Oct. 13, 2021

Bio-integrated Materials Science

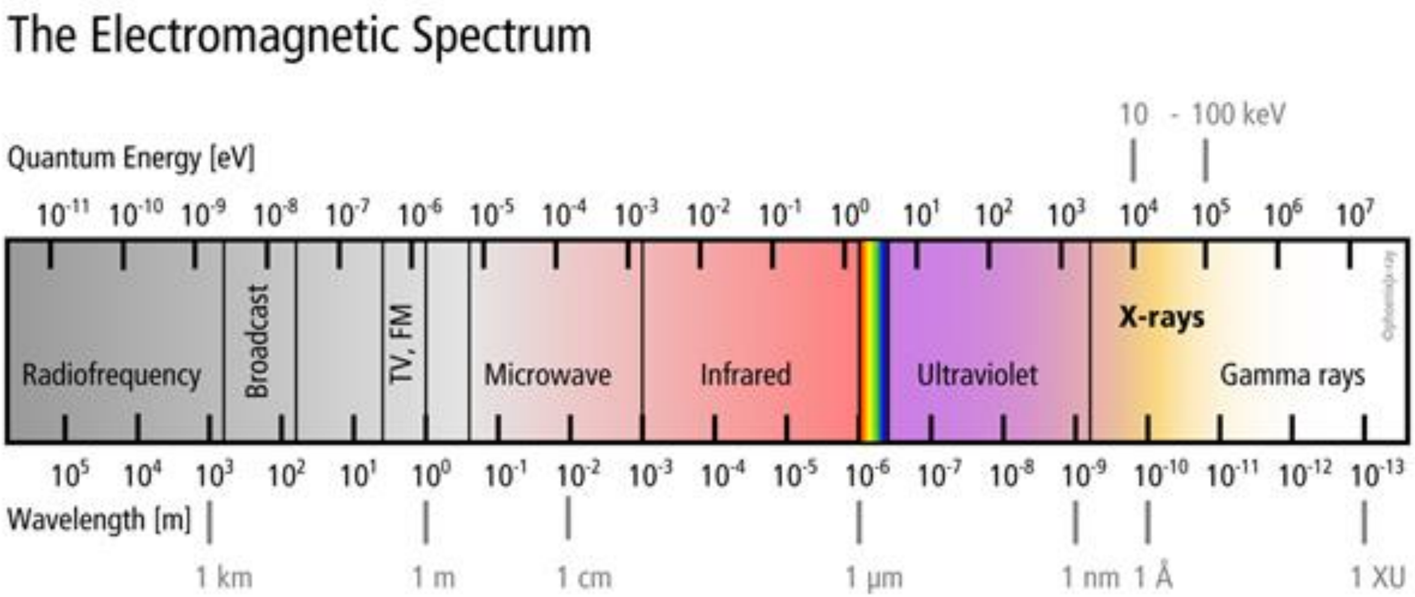
(Online Lectures)

X-ray Diffraction

Lecture 4

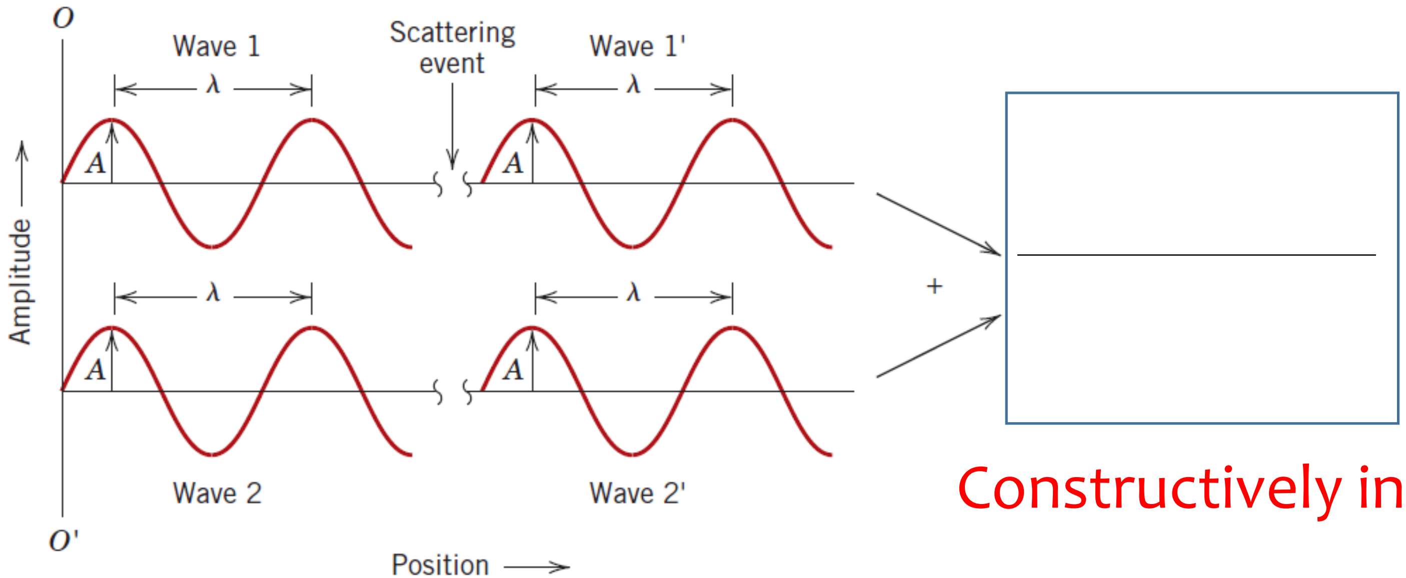
Prof. Jung Heon Lee

X-Ray diffraction

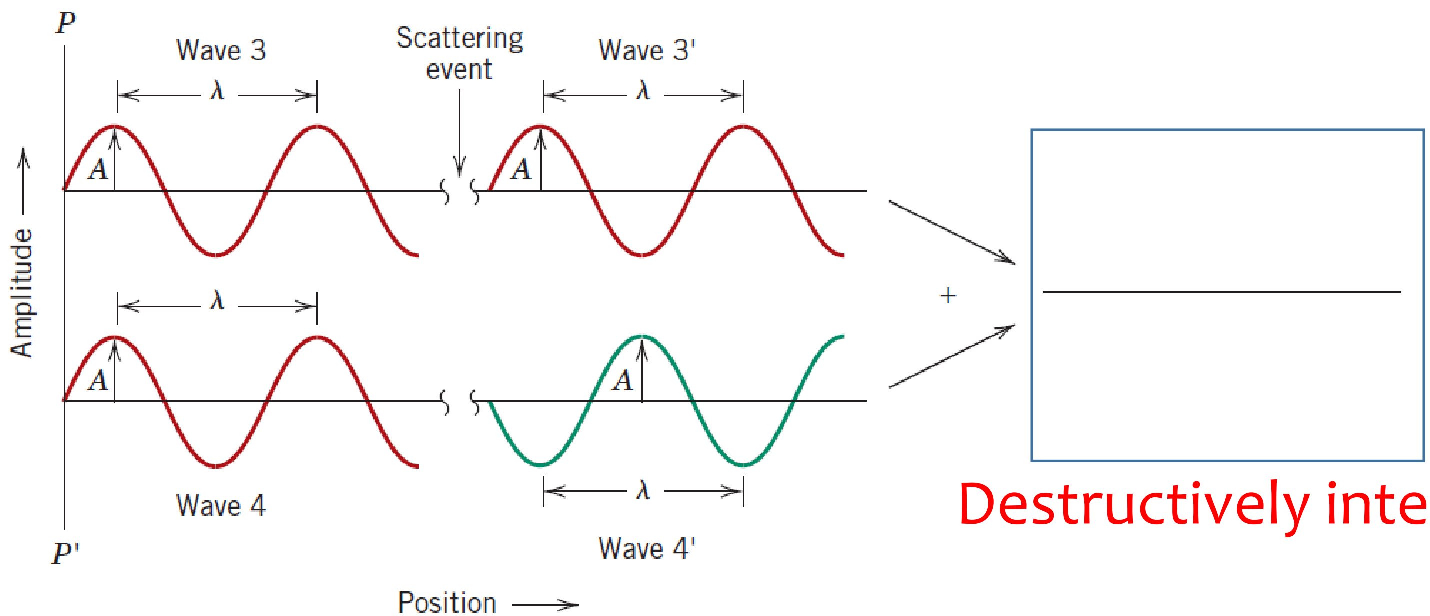


- $\boxed{}$ are electromagnetic radiation with wavelength 0.01-10 nm (visible light ~400-700 nm)
- Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- Spacing is the distance between parallel planes of atoms (~Å).
- Can't resolve spacings $< \lambda$

Interference of wave

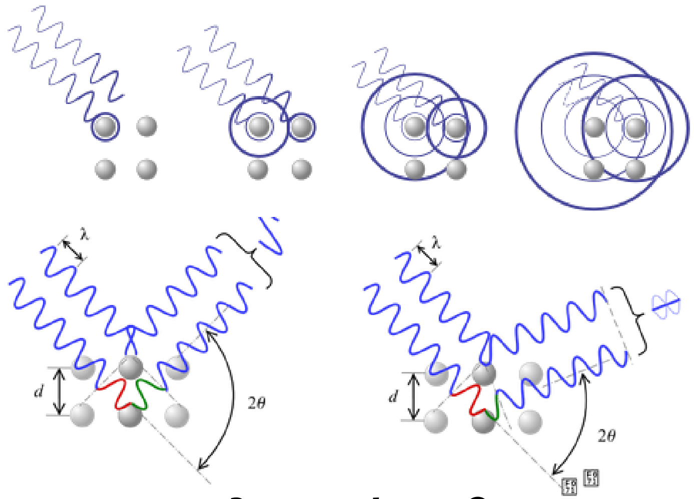


Constructively interfere

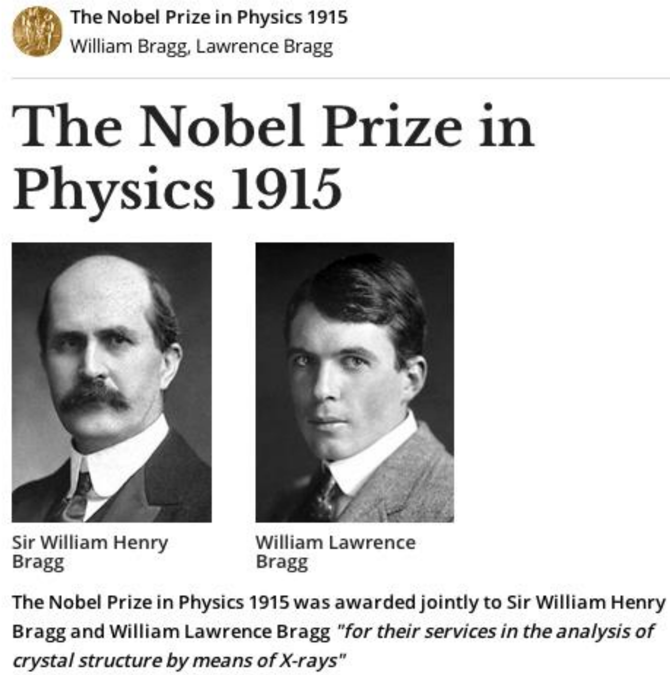


Destructively interfere

X-ray Diffraction



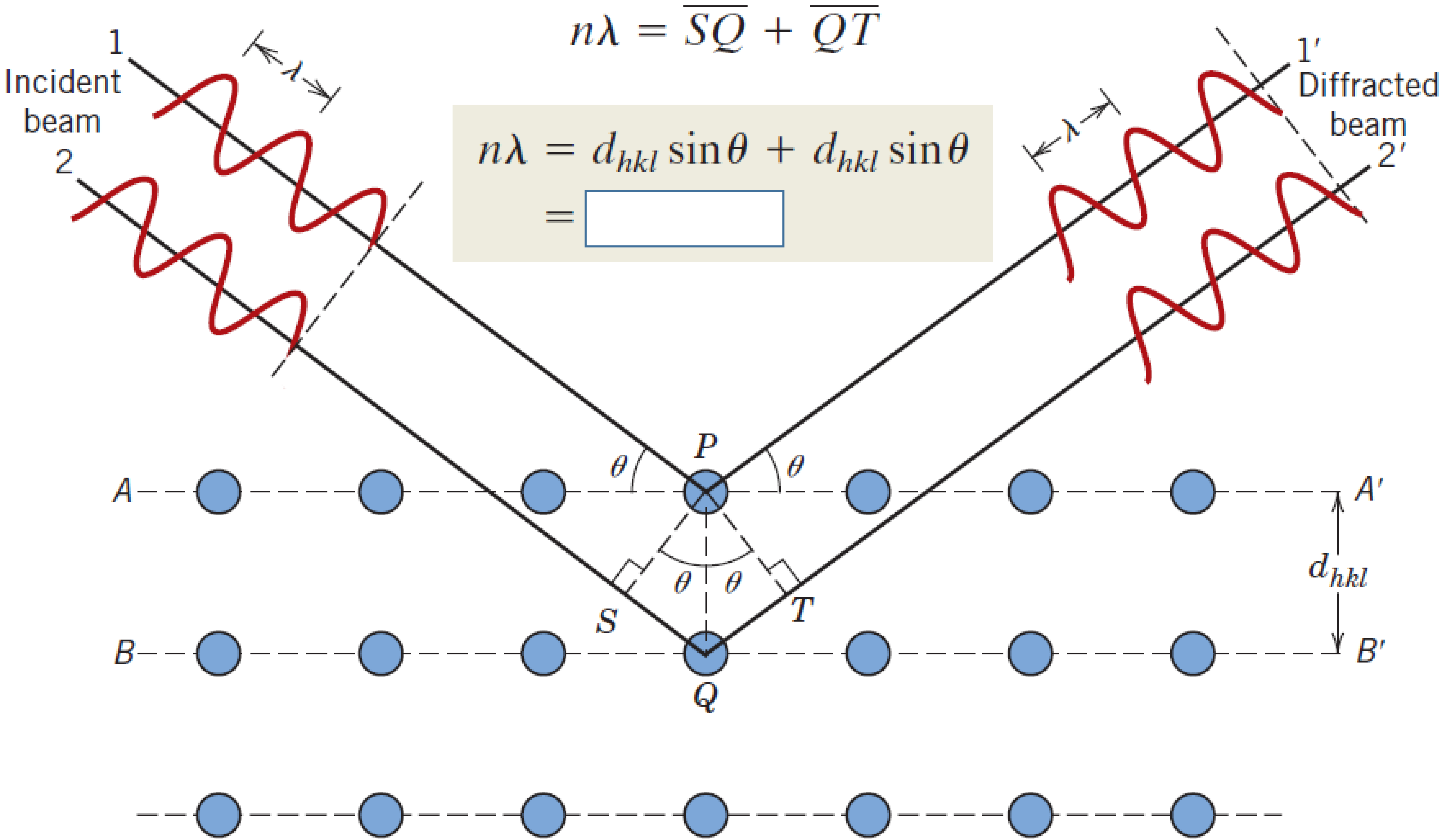
$$n\lambda = 2d\sin\theta$$



- occupied the Cavendish chair of physics at the University of Leeds from 1909.
- He continued his work on X-rays with much success. He invented the X-ray spectrometer and with his son, William Lawrence Bragg, then a research student at Cambridge, founded the new science of X-ray analysis of crystal structure.
- In 1915 father and son were jointly awarded the Nobel Prize in Physics for their studies, using the X-ray spectrometer, of X-ray spectra, X-ray diffraction, and of crystal structure.

http://www.xtal.iqfr.csic.es/Cristalografia/parte_05-en.html
http://en.wikipedia.org/wiki/William_Henry_Bragg

- Incoming X-rays diffract from crystal planes.



X-Rays to determine crystal structure

- Incoming X-rays diffract from crystal planes.

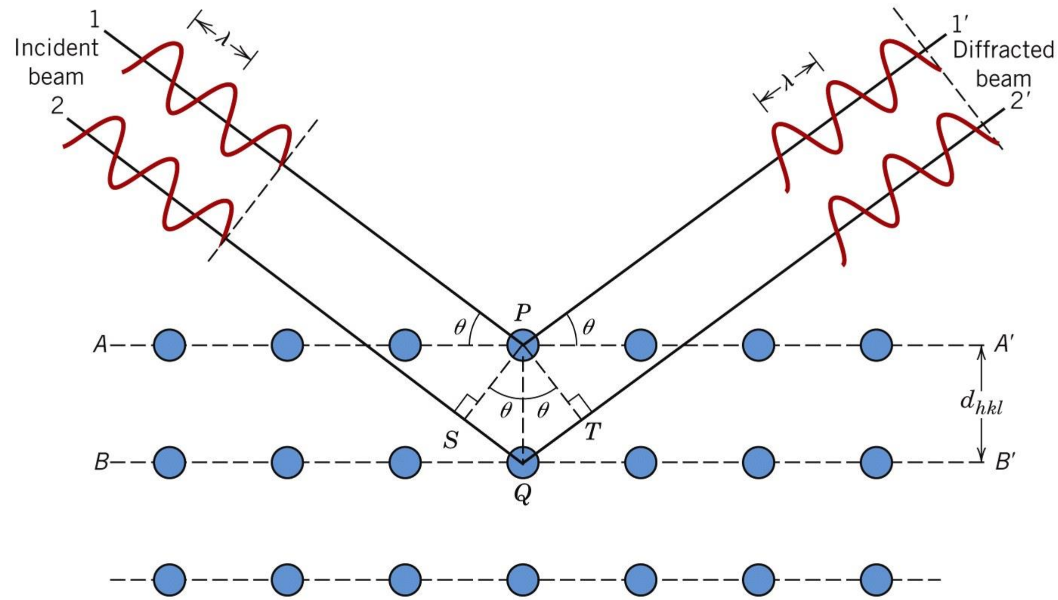


Figure 3.38

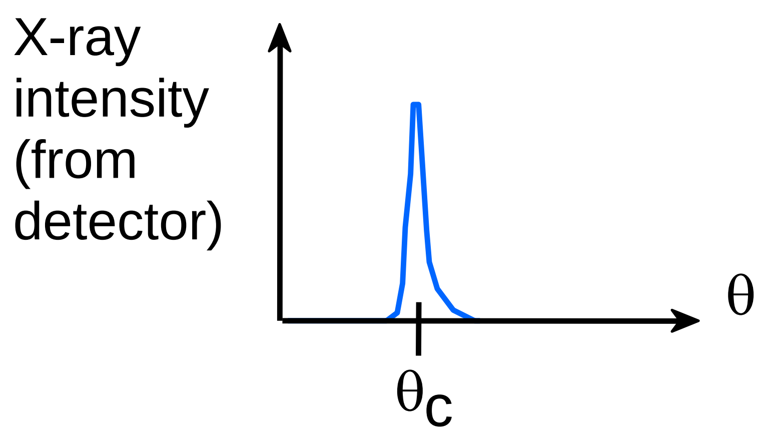
$$n\lambda = 2d\sin\theta$$

lattice spacing of a particular cubic system

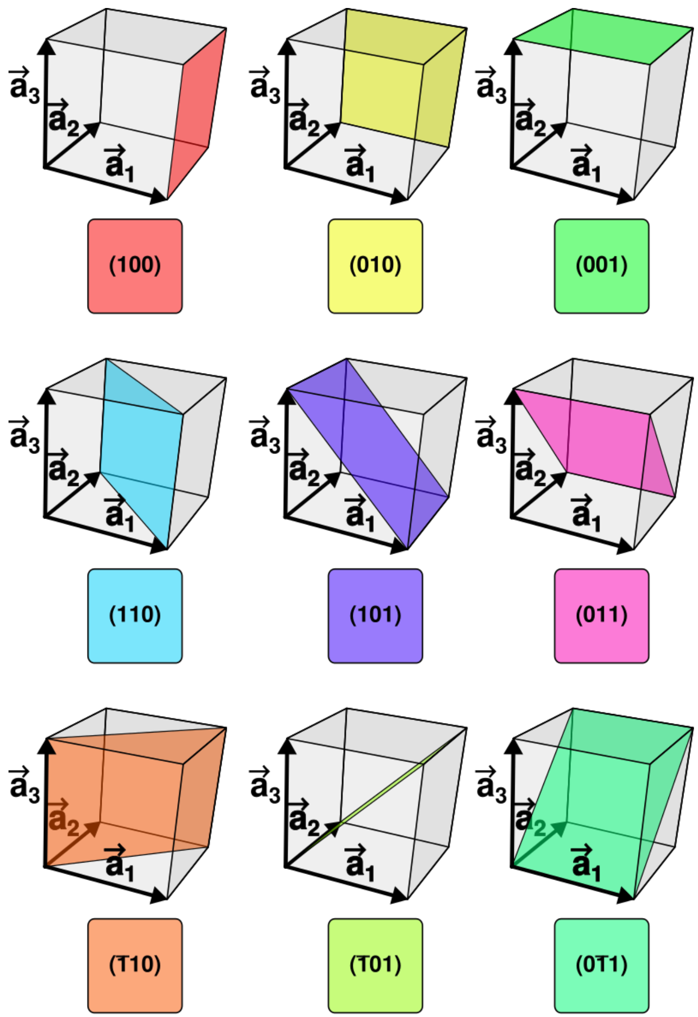
$$d = \boxed{}$$

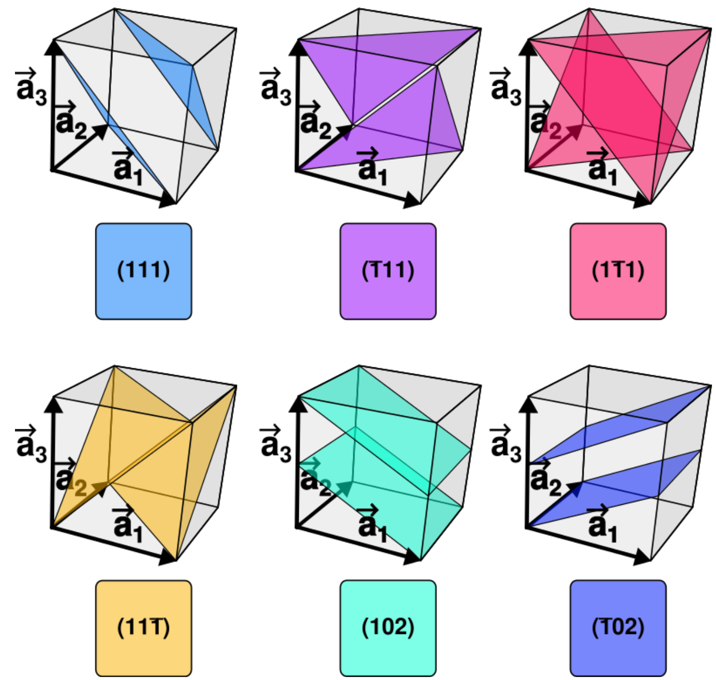
$$\left(\frac{\lambda}{2a}\right)^2 = \frac{\sin^2\theta}{h^2+k^2+l^2}\,.$$

Measurement of critical angle, θ_c, allows computation of planar spacing, *d*.



Crystal structure and miller indices



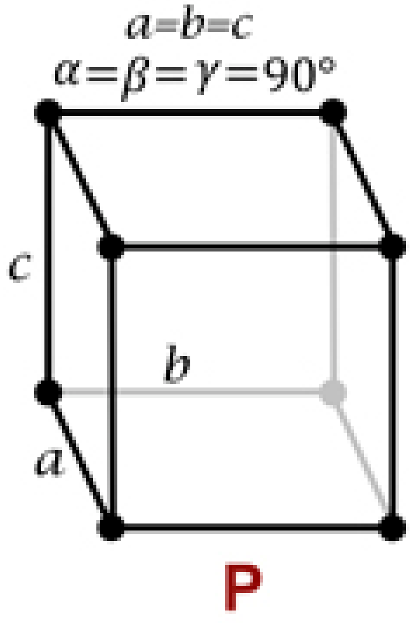


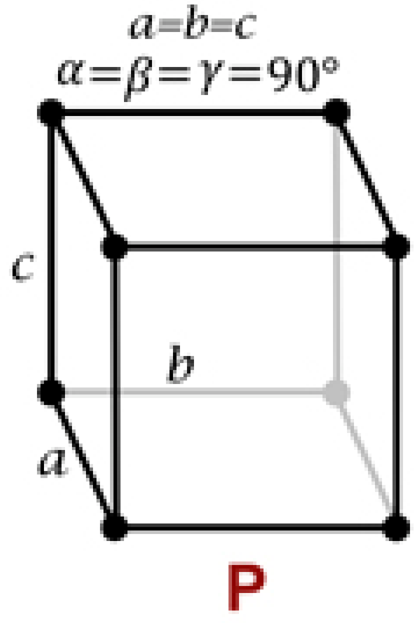
Planes with different Miller indices in cubic crystals.

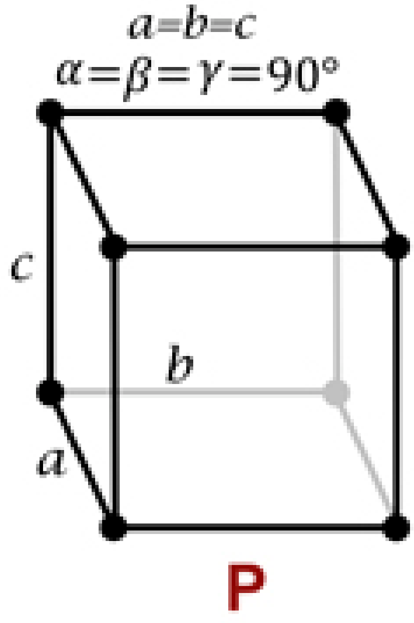
from http://en.wikipedia.org/wiki/Miller_index

Lattice spacing in cubic structure

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







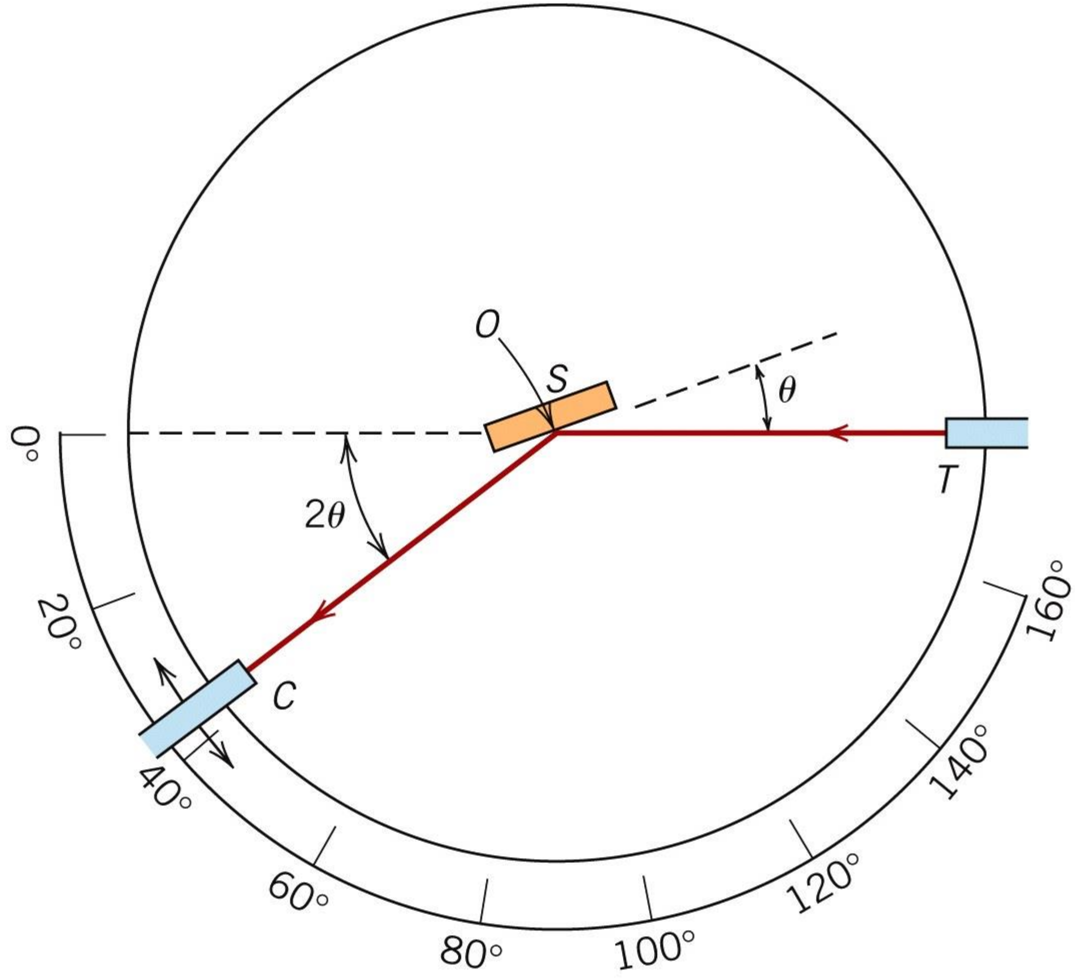
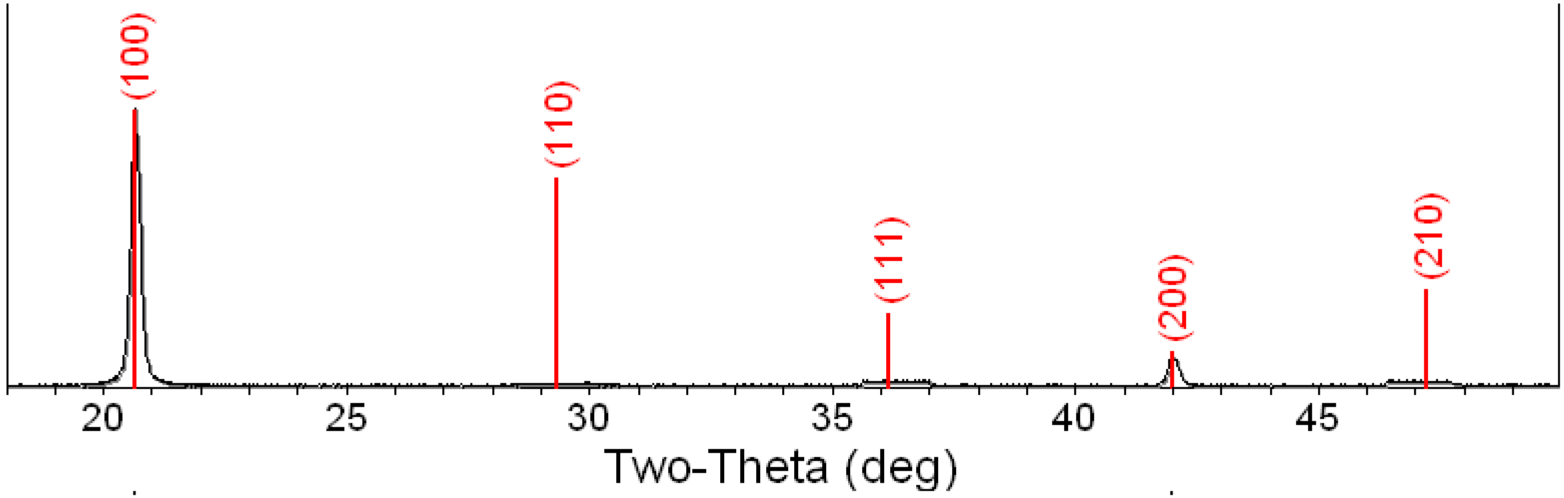
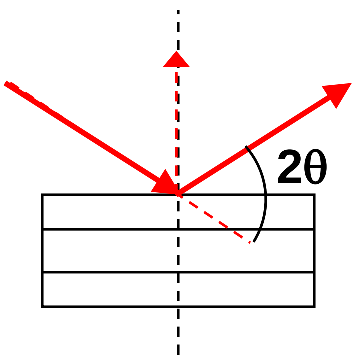


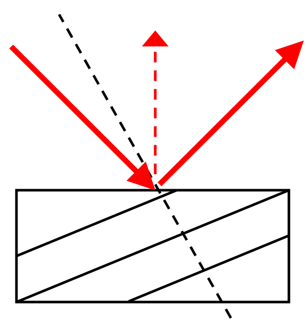
Figure 3.39

A single crystal specimen in a Bragg-Brentano diffractometer would produce ______ family of peaks in the diffraction pattern.

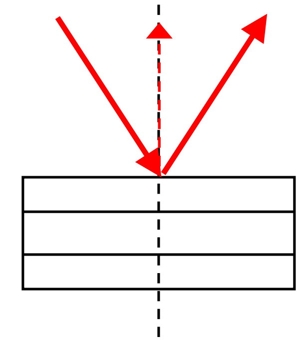




At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.



The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.

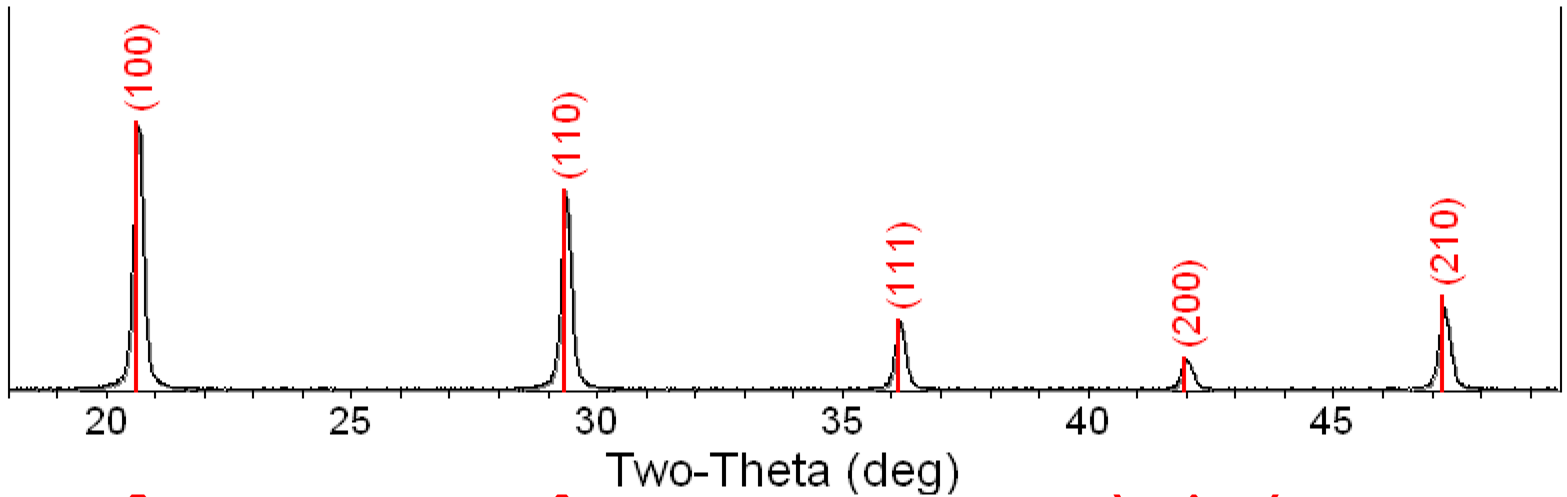


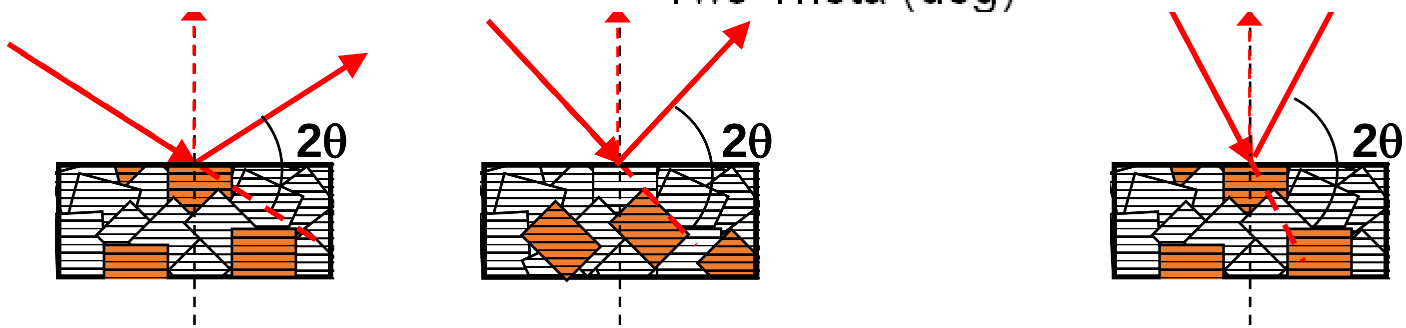
The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d_{200} is ½ d_{100}, they appear at 42 °2θ.

Polycrystalline materials

Figure 3.36

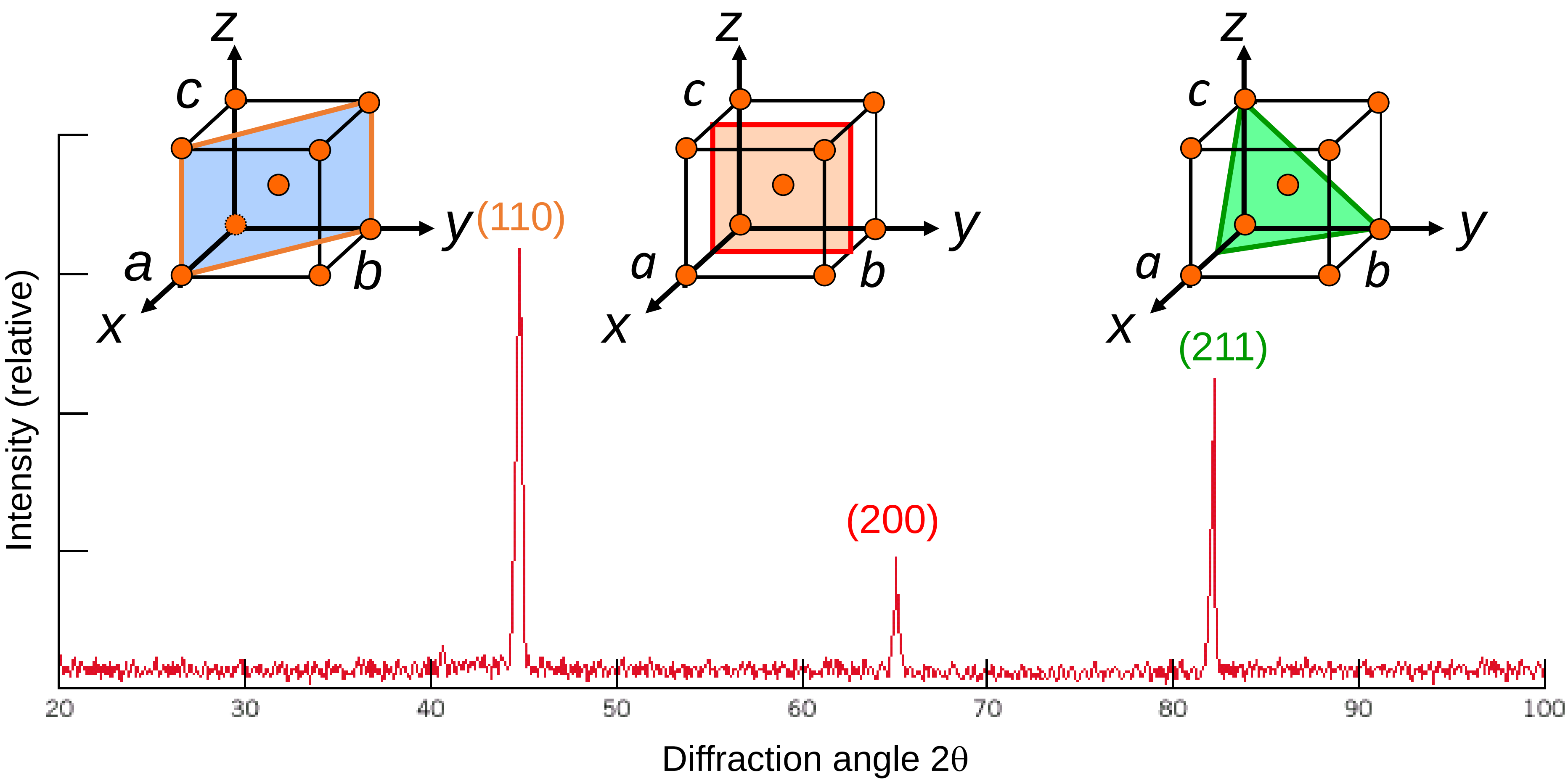
A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed.





- For every set of planes, there will be a small percentage of crystallites that are properly to diffract (the plane perpendicular bisects the incident and diffracted beams).
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.

X-Ray Diffraction Pattern



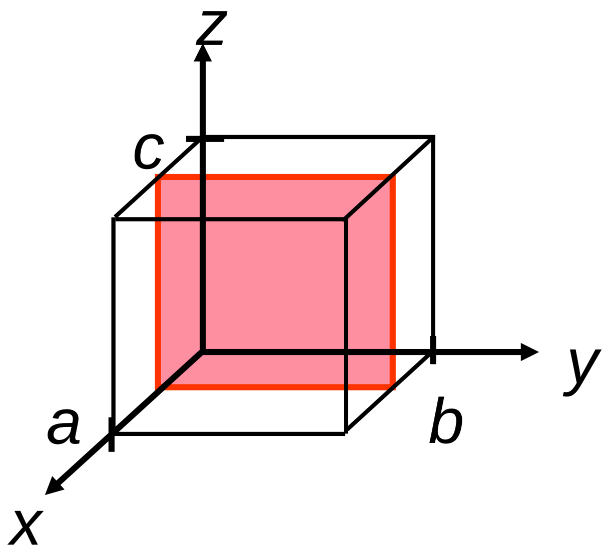
Diffraction pattern for polycrystalline α-iron (BCC)

Adapted from Fig. 3.40, *Callister 4e.*

Where is the peak of (100)?

Where is the peak of (100)?

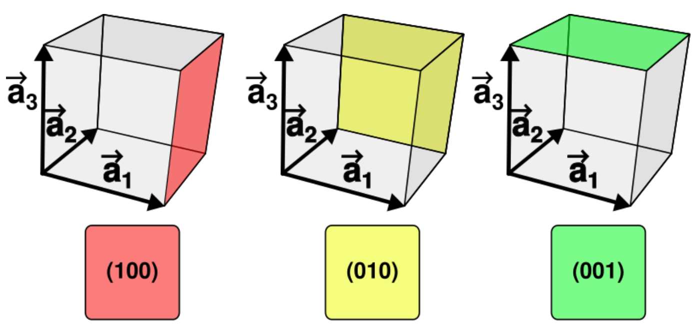
<u>example</u>		a	b	c
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(100)		



Family of Planes {*hkl*}

Ex: $\boxed{\quad\quad}$ = (100), (010), (001),

$(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1})$



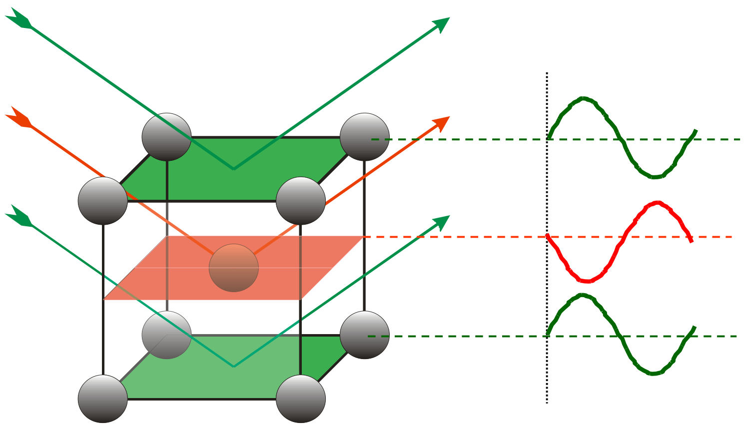
Missing reflections

- Bragg's equation is a negative statement: i.e. just because Bragg's equation is satisfied a 'reflection' $\boxed{}$ be observed.
- Let us consider the case of X-Ray radiation (λ = 1.54 Å) being diffracted from (100) planes of Fe (BCC, a = 2.87 Å = d_{100}).

$$\lambda = 2\, d_{100}\, Sin\theta_{100} \quad Sin\theta_{100} = \frac{\lambda}{2\, d_{100}} = \frac{1.54}{2(2.87)} = 0.268 \quad \theta_{100} = 15.545°$$

But this reflection is absent in BCC Fe

The missing reflection is due to the presence of additional atoms in the unit cell (which are positions at lattice points)



The wave scattered from the middle plane is out of phase with the ones scattered from top and bottom planes. I.e. if the green rays are in phase (path difference of λ) then the red ray will be exactly $\boxed{}$ phase with the green rays (path difference of $\lambda/2$).

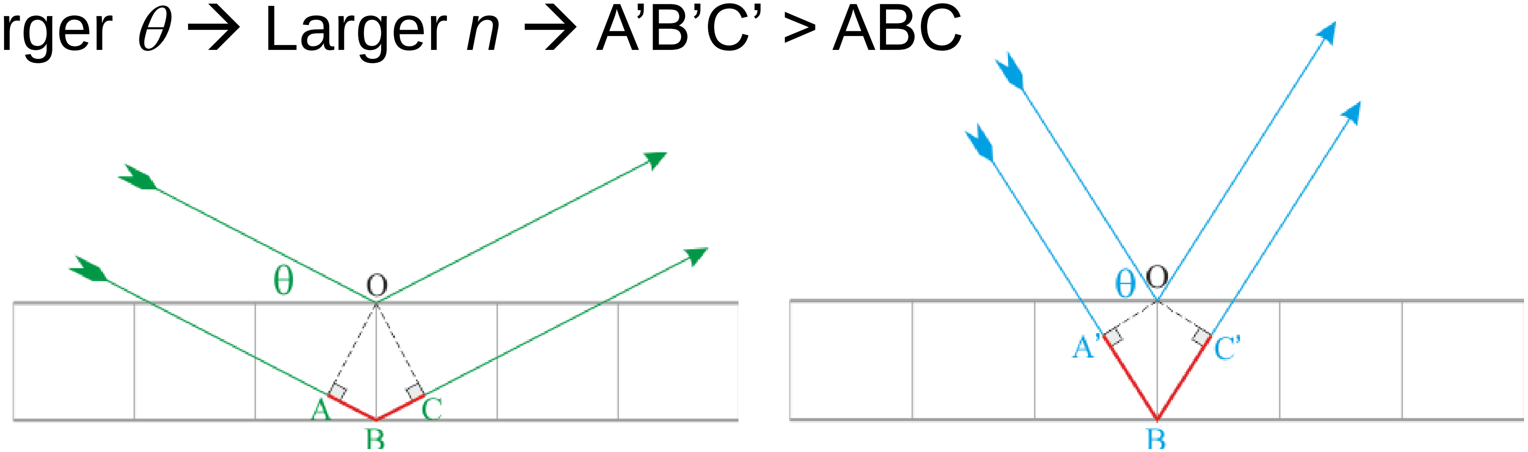
Continuing with the case of BCC Fe…

However, the second order reflection from (100) planes (which is equivalent to the first order reflection from the (200) planes) is observed

$$Sin\theta_{100} = \frac{2\lambda}{2\,d_{100}} = \frac{1.54}{2.87} = 0.536 \qquad \theta_{100}^{2^{nd}\ order} \sim \theta_{200}^{1^{nd}\ order} = 32.45\ ^{\circ}$$

This is because if the green rays have a path difference of 2λ then the red ray will have path difference of λ→ which will still lead to interference!

Larger θ → Larger n → A'B'C' > ABC



Allowed reflections in SC*, FCC*, BCC* & DC crystals

$h^2 + k^2 + l^2$	SC	FCC	BCC	DC
1	100			
2	110		110	
3	111	111		111
4	200	200	200	
5	210			
6	211		211	
7				
8	220	220	220	220
9	300, 221			
10	310		310	
11	311	311		311
12	222	222	222	
13	320			
14	321		321	
15				
16	400	400	400	400
17	410, 322			
18	411, 330		411, 330	
19	331	331		331

Cannot be expressed as $(h^2+k^2+l^2)$

BCC : $h + k + l$ must be even

FCC : h, k, and l must be either all odd or all even

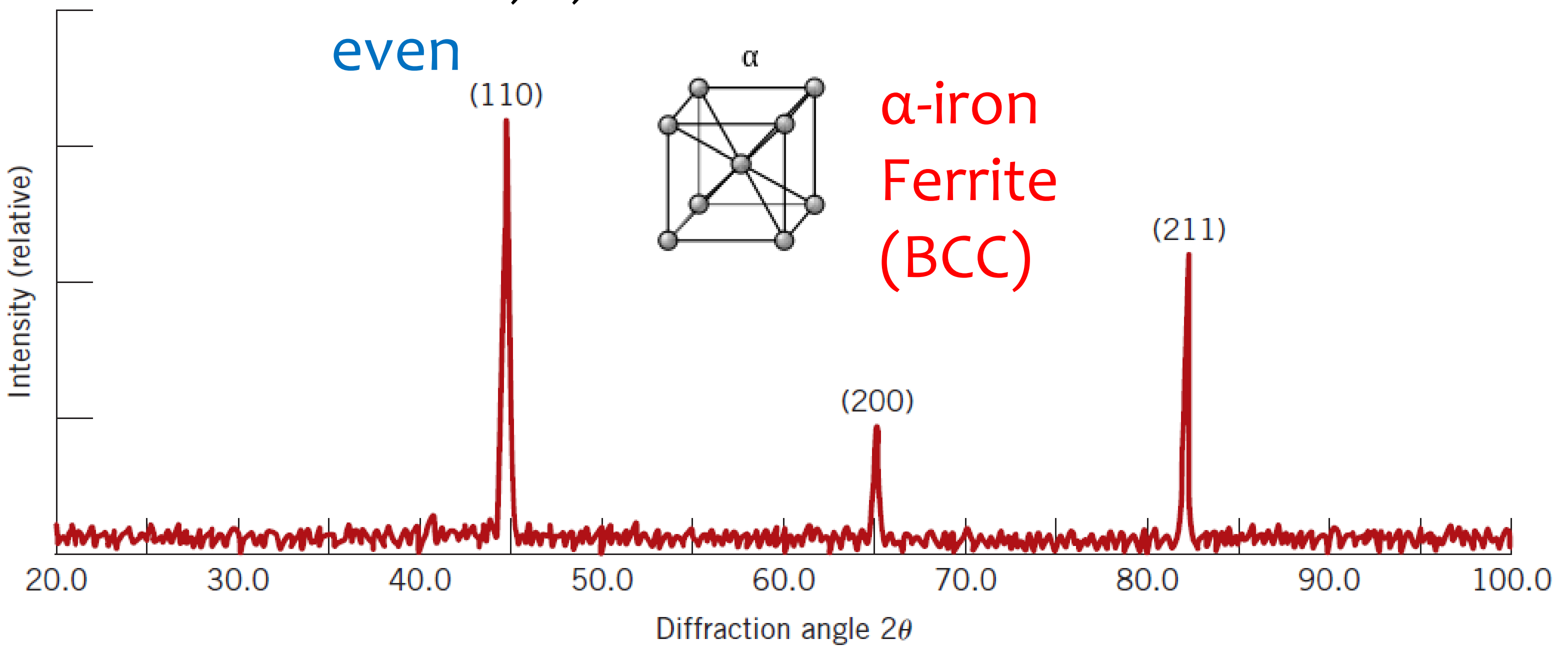
* lattice decorated with monoatomic/monoionic motif

$$
\begin{aligned}
n\lambda &= d_{hkl}\sin\theta + d_{hkl}\sin\theta \\
&= 2d_{hkl}\sin\theta
\end{aligned}
$$

$$
d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}
$$

BCC : *h* + *k* + *l* must be even

FCC : *h*, *k*, and *l* must be either all odd or all even



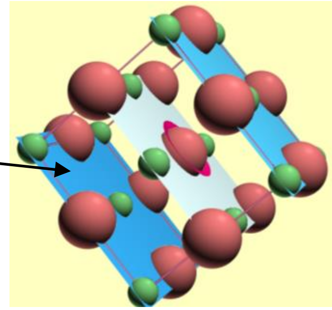
α-iron

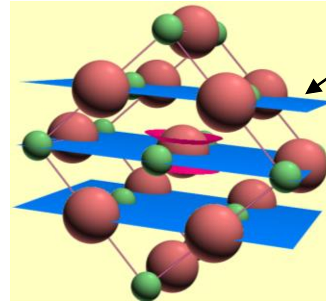
Ferrite

(BCC)

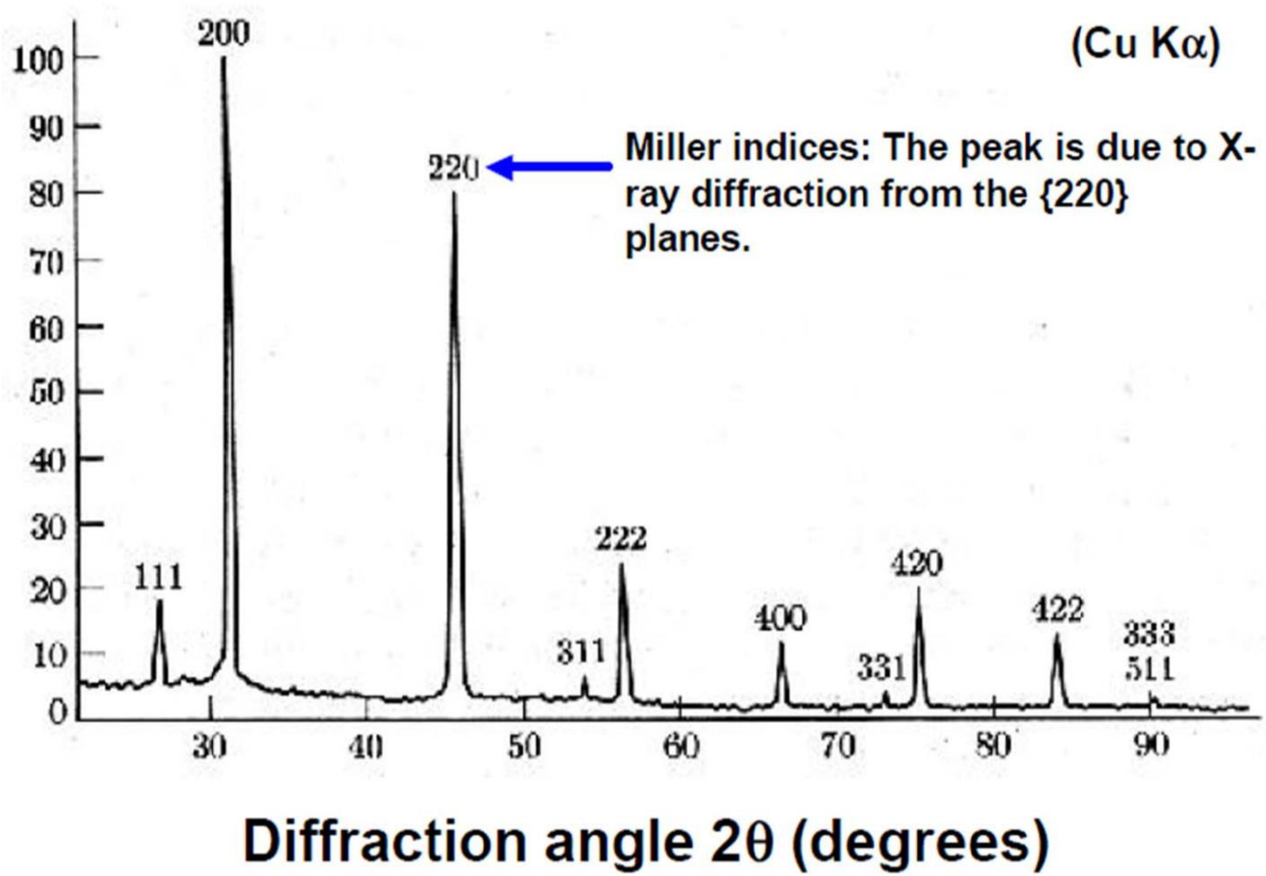
Diffraction pattern for polycrystalline α-iron

The (200) planes of atoms in NaCl





The (220) planes of atoms in NaCl



Interplanar Spacing and Diffraction Angle Computations

For BCC iron, compute (a) the interplanar spacing, and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm. Also, assume that monochromatic radiation having a wavelength of 0.1790 nm is used, and the order of reflection is 1.

Solution

(a) The value of the interplanar spacing d_{hkl} is determined using Equation 3.14, with $a = 0.2866$ nm, and $h = 2$, $k = 2$, and $l = 0$, since we are considering the (220) planes. Therefore,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$= \frac{\boxed{}}{\boxed{}} = 0.1013 \text{ nm}$$

(b) The value of θ may now be computed using Equation 3.13, with $n = 1$, since this is a first-order reflection:

$$\sin\theta = \frac{n\lambda}{2d_{hkl}} = \frac{\boxed{}}{\boxed{}} = 0.884$$

$$\theta = \sin^{-1}(0.884) = \boxed{}$$

The diffraction angle is 2θ, or

$$2\theta = (2)(62.13°) = \boxed{}$$