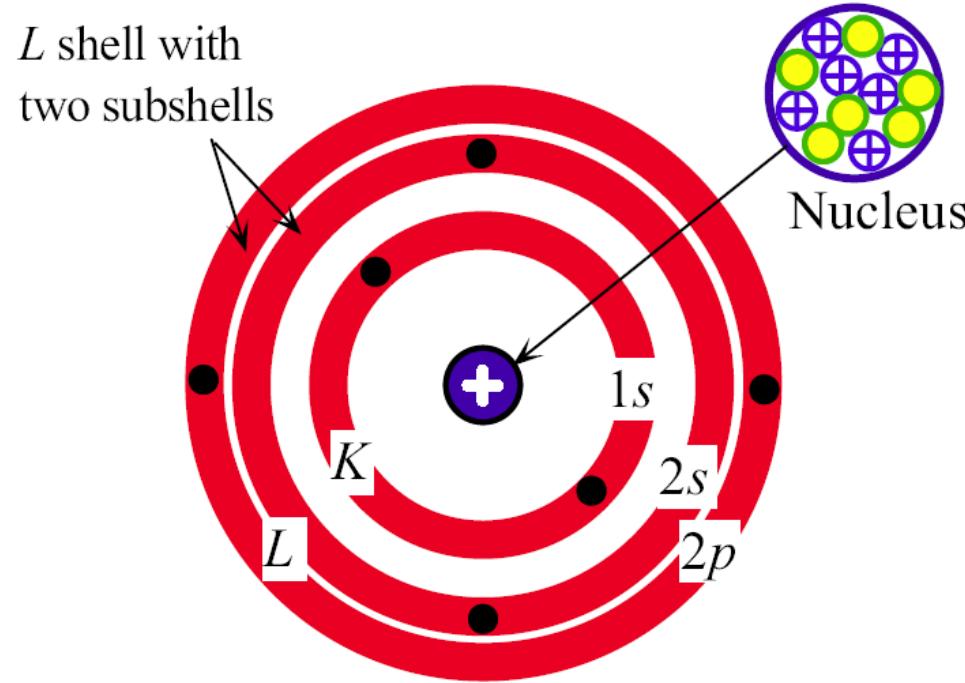


Chapter 1

Elementary Materials Science Concepts



$$1s^2 2s^2 2p^2 \text{ or } [\text{He}]2s^2 2p^2$$

The shell model of the atom in which electrons are confined to live within certain shells and in subshells within shells

Table 1.1 Maximum possible number of electrons in the shells and subshells of an atom

<i>n</i>	Shell	Subshell			
		$\ell = 0$	1	2	3
s	p	d	f		
1	<i>K</i>	2			
2	<i>L</i>	2	6		
3	<i>M</i>	2	6	10	
4	<i>N</i>	2	6	10	14

Virial Theorem

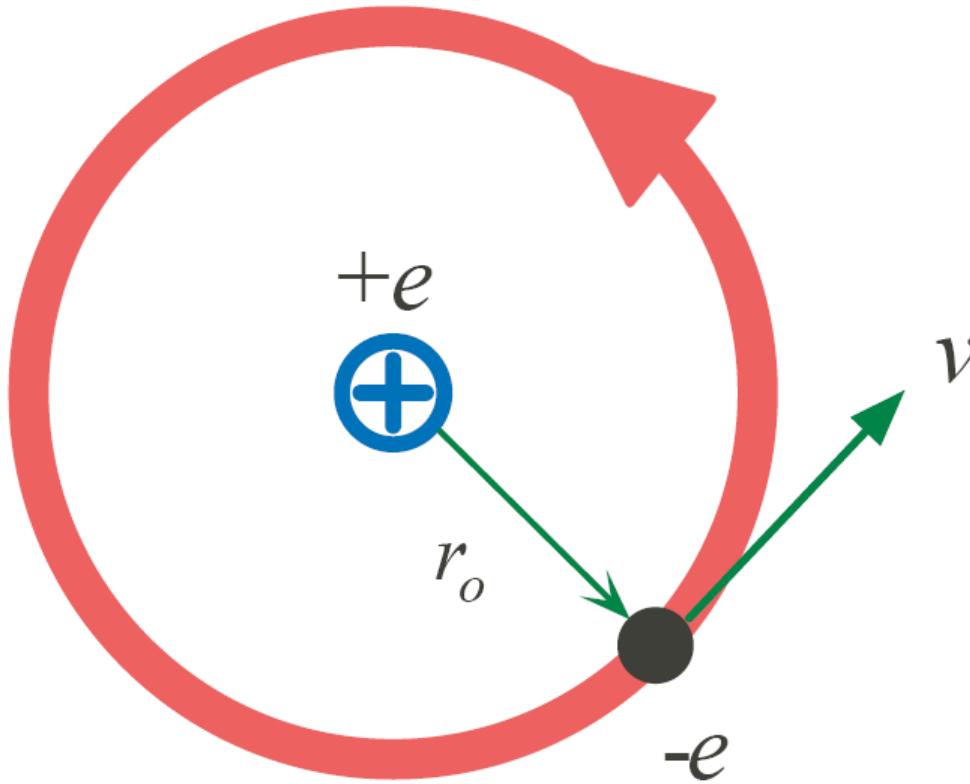
$$\overline{KE} = -\frac{1}{2} \overline{PE}$$

Average kinetic energy is related to the average potential energy

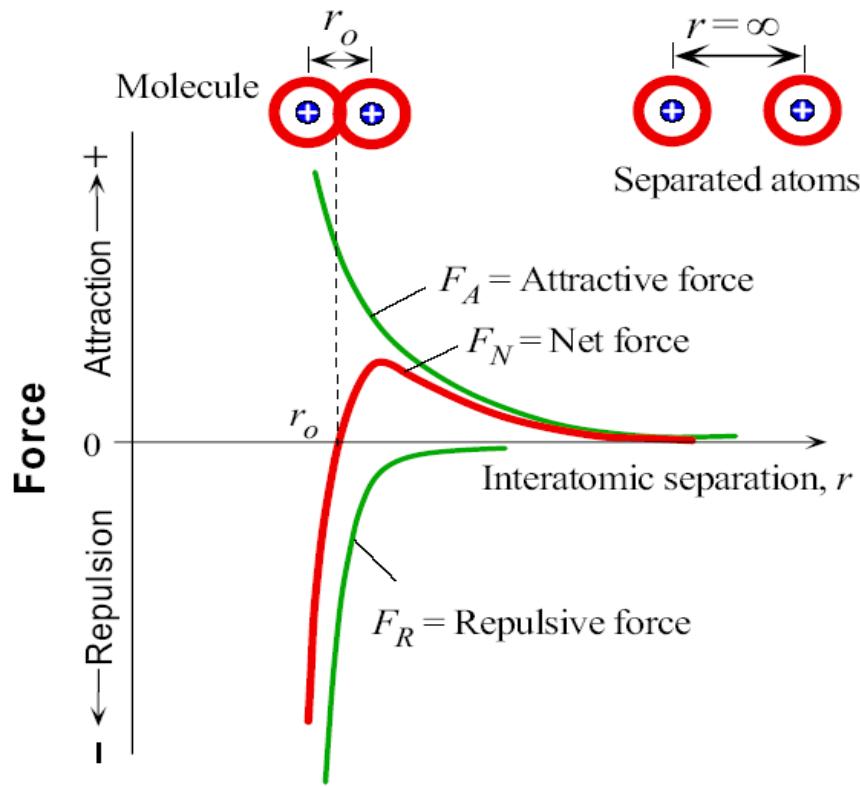
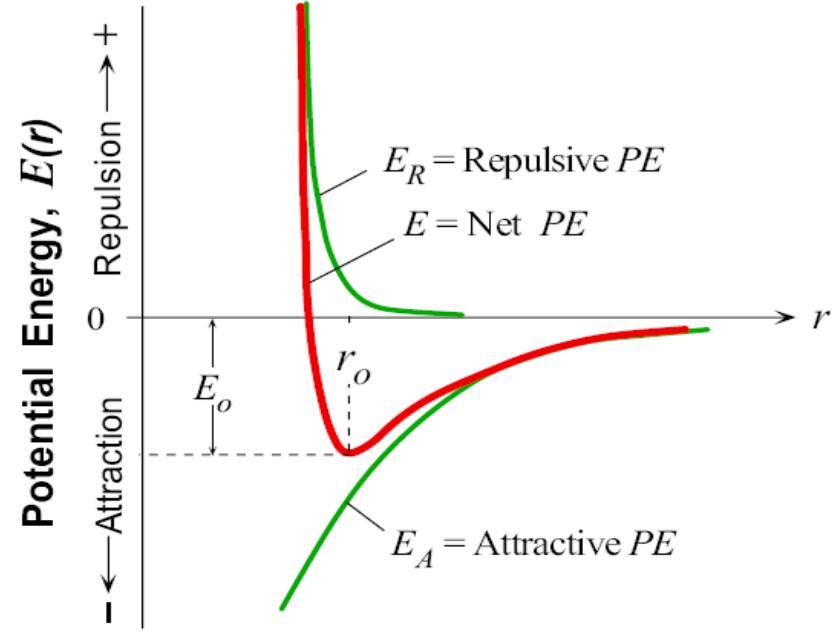
Total Average Energy

$$\overline{E} = \overline{PE} + \overline{KE}$$

Stable orbit has radius, r_o



The planetary model of the hydrogen atom in which the negatively charged electron orbits the positively charged nucleus.

(a) Force vs r (b) Potential energy vs r

- (a) Force vs. interatomic separation
 (b) Energy vs. interatomic separation

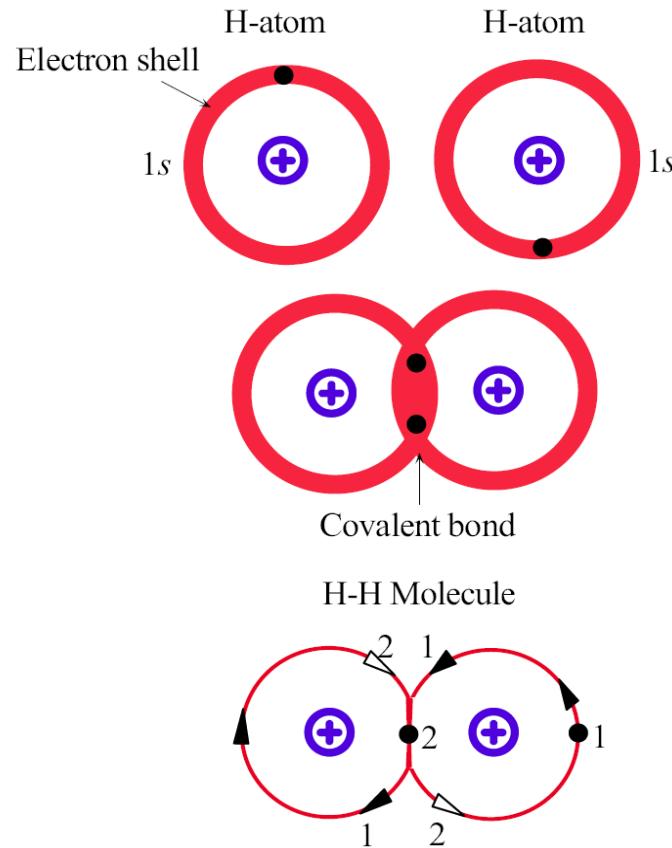
Net Force in Bonding Between Atoms

$$\mathbf{F}_N = \mathbf{F}_A + \mathbf{F}_R = \mathbf{0}$$

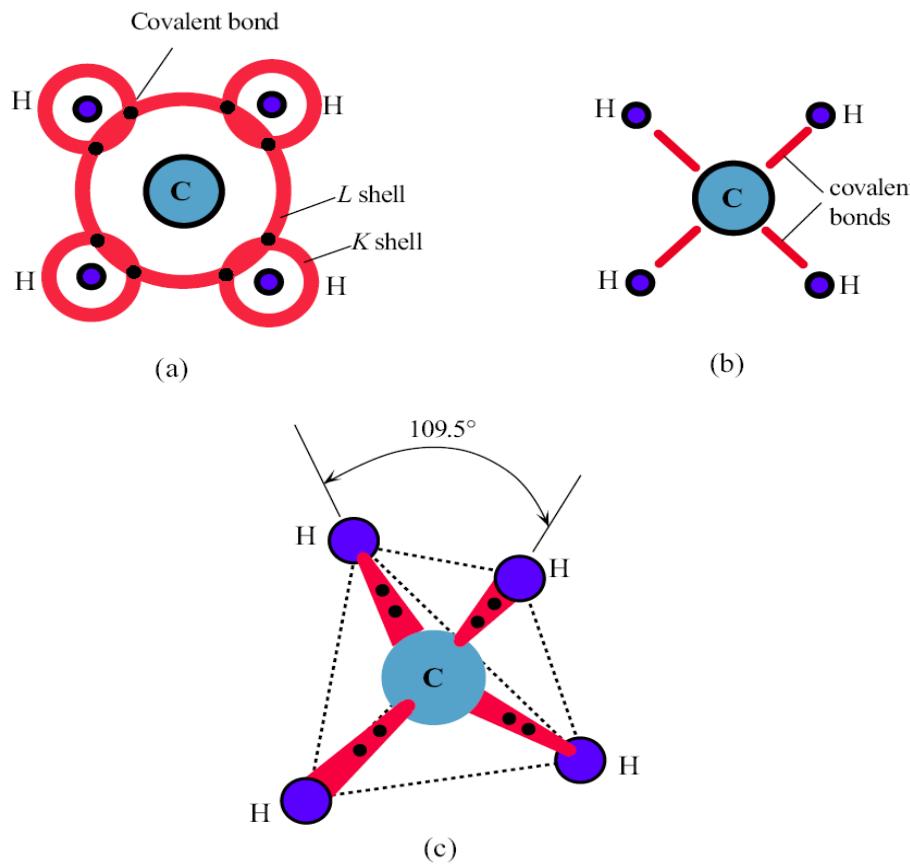
F_N = net force

F_A = attractive force

F_R = repulsive force



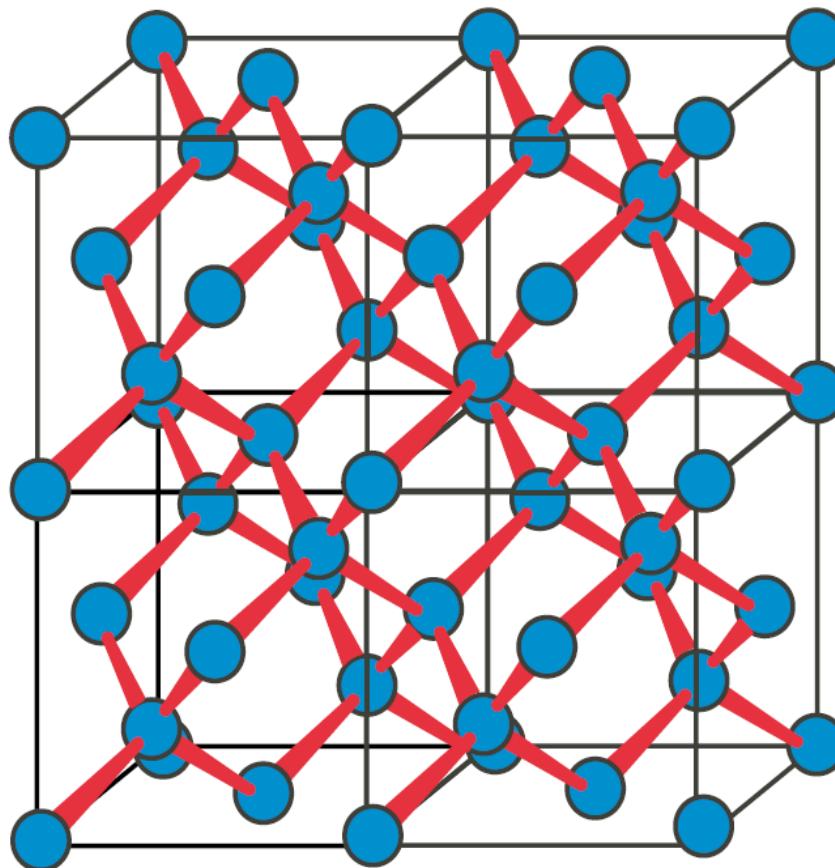
Formation of a covalent bond between two hydrogen atoms leads to the H_2 molecule. Electrons spend majority of their time between the two nuclei which results in a net attraction between the electrons and the two nuclei which is the origin of the covalent bond.



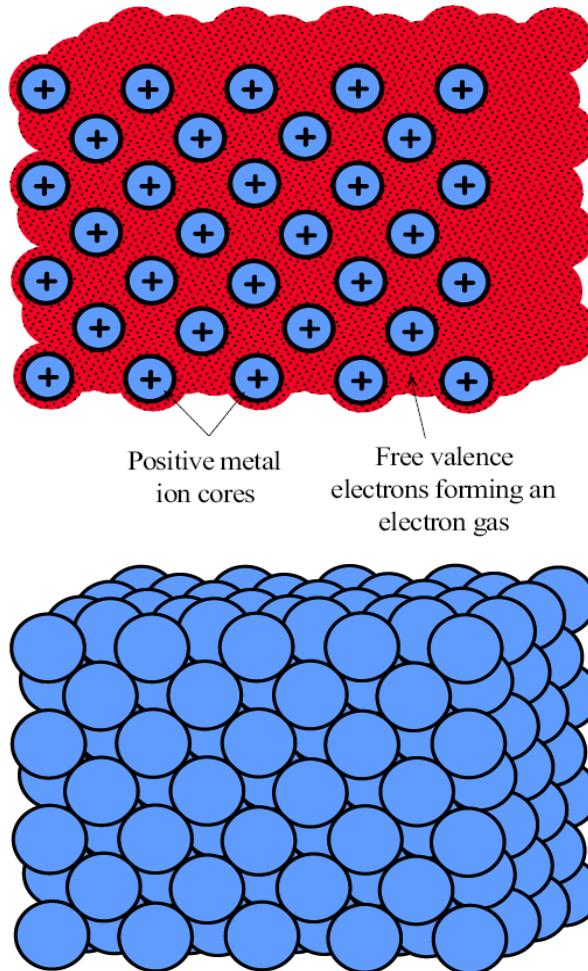
(a) Covalent bonding in methane, CH_4 , involves four hydrogen atoms sharing bonds with one carbon atom. Each covalent bond has two shared electrons. The four bonds are identical and repel each other.

(b) Schematic sketch of CH_4 in paper.

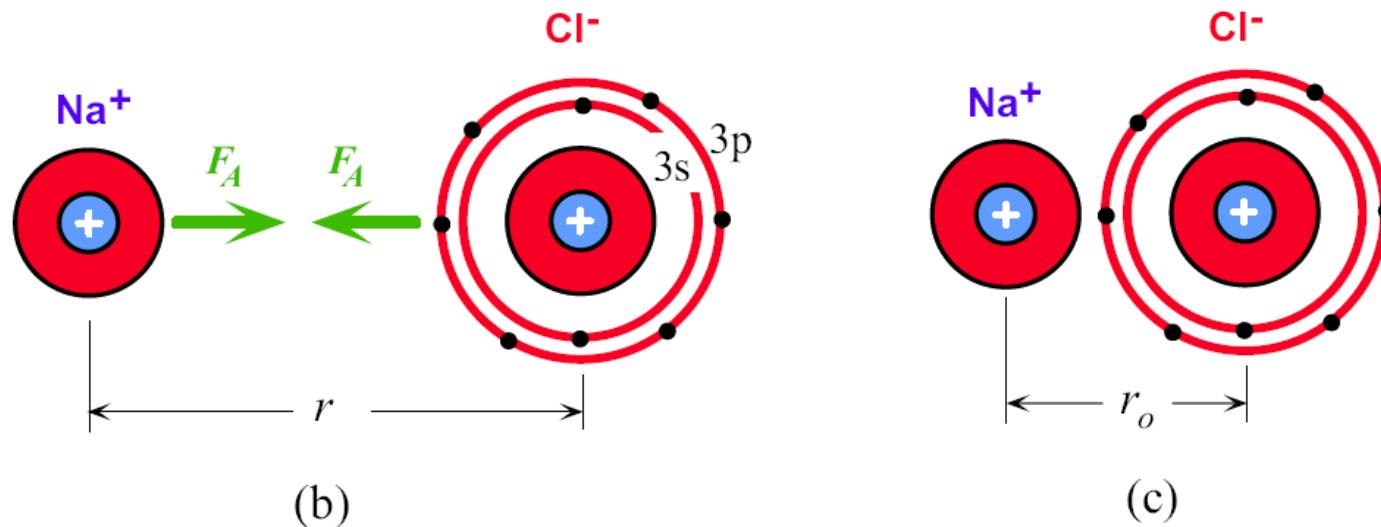
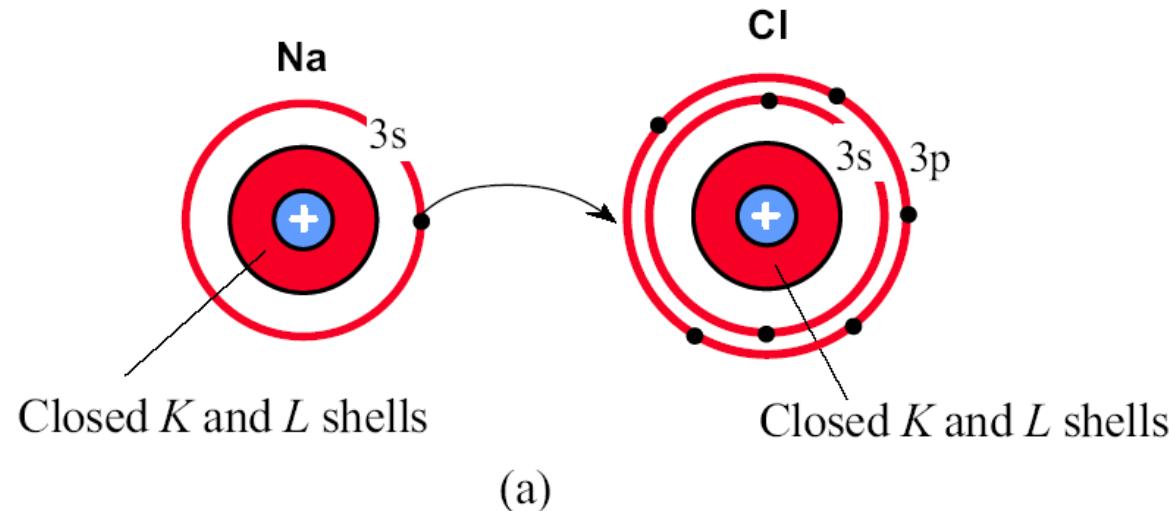
(c) In three dimensions, due to symmetry, the bonds are directed towards the Corners of a tetrahedron.



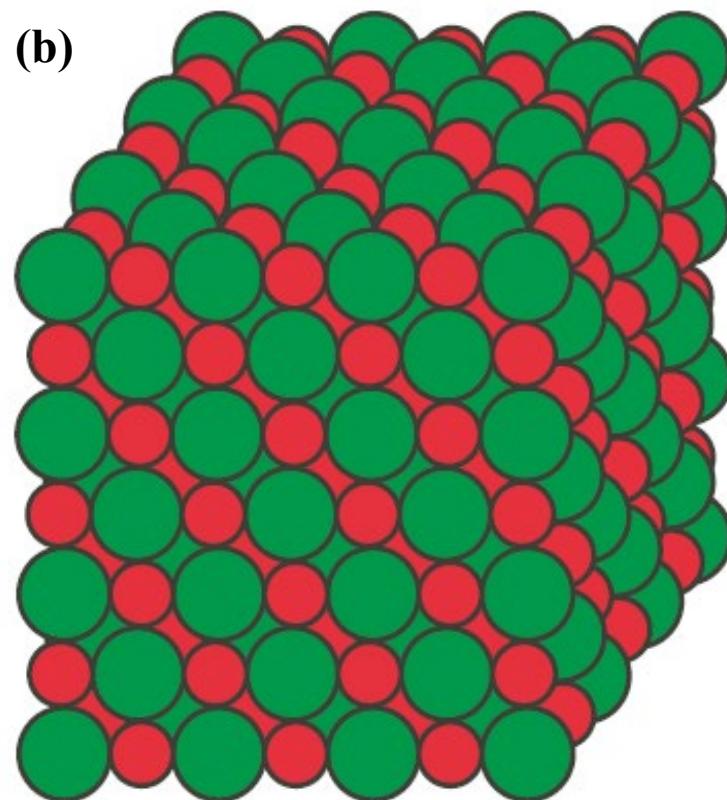
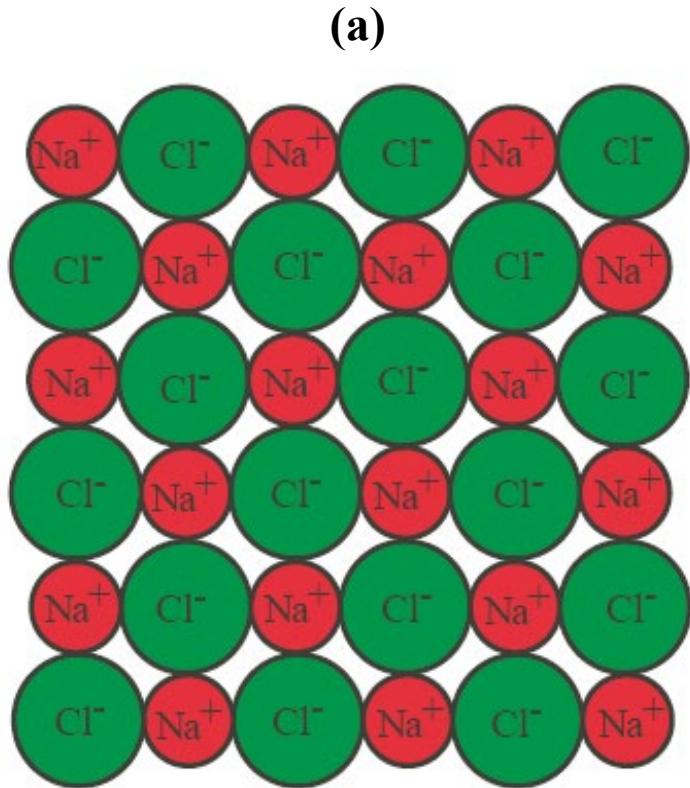
The diamond crystal is a covalently bonded network of carbon atoms. Each carbon atom is covalently bonded to four neighbors forming a regular three dimensional pattern of atoms which constitutes the diamond crystal.



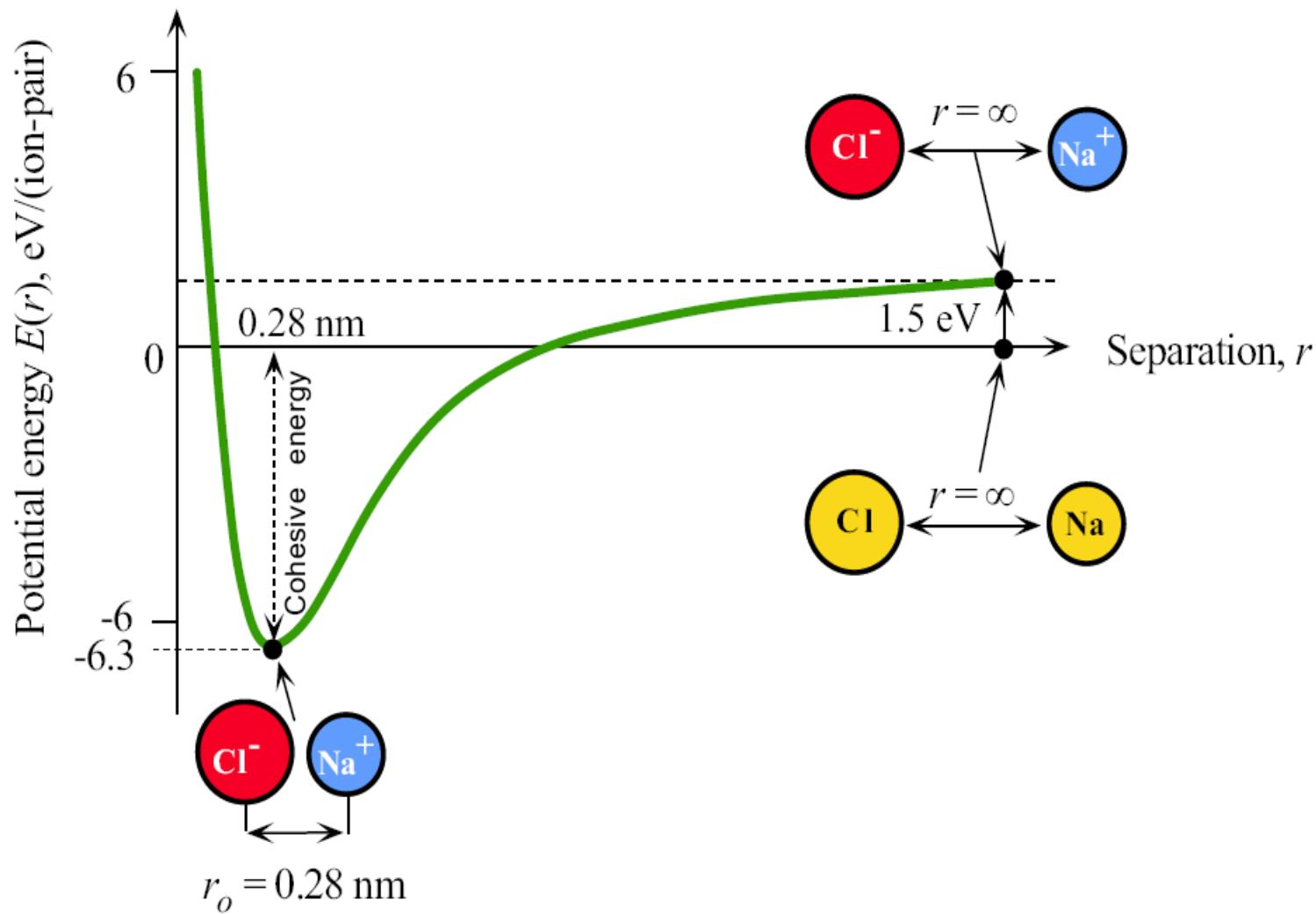
In metallic bonding the valence electrons from the metal atoms form a “cloud of electrons” which fills the space between the metal ions and “glues” the ions together through the coulombic attraction between the electron gas and the positive metal ions.



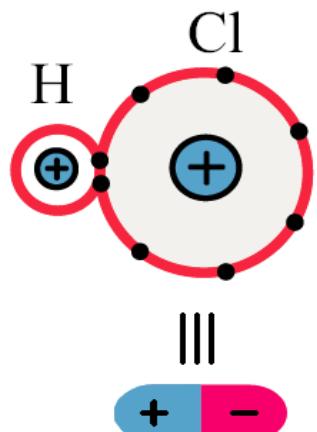
The formation of ionic bond between Na and Cl atoms in NaCl . The attraction
Is due to coulombic forces.



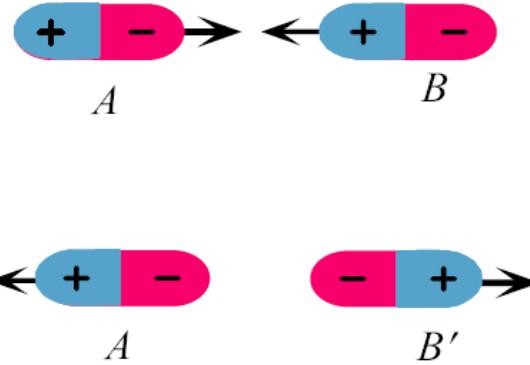
- (a) A schematic illustration of a cross section from solid NaCl. NaCl is made of Cl^- and Na^+ ions arranged alternately so that the oppositely charged ions are closest to each other and attract each other. There are also repulsive forces between the like ions. In equilibrium the net force acting on any ion is zero.
- (b) Solid NaCl.



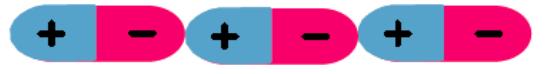
Sketch of the potential energy per ion-pair in solid NaCl. Zero energy corresponds to neutral Na and Cl atoms infinitely separated.



(a)

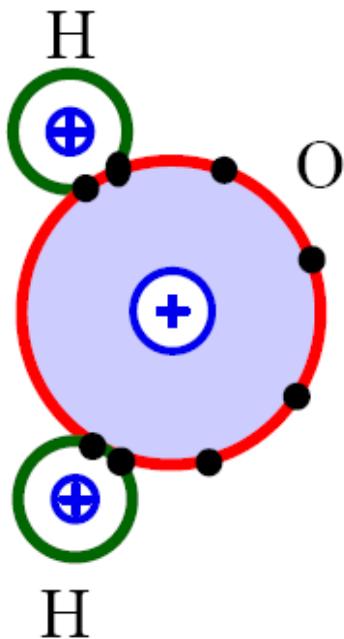


(b)

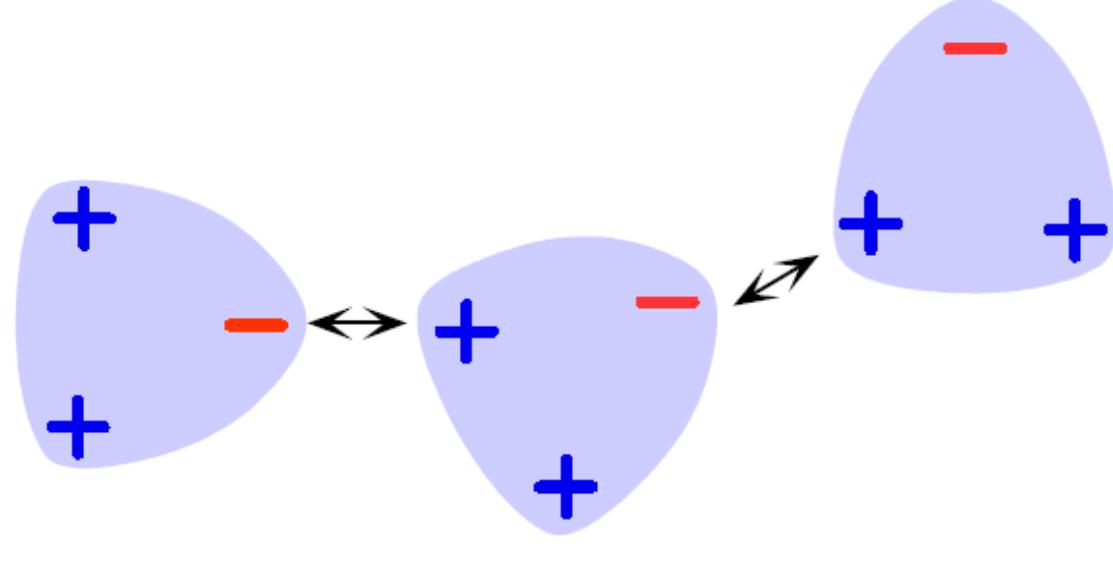


(c)

- (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 Walls bonds.



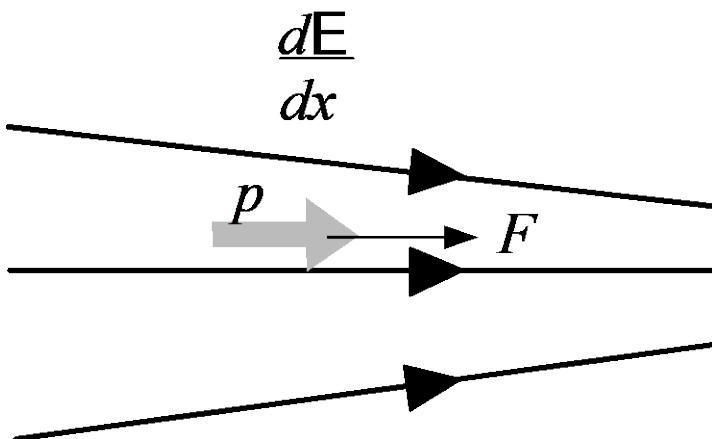
(a)



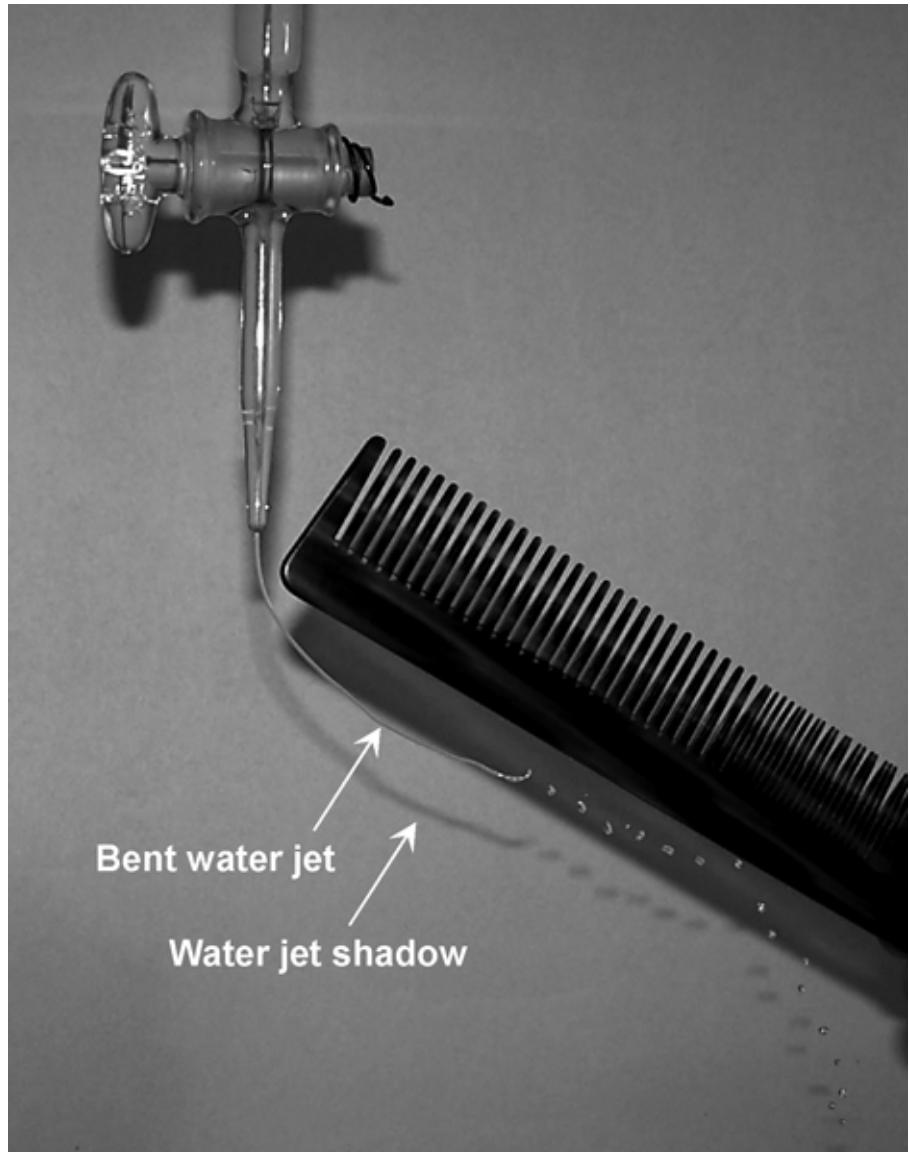
(b)

The origin of van der Walls bonding between water molecules.

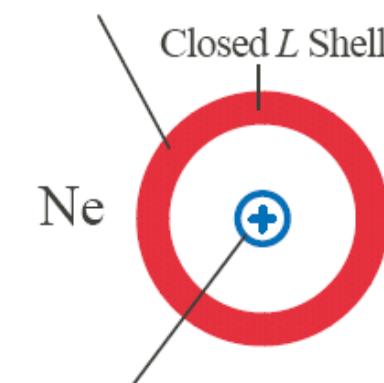
- (a) The H₂O molecule is polar and has a net permanent dipole moment
- (b) Attractions between the various dipole moments in water gives rise to van der Walls bonding



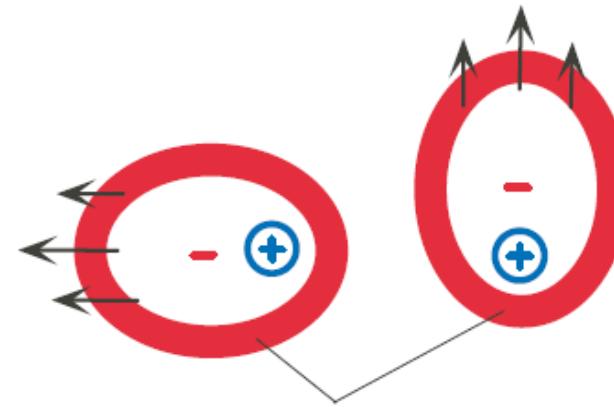
A dipole moment in a nonuniform field experiences a net force F that depends on the dipole moment p and the field gradient dE/dx . When a charged comb (by combing hair) is brought close to a water jet, the field from the comb attracts the polarized water molecules toward higher fields.
[See Question 7.7 in Chapter 7]



Time averaged electron (negative charge) distribution

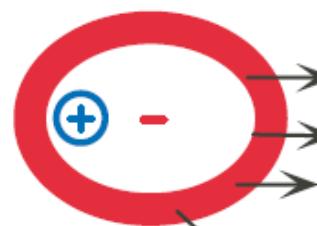


Ionic core
(Nucleus + *K*-shell)



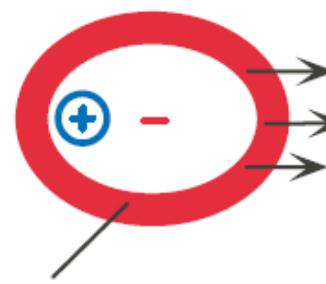
Instantaneous electron (negative charge) distribution fluctuates about the nucleus.

A



van der
Waals force

B



Synchronized fluctuations
of the electrons

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.

Definition of Elastic Modulus

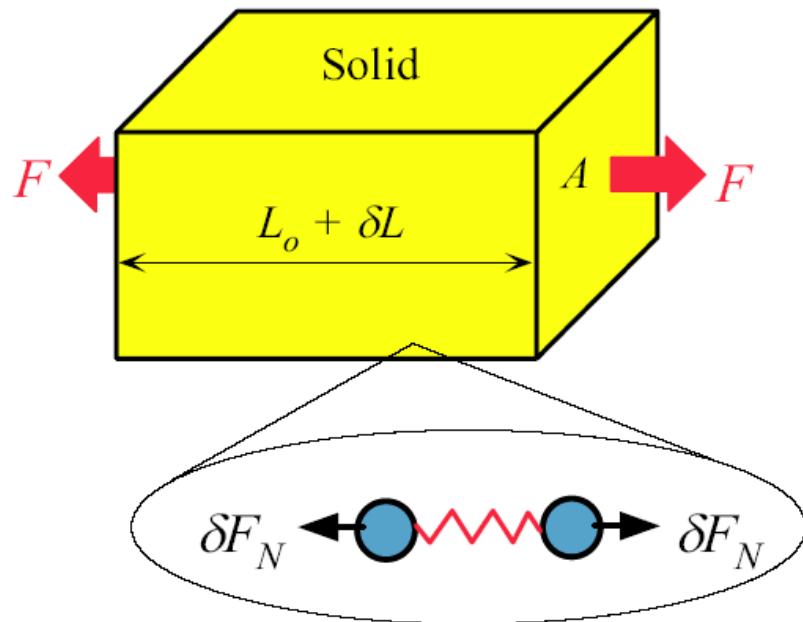
$$\sigma = Y\epsilon$$

σ = applied stress (force per unit area), Y = elastic modulus, ϵ = elastic strain (fractional increase in the length of the solid)

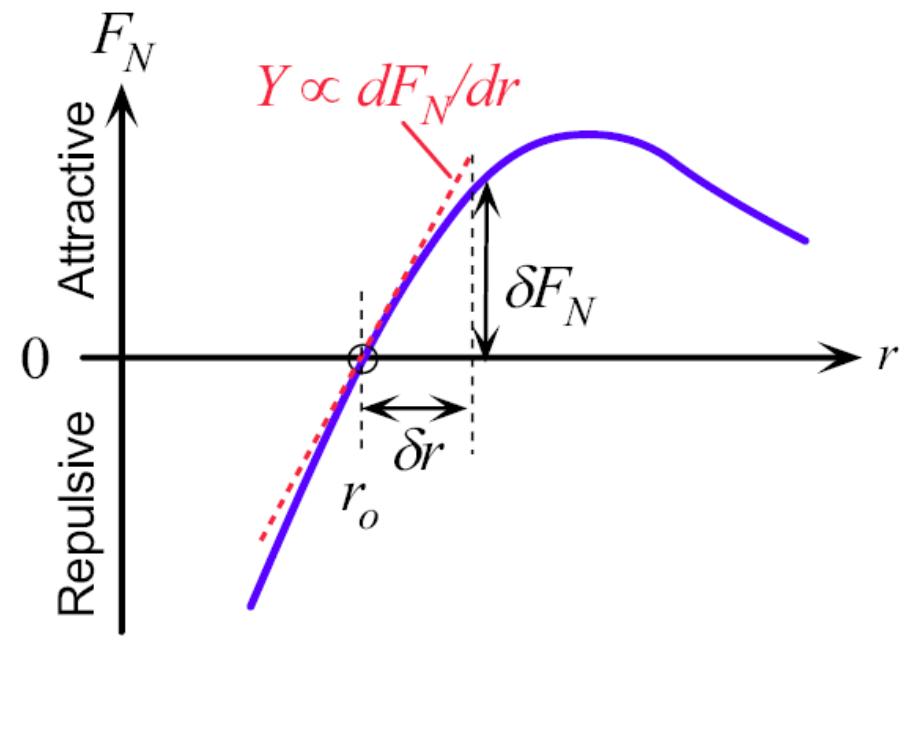
Elastic Modulus and Bonding

$$Y \approx \frac{1}{r_o} \left[\frac{dF_N}{dr} \right]_{r=r_o} \approx \frac{1}{r_o} \left[\frac{d^2 E}{dr^2} \right]_{r=r_o}$$

Y = elastic modulus, r_o = interatomic equilibrium separation, F_N = net force, r = interatomic separation, E = bonding energy



(a)



(b)

(a) Applied forces F stretch the solid elastically from L_o to δL . The force is divided amongst chains of atoms that make the solid. Each chain carries a force δF_N .

(b) In equilibrium, the applied force is balanced by the net force δF_N between the atoms as a result of their increased separation.

Elastic Modulus and Bond Energy

$$Y \approx f \frac{E_{\text{bond}}}{r_o^3}$$

Y = elastic modulus

f = numerical factor (constant) that depends on the type of the crystal and the type of the bond

E_{bond} = bonding energy

r_o = interatomic equilibrium separation

Kinetic Molecular Theory for Gases

$$PV = \frac{1}{3} N m \bar{v^2}$$

P = gas pressure

$\bar{v^2}$ = mean square velocity

N = number of gas molecules

m = mass of the gas molecules

Ideal Gas Equation

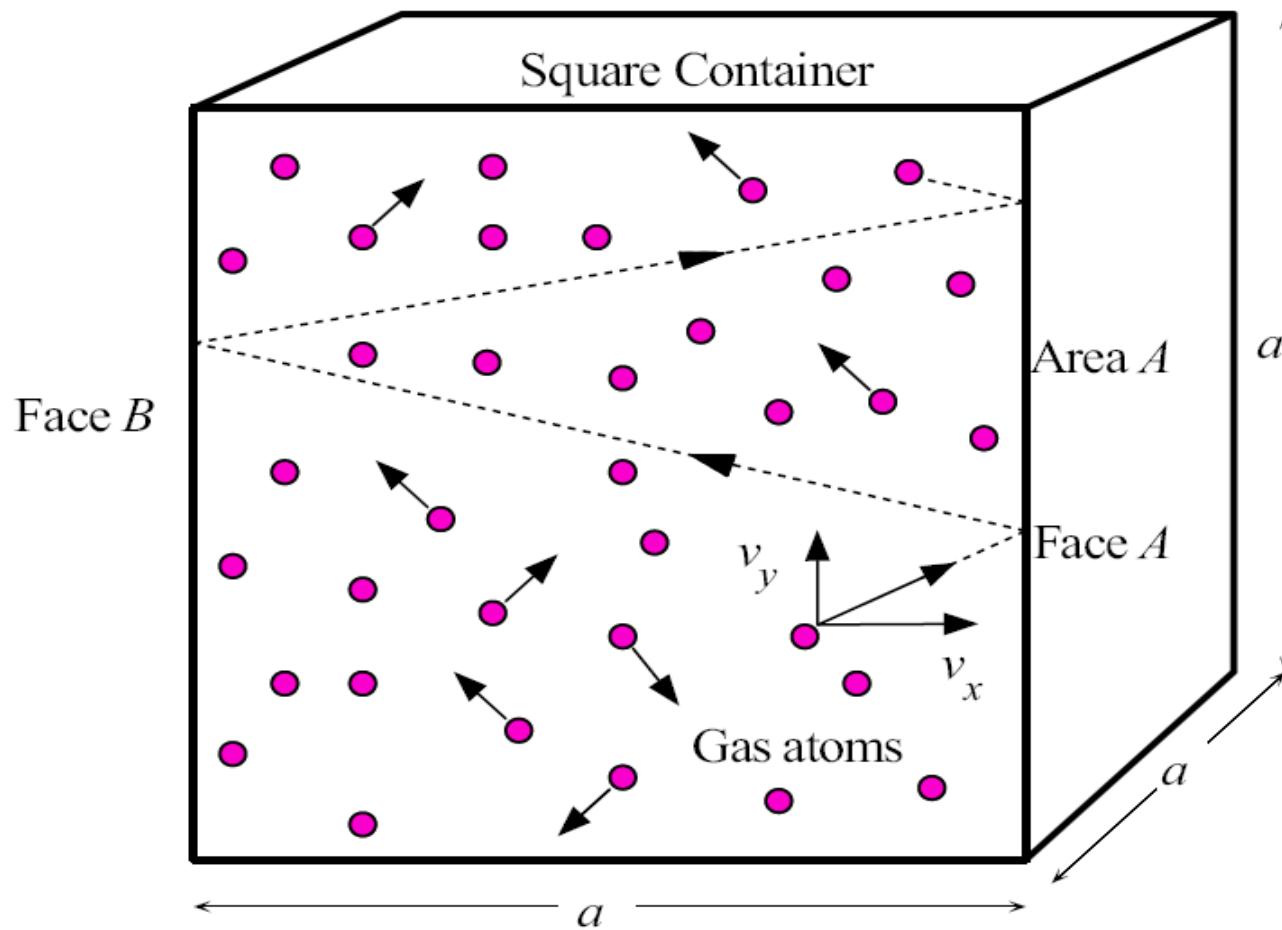
$$PV = (N/N_A)RT$$

N = number of molecules, R = gas constant, T = temperature,
 P = gas pressure, V = volume, N_A = Avogadro's number

Change in Momentum of a Molecule

$$\Delta p = 2mv_x$$

Δp = change in momentum, m = mass of the molecule, v_x = velocity
in the x direction



The gas molecules in the container are in random motion

Rate of Change of Momentum

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{(2a/v_x)} = \frac{mv_x^2}{a}$$

F = force exerted by the molecule, Δp = change in momentum, Δt = change in time, m = mass of the molecule, v_x = velocity in the x direction, a = side length of cubic container

Total Pressure Exerted by N Molecules

$$P = \frac{mN\overline{v_x^2}}{V}$$

P = total pressure, m = mass of the molecule, $\overline{v_x^2}$ = mean square velocity along x , V = volume of the cubic container

Mean Square Velocity

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

Mean square velocities in the x , y , and z directions are the same

Mean Velocity for a Molecule

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}$$

Gas Pressure in the Kinetic Theory

$$P = \frac{Nm\overline{v^2}}{3V} = \frac{1}{3}\rho\overline{v^2}$$

P = gas pressure, N = number of molecules, m = mass of the gas molecule, v = velocity, V = volume, ρ = density.

Mean Kinetic Energy per Atom

$$\overline{KE} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

k = Boltzmann constant, T = temperature

Internal Energy per Mole for a Monatomic Gas

$$U = N_A \left(\frac{1}{2} m \overline{v^2} \right) = \frac{3}{2} N_A k T$$

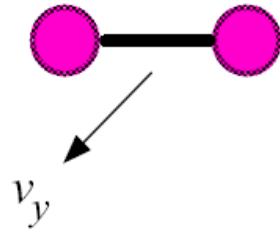
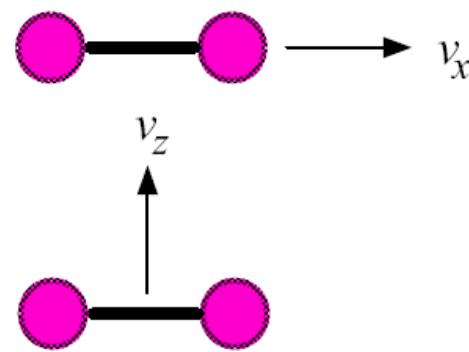
U = total internal energy per mole, N_A = Avogadro's number, m = mass of the gas molecule, k = Boltzmann constant, T = temperature

Molar Heat Capacity at Constant Volume

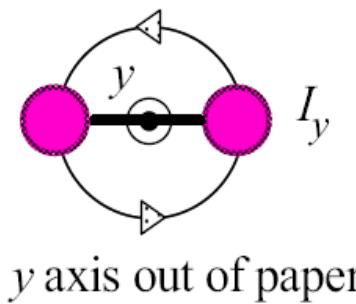
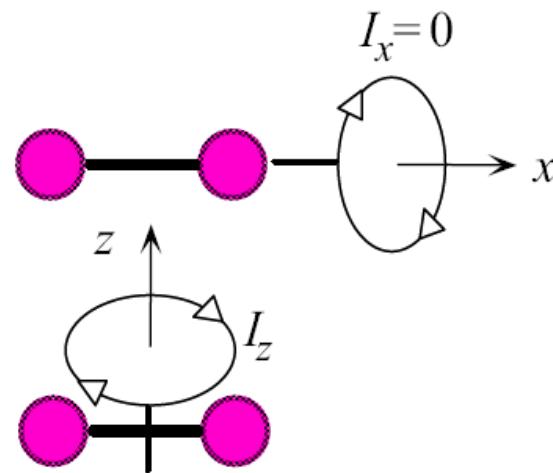
$$C_m = \frac{dU}{dT} = \frac{3}{2} N_A k = \frac{3}{2} R$$

C_m = heat capacity per mole at constant volume ($\text{J K}^{-1} \text{mole}^{-1}$), U = total internal energy per mole, R = gas constant

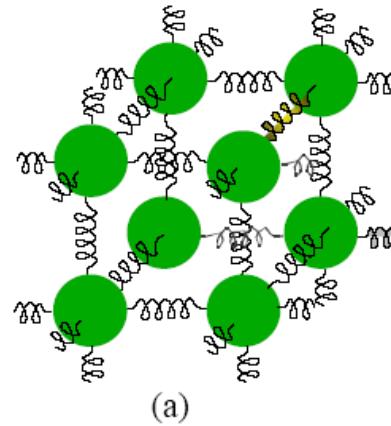
TRANSLATIONAL MOTION



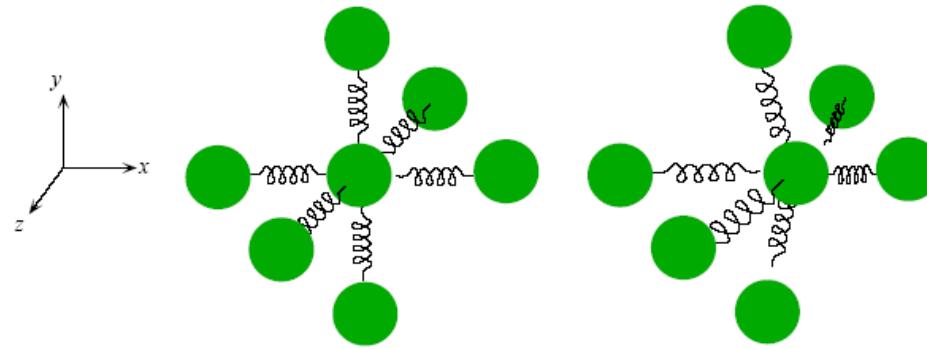
ROTATIONAL MOTION



Possible translational and rotational motions of a diatomic molecule. Vibrational motions are neglected.



(a)



(b)

- (a) The ball and spring model of solids in which the springs represent the interatomic bonds. Each ball (atom) is linked to its nearest neighbors by springs. Atomic vibrations in a solid involve 3 dimensions.
- (b) An atom vibrating about its equilibrium position stretches and compresses its springs to the neighbors and has both kinetic and potential energy.

Internal Energy per Mole

$$U = N_A \cdot 6 \left(\frac{1}{2} kT \right) = 3RT$$

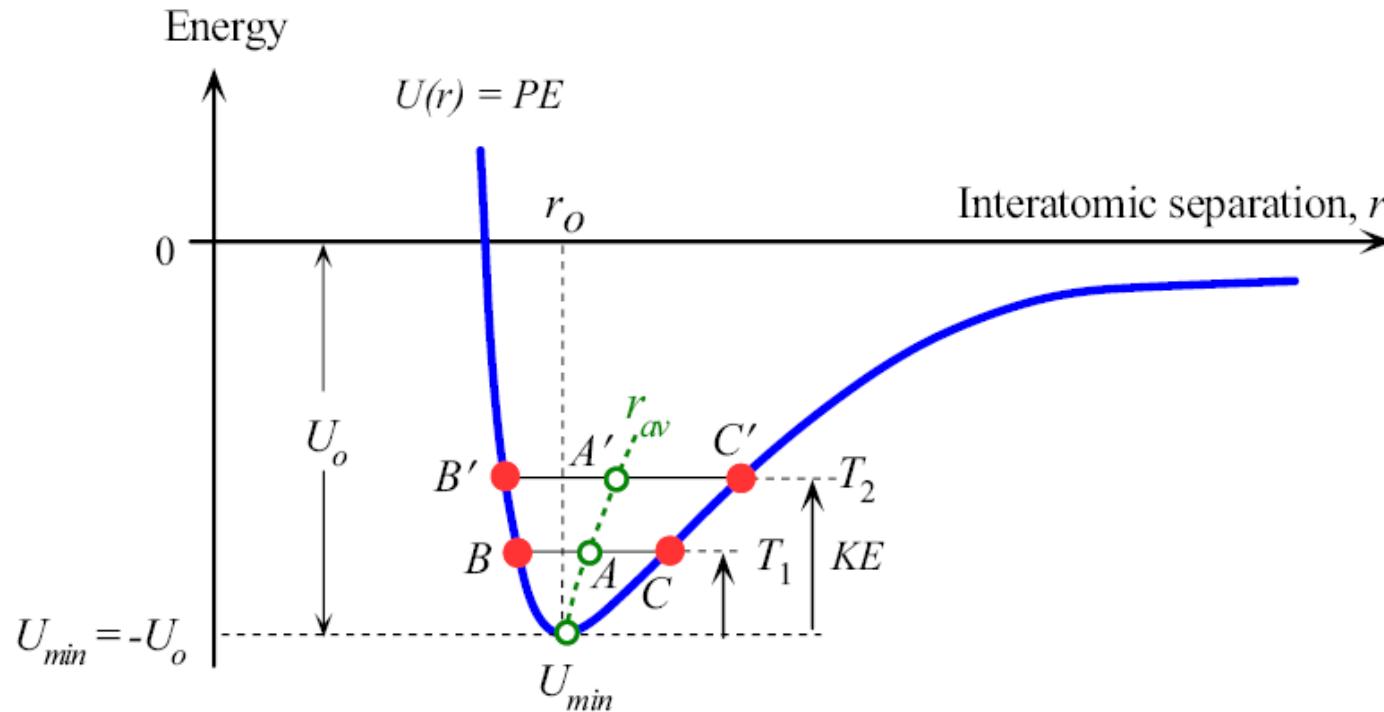
U = total internal energy per mole, N_A = Avogadro's number, R = gas constant, k = Boltzmann constant, T = temperature

Dulong-Petit Rule

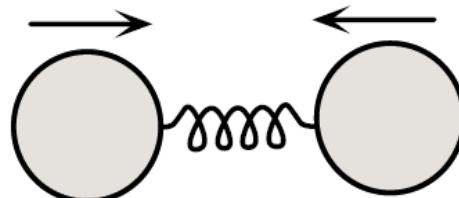
$$C_m = \frac{dU}{dT} = 3R = 25 \text{ J K}^{-1} \text{ mol}^{-1}$$

C_m = Heat capacity per mole at constant volume ($\text{J K}^{-1} \text{ mole}^{-1}$)

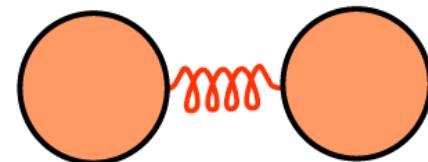
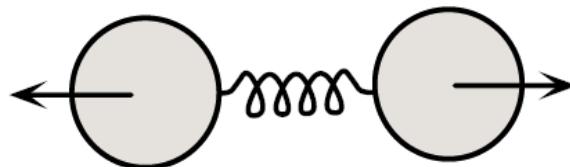
Thermal Expansion



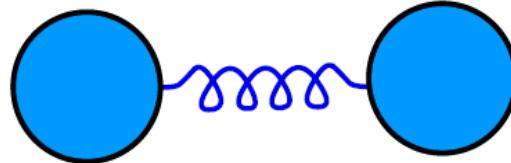
The potential energy PE curve has a minimum when the atoms in the solid attain the interatomic separation $r = r_0$. Due to thermal energy, the atoms will be vibrating and will have vibrational kinetic energy. At $T = T_1$, the atoms will be vibrating in such a way that the bond will be stretched and compressed by an amount corresponding to the KE of the atoms. A pair of atoms will be vibrating between B and C . This average separation will be at A and greater than r_0 .



State A

State B, $KE = 0$,
 $E = U_B$ 

State A

State C, $KE = 0$,
 $E = U_C$

Vibrations of atoms in the solid. We consider, for simplicity a pair of atom. Total energy $E = PE + KE$ and this is constant for a pair of vibrating atoms executing simple harmonic Motion. At B and C KE is zero (atoms are stationary and about to reverse direction of oscillation) and PE is maximum.

Definition of Thermal Expansion Coefficient

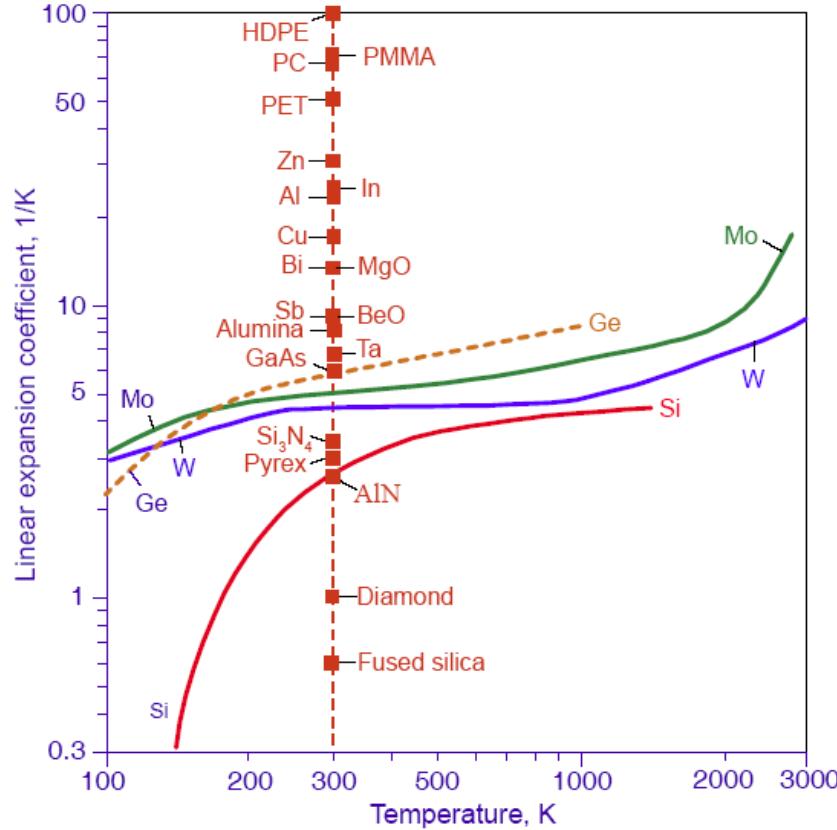
$$\lambda = \frac{1}{L_o} \cdot \frac{\delta L}{\delta T}$$

λ = thermal coefficient of linear expansion or thermal expansion coefficient, L_o = original length, L = length at temperature T

Thermal Expansion

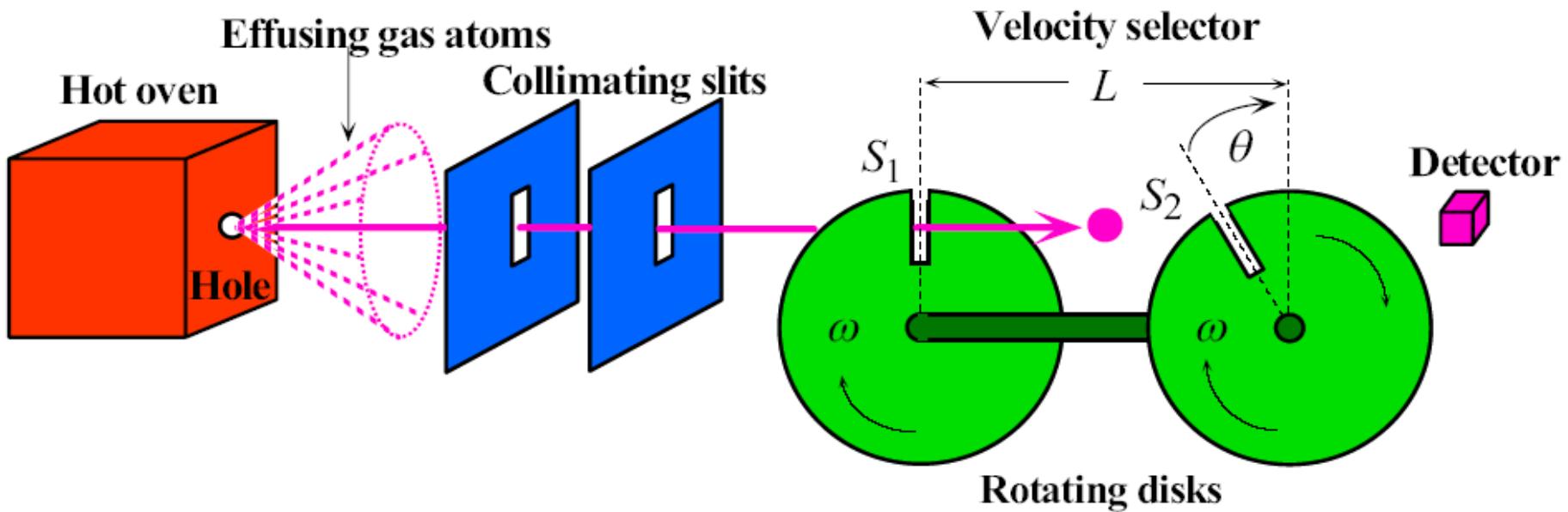
$$L = L_o[1 + \lambda(T - T_o)]$$

L = length at temperature T , L_o = length at temperature T_o



Dependence of the linear thermal expansion coefficient λ (K^{-1}) on temperature T (K) on a log-log plot. HDPE, high density polyethylene; PMMA, Polymethylmethacrylate (acrylic); PC, polycarbonate; PET, polyethylene terephthalate (polyester); fused silica, SiO_2 ; alumina, Al_2O_3 .

SOURCE: Data extracted from various sources including G.A. Slack and S.F. Bartram, *J. Appl. Phys.*, **46**, 89, 1975.

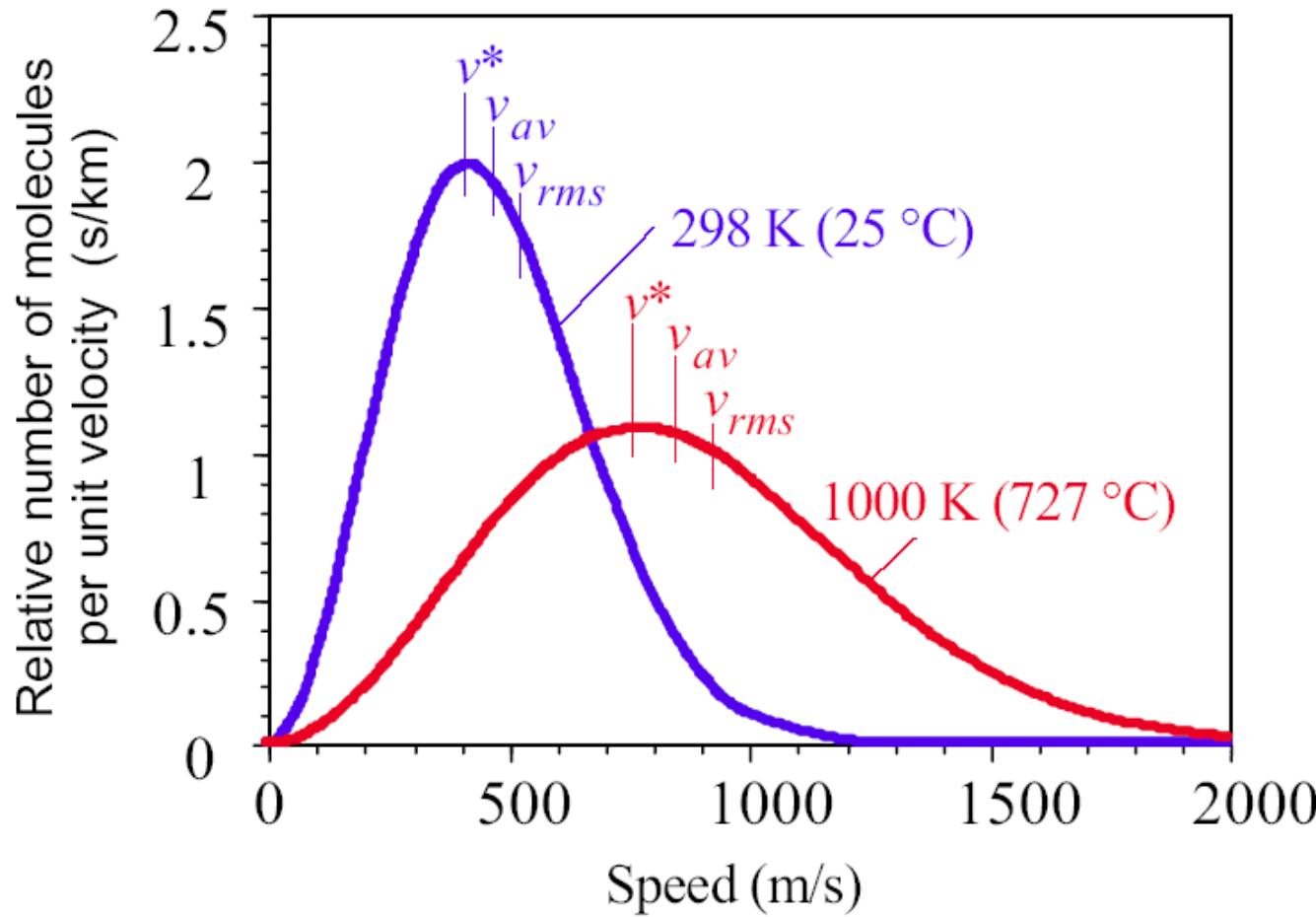


Schematic diagram of a stern type experiment for determining the distribution of molecular velocities

Maxwell-Boltzmann Distribution for Molecular Speeds

$$n_v = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right)$$

n_v = velocity density function, N = total number of molecules, m = molecular mass, k = Boltzmann constant, T = temperature, v = velocity

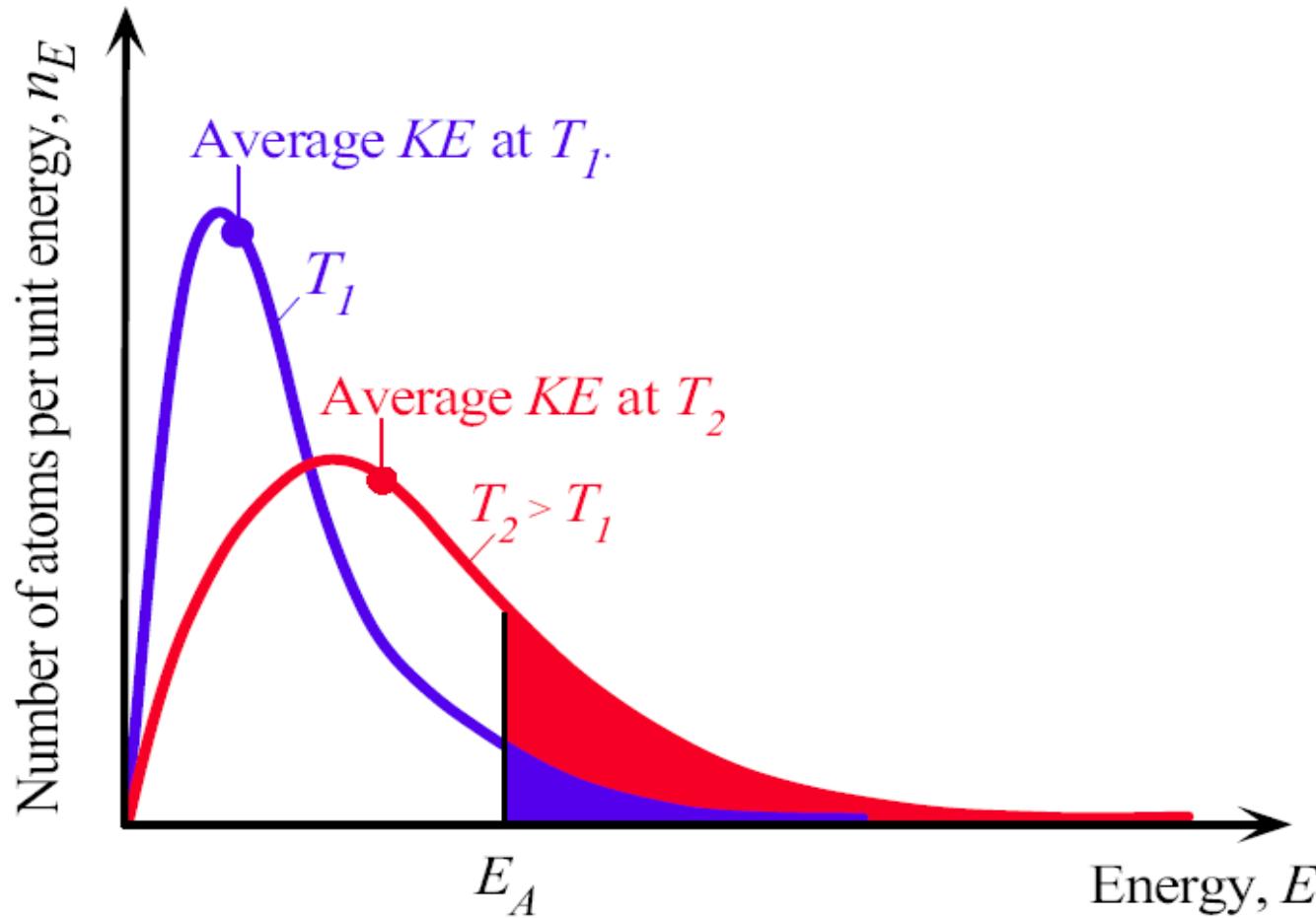


Maxwell Boltzmann distribution of molecular speeds in nitrogen gas at two temperatures. The ordinate is $dN/(Ndv)$, the fractional number of molecules per unit speed interval in $(\text{km}/\text{s})^{-1}$.

Maxwell-Boltzmann Distribution for Translational Kinetic Energies

$$n_E = \frac{2}{\sqrt{\pi}} N \left(\frac{1}{kT} \right)^{3/2} E^{1/2} \exp \left(-\frac{E}{kT} \right)$$

n_E = number of atoms per unit volume per unit energy at an energy E ,
 N = total number of molecules per unit volume, k = Boltzmann constant, T = temperature.

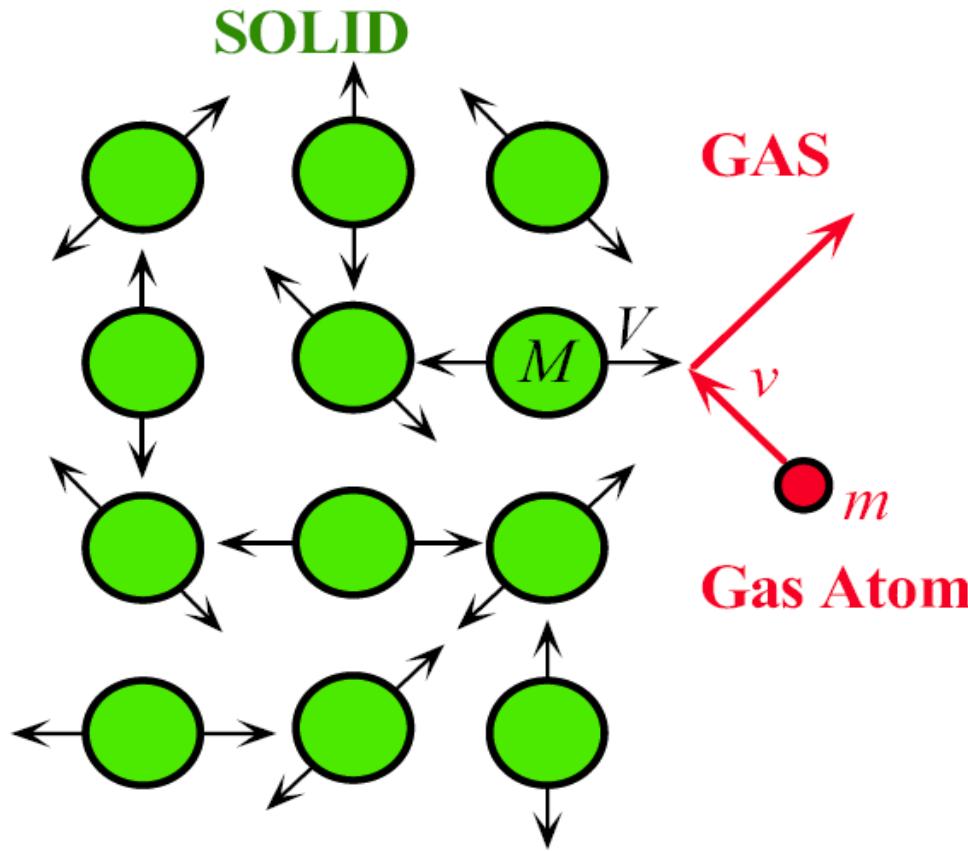


Energy distribution of gas molecules at two different temperatures. The number of molecules that have energies greater than E_A is the shaded area. This area depends strongly on the temperature as $\exp(-E_A/kT)$

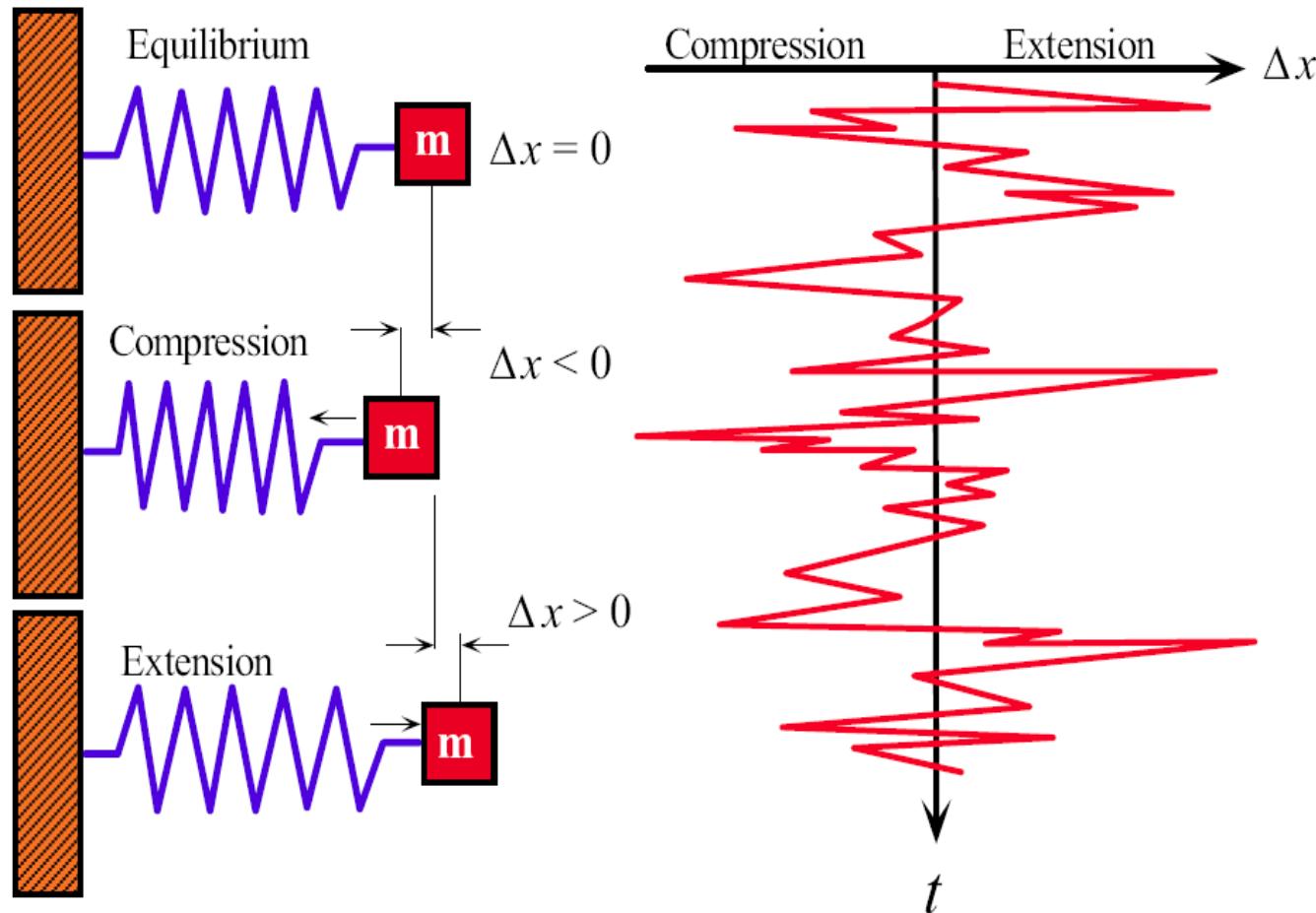
Boltzmann Energy Distribution

$$\frac{n_E}{N} = C \exp\left(-\frac{E}{kT}\right)$$

n_E = number of atoms per unit volume per unit energy at an energy E ,
 N = total number of atoms per unit volume in the system, C = a
constant that depends on the specific system (weak energy
dependence), k = Boltzmann constant, T = temperature



Solid in equilibrium in air. During collisions between the gas and solid atoms, kinetic energy is exchanged.

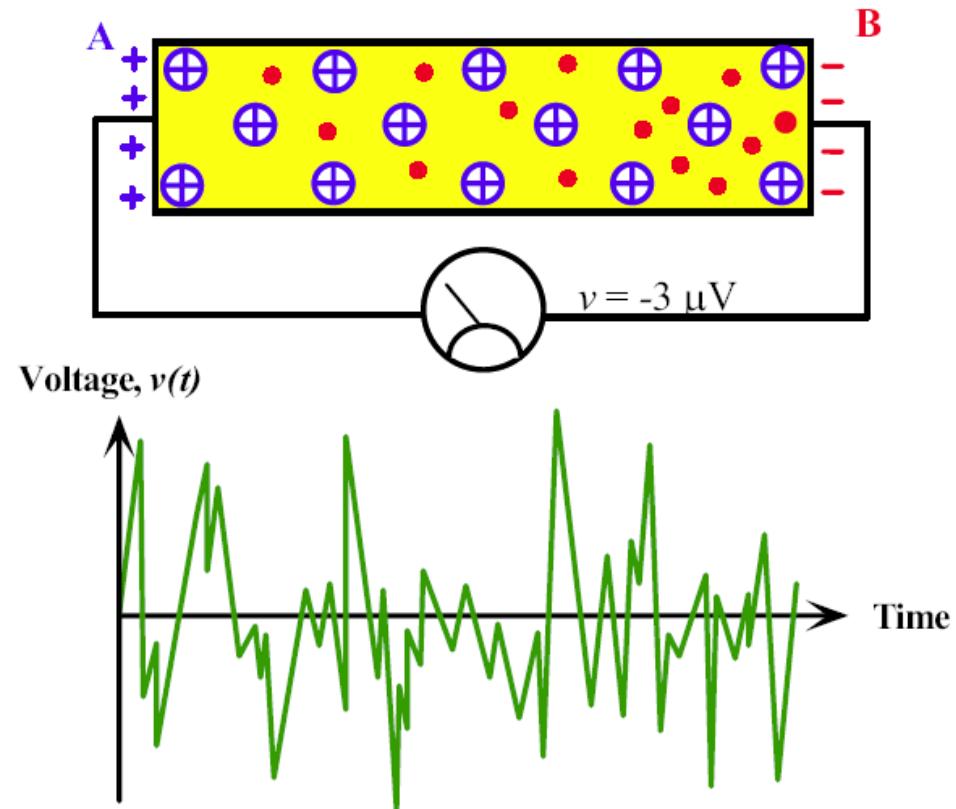
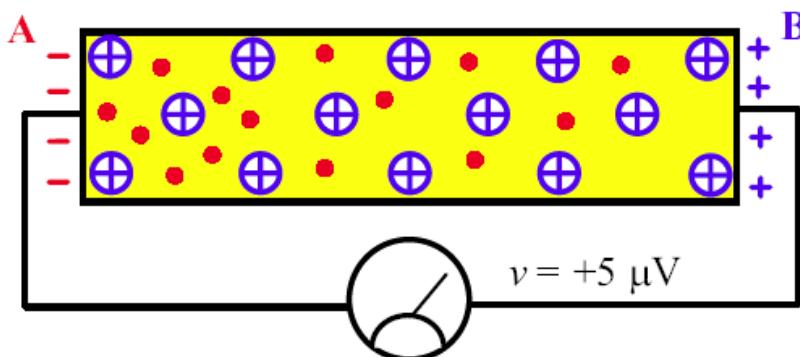
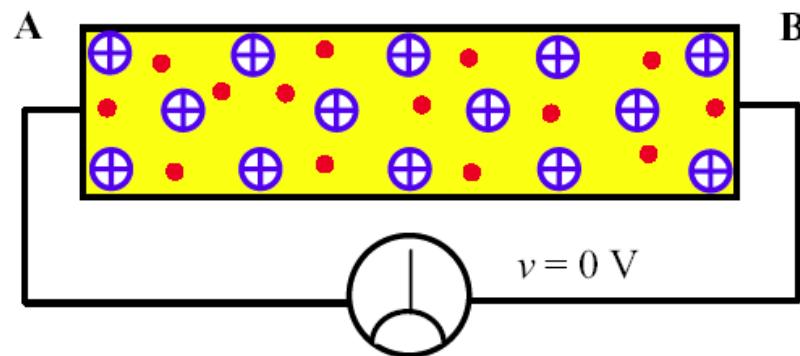


Fluctuations of a mass attached to a spring due to random bombardment of air molecules.

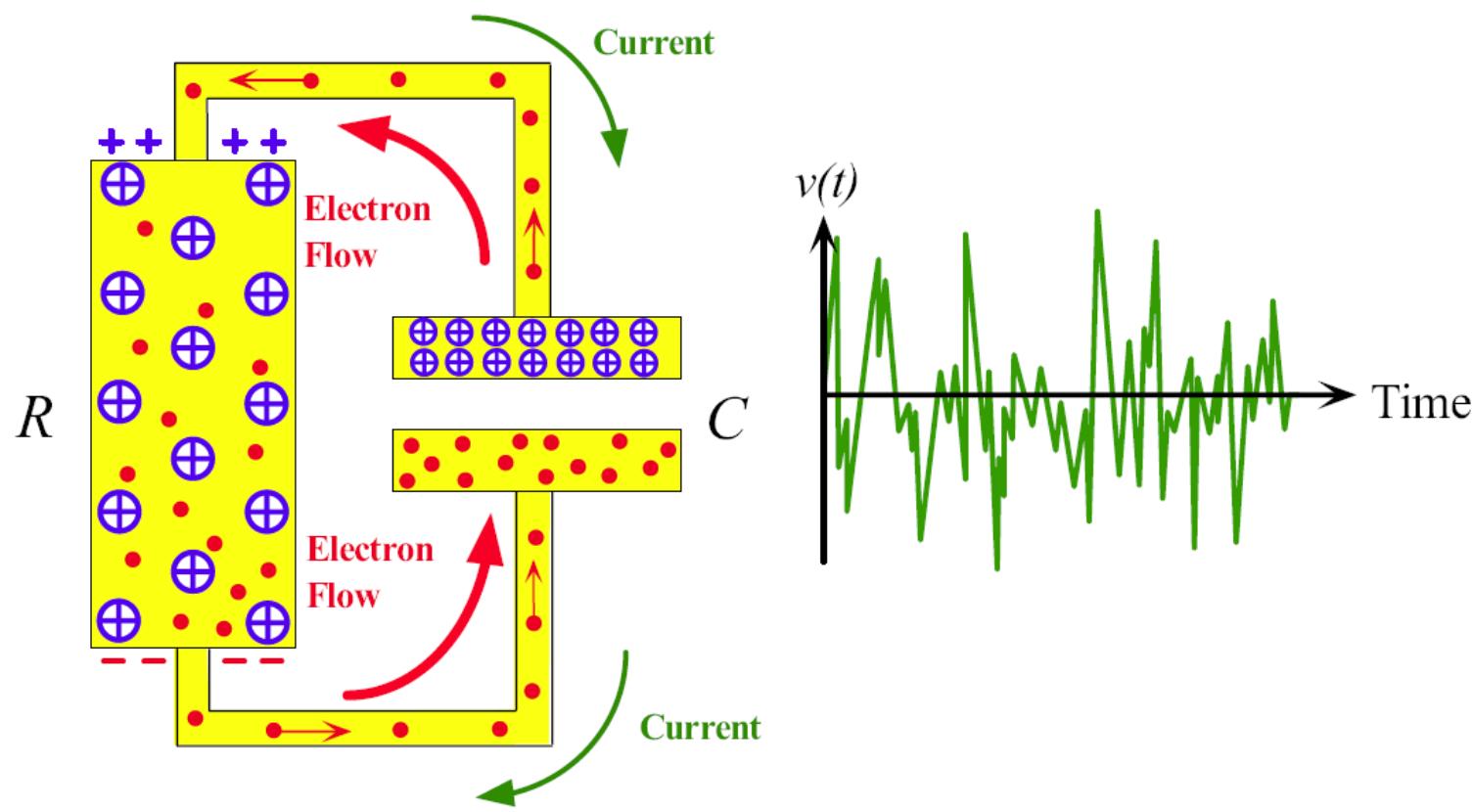
Root Mean Square Fluctuations of a Body Attached to a Spring of Stiffness K

$$(\Delta x)_{\text{rms}} = \sqrt{\frac{kT}{K}}$$

K = spring constant, T = temperature, $(\Delta x)_{\text{rms}}$ = rms value of the fluctuations of the mass about its equilibrium position.



Random motion of conduction electrons in a conductor results in electrical noise.

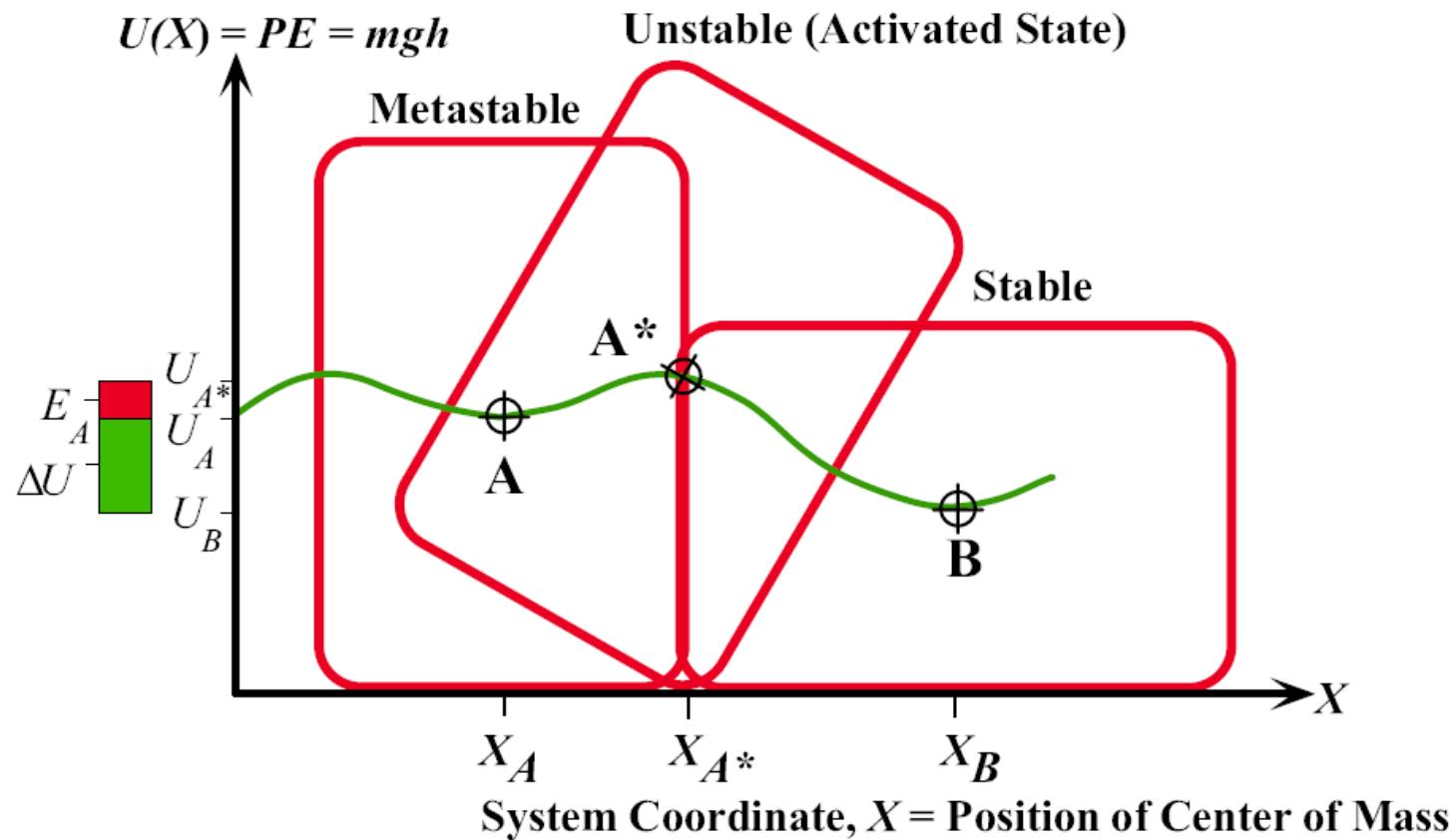


Charging and discharging of a capacitor by a conductor due to the random thermal motions of the conduction electrons.

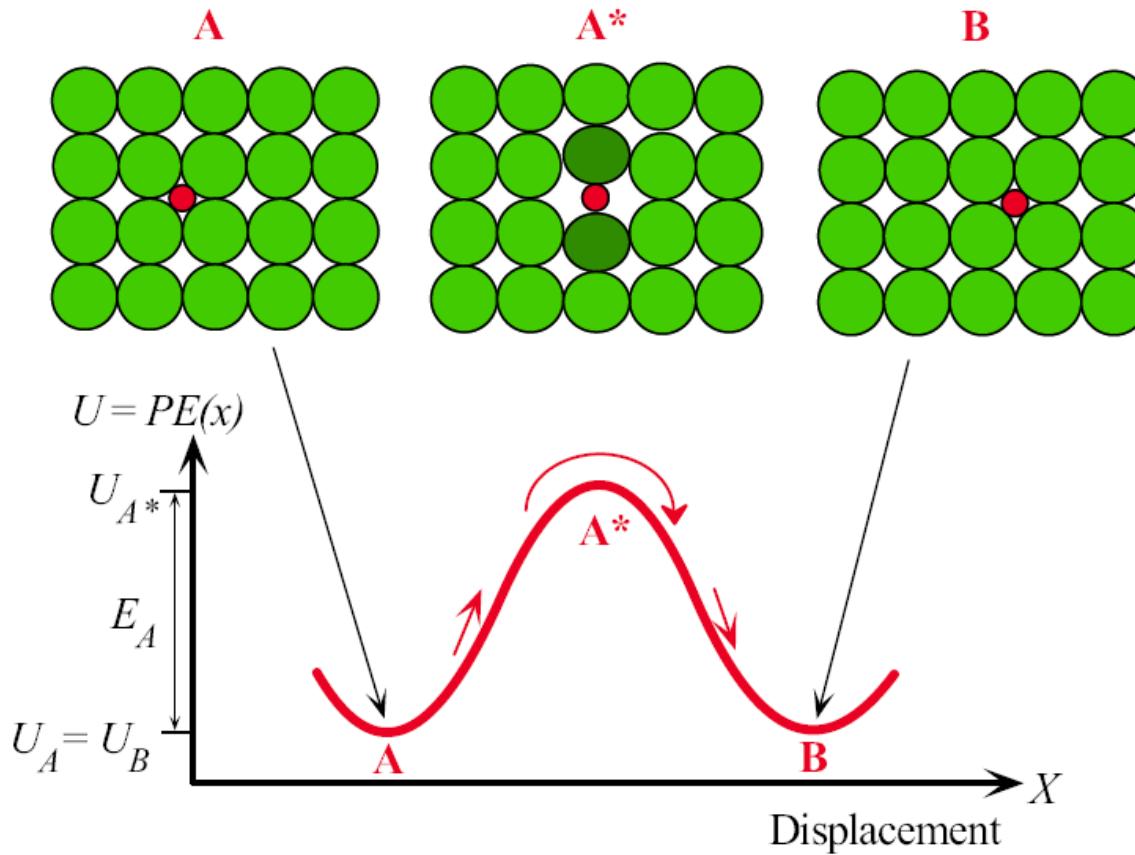
Root Mean Square Noise Voltage Across a Resistance

$$v_{\text{rms}} = \sqrt{4kTRB}$$

R = resistance, B = bandwidth of the electrical system in which noise is being measured, v_{rms} = root mean square noise voltage, k = Boltzmann constant, T = temperature



Tilting a filing cabinet from state A to its edge in state A^* requires an energy E_A . After reaching A^* , the cabinet spontaneously drops to the stable position B . PE of state B is lower than A and therefore state B is more stable than A .



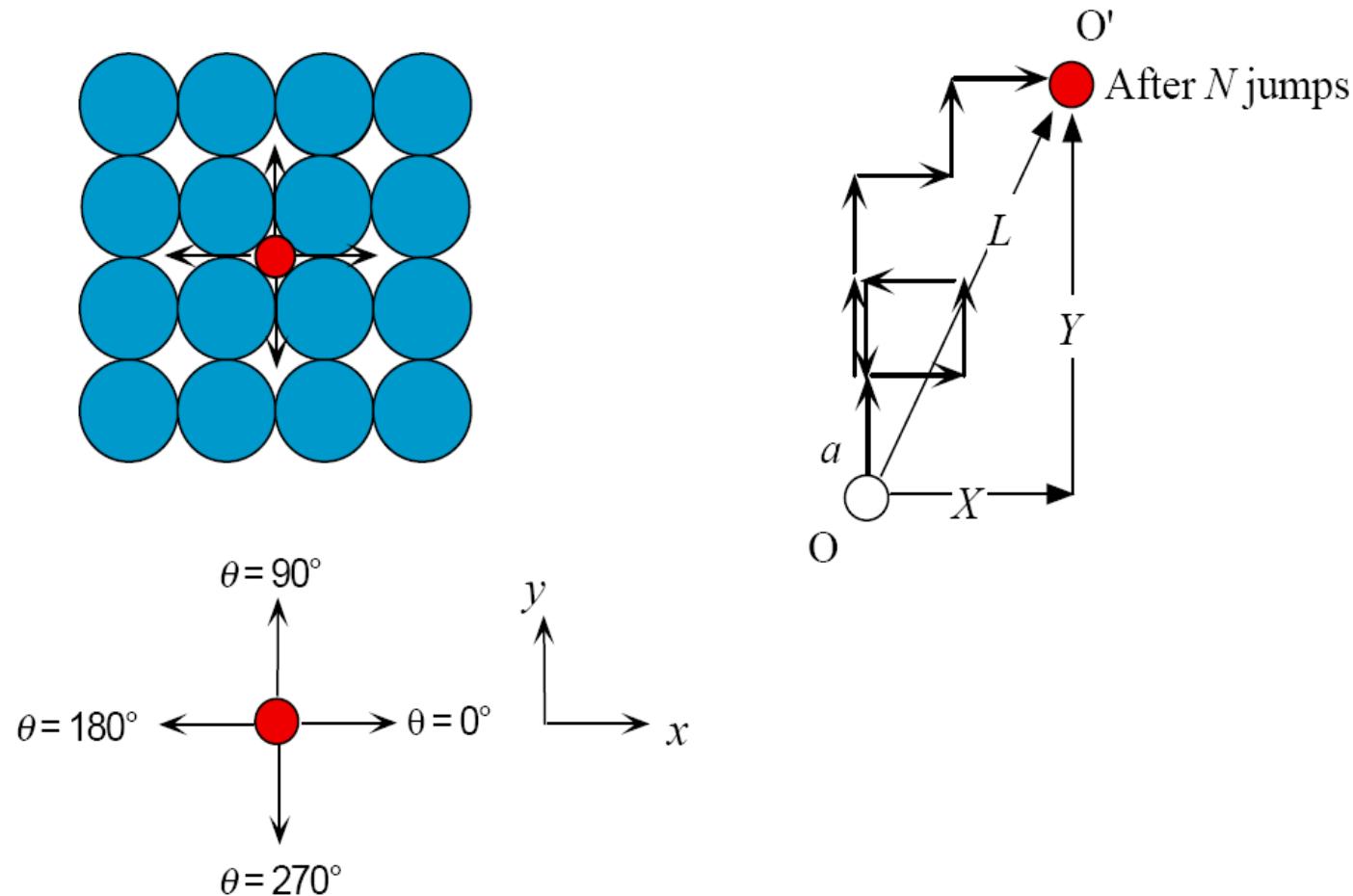
Diffusion of an interstitial impurity atom in a crystal from one void to a neighboring void. The impurity atom at position A must possess an energy E_A to push the host atoms away and move into the neighboring void at B.

Rate for a Thermally Activated Process

$$\vartheta = A v_o \exp(-E_A/kT)$$

$$E_A = U_{A^*} - U_A$$

ϑ = frequency of jumps, A = a dimensionless constant that has only a weak temperature dependence, v_o = vibrational frequency, E_A = activation energy, k = Boltzmann constant, T = temperature, U_{A^*} = potential energy at the activated state A^* , U_A = potential energy at state A .



An impurity atom has four site choices for diffusion to a neighboring interstitial interstitial vacancy. After N jumps, the impurity atom would have been displaced from the original position at O .

Mean Square Displacement

$$L^2 = a^2 \vartheta t = 2Dt$$

L = “distance” diffused after time t , a = closest void to void separation (jump distance), ϑ = frequency of jumps, t = time, D = diffusion coefficient

Diffusion coefficient is thermally activated

$$D = \frac{1}{2} a^2 \vartheta = D_o \exp\left(-\frac{E_A}{kT}\right)$$

D = diffusion coefficient, D_o = constant, E_A = activation energy, k = Boltzmann constant, T = temperature

Crystal Structures

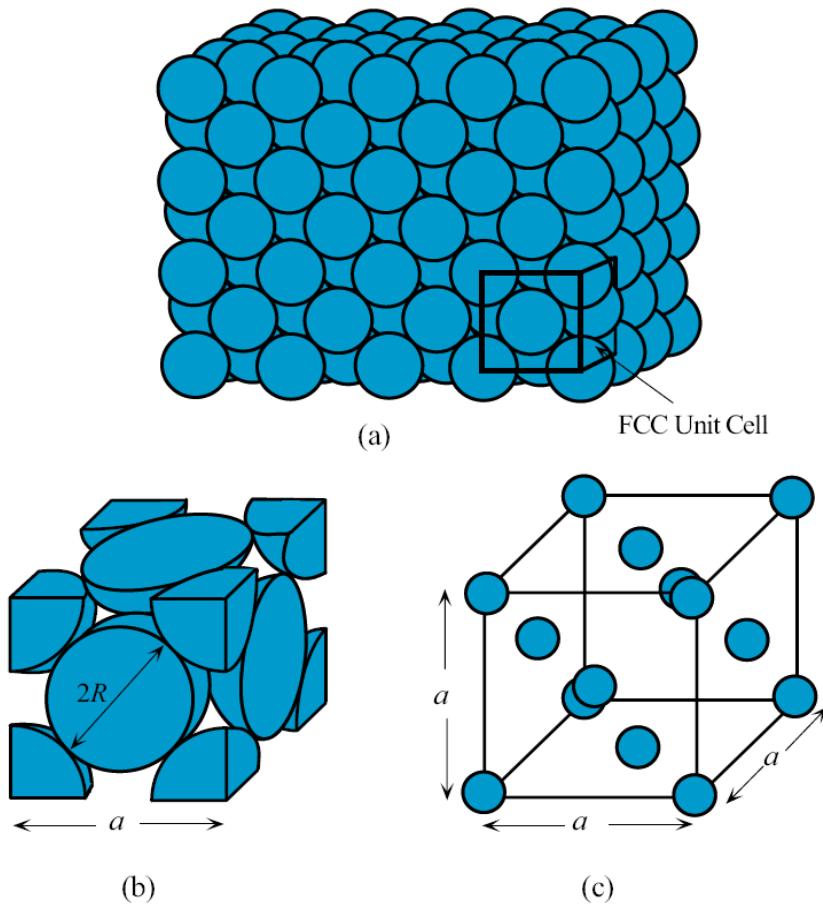


Cubic FeS_2 , iron sulfide, or pyrite, crystals. The crystals look brass-like yellow ("fool's gold").

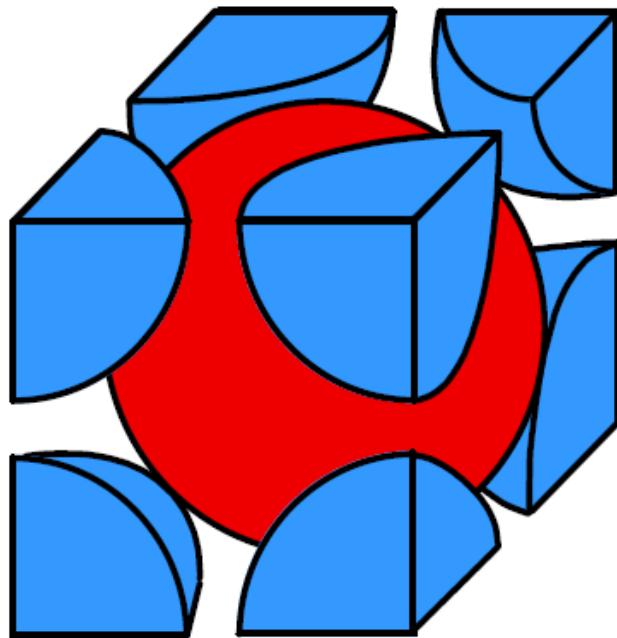
|SOURCE: Photo by SOK

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

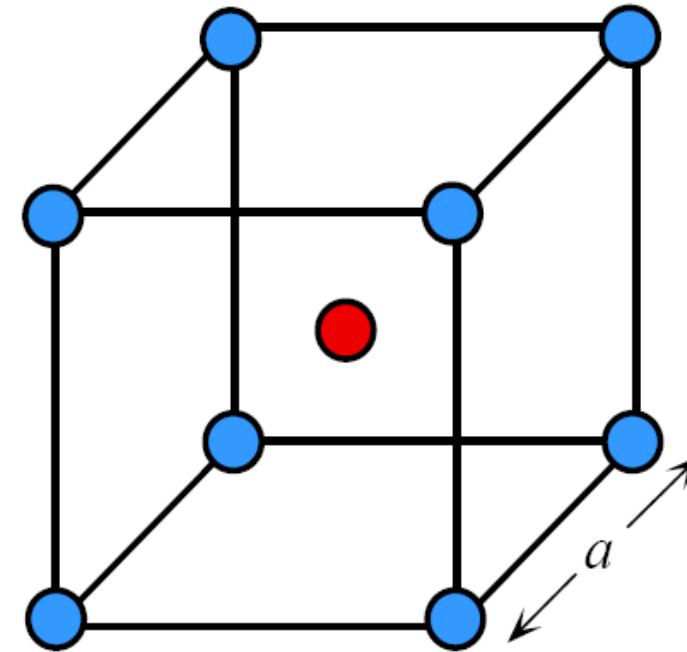
|SOURCE: Photo by SOK



- (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 °C), Ni, Pd, Pt, Rh.



a

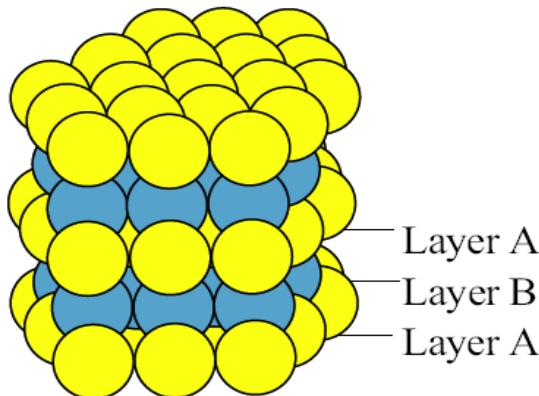


b

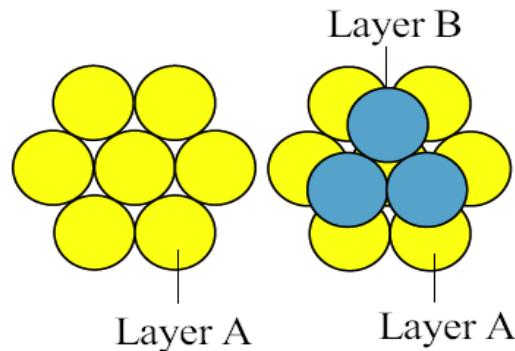
Example: Alkali metals (Li, Na, K, Rb), Cr, Mo, W, Mn, α -Fe (< 912 °C), β -Ti (> 882 °C)

Body centered cubic crystal (BCC) crystal structure.

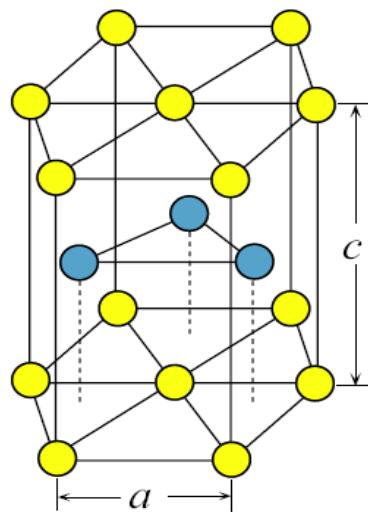
- (a) A BCC unit cell with closely packed hard spheres representing the Fe atoms.
- (b) A reduced-sphere unit cell.



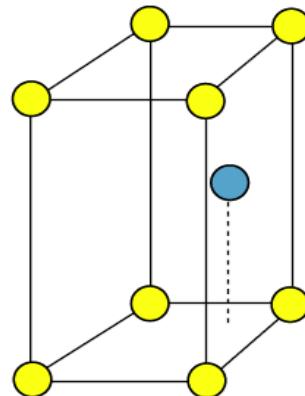
(a)



(b)



(c)



(d)

The Hexagonal Close Packed (HCP) Crystal Structure.

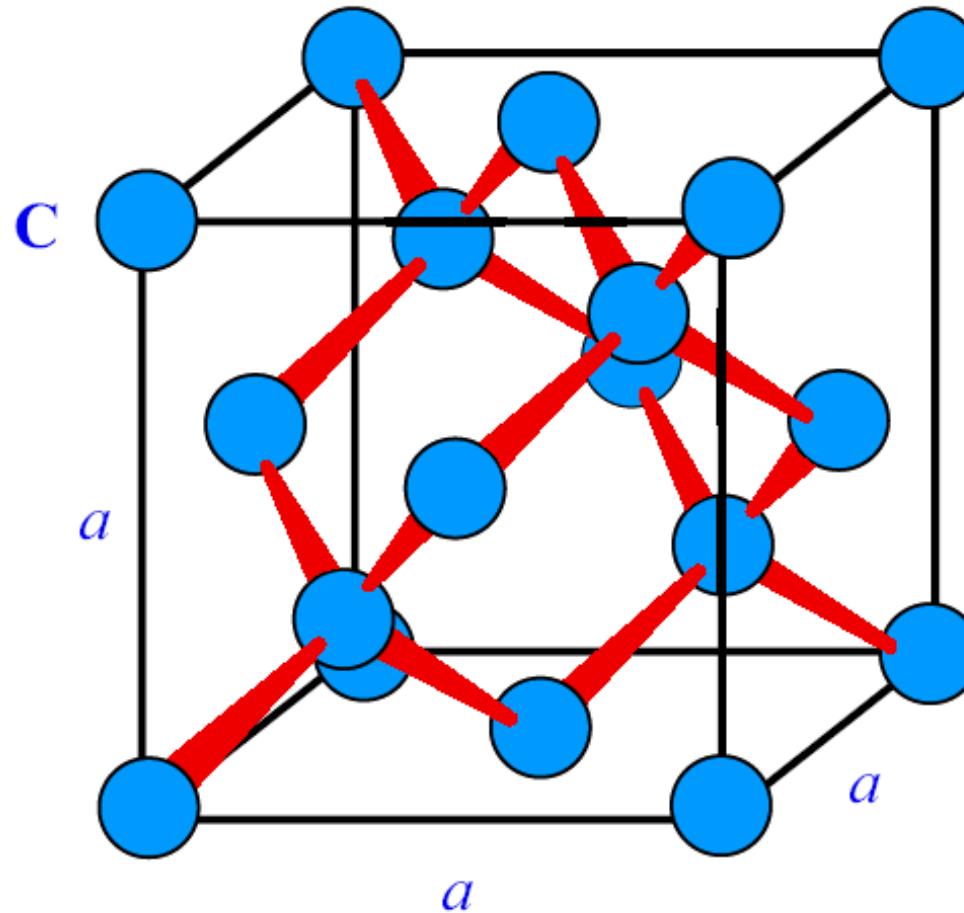
(a) The Hexagonal Close Packed (HCP) Structure. A collection of many Zn atoms. Color difference distinguishes layers (stacks).

(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



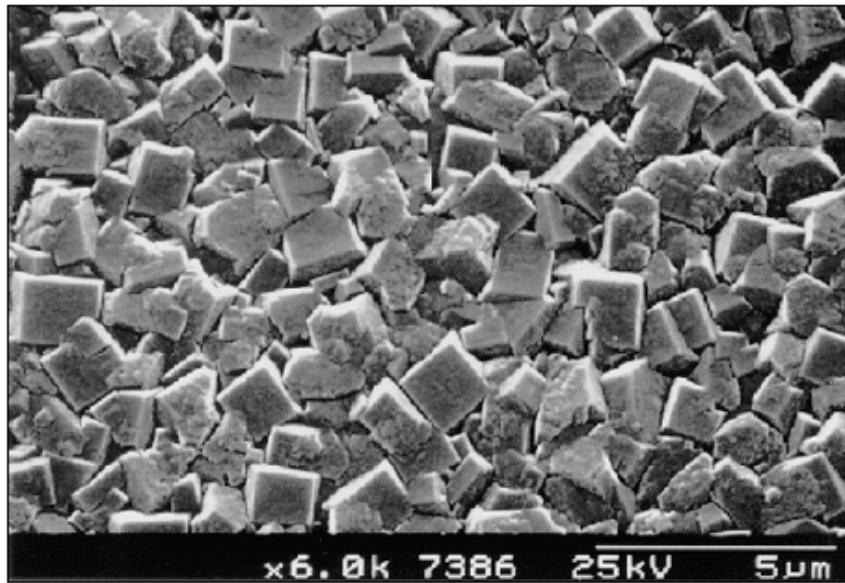
The diamond unit cell is cubic. The cell has eight atoms. Grey Sn (α -Sn) and the Elemental semiconductors Ge and Si have this crystal structure.

Silicon

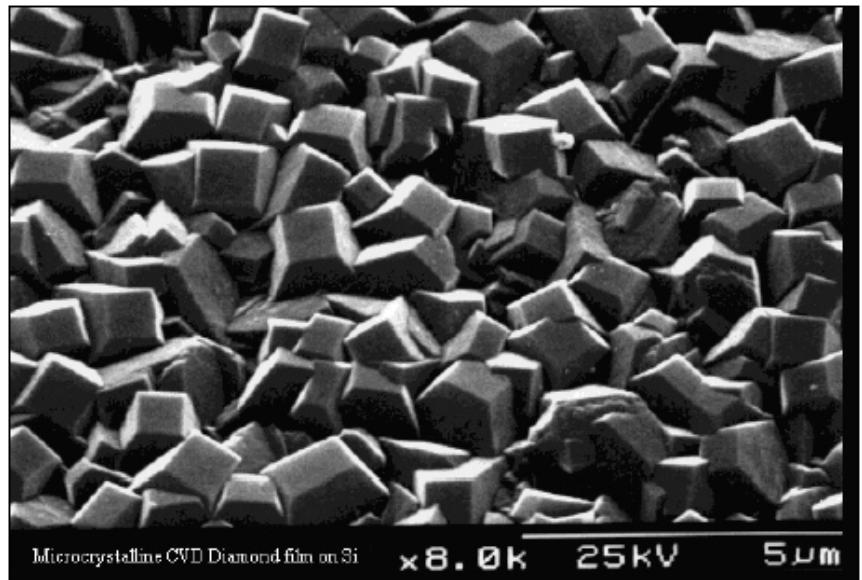


A silicon ingot is a single crystal of Si. Within the bulk of the crystal, the atoms are arranged on a well-defined periodical lattice. The crystal structure is that of **diamond**.

|Courtesy of MEMC, Electronic Materials Inc.



x6.0k 7386 25kV 5 μ m

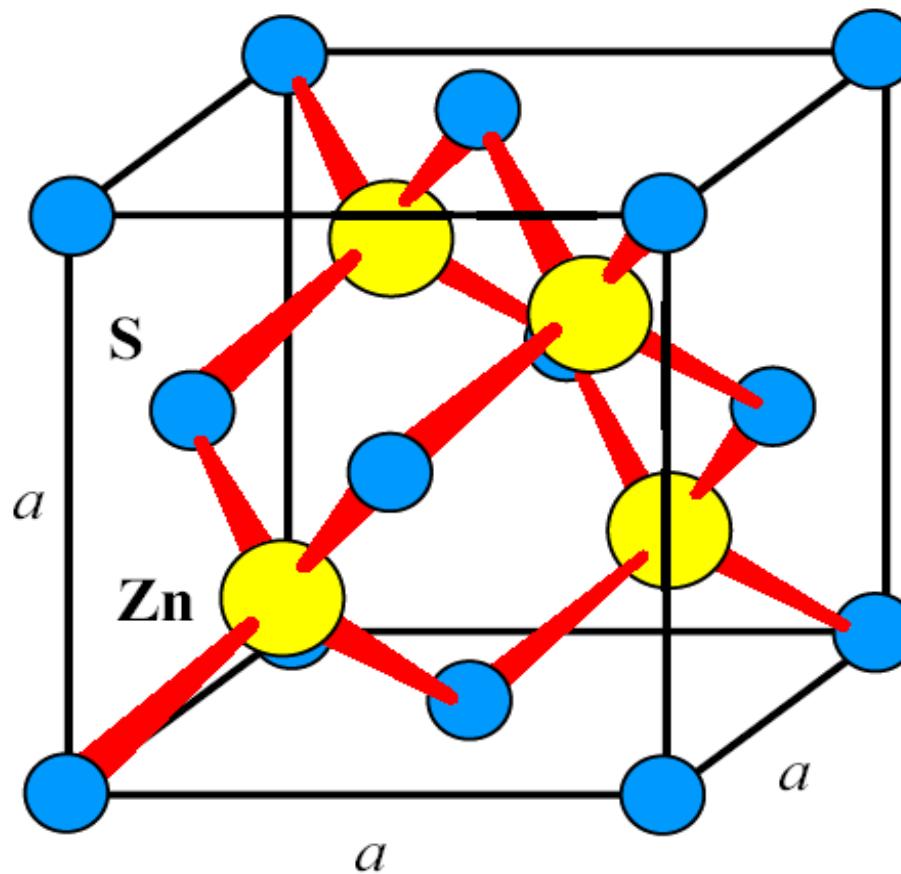


x8.0k 25kV 5 μ m
Microcrystalline CVD Diamond film on Si

| SOURCE: Courtesy of Dr. Paul May, The School of Chemistry, University of Bristol, England.

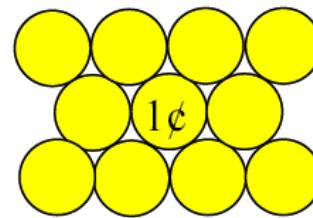
Left: A polycrystalline diamond film on the (100) surface of a single crystal silicon wafer. The film thickness is 6 microns and the SEM magnification is 6000.

Right: A 6-micron-thick CVD diamond film grown on a single crystal silicon wafer. SEM magnification is 8000.

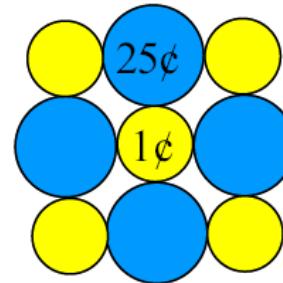


The Zinc blende (ZnS) cubic crystal structure. Many important compound crystal Structures have the zinc blende structure. Examples: AlAs, GaAs, Gap, GaSb, InAs, InP, InSb, ZnS, ZnTe.

Ratio of radii = 1

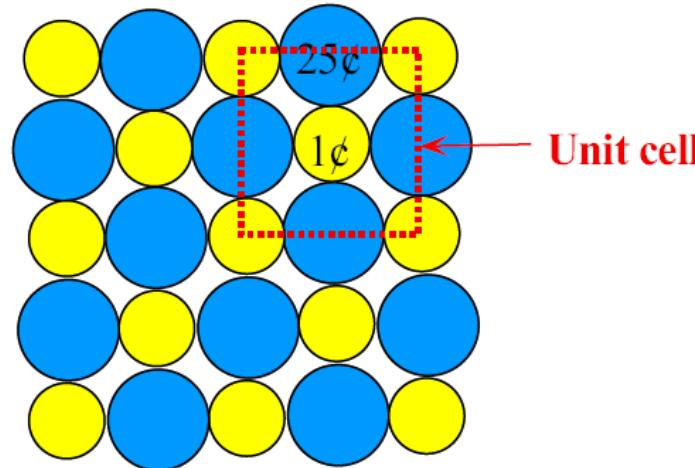


Ratio of radii = 0.75



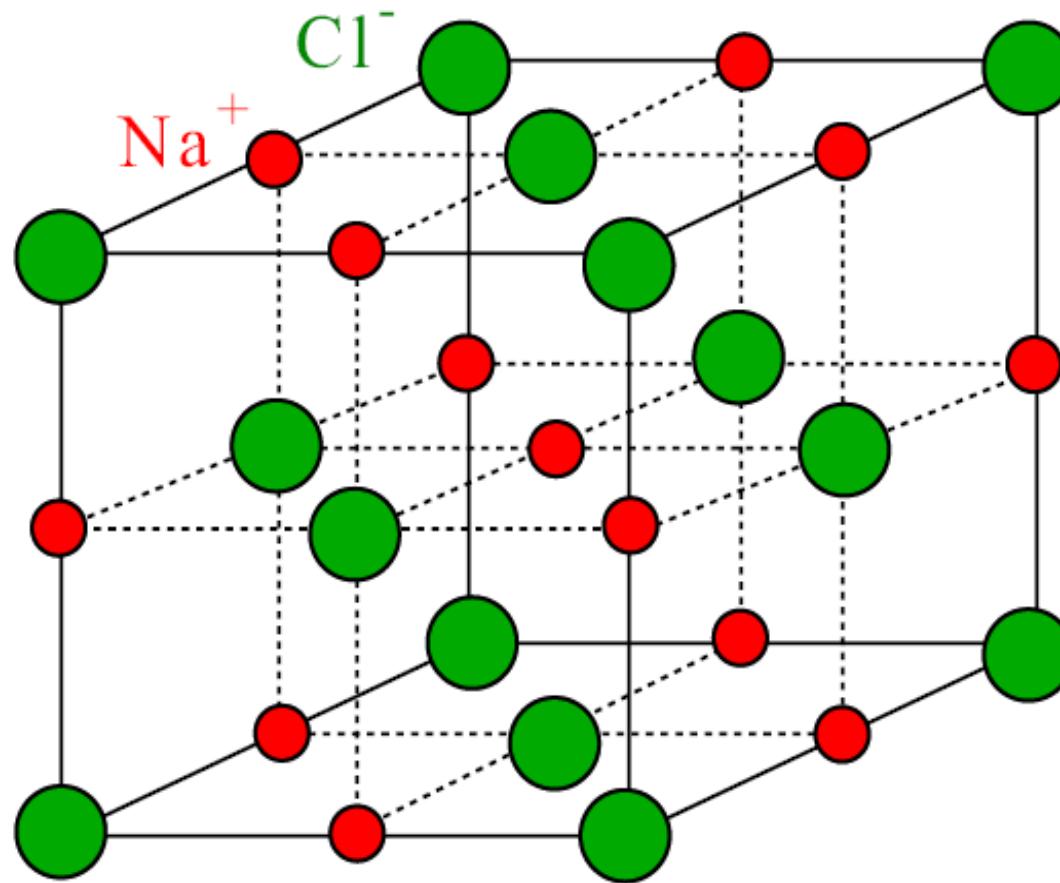
Nearest neighbors = 6

Nearest neighbors = 4



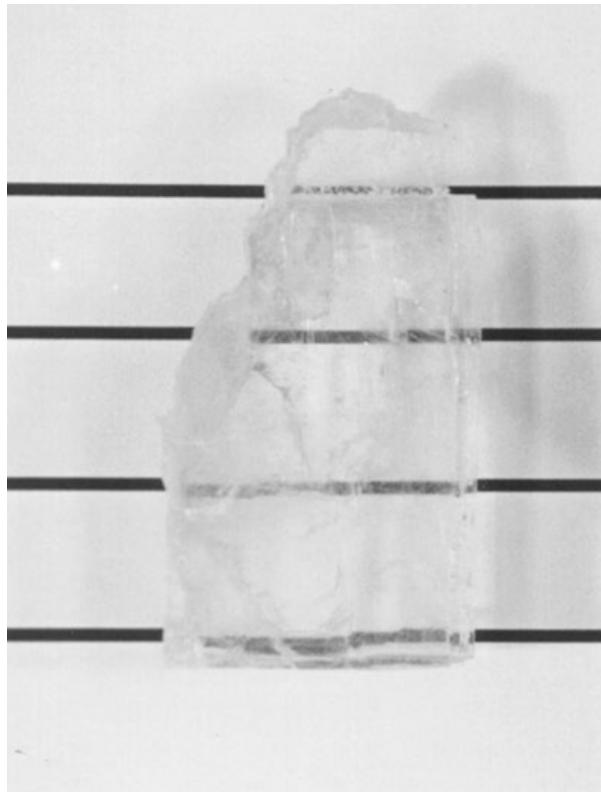
A two-dimensional crystal of pennies and quarters

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

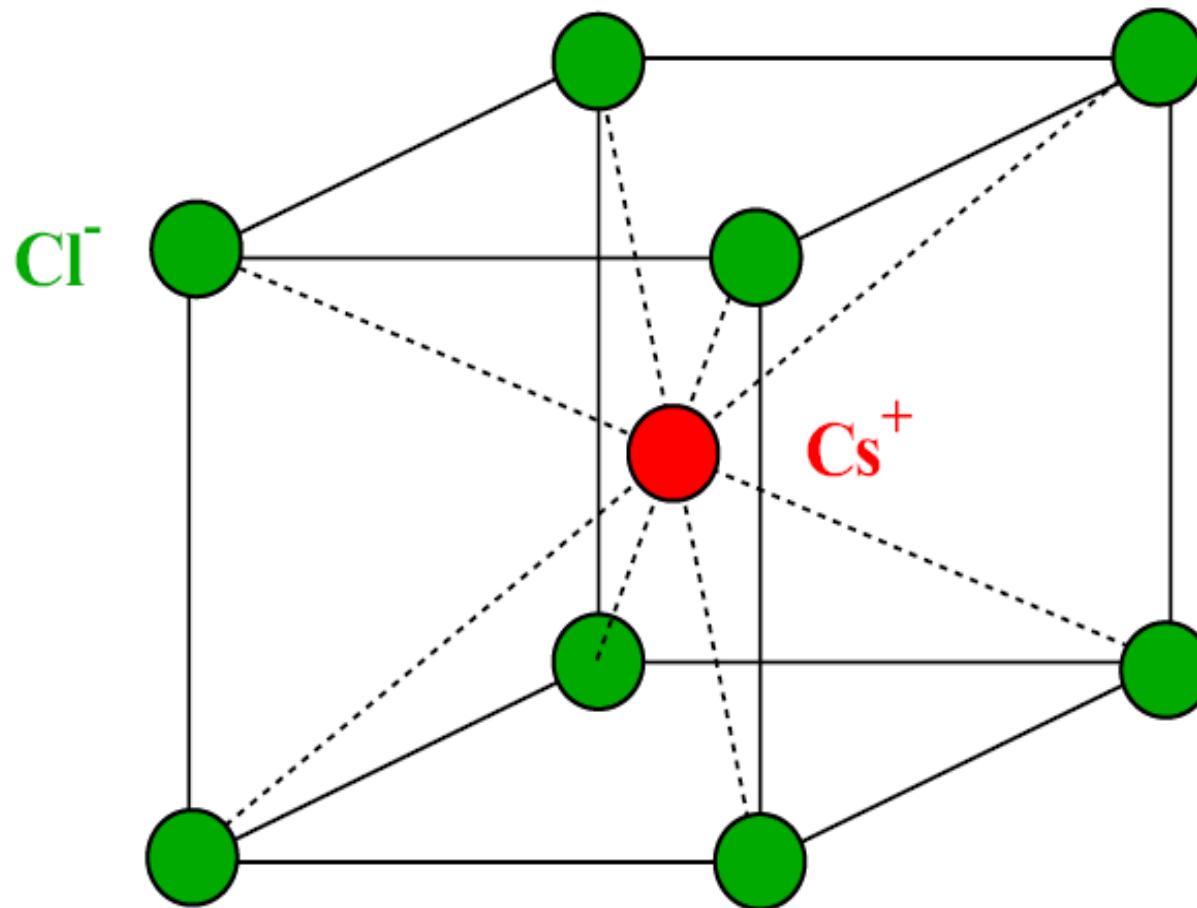


A possible reduced sphere unit cell for the NaCl (rock salt) crystal. An alternative Unit cell may have Na^+ and Cl^- interchanged. Examples: AgCl, CaO, CsF, LiF, LiCl, NaF, NaCl, KF, KCl, MgO.

NaCl or halite crystals are transparent



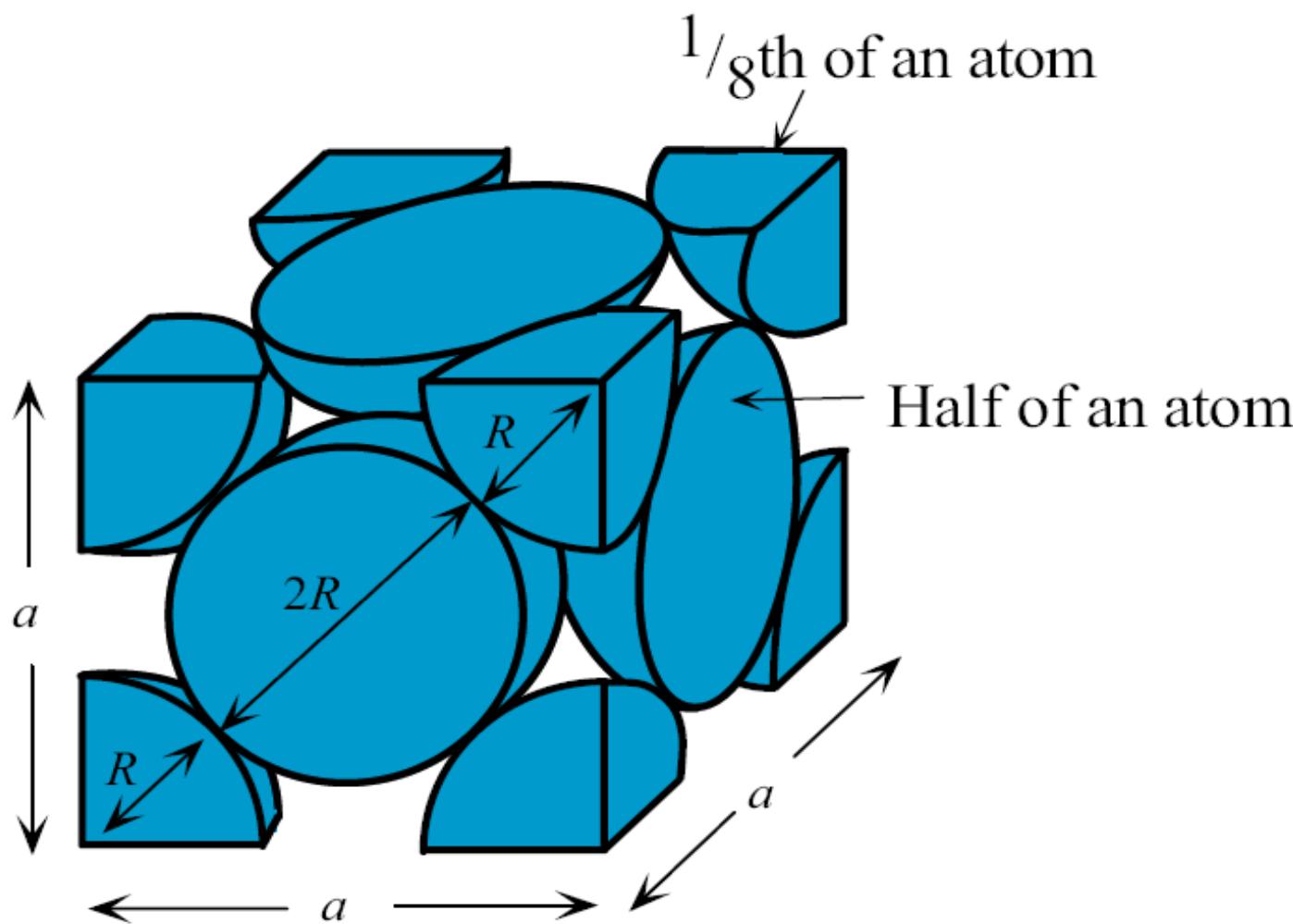
|SOURCE: Photo by SOK



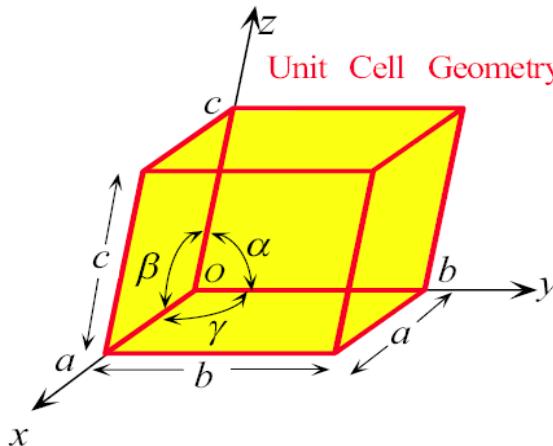
A possible reduced sphere unit cell for the CsCl crystal. An alternative unit cell may have Cs^+ and Cl^- interchanged. Examples: CsCl , CsBr , CsI , TlCl , TlBr , TlI .

Table 1.3 Properties of some important crystal structures

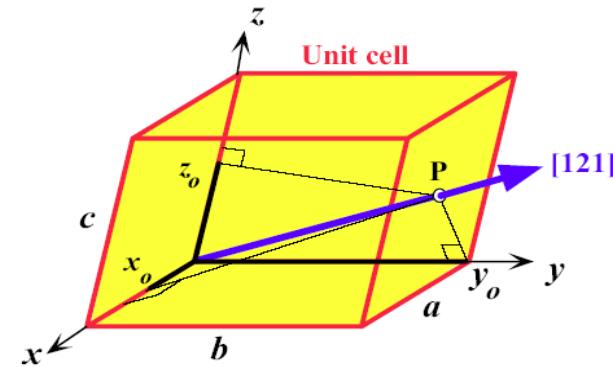
Crystal Structure	a and R (R is the Radius of the Atom)	Coordination Number (CN)	Number of Atoms per Unit Cell	Atomic Packing Factor	Examples
Simple cubic	$a = 2R$	6	1	0.52	No metals (Except Po)
BCC	$a = \frac{4R}{\sqrt{3}}$	8	2	0.68	Many metals: α -Fe, Cr, Mo, W
FCC	$a = \frac{4R}{\sqrt{2}}$	12	4	0.74	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



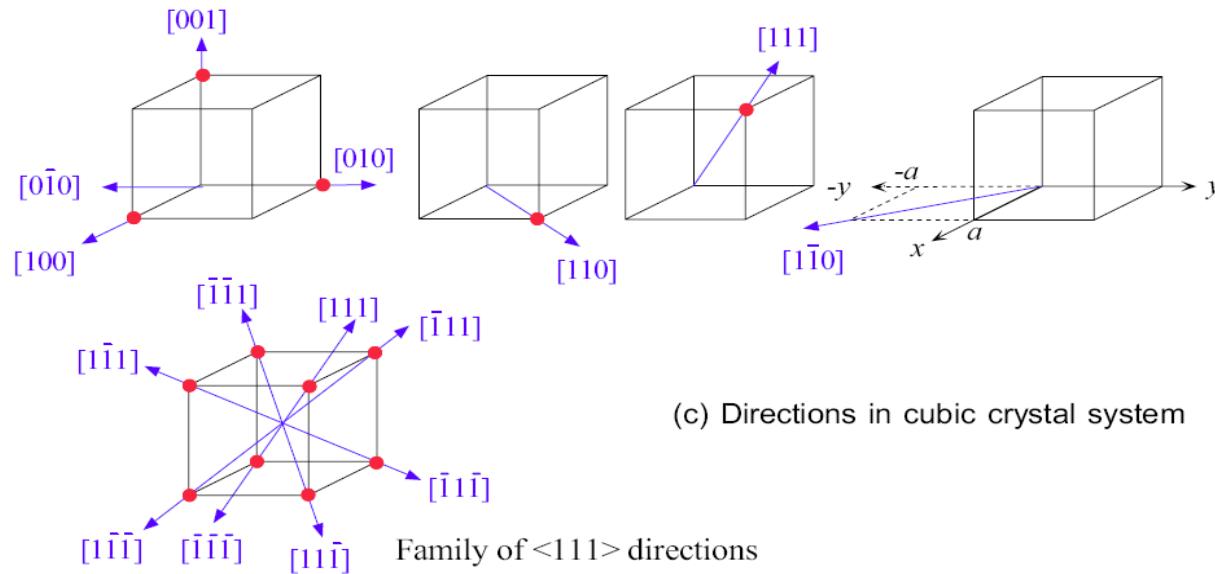
The FCC unit cell. The atomic radius is R and the lattice parameter is a



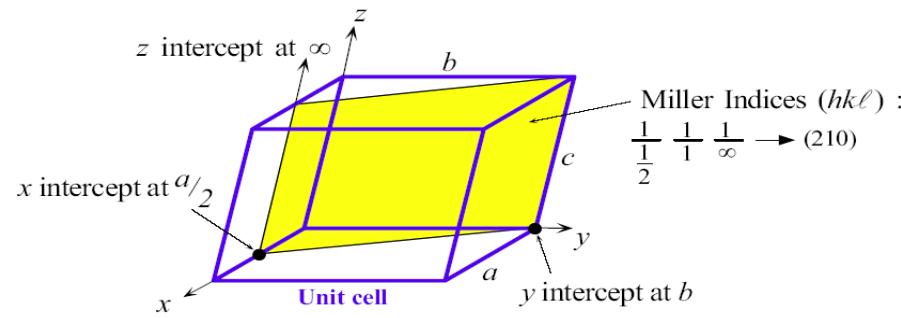
(a) A parallelepiped is chosen to describe geometry of a unit cell. We line the x , y and z axes with the edges of the parallelepiped taking lower-left rear corner as the origin



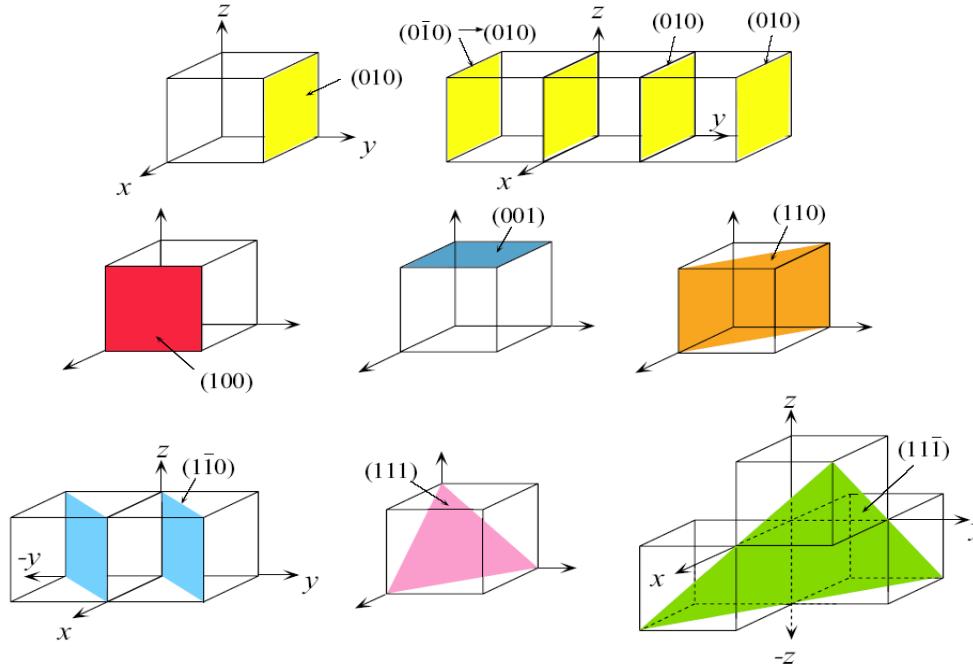
(b) Identification of a direction in a crystal



(c) Directions in cubic crystal system

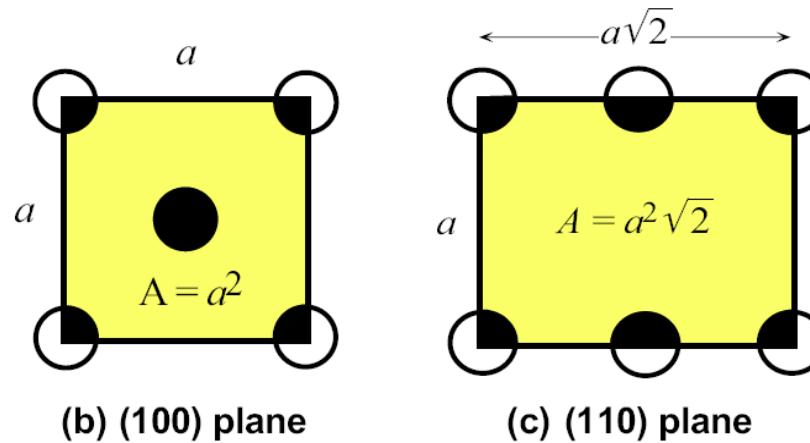
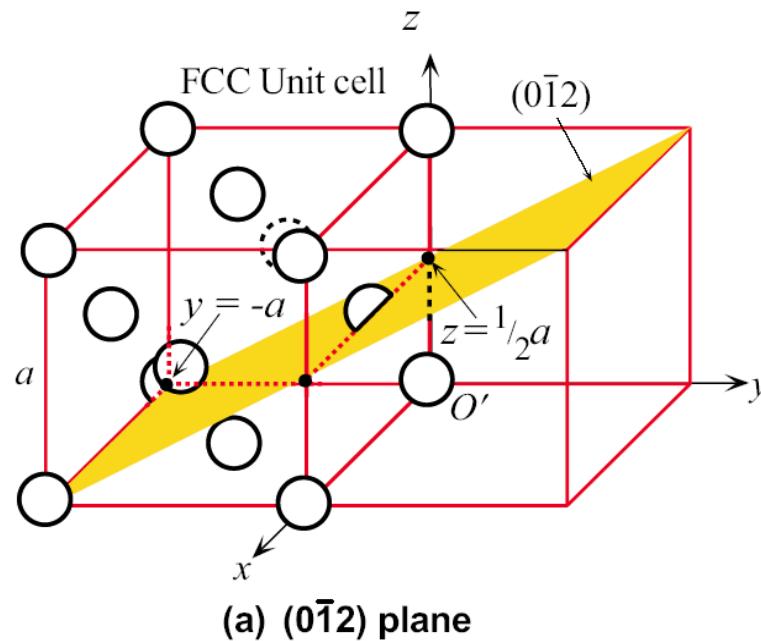


(a) Identification of a plane in a crystal

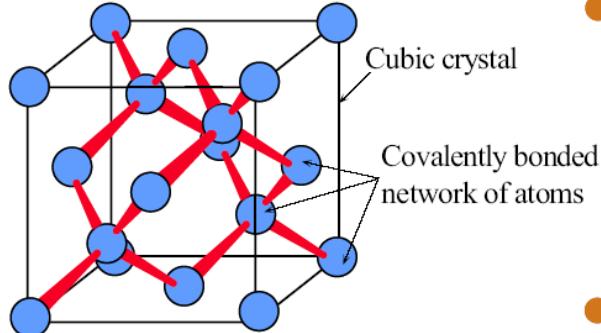


(b) Various planes in the cubic lattice

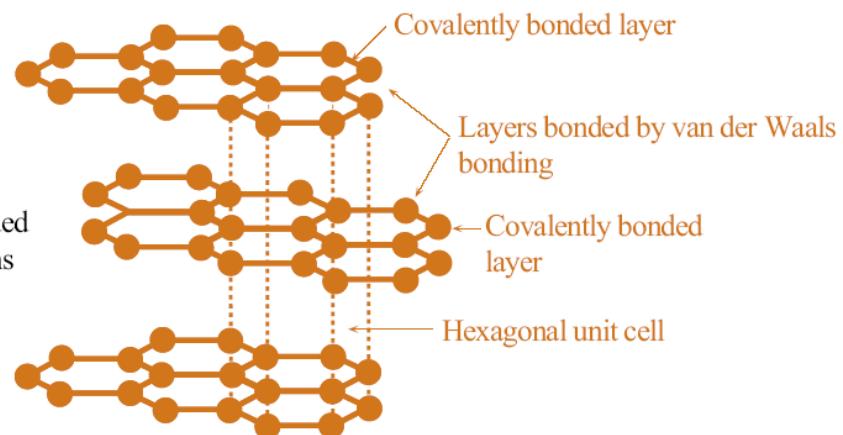
Labeling of crystal planes and typical examples in the cubic lattice



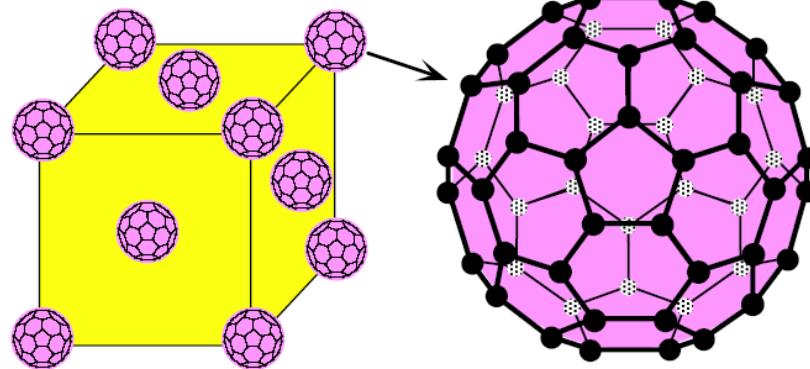
The (012) plane and planar concentrations in an FCC crystal.



(a) Diamond unit cell



(b) Graphite



The FCC unit cell of the Buckminsterfullerene crystal. Each lattice point has a C_{60} molecule

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

(c) Buckminsterfullerene

Three allotropes of carbon

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

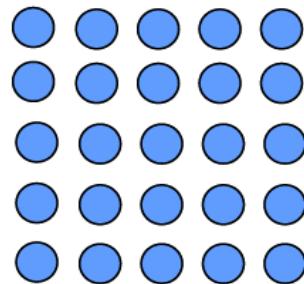
E_v = vacancy formation energy

k = Boltzmann constant

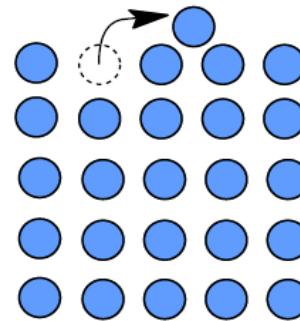
T = temperature (K)

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

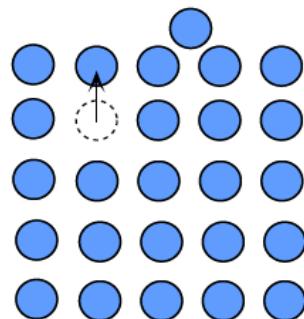
	Graphite	Diamond	Buckminsterfullerene Crystal
Structure	Covalent bonding within layers. Van der Waals bonding between layers. Hexagonal unit cell.	Covalently bonded network. Diamond crystal structure.	Covalently bonded C_{60} spheroidal molecules held in an FCC crystal structure by van der Waals bonding.
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.



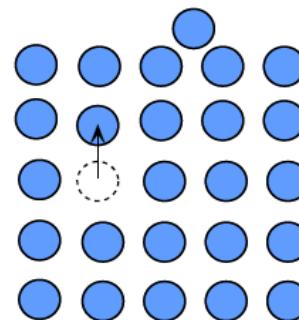
(a) Perfect crystal without vacancies



(b) An energetic atom at the surface breaks bonds and jumps on to a new adjoining position on the surface. This leaves behind a vacancy.

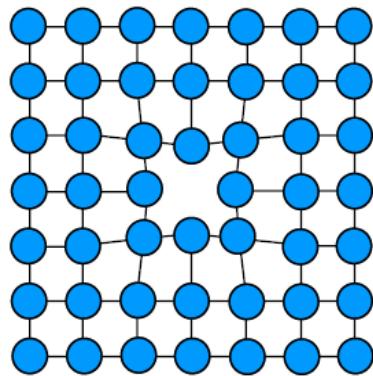


(c) An atom in the bulk diffuses to fill the vacancy thereby displacing the vacancy towards the bulk.

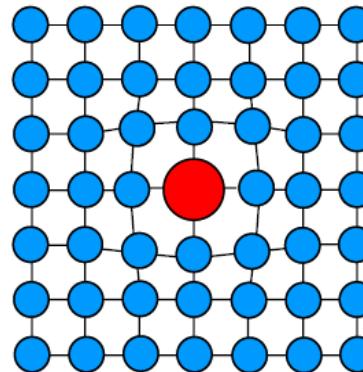


(d) Atomic diffusions cause the vacancy to diffuse into the bulk.

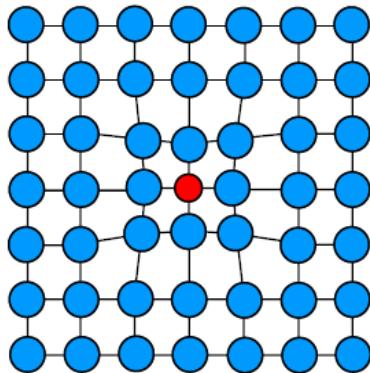
Generation of a vacancy by the diffusion of atom to the surface and the subsequent diffusion of the vacancy into the bulk.



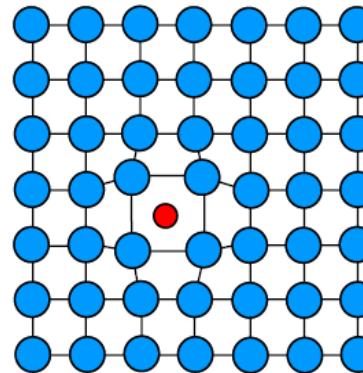
(a) A vacancy in the crystal.



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

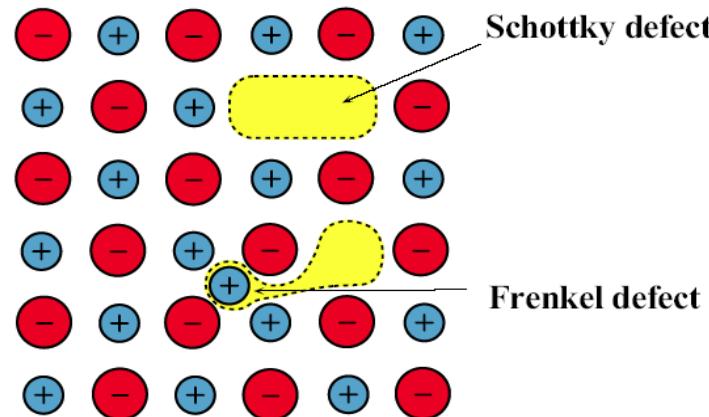


(c) A substitutional impurity in the crystal. The impurity atom is smaller than the host atom.

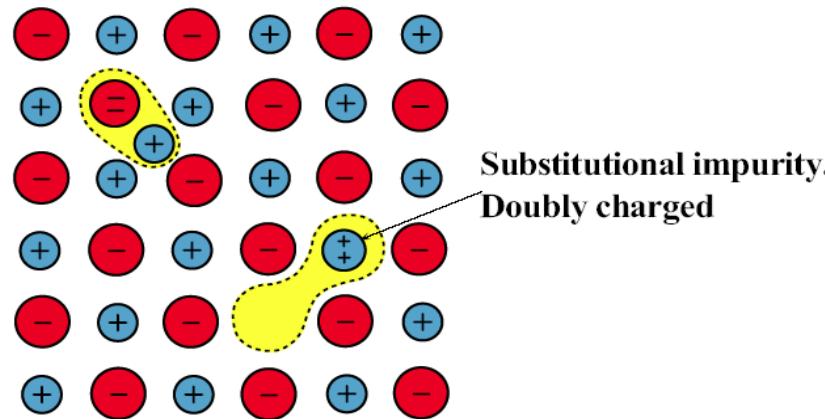


(d) An interstitial impurity in the crystal. It occupies an empty space between host atoms.

Point defects in the crystal structure. The regions around the point defect become distorted; the lattice becomes strained.

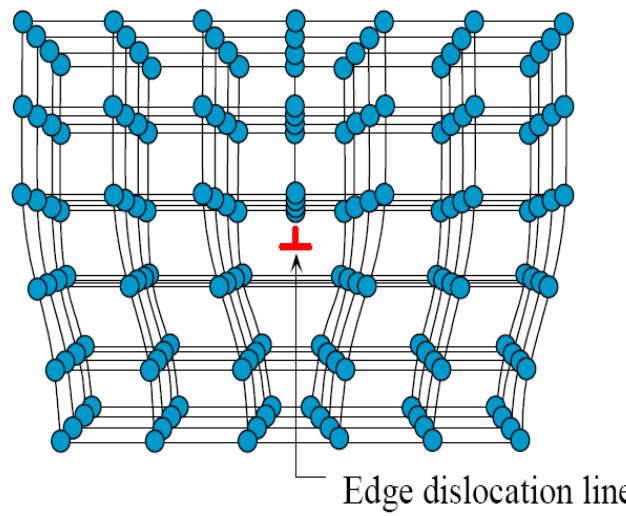


(a) Schottky and Frenkel defects in an ionic crystal.

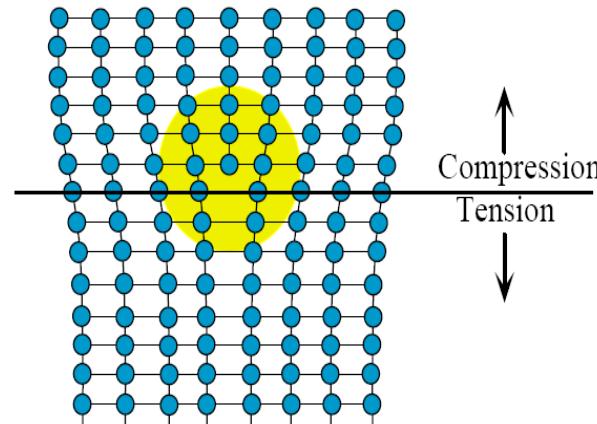


(b) Two possible imperfections caused by ionized substitutional impurity atoms in an ionic crystal.

Point defects in ionic crystals

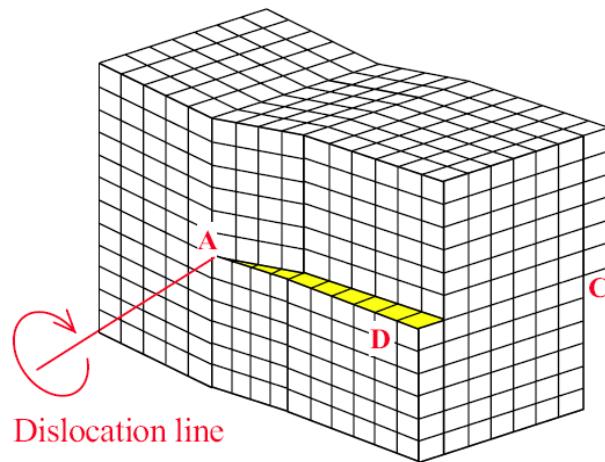


(a) Dislocation is a line defect. The dislocation shown runs into the paper.

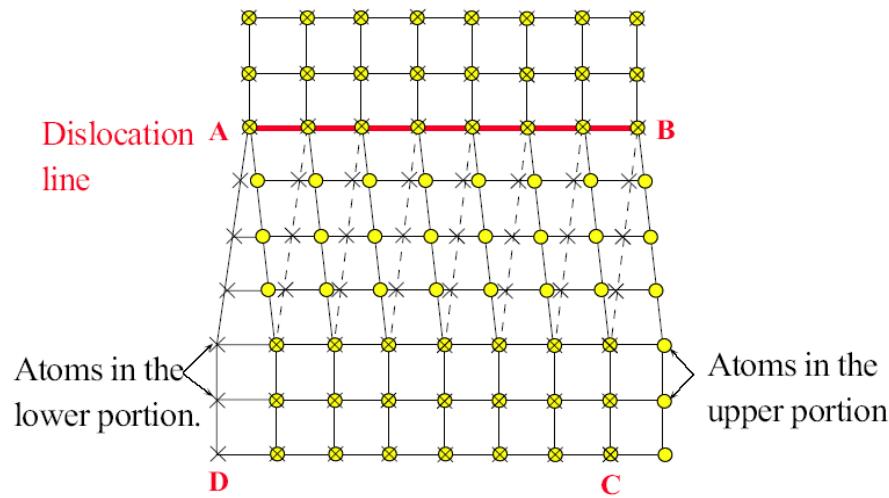


(b) Around the dislocation there is a strain field as the atomic bonds have been compressed above and stretched below the dislocation line

Dislocation in a crystal is a line defect which is accompanied by lattice distortion and hence a lattice strain around it

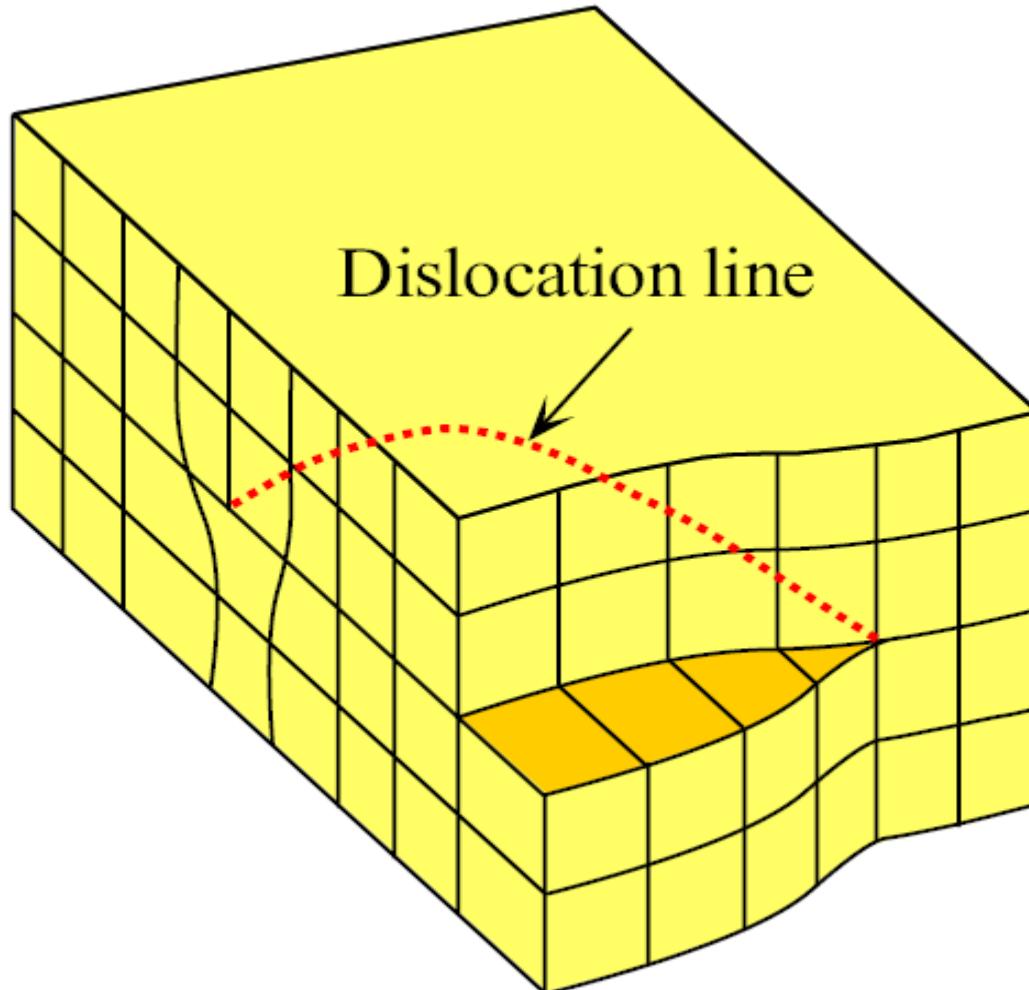


(a) A screw dislocation in a crystal.

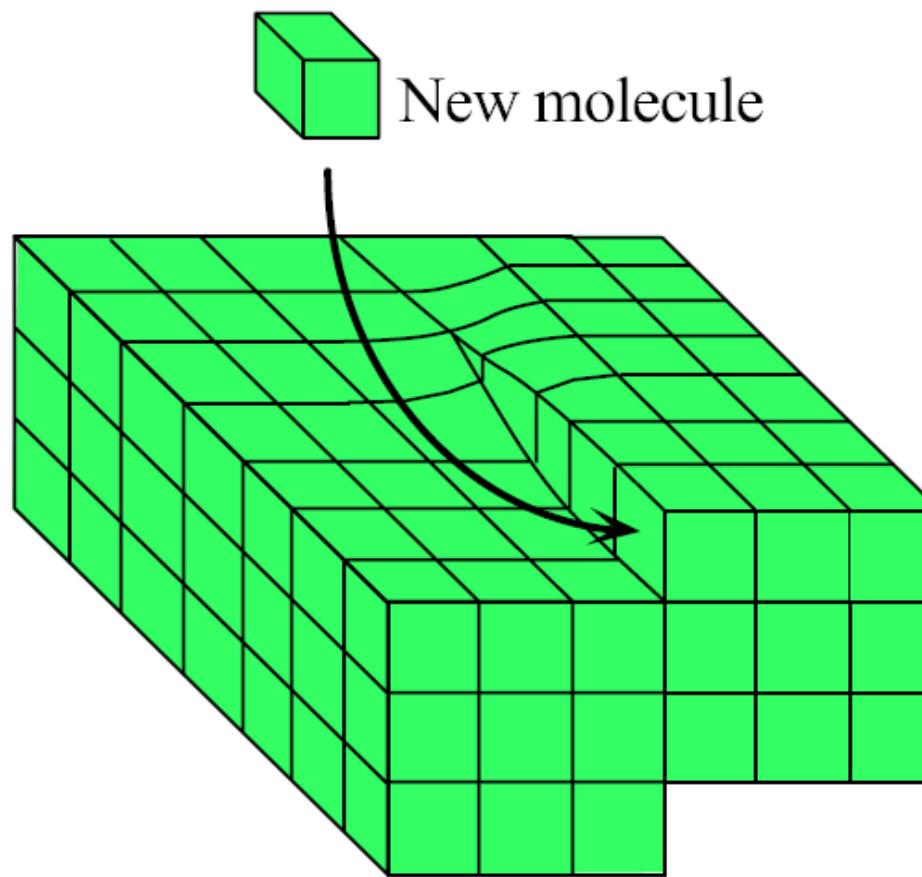


(b) The screw dislocation in (a) as viewed from above.

A screw dislocation involves shearing one portion of a perfect crystal with respect to another portion on one side of a line (AB)



A mixed dislocation

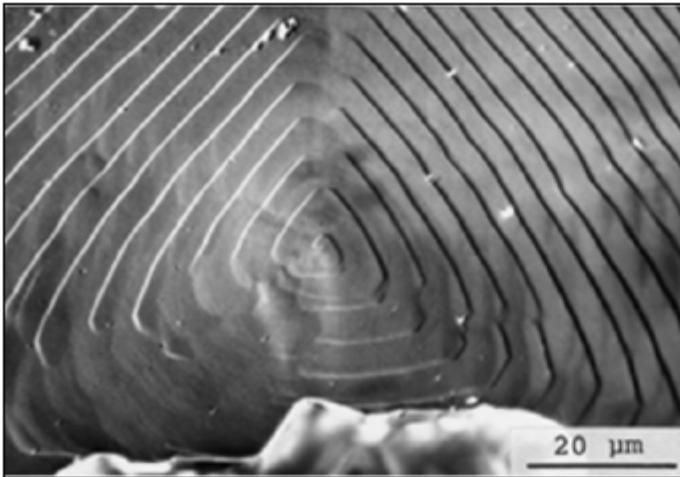


Screw dislocation aids crystal growth because the newly arriving atom can attach to two or three atoms instead of one atom and thereby form more bonds.



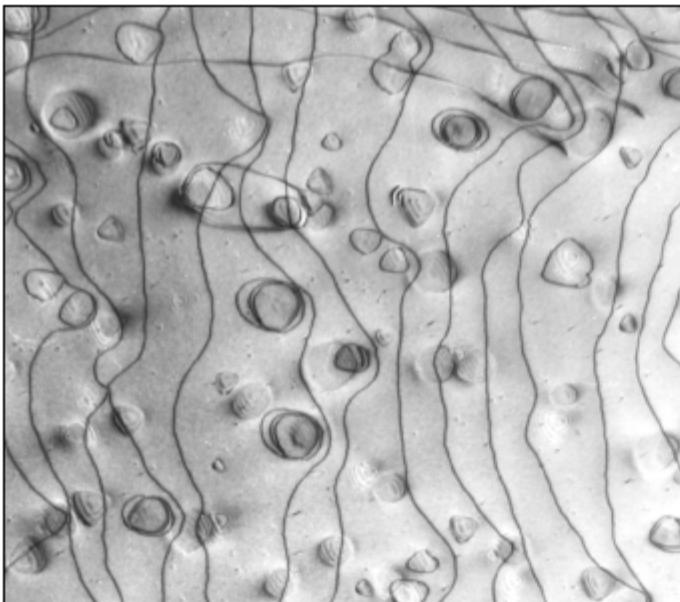
Growth spiral on the surface of a polypropylene crystal due to screw dislocation aided crystal growth.

| SOURCE: Photo by Phillip Geil, Courtesy of Case Western Reserve University.



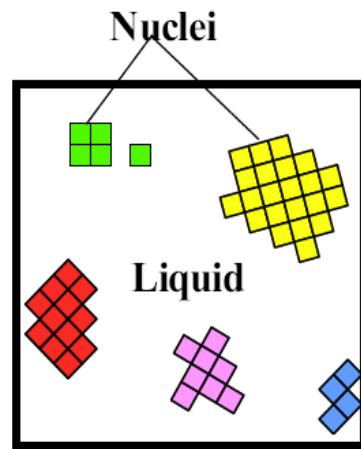
The photograph of the surface of a synthetic diamond grown on the (111) surface of natural diamond from sodium carbonate solvent at 5.5 GPa and 1600 °C.

SOURCE: Courtesy of Dr. Hisao Kanda, National Institute for Materials Science, Ibaraki, Japan.

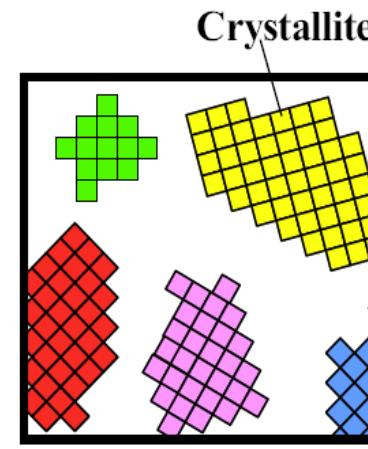


Dislocations can be seen by examining a thin slice of the sample under a transmission electron microscope (TEM). They appear as dark lines and loops as shown here in a Ni-Si alloy single crystal. The loop dislocations are around Ni₃Si particles inside the crystal. The sample had been mechanically deformed, which generates dislocations.

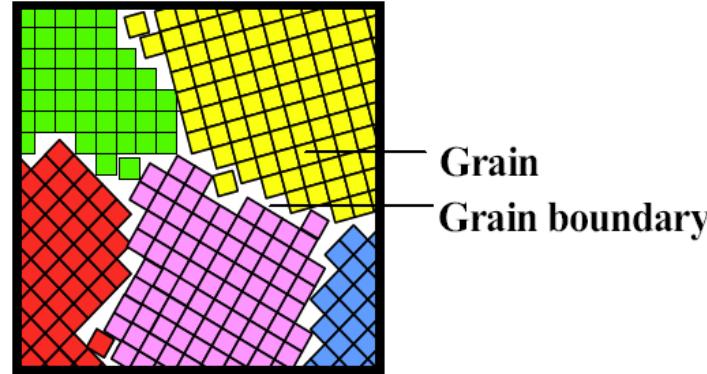
SOURCE: Courtesy of Professor John Humphreys, UMIST, England. (J. Humphreys and V. Ramaswamy in *High Voltage Electron Microscopy*, ed. P. R. Swann. C. J. Humphreys and M. J. Goringe, New York: Academic Press, 1974, p. 26.)



(a)

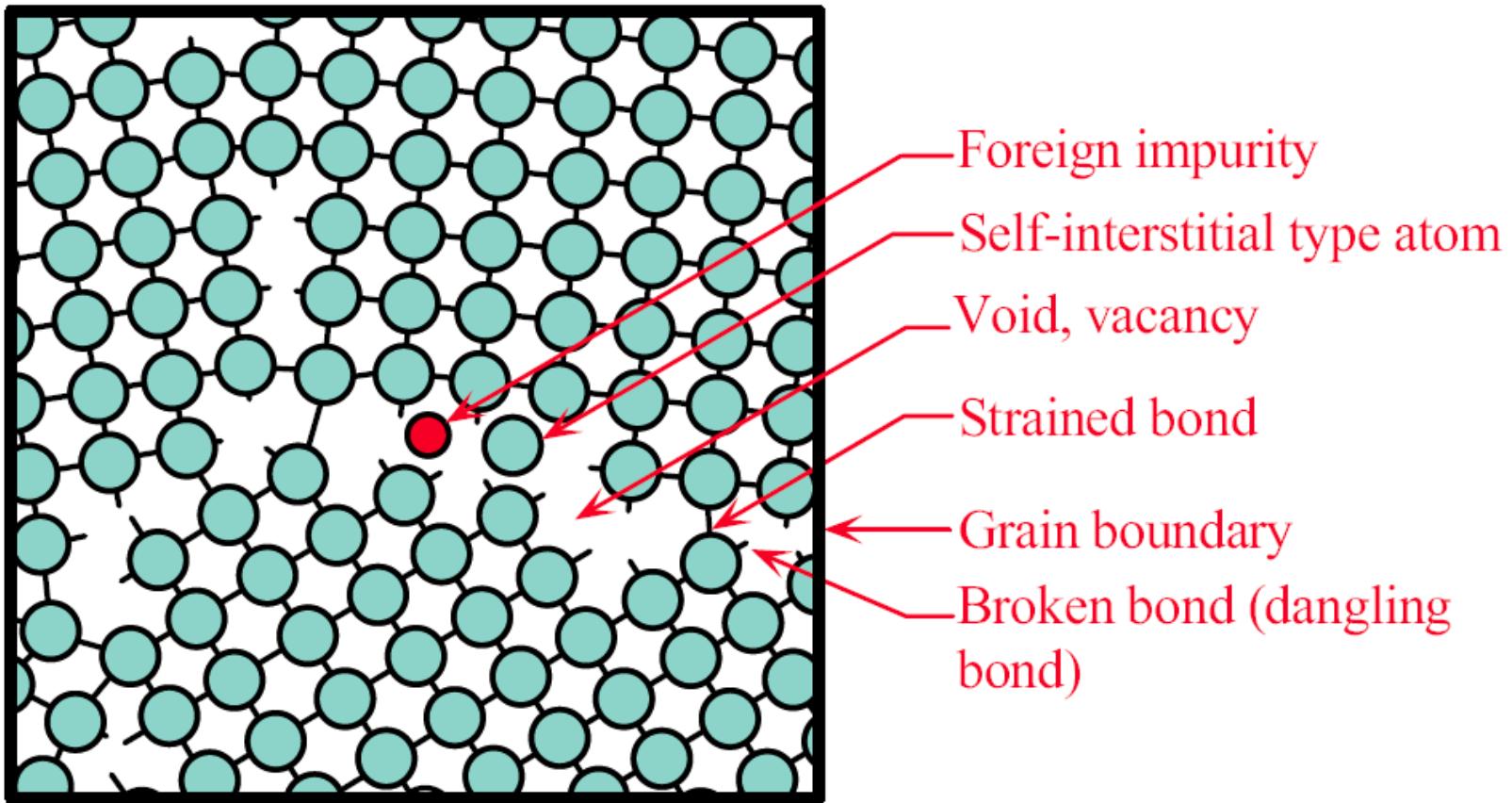


(b)

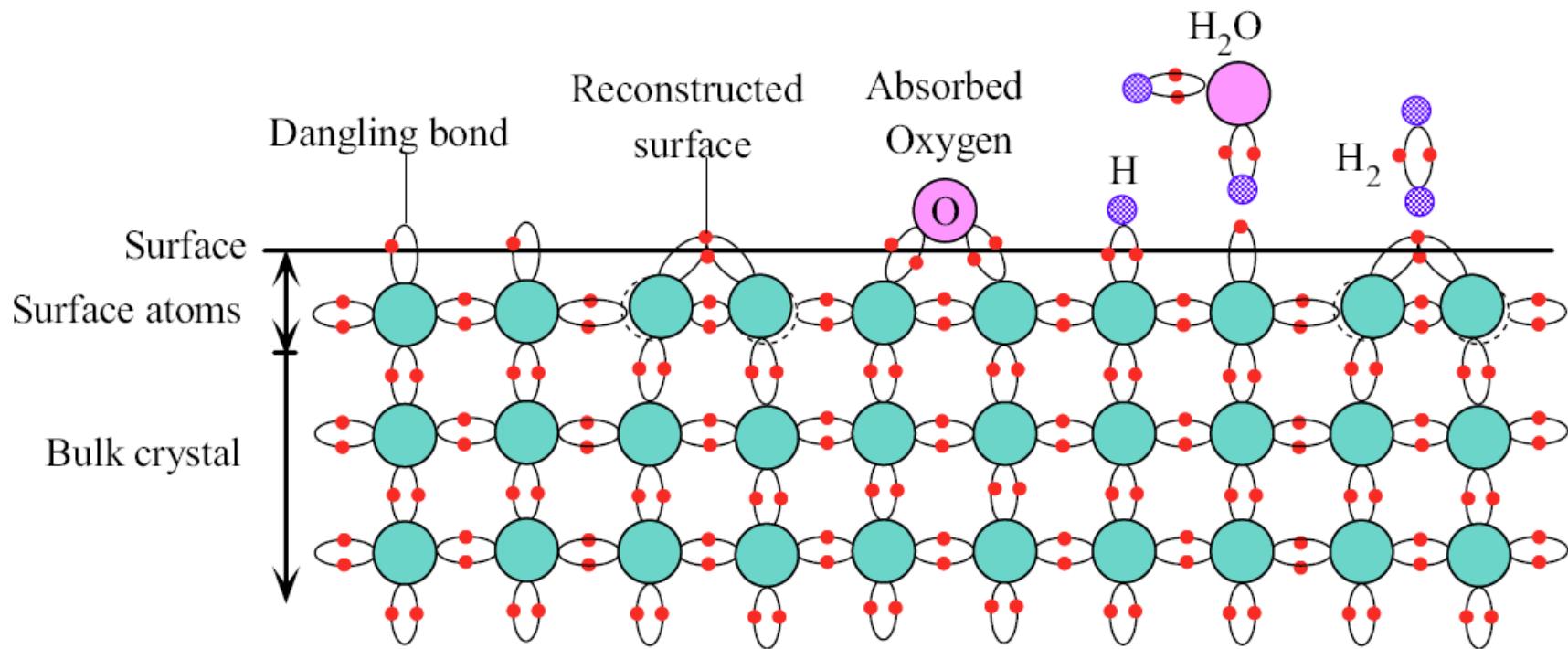


(c)

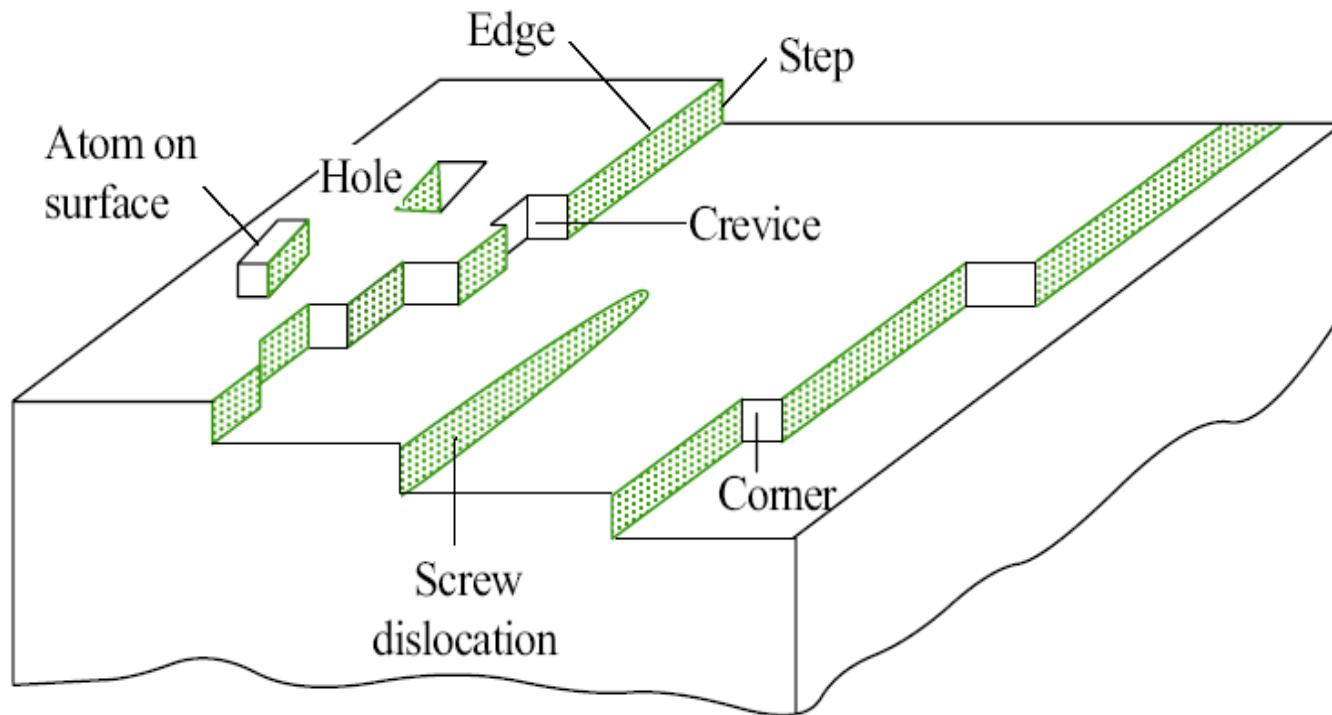
Solidification of a polycrystalline solid from the melt. (a) Nucleation. (b) Growth. (c) The solidified polycrystalline solid. For simplicity cubes represent atoms.



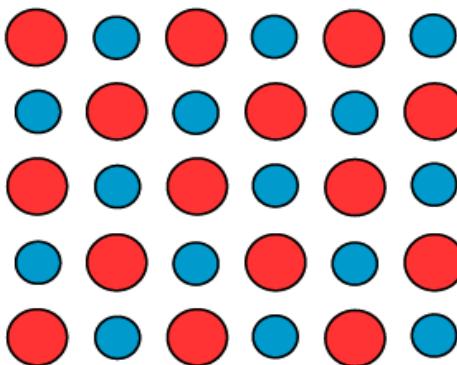
The grain boundaries have broken bonds, voids, vacancies, strained bonds and “interstitial” type atoms. The structure of the grain boundary is disordered and the atoms in the grain boundaries have higher energies than those within the grains.



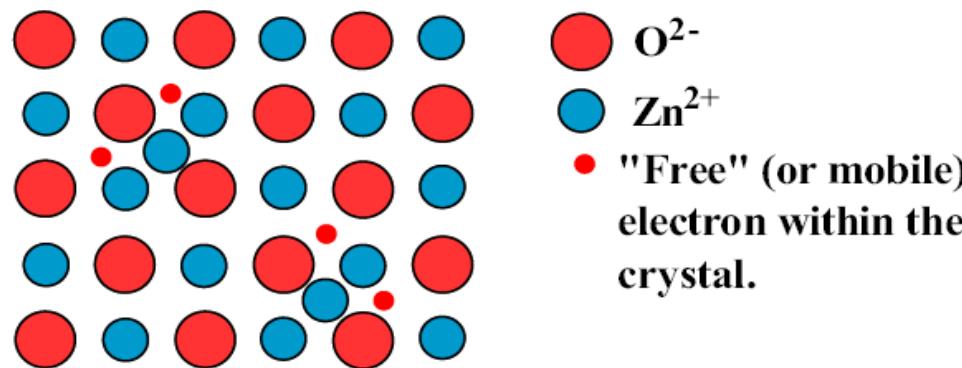
At the surface of a hypothetical two dimensional crystal, the atoms cannot fulfill their bonding requirements and therefore have broken, or dangling, bonds. Some of the surface atoms bond with each other; the surface becomes reconstructed. The surface can have physisorbed and chemisorbed atoms.



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

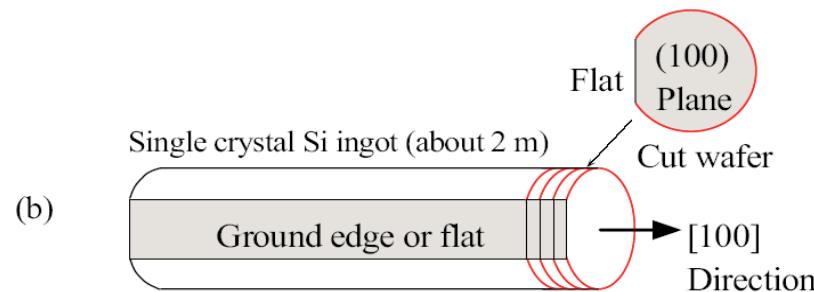
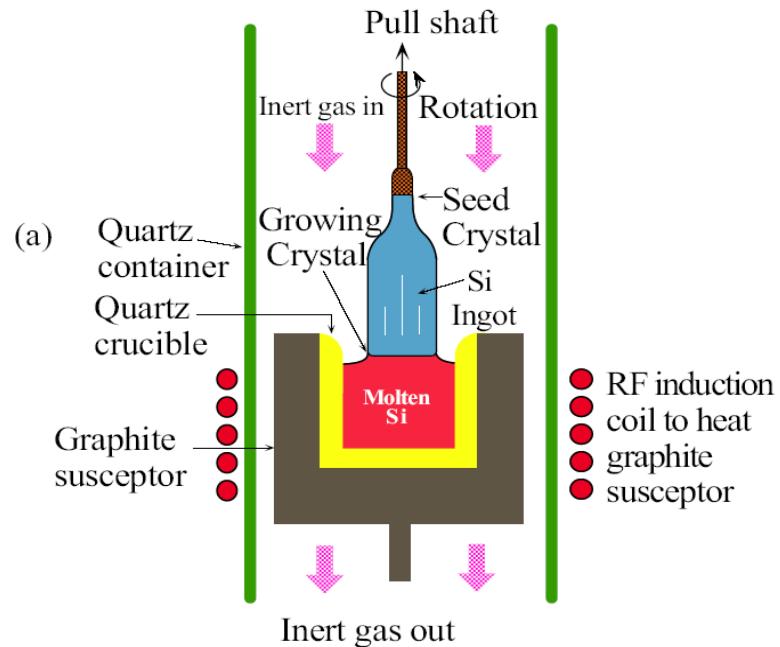


(a) Stoichiometric ZnO crystal with equal number of anions and cations and no free electrons.

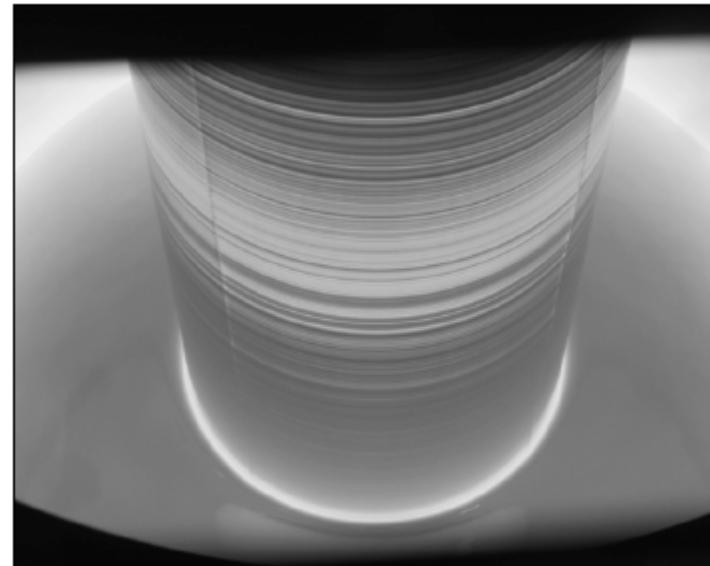
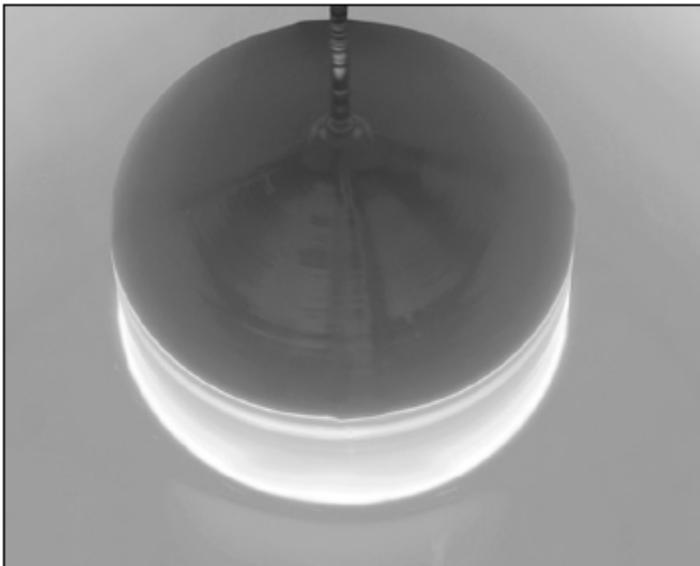


(b) Non-Stoichiometric ZnO crystal with excess Zn in interstitial sites as Zn²⁺ cations.

Stoichiometry and nonstoichiometry and the resulting crystal structure



- (a) Schematic illustration of the growth of a single-crystal Si ingot by the Czochralski technique.
- (b) The crystallographic orientation of the silicon ingot is marked by grounding a flat. The ingot can be as long as 2m. Wafers are cut using a rotating annula diamond saw. Typical wafer thickness is 0.6-0.7 mm.



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

| SOURCE: Courtesy of MEMC Electronic Materials, Inc.

Silicon

90



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.

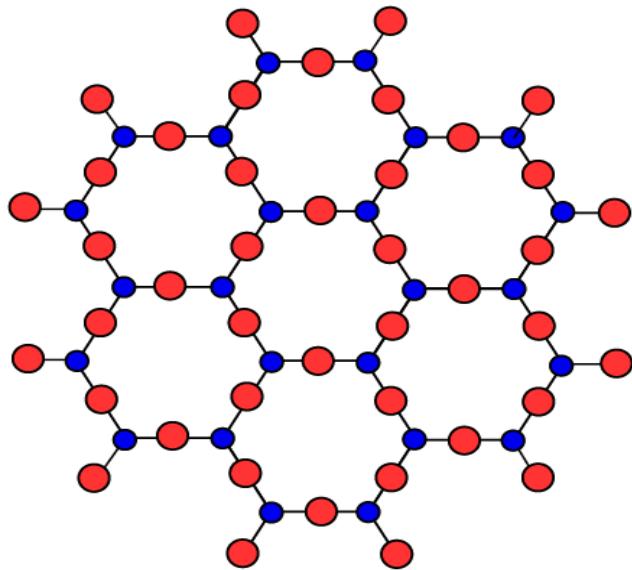


Left: Silicon crystal ingots grown by the
Czochralski crystal drawers in the background
|Courtesy of MEMC, Electronic Materials Inc.

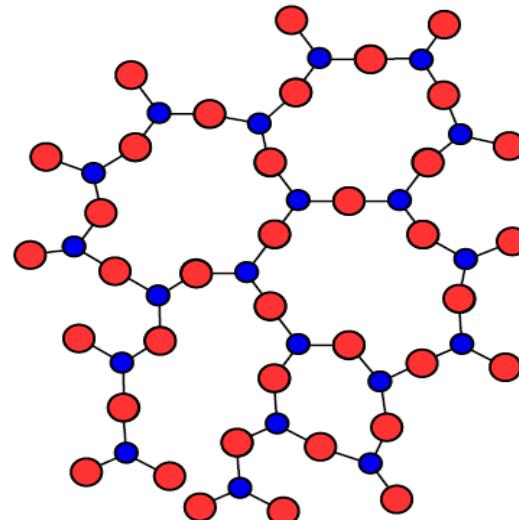


Right: 200 mm and 300 mm Si
|Courtesy of MEMC, Electronic Materials
Inc.

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

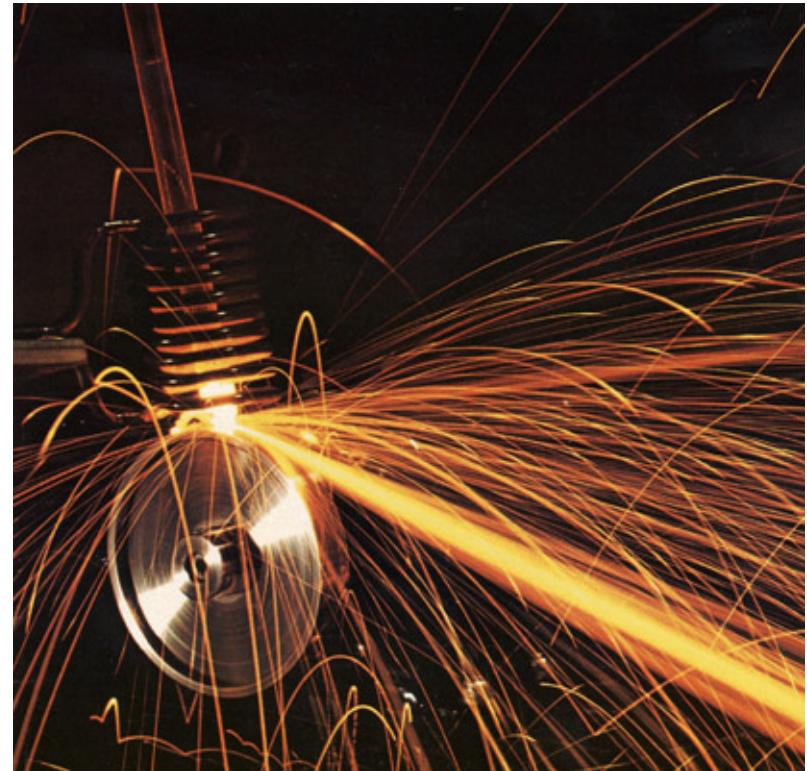
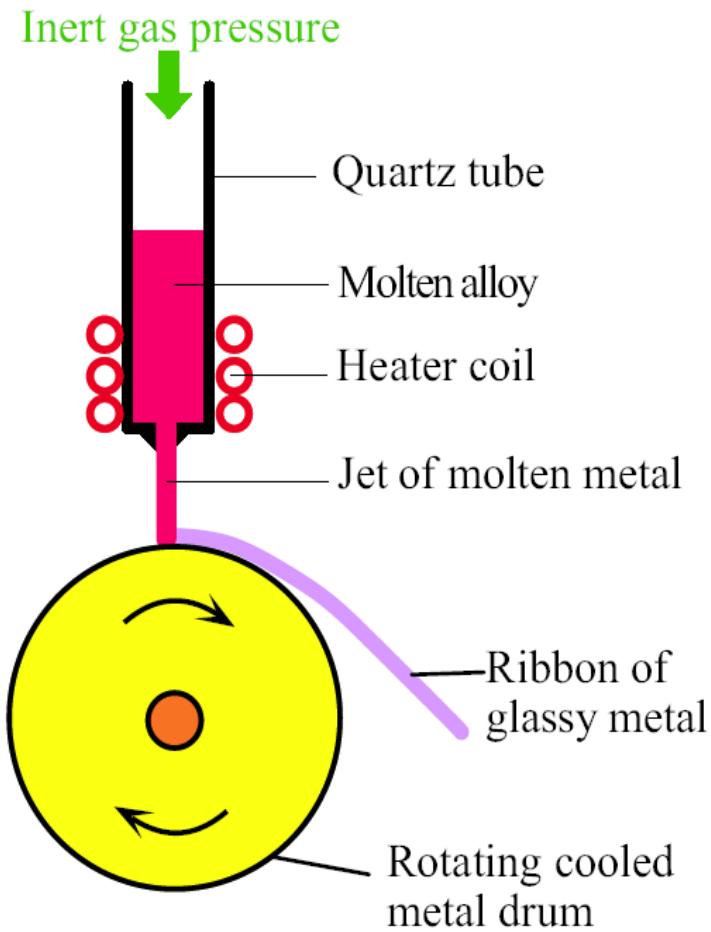


(a) A crystalline solid reminiscent to
crystalline SiO_2 . (Density = 2.6 g cm^{-3})



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

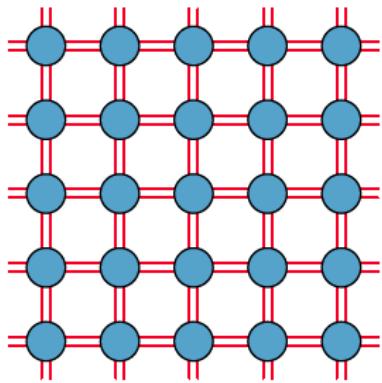
Crystalline and amorphous structures illustrated schematically in two dimensions



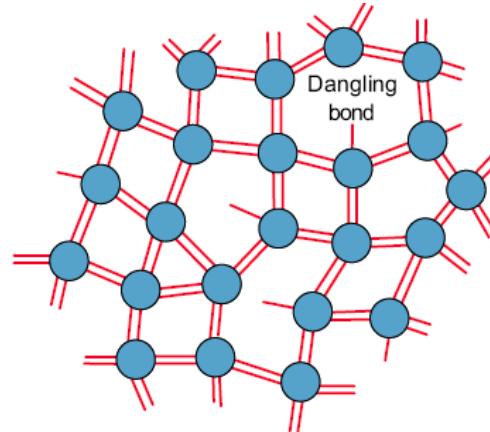
Melt spinning involves squirting a jet of molten metal onto a rotating cool metal drum. The molten jet is instantly solidified into a glassy metal ribbon which is a few microns in thickness. The process produces roughly 1 to 2 kilometers of ribbon per minute.

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

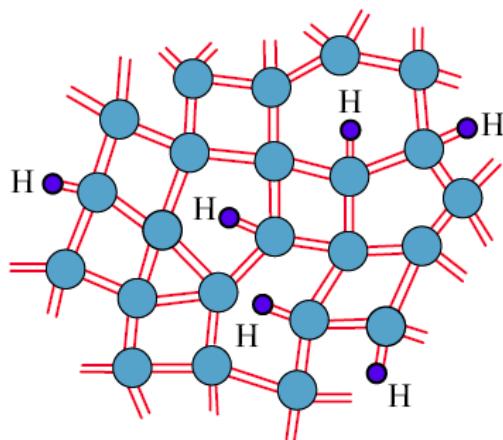
It is possible to rapidly quench a molten metallic alloy, thereby bypassing crystallization, and forming a glassy metal commonly called a metallic glass. The process is called *melt spinning*.



(a) Two dimensional schematic representation of a silicon crystal

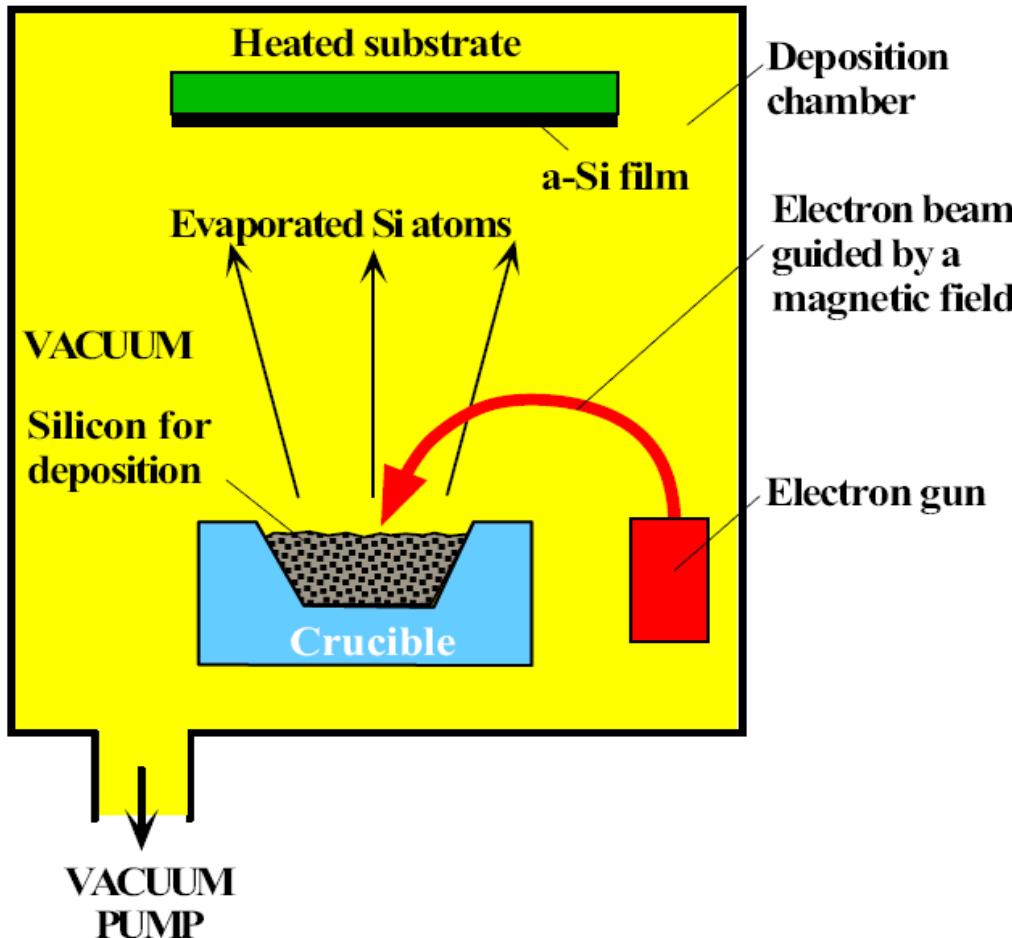


(b) Two dimensional schematic representation of the structure of amorphous silicon. The structure has voids and dangling bonds and there is no long range order.

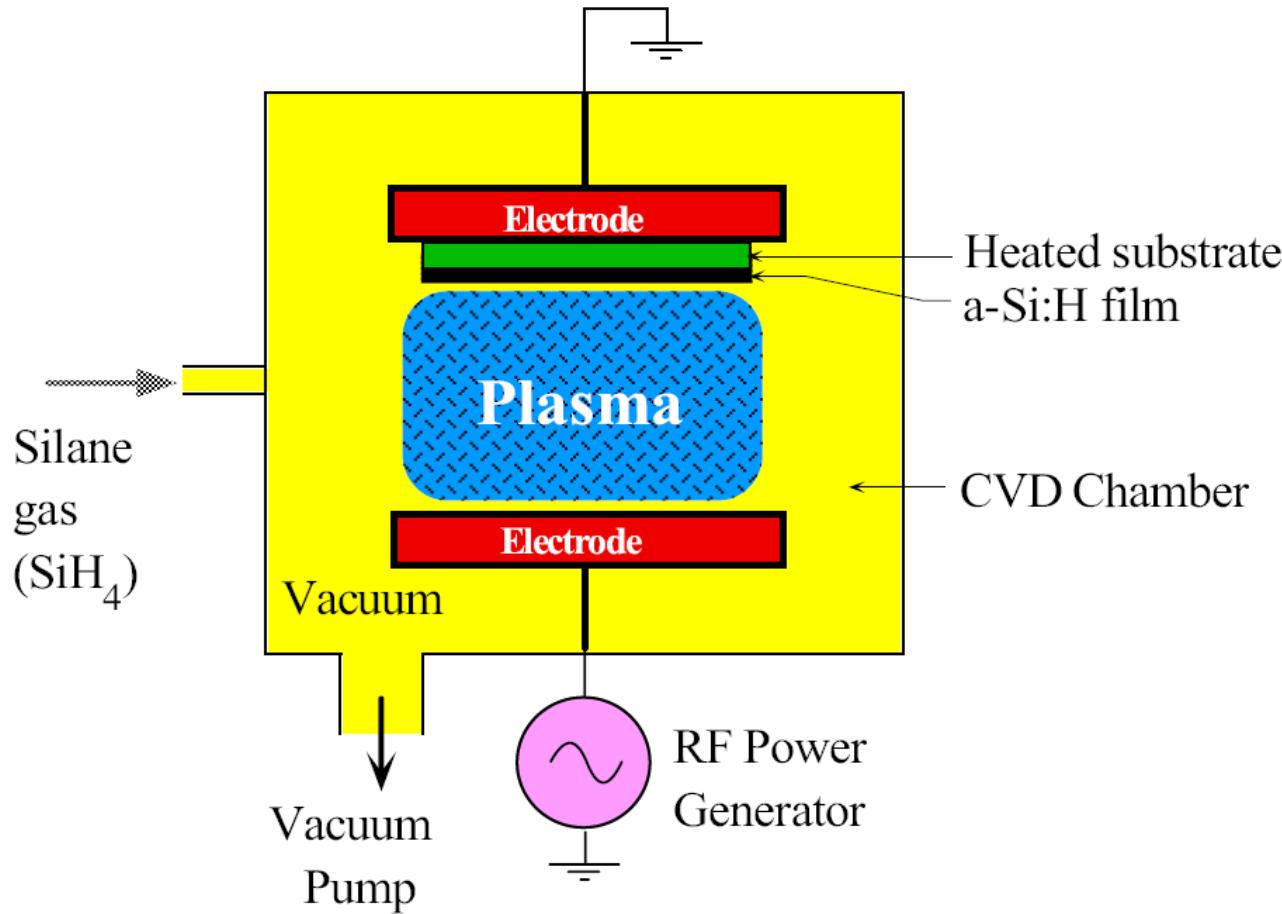


(c) Two dimensional schematic representation of the structure of hydrogenated amorphous silicon. The number of hydrogen atoms shown is exaggerated.

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.



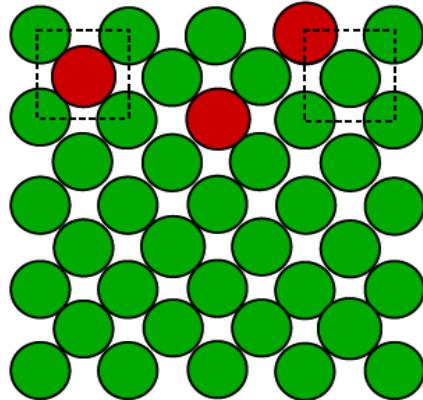
Amorphous silicon, a-Si, can be prepared by an electron beam evaporation of silicon. Silicon has a high melting temperature so that an energetic electron beam is used to melt the crystal in the crucible locally and thereby vaporize Si atoms. Si atoms condense on a substrate placed above the crucible to form a film of a-Si.



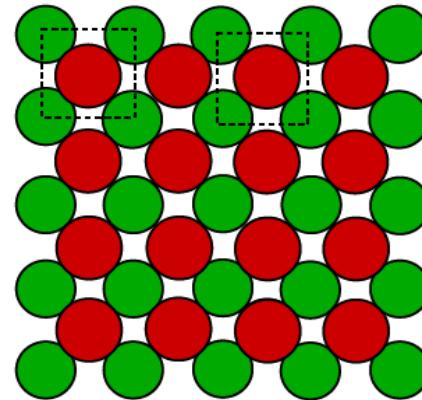
Hydrogenated amorphous silicon, a-Si:H, is generally prepared by the decomposition of silane molecules in a radio frequency (RF) plasma discharge. Si and H atoms condense on a substrate to form a film of a-Si:H

Table 1.5 Crystalline and amorphous silicon

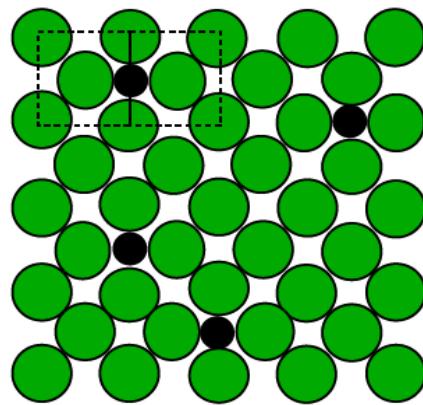
	Crystalline Si (c-Si)	Amorphous Si (a-Si)	Hydrogenated a-Si (a-Si:H)
Structure	Diamond cubic.	Short-range order only. On average, each Si covalently bonds with four Si atoms. Has microvoids and dangling bonds.	Short-range order only. Structure typically contains 10% H. Hydrogen atoms passivate dangling 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.



(a) Disordered Substitutional Solid Solution. Example: Cu-Ni alloys ($\{100\}$ planes)

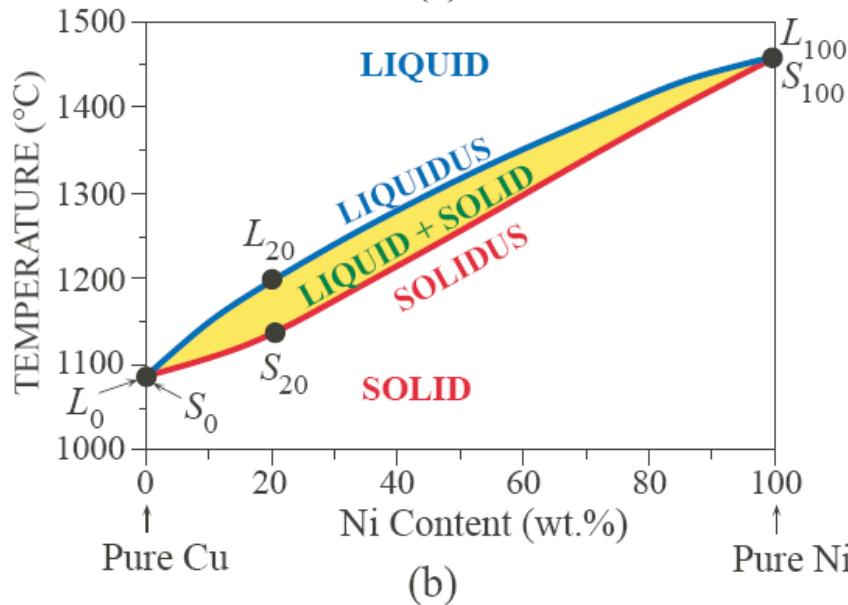
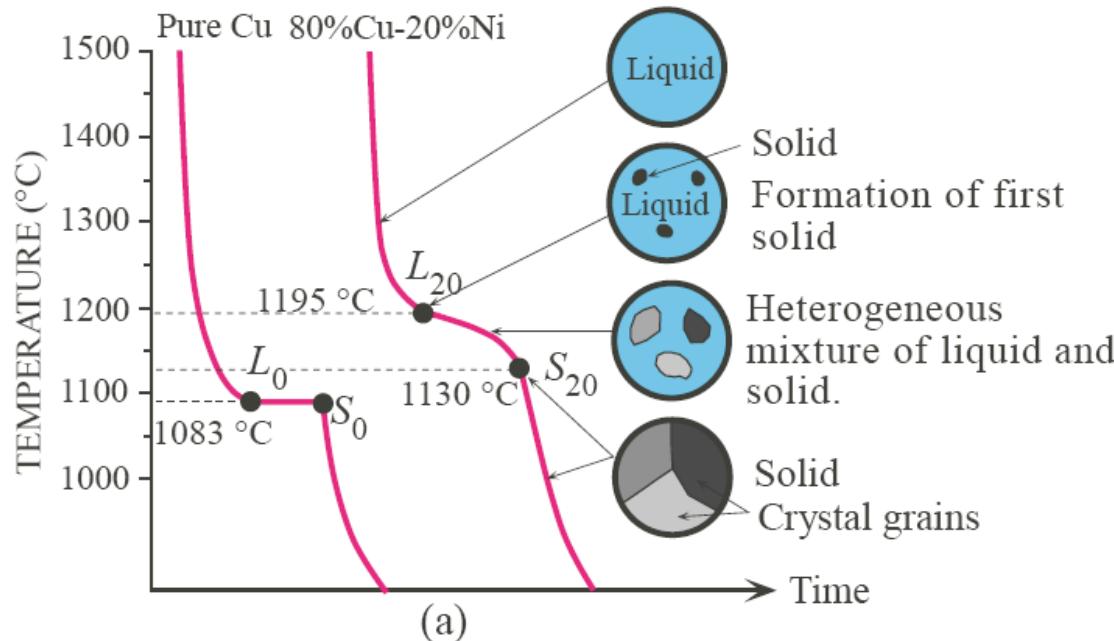


(b) Ordered Substitutional Solid Solution. Example: Cu-Zn alloy of composition 50%Cu-50%Zn. ($\{110\}$ planes).



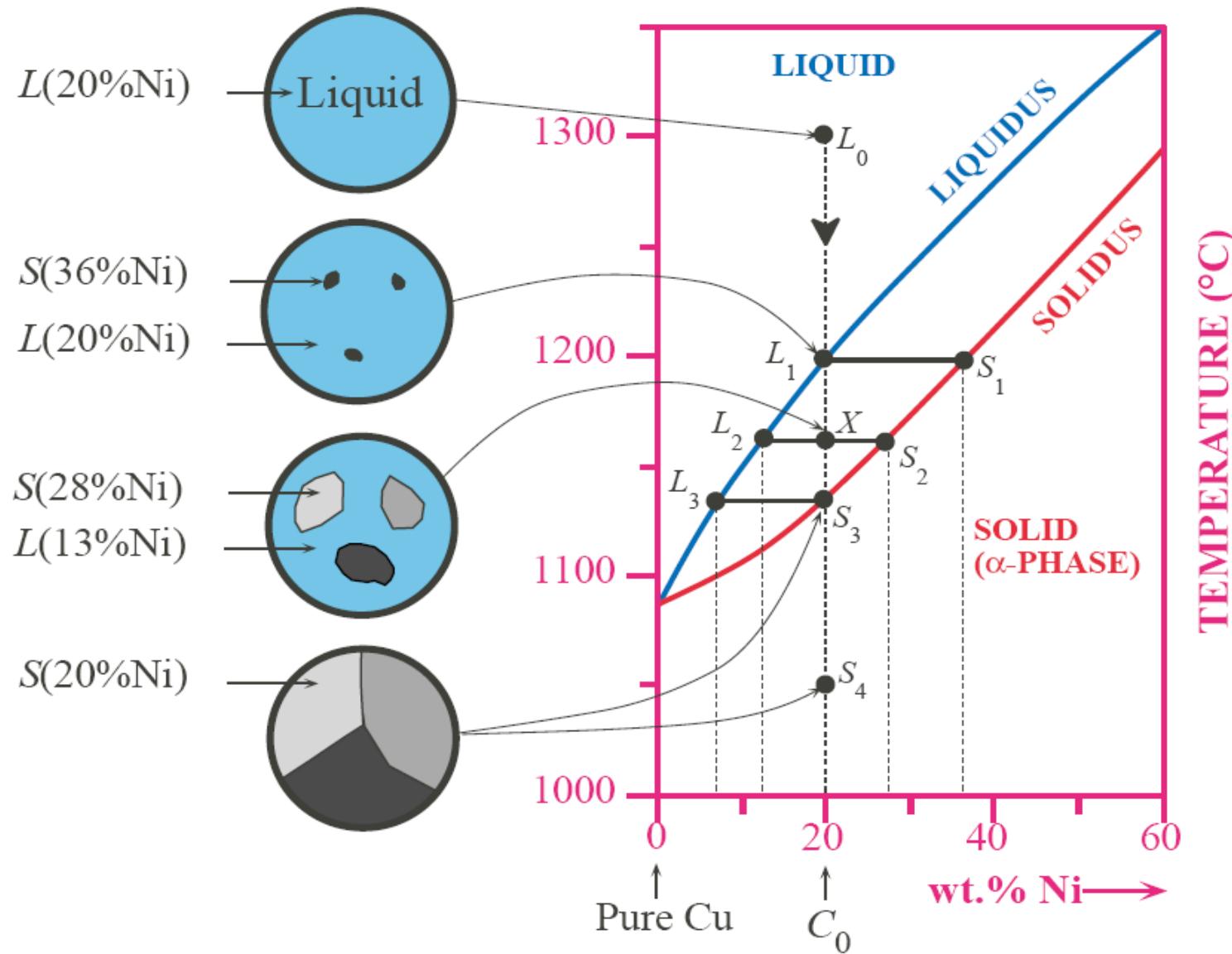
(c) Interstitial Solid Solution. Example: Small number of C atoms in FCC Fe (austenite). ($\{100\}$ planes)

Solid solutions can be disordered substitutional, ordered substitutional and interstitial substitutional



Solidification of an isomorphous alloy such as Cu-Ni.

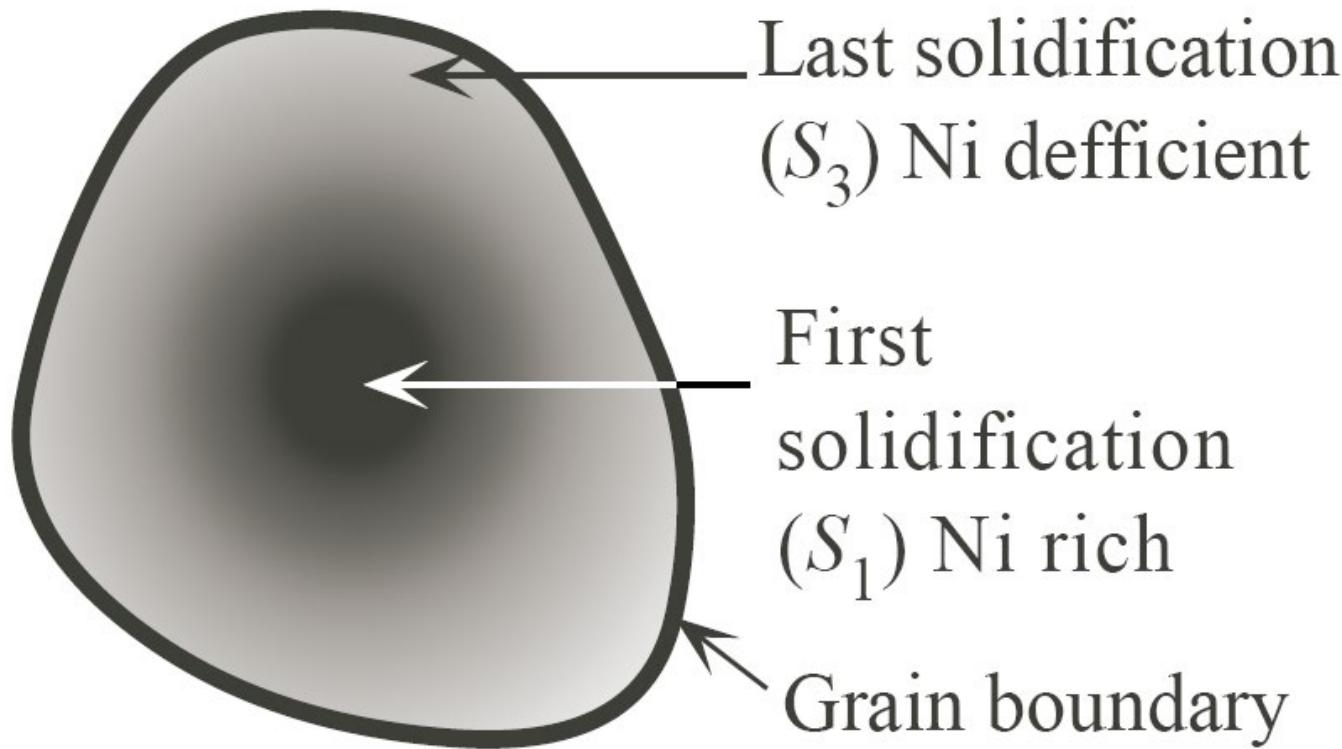
- Typical cooling curves
- The phase diagram marking the regions of existence for the phases



Cooling of a 80%Cu-20%Ni alloy from the melt to the solid state.

Table 1.6 Phase in the 80% Cu–20% Ni isomorphous alloy

Temperature, °C	Phases	Composition	Amount
1300	Liquid only	$L_0 = 20\%$ Ni	100%
1195	Liquid and solid	$L_1 = 20\%$ Ni	100%
		$S_1 = 36\%$ Ni	First solid appears
1160	Liquid and solid	$L_2 = 13\%$ Ni	53.3%
		$S_2 = 28\%$ Ni	46.7%
1130	Liquid and solid	$L_3 = 7\%$ Ni	The last liquid drop
		$S_3 = 20\%$ Ni	100%
1050	Solid only	$S_4 = 20\%$ Ni	100%

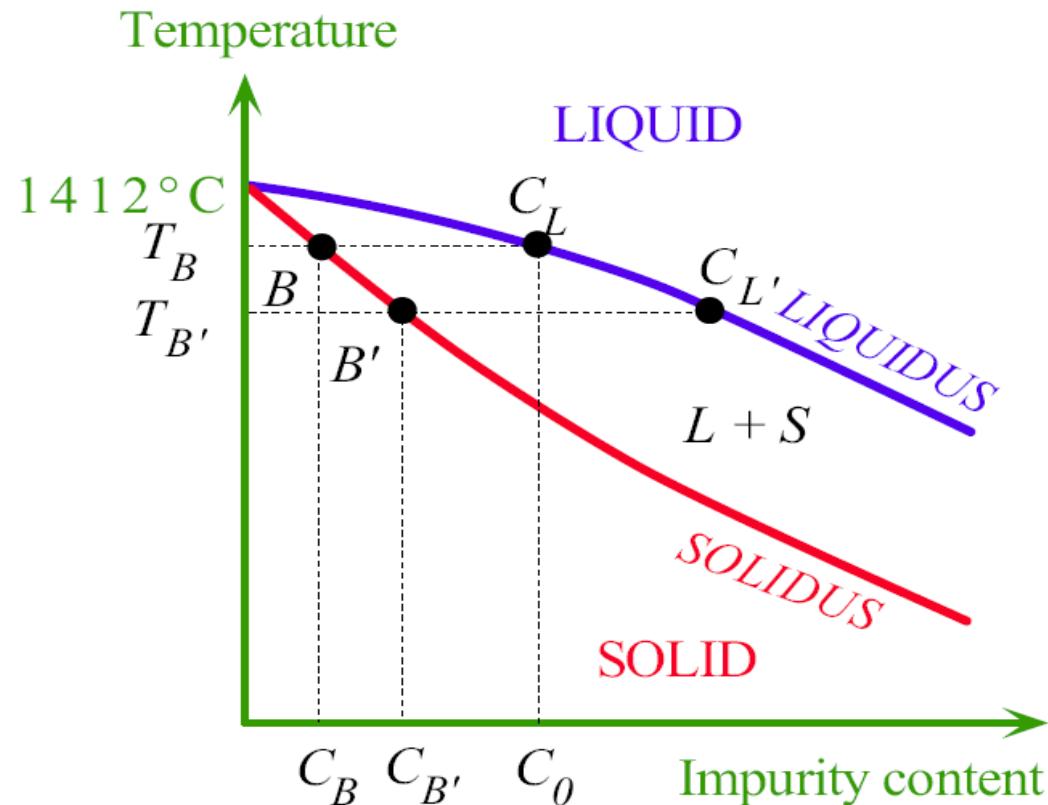


Segregation in a grain due to rapid cooling (nonequilibrium cooling)

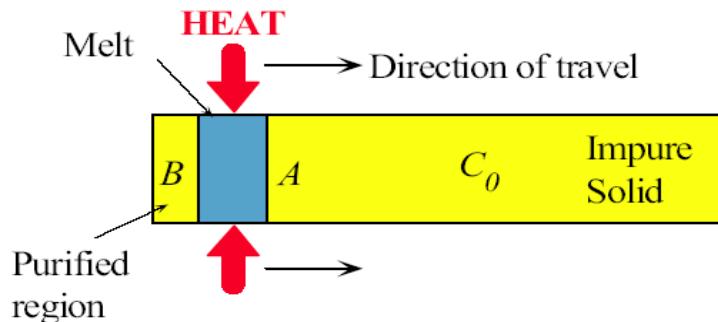
Lever Rule

$$W_L = \frac{C_S - C_O}{C_S - C_L} \quad \text{and} \quad W_S = \frac{C_O - C_L}{C_S - C_L}$$

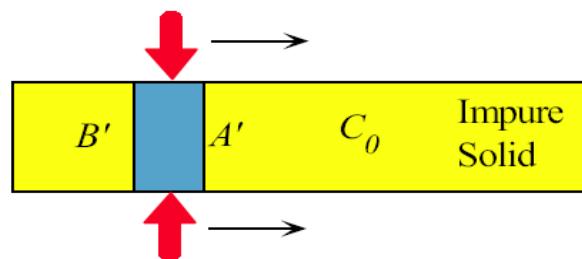
W_L = the weight fraction of the liquid phase, W_S = the weight fraction of the solid phase, C_S = composition of the solid phase, C_L = composition of the liquid phase, C_O = overall composition.



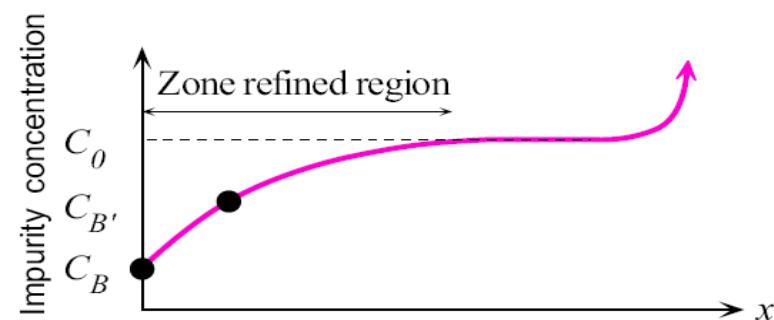
The phase diagram of Si with impurities near the low-concentration region



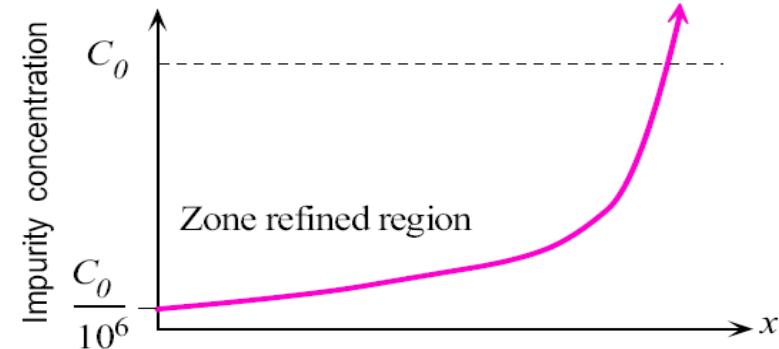
(a) Heat is applied locally starting at one end. The impurity concentration in the refrozen solid at B is $C_B < C_0$. The impurity concentration in the melt is $C_{L'} > C_0$.



(b) As the torch travels towards the right, the refrozen solid at B' has $C_{B'}$ where $C_B < C_{B'} < C_0$. The impurity concentration in the melt is now even greater than $C_{L'}$.

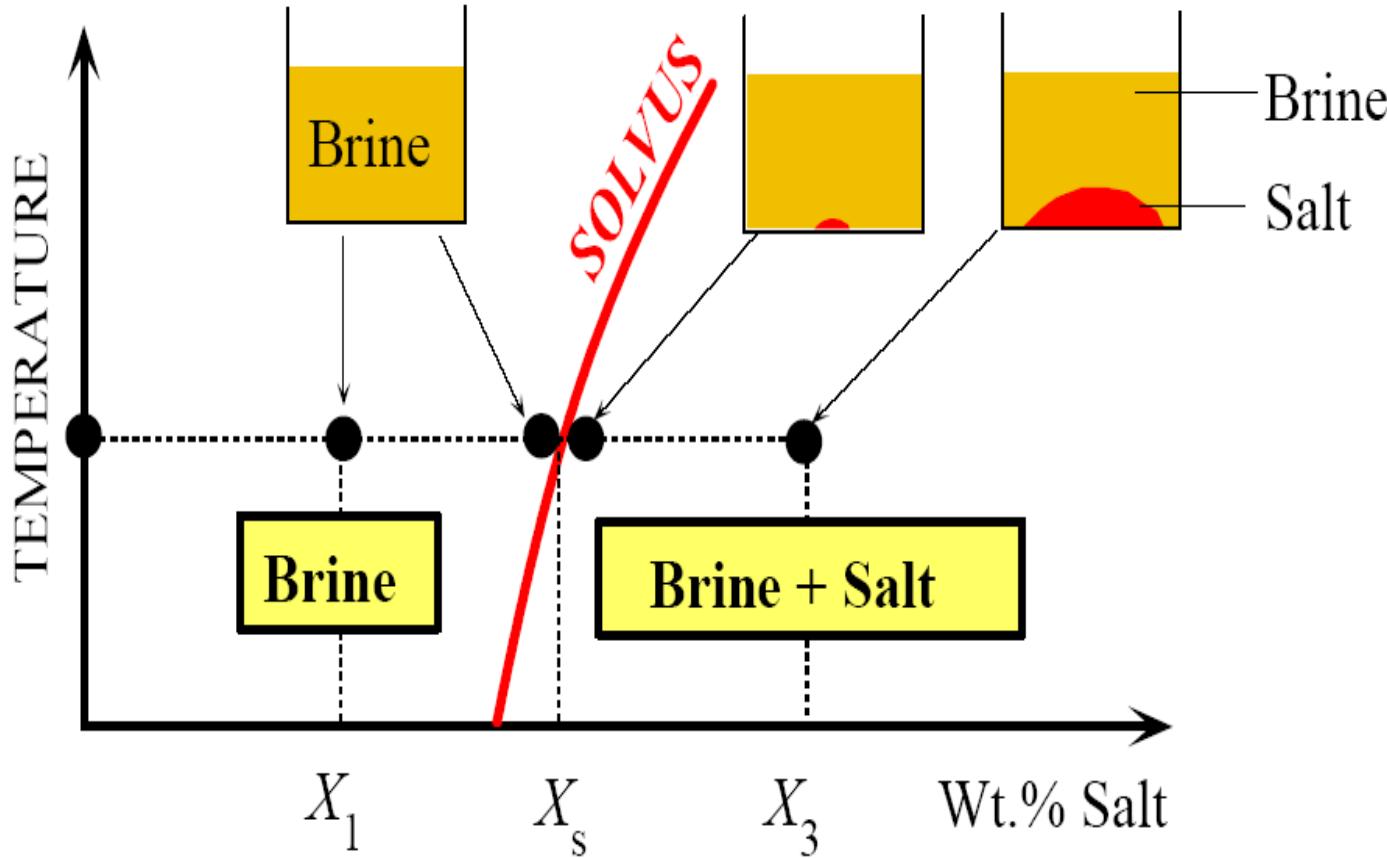


(c) The impurity concentration profile in the refrozen solid after one pass.



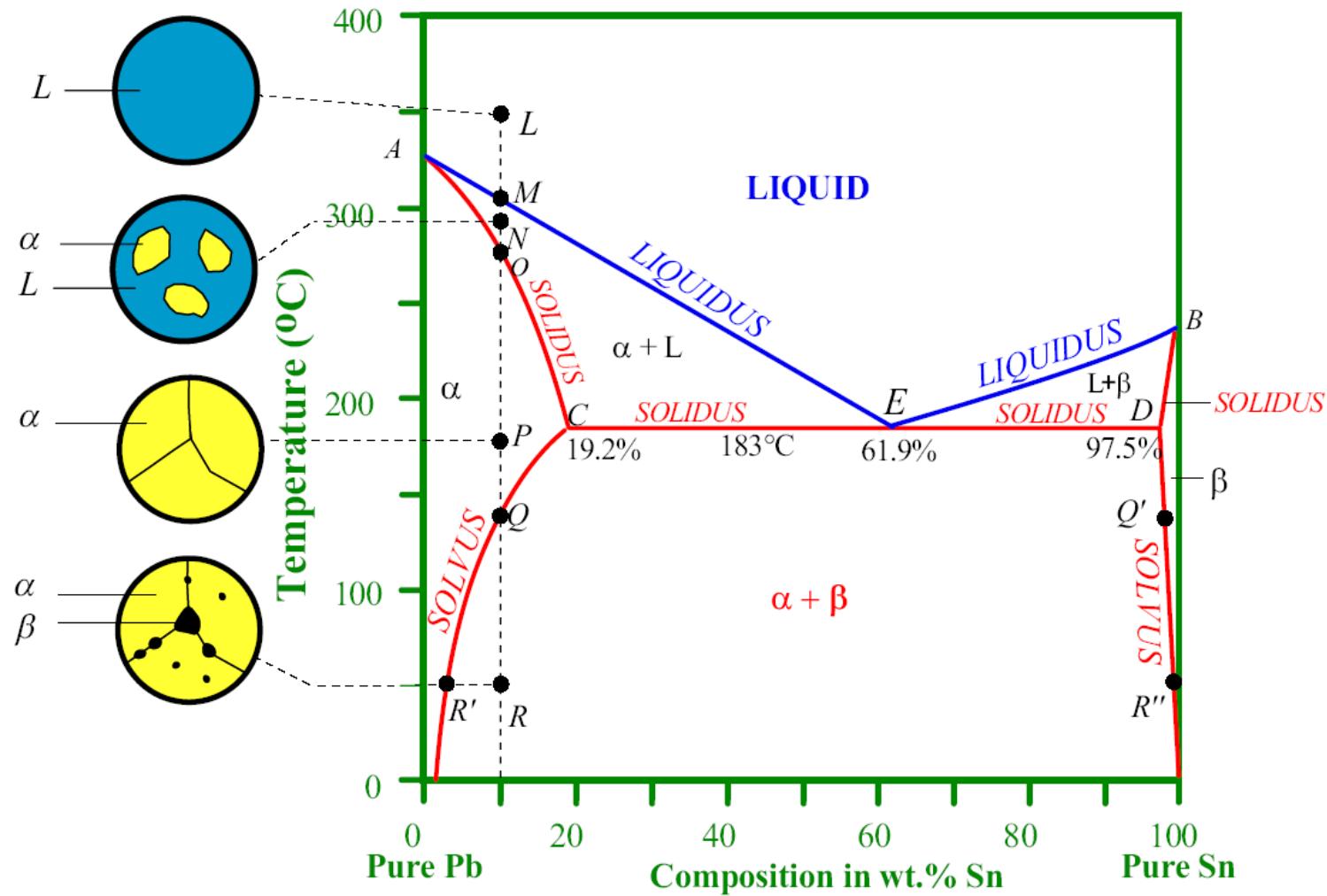
(d) Typical impurity concentration profile after many passes.

The principle of zone refining

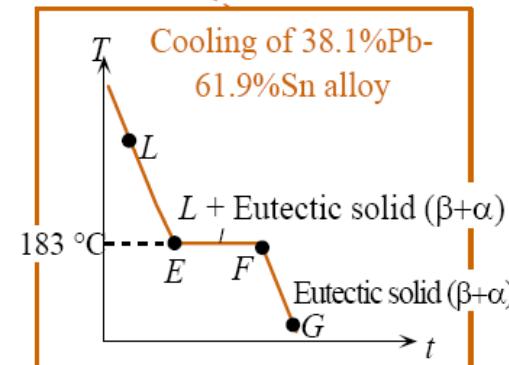
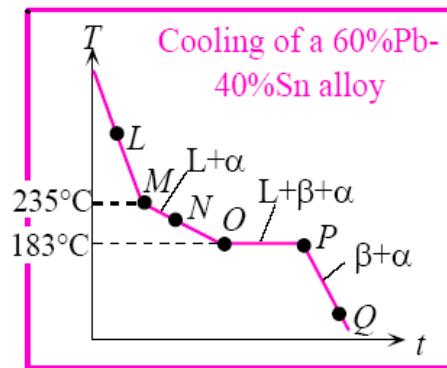
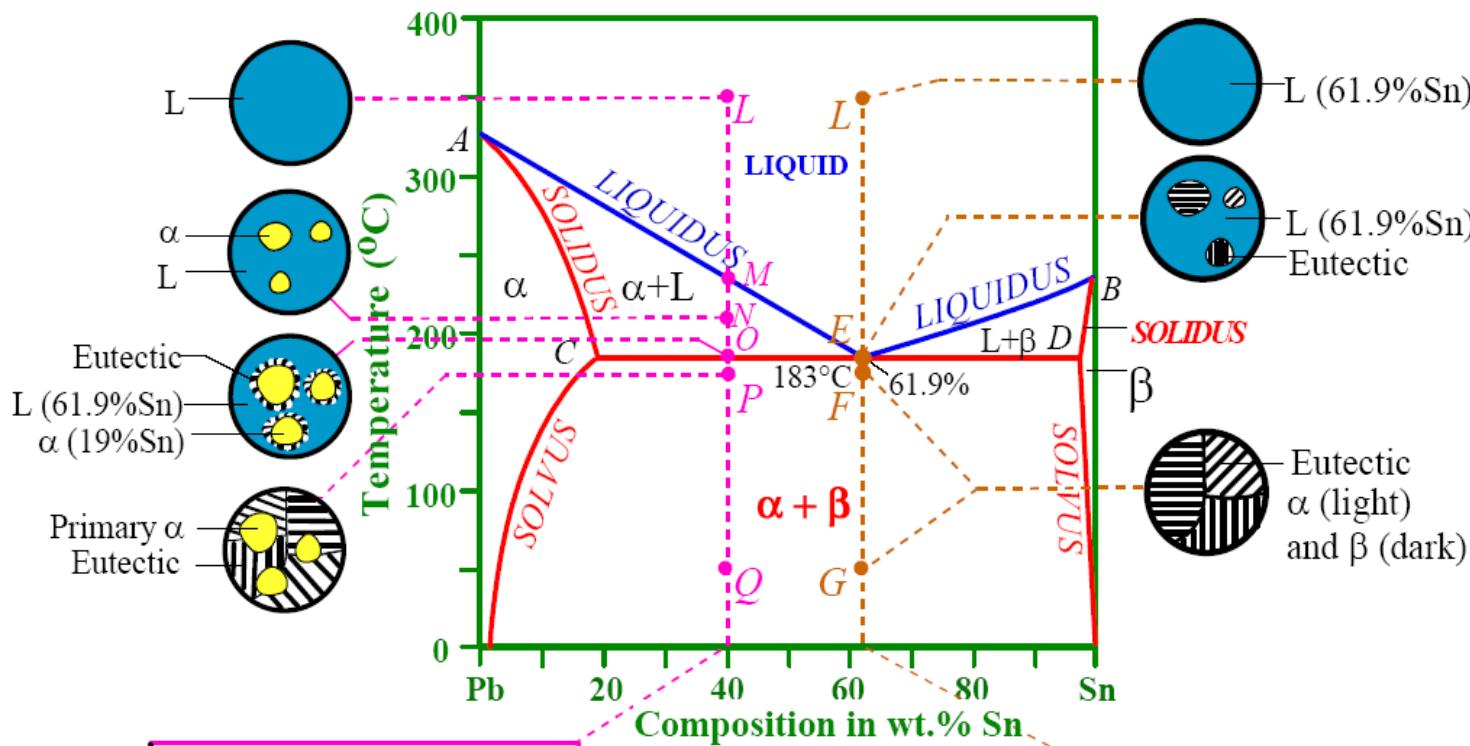


We can only dissolve so much salt in brine (solution of salt in water).

Eventually we reach the solubility limit at X_s , which depends on the temperature. If we add more salt, then the excess salt does not dissolve and coexists with the brine. Past X_s we have two phases, brine (solution) and salt (solid).



The equilibrium phase diagram of the Pb-Sn alloy. The microstructure on the left show the observations at various points during the cooling of a 90% Pb-10% Sn from the melt along the dashed line (the *overall alloy composition* remains constant at 10% Sn).

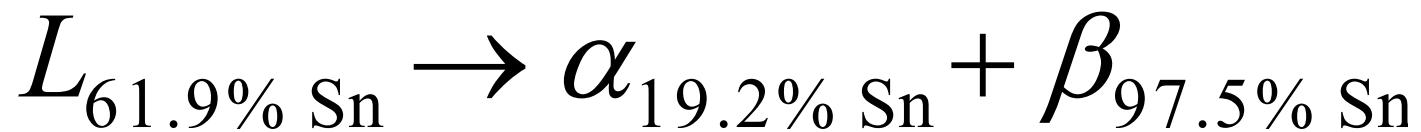


The alloy with the eutectic composition cools like a pure element exhibiting a single solidification temperature at 183°C. The solid has the special eutectic structure. The alloy with the composition 60%Pb-40%Sn when solidified is a mixture of primary α and eutectic solid.

Table 1.7 The 60% Pb–40% Sn alloy

Temperature (°C)	Phases	Composition	Mass (g)	Microstructure and Comment
250	L	40% Sn	100	
235	L	40% Sn	100	The first solid (α -phase) nucleates in the liquid.
	α	15% Sn	0	
210	L	50% Sn	68.7	Mixture of liquid and α phases. More solid forms. Compositions change.
	α	18% Sn	31.3	
183.5	L	61.9% Sn	48.7	Liquid has the eutectic composition.
	α	19.2% Sn	51.3	
182.5	α	19.2% Sn	73.4	Eutectic (α and β phases) and primary α -phase.
	β	97.5% Sn	26.6	

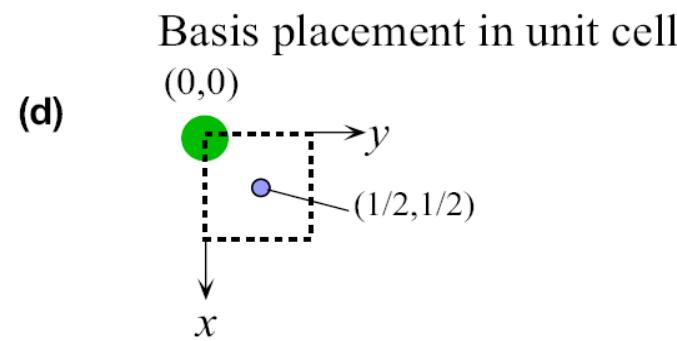
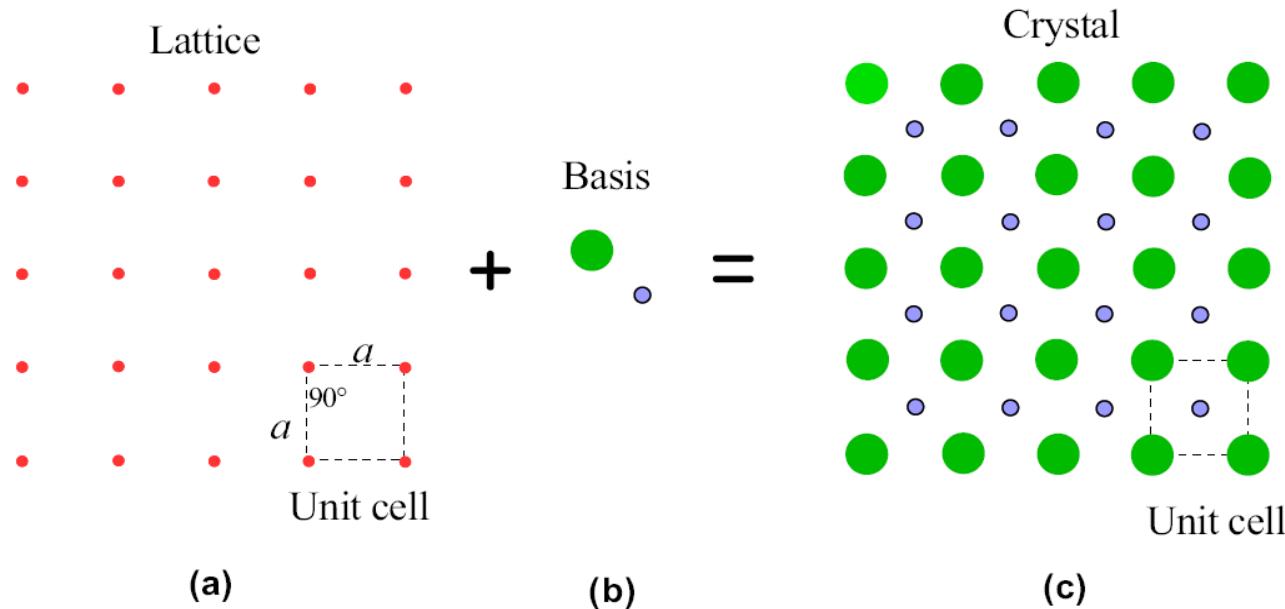
Eutectic Transformation



L = liquid phase

α = Pb-rich solid phase of PbSn

β = Sn-rich solid phase of PbSn

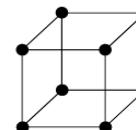


- (a) A simple square lattice. The unit cell is a square with a side a .
- (b) Basis has two atoms.
- (c) Crystal = Lattice + Basis. The unit cell is a simple square with two atoms.
- (d) Placement of basis atoms in the crystal unit cell.

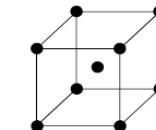
CUBIC SYSTEM

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

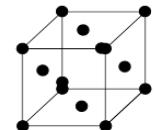
Many metals, Al, Cu, Fe, Pb. Many ceramics and semiconductors, NaCl, CsCl, LiF, Si, GaAs



Simple cubic



Body centered cubic

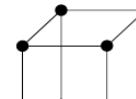


Face centered cubic

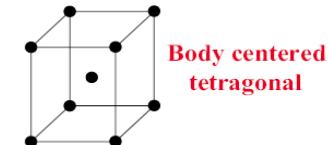
TETRAGONAL SYSTEM

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

In, Sn, Barium Titanate, TiO_2



Simple tetragonal

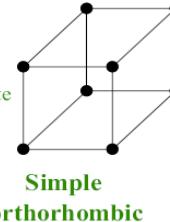


Body centered tetragonal

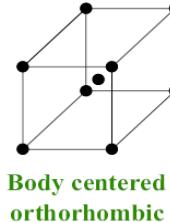
ORTORHOMBIC SYSTEM

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

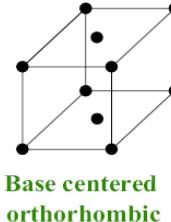
S, U, Pt, Ga (<30°C), Iodine, Cementite (Fe_3C), Sodium Sulfate



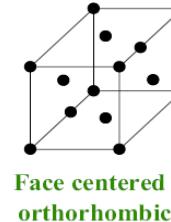
Simple orthorhombic



Body centered orthorhombic



Base centered orthorhombic

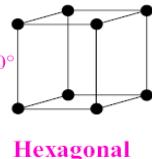


Face centered orthorhombic

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)

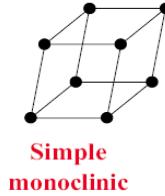


Rhombohedral

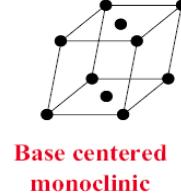
MONOCLINIC SYSTEM

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

α -Selenium, Phosphorus, Lithium Sulfate, Tin Fluoride



Simple monoclinic

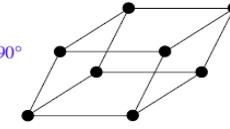


Base centered monoclinic

TRICLINIC SYSTEM

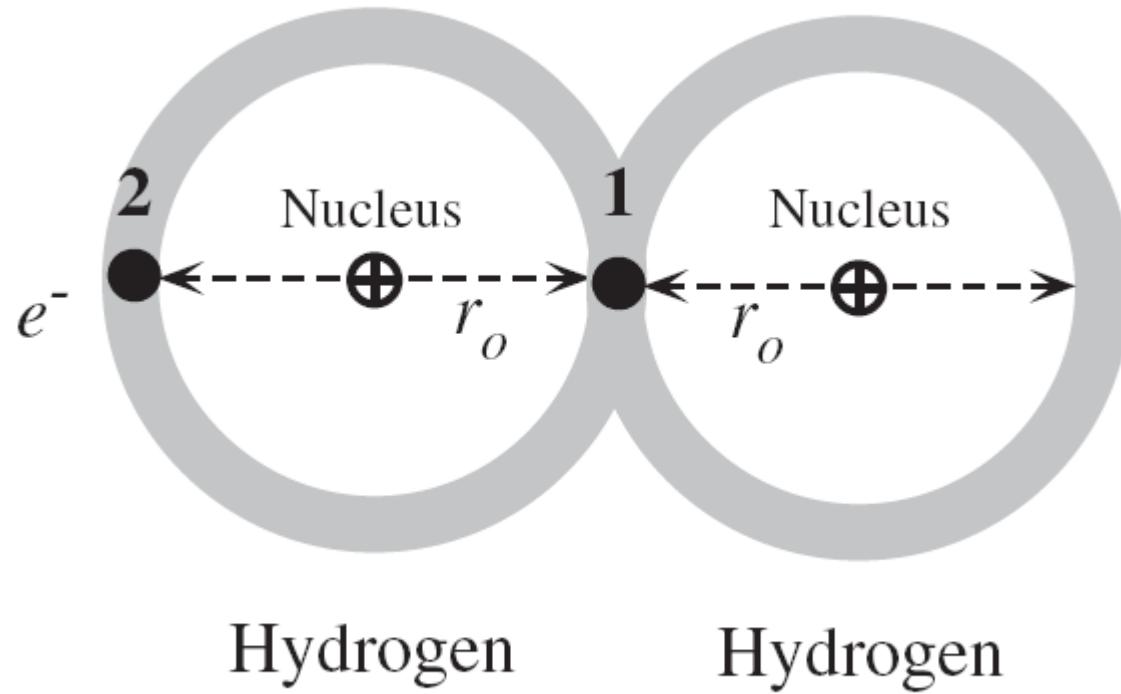
$$a \neq b \neq c \quad \alpha \neq \beta \neq \gamma \neq 90^\circ$$

Potassium dicromate

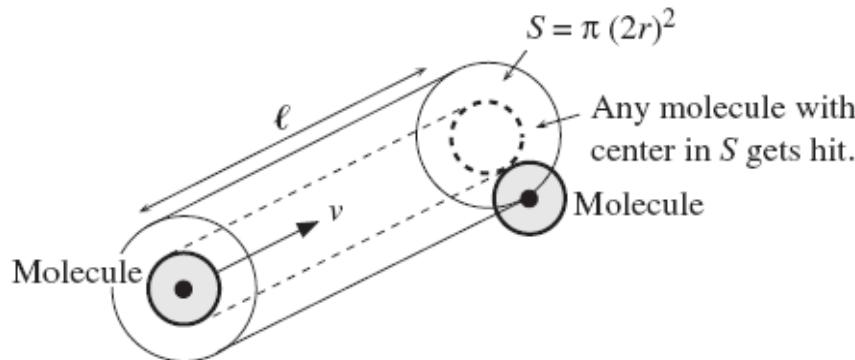


Triclinic

The seven crystal systems (unit cell geometries) and fourteen Bravais lattices.



A simplified view of the covalent bond in H_2 . A snapshot at one instant.

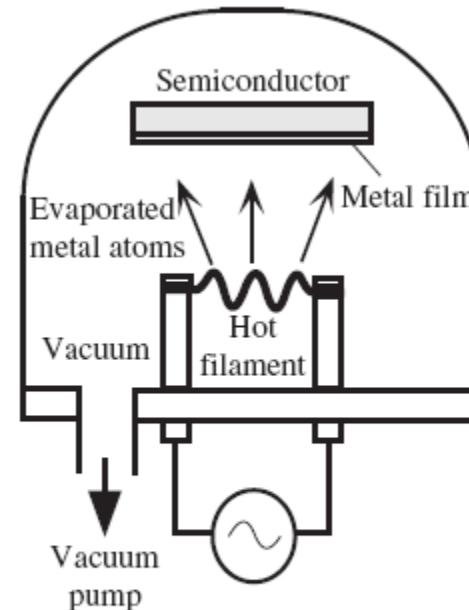


(a) A molecule moving with a velocity v travels a mean distance ℓ between collisions. Since the collision cross-sectional area is S , in the volume $S\ell$ there must be at least one molecule. Consequently, $n(S\ell) = 1$.

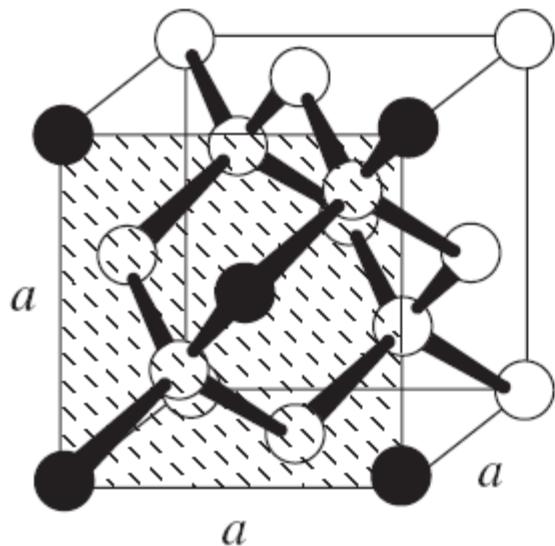


Walter Houser Brattain (1902–1987), experimenting with metal contacts on copper oxide (1935) at Bell Telephone Labs. A vacuum evaporation chamber is used to deposit the metal electrode.

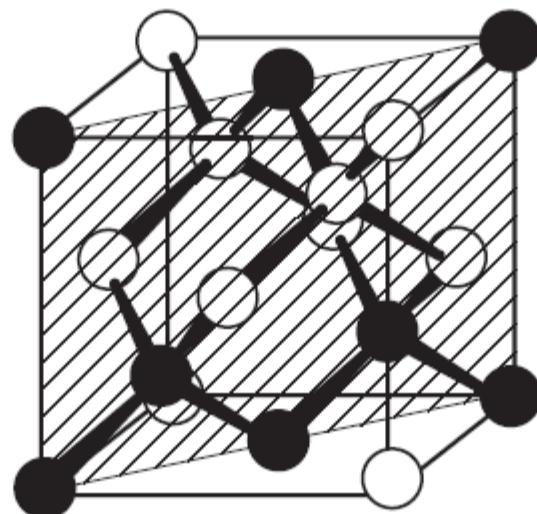
| SOURCE: Bell Telephone Laboratories, courtesy AIP Emilio Segrè Visual Archives.



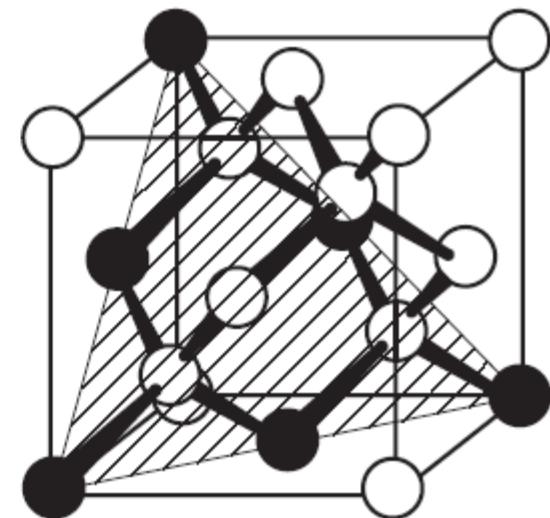
(b) Vacuum deposition of metal electrodes by thermal evaporation.



(100) plane



(110) plane



(111) plane

Diamond cubic crystal structure and planes. Determine what portion of a black-colored atom belongs to the plane that is hatched.

Chapter 3: Fundamentals of Structure of Crystalline Solids

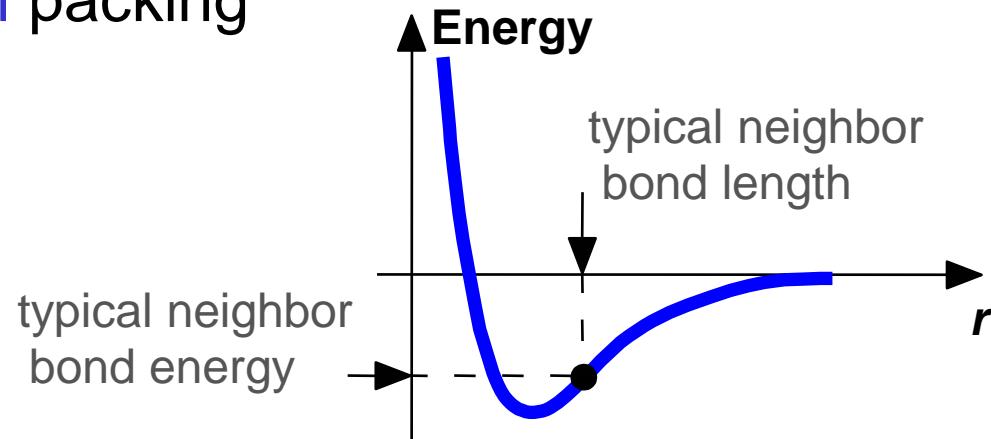
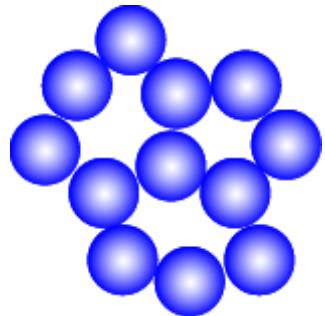
ISSUES TO ADDRESS...

- How do atoms assemble into solid structures in crystalline and non-crystalline materials?
- How do we specify directions and planes in unit cells?
- How do we distinguish between single crystals and polycrystalline materials?
- When do material properties vary with the sample (i.e., part) orientation?

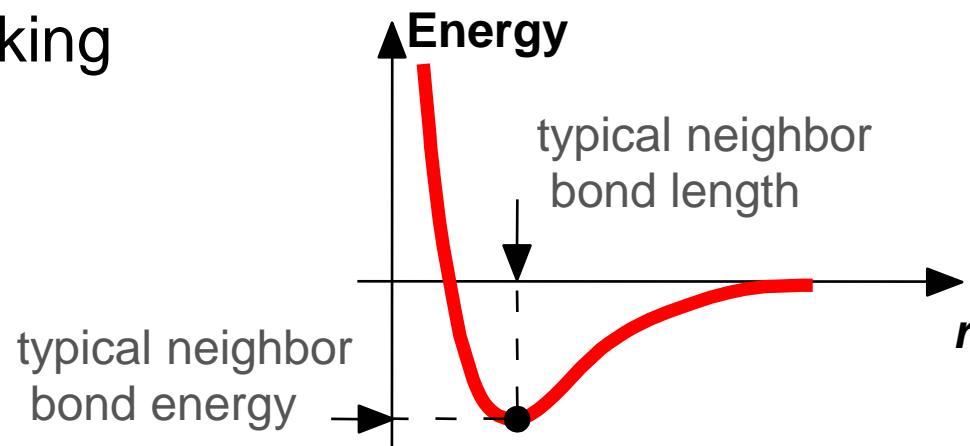
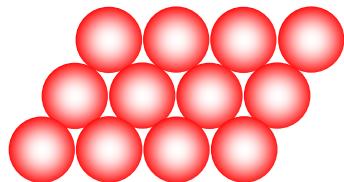


Energy and Packing

- Non dense, **random** packing



- Dense, **ordered** packing

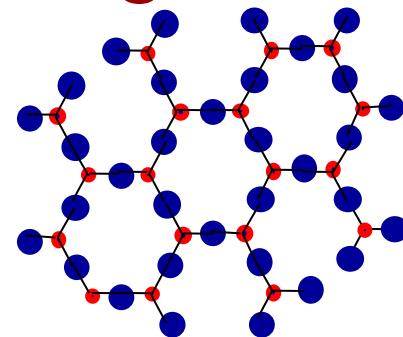


Dense, ordered packed structures tend to have lower energies.

Materials and Packing

Crystalline materials...

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



crystalline SiO₂

From Fig. 3.10(a)

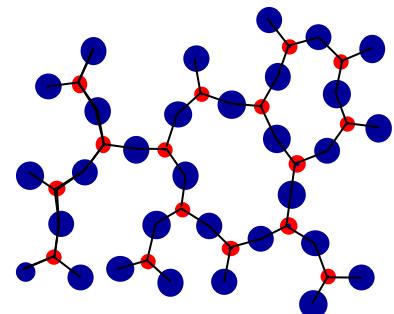
*Callister's Materials Science and Engineering,
Adapted Version.*

Noncrystalline materials...

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

"Amorphous" = Noncrystalline

• Si • Oxygen



noncrystalline SiO₂

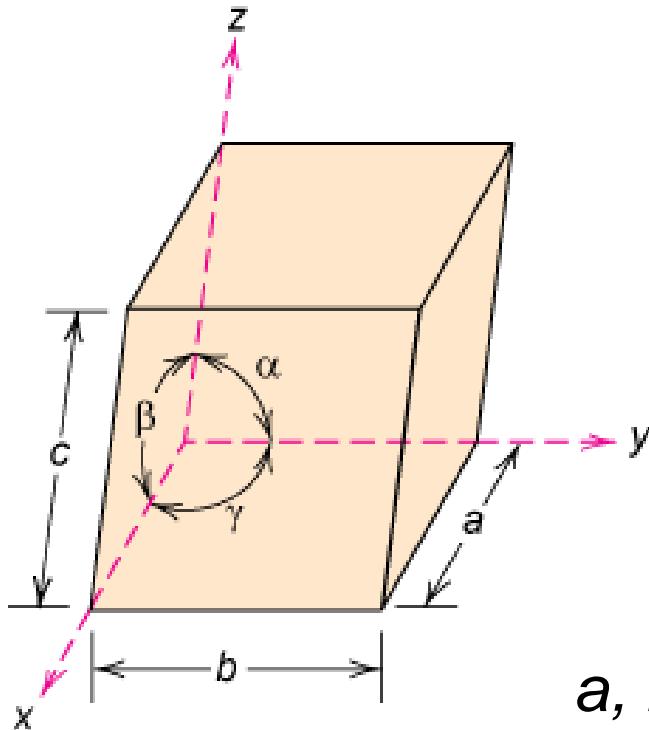
From Fig. 3.10(b)

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



Section 3.3 – Crystal Systems

Unit cell: smallest repetitive volume which contains the complete lattice pattern of a crystal.



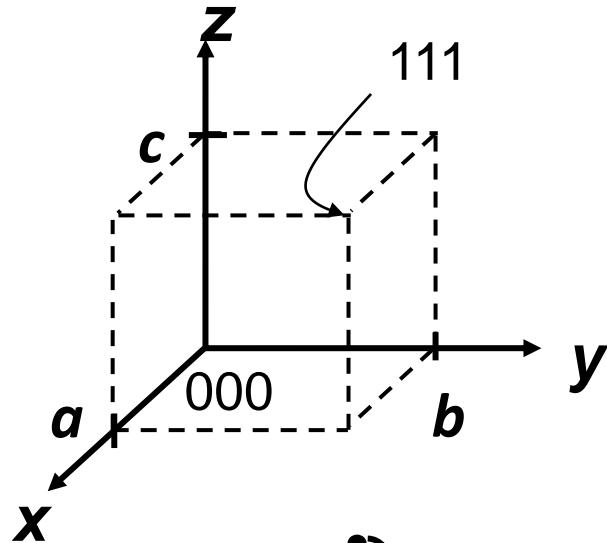
7 crystal systems

14 crystal lattices

a , b , and c are the lattice constants

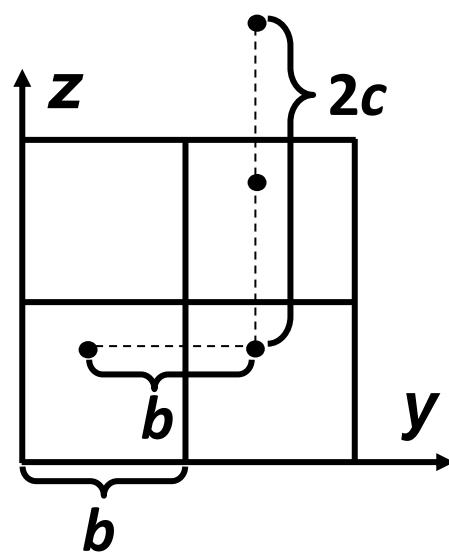
Fig. 3.2
*Callister's Materials
Science and
Engineering,
Adapted Version.*

Section 3.5 Point Coordinates



Point coordinates for unit cell center are

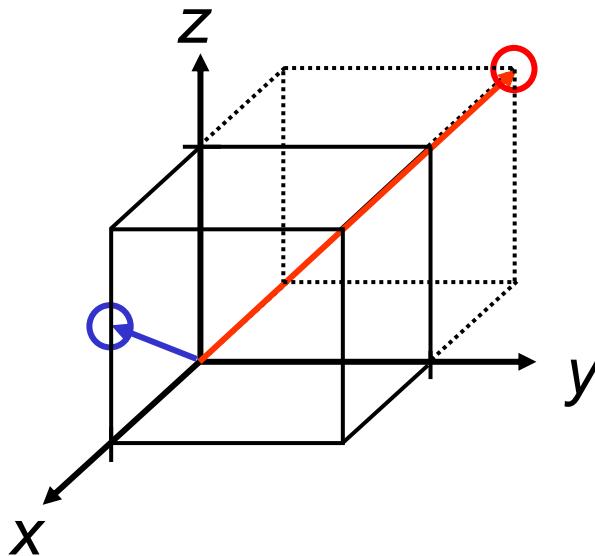
$$a/2, b/2, c/2 \quad \frac{1}{2} \frac{1}{2} \frac{1}{2}$$



Point coordinates for unit cell corner are 111

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

Crystallographic Directions



Algorithm

1. Vector repositioned (if necessary) to pass through origin.
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

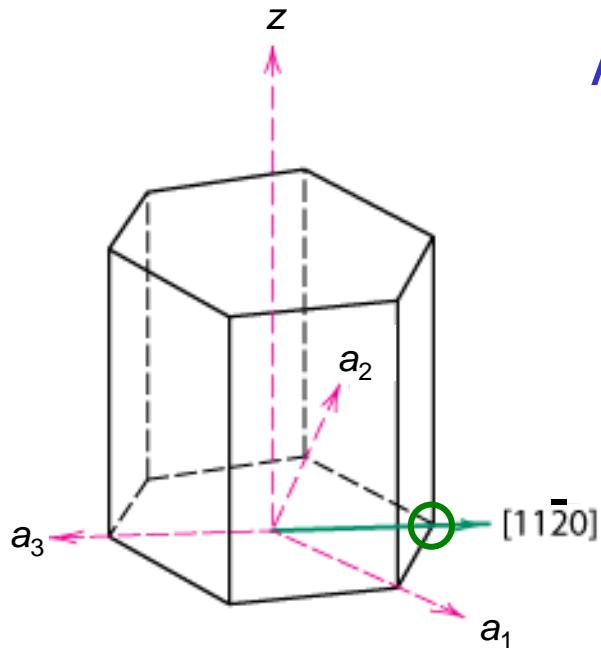
$$[uvw]$$

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

$-1, 1, 1 \Rightarrow [\bar{1}11]$ where overbar represents a negative index

families of directions $\langle uvw \rangle$

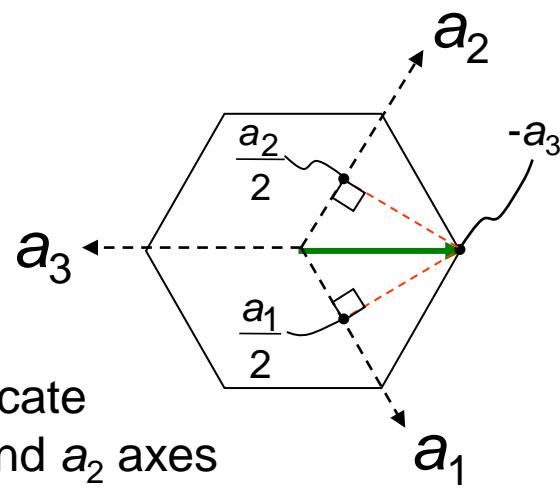
HCP Crystallographic Directions



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

ex: $\frac{1}{2}, \frac{1}{2}, -1, 0 \Rightarrow [11\bar{2}0]$

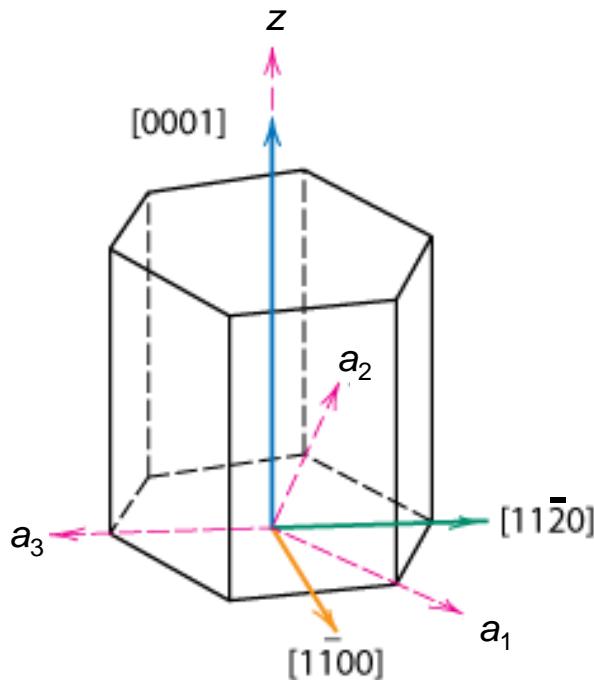
dashed red lines indicate
projections onto a_1 and a_2 axes



HCP Crystallographic Directions

- Hexagonal Crystals

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



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

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

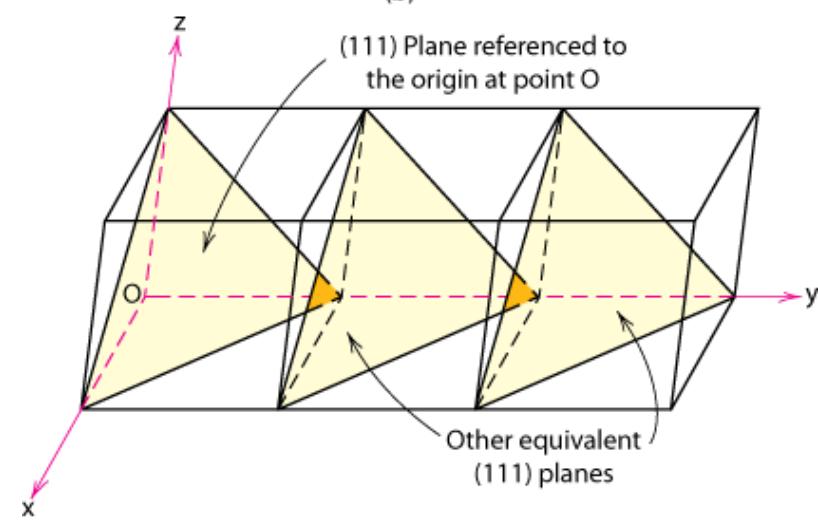
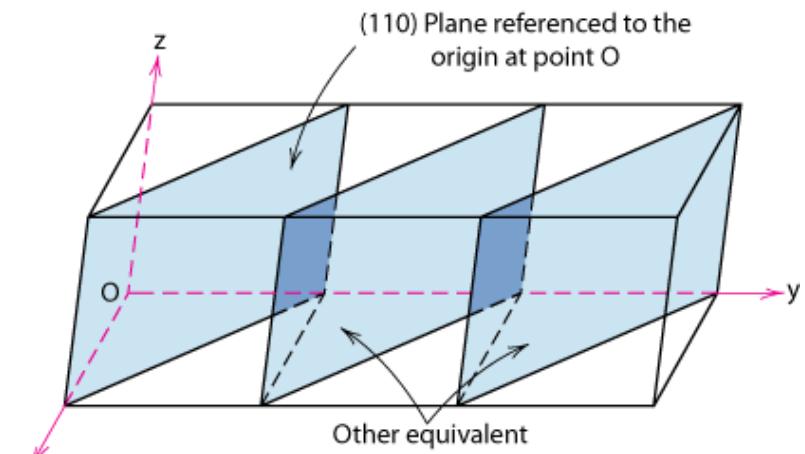
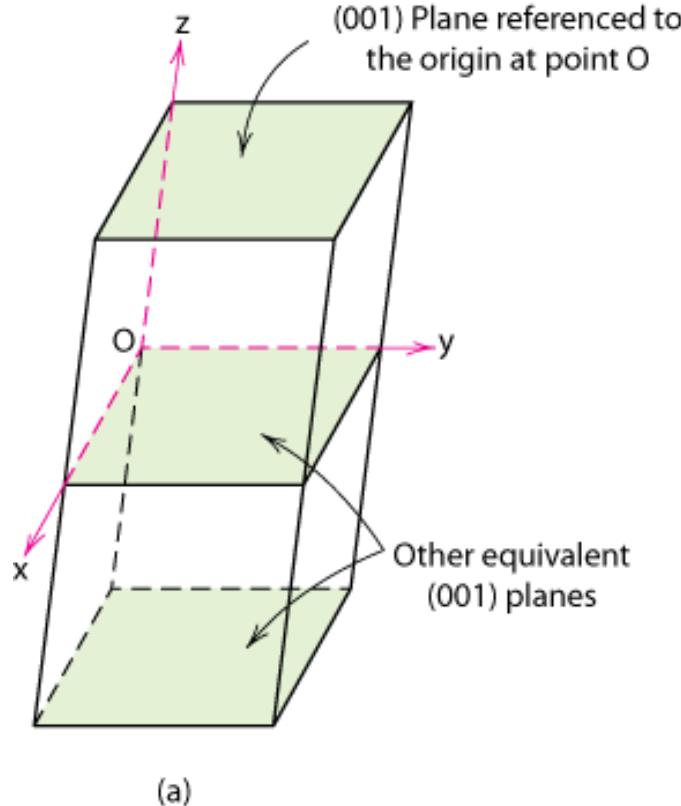
$$v = \frac{1}{3}(2v' - u')$$

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

$$w = w'$$

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

Crystallographic Planes



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

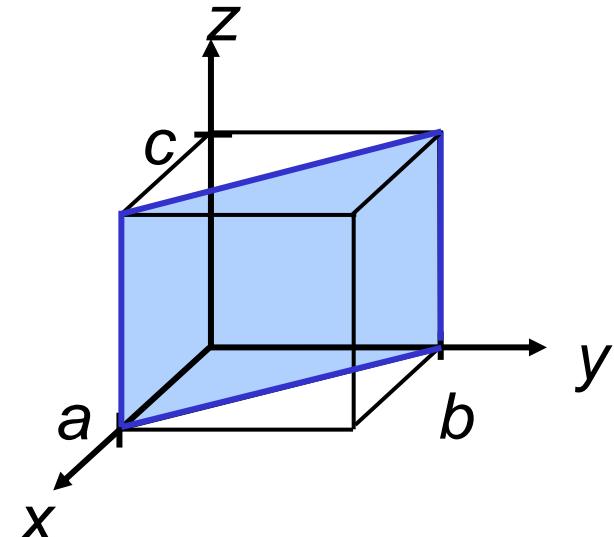
Crystallographic Planes

- Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions & common multiples. All parallel planes have same Miller indices.
- Algorithm
 1. Read off intercepts of plane with axes in terms of a , b , c
 2. Take reciprocals of intercepts
 3. Reduce to smallest integer values
 4. Enclose in parentheses, no commas i.e., (hkl)

Crystallographic Planes

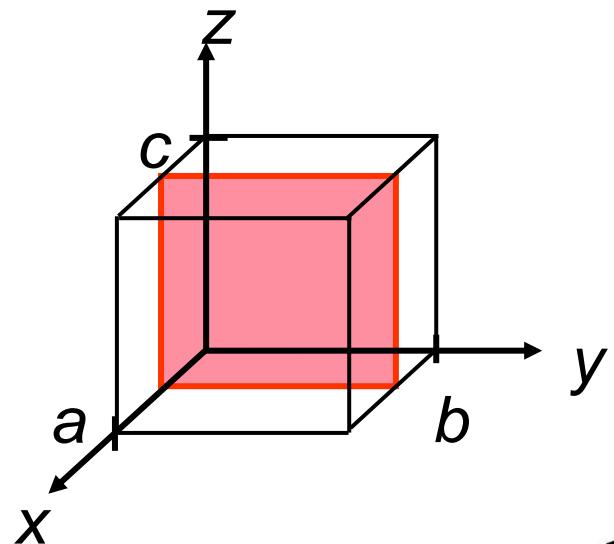
example

	a	b	c
1. Intercept	1	1	∞
2. Reciprocals	1/1	1/1	1/ ∞
	1	1	0
3. Reduction	1	1	0
4. Miller Indices	(110)		



example

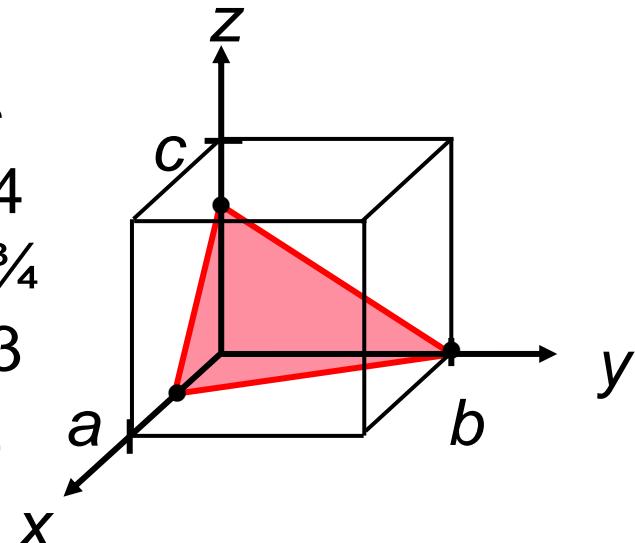
	a	b	c
1. Intercept	1/2	∞	∞
2. Reciprocals	1/½	1/ ∞	1/ ∞
	2	0	0
3. Reduction	2	0	0
4. Miller Indices	(100)		



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)		



Family of Planes $\{hk\}$

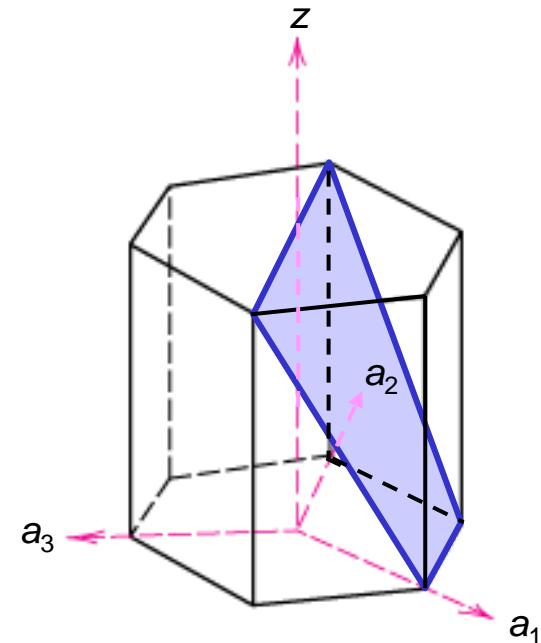
Ex: $\{100\} = (100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$

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	$(10\bar{1}1)$			



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



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.)

Fig. 11.33(c)
*Callister's Materials
Science and
Engineering,
Adapted Version.*
(Fig.11.33(c) courtesy
of Pratt and Whitney).



- Properties of crystalline materials often related to crystal structure.

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

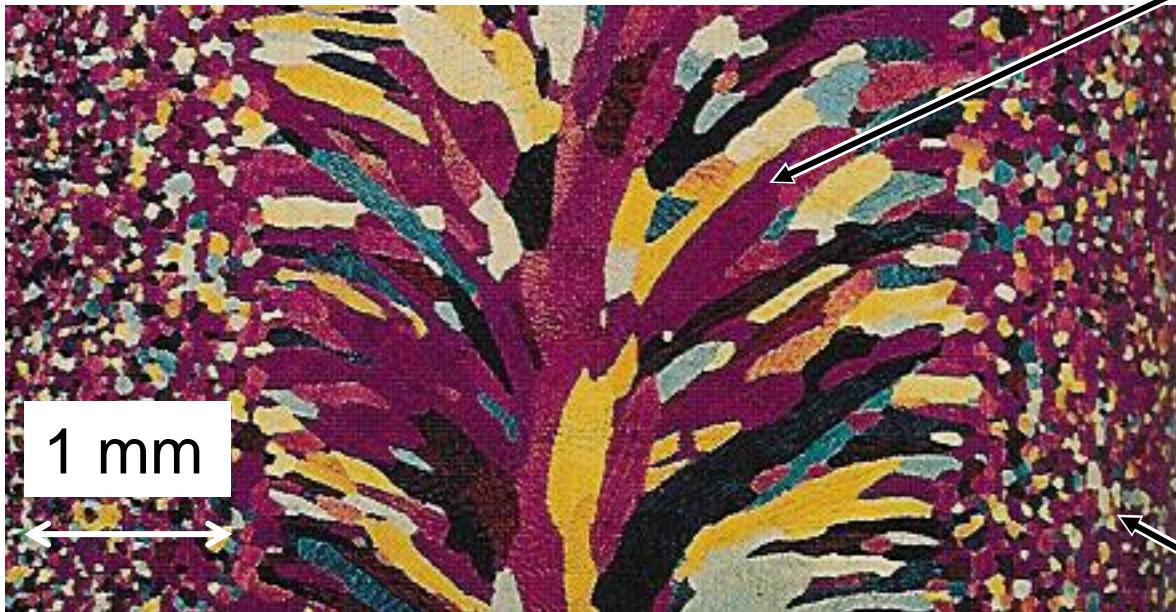


(Courtesy P.M. Anderson)



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)

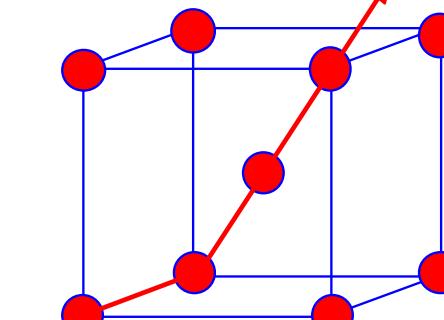
- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If grains are randomly oriented,
overall component properties are not directional.
- Grain sizes typ. range from 1 nm to 2 cm
(i.e., from a few to millions of atomic layers).

Single vs Polycrystals

- Single Crystals

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

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

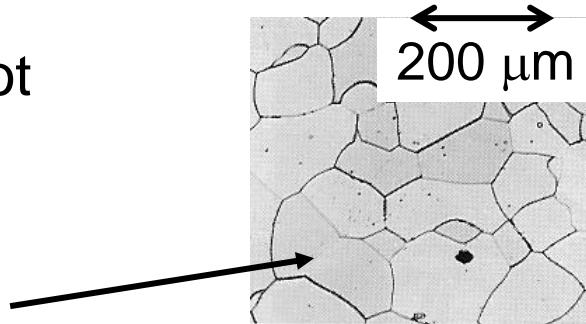


$$E \text{ (edge)} = 125 \text{ GPa}$$

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].)



SUMMARY

- Atoms may assemble into **crystalline** or **amorphous** structures.
- Crystallographic points, directions and planes are specified in terms of indexing schemes.
- Materials can be **single crystals** or **polycrystalline**. Material properties generally vary with single crystal orientation (i.e., they are **anisotropic**), but are generally non-directional (i.e., they are **isotropic**) in polycrystals with randomly oriented grains.

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems:

Chapter 4: Structures of Crystalline Solids

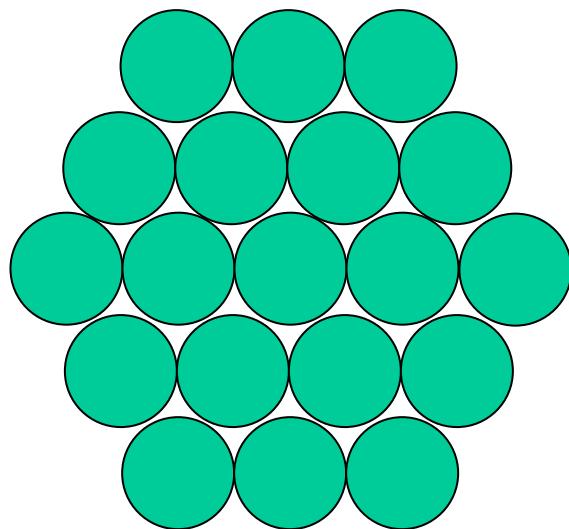
ISSUES TO ADDRESS...

- How do atoms assemble into solid structures in metallic, ceramic and polymeric materials?
- How do the structures of ceramic materials differ from those of metals?
- How do polymeric crystals accommodate the polymer chain?
- How does the density of a material depend on its structure?

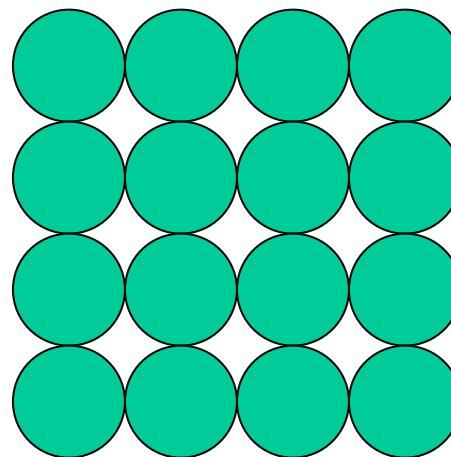


- How can we stack metal atoms to minimize empty space?

2-dimensions



vs.



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

Metallic Crystal Structures

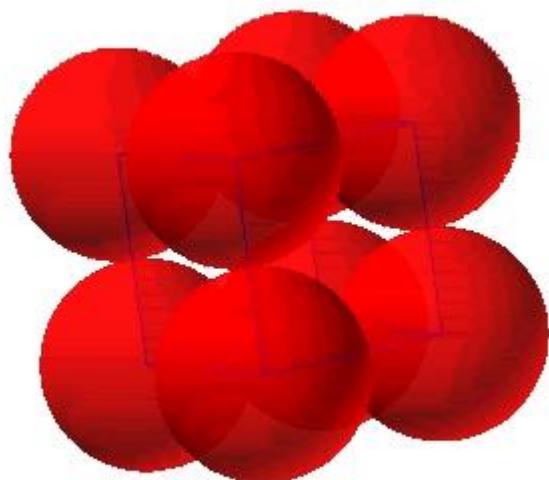
- Tend to be densely packed.
- Reasons for dense packing:
 - Typically, only one element is present, so all atomic radii are the same.
 - Metallic bonding is not directional.
 - Nearest neighbor distances tend to be small in order to lower bond energy.
 - Electron cloud shields cores from each other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

We will examine three such structures...



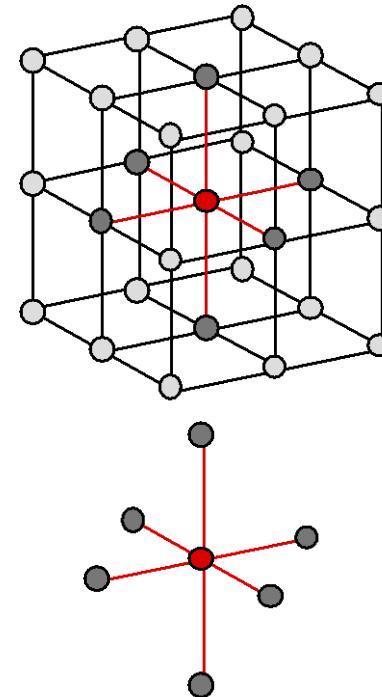
Simple Cubic Structure (SC)

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



(Courtesy P.M. Anderson)

- Coordination # = 6
(# nearest neighbors)

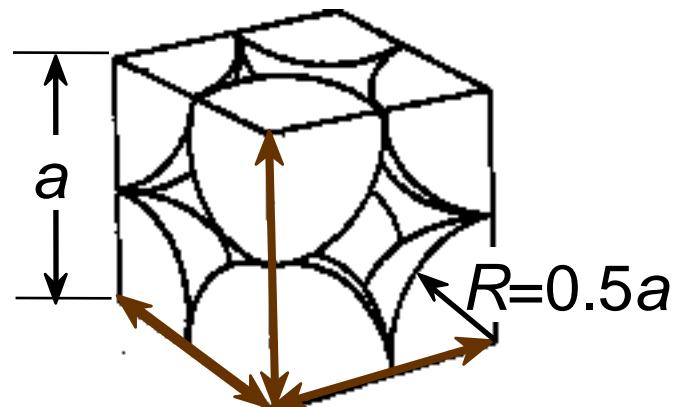


Atomic Packing Factor (APF)

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

*assume hard spheres

- APF for a simple cubic structure = 0.52



close-packed directions

contains $8 \times 1/8 =$

1 atom/unit cell

From Fig. 4.38

Callister's Materials Science and Engineering,
Adapted Version.

$$\text{APF} = \frac{\frac{\text{atoms}}{\text{unit cell}} \cdot \frac{4}{3} \pi (0.5a)^3}{a^3}$$

volume
atom

volume
unit cell

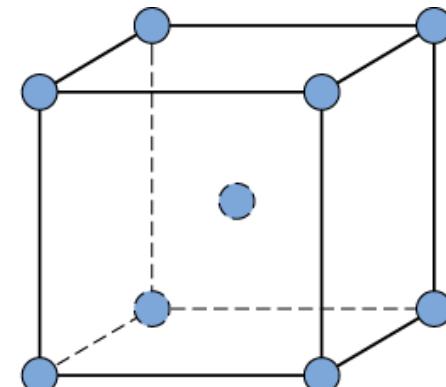
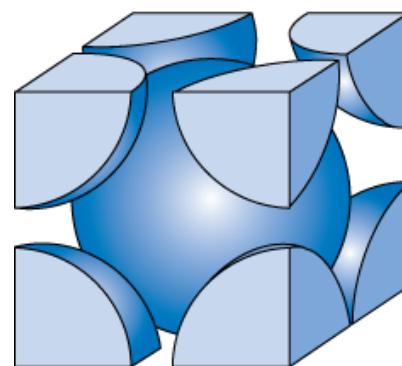
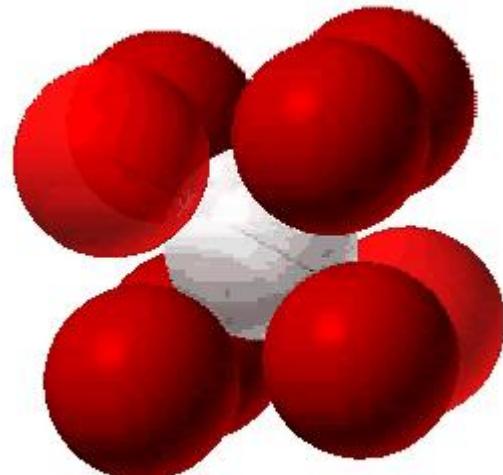
Body Centered Cubic Structure (BCC)

- Atoms touch each other along cube diagonals.

--Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

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

- Coordination # = 8



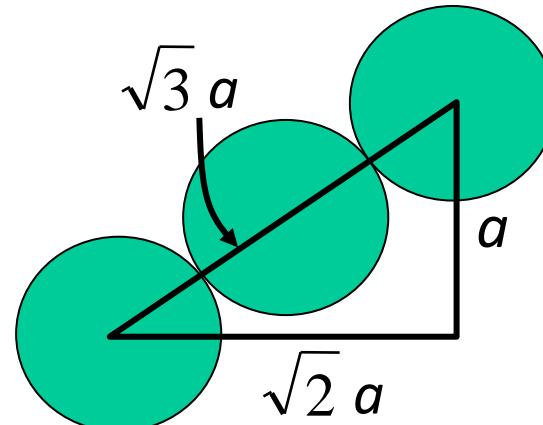
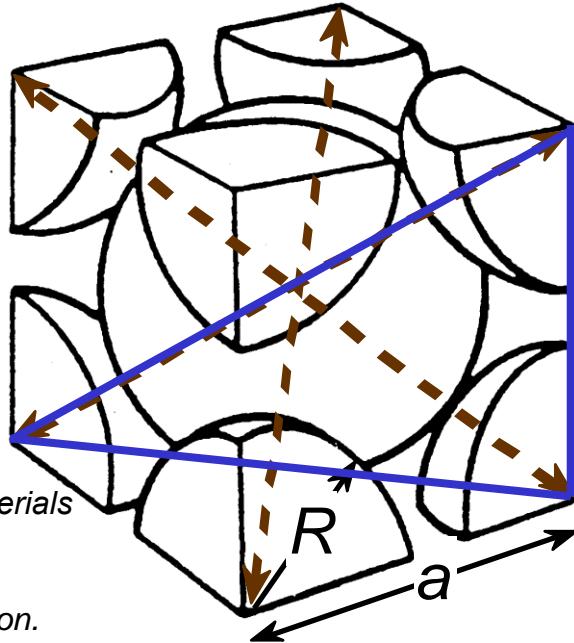
From Fig. 4.2,
Callister's Materials Science and Engineering,
Adapted Version.

(Courtesy P.M. Anderson)

2 atoms/unit cell: 1 center + 8 corners $\times \frac{1}{8}$
Chapter 4 - 6

Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68



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

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

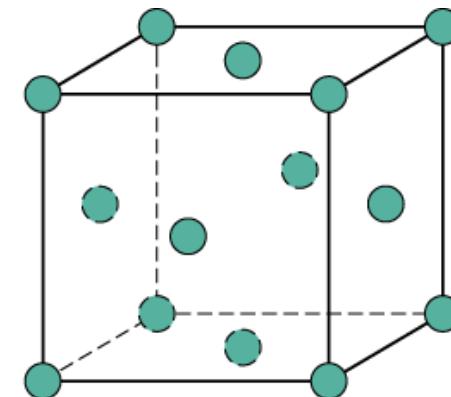
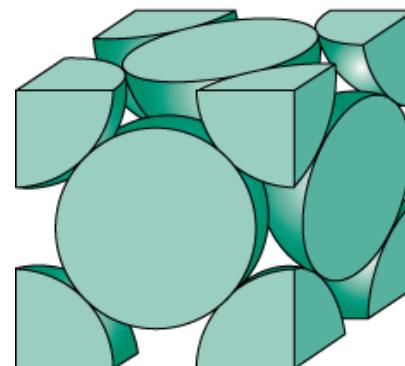
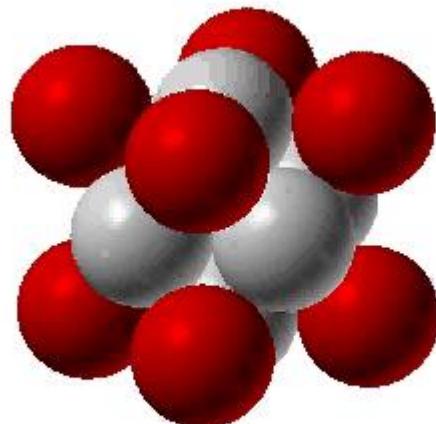
The diagram shows the derivation of the APF for BCC. It starts with the fraction $\frac{\text{atoms}}{\text{unit cell}}$, which is highlighted in green. This is multiplied by 2, highlighted in green, representing the two atoms per unit cell. This is then multiplied by the volume of one atom, highlighted in orange, given by the formula $\frac{4}{3} \pi (\sqrt{3}a/4)^3$. Finally, this is divided by the volume of the unit cell, highlighted in blue, given by 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 $\times \frac{1}{2}$ + 8 corners $\times \frac{1}{8}$

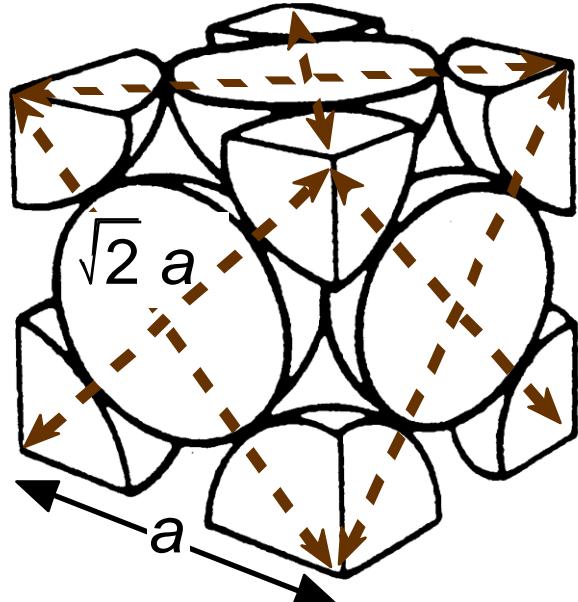
(Courtesy P.M. Anderson)

Chapter 4 - 8



Atomic Packing Factor: FCC

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



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

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

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

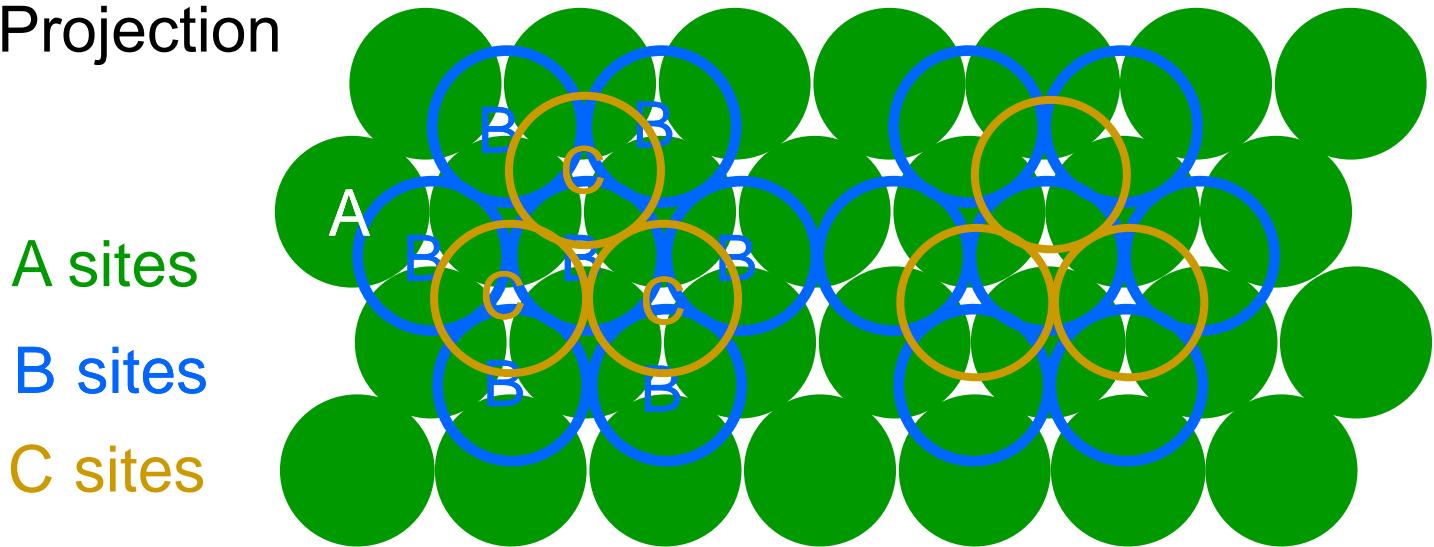
$$\text{APF} = \frac{\frac{\text{atoms}}{\text{unit cell}}}{\frac{\text{volume}}{\text{unit cell}}} = \frac{4 \frac{4}{3} \pi (\sqrt{2}a/4)^3}{a^3}$$

Annotations explain the components of the formula:

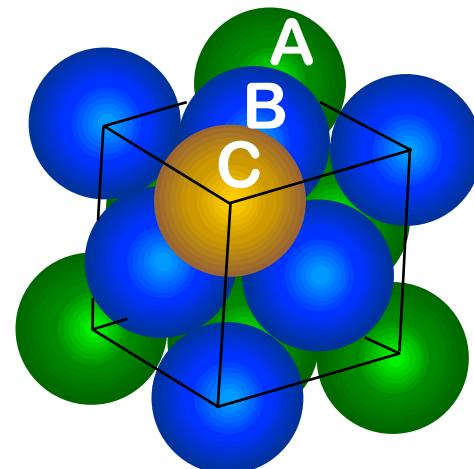
- $\frac{\text{atoms}}{\text{unit cell}}$ is shown in green.
- $\frac{\text{volume}}{\text{atom}}$ is shown in brown.
- $\frac{\text{volume}}{\text{unit cell}}$ is shown in blue.

FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

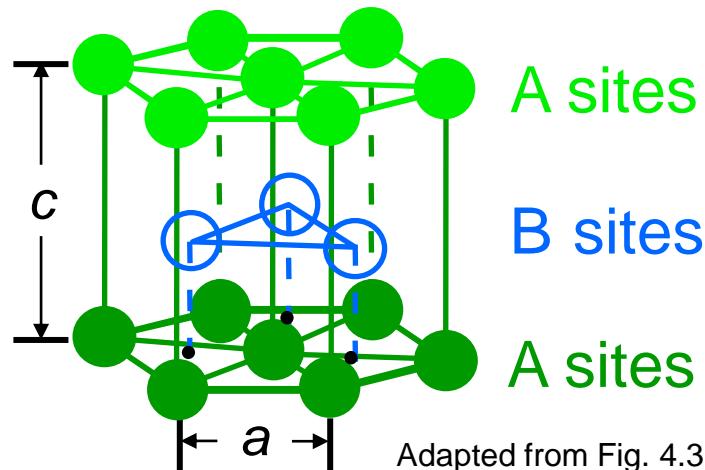


- FCC Unit Cell



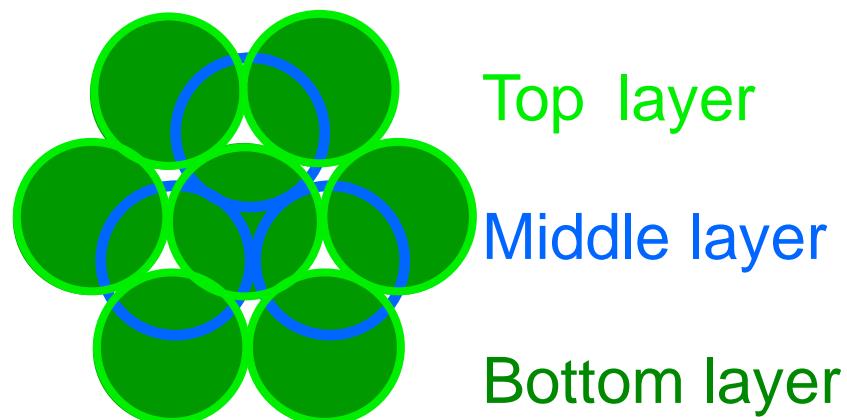
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection



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

- 2D Projection



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

6 atoms/unit cell

ex: Cd, Mg, Ti, Zn

Theoretical Density, ρ

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

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

where

n = number of atoms/unit cell

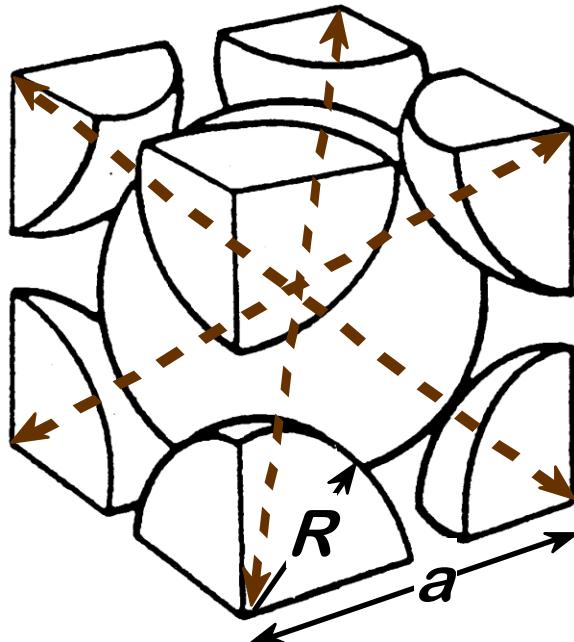
A = atomic weight

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

N_A = Avogadro's number

= 6.023×10^{23} atoms/mol

Theoretical Density, ρ



- Ex: Cr (BCC)

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

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

$$n = 2$$

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

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

Inputs:

- $\frac{\text{atoms}}{\text{unit cell}}$ (green box) = 2
- A (orange box) = 52.00 g/mol
- $\frac{\text{volume}}{\text{unit cell}}$ (blue box) = $a^3 \times 6.023 \times 10^{23}$
- $\frac{\text{atoms}}{\text{mol}}$ (purple box) = 2

Outputs:

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

Densities of Material Classes

In general

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

Why?

Metals have...

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

Ceramics have...

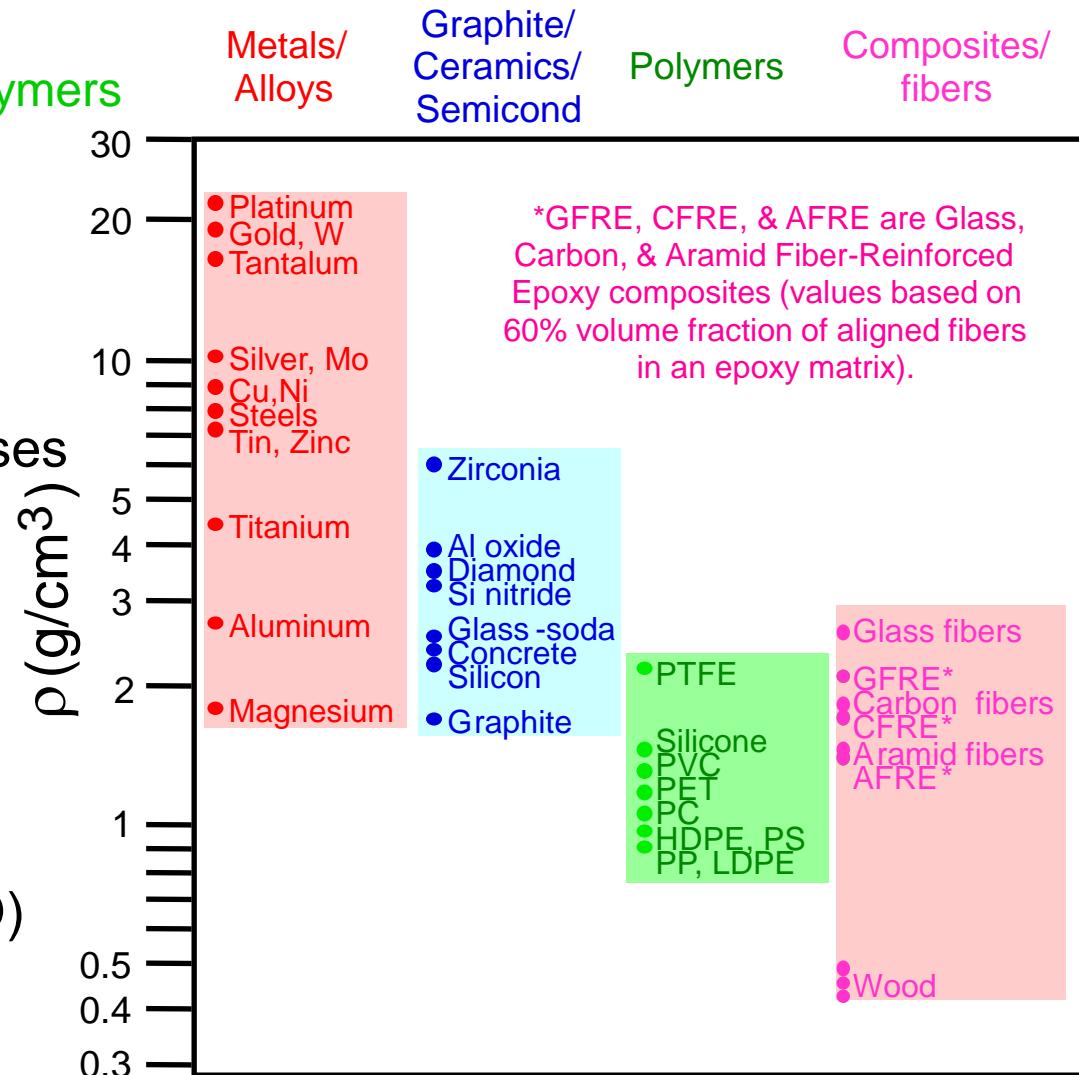
- less dense packing
- often lighter elements

Polymers have...

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

Composites have...

- intermediate values



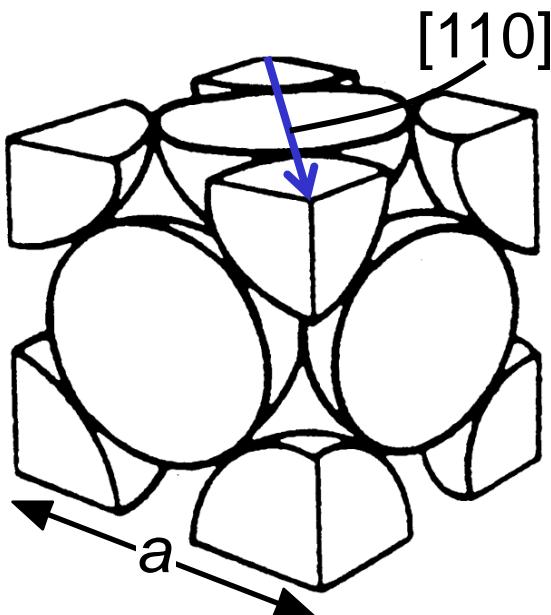
Data from Table B1
Callister's Materials Science and Engineering,
Adapted Version.

Chapter 4 - 14



Linear Density

- Linear Density of Atoms $\equiv LD = \frac{\text{Number of atoms}}{\text{Unit length of direction vector}}$



ex: linear density of Al in [110] direction

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

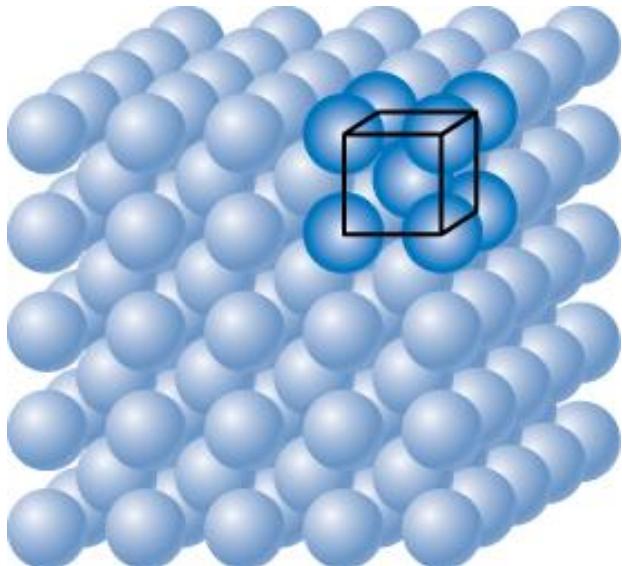
$$LD = \frac{\text{# atoms}}{\text{length}} = \frac{2}{\sqrt{2}a} = 3.5 \text{ nm}^{-1}$$

Atomic Packing of Crystallographic Planes

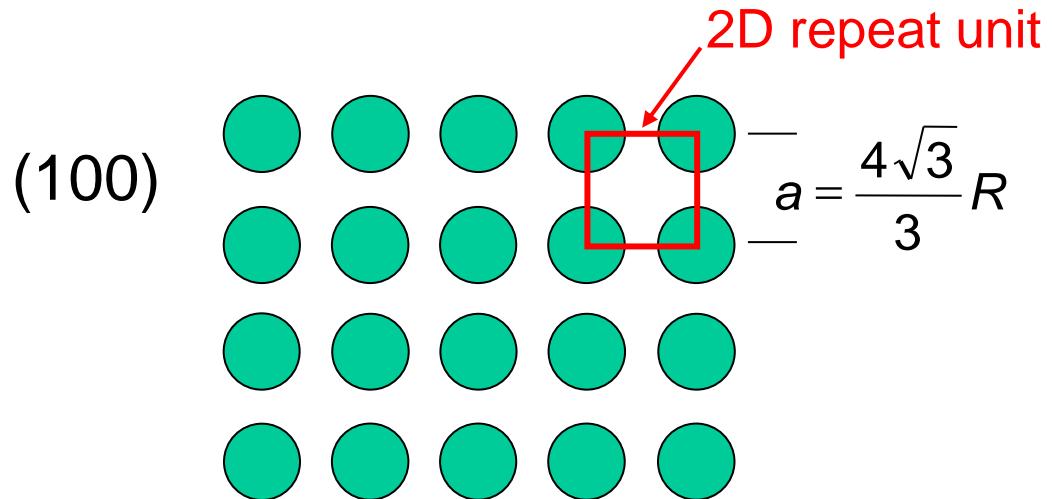
- We want to examine the atomic packing of crystallographic planes
- Iron foil can be used as a catalyst. The atomic packing of the exposed planes is important.
 - a) Draw (100) and (111) crystallographic planes for Fe.
 - b) Calculate the planar density for each of these planes.

Planar Density of (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.



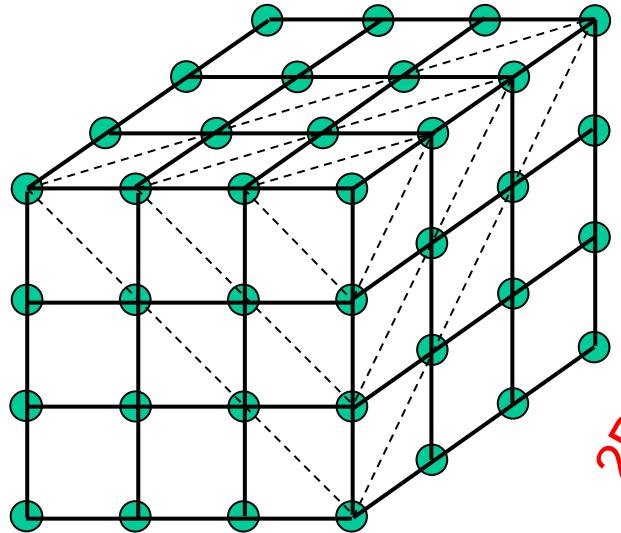
Radius of iron $R = 0.1241 \text{ nm}$

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

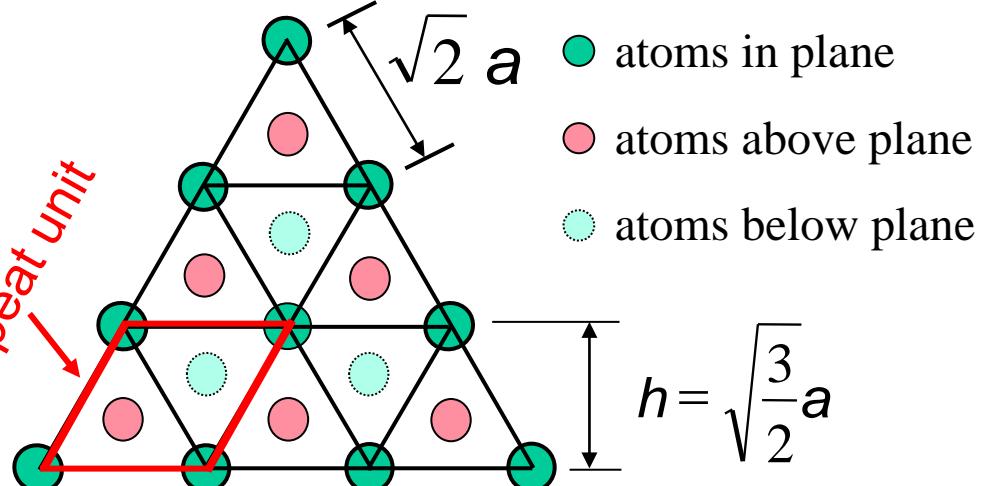
Planar Density of (111) Iron

Solution (cont): (111) plane

1 atom in plane/ unit surface cell



2D repeat unit



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

atoms
—
2D repeat unit

1

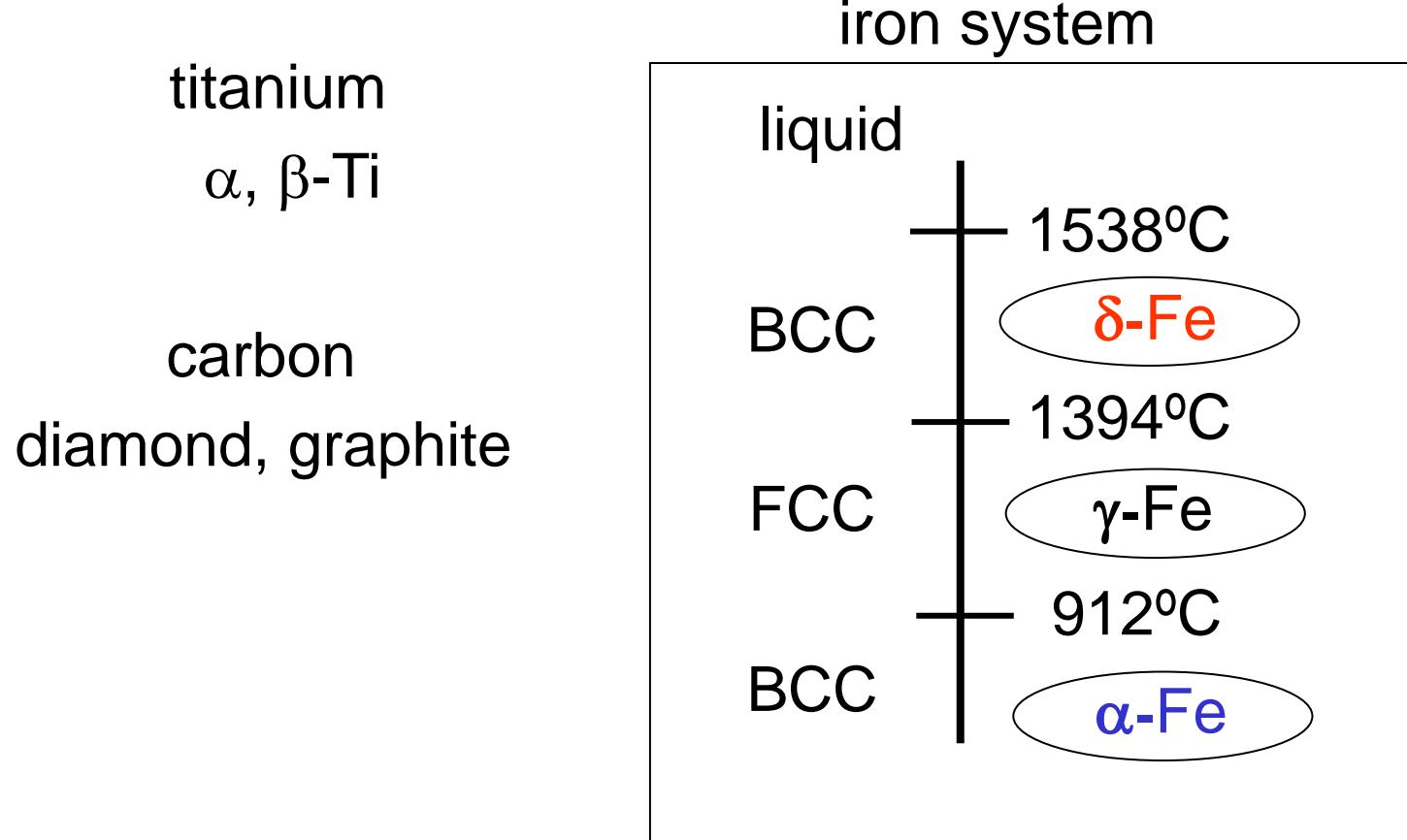
$$\text{Planar Density} = \frac{\text{atoms}}{\frac{\text{area}}{\text{2D repeat unit}}} = \frac{1}{\frac{16\sqrt{3}}{3} R^2} = 7.0 \frac{\text{atoms}}{\text{nm}^2}$$

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



Section 4.9 – Polymorphism

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



Ceramic Crystal Structures

Oxide structures

- oxygen anions much larger than metal cations
- close packed oxygen in a lattice (usually FCC)
- cations in the holes of the oxygen lattice

Site Selection

Which sites will cations occupy?

1. Size of sites

- does the cation fit in the site

2. Stoichiometry

- if all of one type of site is full the remainder have to go into other types of sites.

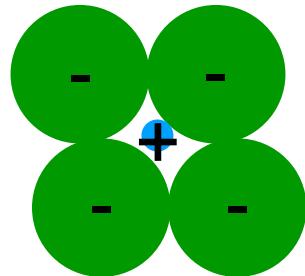
3. Bond Hybridization



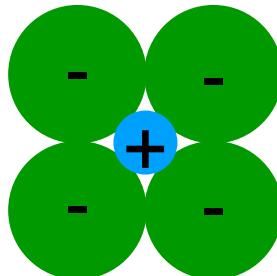
Ionic Bonding & Structure

1. Size - Stable structures:

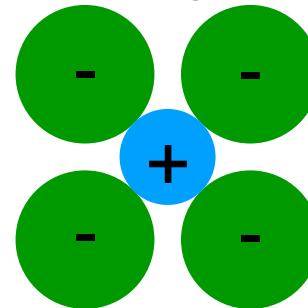
--maximize the # of nearest oppositely charged neighbors.



unstable



stable

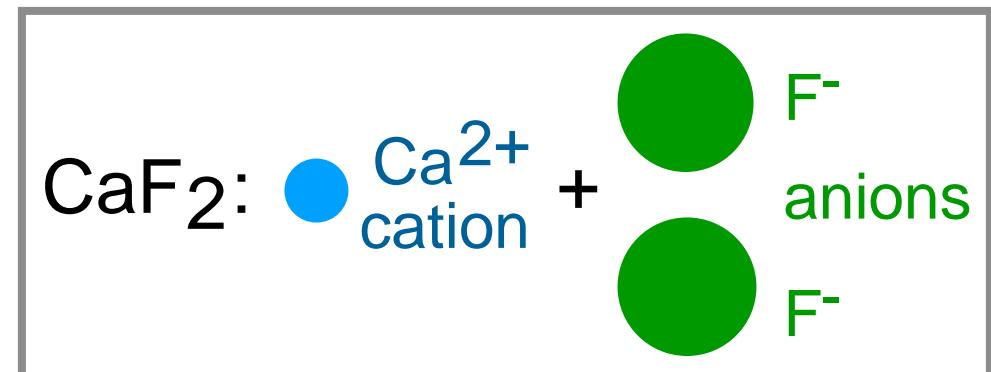


stable

From Fig. 4.10
*Callister's Materials
Science and Engineering,
Adapted Version.*

- **Charge Neutrality:**

--Net charge in the structure should be zero.



--General form: $A_m X_p$



m, p determined by charge neutrality

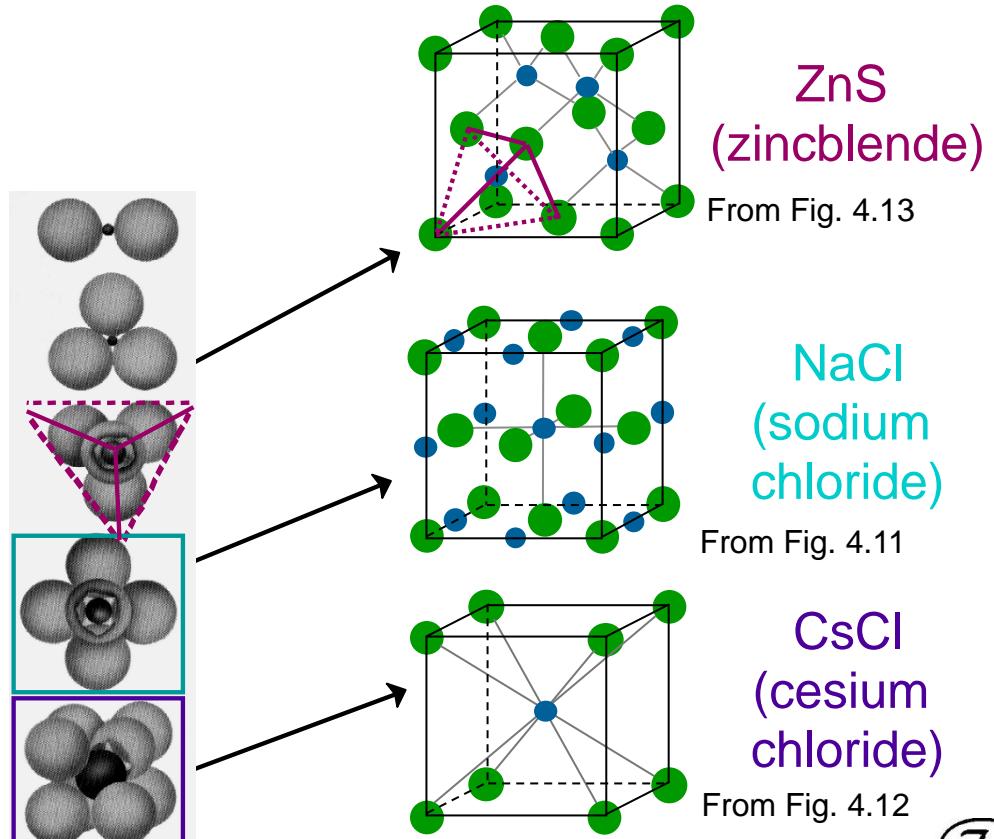
Coordination # and Ionic Radii

- Coordination # increases with $\frac{r_{\text{cation}}}{r_{\text{anion}}}$

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

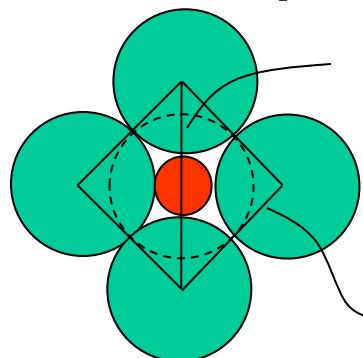
$\frac{r_{\text{cation}}}{r_{\text{anion}}}$	Coord #	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	T_D
0.414 - 0.732	6	O_H
0.732 - 1.0	8	cubic

Adapted from Table 4.3



Cation Site Size

- Determine minimum $r_{\text{cation}}/r_{\text{anion}}$ for O_H site (C.N. = 6)



$$2r_{\text{anion}} + 2r_{\text{cation}} = \sqrt{2}a$$

$$a = 2r_{\text{anion}}$$

$$2r_{\text{anion}} + 2r_{\text{cation}} = 2\sqrt{2}r_{\text{anion}}$$

$$r_{\text{anion}} + r_{\text{cation}} = \sqrt{2}r_{\text{anion}} \quad r_{\text{cation}} = (\sqrt{2} - 1)r_{\text{anion}}$$

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = 0.414$$

Site Selection II

2. Stoichiometry

- If all of one type of site is full the remainder have to go into other types of sites.

Ex: FCC unit cell has 4 O_H and 8 T_D sites.

If for a specific ceramic each unit cell has 6 cations and the cations prefer O_H sites

4 in O_H

2 in T_D



Site Selection III

3. Bond Hybridization – significant covalent bonding

- the hybrid orbitals can have impact if significant covalent bond character present
- For example in SiC
 - $X_{\text{Si}} = 1.8$ and $X_{\text{C}} = 2.5$

$$\% \text{ ionic character} = 100 \{1 - \exp[-0.25(X_{\text{Si}} - X_{\text{C}})^2]\} = 11.5\%$$

- ca. 89% covalent bonding
- both Si and C prefer sp^3 hybridization
- Therefore in SiC get T_D sites



Example: Predicting Structure of FeO

- On the basis of ionic radii, what crystal structure would you predict for FeO?

Cation Ionic radius (nm)

Al³⁺ 0.053

Fe²⁺ 0.077

Fe³⁺ 0.069

Ca²⁺ 0.100

Anion

O²⁻ 0.140

Cl⁻ 0.181

F⁻ 0.133

- Answer:

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.077}{0.140} = 0.550$$

based on this ratio,
--coord # = 6
--structure = NaCl

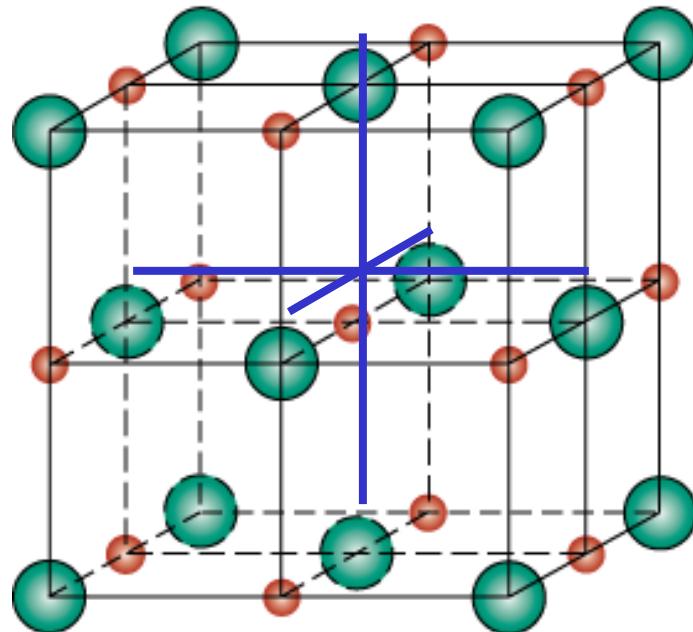
Data from Table 4.4
*Callister's Materials
Science and Engineering,
Adapted Version.*



Rock Salt Structure

Same concepts can be applied to ionic solids in general.

Example: NaCl (rock salt) structure



From Fig. 4.11
Callister's Materials
Science and
Engineering,
Adapted Version.

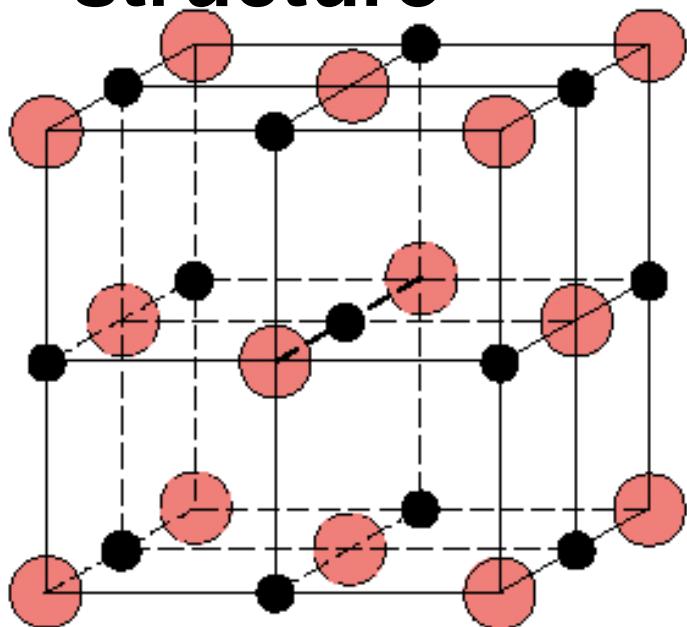
● Na^+ $r_{\text{Na}} = 0.102 \text{ nm}$
● Cl^- $r_{\text{Cl}} = 0.181 \text{ nm}$

$$r_{\text{Na}}/r_{\text{Cl}} = 0.564$$

∴ cations prefer O_H sites

MgO and FeO

MgO and FeO also have the NaCl structure



● O²⁻ $r_O = 0.140 \text{ nm}$
● Mg²⁺ $r_{Mg} = 0.072 \text{ nm}$

$$r_{Mg}/r_O = 0.514$$

∴ cations prefer O_H sites

From Fig. 4.11
Callister's Materials Science and Engineering, Adapted Version.

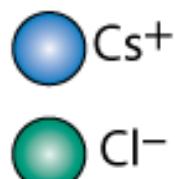
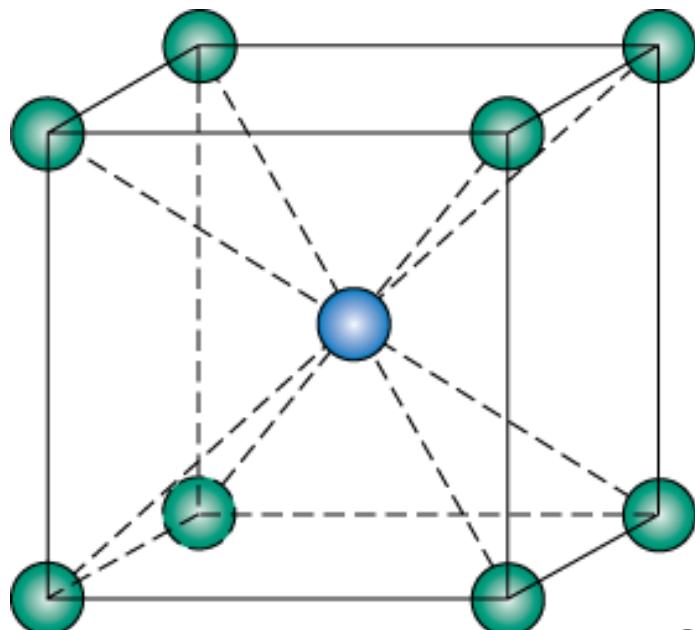
So each oxygen has 6 neighboring Mg²⁺



AX Crystal Structures

AX–Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:



$$\frac{r_{\text{Cs}^+}}{r_{\text{Cl}^-}} = \frac{0.170}{0.181} = 0.939$$

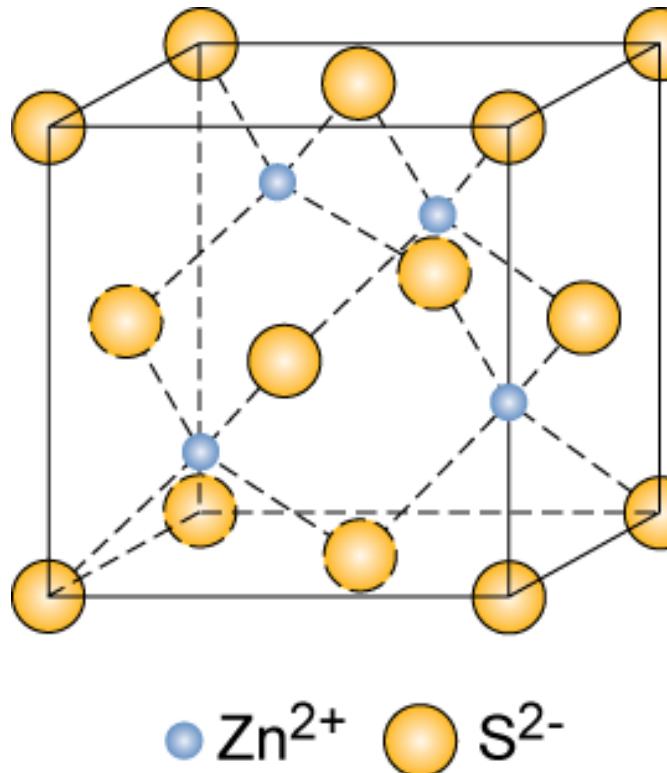
∴ cubic sites preferred

So each Cs^+ has 8 neighboring Cl^-

From Fig. 4.12
*Callister's Materials
Science and
Engineering,
Adapted Version.*

AX Crystal Structures

Zinc Blende structure



From Fig. 4.13
Callister's Materials Science and
Engineering, Adapted Version.

Ex: ZnO, ZnS, SiC

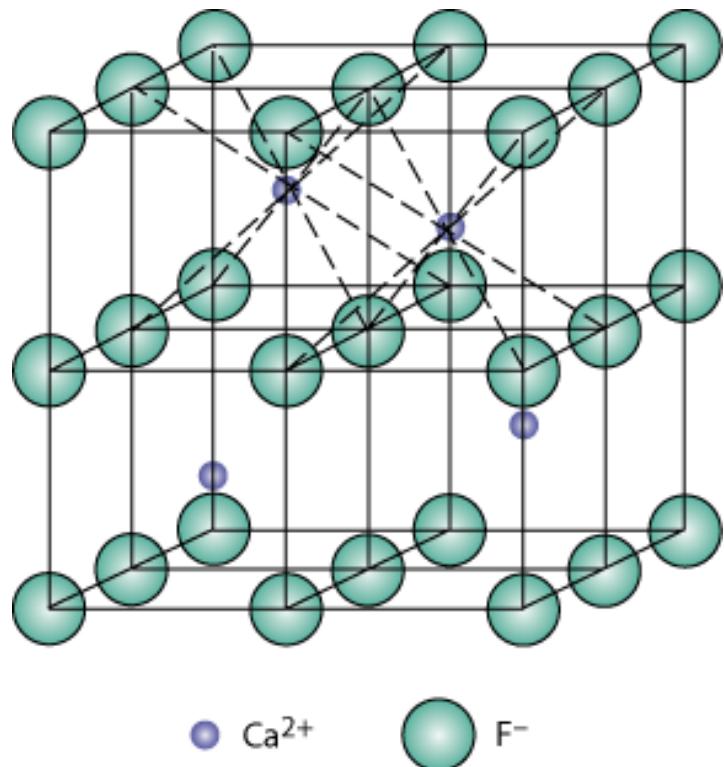
$$\frac{r_{\text{Zn}^{2+}}}{r_{\text{O}^{2-}}} = \frac{0.074}{0.140} = 0.529 \Rightarrow O_H??$$

- Size arguments predict Zn²⁺ in O_H sites,
- In observed structure Zn²⁺ in T_D sites
- **Why is Zn²⁺ in T_D sites?**
 - bonding hybridization of zinc favors T_D sites

So each Zn²⁺ has 4 neighboring O²⁻

AX_2 Crystal Structures

Fluorite structure



- Calcium Fluorite (CaF_2)
- cations in cubic sites
- UO_2 , ThO_2 , ZrO_2 , CeO_2
- antifluorite structure – cations and anions reversed

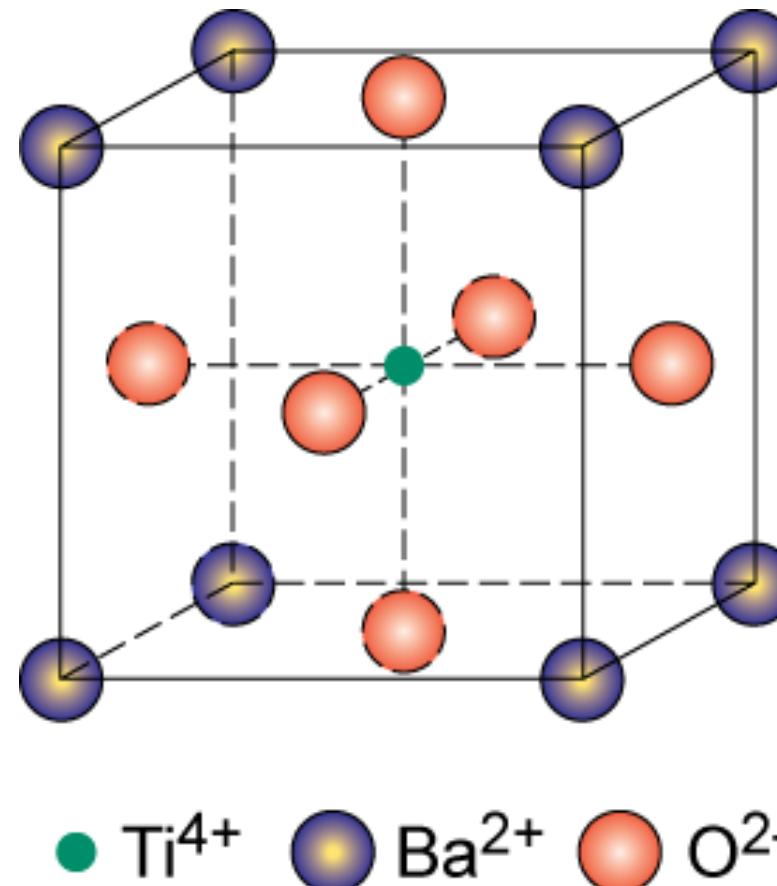
From Fig. 4.14

Callister's Materials Science and Engineering
Adapted Version.

ABX_3 Crystal Structures

Perovskite structure

Ex: complex oxide



From Fig. 4.15
Callister's Materials Science and Engineering
Adapted Version.

Mechanical Properties

We know that ceramics are more brittle than metals. Why?

- Consider method of deformation (will learn later in chapters on mechanical properties – Chapter 9 and 10)
 - slippage along slip planes
 - in ionic solids this slippage is very difficult
 - too much energy needed to move one anion past another anion



Ceramic Density Computation

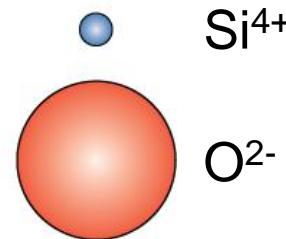
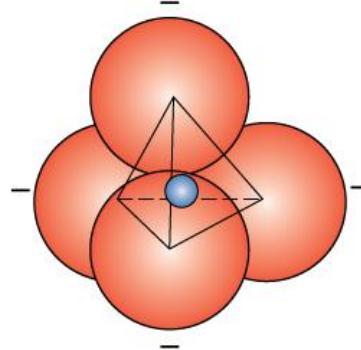
Number of formula units/unit cell

$$\rho = \frac{n'(\Sigma A_C + \Sigma A_A)}{V_C N_A}$$

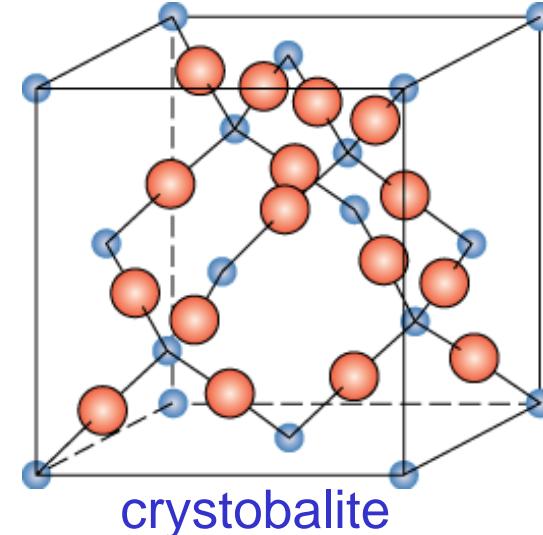
Volume of unit cell

Silicate Ceramics

Most common elements on earth are Si & O



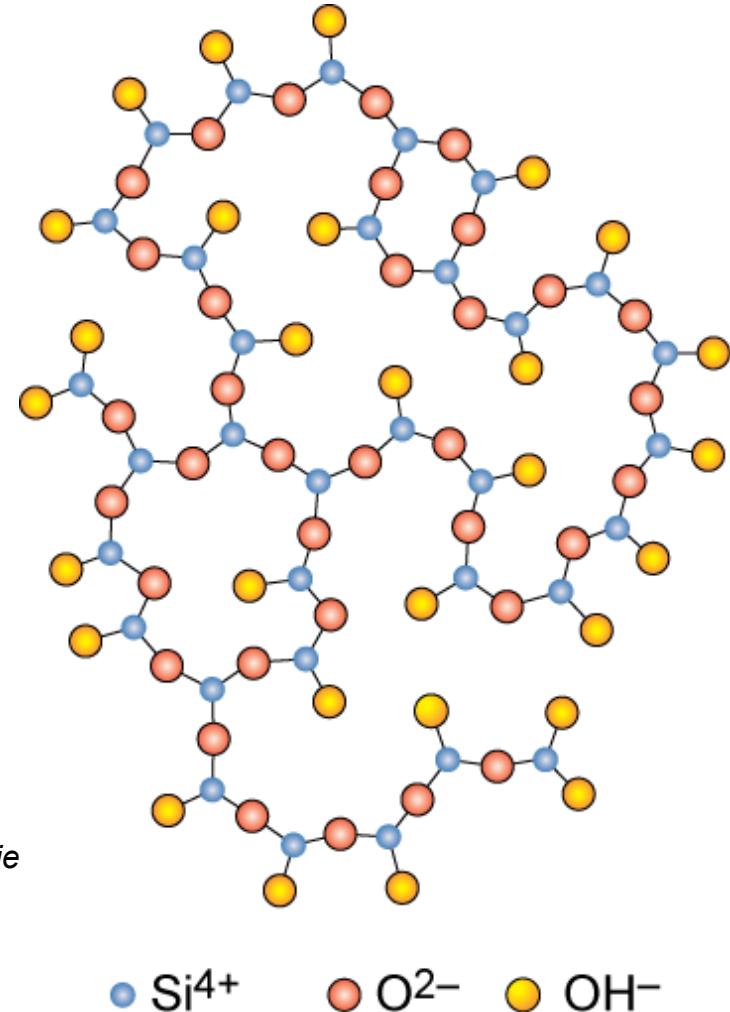
From Figs. 4.18 and 4.19
*Callister's Materials Science
and Engineering*
Adapted Version.



- **SiO_2 (silica) structures are quartz, crystobalite, & tridymite**
- **The strong Si-O bond leads to a strong, high melting material (1710°C)**

Amorphous Silica

- **Silica gels - amorphous SiO_2**
 - Si^{4+} and O^{2-} not in well-ordered lattice
 - Charge balanced by H^+ (to form OH^-) at “dangling” bonds
 - very high surface area $> 200 \text{ m}^2/\text{g}$
 - SiO_2 is quite stable, therefore unreactive
 - makes good catalyst support



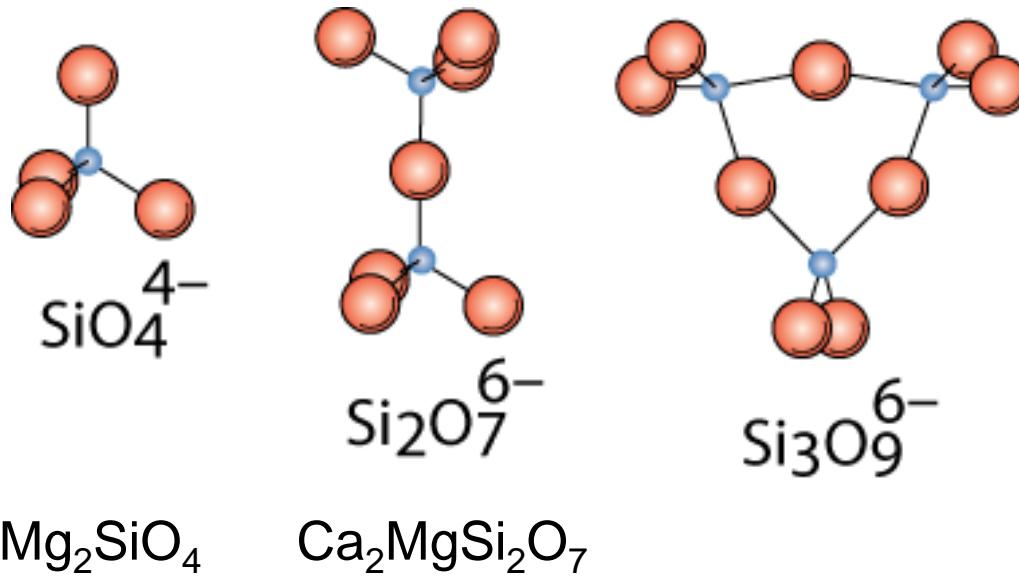
From Fig. 4.20
Callister's Materials Science and Engineering
Adapted Version.

Silica Glass

- **Dense form of amorphous silica**
 - Charge imbalance corrected with “counter cations” such as Na^+
 - Borosilicate glass is the pyrex glass used in labs
 - better temperature stability & less brittle than sodium glass

Silicates

- Combine SiO_4^{4-} tetrahedra by having them share corners, edges, or faces

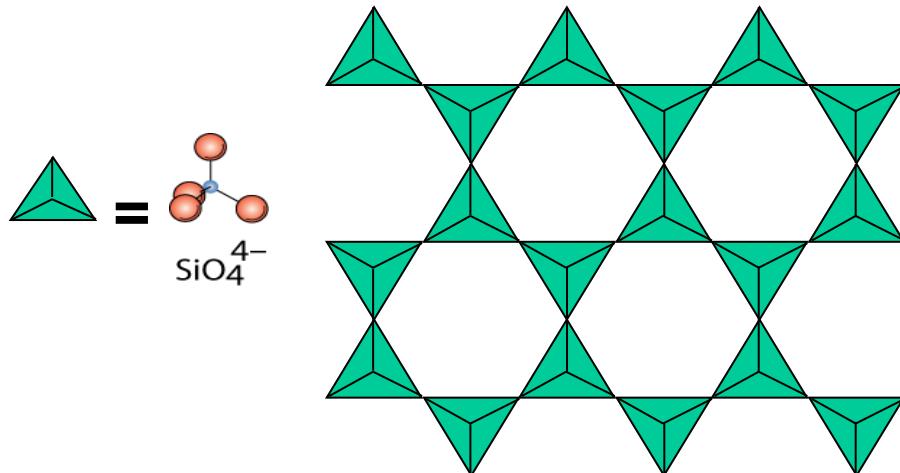


From Fig. 4.21
*Callister's Materials
Science and Engineering
Adapted Version.*

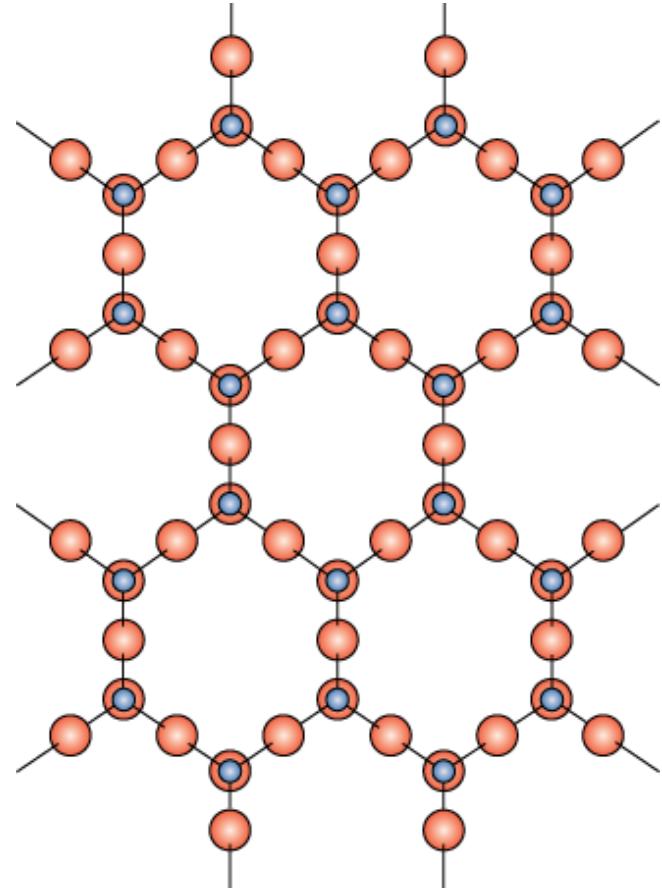
- Cations such as Ca^{2+} , Mg^{2+} , & Al^{3+} act to neutralize & provide ionic bonding

Layered Silicates

- Layered silicates (clay silicates)
 - SiO_4 tetrahedra connected together to form 2-D plane



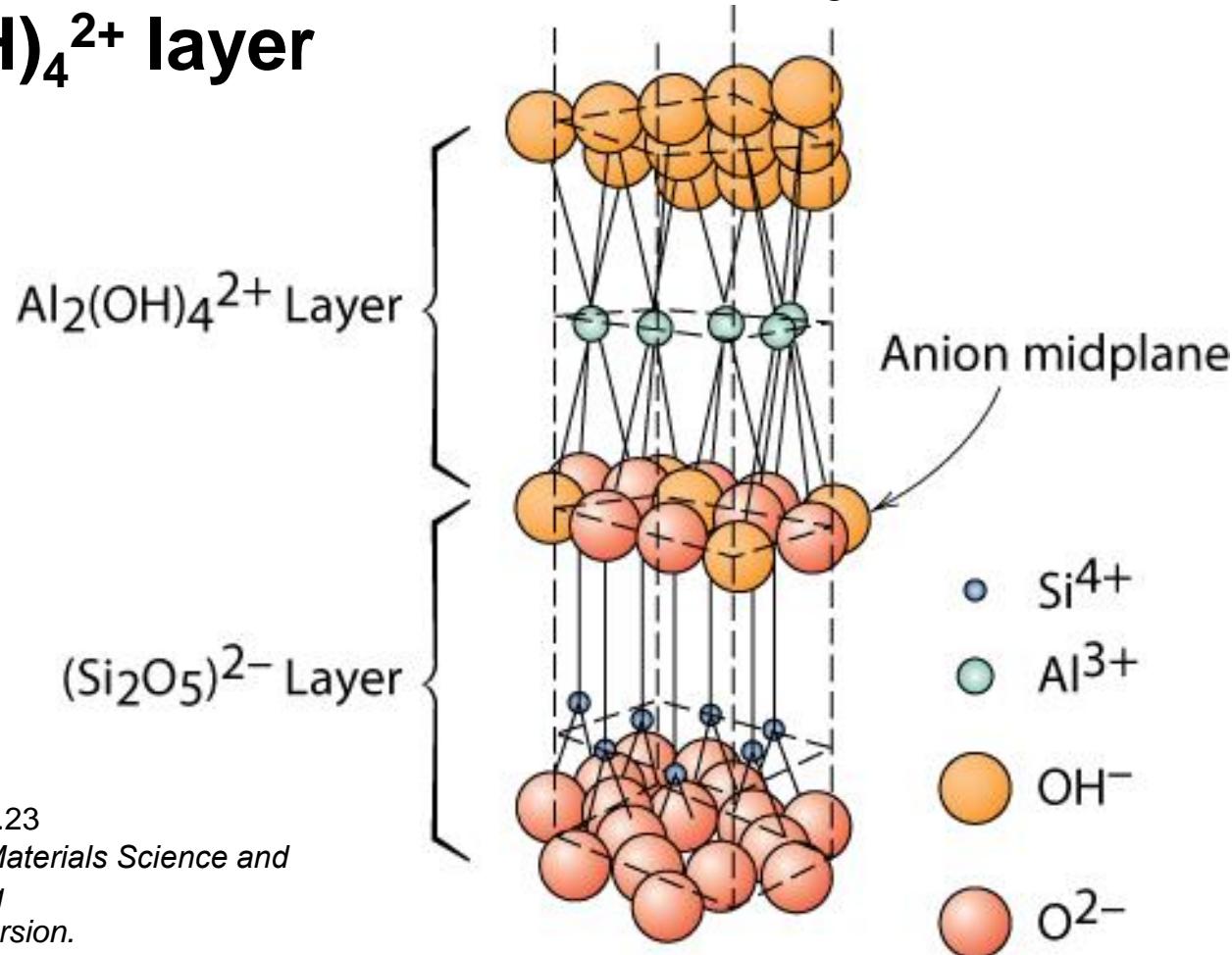
- $(\text{Si}_2\text{O}_5)^{2-}$
- So need cations to balance charge



From Fig. 4.22
Callister's Materials Science and Engineering, Adapted Version.

Layered Silicates

- Kaolinite clay alternates $(\text{Si}_2\text{O}_5)^{2-}$ layer with $\text{Al}_2(\text{OH})_4^{2+}$ layer



From Fig. 4.23
Callister's Materials Science and
Engineering
Adapted Version.

Note: these sheets loosely bound by van der Waal's forces

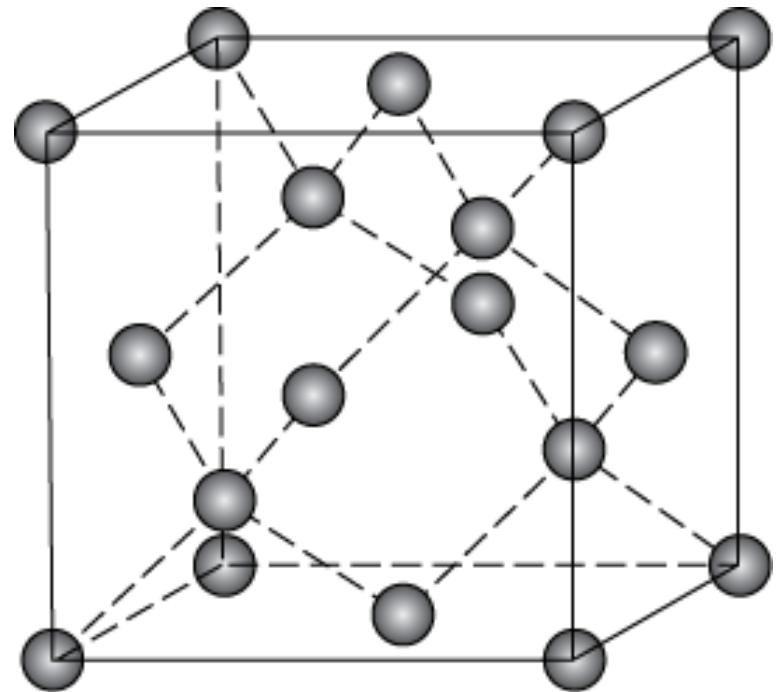
Layered Silicates

- Can change the counterions
 - this changes layer spacing
 - the layers also allow absorption of water
- Micas $KAl_3Si_3O_{10}(OH)_2$
- Bentonite
 - used to seal wells
 - packaged dry
 - swells 2-3 fold in H_2O
 - pump in to seal up well so no polluted ground water seeps in to contaminate the water supply.



Carbon Forms

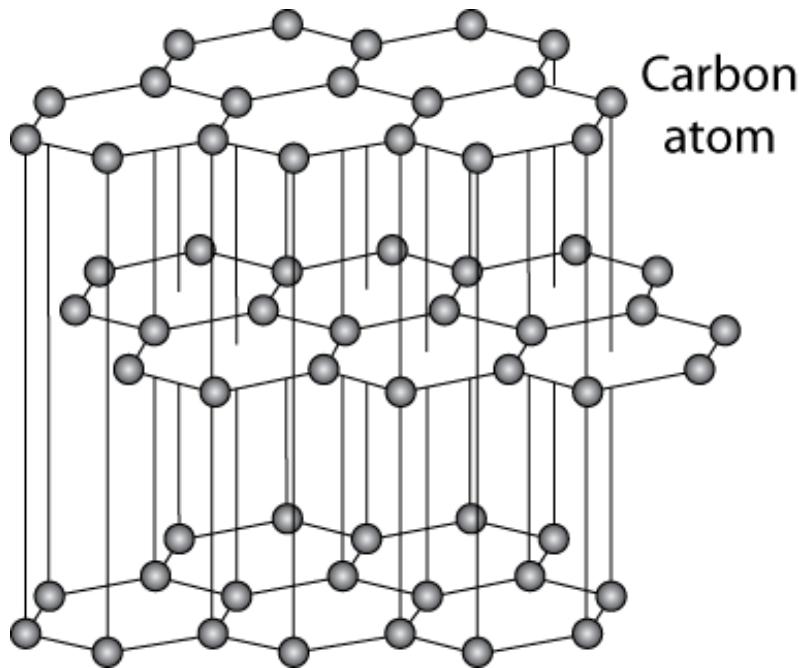
- **Carbon black – amorphous**
 - surface area ca. 1000 m²/g
- **Diamond**
 - tetrahedral carbon
 - hard – no good slip planes
 - brittle – can cut it
 - **large diamonds** – jewelry
 - **small diamonds**
 - often man made - used for cutting tools and polishing
 - **diamond films**
 - hard surface coat – tools, medical devices, etc.



From Fig. 4.24
Callister's Materials Science and Engineering
Adapted Version.

Carbon Forms - Graphite

- **layer structure – aromatic layers**

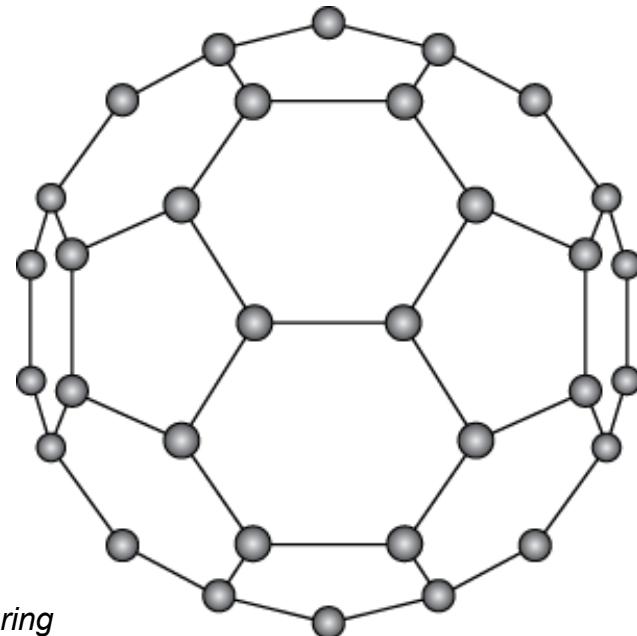
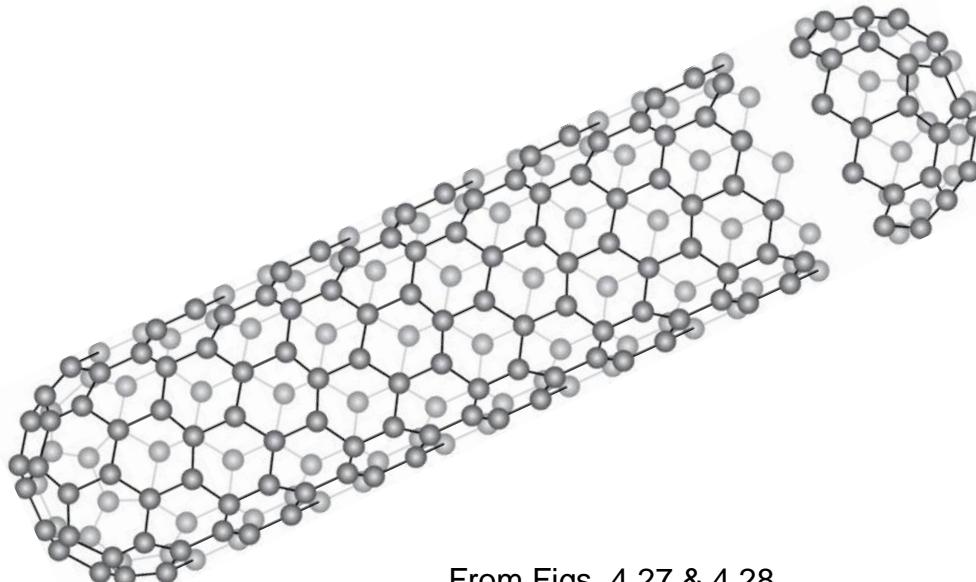


From Fig. 4.26
*Callister's Materials Science and Engineering
Adapted Version.*

- **weak van der Waal's forces between layers**
- **planes slide easily, good lubricant**

Carbon Forms – Fullerenes and Nanotubes

- **Fullerenes or carbon nanotubes**
 - wrap the graphite sheet by curving into ball or tube
 - **Buckminster fullerenes**
 - Like a soccer ball C_{60} - also C_{70} + others

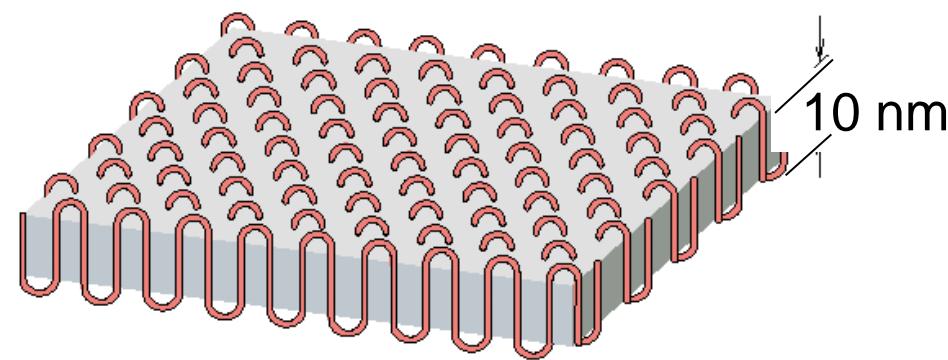


From Figs. 4.27 & 4.28
Callister's Materials Science and Engineering
Adapted Version.

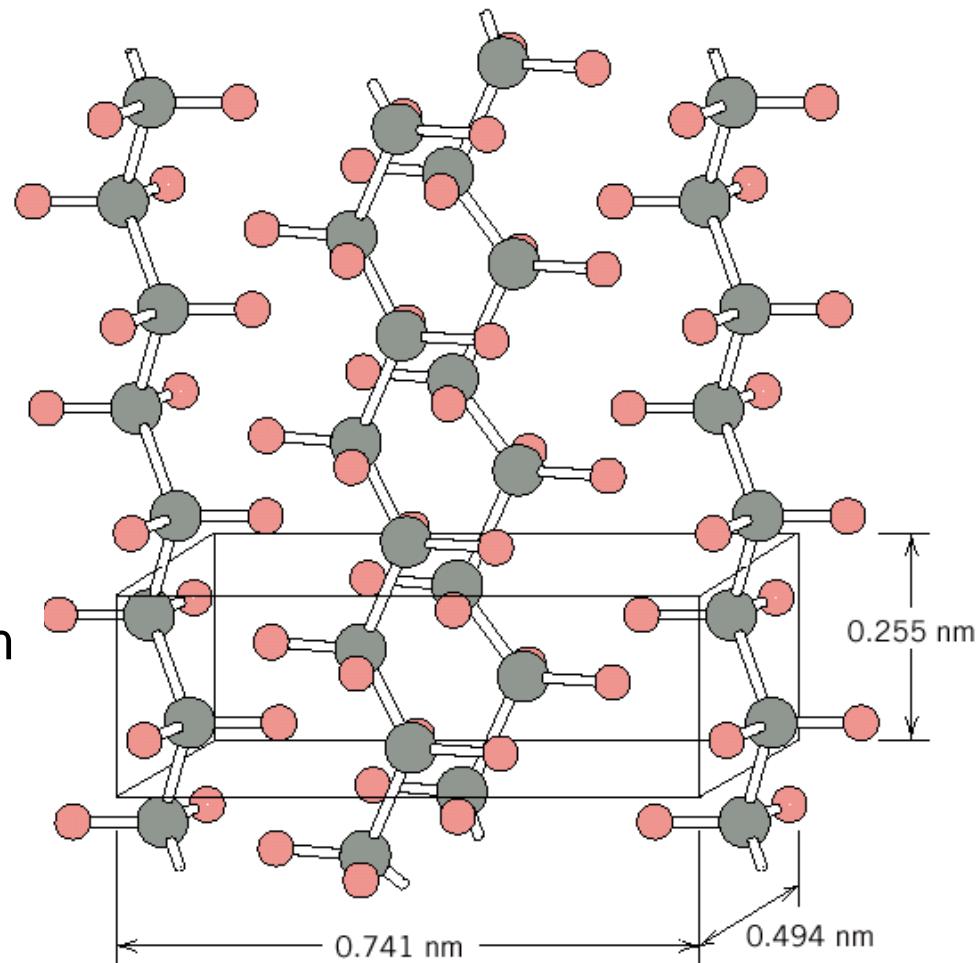
Polymer Crystallinity

Ex: polyethylene unit cell

- Crystals must contain the polymer chains in some way
 - Chain folded structure



From Fig. 4.31
Callister's Materials Science and Engineering
Adapted Version.



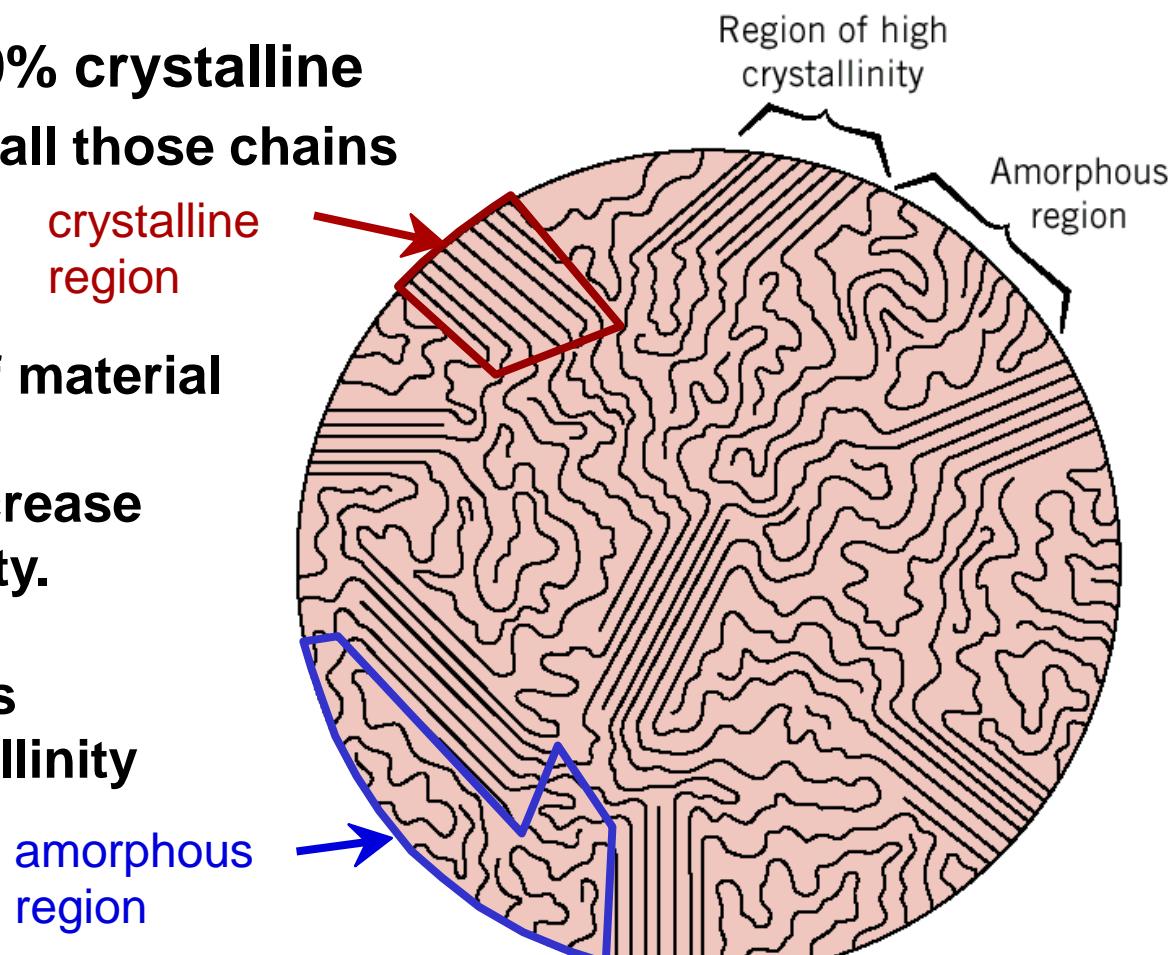
From Fig. 4.29
Callister's Materials Science and Engineering
Adapted Version.



Polymer Crystallinity

Polymers rarely 100% crystalline

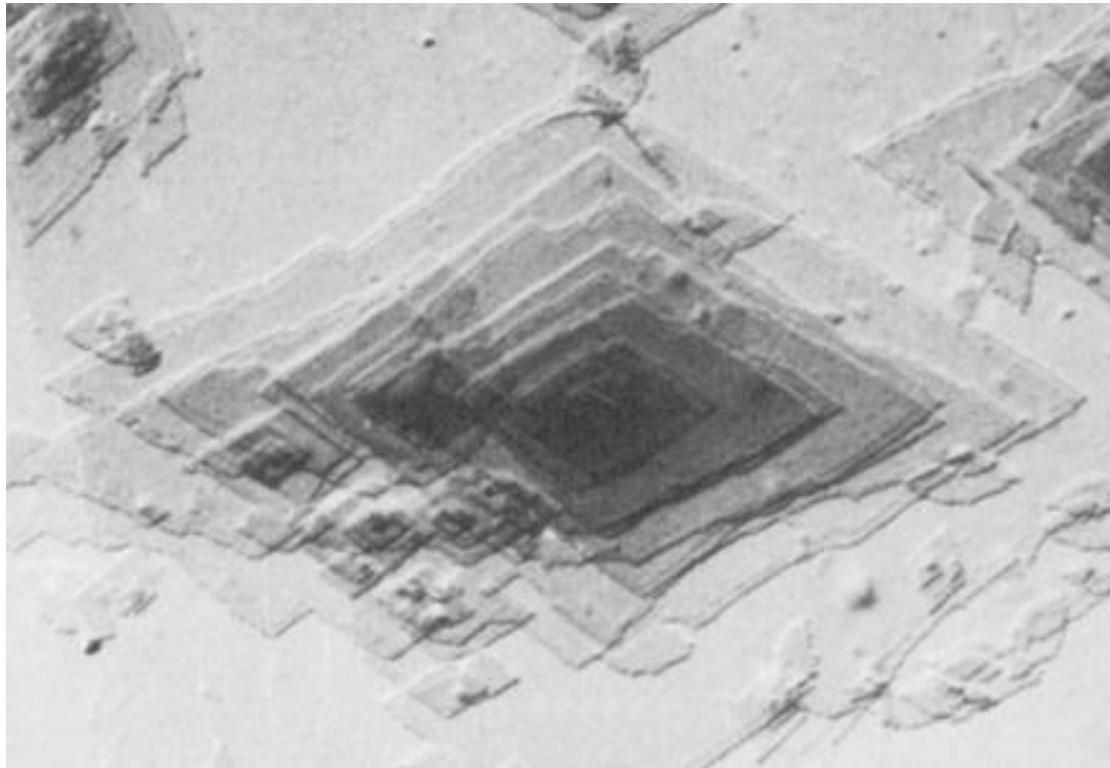
- Too difficult to get all those chains aligned
- **% Crystallinity:** % of material that is crystalline.
 - TS and E often increase with % crystallinity.
 - Annealing causes crystalline regions to grow. % crystallinity increases.



From Fig. 14.11, Callister 6e.
(Fig. 14.11 is from H.W. Hayden, W.G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, John Wiley and Sons, Inc., 1965.)

Polymer Crystal Forms

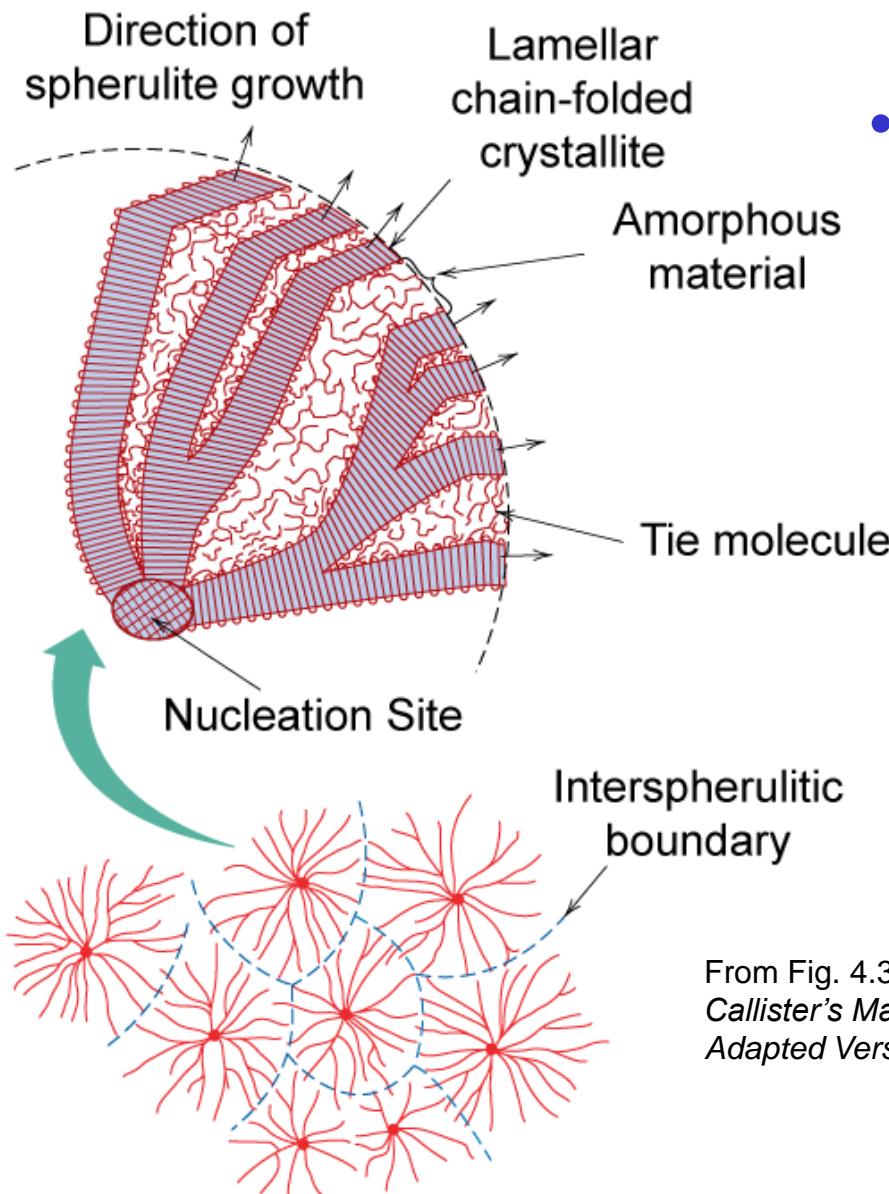
- **Single crystals – only if slow careful growth**



From Fig. 4.30
Callister's Materials Science and Engineering
Adapted Version



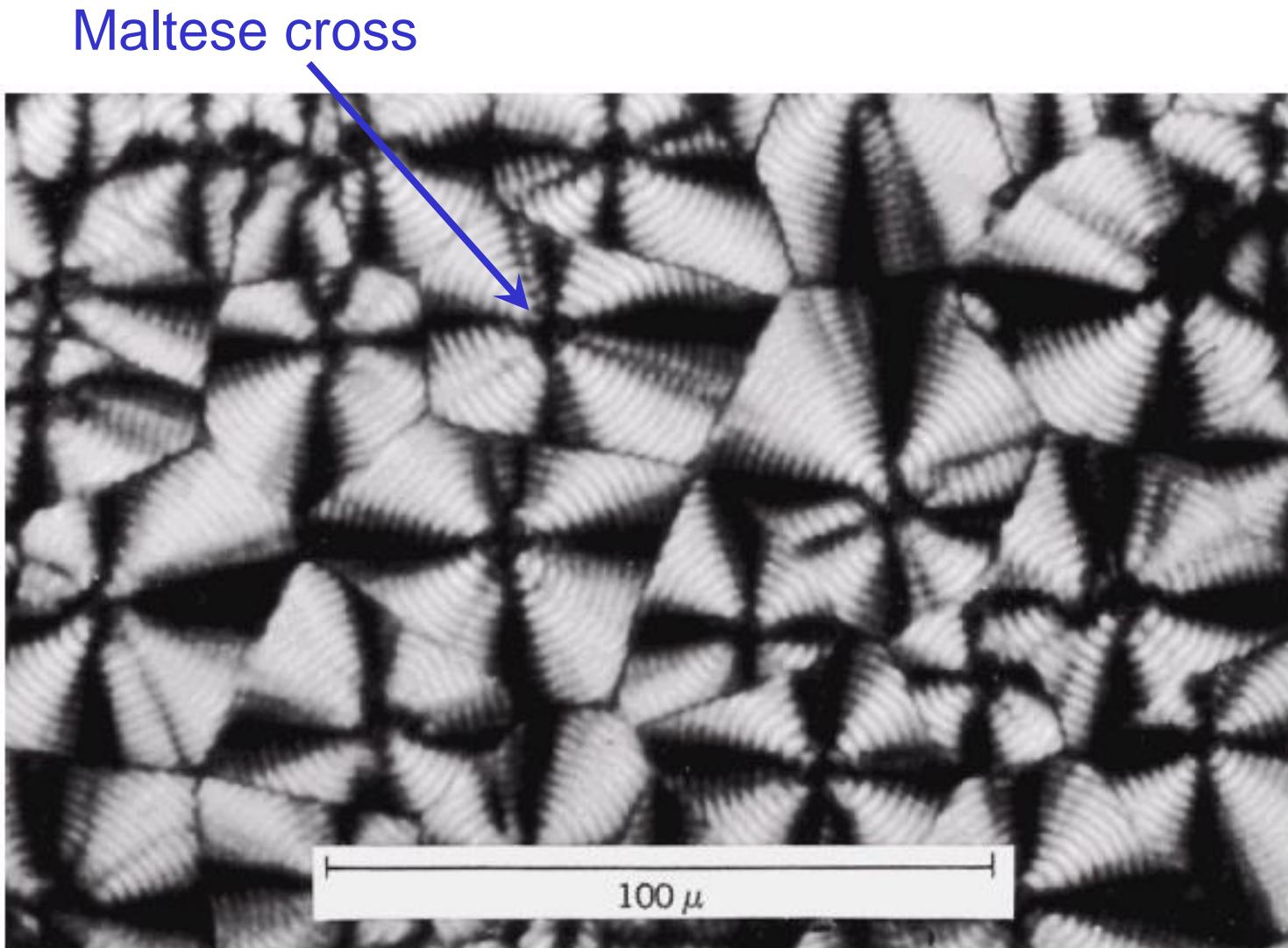
Polymer Crystal Forms



- **Spherulites – fast growth – forms lamellar (layered) structures**

From Fig. 4.32
Callister's Materials Science and Engineering
Adapted Version.

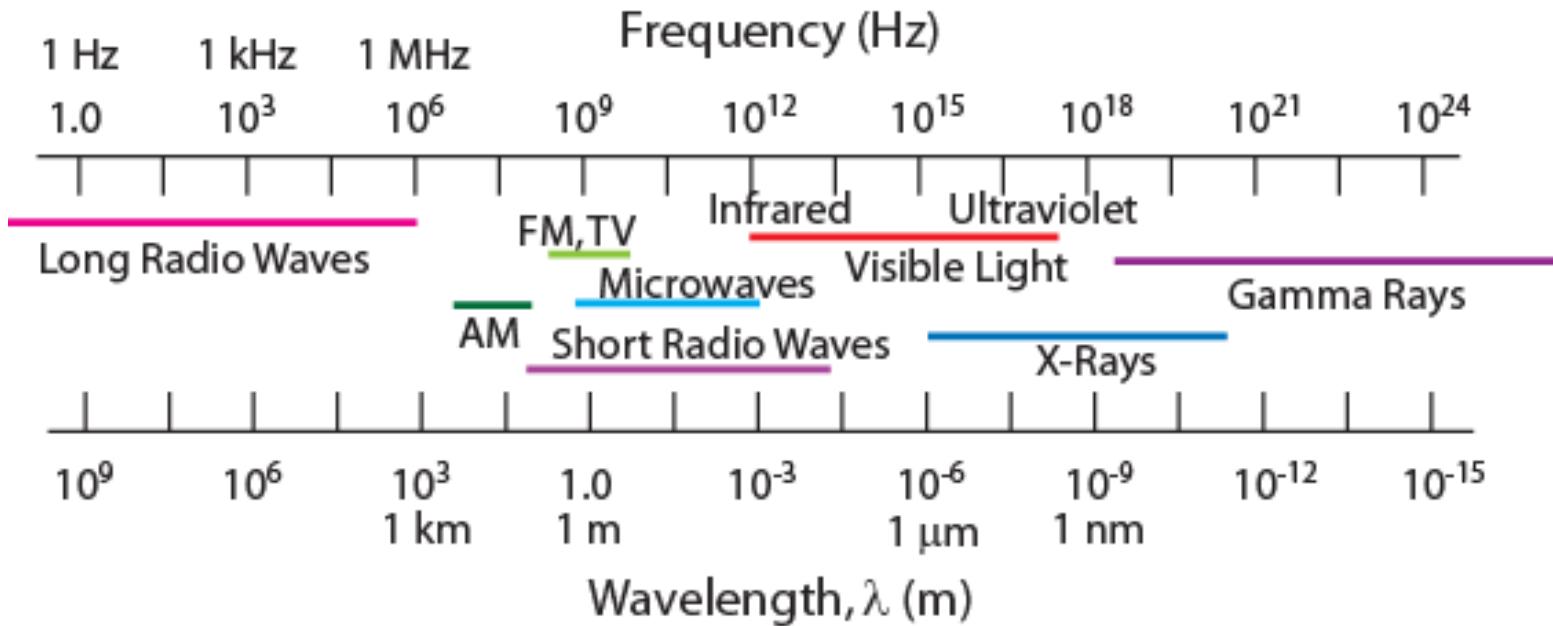
Spherulites – crossed polarizers



From Fig. 4.33
Callister's Materials Science and Engineering
Adapted Version

Section 4.20 - X-Ray Diffraction

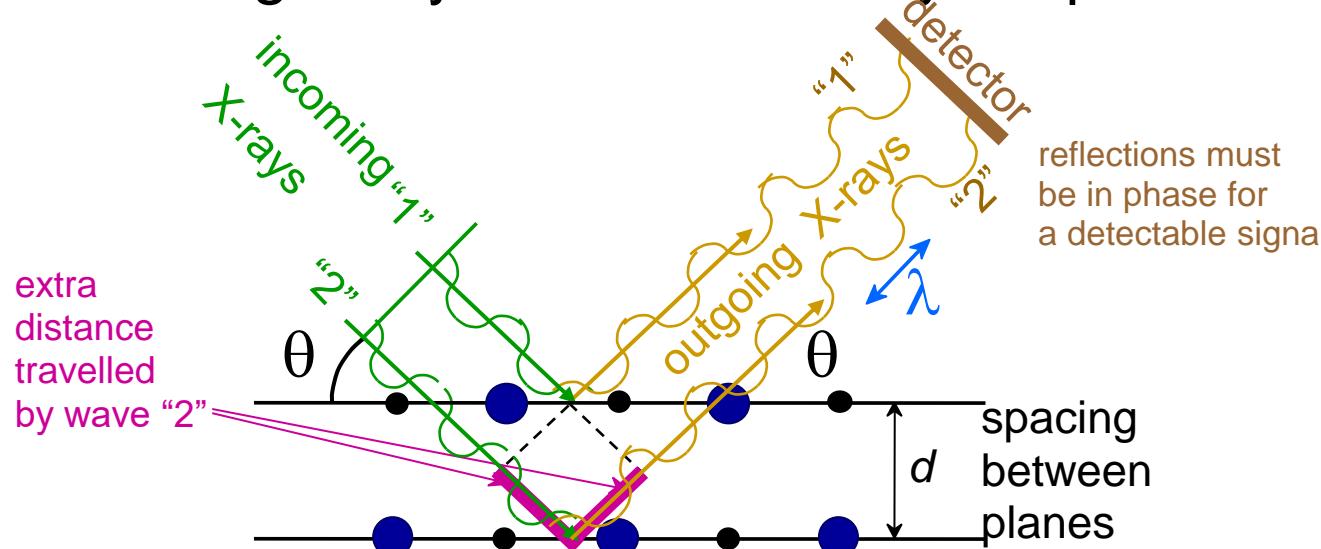
Electromagnetic Spectrum



- Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- Can't resolve spacings $< \lambda$
- Spacing is the distance between parallel planes of atoms.

X-Rays to Determine Crystal Structure

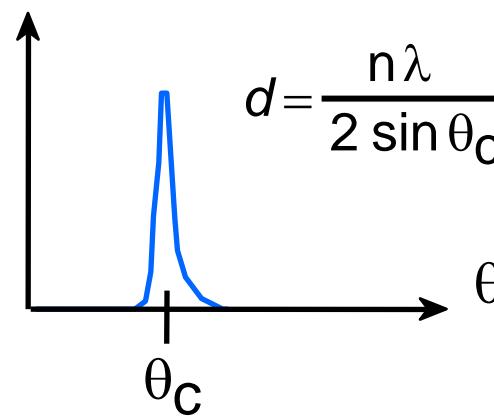
- Incoming X-rays diffract from crystal planes.



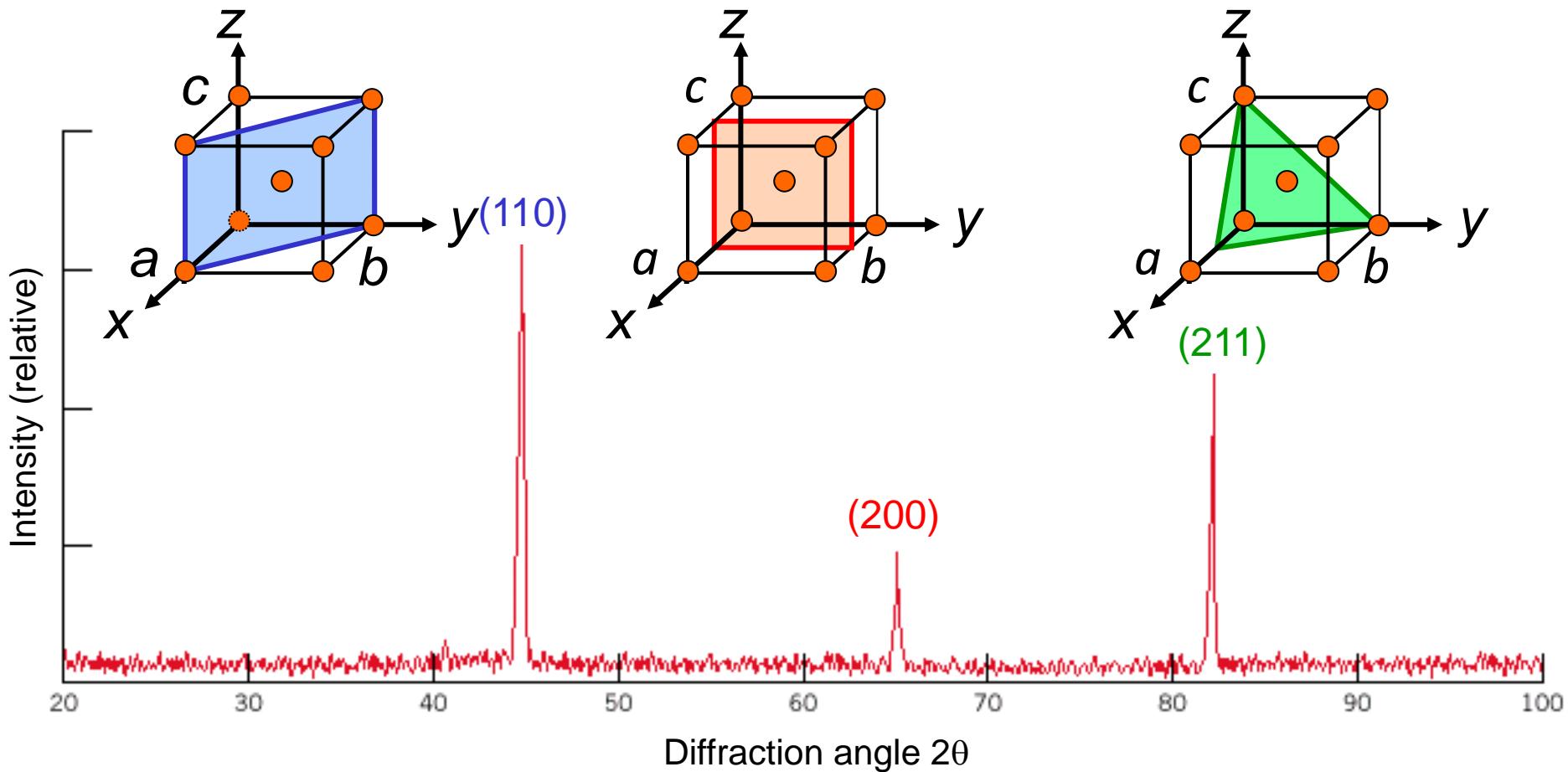
From Fig. 4.35
Callister's Materials
Science and Engineering,
Adapted Version.

Measurement of critical angle, θ_c , allows computation of planar spacing, d .

X-ray intensity (from detector)



X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline α -iron (BCC)

From Fig. 3.20, Callister 5e.

SUMMARY

- Common metallic crystal structures are FCC, BCC, and HCP. Coordination number and atomic packing factor are the same for both FCC and HCP crystal structures.
- We can predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).
- Crystallographic directions and planes are related to atomic linear densities and planar densities.
- Some materials can have more than one crystal structure. This is referred to as polymorphism (or allotropy).

SUMMARY

- Ceramic materials have covalent & ionic bonding.
- Ceramic structures are based on **charge neutrality** and maximizing # of nearest oppositely charged neighbors
- Ceramic structures may be predicted based on the **ratio** of the cation and anion radii
- Polymer structures were described, in particular the **spherulitic** structure of semicrystalline polymer
- X-ray diffraction is used for crystal structure and interplanar spacing determinations.

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: