X-Ray Diffraction in Crystallography (Solid State Physics)

e-content for B.Sc Physics (Honours)
B.Sc Part-III
Paper-VII

Dr. Ayan Mukherjee,
Assistant Professor,
Department of Physics,
Ram Ratan Singh College, Mokama.
Patliputra University, Patna

1. X-Ray (Nature & Generation)

* X-rays are electromagnetic waves with very short wavelength ($\lambda \sim 1A^o$).
i.e. of the same order of magnitude as the lattice constant.
* When high kinetic energy electrons hit a metallic target, X-rays will be emitted.
*Since,

Max. energy a photon can get = K.E of the incident electron

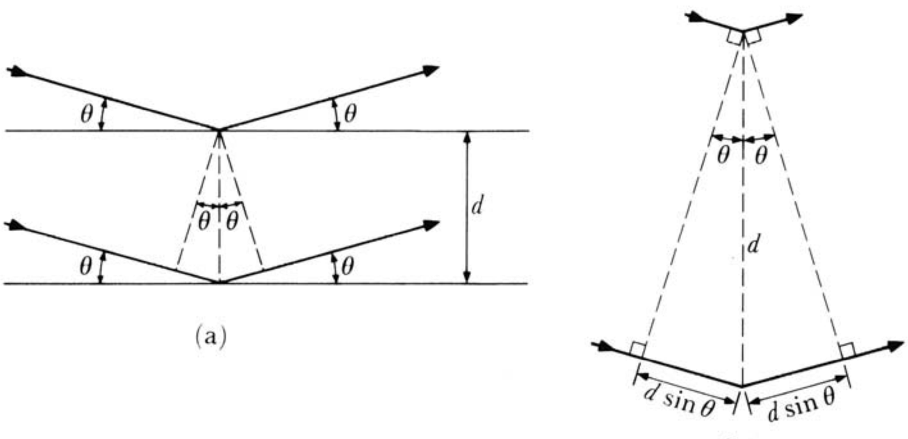
$$h\nu_{max} = eV$$

So, The min. wavelength can be obtained is

$$\lambda_{min} = c/\nu_{max} = 12.3/V \quad A^o.$$

2. Bragg's Law

- Consider an incident beam being reflected by two parallel lattice planes as shown.



(a) (b)

- Bragg's law states the condition for a constructive interference as:

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

Which means that diffraction can not be occurred unless the incident wavelength is

$$\lambda < 2d$$

Interplanar distance (d_{hkl}):

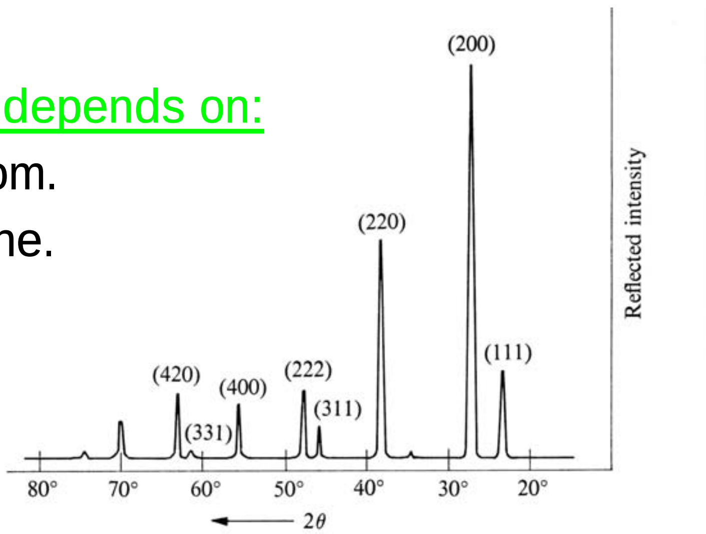
The value of d, the distance between two adjacent planes in the set (hkl) of *a cubic system* is given by,

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

Or:

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

where a is the length of the cube side.



Intensity of reflected waves depends on:

- No. of electrons in each atom.
- Density of atoms in the plane.
- The incident angle θ.
- The order number n.

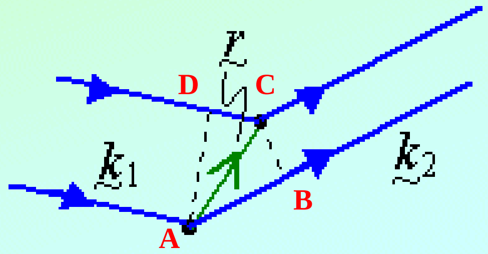
3. Diffraction by a Crystal

- Consider an incident wave being scattered by two lattice points (atoms) as shown.
- Instead of wavelength, the concept of the wavevector ***k***, where $|k| = 2\pi/\lambda$, is often used to characterize the plane-wave and show its direction.

Elastic Scattering: $|\underset{\sim}{k}_1| = |\underset{\sim}{k}_2|$

Phase Difference:

$$\underset{\sim}{k}_2 \cdot \underset{\sim}{r} - \underset{\sim}{k}_1 \cdot \underset{\sim}{r} = \Delta \underset{\sim}{k} \cdot \underset{\sim}{r}$$



- Scattered amplitude is maximum for phase factors equal to unity, ie.

$$\sum_r \exp(i\Delta \mathbf{k}.\mathbf{r}) = \sum_r (\cos\Delta \mathbf{k}.\mathbf{r} - i\sin\Delta \mathbf{k}.\mathbf{r}) = 1$$

Or,

$$\left.\begin{aligned} \Delta \underset{\sim}{k} \cdot \underset{\sim}{a} &= 2\pi h \\ \Delta \underset{\sim}{k} \cdot \underset{\sim}{b} &= 2\pi k \\ \Delta \underset{\sim}{k} \cdot \underset{\sim}{c} &= 2\pi l \end{aligned}\right\} \text{Laue Equations}$$

Solution for such set is of the form: $\Delta \underset{\sim}{k} = \underset{\sim}{G}$

where $\underset{\sim}{G} = h\underset{\sim}{a}^* + k\underset{\sim}{b}^* + l\underset{\sim}{c}^*$ with $\underset{\sim}{a}^* = 2\pi \dfrac{\underset{\sim}{b} \times \underset{\sim}{c}}{\underset{\sim}{a}.\underset{\sim}{b} \times \underset{\sim}{c}}$

$\underset{\sim}{G}$ is called the reciprocal lattice vector.

1. Reciprocal Lattice

- Set of vectors, $G = ha^* + kb^* + lc^*$ defines new lattice: Reciprocal Lattice.

With

$$\mathbf{a}^* = \frac{2\pi}{\Omega}(\mathbf{b}\times\mathbf{c}) \qquad \mathbf{b}^* = \frac{2\pi}{\Omega}(\mathbf{c}\times\mathbf{a}) \qquad \mathbf{c}^* = \frac{2\pi}{\Omega}(\mathbf{a}\times\mathbf{b})$$

Where $\boxed{\Omega = \mathbf{a}.(\mathbf{b}\times\mathbf{c})}$ the volume of the unit cell.

Note that:

$$\mathbf{a}^*.\mathbf{a} = 2\pi \qquad \mathbf{a}^*.\mathbf{b} = \mathbf{a}^*.\mathbf{c} = 0$$

$$\mathbf{b}^*.\mathbf{b} = 2\pi \qquad \mathbf{b}^*.\mathbf{a} = \mathbf{b}^*.\mathbf{c} = 0$$

$$\mathbf{c}^*.\mathbf{c} = 2\pi \qquad \mathbf{c}^*.\mathbf{a} = \mathbf{c}^*.\mathbf{b} = 0$$

  - This is the lattice that is produced by diffraction, ie. a diffraction pattern of a crystal is the mapping of its reciprocal lattice.
- Example: Simple cubic (real) lattice with side α.
  In Cartesian co-ordinates, we have: $a=\alpha i$, $b=\alpha j$ & $c=\alpha k$.

Apply definition of reciprocal vector get:

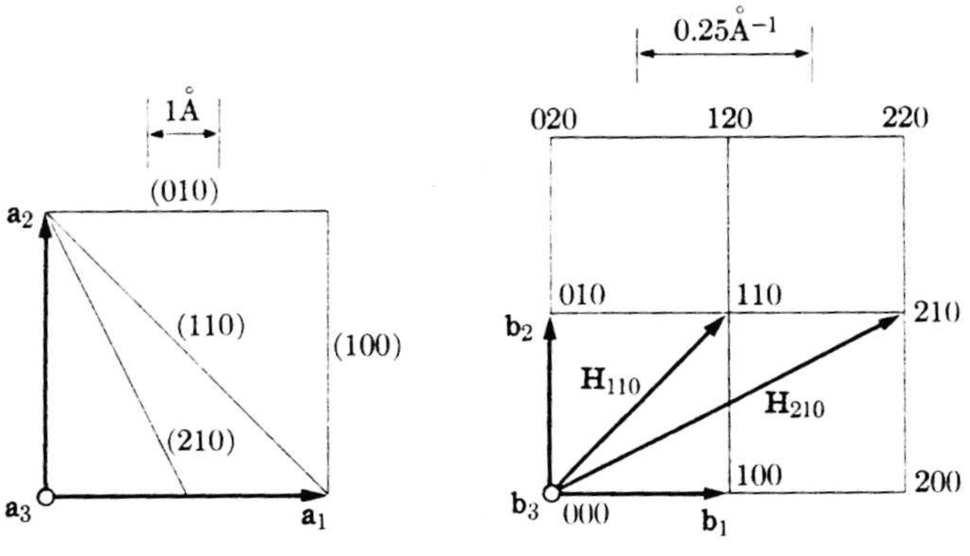
$a^* = (2\pi/\alpha)i$, $b^* = (2\pi/\alpha)j$ & $c^* = (2\pi/\alpha) k$

reciprocal lattice is simple cubic with side $2\pi/\alpha$.

Properties of the reciprocal lattice:

- A vector $\mathbf{G}_{hkl}$ drawn from the origin to any point with coordinates hkl, is perpendicular to the (*hkl*) plane in the real lattice.
- The length of the vector $\mathbf{G}_{hkl}$ is equal to the reciprocal of the spacing *d* of the (*hkl*) planes, or

$$\boxed{G_{hkl} = \frac{2\pi}{d_{hkl}}}$$

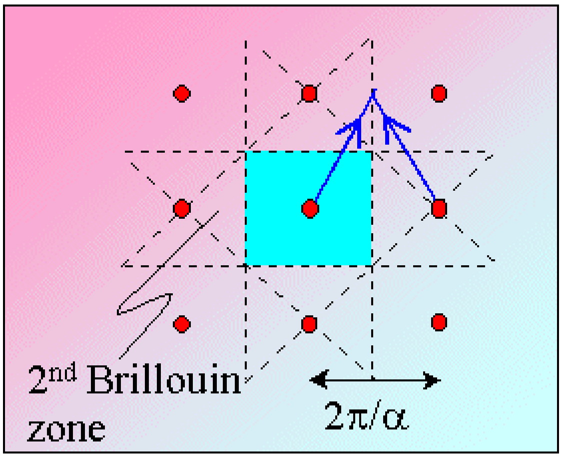


crystal lattice

reciprocal lattice

2. Brillouin Zones

- Use 2-D (square) reciprocal lattice as illustration.



- Define volume in 3D, area in 2D as 1st Brillouin zone (shaded), 2nd Brillouin zone etc.

3. Back to Bragg's law

It was shown before that the condition for a constructive interference between the scattered waves is

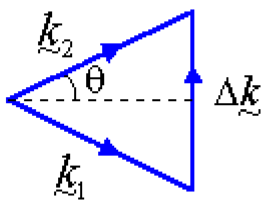
$$\Delta \underset{\sim}{k} = \underset{\sim}{G}$$

and, from the following figure, it is easy to show that for **elastic scattering:**

$$\Delta k = 2k \sin\theta = \frac{4\pi}{\lambda}\sin\theta$$

$$\text{So } \Delta k = \boldsymbol{G} \equiv \frac{4\pi}{\lambda}\sin\theta = \frac{2\pi}{d}$$

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



1. Allowed X-ray diffraction

- Apart from the phase difference, the intensity of the diffracted radiation depends on a number of factors:
- Some are related to the electronic distribution in the atom. And some are related to the structural arrangement of atoms in the crystal.
- Those factors can be expressed by *the structure factor* F_{hkl}

$$\boxed{F_{hkl} = f_a \sum_j e^{i2\pi(hu_j + kv_j + lw_j)}}$$

where f_a is the *atomic form factor* (or **atomic scattering factor**).

Thus, if F_{hkl} is zero for certain indices, then the intensity vanishes, even though the corresponding planes satisfy Bragg's condition.

Example:

The bcc unit cell has two atoms whose coordinates are (u,v,w) = (0,0,0) & (½,½,½). The *structure factor*, for such structure is

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

Hence, if (h+k+l) is odd

$$F_{hkl} = f_a(1-1) = 0$$

And, if (h+k+l) is even

$$F_{hkl} = f_a(1+1) = 2f_a$$

In other words, for the bcc lattice, the diffraction is absent for all planes in which the sum of (h+k+l) is odd and is present for the planes in which the sum of (h+k+l) is even.

2. Methods of X-ray diffraction

There are essentially three methods:

The *rotating-crystal method,*

the *Laue method,*

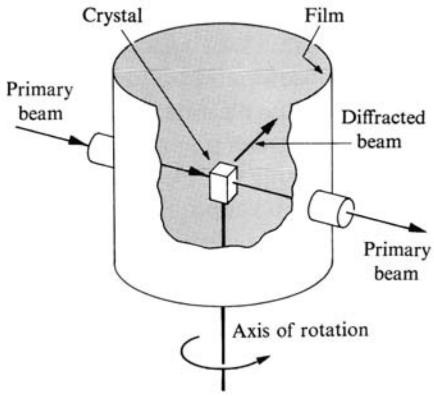
and the *powder method.*

Regardless of the method used, the quantities measured are essentially the same:

i) The scattering angle 2θ between the diffracted and incident beams.

ii) The intensity *I* of the diffracted beam. This quantity determines the cell-structure factor, F_{hkl}.

The rotating-crystal method



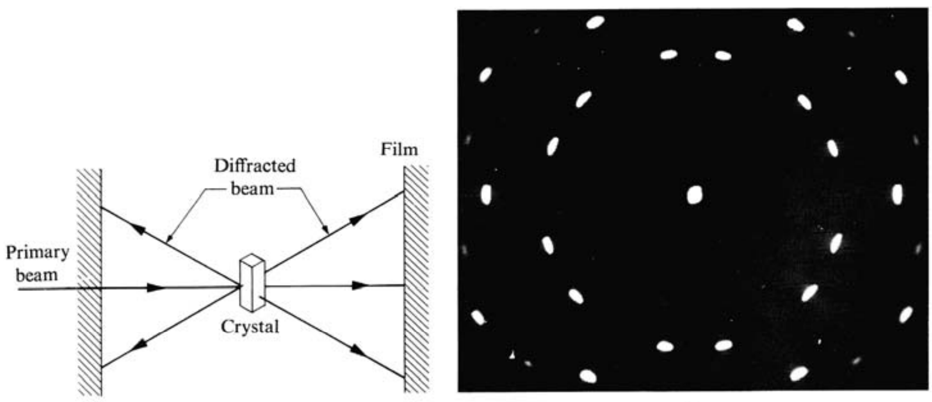
Sample: a single crystal.
Wavelength λ: A monochromatic beam.
Technique: The sample is rotated until a diffraction condition occurs. The diffracted beam, then, will be recorded as a spot on a photographic film.

By recording the diffraction patterns (both angles and intensities) for various crystal orientations, one can determine the shape and size of the unit cell as well as the arrangement of atoms inside the cell.

The Laue method

Sample: a single crystal.
Wavelength λ: A white x-ray beam.
Technique: The sample has a fixed orientation relative to the incident beam. Since λ covers a continuous range, the crystal selects that particular wavelength which satisfies Bragg's law at the present orientation, The diffracted beam is then recorded as a spot on a photographic film.

But si



(a) (b)

is

not measured, one cannot determine the actual values of the interplanar spacings but only their ratios.

The powder method

Sample: a powder or polycrystalline.

Wavelength λ: A monochromatic beam.

Technique: Because of the large number of crystallites which are randomly oriented, there is always enough of these which have the proper orientation relative to the incident monochromatic beam to satisfy Bragg's law. Since both λ and θ are measurable, one can determine the interplanar spacing.

3. Neutron & Electron Diffraction

In addition to x-rays , there are some other forms of radiation that can be used to characterize a crystal if:

- * It has a wave property, so it can interfere.
- *Its wavelength is of the same order of magnitude as the lattice constant.

Since both neutron and electron satisfy those conditions they can be used in diffraction experiments.

The relation between λ (in A°) and the applied field *E* (in electron volts) is:

$$\lambda = \frac{\sqrt{0.08}}{\sqrt{E}} \qquad \text{For neutron}$$

$$\lambda = \frac{\sqrt{150}}{\sqrt{E}} \qquad \text{For electron}$$

Because electrons are light, charged particles, they tend to interact more with atoms and so mostly give information about the surface planes of atoms in a crystal. X-rays tend to interact more with the bulk of the sample and may even pass completely through thin samples. Neutrons interact more with the nuclei of atoms and are especially useful for investigating magnetic interactions and *isotopes*.