MS31007: Materials Science

Chapter 3: Crystal Structure

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Crystal Structure : Solid State Materials

- Lattice structures of common chemical elements.
  Concept of Bravais lattice, definition and examples.
  Primitive vectors of Bravais lattice.
  Primitive/Conventional unit cell.
- Coordination number.
- Examples of common crystal structures.
  - Body-centered cubic lattice.
  - Face-centered cubic lattice.
  - Crystal systems
  - Lattice planes and Miller indices.
- Determination of Lattice Spacing : X-ray Diffraction

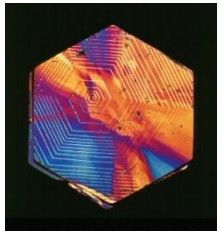
Celestite is a mineral consisting of strontium sulfate ($SrSO_4$). Orthorhombic

Pyrite – FeS_2

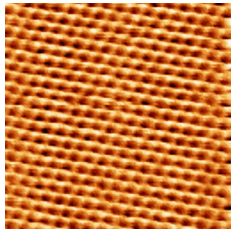
What is solid state materials?

- Single crystals

Long range order and 3D translational periodicity



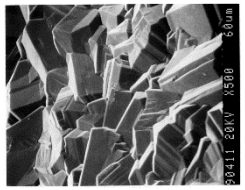
graphite 1.2 mm



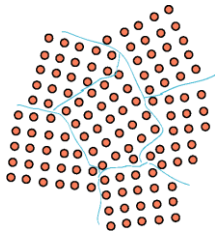
4 nmx4nm

- Polycrystalline crystals

Single crystals assembly

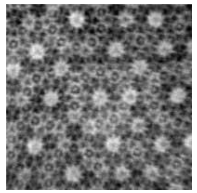


diamond

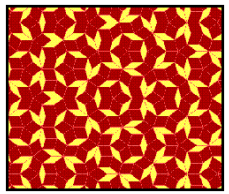


- Quasicrystals

Long range order no 3D translational periodicity

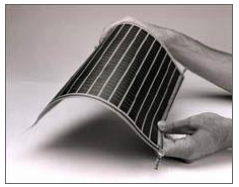


$Al_{72}Ni_{20}Co_8$

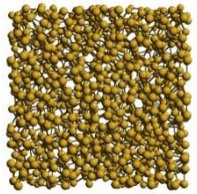


- Amorphous materials

Disordered or random atomic structure



silicon

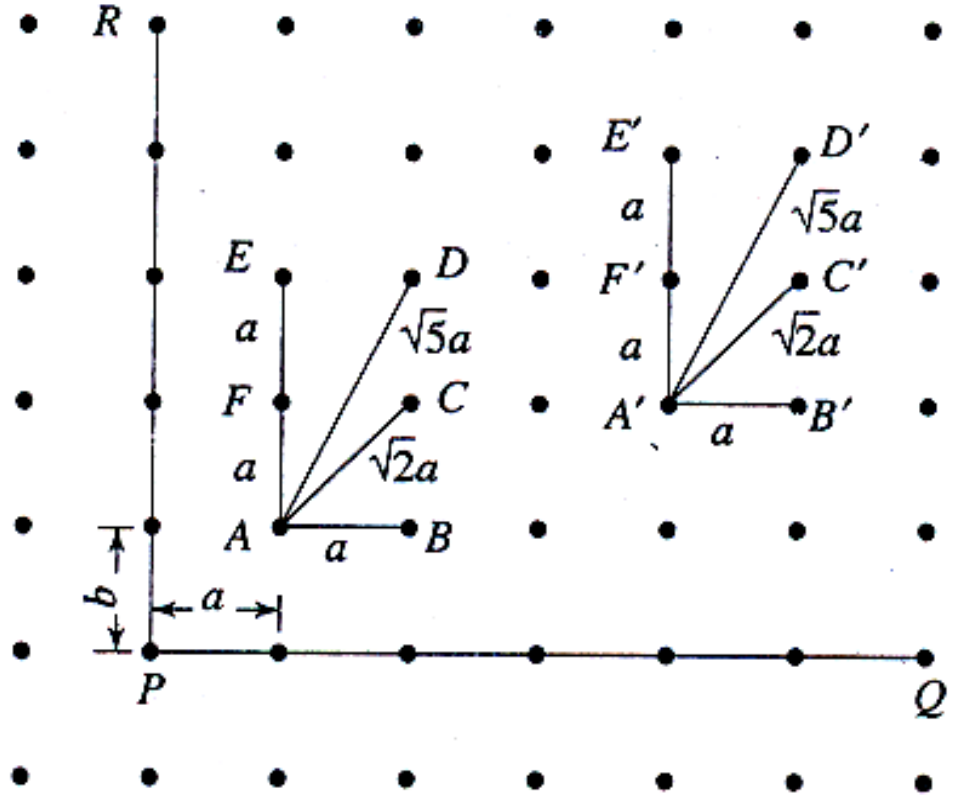


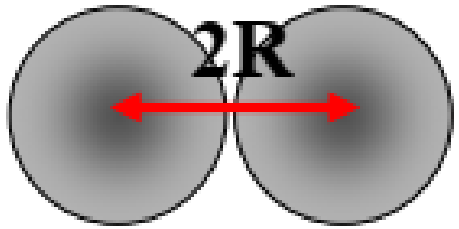
Crystal Structure

Issues that are addressed in this chapter include:

- Periodic array of atoms
- Fundamental types of lattices
- Index system for crystal planes
- Simple crystal structures

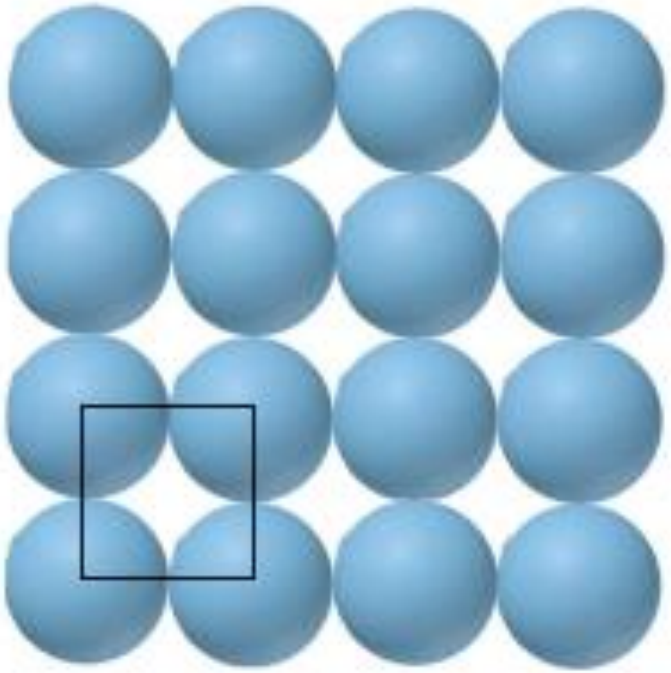
To discuss crystalline structures it is useful to consider atoms as being hard spheres with well-defined radii. In this hard-sphere model, the shortest distance between two like atoms is one diameter of the hard sphere.



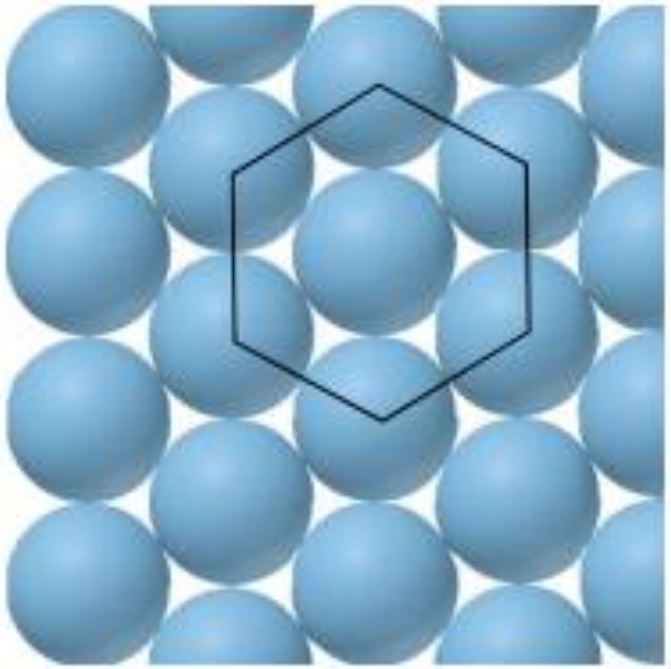


- hard-sphere model

Close-Packing



Square array of circles



Close-packed array of circles

Considering the packing of circles in two dimensions,

-how efficiently do the circles pack for the square array?

- in a close packed array?

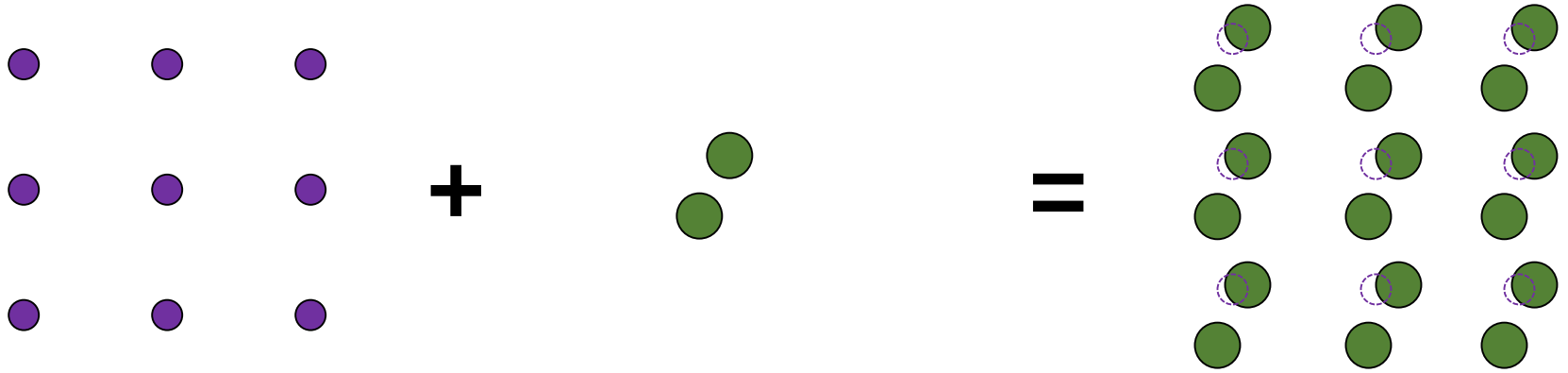
Crystal Structure : Periodic Array of Atoms

- Crystals are composed of a periodic array of atoms.
- Description using a mathematical abstraction

2-Dimensional or 3-Dimensional

The structure of all crystals can be described in terms of a **lattice**, with a group of atoms attached to each lattice point called **basis**:

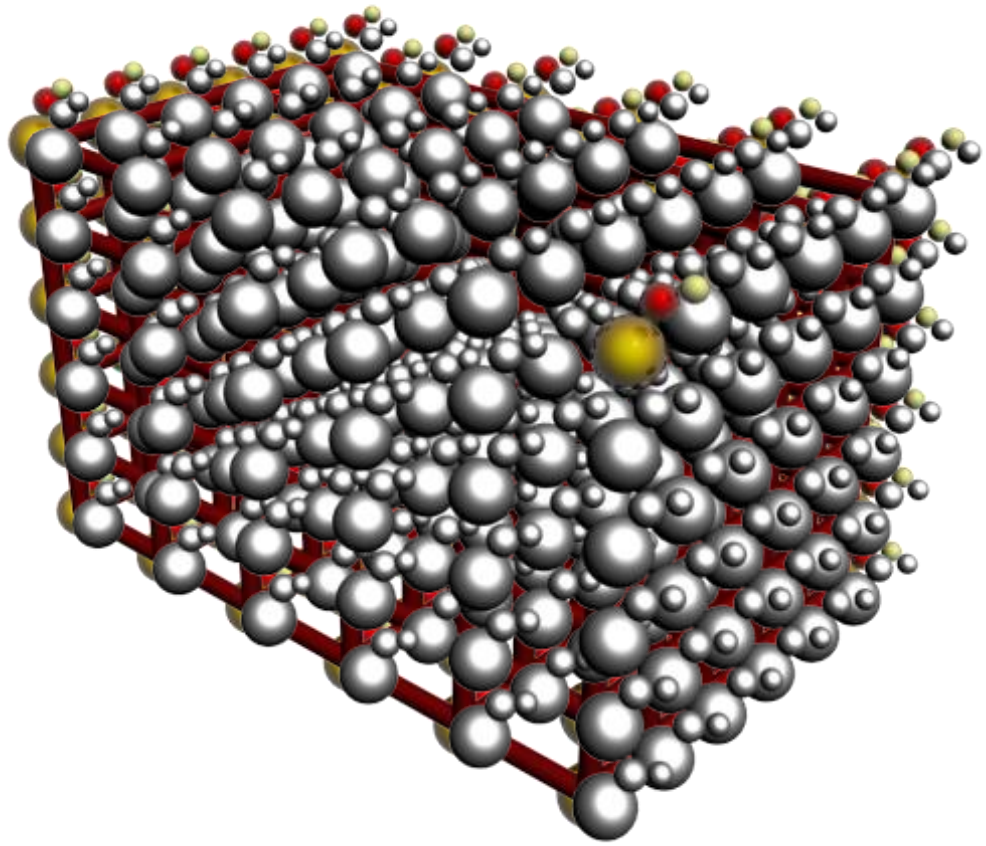
2-Dimensional



Lattice + B**asis** = **Crystal structure**

Periodic Array of Atoms : 3D

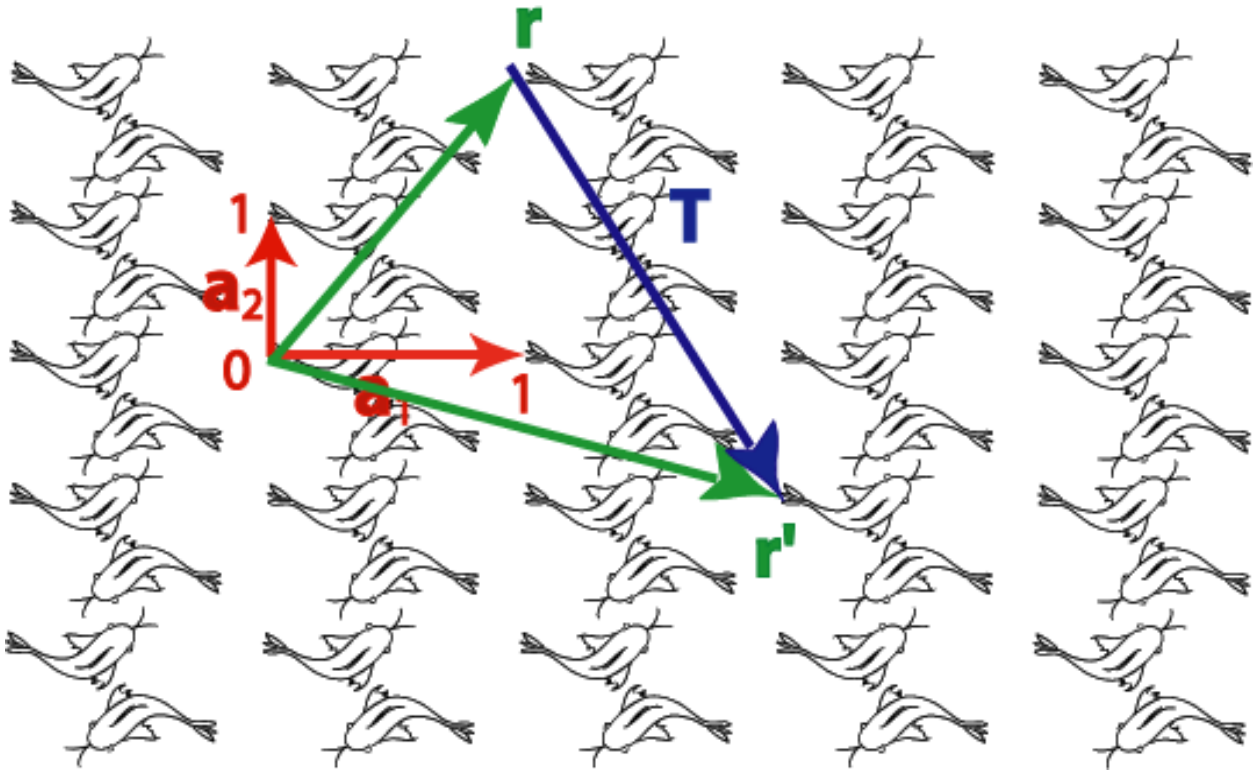
- **Crystal** : Periodic arrangments of atoms in space. 3-Dimensional
- **Lattice** : infinite periodic array of points in space, invariant under translation symmetry.
- **Basis** : atoms or group of atoms attached to every lattice point
- **Lattice + Basis = Crystal**



We can also consider crystalline structure as a lattice of points at atom/sphere centers.

Periodic Array of Atoms

- **Translation vector :** arrangement of atoms looks the same from **r** or **r**’ point
- $\mathbf{r}'=\mathbf{r}+u_1\mathbf{a}_1+u_2\mathbf{a}_2+u_3\mathbf{a}_3$: u_1, u_2 and u_3 integers = lattice constant
- $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ primitive translation vectors
- $\mathbf{T}=u_1\mathbf{a}_1+u_2\mathbf{a}_2+u_3\mathbf{a}_3$ translation vector

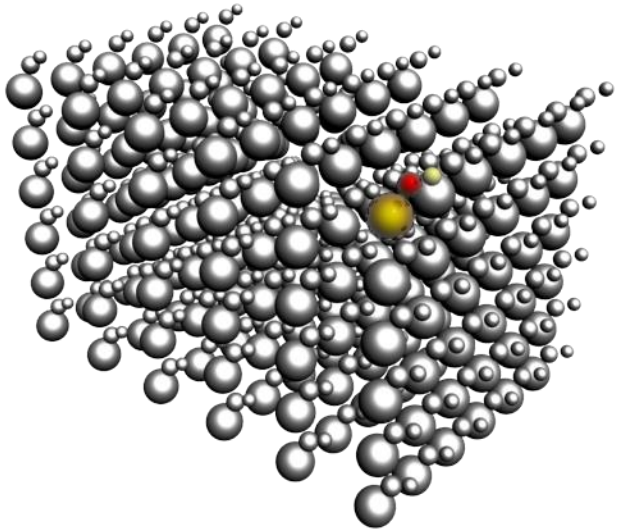


$\mathbf{r} = \mathbf{a}_1+2\mathbf{a}_2$

$\mathbf{r}' = 2\mathbf{a}_1- \mathbf{a}_2$

$\mathbf{T}=\mathbf{r}'-\mathbf{r}=\mathbf{a}_1-3\mathbf{a}_2$

To describe a crystal, it is necessary to specify three things:



1. What is the lattice

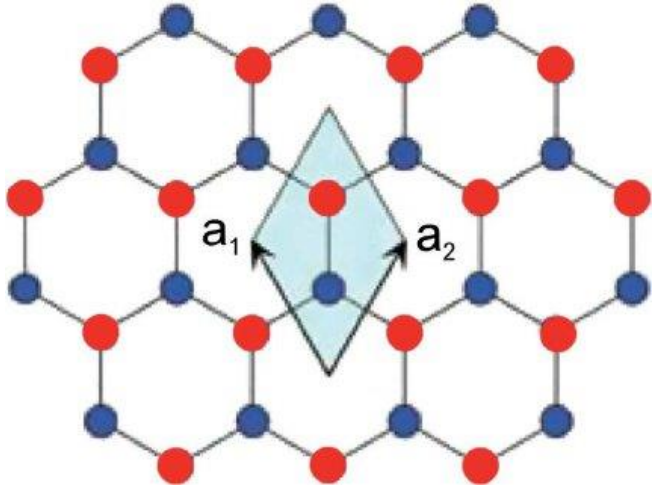
2. What are the lattice translation vectors

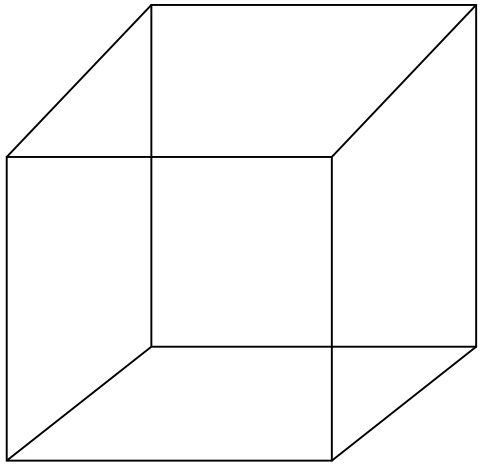
3. What is the basis

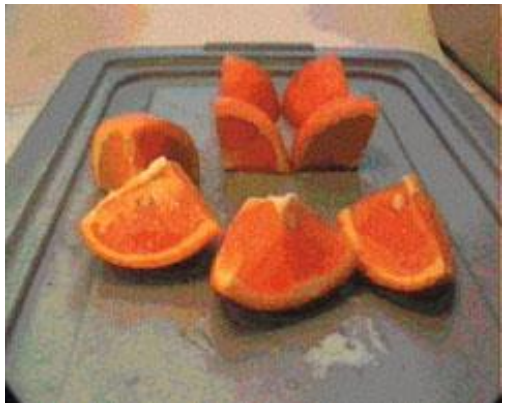
Unit Cell

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

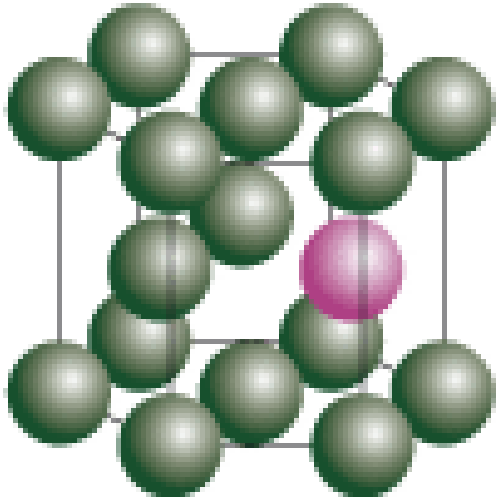
Example: 2D honeycomb net can be represented by translation of two adjacent atoms that form a unit cell for this 2D crystalline structure







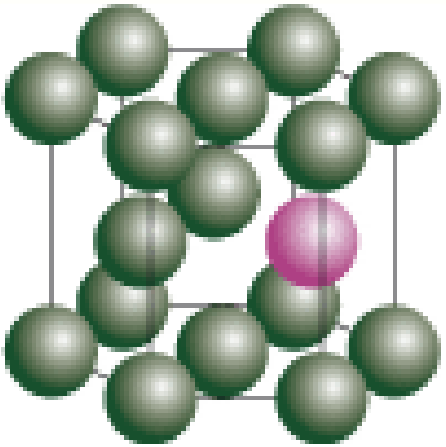
Example of 3D crystalline structure:



Characteristics of Unit Cell

- **Number of atoms / unit cell**
- **Coordination number**

  No. of equidistant nearest neighbouring atoms to a particular atom



- **Atomic Radius (r) :** Half the distance between the nearest neighbouring atoms

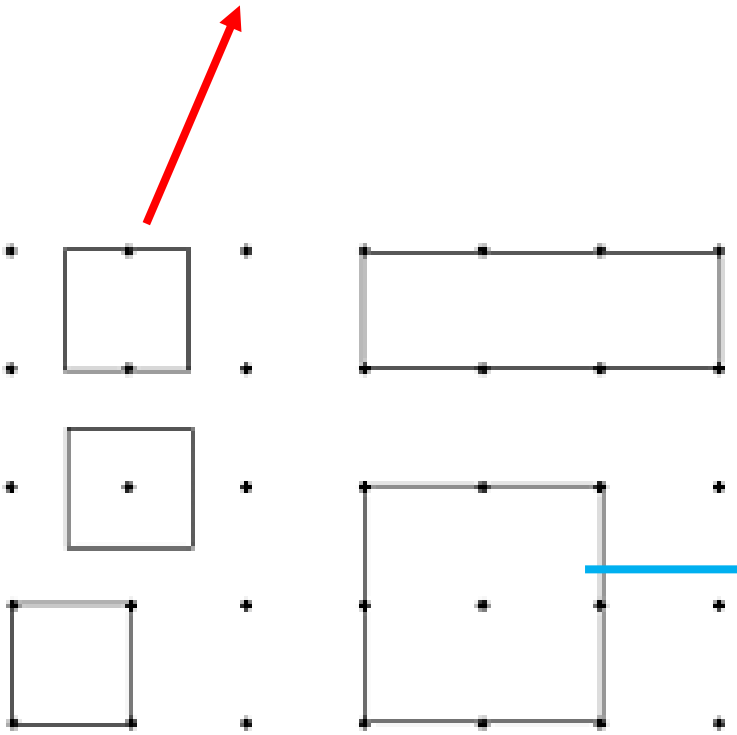
- **Atomic Packing factor or Packing Density**

  Ratio of the volume occupied by the atoms in an unit cell (v) to the volume of the unit cell (V)

Unit Cell : Primitive~ Non-Primitive

❑Primitive unit cells

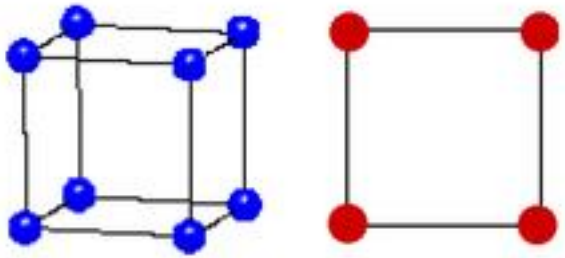
contain only **one lattice point**, which is made up from the lattice points at each of the corners.



❑Non-primitive unit cells

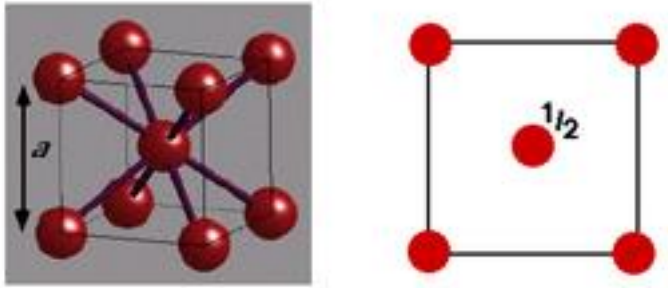
contain additional lattice points, either on a face of the **unit cell** or within the **unit cell**, and so have more than one lattice point per **unit cell**.

- Single lattice point (atom) per cell
- Smallest volume



Simple cubic(sc)
Conventional = Primitive cell
Each atom at the corner is shared by 8 cells

- More than one lattice point (atom) per cell
- Integral multiples of the primitive volume

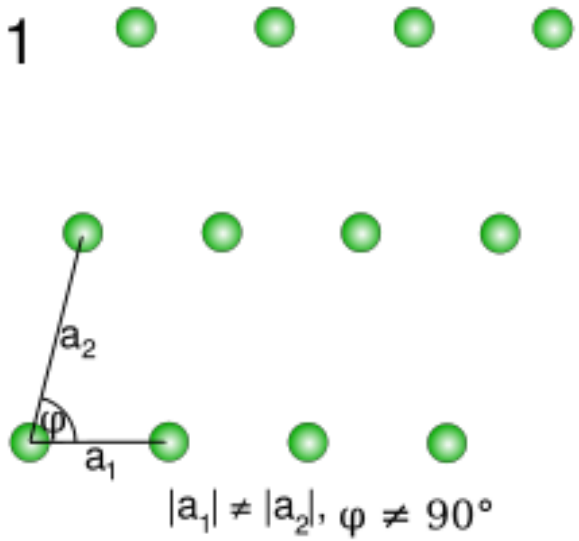


Body centered cubic(bcc)
Conventional ≠ Primitive cell

Bravais Lattice

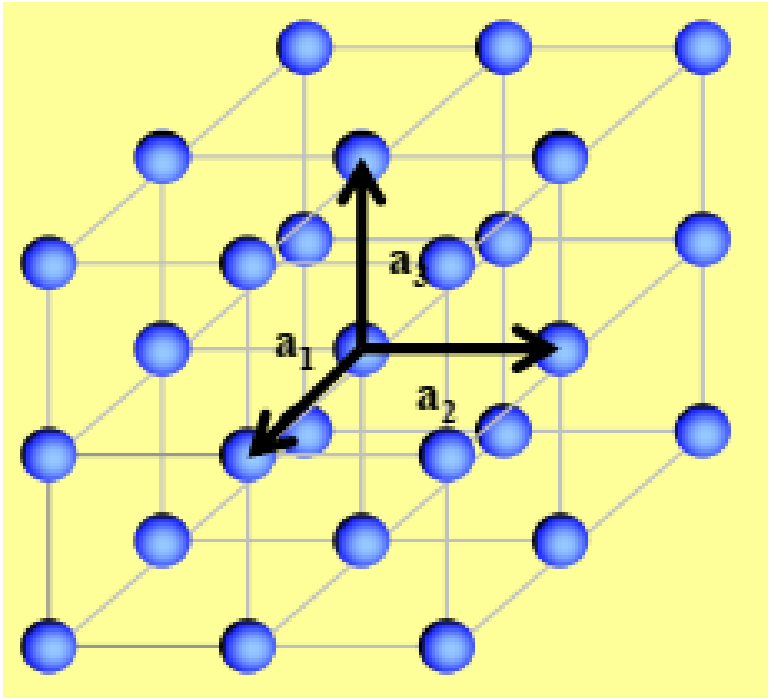
In crystallography, the Bravais lattice concept of an infinite array of discrete points is expanded using the concept of a **unit cell**

The Bravais lattice concept is used to formally define a *crystalline arrangement* and its frontiers.



$$R = n_1 a_1 + n_2 a_2$$

The vectors $\mathbf{a_1}$ and $\mathbf{a_2}$ are primitive vectors.



One of the most common three dimensional Cubic Bravais lattices, the Simple Cubic lattice.

$$R = n_1 a_1 + n_2 a_2 + n_3 a_3$$

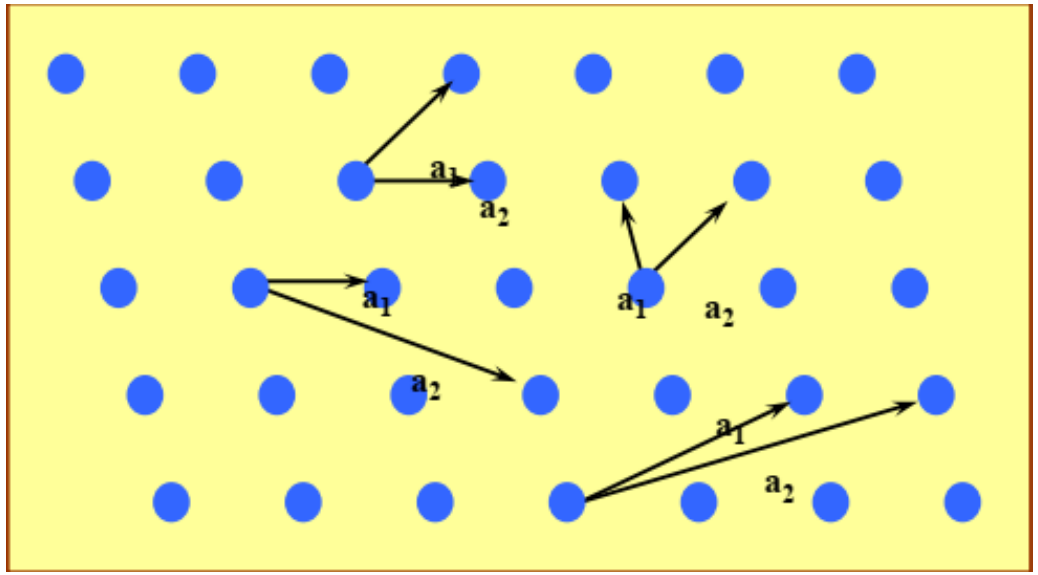
All $\mathbf{a_1}$, $\mathbf{a_2}$, $\mathbf{a_3}$, are of equal length and orthogonal.

Primitive Vectors of a Bravais Lattice

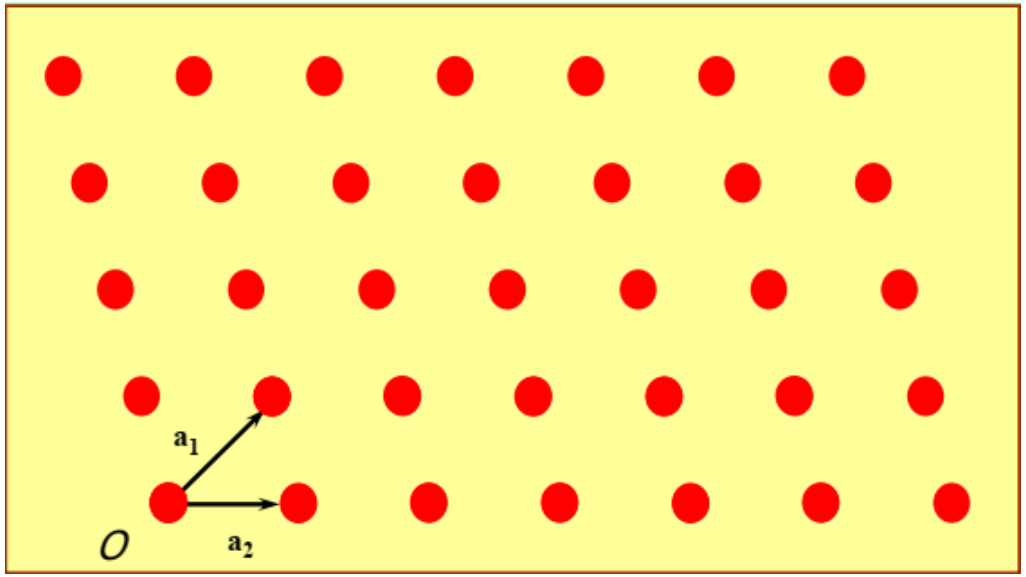
By definition all Bravais lattices must be described by a set of primitive vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ (in 3D).

- The choice of the set of vectors is not unique.
- Four choices of pairs of primitive vectors

in a 2D Bravais Lattice are shown below.



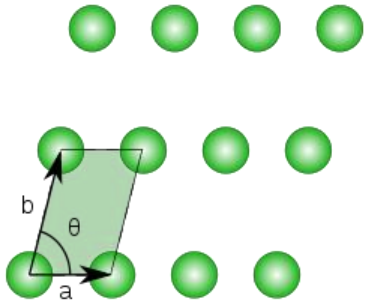
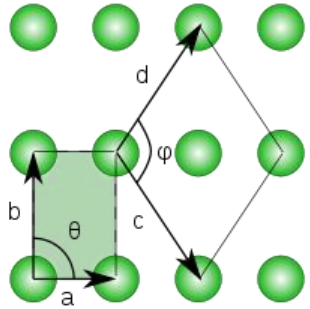
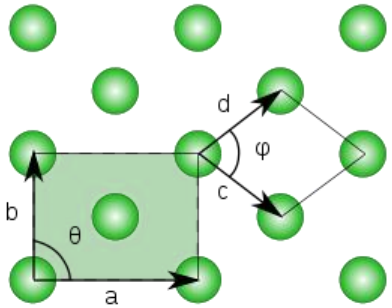
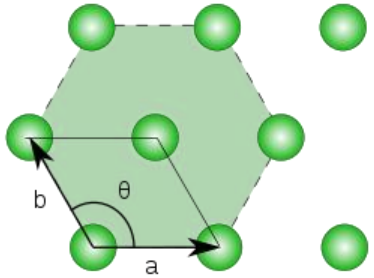
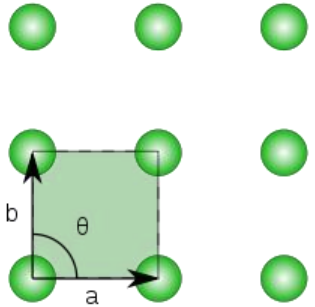
The different pairs of vectors correspond to different choices of primitive vectors in this 2D Bravais Lattice.



- Nominate one point of the lattice to be the origin and select a set of primitive vectors.
- Translating a point through combinations of these two vectors gives our original lattice.

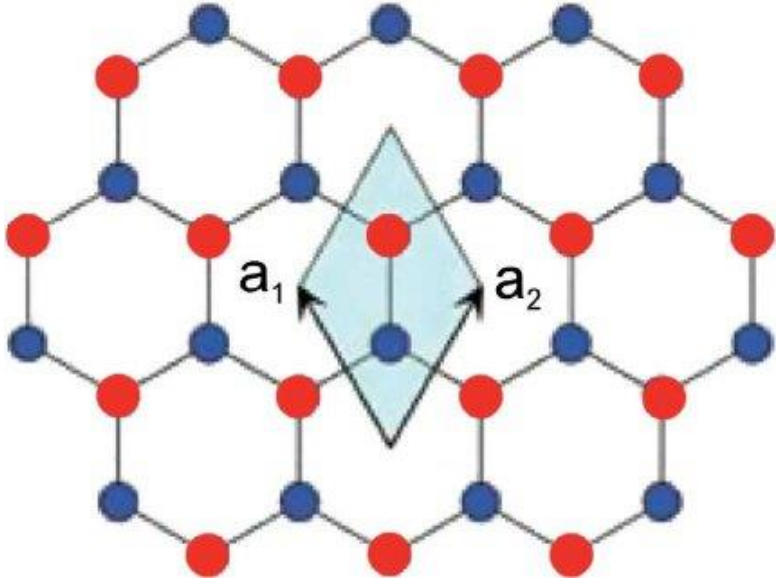
Bravais lattices in 2D

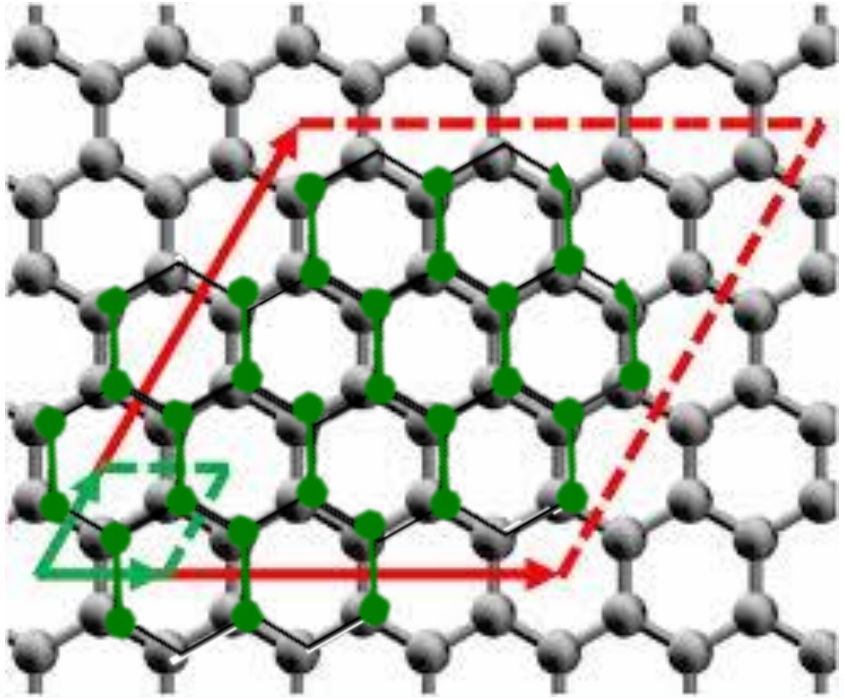
In two-dimensional (2D) space, there are 5 Bravais lattices, grouped into four crystal families.

Oblique lattice	Rectangular lattice	Hexagonal lattice	Square lattice
 1	 2  3 Centered rectangular lattice	 4	 5
$\lvert a\rvert \neq \lvert b\rvert$, $\theta \neq 90°$	$\lvert a\rvert \neq \lvert b\rvert$, $\theta = 90°$ $\lvert c\rvert = \lvert d\rvert$, $\varphi \neq 90°$	$\lvert a\rvert = \lvert b\rvert$, $\theta = 120°$	$\lvert a\rvert = \lvert b\rvert$, $\theta = 90°$
m	o	h	t

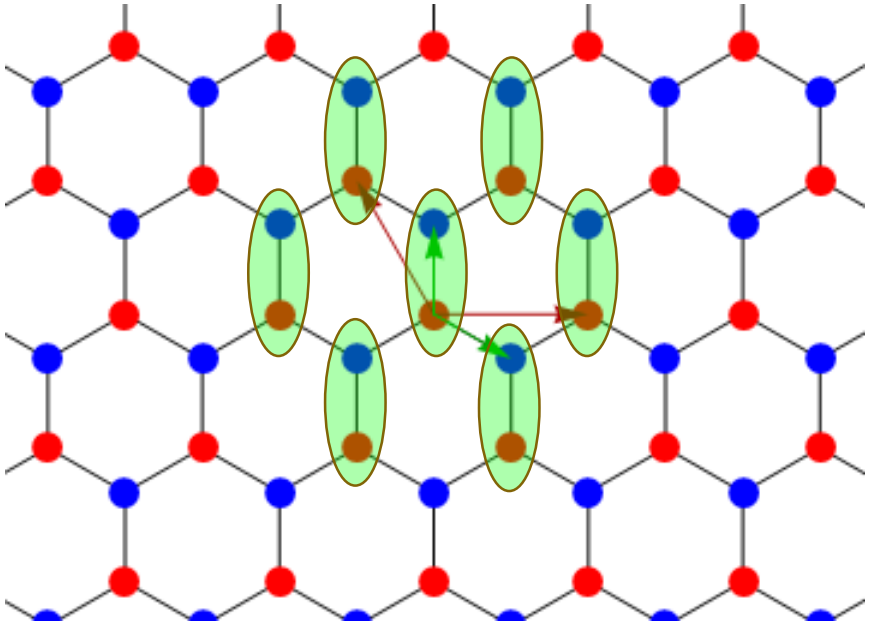
Crystal Structure : Periodic Array of Atoms in 2D

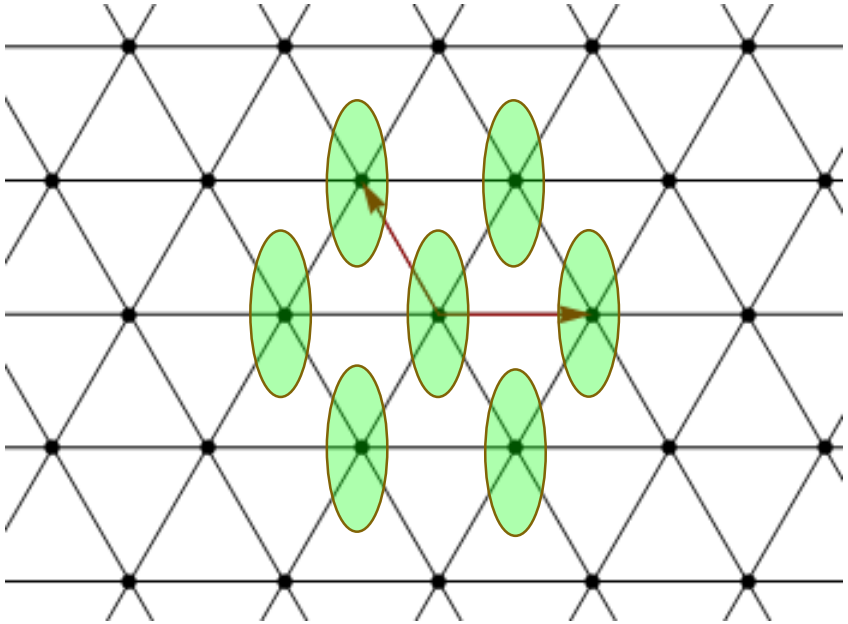
2D honeycomb net can be represented by translation of
two adjacent atoms that form a unit cell
for this 2D crystalline structure





Honeycomb lattice : Graphene





- A honeycomb lattice (left) and a hexagonal lattice (right). The honeycomb lattice is NOT a Bravais lattice. The Bravais lattice of a honeycomb lattice is a hexagonal lattice.
- The red (longer) vectors are lattice vectors. The green (shorter) vectors are NOT lattice vectors.
- **For a Bravais lattice**, all lattice sites are equivalent and any vectors connecting to lattice sites are lattice vectors. These conditions are NOT satisfied here, so this honeycomb lattice is NOT a Bravais lattice.
- To find the Bravais lattice for graphene, we need to use the unit cell which contains two carbon atoms (one blue atom and one red atom). If we do so, we found that the Bravais lattice for this honeycomb lattice (graphene) is a hexagonal lattice.

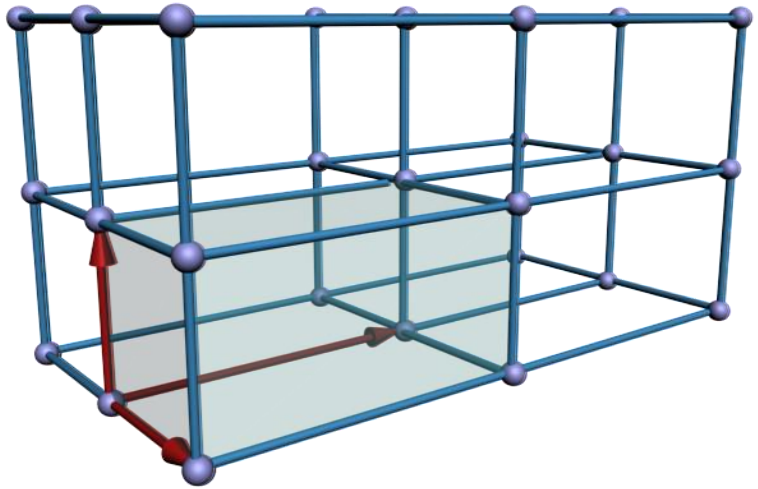
Primitive Cell for 3D Crystals

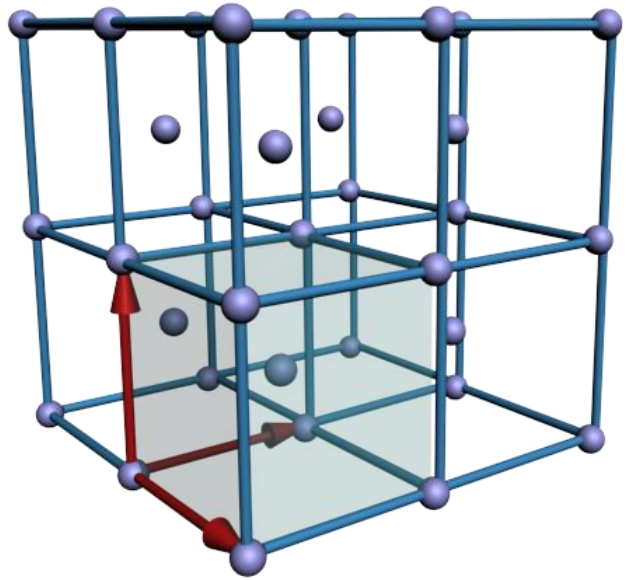
Standard model

- volume associated with one lattice point
- Parallelepiped with lattice points in the corner
- Each lattice point shared among 8 cells
- Number of lattice point/cell=8x1/8=1
- Vc= $|\mathbf{a}_1.(\mathbf{a}_2 x \mathbf{a}_3)|$

Crystallographic unit cell

- larger cell used to display the symmetries of the crystal
- Primitive





Not primitive

Bravais lattices in 3D

In 3D, there are 14 Bravais lattices. These are obtained by combining one of the 7 LATTICE SYSTEM with one of the centering types.

The centering types identify the locations of the lattice points in the unit cell as follows:

- **Primitive (P)**: lattice points on the cell corners only (~simple)
- Base-centered : lattice points on the cell corners with one additional point at the center of each face of one pair of parallel faces of the cell (sometimes called end-centered)
- Body-centered (I): lattice points on the cell corners, with one additional point at the center of the cell
- Face-centered (F): lattice points on the cell corners, with one additional point at the center of each of the faces of the cell