

Handout 5: Reciprocal Space

Useful concepts for the analysis of diffraction data

Chem 6850/8850

X-ray Crystallography

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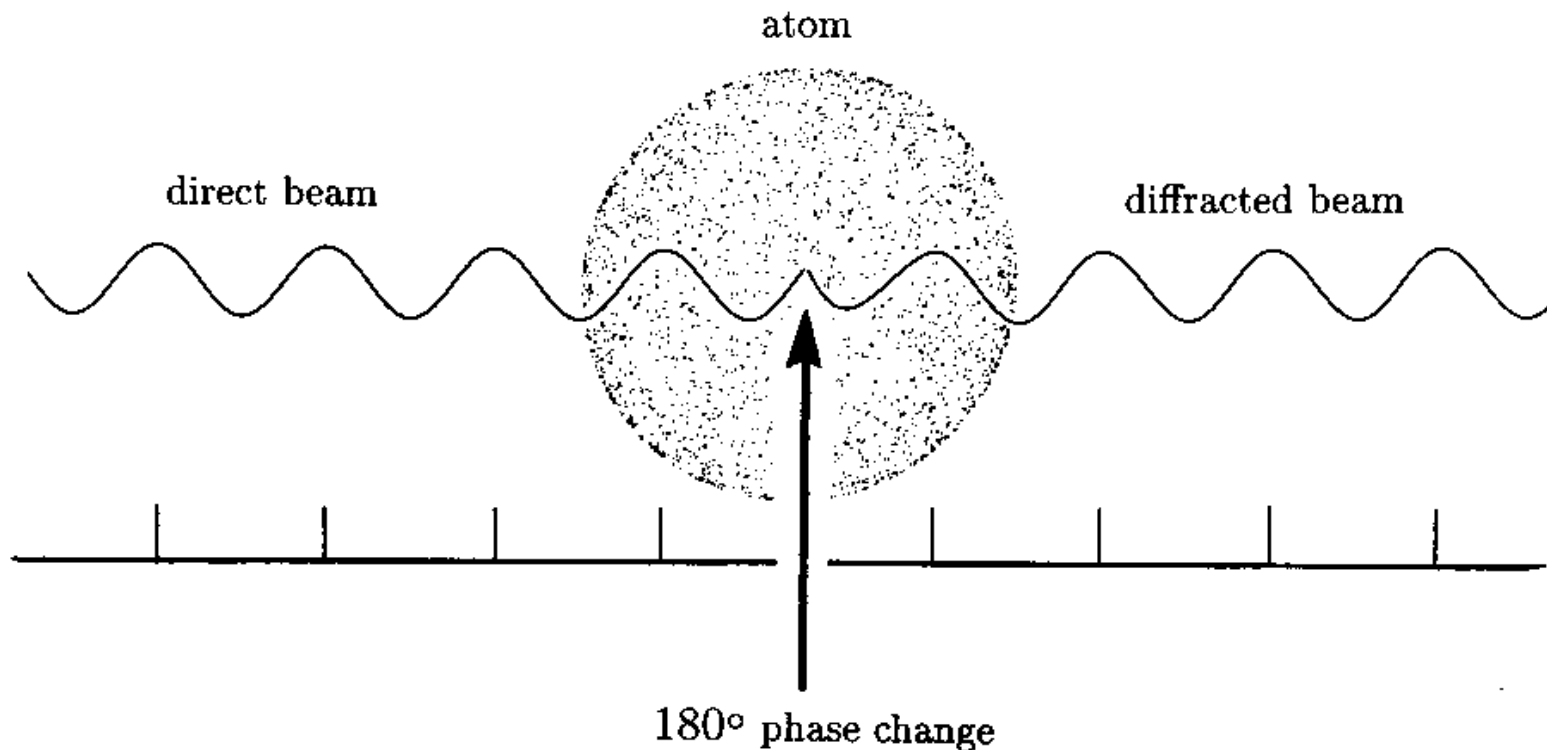
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Concepts versus reality

- **“Reflection from lattice planes” is just a concept that helps us to visualize what is happening in a diffraction experiment**
- **In reality, X-rays are scattered by the electrons in the atoms**
 - X-ray wavelength is similar to size of electron cloud
 - a periodic crystal corresponds to a periodic variation in electron density
 - the scattering event leads to a phase change of 180°
- **Neutrons are scattered by nuclei**
 - nuclei are much smaller than the neutron wavelength
 - neutrons can also interact with magnetic moments in a material



Phase change on scattering



"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

What do we actually measure?

- **We measure the intensity distribution of scattered radiation as a function of scattering angle**
 - for single crystals, we get 3D resolution
 - for powder experiments, all information is compressed into 1D
- **The intensity distribution of scattered radiation is a result of the electron density distribution inside the crystal**
 - the electron density distribution is the same in each unit cell
 - ⇒ periodic array of electron density



Reciprocal space

- **We do not see the periodic electron density directly during a diffraction experiment**
 - we only observe the intensity distribution of X-ray scattering from the crystal(s)
- **The diffraction intensity is correlated to the electron density in the crystal by a Fourier transform**
 - often referred to as direct space and reciprocal space
- **This means that we sample reciprocal space with our diffraction experiments**
 - we can define a reciprocal lattice that corresponds to the direct (crystal) lattice

Real and reciprocal space

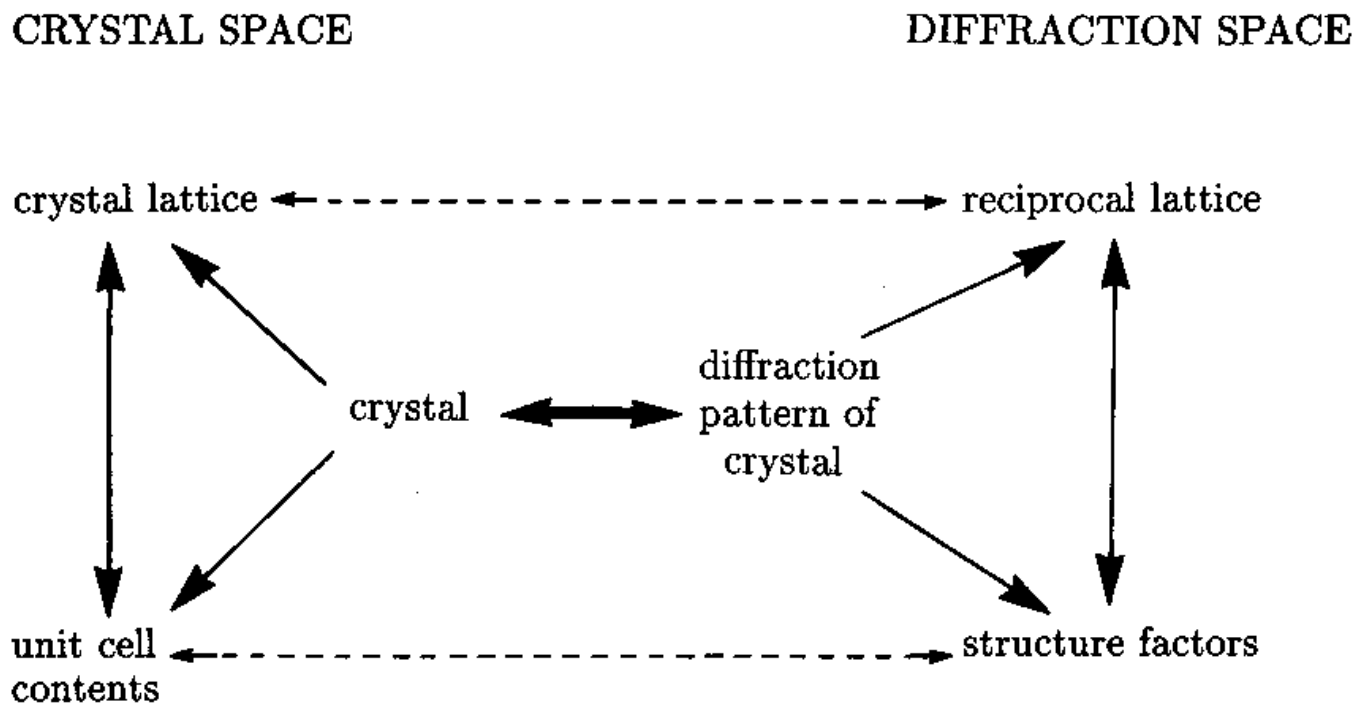


FIGURE 3.11. Relationships between a crystal (in crystal space) and its reciprocal lattice (in diffraction space).

“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.

The reciprocal lattice

- The reciprocal lattice has the same symmetry as the crystal lattice
- It can be derived from the crystal lattice graphically
 - draw lattice planes
 - pick an origin and draw normals to the lattice planes
 - mark points along the normals spaced $d^*(hkl)$ from the origin, where $d^*(hkl) = 1/d(hkl)$
- The reciprocal lattice constants a^* , b^* and c^* are defined so that they correspond to $d^*(100)$, $d^*(010)$ and $d^*(001)$
 - note that the direction of a^* , b^* and c^* will only coincide with that of a , b and c if the crystal lattice has $\alpha = \beta = \gamma = 90^\circ$

The reciprocal lattice – graphical construction

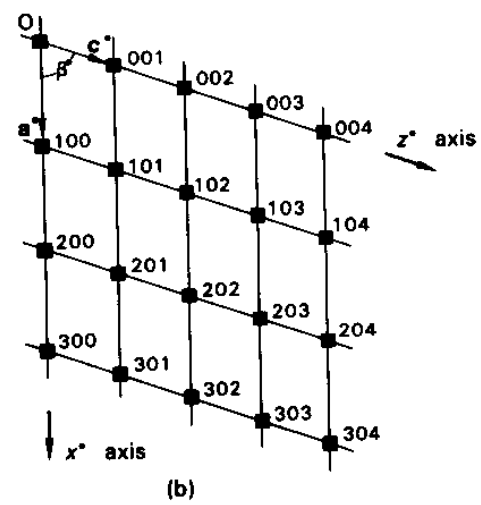
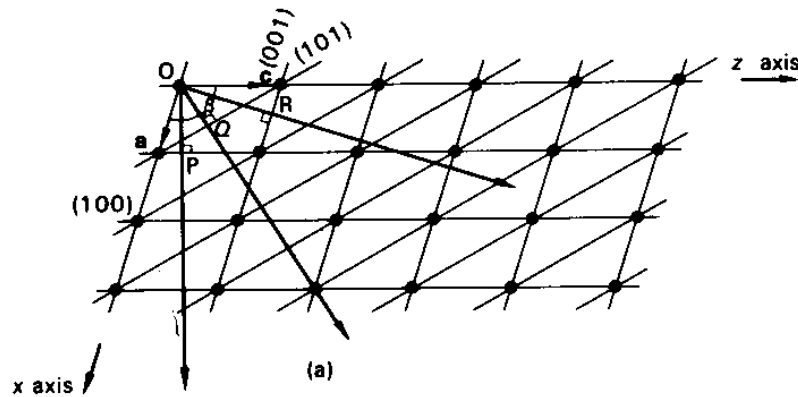


FIGURE 2.15. Direct and reciprocal lattices: (a) monoclinic *P*, as seen in projection along *b*, showing three families of planes; (b) corresponding reciprocal lattice.

“Structure Determination by X-ray Crystallography”, Ladd and Palmer, Plenum, 1994.



Reciprocal lattice constants

- The mathematical definition of the reciprocal lattice constants is

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}$$

$$\mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}$$

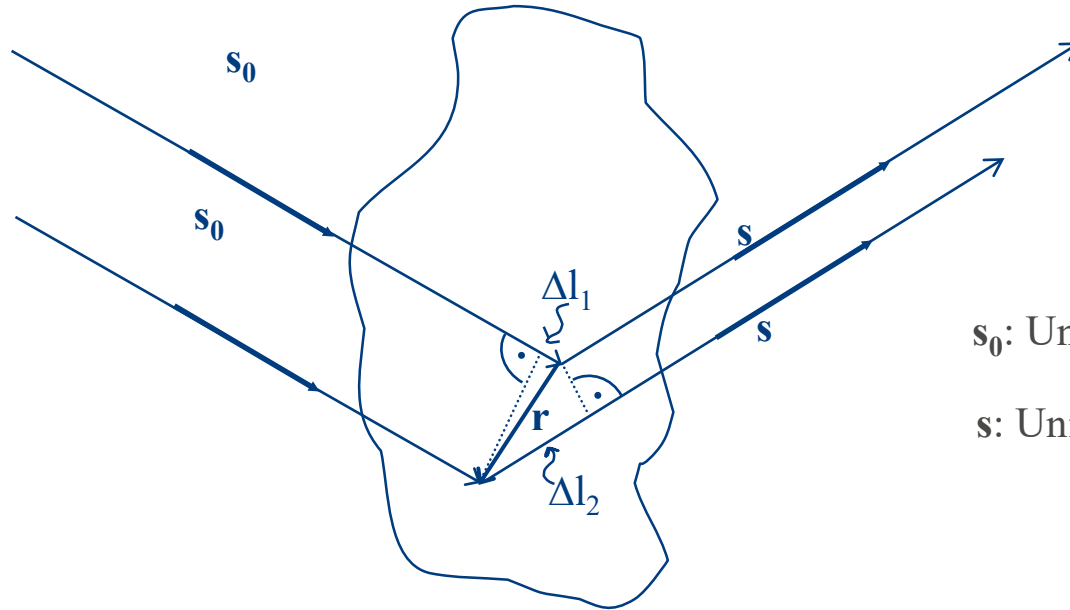
$$\mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}$$

where $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = V$

V = volume of the unit cell

- Note that the cross product returns a vector, while the dot product gives a scalar!

Scattering from a material



s_0 : Unit vector of incoming beam

s : Unit vector of scattered beam

- Assumption: Incoming beam is a plane wave, phase change on scattering is identical for all rays
- According to vector algebra:
 - $\Delta l_1 = -r \cdot s_0$
 - $\Delta l_2 = -r \cdot s$
 - total path difference: $\Delta l = \Delta l_1 - \Delta l_2 = r \cdot (s - s_0)$



Scattering from a material (2)

- Define: Scattering vector

$$\mathbf{S} = \mathbf{s} - \mathbf{s}_0$$

- The phase difference ϕ is given by

$$\phi = 2\pi \frac{\Delta l}{\lambda} = \frac{2\pi}{\lambda} \mathbf{S} \cdot \mathbf{r} = \mathbf{K} \cdot \mathbf{r}$$

- The change in *scattering amplitude*, $dA(\mathbf{s})$, is given by the phase difference and the electron density in the volume element dV_r

$$dA(\mathbf{s}) = e^{-i\mathbf{K} \cdot \mathbf{r}} \rho(\mathbf{r}) dV_r \quad \text{Fourier transform!}$$

$$A(\mathbf{s}) = \int_{V_r}^{\infty} e^{-i\mathbf{K} \cdot \mathbf{r}} \rho(\mathbf{r}) dV_r$$



The relationship between A and ρ

- The scattering amplitude, $A(\mathbf{s})$, and the electron density, $\rho(\mathbf{r})$, are correlated by a Fourier transform

$$A(\mathbf{s}) = \int_{V_r}^{\infty} e^{-i\mathbf{K}\cdot\mathbf{r}} \rho(\mathbf{r}) dV_r \quad \rho(\mathbf{r}) = \int_{V_r}^{\infty} e^{i\mathbf{K}\cdot\mathbf{r}} A(\mathbf{s}) dV_r$$

- Problem: We cannot measure $A(\mathbf{s})$, but only the intensity I , which is given by

$$I = A(\mathbf{s}) \cdot A^*(\mathbf{s})$$

- Note that these equations are valid for *any* material, we have not yet made any assumptions about periodicity!

Scattering from crystals

- To describe the electron density distribution in a crystal, we only need to describe it in one unit cell:

$$\rho(\mathbf{r}) = \rho(\mathbf{r}_0 + \boldsymbol{\tau}_1), \text{ where } \boldsymbol{\tau}_1 = m_1 \mathbf{a} + m_2 \mathbf{b} + m_3 \mathbf{c}$$

- Over all space, this gives us

$$A(\mathbf{s}) = \int_{V_r}^{\infty} e^{-i\mathbf{K} \cdot (\mathbf{r}_0 + \boldsymbol{\tau}_1)} \rho(\mathbf{r}_0) dV_r \quad \text{or}$$

$$A(\mathbf{s}) = \left[\int_{V_r}^{\infty} e^{-i\mathbf{K} \cdot \mathbf{r}_0} \rho(\mathbf{r}_0) dV_r \right] \sum_{m_1} e^{-i\mathbf{K} \cdot m_1 \mathbf{a}} \sum_{m_2} e^{-i\mathbf{K} \cdot m_2 \mathbf{b}} \sum_{m_3} e^{-i\mathbf{K} \cdot m_3 \mathbf{c}}$$

A crystal's interference function

- The summation part in the formula for the scattering amplitude describes a crystal's interference function:

$$\sum_{m_1} e^{-i\mathbf{K}\cdot m_1\mathbf{a}} \sum_{m_2} e^{-i\mathbf{K}\cdot m_2\mathbf{b}} \sum_{m_3} e^{-i\mathbf{K}\cdot m_3\mathbf{c}}$$

remember that $e^{-i\frac{2\pi m_1}{\lambda}\cdot\mathbf{S}\cdot\mathbf{a}} = \cos\left(\frac{2\pi m_1}{\lambda}\cdot\mathbf{S}\cdot\mathbf{a}\right) - i\sin\left(\frac{2\pi m_1}{\lambda}\cdot\mathbf{S}\cdot\mathbf{a}\right)$

- This will lead to reinforcement for

$$\mathbf{a}\cdot\mathbf{S} = n_1\lambda$$

$$\mathbf{b}\cdot\mathbf{S} = n_2\lambda$$

$$\mathbf{c}\cdot\mathbf{S} = n_3\lambda$$

or, using unit vectors

$$\frac{\mathbf{a}}{a}\cdot\frac{\mathbf{S}}{\lambda} = \frac{n_1}{a}$$

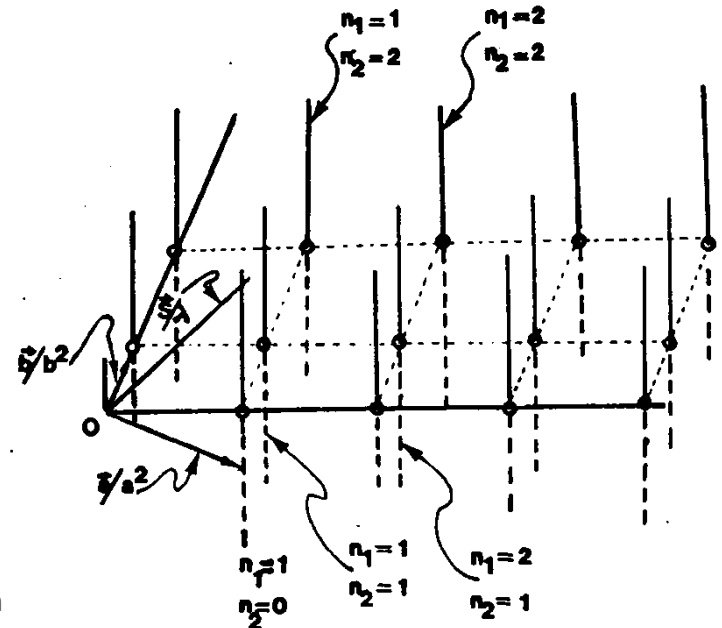
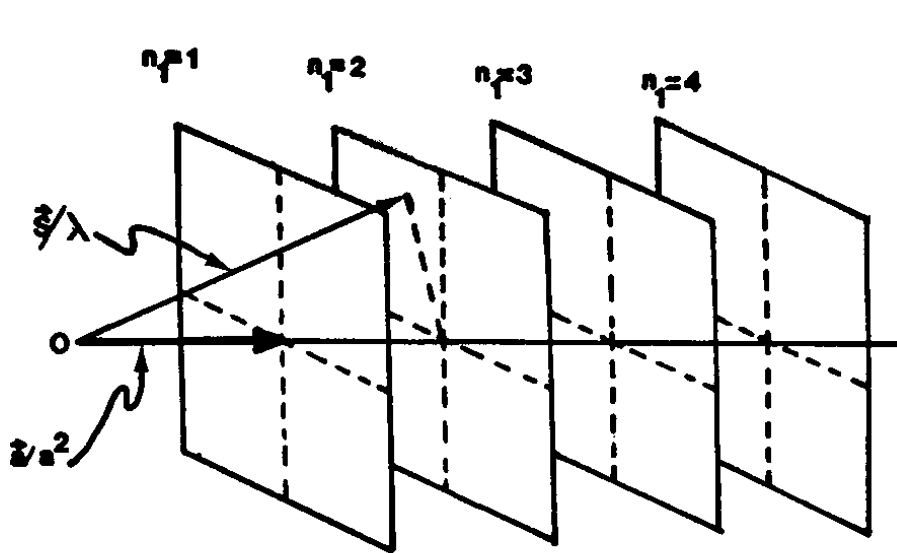
$$\frac{\mathbf{b}}{b}\cdot\frac{\mathbf{S}}{\lambda} = \frac{n_2}{b}$$

$$\frac{\mathbf{c}}{c}\cdot\frac{\mathbf{S}}{\lambda} = \frac{n_3}{c}$$

Laue conditions!

A crystal's interference function (2)

- Each of these conditions describes a family of planes spaced $1/a$ ($1/b$, $1/c$) as a solution for S
 - for a one-dimensional array of scatterers, the solutions are planes
 - for a two-dimensional array, the solutions are lines
 - for a three-dimensional array, the solution consists of points: The reciprocal lattice points



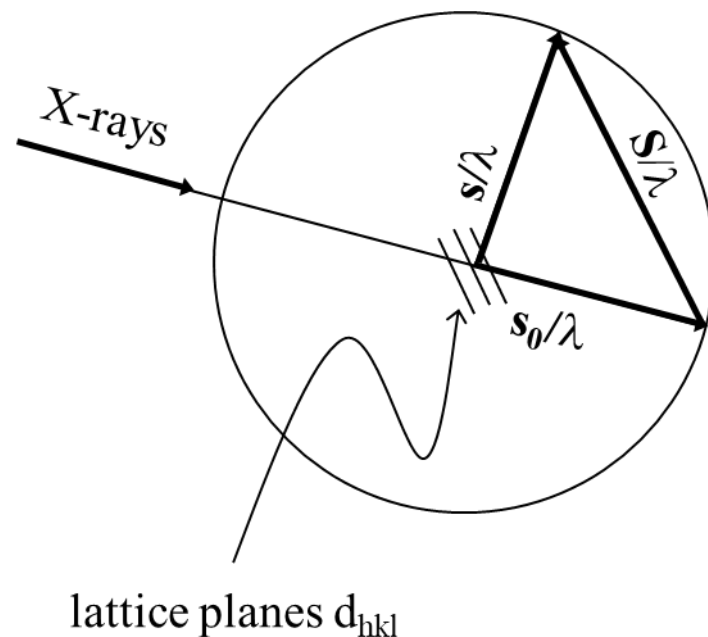
The Ewald sphere

- Remember that we defined

$$\mathbf{S} = \mathbf{s} - \mathbf{s}_0$$

where \mathbf{s} and \mathbf{s}_0 were unit vectors

- We can choose a frame of reference in which \mathbf{s}_0 is fixed, and the end point of the vector \mathbf{s}_0/λ is the origin of reciprocal space
- This allows us to define an *Ewald sphere*, also known as *sphere of reflection*, with radius $1/\lambda$ around the crystal

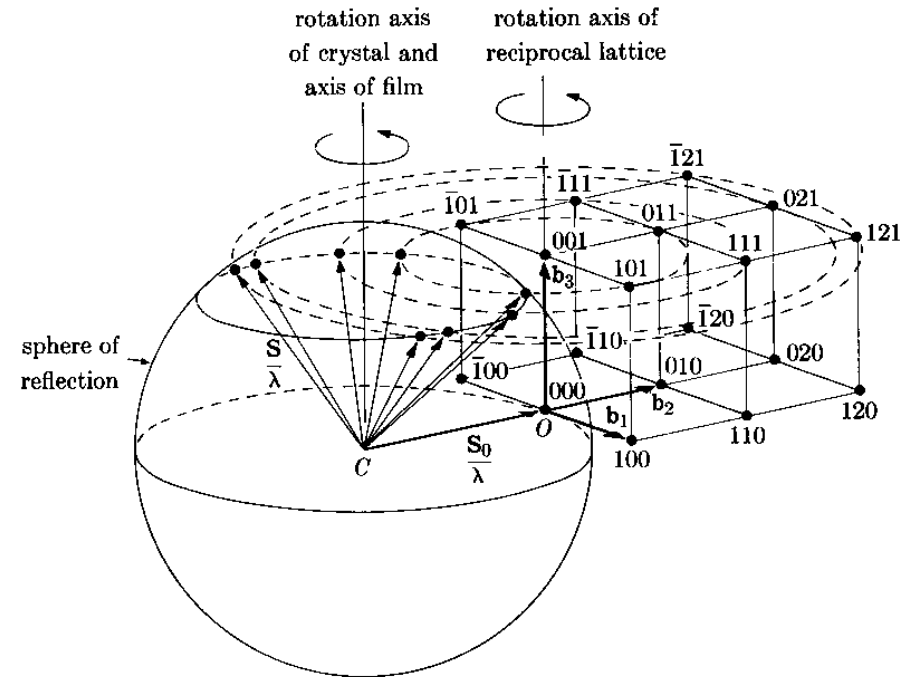


Ray Young, X-ray Monograph



Fulfilling four conditions

- The Ewald construction is also known as *wavelength condition*
- The three Laue conditions and the wavelength condition must be fulfilled simultaneously for diffraction to occur
- This means that a reciprocal lattice point must lie on the Ewald sphere for diffraction to occur
- Rotation of crystal is equivalent to rotation of reciprocal lattice



“Elements of X-ray Diffraction”, Cullity and Stock, Prentice Hall College Div., 3rd edition, 2001.



Bragg's law in reciprocal space

- If we define the distance of a lattice point from the origin of reciprocal space as d^* , we get

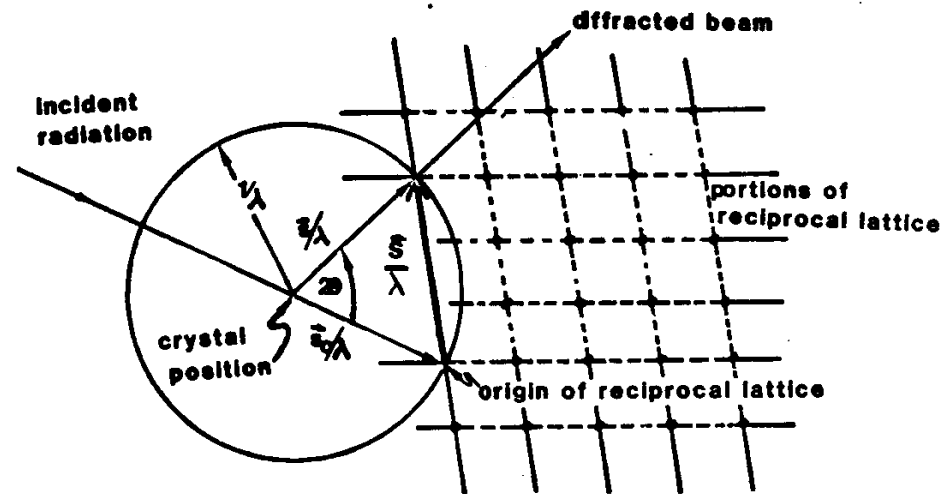
$$\mathbf{d}^* = \frac{\mathbf{S}}{\lambda}$$

- We can also show that

$$\frac{2 \sin \theta}{|\mathbf{d}^*|} = \lambda$$

- It follows that

$$|\mathbf{d}| = \frac{1}{|\mathbf{d}^*|}$$



Ray Young, X-ray Monograph



Calculating d-spacings

- The distance of reciprocal lattice points from the origin of the reciprocal lattice is given by

$$\mathbf{d}^* = h \cdot \mathbf{a}^* + k \cdot \mathbf{b}^* + l \cdot \mathbf{c}^*$$

- h, k and l are the Miller indices
- By definition, d can be calculated from d^* by

$$|\mathbf{d}| = \frac{1}{|\mathbf{d}^*|}$$

- Calculation is only straightforward for orthogonal crystal lattices

d-spacing formulae

TABLE 2.4. Expressions for $d^*(hkl)$ and $d(hkl)$ in the Seven Crystal Systems^a

System	$d^{*2}(hkl)$	$d^2(hkl)$
Triclinic	$h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2klb^*c^* \cos \alpha^* + 2lhc^*a^* \cos \beta^* + 2hka^*b^* \cos \gamma^*$	$K^2/d^{*2}(hkl)$
Monoclinic	$h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2hla^*c^* \cos \beta^*$	$\left\{ \frac{1}{\sin^2 \beta} \left[\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right] + \frac{k^2}{b^2} \right\}^{-1}$
Orthorhombic	$h^2a^{*2} + k^2b^{*2} + l^2c^{*2}$	$\left\{ \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right\}^{-1}$
Tetragonal	$(h^2 + k^2)a^{*2} + l^2c^{*2}$	$\left\{ \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right\}^{-1}$
Hexagonal and trigonal (P)	$(h^2 + k^2 + hk)a^{*2} + l^2c^{*2}$	$\left\{ \frac{4(h^2 + k^2 + hk)}{3a^2} + \frac{l^2}{c^2} \right\}^{-1}$
Trigonal (R) (rhombohedral)	$[h^2 + k^2 + l^2 + 2(hk + kl + hl)(\cos \alpha^*)]a^{*2}$	$a^2(TR)^{-1}$, where $T = h^2 + k^2 + l^2 + 2(hk + kl + hl)[(\cos^2 \alpha - \cos \alpha)/\sin^2 \alpha]$ and $R = (\sin^2 \alpha)/(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)$
Cubic	$(h^2 + k^2 + l^2)a^{*2}$	$\left\{ \frac{h^2 + k^2 + l^2}{a^2} \right\}^{-1} = \frac{a^2}{h^2 + k^2 + l^2}$

^a In the monoclinic system, $d(100) = a \sin \beta$, $d(001) = c \sin \beta$, and hence $a = K/(a^* \sin \beta^*)$ and $c = K/(c^* \sin \beta^*)$.

In the hexagonal system (and trigonal P), $a = b = K/(a^* \sin \gamma^*) = K/(a^* \sqrt{3}/2)$.

In general, the expressions for d^{*2} are simpler in form than the corresponding expressions for d^2 .

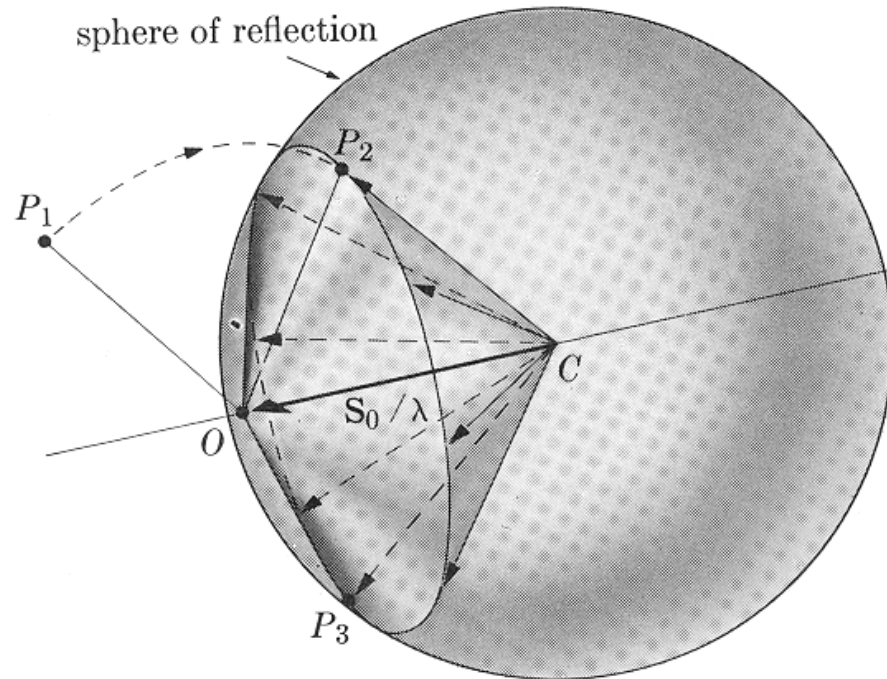
"Structure Determination by X-ray Crystallography", Ladd and Palmer, Plenum, 1994.

Observations from single crystals and powders

- **For a single crystal, there is one orientation in real space, resulting in one orientation of the reciprocal lattice**
 - reciprocal lattice points are resolved and will result in diffraction intensity when they touch the Ewald sphere
- **A powder sample consists of many crystallites with random orientations**
 - we get many overlapping reciprocal lattices, resulting in a “sphere” of reciprocal lattice points that fulfill the Bragg condition at a given 2θ
 - the sphere will intersect the Ewald sphere in a circle
 - we will observe “powder rings”



Powder diffraction rings



“Elements of X-ray Diffraction”, Cullity and Stock, Prentice Hall College Div., 3rd edition, 2001.

Fig. A1-10 Formation of a cone of diffracted rays in the powder method.

- If we assume an infinite number of randomly oriented crystallites, every point P_n at distance d^* from the origin of reciprocal space fulfills the Laue conditions

