



Analytical Methods for Materials

Lesson 16

Scattering and Diffraction Analysis of Materials

Suggested Reading

Chapter 3 in Waseda, pp. 67-75

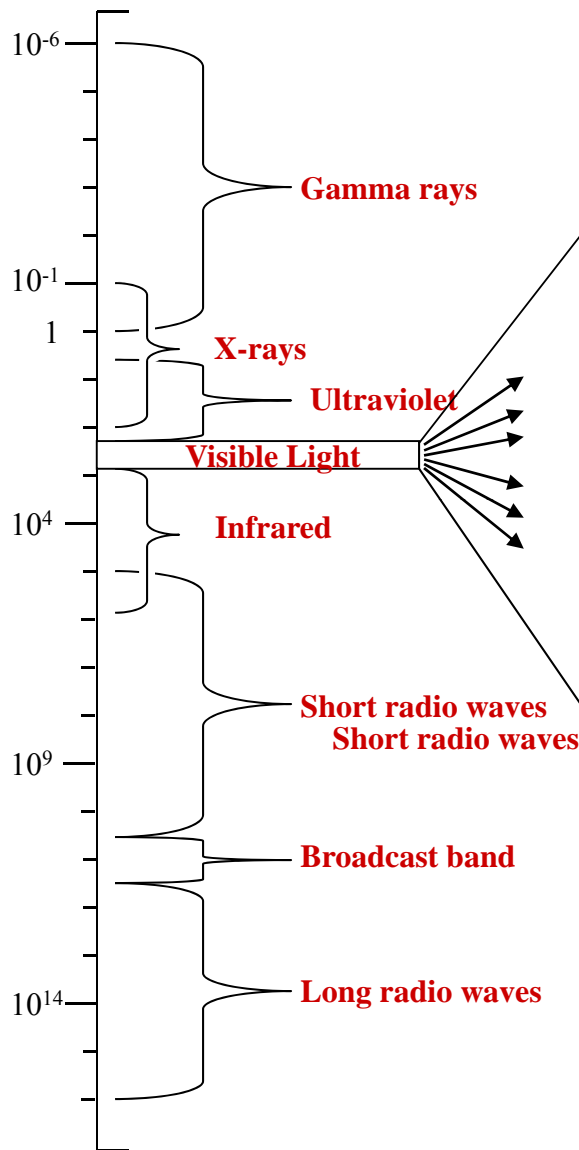
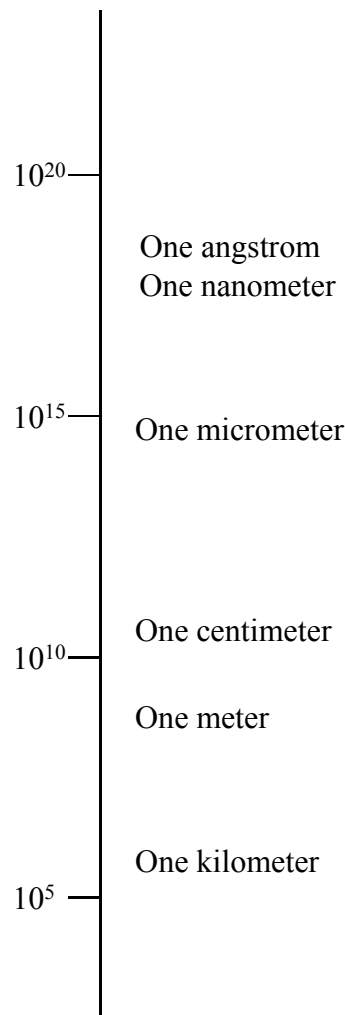
Ch. 6 – B.D. Cullity and S.R. Stock, Elements of X-ray Diffraction, 3rd Edition, Prentice-Hall (2001)

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

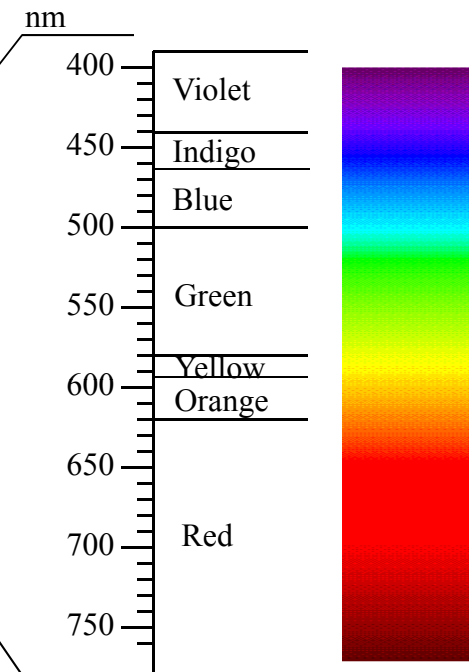
Ch. 7 – Pecharsky and Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, 2nd Edition, Springer (2009)

Frequency in
cycles per second

Wavelength
in nm



Visible Light: $\lambda \sim 6000 \text{ \AA}$
X-rays: $\lambda \sim 0.5 - 2.5 \text{ \AA}$
Electrons: $\lambda \sim 0.05 \text{ \AA}$

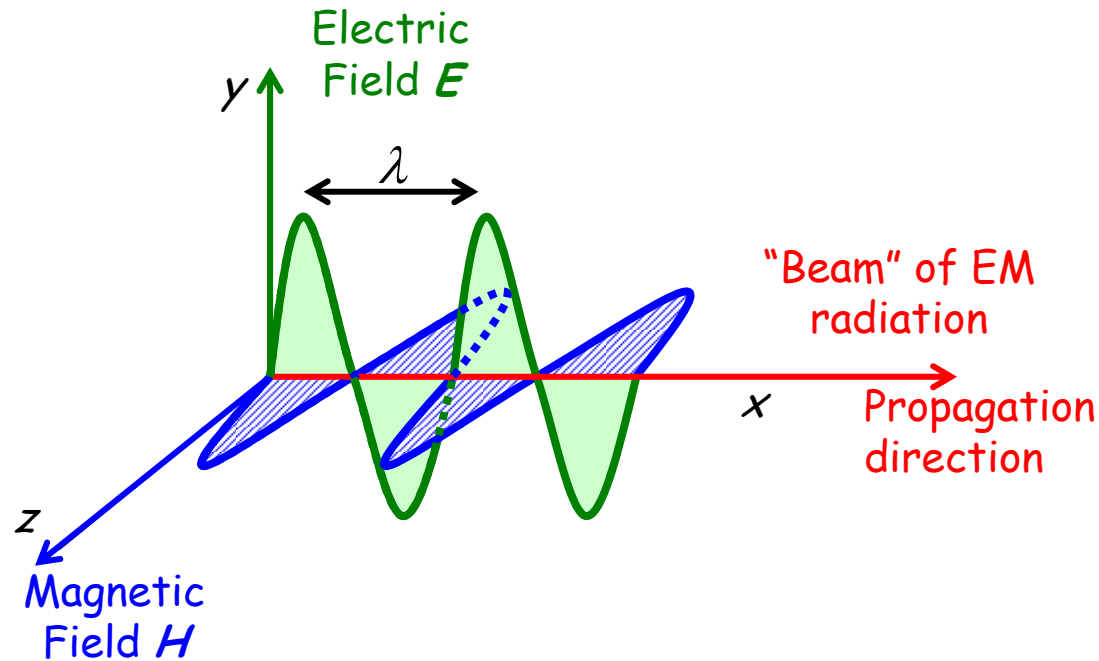


EM Radiation

Self-propagating
waves with
perpendicular
electric and magnetic
components

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

Properties of Electromagnetic Waves



Consist of discrete particles of energy called *photons*.

Photons interact with electrons.

Thus they can be "scattered" by solids.

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

$$h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$$

ν = frequency of the wave

$$c = \text{speed of light} = 3.00 \times 10^8 \text{ m/s}$$

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

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

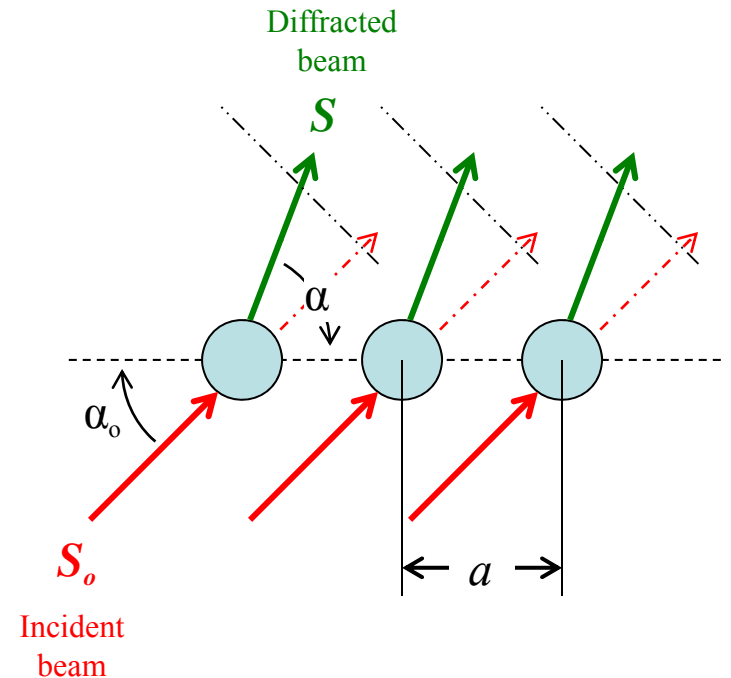
=

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

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

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

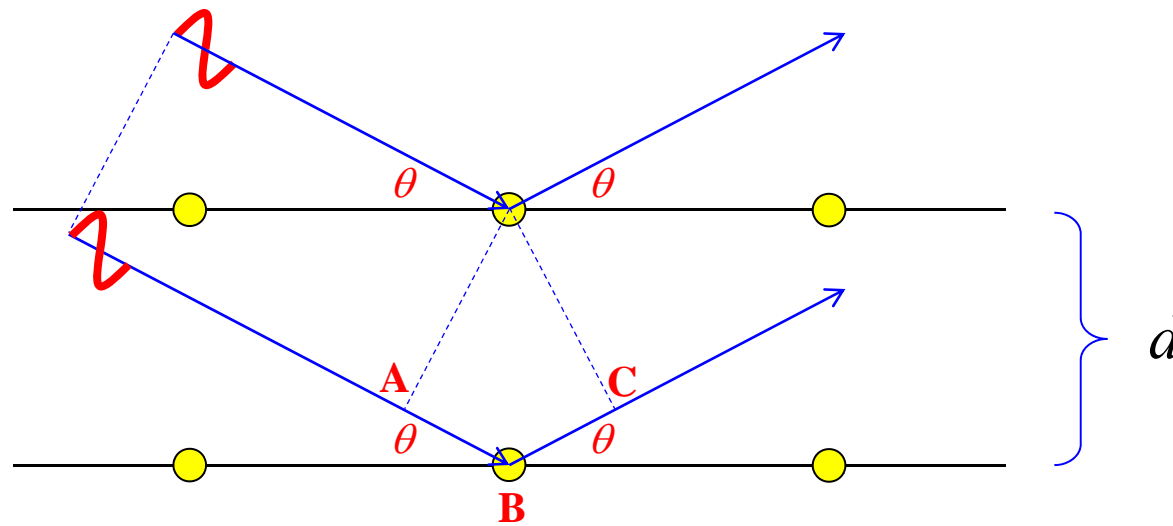
[h, k, l are integers]



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



Bragg's Law

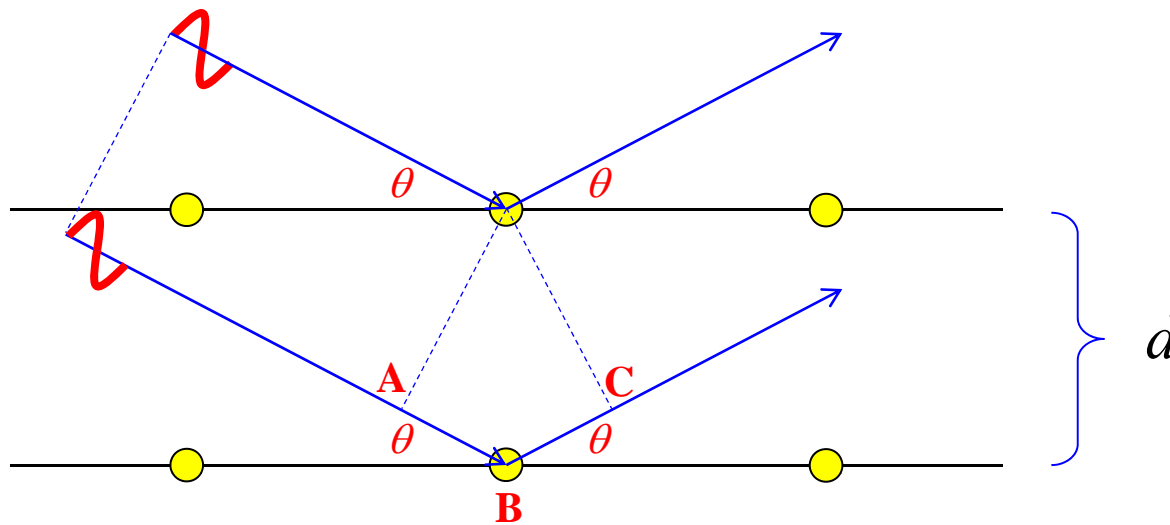


$$\delta = \text{path difference} = AB + BC = 2d \sin \theta$$

\therefore



Bragg's Law



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

For constructive interference $\delta = n\lambda$

\therefore

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

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

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



Bragg's Law

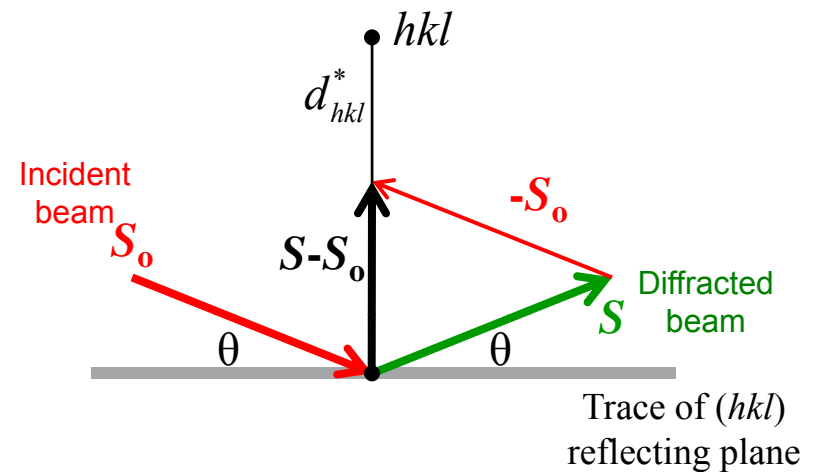
- Bragg's law can be expressed in vector form:

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

$$|d_{hkl}^*| = \frac{1}{d_{hkl}}$$

- 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

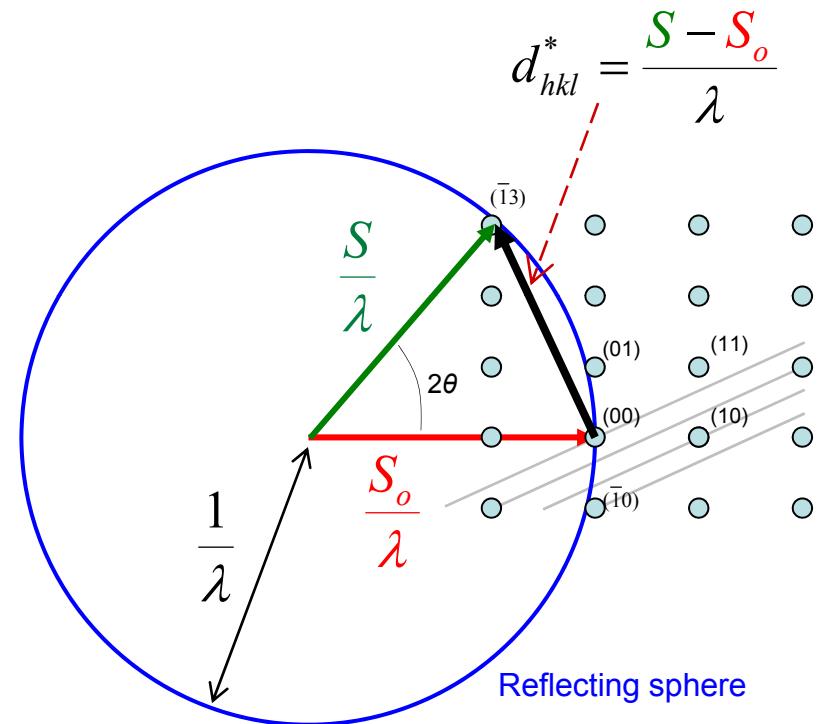
- We can represent the Laue equation graphically.

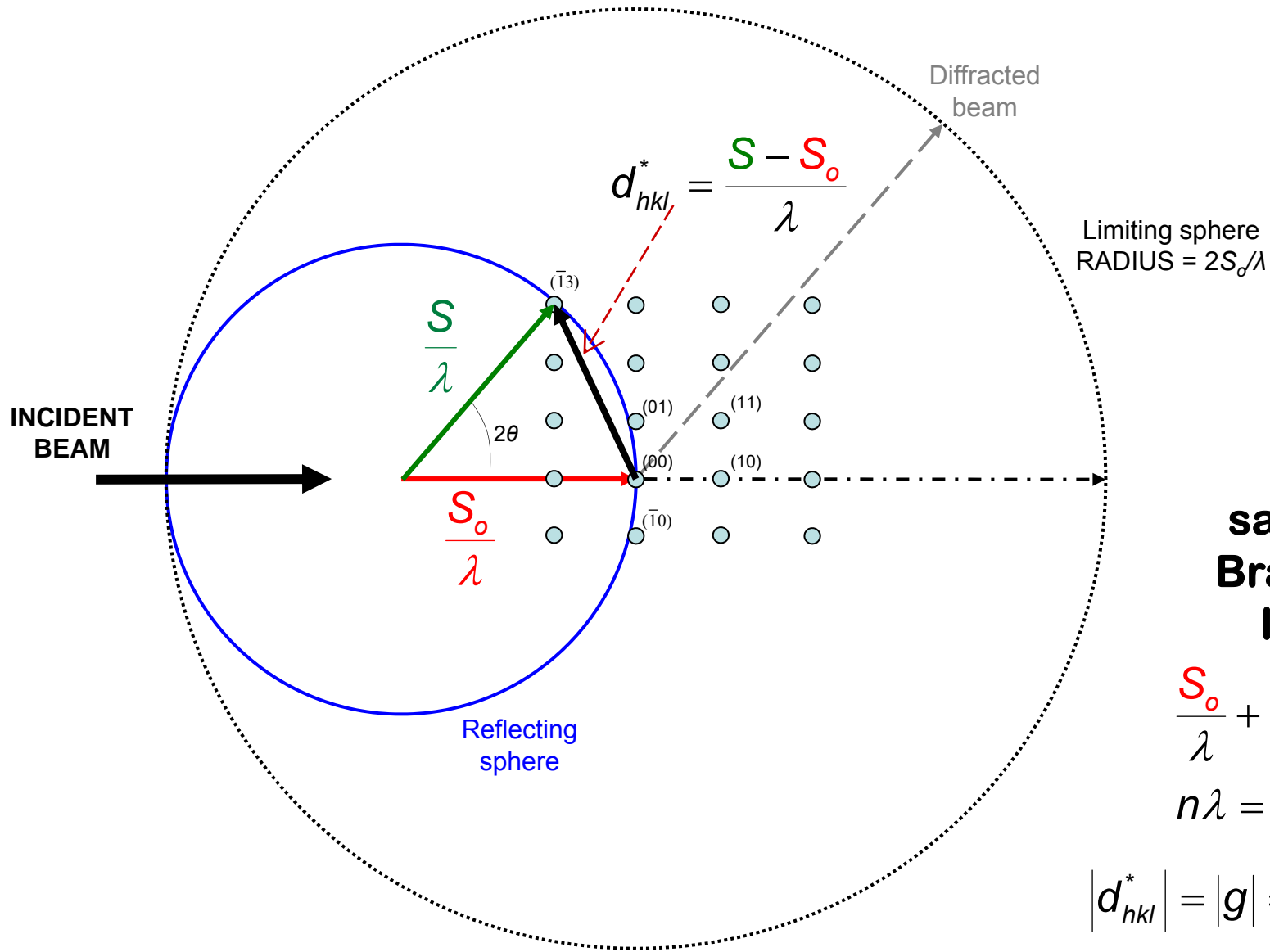
- This is similar to Ewald's sphere.

- **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

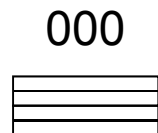
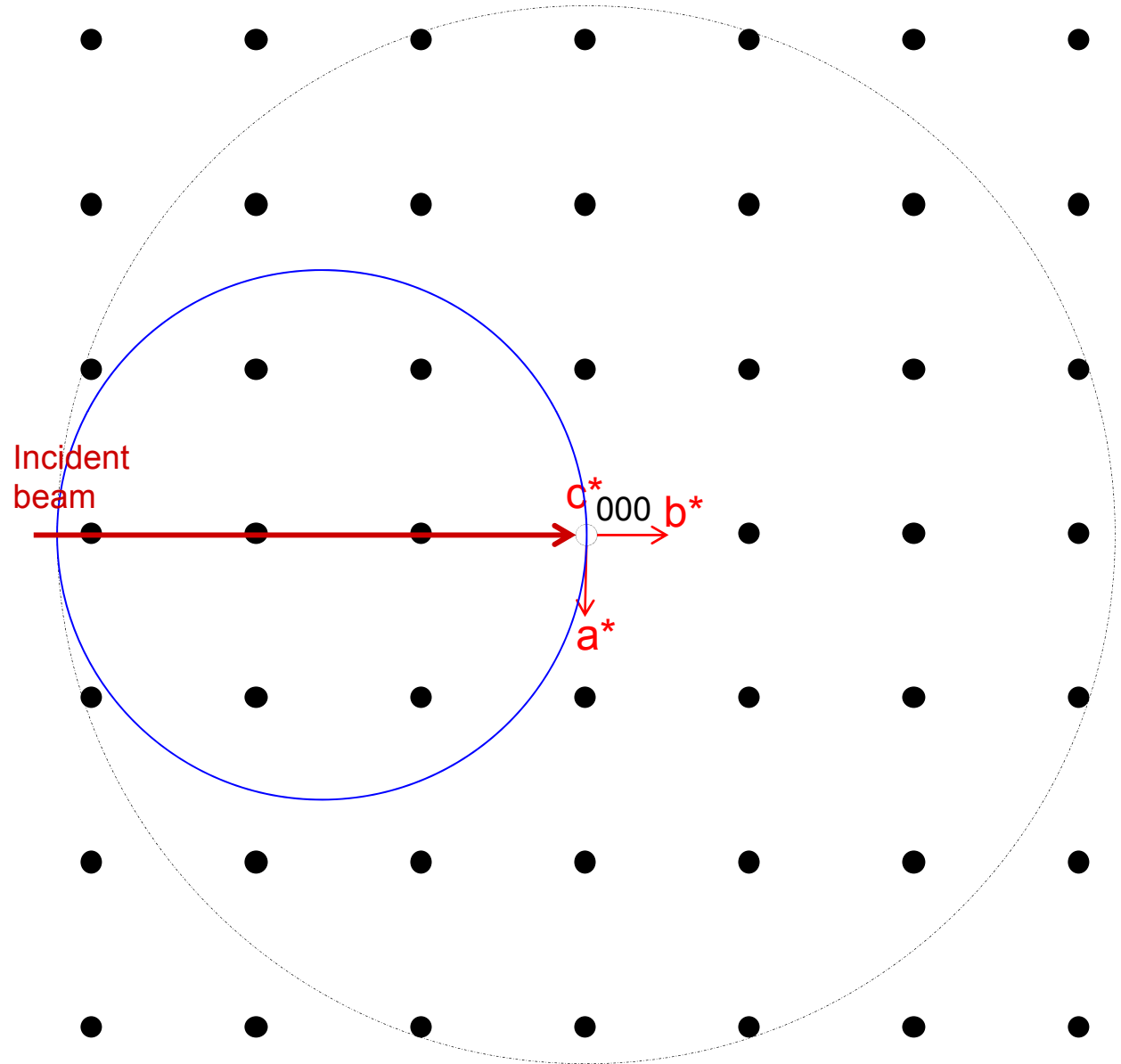
$$\frac{S_o}{\lambda} + d_{hkl}^* = \frac{S}{\lambda}$$

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

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

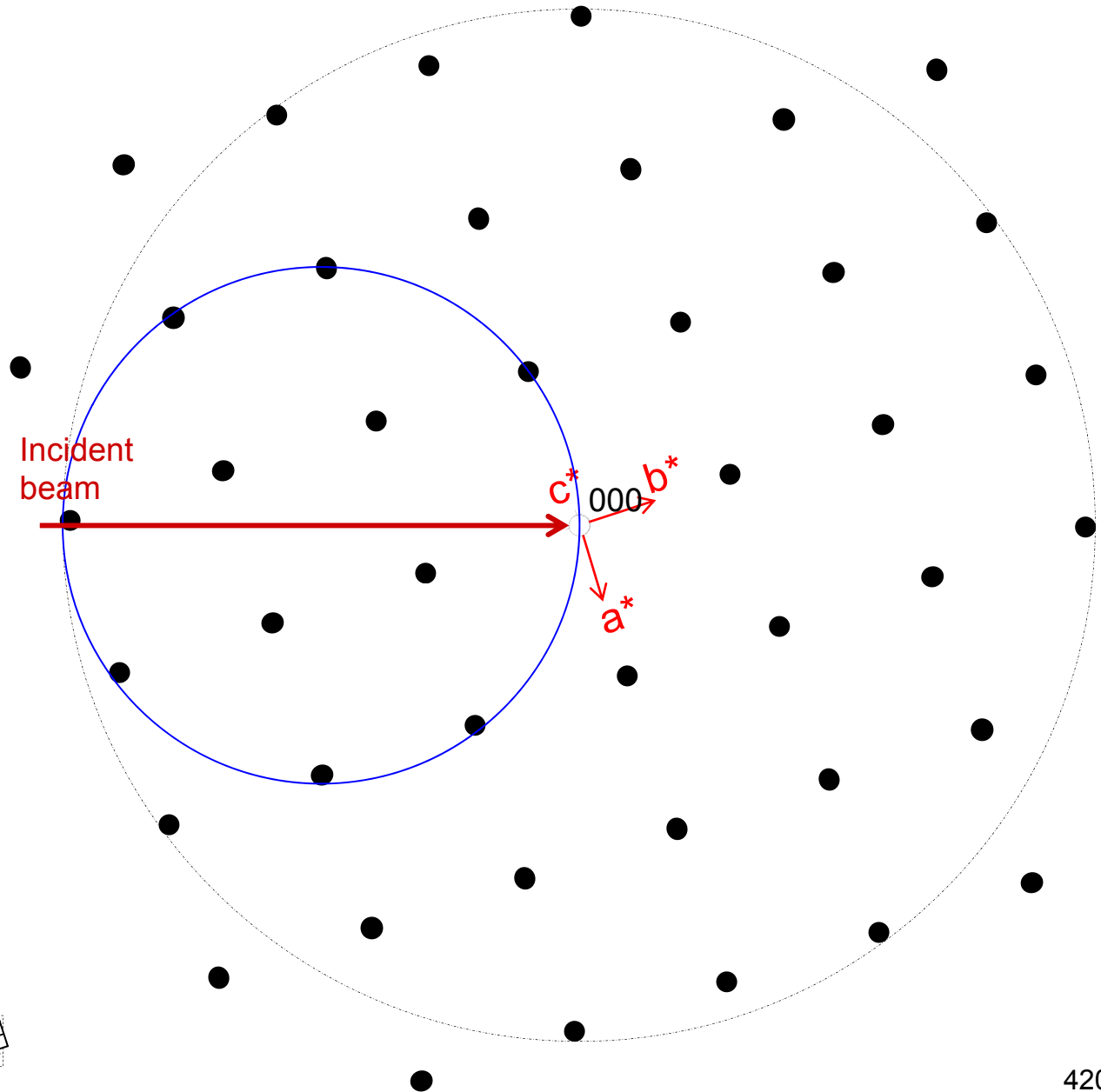
Reciprocal Lattice

- 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 .



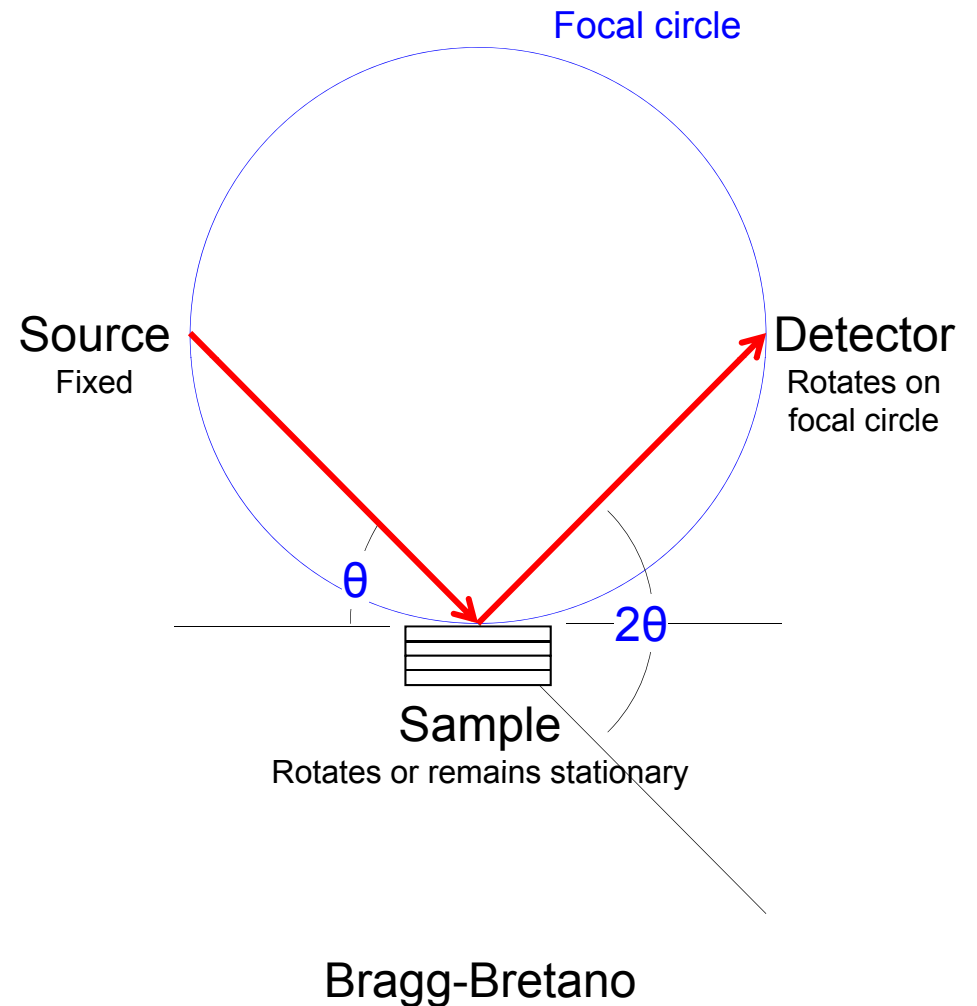
Reciprocal Lattice

- 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 $\theta/2\theta$.
- On instruments such as our Bruker D8 and Philips MPD, the source and detector move while the sample remains stationary.



Diffraction Directions

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

- Cubic:

$$\left. \begin{aligned} \lambda &= 2d \sin \theta \\ &+ \\ \frac{1}{d^2} &= \frac{(h^2 + k^2 + l^2)}{a^2} \end{aligned} \right\} \sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

- 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:

$$\sin^2 \theta_{111} = \frac{\lambda^2}{4a^2} \left(\underset{\substack{\uparrow \\ h}}{1^2} + \underset{\substack{\uparrow \\ k}}{1^2} + \underset{\substack{\uparrow \\ l}}{1^2} \right) = \frac{3\lambda^2}{4a^2}$$

Diffraction Directions

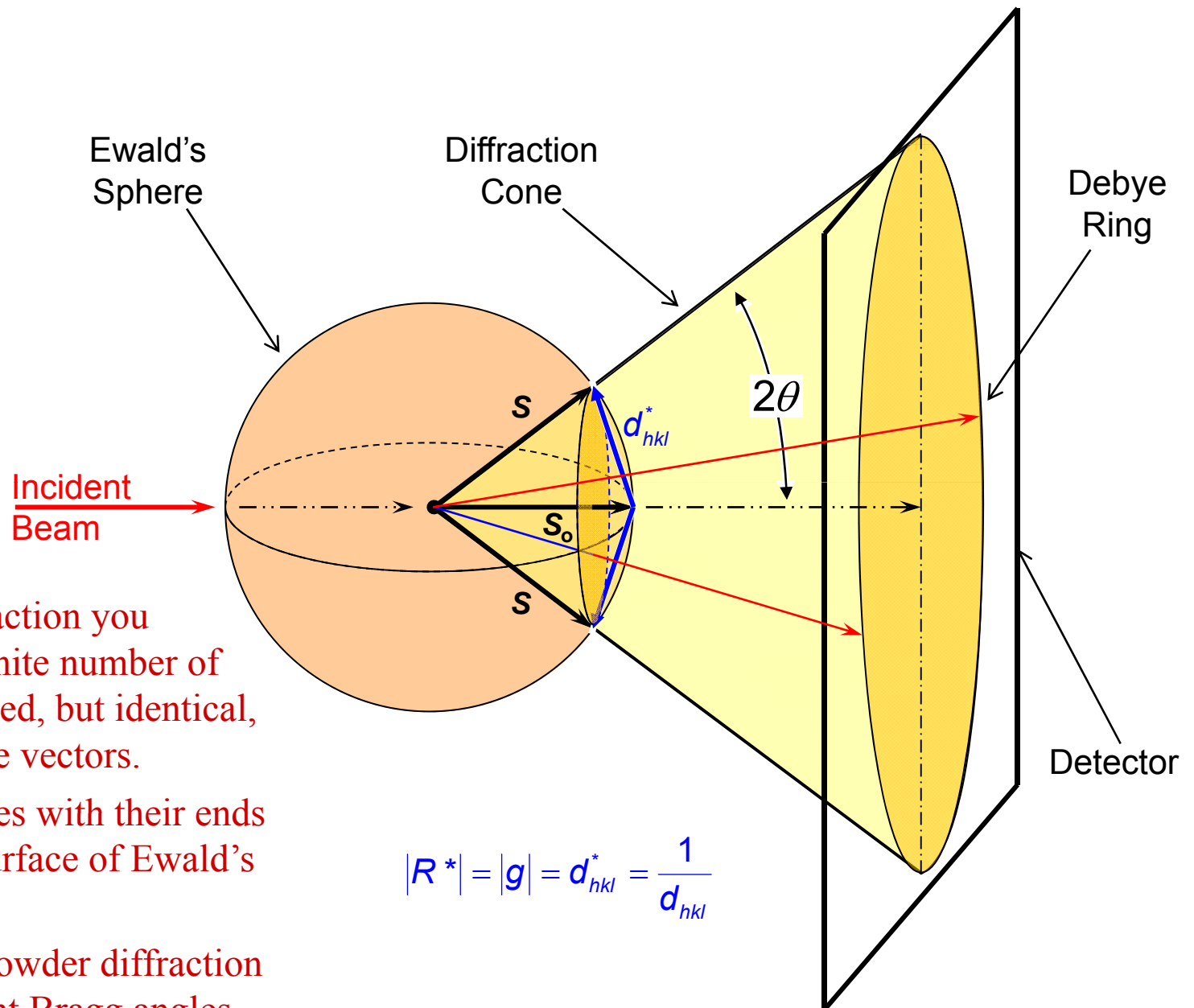
- What about other systems?
- Tetragonal:

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

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

← I've intentionally given you a family here





- 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).

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

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

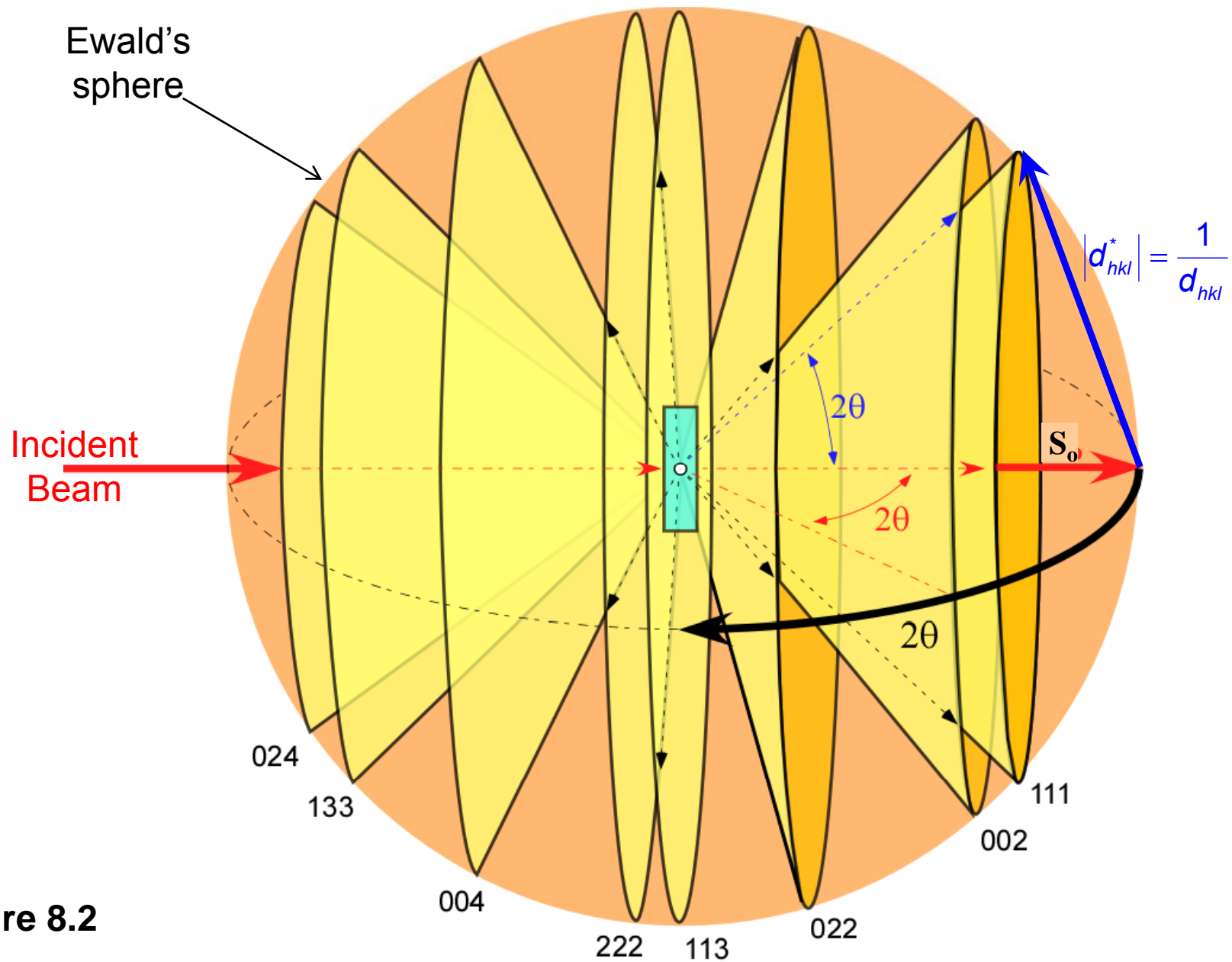
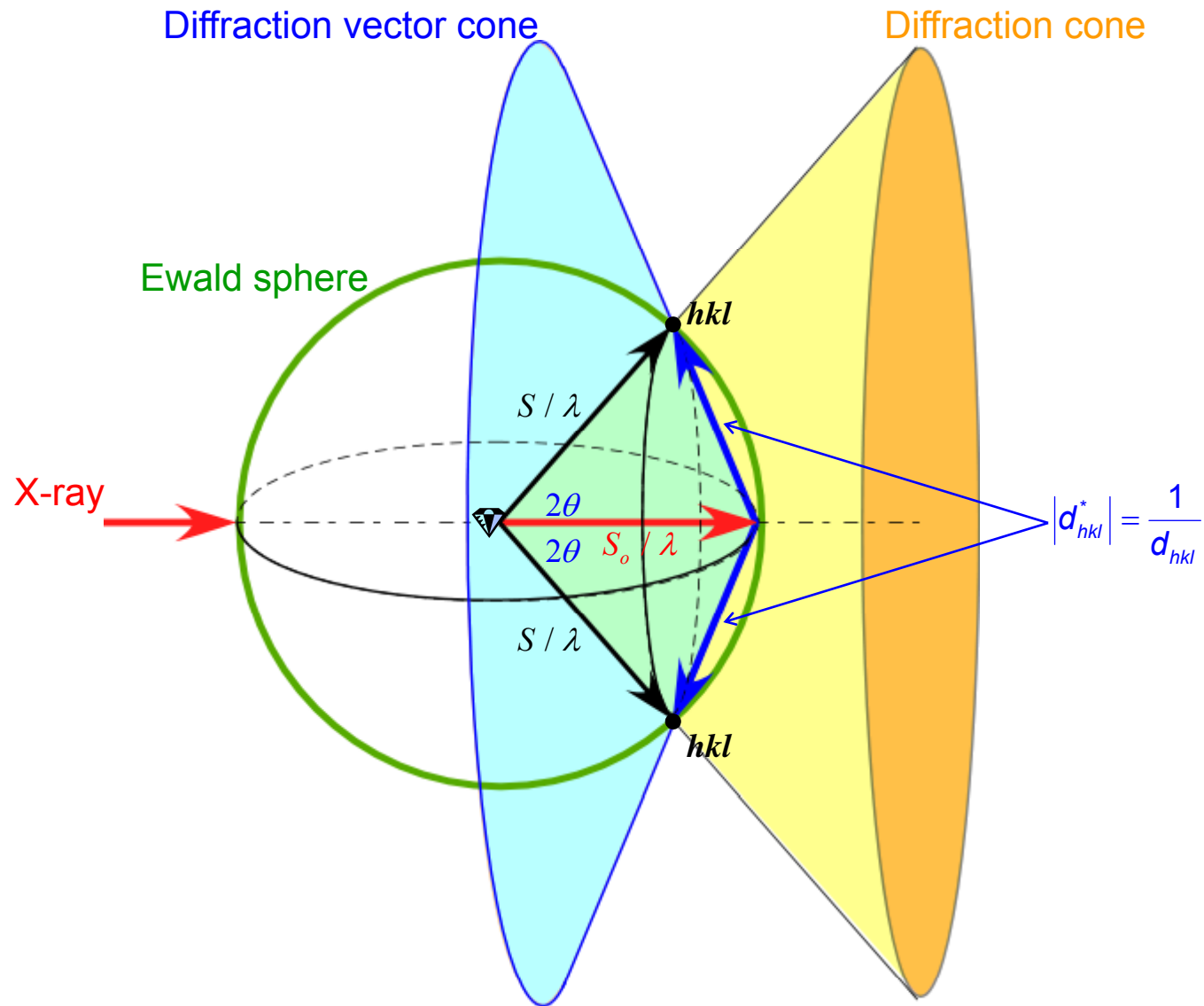
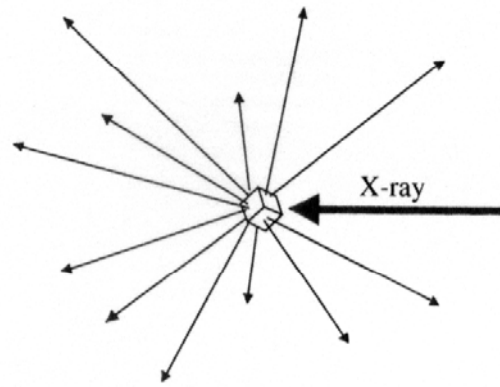


Figure 8.2

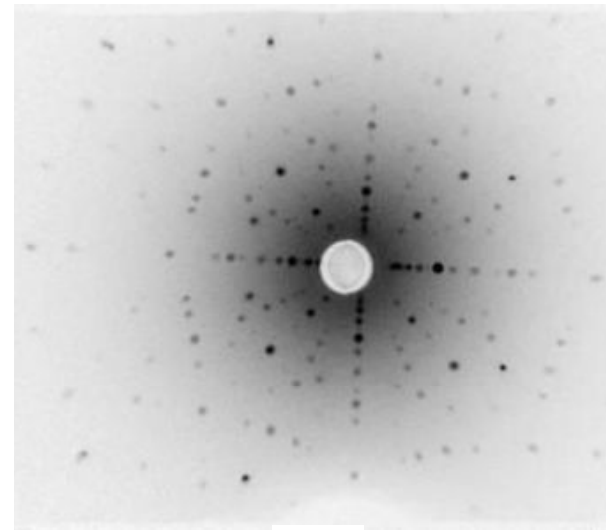
Adapted from Vitalij K. Pecharsky and Peter Y. Zavalij, *Fundamentals of Powder Diffraction and Structural Characterization of Materials*, 2nd Edition, © Kluwer Academic Publishers (2009), p. 154.



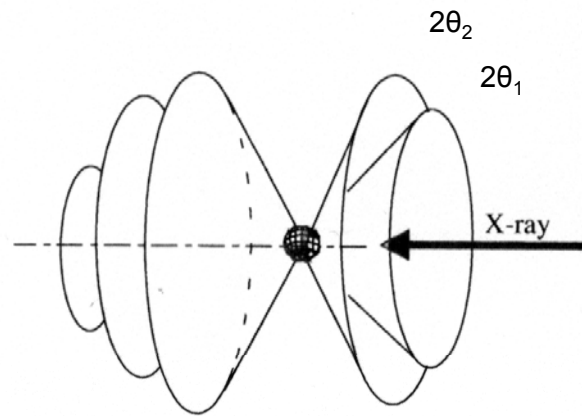
Diffraction cone and diffraction vector cone illustrated on the Ewald sphere.
 Adapted from B.B. He, *Two-Dimensional X-ray Diffraction*, Wiley (2009), p. 20.



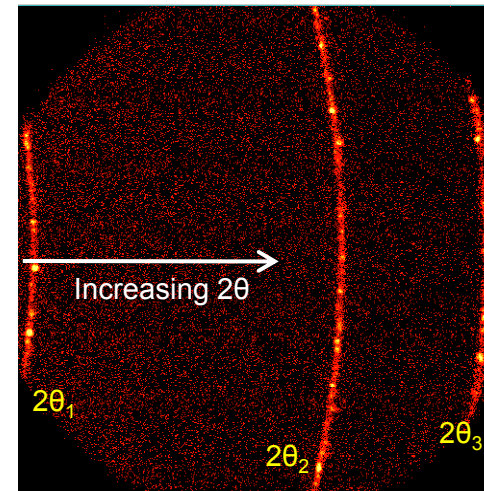
(a)



(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>).

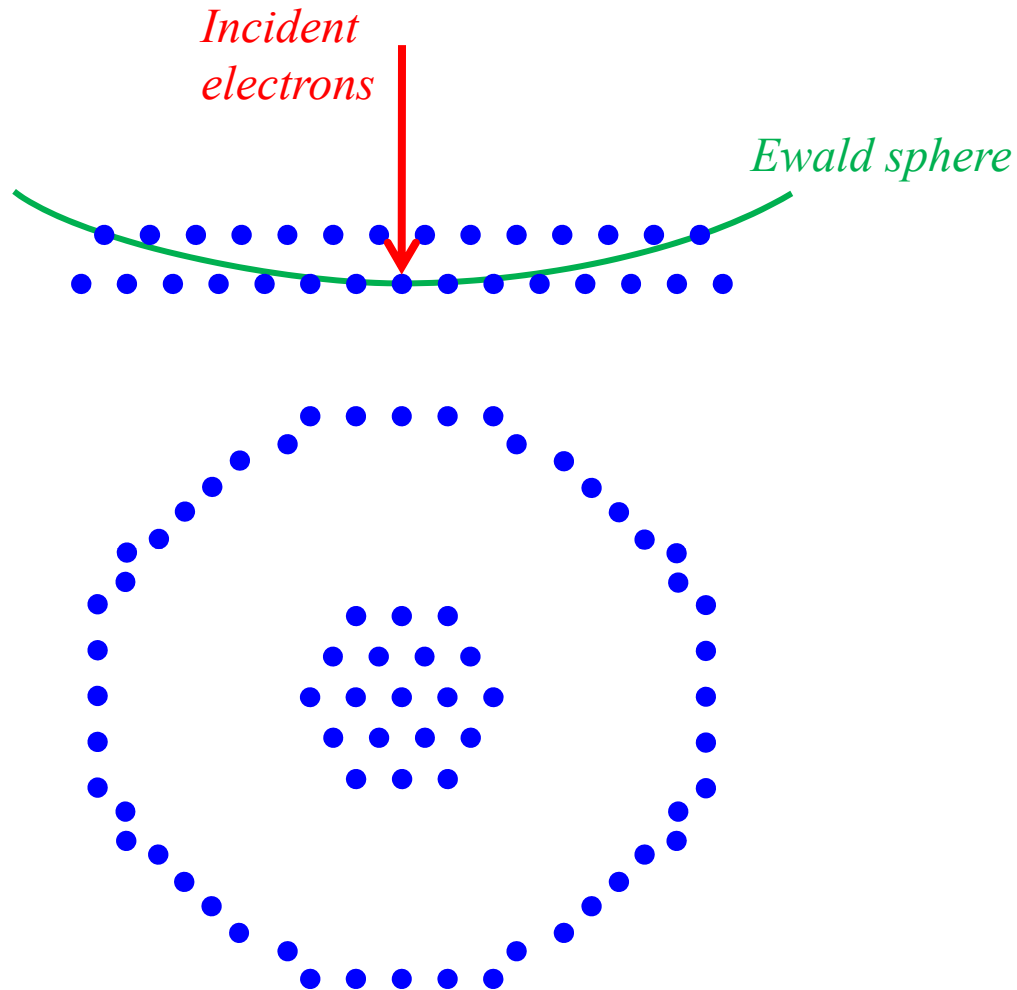
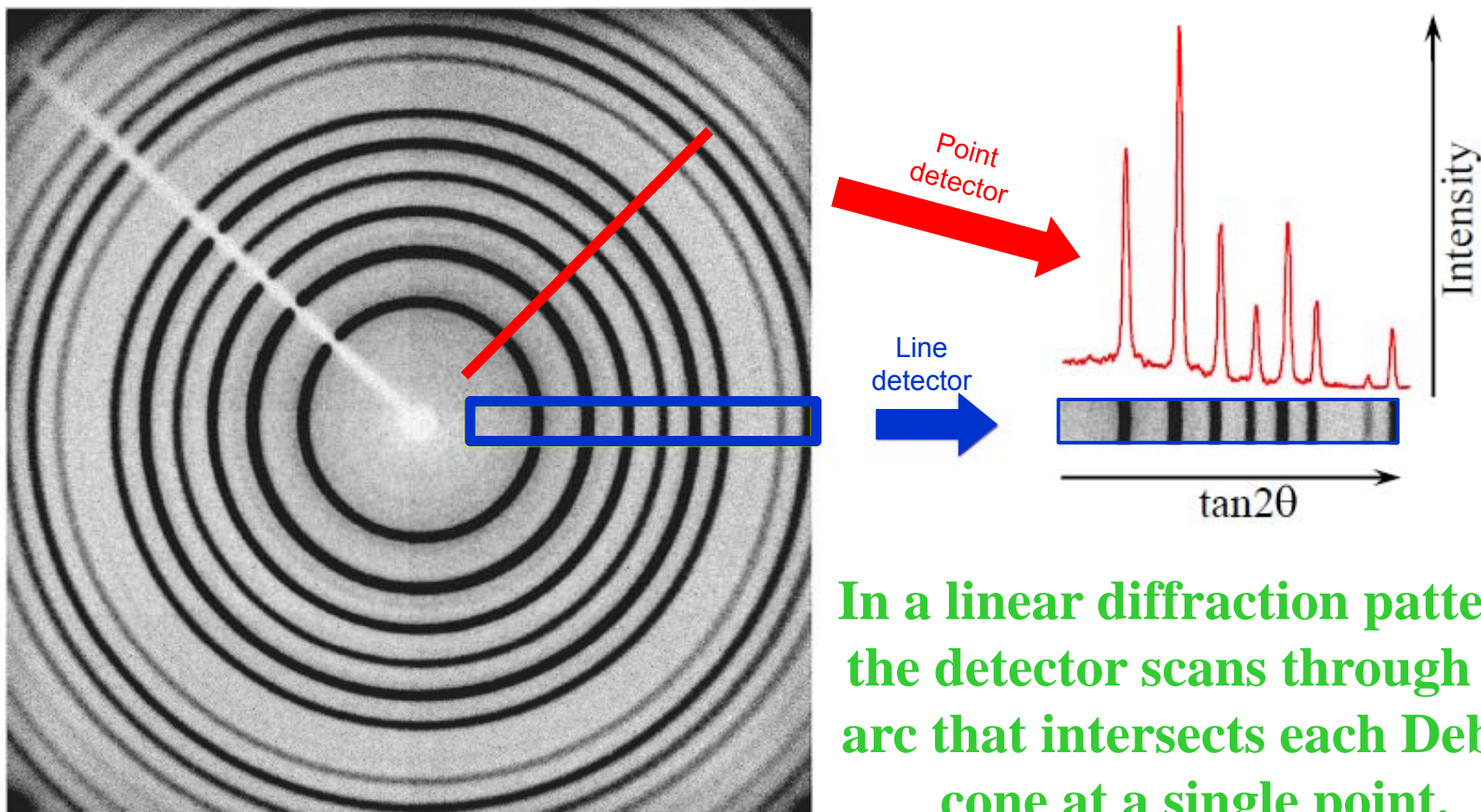


Figure 2.11 Formation of a single crystal diffraction pattern in transmission electron microscopy. The short wavelength of electrons makes the Ewald sphere flat. Thus, the array of reciprocal lattice points in a reciprocal plane touches the sphere surface and generates a diffraction pattern on the TEM 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.