

The Materials Zone

METAL
SEMI-METAL
SEMI-CONDUCTOR
INSULATOR

BAND STRUCTURE

ATOMIC

STATE / VISCOSITY

GAS

SOLID

LIQUID

LIQUID CRYSTALS

Solid Electrolytes

STRUCTURE

AMORPHOUS

QUASICRYSTALS

RATIONAL APPROXIMANTS

CRYSTALS

SIZE

NANO-QUASICRYSTALS

NANOCRYSTALS



Faceted glass objects are sometimes called crystals!

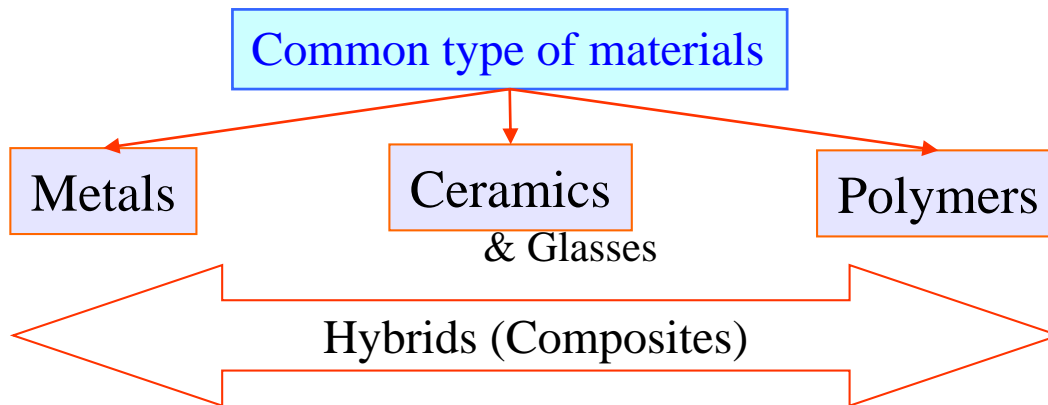
- ❑ Based on **state** (phase) a given material can be **Gas, Liquid** or **Solid**
Intermediate/coexistent states are also possible (i.e. clear demarcations can get blurred).
(Kinetic variables can also affect how a material behaves: e.g. at high strain rates some materials may behave as solids and as a liquid at low strain rates)
- ❑ Based on **structure** (arrangement of atoms/molecules/ions) materials can be **Crystalline, Quasicrystalline** or **Amorphous**.
Intermediate states (say between crystalline and amorphous; i.e. partly crystalline) are also possible. *Polymers are often only partly crystalline.*
- **Liquid Crystals** ('in some sense') are between Liquids and Crystals.
- Similarly **Solid Electrolytes** (also known as* **fast ion conductors** and **superionic conductors**) are also between crystals and liquids. These materials have a sublattice which is 'molten' and the ions in this sublattice are highly mobile (these materials are similar to liquid electrolytes in this sense).
- ❑ Based on **Band Structure** we can classify materials into **Metals, Semi-metals, Semiconductors** and **Insulators**.
- Based on the **size** of the entity in question we can **Nanocrystals, Nanoquasicrystals** etc.

One way of classification does not interfere with another

- ❑ From a *state* perspective we could have a **liquid**, which is a **metal** from the *band structure/conductivity perspective*
→ *Hg is liquid metal at room temperature.*
- ❑ Or we could have a **metal** (*band structure viewpoint*), which is **amorphous** (*structural viewpoint (atomic ordering)*)
→ *ZrTiCuNiBe bulk metallic glass.*
- ❑ Or we could have a **ferromagnetic** material (*from spontaneous spin alignment point of view- a physical property*), which is **amorphous** (e.g.) (*structural viewpoint*)
→ *amorphous Co-Au alloys are ferromagnetic.*

A Common Description

- ❑ Let us consider the common types of *Engineering Materials*.
- ❑ These are **Metals**, **Ceramics**, **Polymers** and various types of **composites** of these.
- ❑ **A composite** is a combination of two or more materials which gives a certain benefit to at least one property → A comprehensive classification is given in the next slide. The term **Hybrid** is a superset of composites.
- ❑ The type of atomic entities (ion, molecule etc.) differ from one class to another, which in turn gives each class a *broad 'flavour'* of properties.
 - Like metals are usually ductile and ceramics are usually hard & brittle
 - Polymers have a poor tolerance to heat, while ceramics can withstand high temperatures
 - Metals are opaque (in bulk), while silicate glasses are transparent/translucent
 - Metals are usually good conductors of heat and electricity, while ceramics are poor in this aspect.
 - If you heat semi-conductors their electrical conductivity will increase, while for metals it will decrease
 - Ceramics are more resistant to harsh environments as compared to Metals
- ❑ **Biomaterials** are a special class of materials which are compatible with the body of an organism ('**biocompatible**'). Certain metals, ceramics, polymers etc. can be used as biomaterials.



Diamond is poor electrical conductor but a good thermal conductor!! (phonons are responsible for this)

Materials

Monolithic

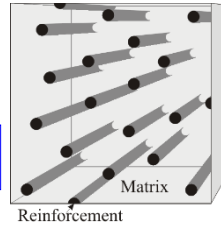
Metals
(& Metallic Alloys)

Ceramics and ceramic alloys
& Glasses

Polymers (& Elastomers)

Hybrids

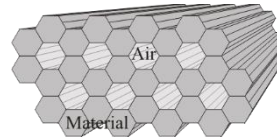
Composite



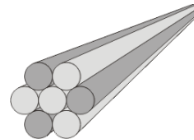
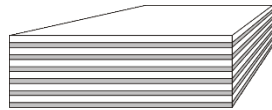
Sandwich



Lattice



Segment



Composites: have two (or more) solid components; usually one is a matrix and other is a reinforcement

Sandwich structures: have a material on the surface (one or more sides) of a core material

Lattice* Structures: typically a combination of material and space (e.g. metallic or ceramic forms, aerogels etc.).

Segmented Structures: are divided in 1D, 2D or 3D (may consist of one or more materials).

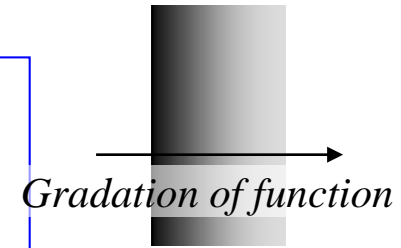
Hybrids are designed to improve certain properties of monolithic materials

Classification of composites.

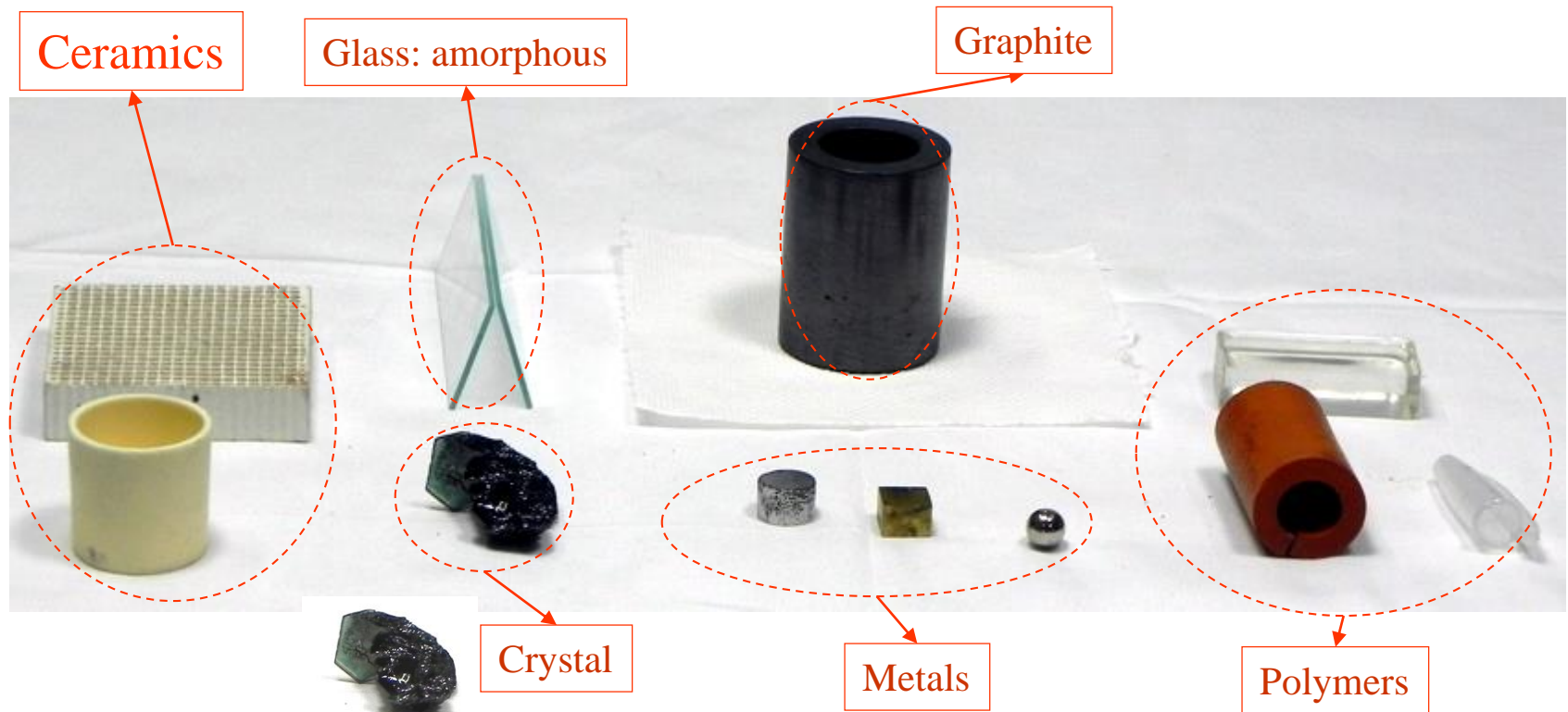
- Based on the matrix: metal matrix, ceramic matrix, polymer matrix.
- Based on the morphology of the reinforcement: particle reinforced (0D), fiber reinforced (1D), laminated (2D).

What are functionally graded materials?

- In functionally graded materials (FGM) the property varies from one side of the material (structure) to the other.
- E.g the outer surface may be made hard and abrasion resistant, while the interior could be made tough.
- The gradation in function could be obtained by composition changes, microstructure differences (via heat treatment), etc.



Common materials: *with various 'viewpoints'*



Common materials: *examples*

- ❑ Metals and alloys
 - Cu, Ni, Fe, NiAl (intermetallic compound), Brass (Cu-Zn alloys).
- ❑ Ceramics & glasses (usually oxides, nitrides, carbides, borides)
 - Oxides (Alumina (Al_2O_3), Zirconia (Zr_2O_3)), Nitrides (Si_3N_4), Borides (MgB_2), Carbides (SiC)).
- ❑ Polymers (thermoplasts, thermosets) (Elastomers)
 - Polythene, Polyvinyl chloride, Polypropylene.

Based on Electrical Conduction

- ❑ Conductors ➤ Cu, Al, NiAl
- ❑ Semiconductors ➤ Ge, Si, GaAs
- ❑ Insulators ➤ Alumina, Polythene* (*also called 'dielectrics'*).

Based on Ductility (*at room temperature ~25 °C*)

- ❑ Ductile ➤ Metals, Alloys.
- ❑ Brittle ➤ Ceramics, Inorganic Glasses, Ge, Si.

MATERIALS SCIENCE & ENGINEERING

Science of Metallurgy

- Thermodynamics
- Kinetics

PHYSICAL

- Structure
- Physical Properties

MECHANICAL

- Deformation Behaviour

ELECTRO-CHEMICAL

- Corrosion

TECHNOLOGICAL

- Extractive
- Casting
- Metal Forming
- Welding
- Powder Metallurgy
- Machining

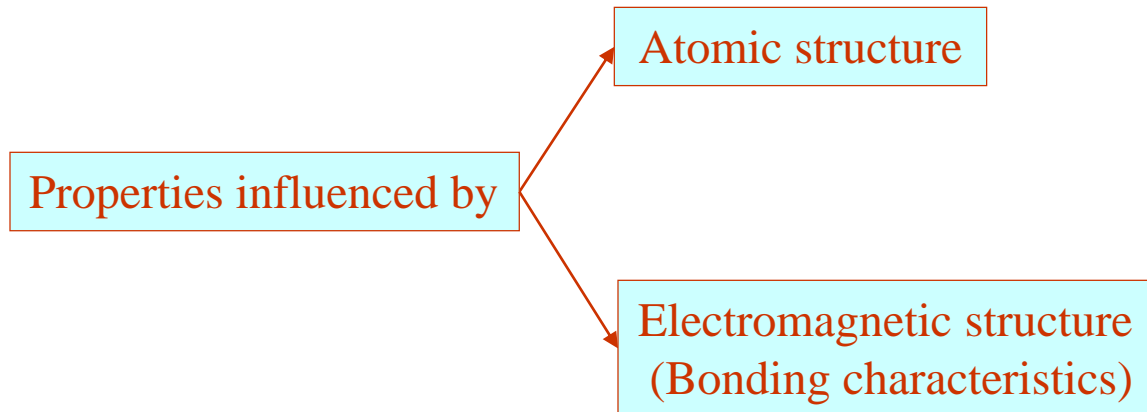
❑ Properties of a material are determined by two important characteristics*:

➤ Atomic structure

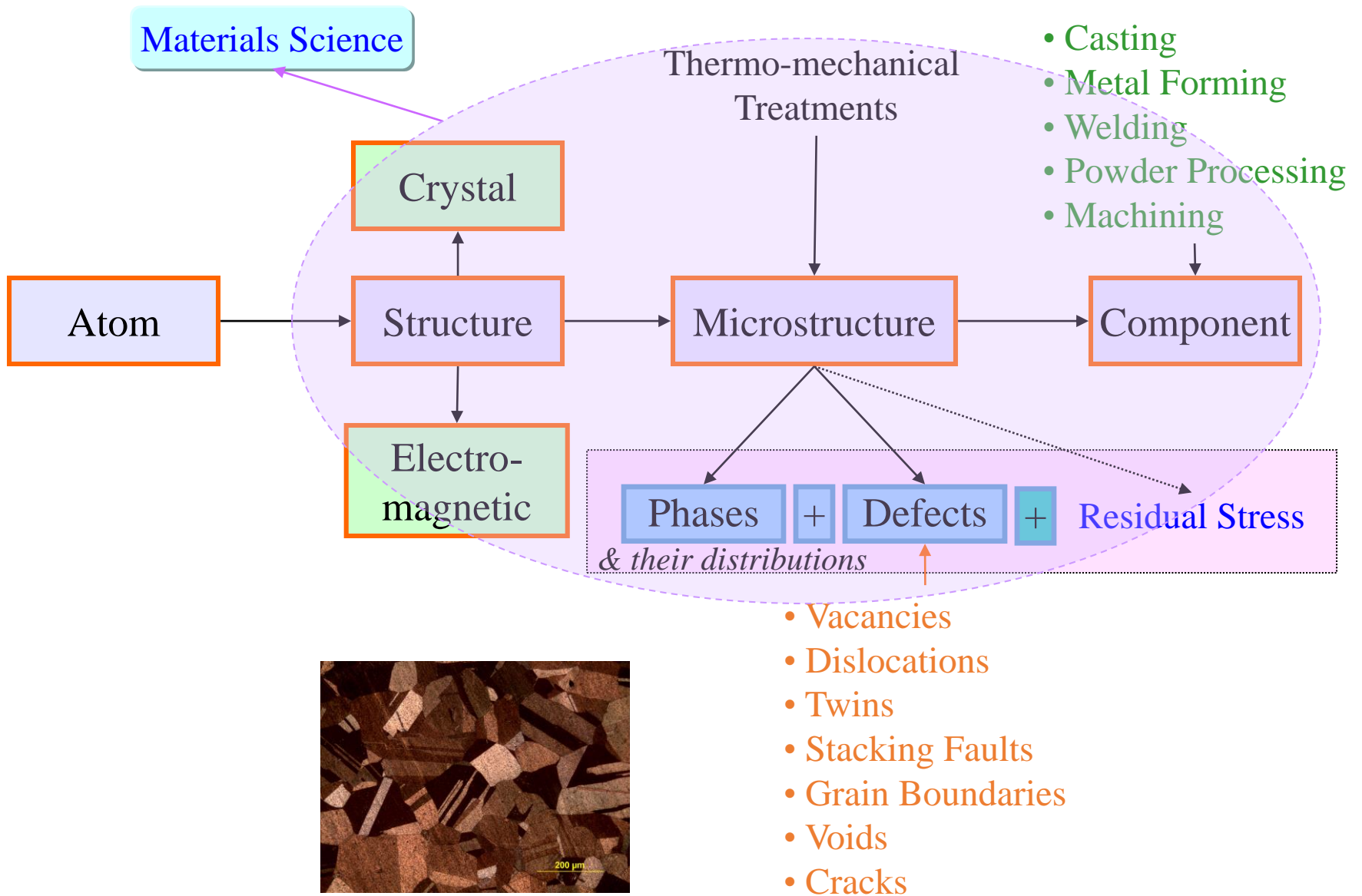
(The way atoms, ions, molecules arranged in the material).

➤ Electromagnetic structure – the bonding character

❑ *Essentially, the electromagnetic structure and processing determine the atomic structure.*



- ❑ In the next three slides we will traverse across lengthscales to demarcate the usual *domain of Materials Science*.
- ❑ Many of the terms and concepts in the slide will be dealt with in later chapters.
- ❑ As we shall see the scale of **Microstructures** is very important and in some sense Materials Scientists are also '*Microstructure Engineers*'!
(Material scientists are **microstructure engineers** who 'worry' about **mechanisms**).
- ❑ There could be issues involved at the scale of the component (i.e. design of the component or its meshing with the remainder of the system), which are traditionally not included in the domain of Materials Science.
 - The inherent resistance of the material to cracks (and stress concentrations) would typically be of concern to materials scientists and not the design of the component.



Processing determines shape and microstructure of a component

❑ Structure could imply two types of structure:

➤ Crystal structure

➤ Electromagnetic structure

▪ *Fundamentally these aspects are two sides of the same coin*

❑ Microstructure can be defined as:

(Phases* + Defect Structure + Residual Stress) *and their distributions*

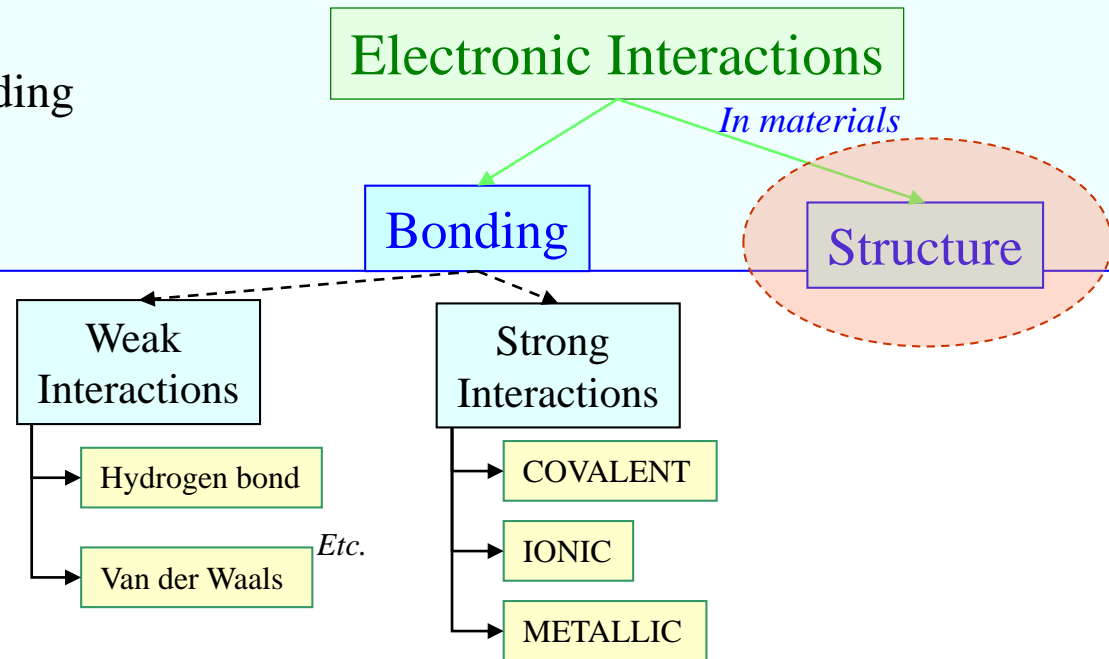
❑ Microstructure can be 'tailored' by thermo-mechanical treatments

❑ A typical component/device could be a *hybrid* with many materials and having *multiple microstructures*

E.g. a pen cap can have plastic and metallic parts

What determines the properties of materials?

- ❑ There are **microstructure 'sensitive' properties** (often called structure sensitive properties) and microstructure **insensitive** properties.
- ❑ ➤ **Microstructure 'sensitive' properties** → Yield stress, hardness, Magnetic coercivity...
- ❑ ➤ **Microstructure insensitive properties** → Density, Elastic modulus...
- ❑ Hence, one has to keep in focus:
 - Atomic structure
 - Electromagnetic structure/Bonding
 - Microstructureto understand the properties.



- ❑ From an alternate perspective:
Electronic interactions are responsible for most the material properties.
From an understanding perspective this can be broken down into Bonding and Structure.

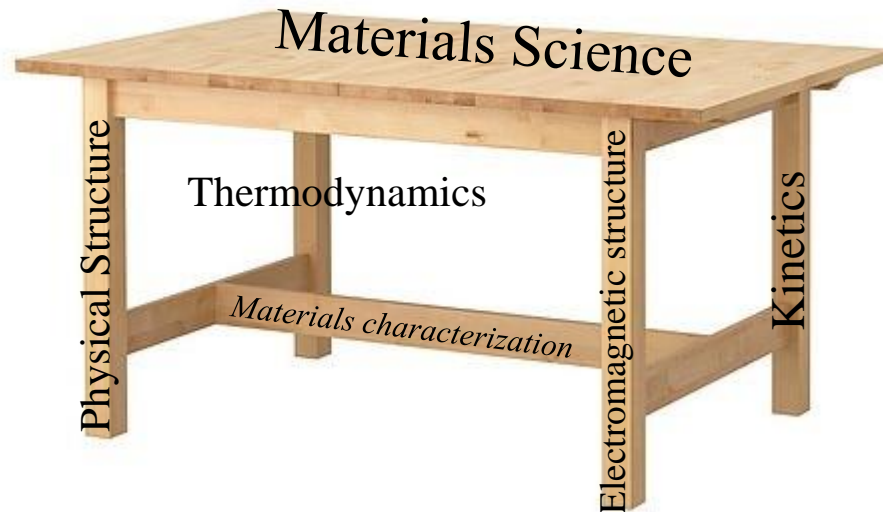
Effect of Bonding on properties: a broad flavour

- ❑ Two important contributing factors to the properties of materials is the nature of bonding and the atomic structure.
- ❑ Both of these are a result of electron interactions and resulting distribution in the material.
- ❑ Note: the energies listed in the table below are approximate.

Bond	Bond Energy eV	Melting point	Hardness (Ductility)	Electrical Conductivity	Examples
Covalent	~1-10	High	Hard (poor)	Usually Low	Diamond, Graphite, Ge, Si
Ionic	~5-15	High	Hard (poor)	Low	NaCl, ZnS, CsCl
Metallic	~0.5-8	Varies	Varies	High	Fe, Cu, Ag
Van der Waals	~0.05-0.5	Low	Soft (poor)	Low	Ne, Ar, Kr
Hydrogen	~0.05-1.5	Low	Soft (poor)	Usually Low	Ice

What are the four founding pillars of materials science?

- ❑ The four pillars of Materials Science and Engineering are (*a simplified view!!!*):
 - Physical structure → Atomic structure (+ Microstructure)
 - Electromagnetic Structure → Electronic and Magnetic structure
 - Thermodynamics
 - Kinetics
- ❑ If one gains understanding of these four pillars, one can comprehend most aspects of Material behaviour and engineer materials for applications.
- ❑ The subject of Materials Engineering can be envisaged as a confluence of Physics, Chemistry, Biology, Mechanical Engineering, etc.

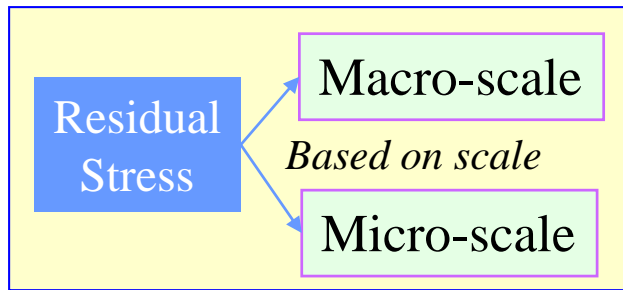


Summary

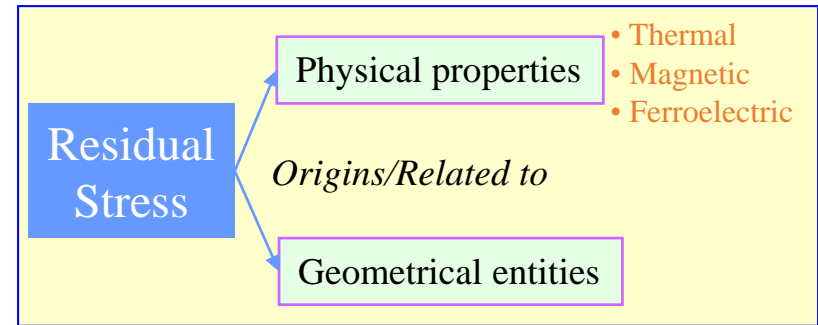
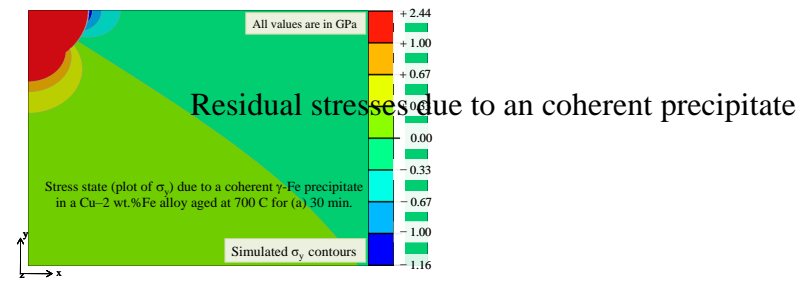
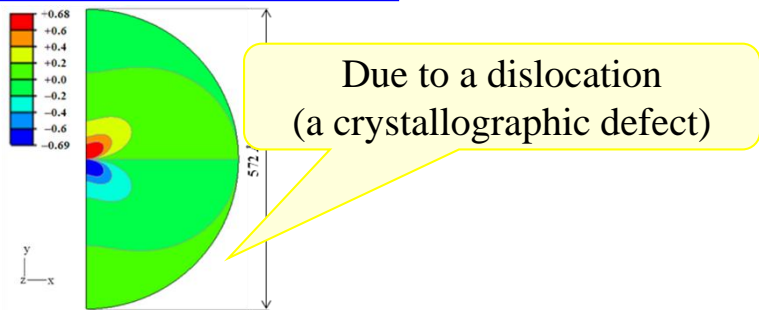
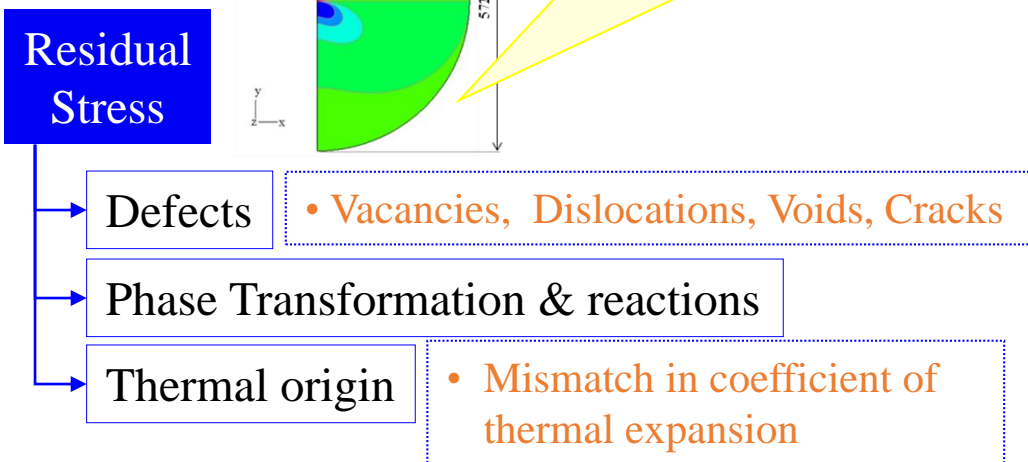
- ❑ The goal of **Materials Science and Engineering** is to design materials with a certain set of **properties**, which gives a certain desired **performance**. Using suitable **processing techniques** the material can be synthesized and processed. The processing also determines the **microstructure** of the material.
- ❑ The material is expected to be used in a structure (e.g. bridge, truss, bolt) or a component (e.g. gear wheel, battery, computer chip, filament of a light bulb).
- ❑ To understand the microstructure the material scientist has to traverse across length scales and has to comprehend the defect structure in the material along with the phases and their distribution. The residual stress state in the material is also very important.
- ❑ Common types of materials available to an engineer are: **Metals, Ceramics and Polymers**. A **hybrid** made out of these materials may serve certain engineering goals better.
- ❑ Materials are also classified based on **Band Structure (Metals, Semi-metals, Semiconductors, Insulators)** or **Atomic Structure (Crystals, Quasicrystals, Amorphous phases)**.

What is 'residual stress' and how can it arise in a material (/component)?

- ❑ The stress present in a material/component in the absence of external loading/forces or constraints (i.e. in a **free-standing** body) is called residual stress.
- ❑ Residual stress can 'be' in the macro-scale or micro-scale and can be deleterious or beneficial depending on the context (diagram below).
- ❑ Residual stress may have multiple origins as in the diagrams below.



- Residual stress can be beneficial (+) or detrimental (-)
- E.g.
 - ⇒ - Stress corrosion cracking
 - ⇒ + Residual Surface Stress in toughened glass

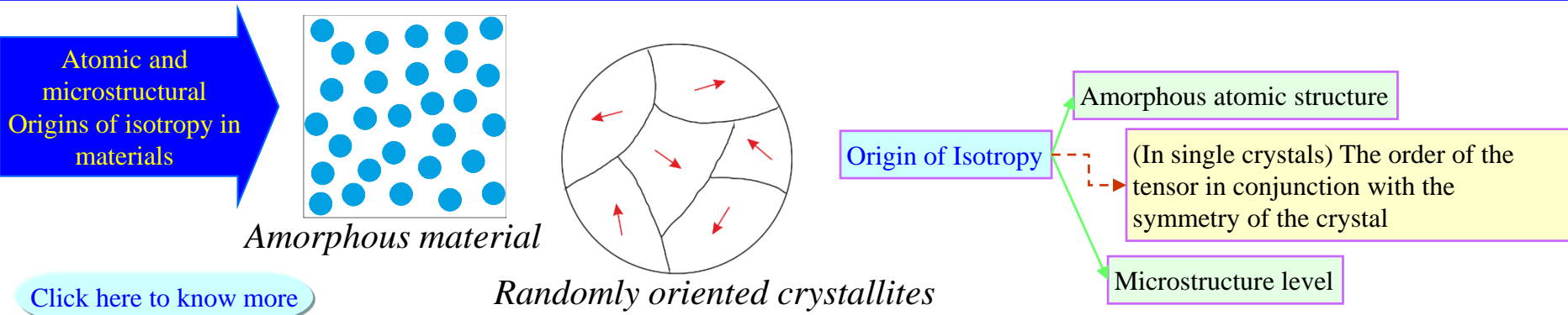


What is the difference between homogeneous and isotropic?

- ❑ In a **homogeneous material** the properties do not change from one position to another. A piece of Cu or an solid solution of Ni in Cu are examples of homogeneous materials, wherein the composition and structure is the same at each point in the material.
- ❑ On the other hand in **heterogeneous material**, the material composition or structure varies from one place to another, which further implies a change in the properties (from one place to another).
- ❑ From a practical standpoint, we usually consider a 'lengthscale' at which the homogeneity is considered. E.g. there might be some compositional variations (and hence local property variations) at the level of a few nanometers, but at the lengthscale of micrometers (microns) these heterogeneities even out and material can be considered homogeneous.
- ❑ In an isotropic material a given property is NOT direction dependent, while in an anisotropic a given property is direction dependent. A material could be isotropic w.r.t. to one property, while could be anisotropic with respect to another. E.g. A single crystal of Cu is isotropic w.r.t. electrical conductivity— a second order tensor property; while is anisotropic w.r.t. elastic modulus— a fourth order tensor property.

How can isotropy arise in a material? (or) How can a material be isotropic?

- ❑ A material can be isotropic (with respect to a property) in three ways.
- ❑ These can arise from:
 - (i) **structure at the atomic level**,
 - (ii) **structure at the microstructural level** or
 - (iii) **tensorial nature of the property** in conjunction with the symmetry of structure (& Neumann's principle). These are explained below.
- (i) The material is disordered (amorphous/glass) and hence all directions are equivalent in the material (on an average). Such a material is truly isotropic.
- (ii) The material may be crystalline, but the crystallites may be oriented randomly (like in a polycrystal) and hence at the lengthscale of the material (which is assumed to be much larger than the crystallite/grain size) the material *appears* to be isotropic.
- (iii) Even single crystals can be isotropic w.r.t. a given property. This depends on the tensorial nature of the property (i.e. is it a second order tensor or a higher order tensor), in conjunction with the symmetry of the crystal (& the Neumann's principle). This point is difficult to explain here and readers may click on the link at the bottom of the page.



ATOMIC STRUCTURE & INTERATOMIC BONDING

BONDING

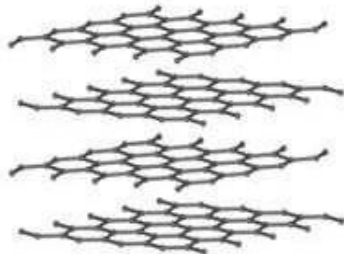
The atomic structures and interatomic bonding directly define the properties of materials

Graphite vs Diamond

Graphite



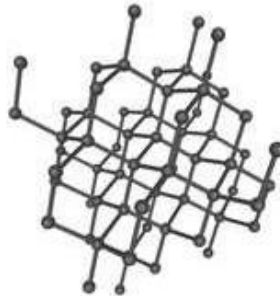
Dull, opaque, soft, common



Diamond



Brilliant, transparent, hard, rare



Example: Carbon as graphite and diamond

FUNDAMENTAL CONCEPTS

Atom consist of:

- ◆ Nucleus (core): protons + neutrons
- ◆ Electrons (e^-)

- Atomic Number (Z):

?

- Atomic Mass (A):

?

- Isotope: **Isotopes** are atoms of the same element that have different numbers of neutrons but the same number of protons and electrons

- Atomic Weight:

?

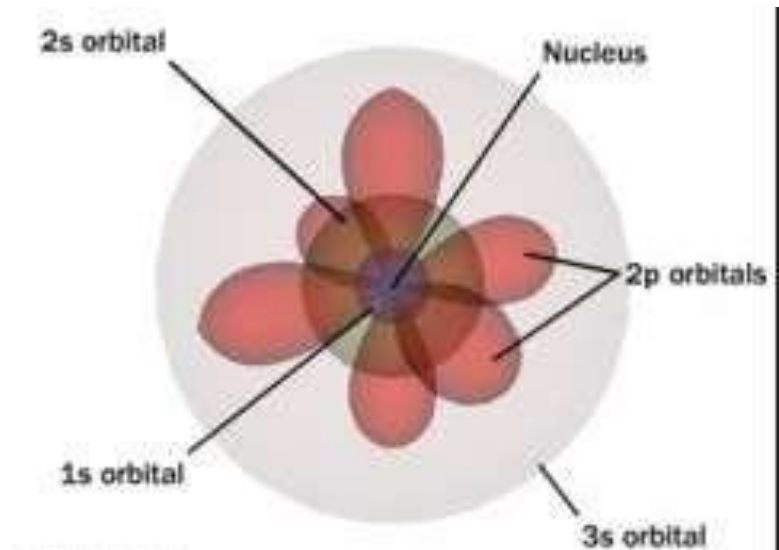
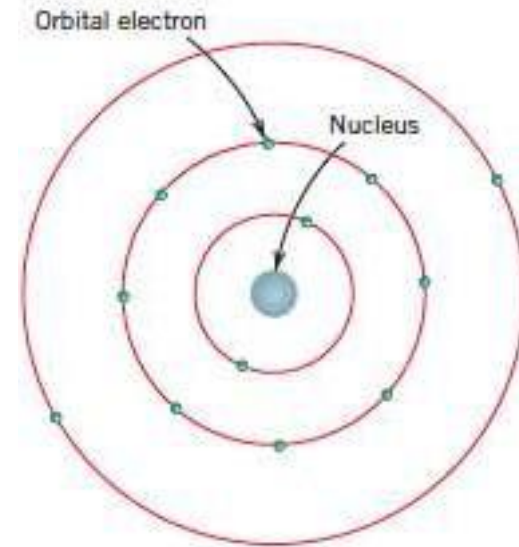
- Atomic Mass Unit (amu):

?

ELECTRONS in ATOMS – ATOMIC MODELS

Bohr Atomic Model:

- ◆ Electrons revolve around nucleus in certain orbitals



ELECTRONS in ATOMS – QUANTUM NUMBERS

- Every electron in an atom is characterized by 4 parameters → **Quantum Numbers** ($n, l, m, \text{no. of electrons}$)
- ' n ' → no. of *shells*
Value of ' n ' = 1, 2, 3 & 4
- ' l ' → no. of *sub-shells*
Value of ' l ' = 0, 1, 2 & 3 or s, p, d & f

value of ' n '	value of ' l '	Name of Subshell
1	0 (s)	1s
2	0 (s)	2s
	1 (p)	2p
3	0 (s)	3s
	1 (p)	3p
	2 (d)	3d
4	0 (s)	4s
	1 (p)	4p
	2 (d)	4d
	3 (f)	4f

ELECTRONS in ATOMS – QUANTUM NUMBERS

- 'm' → no. of *electron orbitals* in *each sub-shell*
- Each electron orbital → max **2** electrons

Subshell	No. of Orbitals (m)	Max No. of Electrons
s	1	2
p	3	6
d	5	10
f	7	14

Shell No.:	Name of Subshell + Max Electrons
1	1s ²
2	2s ²
	2p ⁶
3	3s ²
	3p ⁶
	3d ¹⁰
4	4s ²
	4p ⁶
	4d ¹⁰
	4f ¹⁴

ELECTRONS in ATOMS – ELECTRON CONFIGURATIONS

- **Pauli Exclusion Principle** → each electron state/electron orbital max **2** electrons

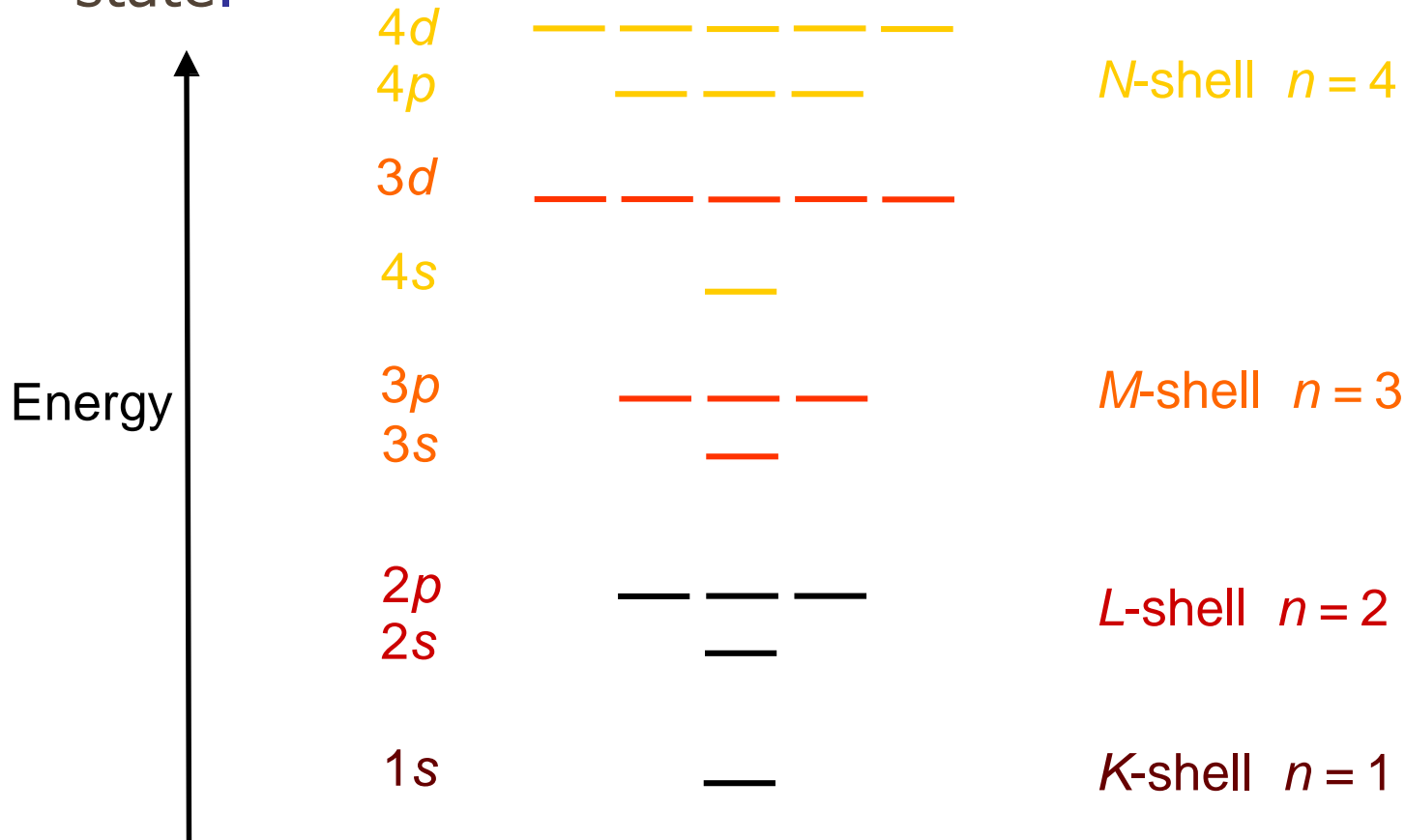
Subshell	No. of Orbitals (m)	Max No. of Electrons
s	1	2
p	3	6
d	5	10
f	7	14

Shell No.:	Name of Subshell + Max Electrons
1	1s ²
2	2s ²
	2p ⁶
3	3s ²
	3p ⁶
	3d ¹⁰
4	4s ²
	4p ⁶
	4d ¹⁰
	7

ELECTRONS in ATOMS – ELECTRON CONFIGURATIONS

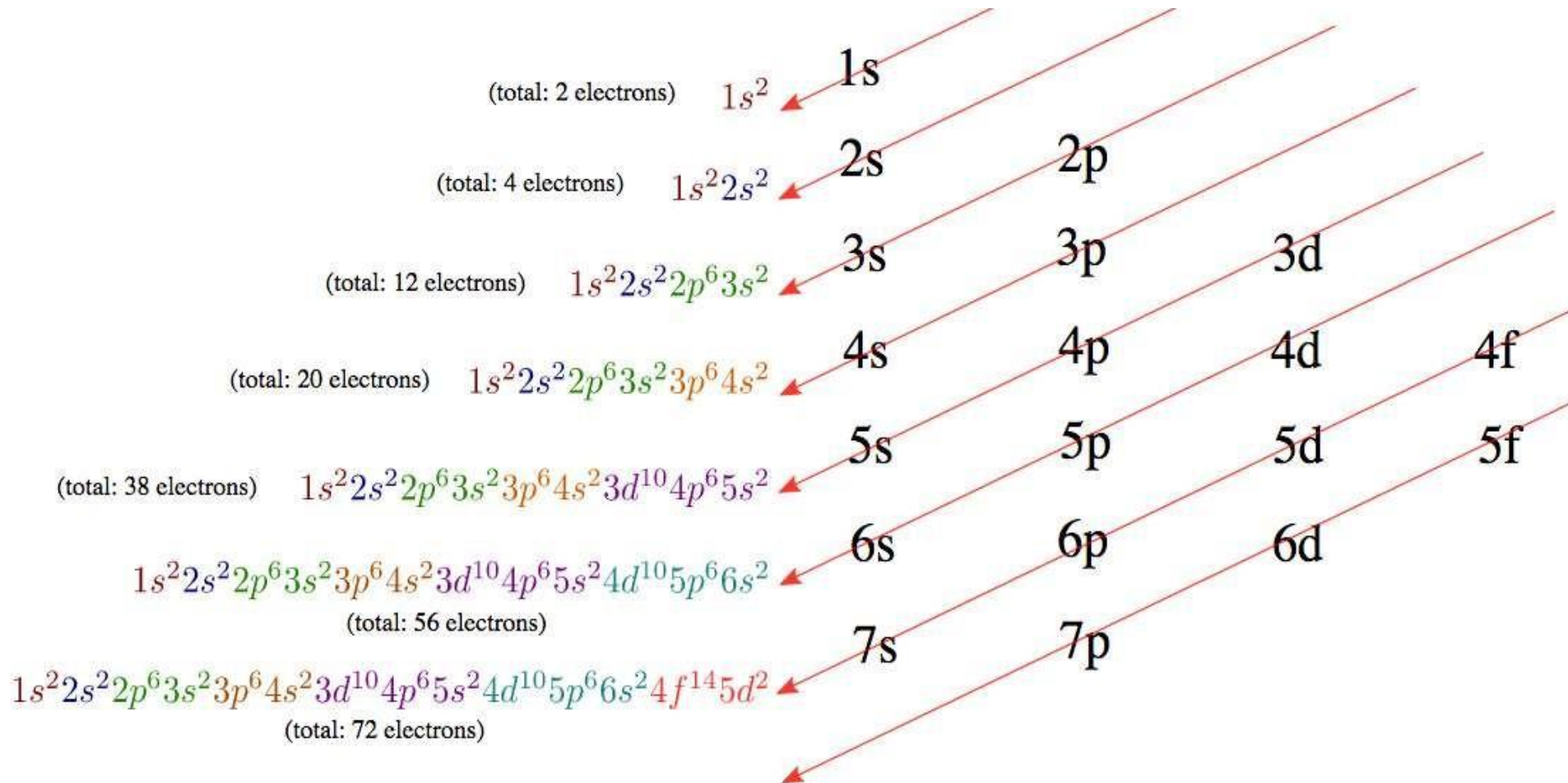
Electrons:

- have discrete energy states
- tend to occupy lowest available energy state.



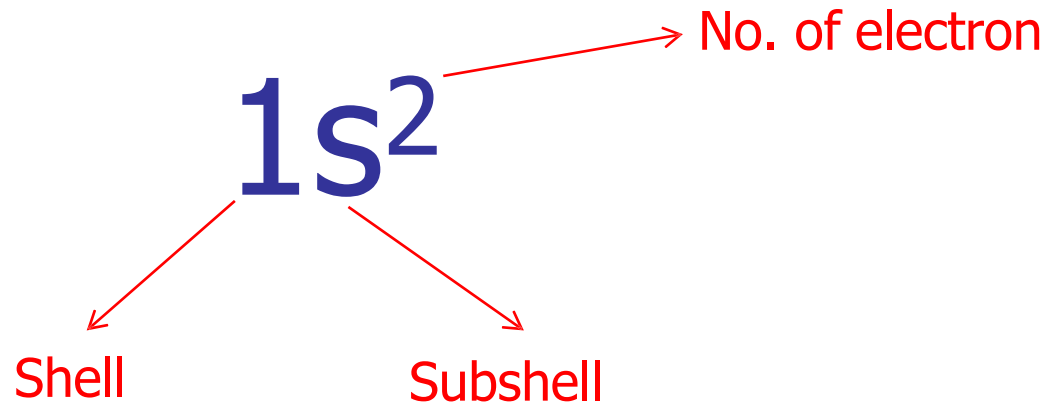
ELECTRONS in ATOMS – ELECTRON CONFIGURATIONS

Hafnium Diagonal Rule for Electron Configuration:



ELECTRONS in ATOMS – ELECTRON CONFIGURATIONS

- **Electron Configuration** → represents the way in which the electron states/electron orbitals are occupied.
- Notation (how to write) : **No. of electrons in each subshell indicate by a script after shell-subshell designation:**



- Examples:
 - Hydrogen (H), $Z=1 \rightarrow 1s^1$
 - Helium (He), $Z=2 \rightarrow 1s^2$
 - Lithium (Li), $Z=3 \rightarrow 1s^2 2s^1$

ELECTRONS in ATOMS – ELECTRON CONFIGURATIONS

Valence electron:

- Electrons that occupy outermost shell,
- Involve in bonding between atoms to form molecules,
- Physical & chemical properties of solids based on valence electron.

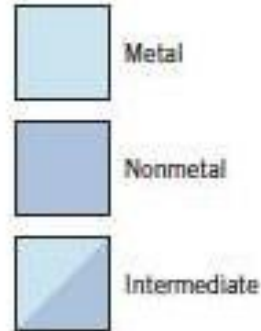
Stable electron configuration:

- Valence electron shell completely filled,
- Max no. of electron in outermost shell → 8 (as in Ne, Ar, Kr)

THE PERIODIC TABLE of ELEMENTS

IA		IIA												0			
1 H 1.0080																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305						VIII					13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.87	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.33	Rare earth series	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.2	76 Os 190.23	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.19	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	Actinide series	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (281)								

Key
 29 ← Atomic number
 Cu ← Symbol
 63.55 ← Atomic weight



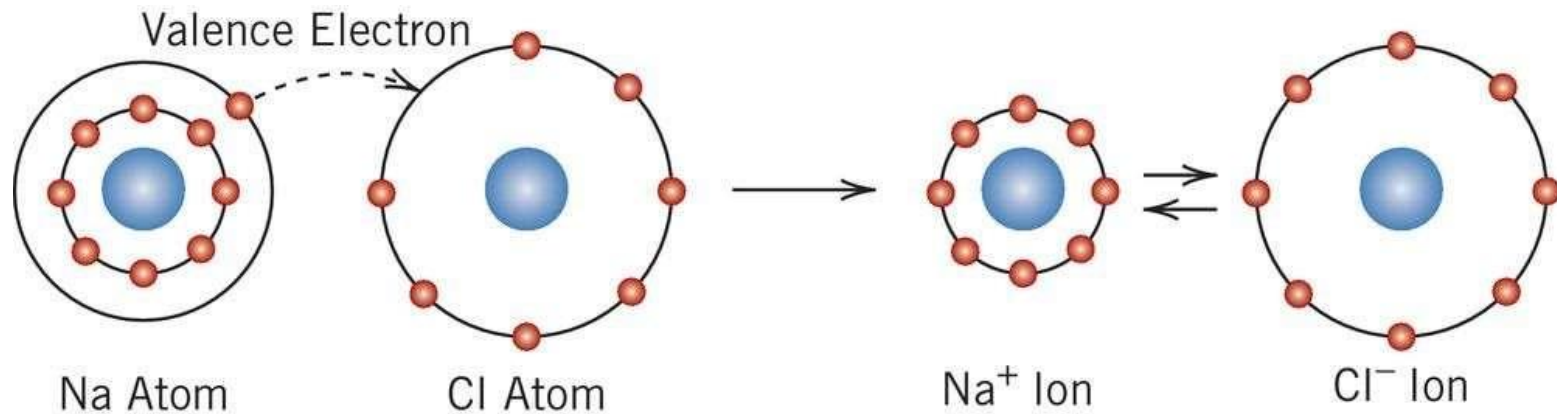
Rare earth series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinide series	89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

THE PERIODIC TABLE of ELEMENTS

- Element → Type of Atom that is distinguished by Its **Atomic Number**
- **Periodic Table of Elements** → Tabular Method of Displaying Elements
- **Same Column** → **Same valence electron** and **similar properties**
 - **Alkali Metal** → Group 1 (Li, Na, K, Rb, Cs): Soft, Low Density, Has **1** valence electron ↔ Very Reactive (React with halogen)
 - **Halogen** → Group VIIA (F, Cl, Br, I): Has **7** valence electrons ↔ Highly Reactive Gas (React with Alkali Metal)
 - **Noble Gas** → Group VIIIA (He, Ne, Ar, Kr, Xe): Odorless, Has **8** valence electrons ↔ Great Chemical Stability

1. Ionic Bonding

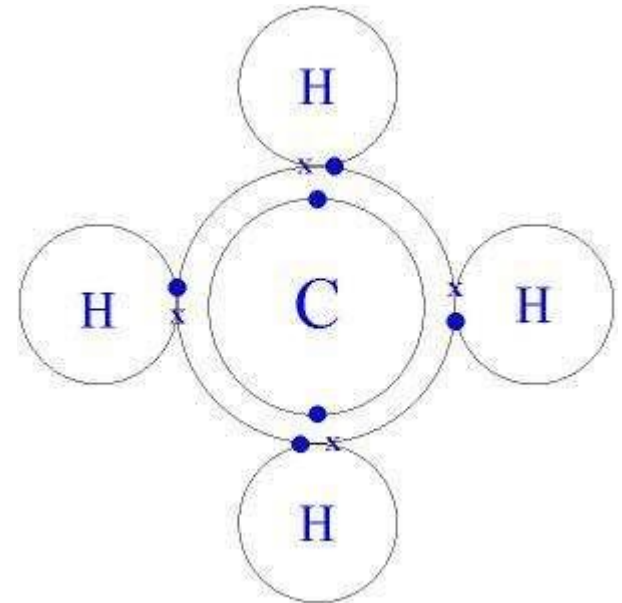
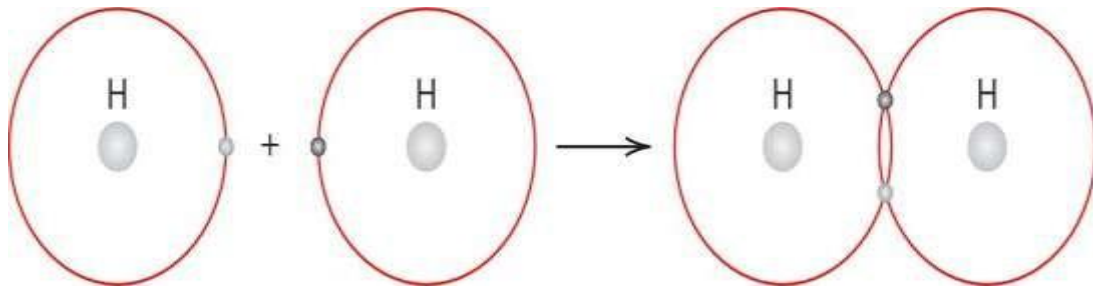
- metal + non-metal, electropositive + electronegative



PRIMARY INTERATOMIC BONDS

2. Covalent Bonding

- Non-metal + non-metal

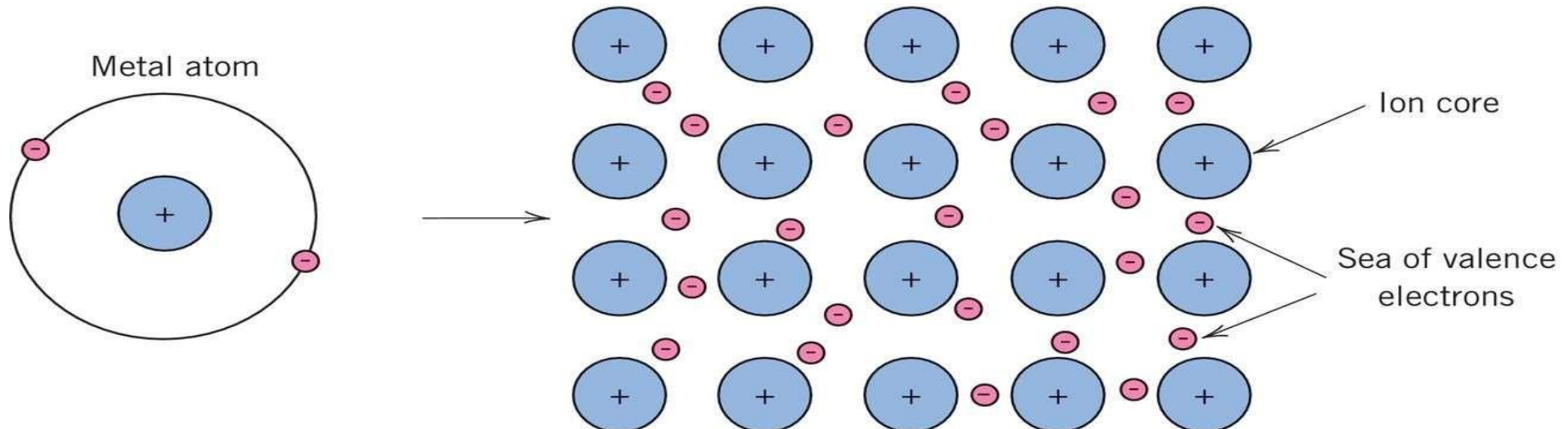


3. Metallic Bonding

- metal + metal

Metallic bonding can be understood as a collective interaction of a mobile electron fluid with metal ions. This type of bonds occurs in the structure of metals, that is, when the number of valence electrons is only a small fraction of the coordination number; then neither an ionic nor a covalent bond can be established.

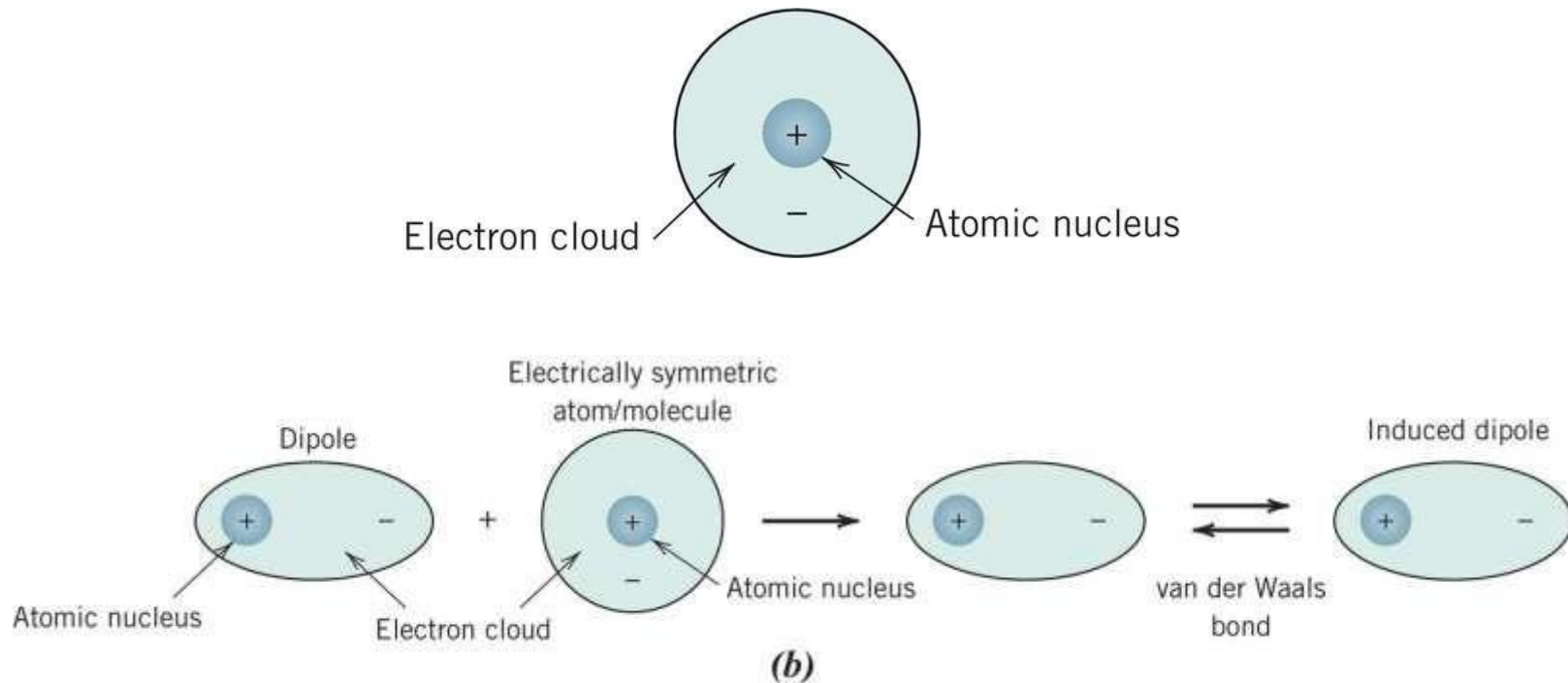
The metallic bond is somewhat weaker than the ionic and covalent bond.



SECONDARY BONDING

Arise due to atomic or molecular **dipoles**

1. Van der Waals bonding:



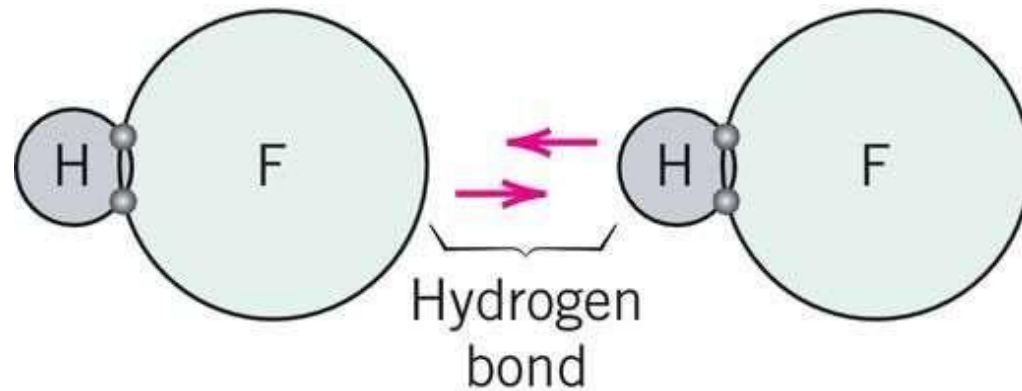
- **Van der Waals forces** (also known as London forces) are the residual attractive or repulsive forces between molecules or atomic groups that do not arise from a covalent bond, or electrostatic interaction of ions or of ionic groups with one another or with neutral molecules. Like hydrogen bonds, van der Waals forces rely on dipoles, a difference in charge between two molecules. But unlike hydrogen bonds the van der Waals dipole usually is not permanent, but transient.

Van der Waals forces are relatively weak compared to covalent bonds, but play a fundamental role in fields as diverse as supramolecular chemistry, structural biology, polymer science, nanotechnology, surface science, and condensed matter physics. Van der Waals forces define many properties of organic compounds, including their solubility in polar and non-polar media.

SECONDARY BONDING

Arise due to atomic or molecular **dipoles**

2. Hydrogen Bonding:



A **hydrogen bond** (or H-bond) results when a hydrogen atom that is covalently bound to an electronegative atom (e.g. O, N, S) is shared with another electronegative atom.

The hydrogen bond is often described as an electrostatic dipole-dipole interaction. However, it also has some features of covalent bonding: it is directional and strong, produces interatomic distances shorter than the sum of the van der Waals radii, and usually involves a limited number of interaction partners.

These hydrogen-bond attractions can occur between molecules (intermolecular) or within different parts of a single molecule (intramolecular). They are stronger than the van der Waals interactions, but weaker than covalent or ionic bonds. This type of bonds can occur in inorganic molecules such as liquid or solid water, in organic molecules or in macromolecules like DNA and proteins.

Hydrogen bonds in liquid water are constantly being made and broken. The lifetime of these single hydrogen bond is very short. Such broken hydrogen bonds will often simply reform.

Properties of metals - Melting Point

- metals have high melting points
- mercury is a liquid at room temperature
- tungsten has a melting point of 3422 degrees
- used in light bulbs and spacecraft parts



Properties of metals - Boiling Point

- in general metals have high boiling points
- it takes a great deal of energy to separate the cations and electrons



Properties of metals - Malleable

- metals can be hammered into sheets
- mobile parts of metallic bonds allow cations and delocalized electrons to slide past each other so metals are malleable and ductile
- delocalized electrons can shift allowing metallic bonds to remain intact



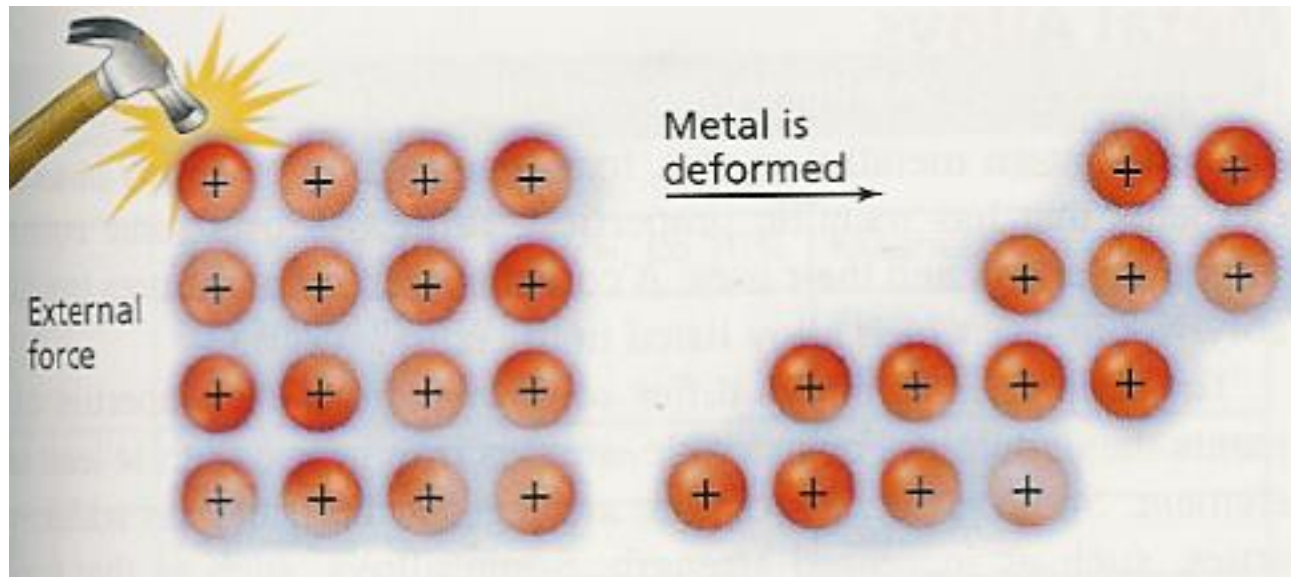


Figure 8-10

An applied force causes metal ions to move through delocalized electrons, making metals malleable and ductile.



Properties of Metals - Durable

- metals are durable because the metallic cations are mobile within the metal, but strongly attracted to the electrons
 - not easily removed
- strength and durability increase as the number of delocalized valence electrons increases



Properties of Metals - Conductors

- metals are good at conducting heat and electricity
 - charged electrons are able to move heat and charge from one place to another quickly



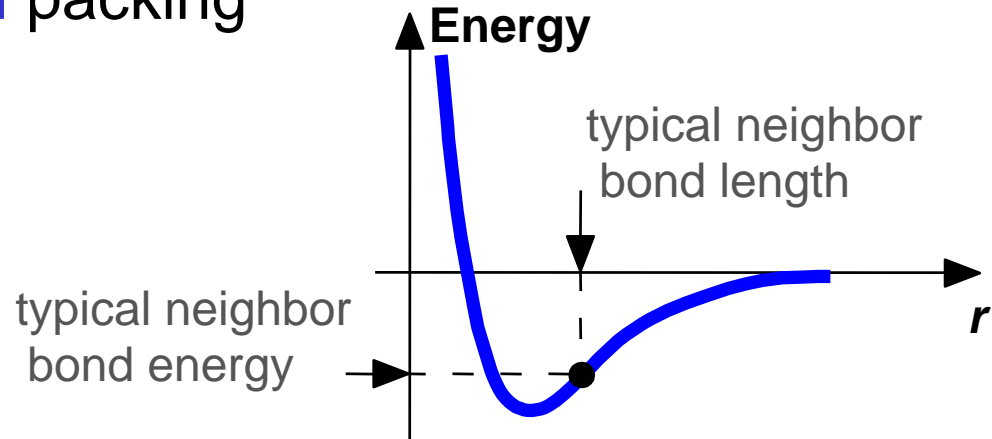
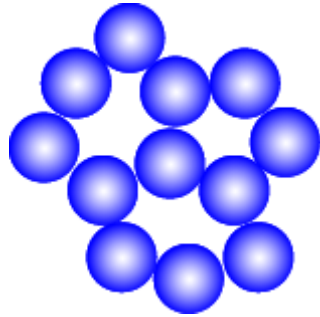
Properties of Metals - Luster

- delocalized electrons can interact with light so they reflect light
 - absorb and release photons (particles of light) and appear shiny

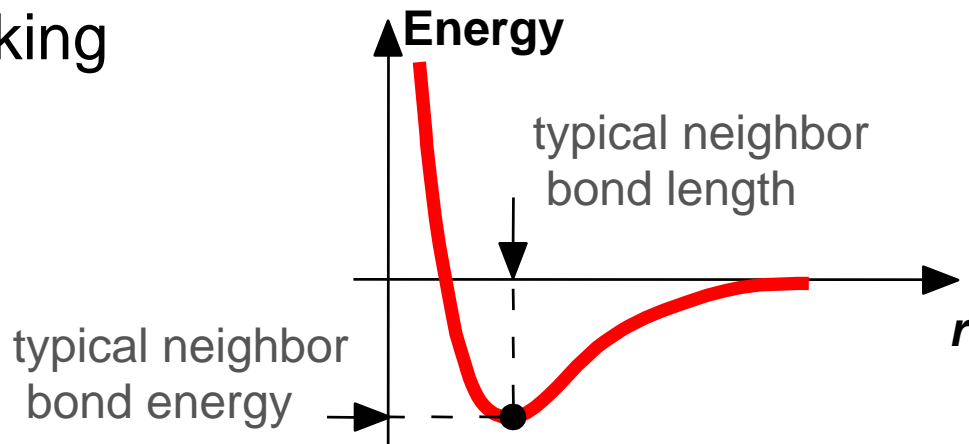
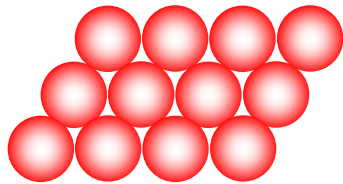


Energy and Packing

- Non dense, **random** packing



- Dense, **ordered** packing



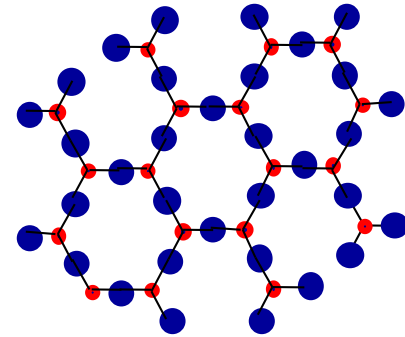
Dense, ordered packed structures tend to have lower energies.



Materials and Packing

Crystalline materials...

- atoms pack in periodic, 3D arrays
- typical of:
 - metals
 - many ceramics
 - some polymers



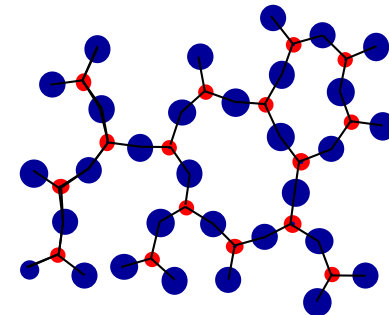
crystalline SiO₂

Adapted from Fig. 3.23(a),
Callister & Rethwisch 8e.

• **Si** • **Oxygen**

Noncrystalline materials...

- atoms have no periodic packing
- occurs for:
 - complex structures
 - rapid cooling



noncrystalline SiO₂

Adapted from Fig. 3.23(b),
Callister & Rethwisch 8e.

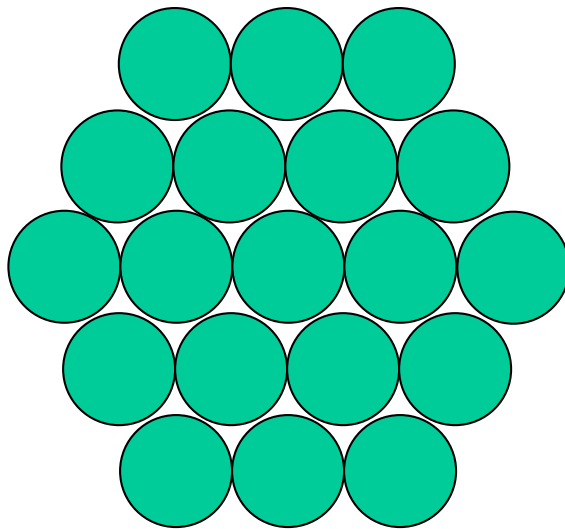
"Amorphous" = Noncrystalline



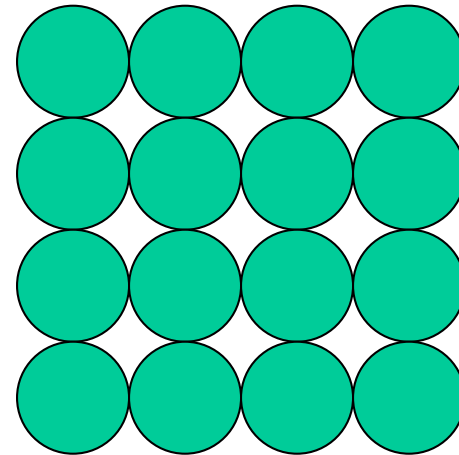
Metallic Crystal Structures

- How can we stack metal atoms to minimize empty space?

2-dimensions



vs.



Metallic Crystal Structures

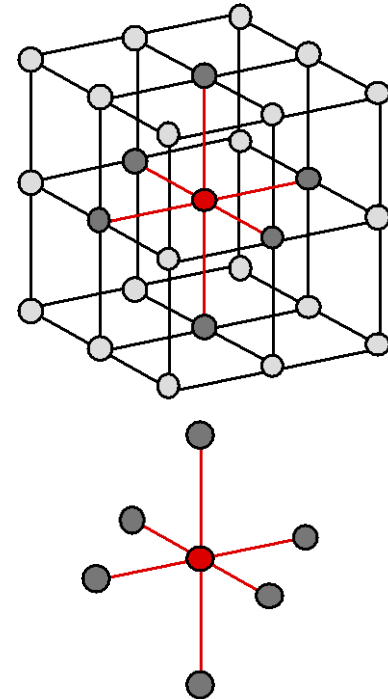
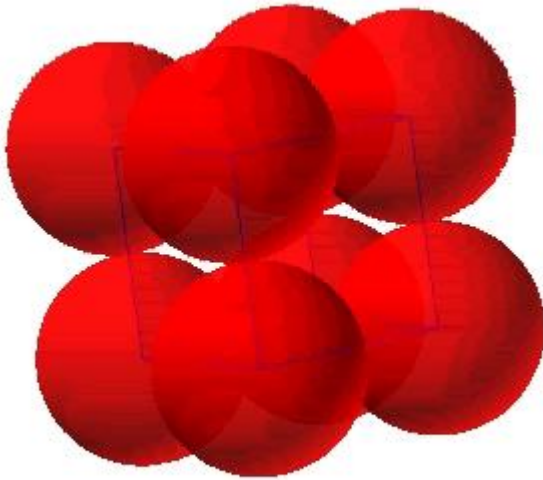
- Tend to be densely packed.
- Reasons for dense packing:
 - Typically, only one element is present, so all atomic radii are the same.
 - Metallic bonding is not directional.
 - Nearest neighbor distances tend to be small in order to lower bond energy.
 - Electron cloud shields cores from each other
- Have the simplest crystal structures.



Simple Cubic Structure (SC)

- Rare due to low packing density (only Po has this structure)
- **Close-packed directions** are cube edges.

- **Coordination # = 6**
(# nearest neighbors)

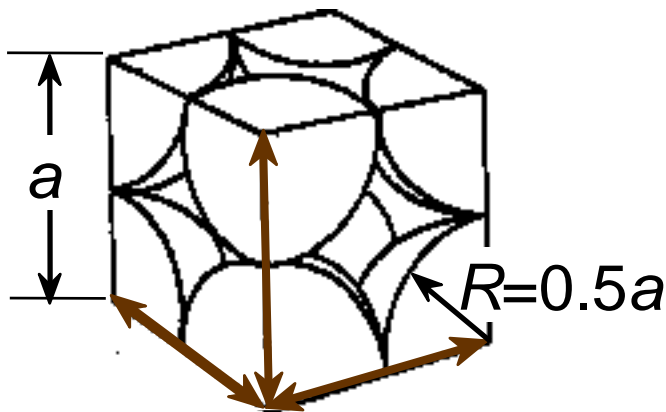


Atomic Packing Factor (APF)

$$\text{APF} = \frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}$$

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

contains $8 \times 1/8 =$

1 atom/unit cell

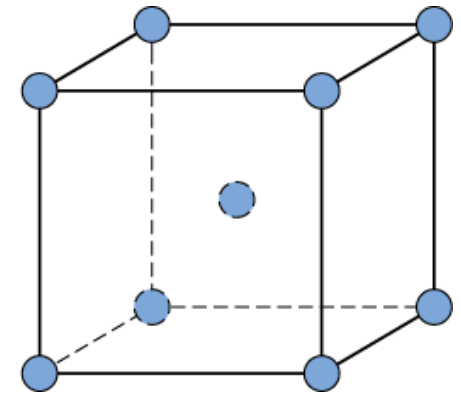
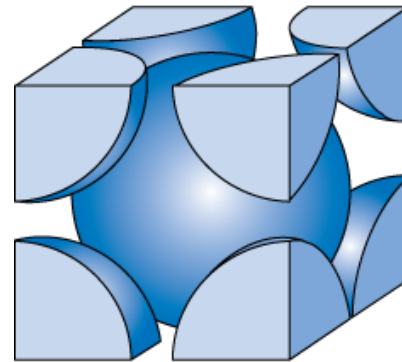
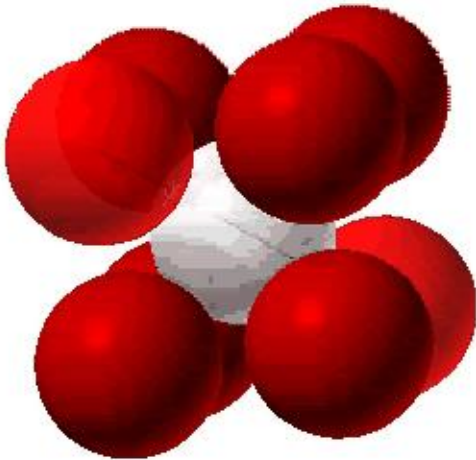
$$\text{APF} = \frac{\overbrace{1}^{\text{atoms}} \overbrace{\frac{4}{3} \pi (0.5a)^3}^{\text{volume atom}}}{\underbrace{a^3}_{\text{volume unit cell}}}$$

Body Centered Cubic Structure (BCC)

- Atoms touch each other along cube diagonals.
 - Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

ex: Cr, W, Fe (α), Tantalum, Molybdenum

- Coordination # = 8



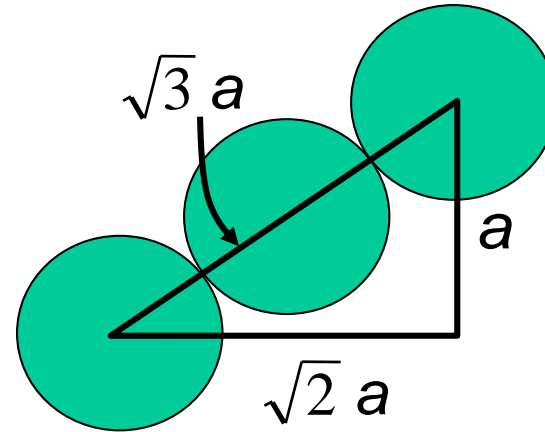
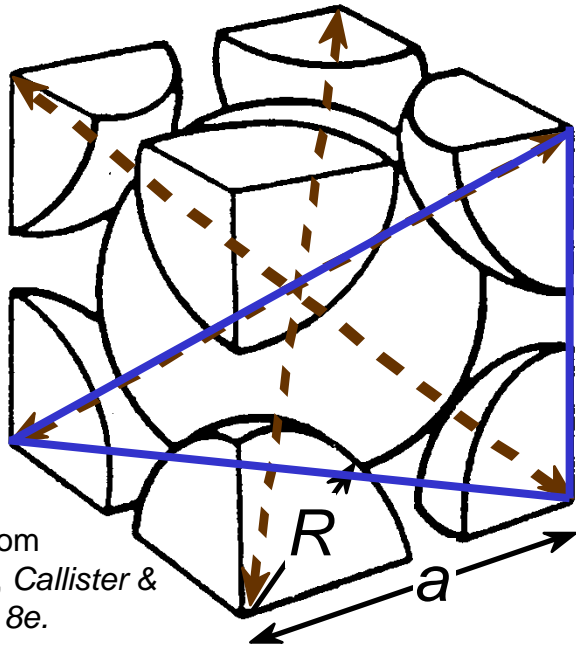
Adapted from Fig. 3.2,
Callister & Rethwisch 8e.

2 atoms/unit cell: 1 center + 8 corners \times 1/8



Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68



Adapted from
Fig. 3.2(a), Callister &
Rethwisch 8e.

$$\text{APF} = \frac{\text{atoms unit cell} \times \text{volume atom}}{\text{volume unit cell}}$$

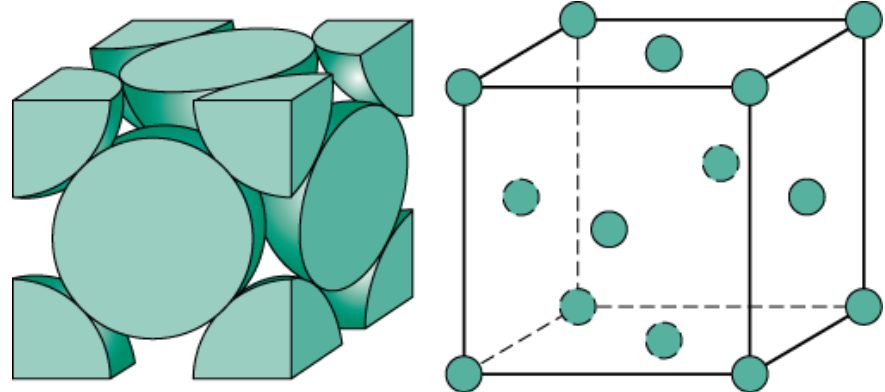
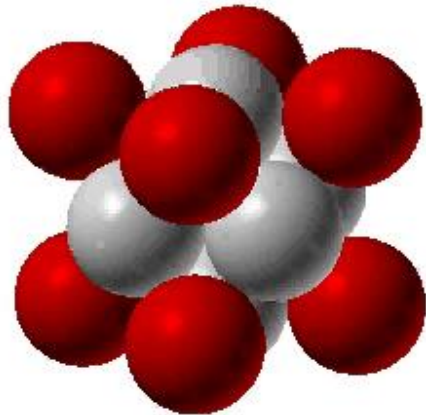
$$\text{APF} = \frac{2 \times \frac{4}{3} \pi (\sqrt{3}a/4)^3}{a^3}$$

Face Centered Cubic Structure (FCC)

- Atoms touch each other along face diagonals.
--Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

- Coordination # = 12



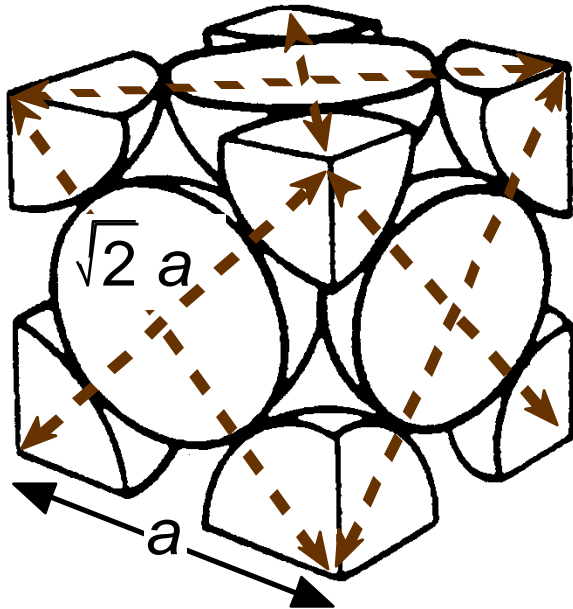
Adapted from Fig. 3.1, *Callister & Rethwisch 8e.*

4 atoms/unit cell: $6 \text{ face} \times \frac{1}{2} + 8 \text{ corners} \times \frac{1}{8}$



Atomic Packing Factor: FCC

- APF for a face-centered cubic structure = 0.74
maximum achievable APF



Unit cell contains:
 $6 \times 1/2 + 8 \times 1/8$
 = 4 atoms/unit cell

$$\text{APF} = \frac{\text{atoms/unit cell} \times \text{volume/atom}}{\text{volume/unit cell}}$$

$$\text{APF} = \frac{4 \times \frac{4}{3} \pi \left(\frac{\sqrt{2}a}{4}\right)^3}{a^3}$$

The diagram shows the calculation of the Atomic Packing Factor (APF) for an FCC unit cell. The numerator is the product of the number of atoms per unit cell (4) and the volume of one atom. The denominator is the volume of the unit cell (a^3).

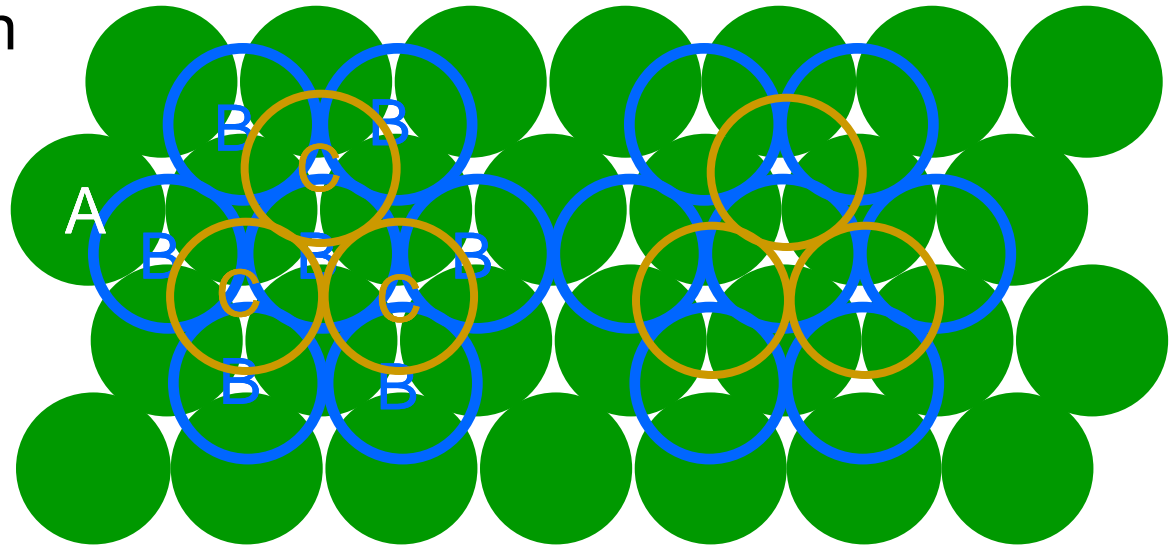
FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

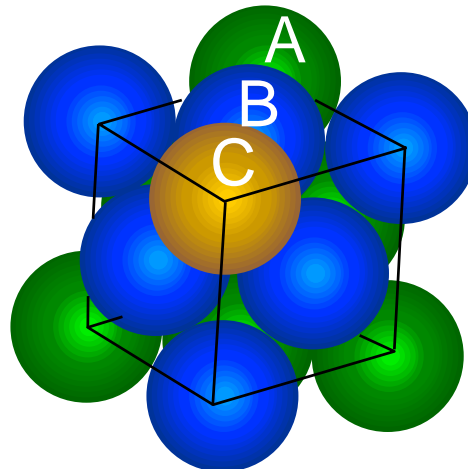
A sites

B sites

C sites

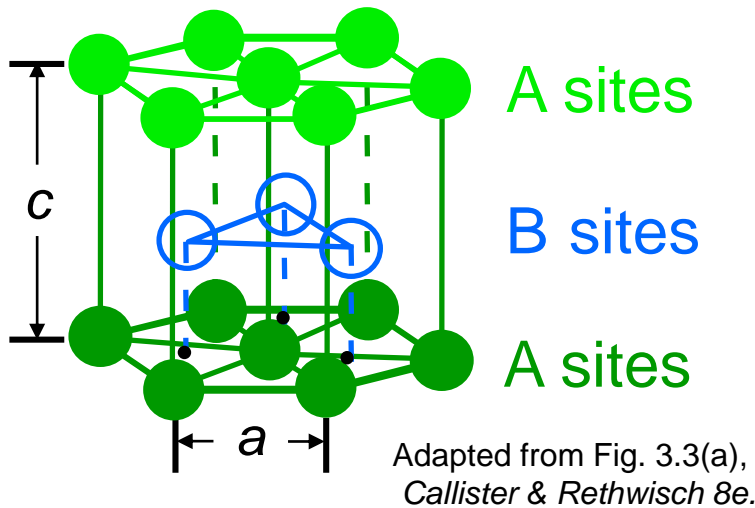


- FCC Unit Cell

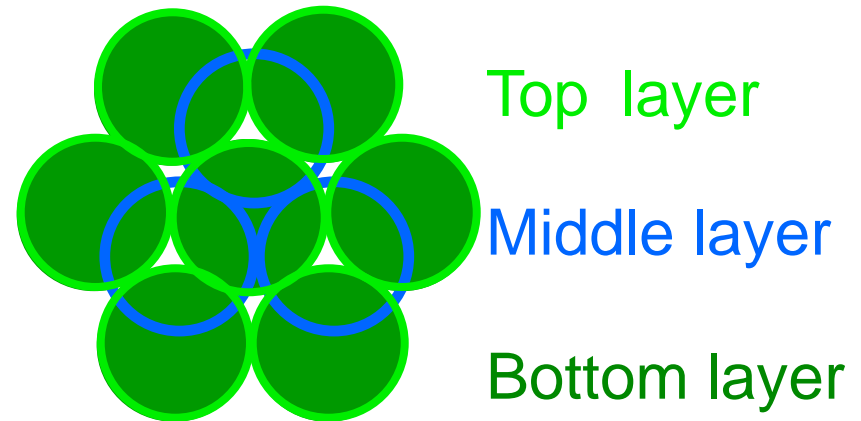


Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



- 2D Projection



- Coordination # = 12
- APF = 0.74

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn



Theoretical Density, ρ

$$\text{Density} = \rho = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}}$$

$$\rho = \frac{nA}{V_C N_A}$$

where

n = number of atoms/unit cell

A = atomic weight

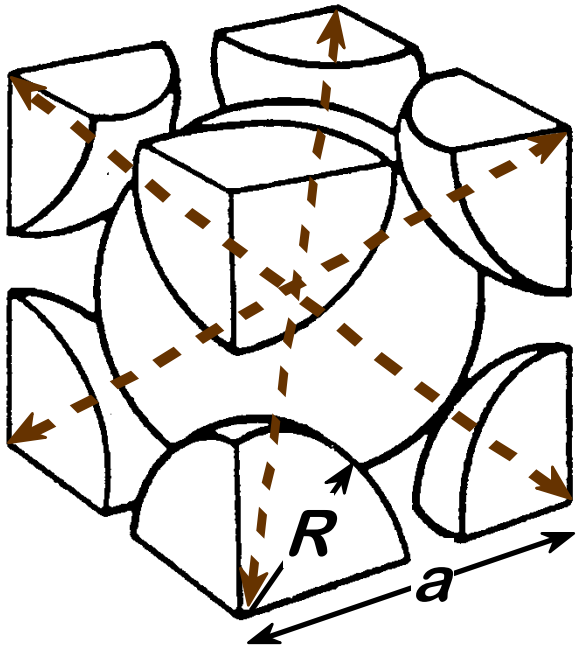
V_C = Volume of unit cell = a^3 for cubic

N_A = Avogadro's number

= 6.022×10^{23} atoms/mol



Theoretical Density, ρ



- Ex: Cr (BCC)

$$A = 52.00 \text{ g/mol}$$

$$R = 0.125 \text{ nm}$$

$$n = 2 \text{ atoms/unit cell}$$

$$a = 4R/\sqrt{3} = 0.2887 \text{ nm}$$

$$\frac{\text{atoms}}{\text{unit cell}} \rightarrow \begin{array}{|c|c|} \hline 2 & 52.00 \\ \hline \end{array} \leftarrow \frac{\text{g}}{\text{mol}}$$

$\rho =$

$\frac{\text{volume}}{\text{unit cell}}$

$$\frac{\begin{array}{|c|c|} \hline a^3 & 6.022 \times 10^{23} \\ \hline \end{array}}{\begin{array}{|c|c|} \hline 2 & 52.00 \\ \hline \end{array}}$$

$\frac{\text{atoms}}{\text{mol}}$

$\rho_{\text{theoretical}}$	$= 7.18 \text{ g/cm}^3$
ρ_{actual}	$= 7.19 \text{ g/cm}^3$

Densities of Material Classes

In general

$$\rho_{\text{metals}} > \rho_{\text{ceramics}} > \rho_{\text{polymers}}$$

Why?

Metals have...

- close-packing (metallic bonding)
- often large atomic masses

Ceramics have...

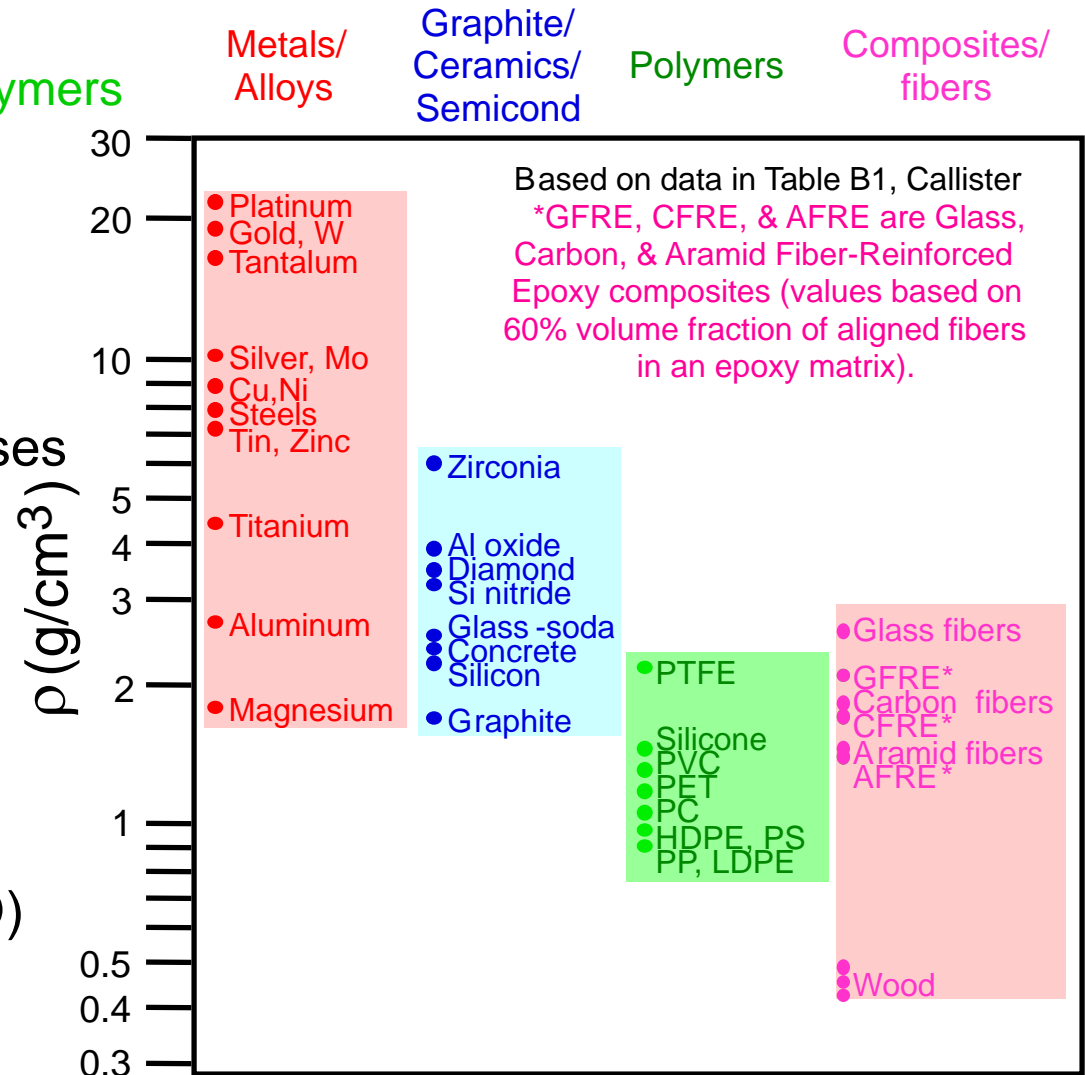
- less dense packing
- often lighter elements

Polymers have...

- low packing density (often amorphous)
- lighter elements (C,H,O)

Composites have...

- intermediate values



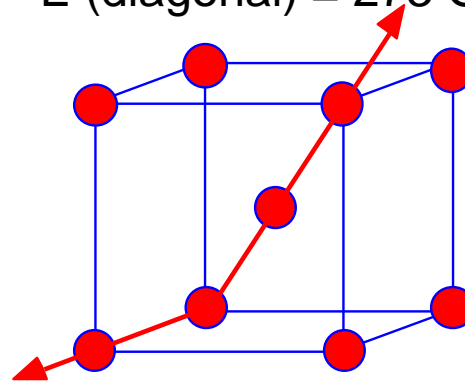
Data from Table B.1, Callister & Rethwisch, 8e.

Single vs Polycrystals

- Single Crystals

- Properties vary with direction: **anisotropic**.
- Example: the modulus of elasticity (E) in BCC iron:

E (diagonal) = 273 GPa

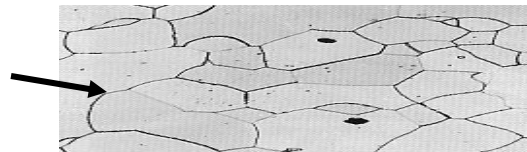
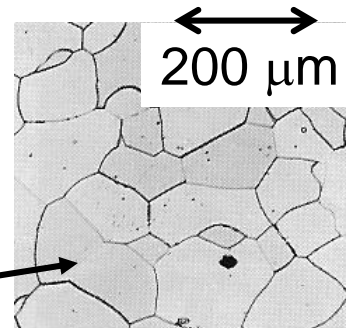


Data from Table 3.3, *Callister & Rethwisch 8e*. (Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

E (edge) = 125 GPa

- Polycrystals

- Properties may/may not vary with direction.
- If grains are randomly oriented: **isotropic**. ($E_{\text{poly iron}} = 210 \text{ GPa}$)
- If grains are **textured**, anisotropic.



Adapted from Fig. 4.14(b), *Callister & Rethwisch 8e*. (Fig. 4.14(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)



Polymorphism

- Two or more distinct crystal structures for the same material (allotropy/polymorphism)

titanium
 α , β -Ti

carbon
diamond, graphite

iron system

