2139-19

School on Synchrotron and Free-Electron-Laser Sources and their Multidisciplinary Applications

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Magnetic and resonant x-ray scattering

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Magnetic and resonant x-ray scattering

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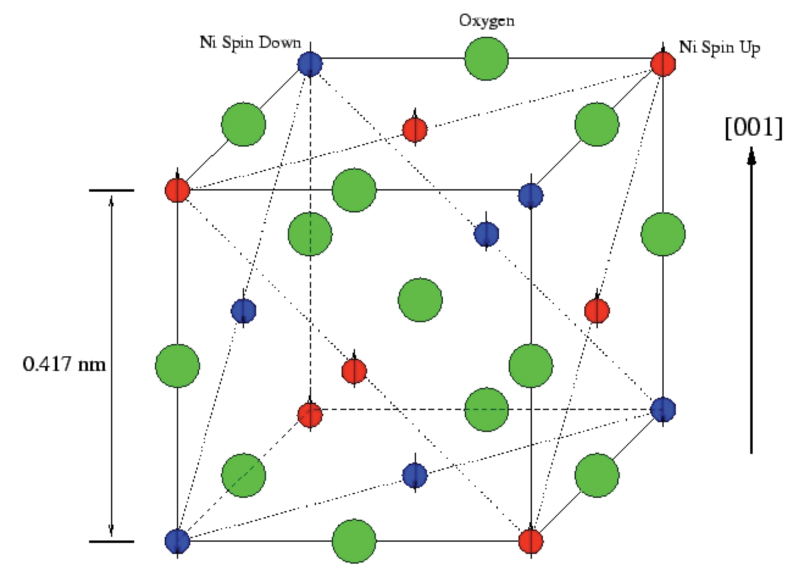
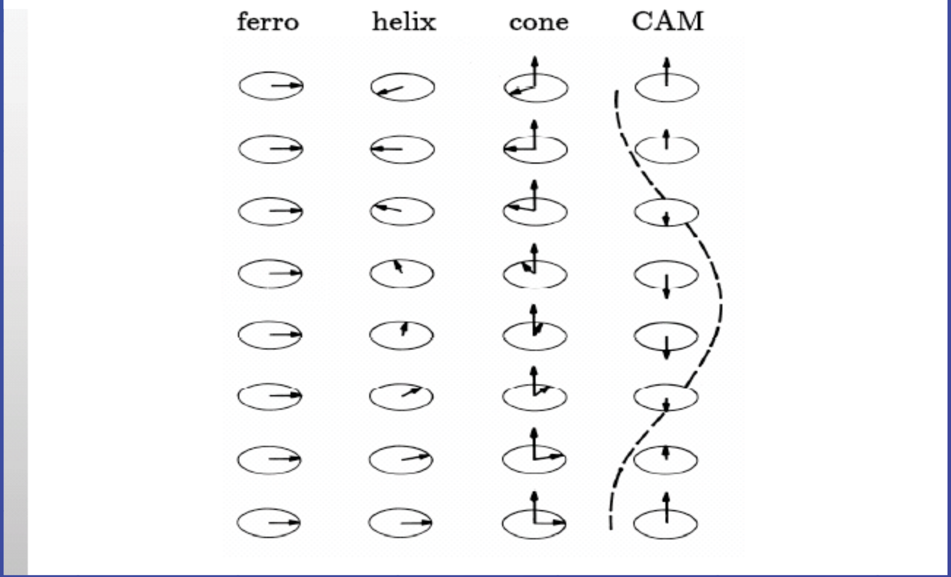
- Purpose and a bit of history
- Theoretical outline: non-resonant and resonant scattering
- Some examples

Large variety of magnetic structures

NiO



Rare Earths

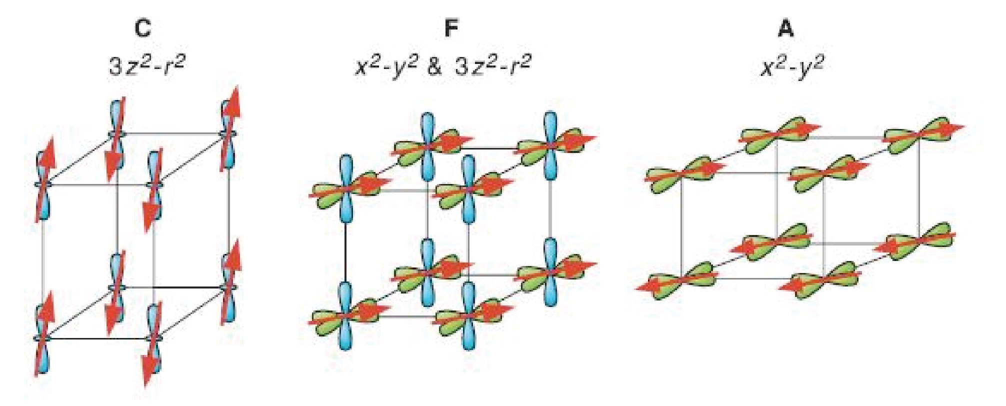


Gd,Tb,Dy Tb,Dy,Ho Ho,Er Er,Tm

Electronic orbital- (and spin-) ordered structures

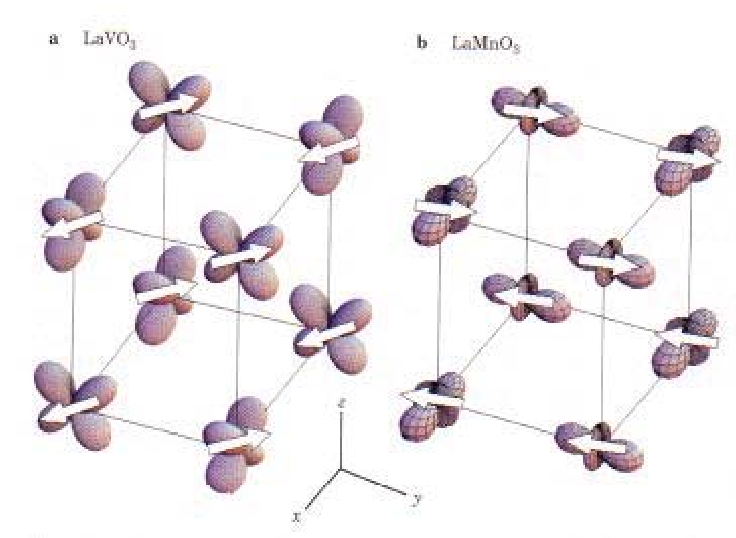
$La_{0.5}Sr_{0.5}MnO_3$ (Coherently strained)

Mn (3d)



$LaVO_3$

V (3d)



$LaMnO_3$

Mn (3d)

Determination of magnetic structures

- Standard probe: **neutron scattering**
- However **x-ray scattering** has some advantages:

  - is useful in the case of small samples

  - very ***high momentum resolution*** (period of incommensurate structures)

  - ***element sensitive*** (resonant)

  - possibility of a ***separate determination of spin and orbital contributions*** to the magnetic moment (by different polarization dependences, non-resonant)

Orbital structure: determination ?

- Orbital order: is often an experimentally hidden degree of freedom in correlated transition-metal oxides
- ***Resonant x-ray scattering: is a promising technique to probe orbital ordering***

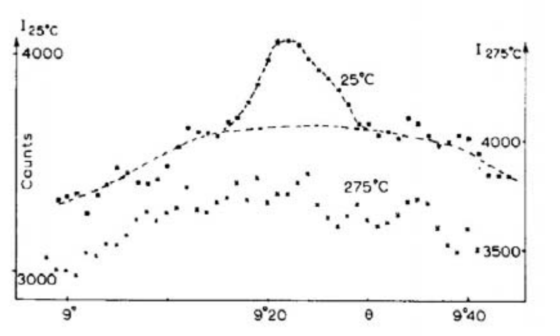
A bit of history

1972) First observation of x-ray magnetic scattering

Antiferromagnetic order in NiO by Bergevin and Brunel,

Phys. Lett. A39, 141 (1972)

Tube source: Counts per 4 hours!

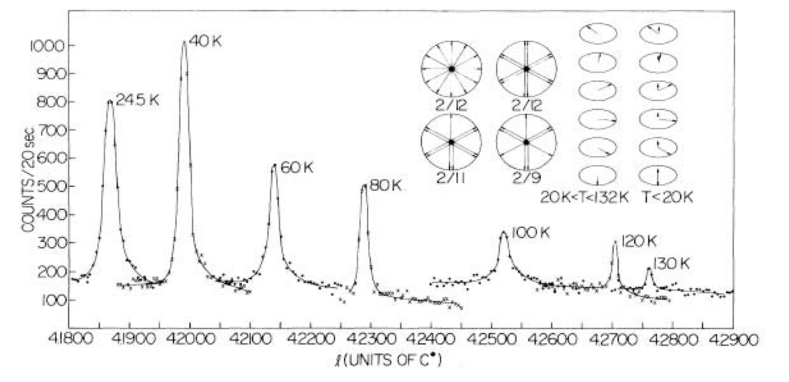


(1985) First Synchrotron radiation studies of magnetism

Magnetic x-ray scattering from Holmium,

Gibbs et al.,Phys. Rev. Lett. 55, 234 (1985)

Synchrotron source: Counts per 20s



More history

(1985) Start of the resonant time

Prediction of resonant effect by Blume, J. Appl. Phys. 57, 3615 (1985)

(1985) First resonant scattering from a ferromagnet

X-ray resonant magnetic scattering from Nickel by Namakawa (1985)

(1988) First resonant scattering from an antiferromagnet

Resonant x-ray scattering from Holmium by Gibbs et al., Phys. Rev. Lett. 61, 1241 (1988)

Since then magnetic and resonant x-ray scattering evolved from scientific curiosities to widely used techniques

Electromagnetic radiation - electron interaction

- Hamiltonian for electrons in an electromagnetic field (Blume 1985):

s_j spin 1/2

$$\vec{\mu}_j = \frac{e\hbar}{mc}\vec{s}_j$$

Kinetic term modified in the presence of the field

$\vec{\mu}_j \cdot \vec{B}$

$$H = \sum_j \frac{1}{2m}\left[\vec{p}_j - \frac{e}{c}\vec{A}(\vec{r}_j)\right]^2 + \sum_{i,j} V(r_{ij}) - \sum_j \frac{e\hbar}{mc}\vec{s}_j \cdot \vec{B}(\vec{r}_j)$$
$$-\frac{e\hbar}{2(mc)^2}\sum_j \vec{s}_j \cdot \left(\vec{E}(\vec{r}_j) \times \left[\vec{p}_j - \frac{e}{c}\vec{A}(\vec{r}_j)\right]\right) + H_{photon}$$

Spin-orbit term modified in the presence of the field

Hamiltonian of the radiation

With the fields **E** and **B** deriving from the vector and scalar potential **A** and ϕ:

$$\vec{B}(\vec{r}_j) = \vec{\nabla} \times \vec{A}(\vec{r}_j)$$

and

$$\vec{E}(\vec{r}_j) = -\vec{\nabla}\Phi(\vec{r}_j) - \frac{1}{c}\frac{\partial \vec{A}}{\partial t}(\vec{r}_j),$$

$$\vec{\nabla} = (\frac{\partial}{\partial x},\frac{\partial}{\partial y},\frac{\partial}{\partial z})$$

- Electromagnetic waves described by the vector potential:

$$\omega_k = ck$$

$$\vec{A}(\vec{r},t) = \sum_{\vec{k},\lambda}\left(\frac{hc^2}{\Omega\omega_k}\right)^{1/2}[\vec{\varepsilon}_\lambda a(\vec{k},\lambda)e^{i(\vec{k}\cdot\vec{r}-w_k t)} + c.c.]$$

Normalization box volume

Polarization vector λ=1,2

$$(\vec{k}\cdot\vec{\varepsilon} = 0)$$

Note: in the second quantization formalism, H_{photon} takes the simple form (quantized radiation field):

$$H_{photon} = \sum_{\vec{k},\lambda}\hbar\omega_k\left(a^+(\vec{k},\lambda)a(\vec{k},\lambda) + 1/2\right),$$

a^+ (a): photon creation (annihilation) operator

- Developing the Hamiltonian:

Hamiltonian for the electrons

$$H \approx \sum_j \frac{\vec{p}_j^{\,2}}{2m} + \sum_{i,j} V(r_{ij}) - \frac{e\hbar}{2(mc)^2} \sum_j \vec{s}_j \cdot \left(\vec{\nabla}\Phi_j \times \vec{p}_j\right)$$

$$+H_{photon}$$

Hamiltonian for the radiation

$$+\underbrace{\frac{e^2}{2mc^2} \sum_j \vec{A}^2(\vec{r}_j)}_{H_1} \underbrace{- \frac{e}{mc} \sum_j \vec{A}(\vec{r}_j) \cdot \vec{p}_j}_{H_2} \underbrace{- \frac{e\hbar}{mc} \sum_j \vec{s}_j \cdot \left(\vec{\nabla} \times \vec{A}(\vec{r}_j)\right)}_{H_3} \underbrace{- \frac{e\hbar}{2(mc)^2} \frac{e}{c^2} \sum_j \vec{s}_j \cdot \left(\frac{\partial A(\vec{r}_j)}{\partial t} \times \vec{A}(\vec{r}_j) \right)}_{H_4}$$

Interaction Hamiltonian
(will be treated as perturbation)

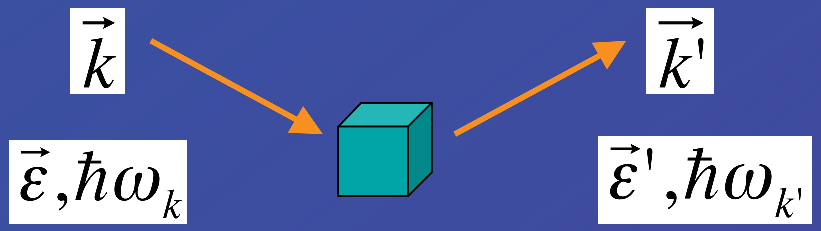
H_2, H_3 → **First order in A**

H_1, H_4 → **Second order in A**

H_3 and H_4 are related to the electron spin (linear dependence)

- We will here focus on elastic scattering

Elastic scattering processes:



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

Electronic ground state

Photon present in the initial state

$$|i>=|0;\ldots,(\vec{\varepsilon}_\lambda,\vec{k}),\ldots>$$

Photon present in the final state

$$|f>=|0;\ldots,(\vec{\varepsilon}'_{\lambda'},\vec{k}'),\ldots>$$

- Probability of transition (per unit time) from state |i> [electronic state |0>, photon (**ε**,**k**)] to state |f> [electronic state |0>, photon (**ε'**,**k'**)] :

(Fermi's "Golden rule")

Second order in A

First order in A

$$W = \frac{2\pi}{\hbar}\left| < f\,|\,H_1 + H_4\,|\,i > + \sum_n \frac{< f\,|\,H_2 + H_3\,|\,n >< n\,|\,H_2 + H_3\,|\,i >}{E_i - E_n}\right|^2 \delta(E_i - E_f)$$

$$= \frac{2\pi}{\hbar}\left|F(\vec{k},\vec{k}',\vec{\varepsilon},\vec{\varepsilon}')\right|^2 \delta(E_i - E_f)$$

F: scattering amplitude

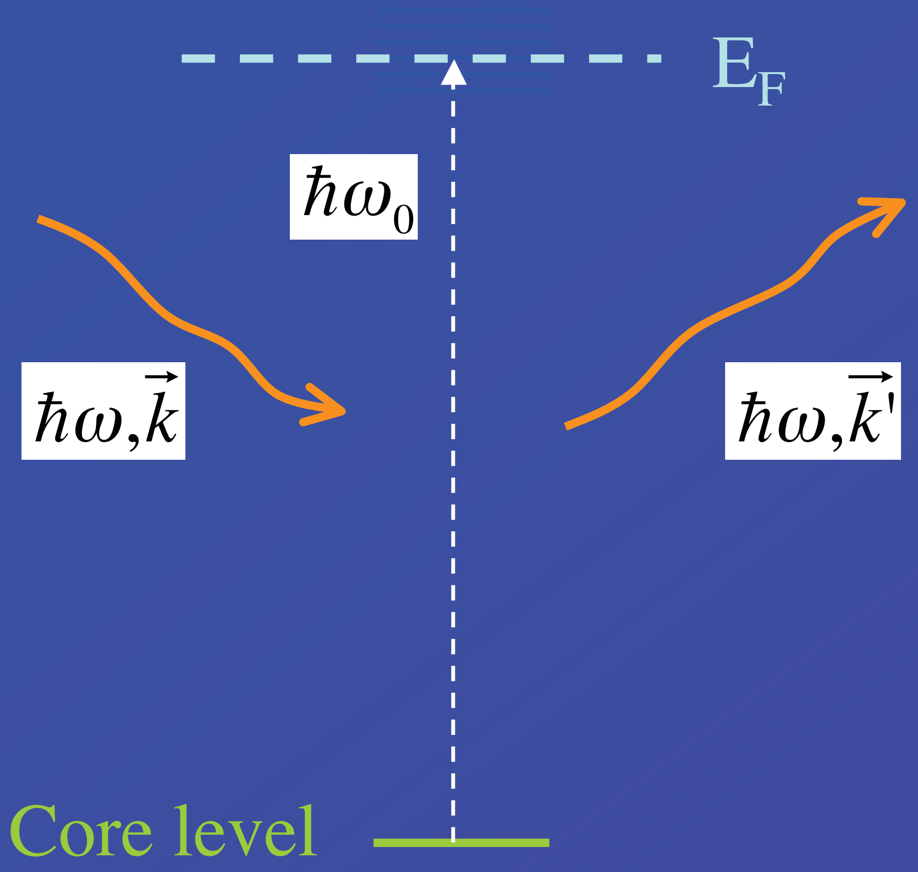
H_1 → Charge or Thompson scattering (crystallography)

$$E_i = E_0 + \hbar\omega_{\vec{k}}$$

A) $\hbar\omega_{\vec{k}} >> E_n - E_0$ → **Non-resonant diffraction**

B) $\hbar\omega_{\vec{k}} \approx E_n - E_0$ → **Resonant diffraction**

Non-resonant and resonant scattering



A) Non resonant:

$$\hbar\omega >> \hbar\omega_0$$

B) Resonant

$$\hbar\omega \approx \hbar\omega_0$$

Non-resonant and resonant scattering

A) Non-resonant case:

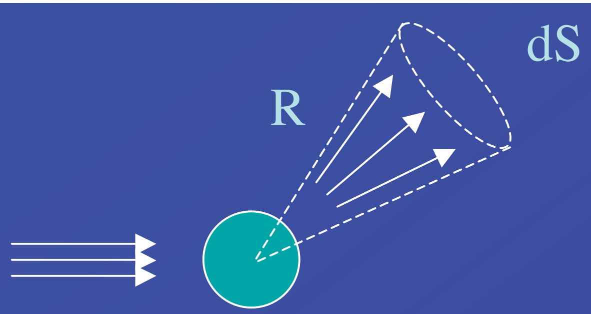
all four H_i contribute

B) Resonant case:

the contribution from $H_2 \sim \sum A(\mathbf{r}_j)\ \mathbf{p}_j$ dominates

- The quantity used to describe the intensity of the elastic scattering is the differential cross section:

$$\frac{d\sigma}{d\Omega} = \frac{\text{Number of photons per unit time scattered within } d\Omega}{\text{Number of incident photons per unit time per unit surface}}$$



$d\Omega = dS/R^2$

- Elastic scattering cross section for an assembly of N atoms:

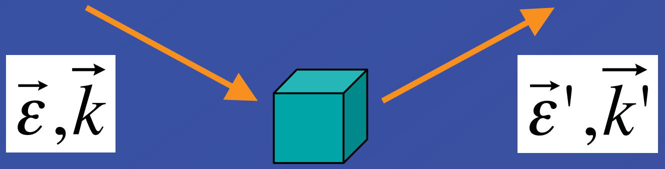
$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2}{mc^2}\right)^2 \left| \sum_N e^{i\vec{q}\cdot\vec{R}_n} F_N(\vec{k},\vec{k}',\vec{\varepsilon},\vec{\varepsilon}') \right|^2 ,$$

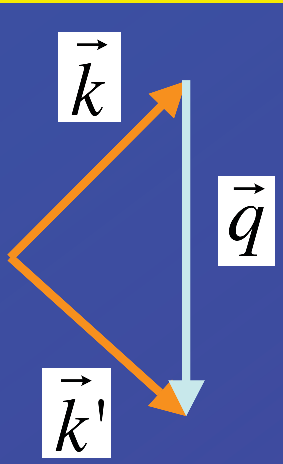
$\vec{q} = \vec{k} - \vec{k}'$

Periodic system: $\vec{q} \equiv \vec{G}_{hkl}$

F_N: atomic scattering amplitude

A) Non-resonant scattering amplitude





$$\vec{q} = \vec{k} - \vec{k}'$$

$$\hat{q} = \frac{\vec{q}}{q}$$

Scattering amplitude

Thompson
(charge scattering)

$$F^{non-res.} \propto \sum_j <0|e^{i\vec{q}\cdot\vec{r}_j}|0> (\vec{\varepsilon}'^* \cdot \vec{\varepsilon})$$

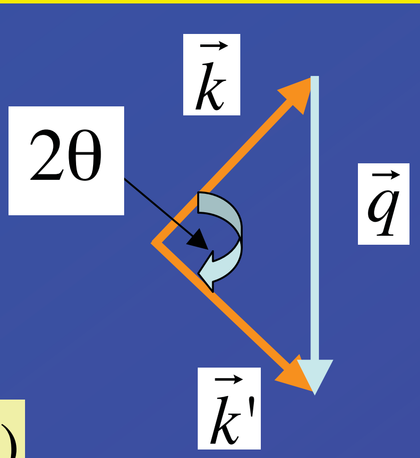
$$-i\frac{\hbar\omega_k}{mc^2}\left[\frac{mc}{e\hbar}<0|\hat{q}\times\left(\vec{M}_L(\vec{q})\times\hat{q}\right)|0>\cdot\vec{P}_L + \frac{mc}{e\hbar}<0|\vec{M}_S(\vec{q})|0>\cdot\vec{P}_S\right]$$

Small factor

Fourier transform of
orbital moment density

Fourier transform of
spin moment density

A) Non-resonant scattering

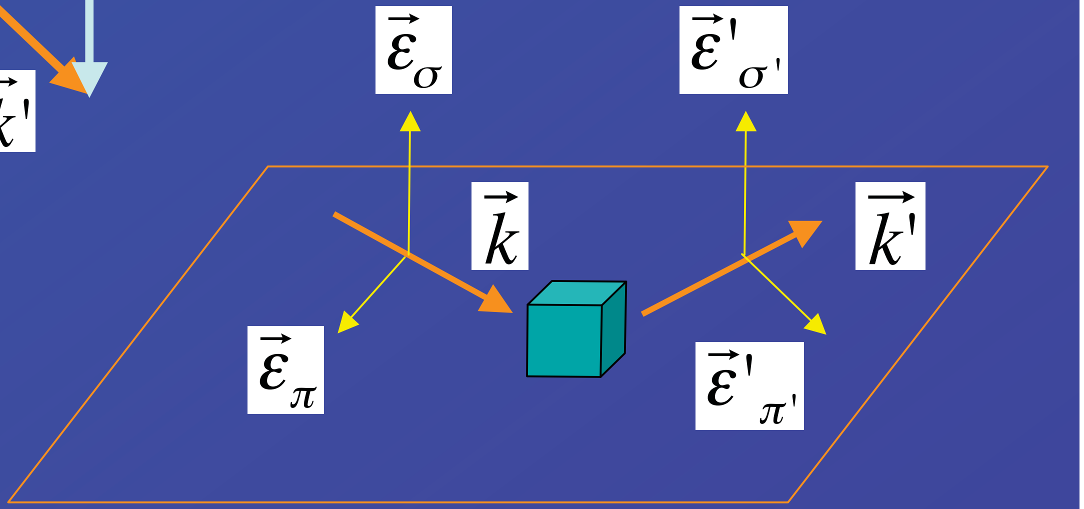


With:

$$\vec{M}_L(\vec{q}) = \sum_j e^{i\vec{q}\cdot\vec{r}_j}\vec{M}_L(\vec{r}_j)$$

$$\vec{M}_S(\vec{q}) = \sum_j e^{i\vec{q}\cdot\vec{r}_j}\vec{s}_j$$

$$\vec{P}_L = (\vec{\varepsilon}'^* \times \vec{\varepsilon})4\sin^2\theta$$



$$\vec{P}_S = \left[\vec{\varepsilon}'^* \times \vec{\varepsilon} + (\hat{k}'\times\vec{\varepsilon}'^*)(\hat{k}'\cdot\vec{\varepsilon}) - (\hat{k}\times\vec{\varepsilon})(\hat{k}\cdot\vec{\varepsilon}'^*) - (\hat{k}'\times\varepsilon'^*)\times(\hat{k}\times\vec{\varepsilon})\right]$$

A) Non-resonant scattering

1) **Has a mall intensity compared to Thompson scattering:**

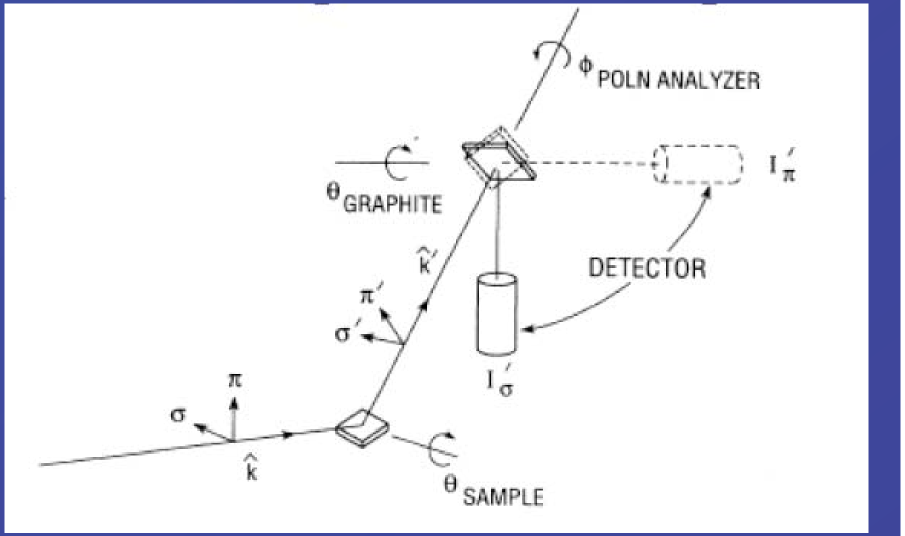
$$\left(\frac{\hbar\omega}{mc^2}\right)^2 \approx \left(\frac{\sim 10keV}{511keV}\right)^2$$

of the order 10^{-4}

2) **Has a very different polarization factors for the orbital M_L and spin M_S contributions to the magnetic moment**

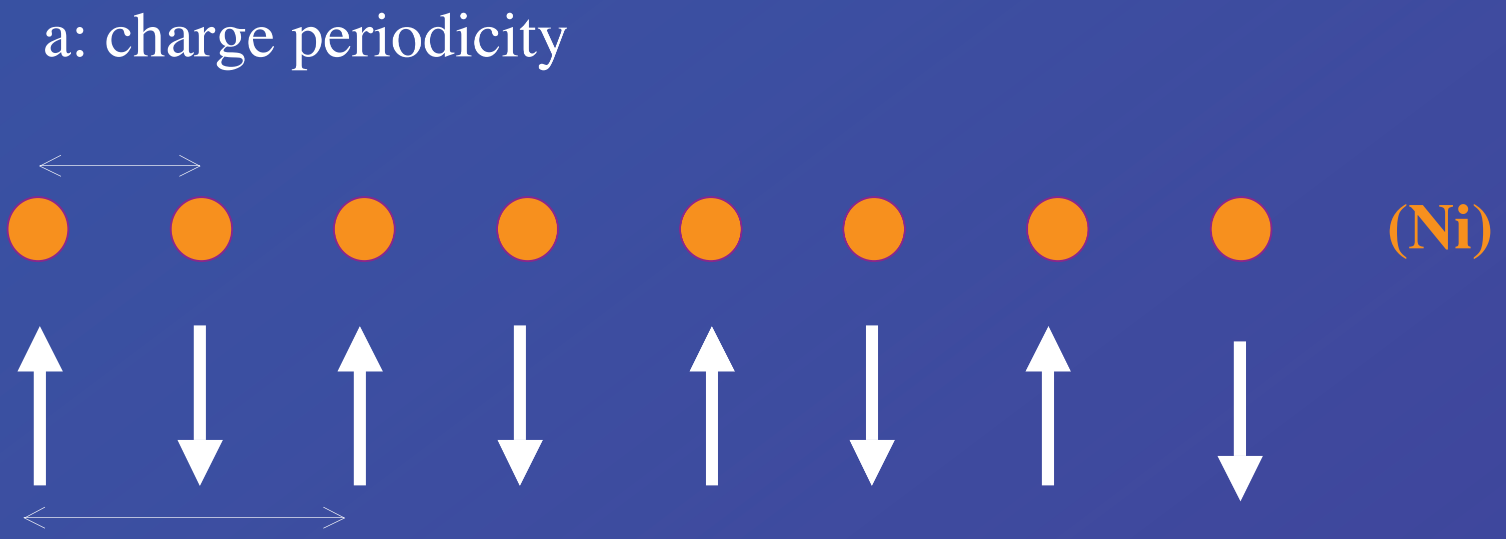
→ **L and S separation**

By selecting the incoming polarization and analyzing the outgoing polarization one can determine the orbital and spin moments



Magnetic scattering for an antiferromagnet

such as NiO

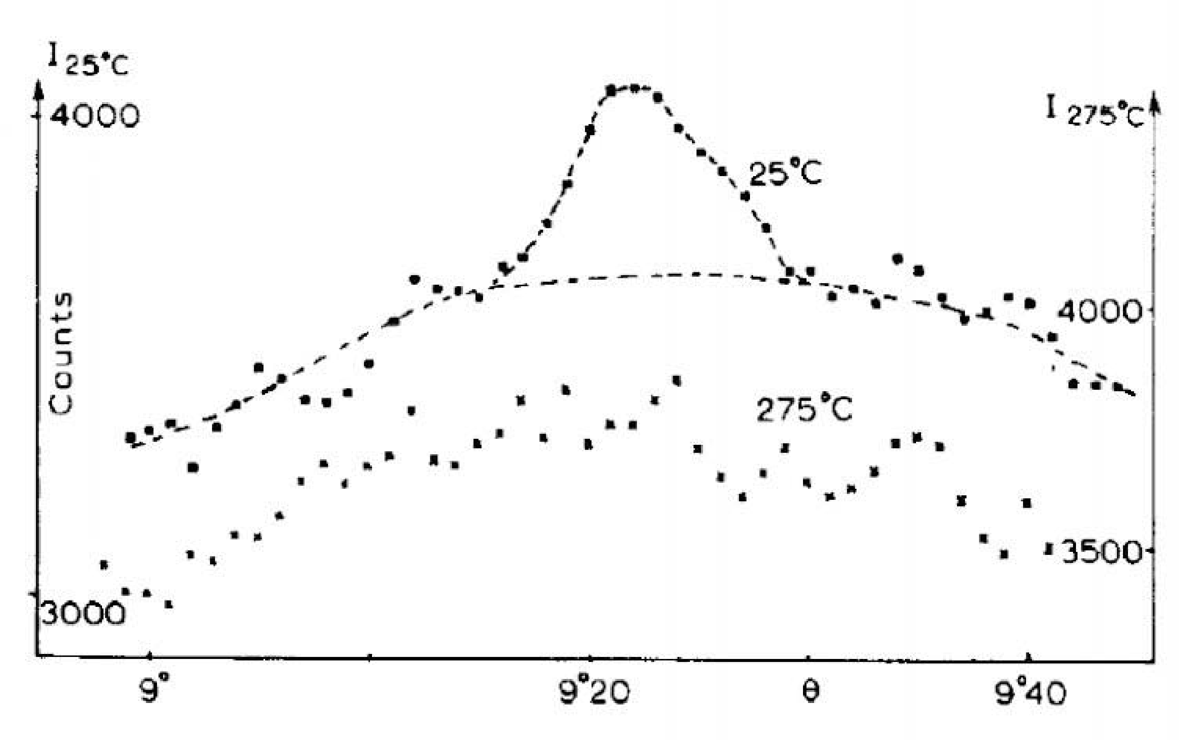

a: charge periodicity

2a: magnetic periodicity → additional reciprocal vectors (superstructure) compared to the charge scattering

First observation of x-ray magnetic scattering

De Bergevin and Brunel, Phys. Lett. A39, 141 (1972)
Antiferromagnetic order in NiO
Laboratory x-ray tube
NiO (3/2.3/2.3/2) reflection

Counts per ~ 4 hours



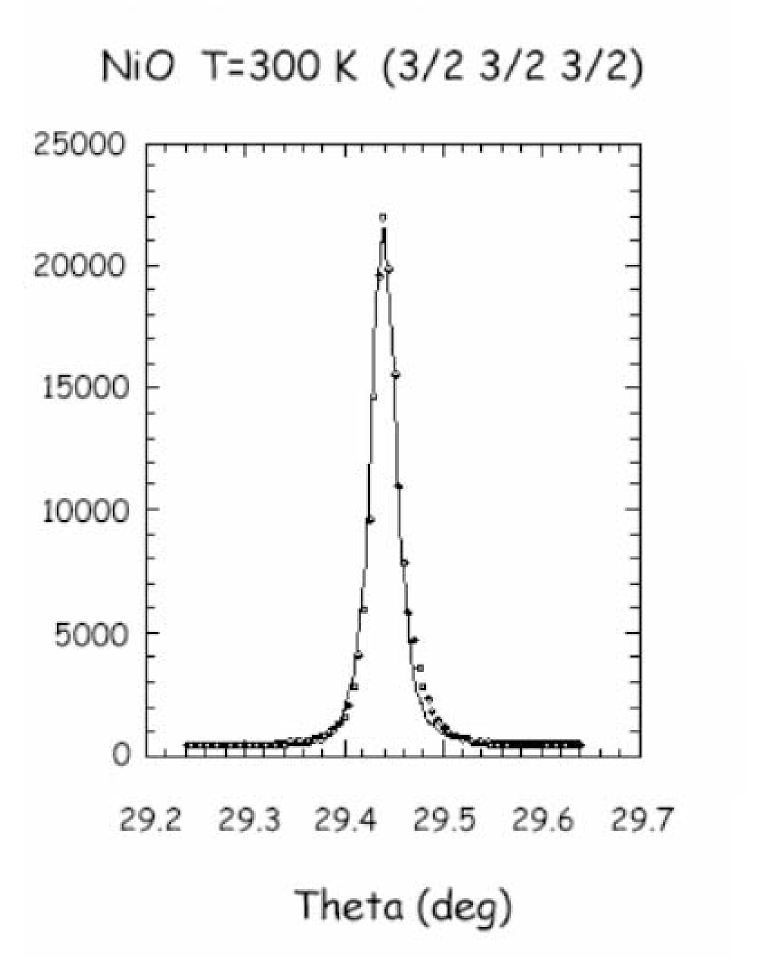
Theta (deg.)

X-ray magnetic scattering in NiO with synchrotron radiation

V. Fernandez et al,, Phys. Rev. B57, 7870 (1998)

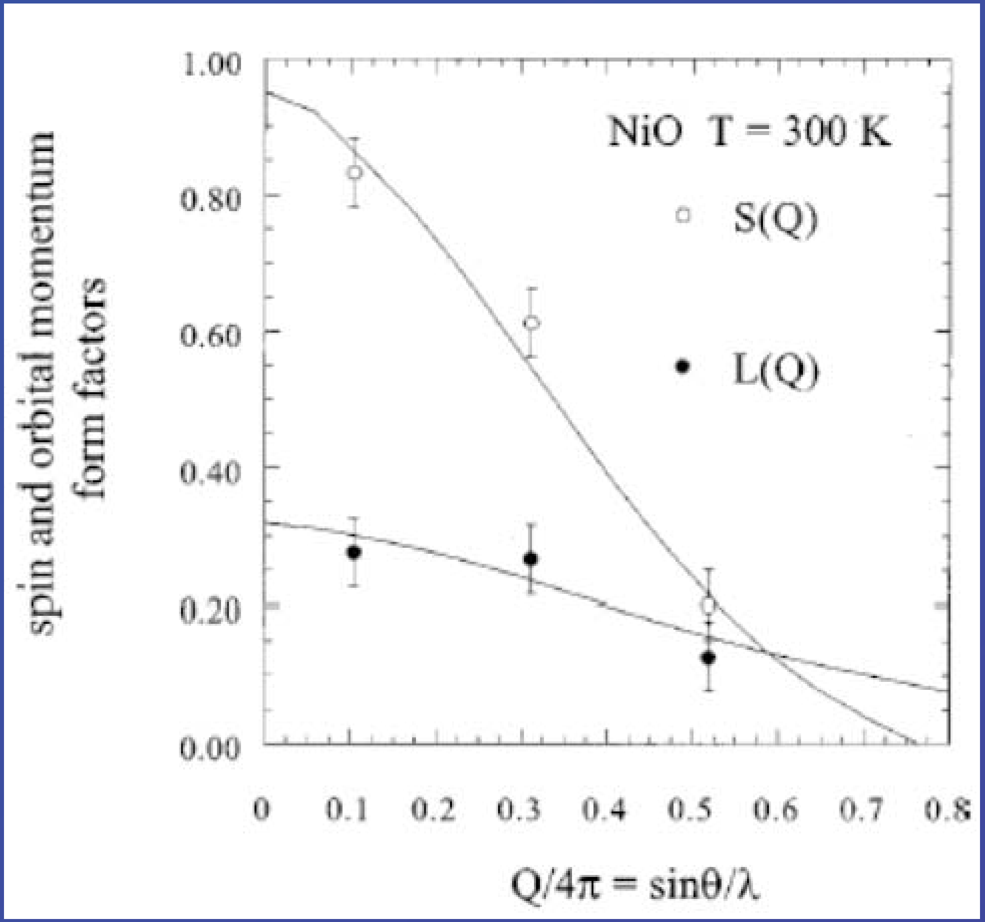
ESRF ID20 Beamline

(counts/s)



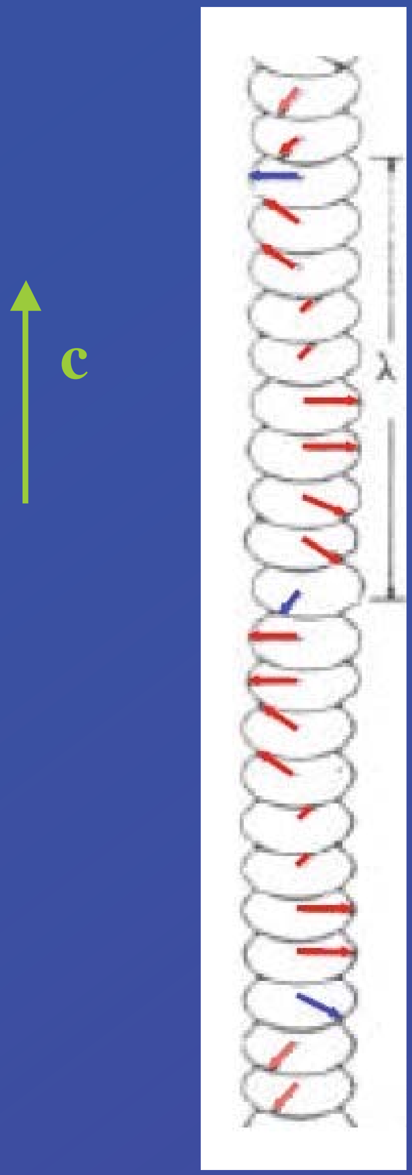
L and S separation for NiO

V. Fernandez et al,, Phys. Rev. B57, 7870



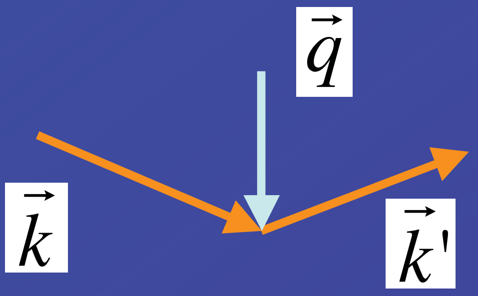
-> L/S=0.34

Application to Holmium magnetic structures



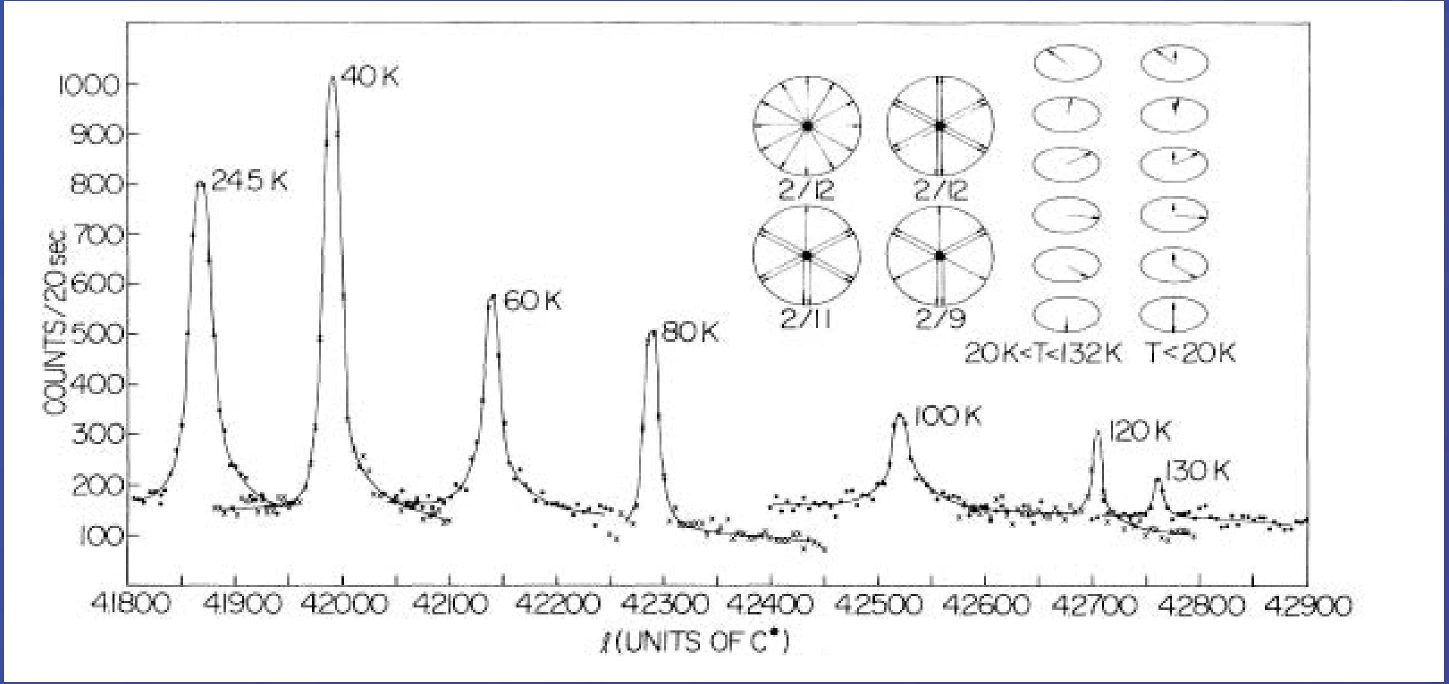
Helical phase (20<T<130K)
s rotate from plane to plane with turn angle that depends on T (incommensurate magnetic spirales; reciprocal vectors: $\boldsymbol{\tau}_m // \mathbf{c}$)
(for T< 20 K cone structure)

Scattering geometry:



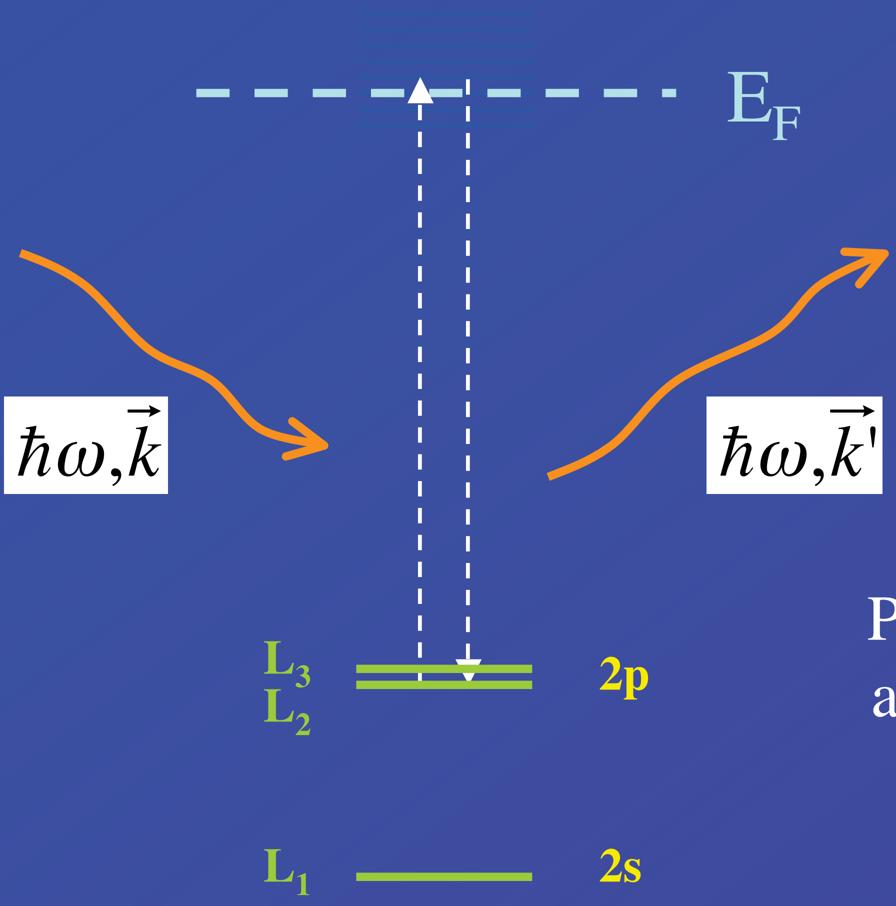
X-ray magnetic scattering in holmium with synchrotron radiation

D. Gibbs et al,, Phys. Lett. 55, 234 (1985)



Excellent momentum resolution

B) Resonant scattering



Photon energy resonant with a core level absorption edge

Resonant elastic x-ray scattering is a second order process in which a core electron is virtually promoted to some intermediate states above the Fermi energy, and subsequently decays to the same core level

B) Resonant scattering amplitude

Scattering amplitude

$$F^{res.} \propto \sum_n \frac{<0|\vec{\varepsilon}^* \cdot \vec{p} e^{i\vec{k}\cdot\vec{r}} \, |n><n|\vec{\varepsilon}' \cdot \vec{p} e^{-i\vec{k}'\cdot\vec{r}} \, |0>}{E_n - E_0 - \hbar\omega + i\Gamma/2}$$

Multipole expansion: $e^{i\vec{k}\cdot\vec{r}} \approx 1 + i\vec{k}\cdot\vec{r} + \ldots$

Strength of the transition depends on:

- -overlap integrals
- -transition order

In transition metals: $L_{2,3}$ edge **2p -> 3d** (dipolar) 0.4-1keV **strong**

B) Resonant magnetic scattering

1) **Has a large intensity** (10^2-10^4 times larger than non-resonant)

2) **Is element sensitive** (from the core level binding energy)

3) **Is less directly related to the magnetic moments** (but is energy dependent -> spectrum)

Dipole-dipole scattering: Hannon-Trammel formula

Hannon et al., Phys. Rev. Lett. 61, 1245 (1988)

$$F^{res.} = -\frac{e^2}{mc^2}\left[(\vec{\varepsilon}'^{*}\cdot\vec{\varepsilon})f^{(0)} - i(\vec{\varepsilon}'^{*}\times\vec{\varepsilon})\cdot\hat{z}_n f^{(1)} + (\vec{\varepsilon}'^{*}\cdot\hat{z}_n)(\vec{\varepsilon}'\cdot\hat{z}_n)f^{(2)}\right]$$

Anomalous dispersion	XRMS (re: circular dichroism)	XRMS (re: linear dichroism)

$\hat{z}_n$ is a unit vector parallel to the magnetic moment of the nth ion

$f^{()}$ are linear combination of the components of the atomic scattering tensor $f_{m,m'}$

Note:the Hannon-trammel formula is valid for local atomic site symmetry C_{4h} or higher - see, e.g., Stojic et al., Phys. Rev. B 72, 104108 (2005)

$L_{2,3}$ edge scattering in *3d* transition-metal compounds

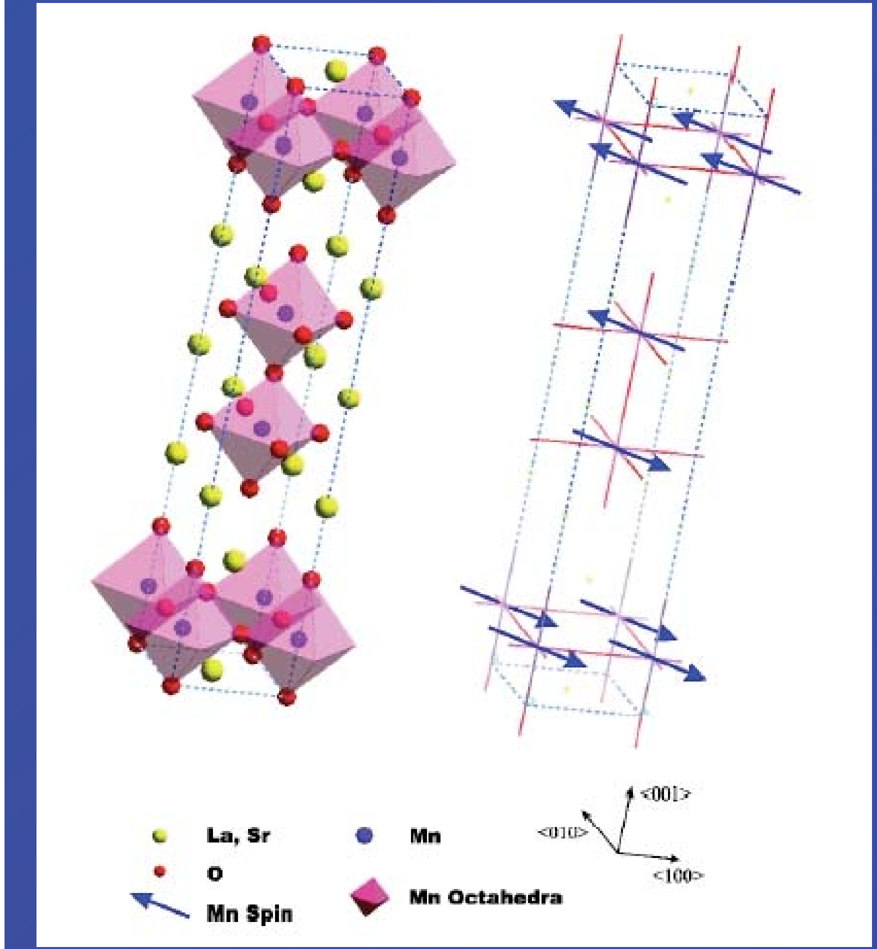
2p -> 3d: directly probes the magnetic electronic states

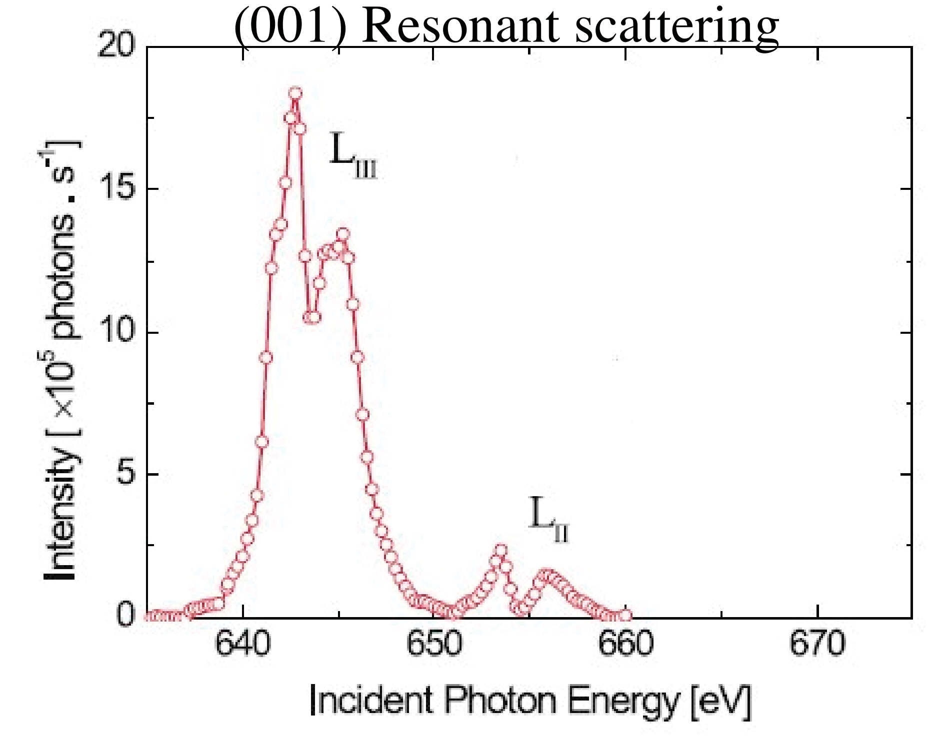
Soft x-ray magnetic scattering probes structures with long periods:

- Artificial superstructures/multilayers
- Complex crystals with large lattice or magnetic unit cells

Soft x-ray resonant magnetic scattering at the Mn $L_{2,3}$ edges in $La_{2-2x}Sr_{1+2x}Mn_2O_7$

Wilkins et al., Phys. Rev. Lett. 90, (2003)



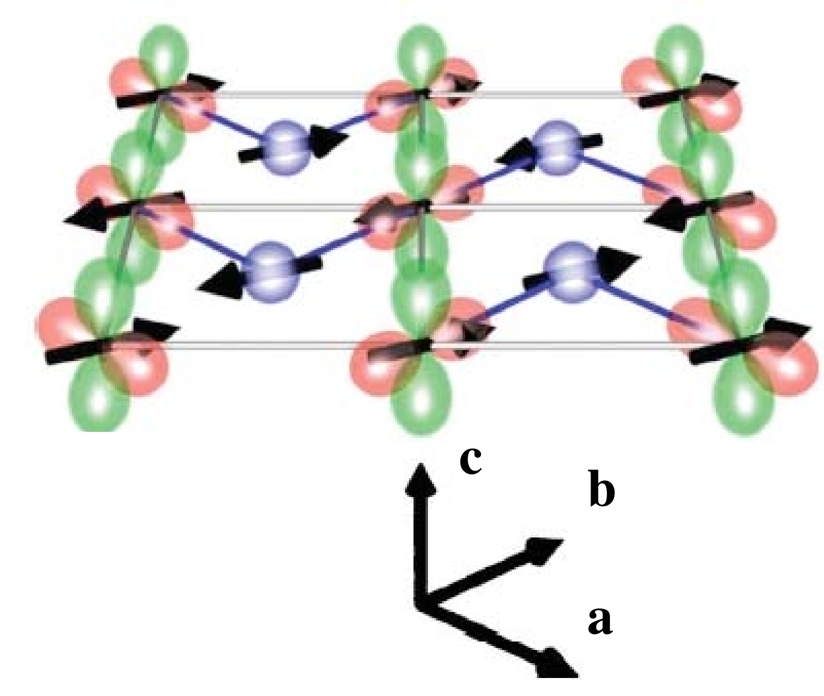


(001) scattering due to AFM magnetic scattering (charge scattering -non-resonant- found to be much weaker)

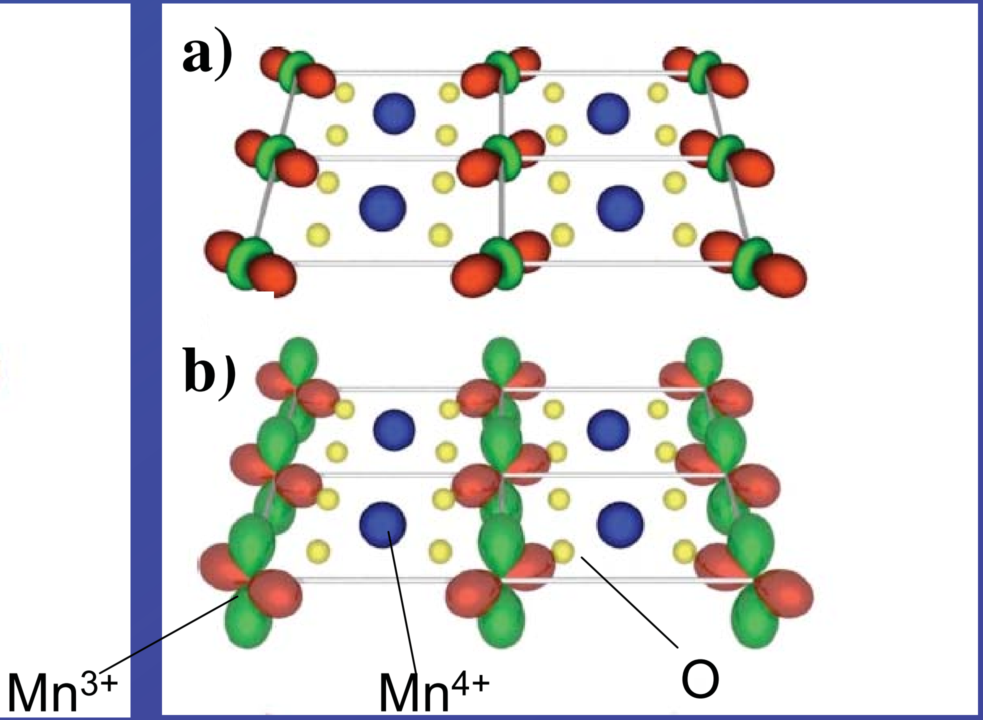
Soft x-ray resonant scattering at the Mn $L_{2,3}$ edges in $La_{0.5}Sr_{1.5}MnO_4$

Wilkins et al., Phys. Rev. B 71, 245102 (2005)

Magnetic order



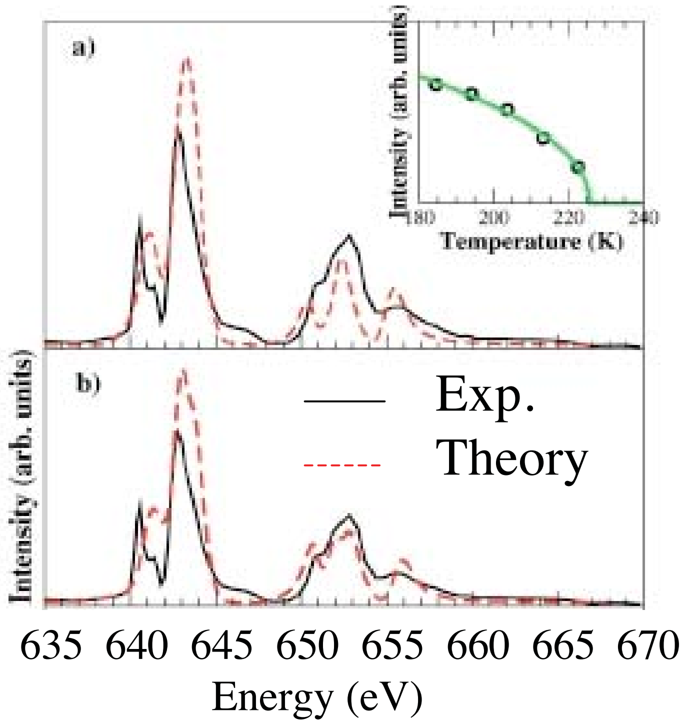
Mn 3*d*-orbital order



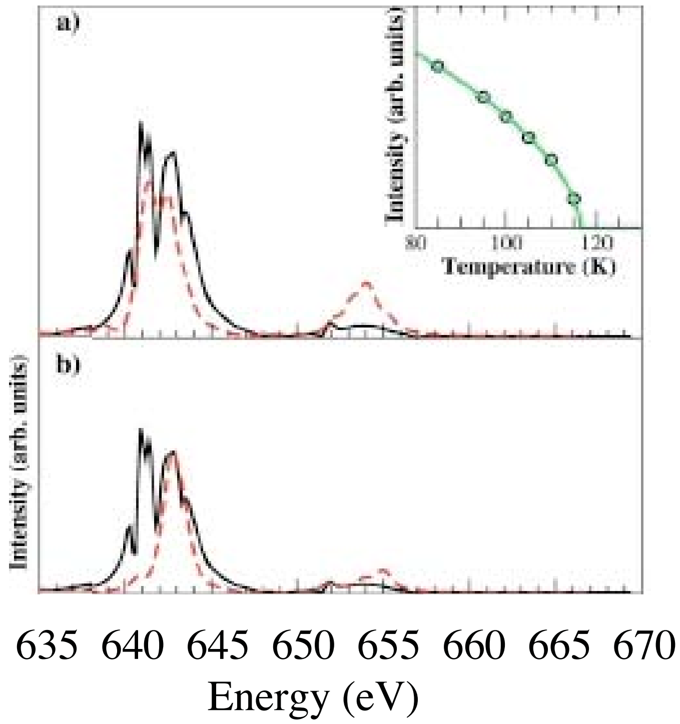
Soft x-ray resonant scattering at the Mn $L_{2,3}$ edges in $La_{0.5}Sr_{1.5}MnO_4$

Wilkins et al., Phys. Rev. B 71, 245102 (2005)

Orbital scattering (1/4,1/4,0)



Magnetic scattering (1/4,-1/4,1/2)



By comparison with atomic multiplet calculations in a crystal field: determination of magnetic & orbital structure; here -> a) x^2-z^2 /y^2-z^2