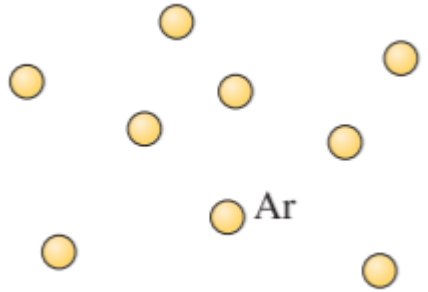
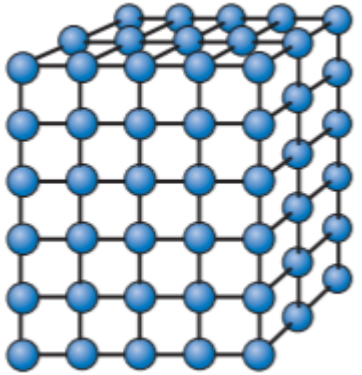
CHAPTER 3

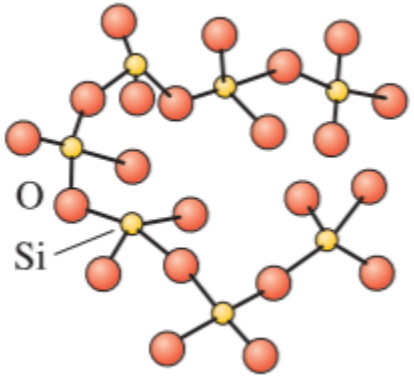
Atomic and Ionic arrangements

Atomic and Ionic arrangements



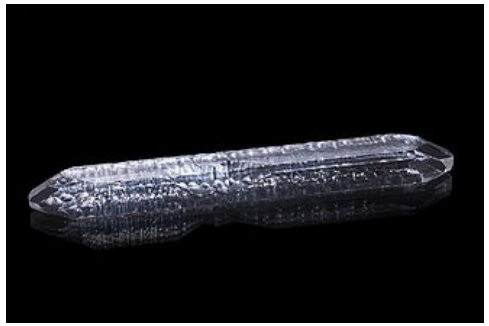
- No Order: Monoatomic gases (Noble gases)
- Amorphous: Short range order. Kinetics of the process by which the material was made did not allow for the formation of periodic arrangements.
- Crystalline: Long-range order. Atoms are situated in a repeating or periodic array over large atomic distances

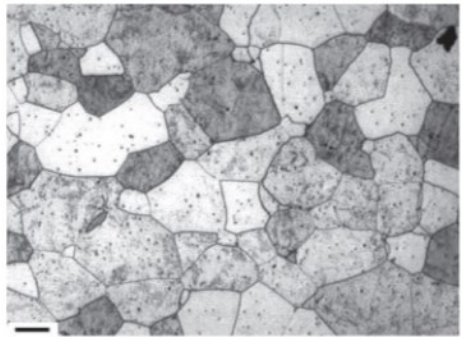


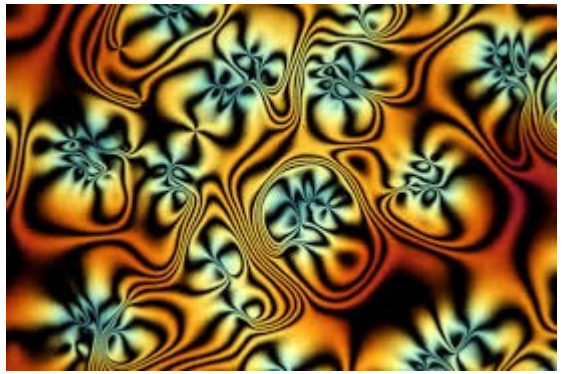


Crystalline Materials

- **Single crystal:** One large crystal (optoelectronics). Absence of defects
- **Polycrystal:** Union of various small crystals (grains). Boundaries between grains are important.
- **Liquids crystals:** Polymers that due to external stimulus go from "normal" liquids to organized liquids.

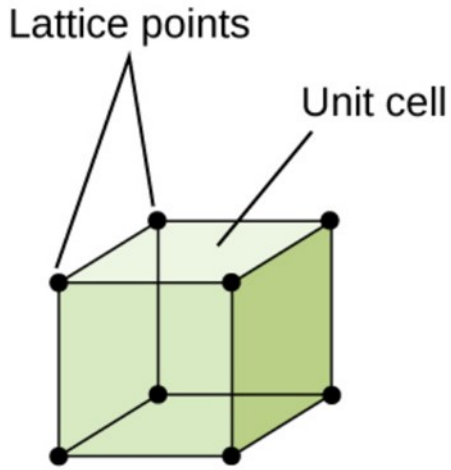




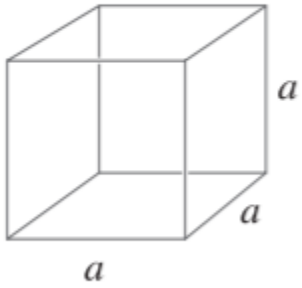


Crystalline structure

- **Lattice:** Collection of points in a periodic patter where, where the surrounding of each point is identical.
- **Basis:** Repetition of a lattice point.
- **Unit cell:** A repetitive pattern of a small groups of atoms form. Simplest and smallest repeating unit in a crystal.

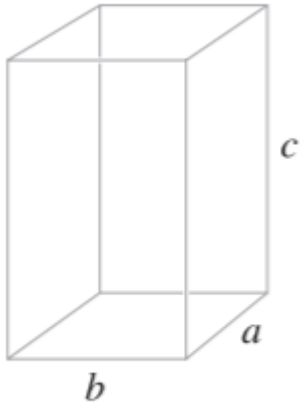


Crystal Systems



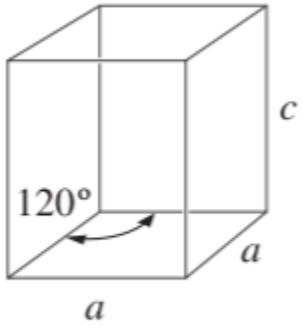
Cubic

$$\alpha = \beta = \gamma = 90°$$
$$V = a^3$$



Orthorhombic

$$a \neq b \neq c$$
$$\alpha = \beta = \gamma = 90°$$
$$V = abc$$

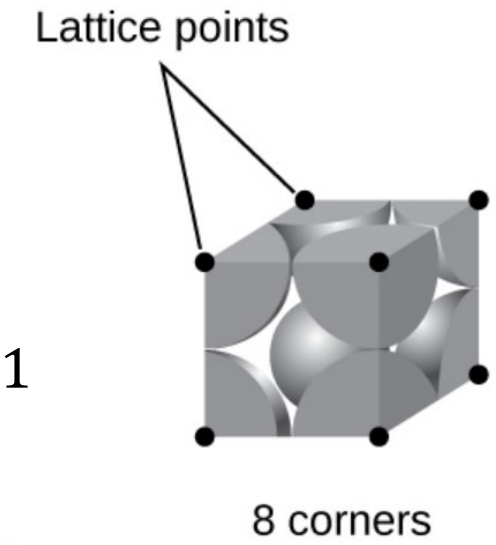


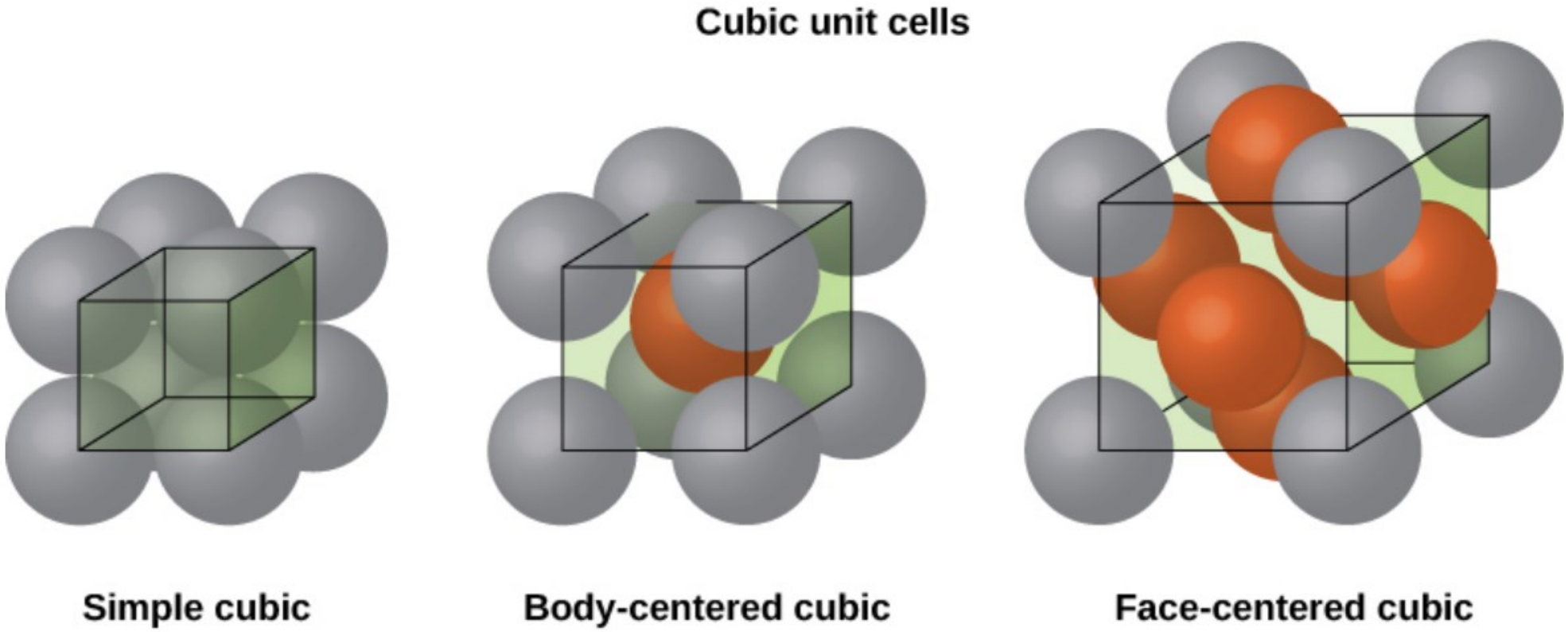
Hexagonal

$$a = b \neq c$$
$$\alpha = 120°$$
$$\beta = 60°$$
$$\gamma = 90°$$
$$V = a^2c$$

Number of lattices per cube

$$\frac{lattice\ points}{unit\ cell} = (\#\ of\ corners) \times \frac{1}{8} + (\#\ of\ faces) \times \frac{1}{2} + (\#\ of\ bodies) \times 1$$





Problem

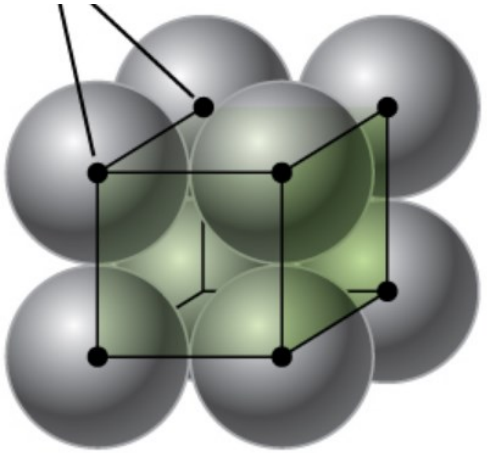
- Calculate the number of lattice points per cubic unit cell:

Simple cubic (SC)

Body centered cubic (BCC)

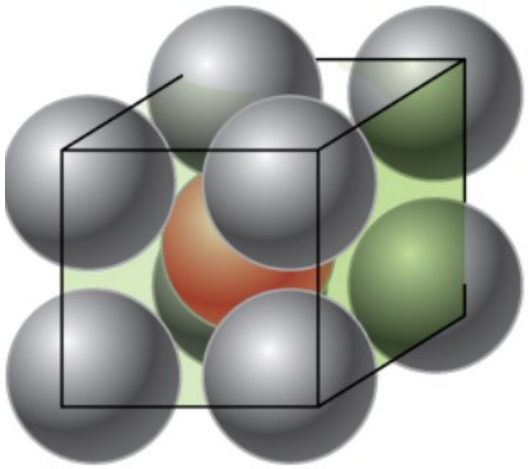
Face centered cubic (FCC)

Number of lattice points: SC



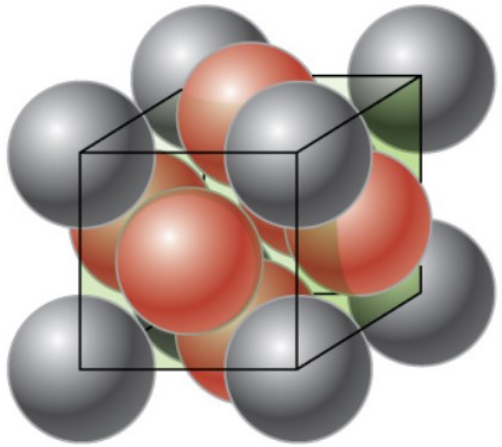
$$\frac{lattice\ points}{unit\ cell} = (\#\ of\ corners) \times \frac{1}{8} + (\#\ of\ faces) \times \frac{1}{2} + (\#\ of\ bodies) \times 1$$

Number of lattice points: BCC



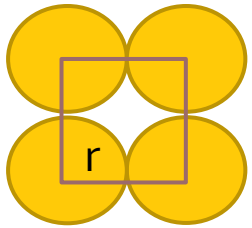
$$\frac{lattice\ points}{unit\ cell} = (\#\ of\ corners) \times \frac{1}{8} + (\#\ of\ faces) \times \frac{1}{2} + (\#\ of\ bodies) \times 1$$

Number of lattice points: FCC



$$\frac{lattice\ points}{unit\ cell} = (\#\ of\ corners) \times \frac{1}{8} + (\#\ of\ faces) \times \frac{1}{2} + (\#\ of\ bodies) \times 1$$

Atomic radius and lattice parameter

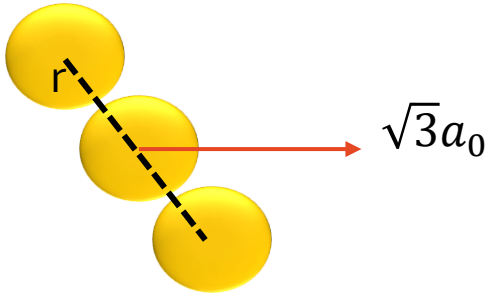


a_0

$a_0 = 2r$

SC

3D

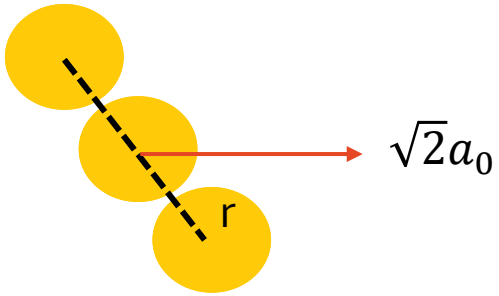


a_0

$a_0 = \frac{4r}{\sqrt{3}}$

BCC

2D



a_0

$a_0 = \frac{4r}{\sqrt{2}}$

FCC

Example

Calculate the radius of aluminum (Al) and iron (Fe)

radius of aluminum (Al)

Table 3-2 Askeland
Table 3.1 Callister
eClass

radius of iron (Fe)

Coordination number and packing factor

- **Coordination number:** number of nearest-neighbor or touching atoms.
- **Packing factor**: fraction of volume occupied by atoms in a unit cell.

$$PF = \frac{\left(\#\frac{atoms}{unit\ cell}\right)(volume\ of\ atom)}{volume\ unit\ cell}$$

Example

- Calculate the packing factor of silver (Ag)

PF of Ag

Table 3-2 Askeland
Table 3.1 Callister

Density

Cubic unit cell

Atomic mass (g/mol)

$$\rho = \frac{\left(\#\frac{atoms}{unit\ cell}\right)(mass\ of\ atom)}{(volume\ of\ unit\ cell)(N_A)}$$

In terms of lattice $(\times 10^{-8} cm)^3$

Avogadro's number $(6.023 \times 10^{23} atoms/mol)$

Example

- Determine the unit cell structure of indium (In). FCC, BCC or SC?

Tetragonal

$a_0 = 0.3252\ nm$

$c_0 = 0.4946\ nm$

Ar(In)= $114.82\ \frac{g}{mol}$

$\rho = 7.286\ \frac{g}{cm^3}$

Unit cell structure of In

Tetragonal

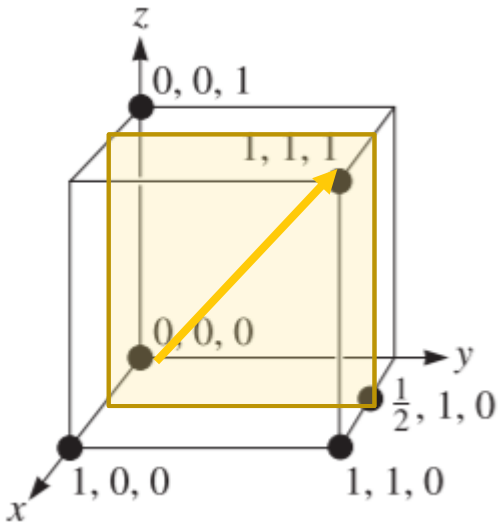
$a_0 = 3.252 \times 10^{-8}\ cm$

$c_0 = 4.946 \times 10^{-8}\ cm$

Ar(In)= $114.82\ \frac{g}{mol}$

$\rho = 7.286\ \frac{g}{cm^3}$

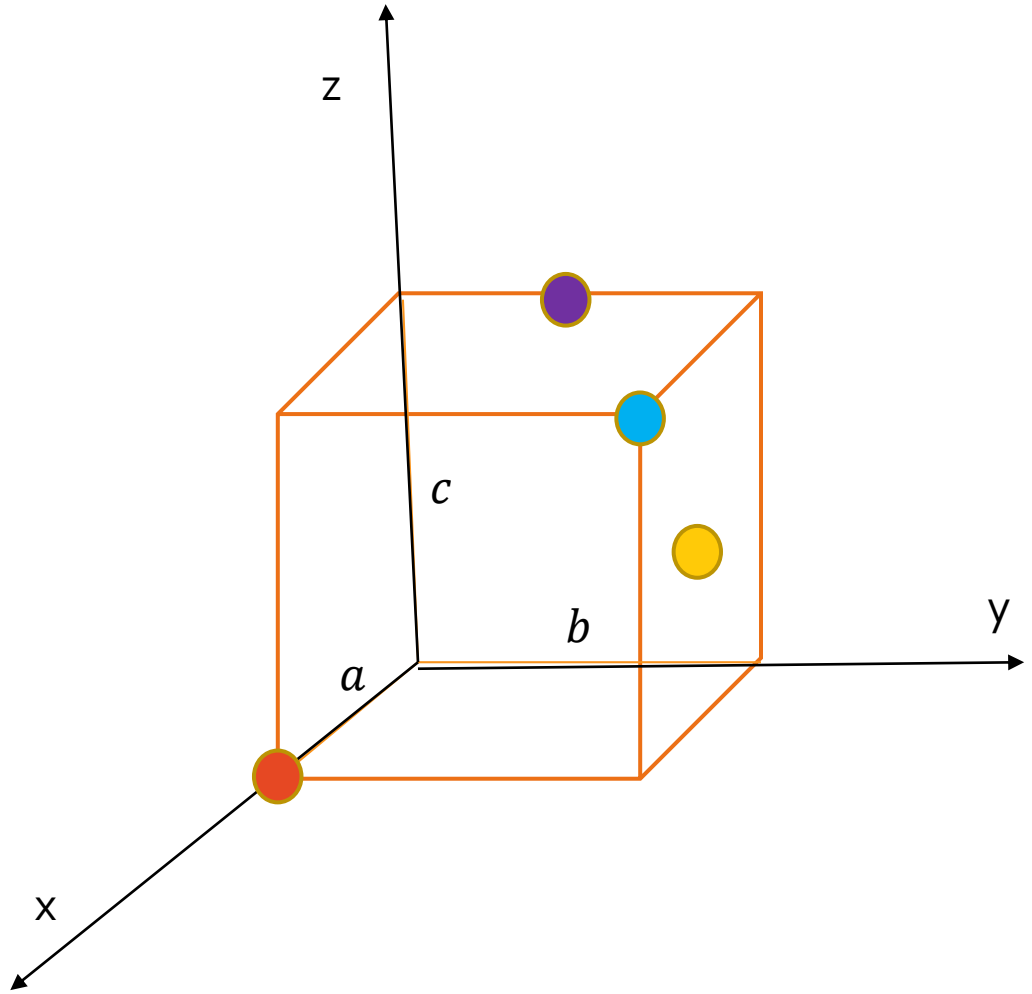
Crystallographic Points, Directions, and Planes



Points: atomic positions
Directions: Vector
Planes: cut section that modifies the interaction with defects

Points

	Point coordinates		
point	X(a)	X(b)	X(c)
●	1	0	0
●	1	1	1
●	0	1/2	1
●	1/2	1	1/2

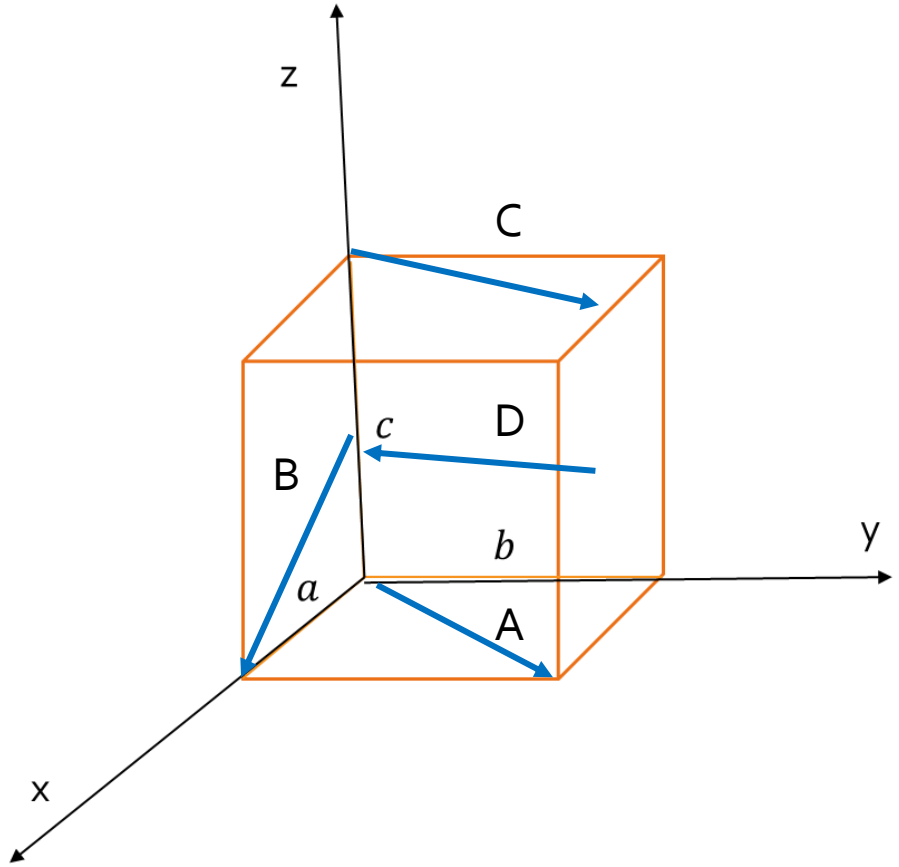


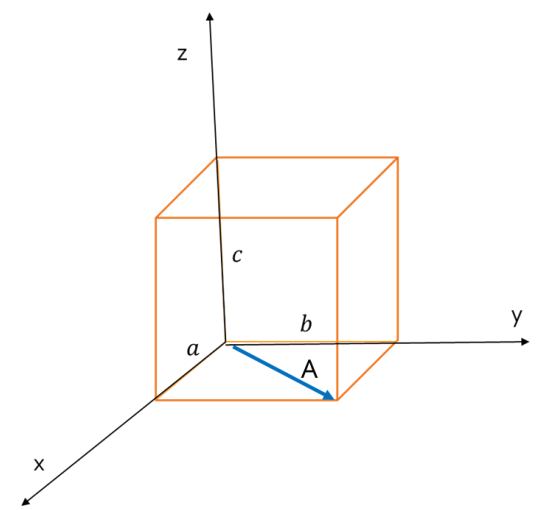
Miller indices: DIRECTIONS

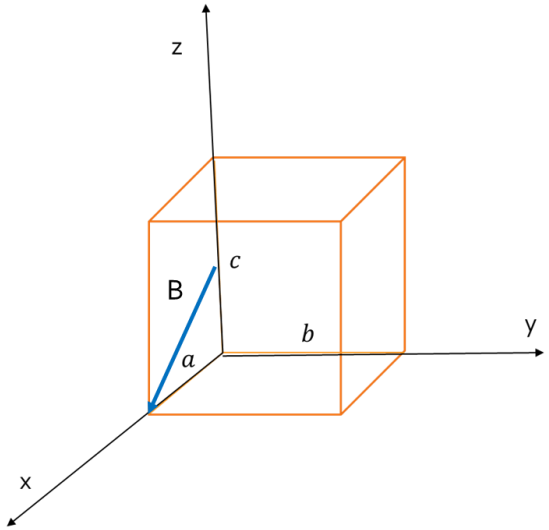
1. Determine the coordinates of 2 points
2. Find vector connecting 2 points
3. Clear fractions
4. Enclose values in [], no commas, no minuses

Example

- Determine the Miller indices or crystallography direction of the following systems




z
c
b
y
a
A
x


z
c
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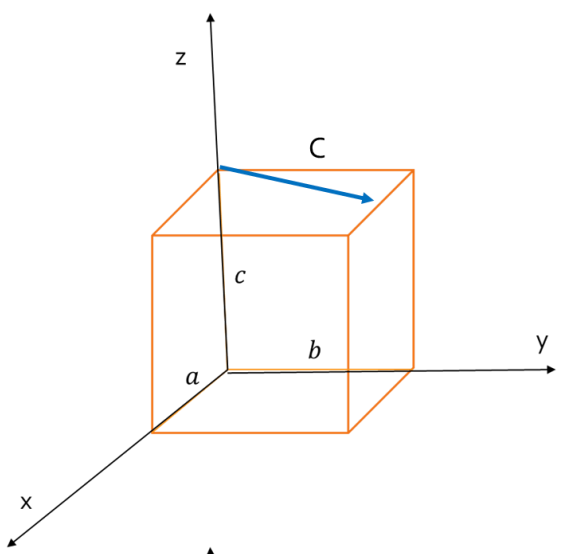
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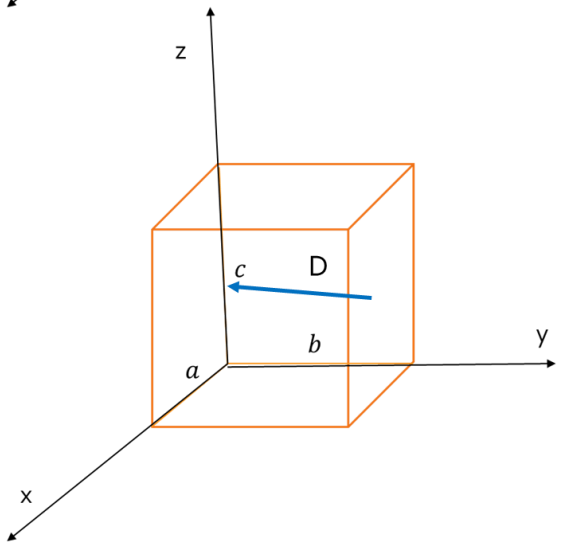
z
c
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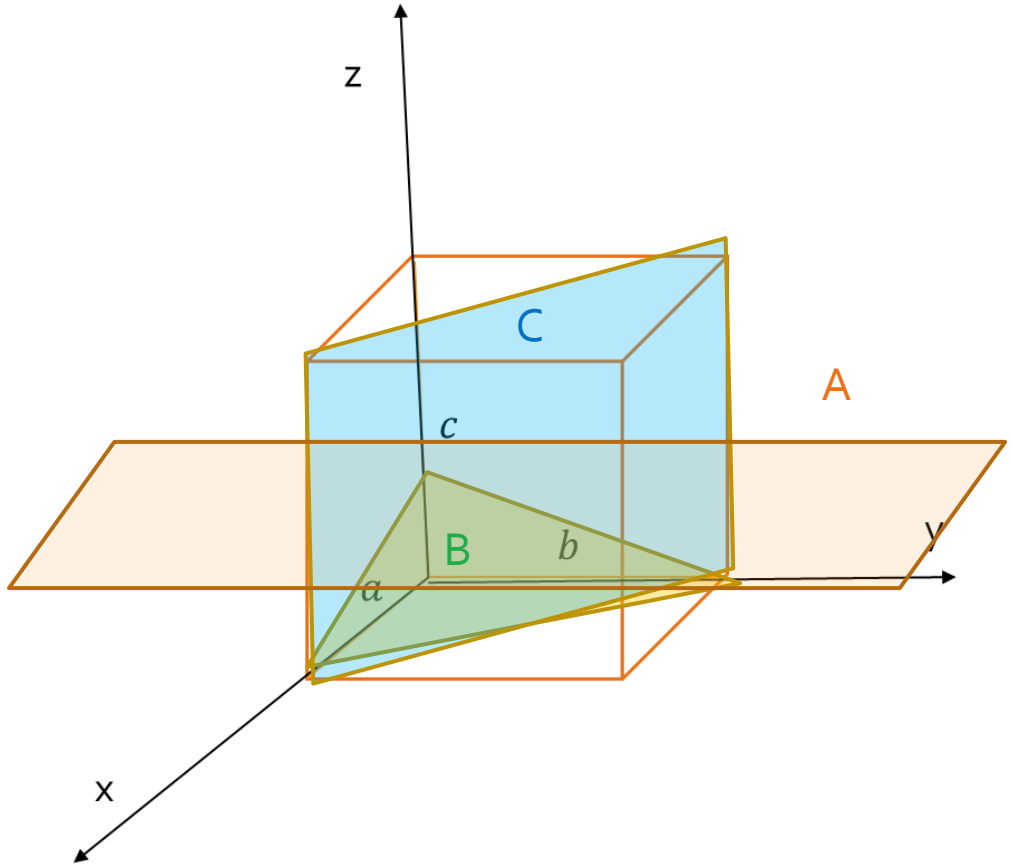
b
y
a
x

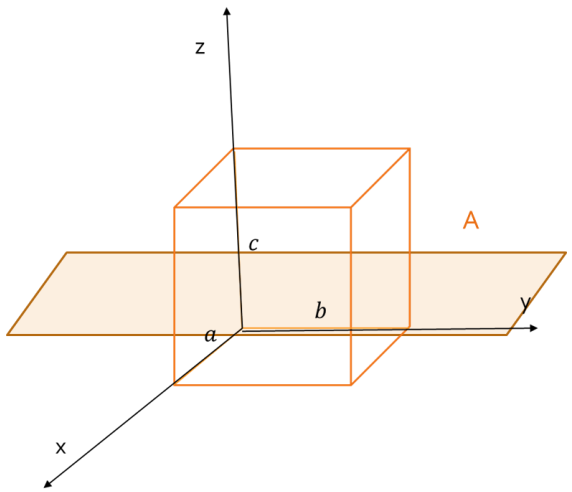
Miller indices: PLANES

1. identify plane intercepts x,y,z
2. take reciprocals of x,y,z
3. clear fractions
4. enclose values in (), commas

Example

- Determine the plane Miller indices of the following systems




z
A
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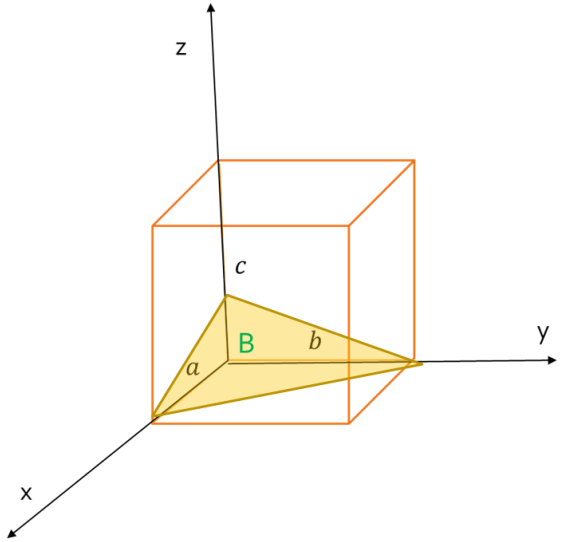
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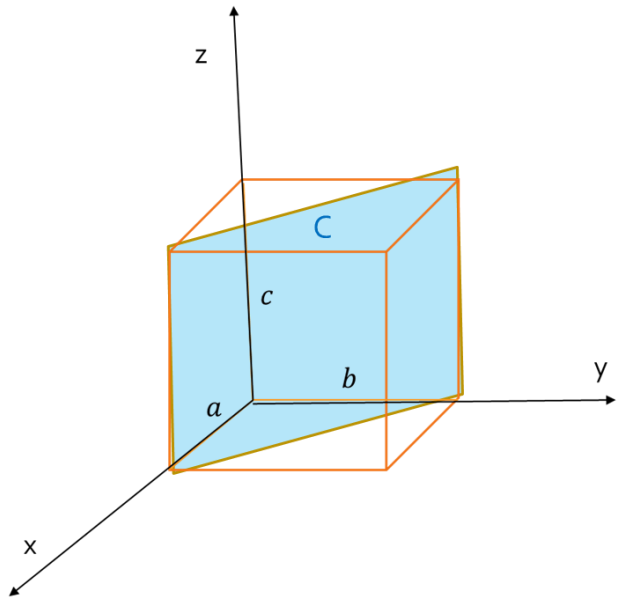
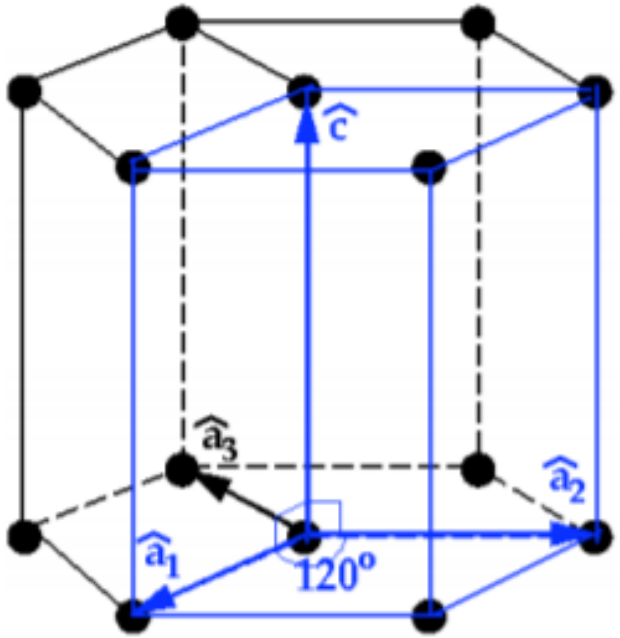

z
C
c
b
y
a
x

Recap: Miler's indices

Directions	Planes
Determine the coordinates of 2 points (Head and tail)	Identify plane intercepts x,y,z (Where they cut the axis)
Find vector connecting 2 points: Subtract the head from the tail	Take reciprocals of x,y,z (1/x,1/y,1/z)
Clear fractions	Clear fractions
Enclose values in [], no commas, no minuses	Enclose values in () or ()* if it is a family of planes, commas, minuses

Hexagonal structure



3 coordinate system:

$$h' = a_1;\ k' = a_2;\ l' = c$$

4 coordinate system:

$$h' = a_1;\ k' = a_2;\ \ i' = a_3;\ \ l' = c$$

$$h = \frac{1}{3}(2h' - k')$$

$$k = \frac{1}{3}(2k' - h')$$

$$i = -\frac{1}{3}(h' + k')$$

$$l = l'$$

Hexagonal coordinates

$$i.\quad a_1 = 1 \quad a_2 = -\frac{1}{2} \quad a_3 = -\frac{1}{2}$$

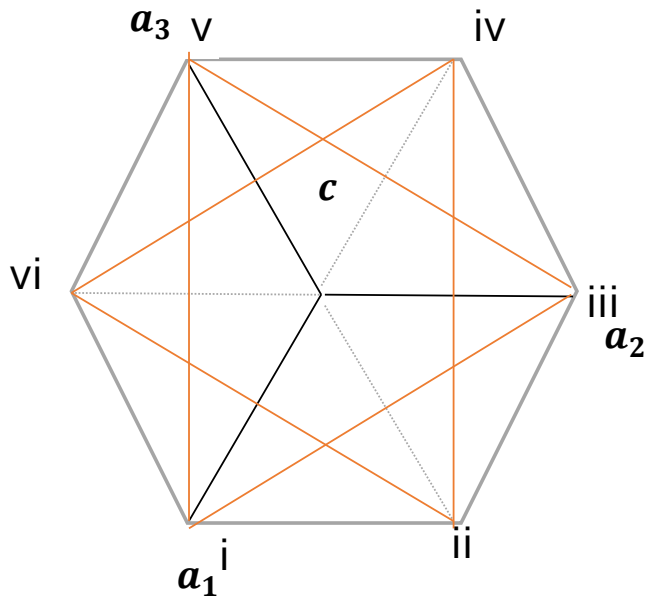
$$ii.\quad a_1 = \frac{1}{2} \quad a_2 = \frac{1}{2} \quad a_3 = -1$$

$$iii.\quad a_1 = -\frac{1}{2} \quad a_2 = 1 \quad a_3 = -\frac{1}{2}$$

$$iv.\quad a_1 = -1 \quad a_2 = \frac{1}{2} \quad a_3 = \frac{1}{2}$$

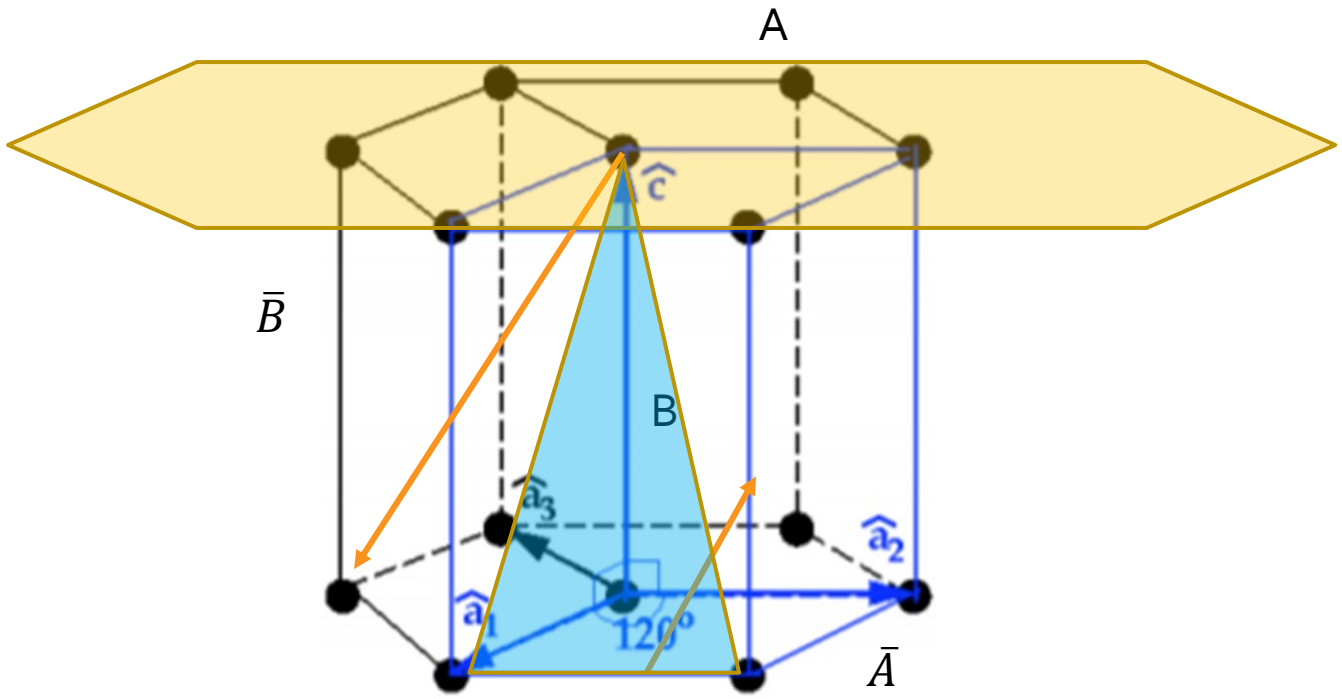
$$v.\quad a_1 = -\frac{1}{2} \quad a_2 = -\frac{1}{2} \quad a_3 = 1$$

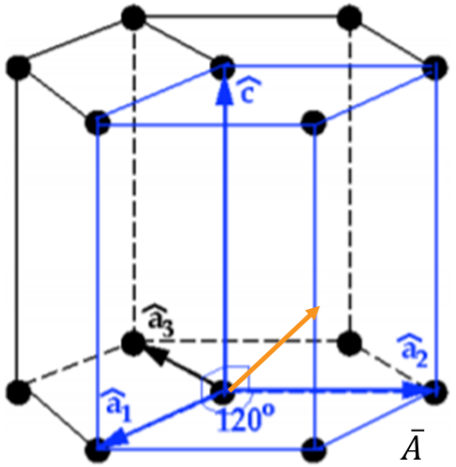
$$vi.\quad a_1 = \frac{1}{2} \quad a_2 = -1 \quad a_3 = \frac{1}{2}$$



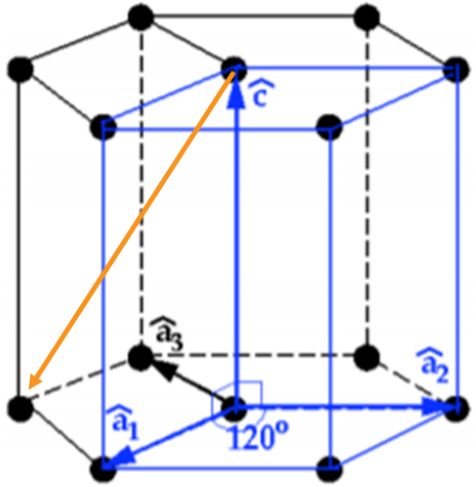
Example

- Determine the plane Miller indices

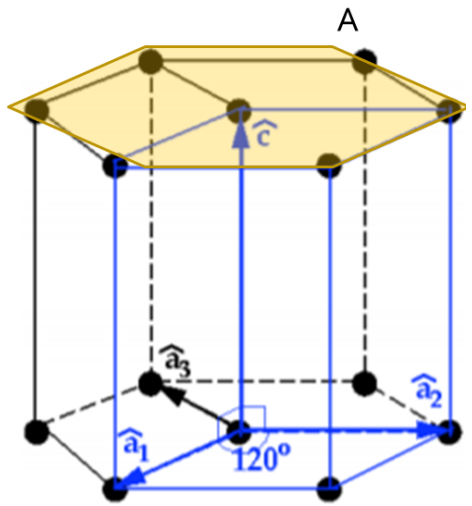




$\bar{A}$



$\bar{B}$


A
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â3
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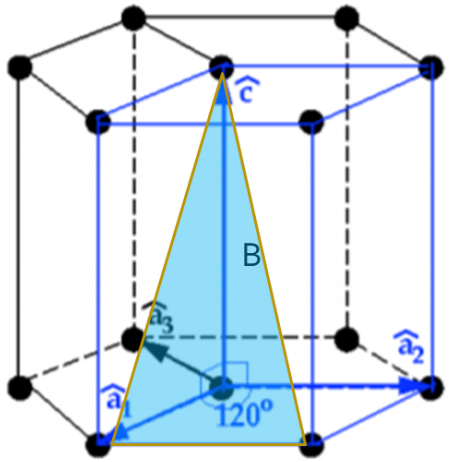
120°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Interplanar Spacing for Cubic System and Tetragonal Systems

The spacing between planes in a family* with the Miller indices h, k and l is denoted by $\mathbf{d_{hkl}}$.

A formula relating this distance to the Miller indices and the lattice constant (a_0) exists for each crystal system. The equation for a cubic system is:

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

$$\#d_{hkl} = \frac{D(distance\ between\ coordinate\ points)}{d_{hkl}}$$

Example

- Determine the number of interplanar spacings in copper (Cu) if the miller indices are [1 1 1]

$\#d_{hkl}$ of Cu

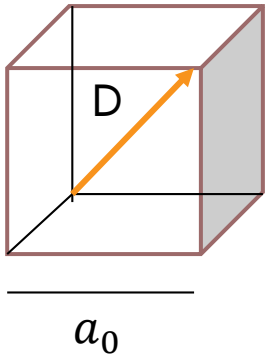
$a_0 = 3.61 \times 10^{-8} cm$

FCC

h=1

k=1

l=1

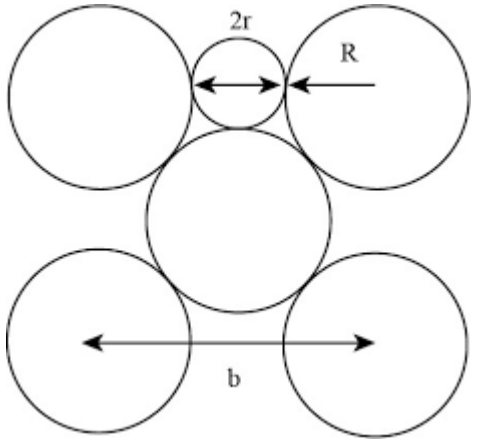


Crystal structure of ionic materials

Closed packed structures of anions with cations filling interstitial sites.

Anions radii> Cations radii

$$Radius\ ratio = \frac{r^+}{r^-}$$



Coordination number

Crystal structure of ionic materials: What does the coordination number tell us?

Radius ratio	Coordination number	Type of structure (Coordination)
< 0.155	2	linear
0.155-0.225	3	triangular
0.225-0.414	4	Tetragonal
0.414-0.732	6	octahedral
0.732-1.0	8	Cubic (SC, BCC, FCC)
>1.0	12	Cubic Closest packed (CCP) Hexagonal closest packed (HCCP)

Crystal structure of ionic materials: Group table

Structure	FCC	FCC	FCC
$\#\ ion/uc$	4 Per Ion	4 per ion	4 Cation +8 Anions
Lattice parameter	$a_0 = 2r_C^+ + 2r_A^-$	$a_0 = \sqrt{\frac{4}{3}}\,(r_C^+ + r_A^-)$	$a_0 = \frac{4(r_C^+ + r_A^-)}{\sqrt{3}}$
Principal example	NaCl	ZnS	CaF2
Most common	MgO	GaAs	UO_2 r^+ $^{-2}$
Other Examples	FeO	III-V Semiconductors	ThO2, CeO2, ZrO2

Example

- For NiO and UO_2, determine (do not assume cubic):

a) Lattice parameter

b) Packing factor

c) Density

NiO

Appendix B (Askeland)

$r_{Ni}^{+2} = 0.069$ nm

$r_0^{-2} = 0.132\ nm$

Table from eClass

Radius ratio	Coordination number	Type of structure (Coordination)
< 0.155	2	linear
0.155-0.225	3	triangular
0.225-0.414	4	Tetragonal
0.414-0.732	6	octahedral
0.732-1.0	8	Cubic (SC, BCC, FCC)
>1.0	12	Cubic Closest packed (CCP) Hexagonal closest packed (HCCP)

NiO

Appendix B (Askeland)

$r_{Ni}^{+2} = 0.069\ \text{nm}$

$r_0^{-2} = 0.132\ nm$

$Ar(Ni) = 57.71 \frac{g}{mol}$

$Ar(O) = 16.0 \frac{g}{mol}$

Table from eClass

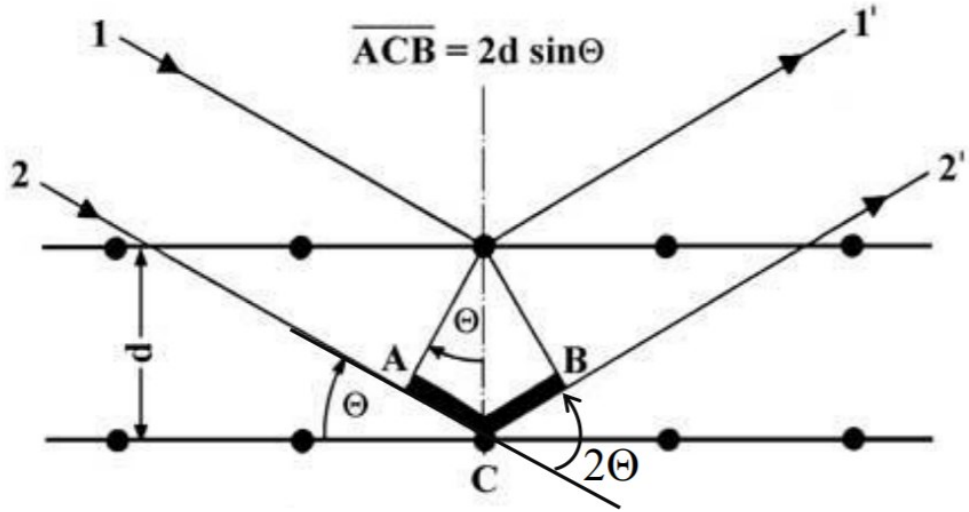
Diffraction Techniques for crystal structures

Bragg's Law: The secondary waves interfere with each other to produce the diffracted beam.

$$\lambda = 2dsin\theta$$

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

$$sin\theta = \left(\frac{\lambda}{2a_0}\right)\sqrt{h^2 + k^2 + l^2}$$



Example

- Diffracted x-ray beam is observed from (2, 2, 0) planes of iron at 2θ angle of 99.1° when x-rays of 0.15418nm. Calculate lattice parameter of iron

$a_0\ of\ Fe$

$\lambda = 0.15418\ nm$

$2\theta = 99.1°$

Plane (2, 2, 0)