GEOMETRY OF CRYSTALS

- Space Lattices
- Motifs
- Crystal Systems

Advanced Reading

**Elementary Crystallography**

M.J. Buerger


**The Structure of Materials**

Samuel M. Allen, Edwin L. Thomas

In this chapter we shall try to understand a **CRYSTAL**

We shall consider some *ideal* mathematical descriptions before taking up examples of *real* crystals (as we shall see these crystals contain atoms, ions or molecules)

The use of Miller indices for directions and planes in lattices and crystals

How to use X-Ray Diffraction for determination of crystal geometry.

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* 3.1 Overview, Geometry of Crystals
  3.2 Miller Indices
  3.3 X-ray Diffraction
In this sub-chapter we shall try to understand a CRYSTAL.

We shall consider some ideal mathematical descriptions before taking up examples of real crystals (as we shall see these crystals contain atoms, ions or molecules).

We will see that the language of crystallography is applicable to all kinds of crystals (those containing atomic entities or mathematical ones).

The real crystals we consider in this chapter are also ‘idealizations’ (i.e. The crystals found in practice have various kinds of defects in them and we shall take up topics related to defects in crystals in the chapter on crystal imperfections (Chapter-5)).
Why study crystal structures?

☐ When we look around much of what we see is non-crystalline (organic things like wood, paper, sand; concrete walls, etc. → some of the things may have some crystalline parts!).

☐ But, many of the common ‘inorganic’ materials are ‘usually*’ crystalline:
  ▪ **Metals:** Cu, Zn, Fe, Cu-Zn alloys
  ▪ **Semiconductors:** Si, Ge, GaAs
  ▪ **Ceramics:** Alumina (Al\(_2\)O\(_3\)), Zirconia (Zr\(_2\)O\(_3\)), SiC, SrTiO\(_3\)

☐ Also, the usual form of crystalline materials (say a Cu wire or a piece of alumina) is polycrystalline and special care has to be taken to produce single crystals

☐ Polymeric materials are *usually* not ‘fully’ crystalline

☐ The crystal structure directly influences the properties of the material
  (as we have seen in the Introduction chapter many additional factors come in)

Why study crystallography?

☐ Gives a terse (concise) representation of a large assemblage of species

☐ Gives the ‘first view’ towards understanding of the properties of the crystal

*Many of the materials which are usually crystalline can also be obtained in an amorphous form*
We shall consider two definitions of a crystal:

1) Crystal = Lattice + Motif
2) Crystal = Space Group + Asymmetric unit (+Wyckoff positions).

The second definition is the more advanced one (the language of crystallographers) and we shall only briefly consider it in this introductory text.

The second definition becomes important as the classification of crystals (7 crystal systems) is made based on symmetry and the first definition does not bring out this aspect.

Note: Since we have this precise definition of a crystal, loose definitions should be avoided (Though often we may live with definitions like: a 3D translationally periodic arrangement of atoms in space is called a crystal).

Initially we shall start with ideal mathematical crystals and then slowly we shall relax various conditions to get into practical crystals.

Note: ‘+’ above does not imply simple addition! More technically it can be thought of as a convolution operation.
Ideal Crystals → Real Crystals → Microstructures → Material → Component

Ideal Crystal

Consider only the Geometrical Entity or only the Physical Property

Crystal*

Put in Crystalline defects & Free Surface & Thermal Vibration

Crystal**

Consider only the Orientational or Positional Order

‘Real Crystal’

Put in Multiple Crystals (Phases) giving rise to interfacial defects

~Microconstituents

Put multiple ~microconstituents Add additional residual stress

Microstructure

Real materials are usually complex and we start with ideal descriptions

Material

Material or Hybrid

Component

* , ** Reduced definition of crystals
♀ That which is NOT associated with defects (crystalline or interfacial) → e.g. thermal residual stresses
Consider only the Geometrical Entity or only the Physical Property

Put in Crystalline defects & Free Surface & Thermal Vibration

Ideal Mathematical Crystal

Part of the infinite crystal

Vacancy shown as an example of a defect

*, ** Reduced definition of crystals
<table>
<thead>
<tr>
<th>Ideal Crystal</th>
<th>Ideal Mathematical Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Considers <em>both</em> Geometrical Entity AND Physical Property/)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Crystal*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Here we consider <em>either</em> geometrical entity OR physical property)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Crystal**</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Consider <em>either</em> the Orientational OR the Positional Order)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>‘Real Crystal’</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Presence of Crystalline defects &amp; Free Surface &amp; Thermal Vibration)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>~Microconstituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Put in Multiple Crystals <em>Phases</em> giving rise to interfacial defects)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Put in multiple ~microconstituents and add additional residual stress*)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Put in many microstructures)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Put in material/s and/or material treatment i.e. temperature/pressure)</td>
</tr>
</tbody>
</table>

*, ** Reduced definition of crystals
* That which is NOT associated with defects (*crystalline or interfacial*)

Some of these aspects will be considered in detail later.
Crystal = \textbf{Lattice} + \textbf{Motif}

\underline{Motif} or \underline{Basis}:
an entity (typically an atom or a group of atoms) associated with each lattice point

\underline{Lattice} ➤ the underlying periodicity of the crystal
\underline{Motif} ➤ Entity \textit{associated} with each lattice points

\underline{Lattice} ➤ how to repeat
\underline{Motif} ➤ what to repeat

\underline{Lattice} ➤ Translationally periodic arrangement of \underline{points}
\underline{Crystal} ➤ Translationally periodic arrangement of \underline{motifs}
Crystal = **Lattice** (*Where to repeat*)

+ **Motif** (*What to repeat*)

---

**Motifs are associated with lattice points**

→ they need NOT *sit* physically at the lattice point

---

Note: Later on we will also consider cases wherein these arrow marks are replaced with atomic entities.
Let us construct the crystal considered before starting with an infinite array of points spaced $a/2$ apart.

Put arrow marks pointing up and down alternately on the points:

What we get is a crystal of lattice parameter ‘$a$’ and not ‘$a/2$’! \(\rightarrow\text{as this lattice parameter is a measure of the repeat distance!}\)

Note: we could have alternately chosen the centres of bottom arrows as lattice points!
An array of points such that every point has identical surroundings

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

Translationally periodic arrangement of points in space is called a lattice

A lattice is also called a Space Lattice
Crystal =

**Space group** *(how to repeat)*

+ **Asymmetric unit** *(Motif’: what to repeat)*

+ Wyckoff positions

---

**Glide reflection operator**

.Symbol g may also be used.

Positions entities with respect to symmetry operators.

*Usually asymmetric units are regions of space which contain the entities (e.g. atoms)*
Symmetry is perhaps the most important principle of nature:

- though often you will have to dig deeper to find this statement

The analogous terms to symmetry are:

Symmetry ⇔ Conservation ⇔ Invariance

The kind of symmetry of relevance to crystallography is geometrical symmetry

The kind of symmetry we encountered in the definition of a lattice is translational symmetry (t)

To know more about symmetry and its role in the definition of crystal structures click here (Very Important!!)
Now let us *make* some crystals

*(to see more examples [click here]*)
Some of the concepts are best illustrated in lower dimensions → hence we shall construct some 1D and 2D crystals before jumping into 3D.

A strict 1D crystal = 1D lattice + 1D motif.

The only kind of 1D motif is a line segment.

An **unit cell** is a representative unit of the structure (*finite part of an infinite structure*)

> which when translationally repeated gives the whole structure.
Other ways of making the same crystal

- We had mentioned before that motifs need not ‘sit’ on the lattice point—they are merely associated with a lattice point
- Here is an example:

![Diagram of a 1D lattice with motifs](image)

**Note:**
For illustration purposes we will often relax this strict requirement of a 1D motif.
- We will put 2D motifs on 1D lattice to get many of the useful concepts across.
  (Actually we have already done this in the example considered before → with an up arrow (↑) and a down arrow (↓))

*looks like 3D due to the shading!

It has been shown in literature that 1D crystals cannot be stable!!
Making a 2D Crystal

- Some aspects we have already seen in 1D → but 2D many more concepts can be clarified in 2D
- 2D crystal = 2D lattice + 2D motif
- As before we can relax this requirement and put 1D or 3D motifs!

(to know more about motifs click here)
Lattice

Motif

$\vec{a}$

$\vec{b}$
As before there are many ways of associating the motif with a lattice point (one of these is shown).

**Note:**
Each motif is identically oriented (*orientationally ordered*) and is associated exactly at the same position with each lattice point (*positionally ordered*).

We will have more to say on this in Chapter 4.
Now let us make some more 2-D crystals
Making a 3D Crystal

- 3D crystal = 3D lattice + 3D motif
- There are 14 distinct lattices possible in 3D called the Bravais lattices
Lattices can be constructed using translation alone.
The definition (& classification) of Crystals is based on symmetry and NOT on the geometry of the unit cell (as often one might feel after reading some books!)
Crystals based on a particular lattice can have symmetry:
- equal to that of the lattice or
- lower than that of the lattice
Based on symmetry crystals are classified into seven types/categories/systems known as the SEVEN CRYSTAL SYSTEMS.
We can put all possible crystals into 7 boxes based on symmetry.

Alternate view
Advanced concept: readers can return to this point later!

Symmetry operators acting at a point can combine in 32 distinct ways to give the 32 point groups.
Lattices have 7 distinct point group symmetries which correspond to the SEVEN CRYSTAL SYSTEMS.
If the definition of Crystals is based on symmetry and the existence of 7 crystal systems is also based on symmetry; then how come we have statements like: $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$ is a cubic crystal?

- This is an important point and requires some clarification.
- Though the definition of crystals (e.g. cubic crystals) are based on symmetry and NOT on the geometry of the unit cell it is true that if we *already have* cubic crystal it is most *preferred/logical* to use parameters like $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$.
- The next slide explains as to why a set of coordinate axis is more preferred for certain geometrical entities using the example of a circle.
- Also see hyperlink below.

Relation between geometry and symmetry in atomic crystals
The centre of symmetry of the object does not coincide with the origin.

The type of coordinate system chosen is not according to the symmetry of the object.

Our choice of coordinate axis does not alter the symmetry of the object (or the lattice)!
What are the symmetries of the 7 crystal systems?

<table>
<thead>
<tr>
<th>Characteristic symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cubic</strong></td>
</tr>
<tr>
<td>Four 3-fold rotation axes (two will generate the other two)</td>
</tr>
<tr>
<td><strong>Hexagonal</strong></td>
</tr>
<tr>
<td>One 6-fold rotation axis (or roto-inversion axis)</td>
</tr>
<tr>
<td><strong>Tetragonal</strong></td>
</tr>
<tr>
<td>(Only) One 4-fold rotation axis (or roto-inversion axis)</td>
</tr>
<tr>
<td><strong>Trigonal</strong></td>
</tr>
<tr>
<td>(Only) One 3-fold rotation axis (or roto-inversion axis)</td>
</tr>
<tr>
<td><strong>Orthorhombic</strong></td>
</tr>
<tr>
<td>(Only) Three $\perp$ 2-fold rotation axes (or roto-inversion axis)</td>
</tr>
<tr>
<td><strong>Monoclinic</strong></td>
</tr>
<tr>
<td>(Only) One 2-fold rotation axis (or roto-inversion axis)</td>
</tr>
<tr>
<td><strong>Triclinic</strong></td>
</tr>
<tr>
<td>None (only translational symmetry)</td>
</tr>
</tbody>
</table>

We have stated that basis of definition of crystals is ‘symmetry’ and hence the classification of crystals is also based on symmetry.

The essence of the required symmetry is listed in the table.

➤ more symmetries may be part of the point group in an actual crystal.

**Note:** translational symmetry is always present in crystals (i.e. even in triclinic crystal).
14 Bravais Lattices divided into 7 Crystal Systems

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Shape of UC</th>
<th>Bravais Lattices</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>1</td>
<td>Cubic</td>
<td>Cube</td>
</tr>
<tr>
<td>2</td>
<td>Tetragonal</td>
<td>Square Prism (general height)</td>
</tr>
<tr>
<td>3</td>
<td>Orthorhombic</td>
<td>Rectangular Prism (general height)</td>
</tr>
<tr>
<td>4</td>
<td>Hexagonal</td>
<td>120° Rhombic Prism</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal</td>
<td>Parallelepiped (Equilateral, Equiangular)</td>
</tr>
<tr>
<td>6</td>
<td>Monoclinic</td>
<td>Parallelogramic Prism</td>
</tr>
<tr>
<td>7</td>
<td>Triclinic</td>
<td>Parallelepiped (general)</td>
</tr>
</tbody>
</table>

Why are some of the entries missing?

- Why is there no C-centred cubic lattice?
- Why is the F-centred tetragonal lattice missing?
- ....?

Refer to slides on Lattice for more on these

<table>
<thead>
<tr>
<th>P</th>
<th>Primitive</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Body Centred</td>
</tr>
<tr>
<td>F</td>
<td>Face Centred</td>
</tr>
<tr>
<td>C</td>
<td>A/B/C- Centred</td>
</tr>
</tbody>
</table>

A Symmetry based concept

‘Translation’ based concept
THE 7 CRYSTAL SYSTEMS
1. **Name of crystal system**

   lattice parameters and relationship amongst them
   *(preferred Unit Cell)*

   - Possible Bravais lattices

Point groups belonging to the crystal system

Diagram of preferred UC
1. Cubic Crystals

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

- Simple Cubic (P) - SC
- Body Centred Cubic (I) – BCC
- Face Centred Cubic (F) - FCC

Point groups \( \Rightarrow 23, \ 43m, \ m\overline{3}, \ 432, \ \frac{4}{m} \ \frac{3}{m} \ \frac{2}{m} \)

- Elements with Cubic structure \( \rightarrow \) SC: F, O, Po
  BCC: Cr, Fe, Nb, K, W, V
  FCC: Al, Ar, Pb, Ni, Pd, Pt, Ge

SC, BCC, FCC are lattices while HCP & DC are crystals!

Note the 3s are in the second position
Examples of elements with Cubic Crystal Structure

- Po (n = 1, SC)
- Fe (n = 2, BCC)
- Cu (n = 4, FCC/CCP)
- C (diamond, n = 8, DC)
Examples of few crystal shapes (*cubic crystal system*)

- **Cube**
- **Tetrakaidecahedron** (*Truncated Octahedron*)
- **Octahedron**
- **Tetrahedron**
The shape of the crystal (*Eumorphic* - well formed) will ‘reflect’ the point group symmetry of the crystal
Note that cubic crystals can have the shape of a cube, an octahedron, a truncated octahedron etc.
(some of these polyhedra have the same rotational symmetry axes; noting that cube and octahedron are regular solids (Platonic) while truncated octahedron with two kinds of faces is not a regular solid)

The external shape is a ‘reflection’ of the symmetry at the atomic level.

Point groups have been included for completeness and can be ignored by beginners.

Cubic crystals can be based on Simple Cubic (SC), Body Centred Cubic (BCC) and Face Centred Cubic Lattices (FCC)
➢ by putting motifs on these lattices.

After the crystal is constructed based on the SC, BCC or FCC lattice, it should have four 3-fold symmetry axes (along the body diagonals)
➢ which crystals built out of atomic entities will usually have
➢ if the crystal does not have this feature it will not be a cubic crystal (even though it is based on a cubic lattice).
2. Tetragonal Crystals

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

- Simple Tetragonal
- Body Centred Tetragonal - BCT

Point groups \( \Rightarrow 4, \quad 4, \quad \frac{4}{m}, \quad 422, \quad 4mm, \quad \frac{4}{2}, \quad \frac{4}{2}, \quad \frac{2}{2}, \quad \frac{2}{m} m m m \)

Elements with Tetragonal structure \( \rightarrow \) In, Sn

*Note the 4 in the first place*
Example of an element with Body Centred Tetragonal Crystal Structure

**Lattice parameter(s)**
\[ a = 3.25 \, \text{Å}, \, c = 4.95 \, \text{Å} \]

**Space Group**
\[ \text{I}4/\text{mmm} \, (139) \]

**Strukturbericht notation**
\[ A6 \]

**Pearson symbol**
\[ t\text{I}2 \]

**Other examples with this structure**
\[ \text{Pa} \]

---

<table>
<thead>
<tr>
<th>In</th>
<th>Wyckoff position</th>
<th>Site Symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>2a</td>
<td>4/mmm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

*Note: All atoms are identical (coloured differently for easy visualization)*
3. Orthorhombic Crystals

- $a \neq b \neq c$
- $\alpha = \beta = \gamma = 90^\circ$

- Simple Orthorhombic
- Body Centred Orthorhombic
- Face Centred Orthorhombic
- End Centred Orthorhombic

Point groups \( \Rightarrow \) 222, 2mm, \( \frac{2}{m} \frac{2}{m} \frac{2}{m} \)

- Elements with Orthorhombic structure \( \rightarrow \) Br, Cl, Ga, I, S, U
Example of an element with Orthorhombic Crystal Structure

Ga

Lattice parameter(s)
\[
a = 2.9 \text{ Å}, \quad b = 8.13, \quad c = 3.17 \text{ Å}
\]

Space Group
Cmcm (63)

Strukturbericht notation

<table>
<thead>
<tr>
<th>Site</th>
<th>Symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>4c</td>
<td>m2m</td>
<td>0.133</td>
<td>0.25</td>
<td>1</td>
</tr>
</tbody>
</table>

Note: All atoms are identical (coloured differently for easy visualization)
4. **Hexagonal Crystals**

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

- **Simple Hexagonal**

  - Point groups $\Rightarrow 6, \bar{6}, \frac{6}{m}, 622, 6mm, \bar{6}m2, \frac{6}{m} \frac{2}{m} \frac{2}{m}$

- **Elements with Hexagonal structure $\rightarrow$ Be, Cd, Co, Ti, Zn**
Example of an element with Hexagonal Crystal Structure

Mg

More about this in the chapter on Structure_of_Solids_Metallic

Note: All atoms are identical (coloured differently for easy visualization)
5. Trigonal/Rhombohedral Crystals

- $a = b = c$
- $\alpha = \beta = \gamma \neq 90^\circ$

- Rhombohedral (simple)

Elements with Trigonal structure $\rightarrow$ As, B, Bi, Hg, Sb, Sm

Point groups $\Rightarrow 3, \overline{3}, 32, 3m, \overline{3} \frac{2}{m}$

Note the 3s are in the first position

Video: Cubic to Trigonal unit cell
Example of an element with Simple Trigonal Crystal Structure

\[ \alpha\text{-Hg} \]

<table>
<thead>
<tr>
<th>~ Hg</th>
</tr>
</thead>
</table>

[111] view

**\( \alpha\text{-Hg} \)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameter(s)</td>
<td>( a = 3.005 \text{ Å} )</td>
</tr>
<tr>
<td>Space Group</td>
<td>R-3m (166)</td>
</tr>
<tr>
<td>Strukturbericht notation</td>
<td>A10</td>
</tr>
<tr>
<td>Pearson symbol</td>
<td>hR1</td>
</tr>
<tr>
<td>Other examples with this structure</td>
<td>( \beta\text{-Po} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wyckoff position</th>
<th>Site Symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>1a</td>
<td>-3m</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
6. Monoclinic Crystals

- Simple Monoclinic
- End Centred (base centered) Monoclinic (A/C)

Point groups $\Rightarrow 2, \bar{2}, \frac{2}{m}$

- Elements with Monoclinic structure $\rightarrow$ P, Pu, Po
7. Triclinic Crystals

- Simple Triclinic

$\alpha \neq \gamma \neq \beta$

Point groups $\Rightarrow 1, \bar{1}$
Note that cubic crystals can have the shape of a cube, an octahedron, a truncated octahedron etc. (*all these polyhedra have the same symmetry*; noting that cube and octahedron are regular solids ([Platonic](#)) while truncated octahedron with two kinds of faces is not a regular solid).

The external shape is a ‘reflection’ of the symmetry at the atomic level.

Point groups have been included for completeness and can be ignored by beginners.

Cubic crystals can be based on Simple Cubic (SC), Body Centred Cubic (BCC) and Face Centred Cubic Lattices (FCC)

> by putting motifs on these lattices.

After the crystal is constructed based on the SC, BCC or FCC lattice, it should have four 3-fold symmetry axes (along the body diagonals)

> which crystals built out of atomic entities will usually have

> if the crystal does not have this feature it will not be a cubic crystal (even though it is based on a cubic lattice) — [more on this here](#).
Now let us consider some simple crystals
- If these spheres were ‘spherical atoms’ then the atoms would be touching each other
- The kind of model shown is known as the ‘Ball and Stick Model’
A note on kind of models used for representation of Crystal Structures

Wire Frame model

Atoms are reduced to points and the focus is on the cell edges

Ball & Stick Model

Both atoms & cell edges are in view (but atoms do not touch each other)

Space Filling Model

Atoms touch each other.
Unit cell edges may not be visible

Void Models

Where the void (actually the polyhedron formed by the vertices of the void) is in full view and everything else is hidden away

Note: though these are called space filling models in reality they do not fill space [as obvious from the space between the atoms (-the voids)]
Body Centred Cubic (BCC) Lattice

+ Sphere Motif

Body Centred Cubic Crystal

Unit cell of the BCC lattice

\[ \text{Atom at } (0, 0, 0) \]
\[ \text{Atom at } (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \]

Space filling model

Central atom is coloured differently for better visibility

Note: BCC is a lattice and not a crystal

So when one usually talks about a BCC crystal what is meant is a BCC lattice decorated with a mono-atomic motif

Video: BCC crystal
Face Centred Cubic (FCC) Lattice + Sphere Motif = Cubic Close Packed Crystal

(Sometimes casually called the FCC crystal)

Note: FCC is a lattice and not a crystal
Face Centred Cubic (FCC) Lattice + Two Ion Motif

Note: This is not a close packed crystal

Has a packing fraction of ~0.67 (using rigid sphere model)

Solved example: packing fraction of NaCl

Video: NaCl crystal

Note that the two ion motif leads to crystal which is not close packed – unlike the mono-atomic (sphere) packing case
Face Centred Cubic (FCC) Lattice + Two Carbon atom Motif

(0,0,0) & (¼, ¼, ¼)

= Diamond Cubic Crystal

Tetrahedral bonding of C (sp³ hybridized)

It requires a little thinking to convince yourself that the two atom motif actually sits at all lattice points!

Note: This is not a close packed crystal

There are no close packed directions in this crystal either!

Video: Diamond crystal
For a well grown crystal (eumorphic crystal) the external shape ‘reflects’ the point group symmetry of the crystal → the confluence of the mathematical concept of point groups and practical crystals occurs here!

The unit cell shapes indicated are the conventional/preferred ones and alternate unit cells may be chosen based on need.

It is to be noted that some crystals can be based on all possible lattices (Orthorhombic crystals can be based on P, I, F, C lattices); while others have a limited set (only P triclinic lattice) → more about this is considered in here
Next (two slides) we shall try to order the 7 crystal systems based on:

- Symmetry and
- the expenditure in terms of lattice parameters (terseness)

Then we shall put the 32 point groups into the 7 boxes (7 crystal systems)

Though this task is a little advanced for this elementary treatment
- it brings out the concept that a given crystal type like cubic crystal does not involve just one symmetry (point group)
- cubic crystals can have lower symmetry than the lattices they are built on (cubic lattices have \( \frac{4}{m} \frac{3}{m} \frac{2}{m} \) symmetry
- we can have cubic crystals without a (pure) 4-fold axis! (e.g. Diamond Cubic crystal does not have a 4-fold it has a \( \frac{4}{4} \) axis)

The concept of terseness is explained in a subsequent slide
Progressive lowering of symmetry amongst the 7 crystal systems

Ordering the 7 Crystal Systems: Symmetry

Arrow marks lead from supergroups to subgroups

Superscript to the crystal system is the order of the lattice point group
As we have noted before, when it comes to crystals symmetry is of paramount importance.

However, we have also seen that a given crystal is ‘best’ described by a certain choice of axes (lattice parameters).

The next slides describes how the lattice parameters can be used to order the seven crystal systems.

To do this a parameter called **terseness** \((t)\) is defined as:

\[
t = (p' - c)
\]

Where, \(p' = (p - e)\)

\(e\) → number of ‘\(=\)’ amongst the lattice parameters \((e.g.\ in\ cubic\ crystals:\ a = b = c; \ \alpha = \beta = \gamma \Rightarrow e = 4)\)

\(c\) → number of constraints (numerical) on lattice parameters \((e.g.\ in\ cubic\ crystals:\ \alpha, \ \beta, \ \gamma = 90^\circ \Rightarrow c = 1)\)

Terseness \((t)\) is a measure of ‘how much do we spend’ on lattice parameters!

The more we spend (larger ‘\(t\)’ number) → the lower down it is in the order.

The less we spend (small ‘\(t\)’ number) → the ‘terser’ we are → higher up in the list.

---

*E.g. for Hexagonal:* there are 6 parameters \((p)\) and 2 ‘\(=\)’ amongst them \((e)\)

\[\Rightarrow p' = (p - e) = (6 - 2) = 4\]

\[c\] the number of numerical constraints on values is 2 \((\alpha, \ \beta = 90^\circ; \ \gamma = 120^\circ)\)

\[t = (p' - c) = (4 - 2) = 2\]
## Calculations

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>p (in 3D)</th>
<th>e</th>
<th>p' = p - e</th>
<th>c</th>
<th>(e + c)</th>
<th>t = p - (e + c) or t = p' - c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>6</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>6</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>6</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Trigonal</td>
<td>6</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Orthorhombic(^1)</td>
<td>6</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Orthorhombic(^2)</td>
<td>6</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>6</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Triclinic</td>
<td>6</td>
<td>0</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>6</td>
</tr>
</tbody>
</table>

\( (e + c) \rightarrow \text{is a measure of ‘how much help’ is available via constraints} \)
Progressive relaxation of the constraints on the lattice parameters amongst the 7 crystal systems

Cubic \((p' = 2, c = 1, t = 1)\)
- \(a = b = c\)
- \(\alpha = \beta = \gamma = 90^\circ\)

Tetragonal \((p' = 3, c = 1, t = 2)\)
- \(a = b \neq c\)
- \(\alpha = \beta = \gamma = 90^\circ\)

Hexagonal \((p' = 4, c = 2, t = 2)\)
- \(a = b \neq c\)
- \(\alpha = \beta = 90^\circ, \gamma = 120^\circ\)

Trigonal \((p' = 2, c = 0, t = 2)\)
- \(a = b = c\)
- \(\alpha = \beta = \gamma \neq 90^\circ\)

Orthorhombic\(^1\) \((p' = 4, c = 1, t = 3)\)
- \(a \neq b \neq c\)
- \(\alpha = \beta = \gamma = 90^\circ\)

Orthorhombic\(^2\) \((p' = 4, c = 1, t = 3)\)
- \(a = b \neq c\)
- \(\alpha = \beta = 90^\circ, \gamma \neq 90^\circ\)

Orthorhombic\(^1\) and Orthorhombic\(^2\) refer to the two types of cells

- \(p'\) = number of independent parameters = \(p - e\) (discounting the number of \(=\))
- \(c\) = number of constraints (positive \(\Rightarrow\) “\(=\) some number“)
- \(t\) = terseness = \((p' - c)\) (is a measure of the ‘expenditure’ on the parameters)

E.g. for Cubic: there are 6 parameters \((p)\) and 4 “\(=\)“ amongst them \((e)\)
\(\Rightarrow p' = (p - e) = (6 - 4) = 2\)
\(c\) the number of numerical constraints on values is 1 (= 90°)
\(t = (p' - c) = (2 - 1) = 1\)

Click here to know more about the two Orthorhombic settings
### Minimum symmetry requirement for the 7 crystal systems

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Characteric symmetry</th>
<th>Point groups</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>Four 3-fold rotation axes</td>
<td>23, 43m, m3, 432, 4 ( \frac{3}{m} \frac{2}{m} )</td>
<td>3 or ( \bar{3} ) in the second place. Two 3-fold axes will generate the other two 3-fold axes.</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>One 6-fold rotation axis (or roto-inversion axis)</td>
<td>6, 6, ( \frac{6}{m} ), 622, 6mm, ( \bar{6} )m2, ( \frac{6}{m} \frac{2}{m} \frac{2}{m} )</td>
<td>6 in the first place</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>(Only) One 4-fold rotation axis (or roto-inversion axis)</td>
<td>4, 4, ( \frac{4}{m} ), 422, 4mm, ( \bar{4} )m2, ( \frac{4}{m} \frac{2}{m} \frac{2}{m} )</td>
<td>4 in first place but no 3 in second place</td>
</tr>
<tr>
<td>Trigonal</td>
<td>(Only) One 3-fold rotation axis (or roto-inversion axis)</td>
<td>3, 3, 32, 3m, ( \frac{3}{m} \frac{2}{m} )</td>
<td>3 or ( \bar{3} ) in the first place</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>(Only) Three ( \perp ) 2-fold rotation axes (or roto-inversion axis)</td>
<td>222, 2mm, ( \frac{2}{m} \frac{2}{m} \frac{2}{m} )</td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>(Only) One 2-fold rotation axis (or roto-inversion axis)</td>
<td>2, ( \bar{2} ), ( \frac{2}{m} )</td>
<td></td>
</tr>
<tr>
<td>Triclinic</td>
<td>None</td>
<td>1, ( \bar{1} )</td>
<td>( \bar{1} ) could be present</td>
</tr>
</tbody>
</table>
Ideal versus Real crystals

- Ideal crystals may have perfect *positional* and *orientational* order with respect to *geometrical entities* and *physical properties*.

- In (defining) real crystals some of these strict requirements may be relaxed:
  - the order considered may be only with respect to the geometrical entity
  - the positional order may be in the average sense
  - the orientational order may be in the average sense

- In addition real crystals:
  - are finite
  - may contain other defects ([Chapter 5](#))
Revision of previous slide:

Later on we shall discuss that motifs can be:

In practice some of the strict conditions imposed might be relaxed and we might call something a crystal even if:

- Orientational order is missing
- There is only average orientational or positional order
- Only the geometrical entity has been considered in the definition of the crystal and not the physical property
The term “morphous” comes from: Late Latin -morphus –morphous or from Greek –morphos which refers to form or shape.

- **Allotropy** → existence of an element in more than one crystal structure.
  - E.g. Fe in CCP (high temperature, γ) and BCC (low temperature, α) forms.

- **Polymorphism** → existence of a crystalline compound in more than one crystal structure.
  - E.g. 3C-SiC (cubic) and 2H-SiC (Wurtzite, hexagonal).

- **Isomorphism** → existence of different materials in same crystal structure.
  - E.g. Ni and Cu in CCP (FCC).

- **Amorphous** → having no crystal structure (~glass).
  - E.g. Window pane silicate glass.
Crystal = Lattice + Motif

- There are 14 Bravais lattices in 3D (which are based on translation)
- Motif is any entity (or entities) which is positioned identically with respect to every lattice point
- There are 32 different ways in which symmetries (rotation, roto-inversion, mirror, inversion) can combine at a point called the 32 point groups
- These Bravais lattices have 7 different symmetries which correspond to the 7 crystal systems
- Conventionally, 7 different unit cells are chosen for these 7 crystal systems
- Real crystals are ‘defected’ in many ways so that some of the symmetries present in an ideal crystal are ‘disturbed’ (either locally or globally).
- The definition of crystals are based on symmetry and not on the geometry of the unit cell.
- Our choice of unit cell cannot alter the crystal system a crystal belongs to.
- Crystals based on a particular lattice can have symmetry equal to or lower than that of the lattice.
- When all symmetry (including translation) is lost the construct is called amorphous.
A cubic crystal is one having **Four** 3-fold axes of rotational symmetry (or maybe roto-inversion axis: \( \overline{3} \)).

- It may or may not have 4-fold axes of symmetry!
- If you *have* a cubic crystal, then you *may* (*i.e. may not also!* ) chose axes like: 
  \[
  a = b = c; \quad \alpha = \beta = \gamma = 90^\circ \quad \text{(but then you are allowed to make other choices!)}
  \]
- A cubic crystal should be defined based on symmetry and not the geometry of the unit cell.
What is a crystal?
- Crystal = Lattice + Motif
- Crystal = Asymmetric Unit + Space Group (+ Wyckoff Positions)
- An array of entities in space, having at least translational symmetry

What constitutes a motif?
- A geometrical entity or a physical property or a combination of both can serve a motif

How is the classification of crystals made into the 7 crystal system?
- The classification is purely based on symmetry
- E.g. if a crystal has only one 4-fold axis then it would be classified as a tetragonal crystal
- This classification is not based on geometry of the unit cell (*as commonly perceived*)
- Ofcourse if one has a cubic crystal, then it will be referred to the cubic axis system

What are the 14 Bravais lattices?
- There are only 14 different ways in which points can be arranged in 3D space such that each point has identical surrounding

What is the relation between the 7 crystal systems and the 14 Bravais lattices?
- Based on symmetry the 14 Bravais lattices can be put into 7 boxes → the 7 crystal systems
- E.g. all lattices with two/four 3-fold axes are put into the box labeled ‘cubic’

What is the relation between the symmetry of a crystal and the symmetry with respect to its properties?
- The properties of a crystal can have a symmetry equal to that of the crystal or a symmetry higher than that of the crystal*
- E.g. cubic crystals (say with $4/m \bar{3} 2/m$ symmetry) have a spherical symmetry w.r.t. to refractive index.

*deriving the actual symmetry is an advanced topic and will not be considered for now
This example pertains to the decoration of 1-dimensional lattice with a two dimensional object.

An infinite one dimensional array of points are spaced equally with spacing ‘a’

- Place an object having the shape of an arrow mark (e.g. ↑) at each point to create a crystal of lattice parameter ‘3a’
- Describe this crystal in terms of a Lattice and a Motif
- How is the symmetry altered on the formation of a crystal?
Solution

Method-1

As the shape only has been specified we can use arrow marks of different sizes

Note: there are an infinite set of possibilities here

Motif:
Method-2

As the shape only has been specified we can use arrow marks of different colours.

Repeat distance 3a

Only lattice points are marked with filled circle

Note: there are an infinite set of possibilities here
Method-3

As the shape only has been specified we can use arrow marks in different orientations.

Repeat distance 3a

Only lattice points are marked with filled circle

Note: there are an infinite set of possibilities here
• How is the symmetry altered on the formation of a crystal?

  ▪ In the above cases the translational symmetry is lowered from ‘a’ to ‘3a’
  ▪ The array of points have a translational symmetry of ‘a’
    → on formation of the crystal only every third point is a lattice point &
    the repeat distance of the crystal is ‘3a’
- Does the array of points at the centres of the Carbon atoms in the graphene sheet as shown below form a lattice?
- Describe the crystal in terms of a lattice and a motif
- What is the unit cell?
The answer is NO!

Not all carbon positions form a lattice
As atoms A & B do not have identical surrounding both cannot be lattice points.
Crystal = Lattice + Motif

Grey atoms sit on the lattice positions

Motif = 1 grey + 1 green (in positions as shown)
Primitive unit cell

Motif for the Graphene Crystal

Contribution of 1 from the corners