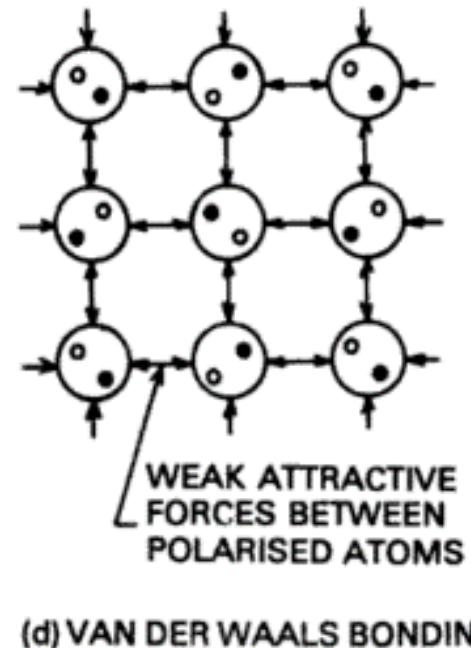
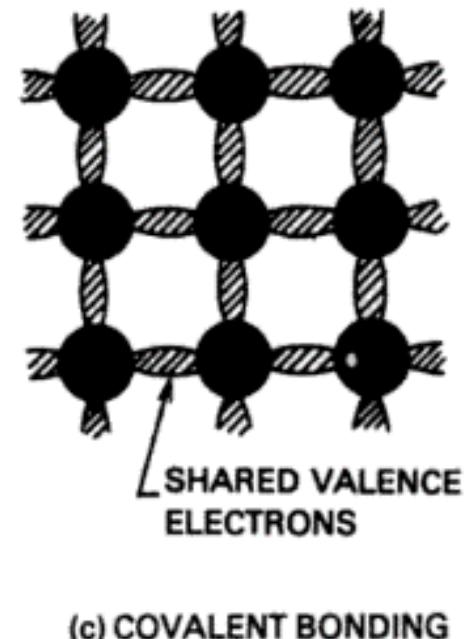
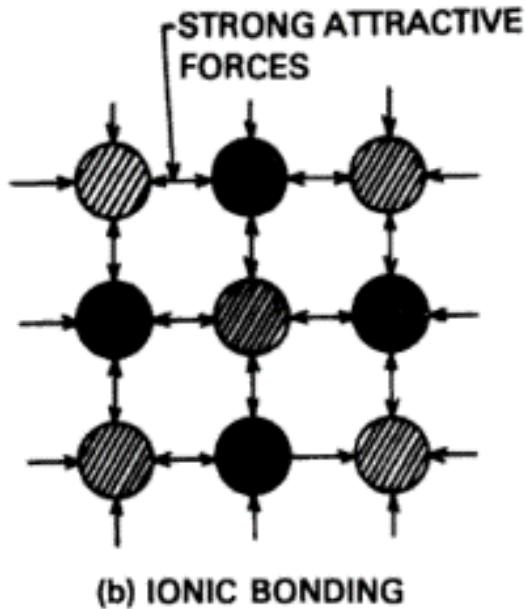
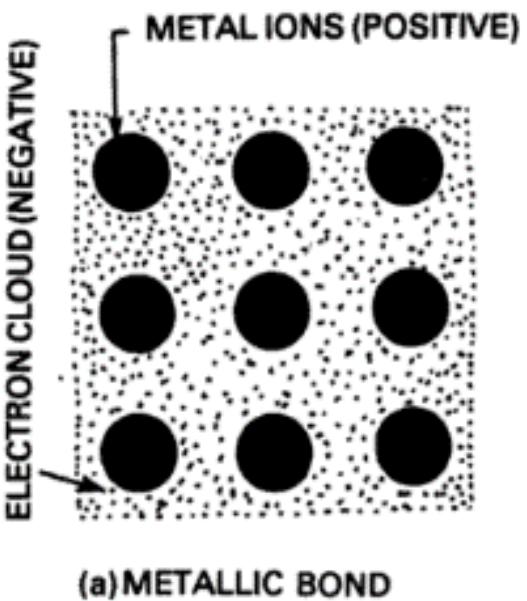


Chapter 1

Elementary Materials Science Concepts

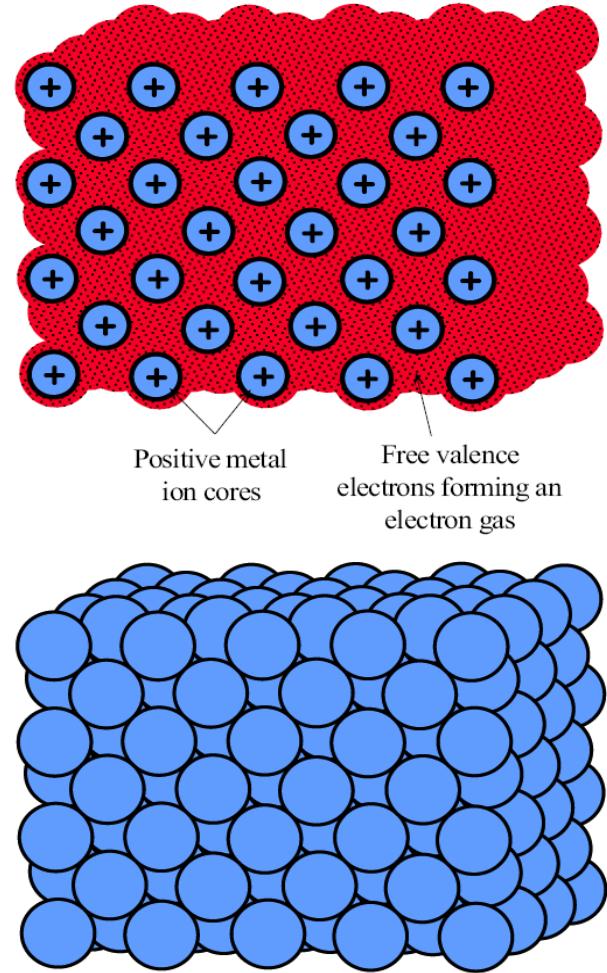
Bonding in Solids

- Properties of an individual atom are determined by its *atomic structure*
 - ✓ Bohr's shell model (1913)
 - ✓ *Energy Levels and Quantum Numbers*: K-, L-, M-shell, etc. and *Principal & Orbital angular momentum quantum nos.*, std. notation: nl^*
- Valence electrons play an important role in producing most of the material properties
- Solid materials can have a very wide range of properties
- This is partly due to the fact that atoms have different types of bonding



(a) Metallic Bond

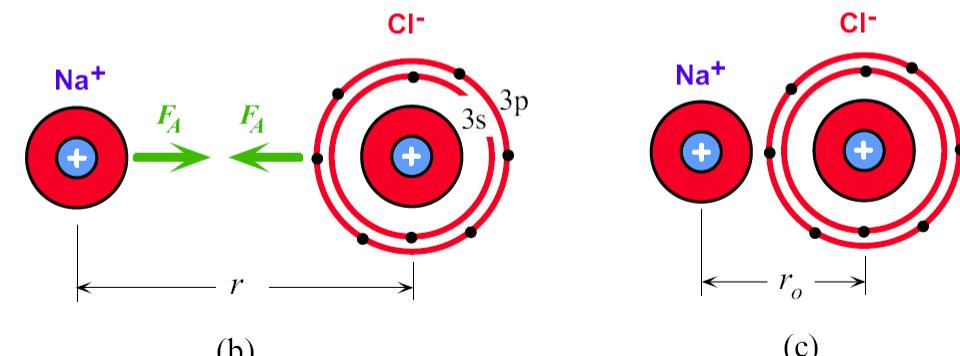
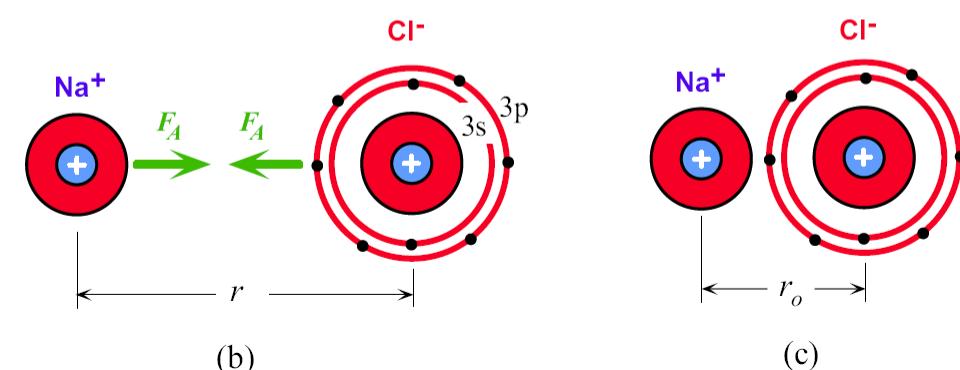
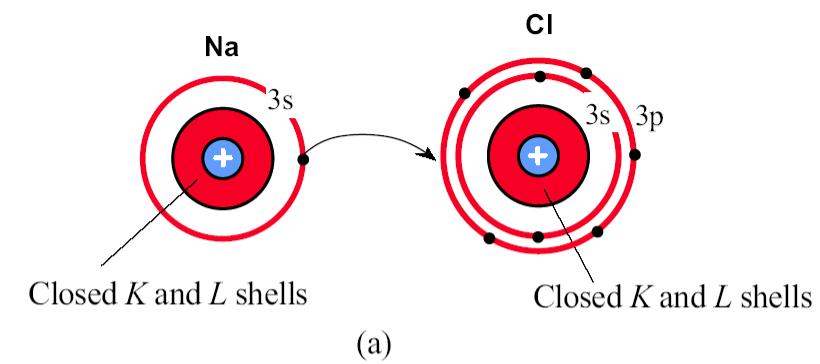
- This bond results when each atom of the metal contributes its valence electrons to the formation of an *electron cloud or electron gas* that spreads throughout the solid metal
- **Bond Characteristic:** conduction of electricity & heat are produced by the free movement of valence electrons through the metal
- “**Free**” valence electrons in the electron gas can respond readily to an applied electric field and drift along the force of the field, which is the reason for the *high electrical conductivity* of metals.
- Furthermore, if there is temperature gradient along metal bar, the free electrons can also contribute to the energy transfer from the hot to the cold regions, since they frequently collide with the metal ions and thereby transfer energy. Metals therefore, typically, also have *good thermal conductivities*; that is, they easily conduct heat.
- **This is why when you touch your finger to a metal it feels cold because it conducts heat “away” from the finger to the ambient (making the fingertip “feel” cold).**
- *All metal conductors show this type of bond.*



In metallic bonding the valence electrons from the metal atoms form a “cloud of electrons” which fills the space between the metal ions and “glues” the ions together through the coulombic attraction between the electron gas and the positive metal ions.

(b) Ionic Bond

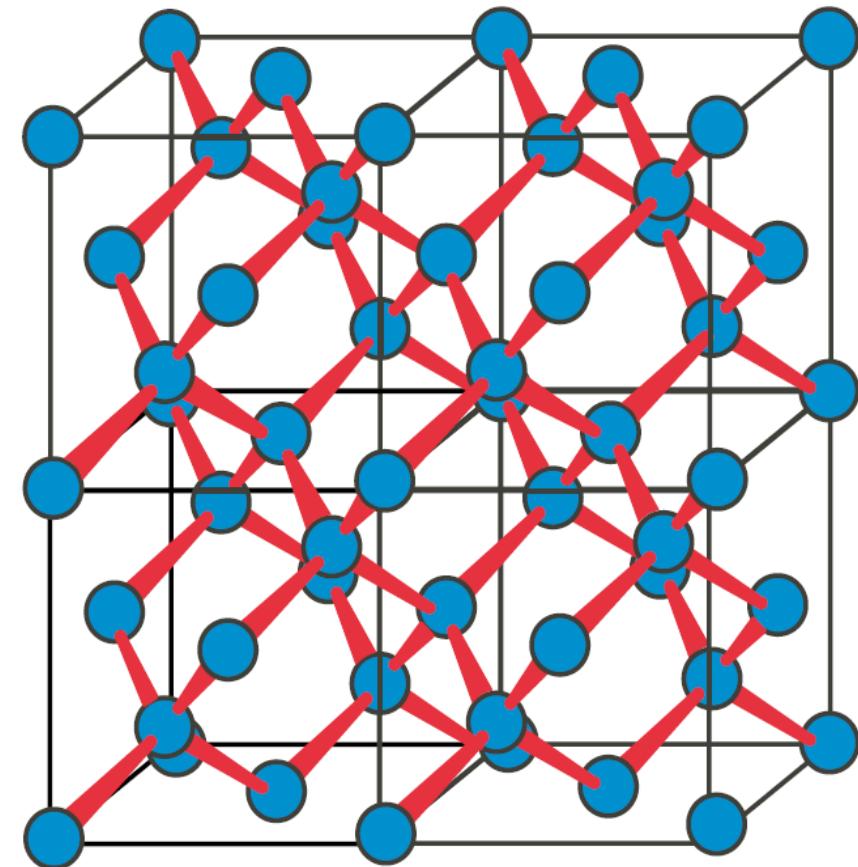
- This bond exists between **two unlike atoms (metal & non-metal)**. If an electron is transferred from a metallic atom to a non-metallic atom, the two resulting ions are held together by electrostatic attraction.
- Examples are the sodium and chlorine atoms. Sodium atom gives away its valence electron and becomes a positive ion (Cation), while chlorine atom takes the electron to fill its last orbit and becomes a negative ion (Anion).
- Since all the electrons are within the rigidly positioned ions, there are no free or loose electrons to wander around in the crystal as in metals. Therefore, ionic solids are typically electrical insulators, have *poor electrical conductivity*.
- Compared to metals and covalently bonded solids, ionically bonded solids have *lower thermal conductivity* since ions cannot readily pass vibrational kinetic energy to their neighbors.
- *Common Salt NaCl, LiF, MgO (magnesia), CsCl, and ZnS are all ionic crystals.*



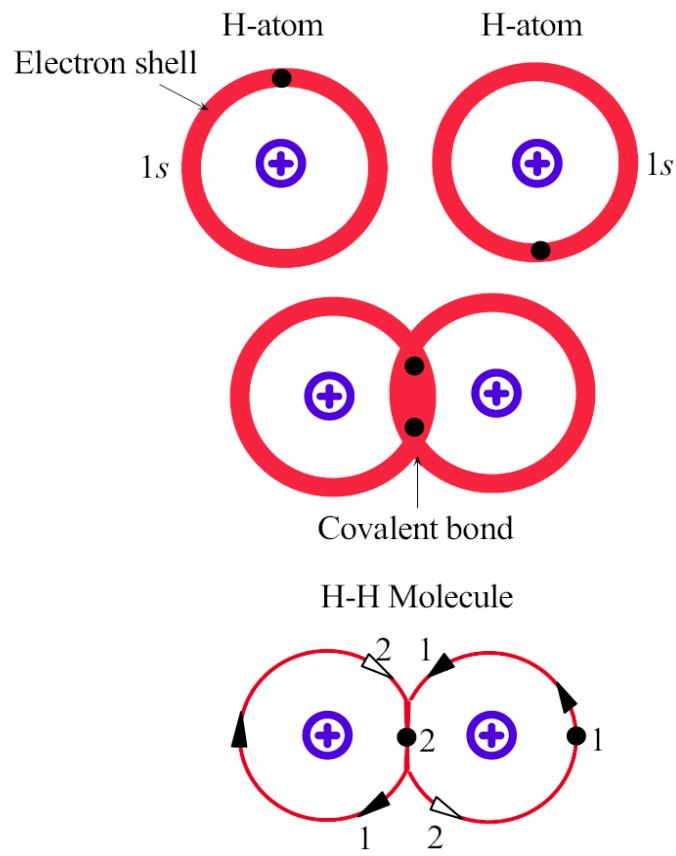
Formation of ionic bond between Na & Cl atoms.
The attraction is due to coulombic forces in NaCl.

(c) Covalent Bond

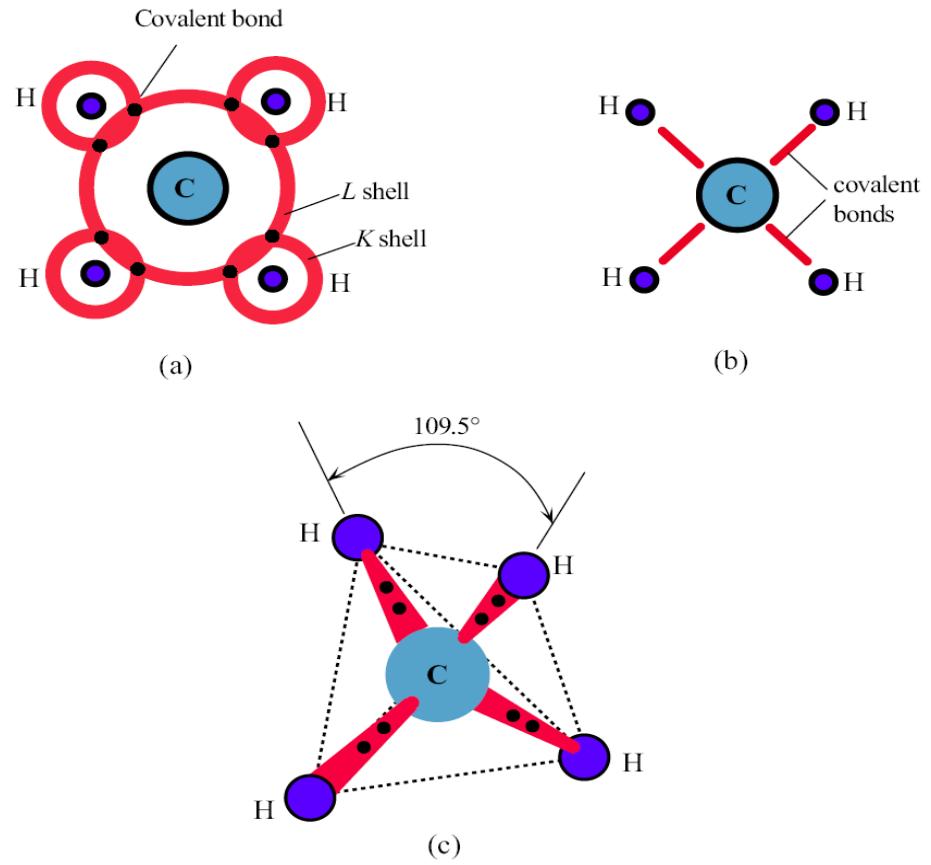
- It is formed by sharing of valence electrons between adjacent atoms, to complete the subshells of each atom.
- Example: *Chlorine molecule*. Outer shell of each Cl atom possesses 7 electrons. Each Cl atom would like to gain an electron, and thus form a stable octet. This can be done by sharing of 2 electrons between pairs of Cl atoms. Each atom contributes 1 electron for the sharing process.
- *Diamond form of carbon*: 4 valence electrons are shared between 4 neighbouring atoms
- Since all the valence electrons are locked in the bonds between the atoms, these electrons are not free to drift in the crystal when an electric field is applied. Consequently, covalent crystals are characterized by *very poor electrical conductivity*.
- *Other examples*: hydrogen, nitrogen, methane (CH_4) etc.



The diamond crystal is a covalently bonded network of carbon atoms. Each carbon atom is covalently bonded to four neighbors forming a regular three dimensional pattern of atoms which constitutes the diamond crystal.



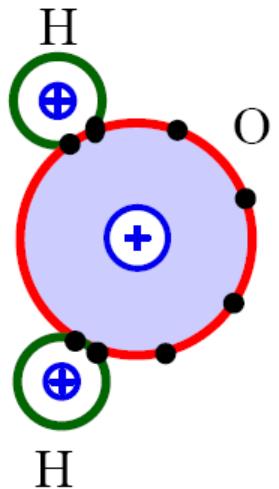
Formation of a covalent bond between two hydrogen atoms leads to the H₂ molecule. Electrons spend majority of their time between the two nuclei which results in a net attraction between the electrons and the two nuclei which is the origin of the covalent bond.



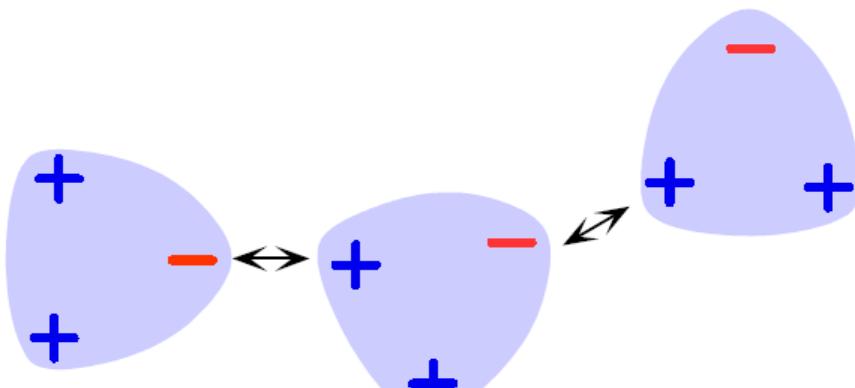
- (a) Covalent bonding in methane, CH₄, involves 4 hydrogen atoms sharing bonds with one carbon atom. Each covalent bond has two shared electrons. The 4 bonds are identical and repel each other.
- (b) Schematic sketch of CH₄ in paper.
- (c) In 3-D, due to symmetry, the bonds are directed towards the corners of a tetrahedron.

(d) van der Waals Bond – secondary bonds

- Inert gases & molecules like CH_4 , which have no valence electrons available for crystalline binding, obtain a weak attractive force as result of polarization of electrical charges.
- *Polarization* is displacement of the centres of positive and negative charges in an electrically neutral atom or molecule when as it is brought close to its neighbouring atom. Its neighbours also become polarized. The resulting weak electrical attraction between neighbouring atoms or molecules is the *van der Waals force*.
- This force can be overcome by disrupting effect of thermal motion of atoms & molecules at higher temperatures.
- Members of the halogen family - fluorine, chlorine, bromine and iodine - all form stable diatomic molecules with covalent bonds. The additional forces which hold the molecules together are of the van der Waals type.
- Elements possessing van der Waals bond have poor electrical conductivity.
- van der Waals bonding is responsible for holding the carbon chains together in polymers. Although the C-to-C bond in a C-chain is due to covalent bonding, the interaction between the C-chains arises from van der Waals forces and the interchain bonding is therefore of secondary nature.
- *Examples of molecular solids; ice, solidified CO_2 (dry ice), O_2 , H_2 , CH_4 , and solid inert gases.*



(a)



(b)

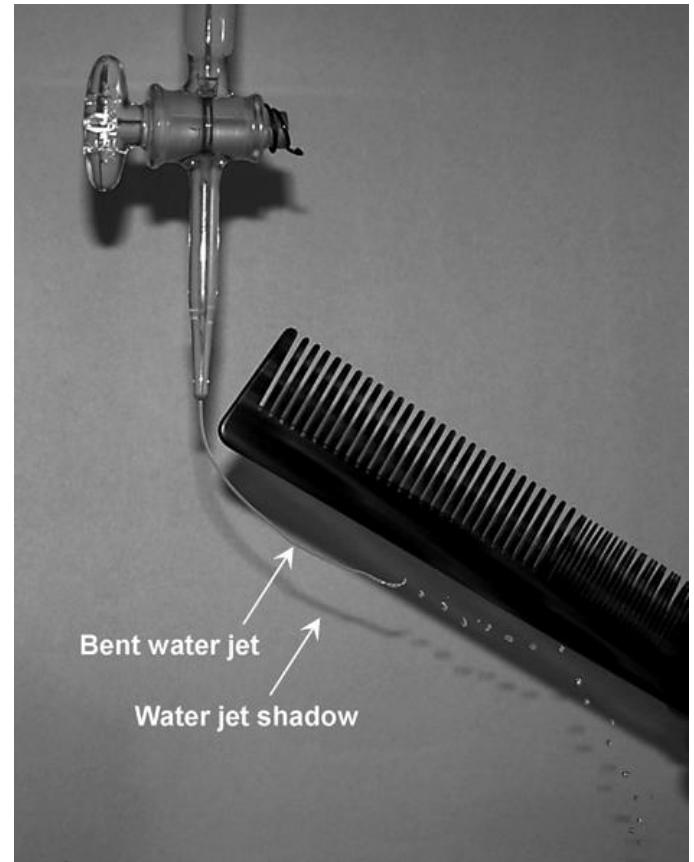
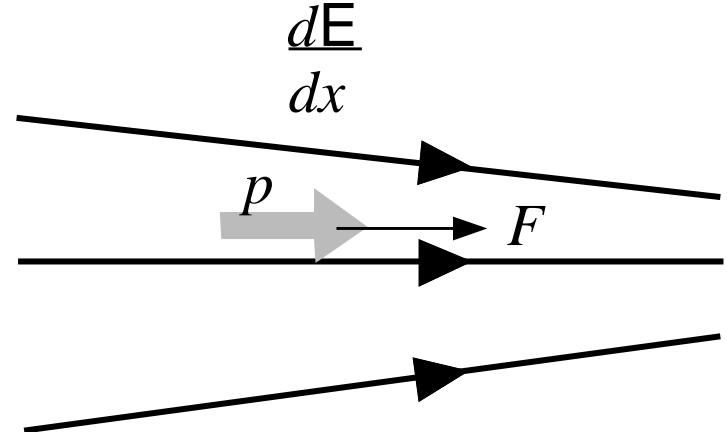
The origin of van der Walls bonding between water molecules.

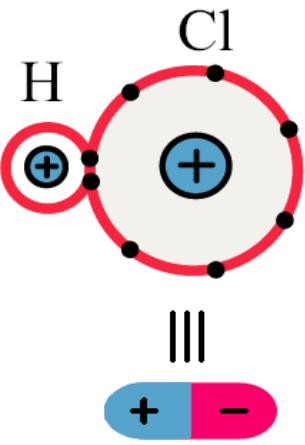
- (a) The H_2O molecule is polar and has a net permanent dipole moment
- (b) Attractions between the various dipole moments in water gives rise to van der Walls bonding

A dipole moment in a nonuniform field experiences a net force F that depends on the dipole moment p and the field gradient dE/dx .

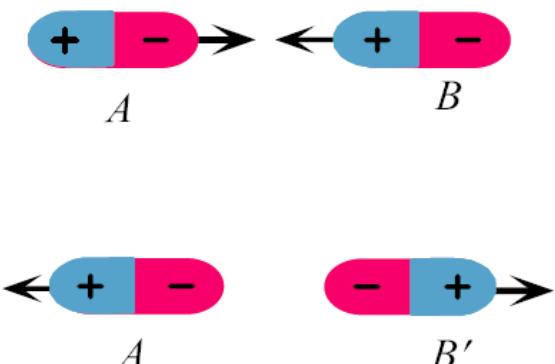
When a charged comb (by combing hair) is brought close to a water jet, the field from the comb attracts the polarized water molecules toward higher fields.

[See Question 7.7 in Chapter 7]

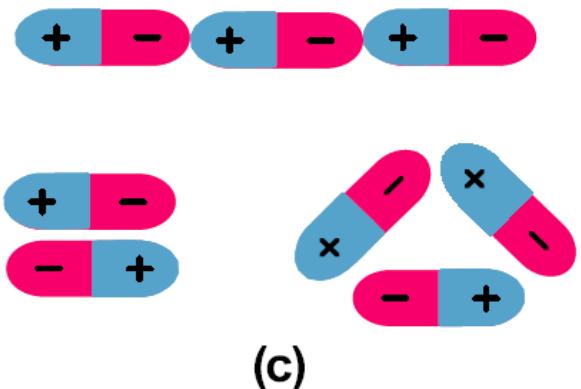




(a)



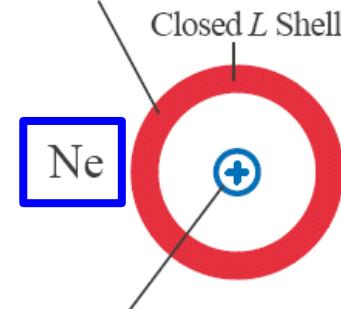
(b)



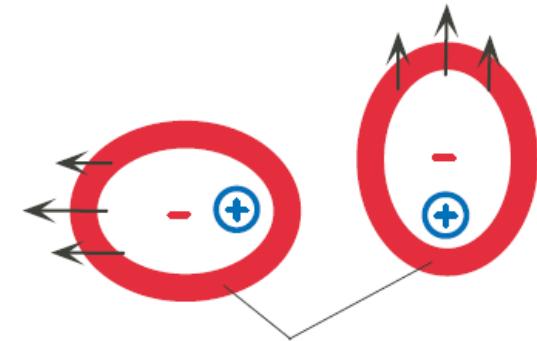
(c)

- (a) A permanently polarized molecule is called an electric dipole moment.
- (b) Dipoles can attract or repel each other depending on their relative orientations.
- (c) Suitably oriented dipoles can attract each other to form van der Waals bonds.

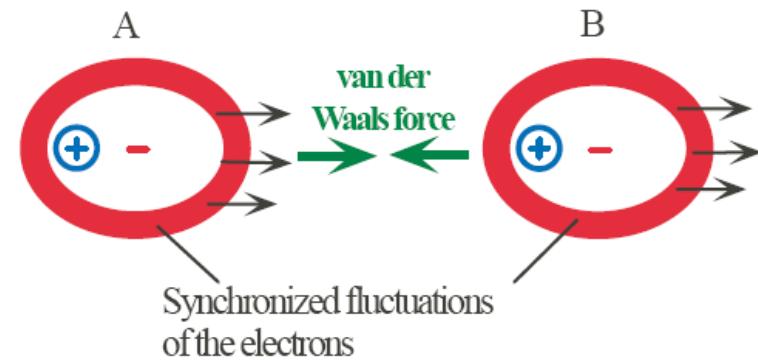
Time averaged electron (negative charge) distribution



Ionic core
(Nucleus + K-shell)



Instantaneous electron (negative charge) distribution fluctuates about the nucleus.



Induced dipole-induced dipole interaction and the resulting van der Waals force

Table 1.2 Comparison of bond types and typical properties (general trends)

Bond Type	Typical Solids	Bond Energy (eV/atom)	Melt. Temp. (°C)	Elastic Modulus (GPa)	Density (g cm ⁻³)	Typical Properties
Ionic	NaCl (rock salt)	3.2	801	40	2.17	Generally electrical insulators. May become conductive at high temperatures.
	MgO (magnesia)	10	2852	250	3.58	High elastic modulus. Hard and brittle but cleavable. Thermal conductivity less than metals.
Metallic	Cu	3.1	1083	120	8.96	Electrical conductor.
	Mg	1.1	650	44	1.74	Good thermal conduction. High elastic modulus. Generally ductile. Can be shaped.
Covalent	Si	4	1410	190	2.33	Large elastic modulus. Hard and brittle.
	C (diamond)	7.4	3550	827	3.52	Diamond is the hardest material. Good electrical insulator. Moderate thermal conduction, though diamond has exceptionally high thermal conductivity.
van der Waals: hydrogen bonding	PVC (polymer)		212	4	1.3	Low elastic modulus. Some ductility.
	H ₂ O (ice)	0.52	0	9.1	0.917	Electrical insulator. Poor thermal conductivity. Large thermal expansion coefficient.
van der Waals: induced dipole	Crystalline argon	0.09	-189	8	1.8	Low elastic modulus. Electrical insulator. Poor thermal conductivity. Large thermal expansion coefficient.

Due to the strong Coulombic attraction between the shared electrons and the positive nuclei, the covalent bond energy is usually the highest for all bond types, leading to very high melting temperatures and very hard solids: diamond is one of the hardest known materials.

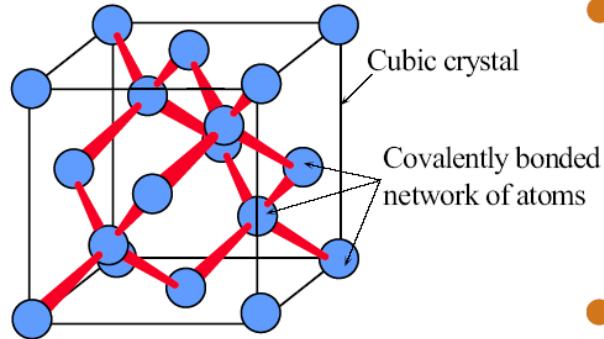
Diamond: stable at very high pressures, an insulator, hardest substance known

Graphite: stable at room temperature, electrical conductor, carbon layers (held together by weak secondary bonds or van der Waals bonds) can readily slide over each other under shear stresses. This is the reason for graphite's lubricating properties.

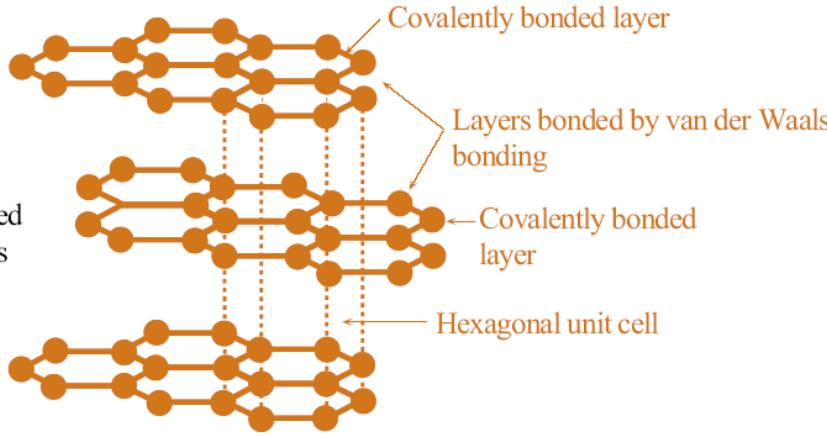
Allotropy or Polymorphism

- Polymorphism or allotropy is a material attribute that allows it to possess more than one crystal structure. Each possible crystal structure is called a polymorph or an allotrope.
- At room temperature, Fe has BCC structure (α -Fe) upto 912 °C (*transition temperature*).
- Between 912-1400 °C, Fe has FCC structure (γ -Fe).
- Above 1400 °C, Fe *again* has BCC structure (δ -Fe).
- Since iron has more than one crystal structure, it is called **polymorphic**.
- Each iron crystal structure is a polymorph or an allotrope.
- When the temperature of a metal is changed, *rearrangement of atoms* in the lattice takes place giving rise to *lower free-energy* to the specific form of metal at particular temperature.
- Among the non-metallic elements, polymorphism is found in phosphorous (white, black and red forms) and carbon (diamond, graphite, etc.).
- Diamond structure of carbon is very different from the layer structure of graphite. Both have widely differing properties, which lead to diverse applications.

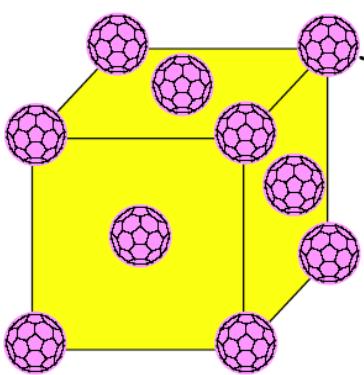
Metal	Temperature range, °C	Crystal structure
Iron	Upto 910	BCC, α -phase
	910-1400	FCC, γ -phase
	1400-1539	BCC, δ -phase
Tin	Upto 12	Cubic, α -phase
	12-231	Tetragonal, β -phase
Cobalt	Upto 421	CPH
	421-1492	FCC
Chromium	Upto 20	CPH
	20-1740	BCC
Titanium	Upto 880	CPH
	880-1710	BCC
Uranium	Upto 668	Orthorhombic
	668-774	Tetragonal
	Above 774	BCC



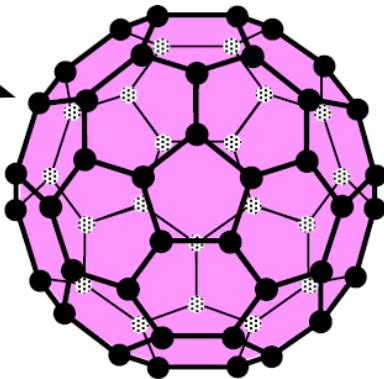
(a) Diamond unit cell



(b) Graphite



The FCC unit cell of the Buckminsterfullerene crystal. Each lattice point has a C_{60} molecule held together by van der Waals forces



Buckminsterfullerene (C_{60}) molecule (the "buckyball" molecule)

(c) Buckminsterfullerene

3 allotropes of carbon

Buckminsterfullerene: another polymorph of carbon

- ✓ 60 carbon atoms bond with each other to form a perfect soccer ball–type molecule
- ✓ C_{60} molecule has 12 pentagons and 20 hexagons
- ✓ Produced in laboratory by a carbon arc in a partial atmosphere of an inert gas (He); also found in the soot of partial combustion
- ✓ It is semiconductor, and its compounds with alkali metals, such as K_3C_{60} , exhibit superconductivity at low temperatures (below 18 K).
- ✓ Mechanically, it is a soft material.

Table 1.4 Crystalline allotropes of carbon (ρ is the density and Y is the elastic modulus or Young's modulus)

	Graphite	Diamond	Buckminsterfullerene Crystal
Structure	Covalent bonding within layers. Van der Waals bonding between layers. Hexagonal unit cell.	Covalently bonded network. Diamond crystal structure.	Covalently bonded C_{60} spheroidal molecules held in an FCC crystal structure by van der Waals bonding.
Electrical and thermal properties	Good electrical conductor. Thermal conductivity comparable to metals.	Very good electrical insulator. Excellent thermal conductor, about five times more than silver or copper.	Semiconductor. Compounds with alkali metals (e.g., K_3C_{60}) exhibit superconductivity.
Mechanical properties	Lubricating agent. Machinable. Bulk graphite: $Y \approx 27 \text{ GPa}$ $\rho = 2.25 \text{ g cm}^{-3}$	The hardest material. $Y = 827 \text{ GPa}$ $\rho = 3.25 \text{ g cm}^{-3}$	Mechanically soft. $Y \approx 18 \text{ GPa}$ $\rho = 1.65 \text{ g cm}^{-3}$
Comment	Stable allotrope at atmospheric pressure	High-pressure allotrope.	Laboratory synthesized. Occurs in the soot of partial combustion.
Uses, potential uses	Metallurgical crucibles, welding electrodes, heating elements, electrical contacts, refractory applications.	Cutting tool applications. Diamond anvils. Diamond film coated drills, blades, bearings, etc. Jewelry. Heat conductor for ICs. Possible thin-film semiconductor devices, as the charge carrier mobilities are large.	Possible future semiconductor or superconductivity applications.

Crystal Structures



Galena is lead sulfide, PbS , and has a cubic crystal structure

|SOURCE: Photo by SOK

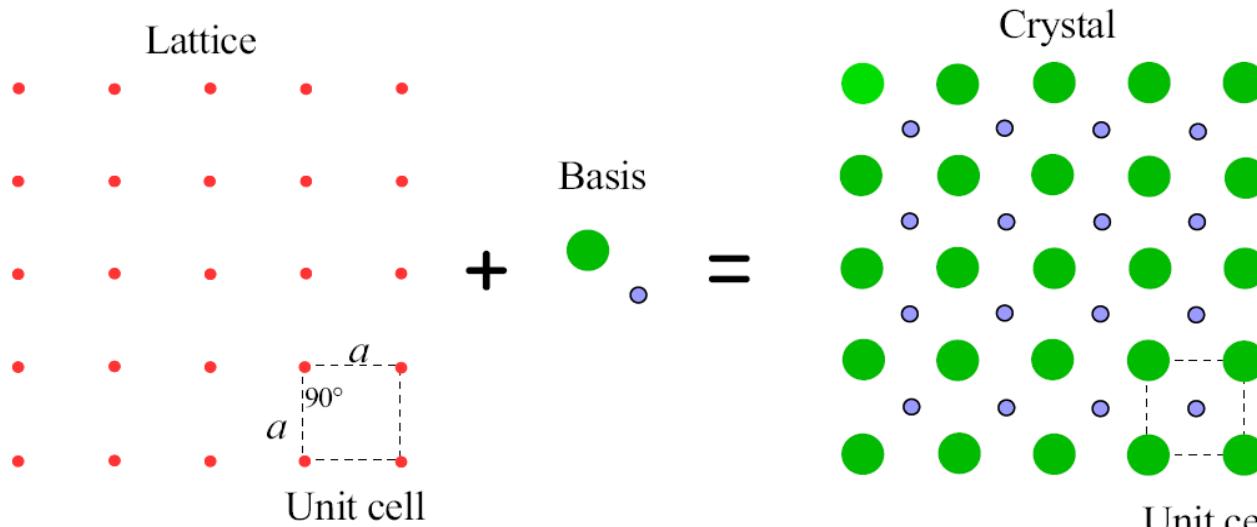


Cubic FeS_2 , iron sulfide, or pyrite, crystals. The crystals look brass-like yellow ("fool's gold").

|SOURCE: Photo by SOK



See 3rd Edition, Additional Topic 1.13 Bravais Lattices: Page 95-98



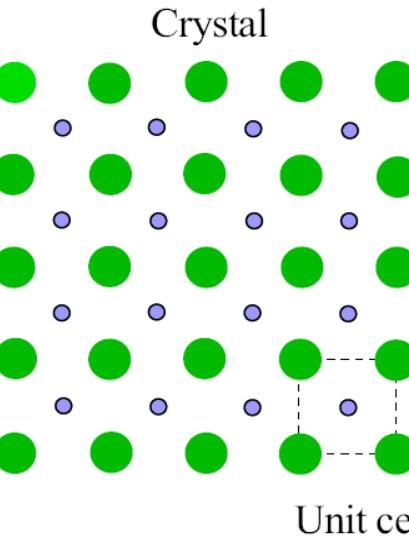
(a)

Basis

$$+ \quad =$$

(b)

Unit cell



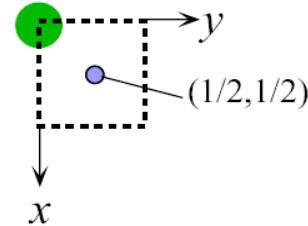
(c)

a
90°
 a

Unit cell

(d)

Basis placement in unit cell
(0,0)

**Figure 1.71: Page 96, 3rd Edition**

(a) A simple square lattice.

The unit cell is a square with a side a .

(b) Basis has two atoms.

(c) **Lattice + Basis = Crystal**.

The unit cell is a simple square with two atoms.

(d) Placement of basis atoms in the crystal unit cell.

- **Lattice** is an infinite *periodic* array of geometric points in space, without any atoms.
- Lattice is a **purely imaginary geometric concept**
- **Basis** represents an atom, a molecule, or a collection of atoms, that is placed at each lattice point to generate the true crystal structure of a substance.
- When we place **basis** at each lattice point, (i.e., an identical group of atoms or molecules), we obtain the actual **crystal structure**.
- Crystal is a lattice plus a basis at each lattice point

- ✓ 14 distinct lattices possible in 3-dimensional (3D) space
 - ✓ Each of these is called a **Bravais lattice**
 - ✓ 7 crystal systems only categorize the unit cells based on the geometry of unit cell and not in terms of the symmetry and periodicity of the lattice points.
 - ✓ One should not confuse the unit-cell geometry with the lattice, which is a periodic array of points.

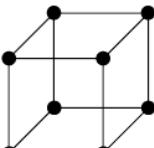
UNIT CELL GEOMETRY

CUBIC SYSTEM

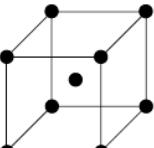
$$a = b = c \quad \alpha = \beta = \gamma = 90^\circ$$

Many metals, Al, Cu, Fe, Pb. Many ceramics and semiconductors, NaCl, CsCl, LiF, Si, GaAs

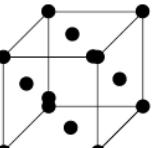
Crystal Structure	Typical Metals
Body centered cubic (BCC)	Cr, α -Fe, Mo, W
Face centered cubic (FCC)	Al, Cu, Au, Ag, Pb, Ni, γ -Fe, α -Sn



Simple cubic



Body centered cubic

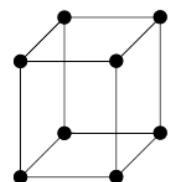


Face centered cubic

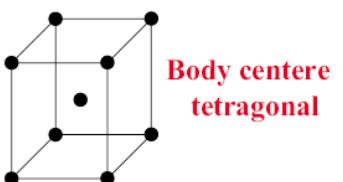
TETRAGONAL SYSTEM

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

In, Sn, Barium Titanate, TiO_2



Simple tetragonal

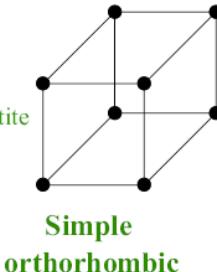


Body centered tetragonal

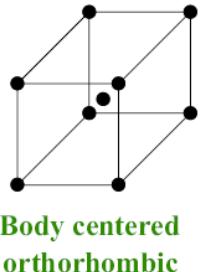
ORTHORHOMBIC SYSTEM

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

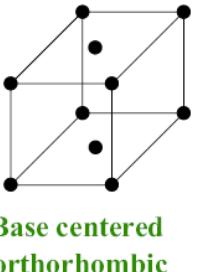
S, U, Pl, Ga (<30°C), Iodine, Cementite (Fe_3C), Sodium Sulfate



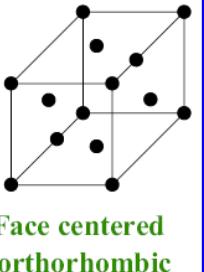
Simple orthorhombic



Body centered orthorhombic



Base centered orthorhombic

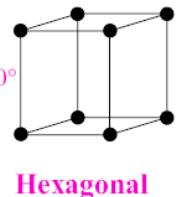


Face centered orthorhombic

HEXAGONAL SYSTEM

$$a = b \neq c \quad \alpha = \beta = 90^\circ ; \gamma = 120^\circ$$

Cadmium, Magnesium, Zinc, Graphite

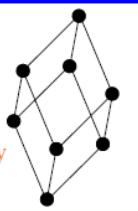


Hexagonal

RHOMBOHEDRAL SYSTEM

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

Arsenic, Boron, Bismuth, Antimony, Mercury (<-39°C)

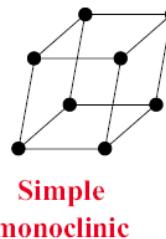


Rhombohedral

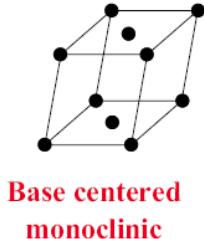
MONOCLINIC SYSTEM

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

α -Selenium, Phosphorus
Lithium Sulfate
Tin Fluoride



Simple monoclinic

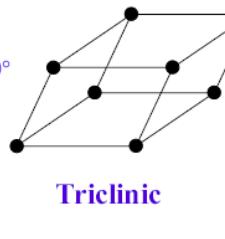


Base centered monoclinic

TRICLINIC SYSTEM

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

Potassium dicromate



Triclinic

SI.

No. Crystal system

Axial lengths and angles

Space lattice

1 Cubic

Three equal axes at right angles

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

2 Tetragonal

Three axes at right angles,

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

3 Orthorhombic

Three unequal axes at right angles

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

4 Rhombohedral

Three equal axes, equally inclined

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

5 Hexagonal

Two equal coplanar axes at 120° , third axis at right angles

$$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$$

6 Monoclinic

Three unequal axes, one pair not at right angle

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

7 Triclinic

Three unequal axes, unequally inclined and none at right angles

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

14 distinct lattices whose unit cells have one of 7 geometries

- ✓ Copper crystal has the FCC Bravais lattice
- ✓ Arsenic, antimony, and bismuth crystals have the rhombohedral Bravais lattice
- ✓ Tin's unit cell belongs to tetragonal crystal system, and its crystal lattice is body-centered tetragonal (BCT)

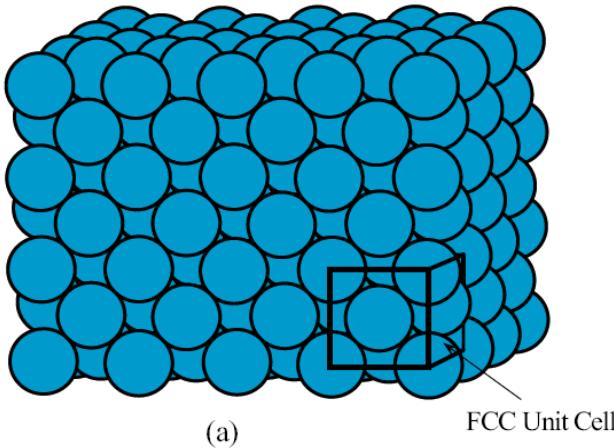
Figure 1.72: Page 97, 3rd Edition

7 crystal systems (unit cell geometries) and 14 Bravais lattices

Lattice, Unit Cell, Bravais lattice, Types of crystals, Voids, etc.

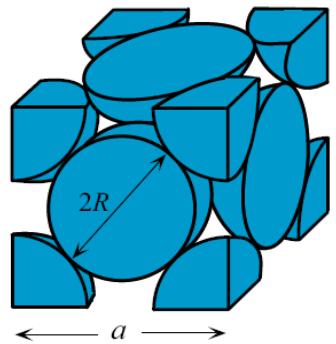
- Important characteristic of a space lattice is that every point has identical surroundings.
- Grouping of atoms whose repetition will produce the crystal is called *unit cell*. It is a building block of the crystal
- The **unit cell** is the most convenient small cell in the crystal structure that carries the properties of the crystal
- Each atom of crystal structure is surrounded by other atoms & all the atoms have identical surroundings.
Coordination number is the number of nearest neighbors around a given atom in the crystal.
- Shape and size of the unit cell is given by 6 lattice parameters: a , b , c , α , β and γ
- Depending upon the relation between these parameters, the unit cells can be divided into 7 groups, known as **crystal systems**.
- 7 different types of crystal systems can be further subdivided into 14 types, depending upon the basic arrangement of atoms within a unit cell. There are 4 different basic arrangements for atoms within a unit cell. They are as follows:
 - ✓ 1. Simple arrangement with lattice points only at cell corners.
 - ✓ 2. Base- or End-centered arrangement with lattice points centered on the opposite faces or ends of the crystal.
 - ✓ 3. Face-centered arrangement with lattice points centered on all faces of the crystal.
 - ✓ 4. Body-centered arrangement with lattice points at the centre of volume of the unit cell.

Each lattice point has one Cu atom and the basis is a single Cu atom

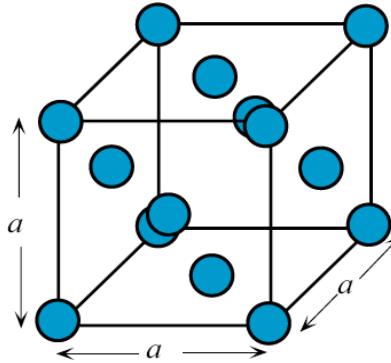


(a)

- ✓ Crystal is essentially a periodic repetition of a small volume (or cell) of atoms in 3D
- ✓ So, it is useful to identify *the repeating unit* to describe the crystal properties through this unit
- ✓ Repetition of the *unit cell* in 3D generates the whole crystal structure



(b)

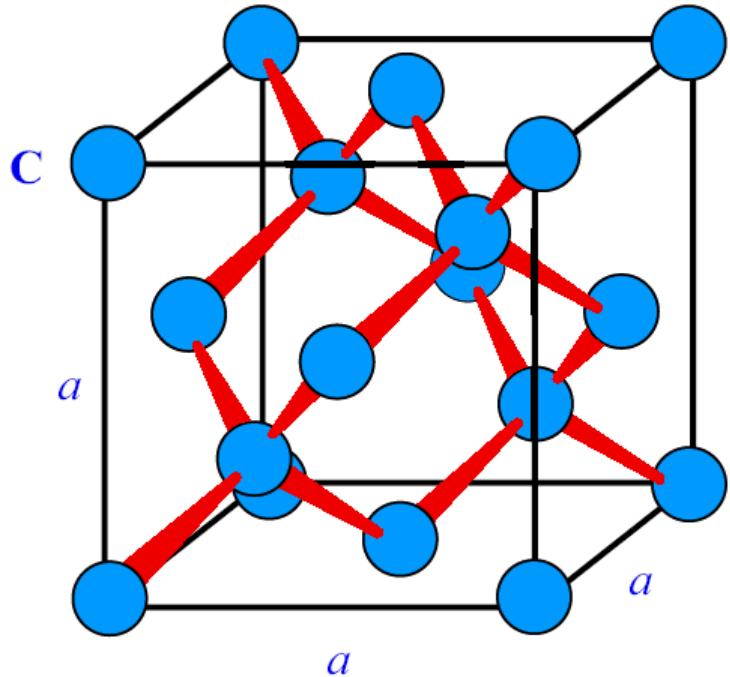


(c)

For clarity, it is often more convenient to draw the unit cell with the spheres reduced, as in Fig.(c)

- (a) The crystal structure of copper is face centered cubic (FCC). The atoms are positioned at well defined sites arranged periodically and there is a long range order in the crystal.
- (b) An FCC unit cell with closed packed spheres.
- (c) Reduced sphere representation of the unit cell. Examples: Ag, Al, Au, Ca, Cu, γ -Fe ($>912^\circ\text{C}$), Ni, Pd, Pt, Rh.

Silicon



Grey Sn (α -Sn),
semiconductors
Ge and Si have
this crystal
structure.

- ✓ Unit cell - cubic structure
- ✓ Atoms at each corner and at center of each face
- ✓ FCC-like structure, **4 atoms within the cell as well**
- ✓ Thus, there are **8 atoms in the unit cell**.
- ✓ Diamond unit cell, in terms of an **FCC lattice** (a geometric arrangement of points) with **each lattice point having a basis of two Si atoms**.
- ✓ If we place the two Si atoms at each site, one right at the lattice point, and other **displaced from it by a quarter lattice distance $a/4$ along the cube edges**, we generate the diamond unit cell.



A silicon ingot is a single crystal of Si. Within the bulk of the crystal, the atoms are arranged on a well-defined periodical lattice. The crystal structure is that of **diamond**.

|Courtesy of MEMC, Electronic Materials Inc.

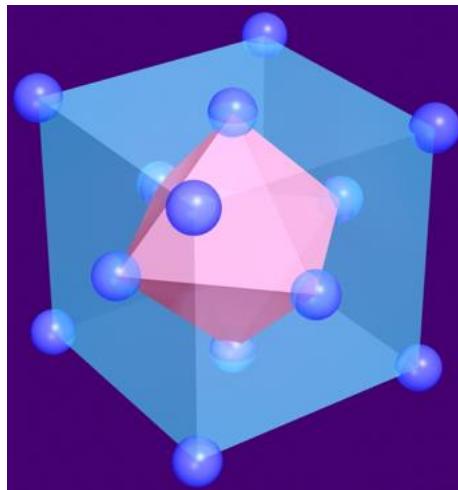
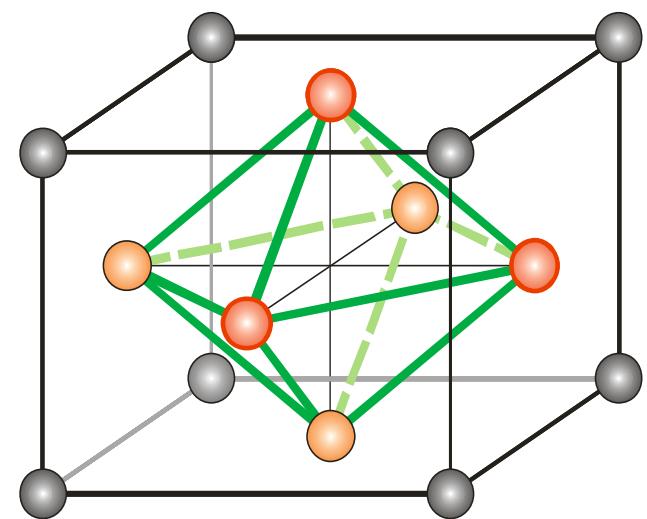
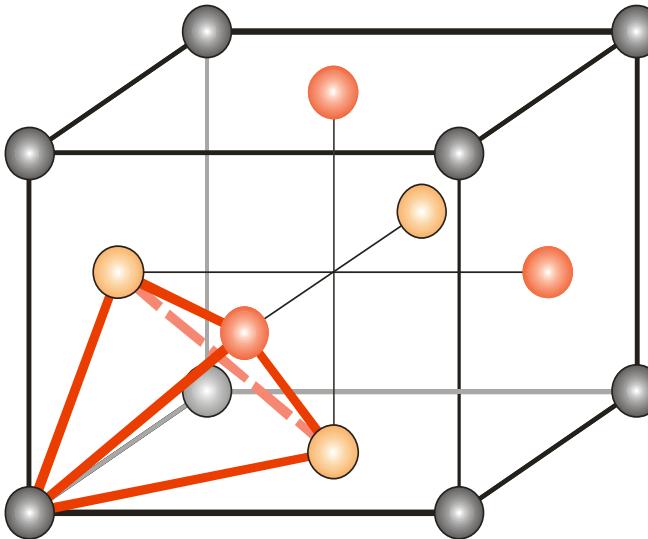
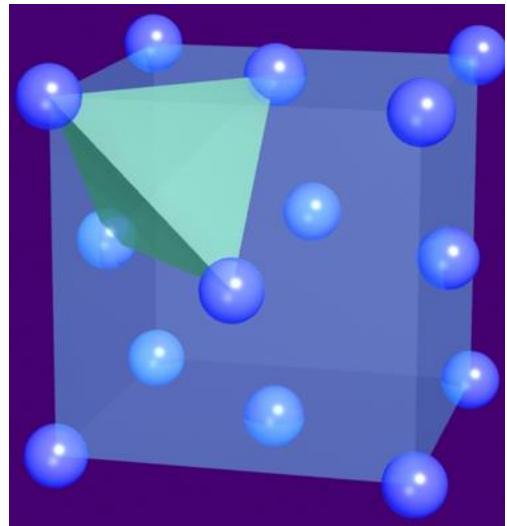
VOIDS

Tetrahedral

TV

Octahedral

OV

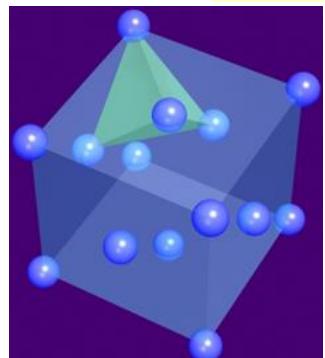


Location of the void:

$\frac{1}{4}$ way along body diagonal $\{ \frac{1}{4}, \frac{1}{4}, \frac{1}{4} \}, \{ \frac{3}{4}, \frac{3}{4}, \frac{3}{4} \}$
+ face centering translations

Location of the void:

At body centre $\{ \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \}$
+ face centering translations



Coordination # = 4
(# nearest neighbors)

Coordination # = 6
(# nearest neighbors)

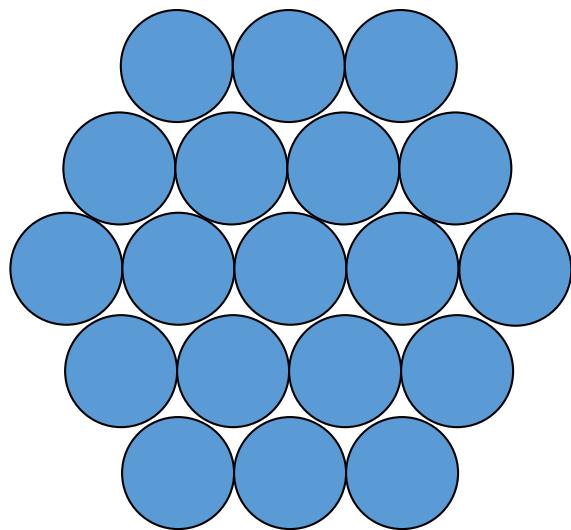
Note: Atoms are coloured differently but are the same

Table 1.3 Properties of some important crystal structures

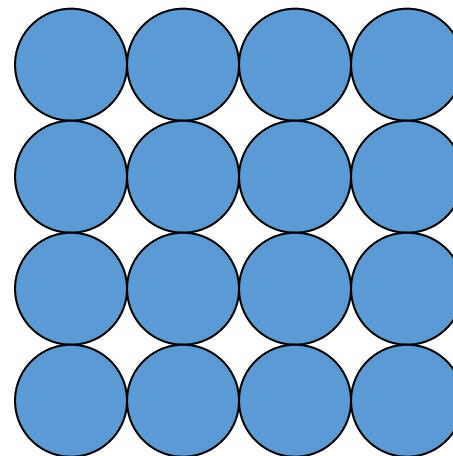
Crystal Structure	a and R (R is the Radius of the Atom)	Coordination Number (CN)	Number of Atoms per Unit Cell	Atomic Packing Factor	Examples
Simple cubic	$a = 2R$	6	1	0.52	No metals (Except Po)
BCC	$a = \frac{4R}{\sqrt{3}}$	8	2	0.68	Many metals: α -Fe, Cr, Mo, W
FCC	$a = \frac{4R}{\sqrt{2}}$	12	4	0.74	Many metals: Ag, Au, Cu, Pt
HCP	$a = 2R$ $c = 1.633a$	12	2	0.74	Many metals: Co, Mg, Ti, Zn
Diamond	$a = \frac{8R}{\sqrt{3}}$	4	8	0.34	Covalent solids: Diamond, Ge, Si, α -Sn
Zinc blende		4	8	0.34	Many covalent and ionic solids. Many compound semiconductors. ZnS, GaAs, GaSb, InAs, InSb
NaCl		6	4 cations 4 anions	0.67 (NaCl)	Ionic solids such as NaCl, AgCl, LiF, MgO, CaO Ionic packing factor depends on relative sizes of ions.
CsCl		8	1 cation 1 anion		Ionic solids such as CsCl, CsBr, CsI

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

2-dimensions



vs.

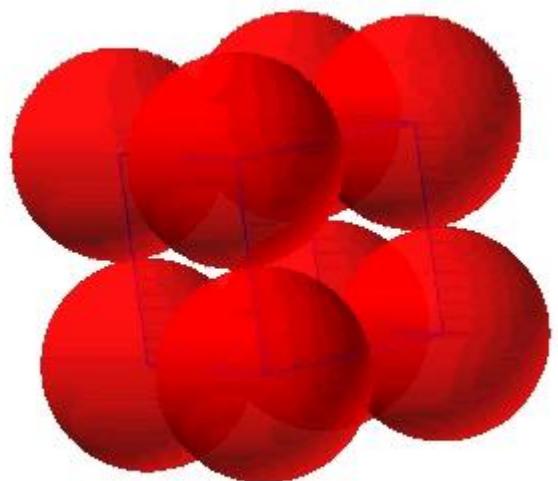


Now stack these 2-D layers to make 3-D structures

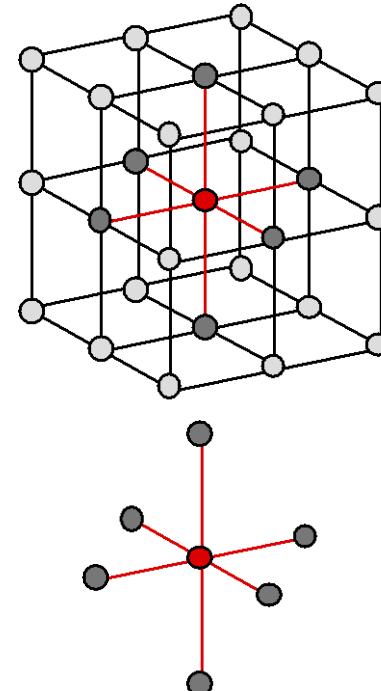
Simple Cubic Structure (SC)

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

- Coordination # = 6
(# nearest neighbors)



(Courtesy P.M. Anderson)

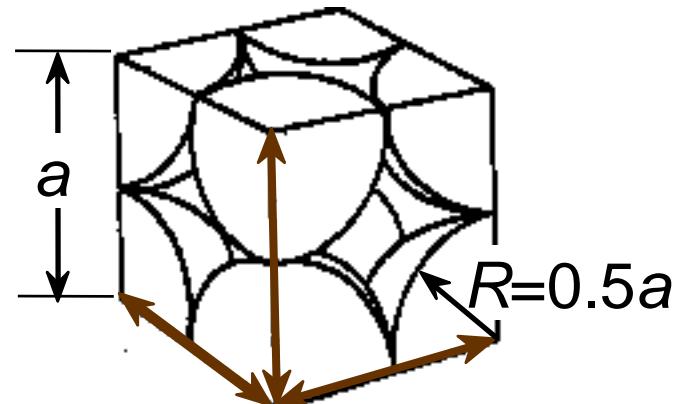


Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52

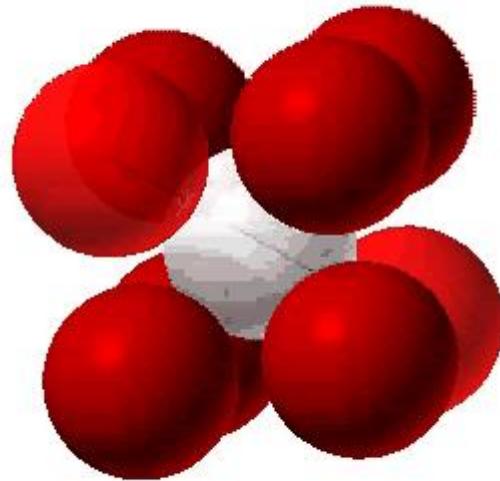


close-packed directions
contains $8 \times \frac{1}{8} =$
 1 atom/unit cell

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

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.

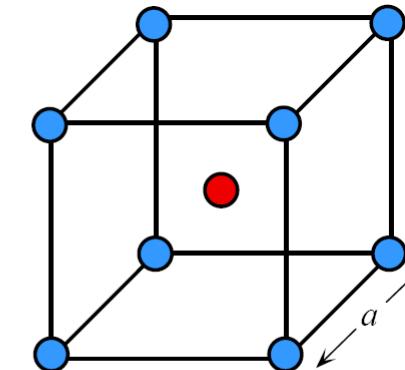
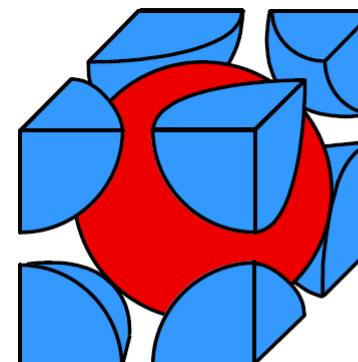


2 atoms/unit cell: 1 center + 8 corners x 1/8

(Courtesy P.M. Anderson)

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

- Coordination # = 8



Example: Alkali metals (Li, Na, K, Rb), Cr, Mo, W, Mn, α -Fe (< 912 °C), β -Ti (> 882 °C)

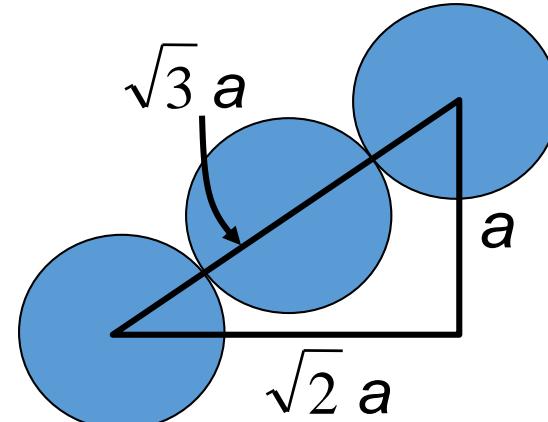
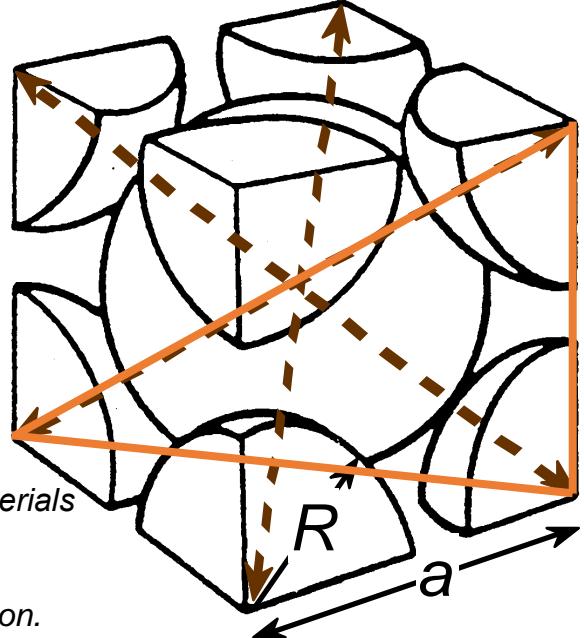
Body centered cubic crystal (BCC) crystal structure.

- (a) BCC unit cell with closely packed hard spheres representing $\frac{24}{24}$ Fe atoms.
- (b) A reduced-sphere unit cell.

Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68

From
Fig. 4.2(a)
*Callister's Materials
Science and
Engineering,
Adapted Version.*



Close-packed directions:
length = $4R = \sqrt{3} a$

$$\text{APF} = \frac{\frac{\text{atoms}}{\text{unit cell}} \cdot \frac{4}{3} \pi (\sqrt{3}a/4)^3}{\frac{\text{volume}}{\text{unit cell}}} \cdot \frac{\text{volume}}{\text{atom}}$$

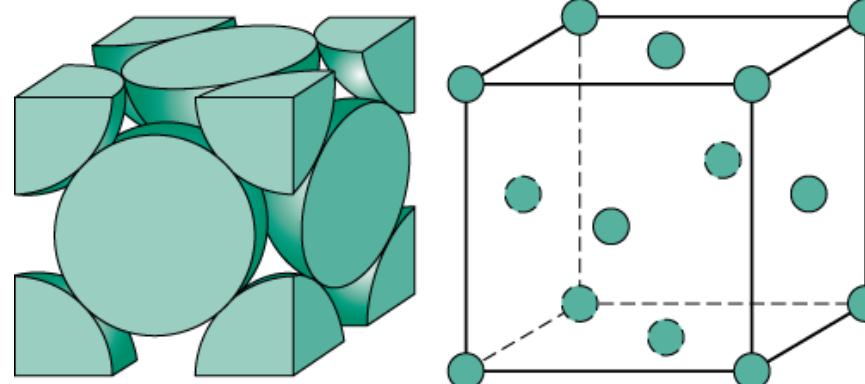
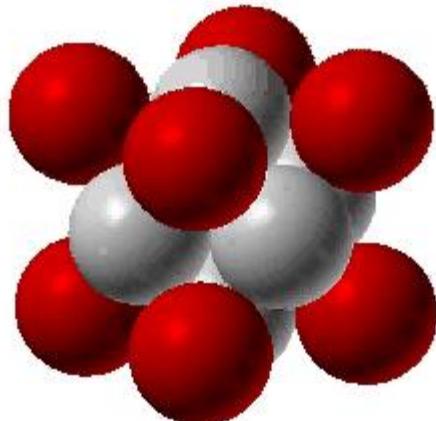
a^3

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



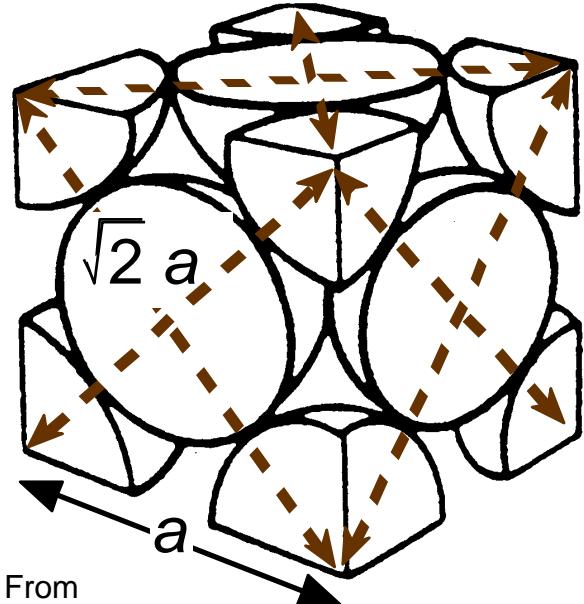
From Fig. 4.1
Callister's Materials Science and Engineering,
Adapted Version.

4 atoms/unit cell: 6 face x 1/2 + 8 corners x 1/8

(Courtesy P.M. Anderson)

Atomic Packing Factor: FCC

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

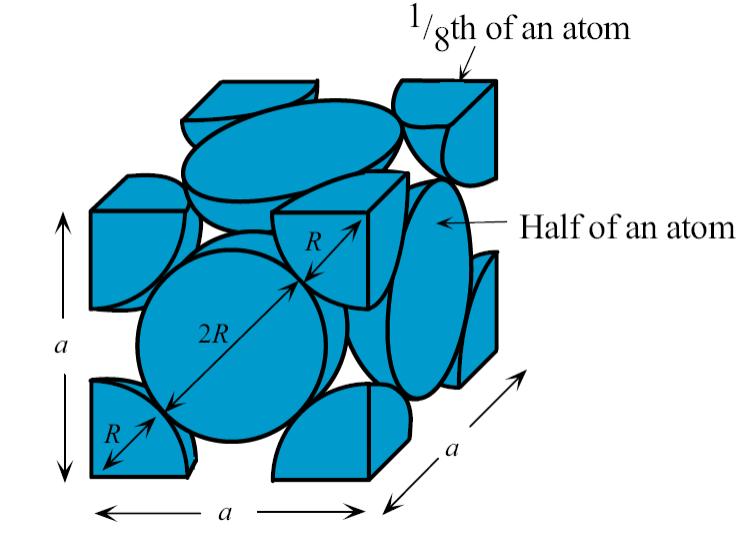


From
Fig. 4.1(a),
*Callister's Materials Science
and Engineering,*
Adapted Version.

Close-packed directions:
length = $4R = \sqrt{2} a$

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

$$\text{APF} = \frac{\frac{\text{atoms}}{\text{unit cell}}}{\frac{\text{volume}}{\text{unit cell}}} = \frac{4 \frac{4}{3} \pi (\sqrt{2}a/4)^3}{a^3}$$

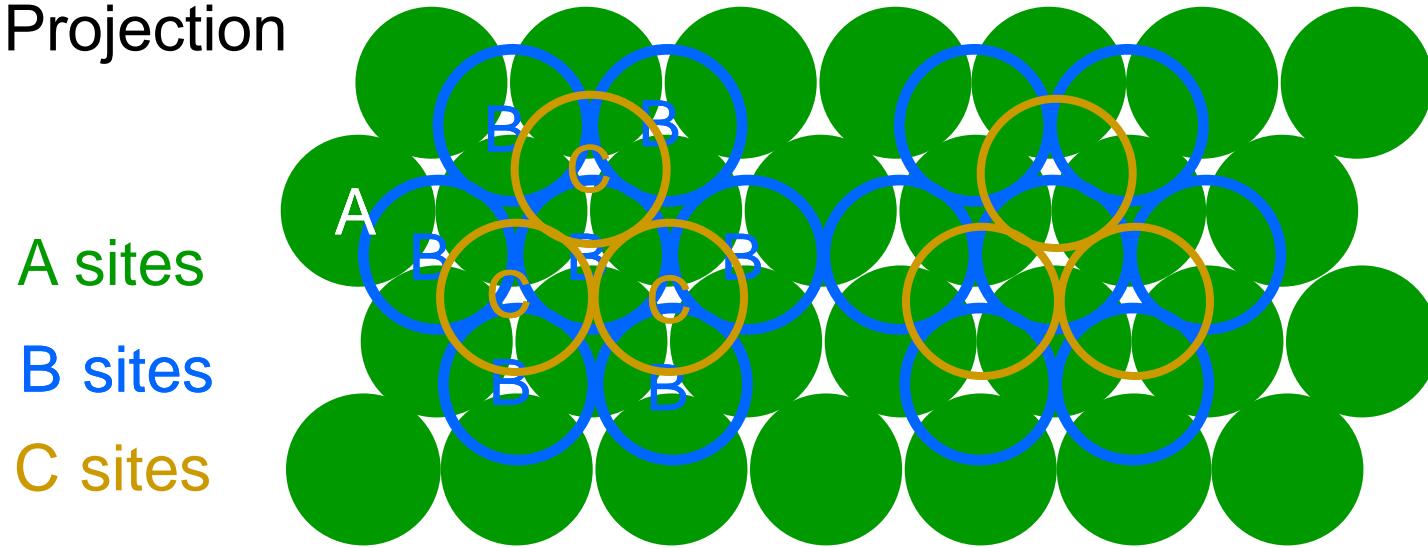


FCC unit cell.
atomic radius is R
lattice parameter is a

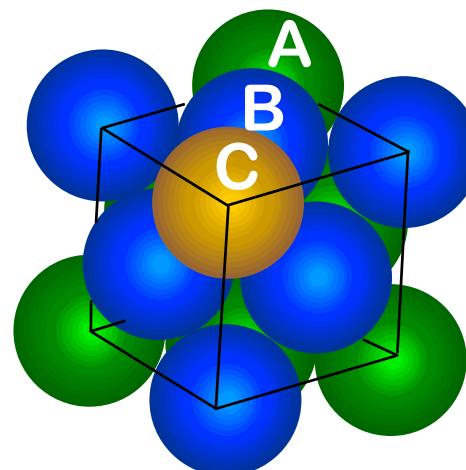
FCC & HCP are **close-packed crystal structure** because the atoms are packed as closely as possible. **74% is max. packing possible** with identical spheres

FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

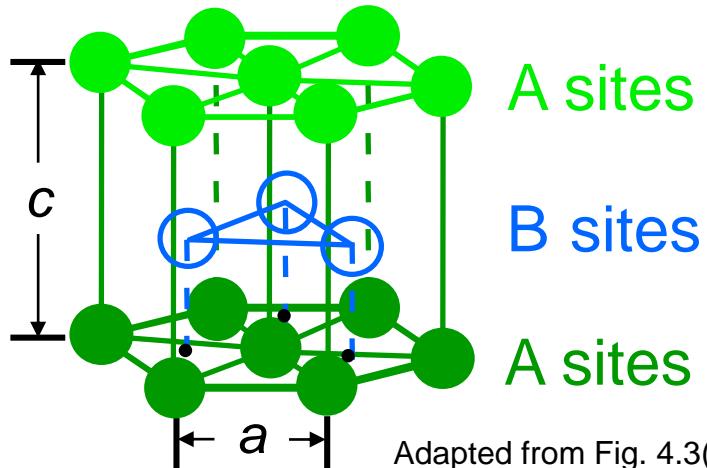


- FCC Unit Cell



Hexagonal Close-Packed Structure (HCP)

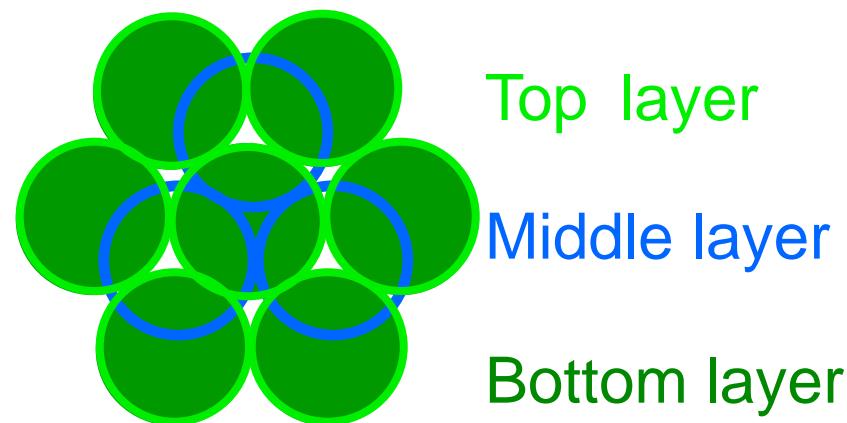
- ABAB... Stacking Sequence
- 3D Projection



Adapted from Fig. 4.3(a),
Callister's Materials Science and Engineering,
Adapted Version.

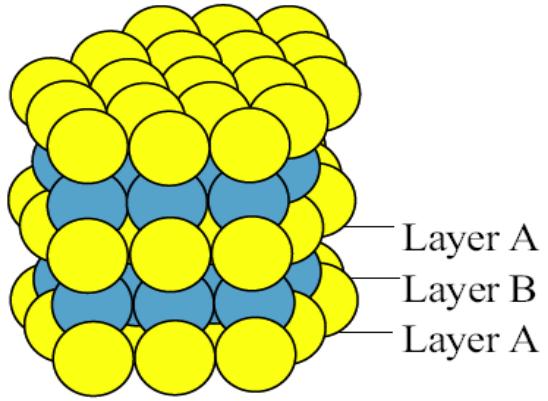
- Coordination # = 12
- APF = 0.74
- $c/a = 1.633$

- 2D Projection

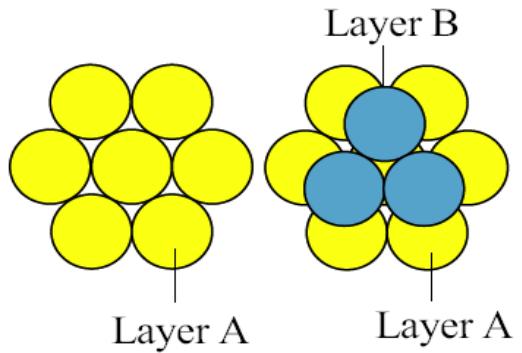


6 atoms/unit cell

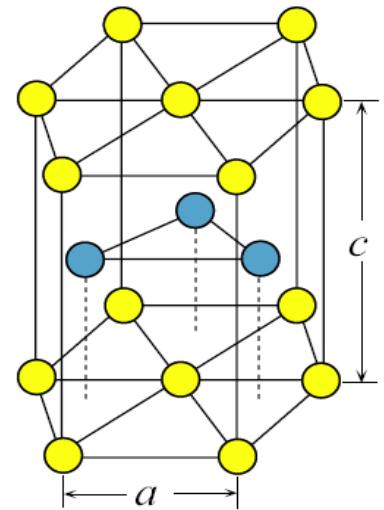
ex: Cd, Mg, Ti, Zn



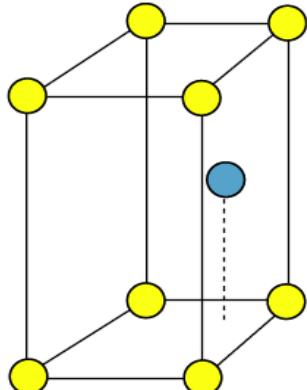
(a)



(b)



(c)



(d)

The Hexagonal Close Packed (HCP) Crystal Structure.

(a) The Hexagonal Close Packed (HCP) Structure. A collection of many Zn atoms. Color difference distinguishes layers (stacks).

(b) The stacking sequence of closely packed layers is ABAB

(c) A unit cell with reduced spheres

(d) The smallest unit cell with reduced spheres.

Examples: Be, Mg, α -Ti ($< 882^\circ\text{C}$), Cr, Co, Zn, Zr, Cd

Theoretical Density, ρ

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

$$\rho = \frac{n A}{V_c N_A}$$

where

n = number of atoms/unit cell

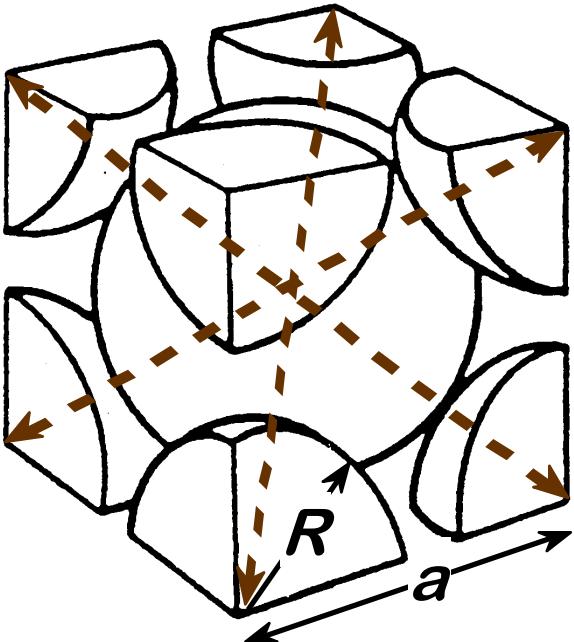
A = atomic weight (g/mol)

N_A = Avogadro's number

= 6.023×10^{23} atoms/mol

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

Theoretical Density, ρ



- Ex: Cr (BCC)

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

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

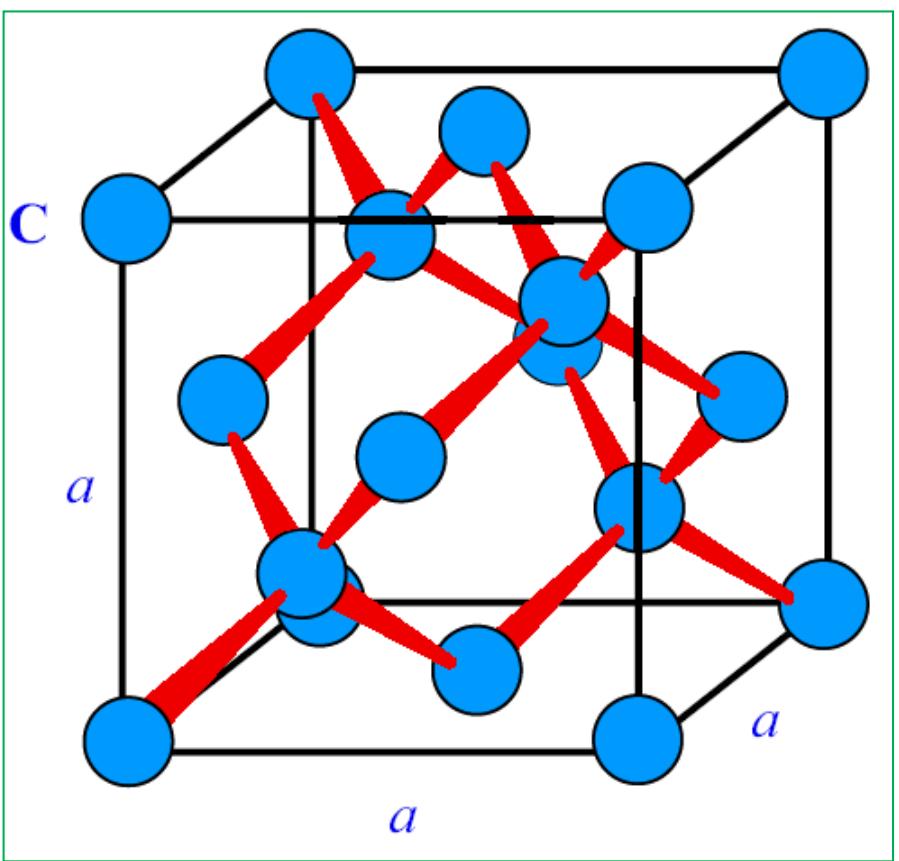
$$n = 2$$

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

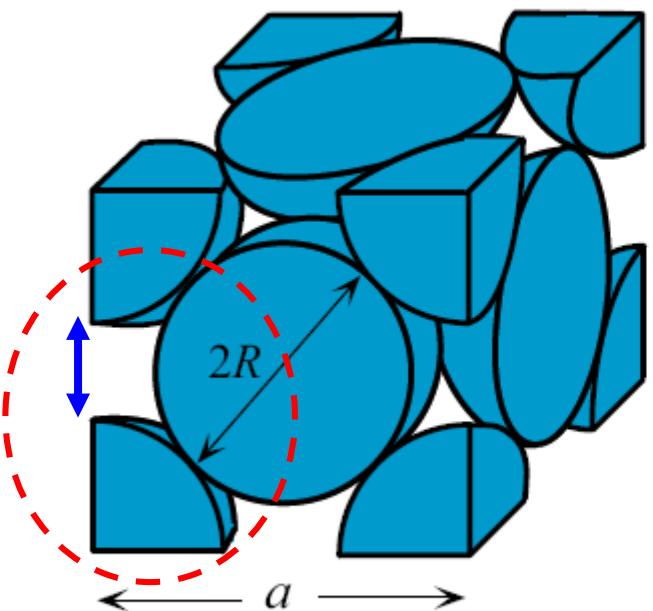
$$\rho = \frac{\frac{\text{atoms}}{\text{unit cell}} \times A}{\frac{\text{volume}}{\text{unit cell}}} = \frac{2 \times 52.00}{a^3 \times 6.023 \times 10^{23}}$$

Atoms per unit cell: 2
Molar mass (A): 52.00 g/mol
Volume per unit cell: a^3
Avogadro's number: 6.023×10^{23} mol⁻¹

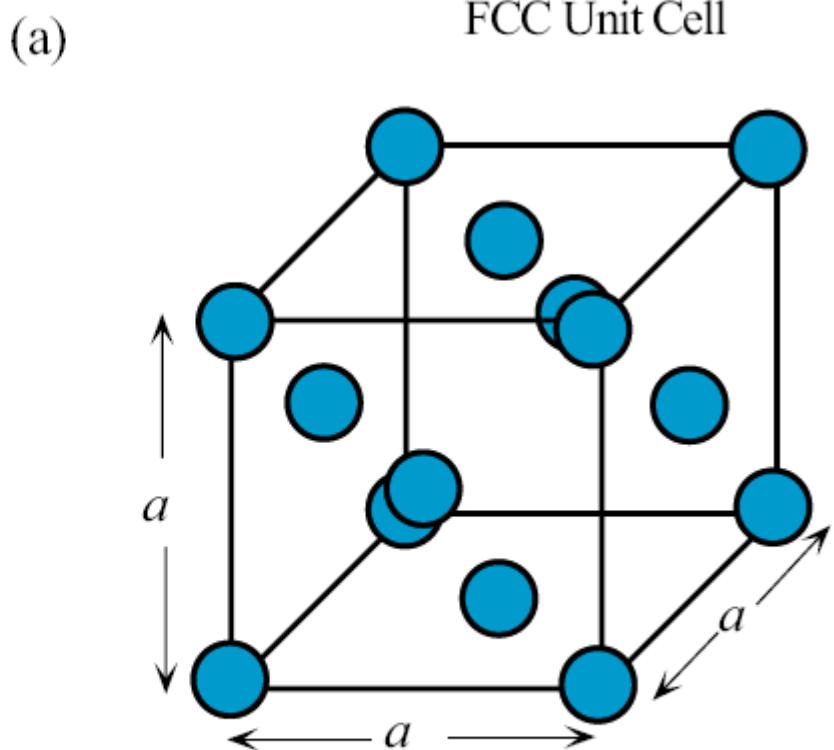
$\rho_{\text{theoretical}} = 7.18 \text{ g/cm}^3$
 $\rho_{\text{actual}} = 7.19 \text{ g/cm}^3$



Grey Sn (α -Sn), semiconductors Ge and Si have this crystal structure.



(b)



(c)

Isn't highest packing in diamond type fcc structure?

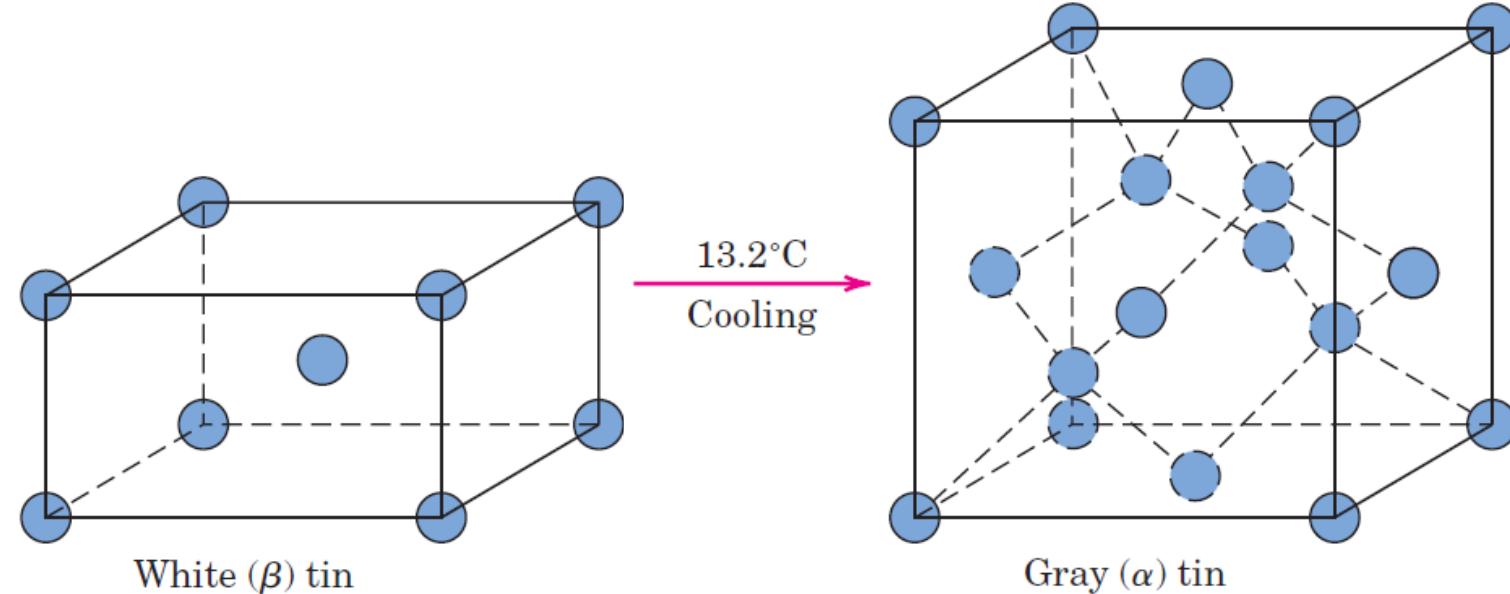
- Discuss just based on hard sphere (not reduced for imagination) model **and same size atoms**. Understand without math calculations

APF: DC < SC < BCC < (FCC=HCP)

Tin (Allotropic Transformation)

- ✓ Tin - experiences an allotropic change at 13.2 °C (55.8 °F)
- ✓ White (or β) tin - BCT crystal structure at room temperature
- ✓ Transforms to gray (or α) tin, which has crystal structure similar to diamond (i.e., diamond cubic crystal structure)

- This change takes place at extremely slow rate
- Lower the temperature, faster the rate
- **27 % increase in volume**
- 1.53 g/cm³ decrease in density (from 7.30 to 5.77 g/cm³).
- This volume expansion results in the disintegration of white tin into a coarse powder of the gray allotrope



(1) Tin pest, transformation of β -Sn into α -Sn

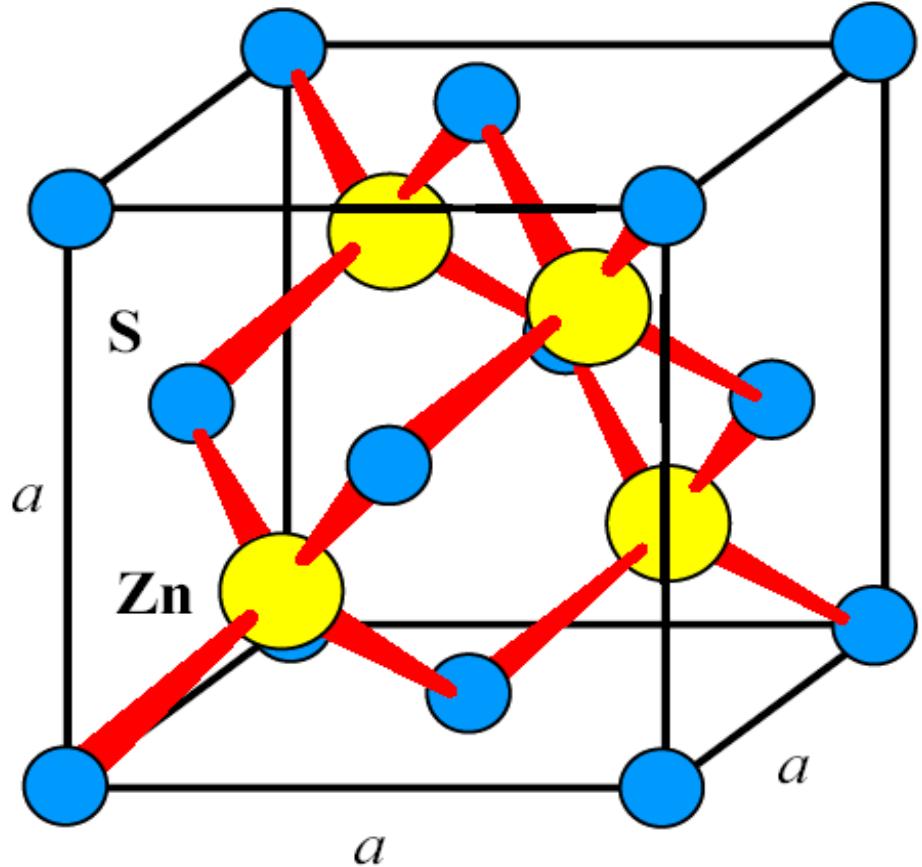
www.youtube.com/watch?v=sXB83Heh3_c

- ✓ Time lapse video of sample maintained at -40 °C
- ✓ 20 shots per hour
- ✓ 1 second of movie correspond 1 hour of real time



(2) Tin pest, Seeding from the centre: www.youtube.com/watch?v=Hb0VoQ-xQhU&NR=1

AX crystal structure: zinc blende or sphalerite structure



Zinc blende (ZnS) cubic crystal structure. Many important compound crystal structures have the zinc blende structure.

Examples: AlAs , GaAs , GaP , GaSb , InAs , InP , InSb , ZnS , ZnTe , and SiC .

- Many important compound semiconductors have this crystal structure, GaAs being the most commonly known
- Unit cell looks like a diamond cubic, but with Zn & S (or Ga & As) atoms alternating positions
- Unit cell is termed the **zinc blende** structure after the mineralogical term for zinc sulfide (ZnS), which has this type of unit cell
- Unit cell can also be described in terms of a fundamental **FCC lattice** and **a basis that has two atoms**, Zn and S (or Ga and As)
- For example, we can place one Zn at each lattice point and one S atom displaced from the Zn by $a/4$ along the cube edges

- All corner and face positions of the cubic cell are occupied by S atoms, while the Zn atoms fill interior tetrahedral positions
- Equivalent structure results if Zn and S atom positions are reversed
- Thus, each Zn atom is bonded to four S atoms, and vice versa

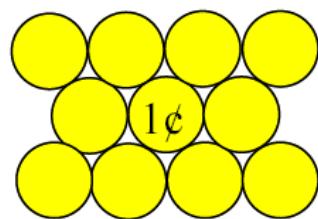
Coordination number is 4; i.e., all atoms are tetrahedrally coordinated

- Most often the atomic bonding is highly covalent in compounds exhibiting this crystal structure

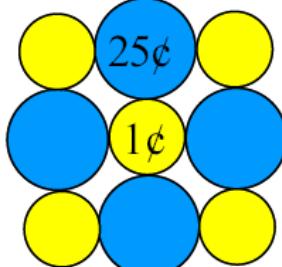
AX crystal structure: sodium chloride (NaCl) or rock salt type

halite crystals
are transparent

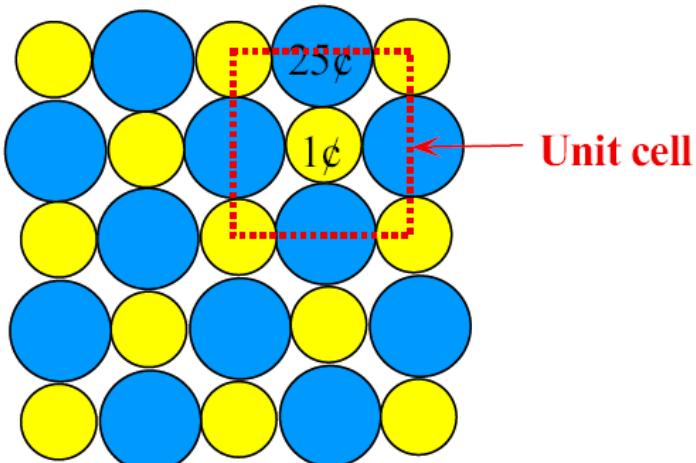
Ratio of radii = 1



Ratio of radii = 0.75

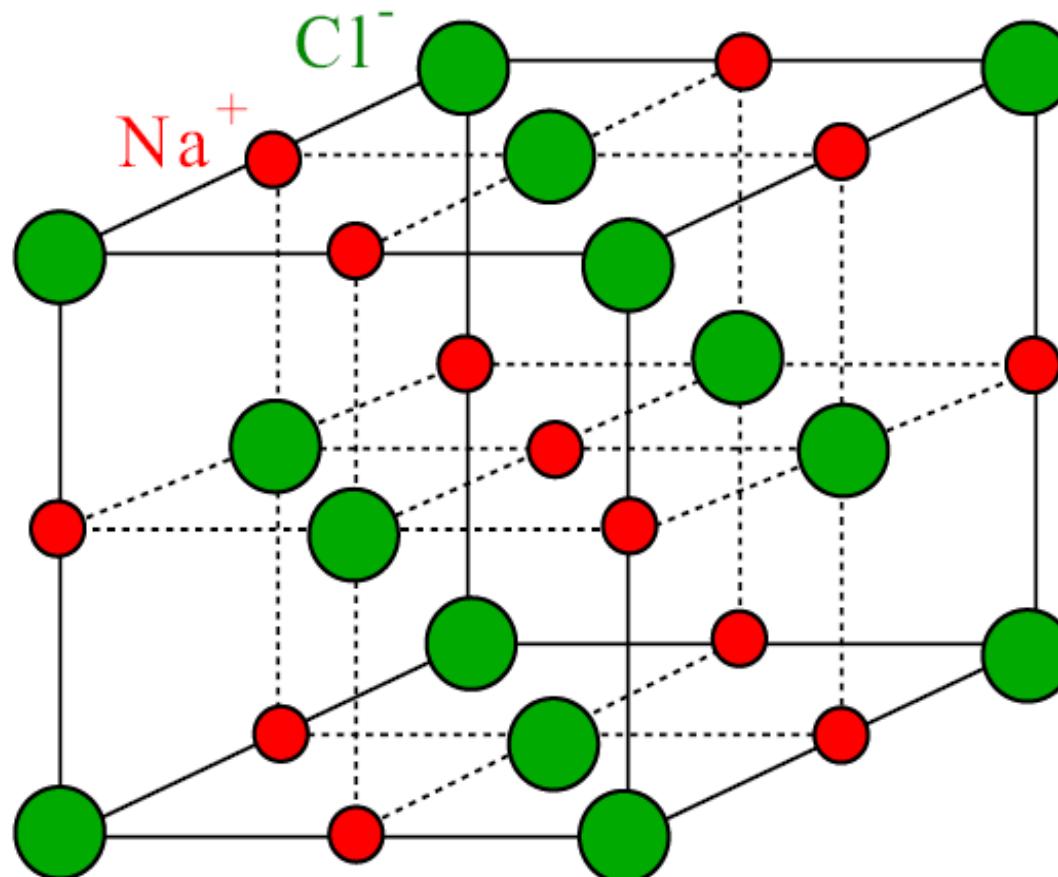


Nearest neighbors = 6



A two-dimensional crystal of pennies and quarters

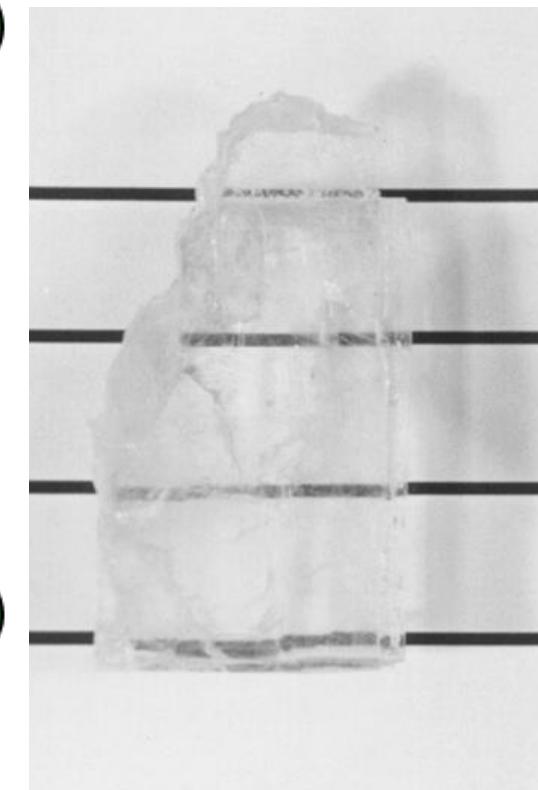
Packing of coins on a table top to build a two dimensional crystal



A possible reduced sphere unit cell for NaCl

Alternative unit cell may have Na^+ & Cl^- interchanged

Examples: AgCl , CaO , CsF , LiF , LiCl , NaF , NaCl , KF , KCl , MgO , MnS , and FeO

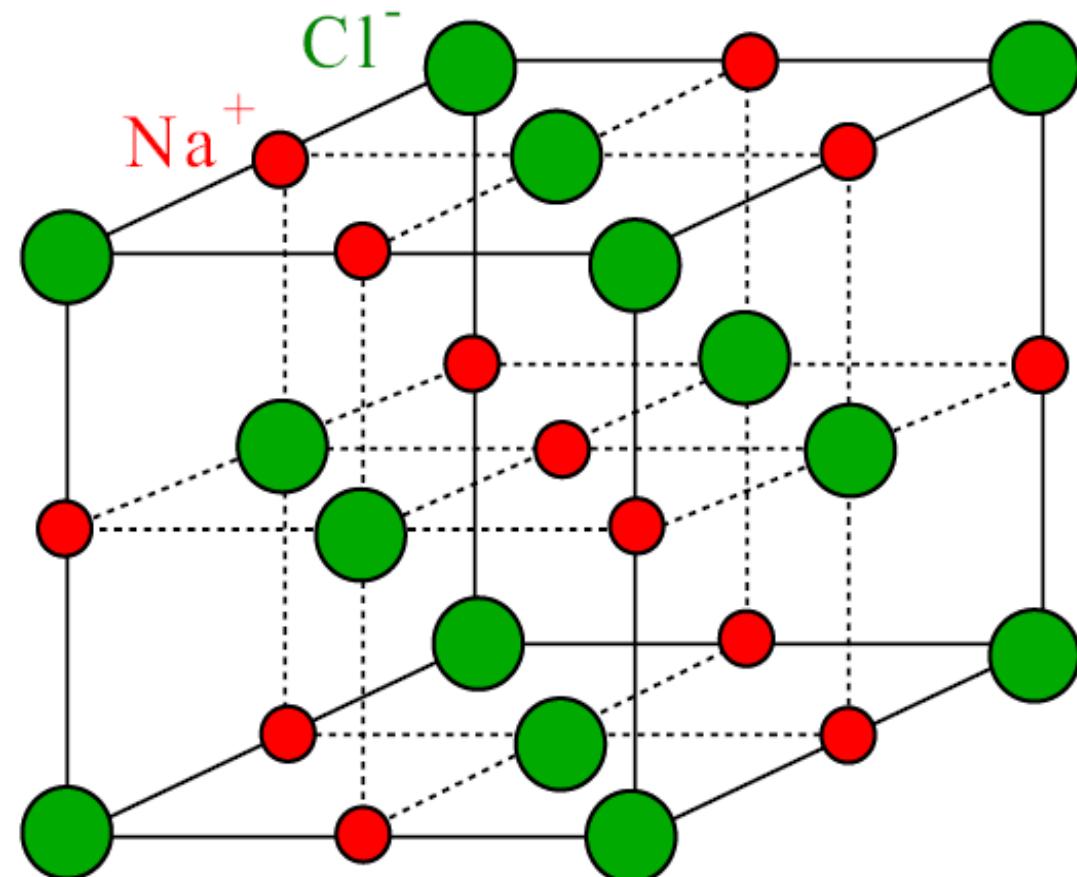


|SOURCE: Photo by SOK

Ionic crystals are often **transparent**, and metallic crystals are always opaque

Maintaining long-range order or symmetry depends on the relative charge & relative size per ion

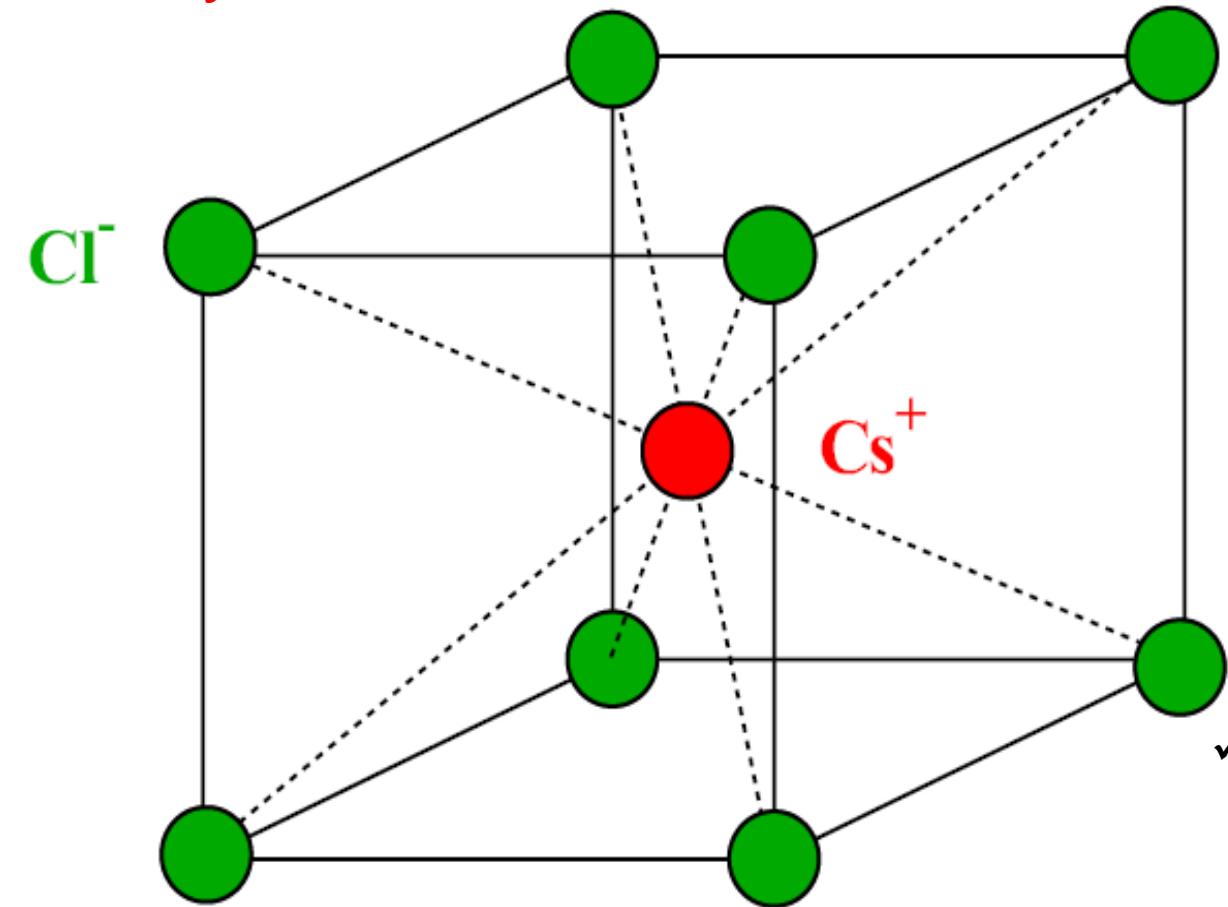
- ❖ 3-D equivalent of the 2-D unit cell of the “penny–quarter” crystal is the **NaCl unit cell**
- ❖ Na ion is about half the size of the Cl ion, which permits 6 nearest neighbors while maintaining long-range order
- Unit cell for this crystal structure is generated from an *FCC arrangement of anions with one cation situated at the cube center and one at the center of each of the 12 cube edges*
- Equivalent crystal structure results from FCC arrangement of cations



- ✓ Repetition of this unit cell in 3-D generates the whole NaCl crystal
- ✓ Coordination number for both cations & anions = 6
- ✓ 2 interpenetrating FCC, 1 composed of the cations, the other of anions

- So, we can describe the whole crystal with **2 interpenetrating FCC unit cells**, each having **oppositely charged ions at the corners and face centers**
- Many ionic solids have the rock salt (NaCl) crystal structure

AX crystal structure: cesium chloride



A possible reduced sphere unit cell for the CsCl crystal.
An alternative unit cell may have Cs^+ and Cl^- interchanged. Examples: CsCl , CsBr , CsI , TlCl , TlBr , TlI .

- ✓ When cation and anions have equal charges and are about the same size, as in the CsCl crystal, the unit cell is called the **CsCl unit cell**
- ✓ Each cation is surrounded by 8 anions (and vice versa), which are at the corners of a cube
- ✓ Coordination number is 8 for both ion types
- ✓ This is not a true BCC unit cell because the atoms at various BCC lattice points are different
- ✓ CsCl - simple cubic lattice with a basis that has one Cl^- ion and one Cs^+ ion
- ✓ Interchange of anions with cations, and vice versa, produces the same crystal structure

Not a BCC crystal structure because ions of 2 different kinds are involved

Ceramic Crystal Structures

- Most ceramic materials are compounds that generally contain metallic and non-metallic elements
- Well known for electrical insulating properties
- Interatomic bonds are either totally ionic, or predominantly ionic but having some covalent character
- Atomic bonding ranges from purely ionic to totally covalent and the degree of ionic character is dependent on the electronegativities of the atoms
- Many technologically important semiconductor materials have mixed bonding, (e.g., GaAs)
- Because ceramics are composed of **at least two elements, and often more**, their crystal structures are generally more **complex** than those for metals

Coordination # and Ionic Radii

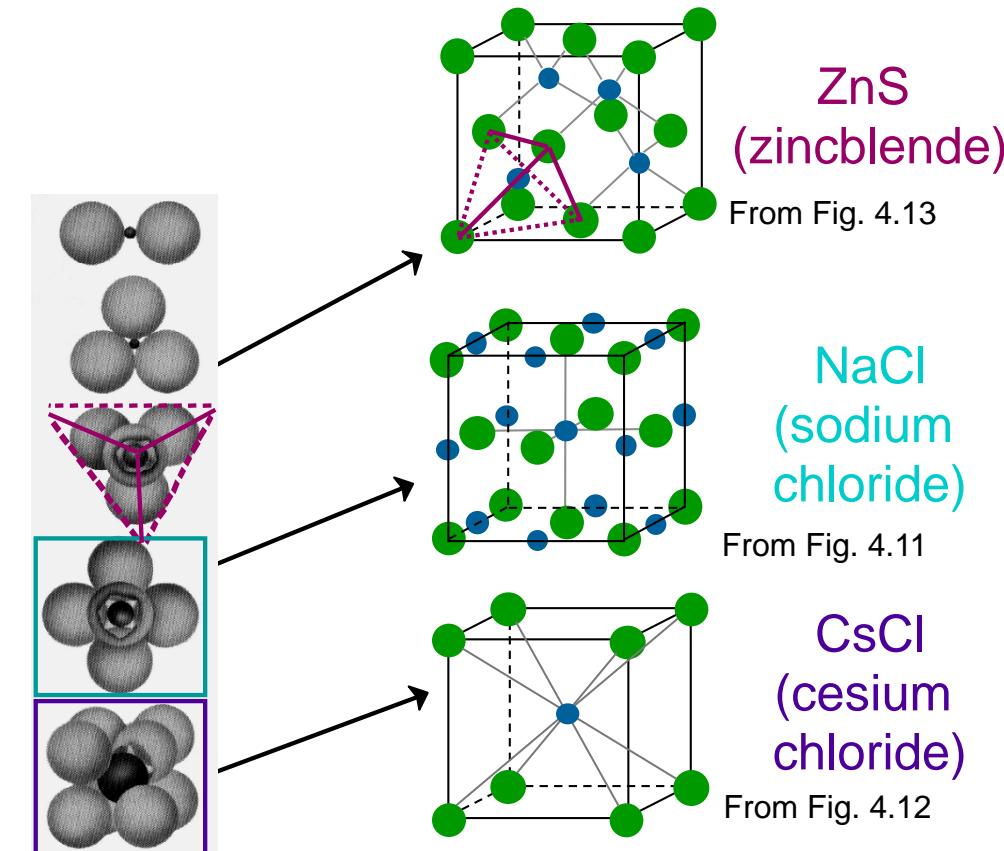
- Coordination # increases with

$$\frac{r_{\text{cation}}}{r_{\text{anion}}}$$

Issue: How many anions can you arrange around a cation?

$\frac{r_{\text{cation}}}{r_{\text{anion}}}$	Coord #	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	T_D
0.414 - 0.732	6	O_H
0.732 - 1.0	8	cubic

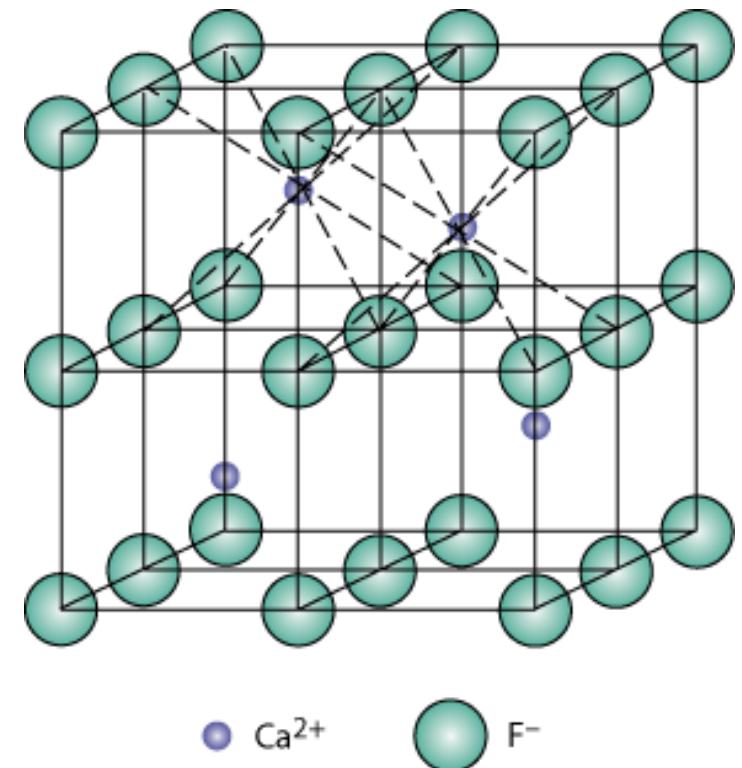
Adapted from Table 4.3



AX_2 Crystal Structures

Fluorite structure

Ex.: UO_2 , ThO_2 , ZrO_2 , CeO_2

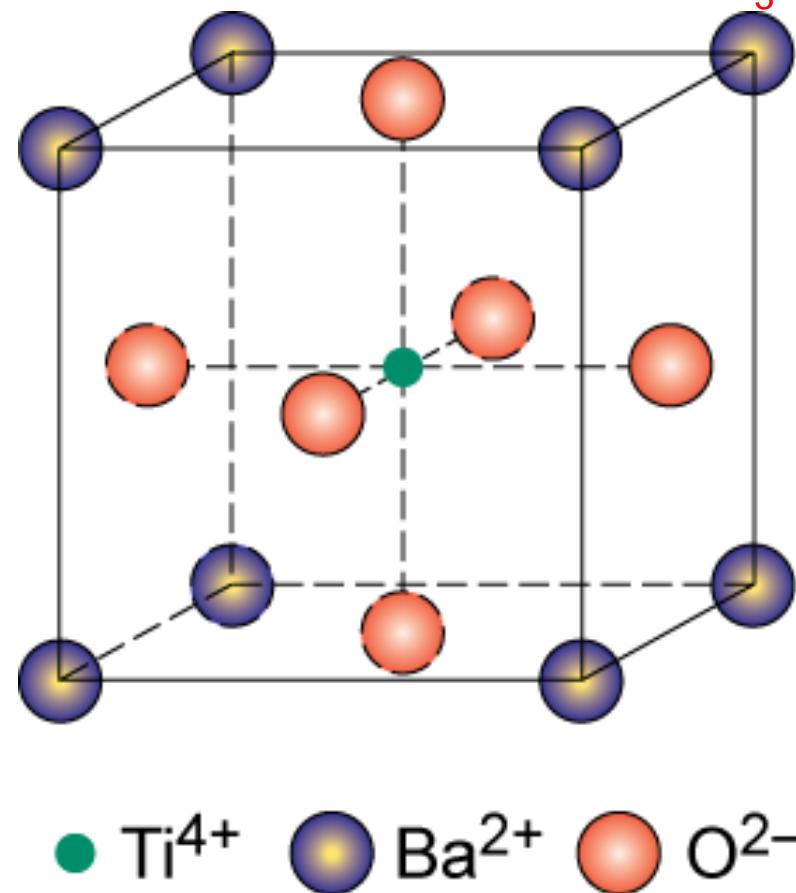


antifluorite structure –
cations and anions reversed

ABX_3 Crystal Structures

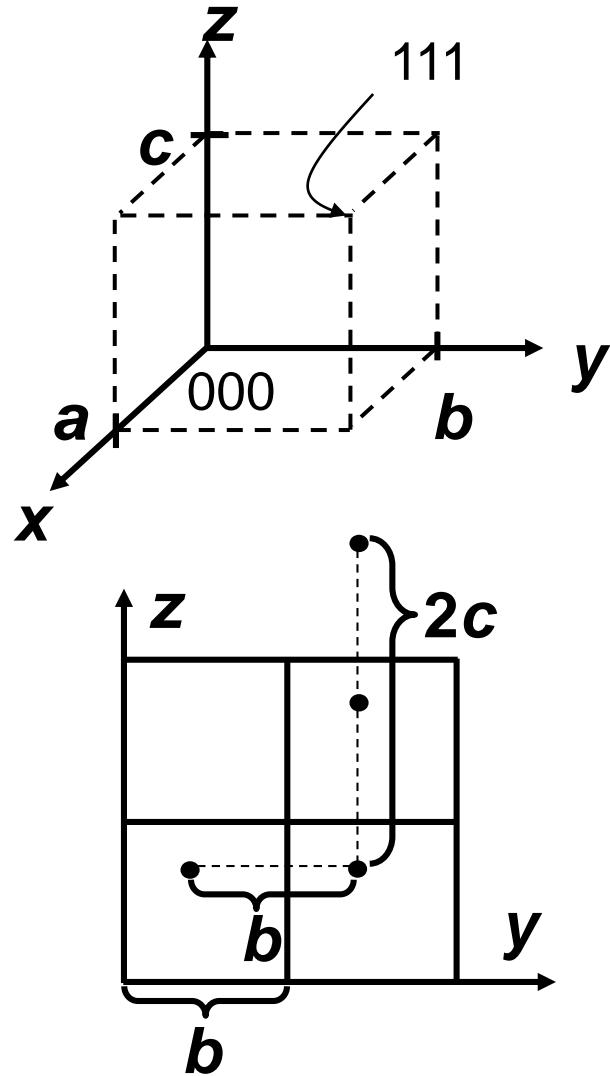
Perovskite structure

Ex: complex oxide, such as
Barium titanate BaTiO_3



- ✓ Ba ions are situated at all eight corners of the cube
- ✓ A single Ti ion is at the cube center
- ✓ O ions located at the center of each of the 6 faces

Point Coordinates



Point coordinates for unit cell center are

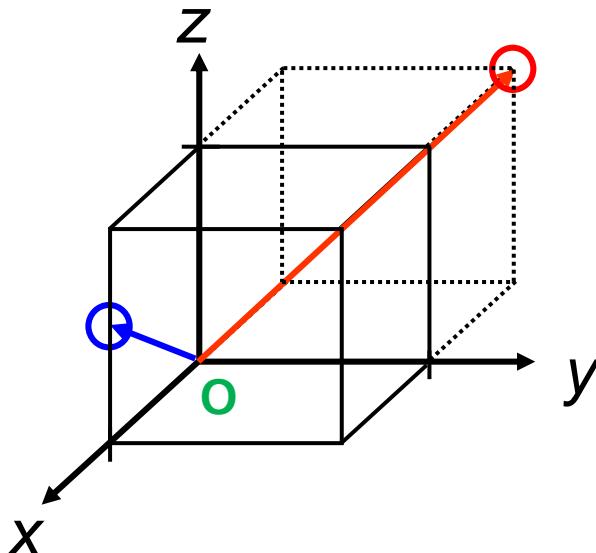
$$a/2, b/2, c/2 \quad 1/2 \ 1/2 \ 1/2$$

Point coordinates for unit cell corner are 111

Translation: integer multiple of lattice constants \rightarrow identical position in another unit cell

- ✓ Indices used to describe a direction within a space lattice are called Miller indices of direction.
- ✓ For convenience, the vector, which passes through origin of the reference coordinates, is ordinarily used to determine the directional indices.
- ✓ A direction within the space lattice is represented by a line passing through the origin & any other point P in space.
- ✓ Then this line may be identified simply by stating the coordinates of point P.
- ✓ The coordinates of the point P, expressed in terms of the lattice parameters a , b and c , and reduced to the smallest integers, are the Miller indices of the direction in question.

Crystallographic Directions



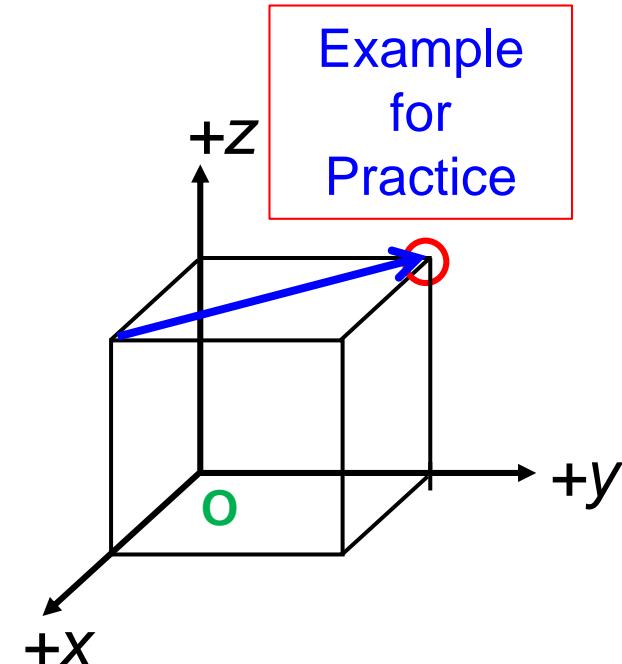
Algorithm

1. Vector repositioned (if necessary) to pass through origin O .
2. Read off projections in terms of unit cell dimensions a , b , and c
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

[uvw]

ex: $1, 0, \frac{1}{2} \Rightarrow 2, 0, 1 \Rightarrow [201]$

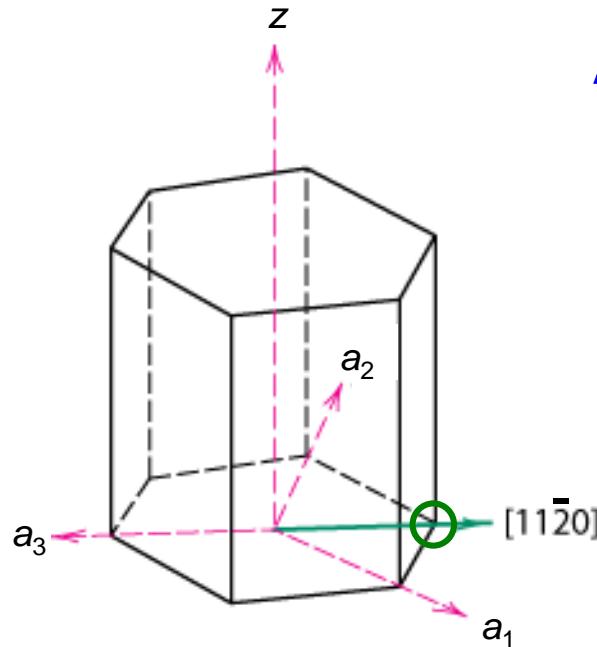
$-1, 1, 1 \Rightarrow [\bar{1}\bar{1}1]$ where overbar represents a negative index



Indices of a direction [uvw] & families of equivalent directions $\langle uvw \rangle$

Ex: $\langle 100 \rangle = [100], [010], [001], [\bar{1}00], [0\bar{1}0], [00\bar{1}]$

HCP Crystallographic Directions



From Fig. 3.6(a)
Callister's Materials Science and Engineering, Adapted Version.

ex: $\frac{1}{2}, \frac{1}{2}, -1, 0$

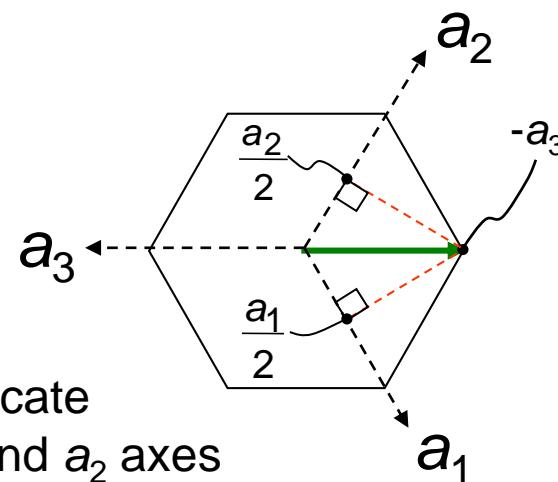
=>

Algorithm

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions a_1 , a_2 , a_3 , or c
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

$[uvtw]$

$[11\bar{2}0]$
dashed red lines indicate
projections onto a_1 and a_2 axes



HCP Crystallographic Directions

- Hexagonal Crystals

- 4 parameter Miller-Bravais lattice coordinates are related to the direction indices (i.e., $u'v'w'$) as follows.

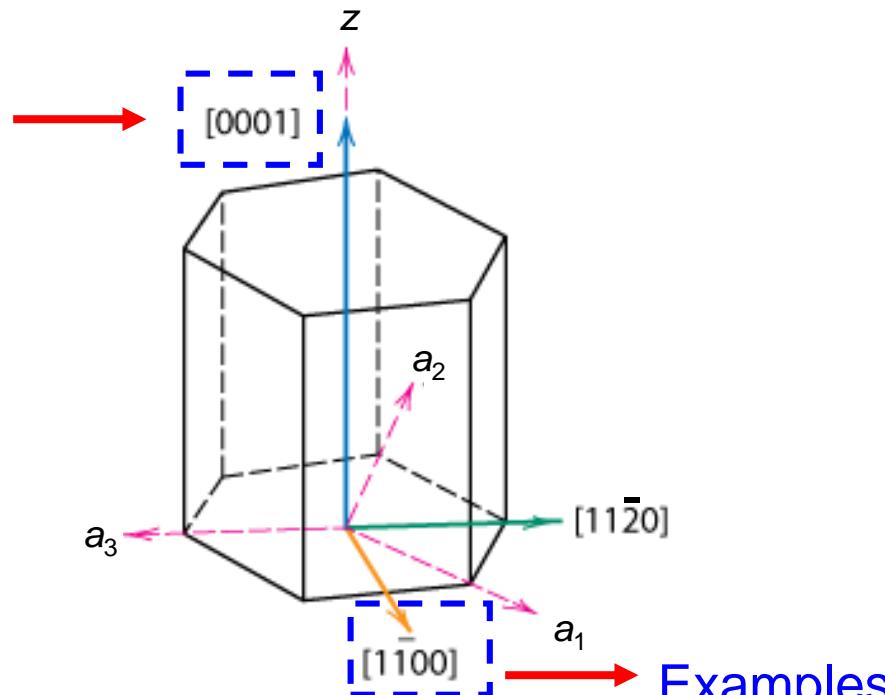
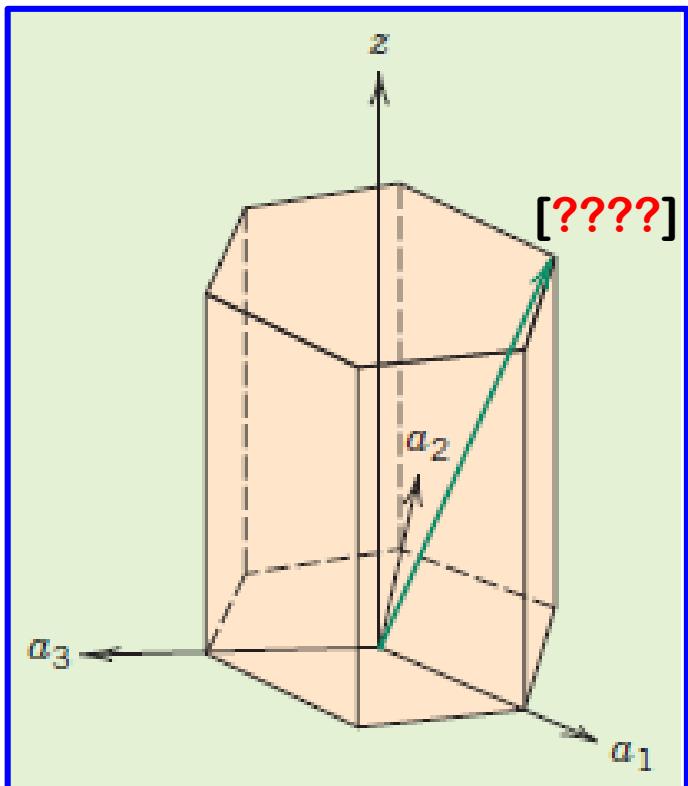


Fig. 3.6(a)
Callister's Materials Science and Engineering,
Adapted Version.

$$[u'v'w'] \rightarrow [uvtw]$$

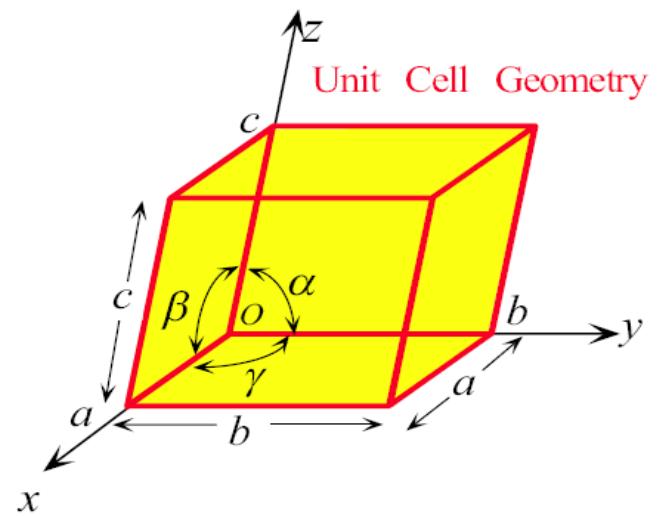
$$u = \frac{1}{3}(2u' - v')$$

$$v = \frac{1}{3}(2v' - u')$$

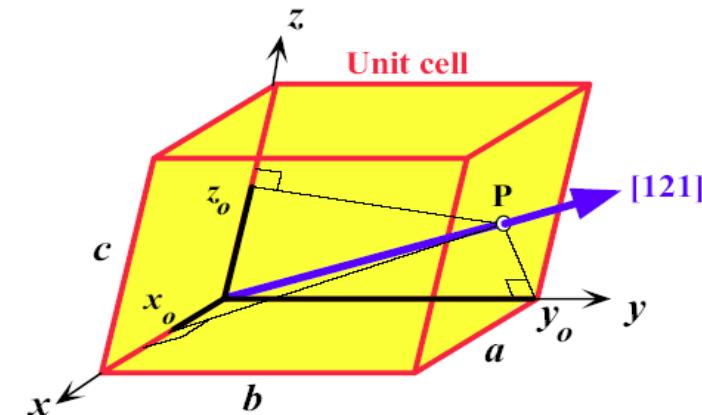
$$t = -(u + v)$$

$$w = w'$$

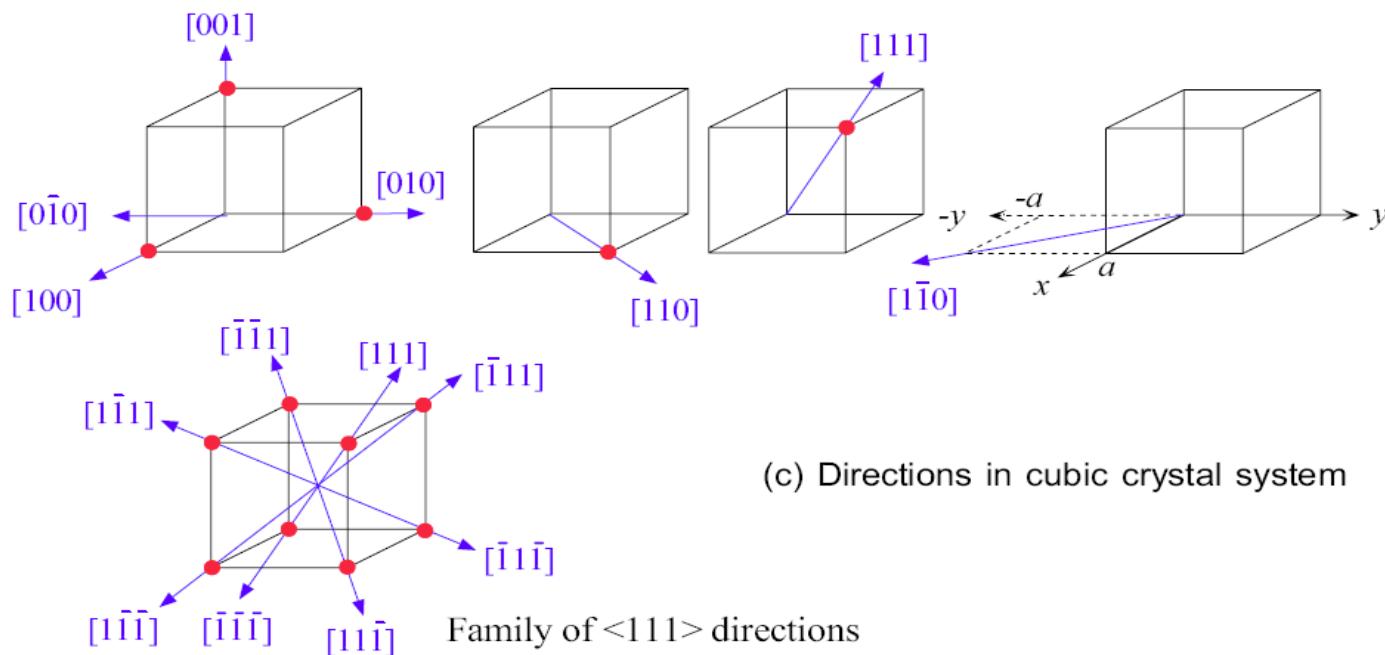
Examples
for
Practice



(a) A parallelepiped is chosen to describe geometry of a unit cell. We line the x, y and z axes with the edges of the parallelepiped taking lower-left rear corner as the origin



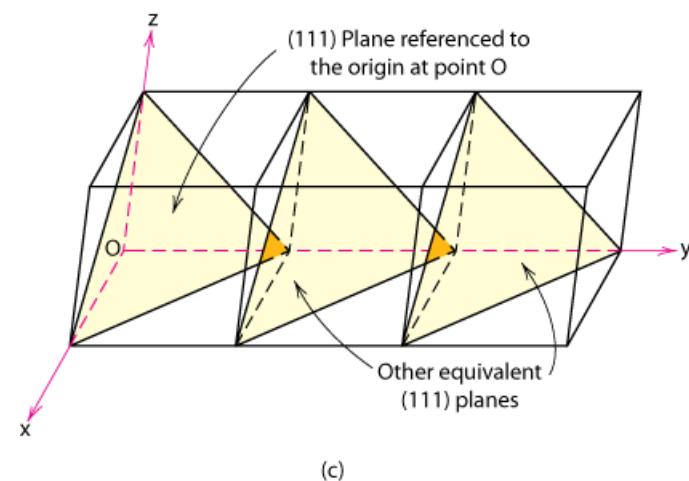
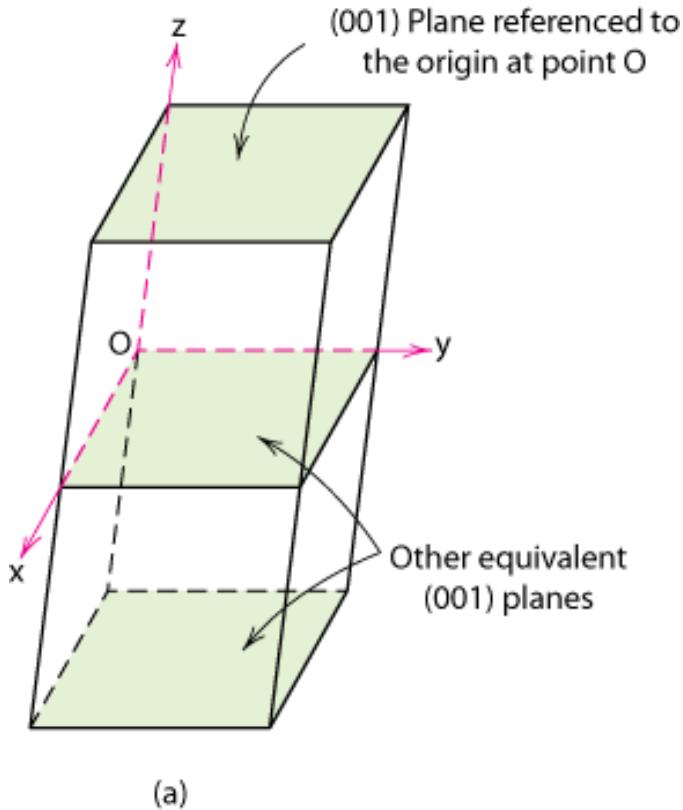
(b) Identification of a direction in a crystal



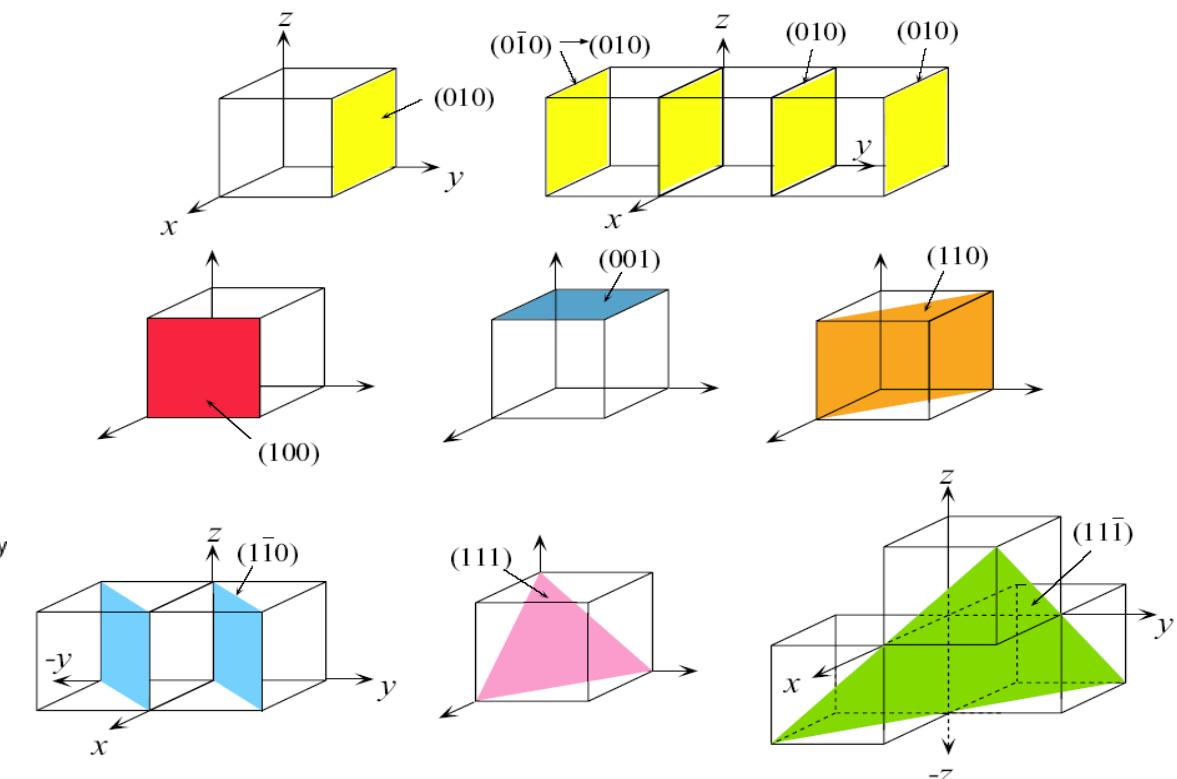
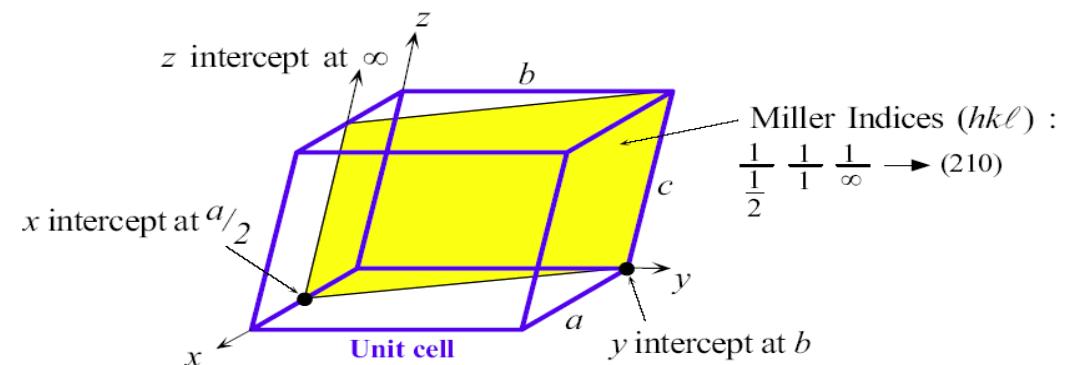
(c) Directions in cubic crystal system

Family of $\langle 111 \rangle$ directions

Crystallographic Planes



From Fig. 3.7
*Callister's Materials Science and Engineering,
 Adapted Version.*



Labeling of crystal planes and typical examples in the cubic lattice

Crystallographic Planes

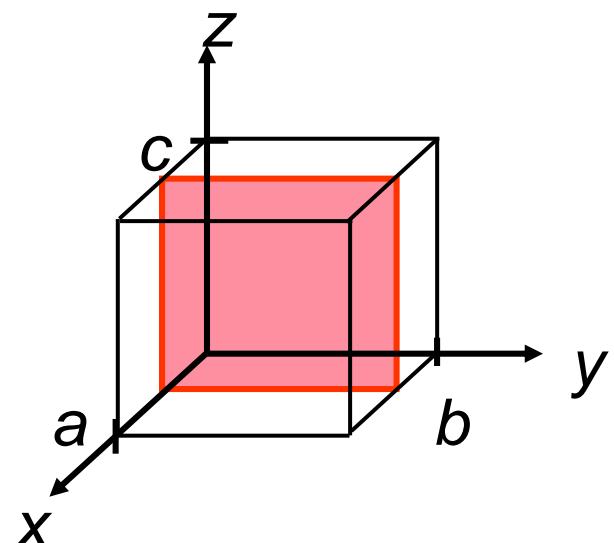
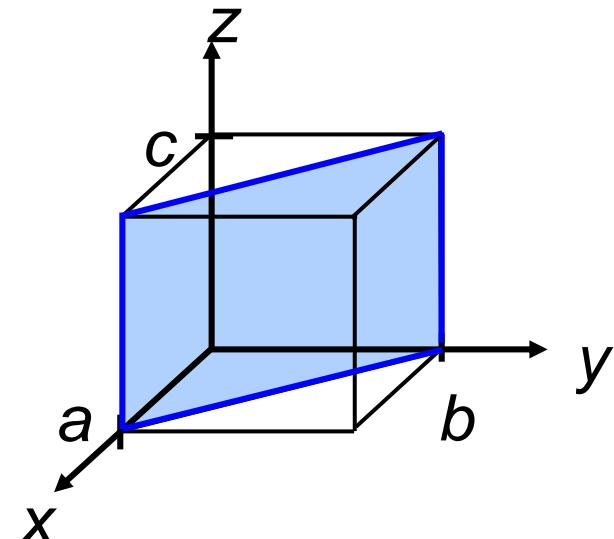
- Miller Indices: Reciprocals of (three) axial intercepts for a plane, cleared of fractions & common multiples.
- Algorithm
 1. Read off intercepts of plane with axes in terms of a, b, c
If plane is parallel to axis, it intercepts the axis at infinity
 2. Take reciprocals of intercepts
 3. Reduce to smallest integer values,
having the same ratio as the reciprocals
 4. Enclose in parentheses, no commas i.e., (hkl)

- ✓ Only gases, liquids, & amorphous solids are truly isotropic, i.e., their properties are same in every plane and every direction.
- ✓ Most crystalline materials are anisotropic, i.e. their properties vary according to the planes or direction along which they are measured; e.g., electrical resistivity, magnetic susceptibility, etc.
- ✓ Hence, it is desirable to have a system of notation to designate different planes and directions through the crystal.
- ✓ Intercepts are measured in terms of the edge lengths or dimensions of the unit cell from the origin along 3 axes.

Crystallographic Planes

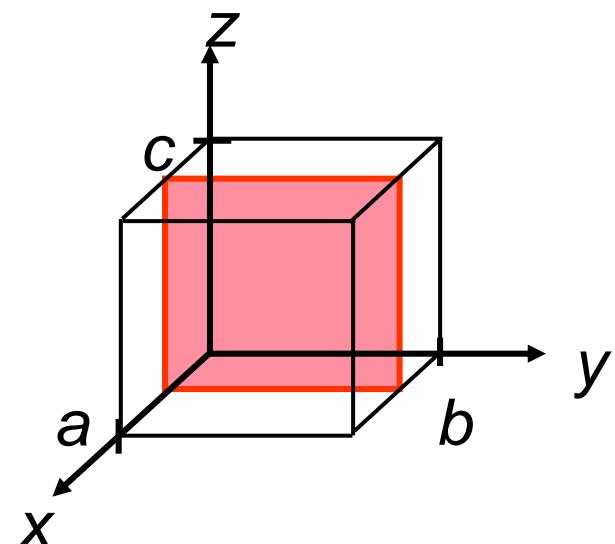
<u>example</u>	a	b	c
1. Intercepts	1	1	∞
2. Reciprocals	$1/1$	$1/1$	$1/\infty$
3. Reduction	1	1	0
4. Miller Indices	(110)		

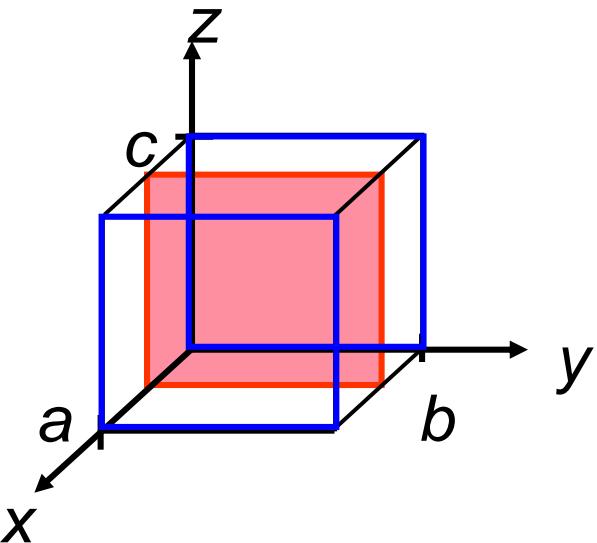
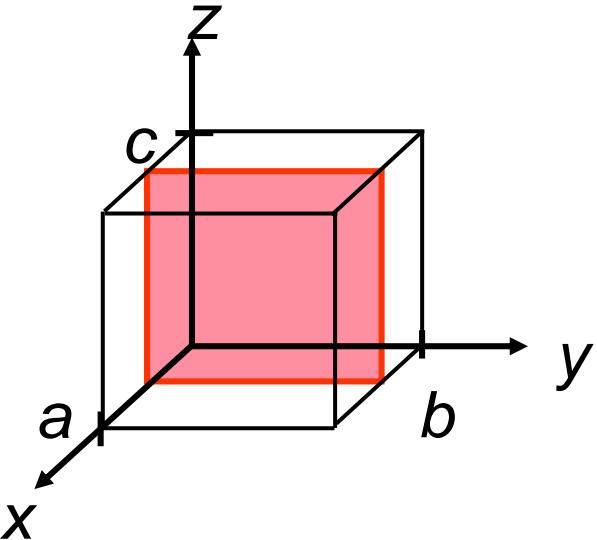
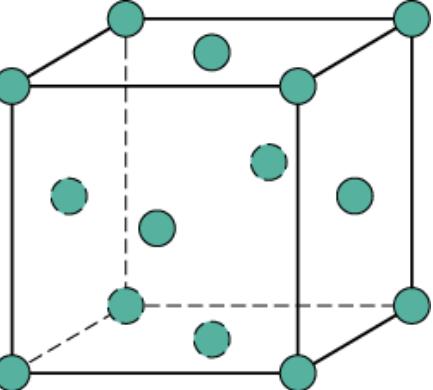
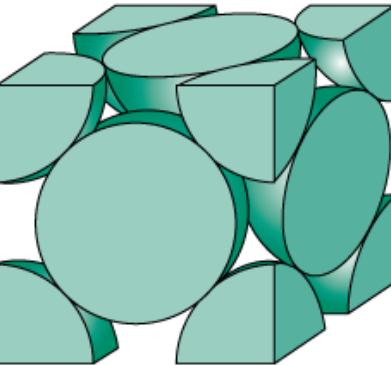
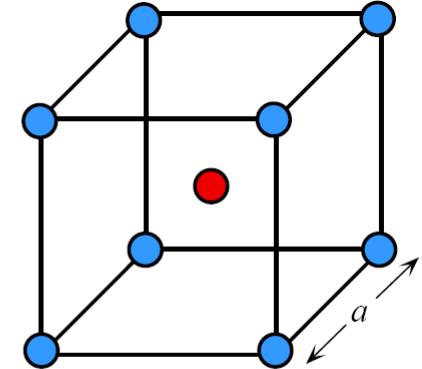
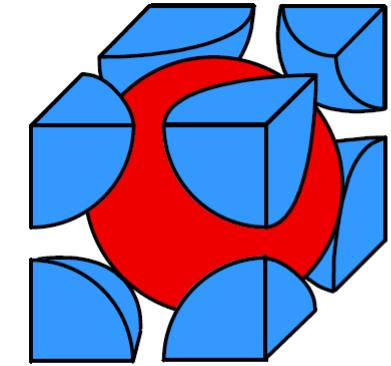
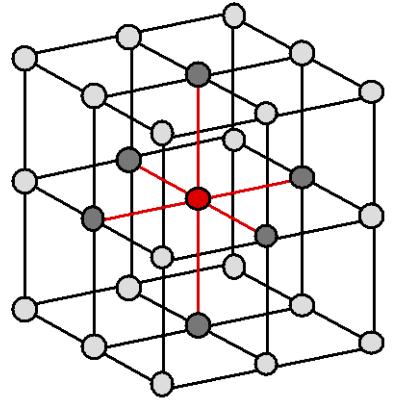
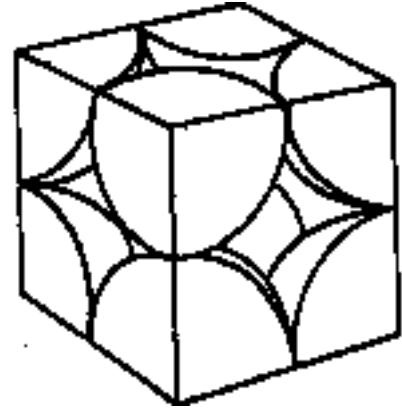
<u>example</u>	a	b	c
1. Intercepts	$1/2$	∞	∞
2. Reciprocals	$1/\frac{1}{2}$	$1/\infty$	$1/\infty$
3. Reduction	2	0	0
4. Miller Indices	(200)		



- Note that NOT all parallel planes are identical
- Planes can have the same Miller indices *only* if they are separated by a multiple of the lattice parameter
- (100) plane is not identical to (200) plane, *even though they are geometrically parallel*

- ✓ In terms of unit cell, plane (100) is face of unit cell cutting x axis at a , whereas (200) is a plane that is halfway inside the unit cell, cutting the x axis at $0.5 a$
- ✓ The planes contain different numbers of atoms
- ✓ (200) plane cannot be shifted by the lattice parameter a to coincide with plane (100)

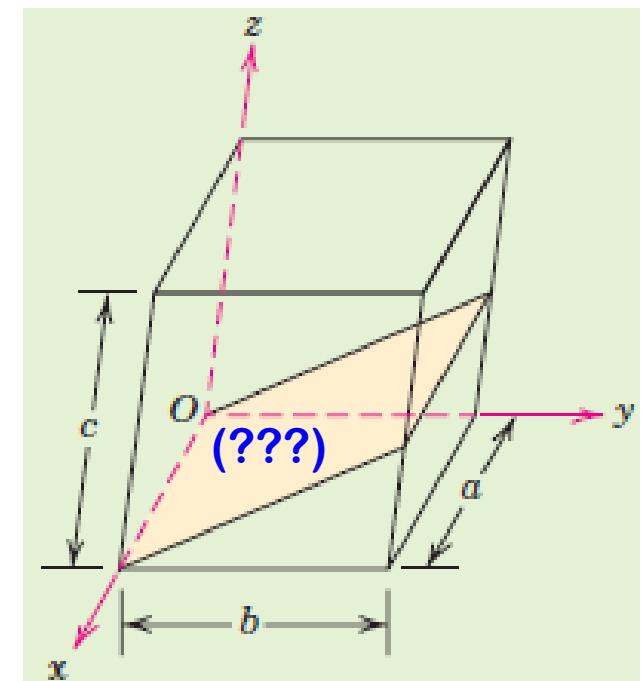
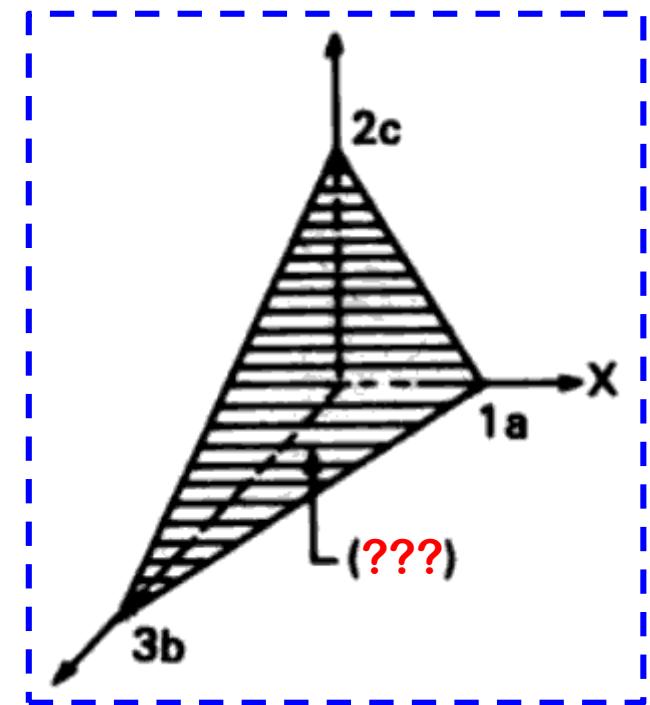
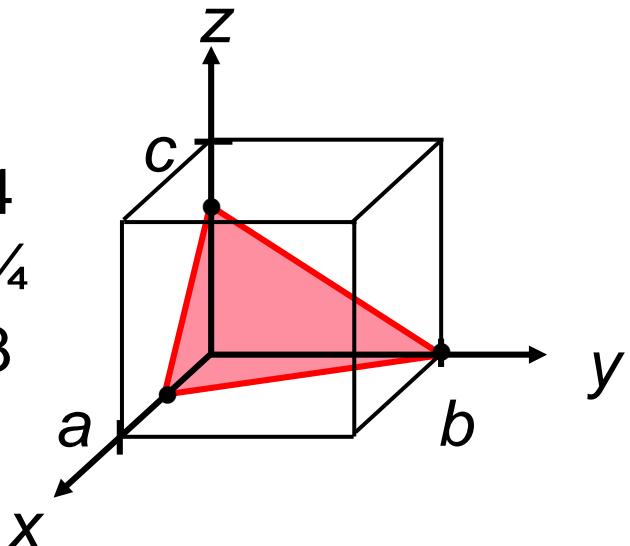




Crystallographic Planes

example

	a	b	c
1. Intercepts	1/2	1	3/4
2. Reciprocals	1/½	1/1	1/¾
	2	1	4/3
3. Reduction	6	3	4
4. Miller Indices	(634)		



Plane (hkl) & Family of Planes $\{hkl\}$

Ex: $\{100\} = (100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$

Crystallographic Planes (HCP)

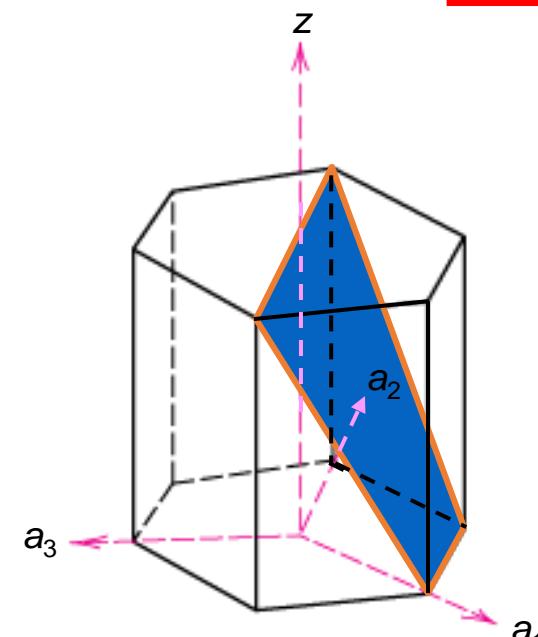
- In hexagonal unit cells the same idea is used

example

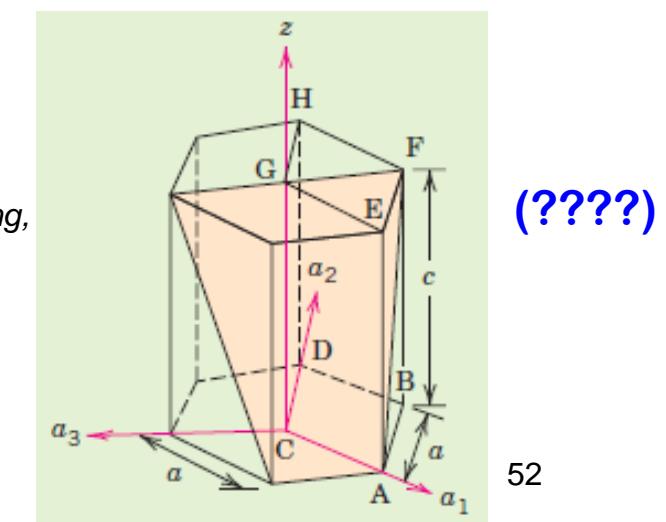
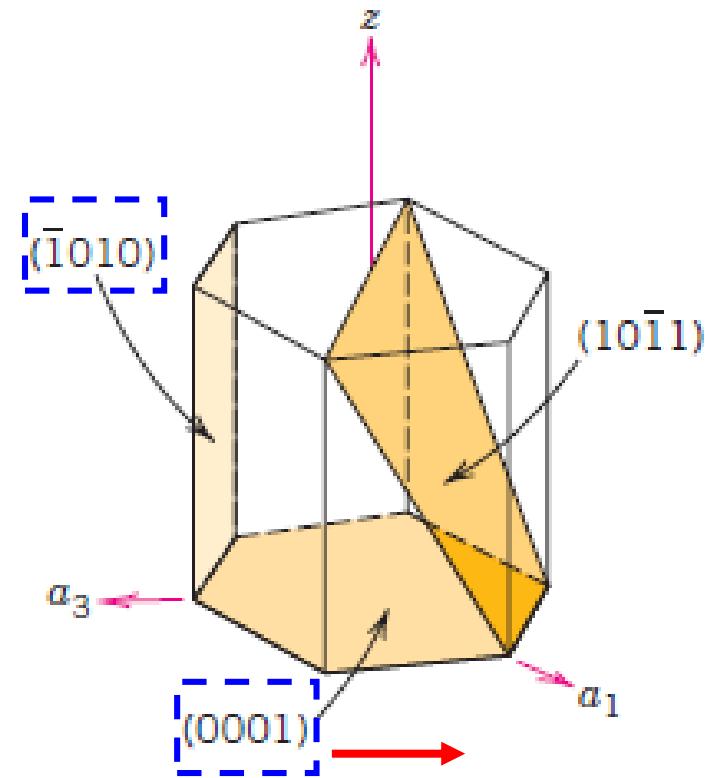
	a_1	a_2	a_3	c
1. Intercepts	1	∞	-1	1
2. Reciprocals	1	$1/\infty$	-1	1
	1	0	-1	1
3. Reduction	1	0	-1	1
4. Miller-Bravais Indices	$(10\bar{1}1)$			

$$i = -(h+k)$$

$$(h k l) \rightarrow (h k i l)$$

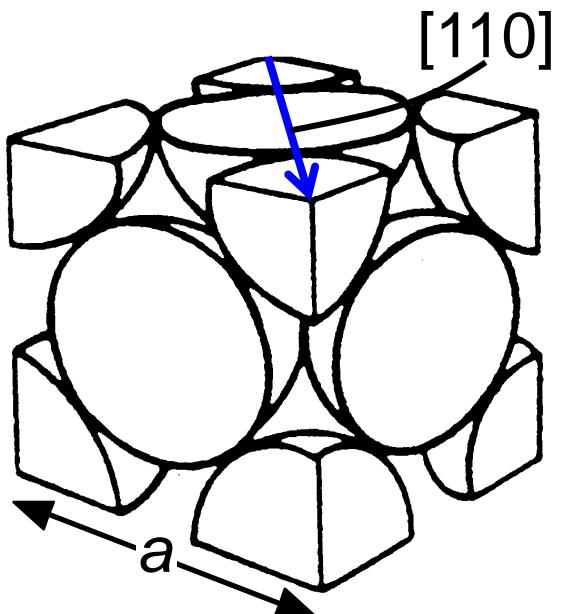


From Fig. 3.6(b)
Callister's Materials Science and Engineering,
Adapted Version.



Linear Density

- Linear Density of Atoms $\equiv LD = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}}$



ex: linear density of Al in [110]
direction

$$a = 0.405 \text{ nm}$$

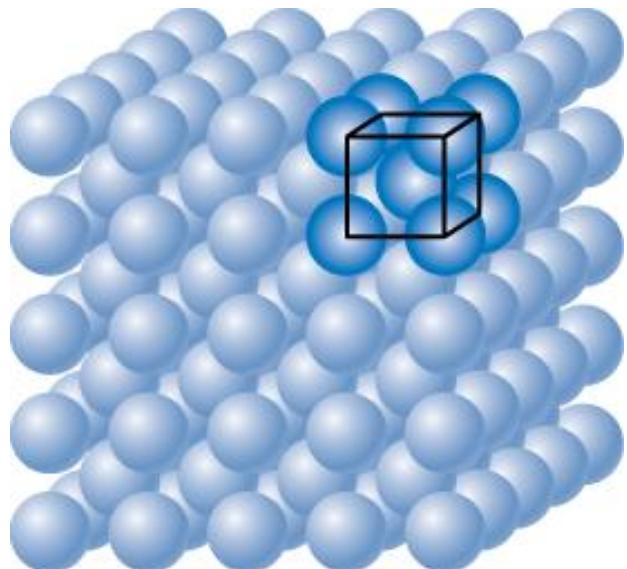
$$LD = \frac{\text{# atoms}}{\text{length}} = \frac{2}{\sqrt{2a}} = 3.5 \text{ nm}^{-1}$$

Atomic Packing of Crystallographic Planes

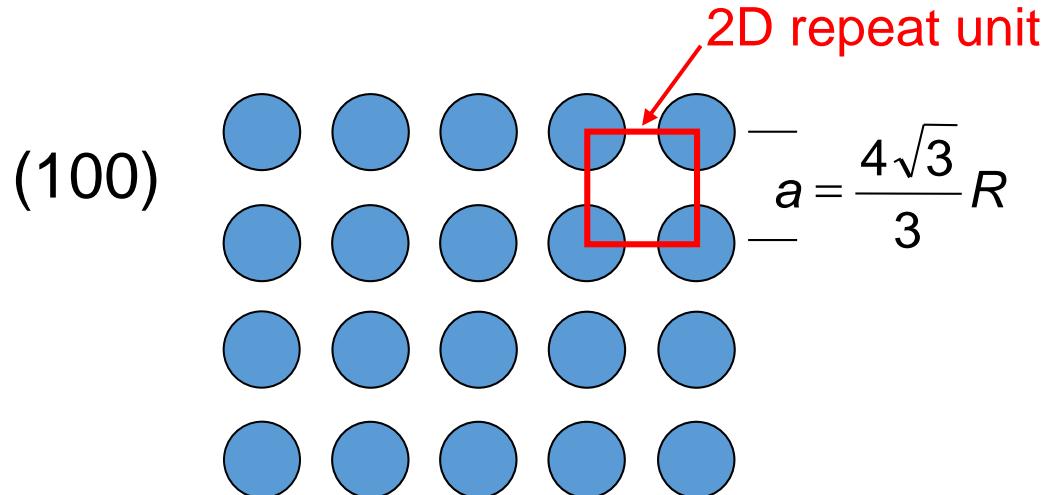
- We want to examine the atomic packing of crystallographic planes
- Iron foil can be used as a catalyst. The atomic packing of the exposed planes is important.
 - a) Draw (100) and (111) crystallographic planes for Fe.
 - b) Calculate the planar density for each of these planes.
- Planar Density of Atoms \equiv $PD = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}}$

Planar Density of (100) Iron

Solution: At $T < 912^{\circ}\text{C}$ iron has the BCC structure.



From Fig. 4.2(c), *Callister's Materials Science and Engineering, Adapted Version*.



Radius of iron $R = 0.1241 \text{ nm}$

$$\text{Planar Density} = \frac{\frac{\text{atoms}}{\text{2D repeat unit}}}{\frac{\text{area}}{\text{2D repeat unit}}} = \frac{1}{\left(\frac{4\sqrt{3}}{3} R\right)^2} = 12.1 \frac{\text{atoms}}{\text{nm}^2} = 1.2 \times 10^{19} \frac{\text{atoms}}{\text{m}^2}$$

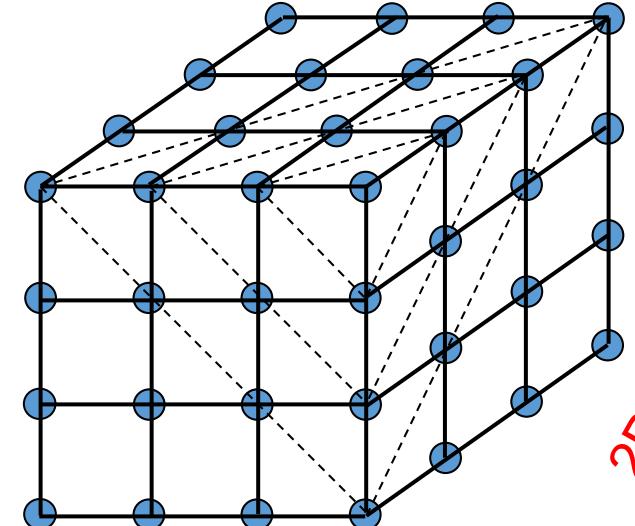
Planar Density of (111) Iron

Please check link <https://images.app.goo.gl/hREBsbUfiQyqtkgK6>, by Arpit Kumar Pandey (19115032) 2nd year EE
 Calculation in link is indeed correct *but with a little correction which is discussed in next 2 slides*

Solution (cont): (111) plane

In this case, no of atoms & repeat area will change according to the choice of your 2D repeat unit,

you can choose either triangle (equilateral triangle) or quadrilateral (parallelogram)

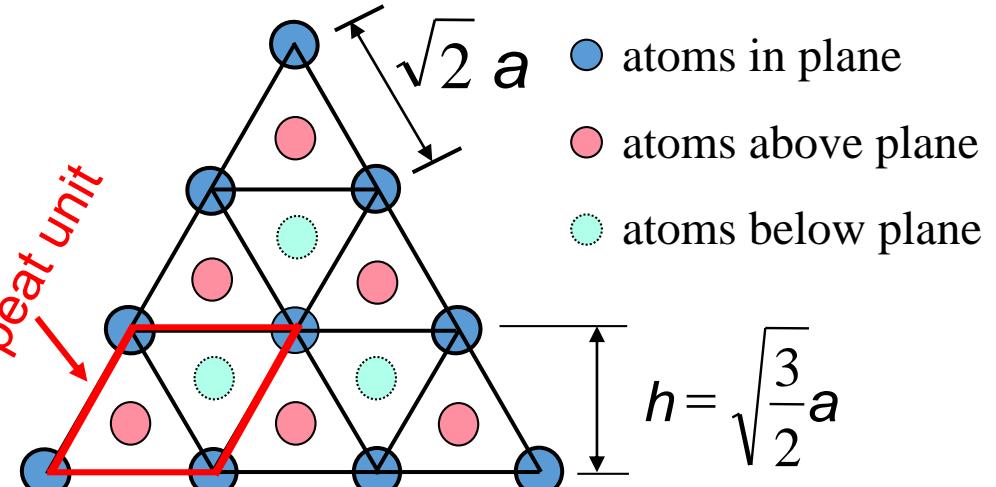


atoms

2D repeat unit

$$\text{Planar Density} = \frac{\text{atoms}}{\frac{\text{area}}{\text{2D repeat unit}}} = \frac{1}{\frac{16\sqrt{3}}{3} R^2}$$

1 atom in plane/ unit surface cell

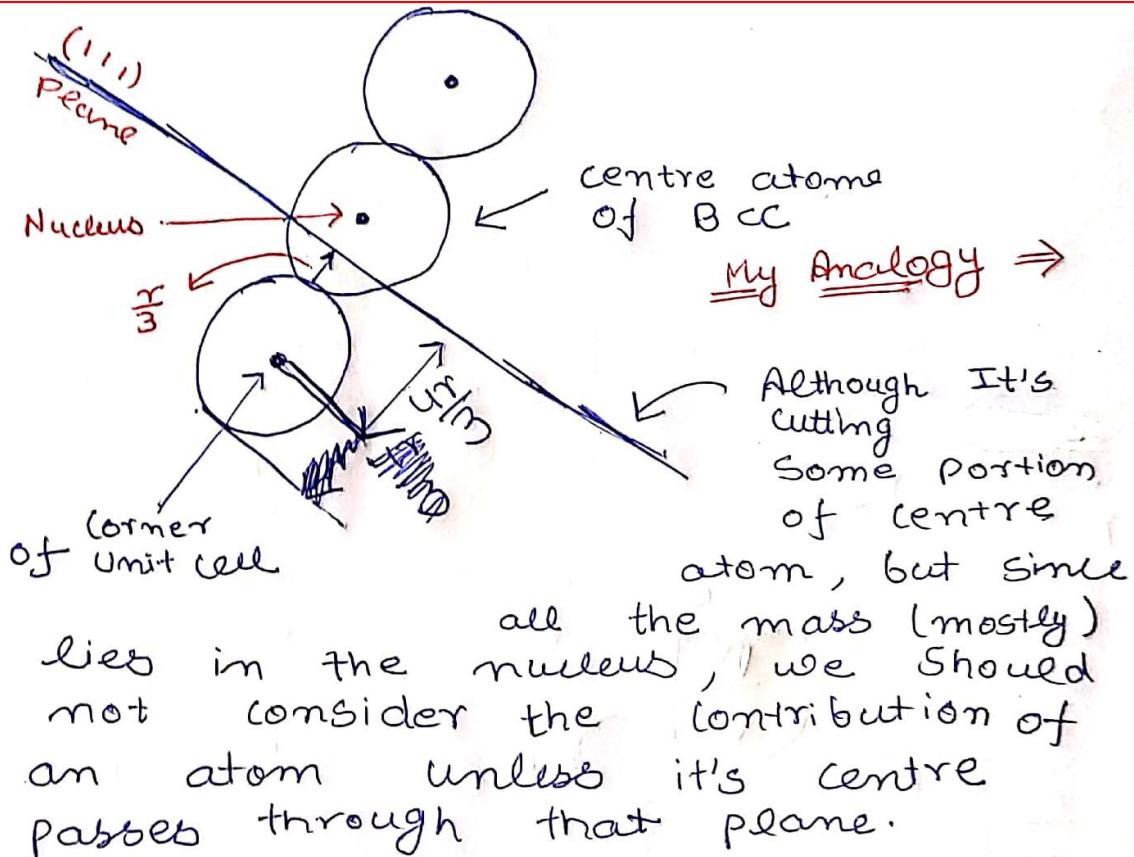


$$\text{area} = \sqrt{2} ah = \sqrt{3} a^2 = \sqrt{3} \left(\frac{4\sqrt{3}}{3} R \right)^2 = \frac{16\sqrt{3}}{3} R^2$$

1

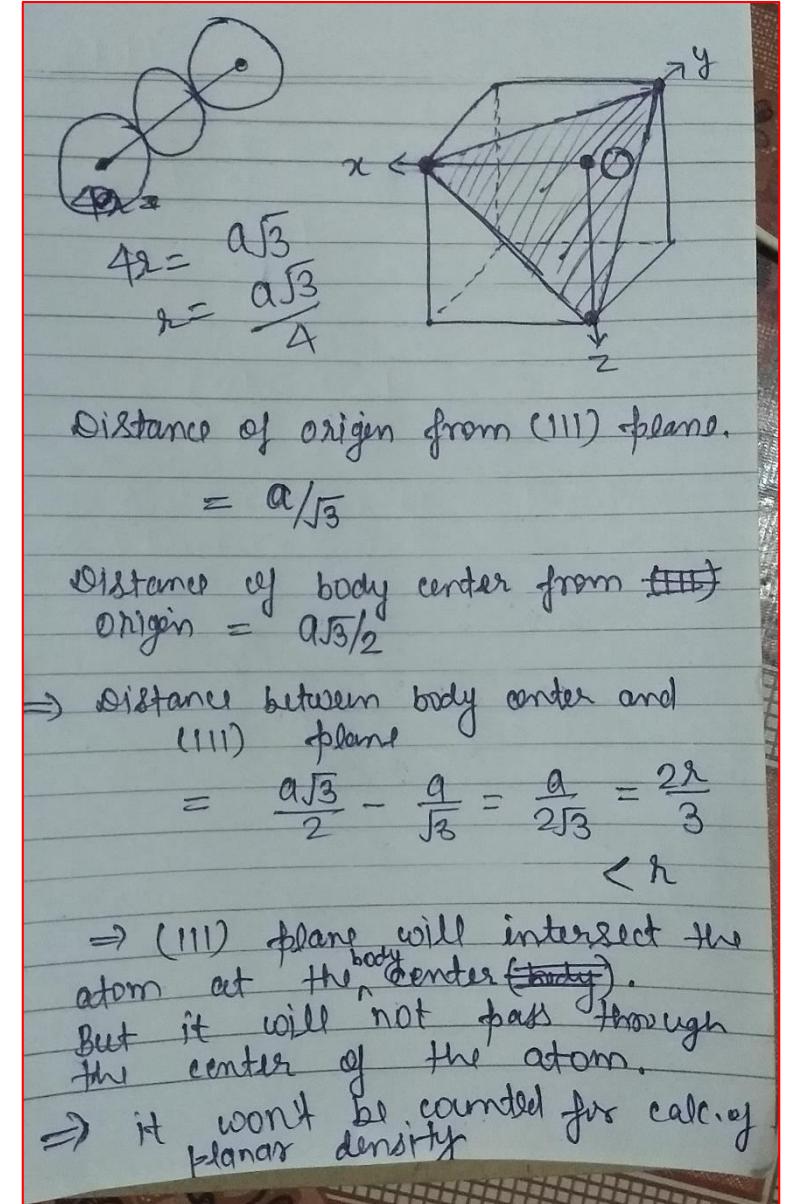
$$= 7.0 \frac{\text{atoms}}{\text{nm}^2}$$

$$0.70 \times 10^{19} \frac{\text{atoms}}{\text{m}^2}$$



Conclusion \rightarrow In Picture Shared by Arpit, calculation is correct but saying that centre atom lies completely outside (111) plane is wrong

- ✓ Please note that the content in both the images are correct, the difference is only in the approach.
- ✓ See left image: Kindly check distance between (111) plane & Nucleus point is $2r/3$ such that $(r/3)+(2r/3)=r$; and $r+(r/3)=4r/3$



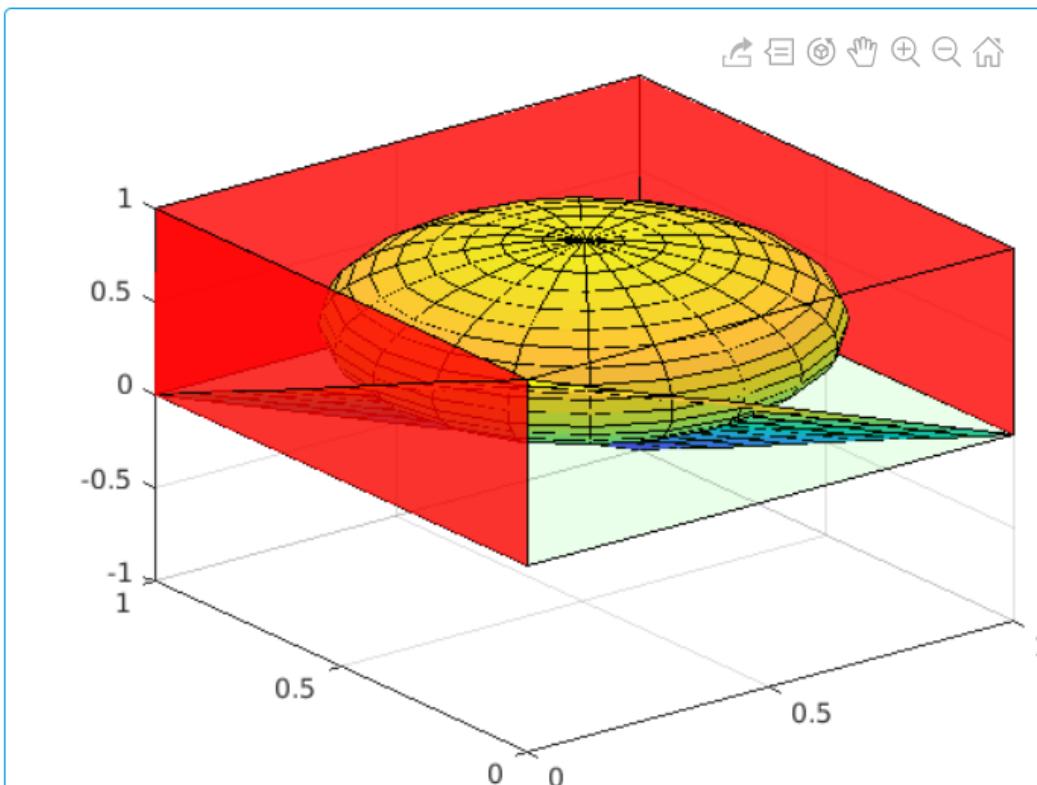
MATLAB Plot

By Anchit Proch (19115024) 2nd year EE

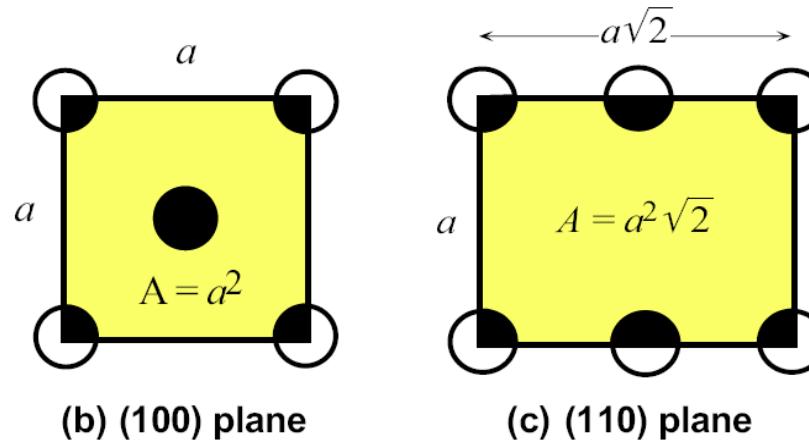
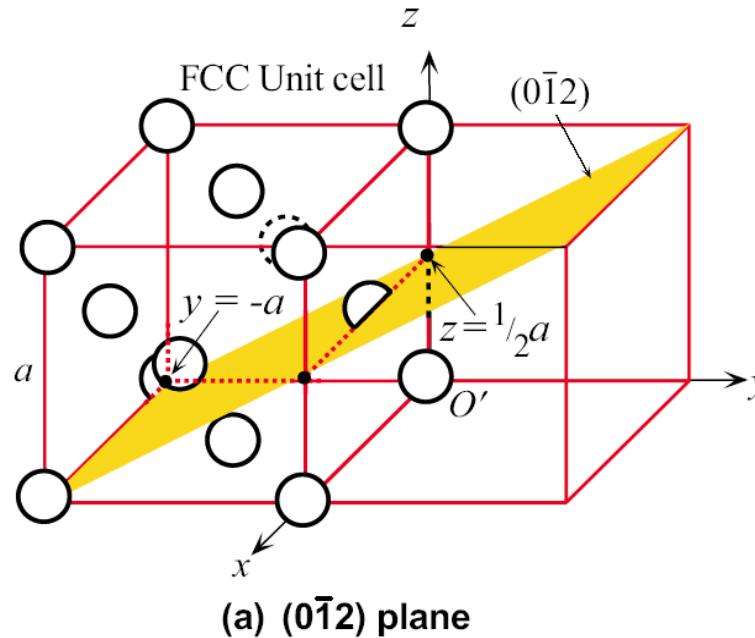
- ✓ The central sphere in BCC and the plane (111) are visualized more efficiently from the plot.
 - ✓ One can also see that the plane partially cuts the atom at the body center of the cube.
 - ✓ The screenshot of the plot and the code, are given below.
- @All : Please be careful, never write planes as (1,1,1). Always write without commas!

```
hold on;
[x,y]=meshgrid(0:0.1:1)
z=ones(size(x))-x-y
surf(x,y,z)
[a,b,c] = sphere;
a=a*(sqrt(3)/4);
b=b*(sqrt(3)/4);
c=c*(sqrt(3)/4);
surf(a+0.5,b+0.5,c+0.5)
hold off;
```

```
-0.5000  0.2000  -0.1000   0.1000  -0.2000  -0.3000  -0.4000  -0.5000
 0.2000  0.1000   0.0000  -0.1000  -0.2000  -0.3000  -0.4000  -0.5000
 0.1000   0.0000  -0.1000  -0.2000  -0.3000  -0.4000  -0.5000  -0.6000
:
:
```



See 3rd Edition, Fig 1.42, Practice Example 1.14 : Page 60-61



The (012) plane and planar concentrations in an FCC crystal.

Examples for Practice

- (1) Calculate the planar density for (100) and (200) planes in simple cubic, which has a lattice parameter of 0.334 nm.
- (2) Determine the planar density and packing fraction for FCC in (111). Can you consider this plane as close-packed? Given, $r = 0.125 \text{ nm}$

- Planar Packing Fraction =
$$\frac{\text{Area of number of atoms centered on a plane}}{\text{Area of plane}}$$

No of atoms on a plane:

BCC (001) type: 1

BCC (011) type: 2

BCC (111) type: $3*(1/6)=(1/2)$

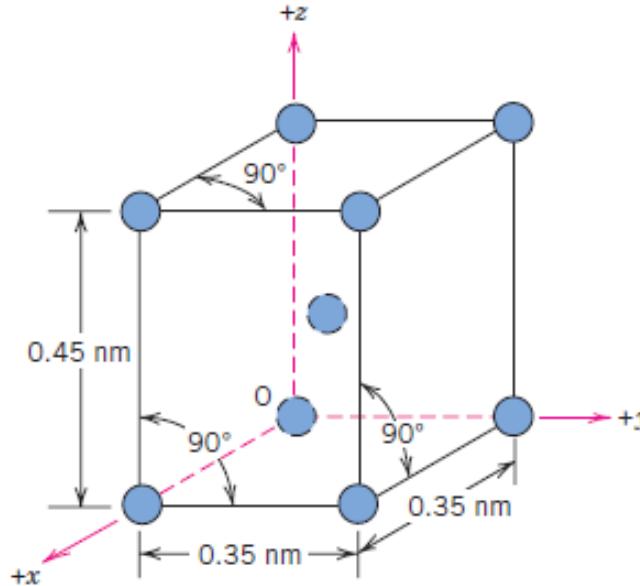
FCC (001) type: 2

FCC (011) type: 2

FCC (111) type: $3*(1/6)+3*(1/2)=2$

Here, *type* is used to represent family of equivalent planes

Examples for Practice



- (1) Consider reduced-sphere unit cell shown in Figure, having origin of the coordinate system positioned at atom labelled with O. For following sets of planes, determine which are equivalent: (100), (010), and (001)
- (2) For tetragonal crystals, cite the indices of directions that are equivalent to [100]

- ✓ For some crystal structures, several nonparallel directions with different indices are actually equivalent; this means that the spacing of atoms along each direction is the same.
- ✓ A “family” of planes contains all those planes that are crystallographically equivalent — that is, having the same atomic packing

Crystal defects - Imperfections in Solids

There is no such thing as a perfect crystal.

- What are these imperfections? Why are they important?

Many of the important properties of materials are due to the presence of imperfections.

- ✓ Quite often, key electrical and mechanical properties are controlled by the defects/imperfections.
- Crystal consists of large number of atoms arranged in a definite pattern which is repetitive in 3-D
- Real crystals deviate from the perfect periodicity of atoms which is assumed in an ideal crystal
- This deviation of atoms from an orderly array of lattice points is termed as *defect or imperfection*
- This deviation is responsible for the changes in the electrical properties of the real crystals.
- For example, integrated circuit microelectronic devices found in our computers, calculators, and home appliances function because of highly controlled concentrations of specific impurities that are incorporated into small, localized regions of semiconducting materials (Extrinsic Semiconduction & Semiconductor Devices)

Types of Imperfections

- Vacancy
- *Impurity*
 - ✓ Interstitial atoms
 - ✓ Substitutional atoms
- Dislocations
(Edge & Screw)
- Grain Boundaries
- Crystal Surfaces
- Stacking faults
- Twin interfaces

Other defects exist in all solid materials that are much larger than those discussed. These include pores, cracks, foreign inclusions, and other phases.

✓ Normally introduced during processing & fabrication steps

Point defects

Line defects

Area / Planar defects

Bulk or Volume defects

Equilibrium Concentration of Vacancies

$$n_v = N \exp\left(-\frac{E_v}{kT}\right)$$

n_v = vacancy concentration, N = number of atoms per unit volume, E_v = vacancy formation energy, k = Boltzmann constant, T = temperature (K)

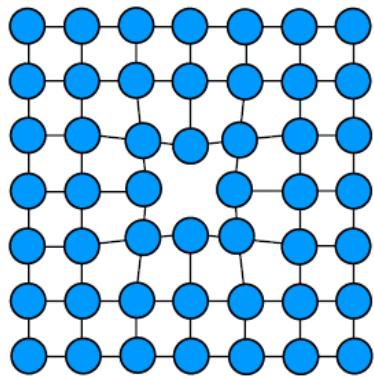
At all temperatures above absolute zero (-273°C), there will always be an equilibrium concentration of vacancies!

Why 100% purity of pure metal/element does not exist or its very difficulty to achieve during the extraction process?

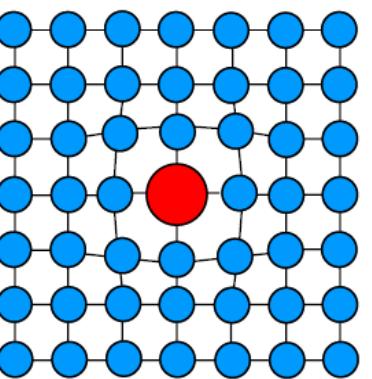
Point defects or point imperfection

- When deviation from periodic arrangement of lattice is localized to vicinity of only few atoms, it is called *point defect*
- Point defects in crystals could be either vacancy or various types of impurities
- *Vacancy or vacant lattice site*, exists when **an atom is missing from a normal lattice position**
 - In all crystals, a definite number of vacant lattice sites exist at temperatures greater than absolute zero
 - This number increases rapidly with increase in temperature
 - Vacancies exist as a requirement of thermal equilibrium and are called ***thermodynamic or equilibrium defects***
- Called *impurity atom* when different type of atom is present either at lattice position or interstitial position
- Called *interstitial* when atom (e.g., C in BCC Fe) is trapped inside crystal at point intermediate between normal lattice positions
- Crystal structure may contain impurities, either naturally or as consequence of intentional addition
 - e.g.; when Si crystal is “doped” with small amount of arsenic (As) atoms, the As atoms substitute directly for Si atoms in Si crystal, i.e., As atoms are **substitutional impurities** (which substitutes directly for the host atom), and the resulting structure is that of a **substitutional solid solution**

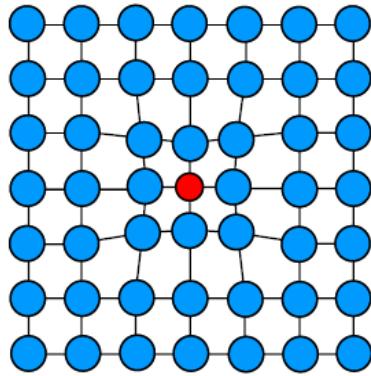
Stoichiometry and nonstoichiometry



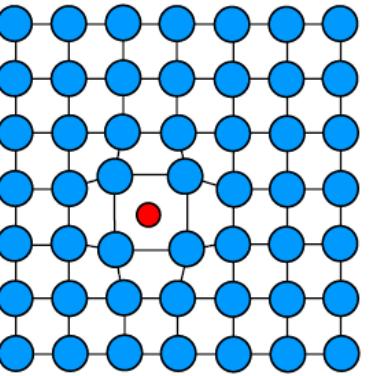
(a) A vacancy in the crystal.



(b) A substitutional impurity in the crystal. The impurity atom is larger than the host atom.



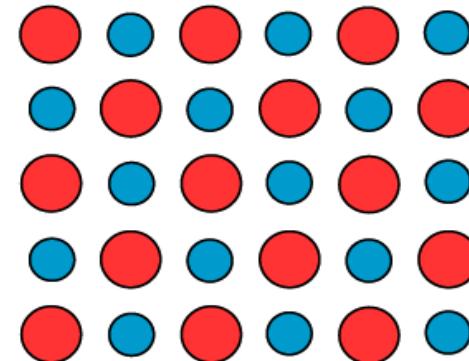
(c) A substitutional impurity in the crystal. The impurity atom is smaller than the host atom.



(d) An interstitial impurity in the crystal. It occupies an empty space between host atoms.

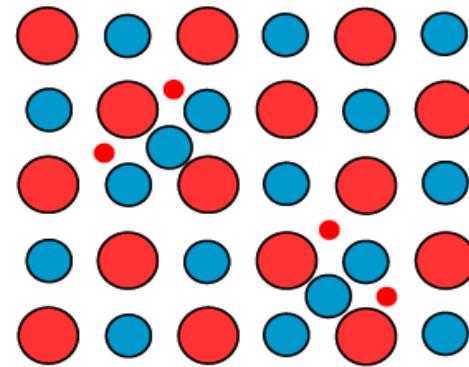
Point defects in the crystal structure.

The regions around the point defect become distorted from perfect periodicity; the lattice becomes *strained around a point defect*.



PC (+ve cation)
NA (-ve anion)

(a) Stoichiometric ZnO crystal with equal number of anions and cations and no free electrons.

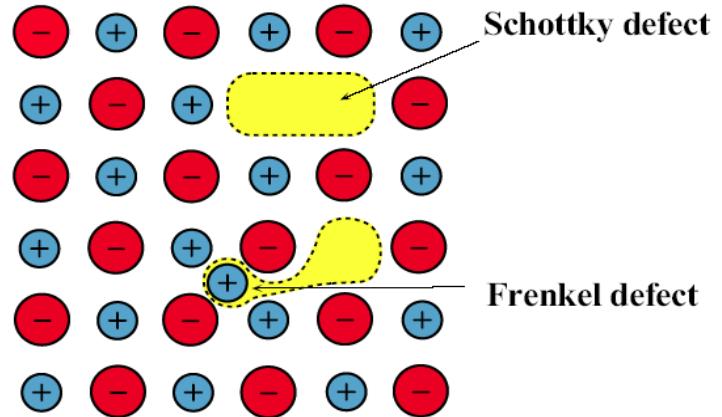


● O^{2-}
● Zn^{2+}
● "Free" (or mobile) electron within the crystal. can contribute to conduction of electricity

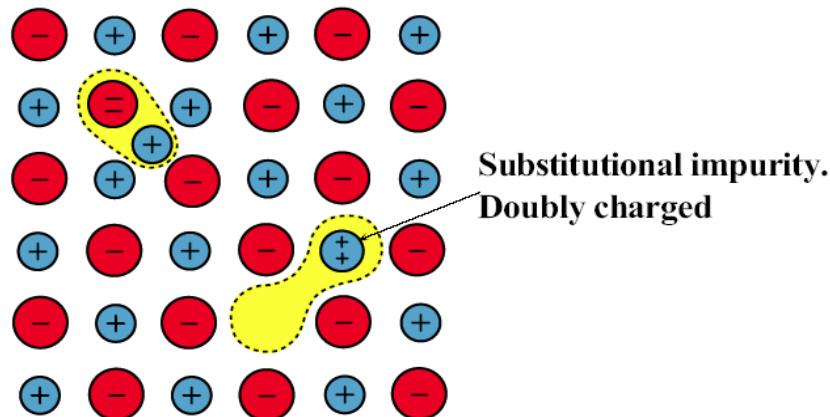
(b) Non-Stoichiometric ZnO crystal with excess Zn in interstitial sites as Zn^{2+} cations.

Resulting structure is *defect structure*, since it deviates from stoichiometry

Defects in Ceramic Structures



(a) Schottky and Frenkel defects in an ionic crystal.



(b) Two possible imperfections caused by ionized substitutional impurity atoms in an ionic crystal.

Point defects in ionic crystals

- **Shottky Defect:** missing cation–anion pair
 - ✓ a paired set of cation and anion vacancies
- **Frenkel Defect:** a cation is out of place
 - ✓ displaced into interstitial position, leaving vacancy at its original site

Defects in ionic crystals:

- Schottky defects are responsible for major optical & electrical properties of alkali halide crystals
- Frenkel defects are predominant in AgCl crystal, *read more from textbook 3rd edition* & also **note about E_{defect} wrt Eq. (1.35)**
- Equilibrium concentration of defects $\sim e^{-Q_D / kT}$

From Fig. 5.4

Callister's Materials Science and Engineering, Adapted Version.

(Fig. 5.4 is from W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley and Sons, Inc., p. 78.)

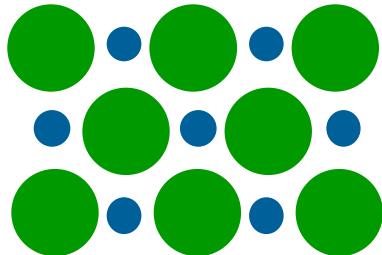
- ✓ Ionic crystals can also have substitutional and interstitial impurities that become ionized in the lattice
- ✓ Most likely type of defect depends on composition of ionic solid and the relative sizes & charges of ions

- Impurities must also satisfy **charge balance = Electroneutrality**

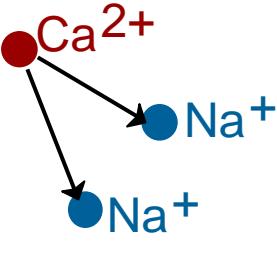
- Ex: NaCl



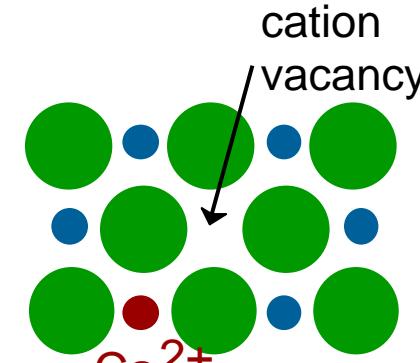
- Substitutional cation impurity



initial geometry

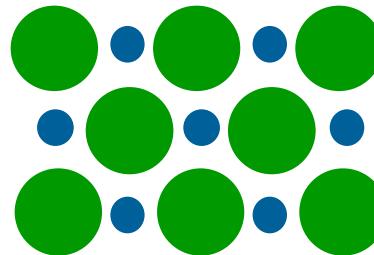


Ca^{2+} impurity

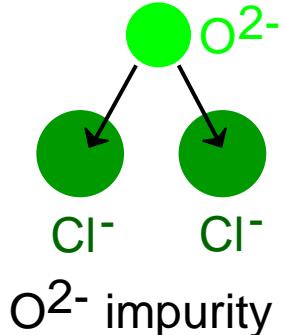


resulting geometry

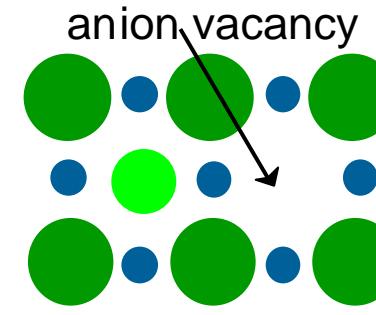
- Substitutional anion impurity



initial geometry



O^{2-} impurity



resulting geometry

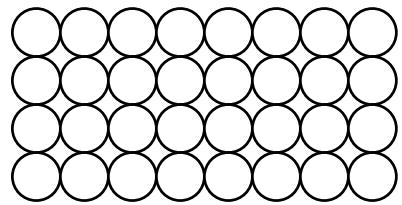
Equilibrium Concentration: Point Defects

- Equilibrium concentration varies with temperature!

$$\frac{N_V}{N} = \exp\left(\frac{-Q_V}{kT}\right)$$

No. of defects
No. of potential defect sites.

Activation energy
Boltzmann's constant
(1.38×10^{-23} J/atom-K)
(8.62×10^{-5} eV/atom-K)



Each lattice site
is a potential
vacancy site

Estimating Vacancy Concentration

- Find the equil. # of vacancies in 1 m³ of Cu at 1000°C.
- Given:

$$\rho = 8.4 \text{ g/cm}^3 \quad A_{\text{Cu}} = 63.5 \text{ g/mol}$$

$$Q_V = 0.9 \text{ eV/atom} \quad N_A = 6.02 \times 10^{23} \text{ atoms/mol}$$

$$\frac{N_V}{N} = \exp\left(\frac{-Q_V}{kT}\right) = 2.7 \times 10^{-4}$$

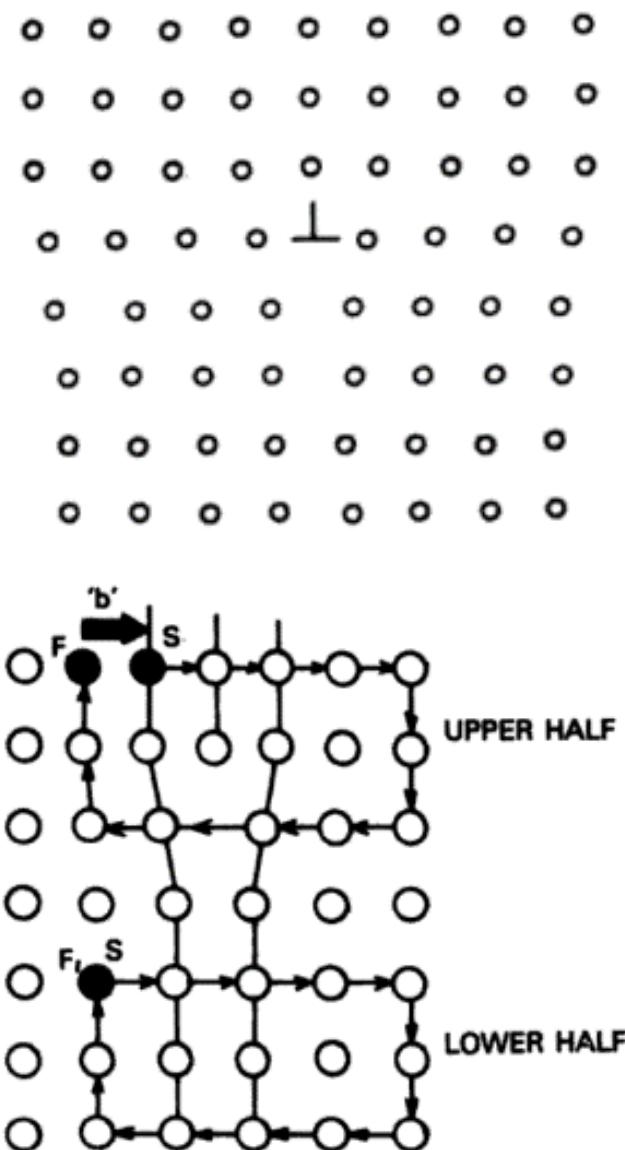
0.9 eV/atom
1273K
 $8.62 \times 10^{-5} \text{ eV/atom-K}$

$$\text{For } 1 \text{ m}^3, N = \rho \times \frac{N_A}{A_{\text{Cu}}} \times 1 \text{ m}^3 = 8.0 \times 10^{28} \text{ sites}$$

- Answer:

$$N_V = (2.7 \times 10^{-4})(8.0 \times 10^{28}) \text{ sites} = 2.2 \times 10^{25} \text{ vacancies}$$

- **Line Defects** obtain their name because they propagate as lines running inside the crystal
- Typical examples of line defects are edge and screw dislocations
- Dislocations move in crystals under an applied stress, and they terminate at the end of crystal through the phenomenon called *slip*. www.youtube.com/watch?v=iKKxTP6xp74
- **Burger's Vector (b)**: indicates the direction in which slip will occur
- Important property of dislocation, indicating extent of lattice displacement caused by dislocation
- Edge dislocation is due to presence of additional half-row of atoms within the lattice
- ✓ If an atom-to-atom circuit is described within a portion of regular lattice, as shown in the lower half of Fig., it will be a complete closed circuit, start (S) and finish (F) of the circuit meeting at the same atom. If, however, a similar circuit is described around the dislocated portion of the lattice, the start and finish will not be coincident as shown in the upper half of Fig. Distance SF will be the Burger's vector b . In an edge dislocation, b vector is normal to the dislocation line.
- In case of screw dislocation, a Burger's circuit describes a helical, or screw, path and b is in the same direction as the line of dislocation. However, the plastic flow under the action of a shearing stress still occurs in the direction of b .



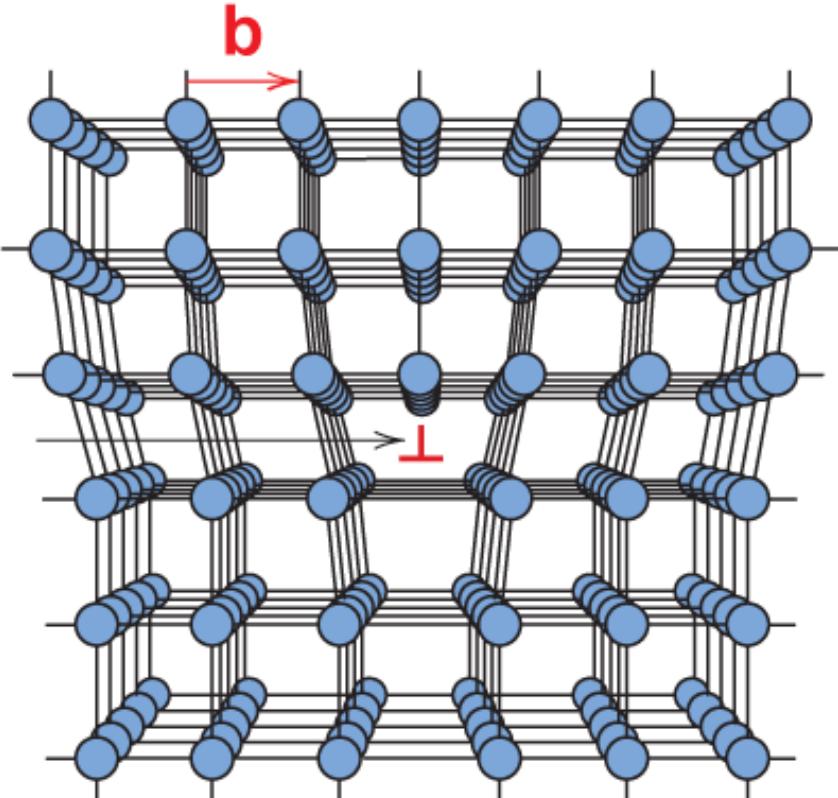
Burger's circuit around an edge dislocation indicating Burger's vector b

Linear Defects (Dislocations)

- Are 1-D defects around which atoms are misaligned
- Edge dislocation:
 - extra half-plane of atoms inserted in a crystal structure
 - $\mathbf{b} \perp$ to dislocation line

Burger's vector, \mathbf{b} : measure of lattice distortion

Burgers vector

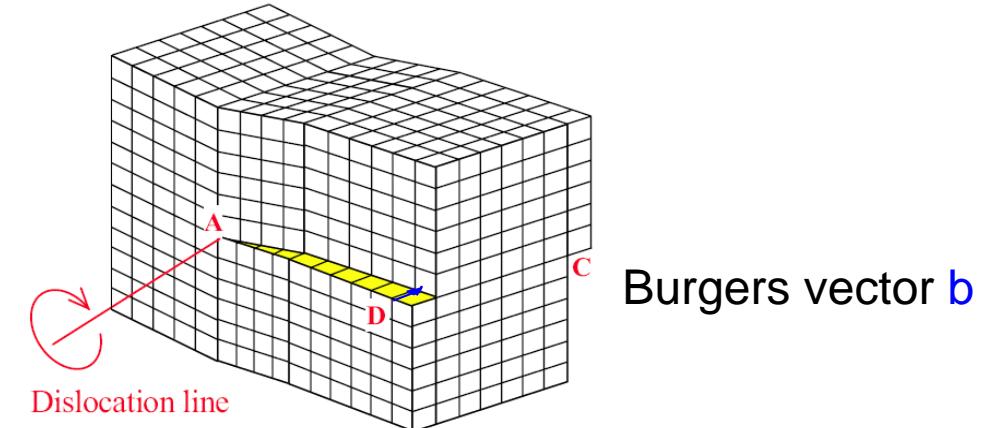


Edge dislocation line

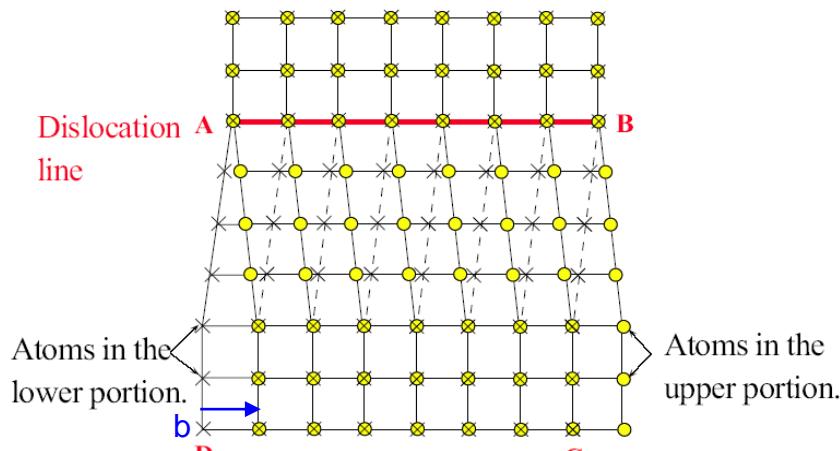
Dislocation can be regarded as a region in the crystal where linear atomic disorder exists

- Screw dislocation:

- spiral planar ramp resulting from shear deformation
- Involves shearing one portion of a perfect crystal w.r.t. another portion on one side of a line (AB)
- $\mathbf{b} \parallel$ to dislocation line



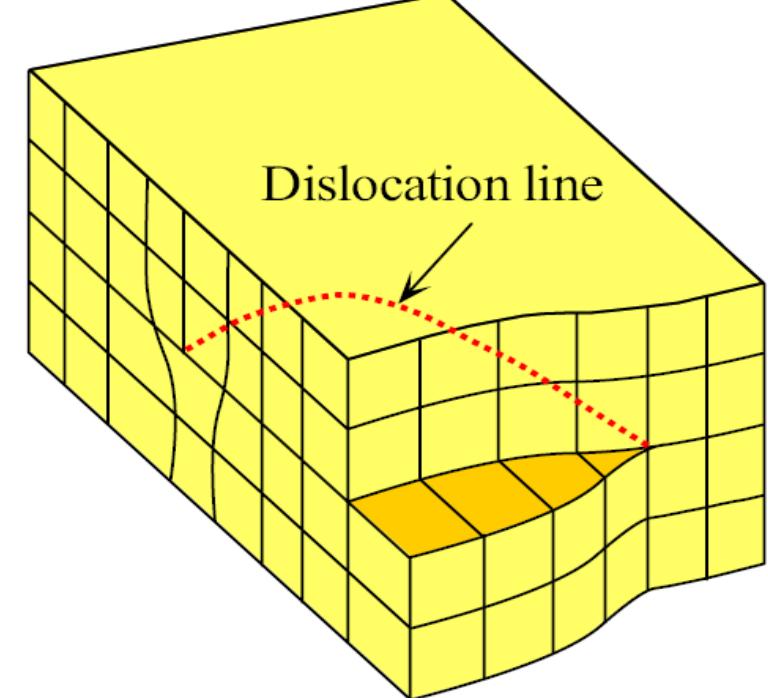
(a) A screw dislocation in a crystal.



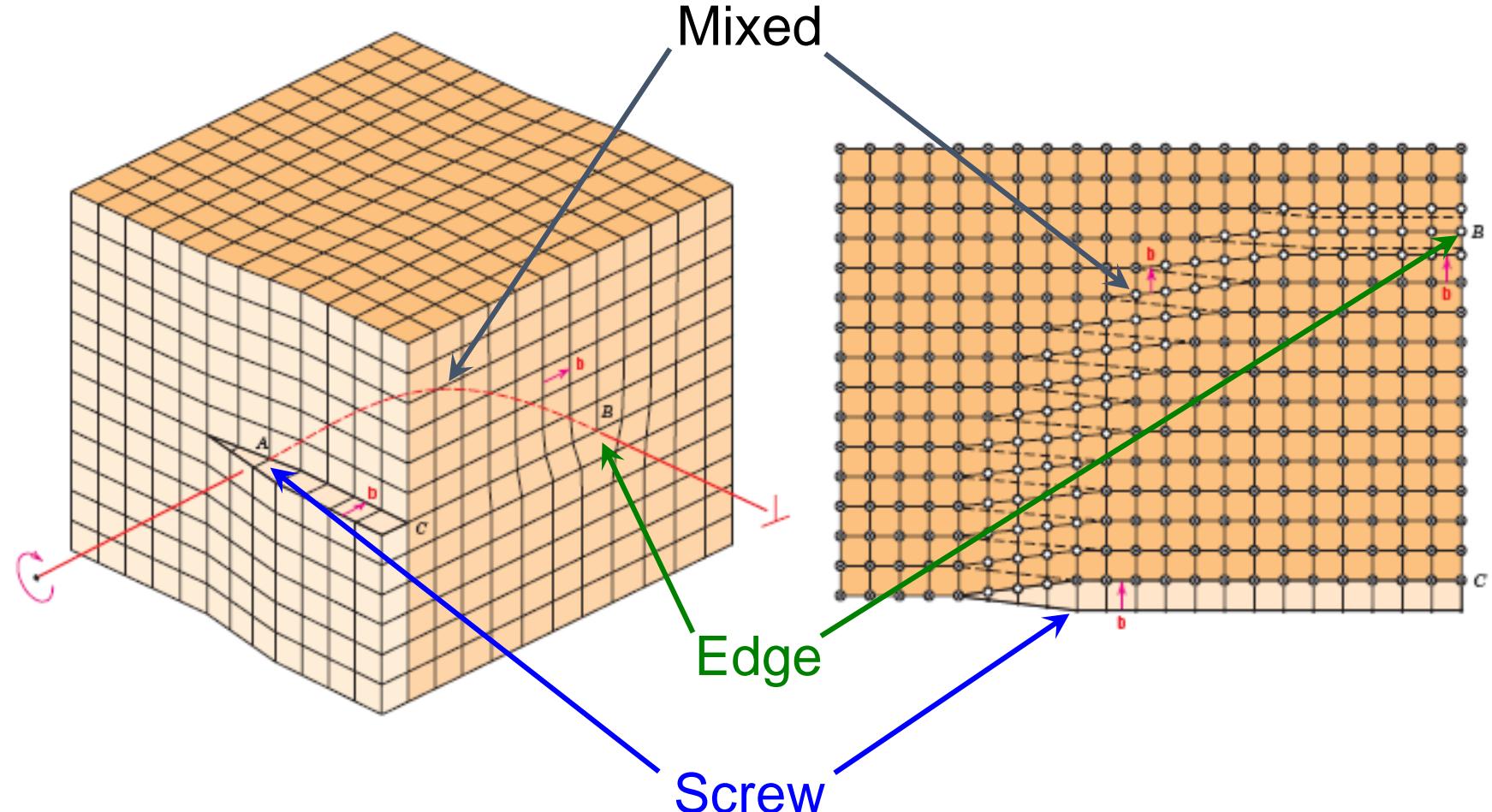
(b) The screw dislocation in (a) as viewed from above.

Edge, Screw, and Mixed Dislocations

In practice, dislocations are rarely of the pure-edge or pure-screw type but are mixed dislocations.



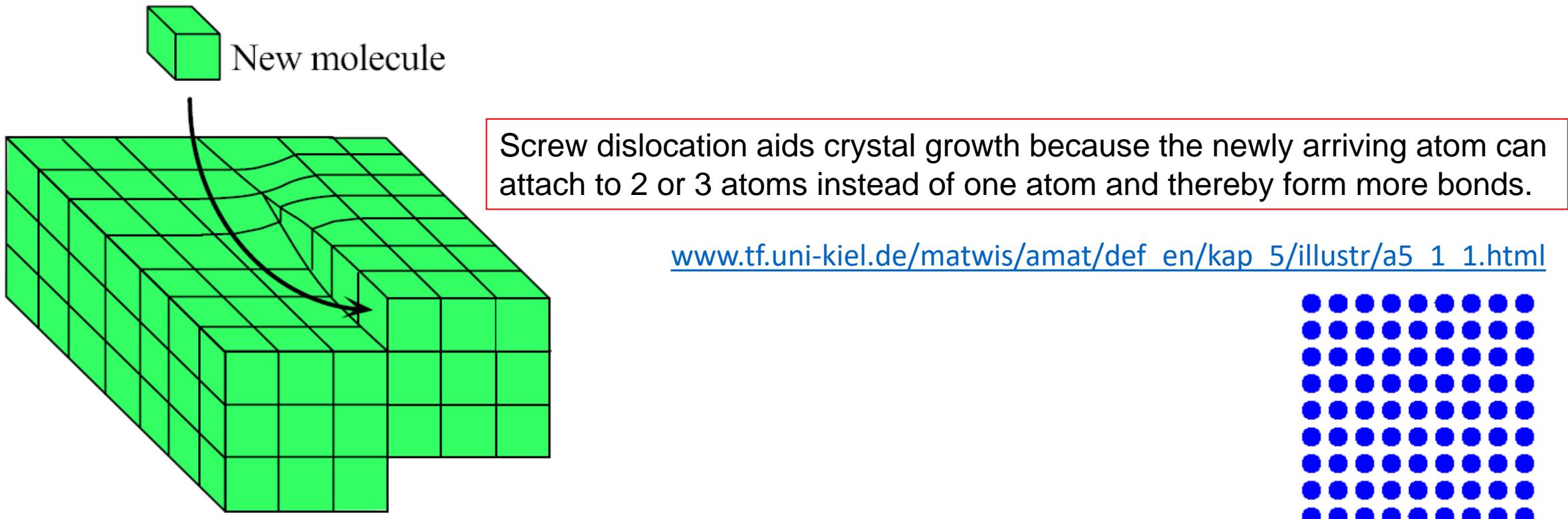
A mixed dislocation



From Fig. 5.9
Callister's Materials Science and Engineering,
Adapted Version.

Dislocations (line defects)

- Dislocations are NOT equilibrium defects and they normally arise when crystal (a) is deformed by stress OR (b) is actually being grown.
- Dislocations increase resistivity of materials, cause significant leakage current in a *pn* junction, and give rise to unwanted noise in various semiconductor devices.
- Fortunately, occurrence of dislocations in semiconductor crystals can be controlled and nearly eliminated; for e.g., Si crystal wafer that is carefully grown may typically have only 1 dislocation line per mm² of crystal, whereas, in a metal interconnection line on a chip, there may be an average of 10⁴–10⁵ dislocation lines per mm² of crystal

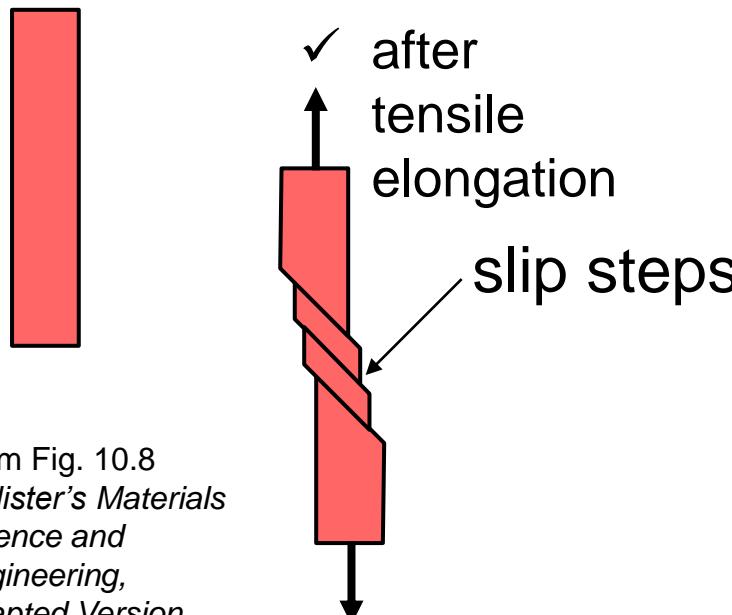


Dislocations:

- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.

Schematic of Zinc (HCP):

- before deformation

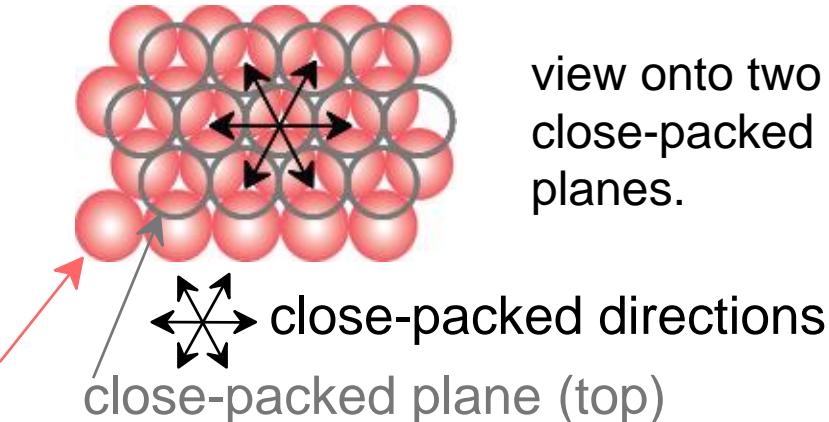


From Fig. 10.8
Callister's Materials
Science and
Engineering,
Adapted Version.

Dislocations & Crystal Structures

- Structure: **close-packed** planes & directions are preferred.

close-packed plane (bottom)

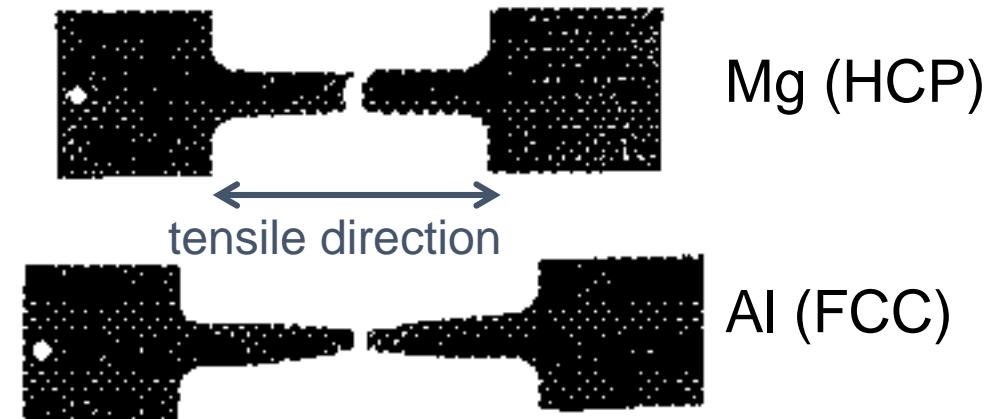


view onto two close-packed planes.

- Comparison among crystal structures:

FCC: many close-packed planes/directions;
HCP: only one plane, 3 directions;
BCC: none

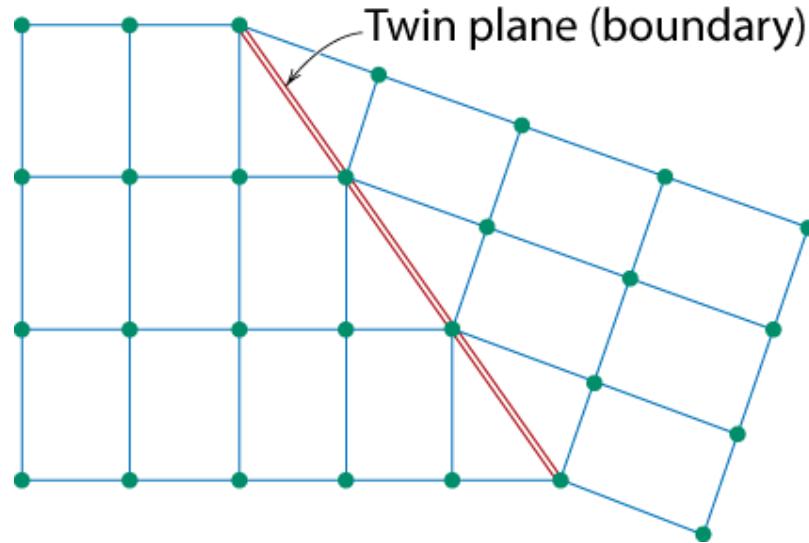
- Specimens that were tensile tested.



Area/Planar Defects in Solids

Twins - Portion of crystal having certain specific orientations w.r.t each other, lattice of one part is mirror image of other
May occur during crystallization from liquid or vapour state, by growth during annealing or during phase transformation

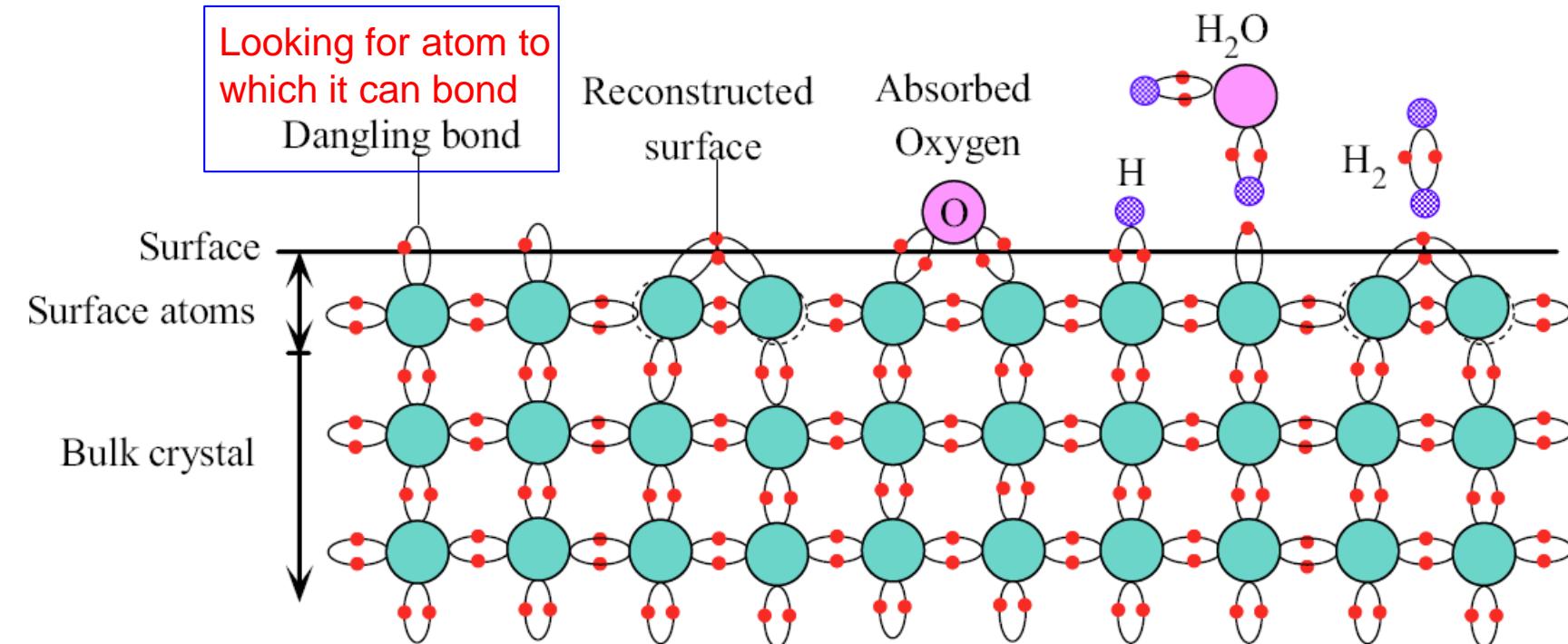
- One case is a **twin boundary (plane)**
 - Essentially a reflection of atom positions across the **twin plane**.



From Fig. 5.13
Callister's Materials Science and Engineering, Adapted Version.

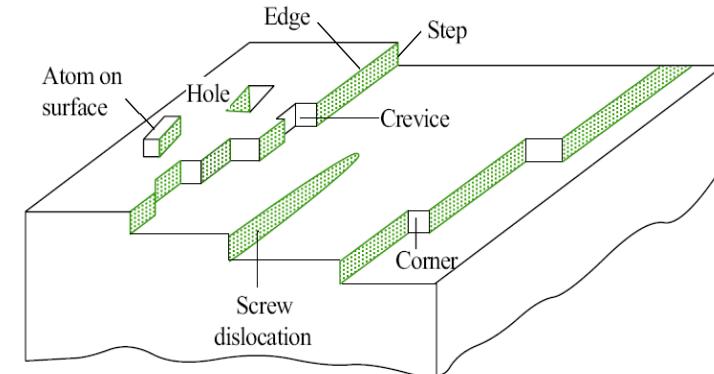
- **Stacking faults**
 - For FCC metals an error in ABCABC packing sequence: Ex: ABC~~A~~BABC
 - ✓ *Stacking faults* are planes where there is an error in the normal sequence of stacking of atom layers
 - ✓ These may be formed during the growth of crystal or may result from motion of partial dislocations
 - ✓ A partial dislocation produces a movement that is less than a full distance

External Surfaces: One of most obvious boundaries is *external surface*, along which the crystal structure terminates. Surface atoms are not bonded to maximum number of nearest neighbors, and are therefore in higher energy state than the atoms at interior positions. Bonds of these surface atoms that are not satisfied give rise to surface energy. To reduce this energy, materials tend to minimize, if at all possible, total surface area. e.g., liquids assume a shape having minimum area—droplets become spherical. Of course, this is not possible with solids, which are mechanically rigid.



At surface of hypothetical 2-D crystal, the atoms cannot fulfill their bonding requirements and therefore have broken, or dangling, bonds. Some of the surface atoms bond with each other; the surface becomes reconstructed. The surface can have physisorbed and chemisorbed atoms.

Surface condition of Si crystal wafer in microelectronics is normally controlled by first etching the surface and then oxidizing it at high temperature to form SiO_2 passivating layer on crystal surface



Typically a crystal surface has many types of imperfections such as steps, ledges, kinks, cervices, holes and dislocations

- **Solidification**- result of casting of molten material

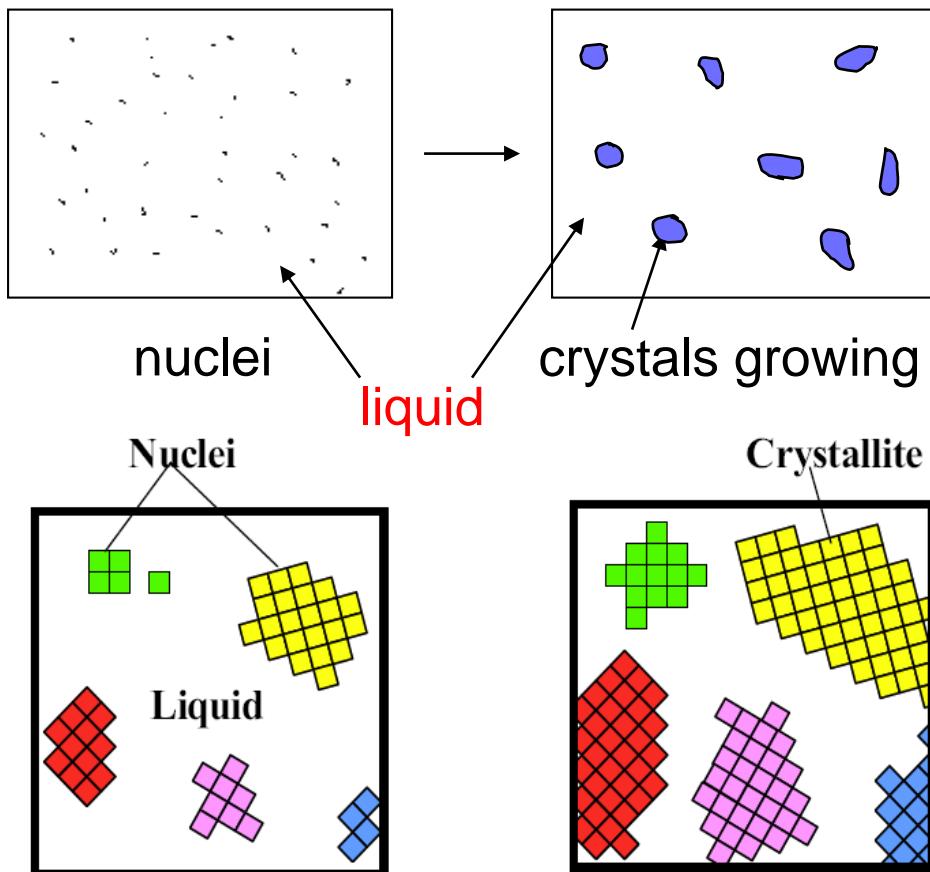
- 2 steps
 - Nuclei form
 - Nuclei grow to form crystals – grain structure

- Start with a molten material – all liquid

Solidification of a polycrystalline solid from melt.

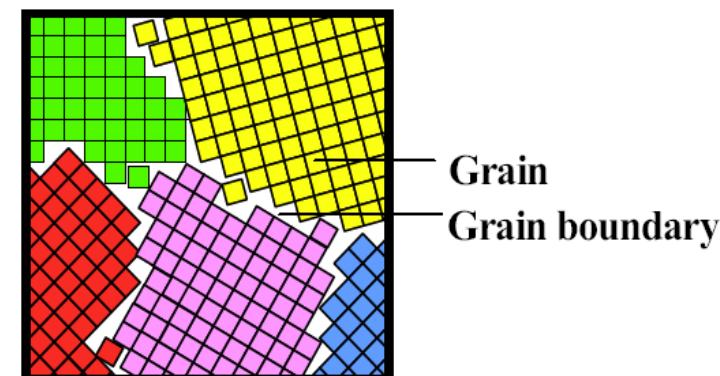
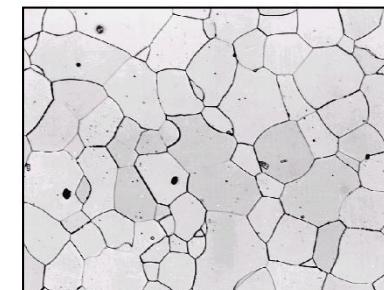
- Nucleation
- Growth
- The solidified polycrystalline solid.

For simplicity cubes represent atoms



(b)

Adapted from Fig.5.19 (b), *Callister's MSE, Adapted Version.*



(c)

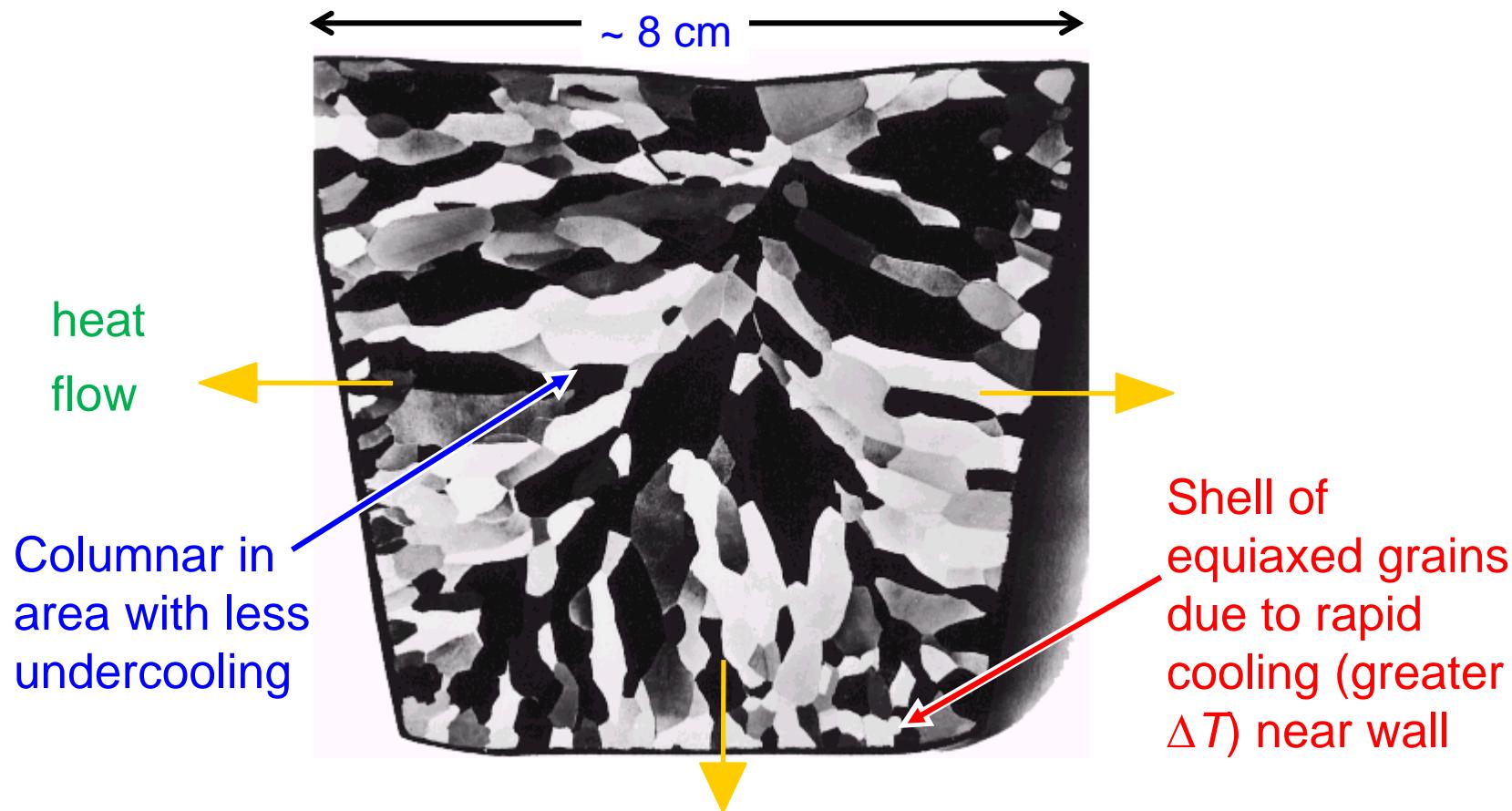
- Crystals grow until they meet each other

- ✓ When liquid is cooled to below its freezing temperature, solidification does not occur at every point in the liquid; rather, it occurs at certain sites called **nuclei**, which are small crystal-like structures containing perhaps 50 to 100 atoms.
- ✓ Liquid atoms adjacent to nucleus - diffuse into nucleus, thereby causing it to grow in size to become a small crystal, or a crystallite, called a **grain**.
- ✓ Since nuclei are randomly oriented when they are formed, the grains have random crystallographic orientations during crystallite growth.
- ✓ As the liquid between the grains is consumed, some grains meet and obstruct each other.
- ✓ At the end of solidification, therefore, the whole structure has grains with irregular shapes and orientations

Solidification

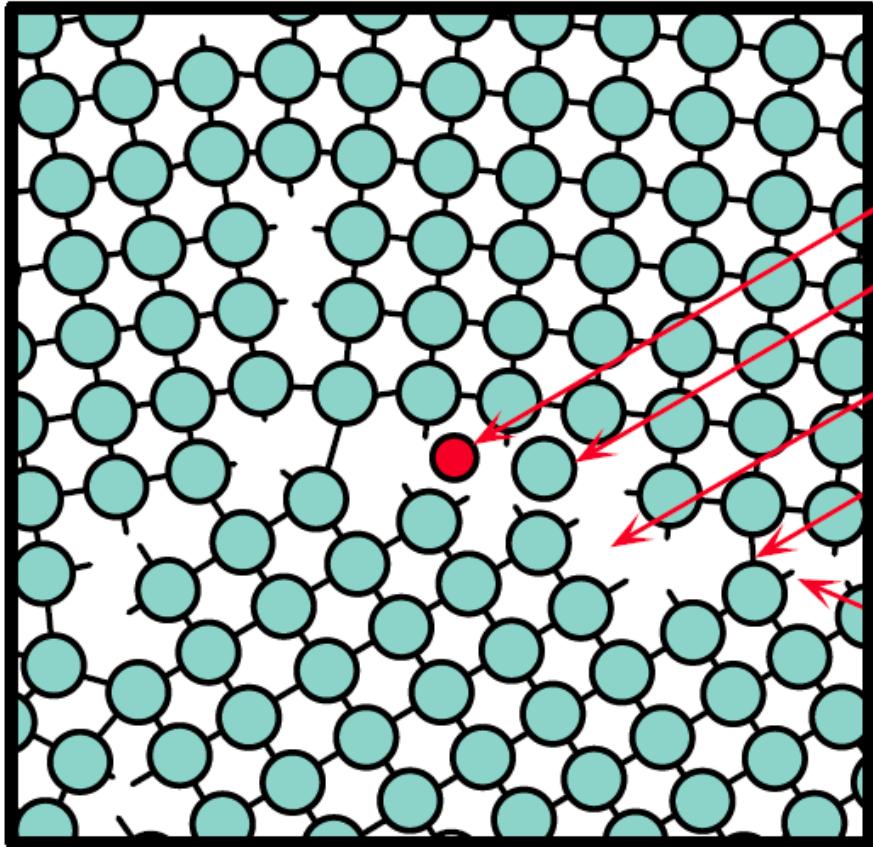
Grains can be

- equiaxed (roughly same size in all directions)
- columnar (elongated grains)



Grain Refiner - added to make smaller, more uniform, equiaxed grains.

From Fig. 5.17
Callister's Materials Science and Engineering,
Adapted Version.



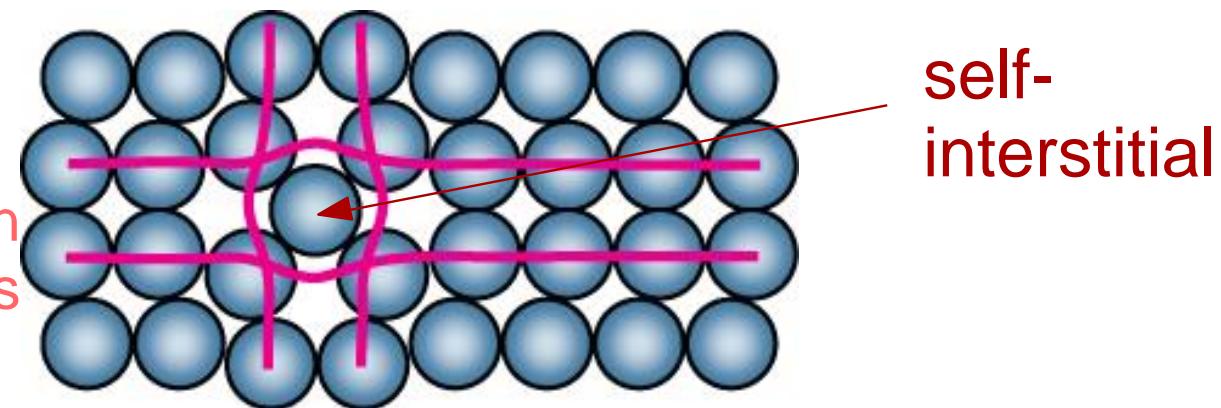
Foreign impurity
Self-interstitial type atom
Void, vacancy
Strained bond
Grain boundary
Broken bond (dangling bond)

Grain boundaries have broken bonds, voids, vacancies, strained bonds and “interstitial” type atoms.

The structure of grain boundary is disordered and atoms in the grain boundaries have higher energies than those within the grains.

- Self-Interstitials:
 - "extra" atoms positioned between atomic sites

distortion
of planes



Grain Boundaries (area/planar defects)

Nonequilibrium defects

- Atoms at grain boundaries cannot follow their natural bonding habits, because the crystal orientation suddenly changes across the boundary.
- *Therefore, there are both voids at grain boundary and stretched & broken bonds. In addition, in this region, there are misplaced atoms that do not follow the crystalline pattern on either side of the boundary.*
- Atoms can diffuse more easily along a grain boundary because (a) less bonds need to be broken due to the presence of voids and (b) the bonds are strained and easily broken anyway.
- Grain boundary represents a high-energy region per atom with respect to the energy per atom within the bulk of the grains themselves.
- At or around room temperature, the atomic diffusion process is slow; thus, the reduction in the grain boundary is insignificant.
- However, at elevated temperatures, atomic diffusion allows big grains to grow, at the expense of small grains, which leads to **grain coarsening (grain growth)** and hence to a reduction in the grain boundary area – this process gives the whole structure a lower potential energy.
- For you as electrical engineers, **grain boundaries become important when designing electronic devices based on polysilicon or any polycrystalline semiconductor.**
- For example, in highly polycrystalline materials, particularly thin-film semiconductors (e.g., polysilicon), the resistivity is invariably determined by polycrystallinity, or grain size, of the material.

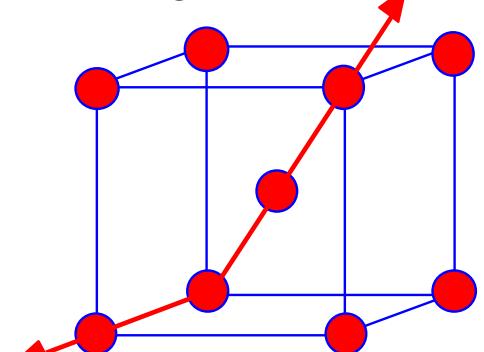
Single crystal & Polycrystalline material

- Metallic materials are generally not in the form of single crystals, but are composed of many small crystals, or grains. These small crystals have random orientations with respect to each other
- Polycrystalline material consists of large number of grain boundaries, where differently oriented *crystals/grains* meet.
- Single crystal exhibits anisotropy, i.e, possesses different properties in different directions
- **Grain = Single Crystal.** *Single Crystal doesn't have any Grain Boundaries, but it can have other defects!*

✓ Single Crystals

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

$$E \text{ (diagonal)} = 273 \text{ GPa}$$



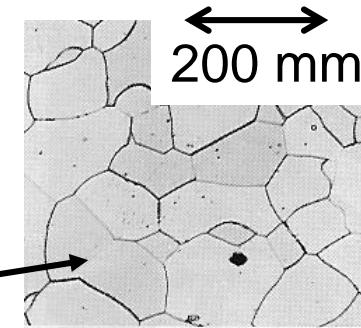
Data from Table 3.2,
*Callister's Materials
Science and
Engineering,
Adapted Version*.
(Source of data is R.W.
Hertzberg, *Deformation
and Fracture Mechanics
of Engineering
Materials*, 3rd ed., John
Wiley and Sons, 1989.)

✓ 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.



From Fig. 5.19(b),
*Callister's Materials
Science and
Engineering,
Adapted Version*.
(Fig. 5.19(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].)

Crystals as Building Blocks

- Some engineering applications require single crystals:

--diamond single crystals for abrasives



(Courtesy Martin Deakins,
GE Superabrasives,
Worthington, OH. Used with
permission.)

--turbine blades



- Properties of crystalline materials often related to crystal structure.

Ex: Quartz fractures more easily along some crystal planes than others.



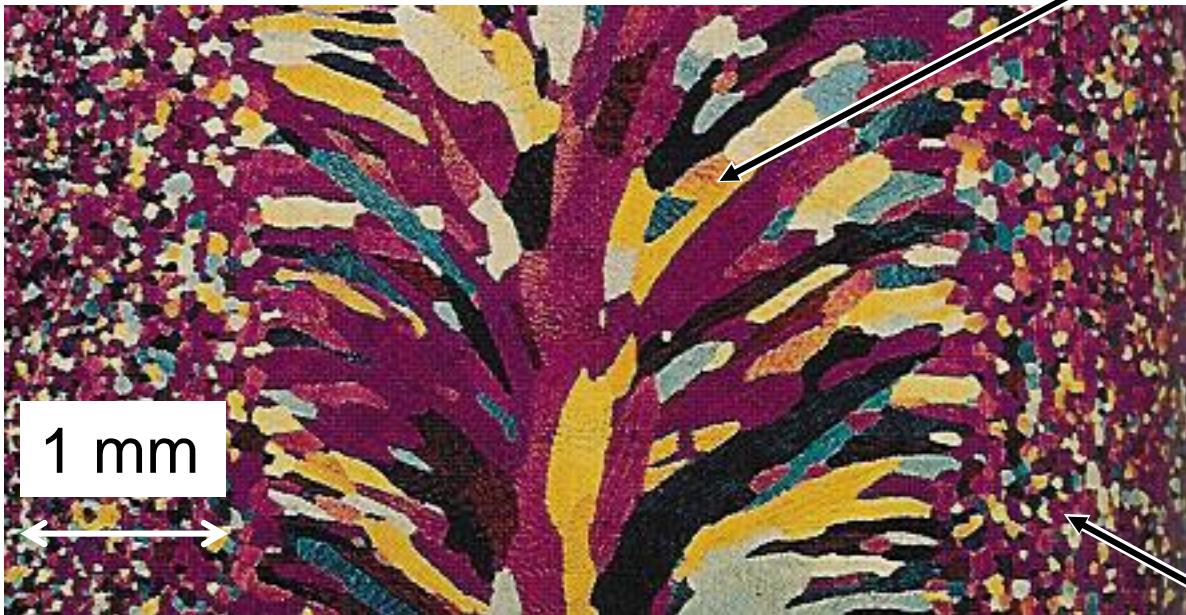
(Courtesy P.M. Anderson)

Polycrystals

- Most engineering materials are polycrystals.

From Fig. K, color inset pages of *Callister 5e*.

(Fig. K is courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)

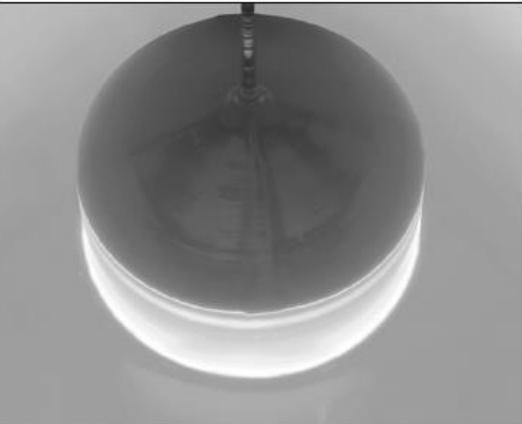


- Nb-Hf-W plate with an electron beam weld.
- **Each "grain" is a single crystal.**
- If grains are randomly oriented, overall component properties are not directional.
- Grain sizes typ. range from 1 nm to 2 cm (i.e., from a few to millions of atomic layers).

(3rd Edition) 1.10: Single-crystal Czochralski Growth

Short video, Crystal Growth to Si Wafer, <https://youtu.be/Q9rgSg5eAhc>
For full video, Silicon WaferFAB, pls see <https://youtu.be/Os8FUHJvgAI>

Silicon



Silicon crystal ingots grown by the Czochralski crystal drawers in the background

200 mm and 300 mm Si

Silicon ingot being pulled from the melt in a Czochralski crystal drawer.

A silicon ingot is a single crystal of Si. Within the bulk of the crystal, the atoms are arranged on a well-defined periodical lattice. The crystal structure is that of **diamond**.

SOURCE: Courtesy of MEMC Electronic Materials, Inc.

(3rd Edition) 1.10: Single-crystal Czochralski Growth

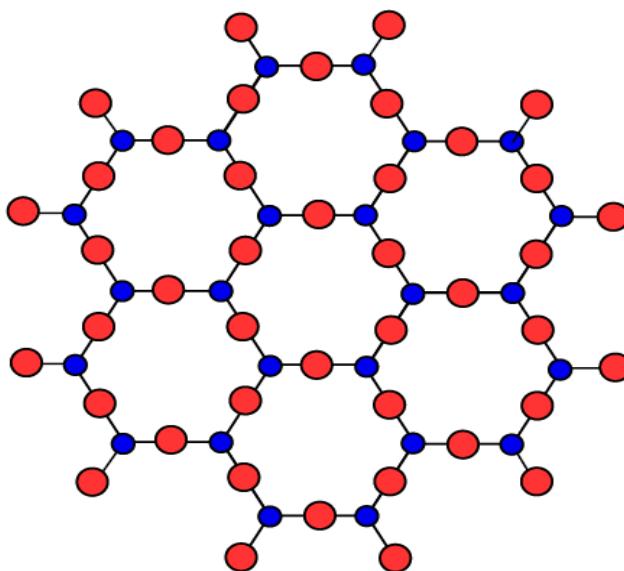
Short video, Crystal Growth to Si Wafer, <https://youtu.be/Q9rgSg5eAhc>
For full video, Silicon WaferFAB, pls see <https://youtu.be/Os8FUHJvqAI>

- Jan Czochralski (1885–1953) discovered the crystal growth technique in 1916.
- He apparently, by accident, dipped his pen into molten tin instead of the ink pot. When he pulled it out, he discovered solidified tin hanging from the nib.
- In 1950s, the researchers at Bell Labs started to use the technique to grow Ge single crystals, which opened the transistor era.
- Czochralski method involves growing a single-crystal ingot from the melt, using solidification on a seed crystal
- A **small dislocation-free crystal**, called a **seed**, is lowered to touch the melt and then slowly pulled out of the melt; a crystal grows by solidifying on the seed crystal.
- To suppress evaporation from the melt and prevent oxidation, argon gas is passed through the system.
- Initially, as the crystal is withdrawn, its cross-sectional area increases; it then reaches constant value determined by the temperature gradients, heat losses, and the rate of pull.
- As melt solidifies on the crystal, heat of fusion is released and must be conducted away; otherwise, it will raise the temperature of crystal and **remelt it**. Area of melt–crystal interface determines rate at which this heat can be conducted away through crystal, whereas rate of pull determines rate at which latent heat is released. Although analysis is not simple one, it is clear that to obtain ingot with large cross-sectional area, pull speed must be slow.
- Typical growth rates are a few millimeters per minute (*48 hours mentioned in video*)
- Also used for growing Ge, GaAs, and InP single crystals, though each case has its own particular requirements
- Final Si crystal inevitably contains oxygen impurities dissolved from the quartz crucible.

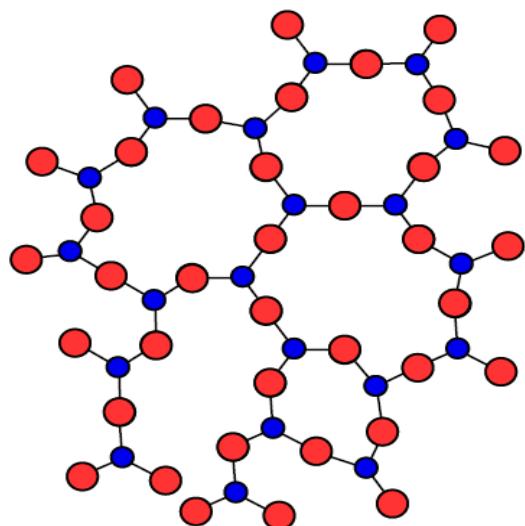
Amorphous and Crystalline

- Atomic arrangements which have repetitive pattern in 3D, are called *crystal structures or crystals*. In such structures, fundamental unit of arrangement repeats itself at regular intervals in 3D, throughout the interior of crystal. Most of the metals are crystalline and consist of crystals.
- *Amorphous structures* are formed when atoms do not have long range repetitive pattern of arrangement and pattern breaks at different places. Common examples of this group are glasses and polymers. Most glasses consist primarily of silicate ions, SiO_2 , to which an appreciable number of large-sized atoms such as sodium have been added. Added *sodium and other atoms*, since they do not fit into the silicate structure very well, make it more difficult for crystallization to occur when the melt is cooled. Glass is *frozen or supercooled liquid* having a very high viscosity.
- Many amorphous solids are formed by *rapidly cooling or quenching* the liquid to temperatures where the atomic motions are so sluggish that crystallization is virtually halted.
- Characteristic property of crystal structure is its periodicity & degree of symmetry. For each atom, the number of neighbors and their exact orientations are well defined; otherwise the periodicity will be lost. Therefore, long-range order results from strict adherence to well-defined bond length and relative bond angle (i.e., exact orientation of neighbors). Crystal is 3-D periodic arrangement of atoms, molecules, or ions.
- Amorphous solid is a solid that exhibits no crystalline structure or long-range order. It only possesses short-range order in the sense that nearest neighbors of atom are well defined by virtue of chemical bonding requirements.

- Silicon (or Arsenic) atom
- Oxygen (or Selenium) atom



(a) A crystalline solid reminiscent to crystalline SiO_2 . (Density = 2.6 g cm^{-3})



(b) An amorphous solid reminiscent to vitreous silica (SiO_2) cooled from the melt (Density = 2.2 g cm^{-3})

Crystalline & amorphous structures illustrated schematically in 2-D

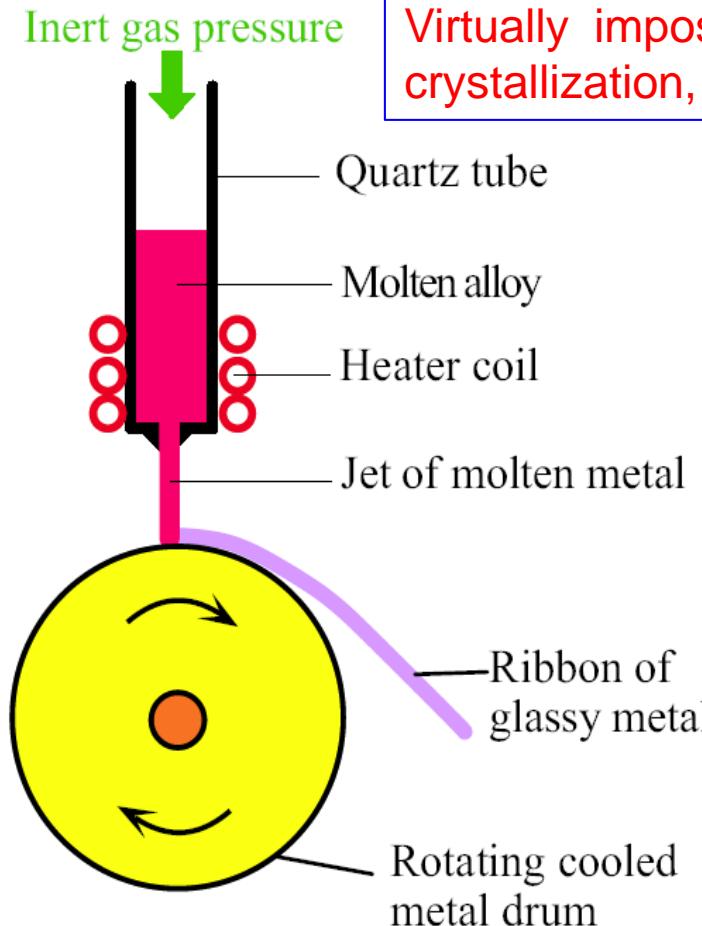
Taking an arbitrary origin, we can predict the position of each atom anywhere in the crystal

As a consequence of the lack of long-range order, amorphous materials do not possess such crystalline defects as grain boundaries and dislocations, which is distinct advantage in certain engineering applications

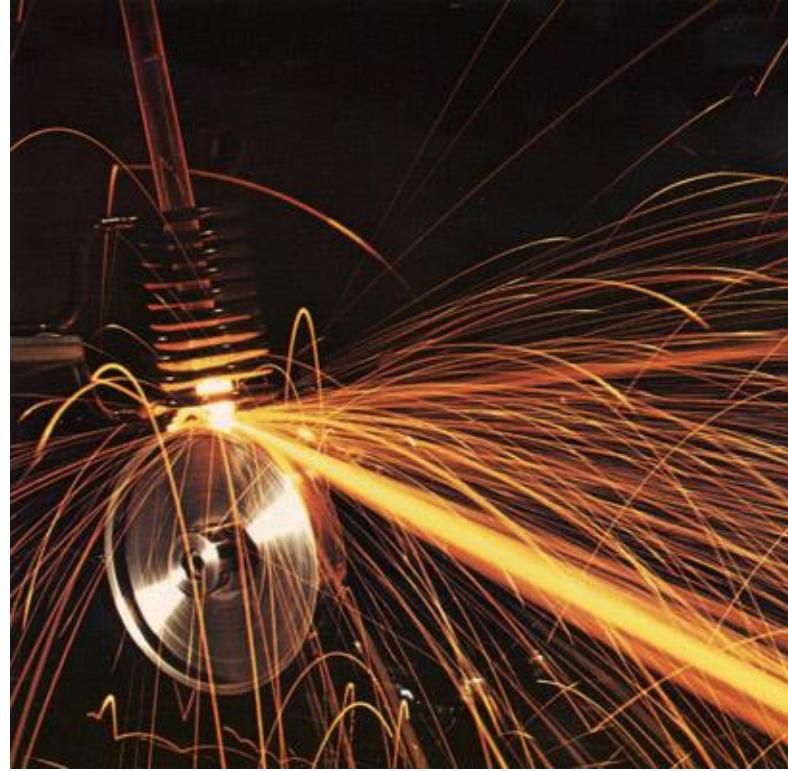
Applications of Glasses & Amorphous Solids

- Ordinary window glass $(\text{SiO}_2)_{0.8}(\text{Na}_2\text{O})_{0.2}$ & majority of glassware are common examples of amorphous solids
- Vitreous silica (SiO_2) mixed with germania (GeO_2) is used extensively in optical fibers
- Insulating oxide layer grown on Si wafer during IC fabrication is amorphous form of SiO_2
- Some intermetallic alloys, such as $\text{Fe}_{0.8}\text{B}_{0.2}$, can be rapidly quenched from liquid to obtain a glassy metal used in low-loss transformer cores
- Arsenic triselenide, As_2Se_3 , has crystal structure that resembles Fig. (a), where As (valency III) bonds with 3 Se atoms, and Se (valency VI) bonds with 2 As atoms
- In amorphous phase, this crystal structure looks like sketch in Fig. (b), in which bonding requirements are only locally satisfied.
- Vapor-grown films of amorphous As_2Se_3 are used in some photoconductor drums in photocopying industry

Whether a liquid forms a glass or a crystal structure on cooling depends on a combination of factors, such as the nature of the chemical bond between the atoms or molecules, the viscosity of the liquid (which determines how easily the atoms move), the rate of cooling, and the temperature relative to the melting temperature



Virtually impossible to quench pure metal, such as Cu (metallic bonding), from melt, bypass crystallization, & form glass. On cooling, Cu ions are quickly shifted w.r.t. each other to form crystal

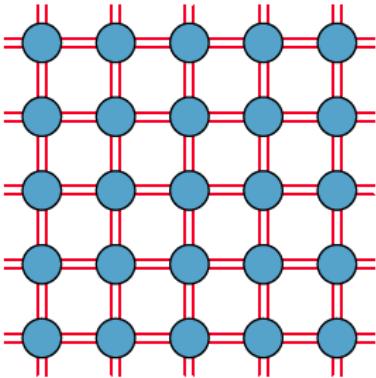


- ✓ Oxides having mixture of covalent & ionic bonds, and highly viscous liquid, readily form glasses
- ✓ Many metal–metal ($\text{Cu}_{66}\text{Zr}_{33}$) & metal–metalloid alloys ($\text{Fe}_{80}\text{B}_{20}$, $\text{Pd}_{80}\text{Si}_{20}$) form glasses if quenched at ultrahigh cooling rates of $10^6\text{--}10^8\text{ }^\circ\text{C/s}$
- ✓ Such cooling rates achieved by squirting thin jet of molten metal against fast-rotating, cooled Cu cylinder. On impact, the melt is frozen within a few milliseconds, producing a long ribbon of metallic glass.

Melt spinning involves squirting a jet of molten metal onto a rotating cool metal drum. The molten jet is instantly solidified into a glassy metal ribbon which is a few microns in thickness. The process produces roughly 1 to 2 kilometers of ribbon per minute.

| SOURCE: Photo courtesy of the Estate of Fritz Goro.

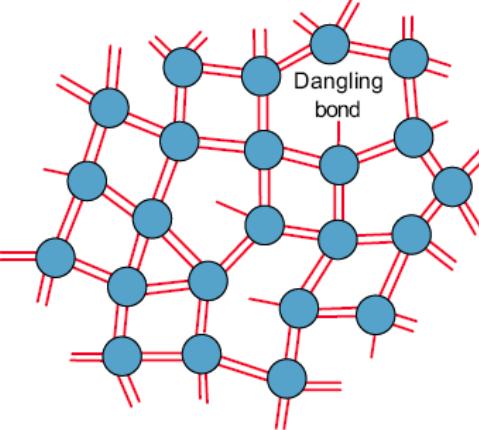
It is possible to rapidly quench a molten metallic alloy, thereby bypassing crystallization, and forming a glassy metal commonly called a metallic glass. The process is called *melt spinning*.



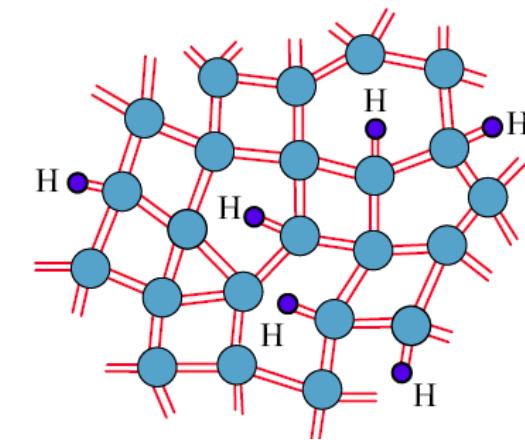
(a) Two dimensional schematic representation of a silicon crystal

Silicon can be grown as a semiconductor crystal or as an amorphous semiconductor film.

Each line represents an electron in a band. A full covalent bond has two lines, and a broken bond has one line.



(b) Two dimensional schematic representation of the structure of amorphous silicon. The structure has voids and dangling bonds and there is no long range order.



(c) Two dimensional schematic representation of the structure of hydrogenated amorphous silicon. The number of hydrogen atoms shown is exaggerated.

Table 1.5 Crystalline and amorphous silicon

	Crystalline Si (c-Si)	Amorphous Si (a-Si)	Hydrogenated a-Si (a-Si:H)
Structure	Diamond cubic.	Short-range order only. On average, each Si covalently bonds with four Si atoms. Has microvoids and dangling bonds.	Short-range order only. Structure typically contains 10% H. Hydrogen atoms passivate dangling bonds and relieve strain from bonds.
Typical preparation	Czochralski technique.	Electron beam evaporation of Si.	Chemical vapor deposition of silane gas by RF plasma.
Density (g cm^{-3})	2.33	About 3–10% less dense.	About 1–3% less dense.
Electronic applications	Discrete and integrated electronic devices.	None	Large-area electronic devices such as solar cells, flat panel displays, and some photoconductor drums used in photocopying.

Thank You

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