

Basics on Diffraction

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**New position : Augure of Jupiter
Calchas**



**« Le cornichon (piclke) est confit dans
du vinaigre, je suis confident du Roi »**

Scattering and diffraction of angstrom wavelength waves (X Ray, electrons, neutrons) is the key to study of atomic structure of condensed matter.

High resolution scattering allows for understanding vibrational, electronic and magnetic behaviour of materials: key importance of combined X, N, E studies

New pulsed sources allow for a time dependent study for out of equilibrium systems

I shall focus on neutron scattering, but keep in mind the importance of combined studies

Outline

Nuclear Diffraction by a stationary target

- Case of a crystal. Comparison with Xray and Electron diffraction
- Taking thermal motion into account : total/Bragg scattering

Inelastic neutron scattering and study of phonons

Magnetic scattering of neutrons

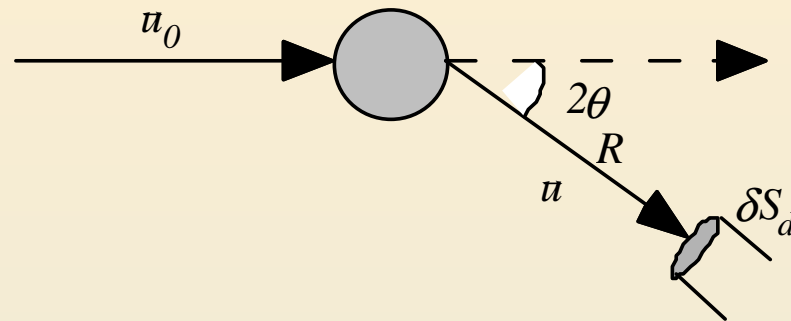
-Basics

-Spin polarized diffraction: access to spin density of materials:
complementarity with Xray high resolution scattering

Reality of crystals: extinction

Scattering cross section

X Rays, electrons, neutrons



$$\delta N(\vec{u}, \vec{u}_0) = F_0 d\sigma = F(\vec{u}, \vec{u}_0) \delta S_d$$

F_0 : incident flux – F : scattered flux

$$\frac{\partial \sigma}{\partial \Omega} = R^2 \frac{F(\vec{u}, \vec{u}_0)}{F_0}$$

Case of energy sensitive detection

$$\delta N(\vec{u}, \vec{u}_0) = F_0 \frac{\partial^2 \sigma}{\partial \Omega \partial E} \delta \Omega_d \delta E_d$$

- *Non relativistic particles*

$$F_{inc} = \frac{\hbar \kappa_0}{m} |\Phi_0|^2 \qquad F_{diff} = \frac{\hbar \kappa_f}{m} |\Phi_f|^2$$

$$\frac{\partial \sigma}{\partial \Omega} = R^2 \frac{\kappa_f}{\kappa_0} \frac{|\Phi_f|^2}{|\Phi_0|^2}$$

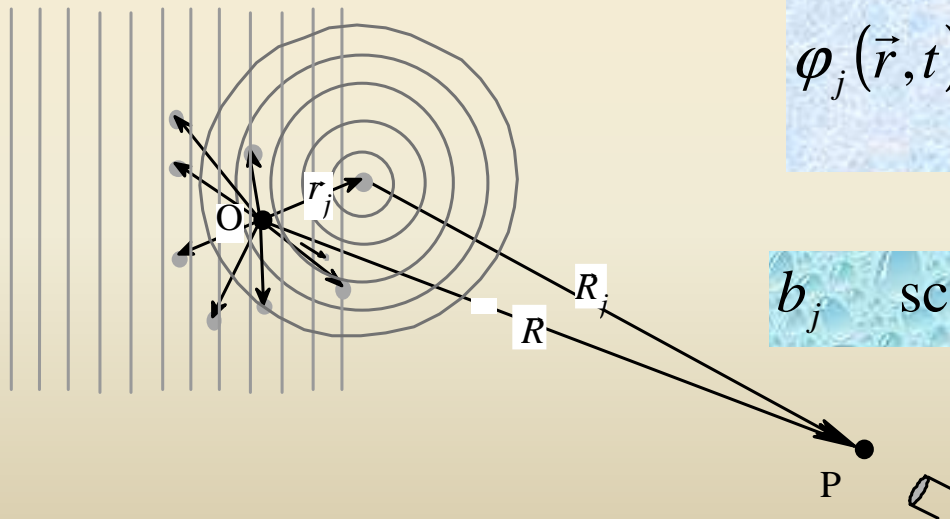
- *Photons: prefactor includes polarization factor of EM beam*

Scattering by a stationary target:

Elementary scatterer:

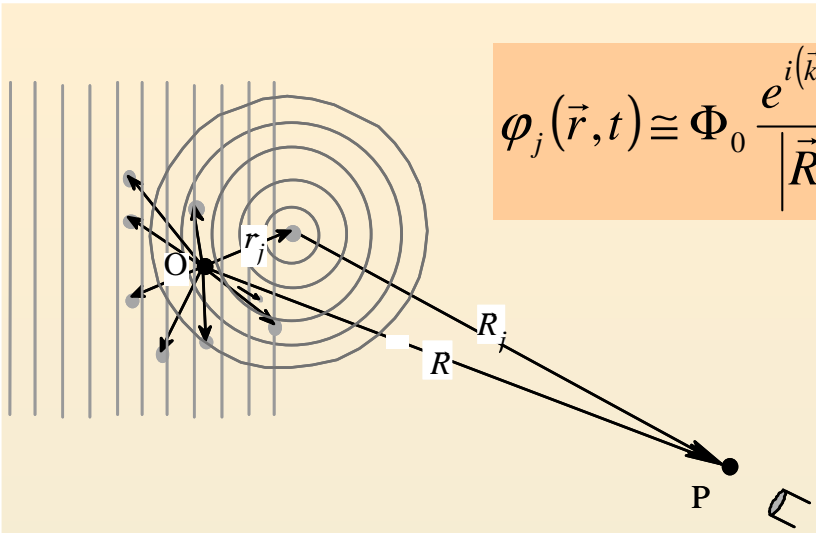
$$\Phi_0(\vec{r}_j, t) = \Phi_0 e^{i(\vec{k}_0 \cdot \vec{r}_j - \omega_0 t)} \quad \vec{R}_j = \vec{R} - \vec{r}_j \quad r_j \ll R$$

Huyghens Fresnel principle: elastic scattering



$$\varphi_j(\vec{r}, t) \cong \Phi_0 \frac{e^{i(\vec{k}_0 \cdot \vec{r}_j - \omega_0 t)}}{|\vec{R} - \vec{r}_j|} \left\{ b_j e^{ik_0 |\vec{R} - \vec{r}_j|} \right\}$$

b_j scattering length of particle

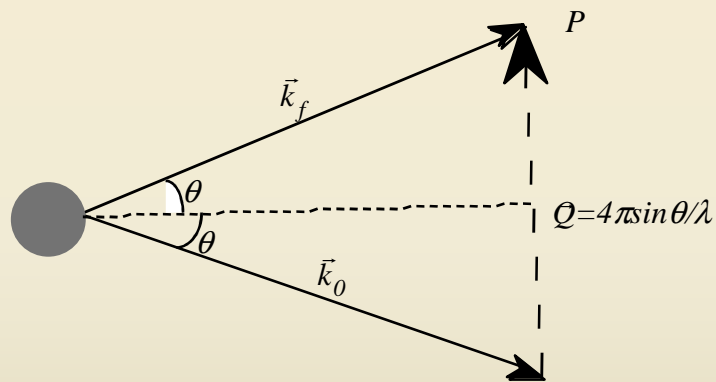


$$\varphi_j(\vec{r}, t) \cong \Phi_0 \frac{e^{i(\vec{k}_0 \vec{r}_j - \omega_0 t)}}{|\vec{R} - \vec{r}_j|} \left\{ a_j e^{ik_0 |\vec{R} - \vec{r}_j|} \right\}$$

Long distance scattering



$$R_j \cong R - \vec{u} \cdot \vec{r}_j$$



$$\vec{k}_f = k_0 \vec{u} \quad \vec{Q} = \vec{k}_0 - \vec{k}_f$$

$$\varphi_j(\vec{r}, t) \cong \Phi_0 \frac{e^{i(k_0 R - \omega_0 t)}}{R} \left\{ b_j e^{i\vec{Q} \cdot \vec{r}_j} \right\}$$

Complex target:

$$\Phi_f(\vec{r}, t) = \Phi_0 \frac{e^{i(k_0 R - \omega_0 t)}}{R} A(\vec{Q})$$



$$A(\vec{Q}) = \sum_{j=1}^N b_j e^{i\vec{Q} \cdot \vec{r}_j}$$

$$\left(\frac{\partial \sigma}{\partial \Omega} \right)_{elastic} = |A(\vec{Q})|^2$$

Scattering function:

$$n(\vec{r}) = \sum_j b_j \delta(\vec{r} - \vec{r}_j)$$



$$A(\vec{Q}) = \int n(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r}$$



$$n(\vec{r}) = \frac{1}{(2\pi)^3} \int A(\vec{Q}) e^{-i\vec{Q} \cdot \vec{r}} d\vec{Q}$$

Crystalline target (periodic scattering function)

$$\begin{aligned} n_0(\vec{r}) &= n(\vec{r}) & \text{if } \vec{r} \in \text{unit cell} \\ &= 0 & \text{otherwise} \end{aligned}$$

$$n(\vec{r}) = \sum_{\vec{L}} n_0(\vec{r} - \vec{L})$$

One defines the structure factor :

$$F(\vec{Q}) = \iiint_{\text{unit cell}} n_0(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r}$$

$$A(\vec{Q}) = F(\vec{Q}) \left[\sum_{\vec{L}} e^{i\vec{Q} \cdot \vec{L}} \right] = \frac{(2\pi)^3}{V} F(\vec{Q}) \left[\sum_{\vec{H}} \delta(\vec{Q} - \vec{H}) \right]$$

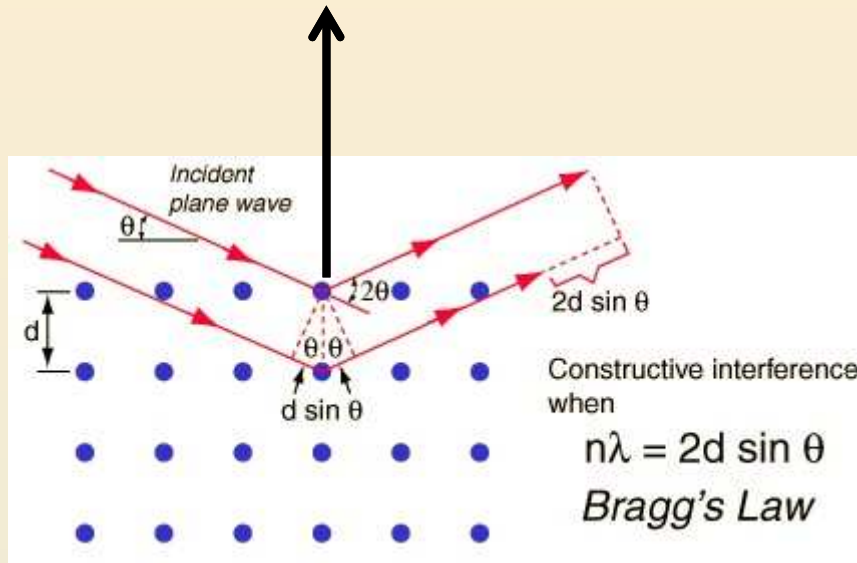
For a finite crystal, with N unit cells

$$A(\vec{H}) = NF(\vec{H})$$

Coherent scattering .

Bragg diffraction conditions.

$\hbar\vec{Q}$ is the momentum transferred to the target by the wave.



$$H = \frac{4\pi \sin \theta}{\lambda}$$

For a finite crystal, there is an opening angle around Bragg condition, of order d/L and one must integrate the peak intensity

Notice that the scattered wave has a phase shift of $\pi/2$ with respect to the incident wave

Case of X Rays

Elementary scatterers are electrons, all undiscernable

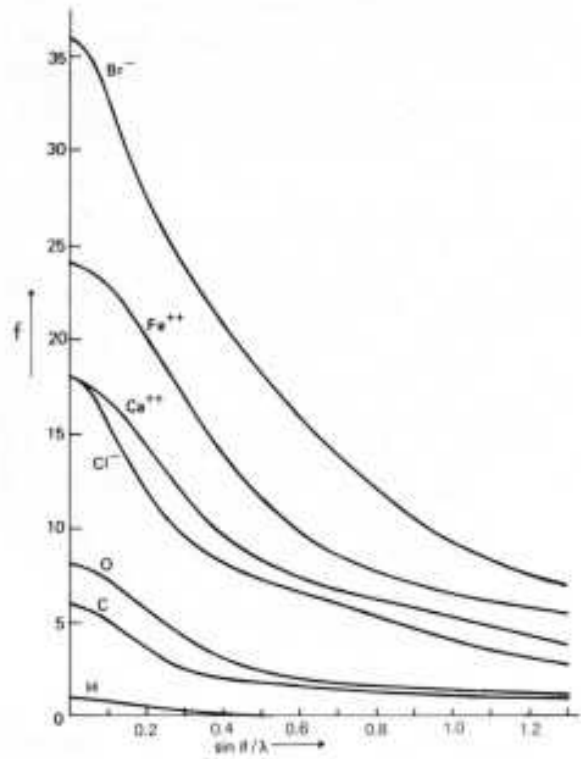
For a 1\AA wavelength, the energy of the photon is about **12000eV**, much higher than cohesive energies in a material

Electron charge density is the effective « target » :

$$A_X(\vec{Q}) = (r_e) \int \rho_e(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d\vec{r}$$

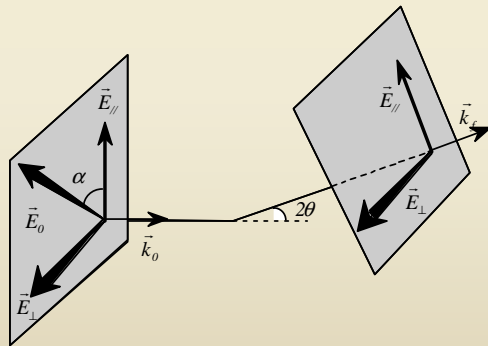
Independent atom approximation

$$\rho_{0,e}(\vec{r}) \approx \sum_n \rho_{at,n}(\vec{r} - \vec{R}_n)$$
$$A_0(\vec{Q}) = \sum_n f_n(Q) e^{i\vec{Q}\cdot\vec{R}_n}$$



Form factors at low scattering angle are proportional to atomic number

They decay as the inverse of atomic radius



$$b \equiv r_0 = \frac{e^2}{4\pi\epsilon_0 mc^2} = 0,28 \cdot 10^{-12} \text{ cm}$$

$$C = \cos^2(2\theta)\cos^2(\alpha) + \sin^2(\alpha)$$

$$\frac{\partial \sigma}{\partial \Omega} = r_0^2 C |A_X(\vec{Q})|^2$$

Neutron waves

Neutrons result from fission of U^{235} and are produced with an **energy** $> 1\text{Mev}$

Moderation via collisions with D_2O , liquid hydrogen, graphite

Neutron life time is about 900 sec

$n \Rightarrow \text{proton} + \text{electron} + \gamma\text{photon}$

Also spallation sources, producing pulsed neutrons

Wave-particle duality

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2}$$

$$m = 1.67510^{-27} \text{ kg}$$

$$\lambda(\text{\AA}) = \frac{0.286}{\sqrt{E(\text{ev})}}$$

$$E(\text{ev}) = \frac{0.082}{\lambda^2}$$

$$\lambda = \frac{30.8}{\sqrt{T}}$$

For $\lambda = 1 \text{\AA}$

$$E = 80 \text{ meV}$$

$$T = 950\text{K}$$

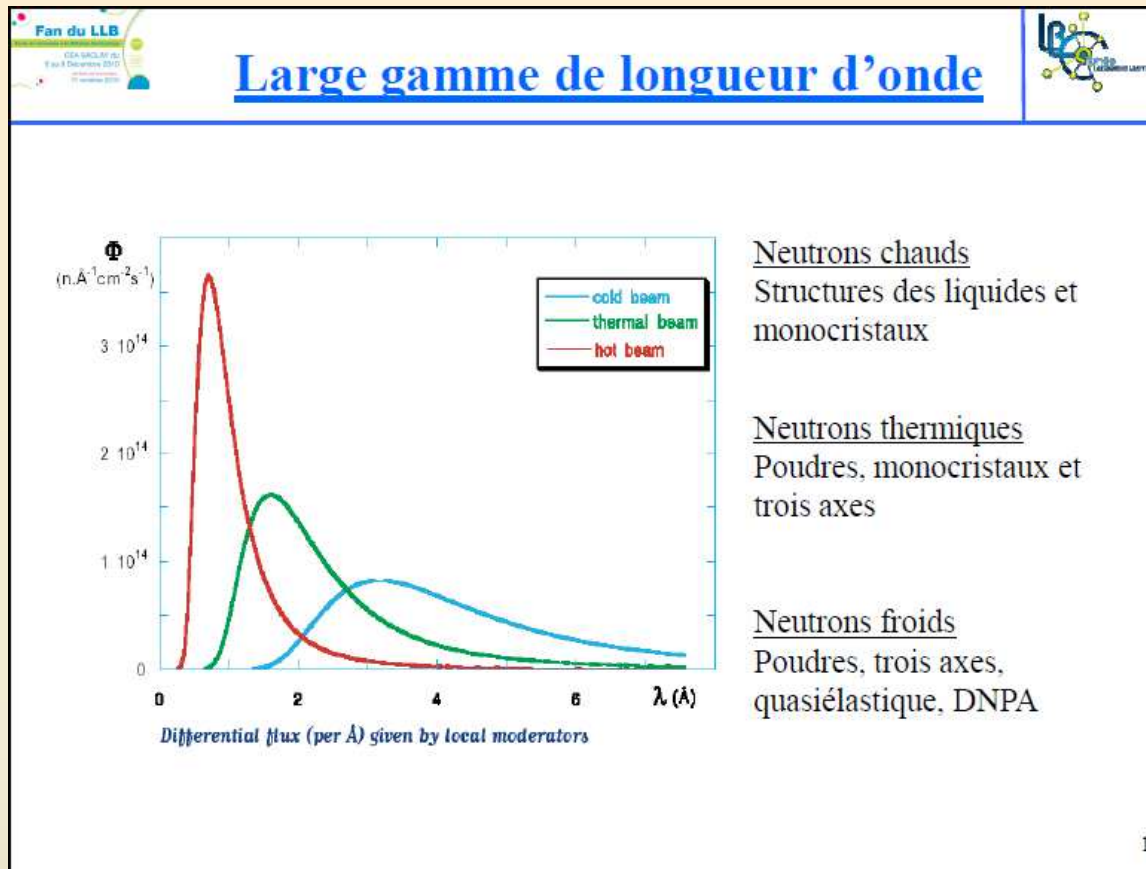
$$v = 4000 \text{ ms}^{-1}$$

Neutron is a fermion, with $\frac{1}{2}$ spin

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$$\mu_n = -\gamma\mu_N\sigma \quad \mu_N = \frac{e\hbar}{2m_p} \quad \gamma = 1.913$$

One talks about « thermal Neutrons », behaving like a perfect gaz flow



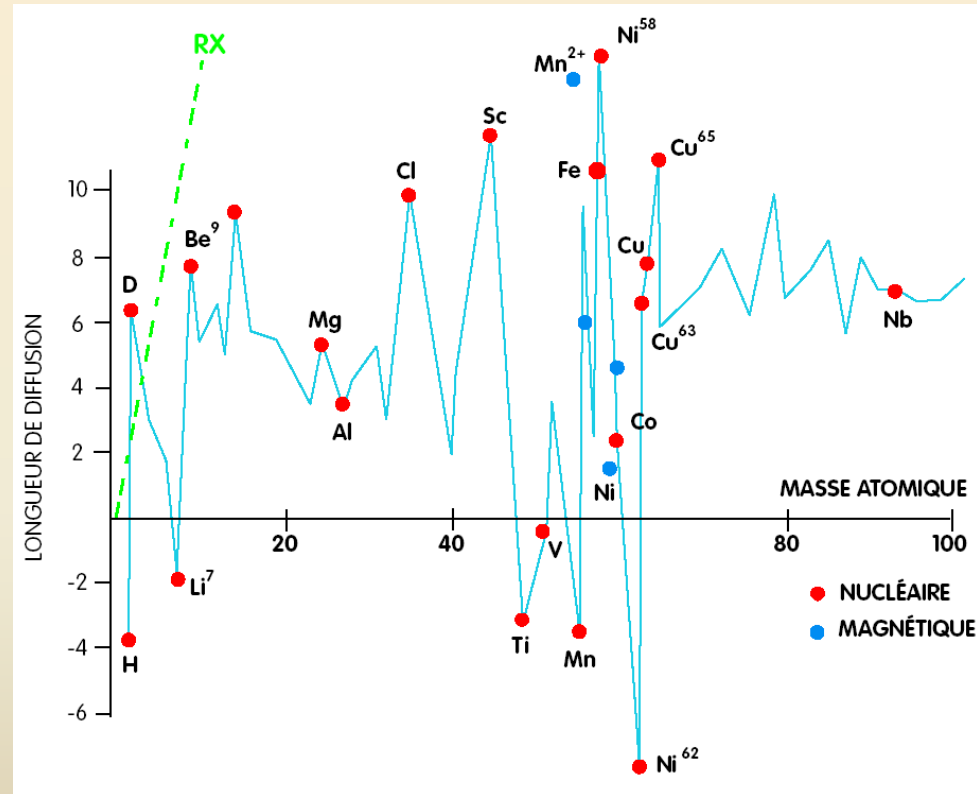
It is necessary to monochromatise the beam, $\lambda \approx \lambda_0$, which also produces significant beam with $\lambda/2$ wavelength

The speed of neutrons is low enough to allow for time of flight detection, besides usual selective absorption

Basic interaction with matter is nuclear interaction, which for study of materials, can be considered as ponctual (range of fm)

$$V_n(\vec{r}) = \frac{2\pi\hbar^2}{m} b \delta(\vec{r} - \vec{R})$$

b is called the scattering length by a nucleus, of the order of 10^{-12} cm



Very significant complementarity towards XRays

Let's consider an incident neutron wave directed towards a nucleus located at origin.

$$\phi_0 \approx e^{i\vec{k}_0 \cdot \vec{r}}$$

When reaching the static nucleus, the neutron wave satisfies the Schrodinger equation

$$\left[-\frac{\hbar^2}{2m} \Delta + \frac{\hbar^2}{2m} b \delta(\vec{r}) \right] \phi = E\phi = \frac{\hbar^2}{2m} k^2 \phi$$

It can be re-written as

$$[\Delta + k^2] \phi = b \delta(\vec{r}) \phi$$

After collision, the neutron is scattered with the same energy, and can be described as a spherical wave. One can show (1st Born approximation, since b is very small compared to λ) that the proper solution (Green function) is

$$G(r) \approx b \frac{e^{ikr}}{r}$$

$$[\Delta + k^2]G = 4\pi\delta(\vec{r})$$

$$G(r) \approx b \frac{e^{ikr}}{r}$$

Complex target

$$[\Delta + k^2]\psi = 4\pi n(\vec{r})\psi$$

$$\psi_f(\vec{R}) = -\int \frac{e^{ik|\vec{R}-\vec{r}'|}}{|\vec{R}-\vec{r}'|} n(\vec{r}') e^{i\vec{k}_0 \cdot \vec{r}'} d\vec{r}'$$

$$\psi_f = -\frac{e^{ikR}}{R} A_{N,e}(\vec{Q}) = \frac{m}{2\pi\hbar^2} \frac{e^{ikR}}{R} \int V(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r}$$

Generalization to electron scattering and beyond

$$A_N(\vec{Q}) = \int n(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d\vec{r}$$
$$A_e(\vec{Q}) = \frac{me^2}{2\pi\hbar^2 \epsilon_0} \frac{\{A_c(\vec{Q}) - A_X(\vec{Q})\}}{Q^2}$$
$$A_c(\vec{Q}) = \sum_j Z_j e^{i\vec{Q}\cdot\vec{R}_j}$$
$$A_X(\vec{Q}) = \int \rho_e(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d\vec{r}$$

$$V_N(\vec{r}) = \frac{2\pi\hbar^2}{m} \sum_j b_j \delta(\vec{r} - \vec{R}_j)$$
$$\Delta V_e(\vec{r}) = -\frac{1}{\epsilon_0} \{\rho_c(\vec{r}) - \rho_e(\vec{r})\}$$
$$V(\vec{r}) = \frac{2\pi\hbar^2}{m} n(\vec{r})$$

It will also apply to magnetic interactions of neutrons with matter
Important complementarity of Xray / Electron scattering

For a stationary crystal, forgetting about surface effects...

$$\left(\frac{\partial \sigma}{\partial \Omega}\right)_{elastic} = |A(\vec{H})|^2 = N^2 |F(\vec{H})|^2$$

Phase problem remains to retrieve the scattering density

$$n(\vec{r}) = \frac{1}{V} \sum_{\vec{H}} F(\vec{H}) e^{-i\vec{H} \cdot \vec{r}}$$

Only the Patterson function can be obtained directly from experiment

$$P(\vec{r}) = \frac{1}{V} \sum_{\vec{H}} |F(\vec{H})|^2 e^{-i\vec{H} \cdot \vec{r}} = n * n$$

$$P(\vec{r}) = \sum_{i, j \in \text{unitcell}} b_i b_j \delta(\vec{r} - \vec{R}_{ij})$$

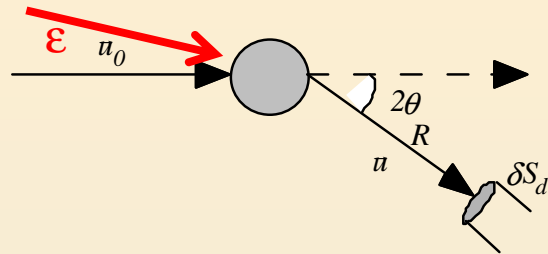
Also direct methods are available for getting the phases

Peaks of $n^2(\vec{r})$ have same location as those of $n(\vec{r})$

Probability relations among the phases of some triplets $F(\vec{H}), [F(\vec{K})F(\vec{H} - \vec{K})]$

Great thanks to David Sayre, Jerome Karle and Herbert Hauptman

Due to finite size, scattering occurs out of exact Bragg condition

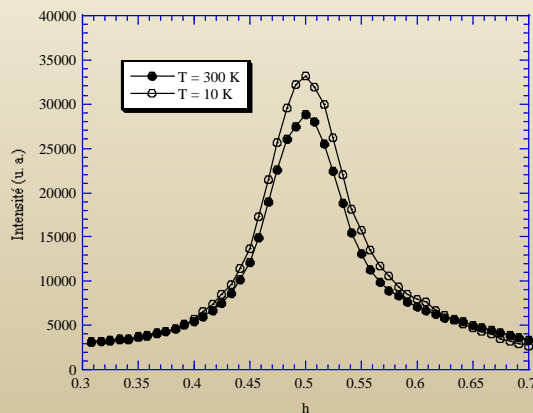


$$\vec{Q} = \vec{H} + \vec{q}$$

For a given position of the crystal (ε), the cross section per unit volume is $\sigma(\varepsilon)$, and after rotation of the crystal, one gets the total « kinematic » diffraction cross section per unit volume :

$$d^3q = (2\pi)^3 \frac{\sin 2\theta}{\lambda^3} d\Omega d\varepsilon$$

$$Q_{kinematic} = \int \sigma(\varepsilon) d\varepsilon = \left| \frac{F}{V} \right|^2 \frac{\lambda^3}{\sin 2\theta} \quad (\text{\AA}^{-1})$$



Raies de surstructure (1/2 1/2 1/2) pour $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN), à $T = 300$ K et 10 K,
le long de la direction [hhh]
spectromètre 6T2 LLB

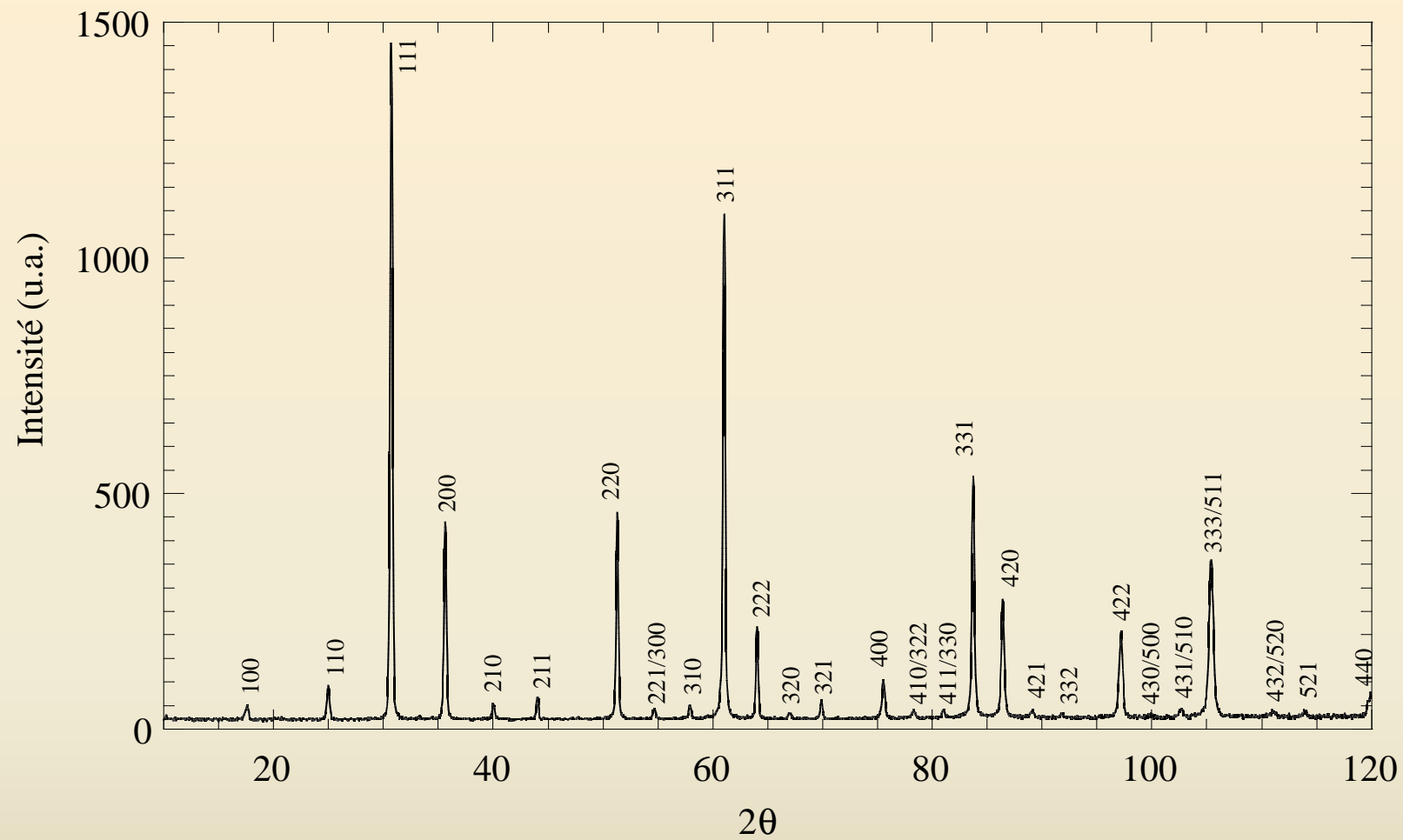


Diagramme de diffraction des neutrons du BaTiO₃ à 401 K : spectromètre 3T2 LLB

There are resolution limits due to the fact that

$$|\vec{H}| \leq \frac{4\pi}{\lambda}$$

There can be a mixture of isotopes in a compound, and moreover there can be a spin coupling between the neutron and scattering nucleus. As a consequence, the scattering length of a given atom can vary from one site to another one

$$A(\vec{Q}) = \sum_{\vec{L}} \sum_j b_{jL} e^{i\vec{Q} \cdot (\vec{R}_j + \vec{L})}$$

The total cross-section is written as the sum of a coherent and an incoherent part

$$\begin{aligned} \langle b_j b_k \rangle &= \langle b_j \rangle \langle b_k \rangle \quad \text{if } j \neq k \\ \langle b_j^2 \rangle &= \langle b_j \rangle^2 + \left[\langle b_j^2 \rangle - \langle b_j \rangle^2 \right] \\ &\quad \text{incoherent} \end{aligned}$$

$$b = b_N + 2B\vec{\sigma} \cdot \vec{I}$$

$$\text{Neutron : } M_N = -\gamma(2\mu_N)\sigma$$

$$\text{Electron : } M_S = -g\mu_B S$$

$$\mu_B = \frac{e\hbar}{2m} = 9.27410^{-24} \text{ JT}^{-1}$$

$$\mu_N = \frac{e\hbar}{2M} = \mu_B / 1836$$

$$\langle b \rangle = \frac{I+1}{2I+1} b_+ + \frac{I}{2I+1} b_-$$

$$\langle b^2 \rangle - \langle b \rangle^2 = \langle b_N^2 \rangle - \langle b_N \rangle^2 + \langle B^2 I(I+1) \rangle$$

	H	D	O	V	Ni
σ_c	1,8	5,6	4,2	0,02	13,4
σ_i	81,2	2	0	5,0	5,0

Isotopic incoherence for Ni
Spin incoherence for H

One gets, besides a coherent Bragg diffraction, where the appropriate scattering length for a nucleus is $\langle b_j \rangle$ an incoherent added intensity

$$\left(\frac{\partial \sigma}{\partial \Omega} \right)_{inc} = N \sum_j \left[\langle b_j^2 \rangle - \langle b_j \rangle^2 \right]$$

Diffraction experiments occur on systems at a given temperature. This creates vibrational disorder of atomic positions. In crystals, those vibrations are phonons

$$A(\vec{Q}) = \sum_{\vec{L}} \sum_n b_n e^{i\vec{Q} \cdot (\vec{R}_n + \vec{L})} e^{i\vec{Q} \cdot \vec{u}_{nL}}$$

$$\langle |A|^2 \rangle = |\langle A \rangle|^2 + \Delta A^2$$

Bragg
diffraction

Thermal diffuse
scattering

$$\langle A(\vec{H}) \rangle = N \langle F(\vec{H}) \rangle$$

$$F(\vec{H}) = \sum_n \langle b_n \rangle e^{i\vec{H} \cdot \vec{R}_n} W_n$$

$$W_n = \langle e^{i\vec{H} \cdot \vec{u}_n} \rangle$$

Debye Waller factor

In the harmonic approximation, one can show exactly

$$W_n = e^{-\frac{1}{2} \langle (\vec{H} \cdot \vec{u}_n)^2 \rangle}$$

For a given frequency

$$W_n \approx e^{-\frac{2\pi^2}{\lambda^2} \left(\frac{\sin \theta}{\lambda}\right)^2 \frac{kT}{m\omega^2}}$$

Debye Waller factor lowers signal for high T, large scattering angle, light atoms, with major contribution from acoustic frequencies.

Anharmonic motion can also be considered

For systems made of molecules or for instance organic fragments linked to a protein, one can model vibrations in terms of intra-molecular (high frequency) and inter-molecular acoustic vibrations !

Static atomic disorder can also lead to a lowering factor, not dependent on T (see extinction !!!)

$$\left\langle e^{i\vec{H} \cdot \vec{u}_n} \right\rangle$$

The other term $\langle \Delta A^2 \rangle$ corresponds to thermal diffuse scattering. See later it's frequency analysis. If no energy analysis is done, it is a diffuse contribution, which is considered as part of background

Parameters progressively introduced in the structure factor and the scattering density function can be adjusted by a refinement of observed data towards the proposed model, via a minimisation with respect to adjustable key parameters (positions, thermal parameters...)

$$R = \sum_H \frac{[I_{obs}(\vec{H}) - I_{mod}(\vec{H})]^2}{\sigma_H^2}$$

Another approach is the maximum entropy method

Besides crystals, many applications to aperiodic structures, disordered solids (glass) and liquids

Model refinement can be very critical



<http://uk.groups.yahoo.com/group/MangloreFriends>

Quantum approach

Fermi Golden Rule

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_f} = \frac{k_f}{k_0} \Sigma(\vec{Q}, \omega)$$

$$\begin{aligned} \Sigma(\vec{Q}, \omega) &= \sum_f \left| \langle \psi_0 | A(\vec{Q}) | \psi_f \rangle \right|^2 \delta(\varepsilon_f - \varepsilon_0 - \hbar\omega) \\ &= \frac{1}{2\pi\hbar} \int e^{-i\omega t} dt \sum_{j,k} \sum_f e^{i(\varepsilon_f - \varepsilon_0)t/\hbar} \langle \psi_0 | a_k e^{i\vec{Q} \cdot \vec{r}_k} | \psi_f \rangle \langle \psi_f | a_j^* e^{-i\vec{Q} \cdot \vec{r}_j} | \psi_0 \rangle \end{aligned}$$

$$\Sigma(\vec{Q}, \omega) = \frac{1}{2\pi\hbar} \int_0^\infty I(\vec{Q}, t) e^{-i\omega t} dt$$

$$I(\vec{Q}, t) = \left\langle \sum_{j,k} a_j^* a_k e^{-i\vec{Q} \cdot \vec{r}_j(t)} e^{i\vec{Q} \cdot \vec{r}_k(0)} \right\rangle$$

$$I(\vec{Q}, t) = \left\langle A(\vec{Q}, 0) A^*(\vec{Q}, t) \right\rangle$$

Space and time correlation function

$$\Sigma(\vec{Q}, \omega) = \frac{1}{2\pi\hbar} \int_0^{\infty} I(\vec{Q}, t) e^{-i\omega t} dt$$

$$I(\vec{Q}, t) = \int \Gamma(\vec{r}, t) e^{i\vec{Q} \cdot \vec{r}} d\vec{r}$$

$$\Gamma(\vec{r}, t) = \int \langle n(\vec{r}', 0) n(\vec{r} + \vec{r}', t) \rangle d\vec{r}'$$

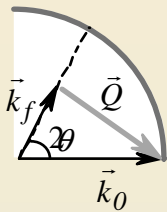
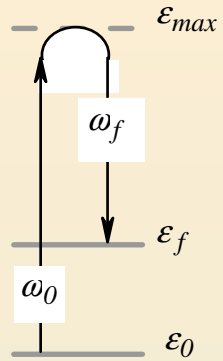
Most general situation

System and beam in a statistical initial state

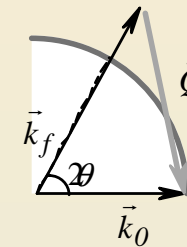
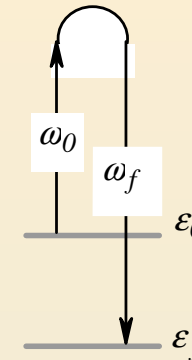
$$\begin{aligned}\Sigma(\vec{Q}, \omega) &= \sum_0 p_0 \sum_f \left| \langle \psi_0 | \tilde{A}(\vec{Q}) | \psi_f \rangle \right|^2 \delta(\varepsilon_0 - \varepsilon_f - \hbar\omega) \\ &= \sum_0 p_0 \sum_f \left| \langle \psi_0, \vec{k}_0 | \tilde{N}(\vec{r}) | \psi_f, \vec{k}_f \rangle \right|^2 \delta(\varepsilon_0 - \varepsilon_f - \hbar\omega)\end{aligned}$$

$$E_f + \varepsilon_f = E_0 + \varepsilon_0$$

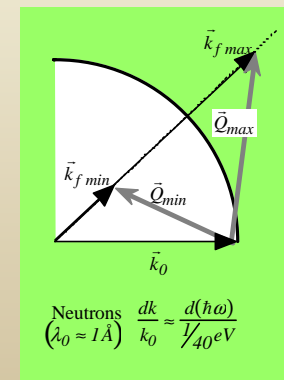
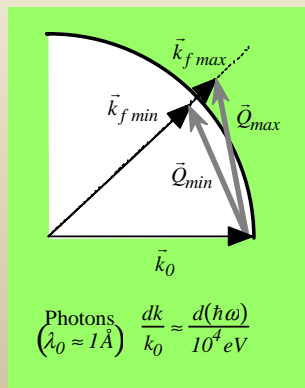
$$\vec{Q} = \vec{k}_0 - \vec{k}_f$$



(a) $\omega > 0$



(b) $\omega < 0$



Total scattering

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{total} = \int \frac{\partial^2\sigma}{\partial\Omega\partial E_f} dE_f = \hbar \int_{-\infty}^{\omega_0} \frac{k_f}{k_0} \Sigma(\vec{Q}, \omega) d\omega$$

$$\omega = \omega_0 - \omega_f \leq \omega_0$$

Static approximation

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{total} = \int \frac{\partial^2\sigma}{\partial\Omega\partial E_f} dE_f = \hbar \int_{-\infty}^{\omega_0} \frac{k_f}{k_0} \Sigma(\vec{Q}, \omega) d\omega$$

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{total} \approx \hbar \int_{-\infty}^{+\infty} \Sigma(\vec{Q}, \omega) d\omega \approx S(\vec{Q})$$

Mostly valid for X Rays

Elastic scattering

$$S_{elastic}(\vec{Q}) = \sum_0 p_0 \left| \langle \psi_0 | \tilde{A}(\vec{Q}) | \psi_0 \rangle \right|^2$$

$$S_{tot}(\vec{Q}) = \sum_0 p_0 \langle \psi_0 | \tilde{A}(\vec{Q}) \tilde{A}^*(\vec{Q}) | \psi_0 \rangle$$

Total scattering

Phonon scattering

Consider inelastic scattering for a model crystal with one atom/cell, where the system will go from vibrational state ψ_n to ψ_m

$$A(\vec{Q}) = b \sum_{\vec{l}} e^{i\vec{Q} \cdot (\vec{l} + \vec{u}_l)} \approx b \left[\sum_{\vec{l}} e^{i\vec{Q} \cdot \vec{l}} \right] + b \left[\sum_{\vec{l}} (\vec{Q} \cdot \vec{u}_l) e^{i\vec{Q} \cdot \vec{l}} \right] + \dots$$
$$= A_0 + A_1$$

Displacement can be decomposed in phonons. We simplify by considering only one phonon, of wave vector q

$$\vec{u}_l = \frac{1}{\sqrt{Nm}} \left(\xi \vec{\epsilon} e^{i\vec{q} \cdot \vec{l}} + c.c. \right)$$
$$\langle \epsilon \rangle = \hbar \omega(\vec{q}) (\bar{n} + 1/2) = \frac{1}{2} \omega^2(\vec{q}) \langle |\xi|^2 \rangle$$

$$A(\vec{Q}) = b \sum_{\vec{l}} e^{i\vec{Q} \cdot (\vec{l} + \vec{u}_l)} \approx b \left[\sum_{\vec{l}} e^{i\vec{Q} \cdot \vec{l}} \right] + b \left[\sum_{\vec{l}} (\vec{Q} \cdot \vec{u}_l) e^{i\vec{Q} \cdot \vec{l}} \right] + \dots$$

$$= A_0 + A_1$$

$$\langle \psi_n | A_0 | \psi_m \rangle = 0 \quad \text{for } m \neq n$$

$$\langle \psi_n | A_1 | \psi_m \rangle \neq 0 \quad \rightarrow \quad \text{for } m = n \pm 1$$

$$\varepsilon_m = \varepsilon_n \pm \hbar\omega$$

Creation or absorption of phonon

$$E_f = E_0 \mp \hbar\omega \quad \frac{\hbar^2 k_f^2}{2m_n} = \frac{\hbar^2 k_0^2}{2m_n} \mp \hbar\omega$$

Energy change can be very pronounced with neutrons, very small with X Rays (need for very high resolution)

$$\langle \psi_n | A | \psi_{n\pm 1} \rangle = b \frac{\vec{Q} \cdot \vec{\varepsilon}}{\sqrt{Nm}} \langle \psi_n | \xi | \psi_{n\pm 1} \rangle \left\{ \sum_{\vec{l}} e^{i(\vec{Q} \pm \vec{q}) \cdot \vec{l}} \right\}$$

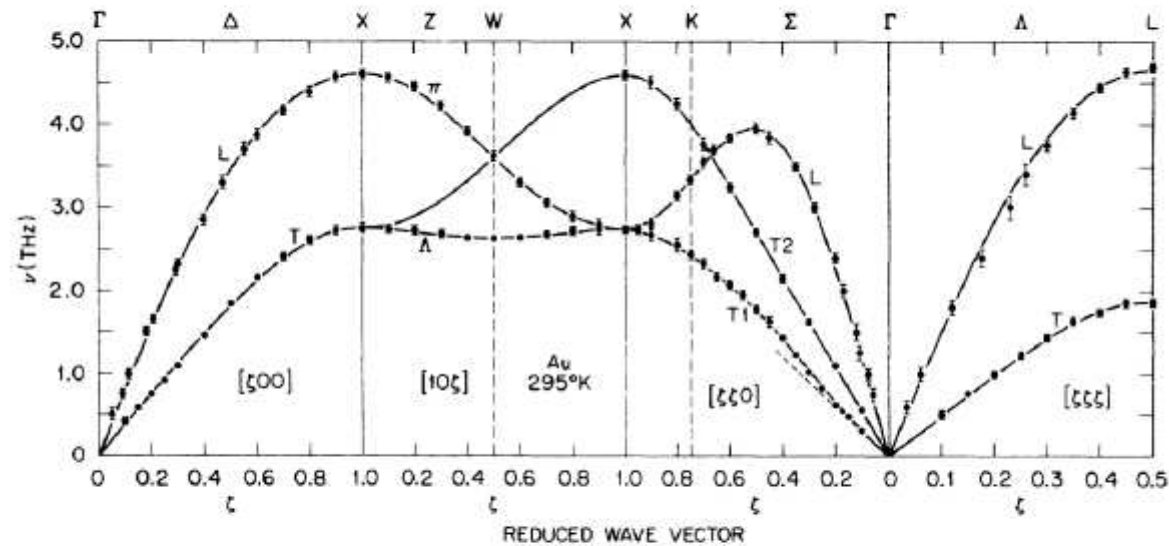
$$\langle \psi_n | A | \psi_{n\pm 1} \rangle = b \frac{\vec{Q} \cdot \vec{\epsilon}}{\sqrt{Nm}} \langle \psi_n | \xi | \psi_{n\pm 1} \rangle \left\{ \sum_{\vec{l}} e^{i(\vec{Q} \pm \vec{q}) \cdot \vec{l}} \right\}$$

One gets diffraction condition (coherent effect)

$$\vec{Q} \pm \vec{q} = \vec{H}$$

In a given scattering direction thus, with energy analyser, one gets ω , \mathbf{k}_f , and therefore \mathbf{q} , $\omega(\mathbf{q})$

Phonon dispersion relation in gold



J. W. Lynn, H. G. Smith, and R. M. Nicklow, *Phys. Rev. B* **8**, 3493 (1973).

Key application of neutrons, in particular for phase transitions

Neutron Magnetic scattering

$\vec{\sigma} \Rightarrow$ neutron spin in units of $\hbar/2 \Rightarrow \sigma_z = \pm 1$

$$\vec{\mu} = \frac{1}{V} \int \vec{m}(\vec{r}) d\vec{r}$$
$$\vec{m}(\vec{r}) = \vec{m}_s(\vec{r}) + \vec{m}_l(\vec{r})$$

Magnetic scattering occurs through dipolar interaction between neutron and electron magnetic moments

$$V_m(\vec{r}) = -\vec{\mu}_n \cdot \vec{B}$$

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

$$\vec{A} = \sum_j \vec{A}_j$$

$$\vec{A}_j = \frac{\mu_0}{4\pi} \vec{\nabla} \left(\frac{1}{R_j} \right) \times \vec{\mu}_j$$

$$F_M(\vec{Q}) = \vec{\sigma} \cdot \vec{\Phi}(\vec{Q})$$

$$\vec{\Phi}(\vec{Q}) = \vec{\Phi}_S(\vec{Q}) + \vec{\Phi}_L(\vec{Q})$$

Spin component

$$F_{M_s}(\vec{Q}) = \vec{\sigma} \cdot \vec{\Phi}_s(\vec{Q})$$

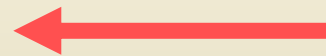
$$\vec{\Phi}_s = r_0 \hat{q} \times \vec{M}_s(\vec{Q}) \times \hat{q} = r_0 \vec{M}_{\perp s}(\vec{Q})$$

$$r_0 = \gamma_e = 1.913 \times r_e = .54 \cdot 10^{-12} \text{ cm}$$

$$\hat{q} = \vec{Q} / Q$$

$$\vec{M}_s(\vec{Q}) = FT[\vec{m}_s(\vec{r})]$$

$$\vec{m}_s(\vec{r}) = \left\langle \sum_j \vec{s}_j \delta(\vec{r} - \vec{r}_j) \right\rangle$$



Spin density

Orbital component, related to current density

$$\vec{j}(\vec{r}) = -\frac{e}{2m} \left\langle \sum_j \{ \vec{p}_j \delta(\vec{r} - \vec{r}_j) + \delta(\vec{r} - \vec{r}_j) \vec{p}_j \} \right\rangle$$

$$F_M(\vec{Q}) = \vec{\sigma} \cdot \vec{\Phi}_l(\vec{Q})$$

$$\vec{\Phi}_l(\vec{Q}) = -\frac{ir_0}{2\pi Q} \hat{q} \times \vec{J}(\vec{Q})$$

$$\vec{J}(\vec{Q}) = FT[\vec{j}(\vec{r})]$$

$$\vec{j}(\vec{r}) = \vec{\nabla} \psi + \vec{\nabla} \times \vec{m}_l(\vec{r})$$

↑

↑

conduction

orbital

$$\vec{\Phi}_L(\vec{Q}) = r_0 \hat{q} \times \vec{M}_L(\vec{Q}) \times \hat{q} = r_0 \vec{M}_{\perp L}(\vec{Q})$$

Orbital magnetisation density defined to any gradient, but magnetic amplitude uniquely defined

$$F_M(\vec{Q}) = r_0 \vec{\sigma} \cdot \vec{M}_{\perp}(\vec{Q})$$

$$\vec{M}(\vec{Q}) = \vec{M}_S(\vec{Q}) + \vec{M}_L(\vec{Q})$$

Case of spin only magnetism, at zero temperature

Magnetization density in units of $2\mu_B$, with a quantization axis Oz (applied field or natural quantization axis)

$$\vec{m}_S(\vec{r}) = \sum_j \vec{\hat{s}}_j \delta(\vec{r} - \vec{r}_j)$$

Ground state eigenstate of \mathbf{S}^2 and \mathbf{S}_z .

$$2M_S = n_\uparrow - n_\downarrow$$

$$m_{S_z}(\vec{r}) = \langle \Psi_{SM_S} | \hat{m}_{S_z} | \Psi_{SM_S} \rangle = M_S s(\vec{r})$$

Normalized spin density

$$s(\vec{r}) = \frac{1}{n_\uparrow - n_\downarrow} \{ \rho_\uparrow(\vec{r}) - \rho_\downarrow(\vec{r}) \}$$

Orbital magnetization

In units of $2\mu_B$

$$\vec{m}_L(\vec{r}) = \frac{1}{4} \left\langle \sum_j \left\{ \vec{l}_j \delta(\vec{r} - \vec{r}_j) + \delta(\vec{r} - \vec{r}_j) \vec{l}_j \right\} \right\rangle$$

$$\vec{L} = \sum_j \vec{l}_j$$

Often, orbital moment is not a constant of motion. Often, spin orbit coupling remains localized, and L remains a reasonably good quantum number. (L^2, S^2, J^2, J_z) are the good quantum numbers

$$\vec{L} + 2\vec{S} = g\vec{J}$$

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

$$\vec{S} = (g-1)\vec{J}$$

$$\vec{L} = (2-g)\vec{J}$$

Neutron elastic scattering

$$I_{\uparrow\uparrow} = \left| F_n + r_0 \vec{\sigma} \cdot \vec{M}_{\perp} \right|^2$$

$$I_{\downarrow\downarrow} = \left| F_n - r_0 \vec{\sigma} \cdot \vec{M}_{\perp} \right|^2$$

$$I_{\uparrow\downarrow} = I_{\downarrow\uparrow} = r_0^2 \left| \vec{\sigma} \times \vec{M}_{\perp} \right|^2$$

If no spin analysis for scattered beam, two cross sections

$$I_{\uparrow} = I_{\uparrow\uparrow} + I_{\uparrow\downarrow}$$

$$I_{\downarrow} = I_{\downarrow\downarrow} + I_{\downarrow\uparrow}$$

$$I_{\uparrow\uparrow} = |F_n + r_0 \vec{\sigma} \cdot \vec{M}_\perp|^2$$

$$I_{\downarrow\downarrow} = |F_n - r_0 \vec{\sigma} \cdot \vec{M}_\perp|^2$$

$$I_{\uparrow\downarrow} = I_{\downarrow\uparrow} = r_0^2 |\vec{\sigma} \times \vec{M}_\perp|^2$$

$$I_\uparrow = I_{\uparrow\uparrow} + I_{\uparrow\downarrow}$$

$$I_\downarrow = I_{\downarrow\downarrow} + I_{\downarrow\uparrow}$$

Unpolarized neutrons

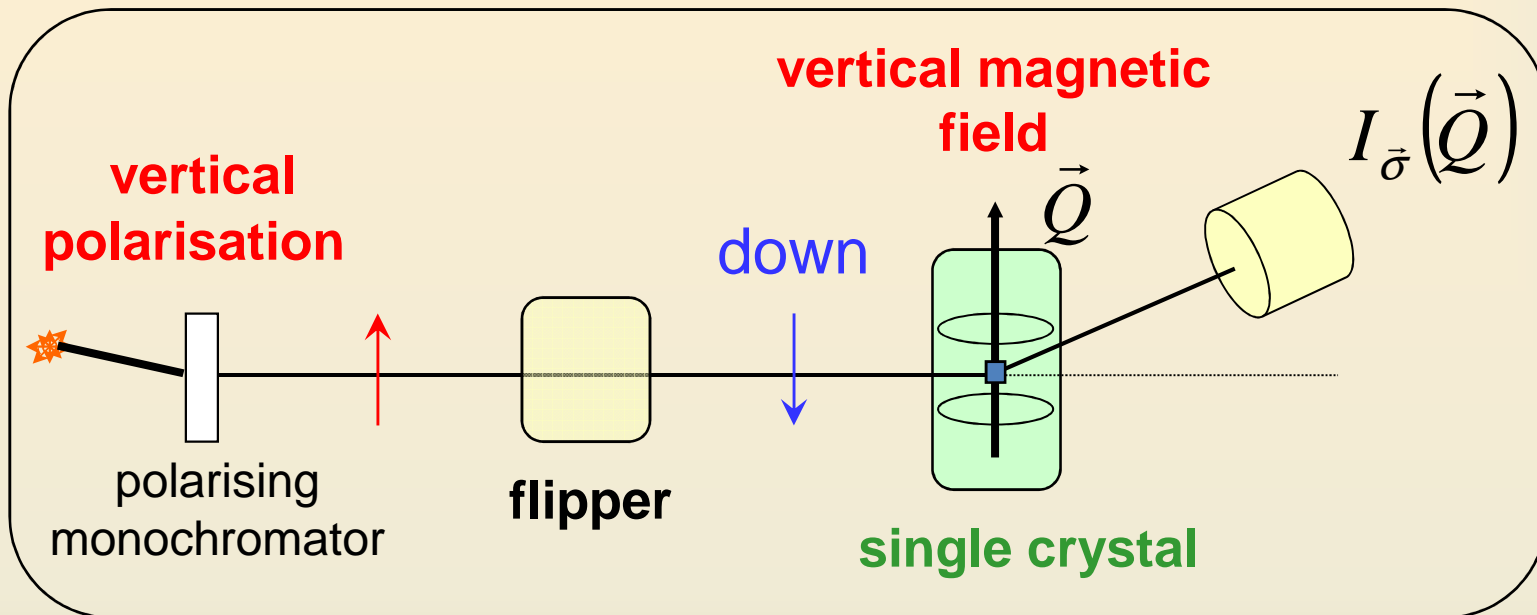
$$I = \frac{1}{2} (I_\uparrow + I_\downarrow) = |F_n|^2 + |F_m|^2$$

$$x = F_m / F_n \quad \Rightarrow \quad I = |F_n|^2 \{1 + x^2\}$$

Magnetic effects hard to observe with unpolarized neutrons

Polarized neutron diffraction

Incident beam of polarized neutrons (spin $\vec{\sigma}$)



$$I_{\vec{\sigma}}(\vec{Q}) \propto \left| F_N(\vec{Q}) + \vec{\sigma} \cdot \vec{M}_{\perp}(\vec{Q}) \right|^2$$

simple case : \vec{Q} in horizontal plane
Magnetization along Oz

$$F_M^\perp = F_M$$

Flipping ratio

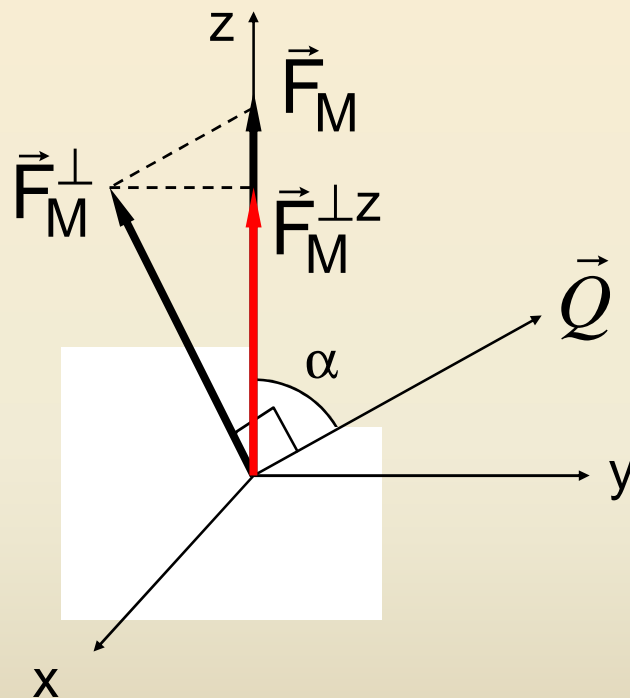
$$R = \frac{I_+}{I_-} = \left(\frac{F_N + F_M}{F_N - F_M} \right)^2 = \left(\frac{1 + \gamma}{1 - \gamma} \right)^2 \quad \text{with } \gamma = \frac{F_M}{F_N}$$

si $F_M \ll F_N$

polarised	$R \cong 1 + 4\gamma$	Linear en F_M
non polarised	$I \propto (F_N^2 + F_M^2)$	negligeable

***advantage of polarized neutrons for
for weak magnetism***

General case : \vec{Q} out of horizontal plane



\vec{F}_M^\perp component of $\vec{F}_M \perp \vec{Q}$

$$F_M^\perp = F_M \sin \alpha$$

$$F_M^{\perp z} = F_M^\perp \sin \alpha = F_M (\sin \alpha)^2$$

\vec{F}_M aligned along vertical axis z

Strong complementarity with X Ray high resolution diffraction, leading to charge density: mainly cohesive contribution towards sum of independent atoms

$$\rho(\vec{r}) = \rho_{\uparrow}(\vec{r}) + \rho_{\downarrow}(\vec{r})$$
$$\delta\rho(\vec{r}) = \rho(\vec{r}) - \rho_{ind.atoms}(\vec{r})$$

$$\rho_{\alpha} = \sum_i n_{i\alpha} |\varphi_{i\alpha}|^2$$
$$n_{\uparrow,\downarrow} = \sum_i n_{i\uparrow,\downarrow}$$

$$s(\vec{r}) = \frac{1}{n_{\uparrow} - n_{\downarrow}} \{ \rho_{\uparrow}(\vec{r}) - \rho_{\downarrow}(\vec{r}) \}$$

P. Coppens and I, with T. Koristzansky, initiated such combined study

Presently a strong project with LLD, CRM2, Spring8 and our lab SPMS
combined refinement of charge and spin,
and also charge / spin and momentum.

Real crystals: extinction

$$\vec{Q} = \vec{H} + \vec{q} = \vec{H} + \frac{1}{\lambda} \vec{\varepsilon}$$

$$d^3q = (2\pi)^3 \frac{\sin 2\theta}{\lambda^3} d\Omega d\varepsilon$$

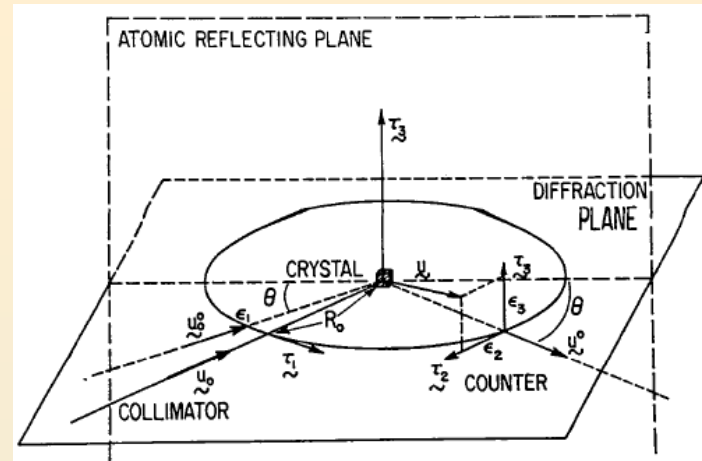
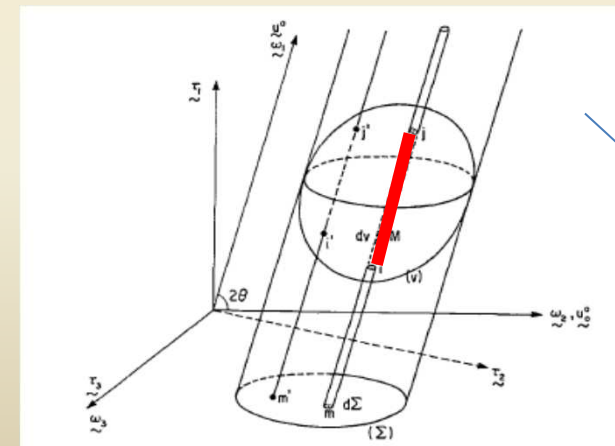


Fig. 1. Definition of the directions of the incident beam \mathbf{u}_0 and of the diffracted beam \mathbf{u} with respect to their ideal values \mathbf{u}_0^0 and \mathbf{u}^0 (defining the diffraction plane), when the Bragg condition is fulfilled. R_0 is the distance between the crystal and the counter.

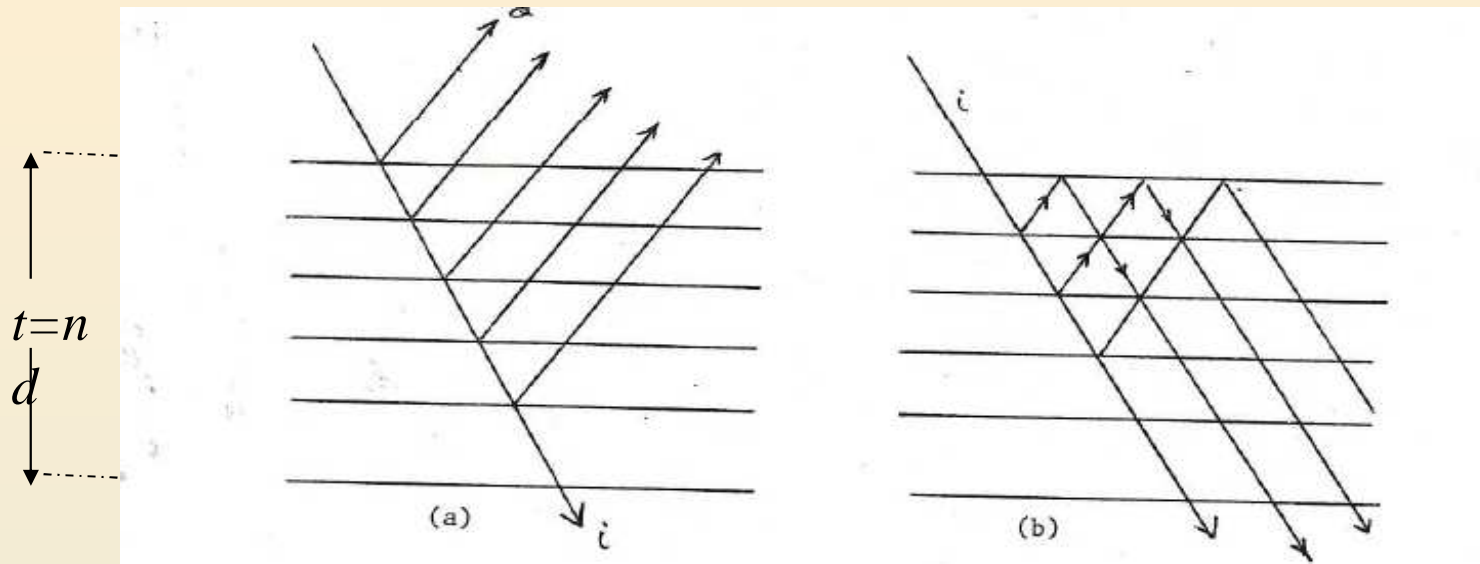
$$\sigma(\varepsilon) = Qv^{-1} \int dv \alpha \frac{\sin^2(\pi\varepsilon\alpha)}{(\pi\varepsilon\alpha)^2} \quad \alpha = l \frac{\sin 2\theta}{\lambda}$$

$$Q_{kinematic} = \int \sigma(\varepsilon) d\varepsilon = \left| \frac{F}{V} \right|^2 \frac{\lambda^3}{\sin 2\theta} \quad (\text{A}^{-1})$$

$$P_k = I_0 v Q_{kinematic}$$



Reflected wave by a plane is out of phase by $\pi/2$ with incident wave



n planes : $t=nd$. Number of possible 3-fold scattering

$$1+2+\dots+n = n(n+1)/2 \approx n^2/2$$

Probability of rescattering

$$x_p = Q d n^2/2 = Q t^2 \sin\theta/\lambda$$

Critical extinction length Λ

$$\Lambda = \left(\frac{\lambda}{Q \sin 2\theta} \right)^{1/2} = \frac{V}{F\lambda} = \left(\frac{d}{Q} \right)^{1/2}$$

In case of perfect regions $t > \Lambda$, diffraction power

$$Q\Lambda = \frac{F\lambda^2}{V \sin 2\theta}$$

Natural width of perfect crystal scattering function : d / Λ

Width of $\sigma(\epsilon)$: d / t

$$\Lambda = \left(\frac{\lambda}{Q \sin 2\theta} \right)^{1/2} = \frac{V}{F\lambda} = \left(\frac{d}{Q} \right)^{1/2}$$

Generally, Λ around $50\mu\text{m}$

If $t > \Lambda$, dynamical regime

If $t < \Lambda$, mixed regime, for which an extinction theory is applicable. This is favoured by using small wavelenths (gamma, synchrotron)

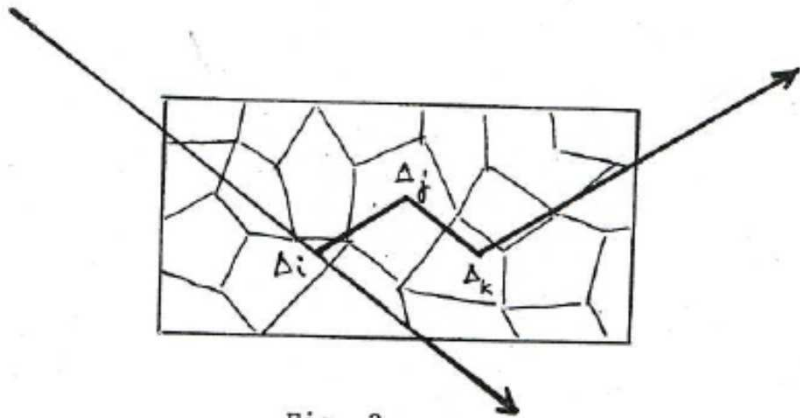


Fig. 3

Mosaic model

$W(\varepsilon)$ mosaic spread function, width η

$\sigma(\varepsilon)$, of width $\beta = d/t$ becomes $\bar{\sigma}(\varepsilon) = \int \sigma(\varepsilon + \tau)W(\tau)d\tau$

width of $\bar{\sigma} \approx \Delta = \beta + \eta$ secondary extinction parameter: $x_s = QT / \Delta$

type 2 extinction: $\eta \ll \beta$ $\bar{\sigma} = \sigma(\varepsilon)$ $x_s = QT / \beta = tT / \Lambda^2$

type 1 extinction: $\eta \gg \beta$ $\bar{\sigma} = QW(\varepsilon)$ $x_s = QT / \eta = t^*T / \Lambda^2$ with $t^* = d / \eta$

In this case primary extinction to be considered: $Q \Rightarrow Qy_p(x_p)$

$$y = y_p(x_p)y_s(y_p x_s)$$

Darwin's equations

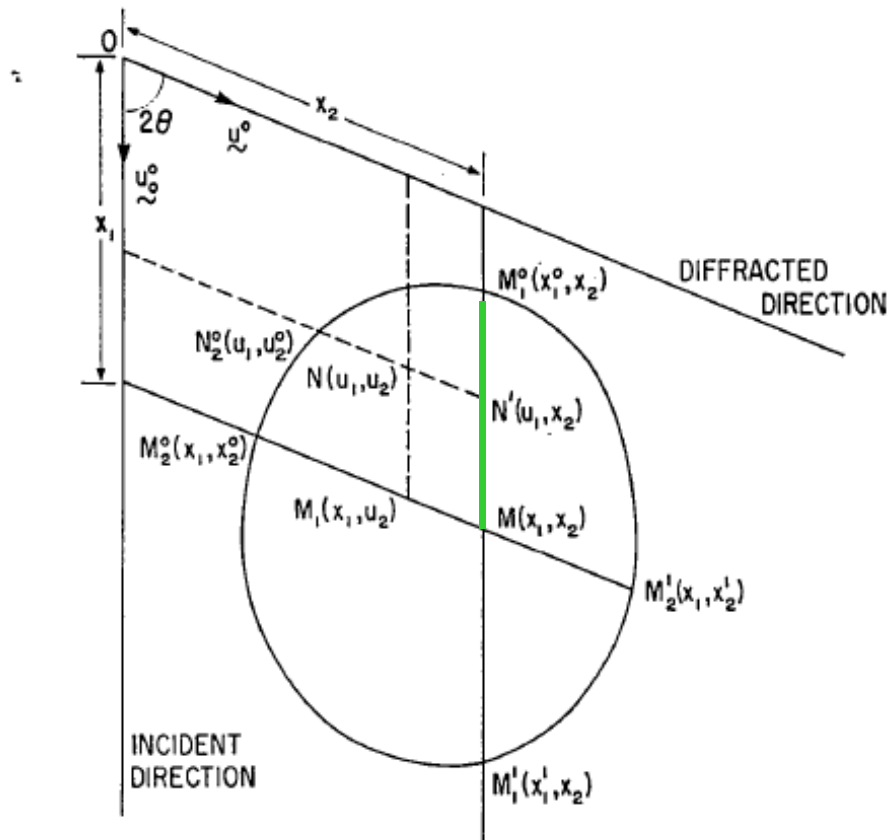


Fig. 2. Section of the crystal in a plane parallel to u_0^0 and u^0 , the incident and diffracted directions. The coordinates of each point of interest are written in parentheses. $t_1 = \overline{M_1^0 M}$; $t_2 = \overline{M_2^0 M}$; $t_2' = \overline{M M_2^1}$.

$$t_1 = \overline{M_1^0 M} = x_1 - x_1^0$$

$$t_2 = \overline{M_2^0 M} = x_2 - x_2^0$$

$$t_2' = \overline{M M_2^1} = x_2^1 - x_2,$$

$$I_0(M_1^0) = \mathcal{J}_0$$

$$I(M_2^0) = 0.$$

$$\frac{\partial I_0}{\partial x_1} = -(\sigma + \mu)I_0 + \sigma I$$

$$\frac{\partial I}{\partial x_2} = -(\sigma + \mu)I + \sigma I_0$$

Energy conservation besides absorption

Coherence is forgotten about

Huge problems with Xray and neutron diffraction, in particular due to rather large samples, *Unability to refine simple basic structures !*

Many applications from BC approach

We could justify parameters studying the occurrence of domains at ferro-electric transition in Rb and K dihydrogeno-phosphate, as a function of temperature

*Our Doliprane seems still to be OK. But nobody talks anymore about it.
Be aware of $H_1 N_1$*

Strong improvements due to higher source flux and therefore use of much smaller crystals

Acta Cryst. (1976). A32, 945

**Polarized Neutron Diffraction –
A Tool for Testing Extinction Models: Application to Yttrium Iron Garnet**

BY MICHEL BONNET, ALAIN DELAPALME AND PIERRE BECKER*

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$$R = \frac{I_{\uparrow\uparrow} y_{\uparrow\uparrow} + I_{\uparrow\downarrow}}{I_{\downarrow\downarrow} y_{\downarrow\downarrow} + I_{\downarrow\uparrow}}$$

If σ_{+-} is small, one can simplify as

$$R = R_k \frac{y_{\uparrow}}{y_{\downarrow}}$$

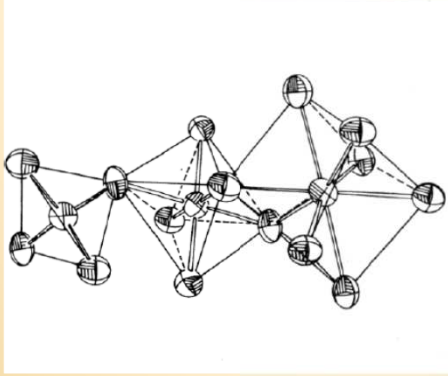
Table 4. Results for YIG-4 $6\bar{4}2$ reflexion; flipping ratio, corrected magnetic structure factor, primary and secondary extinction factor for each spin state, as functions of thickness and wavelength

Quantities in parentheses are standard deviations.

t (mm)	R	F_M Gauss	F_M Lorentz	$y_{\bar{F}}^+$	$y_{\bar{F}}^-$	$y_{\bar{S}}^+$	$y_{\bar{S}}^-$	y^+/y^-
1.00	0.784	18.24	16.13	0.96	0.94	0.45	0.36	1.27
1.10	(0.004)	(0.8)	(0.8)					
1.00	0.762	17.54	16.57	0.97	0.96	0.53	0.43	1.25
0.92	(0.003)	(0.7)	(0.7)					
1.00	0.759	16.51	16.25	0.98	0.97	0.58	0.48	1.23
0.812	(0.003)	(0.6)	(0.6)					
0.3	0.711	16.62	17.27	0.96	0.94	0.71	0.61	1.19
1.10	(0.004)	(0.5)	(0.5)					
0.3	0.671	16.43	17.30	0.98	0.97	0.82	0.73	1.13
0.812	(0.003)	(0.4)	(0.4)					
0.3	0.669	16.07	16.91	0.98	0.97	0.84	0.77	1.11
0.74	(0.003)	(0.4)	(0.4)					
0.3	0.637	16.32	16.84	0.99	0.99	0.92	0.88	1.06
0.5	(0.003)	(0.3)	(0.3)					
powder	0.608	16.65	16.65	1	1	1	1	1
1.104	(0.005)	(0.4)	(0.4)					

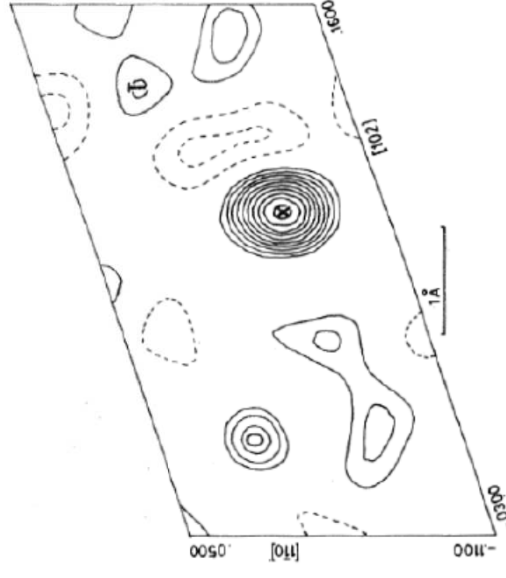
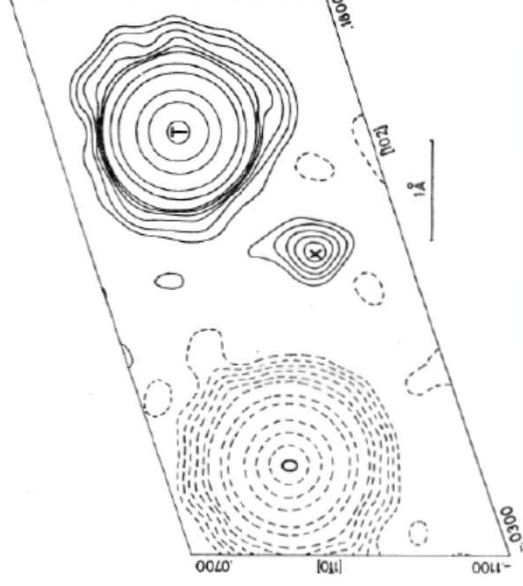
Polarized neutron study of covalency in YIG

M. Bonnet, A. Delapalme, H. Fuess, P. Becker



J. Phys. Chem. Solids, 40, 863 – 876, 1979

Spin density in the $\text{Fe}_0 - \text{O} - \text{Fe}_T$
plane: contours $.02 \mu_B$



Deformation spin density

Norio Kato (1923–2002)



Extinction is like cold: everybody suffers from it, but very few die from it !

I do hope that studies about « extinction cold » in pathological labs will connect with reliable prescription of home doctors to crystallographers and they will then enjoy their better life in crystallography

Conversion from Darwinism to Katolicism

BALHADDad in the world of Physics Equations de Takagi

Norio Kato made key studies which were the basis of the work performed with Mostafa Al Haddad

$$\begin{aligned}\partial D_0 / \partial s_0 &= i\kappa_{-h} \varphi(s_0, s_h) D_h(s_0, s_h) \\ \partial D_h / \partial s_h &= i\kappa_h \varphi^*(s_0, s_h) D_0(s_0, s_h),\end{aligned}$$

$$\kappa_h = \frac{1}{\Lambda}$$

$$\varphi(s_0, s_h) = \exp(2\pi i \mathbf{h} \cdot \mathbf{u}),$$

$$E = \langle \varphi(s_0, s_h) \rangle$$

Long range order parameter,
static Debye Waller factor

$$E = \exp \left[- (2\pi^2/3) h^2 \langle u^2 \rangle \right],$$

Could be applied to eigen Bloch states of disordered solids

We must try to maximize the effect of our interaction with humans (each being perfect if fully isolated). But we should keep in mind the mosaicity of human population

