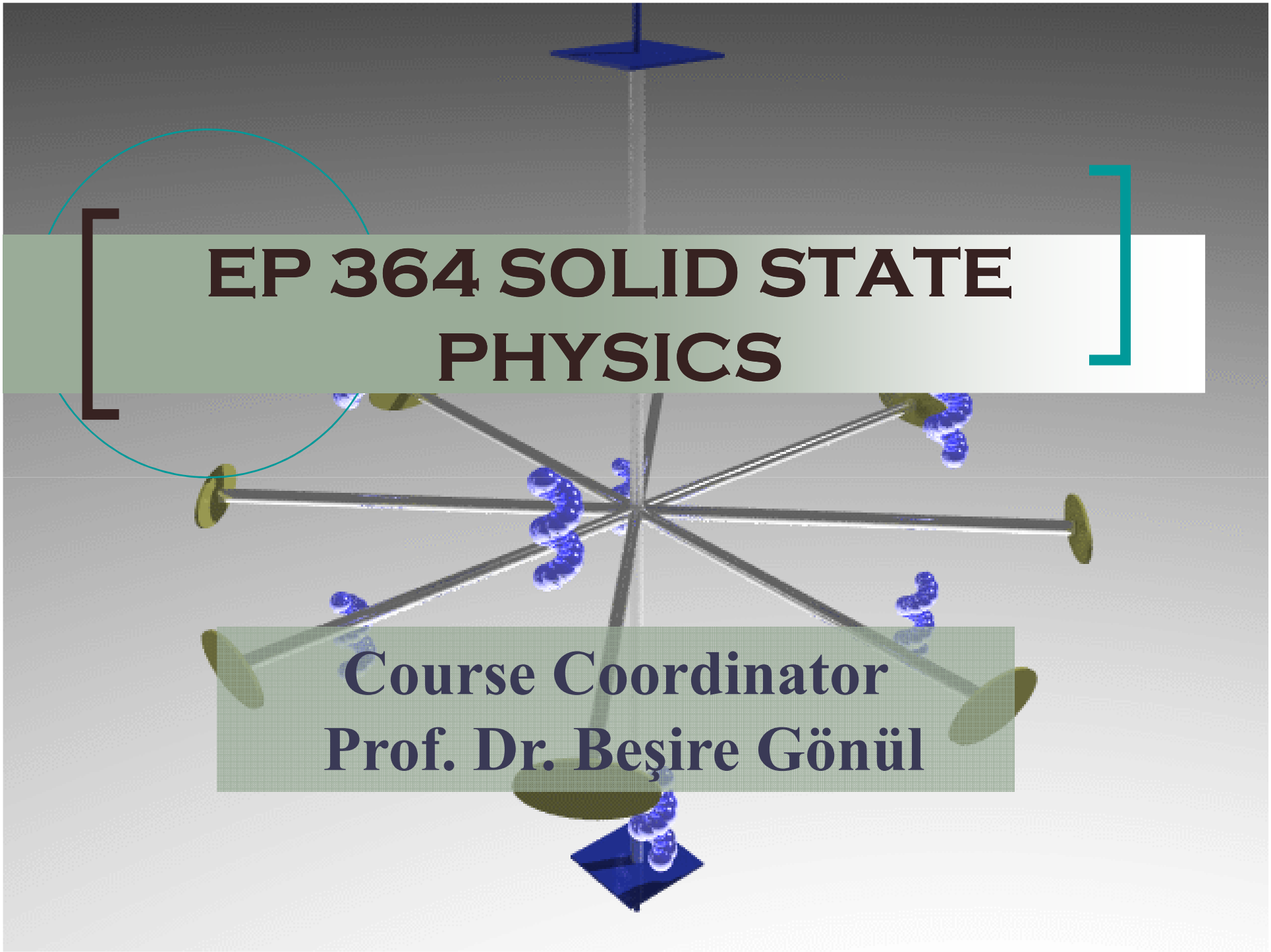
EP 364 SOLID STATE PHYSICS



Course Coordinator
Prof. Dr. Beşire Gönül

INTRODUCTION

- AIM OF SOLID STATE PHYSICS
- WHAT IS SOLID STATE PHYSICS AND WHY DO IT?
- CONTENT
- REFERENCES

Aim of Solid State Physics

- Solid state physics (SSP) explains the properties of solid materials as found on earth.
- The properties are expected to follow from Schrödinger's eqn. for a collection of atomic nuclei and electrons interacting with electrostatic forces.
- The fundamental laws governing the behaviour of solids are known and well tested.

Crystalline Solids

- We will deal with crystalline solids, that is solids with an atomic structure based on a regular repeated pattern.
- Many important solids are crystalline.
- More progress has been made in understanding the behaviour of crystalline solids than that of non-crystalline materials since the calculation are easier in crystalline materials.

What is solid state physics?

- Solid state physics, also known as condensed matter physics, is the study of the behaviour of atoms when they are placed in close proximity to one another.

- In fact, condensed matter physics is a much better name, since many of the concepts relevant to solids are also applied to liquids, for example.

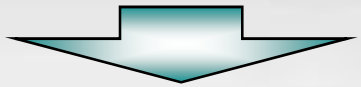
What is the point?

- Understanding the electrical properties of solids is right at the heart of modern society and technology.

- The entire computer and electronics industry relies on tuning of a special class of material, the semiconductor, which lies right at the metal-insulator boundary. Solid state physics provide a background to understand what goes on in semiconductors.

Solid state physics (SSP) is the applied physics

- New technology for the future will inevitably involve developing and understanding new classes of materials. By the end of this course we will see why this is a non-trivial task.

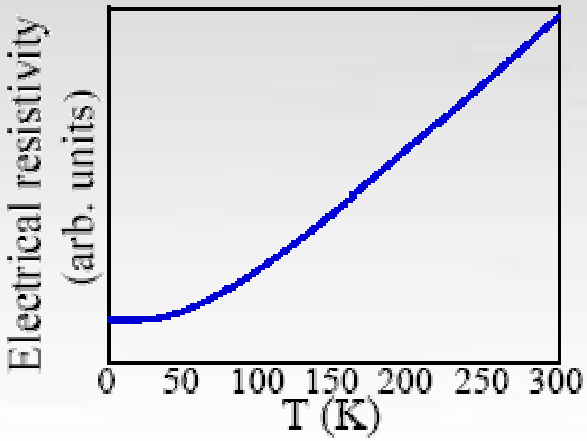


- So, SSP is the applied physics associated with technology rather than interesting fundamentals.

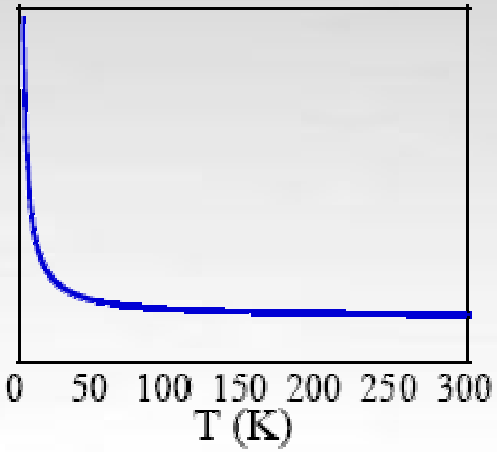
Electrical resistivity of three states of solid matter

- How can this be? After all, they each contain a system of atoms and especially electrons of similar density. And the plot thickens: graphite is a metal, diamond is an insulator and buckminster-fullerene is a superconductor.

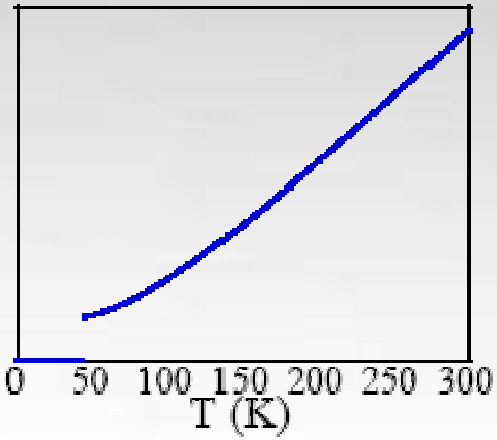
They are all just carbon!



Metal

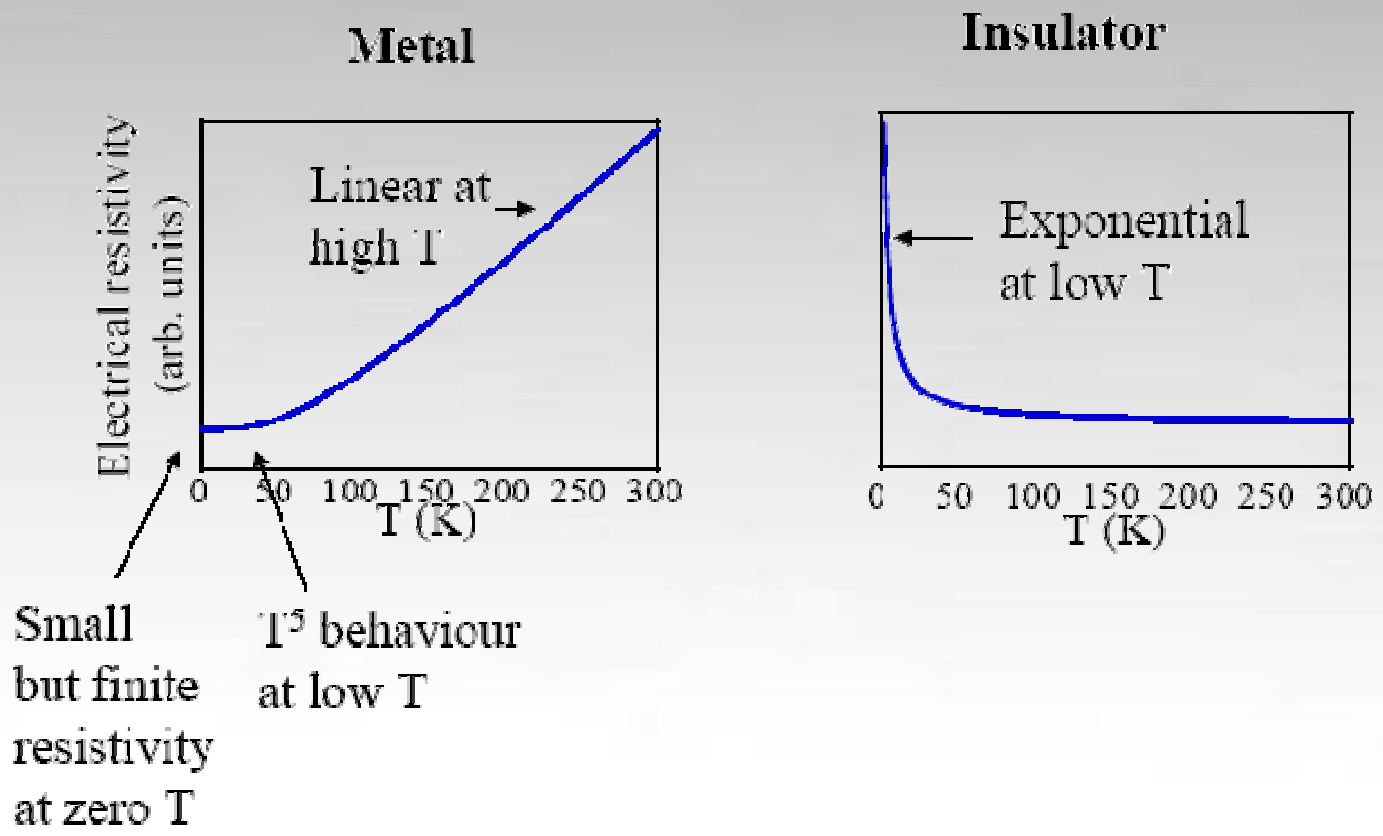


Insulator



Superconductor

- Among our aims - understand **why** one is a metal and one an insulator, and then the physical origin of the marked features.
- Also think about thermal properties etc. etc.



CONTENT

- **Chapter 1.** Crystal Structure
- **Chapter 2.** X-ray Crystallography
- **Chapter 3.** Interatomic Forces
- **Chapter 4.** Crystal Dynamics
- **Chapter 5.** Free Electron Theory

CHAPTER 1. CRYSTAL STRUCTURE

- Elementary Crystallography
  - Solid materials (crystalline, polycrystalline, amorphous)
  - Crystallography
  - Crystal Lattice
  - Crystal Structure
  - Types of Lattices
  - Unit Cell
  - Directions-Planes-Miller Indices in Cubic Unit Cell
- Typical Crystal Structures
  (3D– 14 Bravais Lattices and the Seven Crystal System)
- Elements of Symmetry

CHAPTER 2.
X-RAY CRYSTALLOGRAPHY

- X-ray
- Diffraction
  - Bragg equation
- X-ray diffraction methods
  - Laue Method
  - Rotating Crystal Method
  - Powder Method
- Neutron & electron diffraction

CHAPTER 3. INTERATOMIC FORCES

- Energies of Interactions Between Atoms
- Ionic bonding
  - NaCl
- Covalent bonding
  - Comparision of ionic and covalent bonding
- Metallic bonding
- Van der waals bonding
- Hydrogen bonding

CHAPTER 4. CRYSTAL DYNAMICS

- Sound wave
- Lattice vibrations of 1D cystal
  - Chain of identical atoms
  - Chain of two types of atoms
- Phonons
  - Heat Capacity
  - Density of States
  - Thermal Conduction
- Energy of harmonic oscillator
  - Thermal energy & Lattice Vibrations
  - Heat Capacity of Lattice vibrations

CHAPTER 5.
FREE ELECTRON THEORY

- Free electron model
- Heat capacity of free electron gas
- Fermi function, Fermi energy
- Fermi dirac distribution function
- Transport properties of conduction electrons

REFERENCES

- Core book:

  Solid state physics, J.R.Hook and H.E.Hall, Second edition (Wiley)

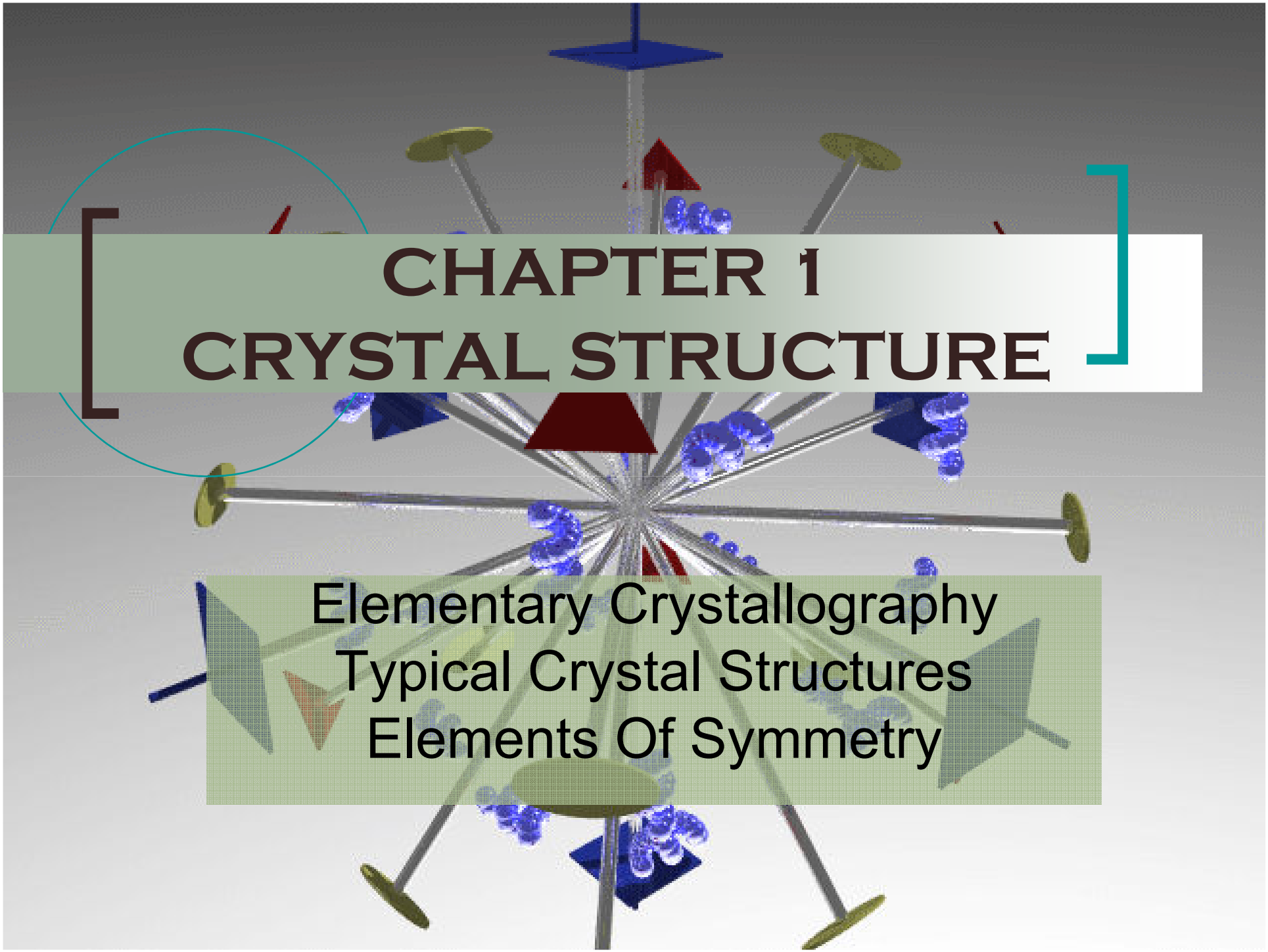
- Other books at a similar level:

  Solid state physics, Kittel (Wiley)

  Solid state physics, Blakemore (Cambridge)

  Fundamentals of solid state physics, Christman (Wiley)

- More advanced: Solid state physics, Ashcroft and Mermin



CHAPTER 1
CRYSTAL STRUCTURE

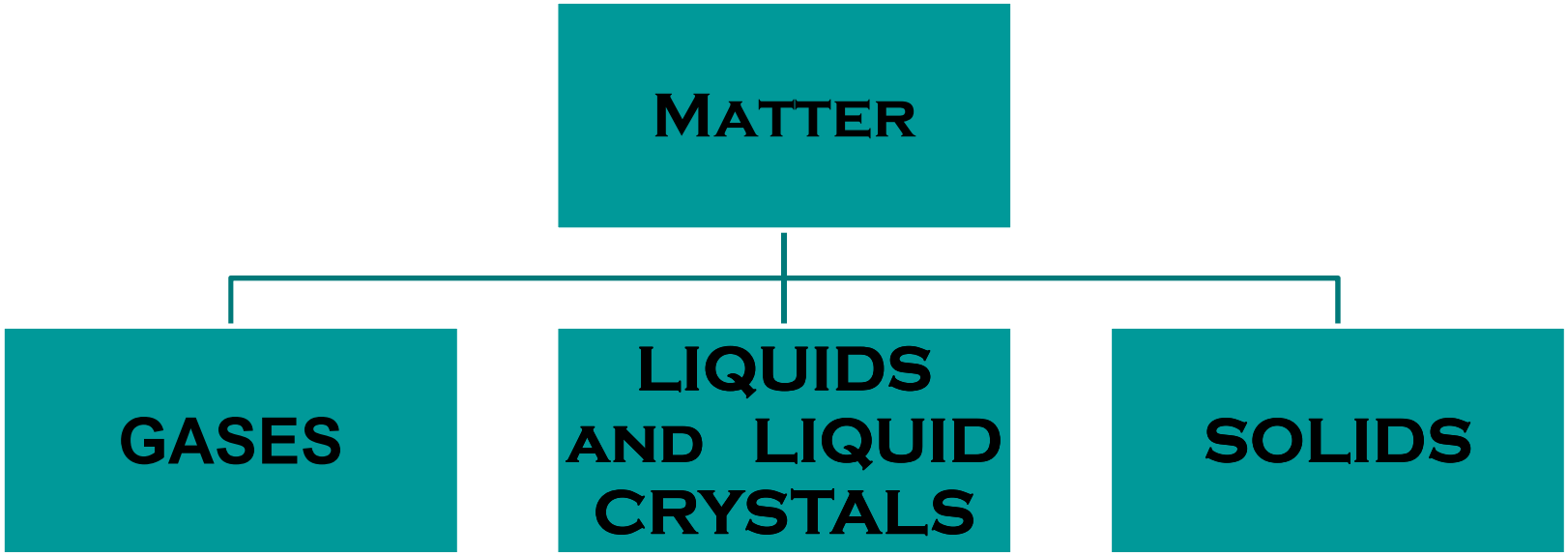
Elementary Crystallography
Typical Crystal Structures
Elements Of Symmetry

Objectives

By the end of this section you should:

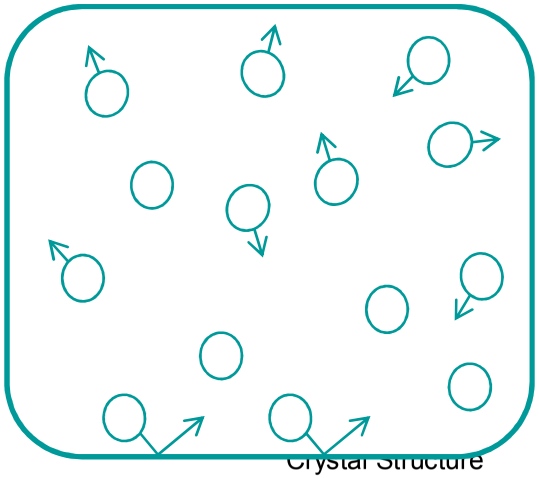
- be able to identify a unit cell in a symmetrical pattern
- know that there are 7 possible unit cell shapes
- be able to define cubic, tetragonal, orthorhombic and hexagonal unit cell shapes

MATTER



Gases

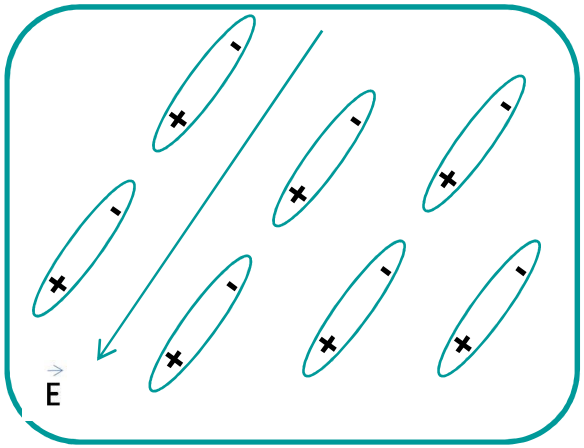
- Gases have atoms or molecules that do not bond to one another in a range of pressure, temperature and volume.
- These molecules haven't any particular order and move freely within a container.



Liquids and Liquid Crystals

- Similar to gases, liquids haven't any atomic/molecular order and they assume the shape of the containers.
- Applying low levels of thermal energy can easily break the existing weak bonds.

Liquid crystals have mobile molecules, but a type of long range order can exist; the molecules have a permanent dipole. Applying an electric field rotates the dipole and establishes order within the collection of molecules.



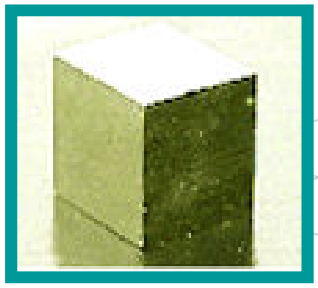
Crytals

- Solids consist of atoms or molecules ***executing thermal motion*** about an equilibrium position ***fixed at a point*** in space.
- Solids can take the form of crystalline, polycrstalline, or amorphous materials.
- Solids (at a given temperature, pressure, and volume) have stronger bonds between molecules and atoms than liquids.
- Solids require more energy to ***break the bonds.***

ELEMENTARY CRYSTALLOGRAPHY

SOLID MATERIALS

- CRYSTALLINE
  - Single Crystal
- POLYCRYSTALLINE
- AMORPHOUS (NON-CRYSTALLINE)

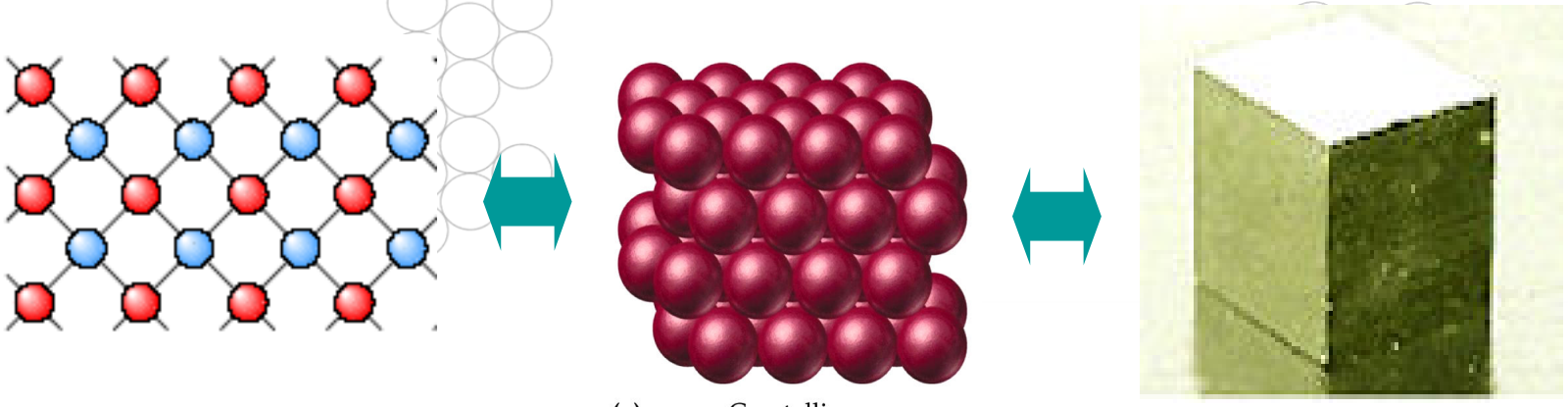


Types of Solids

- Single crsytal, polycrystalline, and amorphous, are the three general types of solids.
- Each type is characterized by the size of ordered region within the material.
- An ordered region is a spatial volume in which atoms or molecules have a regular geometric arrangement or periodicity.

Crystalline Solid

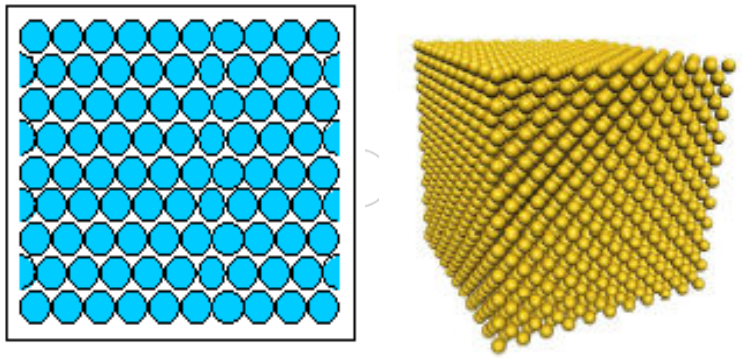
- Crystalline Solid is the solid form of a substance in which the ***atoms or molecules*** are arranged in a definite, repeating pattern in three dimension.
- Single crystals, ideally have a high degree of order, or regular geometric periodicity, throughout the ***entire volume of the material***.



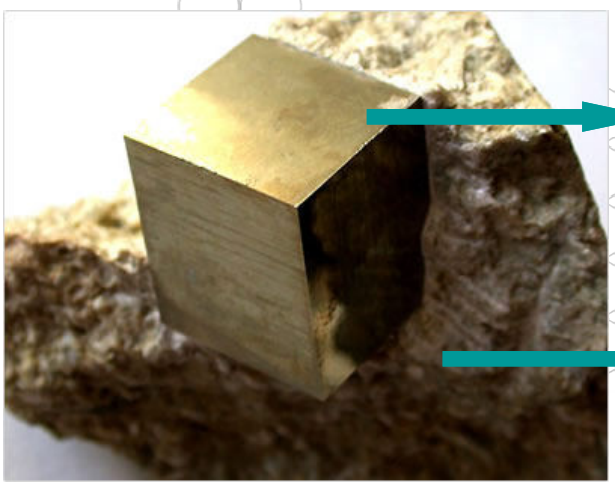
(a) Crystalline solid

Crystalline Solid

- Single crystal has an atomic structure that repeats periodically across its whole volume. Even at infinite length scales, each atom is related to every other equivalent atom in the structure by translational symmetry

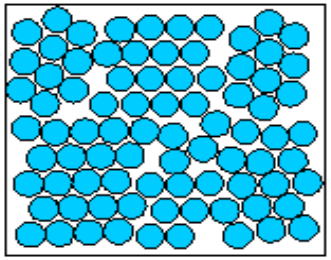


Single Crystal



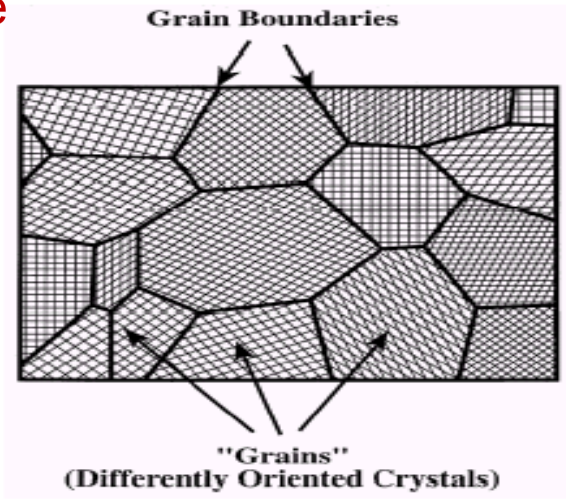
Polycrystalline Solid

- Polycrystal is a material made up of an aggregate of ***many small single crystals*** (also called crystallites or grains).
- Polycrystalline material have a high degree of order over many atomic or molecular dimensions.
- These ***ordered regions,*** or single crytal regions, vary in size and orientation wrt one another.
- These regions are called as ***grains (domain)*** and are separated from one another by ***grain boundaries.*** *The atomic order can vary from one domain to the next.*
- The grains are usually ***100 nm - 100 microns in diameter***. Polycrystals with grains that are <10 nm in diameter are called nanocrystalline



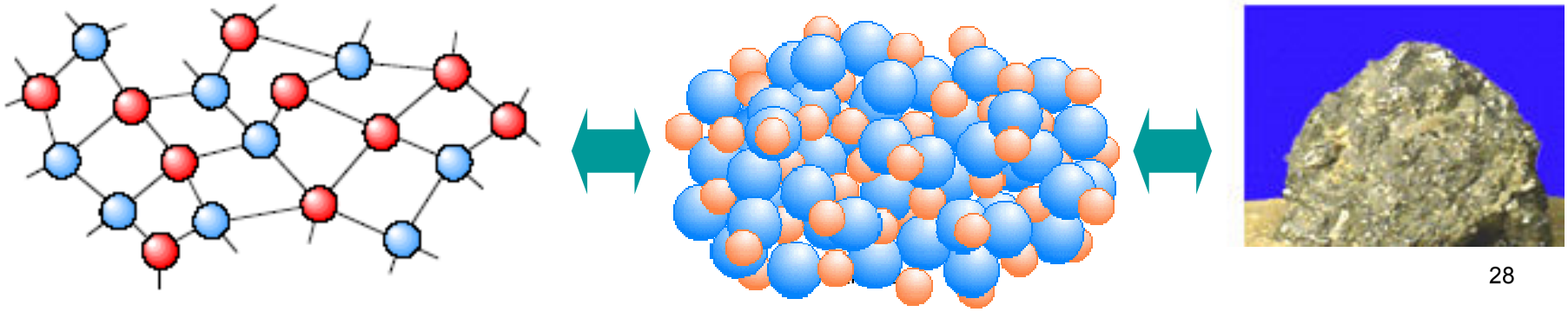
Polycrystalline Pyrite form (Grain)

Crystal Structure



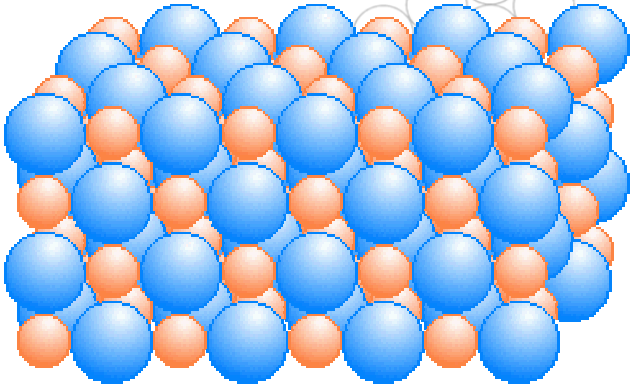
Amorphous Solid

- Amorphous (Non-crystalline) Solid is composed of randomly orientated atoms , ions, or molecules that do not form defined patterns or lattice structures.
- Amorphous materials have order only within a few atomic or molecular dimensions.
- Amorphous materials do not have any long-range order, but they have varying degrees of short-range order.
- Examples to amorphous materials include amorphous silicon, plastics, and glasses.
- Amorphous silicon can be used in solar cells and thin film transistors.



Departure From Perfect Crystal

- Strictly speaking, one cannot prepare a perfect crystal. For example, even the surface of a crystal is a kind of imperfection because the periodicity is interrupted there.
- Another example concerns the thermal vibrations of the atoms around their equilibrium positions for any temperature T>0°K.

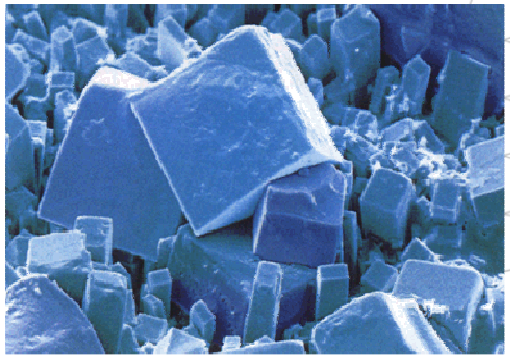


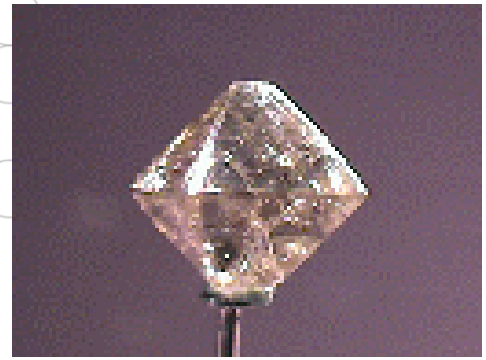
- As a third example, actual crystal always contains some foreign atoms, i.e., impurities. These impurities spoils the perfect crystal structure.

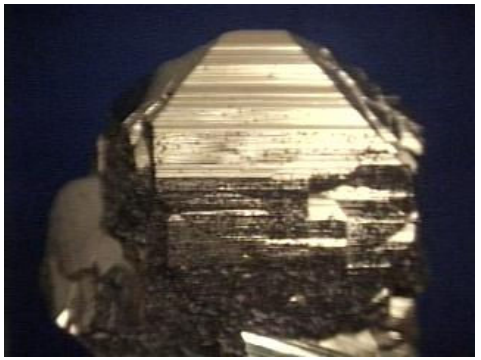
CRYSTALLOGRAPHY

What is crystallography?

The branch of science that deals with the geometric description of crystals and their internal arrangement.







Crystallography

Crystallography is essential for solid state physics

- Symmetry of a crystal can have a profound influence on its properties.
- Any crystal structure should be specified completely, concisely and unambiguously.
- Structures should be classified into different types according to the symmetries they possess.

ELEMENTARY CRYSTALLOGRAPHY

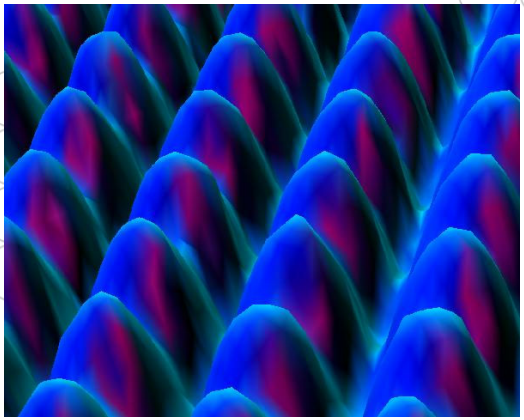
- A basic knowledge of crystallography is essential for solid state physicists;
  - to specify any crystal structure and
  - to classify the solids into different types according to the symmetries they possess.
- Symmetry of a crystal can have a profound influence on its properties.
- We will concern in this course with solids with simple structures.

CRYSTAL LATTICE

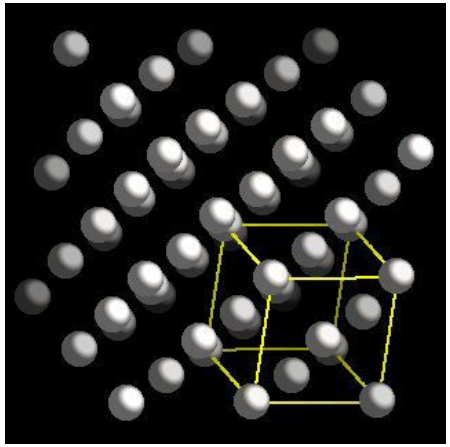
What is crystal (space) lattice?

In crystallography, only the geometrical properties of the crystal are of interest, therefore one replaces each atom by a geometrical point located at the equilibrium position of that atom.

Platinum



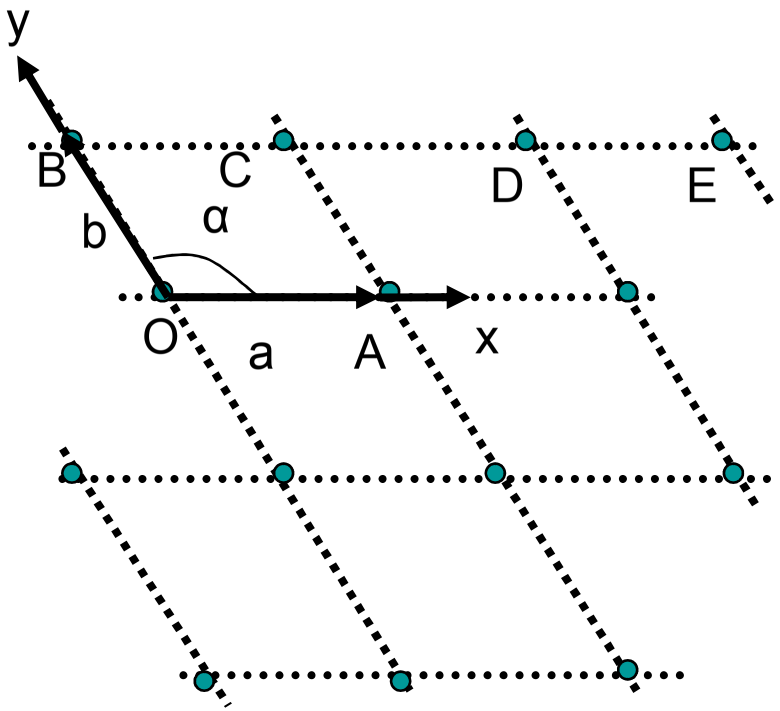
Platinum surface
(scanning tunneling microscope)



Crystal lattice and structure of Platinum

Crystal Lattice

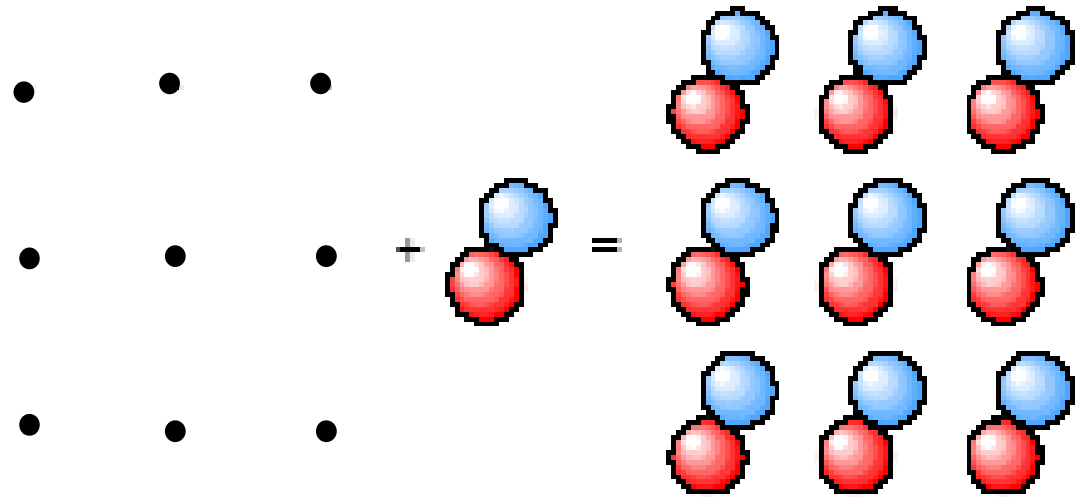
- An infinite array of points in space,
- Each point has identical surroundings to all others.
- Arrays are arranged exactly in a periodic manner.



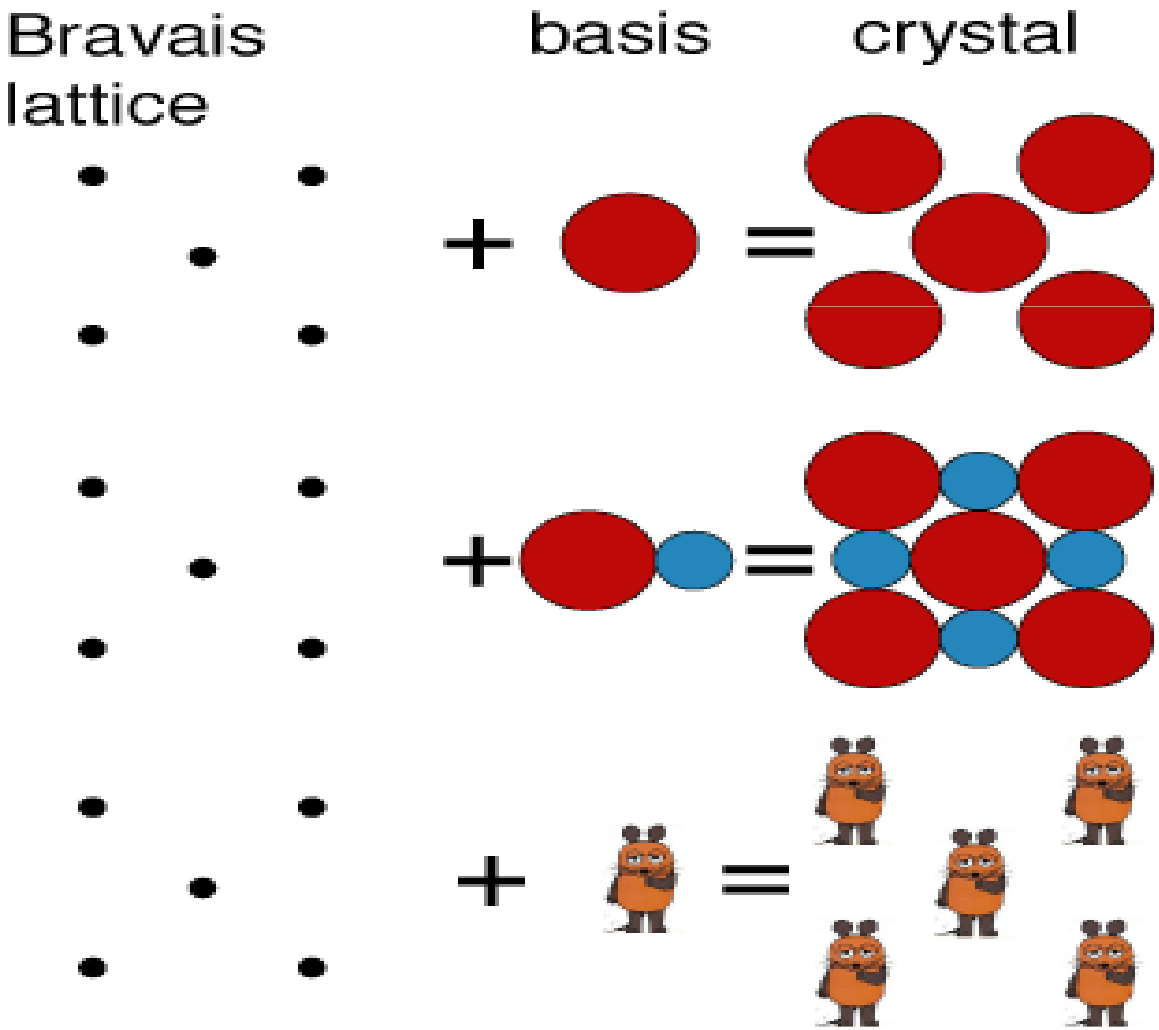
Crystal Structure

- Crystal structure can be obtained by attaching atoms, groups of atoms or molecules which are called basis (motif) to the lattice sides of the lattice point.

Crystal Structure = Crystal Lattice • + Basis

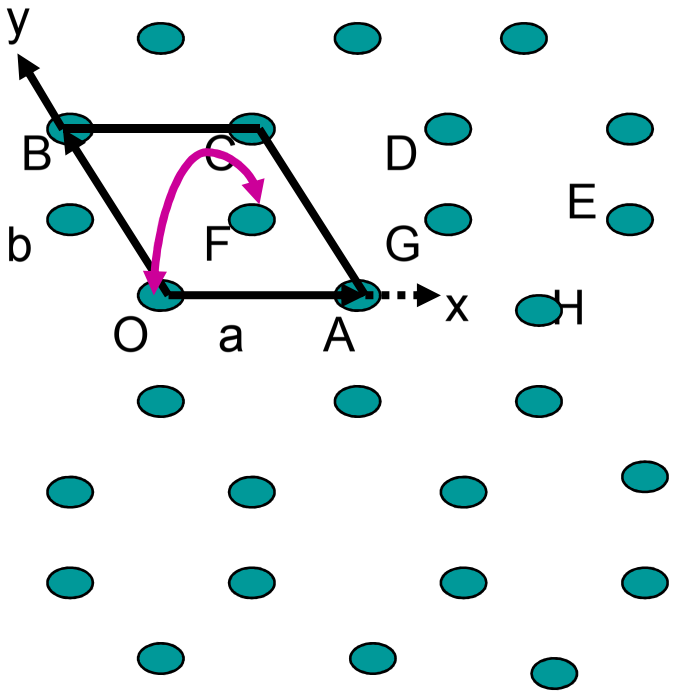


A two-dimensional Bravais lattice with different choices for the basis

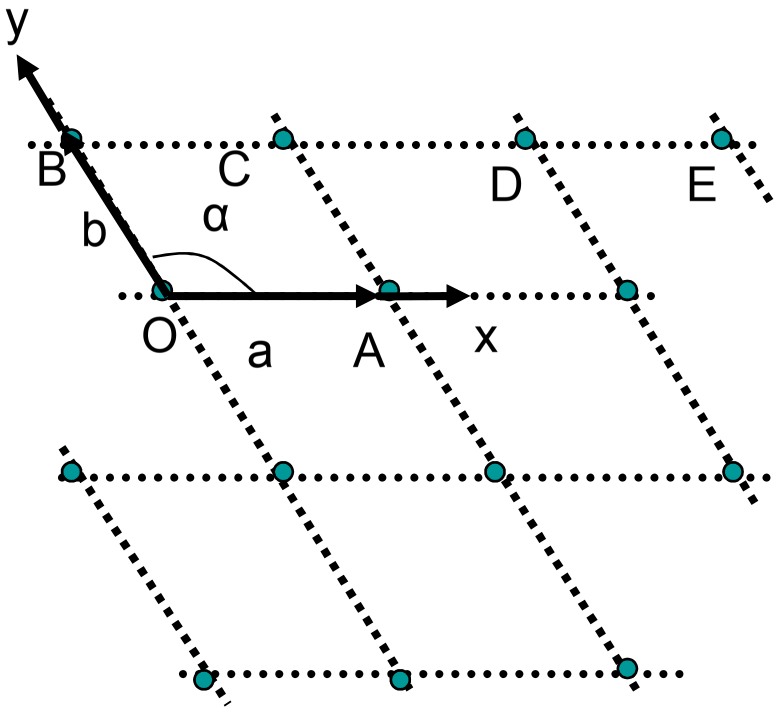


Basis

- **A group of atoms which describe crystal structure**



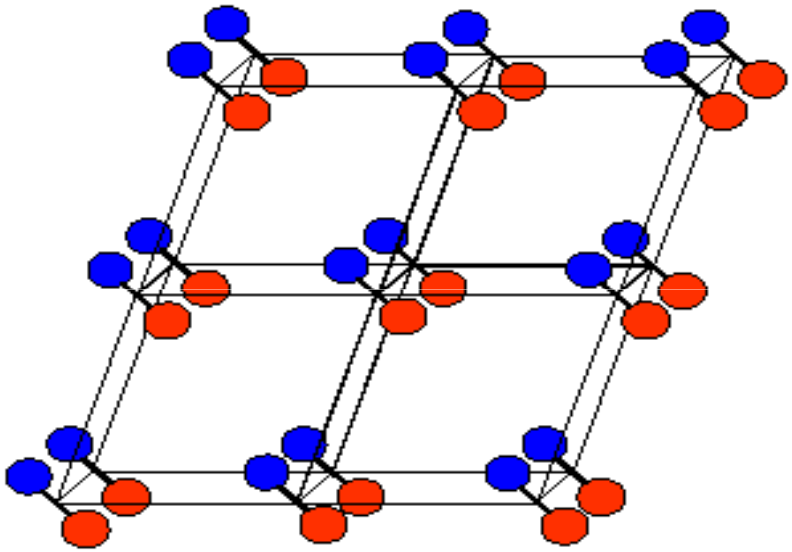
a) Situation of atoms at the corners of regular hexagons



b) Crystal lattice obtained by identifying all the atoms in (a)

Crystal structure

- Don't mix up atoms with lattice points
- Lattice points are infinitesimal points in space
- Lattice points do not necessarily lie at the centre of atoms

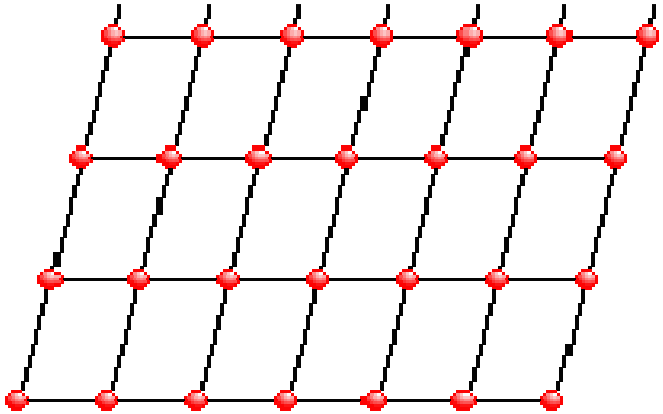


Crystal Structure = Crystal Lattice • + Basis

Crystal Lattice

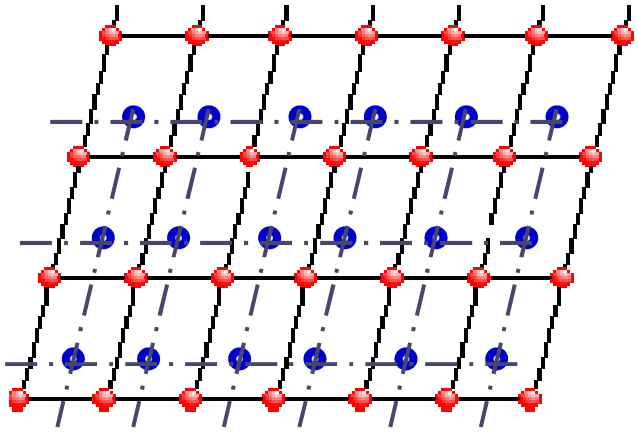
Bravais Lattice (BL)

- All atoms are of the same kind
- All lattice points are equivalent



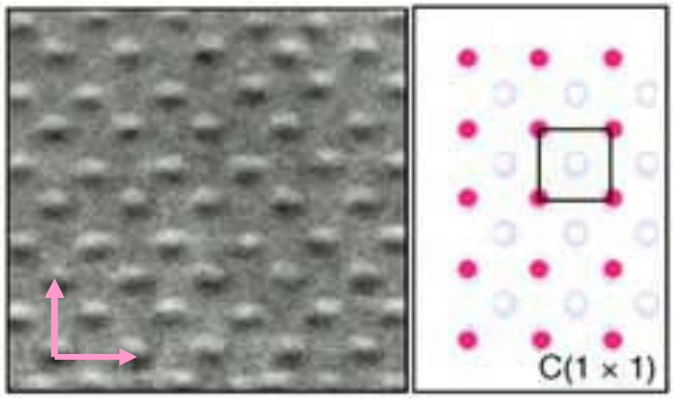
Non-Bravais Lattice (non-BL)

- Atoms can be of different kind
- Some lattice points are not equivalent
- A combination of two or more BL



Types Of Crystal Lattices

1) Bravais lattice is an infinite array of discrete points with an arrangement and orientation that appears exactly the same, from whichever of the points the array is viewed. Lattice is invariant under a translation.



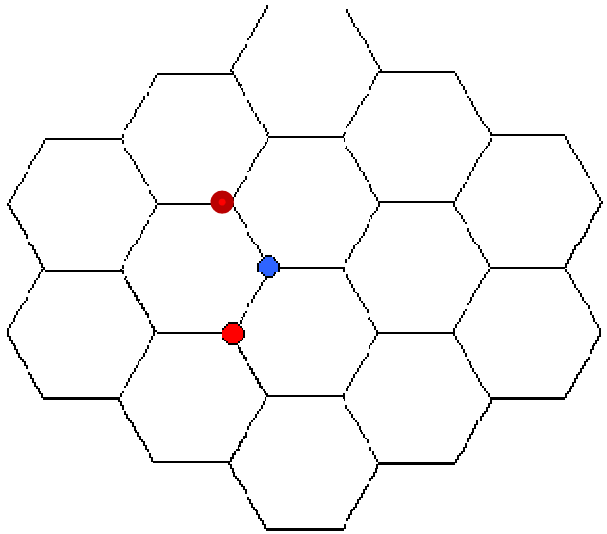
Nb film

Types Of Crystal Lattices

2) Non-Bravais Lattice

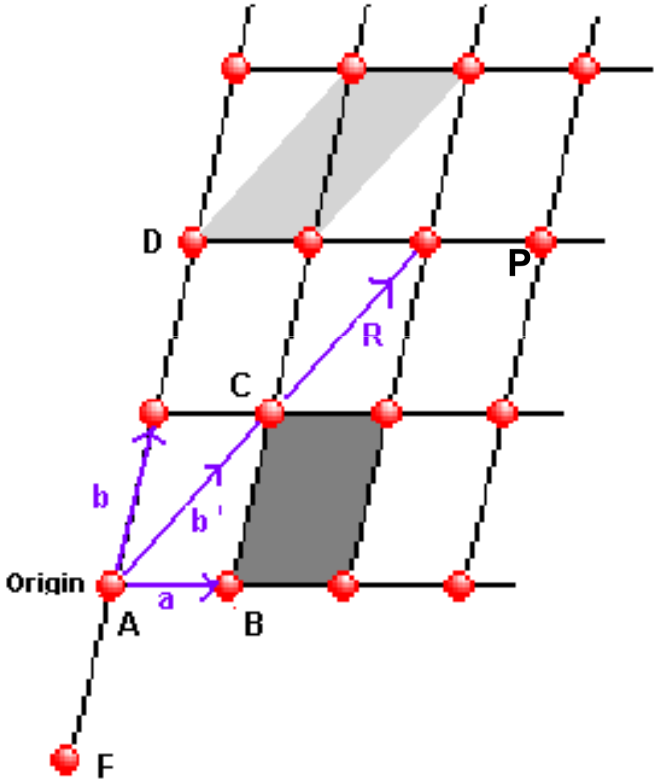
Not only the arrangement but also the orientation must appear exactly the same from every point in a bravais lattice.

- The red side has a neighbour to its immediate left, the blue one instead has a neighbour to its right.
- Red (and blue) sides are equivalent and have the same appearance
- Red and blue sides are not equivalent. Same appearance can be obtained rotating blue side 180º.



Honeycomb

Translational Lattice Vectors – 2D



Point D(n1, n2) = (0,2)

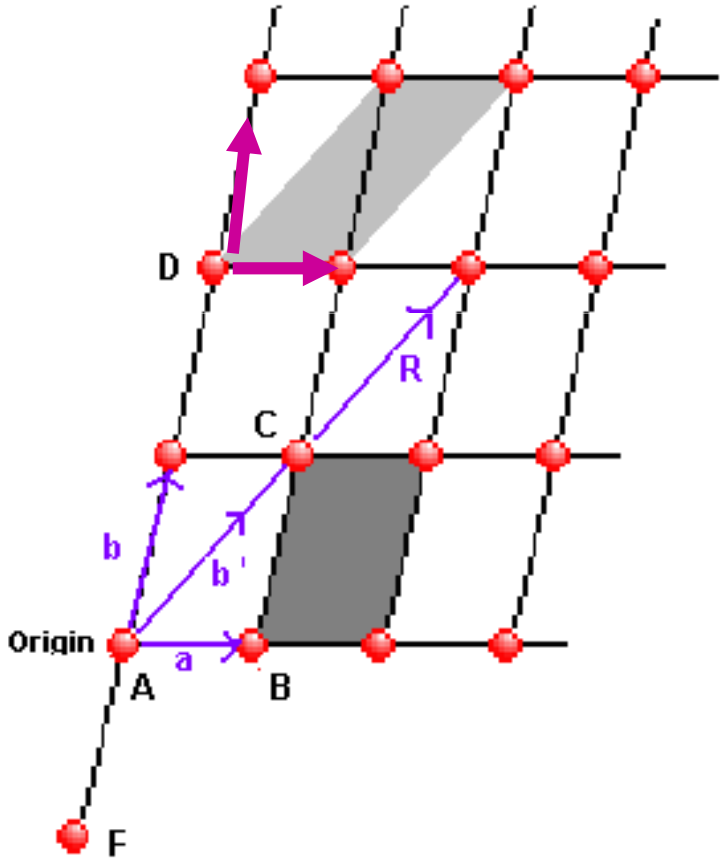
Point F (n1, n2) = (0,-1)

A space lattice is a set of points such that a translation from any point in the lattice by a vector;

$$R_n = n_1\, a + n_2\, b$$

locates an exactly *equivalent* point, *i.e.* a point with the same environment as *P* . This is translational symmetry. The vectors *a*, *b* are known as lattice vectors and (n_1, n_2) is a pair of integers whose values depend on the lattice point.

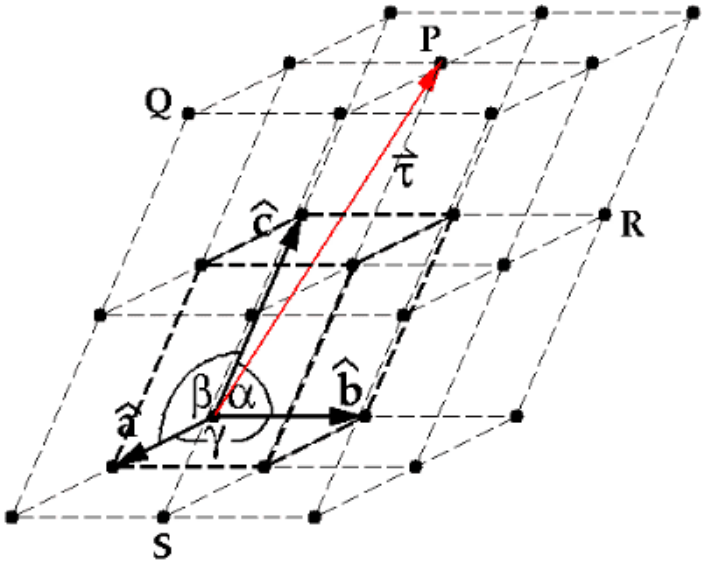
Lattice Vectors – 2D



- The two vectors a and b form a set of lattice vectors for the lattice.
- ***The choice of lattice vectors is not unique***. Thus one could equally well take the vectors a and b' as a lattice vectors.

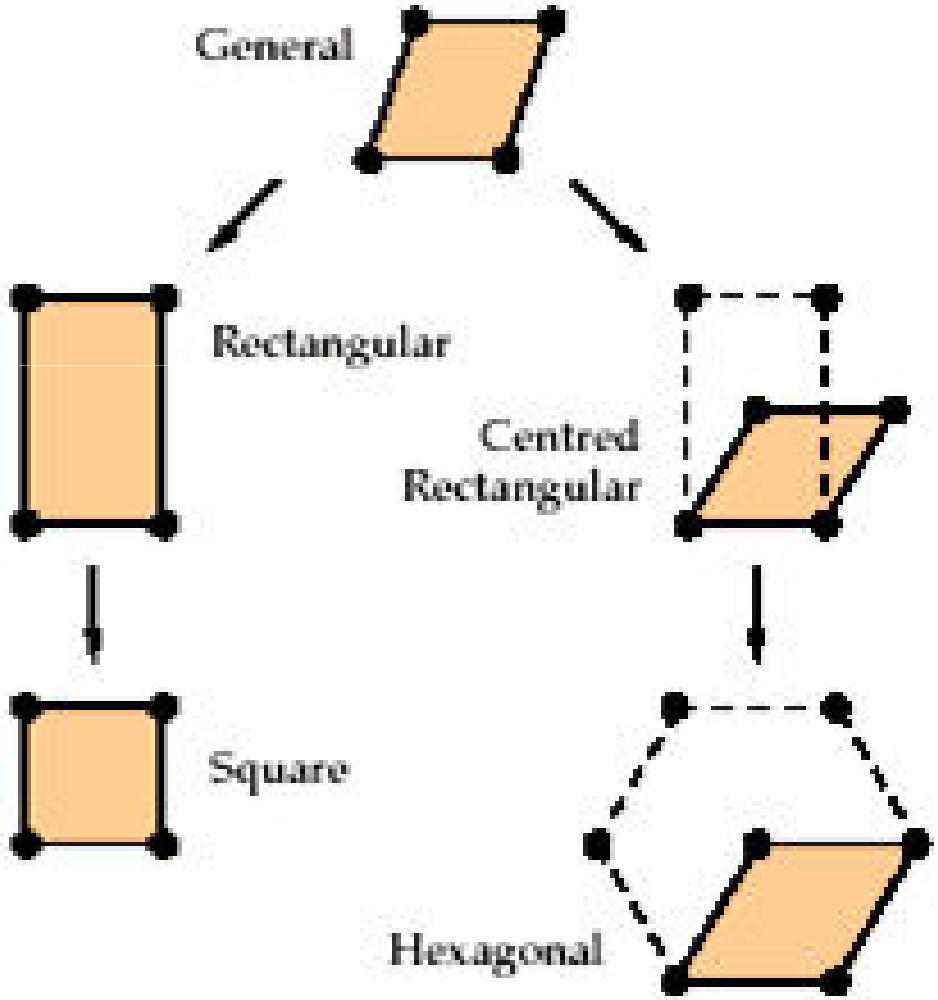
Lattice Vectors – 3D

An ideal three dimensional crystal is described by 3 fundamental translation vectors a, b and c. If there is a lattice point represented by the position vector r, there is then also a lattice point represented by the position vector where *u*, *v* and *w* are arbitrary integers.



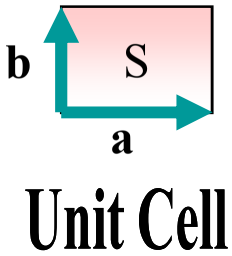
$$\mathbf{r'} = \mathbf{r} + u\,\mathbf{a} + v\,\mathbf{b} + w\,\mathbf{c} \qquad (1)$$

Five Bravais Lattices in 2D

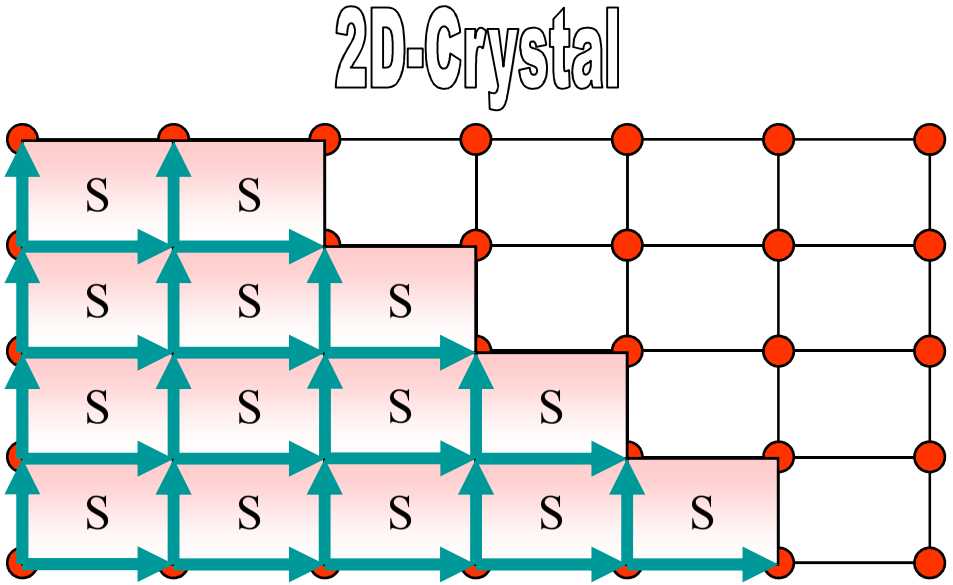


Unit Cell in 2D

- The smallest component of the crystal (group of atoms, ions or molecules), which when stacked together with pure translational repetition reproduces the whole crystal.



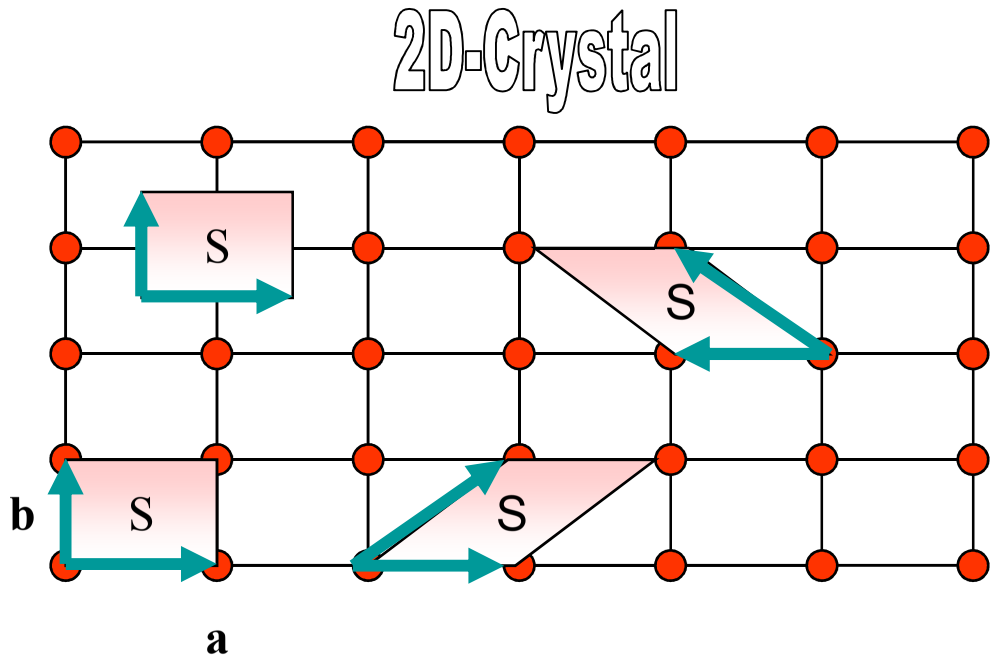
Unit Cell



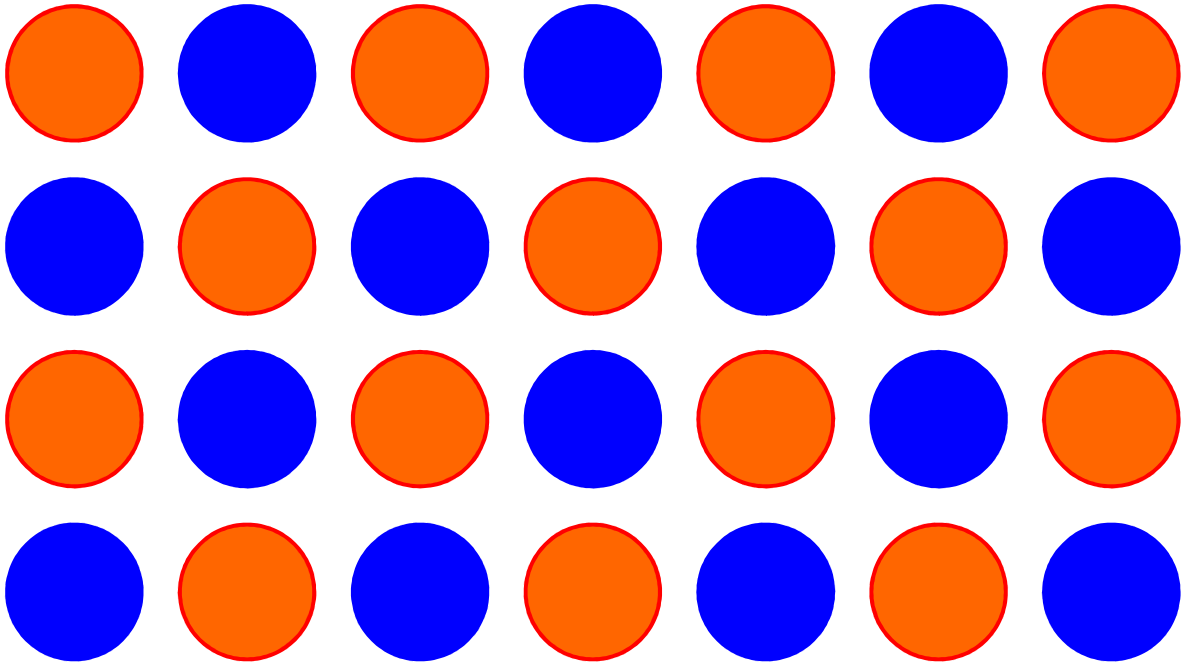
Unit Cell in 2D

- The smallest component of the crystal (group of atoms, ions or molecules), which when stacked together with pure translational repetition reproduces the whole crystal.

The choice of unit cell is not unique.

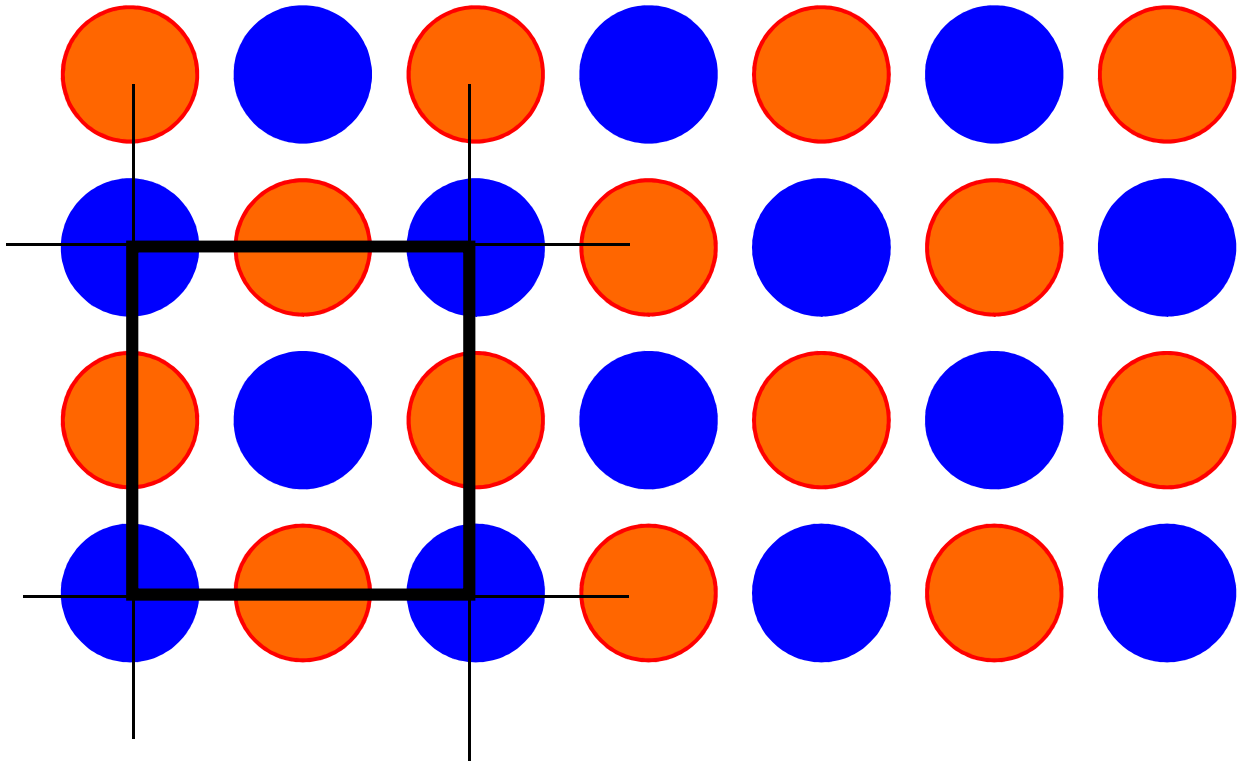


2D Unit Cell example -(NaCl)

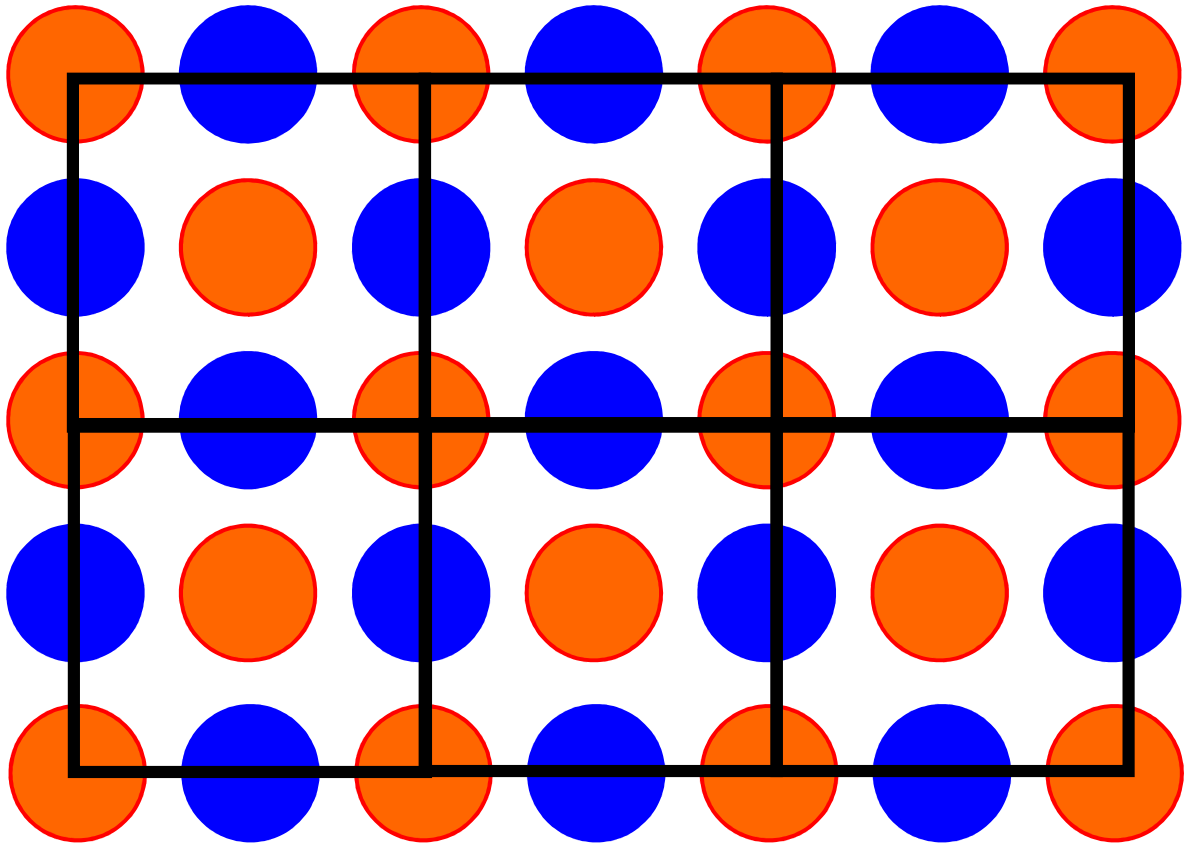


We define **lattice points** ; these are points with *identical environments*

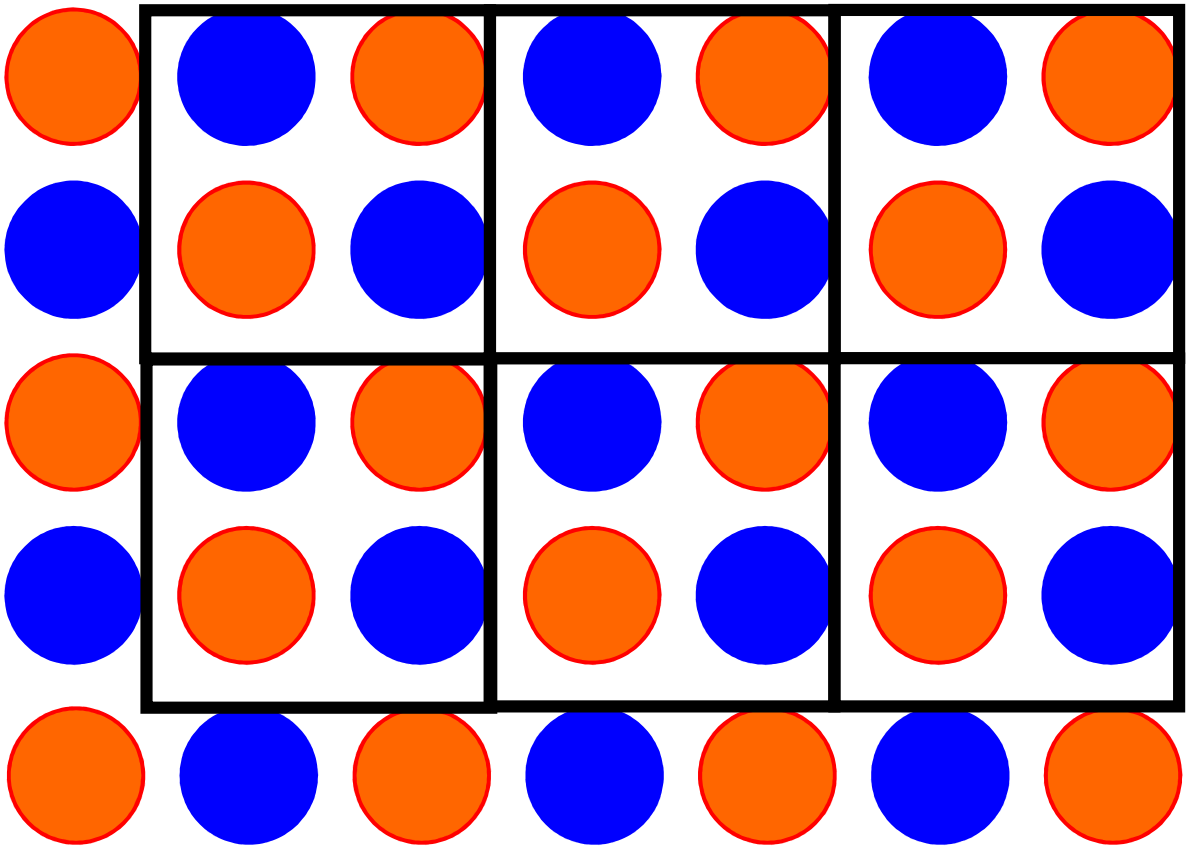
Choice of origin is arbitrary - lattice points need not be atoms - **but** unit cell size should always be the same.



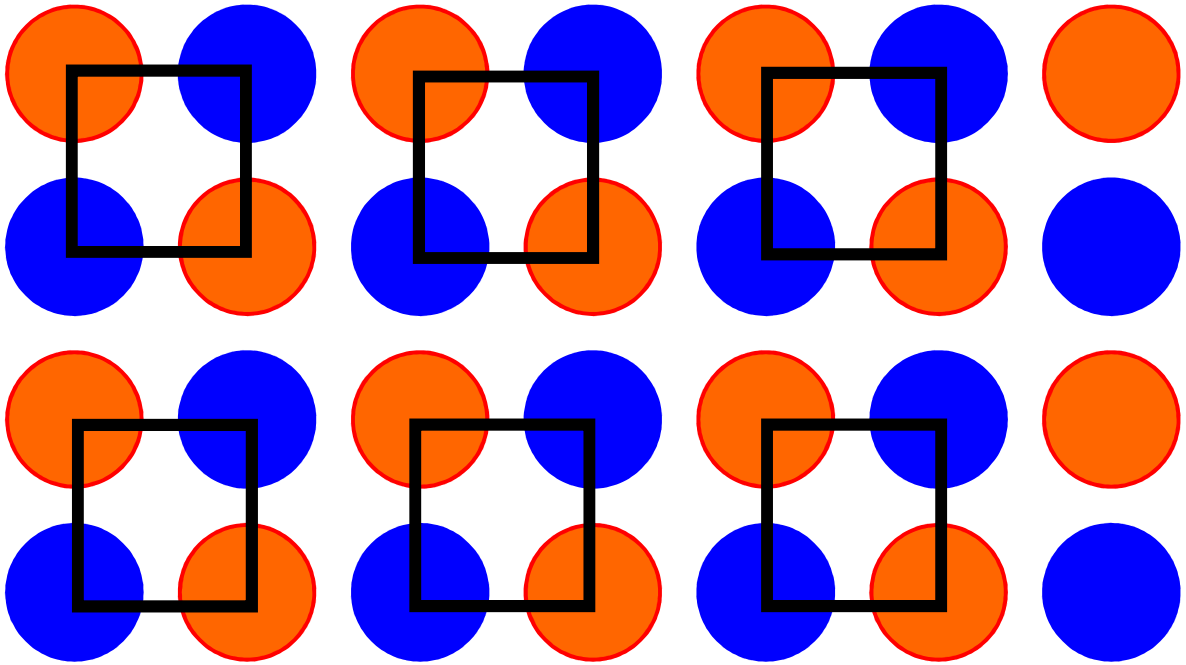
This is also a unit cell - it doesn't matter if you start from Na or Cl



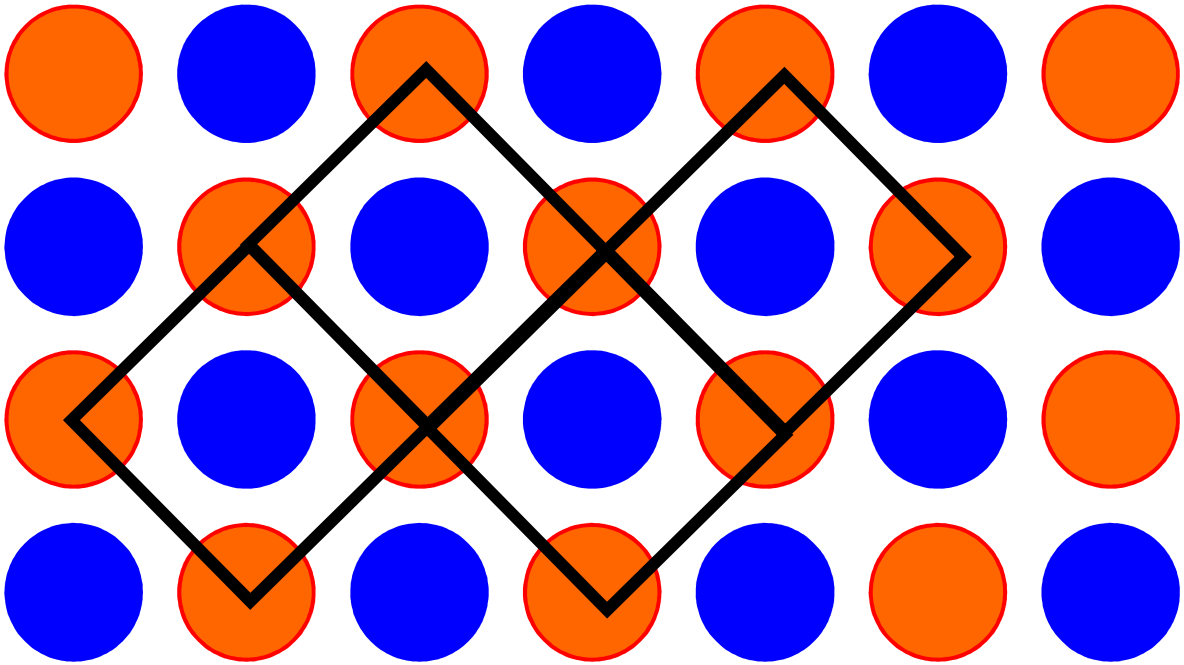
- or if you don’t start from an atom



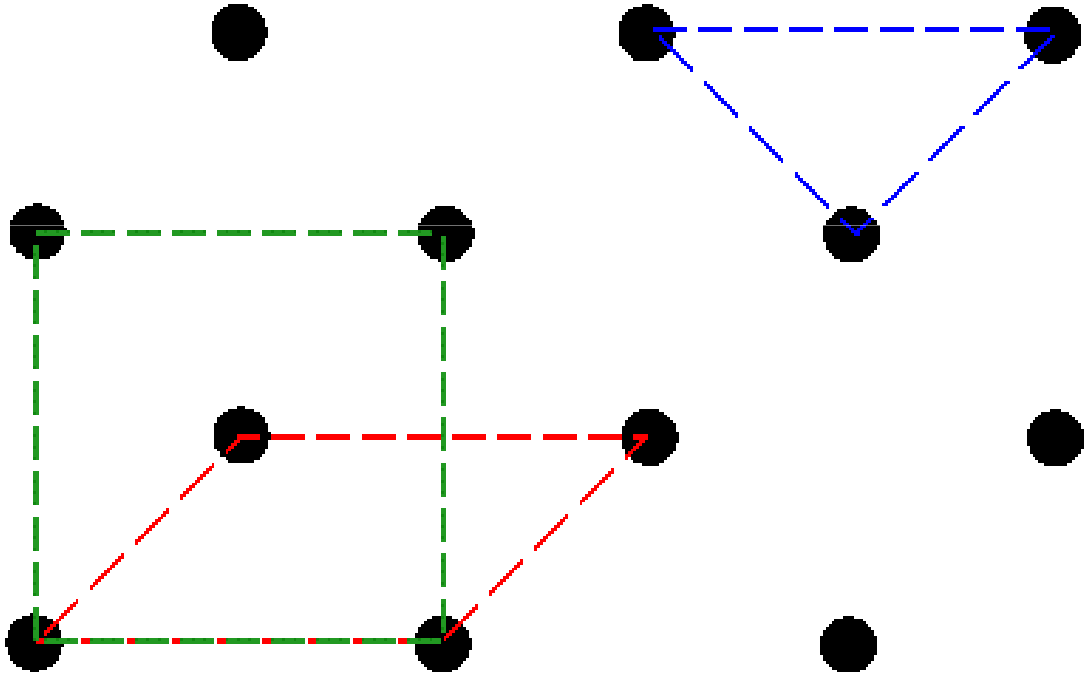
This is NOT a unit cell even though they are all the same - empty space is not allowed!



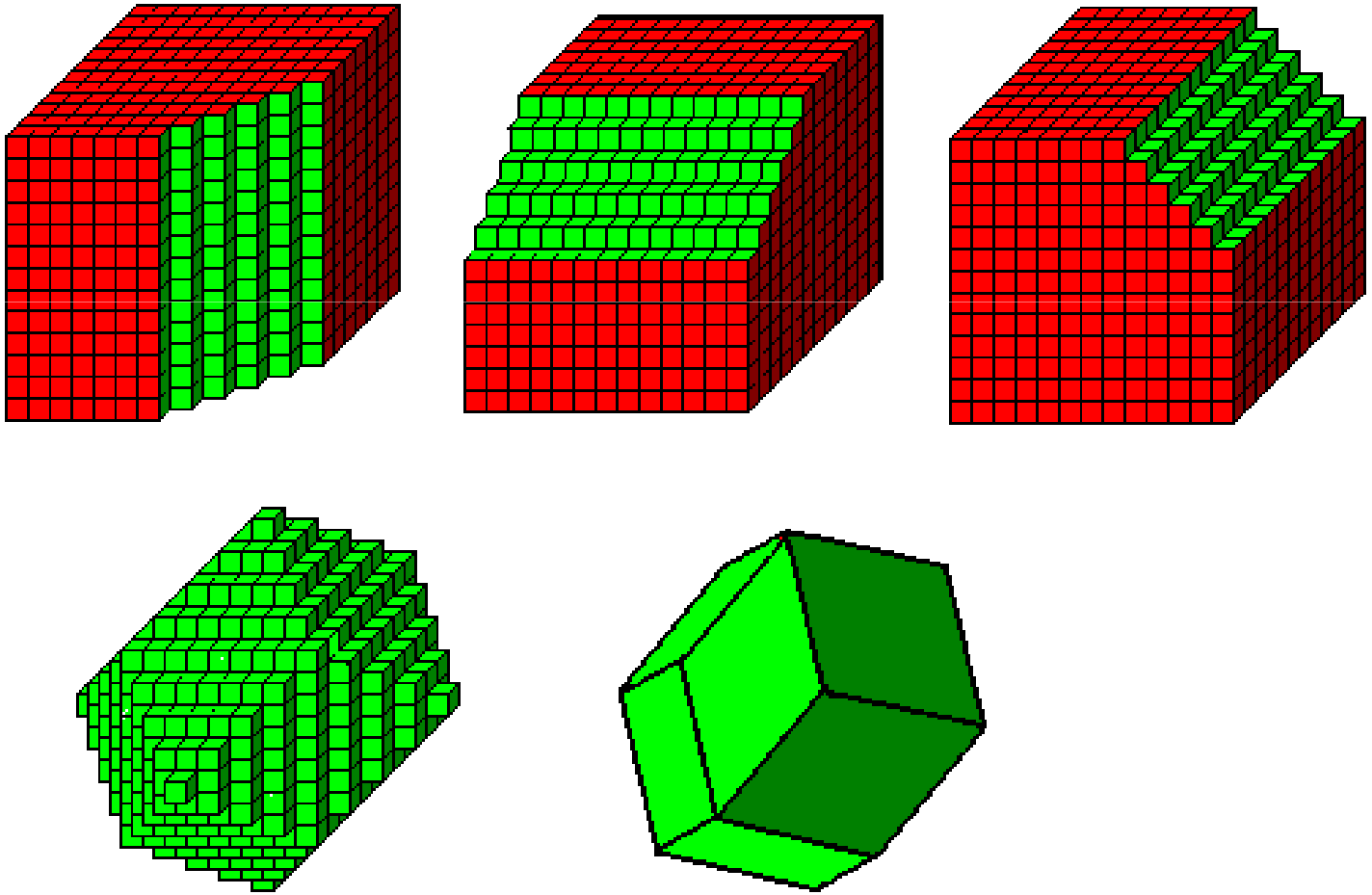
In 2D, this IS a unit cell
In 3D, it is NOT



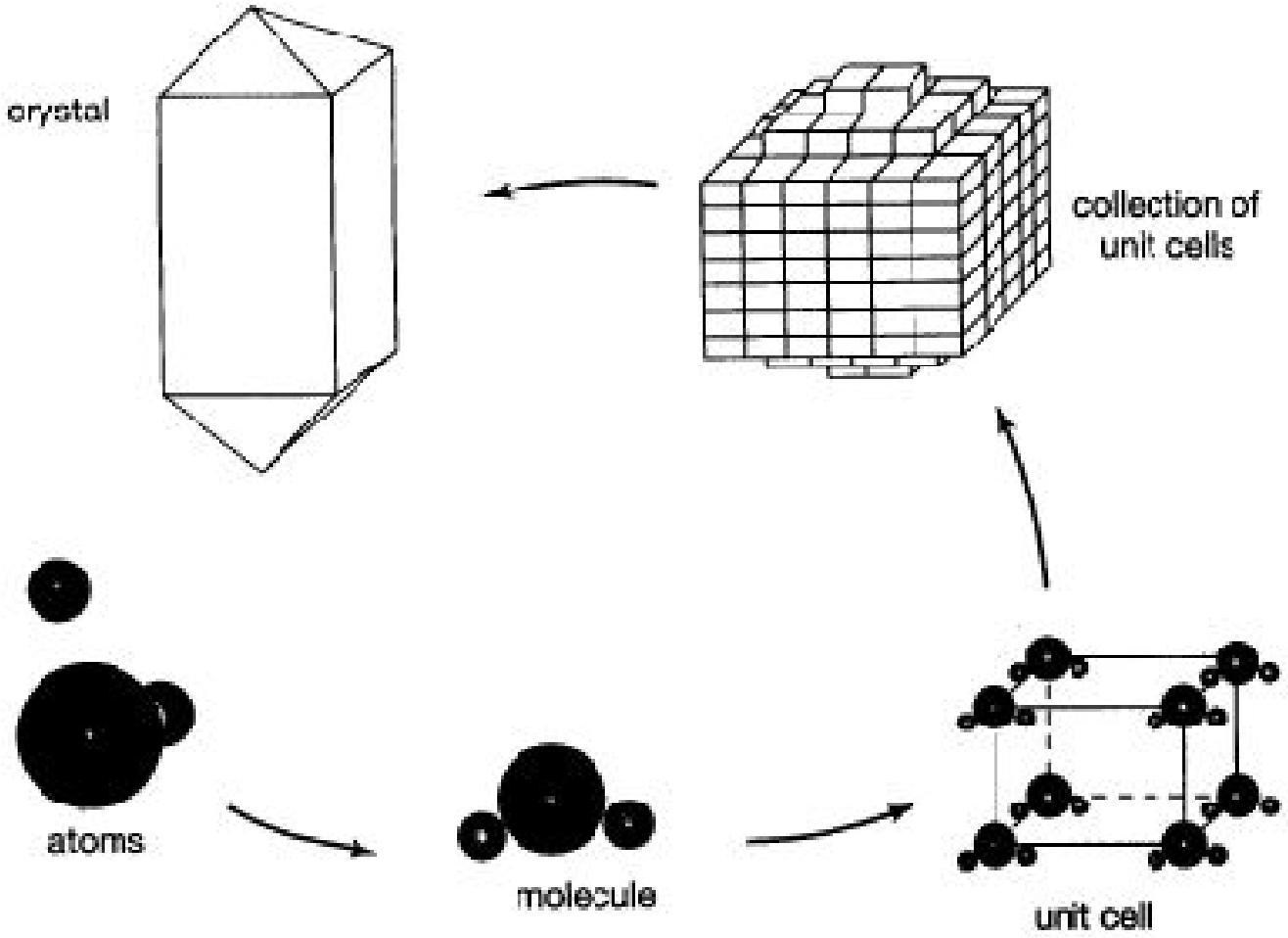
Why can't the blue triangle be a unit cell?



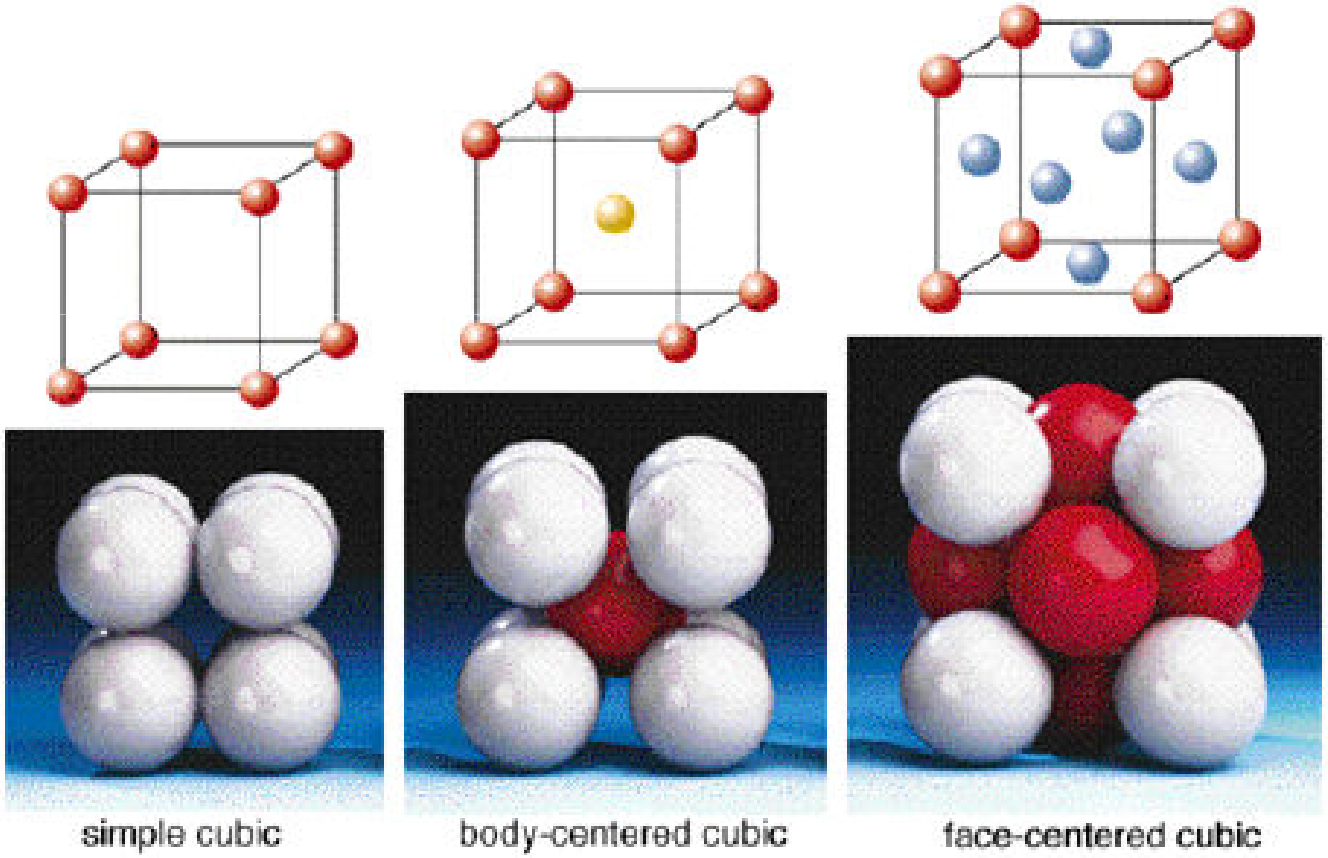
Unit Cell in 3D



Unit Cell in 3D



Three common Unit Cell in 3D



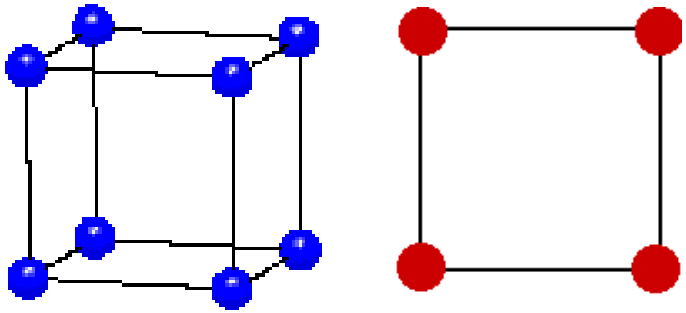
UNIT CELL

Primitive

- Single lattice point per cell
- Smallest area in 2D, or
- Smallest volume in 3D

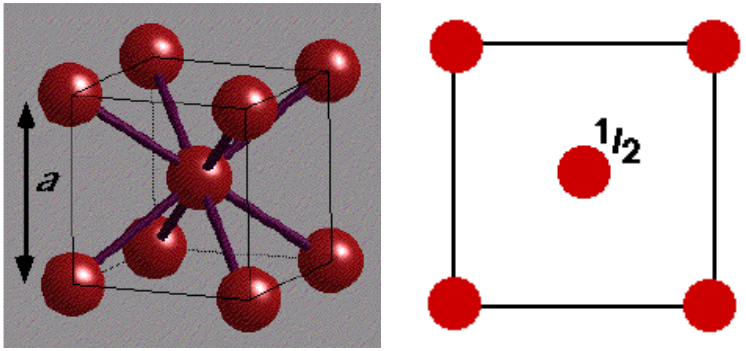
Conventional & Non-primitive

- More than one lattice point per cell
- Integral multibles of the area of primitive cell



Simple cubic(sc)

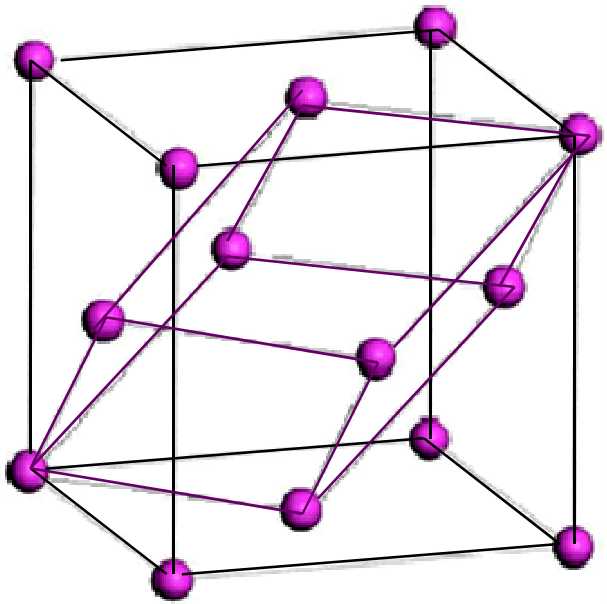
Conventional = Primitive cell



Body centered cubic(bcc)

Conventional ≠ Primitive cell

The Conventional Unit Cell

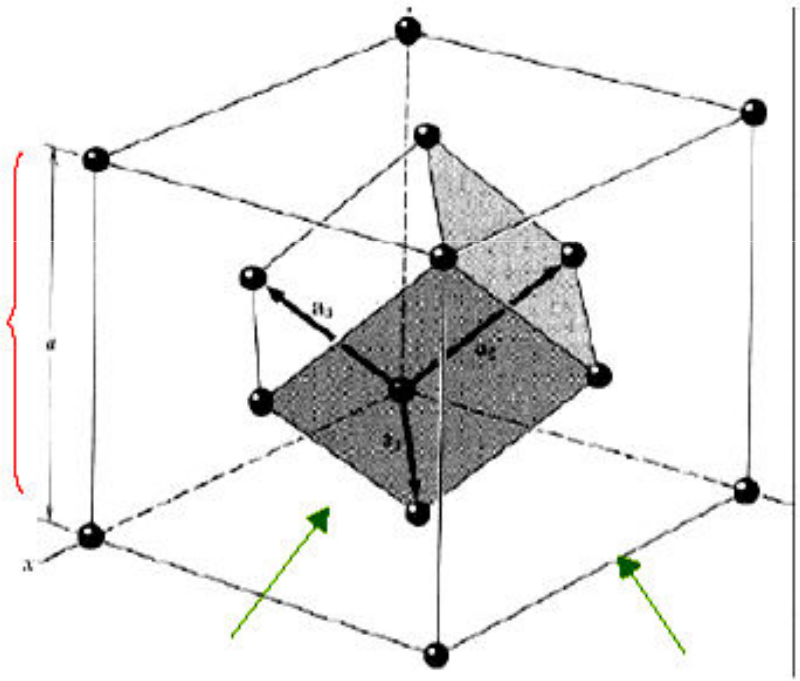


FCC Bravais lattice

- A unit cell just fills space when translated through a subset of Bravais lattice vectors.
- The conventional unit cell is chosen to be larger than the primitive cell, but with the full symmetry of the Bravais lattice.
- The size of the conventional cell is given by the lattice constant a.

Primitive and conventional cells of FCC

lattice constant



primitive vectors

$$\vec{a}_1 = \frac{a}{2}(\hat{x} + \hat{y}),$$

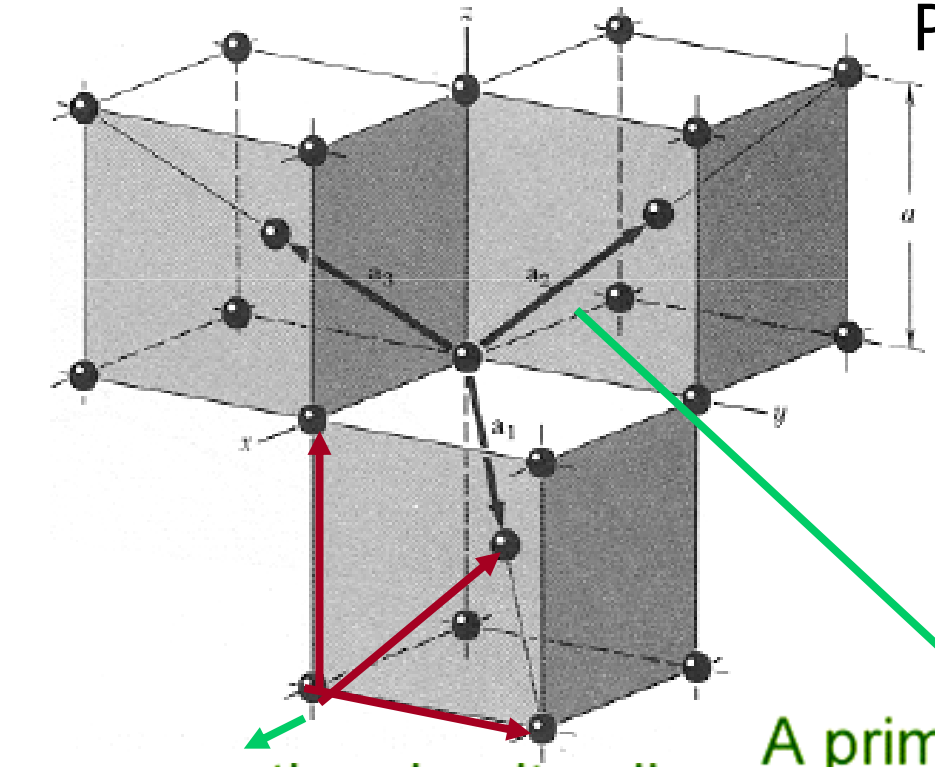
$$\vec{a}_2 = \frac{a}{2}(\hat{y} + \hat{z}),$$

$$\vec{a}_3 = \frac{a}{2}(\hat{z} + \hat{x}).$$

A primitive unit cell

a conventional unit cell

Primitive and conventional cells of BCC



a conventional unit cell

A primitive unit cell

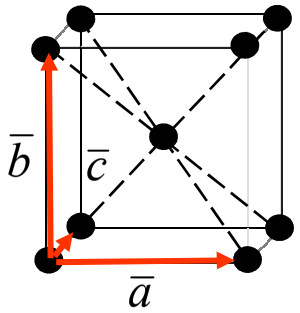
Primitive Translation Vectors:

$$\vec{a}_1 = \frac{1}{2}(\hat{x} + \hat{y} - \hat{z})$$

$$\vec{a}_2 = \frac{1}{2}(-\hat{x} + \hat{y} + \hat{z})$$

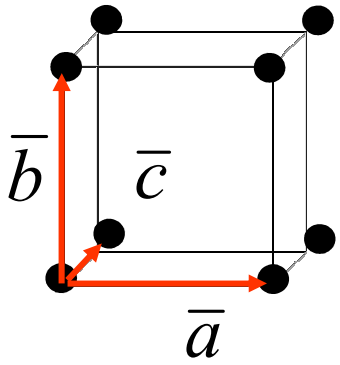
$$\vec{a}_3 = \frac{1}{2}(\hat{x} - \hat{y} + \hat{z})$$

Primitive and conventional cells



Body centered cubic (bcc):
conventional ≠primitive cell

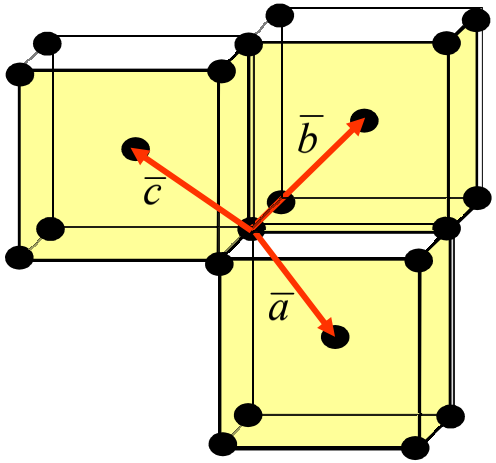
Fractional coordinates of lattice points in conventional cell:
000,100, 010, 001, 110,101, 011, 111, ½ ½ ½



Simple cubic (sc):
primitive cell=conventional cell

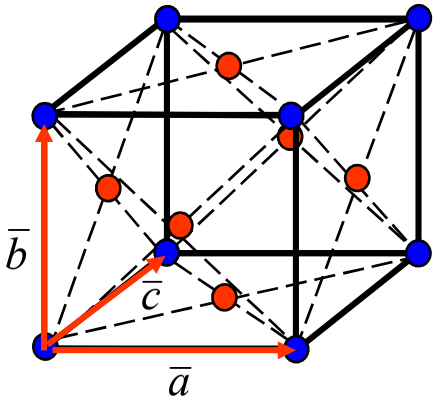
Fractional coordinates of lattice points:
000, 100, 010, 001, 110,101, 011, 111

Primitive and conventional cells



Body centered cubic (bcc):
primitive (rombohedron) ≠conventional cell

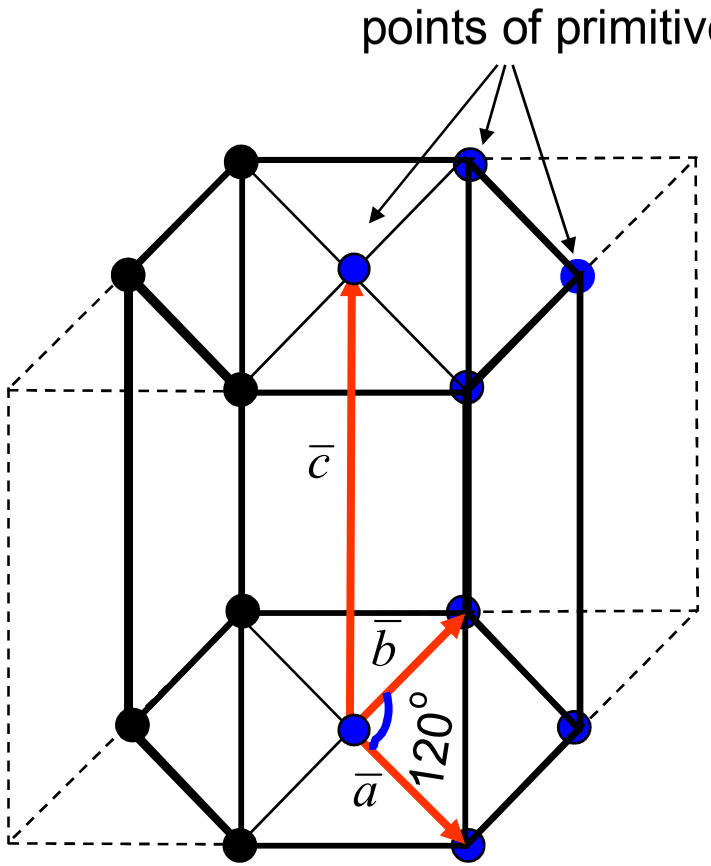
Fractional coordinates:
000, 100, 101, 110, $1\bar{1}0$,$10\bar{1}$, $01\bar{1}$, 211, 200



Face centered cubic (fcc):
conventional ≠ primitive cell

Fractional coordinates:
000,100, 010, 001, 110,101, 011,111, ½ ½ 0, ½ 0 ½, 0 ½ ½ ,½1 ½ , 1 ½ ½ , ½ ½ 1

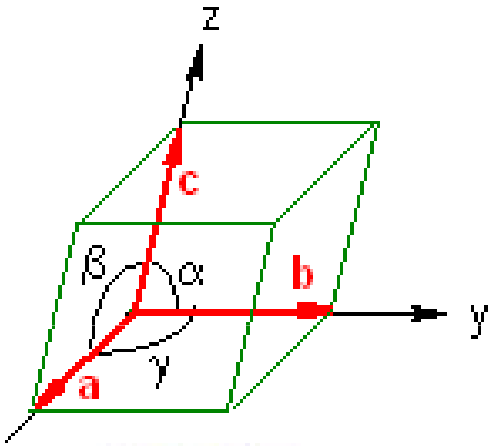
Primitive and conventional cells-hcp

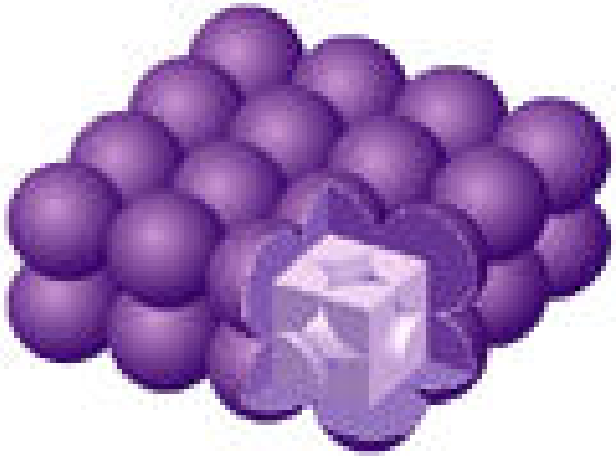


Hexagonal close packed cell (hcp):
conventional =primitive cell

Fractional coordinates:
100, 010, 110, 101,011, 111,000, 001

Unit Cell





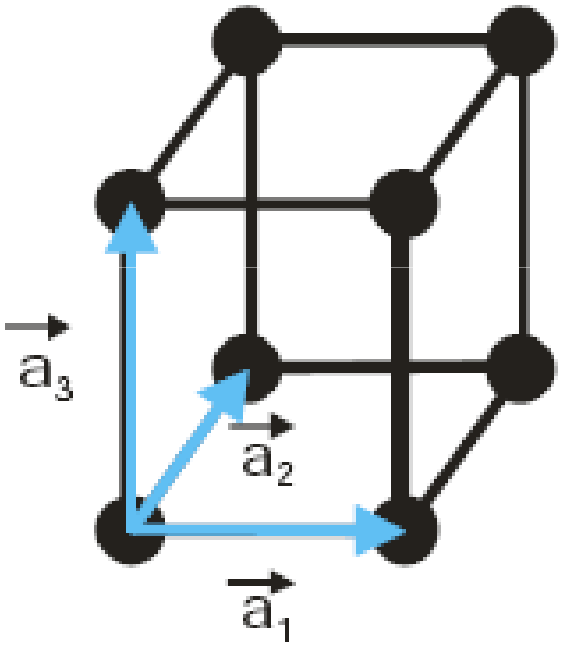
- The unit cell and, consequently, the entire lattice, is *uniquely* determined by the six lattice constants: a, b, c, α, β and γ.
- Only 1/8 of each lattice point in a unit cell can actually be assigned to that cell.
- Each unit cell in the figure can be associated with 8 x 1/8 = 1 lattice point.

Primitive Unit Cell and vectors

- A primitive unit cell is made of primitive translation vectors a_1 ,a_2, and a_3 such that there is no cell of smaller volume that can be used as a building block for crystal structures.

- A primitive unit cell will fill space by repetition of suitable crystal translation vectors. This defined by the parallelpiped a_1, a_2 and a_3. The volume of a primitive unit cell can be found by

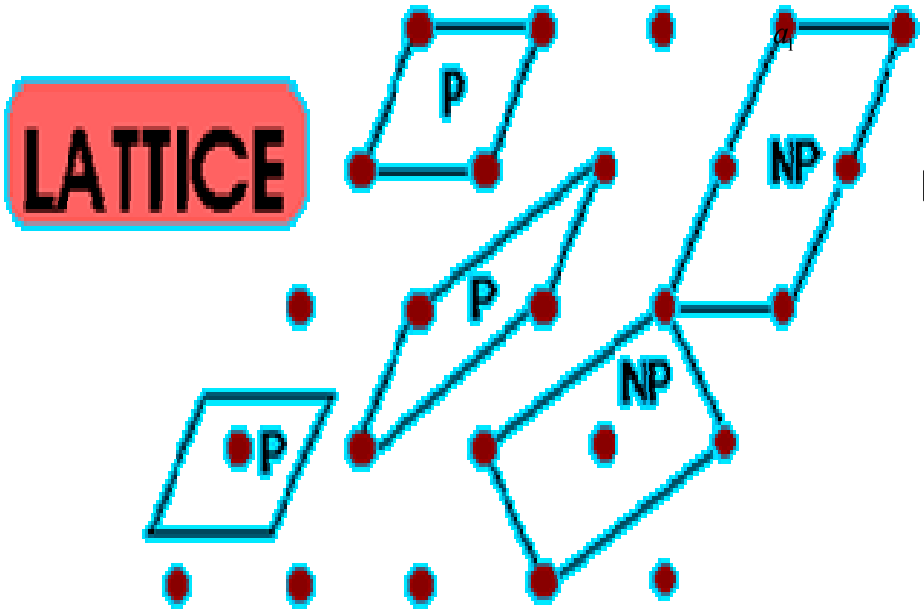
- $V = a_1.(a_2 \times a_3)$ (vector products)



Cubic cell volume = a^3

Primitive Unit Cell

- The primitive unit cell must have only one lattice point.
- There can be different choices for lattice vectors , but the volumes of these primitive cells are all the same.

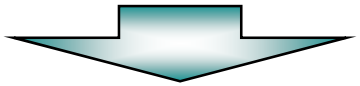


P = Primitive Unit Cell
NP = Non-Primitive Unit Cell

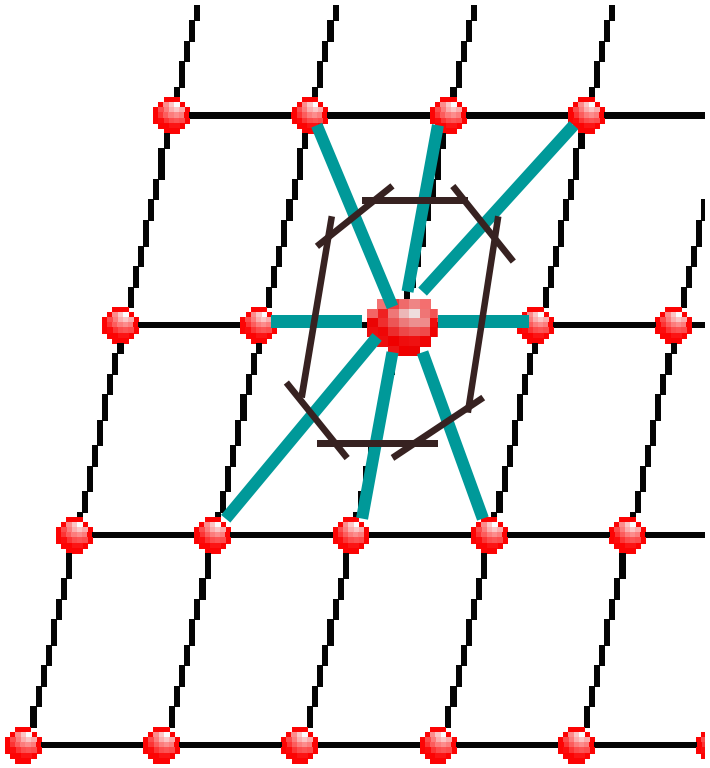
Wigner-Seitz Method

A simply way to find the primitive cell which is called Wigner-Seitz cell can be done as follows;

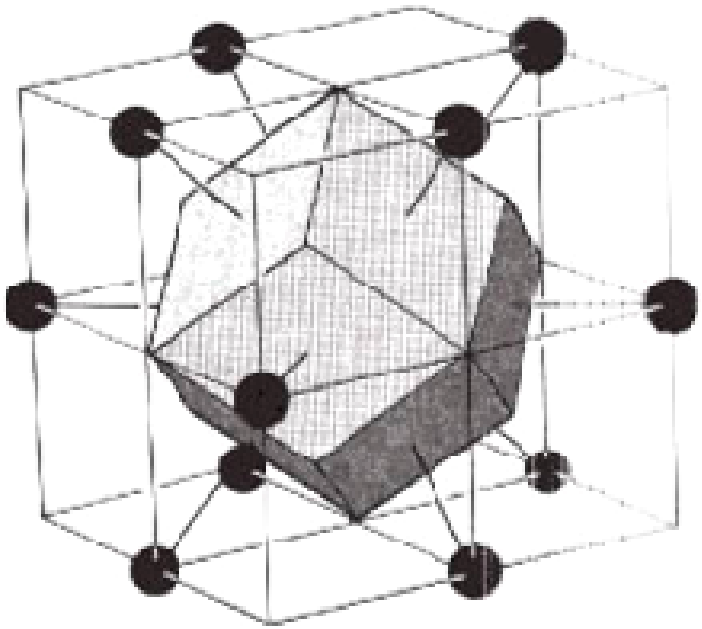
1. Choose a lattice point.
2. Draw lines to connect these lattice point to its neighbours.
3. At the mid-point and normal to these lines draw new lines.



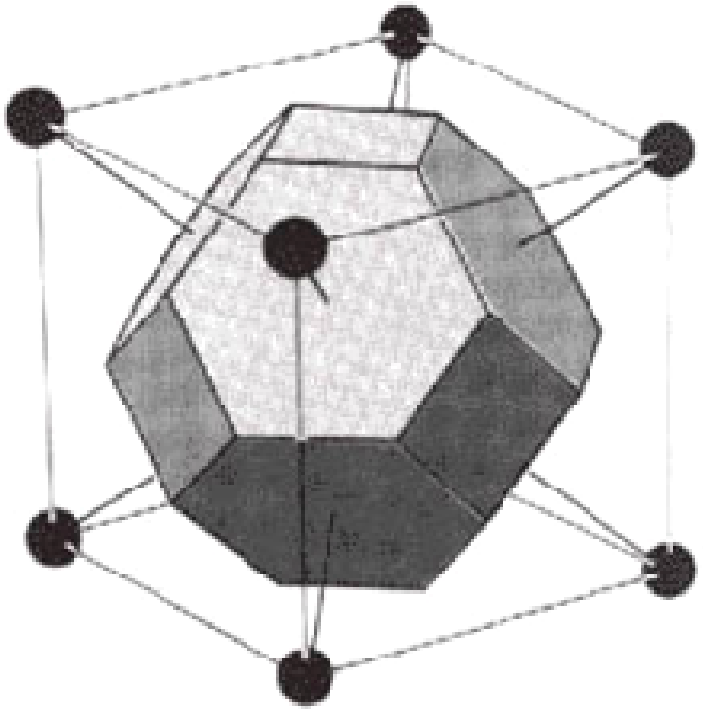
The volume enclosed is called as a Wigner-Seitz cell.



Wigner-Seitz Cell - 3D

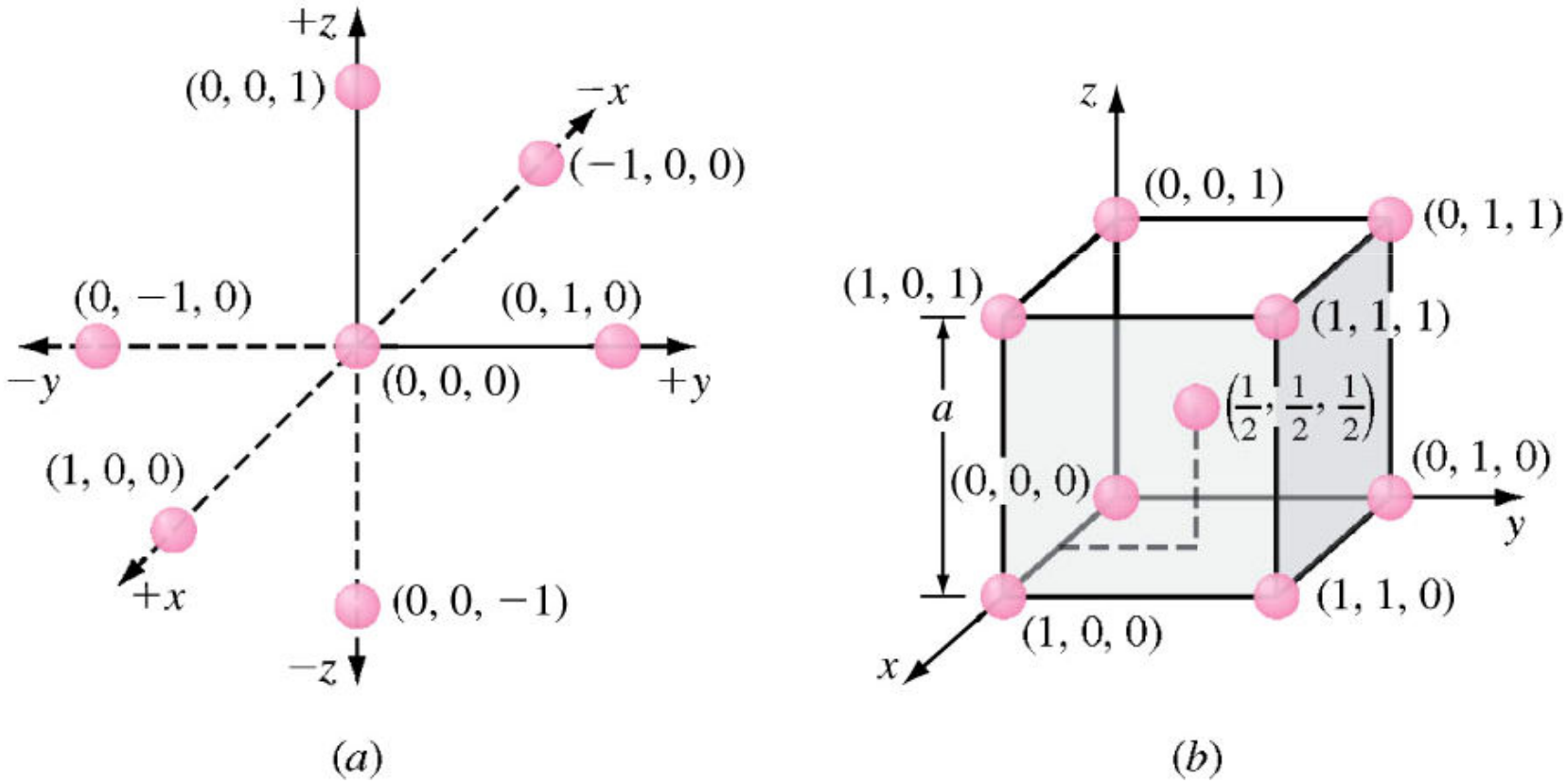


f.c.c Wigner-Seitz cell



b.c.c Wigner-Seitz cell

Lattice Sites in Cubic Unit Cell



Crystal Directions

- **We choose one lattice point on the line as an origin, say the point O. Choice of origin is completely arbitrary, since every lattice point is identical.**
- **Then we choose the lattice vector joining O to any point on the line, say point T. This vector can be written as;**

$$R = n_1 a + n_2 b + n_3 c$$

- **To distinguish a lattice direction from a lattice point, the triple is enclosed in square brackets [...] is used.$[n_1 n_2 n_3]$**
- **$[n_1 n_2 n_3]$ is the smallest integer of the *same relative ratios*.**

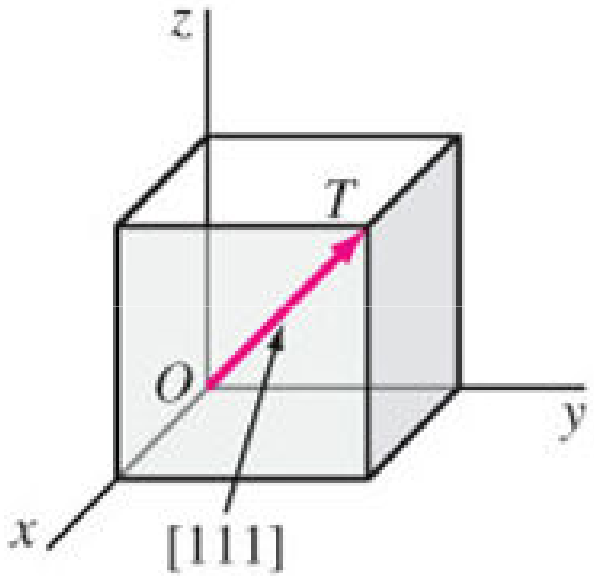
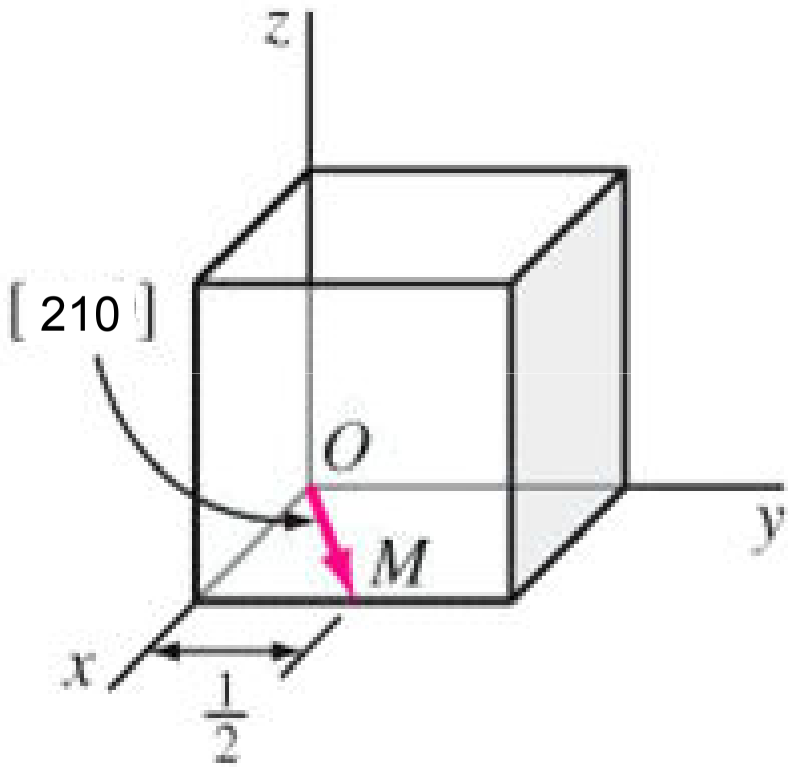


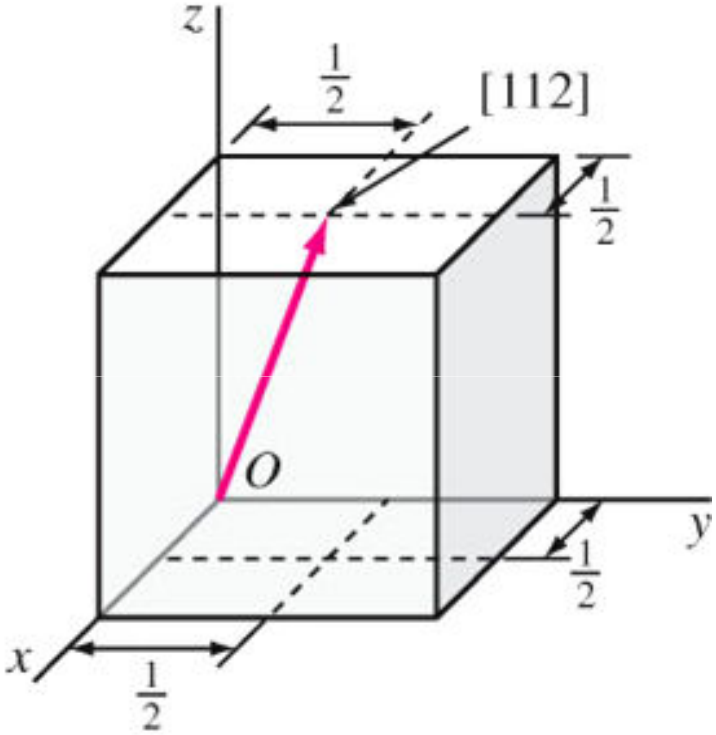
Fig. Shows [111] direction

Examples



X = 1 , Y = ½ , Z = 0

[1 ½ 0] ⇨ [2 1 0]



X = ½ , Y = ½ , Z = 1

[½ ½ 1] ⇨ [1 1 2]

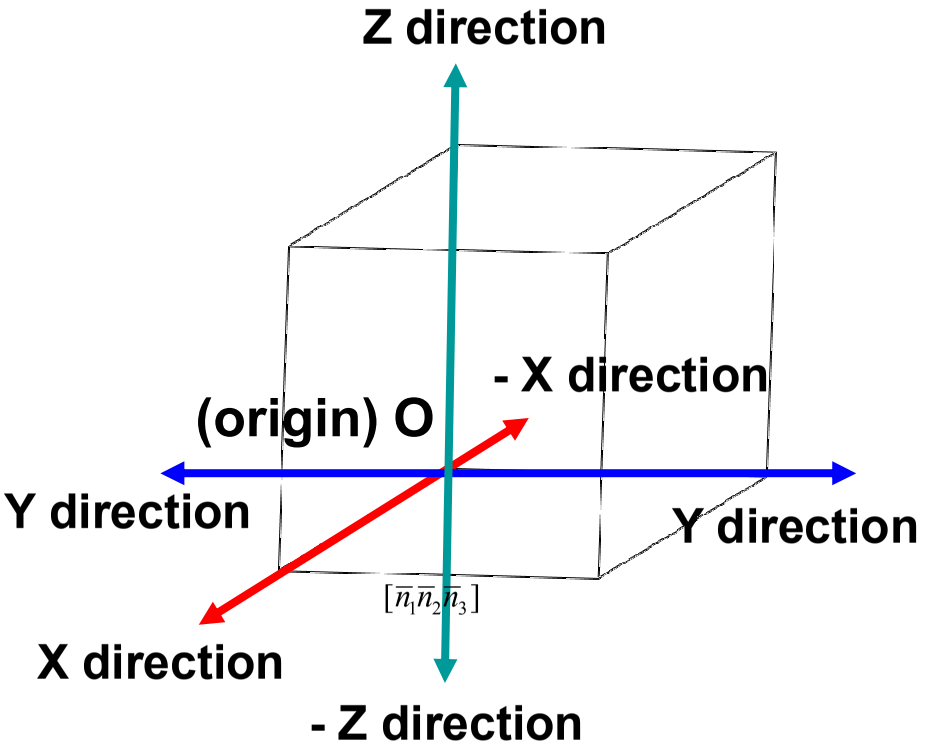
Negative directions

- When we write the direction $[n_1 n_2 n_3]$ depend on the origin, negative directions can be written as

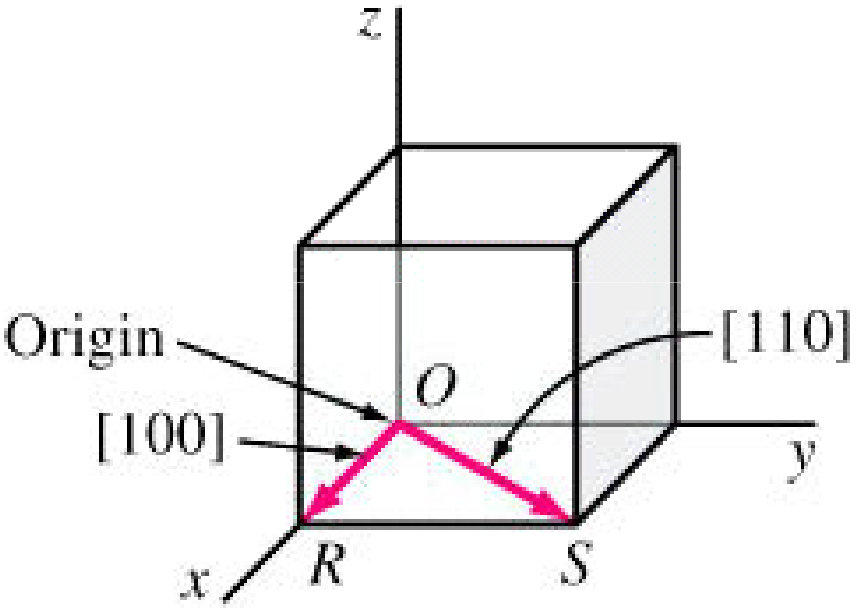
$$[\bar{n}_1 \bar{n}_2 \bar{n}_3]$$

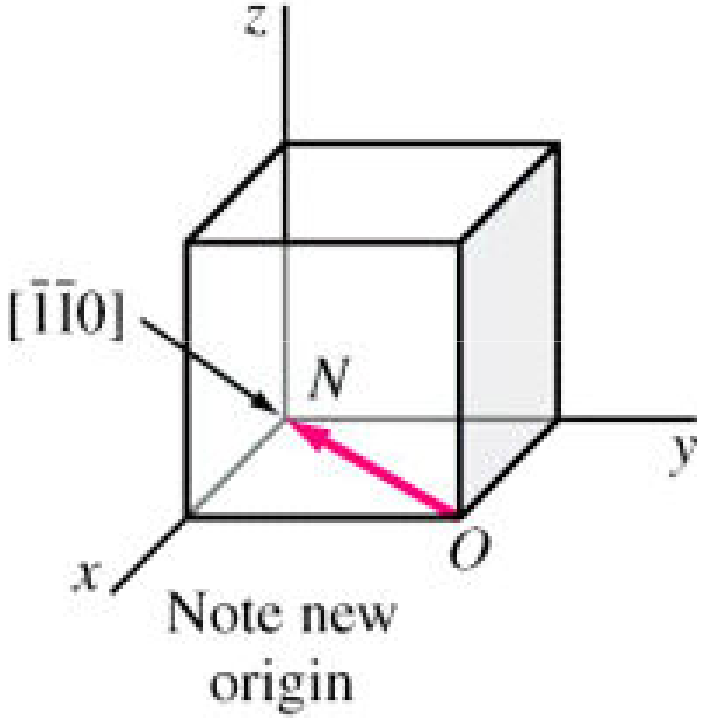
- $R = n_1 a + n_2 b + n_3 c$

Direction must be smallest integers.



Examples of crystal directions

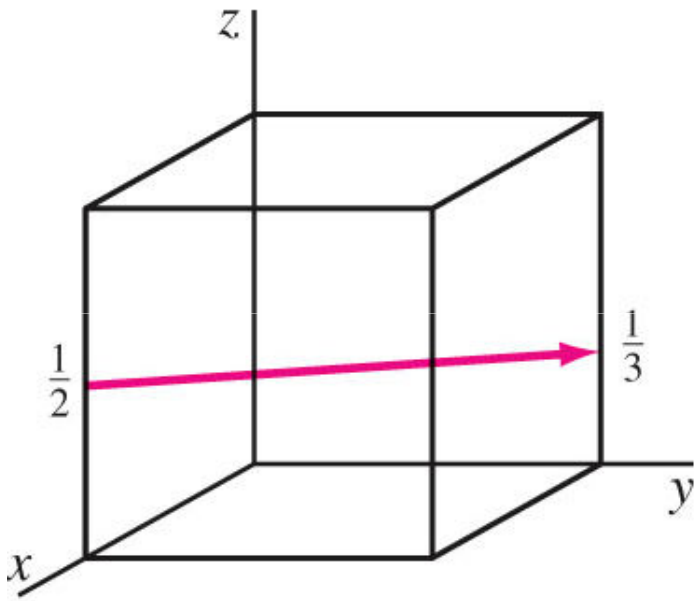




X = 1 , Y = 0 , Z = 0 ⇒ [1 0 0]

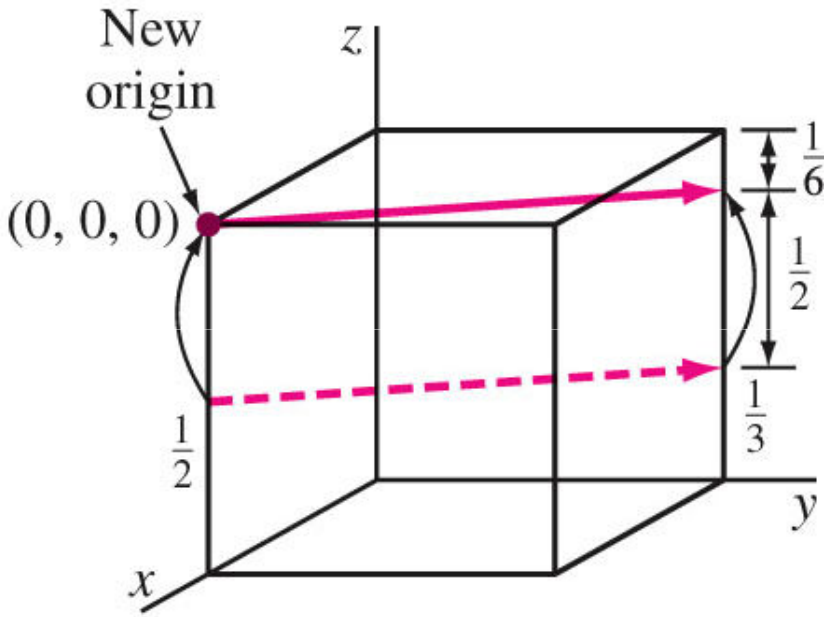
X = -1 , Y = -1 , Z = 0 ⇒ [$\bar{1}$10]

Examples



(a)

We can move vector to the origin.



(b)

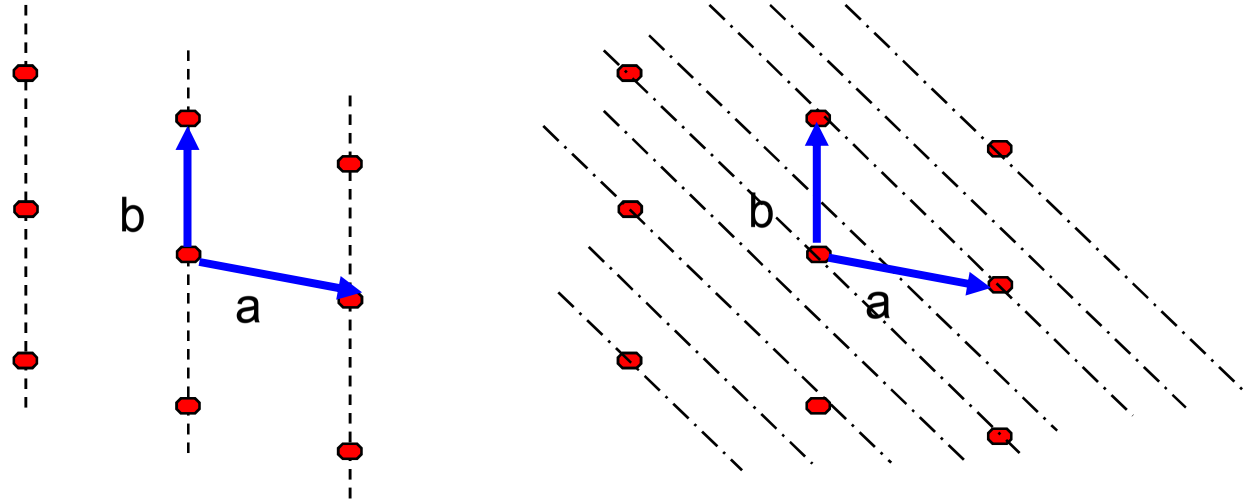
X =-1 , Y = 1 , Z = -1/6

[-1 1 -1/6] ⇨ [$\bar{6}$ 6 $\bar{1}$]

Crystal Planes

- Within a crystal lattice it is possible to identify sets of equally spaced parallel planes. These are called lattice planes.
- In the figure density of lattice points on each plane of a set is the same and all lattice points are contained on each set of planes.

The set of planes in 2D lattice.



Miller Indices

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

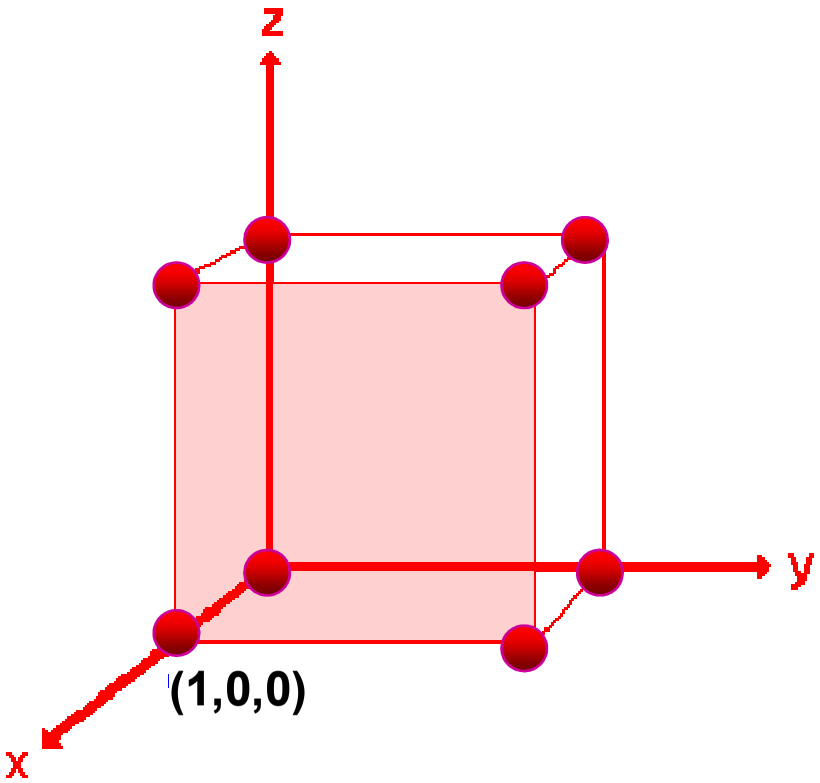
To determine Miller indices of a plane, take the following steps;

1) Determine the intercepts of the plane along each of the three crystallographic directions

2) Take the reciprocals of the intercepts

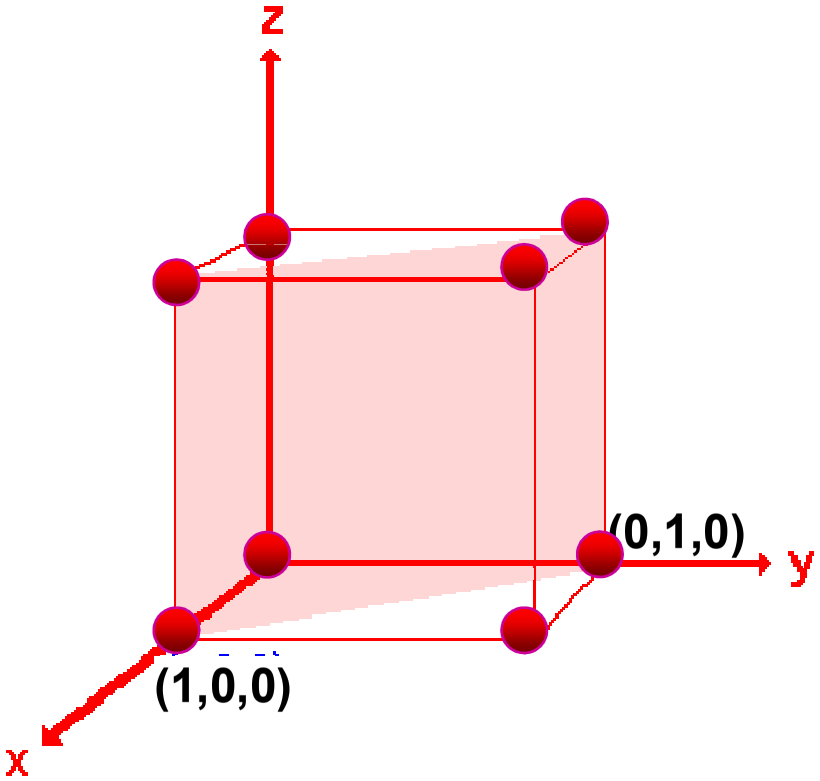
3) If fractions result, multiply each by the denominator of the smallest fraction

Example-1



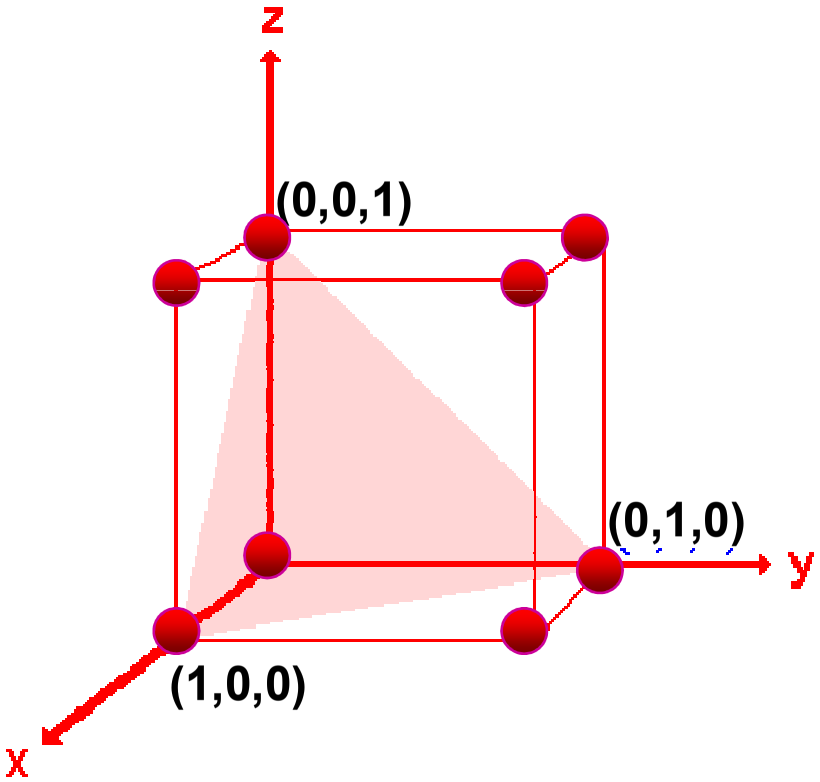
Axis	x	y	z
Intercept points	1	∞	∞
Reciprocals	1/1	1/ ∞	1/ ∞
Smallest Ratio	1	0	0
Miller İndices (100)			

Example-2



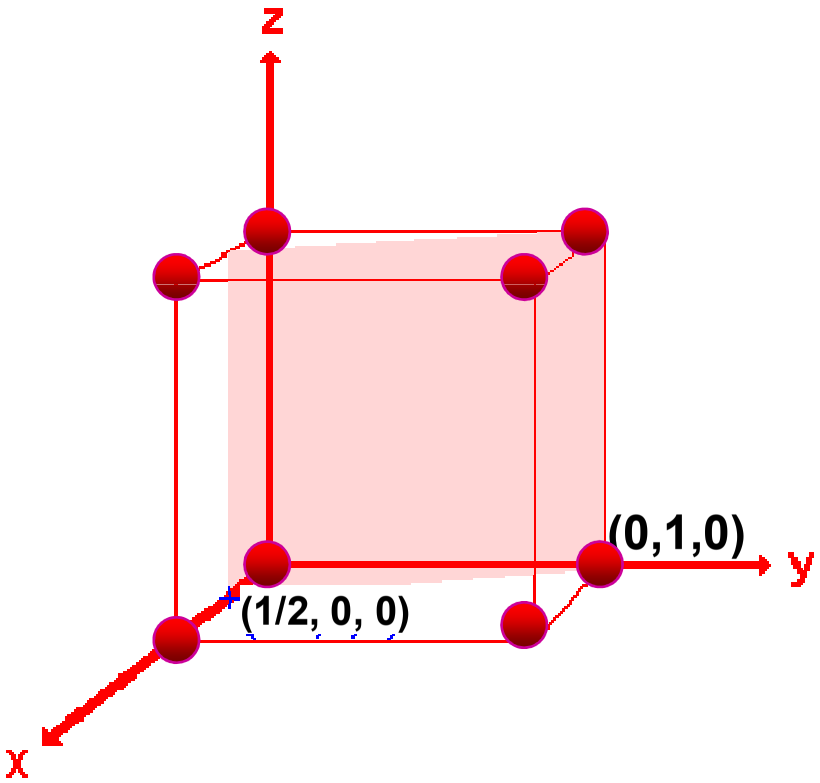
Axis	x	y	z
Intercept points	1	1	∞
Reciprocals	1/1	1/ 1	1/ ∞
Smallest Ratio	1	1	0
Miller İndices (110)			

Example-3



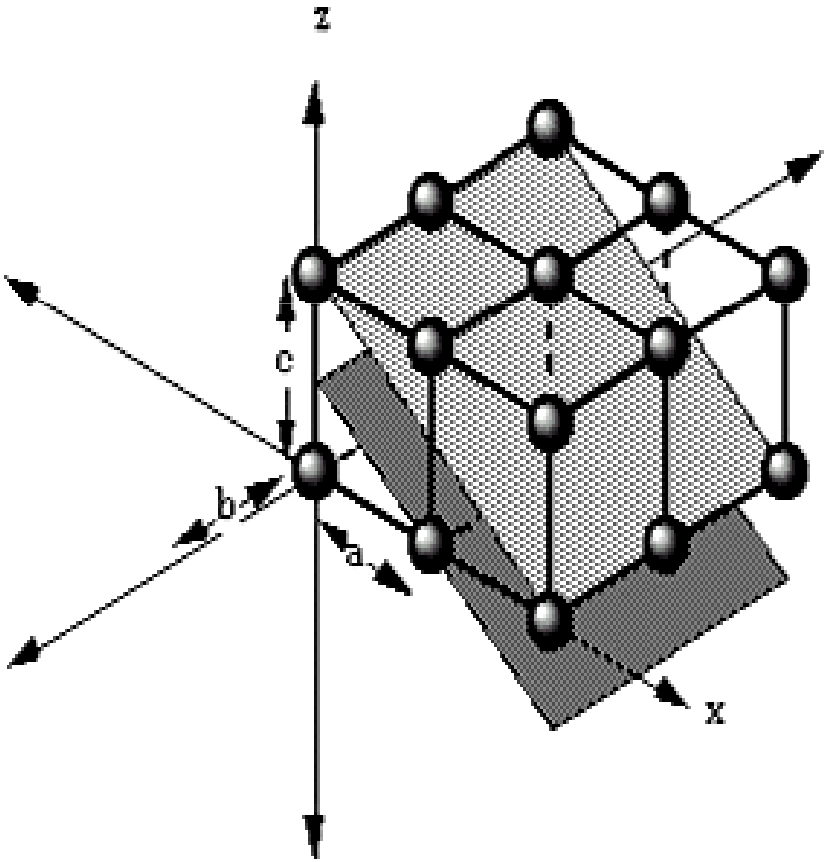
Axis	x	y	z
Intercept points	1	1	1
Reciprocals	1/1	1/ 1	1/ 1
Smallest Ratio	1	1	1
Miller İndices (111)			

Example-4



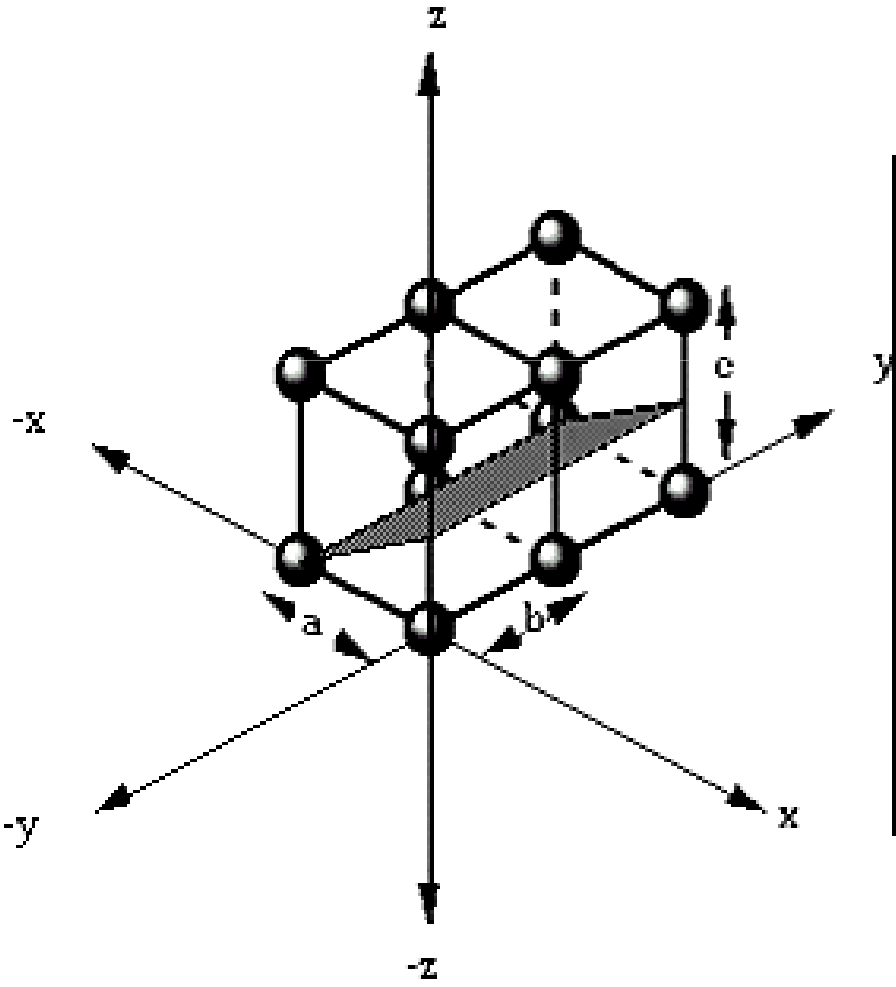
Axis	x	y	z
Intercept points	1/2	1	∞
Reciprocals	1/(½)	1/ 1	1/ ∞
Smallest Ratio	2	1	0
Miller İndices (210)			

Example-5



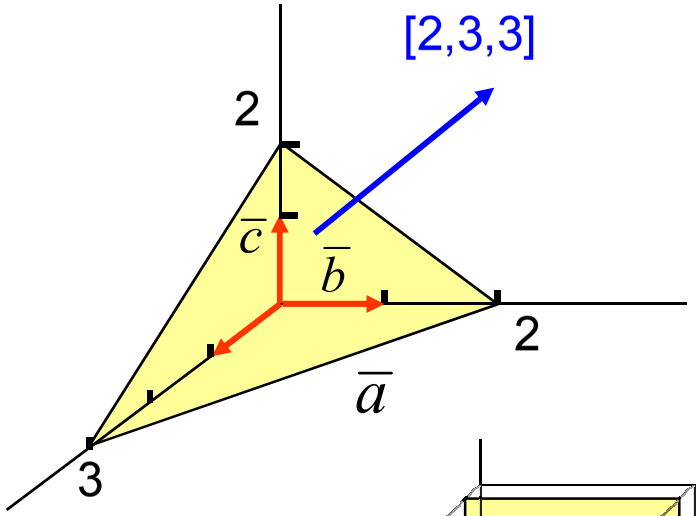
Axis	a	b	c
Intercept points	1	∞	½
Reciprocals	**1/1**	**1/ ∞**	**1/(½)**
Smallest Ratio	1	0	2
Miller İndices (102)			

Example-6



Axis	a	b	c
Intercept points	-1	∞	½
Reciprocals	**1/-1**	**1/ ∞**	**1/(½)**
Smallest Ratio	-1	0	2
Miller İndices $(\bar{1}02)$			

Miller Indices

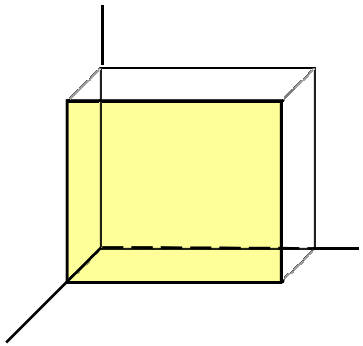


Plane intercepts axes at $3\bar{a}, 2\bar{b}, 2\bar{c}$

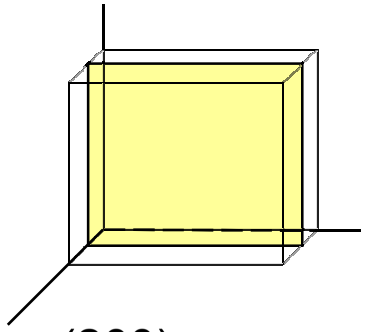
Reciprocal numbers are: $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$

Indices of the plane (Miller): (2,3,3)

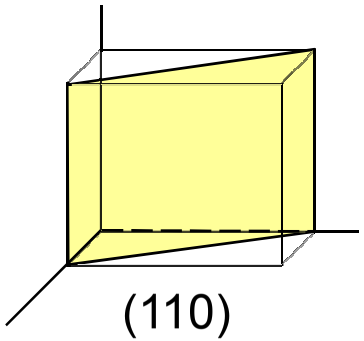
Indices of the direction: [2,3,3]



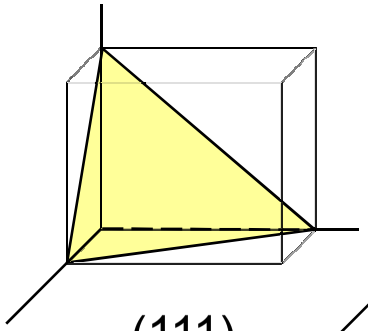
(100)



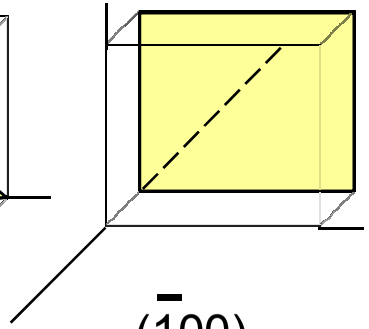
(200)



(110)

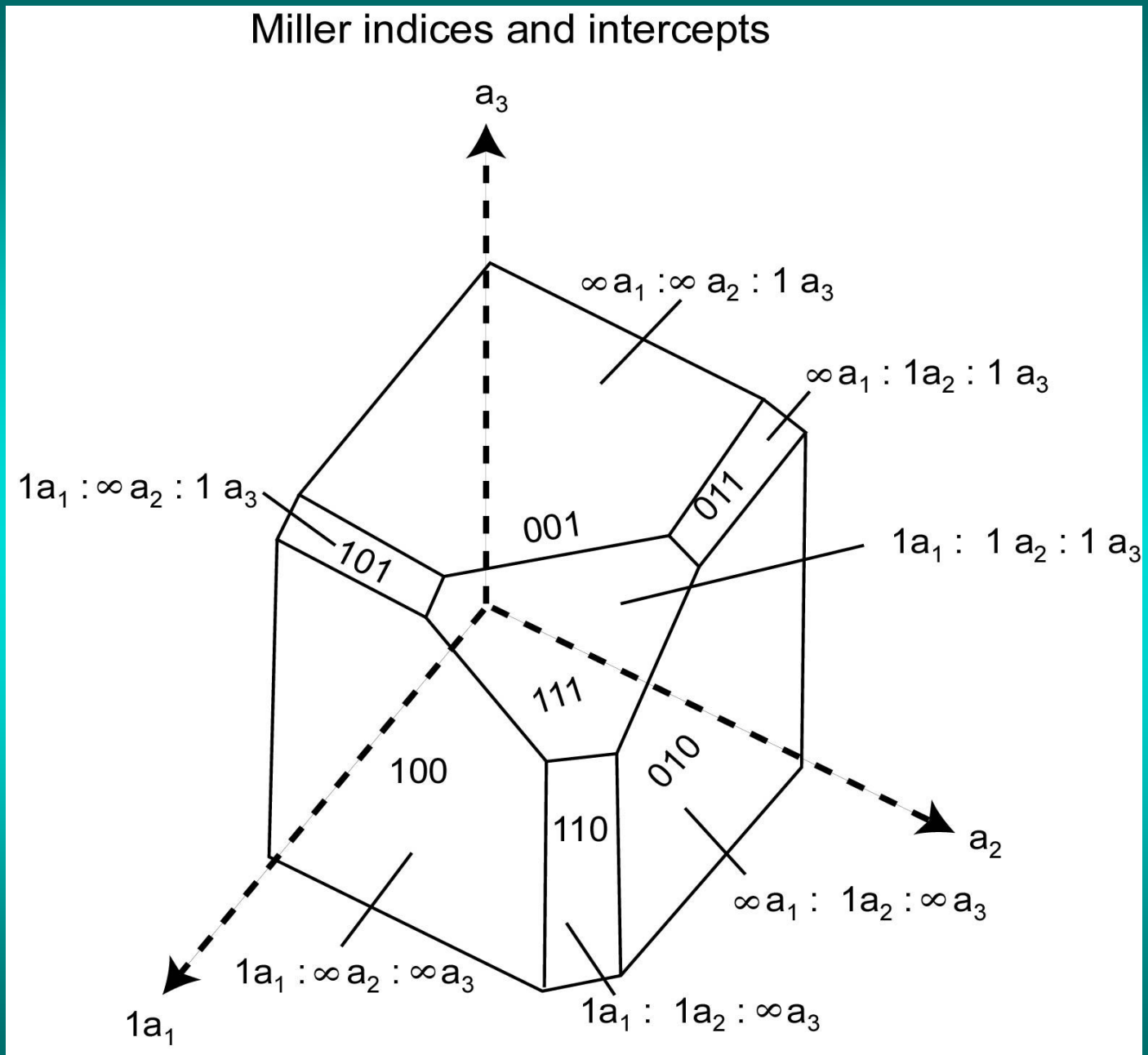


(111)

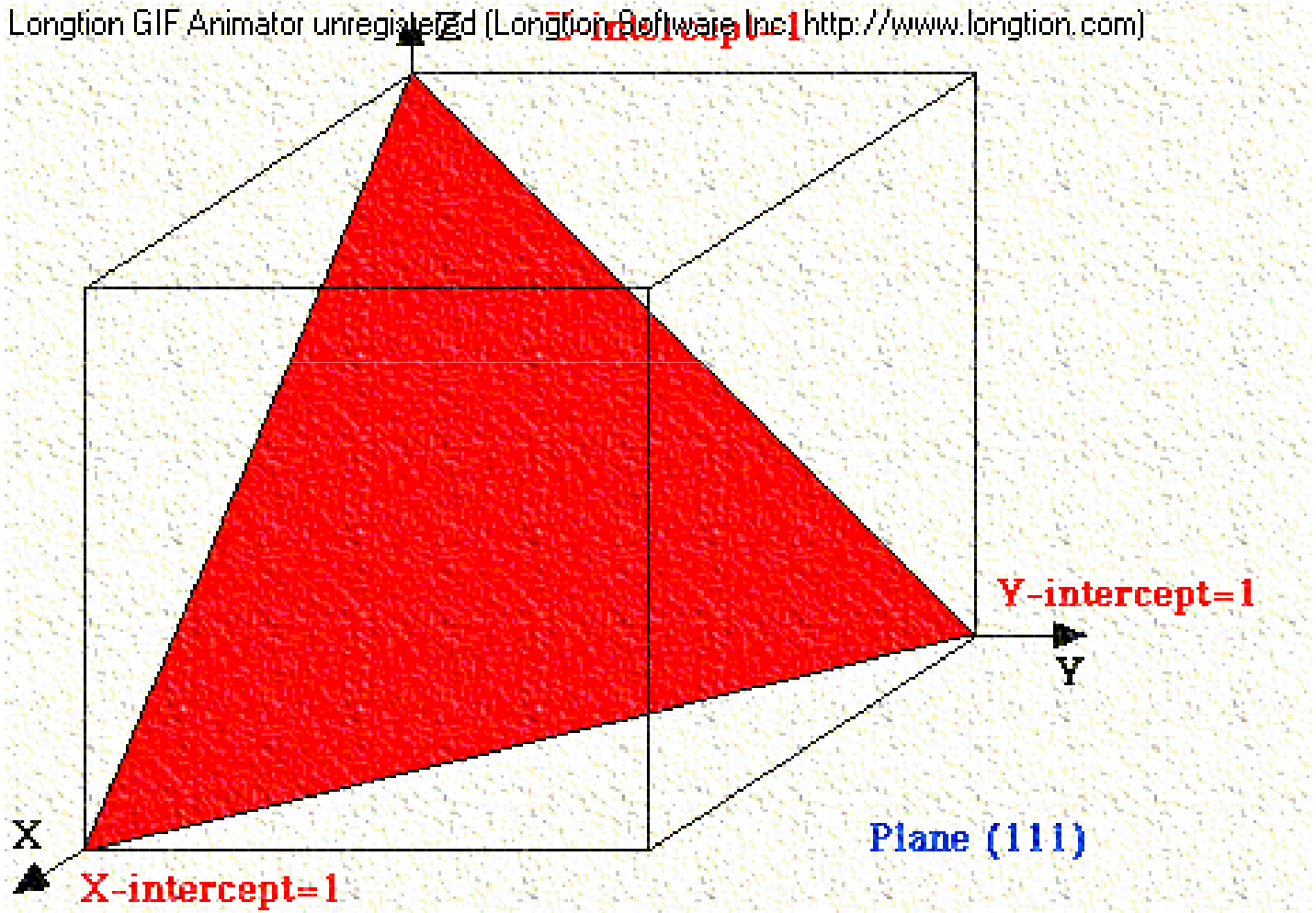


($\bar{1}00$)

Miller indices and intercepts



Example-7


Longtion GIF Animator unregistered (Longtion Software Inc. http://www.longtion.com)
Z-intercept=1
Y-intercept=1
Y
X
X-intercept=1
Plane (111)

Indices of a Family or Form

- 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.

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

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

Thus indices {h,k,l} represent all the planes equivalent to the plane (hkl) through rotational symmetry.

TYPICAL CRYSTAL STRUCTURES

3D – 14 BRAVAIS LATTICES AND THE SEVEN CRYSTAL SYSTEM

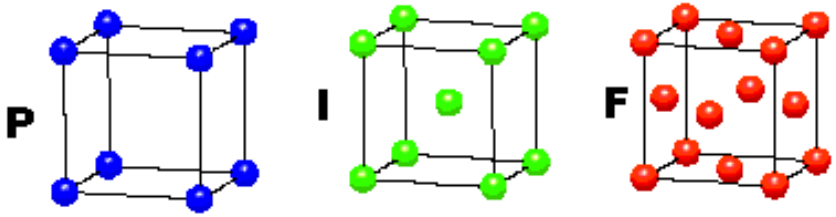
- There are only seven different shapes of unit cell which can be stacked together to completely fill all space (in 3 dimensions) without overlapping. This gives the seven crystal systems, in which all crystal structures can be classified.

- Cubic Crystal System (SC, BCC,FCC)
- Hexagonal Crystal System (S)
- Triclinic Crystal System (S)
- Monoclinic Crystal System (S, Base-C)
- Orthorhombic Crystal System (S, Base-C, BC, FC)
- Tetragonal Crystal System (S, BC)
- Trigonal (Rhombohedral) Crystal System (S)

CUBIC

$a = b = c$

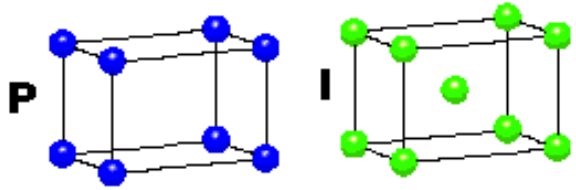
$\alpha = \beta = \gamma = 90°$



TETRAGONAL

$a = b \neq c$

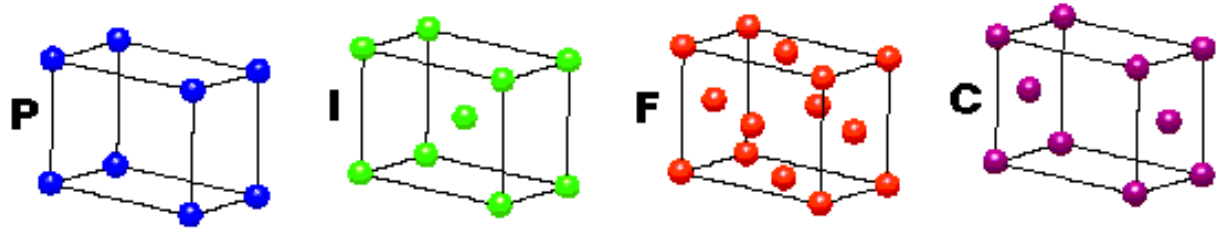
$\alpha = \beta = \gamma = 90°$



ORTHORHOMBIC

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

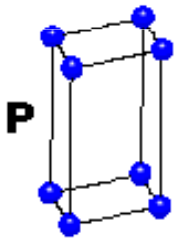


HEXAGONAL

$a = b \neq c$

$\alpha = \beta = 90°$

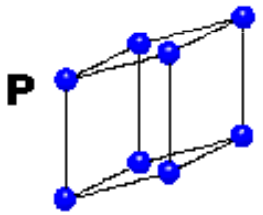
$\gamma = 120°$



TRIGONAL

$a = b = c$

$\alpha = \beta = \gamma \neq 90°$

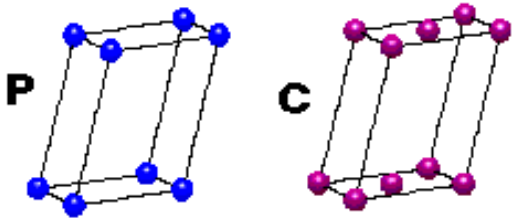


MONOCLINIC

$a \neq b \neq c$

$\alpha = \gamma = 90°$

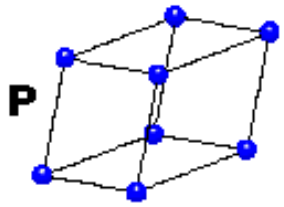
$\beta \neq 120°$



TRICLINIC

$a \neq b \neq c$

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



4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices

Coordination Number

- Coordination Number (CN) : The Bravais lattice points closest to a given point are the nearest neighbours.
- Because the Bravais lattice is periodic, all points have the same number of nearest neighbours or coordination number. It is a property of the lattice.
- A simple cubic has coordination number 6; a body-centered cubic lattice, 8; and a face-centered cubic lattice,12.

Atomic Packing Factor

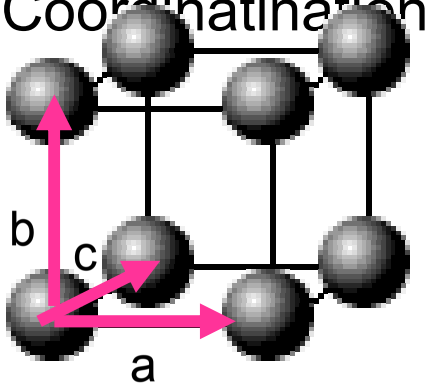
- Atomic Packing Factor (APF) is defined as the volume of atoms within the unit cell divided by the volume of the unit cell.

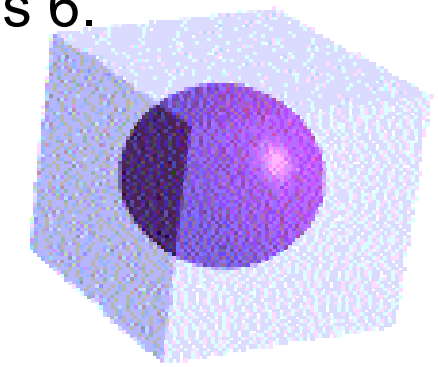
$$\text{APF} = \frac{\text{Volume of Atoms in Unit Cell}}{\text{Volume of Unit Cell}}$$

1-CUBIC CRYSTAL SYSTEM

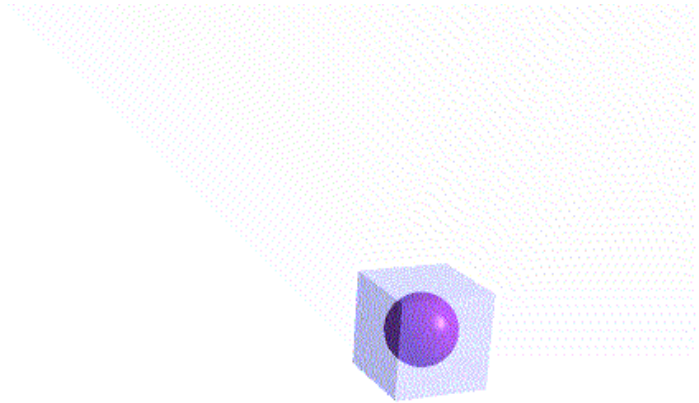
a- Simple Cubic (SC)

- Simple Cubic has one lattice point so its primitive cell.
- In the unit cell on the left, the atoms at the corners are cut because only a portion (in this case 1/8) belongs to that cell. The rest of the atom belongs to neighboring cells.
- Coordinatination number of simple cubic is 6.

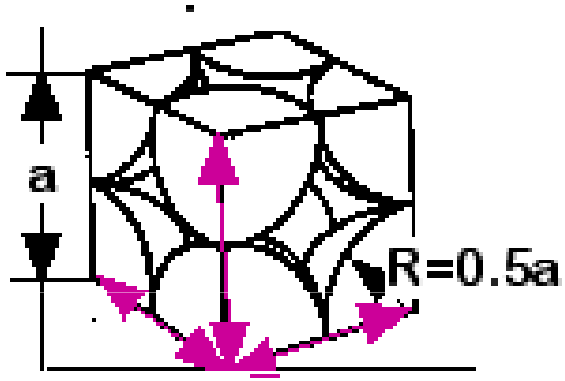




a- Simple Cubic (SC)



Atomic Packing Factor of SC



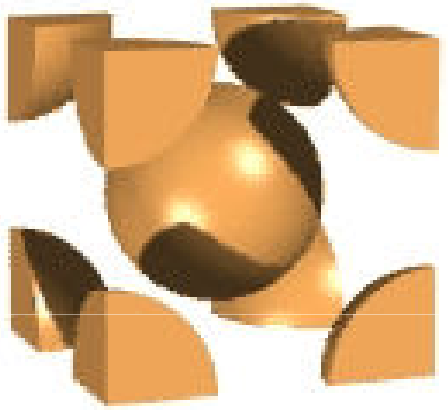
contains 8 x 1/8 =
1atom/unit cell

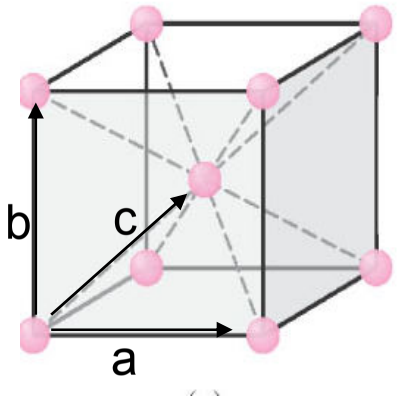
APF = 0.52 for simple cubic

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

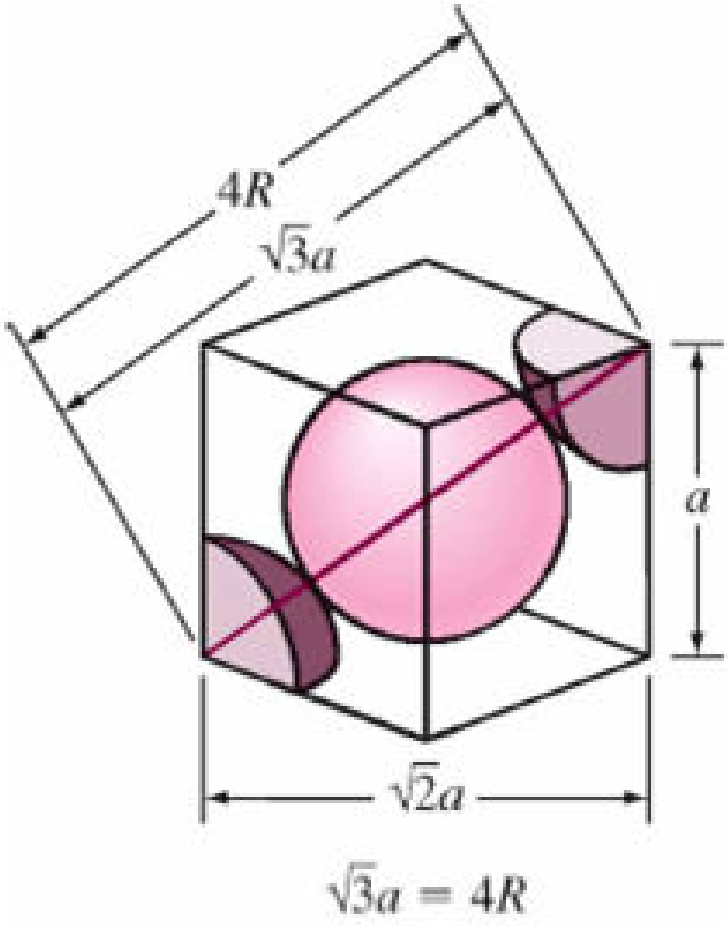
b-Body Centered Cubic (BCC)

- BCC has two lattice points so BCC is a non-primitive cell.
- BCC has eight nearest neighbors. Each atom is in contact with its neighbors only along the body-diagonal directions.
- Many metals (Fe,Li,Na..etc), including the alkalis and several transition elements choose the BCC structure.





Atomic Packing Factor of BCC



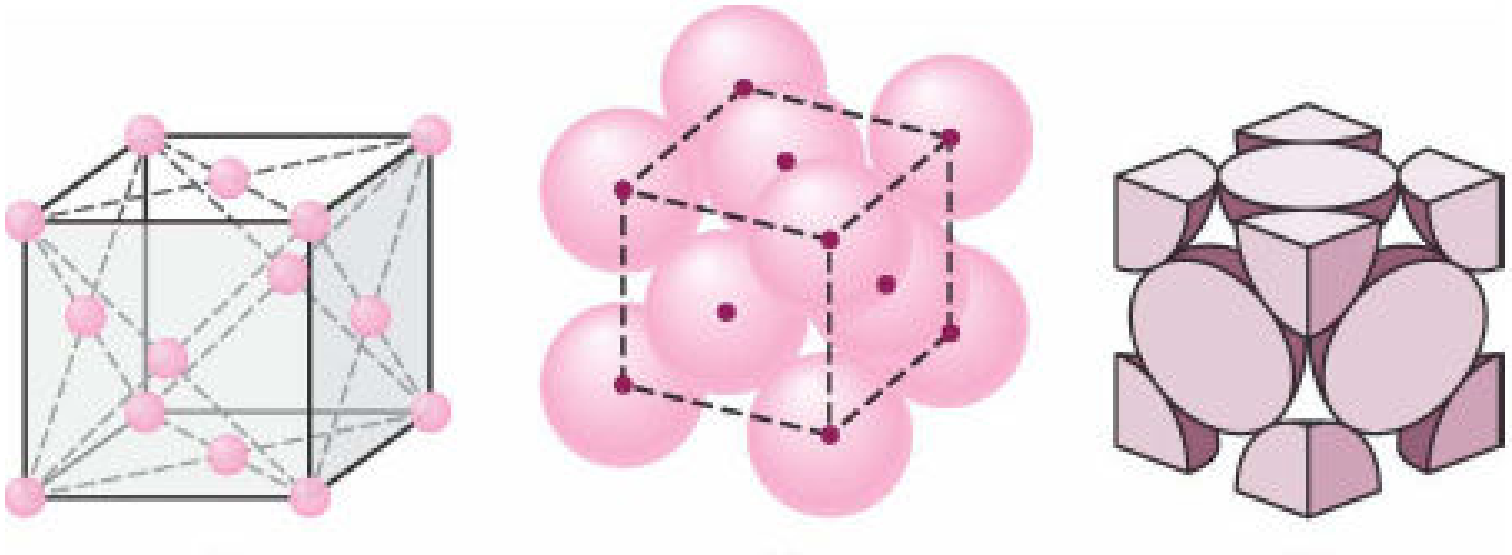
$$APF_{BCC} = \frac{V_{atoms}}{V_{unit\ cell}} = 0.68$$

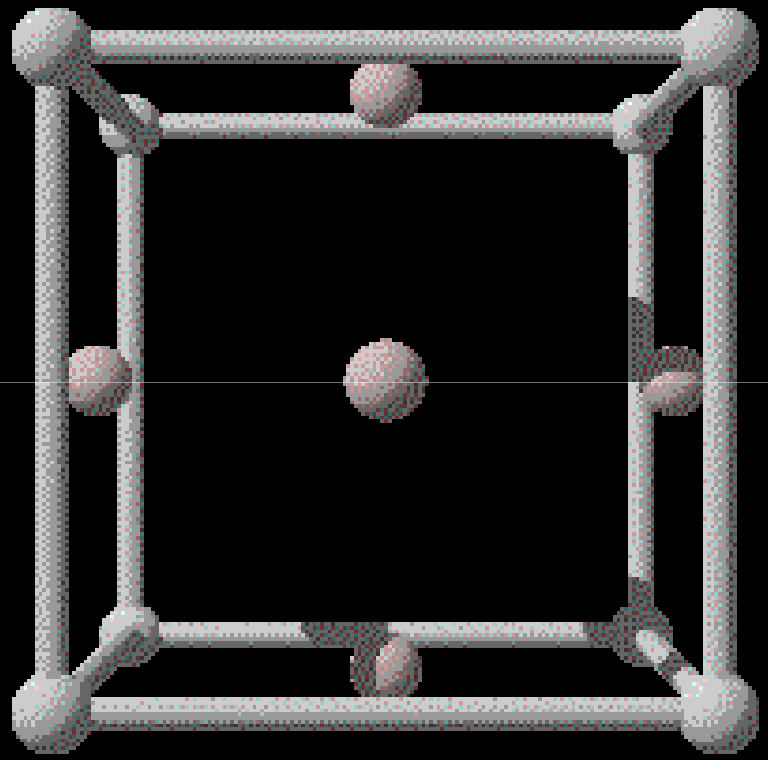
$$APF = \frac{\text{atom}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \cdot \frac{\text{volume}}{\text{unit cell}}$$

$$APF = \frac{2 \cdot \frac{4}{3}\pi (0{,}433a)^3}{a^3}$$

c- Face Centered Cubic (FCC)

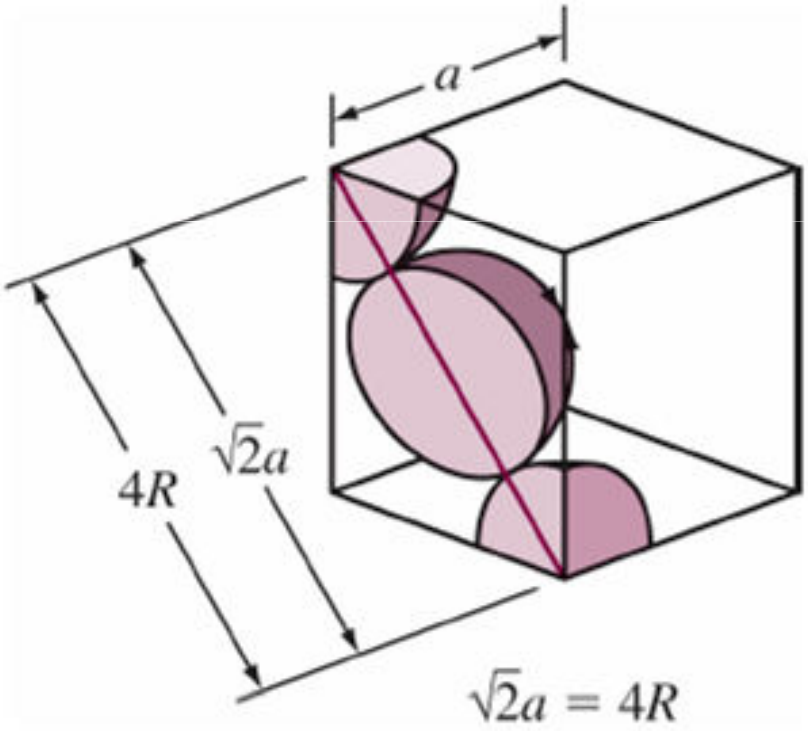
- There are atoms at the corners of the unit cell and at the center of each face.
- Face centered cubic has 4 atoms so its non primitive cell.
- Many of common metals (Cu,Ni,Pb..etc) crystallize in FCC structure.





Face centered cubic unit cell

Atomic Packing Factor of FCC



$$APF_{FCC} = \frac{V_{atoms}}{V_{unit\ cell}} = \mathbf{0,74}$$

$$APF = \frac{\text{atom}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}}$$

$$APF = \frac{4 \cdot \frac{4}{3}\pi(0{,}353a)^3}{a^3}$$

Unit cell contents

Counting the number of atoms within the unit cell

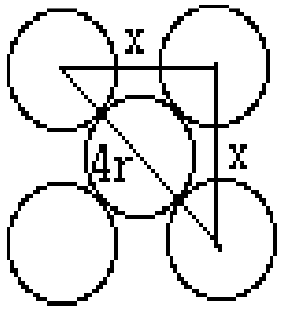
Atoms	**Shared Between:**	**Each atom counts:**
corner	8 cells	1/8
face centre	2 cells	1/2
body centre	1 cell	1
edge centre	2 cells	1/2

lattice type	**cell contents**	
P	1	[=8 x 1/8]
I	2	[=(8 x 1/8) + (1 x 1)]
F	4	[=(8 x 1/8) + (6 x 1/2)]
C	2	[=(8 x 1/8) + (2 x 1/2)]

Example; Atomic Packing Factor

It is very easy to show that the filling of space by spheres is 74%
e.g. for the fcc unit cell of cubic close packing (CCP) with an ABC layer repeat

For spheres of radius, r, touching along the **face diagonal**, the cubic unit cell parameter is calculated as $x = 2\sqrt{2}\,r$



total unit cell volume = x^3

$= 16\sqrt{2}\,r^3$

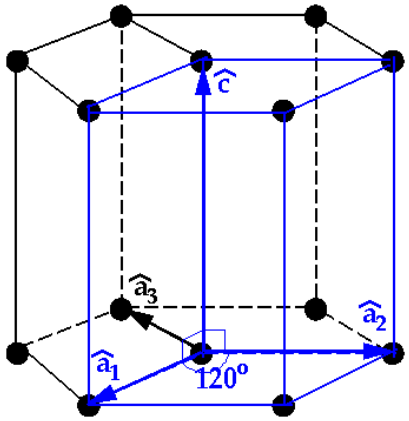
occupied volume = 4 spheres

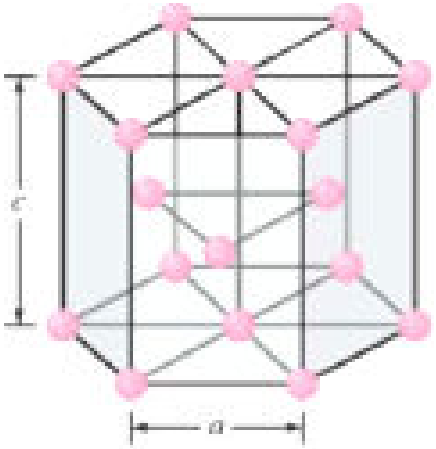
$= \frac{16\pi r^3}{3}$

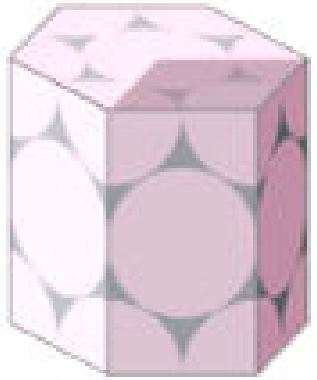
space filling = $\frac{\pi}{3\sqrt{2}}$ = **74.05 %**

2 - HEXAGONAL SYSTEM

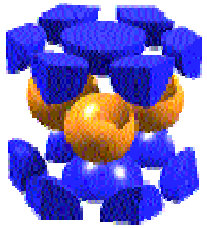
- A crystal system in which three equal coplanar axes intersect at an angle of 60 , and a perpendicular to the others, is of a different length.



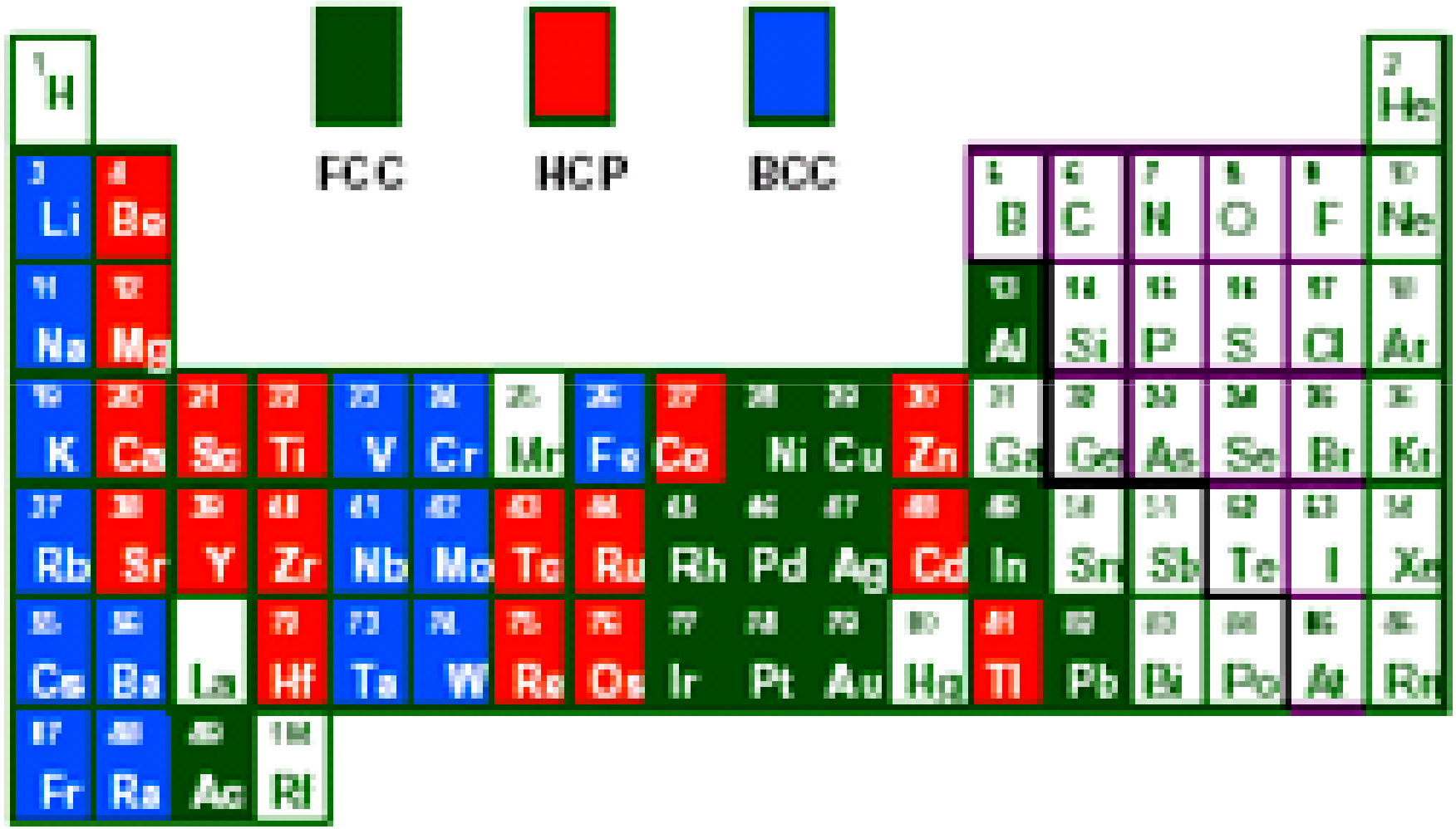




2 - HEXAGONAL SYSTEM

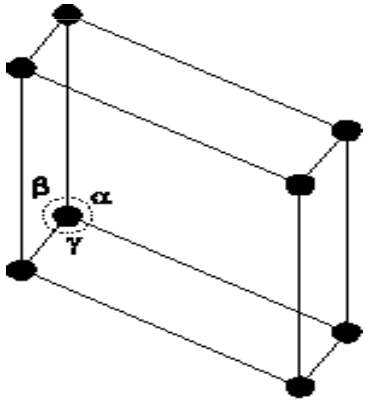


Atoms are all same!


FCC
HCP
BCC
H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Kr
Rb
Sr
Y
Zr
Nb
Mo
Tc
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Xe
Cs
Ba
La
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Po
At
Rn
Fr
Ra
Ac
Rf

3 - TRICLINIC
4 - MONOCLINIC CRYSTAL SYSTEM

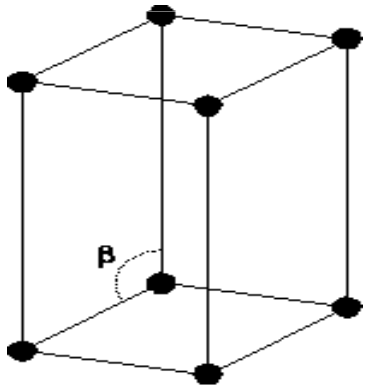
- Triclinic minerals are the least symmetrical. Their three axes are all different lengths and none of them are perpendicular to each other. These minerals are the most difficult to recognize.



Triclinic (Simple)

$\alpha \neq ß \neq \gamma \neq 90$

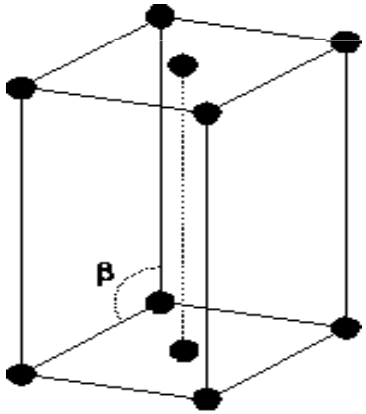
$^{o}a \neq b \neq c$



Monoclinic (Simple)

$\alpha = \gamma = 90^{o}, ß \neq 90^{o}$

$a \neq b \neq c$

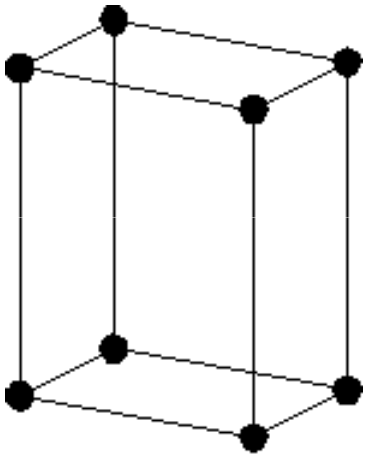


Monoclinic (Base Centered)

$\alpha = \gamma = 90^{o}, ß \neq 90^{o}$

$a \neq b \neq c,$

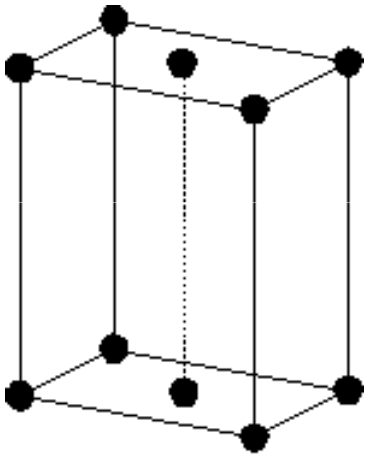
5 - ORTHORHOMBIC SYSTEM



Orthorhombic (Simple)

$\alpha = ß = \gamma = 90^o$

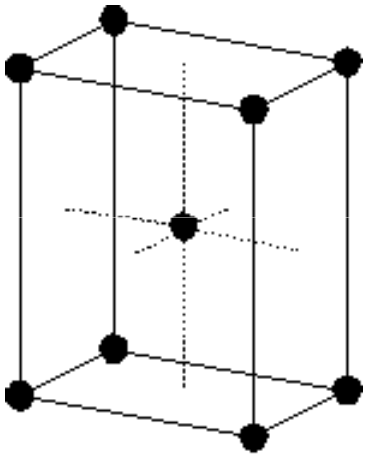
$a \neq b \neq c$



Orthorhombic (Base-centred)

$\alpha = ß = \gamma = 90^o$

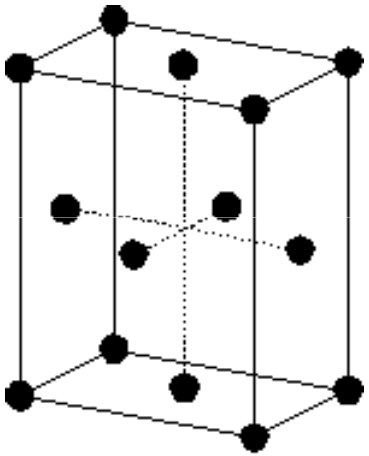
$a \neq b \neq c$



Orthorhombic (BC)

$\alpha = ß = \gamma = 90^o$

$a \neq b \neq c$

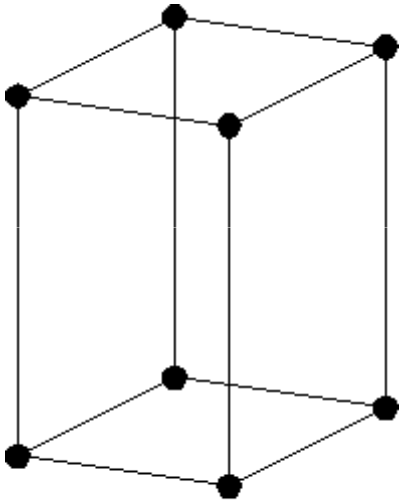


Orthorhombic (FC)

$\alpha = ß = \gamma = 90^o$

$a \neq b \neq c$

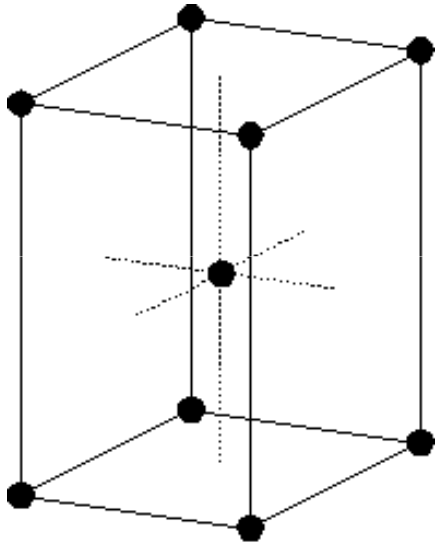
6 – TETRAGONAL SYSTEM



Tetragonal (P)

$\alpha = ß = \gamma = 90^o$

$a = b \neq c$

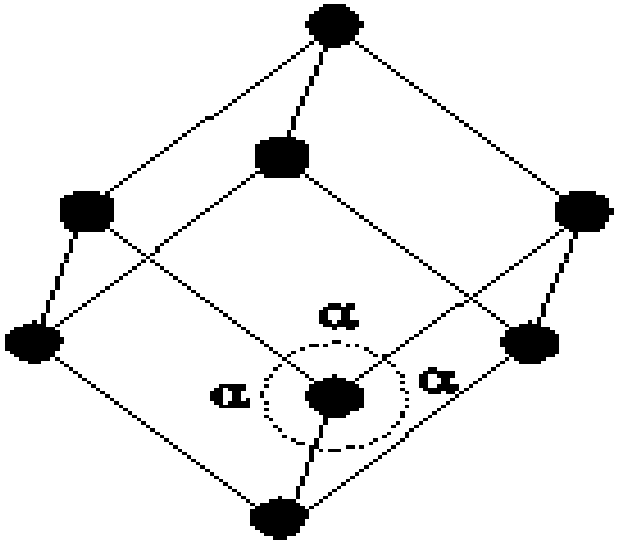


Tetragonal (BC)

$\alpha = ß = \gamma = 90^o$

$a = b \neq c$

7 - Rhombohedral (R) or Trigonal



Rhombohedral (R) or Trigonal (S)

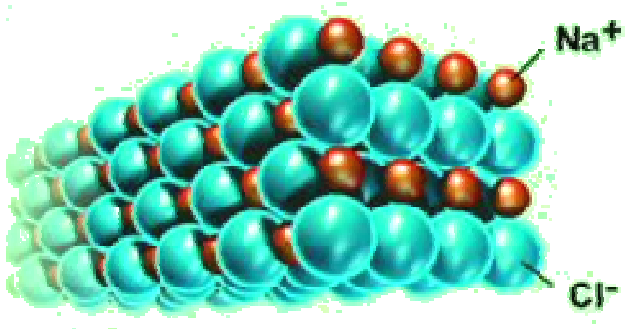
$a = b = c, \alpha = ß = \gamma \neq 90^o$

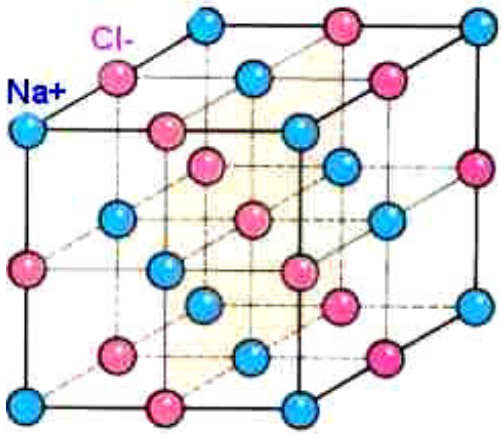
THE MOST IMPORTANT CRYSTAL STRUCTURES

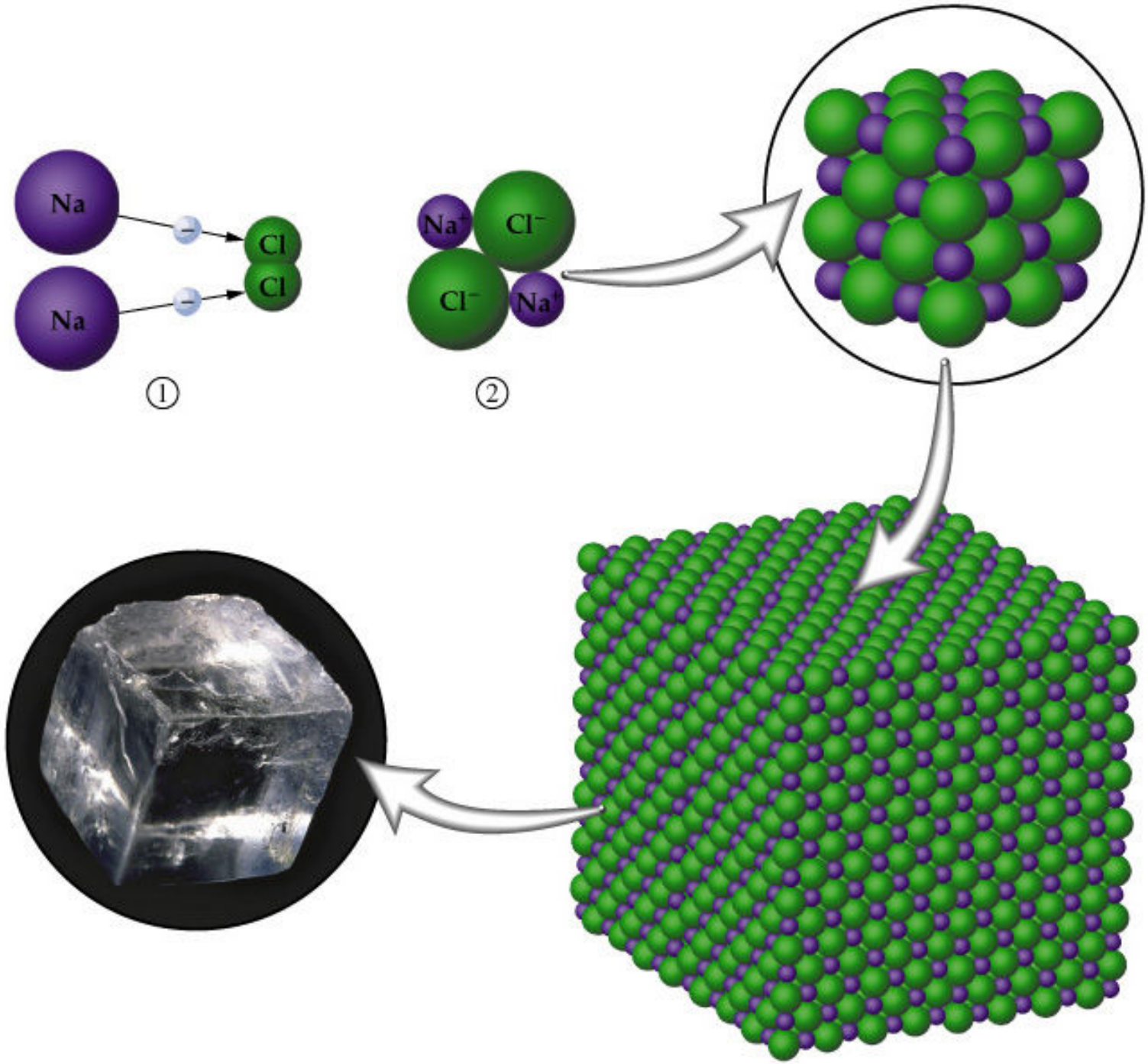
- Sodium Chloride Structure $Na^{+}Cl^{-}$
- Cesium Chloride Structure $Cs^{+}Cl^{-}$
- Hexagonal Closed-Packed Structure
- Diamond Structure
- Zinc Blende

1 – Sodium Chloride Structure

- **Sodium chloride also crystallizes in a cubic lattice, but with a different unit cell.**
- **Sodium chloride structure consists of equal numbers of sodium and chlorine ions placed at alternate points of a simple cubic lattice.**
- **Each ion has six of the other kind of ions as its nearest neighbours.**

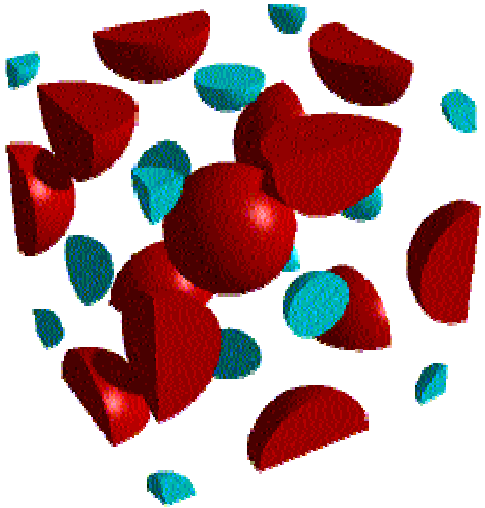




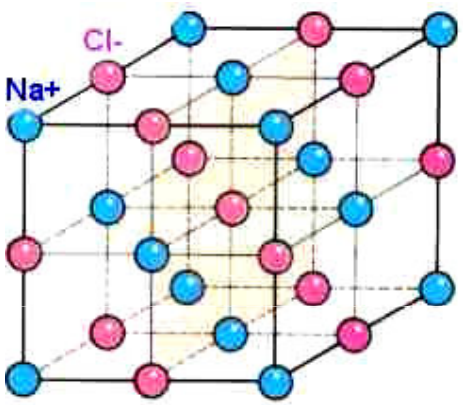

Na
Na
Cl
Cl
①
Na⁺
Cl⁻
Cl⁻
Na⁺
②

Sodium Chloride Structure

- **If we take the NaCl unit cell and remove all the red Cl ions, we are left with only the blue Na. If we compare this with the fcc / ccp unit cell, it is clear that they are identical. Thus, the Na is in a fcc sublattice.**



Sodium Chloride Structure



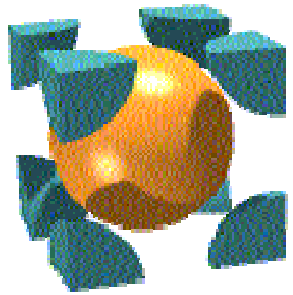
- This structure can be considered as a face-centered-cubic Bravais lattice with a basis consisting of a sodium ion at 0 and a chlorine ion at the center of the conventional cell,

$$a\ /\ 2\ (\vec{x} + \vec{y} + \vec{z}\ )$$

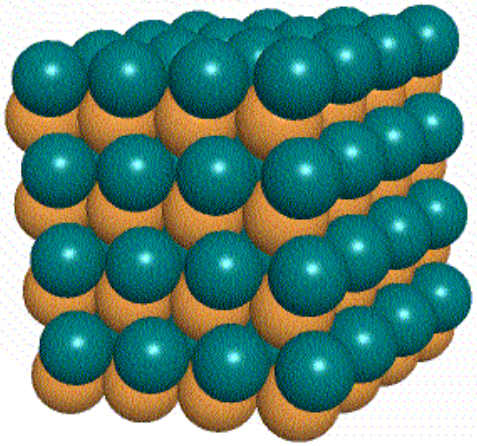
- LiF,NaBr,KCl,LiI,etc
- The lattice constants are in the order of 4-7 angstroms.

2-Cesium Chloride Structure Cs^+Cl^-

- **Cesium chloride crystallizes in a cubic lattice. The unit cell may be depicted as shown. (Cs+ is teal, Cl- is gold).**



- ***Cesium chloride consists of equal numbers of cesium and chlorine ions, placed at the points of a body-centered cubic lattice so that each ion has eight of the other kind as its nearest neighbors.***



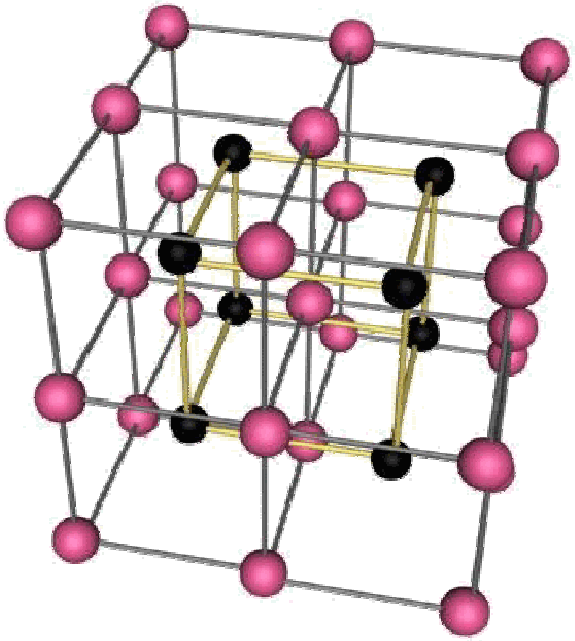
Cesium Chloride Structure Cs^+Cl^-

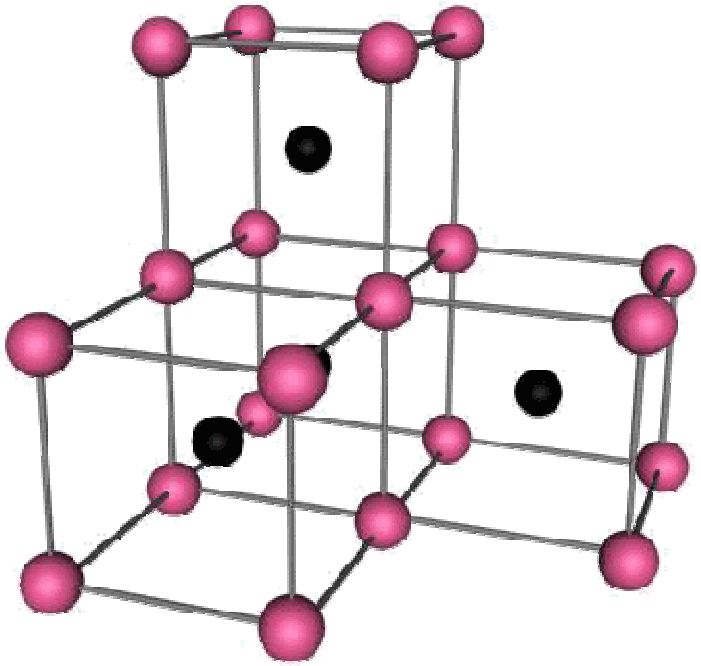
- The translational symmetry of this structure is that of the simple cubic Bravais lattice, and is described as a simple cubic lattice with a basis consisting of a cesium ion at the origin **0** and a chlorine ion at the cube center

$$a/2(\vec{x}+\vec{y}+\vec{z})$$

- CsBr,CsI crystallize in this structure.The lattice constants are in the order of 4 angstroms.

Cesium Chloride Cs^+Cl^-

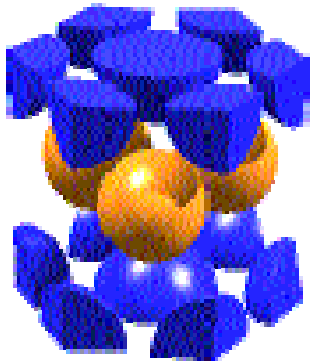


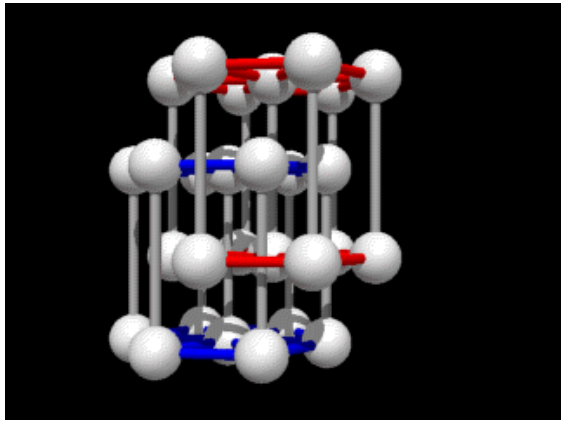


8 cell

3–Hexagonal Close-Packed Str.

- **This is another structure that is common, particularly in metals. In addition to the two layers of atoms which form the base and the upper face of the hexagon, there is also an intervening layer of atoms arranged such that each of these atoms rest over a depression between three atoms in the base.**

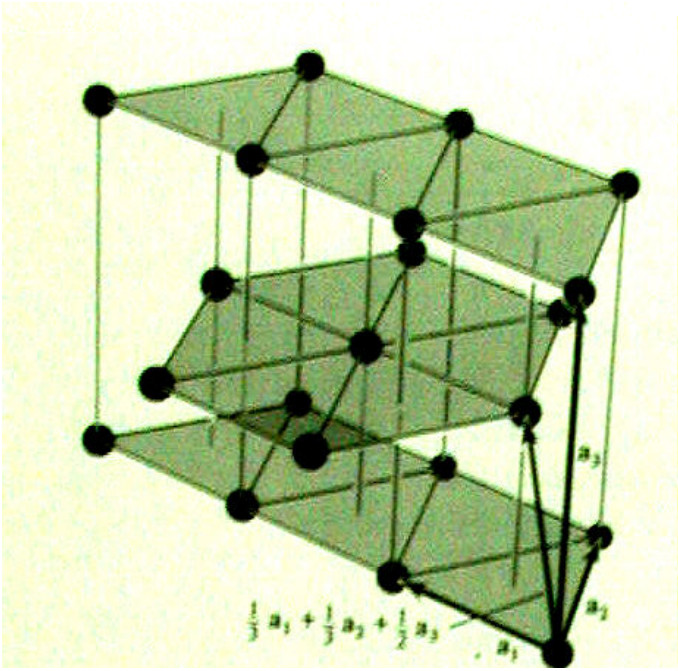


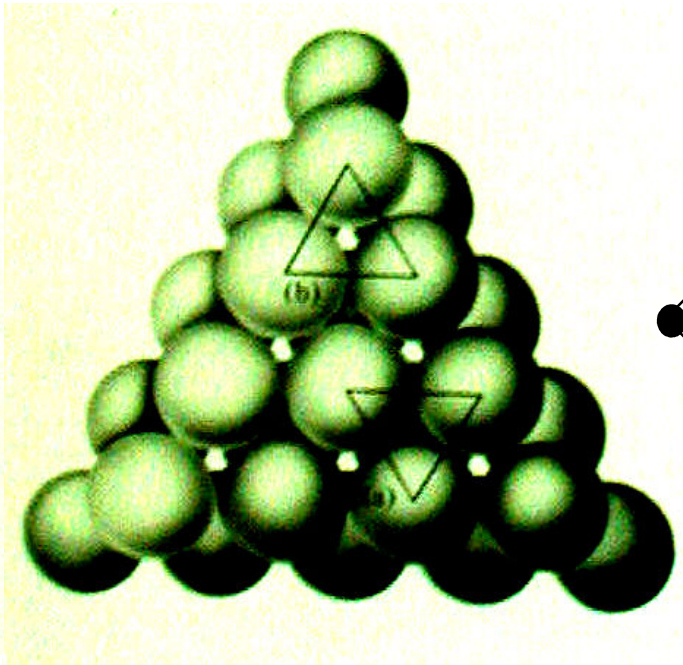


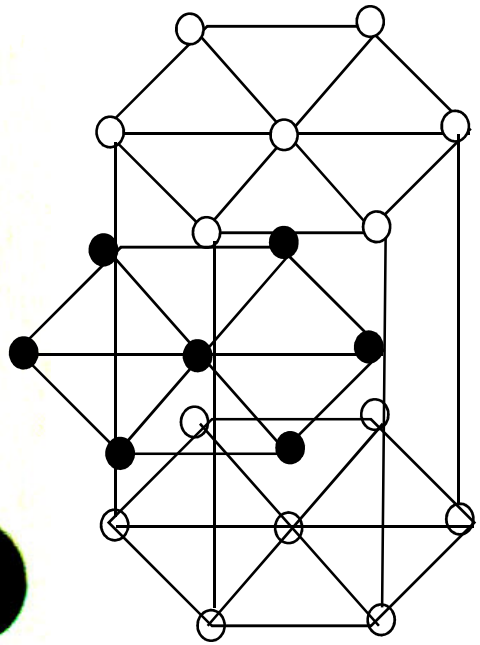
Hexagonal Close-packed Structure

Bravais Lattice : Hexagonal Lattice
He, Be, Mg, Hf, Re (Group II elements)
ABABAB Type of Stacking

a=b a=120, c=1.633a,
basis : (0,0,0) (2/3a ,1/3a,1/2c)

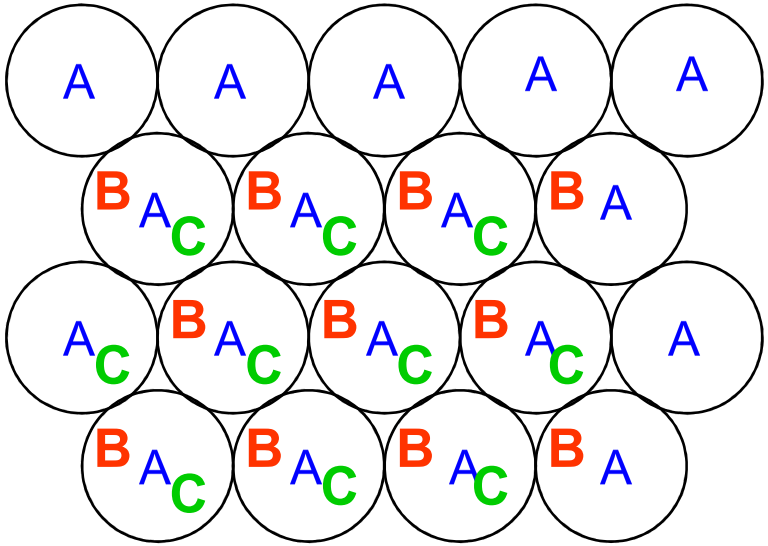






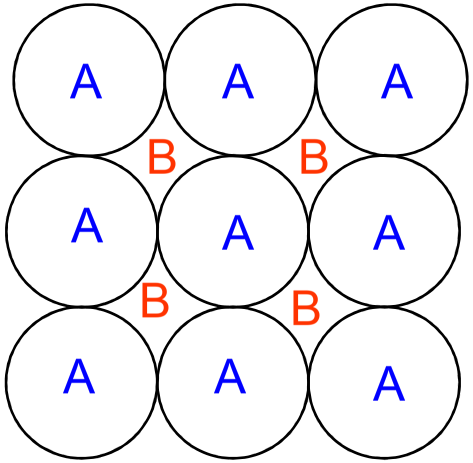
Packing

Close pack



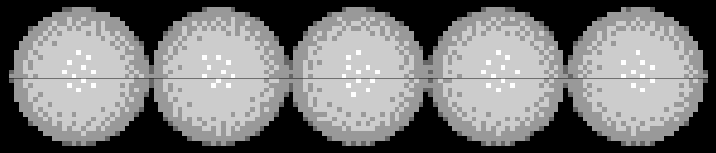
Sequence ABABAB..
-hexagonal close pack

Sequence ABCABCAB..
-face centered cubic close pack



Sequence AAAA…
- simple cubic

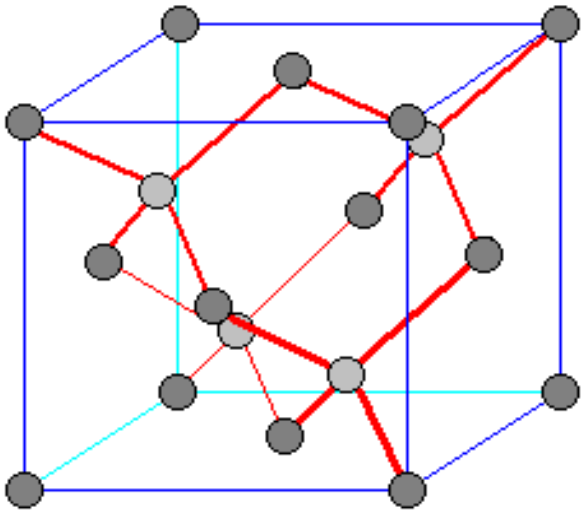
Sequence ABAB…
- body centered cubic

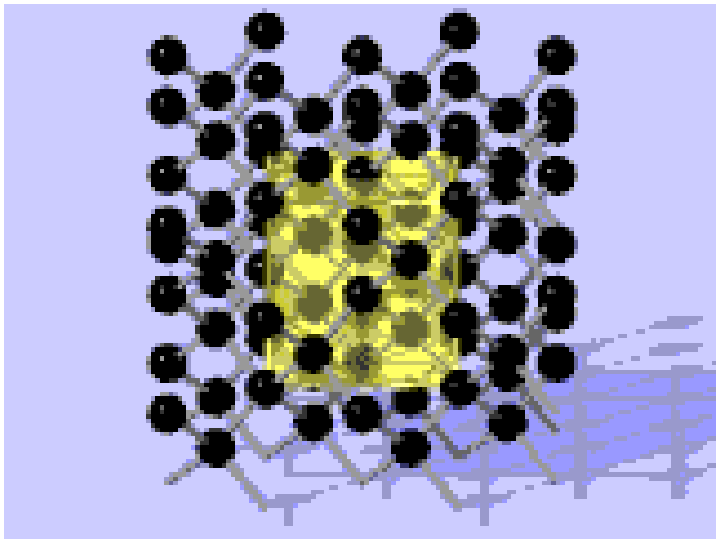


To pack spheres as close as possible
we start with a single row.

4 - Diamond Structure

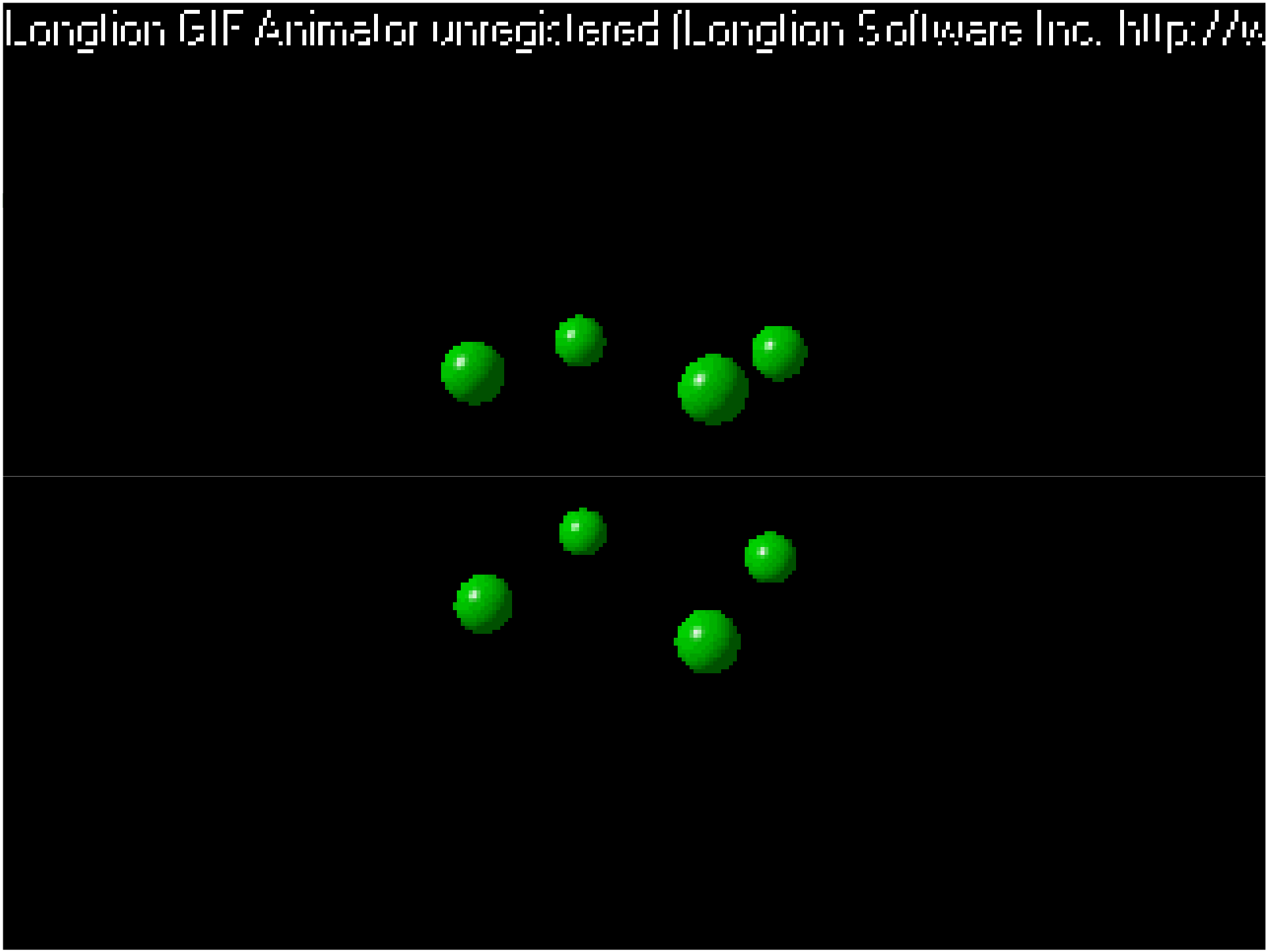
- **The diamond lattice is consist of two interpenetrating face centered bravais lattices.**
- **There are eight atom in the structure of diamond.**
- **Each atom bonds covalently to 4 others equally spread about atom in 3d.**





4 - Diamond Structure

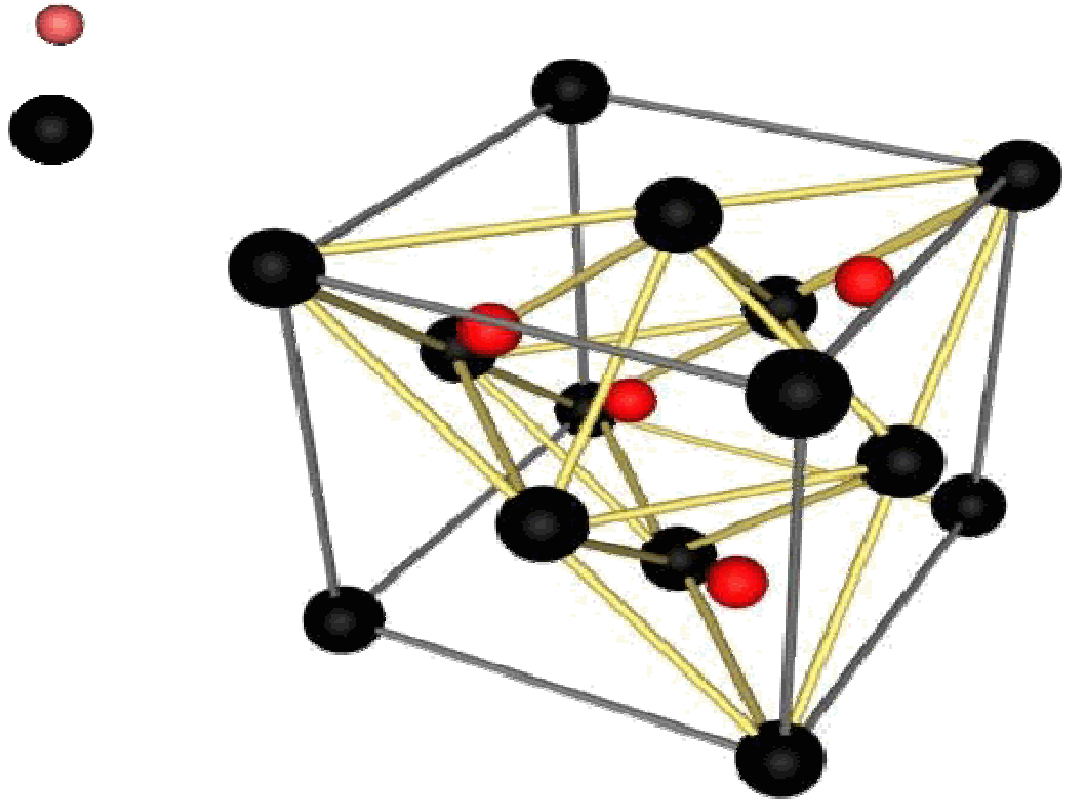
- The coordination number of diamond structure is 4.
- The diamond lattice is not a Bravais lattice.
- Si, Ge and C crystallizes in diamond structure.


Longlion GIF Animator unregistered [Longlion Software Inc. http://w

5- Zinc Blende

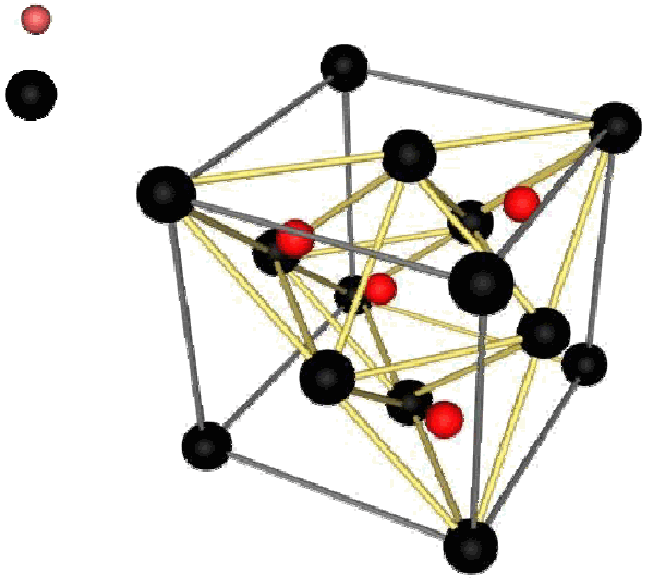
- Zincblende has equal numbers of zinc and sulfur ions distributed on a diamond lattice so that each has four of the opposite kind as nearest neighbors. This structure is an example of a lattice with a basis, which must so described both because of the geometrical position of the ions and because two types of ions occur.
- AgI,GaAs,GaSb,InAs,

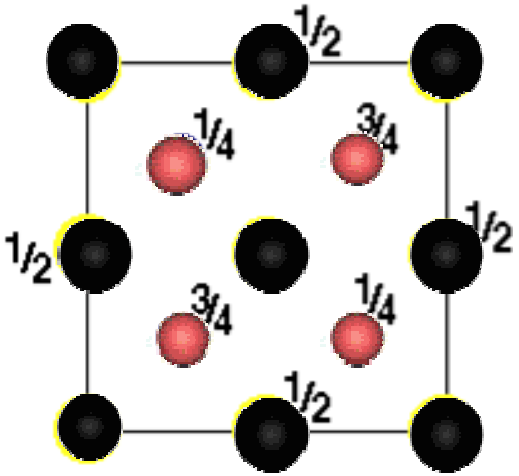
5- Zinc Blende



5- Zinc Blende

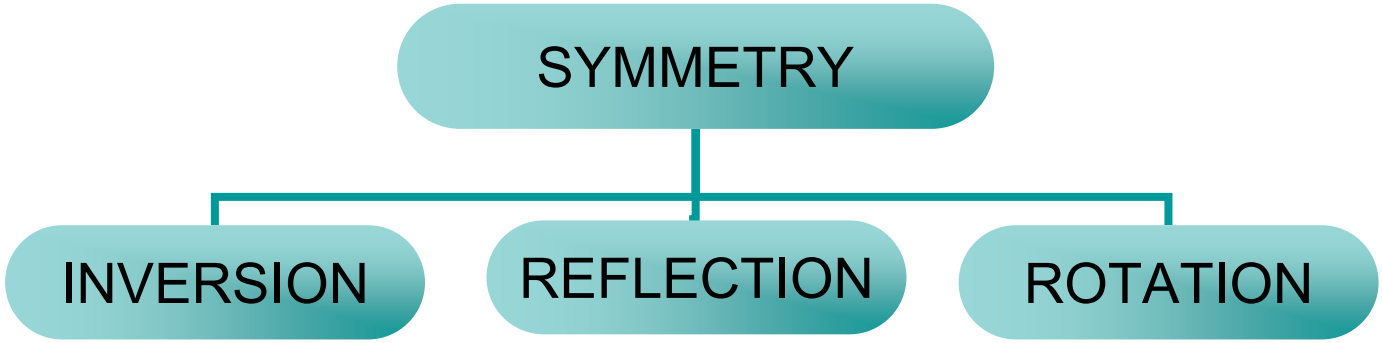
Zinc Blende is the name given to the mineral ZnS. It has a cubic close packed (face centred) array of S and the Zn(II) sit in tetrahedral (1/2 occupied) sites in the lattice.





ELEMENTS OF SYMMETRY

- Each of the unit cells of the 14 Bravais lattices has one or more types of symmetry properties, such as inversion, reflection or rotation,etc.



Lattice goes into itself through Symmetry without translation

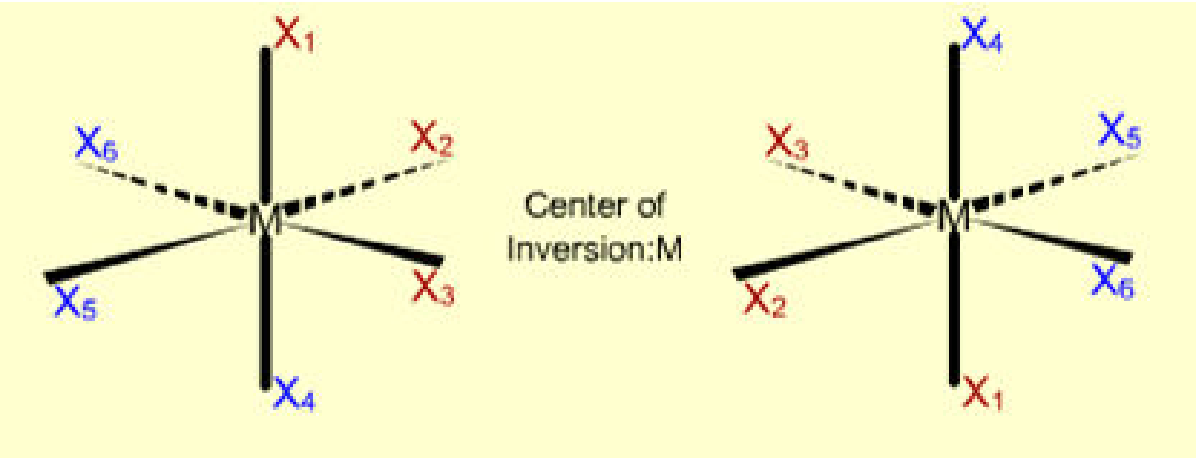
Operation	Element
Inversion	Point
Reflection	Plane
Rotation	Axis
Rotoinversion	Axes

Inversion Center

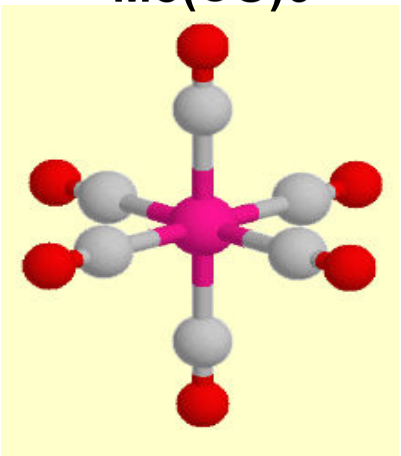
- A center of symmetry: A point at the center of the molecule.

(x,y,z) --> (-x,-y,-z)

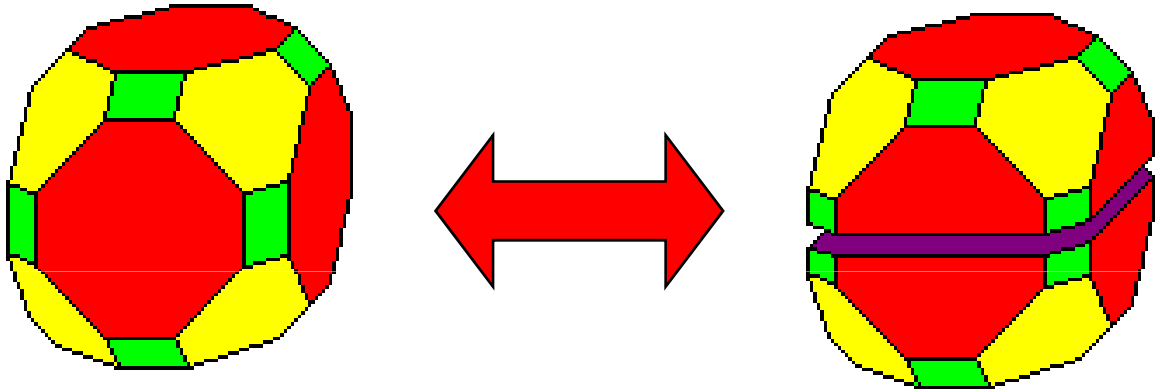
- Center of inversion can only be in a molecule. It is not necessary to have an atom in the center (benzene, ethane). Tetrahedral, triangles, pentagons don't have a center of inversion symmetry. All Bravais lattices are inversion symmetric.



Mo(CO)6

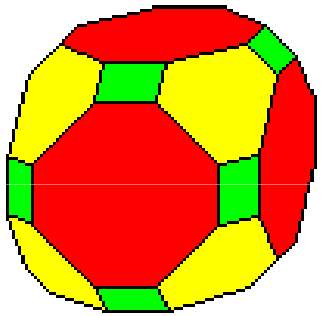


Reflection Plane

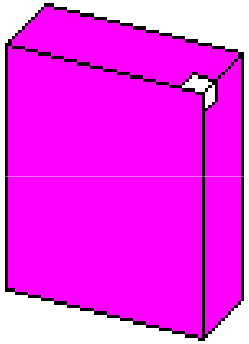


- A plane in a cell such that, when a mirror reflection in this plane is performed, the cell remains invariant.

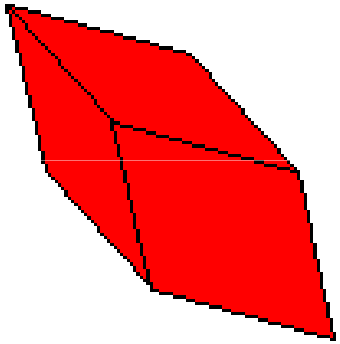
Examples



Monoclinic



Triclinic



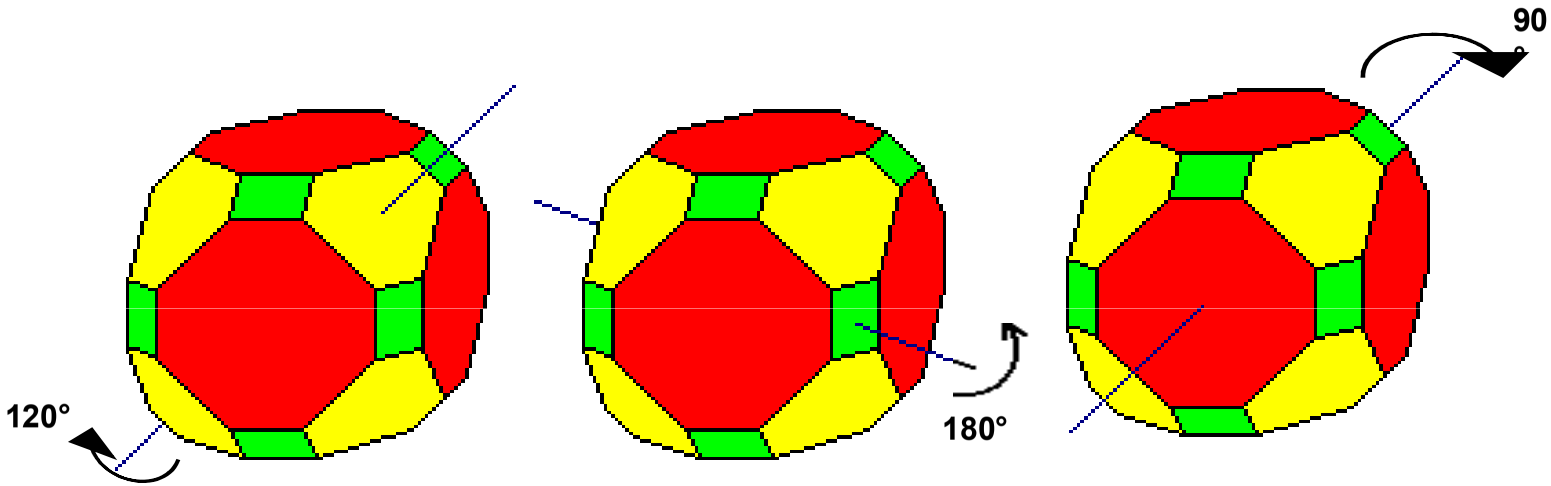
- Triclinic has no reflection plane.
- Monoclinic has one plane midway between and parallel to the bases, and so forth.

Rotation Symmetry

We can not find a lattice that goes into itself under other rotations

- A single molecule can have any degree of rotational symmetry, but an infinite periodic lattice – can not.

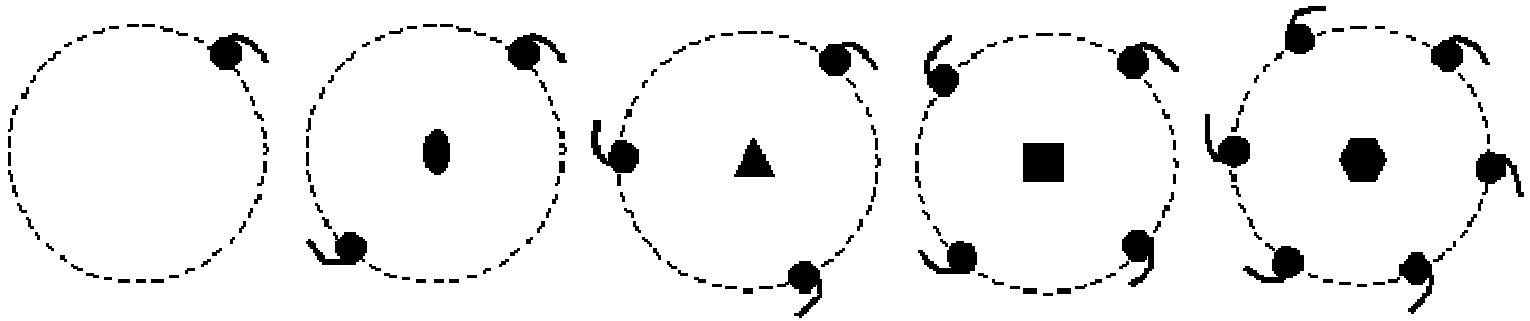
Rotation Axis



- This is an axis such that, if the cell is rotated around it through some angles, the cell remains invariant.

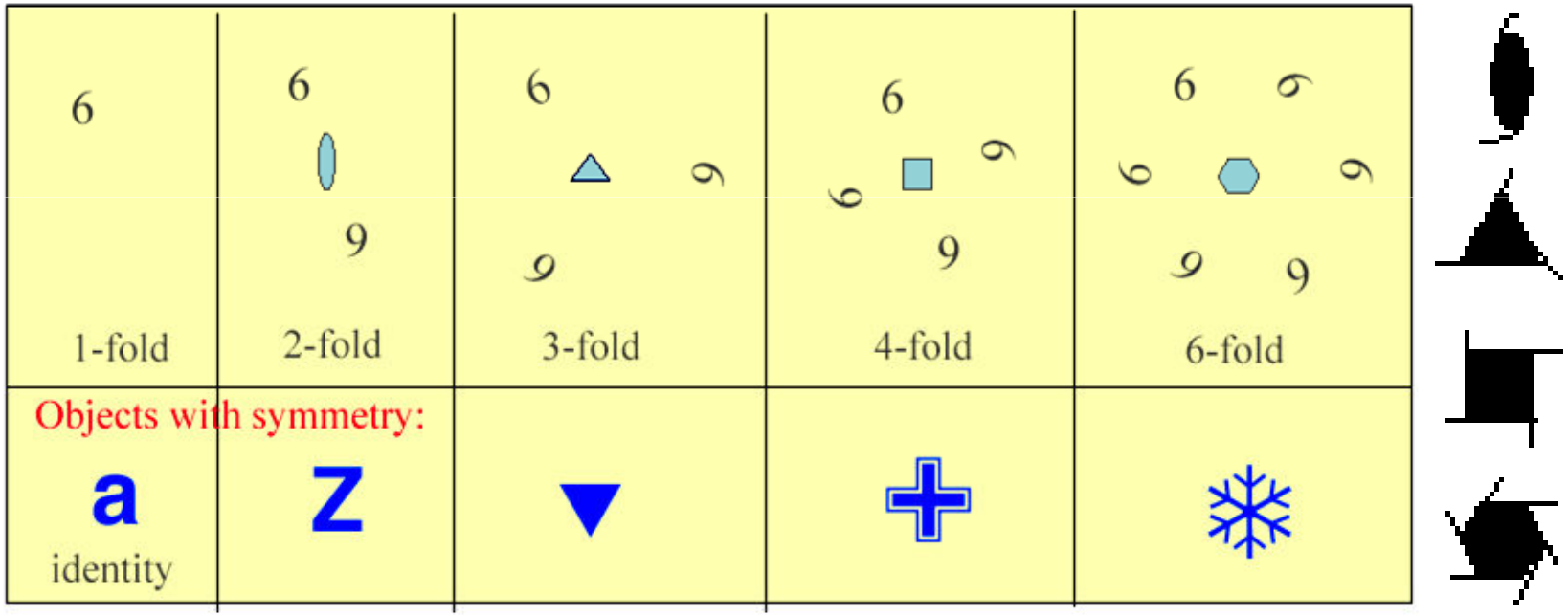
- The axis is called n-fold if the angle of rotation is $2\pi/n$.

Axis of Rotation

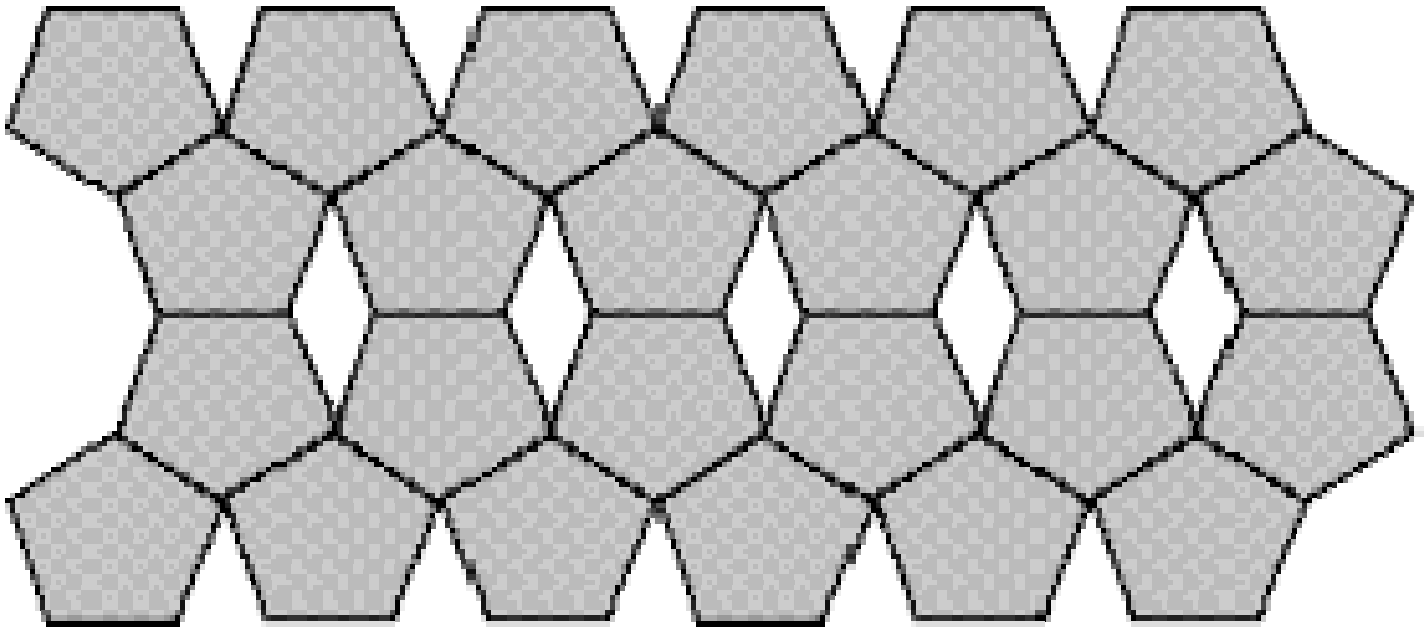


Fold (n)	1	2	3	4	6
Angles	360	180	120	90	60

Axis of Rotation



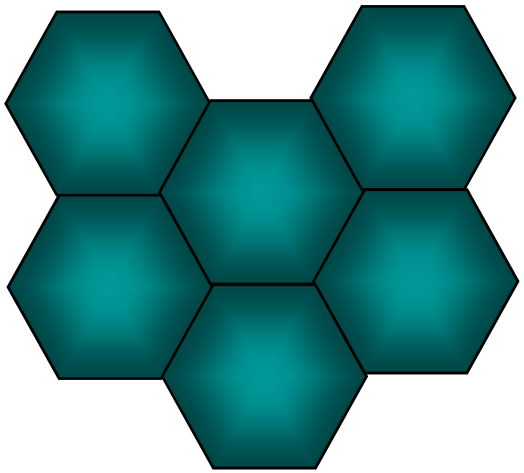
5-fold symmetry

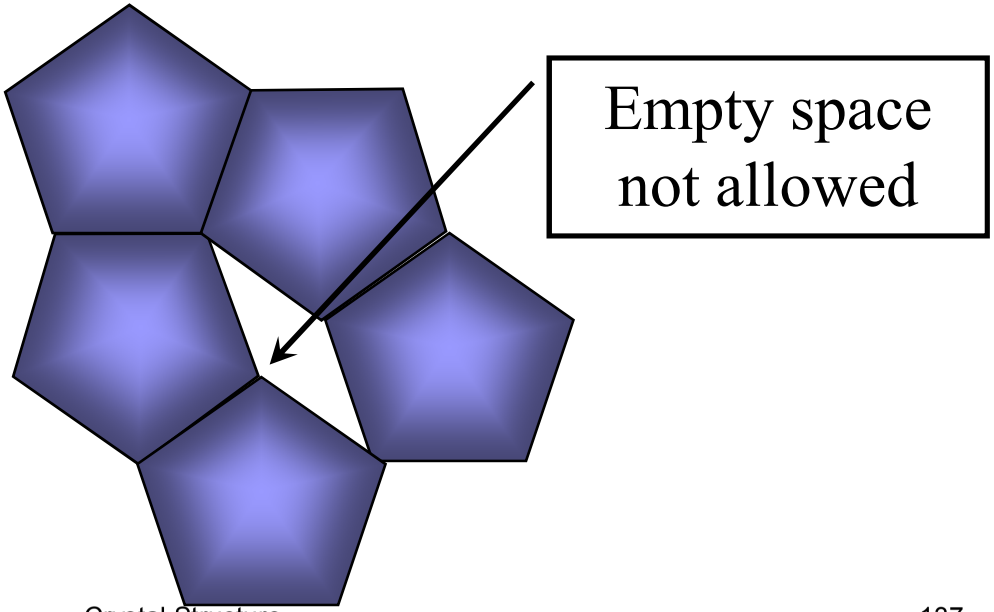


Can not be combined with translational periodicity!

Group discussion

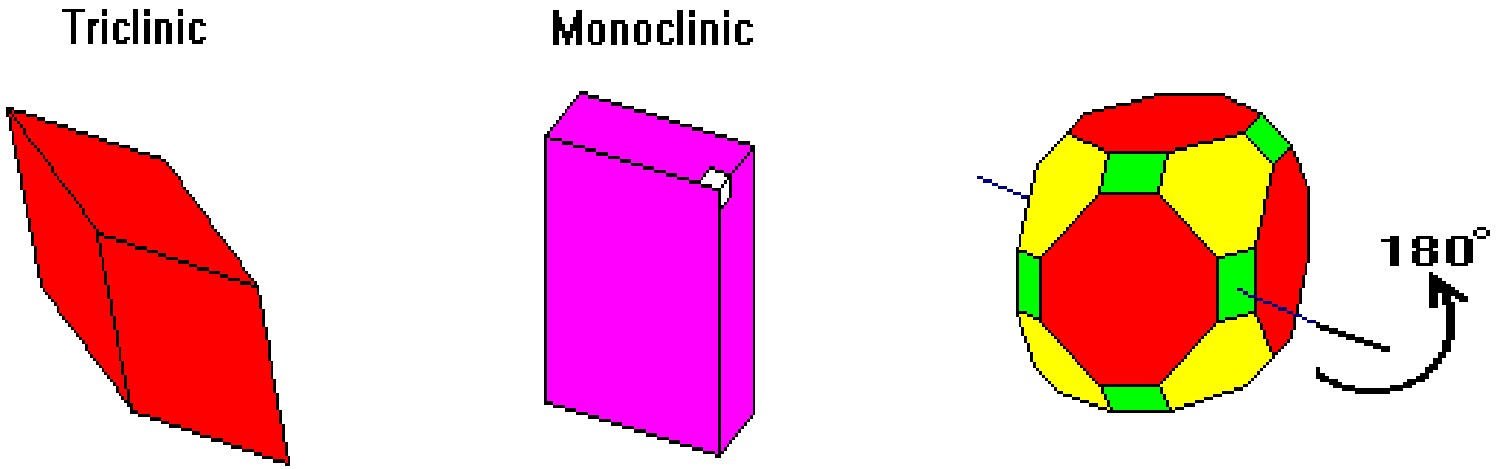
- Kepler wondered why snowflakes have 6 corners, never 5 or 7.By considering the packing of polygons in 2 dimensions, demonstrate why pentagons and heptagons shouldn't occur.



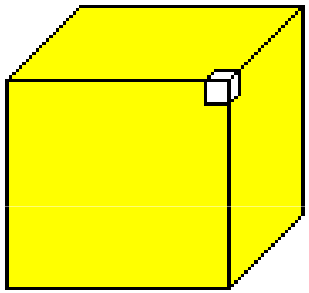


Examples

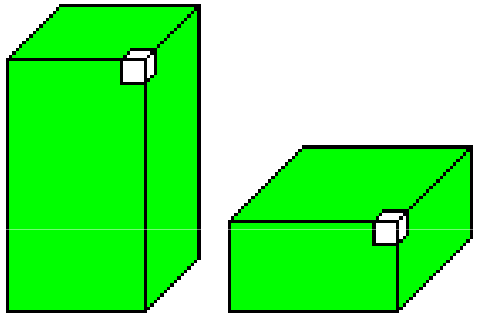
- Triclinic has no axis of rotation.
- Monoclinic has 2-fold axis (θ= 2π/2 =π) normal to the base.



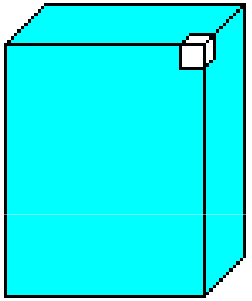
Cubic (Isometric)



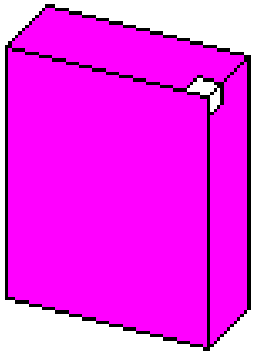
Tetragonal



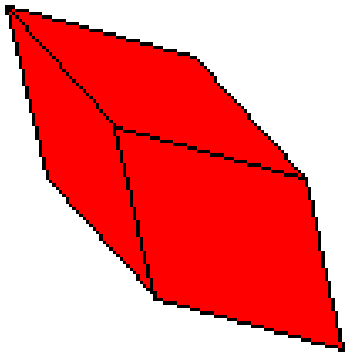
Orthorhombic



Monoclinic



Triclinic



Hexagonal