Analytical Methods for Materials

Lesson 16

Scattering and Diffraction Analysis of Materials

Suggested Reading

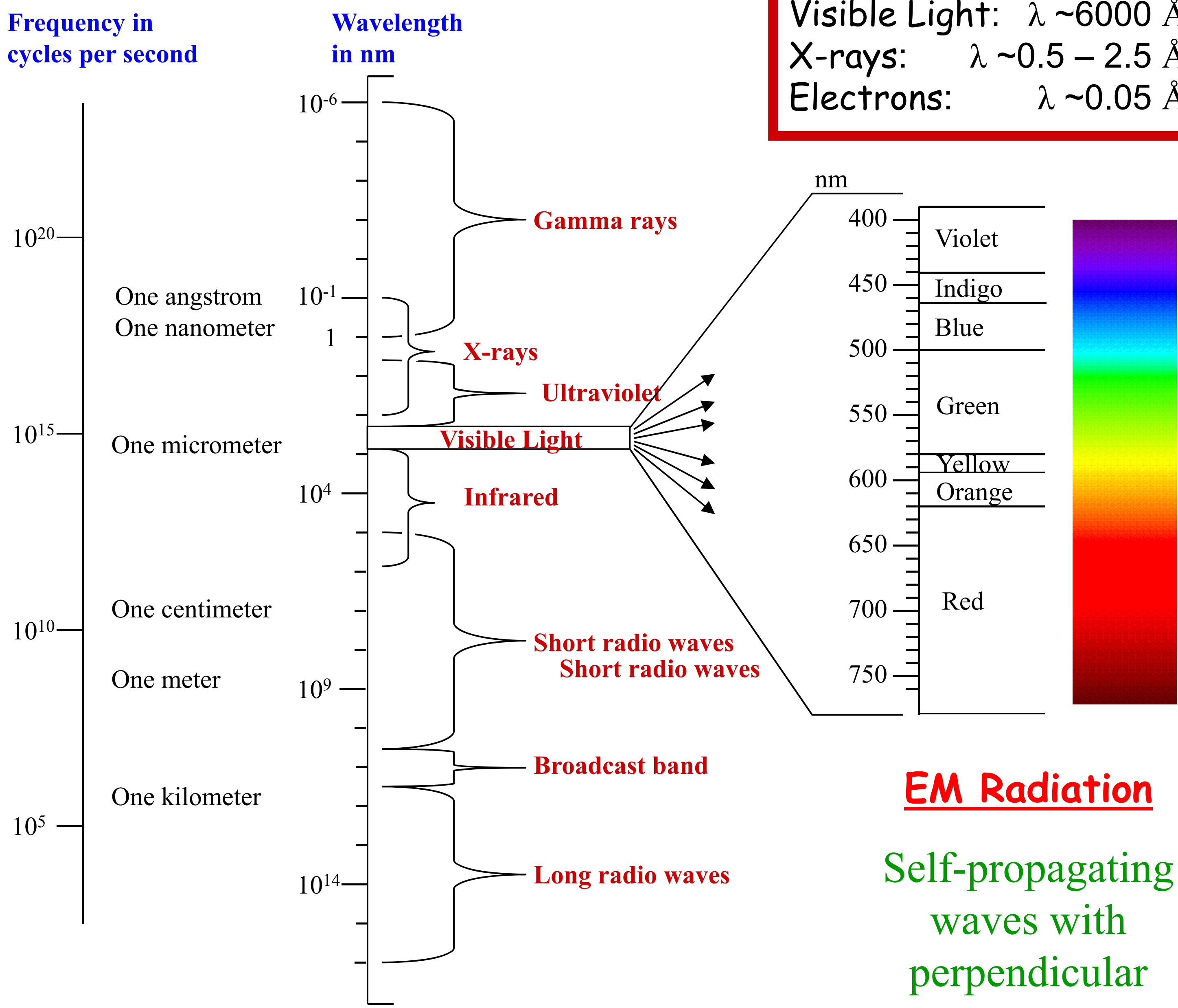
Chapter 3 in Waseda, pp. 67-75

Ch. 6 – B.D. Cullity and S.R. Stock, Elements of X-ray Diffraction, 3rd Edition, Prentice-Hall (2001)

Chs. 11-14 – M. DeGraef and M.E. McHenry, Structure of Materials, Cambridge (2007).

Ch. 7 – Pecharsky and Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, 2nd Edition, Springer (2009)

Visible Light: λ ~6000 Å
X-rays: λ ~0.5 – 2.5 Å
Electrons: λ ~0.05 Å

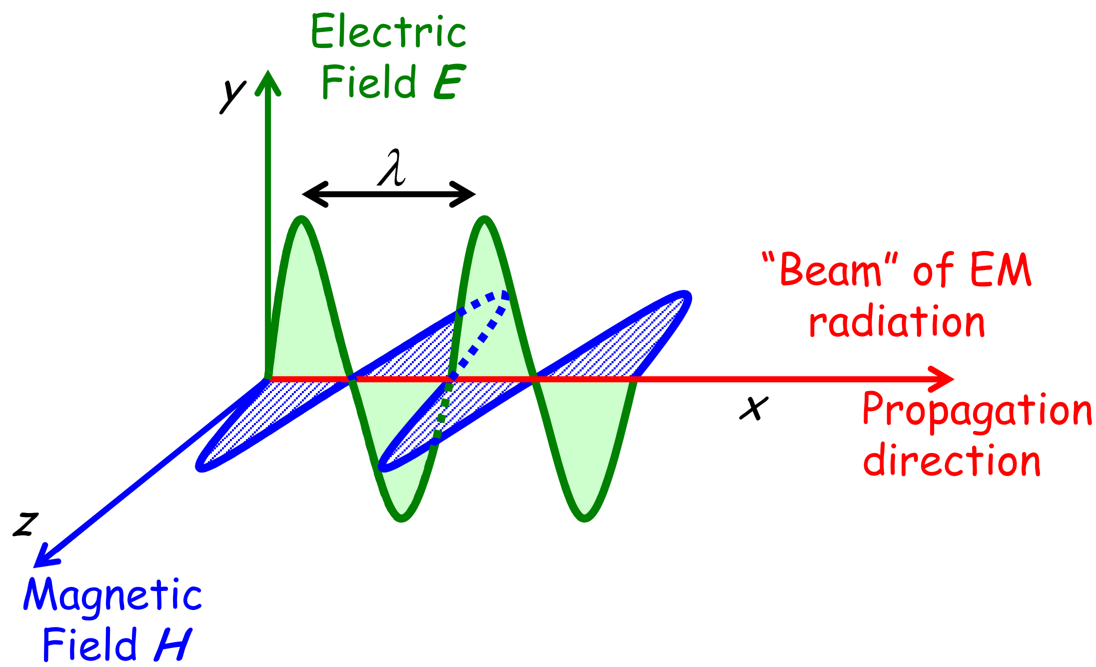


Spectrum of electromagnetic (EM) radiation as a function of frequency (s^{-1}) and wavelength (nm).

EM Radiation

Self-propagating waves with perpendicular electric and magnetic components

Properties of Electromagnetic Waves



Consist of discrete particles of energy called *photons*.

Photons interact with electrons.

Thus they can be "scattered" by solids.

$$E = \text{photon of energy} = h\nu = \frac{hc}{\lambda}$$

$$h = \text{Planck's constant} = 6.626\times10^{-34}\ \text{J}\cdot\text{s}$$

$$\nu = \text{frequency of the wave}$$

$$c = \text{speed of light} = 3.00\times10^{8}\ \text{m/s}$$

$$\lambda = \text{wavelength of radiation}$$

Scattering of EM Radiation by Crystals

- For a material to yield a diffraction pattern, $\lambda_{\text{EM rad.}} \leq d_{\text{hkl}}$.

- This limits us to using:
  - Neutrons
  - Electrons
  - **X-rays → Let's focus on these for right now**

- X-ray scattering (i.e., absorption + re-emission):
  - Elastic (little or no energy loss → diffraction peak)
  - Inelastic (energy loss → no diffraction peak)

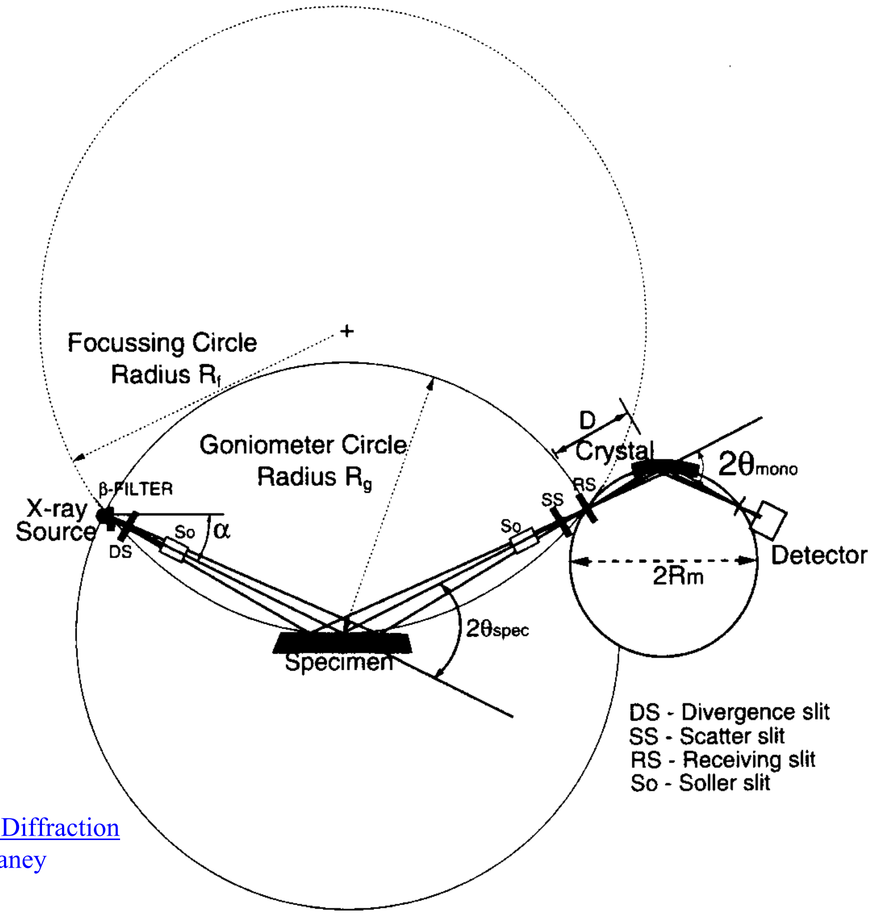
X-ray Powder Diffractometer

- Used to assess the crystal structure of a material. How X-rays diffract is sensitive to atom locations in a unit cell.

- Variations on basic equipment are used to assess:
  – Single crystal orientation
  – Polycrystalline orientations (i.e., texture)
  – Residual stresses
  – Thin film epitaxy
  – Etc…

Geometry of the X-ray Diffractometer

- Generically, diffractometers consist of:
  - X-ray source
  - X-ray detector
  - Specimen to be examined
  - Other things
    - Monochromators
    - Filters
    - Slits
    - Etc…



D.J. Dyson, X-ray and Electron Diffraction Studies in Materials Science, Maney Publishing, London (2004)

Fig. 5.5 The geometry of the diffractometer arrangement: DS is the divergence slit, SS is the scatter slit, RS is the receiving slit, So is the soller slit.

Laue's Equations

- When scattering occurs there is a change in the path of the incident radiation.

δ_n = path difference between incident and scattered beams

(1) $= n\lambda$ where n is an integer

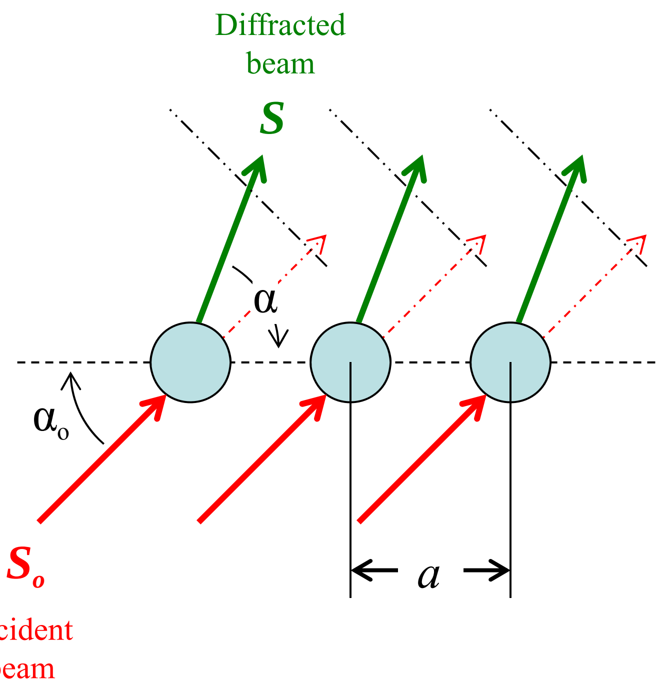
For constructive interference

$$\delta_x = a(\cos\alpha - \cos\alpha_o) = a(S - S_o) = h\lambda$$

$$\delta_y = b(\cos\beta - \cos\beta_o) = b(S - S_o) = k\lambda$$

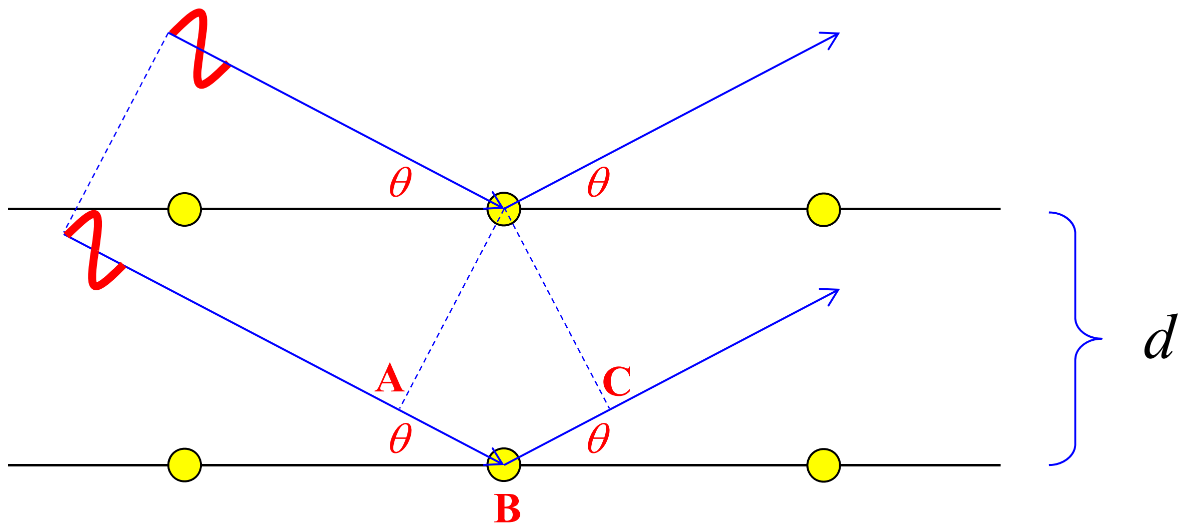
$$\delta_z = c(\cos\gamma - \cos\gamma_o) = c(S - S_o) = l\lambda$$

[h, k, l are integers]



- Constructive interference occurs when all three equations are satisfied simultaneously.

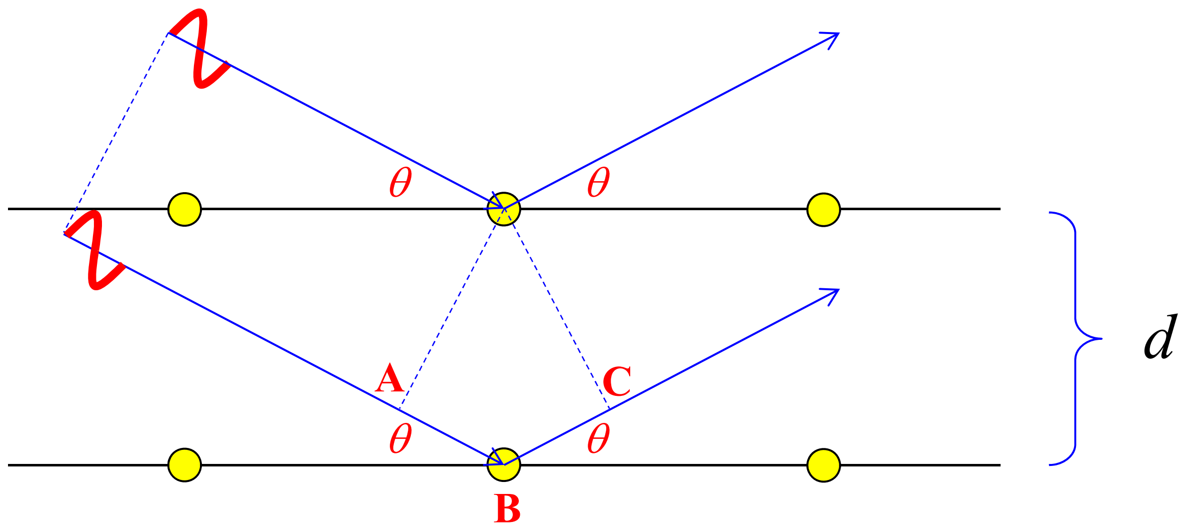
Bragg's Law



$$\delta = \text{ path difference} = AB + BC = 2d\sin\theta$$

$$\therefore$$

Bragg's Law



$$\delta = \text{ path difference} = AB + BC = 2d\sin\theta$$

$$\text{For constructive interference } \delta = n\lambda$$

$$\therefore$$

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

$$d_{hkl} = \frac{d}{n}$$

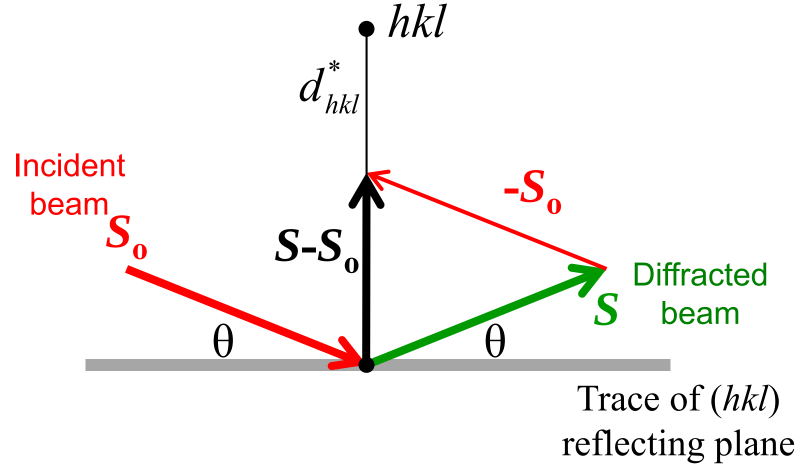
$$\lambda = 2d_{hkl}\sin\theta \text{ (or } n\lambda = 2d\sin\theta)$$

Bragg's Law

- Bragg's law can be expressed in vector form:

$$S - S_o = 2\sin\theta = \lambda d^*_{hkl}$$

$$\left| d^*_{hkl} \right| = \frac{1}{d_{hkl}}$$



- Thus:

$$\frac{S - S_o}{\lambda} = d^*_{hkl} = ha^* + kb^* + lc^*$$

- This tells us that constructive interference occurs when ***S*–*S*$_o$** coincides with the reciprocal lattice vector of the reflecting planes.

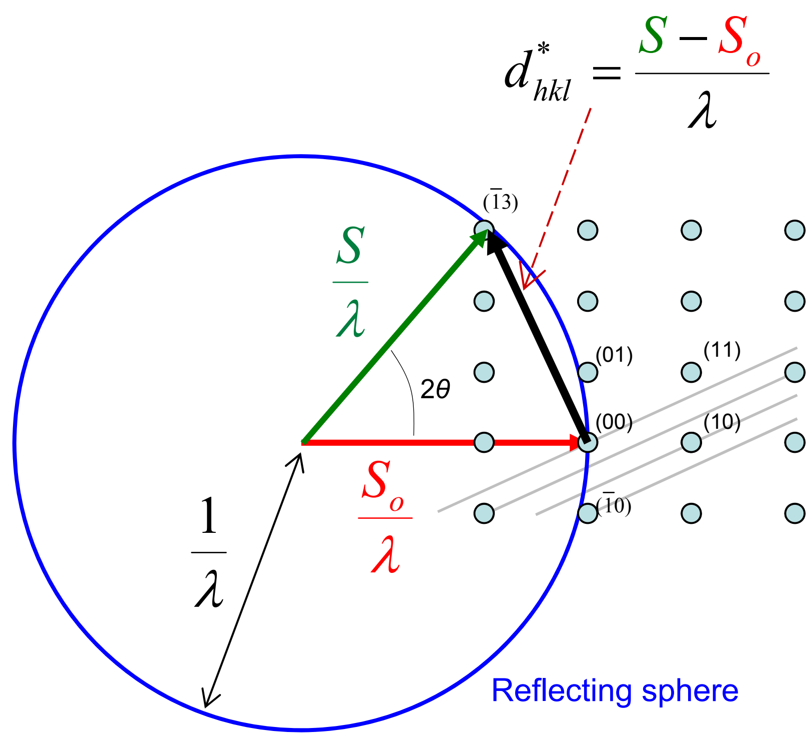
Laue's Equations and the Reciprocal Lattice

- Can represent the Laue equation (i.e., diffraction) graphically.

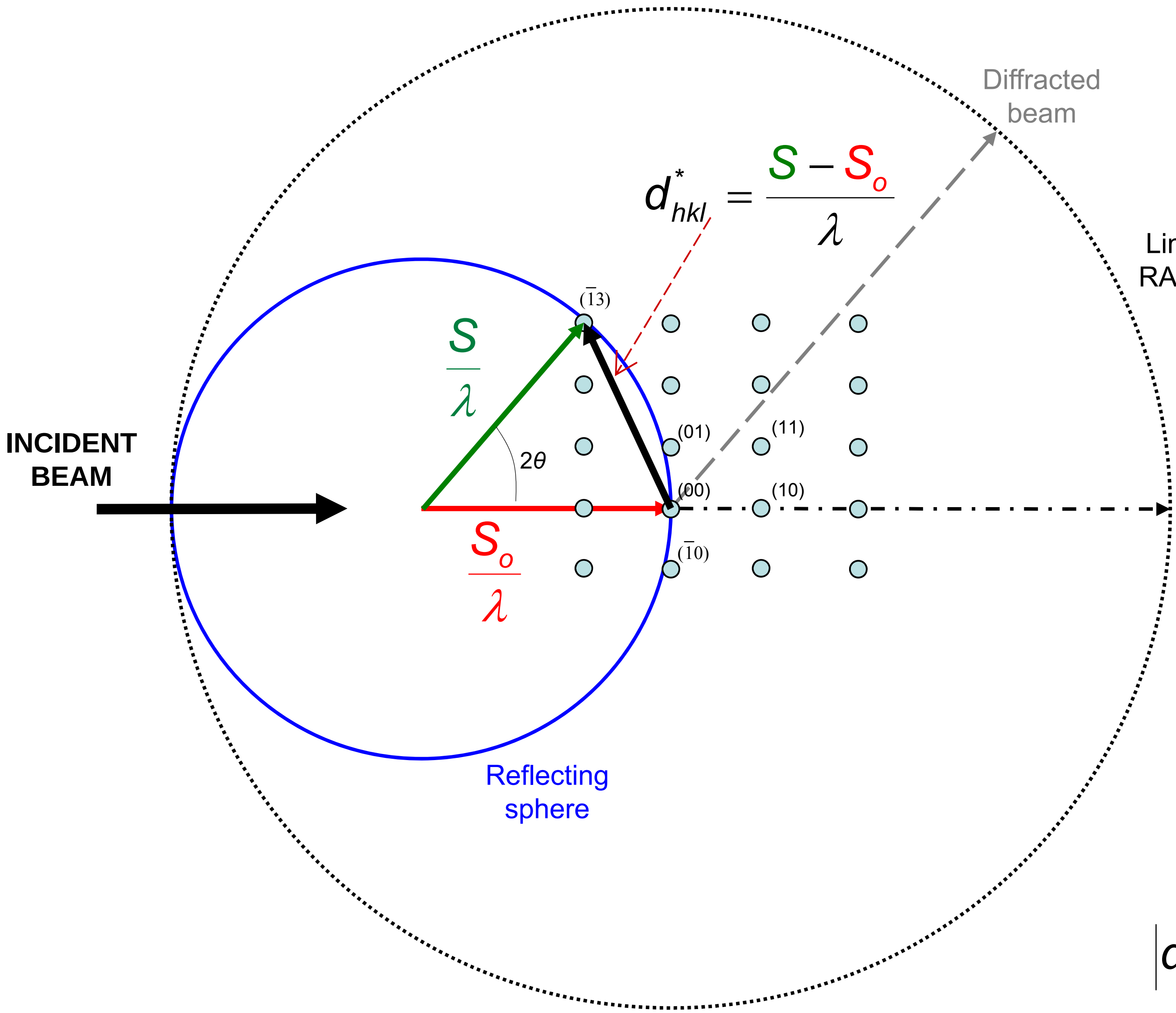
- This is similar to Ewald's sphere.

- **For diffraction** to be observed (*i.e.* Bragg's law satisfied) ***S*** **must end on a reciprocal lattice point**.

- Point's satisfying this criteria represent planes that are oriented for diffraction



- Bragg's law, which describes diffraction in terms of scalars, is generally used for convenience.



To satisfy Bragg's law

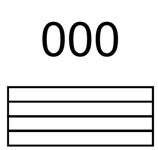
$$\frac{S_o}{\lambda} + d^*_{hkl} = \frac{S}{\lambda}$$

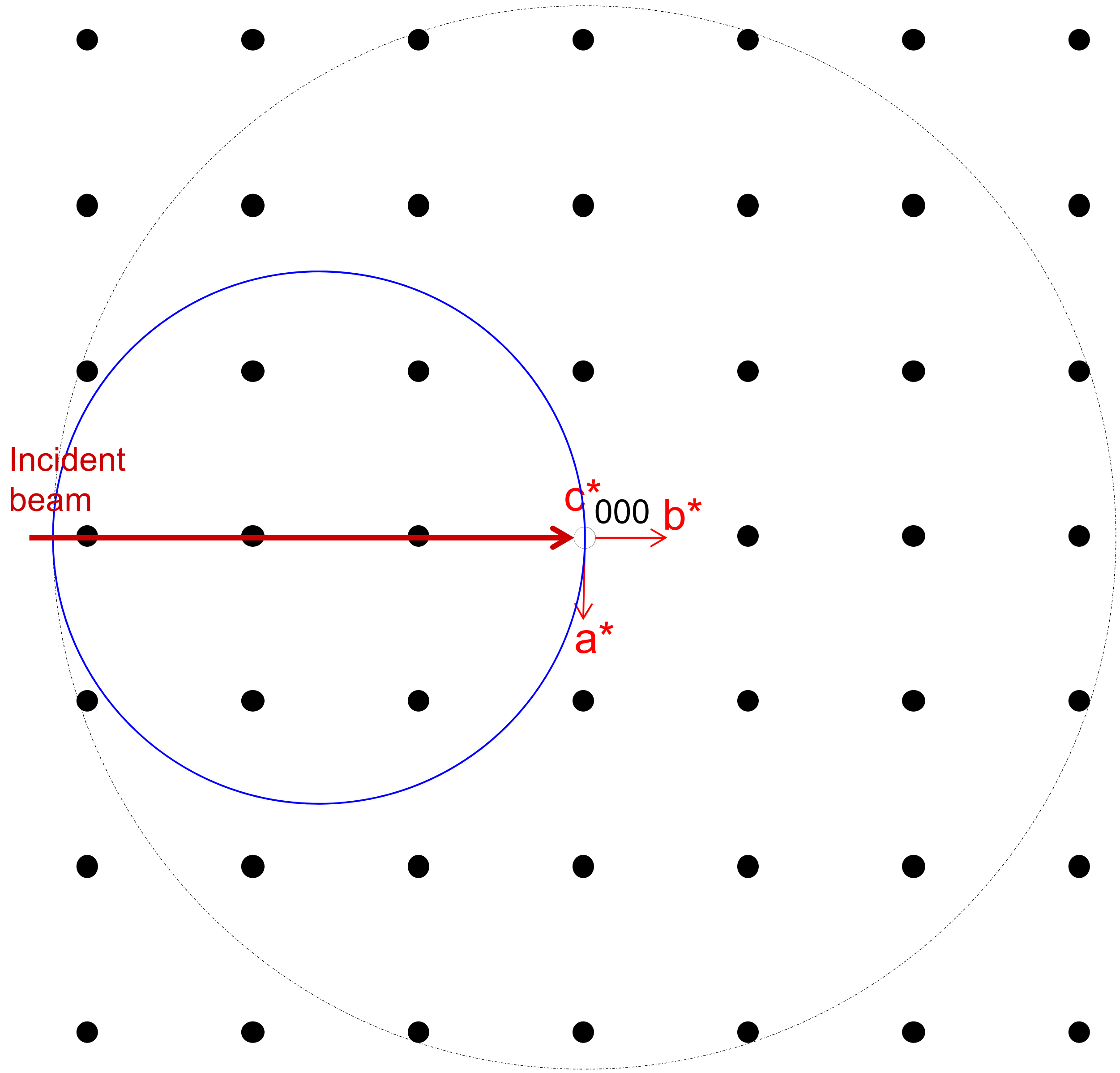
$$n\lambda = 2d\sin\theta$$

$$\left|d^*_{hkl}\right| = \left|g\right| = \frac{1}{d} = \frac{2\sin\theta}{n\lambda}$$

Reciprocal Lattice

- The lattice constructed from all diffraction vectors (i.e., *g*) for a crystal defines possible Bragg reflections.
- Points that intersect the reflecting sphere will satisfy Bragg's law.
- Changes in wavelength (λ) changes the circle radius, which can lead to diffraction. However, we generally do not change λ.



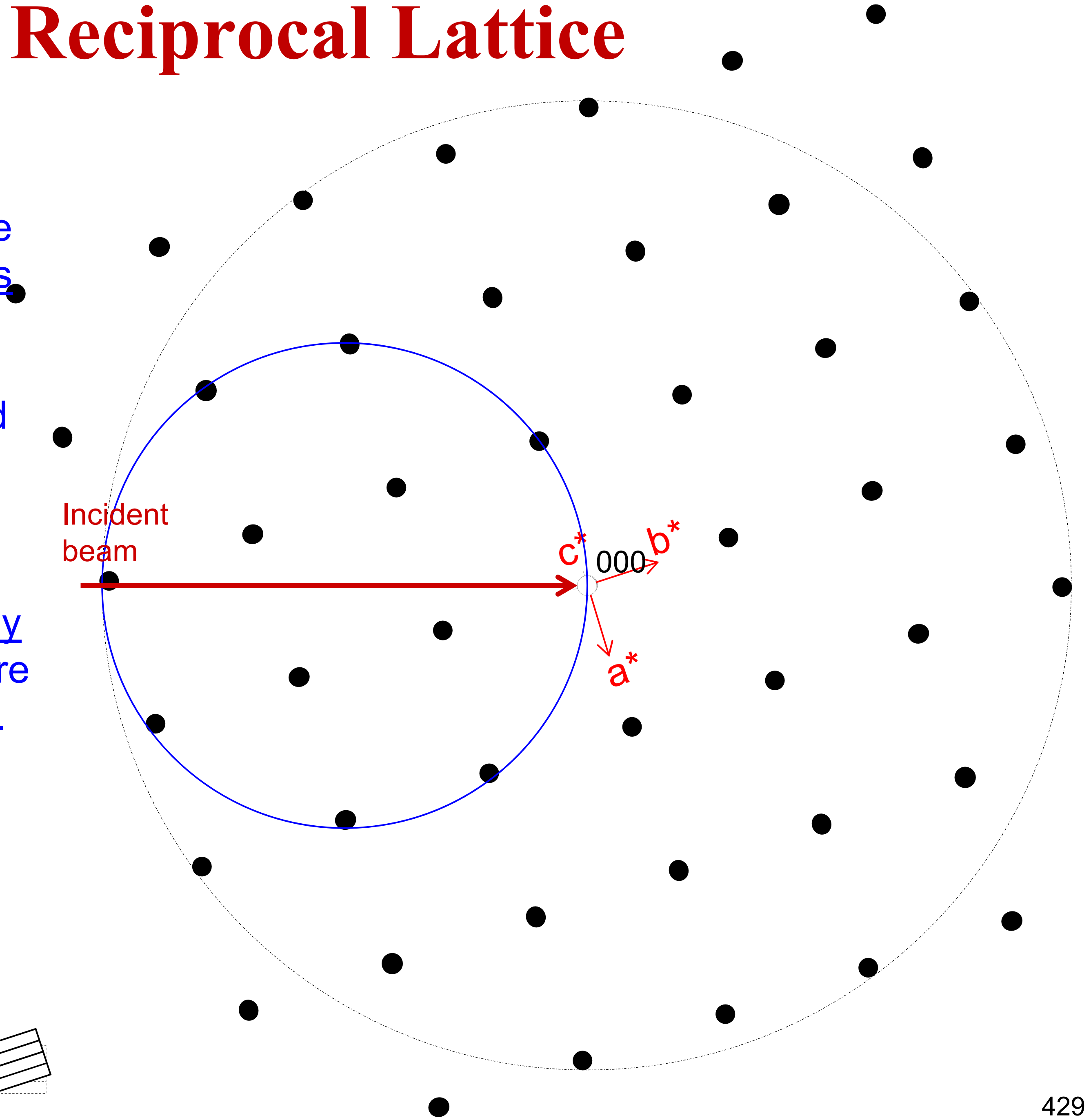


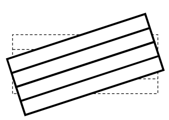
Reciprocal Lattice

- A change in orientation of the incident beam relative to the crystal changes the orientation of the reciprocal lattice, reflecting sphere, and limiting sphere.

- Change will eventually yield a condition where diffraction is possible.

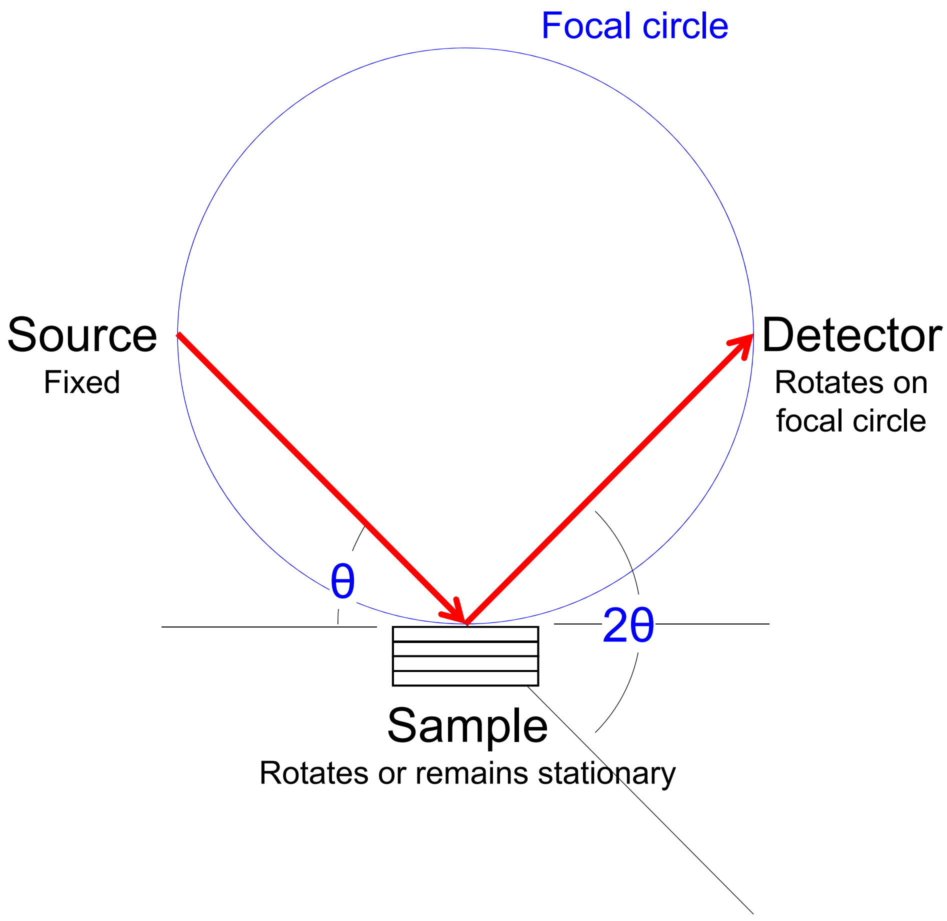
- We mentioned this a few lectures ago.





X-ray Diffractometer

- X-ray source is generally fixed.
- Rotate sample and detector to adjust θ/2θ.
- On instruments such as our Bruker D8 and Philips MPD, the source and detector move while the sample remains stationary.



Bragg-Bretano

Diffraction Directions

- We can determine which reflections are allowed by combining Bragg's law with the interplanar spacing equations for a crystals.
- Cubic:

$$\left.\begin{array}{c} \lambda = 2d\sin\theta \\ + \\ \dfrac{1}{d^2} = \dfrac{\left(h^2+k^2+l^2\right)}{a^2} \end{array}\right\rangle \quad \sin^2\theta = \frac{\lambda^2}{4a^2}\left(h^2+k^2+l^2\right)$$

- This equation predicts, for a particular incident λ and a particular cubic crystal of unit cell size a, all of the possible Bragg angles for the diffracting planes (hkl)

Diffraction Directions – cont'd

- Example:

  What are the possible Bragg angles for {111} planes in a cubic crystal?

- Solution:

$$\sin^2\theta_{111} = \frac{\lambda^2}{4a^2}\left(1^2 + 1^2 + 1^2\right) = \frac{3\lambda}{4a^2}$$

h k l

Diffraction Directions

- What about other systems?

- Tetragonal:

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

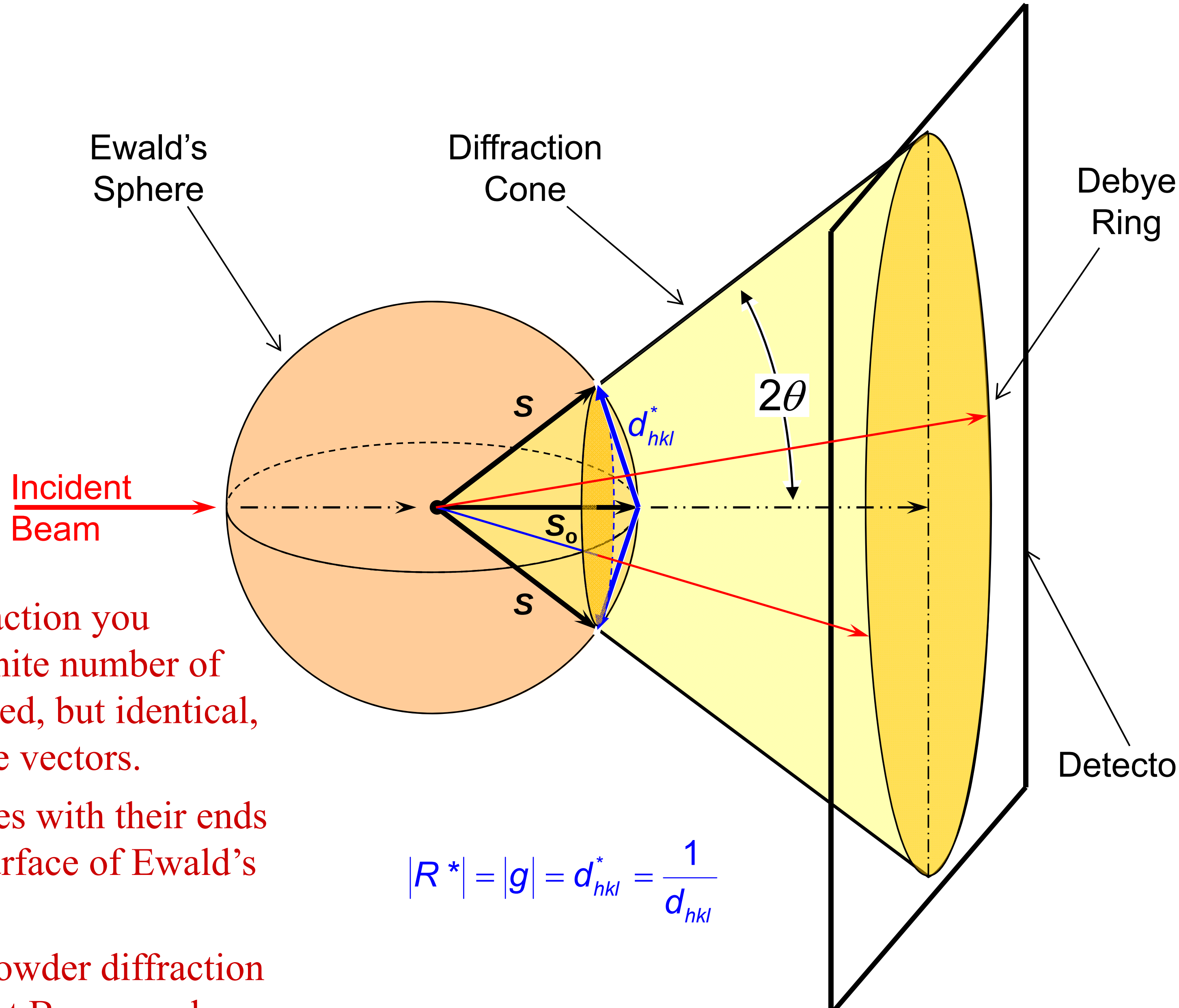
$$+$$

$$\frac{1}{d^2} = \frac{\left(h^2+k^2\right)}{a^2} + \frac{\left(l^2\right)}{c^2}$$

$$\sin^2\theta = \frac{\lambda^2}{4a^2}\left(\frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}\right)$$

- Solution: must know c and a. Will be one peak.
- What about {110}?

I've intentionally given you a family here



$$|R^*| = |g| = d^*_{hkl} = \frac{1}{d_{hkl}}$$

- In powder diffraction you generate an infinite number of randomly oriented, but identical, reciprocal lattice vectors.
- They form circles with their ends placed on the surface of Ewald's sphere.
- They produce powder diffraction cones at different Bragg angles (see the next slide).

Adapted from Vitalij K. Pecharsky and Peter Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, © Kluwer Academic Publishers (2005)

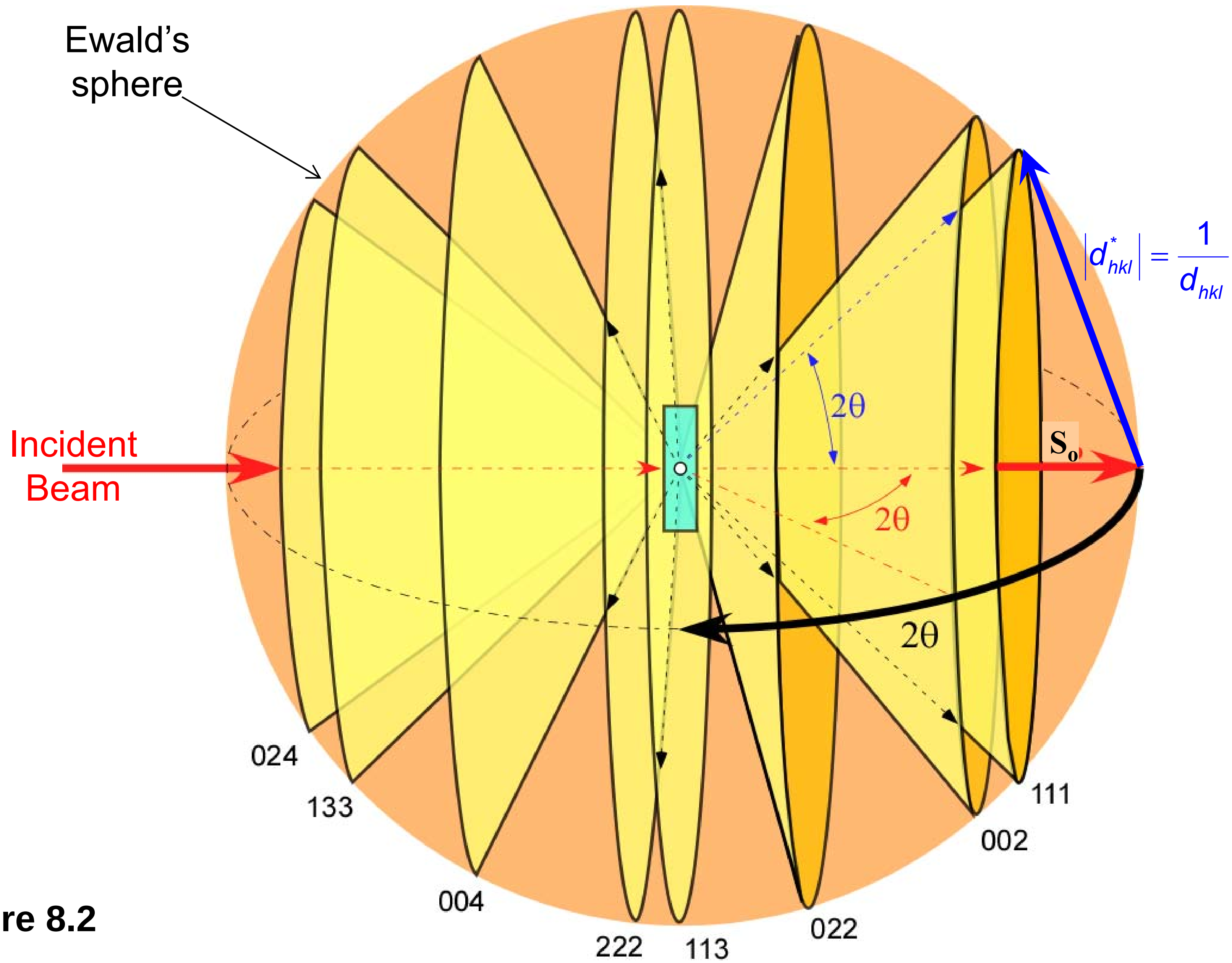
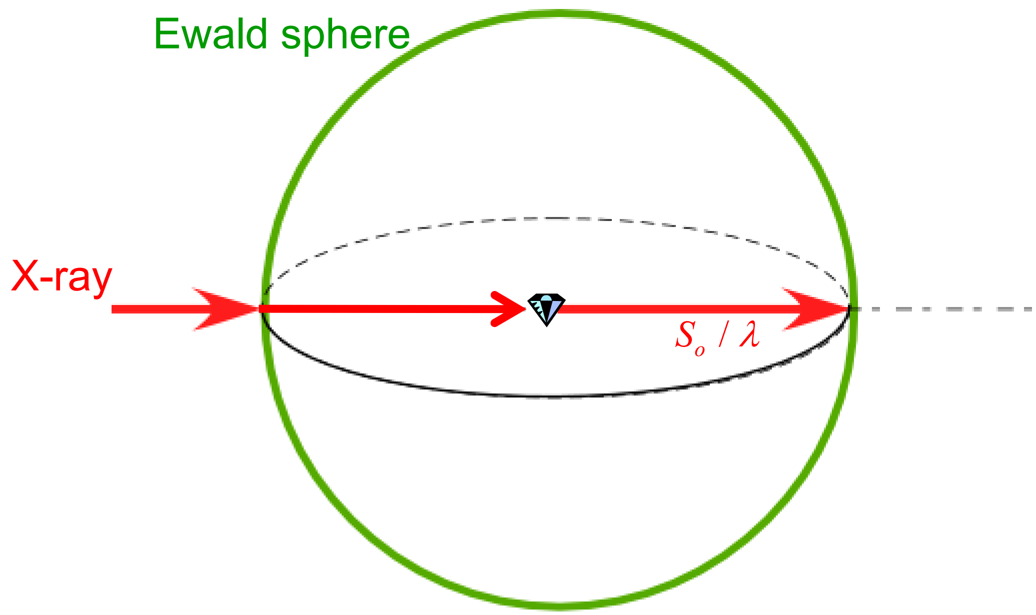
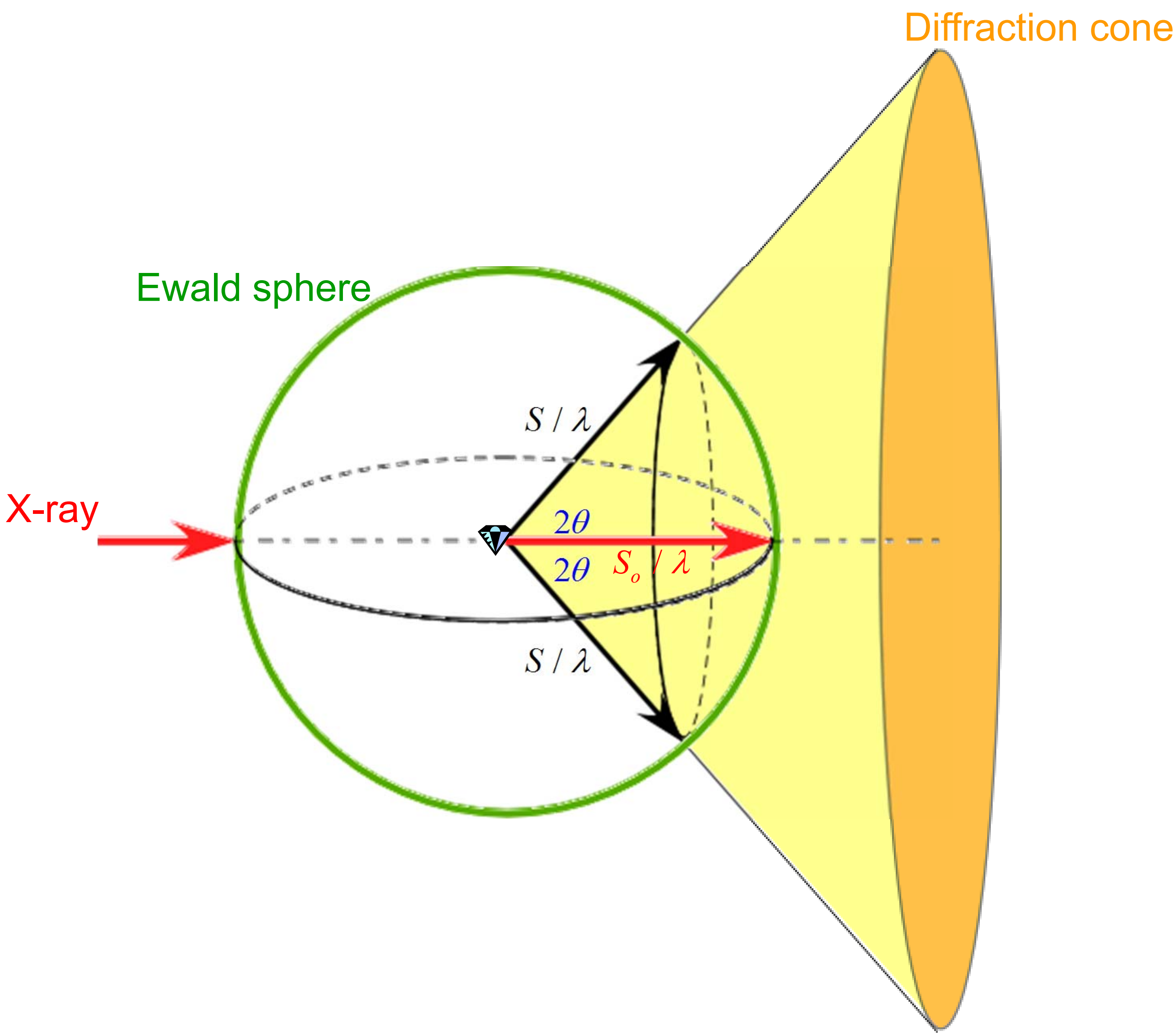
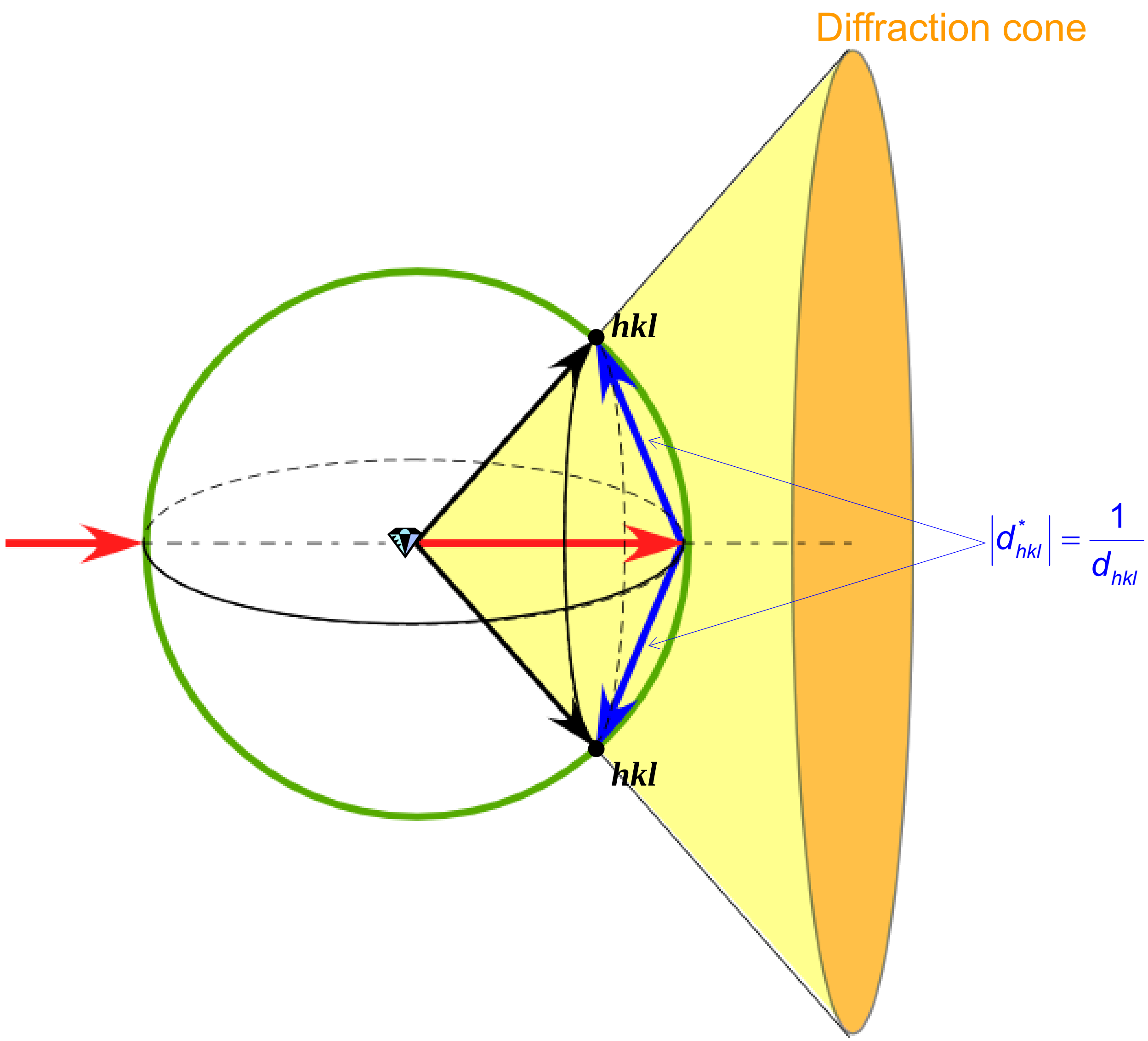


Figure 8.2

Adapted from Vitalij K. Pecharsky and Peter Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, 2nd Edition, © Kluwer Academic Publishers (2009), p. 154.

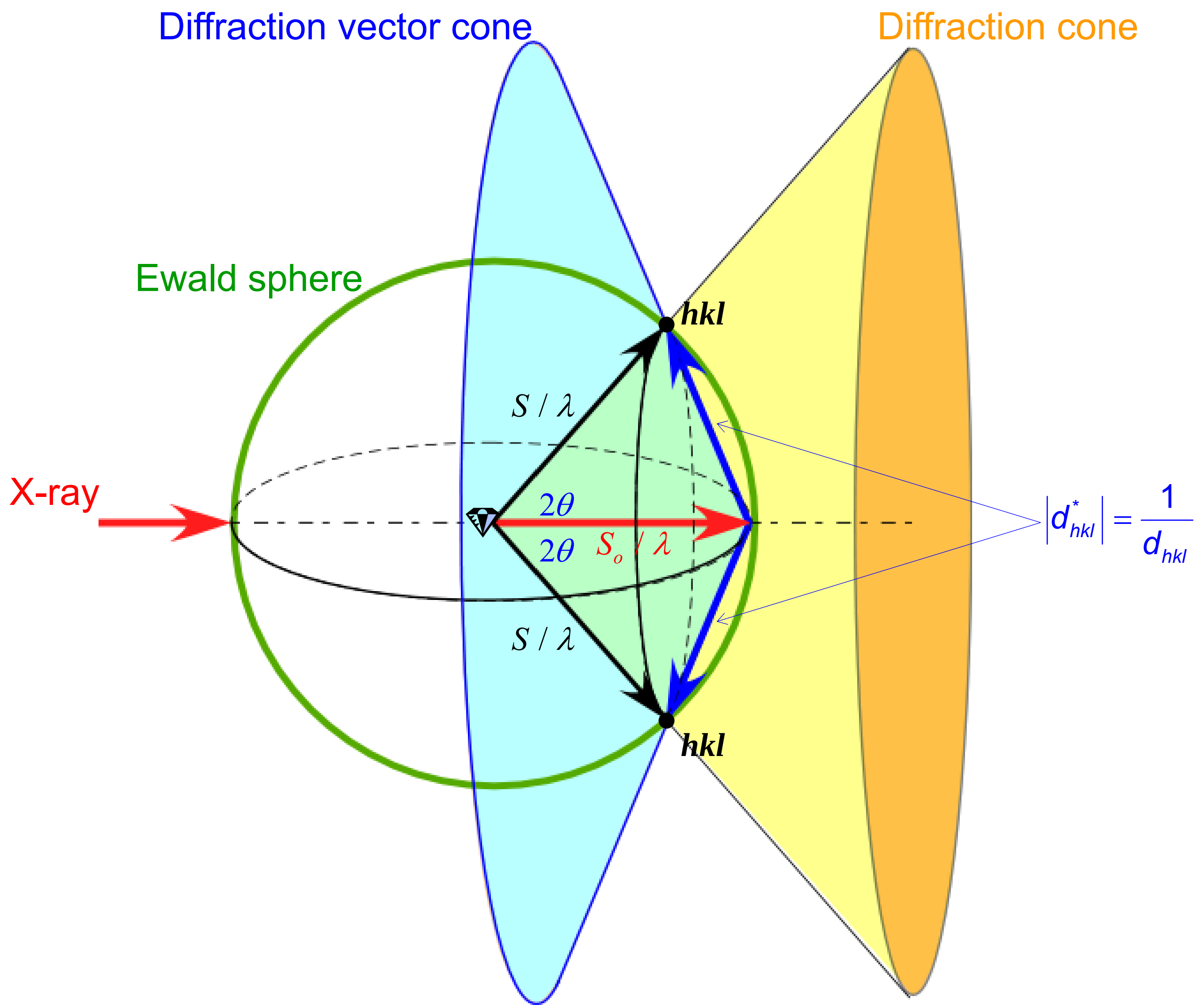

Ewald sphere
X-ray
S_o / λ


Diffraction cone
Ewald sphere
X-ray
S / λ
2θ
2θ
S_o / λ
S / λ



Diffraction cone and diffraction vector cone illustrated on the Ewald sphere.

Adapted from B.B. He, Two-Dimensional X-ray Diffraction, Wiley (2009), p. 20.



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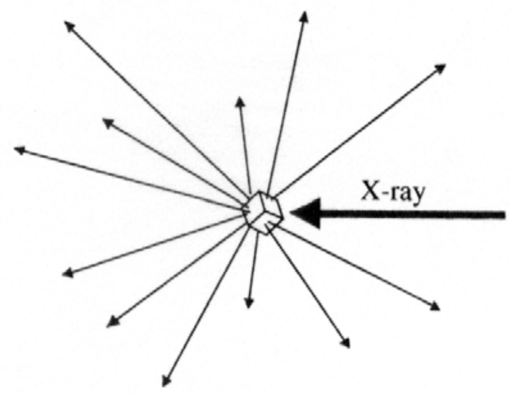
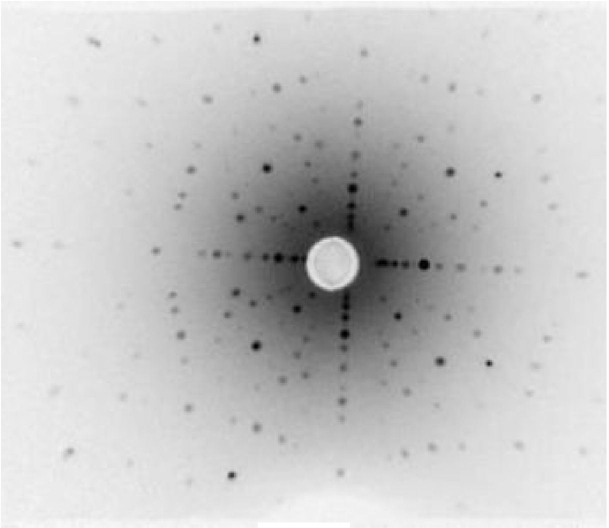
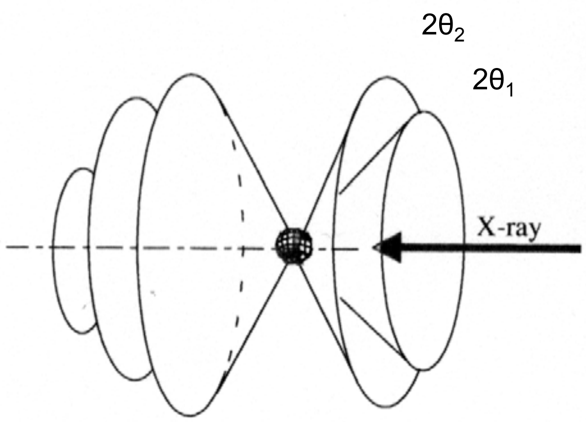


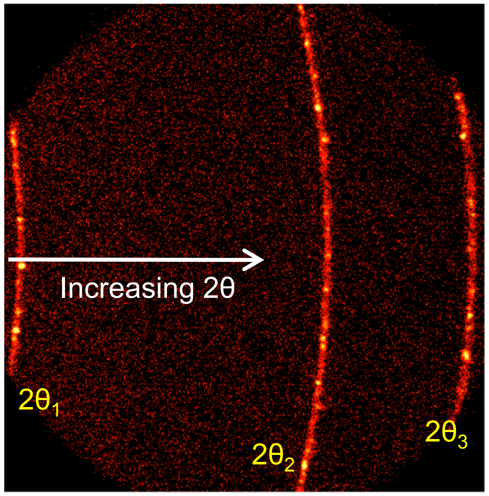
(a)



(b)



(c)



(d)

X-ray diffraction patterns: (a) from single crystal, (b) Laue diffraction pattern from single crystal, (c) diffraction cones from polycrystalline solid, and (d) diffraction frame from a polycrystalline solid. (a) and (c) from B.B. He, *Two-Dimensional X-ray Diffraction*, Wiley (2009), p. 22. (d) from Photonic Science (http://photonic-science.co.uk).

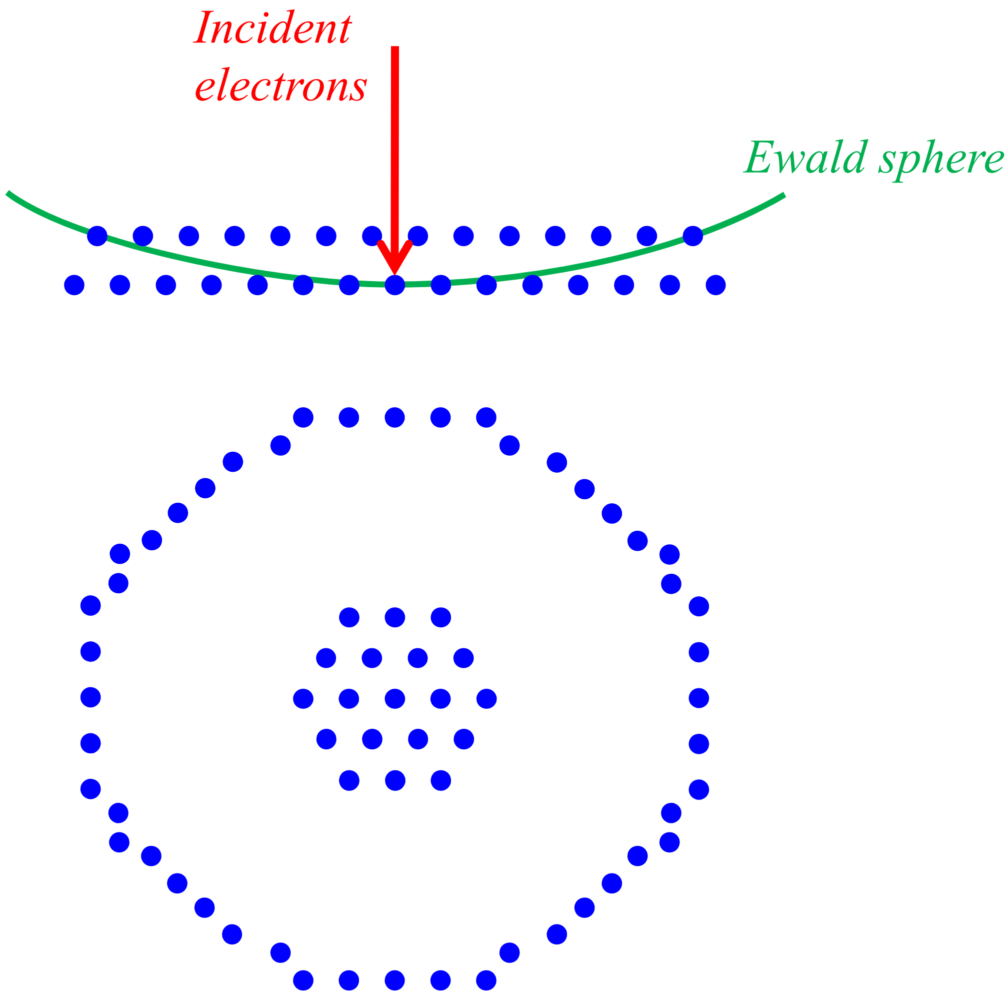
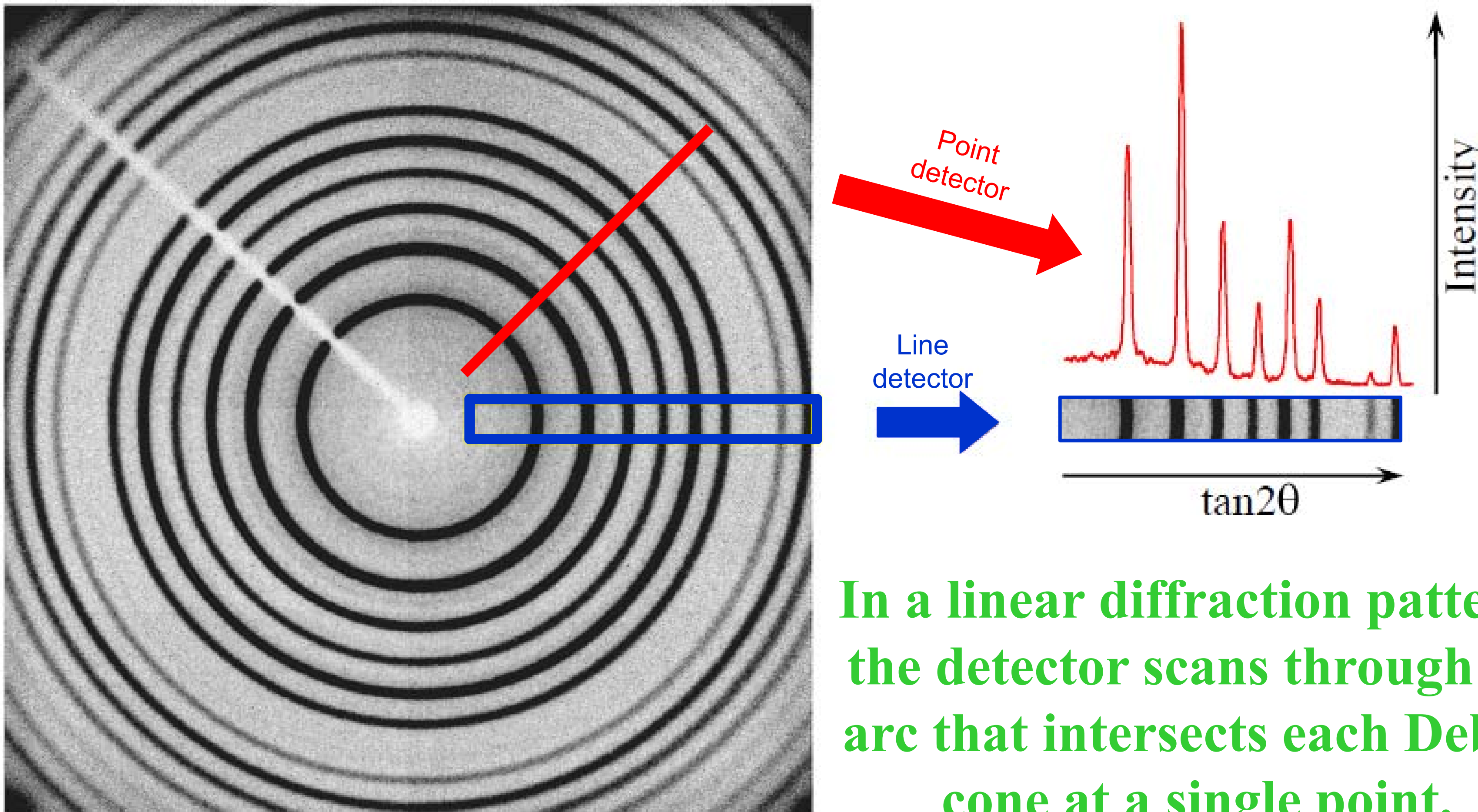


Figure 2.11 Formation of a single crystal diffraction pattern in transmission electron microscopy. The short wavelength of electrons makes the Ewald sphere flat. Thus, the array of reciprocal lattice points in a reciprocal plane touches the sphere surface and generates a diffraction pattern on the TEM screen. Adapted from Y. Leng, *Materials Characterization,* Wiley (2008), p. 55.



In a linear diffraction pattern, the detector scans through an arc that intersects each Debye cone at a single point.

This gives the appearance of a discrete diffraction peak.

Figure 8.4

Adapted from Vitalij K. Pecharsky and Peter Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, 2nd Edition, © Kluwer Academic Publishers (2009), p. 156.

Synopsis

- The Ewald sphere construction allows us to represent Bragg diffraction graphically relative to the reciprocal lattice.

- Reciprocal lattice points lying on the Ewald sphere satisfy Bragg’s law yielding strong diffraction spots/peaks.