Chapter 5

What is XRD used for?

XRD uses x-rays to probe the structure of matter.

Because x-ray wavelengths (~ 0.1 nm) are roughly similar to interatomic spacings in most crystals (~ 0.5 nm), strong diffraction effects are seen.

The crystal structure and even the crystallite spacing and orientation in space can be determined using XRD.

What is the expression for the intensity of scattered x-rays and what condition must be met?

When the crystal contains very many unit cells, the terms with $e^{i(G-K)r}$ oscillate about zero and contribute nothing to the integral except when $G = K$:

$$\int e^{i(G-K)r} dr = \begin{cases} V, & G = K \\ 0, & otherwise \end{cases}$$

The intensity $I(K)$ at such a condition is given by:

$$I(K = G) \propto |\rho_G|^2$$

The condition $G = K$ is the key equation in x-ray diffraction of crystals. We represent it by a variety of graphical methods but one of the most common is the Ewald sphere

Note: $\boldsymbol{K} = k - k_0$ is the vector representing the diffracted x-ray k-vector (k) minus the incident x-ray k-vecotr (k_0), both of which having length = $\frac{2\pi}{\lambda}$, and $\boldsymbol{G} = h\boldsymbol{g_1} + k\boldsymbol{g_2} + l\boldsymbol{g_3}$ is the reciprocal lattice vector.

Provide a qualitative description of the Ewald Sphere

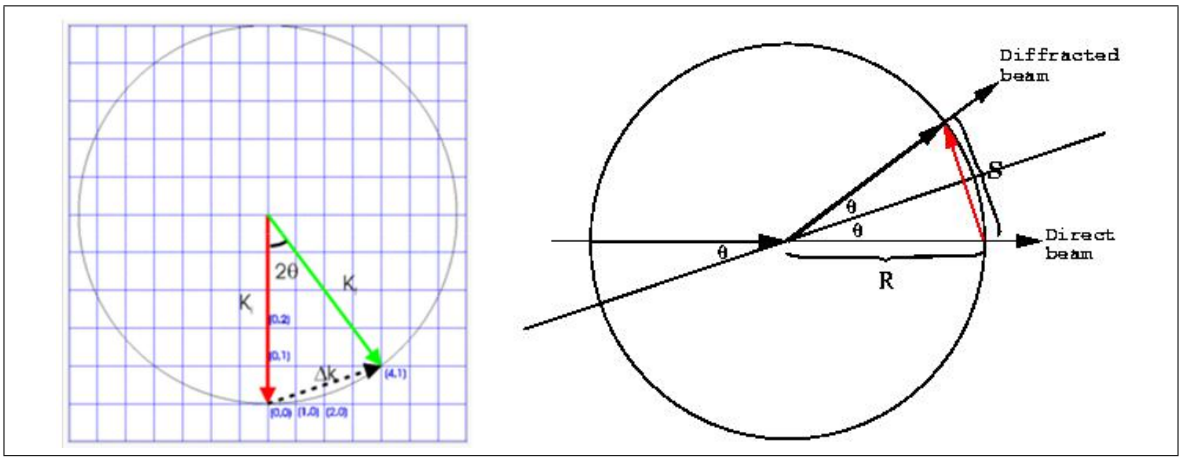
The Ewald sphere is the surface, in reciprocal-space, that all experimentally-observed scattering arises from. (Strictly, only the elastic scattering comes from the Ewald sphere; inelastic scattering is so-called 'off-shell'.) A peak observed on the detector indicates that a reciprocal-space peak is intersecting with the Ewald sphere.

- The Ewald sphere allows you to visualize a diffraction experiment.
- Diffraction only occurs when a reciprocal lattice point intersects the Ewald sphere.
- The diffracted beam will "travel" from the center of the Ewald sphere through the point where its reciprocal lattice point intersects the sphere.
- The radius of the Ewald sphere is $\frac{2\pi}{\lambda}$.
- The Ewald sphere construction is entirely equivalent to Bragg's diffraction law.

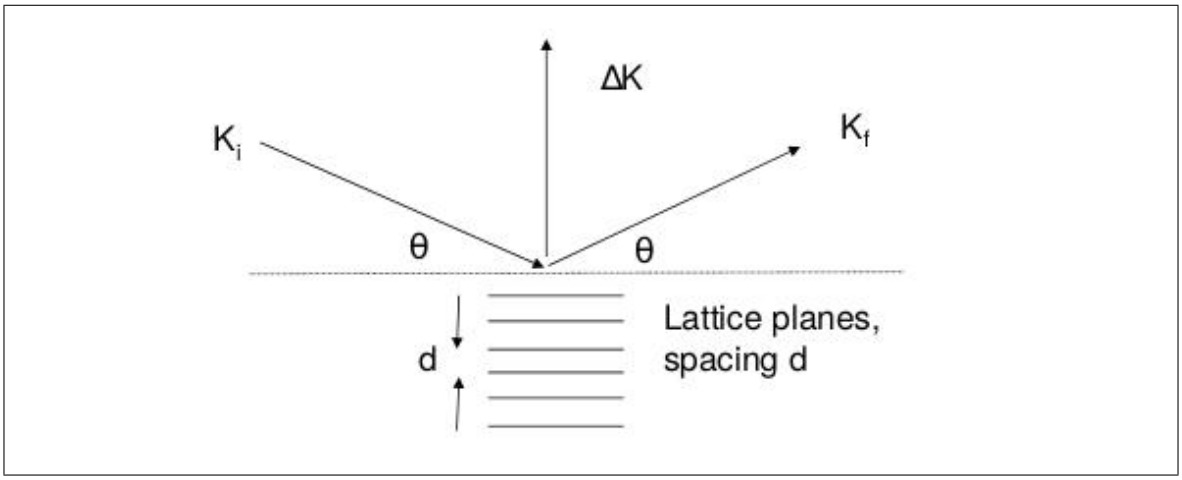
Construct the Ewald sphere, declaring any assumptions made.

1. The incident electron k-vector (K_i) magnitude defines the radius of the circle ($K = \frac{2\pi}{\lambda}$).
2. The diffracted electron k-vector (K_f) must be the same length: *elastic* process.
3. A circle is drawn of radius K.
4. K_i is drawn as a arrow with tail at the centre and tip at circumference.
5. The reciprocal lattice of the material is superimposed to scale and the $(0, 0, 0)$ zone centre placed at the tip of K_i. The orientation of the reciprocal lattice is determined by the real orientation of the crystal with respect to the electron beam.
6. Diffracted electrons can only occur at angles 2θ, such that $\Delta K = K_f - K_i$ are vectors of the material reciprocal lattice, i.e. where the circle "cuts" a reciprocal lattice point.

The Ewald sphere is drawn below. Two different diagrams are provided in order to give a clearer uderstanding:



A diagram of the diffraction as an interaction with the crystal interface is given below:



From the Ewald sphere construction, show that Bragg's law holds

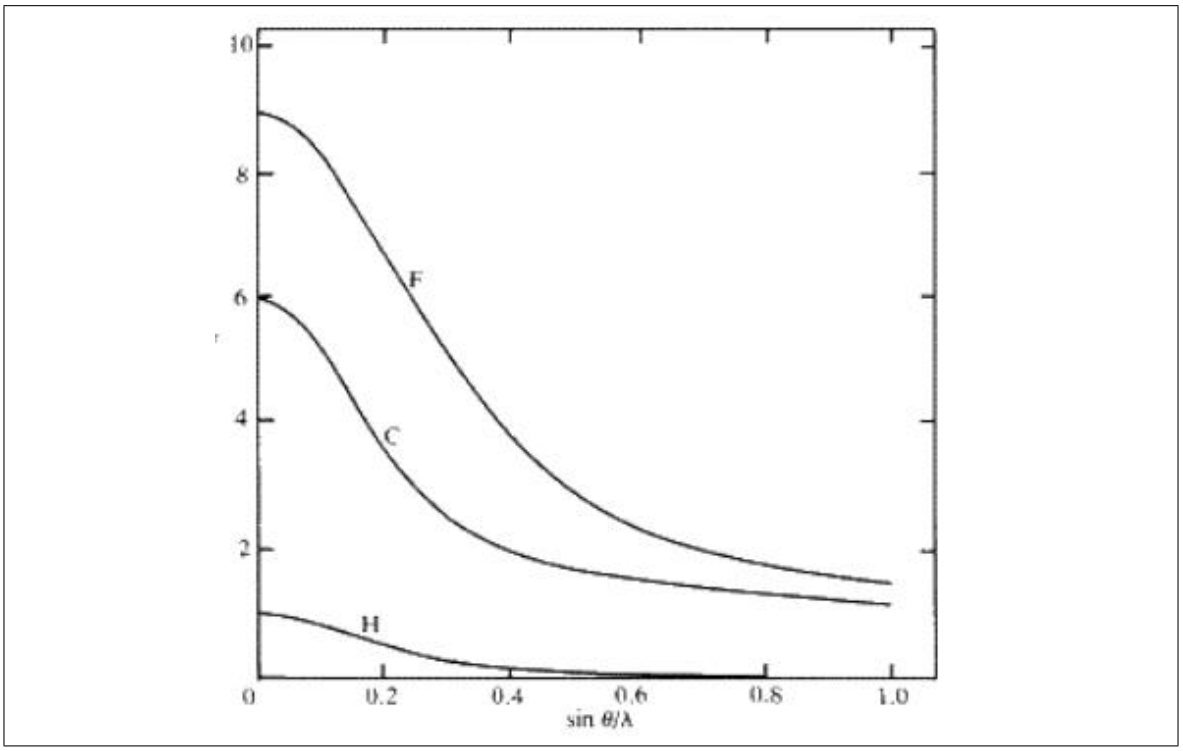
The magnitudes of K_i and K_f are equal to $K = \frac{2\pi}{\lambda}$. And $\Delta K = \frac{2\pi}{d}$, corresponding to the spacing, d, between two points on the lattice, but in reciprocal space (wavenumber/momentum space).

So we have,

$$\begin{aligned} K\sin\theta + K\sin\theta &= \Delta K \\ 2K\sin\theta &= \Delta K \\ 2\left(\frac{2\pi}{\lambda}\right)\sin\theta &= \frac{2\pi}{d} \\ \therefore \lambda &= 2d\sin\theta \end{aligned}$$

What is the shape of the atomic form factor as a function of $\sin\theta/\lambda$?

In general the atomic form factor, f_α, has a shape (as a function of $\sin(\theta)/\lambda$) somewhat like the forms shown, for all atoms. Note that at $\theta = 0$, the y-axis is just the atomic number, Z of the species.



Give expressions for the structure factor, S_G, and the scattering density, ρ_G

$$S_G = \sum_\alpha f_\alpha e^{-iG.r_\alpha}$$

$$\rho_G = \frac{S_G}{V_c}$$

where V_c is the volume of a unit cell for the crystal.

And thus the intensity of a particular reflection is determined by the structure factor and the atomic form factor by,

$$I(K = G) \propto \frac{|S_G|^2}{V_c^2} = \frac{1}{V_c^2} \left| \sum_\alpha f_\alpha e^{-iF.r_\alpha} \right|^2$$

Give 4 uses for x-ray diffraction

1. To determine the crystal structure of unknown crystalline phases
2. To determine the orientation and lattice constants of known crystalline phases
3. To determine the crystal quality of thin and bulk crystal phases
4. To determine the relative orientation of e.g. a thin epitaxial crystalline film on a crystalline substrate

List some prerequisites needed for x-ray diffraction

For diffraction applications, a monochromatic x-ray source is needed.

Generally one uses the stronger Kα characteristic line radiation.

Clearly some filtering of the x-ray source is required to remove e.g. Kβ radiation and the bremmstrahlung continuum radiation.

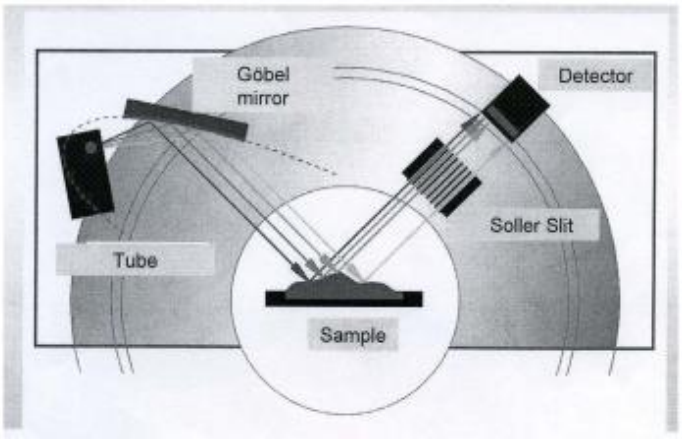
List the components of a thin film texture diffractometer and provide a diagram

The x-ray diffractometer used in DCU is a so-called thin film texture diffractometer.

It operates in a parallel beam geometry has a few main parts:

1. X-ray source
2. Goebel mirror collimator
3. Sample mount and goniometer
4. Detector

The optics look more or less as below and the system is a parallel beam geometry:

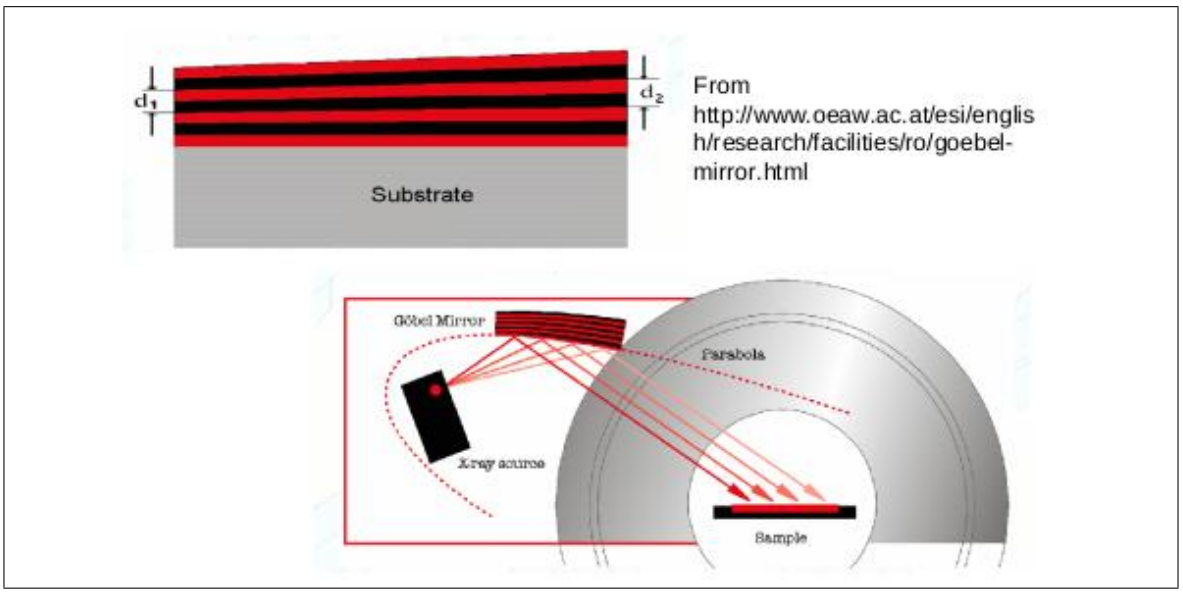


What is the purpose of a Goebel mirror?

The purpose of the Goebel mirror is to collimate the divergent beam (effectively coming from a point-like source on the tube anode).

The Goebel mirror is a multi-layer mirror with stacks of high and low Z materials alternating.

By either bending the layers (generally into a section of a parabola, with the x-ray source at the parabola focus) or allowing the layer thicknesses to vary across the mirror surface one can cause a collimating action.

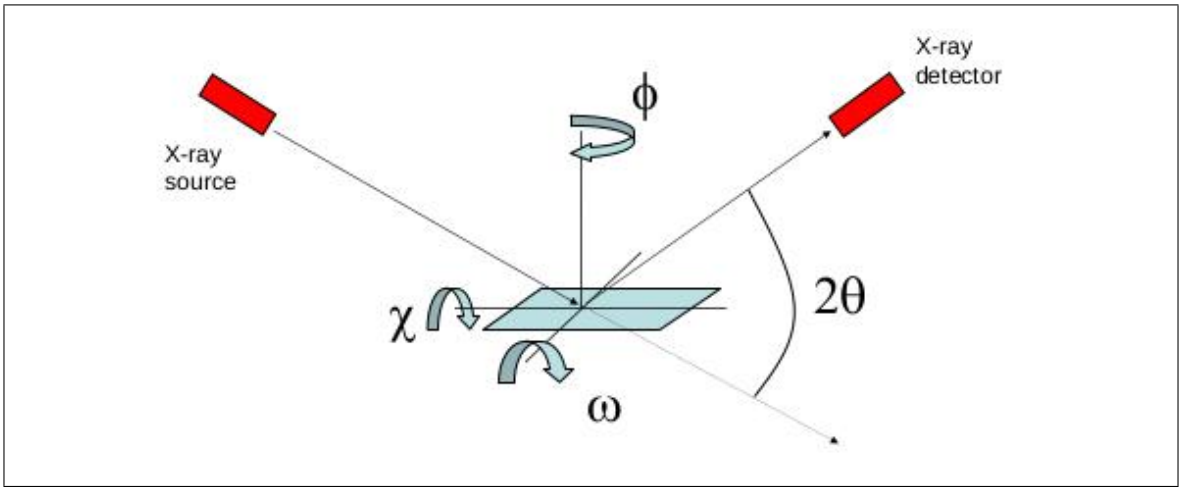


Discuss the use of a goniometer

The sample sits on a mount which allows its orientation to be altered – a goniometer.

Depending on the number of degrees of freedom of this goniometer and the allowed movement of the source and/or detector the XRD system can be called a "one-circle" diffractometer, "two circle" etc.

The DCU system is a "four-circle" diffractometer, a three circle goniometer plus a moveable detector.



The ability to change χ, ω, φ and 2ϑ independently is why such systems are called "four circle".

How are the diffracted x-rays detected?

The x-rays are detected by a scintillation detector (single photon detector) with a set of collimating slits in front of it (to remove any randomly scattered non-parallel x- rays).

When the incident x-ray strikes the fluorescent crystal (scintillator) at the front of the detector a visible photon is produced.

A photocathode struck by the photon ejects an electron.

A series of dynodes after the scintillator/photocathode amplifies the electron into a detectable electrical pulse. (A dynode is an electrode in a vacuum tube that serves as an electron multiplier through secondary emission.)