Chapter 1

Crystal Structure

PHYS 432

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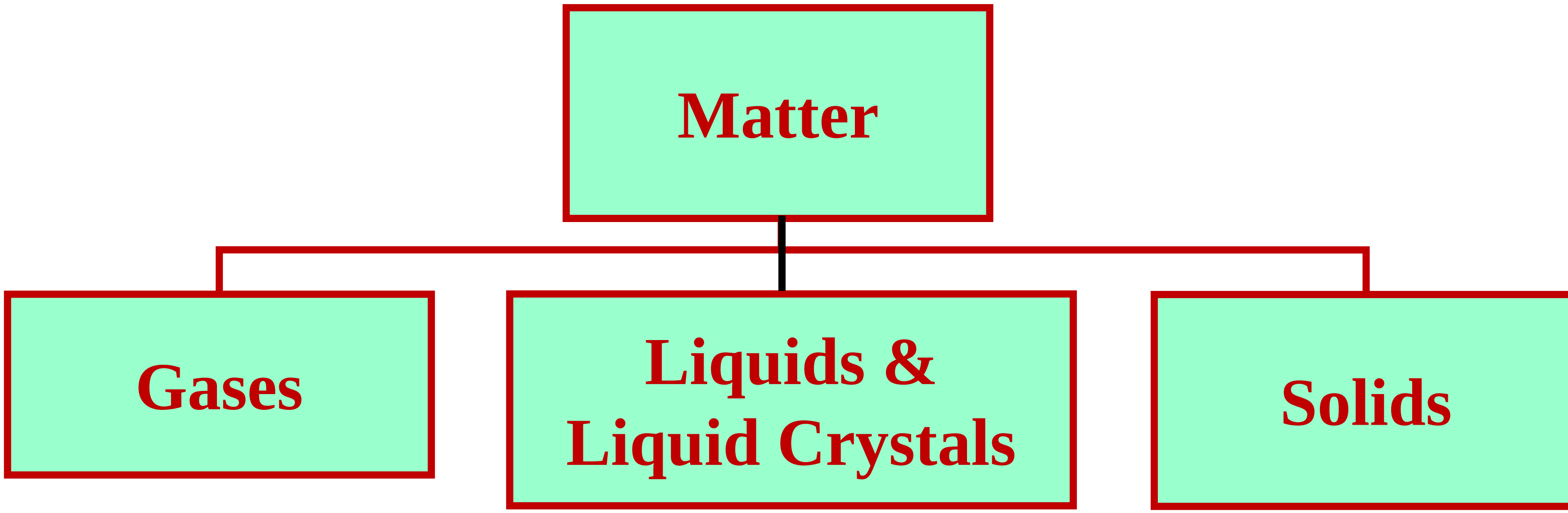
The (Common) Phases of Matter



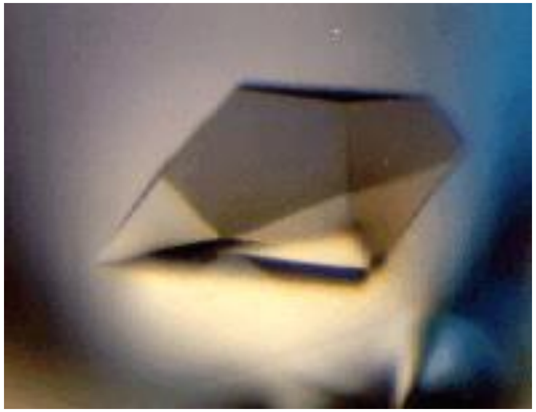
"Condensed Matter" includes ***Liquids, Liquid crystals, and Solids.***

However, our focus in this course is on studying the physics of ***Solids!***

"Solid State Physics"

Crystals are Everywhere!



What are Crystals?

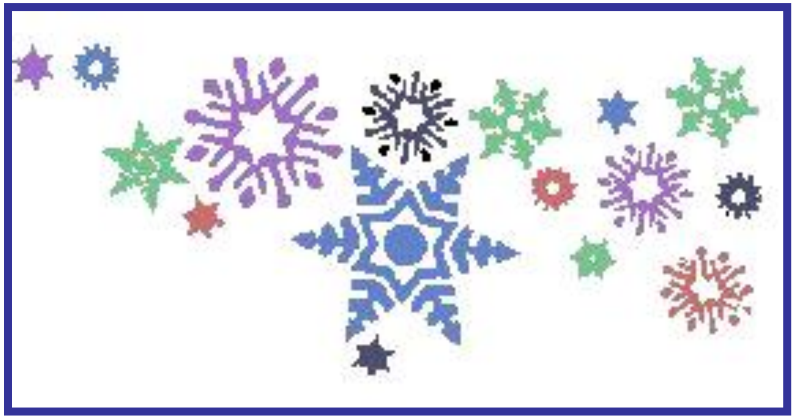
- A crystal or crystalline solid is a solid material whose constituent atoms, molecules, or ions are arranged in an orderly, repeating pattern extending in all three spatial dimensions.

Early ideas

- **All crystals are solids, but all solids are not crystalline!** For example, window glass may not be crystalline.

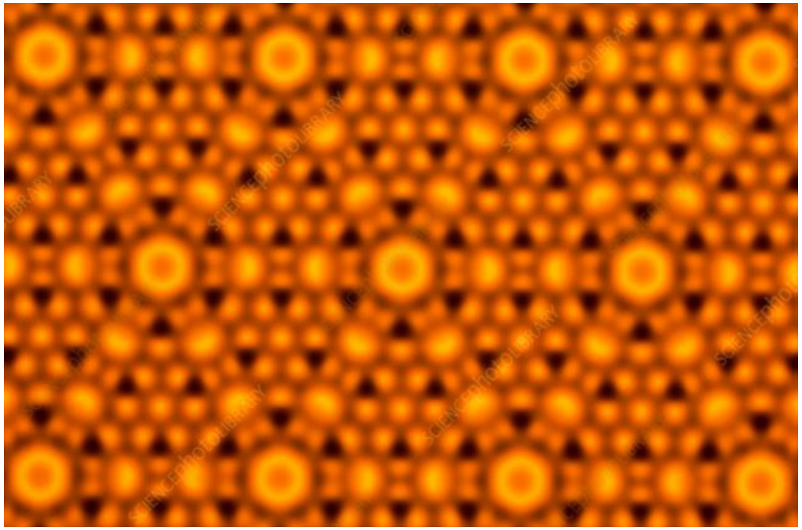
- Crystals have symmetry (**As first reported by Kepler who studied snowflakes!!**) & **long range order in atomic or molecular arrangement.**

- Spheres & small shapes can be packed to produce regular shapes.



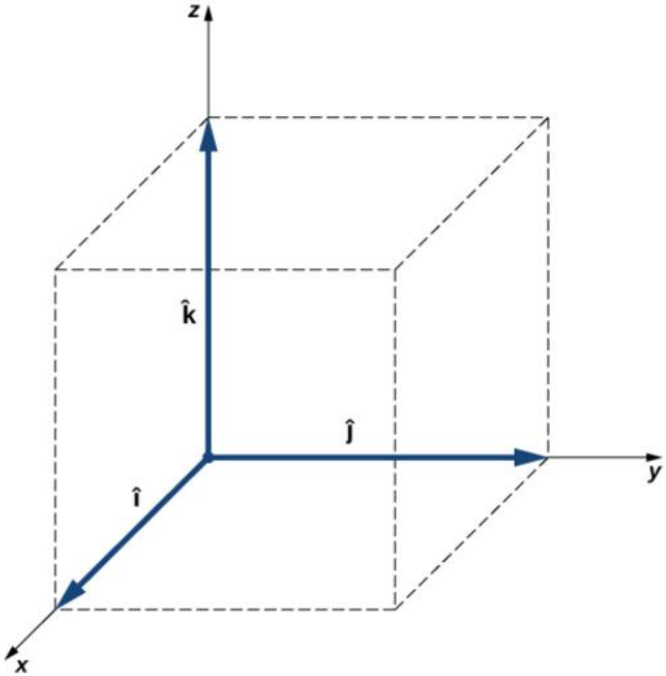
- Early studies led to the correct idea that crystals are regular three-dimensional arrays of atoms and molecules.

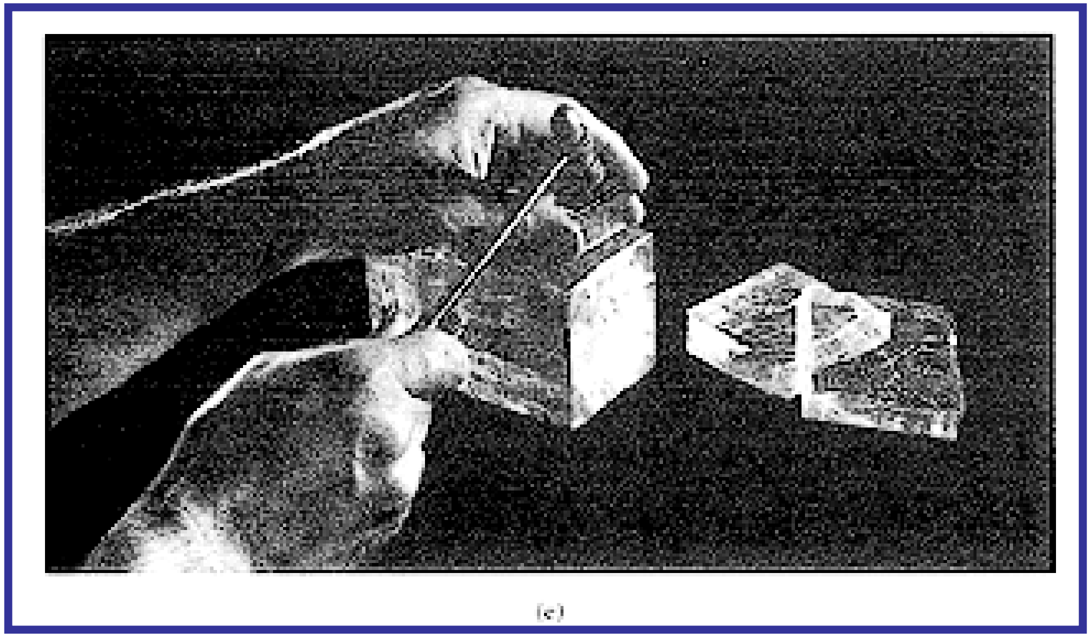
- A single ***unit cell*** is repeated indefinitely along three principal directions that are not necessarily perpendicular.



Experimental Evidence of periodic structures

• Early crystallographers noted that the index numbers that define plane orientations are exact integers. For example, (100), (110), (111) etc.

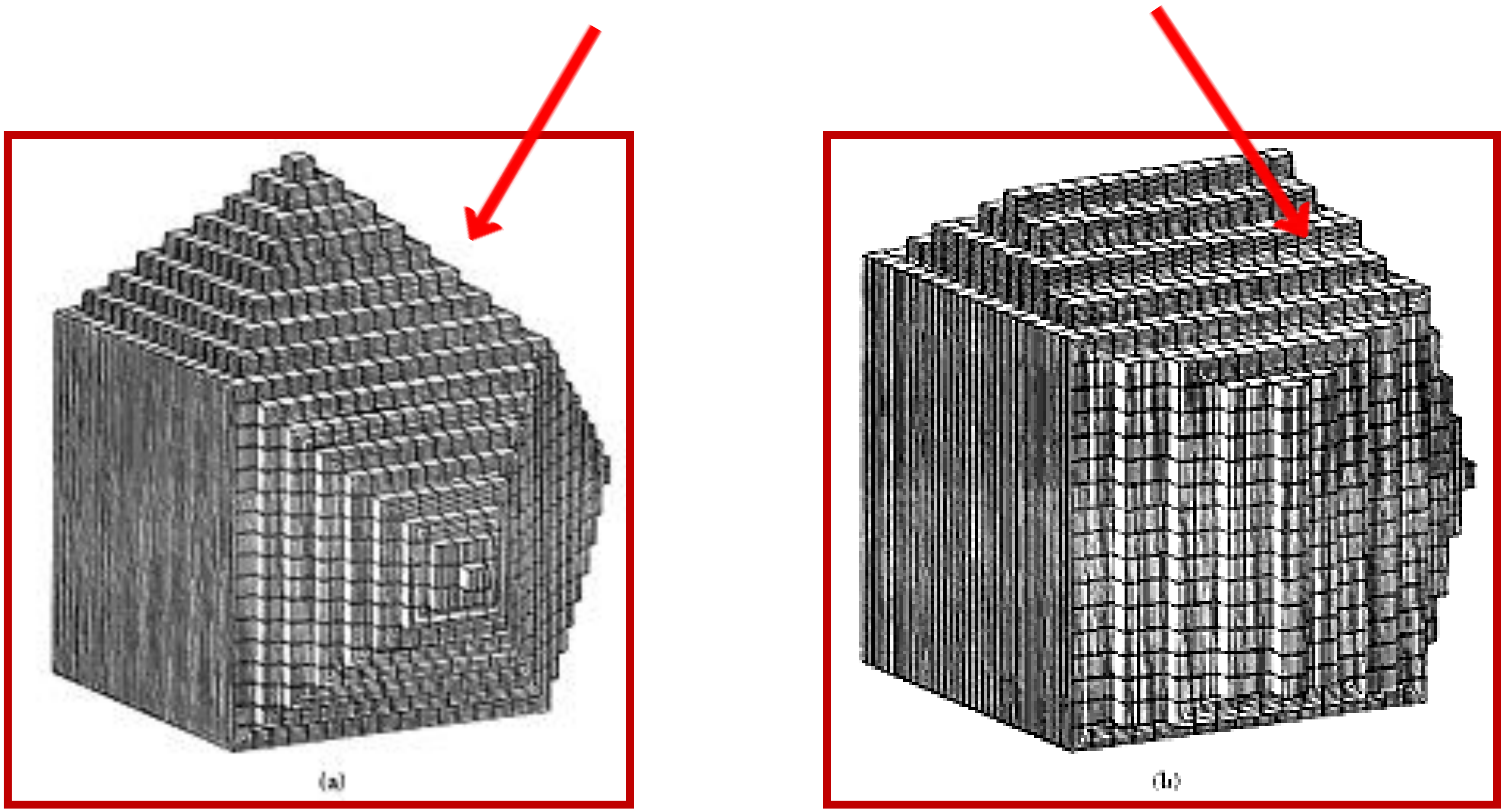




Cleaving a Crystal

Periodic Arrays of Atoms

- The external appearance of crystals gives some clues.
- The figure shows that when a crystal is cleaved, we can see that it is built up of identical "building blocks".

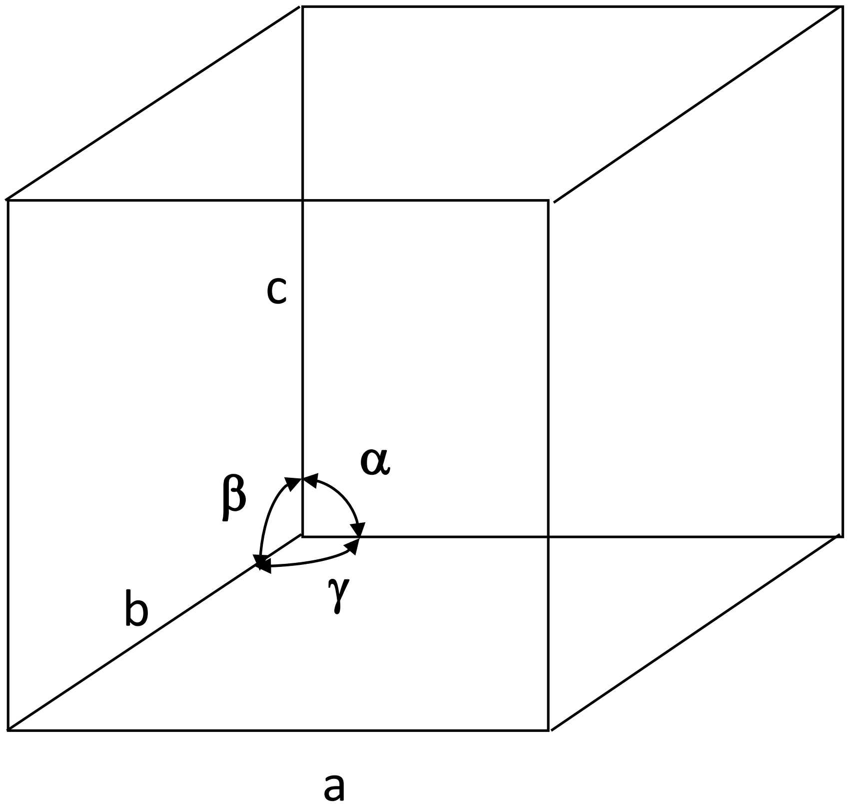


Crystallography

• A branch of science dealing with the geometric description of crystals and their internal arrangements.

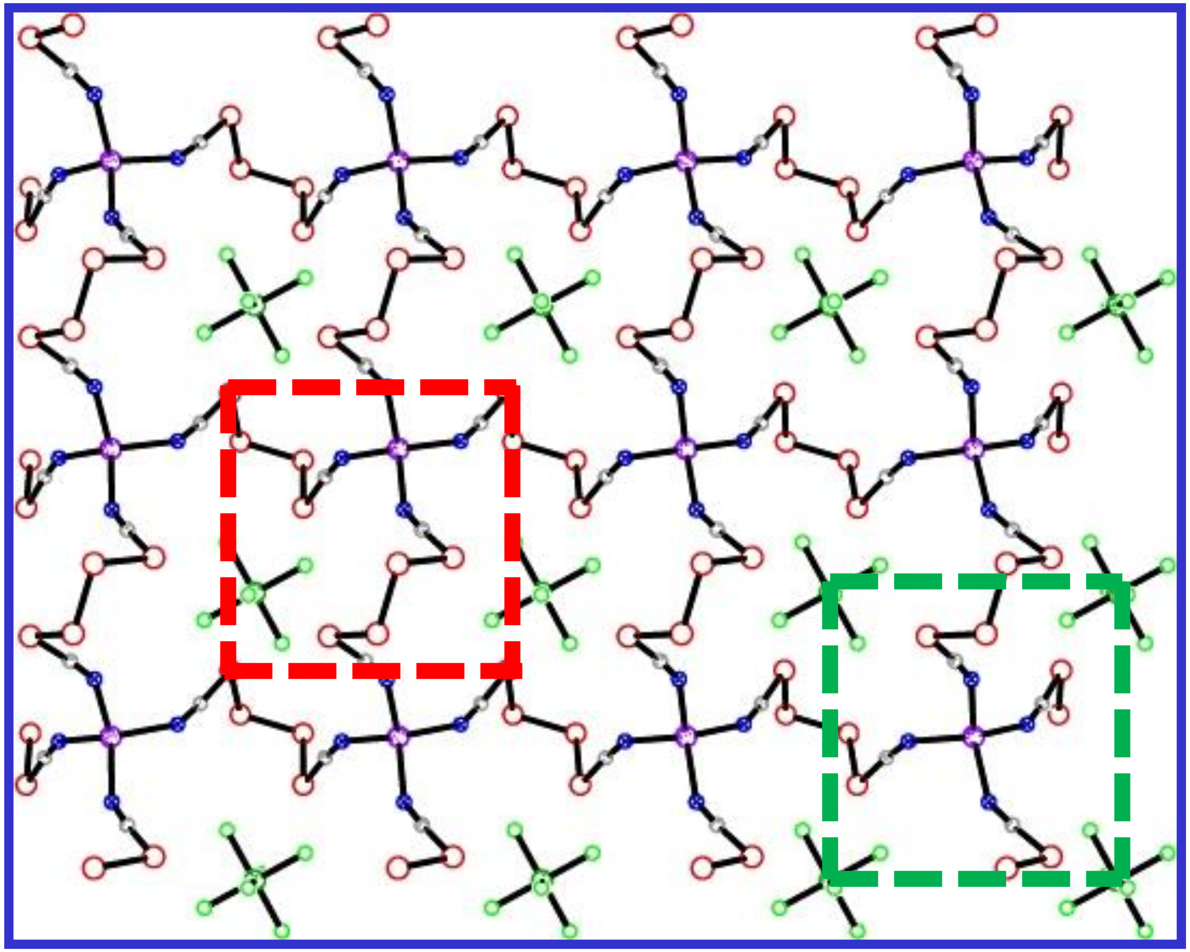
• It is also the science of crystals and the math used to describe them.

Unit Cell Description in Terms of Lattice Parameters

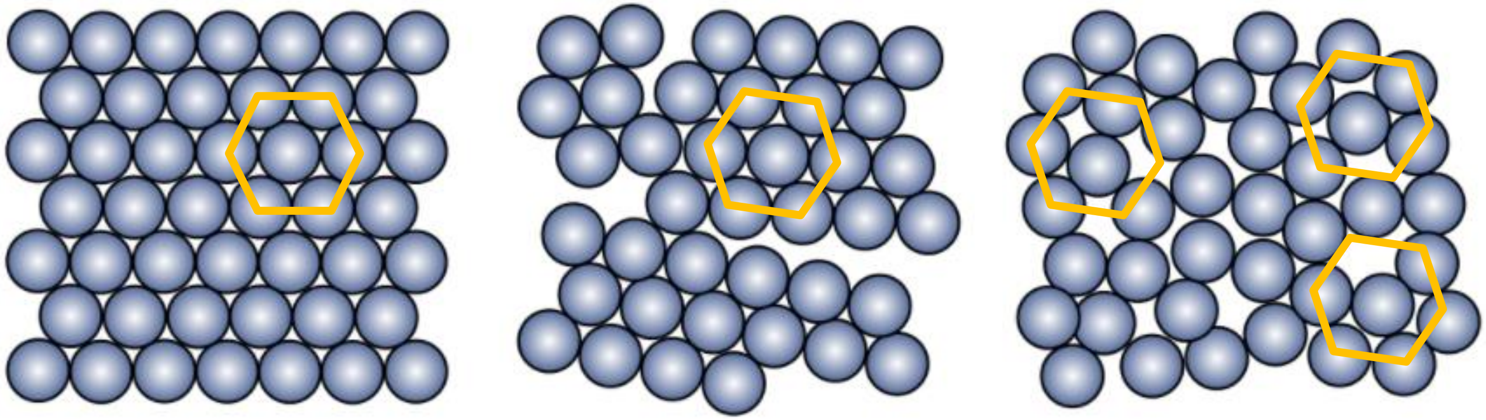


- **a ,b,** and **c** define the edge lengths (lattice constants) & are referred to as the **crystallographic axes**.
- The angles between these axes are **α, β,** and **γ**.
- The lattice parameters **a ,b, c, α, β,** and **γ** give dimensions of a unique unit cell.
- The unit cell is a building block for a crystal.

The Choice of the Unit Cell is ***Not Unique***!



- What is the difference between the following three figures?

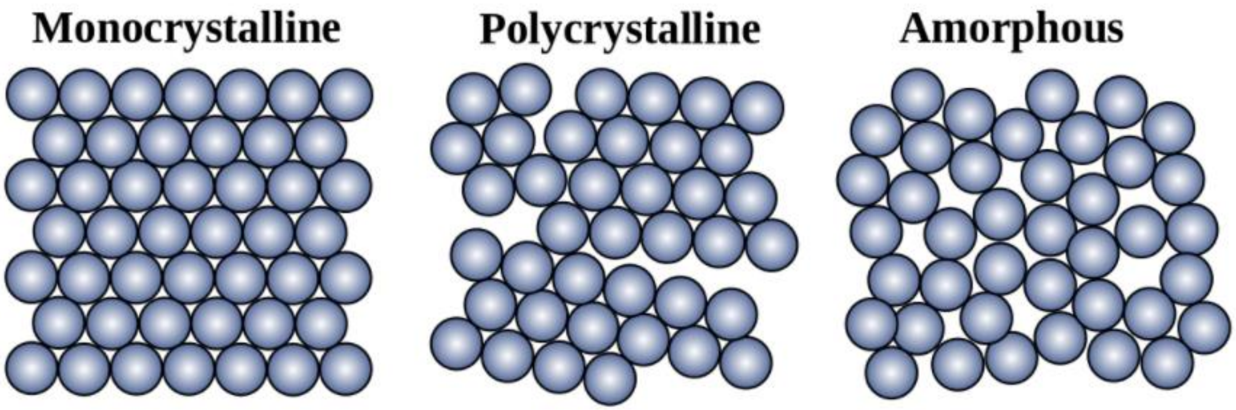


The Three General Types of Solids

- Single Crystal/Monocrystalline, Polycrystalline, and Amorphous

- Each type is characterized by the size of the ordered region within the material. An ordered region is a spatial volume in which atoms or molecules have a regular geometric arrangement or periodicity.

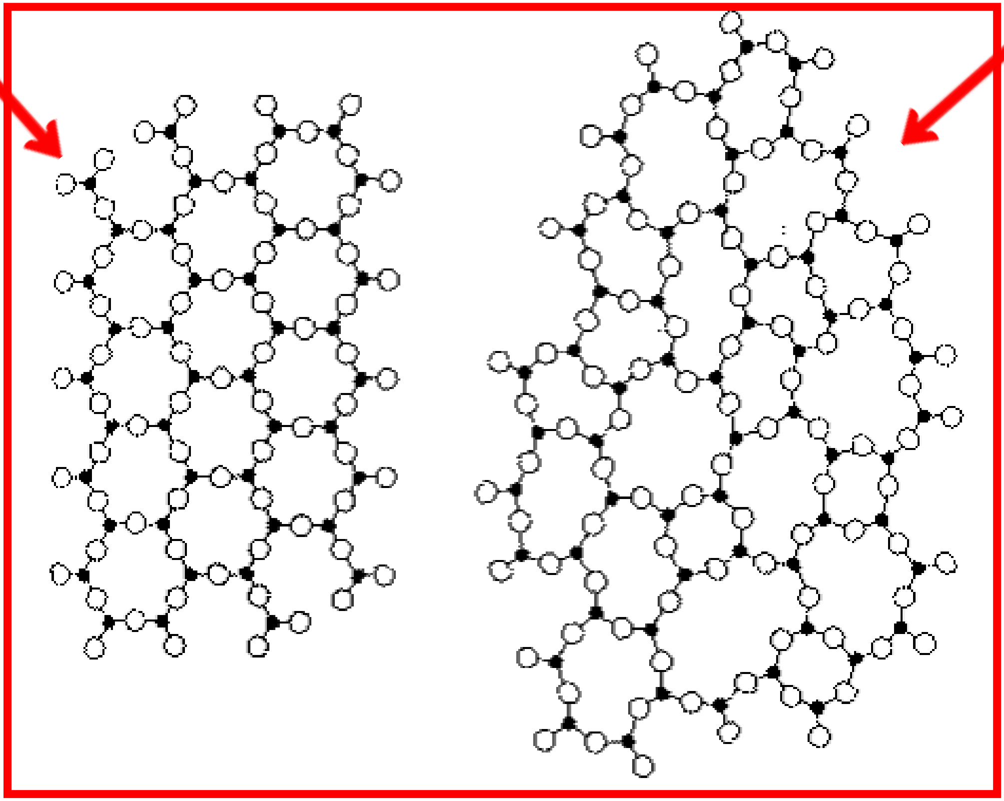
- In monocrystalline solids atoms/molecules have both short range and long range orders in the entire volume of the crystal.
- In polycrystalline solids atoms/molecules have short range and medium range orders in the crystal.
- In amorphous solids atoms/molecules may have short range order but no long medium or long range orders in the crystal.



The Three General Types of Solids

- **Crystals**:
  Short-range Order
  Long-range Order

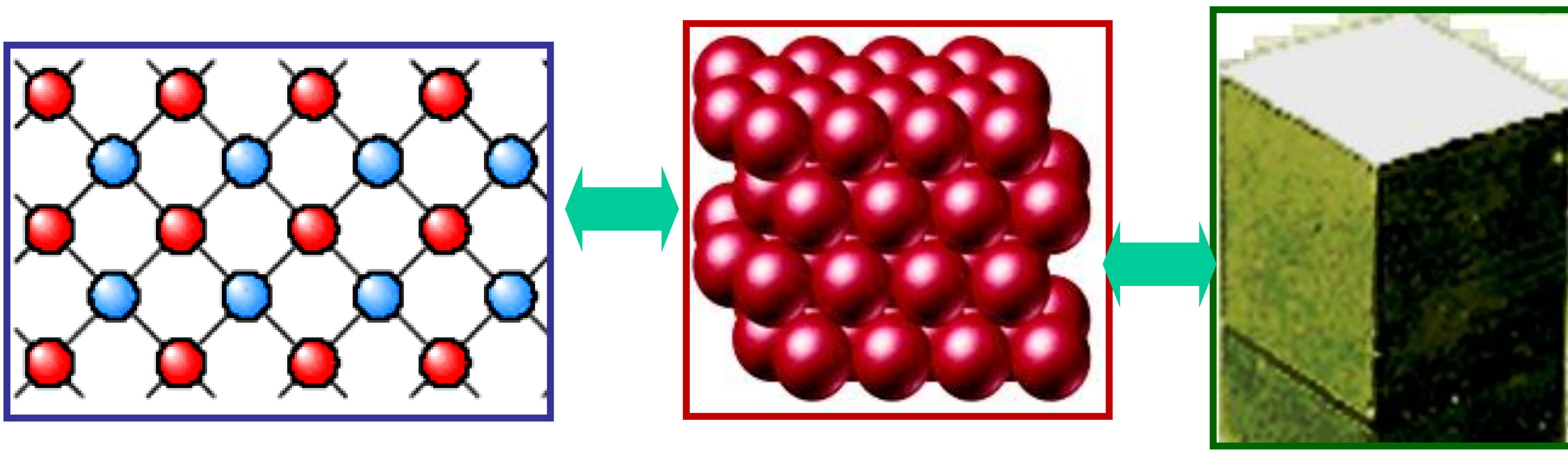
- **Amorphous solids**:
  ~Short-range Order
  No Long-range Order



Crystalline Solids

- A crystalline solid is the solid form of a substance in which the atoms or molecules are arranged in a definite, repeating pattern in three dimensions.

- Single crystals, ideally have a high degree of order, or regular geometric periodicity, throughout the entire volume of the material.



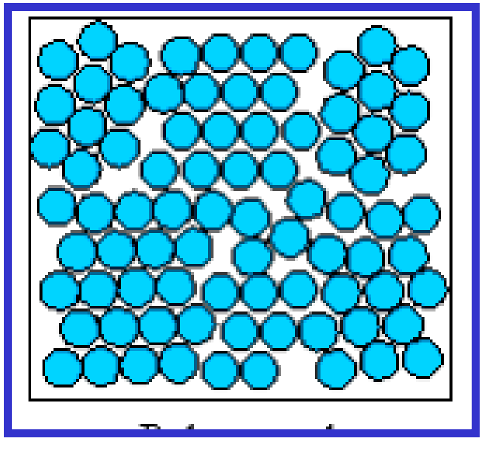
Polycrystalline Solids

- A Polycrystalline Solid is made up of an aggregate of many small single crystals (crystallites or grains).

- Polycrystalline materials have a high degree of order over many atomic or molecular dimensions.

- These ordered regions, or single crystal regions, vary in size and orientation with respect to one another.

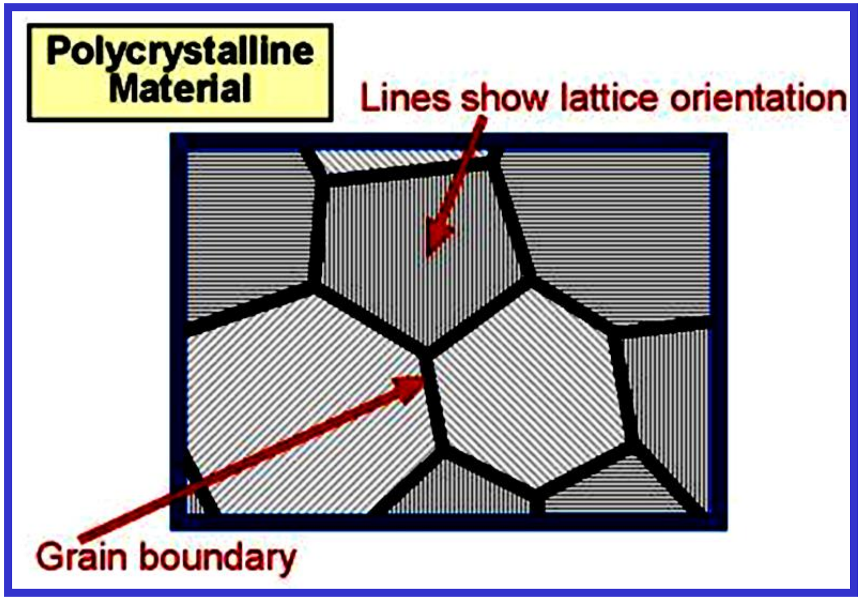
- These regions are called grains (or domains) and are separated from one another by grain boundaries.



Polycrystalline Solids

- In Polycrystalline Solids, the atomic order can vary from one domain to the next. The grains are usually 5 nm - 100 μm in diameter.

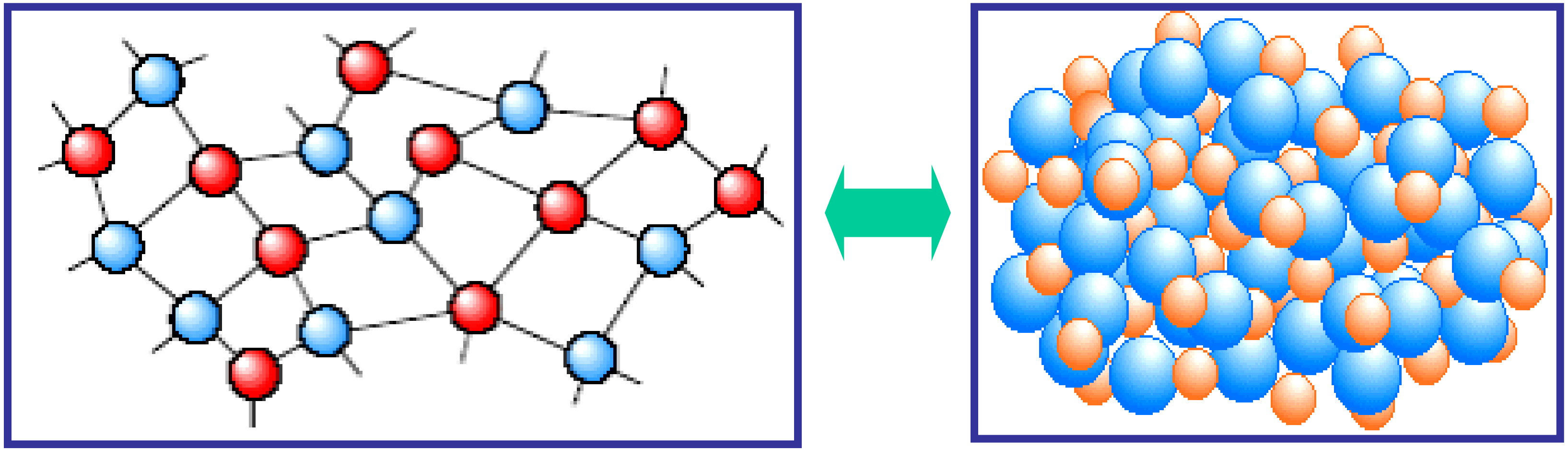
- Polycrystals with grains that are < 10 nm in diameter are called nanocrystallites.



Amorphous Solids

- Amorphous Solids are composed of randomly oriented atoms, ions, or molecules that do not form defined patterns or lattice structures.

- Examples of amorphous materials include amorphous silicon, plastics, polymers, glasses.



Amorphous Solids

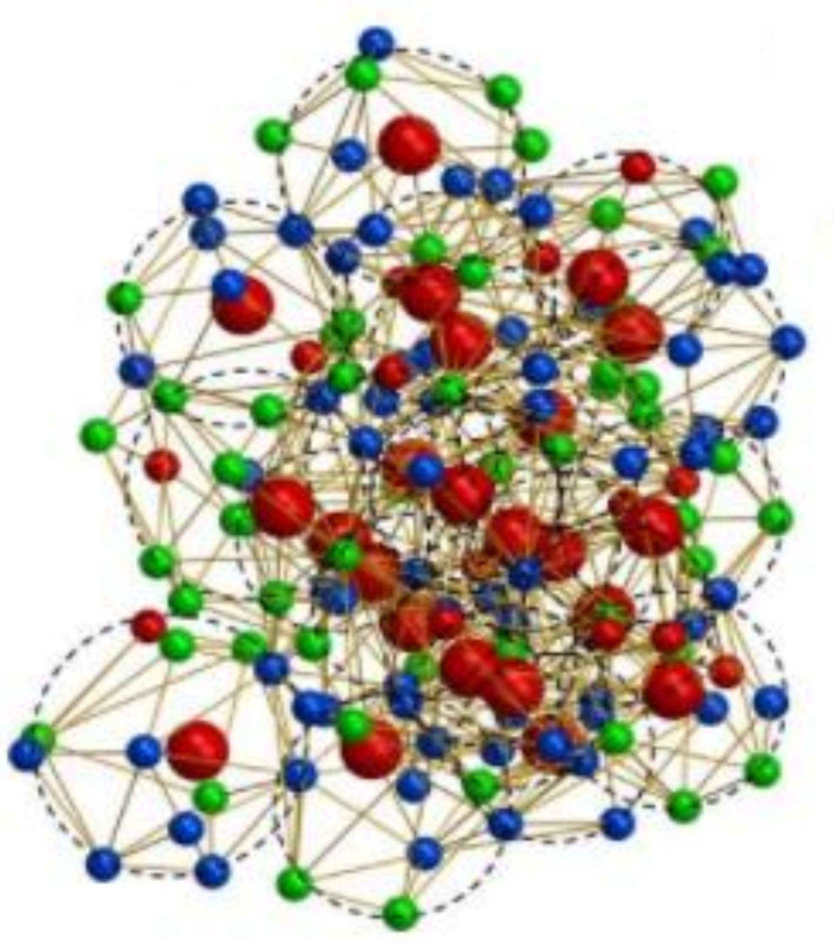


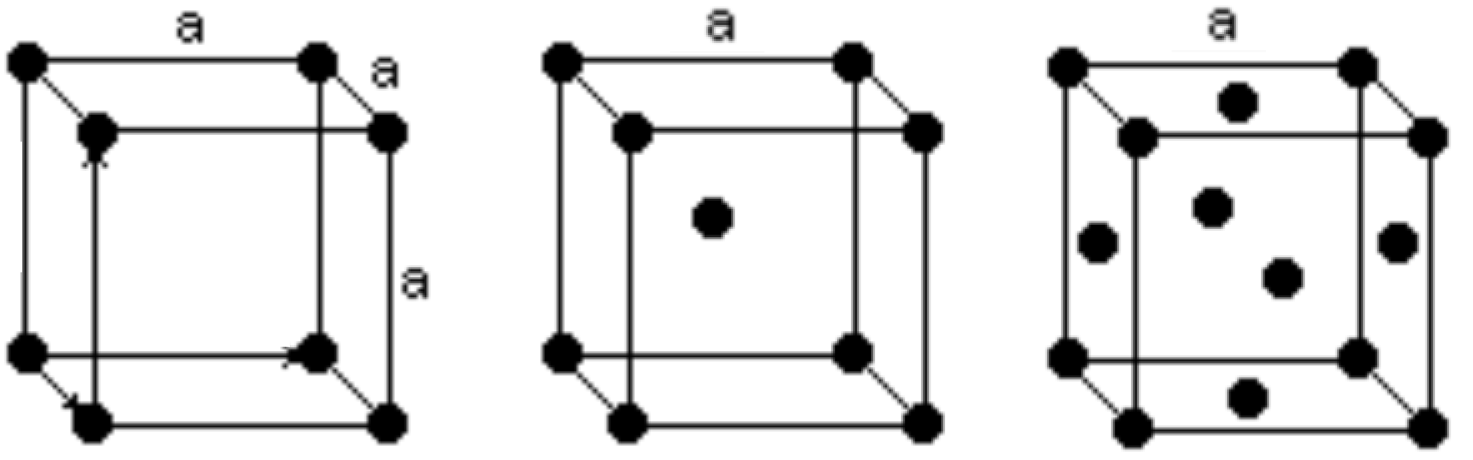
Illustration of a continuous random network structure of the atoms in an amorphous solid

Difference between Crystalline and Amorphous Solid

Properties	**Crystalline solids**	**Amorphous solids**
Structure	The constituent particles, atoms, ions or molecules are arranged in regular and definite three dimensional patterns. For example, sodium chloride, diamond, sugar etc.	The constituent particles are arranged in irregular three dimensional patterns.
Cutting with a sharp cutter	Gives clean, sharp cleavage.	Unclean cleavage.
X-ray, electron, and neutron diffraction	Produce interference fringes/peaks in the diffraction spectra	Do NOT produce any interference fringes/peaks in the diffraction spectra
Melting point	They have a sharp and definite melting point.	Melting point is not definite. It can melt over a range of temperatures.
Heat of fusion	Definite	Not definite.
Physical properties	Mostly show anisotropic physical properties in different directions.	These are isotropic, that is their physical properties are mostly identical in all directions.

- **Crystals, Lattice and Basis**
- **Primitive Lattice Cell**
- **Wigner-Seitz Primitive cell**
- **Bravais and non-Bravais Lattices**
- **Index System for Crystal Planes and Directions**

- Describe similarities and differences between the following three crystal structures.



Crystals

- The periodic array of atoms, ions, or molecules that form the solid is called the Crystal Structure

Crystal Structure ≡ Space (Crystal) Lattice + Basis

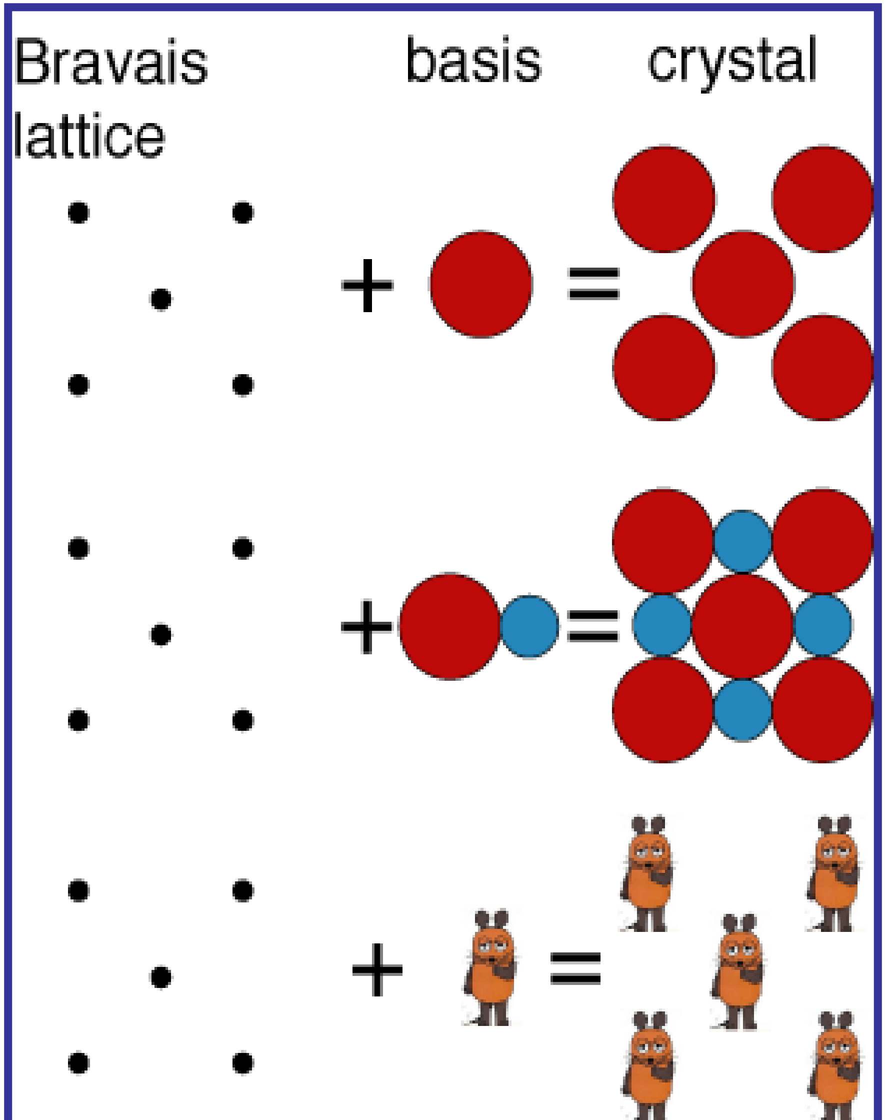
- The Space (Crystal) Lattice is a regular periodic arrangement of points in space, and is purely a mathematical abstraction.

$$r' = r + u_1 a_1 + u_2 a_2 + u_3 a_3$$

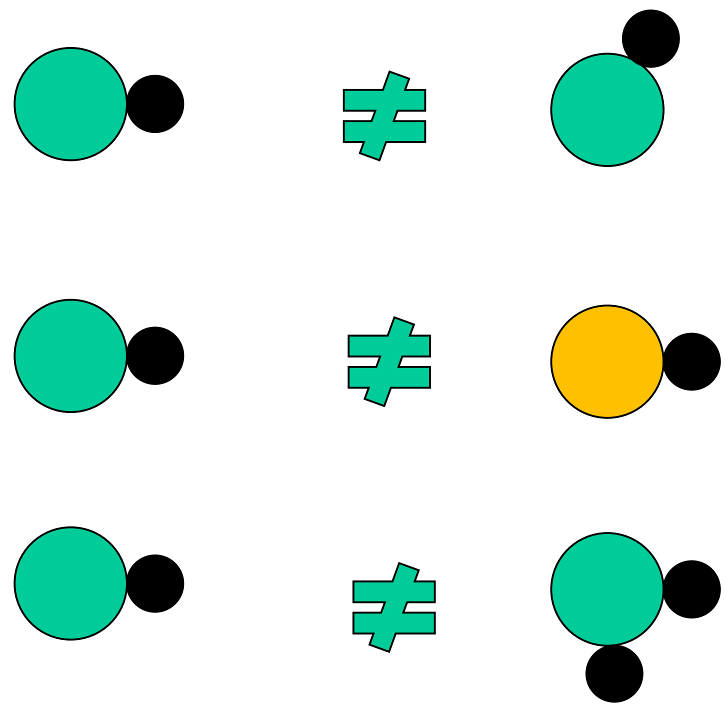
- A crystal structure is formed by "putting" the identical atoms (or group of atoms) on the points of the space lattice.

This group of atoms is called the basis.

A Two-Dimensional (Bravais) Lattice with Different Choices for the Basis



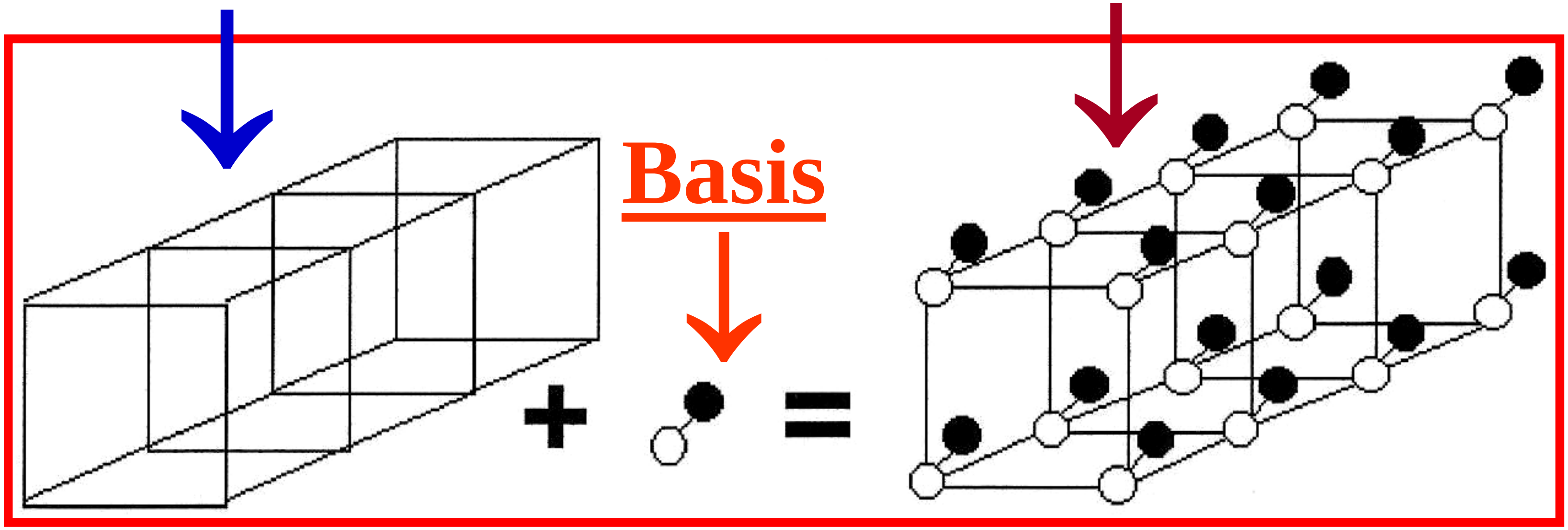
Every basis in a crystal is identical to every other in composition, arrangement, and orientation.



Crystal Structure ≡ Lattice + Basis

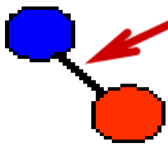
Lattice

Crystal Structure



The atoms do not necessarily lie at lattice points!

Basis

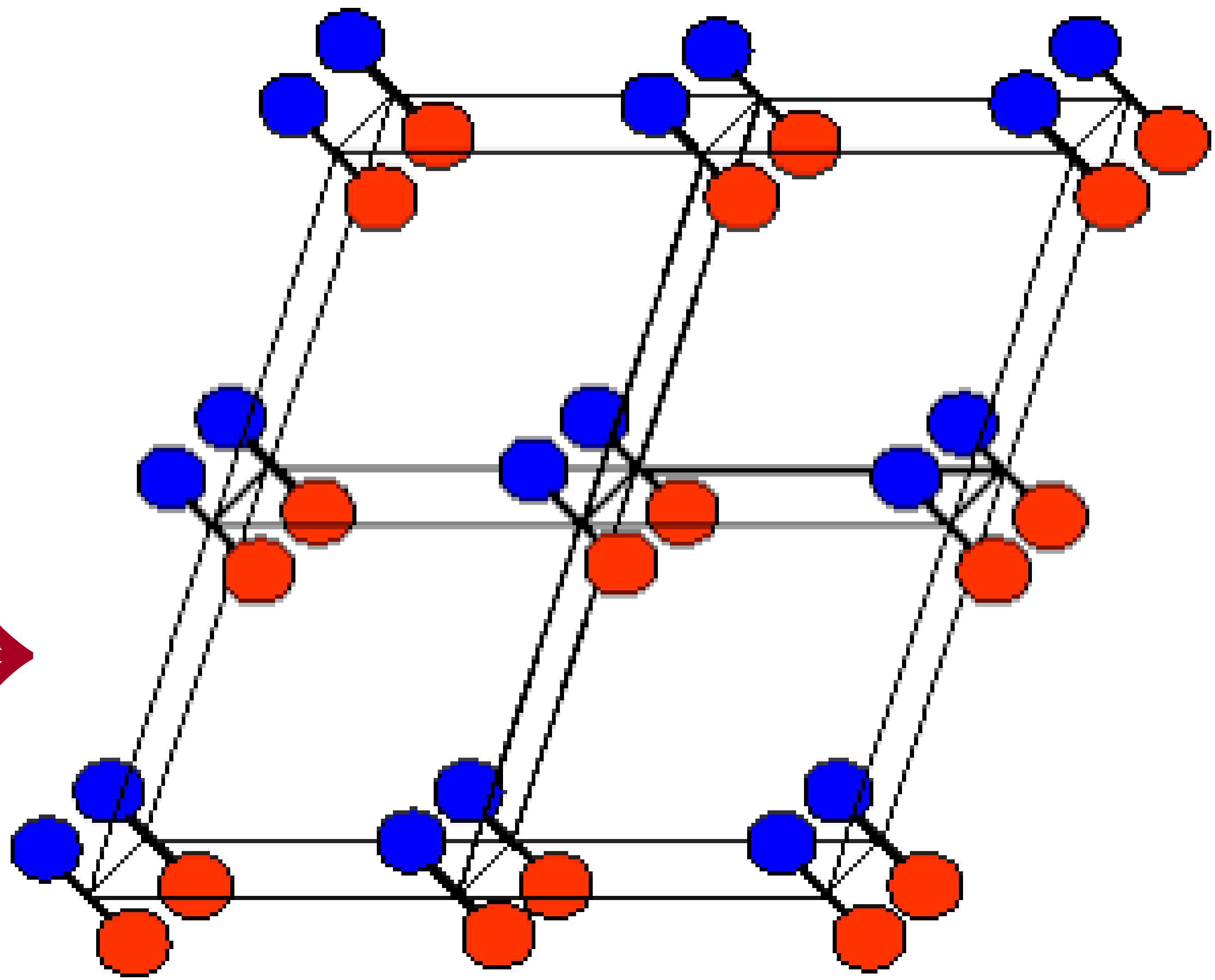


\+

Lattice

↓

Crystal Structure →

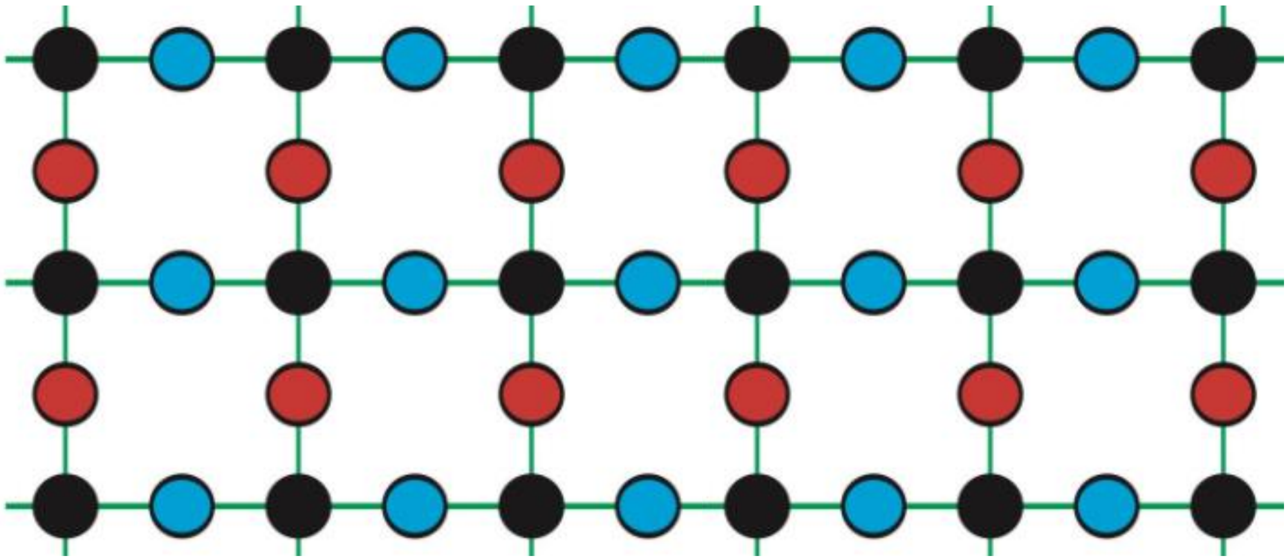


Crystal Lattice

- Since lattice is a regular periodic arrangement of points in space, therefore it should be invariant under translation operation with **r**:

$$\boldsymbol{r}' = \boldsymbol{r} + u_1\boldsymbol{a_1} + u_2\boldsymbol{a_2} + u_3\boldsymbol{a_3}$$

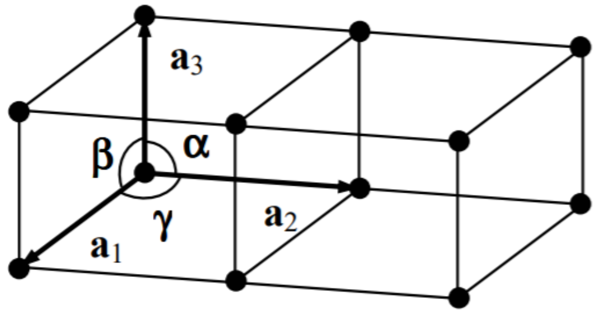
- Here u_1, u_2, u_3 are arbitrary integers and $\boldsymbol{a_1}$, $\boldsymbol{a_2}$, $\boldsymbol{a_3}$ are translational vectors. The set of points defined by r' for all u_1, u_2, u_3 defines the lattice.



Primitive Lattice Cell

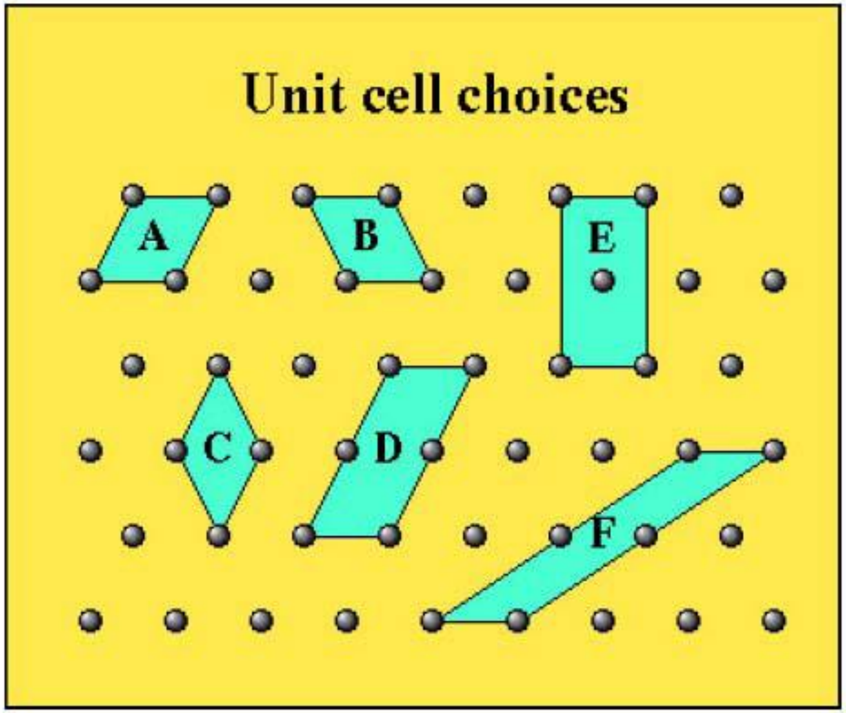
- Primitive lattice cell serve as a building block for the crystal structure and has the smallest volume $V = |\boldsymbol{a_1}.(\boldsymbol{a_2} \times \boldsymbol{a_3})|$ than any other cell.

- The basis associated with a primitive cell is called a primitive basis. No basis contains fewer atoms than a primitive basis contains.



Choice of primitive cells

- Which unit cell is a good choice?
- A, B, and C are primitive unit cells. Why?
- D, E, and F are not. Why?
- Notice: the volumes of A, B, and C are the same. Also, the choice of origin is different, but it doesn't matter
- Also: There is only one lattice point in the primitive unit cells.

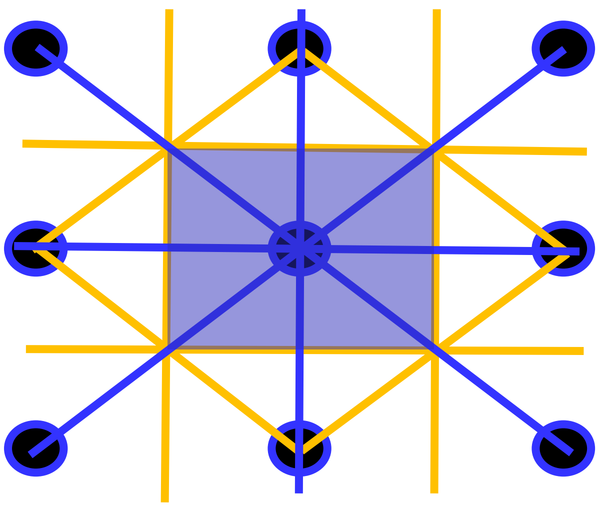


Wigner-Seitz Primitive cell

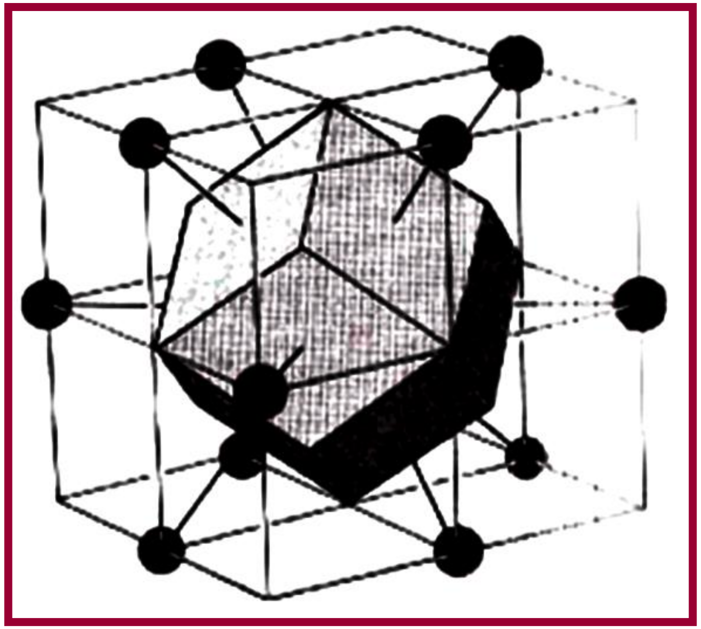
- The choice of primitive cell is not unique. A primitive cell may also be chosen following this procedure:

- First, draw lines to connect a given lattice point to all nearby lattice points.

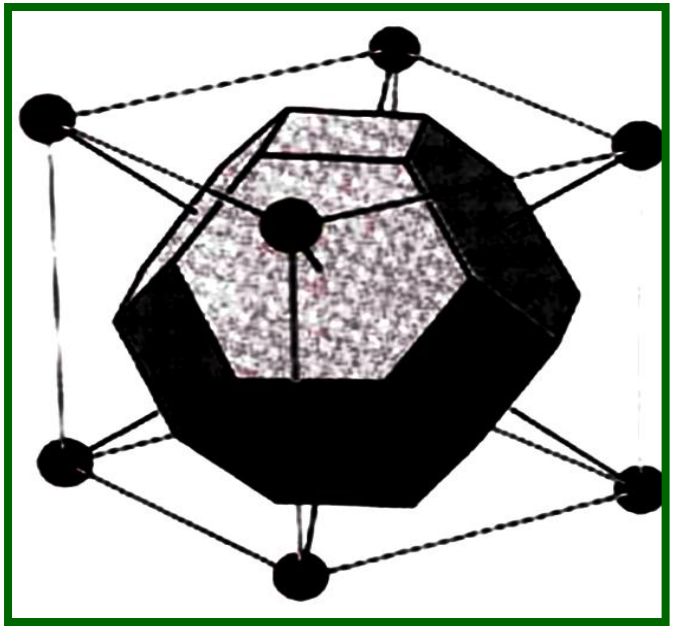
- Second, at the midpoint and normal to these lines, draw new lines or planes. The smallest volume enclosed in this way is the Wigner-Seitz primitive cell.



3D Wigner-Seitz Primitive cell



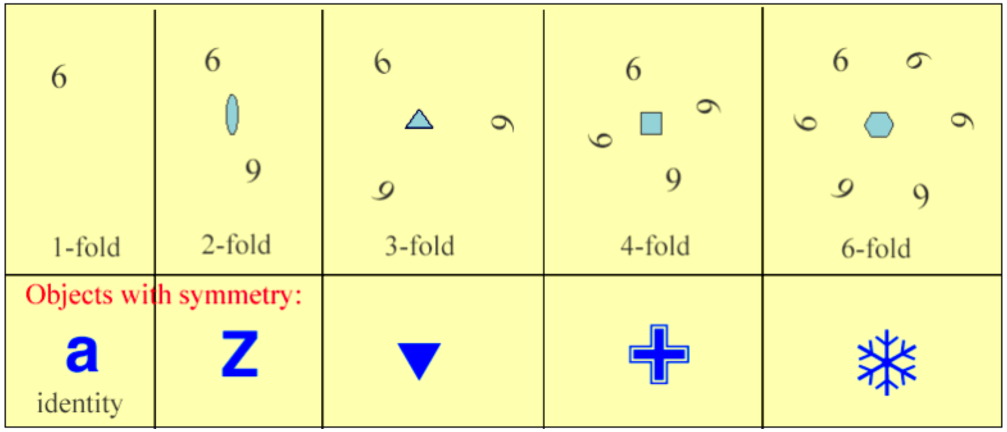
Face Centered Cubic (FCC)
Wigner-Seitz Cell



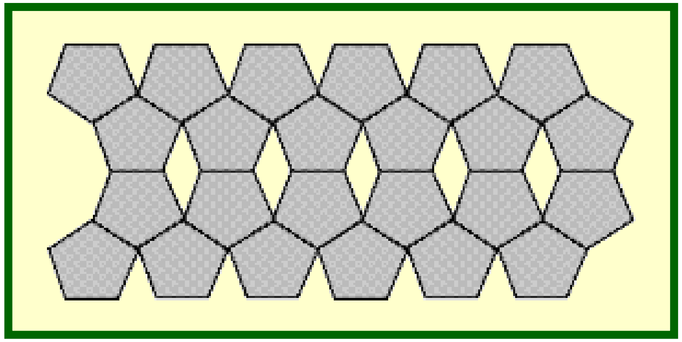
Body Centered Cubic (BCC)
Wigner-Seitz Cell

Fundamental Types of Lattices

- Crystal lattices can be carried or mapped into themselves by the lattice translations, inversion, reflection, rotation, or a combination of these symmetric operations. An example of rotational symmetry is given below.



(5-fold)

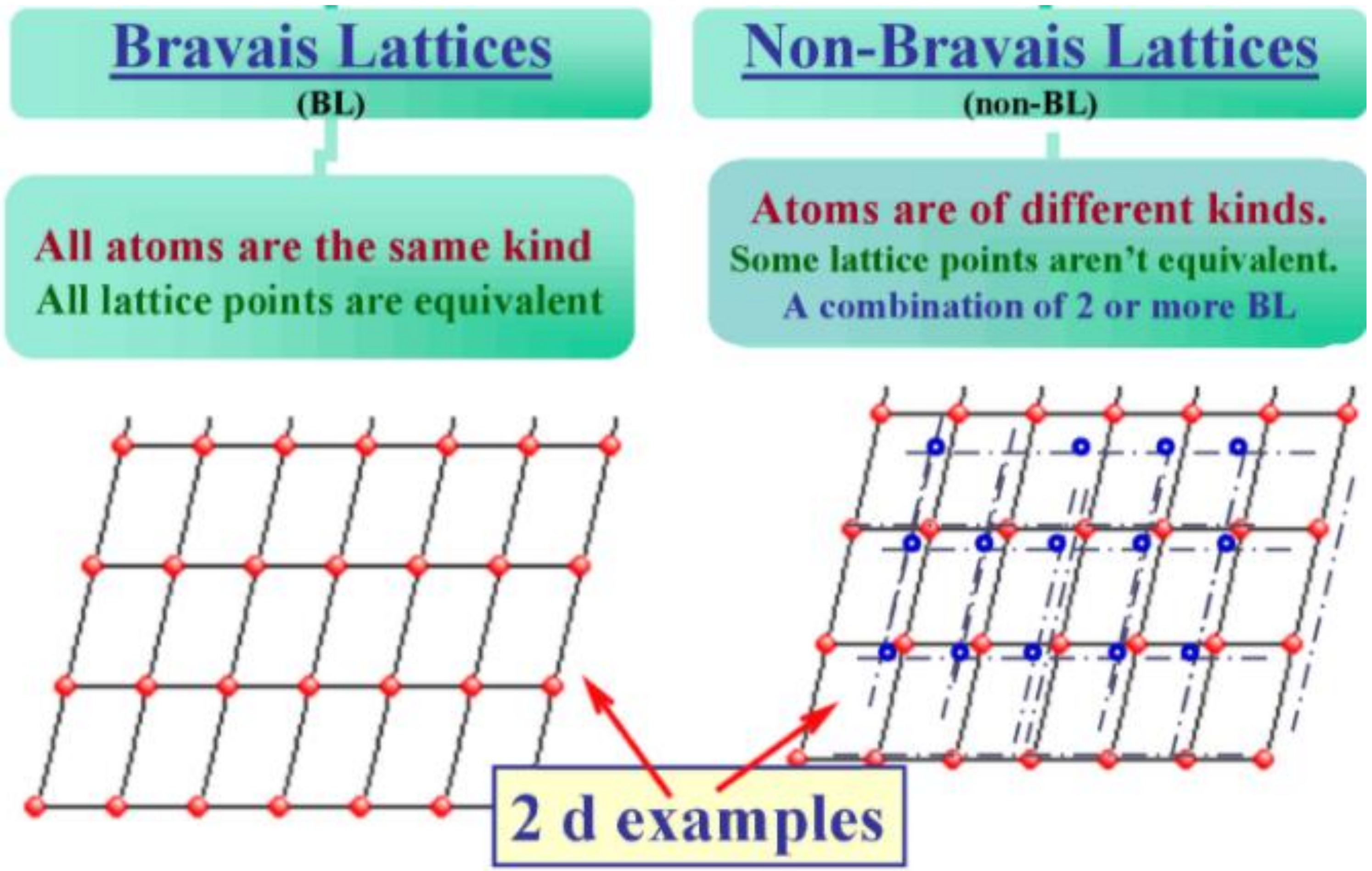


We cannot find a lattice that goes into itself under other rotations, such as by $2\pi/7$ (7-fold) radians or $2\pi/5$ (5-fold) radians.

Bravais and non-Bravais Lattices

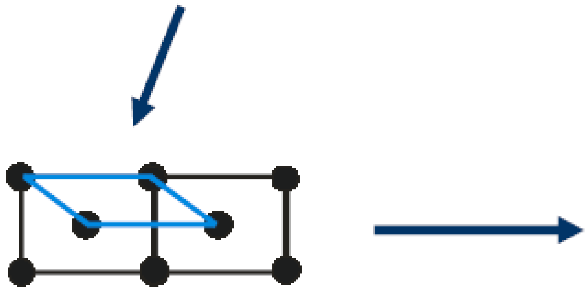
- **Bravais lattice** all lattice points are equivalent and hence by necessity all atoms in the crystal are of the same kind.

- **Non-Bravais lattice**: some of the lattice points are non-equivalent, are often referred to as a lattice with a basis.

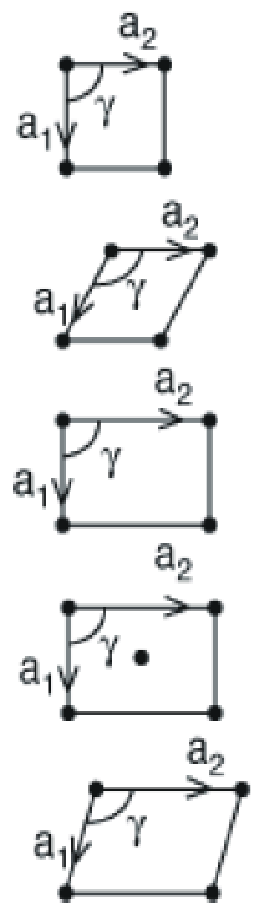


2D lattices Bravais Lattices (5 lattice types)

Note that this is the proper primitive cell for the centered rectangular lattice type (why? It contains only one lattice point)



(this is called a rhombus)



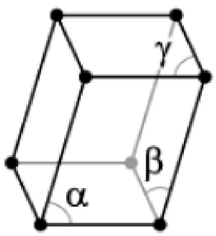
square	$a_1 = a_2$	$\gamma = 90°$
hexagonal	$a_1 = a_2$	$\gamma = 120°$
rectangular	$a_1 \neq a_2$	$\gamma = 90°$
centered rectangular	$a_1 \neq a_2$	$\gamma = 90°$
oblique	$a_1 \neq a_2$	$\gamma \neq 90°$

7 crystal systems and 14 Bravais lattices in 3D

triclinic

$a \neq b \neq c$

$\alpha, \beta, \gamma \neq 90°$

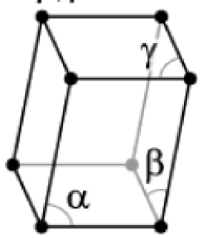


monoclinic

$a \neq b \neq c$

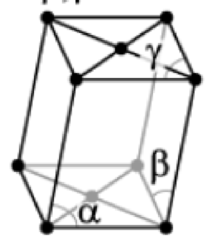
P

$\alpha \neq 90°$
$\beta, \gamma = 90°$



C

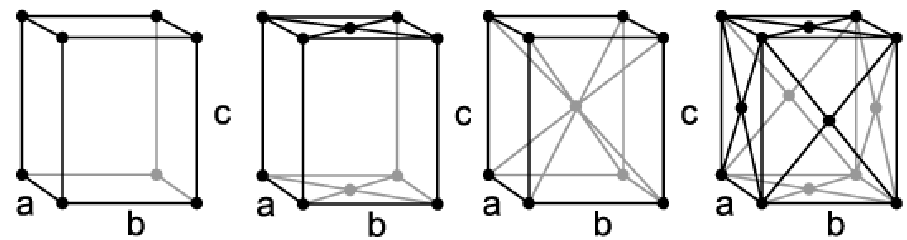
$\alpha \neq 90°$
$\beta, \gamma = 90°$



orthorhombic

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

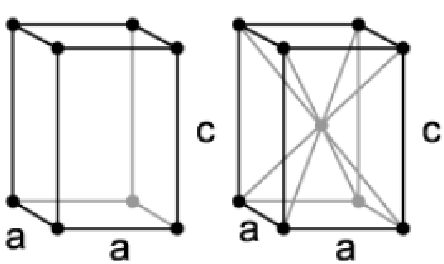
P **C** **I** **F**



tetragonal

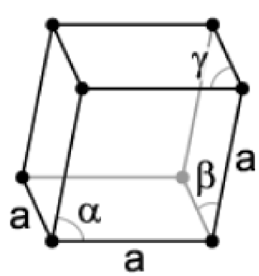
$a = b \neq c,$
$\alpha = \beta = \gamma = 90°$

P **I**



rhombohedral (trigonal)

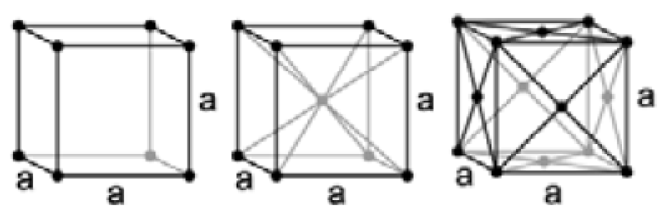
$a = b = c,$
$\alpha = \beta = \gamma \neq 90°$



cubic

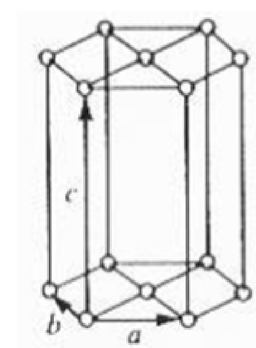
$a = b = c,$
$\alpha = \beta = \gamma = 90°$

P **I** **F**

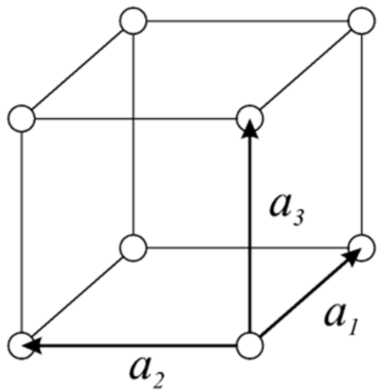


hexagonal

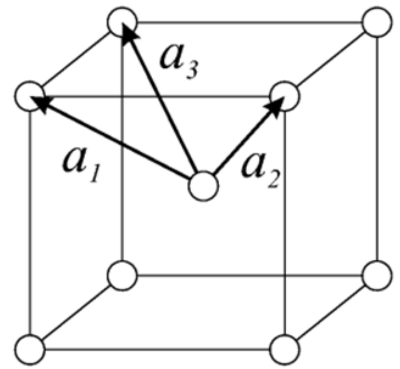
$a = b \neq c,$
$\alpha = \beta = 90°$
$\gamma = 120°$



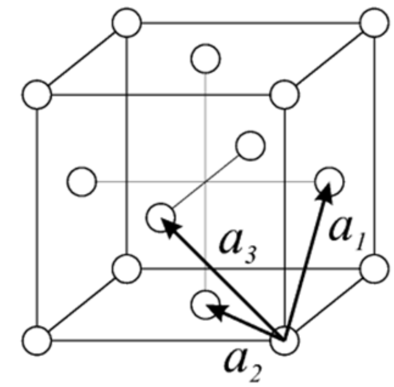
Cubic Lattices: SC, BCC, and FCC



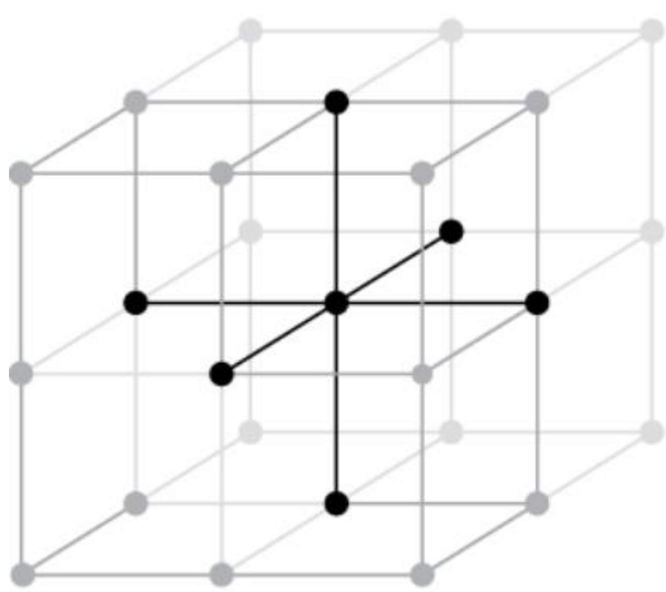
simple cubic

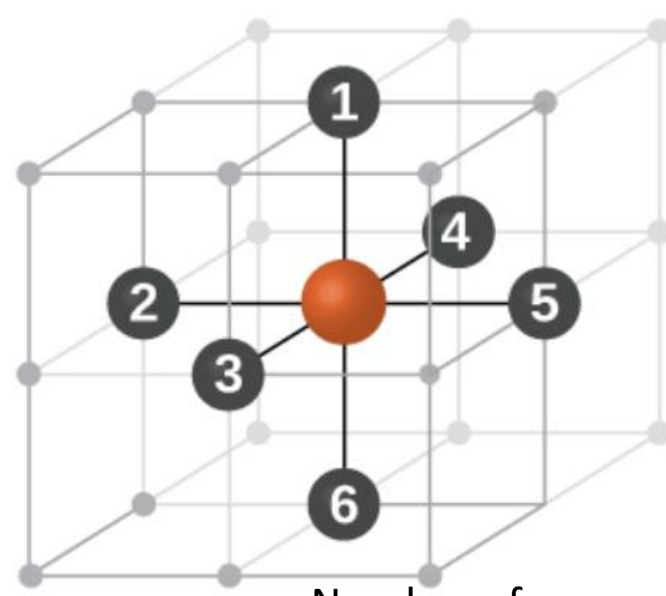


Body centered cubic



Face centered cubic

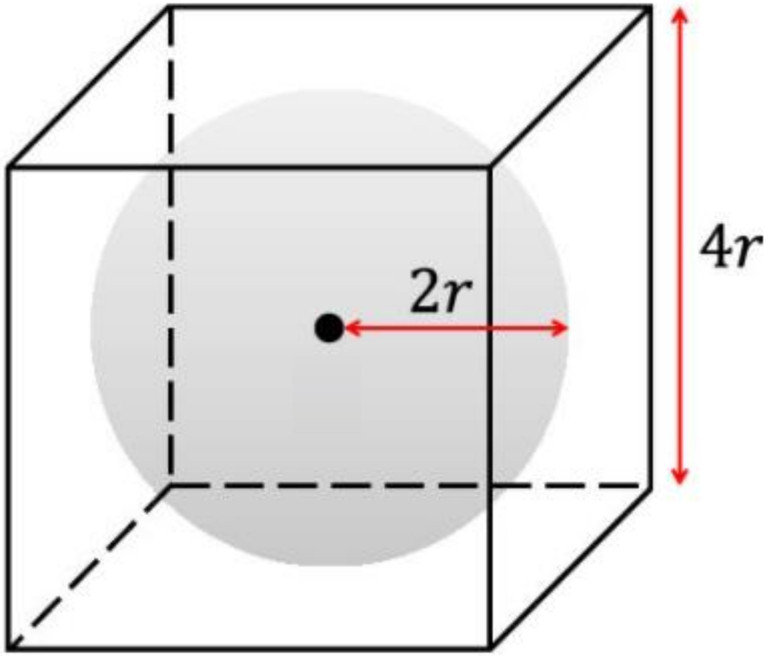




Number of nearest neighbors = 6

- **Cubic Lattices: SC, BCC, and FCC**
- **Crystal Planes**
- **Planar Density and Planar Packing Fraction**
- **Index System for Crystal Planes and Directions**
- **Miller Indices**

- How much volume of the cube is occupied by the ball?
- How much volume of the cube is empty?



Cubic Lattices: SC, BCC, and FCC

	Simple	Body-centered	Face-centered
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	a	$3^{1/2}a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction[a]	$\frac{1}{6}\pi$ $=0.524$	$\frac{1}{8}\pi\sqrt{3}$ $=0.680$	$\frac{1}{6}\pi\sqrt{2}$ $=0.740$

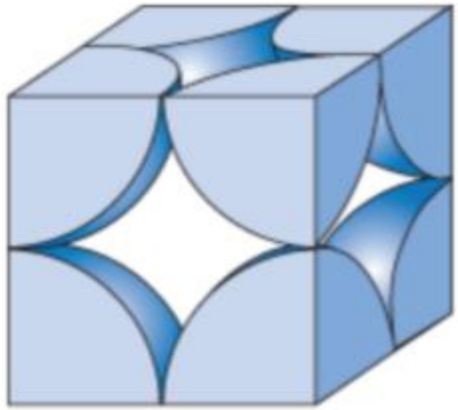
Simple Cubic Crystal

Packing fraction (PF): *(Maxmimum portion of the available volume that can be filled with hard spheres*

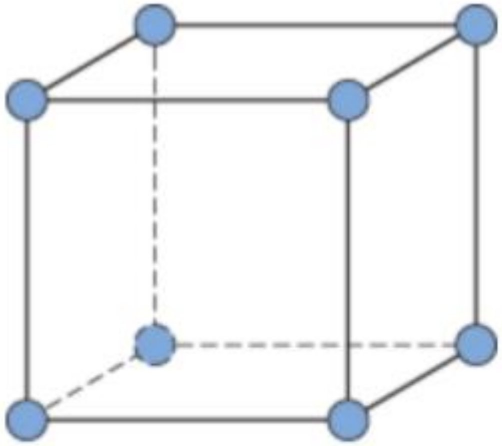
or

Volume occupied by atoms/Volume of the unit cell)

$$PF = \frac{\frac{4}{3}\pi\left(a/2\right)^3}{a^3} = \frac{\pi}{6} = 0.524$$



(a)



(b)

Number of nearest neighbors = 6

Nearest neighbors distance = *a*

Number of next nearest neighbors = 12

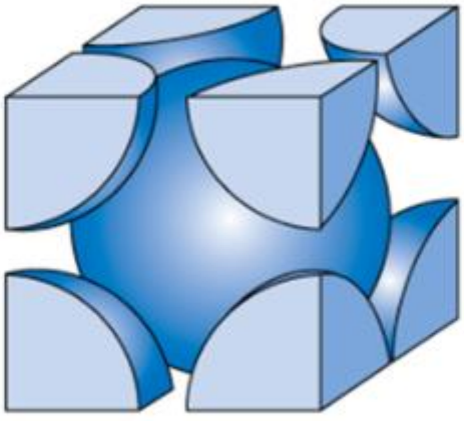
Next nearest neighbors distance = $2^{1/2}$a

Body Centered Cubic

Packing fraction (PF): *(Maxmimum portion of the available volume that can be filled with hard spheres*

or

Volume occupied by atoms/Volume of the unit cell)



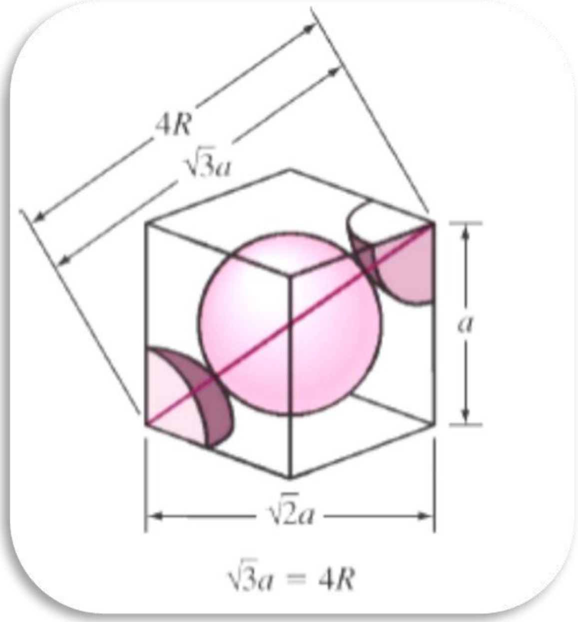
$$PF = \frac{2 \times \frac{4}{3}\pi\left(\frac{\sqrt{3}\,a}{4}\right)^3}{a^3} = \frac{\pi\sqrt{3}}{8} = 0.680 = 68.0\ \%$$

Number of nearest neighbors = 8

Nearest neighbors distance = $\sqrt{3}\,\frac{a}{2} = 0.866a$

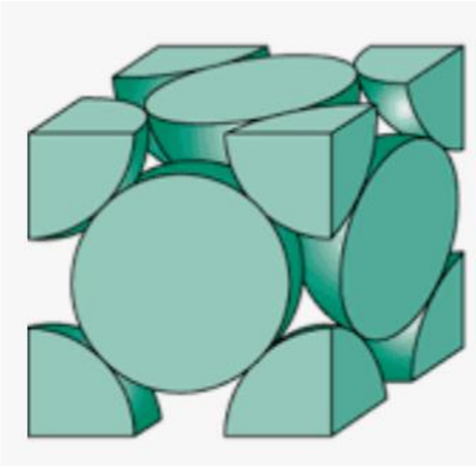
Number of next nearest neighbors = 6

Next nearest neighbors distance = *a*



Face Centered Cubic

Packing fraction (PF): *(Maxmimum portion of the available volume that can be filled with hard spheres*
or
Volume occupied by atoms/Volume of the unit cell)



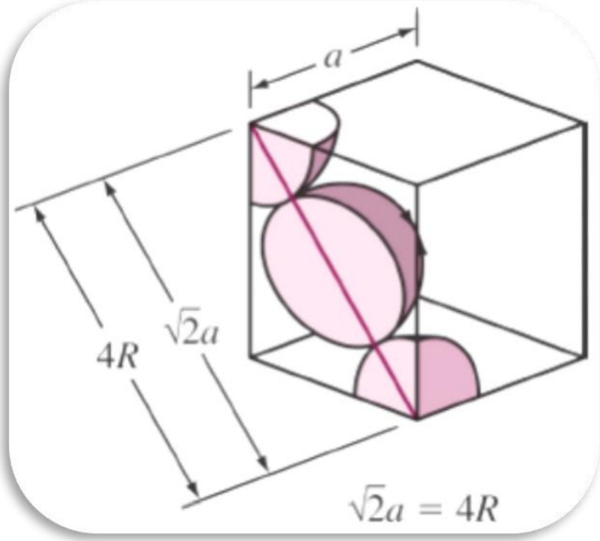
$$PF = \frac{4 \times \frac{4}{3}\pi\left(\frac{\sqrt{2}\,a}{4}\right)^3}{a^3} = \frac{\pi\sqrt{2}}{6} = 0.740 = 74.0\ \%$$

Number of nearest neighbors = 12

Nearest neighbors distance = $\frac{a}{\sqrt{2}} = 0.707a$

Number of next nearest neighbors = 6

Next nearest neighbors distance = *a*

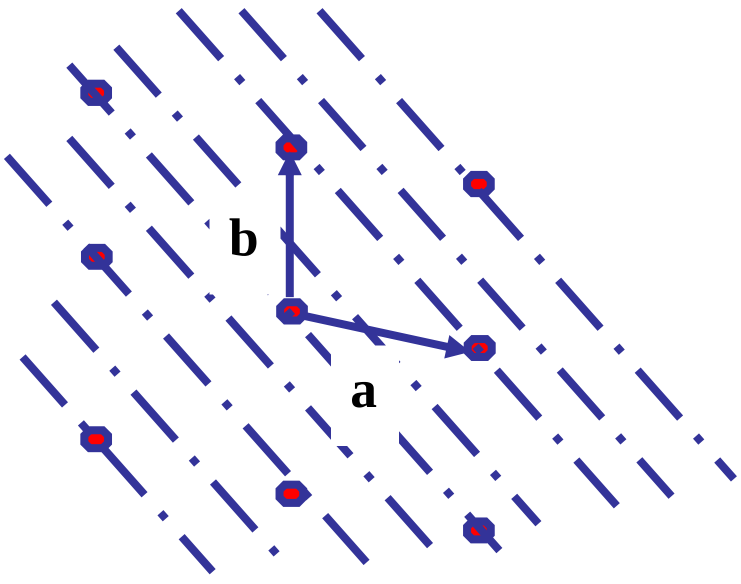


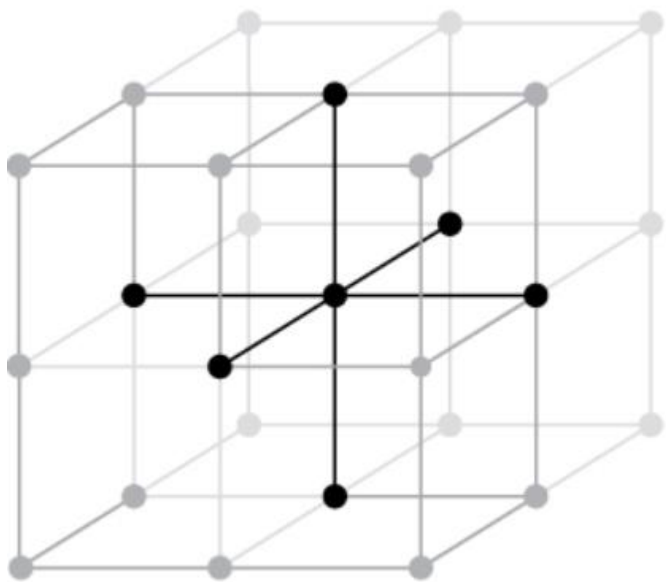
Crystal Planes

- Within a crystal lattice, it is possible to identify sets of equally spaced parallel planes.

These are called *crystal/lattice planes*.

- In a set of crystal planes, the density of lattice points and planar packing fraction for all planes is same.



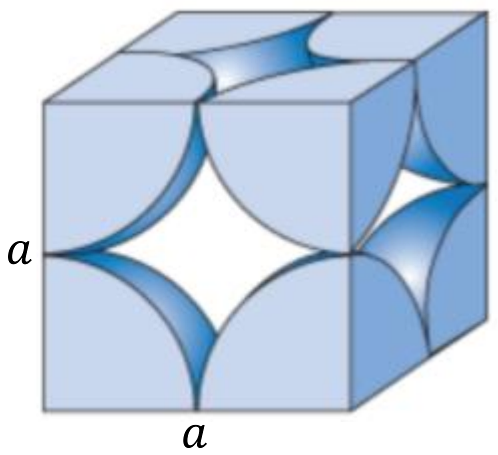


Planar density and Packing Fraction

Planar Density (PD): Number of *atoms in a plane /area of the plane)*

Planar density for SC (100) plane.

$$PD_{100} = \frac{1}{a^2}$$



Planar Packing fraction (PPF): *(Maxmimum portion of the available area in a plane that can be filled with hard spheres*

or

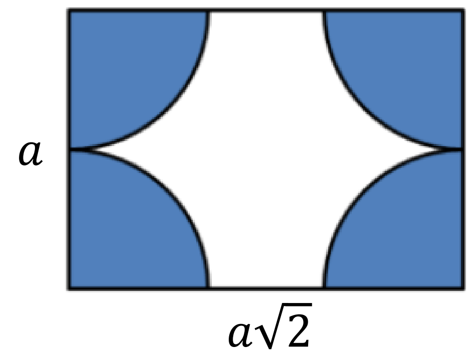
Cross sectional of *atoms in a plane/area of the plane)*

$$PPF_{100} = \frac{1 \times \pi R^2}{a^2} = \frac{\pi R^2}{(2R)^2} = 0.785 = 78.5\ \%$$

Planar density and Packing Fraction

Planar density for SC (110) plane:

$$PD_{100} = \frac{1}{a^2\sqrt{2}}$$

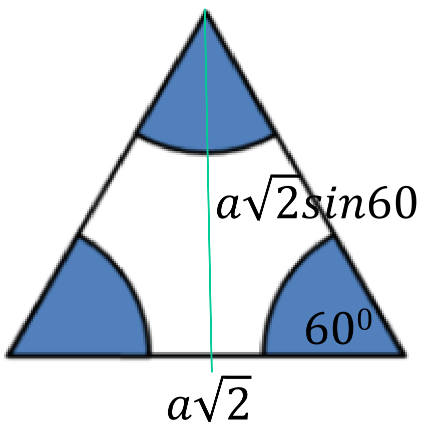


Planar Packing fraction SC (110) plane:

$$PPF_{100} = \frac{1 \times \pi R^2}{a^2} = \frac{\pi R^2}{(2R)^2\sqrt{2}} = 0.555 = 55.5\ \%$$

Planar density for SC (111) plane:

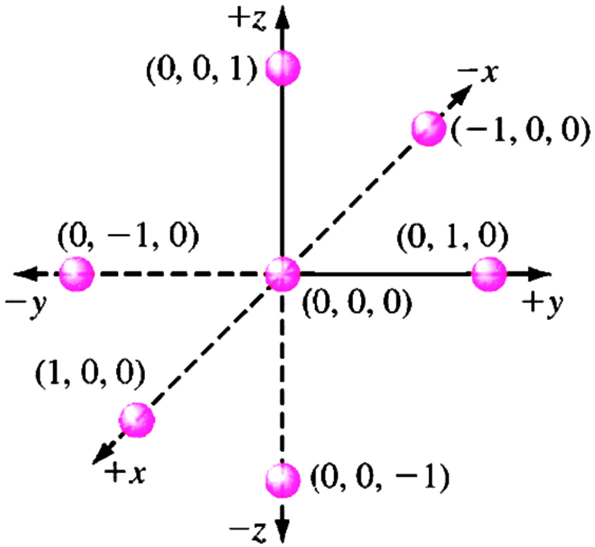
$$PD_{100} = \frac{1/2}{a^2\sqrt{3}/2} = \frac{1}{a^2\sqrt{3}}$$

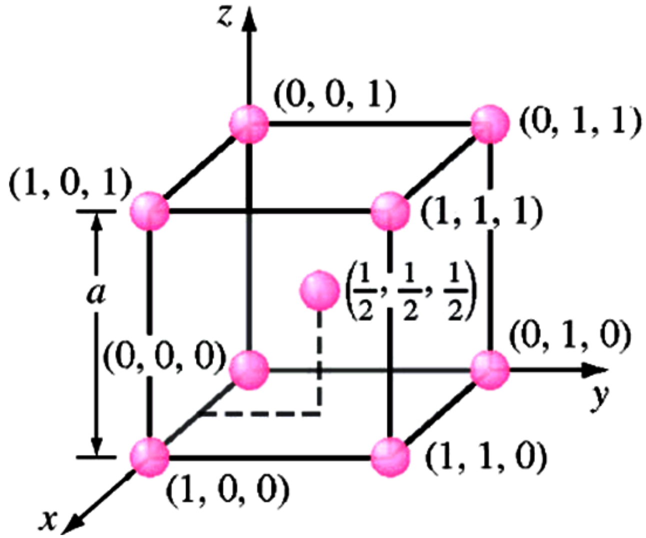


Planar Packing fraction SC (111) plane:

$$PPF_{100} = \frac{1 \times \pi R^2}{a^2} = \frac{\pi R^2}{(2R)^2\sqrt{3}} = 0.453 = 45.3\ \%$$

Index System for Crystal Planes





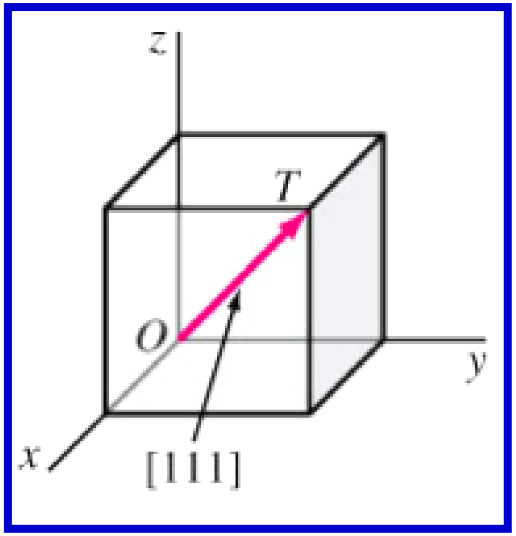
- The <u>**standard notation is shown in the figure**</u>. It is understood that <u>***all distances are in units of the cubic lattice constant a***</u>, which is the length of a cube edge for the material of interest.

Directions in a Crystal: Standard Notation

- Choose an origin, O. This choice is arbitrary, because every lattice point has identical symmetry. Then, consider the lattice vector joining O to any point in space, say point **T** in the figure. As we've seen, this vector can be written

$$\mathbf{T} = n_1\mathbf{a_1} + n_2\mathbf{a_2} + n_3\mathbf{a_3}$$

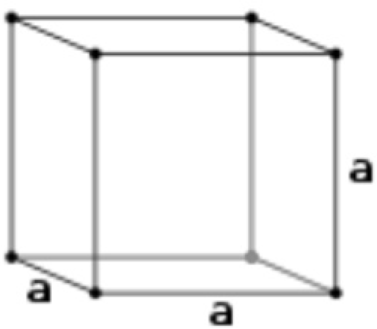
$$\mathbf{T} = a\,\boldsymbol{i} + a\,\boldsymbol{j} + a\,\boldsymbol{k}$$



[111] direction

Primitive lattice vectors of SC, BCC, and FCC

Simple Cubic (SC)



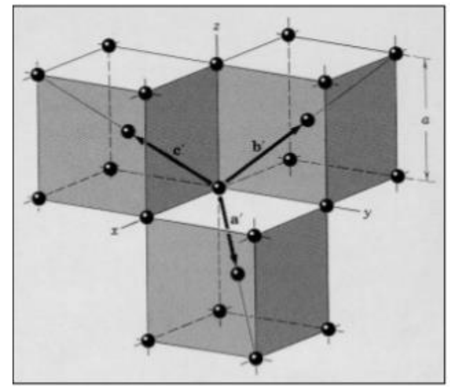
- Primitive translation vectors

$$\vec{a}' = a\hat{x}$$

$$\vec{b}' = a\hat{y}$$

$$\vec{c}' = a\hat{z}$$

Body-centered cubic (BCC)



- Primitive translation vectors

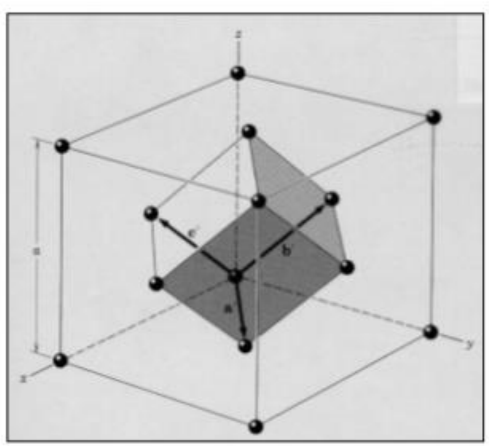
$$\vec{a}' = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z})$$

$$\vec{b}' = \frac{a}{2}(-\hat{x} + \hat{y} + \hat{z})$$

$$\vec{c}' = \frac{a}{2}(\hat{x} - \hat{y} + \hat{z})$$

orthogonal vectors of unit length

Face-centered cubic (FCC)



- Primitive translation vectors

$$\vec{a}' = \frac{a}{2}(\hat{x} + \hat{y});$$

$$\vec{b}' = \frac{a}{2}(\hat{y} + \hat{z})$$

$$\vec{c}' = \frac{a}{2}(\hat{z} + \hat{x}).$$

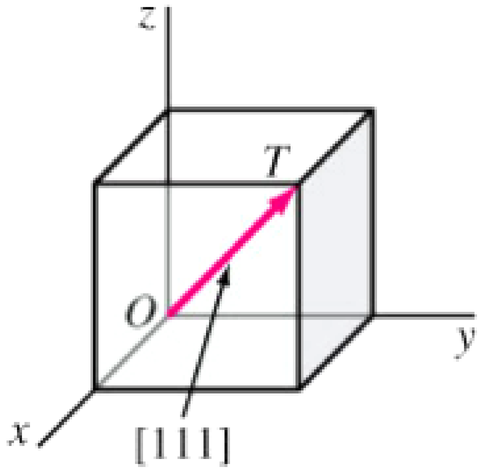
Miller Indices

Miller Indices (hkl) are a symbolic vector representation for the orientation of an atomic plane in a crystal lattice & are defined as the ***reciprocals of the fractional intercepts*** which the plane makes with the crystallographic axes.

Miller indices for a *Lattice Direction* in a cube is indicated by 3 integers enclosed in square brackets [hkl], and h, k, l are the smallest integers possible for the *relative ratios*.

Miller Indices for Directions in a Crystal

- The direction [hkl] is perpendicular to the plane (hkl) having the same indices. This may not be true for other crystal types.



[111] direction

A lattice Vector

$\mathbf{T} = n_1\mathbf{a_1} + n_2\mathbf{a_2} + n_3\mathbf{a_3}$

[111], [222], [333], [444] … are all equivalent directions.

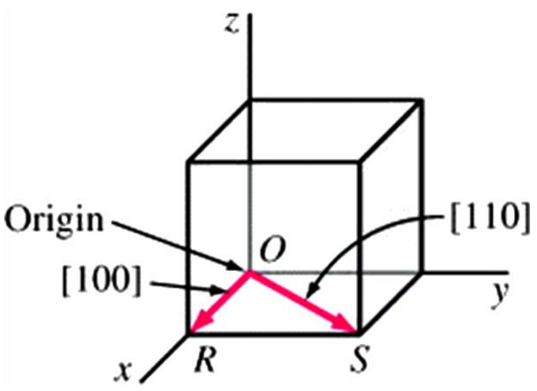
Negative Directions

- When we write the direction [hkl] depending on the origin, negative directions are written as

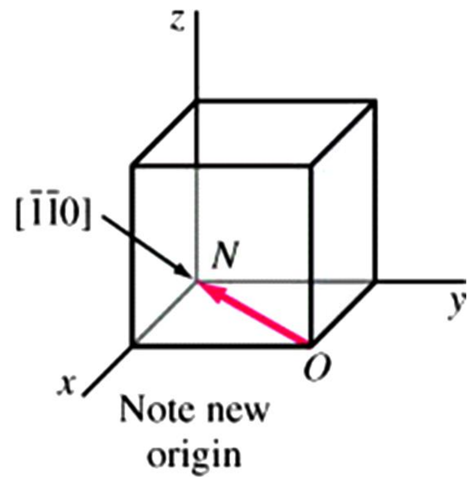
$$\mathbf{R} = n_1\mathbf{a_1} + n_2\mathbf{a_2} - n_3\mathbf{a_3}$$

With a bar above or below the negative integers such as $[hk\bar{l}]$.

To specify the direction, the smallest possible integers must be used.



X = 1, Y = 0, Z = 0
[100]



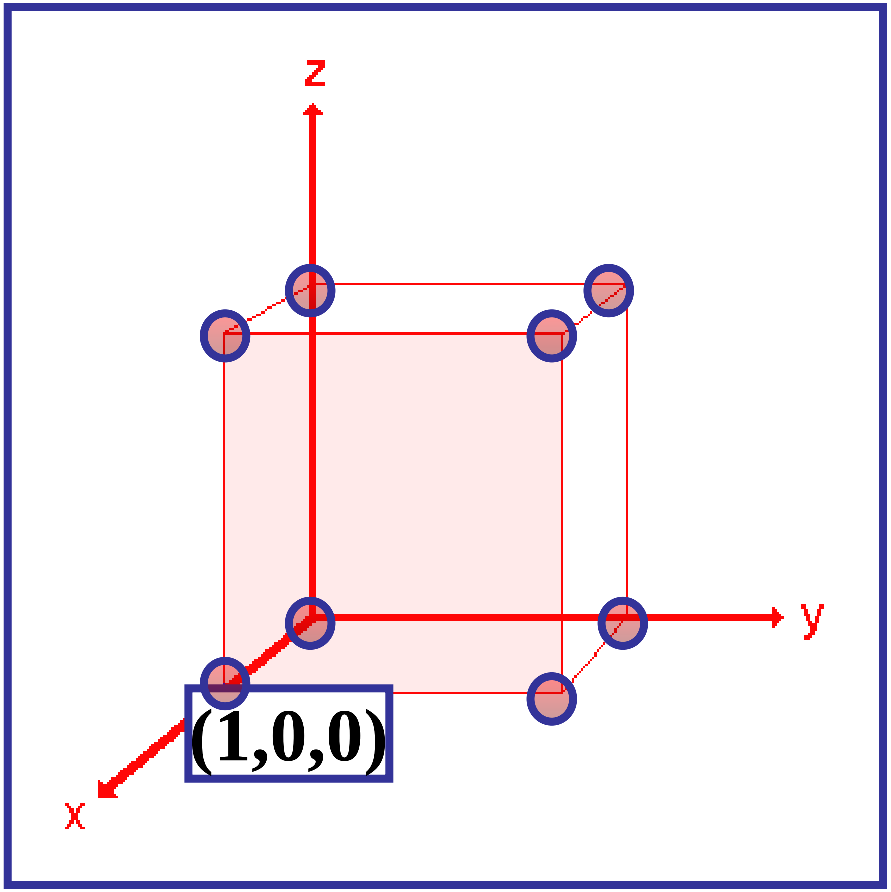
X = -1, Y = -1, Z = 0
$[\bar{1}\bar{1}0]$

Miller Indices

- To find the Miller indices of a plane, take the following steps:

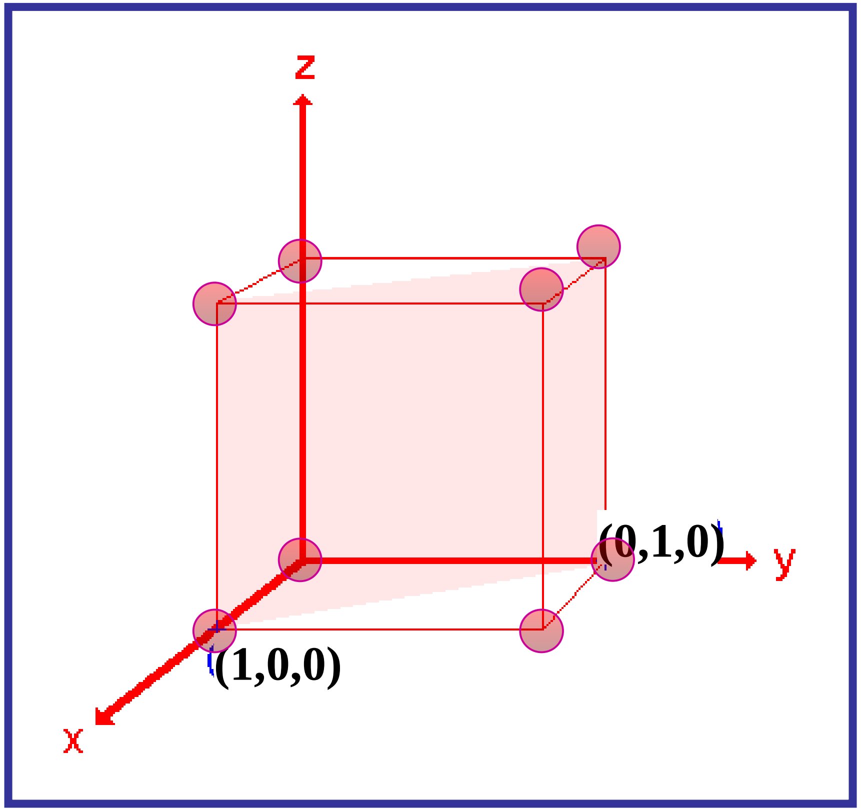
1. **Determine the intercepts** of the plane along each of the three crystallographic directions.
2. **Take the reciprocals** of the intercepts.
3. **If fractions result**, multiply each by the denominator of the ***smallest fraction*****.**

Example 1: (100) Plane



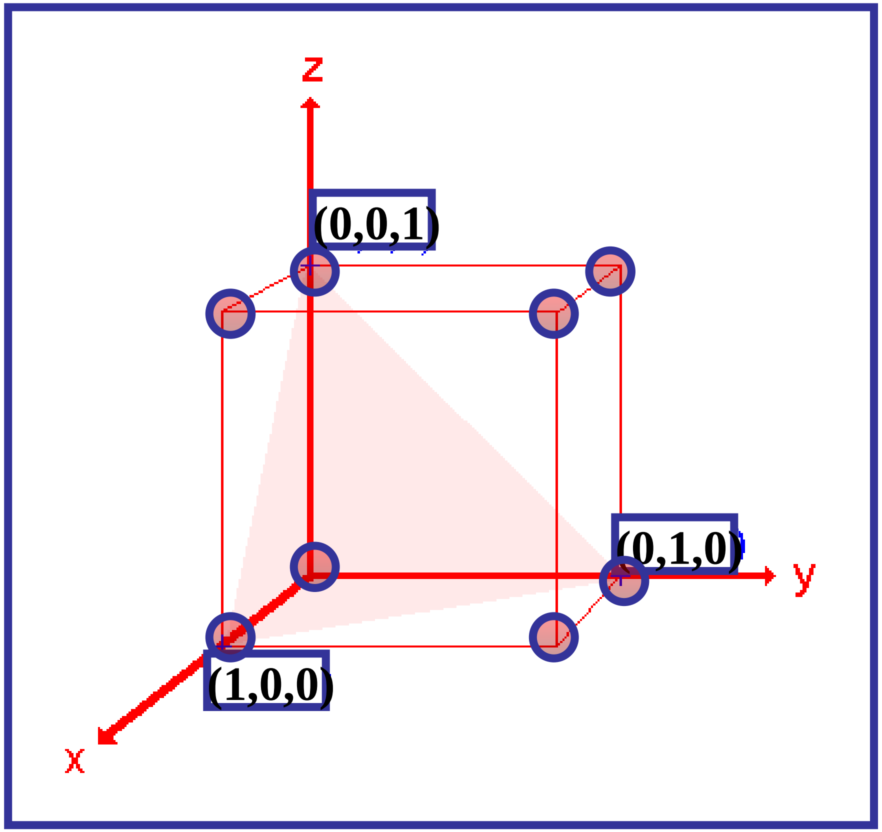
Axis	X	Y	Z
Intercept points	1	∞	∞
Reciprocals	1/1	1/ ∞	1/ ∞
Smallest Ratio	1	0	0
Miller İndices (100)			

Example 2: (110) Plane



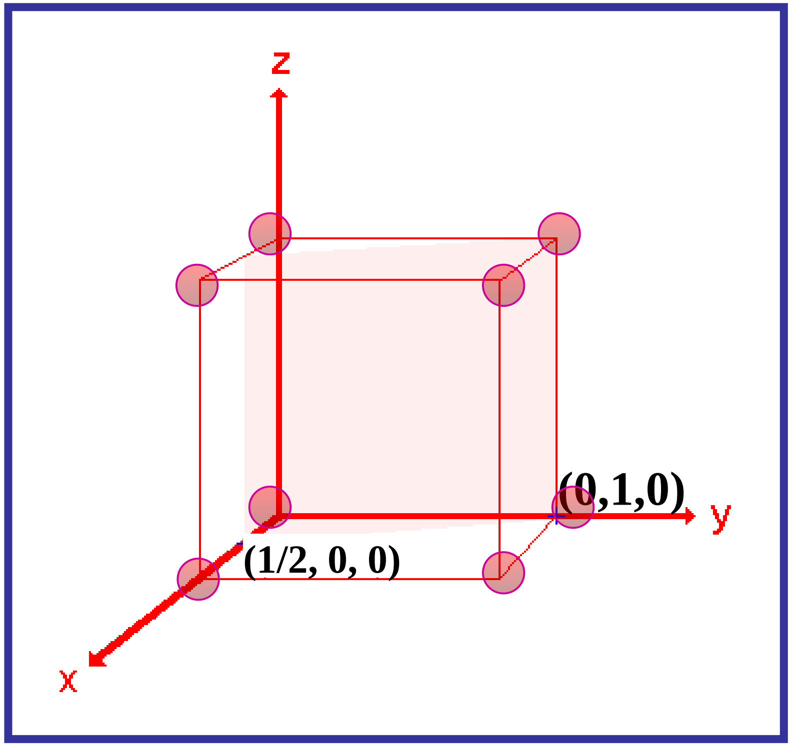
Axis	X	Y	Z
Intercept points	1	1	∞
Reciprocals	1/1	1/ 1	1/ ∞
Smallest Ratio	1	1	0
Miller İndices (110)			

Example 3: (111) Plane



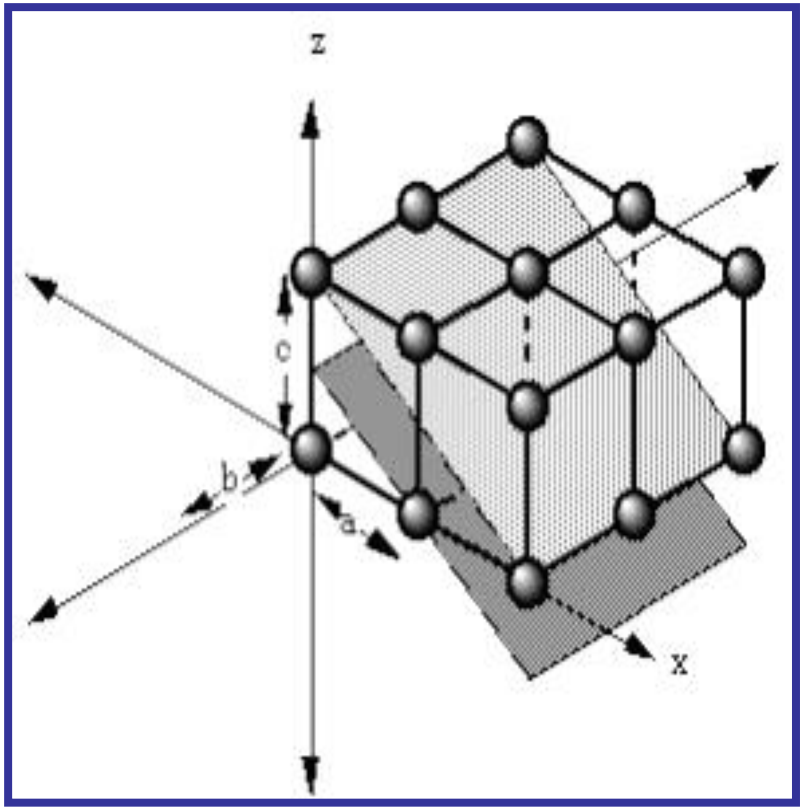
Axis	X	Y	Z
Intercept points	1	1	1
Reciprocals	1/1	1/ 1	1/ 1
Smallest Ratio	1	1	1
Miller İndices (111)			

Example 4: (210) Plane



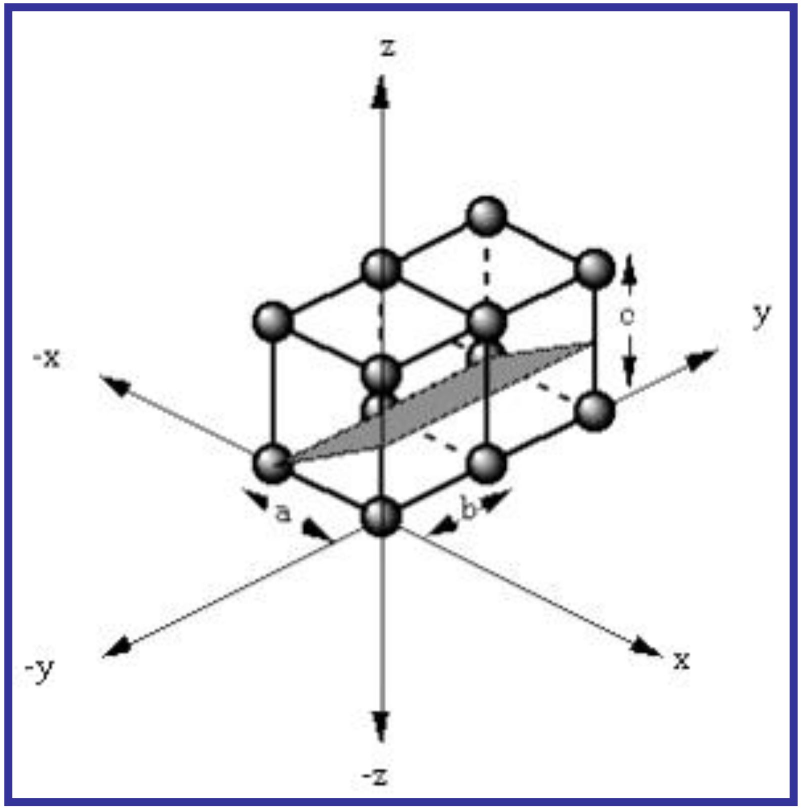
Axis	X	Y	Z
Intercept points	1/2	1	∞
Reciprocals	1/(½)	1/ 1	1/ ∞
Smallest Ratio	2	1	0
Miller İndices (210)			

Example 5: (102) Plane



Axis	a	b	c
Intercept points	1	∞	½
Reciprocals	1/1	1/ ∞	1/(½)
Smallest Ratio	1	0	2
Miller İndices (102)			

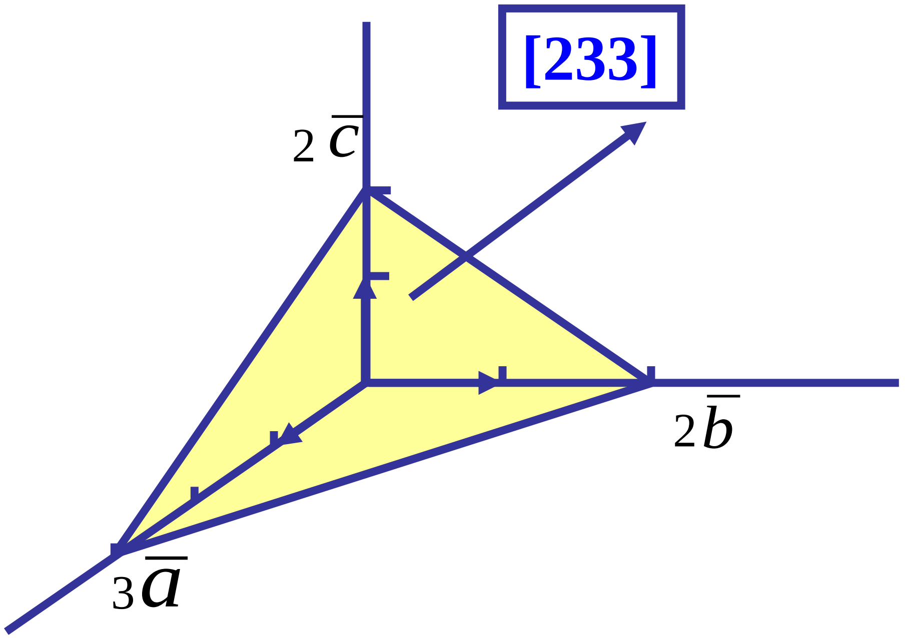
Example 6: (ī02) Plane



Axis	a	b	c
Intercept points	-1	∞	½
Reciprocals	1/-1	1/ ∞	1/(½)
Smallest Ratio	-1	0	2
Miller İndices (ī02)			

Examples of Miller Indices

- Consider the plane shaded in yellow:



Plane intercepts axes at $3\bar{a}, 2\bar{b}, 2\bar{c}$

Reciprocal numbers are: $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$

Miller Indices of the plane: (233)

Indices of the direction: [233]

Indices of a Family of Planes and Directions

- Sometimes. when the unit cell has rotational symmetry, several nonparallel planes may be equivalent by virtue of this symmetry, in which case it is convenient to **lump all these planes in the same Miller Indices**, but with curly brackets.

$$\{100\} \equiv (100),(010),(001),(0\bar{1}0),(00\bar{1}),(\bar{1}00)$$

$$\{111\} \equiv (111),(11\bar{1}),(1\bar{1}1),(\bar{1}11),(\bar{1}\bar{1}\bar{1}),(\bar{1}\bar{1}1),(\bar{1}1\bar{1}),(1\bar{1}\bar{1})$$

- So, indices **{hkl}** represent all of the planes equivalent to the plane **(hkl)** through rotational symmetry.

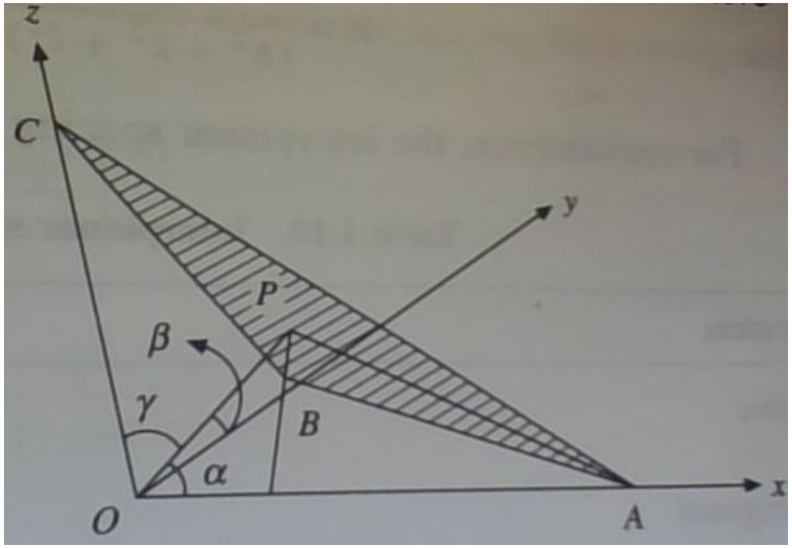
- Similarly, a family of crystallographic directions is represented by <hkl>.

- <100> ≡ [100], [010], [001], $[\underline{1}00]$ …

- **Interplanar Spacing**
- **Special Crystal Structures**
- **Indices for HCP planes and directions**
- **Departures from the “Perfect Crystal”**

Interplanar Spacing

- Interplanar spacing between two adjacent planes, d_{hkl}, is the shortest distance between the planes.



- Intercepts of the plane are $OA = a/h$, $OB = b/k$, and $OC = c/l$.

- OP (d_{hkl}) makes angles α, β, and γ with the three axis.

$$cos\alpha = \frac{OP}{OA} = \frac{d_{hkl}}{a/h}, \qquad cos\beta = \frac{OP}{OB} = \frac{d_{hkl}}{b/k}, \qquad cos\gamma = \frac{OP}{OC} = \frac{d_{hkl}}{c/l}$$

$$cos^2\alpha + cos^2\beta + cos^2\gamma = 1$$

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}}$$

Interplanar spacing of simple cubic crystal

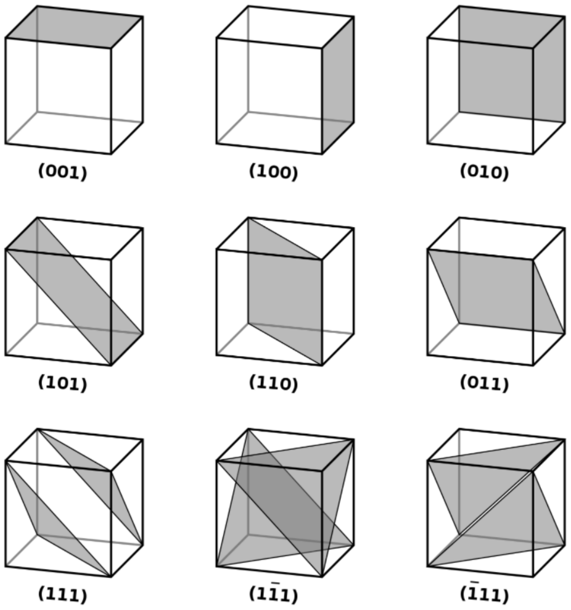
- Determine interplanar spacing for two consecutive (100), (110) and (111) planes in a simple cubic crystal.

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

- For $(100), h = 1, k = 0, l = 0$ $$d_{100} = a$$

- For $(110), h = 1, k = 1, l = 0$ $$d_{110} = \frac{a}{\sqrt{2}}$$

- For $(111), h = 1, k = 1, l = 1$ $$d_{111} = \frac{a}{\sqrt{3}}$$



Calculating Angle between Two Planes

For cubic crystals, the angle, ϕ between two planes, $(h_1\, k_1\, l_1)$ and $(h_2\, k_2\, l_2)$ is given by:

$$\cos\phi = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2}\sqrt{h_2^2 + k_2^2 + l_2^2}}$$

Example:

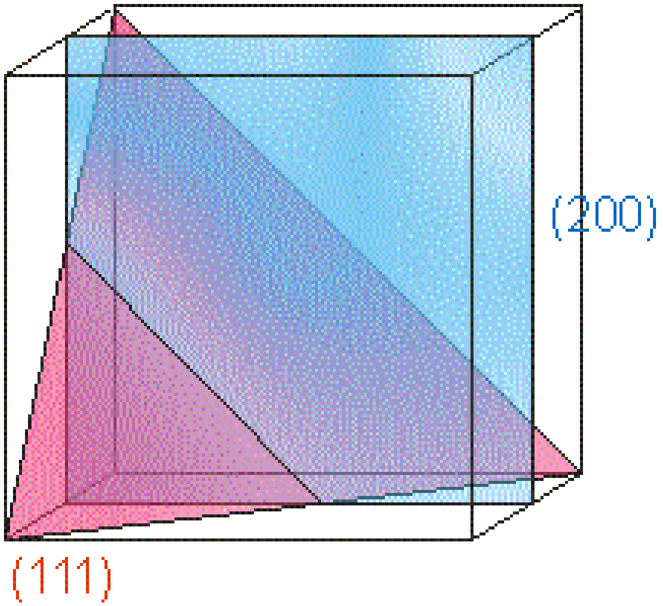
Calculate the angle between the (111) and (200) planes.

From the above,

$$\cos\phi = \frac{(1\times 2) + (1\times 0) + (1\times 0)}{\sqrt{1+1+1}\sqrt{4+0+0}}$$

$$\cos\phi = \frac{1}{\sqrt{3}}$$

which produces the result, $\phi = 54.75°$.



SIMPLE CRYSTAL STRUCTURES

In the following section we will discuss simple crystal structures of general interest:

- sodium chloride,
- cesium chloride,
- hexagonal close-packed,
- diamond,
- cubic zinc sulfide

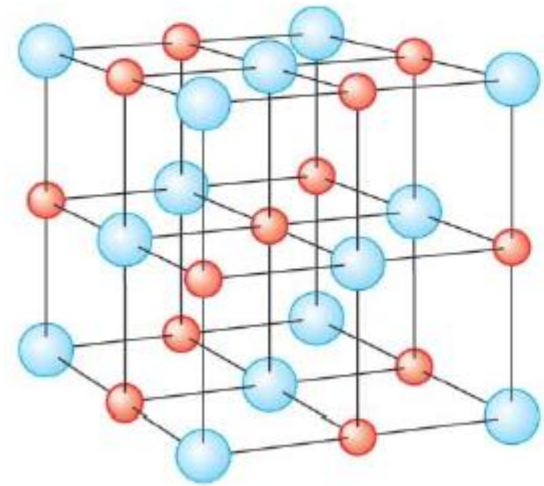
Sodium Chloride Structure

The NaCl structure is FCC

• The basis consists of one Na atom and one Cl atom, separated by one-half of

the body diagonal of a unit cube

• There are four units of NaCl in each unit cube



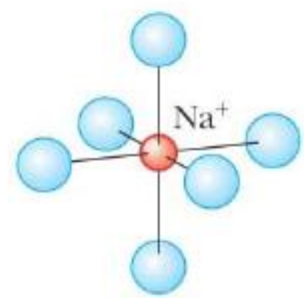
(a)

Atom positions:

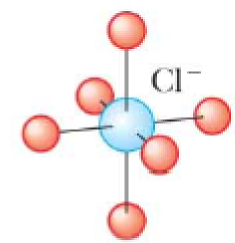
Cl : 000 ; ½½0; ½0½; 0½½

Na: ½½½; 00½; 0½0; ½00

• Each atom has 6 nearest neighbors of the opposite kind



(b)



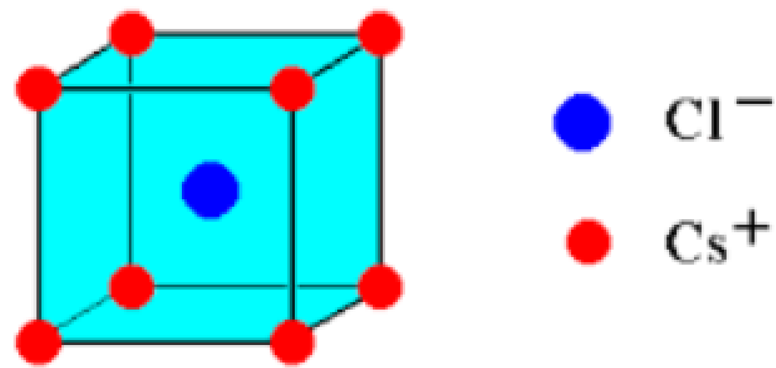
(c)

Cesium Chloride Structure

The CsCl structure is **simple cubic**

• The basis consists of one Cs^{+} ion and one Cl^{-} ion, with each atom at the center of a cube of atoms of the opposite kind

• There is on unit of CsCl in each unit cube.



Atom positions:

Cs^{+} : 000

Cl^{-} : ½½½ (or vice-versa)

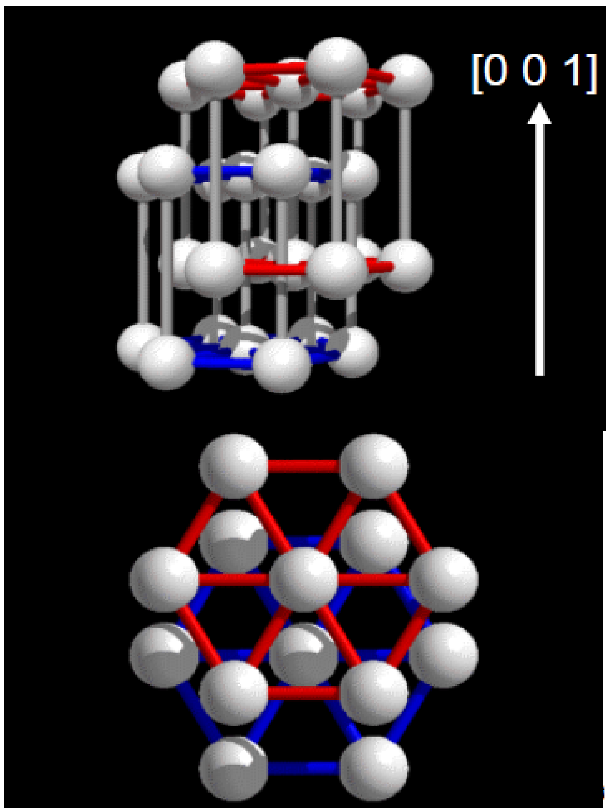
• Each atom has 8 nearest neighbors of the opposite kind

Closed-packed structures

The FCC and hexagonal closed-packed structures (HCP) are formed from packing in different ways. FCC (sometimes called the cubic closed-packed structure, or CCP) has the stacking arrangement of ABCABCABC… HCP has the arrangement ABABAB….

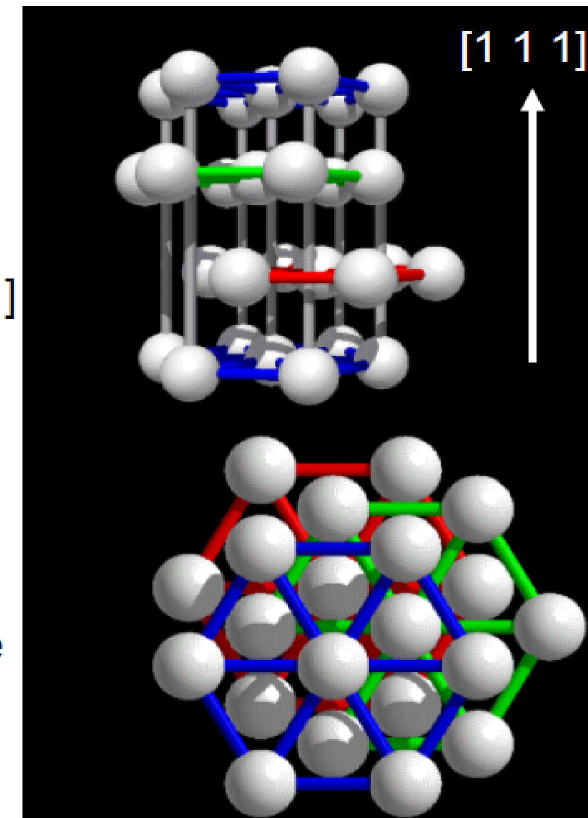
HCP

ABAB sequence



FCC (CCP) (looking along [111] direction

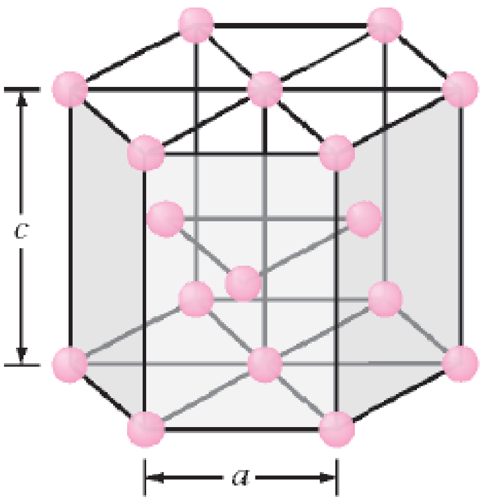
ABCABC sequence

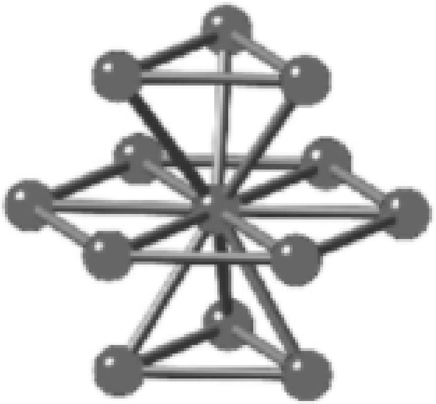


HCP Structure

- Metals do not crystallize into the simple hexagonal crystal structure because the packing factor is too low. The atoms can attain a lower energy and a more stable condition by forming the HCP structure.

- The Packing fraction of the HCP crystal structure is 0.74, the same as that for the FCC crystal structure.





- In HCP and FCC structures the atoms are packed as tightly as possible.

- In each structure, every atom is surrounded by 12 other atoms, thus both structures have a coordination number of 12.

HCP Structure

•The total number of atoms in HCP unit cell:

$$3 \times 1 + \ 2 \times {}^{1}/_{2} + 12 \times {}^{1}/_{6} = \ 6.$$

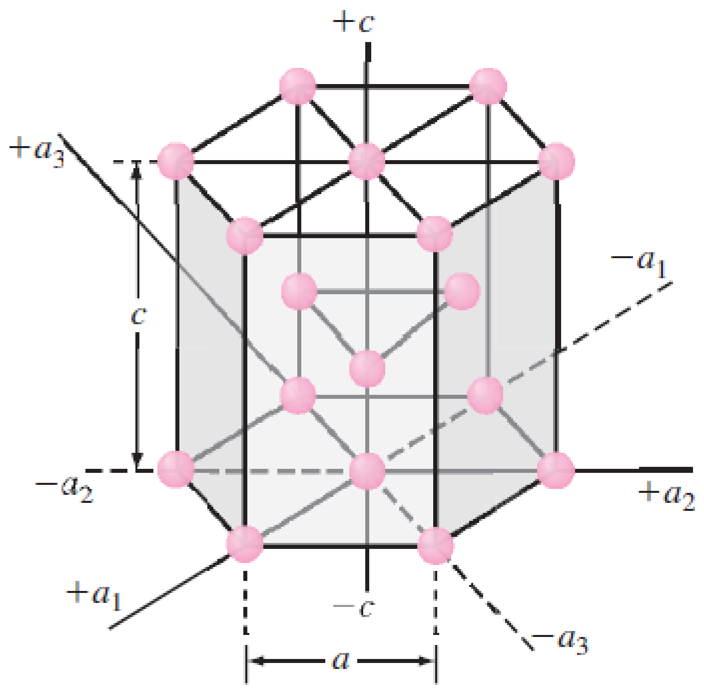
•The ratio of the height *c of the hexagonal prism of the HCP crystal structure* to its basal side *a is called the c/a ratio.*

•*The c/a ratio for an ideal HCP* crystal structure consisting of uniform spheres packed as tightly together as possible is 1.633.


unit cell

Indices for HCP planes and directions

Crystal planes in HCP unit cells are commonly identified by using four indices (known as Miller-Bravais indices) instead of three and are denoted by letters *h, k, i, and l.*



These four-digit hexagonal indices are based on a coordinate system with four axes. There are three basal axes, a_1, a_2, *and* a_3, *which make 120◦ with each other. The fourth axis or c axis is the* vertical axis located at the center of the unit cell.

The three Miller indices $[HKL]$ and the four Miller-Bravais indices $[hkil]$ are connected as given below.

$$h = (2H - K)/3, \qquad k = (2K - H)/3$$

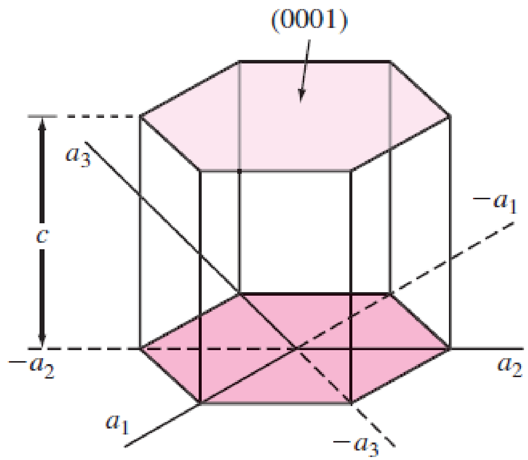
$$i = -(h + k), \qquad l = L$$

Special Cases: Miller Indices For Hexagonal Crystals
Planes and Directions in Cubic Crystals

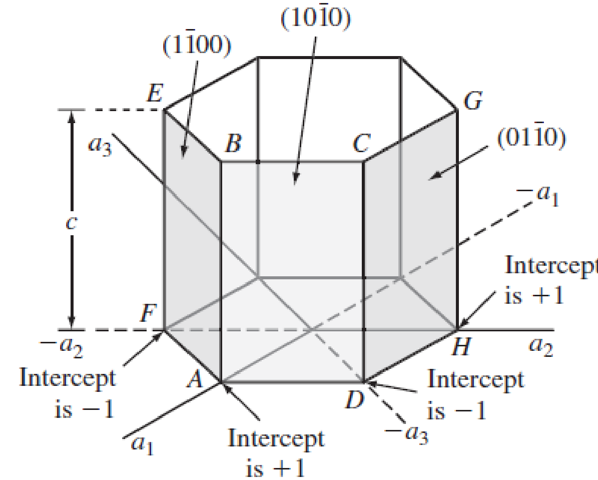
- The justification for using four indices in the case of hexagonal crystals relates to the fact that equivalent planes are not directly apparent if only three indices are used (as is illustrated in the following example).
- (0 1 0) → (0 1 $\underline{1}$ 0)
  (1 0 0) → (1 0 $\underline{1}$ 0)
  (1 1 0) → (1 1 $\underline{2}$ 0) These two planes are equivalent
  ($\underline{1}$ 2 0) → ($\underline{1}$ 2 $\underline{1}$ 0) although it is not initially apparent

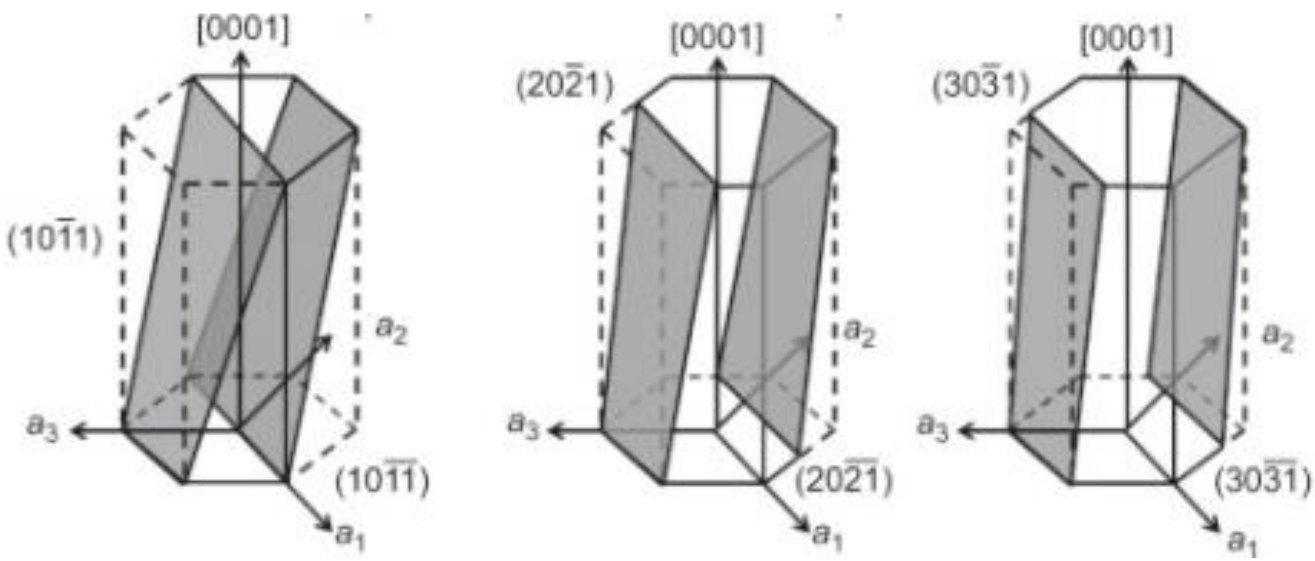
Indices for HCP planes and directions

Basal plane



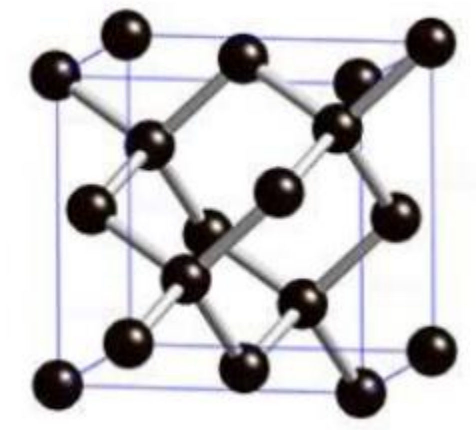
Prism planes





Diamond structure

Diamond structure is adopted by solids with four symmetrically placed covalent bonds. This is the situation in silicon, germanium, and grey tin, as well as in diamond.

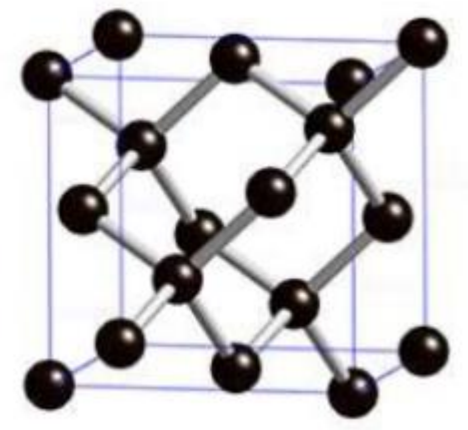


Diamond structure represents two inter-penetrating fcc sublattices displaced from each other by one quarter of the cube diagonal distance.

Atom positions:

Diamond has the translational symmetry of FCC lattice with a basis of two atoms, one at 000 and the other at ¼¼¼.

Diamond structure

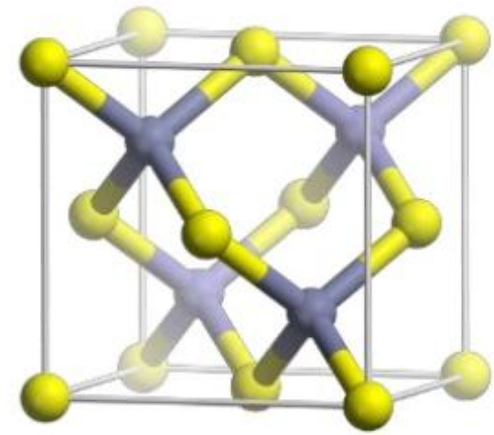


Each atom has 4 nearest neighbors and 12 next nearest neighbors.

The diamond structure is relatively empty: the maximum proportion of the available volume which may be filled by hard spheres is only 0.34, which is 46 percent of the filling factor for close-packed structures such as FCC and HCP.

Cubic Zinc Sulfide Structure

The cubic zinc sulfide (zinc blende) structure results when Zn atoms are placed on one FCC lattice and S atoms on the other FCC lattice.

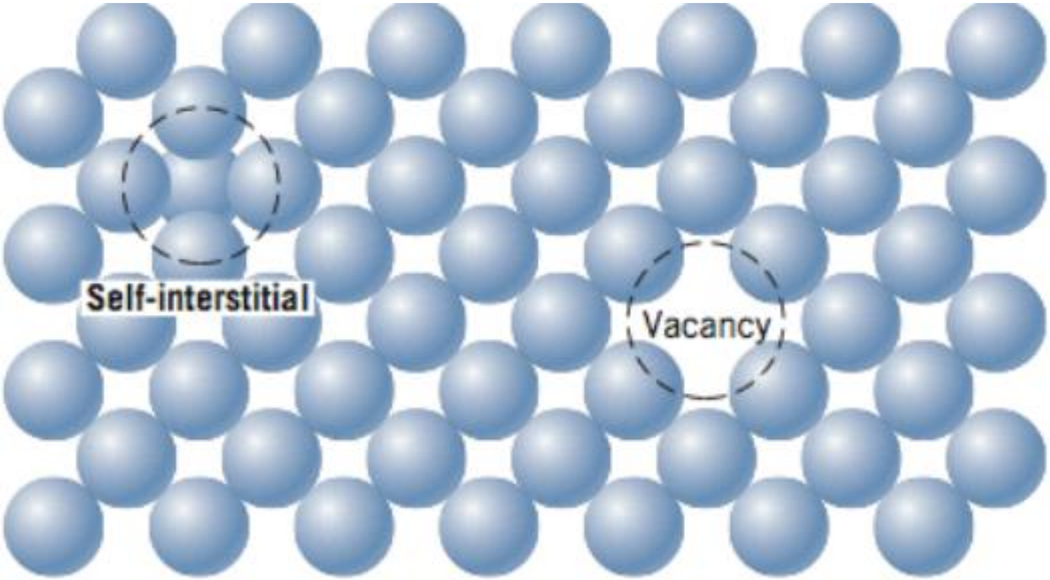


The diamond structure allows a center-of-inversion symmetry operation at the midpoint of every line between nearest-neighbor atoms. The inversion operation carries an atom at **r** into an atom at **-r**. The cubic ZnS structure does not have inversion symmetry.

Crystal	a	Crystal	a
SiC	4.35 Å	ZnSe	5.65 Å
ZnS	5.41	GaAs	5.65
AlP	5.45	AlAs	5.66
GaP	5.45	InSb	6.46

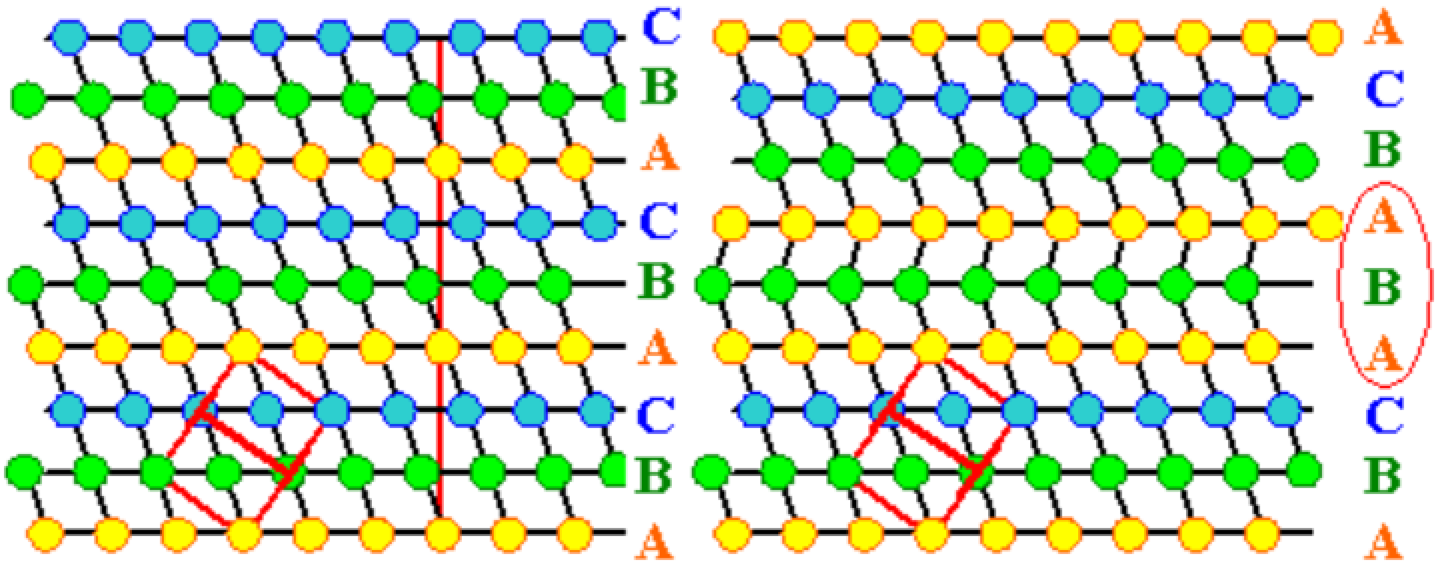
Departures from the "Perfect Crystal"

- Real Crystals always have foreign atoms (impurities), missing atoms (vacancies), & atoms between lattice sites (interstitials) where they should not be. Each of these conditions spoils the perfect crystal structure.



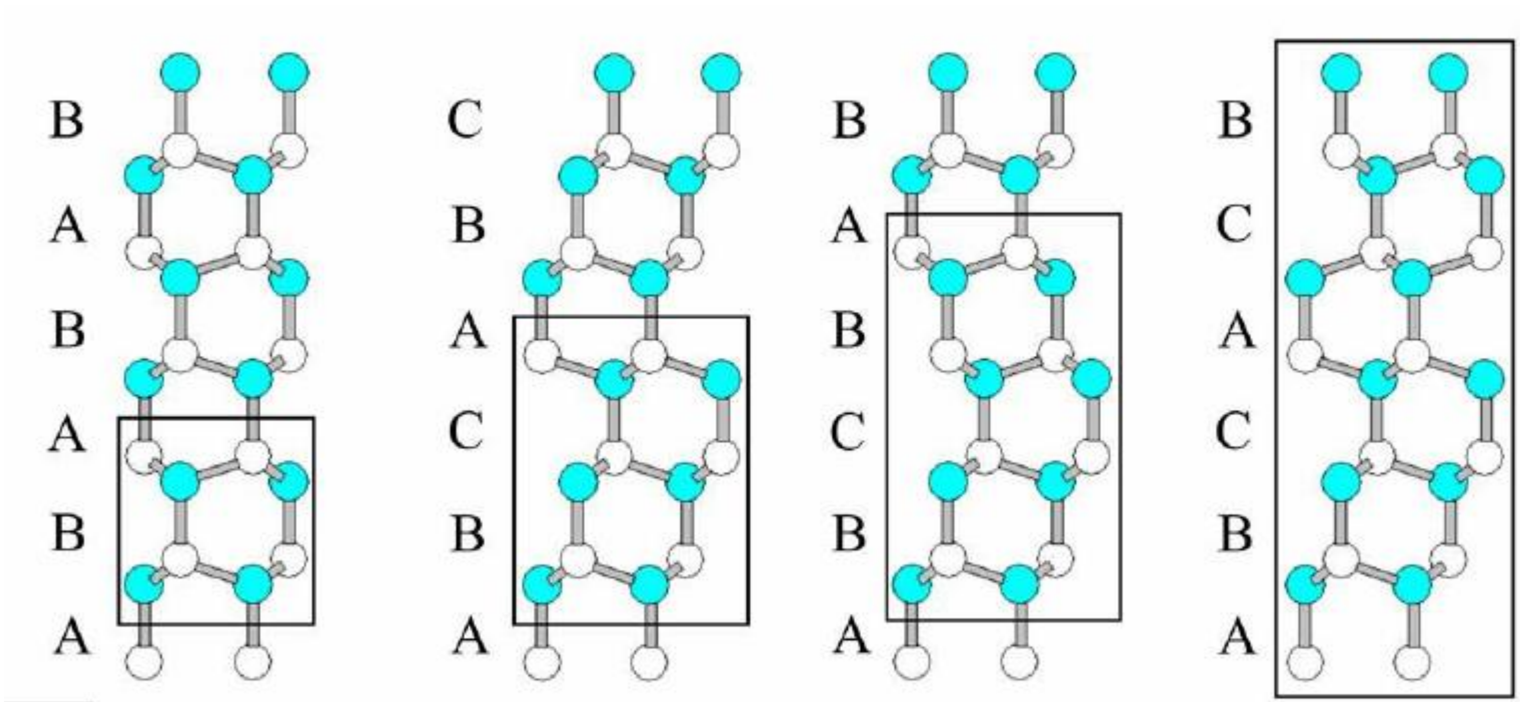
Departures from the "Perfect Crystal"

- Random stacking: Sometimes a crystal structure depart from its perfect crystal sequencing such as structure of ABCABCABC sequence is produced in ABC**ABA**BCA.



Departures from the "Perfect Crystal"

- Polytypism is characterized by a stacking sequence with a long repeat unit along the stacking axis. The best known example is zinc sulfide, ZnS, in which more than 150 polytypes have been identified, with the longest periodicity being 360 layers.



1. ***Tetrahedral angles.*** The angles between the tetrahedral bonds of diamond are the same as the angles between the body diagonals of a cube, as in Fig. 10. Use elementary vector analysis to find the value of the angle.

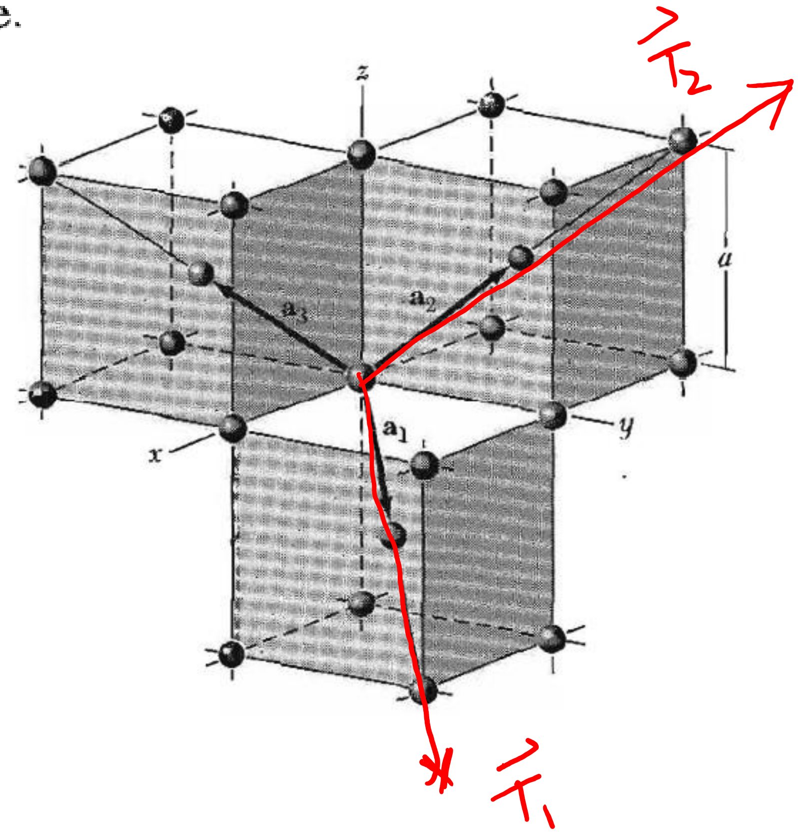
$\vec{T}_1 = \hat{i} + \hat{j} - \hat{k}$

$\vec{T}_2 = -\hat{i} + \hat{j} + \hat{k}$

$\theta = \cos^{-1}\left(\frac{\vec{T}_1 \cdot \vec{T}_2}{|\vec{T}_1|\,|\vec{T}_2|}\right)$

$= \cos^{-1}\left(\frac{-1+1-1}{\sqrt{3}\,\sqrt{3}}\right) = \cos^{-1}\left(\frac{-1}{3}\right)$

$\boxed{\theta = 109.5^\circ}$

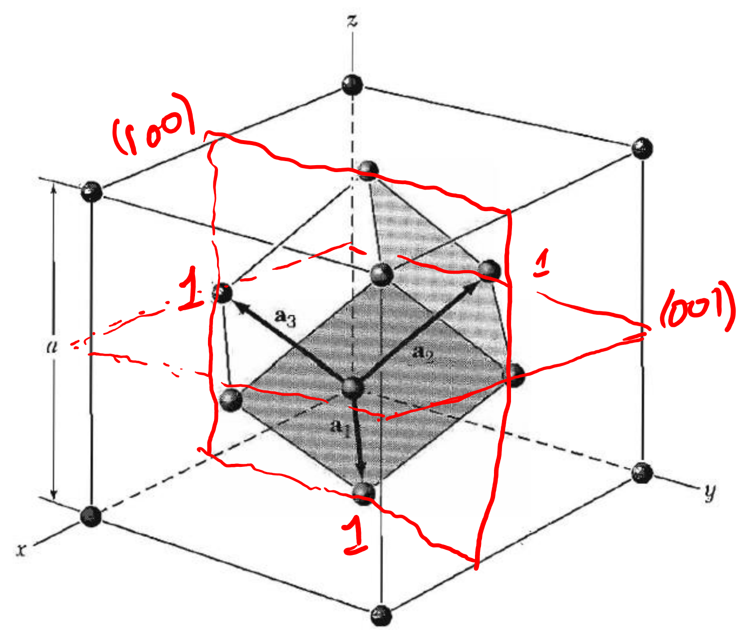


2. *Indices of planes.* Consider the planes with indices (100) and (001); the lattice is fcc, and the indices refer to the conventional cubic cell. What are the indices of these planes when referred to the primitive axes of Fig. 11?

Conventional → Primitive

(100) → (101)

(001) → (011)



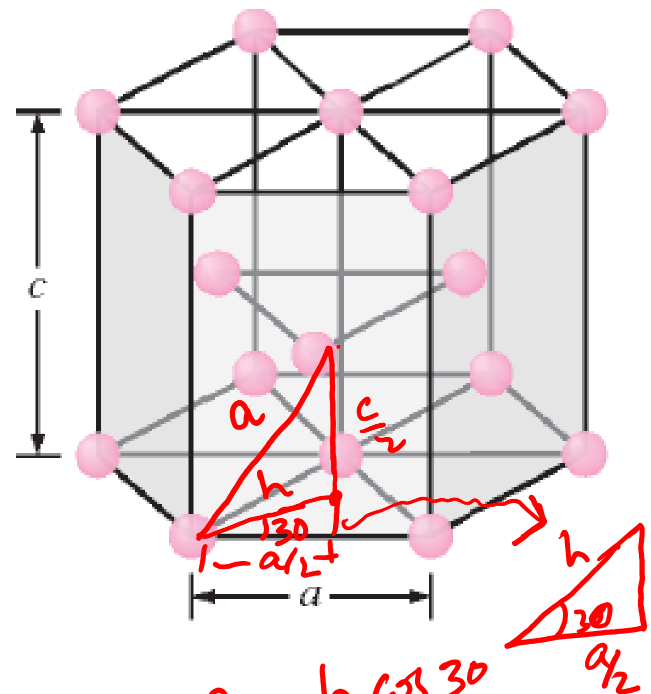
3. *Hcp structure.* Show that the c/a ratio for an ideal hexagonal close-packed structure is $(\frac{8}{3})^{1/2} = 1.633$. If c/a is significantly larger than this value, the crystal structure may be thought of as composed of planes of closely packed atoms, the planes being loosely stacked.

$$a^2 = \left(\frac{c}{2}\right)^2 + h^2$$

$$a^2 = \frac{c^2}{4} + \frac{a^2}{3}$$

$$a^2\left(\frac{2}{3}\right) = \frac{c^2}{4}$$

$$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$$



$$\frac{a}{2} = h\cos 30$$

$$\frac{a}{2} = h\frac{\sqrt{3}}{2}$$

$$h = \frac{a}{\sqrt{3}}$$