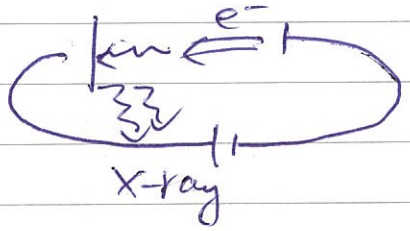
General Consideration of Scattering expt.

Photons, neutrons & electrons are three types of particles widely used in scattering expts. Their characteristics are different:

	X-ray	neutron	electron
charge	0	0	$-e$
mass	0	1.67×10^{-27} kg	9.11×10^{-31} kg
E (typical)	12 keV	0.02 eV (thermal)	60 keV
λ	1 Å	2 Å	0.05 Å
attenuation length	100 μm	5 cm	1 μm

The x-ray scattering is the one that is mostly common used. It only interacts with electrons. Early generation of X-ray is by the collision of electrons with a metal. However, in this generation, 99% of energy is dissipated in heat.



For monochromatic X-ray, the obtained power is less than 10 W.

In the modern X-ray scattering expt, one uses X-ray generated by a synchrotron. The power can go to 1000 W, or even more.

- neutrons: interact with nuclei & (weakly with) electron spins
  - Can probe magnetic structures of the materials.
  - Can be elastic or inelastic
  - ⇒ hence can probe phonons.

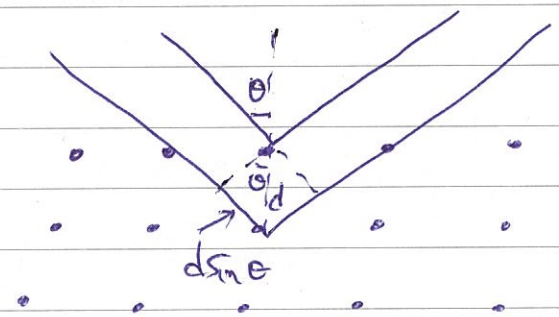
- electrons: interact strongly with matter. (electron diffraction)
  Because it's too strong, it's easily getting multiple collisions, unless the sample is ≲ 100 Å. (& damage the sample) electrons interact with nuclei & e^- with electrostatic potentials.
  Experiments are usually performed in a transmission electron microscope (TEM) or a scanning " " (SEM) back-scattered secondary e

We will focus on X-ray scattering here.

X-ray scattering from crystals

Why there are peaks? (Hints: U.H. & Laue, Bragg)

Bragg formulation



Bragg interpreted peaks by regarding a crystal as made out parallel planes

θ = incident angle

d = distance between planes

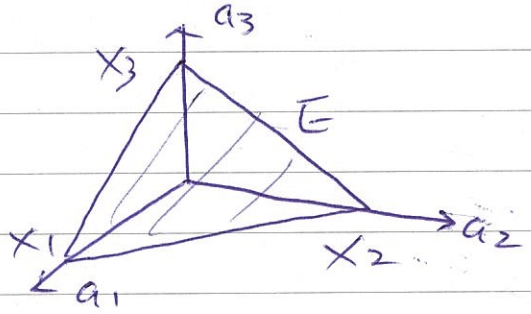
Peaks result from constructive interference.

$\therefore 2d\sin\theta = n\lambda$ (Bragg condition)

Characterization of lattice planes, directions:

Miller indices

(i)



$\frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3} = h : k : \ell$

(integers with no common factors)

E is represented by (h, k, ℓ) (the family of planes $\perp E$)

for negative integer use $\bar{n}$ to represent $-n$

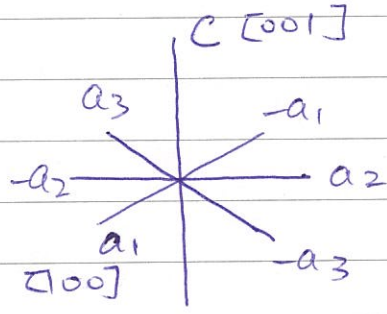
(ii) direction $[\ell\ m\ n]$

e.g. $[100]$ $[010]$ $[001]$ $[\bar{1}00]$ $[0\bar{1}0]$ $[00\bar{1}]$ collectively $\langle 100 \rangle$

planes : (100) (010) (001) collectively as $\{100\}$.

Hexagonal systems are indexed differently:
(Bravais-Miller index)

4 axes: to reflect the symmetry among a_1, a_2, a_3, one adds one more

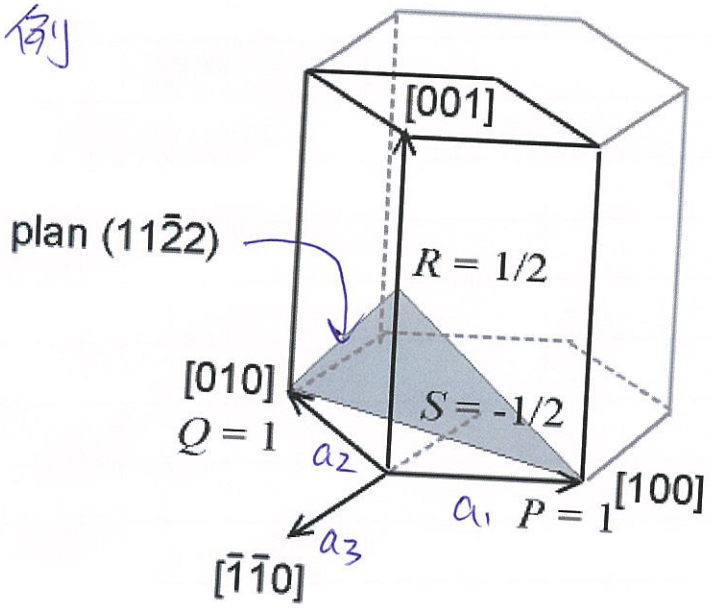


(h, k, i, ℓ)
a_1 a_2 ↑ C

$i = -h-k$ = redundant index

$= \frac{1}{s}$, s = intercept of the plane with $\vec{a_3}$

例



Indexed by this method, it would reflect symmetry easier:

Miller indices
(110) (1$\bar{1}$0)
($\bar{1}$10) are ~~3-sym.~~
3 planes (∥ C axis)
that are symmetric

⇒ (11$\bar{2}$0) (1$\bar{1}$10) ($\bar{1}$110) in Bravais-Miller index exhibit the symmetry more explicitly.

Lattice planes & reciprocal lattices

Since any plane can be expressed as

$\vec{K} \cdot \vec{r} = \text{const.} = A$,

If one write $\vec{K}$ in terms of reciprocal primitive vectors $\vec{g}_1$, $\vec{g}_2$ & $\vec{g}_3$,

$$\vec{K} = l\vec{g}_1 + m\vec{g}_2 + n\vec{g}_3$$

We find that for interceptions, $\vec{r} = x_1\vec{a}_1$, $x_2\vec{a}_2$ or $x_3\vec{a}_3$, $\vec{K}\cdot\vec{r} = 2\pi l x_1$, $2\pi m x_2$, or $2\pi n x_3$

$\vec{K}\cdot\vec{r}$ = Const

$\therefore l : m : n = \frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3} = h : k : l$

Given a family of parallel planes, d = distace between successive plane, we can form $e^{i\vec{K}\cdot\vec{r}}$ with

$\vec{K} = \frac{2\pi}{d}\hat{n}$, $\hat{n} \perp$ planes. $e^{i\vec{K}\cdot\vec{r}}$ = const on each plane.

Since $\vec{K}\cdot\vec{r} = Kd = 2\pi$ for successive planes, $e^{i\vec{K}\cdot\vec{r}}$ has the same value on all planes. Now, one of the plane contains $r=0$, $\therefore e^{i\vec{K}\cdot\vec{r}} = 1$ for all planes, i.e., all $\vec{R}$! $\therefore \vec{K}$ is a vector in reciprocal vector space with l, m & n being integers!

$\therefore$ Miller index $[h,k,l]$ is also the normal vector to the plane and a vector in reciprocal lattice!

Laue's condition & Lattice sum

The Bragg condition can be better understood by using the lattice sum.

$$I = I_0 \left| \sum_i e^{i\vec{q}\cdot\vec{r}_i} \right|^2$$

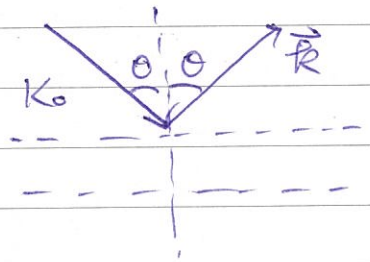
if $e^{i\vec{q}\cdot\vec{r}_i} = 1$ for all i, the I is maxium & $I = N^2 I_0$!

The $e^{i\vec{q}\cdot\vec{r}_i} = 1$ for all r_i, implies $\vec{q} =$ reciprocal lattice vector $\vec{K}$!

i.e. $\vec{k}_0 - \vec{k} = \vec{K}$ = reciprocal lattice vector

This is known as Laue's condition for peaks.

Apparently, it is equivalent to the Bragg condition in the elastic scattering: $k_0 = k = \frac{2\pi}{\lambda}$



$$2k\sin\theta = K = \frac{2\pi}{d} \times n$$

$$\therefore 2d\sin\theta = n\lambda$$

Lattices with identical atoms

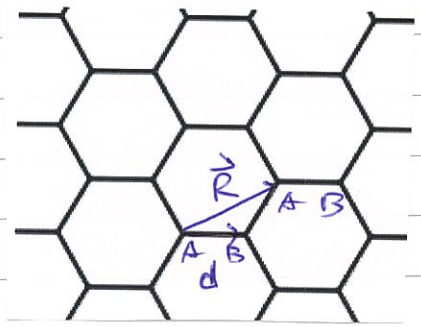
This is the case we have been discussed so far.

The position of each atom can be written as

$$\vec{r}_i = \vec{R}_i + \vec{d}_j$$

$\vec{R}_i$ = a vector in the Bravais lattice,
$\vec{d}_j$ = a vector describing atoms in the basis

example :



Then, $$\sum_i e^{i\vec{q}\cdot\vec{r}_i} = \left(\sum_i e^{i\vec{q}\cdot\vec{R}_i}\right)\left(\sum_j e^{i\vec{q}\cdot\vec{d}_j}\right)$$

$$I = I_0 \left|\sum_i e^{i\vec{q}\cdot\vec{R}_i}\right|^2 |F_q|^2$$

F_q = geometrical structure factor.

In general, if atoms in the basis are not identical, one includes the <u>atomic form factor</u> f_j. then

$$F_q = \sum_j f_j e^{i\vec{q}\cdot\vec{d}_j}$$

f_j is essentially the scattering contribution from atom (ion) j, it also depends on $\vec{q}$.

$$f_j = f_j(q) = -\int dr\, e^{i\vec{q}\cdot\vec{r}}\, n_j(\vec{r})$$

$n_j(\vec{r})$: electron density in jth atom/ion.

It is clear that the intensity I is determined by two factors: $\sum_i e^{i\vec{q}\cdot\vec{R}_i}$ & F_q

Both Bragg's condition & Laue's condition only deal with $\sum_i e^{i\vec{q}\cdot\vec{R}_i}$. Therefore, they predict all peaks are equally strong! Obviously, the introduction of basis induces F_q so that Bragg's peaks are no longer the same and are proportional to $|F_q|^2$!

In the extreme case, it's also possible that $F_q = 0$ for some q and the Bragg peak completely disappear. This is known as extinction.

* Note that a good analogy of effects due to $\sum_i e^{i\vec{q}\cdot\vec{R}_i}$ & F_q is the interference pattern of two slits with finite width where width induces change in the peak heights.

Example of Lattice sum $\sum_i e^{i\vec{q}\cdot\vec{R_i}}$.

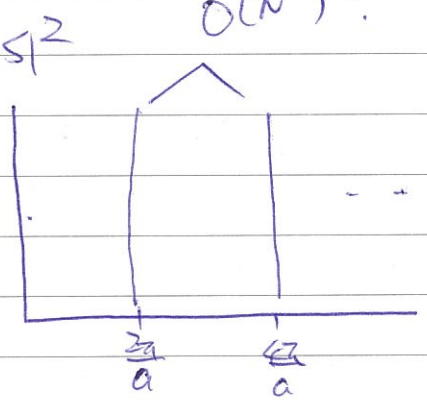
1D lattice

$$\sum_i e^{i\vec{q}\cdot\vec{R_i}} \rightarrow S \equiv \sum_{n=0}^{N-1} e^{inaq}$$

$$e^{iaq} S = \sum_{n=1}^{N} e^{inaq}$$

$$\therefore S = \frac{1 - e^{iNaq}}{1 - e^{iaq}} \qquad |S|^2 = \frac{\sin^2 \frac{Naq}{2}}{\sin^2 aq/2}$$

$\frac{aq}{2} = n\pi$ $\quad |S|^2 = N^2$ ↑ enhancement due to crystalization!

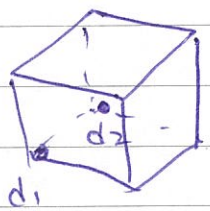


$N \rightarrow \infty$ $\quad \sum_n e^{inaq} \cong \sum_K N \frac{2\pi}{L} \delta\left(q - \frac{2\pi K}{a}\right)$ very sharp peaks

(different from peaks in liquid ...)

example : BCC = Simple cubic with a basis

$d_1 = 0 \qquad d_2 = \left(\frac{a}{2}, \frac{a}{2}, \frac{a}{2}\right)$



$$F_q = 1 + e^{i\vec{q}\cdot\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})}$$

$\vec{q} = \frac{2\pi}{a}(l\hat{x} + m\hat{y} + n\hat{z})$ (Simple cubic)

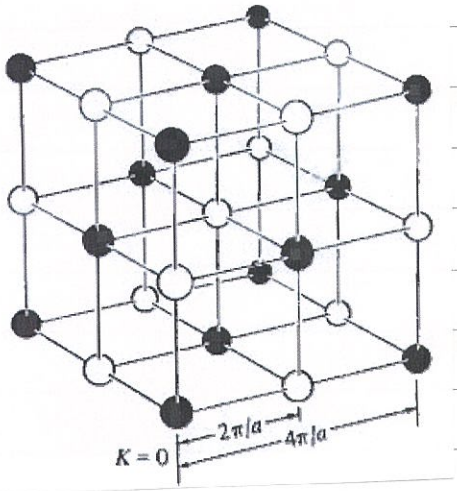
$\therefore F_q = 1 + e^{i\pi(l+m+n)} = 1 + (-1)^{l+m+n}$

$\therefore$ $\ell+m+n$ = odd , $F_g = 0$

= even $F_g = 2$

Simple cubic (reciprocal lattice) then becomes fcc. → see right

One can also treat the BCC as a Bravais lattice and recover the result directly.



The disappearing of peaks is due to the choice of representing the crystal as a lattice with bases.

It is therefore not extinction.

example : diamond lattice (fcc)

$\vec{d}_1 = (0,0,0)$, $\vec{d}_2 = \frac{a}{4}(1,1,1)$

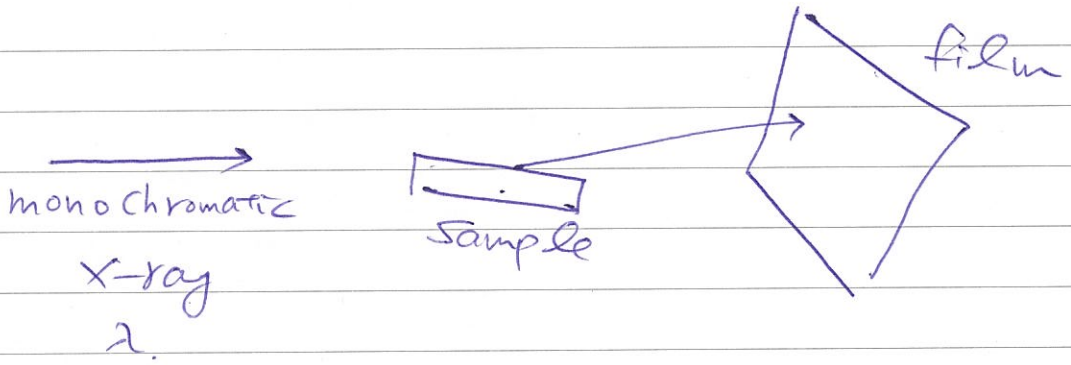
$\vec{g}_1 = \frac{2\pi}{a}(-1,1,1)$, $\vec{g}_2 = \frac{2\pi}{a}(1,-1,1)$, $\vec{g}_3 = (1,1,-1)$ (bcc)

$F_g = 1 + e^{\frac{i\pi}{2}(\ell+m+n)} = \begin{cases} 2 & \ell+m+n = 4n \\ 1 \pm i & \ell+m+n = \text{odd} \\ 0 & \ell+m+n = 2(2n+1) \end{cases}$

extinctions →

Experimental methods

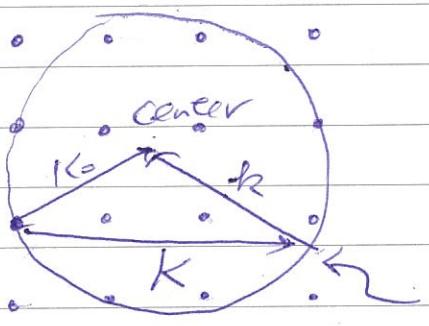
From Bragg's condition, it may seem to be straightforward to perform the expt: (& Laue's)



After some reflection, this clearly doesn't work and can be sumarized by the Ewald construction:

$\vec{K_0} - \vec{k} = \vec{K}$ = reciprocal lattice vector

$K_0 = k$



circle at reciprocal lattice space

Ewald sphere

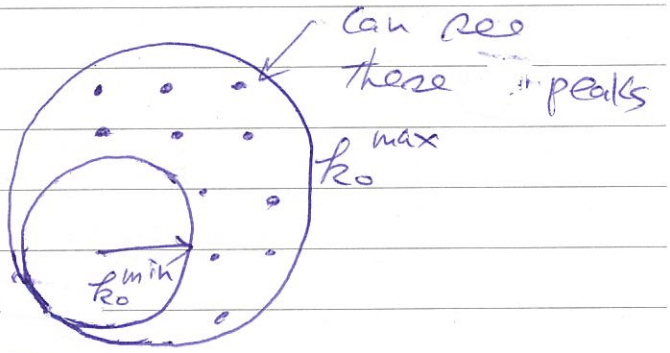
K is not necessarily a reciprocal lattice vector! not a lattice point

3 solutions :

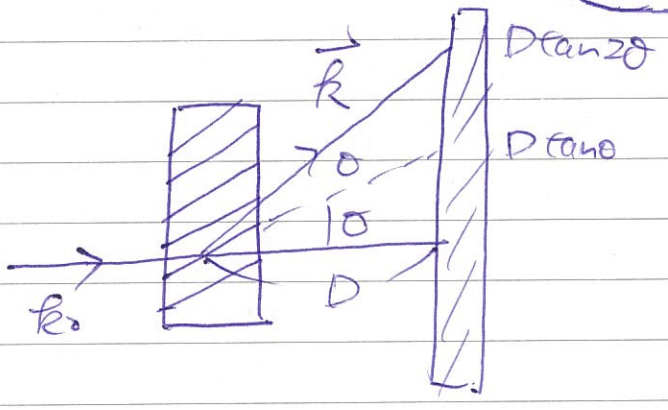
(i) Laue method

Using continuous spectrum of x-ray.

Bremsstrahlung with tungsten anode.



then, $k_0^{min} \leq k_0 \leq k_0^{max}$

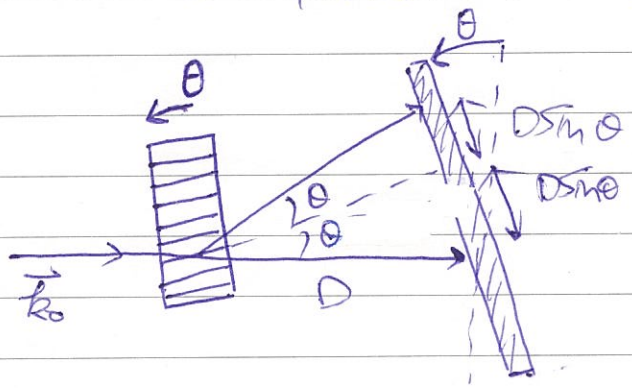


disadvantage : there are intensity variation for I_0, it would then be difficult to pin down the intensity changes due to $|F_g|^2$

but this is a good way to orient the sample with known lattice parameters.

(ii) rotating crystal method

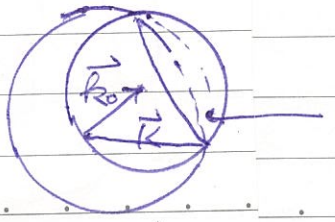
In contrast to change magnitude of $\vec{k}_0$, one can rotate $\vec{k}_0$ or equivalently rotate the sample. Then reciprocal lattice vectors can go across Ewald sphere and be observed



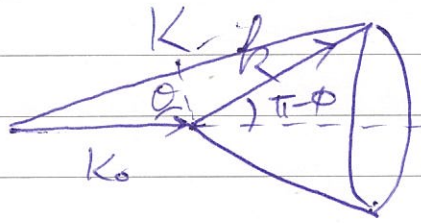
(iii) Powder Method (Debye-Scherrer Method)

By making the sample into small crystals with all possible orientation, effectively the crystal is rotated via all angles.

Hence while $\vec{k}_0$ is fixed, reciprocal lattice vector $\vec{K}$ is rotated and becomes another sphere. Their interception is a ring:



Therefore, each K generates a cone



$K = 2k \sin \Phi/2$

$= 2k \sin\theta$

+ lattice parameters (such as lattice constant a..)

Using these informations (magnitudes of K), one can often construct the reciprocal lattice and then the real lattice (Bravais), (not resolve basis)

In practice, one finds the crystal structure using x-ray from synchrotron. The initial crystal orientation is usually chosen such that $\vec{K}_0 \perp$ one of facets in the well-formed sample.

From the preliminary data, one tries to determine allowed symmetry & unit-cell dimensions. Then one determines what the following angle to be rotated.

In the process of identifying the lattice symmetry (cubic, tetragonal, orthorhombic, ...), it is essentially a trial-and-error process.

→ then one uses information: density, chemical composition

determine # of atoms in each unit cell

→ find positions of atoms using relative intensities of diffraction lines.

X-ray phase problem

As mentioned, what is probed by scattering expt is the correlation function.

In x-ray scattering expt, the obtained data are $I(\vec{q}) = I_0 \langle n(\vec{q}) n(-\vec{q}) \rangle = I_0 \langle |n(\vec{q})|^2 \rangle$. not $n(\vec{q})$ itself! ~~but $|n(\vec{q})|$~~!

If we perform Fourier transformation,

we get: $\because I(\vec{q}) = I_0 \int d\vec{r}_1 \int d\vec{r}_2 \, e^{i\vec{q}\cdot(\vec{r}_1 - \vec{r}_2)} \langle n(\vec{r}_1) n(\vec{r}_2) \rangle$

$= I_0 \int d\vec{R} e^{i\vec{q}\cdot\vec{R}} \int d\vec{r}_1 \langle n(\vec{r}_1) n(\vec{r}_1 - \vec{R}) \rangle$

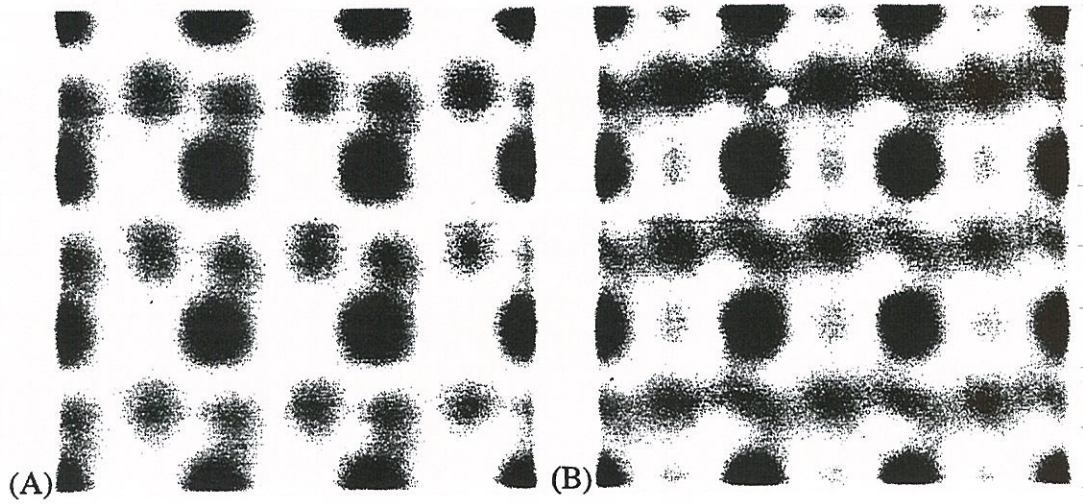
$\therefore I(\vec{R}) \equiv \int I(\vec{q}) e^{-i\vec{q}\cdot\vec{r}} \propto \int d\vec{r}_1 \langle n(\vec{r}_1) n(\vec{r}_1 - \vec{R}) \rangle$

Which is the correlation of density $n(r)$, not directly the data of $n(r)$!

The problem can be traced because we measure $|n(\vec{q})|$ not $n(\vec{q})$ itself!

If we can ... determine the phase of $n(\vec{q})$, (i.e., measuring the electric field, not the intensity), then $n(\vec{q})$ is known so that $n(\vec{r})$ can be exactly constructed! This is known as the x-ray phase problem.

In practice, one can device a known structure and compare $I(R)$ with $n(R)$. (see below) They may differ a lot.



However, if one can include a heavy atom into the crystal while the crystal structure is not changed, one can use it to pin down positions of other atoms! This is usually done in determining the protein structure. Its reason can be easily understood by putting the heavy atom at $r=0$, then $I(\vec{R}) \sim \int dr_1 n(r_1) n(r_1-R) >$

$\sim \langle n(0) n(-R) \rangle + \langle n(R) \cdot n(0) \rangle$

$\sim n(0) \langle n(R) \rangle \propto$ density of atoms!

Neutron scattering and magnetic structure

Neutrons don't carry net charge but carries spin. Therefore, their scatterings are mainly due to nuclei & magnetic structures of electrons. The scatterings from nuclei can probe phonons and we will discuss it later.

For probing magnetic structures due to spins, of electrons, we have

$$\vec{\mu}_e = -2\mu_B \vec{S}_e \qquad \mu_B = \frac{e\hbar}{2m_e}$$

$$\vec{\mu}_n = -g_n \mu_N \vec{S}_n, \qquad \mu_N = \frac{e\hbar}{2m_n}$$

$$= -\gamma \mu_N \vec{\sigma}_n \qquad \vec{\sigma}_n = \text{Pauli matrix}$$

$$\gamma = g_n/2 = 1.913$$

The magnetic field due to μ_e is

$$\vec{B} = \vec{\nabla} \times \vec{A}_e = \frac{\mu_0}{4\pi} \vec{\nabla} \times \left[\vec{\mu}_e \times \nabla \frac{1}{r}\right]$$

$$\vec{A}_e = \frac{\mu_0}{4\pi} \vec{\mu}_e \times \nabla \frac{1}{r}$$

$$\therefore H = -\vec{\mu}_n \cdot \vec{B} = \frac{-\mu_0}{4\pi} (2\gamma \mu_N \mu_B) \vec{\sigma}_n \cdot \left[\vec{\nabla} \times \left(\vec{S}_e \times \nabla \frac{1}{r}\right)\right]$$

$\therefore$ For a single electron spin, one has

$$I \propto |H(\vec{q})|^2 \propto \left| \frac{1}{q^2} \vec{\sigma}_n \cdot \underbrace{\vec{q} \times (\vec{S}_e) \times \vec{q}}_{\vec{S}_e^{\perp} \text{ (only components transverse to } \vec{q} \text{ contribute}} \right|^2$$

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For many spins, $\frac{1}{r} \to \left|\frac{1}{r-r_i}\right|$, each $\vec{S}_e$ is associated with a phase factor $e^{-i\vec{q}\cdot\vec{r}_i}$.

$$\therefore I \propto \left\langle \left| \frac{1}{q^2} \vec{\sigma}_n \cdot \vec{q} \times \underbrace{\left(\sum_i \vec{S}_i e^{-i\vec{q}\cdot\vec{r}_i} \right)}_{\vec{A}} \times \vec{q} \right|^2 \right\rangle$$

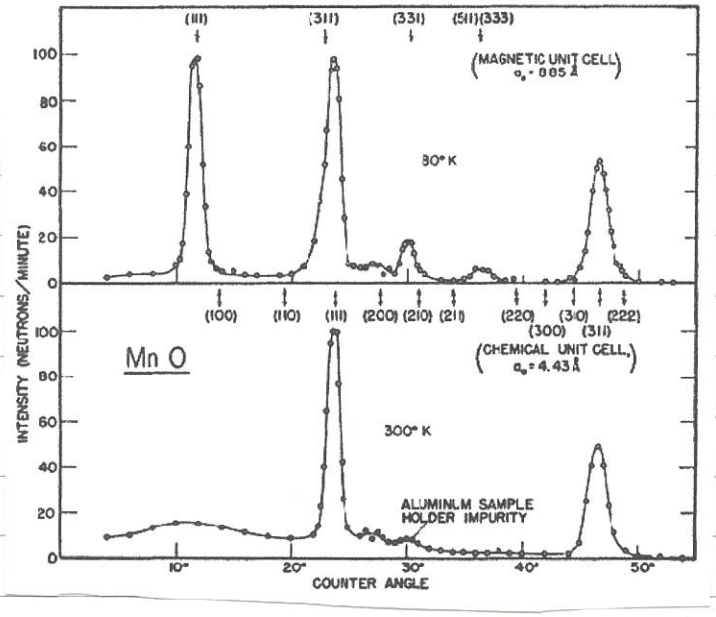
$$\propto \langle \vec{S}^{\perp}_{\vec{q}} \cdot \vec{S}^{\perp}_{\vec{q}} \rangle \quad \text{for unpolarized neutrons:}$$

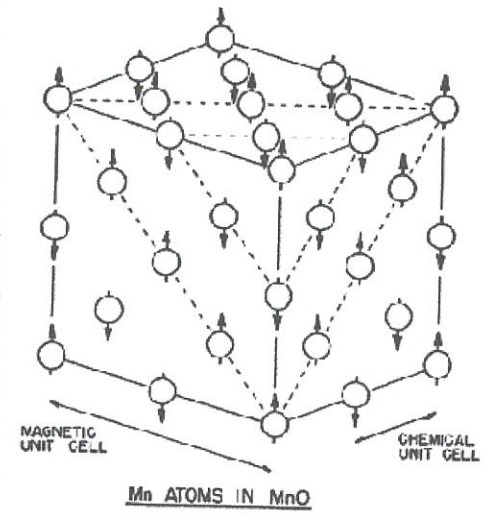
$$\langle \sigma_n^{\alpha} \sigma_n^{\beta} \rangle = \delta_{\alpha\beta}$$

$$\langle \sigma_n^{\alpha} A_{\alpha} \sigma_n^{\beta} A_{\beta} \rangle = \langle A_{\alpha} A_{\alpha} \rangle$$

This is the case of elastic scattering.

Using neutron scatterings, in 1948, Clifford Shull (Phys. Rev. 76, 1256, 1948 & 83, 333, 1951) first confirmed so-called antiferromagnetic structure in MnO. In general, magnetic structures have their own symmetry groups, known as magnetic space groups.





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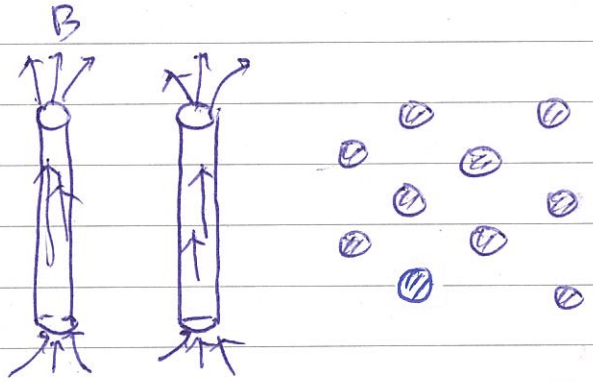
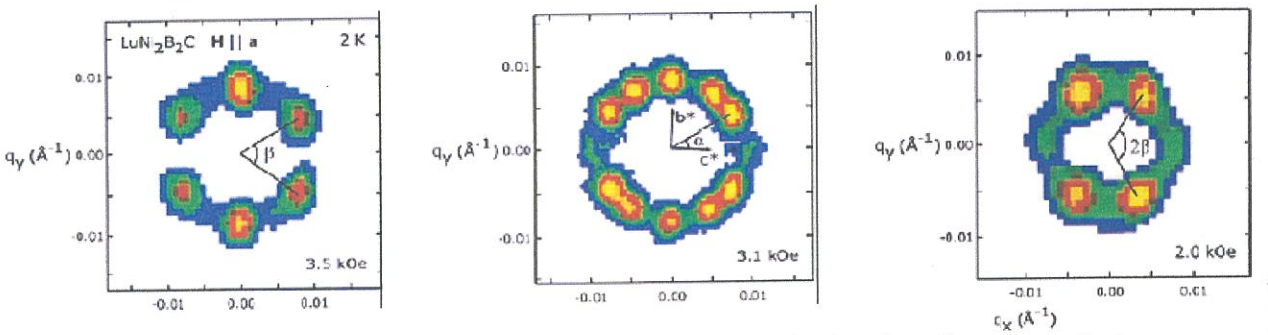
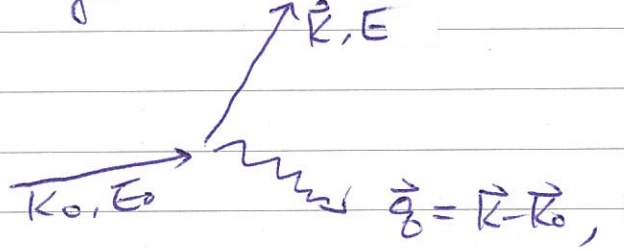
In addition to electron spins, neutrons can also probe magnetic fields. For example, vortices in superconductors form a lattice:





Small angle neutron diffraction patterns from flux lines lattice in a type-II superconductor
Note that the structure of the flux line lattice changes as a function of magnetic field
(M.R. Eskildsen et al., PRL 86, 320 (2001))

Inelastic scattering: In addition to elastic scattering, neutrons can also excite the system and loose energy during scattering



Clearly, in this case, one has to replace $\vec{S}_i e^{-i\vec{q}\cdot\vec{r}_i}$ by $\vec{S}_i e^{i(\omega t - \vec{q}\cdot\vec{r}_i)}$

For unpolarized neutrons,

$$I = I(q,\omega) \propto \langle \vec{S}_\perp(\omega,\vec{q}) \cdot \vec{S}_\perp(\omega,\vec{q}) \rangle$$

Dynamical correlation function & dynamical spin susceptibility

Since $\langle S^\alpha(\omega,\vec{q}) S^\beta(\omega,-\vec{q})\rangle = \int dt \frac{1}{N} \sum_{R_{ij}} \langle e^{-i\vec{q}\cdot\vec{R}_{ij}} S_i^\alpha(0) S_j^\beta(t)\rangle e^{i\omega t}$,

$S^{\alpha\beta}(\omega,q)$

what is probed in inelastic neutron expts is the dynamical correlation function

$$\langle S_i^\alpha(t) S_j^\beta(t')\rangle.$$

The dynamical correlation function is related to the dynamical susceptibility (response function) χ defined by

$$\langle S_i^\alpha(t)\rangle = \int dt' \sum_{j\beta} \chi_{ij}^{\alpha\beta}(t-t') B_j^\beta(t')$$

χ: dynamical susceptibility

via the so-call fluctuation–dissipation theorem

$$S^{\alpha\beta}(\omega,q) = \frac{1}{\pi} \frac{\mathrm{Im}\,\chi^{\alpha\beta}(\omega,q)}{1 - e^{\hbar\omega\beta}}$$

We shall defer the detailed discussion on this theorem later.

X-ray magnetic scattering and inelastic X-ray scattering (IXS)

Light also interacts with magnetic structures via the interaction:

$$-\vec{\mu}\cdot\vec{B} = -\vec{\mu}\cdot\vec{E}\times\vec{v} = -\frac{e\hbar}{2mc}\vec{s}\cdot\vec{E}\times\frac{(\vec{p}-e\vec{A}/c)}{mc}$$

$$\rightarrow \frac{(e/c)^2}{2m^2c^2}\vec{s}\cdot\dot{\vec{A}}\times\vec{A} = V_m$$

(the other terms $-\vec{\mu}\cdot\vec{B} = -\frac{e\hbar}{2mc}\vec{s}\cdot\vec{v}\times\vec{A}$)

Charge interaction: $\frac{1}{2m}(\vec{p}-\frac{e}{c}\vec{A})^2$

$$\rightarrow \frac{-e}{mc}\vec{A}\cdot\vec{p} \;\&\; \boxed{\frac{e^2}{2mc^2}A^2} \equiv V_e$$

$$\frac{V_m}{V_e} \sim \frac{\hbar\omega}{mc^2} \sim 10^{-3} \quad \text{for } \hbar\omega \sim 6000\,V$$

$$\therefore \frac{I_m}{I_e} \sim 10^{-6}$$

∴ Typical direct magnetic X-ray scattering is small. However with high intensity provided by synchrotron, it is still possible to do magnetic X-ray scattering. In addition to direct scattering, resonant scattering & inelastic scattering (IXS) are also possible and being developed.