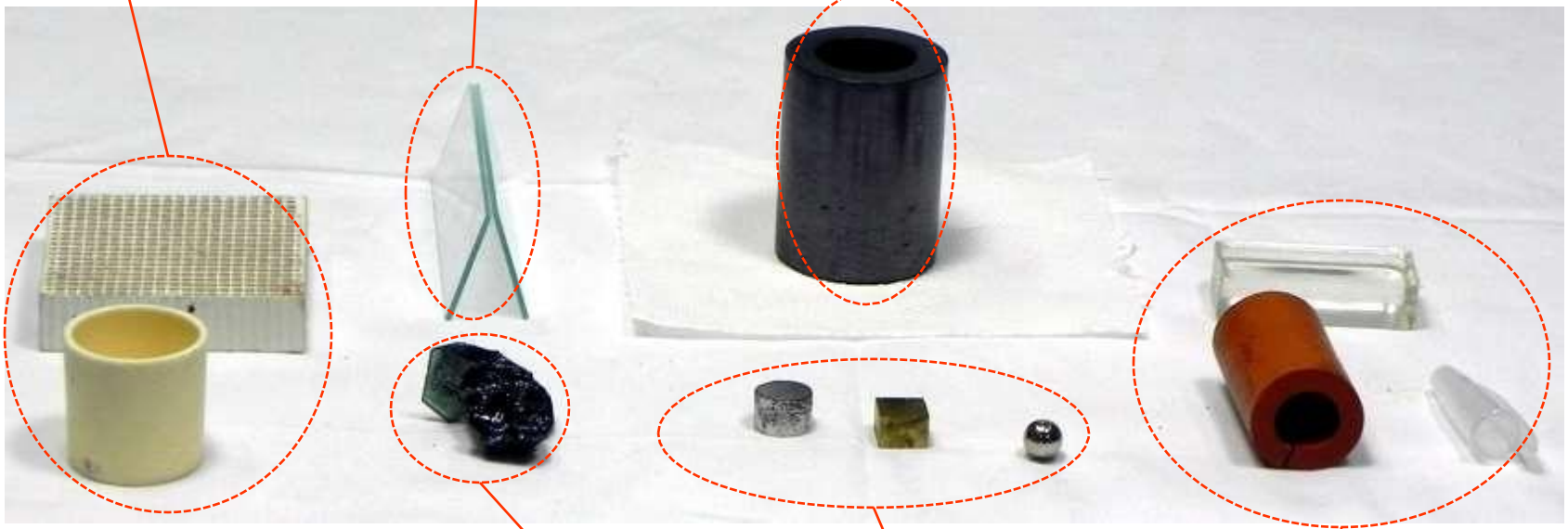
CRYSTAL STRUCTURES

What is space lattice?

- Space lattice is the distribution of points in 3D in such a way that every point has identical surroundings, i.e., it is an infinite array of points in three dimensions in which every point has surroundings identical to every other point in the array.

Common materials: *with various 'viewpoints'*



Graphite

Glass: amorphous

Ceramics

Crystal

Metals

Polymers

Common materials: *examples*

- Metals and alloys ➢ Cu, Ni, Fe, NiAl (intermetallic compound), Brass (Cu-Zn alloys)
- Ceramics (usually oxides, nitrides, carbides) ➢ Alumina (Al_2O_3), Zirconia (Zr_2O_3)
- Polymers (thermoplasts, thermosets) (Elastomers)➢ Polythene, Polyvinyl chloride, Polypropylene

Based on Electrical Conduction

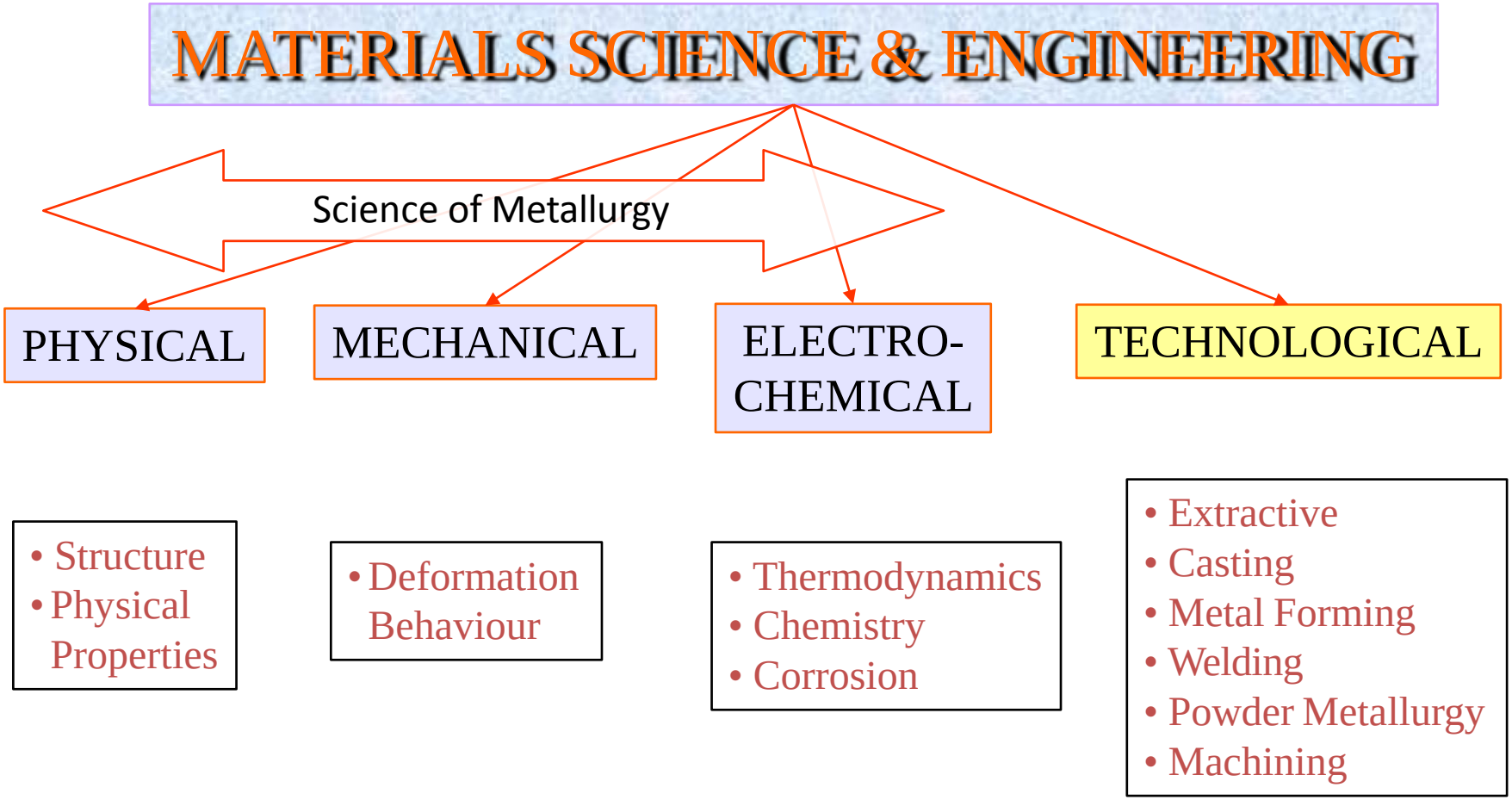
- Conductors ➢ Cu, Al, NiAl
- Semiconductors ➢ Ge, Si, GaAs
- Insulators ➢ Alumina, Polythene*

Based on Ductility

- Ductile ➢ Metals, Alloys
- Brittle ➢ Ceramics, Inorganic Glasses, Ge, Si

** some special polymers could be conducting*

- The broad scientific and technological segments of Materials Science are shown in the diagram below.
- To gain a comprehensive understanding of materials science, all these aspects have to be studied.



Definition 1

Crystal = Lattice + Motif

Motif or Basis:
typically an atom or a group of atoms associated with each lattice point

Lattice ➢ the underlying periodicity of the crystal
Basis ➢ Entity associated with each lattice points

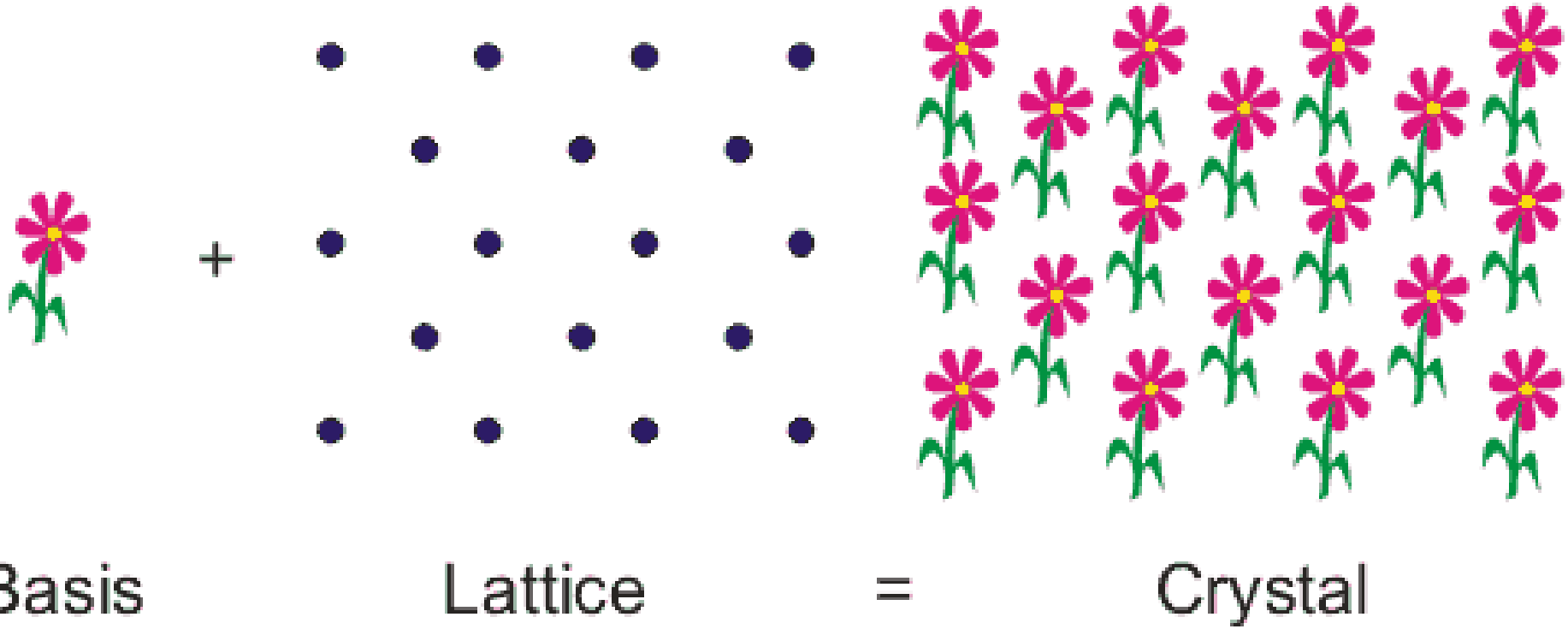
Lattice ➢ how to repeat
Motif ➢ what to repeat

Lattice

Translationally periodic arrangement of points

Crystal

Translationally periodic arrangement of motifs


Basis
Lattice
=
Crystal

Space Lattice

A lattice is also called a Space Lattice

An array of points such that every point has *identical surroundings*

- **In Euclidean space ⇒ infinite array**
- **We can have 1D, 2D or 3D arrays (lattices)**

or

Translationally periodic arrangement of points in space is called a lattice

Unit cell: A unit cell is the sub-division of the space lattice that still retains the overall characteristics of the space lattice.

Primitive cell: the smallest possible unit cell of a lattice, having lattice points at each of its eight vertices only.

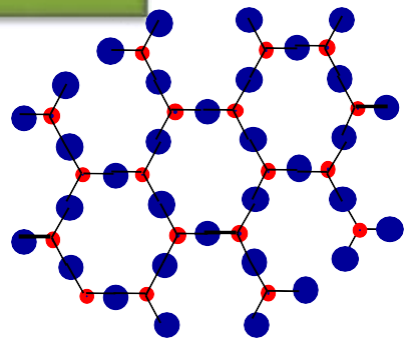
A primitive cell is a minimum volume cell corresponding to a single lattice point of a structure with translational symmetry in 2 dimensions, 3 dimensions, or other dimensions.

A lattice can be characterized by the geometry of its *primitive cell*.

Materials and Packing

Crystalline materials...

- atoms pack in periodic, 3D arrays
- typical of: -metals
  -many ceramics
  -some polymers

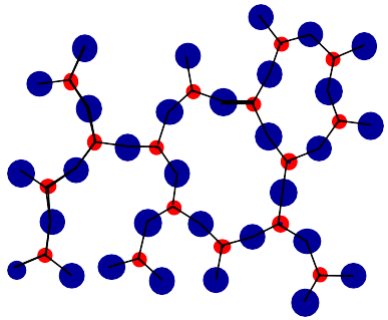


crystalline SiO_2 (Quartz)

Si Oxygen

Non-crystalline materials...

- atoms have no periodic packing
- occurs for: -complex structures
  -rapid cooling

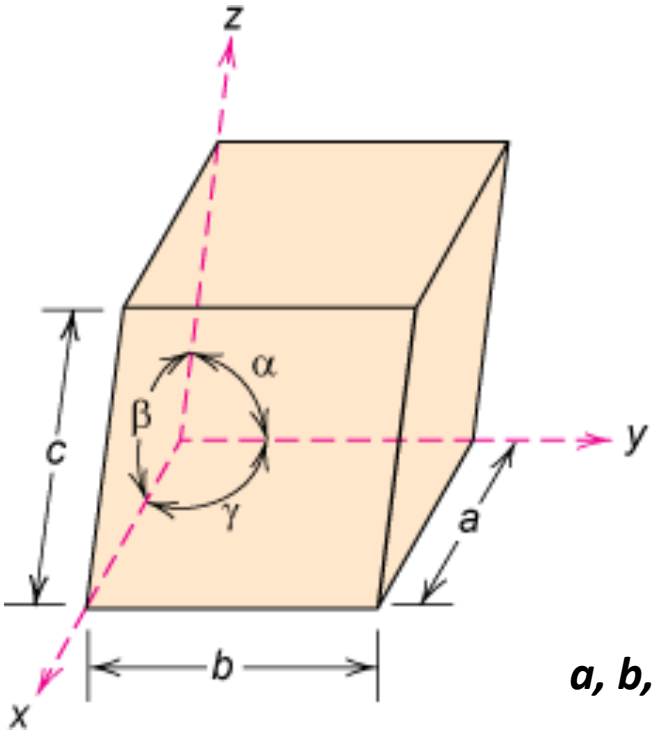


"Amorphous" = Noncrystalline

noncrystalline SiO_2 (Glass)

Crystal Systems

Unit cell: smallest repetitive volume which contains the complete lattice pattern of a crystal.



7 crystal systems

14 crystal lattices

***a, b,* and *c* are the lattice constants**

The Unite Cell is the smallest group of atom showing the characteristic lattice structure of a particular metal.
It is the building block of a single crystal.
A single crystal can have many unit cells.

Crystal systems

Cubic	Three equal axes, mutually perpendicular $a=b=c \quad \alpha=\beta=\gamma=90^\circ$
Tetragonal	Three perpendicular axes, only two equal $a=b\neq c \quad \alpha=\beta=\gamma=90^\circ$
Hexagonal	Three equal coplanar axes at 120˚ and a fourth unequal axis perpendicular to their plane $a=b\neq c \quad \alpha=\beta=90^\circ \quad \gamma=120^\circ$
Rhombohedral	Three equal axes, not at right angles $a=b=c \quad \alpha=\beta=\gamma\neq90^\circ$
Orthorhombic	Three unequal axes, all perpendicular $a\neq b\neq c \quad \alpha=\beta=\gamma=90^\circ$
Monoclinic	Three unequal axes, one of which is perpendicular to the other two $a\neq b\neq c \quad \alpha=\gamma=90^\circ\neq\beta$
Triclinic	Three unequal axes, no two of which are perpendicular $a\neq b\neq c \quad \alpha\neq\beta\neq\gamma\neq90^\circ$

Some engineering applications require single crystals:

--diamond single crystals for abrasives

--turbine blades

What is coordination number?

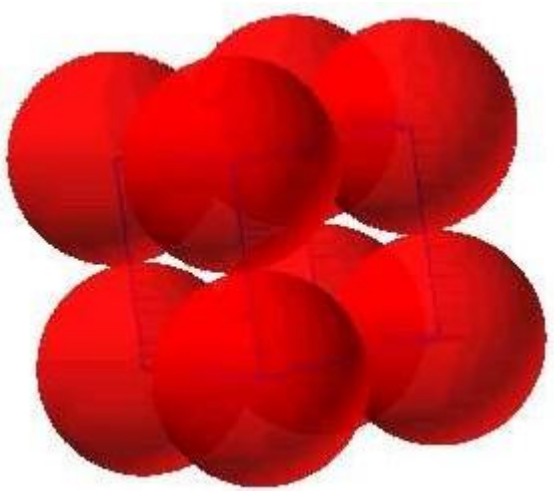
- *The **coordination number** of a central atom in a crystal is the number of its nearest neighbours.*

What is lattice parameter?

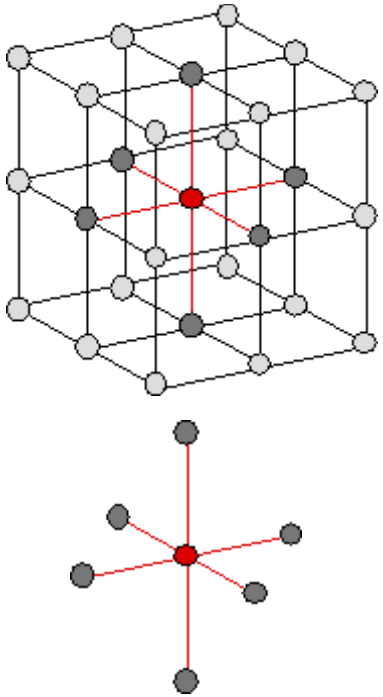
- *The **lattice constant**, or **lattice parameter**, refers to the physical dimension of unit cells in a crystal **lattice**.*
- ***Lattices** in three dimensions generally have three **lattice constants**, referred to as a, b, and c.*

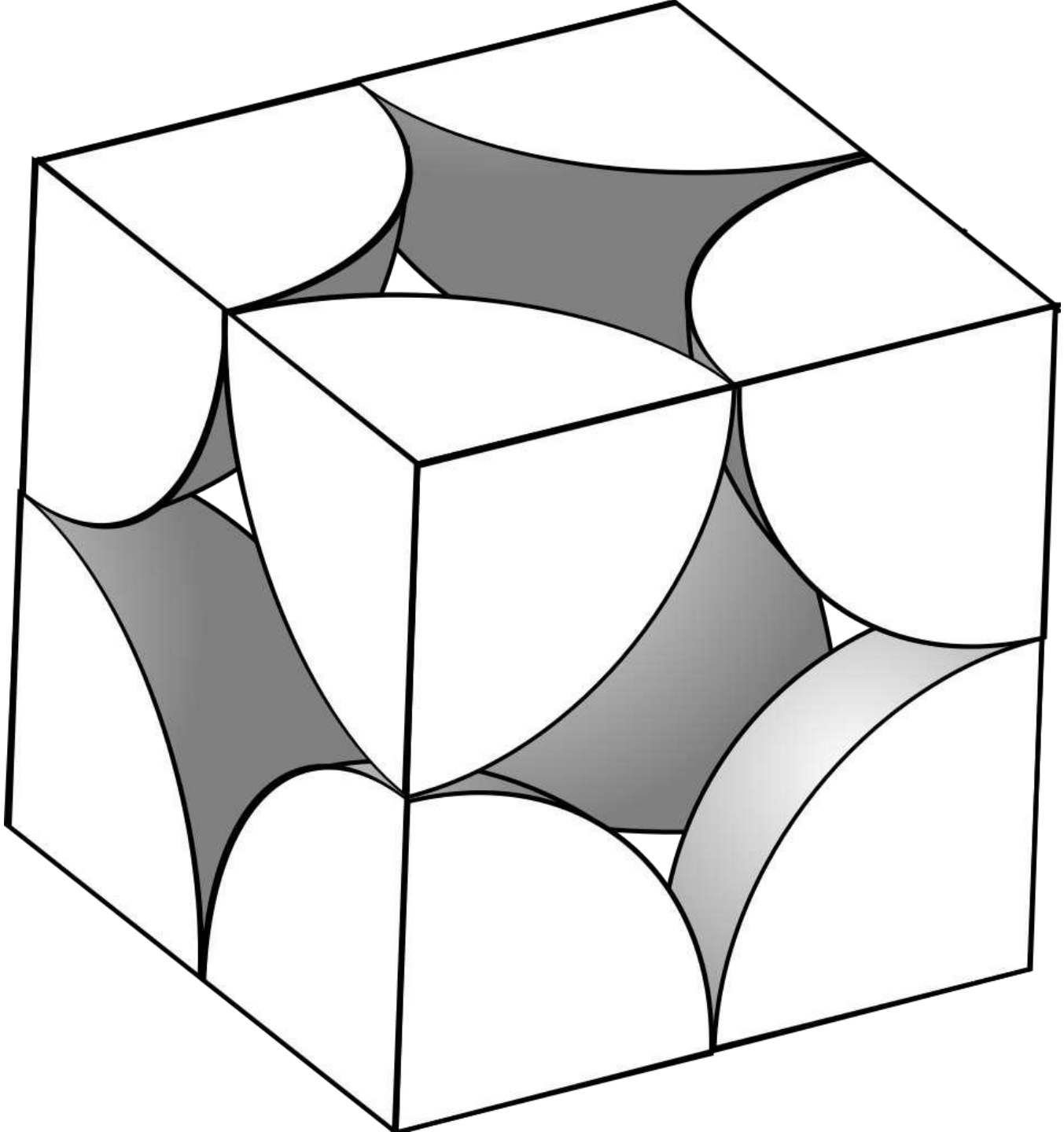
Simple Cubic Structure (SC)

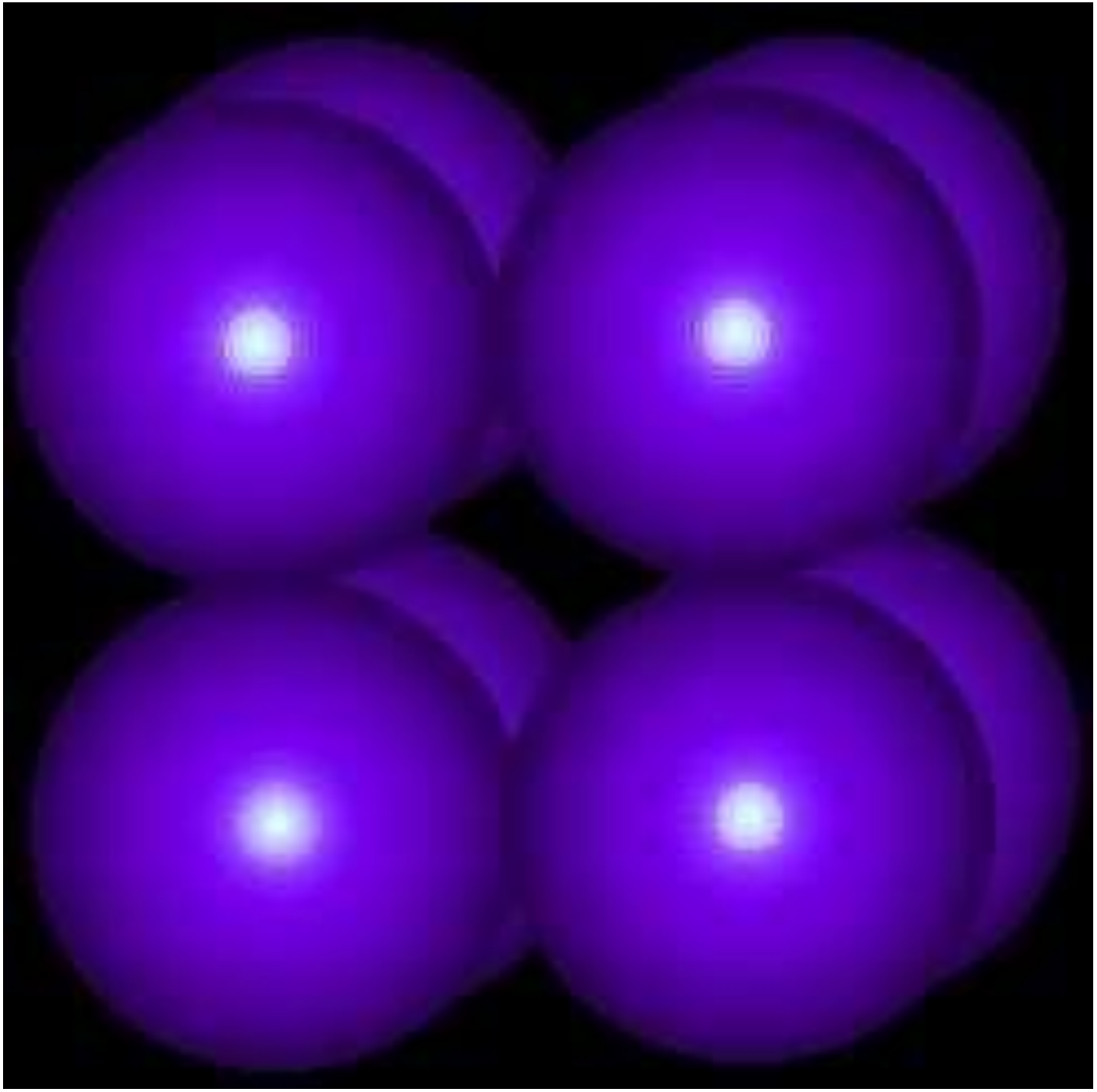
- **Rare due to low packing density (only Po has this structure)**
- **Close-packed directions are cube edges.**



- **Coordination # = 6**
  (# nearest neighbors)





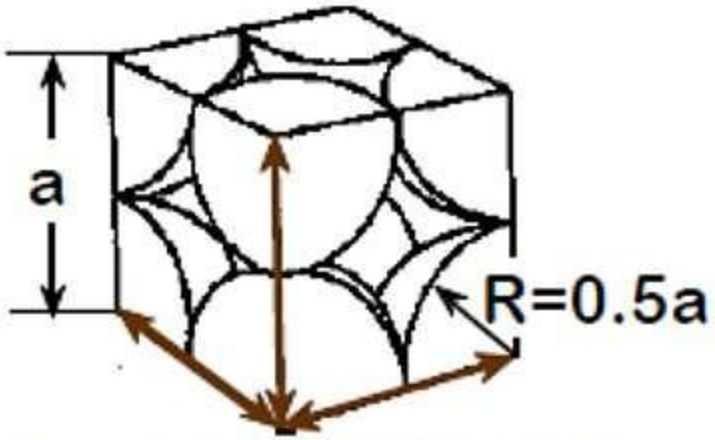


Atomic Packing Factor (APF)

$$APF = \frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}$$

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

contains 8 x 1/8 =
1 atom/unit cell

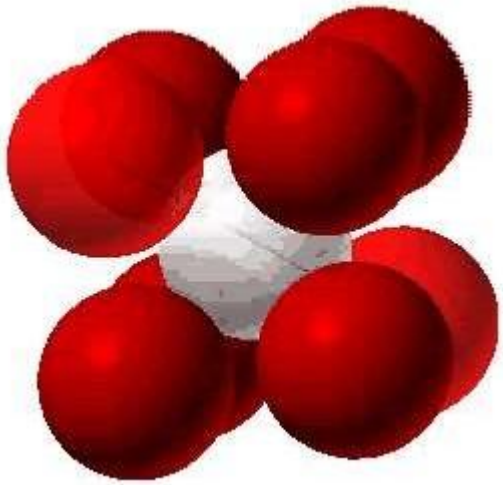
$$APF = \frac{\frac{\text{atoms}}{\text{unit cell}} \times \frac{\text{volume}}{\text{atom}}}{\frac{\text{volume}}{\text{unit cell}}} = \frac{1 \times \frac{4}{3}\pi (0.5a)^3}{a^3}$$

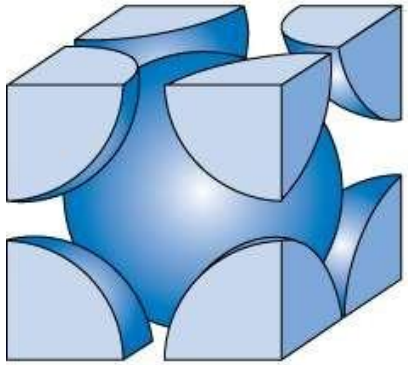
Body Centered Cubic Structure (BCC)

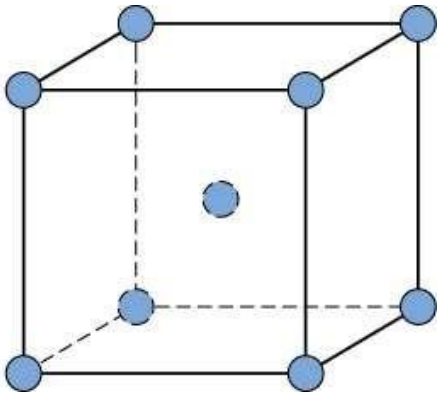
- **Atoms touch each other along cube diagonals.**
  - **--Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.**

ex: Cr, W, Fe (α), Tantalum, Molybdenum

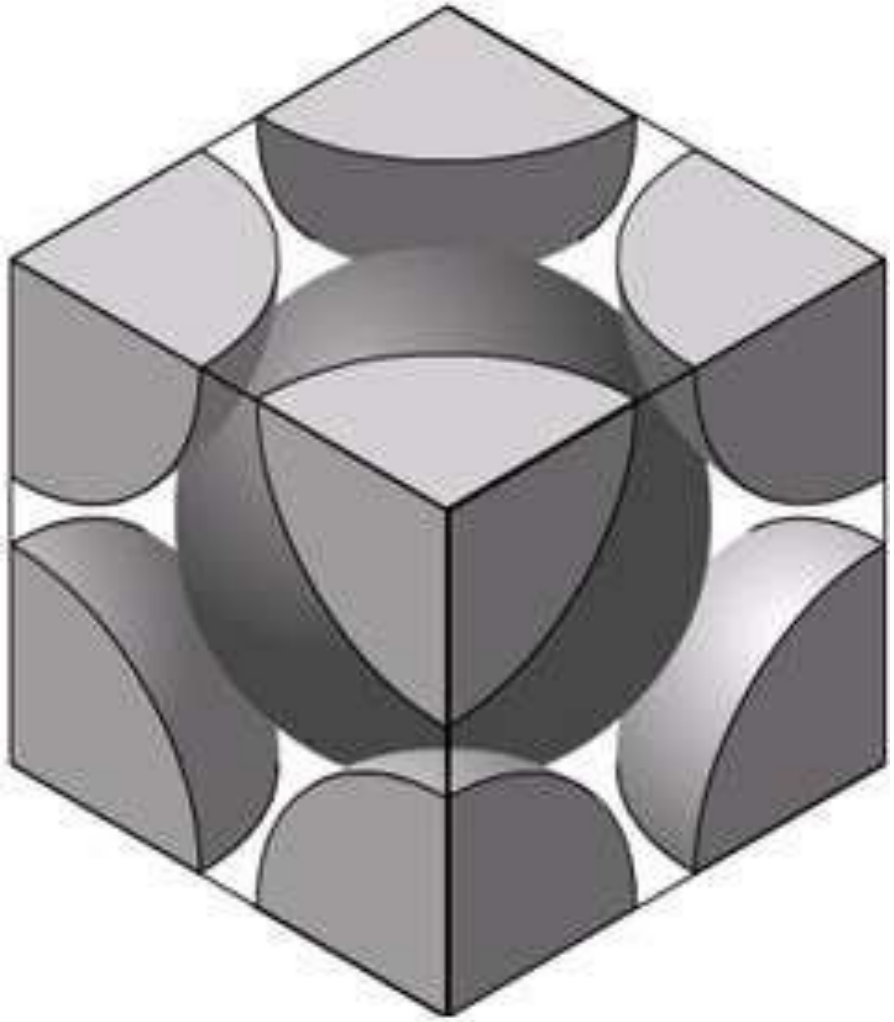
- **Coordination # = 8**

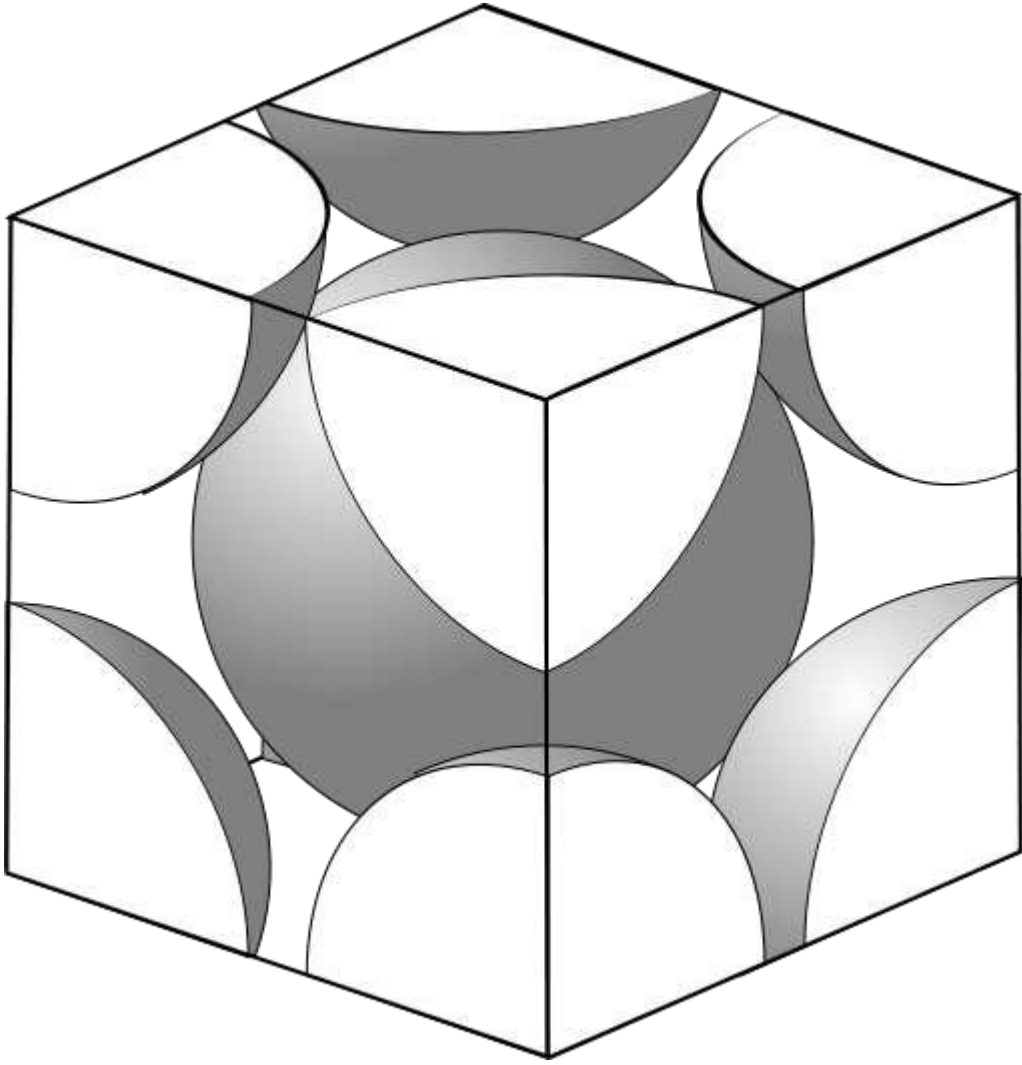


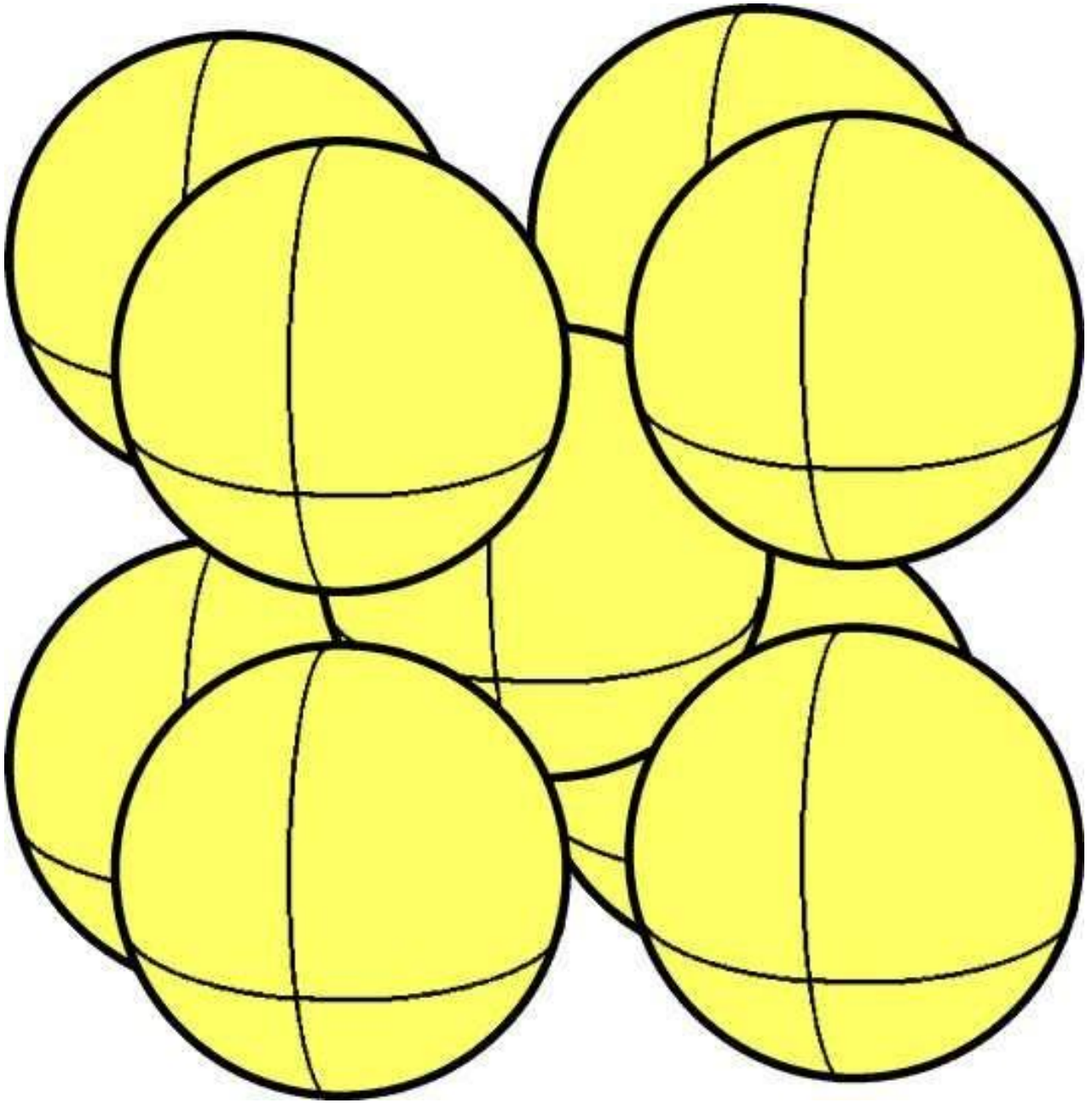




2 atoms/unit cell: 1 center + 8 corners x 1/8

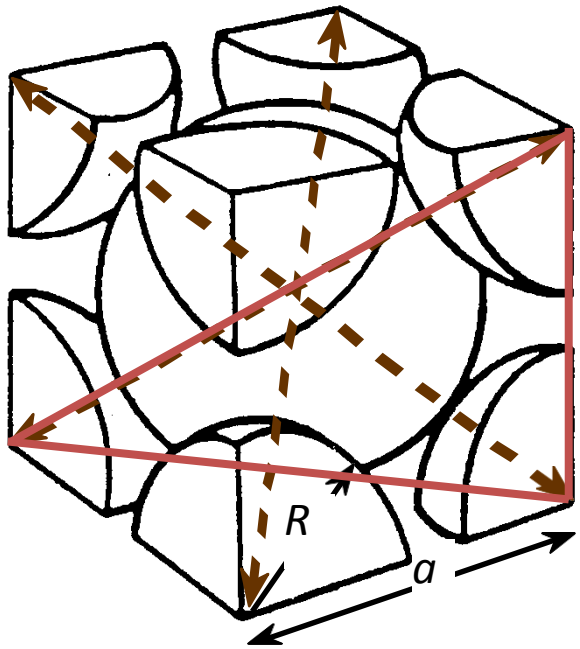


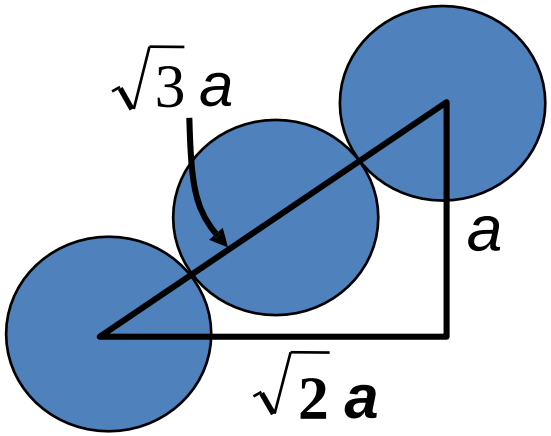




Atomic Packing Factor: BCC

- **APF for a body-centered cubic structure = 0.68**





Close-packed directions:

length = 4*R* = $\sqrt{3}\,a$

$$\text{APF} = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{2 \cdot \frac{4}{3}\pi \left(\sqrt{3}\,a/4\right)^3}{a^3}$$

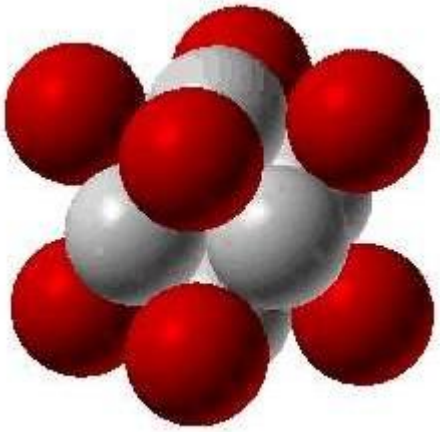
Face Centered Cubic Structure (FCC)

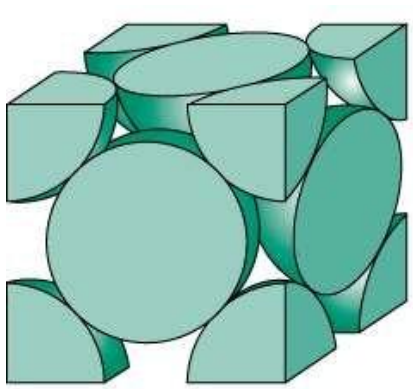
- **Atoms touch each other along face diagonals.**

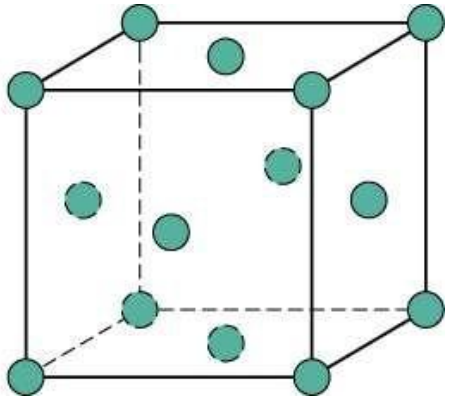
  --Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

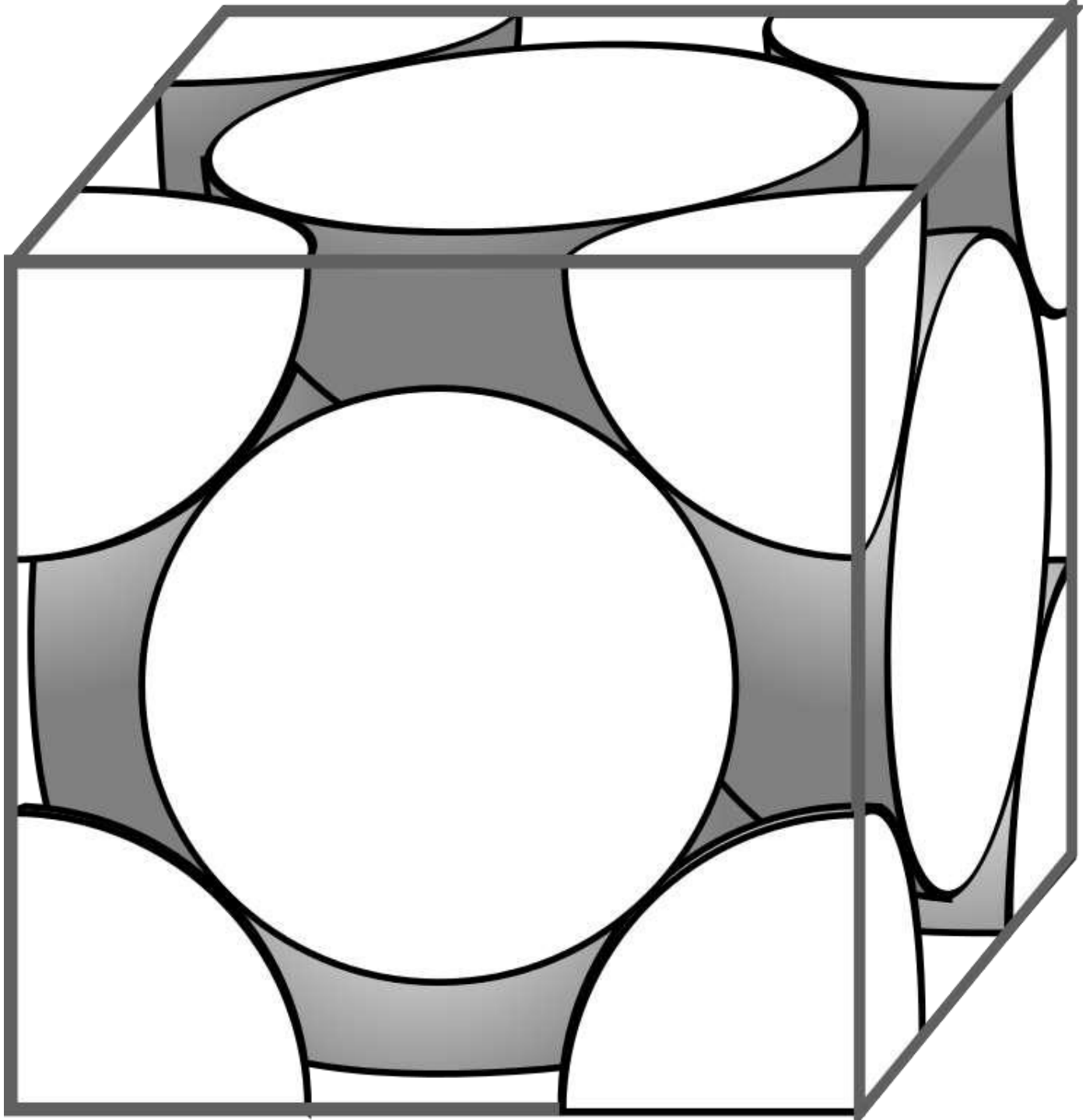
- **Coordination # = 12**







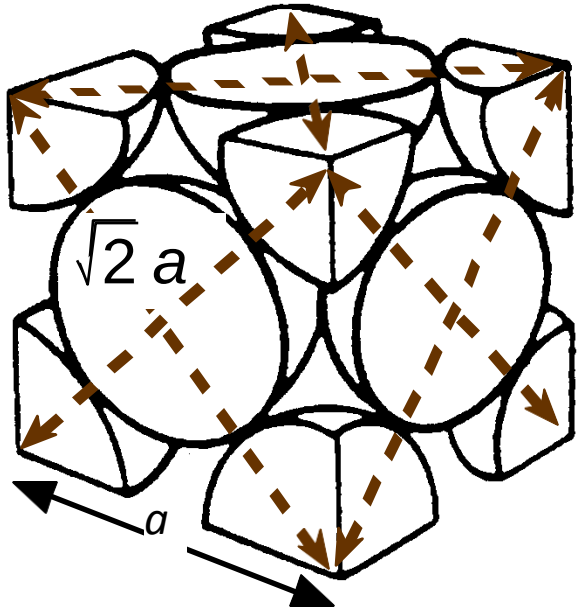
4 atoms/unit cell: 6 face x 1/2 + 8 corners x 1/8



Atomic Packing Factor: FCC

- APF for a face-centered cubic structure = 0.74

maximum achievable APF



Close-packed directions:

length = $4R = \sqrt{2}\,a$

Unit cell contains:

6 x 1/2 + 8 x 1/8

= 4 atoms/unit cell

$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{4 \cdot \frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3}{a^3}$$

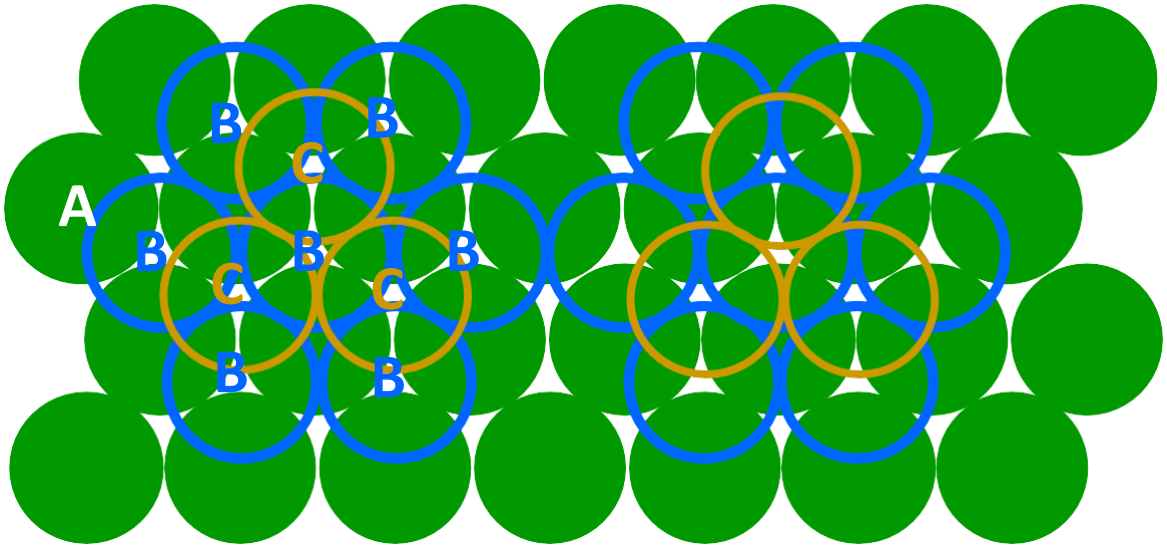
FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

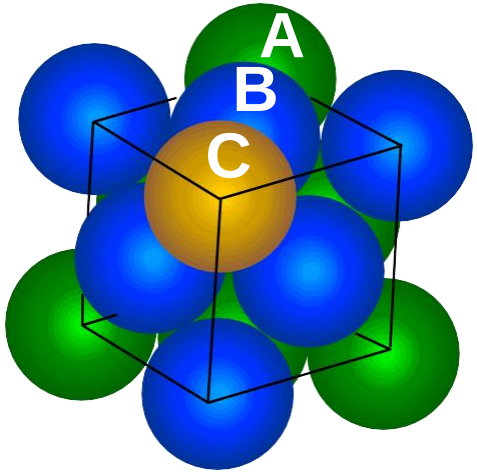
A sites

B sites

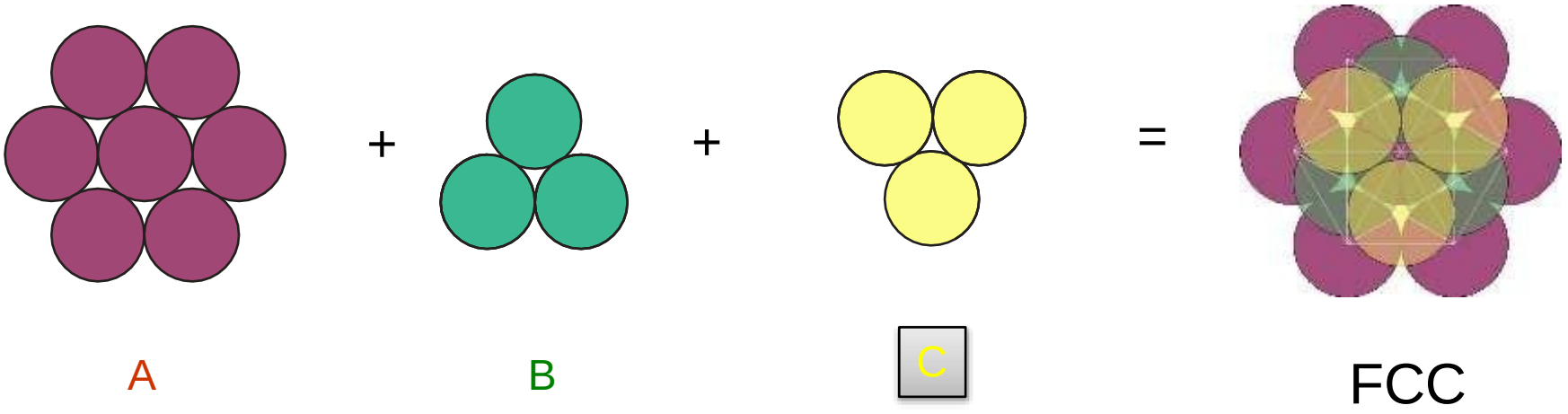
C sites

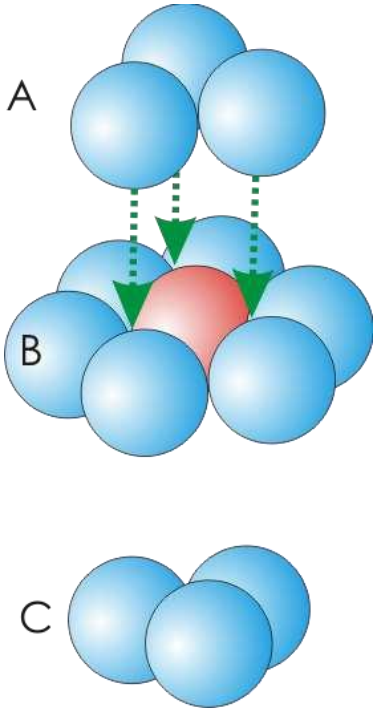


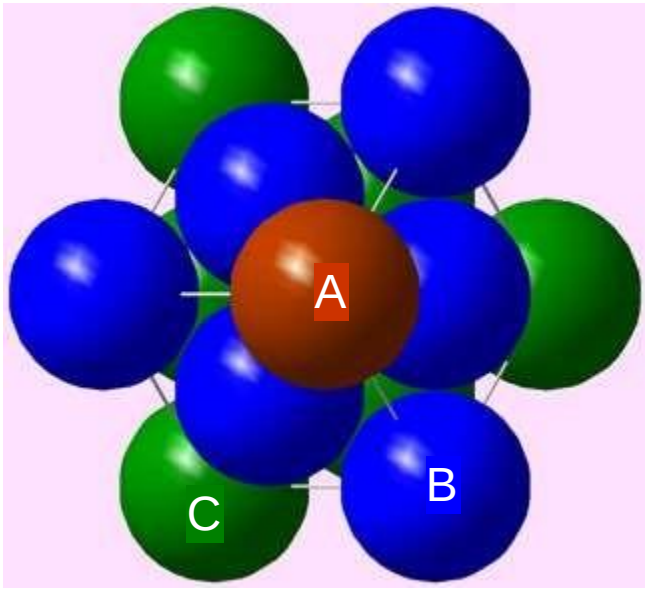
- FCC Unit Cell

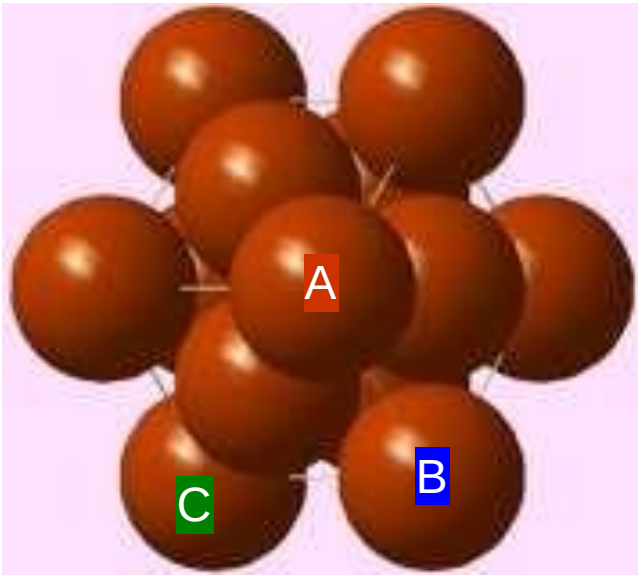


Putting atoms in the B position in the II layer and in C positions in the III layer we get a stacking sequence → ABC ABC ABC…. ➢ The CCP (FCC) crystal

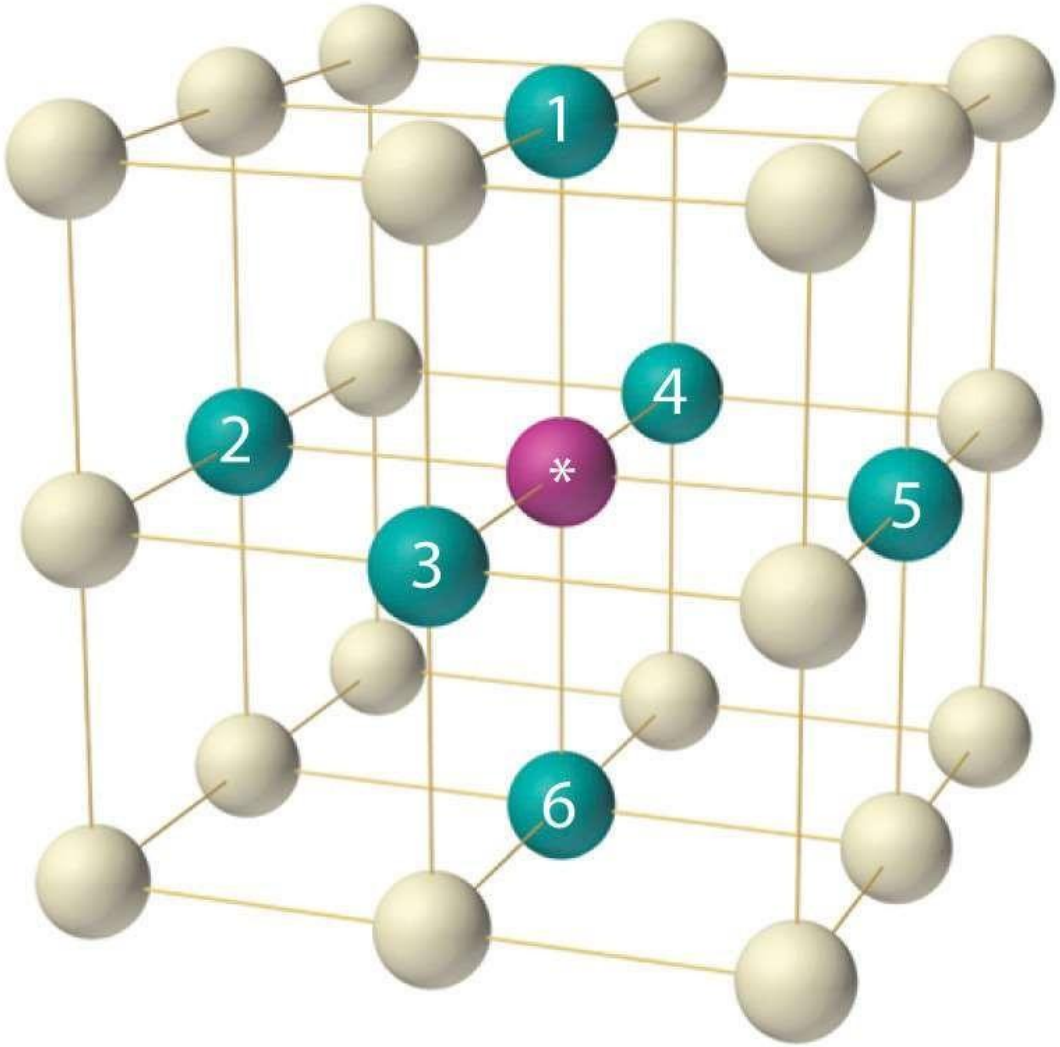




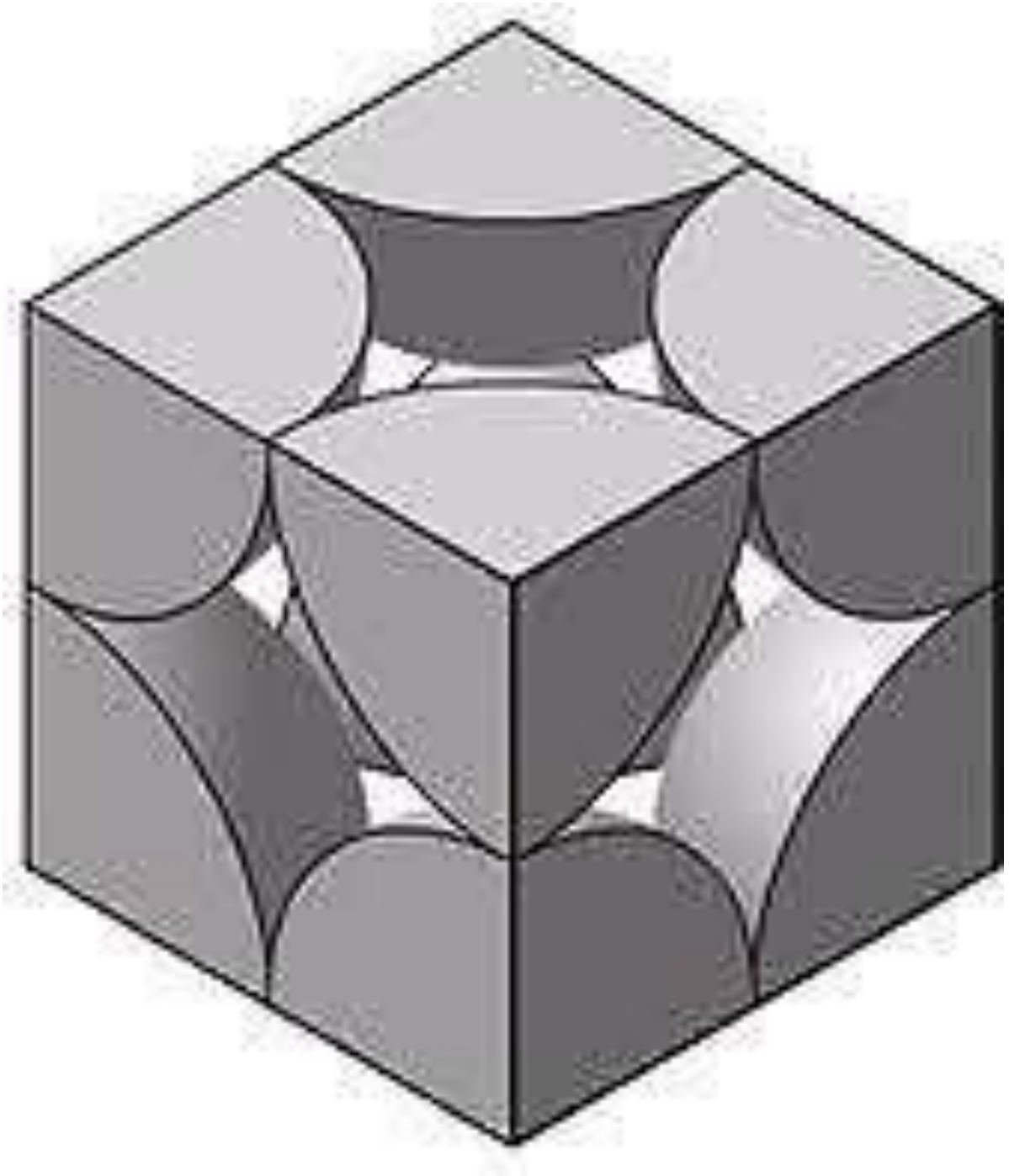




SC-coordination number

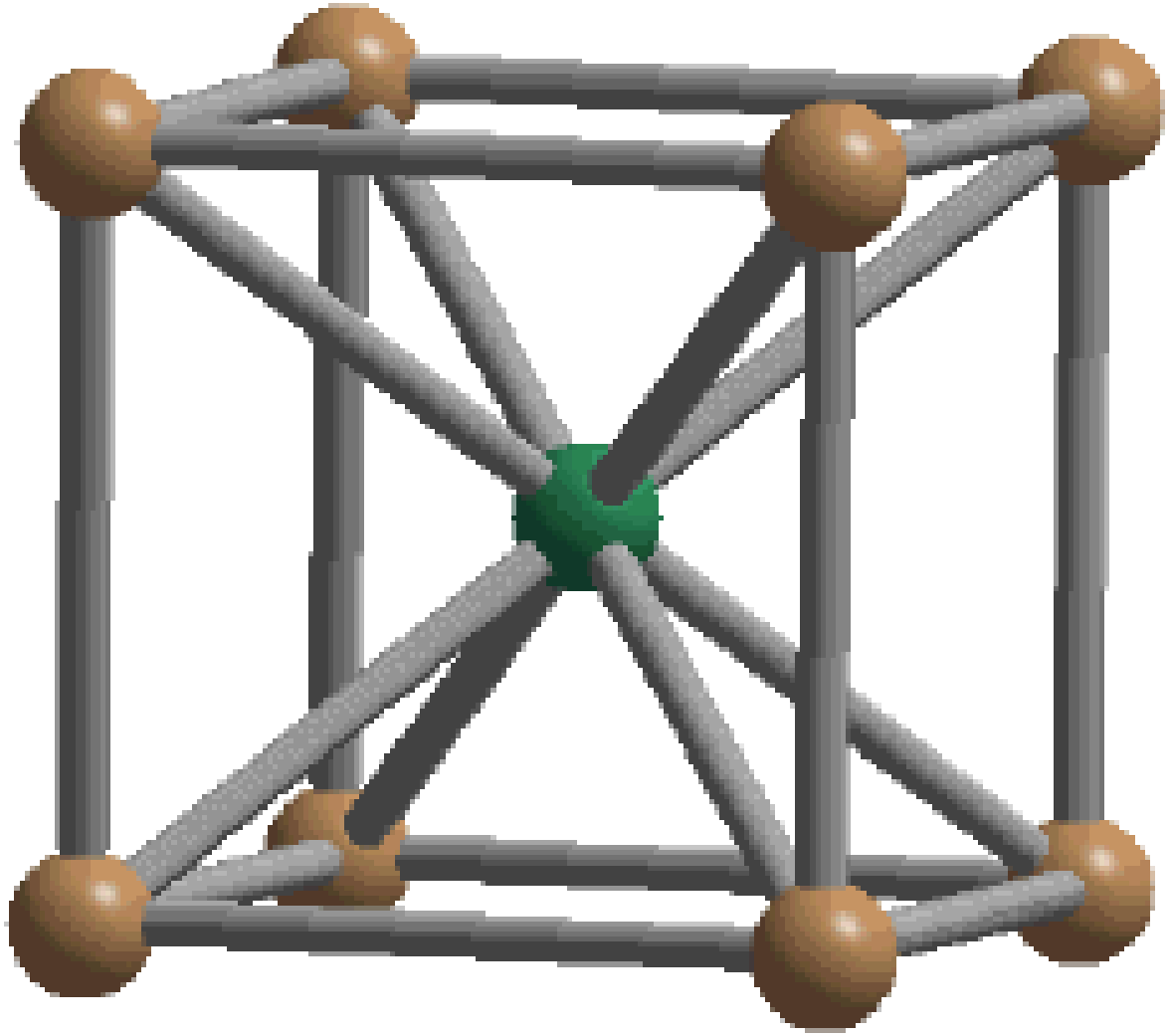


6



- **Coordination # = 6**
  (# nearest neighbors)

BCC-coordination number



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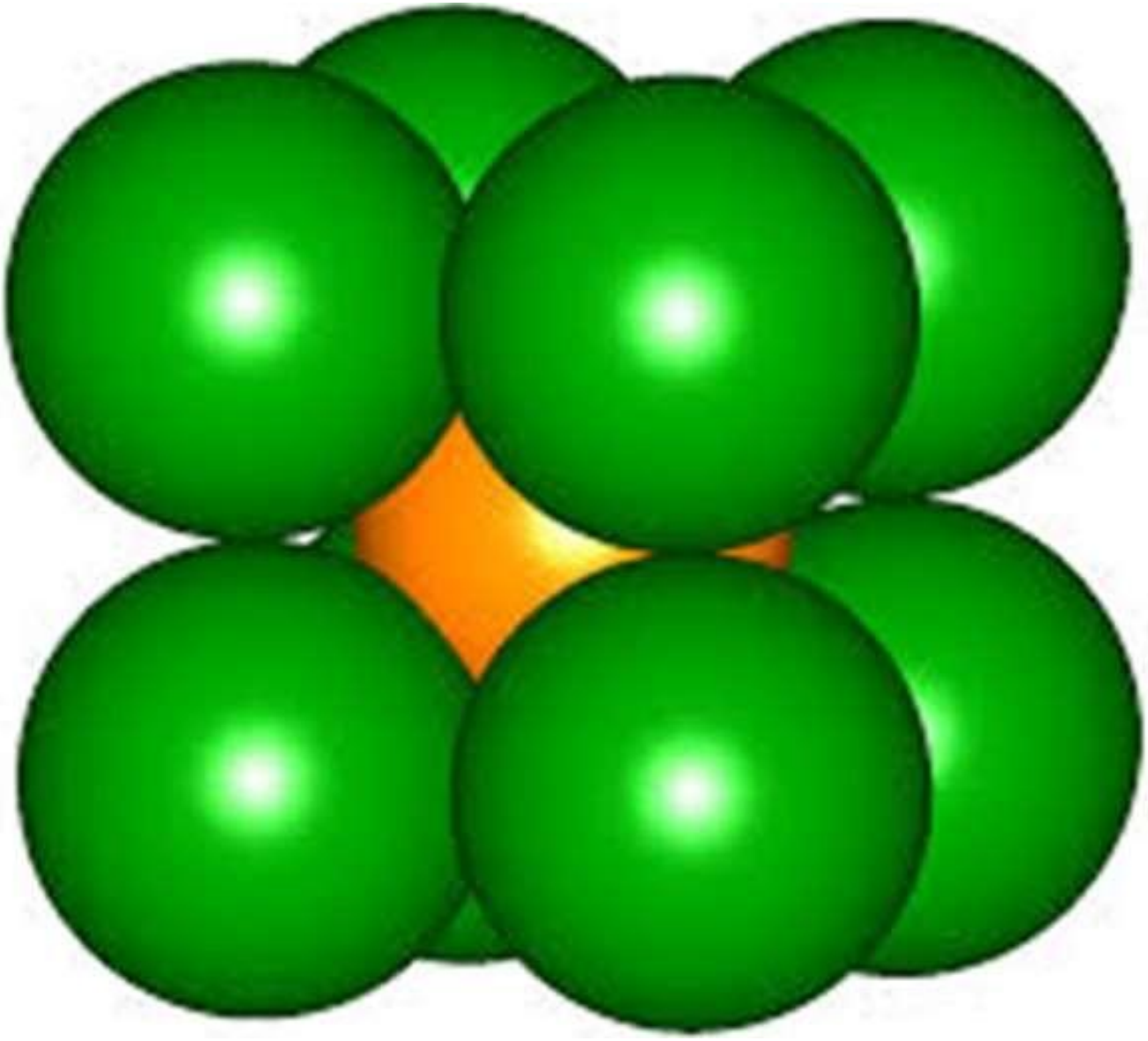
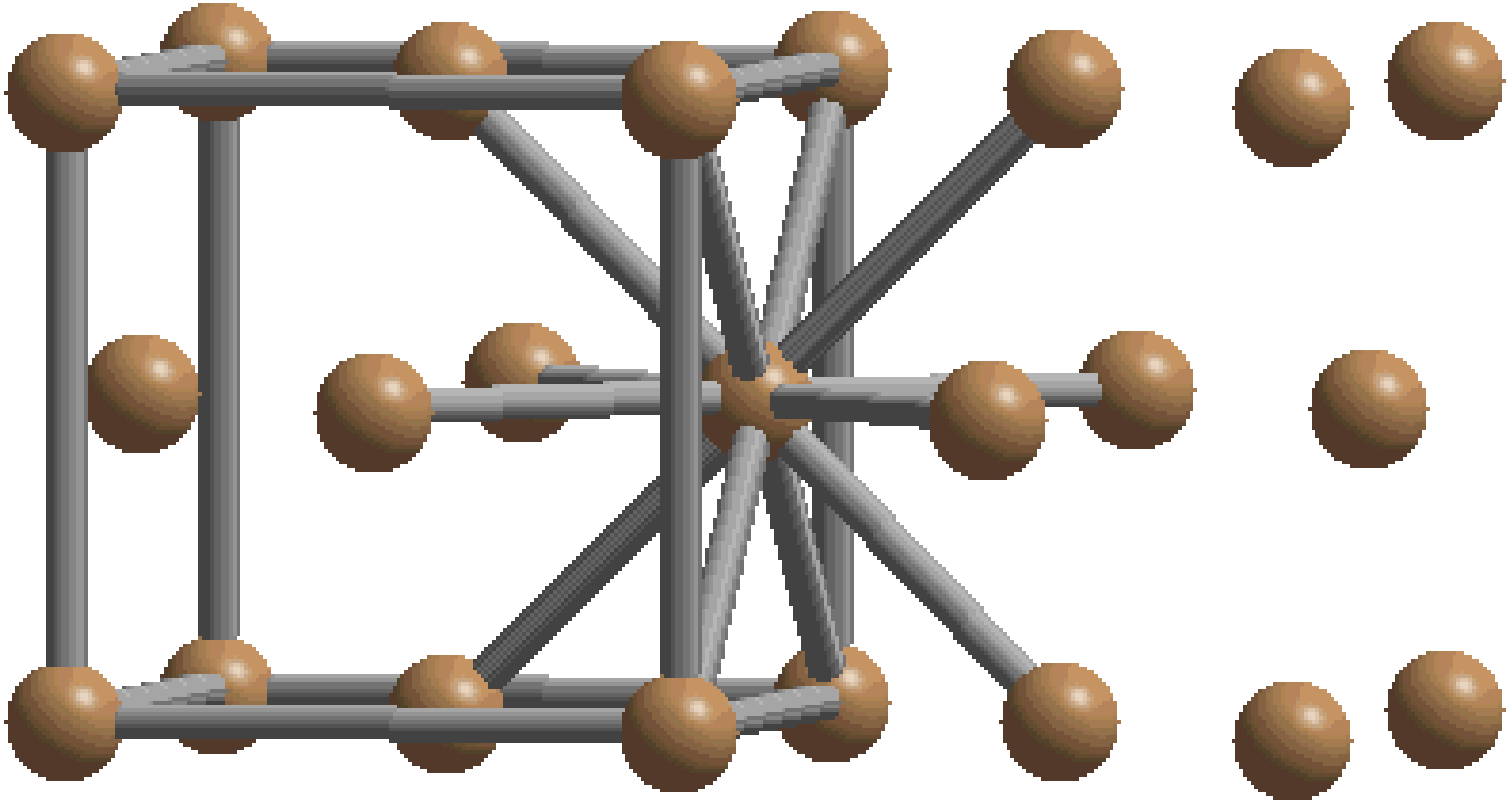
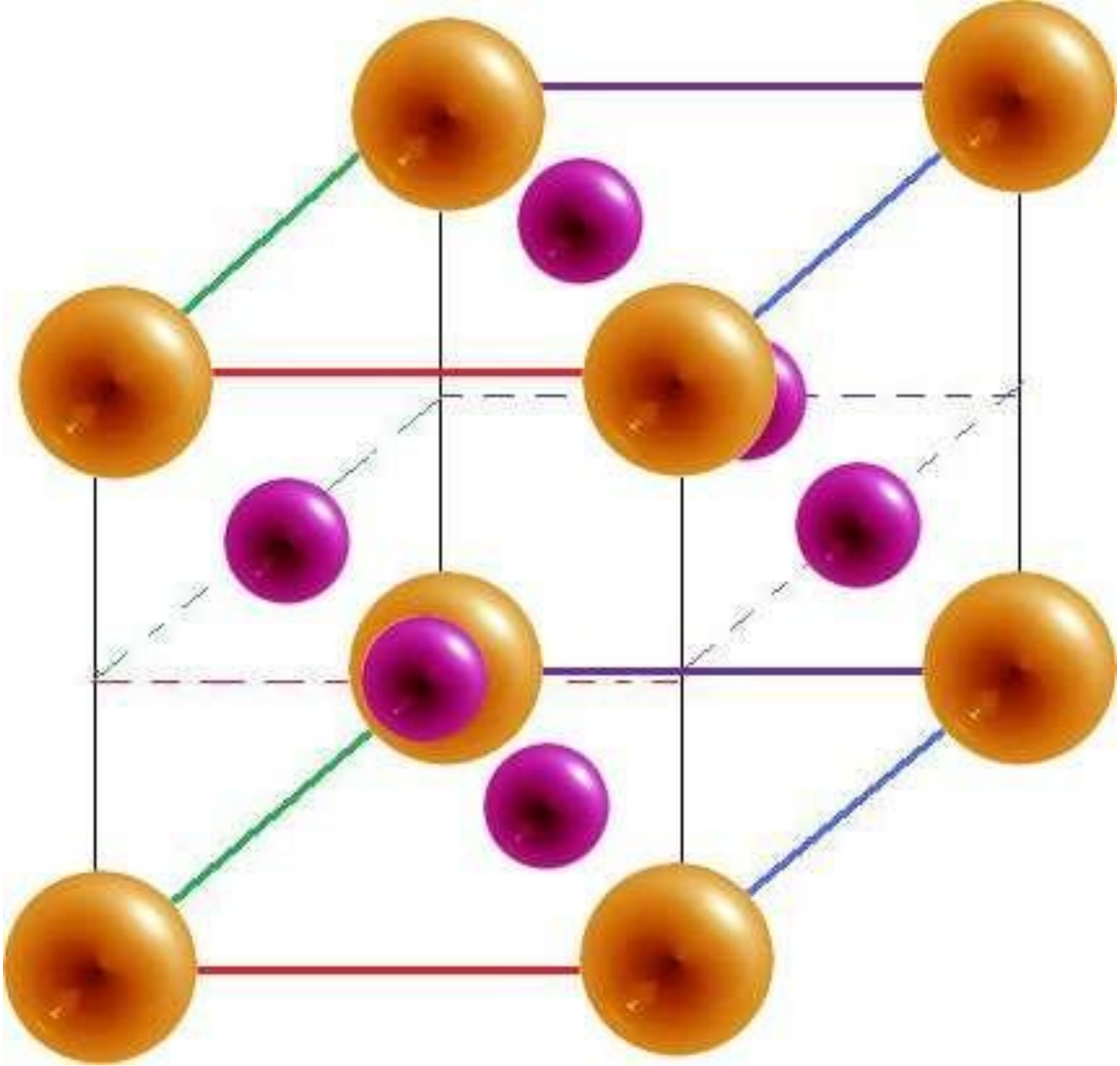


FCC-coordination number



4+4+4=12



Theoretical Density, ρ

$$\text{Density} = \rho = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}}$$

$$\rho = \frac{n A}{V_C N_A}$$

where n = number of atoms/unit cell

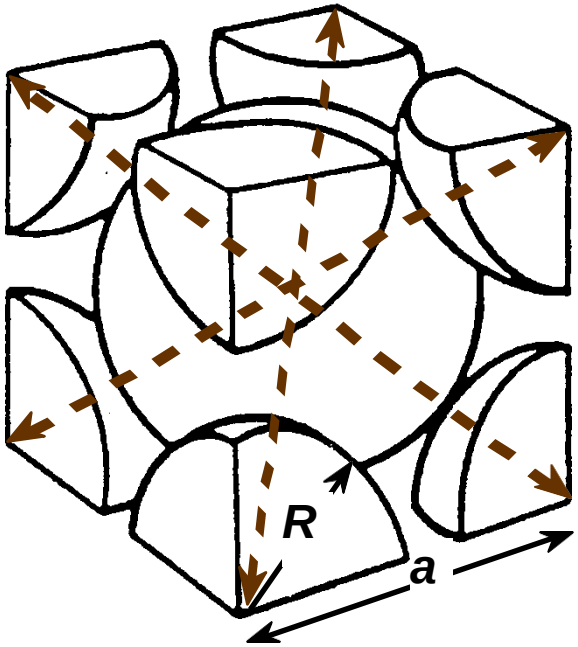
A = atomic weight

V_C = Volume of unit cell = a^3 for cubic

N_A = Avogadro's number

= 6.023×10^{23} atoms/mol

Theoretical Density, ρ



- Ex: Cr (BCC)

  A = 52.00 g/mol

  R = 0.125 nm

  n = 2

$$a = 4R/\sqrt{3} = 0.2887 \text{ nm}$$

$$\rho = \frac{\text{atoms}}{\text{unit cell}} \times \frac{\text{g}}{\text{mol}} \Big/ \left(\text{volume} \times \frac{\text{atoms}}{\text{mol}} \right)$$

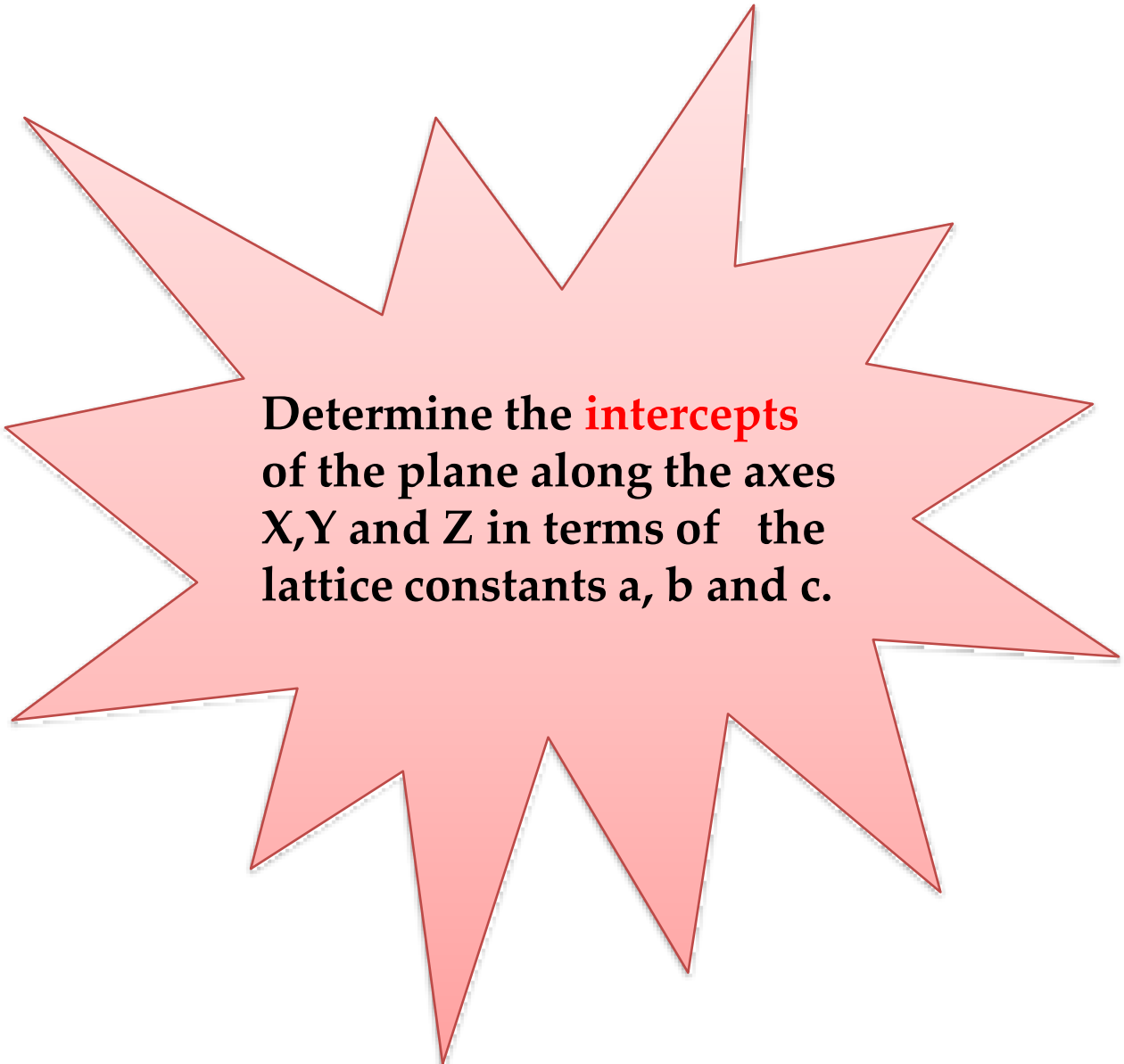
$$\rho = \frac{2 \times 52.00}{a^3 \times 6.023 \times 10^{23}}$$

$\rho_{theoretical}$	= 7.18 g/cm³
ρ_{actual}	= 7.19 g/cm³

Miller indices

Miller indices: defined as the reciprocals of the intercepts made by the plane on the three axes.

Procedure for finding Miller indices



Step 2

Determine the reciprocals of these numbers.

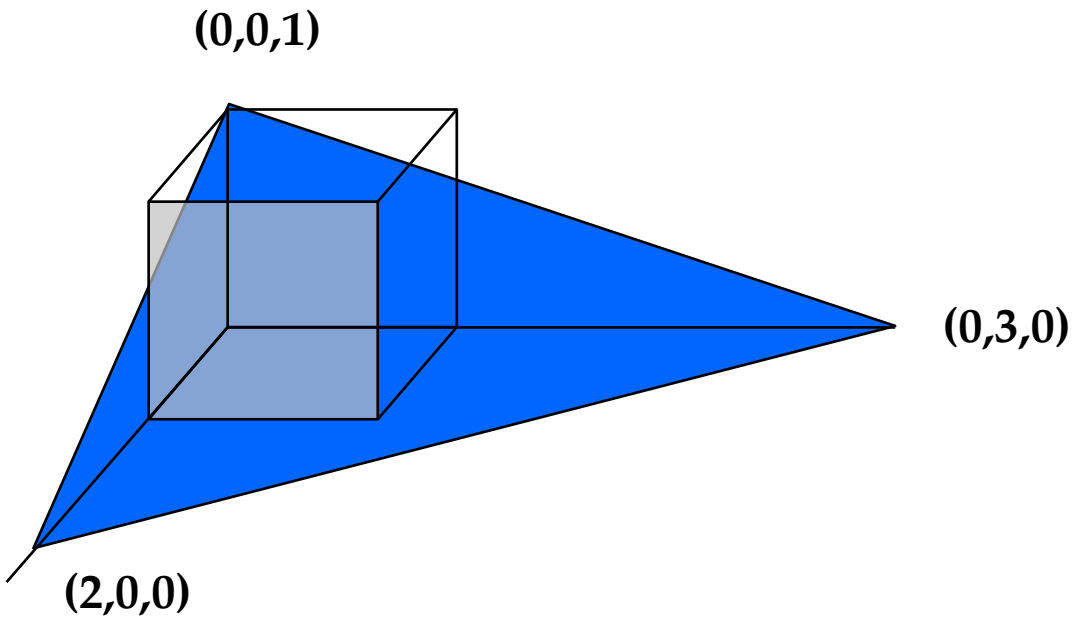
Step 3

Find the least common denominator (*lcd*) and multiply each by this *lcd*

Step 4

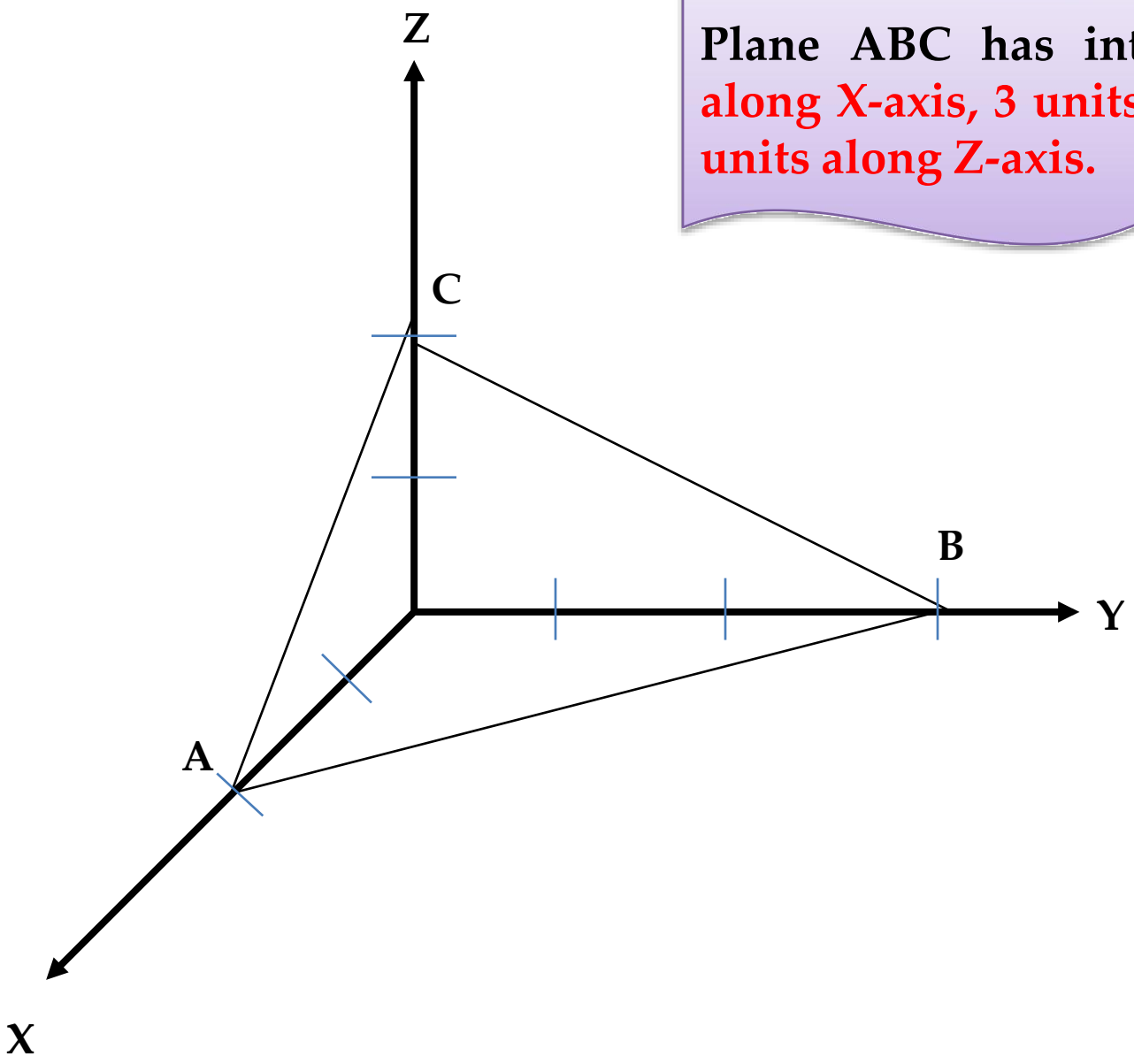
The result is written in parenthesis.
This is called the `Miller Indices' of the plane in the form (h k l).

Miller Indices for planes



- Find intercepts along axes → 2 3 1
- Take reciprocal → 1/2 1/3 1
- Convert to smallest integers in the same ratio → 3 2 6
- Enclose in parenthesis → (326)

Plane ABC has intercepts of 2 units along X-axis, 3 units along Y-axis and 2 units along Z-axis.



DETERMINATION OF 'MILLER INDICES'

Step 1: The intercepts are 2, 3 and 2 on the three axes.

Step 2: The reciprocals are 1/2, 1/3 and 1/2.

Step 3: The least common denominator is '6'.
Multiplying each reciprocal by lcd, we get, 3,2 and 3.

Step 4: Hence Miller indices for the plane ABC is (3 2 3)

IMPORTANT FEATURES OF MILLER INDICES

For the cubic crystal especially, the important features of Miller indices are,

- **A plane which is parallel to any one of the co-ordinate axes has an intercept of infinity (∞).**
- **Therefore the Miller index for that axis is zero; i.e. for an intercept at infinity, the corresponding index is zero.**
- **A plane passing through the origin is defined in terms of a parallel plane having non zero intercepts.**
- **All equally spaced parallel planes have same 'Miller indices' i.e. The Miller indices do not only define a particular plane but also a set of parallel planes.**
- **Thus the planes whose intercepts are 1, 1,1; 2,2,2; -3,-3,-3 etc., are all represented by the same set of Miller indices.**

Worked Example:

✓ *Calculate the miller indices for the plane with intercepts 2a, - 3b and 4c the along the crystallographic axes.*

- **The intercepts are 2, - 3 and 4**

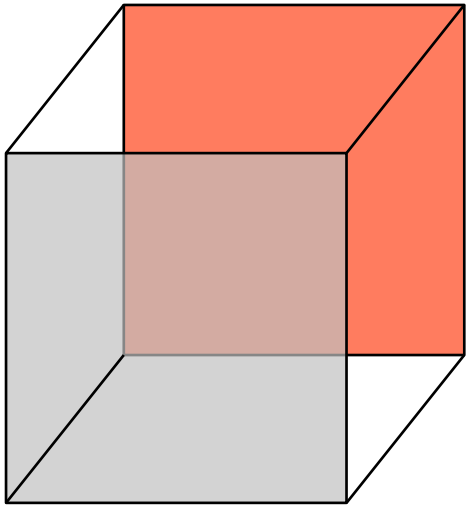
✓ **Step 1: The intercepts are 2, -3 and 4 along the 3 axes**

✓ **Step 2: The reciprocals are**

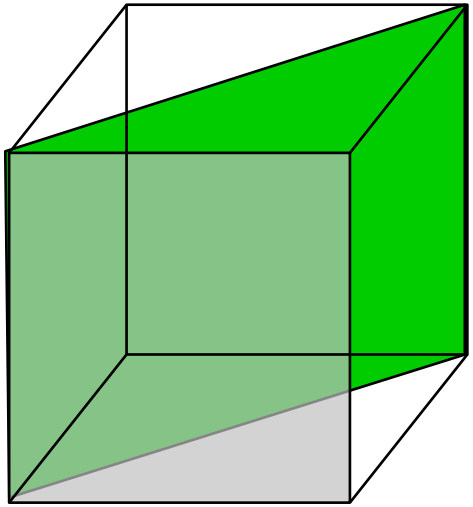
✓ **Step 3: The least common denominator is 12.**

Multiplying each reciprocal by lcd, we get 6 -4 and 3

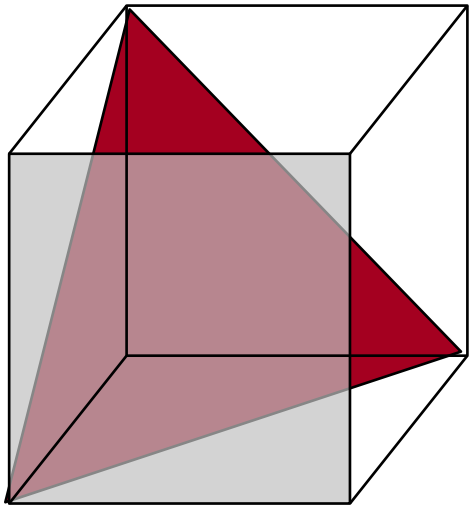
Step 4: Hence the Miller indices for the plane is $(6\ 4\ 3)$



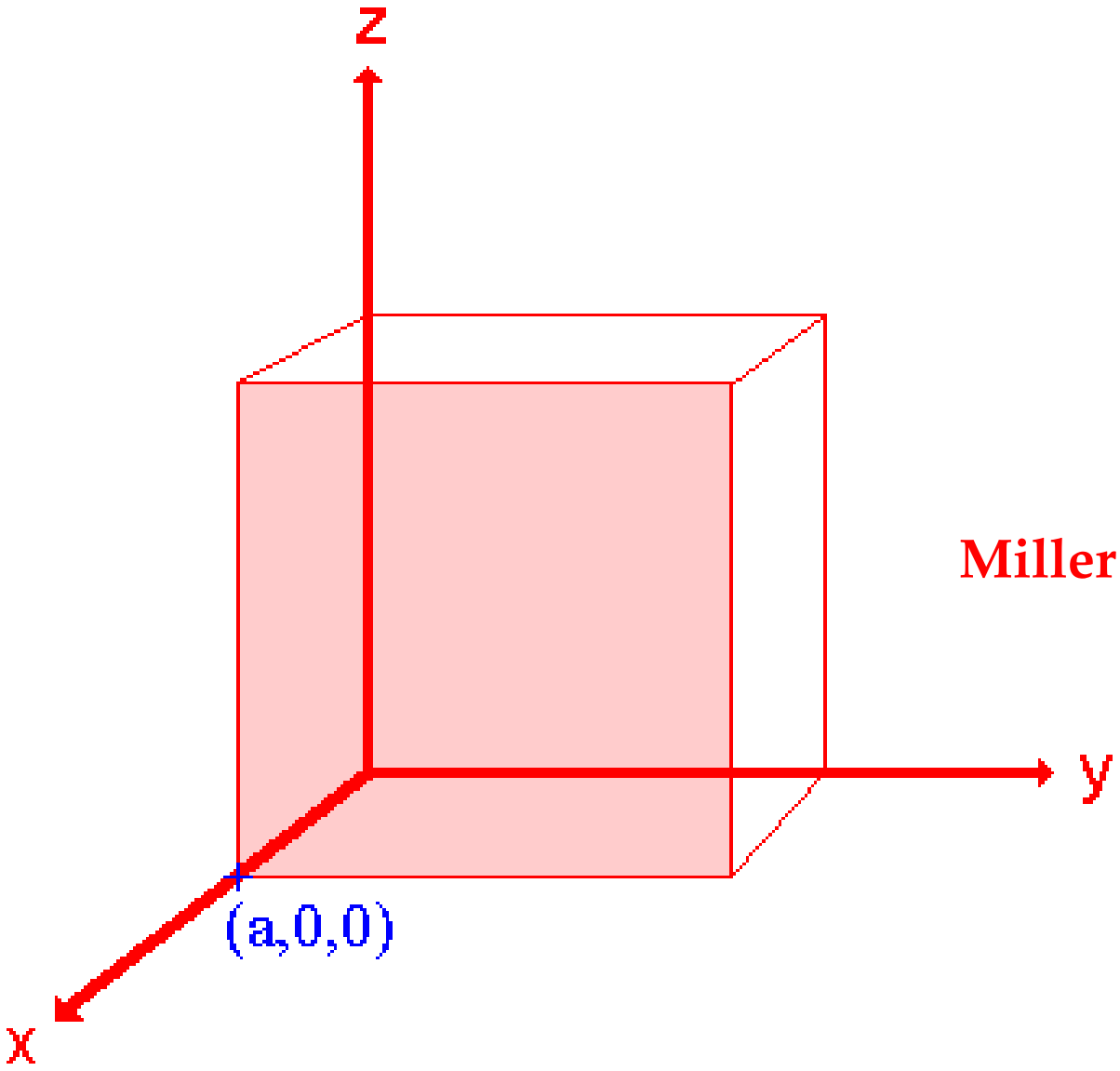
Intercepts → 1 ∞ ∞
Plane → (100)
Family → {100} → 3



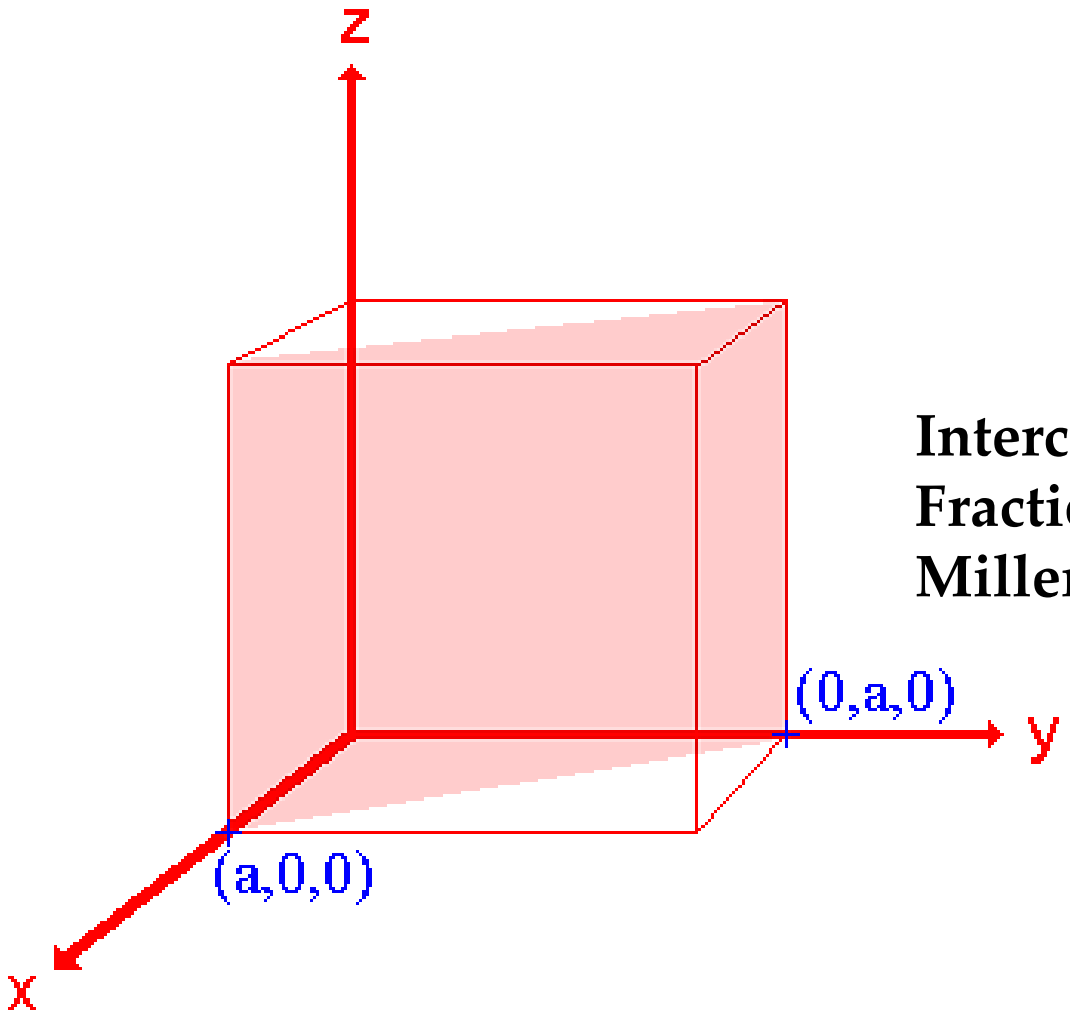
Intercepts → 1 1 ∞
Plane → (110)
Family → {110} → 6



Intercepts → 1 1 1
Plane → (111)
Family → {111} → 8
(Octahedral plane)



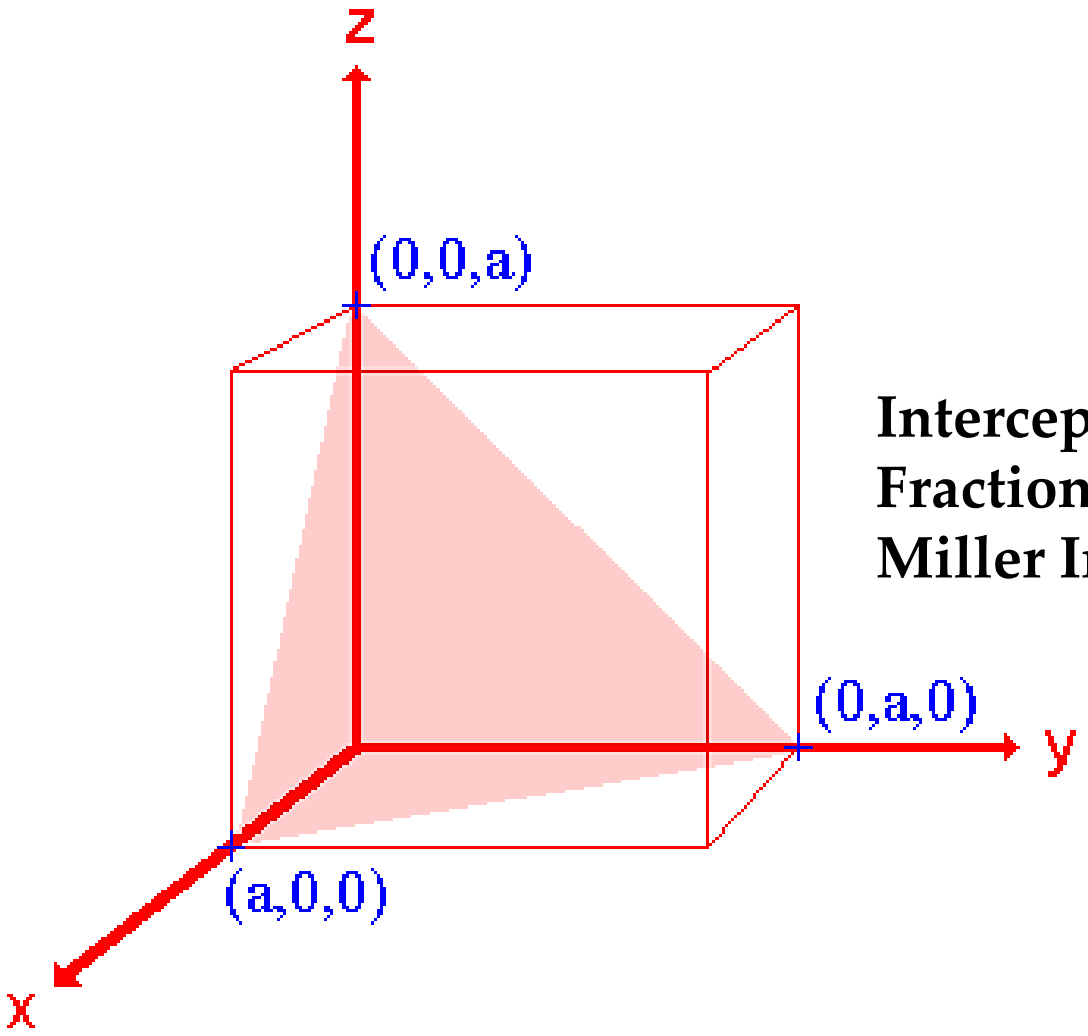
Miller Indices : (100)



Intercepts : a , a , ∞

Fractional intercepts : 1 , 1 , ∞

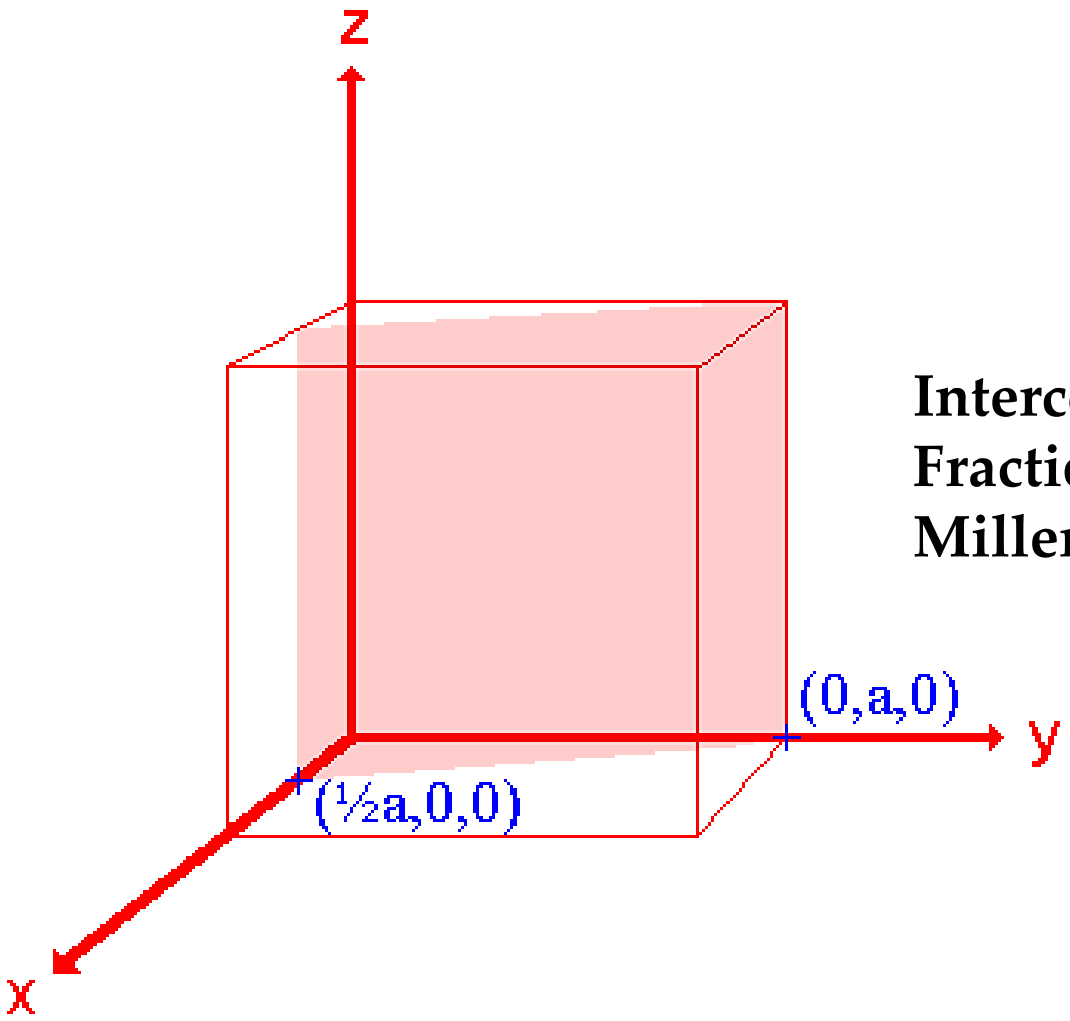
Miller Indices : (110)



Intercepts : a , a , a

Fractional intercepts : 1 , 1 , 1

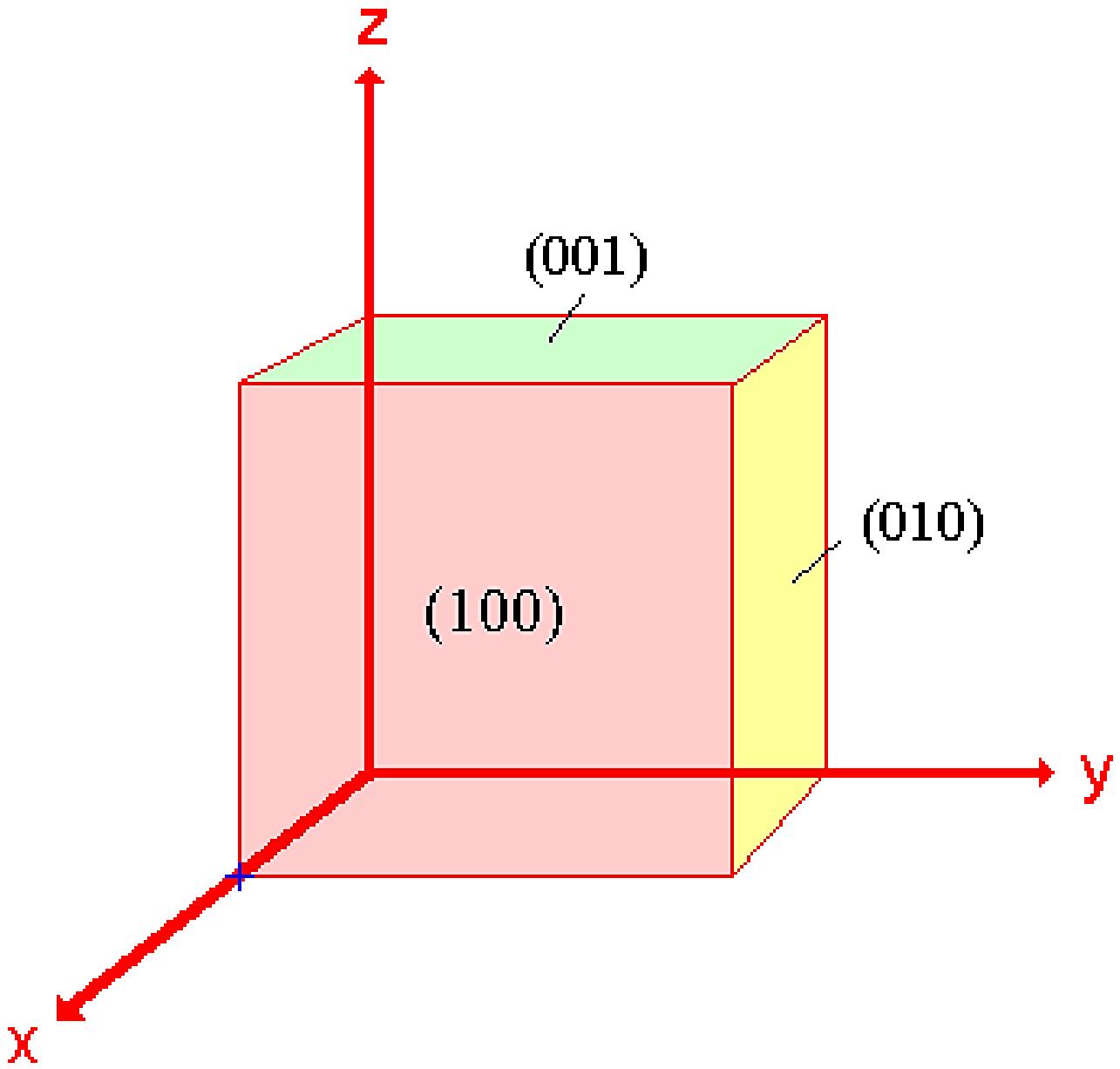
Miller Indices : (111)

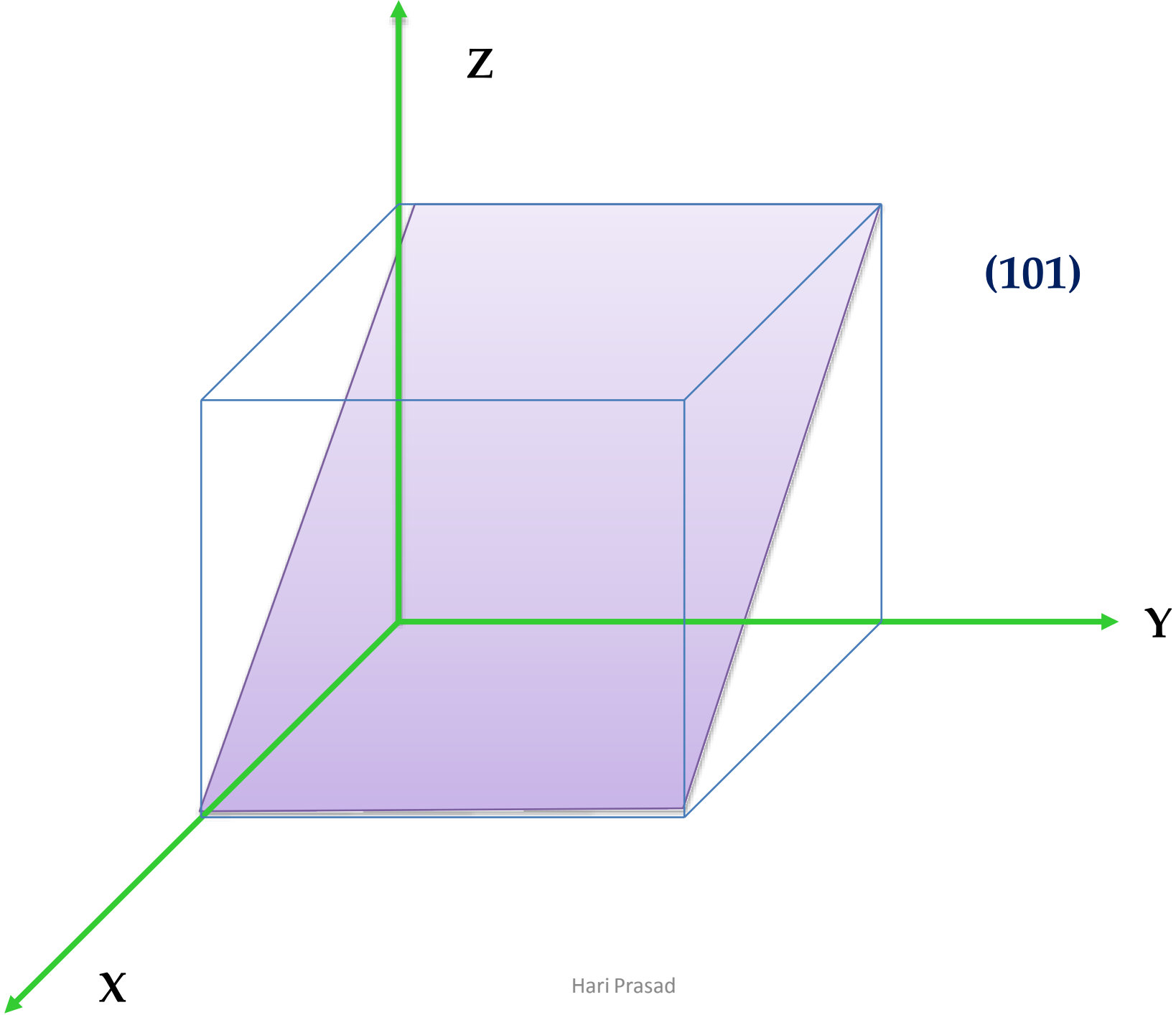


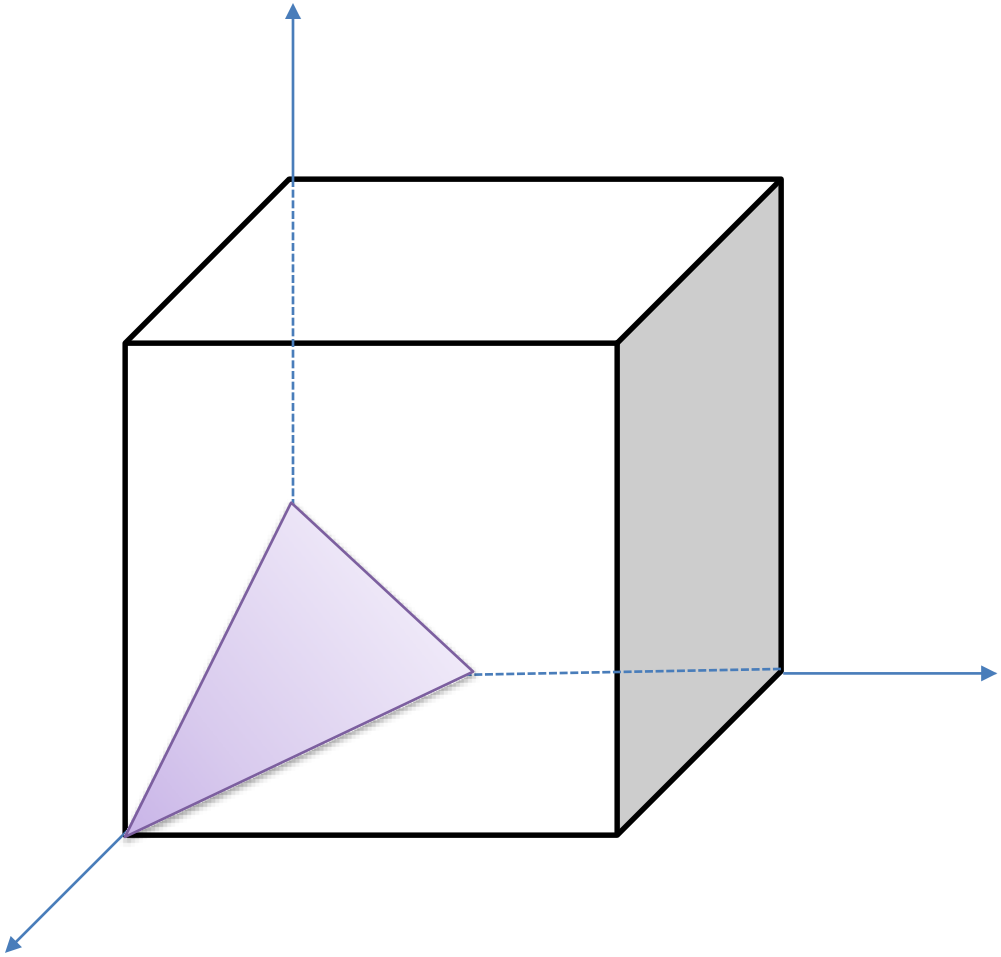
Intercepts : ½ *a* , *a* , ∞

Fractional intercepts : ½ , 1 , ∞

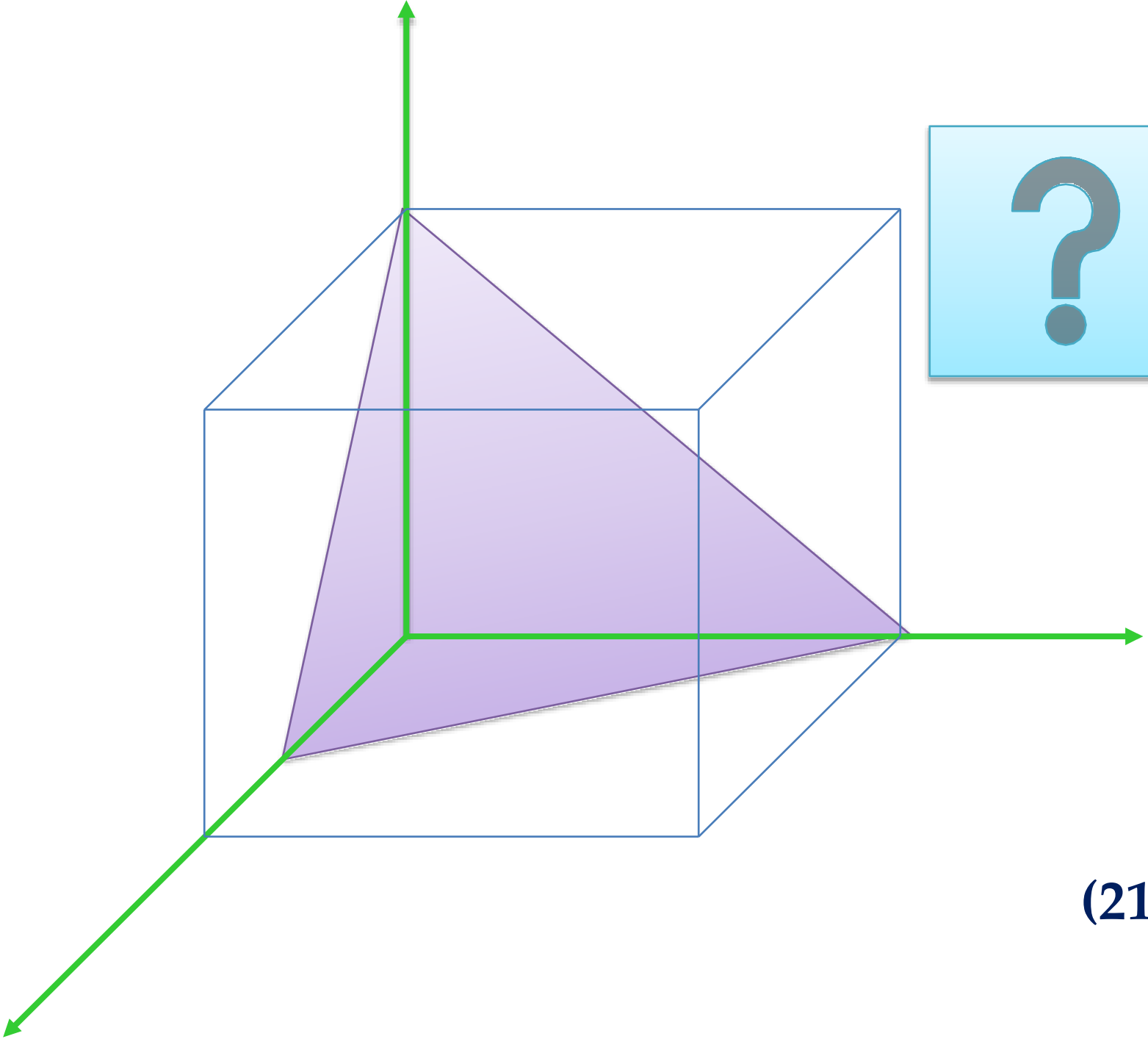
Miller Indices : (210)


z
(001)
(010)
(100)
y
x


Z
Y
X
(101)



(122)



(211)

Crystallographic Directions

- **The crystallographic directions are fictitious lines linking nodes (atoms, ions or molecules) of a crystal.**
- **Similarly, the crystallographic planes are fictitious *planes* linking nodes.**
- **The length of the vector projection on each of the three axes is determined; *these are measured in terms of the unit cell dimensions a, b, and c.***

- To find the Miller indices of a direction, Choose a perpendicular plane to that direction.
- Find the Miller indices of that perpendicular plane.
- The perpendicular plane and the direction have the same Miller indices value.
- Therefore, the Miller indices of the perpendicular plane is written within a square bracket to represent the Miller indices of the direction like [ ].