Crystal Structure and Microstructure

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MATERIALS SCIENCE & ENGINEERING
AN INTRODUCTORY E-BOOK

http://home.iitk.ac.in/~anandh/E-book.htm
What determines the properties of materials?

- Cannot just be the composition!
  - Few 10s of ppm of Oxygen in Cu can degrade its conductivity
- Cannot just be the amount of phases present!
  - A small amount of cementite along grain boundaries can cause the material to have poor impact toughness
- Cannot just be the distribution of phases!
  - Dislocations can severely weaken a crystal
- Cannot just be the defect structure in the phases present!
  - The presence of surface compressive stress toughens glass

The following factors put together determines the properties of a material:
- Composition
- Phases present and their distribution
- Defect Structure (in the phases and between the phases)
- Residual stress (can have multiple origins and one may have to travel across lengthscales)

These factors do NOT act independent of one another (there is an interdependency)

Hence, one has to traverse across lengthscales and look at various aspects to understand the properties of materials.
Processing determines shape and microstructure of a component
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).
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.
Consider only the Geometrical Entity 
or only the Physical Property

Put in Crystalline defects
& Free Surface
& Thermal Vibration

Put multiple ~microconstituents
Add additional residual stress

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

Real materials are usually complex and we start with ideal descriptions

* *, ** Reduced definition of crystals

❖ That which is NOT associated with defects (crystalline or interfacial) → e.g. thermal residual stresses
Crystal = Lattice + Motif

**Motif or Basis:**
an entity (typically an atom or a group of atoms) associated with each lattice point

**Lattice**: the underlying periodicity of the crystal

**Motif**: Entity associated with each lattice point

Lattice ➢ how to repeat
Motif ➢ what to repeat

**Lattice**
Translationally periodic arrangement of **points**

**Crystal**
Translationally periodic arrangement of **motifs**
Crystal =

**Lattice** (*Where to repeat*)

+ 

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

\[ \text{Crystal} = \text{Lattice} + \text{Motif} \]
An array of points in space such that every point has *identical surroundings*

- This automatically implies two properties of lattices
  - In **Euclidean space** lattices are infinite (infinite array)
  - Lattices ‘have translational periodicity’

or

Translationally periodic arrangement of points in space is called a lattice

- We can have 1D, 2D or 3D arrays (lattices)
  
The motif associated with these lattices can themselves be 1D, 2D or 3D ‘entities’.
Crystal

As before there are many ways of associating the motif with a lattice point (one of these is shown).

In many places the ‘infinity’ will be left out (it is implied).
Square Lattice

Triangle Motif

Rectangle Crystal

Symmetry of the lattice and crystal different ⇒ NOT a Square Crystal

For sake of clarity all axes have not been marked

Isn’t this amazing → square lattice with a triangle motif giving a rectangle crystal!

Here the word square does not imply the shape in the usual sense.
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

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

Alternate view: Advanced concept: readers can return to this point later!
What are the symmetries of the 7 crystal systems?

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Characteristic Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>Four 3-fold rotation axes (two will generate the other two)</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>One 6-fold rotation axis (or roto-inversion axis)</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>(Only) One 4-fold rotation axis (or roto-inversion axis)</td>
</tr>
<tr>
<td>Trigonal</td>
<td>(Only) One 3-fold rotation axis (or roto-inversion axis)</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>(Only) Three ⊥ 2-fold rotation axes (or roto-inversion axis)</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>(Only) One 2-fold rotation axis (or roto-inversion axis)</td>
</tr>
<tr>
<td>Triclinic</td>
<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).
### Crystal System

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Shape of UC</th>
<th>Bravais Lattices</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Cubic</td>
<td>Cube</td>
<td>P I F C</td>
</tr>
<tr>
<td>2 Tetragonal</td>
<td>Square Prism (general height)</td>
<td>P I F C</td>
</tr>
<tr>
<td>3 Orthorhombic</td>
<td>Rectangular Prism (general height)</td>
<td>P I F C</td>
</tr>
<tr>
<td>4 Hexagonal</td>
<td>120° Rhombic Prism</td>
<td>P I F C</td>
</tr>
<tr>
<td>5 Trigonal</td>
<td>Parallelepiped (Equilateral, Equiangular)</td>
<td>P I C</td>
</tr>
<tr>
<td>6 Monoclinic</td>
<td>Parallogramic Prism</td>
<td>P I C</td>
</tr>
<tr>
<td>7 Triclinic</td>
<td>Parallelepiped (general)</td>
<td>P I C</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?
- ....?
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 \( \Rightarrow 23, \overline{43}m, \ m\overline{3}, \ 432, \ \frac{4}{m} \overline{3}, \ rac{2}{m} \)

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

Note: here SC, BCC & FCC are lattices
Note: Ge has two atoms per lattice point (has DC crystal structure)

SC, BCC, FCC are lattices while HCP & DC are crystals!
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**
- **Octahedron**
- **Tetrakaidecahedron** *(Truncated Octahedron)*
- **Tetrahedron**
Simple Cubic (SC) Lattice + Sphere Motif

- 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’
Body Centred Cubic (BCC) Lattice + Sphere Motif = Body Centred Cubic Crystal

*Note: BCC is a lattice and not a crystal*

**Unit cell of the BCC lattice**

- Atom at (0, 0, 0)
- Atom at (½, ½, ½)

**Space filling model**

So when one usually talks about a BCC crystal what is meant is a BCC lattice decorated with a mono-atomic motif
Face Centred Cubic (FCC) Lattice + Sphere Motif = Cubic Close Packed Crystal

(Sometimes casually called the FCC crystal)

Unit cell of the FCC lattice

All atoms are identical - coloured differently for better visibility.

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

Note: FCC is a lattice and not a crystal.

Video: FCC crystal
Face Centred Cubic (FCC) Lattice + Two Ion Motif

NaCl Crystal

Note: This is not a close packed crystal. Has a packing fraction of ~0.67 (using rigid sphere model)
Face Centred Cubic (FCC) Lattice + Two Carbon atom Motif (0,0,0) & (¼, ¼, ¼) = Diamond Cubic Crystal

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!
## Minimum symmetry requirement for the 7 crystal systems

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Characteristic 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, m(\overline{3}), 432, (\frac{4}{m} \frac{3}{m} \frac{2}{m})</td>
<td>3 or (\overline{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, (\overline{6}), (\frac{6}{m}), 622, 6mm, (\overline{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, (\overline{4}), (\frac{4}{m}), 422, 4mm, (\overline{4}2m), (\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, (\overline{3}), 32, 3m, (\overline{3} \frac{2}{m})</td>
<td>3 or (\overline{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, (\overline{2}), (\frac{2}{m})</td>
<td></td>
</tr>
<tr>
<td>Triclinic</td>
<td>None</td>
<td>1, (\overline{1})</td>
<td>(\overline{1}) could be present</td>
</tr>
</tbody>
</table>
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).
Positional Order

High T disordered

\[ G = H - TS \]

Low T ordered

SL-1 occupied by Cu and SL-2 occupied by Zn. Origin of SL-2 at \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\)

In a strict sense this is not a crystal! (i.e. it is amorphous)

Called a Disordered solid solution (a crystal in the probabilistic occupational sense)

A compound (intermediate or intermetallic compound)

Probabilistic occupation of each BCC lattice site:
50% by Cu, 50% by Zn

50% Cu

Probabilistic occupation

50% Zn

470°C

being a second order transition this temperature is not 'sharp'

In a strict sense this is not BCC

Note: this is not BCC

Diagrams not to scale
Do BCC crystals have 2 atoms per cell?

A: need NOT

Some examples of BCC crystals

In the conventional (natural choice of UC) there are no atoms at (0,0,0) and (½, ½, ½)!!

Fe

n = 2

Cu$_5$Zn$_8$

$\gamma$-Brass

n = 52

$\alpha$Mn

n = 58

c158
Do elements have simple crystal structures?

A: need NOT

Structure of Elements

Po

$\alpha$Mn

Fe

C (diamond)

Cu

$\beta$Mn

$\alpha$Mn
There are structure sensitive properties (like yield strength and fracture toughness) and structure insensitive* properties (like density and Young’s modulus).\textbf{ The word structure in this context (usually) implies microstructure.}

We have also stated that Material Engineers can also be called microstructure engineers. Processing used to create the component or the sample determines its microstructure. In this context we should keep in view the materials tetrahedron (as below).

Traditionally, the structure seen at high magnifications (of an optical microscope—say at 500× or 1000×), is known as microstructure (in some sense it is the ‘micron-scale structure’).

As we would like to get an handle on the structure sensitive properties, we study microstructures → i.e. we want to do structure-property correlations.

This implies that the definition based on magnification is unsatisfactory. Additionally, if we do imaging at even higher magnification (say in an TEM) the structure we see will have to be termed as ‘nanostructure’ (‘nanometer-scale-structure’).

Keeping the above in view, there is a need for a ‘functional’ definition of a microstructure, which can give us an handle on the properties.

\* The word is ‘sensitive’ and not ‘dependent’! (i.e there can be a dependence).
A functional definition of a microstructure can be given as:

\[
\text{Phases (including morphology)} + \text{Defects} + \text{Residual Stress} \text{ and their distributions.}
\]

The above also includes \textit{defects between the phases} and those arising from a \textit{global view of the sample} (like misorientation between grains, crystallographic texture, etc.).

The most difficult part to understand is: “how is residual stress part of microstructure?”

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**Thermo-mechanical Treatments**

**Microstructure**

- Phases
- Defects
- Residual Stress & their distributions

- Vacancies
- Dislocations
- Twins
- Stacking Faults
- Grain Boundaries
- Voids
- Cracks

*Processing determines shape and microstructure of a component*
The distribution of phases is an important factor which determines the properties of a material. For a fixed volume fraction (or weight fraction) of phases present; the shape, connectivity and distribution of the phases will play a decisive role in determining the properties of the material.

To understand this let us consider 4 different distributions of a brittle phase (B) in a tough ‘matrix’ phase (A)– keeping the *volume fraction of B constant*. B is ‘incoherent’ with matrix.

(a) B forms a continuous network → leads to poor fracture toughness due to continuous path for crack propagation along B.
(b) B is needle shaped with ‘sharp’ features → sharp features lead to stress concentration leading to crack initiation (which then connect via the brittle phase B and lead to low fracture toughness).
(c) B is in the form of large spheres with more interparticle spacing
(d) B is in the form of small spheres with less interparticle spacing as compared to (c) → this material has more strength as compared to (c) dislocations have to bow around closer spaced obstacles.

Phase B can even be nanosized

Four distributions of phase-B (a brittle but hard phase) in phase-A (the tough phase) is considered.
Let us further consider two examples of real microstructures.

Cementite a brittle phase is present as a continuous phase along the ‘prior’ austenite grain boundaries (highlighted in yellow), making the material brittle in impact → cracks propagate along this continuous path of brittle phase.

It is to be noted that, there is cementite also present within the prior austenite grains— but its effect is not as deleterious in impact, as the continuous layer of cementite along prior austenite grain boundaries.

In (b) there is an amorphous phase along the grain boundaries of Si₃N₄ ceramic, giving rise to a similar situation (i.e. a weakened material in impact).
Residual stresses are those which arise in a body in the absence of external loads or constraints. Residual stress can be beneficial or deleterious, depending on the context. Processing used to make the material/component can give rise to residual stresses. Vacancies and dislocations give rise to stress fields at the atomic scale, while residual thermal stresses could pervade the entire component.

Some points in this regard are:

a) the stress fields associated with GP zones in Al-Cu alloys is of the same scale as dislocation stress fields
b) large cracks in the material can lead to macroscopic stress fields, while micro-cracks may have much smaller effective region of stress fields
c) in micron sized components, the scale of thermal residual stress may be expected to be smaller than that in their large scale counterparts.

In the example of GP zones in Al-Cu alloys, the stress/strain fields are intricately associated with the distribution of GP zones (~ the phases); which further highlights the importance of adopting a definition of microstructure as done in here.
The reason for elevating residual stress to be an integral part of the definition of microstructure will become further clear in the next two examples considered.

It is well known that nucleation is preferred at any of the high-energy sites in a material (heterogeneous nucleation). Typical examples of heterogeneous nucleation sites are: surfaces, internal interfaces (grain boundaries, interphase boundaries, stacking faults etc.), crystallographic defects (dislocations), cracks, voids etc. Stressed (and hence strained) regions also can act like heterogeneous nucleation sites.

If a 3 stage process of the growth of epitaxial islands is followed: (i) growth of islands, (ii) capping the islands with a layer, (iii) growing a layer of islands above the capped layer → It is observed that the second layer of islands nucleate in the highly strained region of the capping layer (usually right above the layer below). **Strained regions acts like a preferred nucleation site.**