Physics of Materials:
Classification of Solids

It is evident that many years of research by a great many people, both before and after the discovery of the transistor effect, has been required to bring our knowledge of semiconductors to its present development. We were fortunate to be involved at a particularly opportune time and to add another small step in the control of Nature for the benefit of mankind.

- John Bardeen, 1956 Nobel lecture

Dr. Anurag Srivastava

Atal Bihari Vajpayee

Indian Institute of Information Technology and Management, Gwalior

Classification of Solids,

On The basis of Geometry and Bonding (Intermolecular forces)

CLASSIFICATION OF SOLIDS BASED ON ATOMIC ARRANGEMENT

AMORPHOUS	QUASICRYSTALS	CRYSTALS
~~Ordered~~ + ~~Periodic~~	Ordered + ~~Periodic~~	Ordered + Periodic

- There exists at least one crystalline state of lower energy (G) than the amorphous state (glass)
- The crystal exhibits a sharp melting point
- *"Crystal has a higher density"!!*
- A quasiperiodic crystal, or **quasicrystal**, is a structure that is ordered but not periodic. A quasicrystalline pattern can continuously fill all available space, but it lacks translational symmetry.

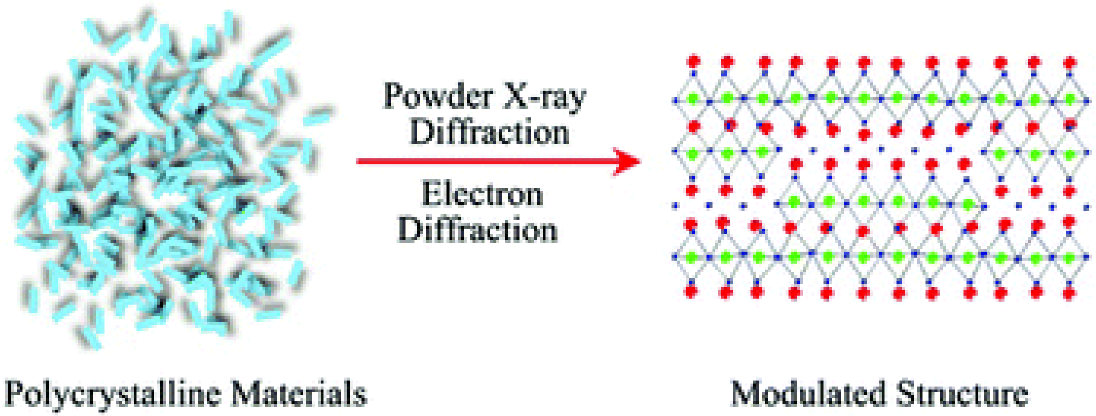
CLASSIFICATION OF SOLIDS BASED ON ATOMIC ARRANGEMENT

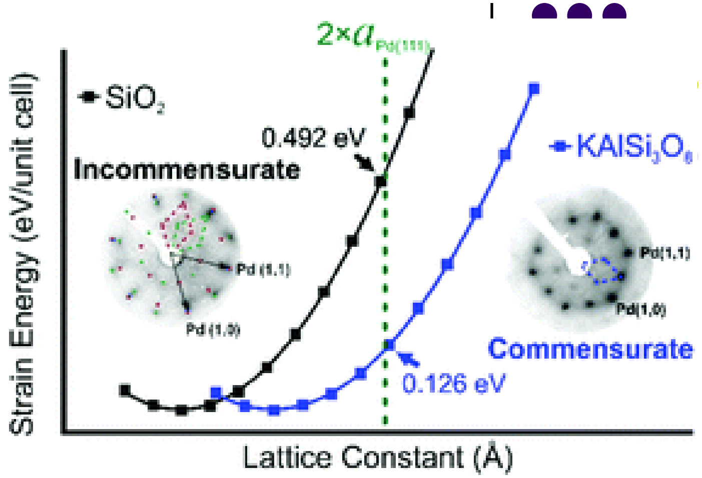
- AMORPHOUS
- QUASICRYSTALS
- CRYSTALS

ADDITIONAL POSSIBLE STRUCTURES

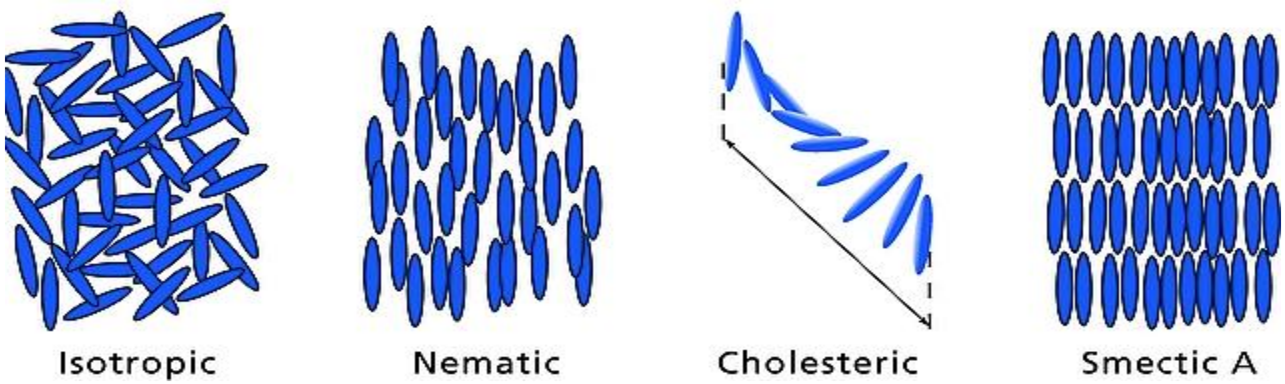
- Modulated structures
- Incommensurately Modulated structures
- Liquid crystals

- ✓ Modulated crystal structures belong to that kind of crystal structures, in which atoms suffer from certain substitutional and/or positional fluctuation. If the period of fluctuation matches that of the three-dimensional unit cell then a superstructure results, otherwise an incommensurate modulated structure is obtained.
- ✓ Incommensurate modulated phases can be found in many important solid state materials. In many cases, the transition to the incommensurate modulated structure corresponds to a change of certain physical properties. A common feature of incommensurate modulated structures is that they do not have 3-dimensional periodicity. However incommensurate modulated structures can be regarded as the 3-dimensional hypersection of a 4- or higher-dimensional periodic structure.
- ✓ Liquid crystals (LCs) are highly structured liquids, with orientational (**nematic**,**cholesteric**) and positional (smectic) order of constituent molecules . The type of molecular order is controlled by shape and chirality of LC molecules, with over a hundred known LC phase,





Commensurate: corresponding in size or degree; in proportion
Incommensurate: out of keeping or proportion with



THE ENTITY IN QUESTION

- GEOMETRICAL
  - E.g. Atoms, Cluster of Atoms Ions, etc.
- PHYSICAL
  - E.g. Electronic Spin, Nuclear spin

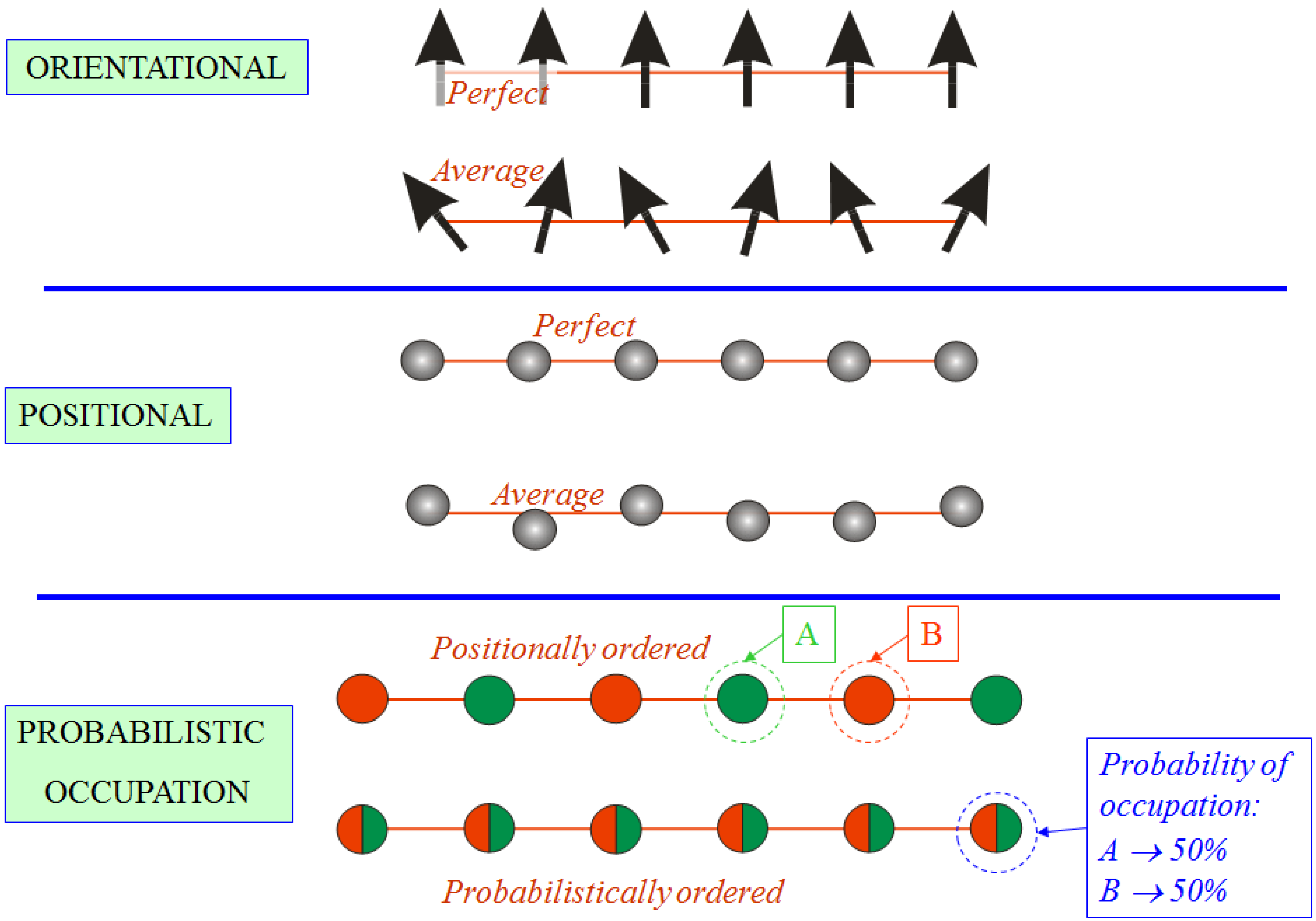
ORDER

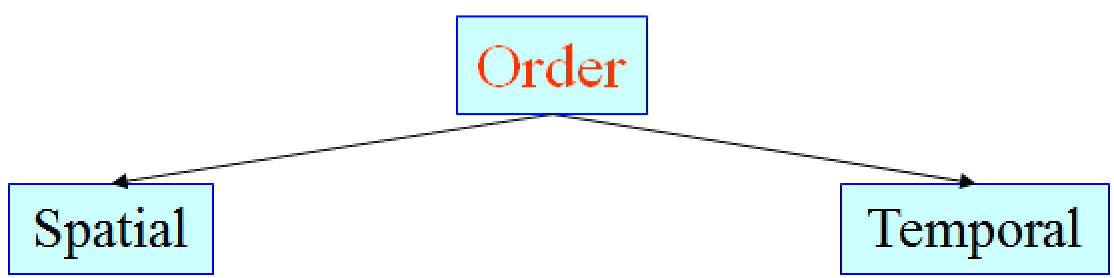
- ORIENTATIONAL
- POSITIONAL

Order-disorder of: POSITION, ORIENTATION, ELECTRONIC & NUCLEAR SPIN

ORDER

- TRUE
- PROBABILISTIC


ORIENTATIONAL
Perfect
Average
POSITIONAL
Perfect
Average
PROBABILISTIC OCCUPATION
Positionally ordered
A
B
Probabilistically ordered
Probability of occupation:
A → 50%
B → 50%


Order
Spatial
Temporal

Range of Spatial Order

- Short Range (SRO)
- Long Range Order (LRO)

Class/ example(s) ↓	Short Range		Long Range	
	Ordered	Disordered	Ordered	Disordered
Crystals[*]/ Quasicrystals	✓		✓	
Glasses[#]	✓			✓
Crystallized virus[$]		✓	✓	
Gases		✓		✓

Notes:

* In practical terms crystals are disordered both in the short range *(thermal vibrations)* and in the long range *(as they are finite)*

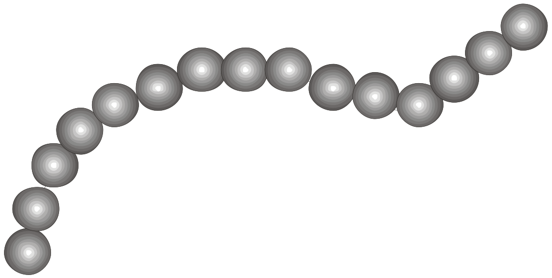
\# ~ Amorphous solids

$ Other examples could be: colloidal crystals, artificially created macroscopic crystals

➢ Liquids have short range spatial order but NO temporal order

Factors affecting the formation of the amorphous state

- When primary bonds are 1D or 2D and secondary bonds aid in the formation of the crystal
- The crystal structure is very complex



- When the free energy difference between the crystal and the glass is small $\Rightarrow$ Tendency to crystallize would be small

- Cooling rate $\rightarrow$ fast cooling promotes amorphization
  - "fast" depends on the material in consideration
  - Certain alloys have to be cooled at 10^6 K/s for amorphization
  - Silicates amorphizes during air cooling

विद्यार्थिनामृतं ज्ञानम्

CRYSTALS

Molecular

- *Molecule held together by primary covalent bonds*
- *Intermolecular bonding is van der walls*

Non-molecular

- COVALENT
- IONIC
- METALLIC

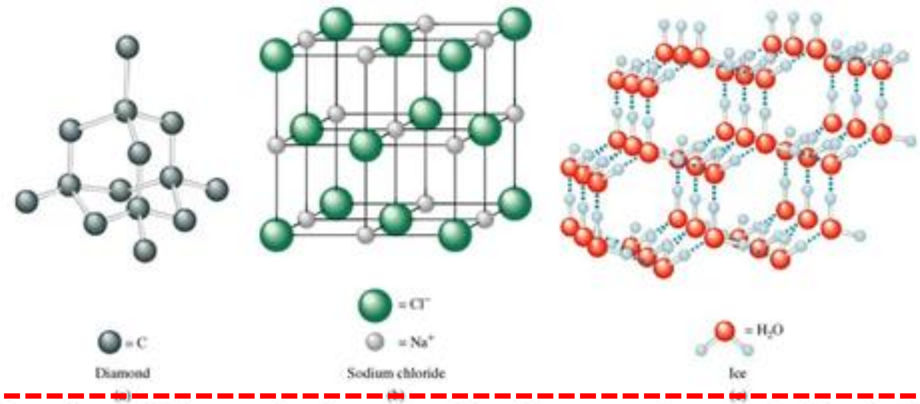
CLASSIFICATION OF SOLIDS BASED ON BONDING

- COVALENT
- IONIC
- METALLIC

1) metallic solids- delocalized nondirectional covalent bonding

2) network solids- atoms bond with strong directional covalent bonds that lead to giant molecules (networks)

3) Group 8 solids- noble gas elements are attracted by London dispersion forces



- Atomic solids- substances that have atoms at the lattice points
  - C, B, Si and all metals
- Ionic solids- have ions at the points of the lattice
  - NaCl
- Molecular solid- have discrete covalently bonded molecules at lattice points
  - ice

The **London** dispersion **force** is the weakest intermolecular **force**. The **London** dispersion **force** is a temporary attractive **force** that results when the electrons in two adjacent atoms occupy positions that make the atoms form temporary dipoles. This **force** is sometimes called an induced dipole-induced dipole attraction.

Structure and Bonding in Metals

- Metals-
  - high thermal conductivity
  - electric conductivity
  - Malleability
  - Ductility

Due to nondirectional covalent bonding

Bonding models for metals

- Indicates the bonding is STRONG and NONDIRECTIONAL
  - –difficult to separate metals atoms, but easy to move them

Alloys

A substance that contains mixture of elements and has metallic properties

- **Substitutional alloy-** some of the host metal atoms are *replaced* by other metal atoms of similar size
  - Brass (1/3 of copper atoms replaced with zinc)
  - Pewter (85%Sn, 7%Cu, 6%Bi, 2%At)

- **Interstitial alloy-** formed when some of the holes in a close packed metal structure are occupied by smaller atoms
  - Steel (carbon atoms into iron)

Approximate Strengths of Interactions between atoms

Bond Type	kJ/mol
Covalent Bond	250
Electrostatic	5
van der Waals	5
Hydrogen bond	20

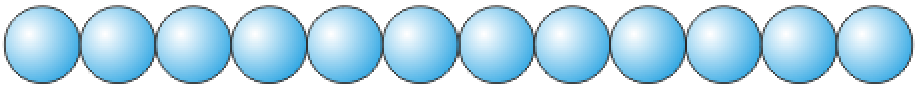
METALLIC

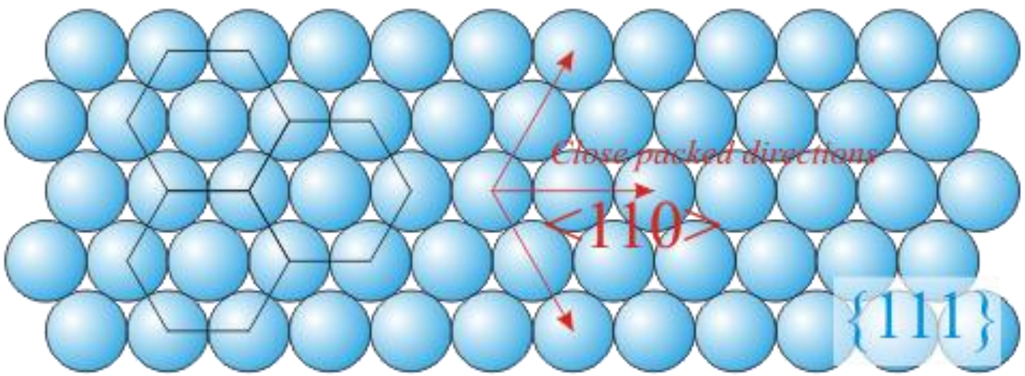
- Positive ions in a free electron cloud
- Metallic bonds are non-directional
- *Each atoms tends to surround itself with as many neighbours as possible!*
- *Usually* high temperature (wrt to MP) → BCC (Open structure)
- The partial covalent character of transition metals is a possible reason for many of them having the BCC structure at low temperatures

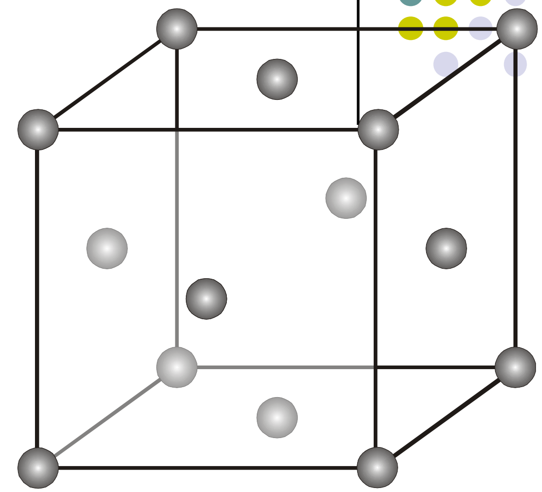
- FCC → Al, Fe (910 - 1410ºC), Cu, Ag, Au, Ni, Pd, Pt
- BCC → Li, Na, K , Ti, Zr, Hf, Nb, Ta, Cr, Mo, W, Fe (below 910ºC),
- HCP → Be, Mg, Ti, Zr, Hf, Zn, Cd
- Others → La, Sm Po, α-Mn, Pu

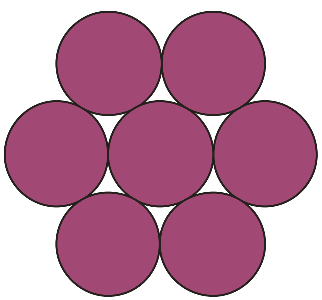
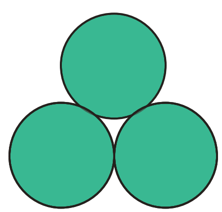
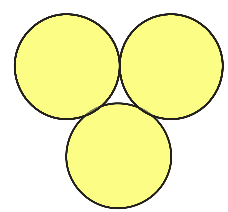
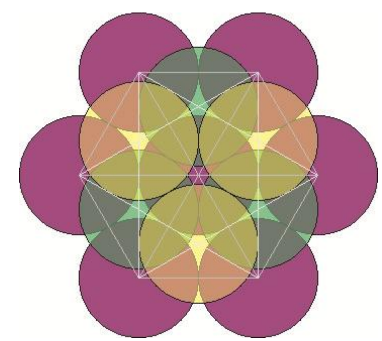
CLOSE PACKING

FCC





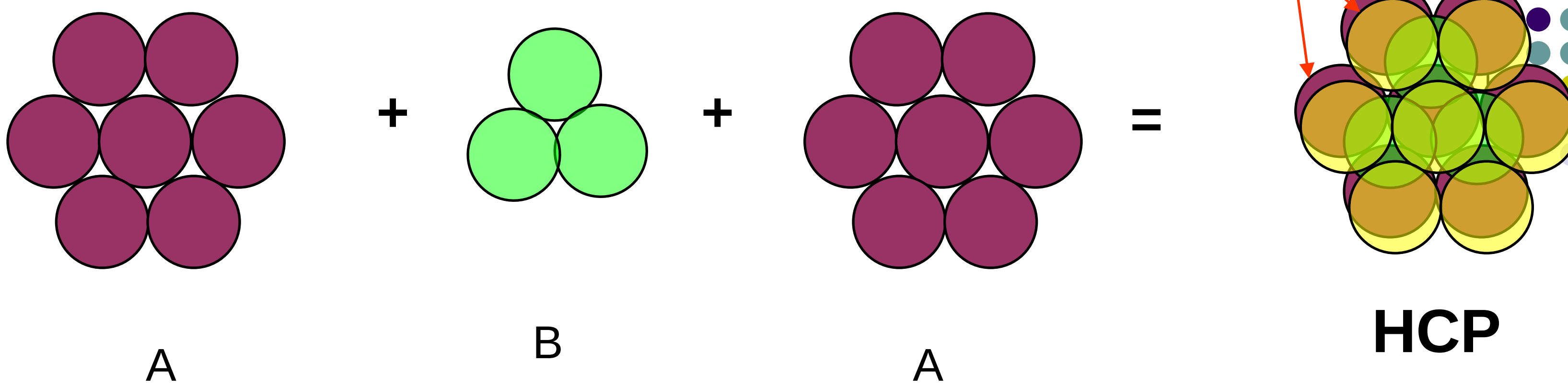


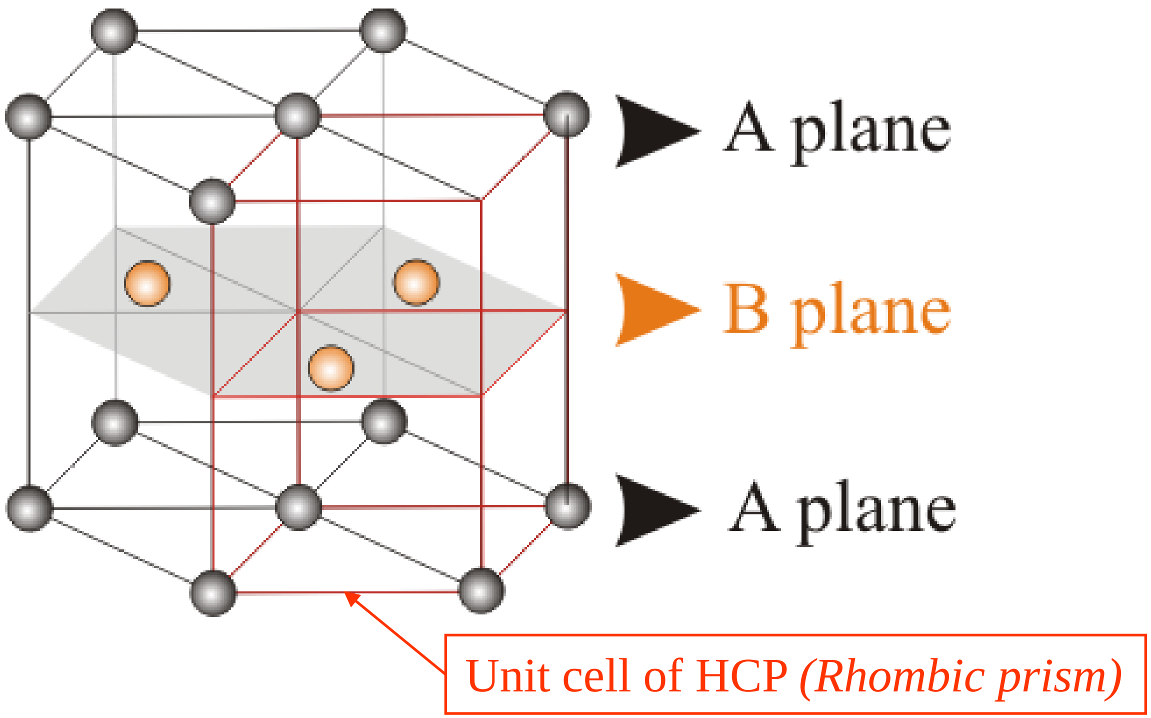
 +  +  = 

A B C **FCC**

Note: Atoms are coloured differently but are the same

HCP





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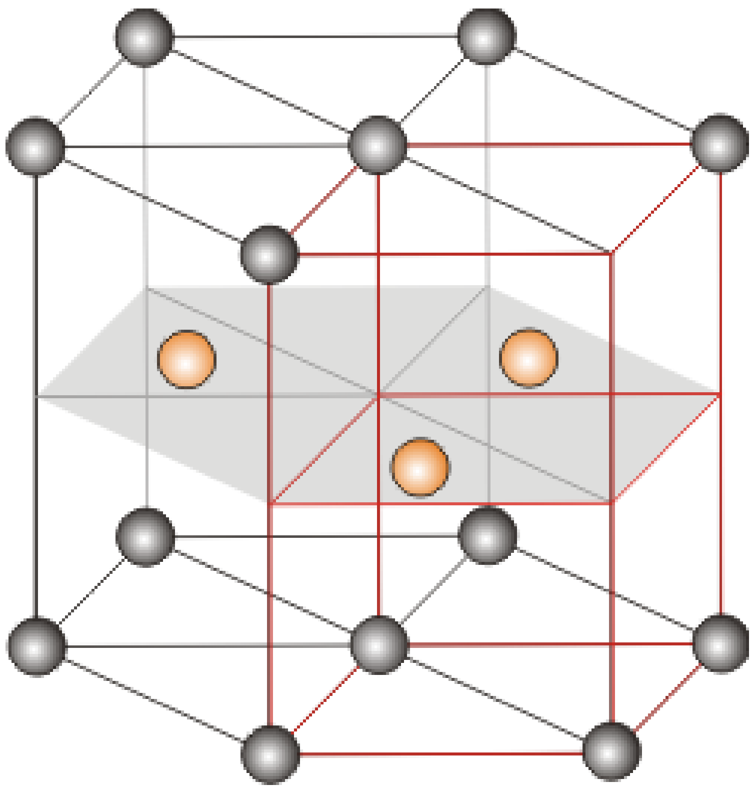
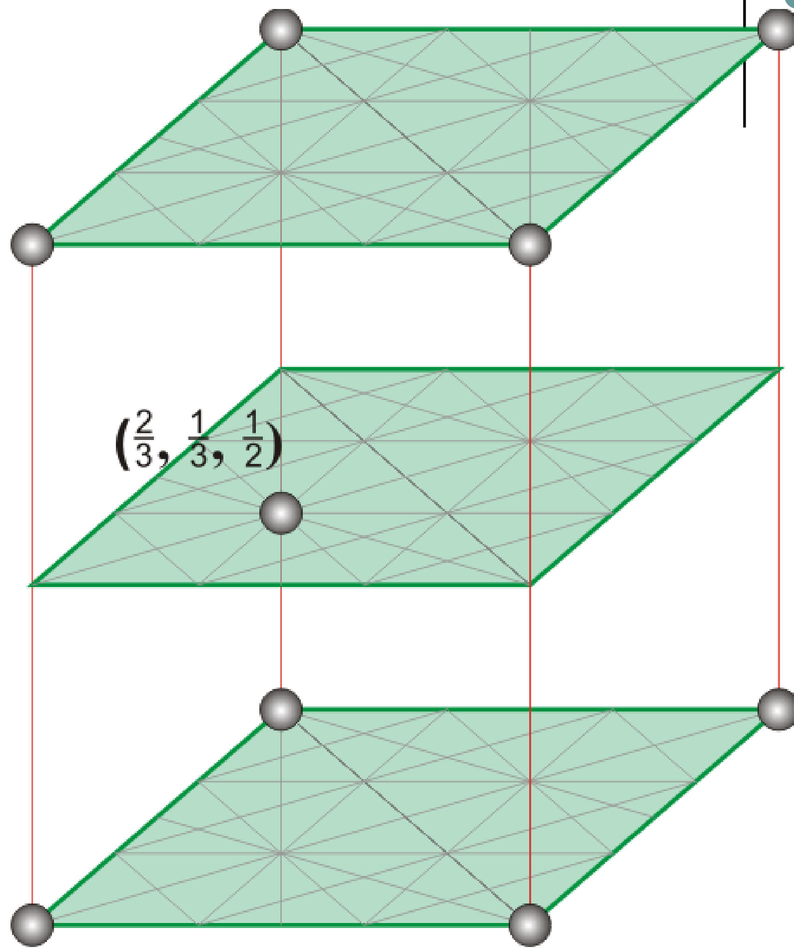




Atoms: (0,0,0), (⅔, ⅓,½)

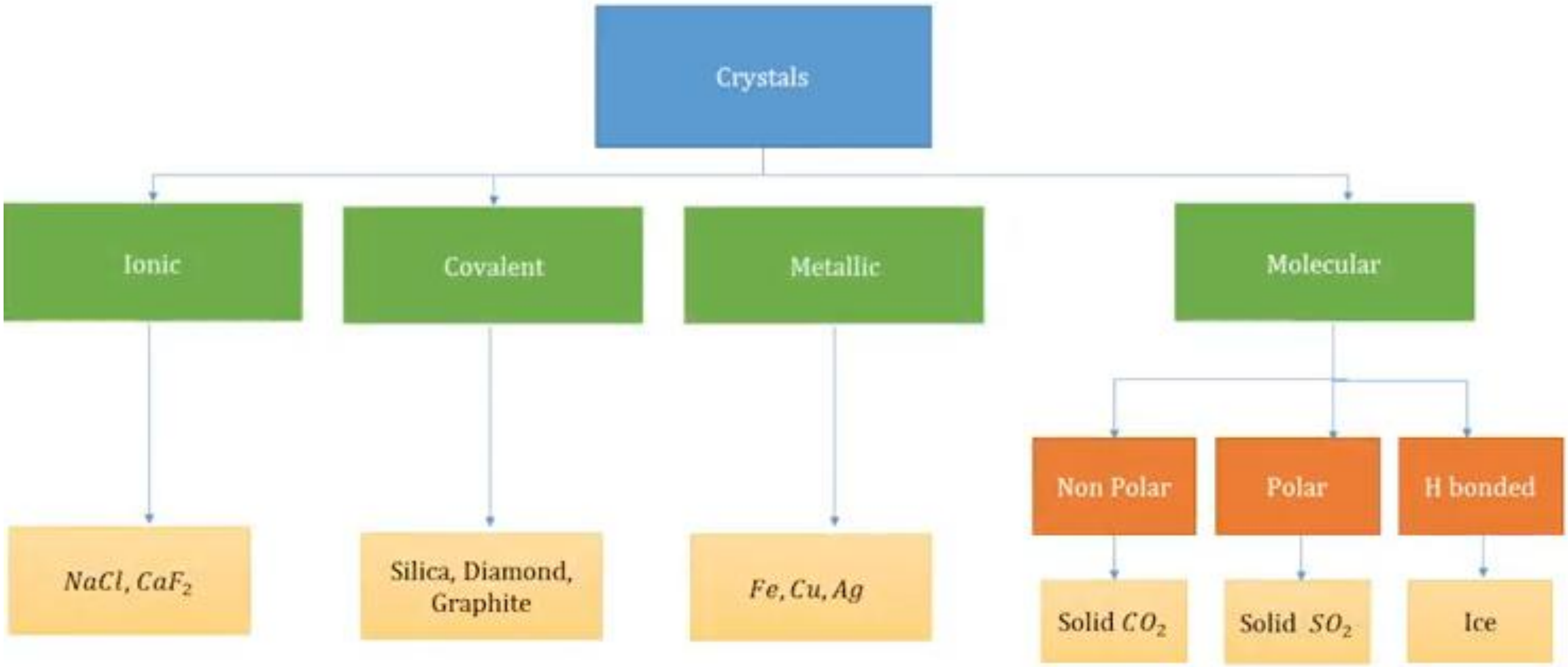
Note: diagrams not to scale

PACKING FRACTION / Efficiency

$$\text{Packing Fraction} = \frac{\text{Volume occupied by atoms}}{\text{Volume of Cell}}$$

	SC*	BCC*	CCP	HCP
Relation between atomic radius (r) and lattice parameter (a)	a = 2r	$\sqrt{3}a = 4r$	$\sqrt{2}a = 4r$	a = 2r $c = 4r\sqrt{\frac{2}{3}}$
Atoms / cell	1	2	4	2
Lattice points / cell	1	2	4	1
No. of nearest neighbours	6	8	12	12
Packing fraction	$\frac{\pi}{6}$	$\frac{\sqrt{3}\pi}{8}$	$\frac{\sqrt{2}\pi}{6}$	$\frac{\sqrt{2}\pi}{6}$
	= 0.52	= 0.68	= 0.74	= 0.74

** Crystal formed by monoatomic decoration of the lattice*



Crystals
Ionic
Covalent
Metallic
Molecular
Non Polar
Polar
H bonded
$NaCl, CaF_2$
Silica, Diamond, Graphite
Fe, Cu, Ag
Solid CO_2
Solid SO_2
Ice