

ANALYTICAL TECHNIQUES (PH 517)

1. Xray & electron diffraction : basic theory, how to analyze data.
Crystals, powder, thin film,
Reciprocal space map
Neutron diffraction, briefly
diffraction
2. Spectroscopic methods : Basic theory, how does the data look?
How to extract relevant information?
Scattering and the dynamic structure factor.
Raman, Infra-red
Photoemission spectra (ESCA/XPS, UPS)
Auger electron spectra
Angle resolved photoemission (ARPES)
Inverse Photoemission process
spectroscopy
3. NMR and ESR : Analysing simple spectra:
Chemical shifts, Splitting of lines.
How to analyse molecular structure
Magic angle spinning.
resonance
4. Synchronous detection, PID Control, FFT & spectrum analysis.
signal processing

HOW DO EXPERIMENT AND THEORY TALK TO EACH OTHER ?

1 + 1 + 1 hrs per week. (Lecture + data analysis) SLOT 2

2 x Quiz + Midsem + Endsem + Term Paper (?)
2x15 + 20 + 40 + 10 (approx weightage)

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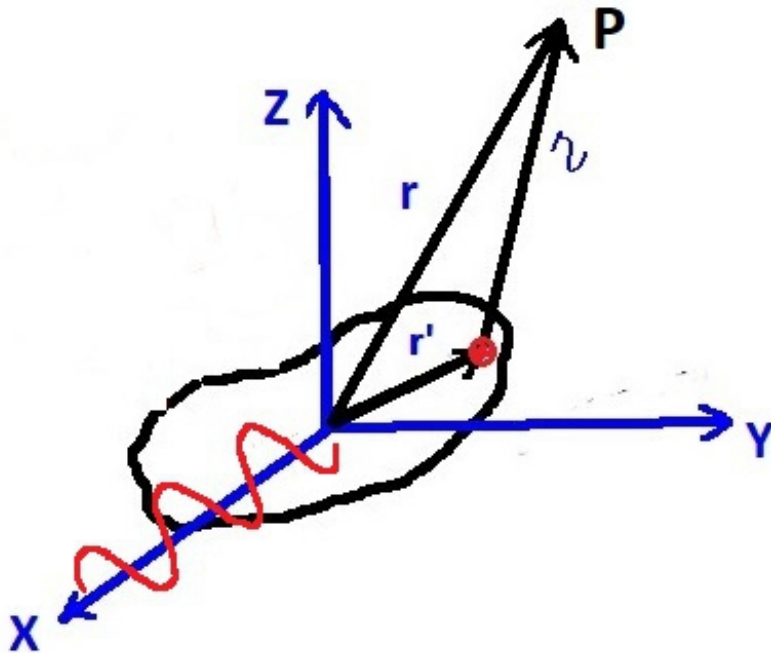
WHAT ARE YOU EXPECTED TO BE ABLE TO DO ALREADY ?

1. Quantum Mechanics at the level of QM-2 as taught here
2. Electromagnetic Theory at a better level than the first year course!
3. Basic understanding of Fourier Analysis and related mathematical methods
4. It helps if you can do a bit of numerical analysis, write your own little codes!
5. Have a sense of order of magnitude of various quantities.

1. X-ray diffraction

Electromagnetic wave incident on a free electron: What happens ?

1. Electron may absorb some energy and a wave (photon) of a different energy goes out : Compton scattering.
2. The electric field makes the electron oscillate (accelerate). It radiates at the same frequency and phase. Elastic scattering.
3. The elastic scattering from many sites can interfere. Inelastic collisions cannot give rise to interference, coherence.



Radiation falls on a localized charge distribution.

What is the electric field at P, a far away point $r \gg r'$?

Radiation from an accelerated charge driven by incident EM wave

Instantaneous Dipole moment defined as

$$\vec{p}(t_0) = \int d\vec{r}' \vec{r}' \rho(\vec{r}', t_0)$$

Revise the concept of retarded potential as applied to calculating radiation.

$$\vec{E}(\vec{r}, t) = \frac{\mu_0}{4\pi r} [(\hat{r} \cdot \ddot{\vec{p}})\hat{r} - \ddot{\vec{p}}]$$

$$\vec{B}(\vec{r}, t) = -\frac{\mu_0}{4\pi r c} [\hat{r} \times \ddot{\vec{p}}]$$

What happens if we assume

$$\ddot{\vec{p}} = \alpha \vec{E}_0 \cos \omega t$$

For a free particle : $\ddot{\vec{p}} = q \ddot{\vec{x}} = \frac{q^2}{m} \vec{E}_0$

Two polarisations: the E field can be either along y or z.

$$\vec{E}_I = \frac{\mu_0 q^2}{4\pi m} E_{0Z} \left(\frac{\sin \theta}{r} \right) \hat{e}_\theta$$

$$\vec{E}_{II} = -\frac{\mu_0 q^2}{4\pi m} E_{0Y} \left(\frac{\cos \theta \sin \phi}{r} \hat{e}_\theta + \frac{\cos \phi}{r} \hat{e}_\phi \right)$$

When can the scattered beam be polarized?

For unpolarized incident wave : $E_{0Z}^2 = E_{0Y}^2 = \frac{E_0^2}{2}$

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Radiation from an accelerated charge driven by incident EM wave

$$E_I^2 + E_{II}^2 = \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{q^2}{m} \right)^2 \frac{E_0^2}{2} \left(\frac{1 + \sin^2 \theta \cos^2 \phi}{r^2} \right)$$

$$\sin \theta \cos \phi = \hat{i} \cdot \hat{\epsilon}_r \quad (\text{call this angle } \psi)$$

Angle between incident wavevector and scattering direction

$$I_{coherent}(\psi) = \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{q^2}{m} \right)^2 I_0 \left(\frac{1 + \cos^2 \psi}{2} \right) \frac{1}{r^2}$$

$$P_{coherent} = \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{q^2}{m} \right)^2 I_0 \int_0^\pi \left(\frac{1 + \cos^2 \psi}{2} \right) \frac{1}{r^2} 2\pi r^2 \sin \psi d\psi$$

$$P_{coherent} = \frac{4\pi}{3} \left(\frac{q^2}{4\pi\epsilon_0 mc^2} \right)^2 I_0$$

What is the dimension of the quantity in bracket?

Calculate the magnitude.

What does it tell you about the electron as a scatterer of EM radiation?

**A proton would scatter $\sim 10^6$ times less.
The scattering is independent of frequency !**

Thomson scattering and classical cross section of an electron

If we assume that the energy stored in the electron's electric field can be equated to its rest mass, we will get a number very close to this.

This is a very small length $\sim 10^{-15}$ m!!

What are these other processes that can come in to the picture?

Internal energy levels in the atom/molecule/solid....absorption edges.

When in Rayleigh scattering the correct process?

When in Mie scattering the correct process?

The correction due to (incoherent) Compton scattering:

$$\Delta \lambda = \frac{2h}{mc} \sin^2 \theta$$

$$I_e \rightarrow I_e \times \left(\frac{\lambda}{\lambda + \Delta \lambda} \right)^3$$

Rayleigh scattering : electron "bound" to an object

$$m \ddot{\vec{x}} = -m \omega_0^2 \vec{x} - e \vec{E}_0 \cos \omega t$$

$$\vec{x} = \frac{e \vec{E}_0}{m(\omega^2 - \omega_0^2)} \cos \omega t$$

Natural frequency of the system arises from binding strength.

e.g. binding to a molecule

This leads to a "Rayleigh" cross section

$$\sigma = \left(\frac{\omega}{\omega_0} \right)^4 \sigma_{Thomson} \quad (\omega \ll \omega_0)$$

An atom would scatter less than a free electron in general.

A "metal" would scatter more than an "insulator".

What would happen when natural frequency comes into picture?

How much does an atom with N electrons scatter ?

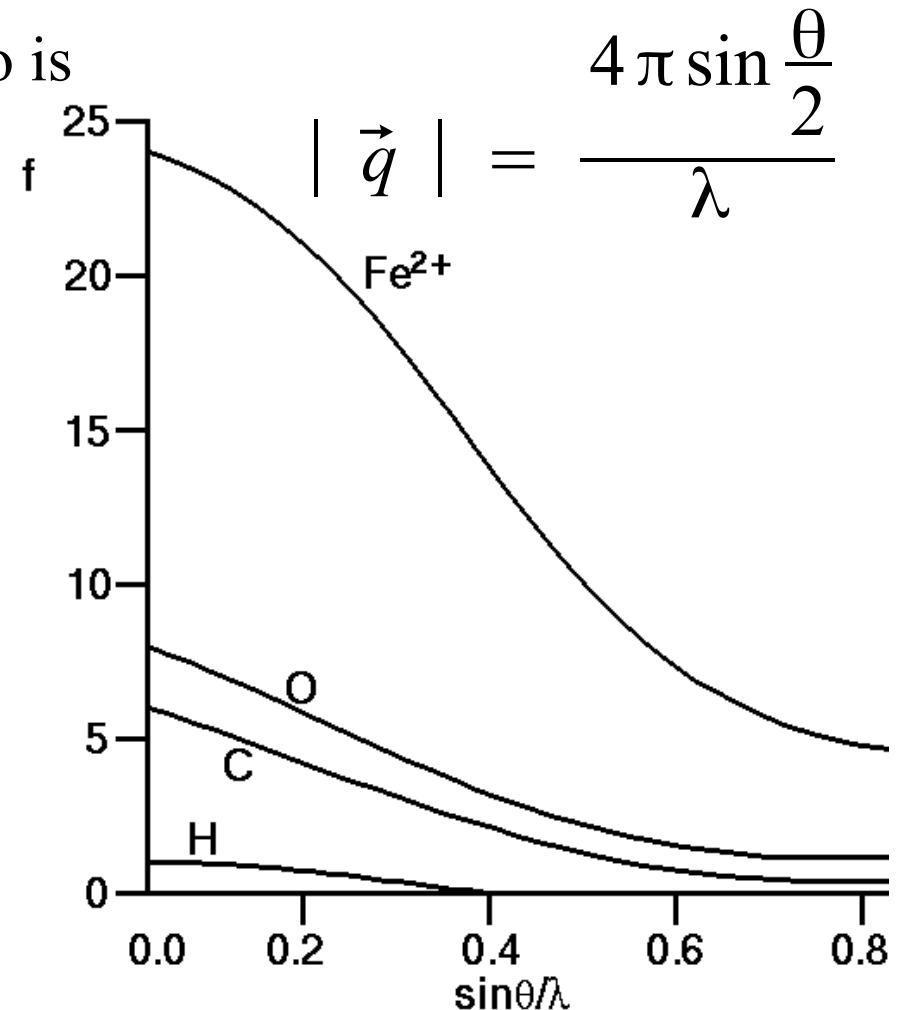
$$\text{atomic form factor} = \frac{\text{Amplitude of the wave scattered by the atom}}{\text{Amplitude scattered by a single electron}}$$

Neglecting some small correction, the ratio is

$$\frac{I_{coh}(\vec{q})}{I_e} = \left(\sum_{j=1}^N f_j \right)^2$$
$$f_j = \int \rho(\vec{r}_j) e^{i\vec{q} \cdot \vec{r}} d^3\vec{r}$$

where \vec{q} is the scattering wave vector.

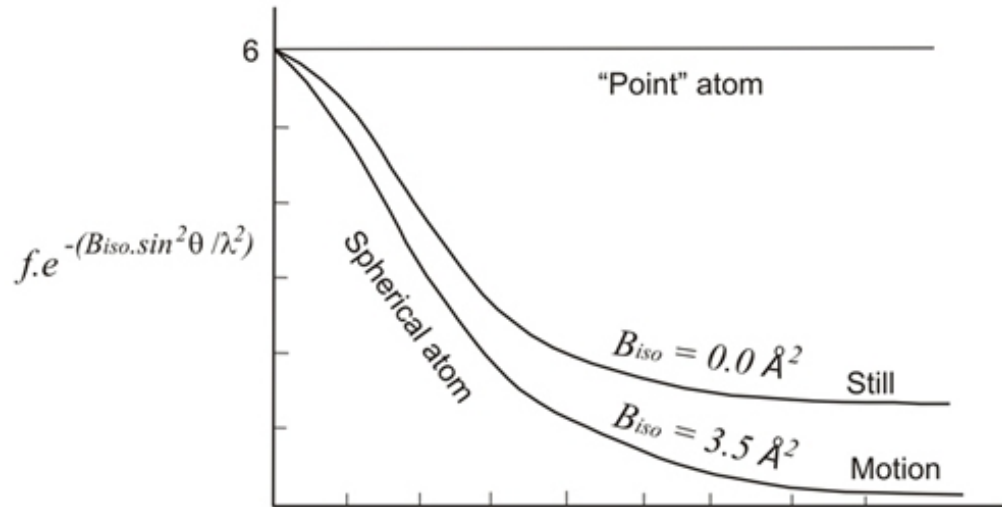
$$\text{For } \vec{q} = 0 \quad \sum_{j=1}^N f_j = N$$



This quantity is extensively tabulated.
See : International tables for crystallography
<http://it.iucr.org/Cb/ch6o1v0001/>

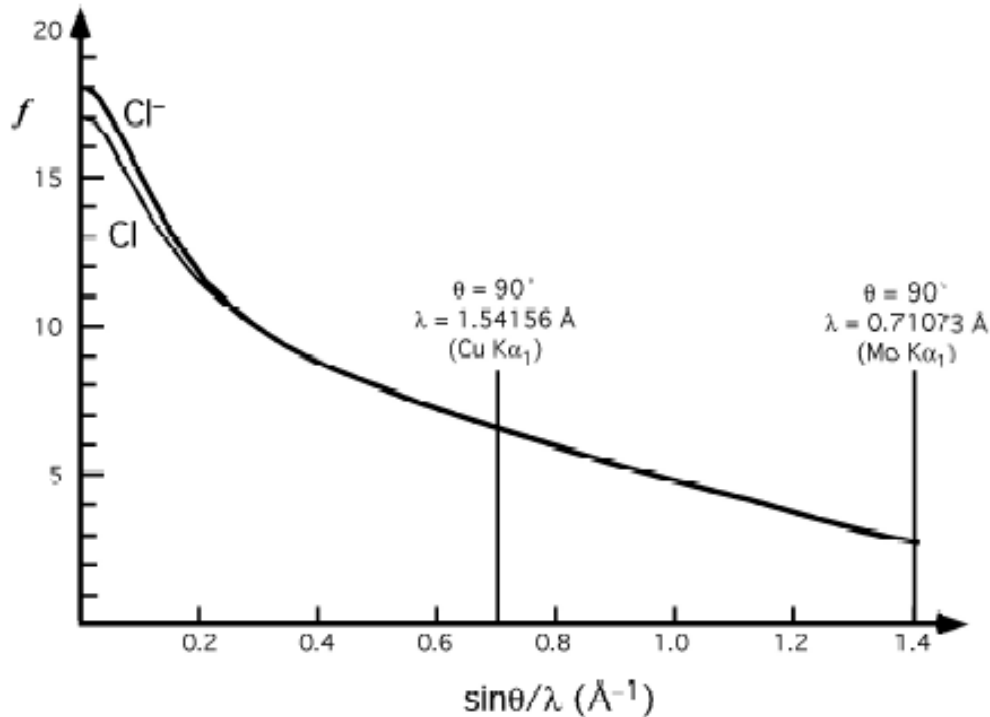
Justify the x-axis unit....

What happens if the atom is not static but vibrates ?



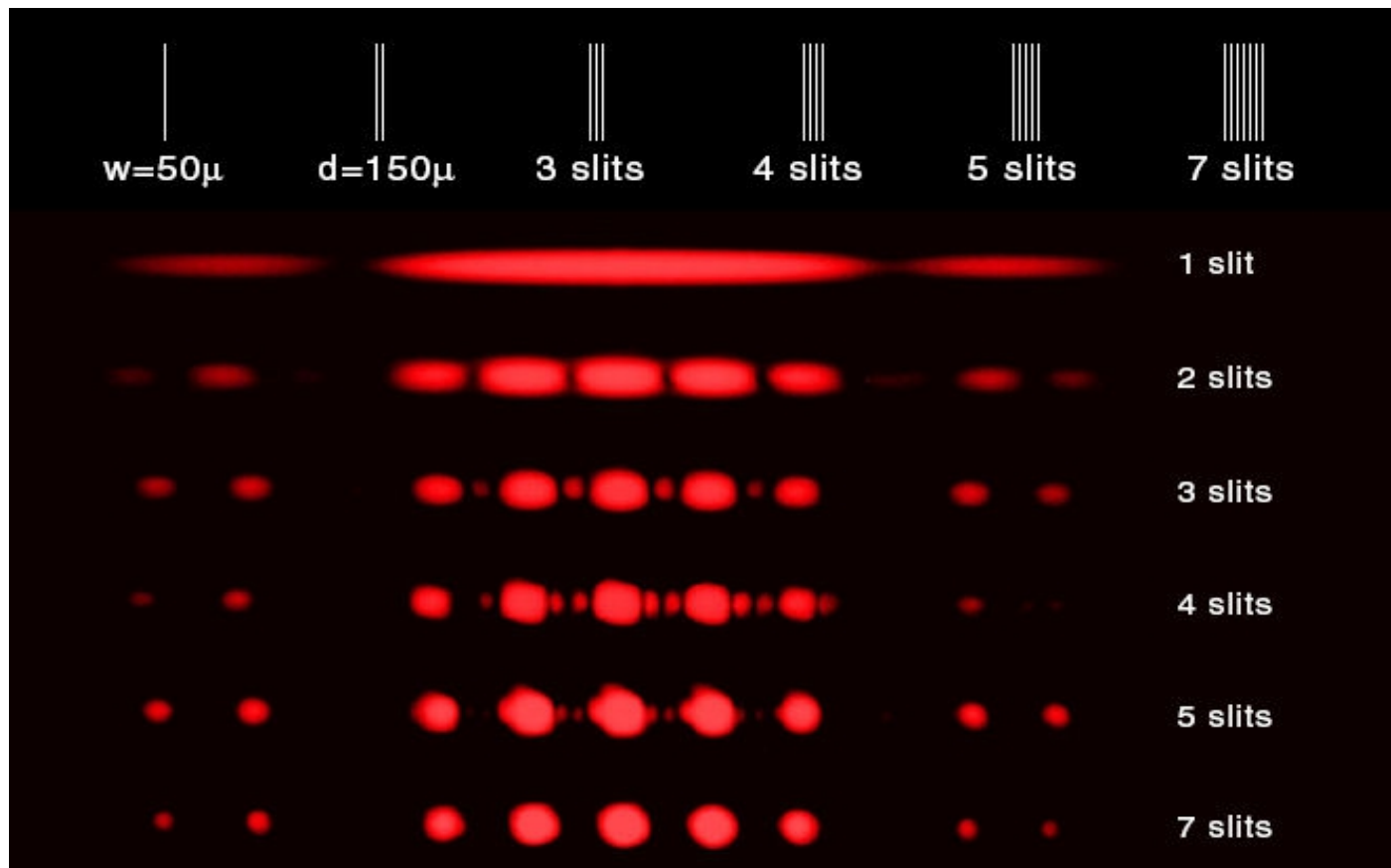
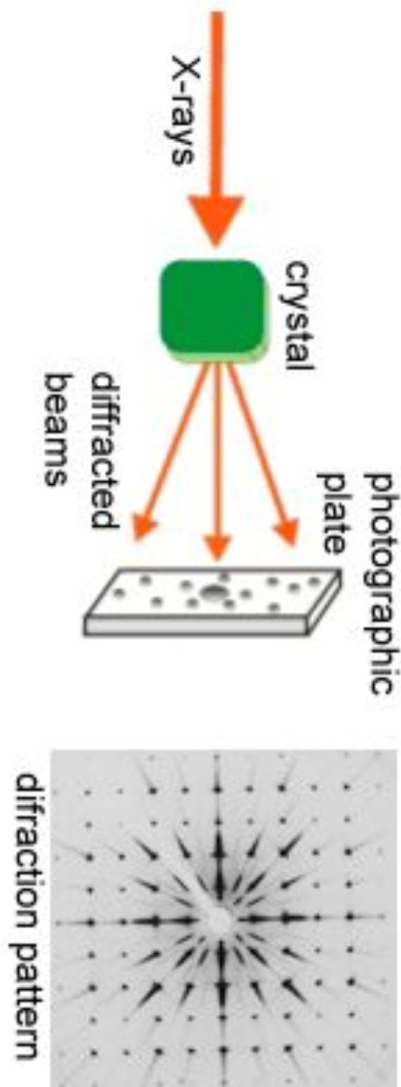
$$f(2\theta)_{motion} = f(2\theta)_{still} \cdot \exp\left[\frac{-8\pi^2 B \sin^2 \theta}{\lambda^2}\right]$$

$B(\text{Å}^2)$ is the displacement parameter



Notice the difference between the ion and the atom is at small theta

X ray scattering by a group of atoms : similarity to light falling on a grating



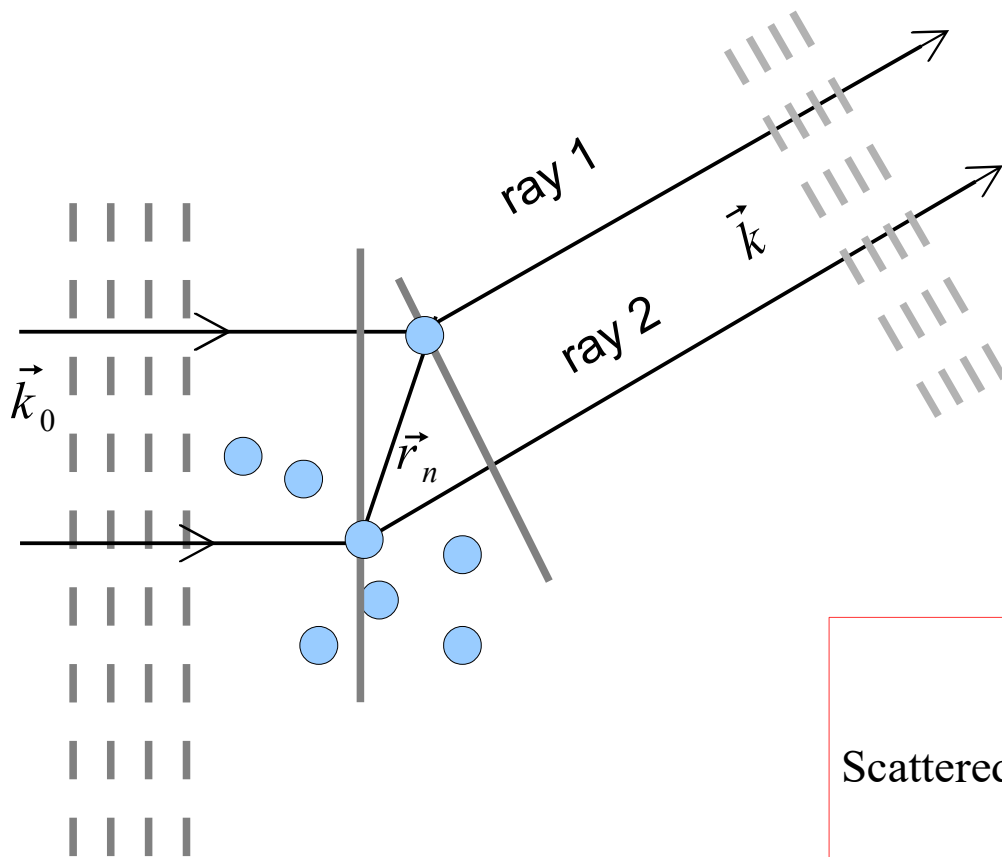
<http://labman.phys.utk.edu/phys136/modules/m9/diff.htm>

The two phenomena are very similar.

The slits for the X-ray grating are formed by the atoms in the crystal lattice.

However crystals, liquids, amorphous solids, films – all can be analysed with X-rays.

X ray scattering by a group of atoms : How to treat the problem?



The atomic positions may or may not be regular.

$$|\vec{k}| = |\vec{k}_0| = \frac{2\pi}{\lambda}$$

$$\vec{k} - \vec{k}_0 = \vec{q}$$

$$\text{Path diff} = (\hat{k} - \hat{k}_0) \cdot \vec{r}_n$$

$$\text{Phase diff} = \vec{q} \cdot \vec{r}_n$$

$$\text{Scattered amplitude} \propto f(\vec{q}) \sum_n e^{i\vec{q} \cdot \vec{r}_n}$$

We have assumed that the outgoing spherical wave can be treated as a plane wave over a small area at a large distance.

Works for any collection of SIMILAR static atoms.

When is this sum large/small ?

Can you see the connection with Fourier transforms?

An important picture to keep in mind....

$\sum e^{i\vec{q}\cdot\vec{r}_j}$ is also the fourier transform
of the number density function

$$n(\vec{r}) = \sum \delta(\vec{r} - \vec{r}_j).$$

However at $\vec{q} = 0$ it has a big peak

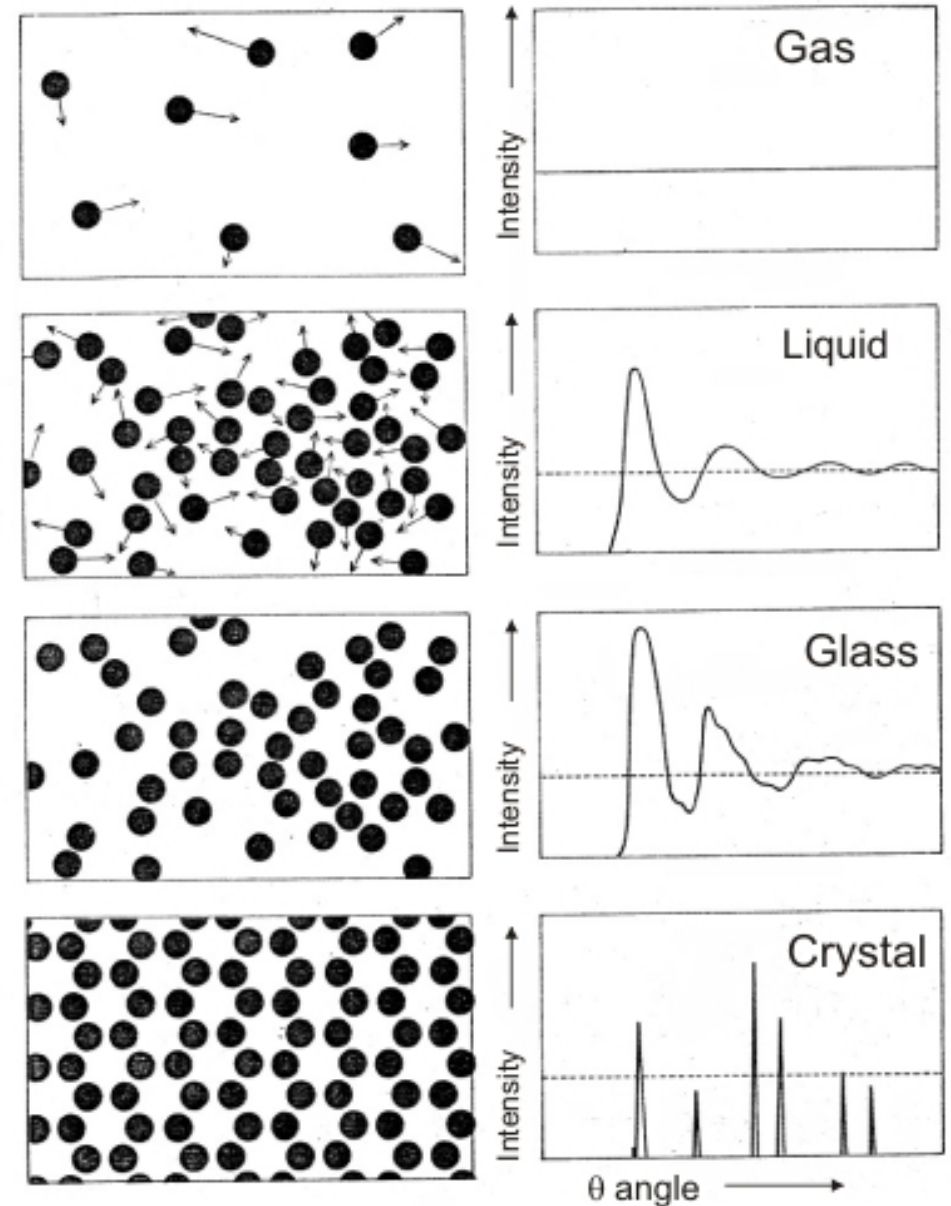
The peak can be eliminated by defining

$$S(\vec{q}) = \frac{1}{N} \left(\left| \sum e^{i\vec{q}\cdot\vec{r}_j} \right|^2 - N^2 \delta(\vec{q}) \right)$$

This is the *structure factor*

that keeps coming up in many contexts.

It is possible to thermal average $S(\vec{q})$



A diffraction experiment ultimately measures the structure factor.

Fourier transform of a periodic function like $\rho(\vec{r}) = \rho(\vec{r} + \vec{R}_n)$

$$\begin{aligned} F(\vec{q}) &= \int_{vol} d^3\vec{r} e^{i\vec{q}\cdot\vec{r}} \rho(\vec{r}) \\ &= \int_{vol} d^3\vec{r} e^{i\vec{q}\cdot\vec{r}} \rho(\vec{r} + \vec{R}_n) \\ &= e^{-i\vec{q}\cdot\vec{R}_n} \times \int_{vol} d^3\vec{r} e^{i\vec{q}\cdot(\vec{r} + \vec{R}_n)} \rho(\vec{r} + \vec{R}_n) \\ F(\vec{q}) &= e^{-i\vec{q}\cdot\vec{R}_n} \times F(\vec{q}) \end{aligned}$$

Infinite extent of the volume plays a role. For finite objects also the result is very nearly correct.

\therefore unless $e^{-i\vec{q}\cdot\vec{R}_n} = 1$, $F(\vec{q}) \equiv 0$

So how to find these special vectors \vec{q} ?? How many such vectors exist ?

Observation : if we can find a set of vectors $\{\vec{b}_1, \vec{b}_2, \vec{b}_3\}$ such that

$$\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$$

Then our problem is solved in any dimension.

It is surprisingly easy to solve $\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$

In N dimension we would have NxN linear equations.

There are exactly NxN unknowns (the components of b1,b2,b3)

The problem in 2D (four unknowns, four linear equations)

$$\begin{aligned}\vec{a}_1 \cdot \vec{b}_1 &= 2\pi &\Rightarrow & a_{1x} b_{1x} + a_{1y} b_{1y} = 2\pi \\ \vec{a}_1 \cdot \vec{b}_2 &= 0 &\Rightarrow & a_{1x} b_{2x} + a_{1y} b_{2y} = 0 \\ \vec{a}_2 \cdot \vec{b}_1 &= 0 &\Rightarrow & a_{2x} b_{1x} + a_{2y} b_{1y} = 0 \\ \vec{a}_2 \cdot \vec{b}_2 &= 2\pi &\Rightarrow & a_{2x} b_{2x} + a_{2y} b_{2y} = 2\pi\end{aligned}$$

When is this not solvable? What does it physically mean?
Be very clear about this point!

Now frame the problem in 3D.
Make the connection with the format textbooks usually
give the result.

Again, when does the 3D case not have a solution?

It is surprisingly easy to solve $\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$

In 3D exactly the same procedure leads to the standard equations

$$\vec{b}_1 = \frac{2\pi}{V} \vec{a}_2 \times \vec{a}_3$$

$$\vec{b}_2 = \frac{2\pi}{V} \vec{a}_3 \times \vec{a}_1$$

$$\vec{b}_3 = \frac{2\pi}{V} \vec{a}_1 \times \vec{a}_2$$

where $V = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$

Chose any three integers (hkl)
with no common factor between them

Then construct the vector

$$\vec{G}_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

What are the properties of \vec{G} ?

Why is this
condition
important ?

Classify all points in the direct lattice according to the value of

$$\vec{G} \cdot \vec{R}_n = (\text{integer}) \times 2\pi$$

$$\vec{G} \cdot \vec{r} = \text{constant} \Rightarrow \text{plane to which } \vec{G} \text{ is a normal}$$

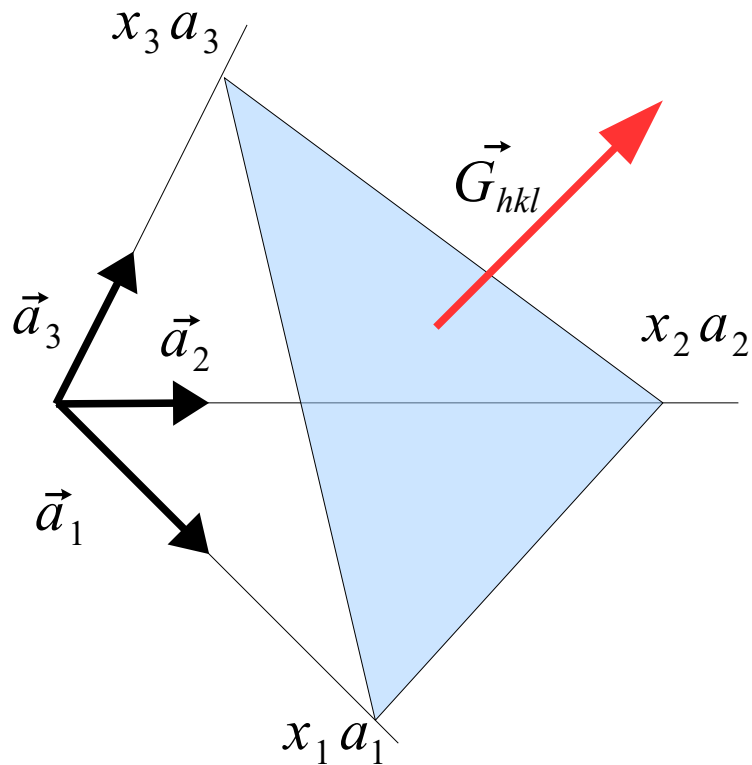
This plane is called the (hkl) plane and will keep coming
back in our analysis again and again !

Properties of the (hkl) plane

Consider the co-ordinate system formed by $\vec{a}_1, \vec{a}_2, \vec{a}_3$

!! They are not necessarily orthogonal !!

Q: How does the (hkl) plane cut these axes ?



$$x_1 : x_2 : x_3 \equiv \frac{1}{h} : \frac{1}{k} : \frac{1}{l}$$

(hkl) should be mutually prime

Proof

$$\vec{G}_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

$$\vec{G} \cdot \vec{r} = 2m\pi$$

$$\therefore h\vec{b}_1 \cdot x_1 \vec{a}_1 = k\vec{b}_2 \cdot x_2 \vec{a}_2 = l\vec{b}_3 \cdot x_3 \vec{a}_3 = 2m\pi$$

Result follows...

The normal vector defines a family of planes.
The constant "m" changes for each plane.
How are these planes spaced?

Properties of the (hkl) plane

$e^{i\vec{G}\cdot\vec{r}}$ looks like a plane wave propagating in the lattice.

In two successive wavefronts (same phase surface) the value of $\vec{G}\cdot\vec{r}$ changes by $2\times\pi$

The perpendicular distance between them is the wavelength of the wave ?

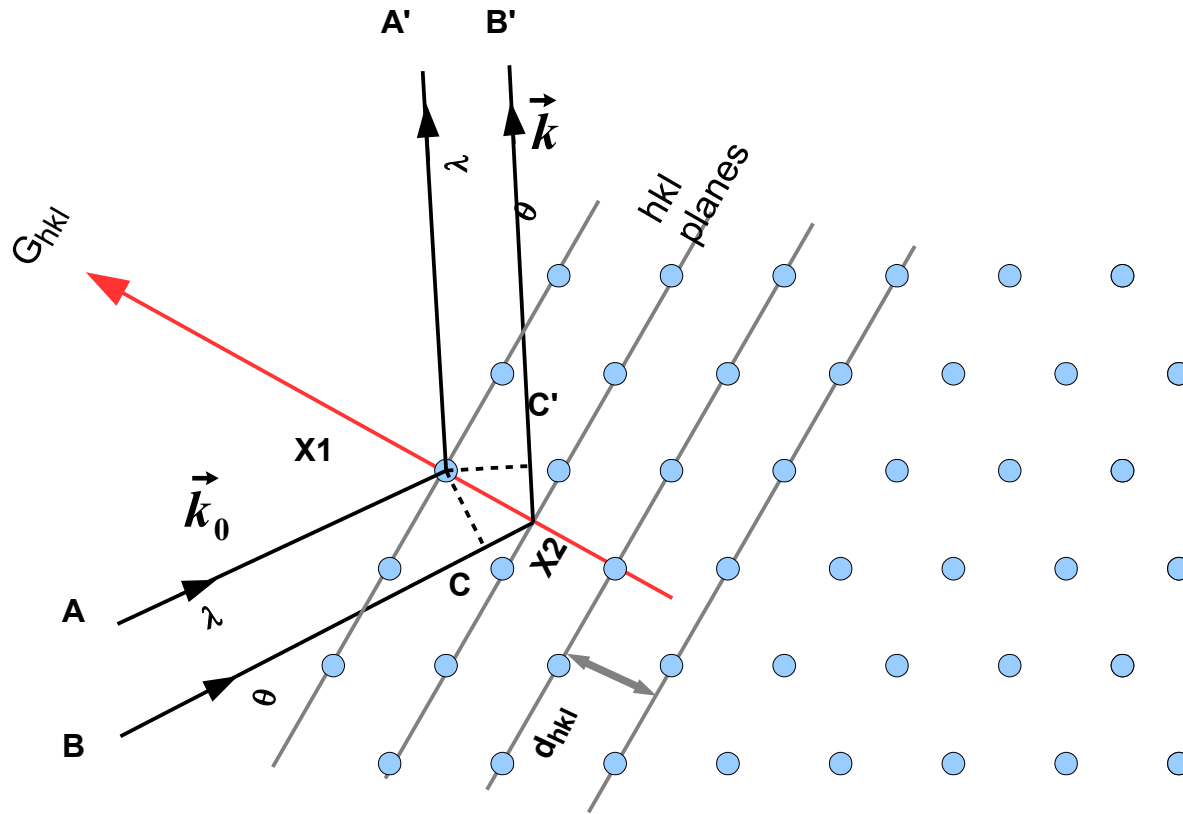
Separation between two successive planes $d_{hkl} = \frac{2\pi}{|\vec{G}|}$

The density of points in an hkl plane $n_{hkl} = \frac{d_{hkl}}{V}$ per unit area

If the numbers hkl are large, then the plane is sparsely populated. Hence the spacing between them is necessarily small.

$I(\vec{q})$ will be large only if $\vec{q} = \vec{G}$

The Bragg diffraction condition



$$BX_2B' - AX_1A' = 2d_{hkl} \sin \theta = n \lambda$$

$$|\vec{G}|^2 = (\vec{k} - \vec{k}_0)^2$$

$$G^2 = \left(\frac{2\pi}{\lambda}\right)^2 2(1 - \cos 2\theta)$$

Using $d_{hkl} = \frac{2\pi}{|\vec{G}|}$ the same result follows

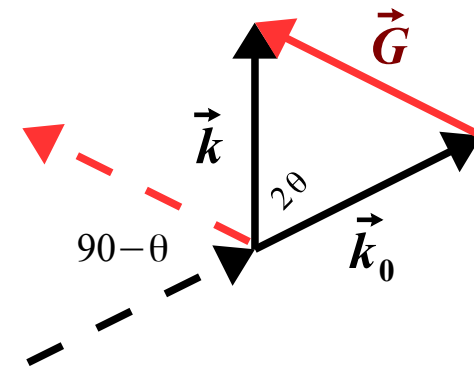
Visualise the crystal as a stack of hkl plane slices.

G_{hkl} is the normal

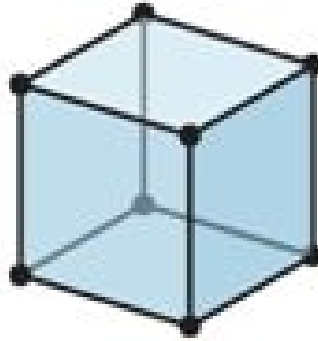
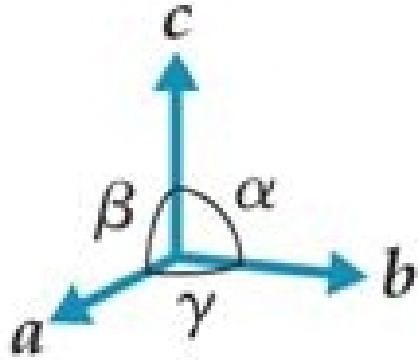
θ is the angle made with the plane. Not the normal.

When will reflections from each layer constructively interfere?

Is this condition same as $q=G$?



The calculation of $d_{hkl} = 2\pi/G_{hkl}$

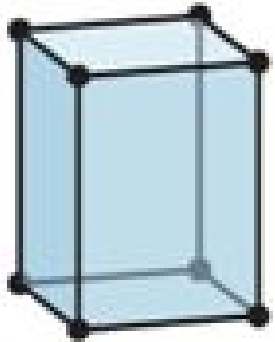


CUBIC (Simple cubic, BCC, FCC)

$$a = b = c$$

$$\alpha = \beta = \gamma = 90$$

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

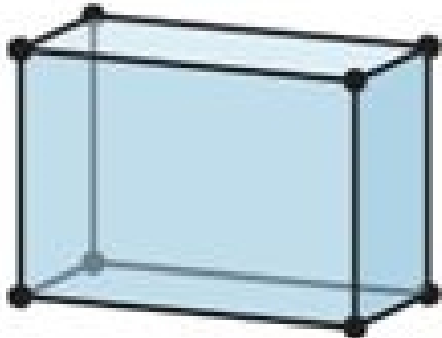


TETRAGONAL

$$a = b \neq c$$

$$\alpha = \beta = \gamma = 90$$

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$



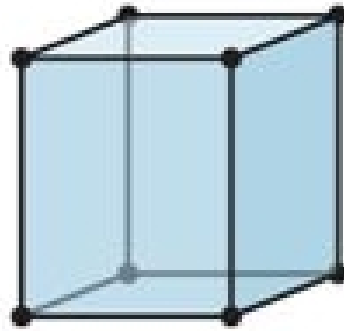
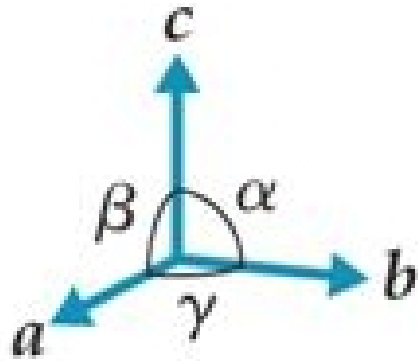
ORTHORHOMBIC

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

The calculation of $d_{hkl} = 2\pi / G_{hkl}$



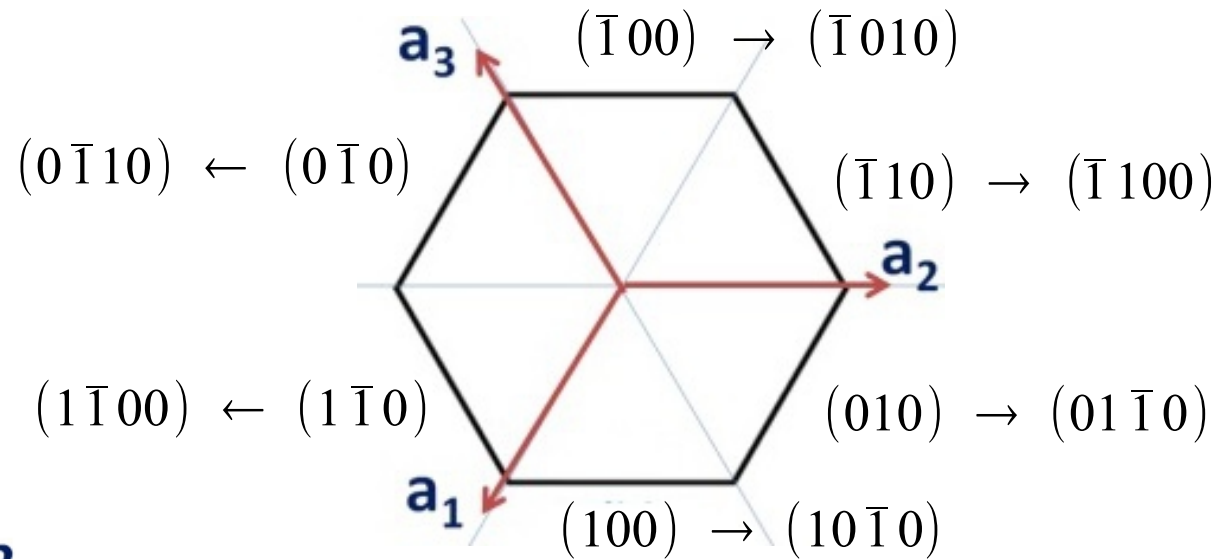
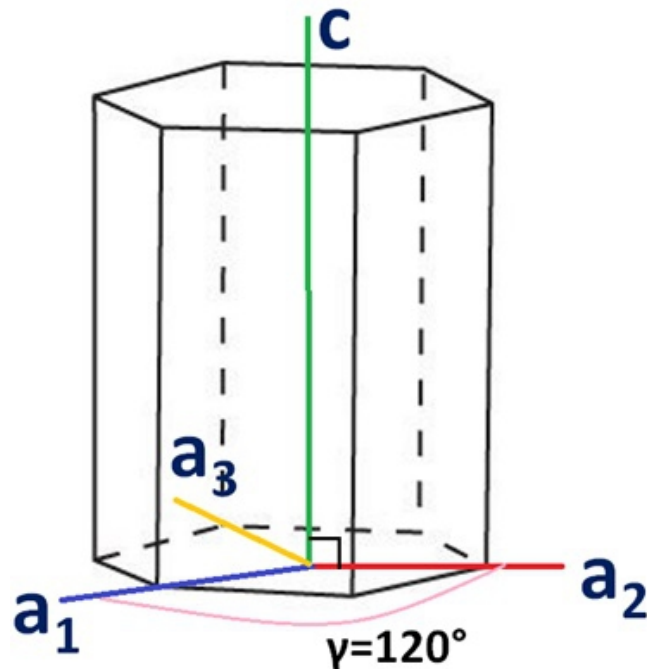
HEXAGONAL

$$a = b \neq c$$

$$\alpha = \beta = 90, \quad \gamma = 120$$

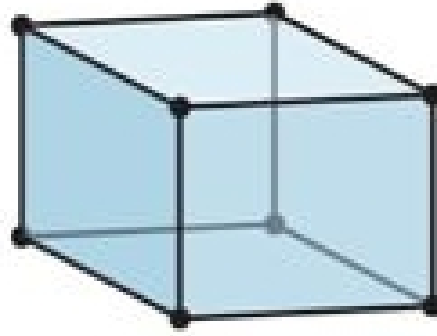
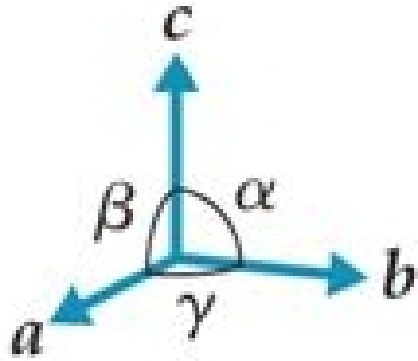
$$\frac{1}{d^2} = \frac{4(h^2 + k^2 + hk)}{3a^2} + \frac{l^2}{c^2}$$

The hexagonal cell is not the primitive cell, but most convenient for visualizing the symmetry.



The six symmetrical planes now have similar looking indices. $h + k + i = 0$ always holds.

The calculation of $d_{hkl} = 2\pi/G_{hkl}$



MONOCLINIC

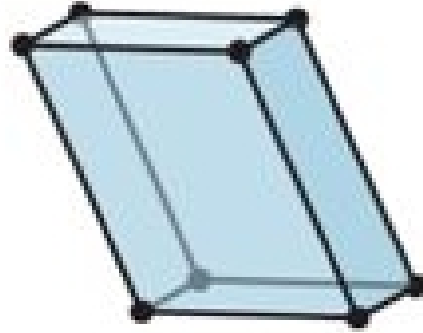
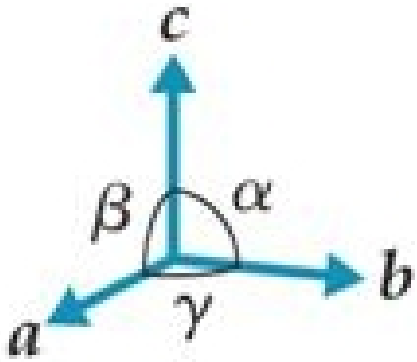
$$a \neq b \neq c$$

$$\alpha = \gamma = 90, \quad \beta \neq 90$$

$$\frac{1}{d^2} = \frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 \sin^2 \beta} - \frac{2hl \cos \beta}{ac \sin^2 \beta}$$

The calculation of $d_{hkl} = 2\pi/G_{hkl}$

TRICLINIC



$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90$$

$$\frac{1}{d^2} = \frac{S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl}{V^2}$$

$$V = abc \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$

$$S = a^2 b^2 c^2 \begin{pmatrix} \frac{\sin^2 \alpha}{a^2} & \frac{\cos \alpha \cos \beta - \cos \gamma}{ab} & \frac{\cos \gamma \cos \alpha - \cos \beta}{ac} \\ \frac{\cos \alpha \cos \beta - \cos \gamma}{ab} & \frac{\sin^2 \beta}{b^2} & \frac{\cos \beta \cos \gamma - \cos \alpha}{bc} \\ \frac{\cos \gamma \cos \alpha - \cos \beta}{ac} & \frac{\cos \beta \cos \gamma - \cos \alpha}{bc} & \frac{\sin^2 \gamma}{c^2} \end{pmatrix}$$

The effect of lattice + basis

Associated with each lattice point is a basis,

so the electron density is: $\sum_{R_n} f(\vec{r} - \vec{R}_n)$

The fourier transform of such a function is

$$\left(\sum_{\text{lattice}} e^{i\vec{q} \cdot \vec{R}_n} \right) \int_{\text{unit cell}} f(\vec{r}) e^{i\vec{q} \cdot \vec{r}} d^3 \vec{r}$$

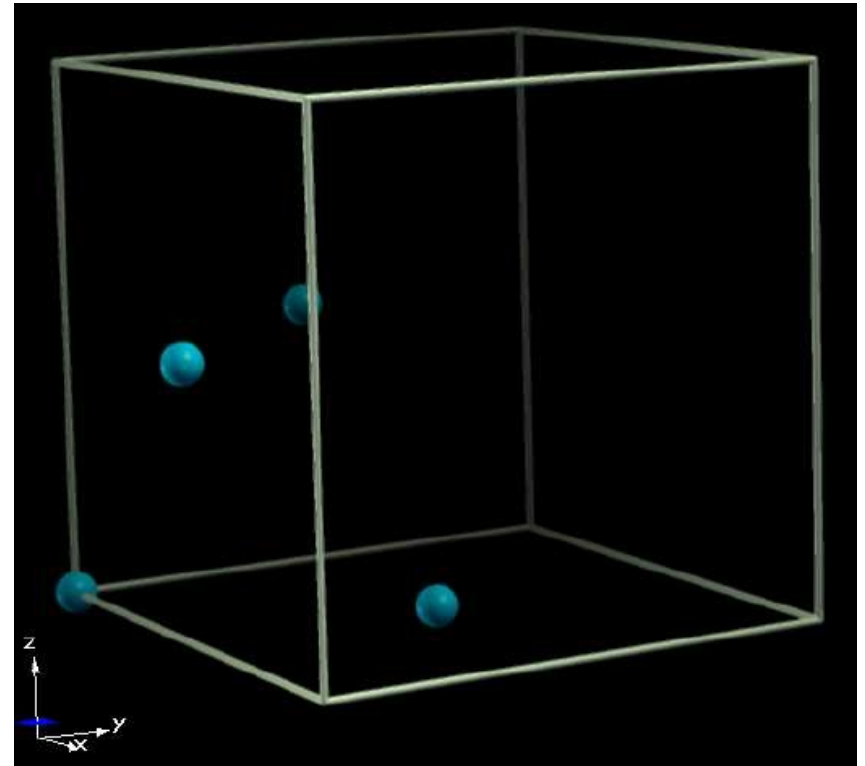
The basis atoms are located at

$$\vec{r}_i = x_i \vec{a}_1 + y_i \vec{a}_2 + z_i \vec{a}_3$$

For $\vec{q} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$

$$\int_{\text{unit cell}} f(\vec{r}) e^{i\vec{q} \cdot \vec{r}} d^3 \vec{r} = \sum_i e^{i2\pi(x_i h + y_i k + z_i l)} \times f_i(\vec{q})$$

F_{hkl} (The structure factor) atomic form factor

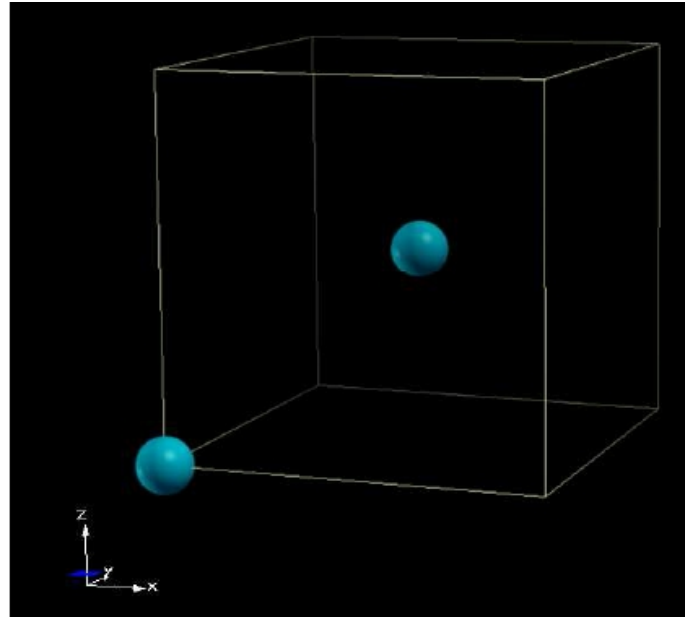
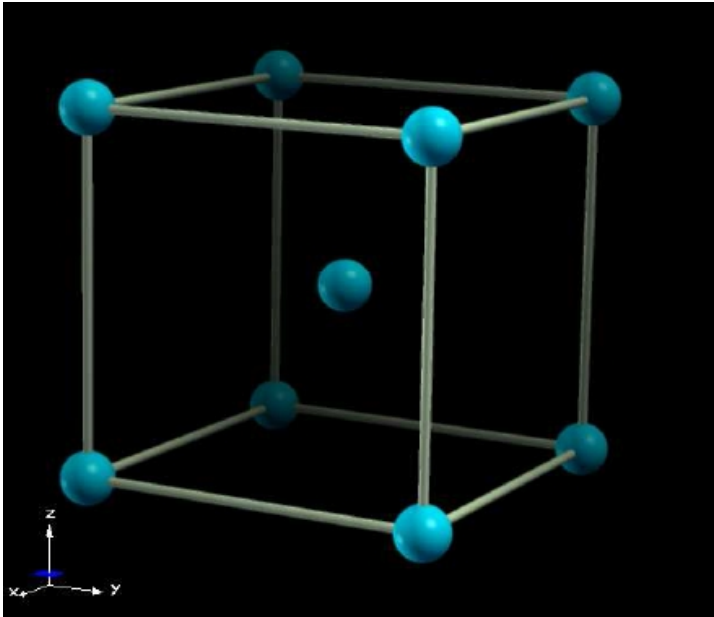


Basis atoms of the FCC

1. 0.0, 0.0, 0.0
2. 0.5, 0.5, 0.0
3. 0.5, 0.0, 0.5
4. 0.0, 0.5, 0.5

Some (hkl) reflections will be killed by the structure factor

The structure factor for BCC lattice

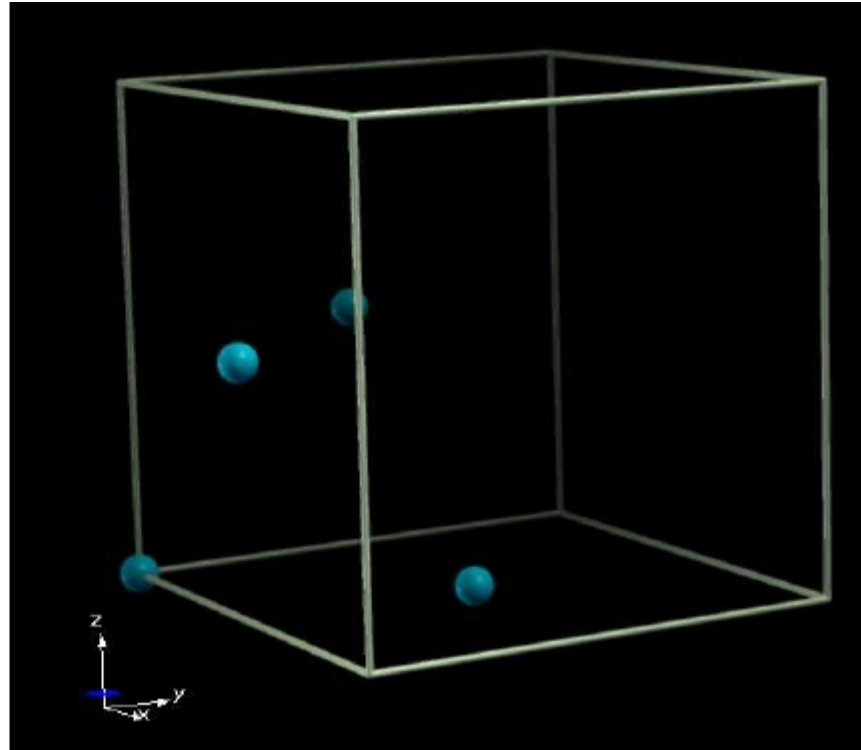
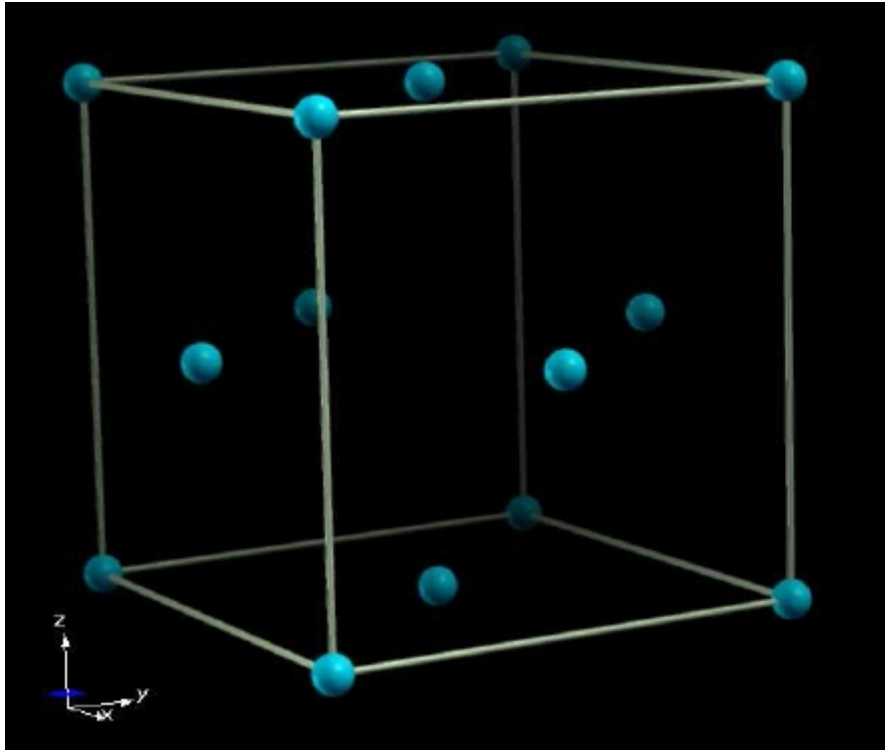


$$F_{hkl} = 1 + e^{i\pi(h+k+l)}$$

Atom positions : $(0,0,0)$
 $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$

$h+k+l$ must be even, assuming identical basis atoms

The structure factor for FCC lattice

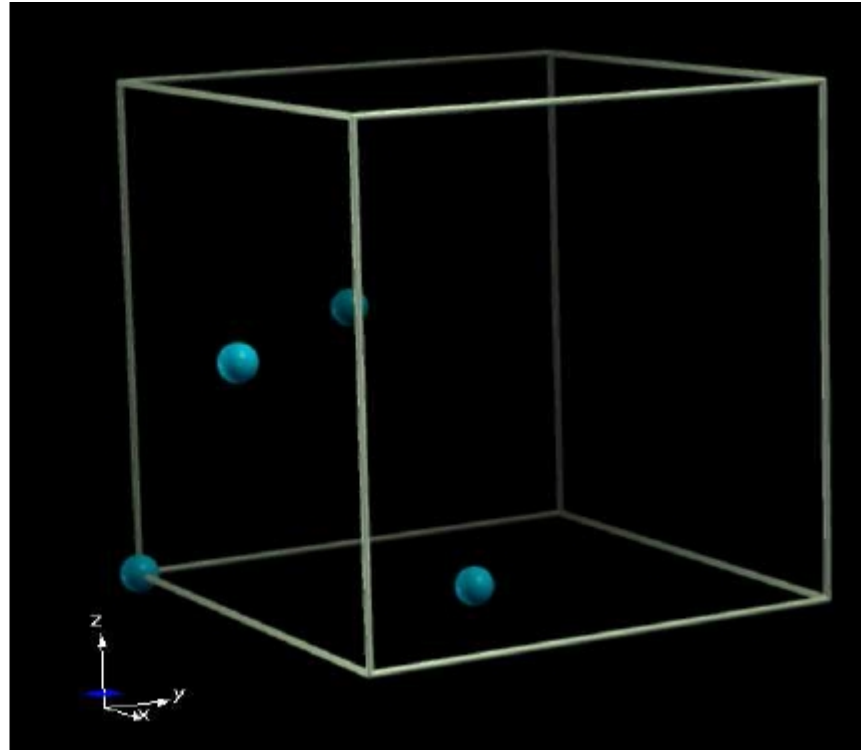
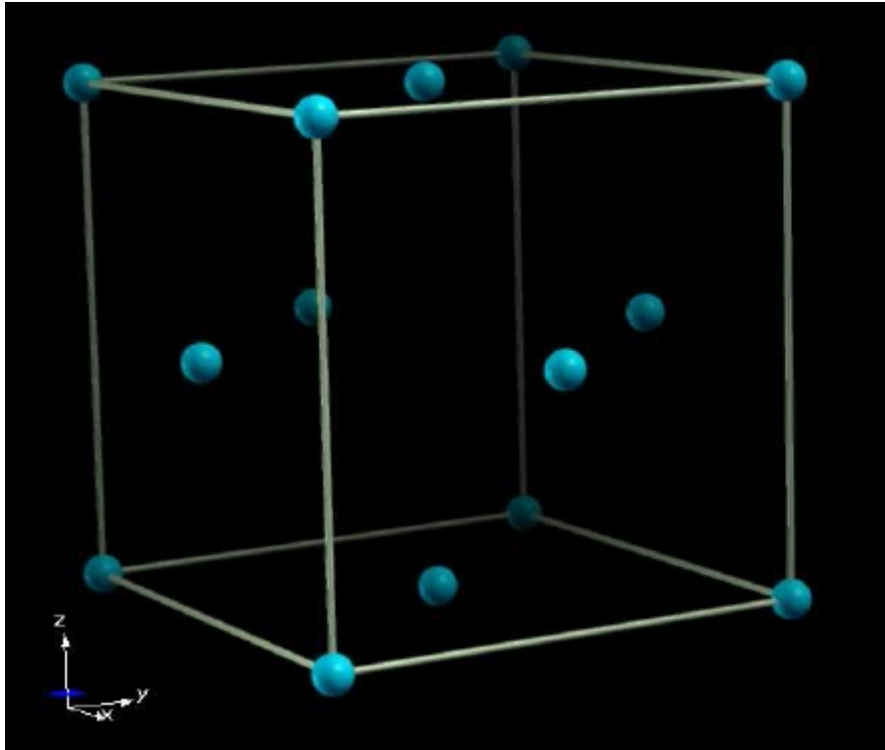


$$F_{hkl} = 1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}$$

(hkl) must be all even or all odd, assuming identical basis atoms.

$$\text{Atom positions: } \begin{pmatrix} 0,0,0 \\ \frac{1}{2}, \frac{1}{2}, 0 \\ 0, \frac{1}{2}, \frac{1}{2} \\ \frac{1}{2}, 0, \frac{1}{2} \end{pmatrix}$$

The structure factor for FCC lattice

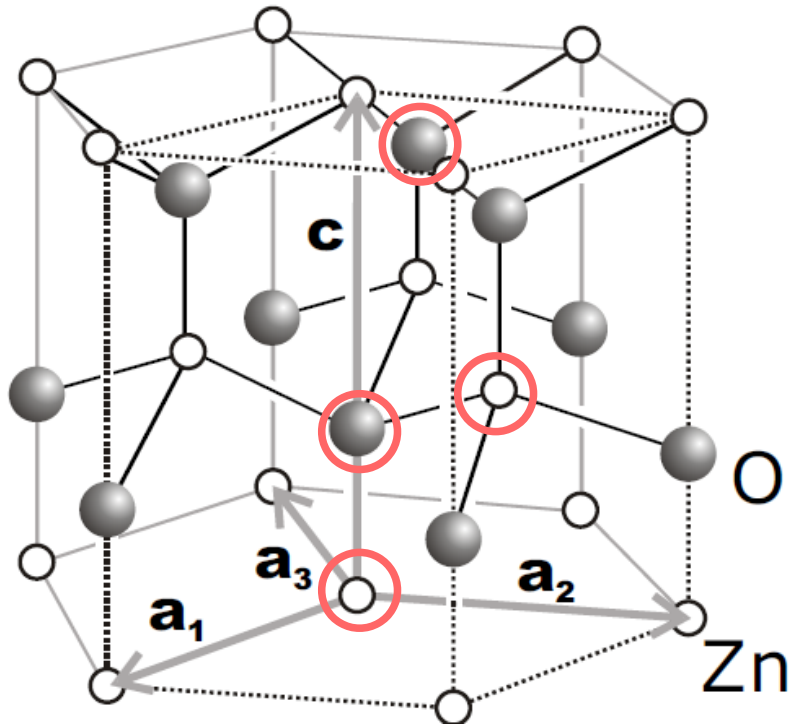


$$F_{hkl} = 1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)}$$

(hkl) must be all even or all odd, assuming identical basis atoms.

$$\text{Atom positions: } \begin{pmatrix} 0,0,0 \\ \frac{1}{2}, \frac{1}{2}, 0 \\ 0, \frac{1}{2}, \frac{1}{2} \\ \frac{1}{2}, 0, \frac{1}{2} \end{pmatrix}$$

The structure factor for Wurtzite (ZnO) lattice



Wurtzite

ZnO

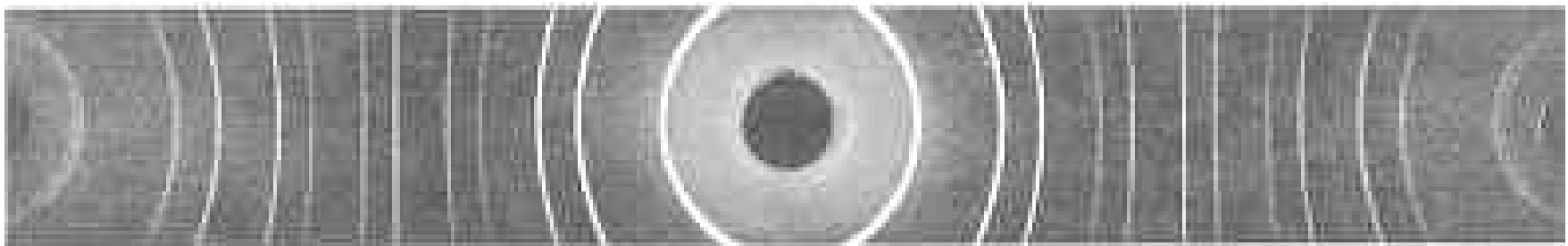
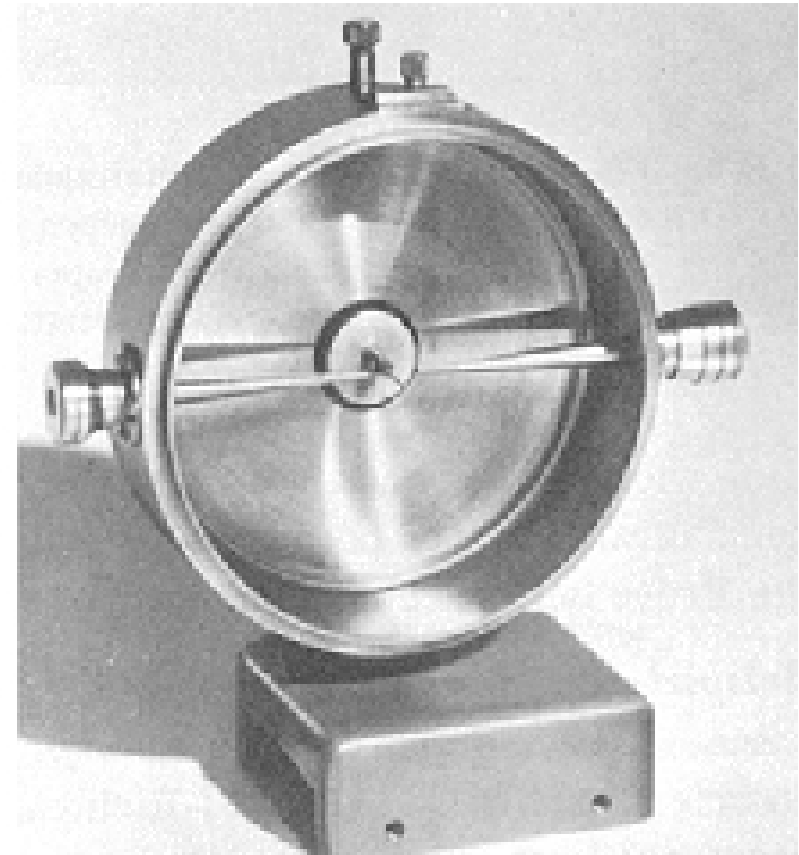
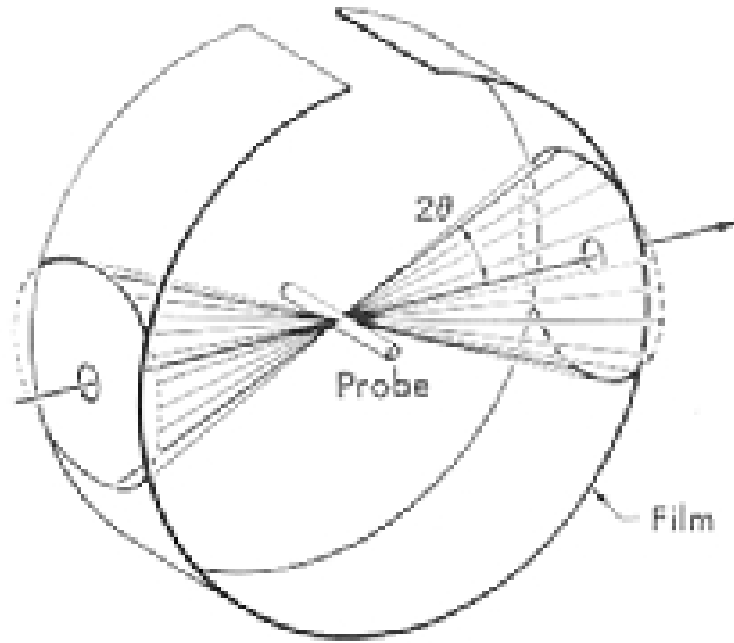
$$Zn : \left(0, 0, \frac{3}{8} \right) , \left(\frac{1}{3}, \frac{2}{3}, \frac{7}{8} \right)$$

$$O : (0, 0, 0) , \left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2} \right)$$

$$F_{hkl} = f_o \left(1 + e^{i 2\pi \left(\frac{h}{3} + \frac{2k}{3} + \frac{l}{2} \right)} \right) + f_{Zn} \left(e^{i 2\pi \frac{3l}{8}} + e^{i 2\pi \left(\frac{h}{3} + \frac{2k}{3} + \frac{7l}{8} \right)} \right)$$

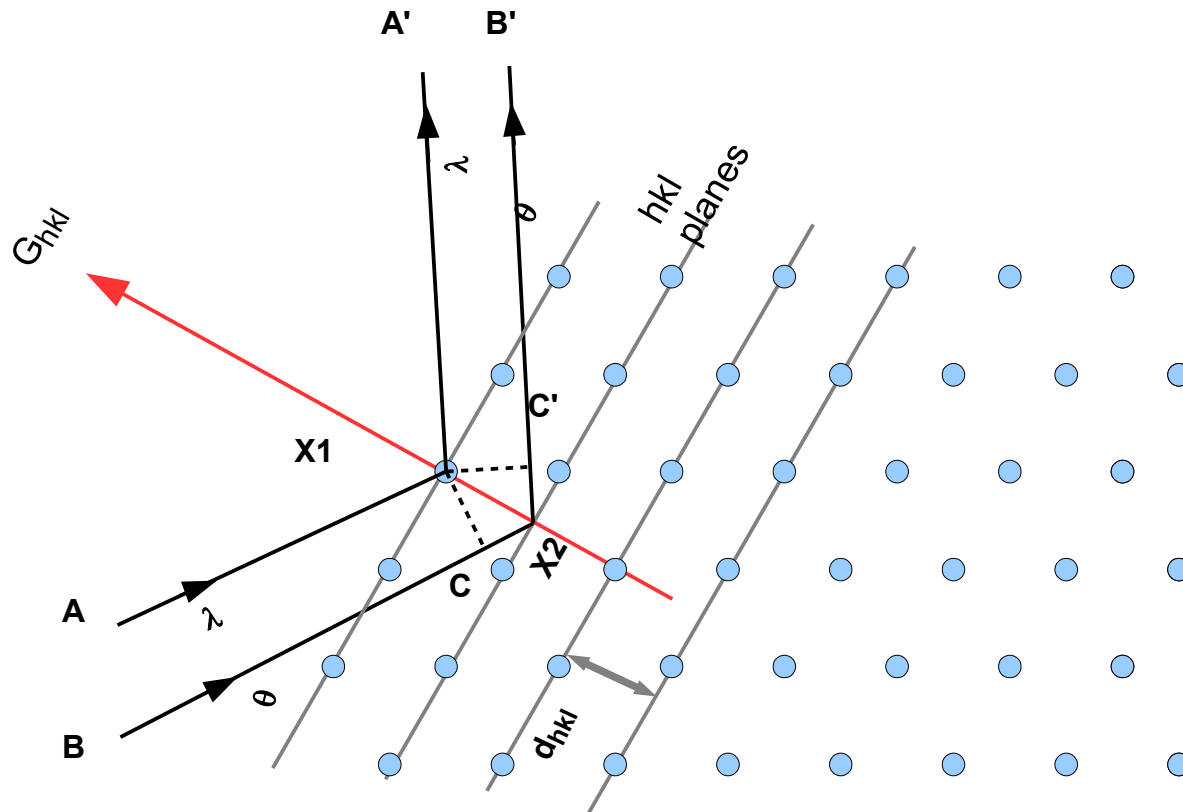
How does powder diffraction work ?

Probably the most used X-ray technique..



Debye Scherer camera and the output it produces. The radius is so arranged such that 1mm on the film = 1 degree angle.

How does powder diffraction work ?



Keep the incident ray fixed.

Rotate G_{hkl} about the the incident ray, keeping the angle between the two fixed.

The outgoing ray will also rotate tracing out a cone with vertical angle 2θ .

In a powder small crystals of all orientation would be found, naturally producing the rings.

Q: What should be the total diffracted intensity at an angle θ ?

How many particles are oriented to diffract at θ ?

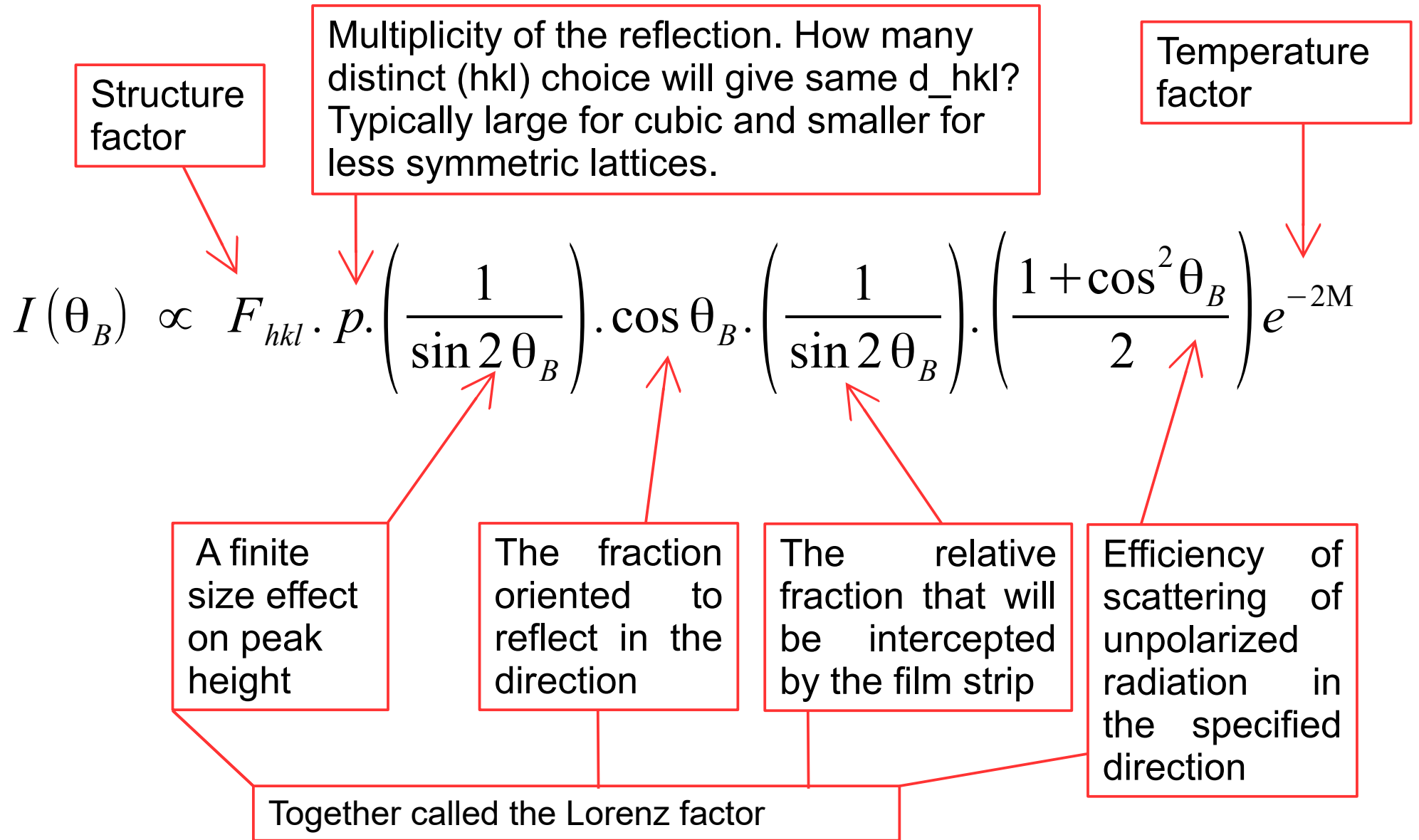
How much of the diffracted intensity is intercepted by a film strip?

How does the line broadening affect the peak height?

What is the multiplicity of the "reflection"?

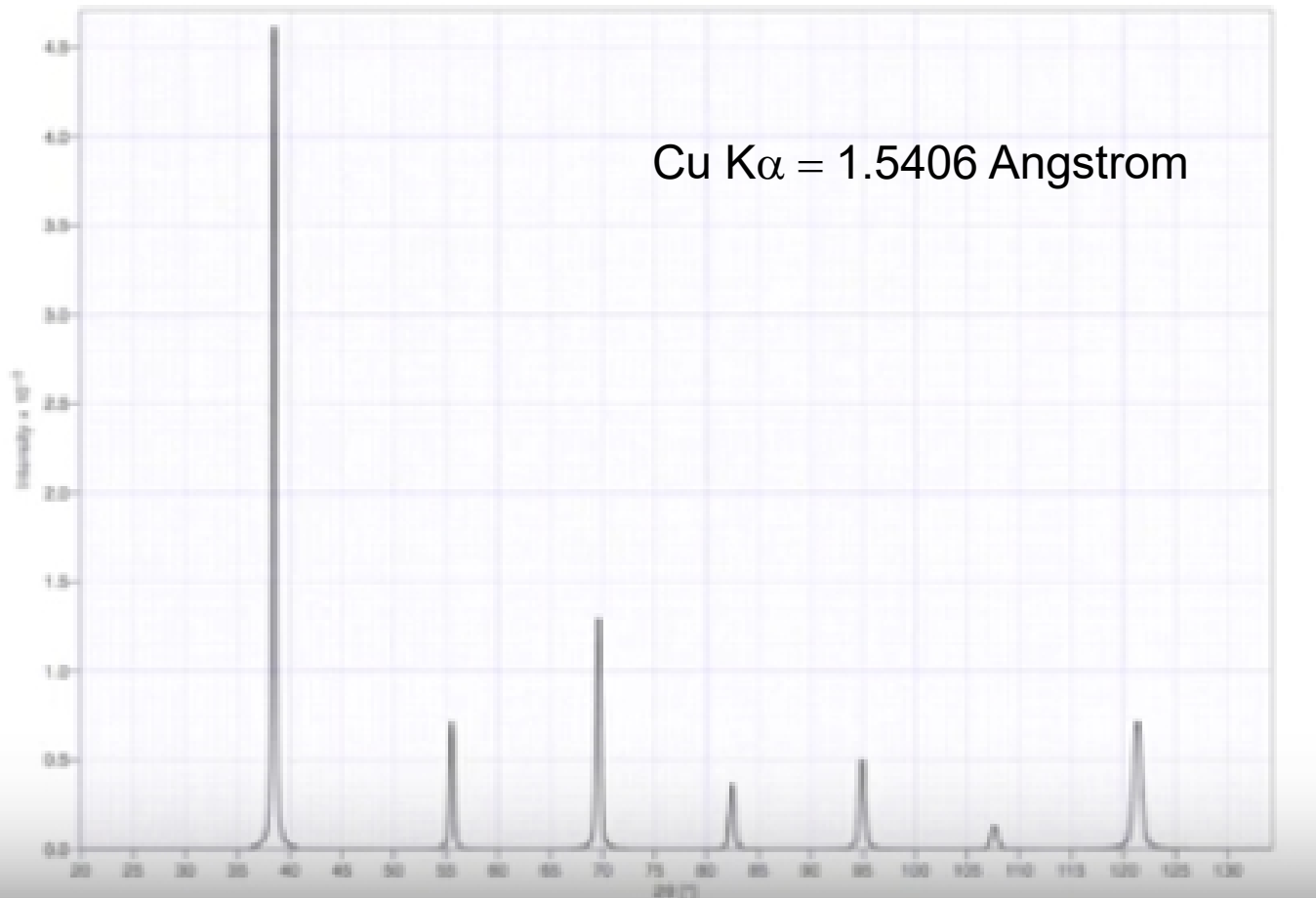
What is the factor due to addition of two possible polarisation direction?

The relative peak height for a certain "reflection"



Note: This is NOT a formula for lineshape. This only gives the peak height.

A very simple example : labelling the (hkl) peaks

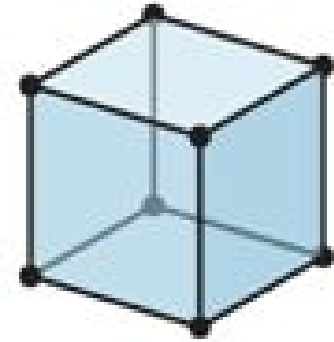


Data: University of Sheffield

Question: What is the lattice constant ?
Can you work out the lattice type ?

A very simple example : labelling the (hkl) peaks

$$\begin{aligned}2 d_{hkl} \sin \theta_{hkl} &= \lambda \\ \sin^2 \theta_{hkl} &= \frac{\lambda^2}{4 d_{hkl}^2} \\ &= \frac{\lambda^2}{4 a^2} (h^2 + k^2 + l^2) \\ \frac{\sin^2 \theta_{h'k'l'}}{\sin^2 \theta_{hkl}} &= \frac{h'^2 + k'^2 + l'^2}{h^2 + k^2 + l^2}\end{aligned}$$



$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

for a cubic system ONLY

cubic system \rightarrow simple cubic/BCC/FCC

Assume that (hkl) begins with (100)

This may NOT always be correct !!

You have to account for ALL the peaks

Obvious assumption : this is NOT a mix of two materials

Finite crystal size : $N_1 a_1 \times N_2 a_2 \times N_3 a_3$: What is $\sum e^{i\vec{q} \cdot \vec{r}_n} = ?$

Consider

$$\vec{q} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3 \quad : \text{ allow } m_1, m_2, m_3 \text{ to be fractions}$$

$$\vec{r}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \quad : n_1, n_2, n_3 \text{ are integers}$$

Then

$$\sum e^{i\vec{q} \cdot \vec{r}_n} = \left(\sum_{n_1=0}^{N_1-1} e^{i2\pi m_1 n_1} \right) \left(\sum_{n_2=0}^{N_2-1} e^{i2\pi m_2 n_2} \right) \left(\sum_{n_3=0}^{N_3-1} e^{i2\pi m_3 n_3} \right)$$

$$= \frac{e^{i2\pi N_1 m_1} - 1}{e^{i2\pi m_1} - 1} \frac{e^{i2\pi N_2 m_2} - 1}{e^{i2\pi m_2} - 1} \frac{e^{i2\pi N_3 m_3} - 1}{e^{i2\pi m_3} - 1}$$

$$|f(\vec{q})|^2 = \frac{\sin^2 N_1 \pi m_1}{\sin^2 \pi m_1} \frac{\sin^2 N_2 \pi m_2}{\sin^2 \pi m_2} \frac{\sin^2 N_3 \pi m_3}{\sin^2 \pi m_3}$$

**Prove this
assertion and
calculate the
peak width**

This function has sharp peaks when m_1, m_2, m_3 are all integers

Finite crystal size : $N_1 a_1 \times N_2 a_2 \times N_3 a_3$: What is $\sum e^{i\vec{q} \cdot \vec{r}_n} = ?$

But as soon as $\delta m_1 = \frac{1}{N_1}, \delta m_2 = \frac{1}{N_2}, \delta m_3 = \frac{1}{N_3}$ $f(\vec{q}) = 0$ again

\therefore Within a region bounded by $\frac{\vec{b}_1}{N_1}, \frac{\vec{b}_2}{N_2}, \frac{\vec{b}_3}{N_3}$, $f(\vec{q}) \neq 0$

The q -space volume enclosed by this patch is

$$\frac{\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)}{N_1 N_2 N_3} = \frac{(2\pi)^3}{v_{\text{unit cell}} N_1 N_2 N_3} = \frac{(2\pi)^3}{V_{\text{sample}}} = (\delta q)^3$$

For elastic scattering $|\vec{q}| = \frac{4\pi}{\lambda} \sin \theta$

combine the two results :

$$\delta(2\theta) = \frac{K \lambda}{\sqrt[3]{V} \cos \theta}$$

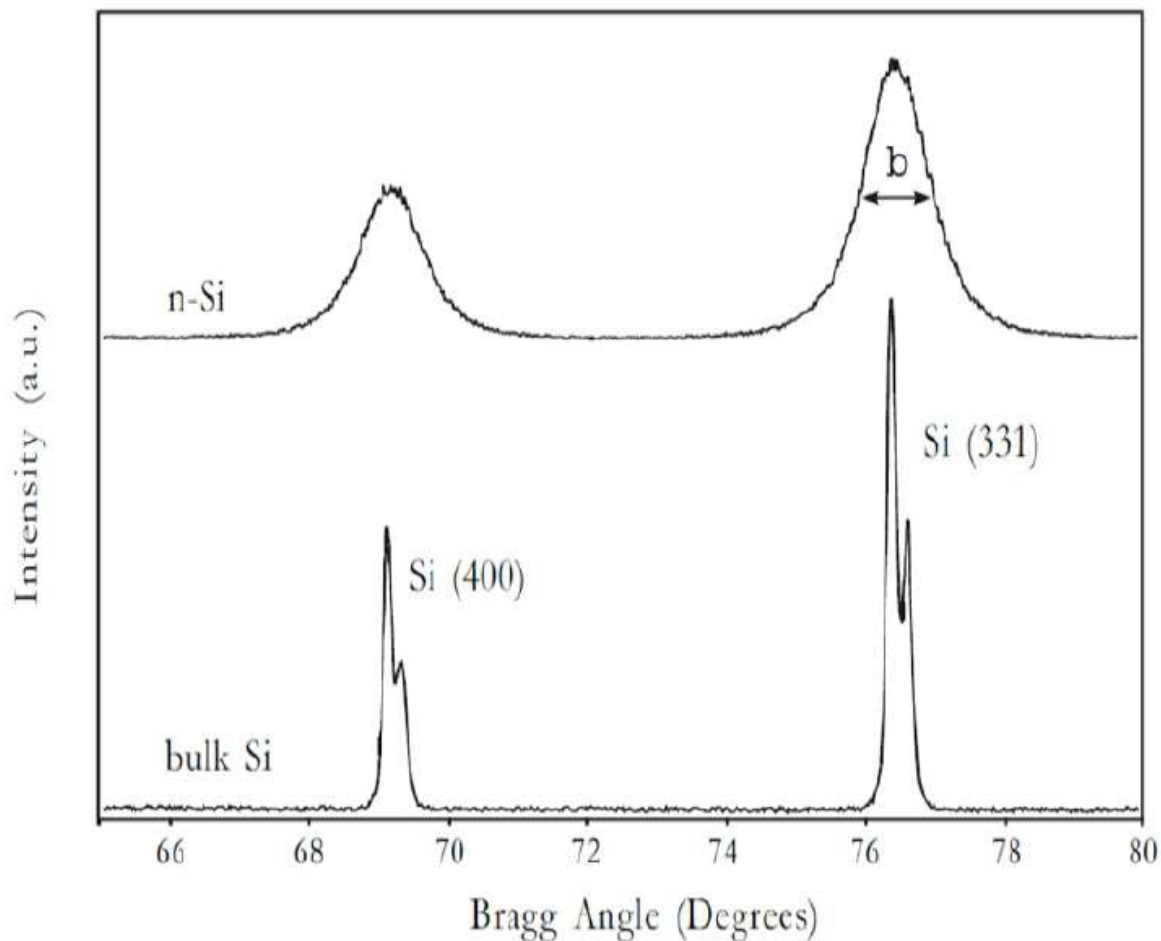
In RADIANS
not degrees!

Small particles will give a large linewidth.

The coefficient K , depends on the shape of the sample. For spheres it is 0.9.

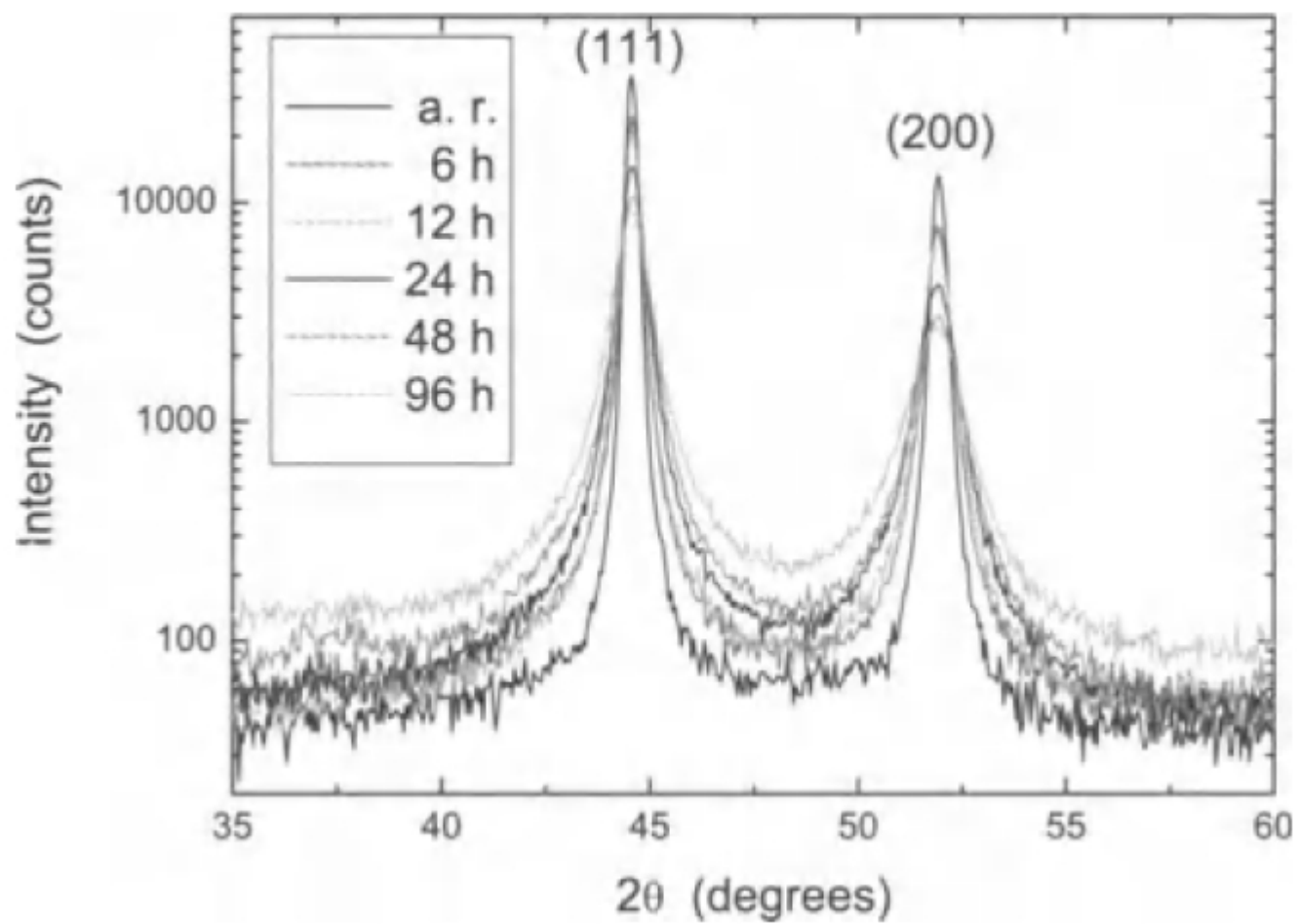
This is the Debye-Scherrer result.

An example of line broadening

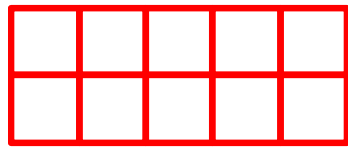


Q: What is the estimated size of the nanocrystalline particles?

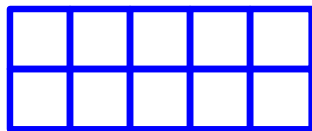
The method is not useful once the size of the grain is about 500 nanometer. For crystallites of that size, the line-broadening becomes smaller than the inherent broadening of the instrument.....



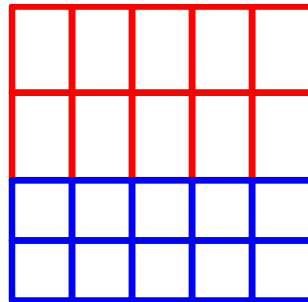
What other factors also broaden the peaks ?



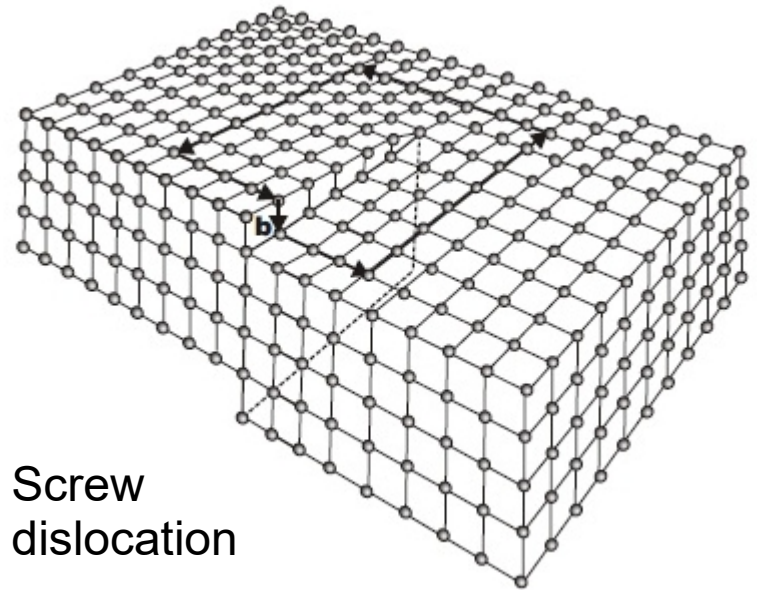
Film



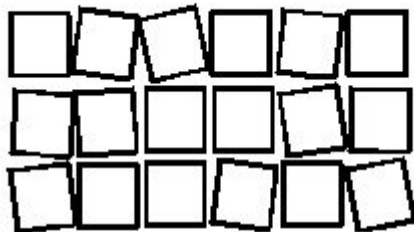
Substrate



Strained
film on
substrate

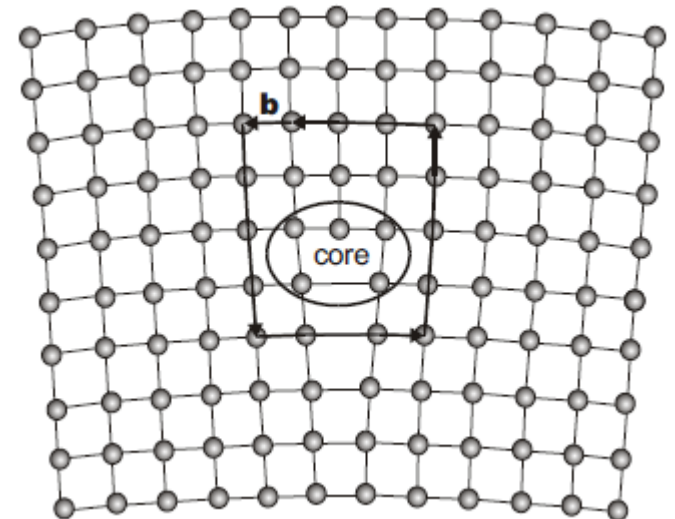


Screw
dislocation



Highly exaggerated representation
of crystal mosaicity

edge
dislocation

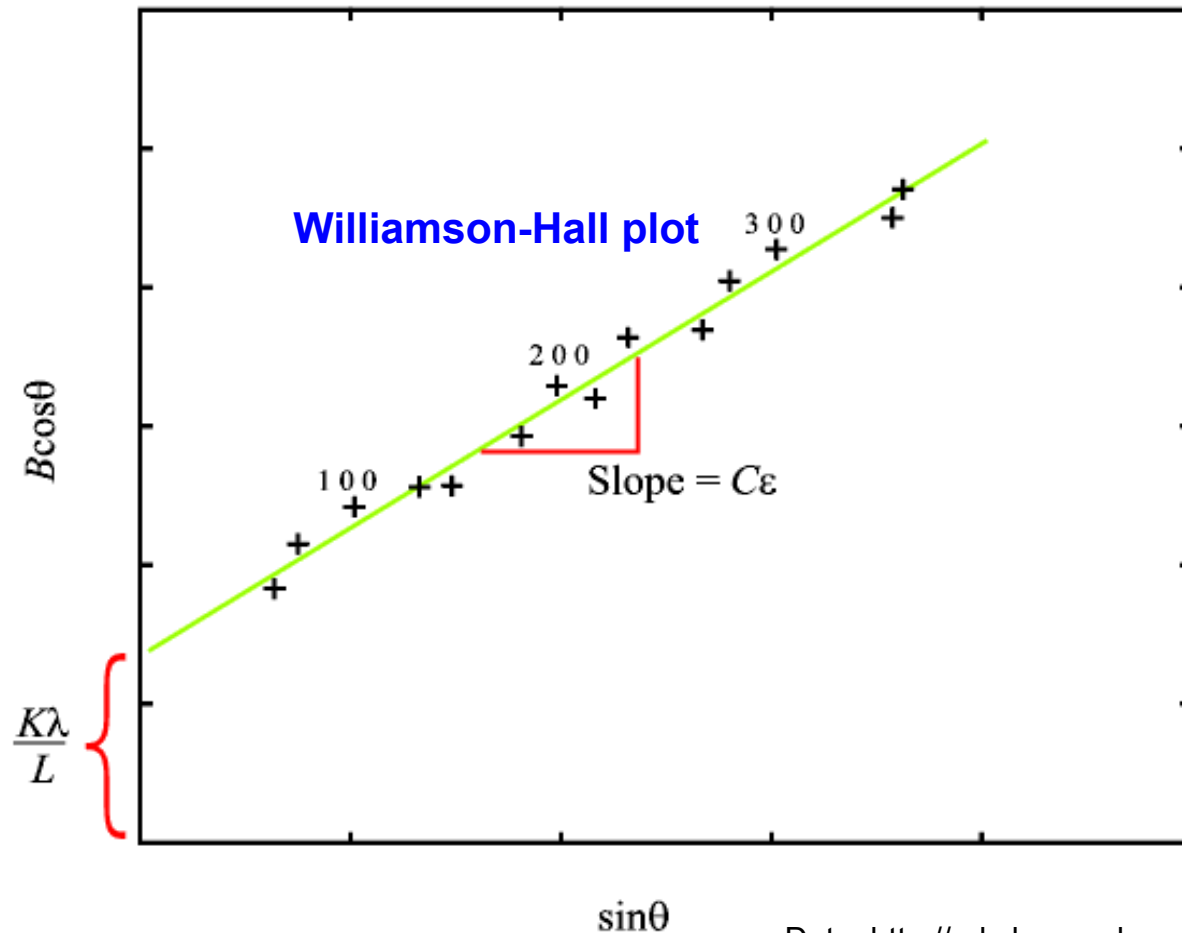


What other factors also broaden the peaks ?

Due to grain size : $\delta\theta = \frac{K\lambda}{L\cos\theta}$

Due to strain : $\delta\theta = C\epsilon\tan\theta$

$$\therefore (\delta\theta)_{\text{total}} \cos\theta = \frac{K\lambda}{L} + C\epsilon \sin\theta$$



Approximate & easy:
W.H.Hall
(Acta Metall. 1, 22-31 (1953)).

More refined method:
B.E.Warren and B.L.Averbach
(J.Appl.Phys. 21, 595(1950))

How lattice vibrations affect X-ray lines: Debye Waller factor

The instantaneous position of a lattice point : $\vec{r}_n + \vec{u}_n(t)$

The structure factor that will determine the line intensity

$$S(\vec{q}) = \left\langle \sum_n e^{i\vec{q} \cdot \vec{r}_n} e^{i\vec{q} \cdot \vec{u}_n} \right\rangle = \left(\sum_n e^{i\vec{q} \cdot \vec{r}_n} \right) \left\langle e^{i\vec{q} \cdot \vec{u}_n} \right\rangle$$

Thermal average of a time varying quantity

The mean positions do not change with time. This sum is the **static structure factor**: no time dependence

This average should be same for every lattice point, so needs to be done once only

We will do this using classical statistical physics. It is also possible to do this quantum mechanically.

How lattice vibrations affect X-ray lines: Debye Waller factor

$$\langle e^{i\vec{q}\cdot\vec{u}_n} \rangle = \frac{\int e^{-\beta H} e^{iq_x x} e^{iq_y y} e^{iq_z z} dx dy dz dp_x dp_y dp_z}{\int e^{-\beta H} dx dy dz dp_x dp_y dp_z}$$

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2$$

We assume SHM of each lattice point (or normal mode). If there is anharmonicity, the result will not be valid.

In this case x and the p integrals decouple very easily...

The p integral will also cancel from the numerator and denominator.

$$\langle e^{i\vec{q}\cdot\vec{u}_n} \rangle = \left(\frac{\int e^{iq_x x} e^{-\beta m \omega^2 x^2 / 2} dx}{\int e^{-\beta m \omega^2 x^2 / 2} dx} \right) \times \text{similar integral on } y, z$$

How lattice vibrations affect X-ray lines: Debye Waller factor

Complete the square on the numerator to get a Gaussian integral...

$$\frac{\int e^{-\frac{\beta m \omega^2}{2} \left[x^2 - 2i \frac{q_x}{\beta m \omega^2} + \left(\frac{-i q_x}{\beta m \omega^2} \right)^2 \right]} e^{-\frac{q_x^2}{2\beta m \omega^2}} dx}{\int e^{-\frac{\beta m \omega^2}{2} x^2} dx}$$

This gives

$$\left\langle e^{i\vec{q} \cdot \vec{u}_n} \right\rangle = e^{-\frac{q_x^2}{2\beta m \omega^2}} e^{-\frac{q_y^2}{2\beta m \omega^2}} e^{-\frac{q_z^2}{2\beta m \omega^2}}$$

classical equipartition $\frac{1}{2} m \omega^2 \langle x^2 \rangle = \frac{1}{2} kT$

How lattice vibrations affect X-ray lines: Debye Waller factor

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \langle u^2 \rangle / 3 = \frac{1}{\beta m \omega^2}$$

$$\therefore \left| \langle e^{i \vec{q} \cdot \vec{u}_n} \rangle \right|^2 = e^{-q^2 \langle u^2 \rangle / 3} \quad (\vec{q} = \vec{G})$$

The intensity peak gets reduced but not broadened by the "Debye Waller factor"

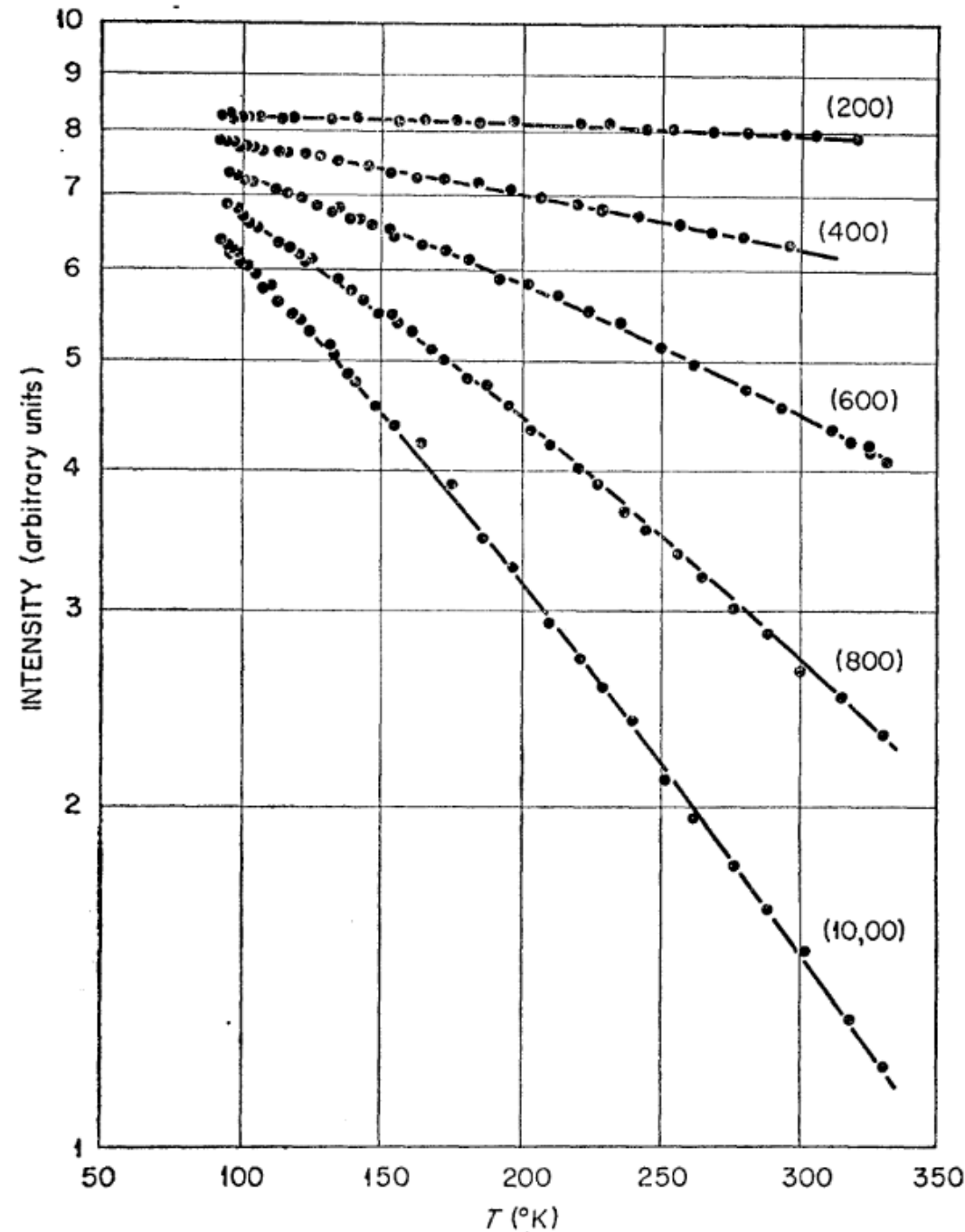
To do this quantum mechanically...use

The Bloch identity : $\langle e^C \rangle = e^{\langle C^2 \rangle / 2}$

It holds if C is a linear combination of a and a^+

The average is a thermal average as before

How lattice vibrations affect X-ray lines: Debye Waller factor

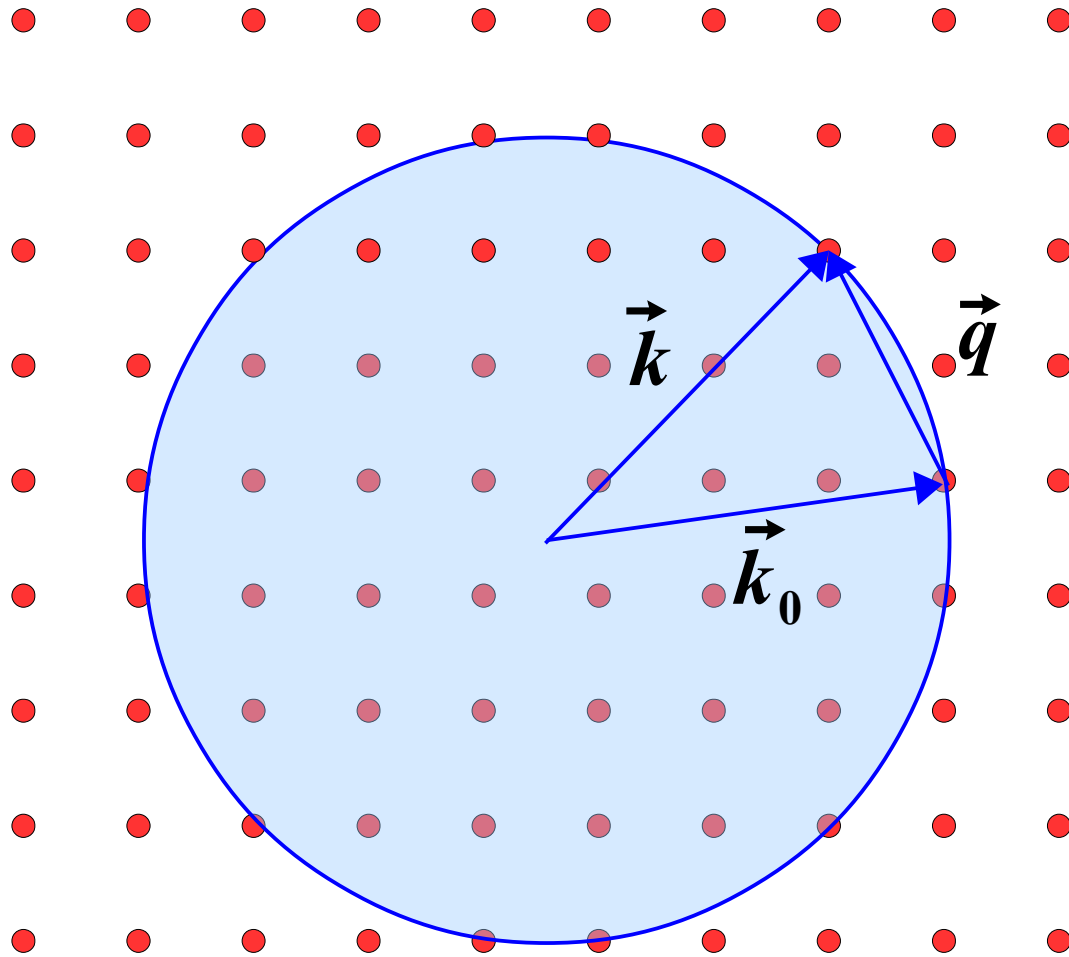


The intensity peak gets reduced but not broadened by the "Debye Waller factor"

The intensity of the (h00) lines of Aluminium. h=odd lines are forbidden for FCC.

The data is from R.M. Nicklow and R.A. Young, *PRB* **152**, 591 (1966)

Ewald sphere



Draw the reciprocal lattice

typical spacing $\sim \frac{2\pi}{a}$

Draw the incident beam circle

radius = $\frac{2\pi}{\lambda}$

Relative size

$a \sim 5 \text{ \AA}$ $\lambda \sim 1 \text{ \AA}$

What if $\lambda \ll a$?

The sphere is NOT centered at a reciprocal lattice point.
But is made to pass through one point, take that to be the origin for reciprocal lattice.

The allowed diffraction directions are obvious.

Ewald sphere

The reciprocal lattice points have finite widths.

The Ewald sphere is also NOT infinitely thin, why ?

What is the consequence of these two facts?

Now suppose we had an electron beam (~10-100 keV).
How would the Ewald sphere look ?

Can you see how electron diffraction will differ from X-ray diffraction?
Which should pick up the symmetry of the lattice more easily?

$$\lambda_{\text{X-ray}} = \frac{hc}{E} = 1.54 \text{ \AA} @ 8 \text{ keV}$$

$$\lambda_{\text{electron}} = \frac{h}{\sqrt{2m_0 eV (1 + eV / 2m_0 c^2)}} = 0.037 \text{ \AA} @ 100 \text{ keV}$$

$$V^* = V (1 + eV / 2m_0 c^2) \quad \text{is called the relativistic potential}$$

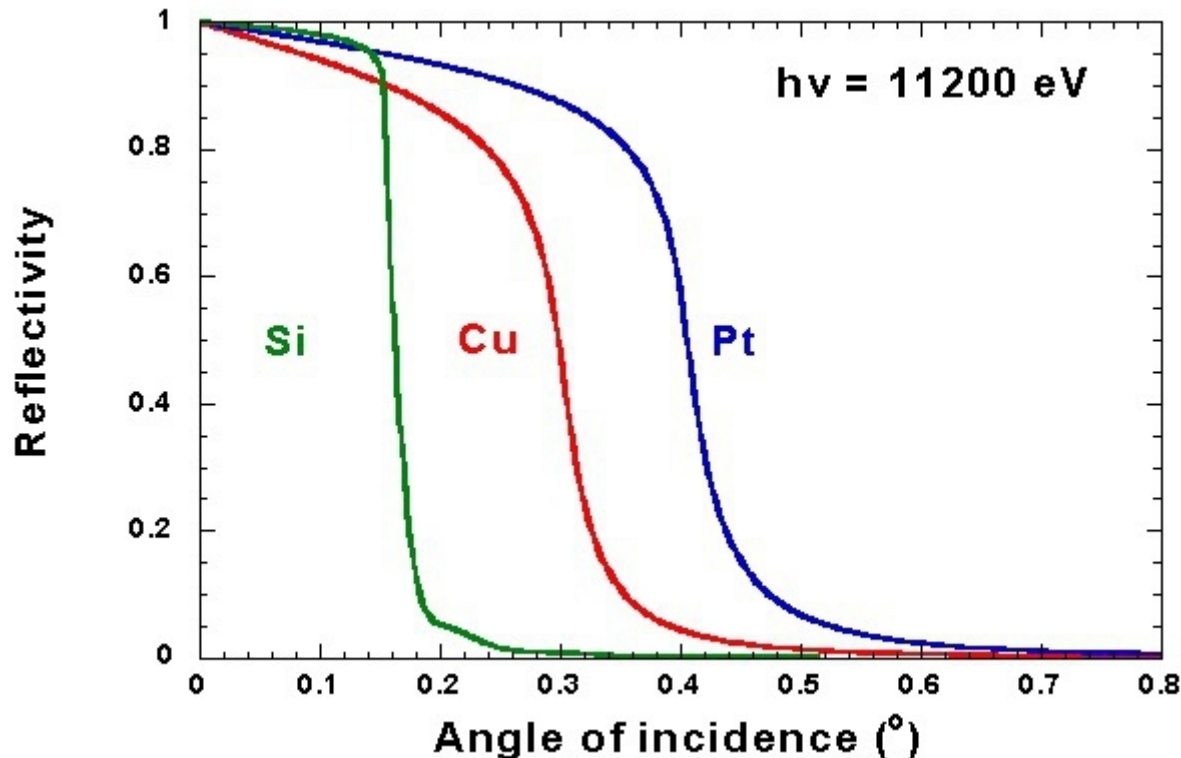
Small angle X ray diffraction : Total external reflection

The refractive index of materials at X-ray frequencies is slightly less than 1.

Vacuum has $n = 1$ exactly.

So xray travelling from vacuum to a medium (say a thin film) is like light travelling from water to air (denser to rarer medium!)

This means there must be an angle of total reflection. This is typically less than 0.2 degrees.



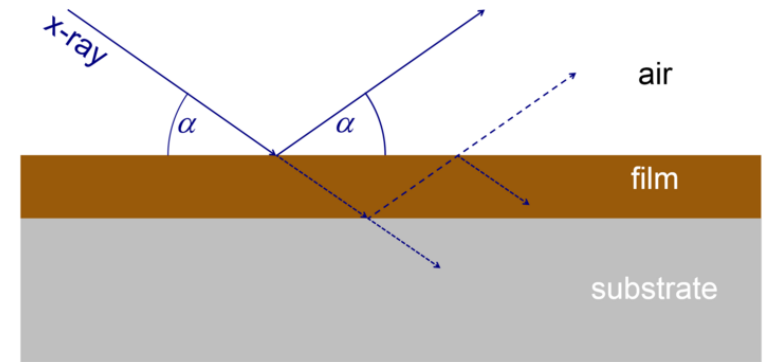
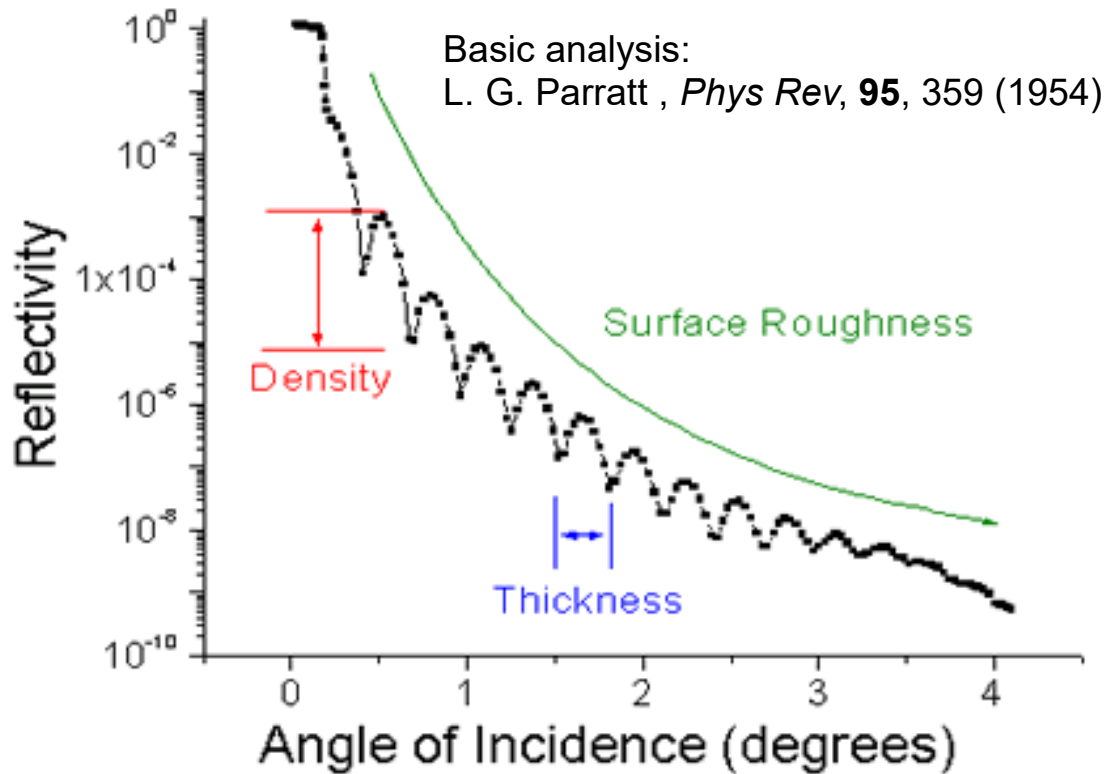
Data: http://www-project.slac.stanford.edu/ssrltxrf/total_reflection.htm

$n = (1 - \delta) + i\beta$
 β, δ can be related
to atomic form factors

What information does
the window between
 $\sim 0.5^\circ - 5^\circ$ contain?

These angles are too
small to be Bragg
angles. Why?

What information is contained at small angles ? Why?



$$2d \sin \alpha = \lambda$$

$$d \approx \frac{\lambda}{2 \Delta \alpha}$$

film may be
amorphous or crystalline.
practical range $\sim 1 \text{ nm} - 1 \mu \text{ m}$

$$h(z) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-z^2/2\sigma^2} \Rightarrow R(q_z) \propto e^{-\sigma^2 q_z^2/2}$$

However this method works only on very smooth mirrorlike films. If you cannot see your reflection on the film....the method is unlikely to work!

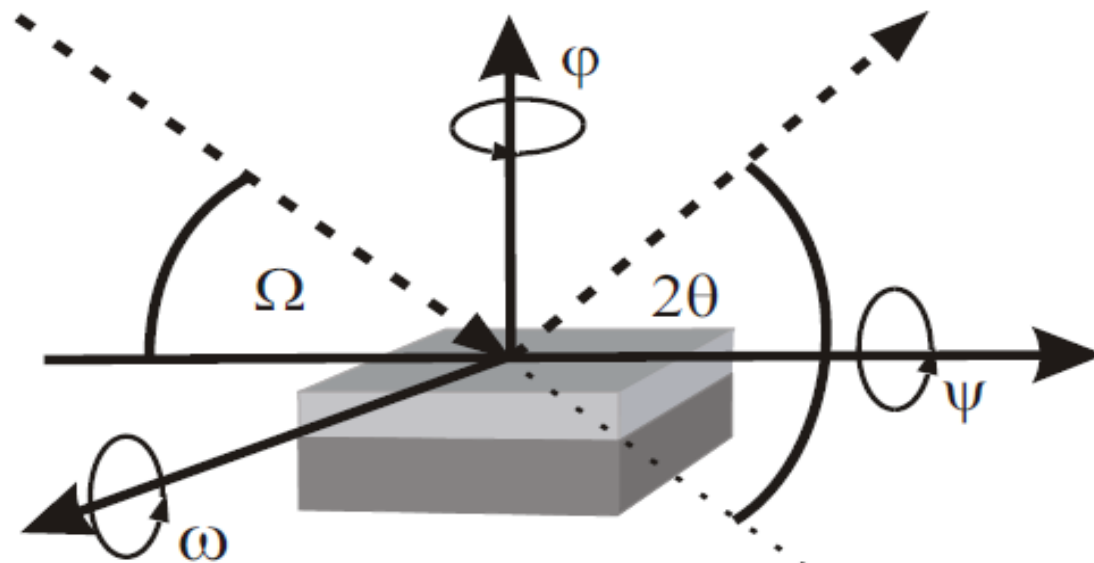
Reciprocal space map

The finite spread of each q vector contains information about deviations from perfect regularity – due to strain, defects, mosaics, lattice mismatch between substrate and epitaxial film etc, other than just finiteness of the volume.

Reciprocal space mapping tries to get this information.

Incident beam

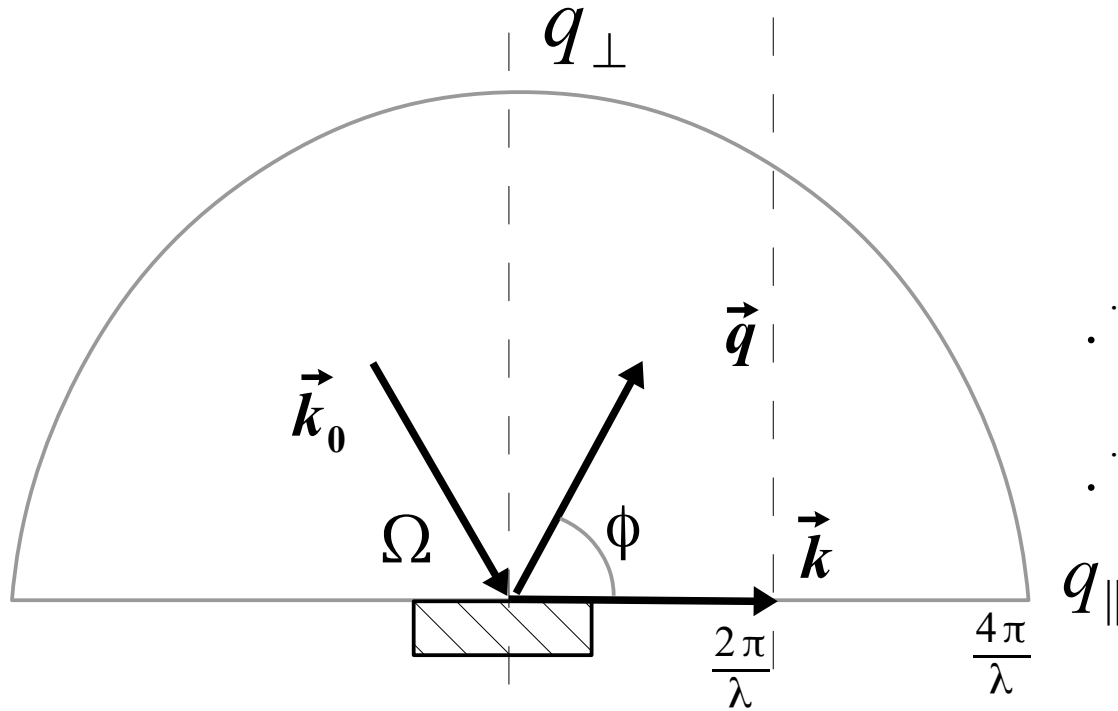
detector location



substrate with
epitaxial layer

**Detector cannot go below
the sample.**

Reciprocal space map : Which values of q are allowed ?



$$|\vec{q}| \sin \phi > \frac{2\pi}{\lambda} \cos\left(\frac{\pi}{2} - 2\phi\right)$$

$$\therefore |\vec{q}| \sin \phi > \frac{2\pi}{\lambda} 2 \sin \phi \cos \phi$$

$$\therefore |\vec{q}| > \frac{4\pi}{\lambda} \cos \phi$$

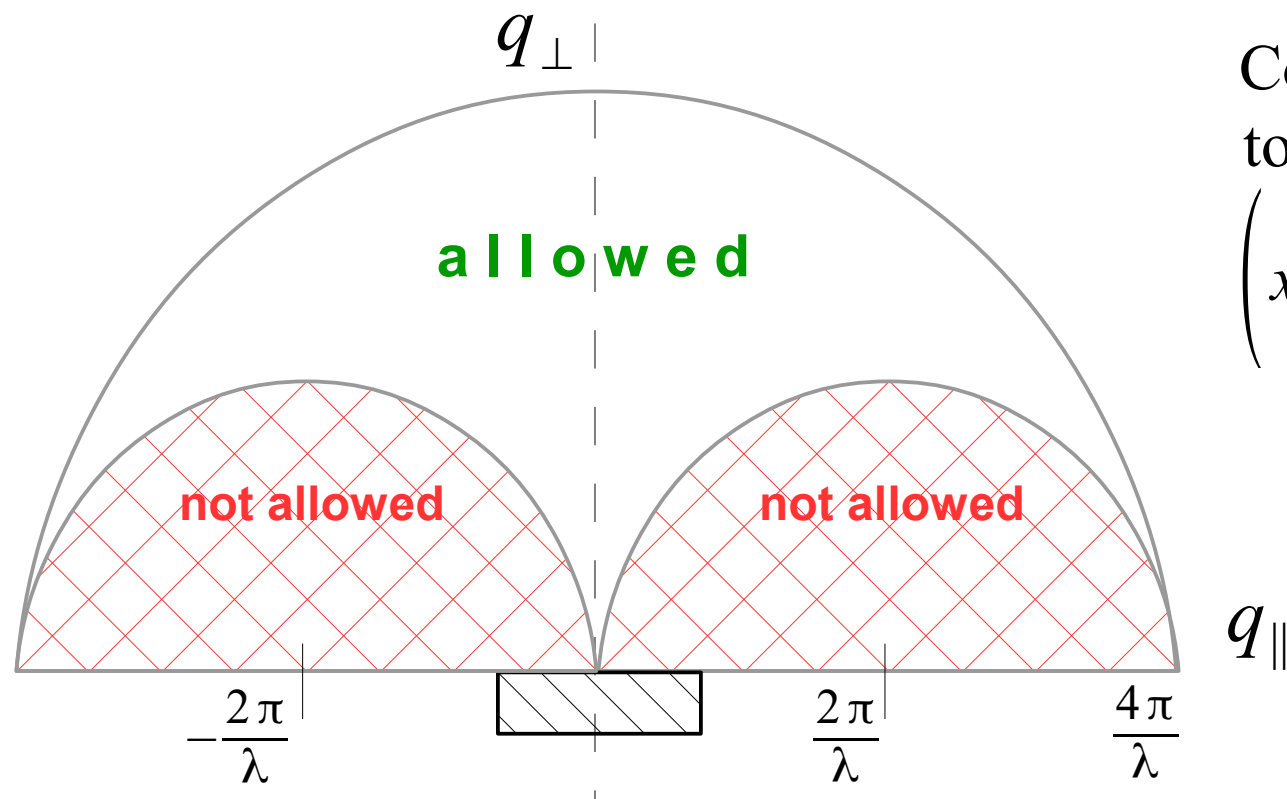
If q points along the normal then any value of q is allowed.

If q is along the x -axis then only allowed value is: $q_{\parallel} = 4\pi/\lambda$

For a direction ϕ the orientation of the relevant hkl planes are shown.

The reflected ray must lie on the upper half (no detector below the sample)

Reciprocal space map : Which values of q are allowed ?



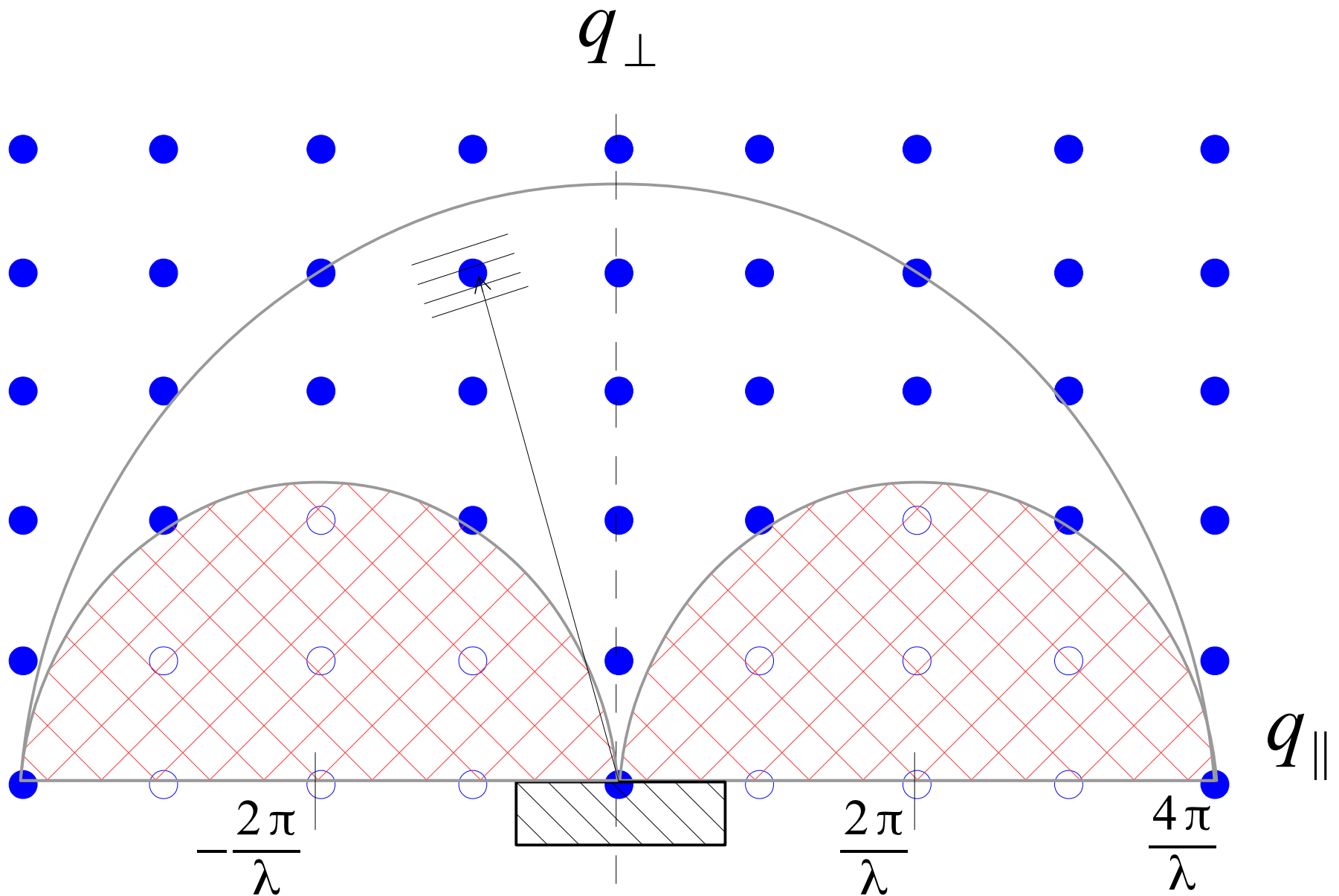
Convert $r = a \cos \theta$
to cartesian

$$\left(x \pm \frac{a}{2}\right)^2 + y^2 = \frac{a^2}{4}$$

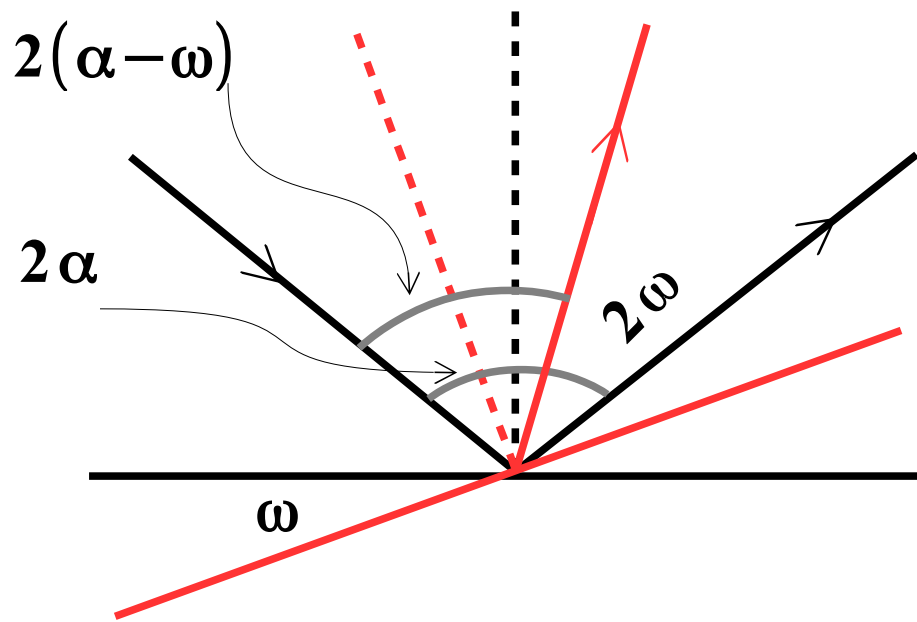
$$\left(q_{\parallel} - \frac{2\pi}{\lambda}\right)^2 + q_{\perp}^2 \geq \left(\frac{2\pi}{\lambda}\right)^2$$

$\frac{4\pi}{\lambda}$ is called the reciprocal lattice unit (r.l.u.)

Scanning the reciprocal space



The $\Omega - 2\theta$ scan or the coupled scan



The incident ray remains the same.
The sample rotates by an angle.
Reflected ray rotates by 2 x angle.

If sample rotates by ω
Detector needs to rotate by 2ω

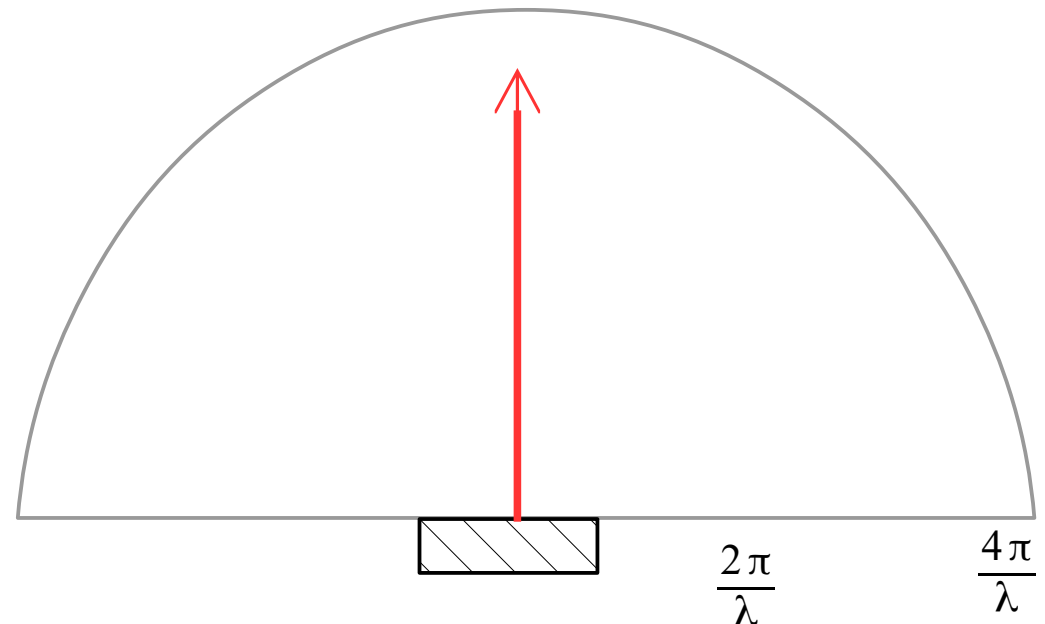
In some instruments the sample is fixed. Xray tube and detector both move at the same rate.

Such a scan picks up the same family of reflections (e.g. 00L)

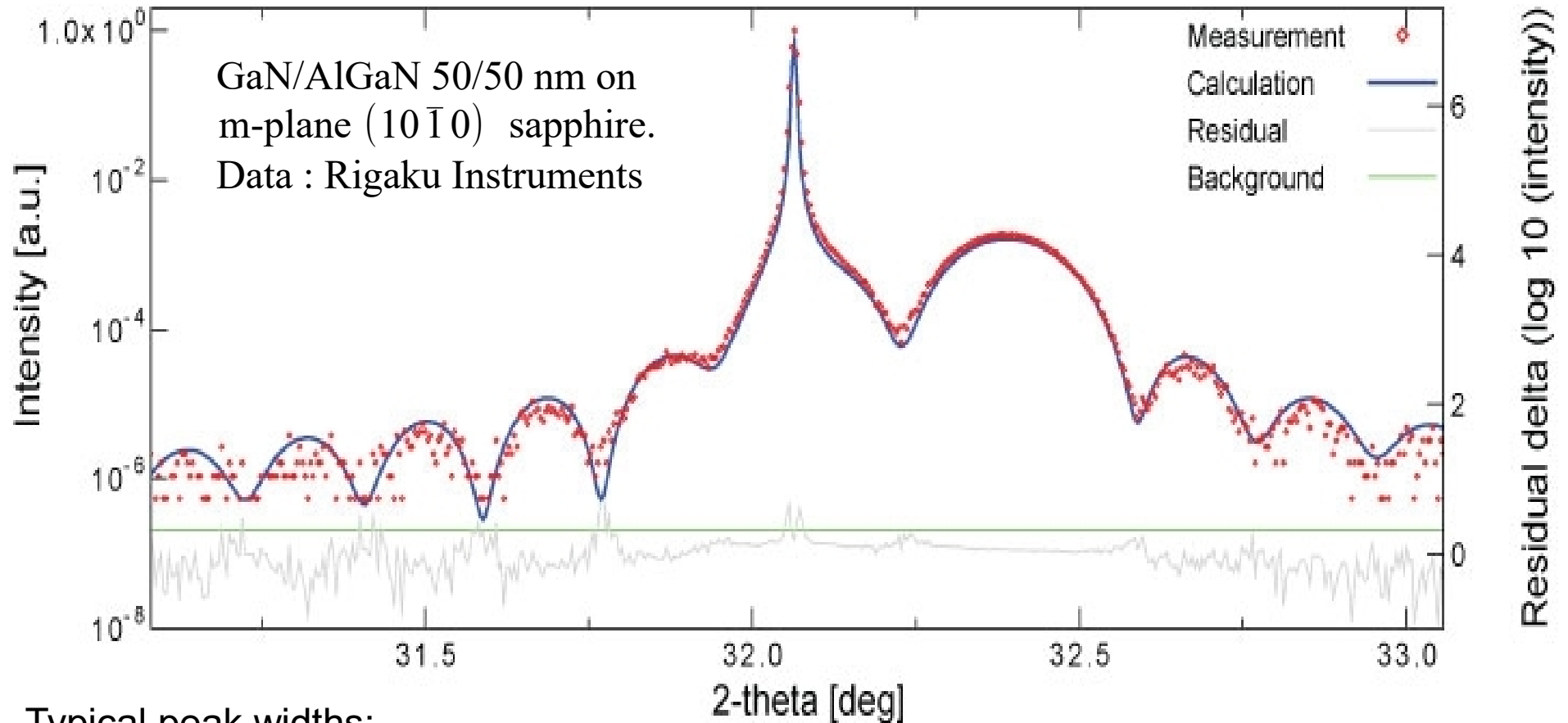
The scattering vector direction remains fixed. Magnitude changes.

Finite width of 00L peaks in perpendicular direction due to grain size/ film thickness.

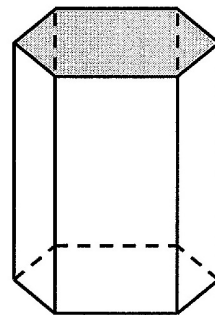
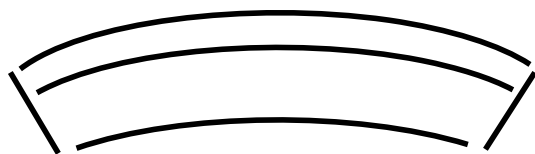
Distance between the secondary maxima is also related of the same.



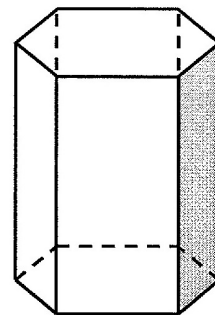
The $\Omega - 2\theta$ scan or the coupled scan



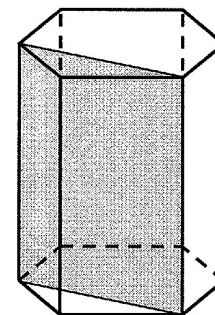
Typical peak widths:
(~ 100 arcsec)



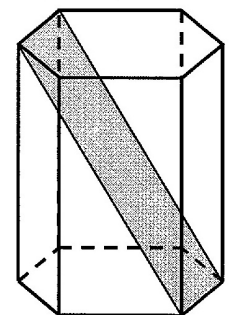
c
(0001)



m
($10\bar{1}0$)

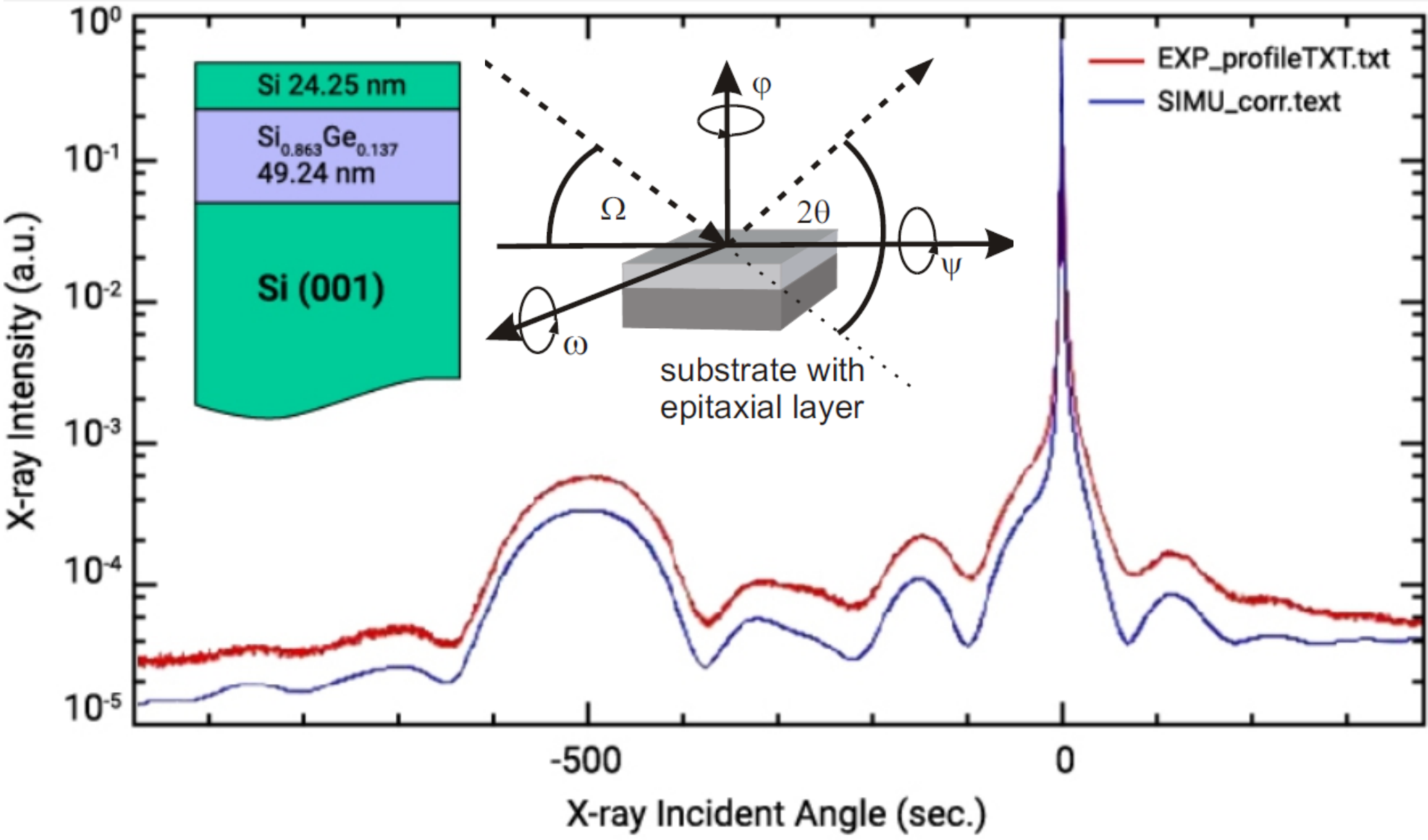


a
($11\bar{2}0$)



r
($10\bar{1}2$)

The rocking curve : fix detector and incident beam. Vary ω a bit

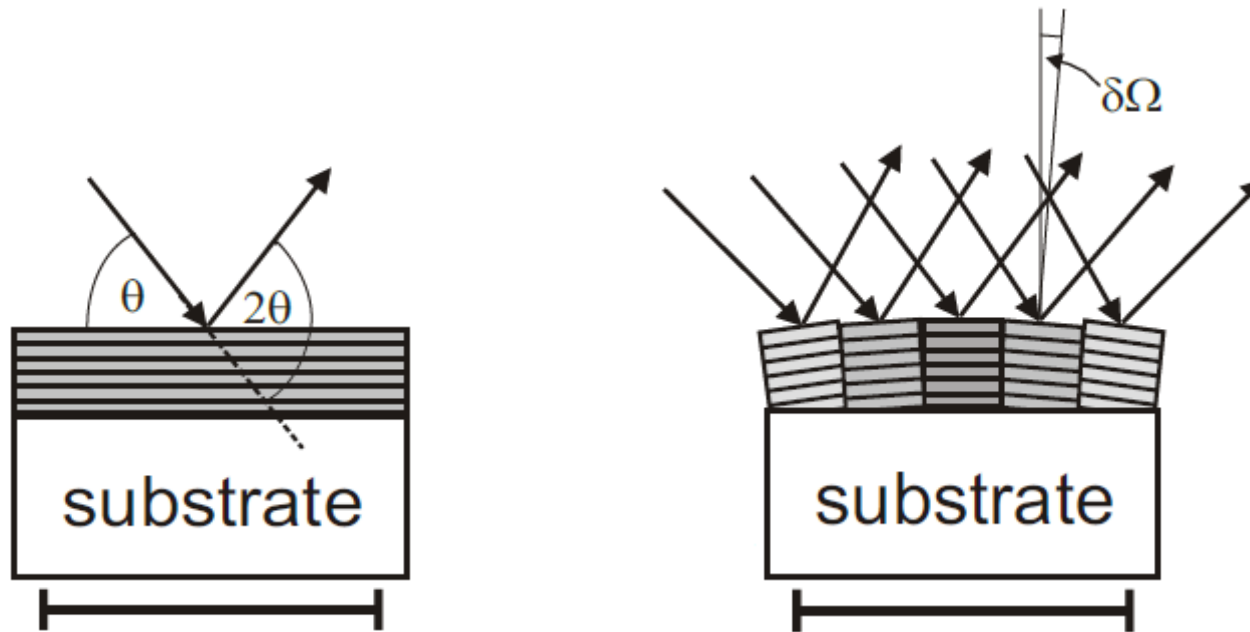


Broadening of the symmetric reflections

The symmetric (00L) reflections are broadened:

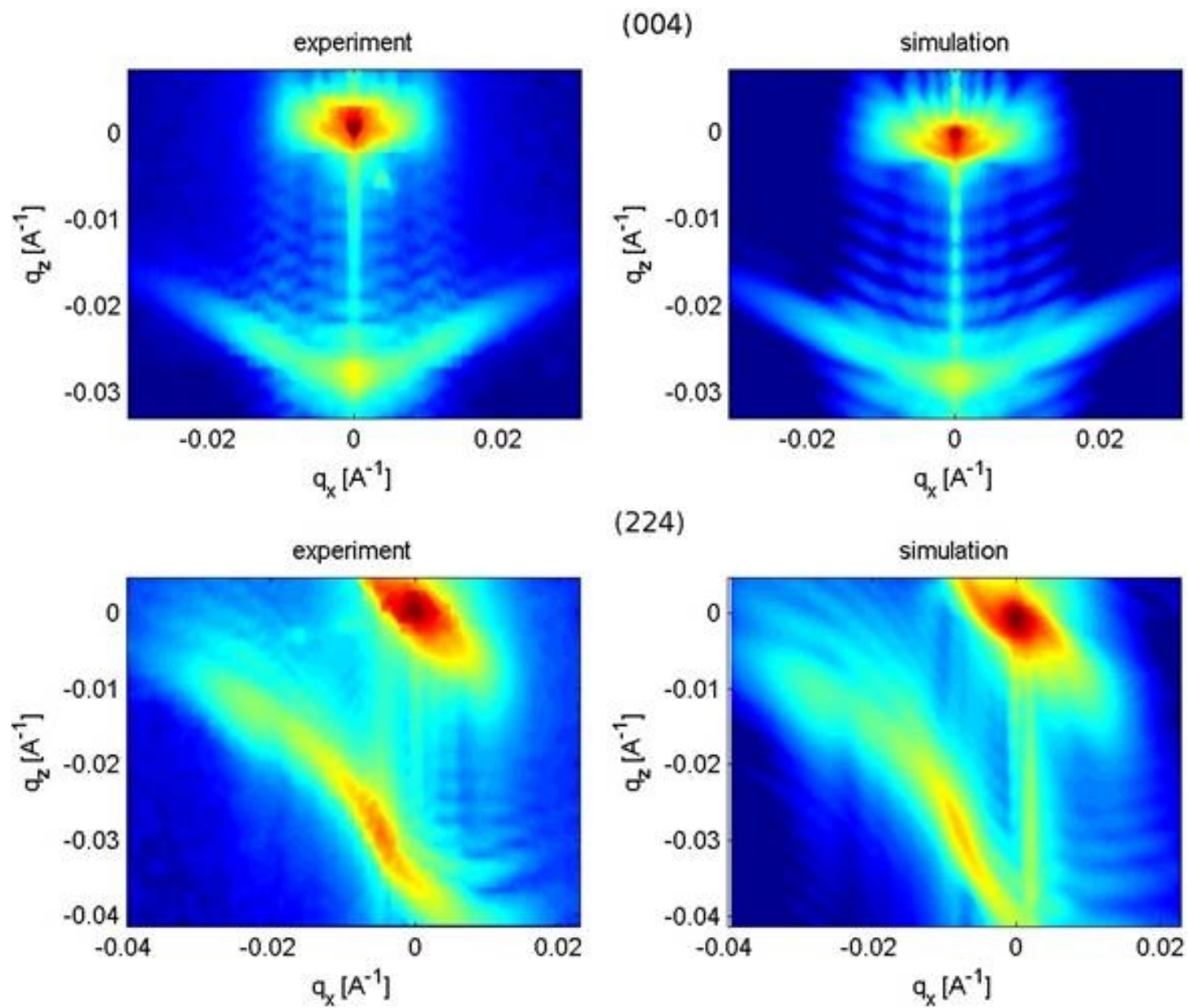
In vertical direction : size of the grain in vertical direction.

In lateral direction: tilt + lateral coherence length of the X-ray beam.



The twist of the grains will not affect this. How can we measure that?

Examples of reciprocal lattice maps

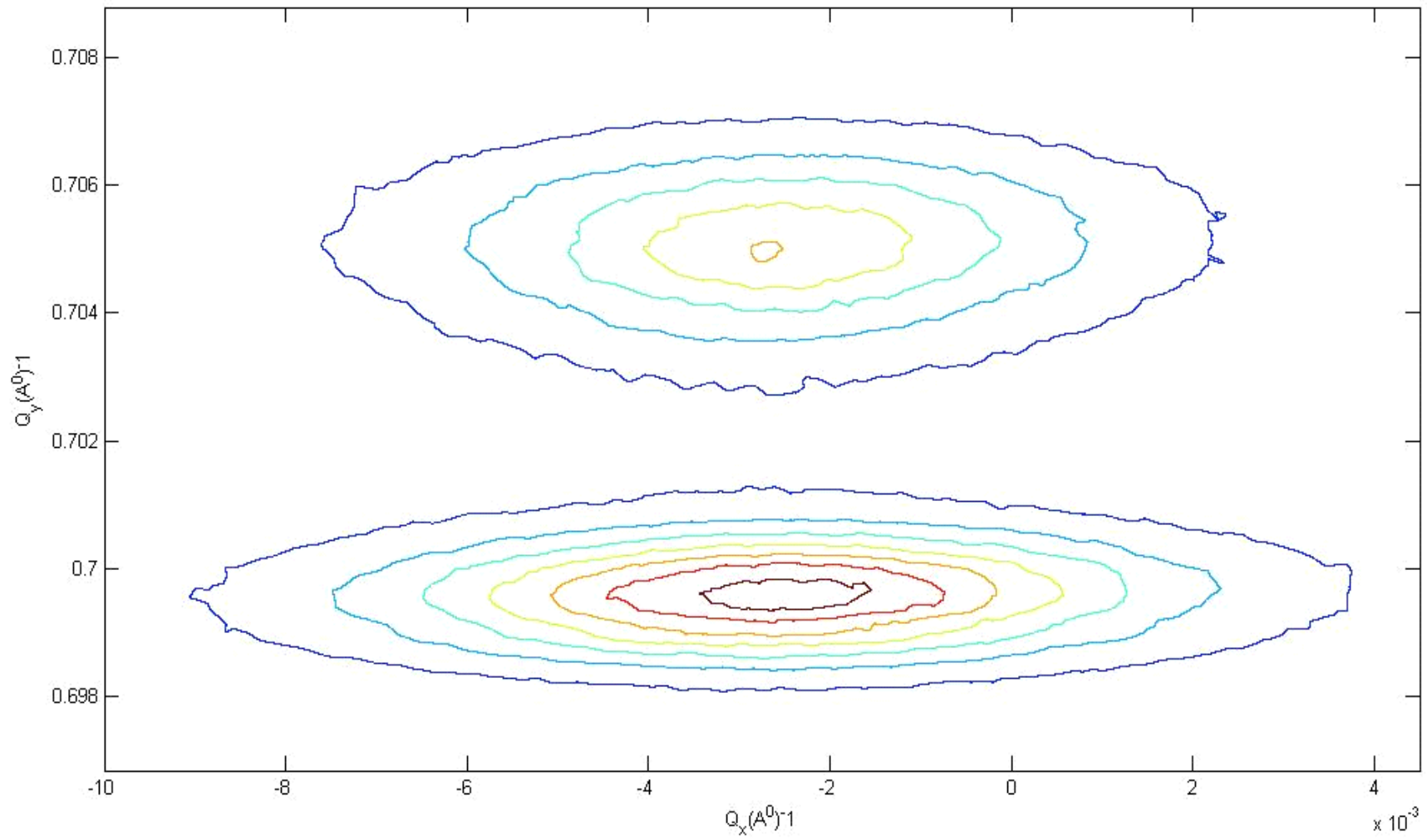


(Ga,Mn)As micro-wires on GaAs substrate: Strain field simulation.

Simulation of reciprocal space maps from elastic strain field in periodical nanostructures, L. Horak, J. Matejova

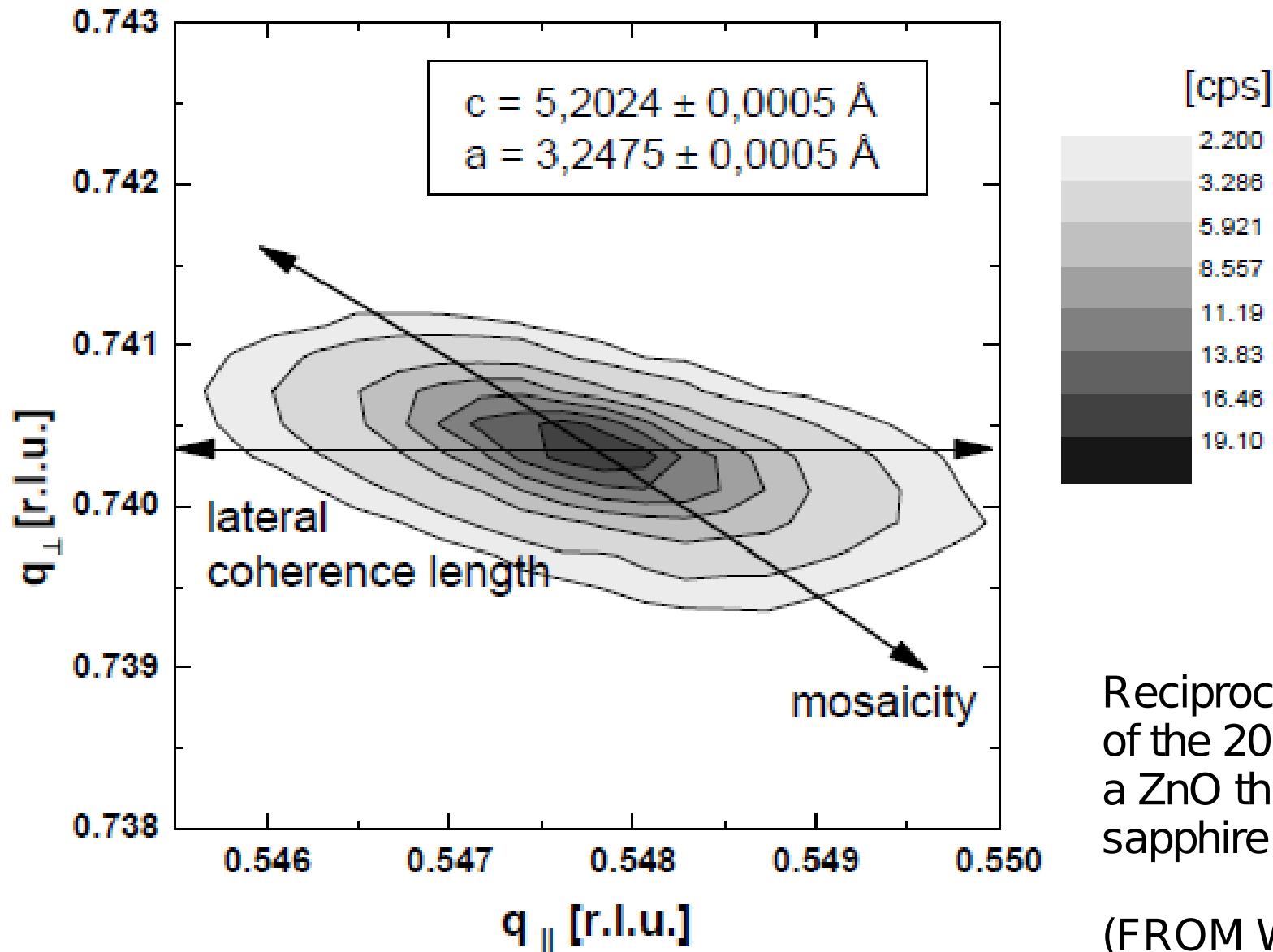
Examples of reciprocal lattice maps

(004) RSM of GeSn grown at $T_{\text{Ge}}=850^{\circ}\text{C}$, $T_{\text{G}}=150^{\circ}\text{C}$ and $T_{\text{Sn}}=900^{\circ}\text{C}$ (Sn% is 3.7)



Data: Krista R & S. Mahapatra

Examples of reciprocal lattice maps



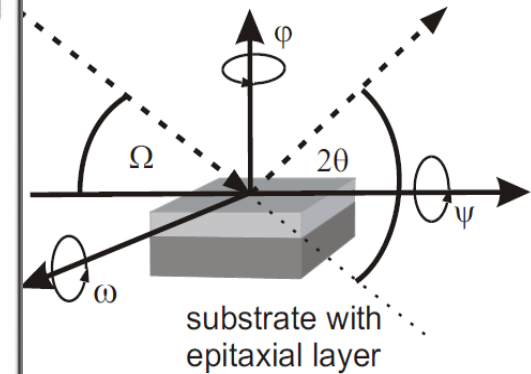
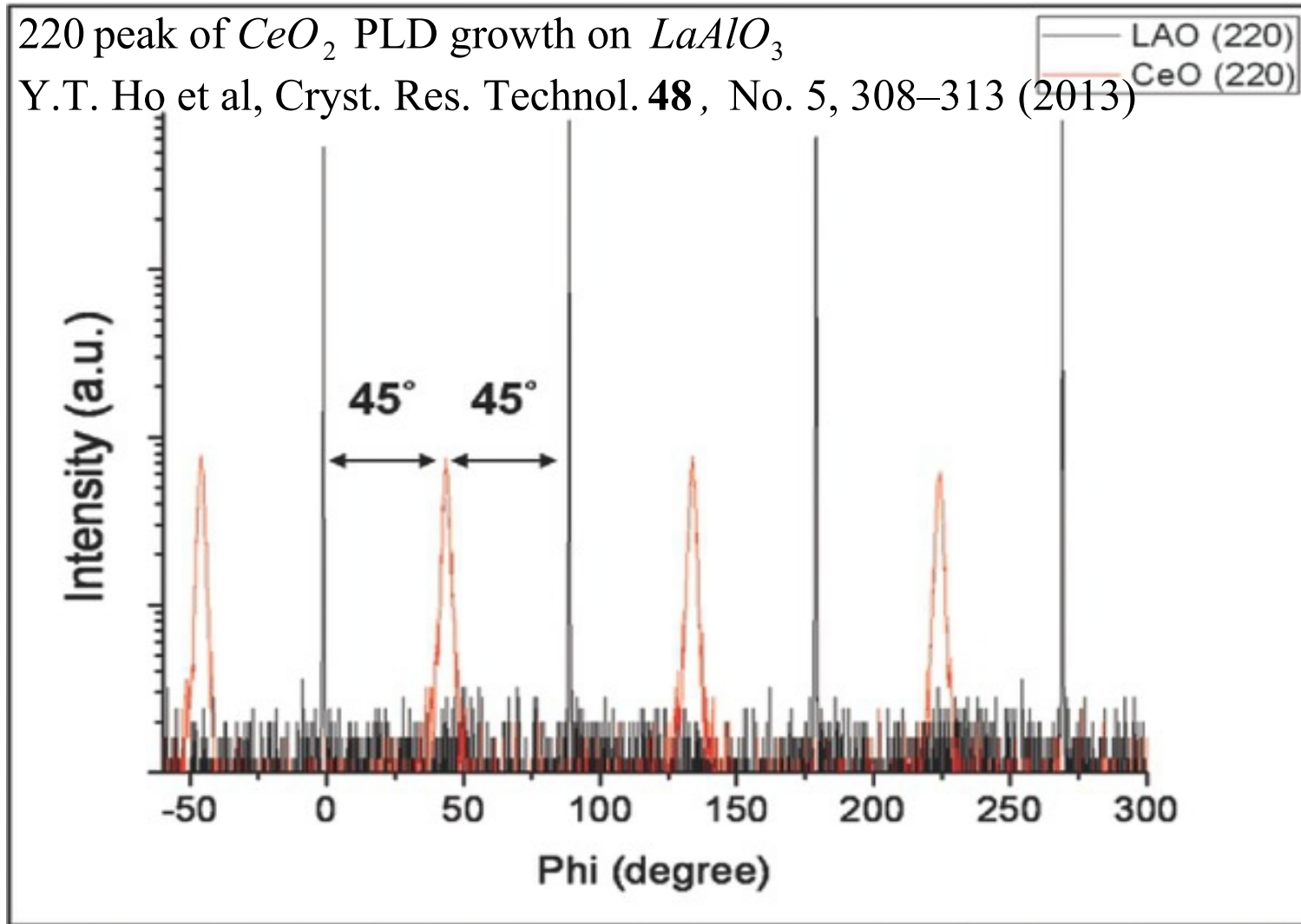
Reciprocal space map of the 205 reflection of a ZnO thin film on sapphire.

(FROM Walter Schottky Instt.)

The Φ scan : angle between the lattice of the film and the substrate

220 peak of CeO_2 PLD growth on $LaAlO_3$

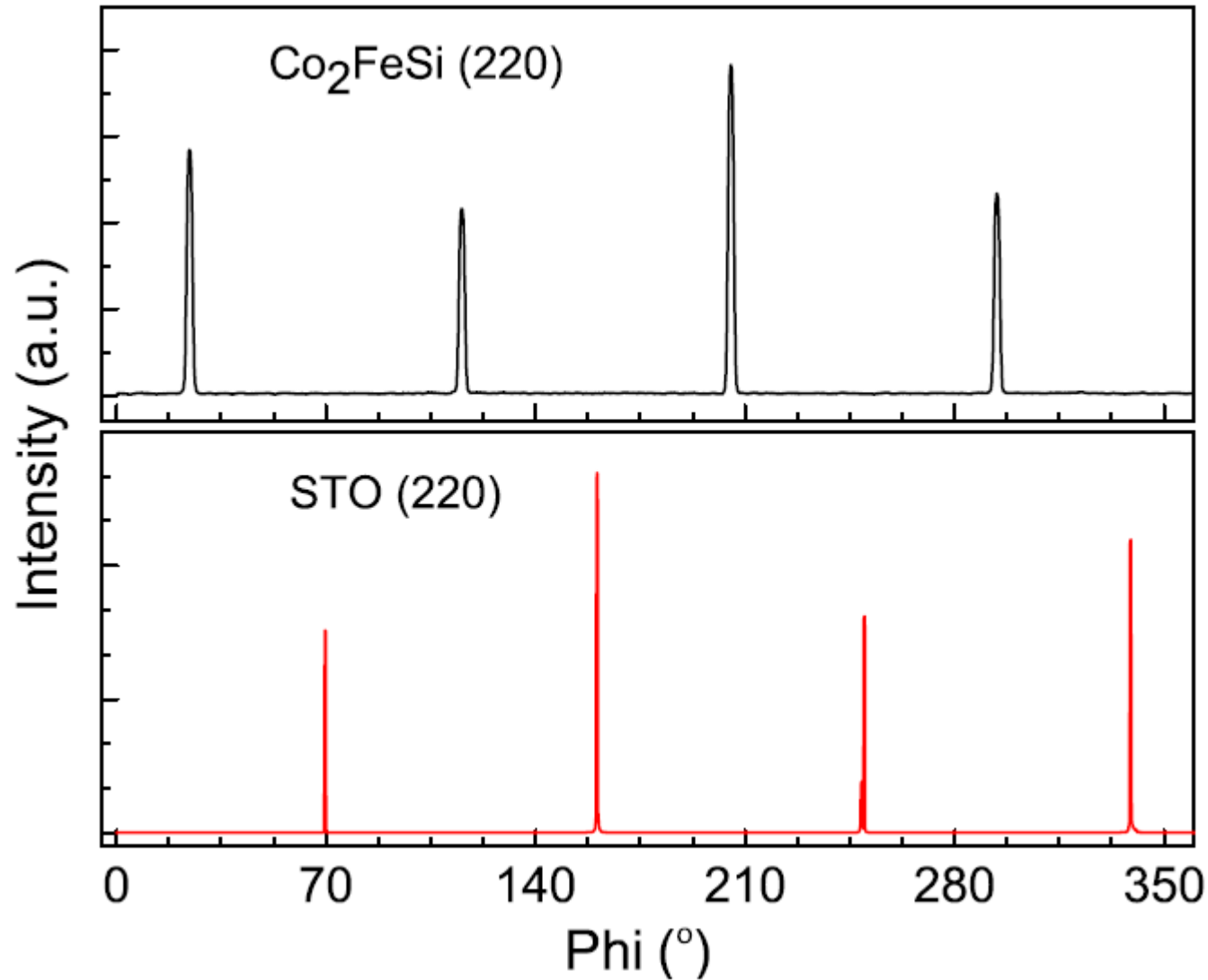
Y.T. Ho et al, Cryst. Res. Technol. **48**, No. 5, 308–313 (2013)



As the sample is rotated about the vertical axis, the reciprocal lattice also rotates. The rotational symmetry of the specific spot & the angular relation between the in-plane lattice vectors of the substrate and the film shows up.

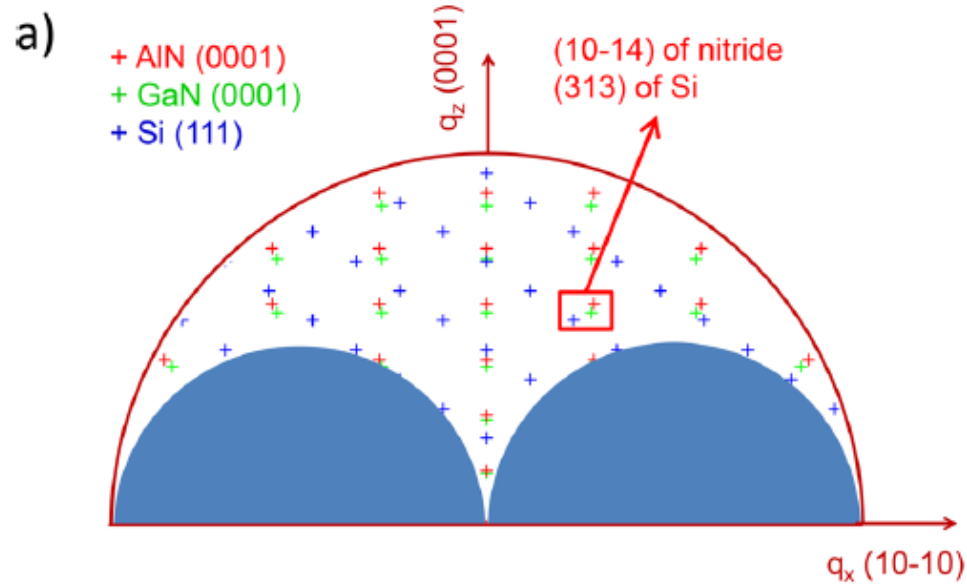
Note: CeO_2 is a high dielectric constant material ($K \sim 25$)

The Φ scan : another example



220 peak of : CO_2FeSi Laser ablation growth on $SrTiO_3$
Anupam et al, J. Phys. D: Appl. Phys. 43 (2010) 255002

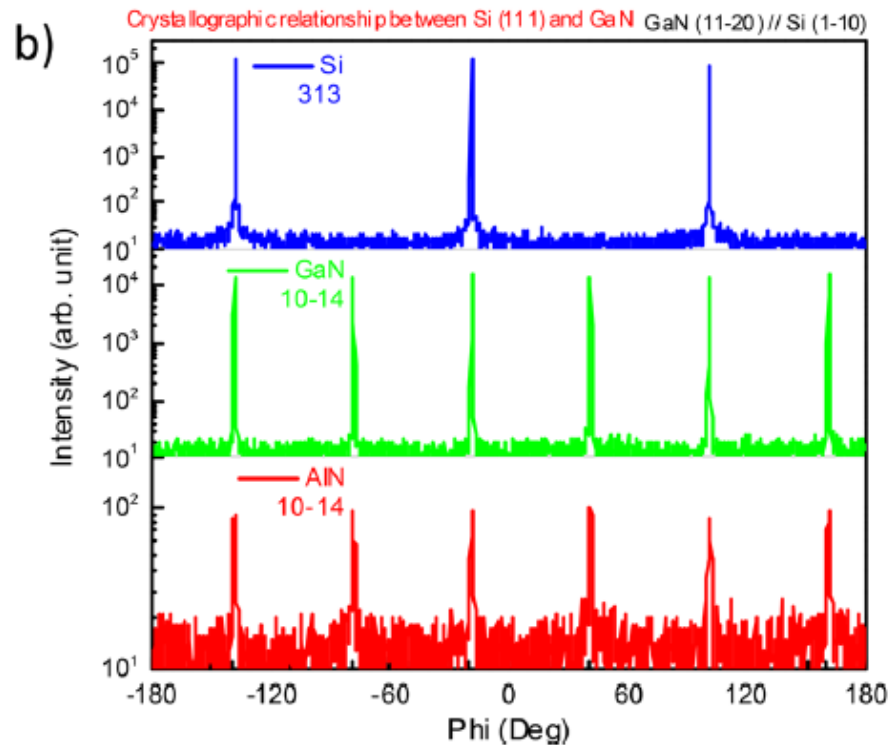
The Φ scan : another example



Kadir et al, Applied Physics Letters, **105**, 232113 (2014)

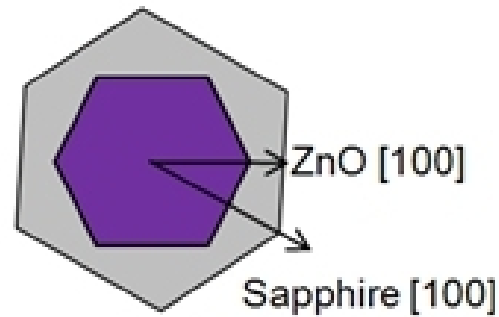
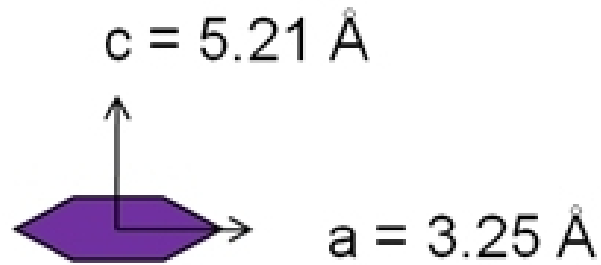
Determination of alloy composition and strain in multiple AlGaIn buffer layers in GaN/Si system

Notice how the reciprocal lattice structure and the phi-scan have been utilised

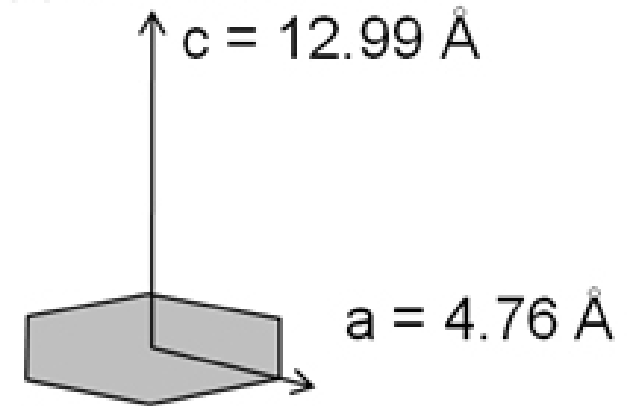


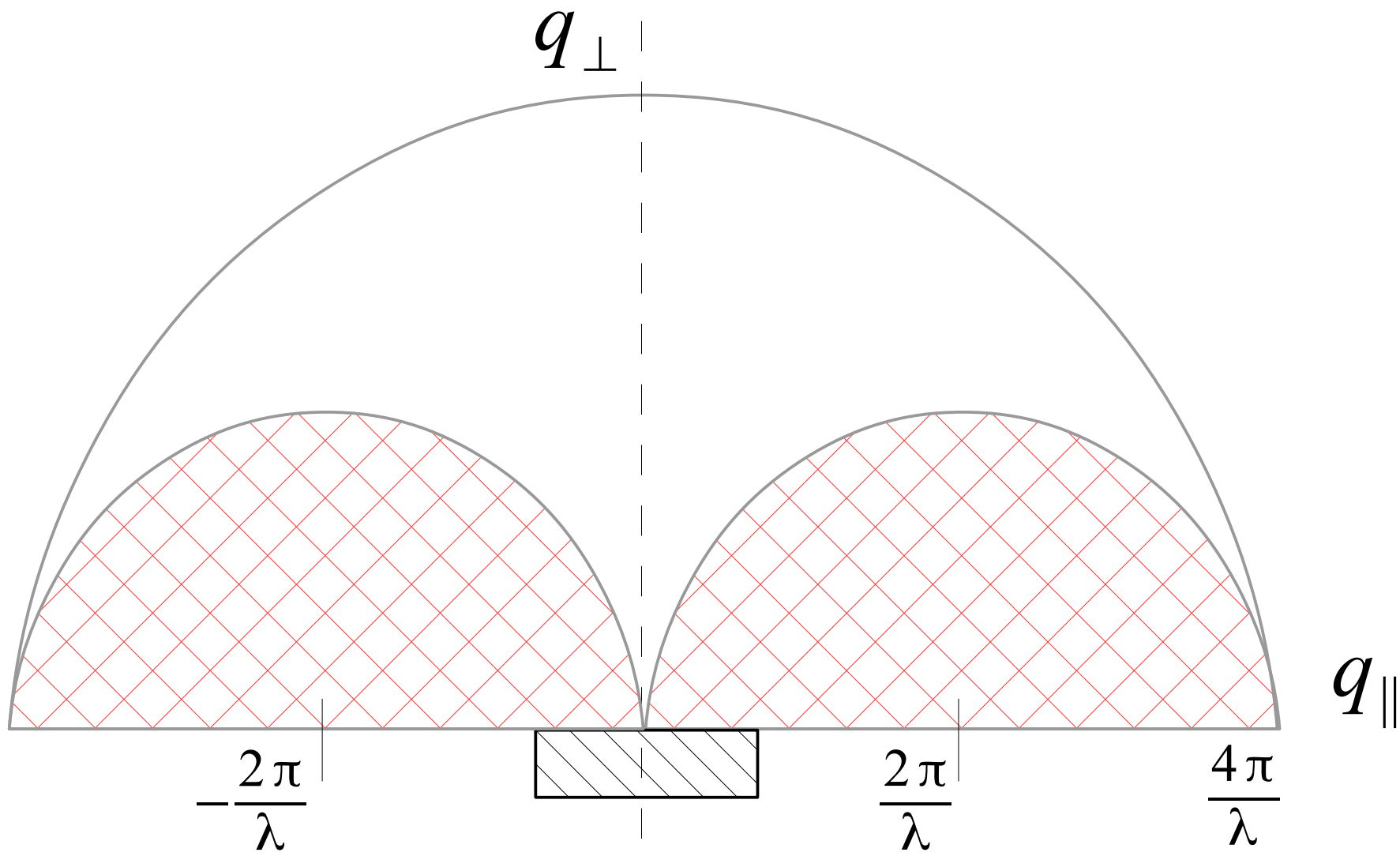
The Φ scan : a frequently encountered relative orientation

ZnO layer



Sapphire substrate





2. Electron and Neutron diffraction

The mean free path in air : a few numbers

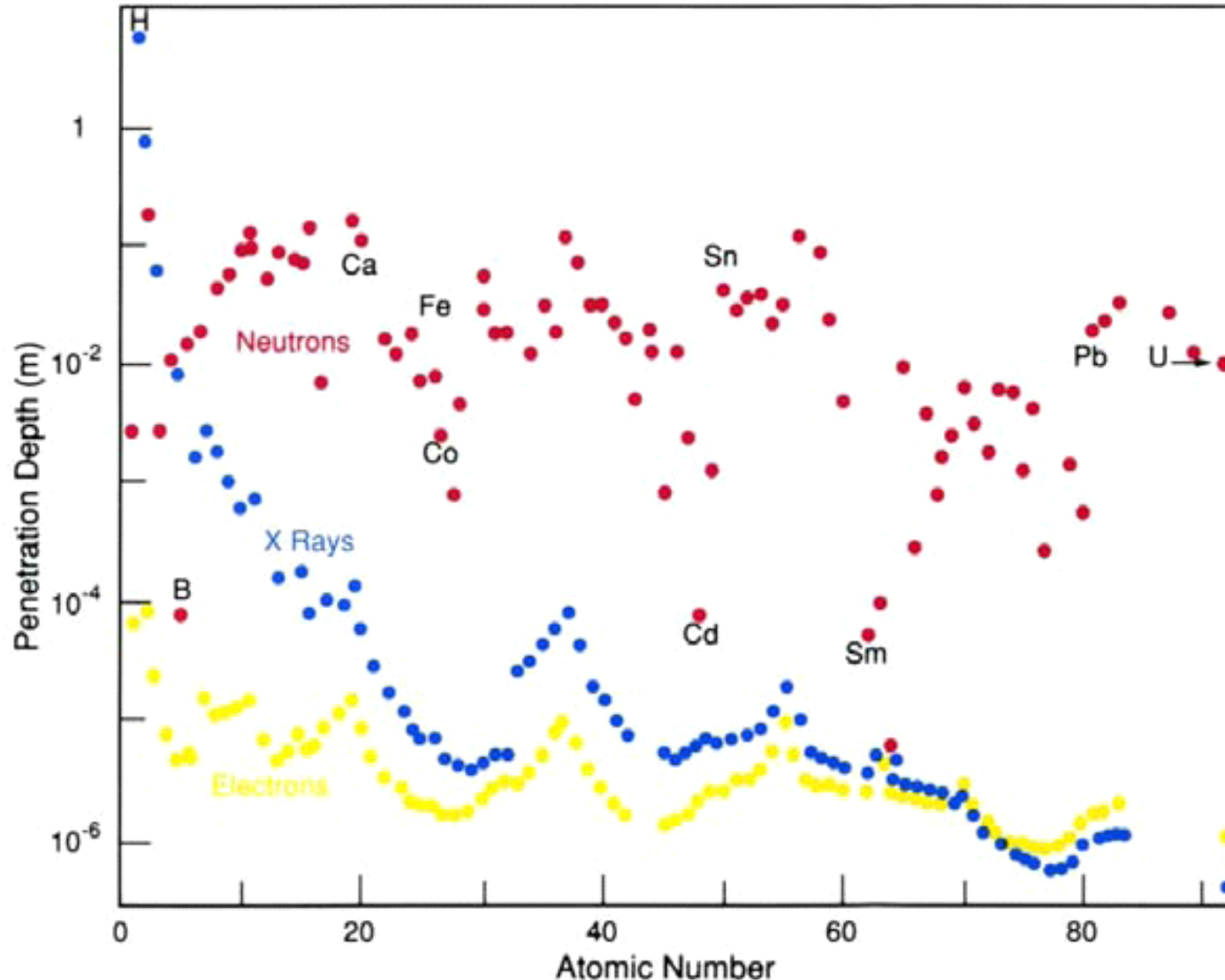
Air Pressure (mbar)	How to get this pressure?	Molecules (cm ⁻³)	Mean free path of air molecules	
1013	atm	$\sim 3 \times 10^{19}$	< 100 nm	
100		$\sim 10^{18}$	few μm	
10^{-3}	Rotary pumps	$\sim 10^{12}$	few cm	
10^{-6}	diffusion/ turbomolecular pumps	$\sim 10^9$	> 1 m (larger than a typical vacuum chamber)	Typical requirement for electron diffraction/imaging

$$l \approx \frac{1}{n \pi \sigma^2}$$

$p = nkT$

Electrons interact very strongly with matter...including air molecules. So any electron diffraction/imaging has to be done in high vacuum. Not required for x-rays in general.

X ray, neutron and electron : comparison of penetration depths



Q: If $\lambda = 1 \text{ \AA}$
 $E = ?$

$$E_{\text{Xray}} = \frac{hc}{\lambda} \approx 1.2 \times 10^4 \text{ eV}$$

$$E_{\text{Neutron}} = \frac{1}{2m_N} \left(\frac{h}{\lambda} \right)^2 \approx 82 \text{ meV}$$

$$E_{\text{electron}} = \frac{1}{2m_e} \left(\frac{h}{\lambda} \right)^2 \approx 150 \text{ eV}$$

For electrons at $\sim 10\text{--}100 \text{ kV}$, relativistic correction may be 5-10%

$$E^2 = p^2 c^2 + m_0^2 c^4$$

$$E = eV + m_0 c^2$$

$$\lambda = h/p$$

$$\lambda = \frac{h}{\sqrt{2eV m_0 (1 + eV/2m_0 c^2)}}$$

Neutron and electron : energies and wavelengths

<i>V (kV)</i>	Electrons	<i>Wavelength λ (nm)</i>	
		<i>Uncorrected</i>	<i>Relativistically corrected</i>
20		0.0086	0.0086
40		0.0061	0.0060
60		0.0050	0.0049
80		0.0043	0.0042
100		0.0039	0.0037
200		0.0027	0.0025
300		0.0022	0.0020
400		0.0019	0.0016
500		0.0017	0.0014
1000		0.0012	0.0009

Fast neutrons: >1 eV, 0.1 MeV or 1 MeV (Depending on the definition)

Slow neutrons: ≤ 0.4 eV.

Epithermal : 0.025 eV \sim 1 eV.

Hot neutrons : ~ 0.2 eV.

Thermal neutrons: ~ 0.025 eV.

Cold neutrons: 5×10^{-5} eV ~ 0.025 eV.

Very cold neutrons: 3×10^{-7} eV $\sim 5 \times 10^{-5}$ eV.

Ultra cold neutrons: $\sim 3 \times 10^{-7}$ eV.

Continuum region neutrons: 0.01 MeV \sim 25 MeV.

Resonance region neutrons: 1 eV \sim 0.01 MeV.

Low energy region neutrons: < 1 eV

Neutron and electron : energies and wavelengths

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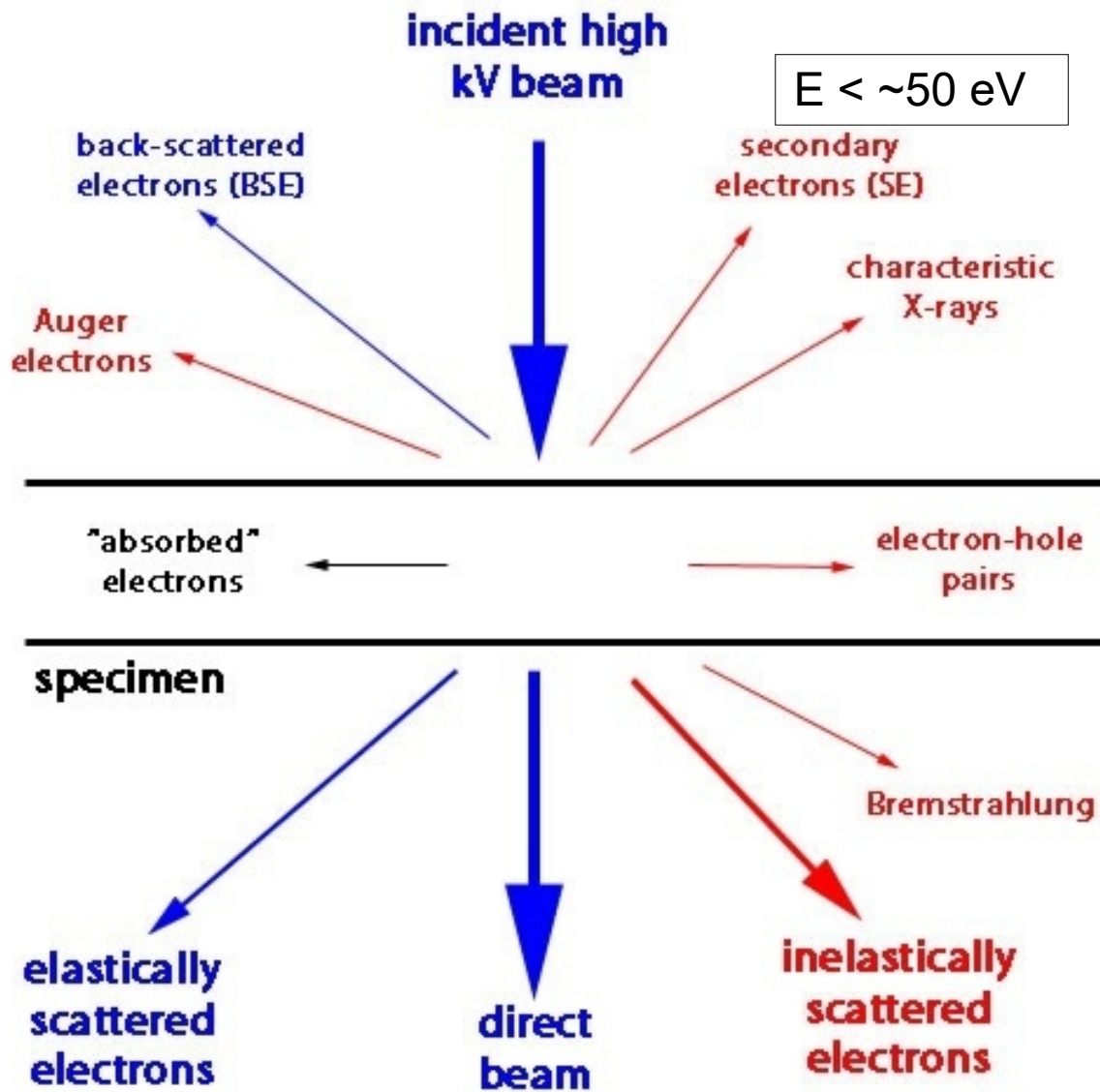
Ultra cold neutrons: $\sim 3 \times 10^{-7}$ eV.

Continuum region neutrons: 0.01 MeV \sim 25 MeV.

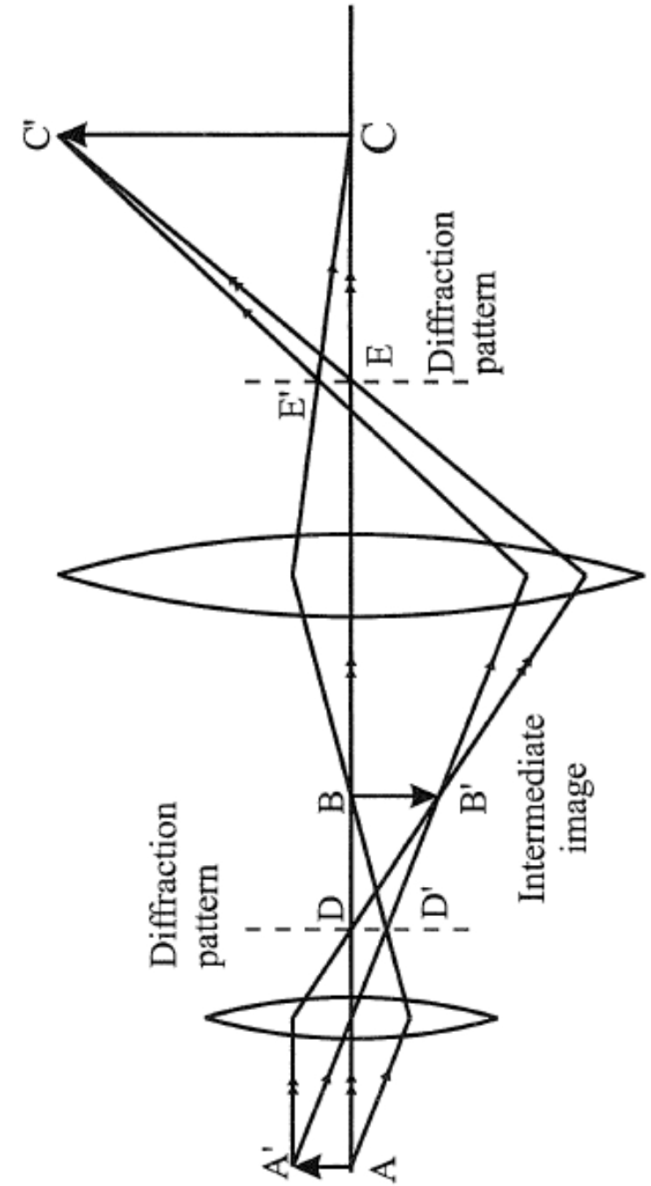
Resonance region neutrons: 1 eV \sim 0.01 MeV.

Low energy region neutrons: < 1 eV

Many processes that happen when electron beam hits matter



modified from Williams & Carter (1996) Fig. 1.3



**Image and diffraction.
What is the difference?**

Step 1: How is an electron beam generated ?

Generating the beam of electrons:

Thermionic emission : Tungsten work fn ~ 5 eV

Work function lowered in Thoriated Tungsten, LaB6 etc to about ~ 3 eV

Required vacuum at filament $\sim 1e-5$ mbar

Simpler technique but has certain limitations.

Beam divergence

Energy spread

Limited in brightness

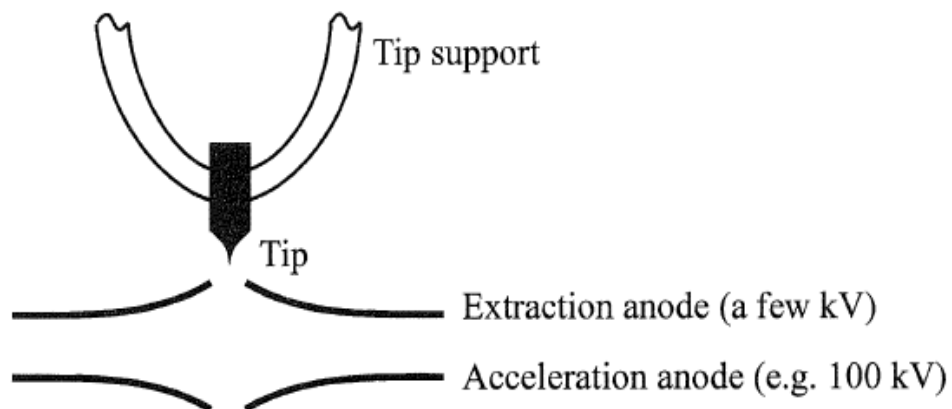
Field emission

Needs extremely sharp tip (< 100 nm) &

Requires very large electric field $> 1e9$ V/m in Ultra high vacuum ($\sim 1e-9$ mbar)

Strong electric field leads to tunneling of electrons (Fowler -Nordheim process)

~ 0.5 eV energy spread



Step 2: How is an electron beam focussed?

Electrostatic Lens :

Cylindrical

Quadrupolar

Magnetic Lens

Solenoidal

Potentials with axial symmetry : An useful relation

$$\nabla^2 V = \frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial V}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2 V}{\partial \phi^2} + \frac{\partial^2 V}{\partial z^2} = 0$$

If the beam does not change the potential

$$\frac{\partial V}{\partial \rho} + \rho \frac{\partial^2 V}{\partial \rho^2} + \rho \frac{\partial^2 V}{\partial z^2} = 0$$

Axially symmetric

If $V(0,z)$ is known the complete potential & trajectory can be determined.

First solve a generic problem for axially symmetric solution of laplace eqn

$$\frac{\partial V}{\partial \rho} + \rho \frac{\partial^2 V}{\partial \rho^2} + \rho \frac{\partial^2 V}{\partial z^2} = 0$$

$$V(\rho, z) = \sum_{n=0}^{\infty} A_{2n}(z) \rho^{2n}$$

$$V(0, z) = A_0(z)$$

Can couple even powers to even powers only.

Consider the powers of ρ .

First & second term will reduce power by 1.

Third term increases the power by 1.

No coupling between ρ^n and ρ^{n+1} possible.

$$\sum_{n=1}^{\infty} A_{2n}(z) \cdot 2n \cdot \rho^{2n-1} + \sum_{n=1}^{\infty} A_{2n}(z) \cdot 2n \cdot (2n-1) \cdot \rho^{2n-1} + \sum_{n=0}^{\infty} \left(\frac{d^2}{dz^2} A_{2n}(z) \right) \rho^{2n+1}$$

Trajectory calculation in paraxial approximation

$$\sum_{n=1}^{\infty} A_{2n}(z) \cdot 2n \cdot \rho^{2n-1} + \sum_{n=1}^{\infty} A_{2n}(z) \cdot 2n \cdot (2n-1) \cdot \rho^{2n-1} + \sum_{n=0}^{\infty} \left(\frac{d^2}{dz^2} A_{2n}(z) \right) \rho^{2n+1}$$

Consider the coefficient of ρ

$$A_2(2+2.1) + A_0''(z) = 0 \quad \Rightarrow \quad A_2 = -\frac{A_0''}{4}$$

Consider the coefficient of ρ^3

$$A_4(4+4.3) + A_2''(z) = 0 \quad \Rightarrow \quad A_4 = \frac{A_0''''}{64}$$

Can you write the general term in the expansion ?

Try to find the pattern of the coefficients.

$$\frac{(-1)^n}{(n!)^2} \left(\frac{\rho}{2} \right)^{2n} A_0^{(2n)}(z)$$

The series solution is then :

$$V(\rho, z) = V(0, z) - \frac{V''(0, z)}{4} \rho^2 + \frac{V''''(0, z)}{64} \rho^4 - \dots$$

$$E_r = -\frac{\partial V}{\partial \rho} = \frac{1}{2} \rho V''(0, z)$$

$$E_z = -\frac{\partial V(0, z)}{\partial z} = -V'(0, z)$$

Correct to first order

Terms of order ρ^2 and higher dropped

Trajectory calculation in paraxial approximation but relativistic

Recall this expression for momentum of a fast electron and define a "relativistic potential":

$$p_{\text{electron}} = \sqrt{2 m_0 e V (1 + e V / 2 m_0 c^2)}$$

$$= \sqrt{2 m_0 e V^*}$$

$$V^* = V (1 + 2 \epsilon V)$$

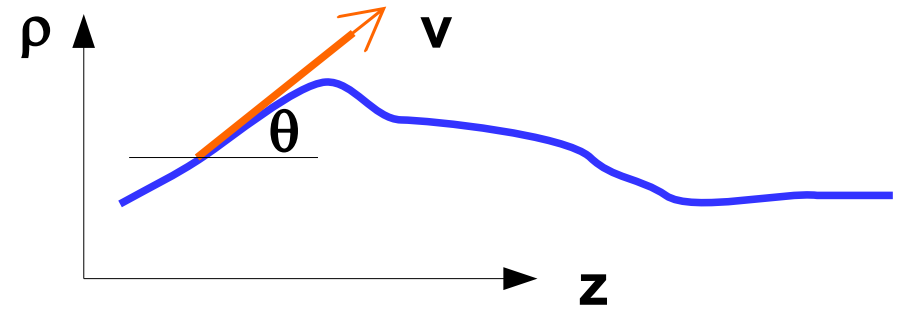
$$\epsilon = e / 2 m_0 c^2$$

Now the equation of motion is:

$$\frac{d}{dt} (m v_{\rho}) = -e E_{\rho}$$

$$\frac{dz}{dt} \cdot \frac{d}{dz} (m v \sin \theta) = -e E_{\rho}$$

$$v \cos \theta \cdot \frac{d}{dz} (m v \sin \theta) = -e E_{\rho}$$



$$\frac{d\rho}{dz} = \tan \theta$$

$$m v = \sqrt{2 e m_0 V^*}$$

$$m = m_0 (1 + 2 \epsilon V)$$

$$\frac{\sqrt{2 e V^*}}{1 + 2 \epsilon V} \cos \theta \frac{d}{dz} [(\sin \theta) \sqrt{2 e V^*}] + e E_{\rho} = 0$$

Trajectory calculation in paraxial approximation but slow...

The previous equation will reduce to :

$$\frac{d^2 \rho}{d z^2} + \left(\frac{V_0'}{V_0} \right) \frac{d \rho}{d z} + \left(\frac{V_0''}{4 V_0} \right) \rho = 0 \quad \text{If} \quad \left(\frac{d \rho}{d z} \right)^2 \ll 1$$

Substitute $f = \rho V^{1/4}$

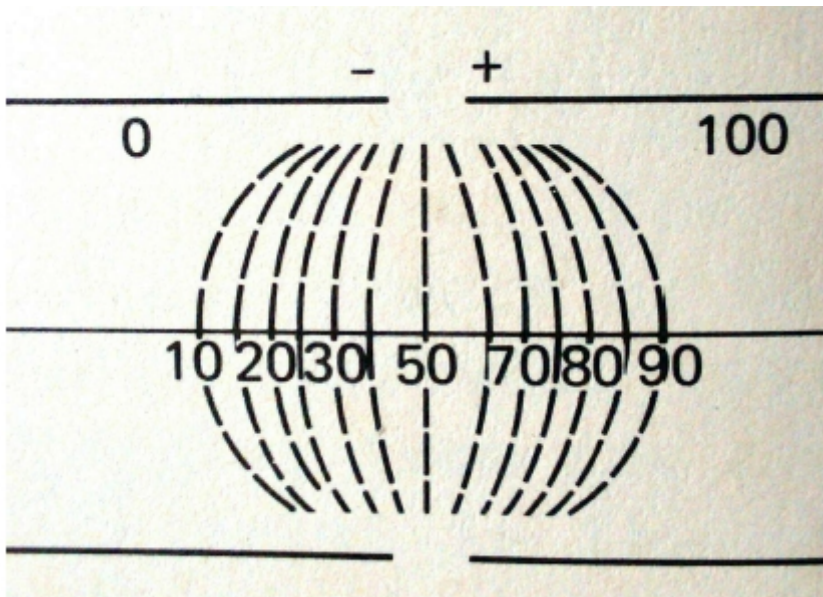
$$\frac{d^2 f}{d z^2} + \frac{3}{16} \left(\frac{V_0'}{V_0} \right)^2 f = 0$$

There is no e/m ratio in the equation

The trajectory depends on the shape of the potential field.

Paths of electrons and light : Bethe's observation

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$



$$v_{1\parallel} = v_{2\parallel}$$

Choose $\phi = 0$ position, so that

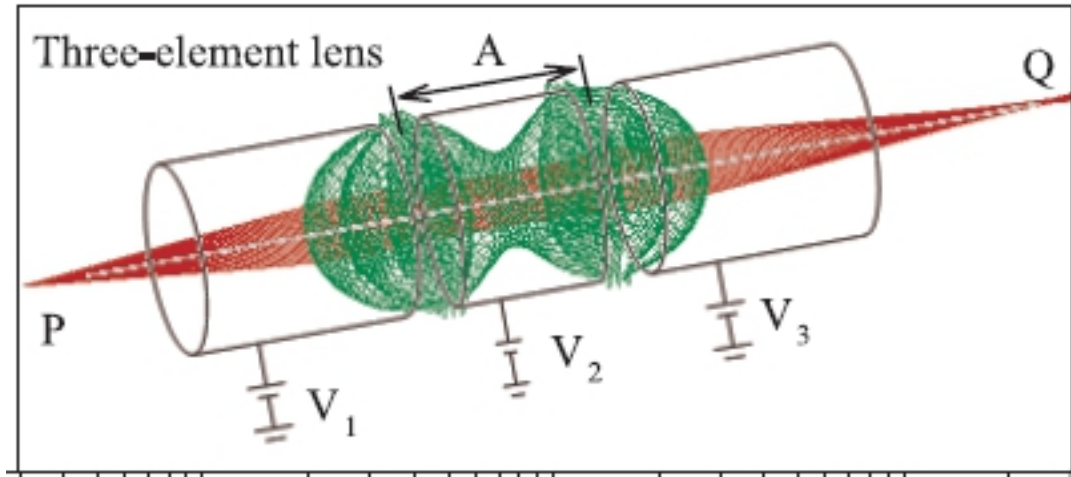
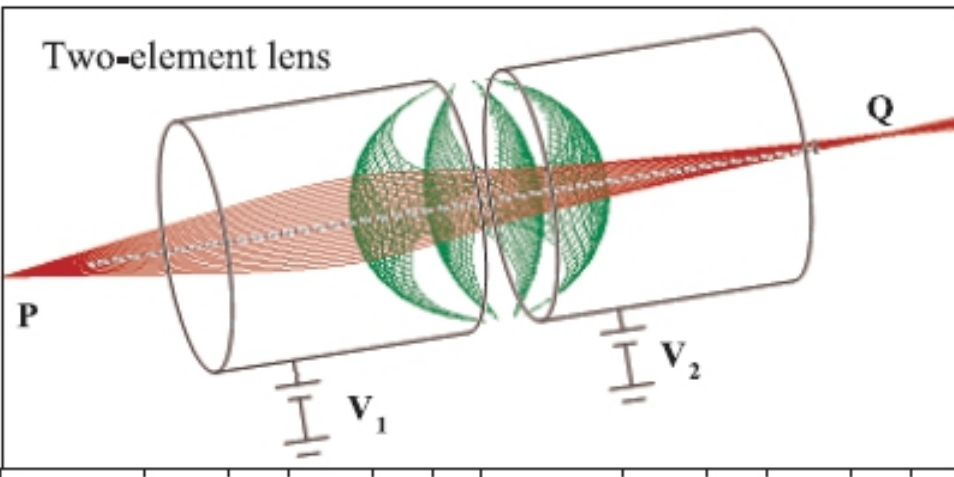
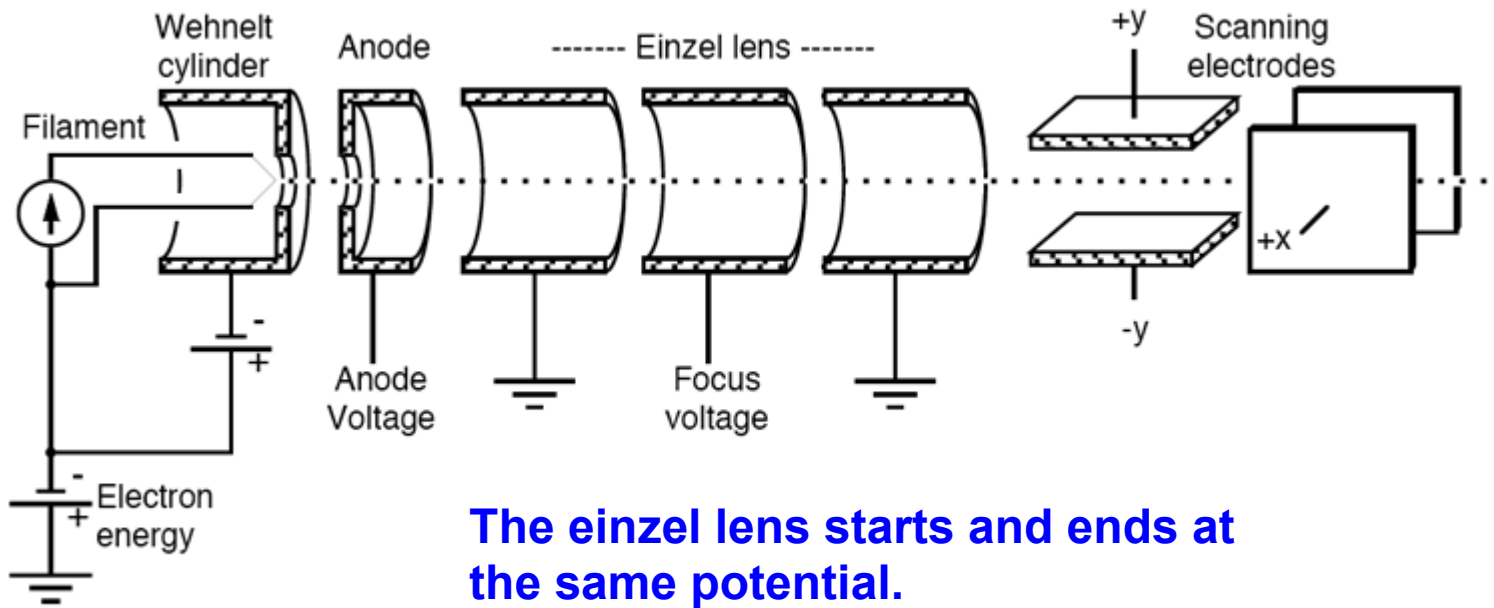
$$\frac{mv^2}{2} + q\phi = 0 \quad \Rightarrow \quad v \propto \sqrt{\phi}$$

$$\frac{\sqrt{\phi_1}}{v_1} v_{1\parallel} = \frac{\sqrt{\phi_2}}{v_2} v_{2\parallel}$$

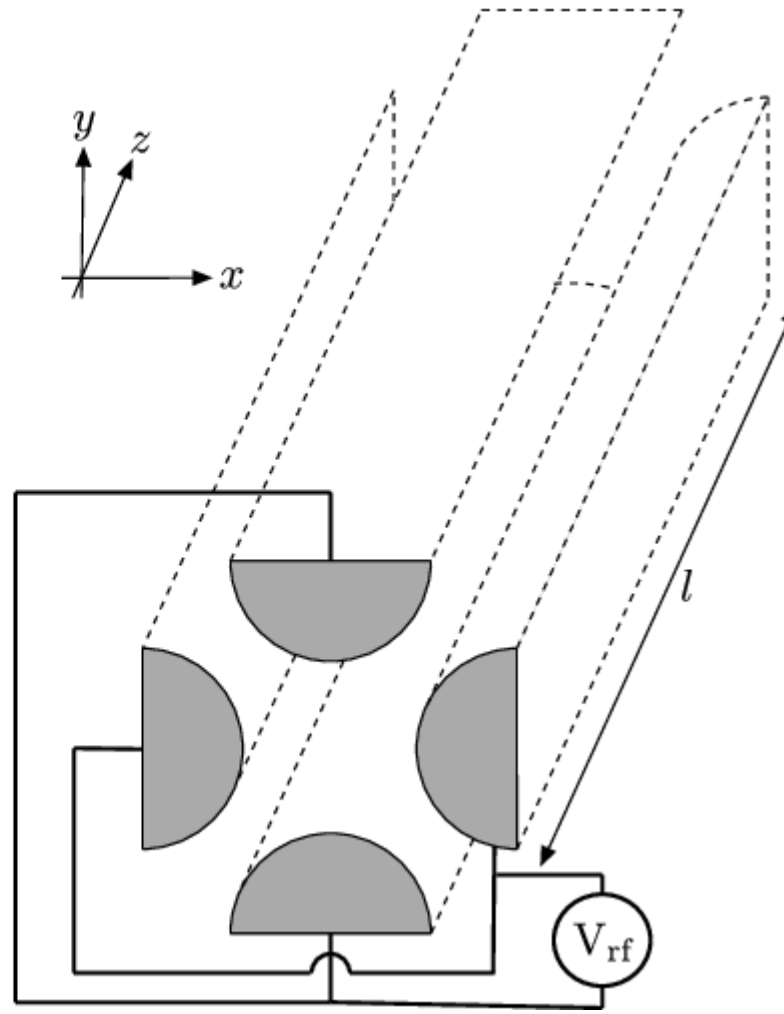
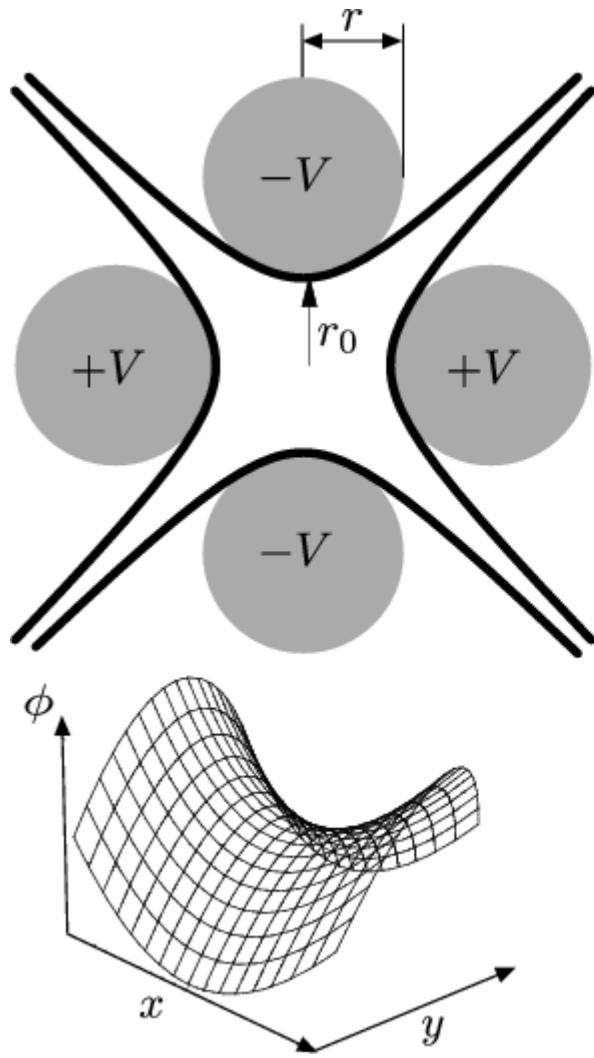
$$\sqrt{\phi_1} \sin \theta_1 = \sqrt{\phi_2} \sin \theta_2$$

square root of $\sqrt{\phi} \rightarrow$ refractive index

Einzel (= single) electrostatic lens



Quadrupole electrostatic lens : not axially symmetric



**Useful for
correcting
astigmatic
error
features in
images.**

The magnetic lens : axially symmetric field of a coil

In a current free region each component of the magnetic field satisfies Laplace's equation. The expansion would be like that of the scalar potential.

Divergence is of course always zero.

This implies:

$$B_z(\rho, z) = B_z(0, z) - \frac{B_z^{(2)}}{4} \rho^2 + \frac{B_z^{(4)}}{64} \rho^4 - \dots$$

$$\text{Since } \nabla \cdot \vec{B} = 0 \Rightarrow \frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho B_\rho) + \frac{\partial B_z}{\partial z} = 0$$

Hence

$$B_\rho(\rho, z) = -B_0^{(1)}(z) \frac{\rho}{2} + B_0^{(3)}(z) \frac{\rho^3}{16} - B_0^{(5)}(z) \frac{\rho^5}{256} + \dots$$

Typically B_z component would be highest in the middle of a coil.
So the derivative will be small.

So the B_r component will be smallest there.

Denotes 2nd, 4th
derivatives

The magnetic lens : equation of the trajectory

$$\ddot{\rho} - \rho \dot{\theta}^2 = \frac{|e|}{m} (B_{\theta} \dot{z} - B_z \rho \dot{\theta})$$

$$\frac{1}{\rho} \frac{d}{dt} (\rho^2 \dot{\theta}) = \frac{|e|}{m} (B_z \dot{\rho} - B_{\rho} \dot{z})$$

$$\ddot{z} = \frac{|e|}{m} (B_{\rho} \rho \dot{\theta} - B_{\theta} \dot{\rho})$$

With $B_{\theta} = 0$ and neglecting terms of $\sim \rho^2$:

$$\ddot{z} \approx 0$$

$$\dot{\theta} = \frac{|e|}{2m} B_z(0, z)$$

$$\ddot{\rho} = -\rho \left(\frac{e B_z}{2m} \right)^2$$

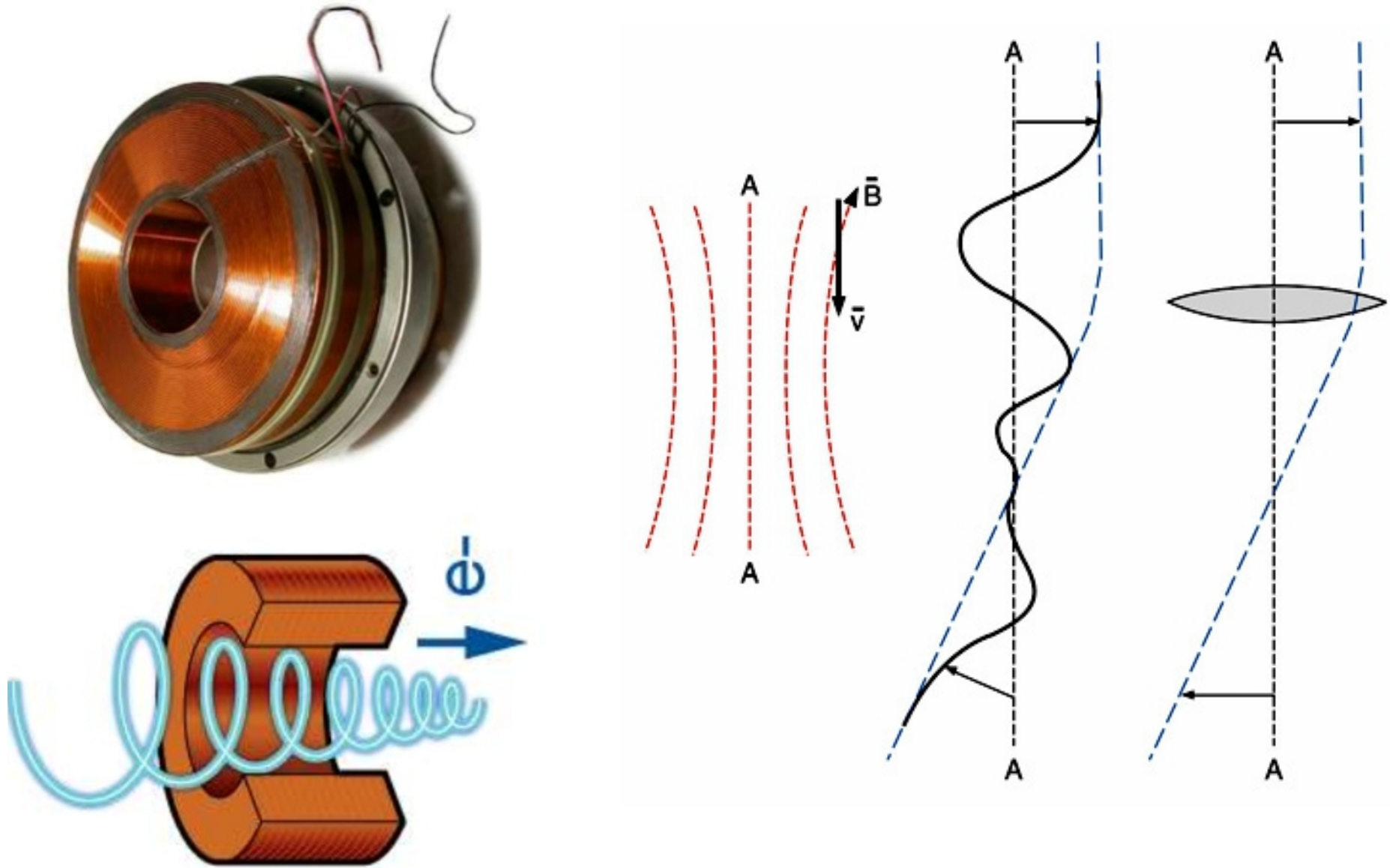
$$\frac{d^2 \rho}{d z^2} + \frac{|e|}{8 m V} B_z^2 \rho = 0$$

V is the electrostatic potential through which it has been accelerated.

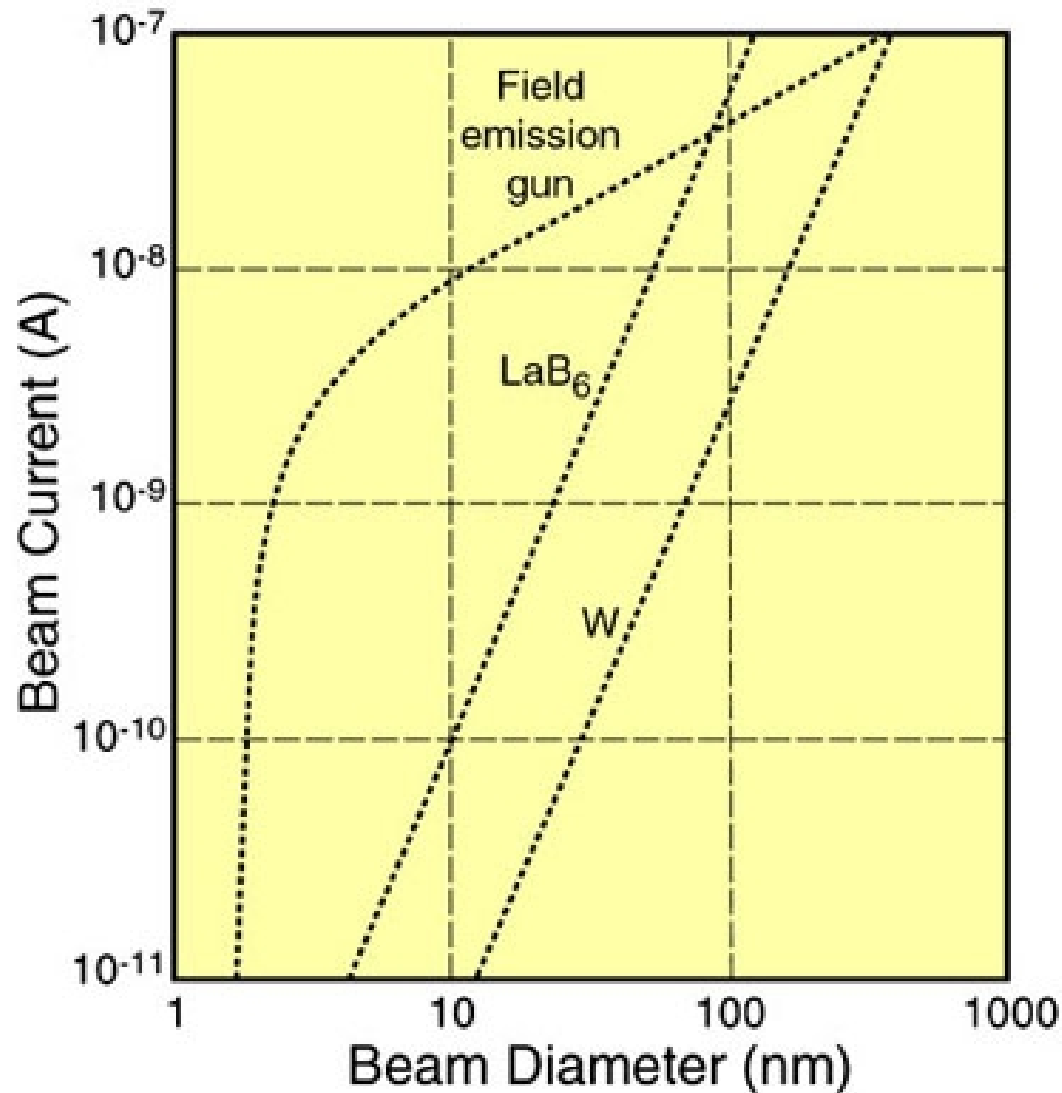
Bz is evaluated on the axis.

Magnetic lens gives better focussing but also rotates the image

The magnetic lens : how do they look & rotation of the trajectory

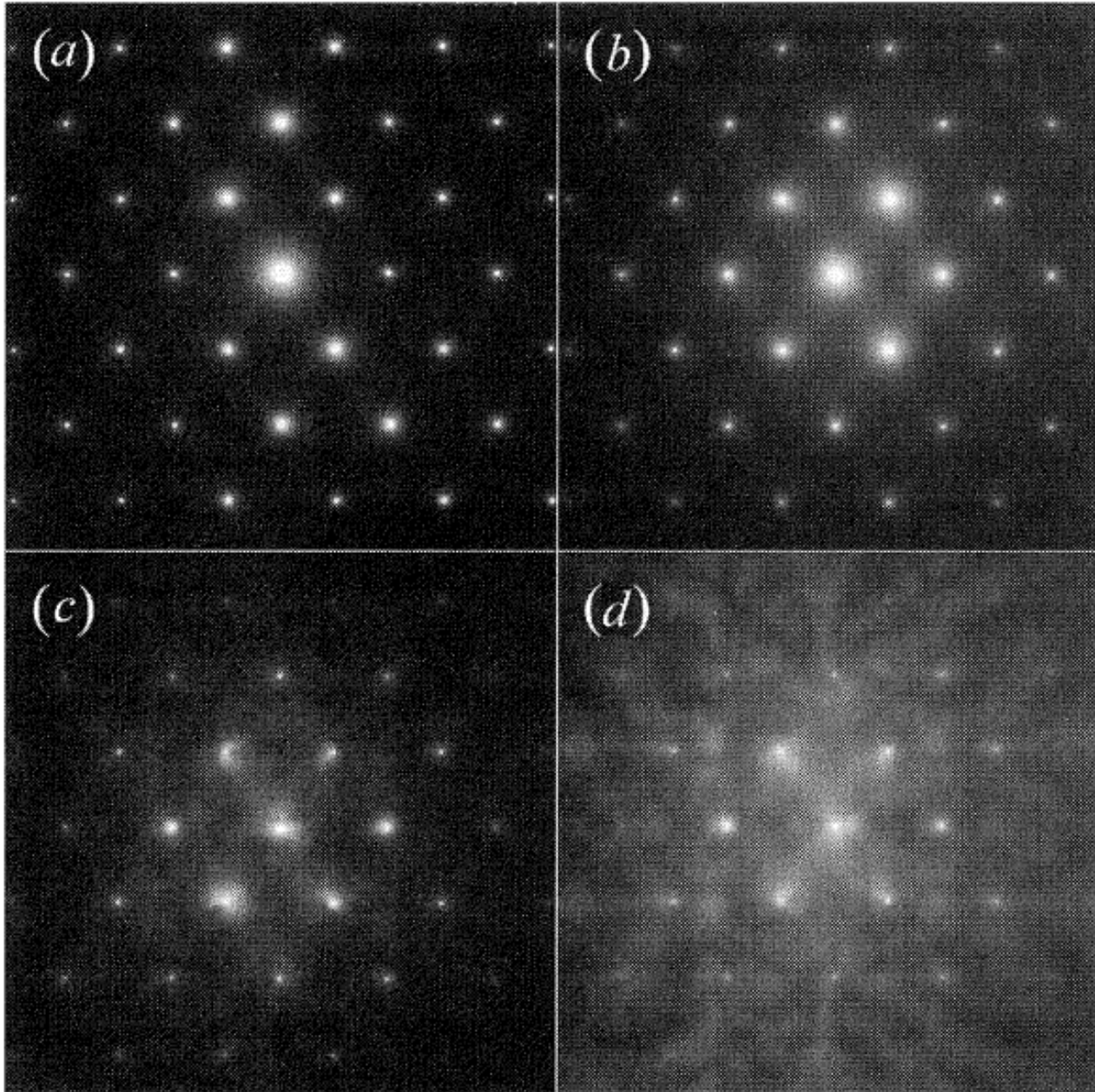


What are the typical beam diameters and beam currents?



This also means that the area of the sample seen by the beam at once is much smaller than an X-ray beam.

Electron diffraction requires thin samples < 100 nm



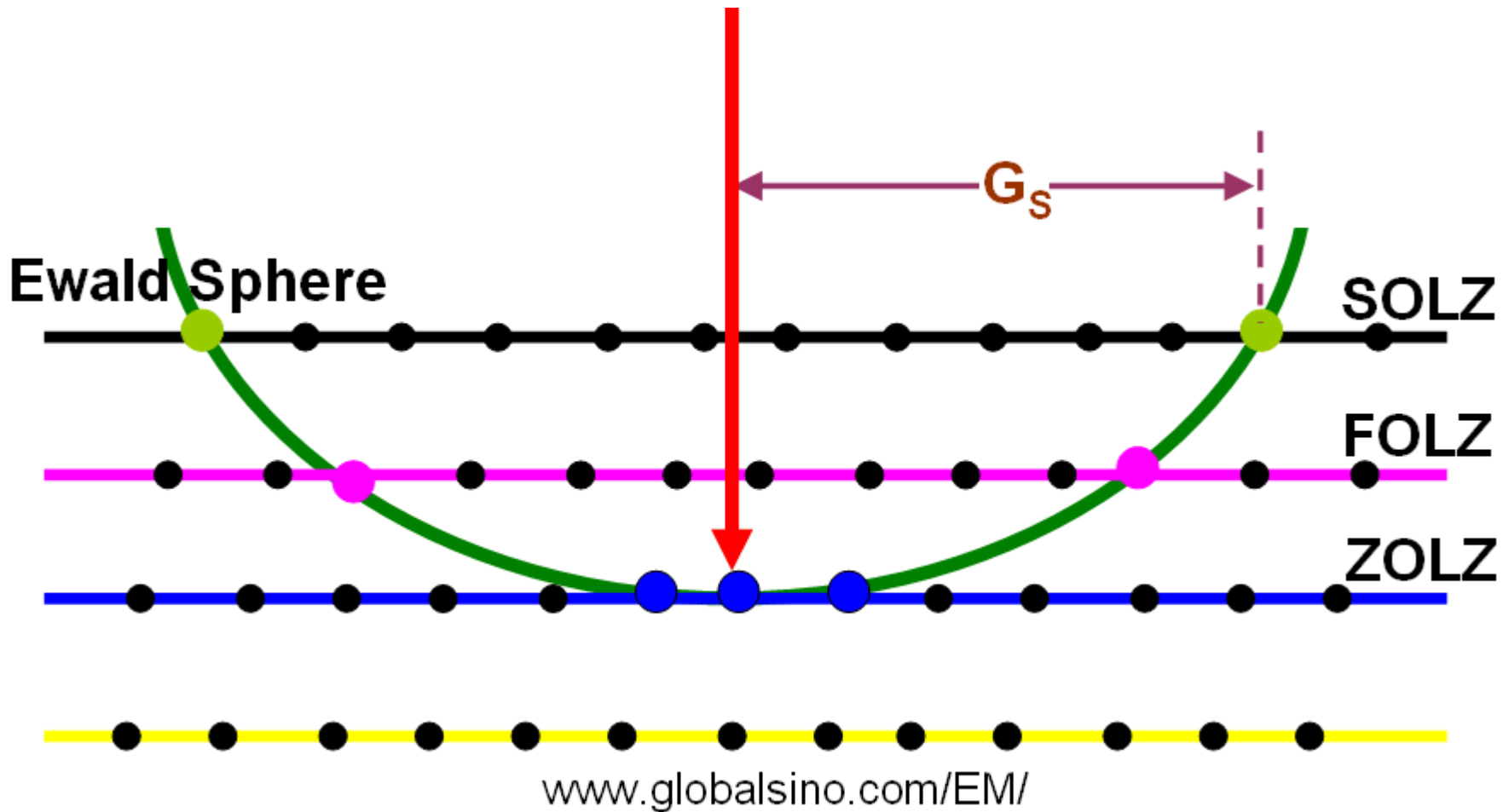
Electron diffraction from Silicon crystal with beam incident along $[110]$.

The pattern starts getting indistinct as progressively thicker regions are probed.

Thickness increases from $a \rightarrow b \rightarrow c \rightarrow d$

[Electron microscopy: Goodhew, Humphrey, Beanland]

Diffraction spots: Zero – First – SecondHigher order Laue zones.

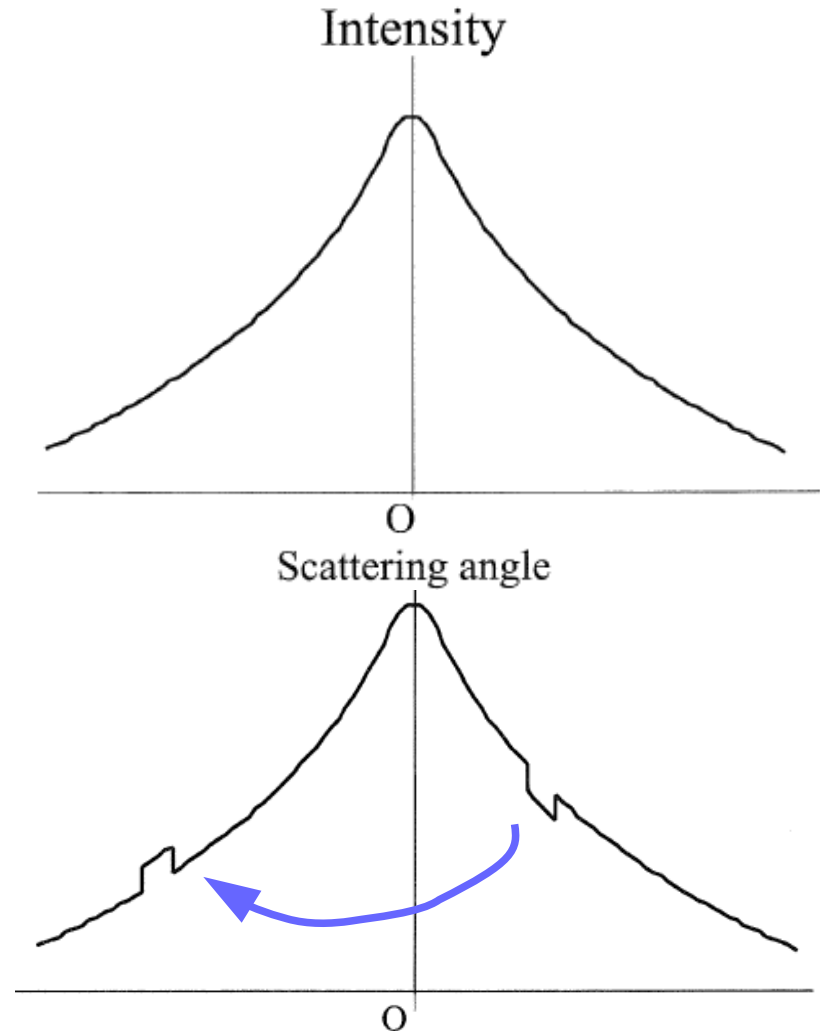
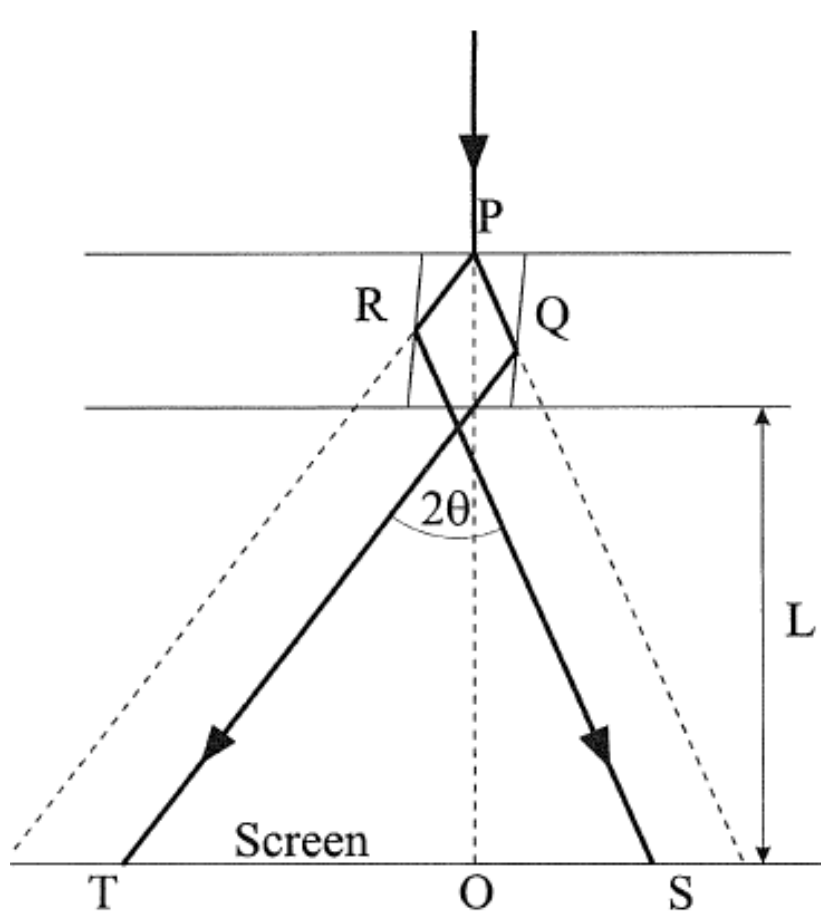


Thin sample → Reciprocal lattice points have some width.

Inelastic scattering followed by elastic (Bragg) scattering: Kikuchi lines

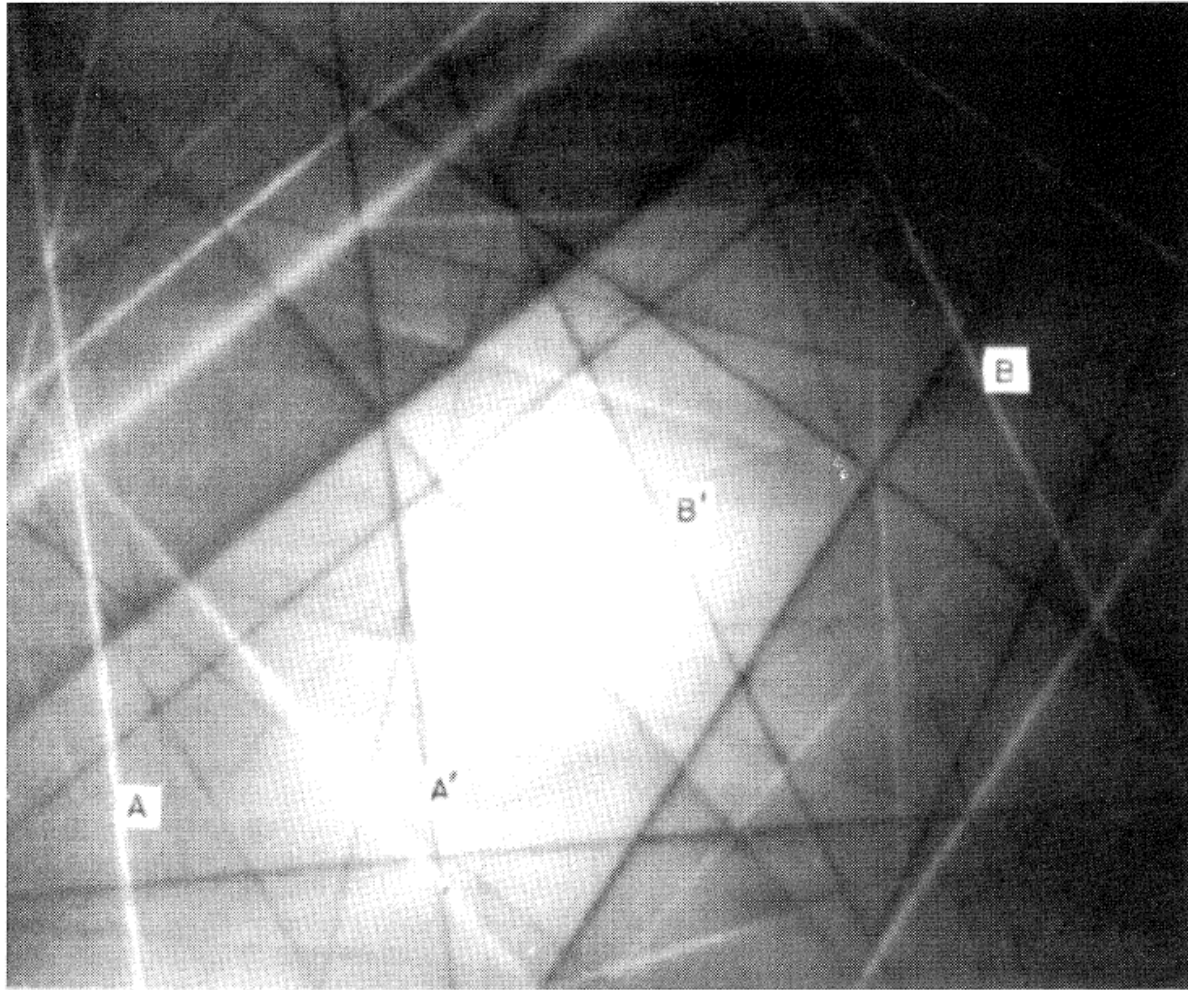
Electrons scatter strongly inside a material so multiple scattering is common, particularly if the sample is slightly thicker.

Unique feature is a pair of bright & dark lines, separated by 2θ – the Bragg angle corresponding to the particular plane giving rise to this:



Figures are taken from : [Electron microscopy: Goodhew, Humphrey, Beanland]

Inelastic scattering followed by elastic (Bragg) scattering: Kikuchi lines



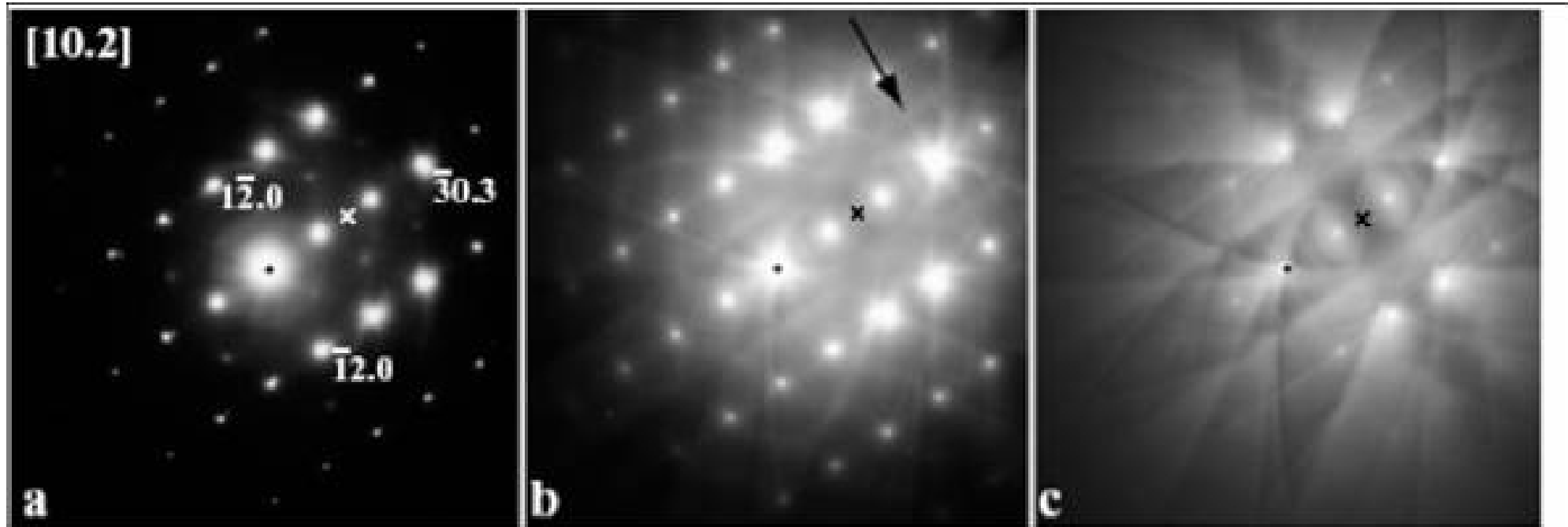
The angular separation between the dark and bright lines would be same as

$$2d(\sin \theta) = \lambda$$

Theta can be calculated from the sample to screen distance.

Sample:
Aluminium

Inelastic scattering followed by elastic (Bragg) scattering: Kikuchi lines



Ti [10.2] patterns at increasing foil thickness

<http://www.globalsino.com/micro/TEM/TEM9966.html>

What happens when the crystal is polycrystalline?

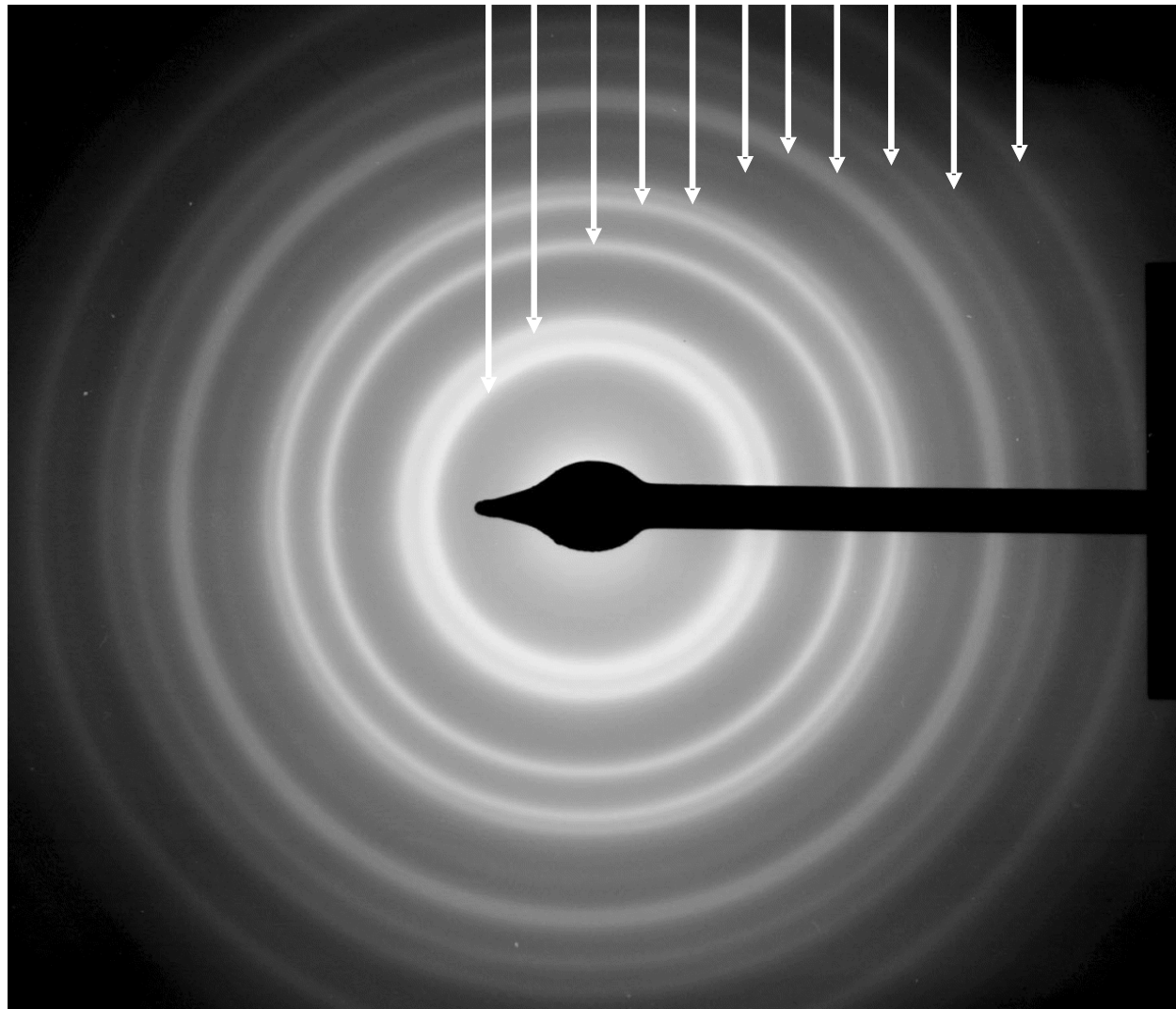
The spots become rings.

An intensity vs radial distance can be converted to an intensity vs 2θ scan, similar to what we get from a powder diffraction.

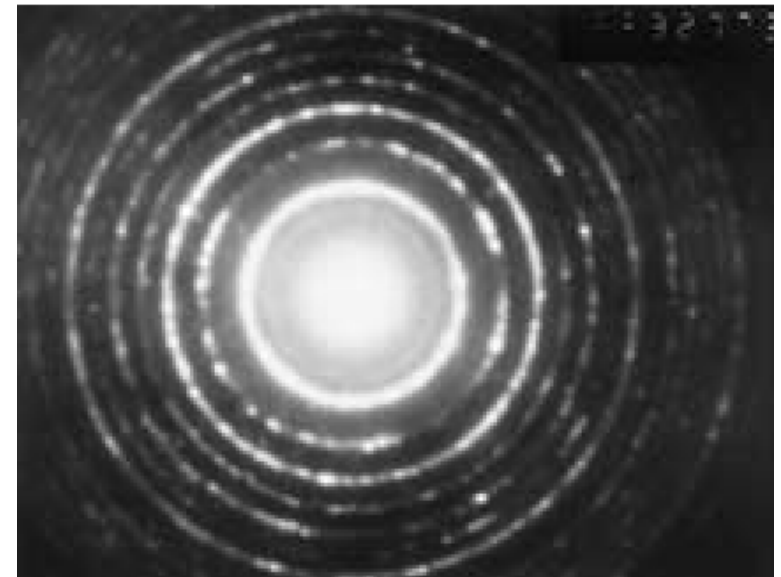
The difference is that the angles would be extremely small, because λ/d is very small.

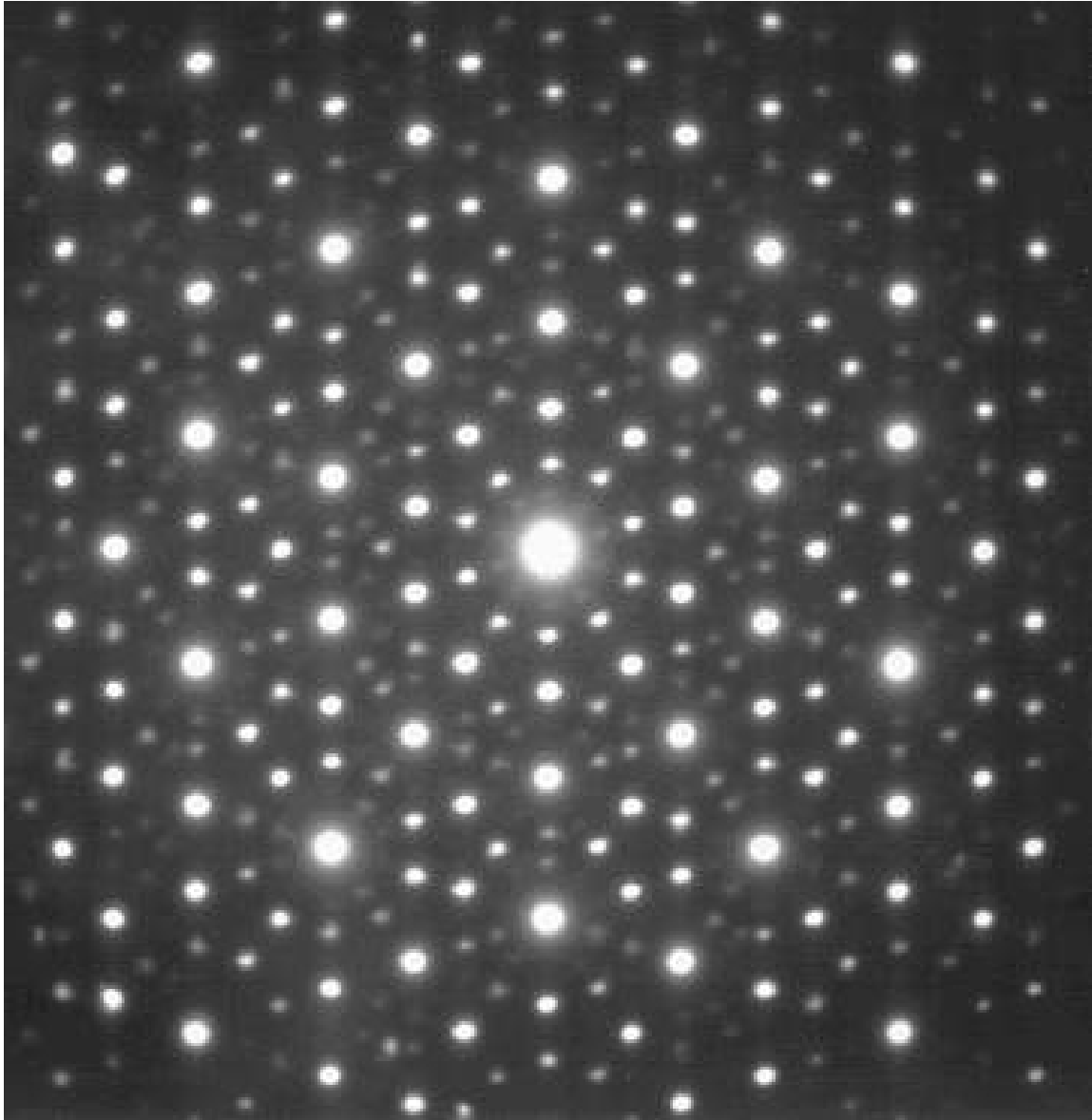
Sample: Silver

(111)
Ag (200)
Ag (220)
Ag (311)
Ag (222)
Ag (400)
Ag (331)
Ag (420)
Ag (422)
Ag (333)
Ag (531)



Sample: Bi-Sr-Ca-Cu-O





What is unusual about this electron diffraction pattern ?

The atomic form factor of an atom for X-ray and neutron

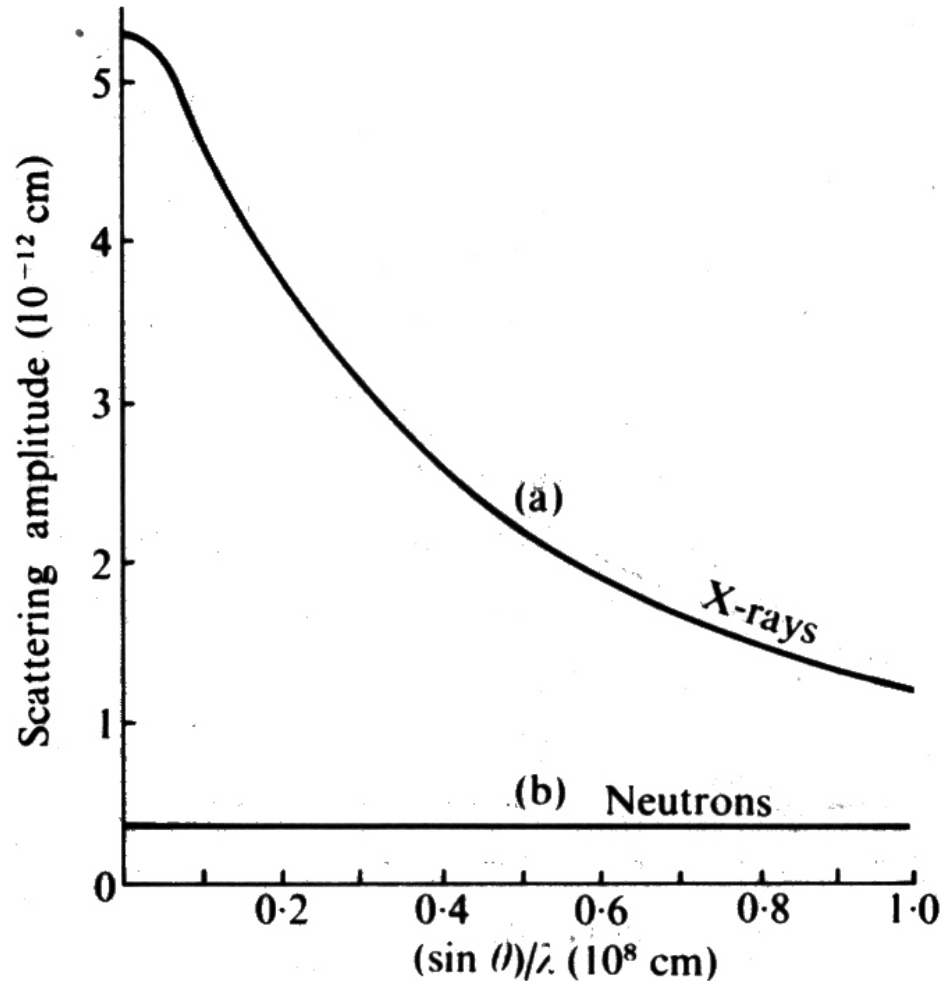


FIG. 16. X-ray and neutron scattering amplitudes for a potassium atom.

Size of the nucleus is much smaller than the wavelength of the thermal neutron.

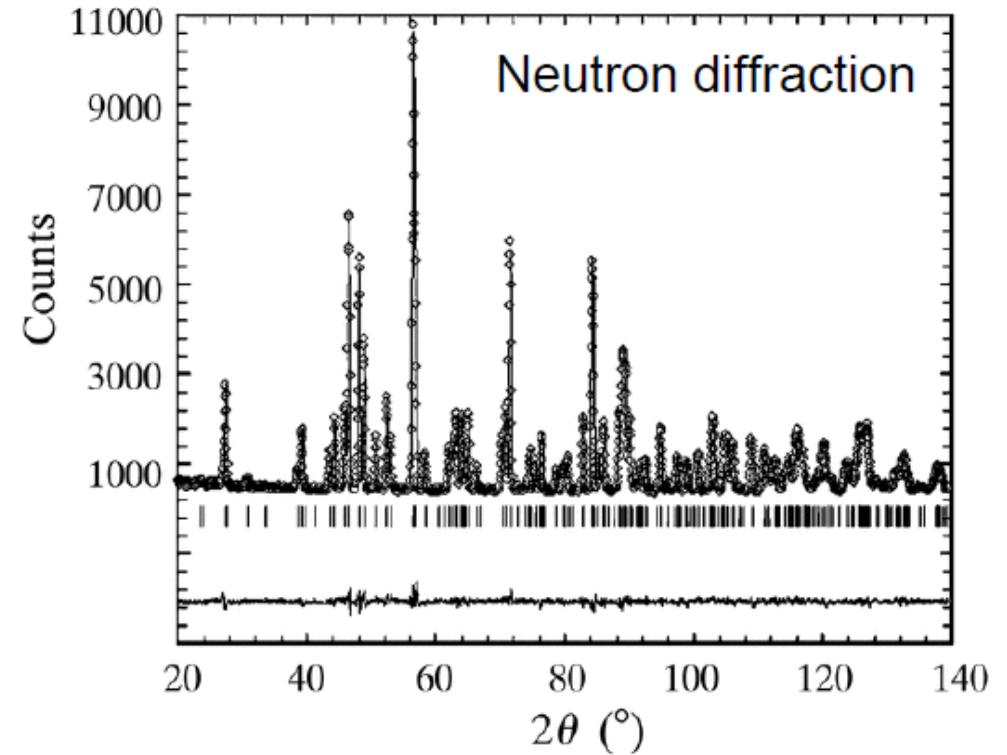
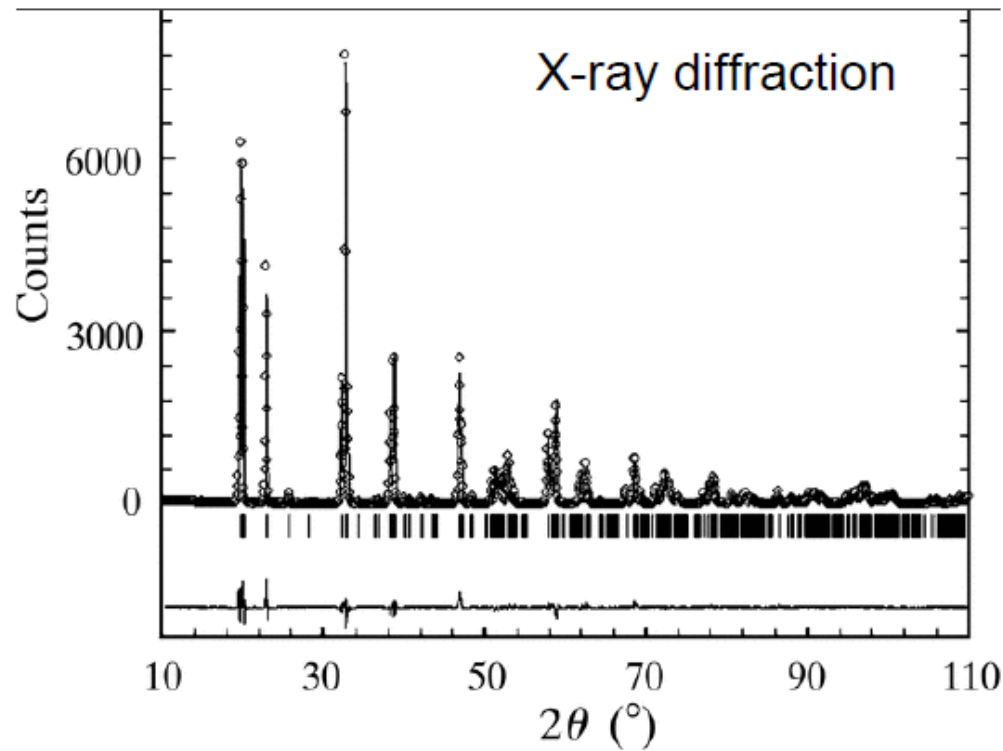
Neutrons do not see the free electrons.

The nucleus is like a point scatterer for a thermal neutron.

So there is no angle dependence of the scattering amplitude.

However neutrons have spin and will see magnetic moments of ions in the lattice.

What is the consequence of not having an angle dependence?

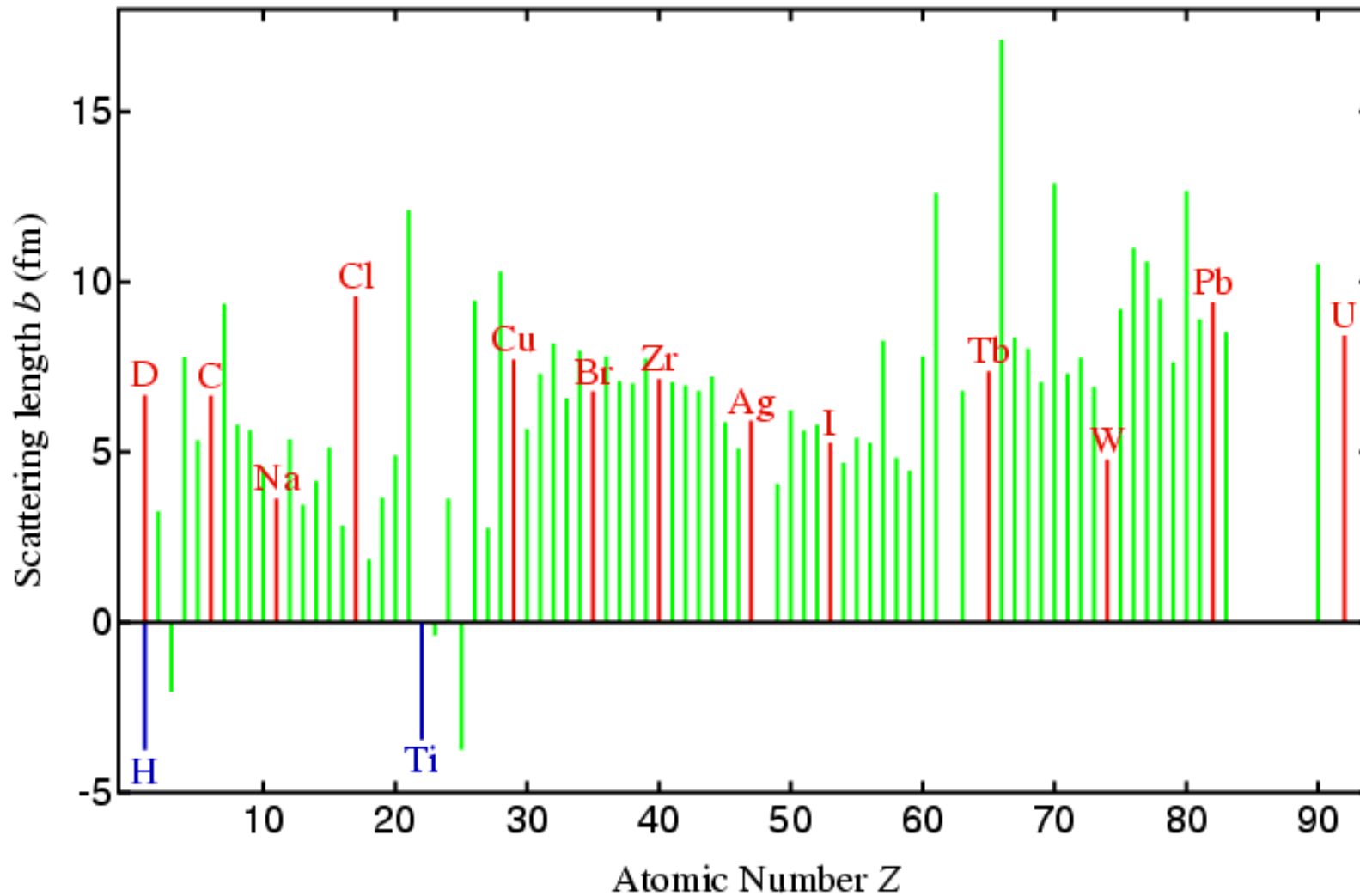


Ca_2MgWO_6 [J.H. Yang et al., Acta Crystallogr. C59, i86 (2003)]

The drop in intensity with increasing angle is a lot less.
So one sees more features in neutron diffraction of the same compound.

However for materials with non-zero nuclear spins, incoherent scattering of neutrons also occur.

The coherent scattering of neutrons by elements

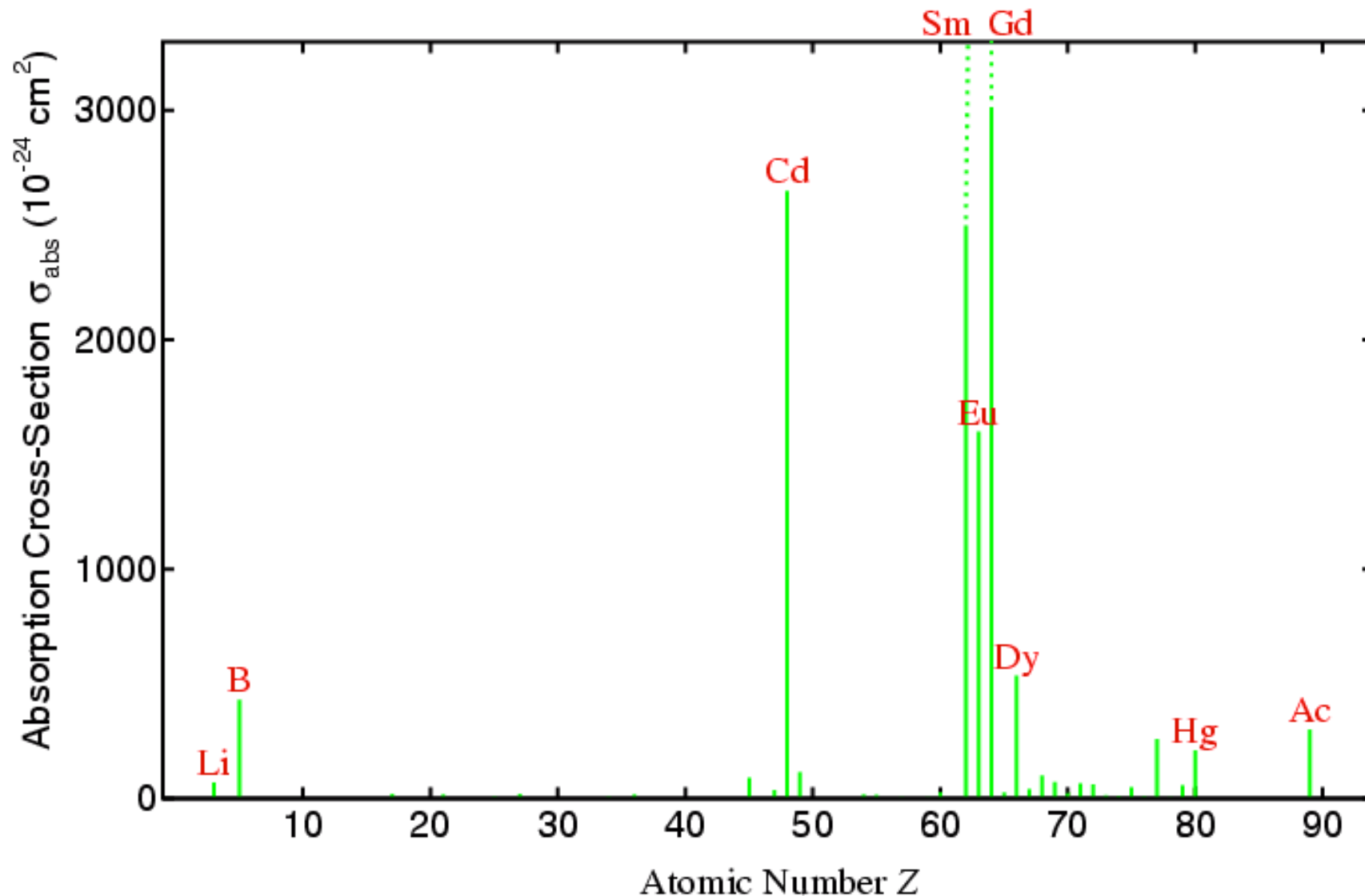


<http://pd.chem.ucl.ac.uk/pdnn/inst3/neutrons.htm>

No systematic trend with atomic number/mass.

Adjacent elements in the periodic table may have very different scattering cross sections

The incoherent scattering of neutrons by elements



<http://pd.chem.ucl.ac.uk/pdnn/inst3/neutrons.htm>

This will give rise to a diffuse background, similar to what inelastic scattering of X-rays does to diffracted intensity of X-rays

The structure factor for neutron scattering has two components

$$F_{hkl}^2 = F_{(\text{Nucl}), hkl}^2 + \left[1 - (\hat{G}_{hkl} \cdot \hat{m})^2 \right] F_{(\text{Mag}), hkl}^2$$

Neutron magnetic moment, in nuclear (Bohr) magneton

Direction of atomic magnetic moments

$$F_{(\text{Mag}), hkl} = \sum_{\alpha=1}^N \left(\frac{e^2 \gamma}{2m_e c^2} gS \right) \times f_m e^{2\pi i(hx_\alpha + ky_\alpha + lz_\alpha)} \times e^{-M}$$

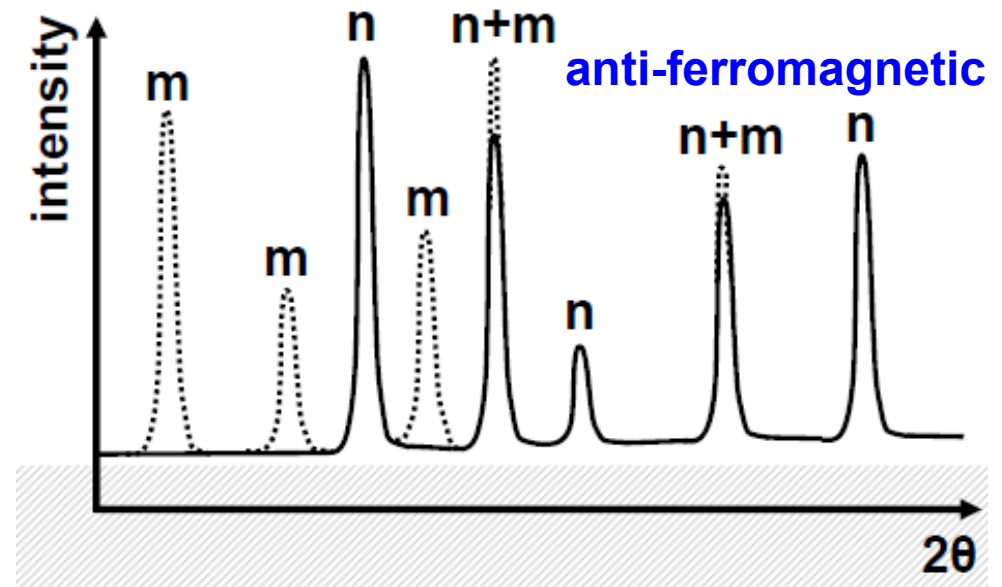
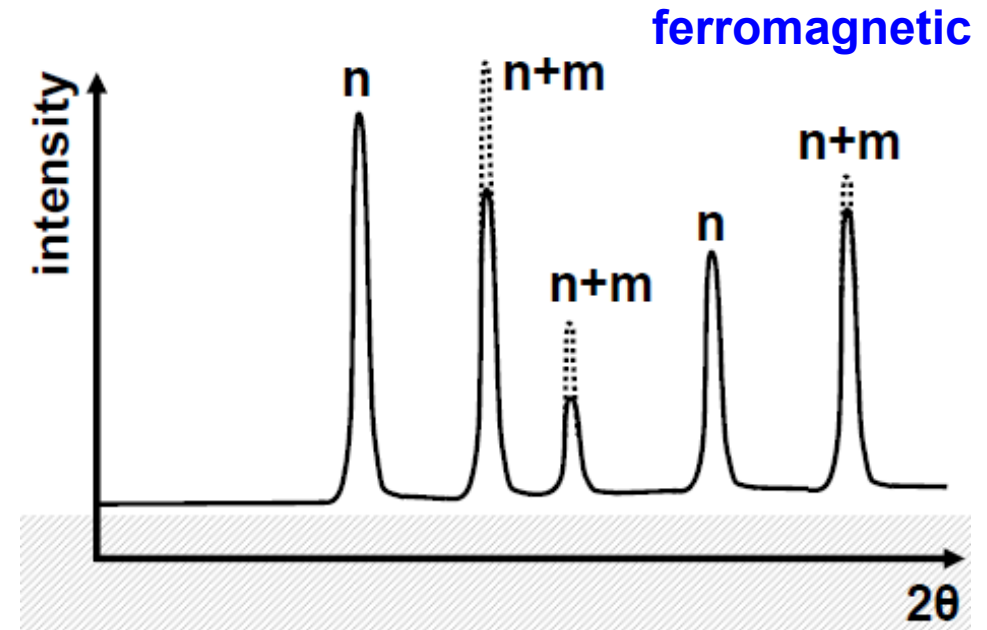
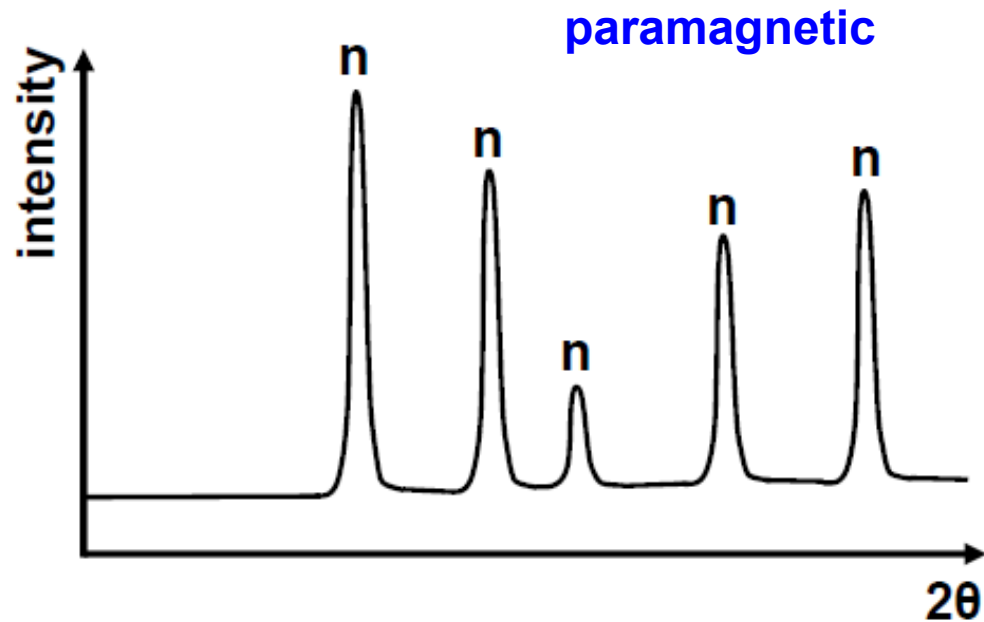
Sum over the basis atoms

Lande $g = 2$
&
Electron spin.
 $S = 1/2$
Not $1/2 (1/2 + 1)$

Magnetic form factor

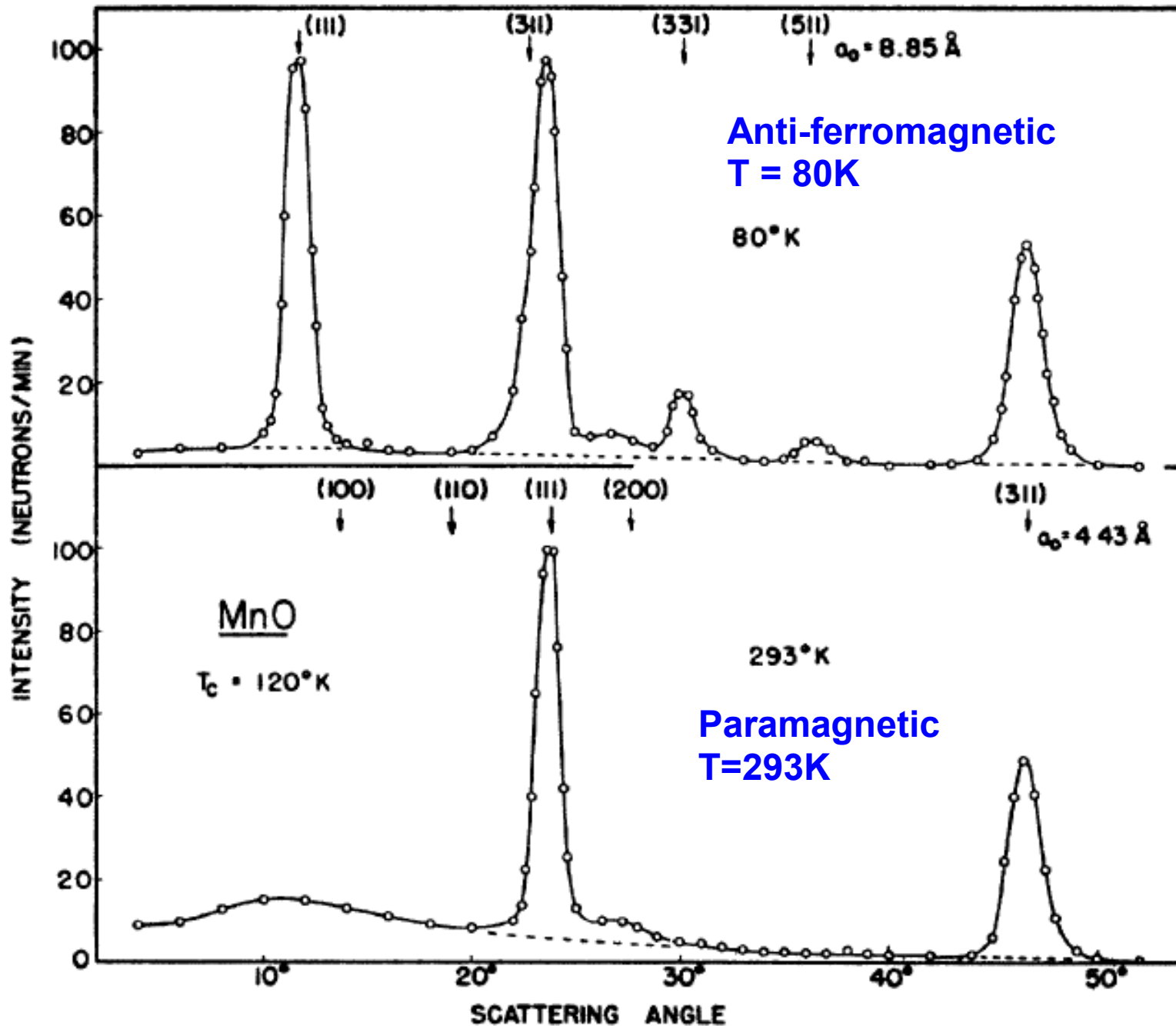
Thermal factor

What qualitative change is seen in a para to ferro/anti-ferro transition?



In anti-ferromagnetic phase the magnetic unit cell and lattice unit cell are different.

Anti ferromagnetic ordering in MnO (Curie Temp = 120K)



The unit cell is taken to be different in the para and the anti-ferro phase. So the indexing of the peaks also become different.

C.G Shull et al.
Phys Rev **83**,
333 (1951)

3. Spectroscopic methods

Typical questions asked : what are the suitable probes ?

What are the elements present in the sample?

The probe should be able to "fingerprint" the atoms irrespective of the valence state they are in.

So the "core levels" should be identified (~100 eV – 1keV)
High energy probes needed. These are typically
XPS (X-ray photoelectron spectroscopy) also called :
ESCA (Electron spectroscopy for Chemical Analysis)
UPS (Ultra violet Photoelectron Spectroscopy)

Relatively high energy probes.
Periodicity of lattice plays almost no role.

What kind of bonds are there ?

Bonds are usually identified by their spring constants.
Usually Raman spectrum.

What is the electronic band structure? Band gaps?

Optical absorption, Photoluminescence, Angle resolved
Photo-emission (ARPES)

Relatively low energy probes

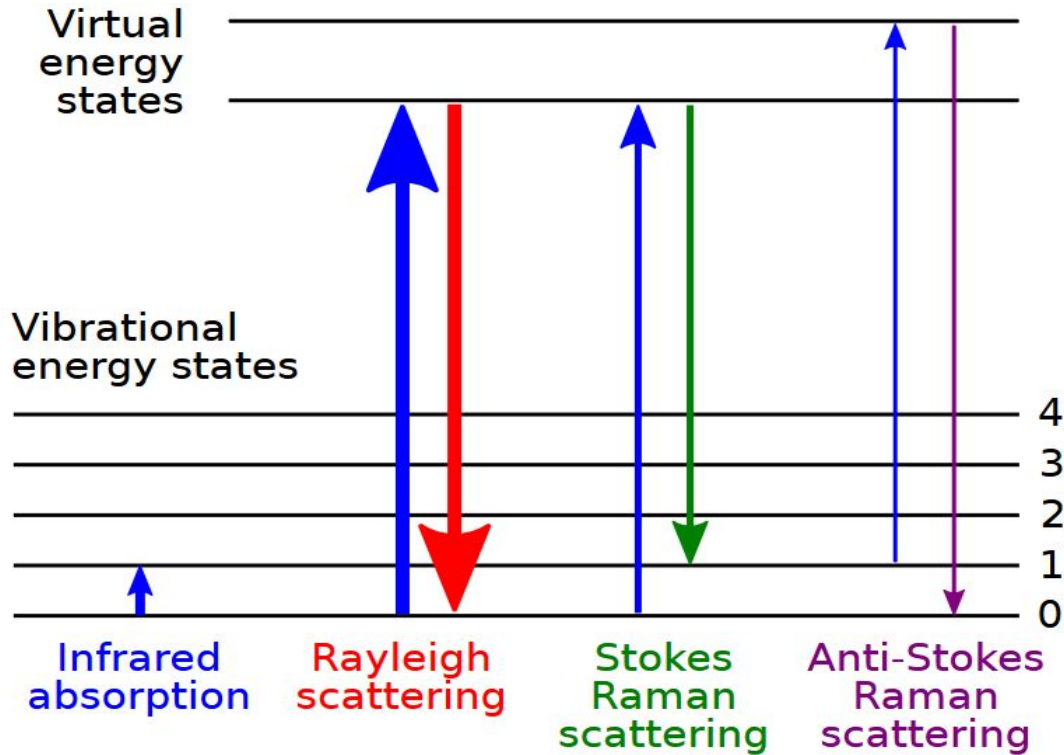
What is the phonon band structure?

Raman & Brillouin scattering
Thermal neutron scattering

Similar questions for molecules.....functional groups, excited states, type of bond...

Scattering from molecules and solids

Molecules:



Raman scattering is a weak process: 1 in $10^6 - 10^7$ incident photons

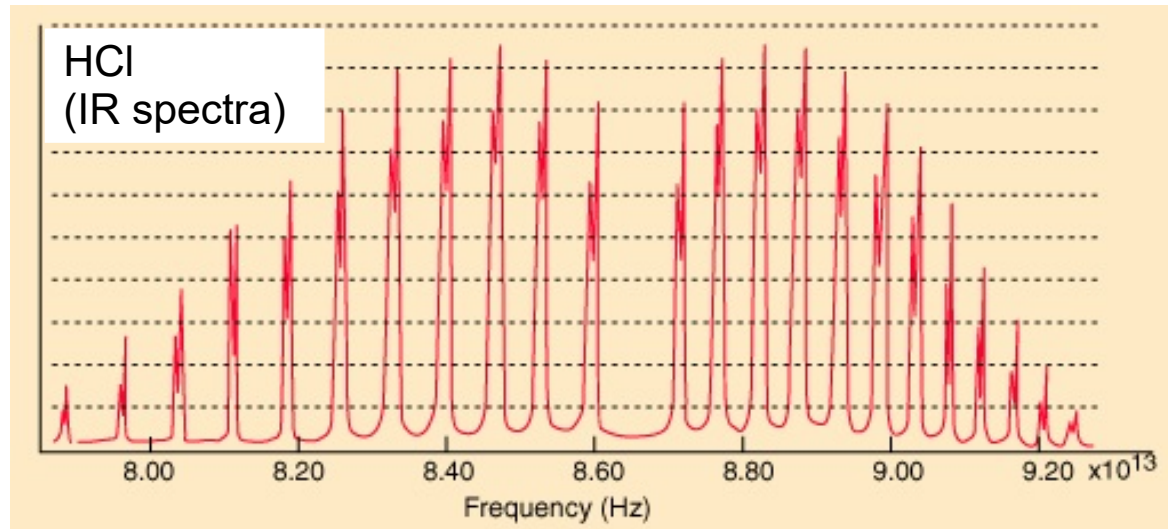
Most of the incident radiation will be "Rayleigh scattered" (no change in energy)

$$I = I_0 \frac{8\pi N \alpha^2}{\lambda^4} \left(\frac{1 + \cos^2 \theta}{R^2} \right)$$

α : polarizability

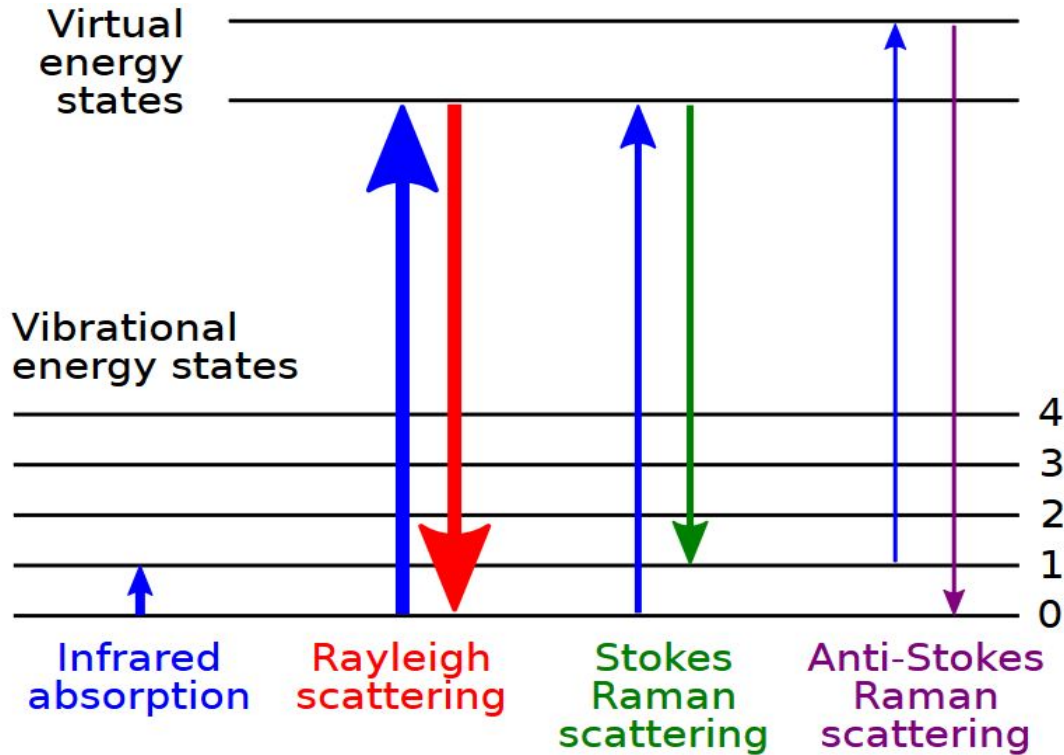
Selection rule for vibrational levels

$\Delta v = \pm 1$: why?
vibration & rotation ?



Scattering from molecules and solids

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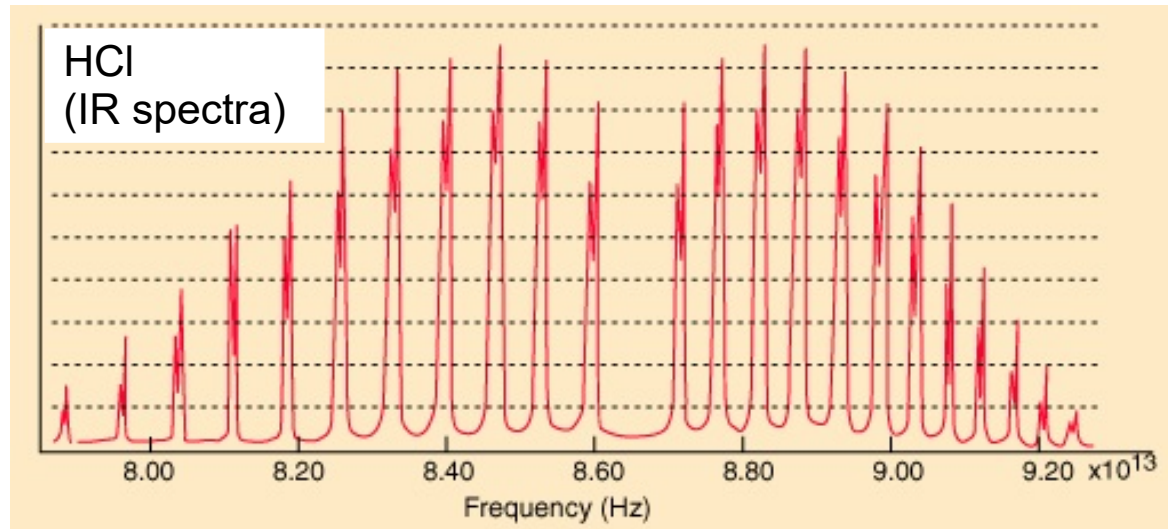
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Selection rule for vibrational levels

$\Delta v = \pm 1$: why?
vibration & rotation ?



How stiff are the molecular springs (bonds)?

Suppose spectra of a diatomic molecule A-B is given

$$\omega = \sqrt{\frac{k}{\mu}}$$









Calculate the reduced mass μ

Then calculate $k = 480 \text{ Nm}^{-1}$ for HCl

So $\sim 0.5 \text{ kg}$ will stretch this by 1 cm

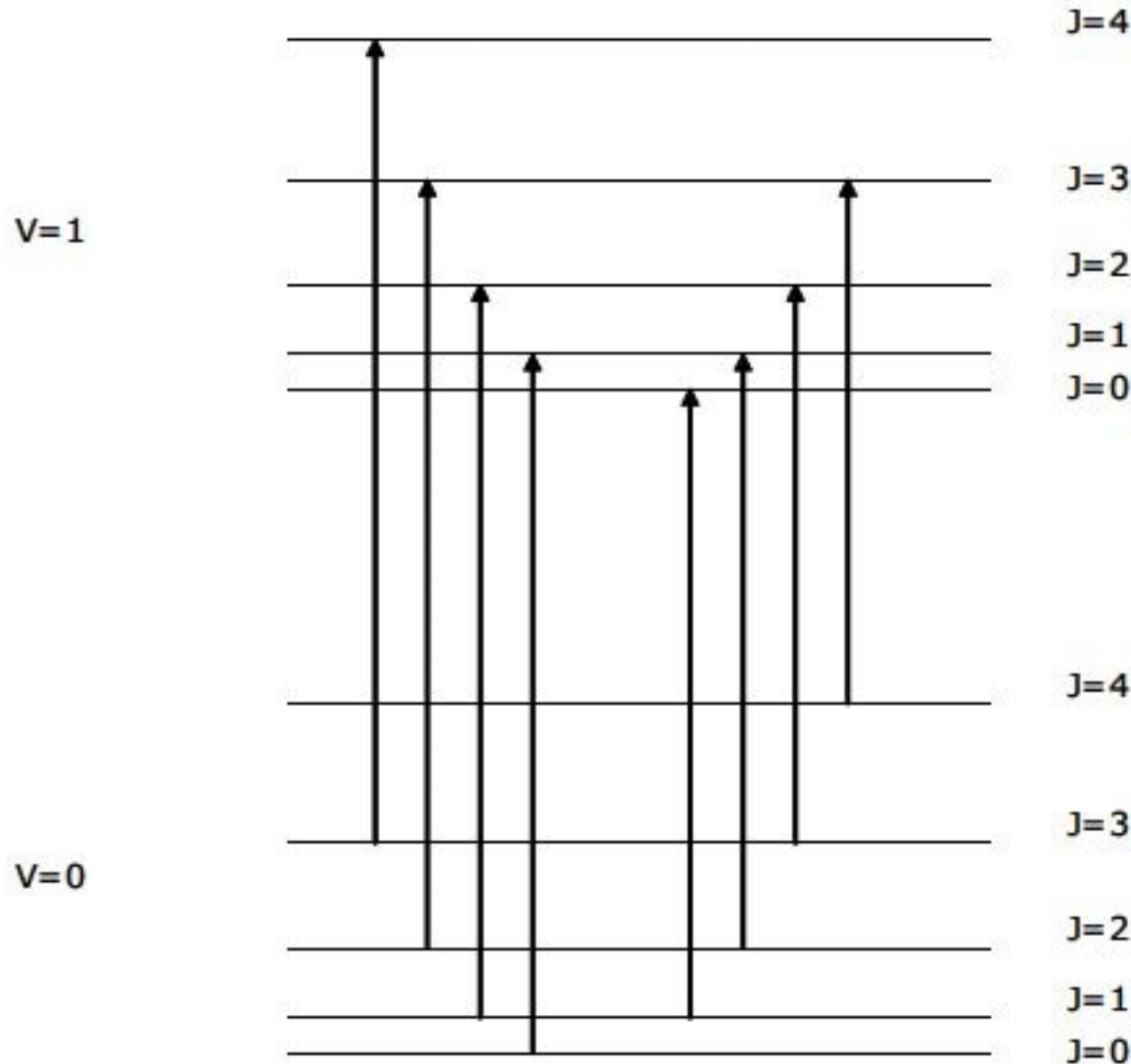
($1 \text{ N} = 10^5 \text{ dyne}$)

Molecule	$\nu \text{ (cm}^{-1}\text{)}$	$k \text{ (dynes cm}^{-1}\text{)}$
HF	3958	8.8×10^5
HCl	2885	4.8×10^5
HBr	2559	3.8×10^5
HI	2230	2.9×10^5
F_2^a	892	4.5×10^5
Cl_2^a	557	3.2×10^5
Br_2^a	321	2.4×10^5
I_2^a	213	1.7×10^5
CO	2143	18.7×10^5
NO	1876	15.5×10^5

Bond	$k \text{ (dynes cm}^{-1}\text{)}$
	4.5×10^5
	5.2×10^5
	9.6×10^5
	15.6×10^5
	12.1×10^5
	17.7×10^5
	5.9×10^5
	4.8×10^5

Data: R.S Drago : Physical Methods for Chemists

Which energy levels do the transitions correspond to ?



Q branch : $\Delta J=0$
 P branch : $\Delta J=-1$
 R branch : $\Delta J=+1$

As the "dumb-bell" rotates, the spring stretches out a little changing the rotational inertia

$$E(v, J) = \hbar \omega \left(v + \frac{1}{2} \right) + B_e J(J+1) - D_e J^2(J+1)^2 - \alpha \left(v + \frac{1}{2} \right) J(J+1)$$

Uncoupled rotation & vibration

Interaction between rotation & vibration

Rotation of the molecules (typically matches microwave energies)

$$H = \frac{\hat{J}^2}{2I} + \vec{p} \cdot \vec{E}$$

\vec{p} is the pre-existing electric dipole moment

$$E_J = \hbar^2 \frac{J(J+1)}{2I}$$

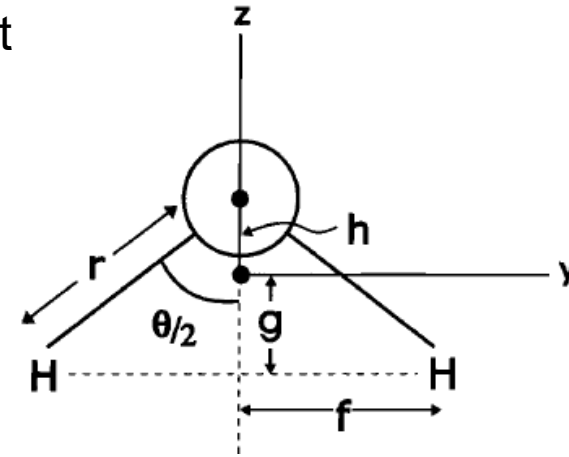
$$W = \langle J' M' | \vec{p} \cdot \vec{E} | J M \rangle$$

selection rule (moment parallel to rotor axis)

$$\Delta J = \pm 1 \quad \Delta M = 0 \quad \text{if } M = 0$$

$$\Delta J = 0, \pm 1, \quad \Delta M = 0 \quad \text{if } M \neq 0$$

$$\therefore \nu = \frac{E_{J+1} - E_J}{h} = \frac{\hbar}{2\pi I} (J+1)$$



Spherical rotor:
All moments of inertia are equal.

Symmetric rotor :
Two moments are equal

Linear rotor:
One moment is zero.

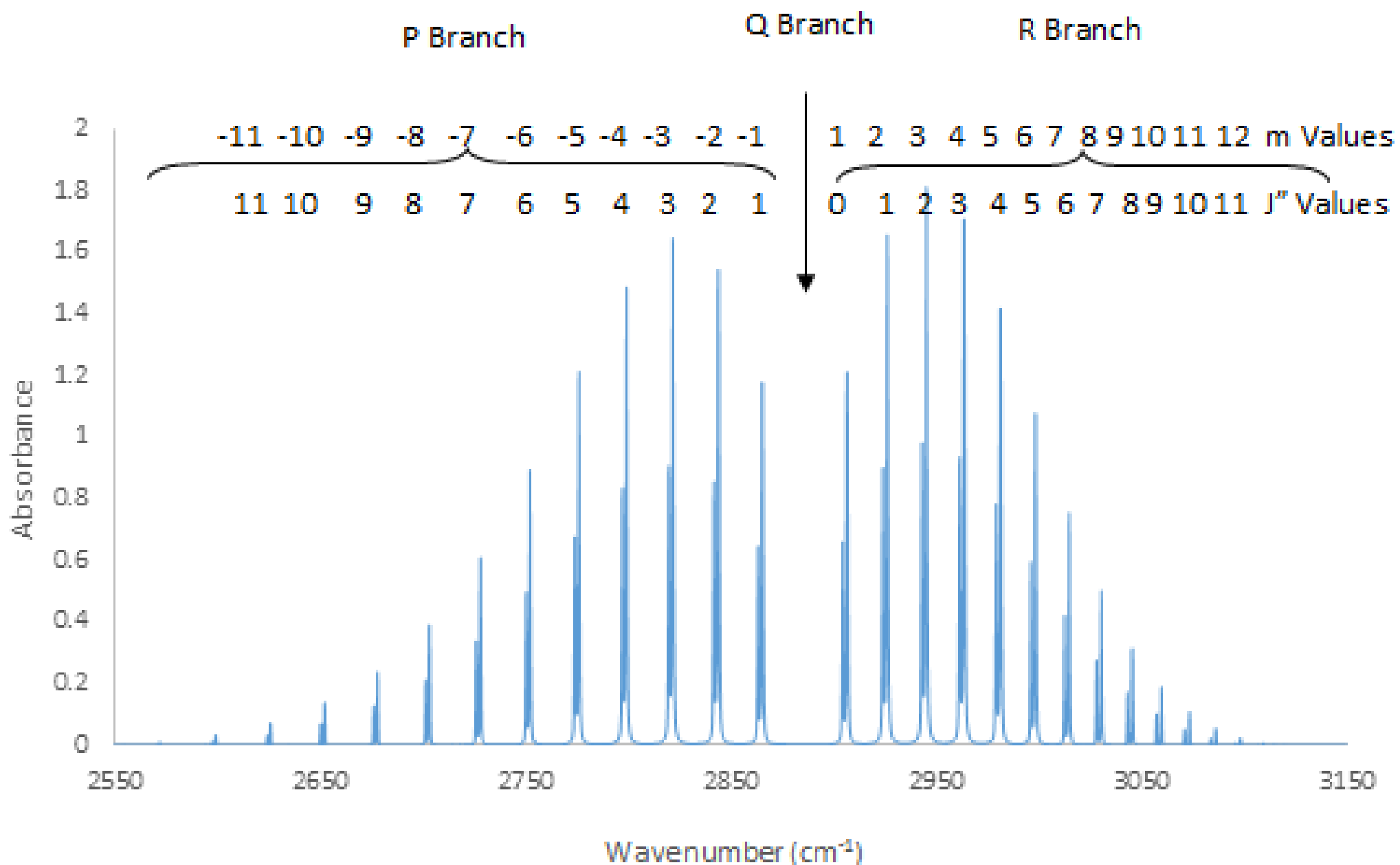
Asymmetric rotor:
All moments are unequal.

The matrix elements are to be calculated between spherical harmonics. \vec{p} is fixed, \vec{E} is the electric field of incident radiation. Selection rules tell you which integrals will NOT vanish.

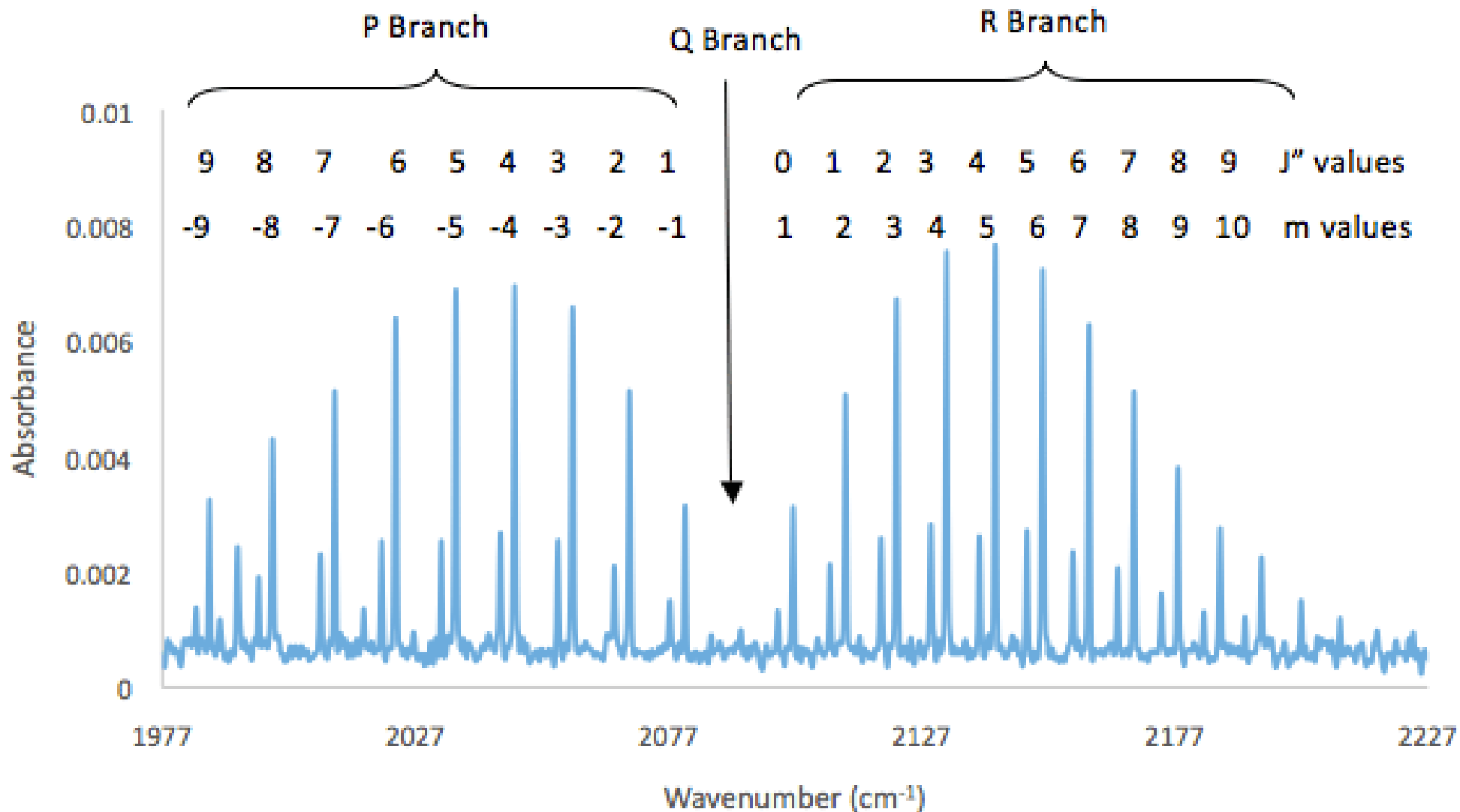
The typical values of the absorption are in the microwave to IR

Note that the rotational inertia is a measure of the size of the molecule.

A traditional example : IR spectra of HCl molecule

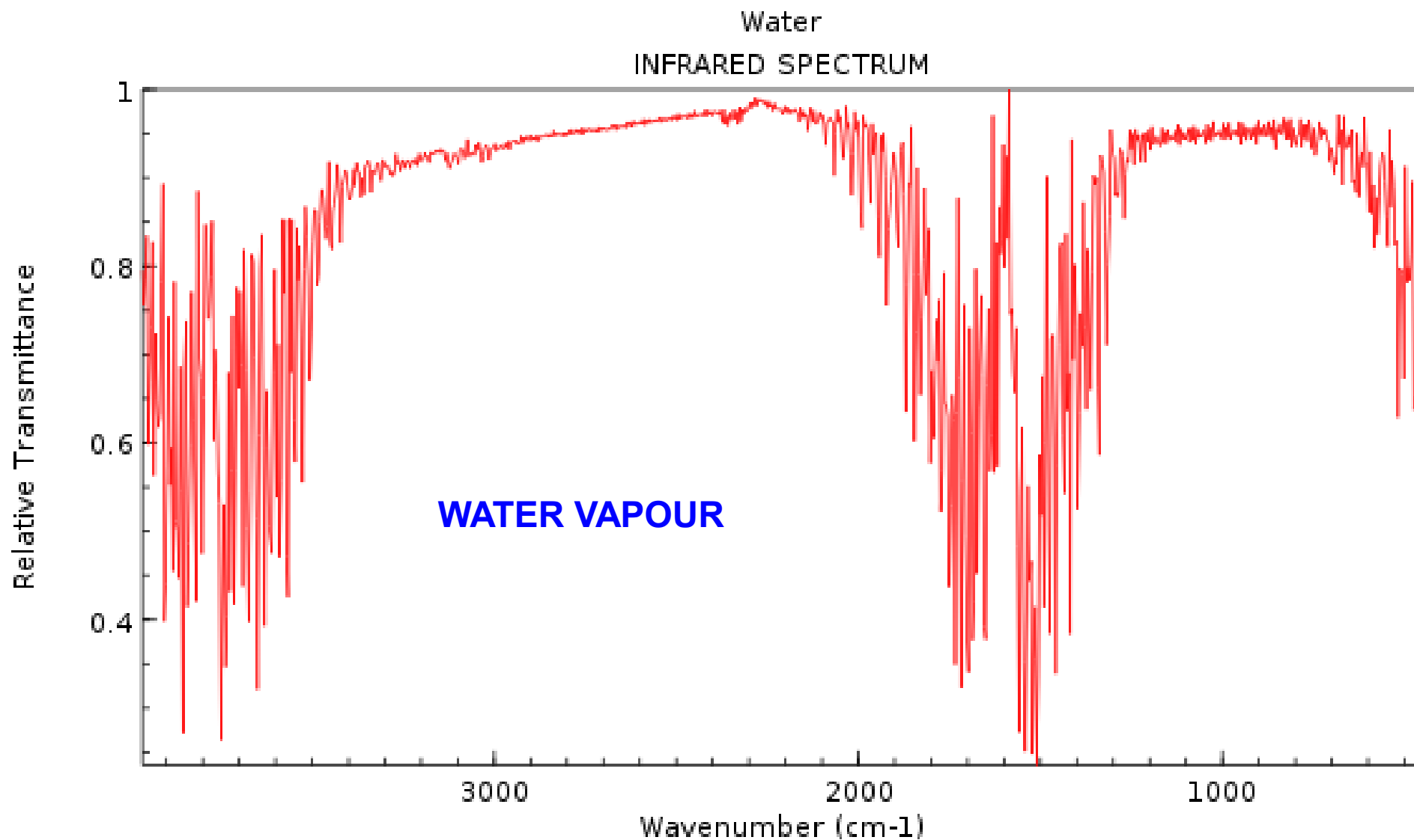


What changes if H is replaced with D ?



Notice the change in the x values, but the overall pattern is still same

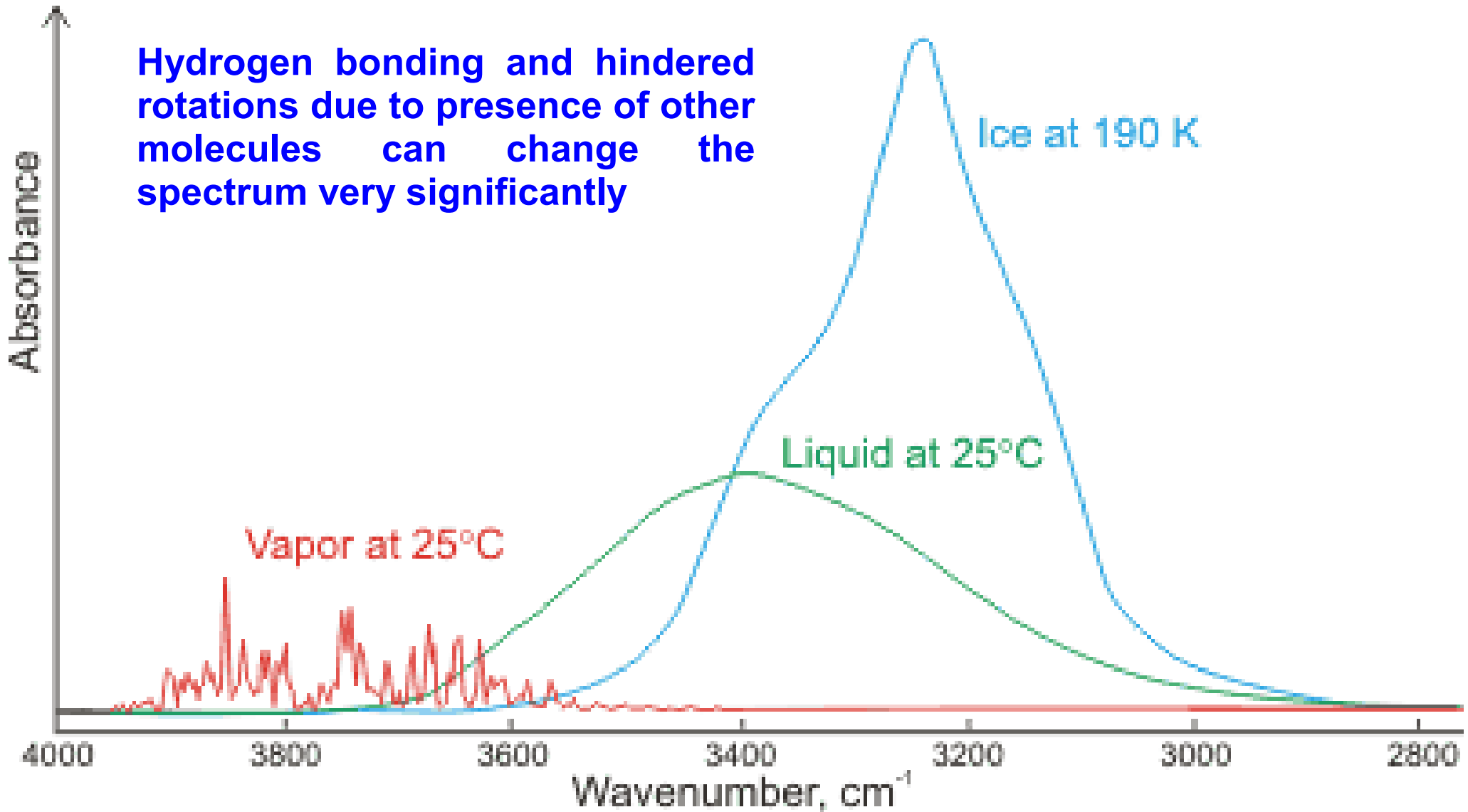
IR spectra in gas liquid & solid phase would be different



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry/>)

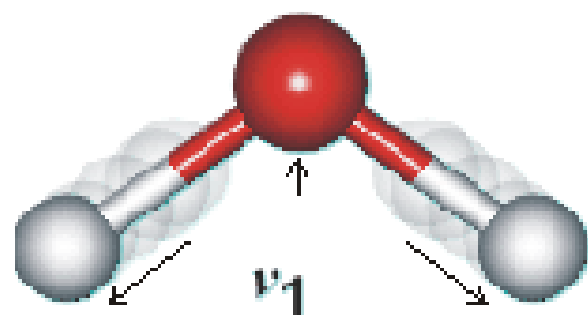
IR spectra in gas liquid & solid phase would be different

Hydrogen bonding and hindered rotations due to presence of other molecules can change the spectrum very significantly

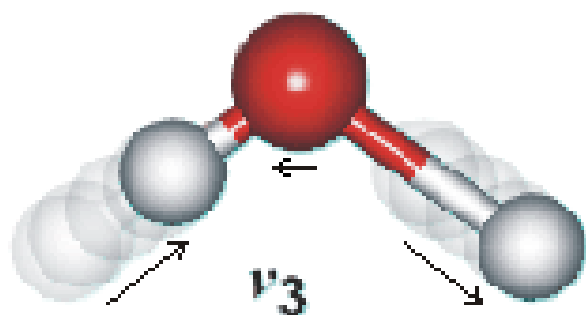


Data from : http://www1.lsbu.ac.uk/water/water_vibrational_spectrum.html
(A collection of lot of data about the spectrum of water and its molecular dynamics)

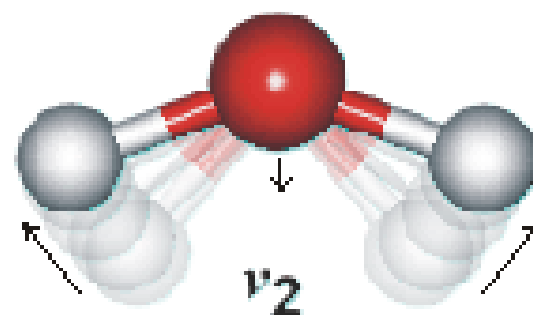
Vibrations of the H_2O molecule : matches IR frequencies



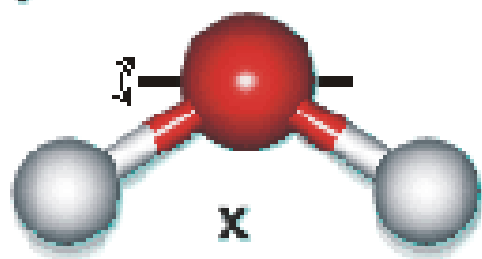
symmetric stretch



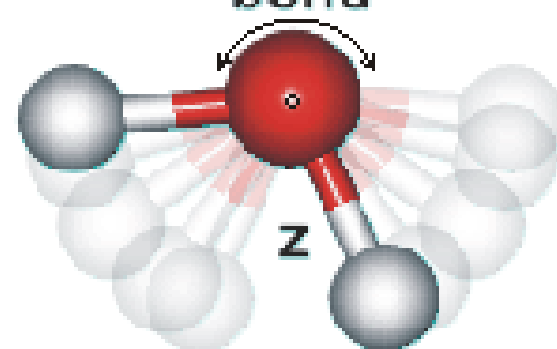
asymmetric stretch



bend

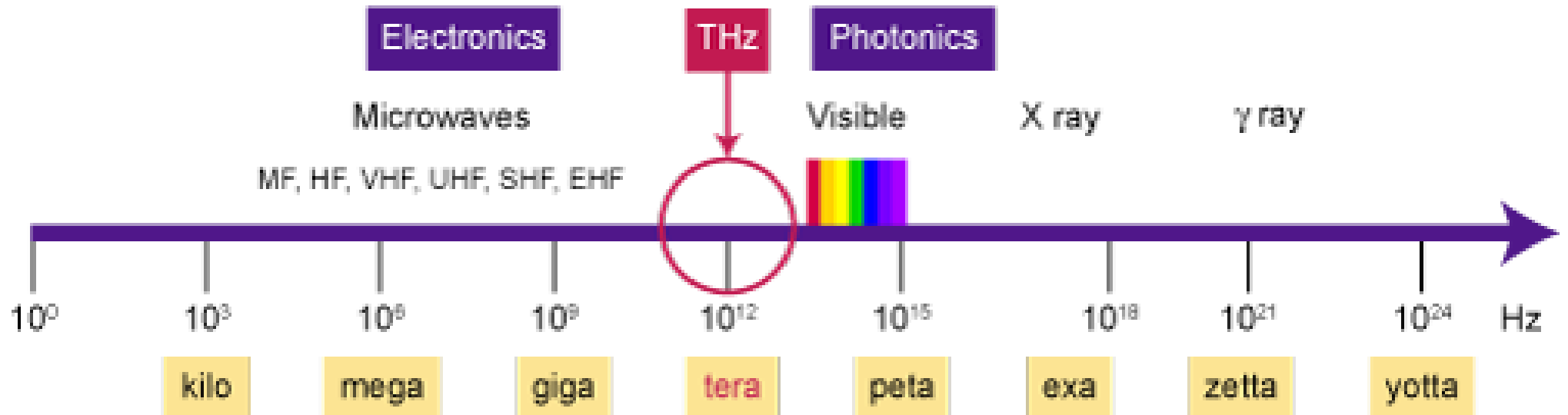


librations



http://www1.lsbu.ac.uk/water/water_vibrational_spectrum.html

What is the Terahertz gap ?



Vibration-Rotation spectra : the overall picture

Consider a AB type molecule.

Write the problem in terms of reduced mass and relative distance.

Quantize this harmonic oscillator about equilibrium "bond length".

The eigenstates are Hermite polynomials as usual.

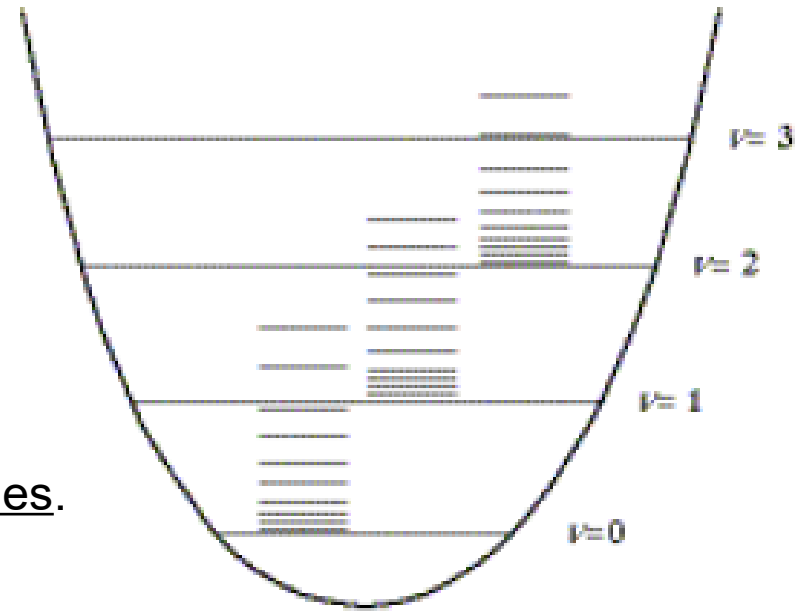
The dipole moment may fluctuate as the bond stretches.
For symmetric diatomic molecules (N₂, H₂, O₂) this does not happen. That is why they are "IR-inactive".

p.E type matrix element would give zero if p is fixed, between states n and n+1 or n-1, due to the nature of the hermite polynomials.

But if p changes proportional to the change in normal co-ordinate then the matrix element would be non-zero between n and n ± 1.

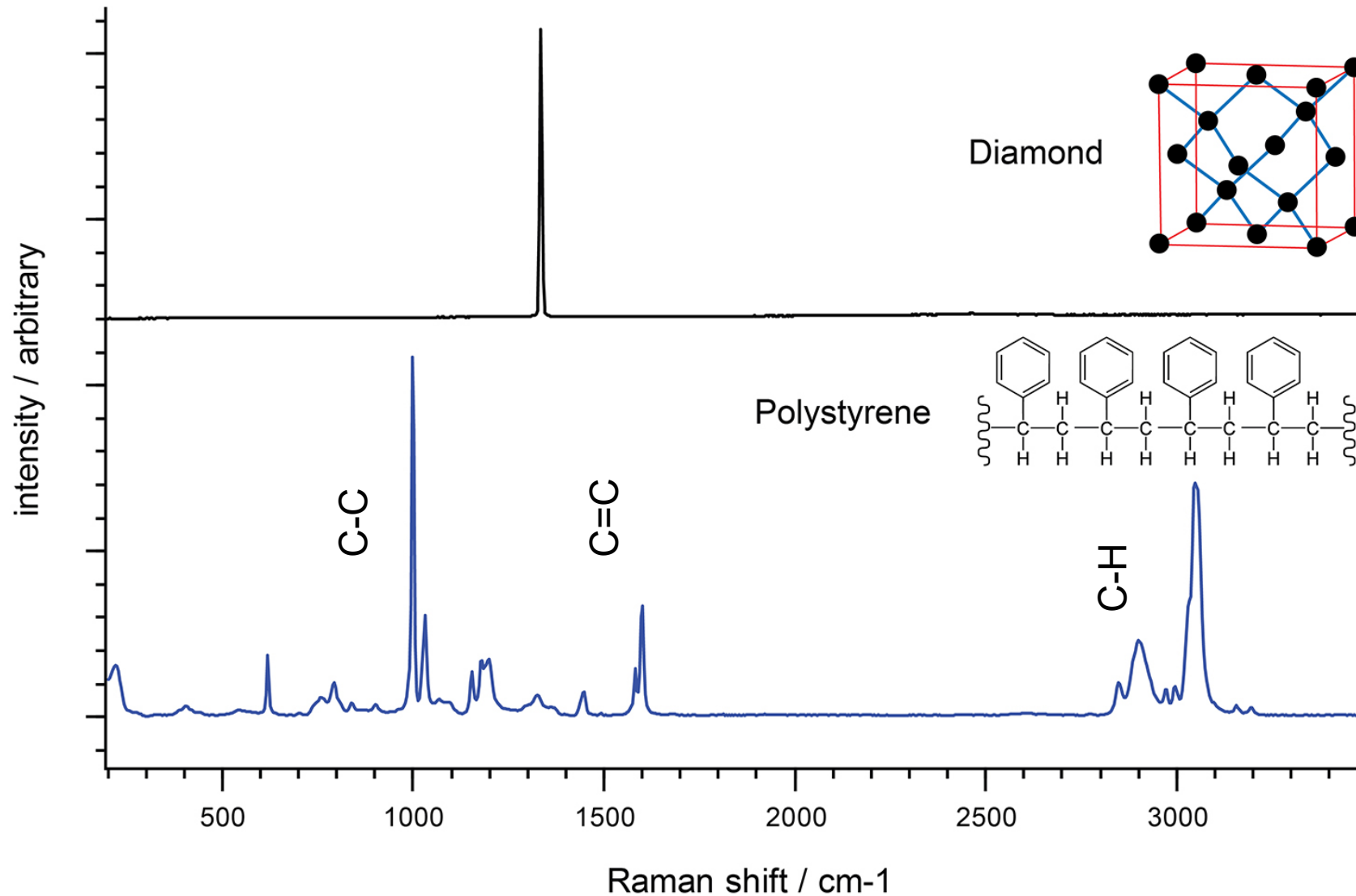
So the first order derivative of the dipole moment w.r.t the relevant normal co-ordinate must be non-zero

This is the selection rule.



**Vibration +
Rotation**

Raman spectra : identifying the vibrations & characteristic lines



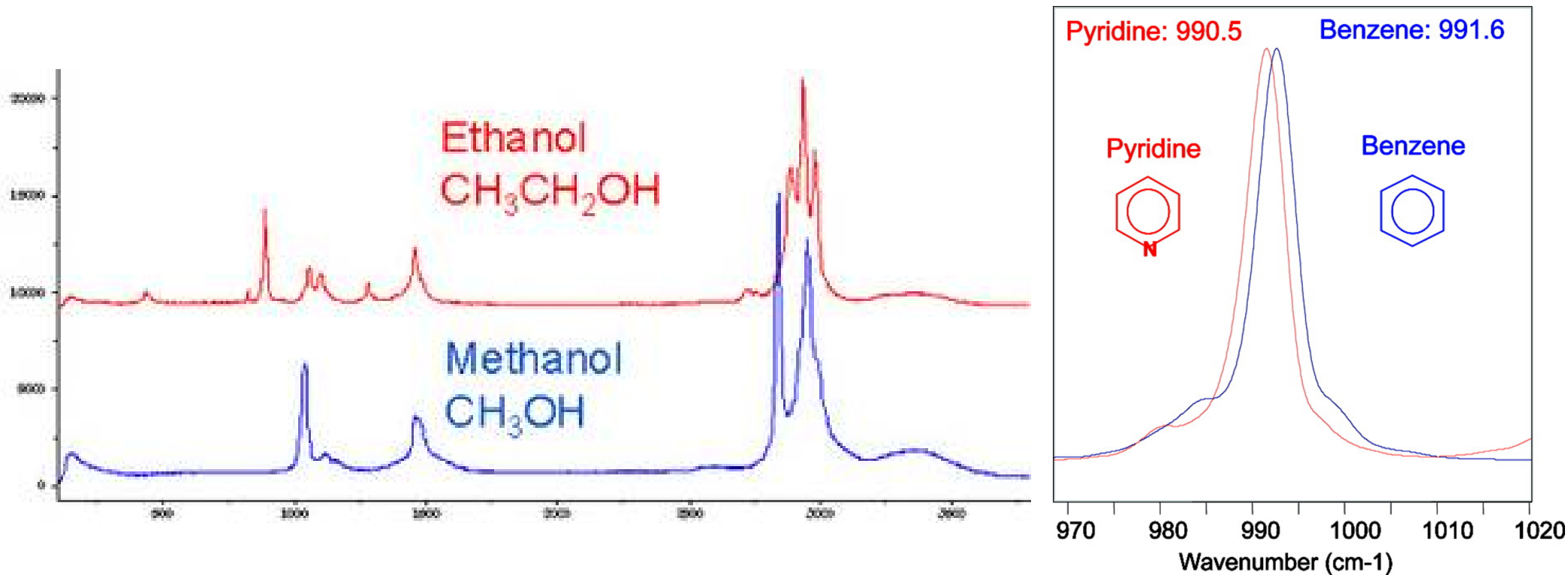
Where does the 1330 line in diamond come from?

Which stretch should give higher freq? Why? C-C or C-H

Data: Renishaw instruments

Classical normal mode problem for molecules:
N atoms \rightarrow 3N normal co-ordinates : masses known, find eigenfrequencies
Subtract : 3 + 3 degrees of freedom for rotation + translation
2 + 3 degrees of freedom for rotation + translation (linear molecule)
Enumerate degeneracies, symmetries

Raman spectra : identifying the vibrations & characteristic lines



Molecules with similar/nearly similar sections give signatures at close wavenumbers.
From known spectral lines \rightarrow identify functional groups/ bond stretches.

What are the selection rules of Raman lines?

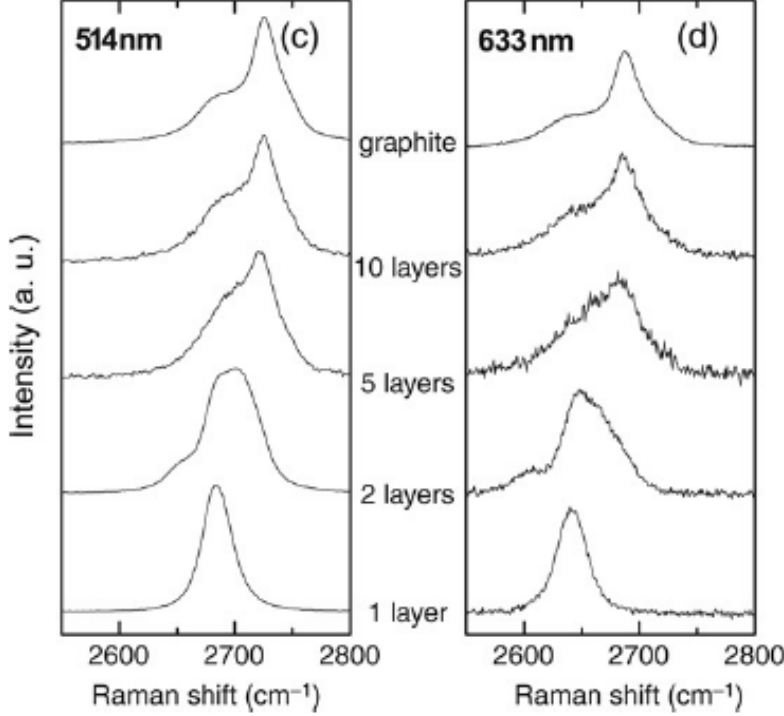
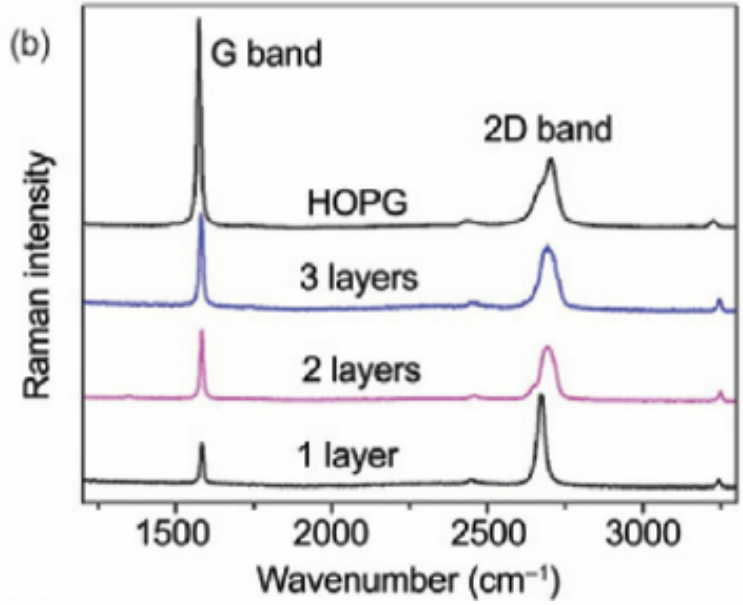
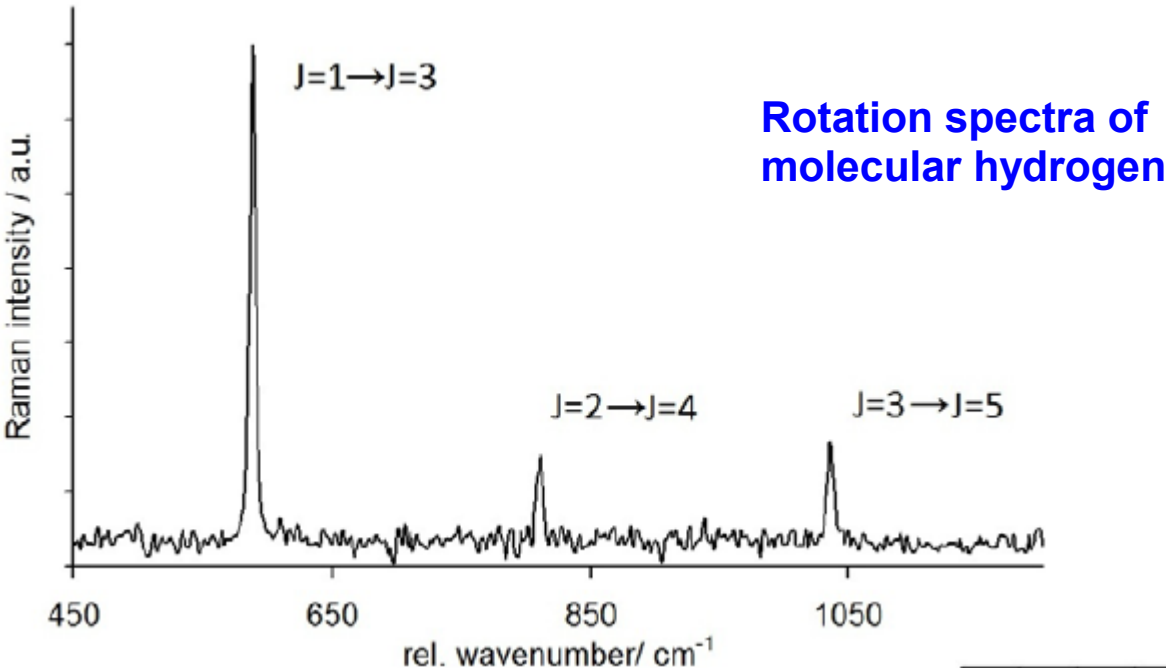
Handwaving argument....

Two transitions are involved : So J should change by 0 or 2.

More rigorous analysis : See I.M. Millis, *Molecular Physics*, **7**, 549 (1964)

Molecular Physics, **8**, 363 (1963)

Raman spectra : identifying the vibrations & characteristic lines



**Graphene/
HOPG**

Data:
A Ferrari
Solid State Comm.
143, 37 (2007)

Raman & Brillouin scattering

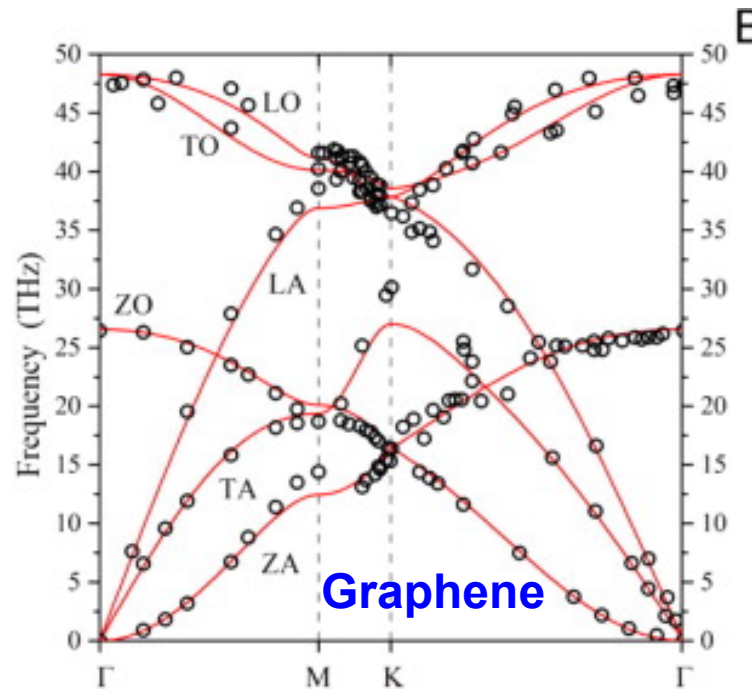
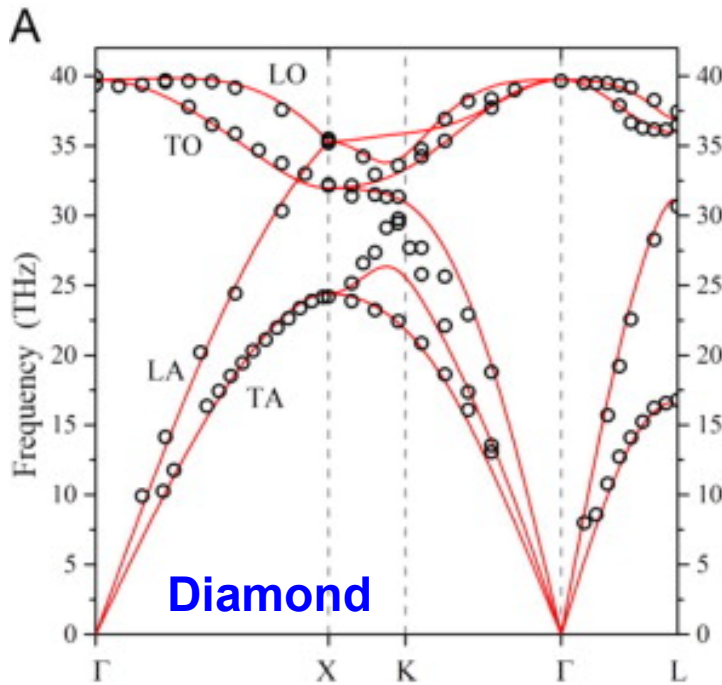
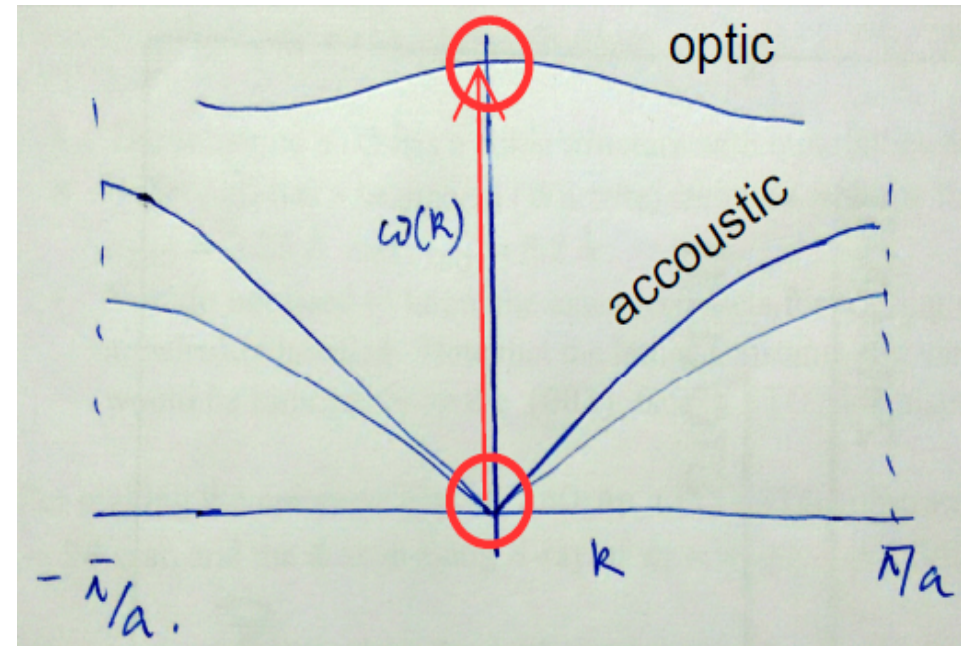
Both involve emission/absorption of a phonon :

Raman : OPTIC branches :
so higher in energy (\sim THz typically)

Brillouin : ACCOUSTIC branches :
so lower in energy (\sim Ghz typically)

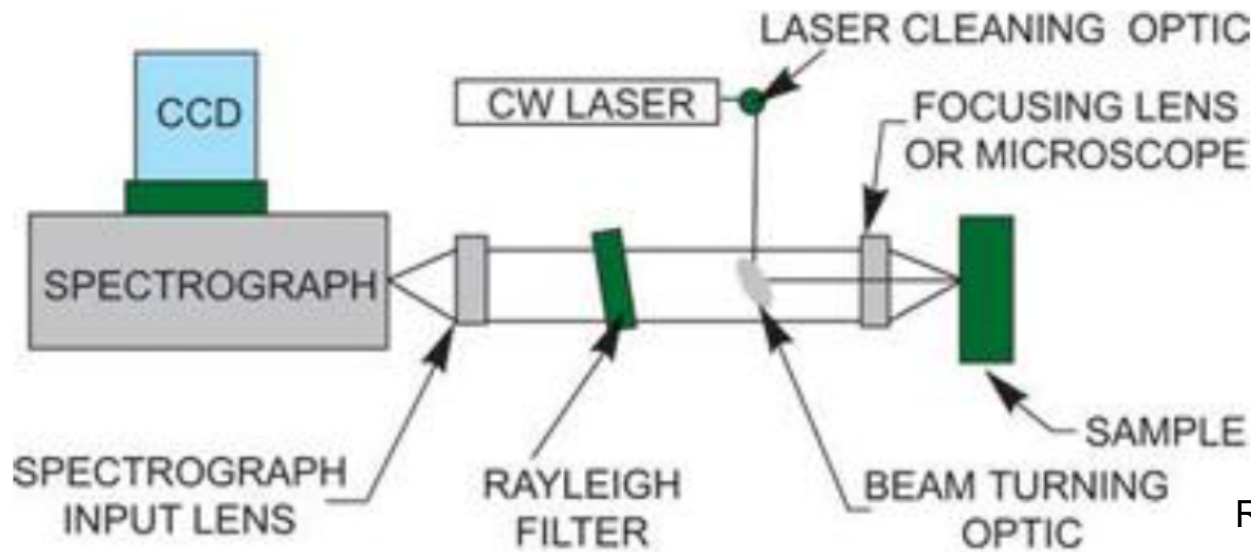
Since the shifts are much smaller, scattering by acoustic phonon gives energy shifts that require Fabry-Perot type arrangement to analyse.

Raman shifts can usually be distinguished by grating.



Phonon spectrum of diamond:
Where does the 1332 cm^{-1} line come from?

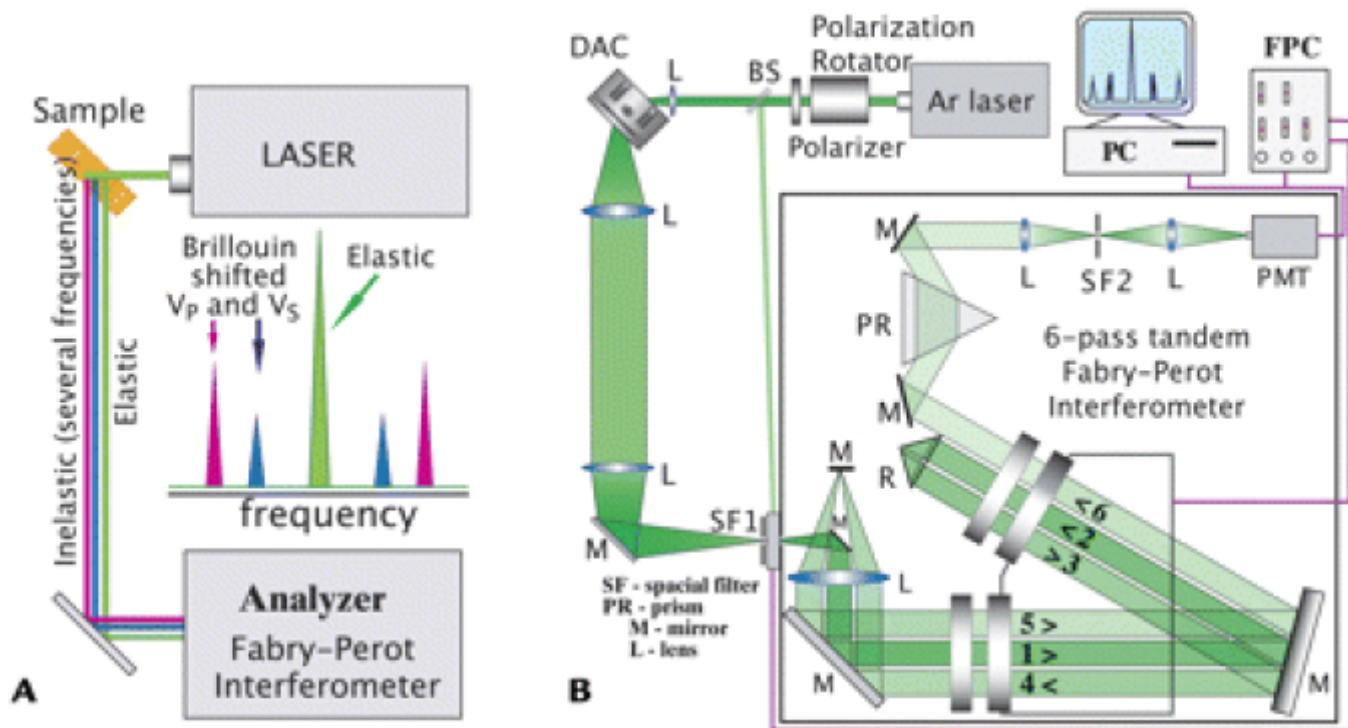
Brillouin scattering detection is more complex than Raman....



Fairly simple, very little sample preparation required.

Even some portable versions are available now.

Raman Spectroscopy. R.L. McCreery



Requires the resolution of a Fabry-Perot interferometer, since the energy shifts are far smaller.

Serc.carleton.edu/NAGTW_orkshops/mineralogy/mineral_physics/brillouin.html

Connecting elastic and inelastic scattering : dynamic structure factor

Consider a slow enough particle (\vec{k}) scattering off a sample (Φ) with a periodic structure

$$\left| \vec{k}_i, \Phi_i \right\rangle \rightarrow \left| \vec{k}_f, \Phi_f \right\rangle \quad \left| \quad V(\vec{r}) = \sum_n v(\vec{r} - \vec{R}_n) \quad \right| \quad V_{\vec{q}} = v_{\vec{q}} \sum_{\text{lattice}} e^{i\vec{q} \cdot \vec{R}_n}$$

$$P_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \left\langle \vec{k}_f, \Phi_f \left| V(\vec{r}) \right| \vec{k}_i, \Phi_i \right\rangle \right|^2 \delta(E_f + \epsilon_f - E_i - \epsilon_i)$$

$$\delta N_{i \rightarrow f} = P_{i \rightarrow f} \times \frac{L^3}{(2\pi)^3} d^3 \vec{k}_f = P_{i \rightarrow f} \times \frac{L^3}{(2\pi)^3} k_f \frac{M}{\hbar^2} d\epsilon_f d\Omega$$

Compare this with the incident particle current

$$\vec{j} = \rho \vec{v} = |\psi_i|^2 \frac{\hbar \vec{k}_i}{M} = \frac{\hbar \vec{k}_i}{MV} \quad \left(\text{assume : } \psi_i = \frac{1}{\sqrt{V}} e^{i\vec{k}_i \cdot \vec{r}} \right)$$

$$|j| d^2 \sigma = \delta N_{i \rightarrow f} \quad \text{Definition of the scattering cross-section}$$

$$\frac{d^2 \sigma}{d\epsilon_f d\Omega} = \frac{(MV)^2}{h^3} \frac{k_f}{k_i} \times \left(\frac{2\pi}{\hbar} \sum_f \left\langle \Phi_f \left| V_{\vec{q}} \right| \Phi_i \right\rangle^* \left\langle \Phi_f \left| V_{\vec{q}} \right| \Phi_i \right\rangle \delta(E_f + \epsilon_f - E_i - \epsilon_i) \right)$$

We only measure the state of the outgoing particle. So all the possible states of the sample must be summed over. That is the origin of the sum over f

Connecting elastic and inelastic scattering : dynamic structure factor

$$\sum_f P_{i \rightarrow f} = \frac{2\pi}{\hbar} |v_q|^2 \sum_f \langle \Phi_i | \sum e^{-i\vec{q} \cdot \vec{R}_m} | \Phi_f \rangle \langle \Phi_f | \sum e^{i\vec{q} \cdot \vec{R}_n} | \Phi_i \rangle \delta(E_f - E_i + \hbar\omega)$$

$$\delta(E_f - E_i + \hbar\omega) = \frac{1}{\hbar} \int \frac{dt}{2\pi} e^{i((E_f - E_i)/\hbar + \omega)t}$$

Notice how the index f has been switched and the complex conjugation removed

$$H | \Phi_f \rangle = E_f | \Phi_f \rangle$$

Heisenberg representation

$$\therefore \sum_{\Phi_f} P_{i \rightarrow f} = \frac{2\pi}{\hbar^2} |v_q|^2 \sum_{fmn} \int \frac{dt}{2\pi} e^{i\omega t} \langle \Phi_i | e^{-i\vec{q} \cdot \vec{R}_m} | \Phi_f \rangle \langle \Phi_f | e^{iHt/\hbar} e^{i\vec{q} \cdot \vec{R}_n} e^{-iHt/\hbar} | \Phi_i \rangle$$

$$= \frac{2\pi}{\hbar^2} |v_q|^2 \times \sum_{mn} \int \frac{dt}{2\pi} e^{i\omega t} \langle \Phi_i | e^{-i\vec{q} \cdot \vec{R}_m^{\vec{0}}} e^{i\vec{q} \cdot \vec{R}_n^{\vec{0}}(t)} | \Phi_i \rangle$$

The time dependence has come in because the lattice points creating the potential are not stationary – this is how the phonons enter into the picture.

Second we need to do a THERMAL average over the initial states, because the sample sits at some finite temperature.

$$\vec{R}_m(t) = \vec{R}_m^0 + \vec{u}_m(t)$$

\vec{R}_m^0 : equilibrium position

Follow the standard notation for thermal average of an expectation value.

Connecting elastic and inelastic scattering : dynamic structure factor

$$\sum_{mn} \int \frac{dt}{2\pi} e^{i\omega t} \langle \Phi_i | e^{-i\vec{q} \cdot \vec{R}_m(0)} e^{i\vec{q} \cdot \vec{R}_n(t)} | \Phi_i \rangle$$

$$= \sum_{mn} e^{i\vec{q} \cdot (\vec{R}_m^0 - \vec{R}_n^0)} \int \frac{dt}{2\pi} e^{i\omega t} \langle e^{-i\vec{q} \cdot \vec{u}_m(0)} e^{i\vec{q} \cdot \vec{u}_n(t)} \rangle$$

$$\langle A \rangle = \frac{\sum_i \langle \Phi_i | A | \Phi_i \rangle e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

Called the
thermal average

$$S(\vec{q}, \omega) = \frac{1}{N} \sum_{mn} e^{i\vec{q} \cdot (\vec{R}_m^0 - \vec{R}_n^0)} \int \frac{dt}{2\pi} e^{i\omega t} \langle e^{-i\vec{q} \cdot \vec{u}_m(0)} e^{i\vec{q} \cdot \vec{u}_n(t)} \rangle$$

$$\frac{d^2 \sigma}{d\epsilon d\Omega} = \frac{(ML^3)^2}{h^3} \frac{k_f}{k_i} \frac{2\pi}{\hbar^2} N |\nu_{\vec{q}}|^2 \times S(\vec{q}, \omega)$$

The dynamic structure factor is a characteristic of the lattice only, irrespective of what (light, electron, neutron) is being scattered by the crystal.

Evaluating the dynamic structure factor

For harmonic vibrations a remarkable result holds for thermal averaging

Given two matrices or operators A and B which are both linear in \vec{r} and \vec{p}

$$\left\langle e^A e^B \right\rangle = e^{\langle A^2 + B^2 + 2AB \rangle / 2}$$

in general $[A, B] \neq 0$

$$\begin{aligned} \left\langle e^{i\vec{q} \cdot \vec{u}_m(0)} e^{i\vec{q} \cdot \vec{u}_n(t)} \right\rangle &= e^{-\langle (\vec{q} \cdot \vec{u}_m(0))^2 \rangle / 2} \times e^{-\langle (\vec{q} \cdot \vec{u}_n(t))^2 \rangle / 2} \times e^{-\langle (\vec{q} \cdot \vec{u}_m(0)) (\vec{q} \cdot \vec{u}_n(t)) \rangle} \\ &= e^{-q^2 \langle u^2 \rangle / 2} \times e^{-q^2 \langle u^2 \rangle / 2} \times e^{-\langle (\vec{q} \cdot \vec{u}_m(0)) (\vec{q} \cdot \vec{u}_n(t)) \rangle} \\ &= e^{-q^2 \langle u^2 \rangle} \times e^{-\langle (\vec{q} \cdot \vec{u}_m(0)) (\vec{q} \cdot \vec{u}_n(t)) \rangle} \end{aligned}$$

All sites m, n are equivalent so their r.m.s amplitude would be same

$$S(\vec{q}, \omega) = e^{-q^2 \langle u^2 \rangle} \sum_n e^{i\vec{q} \cdot \vec{R}_n^0} \int \frac{dt}{2\pi} e^{i\omega t} e^{\langle (\vec{q} \cdot \vec{u}_0(0)) (\vec{q} \cdot \vec{u}_n(t)) \rangle}$$

The $1/N$ factor cancels after one of the indices (in this case m) is summed over.

The exponential can now be simple expanded and evaluated term by term!

Evaluating the dynamic structure factor : expand term by term

$$S(\vec{q}, \omega) = e^{-q^2 \langle u^2 \rangle} \sum_n e^{i\vec{q} \cdot \vec{R}_n^0} \int \frac{dt}{2\pi} e^{i\omega t} \left[1 + \langle ((\vec{q} \cdot \vec{u}_0(0))(\vec{q} \cdot \vec{u}_n(t))) \rangle + \dots \right]$$

The first term is just 1 : The integral reproduces the static structure factor which gives the correct intensity for elastic scattering including the Debye-Waller factor for temperature.

The second term can be evaluated by writing $u_n(t)$ in terms of the creation annihilation operators as applicable to a harmonic oscillator.

$$u_n(t) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} \sqrt{\frac{\hbar}{2m\omega_k}} \left[a_k e^{i(\vec{k} \cdot \vec{R}_n^0 - \omega_k t)} + a_k^+ e^{-i(\vec{k} \cdot \vec{R}_n^0 - \omega_k t)} \right]$$

The operator is written in terms of the fourier transform of the raising/lowering operators.

$$S_1(\vec{q}, \omega) = e^{-q^2 \langle u^2 \rangle} \left(\frac{\hbar^2 q^2}{2m} \right) \sum_{\vec{k}, n} \frac{1}{\hbar \omega_k} \left[e^{-i(\vec{k} - \vec{q}) \cdot \vec{R}_n} n_k \delta(\omega - \omega_k) + e^{-i(\vec{k} + \vec{q}) \cdot \vec{R}_n} (n_k + 1) \delta(\omega + \omega_k) \right]$$

Here the phonon $\omega(\vec{k})$ is created, n_k is the boson occupation probability

The wave vector of the incident particle changes by \vec{q}

Notice how the exponential sum forces the requirement

$$\vec{k} - \vec{q} = \vec{G} \quad (\text{a reciprocal lattice vector})$$

Notice how temperature enters in two ways in inelastic process

Evaluating the dynamic structure factor : expand term by term

$$S(\vec{q}, \omega) = e^{-q^2 \langle u^2 \rangle} \sum_n e^{i\vec{q} \cdot \vec{R}_n^0} \int \frac{dt}{2\pi} e^{i\omega t} \left[1 + \langle ((\vec{q} \cdot \vec{u}_0(0))(\vec{q} \cdot \vec{u}_n(t))) \rangle + \dots \right]$$

The first term is just 1 : The integral reproduces the static structure factor which gives the correct intensity for elastic scattering including the Debye-Waller factor for temperature.

The second term can be evaluated by writing $u_n(t)$ in terms of the creation annihilation operators as applicable to a harmonic oscillator.

$$u_n(t) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} \sqrt{\frac{\hbar}{2m\omega_k}} \left[a_k e^{i(\vec{k} \cdot \vec{R}_n^0 - \omega_k t)} + a_k^+ e^{-i(\vec{k} \cdot \vec{R}_n^0 - \omega_k t)} \right]$$

The operator is written in terms of the fourier transform of the raising/lowering operators.

$$S_1(\vec{q}, \omega) = e^{-q^2 \langle u^2 \rangle} \left(\frac{\hbar^2 q^2}{2m} \right) \sum_{\vec{k}, n} \frac{1}{\hbar \omega_k} \left[e^{-i(\vec{k} - \vec{q}) \cdot \vec{R}_n} n_k \delta(\omega - \omega_k) + e^{-i(\vec{k} + \vec{q}) \cdot \vec{R}_n} (n_k + 1) \delta(\omega + \omega_k) \right]$$

Here the phonon $\omega(\vec{k})$ is created, n_k is the boson occupation probability

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Notice how the exponential sum forces the requirement

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Notice how temperature enters in two ways in inelastic process

Two generic conservation laws for scattering from a crystal

$$E_f - E_i = \pm \hbar \omega(\vec{q})$$

The wave-vector conservation looks like momentum conservation. But it is not momentum.

$$\vec{k}_f - \vec{k}_i = \vec{q} + \vec{G}$$

Notice the presence of an arbitrary reciprocal lattice vector.

Incident particle $\rightarrow i$

Outgoing particle $\rightarrow f$: $w(q)$ is the excitation created or destroyed

When will the additional factor of G come into play?

In a situation where the incident particle has a wave vector comparable in size with the Brillouin zone.

In case where the G comes into play and brings back the resultant vector into the first Brillouin zone – the process is called UMKLAPP (flip over)

It is possible with neutrons, X-rays. (estimate the wave-vector ratio)
Very improbable with visible light.

Wavevector $\sim \pi/a$

Visible light $\sim 10^{-3}$ of the zone vector

X-ray, thermal neutron \sim comparable in size to Brillouin zone

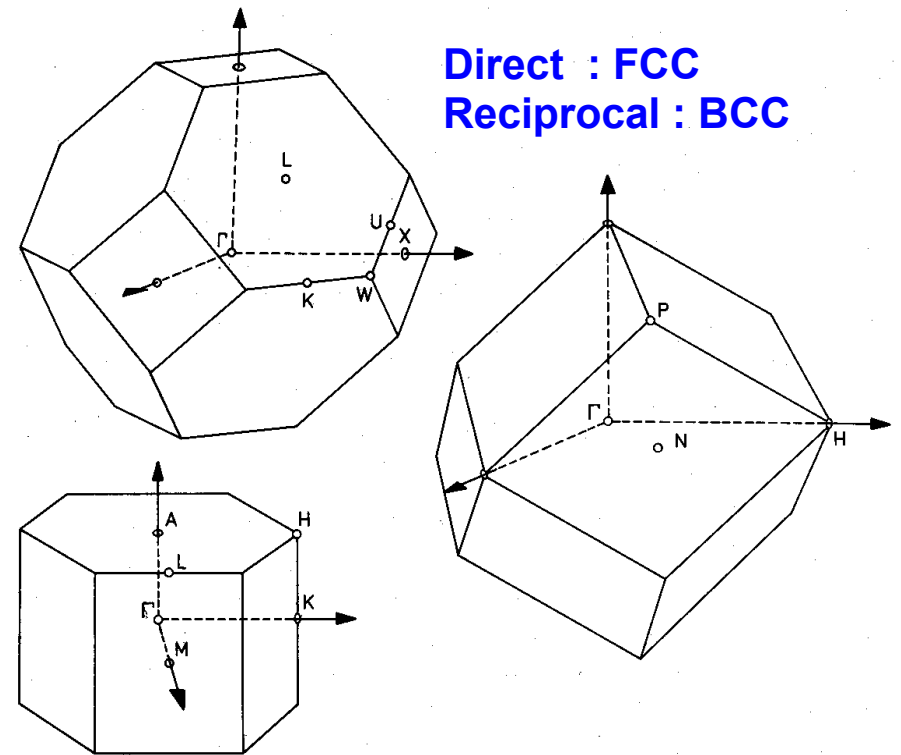
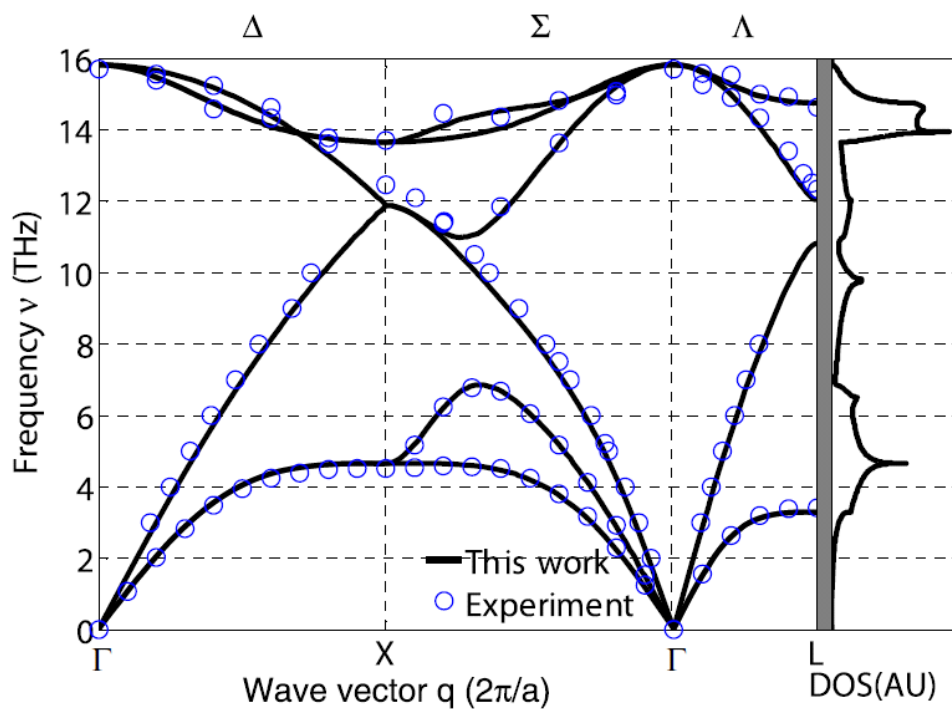
Some examples of phonon dispersion : Silicon

In a 3D crystal there would always be 3 acoustic modes (this can be proved)

If the unit cell has p atoms, then there should be $3p-3$ optical modes.

Many degeneracies are possible. (Calculations : Lattice Dynamics + refinements)

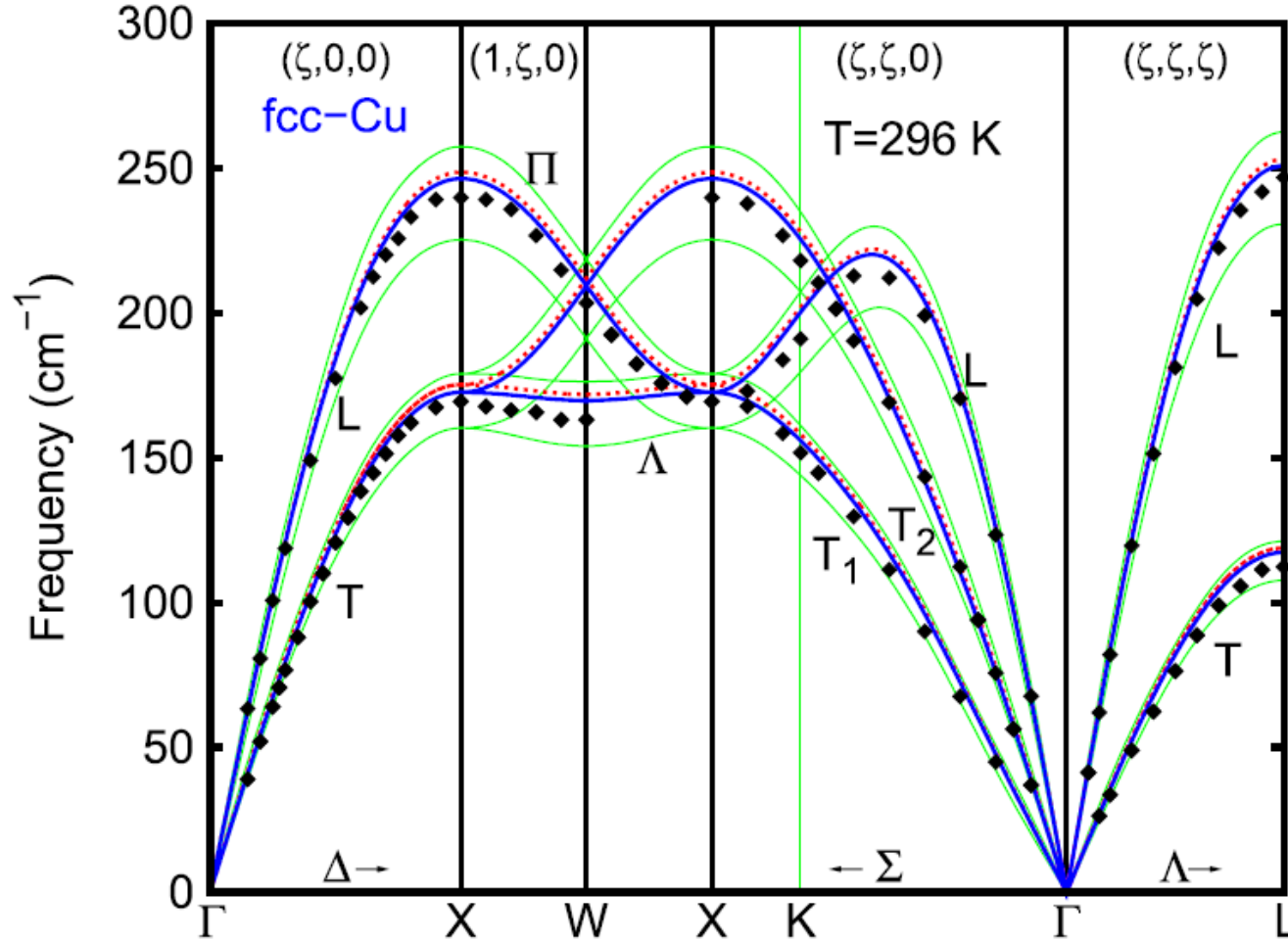
Plotting the dispersion is done following exactly the same convention as electronic band structure...from zone center towards various special points.



Direct : FCC
Reciprocal : BCC

Direct : Hexagonal
Reciprocal: Hexagonal

Some examples of phonon dispersion : FCC - Cu



Methods used to map out phonon $\omega(\mathbf{q})$

Inelastic neutron scattering

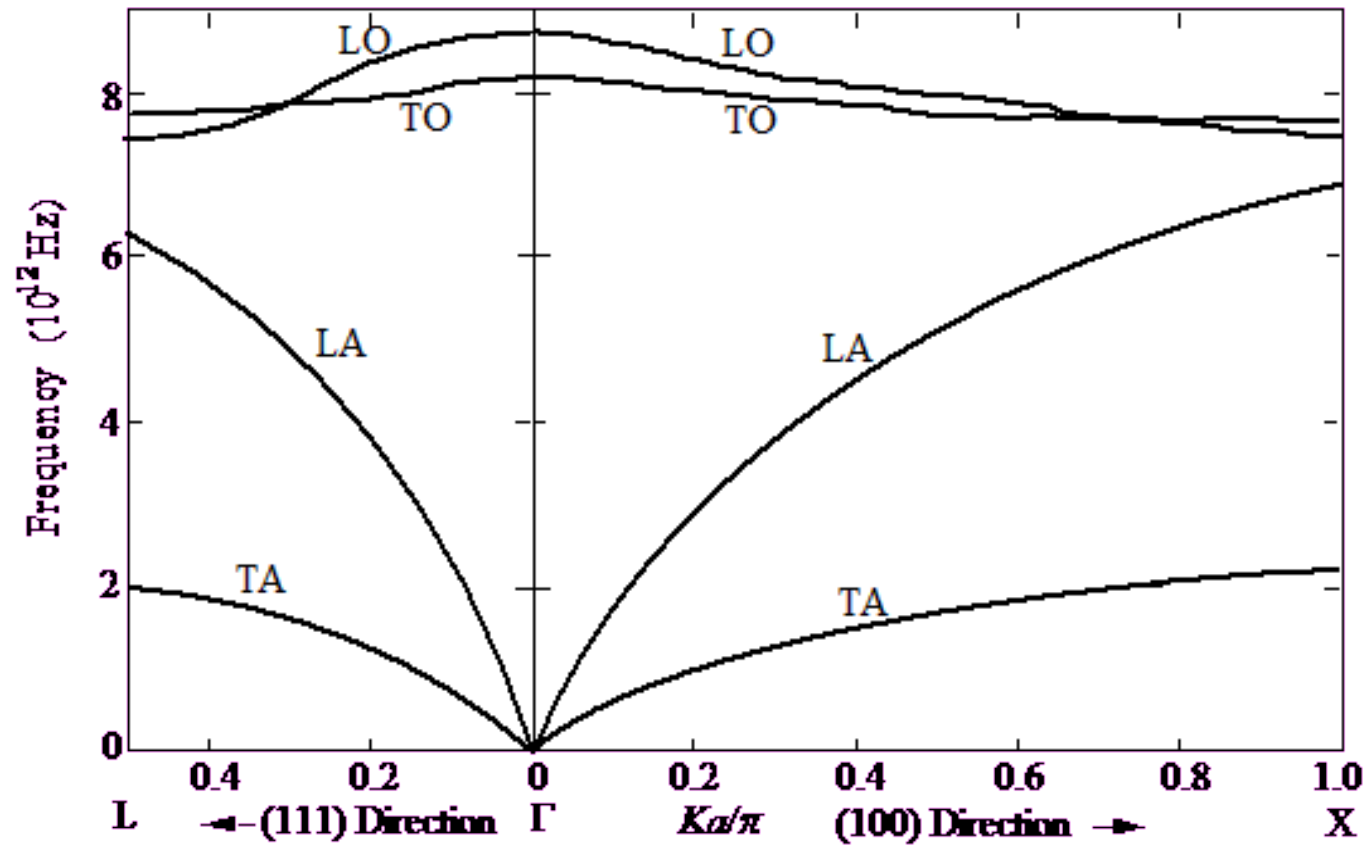
High Resolution Electron Energy Loss scattering (HREELS)

Inelastic Helium atom scattering (HAS)

A. Dal Corso, *J. Phys.: Condens. Matter*, **25**, 145401 (2013)

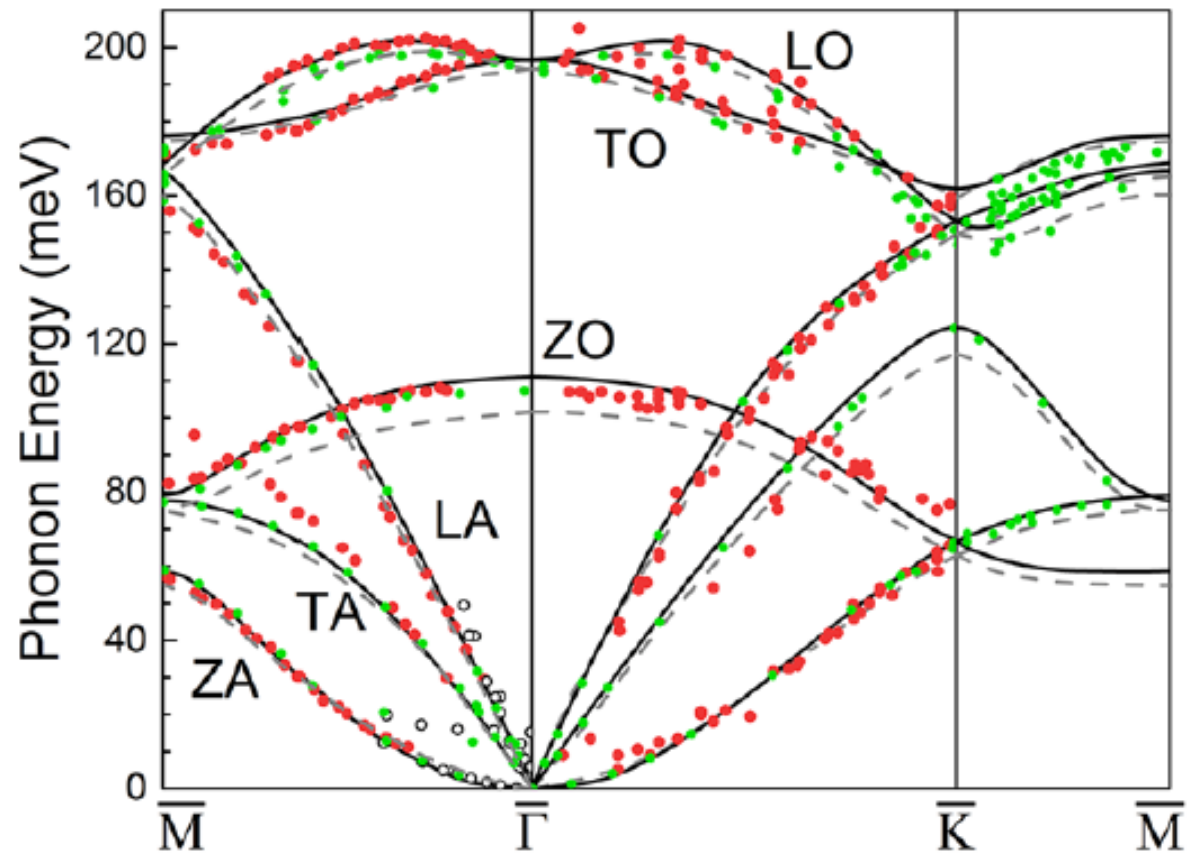
Model calculation results & inelastic neutron diffraction data

Some examples of phonon dispersion : GaAs



GaAs...notice that frequencies are lower than Si.
For diamond it was much higher.

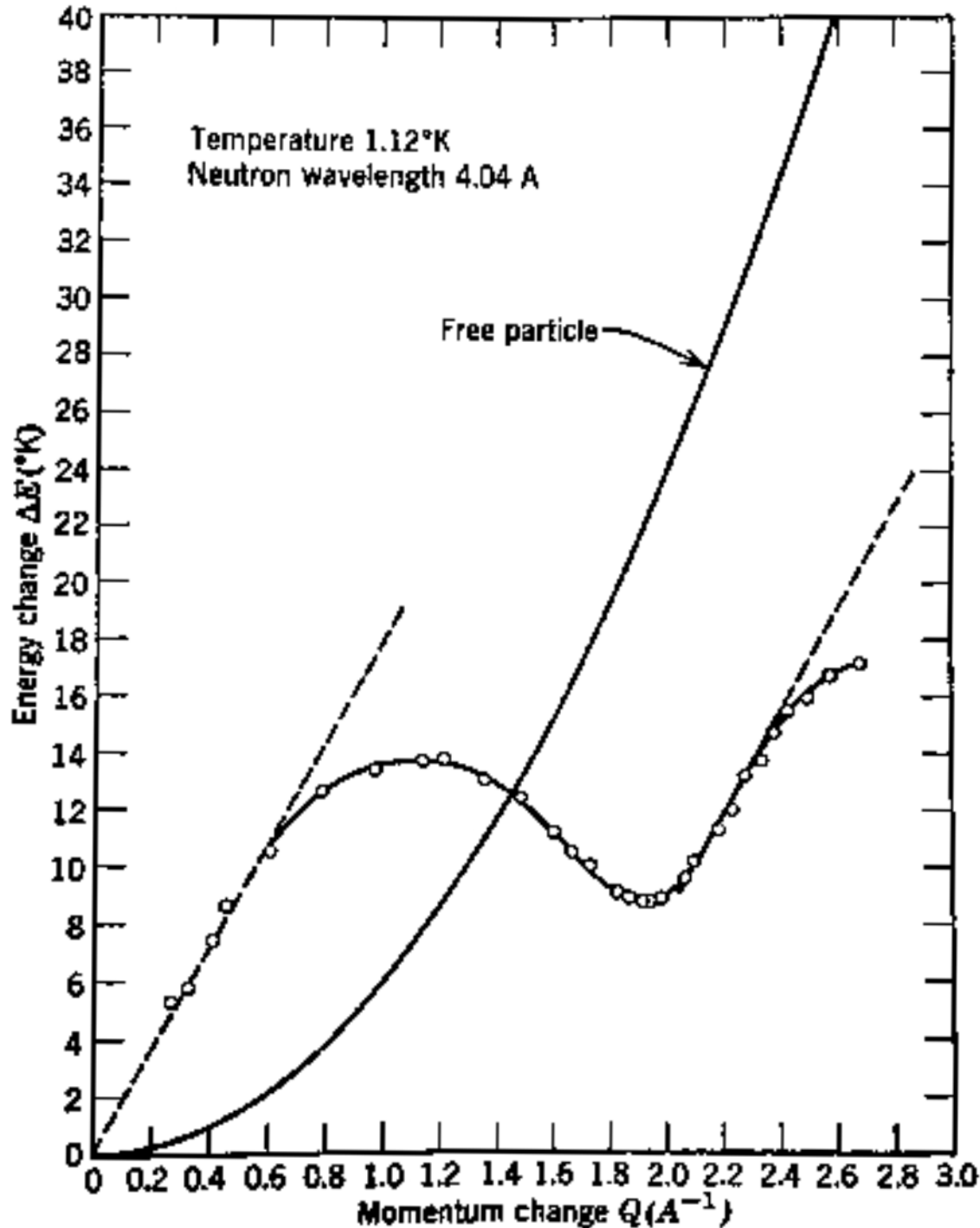
Some examples of phonon dispersion : Graphene



Al Taleb et al
J Phys. Condensed
matter: 28, 103005
(2016)

Figure 2. Phonon dispersion of graphite from HREELS (red dots, [54, 55]), inelastic x-ray scattering (green dots, [53]) and inelastic neutron scattering (open circles, [56]). DFT calculations for Gr are shown by gray-dashed lines [57] and solid lines [58].

Excitation spectrum of a liquid by neutron scattering : Superfluid Helium



The principles are the same.

But here momentum is real.
Unlike phonons in solid, that do not carry real momentum.

There is NO additional reciprocal lattice vector.

The minima at a finite Q is a special feature of a superfluid.

C. Kittel, Quantum theory of solids.

X-ray photoelectron spectroscopy : XPS (ESCA)

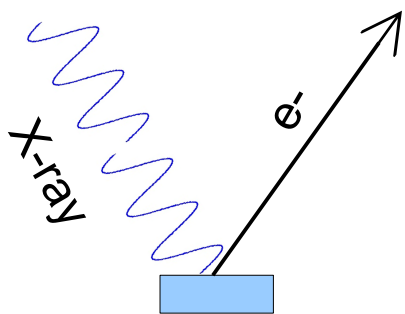
An atom is identified by its energy levels.

The outer levels overlap forming bands (Valence & Conduction bands)

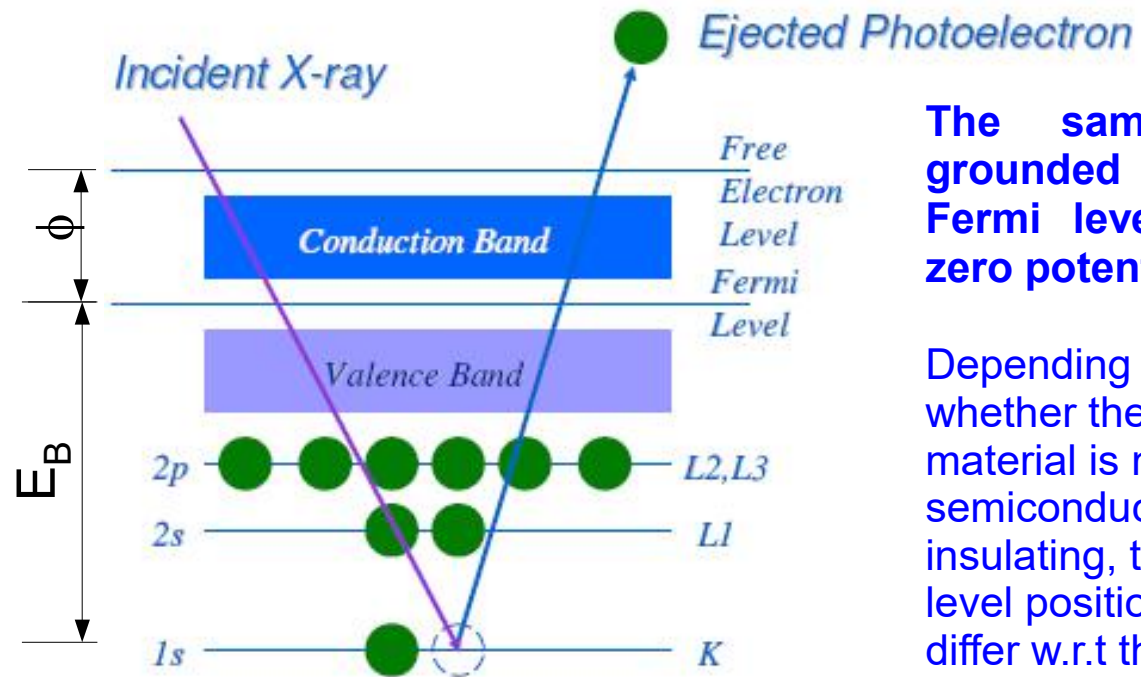
The core levels are virtually unaffected by the ionisation state, chemical bonding state of the outer electrons.

These core levels thus act as a fingerprint of the atom, irrespective of what solid it is in.

$$KE = h\nu - (E_B + \phi)$$



Basic idea : very simple!
Like photoelectric effect.



The sample is grounded means Fermi level is at zero potential.

Depending on whether the material is metallic, semiconducting or insulating, the fermi level position will differ w.r.t the bands.

XPS: Experimental aspects

What kind of X-ray to use?

We are not looking for diffracted spots....

Want a sharply defined energy

About 1 keV needed to probe core levels

Commonly used

Ultra high vacuum needed. Why?

The detector sees the electrons and analyses their energies.

Without very high vacuum, the electrons are going to scatter off gas molecules.

$$P \sim 1 \times 10^{-9} \text{ mbar}$$

X-ray lines

Line	Energy, eV	Width, eV
Y $M\zeta$	132.3	0.47
Zr $M\zeta$	151.4	0.77
Nb $M\zeta$	171.4	1.21
Mo $M\zeta$	192.3	1.53
Ti $L\alpha$	395.3	3.0
Cr $L\alpha$	572.8	3.0
Ni $L\alpha$	851.5	2.5
Cu $L\alpha$	929.7	3.8
Mg $K\alpha$	1253.6	0.7
Al $K\alpha$	1486.6	0.85
Si $K\alpha$	1739.5	1.0
Y $L\alpha$	1922.6	1.5
Zr $L\alpha$	2042.4	1.7
Ti $K\alpha$	4510.0	2.0
Cr $K\alpha$	5417.0	2.1
Cu $K\alpha$	8048.0	2.6

XPS: Experimental aspects

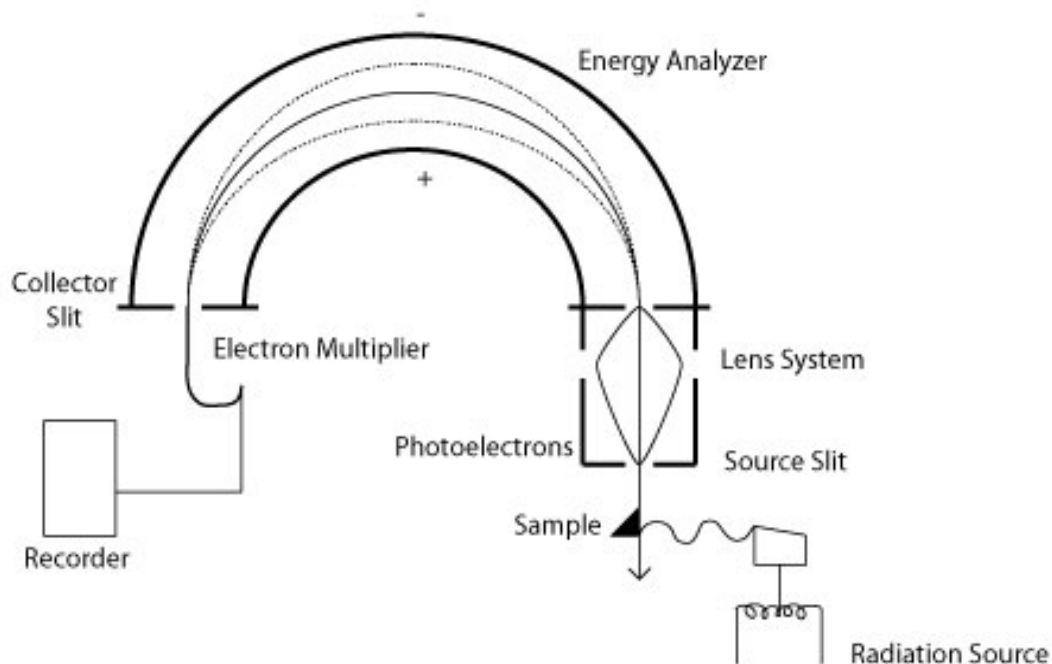
What elements can be detected?

Hydrogen, Helium are too light. Otherwise all elements from Lithium upwards.

However only the top ~ 5-10 nm of the sample actually responds. Electrons emitted from deeper layers will not be able to come out.

So surface contamination must be avoided.

This is also another reason why very high vacuum ($1\text{e-}9$ mbar) is needed.



The electric field is radial and of known value set by the user.

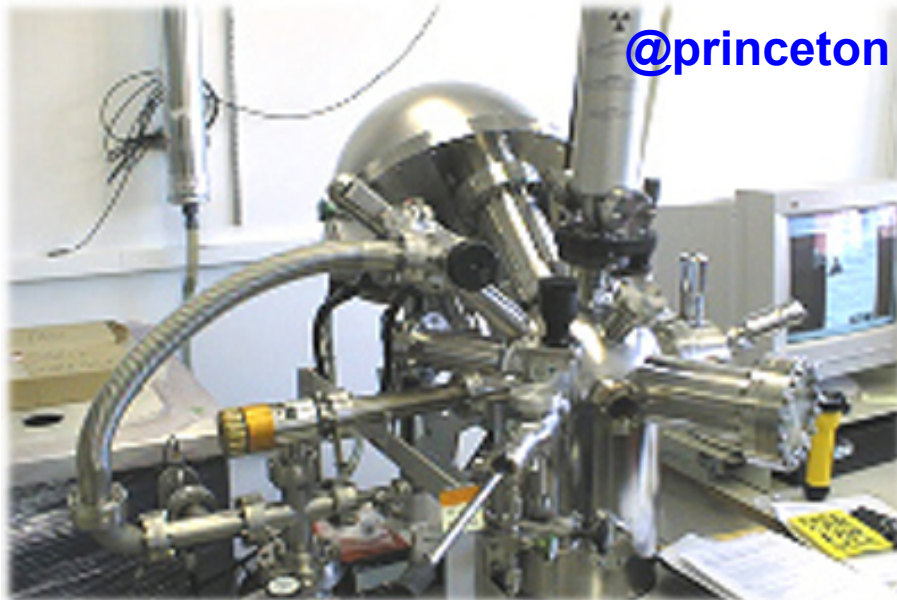
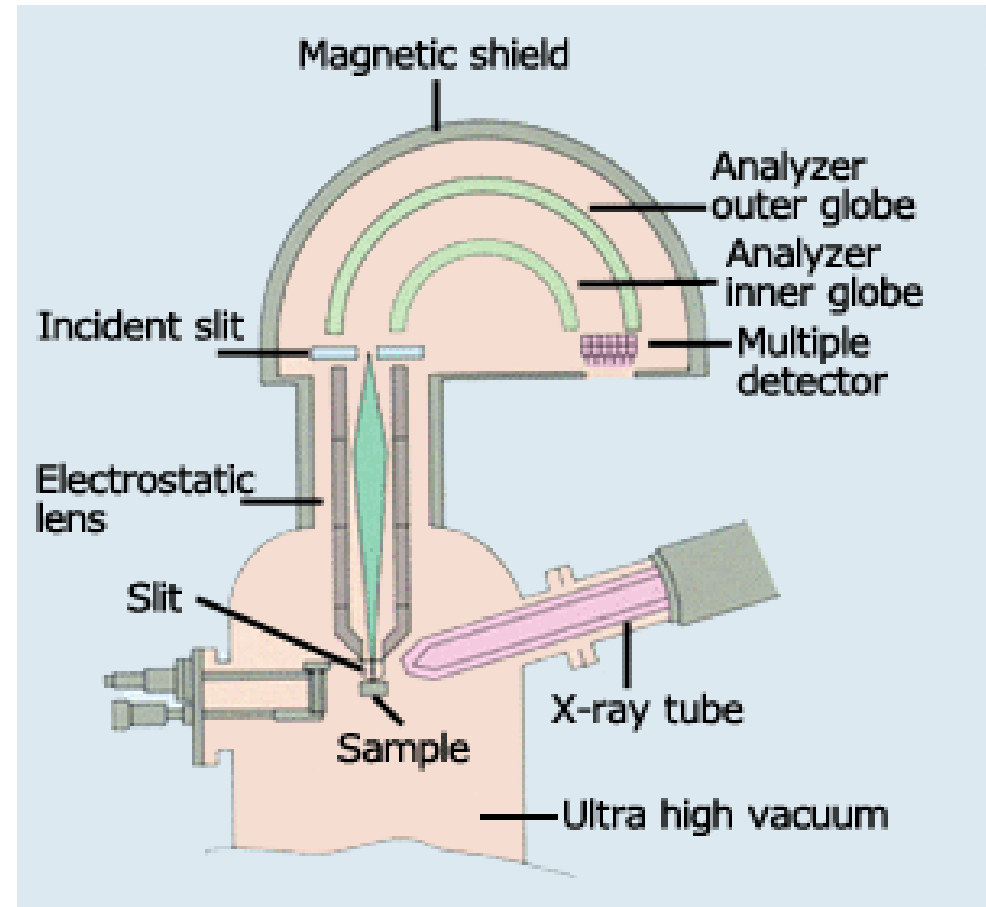
If the entry and the exit points are fixed, then electrons with a specific energy only will pass.

The spectrum is a plot of the intensity vs KE.

Resolution ~ 0.5 eV

Detection limit ~ 0.1 – 1 %

XPS: Experimental aspects : How does an ESCA/XPS look ?



Resolution ~ 0.5 eV

Detection limit ~ 0.1 – 1 %

XPS and its relation to the three electron Auger process

Consider an atom with a vacancy in a core state (say K shell)

The FIRST electron left the atom in an **unstable state with one vacancy**.

It does not matter how this first vacancy was created (hit with an electron or a photon...)

An outer SECOND electron can now drop into the vacant state, releasing another photon in the process. (e.g. $L \rightarrow K$)

This photon may be emitted as a characteristic line. (atom left with 1 vacancy)

But the photon may be reabsorbed by a THIRD electron in the atom and if the energy is in excess of the binding energy of this THIRD electron, that will be emitted.

Finally The atom will be left with 2 vacancies.

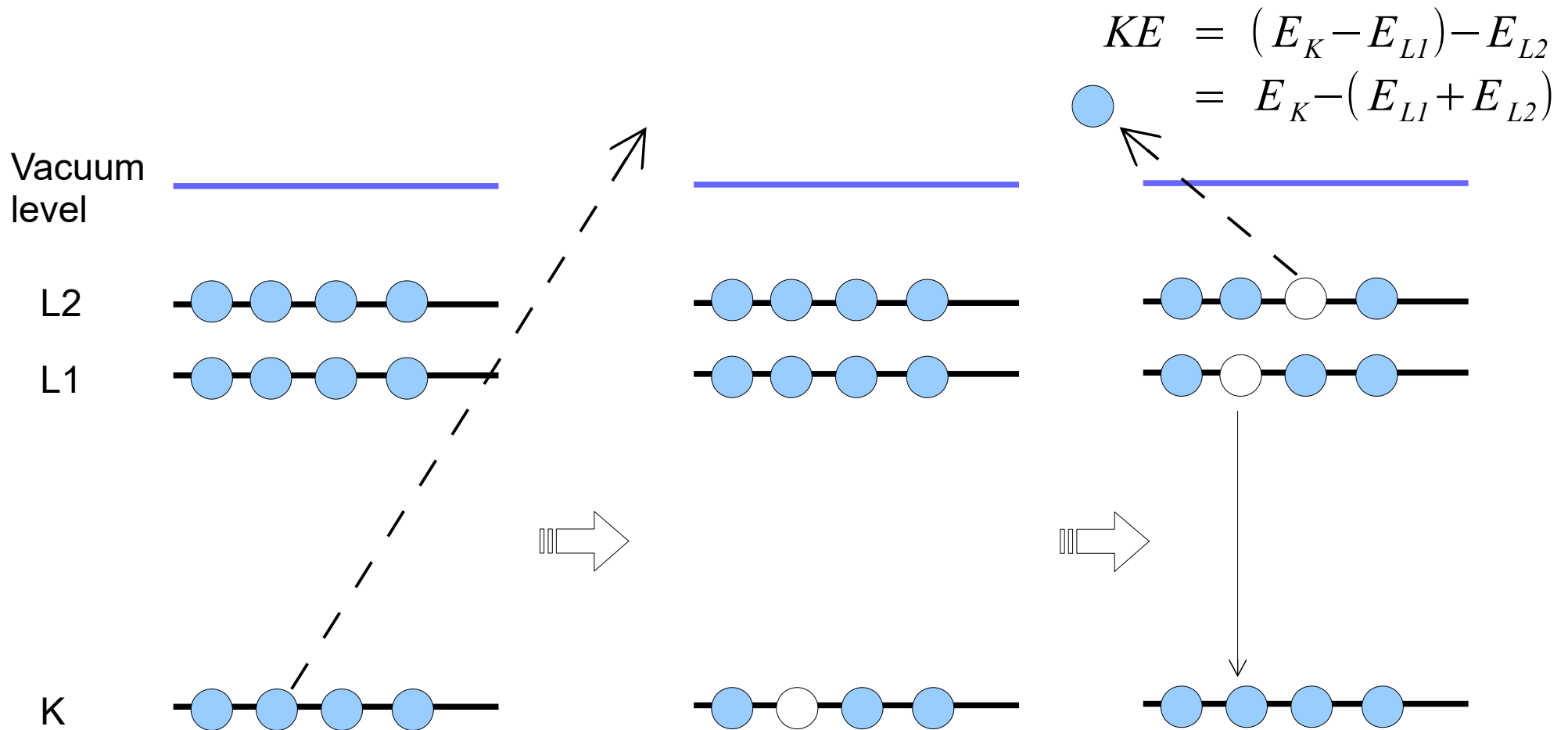
This THREE electron process is called the Auger process. (The mechanism was discovered by Meitner and Auger)

Since three electrons are needed, only atoms with $Z > 2$ can show Auger emission.

The electrons detected in the XPS spectra can also be Auger electrons.

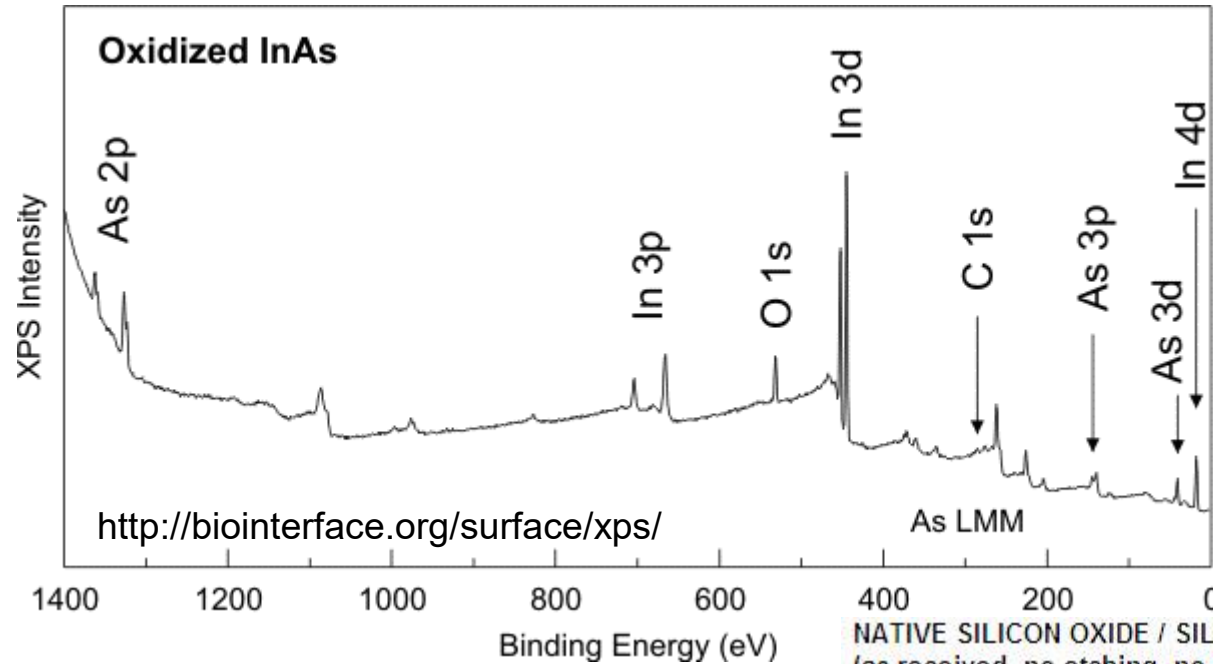
Historically derivative of the intensity used to be plotted to suppress the background slope.

XPS and its relation to the three electron Auger process



Many combinations will be possible in a real atom.
These would be labelled with three indices...e.g. KL1L2

Sample XPS spectra : finding surface contamination/impurity



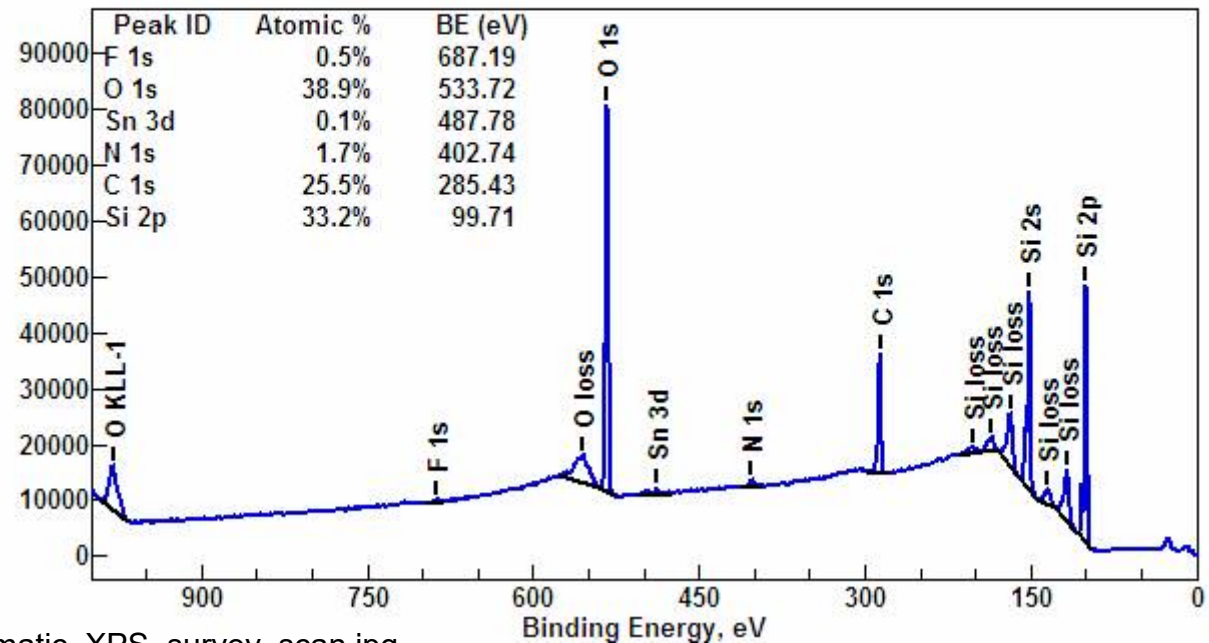
NATIVE SILICON OXIDE / SILICON WAFER (90 DEG TOA)
(as received, no etching, no cleaning)

System Name: XI ASCII
Pass Energy: 150.00 eV
Shift (Bias): 0.0 (0.0) eV
Thursday 6/2/1988

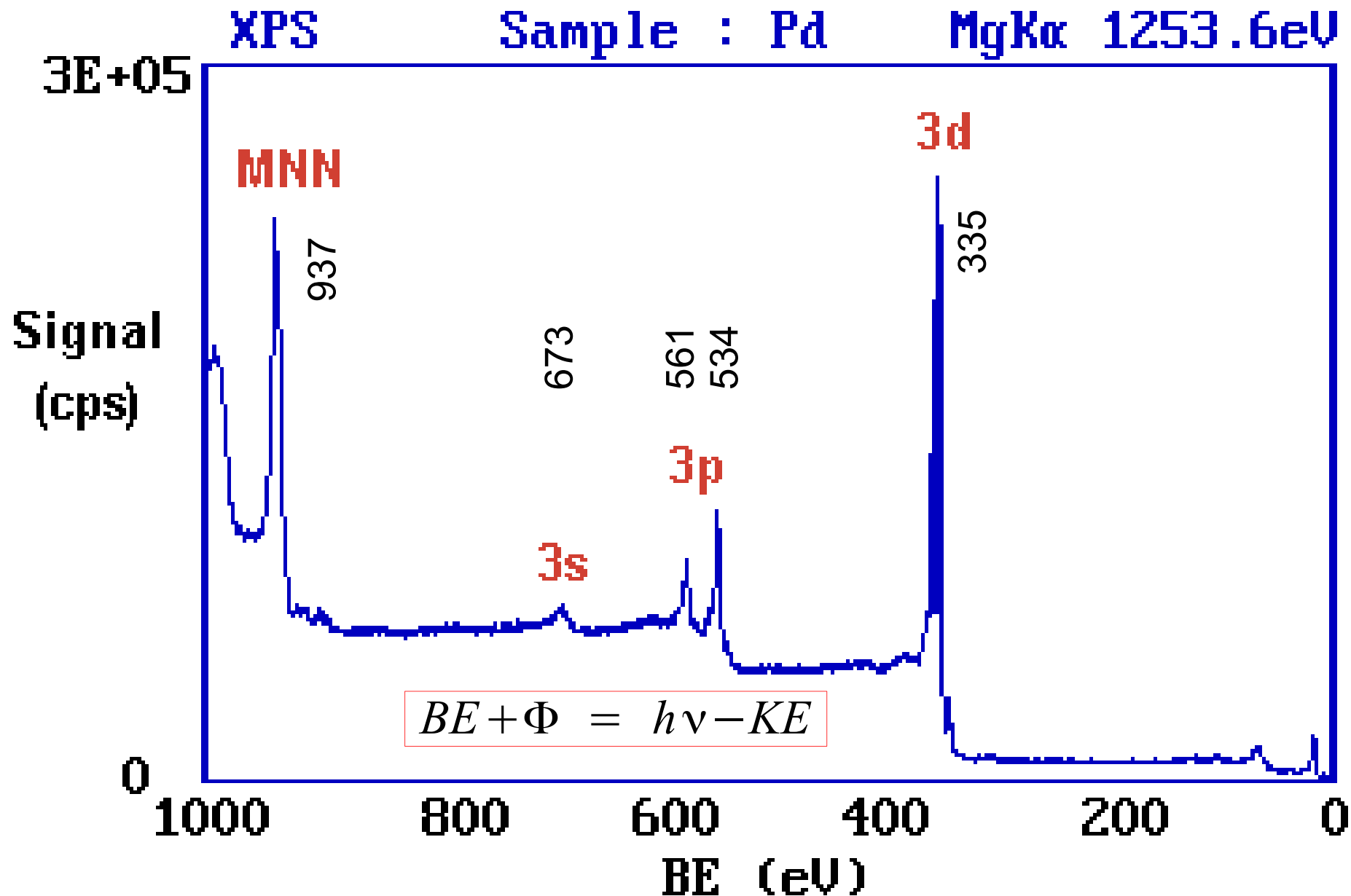
Identify the lines from known values – use standard spectral line libraries....

Quantitative analysis:
Peak area...
But absorption cross section of every level is not necessarily same.

Counts



Sample XPS spectra :Auger and XPS both will be present together



Sample XPS spectra :Binding energy data for Palladium

Electron binding energies

Electron binding energies for palladium. All values of **electron binding energies** are given in eV. The binding energies are quoted relative to the vacuum level for rare gases and H₂, N₂, O₂, F₂, and Cl₂ molecules; **relative to the Fermi level for metals**; and relative to the top of the valence band for semiconductors.

Label	Orbital	eV [literature reference]
-------	---------	---------------------------

K	1s	24350 [1]
---	----	-----------

L _I	2s	3604 [1]
----------------	----	----------

L _{II}	2p _{1/2}	3330 [1]
-----------------	-------------------	----------

L _{III}	2p _{3/2}	3173 [1]
------------------	-------------------	----------

M _I	3s	671.6 [3]
----------------	----	-----------

M _{II}	3p _{1/2}	559.9 [3]
-----------------	-------------------	-----------

M _{III}	3p _{3/2}	532.3 [3]
------------------	-------------------	-----------

M _{IV}	3d _{3/2}	340.5 [3]
-----------------	-------------------	-----------

M _V	3d _{5/2}	335.2 [3]
----------------	-------------------	-----------

N _I	4s	87.1 [2, values derived from reference 1]
----------------	----	---

N _{II}	4p _{1/2}	55.7 [3, one-particle approximation not valid owing to short core-hole lifetime]
-----------------	-------------------	--

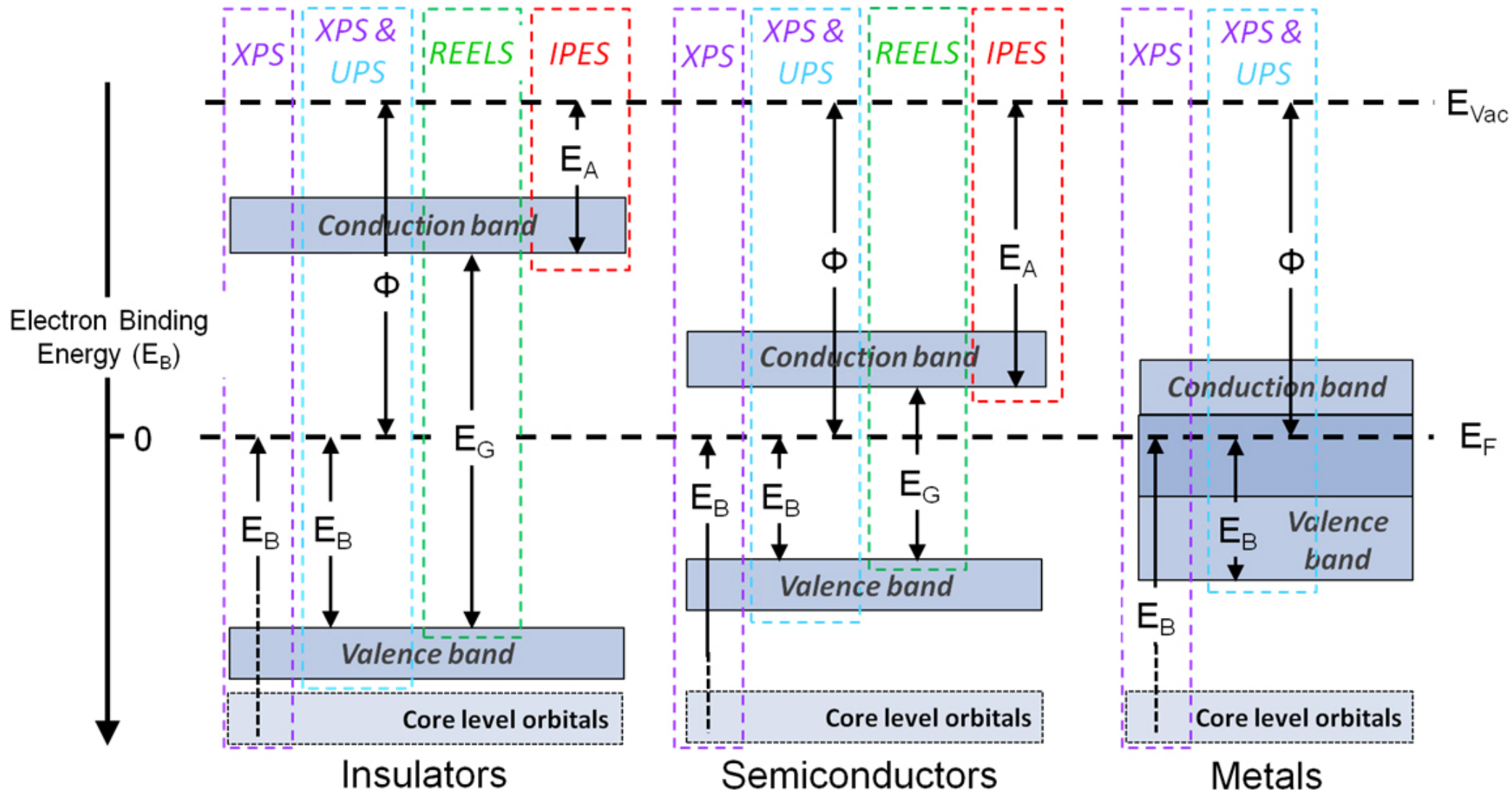
N _{III}	4p _{3/2}	50.9 [3]
------------------	-------------------	----------

Identify the transitions in the previous spectra and Auger electron

References

1. J. A. Bearden and A. F. Burr, "Reevaluation of X-Ray Atomic Energy Levels," *Rev. Mod. Phys.*, 1967, **39**, 125.
2. M. Cardona and L. Ley, Eds., *Photoemission in Solids I: General Principles* (Springer-Verlag, Berlin) with additional corrections, 1978.
3. Gwyn Williams WWW table of values

The scope of various photoemission processes : overview



Where does one find
10-100 eV photons?

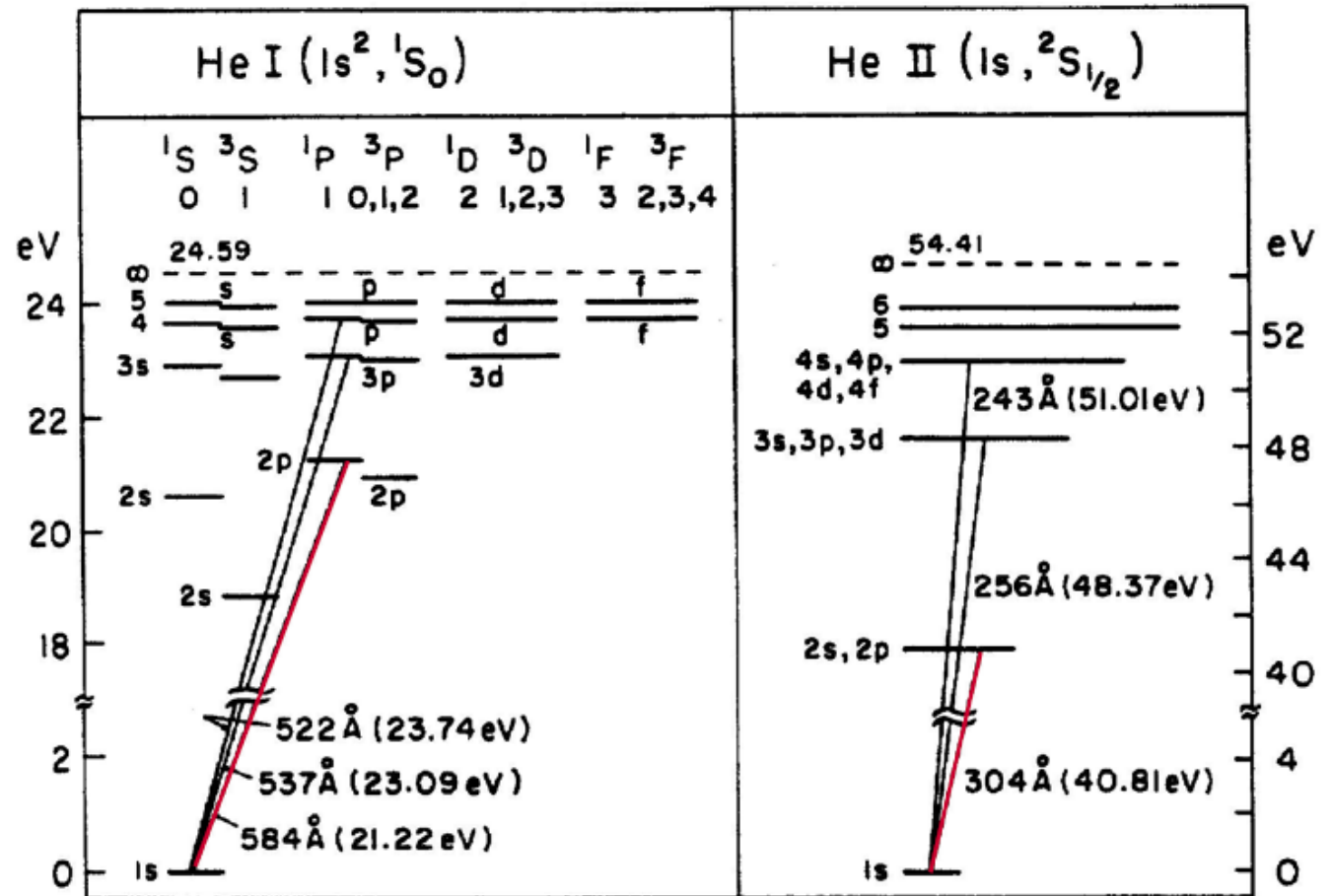
Ne I 16.6eV

Ne II 26.8eV

He I 21.2eV

He II 40.8eV

Synchrotron
radiation



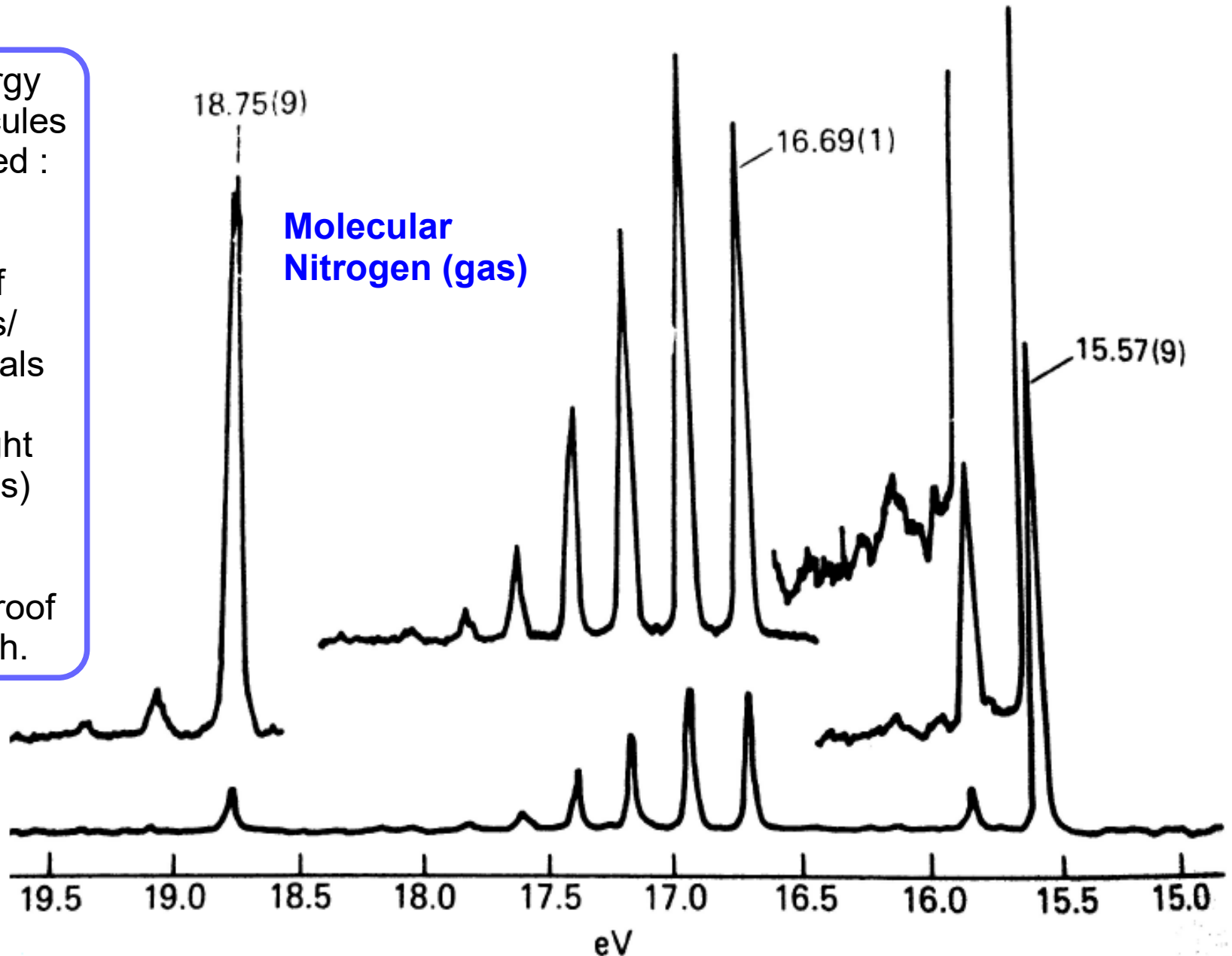
UPS applied to a gas : Electronic levels of molecular N_2

Electronic energy levels of molecules can be predicted :

Linear Combination of Atomic Orbitals/
Molecular orbitals

(similarity to tight binding in solids)

UPS gives the simplest test/proof of this approach.



Band alignment at interfaces using photoemission

We need to understand how the energy levels of two materials in contact evolve/behave. Interfaces are essential in almost any device!

There is a generic class of problems.....

Molecule with metal (Q: How does vacuum level, HOMO-LUMO/Fermi levels align....)
Molecular electronics, organic semiconductor solar cell/devices...

Metal with Semiconductor (The Schottky barrier problem)

Free surface of a semiconductor (Band bending and location of surface states)

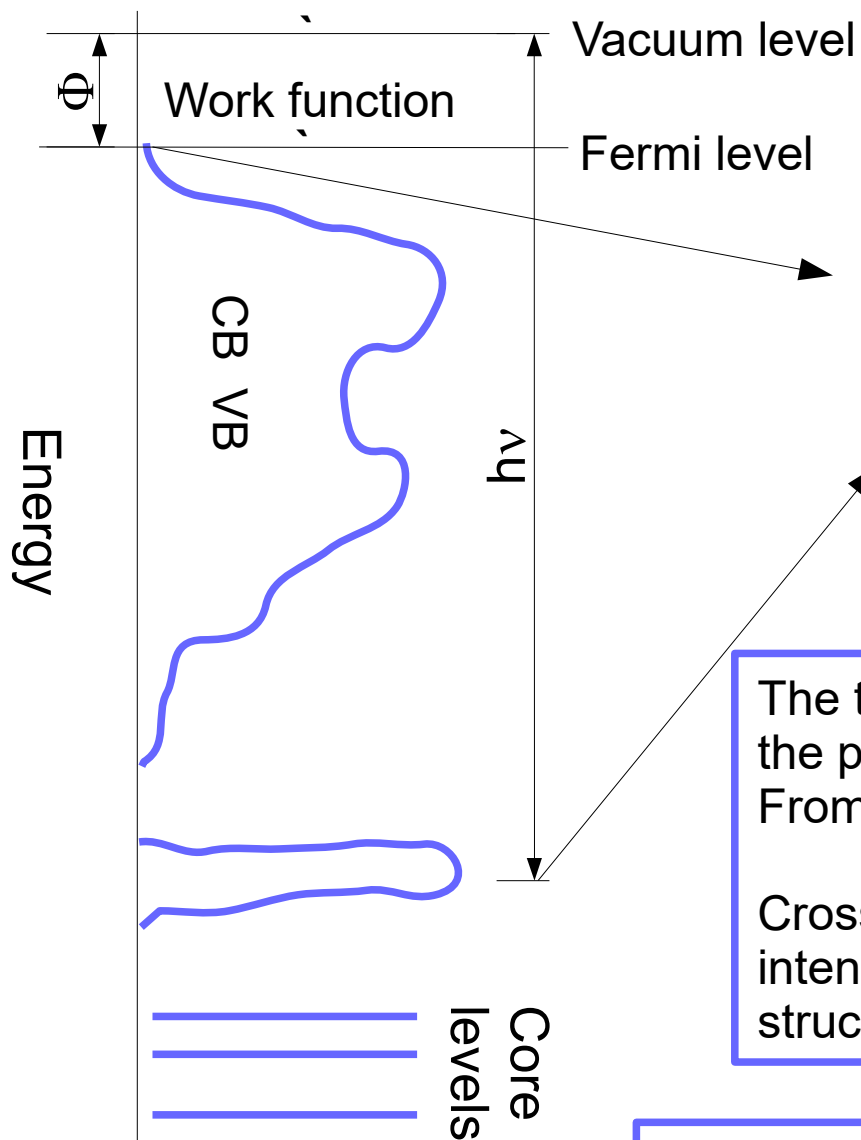
Semiconductor-Semiconductor (The heterointerface, conduction and valence band offsets)

We need to understand the behaviour of the energy levels in the $\sim 1-10$ nm region near the surface and within $\sim 1-10$ eV typically.

No single technique is sufficient to answer all the questions....
But Photoemission (UPS) is one of the useful probes.

**This is NOT a fingerprinting type spectroscopy problem....
cannot match features to known spectral lines etc..**

Determining the work function Φ



Photons with $E = h\nu$ incident on the surface
A typical $E = 21.2$ eV

Electrons coming from here should have
 $KE = h\nu - \Phi$

Electrons coming from here should have
 $KE = 0$

**How would something with $KE \rightarrow 0$
reach the detector? Ans: Small bias**

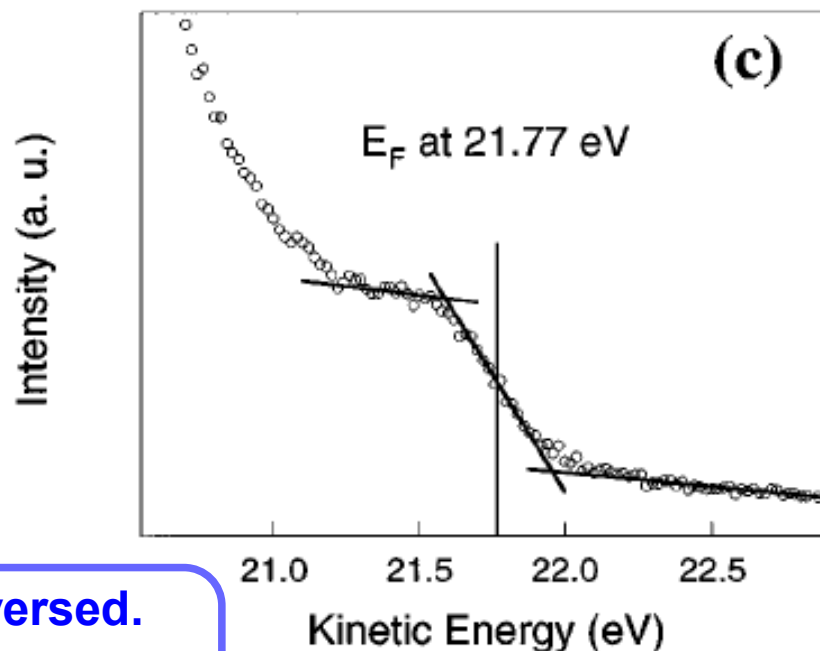
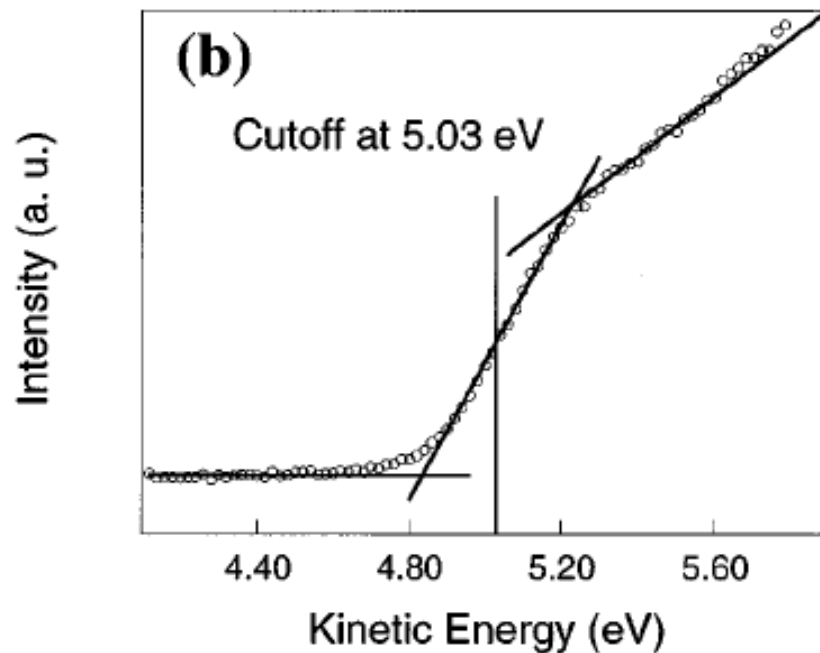
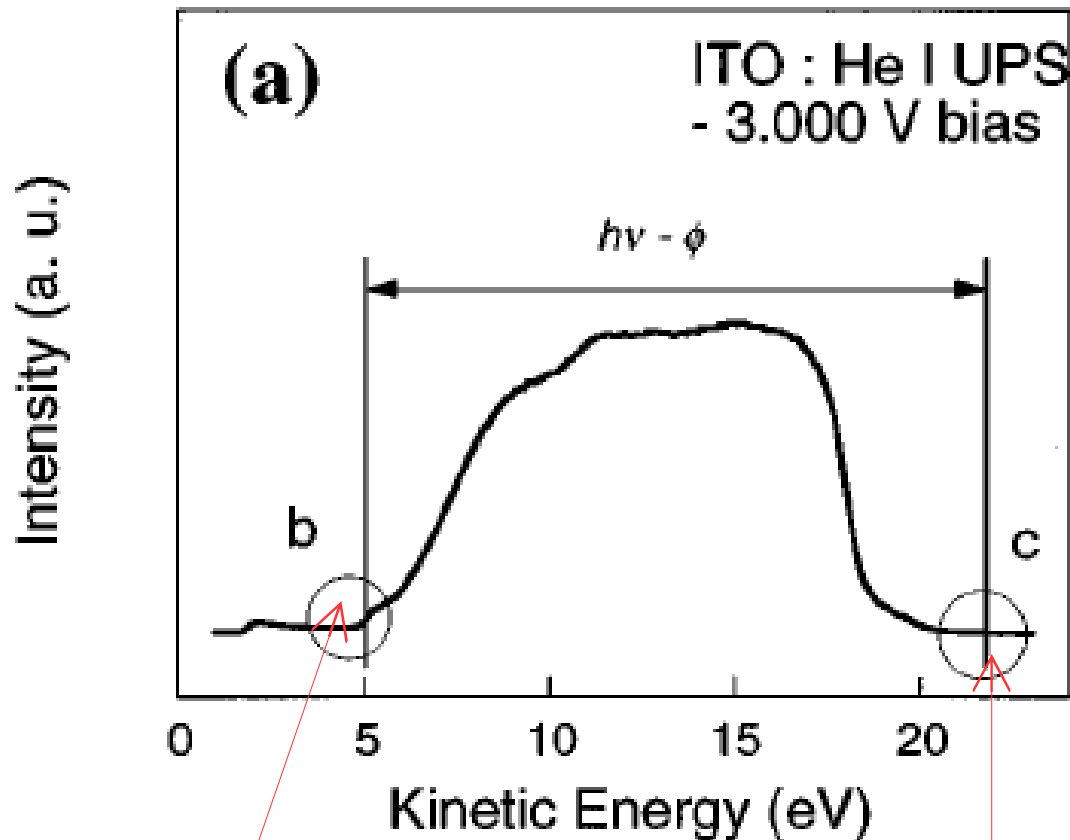
The total spread of the KE is Φ less than the energy of the photon.
From this determine the work function.

Cross sections for typical s,p,d bands are not same, so intensity depends on incident photon energy, band structure details of the material.

UPS will only see occupied states

The measured work function is sensitive to surface conditions, which crystal facet the electron is coming out from, etc.
 ~ 1 - 2 eV spread is possible due to these.

Determining the work function Φ : An example



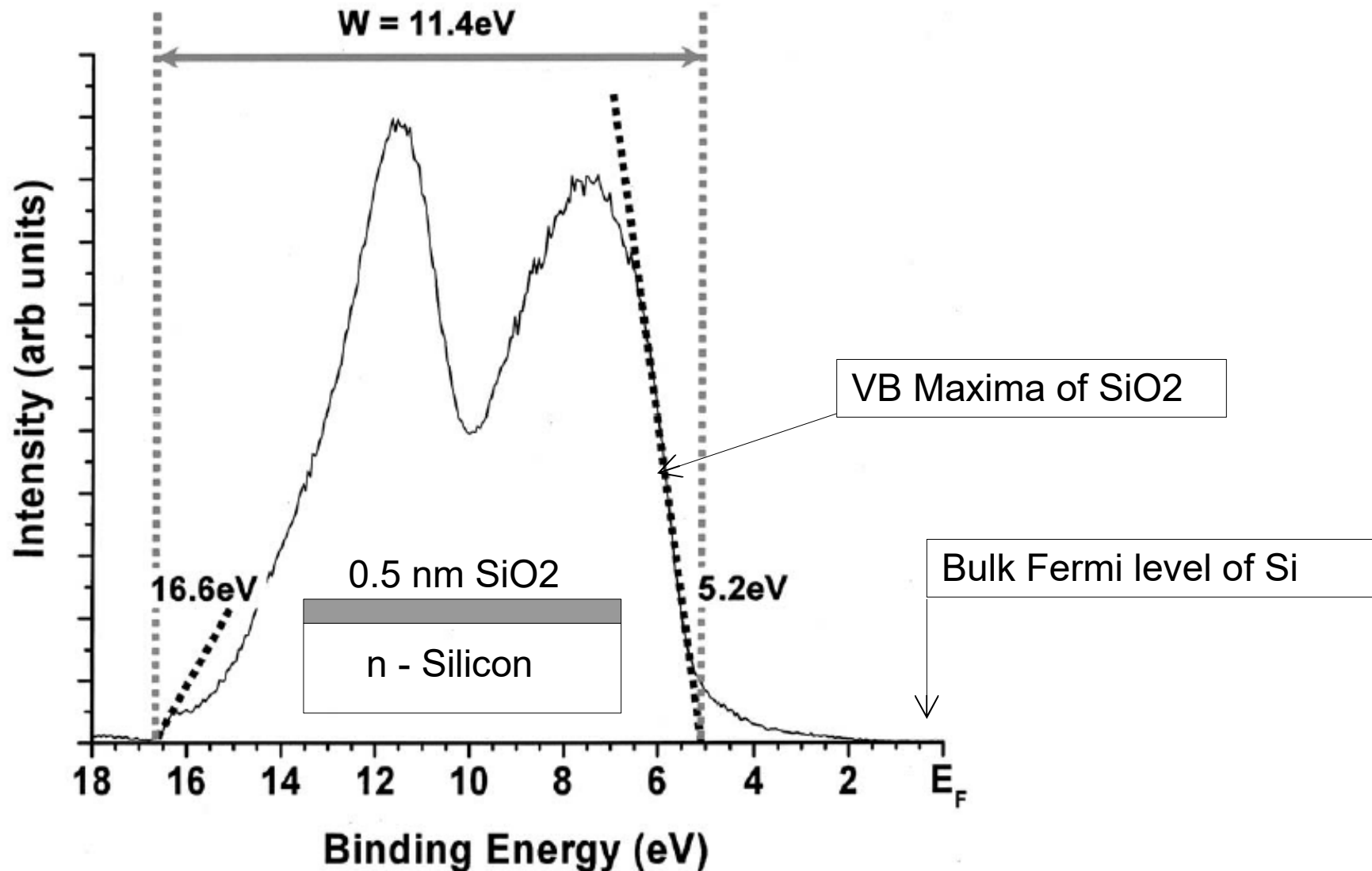
Indium Tin Oxide: commonly used transparent electrode.
Y Park et al. *Applied Physics Letters* **68**, 2699 (1996)

Emission edge.
The deepest electrons
Least sensitive to
temperature etc.

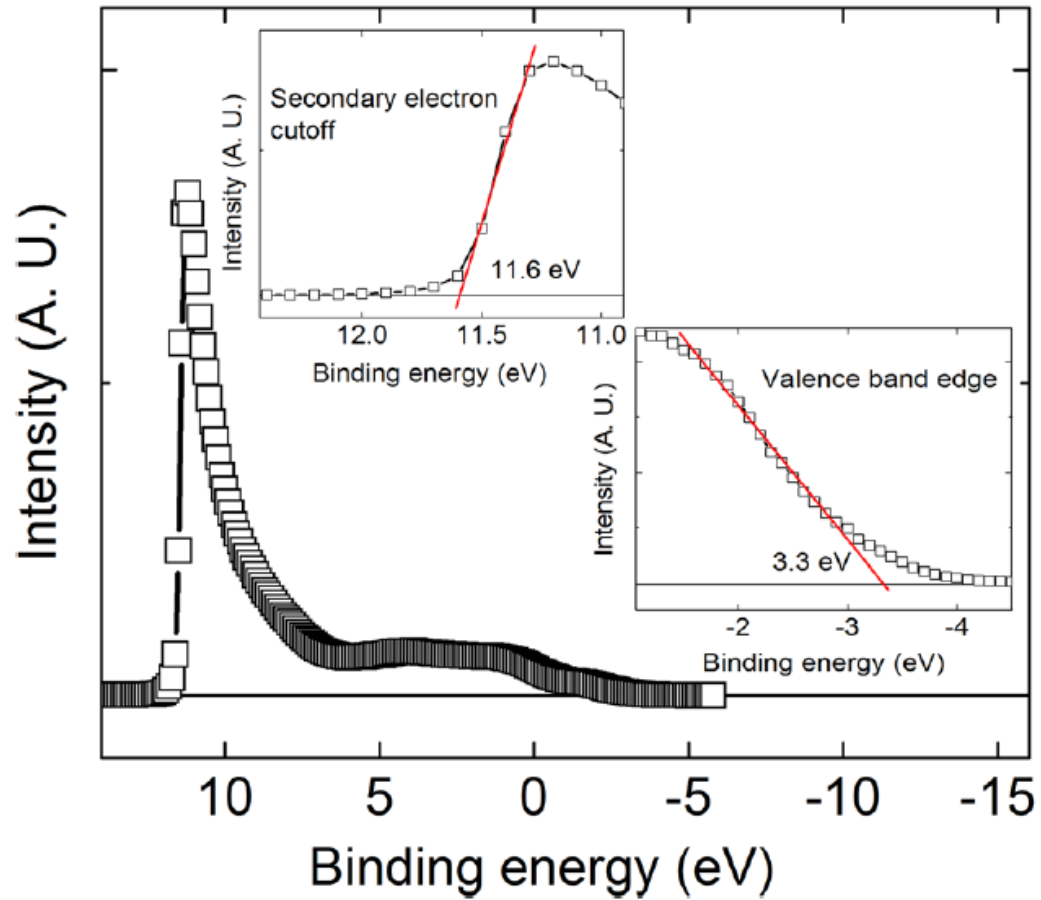
Fermi level
More sensitive to
temperature.

**If plotted against Binding Energy, the plot will be reversed.
Larger KE \rightarrow Smaller BE**

Band alignment at an interface : An example



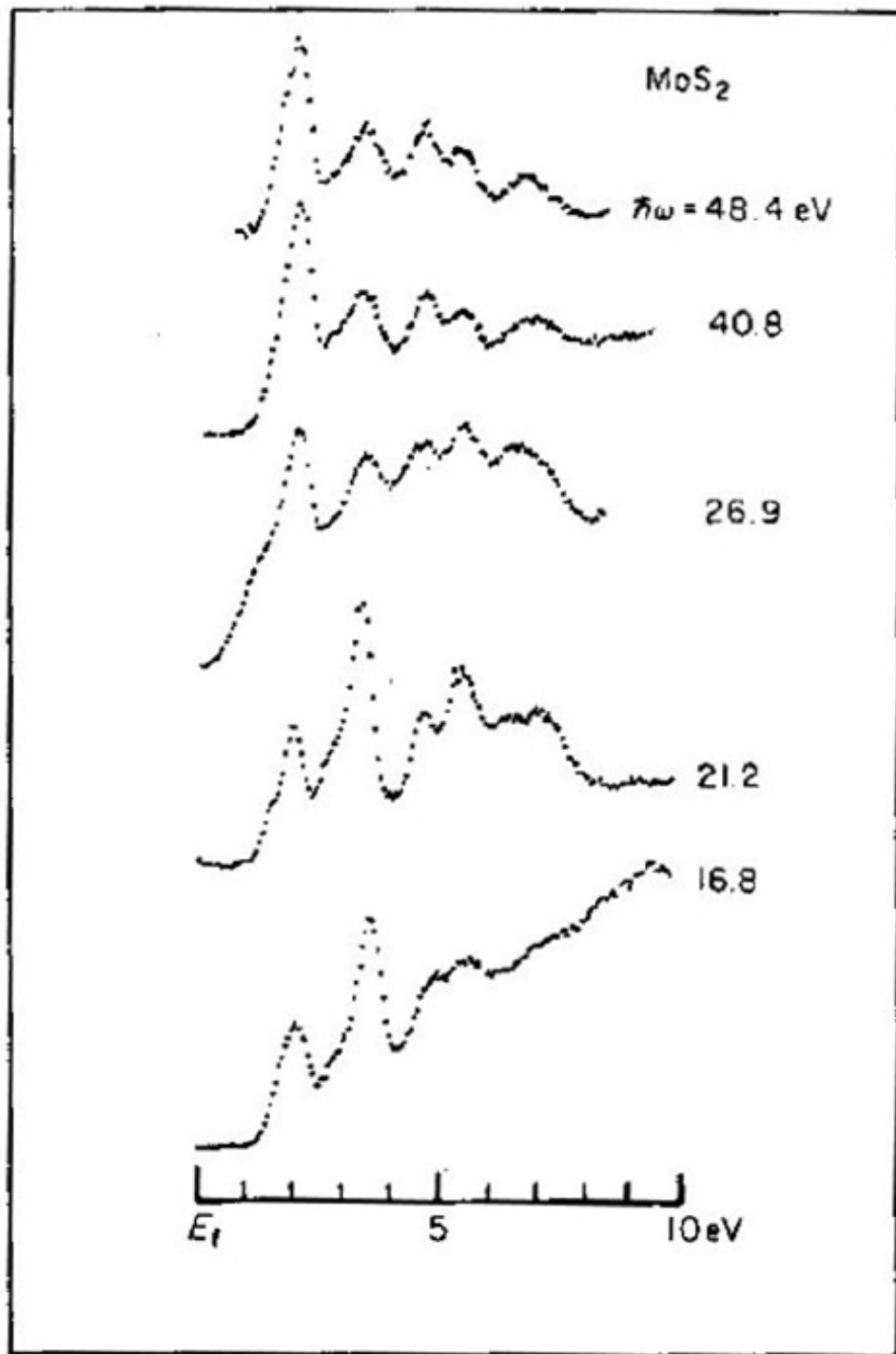
Data: C. G. Fulton et al, *Journal of Applied Physics*, **99**, 063708 (2006)



BiFeO₃ : UPS data

Wei Ji, *Applied Physics Letters*, **103**, 062901 (2013)

UPS at different incident photon energies: An example



UPS spectra of MoS₂ measured with different incident photon energies.

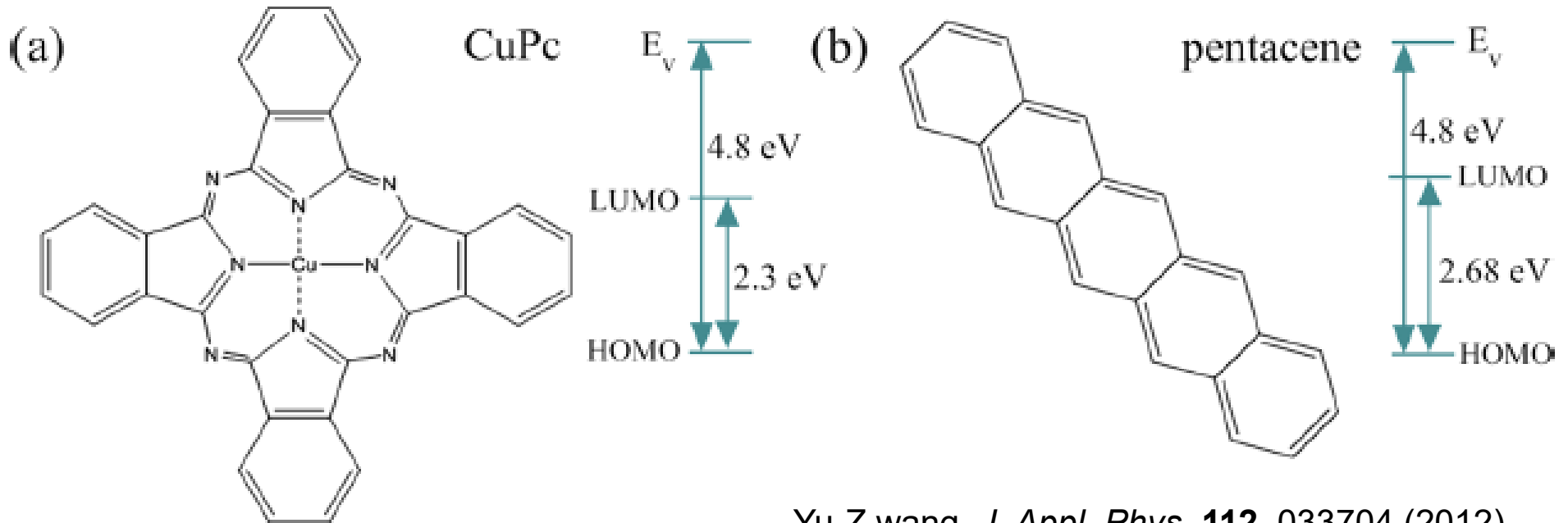
Notice the large qualitative difference.

<http://www.wsu.edu/~scuderio>

Semiconductor analogy of molecules

In molecules : Valence band maxima → HOMO (Highest Occupied Molecular Orbital)
Conduction band minima → LUMO (Lowest Unoccupied Molecular Orbital)

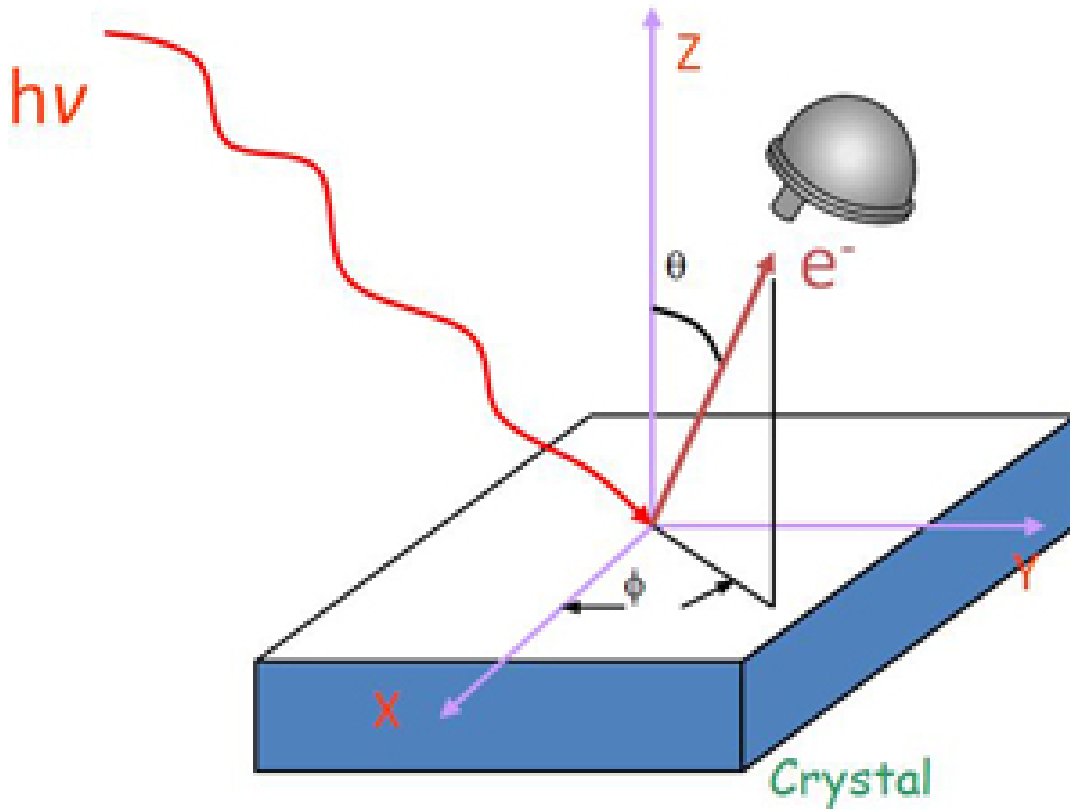
Work function → HOMO to Vacuum level



Yu-Z wang, *J. Appl. Phys.* **112**, 033704 (2012)

The typical energy values indicate that UPS can be useful.....
What would one expect to see ?

Angle Resolved Photoelectron Emission Spectroscopy (ARPES)



It is a probe of the band structure.

Experimentally one measures:

Energy of the emitted electron &
Angle of emission of the electron.

The problem is to infer the $E(k)$ relation
from this data.

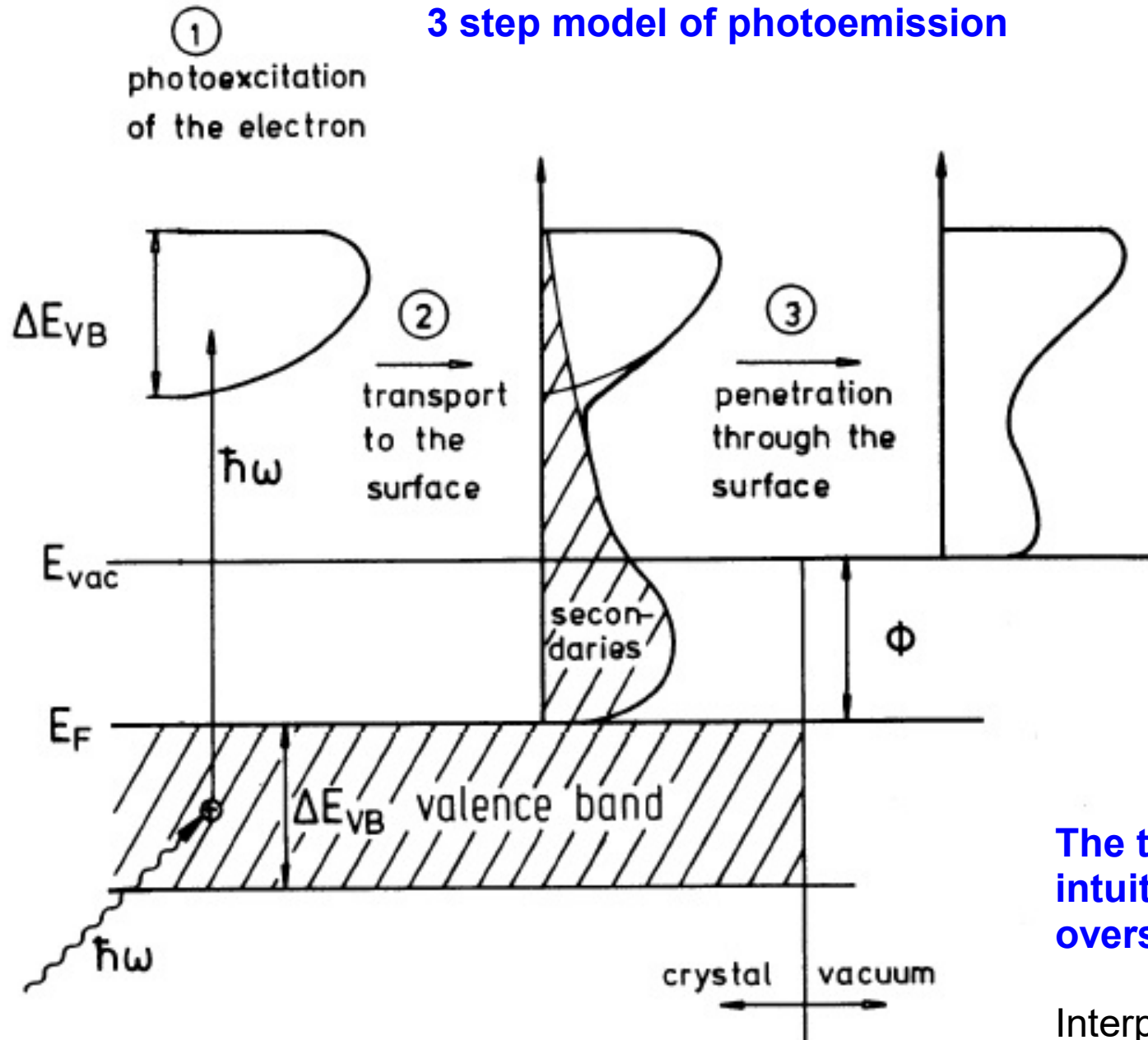
The UV-photon energy is $\sim 20-100$ eV.
So the k-vector of the photon is still
much smaller compared to the Brillouin
zone dimensions. So transitions are
almost vertical.

Modelling this process is not as simple as photoelectric effect. Why?

To be quantitatively correct one needs to model the Bloch eigenstate wavefunction, propagation of the generated electron to the surface, the emission process including the effect of short lived gap states + surface states.

Angle Resolved Photoelectron Emission Spectroscopy (ARPES)

3 step model of photoemission



Photon of 100 eV will have a wavevector of $\sim 1\%$ of the Brillouin zone size.

The three step model is intuitive, but has certain oversimplifications.

Interpretation of ARPES data is more complex.....

ARPES : Using the nearly free electron model for the transitions

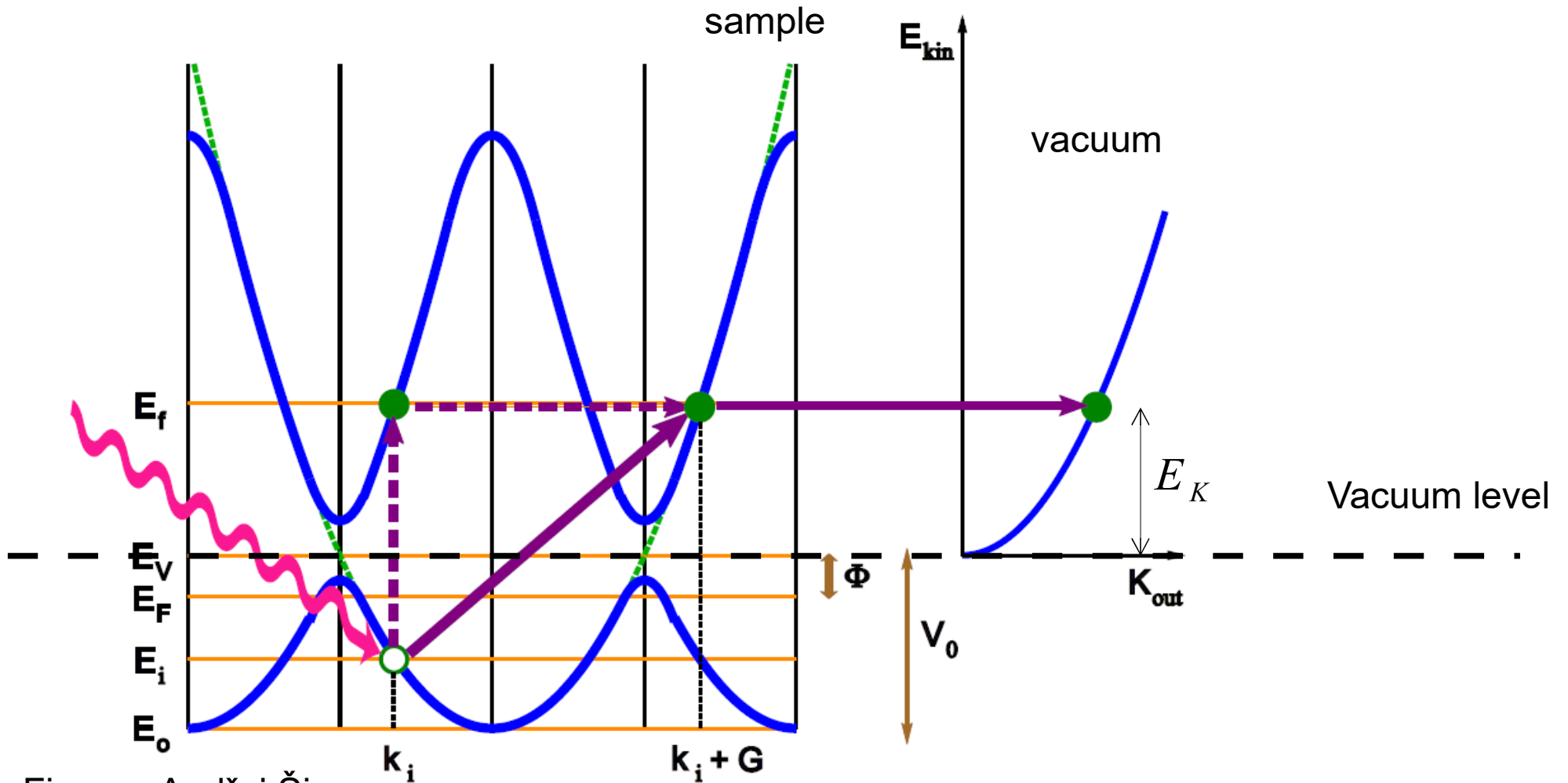


Figure : Andrej Šipr

Notice the use of the repeated zone scheme to draw the NEARLY FREE ELECTRON parabolas...

$$E_f - E_0 = E_K + \Phi + (E_i - E_0)$$

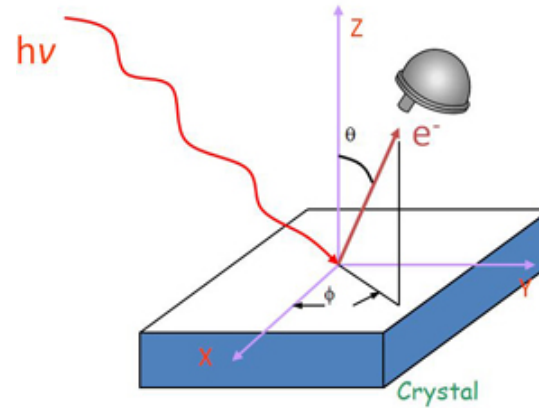
$$E_f - E_0 = \frac{\hbar^2}{2m^*} \left[(k_{\parallel} + G_{\parallel})^2 + (k_{\perp} + G_{\perp})^2 \right]$$

Parallel and perpendicular w.r.t. sample surface.

Transition matrix elements between Bloch states will have the additional G vector. Why ?

ARPES : Using the nearly free electron model for the transitions

$$\left. \begin{aligned} K_x &= \frac{1}{\hbar} \sqrt{2mE_K} \sin\theta \cos\phi \\ K_y &= \frac{1}{\hbar} \sqrt{2mE_K} \sin\theta \sin\phi \\ K_z &= \frac{1}{\hbar} \sqrt{2mE_K} \cos\theta \end{aligned} \right\} \begin{array}{l} K_{\parallel} \\ \\ K_{\perp} \end{array}$$



$E_K, K_{\parallel}, K_{\perp}$
are measured

As the electron emerges from the solid the K_{\parallel} is conserved as in a barrier penetration problem.

$$E_K = h\nu - \Phi - (E_F - E_i)$$

$$K_{\parallel} = k_{\parallel} + G_{\parallel}$$

$$\therefore k_{\parallel} = \frac{1}{\hbar} \sqrt{2mE_K} \sin\theta - G_{\parallel}$$

$$k_{\perp} = \frac{1}{\hbar} \sqrt{2m \left[E_K \cos^2\theta + (E_V - E_0) \right]} - G_{\perp}$$

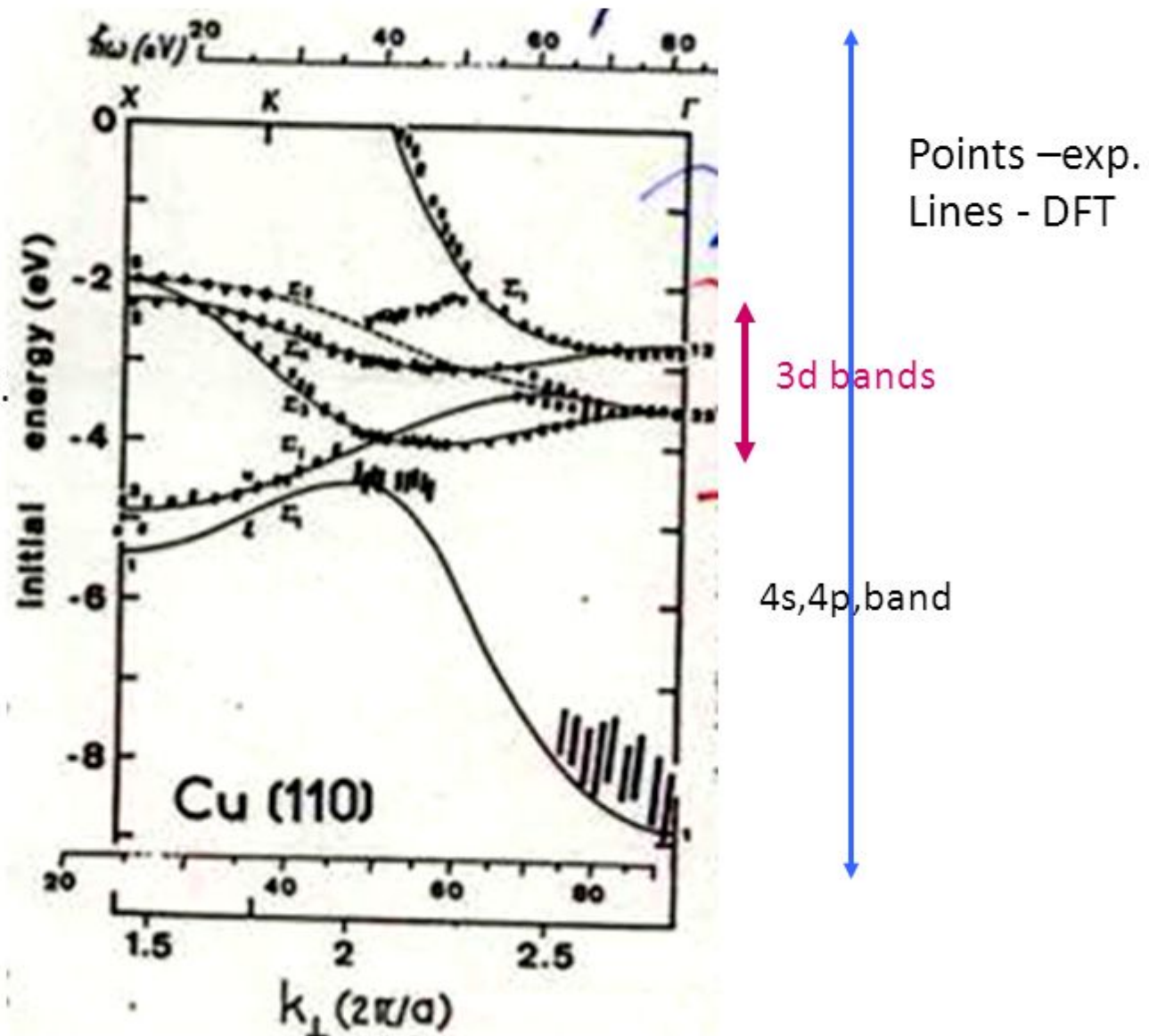
Need to
model / guess

ARPES : What does one see ? Copper

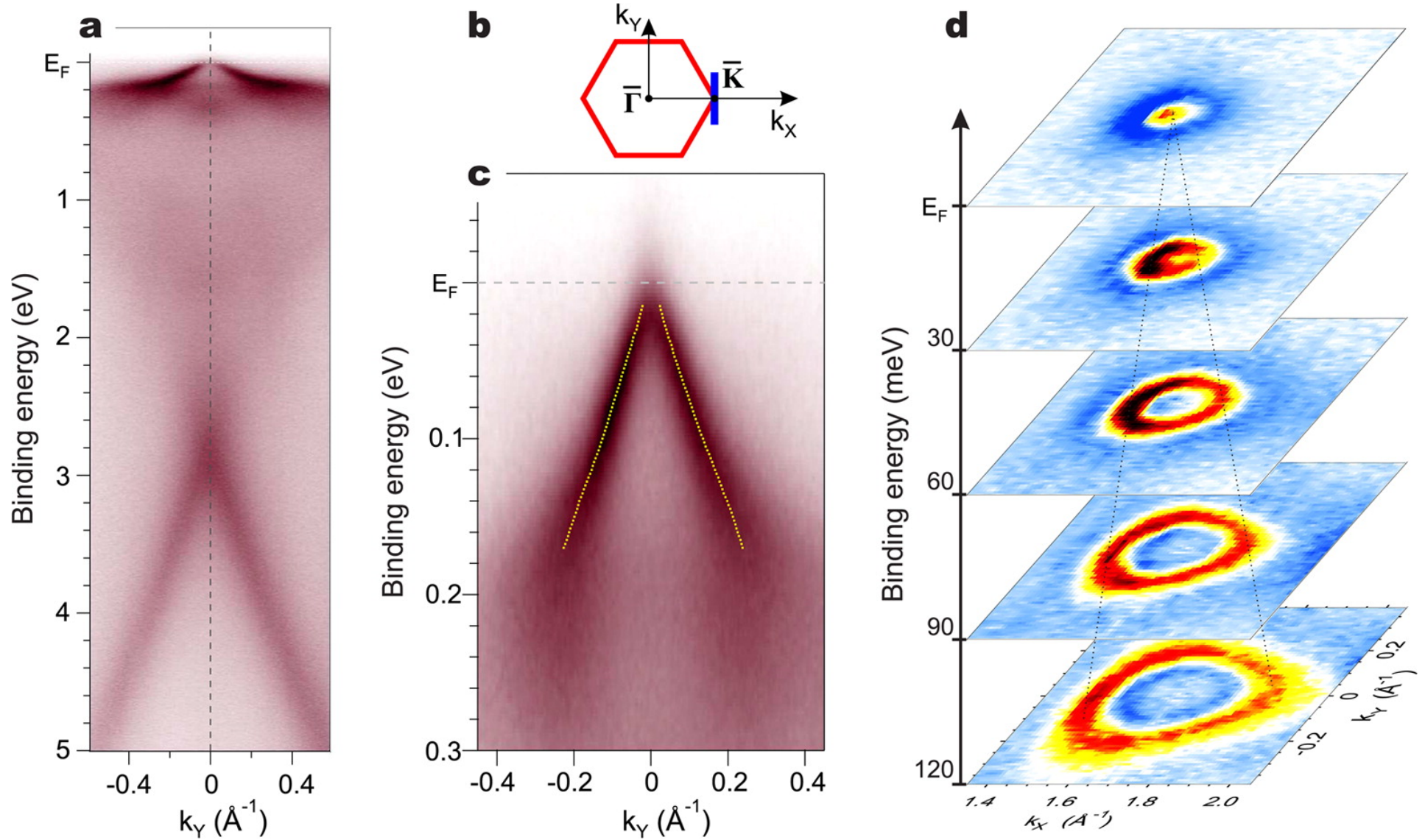
Angular resolved photoelectron spectroscopy (ARPES) of Cu metal
Thiry et al 1979

ARPES Cu

Cu is d10 so one d hole
Has no other d holes to
Correlate with so 1 part.
Theory works FOR N-1
if the only Important
interaction is the d-d
interaction.



ARPES : What does one see ? Graphene

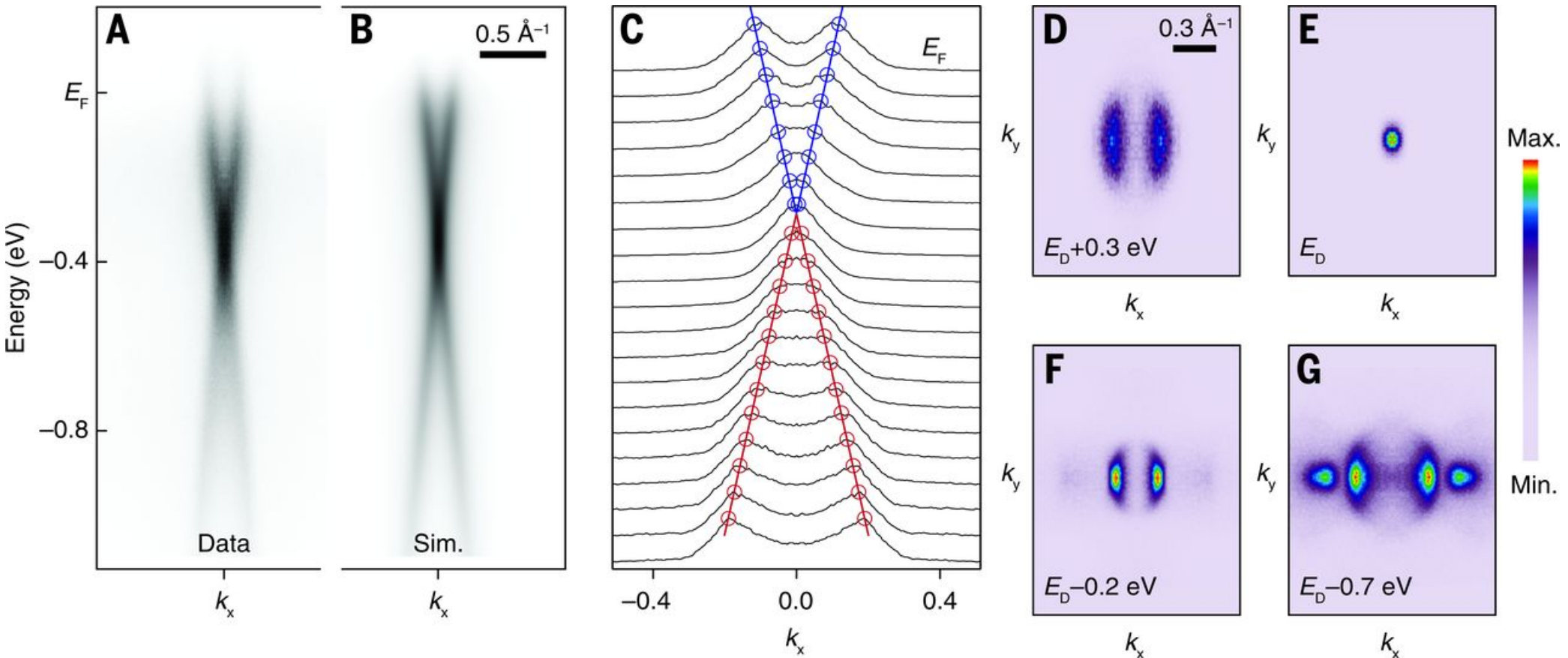


Graphene supported on Cobalt (0001)

D. Usachov et al, *Nano Lett.* **15**, 2396 (2015)

BESSY synchrotron facility, using 40 eV photon

ARPES : What does one see ? Black Phosphorous



Semimetal state of Black Phosphorous:: $T = 15\text{K}$

Jimin Kim et al.

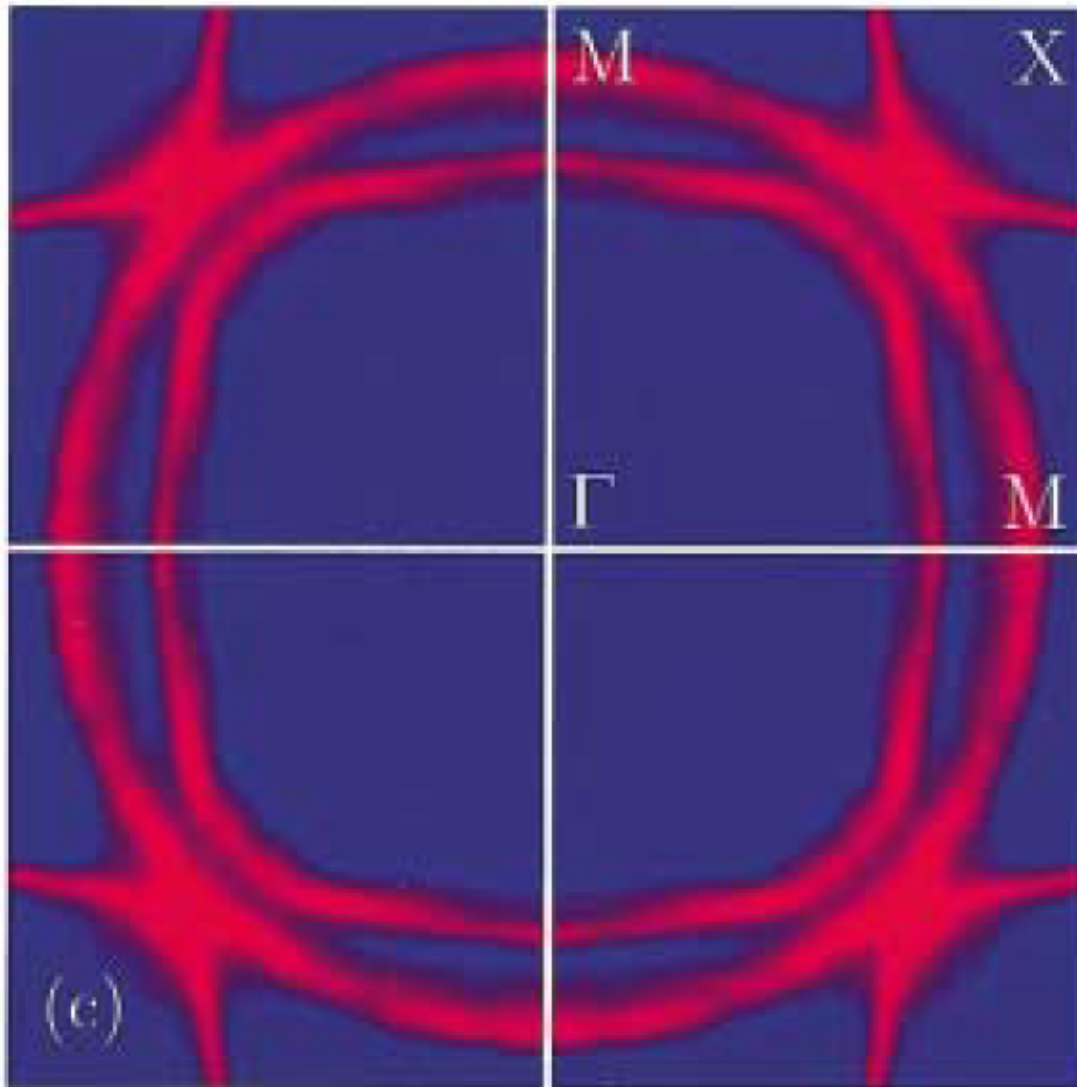
Science 14 Aug 2015:

Vol. 349, Issue 6249, pp. 723-726

Semimetal : Small overlap between Valence and Conduction band

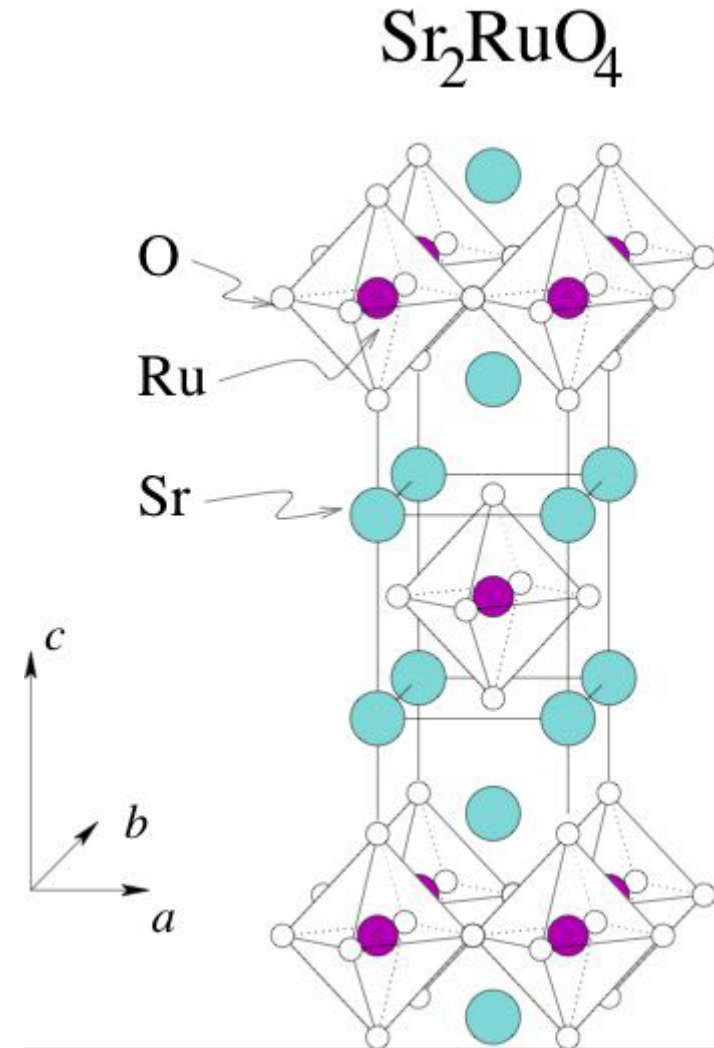
E_D denotes the "Dirac Point"

ARPES : What does one see ? Sr_2RuO_4 (Superconductor)

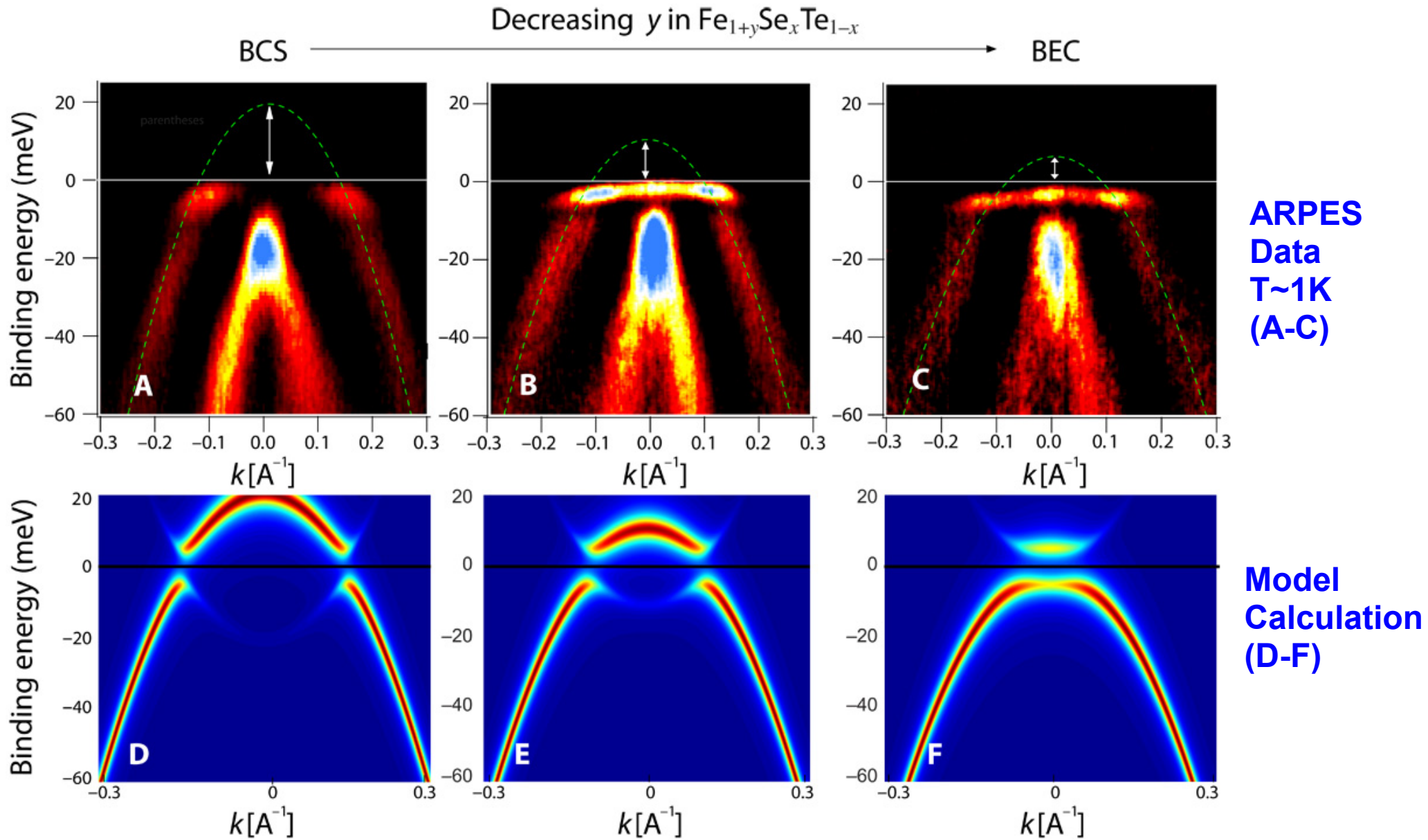


Sr_2RuO_4 cleaved at 180 K

$T = 10 \text{ K}$ $h\nu = 28 \text{ eV}$



ARPES : What does one see ? An Iron containing superconductor



Sahar Rinott et al: Science Advances 21 Apr 2017: Vol. 3, no. 4, e1602372
Note: The data can only show the states below the Fermi level.

ARPES : What we have not discussed.....

What is the correct final state of the electron?

A free particle outside, rapidly decaying inside....

The emitted electron crosses a few atomic layers → diffraction?

It does happen and can be detected as oscillations over the background.

The wavefunction of the $N-1$ electrons must relax. Single particle energy levels cannot be the full story.

Correct, only for non-interacting electrons. What ARPES measures is the "spectral function" of an interacting N -particle system.

Inverse Photoemission spectroscopy : probe the unfilled states

Basic idea: Hit a material with an electron beam. Detect photons which come out.

These are very low energy electrons : less than ~ 20 eV. (Unlike electron microscopes!)

EITHER :

Vary the energy of the electron beam & keep detector at fixed frequency.

Called Bremsstrahlung Isochromat Spectroscopy (BIS)

UV detector with a bandpass $\sim 10 \pm 0.5$ eV is common.

OR

Keep electron beam energy fixed. Detect emitted photons at all frequencies.

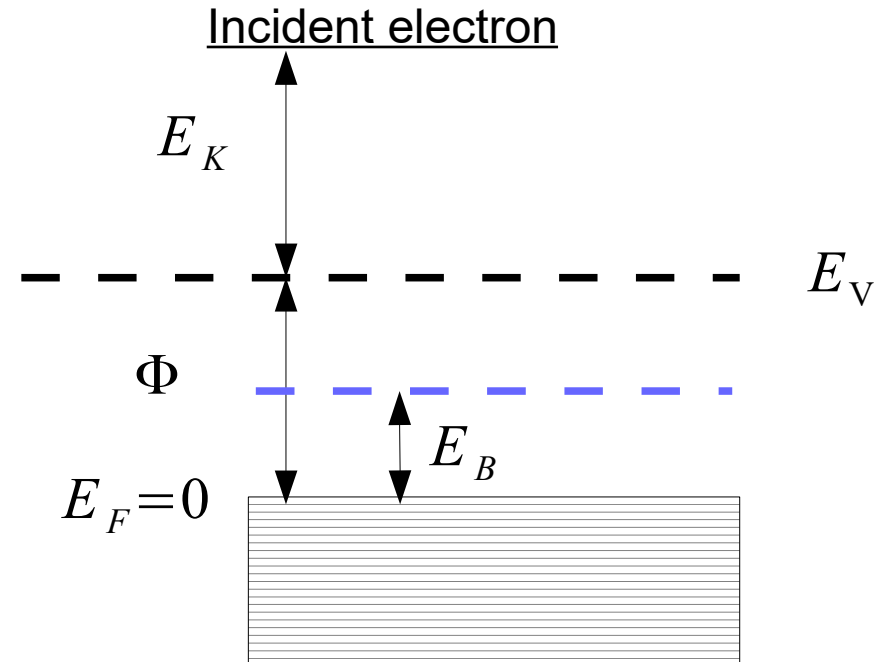
Inverse Photoemission Spectroscopy. (IPES)

Photoemission is not the only energy loss process for the electrons. The process has a small probability. Photon counts in IPES is low (~ 100 cts/sec/Sr).

The angle-resolved version is called K-resolved IPES (KRIPES)

Inverse Photoemission spectroscopy :What is it useful for

$$E_K + \Phi = \hbar \omega + E_B$$

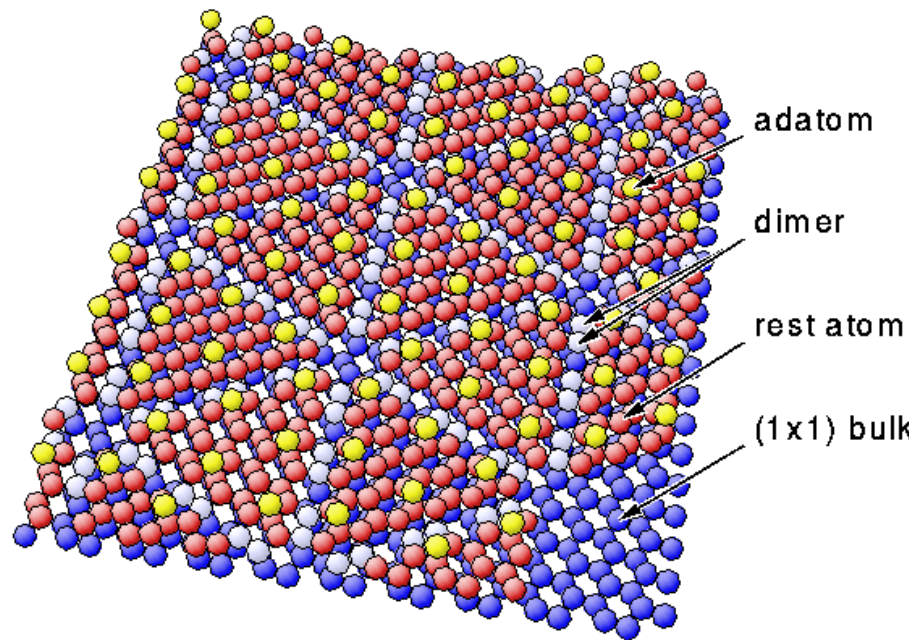


Antibonding states of molecules. (The unfilled Molecular Orbitals)

Surface states of semiconductors (Usually they are in the bandgap region)

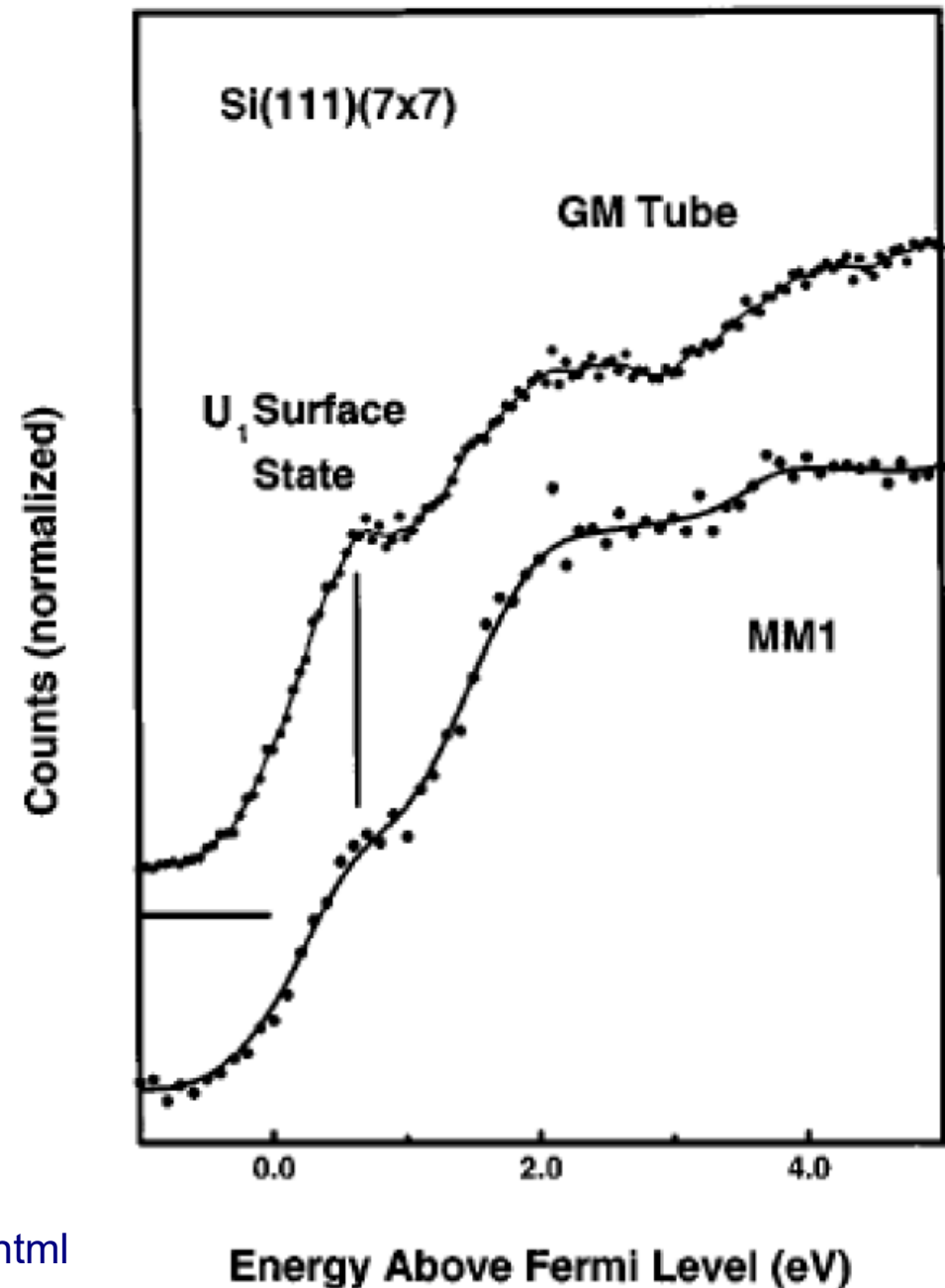
Conduction band states of materials, that are unfilled

Inverse Photoemission spectroscopy : Surface states of Silicon



Si(111)-(7x7) DAS model (Takayanagi/Tong)

BALSAC I



<http://www.fhi-berlin.mpg.de/~hermann/Balsac/pictures.html>

Hill and McLean, Rev Sci Inst, 69, 261, (1998).

3. Magnetic Resonance

What does a small dipole do in a magnetic field ?

Magnetic moment and Angular momentum are related by gyromagnetic ratio.

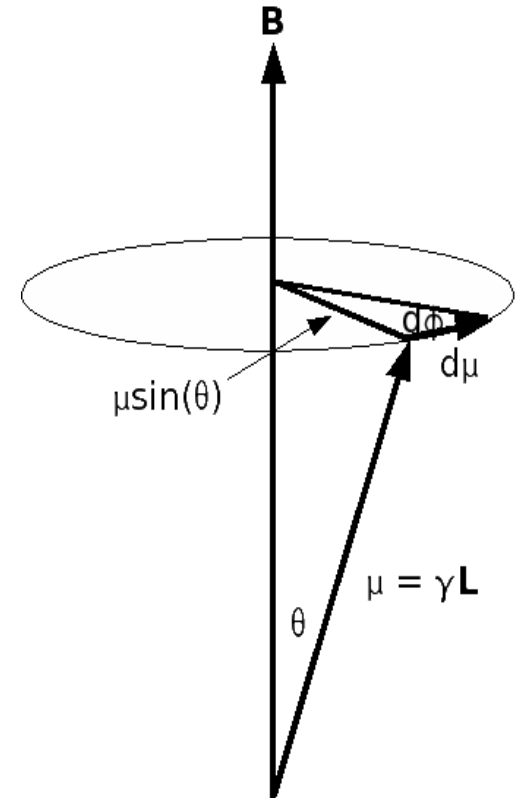
The torque (τ) on a magnetic dipole in a magnetic field is simple to write.

$$\left. \begin{aligned} \vec{\mu} &= \gamma \vec{L} \\ \vec{\tau} &= \vec{\mu} \times \vec{B} \end{aligned} \right\} \Rightarrow \frac{d\vec{\mu}}{dt} = \gamma \vec{\mu} \times \vec{B}$$

Precession about \vec{B} with angular velocity $\omega = \gamma |\vec{B}|$

The angle θ is not restricted.

$$\text{If } \vec{B} = (0, 0, B) \text{ Then } \left\{ \begin{aligned} \frac{d\mu_x}{dt} &= \gamma \mu_y B \\ \frac{d\mu_y}{dt} &= -\gamma \mu_x B \\ \frac{d\mu_z}{dt} &= 0 \end{aligned} \right.$$



What does a small dipole do in a magnetic field ?

Quantum picture requires the time evolution to come from a commutator with the Hamiltonian , not force or torque.

$$\begin{aligned} H &= -\vec{\mu} \cdot \vec{B} & \vec{B} &= (0, 0, B) \\ &= -\gamma S_z B & & \text{The eigenstates are obvious...} \end{aligned}$$

$$[S_i, S_j] = i\hbar \epsilon_{ijk} S_k$$

$$\begin{aligned} \frac{d\mu_x}{dt} &= \frac{i}{\hbar} [H, \mu_x] = i \frac{\gamma B}{\hbar} \gamma [-S_z, S_x] = \gamma B (\gamma S_y) = \gamma B \mu_y \\ \frac{d\mu_y}{dt} &= \frac{i}{\hbar} [H, \mu_y] = i \frac{\gamma B}{\hbar} \gamma [-S_z, S_y] = -\gamma B (\gamma S_x) = -\gamma B \mu_x \\ \frac{d\mu_z}{dt} &= \frac{i}{\hbar} [H, \mu_z] = i \frac{\gamma B}{\hbar} \gamma [-S_z, S_z] = 0 \end{aligned}$$

Take expectation of both the sides.

The same set of equations recovered for the components.

Note that there is no \hbar in the final result.

What can cause transitions between the up & down states ?

To make a spin " flip " we require the raising or lowering operators.

These are linear combinations of S_x and S_y

So the perturbing field must be along x or y direction, with its frequency $\omega = \gamma B$

$$H_1 = -\gamma \hbar B_1 \cos \omega t S_x$$

The two spin 1/2 coupling : energy levels, allowed transitions etc

$$H = \nu_1 S_{1z} + \nu_2 S_{2z} + J \vec{S}_1 \cdot \vec{S}_2$$

$$H_1 = \lambda(t) (\nu_1 S_{1x} + \nu_2 S_{2x})$$

perturbation (H1) is a time varying field in x direction

Using the m1m2 basis to write the hamiltonian matrix

	$ \alpha_1 \alpha_2\rangle$	$ \alpha_1 \beta_2\rangle$	$ \beta_1 \alpha_2\rangle$	$ \beta_1 \beta_2\rangle$
$\langle \alpha_1 \alpha_2 $	$\frac{\nu_1 + \nu_2}{2} + \frac{J}{4}$	0	0	0
$\langle \alpha_1 \beta_2 $	0	$\frac{\nu_1 - \nu_2}{2} - \frac{J}{4}$	$\frac{J}{2}$	0
$\langle \beta_1 \alpha_2 $	0	$\frac{J}{2}$	$\frac{\nu_2 - \nu_1}{2} - \frac{J}{4}$	0
$\langle \beta_1 \beta_2 $	0	0	0	$\frac{-\nu_1 - \nu_2}{2} + \frac{J}{4}$

$H =$

Make use of the block diagonal form and solve....

The two spin 1/2 coupling : energy levels, allowed transitions etc

E

$$\begin{aligned} & \frac{\nu_1 + \nu_2}{2} + \frac{J}{4} \\ & -\frac{J}{4} + \sqrt{\left(\frac{\nu_1 - \nu_2}{2}\right)^2 + \frac{J^2}{4}} \\ & -\frac{J}{4} - \sqrt{\left(\frac{\nu_1 - \nu_2}{2}\right)^2 + \frac{J^2}{4}} \\ & -\frac{\nu_1 + \nu_2}{2} + \frac{J}{4} \end{aligned}$$

define

$$D = \sqrt{\left(\frac{\nu_1 - \nu_2}{2}\right)^2 + \frac{J^2}{4}}$$

$$\tan \phi = \frac{J}{\nu_1 - \nu_2}$$

$|\Psi\rangle$

$$|\Psi_1\rangle = |\alpha_1 \alpha_2\rangle$$

$$|\Psi_2\rangle = \cos \frac{\phi}{2} |\alpha_1 \beta_2\rangle + \sin \frac{\phi}{2} |\beta_1 \alpha_2\rangle$$

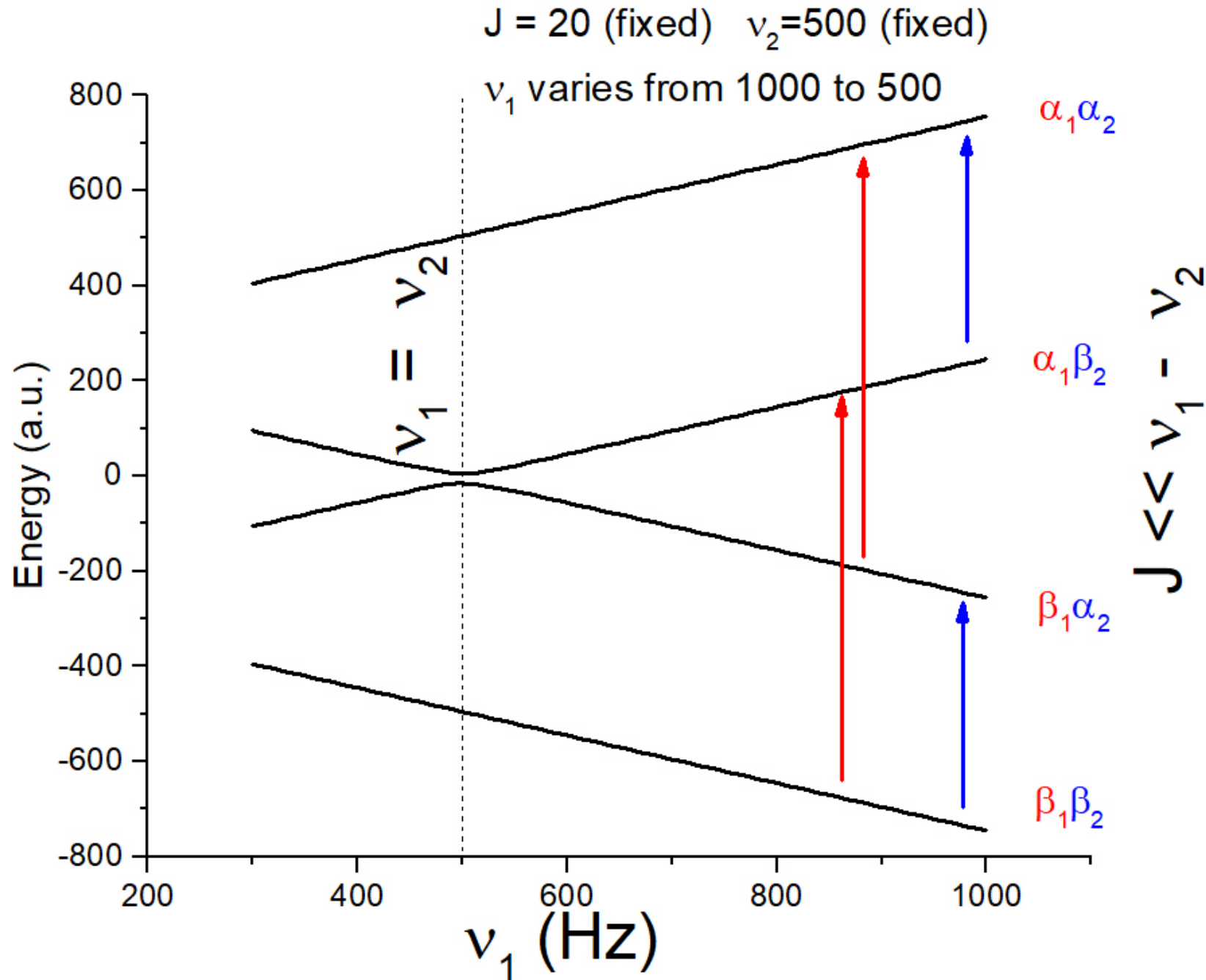
$$|\Psi_3\rangle = \cos \frac{\phi}{2} |\beta_1 \alpha_2\rangle - \sin \frac{\phi}{2} |\alpha_1 \beta_2\rangle$$

$$|\Psi_4\rangle = |\beta_1 \beta_2\rangle$$

when is $\langle \Psi_f | H_1 | \Psi_i \rangle \neq 0$?

what if $\nu_1 \rightarrow \nu_2$

The two spin 1/2 coupling : energy levels, allowed transitions etc



The two spin 1/2 coupling : energy levels, allowed transitions etc

$$\text{If } (\nu_1 - \nu_2) \gg \frac{J}{2}$$

Then

$$E_1 - E_3 = \nu_1 + J/2$$

$$E_2 - E_4 = \nu_1 - J/2$$

$$E_1 - E_2 = \nu_2 + J/2$$

$$E_3 - E_4 = \nu_2 - J/2$$

But if $\nu_1 \approx \nu_2 = \nu$?

Then

$$E_1 - E_3 = \nu + J$$

$$E_2 - E_4 = \nu$$

$$E_1 - E_2 = \nu$$

$$E_3 - E_4 = \nu - J$$

**Each transition splits into two lines.
The splitting is by J units**

**The transitions 1 → 3 & 3 → 4 will
NOT be seen. Why ?**

$$H_1 = \lambda(t) (\nu_1 S_{1x} + \nu_2 S_{2x}) \\ \propto \nu_1 (S_{1+} + S_{1-}) + \nu_2 (S_{2+} + S_{2-})$$

Then calculate

$$\langle \Psi_3 | H_1 | \Psi_1 \rangle \quad \& \quad \langle \Psi_3 | H_1 | \Psi_4 \rangle$$

**The resonance freq ν depends
on the applied magnetic field.**

**J does NOT depend on the field.
Typical magnitude for many
hydrocarbon/organic compound:
J ~ 1-20 Hz**

The two spin 1/2 coupling : energy levels, allowed transitions etc

$$\begin{aligned} & \langle \Psi_3 | H_1 | \Psi_1 \rangle \\ &= \cos \frac{\phi}{2} \langle \beta_1 \alpha_2 | H_1 | \alpha_1 \alpha_2 \rangle - \sin \frac{\phi}{2} \langle \alpha_1 \beta_2 | H_1 | \alpha_1 \alpha_2 \rangle \\ &= \cos \frac{\phi}{2} \langle \beta_1 \alpha_2 | \nu_1 (S_{1+} + S_{1-}) + \nu_2 (S_{2+} + S_{2-}) | \alpha_1 \alpha_2 \rangle \\ &\quad - \sin \frac{\phi}{2} \langle \alpha_1 \beta_2 | \nu_1 (S_{1+} + S_{1-}) + \nu_2 (S_{2+} + S_{2-}) | \alpha_1 \alpha_2 \rangle \\ &= \nu_1 \cos \frac{\phi}{2} - \nu_2 \sin \frac{\phi}{2} \quad \text{As } \nu_1 \rightarrow \nu_2, \phi \rightarrow \frac{\pi}{2} \quad \text{So this will go to zero} \end{aligned}$$

Show that : $\langle \Psi_3 | H_1 | \Psi_4 \rangle \rightarrow 0$ as well

This implies that when the two spins (e.g. protons) become equivalent no signal splitting will show up, even though the coupling exists.

Equivalent nuclei do not split each other's signal

Only one transition will be seen (e.g in CH₃-CH₃, even though 6 protons are there)

This is one of the key factors for interpreting NMR spectra of molecules

The chemical shift and Hydrogen (proton) NMR

Bare proton will resonate at $\nu = \left(\frac{\gamma}{2\pi}\right)B : 42.577 \text{ MHz.Tesla}^{-1}$

In a chemical compound different hydrogen nuclei see slightly (few ppm) different field than what is applied from outside.

This is due to a small screening/enhancement of the applied field by the surrounding electron clouds in the chemical bonds. This small shift is called the chemical shift.

Usually magnetic resonance is measured by keeping the frequency fixed and slowly sweeping the magnetic field. A huge range 60 - 900 Mhz is available.

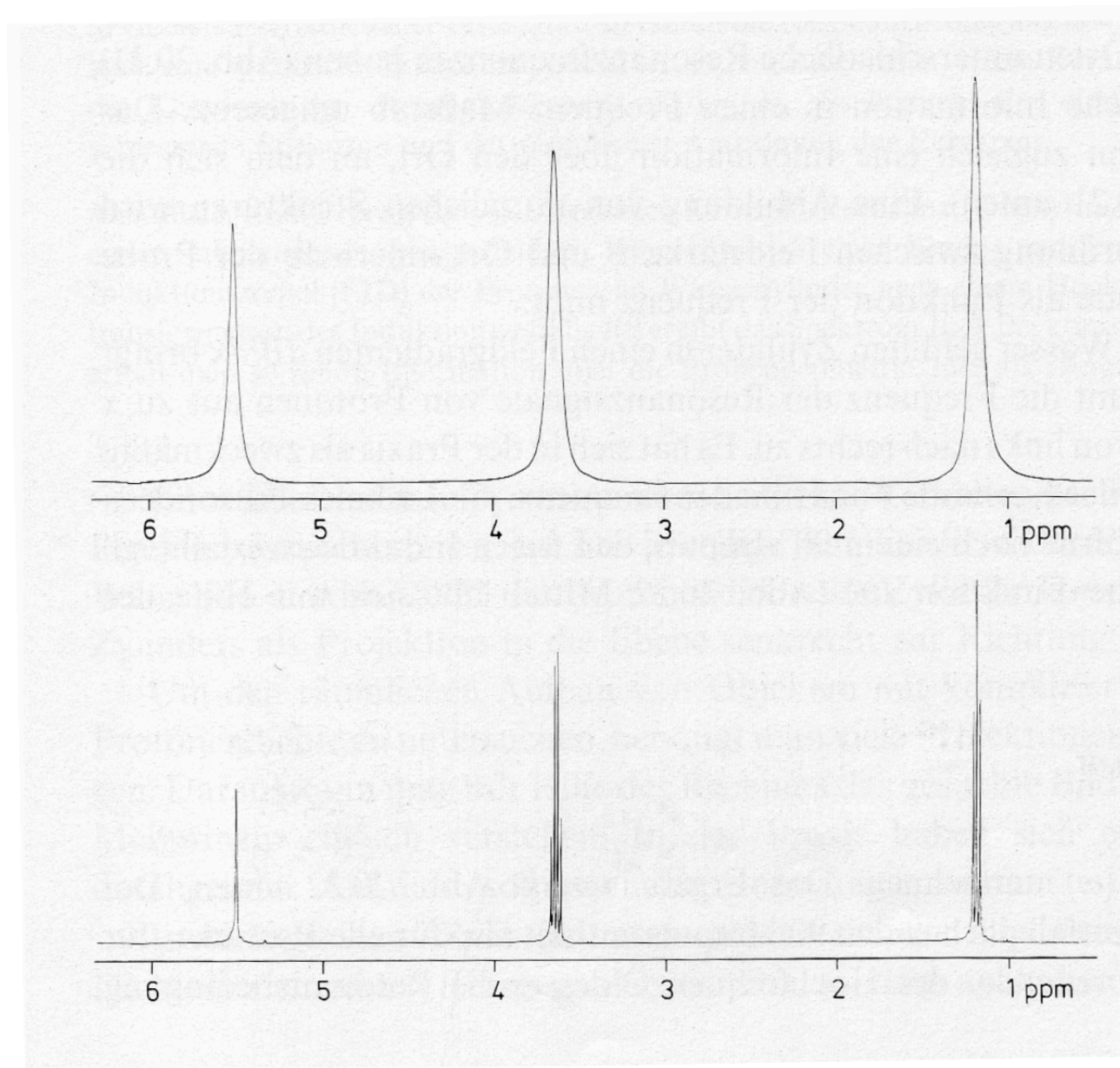
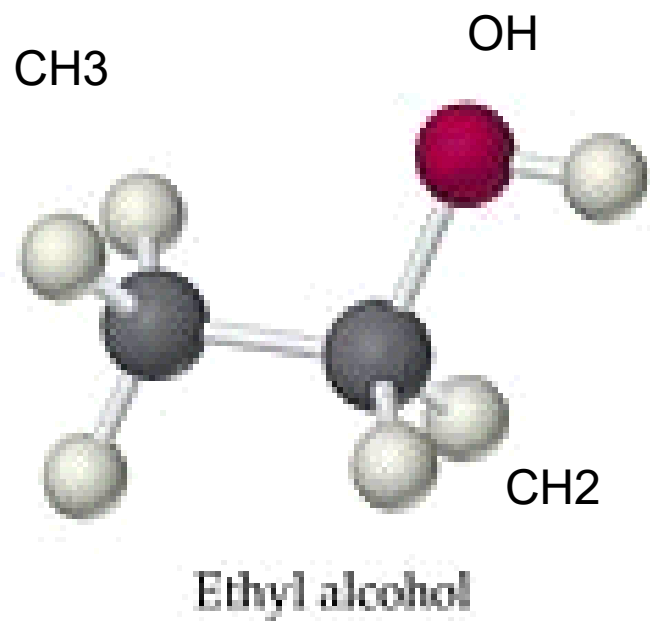
Higher this frequency, better will be the resolution of the measurement.

The difference is expressed with respect to a standard Tetra-methyl Silane $(\text{CH}_3)_4\text{Si}$ rather than a bare proton – this is operationally more practical.

First convert $\Delta B \rightarrow \Delta \nu$ Then $\delta = \frac{\Delta \nu \times 10^6}{\text{operating frequency}}$

δ is called the chemical shift of a particular hydrogen

The chemical shift and Hydrogen (proton) NMR : $C H_3 C H_2 O H$



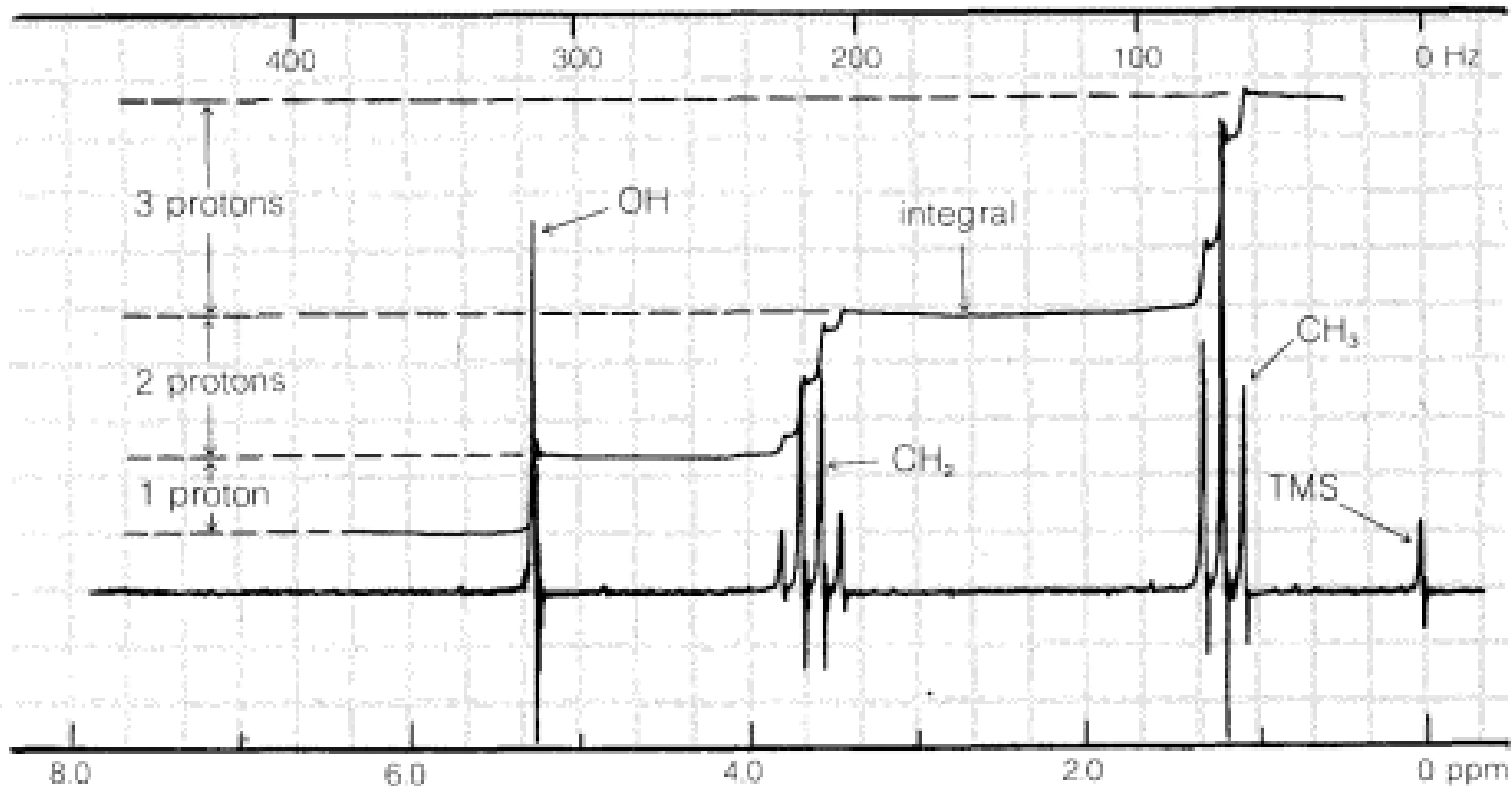
Three types of protons.

Three resonances

Yu & Proctor (1950)

But there is more....

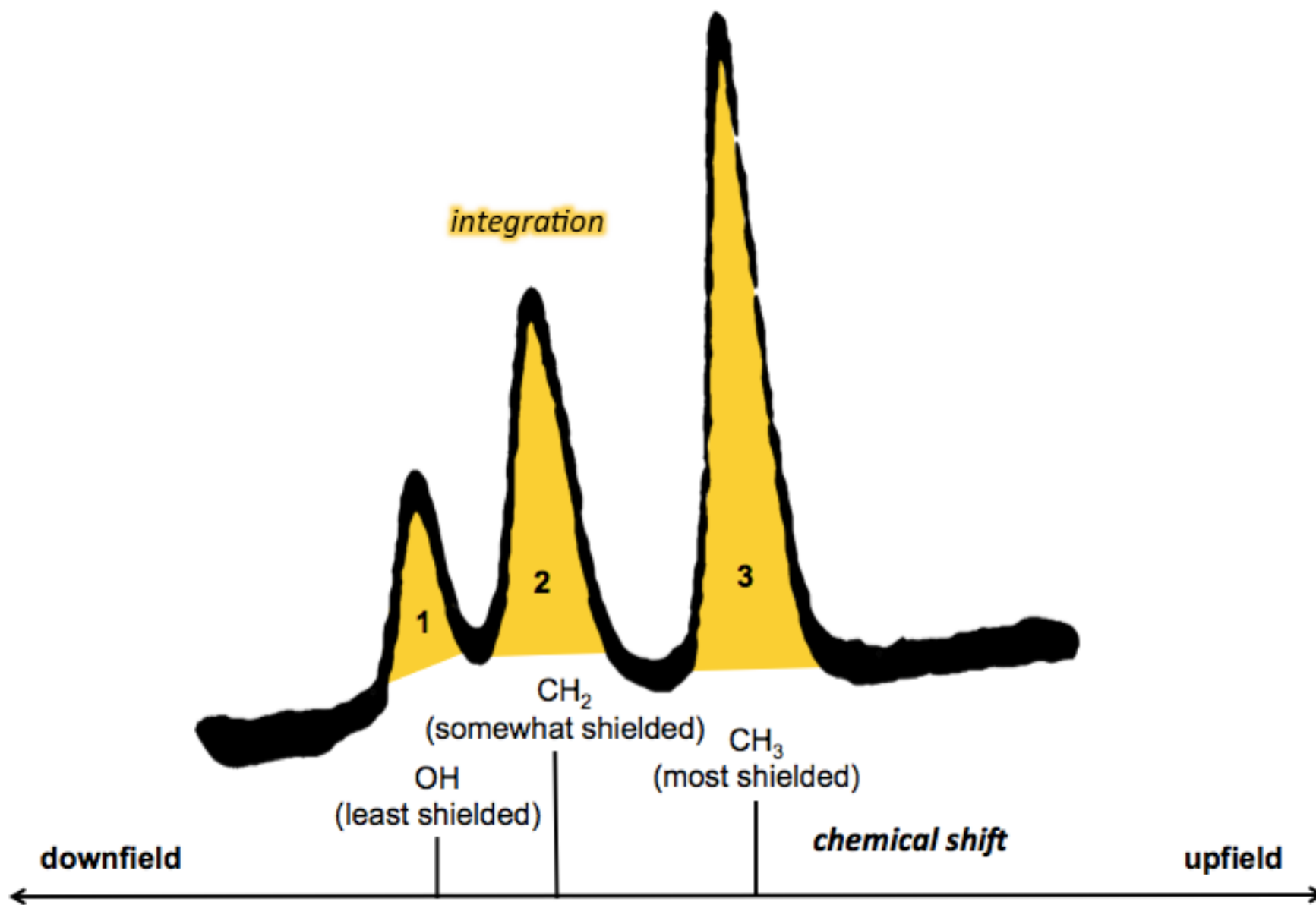
$C H_3 C H_2 O H$ Fine structure and peak area ratios



The fine structure & the peak area ratio....

chem.libretexts.org
Basic Principles of Organic Chemistry
(Roberts and Caserio)

$C H_3 C H_2 O H$ Fine structure and peak area ratios



Typical chemical shifts of various functional groups

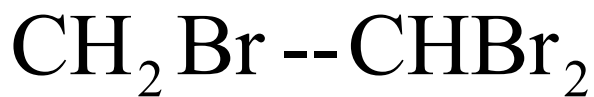
CHARACTERISTIC PROTON CHEMICAL SHIFTS		
Type of proton		Chemical shift δ ppm
Cyclopropane		0.2
Primary	$\begin{array}{c} \text{H} \\ \\ \text{RC}-\text{H} \\ \\ \text{H} \end{array}$	0.9
Secondary	$\begin{array}{c} \text{H} \\ \\ \text{R}_2\text{C}-\text{H} \end{array}$	1.3
Tertiary	$\text{R}_3\text{C}-\text{H}$	1.5
Vinylc	$\text{C}=\text{C}-\text{H}$	4.6-5.9
Acetylenic	$\text{C}\equiv\text{C}-\text{H}$	2-3
Aromatic	$\text{Ar}-\text{H}$	6-8.5
Benzylic	$\text{Ar}-\text{C}-\text{H}$	2.2-3
Allylic	$\text{C}=\text{C}-\text{C}-\text{H}$	1.7
Fluorides	$\text{H}-\text{C}-\text{F}$	4-4.5
Chlorides	$\text{H}-\text{C}-\text{Cl}$	3-4
Bromides	$\text{H}-\text{C}-\text{Br}$	2.5-4
Iodides	$\text{H}-\text{C}-\text{I}$	2-4
Alcohols	$\text{H}-\text{C}-\text{OH}$	3.4-4
Ethers	$\text{H}-\text{C}-\text{OR}$	3.3-4
Esters	$\text{RCOO}-\text{C}-\text{H}$	3.7-4.1
Esters	$\text{H}-\text{C}-\text{COOR}$	2-2.2
Acids	$\text{H}-\text{C}-\text{COOH}$	2-2.6
Carbonyl compounds	$\text{H}-\text{C}-\text{C}=\text{O}$	2-2.7

CHARACTERISTIC PROTON CHEMICAL SHIFTS		
Type of proton		Chemical shift δ , ppm
Aldehydic	$\begin{array}{c} \text{H} \\ \\ \text{RC}=\text{O} \end{array}$	9-10
Hydroxylic	$\text{RO}-\text{H}$	1-5.5
Phenolic	$\text{ArO}-\text{H}$	4-12
Enolic	$\text{C}=\text{C}-\text{O}-\text{H}$	15-17
Carboxylic	$\text{RCOO}-\text{H}$	10.5-12
Amino	$\begin{array}{c} \text{H} \\ \\ \text{RN}-\text{H} \end{array}$	1-5

The shifts are measured with respect to the resonance location of the hydrogens in $(\text{CH}_3)_4\text{Si}$: Tetra-methyl Silane

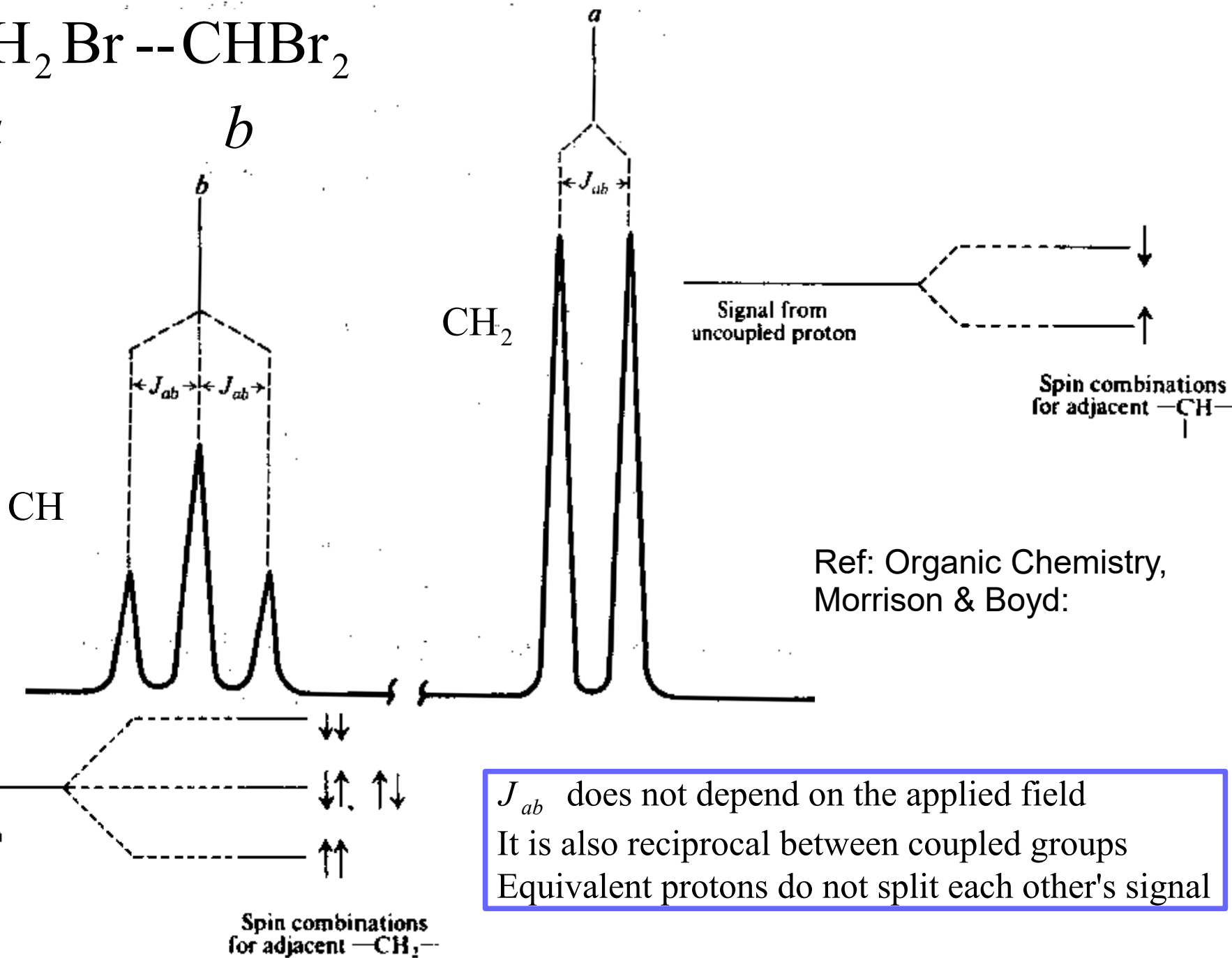
Ref: Organic Chemistry,
Morrison & Boyd:

Typical pattern of peak splitting



a

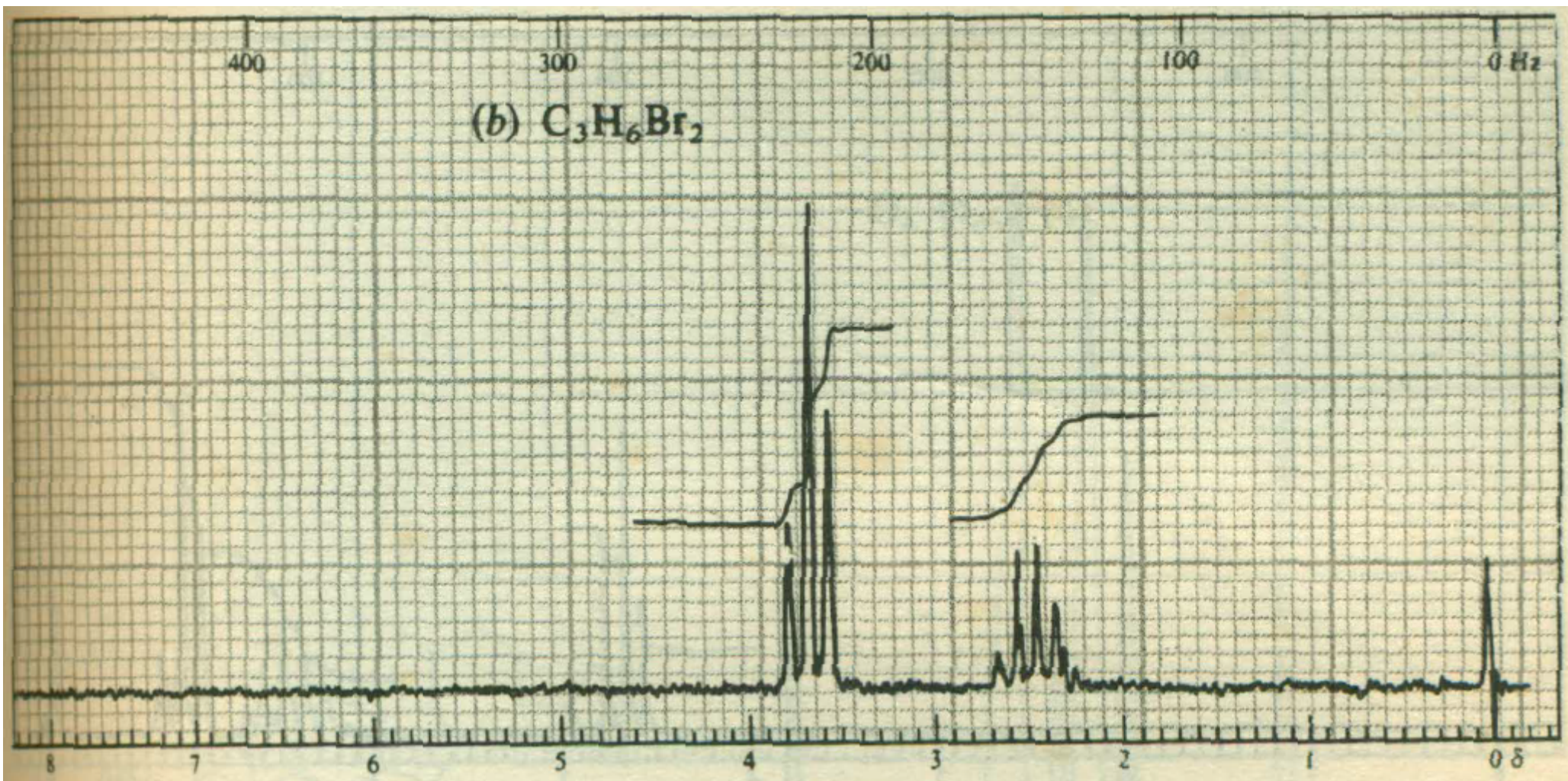
b



Ref: Organic Chemistry,
Morrison & Boyd:

J_{ab} does not depend on the applied field
It is also reciprocal between coupled groups
Equivalent protons do not split each other's signal

Working out the structural formula $C_3H_6Br_2$



Try to solve a simple structure....

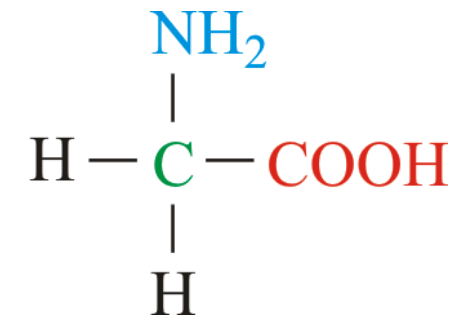
How much should be the dipolar broadening ?

The observed width of the resonance is $\sim 0.1 - 1$ Hz in liquids

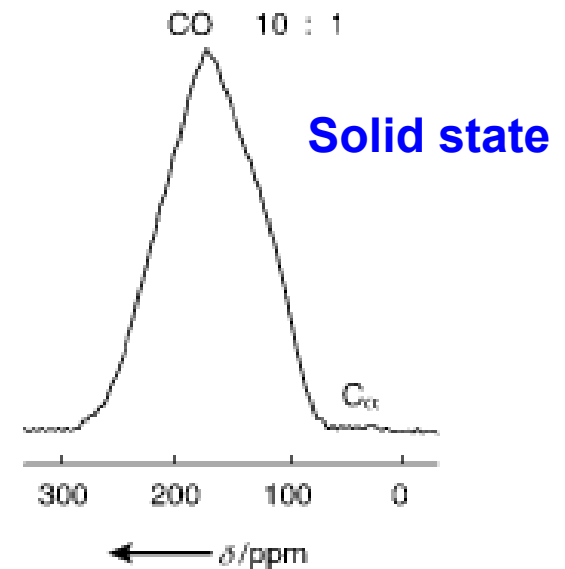
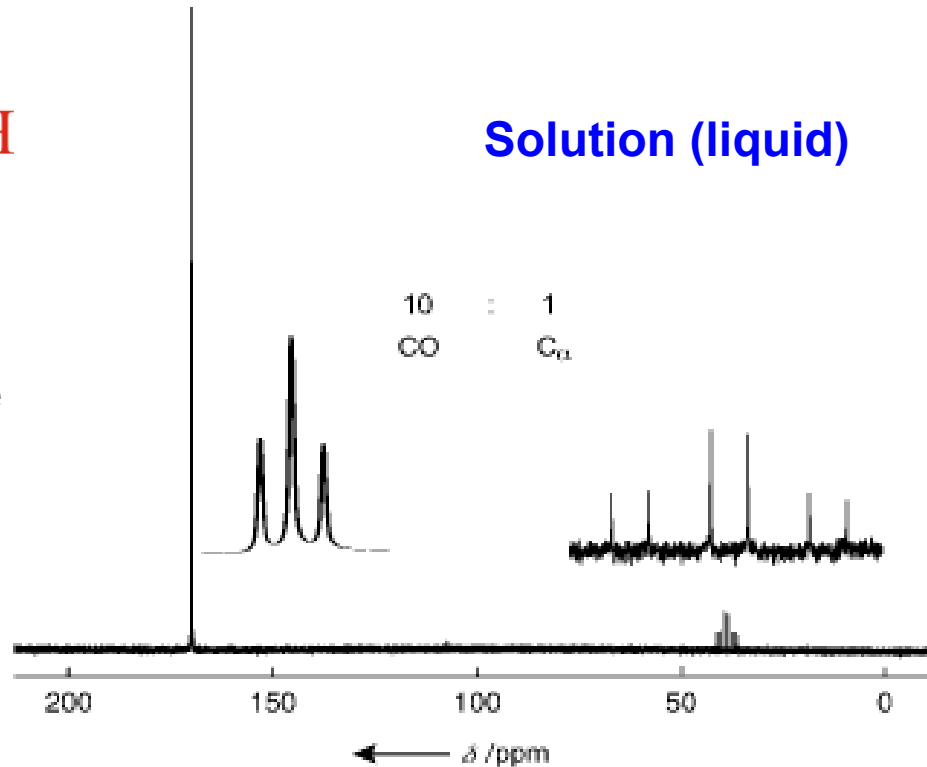
It is MUCH LARGER in solids ~ 1 KHz or more.

Frozen water (ice) will give a broad resonance, liquid water a very narrow one!

This is a generic fact



¹³C NMR of Glycine



How much should be the dipolar broadening ?

Each dipole creates a small field in the neighbouring location,

This "extra" part may reduce/enhance the external field, giving rise to the width

If μ_N is the magnetic moment of a dipole

$$\delta B \approx \frac{\mu_0 \mu_N}{4\pi r^3}$$

$$\delta \nu = \left(\frac{\gamma}{2\pi}\right) \frac{\mu_0 \mu_N}{4\pi r^3}$$
$$\approx 5 \text{ KHz}$$

$$\gamma = 42.57 \text{ MHz/T}$$

Proton gyromagnetic ratio

$$\mu_N = 5.05 \times 10^{-27} \text{ J/T}$$

Nuclear magneton

$$r \approx 2 \text{ \AA}$$

Typical distance in solids

This is the correct order of magnitude for solids.

In case of a liquid the molecules continuously change their relative orientation w.r.t one another.

This molecular tumbling almost averages out the random dipolar field. (**Motional narrowing**)

Modeling the dipole-dipole interaction

The energy of interaction of two classical magnetic dipoles is given by :

$$E = \frac{\mu_0}{4\pi} \left[\frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} - 3 \frac{(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^5} \right] \quad (\vec{\mu} \rightarrow \gamma \hbar I : x = r \sin \theta \cos \phi \dots\dots)$$
$$= \frac{\mu_0}{4\pi} \frac{\gamma_1 \gamma_2}{r^3} [A + B + C + D + E + F]$$

QM correspondence

$$A = I_{1z} I_{2z} (1 - 3 \cos^2 \theta)$$

$$B = -\frac{1}{4} [I_{1+} I_{2-} + I_{1-} I_{2+}] (1 - 3 \cos^2 \theta)$$

$$C = -\frac{3}{2} [I_{1+} I_{2z} + I_{1z} I_{2+}] \sin \theta \cos \theta e^{-i\phi}$$

$$D = -\frac{3}{2} [I_{1-} I_{2z} + I_{1z} I_{2-}] \sin \theta \cos \theta e^{i\phi}$$

$$E = -\frac{3}{4} I_{1+} I_{2+} \sin^2 \theta e^{-2i\phi}$$

$$F = -\frac{3}{4} I_{1-} I_{2-} \sin^2 \theta e^{2i\phi}$$

Most of the contribution to the deviation from simple spin states comes from these two terms. Why ?

Modeling the dipole-dipole interaction

Do the pairwise sum to get the full contribution.

$$H_{dipole} = \frac{1}{2} \left(\frac{\mu_0}{4\pi} \right) \sum_{j=1}^N \sum_{k=1}^N \left[\frac{\vec{\mu}_j \cdot \vec{\mu}_k}{r_{jk}^3} - 3 \frac{(\vec{\mu}_j \cdot \vec{r}_{jk})(\vec{\mu}_k \cdot \vec{r}_{jk})}{r_{jk}^5} \right]$$
$$\approx \frac{1}{4} \left(\frac{\mu_0}{4\pi} \right) \gamma^2 \hbar^2 \sum_{j=1}^N \sum_{k=1}^N \frac{1 - 3 \cos^2 \theta_{jk}}{r_{jk}^3} \left[3 I_{jz} I_{kz} - \vec{I}_j \cdot \vec{I}_k \right]$$

molecular motion in liquids
leads to an averaging over θ

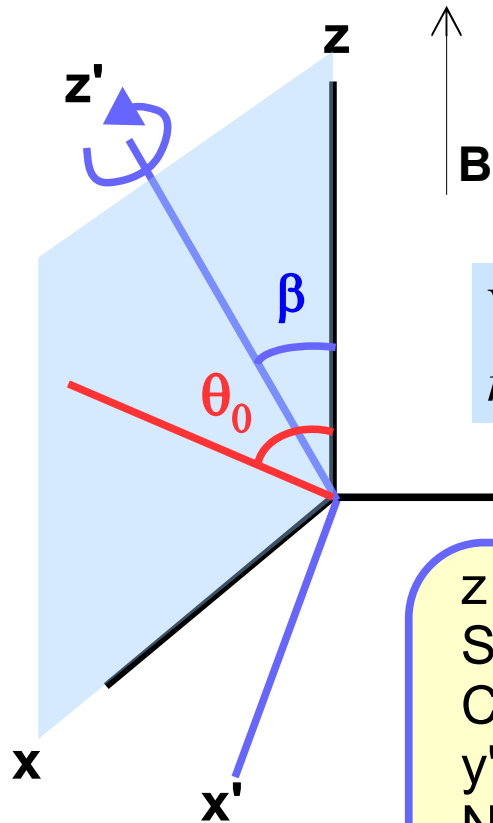
The average $\langle \cos^2 \theta \rangle = 1/3$
over the surface of a sphere.

But this does not happen in solids.
Relative orientations are fixed.

Question: Can we somehow make this averaging happen in a solid?
Can we make a solid appear as a liquid as far as NMR is concerned?

Answer : Spin the sample very fast (few kHz!) in a particular way.
Why does it work?

Modeling the dipole-dipole interaction : motional narrowing



The vector connecting the two dipoles is along θ_0
 β is the axis around which the sample (and hence the vector connecting the dipole pair) is set spinning.

What would be the average $\langle \cos^2 \theta \rangle$ seen by the fixed frame?
 $n_x' = \sin(\theta_0 - \beta) \cos \omega t$, $n_y' = \sin(\theta_0 - \beta) \sin \omega t$, $n_z' = \cos(\theta_0 - \beta)$

z direction is fixed by the B field.
 Sample will be rotated around z' axis.
 Chose the axes such that the z' axis lies in the xz plane
 y' axis can be made to coincide with y
 No loss of generality in this.

At $t=0$ let the θ_0 also lie in the xz plane.
 This is simply a choice of the time $t=0$. No loss of generality.

$$\begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = \begin{pmatrix} \cos \beta & 0 & \sin \beta \\ 0 & 1 & 0 \\ -\sin \beta & 0 & \cos \beta \end{pmatrix} \begin{pmatrix} n'_x \\ n'_y \\ n'_z \end{pmatrix}$$

**Rotation matrix
 between the two
 frames , with common
 y axis**

Motional narrowing → making a solid appear like a liquid

$$\begin{aligned}\cos \theta &= n_z = -\sin \beta n'_x + \cos \beta n'_z \\ &= -\sin \beta \sin(\beta - \theta_0) \cos \omega t + \cos \beta \cos(\beta - \theta_0) \\ \therefore \langle \cos^2 \theta \rangle &= \sin^2 \beta \sin^2(\beta - \theta_0) \langle \cos^2 \omega t \rangle + \cos^2 \beta \cos^2(\beta - \theta_0)\end{aligned}$$

The $\cos \omega t$ term will average to zero over a cycle.

$$\begin{aligned}\langle \cos^2 \theta \rangle &= \sin^2 \beta \sin^2(\beta - \theta_0) \left(\frac{1}{2} \right) + \cos^2 \beta \cos^2(\beta - \theta_0) \\ 3 \langle \cos^2 \theta \rangle - 1 &= \left(\frac{3}{2} \right) \sin^2 \beta \sin^2(\beta - \theta_0) + 3 \cos^2 \beta \cos^2(\beta - \theta_0) - 1 \\ &= \frac{1}{2} (1 - 3 \cos^2 \beta) (1 - 3 \cos^2(\beta - \theta_0))\end{aligned}$$

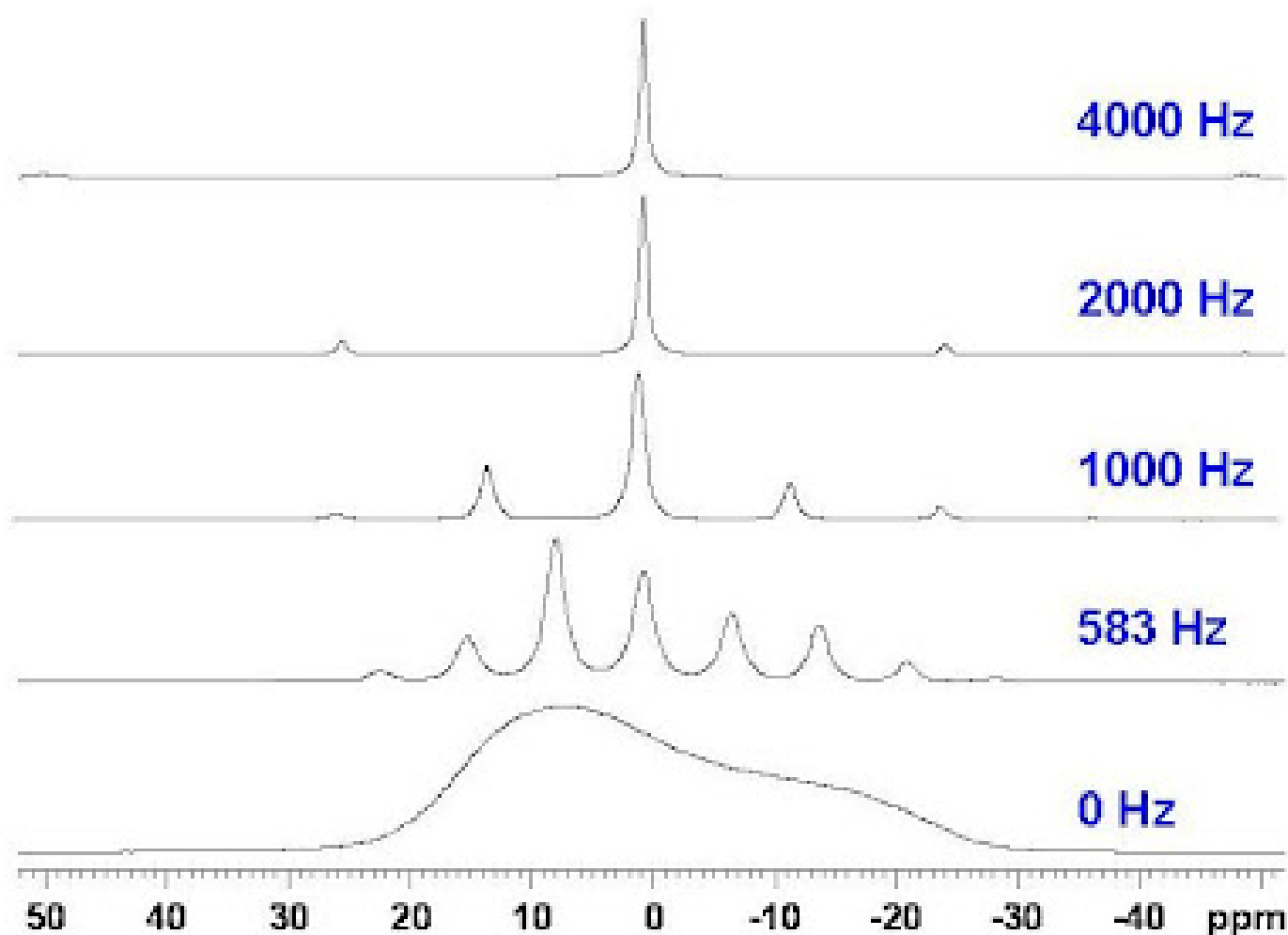
Work out the factorisation

So if we set the angle β such that $(1 - 3 \cos^2 \beta = 0) \Rightarrow \beta = 54.4^\circ$
Then irrespective of anything else the average of the LHS will be zero
Like what happens for a liquid

This is called the "Magic Angle Spinning"

An example of Magic Angle Spinning : solid appears like a liquid

³¹P CPMAS Ammonium Dihydrogen Phosphate



Rabi oscillations → oscillations of the up-down population

Main field in z direction & Perturbing field applied in xy plane (oscillating/rotating)

Population of the up & down states keep oscillating. (...see any QM standard textbook)

$$\text{For spin } 1/2: I_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad I_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad I_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad |\alpha\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad |\beta\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$H_0 = -\gamma \hbar B_0 I_z$$

$$H_1 = -\gamma \hbar B_1 (I_x \cos \omega t + I_y \sin \omega t)$$

Do not assume
resonant frequency

$$|\Psi(t)\rangle = c_\alpha(t)|\alpha\rangle + c_\beta(t)|\beta\rangle$$

$$\text{with : } c_\alpha(t=0) = 1 \quad \& \quad c_\beta(t=0) = 0 \quad \& \quad \omega_0 = \gamma B_0$$

$$|c_\beta(t)|^2 = \frac{\gamma^2 B_1^2}{\gamma^2 B_1^2 + (\omega - \omega_0)^2} \sin^2 \left(\sqrt{\frac{\gamma^2 B_1^2 + (\omega_0 - \omega)^2}{4}} t \right)$$

$$|c_\alpha(t)|^2 = 1 - |c_\beta(t)|^2$$

Rotation and relaxation of the bulk magnetisation

Population oscillations have maximum amplitude when denominator is minimum.

If the perturbation is kept on for a small amount of time:
what would be the final state?

The rotating axis formulation helps to visualize this.

Bulk magnetization is the sum total of the spin moments: So

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1}$$

$$\frac{dM_x}{dt} = \gamma(\vec{M} \times \vec{B})_x - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = \gamma(\vec{M} \times \vec{B})_y - \frac{M_y}{T_2}$$

The most common relaxation mechanism is exponential.

Think of it like a spring coming back to equilibrium

The relaxation of M_z is not energy conserving as far as the spins are concerned

Relaxation of M_x and M_y do not require energy loss.

Different mechanismsso different relaxation times.

How would this look like from a co-ordinate system rotating about the shared z-axis?

The rotating axis formulation : Bloch equations

$$\vec{M} = \hat{i} M_x + \hat{j} M_y + \hat{k} M_z$$

$$\frac{d\vec{M}}{dt} = \left[M_x \frac{d\hat{i}}{dt} + M_y \frac{d\hat{j}}{dt} + M_z \frac{d\hat{k}}{dt} \right] + \left[\hat{i} \frac{dM_x}{dt} + \hat{j} \frac{dM_y}{dt} + \hat{k} \frac{dM_z}{dt} \right]$$

$$= \vec{\omega} \times \vec{M} + \frac{\delta \vec{M}}{\delta t}$$

← seen from the rotating frame

$$\frac{\delta \vec{M}}{\delta t} = \frac{d\vec{M}}{dt} - \vec{\omega} \times \vec{M}$$

$$= \gamma \vec{M} \times \vec{B} + \vec{M} \times \vec{\omega}$$

$$= \vec{M} \times \left[\hat{k} \left(\gamma B_0 + \omega_z \right) + \gamma \vec{B}_1 \right]$$

Chose ω such that this is zero

The unit vectors of the rotating co-ordinate also change when viewed from the "inertial" frame

The effective equation will then only have the perturbing field + relaxation

The rotating axis formulation : Bloch equations

$$\frac{\delta \vec{M}}{\delta t} = \gamma \vec{M} \times \hat{i} B_1$$

Consider the time for which the perturbation is on. The rotating B1 field is static in the rotating frame. Neglect relaxation during the short time

This is a rigid rotation if seen from the rotating frame

Keep the pulse on for a time such that $\gamma B_1 t = \pi, \pi/2$

Then the field is switched off

Go back to inertial frame, analyze relaxation

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1}$$

The relaxation of Mz induces a decaying voltage in the detection coil. The relaxation time T1 can be found from this.

$$\begin{aligned} \frac{dM_x}{dt} &= \gamma M_y B_0 - \frac{M_x}{T_2} \\ \frac{dM_y}{dt} &= -\gamma M_x B_0 - \frac{M_y}{T_2} \end{aligned}$$

Multiply the second eqn by i
Solve for $M_x + i M_y$:: OR diagonalise

$$\frac{d}{dt} \begin{pmatrix} M_x \\ M_y \end{pmatrix} = - \begin{pmatrix} 1/T_2 & -\gamma B_0 \\ \gamma B_0 & 1/T_2 \end{pmatrix} \begin{pmatrix} M_x \\ M_y \end{pmatrix}$$

The rotating axis formulation : Bloch equations

$$M_z(t) = M_0 \left(1 - e^{-t/T_1} \right) + M_z(0) e^{-t/T_1}$$

$$M_x(t) = \left[M_x(0) \cos(\gamma B_0 t) + M_y(0) \sin(\gamma B_0 t) \right] e^{-t/T_2}$$

$$M_y(t) = \left[M_y(0) \cos(\gamma B_0 t) - M_x(0) \sin(\gamma B_0 t) \right] e^{-t/T_2}$$

The magnitude $\left(M_x^2 + M_y^2 \right)^{1/2}$ decays as $\sim e^{-t/T_2}$

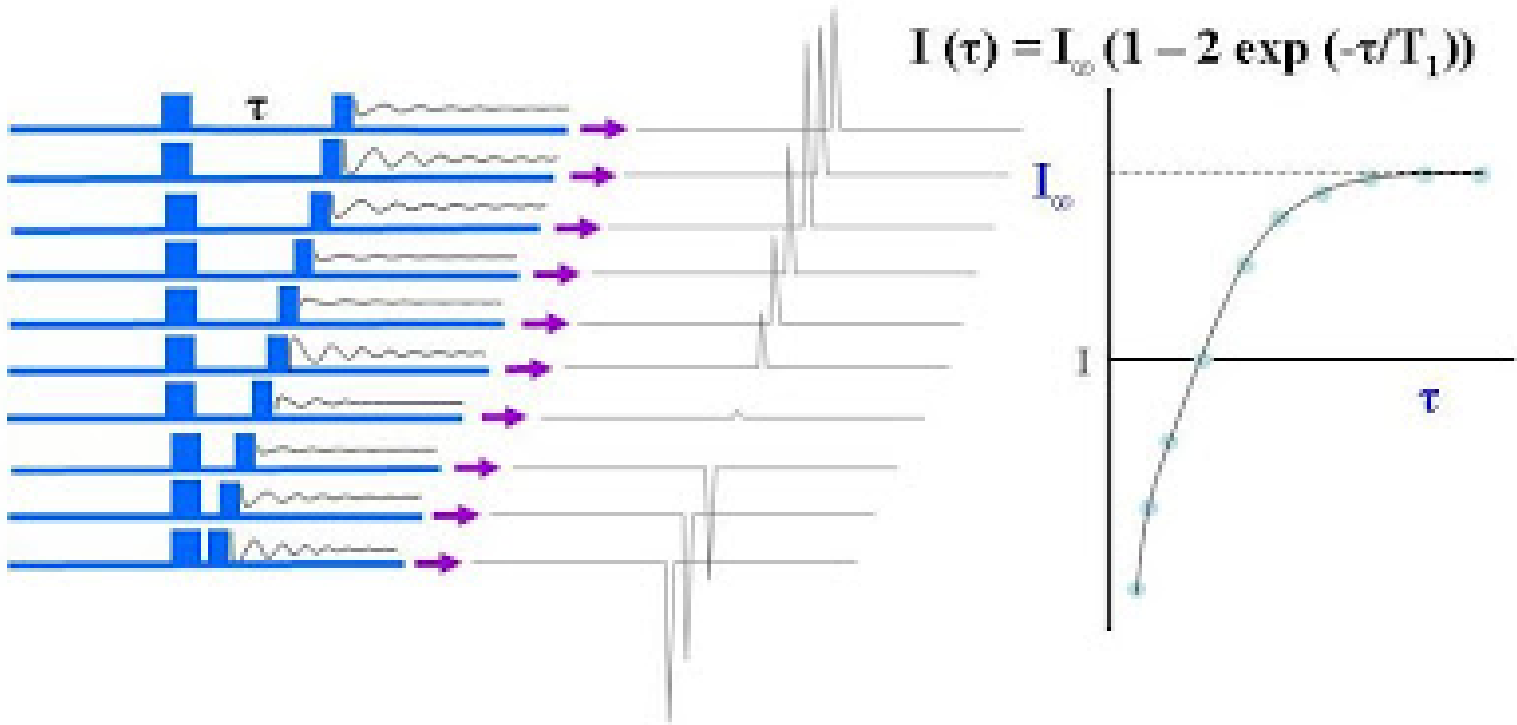
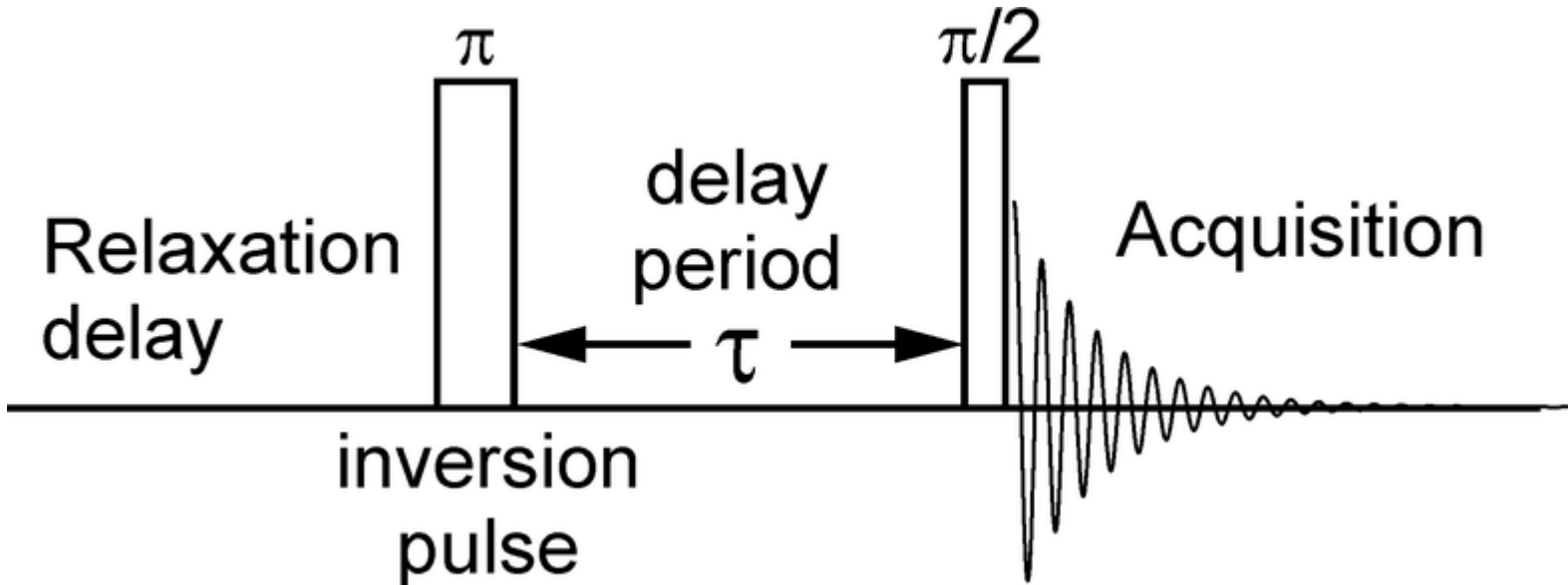
T1 is the spin-lattice relaxation time in a solid

T2 is the spin-spin relaxation time

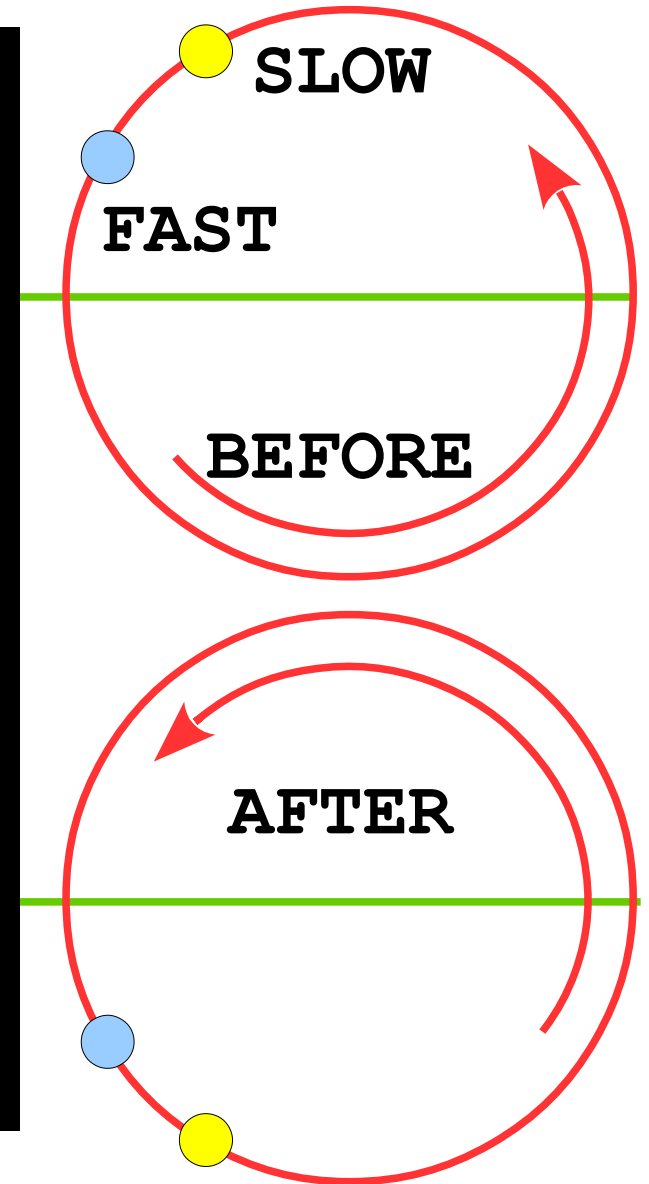
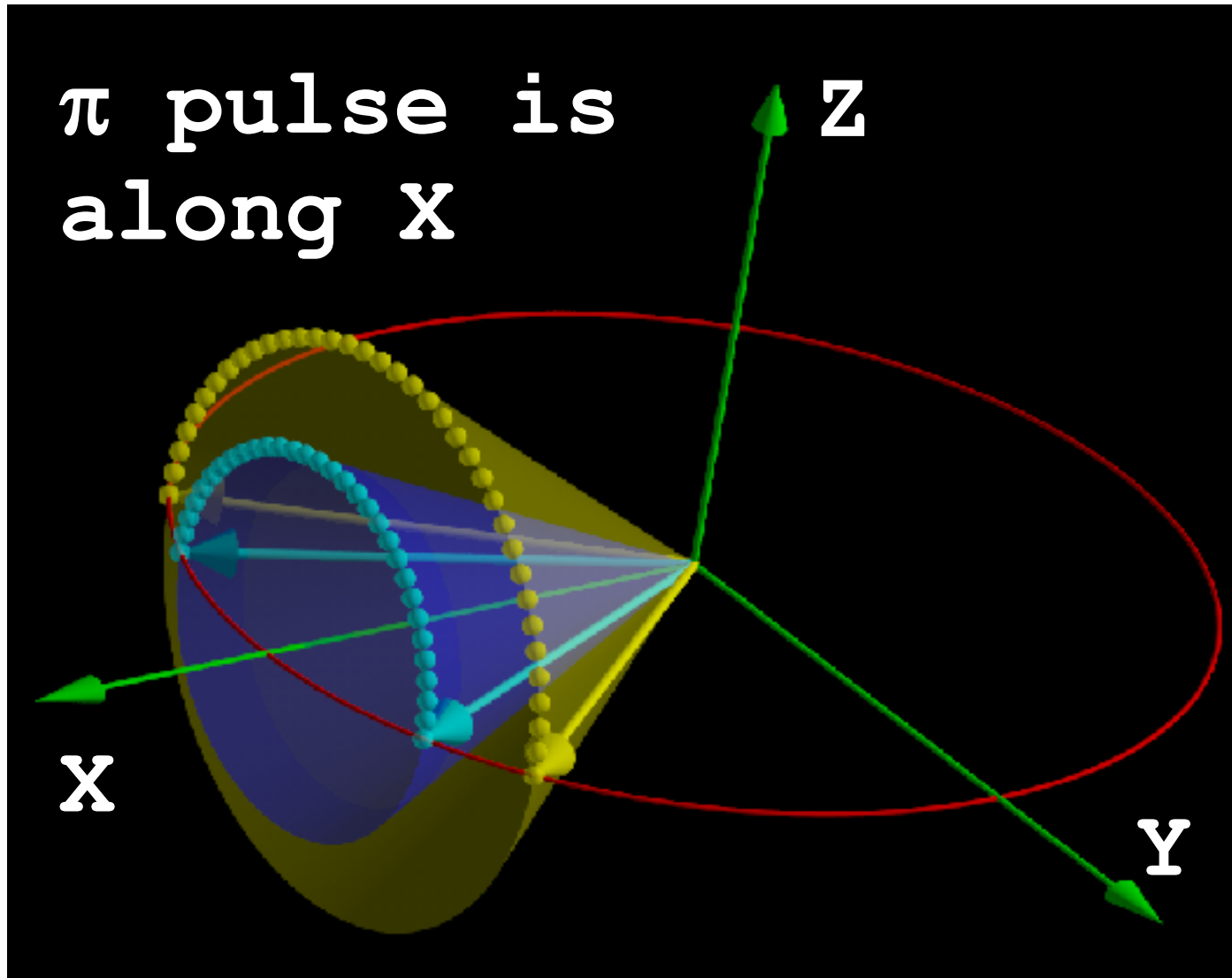
Generally T1 >> T2 (millisecond/ microsecond)

How would one measure T1 and T2 ?

Measuring T_1 by inversion recovery sequence : $\pi - \tau - \pi/2$



Effect of π pulse : when M is in the xy plane



$$\frac{\delta \vec{M}}{\delta t} = \gamma \vec{M} \times \hat{i} B_1$$

After the pulse the fast dot will trail by exactly the same amount it was leading by. The gap will start closing.

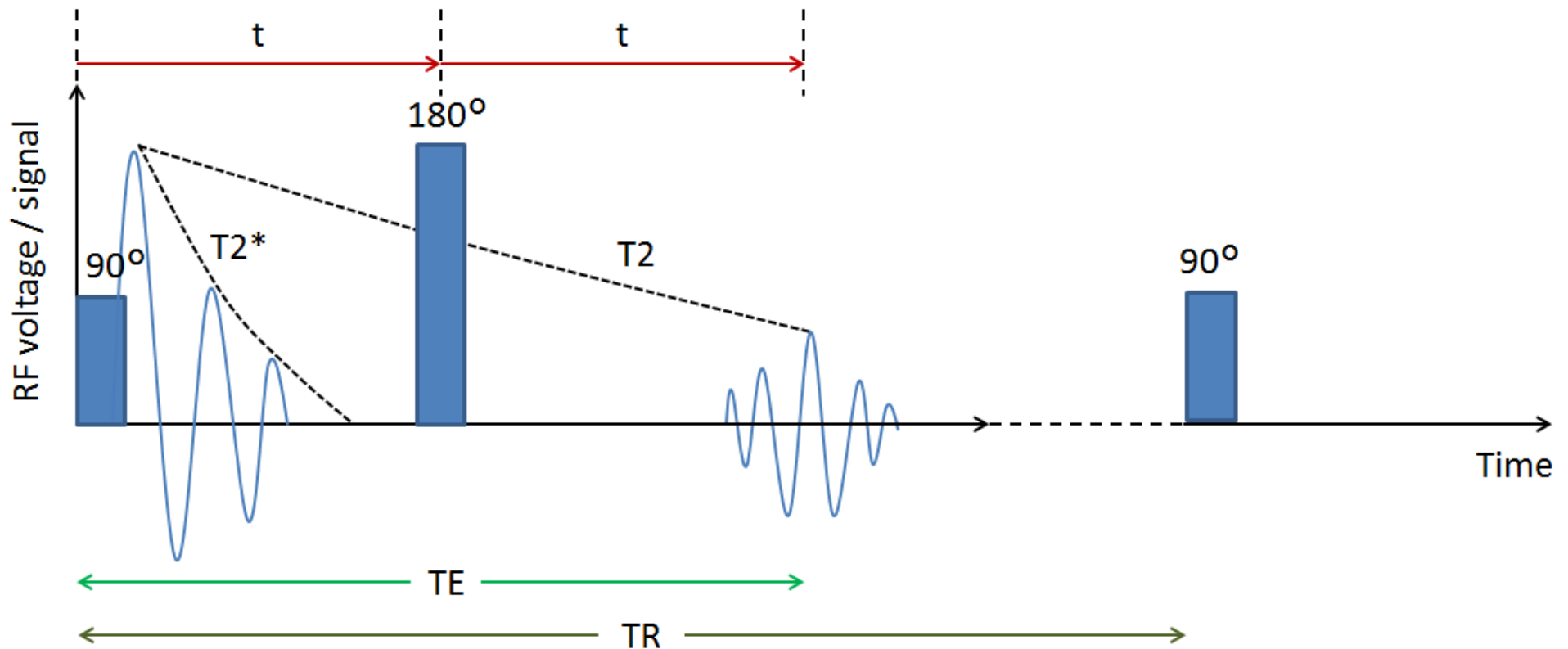
Measuring T_2 by spin-echo sequence : $\pi/2 - \tau - \pi - \tau$

There are small inhomogeneities in the magnetic field

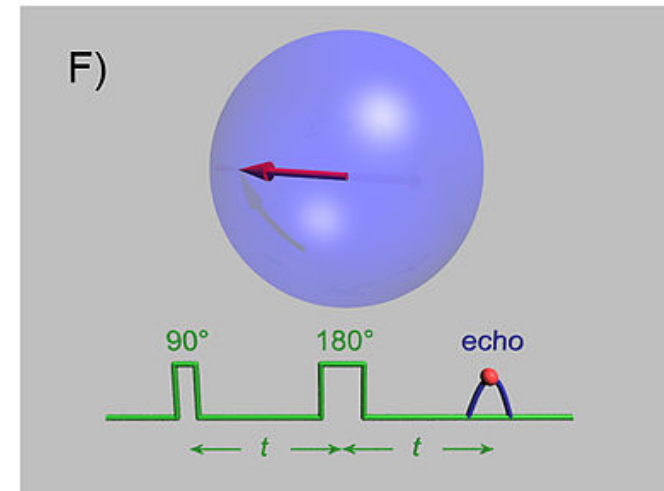
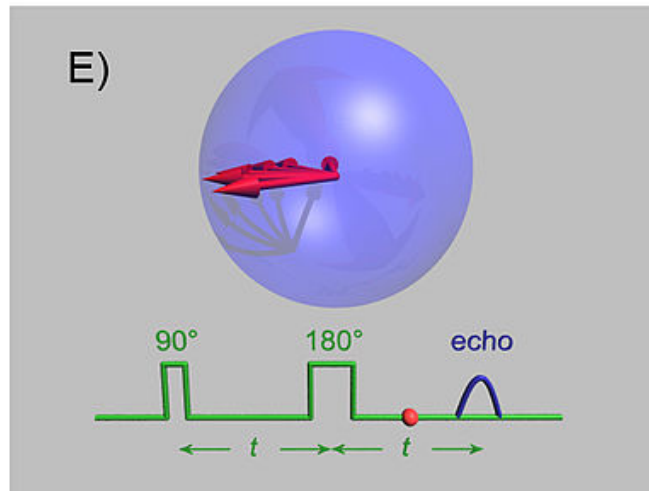
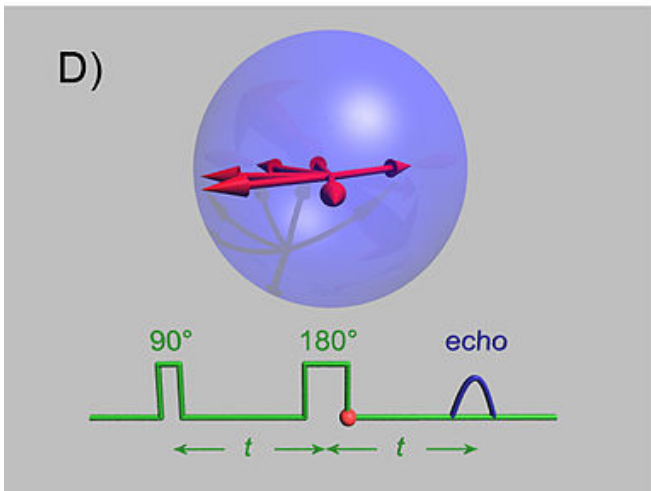
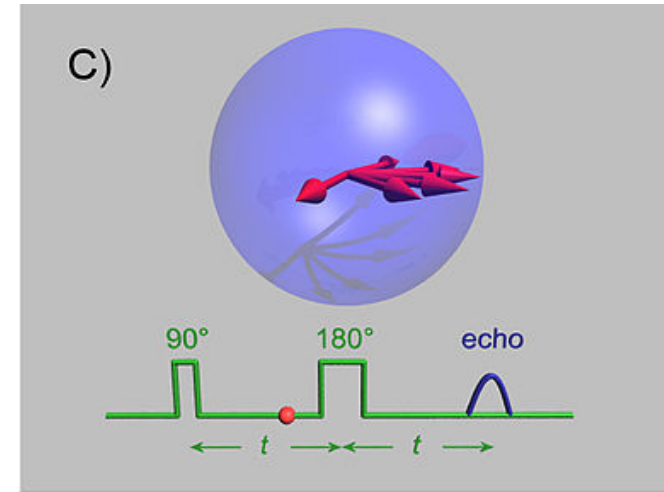
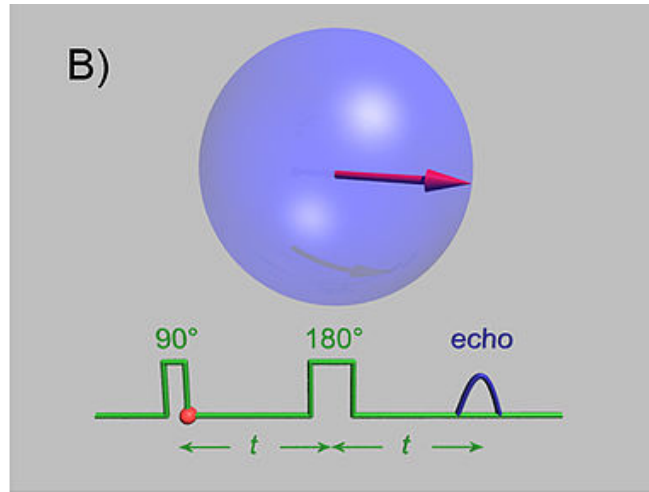
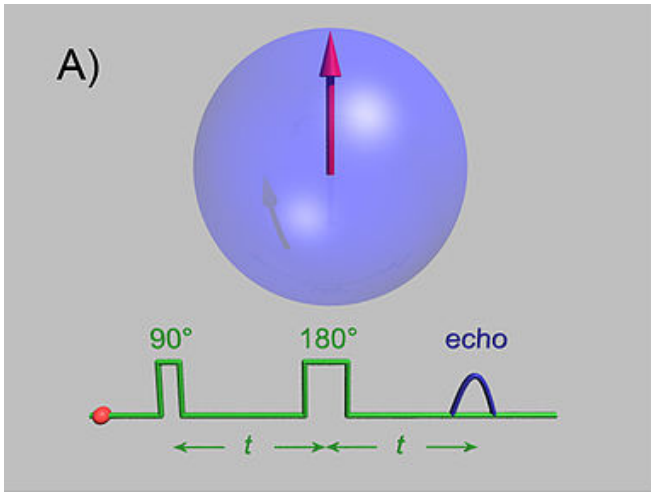
This will cause the spins to "rotate" at slightly different rates.

This will cause them to "debunch" giving a wrong measure of decay due to interaction.

A trick of overcoming the inhomogeneity is the spin echo sequence.



Measuring T_2 by spin-echo sequence : $\pi/2 - \tau - \pi - \tau$



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