# Crystal structure from X-ray diffraction

Atomic distances ~ $\dot{A}$, need radiation of comparable wavelength to probe it;

$E = \frac{hc}{\lambda} = 12.3\ KeV$ ; X-rays have this kind of energies.

Bragg condition and Laue condition – two equivalent ways at looking at X-ray diffraction in crystals.

Bragg condition for X-ray diffraction: Bragg's considered specular reflection of X-rays from different families of planes in the crystal – constructive interference will give rise to characteristic peaks at certain energies and incident directions.

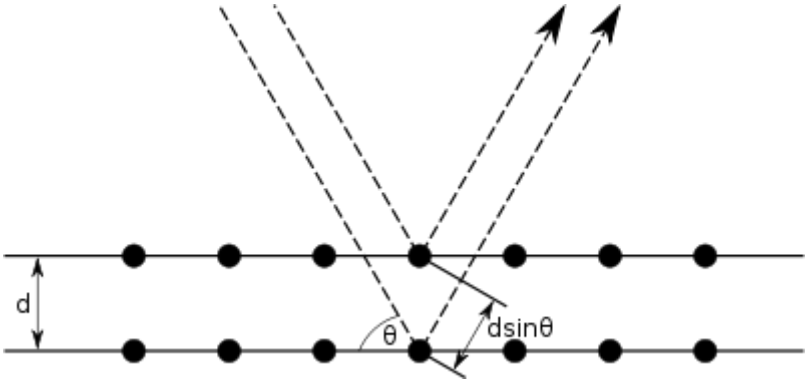


**Figure 1: Bragg reflection**

Conditions for sharp reflected intensity:

1. Rays are specularly reflected – no energy loss – mostly valid as most of the scattering is elastic.
2. Rays reflected from adjacent planes interfere constructively.

Path difference is 2dsinθ; this should equal nλ - Bragg condition for X-ray diffraction peak is

$$2dsin\theta = n\lambda$$

Laue condition for X-ray diffraction: Bragg treatment required the description of the lattice in terms of infinite number of families of planes in the lattice – Laue treatment is in terms of the Reciprocal lattice vectors.

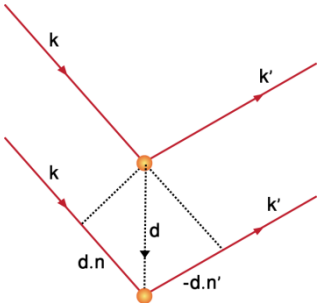


**Figure 2: Laue scattering**

Consider the incident wave $\boldsymbol{k}$ scattered in all directions by the ions/atoms at the lattice sites. The path difference between the incident and scattered wave of wavevector $\boldsymbol{k'}$ should be equal to $m\lambda$ for constructive interference:

$$\boldsymbol{d}.\boldsymbol{n} + (-\boldsymbol{d}.\boldsymbol{n}') = \boldsymbol{d}.(\boldsymbol{n} - \boldsymbol{n}') = m\lambda$$

or

$$\boldsymbol{d}.(\boldsymbol{k} - \boldsymbol{k}') = 2\pi m$$

This should be valid for any pair of lattice sites separated by the lattice vectors $\boldsymbol{R}$ and for all values of $m$; so

$$\boldsymbol{R}.(\boldsymbol{k} - \boldsymbol{k}') = 2\pi m$$

Equivalently;

$$\boldsymbol{e}^{\boldsymbol{iR}.(\boldsymbol{k}-\boldsymbol{k}')} = 1;\ \text{for all } \boldsymbol{R} \text{ in Bravais lattice}$$

This shows that the change in wave vector of the incident radiation for the interference to be constructive should be a reciprocal lattice vector; $\boldsymbol{k} - \boldsymbol{k}' = \boldsymbol{K}$.

Geometrical interpretation: $k' = |\boldsymbol{k}'| = k = |\boldsymbol{k} - \boldsymbol{K}|$; hence $K = 2\boldsymbol{k}.\widehat{\boldsymbol{K}}$ implying that the projection of incident wave vector $\boldsymbol{k}$ along $\boldsymbol{K}$ should be half the length of $\boldsymbol{K}$. This implies that there will be Laue peak when the tip of the incident wave vector lies on the plane bisecting the line joining the origin and any reciprocal lattice point – this is called the Bragg plane.

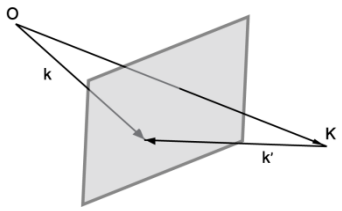


**Figure 3: geometrical interpretation of Laue scattering**

Equivalence of Laue and Bragg pictures:

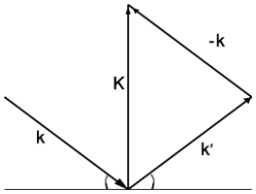


**Figure 4: Equivalence of Bragg and Laue pictures**

Laue reflection with **K=k-k'** can be thought of as Bragg reflection from lattice planes perpendicular to the reciprocal lattice vector **K**. The length of K will be related to the lattice spacing of these planes $d$ by $K = 2\pi n/d$. From Figure 4, $K = 2ksin\theta$ and hence we get Bragg condition $2dsin\theta = n\lambda$. This tells us that Laue reflection corresponding to a change in reciprocal lattice vector by $\boldsymbol{K}$ is equivalent to Bragg reflection from a family of lattice planes perpendicular to $\boldsymbol{K}$. $n$ is the ratio of the lengths of $\boldsymbol{K}$ to the shortest reciprocal lattice vector perpendicular to the plane.

Ewald Construction: Reciprocal lattice is a collection of discrete points – hence condition for Laue diffraction is difficult to satisfy for any ***k*** and ***k'***. Solution – use Ewald construction. With the tip of the incident wave vector as center, draw a sphere of radius |***k***|. Any reciprocal lattice point which lies on the surface of this sphere will satisfy the Laue condition and hence will produce Laue scattering peak.

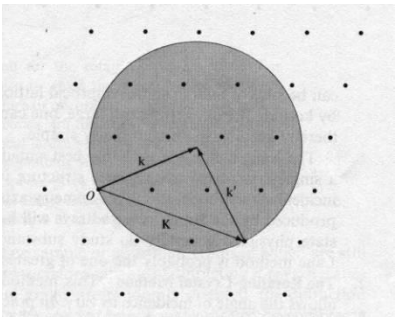


**Figure 5: Ewald construction**

How to ensure that for a given incident wave-vector we will get diffraction peaks? - Can get diffraction peaks by either varying the angle of incidence or the wavelength of incident radiation.

General techniques to obtain the diffraction peaks:

1. Laue Method: Keep the angle of incidence fixed but vary the wavelength – Ewald sphere will cover region between two spheres with max. and min. wavelength – all Reciprocal lattice points within this sphere will give Bragg peaks – best suited for single crystalline specimens.

2. Rotating crystal method: Keep the wavelength fixed but vary the angle of incidence – rotate the crystal about an axis – Ewald sphere remains fixed in space while the reciprocal lattice rotates along with the crystal lattice about the same axis and by same amount – each reciprocal lattice point makes a circle about the rotation axis – whenever this intersects with the Ewald sphere there will be a Bragg peak.

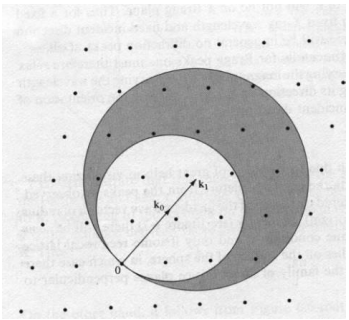


**Figure 6: Laue method**

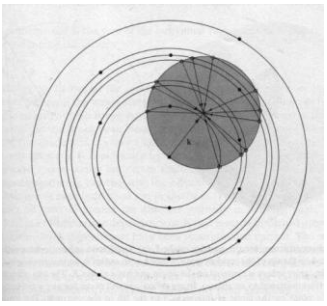

**Figure 7: Rotating crystal method**

3. Debye-Scherrer/powder method: Used for powder specimens – size of crystallites still big enough to cause diffraction – incident angle and wavelength are kept fixed – sample I rotated about fixed axis – all crystallites randomly oriented – so equivalent to rotating the reciprocal lattice over all possible axes of rotation – diffraction pattern equivalent to that of single crystal at all possible orientations to incident radiation.

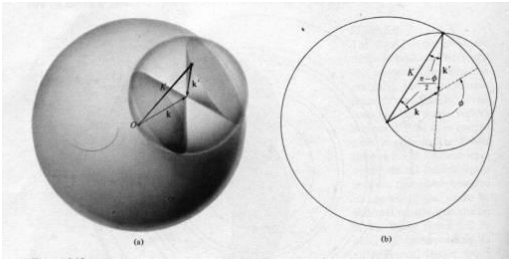

**Figure 8: Debye-Scherrer/powder method**

## Geometrical Structure Factor:

Till now dealt with lattice with a monoatomic basis. Consider a lattice with a multiple unit basis – identical scatterers at $\boldsymbol{d}_i$ – phase difference between rays scattered at $\boldsymbol{d}_i$and $\boldsymbol{d}_j$ is $\propto e^{i\boldsymbol{K}.(\boldsymbol{d}_i-\boldsymbol{d}_j)}$ - the amplitude of radiation scattered from the lattice site $\propto \sum_i e^{i\boldsymbol{K}.\boldsymbol{d}_i}$ - this is the geometric structure factor.

$$S_K = \sum_i e^{i\boldsymbol{K}.\boldsymbol{d}_i}$$

Intensity of scattered radiation $I \propto |S_K|^2$. Effect of $S_K$ is most dramatic when it vanishes
E.g. – For BCC lattice, $d_1 = 0, d_2 = \frac{a}{2}(\boldsymbol{x}+\boldsymbol{y}+\boldsymbol{z})$; any general $\boldsymbol{K}$ in the cubic system is $K = \frac{2\pi}{a}(n_1\boldsymbol{x} + n_2\boldsymbol{y} + n_3\boldsymbol{z})$. Then

$$S_K = \sum_i e^{i\boldsymbol{K}.\boldsymbol{d}_i} = 1 + \exp\{i\pi(n_1+n_2+n_3)\} = 1 + (-1)^{n_1+n_2+n_3}$$

$$= 2 \text{ for } n_1+n_2+n_3 \text{ even}$$
$$= 0 \text{ for } n_1+n_2+n_3 \text{ odd}$$

This converts the Simple cubic reciprocal lattice into FCC.