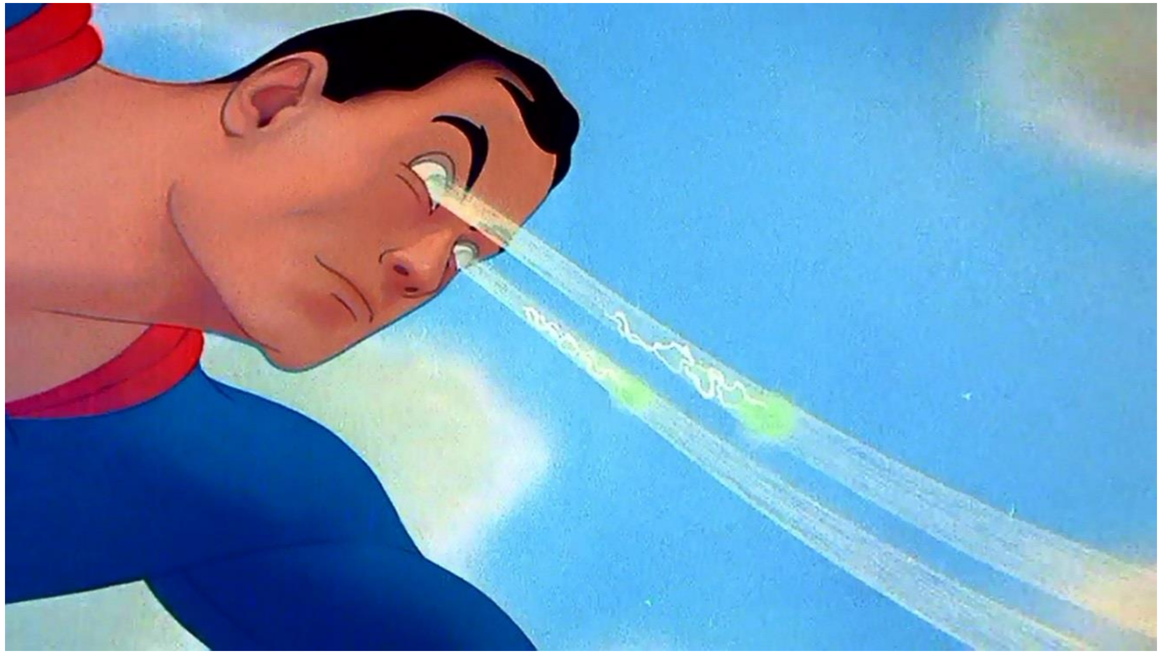
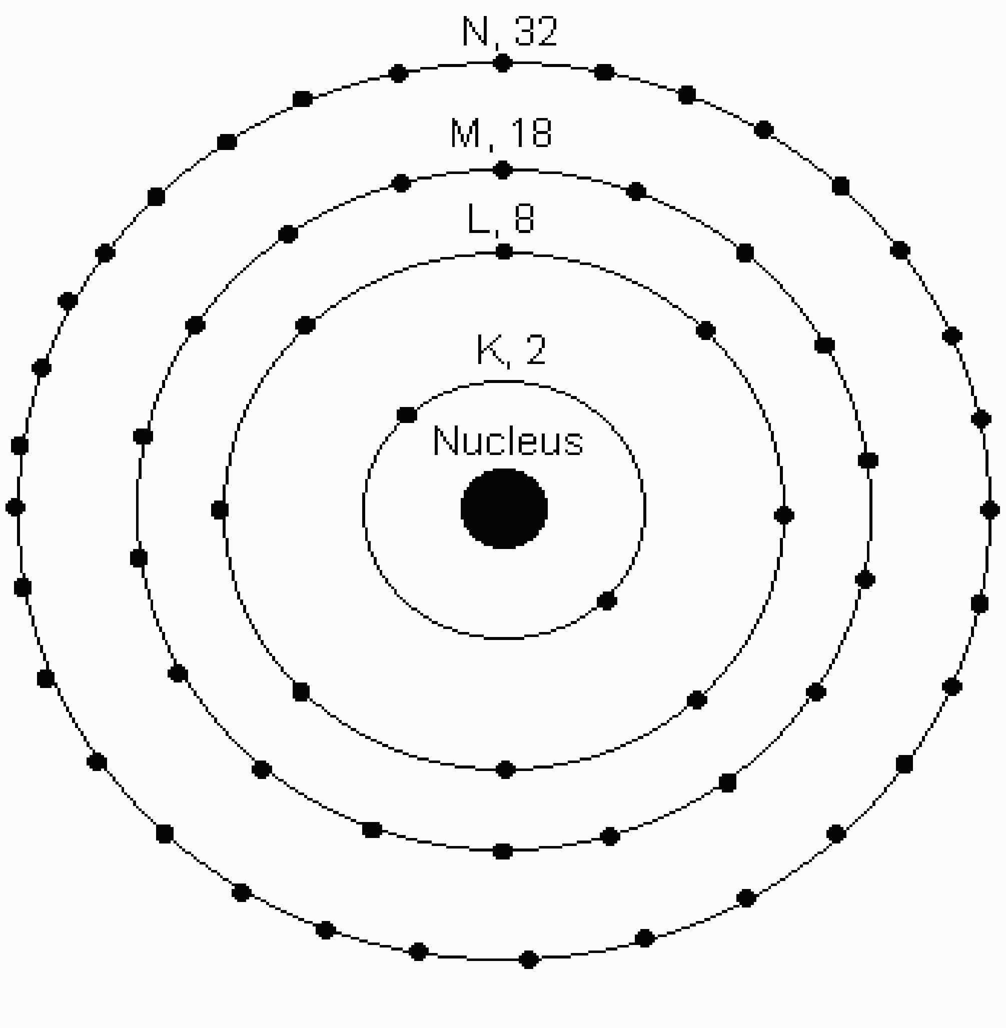
3-X-Ray Diffraction



Primer in Materials Science

Spring 2021

Atom Structure



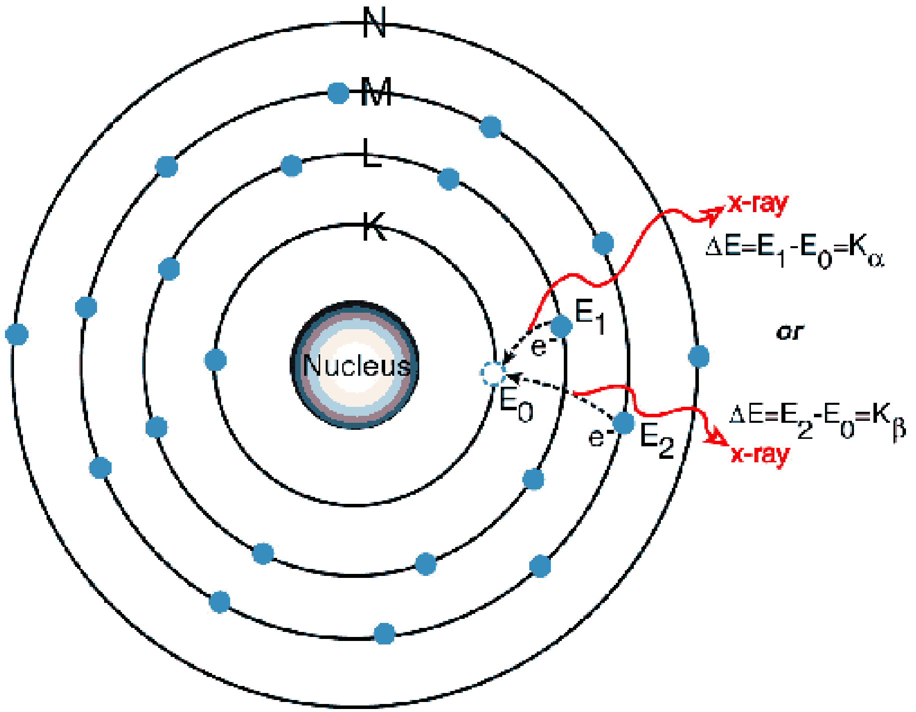
Quantum numbers

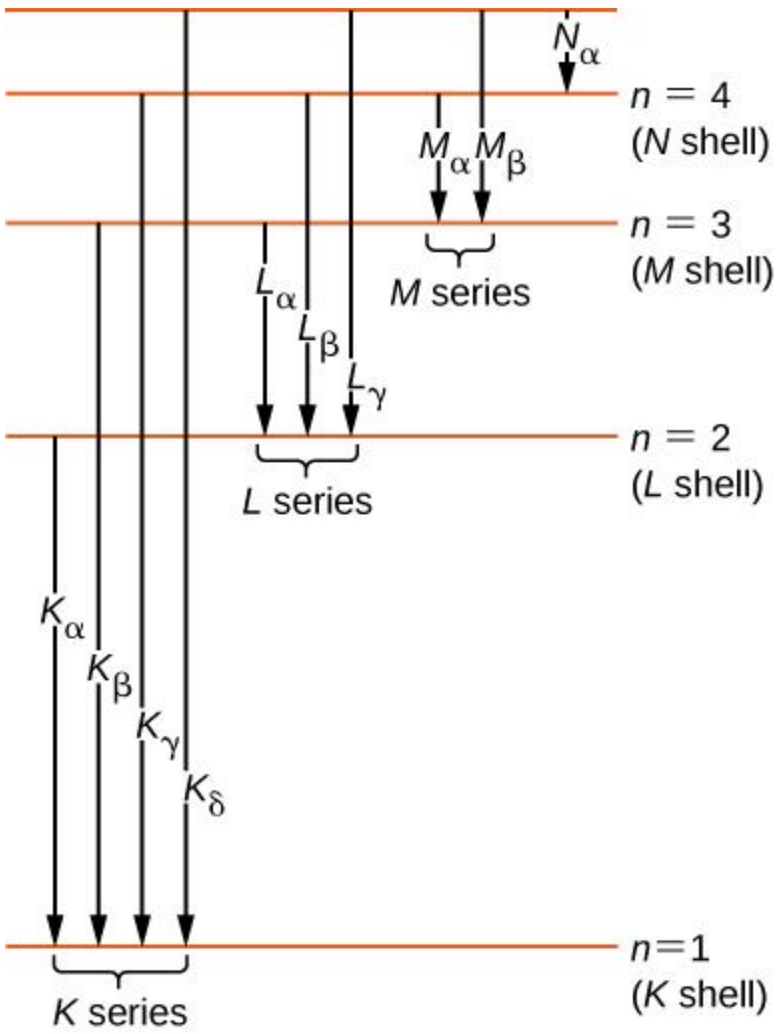
The energy level to which each electron belongs is determined by four quantum numbers

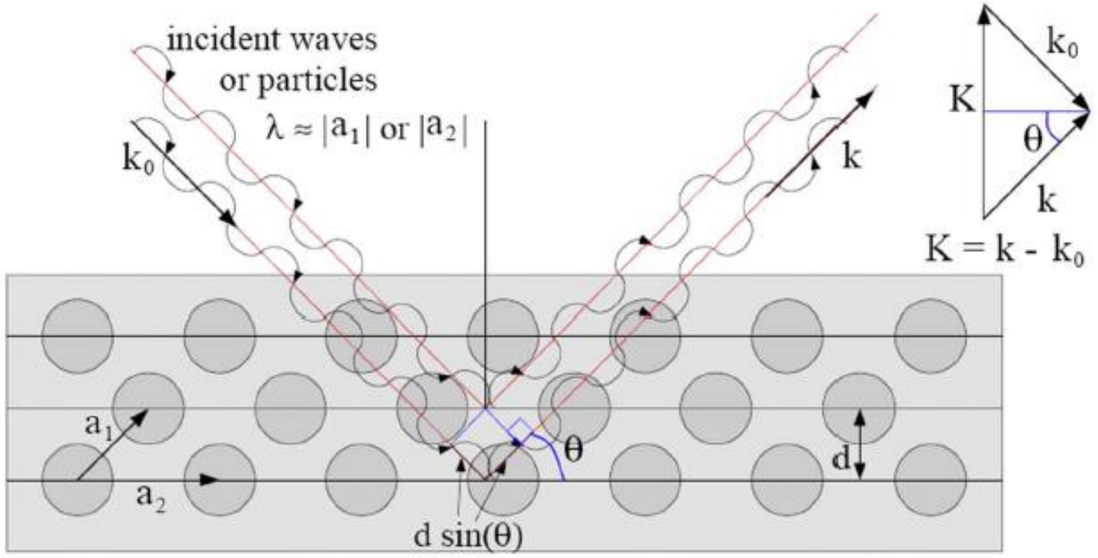
- n – this principle quantum number assigned integral values 1, 2, 3, 4, 5 , … that refer to the quantum shell to which the electron belongs. Quantum shells are also assigned a letter. n=1 is K, n=2 is L, n=3 is M, and so on
- l - is the azimuthal quantum number which determines the angular momentum of the electron. l= 0,1,2,…n-1. the azimuthal quantum numbers are designated by lower case letters. s for l=0, p for l=1, d for l=2, f for l=3, etc.
- There are another two quantum numbers: m_l=-l…-1,0,1…l; m_s=1/2, -1/2 (for electron)

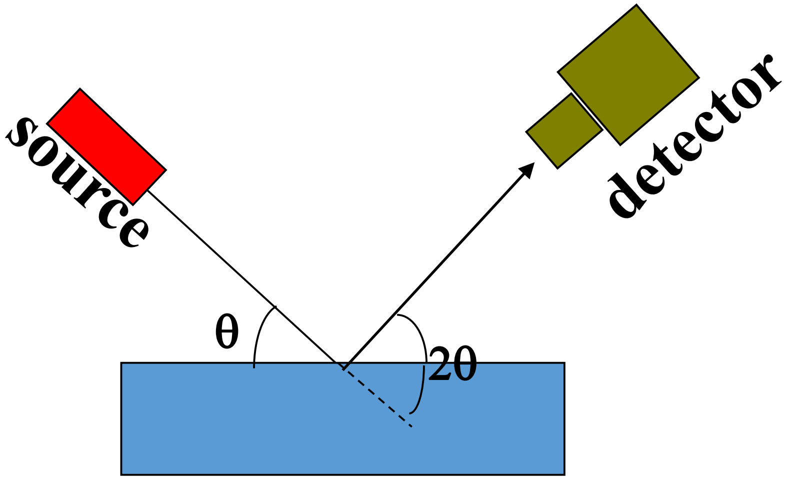
X-Ray

Selection rule: The change in orbital angular momentum can be Δl= ± 1









Bragg's Law:

1) We can get a diffraction only from planes that are parallel to the surface (the incident angle = the diffracted angle = θ).

2)

$$\left|\vec{K}\right| = n\left|\vec{H}_{hkl}\right|$$

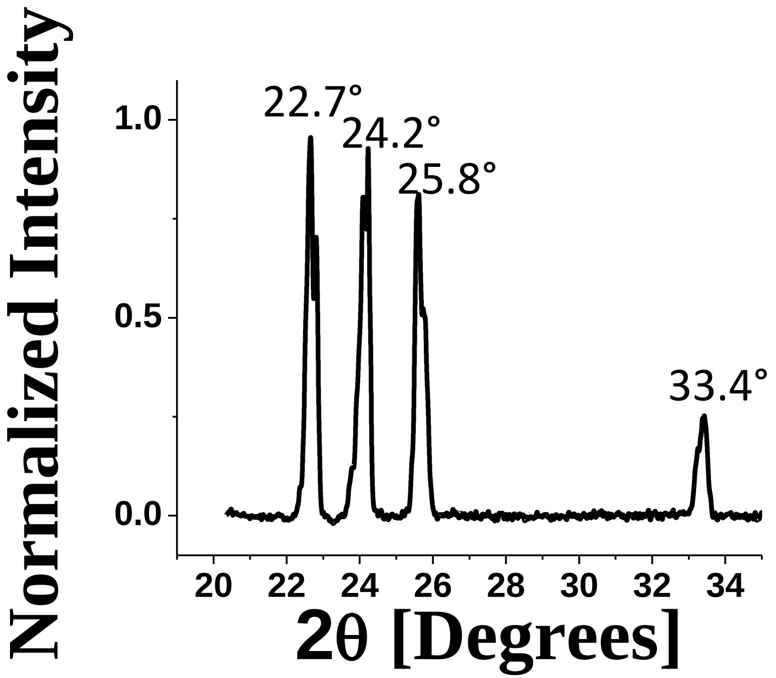
$$\left|\vec{K}\right| = 2\left|\vec{k}\right|\sin\theta \qquad \left|\vec{k}\right| = \frac{1}{\lambda};\left|\vec{H}_{hkl}\right| = \frac{1}{d_{hkl}}$$

$$\frac{n}{d_{hkl}} = 2\frac{1}{\lambda}\sin\theta$$

$$n\lambda = 2d_{hkl}\sin\theta$$

Example 3.1

Fine the d-spacing from the following x-ray diffraction of hexagonal ice, if λ=1.54Å.



$$d_1 = \frac{1.54}{2\sin(11.35°)} = 3.91\ \text{Å}$$

d_2= 3.67Å

d_3= 3.45Å

d_4= 2.68Å

Structure Factor

$$e^{ix} = \cos x + i \sin x$$

$$e^{2\pi i} = 1; e^{\pi i} = -1; e^{\frac{1}{2}\pi i} = i$$

$$F = \sum_j f_{A_j} e^{2\pi i \vec{H} \cdot \vec{r}_j}$$

|F|= 0, forbidden diffraction

$$I \approx F^2$$

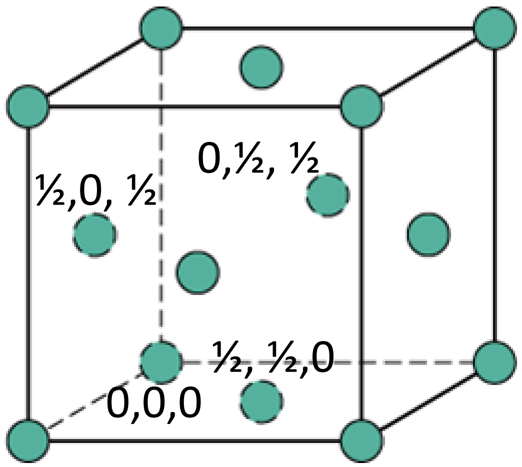
For orthogonal system :

$$F = \sum_j f_{A_j} e^{2\pi i (hx_j + ky_j + lz_j)}$$

Example 3.2

Determine the allowed and forbidden diffractions for FCC and Diamond structures.

FCC:



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

Allowed diffractions: h,k,l are all odd or all even

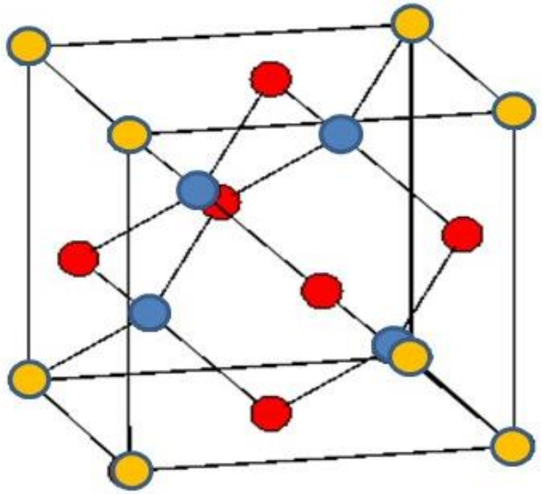
Forbidden diffractions: h,k,l are mixed

Diamond:

Diamond structure can be described as two FCC in 0,0,0 and ¼, ¼, ¼ lattice site.

FCC#1: 0,0,0 0,½, ½   ½,0, ½   ½, ½,0

FCC#2: ¼,¼,¼   ¼, ¾, ¾   ¾, ¼, ¾   ¾, ¾ ¼



$$F = F_{FCC}(1 + e^{\frac{1}{2}\pi i(h+k+l)})$$

Allowed diffractions: h,k,l are all odd; if h,k,l are all even, h+k+l=4n

Forbidden diffractions: h,k,l are mixed or h,k,l are all even, h+k+l≠4n

Example 3.3

Derive the expression for diffraction peak broadening that comes from grain size and microstrain.

Grain Size:

The uncertainty principle: $\Delta K \times \Delta X = 1$

$$\Delta X = D$$

$$\Delta K = 2\Delta\theta\cos\theta \cdot \frac{1}{\lambda}$$

$$\Downarrow$$

$$D = \frac{\lambda}{2\Delta(\theta)\cdot\cos(\theta)}$$

Microstrain:

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

$$0 = 2\Delta d \sin\theta + 2d\Delta\theta \cos\theta$$

$$\varepsilon = \frac{\langle \Delta d \rangle}{d} = \frac{\Delta(\theta)}{\tan(\theta)}$$

Grain Size, D (Sherrer Eq.):

$$D = \frac{0.9 \cdot \lambda}{\Delta(2\theta) \cdot \cos(2\theta/2)}$$; Lorentzian, *M(θ)*

Strain, ε:

$$\varepsilon = \frac{\langle \Delta d \rangle}{d} = \frac{\Delta(2\theta)}{2\tan(2\theta/2)}$$; Gaussian, *N(θ)*

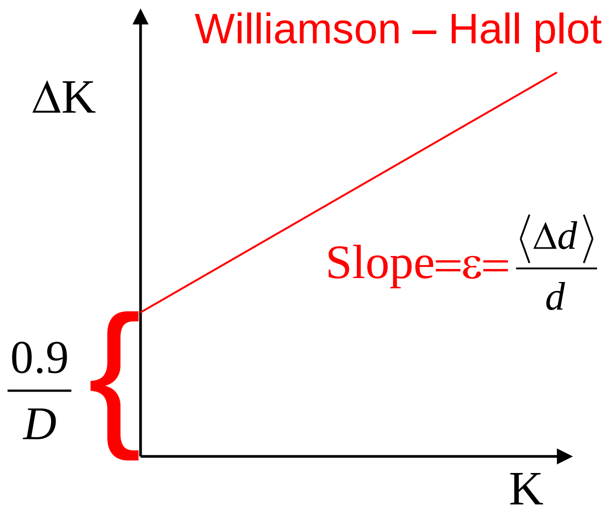
Grain Size+Strain =Voigt Function:

$$F(\theta) = \int M(\theta') \cdot N(\theta - \theta') \partial\theta'$$

Williamson – Hall plot (assuming two Lorentzians):

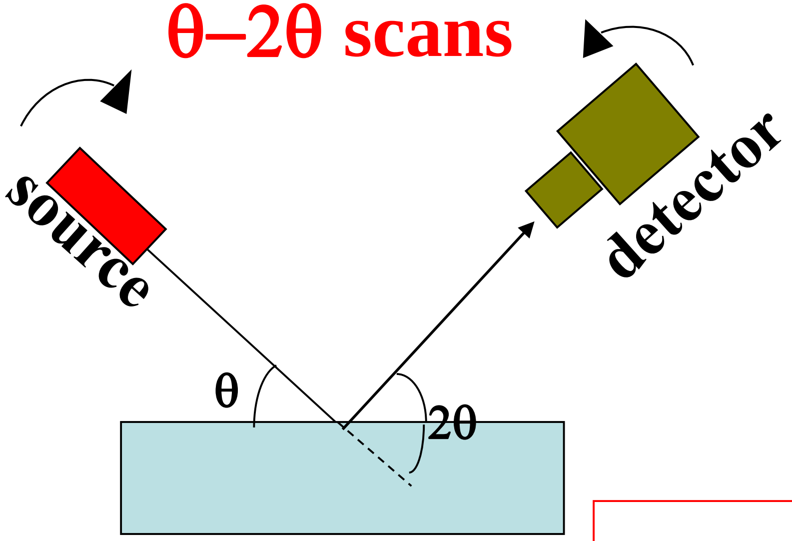
$$K = \frac{2 \cdot \sin(2\theta/2)}{\lambda}$$

$$\frac{\Delta(2\theta) \cdot \cos(2\theta/2)}{\lambda} = \Delta K = \frac{0.9}{D} + K \cdot \frac{\langle \Delta d \rangle}{d}$$

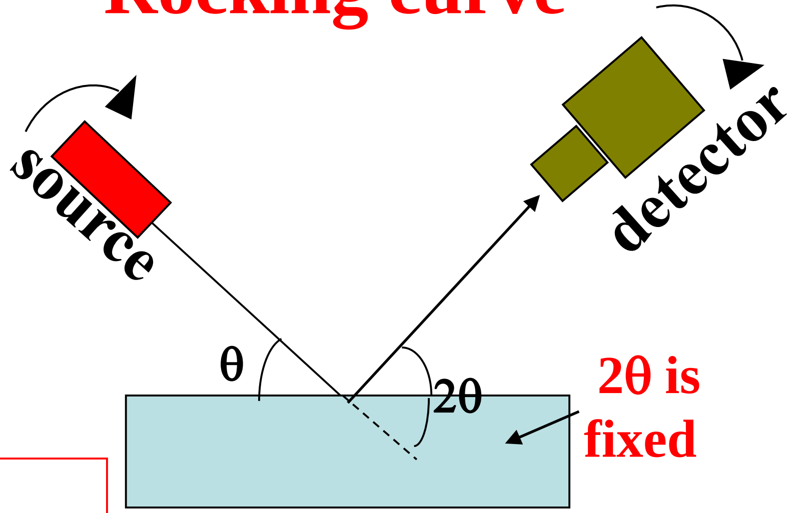


XRD

θ–2θ scans

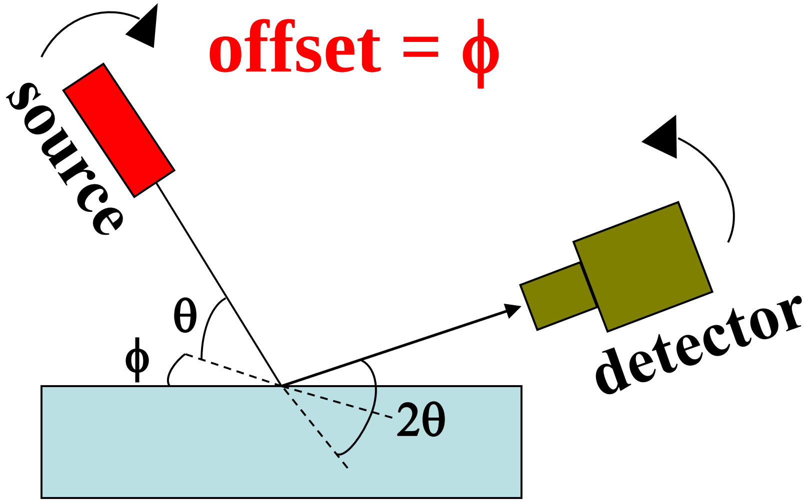


Rocking curve



$$d = \frac{\lambda}{2 \cdot \sin(2\theta / 2)}$$

θ–2θ scans with offset = ϕ



Static detector