WHAT DO WE SEE WITH X-RAYS IN MAGNETISM

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OUTLINES

1. Introduction: synchrotron radiation and magnetism
2. Basic photon-matter interaction: absorption and scattering
3. Theory of electron-photon interaction

   classical, semi-classical and relativistic
4. Magnetic and Resonant exchange scattering
5. Examples of applications

Books:
"Synchrotron Radiation: Basics, Methods and Applications", Ed. Mobilio, Boschierini, Meneghini, Sringer-Heidelberg 2015
Jens Als-Nielsen and Des McMorrow , "Elements of Modern X-ray Physics", Second edition, John Wiley & Sons, Ltd Publication, (2011).

INGREDIENTS FOR MAGNETISM

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

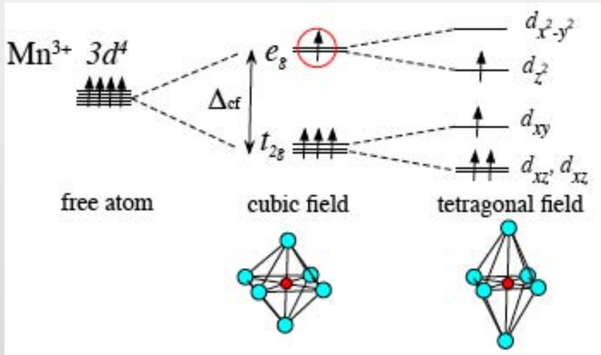
  ex. Rare Earth compounds

Intra atomic exchange → Pauli fermion exclusion → Spin-orbit coupling →

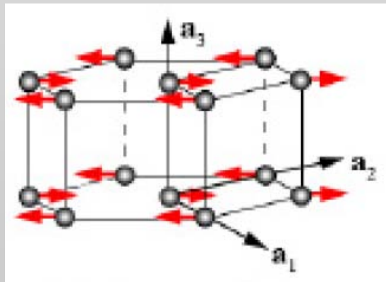
Hund's rules:
max S
max L
J = L+S or |L-S|

- 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

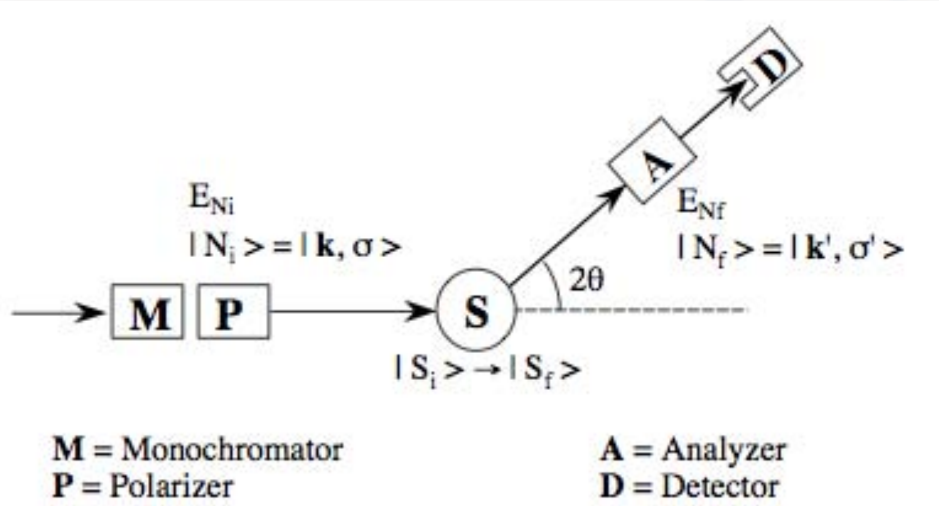


- Inter atomic magnetic interactions induce long range order
  - Isotropic exchange H=J **S·S** (Heisenberg)
  - Anisotropic exchange H=**S** J̲ **S** (Dzyaloshinsky-Moriya)
  - Super-exchange and double-exchange
  - Itinerant exchange (RKKY)



SCATTERING EXPERIMENTS

Determination of temporal evolution of the physical state of a large number of particle at the thermal equilibrium.
Measurement 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'**
Spin	σ => σ'

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:

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

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 $<S_f|$:

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

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

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

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

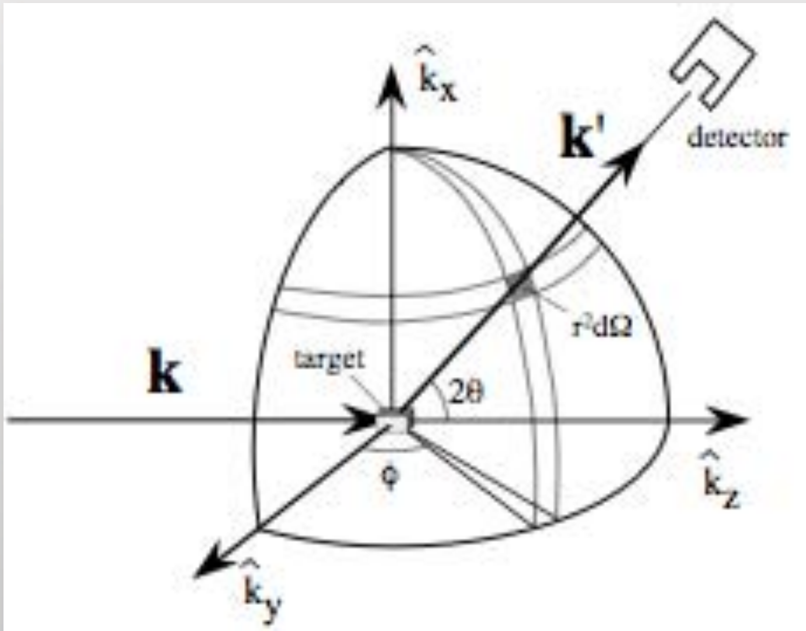
Differential scattering cross-section

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

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

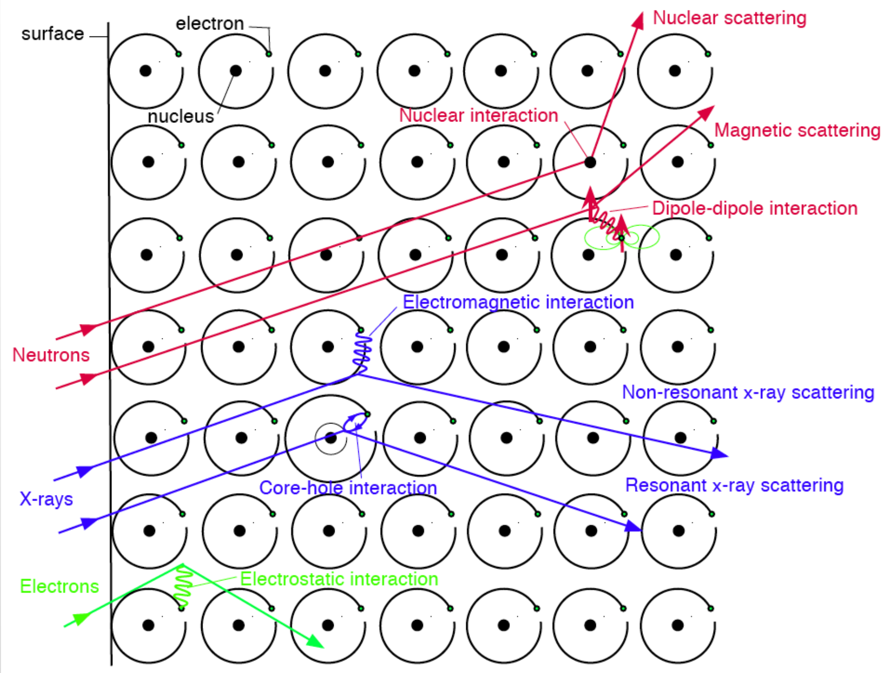
Total scattering cross-section

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



MAGNETIC PROBES

Neutron and x-ray magnetic scattering are a powerfull probe to study the magnetism in condensed matter.



Neutron scattering (Cold-Thermal)

- Bulk sensitivity (low absorp., ~10 cm)
- Amplitudes: Nuclear/Magnetic ~ 1
- High E-resolution
- **Unpolarized source**
- Soft interaction neutron-sample
- Well established sample environment

X-ray scattering (3-30 keV)

- Surface sensitivity (high absorp., ~10 μm)
- Amplitudes: Charge/Magnetic ~ 10^5
- High Q-resolution
- **Polarized source**
- **Easy Focusing**
- Hard probe (T-heating, sample damage)...

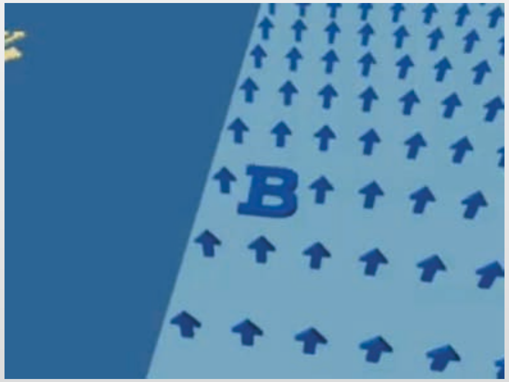
WHAT THE SYNCHROTRON RADIATION?

Electromagnetic radiation emitted when **charge particles** moving at ultra-relativistic energies are forced to change direction under the action of a magnetic field.

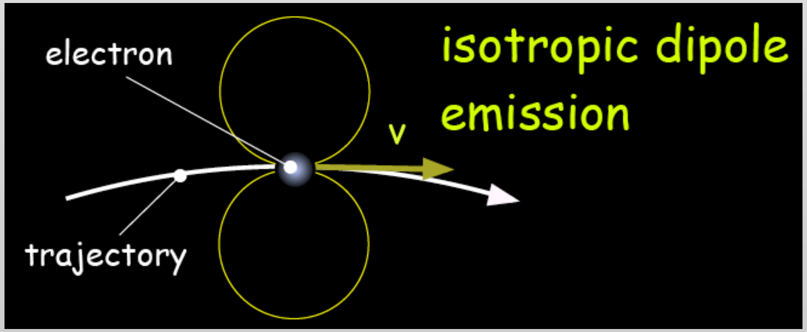
$E > m_0c^2 \sim 0.511$ MeV $\gamma = E/m_0c^2$ $\gamma \sim 1957\ E[GeV]$

Classical emission $v_e << c$
Lorenz Force **F**=q (**E**+**v**x**B**)

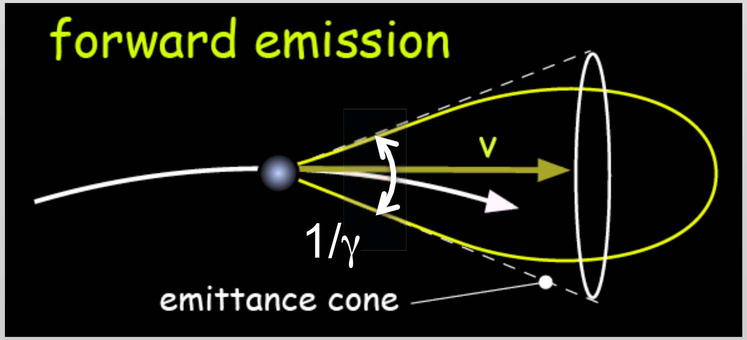
Relativistic emission when $v_e \sim c$
Forward direction emittance cone $1/\gamma \sim 1$mrad



Notice: 1mrad~0.057 deg!



Ex: Radio waves



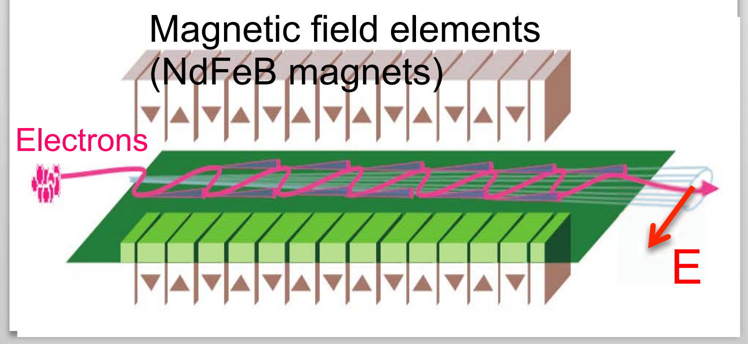
Synchrotron emission

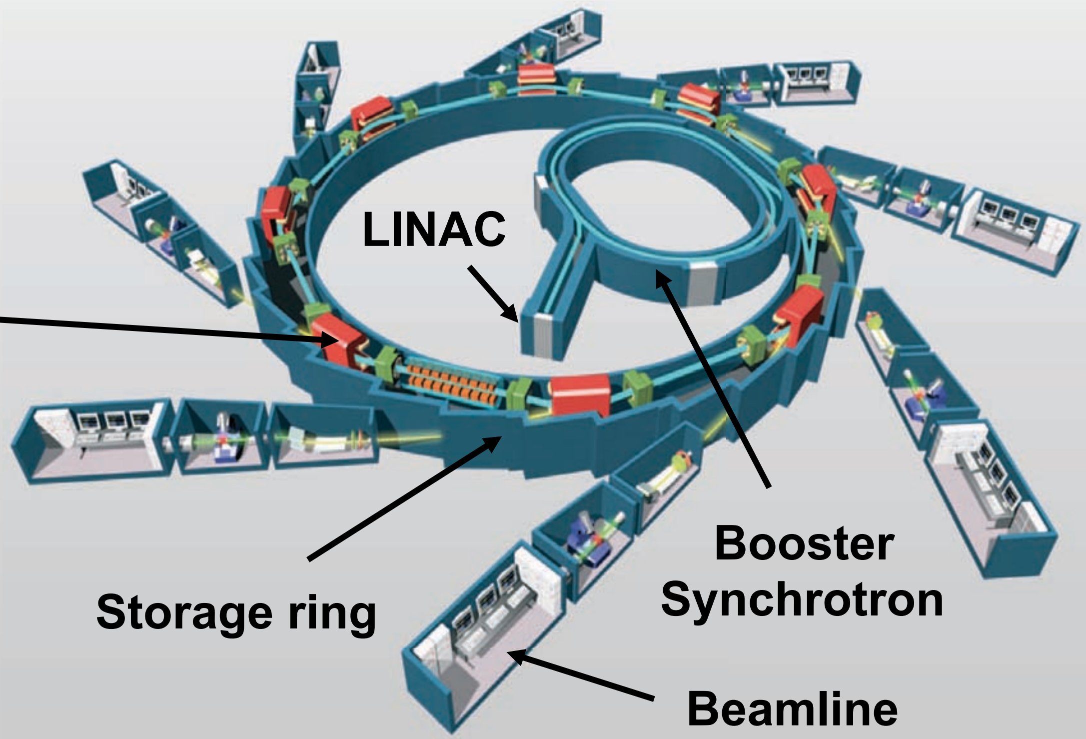
The Synchrotron is a “storage ring” where the **electrons** are first accelerated by a booster at high energies and then constrained on a circular orbit.

ESRF:
Energy: 6.02 GeV
Circumference: 844 m
Maximum current: 200 mAmp

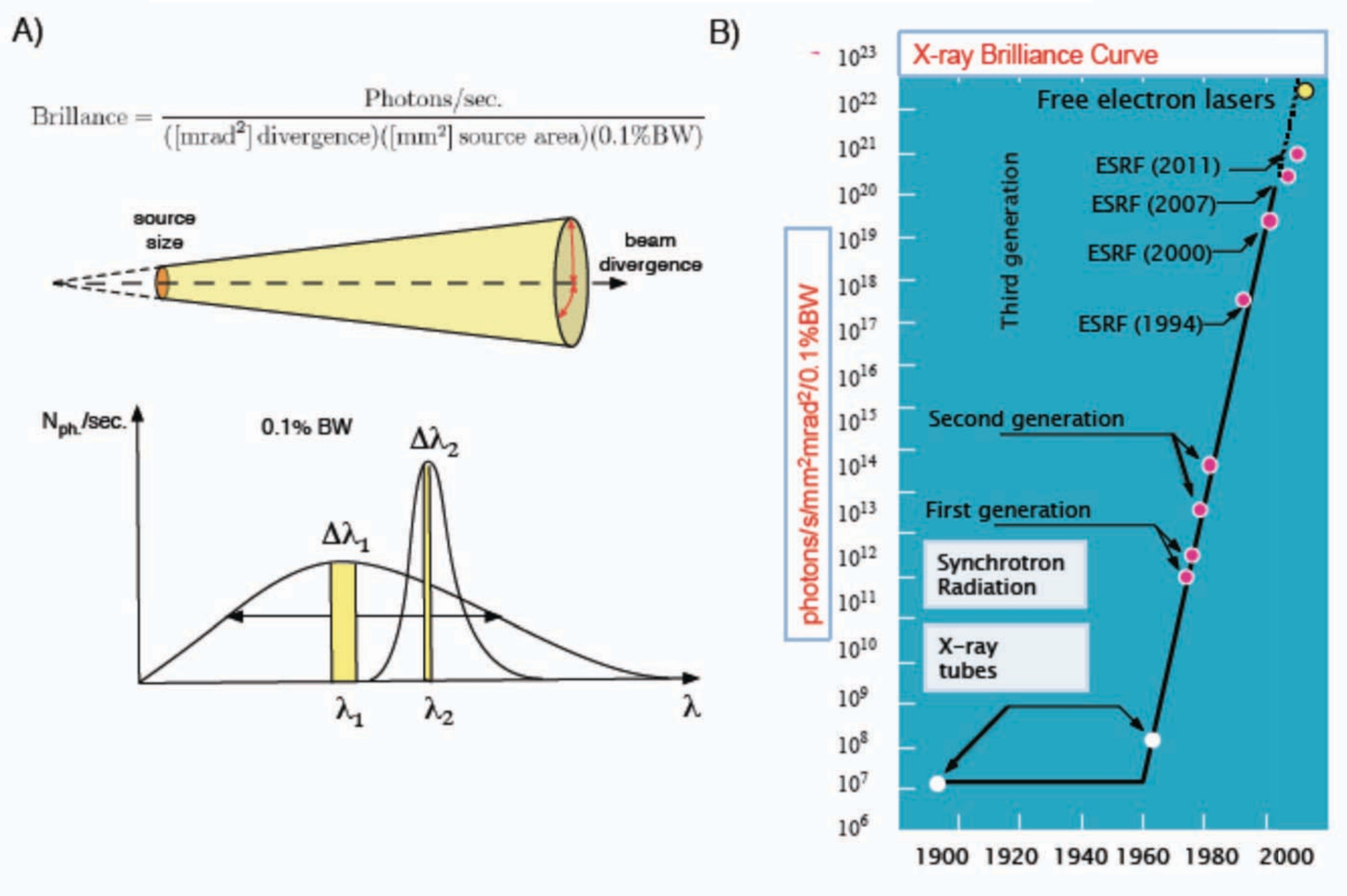
The electrons trajectory is modulated by a spatial periodic magnetic field (undulators).
The radiation emitted by a given electron at one oscillation is in phase with the radiation from the following oscillations.

Insertion devices: Undulators





BRILLANCE OF THE SYNCHROTRON SOURCES



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:

$$\mathrm{B} = \nabla \times \mathrm{A}$$
$$\mathrm{E} = -\nabla\Phi - \frac{1}{c}\frac{\partial \mathrm{A}}{\partial t}$$

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.

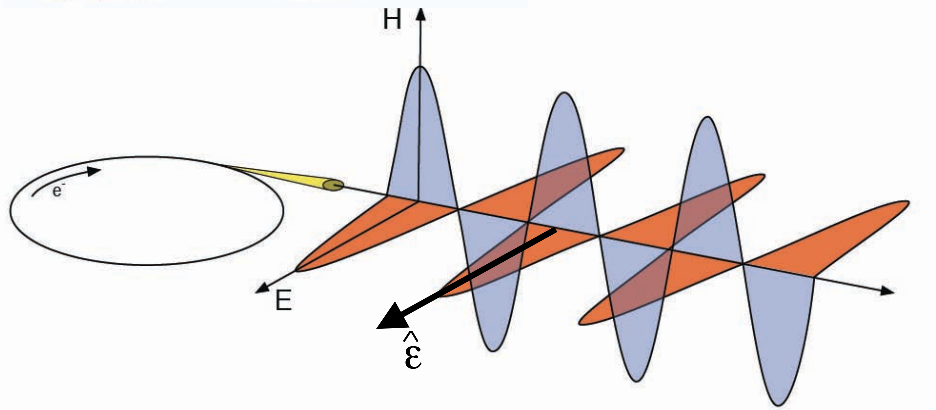
Energy
[keV] = ħω=hc/λ = 12.398 / λ [Å]

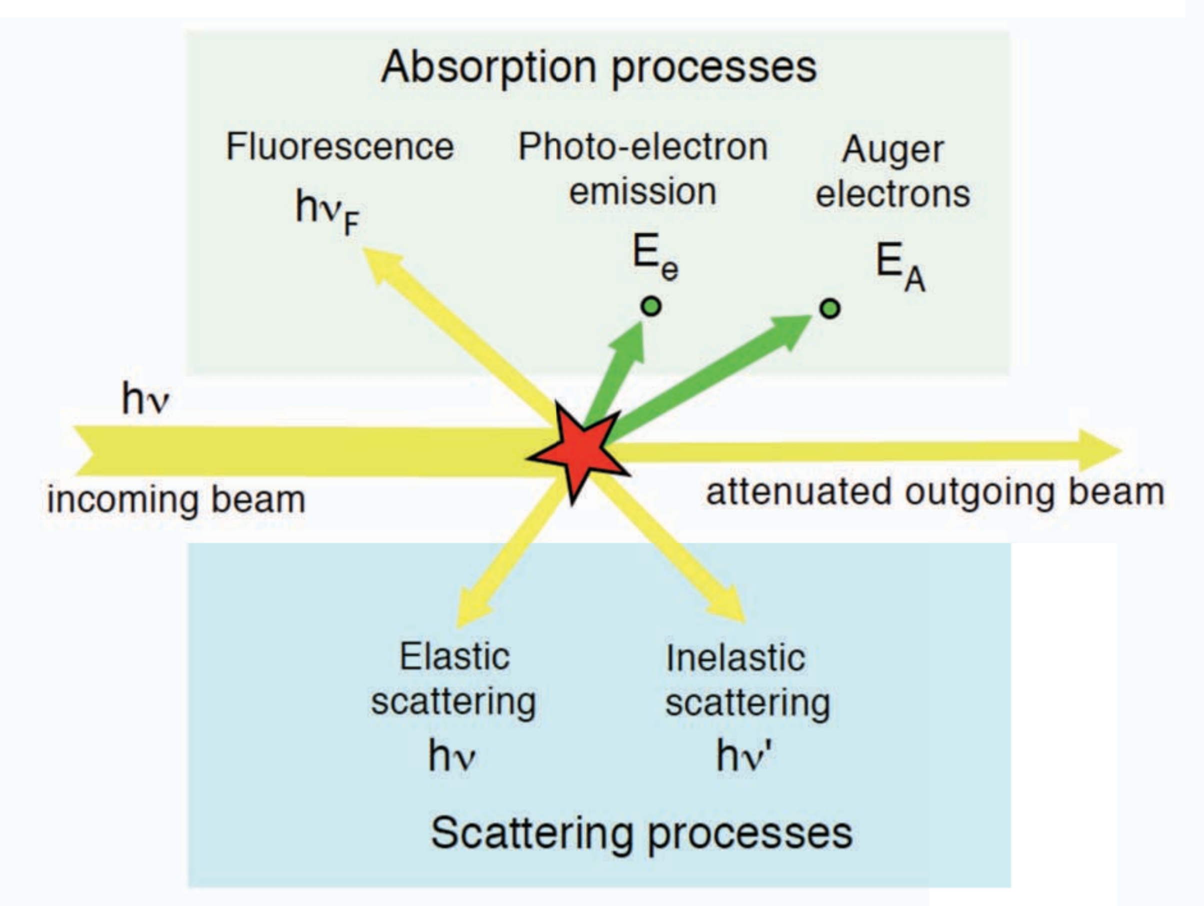
Spectral intensity
$I_0(\omega) = \langle E_0^2 \rangle = N(\omega)\, \hbar\omega$

ex. 1 Å = 12.398 keV

Transverse EM waves

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





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

X-RAYS SCATTERING: FREE ELECTRONS

- Hypotesis: electron are at rest
- The electric field E_{in} of the incident x-rays act as a force **F**=**E**q
- The electron accelerates and radiates a spherical wave E_{rad}

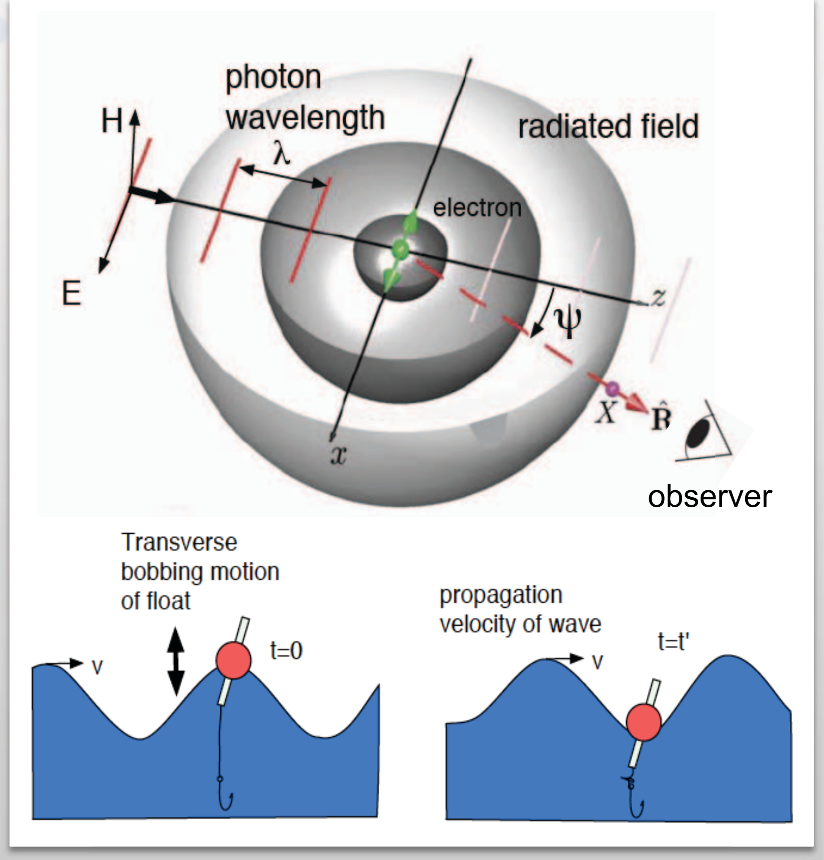
Istantaneous radiated spherical field E_{rad} :
- proportional to the electron acceleration
- anti-phase with respect E_{in}
- decreases with cos(ψ)

$$\frac{E_{rad}(R,t)}{E_{in}} = -\left(\frac{e^2}{4\pi\epsilon_0 mc^2}\right)\frac{e^{ikR}}{R}\cos\psi$$

Thomson scattering length:

$$r_0 = \left(\frac{e^2}{4\pi\epsilon_0 mc^2}\right) = 2.82\times10^{-5}\ \text{Å}$$

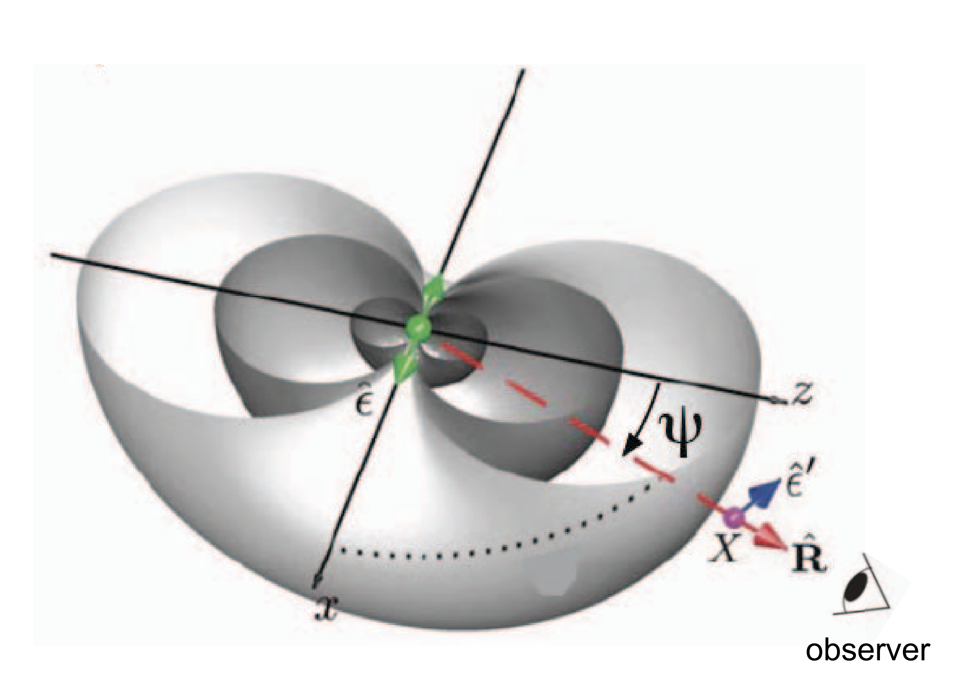
m = the electron mass
e= electron charge

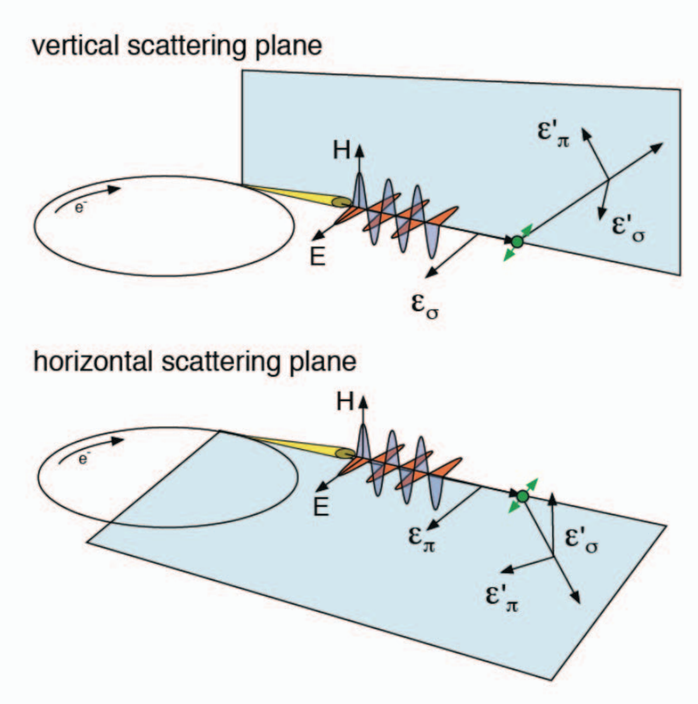


POLARIZATION DEPENDENCE OF THOMSON SCATTERING

The differential cross section for the Thomson scattering depends from the incident and scattered photon polarizations

$$\left(\frac{d\sigma}{d\Omega}\right) = r_0^2 \left|\hat{\varepsilon}\cdot\hat{\varepsilon}'\right|^2 \quad P = \left|\hat{\varepsilon}\cdot\hat{\varepsilon}'\right|^2 = \begin{cases} 1 & \text{synchrotron: vertical scattering plane} \\ \cos^2\psi & \text{synchrotron: horizontal scattering plane} \\ \frac{1}{2}\left(1+\cos^2\psi\right) & \text{unpolarized source} \end{cases}$$



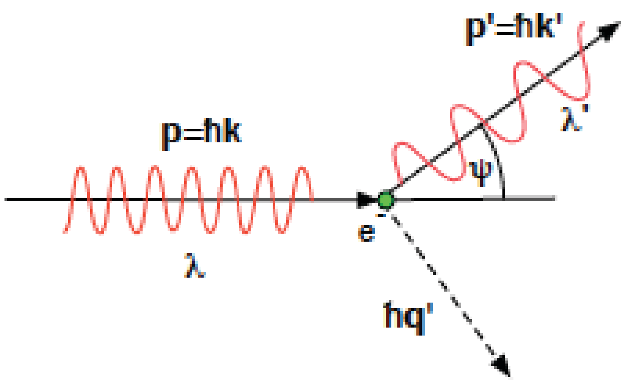


Compton scattering:
Inelastic collision between a photon and an electron at the rest in which part of the the photon energy is transferred to the electron.
This scattering is **incoherent!**

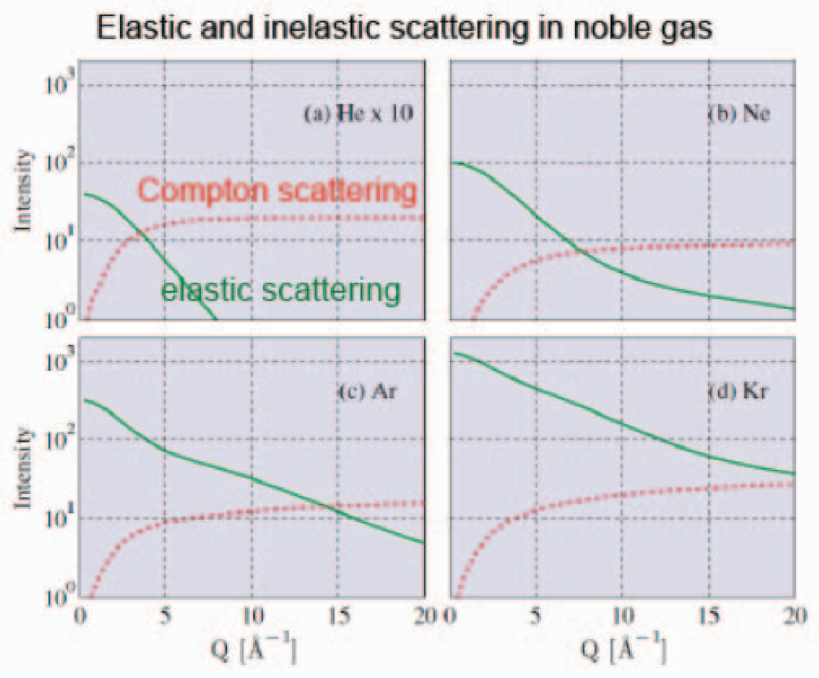
Compton scattering wavelenght

$$\lambda' = \lambda + \frac{h}{m_e c^2}(1 - \cos\psi) = \lambda + \lambda_c(1 - \cos\psi)$$

$$\lambda_c = \frac{h}{m_e c^2} = 0.0243 \quad \text{Å}$$



$$m_e c^2 + \hbar c k = \sqrt{(m_e c^2)^2 + (\hbar c q')^2} + \hbar c k'$$

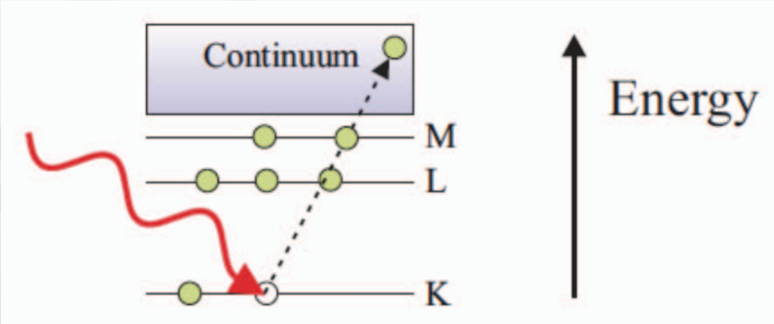


ABSORPTION/EMISSION PROCESSES

Absorption and emission processes are tools for basic analysis of the electronic structure of atom, molecules and solids over different energy scales.

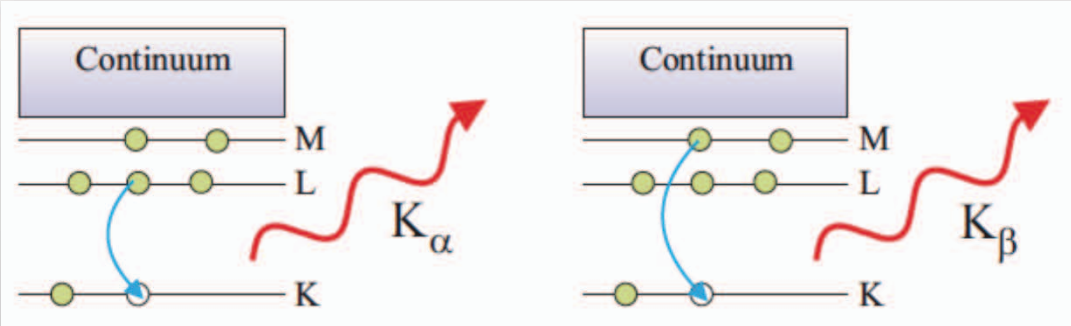
Photo-electric absorption

Photon absorbed and electron emitted in the continuum



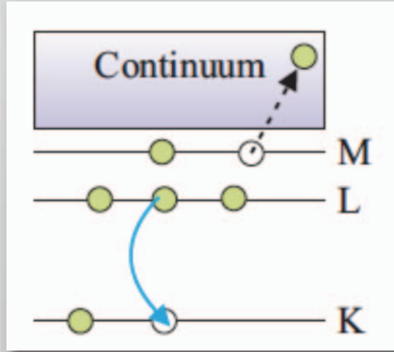
Fluorescent emission

An electron from the outer shell fill the hole and emit a photon



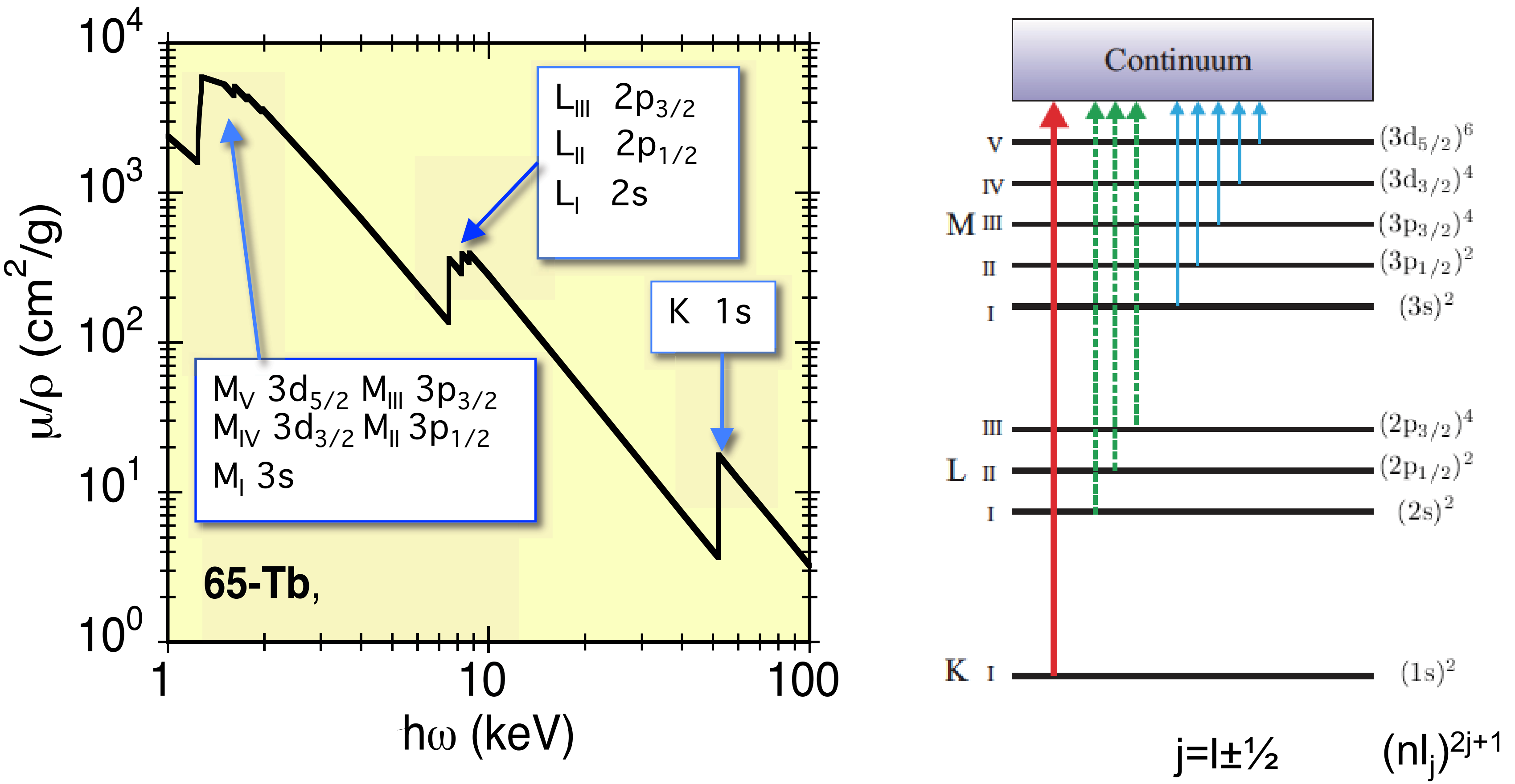
Auger electron emission

The atom relax into the ground state by emitting an electron



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.



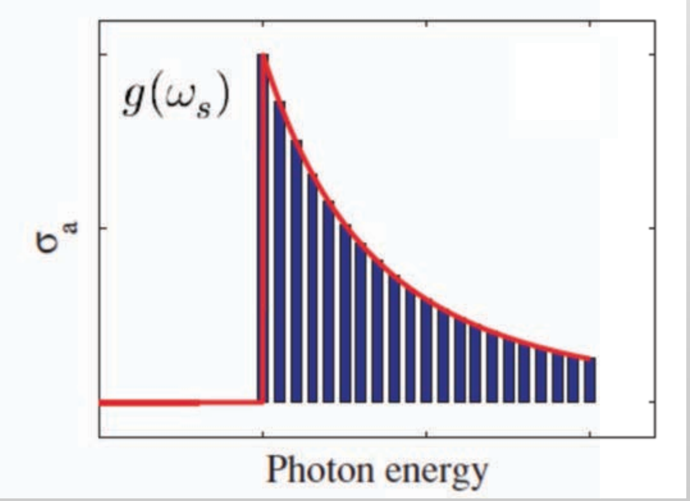
BOUND ELECTRONS AND DISPERSION CORRECTIONS

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".

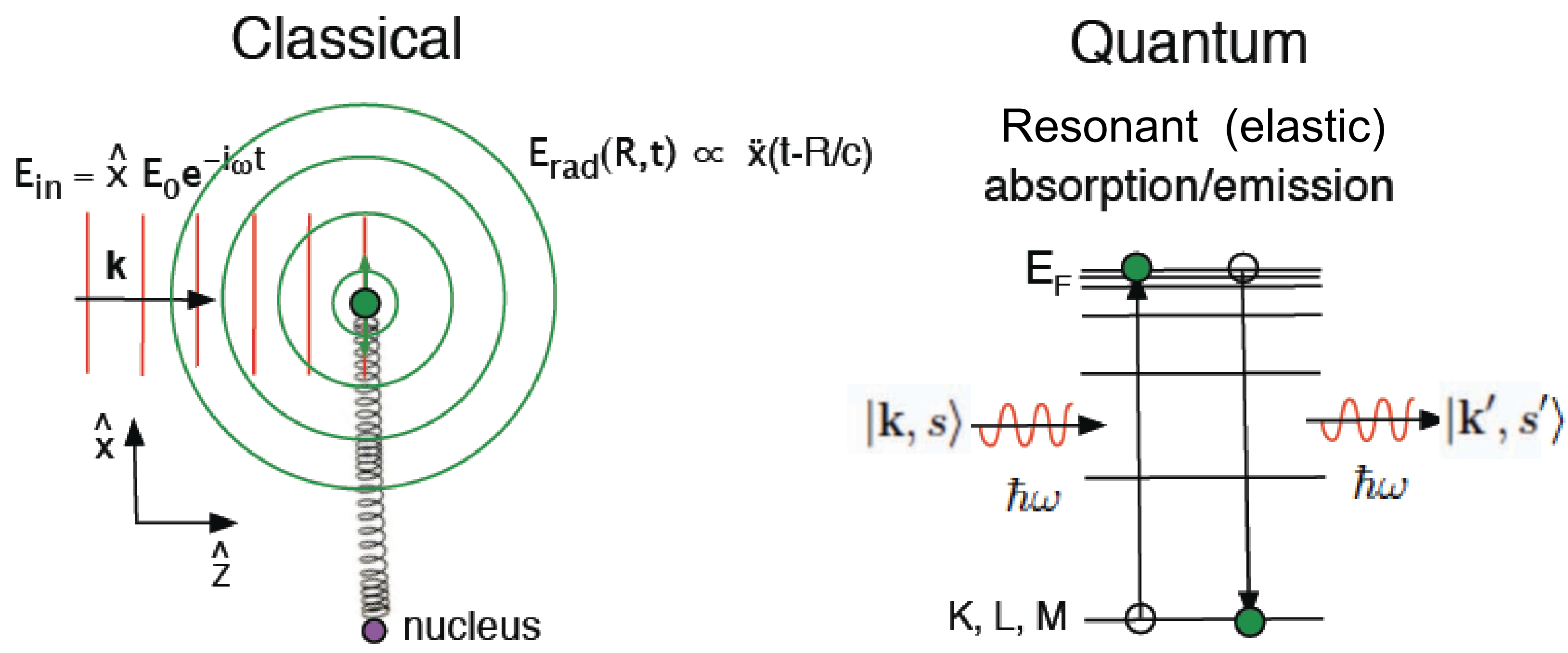
$$f(\mathbf{Q},\omega) = f^0(\mathbf{Q}) + f'(\omega) + i\,f''(\omega)$$

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 $\sigma_a(\omega = \omega_s)$.



BOUND ELECTRONS: RESONANT OSCILLATION

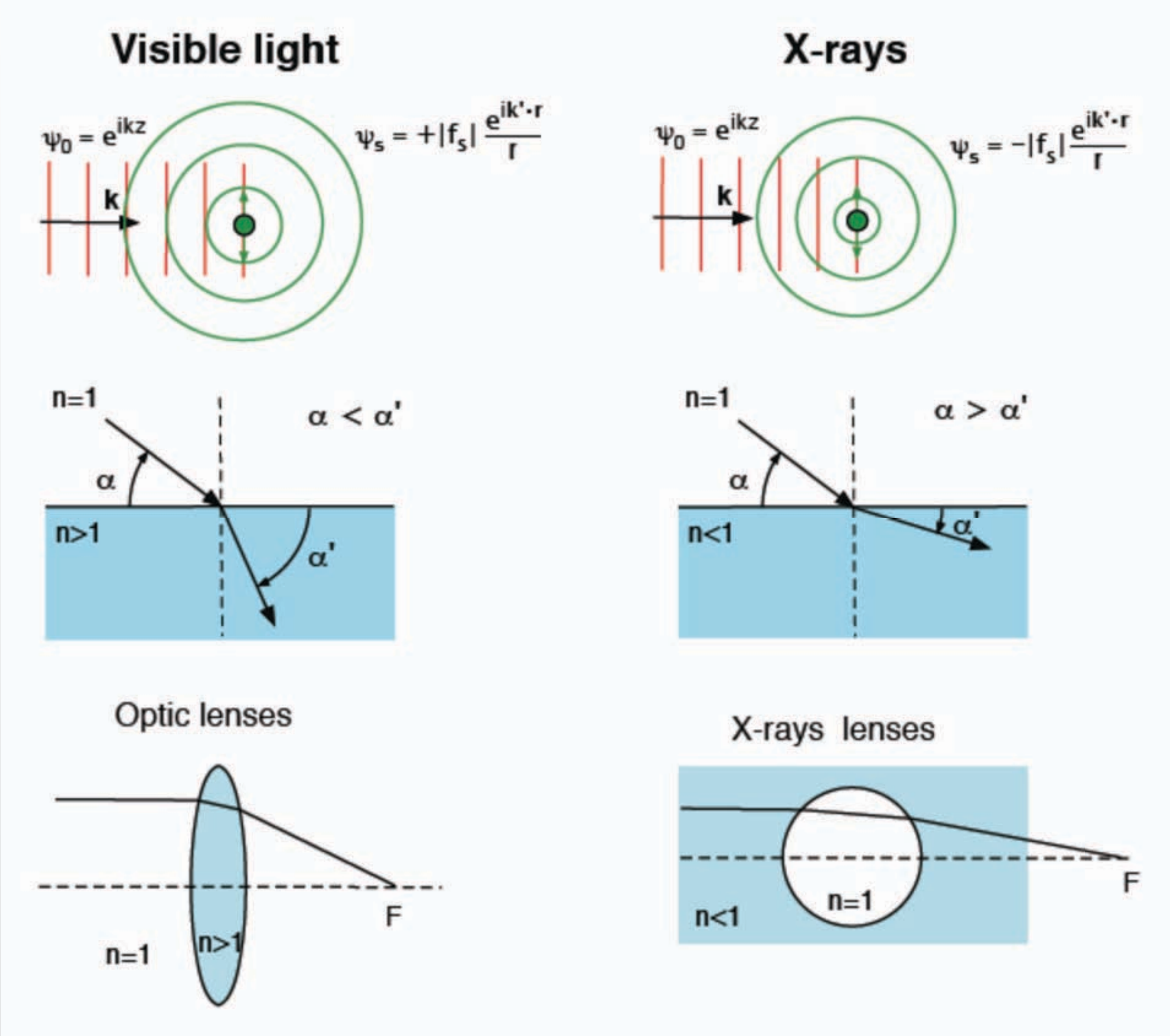
The electron be subject to the electric field E_{in} of an incident X-ray beam and to a damping term proportional to the electron velocity $\Gamma\dot{x}$ which represents dissipation of energy.



Γ= damping factor
ω= frequency

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

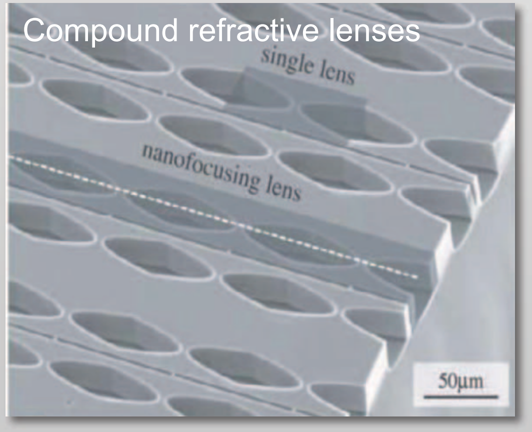
Snell law: $n_1\cos\alpha = n_2\cos\alpha'$



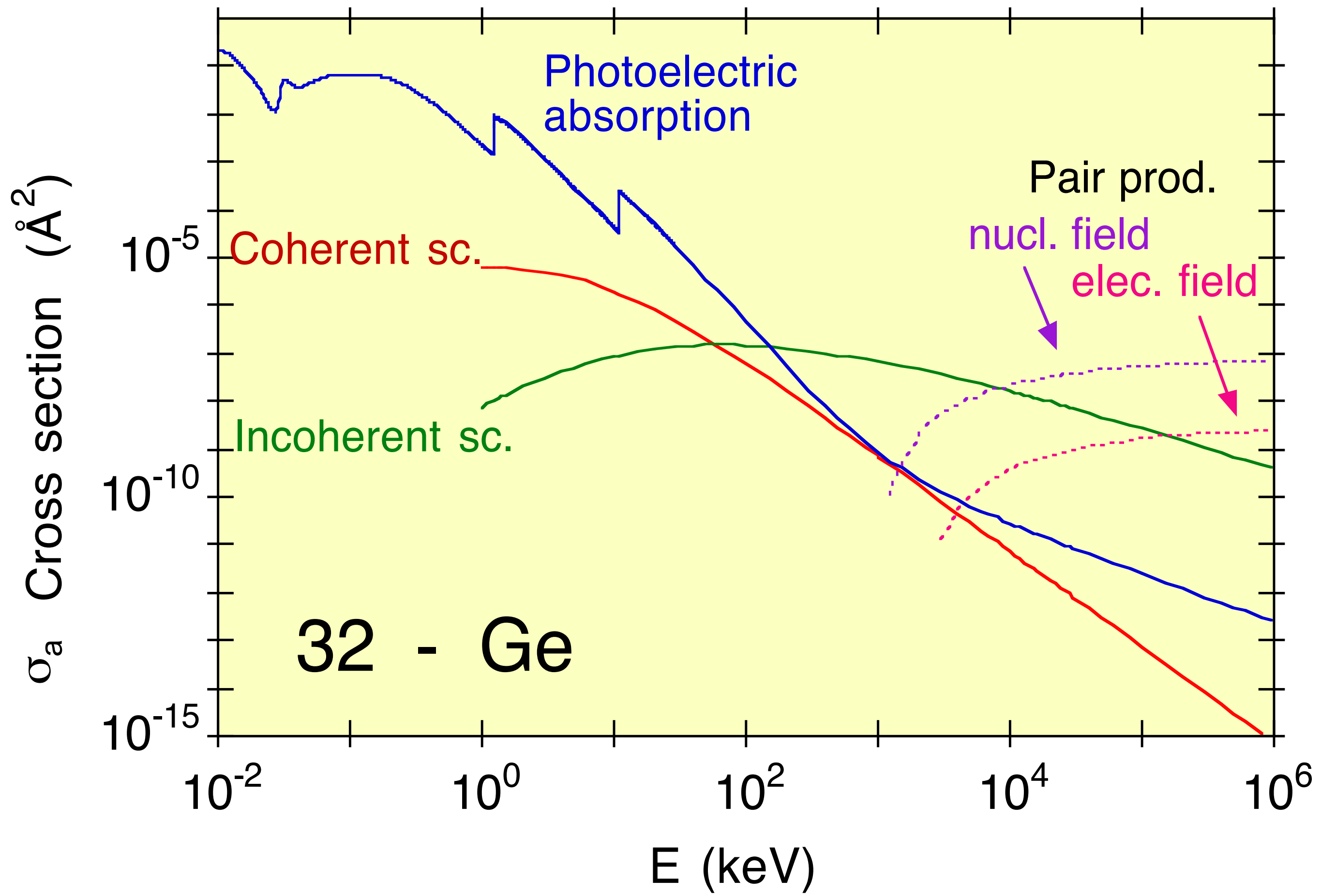
Refraction index
for X-rays:

$$n = 1 - \delta + i\beta$$

$\delta(\text{air}) \sim 10^{-8}$
$\delta(\text{solids}) \sim 10^{-5}$
$\beta \sim 10^{-8} << \delta$



CROSS SECTIONS

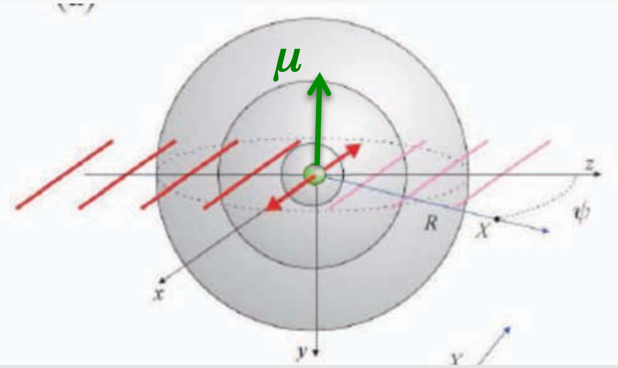


MAGNETIC INTERACTION

The magnetic interaction is a relativistic correction to the Thomson scattering

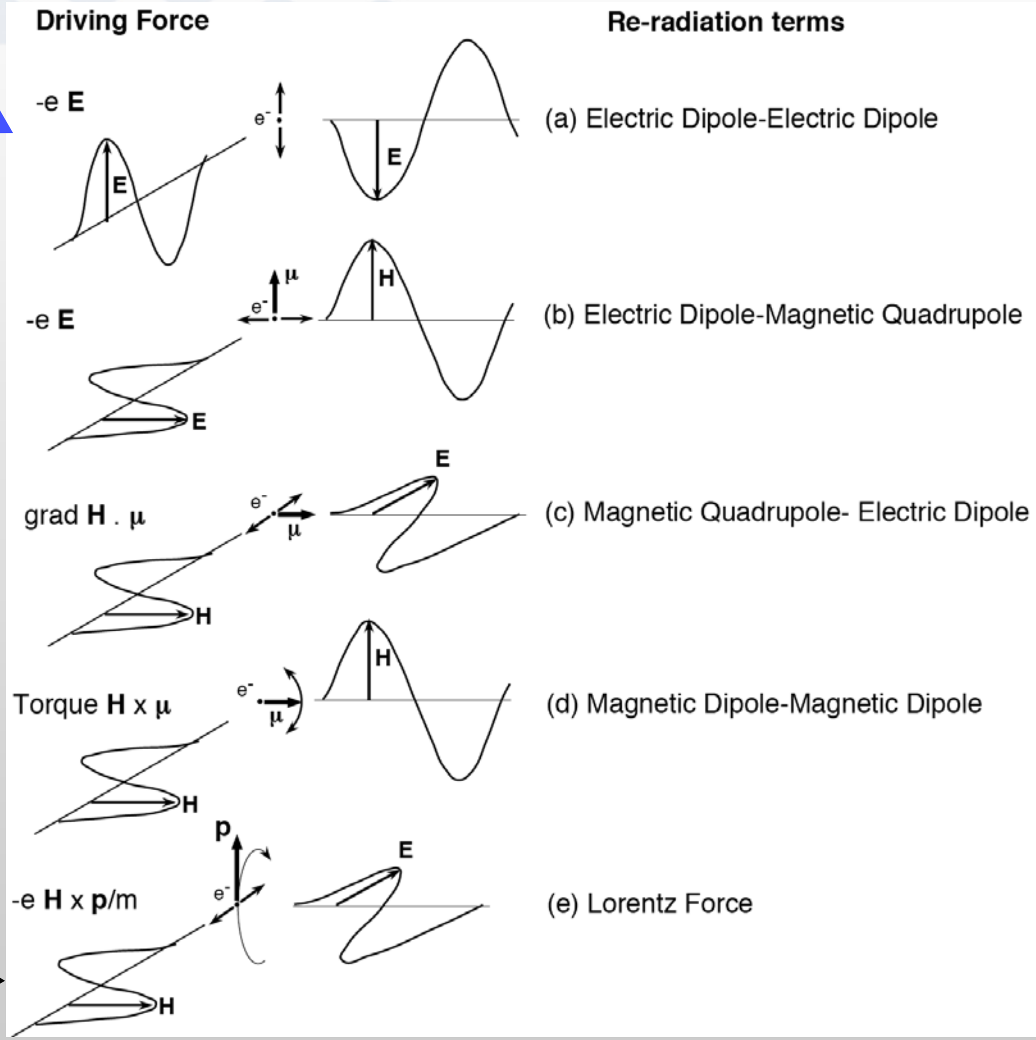
*... a **classical interpretation** from de Bergevin and Brunel (Acta Cryst, 1981)*

Thomson scattering



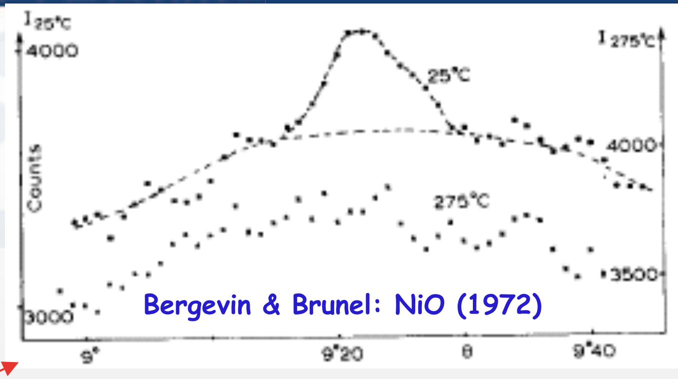
Spin-dependent scattering

Orbital motion



Theory photon-electron interaction

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

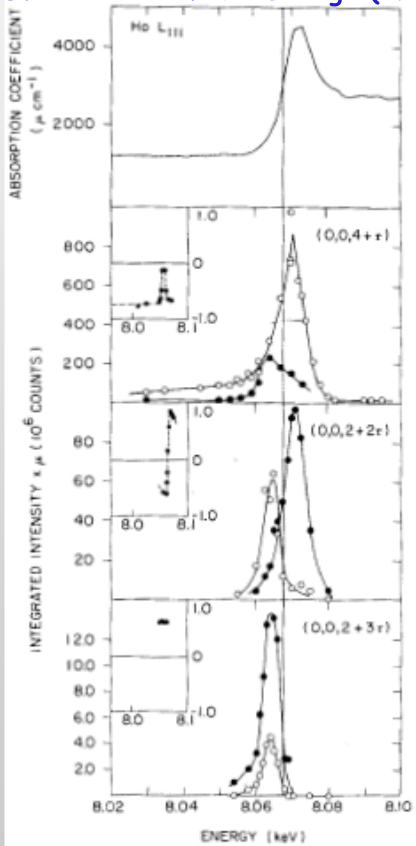


Bergevin & Brunel: NiO (1972)

Pre-synchrotron works

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

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

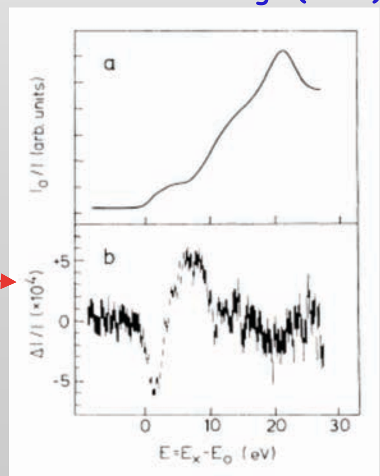


2nd generation synchrotron works

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)

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

$$H \Psi = E \Psi \qquad \Psi(r_1, r_2, \ldots r_n; R_1, R_2, \ldots R_N)$$

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 $|\Psi_i\rangle$ and a final $\langle\Psi_f|$ 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)

The semi-classical description of the interaction assumes a plane wave perturbation:

1) Absorption processes (non-relativistic quantum description)
depends from the first order term in the potential vector A

$$W_{fi}^{abs} = \frac{2\pi}{\hbar}\left|\langle\Psi_f| - \frac{e}{mc}\sum_j \mathbf{A}_k(r_j)e^{\mathbf{k}\cdot\mathbf{r}_j}\cdot\mathbf{p}_j|\Psi_i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$

$$\mu = -\frac{1}{I}\frac{dI}{dx} = \sum_f \frac{2\pi c}{\omega^2 A_k^2} N\hbar\omega W_{fi}^{abs}$$

2) Scattering processes (non-relativistic quantum description)
local current density $\mathbf{j}_{nm}(\mathbf{r},t)$ of the electron in the state $\Psi(\mathbf{r},t)$
the time-dependent current emits electromagnetic waves

$$\mathbf{j}_{nm} = \frac{1}{2m}\sum_j(\Psi_n^*\hat{p}_j\Psi_m - \Psi_n\hat{p}_j\Psi_m^*) - \sum_j\frac{eA(r_j,t)}{2m}(\Psi_n^*\Psi_m + \Psi_n\Psi_m^*)$$

Current density matrix elements

Modification of electron momentum due to E.M. field

Elastic scattering (Thomson): diagonal elements of current operators
Inelastic scattering (Compton): non-diagonal elements

From the semi-classical approach we consider a plane wave perturbation:

$$\mathbf{j}_{nm} = -\sum_j \frac{e\mathbf{A}(\mathbf{r}_j,t)}{2m}(\Psi_n^*\Psi_m + \Psi_n\Psi_m^*)$$

$$\mathbf{j}_{nm} = -\sum_j \frac{e\mathbf{A}_k}{2m} e^{\mathbf{k}\cdot\mathbf{r}_j}(\psi_n^*\psi_m e^{(\omega_m-\omega_n-\omega)t} + \psi_n\psi_m^* e^{(\omega_m-\omega_n-\omega)t})$$

$$\omega_m = \omega_n$$

$$\omega' = \omega - (\omega_m - \omega_n)$$

Thomson scattering cross section

$$\left(\frac{d\sigma}{d\Omega}\right)_{el} = r_o^2 cos^2\theta \left| \langle\Psi_n| \sum_j e^{-jqr_j} |\Psi_n\rangle \right|^2$$

Compton scattering cross section

$$\left(\frac{d\sigma}{d\Omega}\right)_{inel.} = r_o^2 cos^2\theta \sum_{m\neq n} \frac{\omega'}{\omega} \left| \langle\Psi_m| \sum_j e^{-jqr_j} |\Psi_n\rangle \right|^2$$

Notice that in the limit of high energies the sum of elastic and inelastic cross sections is equal to the classical Thomson cross section of Z point free electrons.

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", wavevector **k** and polarization "ε",

$$|n_{k1,\epsilon1}; \ldots n_{k,\epsilon}; \ldots n_{k_t,\epsilon_t}\rangle$$

and the creation and annihilation operators, "a†" and "a" defined as:

$$a^\dagger_{k,\epsilon}|n_{k1,\epsilon1}; \ldots n_{k,\epsilon}; \ldots n_{k_t,\epsilon_t}\rangle = \sqrt{n_{k,\epsilon}+1}|n_{k1,\epsilon1}; \ldots n_{k,\epsilon}+1; \ldots n_{k_t,\epsilon_t}\rangle$$

$$a_{k,\epsilon}|n_{k1,\epsilon1}; \ldots n_{k,\epsilon}; \ldots n_{k_t,\epsilon_t}\rangle = \sqrt{n_{k,\epsilon}}|n_{k1,\epsilon1}; \ldots n_{k,\epsilon}-1; \ldots n_{k_t,\epsilon_t}\rangle$$

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:

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

RELATIVISTIC INTERACTIONS

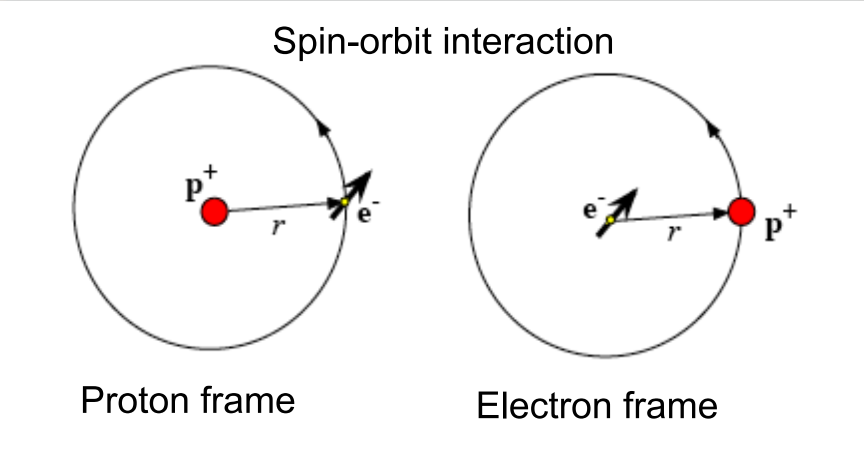
The interaction Hamiltonian is obtained from the **Dirac equation** in the limit of low velocities and taking the terms o(v/c).

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:

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

- 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'

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

A^2: quadratic terms ($a_{ks}^\dagger a_{k's'}$, $a_{ks}^\dagger a_{k's'}$, …)

A: linear terms ($a_{ks}^\dagger$ and a_{ks})

Absorption processes => must contain only the photon annihilation operator $a_{k,s}$ we need consider only the linear terms in the **A**

Scattering processes => involve both the photon operators $a_{ks}^\dagger$ and a_{ks} only the quadratic terms $\mathbf{A}^2$ are retained

Ex. : **Elastic scattering processes:**
conserves the number of photons. A(r) is linear in $a_{ks}^\dagger$ and a_{ks}
- 1^{st} order perturbation: QUADRATIC terms in A(r) (H'_1 and H'_4)
- 2^{nd} order perturbation: LINEAR terms in A(r) (H'_2 and H'_3)

Fermi's Golden rule:

$$W = \frac{2\pi}{\hbar} \Big| < a\,;\, \mathbf{k}'\,\epsilon'|\, H'_1 + H'_4\, |a\,;\, \mathbf{k}\,\epsilon > \quad \leftarrow \textit{1st order}$$

$$+ \sum_n \frac{< a\,;\, \mathbf{k}'\,\epsilon'|\, H'_2 + H'_3\, |n >< n|\, H'_2 + H'_3\, |a\,;\, \mathbf{k}\,\epsilon >}{E_a + \hbar\omega_k - E_n} \Big|^2 \quad \leftarrow \textit{2nd order}$$

$$|i\rangle = |a;\mathbf{k},\epsilon\rangle,\ \ |f\rangle = |b;\mathbf{k}',\epsilon'\rangle$$

X-RAYS SCATTERING AMPLITUDES

M. Blume, J. Appl. Phys. 57, 3615 (1985)
M. Blume,*"Resonant anomalous x-ray scattering"*, ed. G. Materlik, (1994).

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

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

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

n= unit cell atomic site

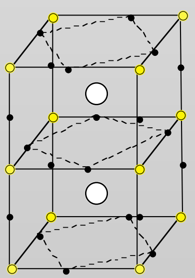
Site selectivity
- Space group symmetries
- Extinction rules

Atomic scattering amplitudes
- Atomic properties (photon-electron interactions)
- Electronic order parameters

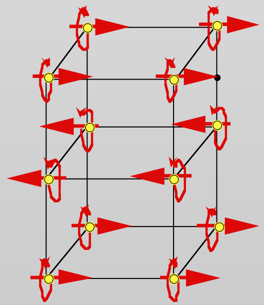
$$f = f_0 + f^{magn.} + f' + i f''$$

CHARGE (Thomson)	MAGNETIC	RESONANT
E=10-50 keV	E=3.0-10 keV	E=3-20 keV
$Z\, r_0 \sim 1\text{-}95\, r_0$	$\hbar\omega/mc^2\, Z^{magn.}\, r_0 \sim 0.001\text{-}0.03\, r_0$	$Z^{res.}\, r_0 \sim 0.01\text{-}100\, r_0$

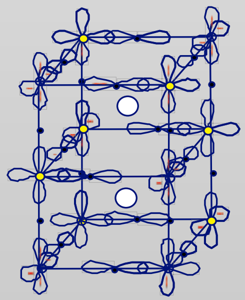
Structural characterization



Magnetic structure determination



Valence electronic anisotropies



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

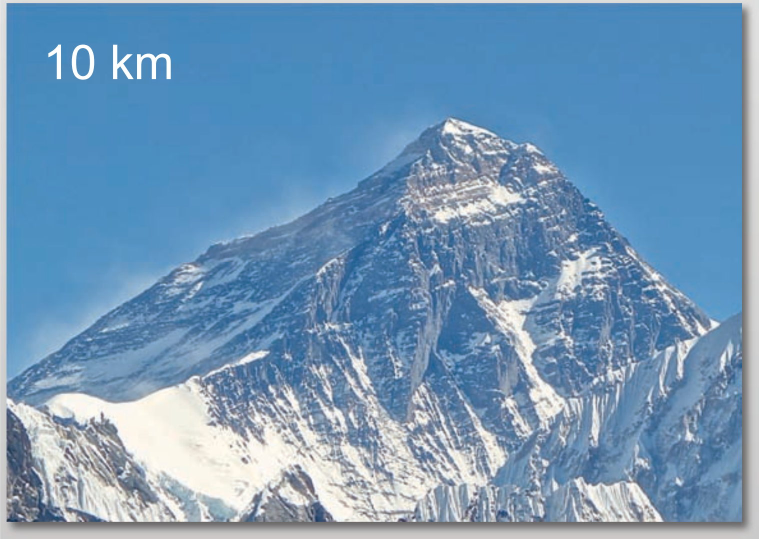
$I_{res.}$~10^3-10^5 cts/s

MAGNETIC

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

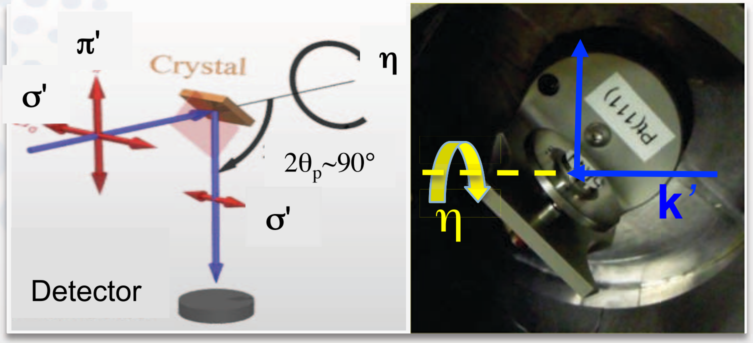
CHARGE (Thomson)

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



X-rays Polarization analyser

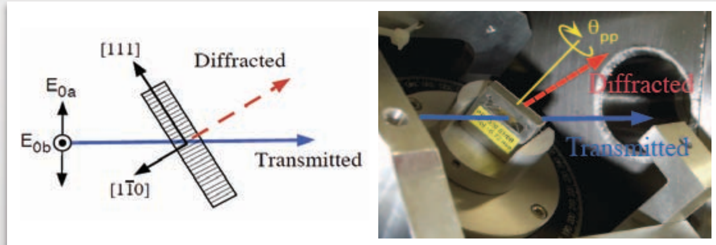
- Thomson selection rules (ε·ε')
- Bragg diffraction by a crystal analyzer $2\theta_p$~90°
- η = rotation about scattered wavevector k'



Phase plate retarder

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

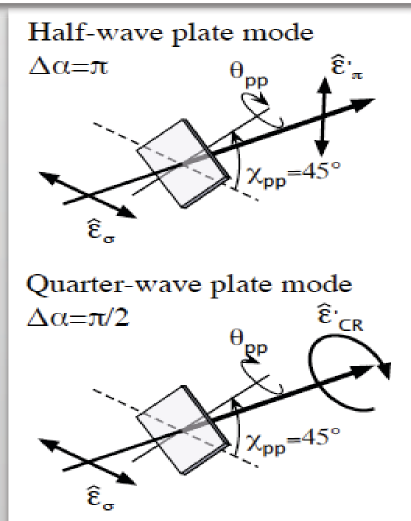
$$\Delta\alpha = \frac{2\pi}{\lambda}(n_\sigma - n_\pi)d = -\frac{\pi}{2}\left[\frac{r_e^2\lambda^3 Re(F_h F_{\bar{h}}) sin2\theta_{pp}}{\pi^2 V^2 \Delta\theta_{pp}}\right] d$$



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%)

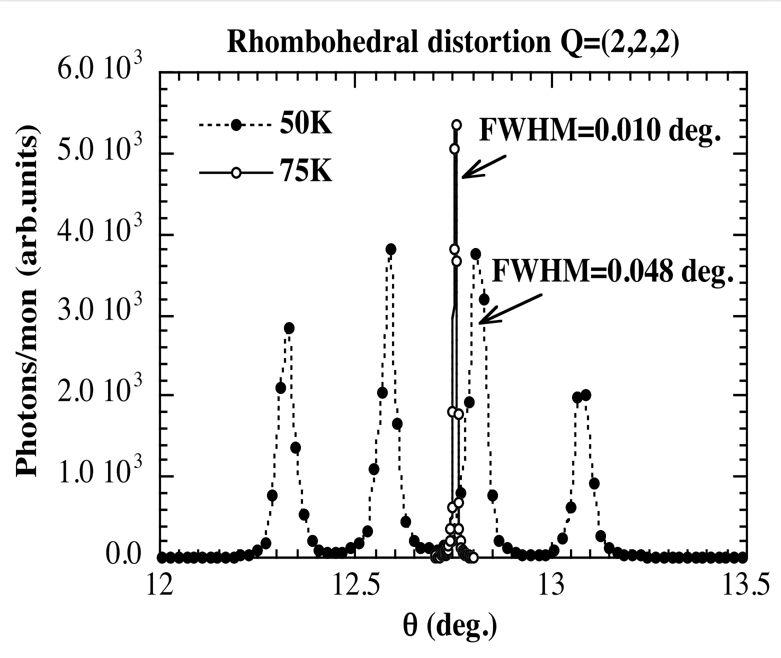
Linear Polarization Scan ($\Delta\alpha=\pi$)
-Continous rotation of χ



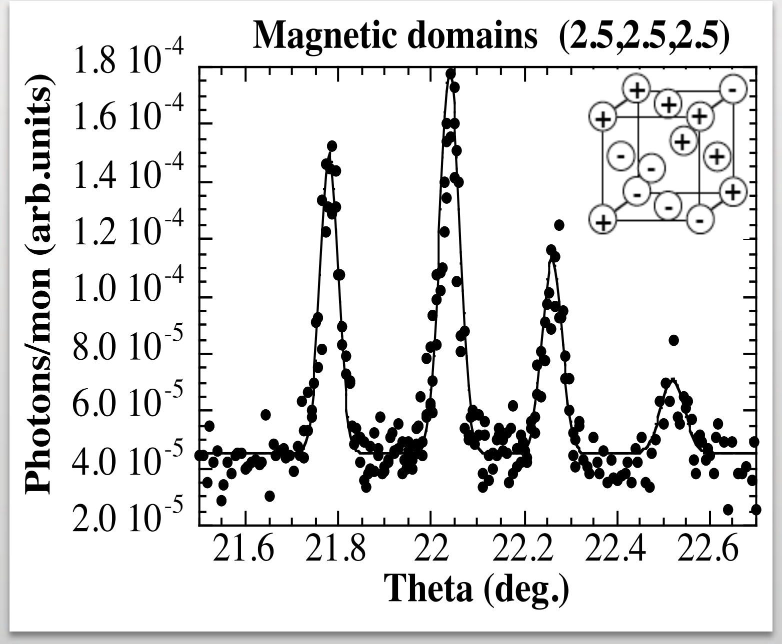
The high-Q resolution allow the separation of crystallographic and magnetic reflections.

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

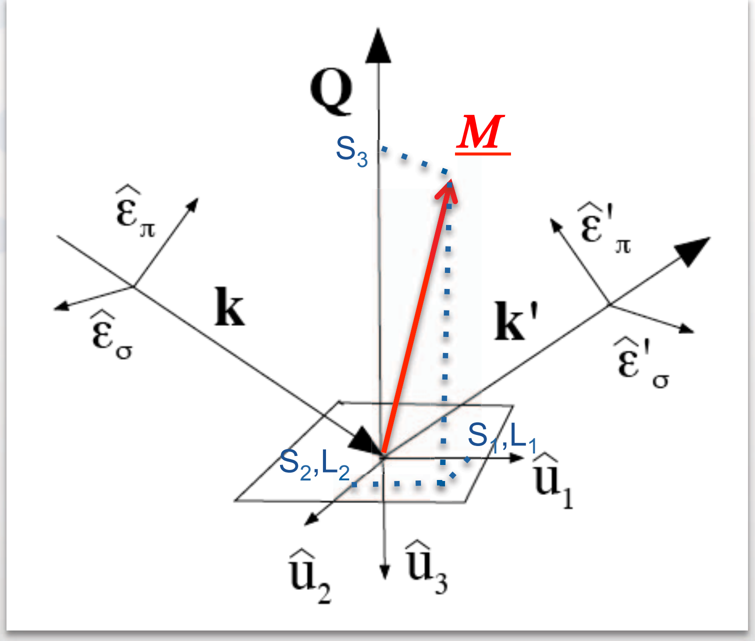
Thomson scattering



Non-resonant magnetic scattering



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



- *Jones's matrices for NRMS:*

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

(σ−σ', π−σ' above; σ−π', π−π' below)

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

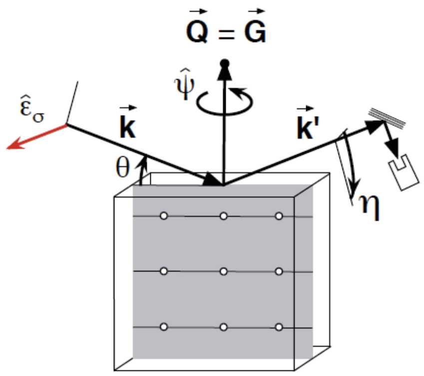
$$\begin{aligned} \hat{u}_1 &= (\hat{k}+\hat{k}')/2\cos\theta \\ \hat{u}_2 &= (\hat{k}\times\hat{k}')/\sin 2\theta \\ \hat{u}_3 &= (\hat{k}-\hat{k}')/2\sin\theta \end{aligned}$$

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

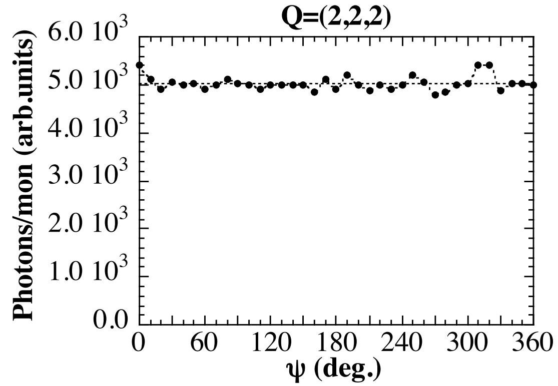
Fourier transforms of spin and orbital magnetization densities

AZIMUTHAL LINEAR X-RAY POLARIMETRY

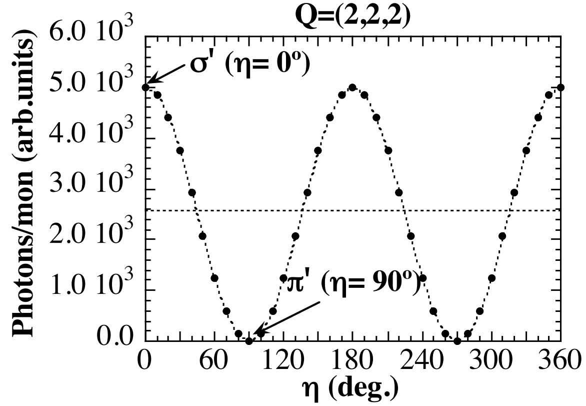
Charge scattering



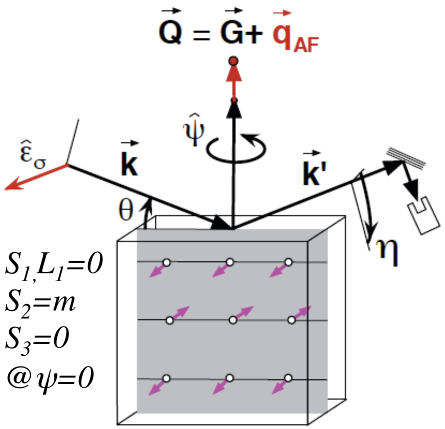
Azimuthal scans



Polarization analysis



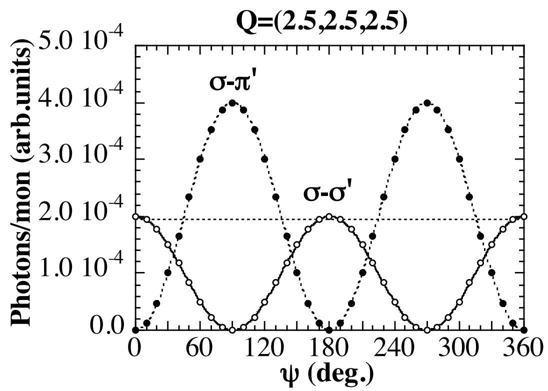
Magnetic scattering



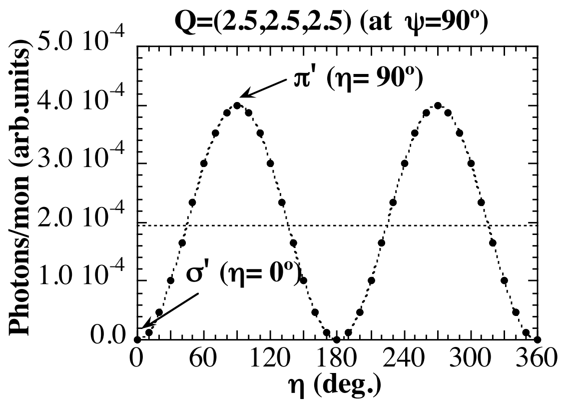
$M_{\sigma\sigma} \sim S_2 \sin 2\theta,$

$M_{\sigma\pi} \sim 2 \sin^2\theta \cos\theta \, (L_1+S_1)$

Azimuthal scans



Polarization analysis ψ=90°



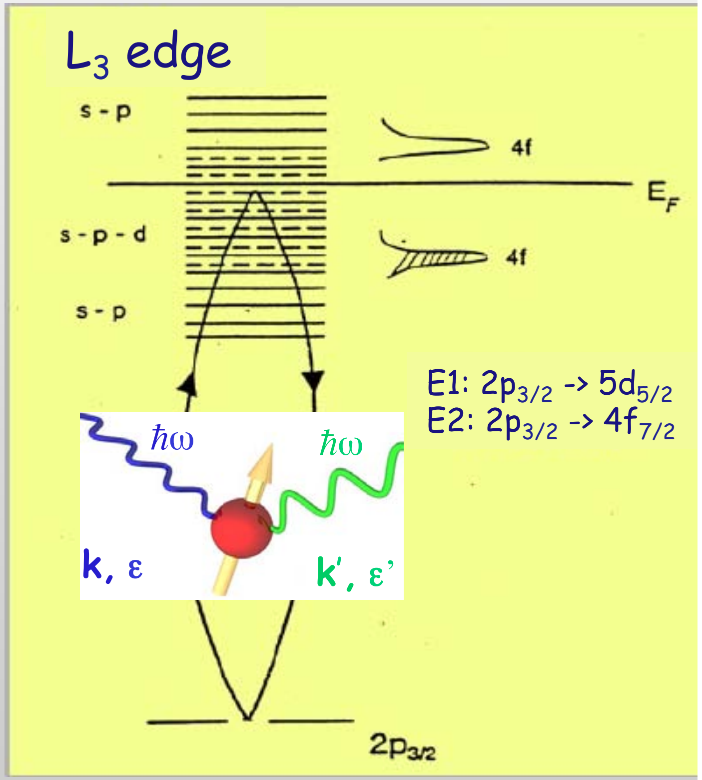
RESONANT X-RAY SCATTERING

$$f^{RXS} \approx -\frac{1}{m}\sum_c \frac{E_g - E_c}{\hbar\omega_k} \cdot \frac{\langle g|\sum_j e^{-i\mathbf{k}'\cdot\mathbf{r}_j}\hat{\epsilon}'^* \cdot \mathbf{p}_j|c\rangle\langle c|\sum_j e^{i\mathbf{k}\cdot\mathbf{r}_j}\hat{\epsilon}\cdot\mathbf{p}_j|g\rangle}{E_g - E_c + \hbar\omega_k - i\Gamma_c/2}$$

- Enhancement of scattering amplitude near absorption edge
- Excitation of a inner-shell electron into an empty valence state
- Sensitivity to the local degeneration of valence-electron states

- Local symmetries of bound electrons
- Tensorial structure factor
- Forbidden lattice reflections
- Polarization effects (links with magneto-optics)
- Mixing diffraction and atomic spectroscopy

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 **A**(**r**) 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

Geometrical and polarization dependence

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

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

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

Matrix elements

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

E1: ELECTRIC-DIPOLE TRANSITIONS

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

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

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

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

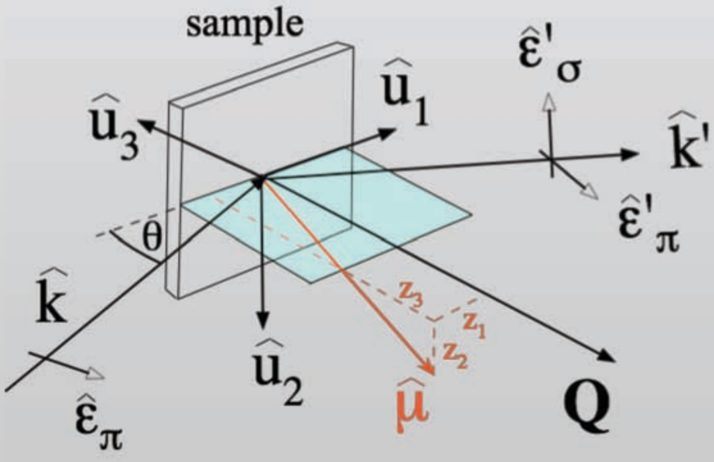
$$F^{(2)}_{E1} = \frac{3}{16\pi}[2F_{10} - F_{11} - F_{1-1}]$$ ← *Electric quadrupole*

- Polarization dependence for magnetic dipole:
  - Horizonthal scattering geometry
  - π-incident polarization

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

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

z_i magnetic dipole component along u_i



E1: ELECTRIC-DIPOLE TRANSITIONS

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

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

$$F_{E1}^{(0)} = \frac{3}{16\pi}[F_{11} + F_{1-1}] \quad \longleftarrow \textit{Charge scattering}$$

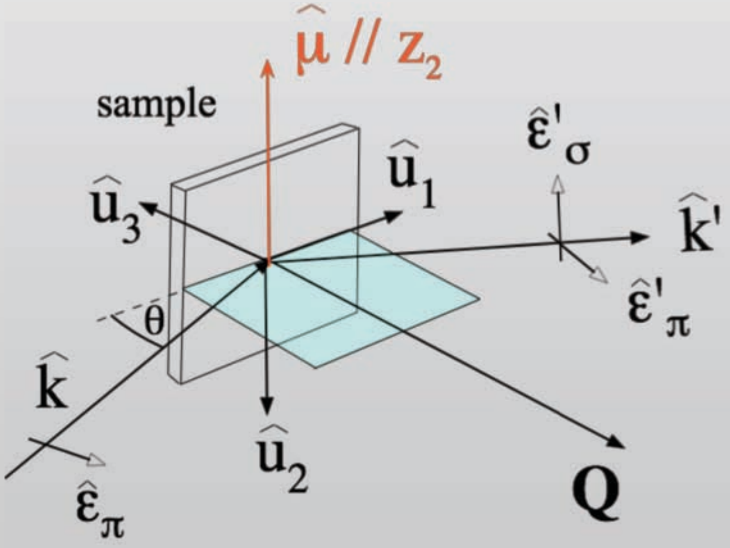
$$F_{E1}^{(1)} = \frac{3}{16\pi}[F_{11} - F_{1-1}] \quad \longleftarrow \textit{Magnetic dipole}$$

$$F_{E1}^{(2)} = \frac{3}{16\pi}[2F_{10} - F_{11} - F_{1-1}] \quad \longleftarrow \textit{Electric quadrupole}$$

- Polarization dependence for magnetic dipole:
  - Horizonthal scattering geometry
  - π-incident polarization

$\varepsilon_\pi - \varepsilon'_\sigma$	0
$\varepsilon_\pi - \varepsilon'_\pi$	$-z_2 \sin 2\theta$

z_i magnetic dipole component along u_i



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

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

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

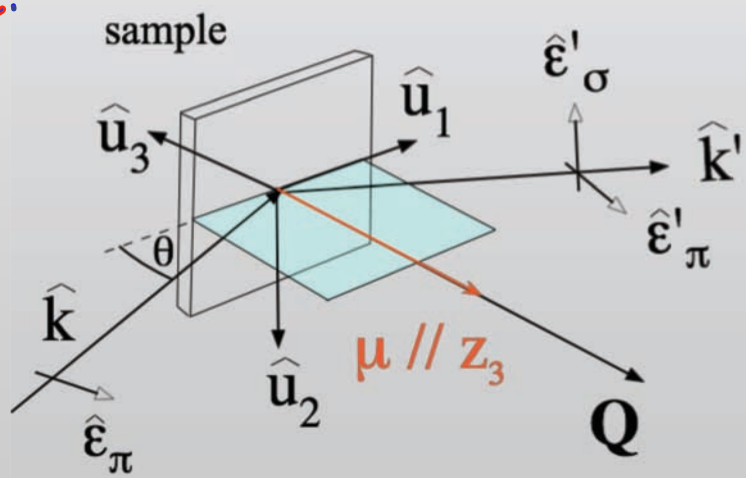
$$F_{E1}^{(1)} = \frac{3}{16\pi}[F_{11} - F_{1-1}]$$ ← *Magnetic dipole*

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

- Polarization dependence for magnetic dipole:
  - Horizonthal scattering geometry
  - π-incident polarization

$\varepsilon_\pi - \varepsilon'_\sigma$	$z_3 \sin\theta$
$\varepsilon_\pi - \varepsilon'_\pi$	0

z_i magnetic dipole component along u_i



RXS ABSORPTION EDGES
ELEMENT AND SHELL SELECTIVITY

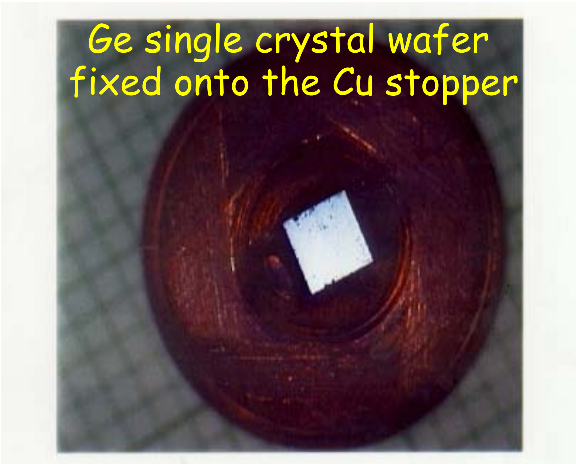
Series	Abs. edge	Energy (keV)	λ (Å)	Shells	Type	Resonant amplitude
3d	$L_{2,3}$	*0.4–1.0*	*12–30*	*2p→3d*	*E1*	*≈100*
	K	4.5–9.5	1.3–2.7	1s→4p	E1	≈0.02
				1s→3d	E2	≈0.01
5d	$\mathrm{L}_{2,3}$	5.4–14	0.9–2.2	*2p→5d*	E1	≈1-10
4f	$\mathrm{L}_{2,3}$	5.7–10.3	1.2–2.2	2p→5d	E1	≈0.10
				2p→4f	E2	≈0.05
	$M_{4,5}$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

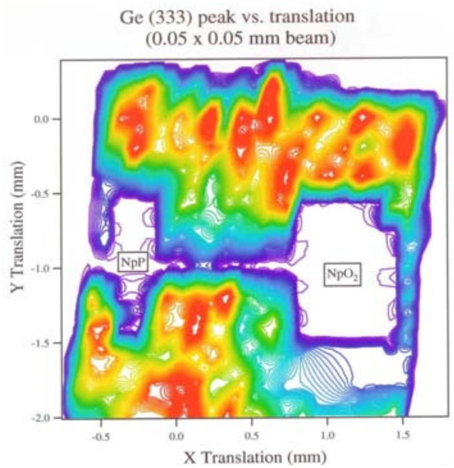
RXS AT M-EDGES OF ACTINIDES: CHEMICAL SELECTIVITY

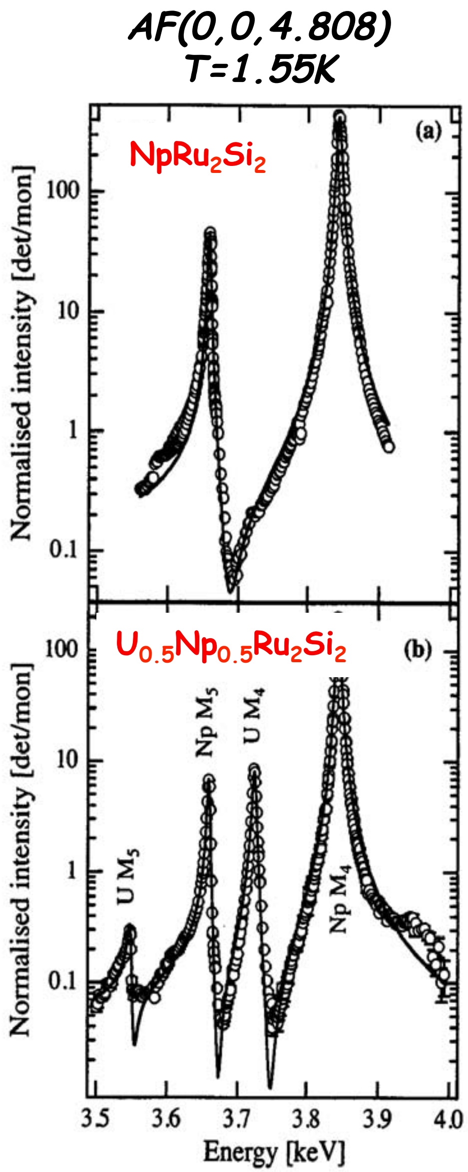
Resonant magnetic scattering in $(U_{0.5}Np_{0.5})Ru_2Si_2$ solid solution
E. Lidstrom et al., Phys. Rev. B 61, 1375 (2000)

Actinide Sample:
mounted on 2x2 mm^2 Ge(111) wafer
volume 0.1 mm^3, **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







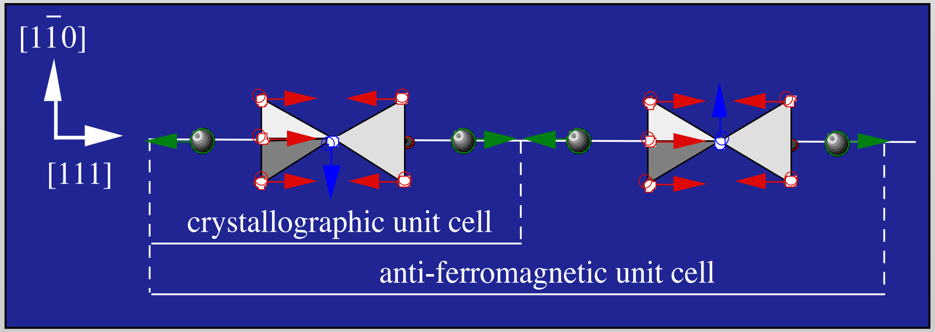
On the magnetic ground state of $Ce(Co_xFe_{1-x})_2$

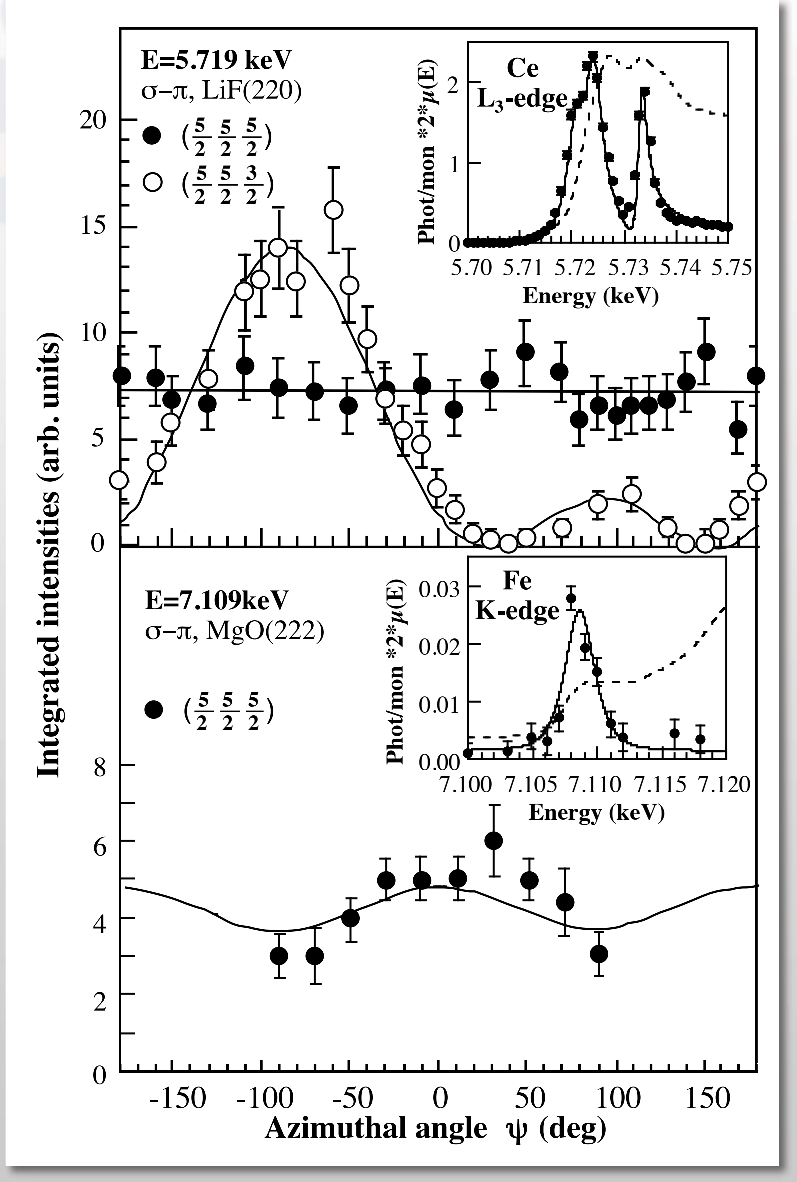
L. Paolasini, et al. Phys. Rev. Lett. 90 (2003) 57201;
ibid: Phys. Rev. B 77 (2008) 094433

- 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)





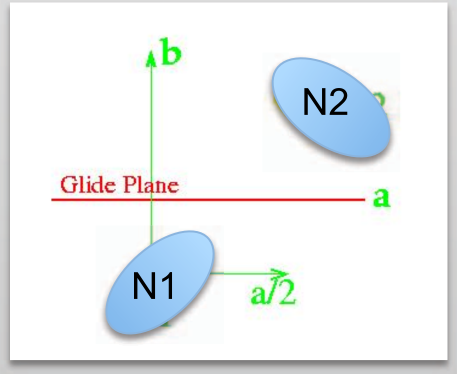
Interplay between orbital and magnetic ordering in $KCuF_3$
R. Caciuffo, et al., Phys. Rev. B 63 (2002) 174425; ibid. L. Paolasini, Phys. Rev. Letters 88 (2002) 106403.

Scientific background

- Mott-Hubbard insulator
- Model system for orbital ordering

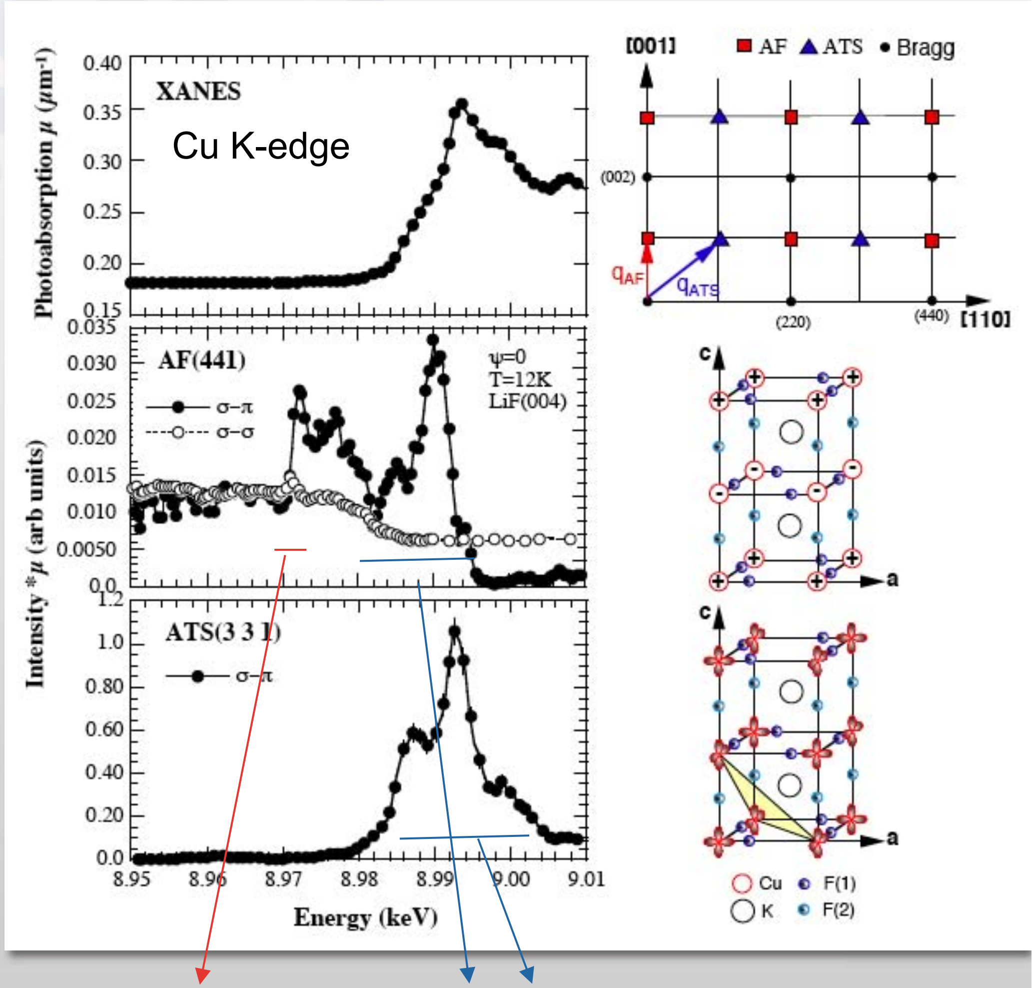
Experimental results

- 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)



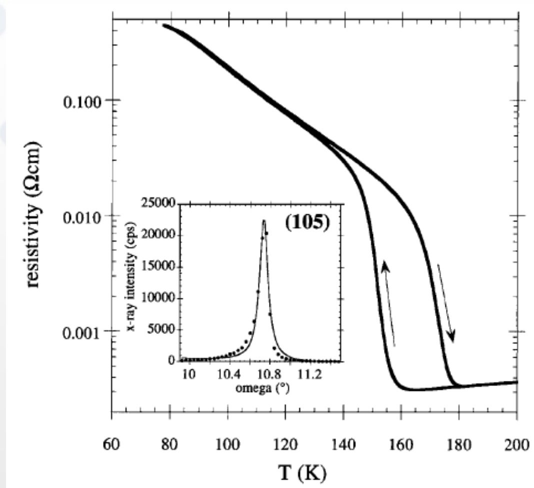
Violation of the extinction rules

f(N1)+f(N2)exp[iπh]



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.

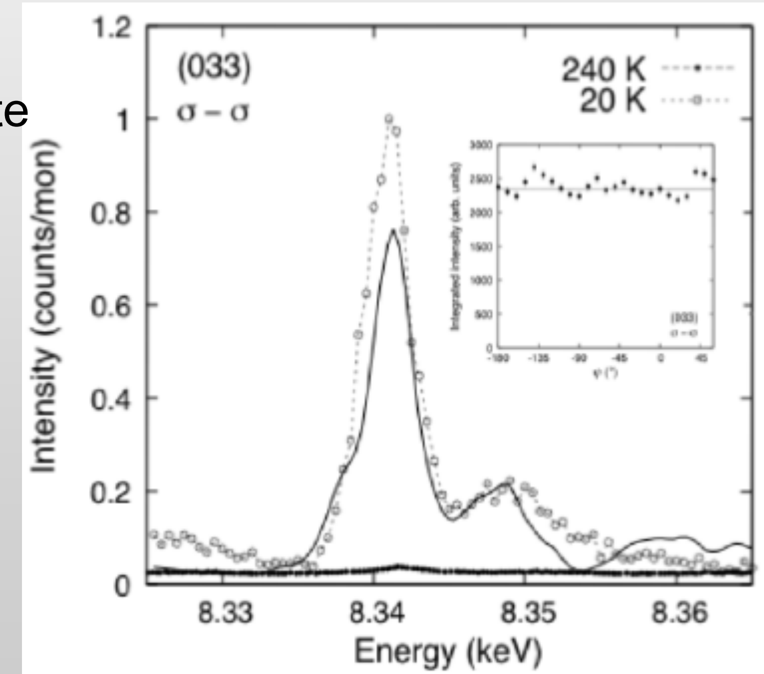


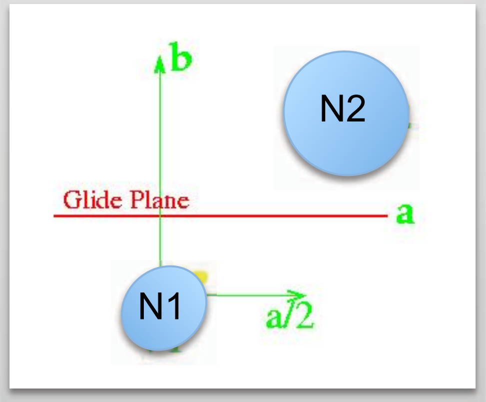
- Prototype of bandwidth-controlled metal-insulator
- Metal/insulator transition T_{MI}=150-170K

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

  $Nd^{3\pm\delta}$ where δ~0.45±0.04





Violation of the extinction rules

f(N1)≠f(N2)

Complementary polarized neutron and resonant x-ray magnetic reflectometry

E. Kravtsov, et al., Phys. Rev B 79 (2009) 134438.

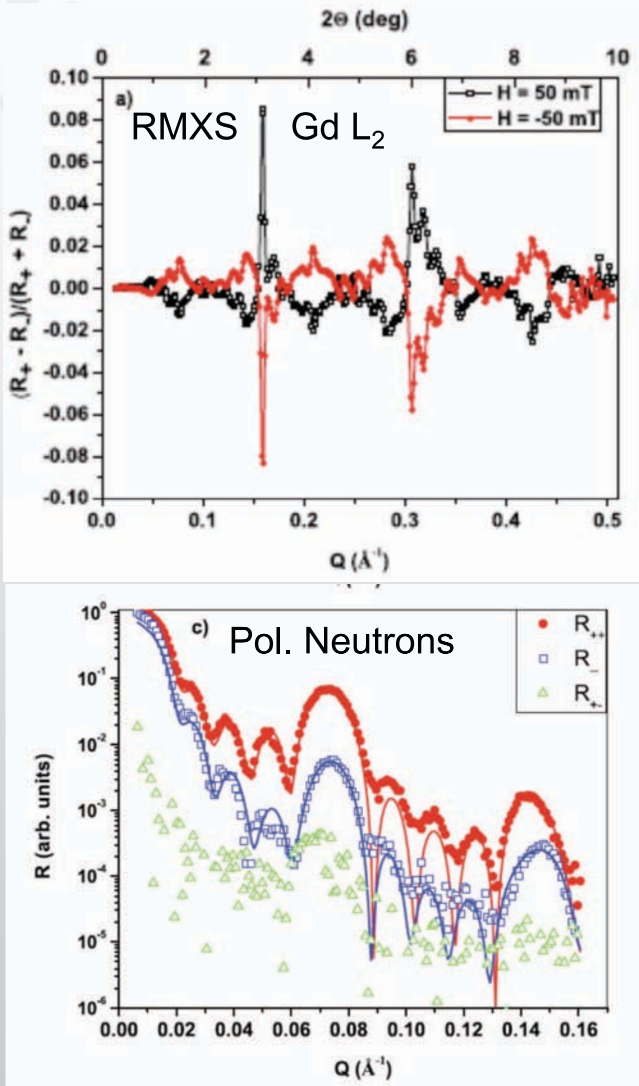
RMX reflectivity (circular polarization)
Polarized neutron reflectivity

Element-specific magnetization profile in the multilayer (Fe35 Å /Gd50 Å)$_5$

Asymmetric termination Fe-top, Gd-bottom lead to unique low-temperature magnetic phases.

Significant twisting of Fe and Gd magnetic moments

Nonuniform distribution of vectorial magnetization within Gd layers. A



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)

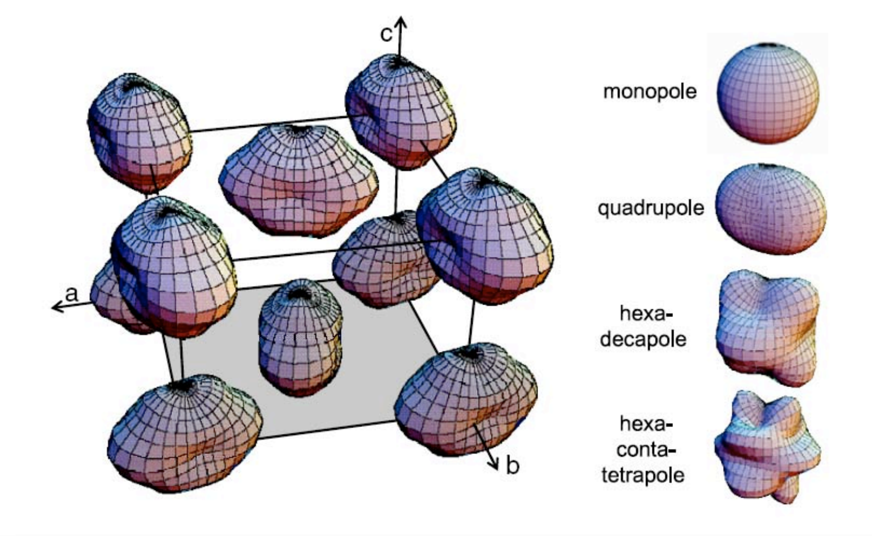
Dubovik, V.M. & Tugushev, V.V., Physics Reports 187, 145-202 (1990)
Di Matteo, J. Phys. D: Appl. Phys. 45 163001 (2012).

Charge distribution $\rho(\mathbf{x})$:

Electrostatic energy

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

Charge multipoles



Permanent currents $\mathbf{j}(\mathbf{x})$:

Magnetic energy

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

Irrotational (rotor free)

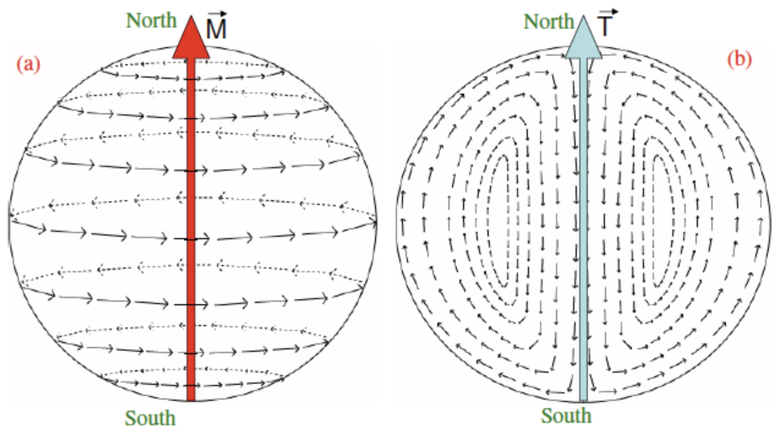
$$\vec{\nabla} \cdot \vec{J} = \vec{\nabla} \cdot \vec{J}_{\parallel} \equiv -\partial_t \rho$$

Stationary states

Solenoidal (divergenceless)

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

Toroidal moment M *Poloidal moment T*



ψ(x) scalar χ(x) pseudo-scalar

SYMMETRY TRANSFORMATIONS

Symmetry transformation of coordinate system

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)

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

$j=0:$

$$T^{(0)}_0 = \frac{1}{3}\,(D^{xx}+D^{yy}+D^{zz})$$

$j=1:$

$$T^{(1)}_0 = \frac{1}{2}\,(D^{xy}-D^{yx})$$

$$T^{(1)}_{\pm1} = \mp\frac{1}{2\sqrt{2}}\,[(D^{yz}-D^{zy}) \mp i(D^{xz}-D^{zx})]$$

$j=2:$

$$T^{(2)}_0 = D^{zz} - T^{(0)}_0$$

$$T^{(2)}_{\pm1} = \mp\sqrt{\frac{2}{3}}\,\frac{1}{2}[(D^{xz}+D^{zx}) \mp i(D^{yz}+D^{zy})]$$

$$T^{(2)}_{\pm2} = \frac{1}{\sqrt{6}}[2D^{xx}-2D^{yy} \pm i(D^{xy}+D^{yx})]$$

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

⇒Exchange of αβγδ indexes

- j=1,3 pure magnetic terms: antisymmetric with respect to the time-reversal symmetry

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

Product of irreducible spherical tensors X_q and F_q.
The rank q depends on the order of multipole in the EM field expansion:

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

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
$F^3(E1\text{-}E2)+F^4(E2\text{-}E2)$

ATS
$(h0.\text{-}h)_m$ $h_m=2n+1$

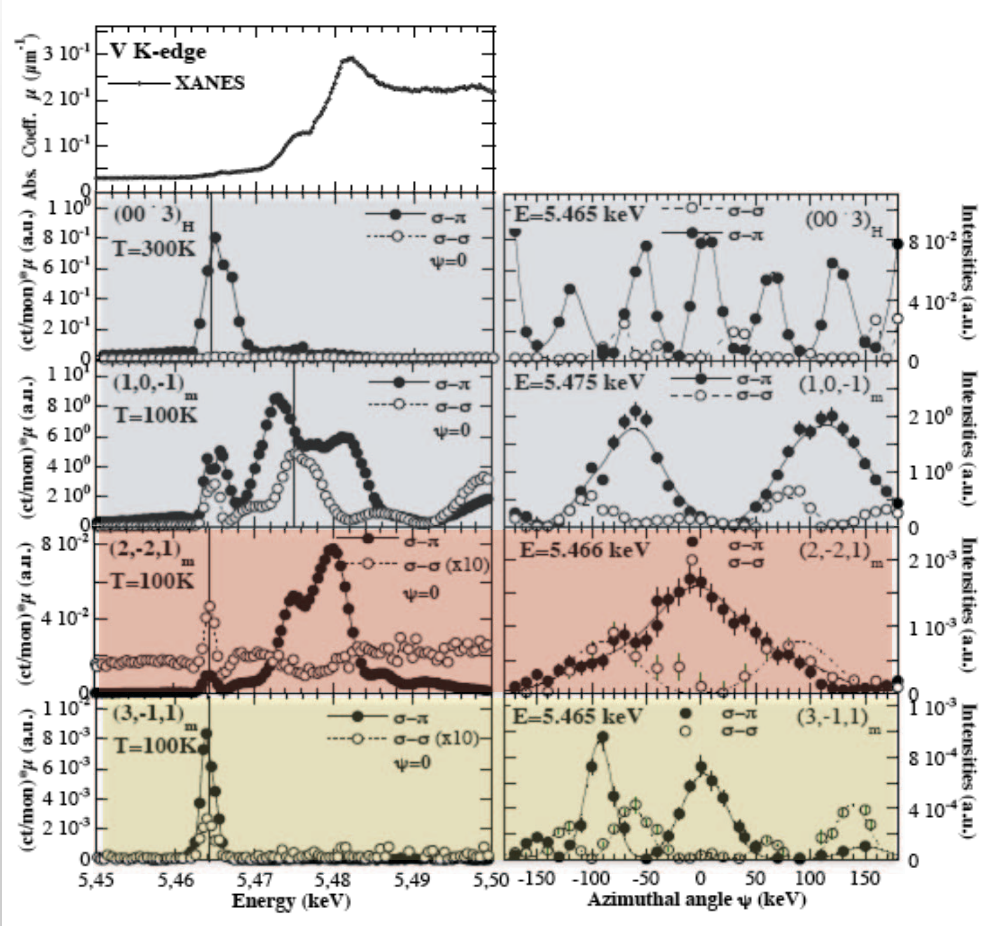
Electric quadrupole
$F^2(E1\text{-}E1)$ (dominant contribution)

AF reflections
k_m+l_m=even and h_m=even

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

Special reflections
k_m+l_m=even and h_m=odd

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



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*

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

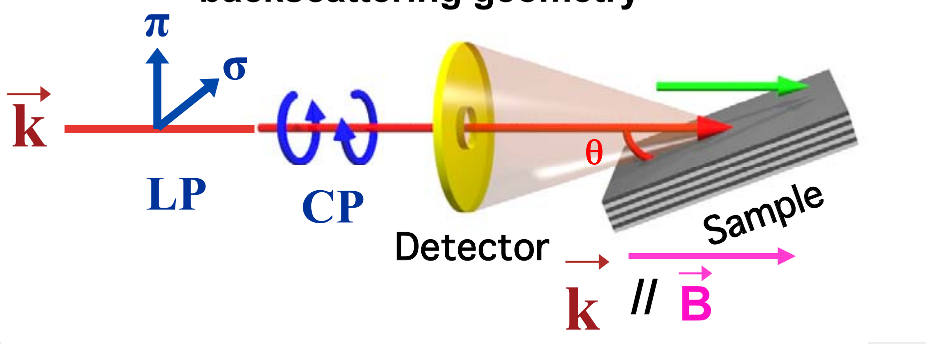
XnrLD (optical activity)
(X-ray non-reciprocal linear dichroism)
- *Spin and orbital moment determination*

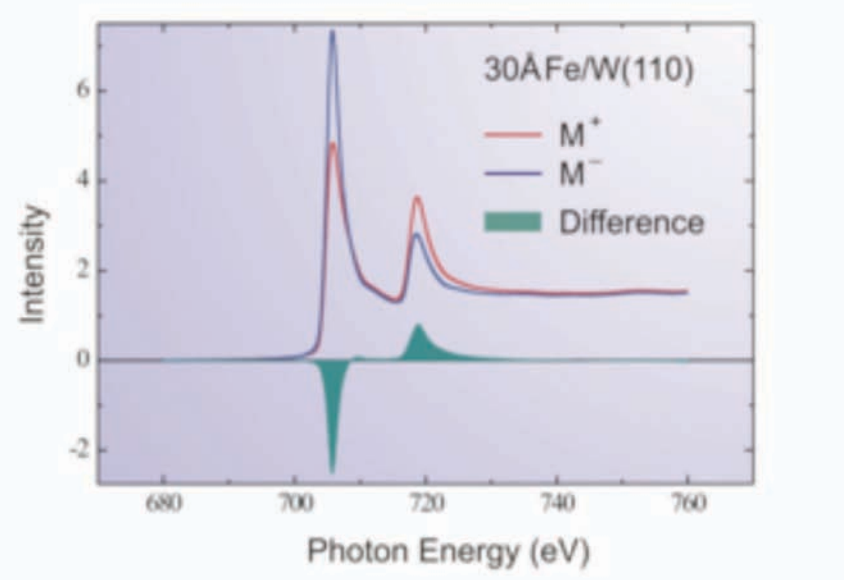
$$\Delta\mu = \mu^{\parallel}(H\uparrow) - \mu^{\perp}(H\uparrow) \quad W^{(2)} = [L \otimes n]^{(2)}$$

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

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

Total Fluorescence Yield in backscattering geometry

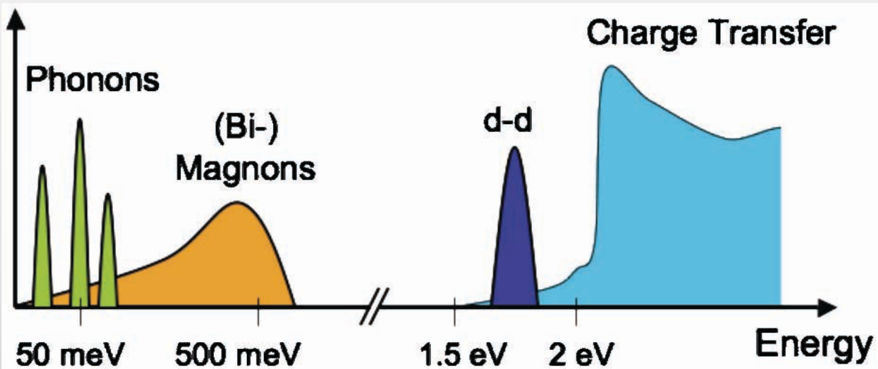




Ament et al., REVIEWS OF MODERN PHYSICS, VOLUME ***83**, 705 (2011)*

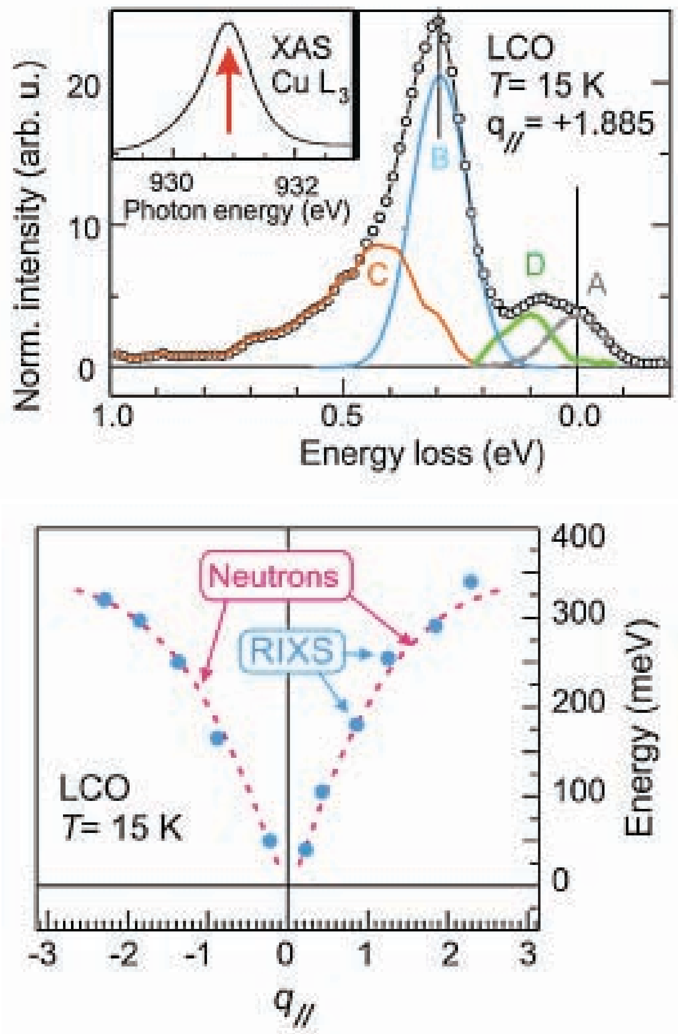
Probe elementary excitations in complex materials by measuring their energy, momentum, and polarization dependence.

Determining the low-energy charge, spin, orbital, and lattice excitations of solids



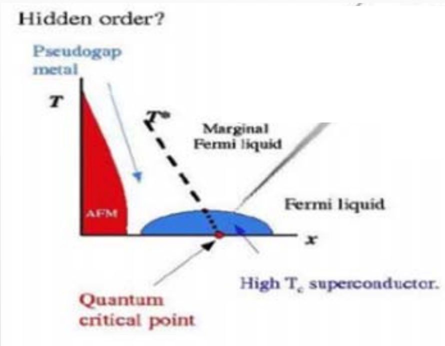
- Aggressive improvement of energy resolution, but still high with respect neutron inelastic energies
- Hard x-rays edges limited by resonance enhancement
- Future perspectives for advances X-FEL

Braicovich et al. (2010)



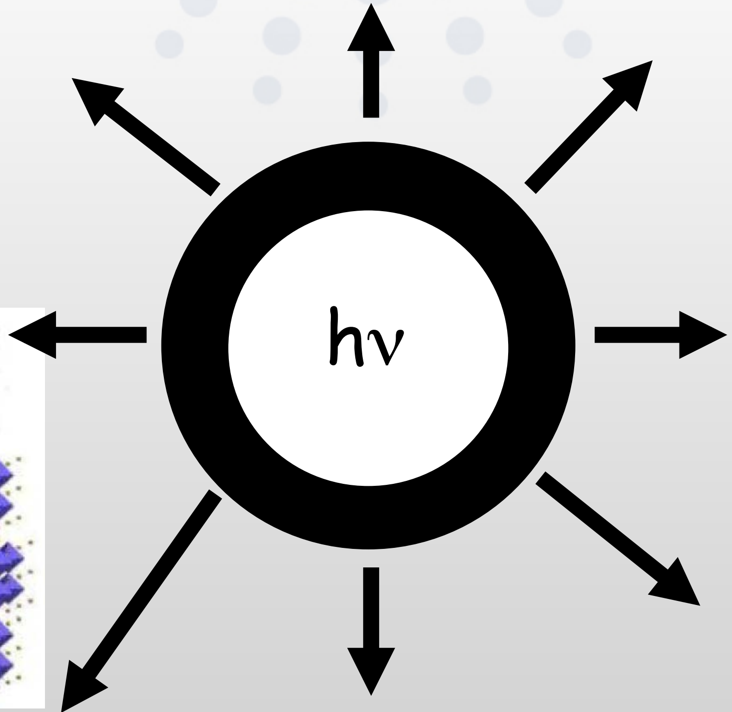
SYNCHROTRON RESEARCH ON MAGNETISM

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

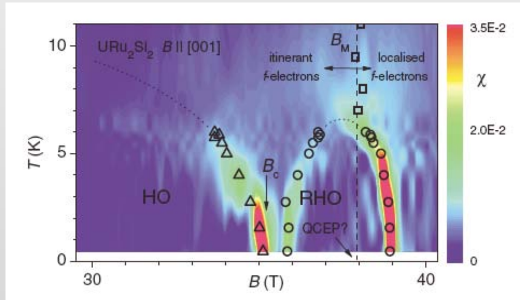


Magnetic phase diagram
-Structural phase transitions
- Metamagnetic transitions
- Lock-in transitions

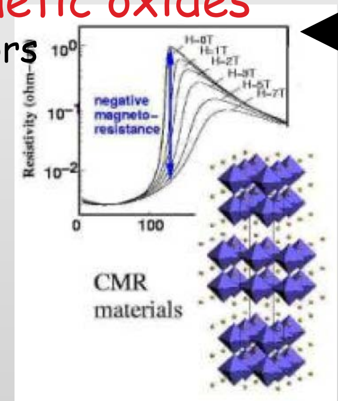
Quantum low dimensional antiferromagnetics
- Spin-1 Haldane chains
- Spin ladders
- Magnetization plateaus



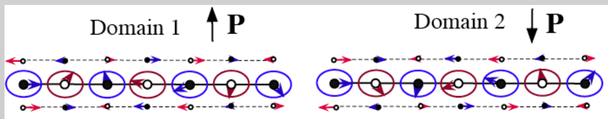
Heavy fermions
- Quantum criticality
- Hidden order parameter
- Metamagnetism



Doped magnetic oxides
- Mott-insulators
- CMR

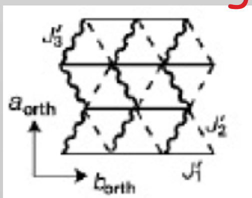


Multiferroics
- Magnetoelectricity
- Magnetic/FE coupling



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

Frustrated magnetism



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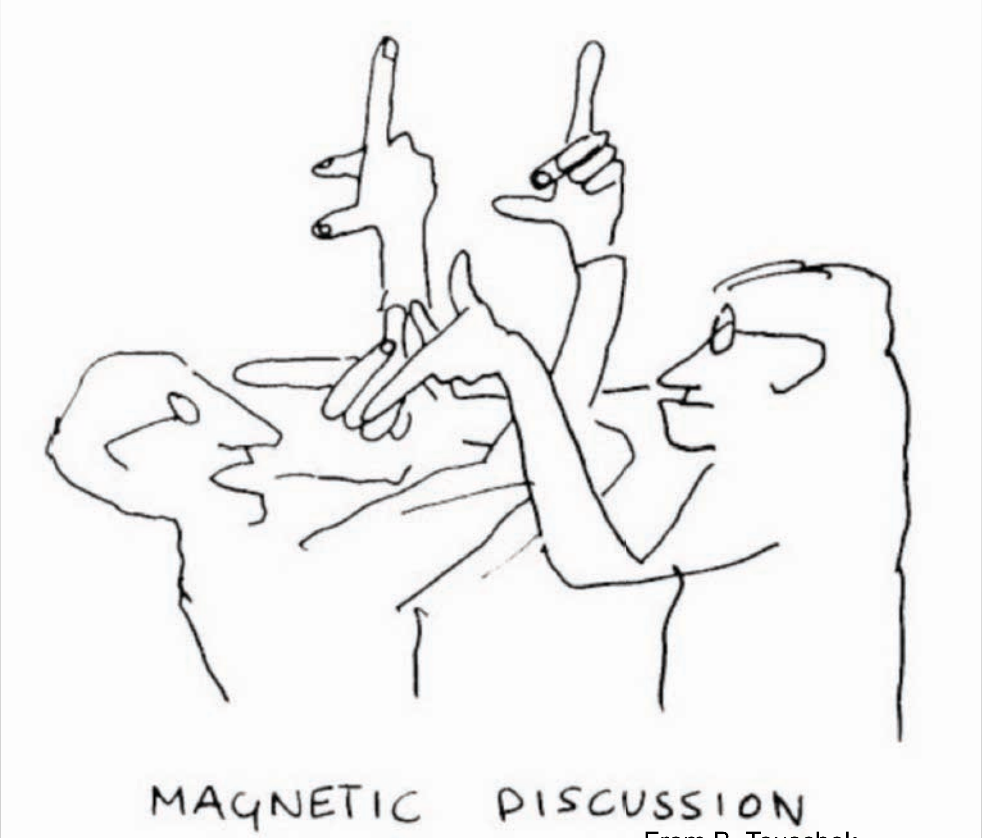

From B. Touschek