

Materials Science and Engineering I

Chapter 3



Chapter 3 Outline

How do atoms arrange themselves to form solids?

Fundamental concepts and language

□ Unit cells

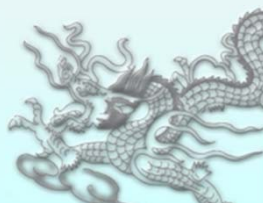
□ Crystal structures

- ◆ Face-centered cubic
- ◆ Body-centered cubic
- ◆ Hexagonal close-packed

□ Close packed crystal structures

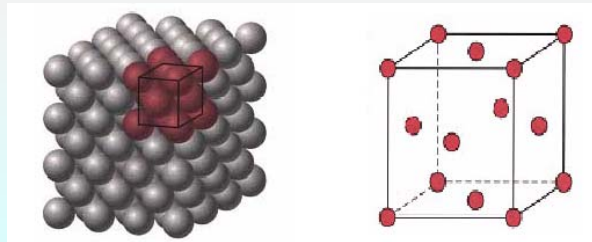
□ Density computations

□ Types of solids

- ◆ Single crystal
 - ◆ Polycrystalline
 - ◆ Amorphous
- 

Crystal structure

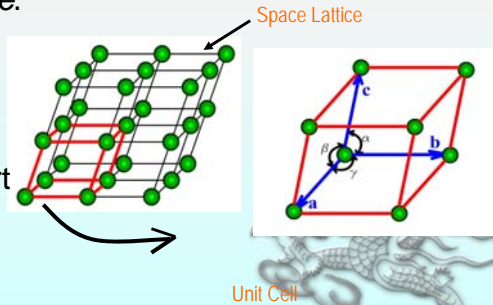
To discuss crystalline structures it is useful to consider atoms as being hard spheres with well-defined radii. In this hard-sphere model, the shortest distance between two like atoms is one diameter. We can also consider crystalline structure as a lattice of points at atom/sphere centers.



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The Space Lattice and Unit Cells

- ◆ Atoms, arranged in repetitive 3-Dimensional pattern, in long range order (LRO) give rise to *crystal structure*.
- ◆ Properties of solids depends upon crystal structure and bonding force.
- ◆ An imaginary network of lines, with atoms at intersection of lines, representing the arrangement of atoms is called *space lattice*.
- ◆ **Unit cell** is that block of atoms which repeats itself to form space lattice.
- ◆ Materials arranged in short range order are called

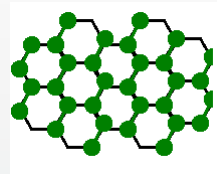


amorphous materials

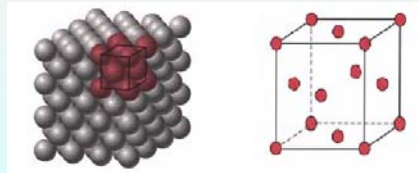
Unit cell

The unit cell is the smallest structural unit or building block that can describe the crystal structure. Repetition of the unit cell generates the entire crystal.

Example: 2D honeycomb net can be represented by translation of two adjacent atoms that form a unit cell for this 2D crystalline structure



Example of 3D crystalline structure:

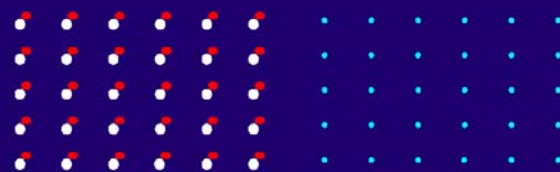


Different choices of unit cells possible, generally choose parallelepiped unit cell with highest level of symmetry

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基元和晶體結構 (Basis and the Crystal Structure)

Crystal
periodic array of atoms : point lattice + basis

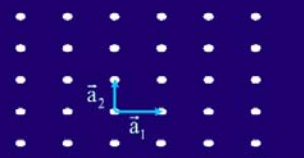


● Point lattice – mathematical points in space

$$\vec{r}' = \vec{r} + u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$$

$$u_1, u_2, u_3 \in \text{integer}$$

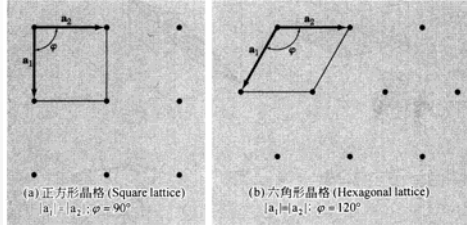
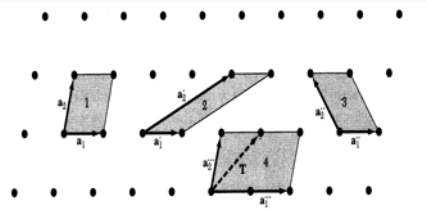
$$\vec{a}_1, \vec{a}_2, \vec{a}_3 = \text{lattice vectors}$$



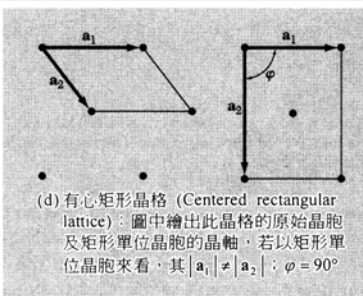
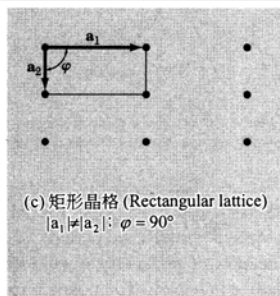
二維晶格類型 (Two-Dimensional Lattice Types)

斜晶格 (oblique lattice)

特殊晶格類型 (special lattice type)

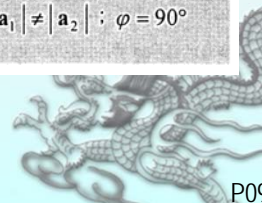
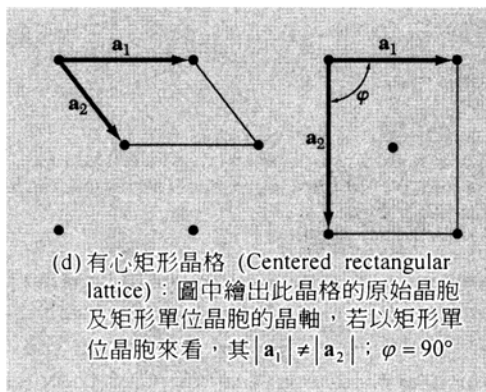
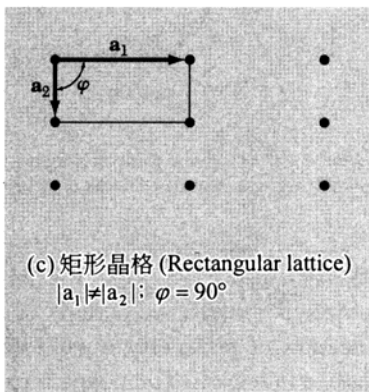


特殊晶格類型 (special lattice type)



P09

特殊晶格類型 (special lattice type)

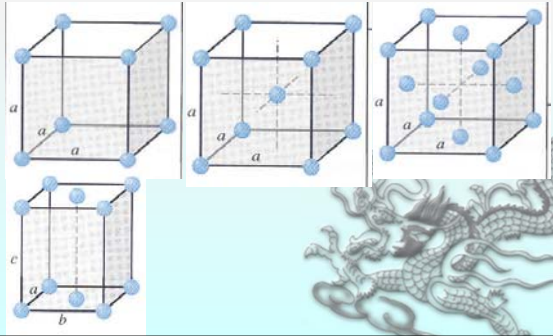


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Crystal Systems and Bravais Lattice

- ◆ Only seven different types of unit cells are necessary to create all point lattices.
- ◆ According to Bravais (1811-1863), fourteen standard unit cells can describe all possible lattice networks.
- ◆ The four basic types of unit cells are

- Simple
- Body Centered
- Face Centered
- Base Centered



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三維晶格類型 (Three-Dimensional Lattice Types)

The seven crystal systems divided into fourteen Bravais lattices

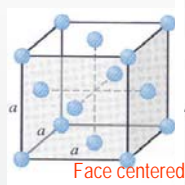
System	Number of lattices	Unit cell characteristics	Characteristic symmetry elements
Triclinic	1: Simple	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$	None
Monoclinic	2: Simple, Base-Centered	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = 90^\circ \neq \gamma$	One 2-fold rotation axis
Orthorhombic	4: BCC, FCC Simple, Base-Centered	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$	Three mutually orthogonal 2-fold rotation axes
Tetragonal	2: Simple, BCC	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$	One 4-fold rotation axis
Cubic	3: Simple, BCC, FCC	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$	Four 3-fold rotation axes
Trigonal	1: Simple	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120^\circ \neq 90^\circ$	One 3-fold rotation axis
Hexagonal	1: Simple	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	One 3-fold rotation axis

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Types of Unit Cells

◆ Cubic (立方)

- > $a = b = c$
- > $\alpha = \beta = \gamma = 90^\circ$



Unit Cell

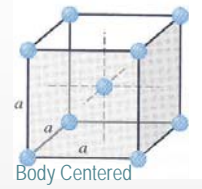
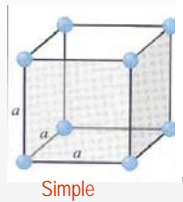
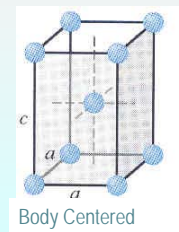
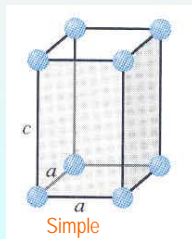


Figure 3.2

◆ Tetragonal (正方)

- > $a = b \neq c$
- > $\alpha = \beta = \gamma = 90^\circ$

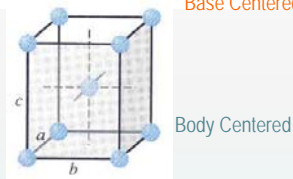
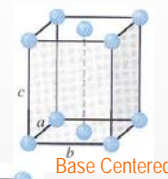
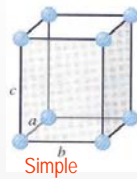
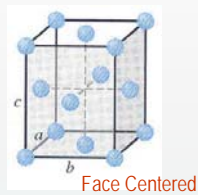


After W.G. Moffatt, G.W. Pearsall, & J. Wulff, "The Structure and Properties of Materials," vol. I: "Structure," Wiley, 1964, p.47.)

Types of Unit Cells

◆ Orthorhombic (斜方)

- > $a \neq b \neq c$
- > $\alpha = \beta = \gamma = 90^\circ$



◆ Rhombohedral (菱方)

- > $a = b = c$
- > $\alpha = \beta = \gamma \neq 90^\circ$

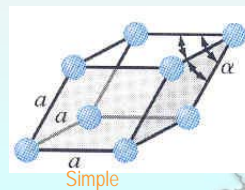


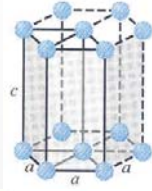
Figure 3.2

After W.G. Moffatt, G.W. Pearsall, & J. Wulff, "The Structure and Properties of Materials," vol. I: "Structure," Wiley, 1964, p.47.)

Types of Unit Cells

◆ Hexagonal (六方)

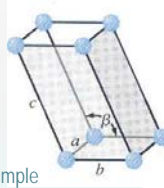
- > $a = b \neq c$
- > $\alpha = \beta = 90^\circ \neq \gamma = 120^\circ$



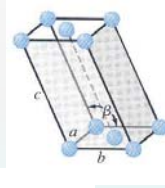
Simple

◆ Monoclinic (單斜)

- > $a \neq b \neq c$
- > $\alpha = \gamma = 90^\circ \neq \beta$



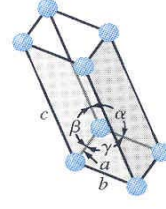
Simple



Base
Centered

◆ Triclinic (三斜)

- > $a \neq b \neq c$
- > $\alpha \neq \beta \neq \gamma \neq 90^\circ$



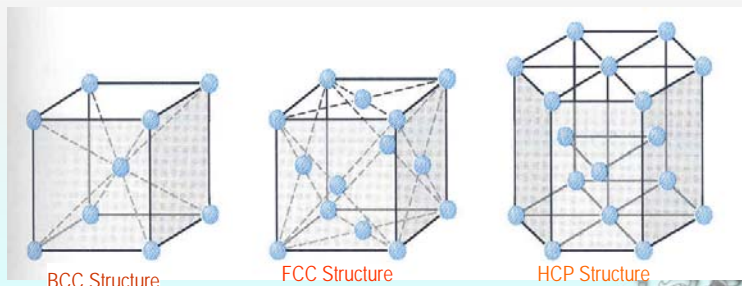
Simple

Figure 3.2

After W.G. Moffatt, G.W. Pearsall, & J. Wulff, "The Structure and Properties of Materials," vol. I: "Structure," Wiley, 1964, p.47.)

Principal Metallic Crystal Structures

- ◆ 90% of the metals have either Body Centered Cubic (BCC), Face Centered Cubic (FCC) or Hexagonal Close Packed (HCP) crystal structure.
- ◆ HCP is denser version of simple hexagonal crystal structure.



BCC Structure

FCC Structure

HCP Structure

Figure 3.3

Body Centered Cubic (BCC) Crystal Structure

- ◆ Represented as one atom at each corner of cube and one at the center of cube.
- ◆ Each atom has 8 nearest neighbors.
- ◆ Therefore, *coordination number* is 8.
- ◆ **Examples :-**
 - Chromium (a=0.289 nm)
 - Iron (a=0.287 nm)
 - Sodium (a=0.429 nm)

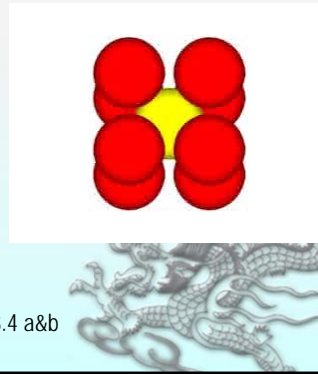
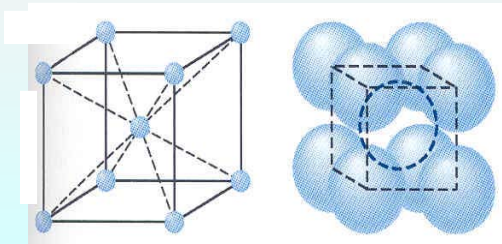
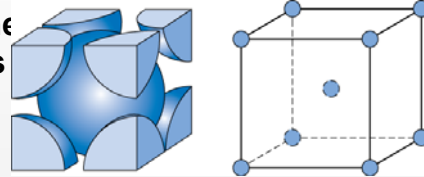


Figure 3.4 a&b

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BCC Crystal Structure (Cont..)

- ◆ Each unit cell has eight 1/8 atom at corners and 1 full atom at the center. Therefore, each unit cell has $(8 \times 1/8) + 1 = 2$ atoms



- ◆ Atoms contact each other at cube diagonal

Therefore, lattice constant $a = \frac{4R}{\sqrt{3}}$

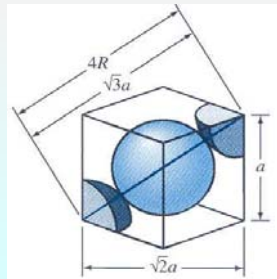


Figure 3.5

Example Problem 3.1

Iron at 20°C is BCC with atoms of atomic radius 0.124 nm. Calculate the lattice constant a for the cube edge of the iron unit cell.

■ Solution

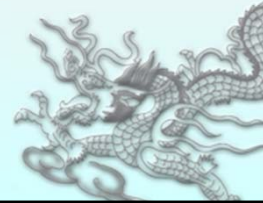
From Fig. 3.5 it is seen that the atoms in the BCC unit cell touch across the cube diagonals. Thus, if a is the length of the cube edge, then

$$\sqrt{3}a = 4R \quad (3.1)$$

where R is the radius of the iron atom. Therefore

$$a = \frac{4R}{\sqrt{3}} = \frac{4(0.124 \text{ nm})}{\sqrt{3}} = 0.2864 \text{ nm} \blacktriangleleft$$

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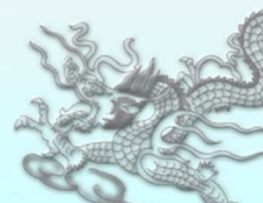
Atomic Packing Factor of BCC Structure

$$\text{Atomic Packing Factor} = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}}$$

$$V_{\text{atoms}} = 2 \times \left(\frac{4\pi R^3}{3} \right) = 8.373R^3$$

$$V_{\text{unit cell}} = a^3 = \left(\frac{4R}{\sqrt{3}} \right)^3 = 12.32 R^3$$

$$\text{Therefore APF} = \frac{8.373 R^3}{12.32 R^3} = 0.68$$



Example Problem 3.2

Calculate the atomic packing factor (APF) for the BCC unit cell, assuming the atoms to be hard spheres.

■ Solution

$$\text{APF} = \frac{\text{volume of atoms in BCC unit cell}}{\text{volume of BCC unit cell}} \quad (3.2)$$

Since there are two atoms per BCC unit cell, the volume of atoms in the unit cell of radius R is

$$V_{\text{atoms}} = (2)(\pi R^3) = 8.373R^3$$

The volume of the BCC unit cell is

$$V_{\text{unit cell}} = a^3$$

where a is the lattice constant. The relationship between a and R is obtained from Fig. 3.5, which shows that the atoms in the BCC unit cell touch each other across the cubic diagonal. Thus

$$\sqrt{3}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{3}} \quad (3.1)$$

Thus,

$$V_{\text{unit cell}} = a^3 = 12.32R^3$$

The atomic packing factor for the BCC unit cell is, therefore,

$$\text{APF} = \frac{V_{\text{atoms/unit cell}}}{V_{\text{unit cell}}} = \frac{8.373R^3}{12.32R^3} = 0.68 \quad \blacktriangleleft$$

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Face Centered Cubic (FCC) Crystal Structure

- ◆ FCC structure is represented as one atom each at the corner of cube and at the center of each cube face.
- ◆ Coordination number for FCC structure is 12
- ◆ Atomic Packing Factor is 0.74
- ◆ Examples :-

- ◆ **Aluminum** ($a = 0.405$)
- ◆ **Gold** ($a = 0.408$)

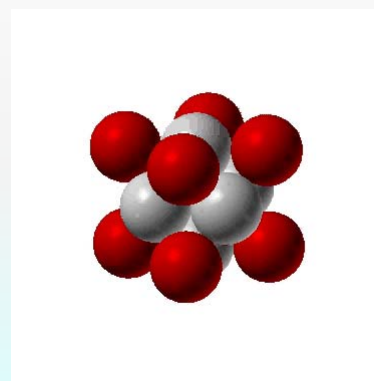
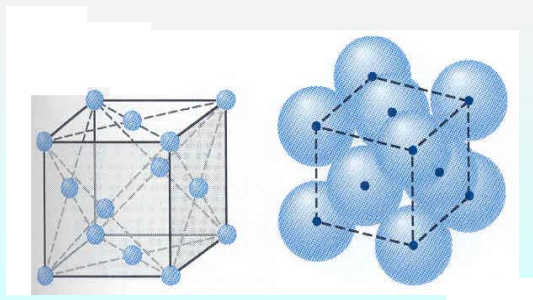


Figure 3.6 a&b

3-11

FCC Crystal Structure (Cont..)

- ◆ Each unit cell has eight $1/8$ atom at corners and six $1/2$ atoms at the center of six faces.

Therefore each unit cell has

$$(8 \times 1/8) + (6 \times 1/2) = 4 \text{ atoms}$$

- ◆ Atoms contact each other across cubic face diagonal

$$\begin{aligned} \text{Therefore, lattice} & \quad 4R \\ \text{constant } a & = \frac{4R}{\sqrt{2}} \end{aligned}$$

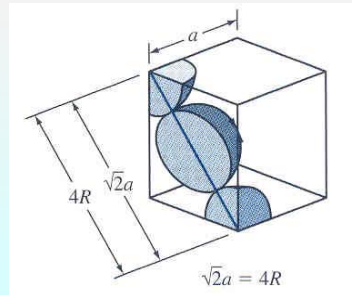
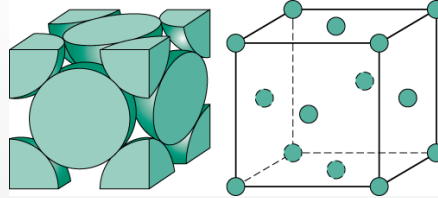


Figure 3.7

Hexagonal Close-Packed Structure

- ◆ The HCP structure is represented as an atom at each of 12 corners of a hexagonal prism, 2 atoms at top and bottom face and 3 atoms in between top and bottom face.
- ◆ Atoms attain higher APF by attaining HCP structure than simple hexagonal structure.
- ◆ The **coordination number is 12, APF = 0.74.**

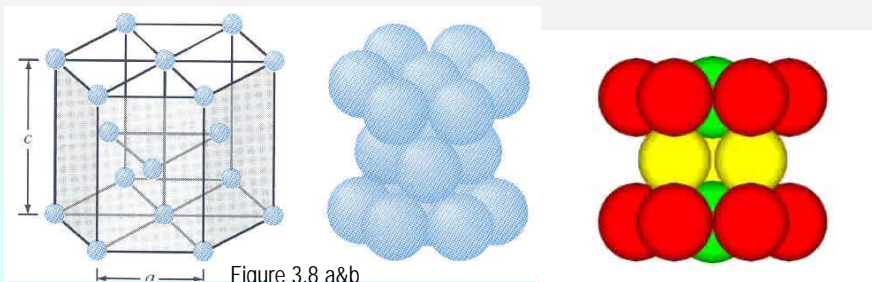


Figure 3.8 a&b

After F.M. Miller, "Chemistry: Structure and Dynamics," McGraw-Hill, 1984, p.296

Example Problem 3.3

- a. Calculate the volume of the zinc crystal structure unit cell by using the following data: pure zinc has the HCP crystal structure with lattice constants $a = 0.2665$ nm and $c = 0.4947$ nm.
 b. Find the volume of the larger cell.

■ Solution

The volume of the zinc HCP unit cell can be obtained by determining the area of the base of the unit cell and then multiplying this by its height (Fig. EP3.3).

- a. The area of the base of the unit cell is area $ABDC$ of Fig. EP3.3a and b . This total area consists of the areas of six equilateral triangles of area ABC of Fig. EP3.3b. From Fig. EP3.3c,

$$\begin{aligned} \text{Area of triangle } ABC &= \frac{1}{2}(\text{base})(\text{height}) \\ &= \frac{1}{2}(a)(a \sin 60^\circ) = \frac{1}{2}a^2 \sin 60^\circ \end{aligned}$$

From Fig. EP3.3b,

$$\begin{aligned} \text{Total area of HCP base, area } ABDC &= (2)(3a^2 \sin 60^\circ) \\ &= a^2 \sin 60^\circ \end{aligned}$$

From Fig. EP3.3a,

$$\begin{aligned} \text{Volume of zinc HCP unit cell} &= (a^2 \sin 60^\circ)(c) \\ &= (0.2665 \text{ nm})^2(0.8660)(0.4947 \text{ nm}) \\ &= 0.0304 \text{ nm}^3 \quad \blacktriangleleft \end{aligned}$$

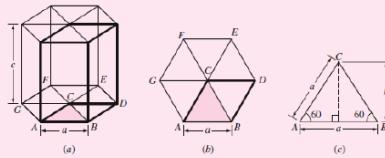


Figure EP3.3

Diagrams for calculating the volume of an HCP unit cell. (a) HCP unit cell. (b) Base of HCP unit cell. (c) Triangle ABC removed from base of unit cell.

- b. From Fig. EP3.3a,

$$\begin{aligned} \text{Volume of the "large" zinc HCP cell} &= 3(\text{volume of the unit cell or primitive cell}) \\ &= 3(0.0304) = 0.0913 \text{ nm}^3 \end{aligned}$$

HCP Crystal Structure (Cont..)

- ◆ Each atom has six $1/6$ atoms at each of top and bottom layer, two half atoms at top and bottom layer and 3 full atoms at the middle layer.

- ◆ Therefore each HCP unit cell has $(2 \times 6 \times 1/6) + (2 \times 1/2) + 3 = 6$ atoms

◆ Examples:-

- Zinc ($a = 0.2665$ nm, $c/a = 1.85$)
- Cobalt ($a = 0.2507$ nm, $c/a = 1.62$)

- ◆ Ideal c/a ratio is 1.633.

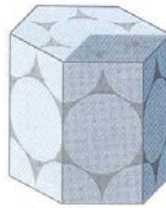
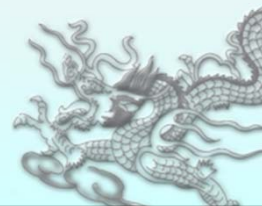
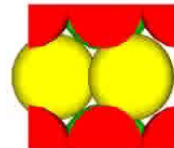


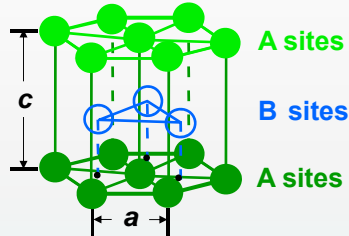
Figure 3.8 c



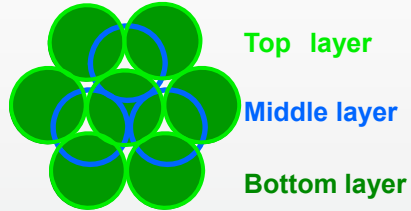
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence

- 3D Projection



- 2D Projection



- Coordination # = 12

6 atoms/unit cell

- APF = 0.74

ex: Cd, Mg, Ti, Zn

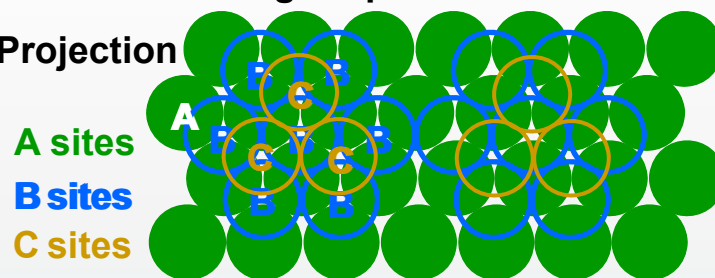
- $c/a = 1.633$

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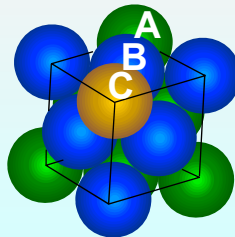
FCC Stacking Sequence

- ◆ ABCABC... Stacking Sequence

- ◆ 2D Projection

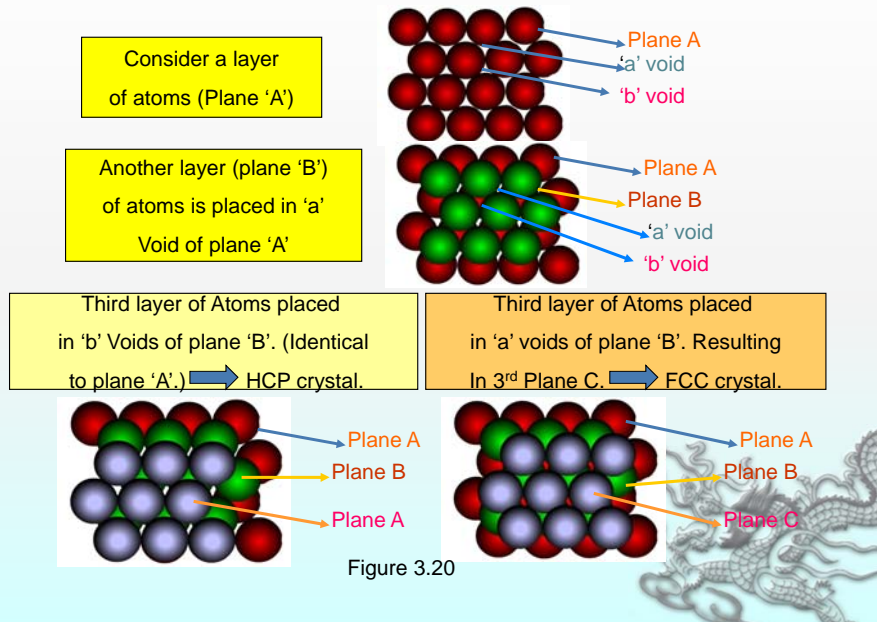


- ◆ FCC Unit Cell



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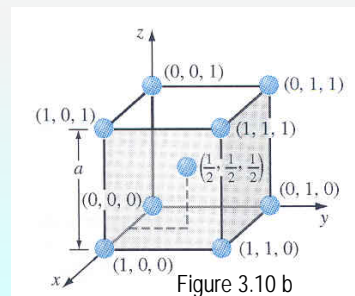
Structural Difference between HCP and FCC



Atom Positions in Cubic Unit Cells

- ◆ Cartesian coordinate system is use to locate atoms.
- ◆ In a cubic unit cell
 - y axis is the direction to the right.
 - x axis is the direction coming out of the paper.
 - z axis is the direction toward top.
 - Negative directions are to the opposite of positive directions.

- ◆ Atom positions are located using unit distances along the axes.



Directions in Cubic Unit Cells

- ◆ In cubic crystals, **Direction Indices** are vector components of directions resolved along each axes and reduced to smallest integers.
- ◆ Direction indices are **position coordinates** of unit cell where the direction vector emerges from cell surface, converted to integers.

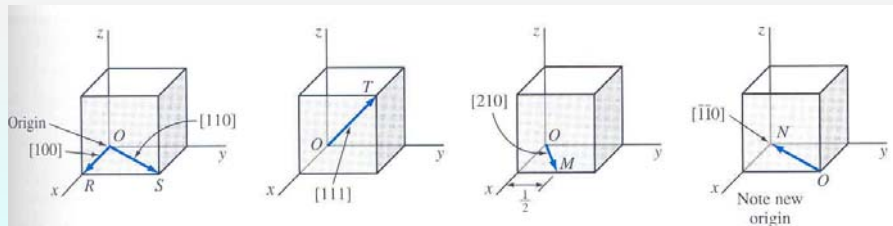


Figure 3.11

Example Problem 3.4

Draw the following direction vectors in cubic unit cells:

- [100] and [110]
- [112]
- $\bar{1}10$
- $\bar{3}2\bar{1}$

■ **Solution**

- The position coordinates for the [100] direction are (1, 0, 0) (Fig. EP3.4a). The position coordinates for the [110] direction are (1, 1, 0) (Fig. EP3.4a).
- The position coordinates for the [112] direction are obtained by dividing the direction indices by 2 so that they will lie within the unit cube. Thus, they are $(\frac{1}{2}, \frac{1}{2}, 1)$ (Fig. EP3.4b).
- The position coordinates for the $\bar{1}10$ direction are (-1, 1, 0) (Fig. EP3.4c). Note that the origin for the direction vector must be moved to the lower-left front corner of the cube.
- The position coordinates for the $\bar{3}2\bar{1}$ direction are obtained by first dividing all the indices by 3, the largest index. This gives $-1, \frac{2}{3}, -\frac{1}{3}$ for the position coordinates of the exit point of the direction $\bar{3}2\bar{1}$, which are shown in Fig. 3.4d.

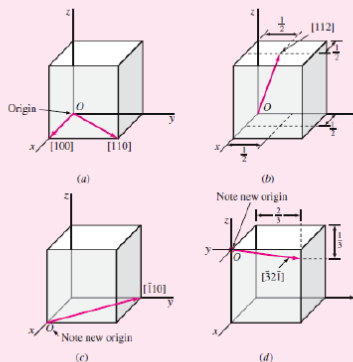


Figure EP3.4

Example Problem 3.5

Determine the direction indices of the cubic direction shown in Fig. EP3.5a.

■ **Solution**

Parallel directions have the same direction indices, and so we move the direction vector in a parallel manner until its tail reaches the nearest corner of the cube, still keeping the vector within the cube. Thus, in this case, the upper-left front corner becomes the new origin for the direction vector (Fig. EP3.5b). We can now determine the position coordinates where the direction vector leaves the unit cube. These are $x = -1$, $y = +1$, and $z = -\frac{1}{6}$. The position coordinates of the direction where it leaves the unit cube are thus $(-1, +1, -\frac{1}{6})$. The direction indices for this direction are, after clearing the fraction $6x$, $(-1, +1, -\frac{1}{6})$, or $[\bar{6}6\bar{1}]$.

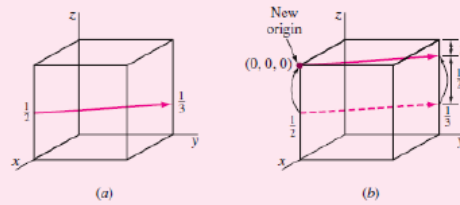


Figure EP3.5

Example Problem 3.6

IMC

Determine the direction indices of the cubic direction between the position coordinates $(\frac{3}{4}, 0, \frac{1}{4})$ and $(\frac{1}{4}, \frac{1}{2}, \frac{1}{2})$.

■ **Solution**

First we locate the origin and termination points of the direction vector in a unit cube, as shown in Fig. EP3.6. The fraction vector components for this direction are

$$\begin{aligned} x &= -(\frac{3}{4} - \frac{1}{4}) = -\frac{1}{2} \\ y &= (\frac{1}{2} - 0) = \frac{1}{2} \\ z &= (\frac{1}{2} - \frac{1}{4}) = \frac{1}{4} \end{aligned}$$

Thus, the vector direction has fractional vector components of $-\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$. The direction indices will be in the same ratio as their fractional components. By multiplying the fraction vector components by 4, we obtain $[\bar{2}21]$ for the direction indices of this vector direction.

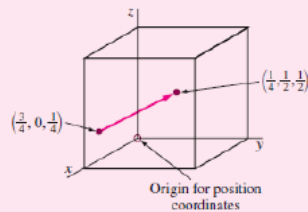
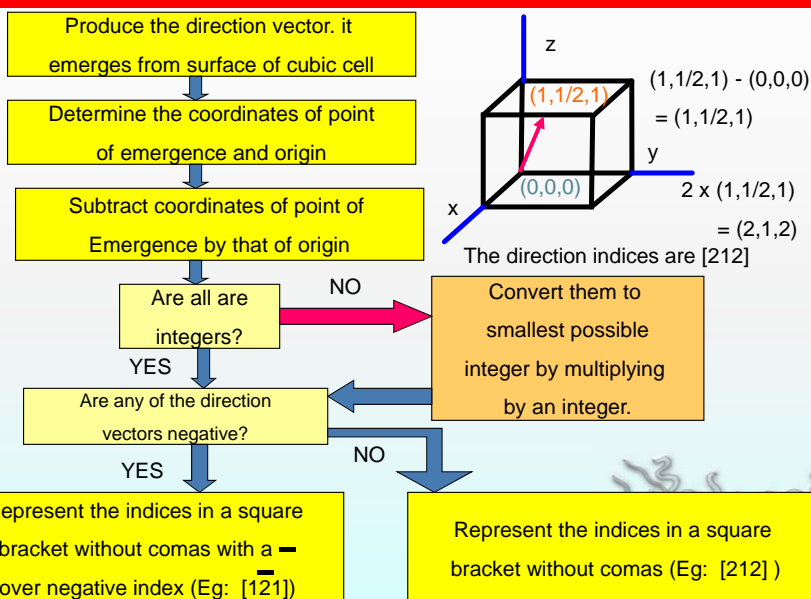


Figure EP3.6

Procedure to Find Direction Indices



3-17

Direction Indices - Example

- ◆ Determine **direction indices** of the given vector.
Origin coordinates are $(\frac{3}{4}, 0, \frac{1}{4})$.
Emergence coordinates are $(\frac{1}{4}, \frac{1}{2}, \frac{1}{2})$.

Subtracting origin coordinates from emergence coordinates,
 $(\frac{1}{4}, \frac{1}{2}, \frac{1}{2}) - (\frac{3}{4}, 0, \frac{1}{4})$
 $= (-\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$

Multiply by 4 to convert all fractions to integers
 $4 \times (-\frac{1}{2}, \frac{1}{2}, \frac{1}{4}) = (-2, 2, 1)$

Therefore, the direction indices are $[\bar{2} 2 1]$

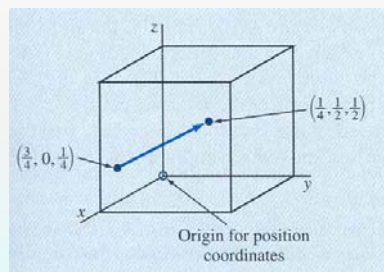
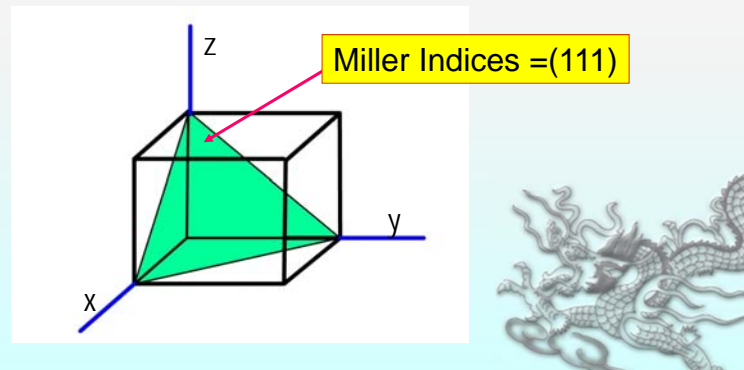


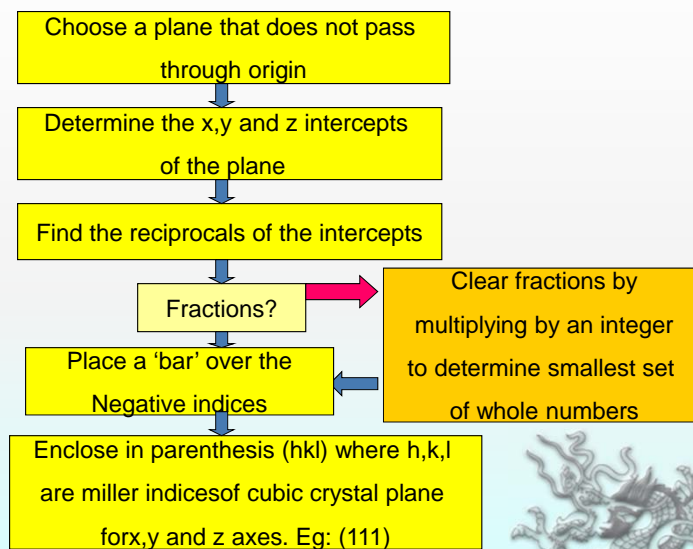
Figure EP3.6

Miller Indices

- ◆ Miller Indices are used to refer to specific lattice planes of atoms.
- ◆ They are reciprocals of the fractional intercepts (with fractions cleared) that the plane makes with the crystallographic x,y and z axes of three nonparallel edges of the cubic unit cell.



Miller Indices - Procedure



Miller Indices - Examples

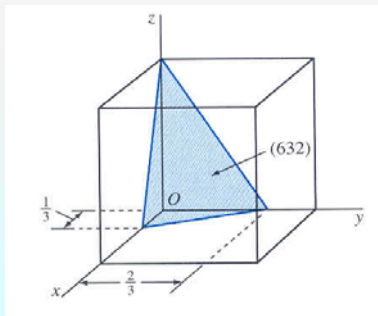
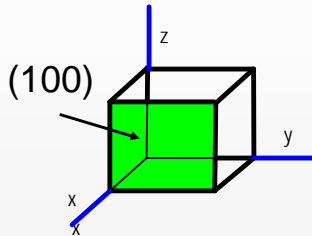


Figure 3.14

- ◆ Intercepts of the plane at x, y & z axes are 1, ∞ and ∞
- ◆ Taking reciprocals we get (1,0,0).
- ◆ Miller indices are (100).

- ◆ Intercepts are $1/3$, $2/3$ & 1.
- ◆ taking reciprocals we get (3, $3/2$, 1).
- ◆ Multiplying by 2 to clear fractions, we get (6,3,2).
- ◆ Miller indices are (632).

Miller Indices - Examples

- ◆ Plot the plane (101)
Taking reciprocals of the indices we get (1 ∞ 1).
 - ◆ The intercepts of the plane are $x=1$, $y= \infty$ (parallel to y) and $z=1$.
- *****
- ◆ Plot the plane (2 2 1)
Taking reciprocals of the indices we get ($1/2$ $1/2$ 1).
 - ◆ The intercepts of the plane are $x=1/2$, $y= 1/2$ and $z=1$.

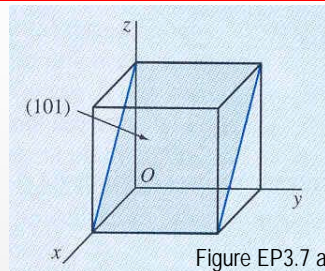


Figure EP3.7 a

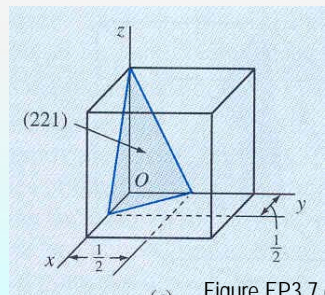
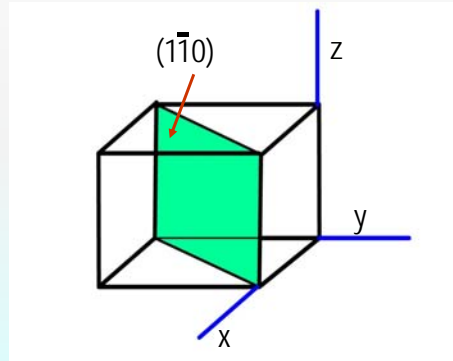


Figure EP3.7 c

Miller Indices - Example

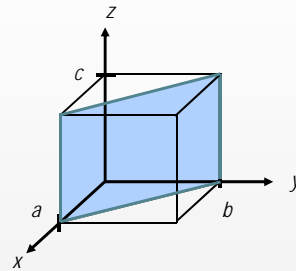
- ◆ Plot the plane $(1\bar{1}0)$
- The reciprocals are $(1, -1, \infty)$
- The intercepts are $x=1, y=-1$ and $z=\infty$ (parallel to z axis)

To show this plane a single unit cell, the origin is moved along the positive direction of y axis by 1 unit.

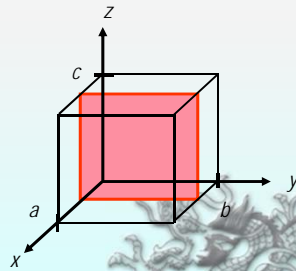


Crystallographic Planes

example	a	b	c
1. Intercepts	1	1	∞
2. Reciprocals	$1/1$	$1/1$	$1/\infty$
3. Reduction	1	1	0
4. Miller Indices	(110)		

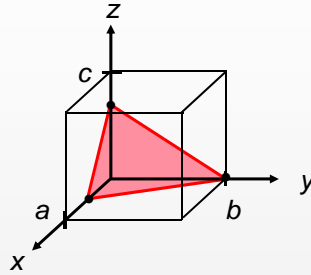


example	a	b	c
1. Intercepts	$1/2$	∞	∞
2. Reciprocals	$1/1/2$	$1/\infty$	$1/\infty$
3. Reduction	2	0	0
4. Miller Indices	(100)		



Crystallographic Planes

example	<i>a</i>	<i>b</i>	<i>c</i>
1. Intercepts	1/2	1	3/4
2. Reciprocals	1/1/2	1/1	1/3/4
3. Reduction	2	1	4/3
4. Miller Indices	(634)		



Other useful facts:

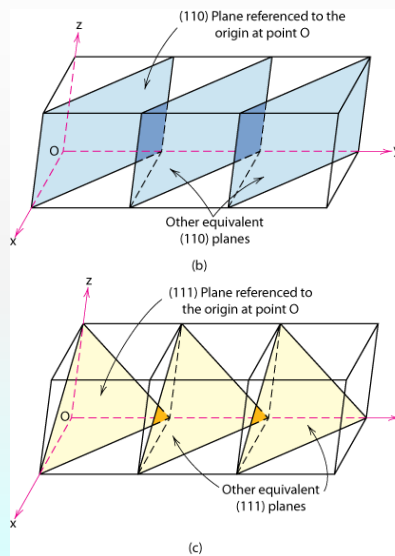
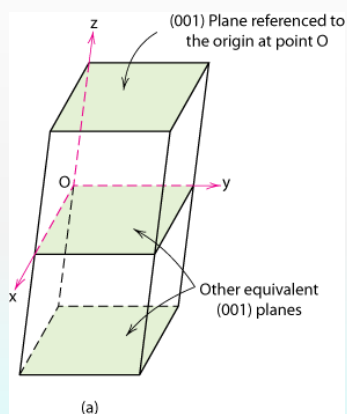
- Family of Planes $\{hkl\}$

Ex: $\{100\} = (100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$

- For cubic systems *only*: $[x\ y\ z]$ is normal to plane $(x\ y\ z)$

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Crystallographic Planes



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Example Problem 3.7

Draw the following crystallographic planes in cubic unit cells:

- a. (101) b. $(1\bar{1}0)$ c. (221)
- d. Draw a (110) plane in a BCC atomic-site unit cell, and list the position coordinates of the atoms whose centers are intersected by this plane.

■ **Solutions**

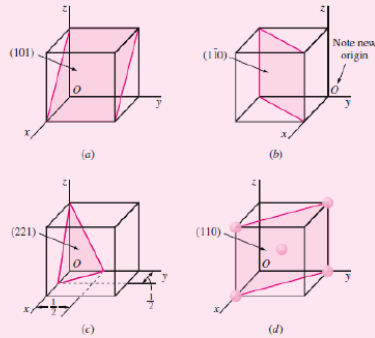


Figure EP3.7
Various important cubic crystal planes.

- a. First determine the reciprocals of the Miller indices of the (101) plane. These are $1, \infty, 1$. The (101) plane must pass through a unit cube at intercepts $x = 1$ and $z = 1$ and be parallel to the y axis (Fig. EP3.7a).
- b. First determine the reciprocals of the Miller indices of the $(1\bar{1}0)$ plane. These are $1, -1, \infty$. The $(1\bar{1}0)$ plane must pass through a unit cube at intercepts $x = 1$ and $y = -1$ and be parallel to the z axis. Note that the origin of axes must be moved to the lower-right back side of the cube (Fig. EP3.7b).
- c. First determine the reciprocals of the Miller indices of the (221) plane. These are $\frac{1}{2}, \frac{1}{2}, 1$. The (221) plane must pass through a unit cube at intercepts $x = \frac{1}{2}$, $y = \frac{1}{2}$, and $z = 1$ (Fig. EP3.7c).

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Example Problem 3.8

Determine the Miller indices of the cubic crystallographic plane shown in Fig. EP3.8a.

■ **Solution**

First, transpose the plane parallel to the z axis $\frac{1}{4}$ unit to the right along the y axis as shown in Fig. EP3.8b so that the plane intersects the x axis at a unit distance from the new origin

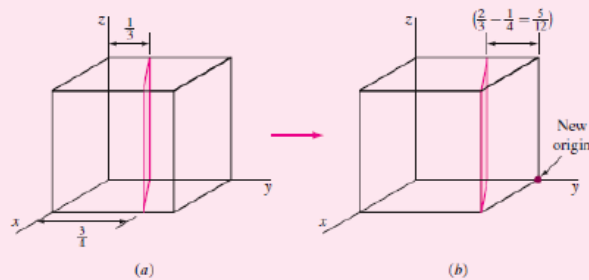


Figure EP3.8

located at the lower-right back corner of the cube. The new intercepts of the transposed plane with the coordinate axes are now $(+1, -\frac{5}{12}, \infty)$. Next, we take the reciprocals of these intercepts to give $(1, -\frac{12}{5}, 0)$. Finally, we clear the $\frac{12}{5}$ fraction to obtain $(5\bar{1}20)$ for the Miller indices of this plane.

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Example Problem 3.9

Determine the Miller indices of the cubic crystal plane that intersects the position coordinates $(1, \frac{1}{2}, 0)$, $(1, 1, \frac{1}{2})$, $(\frac{3}{4}, 1, \frac{1}{4})$, and all coordinate axes.

■ Solution

First, we locate the three position coordinates as indicated in Fig. EP3.9 at A , B , and C . Next, we join A and B , extend AB to D , and then join A and C . Finally, we join A to C to complete plane ACD . The origin for this plane in the cube can be chosen at E , which gives axial intercepts for plane ACD at $x = -\frac{1}{2}$, $y = -\frac{3}{4}$, and $z = \frac{1}{2}$. The reciprocals of these axial intercepts are -2 , $-\frac{4}{3}$, and 2 . Multiplying these intercepts by 3 clears the fraction, giving Miller indices for the plane of $(\bar{6}\bar{4}6)$.

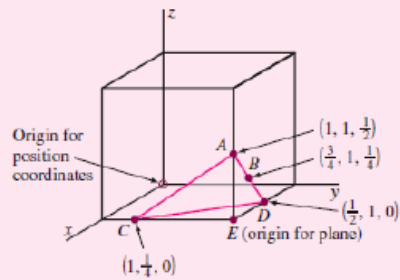


Figure EP3.9

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Miller Indices – Important Relationship

- ◆ Direction indices of a direction perpendicular to a crystal plane are same as miller indices of the plane.

- ◆ Example:-

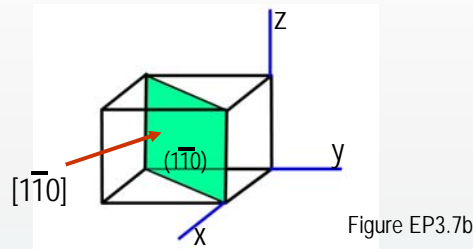


Figure EP3.7b

- ◆ Interplanar spacing between parallel closest planes with same miller indices is given by

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

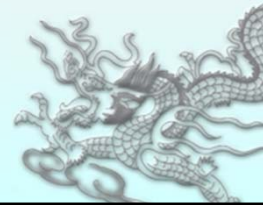
Example Problem 3.10

Copper has an FCC crystal structure and a unit cell with a lattice constant of 0.361 nm. What is its interplanar spacing d_{220} ?

■ **Solution**

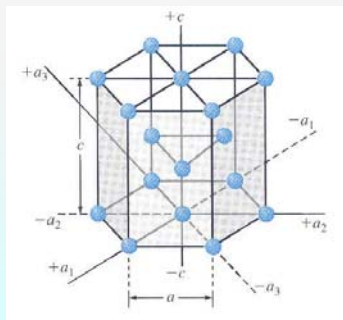
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{0.361 \text{ nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.128 \text{ nm} \blacktriangleleft$$

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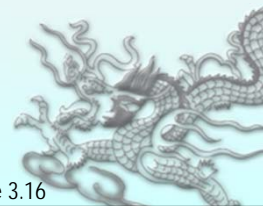
Planes and Directions in Hexagonal Unit Cells

- ◆ Four indices are used (hkil) called as *Miller-Bravais* indices.
- ◆ Four axes are used (a_1 , a_2 , a_3 and c).
- ◆ Reciprocal of the intercepts that a crystal plane makes with the a_1 , a_2 , a_3 and c axes give the h, k, l and i indices respectively.



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Figure 3.16



Hexagonal Unit Cell - Examples

◆ **Basal Planes:-**

Intercepts $a_1 = \infty$
 $a_2 = \infty$
 $a_3 = \infty$
 $c = 1$
 $(hkli) = (0001)$

◆ **Prism Planes :-**

For plane ABCD,
 Intercepts $a_1 = 1$
 $a_2 = \infty$
 $a_3 = -1$
 $c = \infty$
 $(hkli) = (10\bar{1}0)$

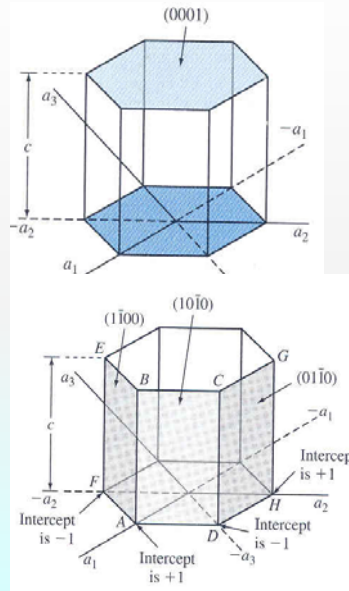


Figure 3.12 a&b

Directions in HCP Unit Cells

- ◆ Indicated by 4 indices [uvtw].
- ◆ u,v,t and w are lattice vectors in a_1 , a_2 , a_3 and c directions respectively.
- ◆ **Example:-**

For a_1 , a_2 , a_3 directions, the direction indices are $[2\bar{1}\bar{1}0]$, $[\bar{1}2\bar{1}0]$ and $[\bar{1}\bar{1}20]$ respectively.

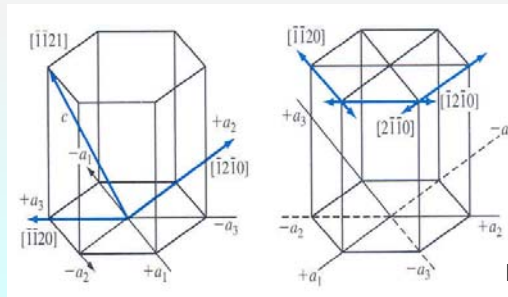
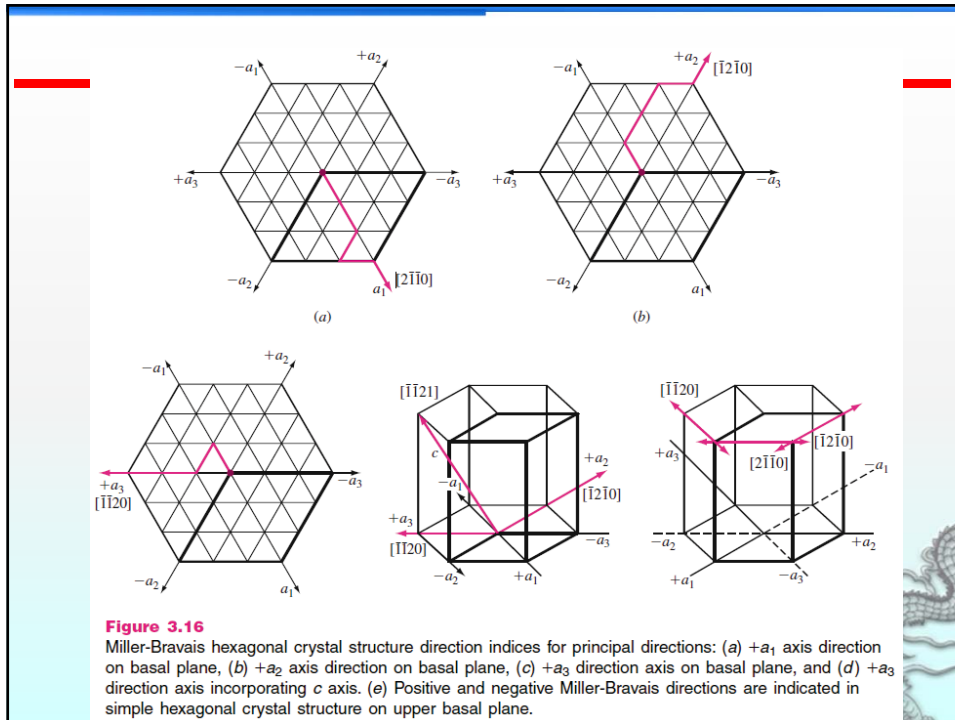
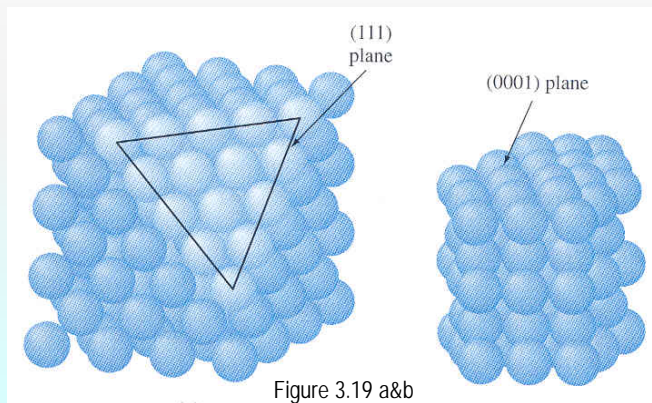


Figure 3.18 d&e



Comparison of FCC and HCP crystals

- ◆ Both FCC and HCP are close packed and have APF 0.74.
- ◆ FCC crystal is close packed in (111) plane while HCP is close packed in (0001) plane.



After W.G. Moffatt, E.W. Pearsall, & J. Wulff, "The Structure and Properties of Materials," vol. I: "Structure," Wiley, 1964, p.51.

Volume Density

◆ Volume density of metal = $\rho_v = \frac{\text{Mass/Unit cell}}{\text{Volume/Unit cell}}$

◆ Example:- Copper (FCC) has atomic mass of 63.54 g/mol and atomic radius of 0.1278 nm.

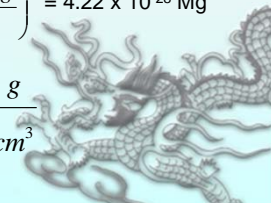
$$a = \frac{4R}{\sqrt{2}} = \frac{4 \times 0.1278 \text{ nm}}{\sqrt{2}} = 0.361 \text{ nm}$$

$$\text{Volume of unit cell} = V = a^3 = (0.361 \text{ nm})^3 = 4.7 \times 10^{-29} \text{ m}^3$$

FCC unit cell has 4 atoms.

$$\text{Mass of unit cell} = m = \frac{(4 \text{ atoms})(63.54 \text{ g/mol})}{4.7 \times 10^{23} \text{ atoms/mol}} \left(\frac{10^{-6} \text{ Mg}}{\text{g}} \right) = 4.22 \times 10^{-28} \text{ Mg}$$

$$\rho_v = \frac{m}{V} = \frac{4.22 \times 10^{-28} \text{ Mg}}{4.7 \times 10^{-29} \text{ m}^3} = 8.98 \frac{\text{Mg}}{\text{m}^3} = 8.98 \frac{\text{g}}{\text{cm}^3}$$



Planar Atomic Density

◆ Planar atomic density = $\rho_p = \frac{\text{Equivalent number of atoms whose centers are intersected by selected area}}{\text{Selected area}}$

◆ Example:- In Iron (BCC, a=0.287), The (110) plane intersects center of 5 atoms (Four 1/4 and 1 full atom).

◆ Equivalent number of atoms = $(4 \times 1/4) + 1 = 2$ atoms
 Area of 110 plane = $\sqrt{2}a \times a = \sqrt{2}a^2$

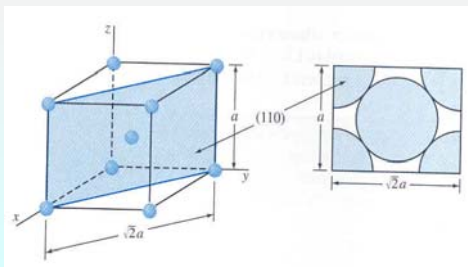
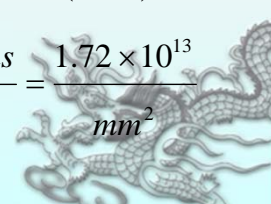


Figure 3.22 a&b

$$\rho_p = \frac{2}{\sqrt{2}(0.287)^2}$$

$$= \frac{17.2 \text{ atoms}}{\text{nm}^2} = 1.72 \times 10^{13} \frac{\text{atoms}}{\text{nm}^2}$$



Calculate the planar atomic density ρ_p on the (110) plane of the α iron BCC lattice in atoms per square millimeter. The lattice constant of α iron is 0.287 nm.

■ **Solution**

$$\rho_p = \frac{\text{equiv. no. of atoms whose centers are intersected by selected area}}{\text{selected area}} \quad (3.6)$$

The equivalent number of atoms intersected by the (110) plane in terms of the surface area inside the BCC unit cell is shown in Fig. 3.22 and is

$$1 \text{ atom at center} + 4 \times \frac{1}{4} \text{ atoms at four corners of plane} = 2 \text{ atoms}$$

The area intersected by the (110) plane inside the unit cell (selected area) is

$$(\sqrt{2}a)(a) = \sqrt{2}a^2$$

Thus, the planar atomic density is

$$\begin{aligned} \rho_p &= \frac{2 \text{ atoms}}{\sqrt{2}(0.287 \text{ nm})^2} = \frac{17.2 \text{ atoms}}{\text{nm}^2} \\ &= \frac{17.2 \text{ atoms}}{\text{nm}^2} \times \frac{10^{12} \text{ nm}^2}{\text{mm}^2} \\ &= 1.72 \times 10^{13} \text{ atoms/mm}^2 \quad \blacktriangleleft \end{aligned}$$

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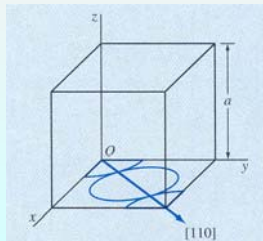
Linear Atomic Density

Number of atomic diameters
intersected by selected length
of line in direction of interest
Selected length of line

◆ **Linear atomic density** = $\rho_l = \frac{\text{Number of atomic diameters intersected by selected length of line in direction of interest}}{\text{Selected length of line}}$

◆ **Example:-** For a FCC copper crystal ($a=0.361$), the [110] direction intersects 2 half diameters and 1 full diameter.

◆ Therefore, it intersects $\frac{1}{2} + \frac{1}{2} + 1 = 2$ atomic diameters.



$$\text{Length of line} = \sqrt{2} \times 0.361 \text{ nm}$$

$$\rho_l = \frac{2 \text{ atoms}}{\sqrt{2} \times 0.361 \text{ nm}} = \frac{3.92 \text{ atoms}}{\text{nm}} = \frac{3.92 \times 10^6 \text{ atoms}}{\text{mm}}$$

Figure 3.23

Example Problem 3.13

Calculate the linear atomic density ρ_l in the [110] direction in the copper crystal lattice in atoms per millimeter. Copper is FCC and has a lattice constant of 0.361 nm.

■ Solution

The atoms whose centers the [110] direction intersects are shown in Fig. EP3.13. We shall select the length of the line to be the length of the face diagonal of the FCC unit cell, which is $\sqrt{2}a$. The number of atomic diameters intersected by this length of line are $\frac{1}{2} + 1 + \frac{1}{2} = 2$ atoms. Thus using Eq. 3.7, the linear atomic density is

$$\begin{aligned}\rho_l &= \frac{2 \text{ atoms}}{\sqrt{2}a} = \frac{2 \text{ atoms}}{\sqrt{2}(0.361 \text{ nm})} = \frac{3.92 \text{ atoms}}{\text{nm}} \\ &= \frac{3.92 \text{ atoms}}{\text{nm}} \times \frac{10^6 \text{ nm}}{\text{mm}} \\ &= 3.92 \times 10^6 \text{ atoms/mm} \leftarrow\end{aligned}$$

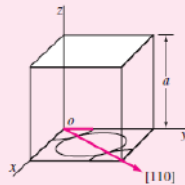
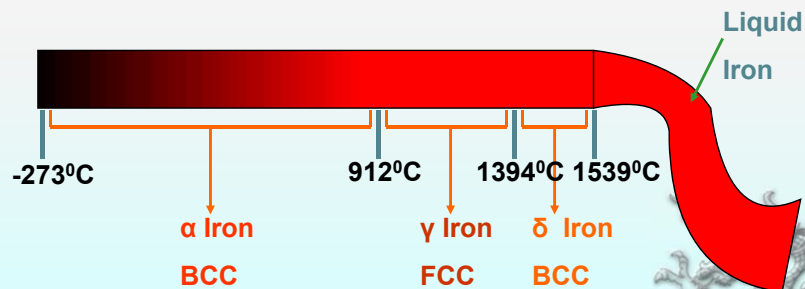


Figure EP3.13
Diagram for calculating the atomic linear density in the [110] direction in an FCC unit cell.

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Polymorphism or Allotropy

- ◆ Metals exist in more than one crystalline form. This is called a polymorphism or an allotropy.
- ◆ Temperature and pressure leads to change in crystalline forms.
- ◆ Example:- Iron exists in both BCC and FCC forms depending on the temperature.



Example Problem 3.14

Calculate the theoretical volume change accompanying a polymorphic transformation in a pure metal from the FCC to BCC crystal structure. Assume the hard-sphere atomic model and that there is no change in atomic volume before and after the transformation.

■ Solution

In the FCC crystal structure unit cell, the atoms are in contact along the face diagonal of the unit cell, as shown in Fig. 3.7. Hence,

$$\sqrt{2}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{2}} \quad (3.3)$$

In the BCC crystal structure unit cell, the atoms are in contact along the body diagonal of the unit cell as shown in Fig. 3.5. Hence,

$$\sqrt{3}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{3}} \quad (3.1)$$

The volume per atom for the FCC crystal lattice, since it has four atoms per unit cell, is

$$V_{\text{FCC}} = \frac{a^3}{4} = \left(\frac{4R}{\sqrt{2}}\right)^3 \left(\frac{1}{4}\right) = 5.66R^3$$

The volume per atom for the BCC crystal lattice, since it has two atoms per unit cell, is

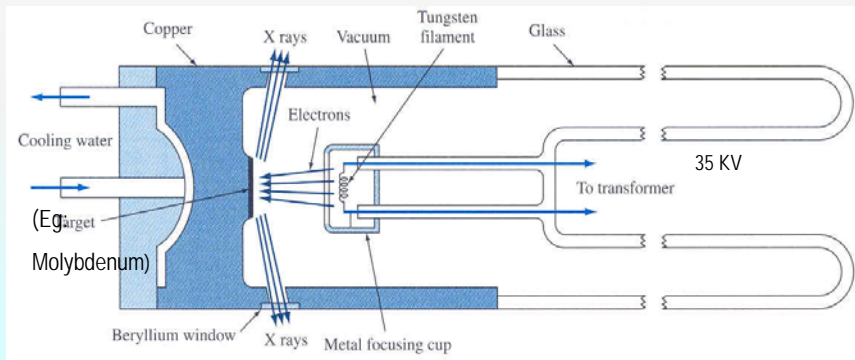
$$V_{\text{BCC}} = \frac{a^3}{2} = \left(\frac{4R}{\sqrt{3}}\right)^3 \left(\frac{1}{2}\right) = 6.16R^3$$

The change in volume associated with the transformation from the FCC to BCC crystal structure, assuming no change in atomic radius, is

$$\frac{\Delta V}{V_{\text{FCC}}} = \frac{V_{\text{BCC}} - V_{\text{FCC}}}{V_{\text{FCC}}} = \frac{(6.16R^3 - 5.66R^3)}{5.66R^3} 100\% = +8.8\% \blacktriangleleft$$

Crystal Structure Analysis

- ◆ Information about crystal structure are obtained using X-Rays.
- ◆ The X-rays used are about the same wavelength (0.05-0.25 nm) as distance between crystal lattice planes.



After B.D. Cullity, "Elements of X-Ray Diffraction," 2d ed., Addison-Wesley, 1978, p.23.

Figure 3.25

X-Ray Spectrum of Molybdenum

- ◆ X-Ray spectrum of Molybdenum is obtained when Molybdenum is used as **target metal**.
- ◆ $K\alpha$ and $K\beta$ are characteristic of an element.
- ◆ For Molybdenum $K\alpha$ occurs at wave length of about 0.07nm.
- ◆ Electrons of $n=1$ shell of target metal are knocked out by bombarding electrons.
- ◆ Electrons of higher level drop down by **releasing energy** to replace lost electrons

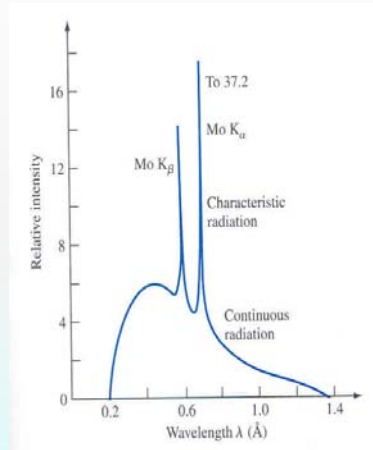
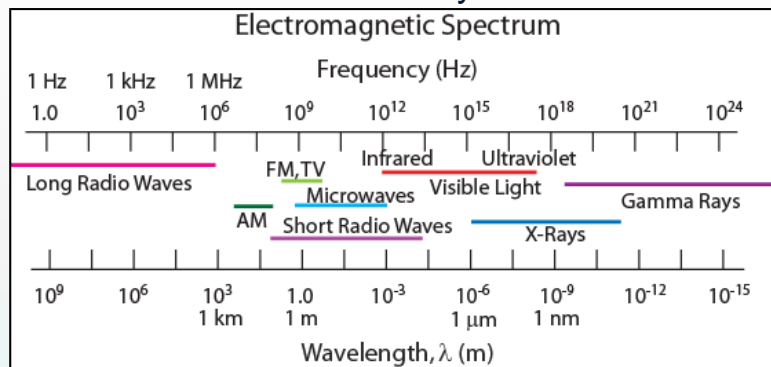


Figure 3.26

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X-Ray Diffraction

How do we **know** what the crystal structures are?



- ◆ Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- ◆ Can't resolve spacings $< \lambda$
- ◆ Spacing is the distance between parallel planes of atoms.

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X-Ray Diffraction

- ◆ Crystal planes of target metal act as **mirrors** reflecting X-ray beam.
- ◆ If rays leaving a set of planes are **out of phase** (as in case of arbitrary angle of incidence) no reinforced beam is produced.
- ◆ If rays leaving are in phase, reinforced beams are produced.

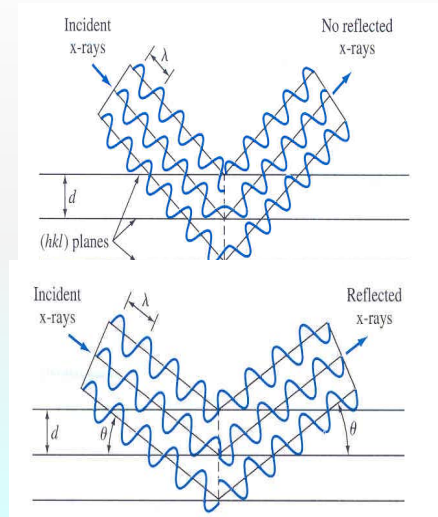
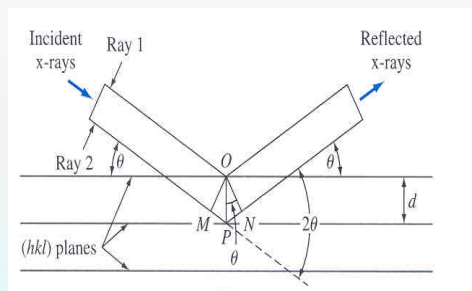


Figure 3.28

After A.G. Gbý and J.J. Hren, "Elements of Physical Metallurgy," 3d ed., Addison-Wesley, 1974, p.201.)

X-Ray Diffraction (Cont..)

- ◆ For rays reflected from different planes to be in phase, the extra distance traveled by a ray should be an integral multiple of wave length λ .



$$n\lambda = MP + PN \quad (n = 1, 2, \dots)$$

n is order of diffraction

If d_{hkl} is interplanar distance,

$$\text{Then } MP = PN = d_{hkl} \cdot \sin\theta$$

Therefore, $\lambda = 2 d_{hkl} \cdot \sin\theta$

Example Problem 3.15

A sample of BCC iron was placed in an X-ray diffractometer using incoming X-rays with a wavelength $\lambda = 0.1541$ nm. Diffraction from the {110} planes was obtained at $2\theta = 44.704^\circ$. Calculate a value for the lattice constant a of BCC iron. (Assume first-order diffraction with $n = 1$.)

■ Solution

$$2\theta = 44.704^\circ \quad \theta = 22.35^\circ$$
$$\lambda = 2d_{hkl} \sin \theta \quad (3.10)$$

$$d_{110} = \frac{\lambda}{2 \sin \theta} = \frac{0.1541 \text{ nm}}{2(\sin 22.35^\circ)}$$
$$= \frac{0.1541 \text{ nm}}{2(0.3803)} = 0.2026 \text{ nm}$$

Rearranging Eq. 3.4 gives

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

Thus,

$$a(\text{Fe}) = d_{110} \sqrt{1^2 + 1^2 + 0^2}$$
$$= (0.2026 \text{ nm})(1.414) = 0.287 \text{ nm} \blacktriangleleft$$

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Structure factor

- ◆ For BCC structure, diffraction occurs only on planes whose miller indices when added together total to an even number.

I.e. $(h+k+l) = \text{even}$ \longrightarrow Reflections present

$(h+k+l) = \text{odd}$ \longrightarrow Reflections absent

- ◆ For FCC structure, diffraction occurs only on planes whose miller indices are either all even or all odd.

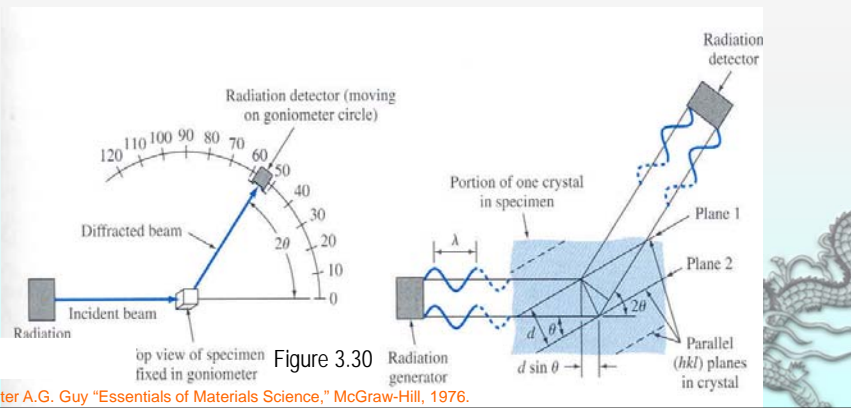
I.e. (h,k,l) all even or odd \longrightarrow Reflections present

(h,k,l) not all even or all odd \longrightarrow Reflections absent.

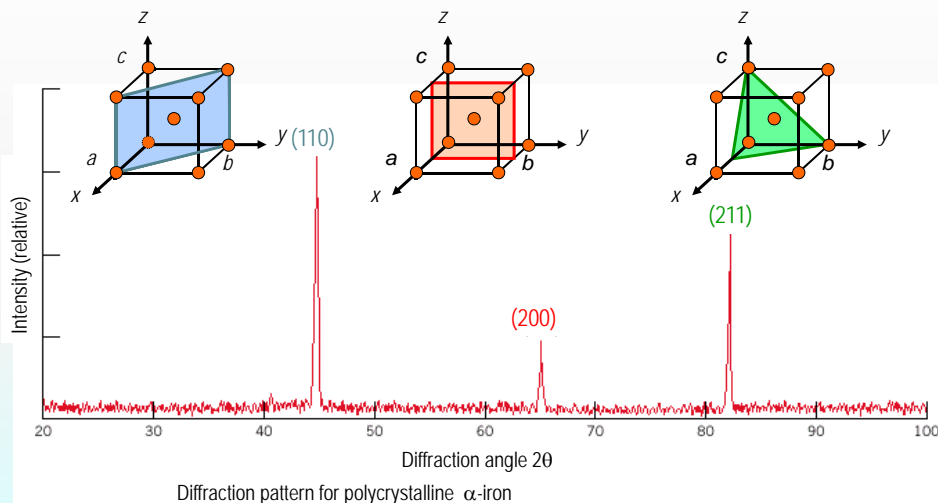
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X-Ray Diffraction Analysis

- ◆ **Powdered specimen** is used for X-ray diffraction analysis as the random orientation facilitates different angle of incidence.
- ◆ Radiation counter detects angle and intensity of diffracted beam.



X-Ray Diffraction Pattern



Adapted from Fig. 3.20, Callister 5e.

Interpreting Diffraction Data

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

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

Substituting for d, $\lambda = \frac{2a \sin \theta}{\sqrt{h^2 + k^2 + l^2}}$

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

**Note that the wavelength λ and lattice constant a are the same
For both incoming and outgoing radiation.**

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Interpreting Diffraction Data (Cont..)

- ◆ **For planes 'A' and 'B' we get two equations**

$$\sin^2 \theta_A = \frac{\lambda^2 (h_A^2 + k_A^2 + l_A^2)}{4a^2} \quad (\text{For plane 'A'})$$

$$\sin^2 \theta_B = \frac{\lambda^2 (h_B^2 + k_B^2 + l_B^2)}{4a^2} \quad (\text{For plane 'B'})$$

Dividing each other, we get

$$\frac{\sin^2 \theta_A}{\sin^2 \theta_B} = \frac{(h_A^2 + k_A^2 + l_A^2)}{(h_B^2 + k_B^2 + l_B^2)}$$

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Interpreting Experimental Data

- ◆ For BCC crystals, the first two sets of diffracting planes are **{110}** and **{200}** planes.

Therefore

$$\frac{\sin^2 \theta_A}{\sin^2 \theta_B} = \frac{(1^2 + 1^2 + 0^2)}{(2^2 + 0^2 + 0^2)} = 0.5$$

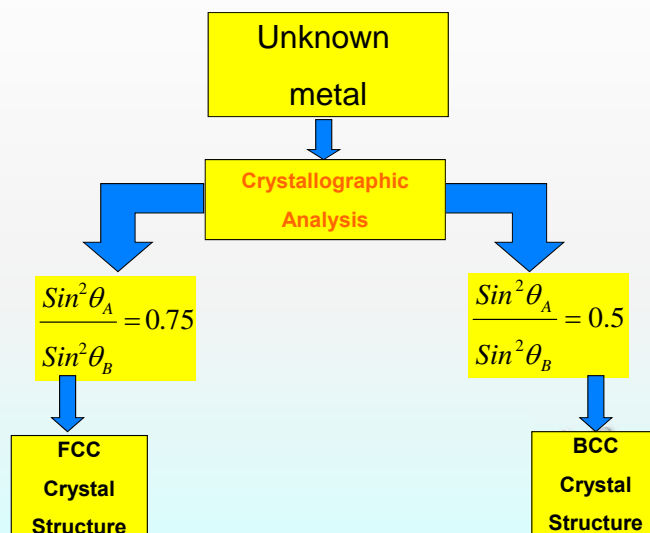
- ◆ For FCC crystals the first two sets of diffracting planes are **{111}** and **{200}** planes

Therefore

$$\frac{\sin^2 \theta_A}{\sin^2 \theta_B} = \frac{(1^2 + 1^2 + 1^2)}{(2^2 + 0^2 + 0^2)} = 0.75$$

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Crystal Structure of Unknown Metal



Example Problem 3.16

An X-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure shows diffraction peaks at the following 2θ angles: 40, 58, 73, 86.8, 100.4, and 114.7. The wavelength of the incoming X-ray used was 0.154 nm.

- a. Determine the cubic structure of the element.
- b. Determine the lattice constant of the element.
- c. Identify the element.

■ **Solution**

a. *Determination of the crystal structure of the element.* First, the $\sin^2 \theta$ values are calculated from the 2θ diffraction angles.

2θ (deg)	θ (deg)	$\sin \theta$	$\sin^2 \theta$
40	20	0.3420	0.1170
58	29	0.4848	0.2350
73	36.5	0.5948	0.3538
86.8	43.4	0.6871	0.4721
100.4	50.2	0.7683	0.5903
114.7	57.35	0.8420	0.7090

Next, the ratio of the $\sin^2 \theta$ values of the first and second angles is calculated:

$$\frac{\sin^2 \theta}{\sin^2 \theta} = \frac{0.117}{0.235} = 0.498 \approx 0.5$$

The crystal structure is BCC since this ratio is ≈ 0.5 . If the ratio had been ≈ 0.75 , the structure would have been FCC.

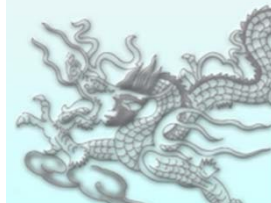
b. *Determination of the lattice constant.* Rearranging Eq. 3.12 and solving for a^2 gives

$$a^2 = \frac{\lambda^2 h^2 + k^2 + l^2}{4 \sin^2 \theta} \tag{3.16}$$

or

$$a = \frac{\lambda}{2} \sqrt{\frac{h^2 + k^2 + l^2}{\sin^2 \theta}} \tag{3.17}$$

Substituting into Eq. 3.17 $h = 1, k = 1, l = 0$ for the h, k, l Miller indices of the first set of principal diffracting planes for the BCC crystal structure, which are the {110} planes, the corresponding value for $\sin^2 \theta$, which is 0.117, and 0.154 nm for λ , the incoming radiation, gives



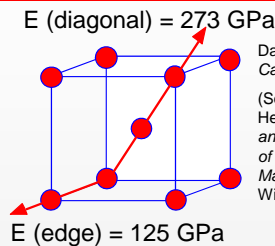
Single vs Polycrystals

- Single Crystals

-Properties vary with

direction: **anisotropic**.
-Example: the modulus

of elasticity (E) in BCC iron:



Data from Table 3.3, Callister 7e.
(Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

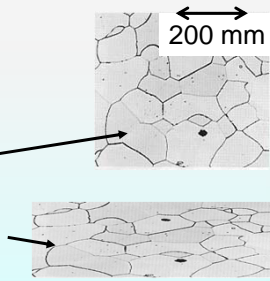
- Polycrystals

-Properties may/may not vary with direction.

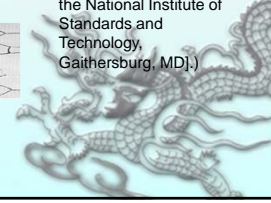
-If grains are randomly oriented: **isotropic**.

($E_{\text{poly iron}} = 210 \text{ GPa}$)

-If grains are **textured**, anisotropic.



Adapted from Fig. 4.14(b), Callister 7e.
(Fig. 4.14(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)



Amorphous Materials

- ◆ Random spatial positions of atoms
- ◆ Polymers: Secondary bonds do not allow formation of parallel and tightly packed chains during solidification.
 - Polymers can be semicrystalline.
- ◆ Rapid cooling of metals (10^8 K/s) can give rise to amorphous structure (metallic glass).

