Elements of Modern X-ray Physics

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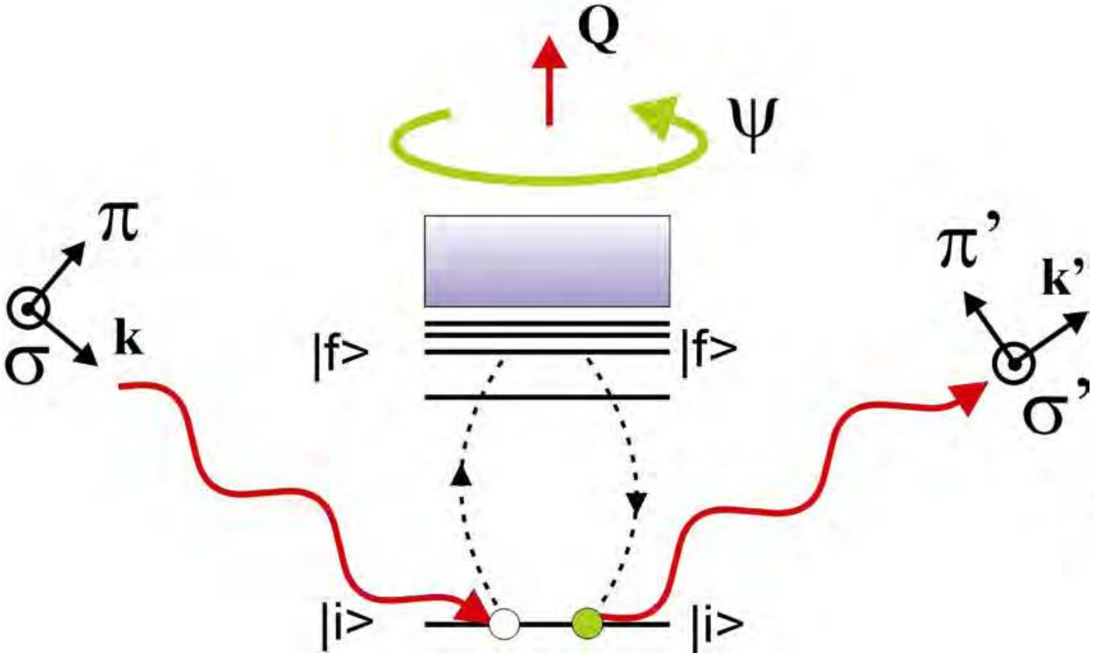
About this course

"To explain the physics underlying the production and exploitation of X-rays with emphasis on application in condensed matter and materials physics"

1. Sources of X-rays
2. X-rays and their interaction with matter: scattering
3. Refraction and absorption of X-rays
4. X-ray imaging

X-rays and their interaction with matter

About this lecture



Scattering amplitude is a tensor

$$A = \epsilon' \cdot f \cdot \epsilon,$$

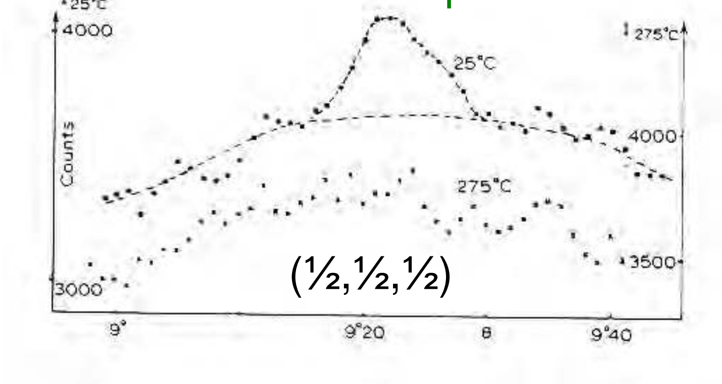
$$f = \sum_n T_n \exp(i\mathbf{Q} \cdot \mathbf{r}).$$

1. Cross-sections and scattering lengths
2. Semi-classical description of elastic scattering
   - Thomson scattering
   - Resonant scattering
   - Relationship between scattering, refraction and absorption
3. Compton scattering
   - Kinematics
   - Klein-Nishina cross-section
4. Quantum mechanical treatment
   - Non-resonant magnetic scattering
   - Resonant scattering from multipoles

X-ray Magnetic Scattering

(1972) X-ray Magnetic Scattering

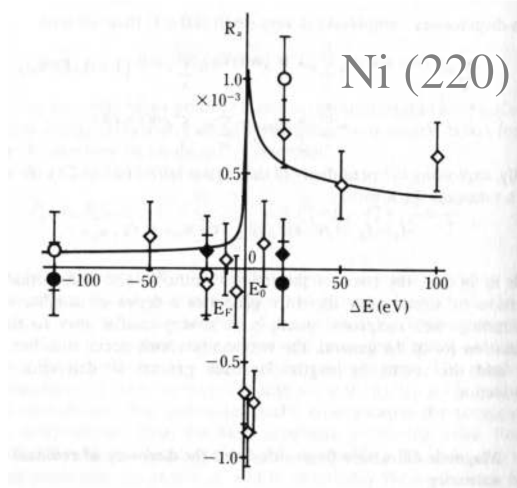
Tube source: Counts per 4 hours!



NiO, de Bergevin and Brunel (1972)

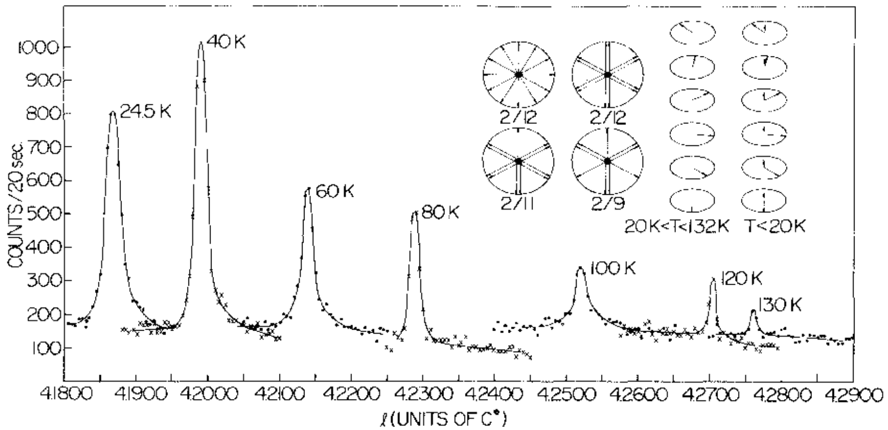
(1985) First Resonant Scattering

Nickel, Namikawa (1985)

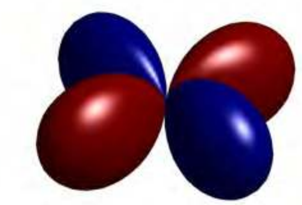


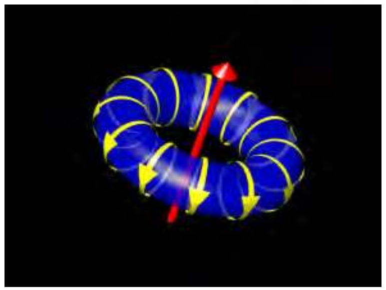
(1985) First Synchrotron Studies

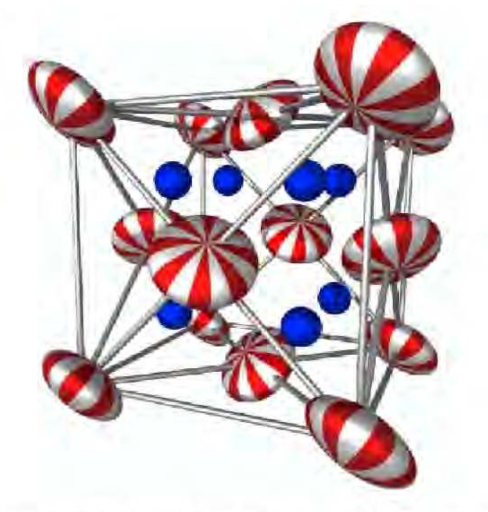
Holmium, Gibbs et al. (1985)



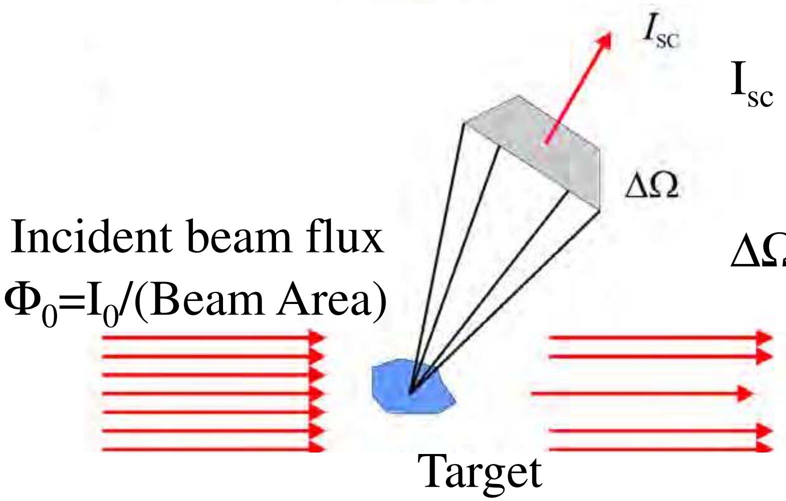
"Modern" Era?!?







Scattering Cross-sections



I_{sc} scattered beam intensity [particles/s]

$\Delta\Omega$ element of solid angle [(Area)/(distance)^2]

Quite generally we expect

$$I_{SC} = \Phi_0 \times \Delta\Omega \times \text{Scattering efficiency factor} = \Phi_0 \times \Delta\Omega \times \left(\frac{d\sigma}{d\Omega}\right)$$

This defines the **Differential Cross - section**

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{\text{Number of particles scattered per second into detector}}{\text{Incident Flux } \times \text{Detector solid Angle}} = \frac{I_{SC}}{\Phi_0 \Delta\Omega}$$

The **Total Cross - section** is obtained by integrating over all solid angle

$$\sigma = \int \left(\frac{d\sigma}{d\Omega}\right) d\Omega$$

This **Partial Differential Cross - section**

$$\left(\frac{d\sigma}{d\Omega dE_f}\right) = \frac{\text{Particles scattered per second into detector in energy window } dE_f}{\text{Incident Flux } \times \text{Detector solid Angle} \times \ dE_f}$$

Photons: Basic Properties and Interactions

	Photon	Neutron
Charge:	**0**	**0**
Mass:	**0**	**1.675 x 10^{-27} Kg**
Spin:	**1**	**½**
Magnetic Moment:	**0**	**-1.913 μ_N**

Scattering lengths:

Sensitivity to Structure:	**r_0=2.82 x 10^{-5} Å** (E field photon and e)	**b~r_0** (Short range nuclear forces)
Sensitivity to Magnetism:	**$r_0(\hbar\omega/mc^2)$** (E, H field photon and e and μ_B)	**b_{mag} ~ r_0** (μ_n.B_{dipp})
Resonant Scattering:	**100 r_0!**	

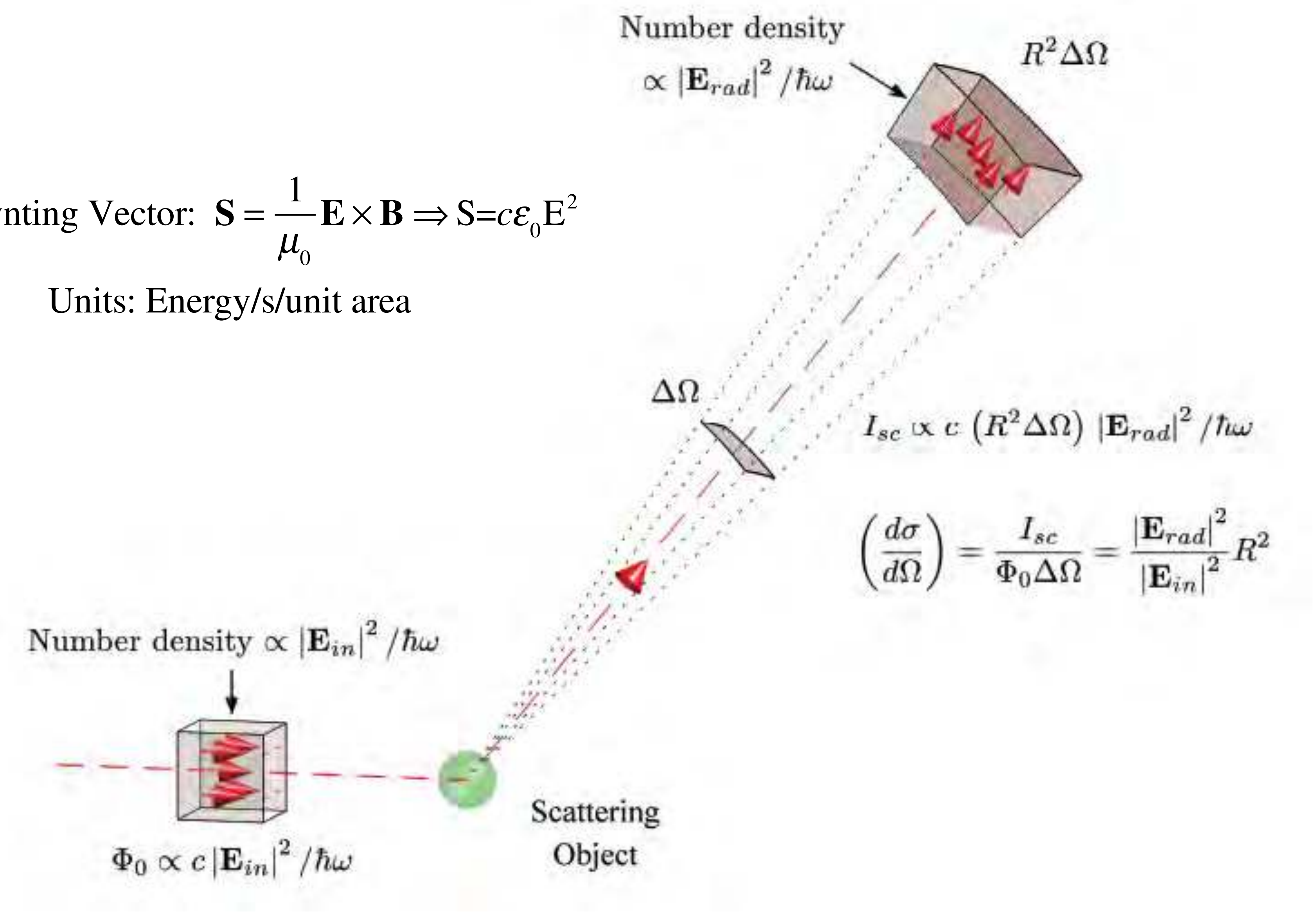
$$r_0 = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{mc^2} = 2.82\times10^{-15}\,m$$

Scattering of an electromagnetic wave

Semi-classical treatment

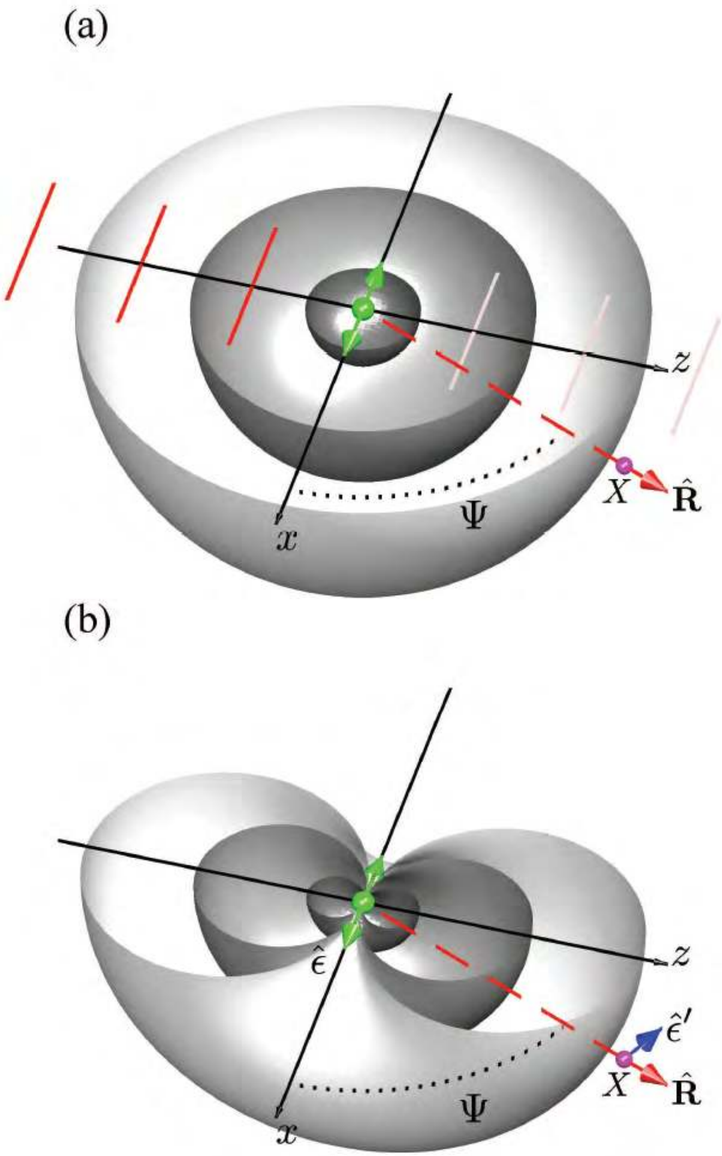
Poynting Vector: $\mathbf{S} = \frac{1}{\mu_0}\mathbf{E}\times\mathbf{B} \Rightarrow S = c\varepsilon_0 E^2$

Units: Energy/s/unit area



Radiation from an accelerating charge

Electric dipole radiation



$$E_{rad} \propto \frac{-e}{R} a_X(t')\sin\Psi \propto \frac{e}{R} a_X(t')(\hat{\varepsilon}\cdot\hat{\varepsilon}') \qquad \text{where } t' = t - R/c$$

The acceleration of the charge is given by

$$a_X(t') = \frac{-eE_0 e^{-i\omega t'}}{m} = \frac{-e}{m}E_{in}e^{i\omega(R/c)} = \frac{-e}{m}E_{in}e^{ikR} \quad \text{where } E_{in} = E_0 e^{-i\omega t}$$

$$\therefore \frac{E_{rad}(R,t)}{E_{in}} \propto \left(\frac{e^2}{m}\right)\frac{e^{ikR}}{R}(\hat{\varepsilon}\cdot\hat{\varepsilon}')$$

$$= -r_0 \frac{e^{ikR}}{R}\left|\hat{\varepsilon}\cdot\hat{\varepsilon}'\right| \qquad \text{from exact treatment}$$

$$r_0 = \left(\frac{e^2}{4\pi\varepsilon_0 mc^2}\right) = 2.82\times 10^{-15}\, m$$

$$\frac{d\sigma}{d\Omega} = \frac{\left|E_{rad}\right|^2 R^2}{\left|E_{in}\right|^2} = r_0^2\left|\hat{\varepsilon}\cdot\hat{\varepsilon}'\right|^2$$

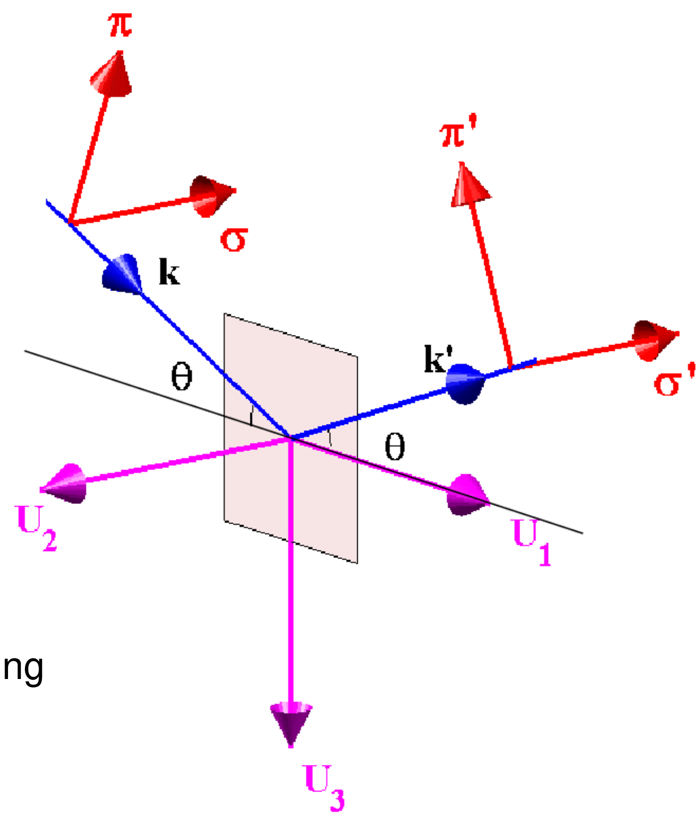
Thomson cross-section

Scattering from the charge of a single, unbound electron

Scattering length:

$$-r_0$$

phase shift of π on scattering (refractive index, $n < 1$)



Polarization dependence:

$$\frac{d\sigma}{d\Omega} = r_0^2 \left|\hat{\varepsilon}\cdot\hat{\varepsilon}'\right|^2 = r_0^2 P$$

with

$$P = \left|\hat{\varepsilon}\cdot\hat{\varepsilon}'\right|^2 = \begin{cases} \left|\hat{\sigma}\cdot\hat{\sigma}'\right|^2 = 1 & \text{Synchrotron: vertical scattering} \\ \left|\hat{\pi}\cdot\hat{\pi}'\right|^2 = \cos^2(2\theta) & \text{Synchrotron: horizontal scattering} \\ \frac{1}{2}(1+\cos^2(2\theta)) & \text{Unpolarised source} \end{cases}$$

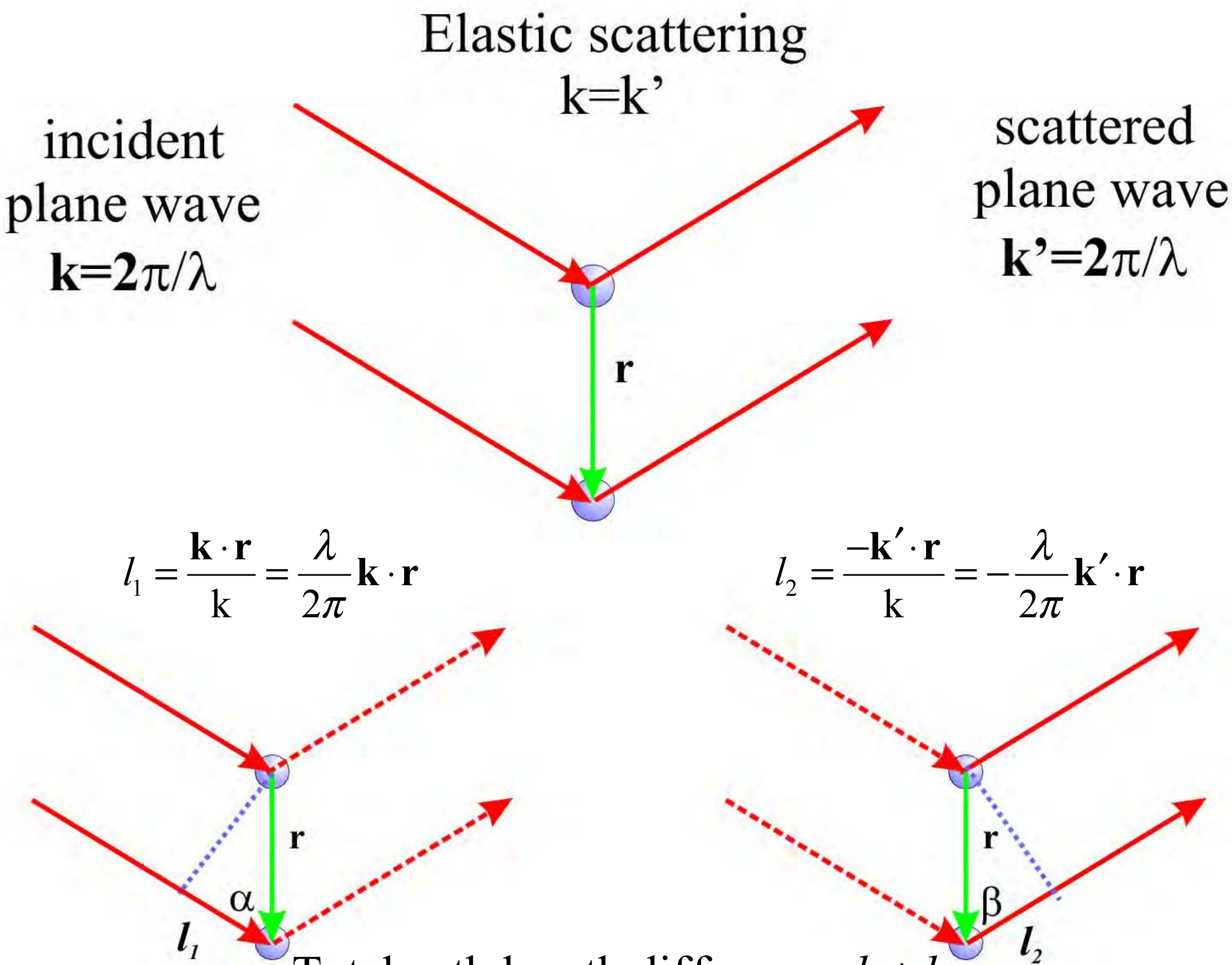
Total scattering cross-section:

$$\sigma_T = \int \frac{d\sigma}{d\Omega} d\Omega = 4\pi r_0^2 \left\langle \left|\hat{\varepsilon}\cdot\hat{\varepsilon}'\right|^2 \right\rangle = 4\pi r_0^2 \frac{2}{3}$$

$$\boxed{\sigma_T = \left(\frac{8\pi}{3}\right) r_0^2}$$

Diffraction: Two point scatterers

Definition of the scattering vector



Total path length difference: $l_1 + l_2$

Total phase difference: $\frac{2\pi}{\lambda}(l_1 + l_2) = (\mathbf{k} - \mathbf{k}')\cdot\mathbf{r} = \mathbf{Q}\cdot\mathbf{r}$

Scattering vector $\mathbf{Q} = \mathbf{k} - \mathbf{k}'$

Diffraction: Two point scatterers

Amplitude and intensity of scattered beam

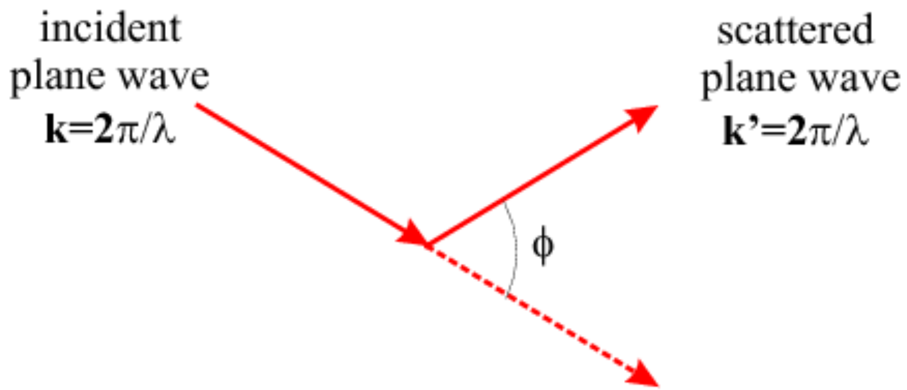
Scattered wave from origin: $\psi_1(\mathbf{x}) = Ae^{i\mathbf{k}'\cdot\mathbf{x}}$

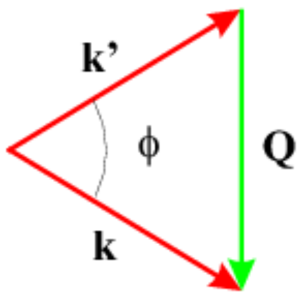
Scattered wave from $\mathbf{r}$: $\psi_2(\mathbf{x}) = Ae^{i\mathbf{k}'\cdot\mathbf{x}}e^{i\mathbf{Q}\cdot\mathbf{r}}$

Total amplitude: $\psi_t = \psi_1(\mathbf{x}) + \psi_2(\mathbf{x}) = Ae^{i\mathbf{k}'\cdot\mathbf{x}} + Ae^{i\mathbf{k}'\cdot\mathbf{x}}e^{i\mathbf{Q}\cdot\mathbf{r}}$

Intensity: $I = |\psi_t|^2 = \psi_t\psi_t^* = 2A^2(1+\cos(\mathbf{Q}\cdot\mathbf{r}))$

Scattering triangle





$$Q = \frac{4\pi}{\lambda}\sin(\phi/2)$$

Scattering from an atom

unbound electrons

Discrete system: scattering amplitude $A(\mathbf{Q}) = -r_0 \sum_{j} e^{i\mathbf{Q}\cdot\mathbf{r}_j}$

Continuous system: $A(\mathbf{Q}) = -r_0 \int \rho(\mathbf{r}) d\mathbf{r}\, e^{i\mathbf{Q}\cdot\mathbf{r}}$ $\rho(\mathbf{r})$: number density of scatterers

X-rays

Atomic form factor defined by $f^0(\mathbf{Q}) = \int \rho(\mathbf{r}) d\mathbf{r}\, e^{i\mathbf{Q}\cdot\mathbf{r}}$

$$f^0(\mathbf{Q}) \to \mathrm{Z} \text{ as } \mathrm{Q} \to 0$$

$$f^0(\mathbf{Q}) \to 0 \text{ as } \mathrm{Q} \to \infty$$

Formally, the atomic form factor is the Fourier transform of the atomic electron density

Example: 1s hydrogenic wave function

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \quad \Rightarrow \quad f^0_{1s}(Q) = \frac{1}{(1+(Qa/2)^2)^2} \qquad \text{with } a = a_0 / Z$$

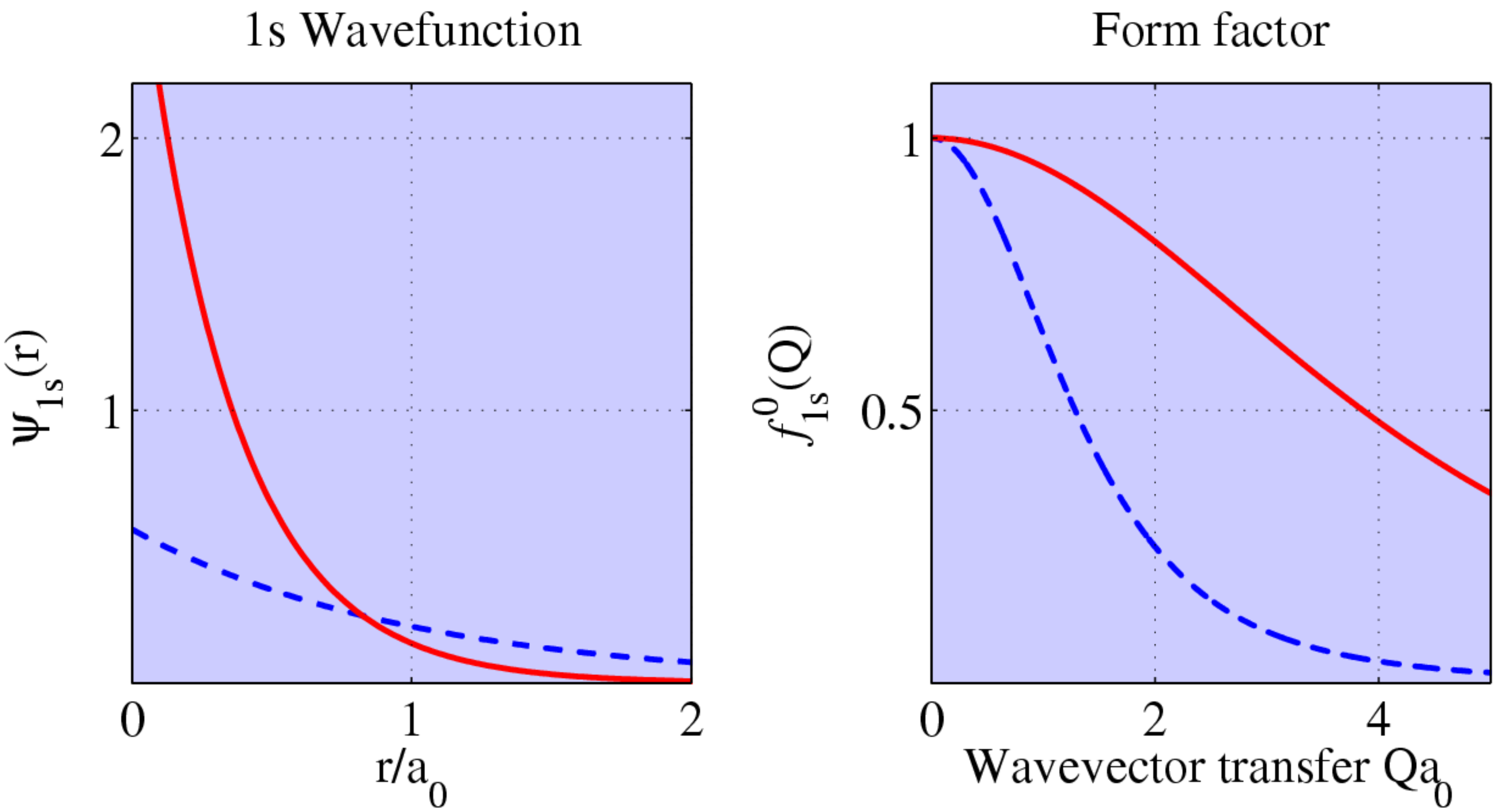
Neutrons

For neutrons $\rho(\mathbf{r}) = \delta(\mathbf{r})$ and $\int \delta(\mathbf{r}) d\mathbf{r}\, e^{i\mathbf{Q}\cdot\mathbf{r}} = 1$

X-ray charge scattering: decrease of scattering intensity with increasing Q

Neutron nuclear scattering: no decrease

Atomic form factor of Hydrogen-Like Atom



Scattering cross-section from a crystal

Laue condition

For lattice sum: $\sum_{\mathbf{R}_n}^{\text{lattice}} e^{i\mathbf{Q}\cdot\mathbf{R}_n}$ large number of terms means cancellation unless special condition is fulfilled where they all add up. This condition requires that

$$\mathbf{Q}\cdot\mathbf{R}_n = 2\pi \times \text{integer}$$

This condition is met if $\mathbf{Q}=\mathbf{G}$ a reciprocal lattice vector since

$\mathbf{R}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ and $\mathbf{G} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^*$ where the primitive reciprocal lattice vectors are defined by $\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi\delta_{ij} \Rightarrow \mathbf{G}\cdot\mathbf{R}_n = 2\pi(hn_1 + kn_2 + ln_3)$

All unit cells therefore scatter in phase when

$$\mathbf{Q}=\mathbf{G} \qquad \text{Laue condition}$$

Can show that $$\left|\sum_{\mathbf{R}_n}^{\text{lattice}} e^{i\mathbf{Q}\cdot\mathbf{R}_n}\right|^2 = N v_c^* \sum_{\mathbf{G}} \delta(\mathbf{Q}-\mathbf{G})$$

Thus $$\left(\frac{d\sigma}{d\Omega}\right)^{Crystal} = N v_c^* \sum_{\mathbf{G}} \left|F(\mathbf{Q})\right|^2 \delta(\mathbf{Q}-\mathbf{G})$$

Unit cell structure factor $$F^{x-rays}(\mathbf{Q}) = r_0 \sum_{\mathbf{r}_j}^{\text{unit cell}} Pf_j(\mathbf{Q})\, e^{i\mathbf{Q}\cdot\mathbf{r}_j} \qquad F^{neutrons}(\mathbf{Q}) = \sum_{\mathbf{r}_j}^{\text{unit cell}} b_j\, e^{i\mathbf{Q}\cdot\mathbf{r}_j}$$

X-ray Resonant Scattering

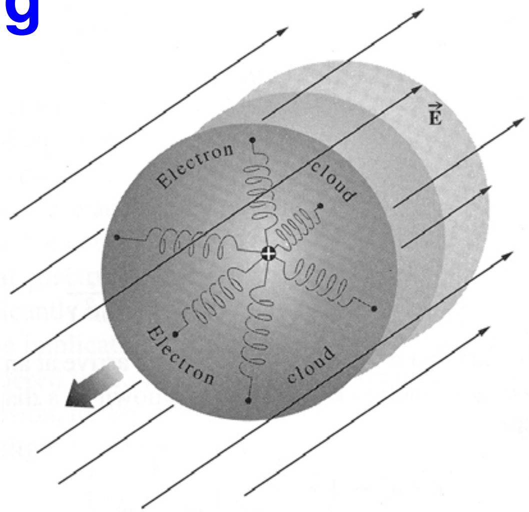
Dispersion corrections

From electrons bound in atoms expect:

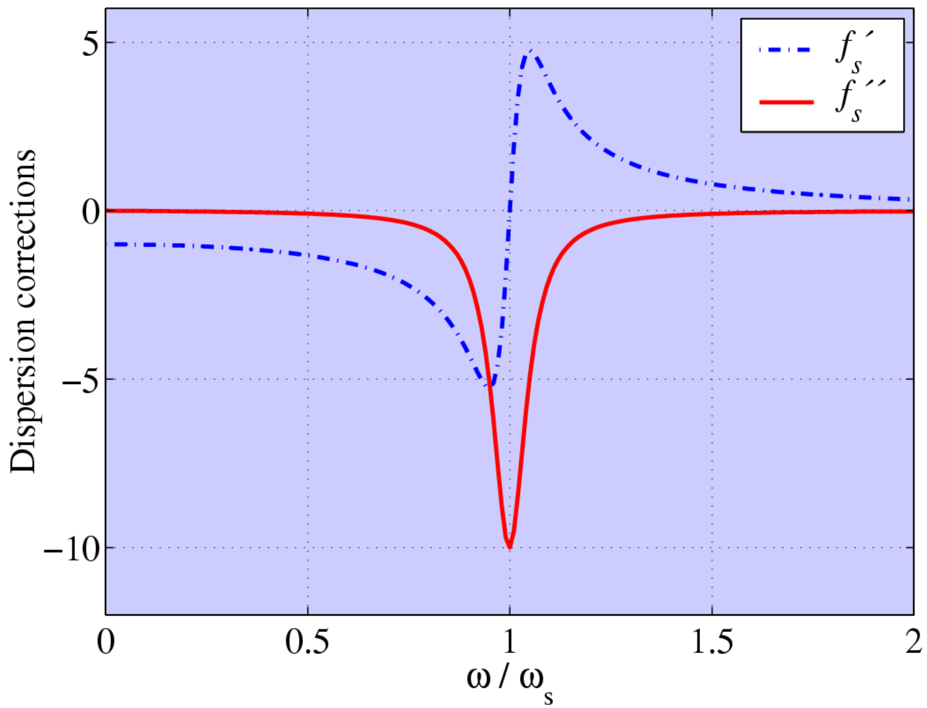
$$f(\mathbf{Q},\omega) = f^0(\mathbf{Q}) + f'(\omega) + i\,f''(\omega)$$

Forced, damped oscillator model

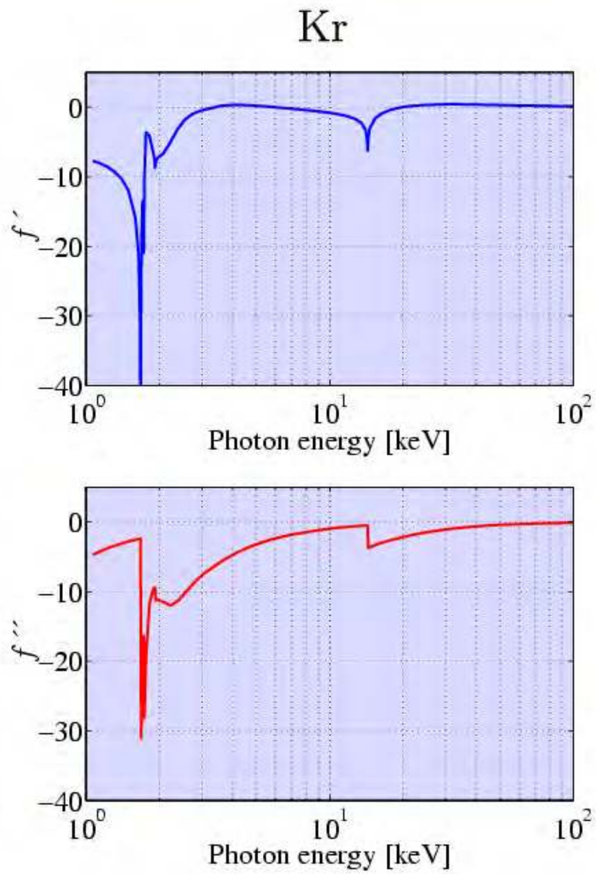
$$\ddot{x} + \Gamma\dot{x} + \omega_r^2 x = -\left(\frac{eE_0}{m}\right)e^{-i\omega t} \Rightarrow x(t) = \left(-\frac{e}{m}\right)\frac{\mathrm{E}_0 e^{-i\omega t}}{\left(\omega_0^2 - \omega^2 - i\omega\Gamma\right)}$$



$$f_s' = \frac{\omega_0^2(\omega^2-\omega_0^2)}{(\omega^2-\omega_0^2)^2+(\omega\Gamma)^2} \quad f_s' = -\frac{-\omega_0^2\omega\Gamma}{(\omega^2-\omega_0^2)^2+(\omega\Gamma)^2}$$



Dispersion corrections



Resonant scattering in crystallography

Breakdown of Friedel's Law

Non-resonant

$$A(Q) = f_1^0 + f_2^0 e^{iQx}$$

$$\Rightarrow I(Q) = (f_1^0)^2 + (f_2^0)^2 + 2 f_1^0 f_2^0 \cos(Qx)$$

$$\therefore I(Q) = I(-Q)$$

Resonant

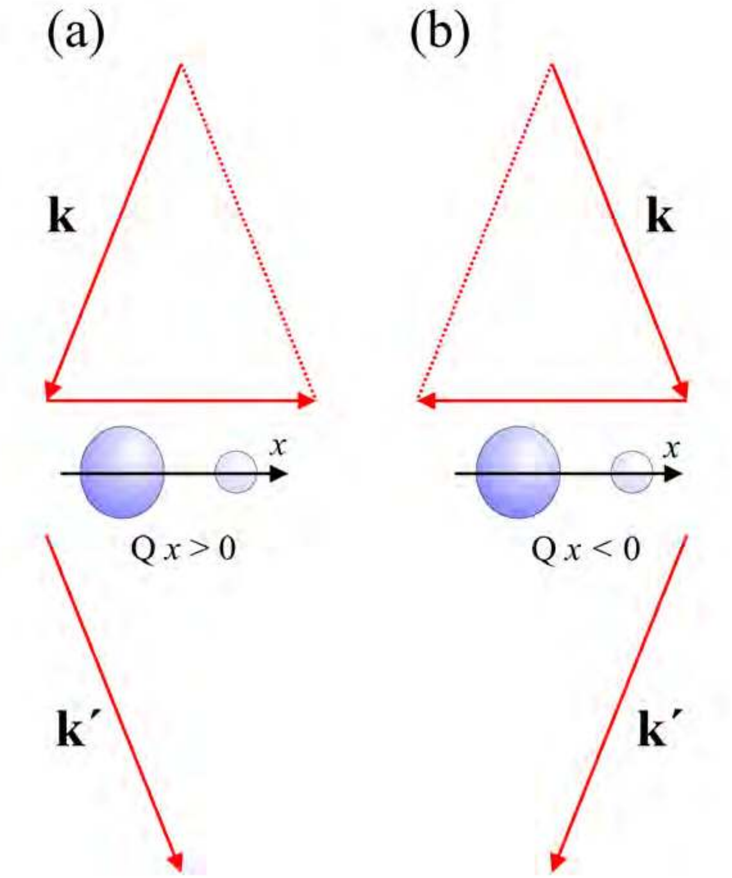
$$f_1 = f_1^0 + f_1{}' + i f_1{}'' \equiv r_1 e^{i\phi_1}$$

$$A(Q) = r_1 e^{i\phi_1} + r_2 e^{i\phi_2} e^{iQx}$$

$$\Rightarrow I(Q) = r_1^2 + r_2^2 + 2 f_1^0 f_2^0 \cos(Qx - \phi_1 + \phi_2)$$

$$\cos(Qx - \phi_1 + \phi_2) \neq \cos(-Qx - \phi_1 + \phi_2)$$

$$\therefore I(Q) \neq I(-Q)$$



Dispersion corrections reveal absolute atomic configurations: route to solution of phase problem, enables MAD, SAD, etc.

Relationship between scattering and refraction

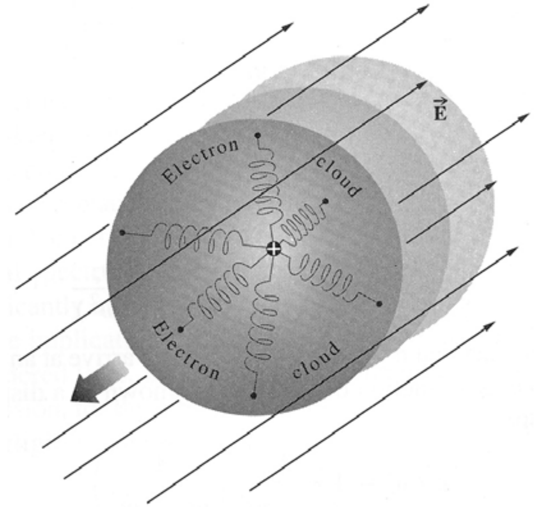
Electric field $\mathbf{E}(t)$=> $\mathbf{P}(t)$ (electric dipole/V)

$$\mathbf{P}(t) = \varepsilon_0 \chi \mathbf{E}(t) = (\varepsilon - \varepsilon_0)\mathbf{E}(t)$$

where

$$\mathrm{P}(t) = \frac{-N e\, x(t)}{V} = -\rho e\, x(t) = -\rho e\left(-\frac{e}{m}\right)\frac{\mathrm{E}_0 e^{-i\omega t}}{\left(\omega_0^2 - \omega^2 - i\omega\Gamma\right)}$$

$$\Rightarrow \frac{\mathrm{P}(t)}{\mathrm{E}(t)} = \varepsilon - \varepsilon_0 = \left(\frac{e^2\rho}{m}\right)\frac{1}{\left(\omega_0^2 - \omega^2 - i\omega\Gamma\right)}$$



The refractive index is defined by

$$n^2 = \frac{c^2}{v^2} = \frac{\varepsilon}{\varepsilon_0}$$

$$\Rightarrow n^2 = 1 + \left(\frac{e^2\rho}{\varepsilon_0 m}\right)\frac{1}{\left(\omega_0^2 - \omega^2 - i\omega\Gamma\right)}$$

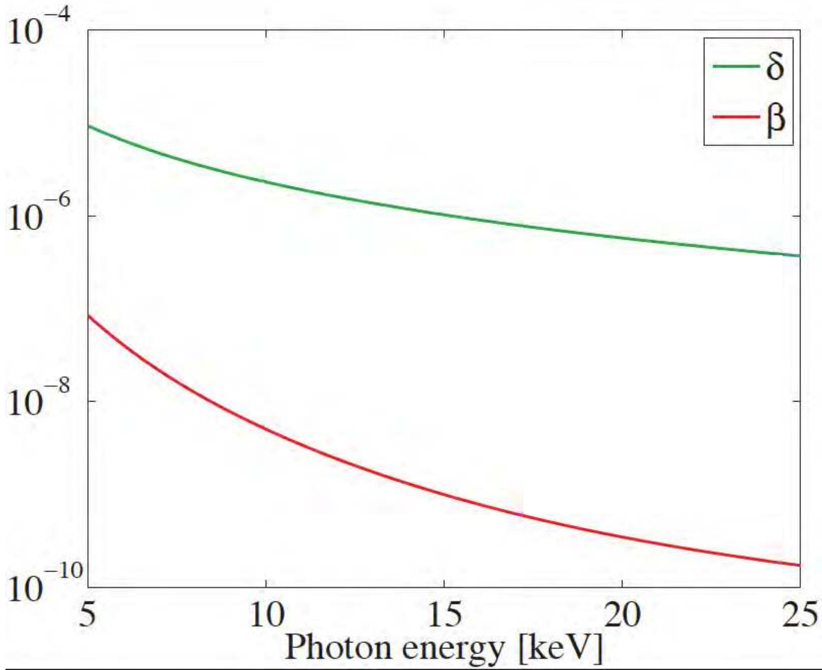
For X-rays, $\omega \gg \omega_0 \gg \Gamma$

$$n \approx 1 - \frac{1}{2}\left(\frac{e^2\rho}{\varepsilon_0 m\omega^2}\right) = 1 - \frac{2\pi\rho r_0}{k^2}$$

$$\boxed{n \approx 1 - \delta + i\beta}$$

Since $\rho = \rho_a f(0)$

$$\delta = \frac{2\pi\rho_a r_0\left(f^0(0) + f'(\hbar\omega)\right)}{k^2} \qquad \beta = -\frac{2\pi\rho_a r_0 f''(\hbar\omega)}{k^2}$$



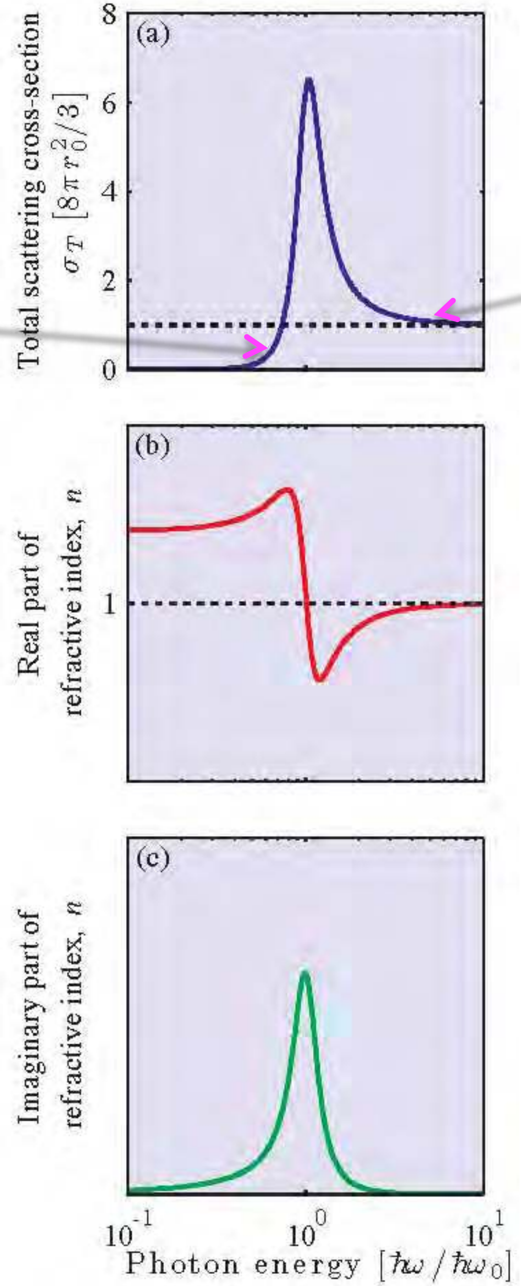
Relationship between scattering and refraction

Resonant scattering

$$f(Q,\hbar\omega) = f^0(Q) + f'(\hbar\omega) + if''(\hbar\omega)$$

Rayleigh scattering
Visible light

Thomson scattering
X-rays



Refractive index

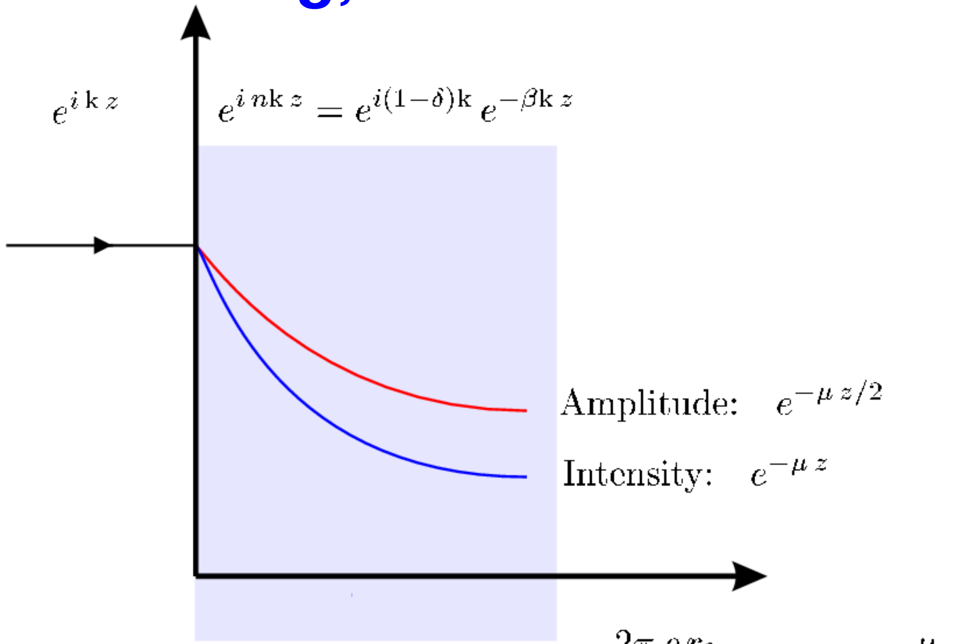
$$n = 1 - \delta + i\beta$$

$$\delta = (f^0(0) + f')\frac{2\pi\rho_a r_0}{k^2}$$

$$\beta = -f''\left(\frac{2\pi\rho_a r_0}{k^2}\right)$$

Scattering and refraction: different ways of understanding the same phenomena

Relationship scattering, refraction and absorption



$n = 1$ $\quad n = 1 - \delta + i\beta \;;\; \delta = \frac{2\pi \rho r_0}{k^2}$ and $\beta = \frac{\mu}{2k}$

$$n = 1 - \delta + i\beta \qquad \delta = \left(\frac{2\pi\rho_a (f^0(0) + f')r_0}{k^2} \right) \quad \beta = -\left(\frac{2\pi\rho_a f'' r_0}{k^2} \right)$$

Absorption coefficient μ defined by $I = I_0 e^{-\mu z}$ and

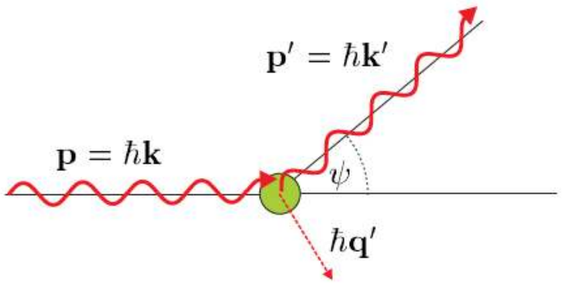
absorption cross-section $\sigma_a = \mu / \rho_a$

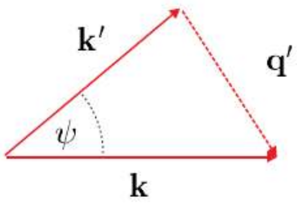
$$f'' = -\left(\frac{k^2}{2\pi\rho_a r_0} \right) \frac{\mu}{2k} = -\left(\frac{k}{4\pi r_0} \right) \sigma_a$$

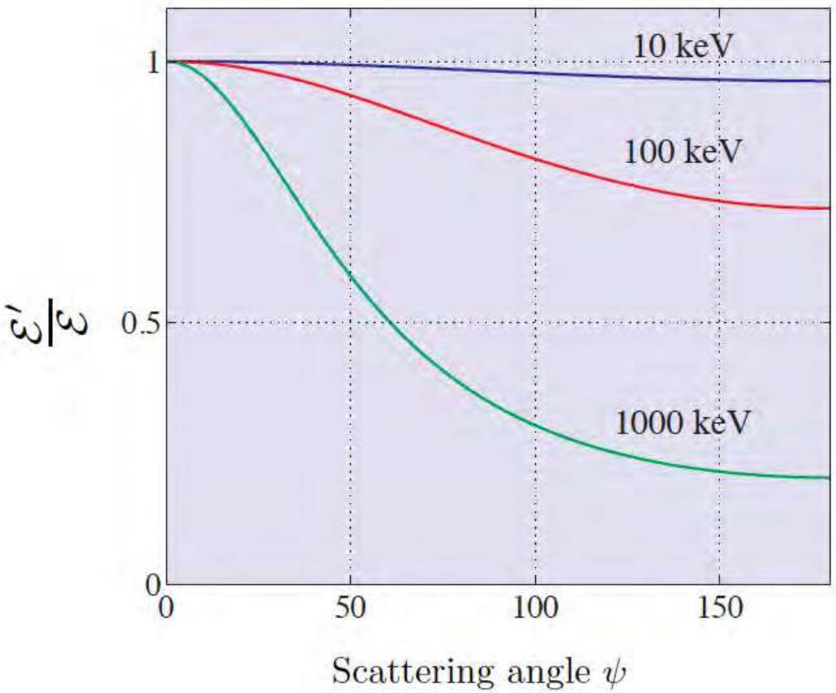
Absorption is proportional to the imaginary part of the forward scattering amplitude (Optical Theorem)

Compton scattering

Kinematics







Kinematics of Compton scattering

Consider a photon incident along the x direction scattering off of a stationary electron. After the scattering event the photon is deflected by an angle ψ in the $x-y$ plane, while the electron moves at an angle ϕ. The momenta and energy before and after the scattering event may be written as

	Initial	*Final*
Momenta	$\begin{pmatrix} \hbar k_i \\ 0 \end{pmatrix} \equiv \begin{pmatrix} \chi_i \\ 0 \end{pmatrix}$	$\begin{pmatrix} \chi_f \cos\psi - \gamma_f \beta_f \cos\phi \\ \chi_f \sin\psi - \gamma_f \beta_f \sin\phi \end{pmatrix}$
Energy	$\chi_i + 1$	$\chi_f + \gamma_f$

where $\chi_{i(f)} = h\nu_{i(f)}/mc^2, etc.$

Conservation of momentum implies that:

$$\chi_i = \chi_f \cos\psi - \gamma_f \beta_f \cos\phi \qquad \text{x-component}$$
$$0 = \chi_f \sin\psi - \gamma_f \beta_f \sin\phi \qquad \text{y-component}$$

Squaring and adding the above equations to eliminate the scattering angle ϕ of the electron yields

$$\gamma_f^2 = 1 + (\chi_i - \chi_f)^2 + 2\chi_i\chi_f (1 - \cos\psi)$$

while from the conservation of energy we have

$$\gamma_f^2 = 1 + (\chi_i - \chi_f)^2 + 2(\chi_i - \chi_f)$$

By comparing the two expressions for γ_f^2 we obtain

$$\frac{\chi_i}{\chi_f} = 1 + \chi_i (1 - \cos\psi)$$

or using the fact that $\chi = \lambda\!\!\!^{-}_C \mathrm{k}$

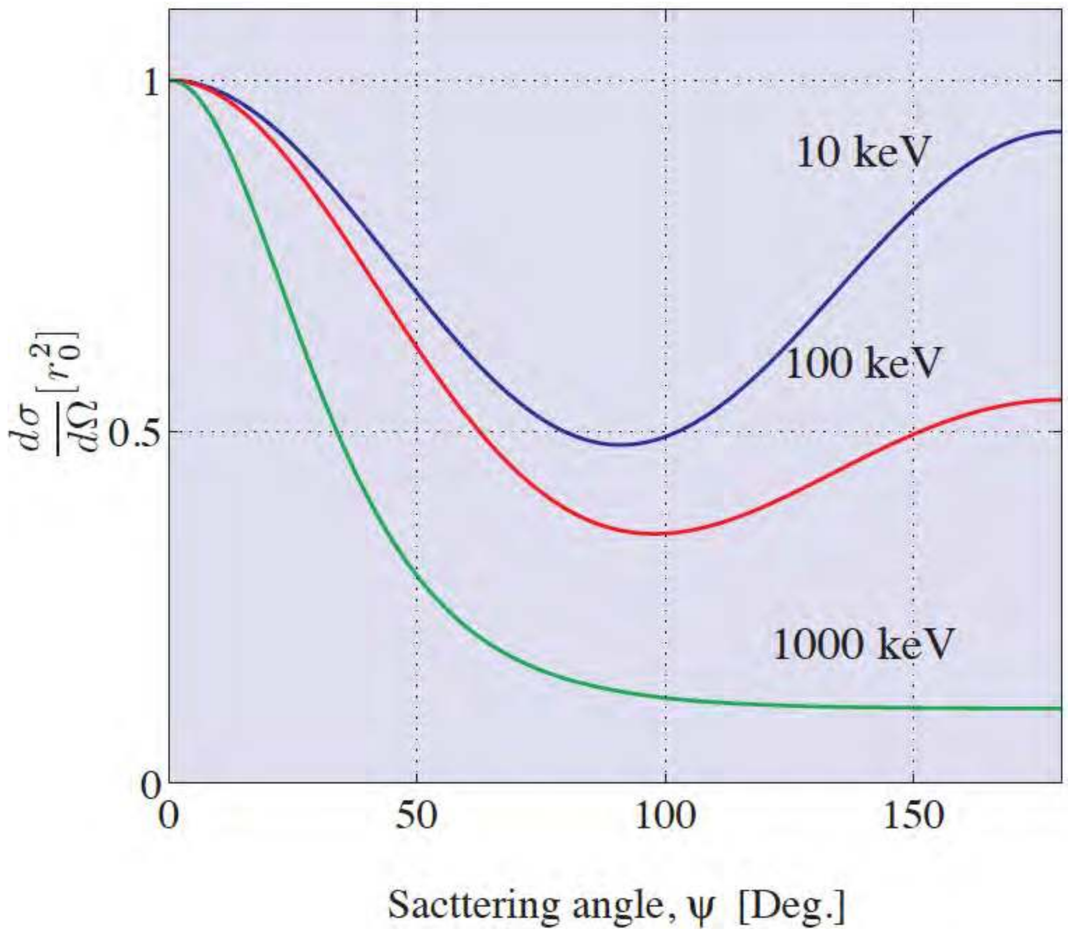
$$\frac{\mathrm{k}_i}{\mathrm{k}_f} = 1 + \lambda\!\!\!^{-}_C \mathrm{k}_i (1 - \cos\psi) = \frac{\mathcal{E}_i}{\mathcal{E}_f} = \frac{\lambda_f}{\lambda_i} \qquad (1)$$

Compton scattering

Klein-Nishina Cross-section

$$\frac{d\sigma}{d\Omega} = \frac{r_0^2}{2}\left(\frac{\mathcal{E}'}{\mathcal{E}}\right)^2 \left[(1+\cos^2\psi) + \frac{\mathcal{E}-\mathcal{E}'}{mc^2}(1-\cos\psi)\right]$$

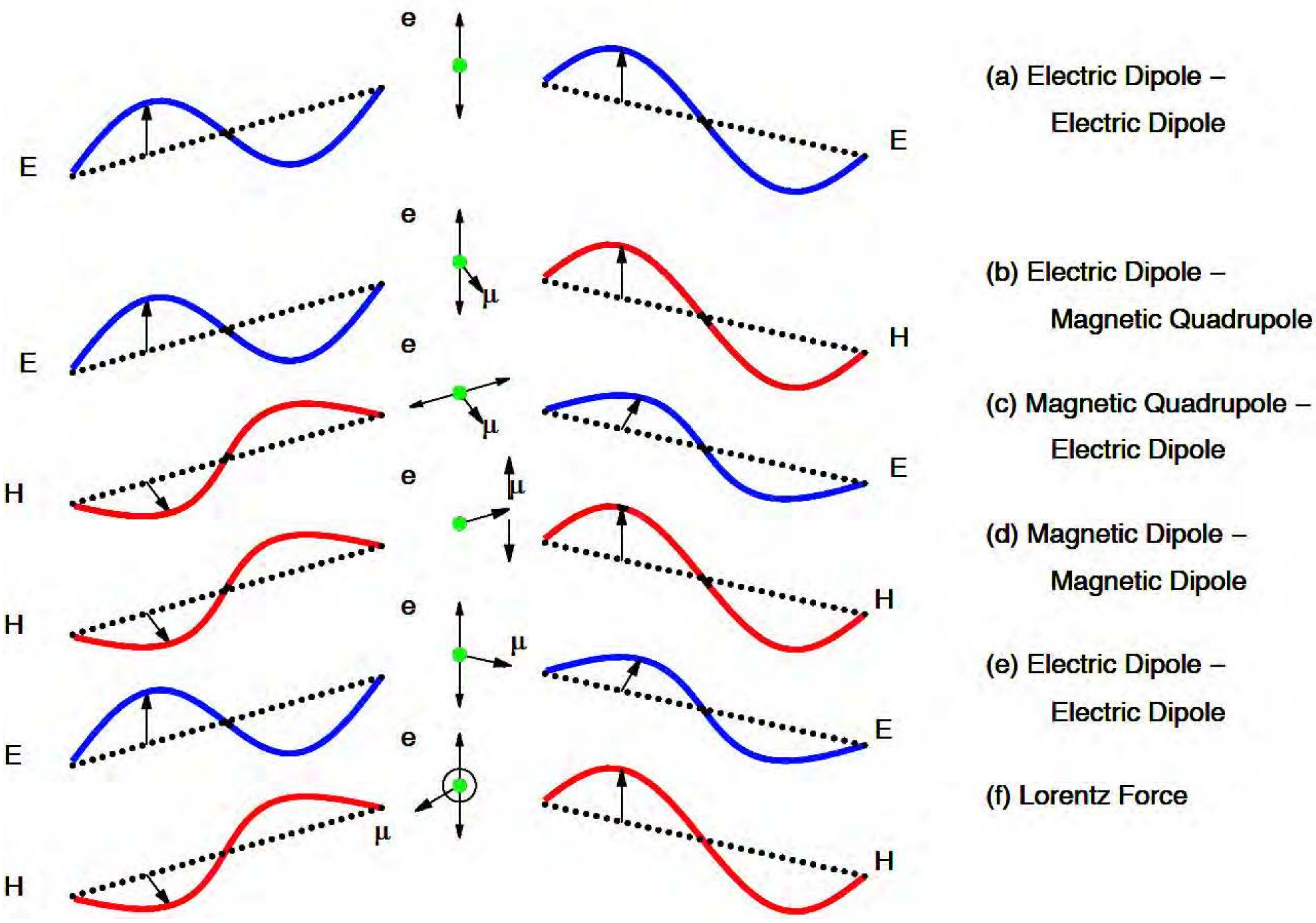
unpolarized source



When $\mathcal{E} \ll mc^2$ $(\Rightarrow \mathcal{E}' \to \mathcal{E})$ or $\psi \to 0$ we recover the Thomson scattering formula

$$\frac{d\sigma}{d\Omega} = \frac{r_0^2}{2}(1+\cos^2\psi)$$

X-rays and their interaction with matter

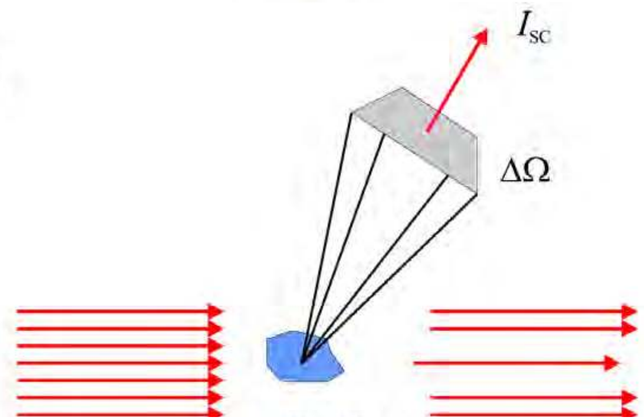


Adapted from de Bergevin and Brunel, 1981

Quantum mechanical description of scattering

Theoretical Framework

Task is to determine the differential cross-section:



$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{\text{Number of particles scattered per second into detector}}{\text{Incident Flux } \times \text{Detector solid Angle}}$$

$$= \frac{W}{\Phi_0(\Delta\Omega)}$$

The transition rate probability W to 2nd order

$$W = \frac{2\pi}{\hbar}\left|\langle f|H_I|i\rangle + \sum_n \frac{\langle f|H_I|n\rangle\langle n|H_I|i\rangle}{\mathcal{E}_i - \mathcal{E}_n}\right|^2 \rho(\mathcal{E}_f)$$

Interaction Hamiltonian H_I: describes interaction between radiation and target

Density of final states

$$\rho(\mathcal{E}_f)\,d\mathcal{E}_f = \rho(\mathbf{k}_f)\,d\mathbf{k}_f$$

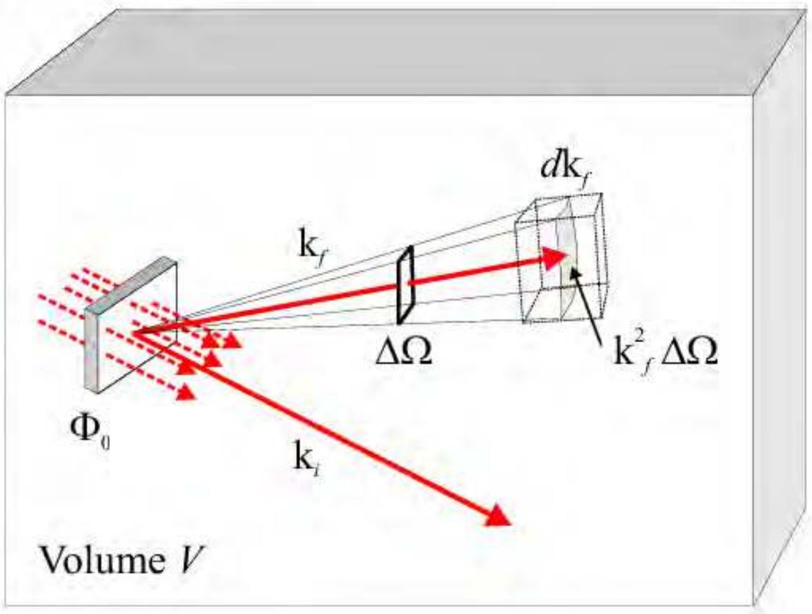
Box normalisation implies

$$\rho(\mathcal{E}_f)\,d\mathcal{E}_f = \rho(\mathrm{k}_f)\;\mathrm{k}_f^2\,\Delta\Omega\,d\mathrm{k}_f$$

$$\therefore \quad \rho(E_f) = \frac{V}{(2\pi)^3}\;\mathrm{k}_f^2\,\Delta\Omega\,\frac{d\mathrm{k}_f}{d\mathcal{E}_f}$$

To first order

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{1}{\Phi_0}\frac{2\pi}{\hbar}\left|\langle f|H_I|i\rangle\right|^2 \frac{V}{(2\pi)^3}\mathrm{k}_f^2\,\frac{d\mathrm{k}_f}{d\mathcal{E}_f}$$



Quantum mechanical description of scattering

Theoretical Framework

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{1}{\Phi_0}\frac{2\pi}{\hbar}\left|\langle f|H_I|i\rangle\right|^2 \frac{V}{(2\pi)^3}\mathrm{k}_f^2 \frac{d\mathrm{k}_f}{d\mathcal{E}_f}$$

For photons, $\Phi_0 = c/V$ and $E = \hbar ck$

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{V}{c}\frac{2\pi}{\hbar}\left|\langle f|H_I|i\rangle\right|^2 \frac{V}{(2\pi)^3}\frac{\mathcal{E}_f^2}{(\hbar c)^2}\frac{1}{\hbar c}$$

$$\left(\frac{d\sigma}{d\Omega}\right) = \left(\frac{V}{2\pi}\right)^2 \frac{\mathcal{E}_f^2}{\hbar^4 c^4}\left|\langle f|H_I|i\rangle\right|^2$$

which for elastic scattering becomes

$$\boxed{\left(\frac{d\sigma}{d\Omega}\right)_{elastic} = \left(\frac{V}{2\pi}\right)^2 \frac{1}{\hbar^4 c^4}\int \mathcal{E}_f^2\left|\langle f|H_I|i\rangle\right|^2 \delta\left(\mathcal{E}_f - \mathcal{E}\right)d\mathcal{E}}$$

Quantizing the Radiation Field

Classical energy of electromagnetic field (free space)

$$\mathcal{E}_{rad} = \varepsilon_0 \int_V \boldsymbol{E} \cdot \boldsymbol{E}\, d\boldsymbol{r} \qquad \text{with } \boldsymbol{E} = -\frac{\partial \boldsymbol{A}}{\partial t}$$

Most general form for Vector potential $\boldsymbol{A}$ is as a Fourier series, of which one term is:

$$\boldsymbol{A}(r,t) = A_0 \hat{\varepsilon}\left[a_{\boldsymbol{k}} \mathrm{e}^{i(\boldsymbol{k}\bullet\boldsymbol{r}-\omega t)} + a_{\boldsymbol{k}}^{*} \mathrm{e}^{-i(\boldsymbol{k}\bullet\boldsymbol{r}-\omega t)} \right]$$

Therefore

$$\mathcal{E}_{rad} = 2\varepsilon_0 \omega^2 A_0^2 a_{\boldsymbol{k}}^{*} a_{\boldsymbol{k}} V = \hbar\omega a_{\boldsymbol{k}}^{*} a_{\boldsymbol{k}} \qquad \text{if } A_0 = \sqrt{\frac{\hbar}{2\varepsilon_0 \omega V}}$$

c.f. Harmonic Oscillator

$$\mathcal{E}_{sho} = \hbar\omega(a_{\boldsymbol{k}}^{\dagger} a_{\boldsymbol{k}} + \frac{1}{2})$$

Suggests radiation field is quantised like an harmonic oscillator with

$$a_{\mathbf{k}} \left| n \right\rangle = \sqrt{\mathrm{n}} \left| \mathrm{n\text{-}1} \right\rangle \qquad \text{and} \qquad a_{\mathbf{k}}^{\dagger} \left| n \right\rangle = \sqrt{n+1} \left| n+1 \right\rangle$$

$$\boxed{\boldsymbol{A}(r,t) = \sum_u \sum_{\boldsymbol{k}} \sqrt{\frac{\hbar}{2\varepsilon_0 \omega V}} \hat{\varepsilon}_u \left[a_{u,\boldsymbol{k}} \mathrm{e}^{i(\boldsymbol{k}\bullet\boldsymbol{r}-\omega t)} + a_{u,\boldsymbol{k}}^{\dagger} \mathrm{e}^{-i(\boldsymbol{k}\bullet\boldsymbol{r}-\omega t)} \right]}$$

Vector potential is LINEAR in photon annihilation and creation operators

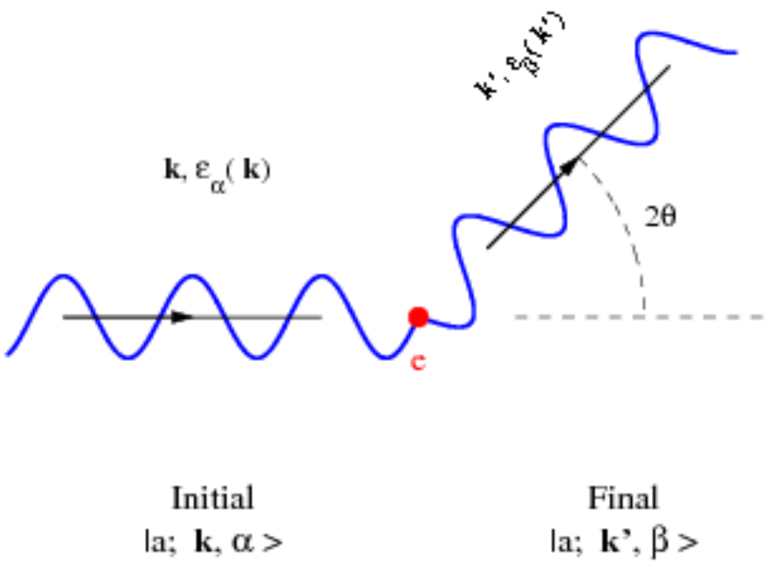
X-ray Scattering: Interaction Hamiltonian

Single Electron in an electromagnetic field (ignore magnetic degrees of freedom to start with) :

$$H_0 = \frac{p^2}{2m} + V$$

Canonical momentum $\boldsymbol{p} \rightarrow \boldsymbol{p} + e\boldsymbol{A}$ with $\boldsymbol{B} = \nabla \times \boldsymbol{A}$ and $\boldsymbol{E} = -\nabla\phi - \dot{\boldsymbol{A}}$

$$H_0 \rightarrow H_0 + \frac{e\boldsymbol{A}\cdot\boldsymbol{p}}{m} + \frac{e^2 A^2}{2m} \Rightarrow \boxed{H_I = \underbrace{\left(\frac{e^2}{2m}\right)A^2}_{H_1} + \underbrace{\left(\frac{e}{m}\right)\boldsymbol{A}\cdot\boldsymbol{p}}_{H_2}}$$



Non-magnetic, Non-resonant scattering

1st order :

$$W = \frac{2\pi}{\hbar}\left|\langle f | H_I | i \rangle\right|^2 \rho\left(\mathcal{E}_f\right)$$

$$H_I = \left(\frac{e^2}{2m}\right)A^2 + \left(\frac{e}{m}\right)\boldsymbol{A}\cdot\boldsymbol{p}$$

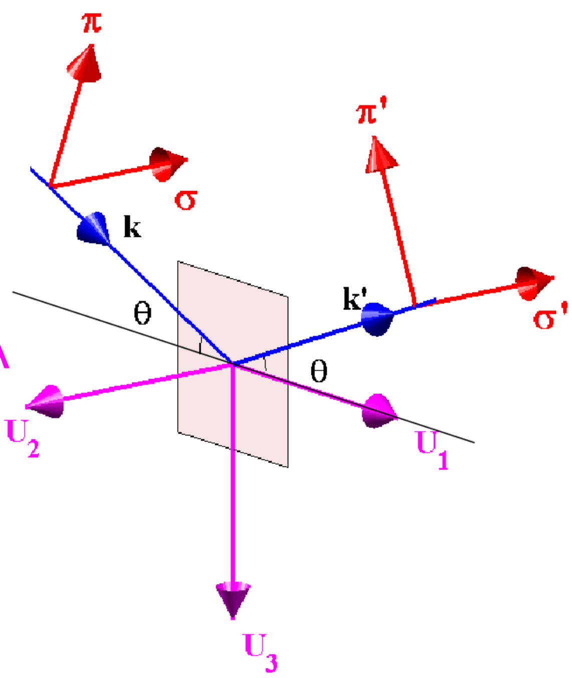
Thomson (Charge) Scattering

$$\left\langle a;\boldsymbol{k}',\beta\right|\left(\frac{e^2}{2m}\right)A^2\left|a;\boldsymbol{k},\alpha\right\rangle = \left\langle \boldsymbol{k}',\beta\right|\left(\frac{e^2}{2m}\right)A^2\left|\boldsymbol{k},\alpha\right\rangle = \left(\frac{e^2\hbar}{2m\varepsilon_0 V\omega}\right)\hat{\varepsilon}_{\alpha,\boldsymbol{k}}\hat{\varepsilon}_{\beta,\boldsymbol{k}}$$

$$\left(\frac{d\sigma}{d\Omega}\right)^{Charge} = \frac{W}{\Phi_0(\Delta\Omega)} = r_0^2\left|\hat{\varepsilon}'\cdot\hat{\varepsilon}\right|^2$$

Differential cross-section for an array of atoms

$$\left(\frac{d\sigma}{d\Omega}\right) = r_0^2(\hat{\varepsilon}'\cdot\hat{\varepsilon})\left|\sum_s f_s^0(Q)\,\mathrm{e}^{i\boldsymbol{Q}\cdot\boldsymbol{R}_s}\right|^2$$



$f_s^0(Q)$ is the atomic form factor and $r_0 = \left(\frac{e^2}{4\pi\varepsilon_0 mc^2}\right) = 2.82 \times 10^{-5}$ Å

Polarization factor refers to E field may be written as

$(\hat{\varepsilon}'\cdot\hat{\varepsilon}) \rightarrow$

	$\hat{\varepsilon}_\perp \equiv \sigma$	$\hat{\varepsilon}_\parallel \equiv \pi$
$\hat{\varepsilon}'_\perp \equiv \sigma'$	1	0
$\hat{\varepsilon}'_\parallel \equiv \pi'$	0	$\cos 2\theta$

Interaction Hamiltonian

X-ray Magnetic Scattering

Single Electron in an electromagnetic field :

$$H_0 = \frac{p^2}{2m} + V$$

Canonical momentum $\boldsymbol{p} \rightarrow \boldsymbol{p} + e\boldsymbol{A}$ with $\boldsymbol{B} = \nabla \times \boldsymbol{A}$ and $\boldsymbol{E} = -\nabla\phi - \dot{\boldsymbol{A}}$

+

Zeeman Interaction :

$$H_Z = g\mu_B \boldsymbol{s}\cdot\boldsymbol{B} = \frac{e\hbar}{m}\boldsymbol{s}\cdot\nabla\times\boldsymbol{A}$$

+

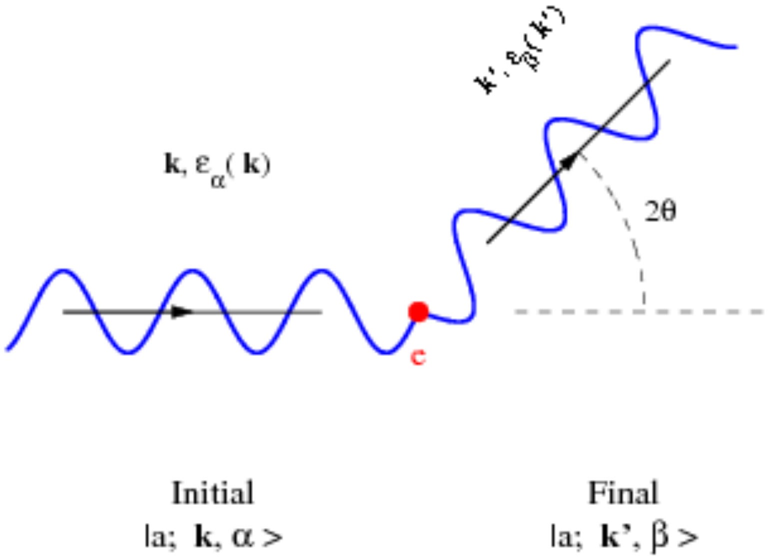
Spin - Orbit Interaction :

$$H_{so} = -\frac{1}{2}\boldsymbol{m}\cdot\boldsymbol{B} = \frac{1}{2}g\mu_B\boldsymbol{s}\cdot\frac{\boldsymbol{E}\times\boldsymbol{v}}{c^2} = \frac{e\hbar}{2m^2c^2}\boldsymbol{s}\cdot\boldsymbol{E}\times\boldsymbol{p} = \left(\frac{e\hbar}{2m^2c^2}\right)\boldsymbol{s}\cdot\left(-\nabla\phi - \dot{\boldsymbol{A}}\right)\times\left(\boldsymbol{p} + e\boldsymbol{A}\right)$$

$$\approx -\left(\frac{e^2\hbar}{2m^2c^2}\right)\boldsymbol{s}\cdot\left(\dot{\boldsymbol{A}}\times\boldsymbol{A}\right)$$

$$H_I = \underbrace{\left(\frac{e^2}{2m}\right)A^2}_{H_1} + \underbrace{\left(\frac{e}{m}\right)\boldsymbol{A}\cdot\boldsymbol{p}}_{H_2} + \underbrace{\left(\frac{e\hbar}{m}\right)\boldsymbol{s}\cdot\nabla\times\boldsymbol{A}}_{H_3} - \underbrace{\left(\frac{e^2\hbar}{2m^2c^2}\right)\boldsymbol{s}\cdot\left(\dot{\boldsymbol{A}}\times\boldsymbol{A}\right)}_{H_4}$$

Non-resonant Magnetic Scattering



1st order : $$W = \frac{2\pi}{\hbar}\left|\langle f | H_I | i \rangle\right|^2 \rho\left(\mathcal{E}_f\right)$$

2nd order : $$W = \frac{2\pi}{\hbar}\left|\sum_n \frac{\langle f | H_I | n \rangle \langle n | H_I | i \rangle}{\mathcal{E}_i - \mathcal{E}_n}\right|^2 \rho\left(\mathcal{E}_f\right)$$

1st order:

$$H_I = \left(\frac{e^2}{2m}\right) A^2 + \left(\frac{e}{m}\right) \boldsymbol{A} \cdot \boldsymbol{p} + \left(\frac{e\hbar}{m}\right) \boldsymbol{s} \cdot \nabla \times \boldsymbol{A} - \left(\frac{e^2\hbar}{2m^2c^2}\right) \boldsymbol{s} \cdot \left(\dot{\boldsymbol{A}} \times \boldsymbol{A}\right)$$

2nd order:

$$H_I = \left(\frac{e^2}{2m}\right) A^2 + \left(\frac{e}{m}\right) \boldsymbol{A} \cdot \boldsymbol{p} + \left(\frac{e\hbar}{m}\right) \boldsymbol{s} \cdot \nabla \times \boldsymbol{A} - \left(\frac{e^2\hbar}{2m^2c^2}\right) \boldsymbol{s} \cdot \left(\dot{\boldsymbol{A}} \times \boldsymbol{A}\right)$$

Summary: 1st Order Scattering Processes

Thomson scattering

$$H_I = \left(\frac{e^2}{2m}\right)A^2 - \left(\frac{e^2\hbar}{2m^2c^2}\right)\boldsymbol{s}\cdot\left(\dot{\boldsymbol{A}}\times\boldsymbol{A}\right)$$

$$\left\langle a;\boldsymbol{k}',\beta\right|\left(\frac{e^2}{2m}\right)A^2\left|a;\boldsymbol{k},\alpha\right\rangle = \left\langle \boldsymbol{k}',\beta\right|\left(\frac{e^2}{2m}\right)A^2\left|\boldsymbol{k},\alpha\right\rangle = \left(\frac{e^2\hbar}{2m\varepsilon_0 V\omega}\right)\hat{\varepsilon}_{\alpha,\boldsymbol{k}}\cdot\hat{\varepsilon}_{\beta,\boldsymbol{k}'}$$

$$\left(\frac{d\sigma}{d\Omega}\right)^{Charge} = \frac{W}{\Phi_0(\Delta\Omega)} = r_0^2\left|\hat{\varepsilon}'\cdot\hat{\varepsilon}\right|^2$$

Magnetic scattering

$$\left\langle a;\boldsymbol{k}',\beta\right| -\left(\frac{e^2\hbar}{2m^2c^2}\right)\boldsymbol{s}\cdot\left(\dot{\boldsymbol{A}}\times\boldsymbol{A}\right)\left|a;\boldsymbol{k},\alpha\right\rangle = i\left(\frac{e^2\hbar^2}{2m^2Vc^2\varepsilon_0}\right)\left\langle\boldsymbol{s}\right\rangle\left(\hat{\varepsilon}_{\alpha,\boldsymbol{k}}\times\hat{\varepsilon}_{\beta,\boldsymbol{k}'}\right)$$

$$\left(\frac{d\sigma}{d\Omega}\right)^{Magnetic} = r_0^2\left(\frac{\hbar\omega}{mc^2}\right)^2\left|\hat{\varepsilon}'\times\hat{\varepsilon}\right|^2\left\langle\boldsymbol{s}\right\rangle^2$$

- Magnetic scattering is weaker than charge by $(\hbar\,\omega/mc^2)^2$ ~0.0001 at 10 keV
- Scattering cross-section is proportional to $\langle s\rangle^2$ => Magnetic crystallography
- Magnetic scattering has a distinctive polarization dependence

Total non-resonant magnetic cross-section

Unique ability to separate spin and orbital moments

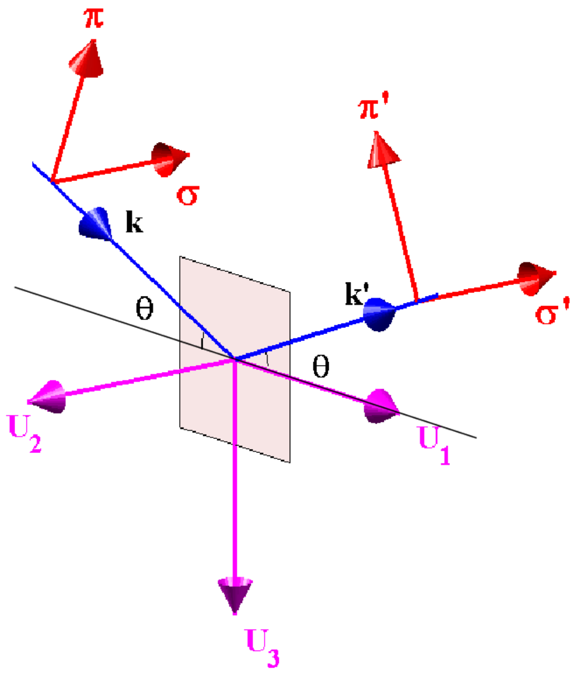
Magnetic scattering length

$$f^{mag}(\boldsymbol{Q}) = i\, r_0 \left(\frac{\hbar\omega}{mc^2}\right)\left[\frac{1}{2}\boldsymbol{L}(\boldsymbol{Q})\cdot A'' + \boldsymbol{S}(\boldsymbol{Q})\cdot B\right]$$

$\boldsymbol{L}(\boldsymbol{Q})$ and $\boldsymbol{S}(\boldsymbol{Q})$ are Fourier transforms

of the atomic and spin magnetization densities

A'' and B contain the dependence on $\boldsymbol{k}, \boldsymbol{k}', \hat{\varepsilon}$ and $\hat{\varepsilon}'$



$$f^{mag}(\boldsymbol{Q}) = i\, r_0 \left(\frac{\hbar\omega}{mc^2}\right) \times$$

	$\hat{\varepsilon}_\perp \equiv \sigma$	$\hat{\varepsilon}_\parallel \equiv \pi$
$\hat{\varepsilon}'_\perp$	$\sin 2\theta S_2$	$-2\sin^2\theta\left[(L_1+S_1)\cos\theta - S_3\sin\theta\right]$
$\hat{\varepsilon}'_\parallel$	$2\sin^2\theta\left[(L_1+S_1)\cos\theta - S_3\sin\theta\right]$	$\sin 2\theta\left[2\sin^2\theta L_2 + S_2\right]$

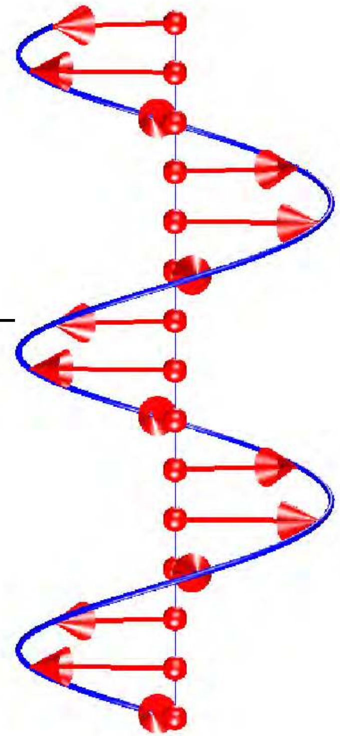
Blume and Gibbs, PRB 1988

Example: scattering from a magnetic spiral

Assume for clarity that

$<\boldsymbol{L}>=0$ and $\boldsymbol{S}=\mathrm{S}(\cos(\mathrm{qa}\ell), \sin(\mathrm{qa}\ell))$

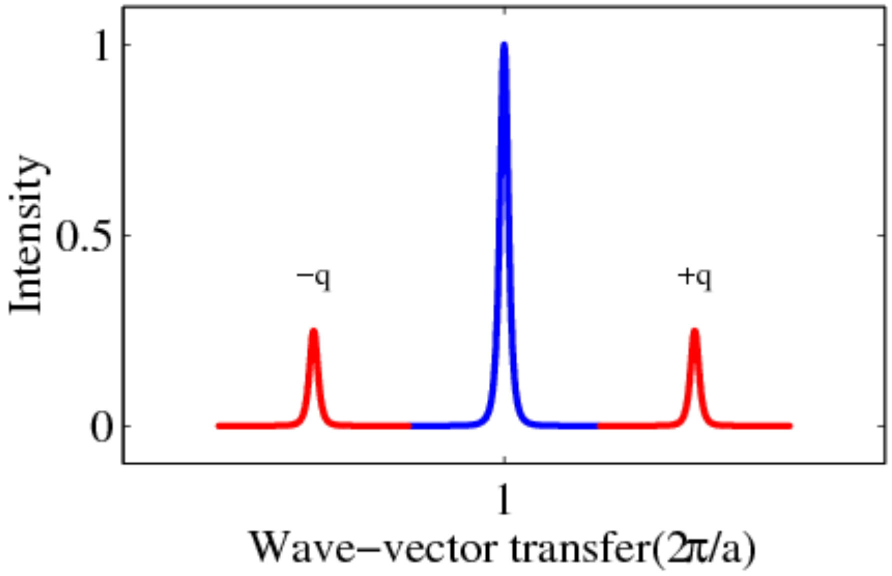
and that experiment is done with σ polarized light and no analyser



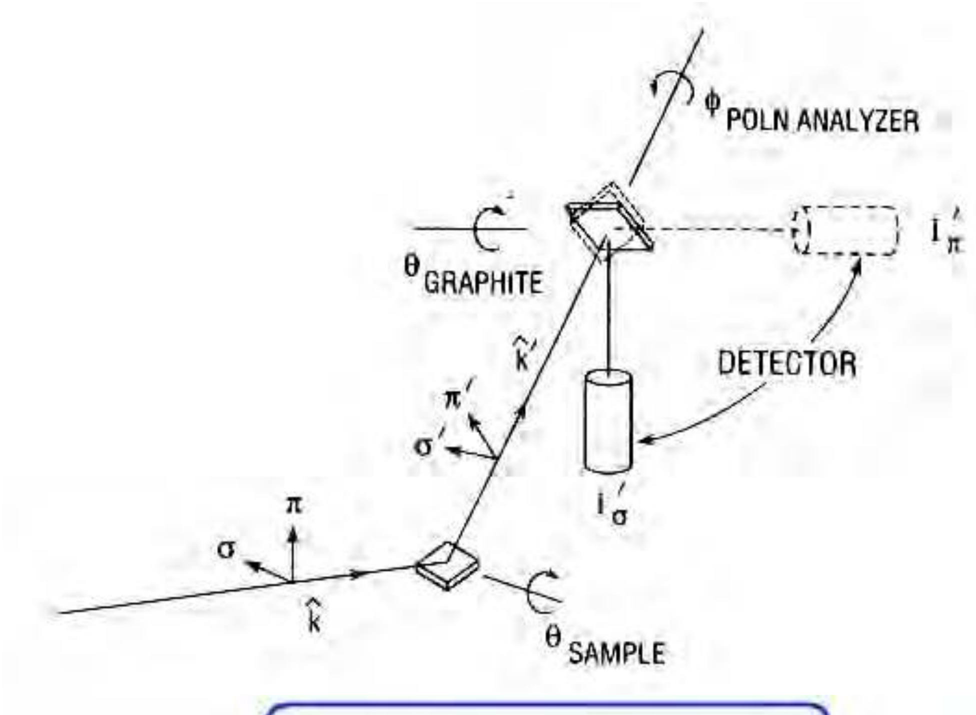
$$f^{mag}(\boldsymbol{Q}) = i\, r_0 \left(\frac{\hbar\omega}{mc^2}\right) \frac{S}{2} \sum_{\ell} e^{i(Q\pm q)a\ell} \times$$

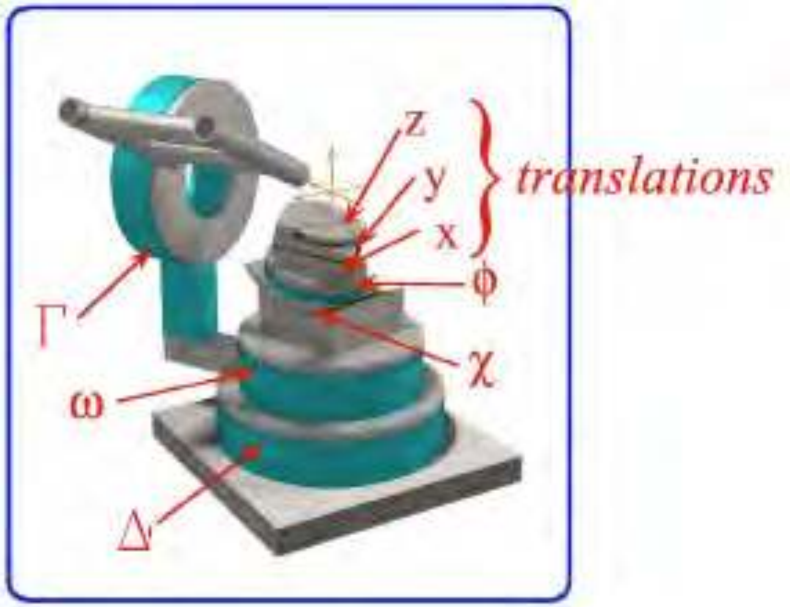
	$\hat{\varepsilon}_{\perp} \equiv \sigma$	$\hat{\varepsilon}_{\parallel} \equiv \pi$
$\hat{\varepsilon}'_{\perp}$	$\pm i \sin 2\theta$	$-2\sin^2\theta\cos\theta$
$\hat{\varepsilon}'_{\parallel}$	$2\sin^2\theta\cos\theta$	$\pm i \sin 2\theta$

$$\left(\frac{d\sigma}{d\Omega}\right)^{Magnetic} = r_0^2 \left(\frac{\hbar\omega}{mc^2}\right)^2 \frac{S^2}{4} \sin^2 2\theta (1+\sin^2\theta) \left(\frac{2\pi}{a}\right) \sum_G \delta(Q - G \pm q)$$



Experimental considerations





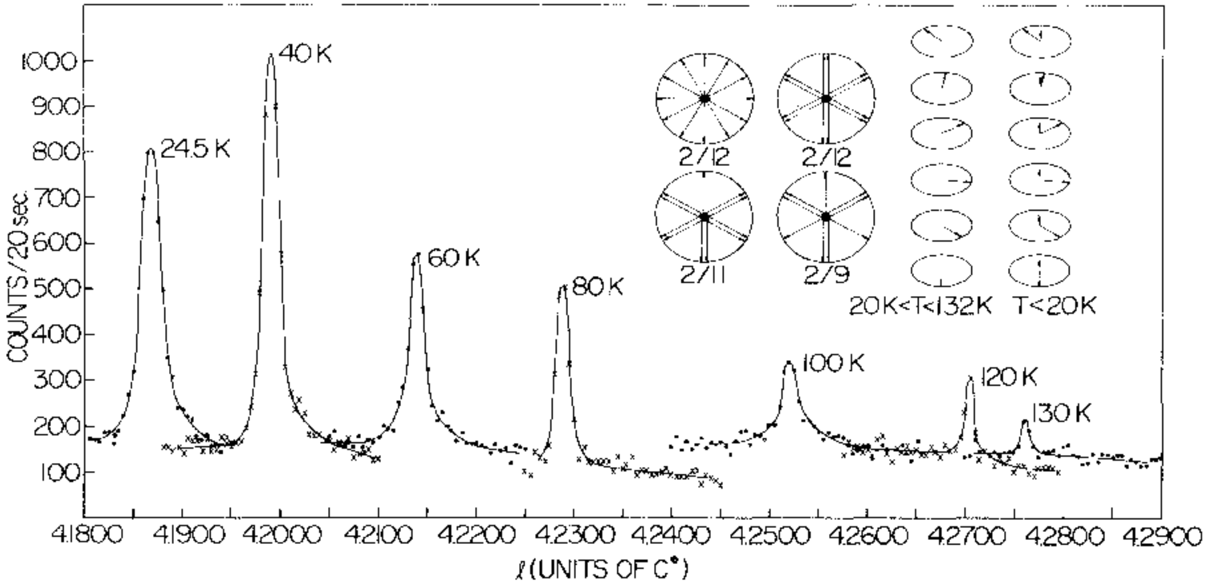
- •High flux beamline
- •Tunable photon energy, 1-15 keV
- •Well defined incident polarization
- •Versatile diffractometer
- •Azimuthal degree of freedom
- •Polarization analysis

First Synchrotron Radiation Studies of Magnetism

Non-Resonant Magnetic scattering from Holmium

Gibbs, Moncton, D'Amico, Bohr and Grier (1985)

Synchrotron Source: Counts per 20s



Advantages of Non-resonant X-ray Magnetic Scattering

- •High-resolution technique (Phase transitions)
- •Separation of orbital and spin magnetization densities
- •Highly focussed beams (Small samples)

Non-resonant X-ray magnetic scattering study of non-collinear order using circularly polarized X-rays

Imaging the electric field control of magnetism in multiferroic $TbMnO_3$

PRL **102,** 237205 (2009) PHYSICAL REVIEW LETTERS week ending 12 JUNE 2009

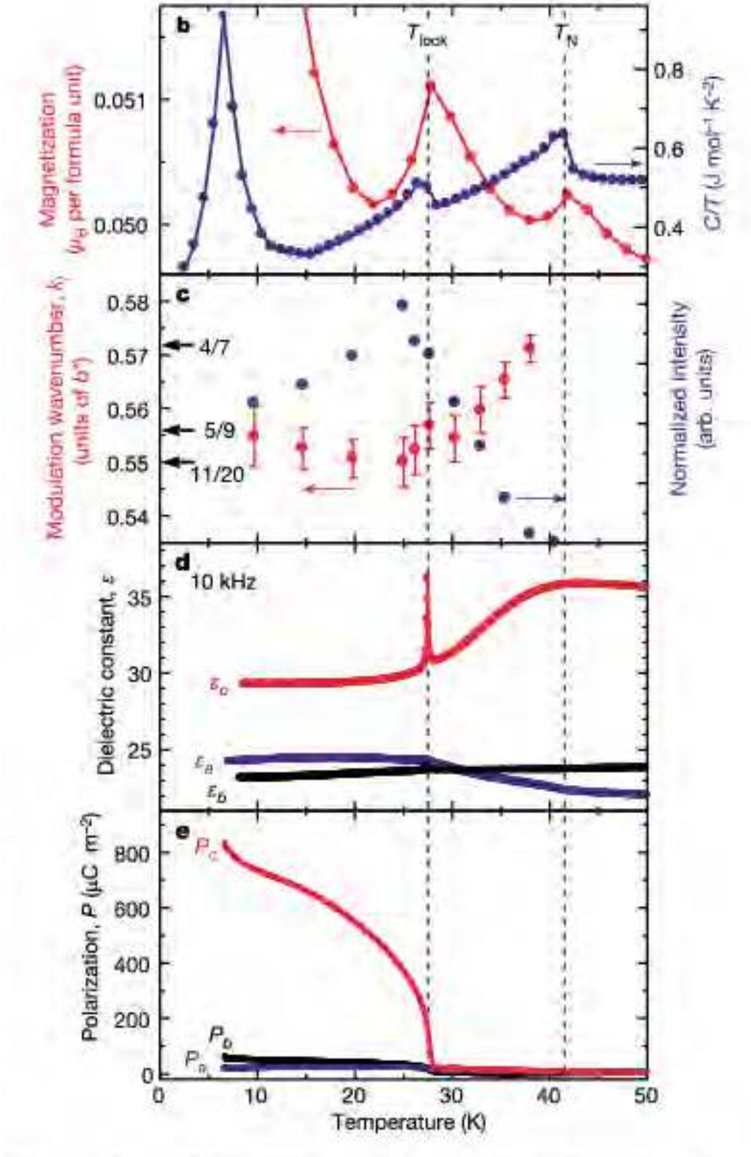
Circularly Polarized X Rays as a Probe of Noncollinear Magnetic Order in Multiferroic $TbMnO_3$

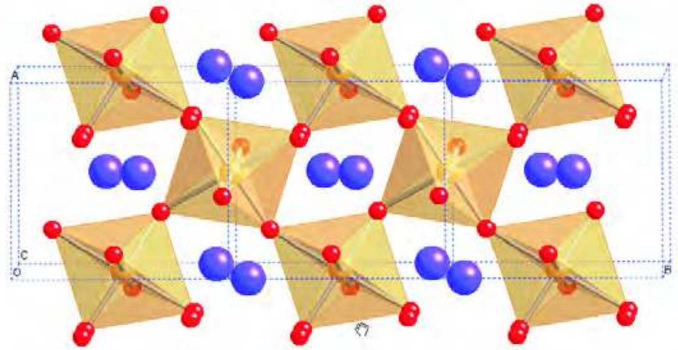
F. Fabrizi,[1,2] H. C. Walker,[1,2,*] L. Paolasini,[1] F. de Bergevin,[1] A. T. Boothroyd,[3] D. Prabhakaran,[3] and D. F. McMorrow[2]

Magnetic Control of Ferroelectric Polarization

Kimura et al. Nature (2004)

$TbMnO_3$

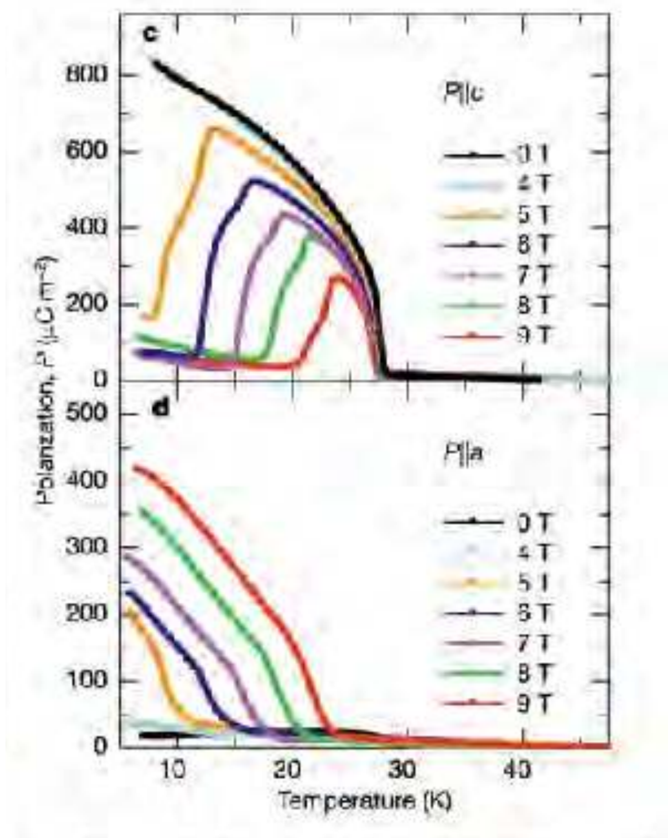




Pbmn

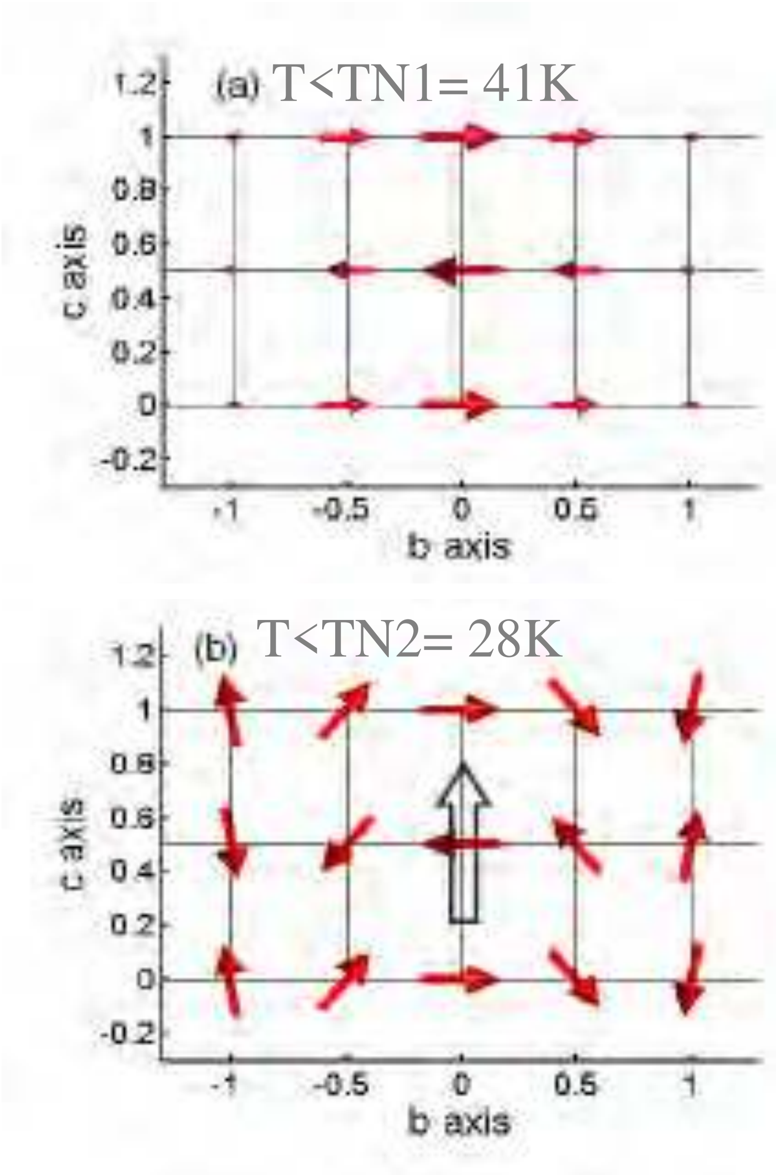
Mn: bar 1

Tb: m



Magnetic inversion symmetry breaking and ferroelectricity in $TbMnO_3$

Kenzelmann et al. PRL (2005)



Neutron Scattering

q_{Mn}=(0 q 1) A-type Fourier components

Γ_3: $m_3[Mn] = (0.0\ 2.9\ 0.0)\mu_B$

$m_3[Tb] = (0.0\ 0.0\ 0.0)\ \mu_B$

Γ_3: $m_3[Mn] = (0\ 3.9\ 0)\ \mu_B$ Γ_2: $m_2[Mn] = (0\ 0\ 2.8)\ \mu_B$

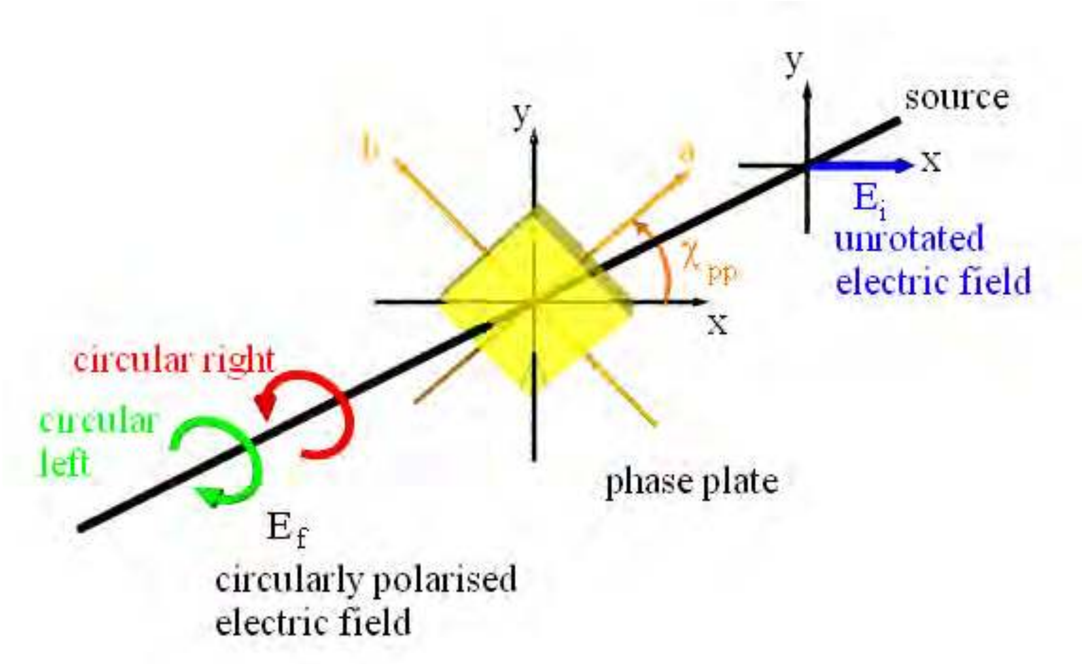
$m_3[Tb] = (0\ 0\ 0)\ \mu_B$ $m_2[Tb] = (1.2\ 0\ 0)\ \mu_B$

Phase between b and c components not fixed by experiment

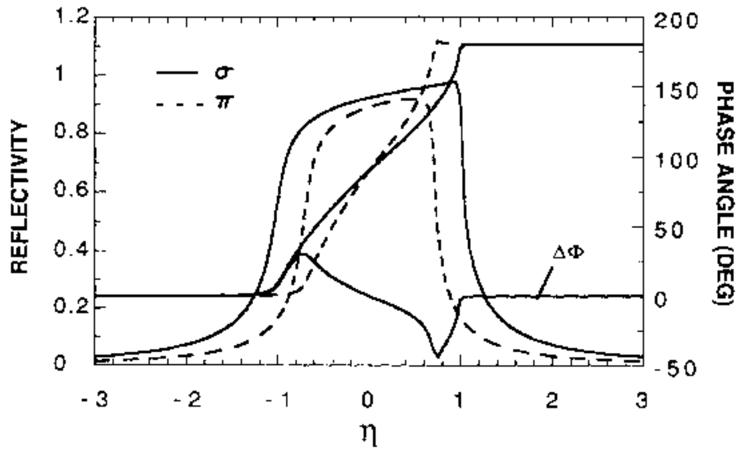
Ferroelectricity from magnetic Frustration!

Production of circularly polarized X-rays

Perfect diamond crystals can act as l/4 wave phase retarder producing circularly polarised light



Batterman PRB (1992)

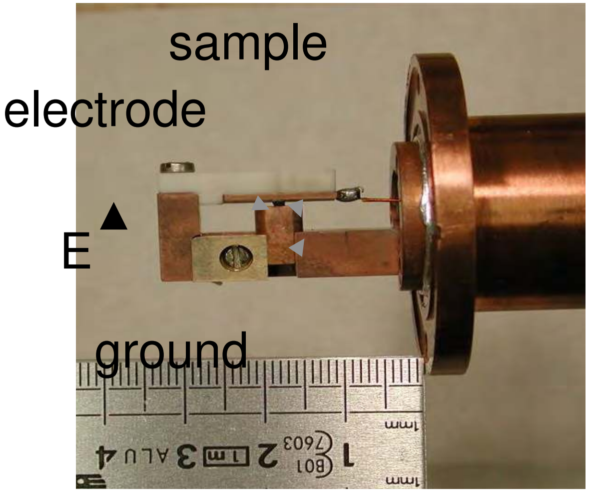


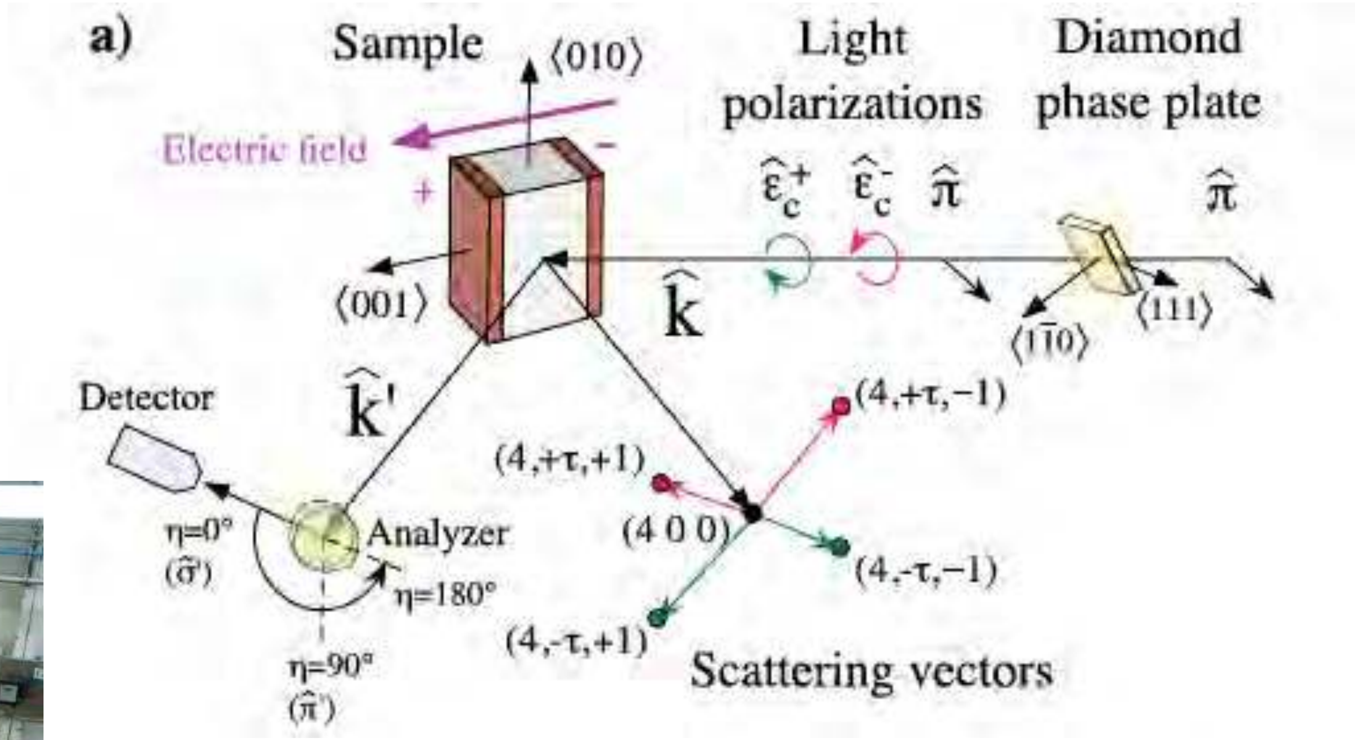
e=7.5 keV: diamond thickness = 1200 mm, Circular polarisation ~ 98%

e=6.15 keV: diamond thickness = 700 mm, Circular polarisation ~ 99%

Handedness of circularly polarised light couples to handedness of chiral spin structures

Diffraction in Applied E&H fields





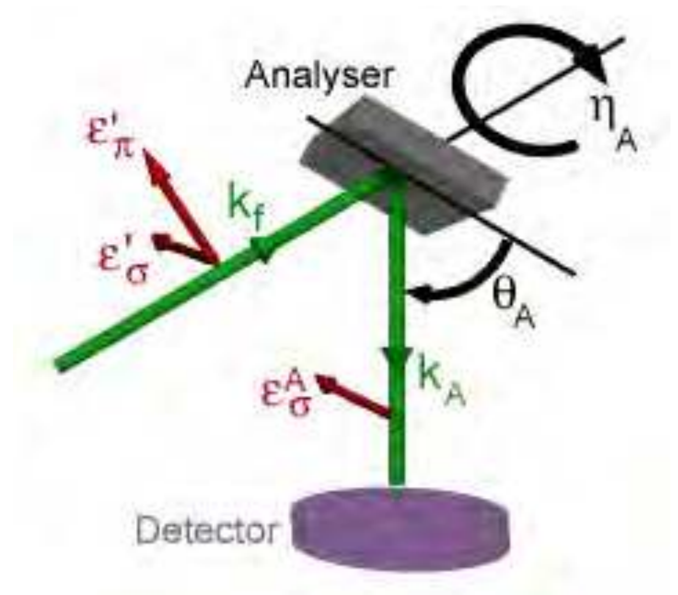
Non-resonant magnetic scattering length:

$$f_{\hat{\sigma}'} \;\propto\; S_b^M + \epsilon\,\alpha\,\gamma\,S_c^M - i\,\beta\,\gamma\,S_b^T$$

$$f_{\hat{\pi}'} \;\propto\; (\epsilon\,\beta\,\gamma)(S_b^T + L_b^T) + i\,(\epsilon\,S_b^M + \alpha\,\gamma\,S_c^M)$$

α=±1: selects sign of τ
β=±1: selects sign of l
γ=±1: selects rcp or lcp

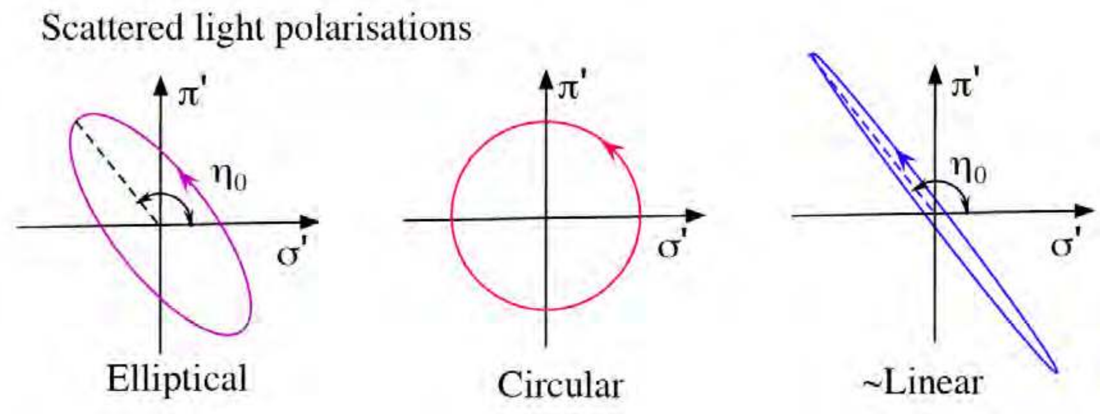
Polarization analysis of the scattered beam

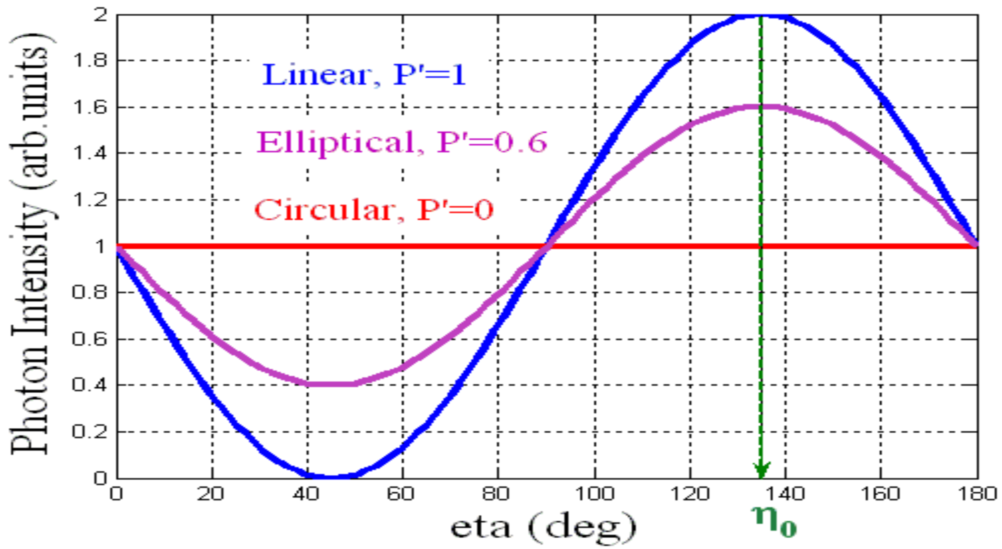


Beam polarization characterised by Stokes Parameters(P_1, P_2, P_3)

Experiment determines linear parameters P_1 and P_2

$$I(\eta) = 1+P_1\cos(2\eta)+P_2\sin(2\eta)=1+P'\cos(2(\eta-\eta_0))$$



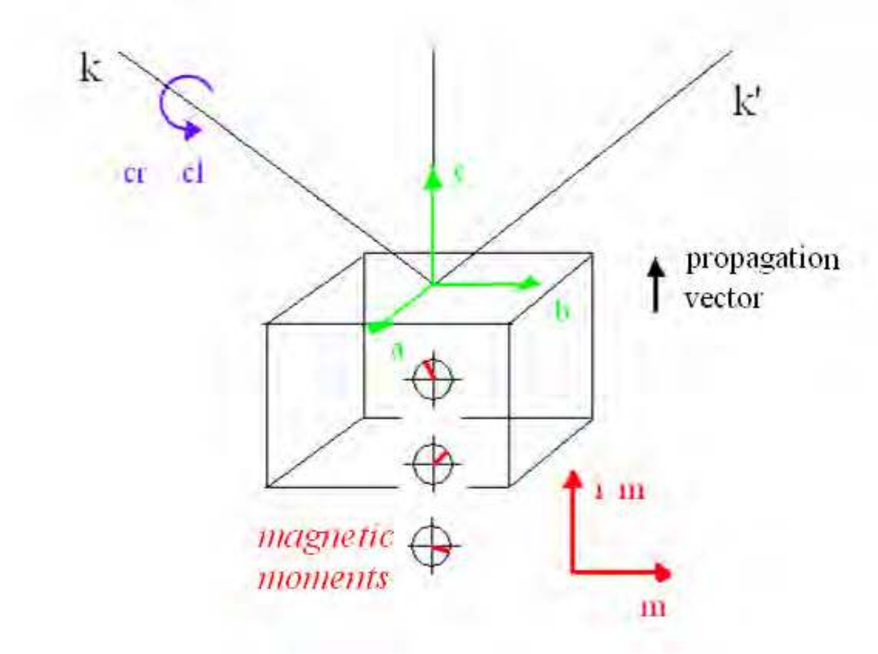


Circularly polarized light and cycloidal domains

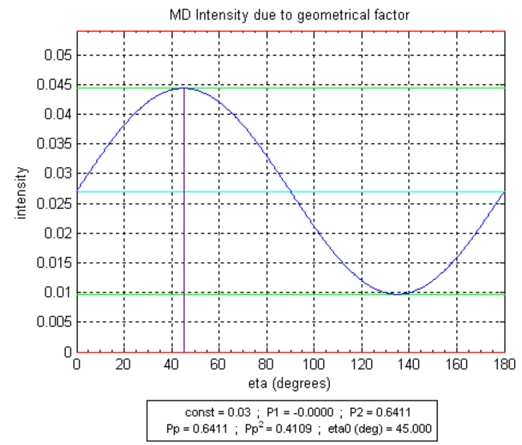
LINEAR LIGHT : Same scattering cross-section for the two cycloidal domains

CIRCULAR LIGHT : Coupling between chirality of the magnetic structure and handedness of the circular light → possible to discriminate

ex. : simple magnetic structure ; non resonant scattering

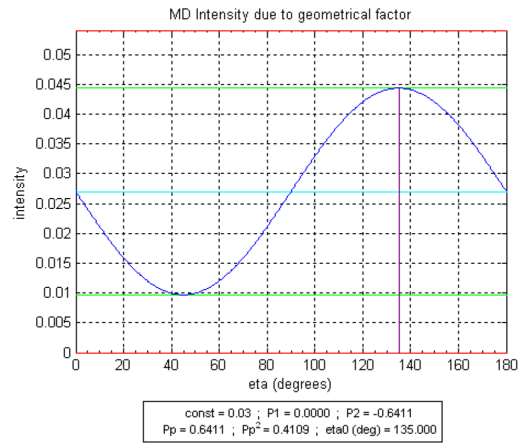


circular right, monochiral domain



$\eta_0 \rightarrow \eta_0 + 90^\circ$

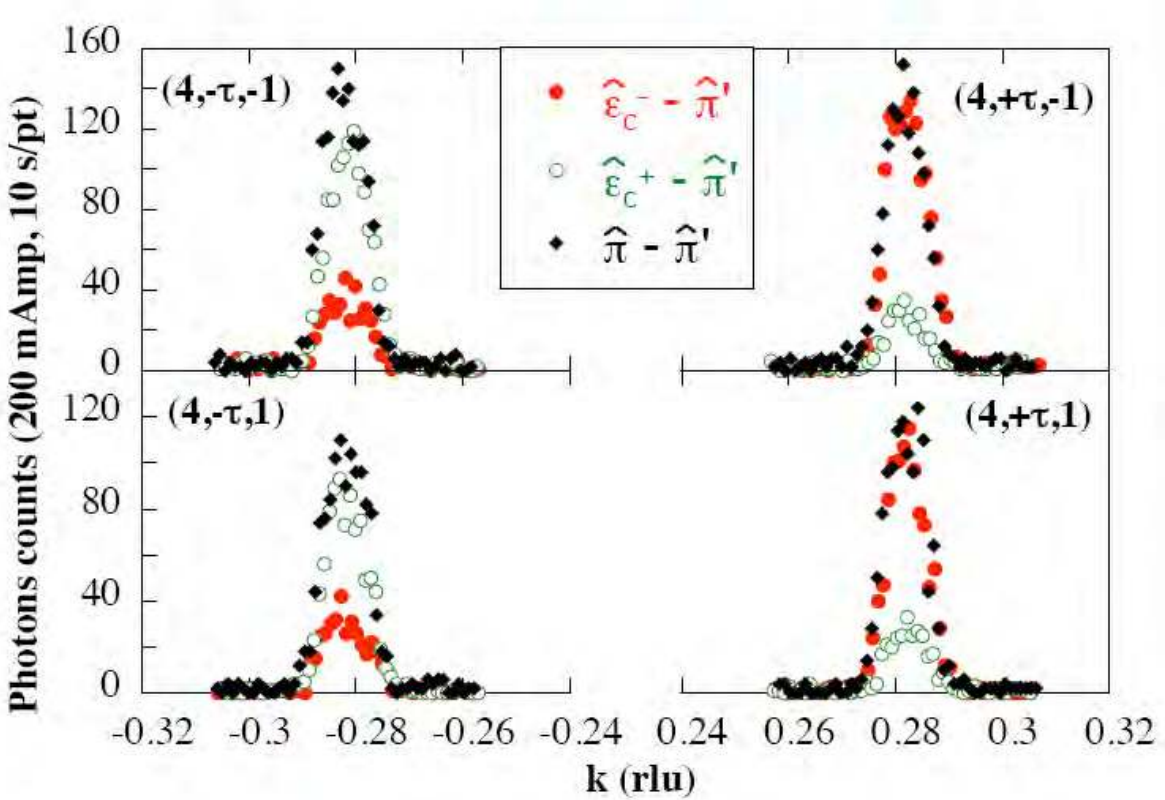
circular left, monochiral domain



Reversing the polarisation =exchanging domains

Domain populations - A-type peak

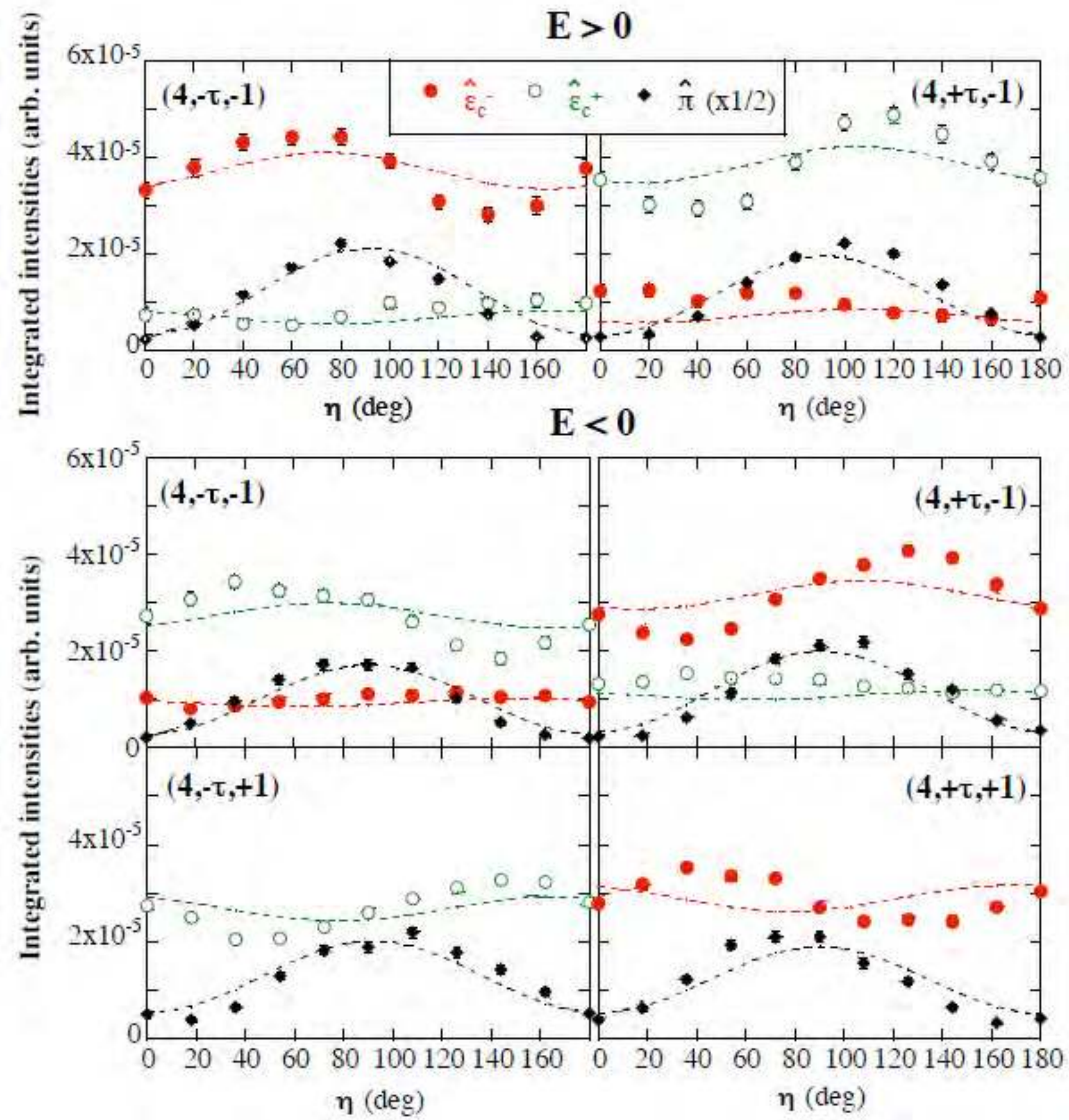
- T=15 K i.e. in FE phase, field cooling -700 V
- E=7.5 keV
- A-type star of wave-vectors
- Measured in π' channel



- All 4 intensities similar for linear polarization (π-π')
- $I(\varepsilon_c^+ - \pi') \neq I(\varepsilon_c^- - \pi')$, complementary behaviour depending on ±τ
- Demonstrates imbalance of cycloidal domains

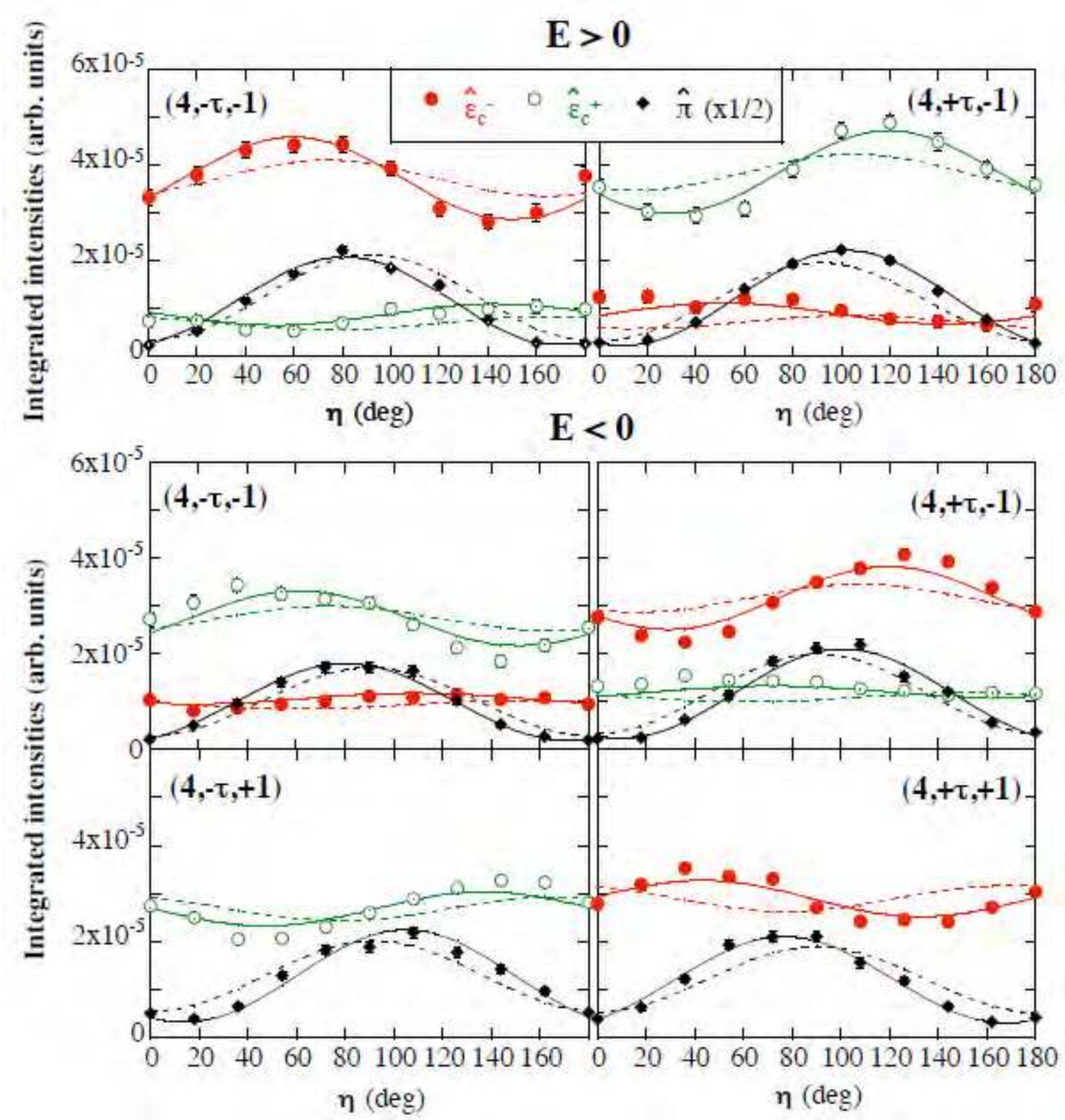
Stokes scans to demonstrate domain reversibility for ±E

Comparison with Kenzelmann model



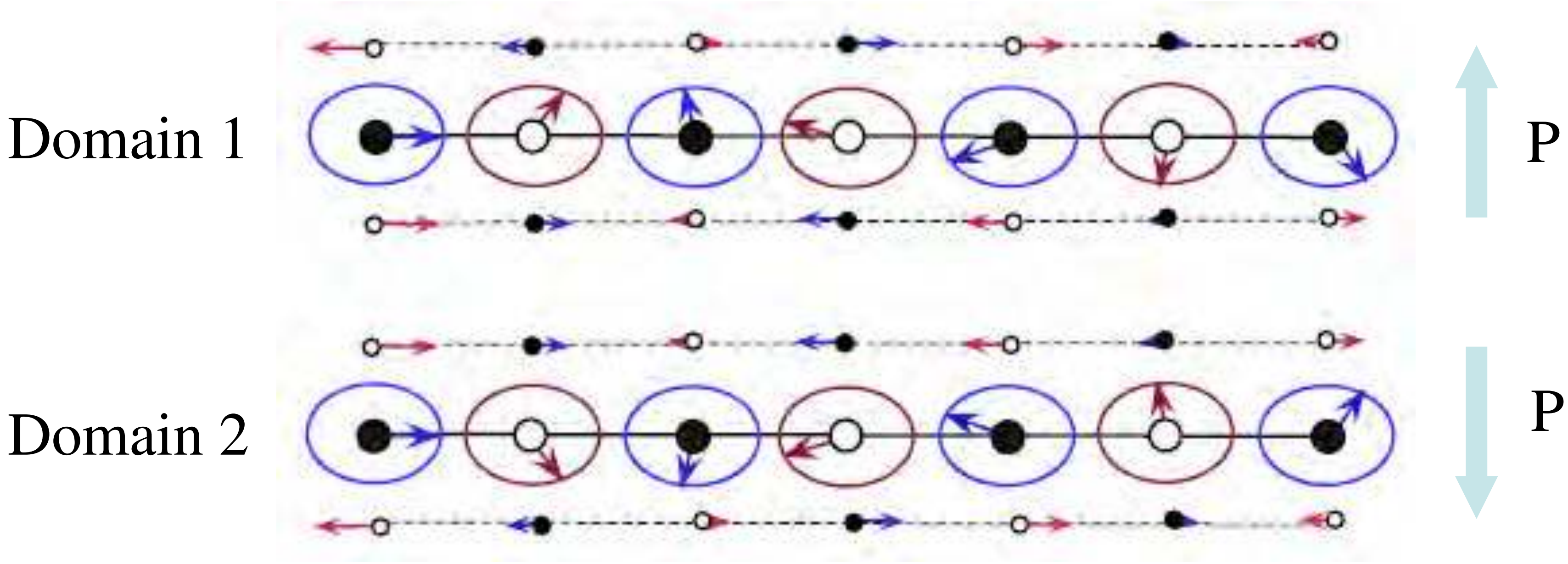
- Dashed lines for Kenzelmann model – IC structure with cycloidal ordering of Mn spins rotating in *bc* plane + Tb moment along *a*
- Unsatisfactory agreement with data

New magnetic structure model



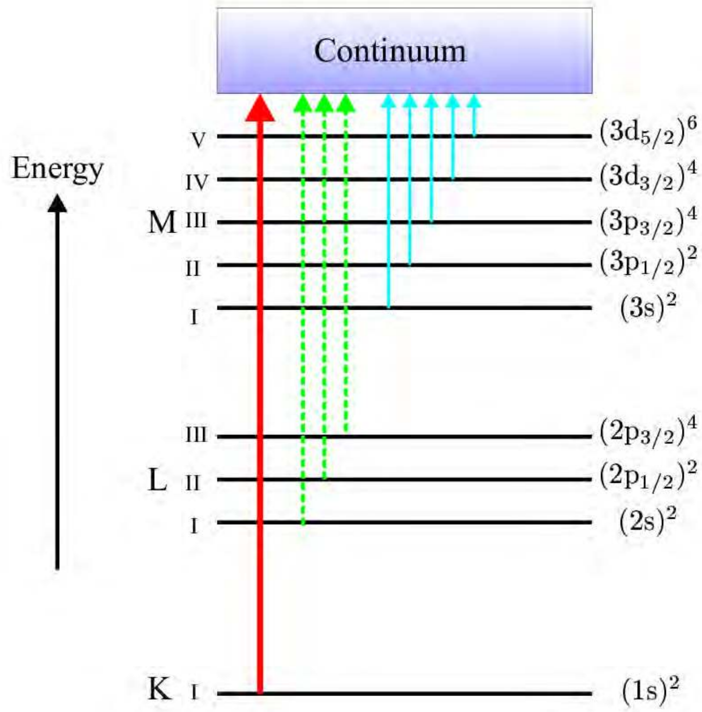
- Additional Tb spin moment component along *b*
- Plus Tb orbital moment equal in size to spin component

Cycloidal domains



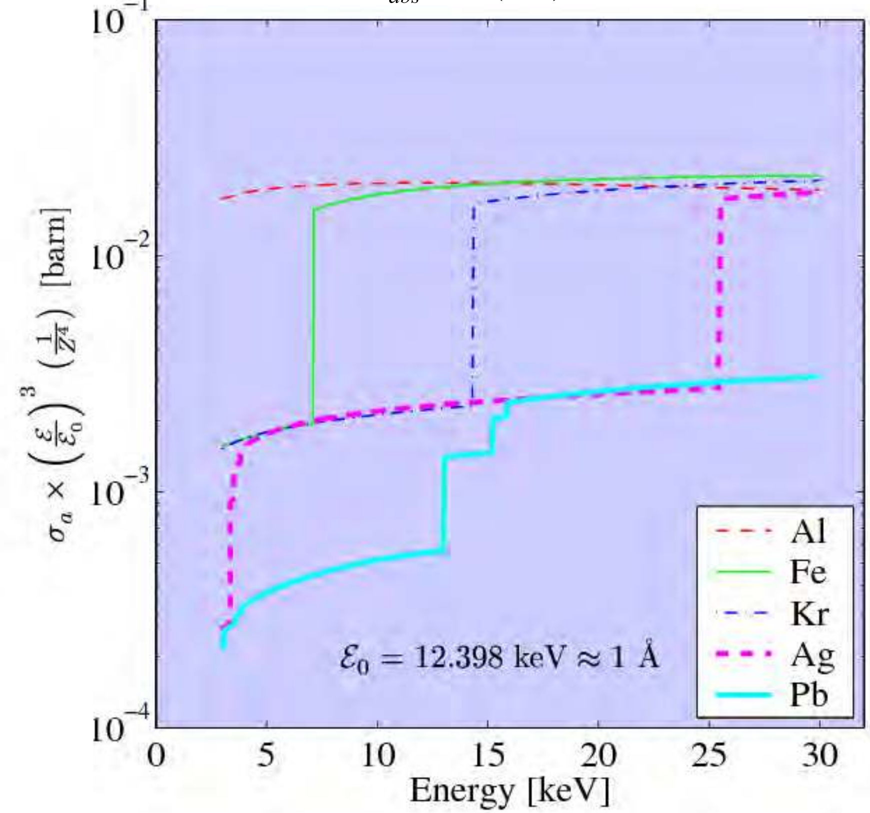
- Projection of domains in *bc* plane with newly determined longitudinal component of Tb moment
- E>0 field cooling → 96±3 % Domain 1
- E<0 field cooling → 93±2 % Domain 2
- Absolute measurement of sense of rotation (chirality)

X-ray absorption edges



Absorption cross-section scales as

$$\sigma_{abs} \propto (\hbar\omega)^{-3} Z^4$$



Absorption coefficient μ defined by $I = I_0 e^{-\mu z}$

In general x-ray scattering length is $f(Q,\hbar\omega) = f_0(Q) + f' + if''$

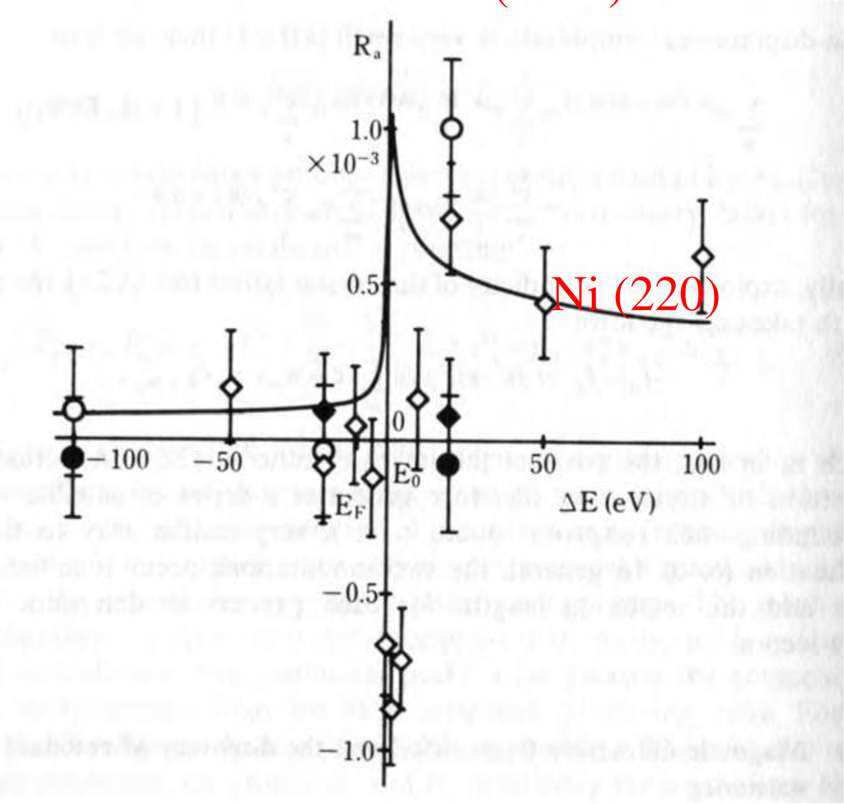
$$f'' = -\left(\frac{k^2}{2\pi\rho_a r_0}\right)\frac{\mu}{2k}$$

Absorption is proportional to imaginary part of the forward scattering amplitude

X-ray Resonant Magnetic Scattering

”Interesting magnetic effects might occur near an absorption edge”Blume (1985)

X-ray Resonant Magnetic Scattering from Nickel
Namikawa (1985)

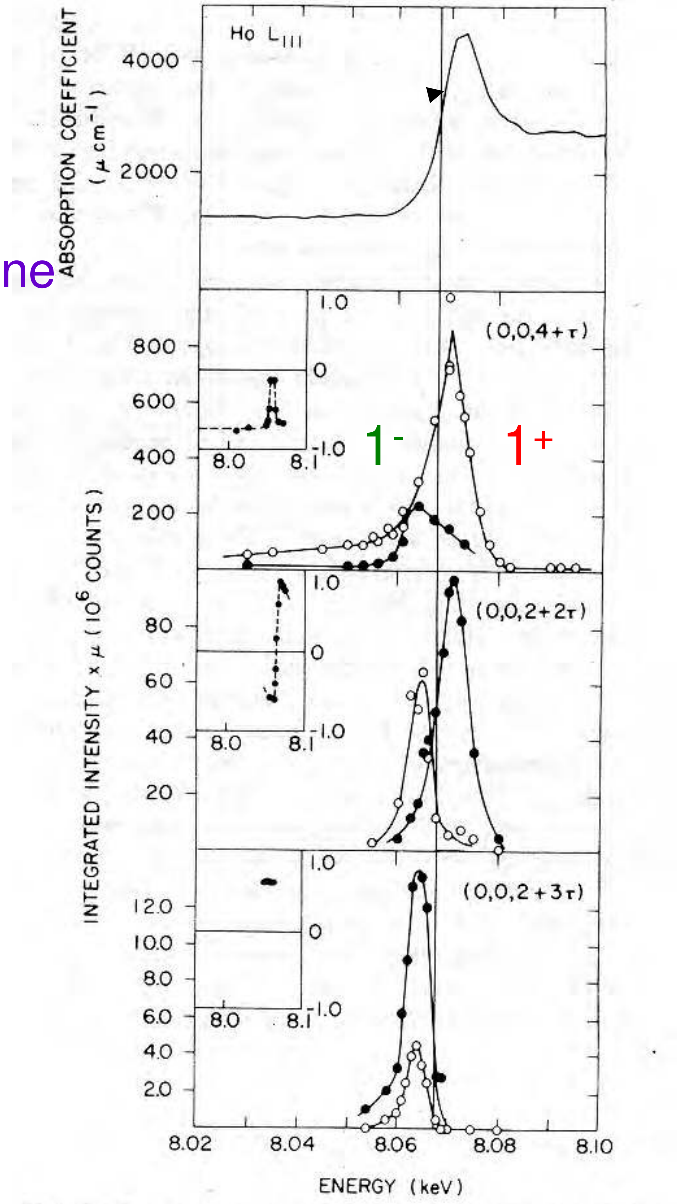


(1985) First Resonant Scattering from a Ferromagnet

Large enhancement of XMRS at L edges of Holmium

Gibbs, Harshman, Isaacs, McWhan, Mills and Vettier (1988)

White Line

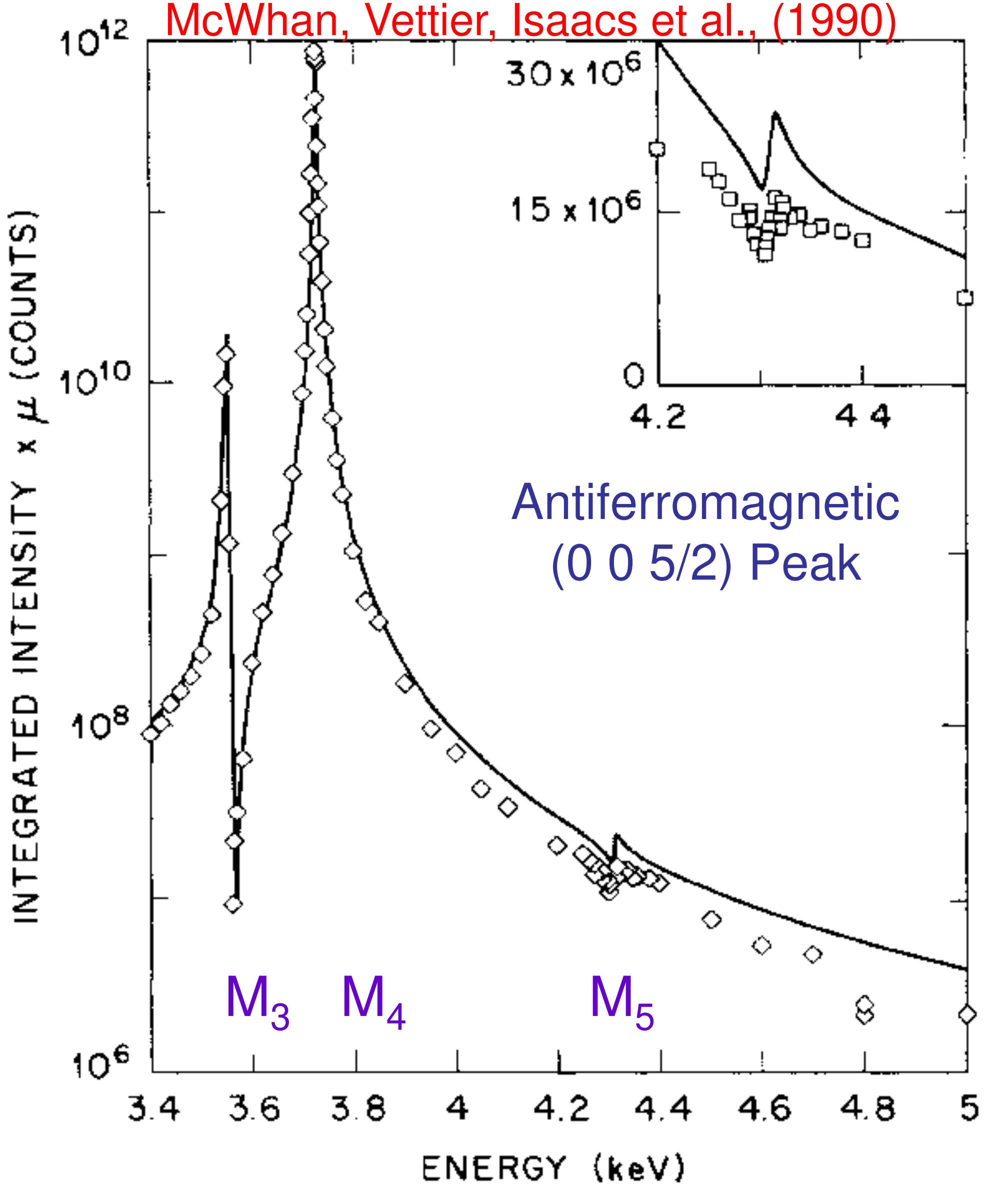


- 100 fold increase when tuned to the L_3 edge
- Two distinct types of transition are observed: one above and one below the edge
- Higher order satellites up to 4th order
- Polarization state changes with order
  - 1^+: rotated, σ->π’
  - 1^- : unrotated, , σ->σ’
- Signal disappears at T_N
- Peaks arise from transitions to bound states
  - 1^+: 2p -> 5d Dipole
  - 1^-: 2p -> 4f Quadrupole

XRMS is Born: A New Element and Electron Shell Sensitive Probe!

XRMS from Actinides

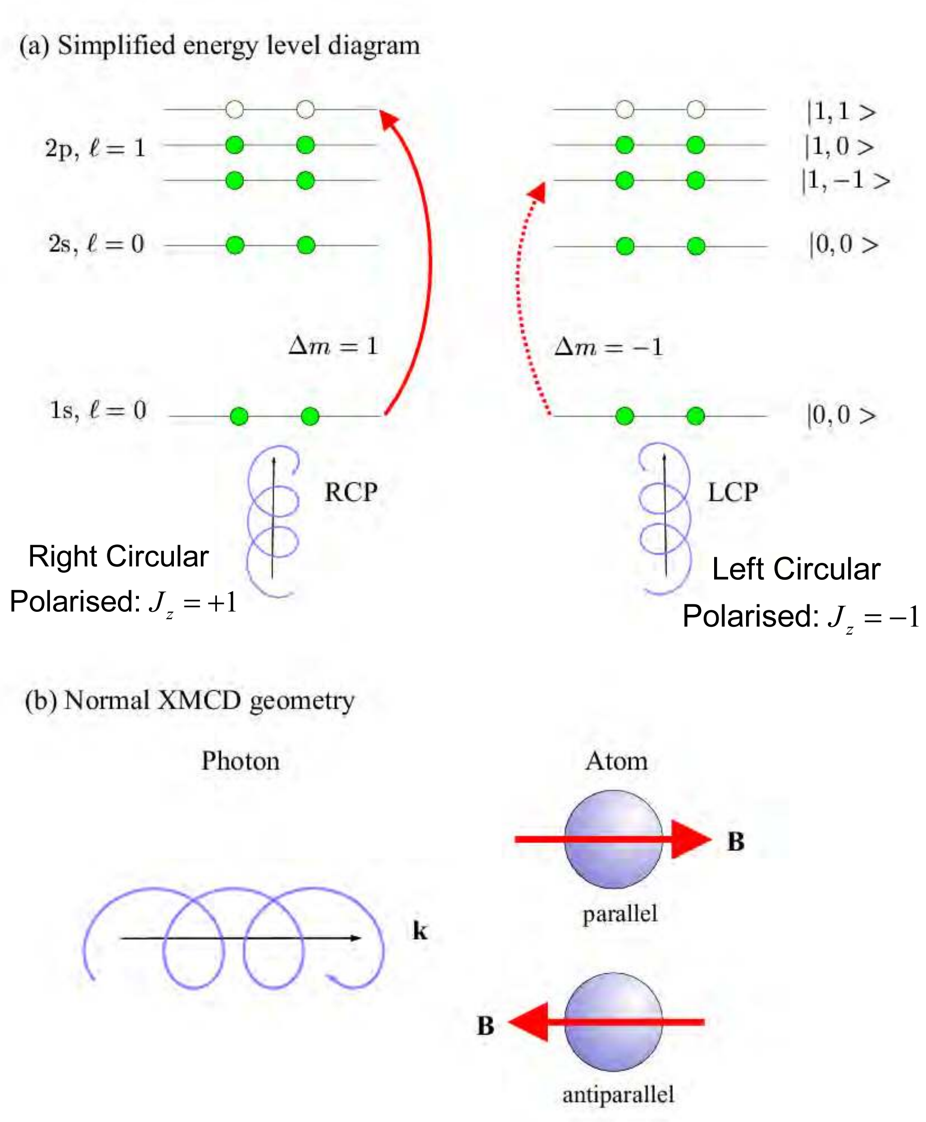
Resonant Scattering Study of UAs
McWhan, Vettier, Isaacs et al., (1990)

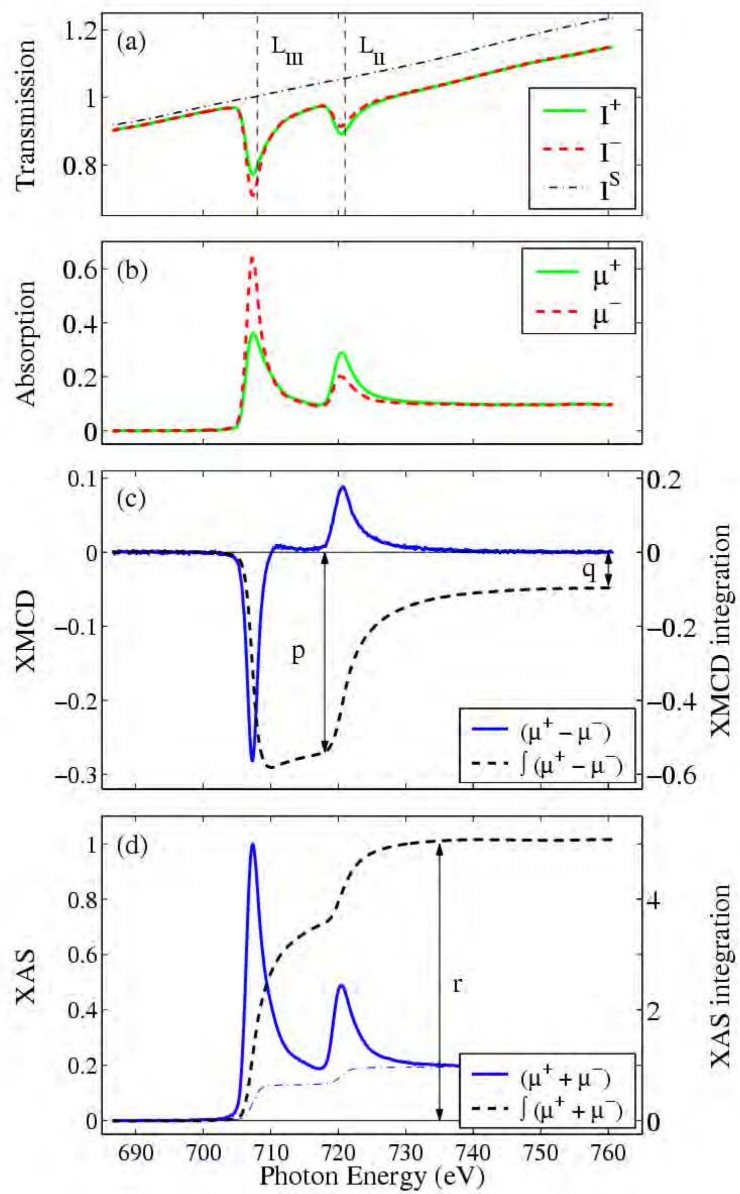


- 10^7 fold increase when tuned to the M_4 edge of U
- Magnetic peak ~1% of Charge peak!
- Fit to sum of three coherent dipole oscillators
- Single Dipole transition at each edge: 3d->5f
- Polarization analysis: rotated σ->π’

X-ray Dichroism

Preferential absorption of one of two orthogonal photon polarization state





Iron thin films, Chen et al. PRL (1995)