.6)×10^{-5}</td>
<td>7.2</td>
</tr>
<tr>
<td>temperature factors</td>
<td>B_{Ni} = 0.37</td>
<td>B_{O} = 0.26</td>
<td></td>
</tr>
</tbody>
</table>

extinction effects to be taken into account when comparing charge and magnetic intensities
non resonant scattering NiO

- magnetic domains measure 3 magnetic peaks \((h/2, h/2, h/2)\)
  \(h=1,3,5\)
not possible to control domains population (even by applying field)
average over orientation with respect to incident polarisation (azimuthal scans)
magnetic peaks show rotated polarisation component
magnetic domains in NiO

- weak reflections from domains with different propagation vectors
  sample almost single T-domain near surface
- rotation about [111] shows S-domains

\[ M_{\sigma \sigma} = \sin(2\theta) \sin\Phi \ S(Q) \]
\[ M_{\sigma \pi} = \sin(2\theta) \sin(\theta)(\cos\Phi \ S(Q) + \cos(\Phi + \Phi_0) \ L(Q)) \]

offset between L and S  no S_3

polarised intensities are shifted in \( \Phi \)
Offset=0
can obtain domain fractions in volume probed by beam:
\( \alpha_1 = 0.26 \pm 0.03 \)  \( \alpha_2 = 0.23 \pm 0.03 \)  \( \alpha_3 = 0.50 \pm 0.02 \)

translations indicate domains size 300\( \mu \)m
averaged intensities
magnetic form factors in NiO

- polarised intensities corrected for width of rocking curve of analyser
  note: change in resolution function (better use crystals with wide band)
  required to obtain fully integrated intensities
- comparison with unpolarised intensities (no analyser) gives analyser reflectivity

- experimental Φ-averaged intensities

\[
\begin{align*}
I_{\sigma\sigma} & \propto (\sin 2\theta)^2 \frac{1}{2} S^2(Q) \\
I_{\sigma\pi} & \propto (\sin 2\theta)^2 (\sin \theta)^2 \frac{1}{2} (S(Q) + L(Q))^2
\end{align*}
\]

<table>
<thead>
<tr>
<th>(h,k,l)</th>
<th>(I_{ext})</th>
<th>(I_{und})</th>
<th>(I_{total})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1/2,1/2,1/2)</td>
<td>((2.8\pm0.1) \times 10^{-5})</td>
<td>((1.32\pm0.08) \times 10^{-6})</td>
<td>((2.35\pm0.2) \times 10^{-4})</td>
</tr>
<tr>
<td>(3/2,3/2,3/2)</td>
<td>((3.45\pm0.1) \times 10^{-5})</td>
<td>((1.7\pm0.05) \times 10^{-5})</td>
<td>((4.5\pm0.3) \times 10^{-4})</td>
</tr>
<tr>
<td>(5/2,5/2,5/2)</td>
<td>((3.5\pm0.1) \times 10^{-6})</td>
<td>((6.2\pm0.2) \times 10^{-6})</td>
<td>((7.7\pm0.4) \times 10^{-5})</td>
</tr>
</tbody>
</table>

- extract \(L(Q)/2S(Q)\) ratio as a function of \(Q\)
magnetic form factors in NiO

- large contribution (17±3%) from orbital moment exists

- increase at large Q indicates broader spatial extent of spin density

Electrons with same spins tend to be further apart!
magnetic form factors in NiO

- comparison of magnetic intensities to charge intensities and extinction corr.
- polarised intensities on absolute scale in electron units

extract $S(Q)$ and $L(Q)$ in real numbers

$S(O)=0.95\pm0.1$ and $L(O)=0.32\pm0.05$

magnetic moment at 300K $2.2\pm0.2\mu_B$

<table>
<thead>
<tr>
<th>$(h,k,l)$</th>
<th>$P^2_{\text{ext}}$</th>
<th>$P^2_{\text{int}}$</th>
<th>$P^2_{\text{total}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(1/2,1/2,1/2)$</td>
<td>$(8.4\pm0.9)\times10^{-6}$</td>
<td>$(4.0\pm0.5)\times10^{-7}$</td>
<td>$(9\pm1)\times10^{-6}$</td>
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<tr>
<td>$(3/2,3/2,3/2)$</td>
<td>$(3.2\pm0.4)\times10^{-5}$</td>
<td>$(1.6\pm0.2)\times10^{-5}$</td>
<td>$(4.8\pm0.5)\times10^{-5}$</td>
</tr>
<tr>
<td>$(5/2,5/2,5/2)$</td>
<td>$(4.2\pm0.5)\times10^{-6}$</td>
<td>$(7.5\pm0.9)\times10^{-6}$</td>
<td>$(1.1\pm0.2)\times10^{-5}$</td>
</tr>
</tbody>
</table>
magnetic form factors in NiO

comparison with other methods

g-factor = 2.2 indicates spin-orbit/10Dq ≈ 0.1 which leads to L ≈ 0.3

neutrons:

pb: neutrons would tell L/S through a fit of data with electronic wave functions

not really known in NiO; atomic wave functions not adequate.
magnetic form factors

through the whole series MnO, CoO, CuO


related to resonant effects
to be discussed later
existence of E2 resonance at K-edge linked to finite $\langle L \rangle$

better knowledge of electronic properties of 3d oxides
magnetism at surfaces

NiO
non-resonant scattering
grazing incidence scattering

A. Barbier et al. PRL 93, 25708 (2004)

depth sensitive
surface ordering
well-defined 2D order

melting of S-domains

C. Vettier Institut Laue Langevin 19 October 2005
non-resonant scattering from ferromagnet

Principle: measurement of flipping ratios
like in neutron diffraction
\[ f_{\text{total}} = f_{\text{charge}} + f_{\text{magnetic}} \text{ with } f_{\text{magnetic}} \ll f_{\text{charge}} \]

If we can flip \( f_{\text{magnetic}} \) by applying H or rotating polarisation
we define
\[ R = \frac{I_+ - I_-}{I_+ + I_-} \]
\[ I_{\pm} = |f_{\text{charge}} +/\mp f_{\text{magnetic}}|^2 \]

in the case of non-resonant scattering \( f_{\text{magnetic}} \) is linear in \( S \) and \( L \).
applying a field can change the sign of \( f_{\text{magnetic}} \) with different incident polarisations.

\( R \) is given by the interference between charge and magnetic scattering.
Since Thomson scattering does not rotate polarisation, interference arises in \( \sigma-\sigma \) and \( \pi-\pi \) channels only (linear polarisation)

in case of general incident polarisation, the full formalism has to be used.
non resonant scattering - ferromagnets

- density matrix
  \[
  \rho = \frac{1}{2} \begin{pmatrix}
  1 + P_1 & P_2 - i P_3 \\
  P_2 + i P_3 & 1 - P_1
\end{pmatrix}
  \]
  \[
  P = \text{tr}(\sigma \rho) \text{ Poincare vector}
  \]

- scattered intensity
  \[
  \frac{d\sigma}{d\Omega} = r_0^2 \text{tr}(\rho') \quad \rho' = M \rho M^+
  \]

- scattered polarisation
  \[
  P = \frac{\text{tr}(\alpha \rho')}{\text{tr}(\rho')}
  \]

- charge scattering  back to equations
  \[
  \frac{d\sigma}{d\Omega_c} = r_0^2 [\rho(Q)]^2 \frac{1}{2} \left[ 1 + \cos^2 2\theta + P_1 (1 - \cos^2 2\theta) \right]
  \]

- pure magnetic terms  complex in the case of general polarisation
  interference between spin and orbital momentum
  beyond this lecture

M. Blume et al. PRB 37, 1779 (1988)
non resonant scattering - ferromagnets

- purely magnetic scattering

\[
\frac{d\sigma}{d\Omega}_m = \frac{1}{2} r_0^2 \left( \frac{hQ}{mc} \right)^2 \left[ (1 + P_1) \cos^2 \theta \left[ S_2^2 + \sin^2 \theta (L_1 + S_1)^2 \right] + \sin^4 \theta S_3^2 \right] + \sin 2\theta \sin^2 \theta (L_1 + S_1) S_3 \\
(1 - P_1) \cos^2 \theta \left[ (2 \sin^2 \theta L_2 + S_2)^2 + \sin^2 \theta (L_1 + S_1)^2 \right] + \sin^4 \theta S_3^2 \\
- \sin 2\theta \sin^2 \theta (L_1 + S_1) S_3
\]

- circular polarisation \( P_3 \)

\[
\frac{d\sigma}{d\Omega}_m = r_0^2 \left( \frac{hQ}{mc} \right)^2 \left( L_1' + S_1' \right) \left[ \sin^2 \theta L_2'' + S_2'' \right] - \left( L_1'' + S_1'' \right) \left[ \sin^2 \theta L_2' + S_2' \right] + \sin^3 \theta \left( S_3' L_2'' - S_3'' L_2' \right)
\]
non resonant scattering - ferromagnets

- interference terms
- linear polarisation $P_1$ centrosymmetric structure
  note that if crystal and magnetic structures are centrosymmetric
  interference occurs through imaginary part of atomic scattering factors

\[
\frac{d\sigma}{d\Omega} = - r_0^2 \left( \frac{\hbar Q}{mc} \right) \begin{pmatrix}
\cos \theta (1 + P_1) \rho''(Q) S_2 \\
\cos \theta \cos 2\theta (1 - P_1) \rho''(Q) \left( 2 \sin^2 \theta L_2 + S_2 \right)
\end{pmatrix}
\]

- circular polarisation $P_3$

\[
\frac{d\sigma}{d\Omega} = - r_0^2 \left( \frac{\hbar Q}{mc} \right) \begin{pmatrix}
\cos \theta \\
\cos 2\theta \left( \rho'(Q) (2 \sin^2 \theta L_2'' + S_2'') - \rho''(Q) (2 \sin^2 \theta L_2' + S_2') \right) \\
1 + \cos 2\theta \sin 2\theta \left[ \rho'(Q) (L_1' + S_1') - \rho''(Q) (L_1'' + S_1'') \right] \\
1/2 \left[ \rho'(Q) S_3' - \rho''(Q) S''_2 \right]
\end{pmatrix}
\]
non resonant scattering - ferromagnets

- assume fully linearly polarised radiation \( P1=\pm 1 \)
  
  incident polarisation \( \sigma \) \( P1=1 \)

\[
R = - \frac{\hbar Q}{mc} \frac{2 \cos \theta \rho''(Q) S_2}{|\rho(Q)|^2 + \left( \frac{\hbar Q}{mc} \right)^2} \approx - \frac{\hbar Q}{mc} \frac{2 \cos \theta \rho''(Q) S_2}{|\rho(Q)|^2}
\]

incident polarisation \( \pi \) \( P1=-1 \)

\[
R = - \frac{\hbar Q}{mc} \frac{2 \cos \theta \rho''(Q) \{2 \sin^2 \theta L_2 + S_2\}}{\cos 2\theta |\rho(Q)|^2 + \left( \frac{\hbar Q}{mc} \right)^2} \approx \frac{\hbar Q}{mc} \frac{2 \cos \theta \rho''(Q) \{2 \sin^2 \theta L_2 + S_2\}}{\cos 2\theta |\rho(Q)|^2}
\]

in principle it is possible to measure \( L \) and \( S \) by changing polarisation
non resonant scattering - ferromagnets

- assume circularly polarised radiation \( P_1=0, P_2=0 \)

scatter geometry: field (\( S \) and \( L \)) in scattering plane but perpendicular to \( Q \)

only \( S_1 \) and \( L_1 \) components

\[
R = \frac{hQ}{mc} \frac{P_3}{\rho(Q)} \frac{(1 + \cos 2\theta) \sin 2\theta \left[ \rho'(Q)(L'_1 + S'_1) - \rho''(Q)(L''_1 + S''_1) \right]}{(1 + \cos^2 2\theta) |\rho(Q)|^2}
\]

we can flip magnetisation or polarisation

if \( 2\theta = 90^\circ \)

\[
R \approx \frac{hQ}{mc} \frac{P_3}{\rho(Q)} \left( L_1 + S_1 \right)
\]

if magnetic field perpendicular to scattering plane \( S_1 = L_1 = 0 \)

\[
R = -\frac{hQ}{mc} \cos \theta \left\{ \frac{(\rho'(Q)S''^2_2 - \rho''(Q)S'_2^2)}{\cos^2 \theta \left[ \rho'(Q)(2\sin^2 \theta L''^2_2 + S''^2_2) - \rho''(Q)(2\sin^2 \theta L'_2 + S'_2) \right]} \right\} - \frac{P_3}{2} \frac{(1 - \cos 2\theta)^2 \rho''(Q)S''_2}{(1 + \cos^2 2\theta) |\rho(Q)|^2}
\]

not very efficient
flipping ratios from ferromagnetic materials

- application to determination of polarisation of synchrotron beams

known magnetic substance; in general $L=0$ and centrosymmetric field in scattering plane: only $S_1$ and $S_3$ components

ideal if $H//k_\parallel\cos\theta+k_\perp$ but $S_2=S_3=0$ is ok

assume $P_2=0$ but with $P_1$ and $P_3$ finite

\[
\frac{d\sigma}{d\Omega}|_I = r_0^2 \left( \frac{hQ}{mc} \right) P_3 \frac{1}{2} \left\{ (1 + \cos2\theta)\sin2\theta \left[ \rho'(Q)(L'_1 + S'_1) - \rho''(Q)(L''_1 + S''_1) \right] \right\}
\]

neglect imaginary parts $f'$ and $f''$

\[
R = 8 \left( \frac{hQ}{mc} \right) P_3 \frac{S(Q)}{\rho(Q)} \frac{\sin\theta \cos^3\theta}{1 + \cos^22\theta + P_1 (1 - \cos^22\theta)}
\]

flipping ratios from ferromagnetic materials

• circular polarisation
  2 types applications
    Bragg scattering to increase sensitivity
    coupling to real part of $\rho(Q)$
    field perpendicular to Q but in scattering plane $2\theta=90^\circ$
    $R \approx \frac{hQ}{mc} \frac{p_3}{\rho(Q)} \frac{(L_1 + S_1)}{(Q)}$

  white beam technique; fixed $2\theta=90^\circ$ value; energy sensitive detector


magnetic Compton scattering
  signal proportional to $P3$
  field in scattering plane  $q \cdot \cos\theta + q'$
non-resonant scattering - summary

what does non-resonant magnetic scattering bring about?

 possibility to use highly collimated beams for magnetism
  surface magnetism
  polarization analysis
  separation of orbital and spin magnetism

however, “weak” intensities
  “good” samples (single crystals) are needed
resonant scattering

As a reminder, probability of transition

\[
\frac{d^2\sigma}{dEdO'} = \frac{w\rho(E)}{c/\Omega}
\]

\[
\rho(E) dE dO' = \frac{\Omega}{(2\pi)^3 \hbar^3 c^3} dE dO'
\]

\[
w = \frac{2\pi}{\hbar} \left| \langle f | H'_1 + H'_4 | i \rangle + \sum_n \frac{\langle f | H'_2 + H'_3 | n \rangle \langle n | H'_2 + H'_3 | i \rangle}{E_0 - E_n + \hbar \omega_K} \right|^2 \times
\]

\[
\times \delta(\hbar(\omega_K - \omega_{K'}))
\]

At the resonance, the leading term is given by

\[
\frac{1}{E_0 - E(\Psi_n) + \hbar \omega_K + i\Gamma_n/2} = \frac{1}{\hbar \omega_K} + \frac{E(\Psi_n) - E_0 - i\Gamma_n/2}{\hbar \omega_K} \times
\]

\[
\times \frac{1}{E_0 - E(\Psi_n) + \hbar \omega_K + i\Gamma_n/2}
\]

absorption and creation of photon - case a
for such process, the leading term is:

\[
\begin{align*}
\langle f | H'_{2} + H'_{3} | n \rangle \langle n | H'_{2} + H'_{3} | i \rangle &= \\
= \left( \frac{\hbar c^{2}}{\Omega_{\mathbf{k}}} \right) \left( \frac{e}{mc} \right)^{2} \langle 0 | \sum_{j=1}^{N} \left[ e_{\lambda'}^{r} \cdot \mathbf{p}_{j} - i\hbar (\mathbf{k} \times e_{\lambda'}^{r}) \cdot s_{j} \right] e^{-i\mathbf{k'} \cdot \mathbf{r}_{j}} | n \rangle \\
&\times \langle n | \sum_{j'=1}^{N} \left[ e_{\lambda} \cdot \mathbf{p}_{j'} + i\hbar (\mathbf{k} \times e_{\lambda}) \cdot s_{j'} \right] e^{i\mathbf{k} \cdot \mathbf{r}_{j'}} | 0 \rangle
\end{align*}
\]

we can distinguish 3 terms:

- \((e' \cdot \mathbf{P})(e \cdot \mathbf{P})\) contribution
- \((e' \cdot \mathbf{P})(k \times e \cdot s) - (k' \times e' \cdot s)(e \cdot \mathbf{P})\) contribution
- \((k' \times e' \cdot s)(k \times e \cdot s)\) contribution

resonant scattering

\((\epsilon' \cdot P)(\epsilon \cdot P)\) contribution

the leading term!

involved algebra and calculation

see lecture by S di Matteo!

basic physical explanation:

- electric transitions
- but exclusion principle leads magnetic sensitivity
- spin polarization of core levels and excited levels

J. P. Hannon et al. PRL 61, 1245 (1988)
resonant scattering

complex expression for scattering amplitude:

\[ f_{EL}^{(x,\text{res})}(k_f e_f; k_0 e_0) = 4\pi\chi f_D \sum_{M=L}^{L} [e_f^* \cdot Y_{LM}^{(e)}(\hat{k}_f) Y_{LM}^{(e)*}(\hat{k}_0) \cdot e_0] F_{LM}^{(e)}(\omega), \]

various approximations: L=1 dipolar, L=2 quadrupolar, ...

\[ F_{LM}^{(e)}(\omega) = \sum_{\alpha, \eta} \left\{ p_\alpha p_\alpha(\eta) \Gamma_x(\alpha M \eta; EL)/\Gamma(\eta) \right\} \frac{x(\alpha, \eta) - i}{x(\alpha, \eta) - i}. \]

with:

\[ \Gamma_x(\alpha M \eta; EL) = 8\pi \left\{ \frac{e^2}{\chi} \right\} \left( \frac{L+1}{L} \right) |(\alpha) \sum_j j_L(kr_j) Y_{LM}(\hat{r}_j)|^2 \]

and:

\[ x(\alpha, \eta) = [\epsilon(\eta) - \epsilon(\alpha) - \hbar \omega]/[\Gamma(\eta)/2]. \]

many quantities to evaluate numerically!
resonant scattering

gеometrical dependence of scattering amplitude

all invariants that can be formed with the quantities involved

dipole: polarisation vectors and quantization axis

quadrupole: same plus x-ray wave-vectors, ..... 

dipole:

\[ f_{E_1}^{(\chi_{\text{res}})} = \frac{3}{4} \chi \{ e_j^* \cdot e_0 [F_{11}^{(e)} + F_{1-1}^{(e)}] - i(e_j^* \times e_0) \cdot \hat{z}_J [F_{11}^{(e)} - F_{1-1}^{(e)}] + \]

\[ + (e_j^* \cdot \hat{z}_J)(e_0 \cdot \hat{z}_J) [2F_{10}^{(e)} - F_{11}^{(e)} - F_{1-1}^{(e)}] \}, \]

\( z_J \) direction of local magnetisation

anomalous scattering: no \( z \), magnetic scattering: terms in \( z \) and \( z^2 \)

no simple link to spin or moment values!
resonant scattering

\[(k' \times \epsilon' \cdot s)(k \times \epsilon \cdot s)\) contribution

at lowest order it has no magnetic sensitivity

but contributes to anomalous scattering

\[(\epsilon' \cdot P)(k \times \epsilon \cdot s) - (k' \times \epsilon' \cdot s)(\epsilon \cdot P)\) contribution

at lowest order

\[
\frac{1}{24}(ka_0)^2 \left\langle a \left| \frac{r_j}{a_0} \right| e \right \rangle^2 \left\{ (\epsilon' \cdot \hat{k})(k \times \epsilon) - (\epsilon \cdot \hat{k}')(k' \times \epsilon') \right\} \cdot \hat{z}_n m_h
\]

\[
\frac{E_a - E_c}{E_a - E_c + \hbar \omega_k - i\Gamma/2}
\]

\[
\left\{ (\epsilon' \cdot \hat{k})(k \times \epsilon) - (\epsilon \cdot \hat{k}')(k' \times \epsilon') \right\} = \begin{bmatrix} 0 & -\hat{k}' + (\hat{k} \cdot \hat{k}')\hat{k} \\ \hat{k}' - (\hat{k} \cdot \hat{k}')\hat{k}' & 2\hat{k}' \times \hat{k} \end{bmatrix}
\]

no dichroism

resonant scattering

focus on the \((\epsilon' \cdot \mathbf{P})(\epsilon \cdot \mathbf{P})\) term

dipole :

\[
f_{E1}^{(\chi_{res})} = \frac{3}{4} \chi \{ \mathbf{e}_f^* \cdot \mathbf{e}_0 [F_{11}^{(e)} + F_{1-1}^{(e)}] - i (\mathbf{e}_f^* \times \mathbf{e}_0) \cdot \mathbf{\hat{z}}_J [F_{11}^{(e)} - F_{1-1}^{(e)}] +
\]

\[
+ (\mathbf{e}_f^* \cdot \mathbf{\hat{z}}_J)(\mathbf{e}_0 \cdot \mathbf{\hat{z}}_J) [2F_{10}^{(e)} - F_{11}^{(e)} - F_{1-1}^{(e)}]\},
\]

\(\mathbf{z}_J\) direction of local magnetisation

anomalous scattering : no \(z\), magnetic terms in \(z\) and \(z^2\)
resonant scattering

simple example/illustration at M edge (for dipole transition!)

assembly of (polarised) ions with simple ground state:

1 hole in the 4f band

Hund’s rule \( l=3, m_l=-3, m_s=-1/2 \quad j=7/2 \quad m_j=7/2 \)

only 1 possible transition possible at M\(_5\) edge

from \( 3d_{5/2}, m_j=5/2 \) to \( 4f_{7/2}, m_j=7/2 \)

\( F_{11} = F_{10} = 0 \)

contributions to 3 terms in scattering amplitude

no resonance at the M\(_4\) edge! (in dipole approximation)

J. B. Goedkoop et al. PRB 37, 2086 (1988)
resonant scattering

connection to absorption/fluorescence

\( Q=0 \) experiments

linear term: non-zero if complex polarisation circular dichroism

quadratic term: linear dichroism, Cotton-Mouton effect

\[
\begin{align*}
    f_{E_1}^{(\chi_{\text{res}})} &= \frac{3}{4} \chi \left\{ e_0^* \cdot e_0 \left[ F_{11}^{(e)} + F_{1-1}^{(e)} \right] - i (e_0^* \times e_0) \cdot \hat{z}_J \left[ F_{11}^{(e)} - F_{1-1}^{(e)} \right] \right. \\
    &\quad + \left. (e_0^* \cdot \hat{z}_J) (e_0 \cdot \hat{z}_J) \left[ 2 F_{10}^{(e)} - F_{11}^{(e)} - F_{1-1}^{(e)} \right] \right\},
\end{align*}
\]

scattering experiments

constant term: “normal anomalous” term non-magnetic

linear term: Bragg peaks corresponding to magnetic lattice symmetry at \( Q_m \) in reciprocal lattice

quadratic term: “resonant” harmonics at \( 2 \times Q_m \)!
resonant scattering

geometry and polarisation dependence

\[ f^{res}_{E1} = F^{(0)} \epsilon' \cdot \epsilon - i F^{(1)} (\epsilon' \times \epsilon) \cdot z + F^{(2)} (\epsilon' \cdot z)(\epsilon \cdot z) \]

\[ = F^{(0)} \begin{pmatrix} 1 & 0 \\ 0 & \cos 2\theta \end{pmatrix} - i F^{(1)} \begin{pmatrix} 0 & z_1 \cos \theta + z_3 \sin \theta \\ z_1 \cos \theta - z_3 \sin \theta & -z_2 \sin 2\theta \end{pmatrix} \]

\[ + F^{(2)} \begin{pmatrix} z_2^2 & -z_2 (z_1 \sin \theta - z_3 \cos \theta) \\ z_2 (z_1 \sin \theta + z_3 \cos \theta) & z_1^2 \sin^2 \theta + z_3^2 \cos^2 \theta \end{pmatrix} \]

no $\sigma$-$\sigma$ scattering in first order
resonant scattering

quadrupolar approximations

\[ f_{E2}^{\text{res}} \text{ contains terms up to } 4^{\text{th}} \text{ order in } z \]

order (0) \hspace{2cm} (k' \cdot k) (\varepsilon' \cdot \varepsilon)

order (1) \hspace{2cm} -i(k' \cdot k) (\varepsilon' \times \varepsilon) \cdot z + [k' \leftrightarrow \varepsilon', k \leftrightarrow \varepsilon]

order (2) \hspace{2cm} (k' \cdot k) (\varepsilon' \cdot z) (\varepsilon \cdot z) + [k' \leftrightarrow \varepsilon'] + [k \leftrightarrow \varepsilon]

\hspace{2cm} + [k' \leftrightarrow \varepsilon', k \leftrightarrow \varepsilon] + (k' \times k) \cdot z (\varepsilon' \times \varepsilon) \cdot z

order (3) \hspace{2cm} -i(k' \cdot z) (k \cdot z) (\varepsilon' \times \varepsilon) \cdot z + [k' \leftrightarrow \varepsilon', k \leftrightarrow \varepsilon]

\hspace{2cm} + [k' \leftrightarrow \varepsilon'] + [k \leftrightarrow \varepsilon]

order (4) \hspace{2cm} (k' \cdot z) (k \cdot z) (\varepsilon' \cdot z) (\varepsilon \cdot z)

more “resonant harmonics”! up to 4xQm
resonant scattering

what does a resonance look like?

UAs simple antiferromagnet
(0,0,5/2) magnetic Bragg peak
diffracted intensity versus photon energy

huge intensities!
Interferences between resonances
\( M_3, M_4, M_5 \) edges
essentially dipole transitions
\( M_4, M_5 \) from 3d to 5f
\( M_3 \) from 3p to 6d

D.B. McWhan et al. PRB 42, 6007 (1990)

C. Vettier Institut Laue Langevin 19 October 2005
resonant scattering

applications:

- large scattered intensities
- chemical selectivity
- electronic selectivity
- probe of electronic densities of states
- Q=0 experiments - reflectometry - absorption - imaging

difficulties:

- how to interpret observed intensities?
- are intensities magnetic in origin?
- experimental limitations - absorption
resonant scattering

large intensities: many examples

but how to predict intensities?

scattering amplitude: matrix elements (dipole/quadrupole)

spin polarisation of electronic levels

presence of spin-orbit coupling!

<table>
<thead>
<tr>
<th>elements</th>
<th>edge</th>
<th>transition</th>
<th>intermediate states</th>
<th>energy (keV)</th>
<th>wavelength (Å)</th>
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<tbody>
<tr>
<td>3d</td>
<td>K</td>
<td>E1,E2</td>
<td>4p, 3d</td>
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<td>1.743</td>
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<td>L3</td>
<td>E1</td>
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<td>E2</td>
<td>5d</td>
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<td>L2,3</td>
<td>E1,E2</td>
<td>5d, 4f</td>
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<td>M4,5</td>
<td>E1</td>
<td>4f</td>
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<td>10.2</td>
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<tr>
<td>5f</td>
<td>L2,3</td>
<td>E1,E2</td>
<td>6d, 5f</td>
<td>17.17</td>
<td>0.722</td>
</tr>
<tr>
<td>U</td>
<td>M4,5</td>
<td>E1</td>
<td>5f</td>
<td>3.74</td>
<td>3.32</td>
</tr>
</tbody>
</table>

\[ \approx 0.01 \, r_0 \]
\[ \approx 1 \, r_0 \]
\[ \approx 0.1 \, r_0 \]
\[ \approx 100 \, r_0 \]
\[ \approx 10 \, r_0 \]
**resonant scattering - chemical selectivity**

**chemical selectivity** : absorption edges energies are element specific

<table>
<thead>
<tr>
<th>element</th>
<th>K edge (eV)</th>
<th>L1 edge (eV)</th>
<th>L2 edge (eV)</th>
<th>L3 edge (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>4492</td>
<td>498</td>
<td>403</td>
<td>399</td>
</tr>
<tr>
<td>Ti</td>
<td>4966</td>
<td>561</td>
<td>461</td>
<td>454</td>
</tr>
<tr>
<td>V</td>
<td>5465</td>
<td>623</td>
<td>520</td>
<td>512</td>
</tr>
<tr>
<td>Cr</td>
<td>5989</td>
<td>696</td>
<td>584</td>
<td>574</td>
</tr>
<tr>
<td>Mn</td>
<td>6539</td>
<td>769</td>
<td>650</td>
<td>639</td>
</tr>
<tr>
<td>Fe</td>
<td>7112</td>
<td>845</td>
<td>720</td>
<td>707</td>
</tr>
<tr>
<td>Co</td>
<td>7709</td>
<td>925</td>
<td>793</td>
<td>778</td>
</tr>
<tr>
<td>Ni</td>
<td>8333</td>
<td>1008</td>
<td>870</td>
<td>853</td>
</tr>
<tr>
<td>Cu</td>
<td>8979</td>
<td>1097</td>
<td>952</td>
<td>932</td>
</tr>
<tr>
<td>Zn</td>
<td>9659</td>
<td>1196</td>
<td>1045</td>
<td>1022</td>
</tr>
</tbody>
</table>

across 3d series

selecting chemical species by tuning photon energies to proper edge
resonant scattering - chemical selectivity

alloys, compounds, intermetallics
hetero-magnetic multilayers,

\( U_{1-x}Np_xRu_2Si_2 \)

antiferromagnetic system
incommensurate structure at \( x=0 \)
(neutron scattering)
magnetic intensity at \((00 \ 4+q)\)
separation of U and Np response

E. Lidström et al. PRB 61, 1375 (2000)
resonant scattering - chemical selectivity

temperature dependence of order parameters:

Np magnetism drives magnetism of U lattice
similarly, different edges couple to different electronic levels:

<table>
<thead>
<tr>
<th>edge</th>
<th>K</th>
<th>L1</th>
<th>L2</th>
<th>L3</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
<th>...</th>
</tr>
</thead>
<tbody>
<tr>
<td>core level</td>
<td>1s1/2</td>
<td>2s1/2</td>
<td>2p1/2</td>
<td>2p3/2</td>
<td>3s1/2</td>
<td>3p1/2</td>
<td>3p3/2</td>
<td>3d3/2</td>
<td>3d5/2</td>
<td>...</td>
</tr>
</tbody>
</table>

at each edge, dipole and quadrupole transitions couple to different bands

Holmium as an example

hexagonal crystal structure

helicoidal magnetic structure

propagating along c-axis

magnetic Bragg peaks at \((h,k,l)+(0,0,\tau)\)
Holmium ordered phase at the L$_3$ edge (8.07 keV)

L$_3$ E1 leads to 5d states, E2 leads to 4f states

D. Gibbs et al. PRL 61, 1241 (1988)
resonant scattering - electronic selectivity

unpolarised resonant harmonics

polarisation analysis
\(\sigma-\sigma\) and \(\sigma-\pi\)

separation \(E_1/E_2\)

d states
f states

D. Gibbs et al. PRB 43, 5663 (1991)
resonant scattering - resonant harmonics

temperature dependence of high-order harmonics

test for scaling theories

mean-field not quite right!

G. Helgesen et al., PRB 50, 2990 (1994)
valence state selectivity

Coexistence of 2 valence states
$\text{Tm}^{2+}(4f^{13})$ and $\text{Tm}^{3+}(4f^{12})$

time scales?

L3 edge  dipole transitions to 5d states

D.B. McWhan et al. PRB 47, 8630 (1993)
resonant scattering - electronic selectivity

application to the observation of induced magnetic moments

Samarium metallic rare-earth

exchange mediated by 5d electrons

spin-polarisation of 5d bands follows 4f polarisation!

A. Stunault at al. PRB 65, 64436 (2002)
resonant scattering - selectivity?

$\text{UGa}_3$ simple antiferromagnet

strong resonance at the M4,5 edges of U

but resonance at K-edge of non-magnetic Ga

similar effects at K-edge of As in UAs!

K-edge transition from s to p bands

no large polarization expected!

not observed with neutrons nor Mössbauer

asymmetry between up/down orbitals . . . .

D. Mannix et al. PRL 86, 4128 (2001)
resonant scattering - spectrometry?

observation of density of unoccupied electronic states!

simple energy line-shapes

UAs : M$_{4,5}$ edges
E1 transition to 5$f$ states

Ho : L$_3$ edge
E1 transition to 4$f$ states
E2 transition to 5$d$ states
Sm: L$_3$ edge
E1 transition to 4$f$ states
complex and broad
E2 transition to 5$d$ states
resonant scattering - spectrometry?

RbMnF$_3$

K edge of Mn$^{2+}$

K-edges are special

E$_1$ transitions to $p$ states

complex and very broad

E$_2$ transitions to $3d$ states

very weak E$_2$

no orbital moment

observed in other systems

difficult to analyse!
Q=0 experiments

XMCD
soft x-ray range (low energy)
circular x-ray polarisation
element sensitivity

XMCD & PhotoElectron Emission Microscopy (PEEM)
imaging of magnetic domain/walls
Co/Cu/Ni trilayer
coupling mechanism through domain wall stray fields
importance for thin film technology

W. Kuch et al. PRB 67, 214403 (2003)
resonant scattering - difficulties

• how to interpret observed intensities?
  no simple connection to magnetic moments
  data analysis involves evaluating band calculations

• experimental limitations - absorption
  large variation through the edge corrections?
  example NiO  K-edge of Ni.
resonant scattering - difficulties

- are intensities magnetic in origin?

**RESONANCE is a very GENERAL PROCESS**
the origin of the resonance can be very diverse

low local symmetry

incident photon promotes an electron (photo-electron) into an available electronic states (outer electronic shells).
these shells are sensitive to **local symmetry of the site**
probabilities of transition (similar to scattering amplitudes) depend on the orientation of the symmetry axes with respect to the incident polarisation (electrical field which actually induces the promotion of the electron)

**atomic structure factors** cannot be longer consider as **spherical objects**; they depend on the orientation of the object with respect to the incident polarisation (incident electrical field)

resonant scattering - difficulties

difficult but classical problem: symmetry allows resonant scattering but physical origin of the resonance to be determined by experiments.

examples:  
- low symmetry of crystal structures
- \( \text{MnF}_2 \) tetragonal structure
- magnetic order (local moments break the symmetry)
- orbital order (degenerate orbitals e.g. in a doublet are occupied preferentially with LRO)

see S. di Matteo
resonant scattering - difficulties

$\text{MnF}_2$

simple bct structure - Mn ions in low symmetry environment D2h

(001) reflex forbidden

Mn K-edge at (001) strong resonance

polarisation and azimuth dependence
resonant scattering - summary

what does resonant magnetic scattering bring about?

- large scattering intensities
- chemical selectivity
- electronic selectivity

- spectroscopy of available states
- imaging methods

can we use x-rays to replace neutron scattering?

NO!

inelastic scattering - and structure determinations
resonant scattering - summary

neutrons methods provide all what we know about magnetic structures

resonant x-ray scattering from UO$_2$ powder at M$_4$ edge!
only one powder line visible

C.G. Shull et al. PR 76, 1256 (1949)

magnetic x-ray scattering - summary

what do x-ray magnetic scattering bring about?

new features - not available before

- L/S separation
- chemical selectivity
- electronic selectivity
- spectroscopy of available states
- studies of micro-samples (surfaces !)
- imaging methods and time-resolved

but requires a lot of care and caution