Aim of Solid State Physics

Solid state physics (SSP) explains the properties of solid materials as found on earth.
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.
CRYSTAL STRUCTURE

Crystal

- 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, polycrystalline, 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.
SOLID MATERIALS

CRYSTALLINE

POLYCRYSTALLINE

AMORPHOUS (Non-crystalline)

Single Crystal
Types of Solids

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

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

Polycrystalline 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 crystal 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.
Amorphous Solid

- 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 (Non-crystalline) Solid is composed of randomly orientated atoms, ions, or molecules that do not form defined patterns or lattice structures.

Amorphous silicon can be used in solar cells and thin film transistors.
- 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 \( T > 0 \, ^\circ\text{K} \). As a third example, actual crystal always contains some foreign atoms, i.e., impurities. These impurities spoils the perfect crystal structure.
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.
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.
- 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 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 \cdot + \text{Basis} \cdot
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

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**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.
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

-Honeycomb

-Red and blue sides are not equivalent. Same appearance can be obtained rotating blue side 180°.
A space lattice is a set of points such that a translation from any point in the lattice by a vector:

\[ R_n = n_1 \mathbf{a} + n_2 \mathbf{b} \]

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

Point \( D(n_1, n_2) = (0,2) \)

Point \( F(n_1, n_2) = (0,-1) \)
- The two vectors $\mathbf{a}$ and $\mathbf{b}$ 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 $\mathbf{a}$ and $\mathbf{b}'$ as a lattice vectors.
Lattice Vectors – 3D

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

\[
\mathbf{r}' = \mathbf{r} + u \mathbf{a} + v \mathbf{b} + w \mathbf{c} \quad (1)
\]
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.
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.
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
Q: Why can't the blue triangle be a unit cell?
Unit Cell in 3D
Unit Cell in 3D

crystal

collection of unit cells

atoms

molecule

unit cell
Three common Unit Cell in 3D

- Simple cubic
- Body-centered cubic
- Face-centered cubic
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 multiples of the area of primitive cell

Simple cubic (sc)

Conventional = Primitive cell

Body centered cubic (bcc)

Conventional ≠ Primitive cell
The Conventional Unit Cell

- 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

A primitive unit cell  a conventional unit cell

primitive vectors

\[ \vec{a}_1 = \frac{a}{2}(\hat{x} + \hat{y}) \]
\[ \vec{a}_2 = \frac{a}{2}(\hat{y} + \hat{z}) \]
\[ \vec{a}_3 = \frac{a}{2}(\hat{z} + \hat{x}) \]
Primitive and conventional cells of BCC

**Primitive Translation Vectors:**

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

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

\[ \vec{a}_3 = \frac{1}{2}(\hat{x} + \hat{y} + \hat{z}) \]
Simple cubic (sc):
primitive cell = conventional cell
Fractional coordinates of lattice points:
000, 100, 010, 001, 110, 101, 011, 111

Body centered cubic (bcc):
conventional ≠ primitive cell
Fractional coordinates of lattice points in conventional cell:
000, 100, 010, 001, 110, 101, 011, 111, \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \)
Body centered cubic (bcc): 
primitive (rombohedron) \( \neq \) conventional cell

Fractional coordinates:
000, 100, 101, 110, 110, 101, 011, 211, 200

Face centered cubic (fcc):
conventional \( \neq \) primitive cell

Fractional coordinates:
000, 100, 010, 001, 110, 101, 011, 111, \( \frac{1}{2} \) \( \frac{1}{2} \) 0, \( \frac{1}{2} \) 0 \( \frac{1}{2} \) \( \frac{1}{2} \), \( \frac{1}{2} \) 1 \( \frac{1}{2} \) \( \frac{1}{2} \), 1 \( \frac{1}{2} \) \( \frac{1}{2} \), \( \frac{1}{2} \) \( \frac{1}{2} \) 1
Hexagonal close packed cell (hcp):  
conventional \text{=} \text{primitive cell}  

Fractional coordinates:  
100, 010, 110, 101, 011, 111, 000, 001
The unit cell and, consequently, the entire lattice, is uniquely determined by the six lattice constants: $a$, $b$, $c$, $\alpha$, $\beta$ and $\gamma$. 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 $8 \times 1/8 = 1$ lattice point.
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 parallelepiped $a_1, a_2$ and $a_3$. The volume of a primitive unit cell can be found by

$$V = a_1.(a_2 \times a_3) \quad \text{(vector products)}$$

- **Cubic cell volume** $= a^3$
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.
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

(a)

(b)
- 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 \([\ldots]\) 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

$X = 1, \ Y = \frac{1}{2}, \ Z = 0$
$[1 \ \frac{1}{2} \ 0] \rightarrow [2 \ 1 \ 0]$

$X = \frac{1}{2}, \ Y = \frac{1}{2}, \ Z = 1$
$[\frac{1}{2} \ \frac{1}{2} \ 1] \rightarrow [1 \ 1 \ 2]$
Negative directions

- When we write the direction $[n_1n_2n_3]$ depend on the origin, negative directions can be written as $[-[n_1n_2n_3]]$.

- $R = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}$

Direction must be smallest integers.
Examples of crystal directions

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

\[ X = -1, Y = -1, Z = 0 \rightarrow [\bar{1}10] \]
Examples

We can move vector to the origin.

(a) $X = -1$, $Y = 1$, $Z = -1/6$

(b) $[\begin{array}{c} -1 \\ 1 \\ -1/6 \end{array}]$ $\rightarrow$ $[\begin{array}{c} 6 \\ 6 \\ 1 \end{array}]$
- 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 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

<table>
<thead>
<tr>
<th>Axis</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept points</td>
<td>1</td>
<td>∞</td>
<td>∞</td>
</tr>
<tr>
<td>Reciprocals</td>
<td>1/1</td>
<td>1/∞</td>
<td>1/∞</td>
</tr>
<tr>
<td>Smallest Ratio</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Miller Indices** (100)
### Example-2

#### Axis

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept points</td>
<td>1</td>
<td>1</td>
<td>∞</td>
</tr>
<tr>
<td>Reciprocals</td>
<td>1/1</td>
<td>1/1</td>
<td>1/∞</td>
</tr>
<tr>
<td>Smallest Ratio</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

#### Miller Indices

(110)
### Example-3

<table>
<thead>
<tr>
<th>Axis</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept points</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Reciprocals</td>
<td>1/1</td>
<td>1/1</td>
<td>1/1</td>
</tr>
<tr>
<td>Smallest Ratio</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

**Miller Indices** (111)
Example-4

<table>
<thead>
<tr>
<th>Axis</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept points</td>
<td>1/2</td>
<td>1</td>
<td>∞</td>
</tr>
<tr>
<td>Reciprocals</td>
<td>1/(1/2)</td>
<td>1/1</td>
<td>1/∞</td>
</tr>
<tr>
<td>Smallest Ratio</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Miller Indices (210)
Example-5

<table>
<thead>
<tr>
<th>Axis</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>1</td>
<td>∞</td>
<td>½</td>
</tr>
<tr>
<td>points</td>
<td>1/1</td>
<td>1/∞</td>
<td>1/½</td>
</tr>
<tr>
<td>Reciprocals</td>
<td>1/1</td>
<td>1/∞</td>
<td>1/(½)</td>
</tr>
<tr>
<td>Smallest Ratio</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

Miller Indices (102)
Example-6

<table>
<thead>
<tr>
<th>Axis</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept points</td>
<td>-1</td>
<td>∞</td>
<td>½</td>
</tr>
<tr>
<td>Reciprocals</td>
<td>1/-1</td>
<td>1/∞</td>
<td>1/(½)</td>
</tr>
<tr>
<td>Smallest Ratio</td>
<td>-1</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

Miller Indices (102)
Miller Indices

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

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) (100)
Miller indices and intercepts

$\infty a_1 : \infty a_2 : 1 a_3$

$1a_1 : \infty a_2 : 1 a_3$

$\infty a_1 : 1 a_2 : 1 a_3$

$1a_1 : 1 a_2 : 1 a_3$

$\infty a_1 : 1 a_2 : \infty a_3$

$1a_1 : \infty a_2 : \infty a_3$

$1a_1 : 1 a_2 : \infty a_3$
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.

\[
\{100\} \equiv (100), (010), (001), (0 \overline{1} 0), (00 \overline{1}), (\overline{1} 0 0)
\]
\[
\{111\} \equiv (111), (11 \overline{1}), (1 \overline{1} 1), (\overline{1} 1 1), (\overline{1} \overline{1} \overline{1}), (\overline{1} \overline{1} 1), (\overline{1} 1 \overline{1}), (1 \overline{1} \overline{1})
\]

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

1- Cubic Crystal System (SC, BCC, FCC)
2- Hexagonal Crystal System (S)
3- Triclinic Crystal System (S)
4- Monoclinic Crystal System (S, Base-C)
5- Orthorhombic Crystal System (S, Base-C, BC, FC)
6- Tetragonal Crystal System (S, BC)
7- Trigonal (Rhombohedral) Crystal System (S)
Crystal Structure

**CUBIC**

\[ a = b = c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

**TETRAGONAL**

\[ a = b \neq c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

**ORTHORHOMBIC**

\[ a \neq b \neq c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

**HEXAGONAL**

\[ a = b \neq c \]
\[ \alpha = \beta = 90^\circ \]
\[ \gamma = 120^\circ \]

**MONOCLINIC**

\[ a \neq b \neq c \]
\[ \alpha = \gamma = 90^\circ \]
\[ \beta \neq 120^\circ \]

**TRICLINIC**

\[ a \neq b \neq c \]
\[ \alpha \neq \beta \neq \gamma \neq 90^\circ \]

---

4 Types of Unit Cell
- **P** = Primitive
- **I** = Body-Centred
- **F** = Face-Centred
- **C** = Side-Centred

7 Crystal Classes → 14 Bravais Lattices
- **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 (APF) is defined as the volume of atoms within the unit cell divided by the volume of the unit cell.

\[ F.F = APF = \frac{\text{Volume of Atoms in Unit Cell}}{\text{Volume of Unit Cell}} \]
1-CUBIC CRYSTAL SYSTEM

نظام المكعب

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

$APF = \frac{4}{3} \pi (0.5a)^3$

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

$APF = \frac{1}{a^3}$

Volume atom

Volume unit cell

APF = 0.52 for simple cubic
- 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

$$APF_{BCC} = \frac{V_{atoms}}{V_{unit\text{cell}}} = 0.68$$
- There are atoms at the corners of the unit cell and at the centre 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

\[
APF_{\text{FCC}} = \frac{V_{\text{atoms}}}{V_{\text{unit cell}}} = 0.74
\]
### Unit cell contents

Counting the number of atoms **within** the unit cell

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Shared Between:</th>
<th>Each atom counts:</th>
</tr>
</thead>
<tbody>
<tr>
<td>corner</td>
<td>8 cells</td>
<td>1/8</td>
</tr>
<tr>
<td>face centre</td>
<td>2 cells</td>
<td>1/2</td>
</tr>
<tr>
<td>body centre</td>
<td>1 cell</td>
<td>1</td>
</tr>
<tr>
<td>edge centre</td>
<td>2 cells</td>
<td>1/2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>lattice type</th>
<th>cell contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1 [=8 \times 1/8]</td>
</tr>
<tr>
<td>I</td>
<td>2 [=(8 \times 1/8) + (1 \times 1)]</td>
</tr>
<tr>
<td>F</td>
<td>4 [=(8 \times 1/8) + (6 \times 1/2)]</td>
</tr>
<tr>
<td>C</td>
<td>2 [=(8 \times 1/8) + (2 \times 1/2)]</td>
</tr>
</tbody>
</table>
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 = $\frac{\pi}{3\sqrt{2}} = 74.05\%$
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
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) -
  \[ \alpha \neq \beta \neq \gamma \neq 90^\circ \]
  \[ a \neq b \neq c \]

- Monoclinic (Simple) -
  \[ \alpha = \gamma = 90^\circ, \beta \neq 90^\circ \]
  \[ a \neq b \neq c \]

- Monoclinic (Base Centered) -
  \[ \alpha = \gamma = 90^\circ, \beta \neq 90^\circ \]
  \[ a \neq b \neq c, \]
5 - ORTHORHOMBIC SYSTEM

Orthorhombic (Simple)
\[ \alpha = \beta = \gamma = 90^\circ \]
\[ a \neq b \neq c \]

Orthorhombic (Base-centred)
\[ \alpha = \beta = \gamma = 90^\circ \]
\[ a \neq b \neq c \]

Orthorhombic (BC)
\[ \alpha = \beta = \gamma = 90^\circ \]
\[ a \neq b \neq c \]

Orthorhombic (FC)
\[ \alpha = \beta = \gamma = 90^\circ \]
\[ a \neq b \neq c \]
6 – TETRAGONAL SYSTEM

Tetragonal (P)
\[ \alpha = \beta = \gamma = 90^\circ \]
\[ a = b \neq c \]

Tetragonal (BC)
\[ \alpha = \beta = \gamma = 90^\circ \]
\[ a = b \neq c \]
7 - Rhombohedral (R) or Trigonal (S)

Rhombohedral (R) or Trigonal (S)

\[ a = b = c, \quad \alpha = \beta = \gamma \neq 90^\circ \]
THE MOST IMPORTANT CRYSTAL STRUCTURES

- Sodium Chloride Structure $\text{Na}^+\text{Cl}^-$
- Cesium Chloride Structure $\text{Cs}^+\text{Cl}^-$
- Hexagonal Closed-Packed Structure
- Diamond Structure
- Zinc Blende
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.
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, \( \frac{a}{2} ( \vec{x} + \vec{y} + \vec{z} ) \)
- LiF, NaBr, KCl, LiI, etc
- The lattice constants are in the order of 4-7 angstroms.
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

\[ a/2(x + y + z) \]

CsBr,Csl crystallize in this structure. The lattice constants are in the order of 4 angstroms.
Cesium Chloride Cs\(^+\)Cl\(^-\)

8 cell
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 hexagonal, 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 Bزاوية=120, c=1.633a,
basis: (0,0,0) (2/3a,1/3a,1/2c)
Sequence ABABABAB...
- hexagonal close pack

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

<table>
<thead>
<tr>
<th>Operation</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inversion</td>
<td>Point</td>
</tr>
<tr>
<td>Reflection</td>
<td>Plane</td>
</tr>
<tr>
<td>Rotation</td>
<td>Axis</td>
</tr>
<tr>
<td>Rotoinversion</td>
<td>Axes</td>
</tr>
</tbody>
</table>
A center of symmetry: A point at the center of the molecule. 

\[(x, y, z) \rightarrow (-x, -y, -z)\]

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

- Triclinic has no reflection plane.
- Monoclinic has one plane midway between and parallel to the bases, and so forth.
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.
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 $2\pi/n$. 

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Axis of Rotation

<table>
<thead>
<tr>
<th>Fold (n)</th>
<th>Angles</th>
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<tbody>
<tr>
<td>1</td>
<td>360</td>
</tr>
<tr>
<td>2</td>
<td>180</td>
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<tr>
<td>3</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
</tr>
</tbody>
</table>
# Axis of Rotation

<table>
<thead>
<tr>
<th>1-fold</th>
<th>2-fold</th>
<th>3-fold</th>
<th>4-fold</th>
<th>6-fold</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
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<td>9</td>
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</tbody>
</table>

**Objects with symmetry:**
- Identity
- A
- Z
- ▼
- +
- ❀
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 \((\theta = \frac{2\pi}{2} = \pi)\) normal to the base.