The geometric construction of Ewald sphere and Bragg condition:

The construction of Ewald sphere must be done such that the Bragg condition is satisfied. This can be done as follows:

i) Draw a wave vector $\vec{k}$ in the direction of x-ray beam. It is chosen to start from a certain origin which represents a reciprocal lattice point.

ii) Draw a sphere of radius $|\vec{k}| = \frac{2\pi}{\lambda}$ about this chosen origin.

iii) A diffracted beam of wave vector $\vec{k}'$ (with a magnitude of $|\vec{k}'| = \frac{2\pi}{\lambda}$) will be formed if the sphere intersects at any other reciprocal lattice point (at the tail of this vector).

iv) A reciprocal lattice vector $\vec{G}$ that connects the reciprocal lattice point (origin) to the reciprocal lattice point (at the tail of diffracted beam vector) such that $\vec{G} = \vec{k}' - \vec{k}$, as shown in figure 42, where $\vec{K} = \vec{G}$ is chosen.

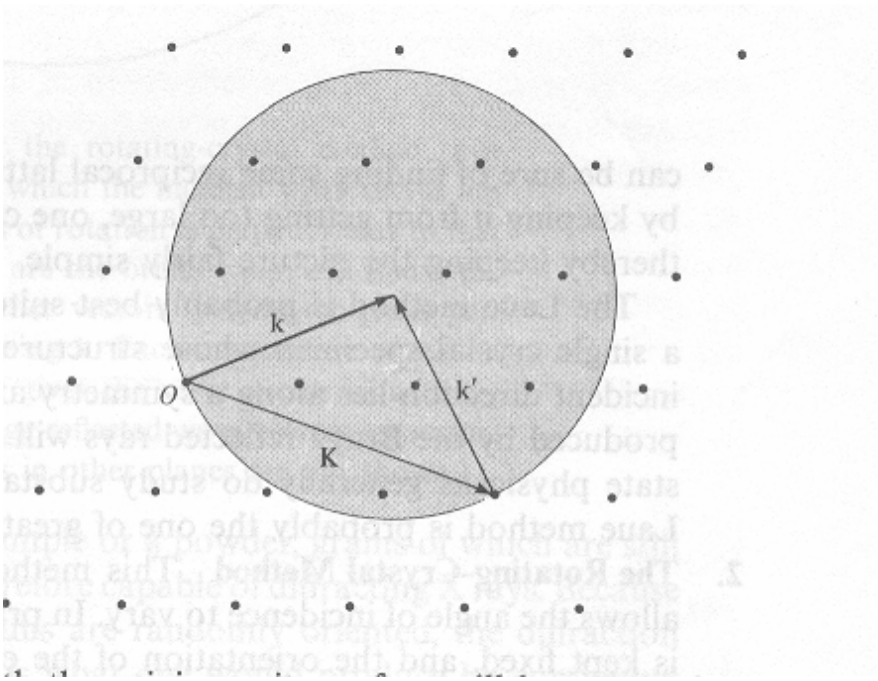

Figure 42: The Ewald sphere construction.

Experimental techniques:

The wave length, in most experiments, is controlled by regulating the energy of the beam particles. The wave length λ of any beam particles can be easily obtained from the relation $\lambda = (\frac{2\pi^2\hbar^2}{mE})^{1/2}$, where m is the mass of the particle and E is the energy of the beam particles. However the wave length λ of photons is $\lambda = (\frac{2\pi\hbar c}{E})$, where *c* is the velocity of light. Photons useful for structure analysis have energies on the order of 10 keV. While electrons have energies on the order of 100eV and protons have energies on the order of 0.1eV.

The wave length λ of the continuous portion of x-ray radiation can be obtained at a minimum $\lambda_{\min} = (\frac{2\pi\hbar c}{eV})$, where V is the accelerating potential of the incident electrons that appear as photons in the x-ray instrument. This wave length has another limit λ_{max}.

The wave length λ of the other portion of x-ray radiation (which represents a series of narrow, intense peaks with certain wavelengths) depends on the characteristic lines of the typical target employed in the x-ray instrument. For example, the average of the K_α lines is at 1.54 $\mathring{A}$ and that of K_β lines is at 1.39 $\mathring{A}$ for a copper target.

Three main experimental methods:

1) Laue method
2) Rotating crystal method.
3) Powder method.

In each of these methods, the main purpose is to make sure that a reasonable number of peaks can be obtained either by using a wide spectrum of wave lengths or a wide variety of crystal orientations. In particular, an incident wave vector $\vec{k}$ will lead to a diffraction peak (or "Bragg reflection") if and only if the head of this wave vector lies on k-space Bragg plane. Thus, to search for Bragg peaks, we must either fix the magnitude of $\vec{k}$ and keep varying its direction (varying the orientation of the crystal with respect to the incident beam direction), or changing the magnitude of $\vec{k}$ (i.e. changing the wave length of the incident beam).

1. The Laue method:

In this method the continuous portion of x-ray radiation is used to illuminate the sample under study. The wave lengths in the range $\lambda_{min} < \lambda < \lambda_{max}$ with values $0.2\,\mathring{A} < \lambda < 3\,\mathring{A}$ may b used. Now a single crystal of fixed orientation from a fixed incident beam direction $\hat{n}$ with the above-mentioned range of wave lengths can be used to get Bragg peaks. The Ewald spheres for the Laue method can be constructed when two vectors are drawn in the same direction with their heads at the same reciprocal point, as shown in figure 43. The longer vector $\vec{k}_o$ has a magnitude $\frac{2\pi}{\lambda_{\min}}$ and is the radius of the large sphere. The

shorter one $\vec{k}_1$ has a magnitude $\frac{2\pi}{\lambda_{\max}}$ and is the radius of the small sphere. However Bragg peaks can be observed corresponding to any reciprocal lattice vectors lying within the region contained between the two spheres. The projection of the reciprocal lattice vectors $\vec{G}$ along the unit vector $\hat{n}$ in the direction of the incident beam may be obtained from:

$$\hat{n} \bullet \vec{G} = -\left|\vec{G}\right| \sin\theta \ ,$$

$$\Rightarrow \sin\theta = -\frac{\hat{n} \bullet \vec{G}}{\left|\vec{G}\right|}$$

Also $\sin\theta = \frac{\left|\vec{G}\right| / 2}{\left|\vec{k}\right|} = \frac{\lambda}{4\pi}\left|\vec{G}\right|$.

Thus the required wave length can be found as:

$$\lambda = -4\pi \frac{\hat{n} \bullet \vec{G}}{\left|\vec{G}\right|^2} .$$

Notes:

1) A given peak may be found when the wavelength for each reciprocal lattice vector is evaluated within the range $\lambda_{min} < \lambda < \lambda_{\max}$ and if the structure factor does exist.
2) The scattering angle from the above-mentioned relation can be used to find the direction of $\vec{G}$ and not its magnitude.
3) Since the range of the wave lengths in the incident beam is limited then the relation $\lambda = -4\pi \frac{\hat{n} \bullet \vec{G}}{\left|\vec{G}\right|^2}$ can be used to place limits on the magnitude of reciprocal lattice vectors.

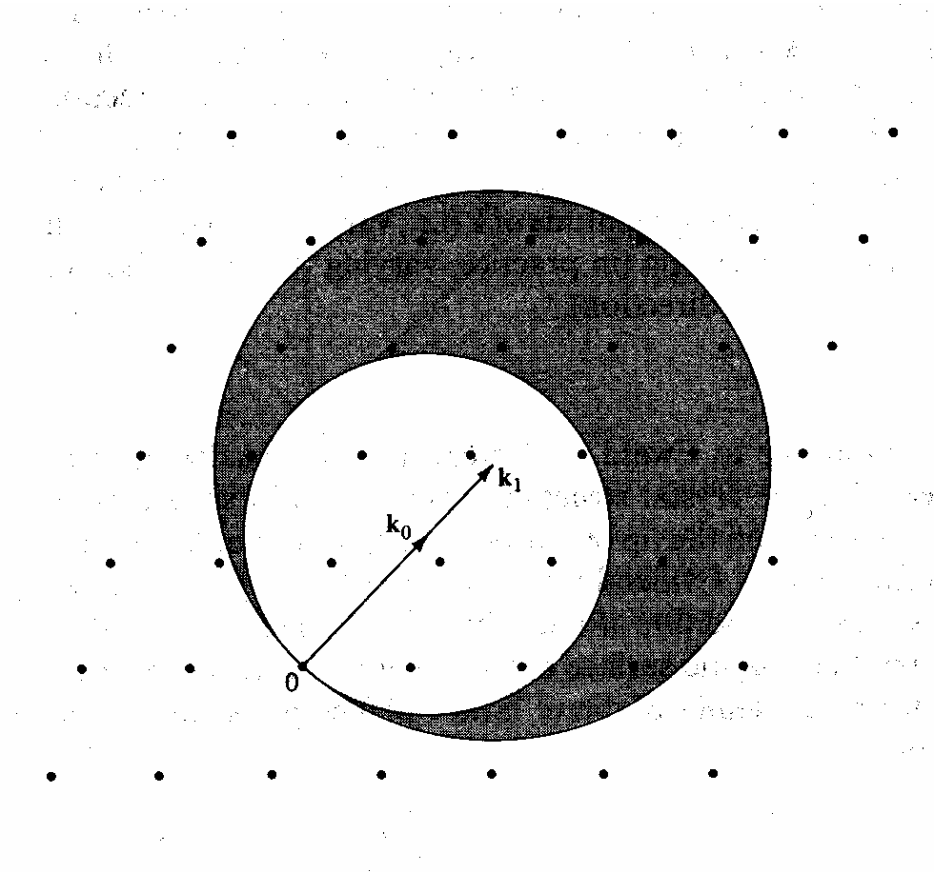

Figure 43: The Ewald spheres construction for the Laue method.

The use of Laue method:

This method is widely used to determine lattice symmetry. In particular, it is used to determine the orientation of a single crystal sample whose structure is known. If the incident direction lies along a symmetry axis of the crystal (i.e. four fold symmetry for NaCl structure) the pattern of spots produced by the Bragg reflected rays will have the same symmetry. This is shown in figure 44.

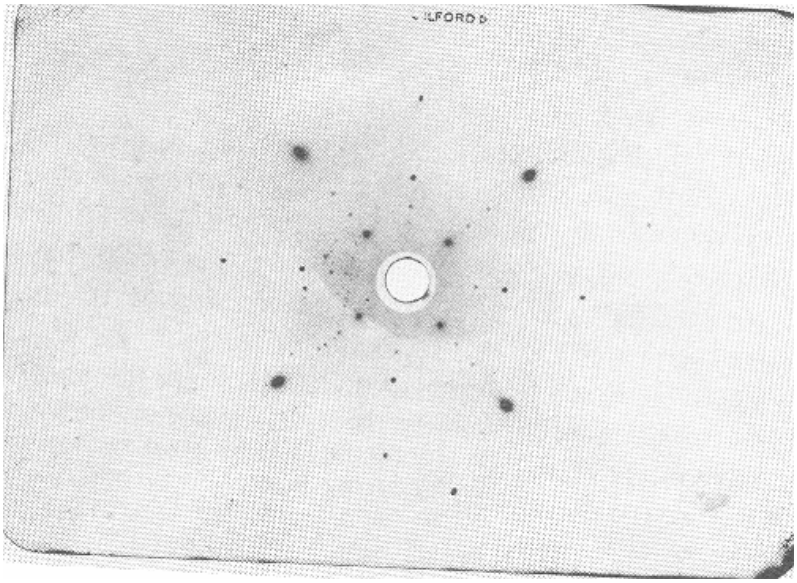

Figure 44: A Laue pattern for NaCl crystal. This pattern shows the four fold symmetry.

2. The rotating-crystal method:

In this method a monochromatic x-ray is used with varying angle of incidence. The direction of the x-ray beam is kept fixed and the orientation of the crystal varied. As the crystal rotates the reciprocal lattice points will rotate about the fixed axis. Thus the Ewald sphere (which is determined by the fixed incident wave vector $\vec{k}$) is fixed in k-space, while the entire reciprocal lattice rotates about the axis of rotation of the crystal. However, as reciprocal lattice rotates, different reciprocal lattice points cross the surface of the Ewald sphere and when a point is on the surface, the corresponding intensity peak is produced, as shown in figure 45.

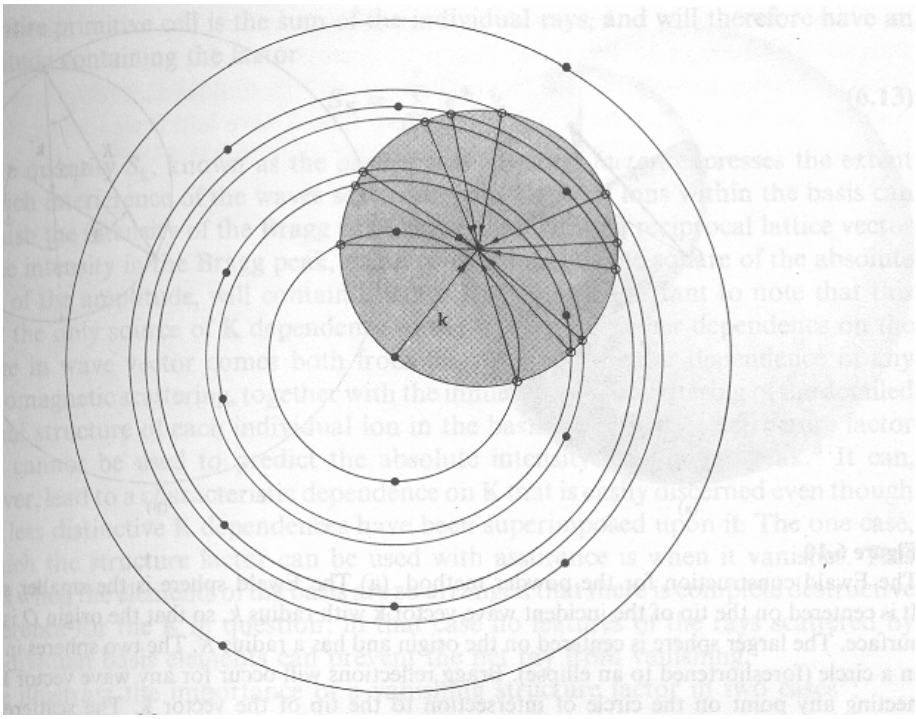

Figure 45: The Ewald construction for the rotating-crystal method.

The use of rotating-crystal method:
It is used to determine the shape and size of the unit cell.

3. The powder method (or Debye-scherrer method):

This method is similar to the previous method in (2) (the rotating-crystal method), but has in addition the axis of rotation is changed over all possible orientations. In this method a polycrystalline sample (or a powder of large number of small randomly oriented crystals) is illuminated by a monochromatic beam. The Bragg peaks will be found by fixing both the incident beam wave vector $\vec{k}$ and the Ewald sphere and then allowing the reciprocal lattice to rotate through all possible angles about the origin so that each reciprocal lattice vector $\vec{K}$ generates a sphere of radius $\vec{k}$ about the origin. Such a sphere will intersect the Ewald sphere in a circle provided that K is less than 2k, as shown in figure 46. The vector joining any point on such a circle with the head of $\vec{k}$ is a wave vector $\vec{k}'$, for which scattered radiation will be observed. Each reciprocal lattice vector of

length less than $4\pi/\lambda$ and non-vanishing structure factors will have a corresponding scattered peak.

$K = 2k\sin\frac{\phi}{2}$.

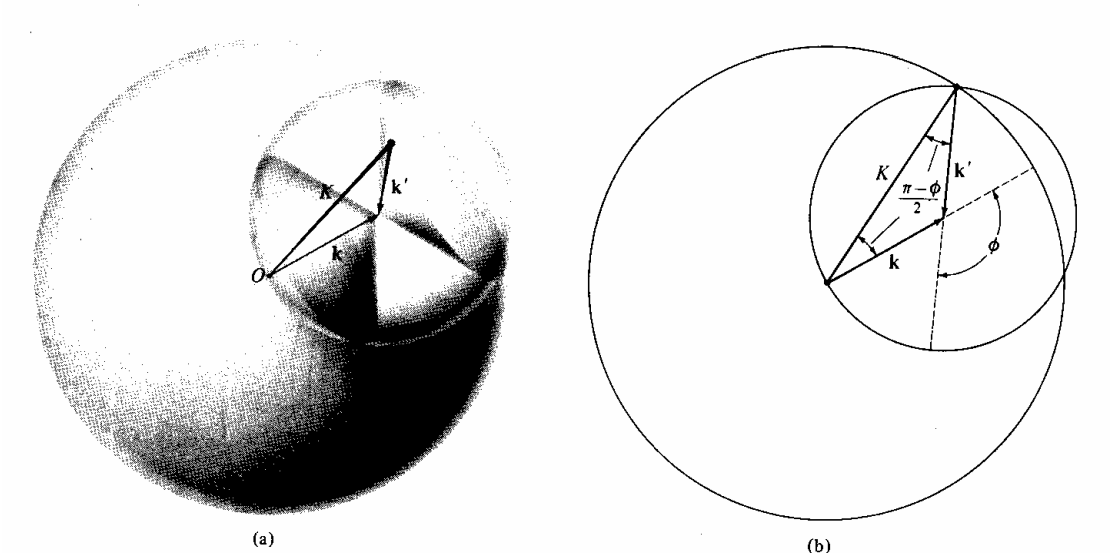

Figure 46: The Ewald construction for the powder method.

A crystal is oriented such that an intense scattered beam occurs with an angle θ. If the crystal is rotated about the direction of the incident beam, the scattered beam rotates around the surface of a cone with apex at the crystal and with an angle of apex equal twice the scattering angle (i.e $\phi = 2\theta$), as shown in figure 47.

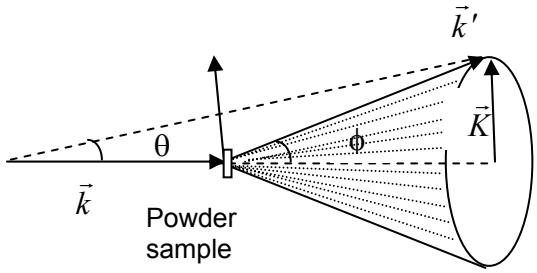

Figure 47: The scattered beam rotates around the surface of a cone with apex at the sample with $\phi = 2\theta$.

The indexing of powder pattern:

The powder pattern on a film may appear as a series of concentric rings, one for each possible scattering angle. If we consider a cubic crystal of edge a, the value of a can be determined experimentally. Now if the simple cubic lattice is used as a basis for the indices, the separation of the $(hk\ell)$ planes is given by: $d = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}}$. By substituting this expression into Bragg law we get $\sin^2\theta = \frac{\lambda^2 N}{4a^2}$, where $N = n^2(h^2 + k^2 + \ell^2)$.

The scattering angle θ is measured for each ring and a value of N is assigned for each ring. Values of N are selected so that their ratios are the same as the ratios of the orresponding values of $\sin^2\theta$. If more than one set of integers has the same ratios, the one with the smallest values is usually selected

e.g. for bcc lattice N must be even because $h + k + \ell$ is even and the square of even is even. Also the square of odd is odd.

For fcc lattice the indices must be all even or all odd.