LECTURE #06

Chapter 3:
X-ray Diffraction and Crystal Structure Determination

Learning Objectives

- To describe crystals in terms of the stacking of planes.
- How to use a dot product to solve for the angles between planes and directions
- Describe a way to determine the crystal structure of a material using X-rays.

Relevant Reading for this Lecture...

- ***Pages 83-87.***

1

Recap of Miller Indices

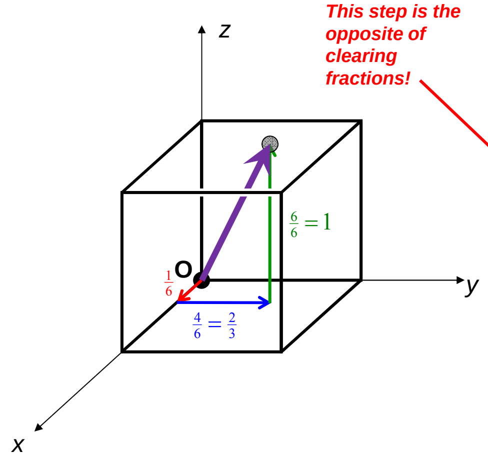
1) Last time we showed how to use vectors and Miller indices to define planes and directions in crystals.

2) Let's start with a worked example of (2) and then move into today's lecture.

2

In class example #2: SOLUTION

In a cubic unit cell, draw correctly a vector with indices [146].



This step is the opposite of clearing fractions!

Select your origin. Put it wherever you want to.

indices	[1	4	6]
Div. by 6	$\frac{1}{6}$	$\frac{4}{6}$	$\frac{6}{6}$

These fractions denote how far to step in the x, y, or z directions (away from the origin).

NOTE: It would be "wise" to select the origin so that you can complete the desired steps <u>within</u> the cell that you are using!

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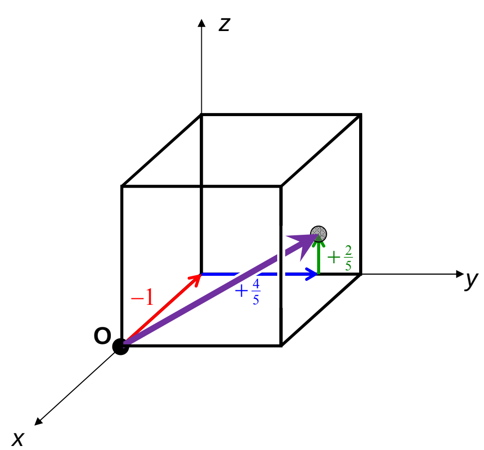
In class example #3:

In a cubic unit cell, draw correctly a vector with indices [$\bar{5}$42].



NOTE: It would be "wise" to select the origin so that you can complete the desired steps <u>within</u> the cell that you are using!

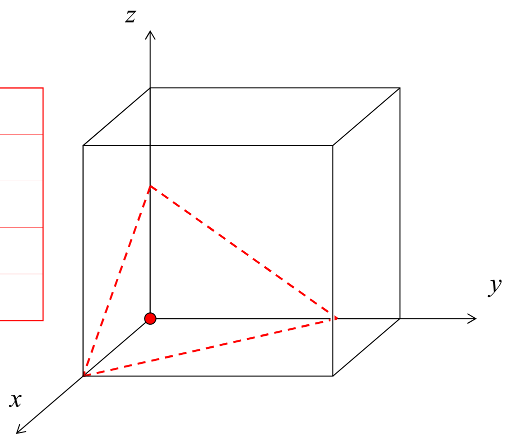
5

4

MILLER INDICES FOR A SINGLE PLANE

What is the plane bounded by the dash lines?

	x	y	z
Intercept			
Reciprocal			
Clear			
INDICES			



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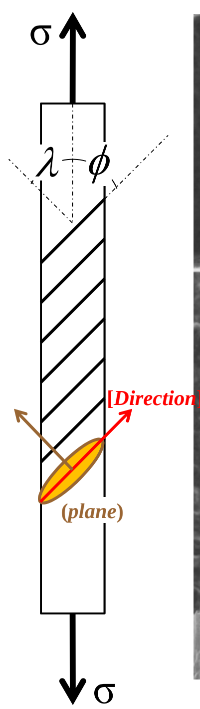
5

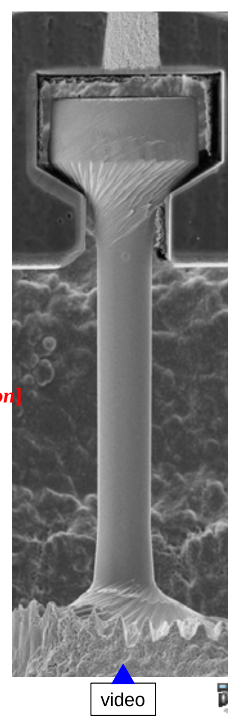
Remember this?

- When materials deform, they normally prefer to deform via shear in the closest packed directions on the closest packed planes!

  The tensile axis is in a different direction than the shear direction.

  We'll address this in more detail when we discuss mechanical properties!





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6

Sometimes it is necessary to determine the angle between a couple of directions or planes.

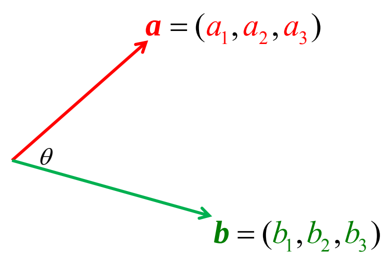
Use the cosine law

Sometimes it may be necessary to determine whether a direction lies on a particular plane.

Use the dot product

7

Vector dot products



*"**a** dot **b**" = sum of each vector index with its counterpart vector*

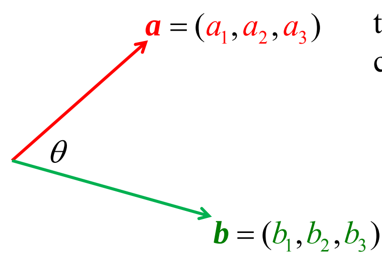
$\vec{a} \cdot \vec{b} = a_1 \times b_1 + a_2 \times b_2 + a_3 \times b_3$

Example: Find the dot product of ***a*** and ***b*** if ***a*** = (1,2,3) and ***b*** = (4,5,6)

$$\boldsymbol{a} \bullet \boldsymbol{b} = (1,2,3) \bullet (4,5,6) = 1 \cdot 4 + 2 \cdot 5 + 3 \cdot 6 = 4 + 10 + 18 = 32$$

8

Finding the angle between 2 vectors



a•b also equals the magnitude of ***a*** times the magnitude of ***b*** times the cosine of the angle between vectors.

$$\boldsymbol{a} \bullet \boldsymbol{b} = a_1 \cdot b_1 + a_2 \cdot b_2 + a_3 \cdot b_3 = |\boldsymbol{a}||\boldsymbol{b}|\cos\theta$$

Vector Magnitudes

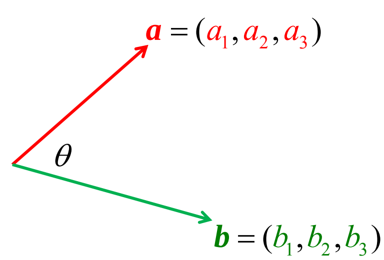
$$|\boldsymbol{a}| = \sqrt{a_1^2 + a_2^2 + a_3^2} \qquad |\boldsymbol{b}| = \sqrt{b_1^2 + b_2^2 + b_3^2}$$

Re-arrange and solve for cos θ. *This yields the familiar cosine law:*

$$\cos\theta = \frac{\boldsymbol{a} \bullet \boldsymbol{b}}{|\boldsymbol{a}||\boldsymbol{b}|} = \frac{a_1 \cdot b_1 + a_2 \cdot b_2 + a_3 \cdot b_3}{\sqrt{a_1^2 + a_2^2 + a_3^2} \times \sqrt{b_1^2 + b_2^2 + b_3^2}}$$

9

Finding the angle between 2 vectors



Example: Find the angle between ***a*** and ***b*** if ***a*** = (1,2,3) and ***b*** = (4,5,6)

$$\cos\theta = \frac{\boldsymbol{a} \bullet \boldsymbol{b}}{|\boldsymbol{a}||\boldsymbol{b}|} = \frac{1 \cdot 4 + 2 \cdot 5 + 3 \cdot 6}{\sqrt{1^2 + 2^2 + 3^2} \times \sqrt{4^2 + 5^2 + 6^2}} = \frac{32}{\sqrt{14}\sqrt{77}} = 0.9746$$

$$\theta = \cos^{-1}(0.9746) = \underline{\underline{12.93°}}$$

10

Angle between planes: Dot Product

We can define planes using vectors perpendicular to them!

Normal vectors have the same indices as the planes!

$$D = u \cdot \vec{a} + v \cdot \vec{b} + w \cdot \vec{c} \qquad D' = u' \cdot \vec{a} + v' \cdot \vec{b} + w' \cdot \vec{c}$$

$$\vec{D} \bullet \vec{D}' = |\vec{D}| \cdot |\vec{D}'| \cos\delta$$

$$\cos\delta = \frac{\vec{D} \cdot \vec{D}'}{|\vec{D}| \cdot |\vec{D}'|} \frac{u \cdot u' + v \cdot v' + w \cdot w'}{\sqrt{u^2 + v^2 + w^2}\sqrt{(u'^2) + (v'^2) + (w'^2)}}$$

Equations work with Miller indices!

11

How to tell if a direction lies on a plane

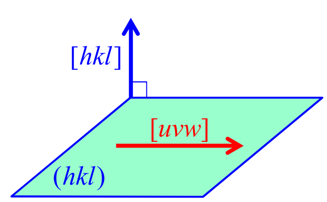
If the dot product of the vector and plane = 0,

then the vector lies on the plane

$$\vec{D} = u\vec{a} + v\vec{b} + w\vec{c} \qquad \vec{P} = h\vec{a} + k\vec{b} + l\vec{c}$$

$$[uvw] \qquad (hkl)$$

$$\vec{D} \cdot \vec{P} = |\vec{D}| \cdot |\vec{P}| \cos\delta = u \cdot h + v \cdot k + w \cdot l = 0$$



12

In Class Example

Which members of the <111> family of directions lie within the (110) plane?

13

In Class Example: SOLUTION

Which members of the <111> family of directions lie within the (110) plane?

The [110] direction is perpendicular (i.e., normal) to the (110) plane.

The directions that lie on this plane will give a zero dot product with [110].

$$[110]\bullet[hkl] = 1\cdot h + 1\cdot k + 0\cdot l$$

Now substitute in the members of the <111> family and see which give a zero dot product. The <111> family is:

$$[111], [\bar{1}11], [1\bar{1}1], [11\bar{1}], [\bar{1}\bar{1}\bar{1}], [1\bar{1}\bar{1}], [\bar{1}1\bar{1}], [\bar{1}\bar{1}1]$$

Substitute each direction in for $[hkl]$ as shown below:

$$[110]\bullet[111] = 1\cdot 1 + 1\cdot 1 + 0\cdot 1 = 2$$

$$[110]\bullet[\bar{1}11] = -1\cdot 1 + 1\cdot 1 + 0\cdot 1 = 0$$ ← **This one is on the (110) plane.**

$$etc...$$

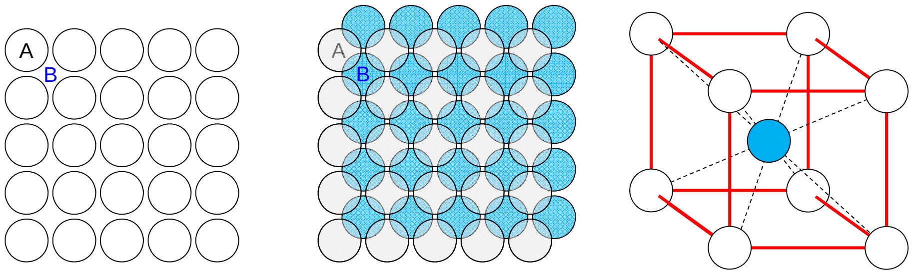
Look for all instances where the dot product = zero.

$$\underline{\underline{\text{SOLUTION: } [\bar{1}11], [1\bar{1}1], [1\bar{1}\bar{1}], \text{ and } [\bar{1}1\bar{1}]}}$$

14

Atomic packing and the unit cell

- We can visualize crystals structures as stacked planes of atoms.



(a) Non-close-packed layer A.

(b) Stack next layer on B sites. Yields ABABAB… stacking. BCC packing.

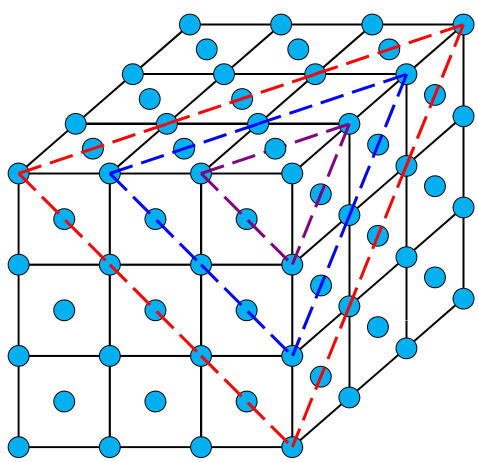
(c) The BCC unit cell

(a) A square grid of spheres. (b) A second layer, B, nesting in the first, A; repeating this sequence gives ABABAB… Packing resulting in (c) the BCC crystal structure.

15

Now that we understand planes – how do crystal structures compare?

Close Packed Stacking Sequence in FCC



16

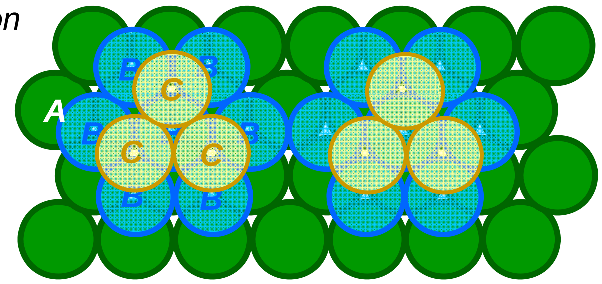
What is the Close Packed Stacking Sequence in FCC?

- ABCABC... Stacking Sequence
- 2D Projection

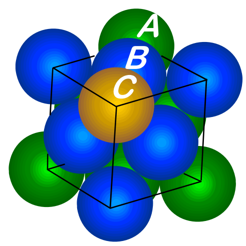
A sites

B sites

C sites



- FCC Unit Cell

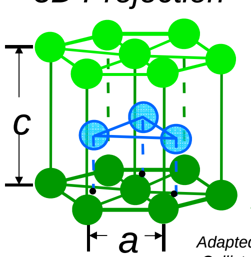


5

17

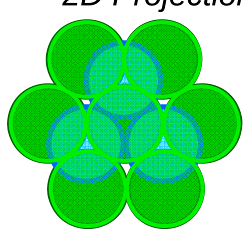
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



Adapted from Fig. 3.3(a), Callister 7e.

- 2D Projection



A: Top layer

B: Middle layer

A: Bottom layer

- Coordination # = 12
- APF = 0.74
- c/a = 1.633

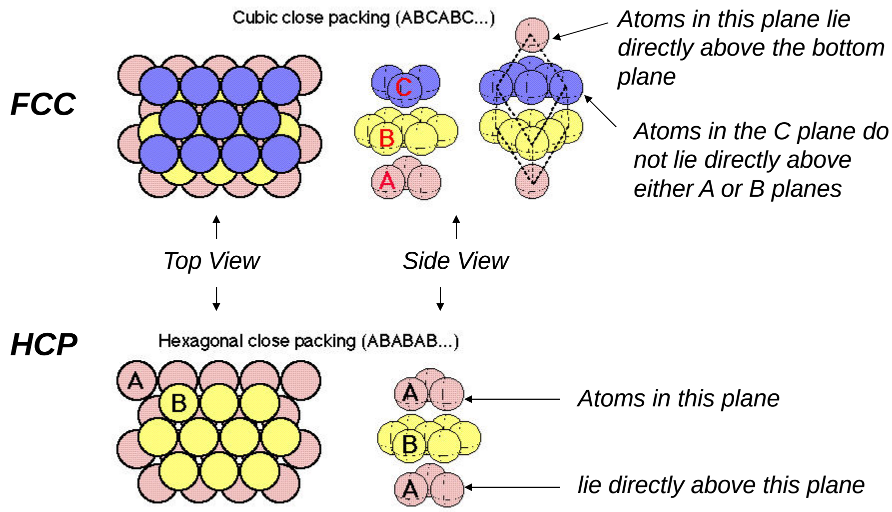
6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

2

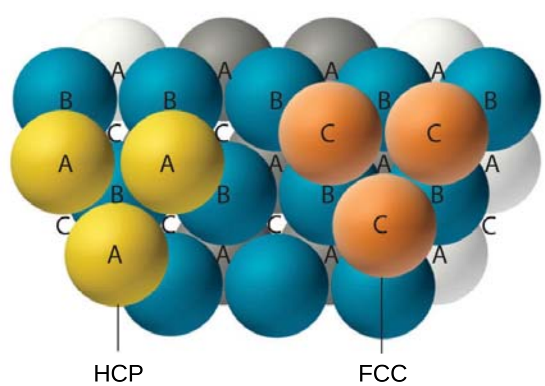
18

A comparison of the stacking sequence of close packed planes in HCP & FCC crystals



19

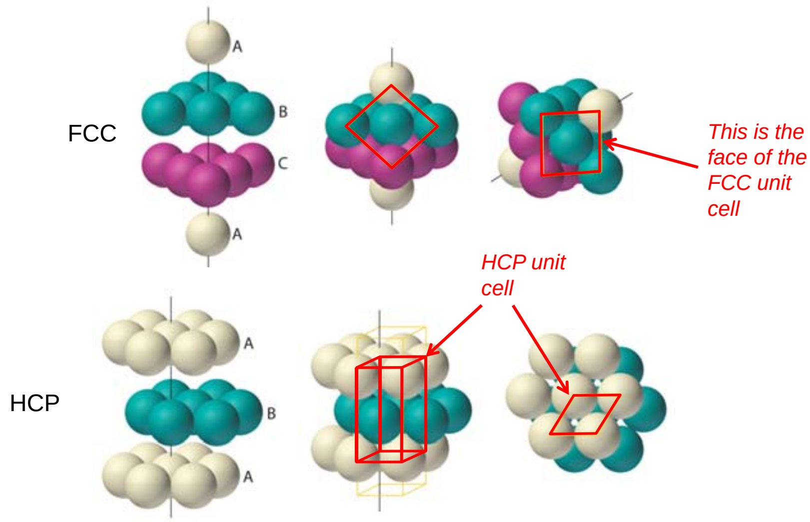
A comparison of HCP and FCC stacking sequence of close packed planes



This is similar to Figs. 3.30 – 3.32 on pages 78 and 79 of your book.

20

A comparison of the stacking sequence of close packed planes in HCP & FCC

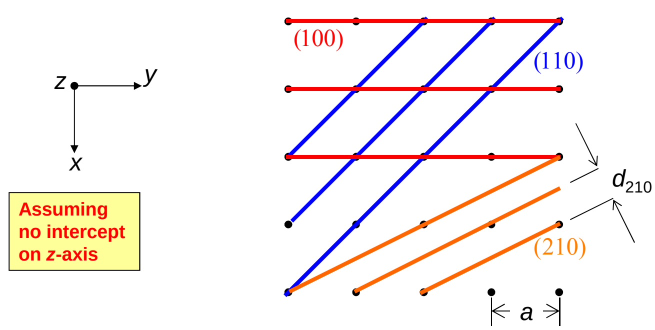


Just another visual to help you out

21

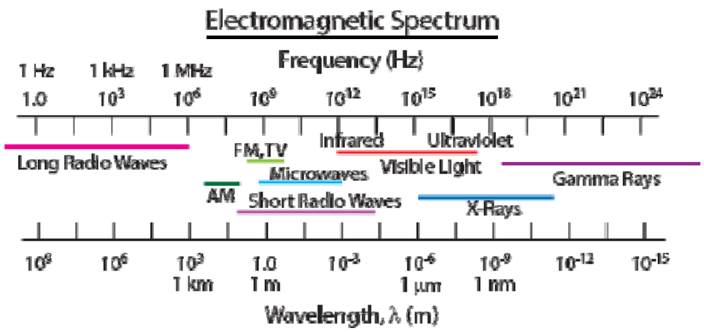
How Can We Determine Crystal Structures?

- Measure the inter-planar spacing.
- The inter-planar spacing in a particular direction is the distance between equivalent planes of atoms.
  - Function of lattice parameter
  - Function of crystal symmetry *(i.e., how atoms are arranged)*



22

How do we Measure this Spacing?
X-Ray Diffraction

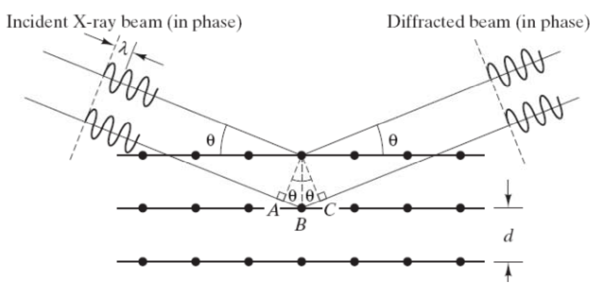


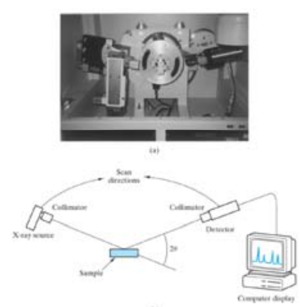
- Diffraction gratings must have spacing comparable to the wavelength (λ) of diffracted radiation (X-rays).
- In crystals: diffraction gratings are planes of atoms. Spacing is the distance between parallel planes of atoms.
- We can only resolve a spacing that is bigger than λ.

  (This is why we use X-rays… they are approximately the same size as planar spacings)

23

Bragg's Law:





Bragg's Law:

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

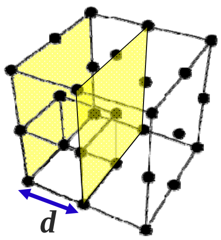
Where:

- θ is half the angle between the diffracted beam and the original beam direction
- λ is the wavelength of X-ray
- d is the interplanar spacing

24

Bragg's Law:

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



Interplanar spacing:

$$d_{hkl} = \frac{d}{n} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} = \frac{\lambda}{2\sin\theta}$$

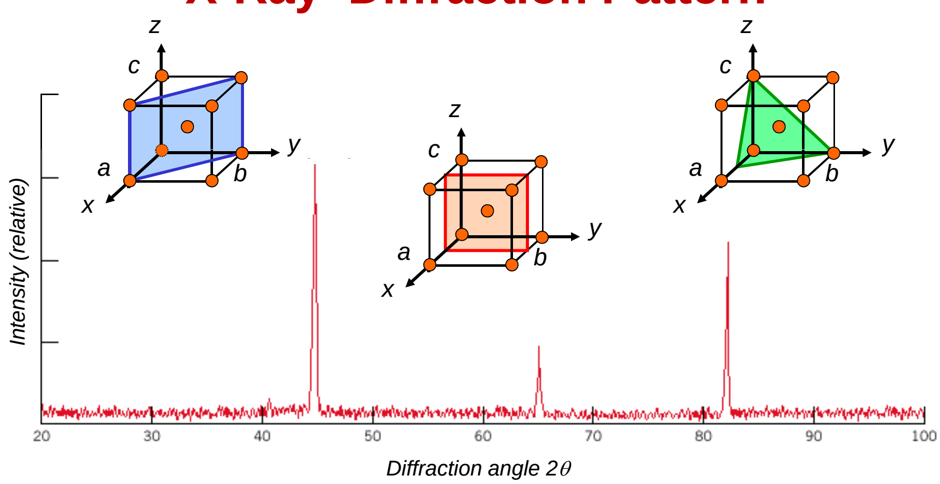
Lattice parameter

Order of reflection (integer)

Miller Indices

25

X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline α-iron (BCC)

Adapted from Fig. 3.40, Callister and Rethwisch 4e. P. 86

3

26

Why do different crystals diffract different planes?

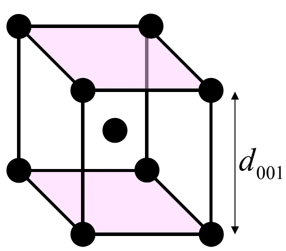
Reflection Rules of X-Ray Diffraction for the Common Metal Structures		
Crystal structure	**Diffraction does not occur when**	**Diffraction occurs when**
Body-centered cubic (bcc)	$h + k + l =$ odd number	$h + k + l =$ even number
Face-centered cubic (fcc)	h, k, l mixed (i.e., both even and odd numbers)	h, k, l unmixed (i.e., are all even numbers or all are odd numbers)
Hexagonal close packed (hcp)	$(h + 2k) = 3n$, l odd (n is an integer)	All other cases

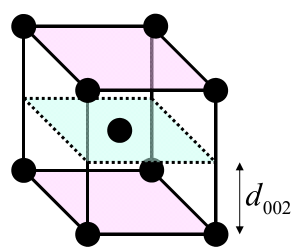
It's based on atomic arrangement.

Thus, there are rules that define which planes diffract.

Some reflections aren't observed. WHY?

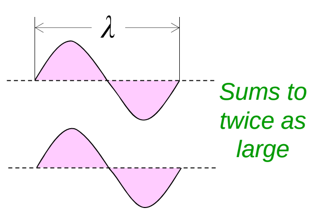
Why is the {100} not an allowed reflection in BCC?

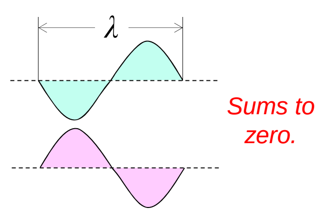




***Diffraction from* (001) planes.**
Diffracted X-rays are in phase
(i.e., they line up perfectly).

***Diffraction from* (002) planes.**
X-rays diffracted from (002)
are shifted 180° out of phase
(i.e., they do not line up perfectly).





Related to equations 3.16 and 3.16 on page 84.

In Class Example

What would be the (*hkl*) indices for the three lowest diffraction-angle peaks for BCC metal?

29

In Class Example: SOLUTION

What would be the (*hkl*) indices for the three lowest diffraction-angle peaks for BCC metal?

First, satisfy reflection criteria for BCC (i.e., $h + k + l$ = even number).

Second, combine *d*-spacing equation with Bragg's Law:

$$d_{hkl} = \frac{d}{n} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} = \frac{\lambda}{2\sin\theta}$$

Re-arrange so that we can determine θ; you will get:

$$\sin\theta = \frac{\lambda}{2a_o}\sqrt{h^2 + k^2 + l^2}$$

Now we plug in *hkl* values such that the reflection rule is satisfied. NOTE: smallest θ corresponds to smallest combination of *hkl* values.

Indices	$h+k+l$	$h^2+k^2+l^2$	*BCC*
100	*odd*	1	*no*
110	**even**	2	**YES** ←
111	*odd*	3	*no*
200	**even**	4	**YES** ←
210	*odd*	5	*no*
211	**even**	6	**YES** ←

A great variation on this question would be:
What are the reflection angles

30

Summary

- We can use the dot product as a means to identify angles between planes and directions (this will be important when we get to mechanical behavior!)
- Crystal structure can be determined by measuring inter-planar spacing.
- We use X-ray Diffraction to measure this spacing.
- Inter-planar spacing can be calculated using:

$$d_{hkl} = \frac{d}{n} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} = \frac{\lambda}{2\sin\theta}$$

- Bragg's Law: $n\lambda = 2d\sin\theta$
- Depending on crystal types, certain {hkl} planes will diffraction and can be used to identify the crystal structure. We have a set of selection rules to help us identify them. (*You do not need to memorize these rules – they would be given to you on an exam, if a question was asked*.)

31