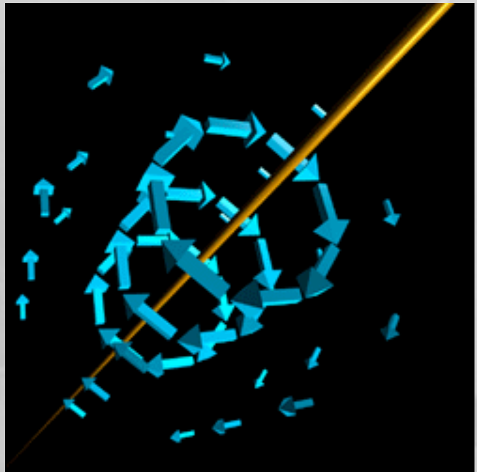
XIII School on Synchrotron Radiation:
Fundamentals, Methods and Applications
Grado, Italy / 14-25 September 2015
SOCIETA' ITALIANA DI LUCE DI SINCROTRONE
Elettra Sincrotrone Trieste

MAGNETIC AND RESONANT X-RAY DIFFRACTION



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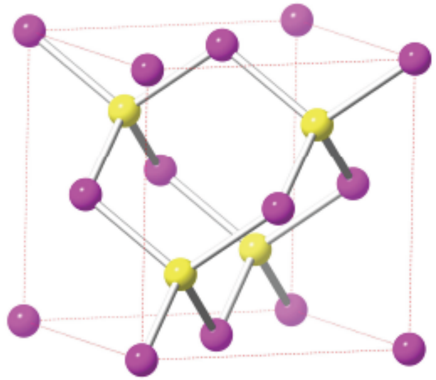
OUTLINES

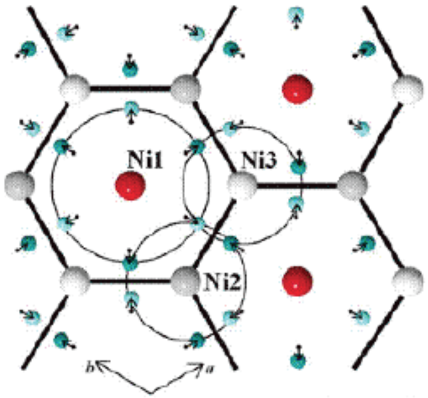
1. Magnetism and magnetic structures
2. Theory of x-ray magnetic and resonant scattering
3. Experimental methods: polarized x-rays
4. Non-resonant magnetic scattering
5. Resonant x-ray scattering and high order multipoles

ELASTIC SCATTERING: GROUNDSTATES AND ORDER

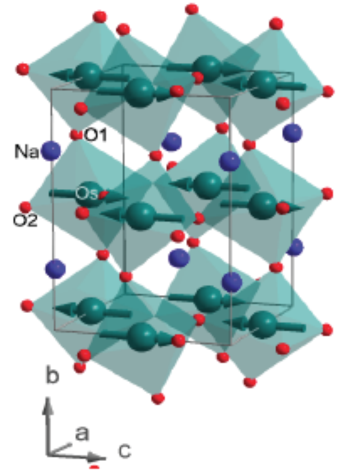
Charge density

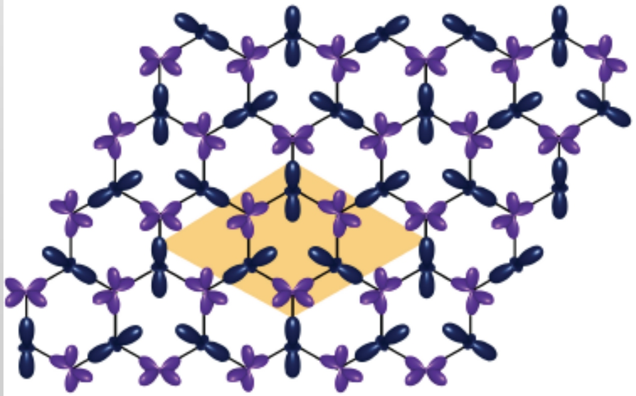


Charge order

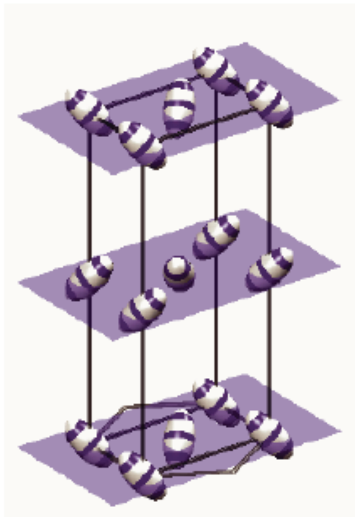


Magnetic order

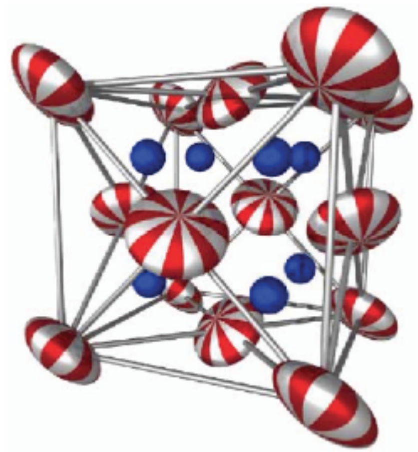




Orbital order



Quadrupolar order



Octupolar order

INGREDIENTS FOR MAGNETISM

- Intra atomic magnetic properties
  - Single ion properties
  - Fine structure

  ex. Rare Earth compounds

Intra atomic exchange

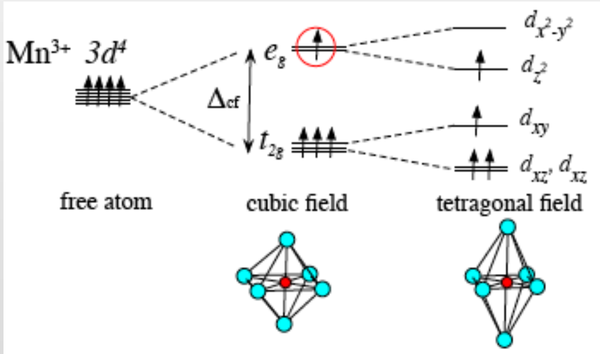
Pauli fermion exclusion

Spin-orbit coupling

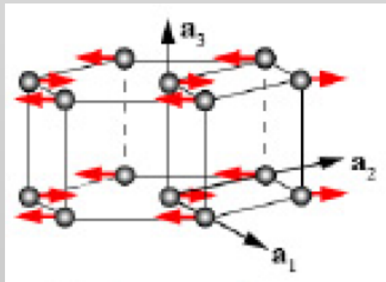
Hund's rules:
max S
max L
J = L+S or |L-S|

- Crystal electric field perturbs the atomic magnetism
  - Coulomb repulsion vs hopping transfer
  - Breaking of Hund rules
  - Quenching of orbital momentum
  - Magnetic anisotropy

  ex. Transition metal oxides



- Inter atomic magnetic interactions induce long range order
  - Isotropic exchange H=J **S·S** (Heisenberg)
  - Anisotropic exchange H=**S** J̲ **S** (Dzyaloshinsky-Moriya)
  - Super-exchange and double-exchange
  - Itinerant exchange (RKKY)



The Structure factor F(hkl) describes the interference between the resultatant waves diffused from each atom in the unit cell for any given reciprocal lattice vector $Q=G_{hkl}$ i.e.:

$$\left(\frac{d\sigma}{d\Omega}\right)_{Bragg} = N\frac{(2\pi)^3}{v_0}\sum_{hkl}\delta(\mathbf{Q}-\mathbf{G}_{hkl})\ |F(hkl)|^2$$

N° unit cell *unit cell volume* ***Laue's condition***

$$F(hkl) = \sum_s f_s\ e^{i\mathbf{G}_{hkl}\cdot\mathbf{d}_s - W_s}$$

Structure factor: information about the atom distribution inside the unit cell

$$f_s = \int_{atom} \rho_s(\mathbf{r}')e^{-i\mathbf{Q}\cdot\mathbf{r}'}d\mathbf{r}'$$

f_s = atomic scattering amplitude for the atoms s related to the Fourier transform of the atomic electron density

MAGNETIC PROPAGATION VECTOR q_m

We want to define a way to describe the magnetic atoms inside an unit cell

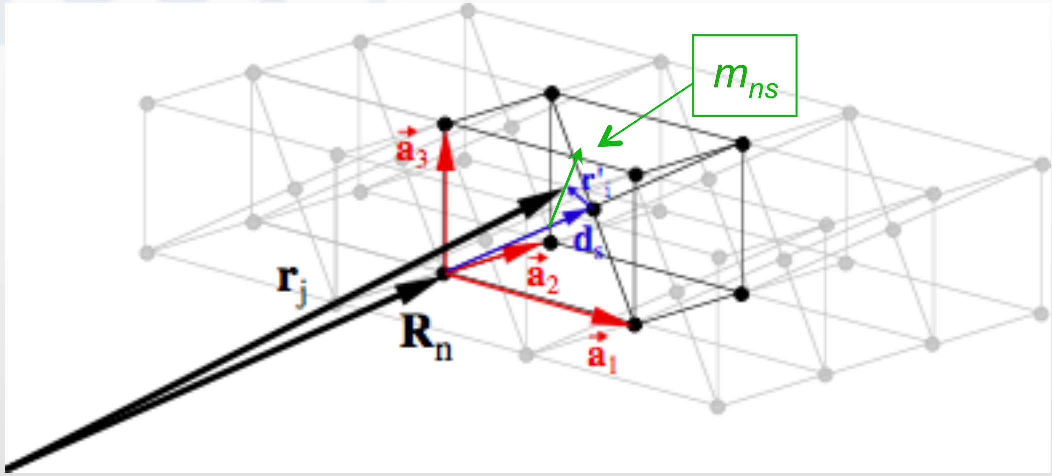
The magnetic propagation vector give information only on the periodicity of a magnetic structure and NOT on the orientation of the magnetic moments

- *The magnetic propagation vector* $\boldsymbol{q}_m$ *is a reciprocal vector*
- $\boldsymbol{q}_m$ *is a eigenfunction of the Translational Group*
- *It is defined inside the 1st Brillouin zone*
- *Describes the periodicity of a magnetic structures*
- *Perpendicular to the planes containing atoms with the same orientation of the magnetic moments*
- *The inverse of its modulus is equal to magnetic interplanar distances*

THE MAGNETIC MOMENT DISTRIBUTION m_{ns}

The magnetic moment distribution m_{ns} relative to the s-atom inside the n^{th}-lattice cell is equal to the Fourier transform:

$$\mathbf{m}_{ns} = \sum_{\mathbf{q}_m} \mathbf{m}_s^{\mathbf{q}_m} \; e^{-i\mathbf{q}_m \cdot \mathbf{R}_n}$$

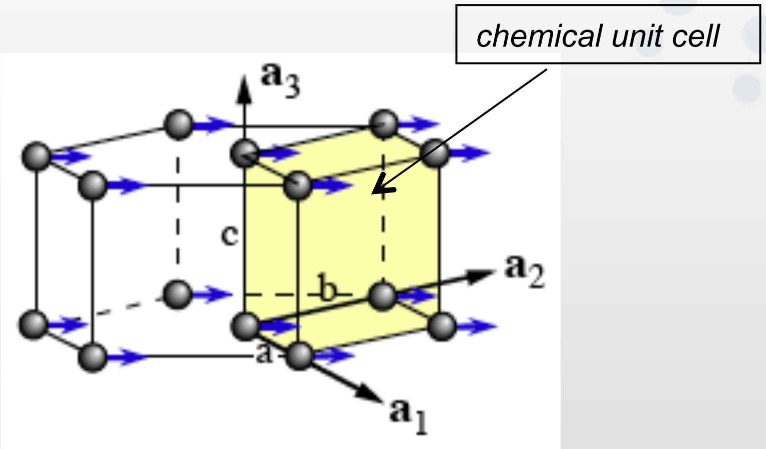


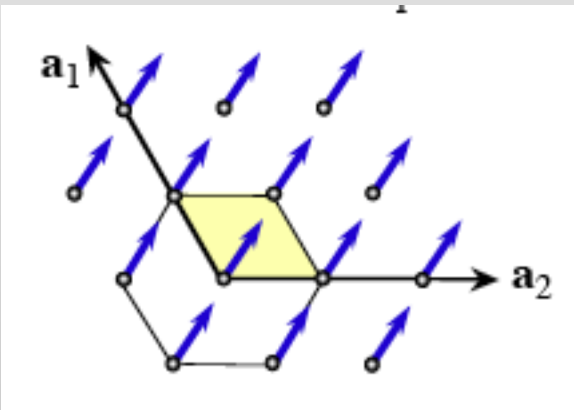
- m_{ns} *is a REAL vector !!!!*
- *The fase factor is real ONLY if q_m correspond to the 1st Brillouin surface (i.e. for ferro and antiferromagnetics)*
- *In general the for any q_m the sum must include $-q_m$ such that :*

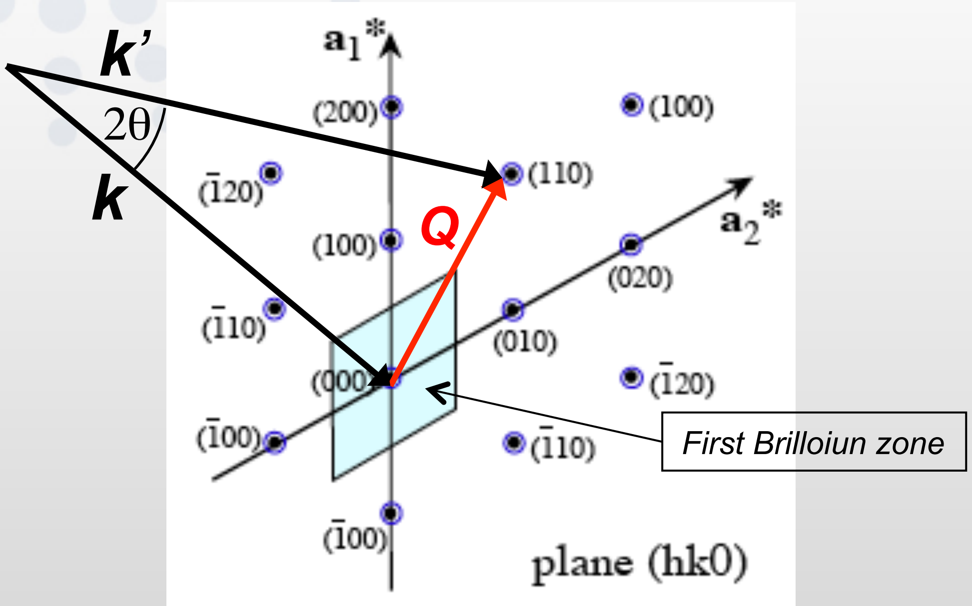
$$\mathbf{m}_{ns} = \mathbf{m}_s^{\mathbf{q}_m} \; e^{-i\mathbf{q}_m \cdot \mathbf{R}_n} + \mathbf{m}_s^{-\mathbf{q}_m} \; e^{i\mathbf{q}_m \cdot \mathbf{R}_n} = 2\,|\mathbf{m}_s^{\mathbf{q}_m}| \; \hat{\mathbf{u}} \; cos(\mathbf{q}_m \cdot \mathbf{R}_n + \phi)$$

Example 1: Ferromagnetic

- *All the magnetic moment* $\mathbf{m}_j$ *are parallel each others*
- *The magnetic and the chemical unit cells coincide*
- *Structural and magnetic reflections coincide*





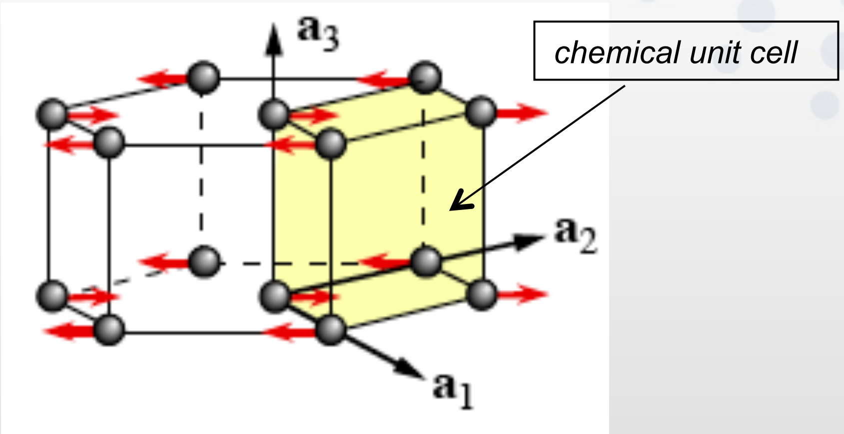


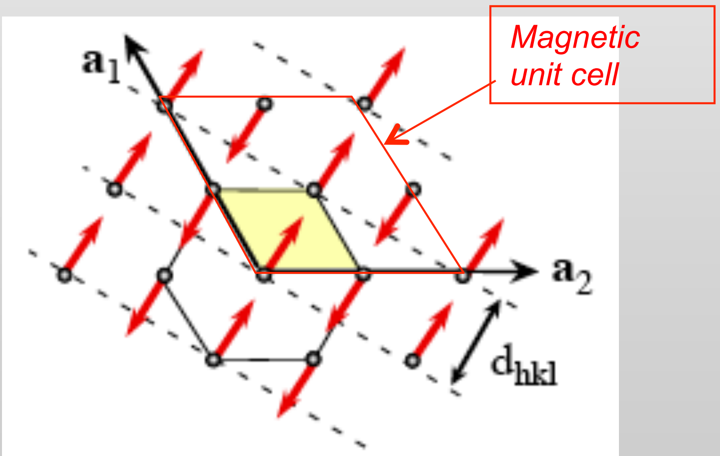
$$\mathbf{q}_m = (0,0,0)$$

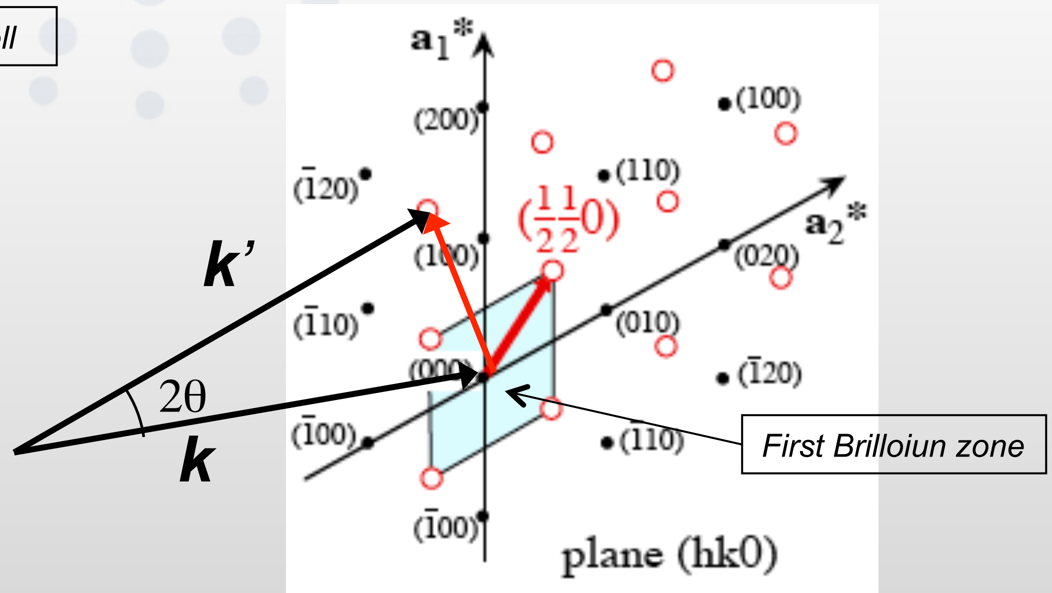
$$\mathbf{m}_{ns} = \mathbf{m}_0 = m_{01}\mathbf{a}_1 + m_{02}\mathbf{a}_2$$

Example 2: Antiferromagnetic

- *Adjacent planes contain antiparallel magnetic moment* $\mathbf{m}_j$
- *Magnetic cell integral multiple of the chemical unit cell (double)*
- *Magnetic reflections correspond to the symmetry points at the surface of the Brillouin zone*







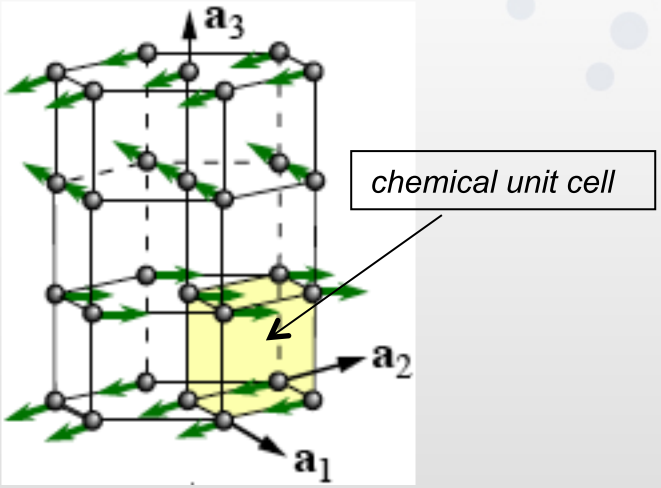
$\mathbf{q}_m$=(1/2,1/2,0)

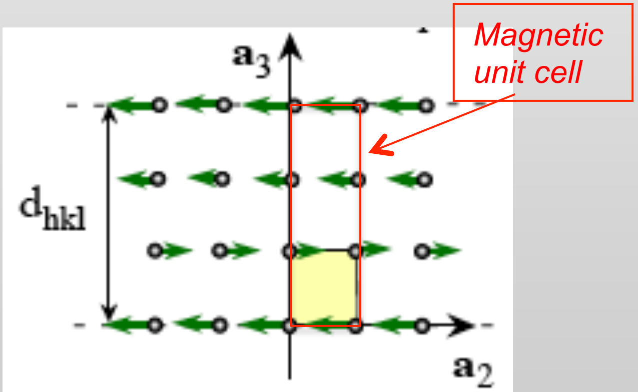
$\mathbf{m}_{ns} = (-)^n\, \mathbf{m}_0 = (-)^n\, (m_{01}\mathbf{a}_1 + m_{02}\mathbf{a}_2)$

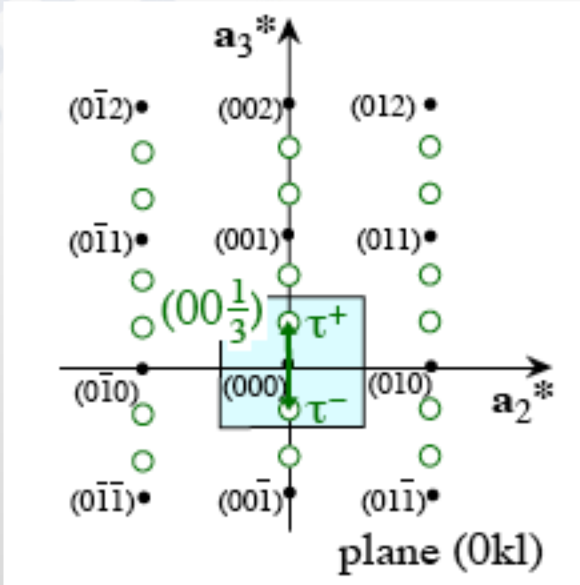
Example 3: Commensurate Helix

- *Propagation vector* $\boldsymbol{q}_m$ *have a non-integral periodicity*
- *In general both* $\boldsymbol{q}_m$ *and* $-\boldsymbol{q}_m$ *exists (indicated* τ^+ *and* τ^-*)*

The propagation vector $\boldsymbol{q}_m$ *inside the 1st Brillouin zone*





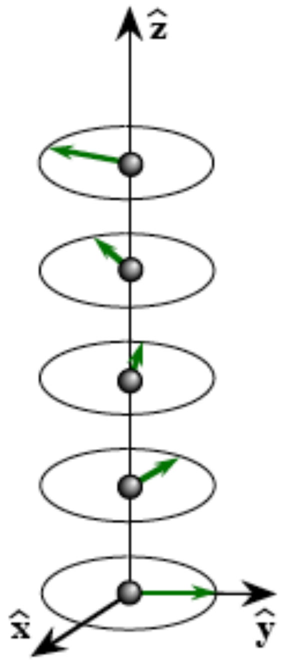


$\mathbf{q_m}$=(0,0,1/3)

$\mathbf{m}_{ns}=m_0[\cos(\mathbf{q}_m \cdot \mathbf{R}_n+\phi)\mathbf{u}_s+\sin(\mathbf{q}_m \cdot \mathbf{R}_n+\phi)\mathbf{v}_s]$

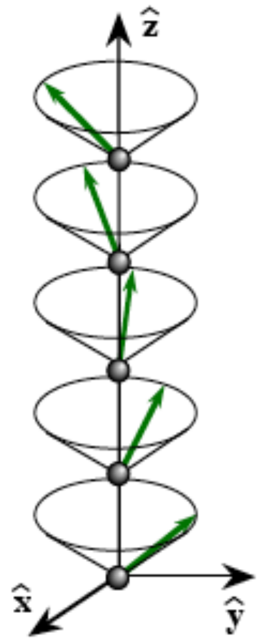
Non-collinear incommensurate magnetic modulations

a) Simple helix



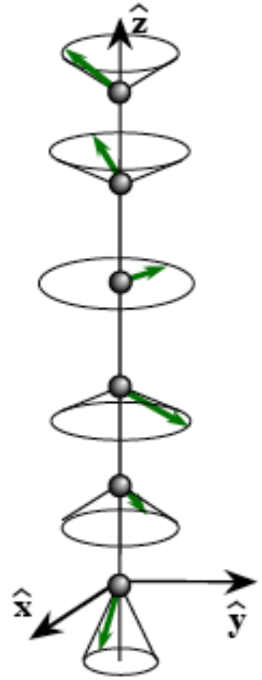
$$m_x = m_0 \cos\theta$$
$$m_y = m_0 \sin\theta$$
$$m_z = 0$$

b) Ferromagnetic helix

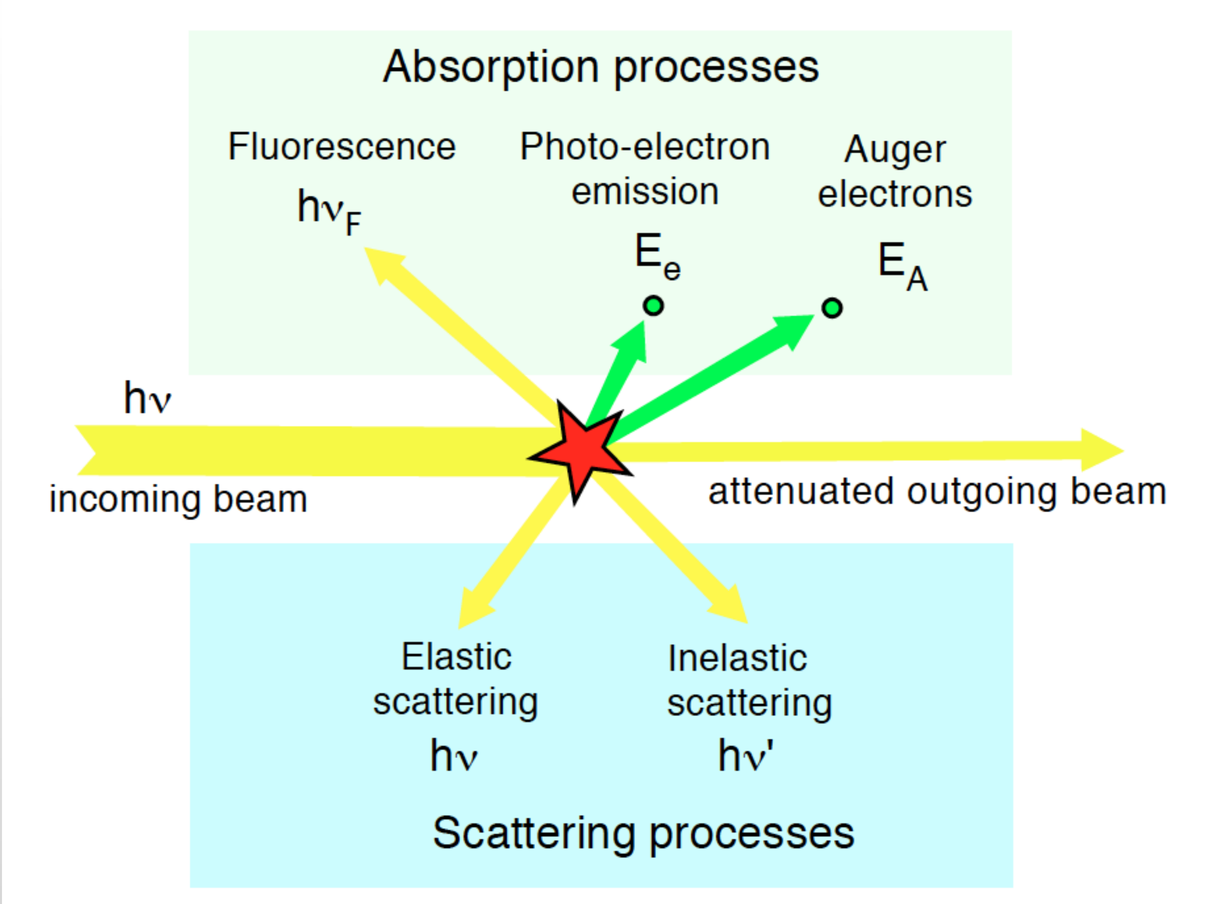


$$m_x = m_0 \cos\theta$$
$$m_y = m_0 \sin\theta$$
$$m_z \neq 0$$

c) Complex helix

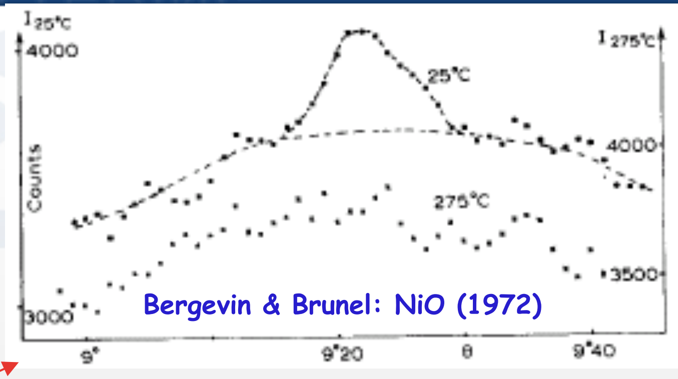


$$m_x = m_0 \cos\theta \sin\beta$$
$$m_y = m_0 \sin\theta \sin\beta$$
$$m_z = \cos\beta$$



Photon absorption :	Excitation with or without emission of electrons	
Photon scattering :	Elastic	=> Thomson and magnetic
	Inelastic	=> Compton (Raman)
	Resonant	=> Elastic or inelastic

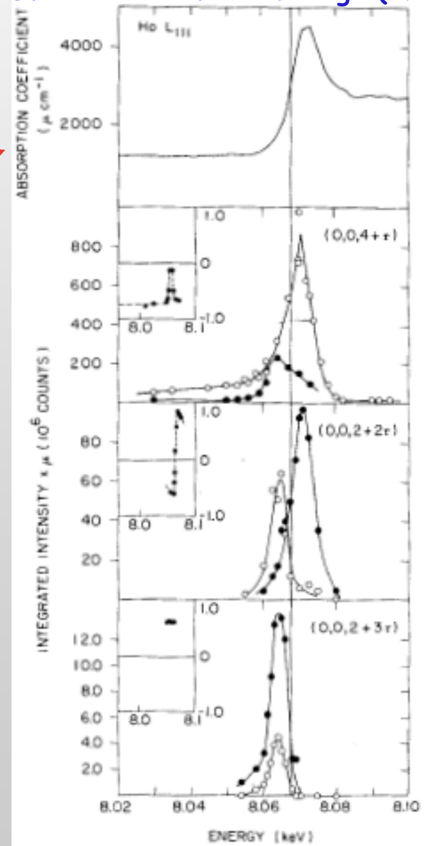
Theory photon-electron interaction
- Klein & Nishina: Compton scattering (1929)
- Bohr (1932)
- Gell-Mann & Goldberg (1954)
- Lowe (1955)



Pre-synchrotron works
- Platzman & Tzoar: Theory (1972)
- de Bergevin & Brunel: Theory and Exp.NiO, Fe_2O_3, MnO (1972,1981,1984)

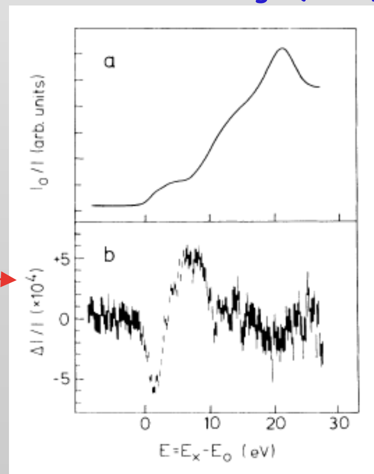
2nd generation synchrotron works

D. Gibbs et al.: Ho L-edge (1985)



Resonant Exchange scattering
- Blume (1985)
- Gibbs, Bohr, Moncton: Exp. Ho (1985,1986)
- Namikawa: Exp. Ni (1985)
- Hannon, Trammel, Blume, Gibbs: theory (1988)
- Vettier, Isaac, McWhan: Exp. UAs (1989)

G. Shutz: Fe K-edge (1987)



Magnetic circular dichroism
- Shutz: Exp. XMCD Fe (1987)
- Carra & Altarelli: Theory (1989)

THE ELECTROMAGNETIC FIELD

The electromagnetic field generated by the electrons is described by the electric **E** and magnetic **B** in term of scalar Φ and vector **A** potential:

$$\mathbf{B} = \nabla \times \mathbf{A}$$

$$\mathbf{E} = -\nabla\Phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}$$

Maxwell equations

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$$

$$\mathbf{B} = \mathbf{B}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$$

$$\mathbf{A} = \mathbf{A}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$$

The synchrotron radiation delivered by insertion devices is a polarized electromagnetic wave with polarization vector ε parallel to the electric field **E** and lying in the synchrotron orbit plane.

Energy

$\mathcal{E}$ [keV] = $\hbar\omega = hc/\lambda = 12.398 / \lambda$ [Å]

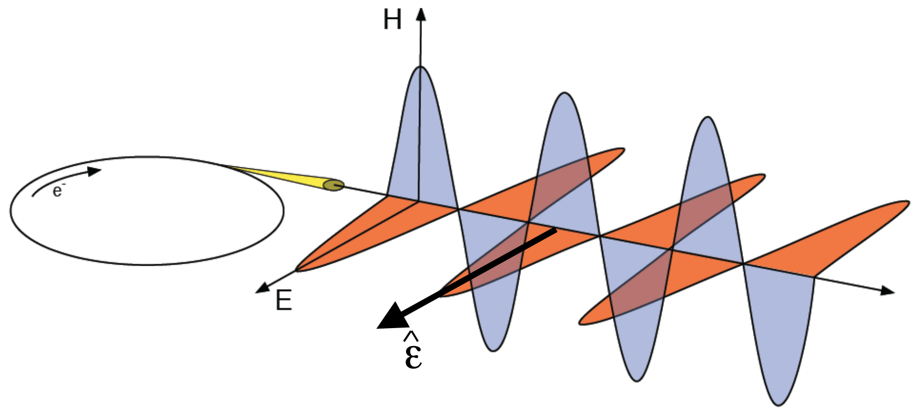
Spectral intensity

$I_0(\omega) = \langle E_0^2 \rangle = N(\omega)\, \hbar\omega$

ex. 1 Å = 12.398 keV

Transverse EM waves

$$\vec{\mathbf{E}}(\vec{\mathbf{r}}, t) = \hat{\epsilon} E_0 e^{i(\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}-\omega t)}$$

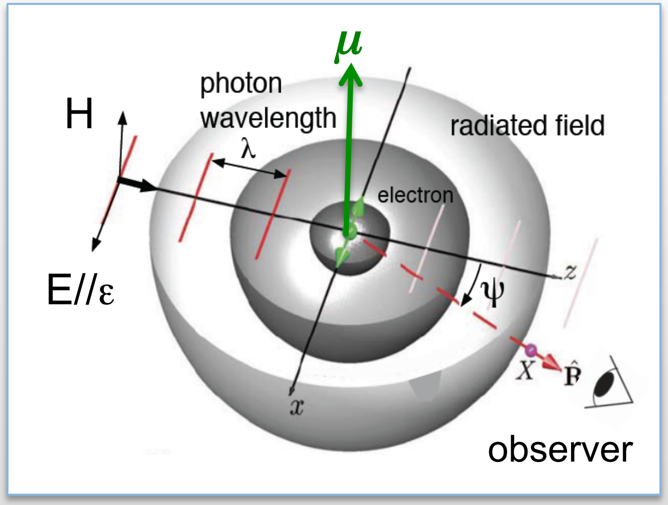


MAGNETIC INTERACTION

The magnetic interaction is a relativistic correction of the Thomson scattering

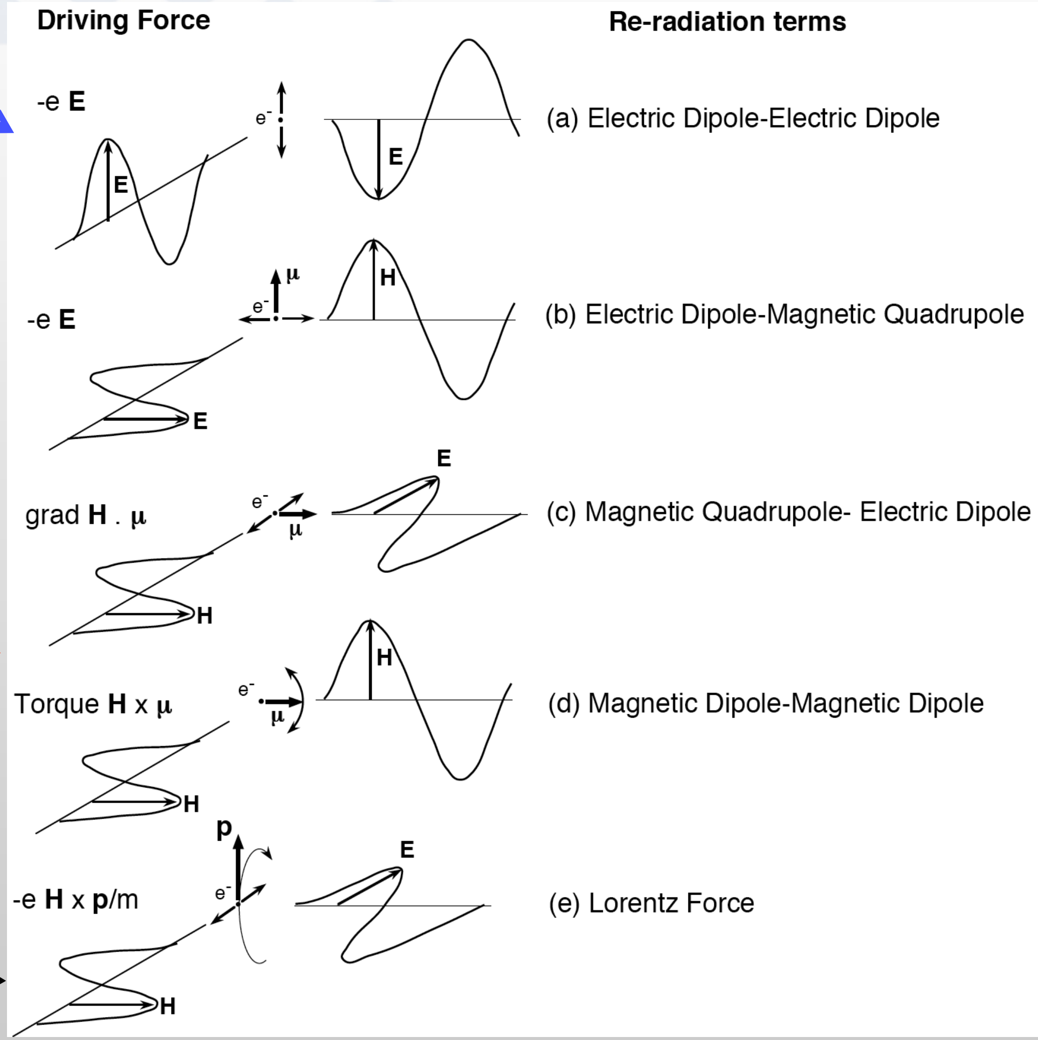
*... a **classical interpretation** from de Bergevin and Brunel (Acta Cryst, 1981)*

Thomson scattering

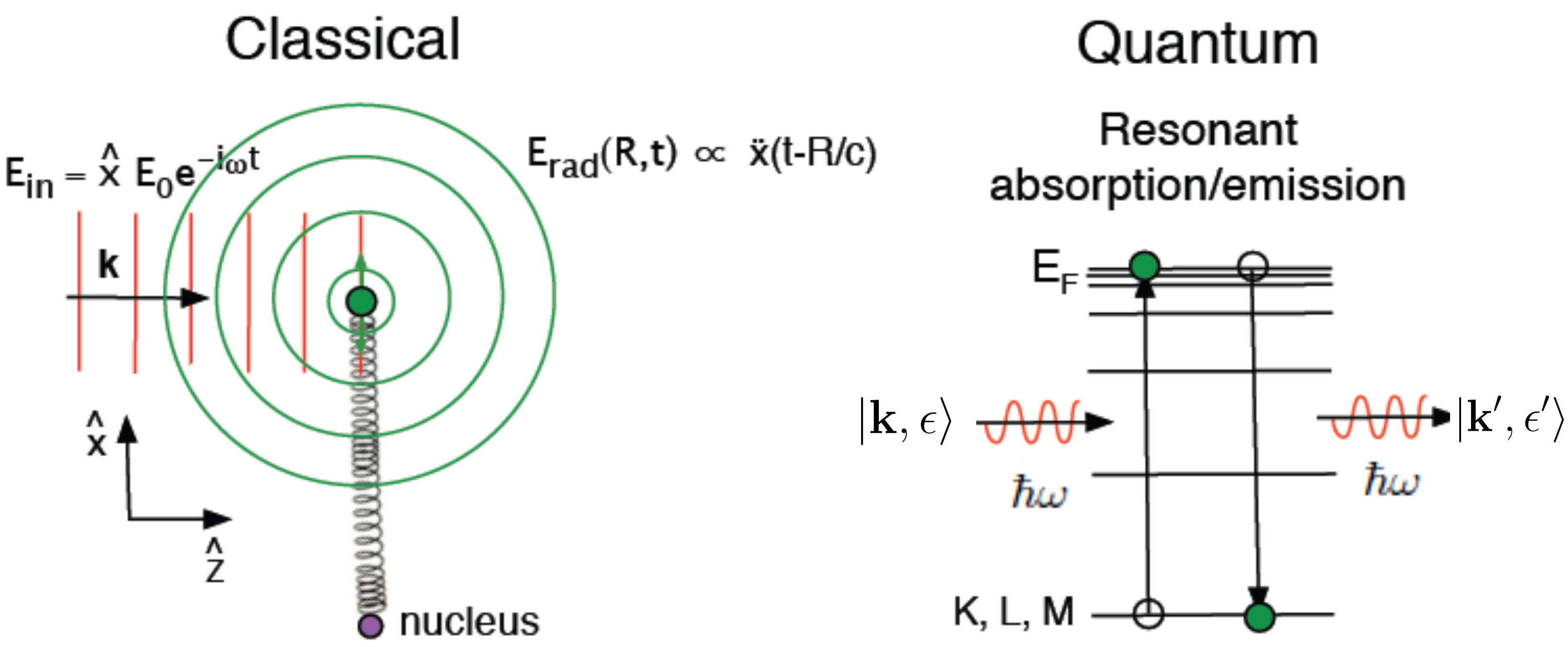


Spin-dependent scattering

Orbital motion



The electron be subject to the electric field E_{in} of an incident X-ray beam and to a damping term proportional to the electron velocity $\Gamma\dot{x}$ which represents dissipation of energy.



Γ= damping factor
ω= frequency

$1/\Gamma$= core-hole lifetime
$\hbar\omega$= resonant energy

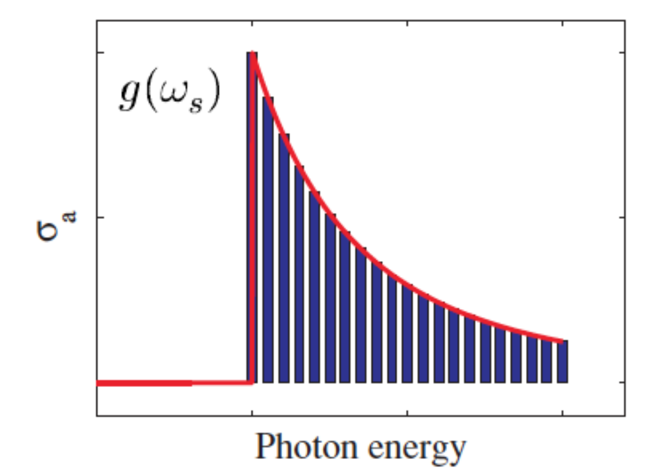
Because the electrons are bound in atoms with discrete energies, a more elaborate model than that of a cloud of free electrons must be invoked.

The scattering amplitude includes two energy dependent term f'(ω) and f"(ω) which are called "dispersion corrections".

$$f(\mathbf{Q},\omega) = f^0(\mathbf{Q}) + f'(\omega) + i\,f''(\omega)$$

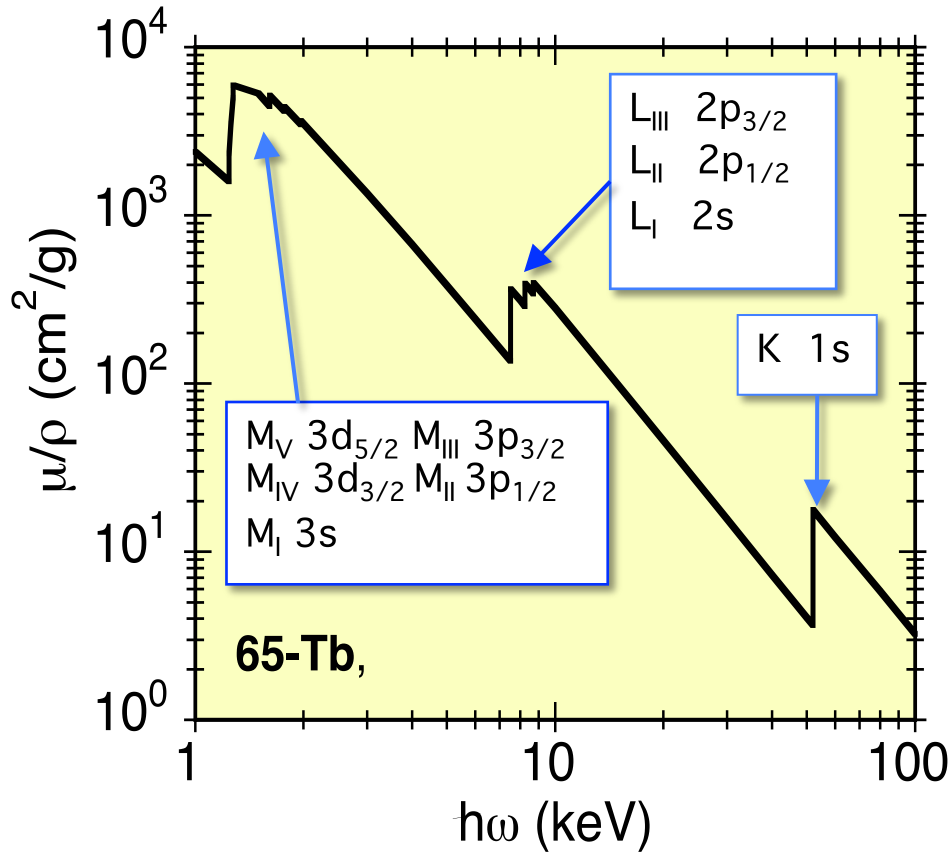
Thomson Dispersion corrections

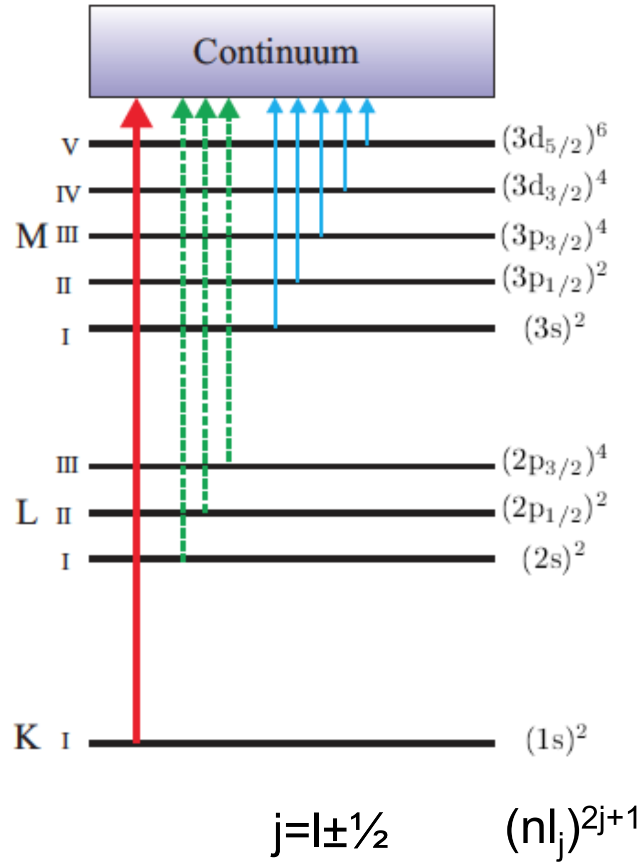
The dispersion corrections are derived by treating atomic electrons as harmonic oscillators. The absorption cross section σ_a is a superposition of oscillators with relative weights, so-called oscillator strengths, $g(\omega_s)$, proportional to $\sigma_a(\omega = \omega_s)$.



X-RAY ABSORPTION EDGES

X-rays energies are able to extract atomic electrons from the atomic core!
The **element-specific** energies of the discontinuous jumps in the x-rays absorption spectra are called absorption edges.





See the lectures of Mobilio and Bertoni!!!!

Matter is described by a wavefunction Ψ solution of **Schrodinger equation**:

$$H\,\Psi = E\,\Psi$$

$$\Psi(r_1, r_2, \ldots r_n; R_1, R_2, \ldots R_N)$$

r_i electron positions R_i Nuclei positions

1) **Born-Oppenheimer approximation:**
   Nuclei at the rest position R_i^0
   An effective Hamiltonian H_{eff} describes the attractive potential of ions on the electrons
2) **Mean field approximation:**
   Electrons move independently in the mean field created by the other electrons
   No electron correlation effects and Ψ depends only from $\mathbf{r}_j$
3) **One electron approximation:**
   The wavefunction of the electron r_n can be single out
   The effective Hamiltonian depends only from the coordinate of this electron

$$\Psi(r_1, r_2, \ldots r_n; R_1^0, R_2^0, \ldots R_N^0) \sim \Psi(r_1, r_2, \ldots r_{n-1}; R_1^0, R_2^0, \ldots R_N^0)\,\psi(r_n)$$

$$H_{eff}(\mathbf{r}_n)\,\psi(r_n) = E\,\psi(r_n)$$

Matter is treated as a quantum mechanical system and the radiation as a classical field

1) **Interaction occurs mainly with the electrons**
   we considers only the electronic transitions
   we suppose to know their eigenstates and the eigenfunctions
2) **The system is composed mainly by N identical microscopic entities**
   Atoms, molecules, clusters …
3) **The electromagnetic wave acts as a time-dependent perturbation**
   modify the electron wavefunction
   transitions between eigenstates

FERMI GOLDEN RULE (second order)

Transition rate W_{fi} per unit of volume between an initial $|\Psi_i>$ and a final $<\Psi_f|$ unperturbed eigenstate

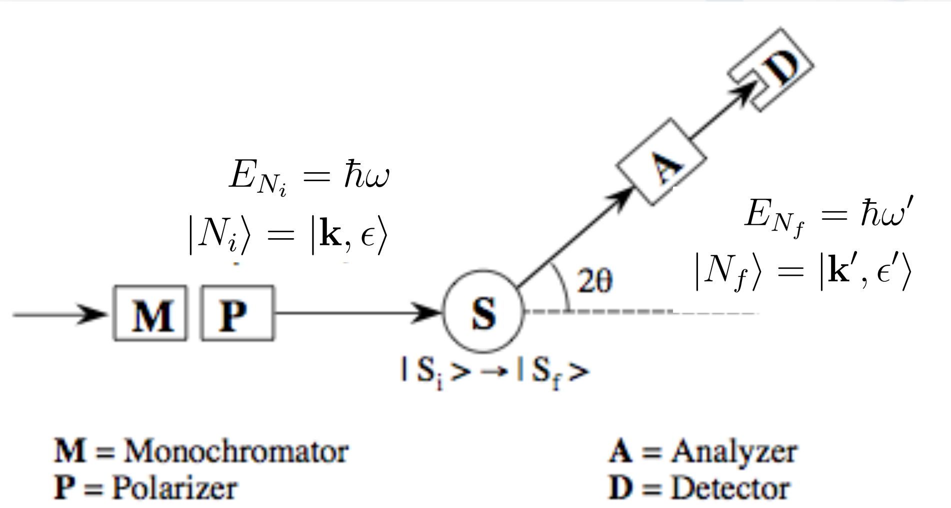
$$W_{fi} = \frac{2\pi}{\hbar} \left| \langle \Psi_f | H_{int} | \Psi_i \rangle + \sum_k \frac{\langle \Psi_f | H_{int} | \Psi_k \rangle \langle \Psi_k | H_{int} | \Psi_i \rangle}{E_i - E_k - \hbar\omega} \right|^2 \delta(E_f - E_i - \hbar\omega)$$

$$H_{int} = \sum_j \left(-\frac{e}{mc} \mathbf{A}(\mathbf{r}_j) \cdot \mathbf{p}_j + \frac{e^2}{2mc^2} A^2(\mathbf{r}_j) \right)$$

Classical limit of Dirac equation
(non-relativistic behaviour of electrons in an electromagnetic field)

SCATTERING EXPERIMENTS

Determination of temporal evolution of the physical state of a large number of particle at the thermal equilibrium.
Measure of the probe dynamical variables N_i and N_f after the interaction with the sample



Magnetic probe

Energy	E_{Ni} => E_{Nf}
Momentum	**Q=k-k'**
Polarization	ε => ε'

Sample

Transition	$\|S_i>$ => $\|S_f>$
Energy	E_{Si} => E_{Sf}

Fermi's Golden rule

Transition probability per unit time of from an initial $|S_i,N_i>$ and a final state $<S_f,N_f|$ of the |sample+probe> system, related to the interaction potential V:

$$W_{N_iS_iN_fS_f} = \frac{2\pi}{\hbar}\sum_{S_iS_f} |\langle S_fN_f|V|S_iN_i\rangle|^2\,\delta(E_{S_i}+E_{N_i}-E_{S_f}-E_{N_f})$$

THE INTERACTION POTENTIAL

In scattering experiments we are interested in the changes of **the probe states** **|**N_i> and <N_f**|** :

$$\mathcal{V} = \langle N_f | V | N_i \rangle$$

Matrix elements of interaction potential V

The probability per unit time that the probe undergoes a transition from the initial state |N_i> to the final state <N_f| is obtained from the previous equation by averaging over the thermal distribution of the sample initial states |S_i> and by summing over all the possible sample final states <S_f|:

$$W_{N_i N_f} = \frac{2\pi}{\hbar} \sum_{S_i S_f} p(S_i) \left| \langle S_f | \mathcal{V} | S_i \rangle \right|^2 \delta(E_{S_i} - E_{S_f} + \hbar\omega)$$

$$p(S_i) = \frac{1}{Z_S} exp(-\frac{E_{S_i}}{K_B T})$$

$$Z_S = \sum_{S_i} exp(-\frac{E_{S_i}}{K_B T})$$

Partition function

This expression relates the change of the state of the probe with the time-evolution of the sample state

Measurable quantity in the scattering experiments
The energy of the probe is comparable with the sample eigenstates

Partial differential scattering cross-section

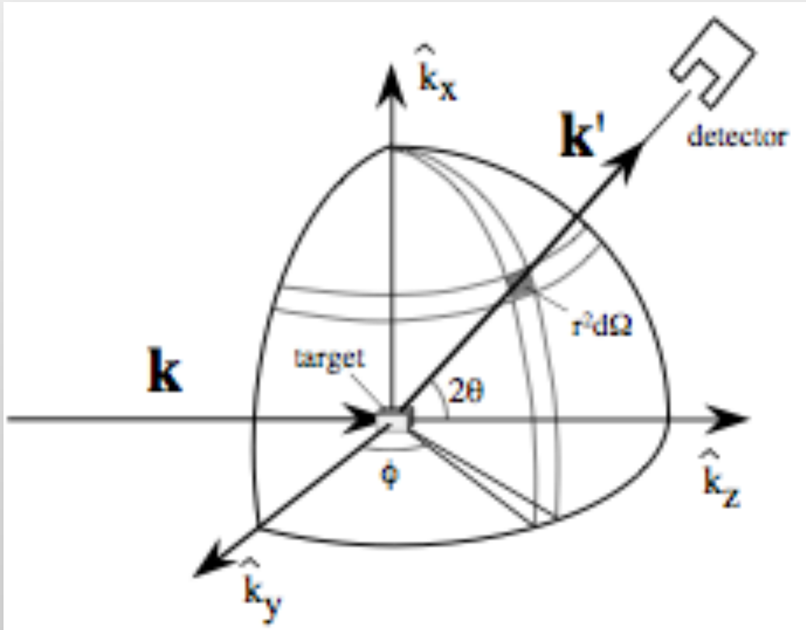
$$\frac{d^2\sigma}{d\Omega dE} = \frac{N_{E_f}(\theta,\phi)}{\Omega_0 \, d\Omega dE}$$

Ratio between the number of scattered particles with energies E_f in the solid angle $\Delta\Omega(\theta, \phi)$ and the incident flux density Ω_0 per unit of solid angle $d\Omega$ and energy dE

Differential scattering cross-section

$$\left(\frac{d\sigma}{d\Omega}\right)_{\sigma,\lambda\rightarrow\sigma',\lambda'} = \frac{1}{\Omega_0}\frac{1}{d\Omega}\sum_{k'\in d\Omega} W_{\mathbf{k},\sigma,\lambda\rightarrow\mathbf{k}'\sigma',\lambda'}$$

$$\sum_{k'\in d\Omega} W_{\mathbf{k},\sigma,\lambda\rightarrow\mathbf{k}'\sigma',\lambda'} = \frac{2\pi}{\hbar^2}\rho_{\mathbf{k}'}\langle\mathbf{k}'\sigma'\lambda'|\mathcal{V}|\mathbf{k}\sigma\lambda\rangle$$



Total scattering cross-section

$$\sigma_{tot} = \int \left(\frac{d\sigma}{d\Omega}\right) d\Omega = 4\pi \int_0^{\pi} \left(\frac{d\sigma}{d\Omega}\right) sin(2\theta) d\theta$$

QUANTIZATION OF EM FIELD

For a complete description of the x-ray-matter interaction we need to consider the **relativistic motion of the electrons in a quantized electromagnetic field.**

The "second quantization" describes the EM field as photon states with an occupation number "$n_{k\varepsilon}$,", wavevector **k** and polarization "ε",

$$|n_{k_1,\epsilon_1}; ...n_{k,\epsilon}; ...n_{k_t,\epsilon_t}\rangle$$

and the creation and annihilation operators, "$a^\dagger$" and "a" are defined as:

$$a^\dagger_{k,\epsilon}|n_{k_1,\epsilon_1}; ...n_{k,\epsilon}; ...n_{k_t,\epsilon_t}\rangle = \sqrt{n_{k,\epsilon}+1}|n_{k_1,\epsilon_1}; ...n_{k,\epsilon}+1; ...n_{k_t,\epsilon_t}\rangle$$

$$a_{k,\epsilon}|n_{k_1,\epsilon_1}; ...n_{k,\epsilon}; ...n_{k_t,\epsilon_t}\rangle = \sqrt{n_{k,\epsilon}}|n_{k_1,\epsilon_1}; ...n_{k,\epsilon}-1; ...n_{k_t,\epsilon_t}\rangle$$

With this assumptions, the harmonic components of an EM field is decomposed in a sum of quantized oscillators. The vector potential **A** then became an operator:

$$\mathbf{A}(\mathbf{r},t) = \sum_{k,\epsilon}\sqrt{\frac{4\pi\hbar c^2}{2V\omega_k}}\left(a_{k,\epsilon}\hat{\epsilon}_{k,\epsilon}e^{i\mathbf{k}\cdot\mathbf{r}-i\omega t} + a^\dagger_{k,\epsilon}\hat{\epsilon}^*_{k,\epsilon}e^{-i\mathbf{k}\cdot\mathbf{r}-i\omega t}\right)$$

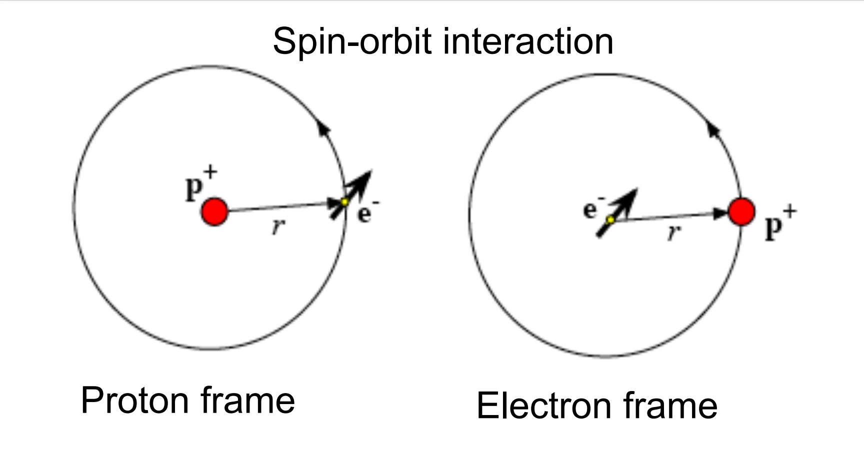
The interaction Hamiltonian is obtained from the **Dirac equation** in the limit of low velocities and taking the terms o(v/c).

Relativistic terms

$$\hat{H}_{int} = \sum_j \left(-\frac{e}{mc}\mathbf{A}(\mathbf{r}_j)\cdot\mathbf{p}_j + \frac{e^2}{2mc^2}\mathbf{A}^2(\mathbf{r}_j) - \frac{e\hbar}{mc}\mathbf{s}_j\cdot\nabla\times\mathbf{A} - \frac{e\hbar}{2m^2c^3}\mathbf{s}_j\cdot\frac{\partial\mathbf{A}}{\partial t}\times\frac{e}{c}\mathbf{A}\right)$$

Zeeman term:
Interaction of electron spins s_j with the magnetic field **B**

Spin-orbit interaction:
interaction between the spin **S** and the orbital part **L** of the electron's wave functions



The mutual interaction between spin magnetic moment μ and magnetic field $\mathbf{B}^p$ is generated by the positive charge of the nucleus rotating around the electron rest frame:

$$H_{so} = -\frac{1}{2}\,\mu\cdot\mathbf{B}^p = \frac{e\hbar^2}{2m_e c^2 r}\frac{dV(r)}{dr}\,\mathbf{L}\cdot\mathbf{S} = \lambda\,\mathbf{L}\cdot\mathbf{S}$$

M. Blume, *"Resonant anomalous x-ray scattering"*, ed. G. Materlik, (1994), p. 494-512, Elsevier Science B.V., Amsterdam.
M. Blume, J. Appl. Phys. 57, 3615 (1985)

1) *Write Hamiltonian to describe charges and photons*
2) *Separate the electric field generated by the charges from that generated by the radiation field*
3) *Expansion of spin-orbit term by A(**r**) (transv. plane waves)*
4) *Exploit the Fermi's Golden rule (2nd order)*
5) *Distinguish non-resonant and resonant x-ray scattering regimes*

$$\mathcal{H} \;=\; \mathcal{H}_{el} + \mathcal{H}_{ph} + \mathcal{H}'$$

Non-interacting electrons — *Non interacting photons* — *Interaction (weak)*

M. Altarelli: *Resonant X-ray Scattering: A Theoretical Introduction*, Lect. Notes Phys. **697**, 201–242 (2006)
www.springerlink.com © Springer-Verlag Berlin Heidelberg 2006

Hamiltonian for electrons and photons in a quantized electromagnetic field

- *Non-interacting electrons H_{el}*

$$\mathcal{H}_{el} = \sum_j \frac{1}{2m}\mathbf{P}_j^2 + \sum_{ij} V(r_{ij}) + \frac{e\hbar}{2(mc)^2}\sum_j \mathbf{s}_j \cdot (\nabla\Phi_j \times \mathbf{P}_j),$$

- *Non-interacting photons H_{ph}*

$$H_{phot} = \sum_{\mathbf{k},\epsilon} \hbar\omega(a^\dagger_{k,\epsilon} a_{k,\epsilon} + \frac{1}{2})$$

- *Interaction term H'*

$$\begin{aligned}
\mathcal{H}' &= \mathcal{H}'_1 + \mathcal{H}'_2 + \mathcal{H}'_3 + \mathcal{H}'_4 \\
&= \frac{e^2}{2mc^2}\sum_j \mathbf{A}^2(\mathbf{r}_j) \\
&\quad -\frac{e}{mc}\sum_j \mathbf{A}(\mathbf{r}_j)\cdot\mathbf{P}_j \\
&\quad -\frac{e\hbar}{mc}\sum_j \mathbf{s}_j\cdot[\nabla\times\mathbf{A}(\mathbf{r}_j)] \\
&\quad -\frac{e\hbar}{2(mc)^2}\frac{e}{c^2}\sum_j \mathbf{s}_j\cdot[\dot{\mathbf{A}}(\mathbf{r}_j)\times\mathbf{A}(\mathbf{r}_j)].
\end{aligned}$$

1st order

2st order

A(r) is linear in a†(**k**,ε) and a(**k**,ε)

Elastic scattering processes conserves the number of photons

- The QUADRATIC terms in A(r) contribute to the 1° order perturbation
  (H'_1 and H'_4)
- The linear terms in A(r) contribute to the 2° order perturbation.
  (H'_2 and H'_3)

$$W = \frac{2\pi}{\hbar} \Big| < a\;;\; \mathbf{k}'\;\epsilon' |\; H'_1 + H'_4 \;| a\;;\; \mathbf{k}\;\epsilon >$$
$$+ \sum_n \frac{< a\;;\; \mathbf{k}'\;\epsilon' |\; H'_2 + H'_3 \;| n >< n |\; H'_2 + H'_3 \;| a\;;\; \mathbf{k}\;\epsilon >}{E_a + \hbar\omega_k - E_n} \Big|^2$$

$$\begin{aligned} |i\rangle &= |a;\mathbf{k},\epsilon\rangle \\ |f\rangle &= |a;\mathbf{k}',\epsilon'\rangle \end{aligned}$$

For resonant elastic scattering: the system have an identical initial and final ground state |a>

X-RAYS SCATTERING AMPLITUDES

$$\frac{d\sigma}{d\Omega} = r_0^2 \left| \sum_n e^{i\mathbf{Q}\cdot\mathbf{R}_n} f_n(\mathbf{k}, \mathbf{k}', \hat{\epsilon}, \hat{\epsilon}', \hbar\omega_k) \right|^2 \qquad f = f_0 + f^{magn.} + f' + if''$$

$$f_0(\mathbf{Q}, \hat{\epsilon}, \hat{\epsilon}') = \langle a \mid \sum_j e^{i\mathbf{Q}\cdot\mathbf{r}_j} \mid a\rangle \hat{\epsilon}' \cdot \hat{\epsilon}.$$

Thomson
Charge density

$$f^{magn.}(\mathbf{Q}) \;=\; -i\frac{\hbar\omega_k}{mc^2}(\mathbf{L}(\mathbf{Q})\cdot\mathbf{P}_L + \mathbf{S}(\mathbf{Q})\cdot\mathbf{P}_S)$$

Polarization dependent terms

$$\mathbf{P}_L \;=\; -\,sin^2\theta\,[\mathbf{Q}\times[(\hat{\epsilon}'^* \times \hat{\epsilon})\times\mathbf{Q}]]$$
$$\mathbf{P}_S \;=\; \hat{\epsilon}'^* \times \hat{\epsilon} + (\hat{\mathbf{k}}' \times \hat{\epsilon}'^*)(\hat{\mathbf{k}}'\cdot\hat{\epsilon}) - (\hat{\mathbf{k}}\times\hat{\epsilon})(\hat{\mathbf{k}}\cdot\hat{\epsilon}'^*) - (\hat{\mathbf{k}}'\times\hat{\epsilon}'^*)\times(\hat{\mathbf{k}}\times\hat{\epsilon})$$

Non-resonant magnetic
Orbital and spin separation
Magnetization density

$$f^{RXS} = +\frac{1}{m}\sum_c \frac{E_g - E_c}{\hbar\omega_k}\left(\frac{\hat{\epsilon}'^* \cdot \langle g|\, \tilde{O}^\dagger(\mathbf{k}')\, |c\rangle\, \langle c|\, \tilde{O}(\mathbf{k})\, |g\rangle \cdot \hat{\epsilon}}{E_g - E_c + \hbar\omega_k - i\Gamma_c/2} - \frac{\hat{\epsilon}\cdot\langle g|\, \tilde{O}(\mathbf{k})\, |c\rangle\, \langle c|\, \tilde{O}^\dagger(\mathbf{k}')\, |g\rangle \cdot \hat{\epsilon}'^*}{E_g - E_c - \hbar\omega_k} \right)$$

Current operators J(k)

$$\hat{O}(\mathbf{k}) \;=\; \sum_j e^{i\mathbf{k}\cdot\mathbf{r}_j}\,[\,\hat{\epsilon}\cdot\mathbf{P}_j - i\hbar(\mathbf{k}\times\hat{\epsilon})\cdot\mathbf{s}_j\,]$$
$$\hat{O}^{+}(\mathbf{k}') \;=\; \sum_j e^{-i\mathbf{k}'\cdot\mathbf{r}_j}\,[\,\hat{\epsilon}'\cdot\mathbf{P}_j + i\hbar(\mathbf{k}'\times\hat{\epsilon}')\cdot\mathbf{s}_j\,]$$

Resonant terms
Core-hole virtual transition
Tensorial amplitudes
High order multipoles

Coherent elastic scattering cross-section for periodic crystals

$$\frac{d\sigma}{d\Omega} = r_0^2 \left| \sum_n \underbrace{e^{i\mathbf{Q}\cdot\mathbf{R}_n}} \underbrace{f_n(\mathbf{k}, \mathbf{k}', \hat{\epsilon}, \hat{\epsilon}', \hbar\omega_k)} \right|^2$$

n= unit cell atomic site

Site selectivity

- *Space group symmetries*
- *Extinction rules*

Atomic scattering amplitudes

- *Atomic properties (photon-electron interactions)*
- *Electronic order parameters*

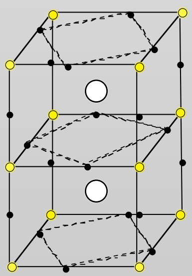
$$f = f_0 + f^{magn.} + f' + i f''$$

CHARGE (Thomson)
E=10-50 keV
$Z\, r_0 \sim$ 1-95 r_0

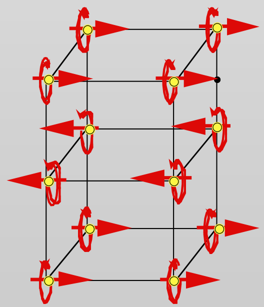
MAGNETIC
E=3.0-10 keV
$\hbar\omega/mc^2\, Z^{magn.}\, r_0 \sim$ 0.001-0.03 r_0

RESONANT
E=3-20 keV
$Z^{res.}\, r_0 \sim$ 0.01-100 r_0

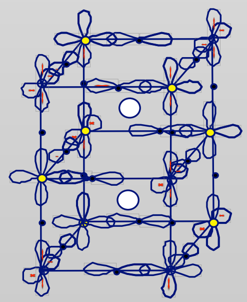
Structural characterization



Magnetic structure determination



Valence electronic anisotropies
Anisotropy tensor susceptibility



High-Q quality samples are required to detect the weak magnetic reflections

$$\frac{\sigma_{mag}}{\sigma_{charge}} \simeq \left(\frac{\hbar\omega_k}{mc^2}\right)^2 \left(\frac{N_m}{N}\right)^2 \langle M\rangle^2 \left(\frac{f_m}{f}\right)^2$$

~ 10^{-6} @ 9 keV

RESONANT (magnetic)

$I_{res.}$~10^3-10^5 cts/s

MAGNETIC

$I_{magn.}$~10^0-10^2 cts/s

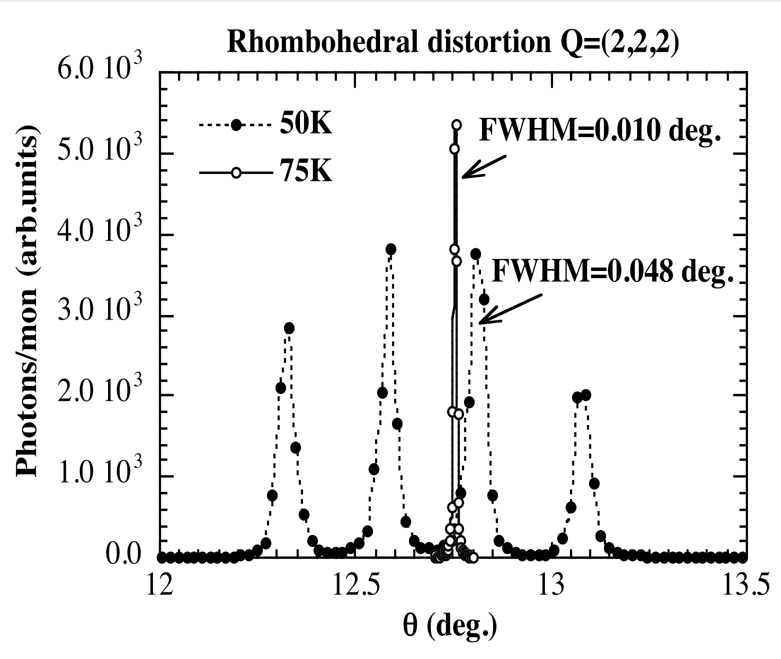
CHARGE (Thomson)

$I_{ch.}$~10^5-10^9 cts/s

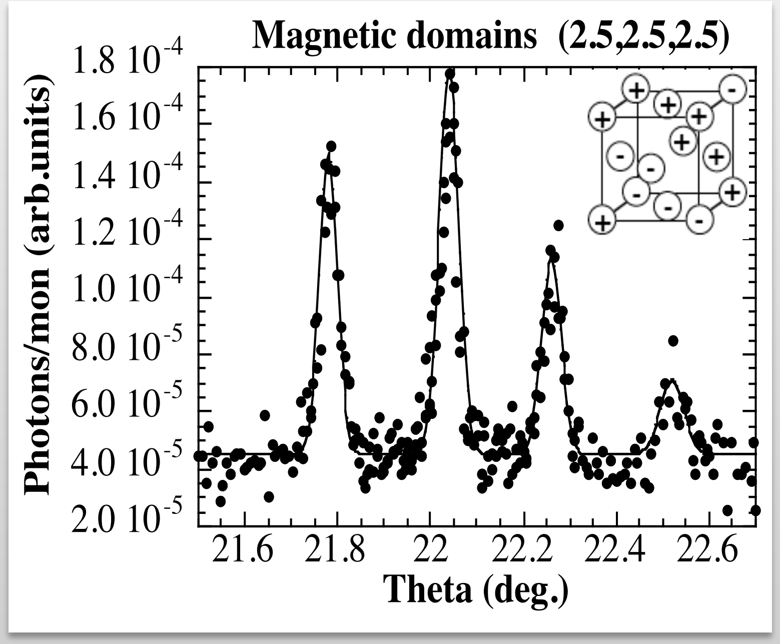
The high-Q resolution allow the separation of crystallographic and magnetic reflections.

Ex. Charge and antiferromagnetic Bragg reflections in $Ce_{0.93}Co_{0.07}Fe_2$

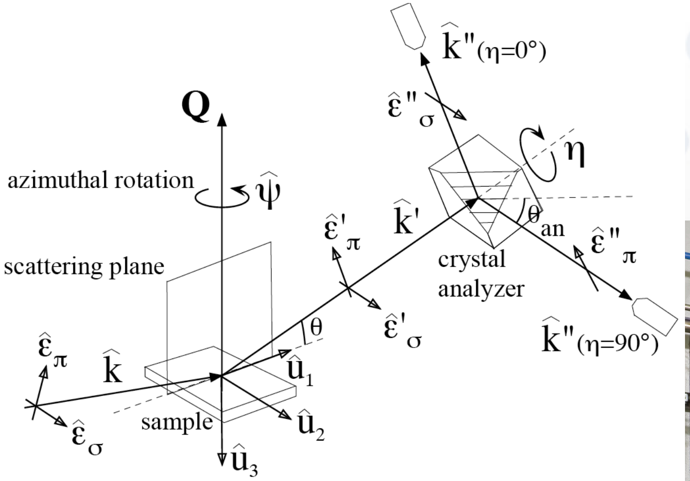
Thomson scattering



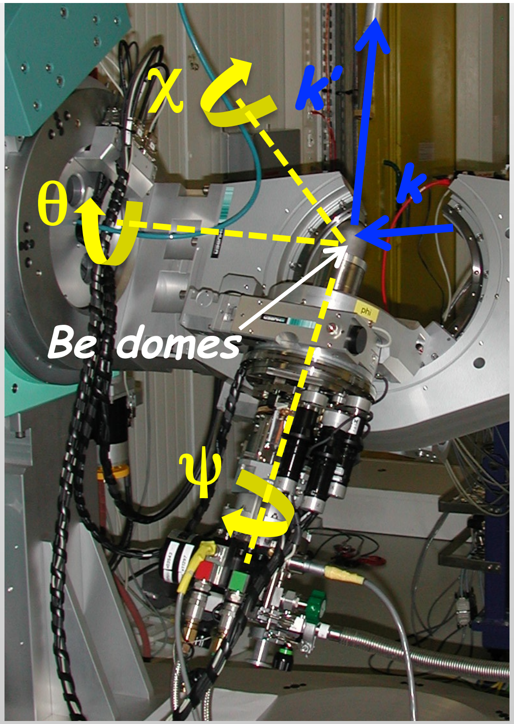
Non-resonant magnetic scattering

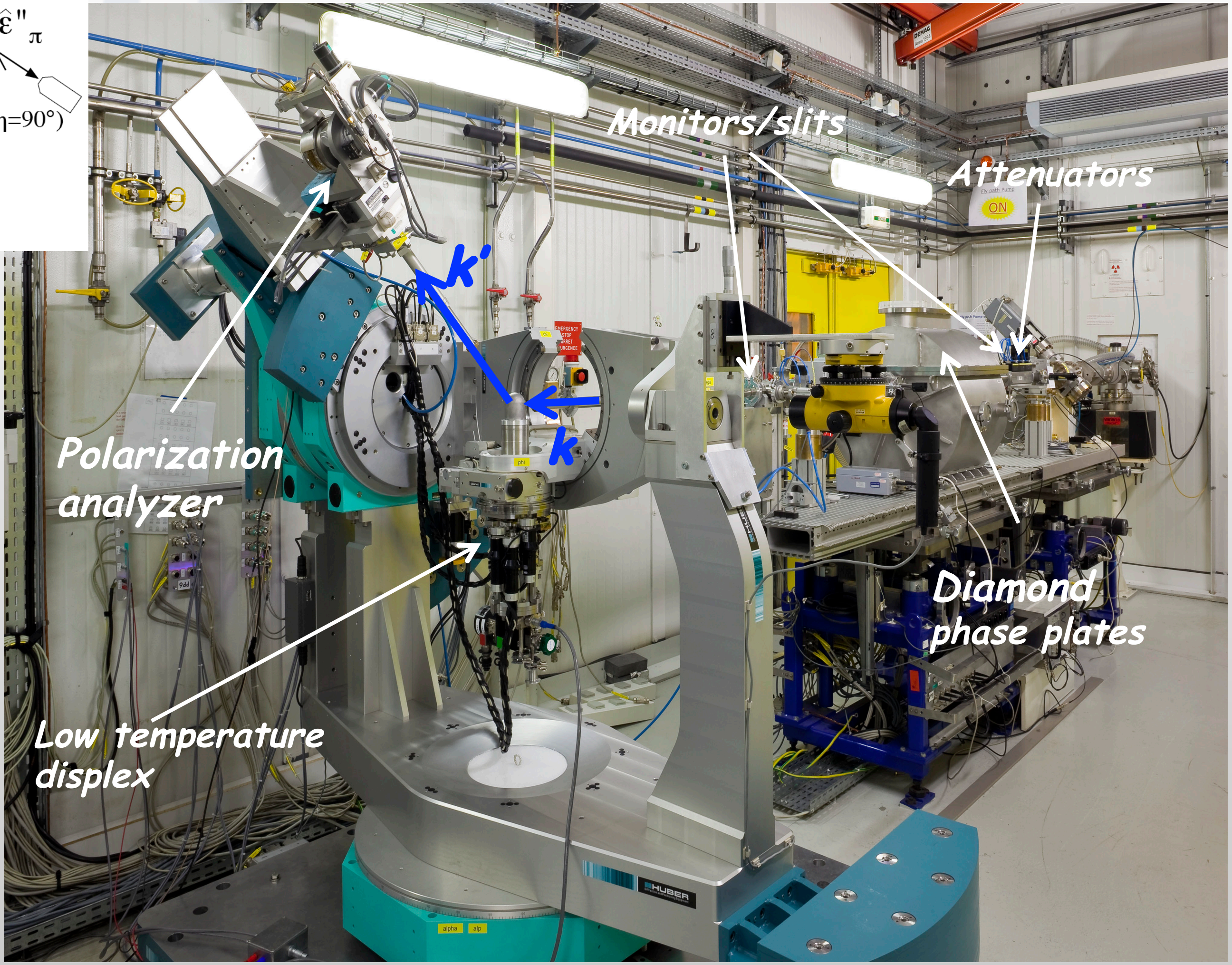


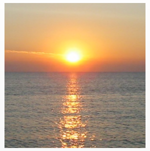
POLARIZED AZIMUTHAL DIFFRACTION



Four-circle diffractometer
Vertical scattering plane

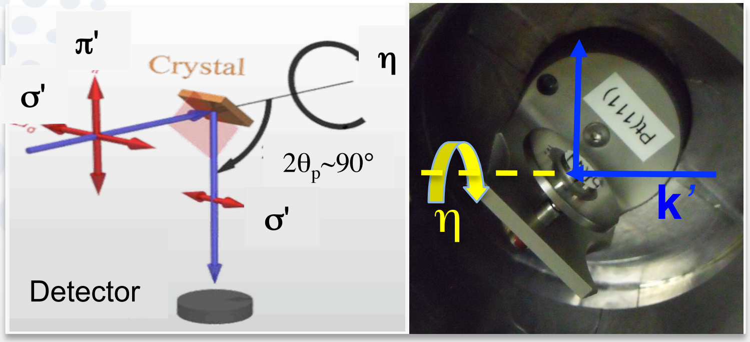


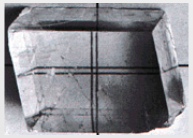




X-rays Polarization analyser

- Thomson selection rules (ε·ε')
- Bragg diffraction by a crystal analyzer $2\theta_p$~90°
- η = rotation about scattered wavevector k'

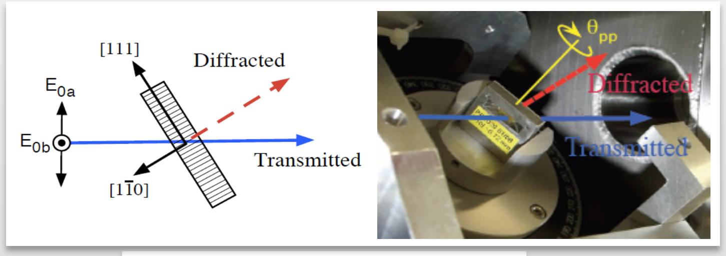




Phase plate retarder

Phase shift $\Delta\alpha$ between the transmitted and incident beam in the dynamical diffraction limit

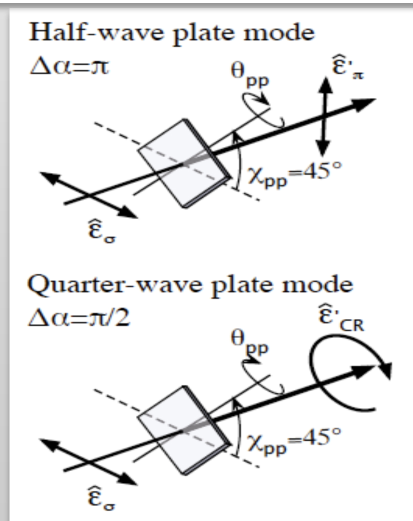
$$\Delta\alpha = \frac{2\pi}{\lambda}(n_\sigma - n_\pi)d = -\frac{\pi}{2}\left[\frac{r_e^2\lambda^3 Re(F_h F_{\bar{h}}) sin2\theta_{pp}}{\pi^2 V^2 \Delta\theta_{pp}}\right] d$$



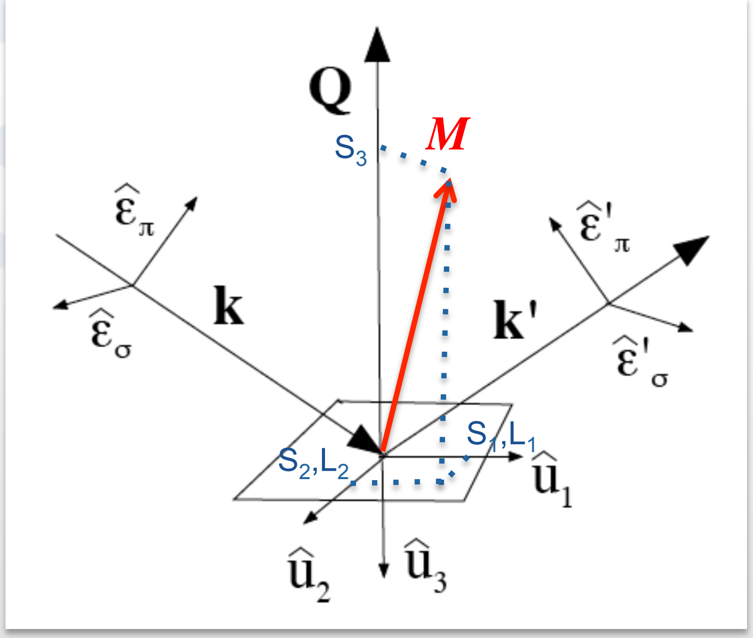
Half wave plate mode ($\Delta\alpha=\pi$)
- Rotation of 90° of liner polarization (when χ=45°)

Quarter wave plate mode ($\Delta\alpha=\pi/2$)
-Circular left/right polarizations (~98-99%)

Linear Polarization Scan ($\Delta\alpha=\pi$)
-Continous rotation of χ



$$f^{magn.}(\mathbf{Q}) \; = \; -i\frac{\hbar\omega_k}{mc^2}\left(\mathbf{L}(\mathbf{Q})\cdot\mathbf{P}_L + \mathbf{S}(\mathbf{Q})\cdot\mathbf{P}_S\right)$$



- *Jones's matrices for NRMS:*

$$f^{non-res}_{mag} = -i\frac{\hbar\omega}{mc^2}\begin{array}{cc} \sigma-\sigma' & \pi-\sigma' \\ \multicolumn{2}{c}{\begin{pmatrix} M_{\sigma\sigma} & M_{\pi\sigma} \\ M_{\sigma\pi} & M_{\pi\pi} \end{pmatrix}} \\ \sigma-\pi' & \pi-\pi' \end{array}$$

$$\begin{aligned} M_{\sigma\sigma} &= S_2 \sin 2\theta \\ M_{\pi\sigma} &= -2\sin^2\theta\,[(\cos\theta)\,(L_1+S_1) - S_3\sin\theta] \\ M_{\sigma\pi} &= 2\sin^2\theta\,[\cos\theta\,(L_1+S_1) + S_3\sin\theta] \\ M_{\pi\pi} &= \sin 2\theta\left[2L_2\sin^2\theta + S_2\right] \end{aligned}$$

$$\begin{aligned} \hat{\mathbf{u}}_1 &= (\hat{\mathbf{k}}+\hat{\mathbf{k}}')/2\cos\theta \\ \hat{\mathbf{u}}_2 &= (\hat{\mathbf{k}}\times\hat{\mathbf{k}}')/\sin 2\theta \\ \hat{\mathbf{u}}_3 &= (\hat{\mathbf{k}}-\hat{\mathbf{k}}')/2\sin\theta \end{aligned}$$

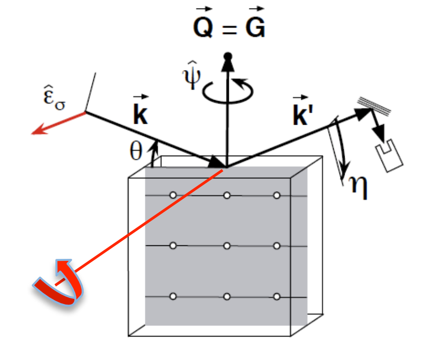
$$\begin{aligned} S_i &= \frac{f_s(Q)\mu_s^i}{g_s\mu_B} \\ L_i &= \frac{f_l(Q)\mu_l^i}{g_l\mu_B} \end{aligned}$$

Fourier transforms of spin and orbital magnetization densities

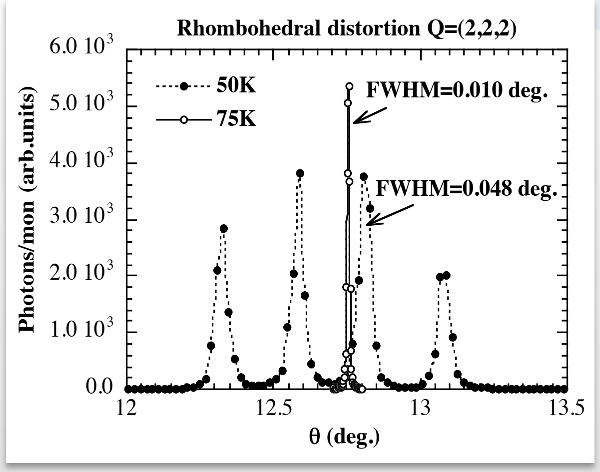
CHARGE SCATTERING

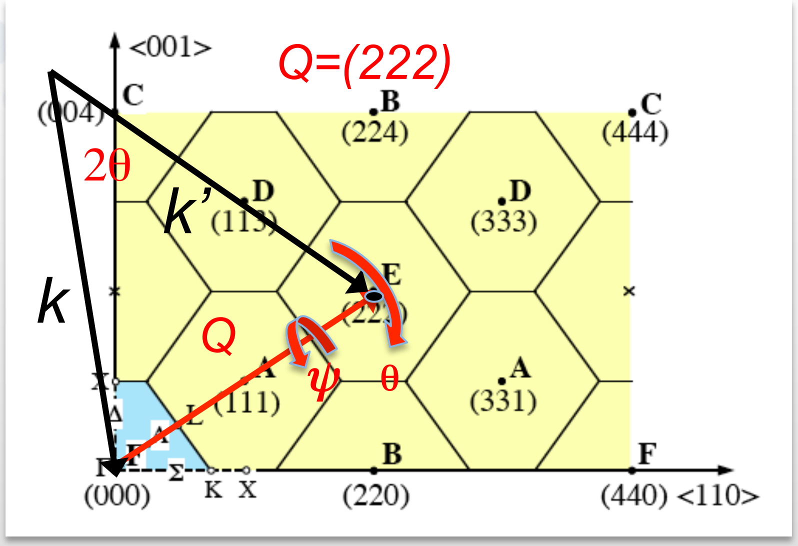
$$f_0(\mathbf{Q}, \hat{\epsilon}, \hat{\epsilon}') = \langle a \mid \sum_j e^{i\mathbf{Q}\cdot\mathbf{r}_j} \mid a \rangle \hat{\epsilon}' \cdot \hat{\epsilon}.$$

- Invariant for the x-rays polarization
- Invariant for the azimuthal rotation



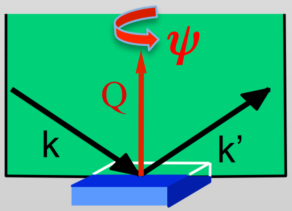
θ rocking angle



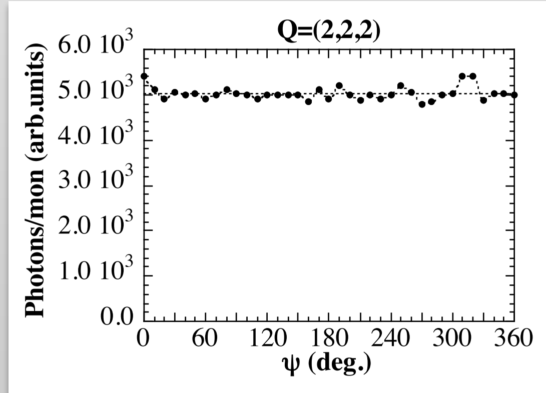


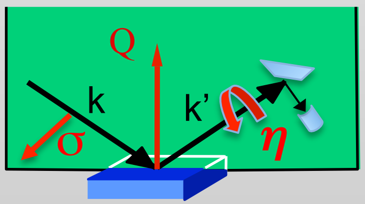
Azimuthal scans

Polarization analysis

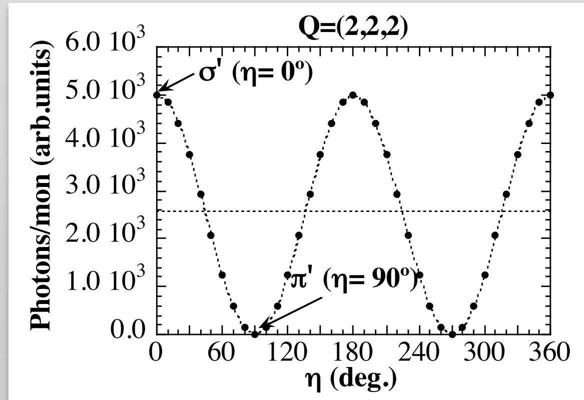


ψ *azimuthal rotation (about the scattering vector Q)*





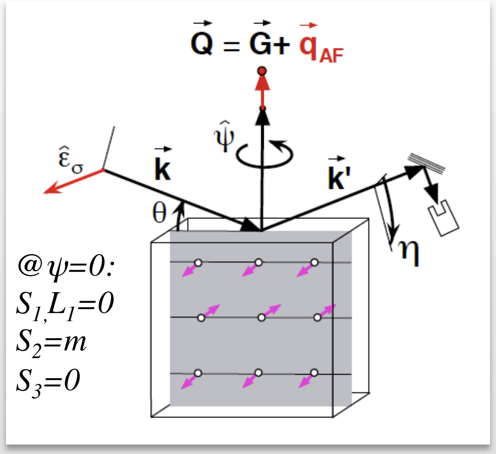
η *polarization angle (about the scattered wavevector k')*

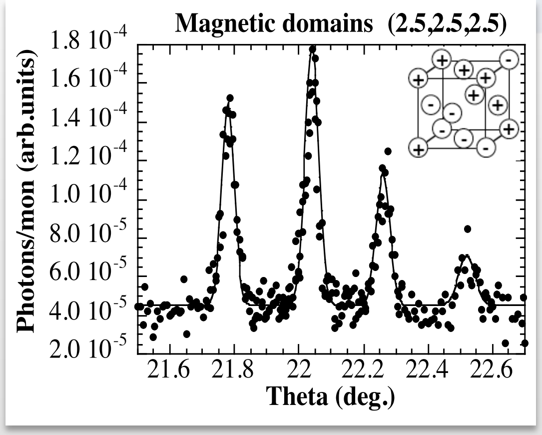


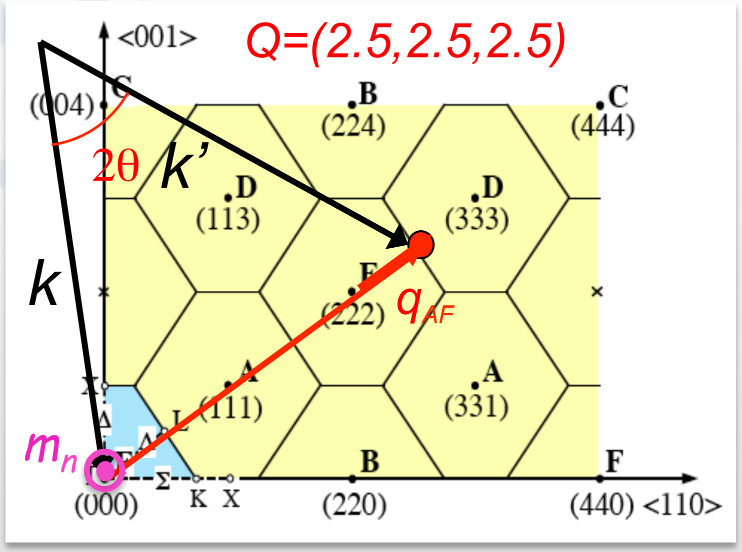
EX.: AF STRUCTURE (NRMS)

- *Magnetic propagation vector => q_{AF} =(1/2,1/2,1/2)*
- *Magnetic moment direction => m_n = [1,-1,0]*

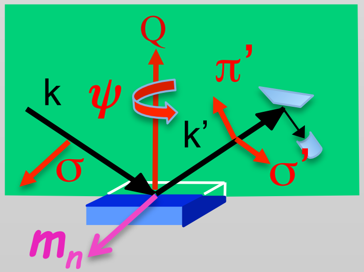
$$f_{\sigma\text{-}\sigma'} \propto M_{\sigma\sigma} \sim S_2 \sin 2\theta,$$
$$f_{\sigma\text{-}\pi'} \propto M_{\sigma\pi} \sim 2\sin^2\theta\,[\cos\theta\,(L_1+S_1) + S_3 \sin\theta]$$

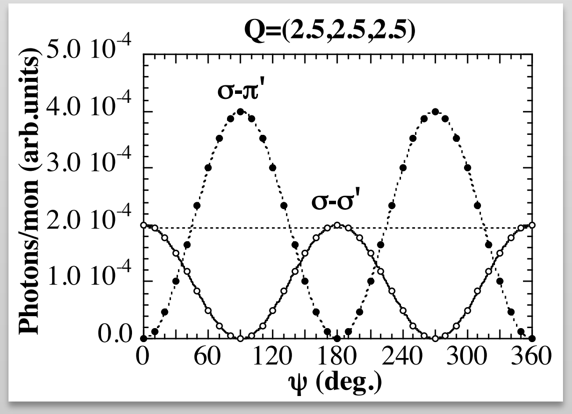




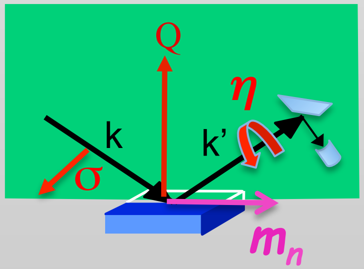


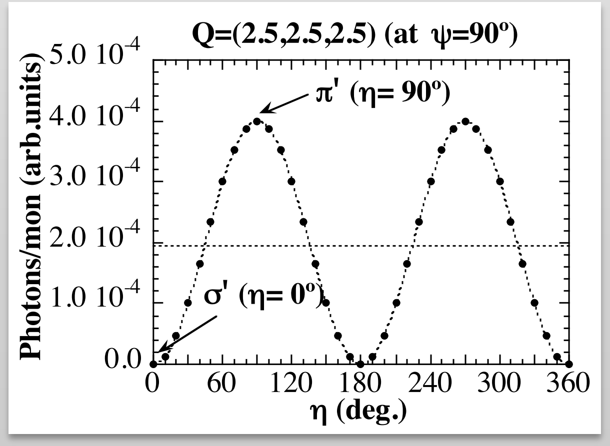
Azimuthal scans





Polarization analysis at ψ=90°





EX.:ORBITAL MAGNETIC MOMENT IN $KCuF_3$

Azimuthal scan :

- *Single magnetic domain probed*
- *Moment lies along the directions <110>*

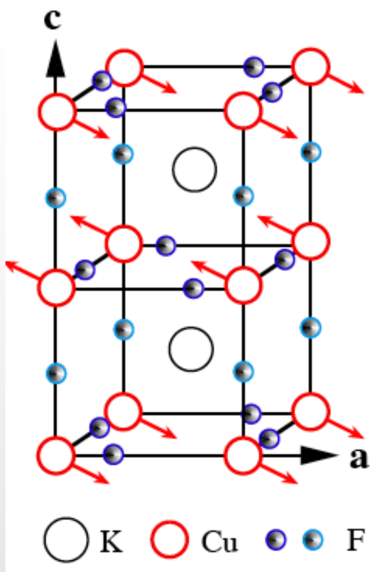
Polarization analysis:

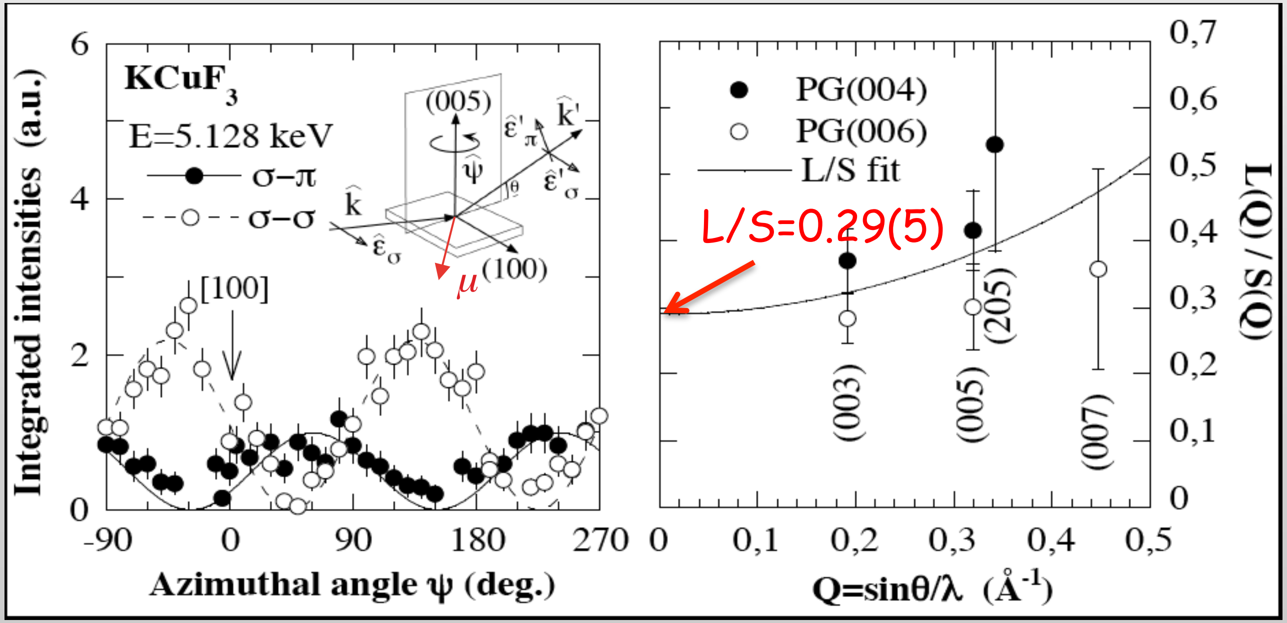
- *Determination of L/S ratio*

$$M_{\sigma\sigma} = S_2 \sin 2\theta$$
$$M_{\pi\sigma} = -2\sin^2\theta\,[(\cos\theta)(L_1+S_1)]$$

$$\frac{L(Q)}{S(Q)} = \frac{\tan(\rho-\frac{\pi}{4})}{\sin\theta}\sqrt{\frac{I_{\sigma\pi}}{I_{\sigma\sigma}}-1}$$

ρ = angle between [100] and $\underline{u}_1$ (azimuth)





From neutrons:
(Hutchings et al. PRB(1969)
$\mu_0 = 0.49\ \mu_{B/Cu^{2+}}$

From NRXS:
$\mu_0 = L+2S = 0.49\ \mu_{B/Cu^{2+}}$
$\mu_L/\mu_S \sim L/2S \sim 0.14$

$\mu_S = 0.43\ \mu_{B/Cu^{2+}}$
$\mu_L = 0.06\ \mu_{B/Cu^{2+}}$

Kramers-Heisenberg formula: resonant terms

$$f = -\left(\frac{r_e}{m_e}\right) \sum_{\eta(\Delta)} \frac{\langle\{\varepsilon' \cdot \mathbf{J}(-\mathbf{q}')|\eta\rangle\langle\eta|\varepsilon \cdot \mathbf{J}(\mathbf{q})\}\rangle}{E - \Delta + i\Gamma/2}$$

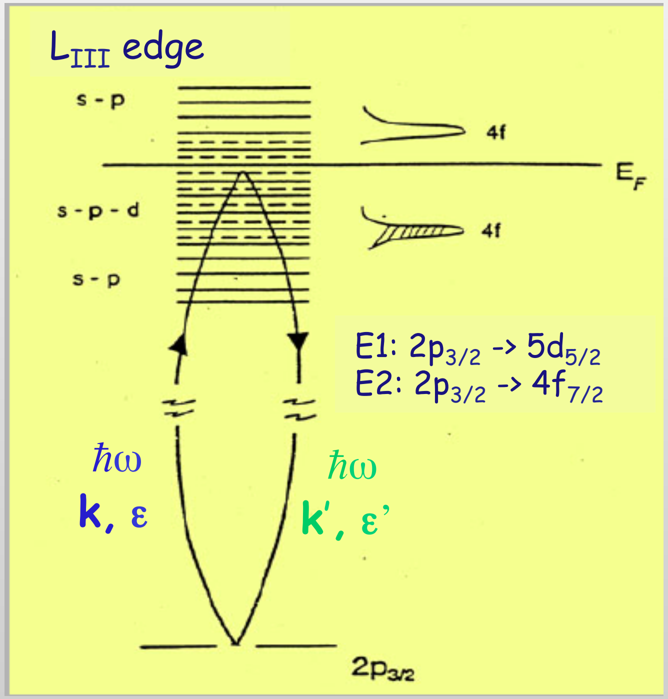
Current operator

$$\mathbf{J}(\mathbf{q}) = \sum(\mathbf{p}_j + i\mathbf{s}_j \times \mathbf{q})e^{i\mathbf{q}\cdot\mathbf{R}_j}$$

- Excitation of a inner-shell electron into an empty valence state
- Enhancement of scattering amplitude near absorption edge (NEXAS)

Sensitivity to the local degeneration of valence-electron states:

- Local symmetries of bound electrons
- Tensorial scettering amplitudes
- Forbidden lattice reflections
- Polarization effects (links with magneto-optics)



E1 = Electric dipole transitions (L=1)
E2 = Electric quadrupole transitions (L=2)

RESONANT MAGNETIC X-RAY SCATTERING AMPLITUDES

J.P. Hannon, G.T. Trammel, M. Blume, and D. Gibbs, Phys. Rev. Lett. 61 (1988) 1245;62 (1989) 263 (E).

- Expansion of spatial part of vector potential in spherical harmonics Y_{LM}
- Spherical symmetry SU(2) broken by an axial vector
- Cubic and centro-symmetric local symmetries

$$f^{RXS} = \sum_{L,M} F_{LM}(\hbar\omega_k)\left[\hat{\epsilon}' \cdot \mathbf{Y}^{(e)}_{L,M}(\hat{\mathbf{k}}')\mathbf{Y}^{*(e)}_{L,M}(\hat{\mathbf{k}}) \cdot \hat{\epsilon}\right]$$

Resonant strength

Scattering geometry (**k**,**k**')
and polarization (ε,ε') dependence

$$F_{LM}(\hbar\omega_k) = \sum_{a,c} p_a p_a(c) \frac{E_a - E_c}{\hbar\omega_k} \frac{\Gamma_x(aMc;EL)/\Gamma_c}{x+i}$$

$$x = \frac{E_a - E_c + \hbar\omega_k}{\Gamma_c/2}$$

$$\Gamma_x(aMc;EL) = 2 * \frac{(4\pi)^2}{((2L+1)!!)^2}\frac{L+1}{L} mc^2 \left|\left\langle a \left| (kr)^L Y^*_{LM}(\hat{\mathbf{r}}_j)\right| c\right\rangle\right|^2$$

L=1 => Electric dipole E1
L=2 => Electric quadrupole E2

Dipole/quadrupole matrix elements

E1: ELECTRIC-DIPOLE TRANSITIONS

Hill, J. and McMorrow, D., Acta Cryst. A **52** (1996)236-244.

Dominant terms in RXS amplitudes at $L_{2,3}$ edges:

$$f_{E1}^{res} = \left[\hat{\epsilon}' \cdot \hat{\epsilon} F_{E1}^{(0)} \boxed{- i(\hat{\epsilon}' \times \hat{\epsilon}) \cdot \mathbf{z}_n F_{E1}^{(1)}} + (\hat{\epsilon}' \cdot \mathbf{z}_n)(\hat{\epsilon} \cdot \mathbf{z}_n) F_{E1}^{(2)}\right]$$

- *Jones's matrices for E1-RXS:*

$$\mathcal{F}_{E1} = F_{E1}^{0} \begin{pmatrix} 1 & 0 \\ 0 & \cos 2\theta \end{pmatrix} \boxed{- iF_{E1}^{1} \begin{pmatrix} 0 & z_1 \cos\theta + z_3 \sin\theta \\ -z_1 \cos\theta + z_3 \sin\theta & -z_2 \sin 2\theta \end{pmatrix}}$$
$$+ F_{E1}^{2} \begin{pmatrix} z_2^2 & -z_2(z_1 \cos\theta - z_3 \sin\theta) \\ z_2(z_1 \cos\theta + z_3 \sin\theta) & -\cos^2\theta(z_1^2 \tan^2\theta + z_3^2) \end{pmatrix}$$

$$F_{E1}^{(0)} = \frac{3}{16\pi}[F_{11} + F_{1-1}]$$ ← Charge scattering (Dispersion corrections)

$$F_{E1}^{(1)} = \frac{3}{16\pi}[F_{11} - F_{1-1}]$$ ← **Magnetic dipole** (RMXS+XMCD)

$$F_{E1}^{(2)} = \frac{3}{16\pi}[2F_{10} - F_{11} - F_{1-1}]$$ ← Electric quadrupole (Anisotropic Tensor Susceptibility +XMLD)

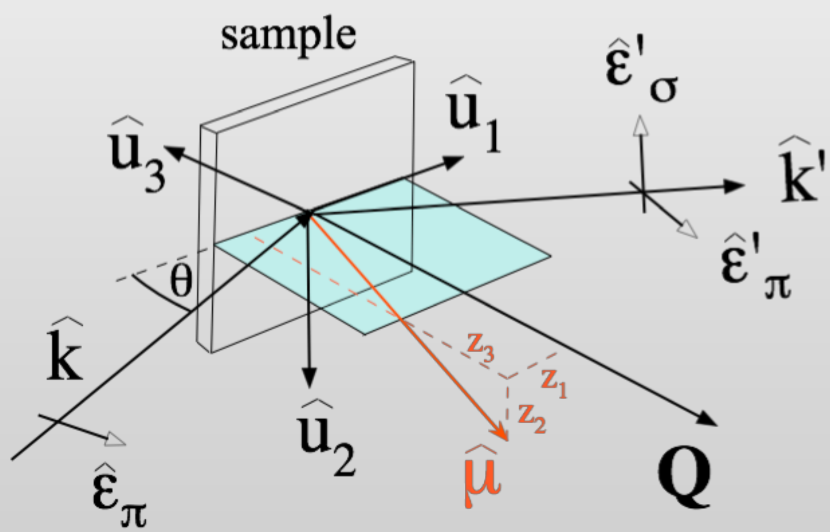
Notice that $F_{E1}^{(p)}$ depends from a linear combination F_{LM} and (p) is a rank tensor!

Ex.: Polarization dependence for magnetic dipole:

- Horizonthal scattering geometry
- π-incident polarization
- Generic moment orientation μ

$\varepsilon_\pi - \varepsilon'_\sigma$ => $z_1 \cos\theta + z_3 \sin\theta$

$\varepsilon_\pi - \varepsilon'_\pi$ => $-z_2 \sin 2\theta$

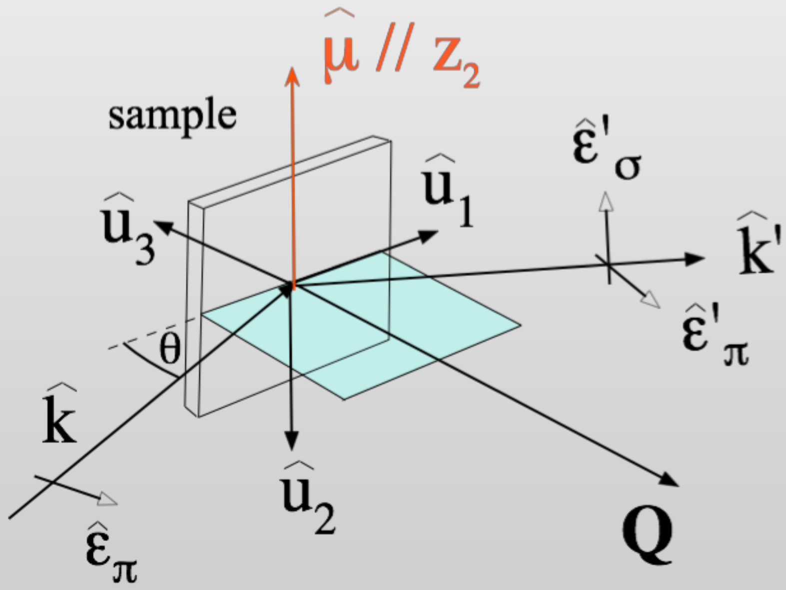


Ex.: Polarization dependence for magnetic dipole:

- Horizonthal scattering geometry
- π-incident polarization
- Moment orientation μ along u_2

$\varepsilon_\pi - \varepsilon'_\sigma$ => 0

$\varepsilon_\pi - \varepsilon'_\pi$ => $-z_2 \sin 2\theta$

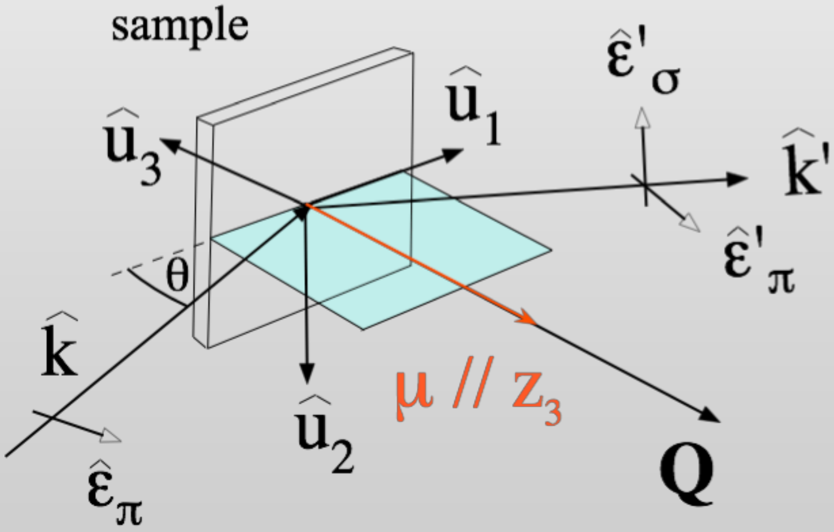


Ex.: Polarization dependence for magnetic dipole:

- Horizonthal scattering geometry
- π-incident polarization
- Moment orientation μ along u_3

$\varepsilon_\pi - \varepsilon'_\sigma$ => $z_3 \sin\theta$

$\varepsilon_\pi - \varepsilon'_\pi$ => 0



RXS ABSORPTION EDGES
ELEMENT AND SHELL SELECTIVITY

The resonance strength is mainly related to the core-hole spin-orbit coupling!

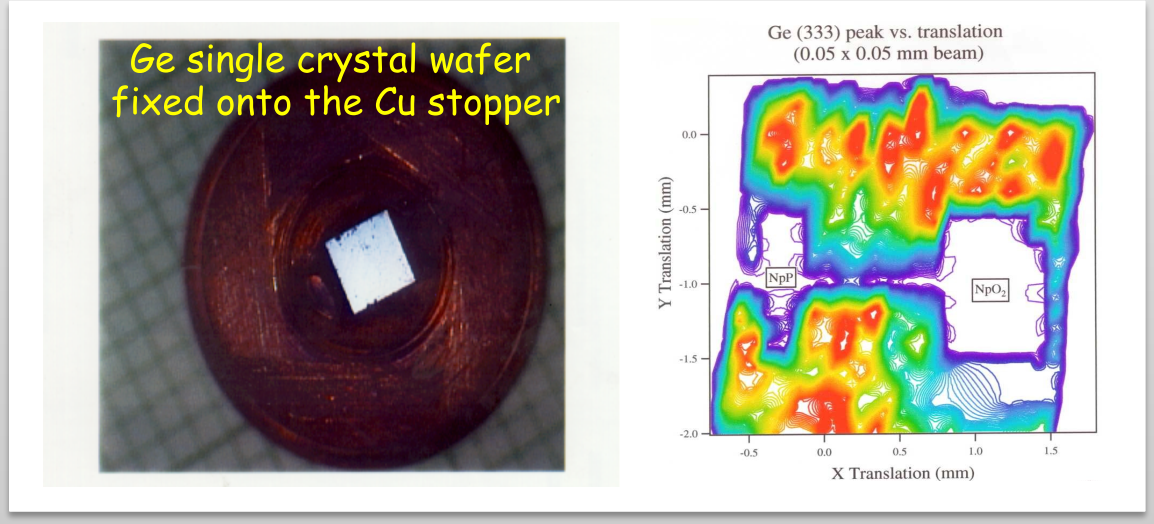
Series	Abs. edge	Energy (keV)	λ (Å)	Shells	Type	Resonant amplitude	
3d	*$L_{2,3}$*	*0.4–1.0*	*12–30*	*2p→3d*	*E1*	*≈100*	huge!!
	K	4.5–9.5	1.3–2.7	1s→4p	E1	≈0.02	weak
				1s→3d	E2	≈0.01	
5d	$L_{2,3}$	5.4–14	0.9–2.2	*2p→5d*	E1	≈1-10	strong
4f	$L_{2,3}$	5.7–10.3	1.2–2.2	2p→5d	E1	≈0.10	quite strong
				2p→4f	E2	≈0.05	weak
	$M_{4,5}$	*0.9–1.6*	*7.7–13.8*	*2d→4f*	*E1*	*≈100-300*	huge!!
5f	$L_{2,3}$	17–21	0.6–0.7	2p→6d	E1	≈0.05	weak
				2p→4f	E2	≈0.01	weak
	$M_{4,5}$	3.5–4.5	2.7–6	3d→5f	E1	≈10.0	strong

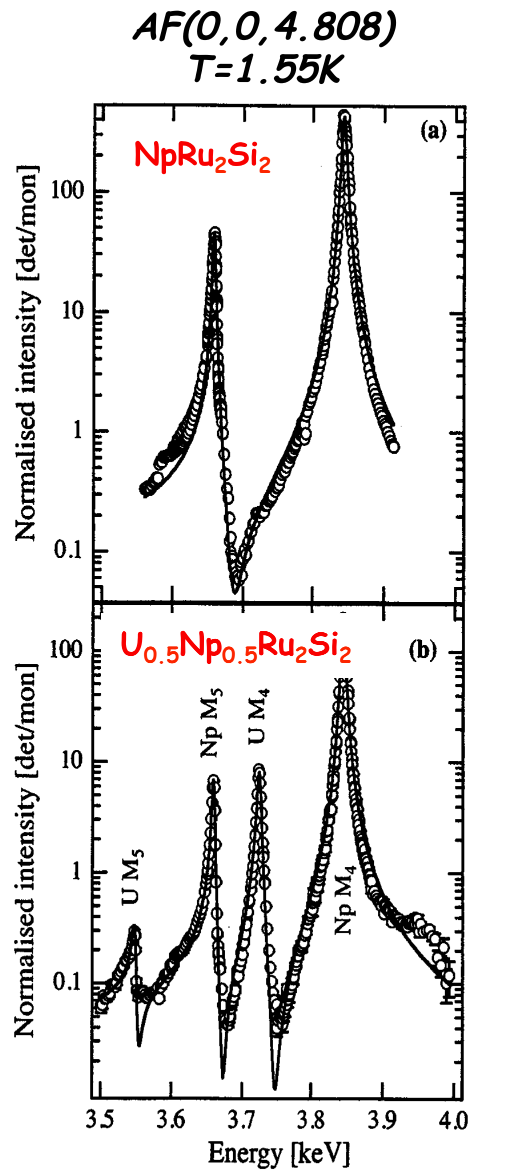
Soft x-rays energies … but with a reduced reciprocal lattice space

Resonant magnetic scattering in $(U_{0.5}Np_{0.5})Ru_2Si_2$ solid solution
E. Lidstrom et al., Phys. Rev. B 61, 1375 (2000)

Actinide Sample:
mounted on 2x2 mm² Ge(111) wafer
volume 0.1 mm³, **30 μg** Np
Element selectivity and sublattice magnetization
Np and U at $M_{4,5}$ edges

Branching ratios between M_4-M_5 edges
Electronic ground state
Exchange and spin-orbit coupling





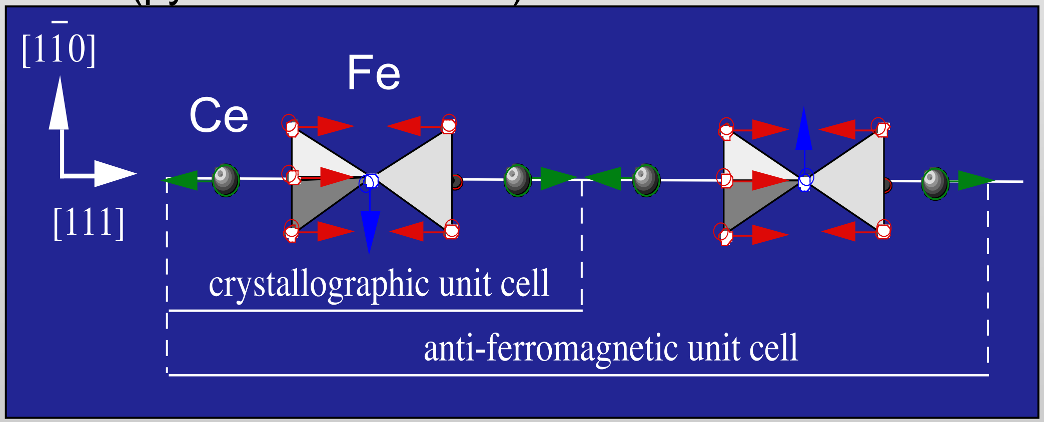
On the magnetic ground state of $Ce(Co_xFe_{1-x})_2$

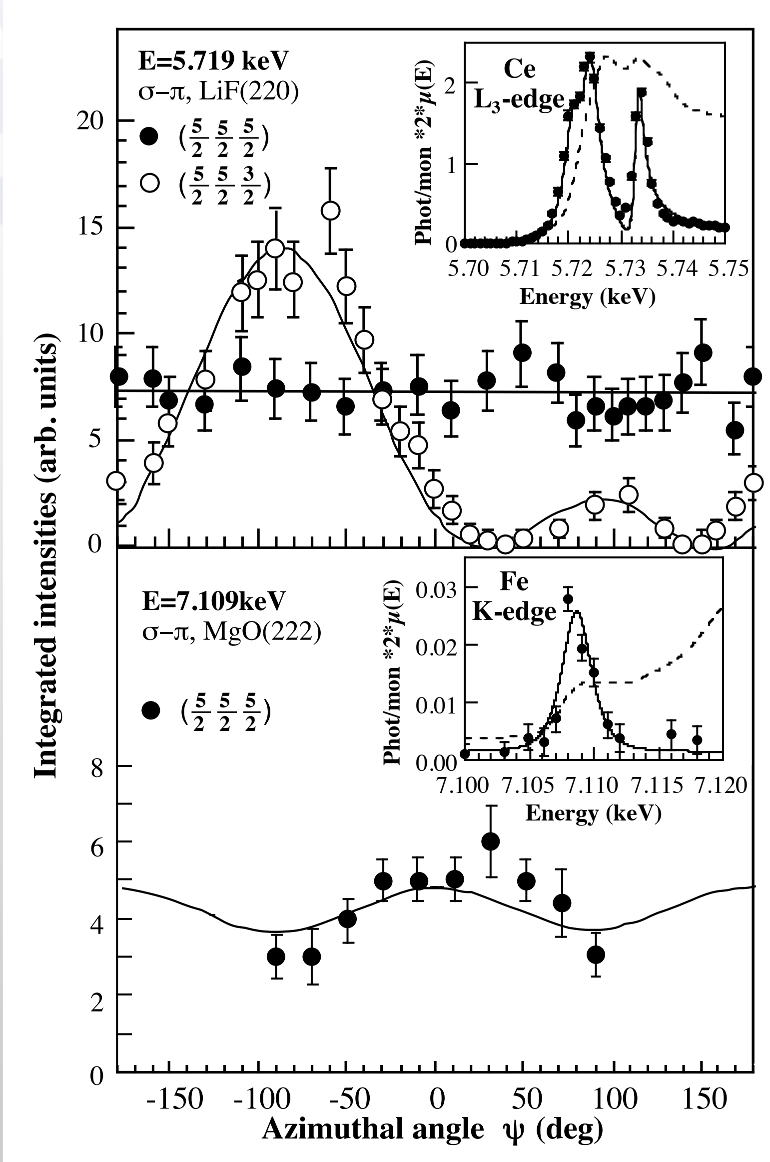
L. Paolasini, et al.,Phys. Rev. Lett. 90 (2003) 57201;
ibid: Phys. Rev. B 77 (2008) 094433

- Laves Phase structure (Fd-4m)
- In pure $CeFe_2$ AF short range fluctuations cohexist with a nominal F state
- Co doping stabilize AF ground state

Experimental results

- Azimuthal dependence at Ce L_3-edge and at Fe K-edge
- Individual sublattice magnetization and non collinear magnetic structure of Fe
- Geometrical frustration of Fe sublattice (pyroclore sublattice)





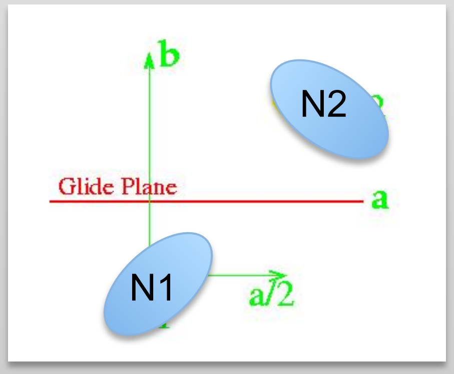
Interplay between orbital and magnetic ordering in $KCuF_3$
R. Caciuffo, et al., Phys. Rev. B 63 (2002) 174425; ibid. L. Paolasini, Phys. Rev. Letters 88 (2002) 106403.

Scientific background

- Mott-Hubbard insulator
- Model system for orbital ordering

Experimental results

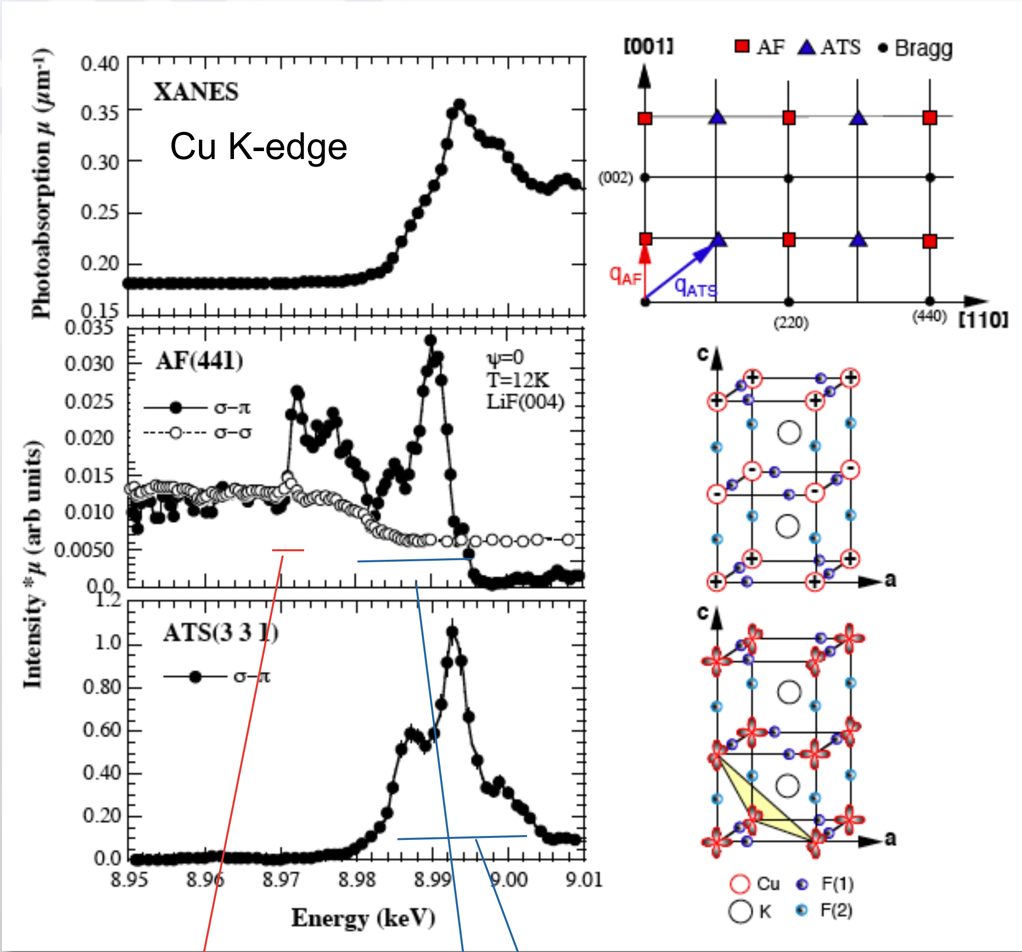
- Orbital and AF order strictly related.
- OO of $d_{y^2-z^2}$ - $d_{x^2-z^2}$ type with q_{OO}=<111>.
- ATS due to the difference in the $2p_{x(y)}$ DOS (Jahn-Teller distortion)



Violation of the extinction rules

f(N1)+f(N2)exp[iπh]

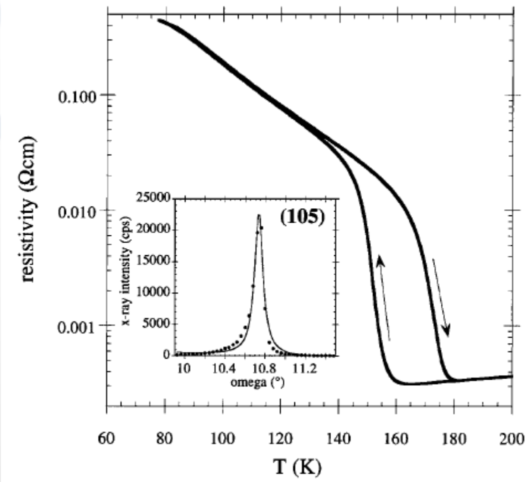
$\boxed{F_{E1}^{(2)}}$



E2 = 1s -> 3d E1 = 1s -> 4p

Direct observation of charge order in epitaxial $NdNiO_3$ films
Staub U. et al., Phys. Rev. Letters 88 (2002) 126402.

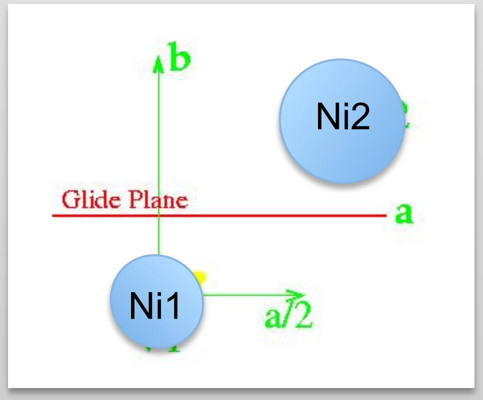
- Prototype of bandwidth-controlled metal-insulator
- Metal/insulator transition T_{MI}=150-170K



Experimental results

- Strong enhancement of RXS at Ni K-edge on the forbidden charge reflection (105)
- ATS due to a charge dis-proportionation at Ni^{3+} site

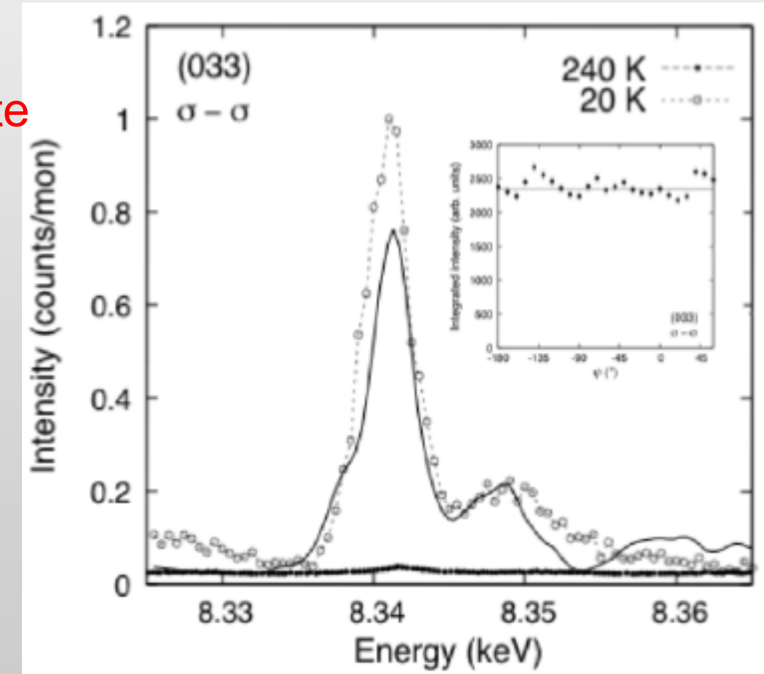
$Ni^{3\pm\delta}$ where δ~0.45±0.04



Violation of the extinction rules

f(Ni1)≠f(Ni2)

$\boxed{F_{E1}^{(2)}}$



DEVELOPMENT OF HANNON'S TERMS FOR NON- CENTROSYMMETRIC SYSTEMS

P. Carra and B. T. Thole, Rev. Mod. Phys. 66, 1509 (1994)

Extension of RXS to all the local symmetries E2-E2

Interpretation of forbidden reflection of Fe_2O_3 in term of charge multipoles

I. Marri and P. Carra, Phys. Rev. B 69, 113101 (2004)

E1-E2 events for non centrosymmetric systems

Interpretation of dichroic signals (parity breaking symmetries)

$$f^{RXS} \approx m \sum_c \frac{(E_c - E_a)^3}{\hbar^3 \omega_k \, (E_a - E_c + \hbar\omega_k - i\Gamma_c/2)}$$

$$\left[\sum_{\alpha\beta} \epsilon'^*_\alpha \, \epsilon_\beta \, D_{\alpha\beta} - \frac{i}{2} \sum_{\alpha\beta\gamma} \epsilon'^*_\alpha \, \epsilon_\beta \left(k_\gamma \, I_{\alpha\beta\gamma} - k'_\gamma \, I^*_{\beta\alpha\gamma} \right) + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \epsilon'^*_\alpha \, \epsilon_\beta \, k'_\gamma \, k_\delta \, Q_{\alpha\beta\gamma\delta} \right]$$

$$D_{\alpha\beta} = \left\langle a \middle| \sum_j r_j^\alpha \middle| c \right\rangle \left\langle c \middle| \sum_i r_i^\beta \middle| a \right\rangle$$

Dipole-Dipole (E1-E1)

$$I_{\alpha\beta\gamma} = \left\langle a \middle| \sum_j r_j^\alpha \middle| c \right\rangle \left\langle c \middle| \sum_i r_i^\beta r_i^\gamma \middle| a \right\rangle$$

Dipole-Quadrupole (E1-E2)

$$Q_{\alpha\beta\gamma\delta} = \left\langle a \middle| \sum_j r_j^\alpha r_j^\beta \middle| c \right\rangle \left\langle c \middle| \sum_i r_i^\gamma r_i^\delta \middle| a \right\rangle$$

Quadrupole-Quadrupole (E2-E2)

TENSOR SYMMETRIES

Space inversion (parity):

• Tensors D and Q are even and I odd

=> Dipole-Quadrupole transitions (E1-E2) allowed for "resonant" atom breaking the site inversion symmetry

Rotation:

• Decomposition of tensor elements ($D^{\alpha\beta}$, $I^{\alpha\beta\psi}$ or $Q^{\alpha\beta\psi\delta}$) in its irreducible components $T^{(j)}$ (with dimension 2j+1)

Ex: For Dipole Dipole (E1-E1)

$$f^{RXS}(dd) \propto \sum_{\alpha\beta} \epsilon'^{\alpha}\epsilon^{\beta} D^{\alpha\beta} = \sum_{j=0,1,2} \sum_{m=-j}^{j} (-1)^{j+m} P^{(j)}_{-m} T^{(j)}_{m}$$

$$\begin{aligned}
&j = 0: \\
&\quad T^{(0)}_0 = \frac{1}{3}\left(D^{xx} + D^{yy} + D^{zz}\right) \\
&j = 1: \\
&\quad T^{(1)}_0 = \frac{1}{2}\left(D^{xy} - D^{yx}\right) \\
&\quad T^{(1)}_{\pm 1} = \mp\frac{1}{2\sqrt{2}}\left[(D^{yz} - D^{zy}) \mp i(D^{xz} - D^{zx})\right] \\
&j = 2: \\
&\quad T^{(2)}_0 = D^{zz} - T^{(0)}_0 \\
&\quad T^{(2)}_{\pm 1} = \mp\sqrt{\frac{2}{3}}\,\frac{1}{2}\left[(D^{xz} + D^{zx}) \mp i(D^{yz} + D^{zy})\right] \\
&\quad T^{(2)}_{\pm 2} = \frac{1}{\sqrt{6}}\left[2D^{xx} - 2D^{yy} \pm i(D^{xy} + D^{yx})\right]
\end{aligned}$$

Time reversal: (exchange k and k' wavevector directions)

⇒Exchange of αβγδ indexes

•j=1 magnetic terms: antisymmetric with respect to the time-reversal symmetry

HIGH ORDER MULTIPOLES

Dubovik, V.M. & Tugushev, V.V., Physics Reports 187, 145-202 (1990)

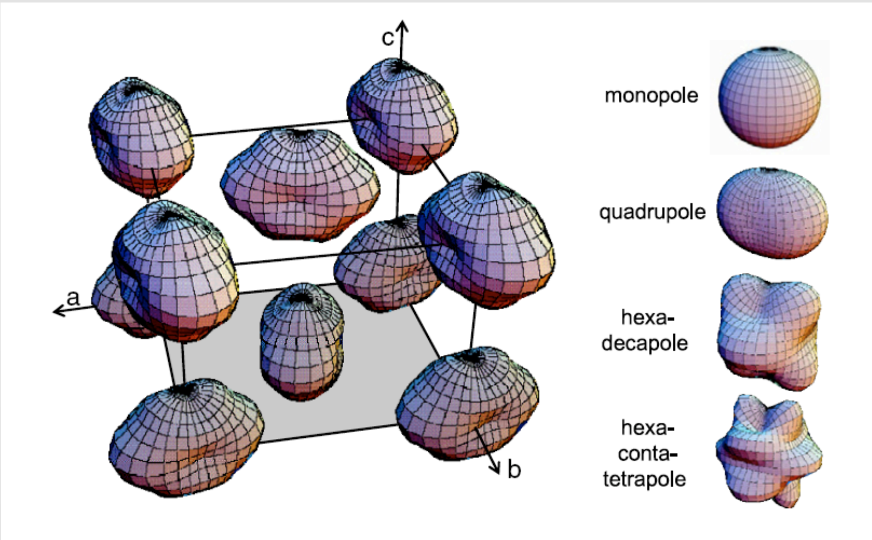
The multipole expansion of the EM field

Charge distribution ρ(x):

Electrostatic energy

$$W_E = \int d^3x \rho(\vec{x})\Phi(\vec{x})$$

Charge multipoles



Permanent currents j(x):

Magnetic energy

$$W_M = \int d^3x \; \vec{J}(\vec{x}) \cdot \vec{A}(\vec{x})$$

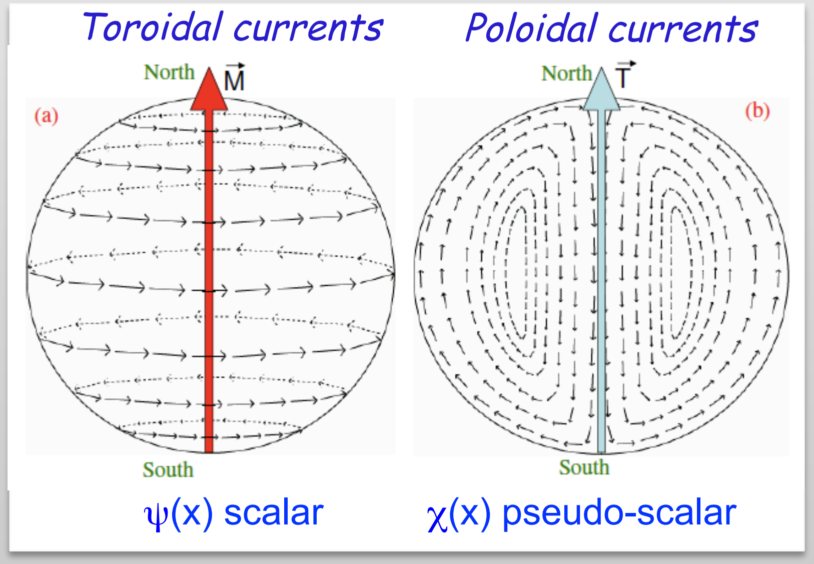
Irrotational (rotor free)

$$\vec{\nabla} \cdot \vec{J} = \cancel{\vec{\nabla} \cdot \vec{J}_{\parallel}} \equiv -\partial_t \rho$$

Stationary states

Solenoidal (divergenceless)

$$\vec{J}_{\perp} = \vec{l}\psi(\vec{x}) + \vec{\nabla} \times (\vec{l}\chi(\vec{x}))$$



CLASSIFICATION OF MULTIPOLES: T AND P

S. Di Matteo, Y. Joly, C.R. Natoli, Phys. Rev. B 72, 144406 (2005)

Product of irreducible spherical tensors $X^{(p)}$ and $F^{(p)}$.

The tensor rank p depends on the order of multipole in the EM field expansion

$$f_j^{RXS} = \sum_{p,q} (-1)^q X_{-q}^{(p)} F_q^{(p)}(j;\omega)$$

p= tensor rank:

p=0 monopole
p=1 dipole
p=2 quadrupole
p=3 octupole
p=4 hexa-decapole
p=5 hexa-conta-tetrapole

Tensor	rank	$\hat{T}$	$\hat{P}$	Type	Multipole
$F^{(0)}(E1-E1)$	0	+	+	charge	monopole
$F^{(0)}(E2-E2)$	0	+	+	charge	monopole
$F^{(1)}(E1-E1)$	1	-	+	magnetic	dipole
$F^{(1)}(E2-E2)$	1	-	+	magnetic	dipole
$F^{(1+)}(E1-E2)$	1	+	-	electric	dipole
$F^{(1-)}(E1-E2)$	1	-	-	polar toroidal	dipole
$F^{(2)}(E1-E1)$	2	+	+	electric	quadrupole
$F^{(2)}(E2-E2)$	2	+	+	electric	quadrupole
$F^{(2+)}(E1-E2)$	2	+	-	axial toroidal	quadrupole
$F^{(2-)}(E1-E2)$	2	-	-	magnetic	quadrupole
$F^{(3)}(E2-E2)$	3	-	+	magnetic	octupole
$F^{(3+)}(E1-E2)$	3	+	-	electric	octupole
$F^{(3-)}(E1-E2)$	3	-	-	polar toroidal	octupole
$F^{(4)}(E2-E2)$	4	+	+	electric	hexadecapole

$P^{+/-}T^{+}$ Electric/charge

$P^{+}T^{-}$ Magnetic

$P^{-}T^{-}$ Magneto-electric

EXPERIMENTAL DETERMINATION OF MULTIPOLAR ORDERED STATES IN V_2O_3

Experiments:

L. Paolasini, et. al J. Electron Spectrosc. Relat. Phenom. 120, 1 (2001)

J. Fernandez-Rodrıguez, V. Scagnoli, C. Mazzoli, F. Fabrizi, S.W. Lovesey, J. A. Blanco, D.S. Sivia, K.S. Knight, F. de Bergevin, and L. Paolasini, Phys. Rev. B **81** (2010) 085107.

Theory:

S. Di Matteo, Y. Joly, A. Bombardi, L. Paolasini, F.de Bergevin, and C.R. Natoli, Phys. Rev. Lett. 91, 257402 (2003)

S. Loversey, J. Fernandez-Rodriguez, J.A. Blanco, D.S. Sivia, K.S. Knight, L. Paolasini, Phys. Rev. B **75** (2007) 014409

ATS
$(00.l)_H$ $l_H=3(2n+1)$

Electric octupole and hexadecapole
F^3(E1-E2)+F^4(E2-E2)

ATS
$(h0.-h)_m$ $h_m=2n+1$

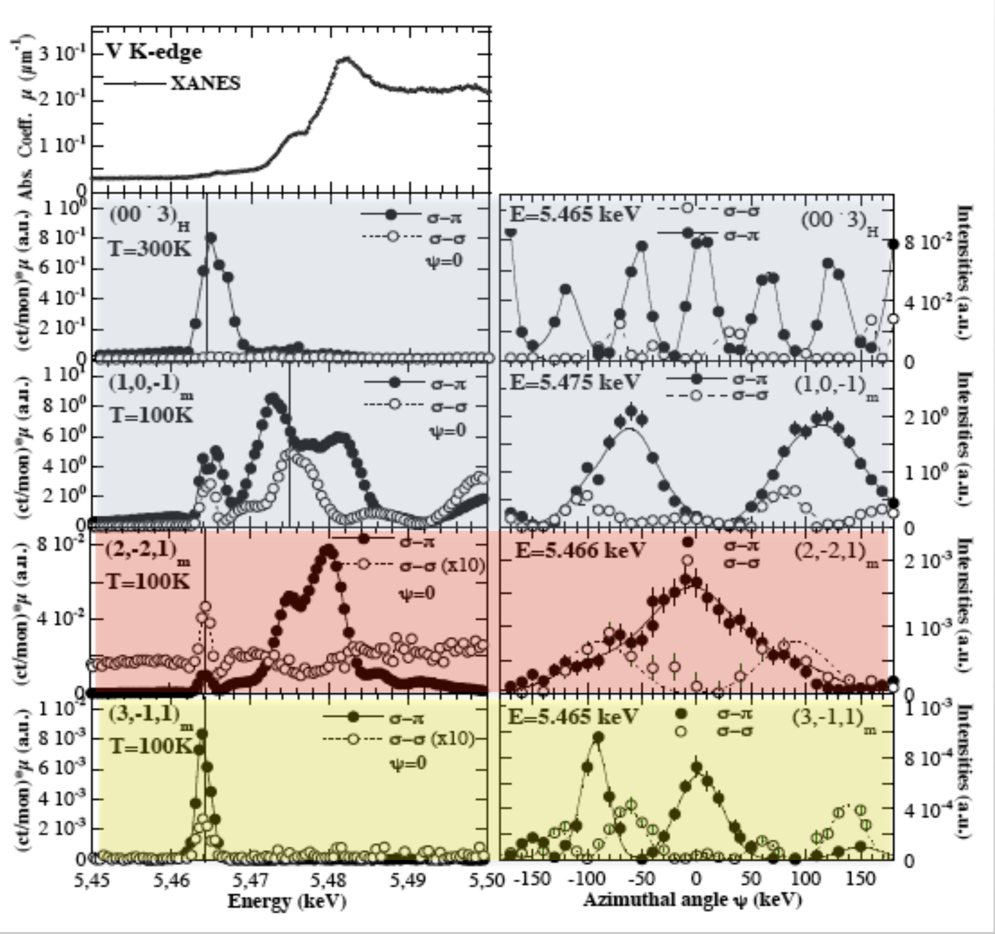
Electric quadrupole
F^2(E1-E1)
(dominant contribution)

AF reflections
k_m+l_m=even and h_m=even

Magnetic dipole and magnetic quadrupole
F^1(E1-E1)+F^{2-}(E2-E2)

Special reflections
k_m+l_m=even and h_m=odd

Polar toroidals and magnetic quadrupole
$F^{(1,3)-}$(E1-E2) and F^2(E2-E2)



Local, Element, Orbital Selective Probe

XLD
(X-ray Linear Dichroism)
- *Local site electronic anisotropies*

$$\Delta\mu = \mu^{\parallel} - \mu^{\perp} \text{ (LD)}$$

XMCD (magneto-optics)
(X-ray Magnetic Circular Dichroism)
- *Spin and orbital moment determination*
- *Ferro-, ferri- and para- magnetism*

$$\Delta\mu = \mu^{+} - \mu^{-} \text{ (CD) ;} \qquad \langle \mathbf{L_z} \rangle, \langle \mathbf{S_z} \rangle \text{ and } \langle \mathbf{T_z} \rangle$$

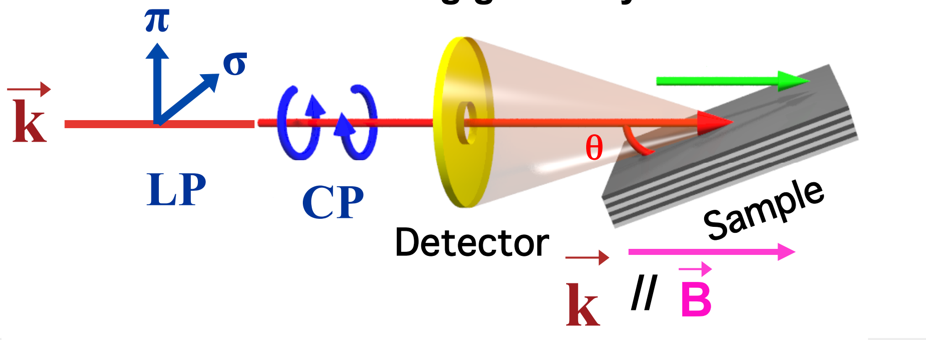
XnrLD (optical activity)
(X-ray non-reciprocal linear dichroism)
- *Spin and orbital moment determination*

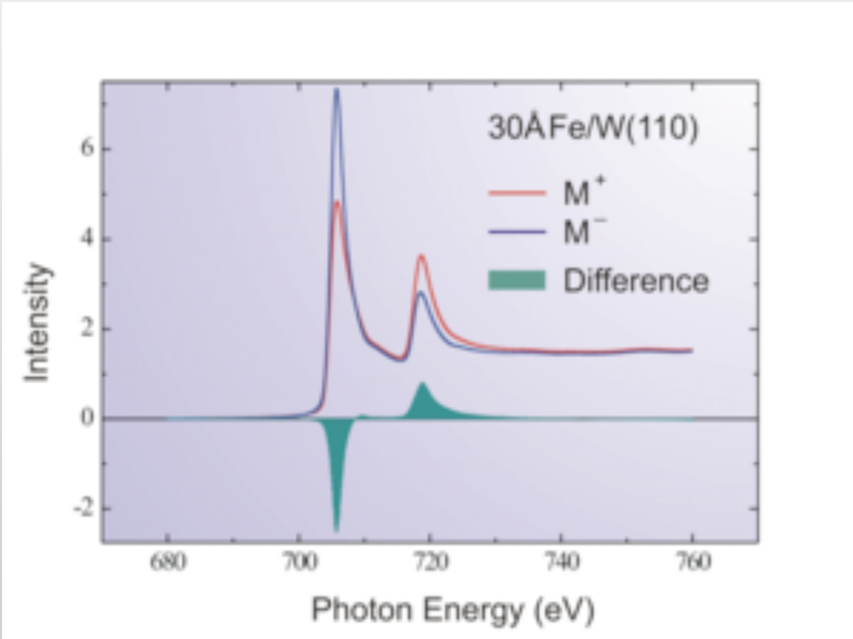
$$\Delta\mu = \mu^{\parallel}(H\uparrow) - \mu^{\perp}(H\uparrow) \qquad W^{(2)} = [L \otimes n]^{(2)}$$

XMχD (optical activity)
(X-ray magneto-chiral dichroism)

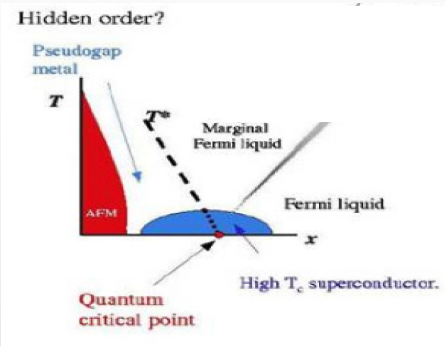
$$\Delta\mu = [\mu^{+}(H\uparrow) + \mu^{-}(H\uparrow)] - [\mu^{-}(H\downarrow) + \mu^{+}(H\downarrow)] \qquad \Omega = \mathrm{i}[n, L^2]/2$$

Total Fluorescence Yield in backscattering geometry





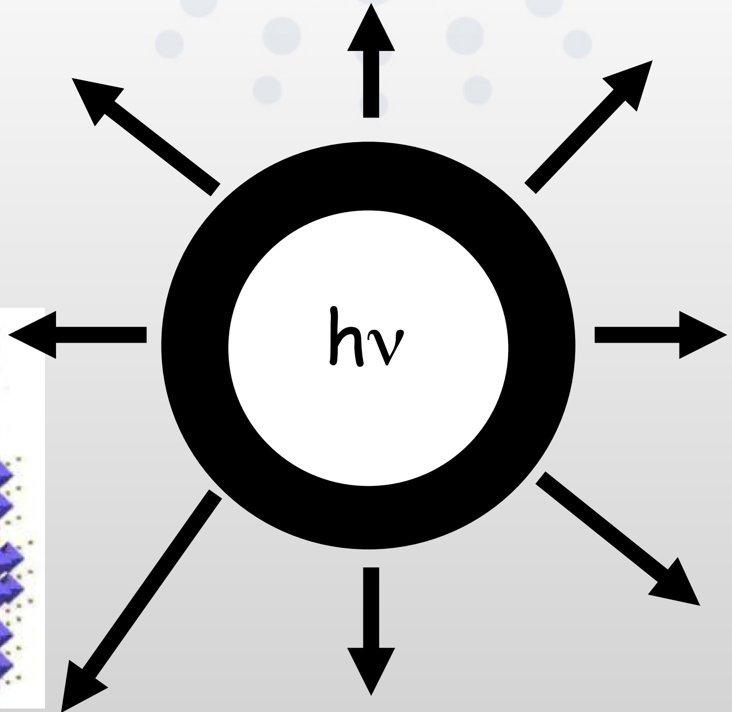
High-T_c superconductors
- Pseudogap state
- Simmetry of pair condensate

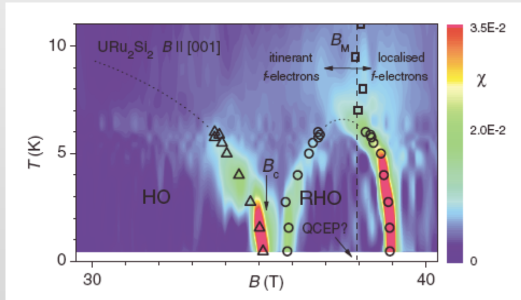


Magnetic phase diagram
-Structural phase transitions
- Metamagnetic transitions
- Lock-in transitions

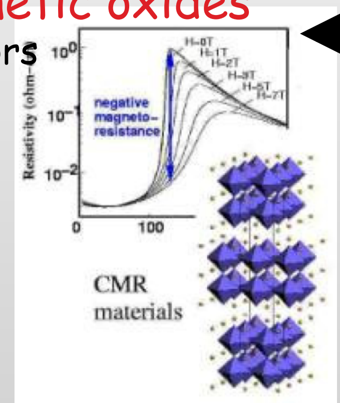
Quantum low dimensional antiferromagnetics
- Spin-1 Haldane chains
- Spin ladders
- Magnetization plateaus

Heavy fermions
- Quantum criticality
- Hidden order parameter
- Metamagnetism

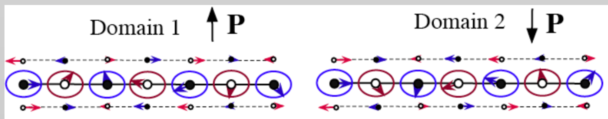




Doped magnetic oxides
- Mott-insulators
- CMR

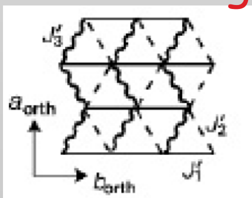


Multiferroics
- Magnetoelectricity
- Magnetic/FE coupling



1D-2D (organic?) conductors
- CDW and SDW
- Superconductivity

Frustrated magnetism



CONCLUSIONS

Site selectivity:

- Disentangle the individual site contributions
- High Q-resolution to resolve small splitting of magnetic Bragg peaks
- Small scattering volumes (small samples, thin films)

Resonant x-ray scattering:

- Chemical and shell selectivity
- RXS: unique information about electronic and magnetic order parameters
- Orbital selectivity and tensorial structure factor
- High order multipoles, orbital ordering, local site anisotropies

Non-resonant magnetic x-ray scattering:

- Determination of L/S ratio of ordered magnetic phases
- Single magnetic domain imaging

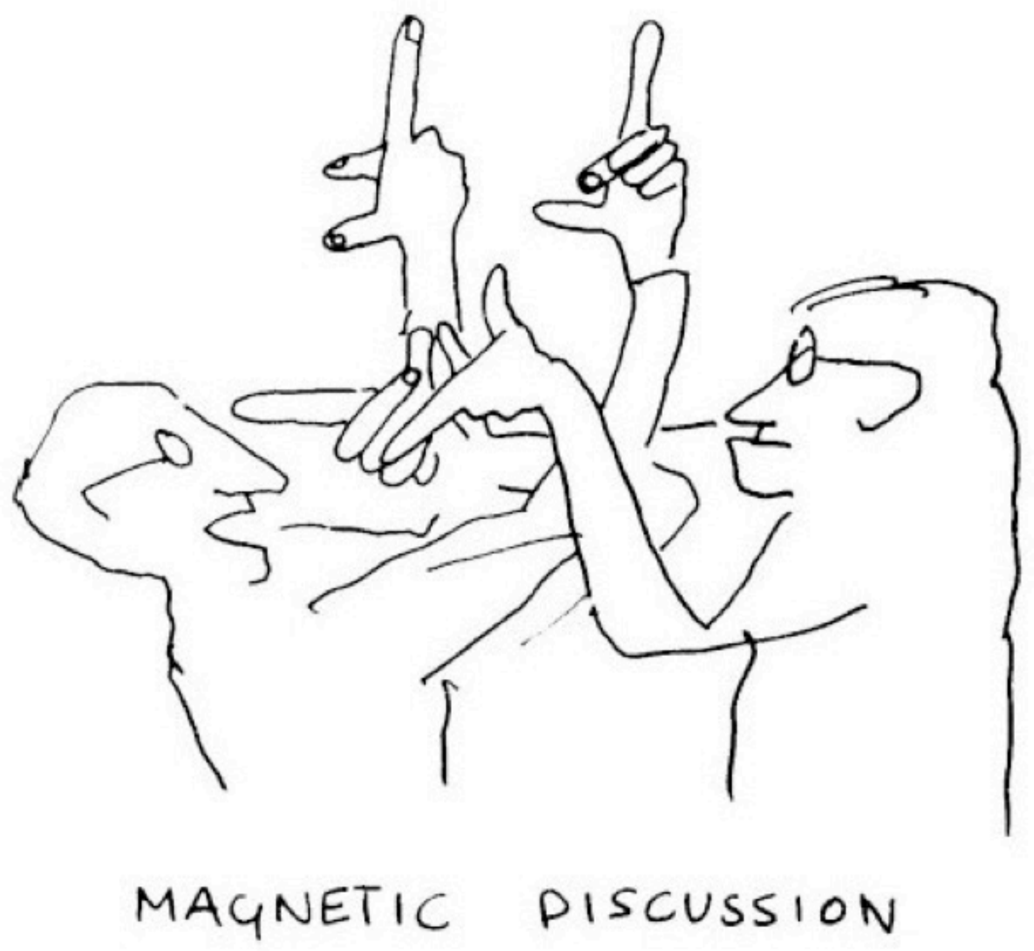
X-ray polarization analysis and control:

- Single out the individual scattering amplitude contributions (f^0, f^{magn}, f^{RXS})
- Circular polarimetry:
    - Handedness of allows the determination of helicity, absolute phase
- Linear polarimetry:
    - Disentangle the resonant x-ray scattering contributions

Extreme conditions:

- Small samples (easy focusing) allows the application of extreme conditions:
    - Combined high pressures, high magnetic and electric fields

Thank you for your attention!



From B. Touschek