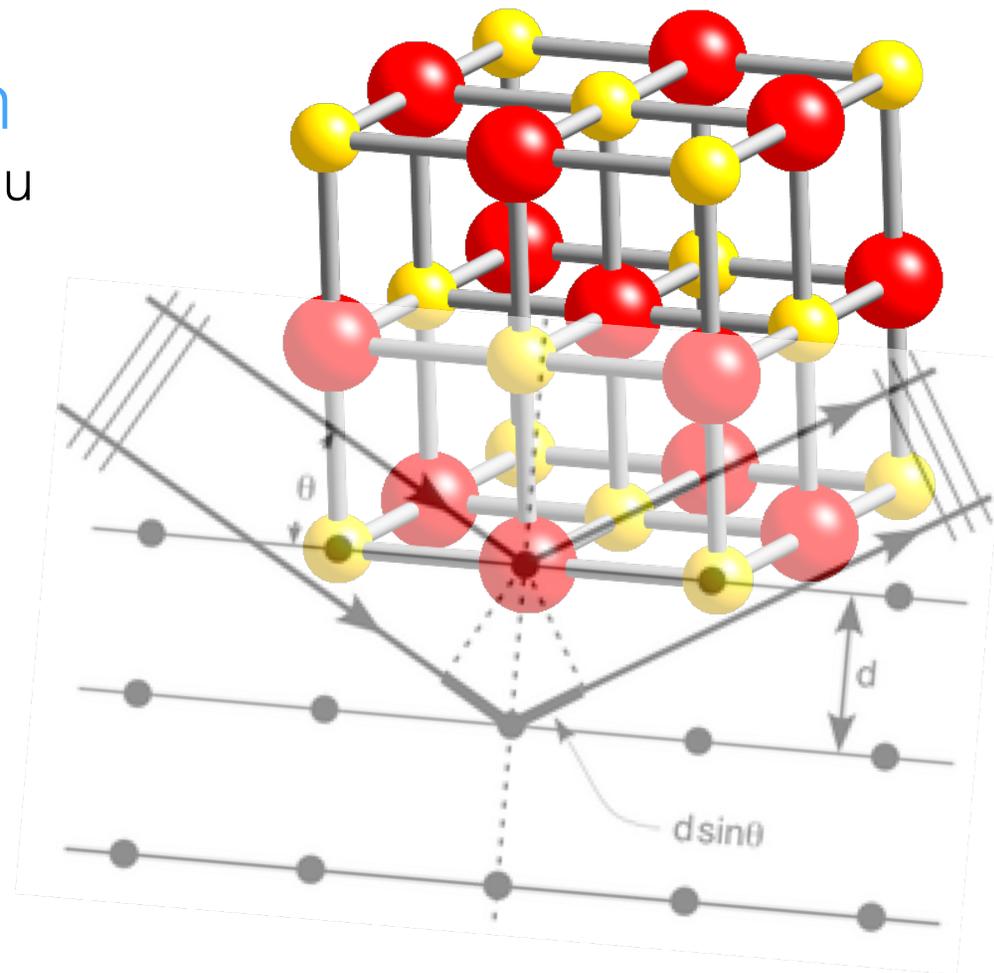


# Principles of X-ray Diffraction (part 1)

Jennifer Jackson  
jackson@gps.caltech.edu

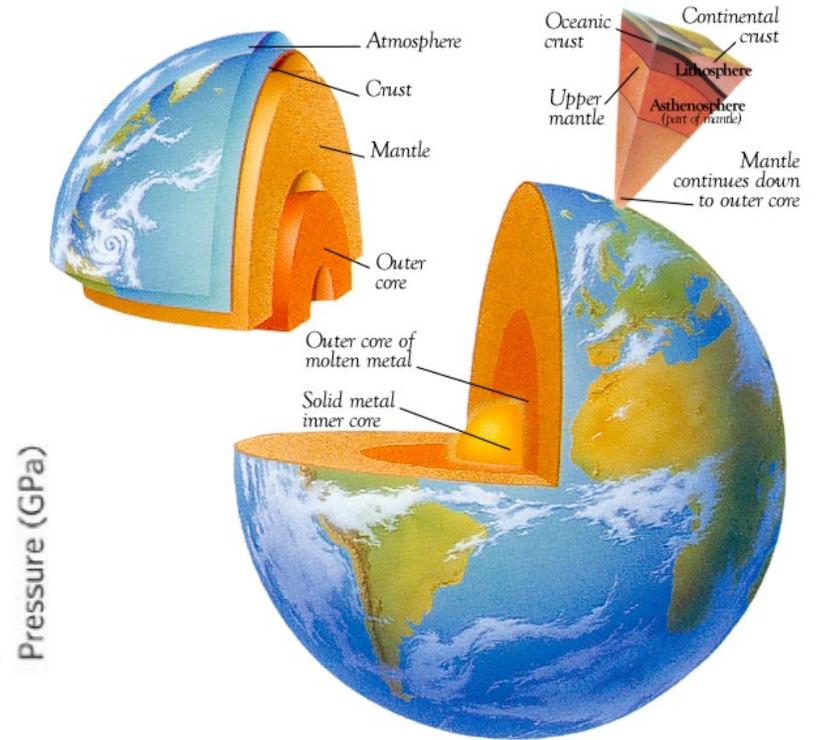
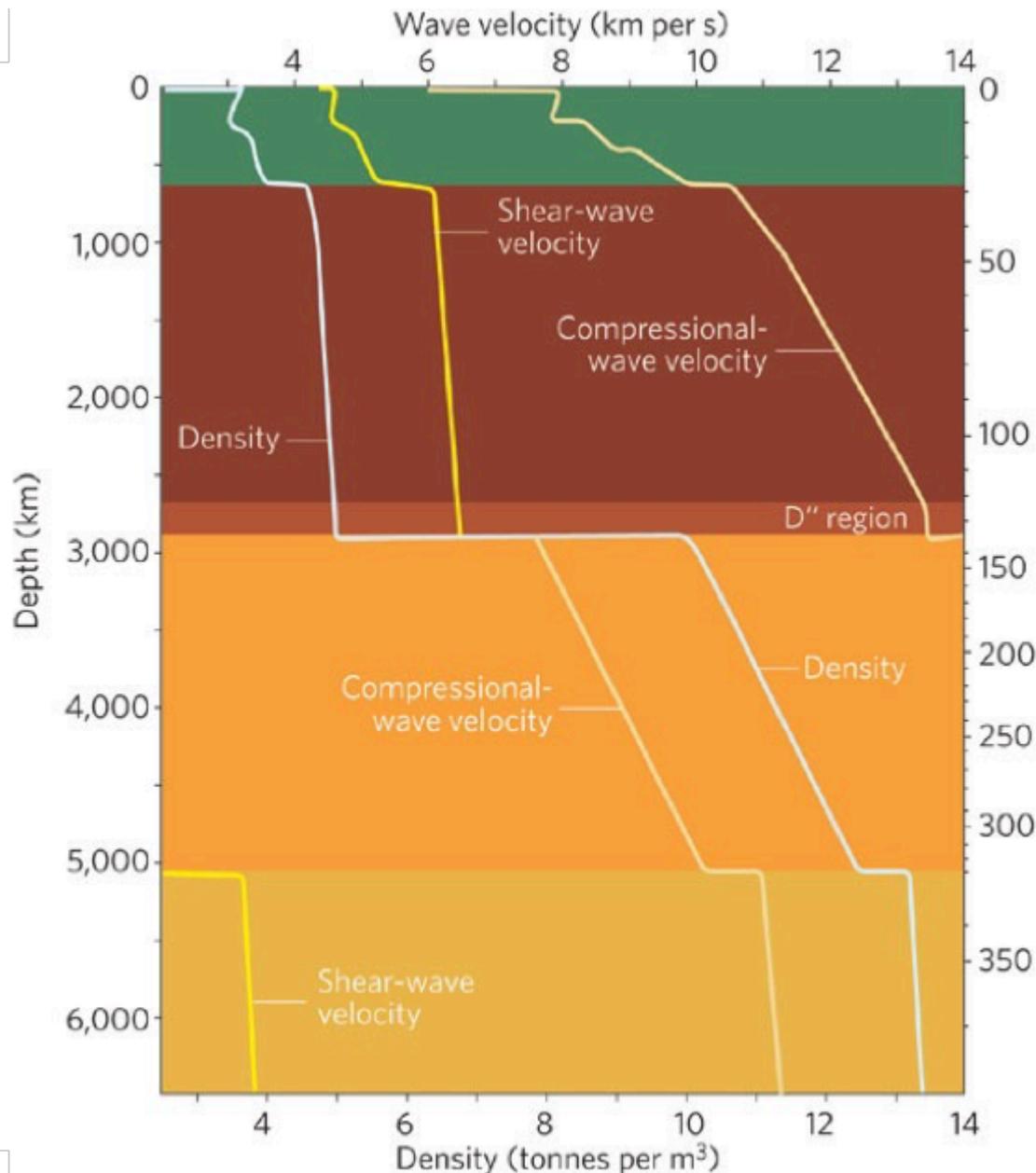
Winter term 2020  
Ge 116



Week 1: Sample preparation for XRD measurements (Jackson's lab, B58, South Mudd)

Lab Schedule:  
TBD

# The first-order structure of Earth's interior: 1D reference Earth models



Preliminary Reference Earth Model (PREM): Dziewonski & Anderson (1981)

Also: AK135 (Kennett *et al.* 1995), Masters & Gubbins (2003), Deuss (2008),

*Figures from: Romanowicz, Nature (2008), Discovery Channel*

# Mantle Mineralogy (Peridotitic)

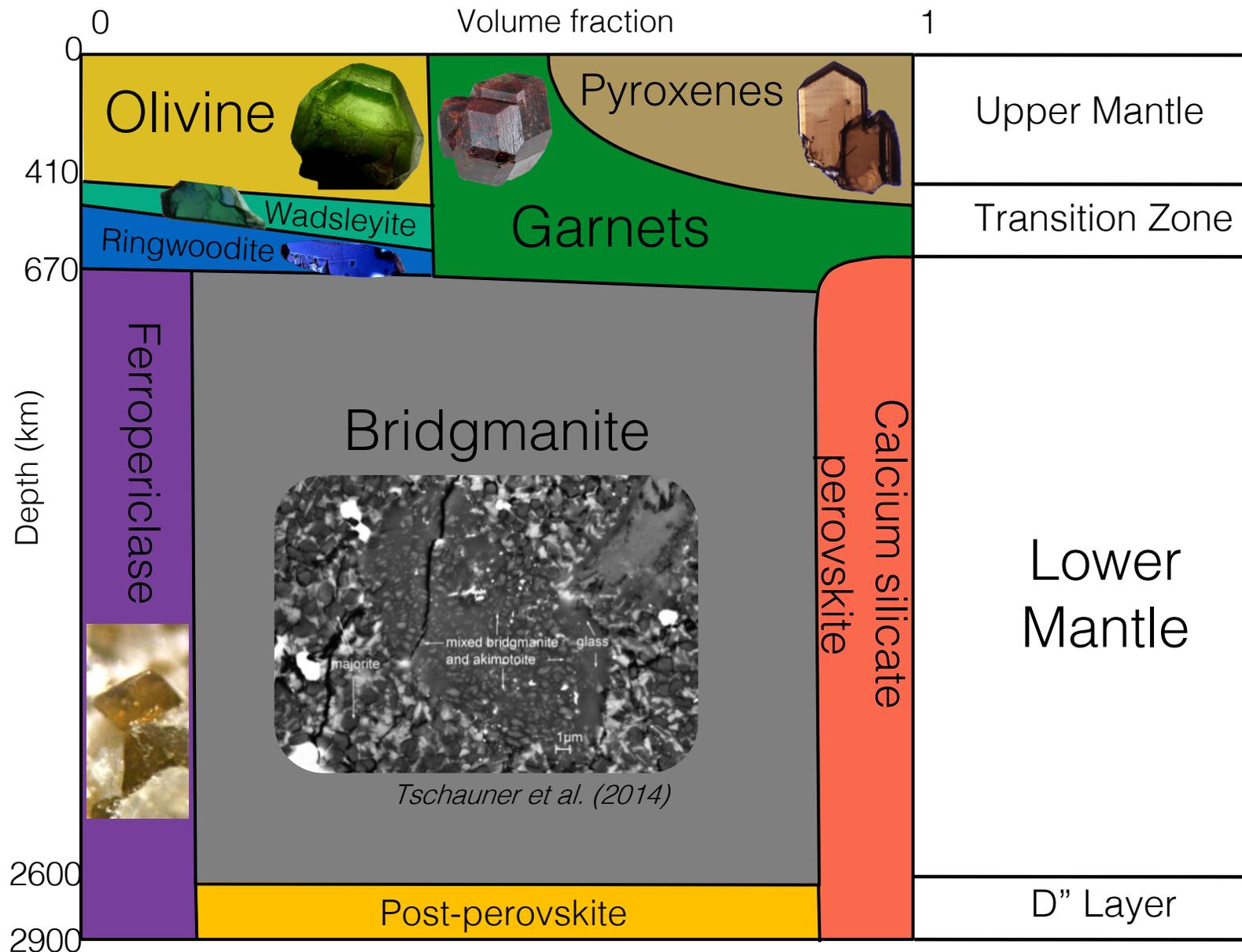
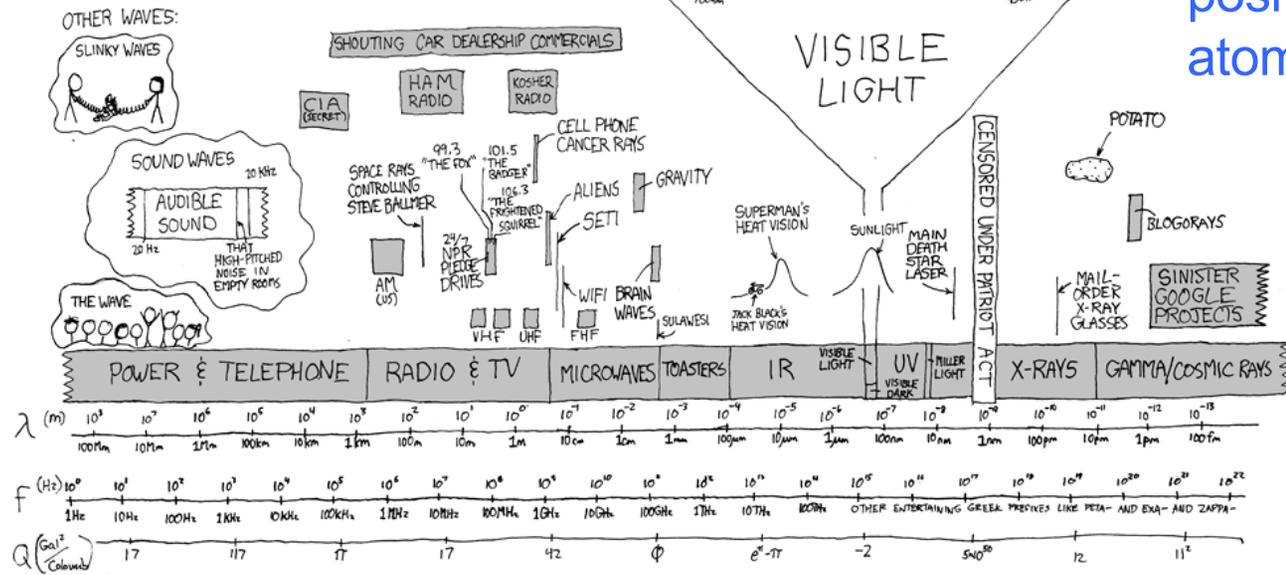


Figure after J. Amodeo; orthopyroxene from minerals.gps.caltech.edu; olivine by Rob Lavinsky; wadsleyite by T. Kawazoe; ringwoodite by Joe Smyth

# THE ELECTROMAGNETIC SPECTRUM

THESE WAVES TRAVEL THROUGH THE ELECTROMAGNETIC FIELD. THEY WERE FORMERLY CARRIED BY THE AETHER, WHICH WAS DECOMMISSIONED IN 1897 DUE TO BUDGET CUTS.

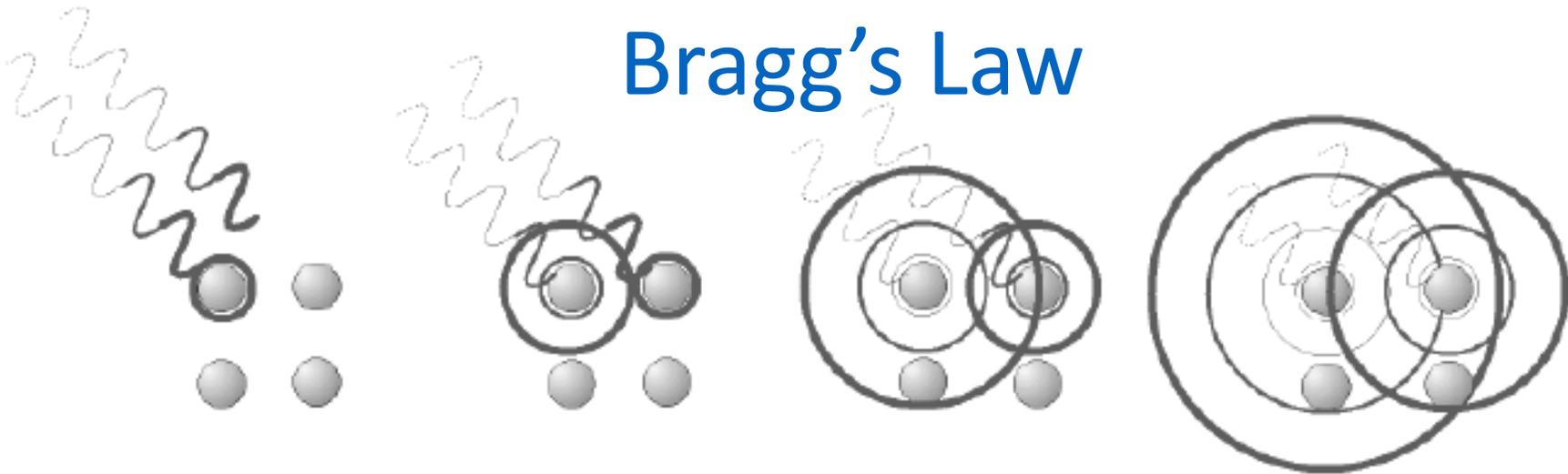


X-rays have wavelengths,  $\lambda$ :  $\sim 0.1 \text{ nm}$  to  $10^{-6} \text{ nm}$ : Comparable to interatomic positions, thus ideal for atomic diffracting conditions



- Discovery of X-rays (Röntgen-rays, Brehmsstrahlung): 1895 by Wilhem Röntgen, Nobel 1901  
*Side note:* Nikola Tesla was already building vacuum tubes and unbeknownst to him, produced such radiation. After Röntgen announced his discovery, Tesla sent him the above image.
- Discovery of diffraction of X-rays by an orderly arrangement of atoms (crystals): 1912 by Max Theodor Felix von Laue, Nobel 1914
- Analysis of crystal structure by x-rays: Sirs W.H. and W.L. Bragg, Nobel 1915
- Also in that year, 1915: Einstein's General Theory of Relativity published. Recognition of Einstein's Theoretical physics and discovery of the photoelectric effect (1021): light as a particle (photon) not just a wave

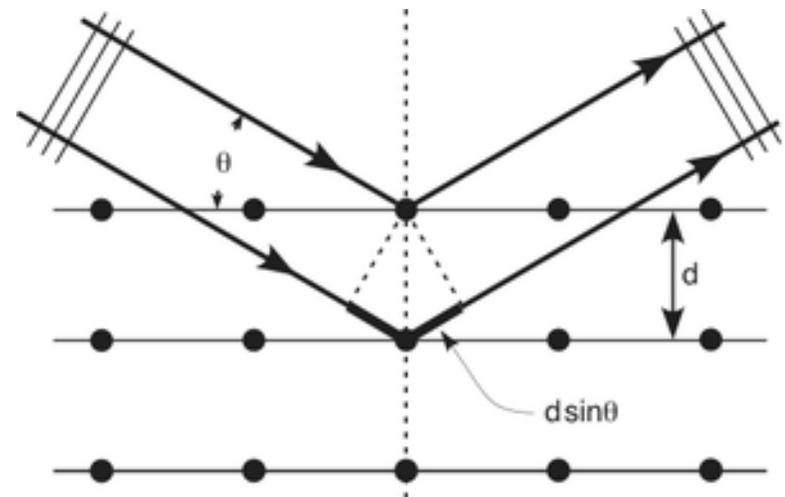
# Bragg's Law



X-rays interact with the electric field surrounding the atoms. The electron cloud re-radiates waves with the same frequency (energy) as the X-rays (elastic scattering). Energy is conserved, only momentum has changed. Those waves interfere with one another creating constructive and destructive interferences. The nature of this interference can be described by *Bragg's law, which is a kinematic description* that states that the interference is constructive when the phase shift is proportional to  $2\pi$ , and considers only single planes (not multiple). This gives the relation:

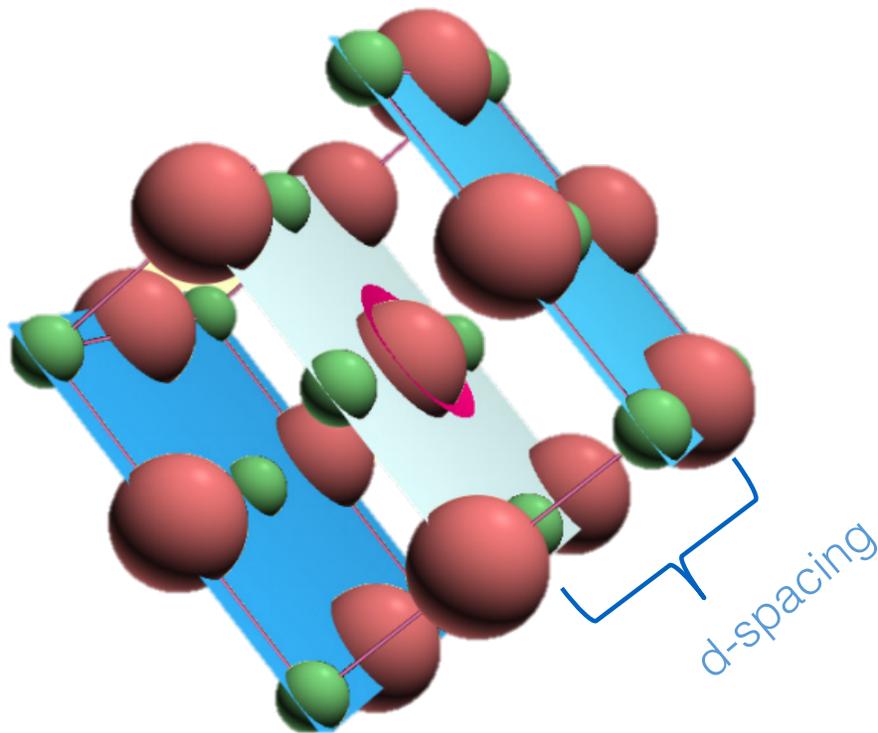
$$n\lambda = 2d \sin \theta$$

Contrast with dynamical diffraction of x-rays:  
Considers multiple reflections from different planes, describes scattering from nearly perfect single crystals (like silicon)

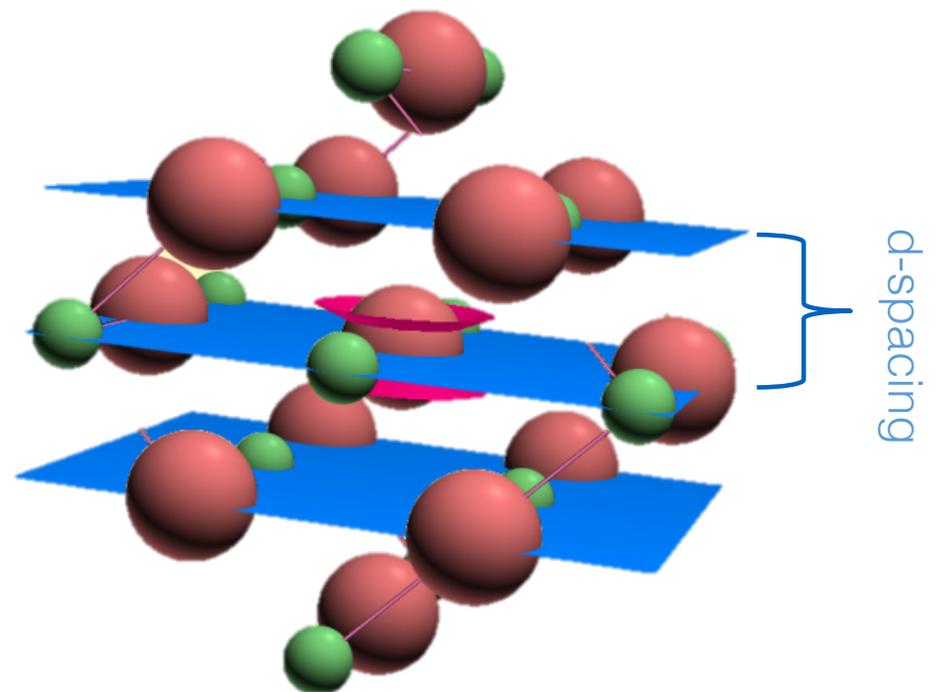


# Crystal Planes

- A crystal has a periodic arrangement of atoms with crystal planes.
- Assume that each crystal plane reflects radiation like a mirror.



(200) planes of NaCl



(220) planes of NaCl

# Miller Indices - Planes

- The orientation of a plane may be defined by how the plane intersects crystallographic axes.
- Brackets (curvy = planes, angular = directions):

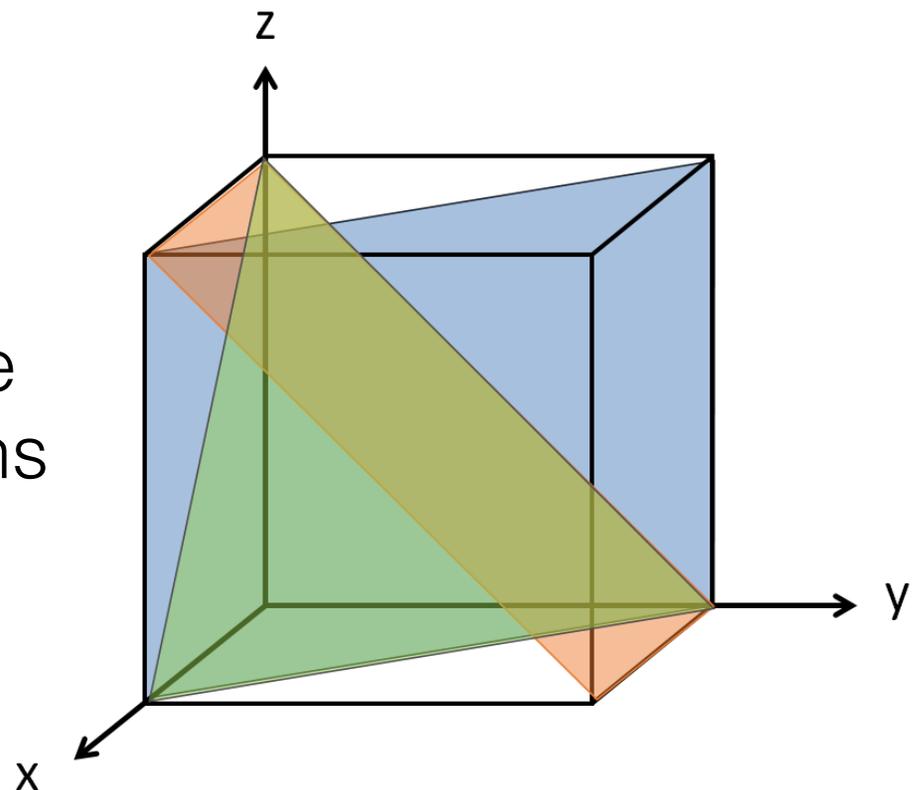
$()$  = plane

$\{ \}$  = set of all planes  
corresponding to  $()$

$[\ ]$  = direction

orthogonal to plane

$\langle \rangle$  = set of all directions  
corresponding to  $[\ ]$

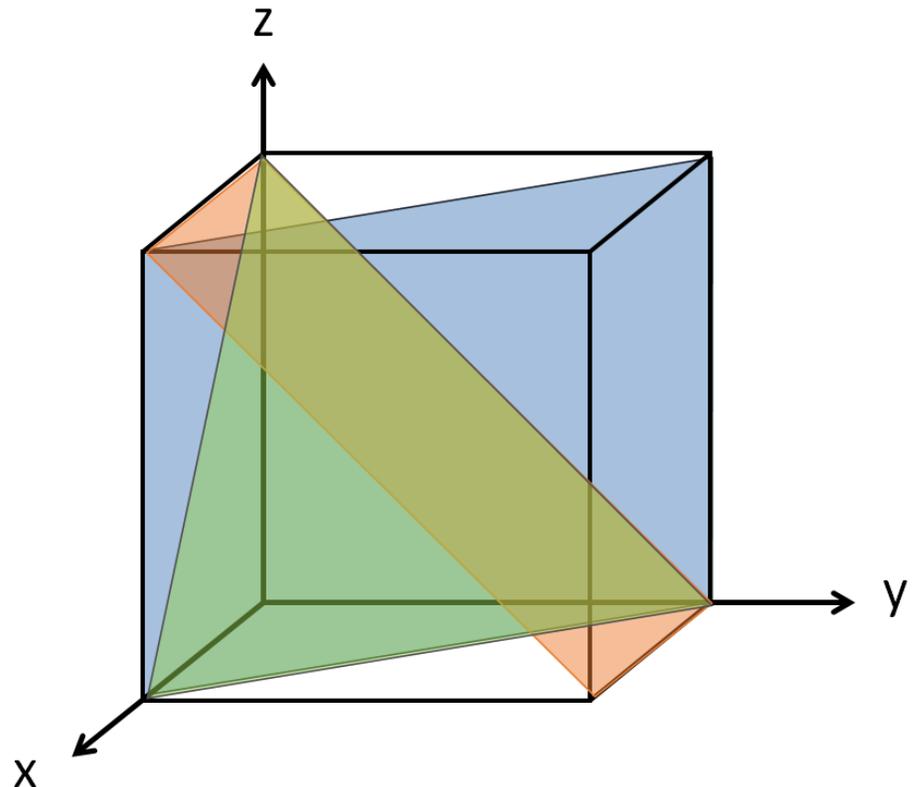


# Miller Indices - Planes

Steps to finding the Miller indices of a plane:

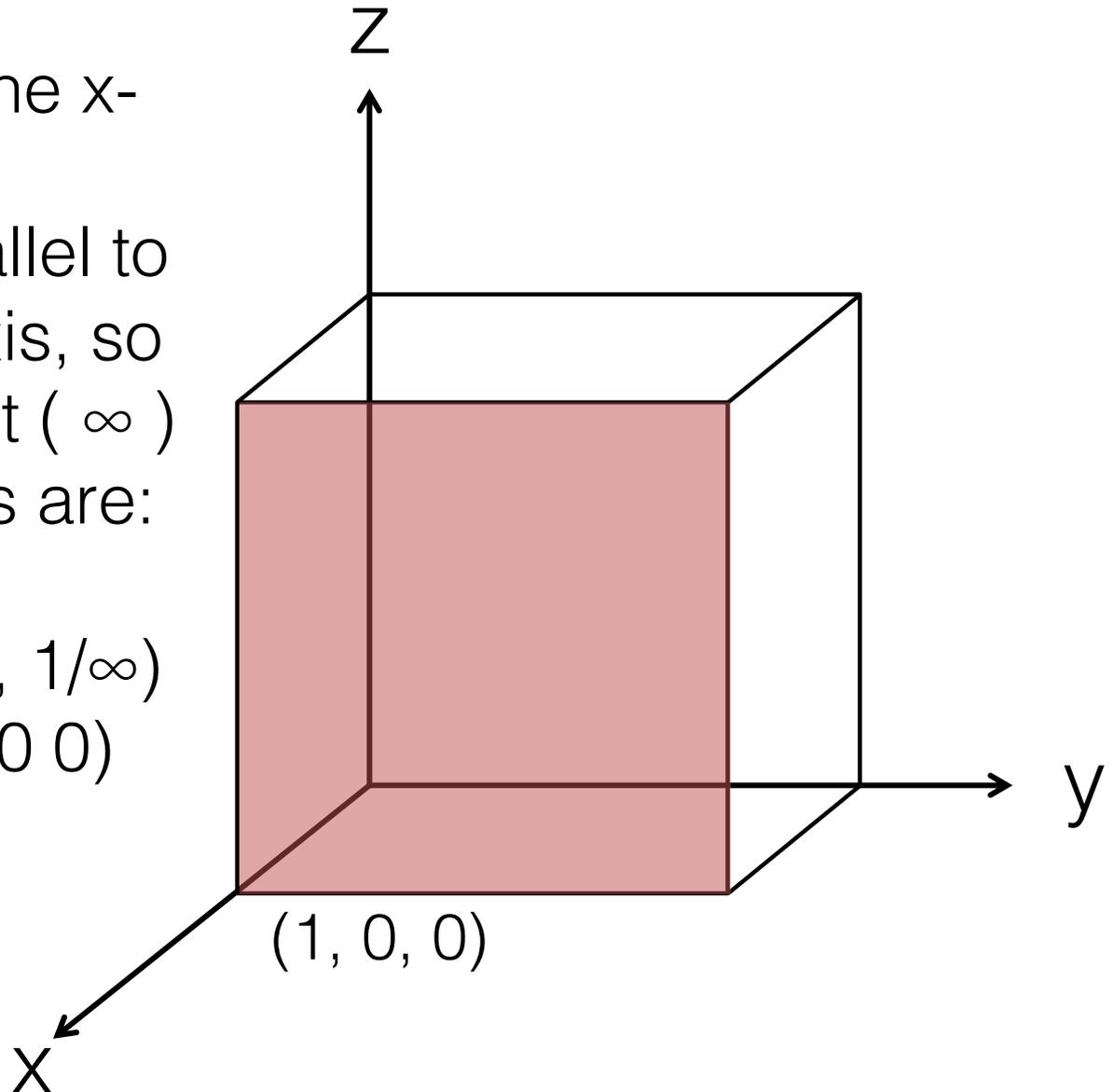
- 1) Identify the intercepts on the x- , y- and z- axes
- 2) Take the reciprocal (inverse):

$$(x, y, z) \rightarrow (1/x, 1/y, 1/z)$$



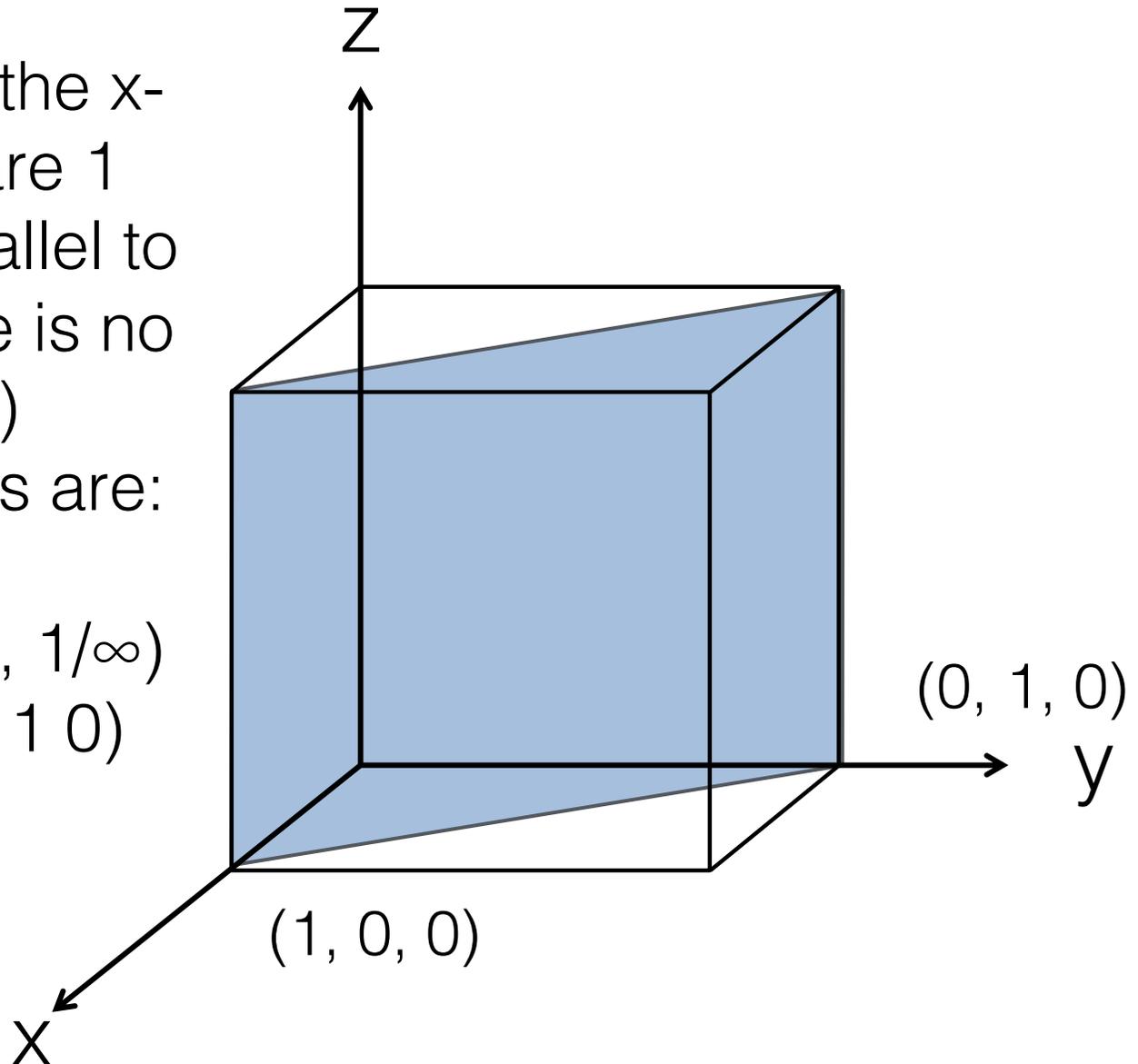
# Miller Indices - Planes

- The intercept on the x-axis is at 1
- The surface is parallel to the y-axis and z-axis, so there is no intercept ( $\infty$ )
- Thus the intercepts are:  
 $(1, \infty, \infty)$
- Inverse:  $(1/1, 1/\infty, 1/\infty)$
- Miller indices:  $(1\ 0\ 0)$



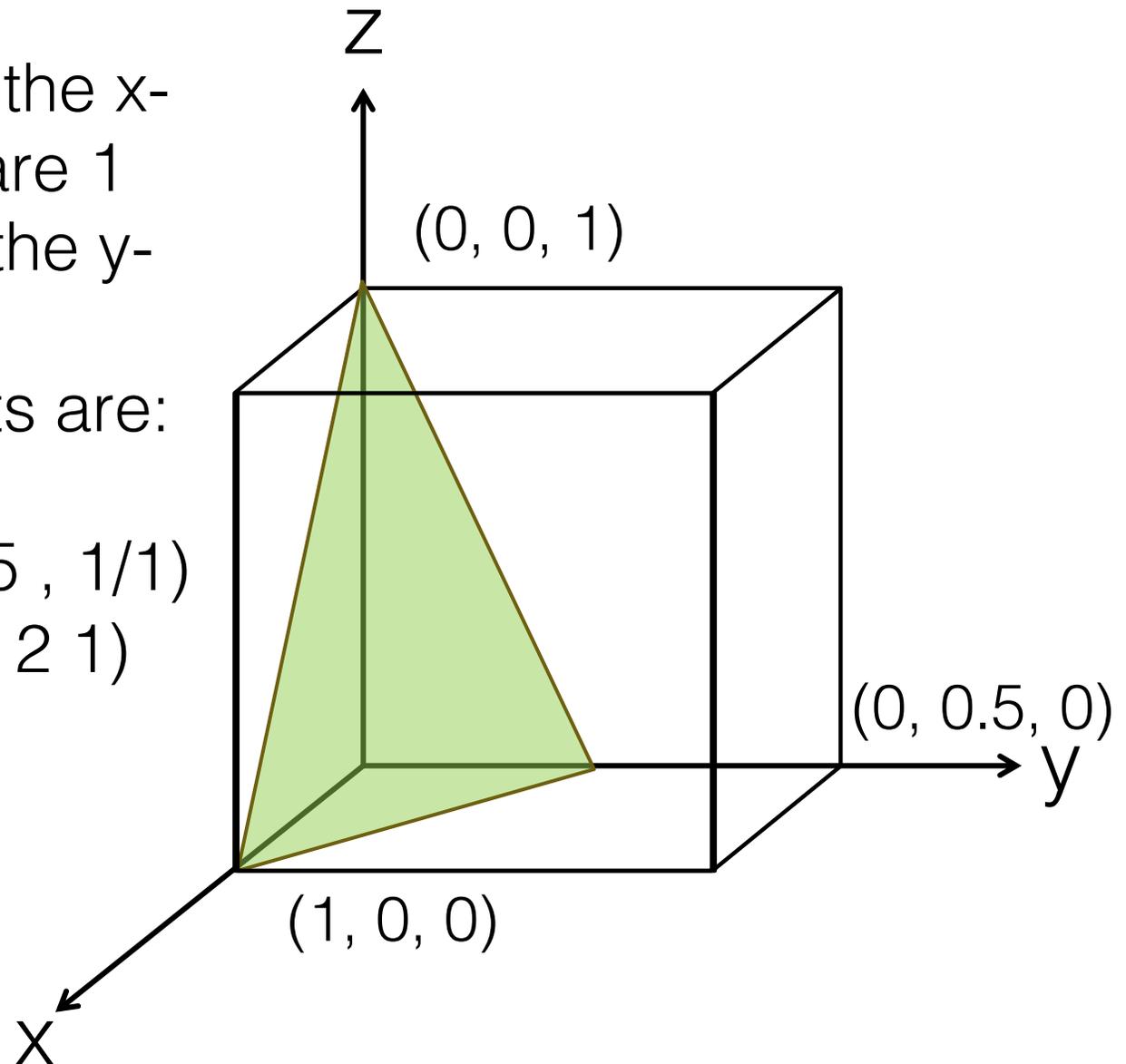
# Miller Indices - Planes

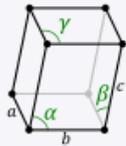
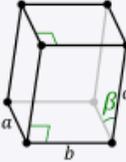
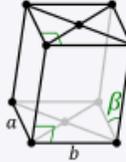
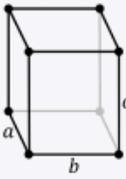
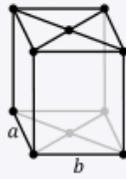
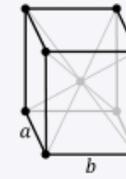
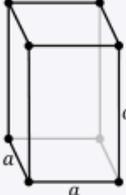
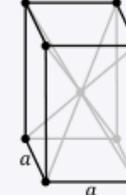
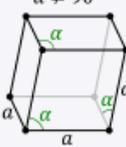
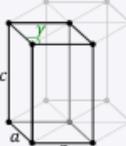
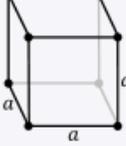
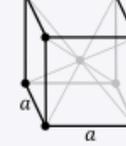
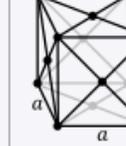
- The intercepts on the x-axis and y-axis are 1
- The surface is parallel to the z-axis, so there is no intercept ( $\infty$ )
- Thus the intercepts are:  
 $(1, 1, \infty)$
- Inverse:  $(1/1, 1/1, 1/\infty)$
- Miller indices:  $(1\ 1\ 0)$



# Miller Indices - Planes

- The intercepts on the x-axis and z-axis are 1
- The intercept on the y-axis is 0.5
- Thus the intercepts are:  $(1, 0.5, 1)$
- Inverse:  $(1/1, 1/0.5, 1/1)$
- Miller indices:  $(1\ 2\ 1)$



Crystal family	Lattice system	Schönflies	14 Bravais Lattices			
			Primitive	Base-centered	Body-centered	Face-centered
triclinic		$C_i$				
monoclinic		$C_{2h}$	$\beta \neq 90^\circ$ $a \neq c$ 	$\beta \neq 90^\circ$ $a \neq c$ 		
orthorhombic		$D_{2h}$	$a \neq b \neq c$ 	$a \neq b \neq c$ 	$a \neq b \neq c$ 	$a \neq b \neq c$ 
tetragonal		$D_{4h}$	$a \neq c$ 		$a \neq c$ 	
hexagonal	rhombohedral	$D_{3d}$	$\alpha \neq 90^\circ$ 			
	hexagonal	$D_{6h}$	$\gamma = 120^\circ$ 			
cubic		$O_h$				

e.g., Klein, en.wikipedia

# Lattice parameters from X-ray Diffraction

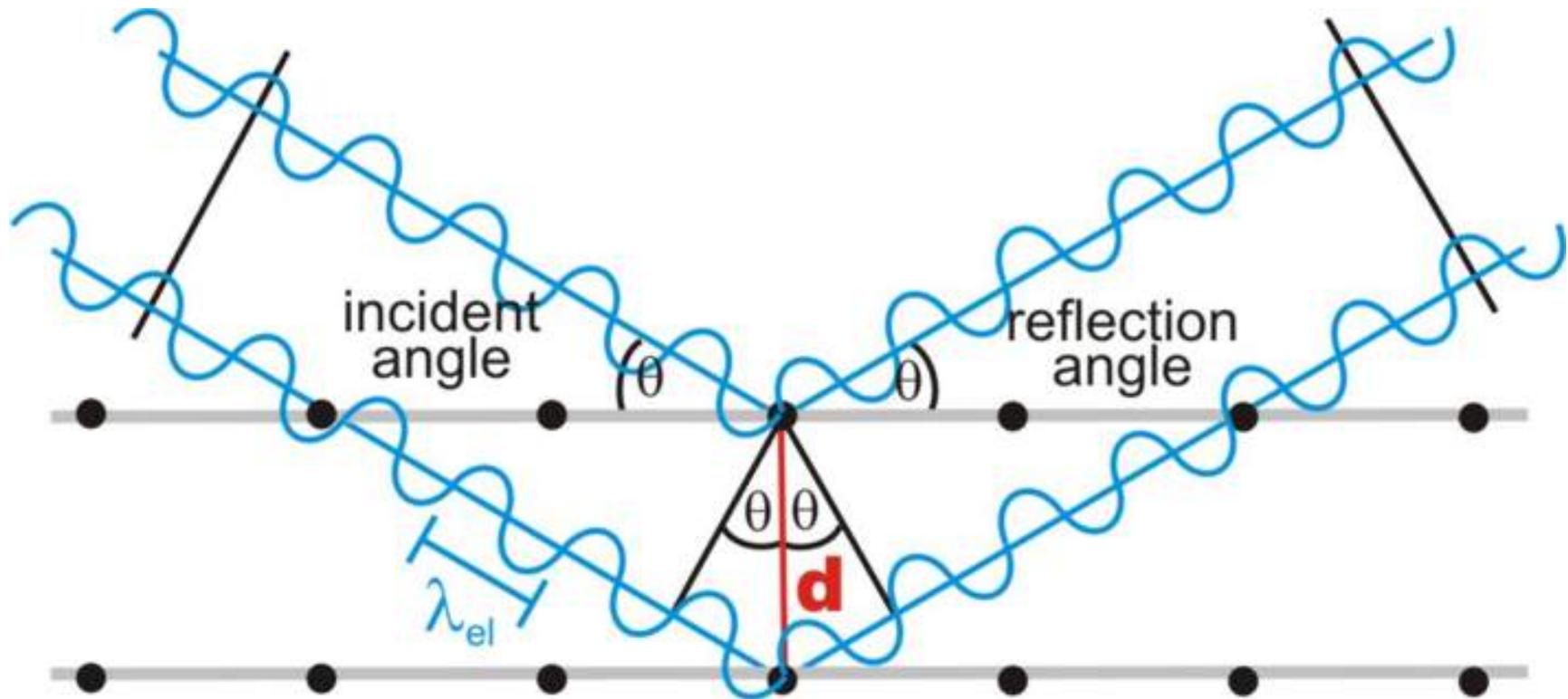
## d-spacing in different crystal systems

---

★ Cubic	$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$
★ Tetragonal	$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
★ Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
★ Hexagonal	$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$
★ Monoclinic	$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$
★ Triclinic -	

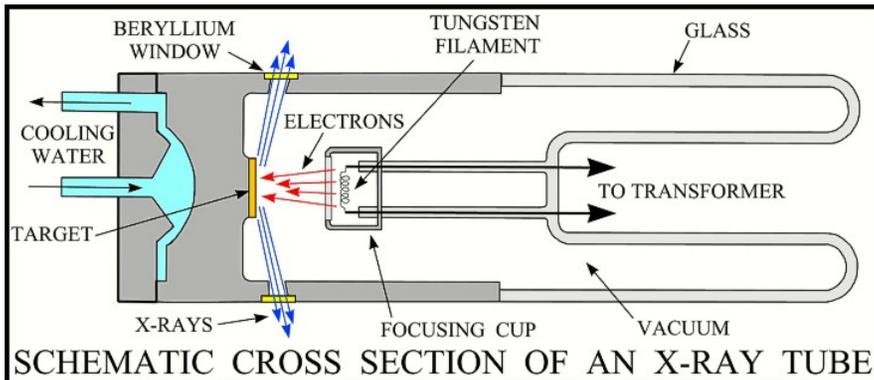
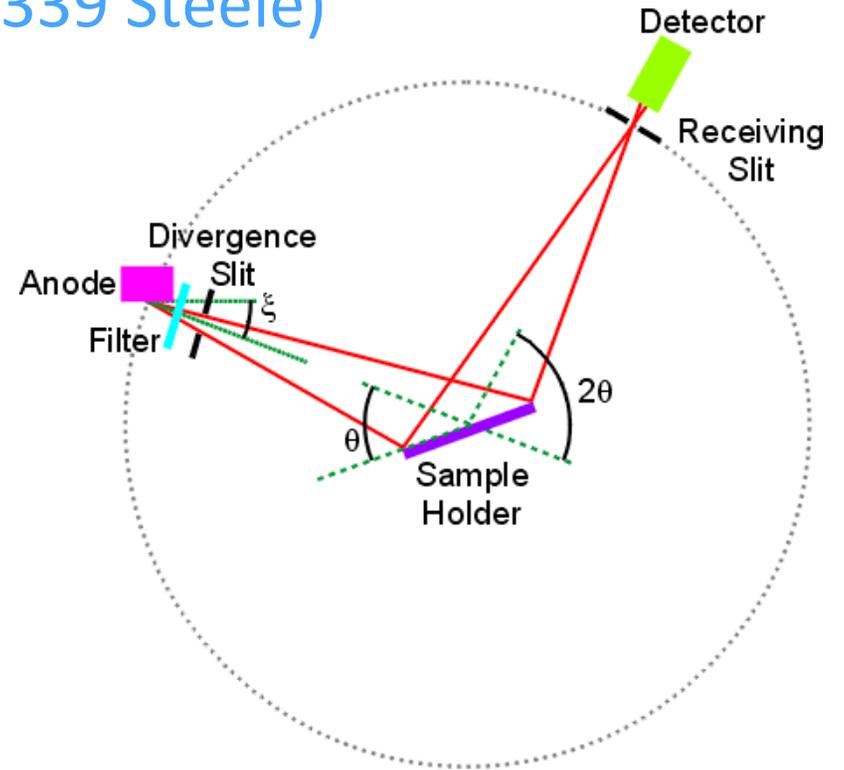
# X-ray Diffraction

$$n\lambda = 2d \sin\theta \quad \text{Bragg's Law}$$



# Week 2: Powder XRD measurements (339 Steele)

## Bragg-Brentano geometry



Target: Cu

Operating energy: 8 keV

Filter: Ni ( $K_{\beta}$  filtered out)

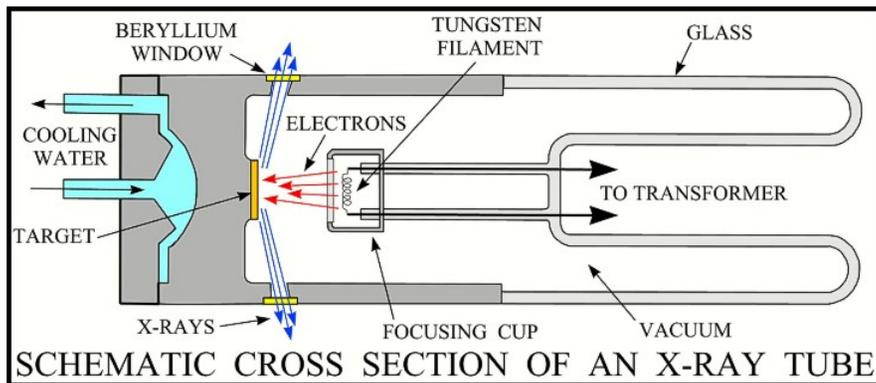
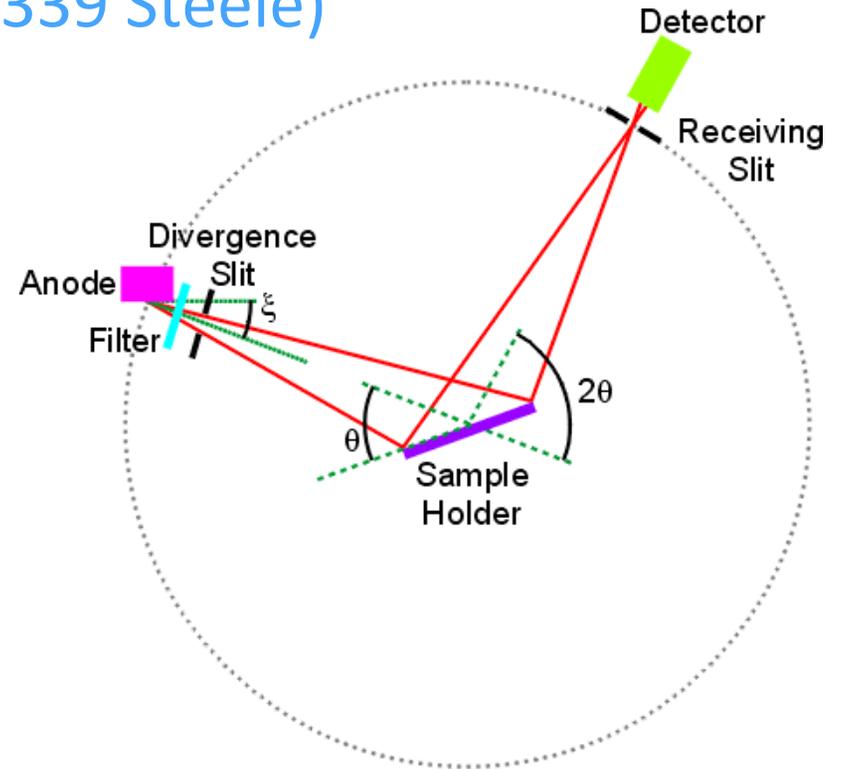
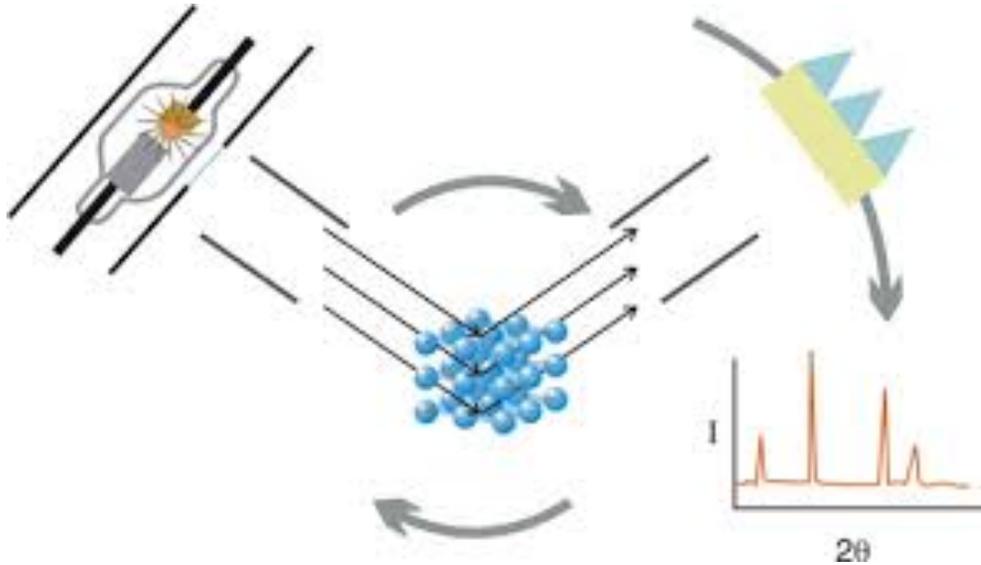
Cu  $K\alpha_1$ ,  $\lambda = 1.54056 \text{ \AA}$

Cu  $K\alpha_2$ ,  $\lambda = 1.54439 \text{ \AA}$

Bragg's law:  $\lambda = 2d_{hkl} \sin\theta$

# Week 2: Powder XRD measurements (339 Steele)

## Bragg-Brentano geometry



Target: Cu

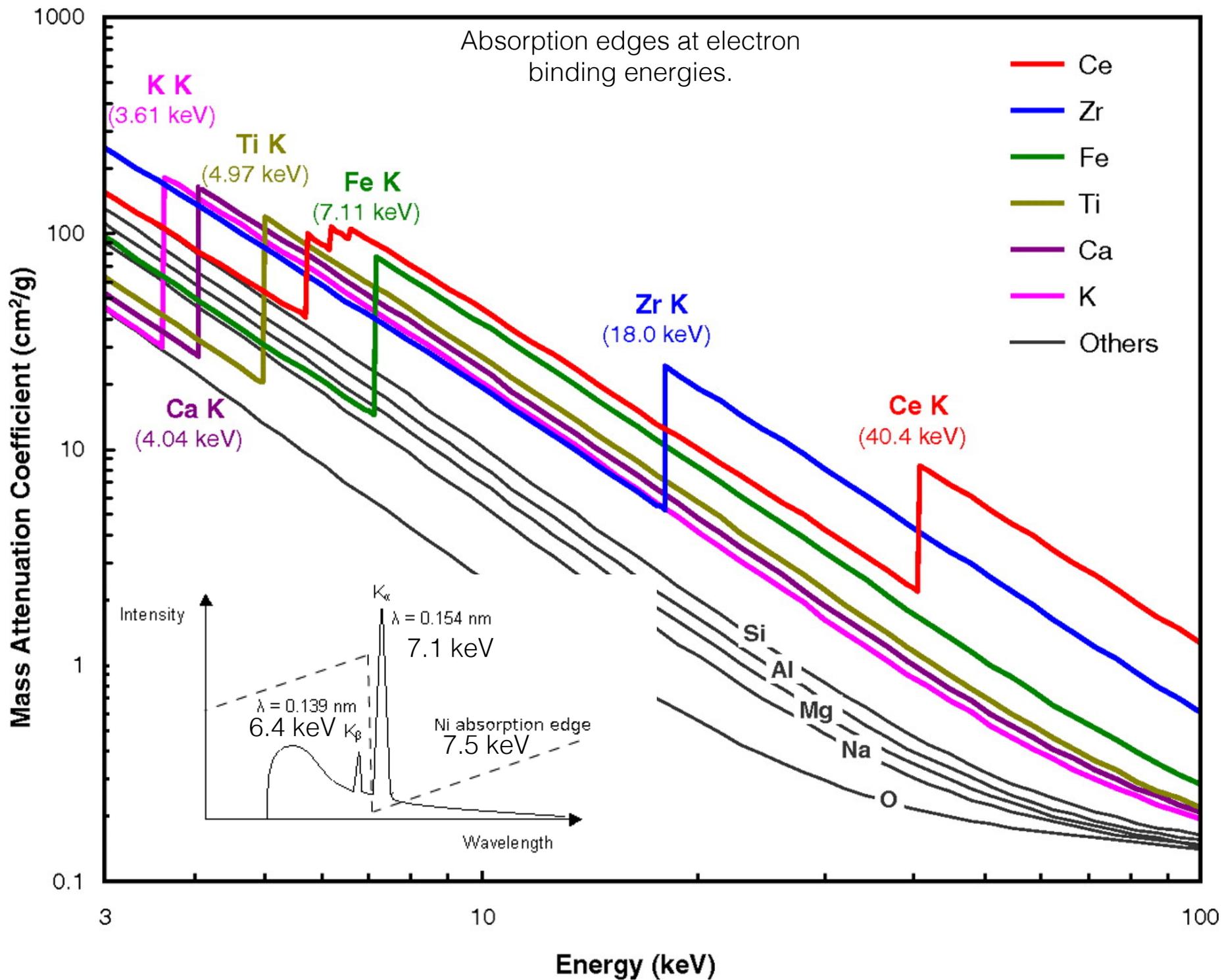
Operating energy: 8 keV

Filter: Ni ( $K_{\beta}$  filtered out)

Cu  $K\alpha_1$ ,  $\lambda = 1.54056 \text{ \AA}$

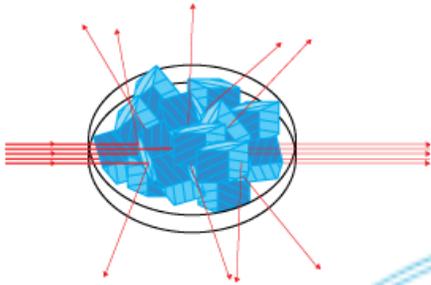
Cu  $K\alpha_2$ ,  $\lambda = 1.54439 \text{ \AA}$

Bragg's law:  $\lambda = 2d_{hkl} \sin\theta$

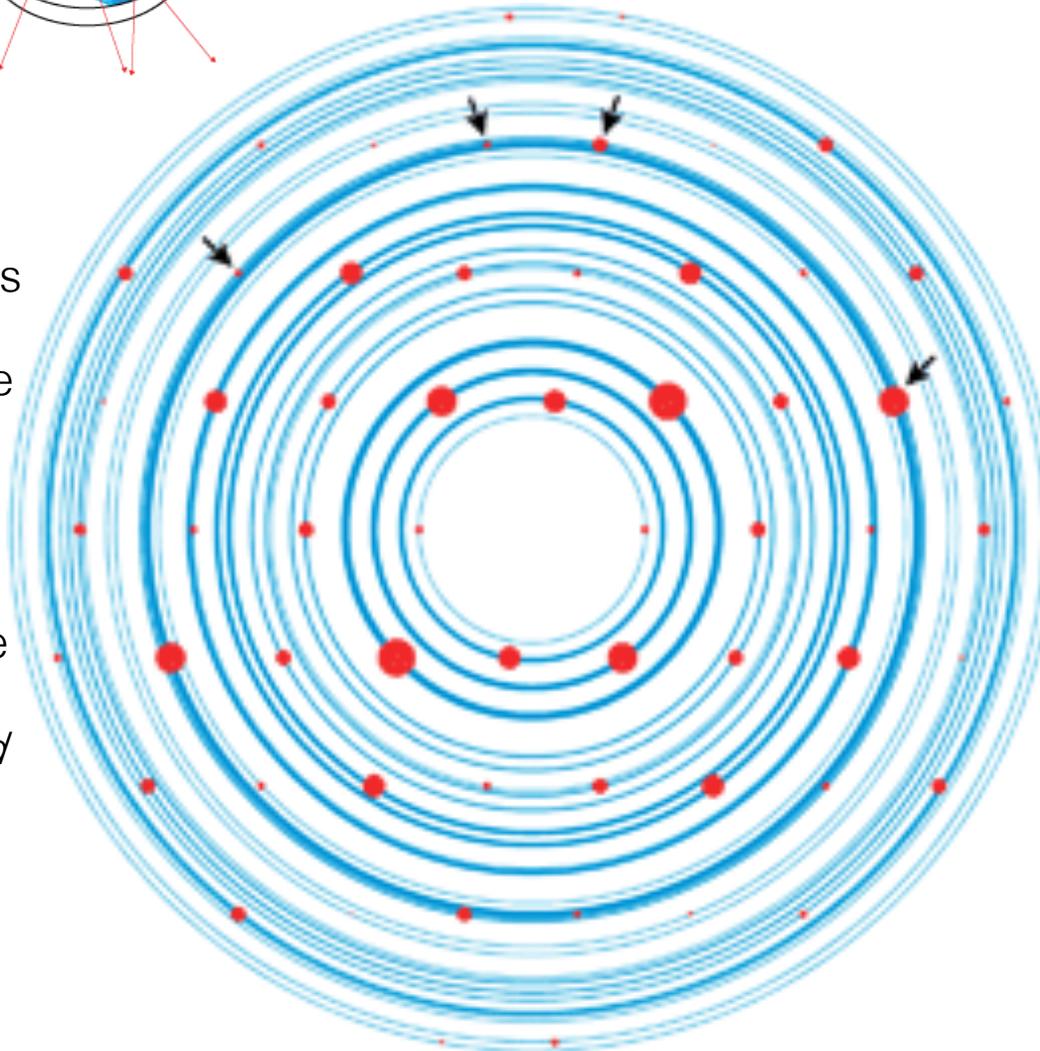


# Powdered vs. Single Crystal XRD

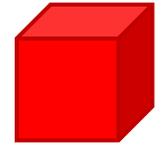
Powdered



- Thousands of crystallites
- Random orientations
- Probing all possible orientations
- Easy to make
- Fast collection time
- *Issues of preferred orientation*
- *Issues of peak overlap*



Single Crystal



- Great for discovering new minerals (determining crystal structure)
- Information about bond lengths, bond angles, site ordering
- Slow collection time
- Rare to have peak overlaps
- *Difficult to synthesize*
- *Twinned samples are challenging*

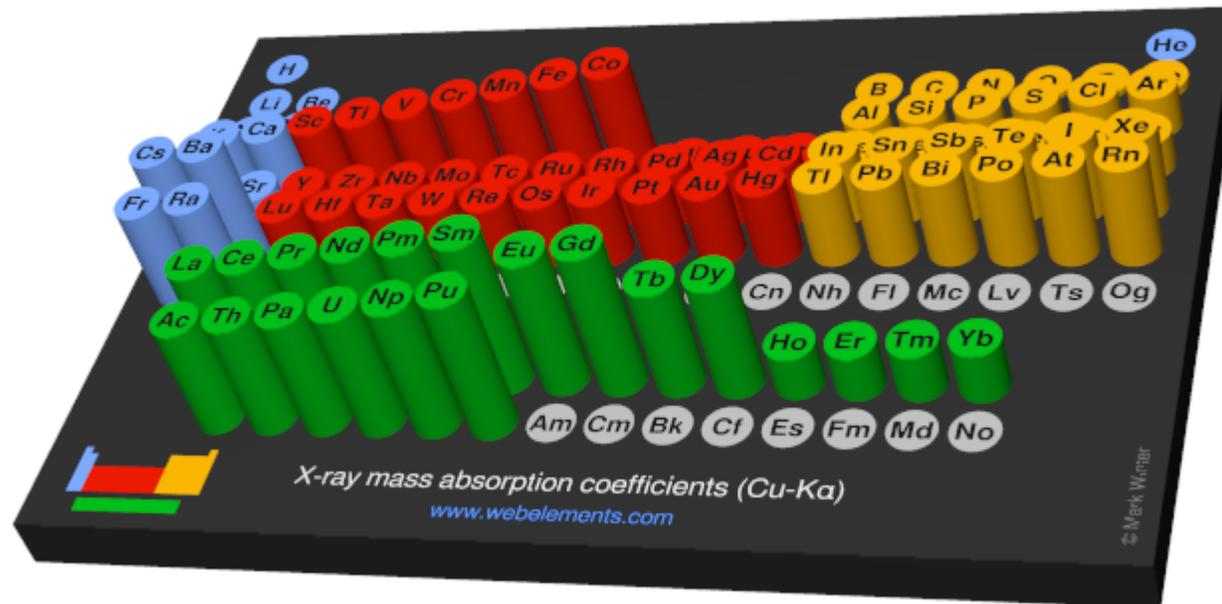
# The intensity of diffracted x-rays

$$I / I_0 \approx k \left[ \sum_j f_j e^{i2\pi(hx_j + ky_j + lz_j)} \right]^2 = kF_{hkl}^2 p(LPF) A(\theta) e^{-2m}$$

Intensity of the diffracted x-ray photons contains all the static information of a crystal: Structure factor,  $F$  (phase information) and the form factors:

- Atomic number, scattering angle ( $F$ ) ; represents electric field scattered by an atom
- Multiplicity,  $p$ : how many diffracting planes contribute to a given peak
- LPF: Lorenz polarization factor
- $A(\theta)$ , absorption ( $I/I_0 = e^{-\mu x}$ ): “Beer-Lambert Law”, where  $\mu = \rho \sigma_{PE}$ 
  - PE: photoelectric cross-section of a material and hence,  $\mu$  is a function of x-ray wavelength,  $\lambda$
- $e^{-2m}$ , atomic thermal motion (Debye-Waller factor)

# X-ray mass absorption coefficients for copper radiation (Cu-K $\alpha$ ) in a 3D periodic table



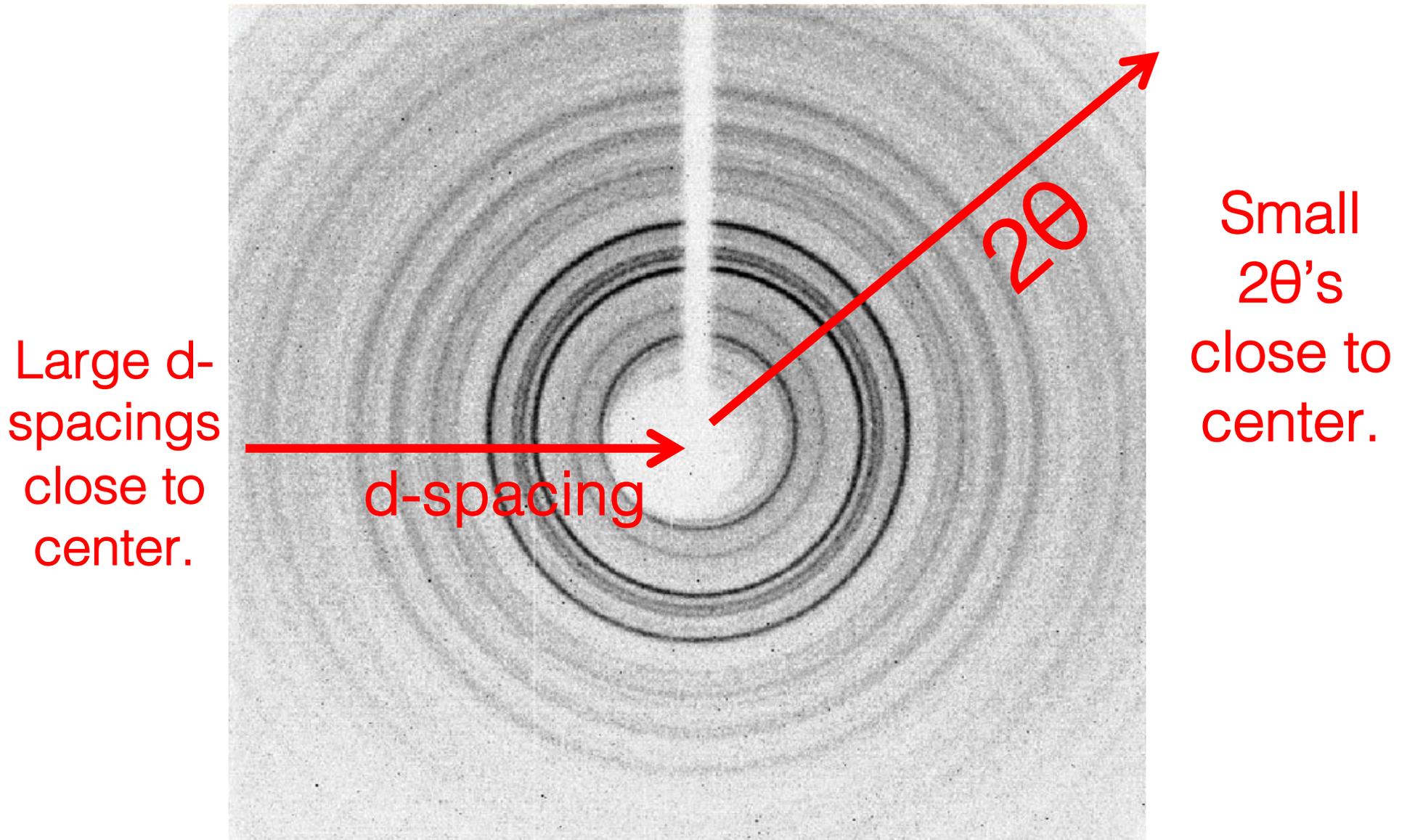
When radiation traverses a layer of an element or compound, it is diminished in intensity by a constant fraction per thickness  $x$  of that element (or compound). The emergent radiant intensity,  $I$ , in terms of incident radiant intensity  $I_0$ , is given by

$$I = I_0 \exp(-\mu x)$$

which defines  $\mu$ , the total linear absorption coefficient. Since the reduction of intensity is determined by the quantity of mass traversed by the primary beam, the absorber thickness is best expressed on a mass basis,  $\text{g}/\text{cm}^2$ . The mass absorption coefficient,  $\mu/\rho$ , expressed in units of  $\text{cm}^2/\text{g}$ , where  $\rho$  is the density of the material, is approximately independent of the physical state of the material.

e.g., G.W.C. Kaye and T.H. Laby in Tables of physical and chemical constants, Longman, London, UK, 15th edition, 1993

# Powdered X-ray Diffraction

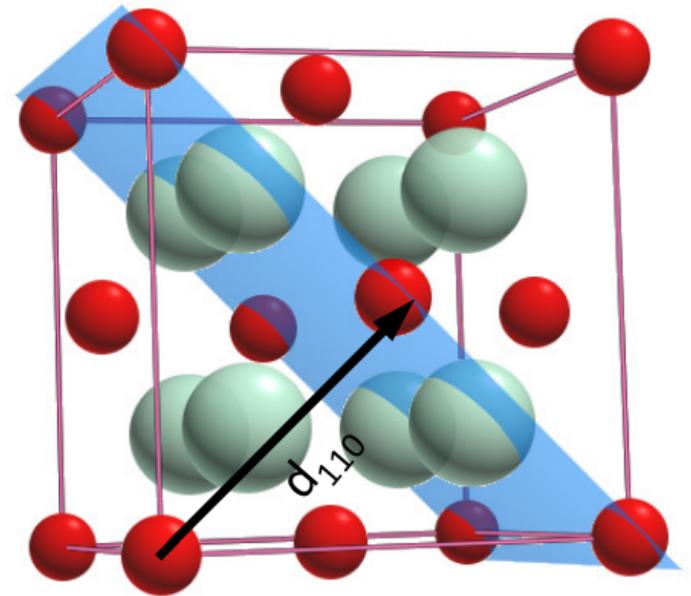


# Integrated Diffraction Pattern

The position of the diffraction peaks are determined by the distance between parallel planes of atoms.

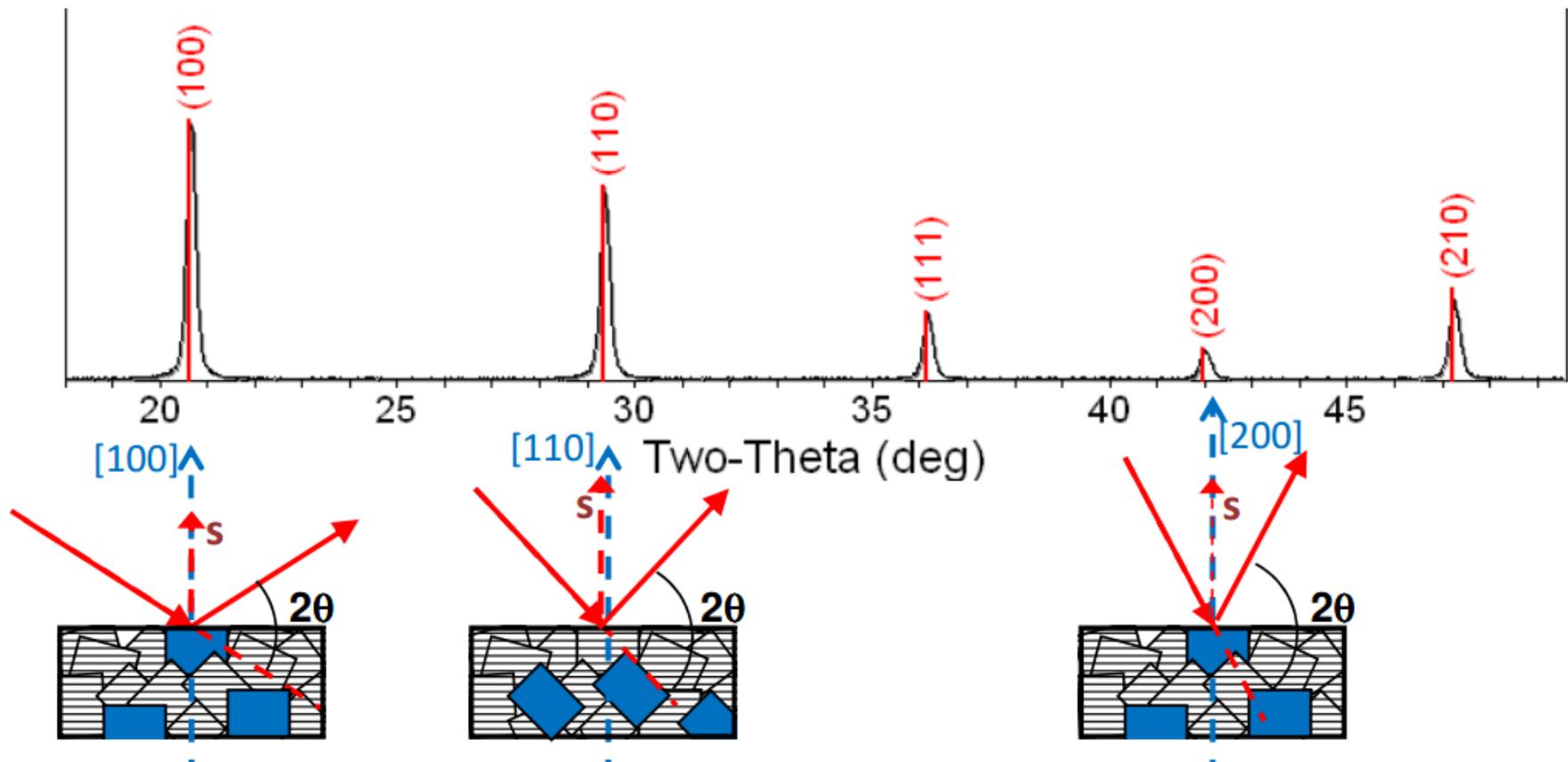
**Bragg's Law**

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

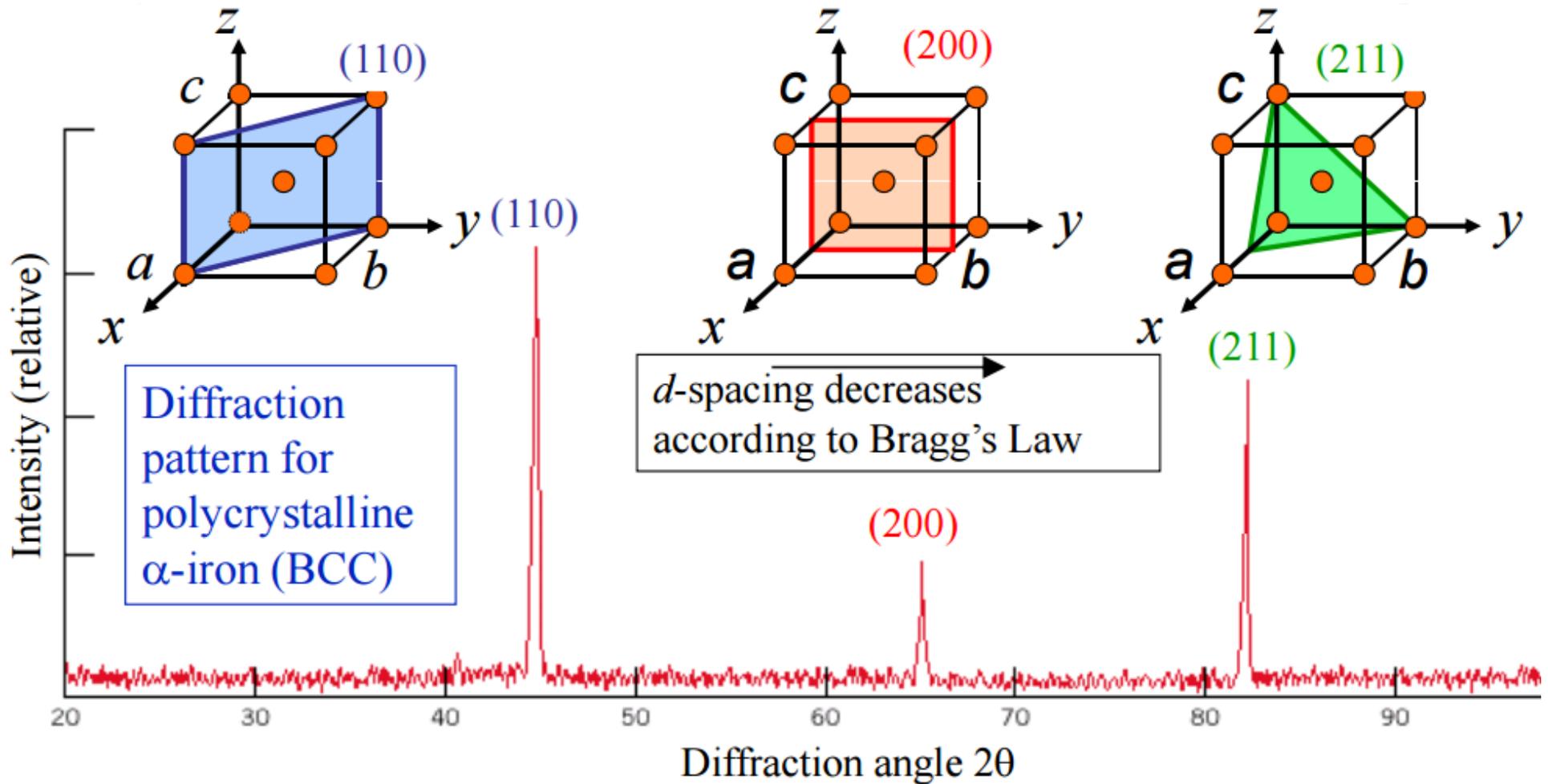


# Integrated Powder Diffraction Pattern

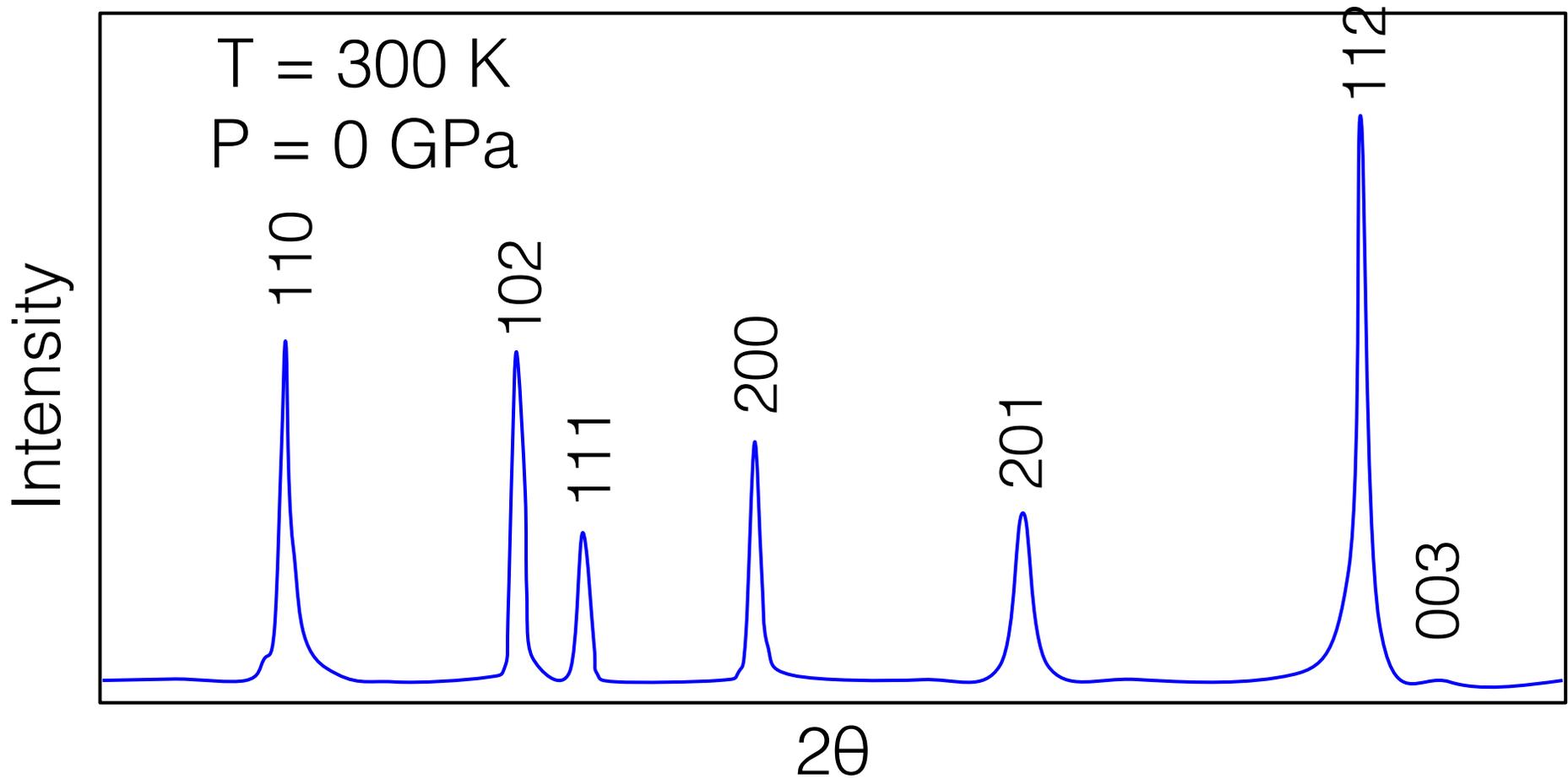
A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed.



# Integrated Powder Diffraction Pattern



# Integrated Diffraction Pattern



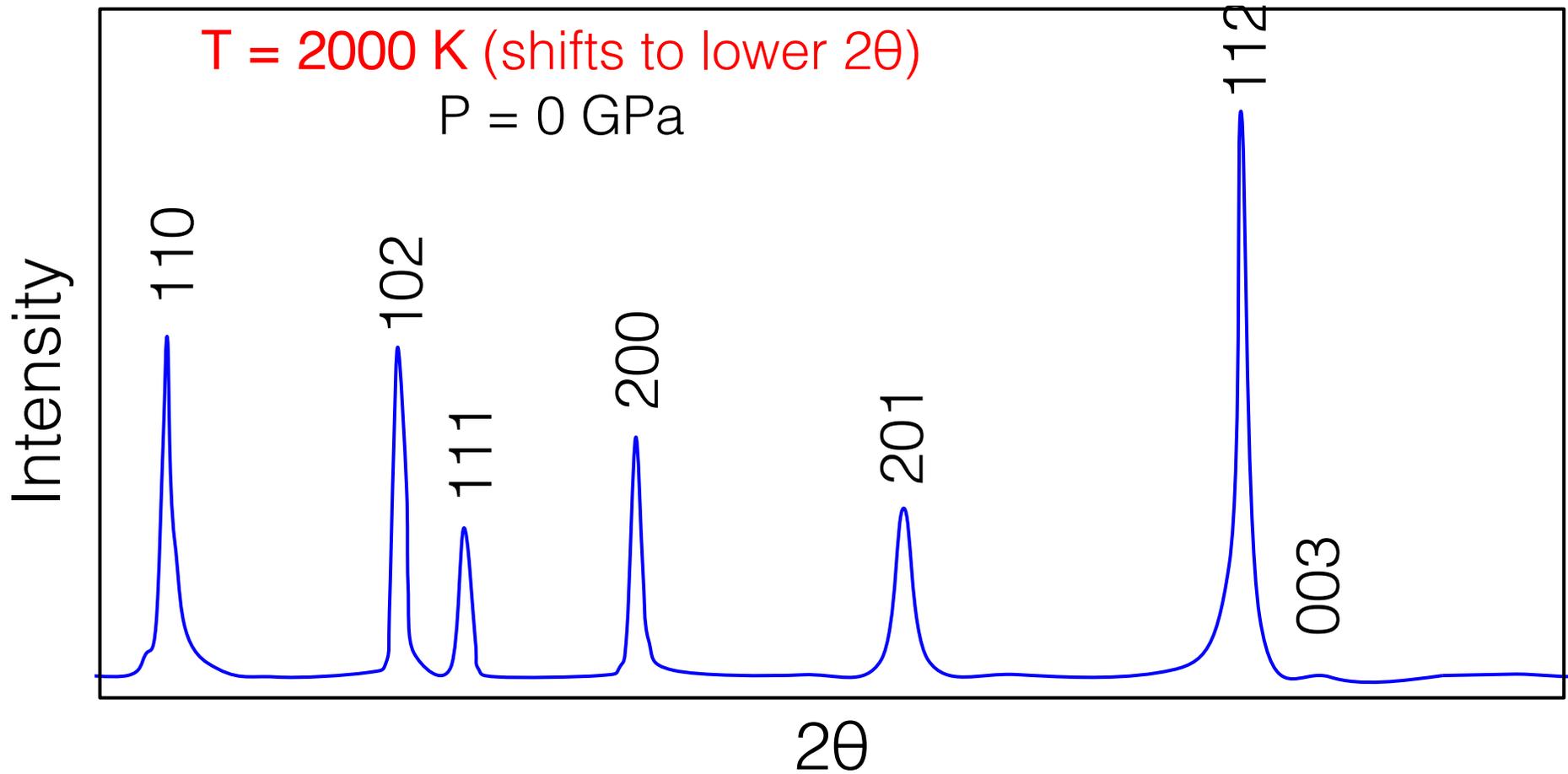
$$n\lambda = 2d \sin\theta$$

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

Thus,  $\theta \sim 1/d$ .

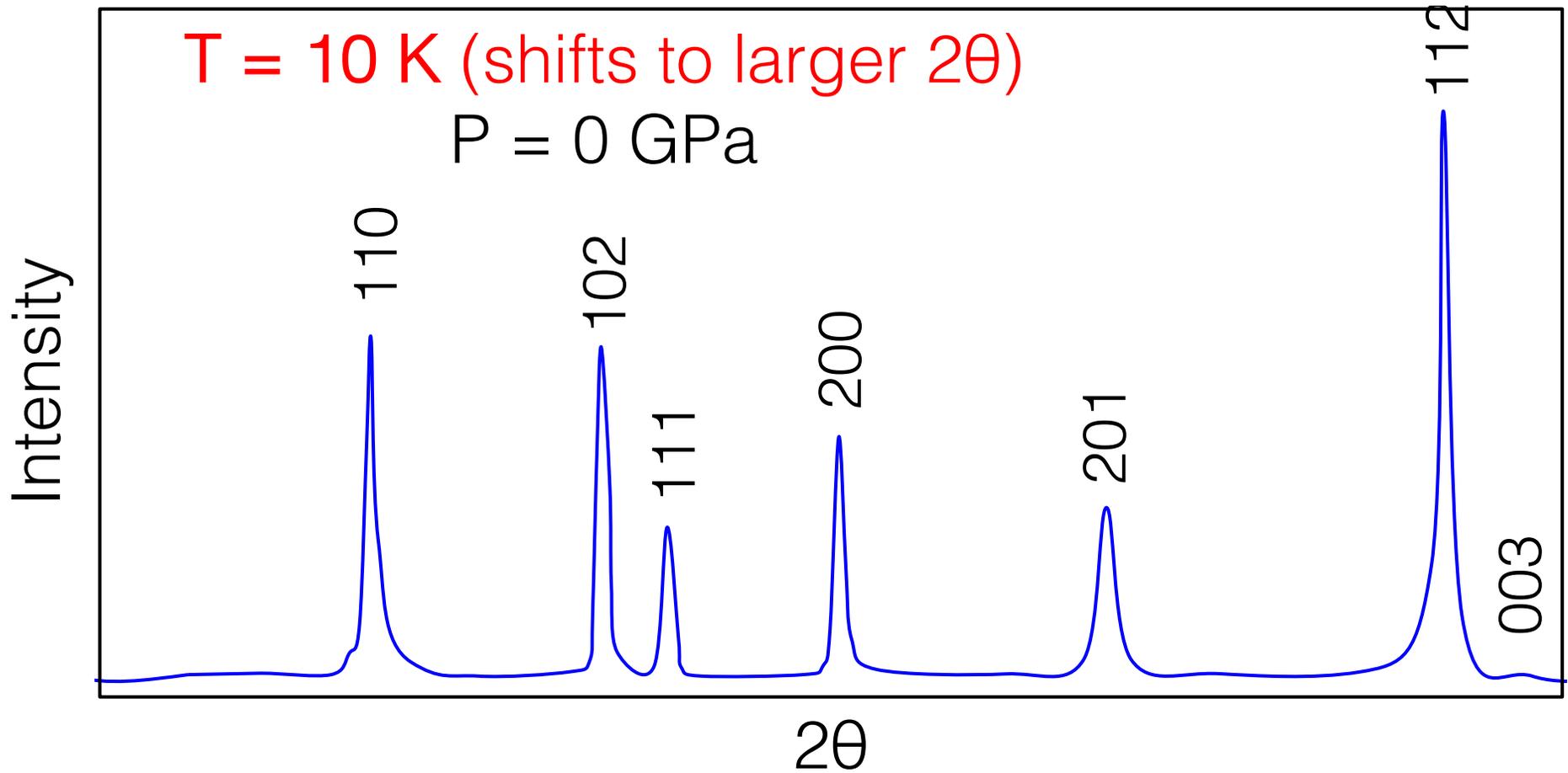
The d-spacing is related to volume:  $d^{1/3} \sim V$ .

# Integrated Diffraction Pattern



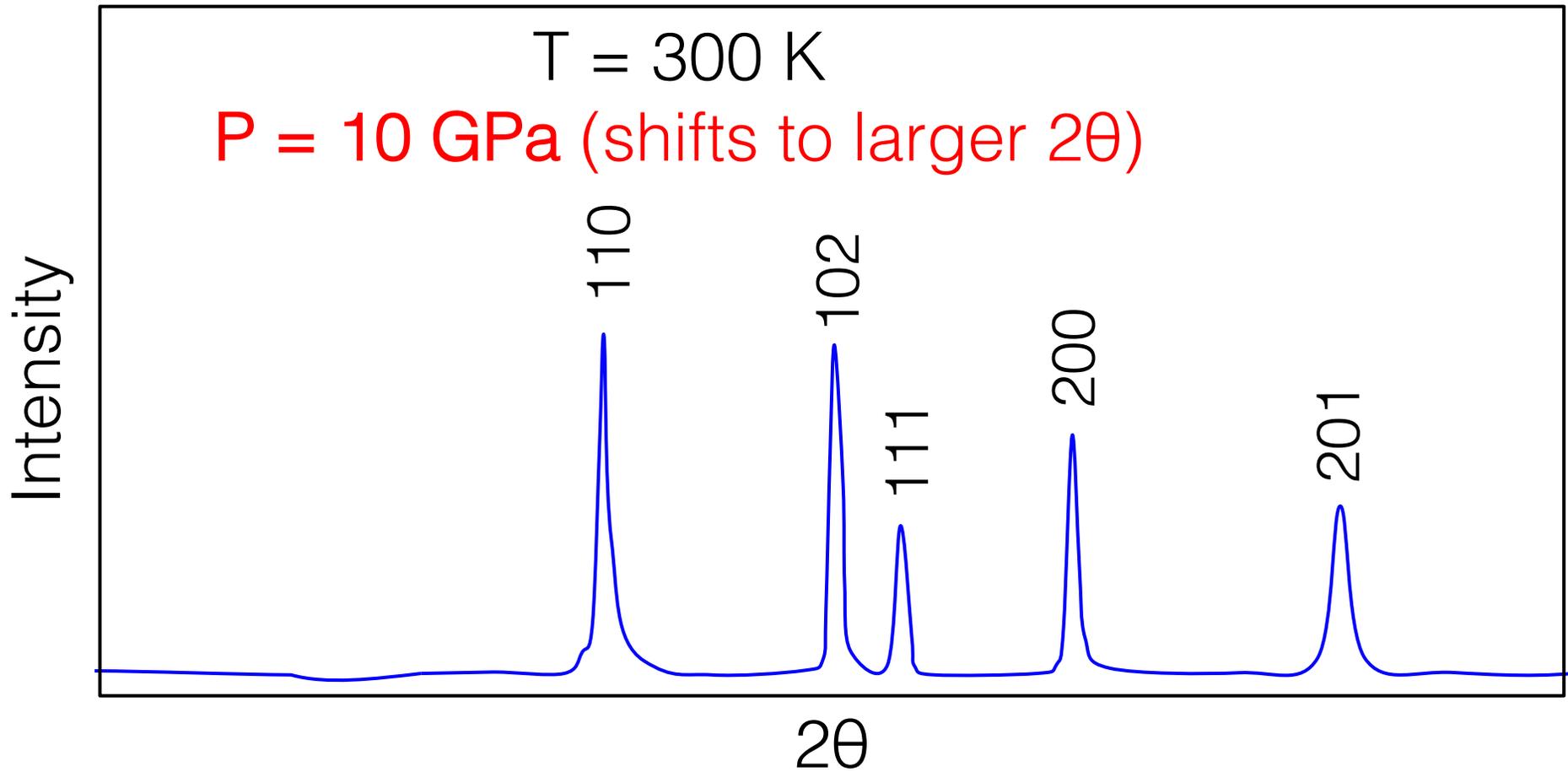
Increasing temperature, increases the volume, which increases the d-spacing and decreases  $2\theta$ .

# Integrated Diffraction Pattern



Decreasing temperature, decreases the volume, which decreases the d-spacing and increases  $2\theta$ .

# Integrated Diffraction Pattern



Increasing pressure, decreases the volume, which decreases the d-spacing and increases  $2\theta$ .