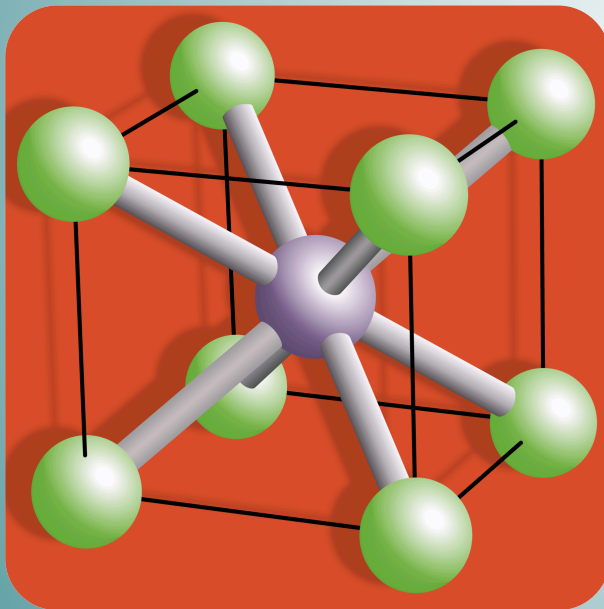# Materials

Topic 3. Crystalline and Amorphous structure

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3.1. STATES OF MATTER

- **Matter can exist in three states: gaseous, liquid and solid.**

- **Gaseous state: according to the kinetic theory gases are formed by small elastic spheres that move randomly in an unceasing way, because they have a high kinetic energy whose value depends exclusively on the temperature.**

$$E = K \cdot T \qquad \text{(K, Boltzmann constan)}$$

- **The particles are very far apart, and there are no interactions between them.**

- **Liquid state:** the particles have lower kinetic energy than in gases, so there are attractive forces between them, with the speed of diffusion being lower in liquids.

- The interaction between molecules and the fact that their compactness is maximum, causes that, unlike gases, liquids are **incompressible**, but retaining the characteristics of **isotropy**.
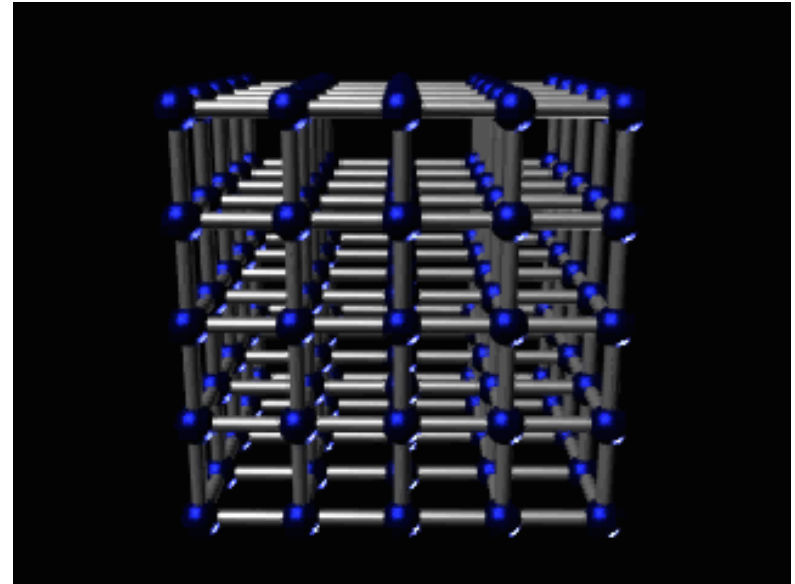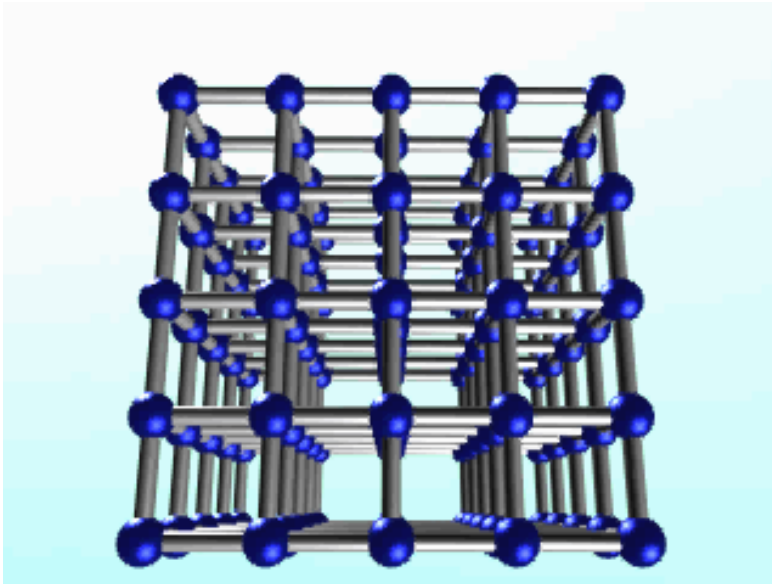
- **Solid state:** the particles are in contact with each other, in fixed positions and with strong mutual attractions.
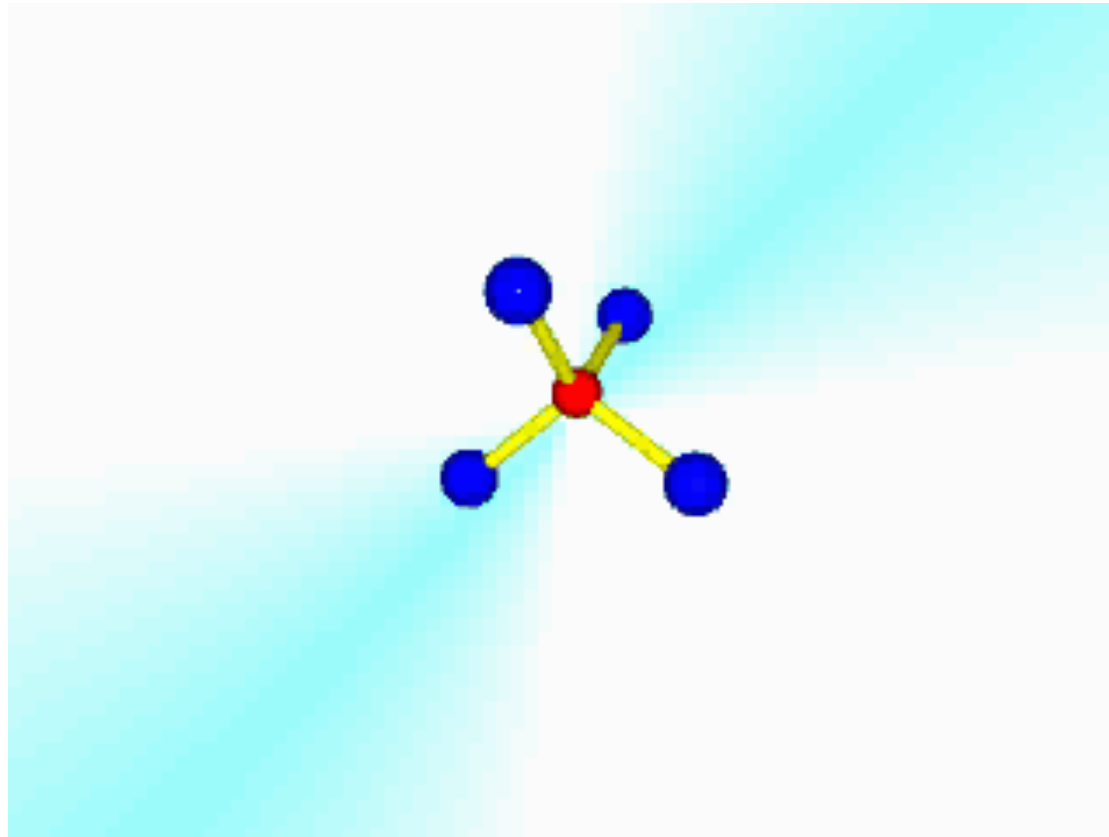
3.2. CRYSTALLINE AND AMORPHOUS SOLIDS

• **Depending on their structural arrangement, solids are classified as:**

  – **Crystalline: constituted by small crystals in which the atoms are packaged according to regular and repetitive three-dimensional patterns.**

– **Amorphous (or glass):** when there is no regularity in the spatial arrangement of their atoms.
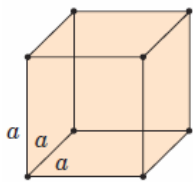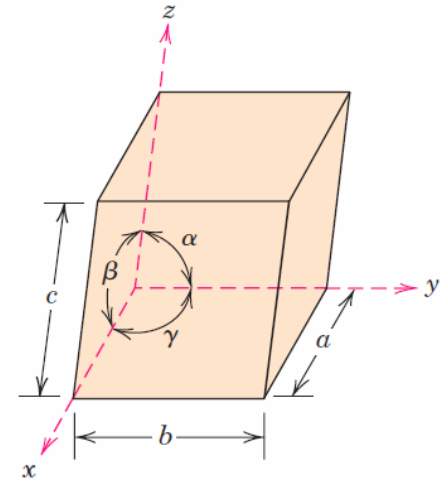
3.3. CRYSTAL LATTICE

• **Any crystal lattice can be described as a model formed by repeating several structural units.**

• **A crystal lattice is a periodic arrangement of points that define a space.**

• **The unit cell is a subdivision of the crystalline network that preserves the general characteristics of the entire network.**

Atoms centers
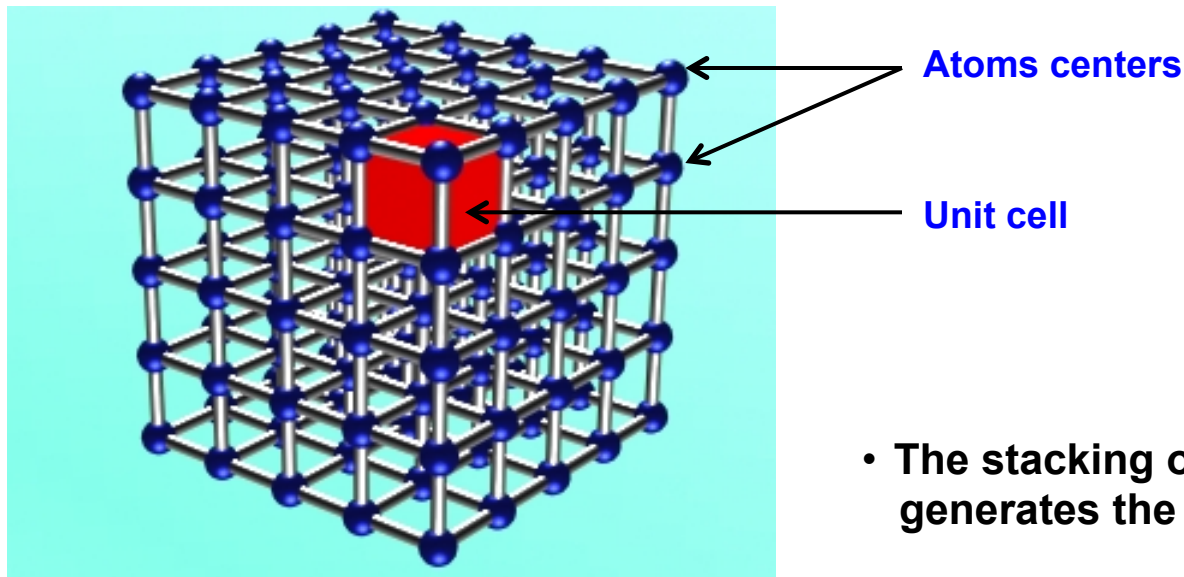
Unit cell

• **The stacking of identical unit cells generates the entire network.**

3.4. CRYSTAL SYSTEMS Y BRAVAIS LATTICE

- **Unit cell with x, y and z coordinate axes, showing:**
  - **Axial lengths (a, b, and c).**
  - **Interaxial angles (α, β, and γ).**

- **Termed as the six lattice parameters of a crystal structure.**

- **There are seven different possible combinations of a, b, and c, and α, β and γ and each of which represents a distinct crystal system.**
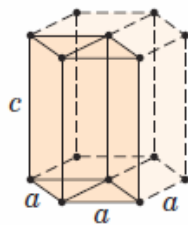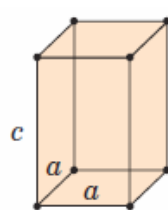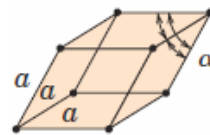
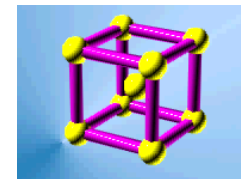| Cubic	Hexagonal	Tetragonal	Rhombohedral (Trigonal)	Orthorhombic	Monoclinic	Triclinic
a = b = c	a = b ≠ c	a = b ≠ c	a = b = c	a ≠ b ≠ c	a ≠ b ≠ c	a ≠ b ≠ c
$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = 90°$ $\gamma = 120°$	$\alpha = \beta = \gamma = 90°$	$\alpha = \beta = \gamma \neq 90°$	$\alpha = \beta = \gamma = 90°$	$\alpha = \gamma = 90° \neq \beta$	$\alpha \neq \beta \neq \gamma \neq 90°$
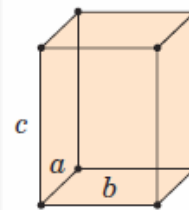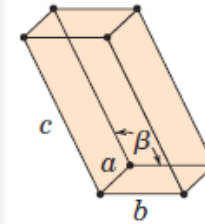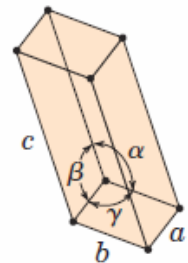
- **There are 14 kinds of unit cells or Bravais Lattice.**

- **According to the location of the nodes:**
  - **Vertex (P).**
  - **Centers of the faces (F).**
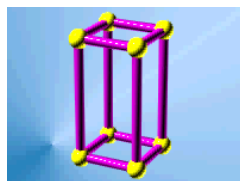 - **Centers of the bases (C).**
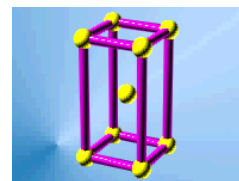 - **Inner (I).**
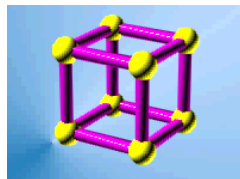
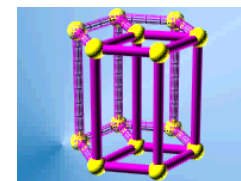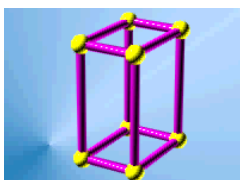Cubic Simple
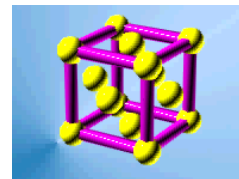
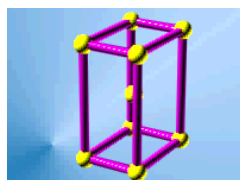Face-centered Cubic

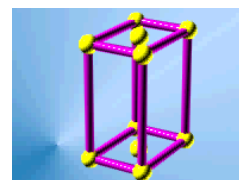Body-centered Cubic

Simple Tetragonal

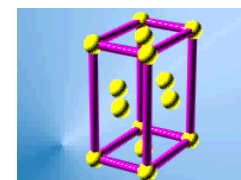Body-centered Tetragonal

Hexagonal

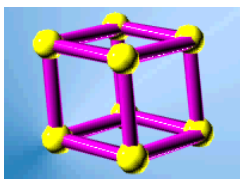Orthorhombic Simple

Body-centered Orthorhombic

Base-centered Orthorhombic

Face-centered Orthorhombic

Rhombohedral
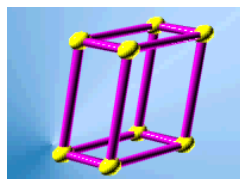
Monoclinic Simple
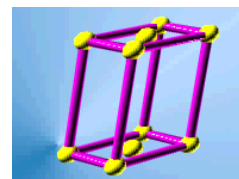
Base-centered Monoclinic
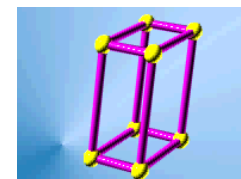
Triclinic

3.5. COMMON CRYSTALLINE STRUCTURES

Cubic Simple (CS)

Face-centered Cubic (FCC)

Body-centered Cubic (BCC)
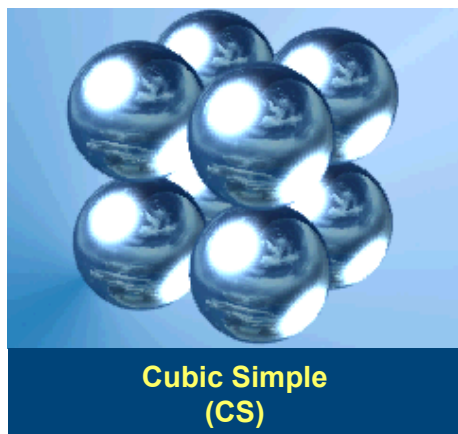
Po
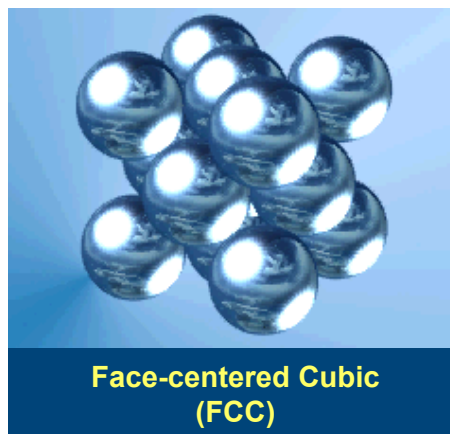
Au, Ag, Pb, Pt, Fe (910 - 1400º C)…

Fe, Li, K, Cr, V, W, Mo…

- **Number of atoms contained in the unit cell:**
  - **The vertex contribute to the counting with 1/8 atom.**
  - **The faces with ½ atom.**
  - **The central nodes with 1 atom.**

$$CS: \; n = 8 \; vertex \cdot \frac{1}{8} \frac{atom}{vertex} = 1 \; atom$$

$$FCC: \; n = 8 \; vertex \cdot \frac{1}{8} \frac{atom}{vertex} + 6 \; faces \times \frac{1}{2} \frac{atom}{face} = 4 \; atoms$$

$$BCC: \; n = 8 \; vertex \cdot \frac{1}{8} \frac{atom}{vertex} + 1 \; central \; atom = 2 \; atoms$$

Cubic Simple (CS) | **Face-centered Cubic (FCC)** | **Body-centered Cubic (BCC)**
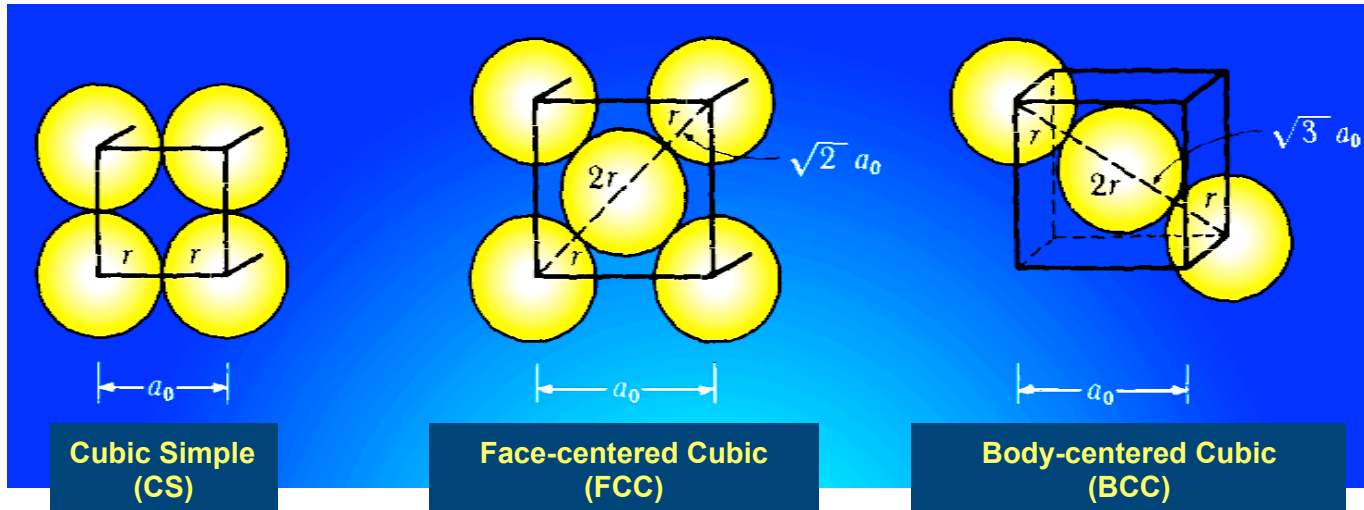
CS structure: atoms touch each other along the edge of the cube.

$$a_0 = 2r \qquad r = atomic\ radious$$

FCC structure: atoms touch each other along the diagonal of the cube face.

$$a_0 = \frac{4r}{\sqrt{2}}$$

BCC structure: atoms touch each other along the diagonal of the cube

$$a_0 = \frac{4r}{\sqrt{3}}$$
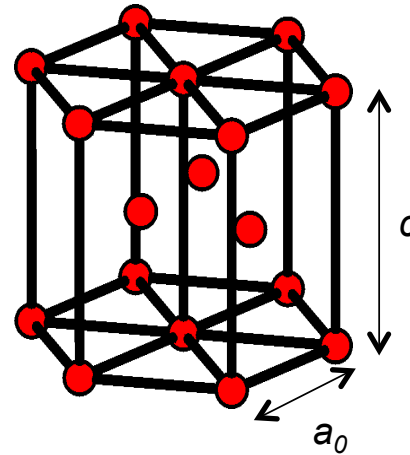
Hexagonal compact (HCP)

Mg, Zn, Ti, Cd, Be, Co, Zr…

$$HCP: \; n = 12 \; vertex \cdot \frac{1}{6} \frac{atom}{vertex} + 3 \; internal \; atoms \; + 2 \; bases \cdot \frac{1}{2} atoms = 6 \; atoms$$

HCP structure: atoms touch each other along the edge of the hexagon.

$$a_0 = 2r \qquad r = \; atomic \; radious$$
$$c = 1.63 \cdot a_0$$
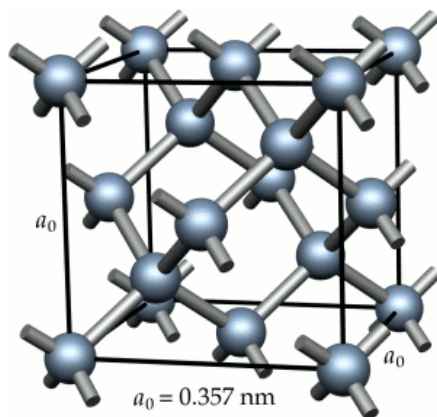
Cubic Diamond

Diamond, Si, Ge, Sn …

Blende type

GaAs, ZnS, TiC, ZrC, VN…
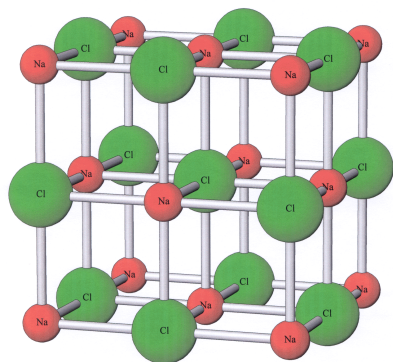
Sodium Chloride type

NaCl, MgO, LiF, KCl, …
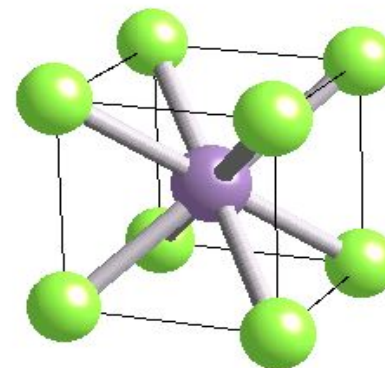
Cesium Chloride type

CsCl, RbCl, AlNi, CuZn, …

3.6. ALLOTROPY AND POLYMORPHISM

- **Each material chooses the structure that provides the least energy (the energy difference among alternative structures is usually small).**

Allotropy

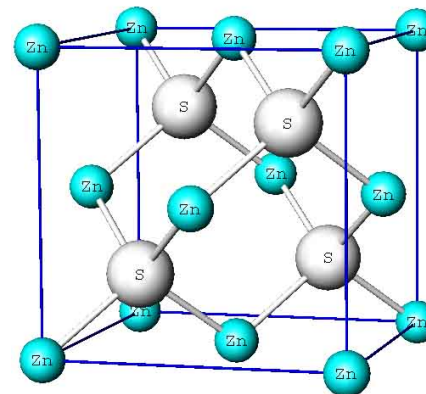| Metal	Crystalline structure –room temperature–	Other temperatures
Ca	FCC	BCC (> 447 °C)
Co	HCP	FCC (> 427 °C)
Hf	HCP	BCC (> 1742 °C)
Fe	BCC	FCC (912 - 1394 °C)
		BCC (> 1394 °C)
Li	BCC	HCP (< - 193 °C)
Na	BCC	HCP (< - 233 °C)
Tl	HCP	BCC (> 234 °C)
Ti	HCP	BCC (> 883 °C)
Y	HCP	BCC (> 1481 °C)
Zr	HCP	BCC (> 872 °C)

Allotropes of Iron, Fe

2.93 Å

δ– iron   body-centred

3.60 Å

γ– iron   face-centred

2.86 Å

α– iron   body-centred
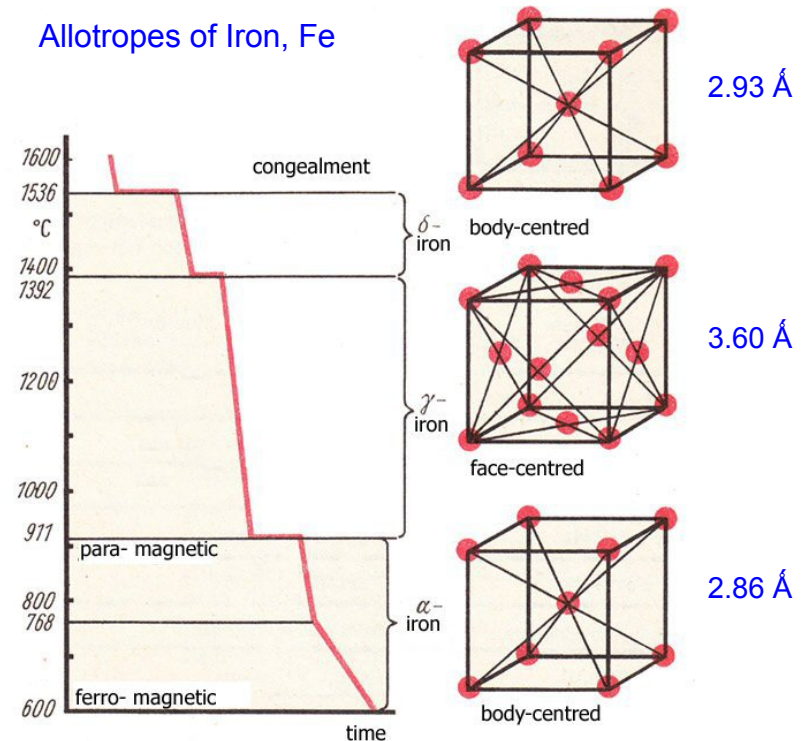
- **Tin disease (pest):**
  Change of Sn white (Sn-β, tetragonal), usual at room temperature, to Sn fragile gray (Sn-α, cubic), which appears at temperatures below 13.2° C with long exposure times.

Inicial state

Exposed for 1.5 years

Exposed for 1.8 años years   20mm

13.2°C
Cooling

White (β) tin   Gray (α) tin
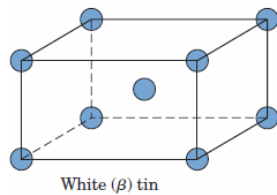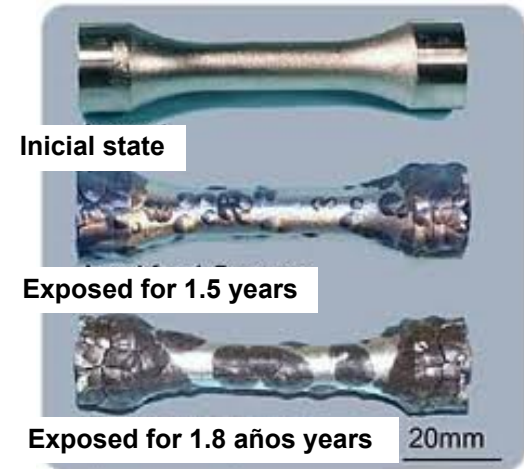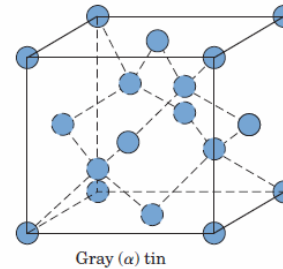
- **Case 1: Napoleon's campaign in Russia, 1812.**

– **Case 2:** Captain Scott's expedition to the South Pole, 1912.

Polymorphism

Quartz
α

Tridymite
β

Cristobalite
β

573 °C
Quartz α <-------------------> Quartz β
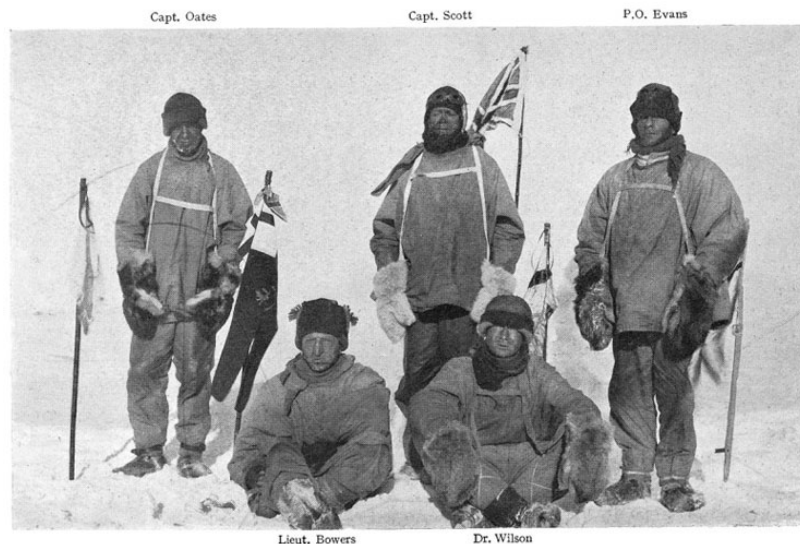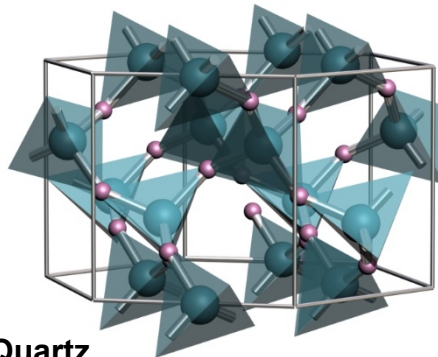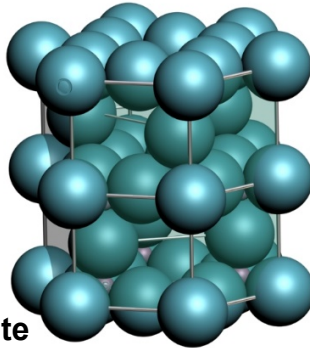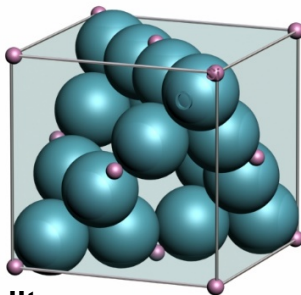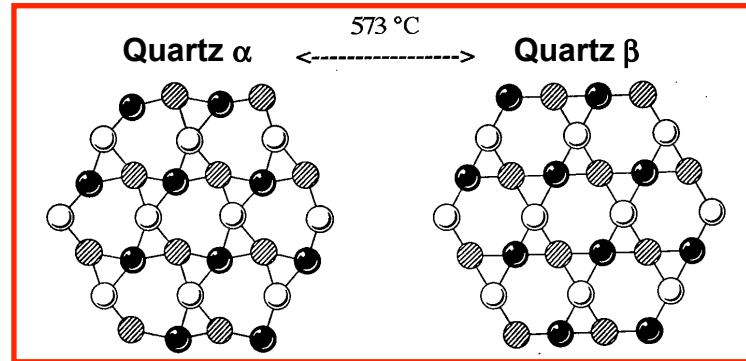
Chemical substance	Mineral	crystal system	specific gravity	Transformation temperature (ºC)
CaCO$_3$	Calcite Aragonite	Rhombohedral Orthorhombic	2,71 2,93	
SiO$_2$	quartz α quartz β tridymite α tridymite β ciristobalite α ciristobalite β	Trigonal Hexagonal Monoclinic Hexagonal Tetragonal Cubic	2.65 2.53 2.27 2.26 2.32 2.20	< 573 > 573 ----- > 870 ----- > 1470

3.7. MILLER INDICES

- **Miller indices represent a crystallographic notation that allows to describe any plane or spatial direction by a set of three numbers.**

1. LATTICE NODES

- **Each node of the lattice is defined by three indices that denote their Cartesian coordinates (x, y, z) in space, with respect to an arbitrary origin.**
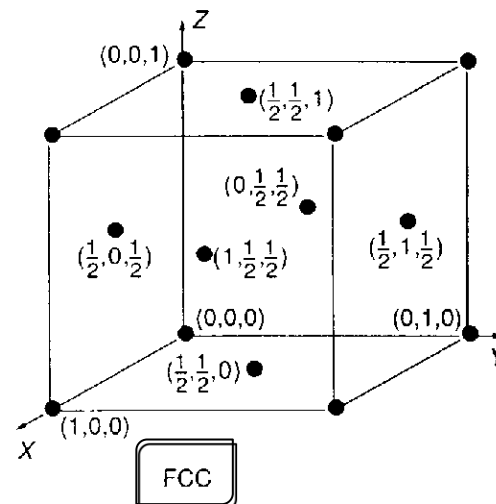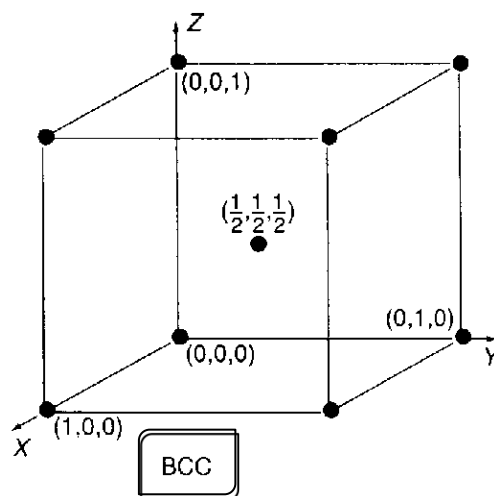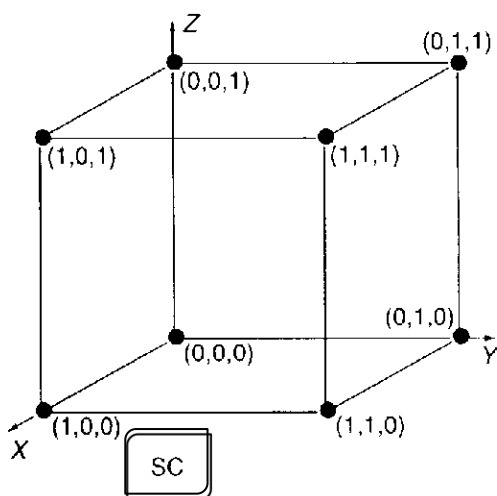
2. DIRECTION INDICES

- **The directions are vectors that connect two lattice nodes in a pre-established direction. The indices of a direction are given by the difference of the coordinates of the points (nodes), reduced to the smaller integers in the same proportion.**

Directions: [u v w]

Family of directions <u v w>
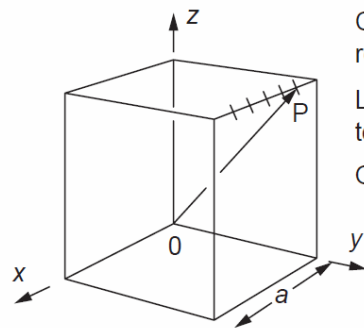
	x	y	z
Coordinates of P relative to 0	$\frac{1}{6}$	1	1
Lowest integers to give same ratio	1	6	6
Quote	[166]		

Collectively ⟨111⟩
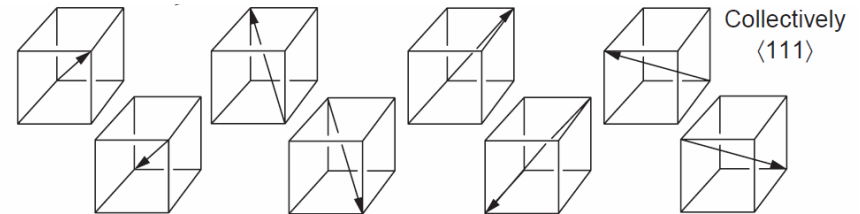
Note — in cubic systems only ! [111] is the normal to (111)
[100] is the normal to (100), etc.

Direction indices for identifying crystal directions, showing how the [166] direction is defined.

The figure shows the family of <111> directions.

[111]   [112]   [1̄12]   [01̄2]   [221]
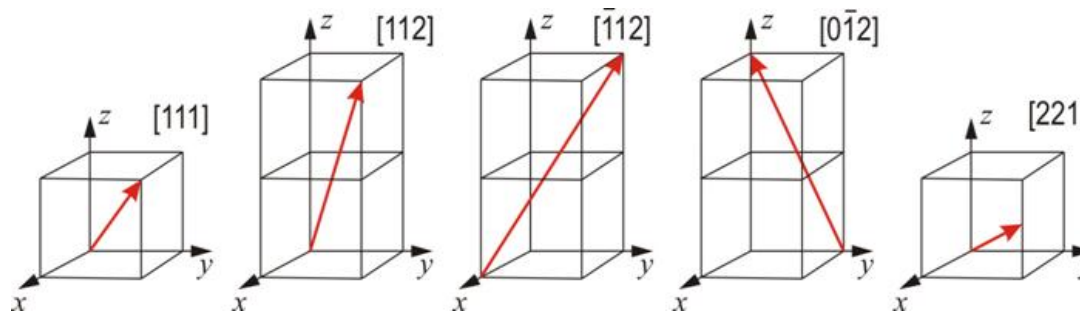
3. PLANE INDICES

- **Crystallographic planes can also be identified by three Miller indices.** Method:

  I.   Epress the cuts of the plane with the axes in units of the lattice parameters of the unit cell.

  II. Calculate the reciprocals of these values.

  III. Reduce the inverse to the minor integer in the same proportion.

Directions: (h k l)

Family of directions {h k l}

Collective description {100}

Family of {100} and of {110} planes
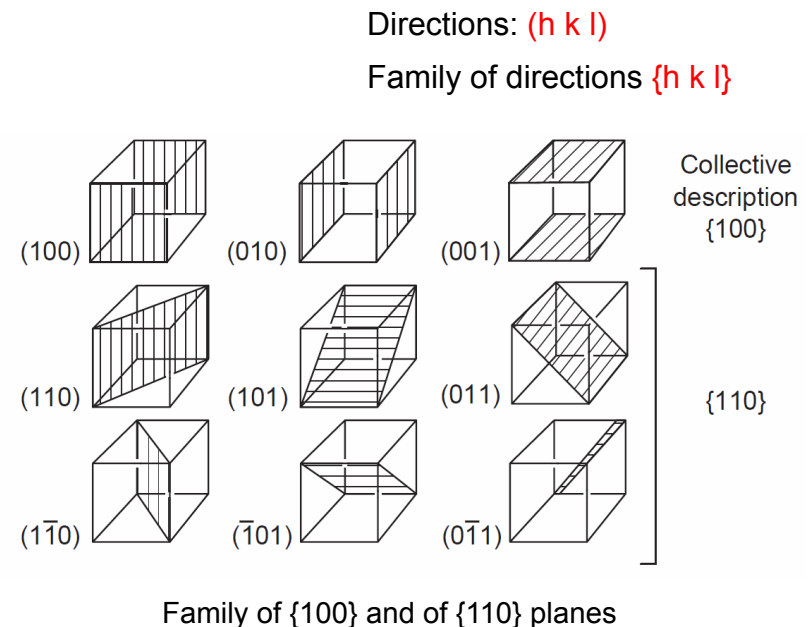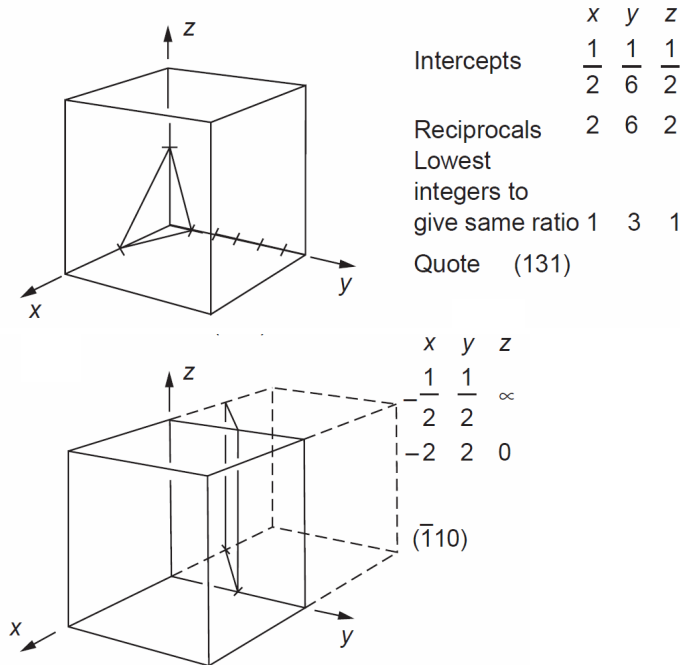
- **Miller indices for identifying crystal planes, showing how the (131) plane and the ($\bar{1}$10) planes are defined.**

- **These rules are not valid for any plane that passes through the origin of coordinates.**

EXAMPLES
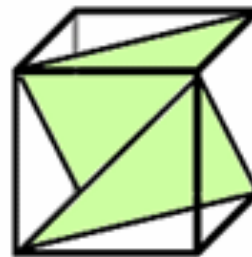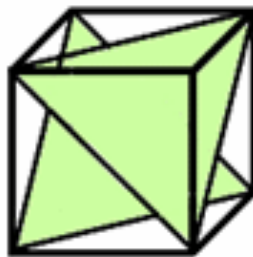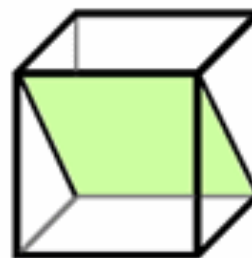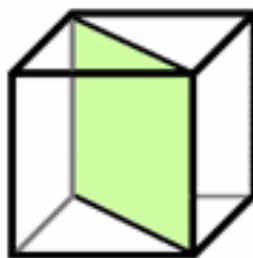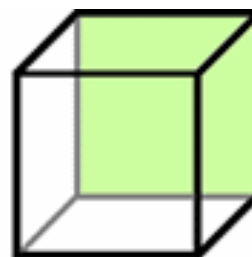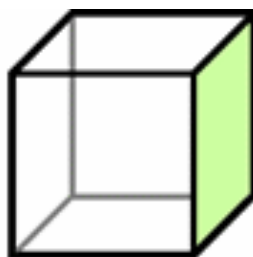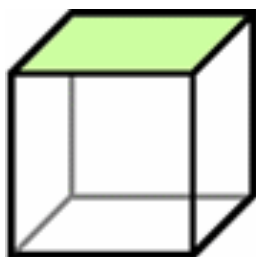
3.8. POLYCRYSTALLINE SOLIDS

• **Most crystalline solids are the set of many small crystals or grains.**
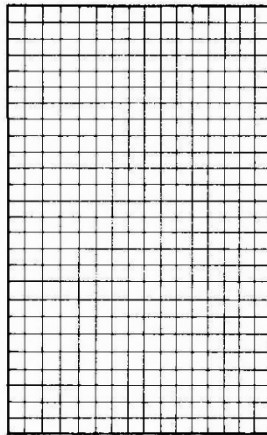
Monocrystalline solid

Polycrystalline solid

0.001 in
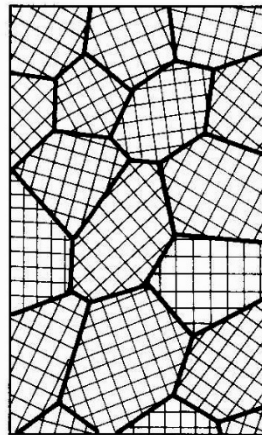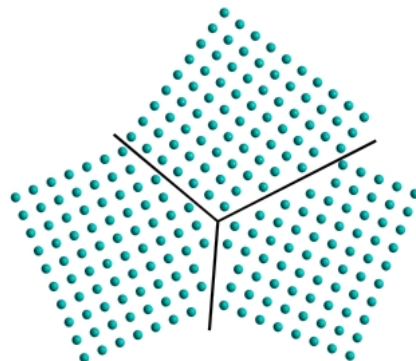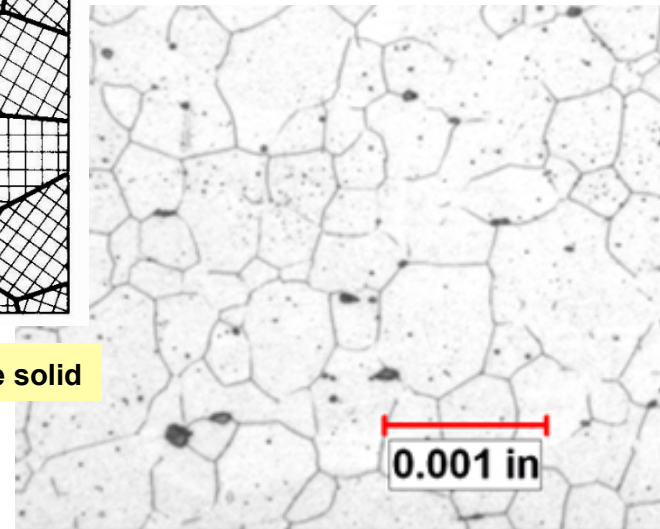
• **The contact between grains is a defect in the spatial arrangement known as grain boundary.**

3.9. POLYMER STRUCTURE

- **Polymers: long chain macromolecules.**

  The atoms that form the skeleton are joined by covalent bonds.

  Carbon ●
  Hydrogen ●
  Chlorine ●

- **Arrangement of chains:**
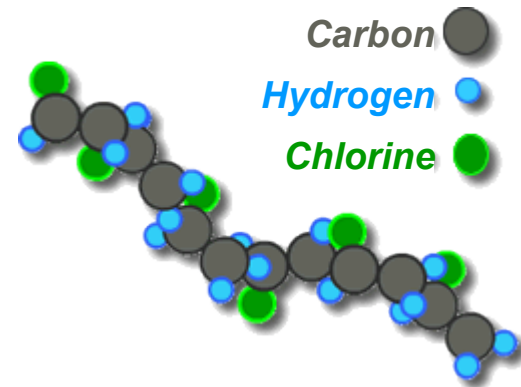
Random (amorphous)
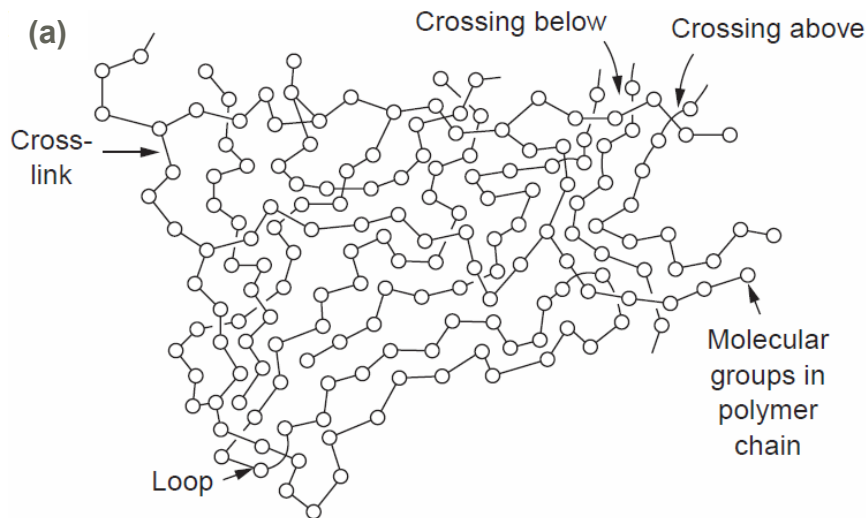
Mixed structure (degree of crystallinity)

(a) Cross-link, Crossing below, Crossing above, Molecular groups in polymer chain, Loop

(b) Amorphous region, Chain branching, Crystalline region, Side groups
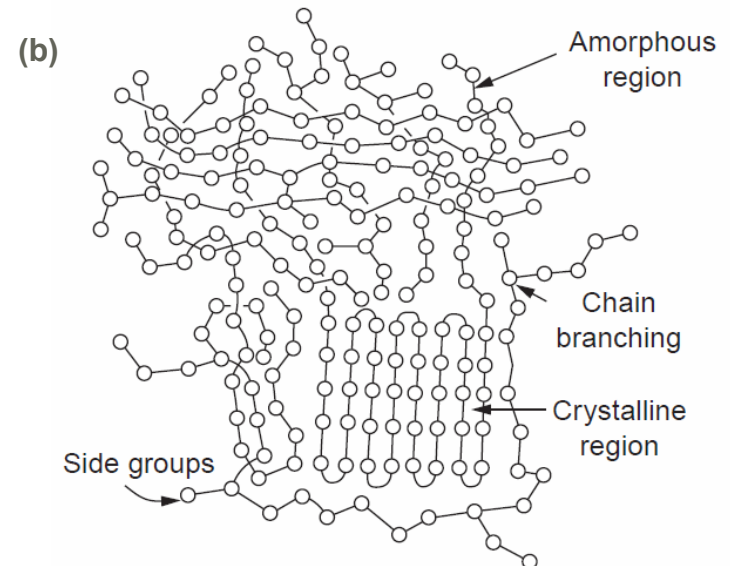
3.10. GLASS STRUCTURE

- **The materials with very complex atomic or molecular structure, can hardly be ordered in crystals, giving rise to amorphous structures, without any order, which are usually isotropic.**

Fast cooling → formation of non-crystalline solid (glass).

Crystalline SiO$_2$ *Amorphous SiO$_2$*

○ O
● Si
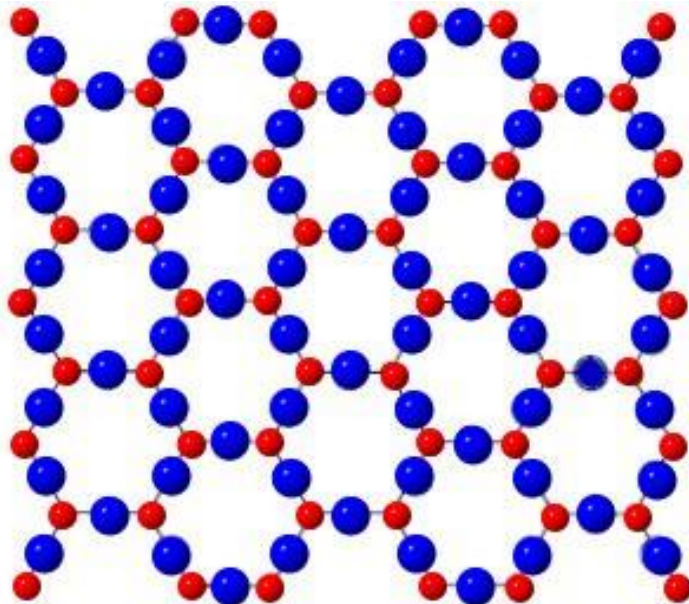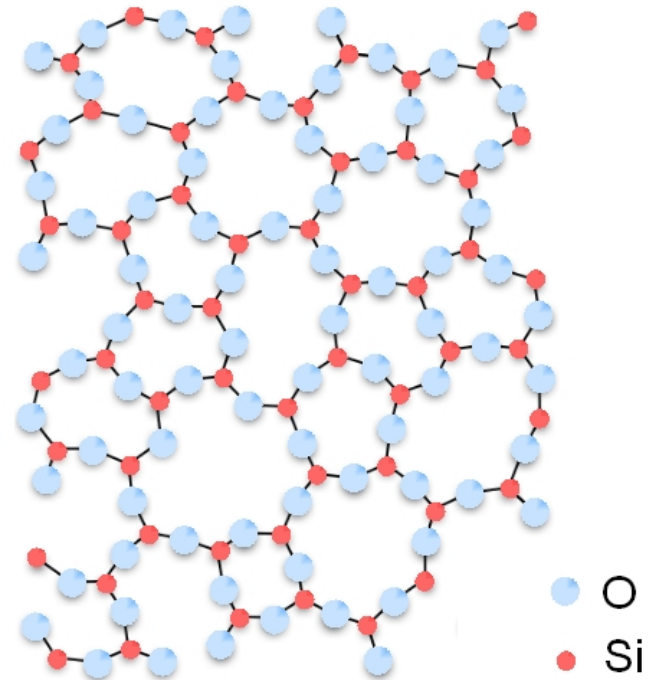
3.11. THE DENSITY OF SOLIDS

- **It reflects the relationship between the mass and the size of the atoms that make up the material, as well as the efficiency with which they are packaged.** A knowledge of the crystal structure of a metallic solid permits computation of its theoretical density through the relationship.

$$\rho = \frac{cell\ mass}{cell\ volume} = \frac{n \cdot m}{V} = \frac{n \cdot M}{N_A \cdot V_C}$$

Where:

- **n:** number of atoms associated with each unit cell.
- **M:** atomic weight.
- **N$_A$:** avogadro´s number ($6.023 \cdot 10^{23}$ atoms/mol).
- **V$_C$:** volumen of the unit cell.

- The Atomic Packing Factor, APF, is defined as the fraction of solid sphere volume in a unit cell, or:

$$APF = \frac{volume\ of\ atoms\ in\ a\ unit\ cell}{total\ unit\ cell\ volume}$$

DATA FOR DENSITY, ρ

Material	ρ (Mg m^{-3})
Osmium	22.7
Platinum	21.4
Tungsten and alloys	13.4–19.6
Gold	19.3
Uranium	18.9
Tungsten carbide, WC	14.0–17.0
Tantalum and alloys	16.6–16.9
Molybdenum and alloys	10.0–13.7
Cobalt/tungsten-carbide cermets	11.0–12.5
Lead and alloys	10.7–11.3
Silver	10.5
Niobium and alloys	7.9–10.5
Nickel	8.9
Nickel alloys	7.8–9.2
Cobalt and alloys	8.1–9.1
Copper	8.9
Copper alloys	7.5–9.0
Brasses and bronzes	7.2–8.9
Iron	7.9
Iron-based super-alloys	7.9–8.3
Stainless steels, austenitic	7.5–8.1
Tin and alloys	7.3–8.0
Low-alloy steels	7.8–7.85
Mild steel	7.8–7.85
Stainless steel, ferritic	7.5–7.7
Cast iron	6.9–7.8
Titanium carbide, TiC	7.2
Zinc and alloys	5.2–7.2

Material	ρ (Mg m^{-3})
Chromium	7.2
Zirconium carbide, ZrC	6.6
Zirconium and alloys	6.6
Titanium	4.5
Titanium alloys	4.3–5.1
Alumina, Al_2O_3	3.9
Alkali halides	3.1–3.6
Magnesia, MgO	3.5
Silicon carbide, SiC	2.5–3.2
Silicon nitride, Si_3N_4	3.2
Mullite	3.2
Beryllia, BeO	3.0
Common rocks	2.2–3.0
Calcite (marble, limestone)	2.7
Aluminum	2.7
Aluminum alloys	2.6–2.9
Silica glass, SiO_2 (quartz)	2.6
Soda glass	2.5
Concrete/cement	2.4–2.5
GFRPs	1.4–2.2
Carbon fibers	2.2
PTFE	2.3
Boron fiber/epoxy	2.0
Beryllium and alloys	1.85–1.9
Magnesium and alloys	1.74–1.88
Fiberglass (GFRP/polyester)	1.55–1.95
Graphite, high strength	1.8
PVC	1.3–1.6
CFRPs	1.5–1.6
Polyesters	1.1–1.5
Polyimides	1.4
Epoxies	1.1–1.4
Polyurethane	1.1–1.3
Polycarbonate	1.2–1.3
PMMA	1.2
Nylon	1.1–1.2
Polystyrene	1.0–1.1
Polyethylene, high-density	0.94–0.97
Ice, H_2O	0.92
Natural rubber	0.83–0.91
Polyethylene, low-density	0.91
Polypropylene	0.88–0.91
Common woods	0.4–0.8
Cork	0.1–0.2
Foamed plastics	0.01–0.6

BAR CHART OF DATA FOR DENSITY, ρ