X-ray Diffraction

Reciprocal lattice

From Wikipedia, the free encyclopedia

In physics, the reciprocal lattice of a lattice (usually a Bravais lattice) is the lattice in which the Fourier transform of the spatial wave function of the original lattice (or *direct lattice*) is represented. This space is also known as *momentum space* or less commonly *k-space*, due to the relationship between the Pontryagin duals momentum and position. The reciprocal lattice of a reciprocal lattice is the original or *direct lattice*.

Mathematical description

Consider a set of points R (R is a vector depicting a point in a Bravais lattice) constituting a Bravais lattice, and a plane wave defined by:

$$e^{i\mathbf{K}\cdot\mathbf{r}} = \cos(\mathbf{K}\cdot\mathbf{r}) + i\sin(\mathbf{K}\cdot\mathbf{r})$$

If this plane wave has the same periodicity as the Bravais lattice, then it satisfies the equation:

$$e^{i\mathbf{K}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{K}\cdot\mathbf{r}}$$
$$\therefore e^{i\mathbf{K}\cdot\mathbf{r}}e^{i\mathbf{K}\cdot\mathbf{R}} = e^{i\mathbf{K}\cdot\mathbf{r}}$$
$$\Rightarrow e^{i\mathbf{K}\cdot\mathbf{R}} = 1$$

Mathematically, we can describe the reciprocal lattice as the set of all vectors K that satisfy the above identity for all lattice point position vectors R. This reciprocal lattice is itself a Bravais lattice, and the reciprocal of the reciprocal lattice is the original lattice, which reveals the Pontryagin duality of their respective vector spaces.

For an infinite three dimensional lattice, defined by its primitive vectors $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$, its reciprocal lattice can be determined by generating its three reciprocal primitive vectors, through the formulae

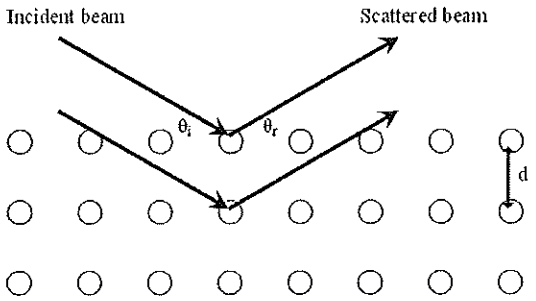
$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$
$$\mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}$$
$$\mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}$$

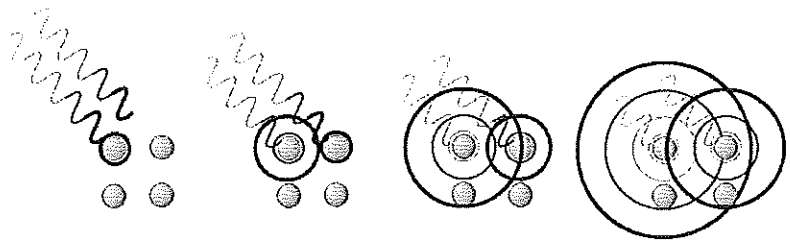
- The reciprocal lattice to an FCC lattice is the body-centered cubic (BCC) lattice.
- That of simple cubic (a), is simple cubic (2pi/a).
- That of BCC is FCC
- That of simple hexagonal (a,c) is simple hexagonal (2pi/c and 4pi/sqrt(3)/a

Bragg's Law

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

- Constructive interference only occurs for certain θ's correlating to a (*hkl*) plane, specifically when the path difference is equal to n wavelengths.



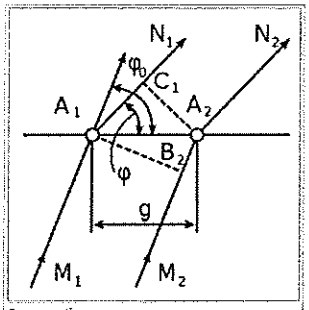


When X-rays are incident on an atom, they make the electronic cloud move as does any electromagnetic wave. The movement of these charges re-radiates waves with the same frequency (blurred slightly due to a variety of effects); this phenomenon is known as Rayleigh scattering (or elastic scattering). The scattered waves can themselves be scattered but this secondary scattering is assumed to be negligible.

Laue equations

From Wikipedia, the free encyclopedia

In crystallography, the Laue equations give three conditions for incident waves to be diffracted by a crystal lattice. They are named after physicist Max von Laue (1879 — 1960). They reduce to the Bragg law.



Laue equation

Equations

Take $\mathbf{k}_i$ to be the wavevector for the incoming (incident) beam and $\mathbf{k}_o$ to be the wavevector for the outgoing (diffracted) beam. $\mathbf{k}_o - \mathbf{k}_i = \Delta\mathbf{k}$ is the scattering vector and measures the change between the two wavevectors.

Take $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ to be the primitive vectors of the crystal lattice. The three Laue conditions for the scattering vector, or the Laue equations, for integer values of a reflection's reciprocal lattice indices (h,k,l) are as follows:

$$\mathbf{a}\cdot\Delta\mathbf{k} = 2\pi h$$
$$\mathbf{b}\cdot\Delta\mathbf{k} = 2\pi k$$
$$\mathbf{c}\cdot\Delta\mathbf{k} = 2\pi l$$

These conditions say that the scattering vector must be oriented in a specific direction in relation to the primitive vectors of the crystal lattice.

Relation to Bragg Law

If $\mathbf{G} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}$ is the reciprocal lattice vector, we know $\mathbf{G}\cdot(\mathbf{a}+\mathbf{b}+\mathbf{c}) = 2\pi(h+k+l)$. The Laue equations specify $\Delta\mathbf{k}\cdot(\mathbf{a}+\mathbf{b}+\mathbf{c}) = 2\pi(h+k+l)$. Whence we have $\Delta\mathbf{k} = \mathbf{G}$ or $\mathbf{k}_o - \mathbf{k}_i = \mathbf{G}$.

From this we get the diffraction condition:

$$\mathbf{k}_0 - \mathbf{k}_i = \mathbf{G}$$
$$(\mathbf{k}_i + \mathbf{G})^2 = \mathbf{k}_0^2$$
$$k_i^2 + 2\mathbf{k}_i\cdot\mathbf{G} + G^2 = k_0^2$$

Since $(\mathbf{k}_0)^2 = (\mathbf{k}_i)^2$ (considering elastic scattering) and $\mathbf{G} = -\mathbf{G}$ (a negative reciprocal lattice vector is still a reciprocal lattice vector):

$$2\mathbf{k}_i\cdot\mathbf{G} = G^2.$$

The diffraction condition $2\mathbf{k}_i\cdot\mathbf{G} = G^2$ reduces to the Bragg law $2d\sin\theta = n\lambda$.

References

- Kittel, C. (1976). *Introduction to Solid State Physics*, New York: John Wiley & Sons. ISBN 0-471-49024-5

Bragg condition's

The diffraction condition can be written in vector form

$$2\mathbf{k}\cdot\mathbf{G} + G^2 = 0$$

k - is the incident wave vector

k' - is the reflected wave vector

G - is a reciprocal lattice vector such that where

$$\mathbf{G} = \Delta\mathbf{k} = \mathbf{k} - \mathbf{k'}$$

the diffraction condition is met

Lattice Constants

The distance between planes of atoms is

$$d(hkl) = 2\pi / |\mathbf{G}|$$

Since **G** can be written as

$$\mathbf{G} = 2\pi/a\ (h^*\mathbf{b}_1 + k^*\mathbf{b}_2 + l^*\mathbf{b}_3)$$

Substitute in **G**

$$d(hkl) = a / (h^2 + k^2 + l^2)^{(1/2)}$$

Or

$$a = d * (h^2 + k^2 + l^2)^{(1/2)}$$

a is the spacing between nearest neighbors

Laue Conditions

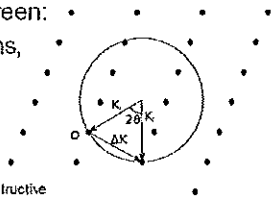
$$\mathbf{a_1}\cdot\Delta\mathbf{k} = 2\pi v_1 \qquad \mathbf{a_2}\cdot\Delta\mathbf{k} = 2\pi v_2$$
$$\mathbf{a_3}\cdot\Delta\mathbf{k} = 2\pi v_3$$

- Each of the above describes a cone in reciprocal space about the lattice vectors a_1, a_2, and a_3.
  - the v_i are integers
- When a reciprocal lattice point intersects this cone the diffraction condition is met, this is generally called the Ewald sphere.

Ewald's sphere

The Ewald sphere is a geometric construct used in electron, neutron, and X-ray crystallography which demonstrates the relationship between:

- ➢the wavevector of the incident and diffracted x-ray beams,
- ➢the diffraction angle for a given reflection,
- ➢the reciprocal lattice of the crystal



A crystal can be described as a lattice of points of equal symmetry. The requirement forconstructive interference in a diffraction experiment means that in momentum orreciprocal space the values of momentum transfer where constructive interference occurs also form a lattice (the reciprocal lattice). For example, the reciprocal lattice of asimple cubic real-space lattice is also a simple cubic structure. Another example, the reciprocal lattice of an FCC crystal real-space lattice is a BCC structure, and vice versa. The aim of the Ewald sphere is to determine which lattice planes (represented by the grid points on the reciprocal lattice) will result in a diffracted signal for a given wavelength, λ, of incident radiation.

The incident plane wave falling on the crystal has a wave vector K_i whose length is $2\pi/\lambda$. The diffracted plane wave has a wave vector K_f. If no energy is gained or lost in the diffraction process (it is elastic) then K_f has the same length as K_i. The difference between the wave-vectors of diffracted and incident wave is defined as scattering vector $\Delta K = K_f - K_i$. Since $K_i$and K_f have the same length the scattering vector must lie on the surface of a sphere of radius $2\pi/\lambda$. This sphere is called the Ewald sphere.

The reciprocal lattice points are the values of momentum transfer where the Bragg diffraction condition is satisfied and for diffraction to occur the scattering vector must be equal to a reciprocal lattice vector. Geometrically this means that if the origin of reciprocal space is placed at the tip of K_i then diffraction will occur only for reciprocal lattice points that lie on the surface of the Ewald sphere.

Small scattering-angle limit

When the wavelength of the radiation to be scattered is much smaller than the spacing between atoms, the Ewald sphere radius becomes large compared to the spatial frequency of atomic planes. This is common, for example, in transmission electron microscopy. In this approximation, diffraction patterns in effect illuminate planar slices through the origin of a crystal's reciprocal lattice. However, it is important to note that while the Ewald sphere may be quite flat, a diffraction pattern taken perfectly aligned down a zone axis (high-symmetry direction) contains precisely zero spots that exactly satisfy the Bragg condition. As one tilts a single crystal with respect to the incident beam, diffraction spots wink on and off as the Ewald sphere cuts through one zero order Laue zone (ZOLZ) after another.

Summary of Bragg & Laue

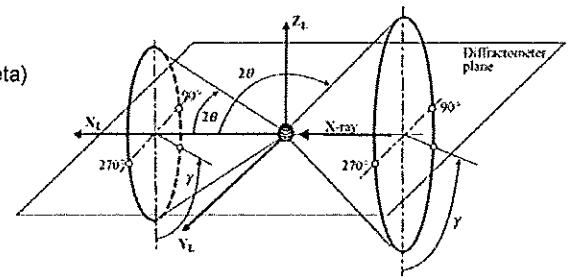
- When a diffraction condition is met there can be a reflected X-ray
  - Extra atoms in the basis can suppress reflections
- Three variables λ, θ, and d
  - λ is known
  - θ is measured in the experiment (2θ)
  - d is calculated
- From the planes (*hkl*)
  - *a* is calculated

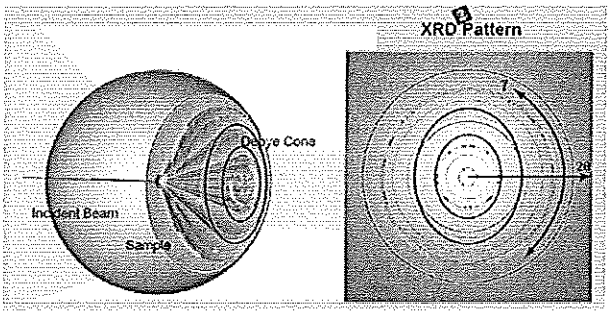
$$d = \frac{n\lambda}{2\sin\theta}$$

$$a = d\sqrt{h^2 + k^2 + l^2}$$

Geometry Conventions

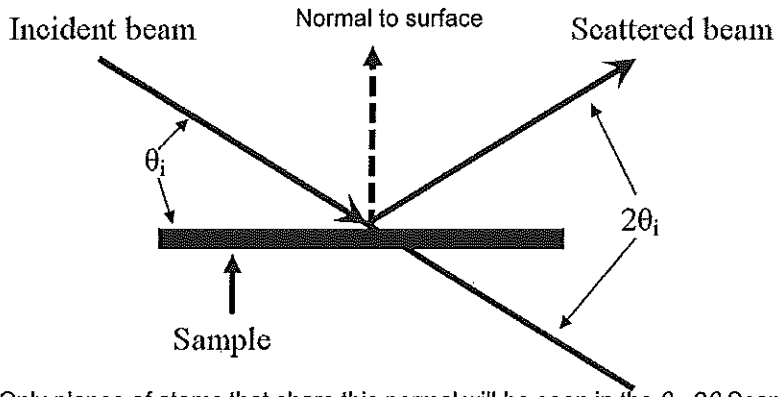
- Bragg-Brentano (theta-2theta)
- theta-theta





θ - 2θ Scan

The θ - 2θ scan maintains these angles with the sample, detector and X-ray source



Only planes of atoms that share this normal will be seen in the θ - 2θ Scan

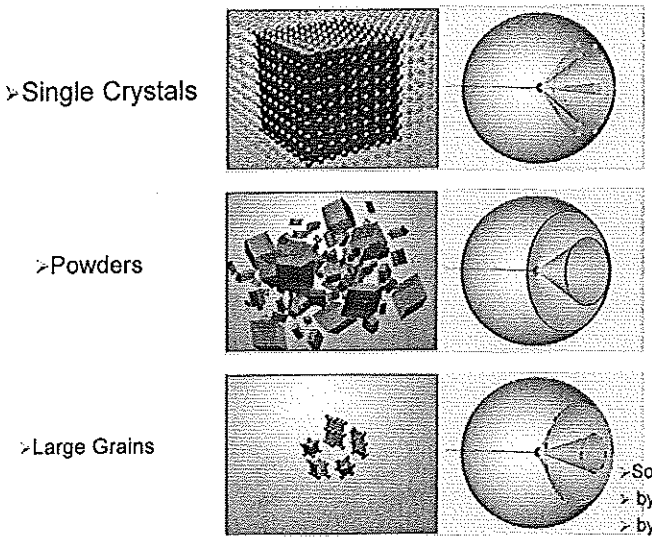
θ - 2θ Scan

The incident X-rays may reflect in many directions but will only be measured at one location so we will require that:

Angle of incidence (θ_i) = Angle of reflection (θ_r)

This is done by moving the detector twice as fast in θ as the source. So, only where $\theta_i = \theta_r$ is the intensity of the reflect wave (counts of photons) measured.

XRD 2D Pattern



➢Source: Particle Size Analysis
➢ by Two-dimensional XRD presenta
➢ by Bob He, Bruker AXS, Inc.

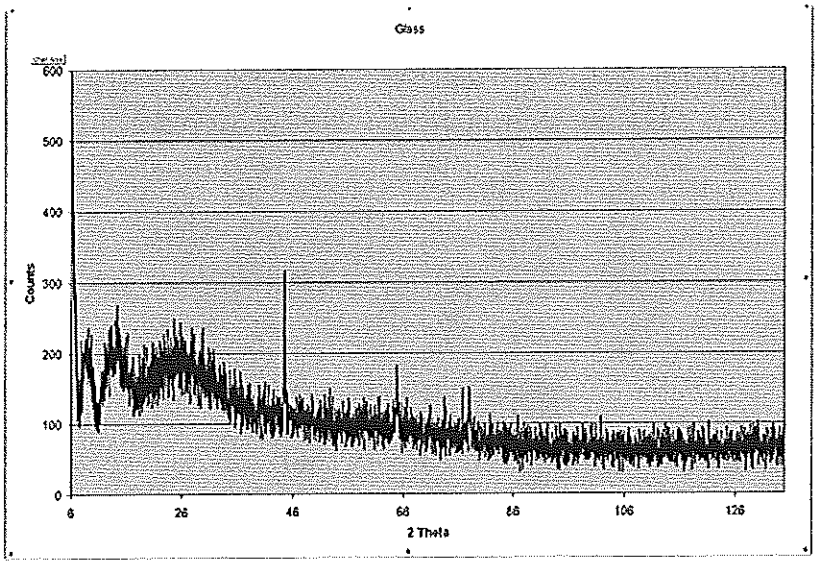
θ - 2θ Scan

The incident X-rays may reflect in many directions but will only be measured at one location so we will require that:

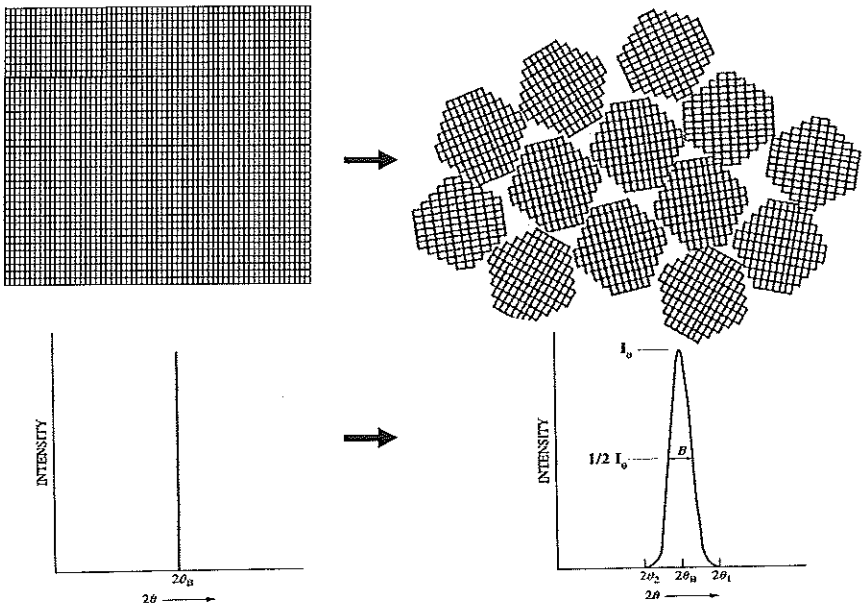
Angle of incidence (θ_i) = Angle of reflection (θ_r)

This is done by moving the detector twice as fast in θ as the source. So, only where $\theta_i = \theta_r$ is the intensity of the reflect wave (counts of photons) measured.

θ - 2θ Scan



Smaller Crystals Produce Broader XRD Peaks



Scherrer's Formula

$$t = \frac{K * \lambda}{B * \cos\theta_B}$$

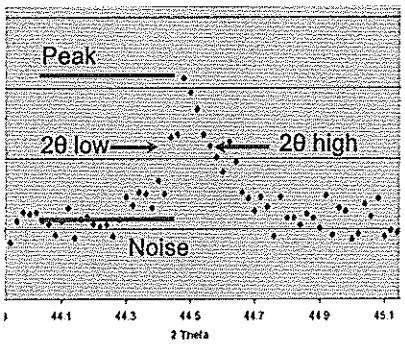
t = thickness of crystallite
K = constant dependent on crystallite shape (0.89)
λ = x-ray wavelength
B = FWHM (full width at half max) or integral breadth
θ_B = Bragg Angle

Scherrer's Formula

What is *B*?

$B = (2\theta \text{ High}) - (2\theta \text{ Low})$

B is the difference in angles at half max



When to Use Scherrer's Formula

- Crystallite size <1000 Å
- Peak broadening by other factors
  - Causes of broadening
    - Size
    - Strain
    - Instrument
  - If breadth consistent for each peak then assured broadening due to crystallite size
- K depends on definition of t and *B*
- Within 20%-30% accuracy at best

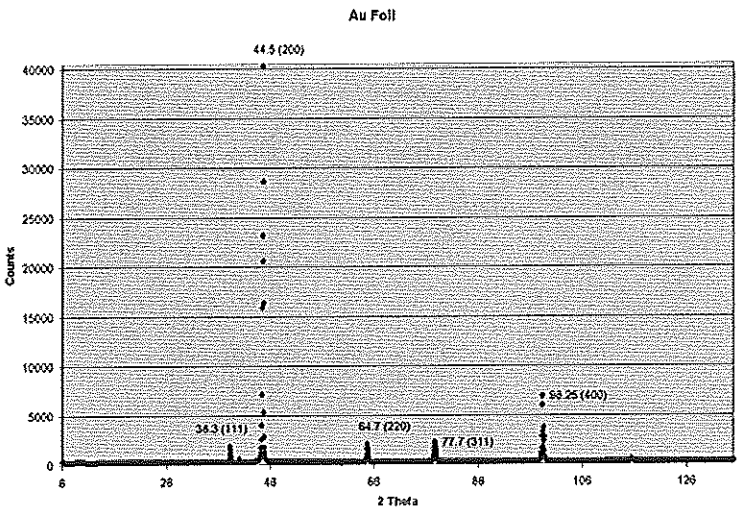
Sherrer's Formula References

Corman, D. Scherrer's Formula: Using XRD to Determine Average Diameter of Nanocrystals.

Data Analysis

- Plot the data (2θ vs. Counts)
- Determine the Bragg Angles for the peaks
- Calculate *d* and *a* for each peak
- Apply Scherrer's Formula to the peaks

Bragg Example



Bragg Example

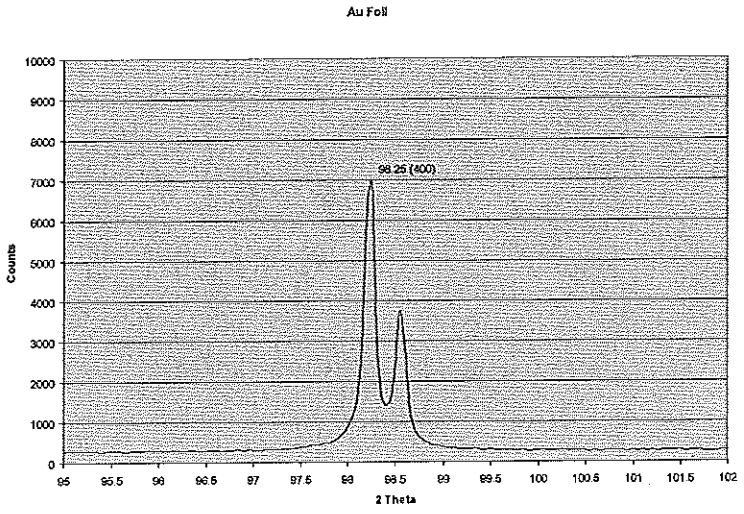
$d = \lambda / (2 \sin \theta_B)$ $\lambda = 1.54$ Å

$= 1.54$ Å $/ (2 * \sin (38.3 / 2))$

$= 2.35$ Å

Simple Right!

Scherrer's Example



Scherrer's Example

$$t = \frac{0.89 * \lambda}{B * \cos\theta_B}$$

t = 0.89*λ / (B Cos θ_B) λ = 1.54 Å

= 0.89*1.54 Å / (0.00174 * Cos (98.25/ 2))

= 1200 Å

B = (98.3 - 98.2)*π/180 = 0.00174

Simple Right!