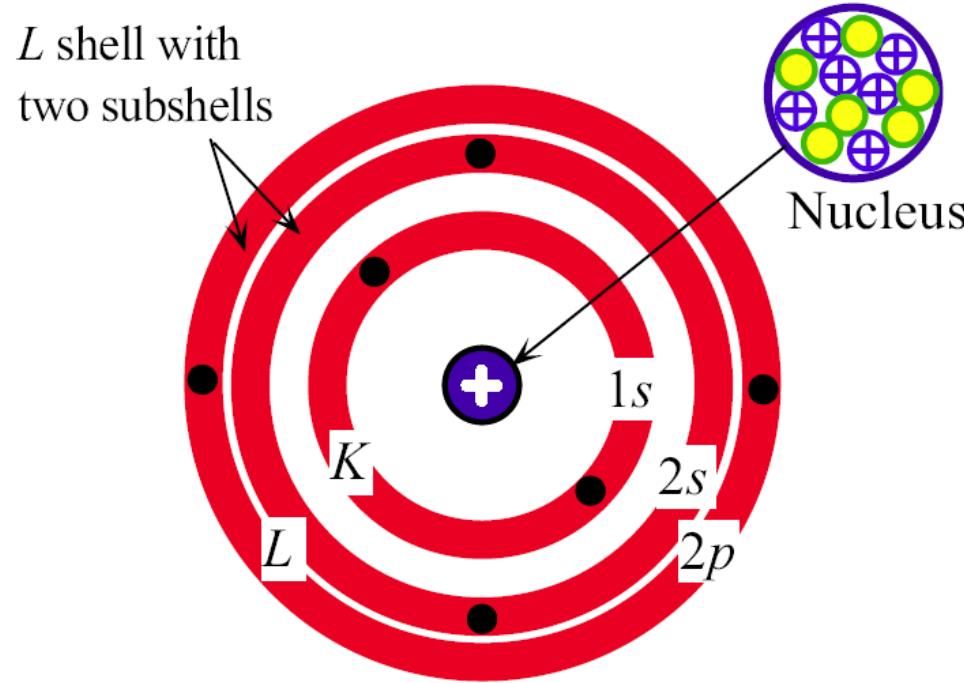


## Chapter 1

# Elementary Materials Science Concepts



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

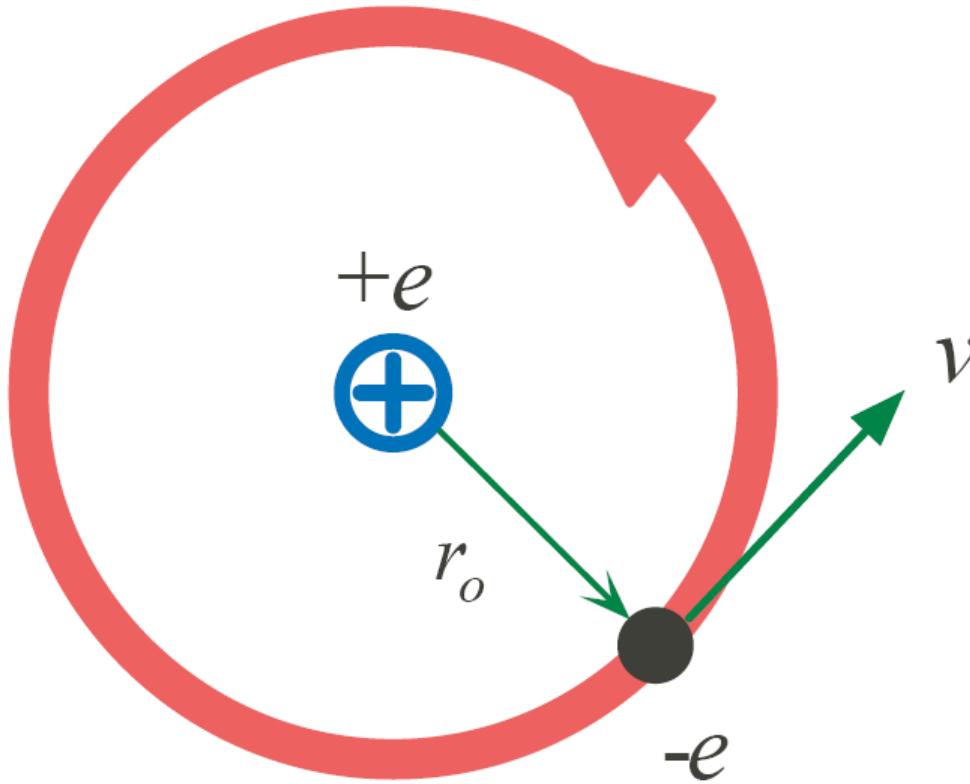
$$\overline{KE} = -\frac{1}{2} \overline{PE}$$

Average kinetic energy is related to the average potential energy

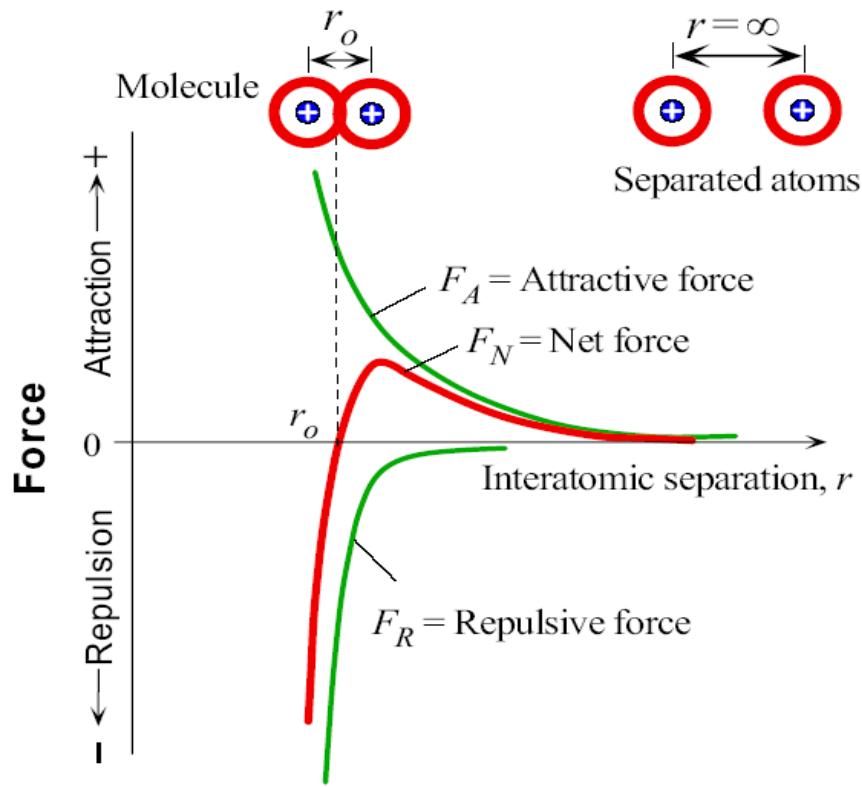
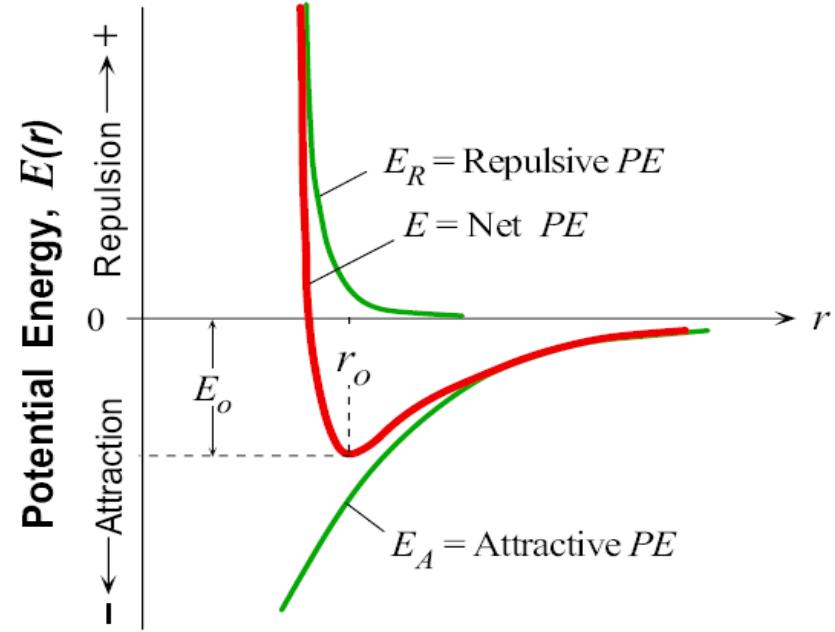
## Total Average Energy

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

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

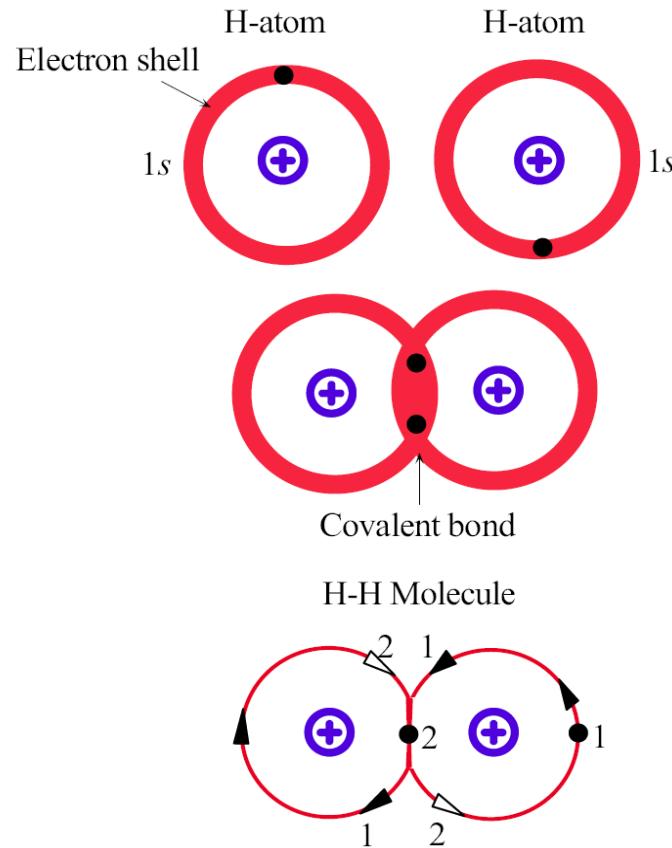
# Net Force in Bonding Between Atoms

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

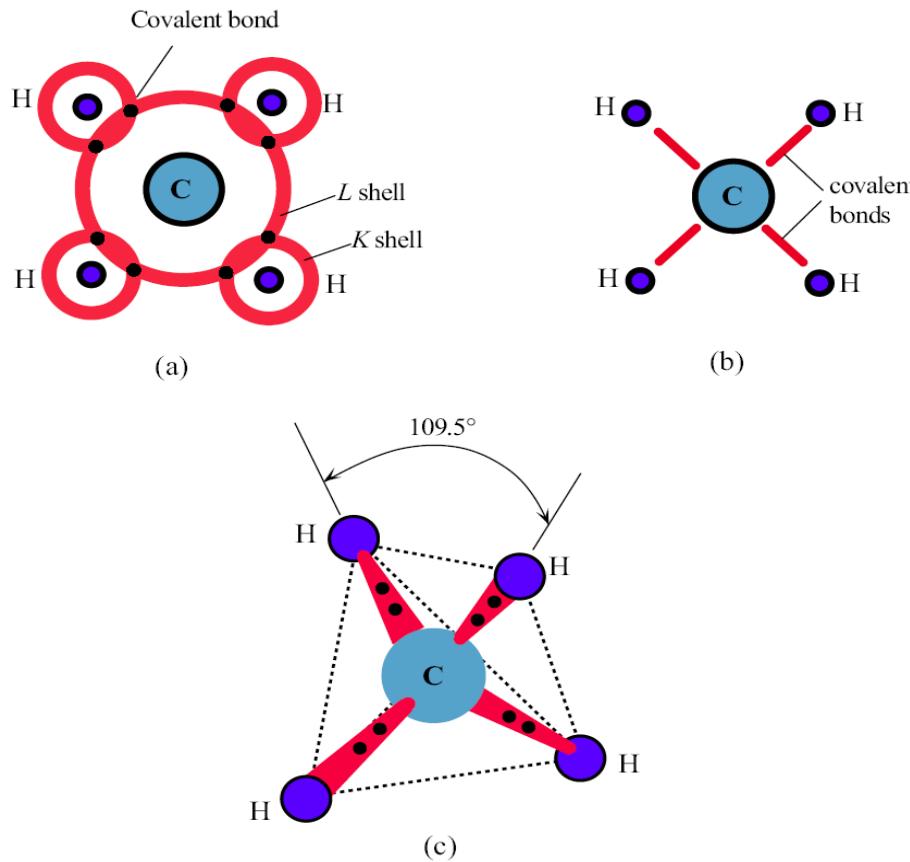
$F_N$  = net force

$F_A$  = attractive force

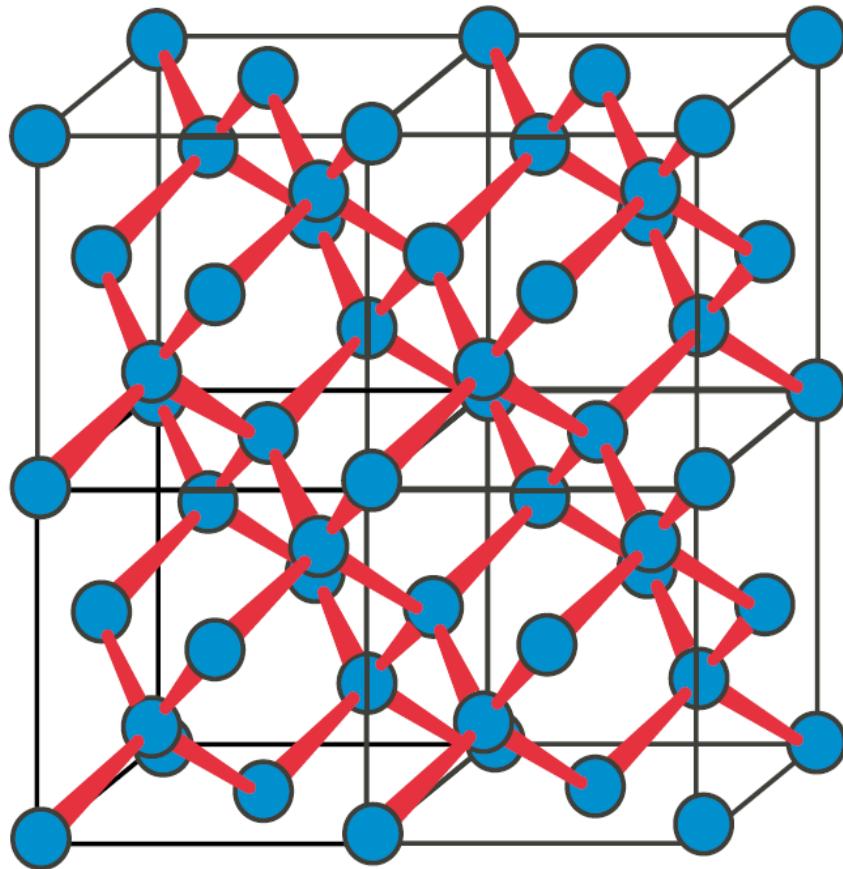
$F_R$  = repulsive force



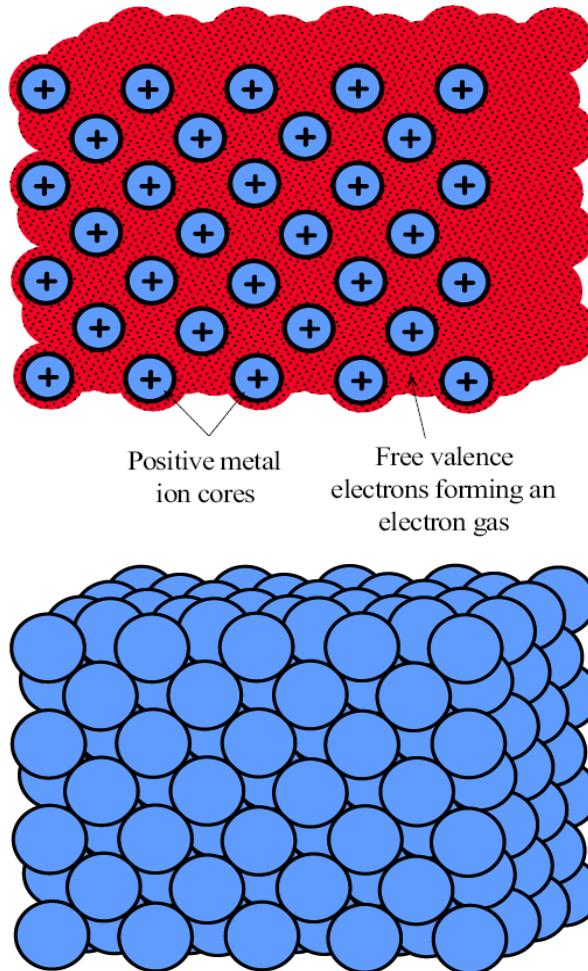
Formation of a covalent bond between two hydrogen atoms leads to the  $\text{H}_2$  molecule. Electrons spend majority of their time between the two nuclei which results in a net attraction between the electrons and the two nuclei which is the origin of the covalent bond.



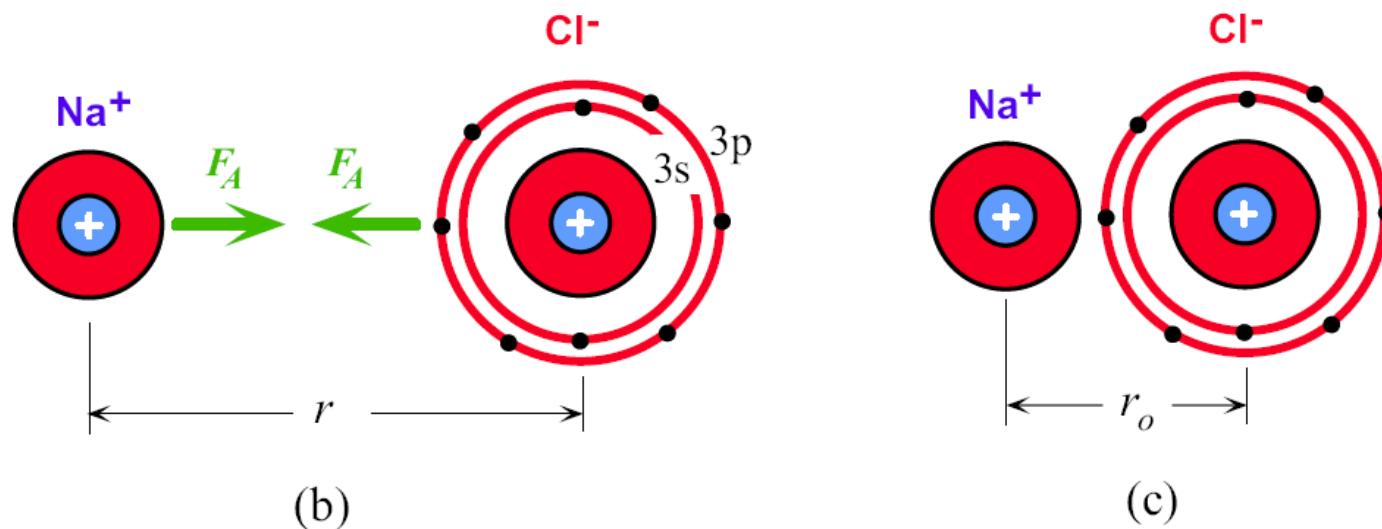
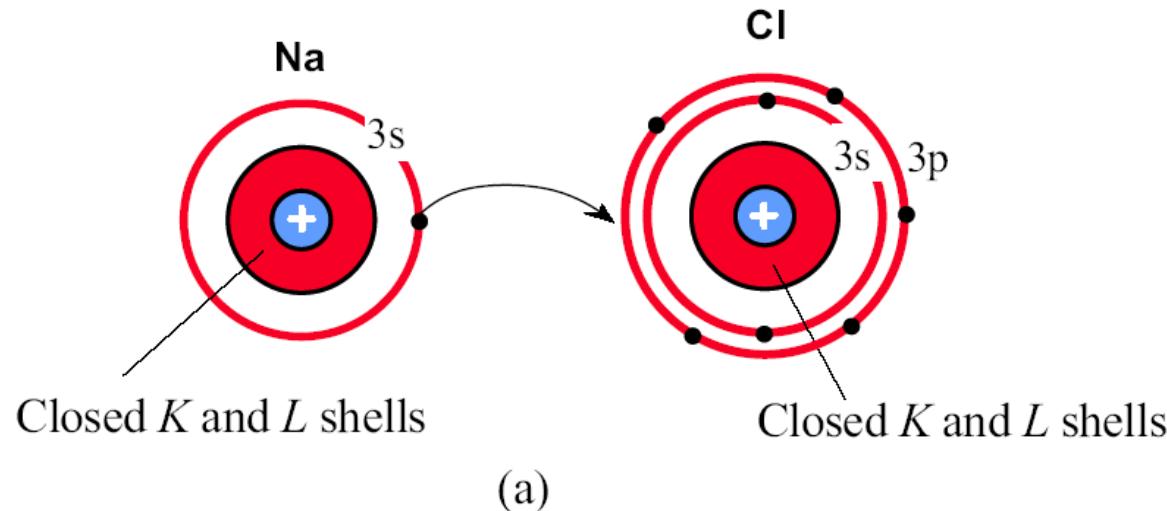
- (a) Covalent bonding in methane,  $\text{CH}_4$ , involves four hydrogen atoms sharing Bonds with one carbon atom. Each covalent bond has two shared electrons. The four bonds are identical and repel each other.
- (b) Schematic sketch of  $\text{CH}_4$  in paper.
- (c) In three dimensions, due to symmetry, the bonds are directed towards the Corners of a tetrahedron.



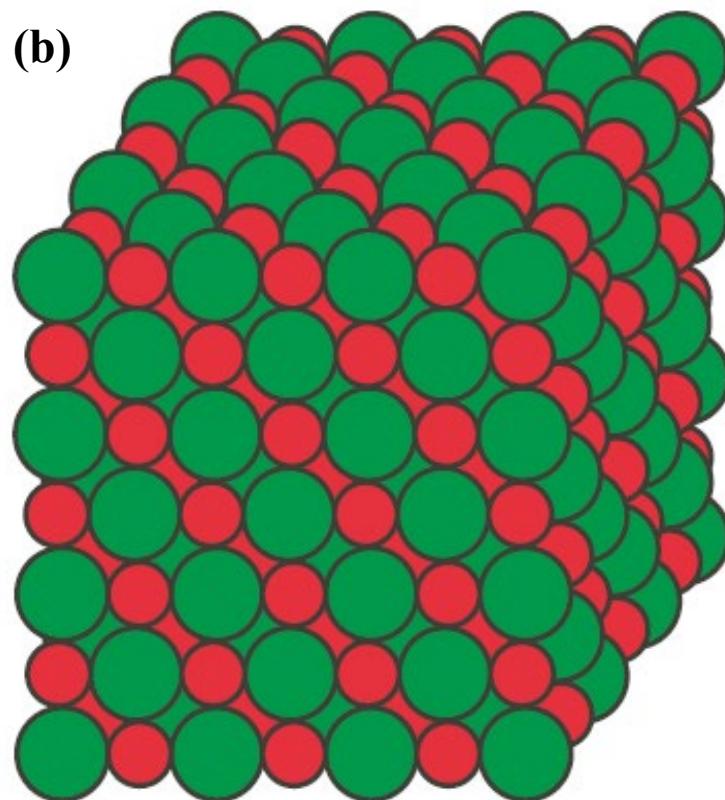
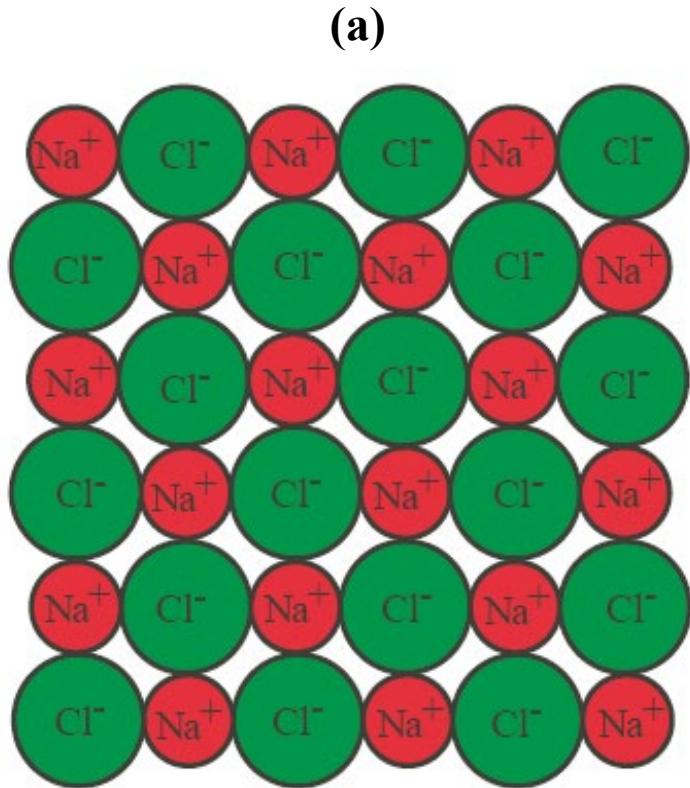
The diamond crystal is a covalently bonded network of carbon atoms. Each carbon atom is covalently bonded to four neighbors forming a regular three dimensional pattern of atoms which constitutes the diamond crystal.



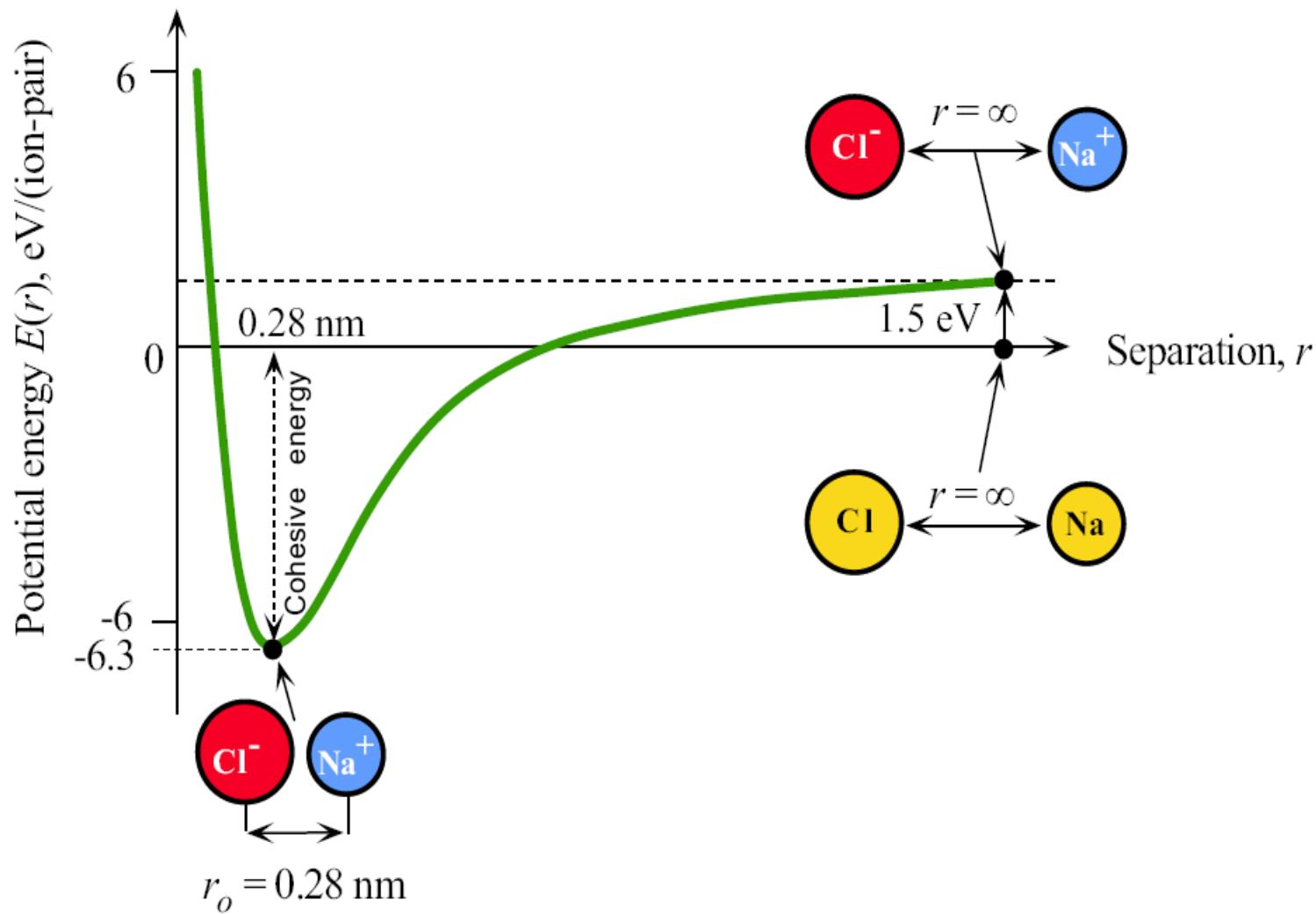
In metallic bonding the valence electrons from the metal atoms form a “cloud of electrons” which fills the space between the metal ions and “glues” the ions together through the coulombic attraction between the electron gas and the positive metal ions.



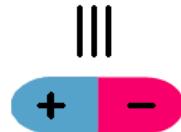
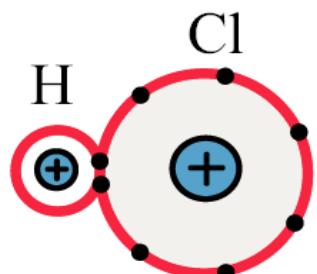
The formation of ionic bond between Na and Cl atoms in  $\text{NaCl}$ . The attraction  
Is due to coulombic forces.



- (a) A schematic illustration of a cross section from solid NaCl. NaCl is made of  $\text{Cl}^-$  and  $\text{Na}^+$  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)

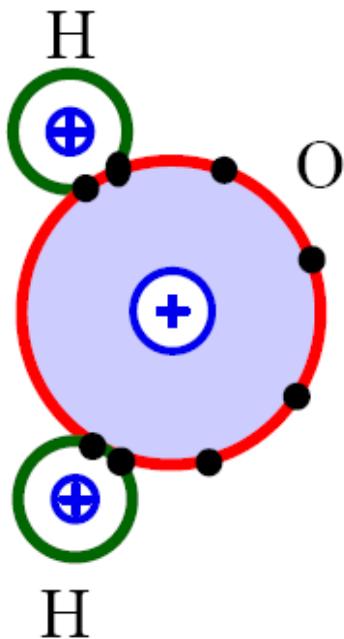


(b)

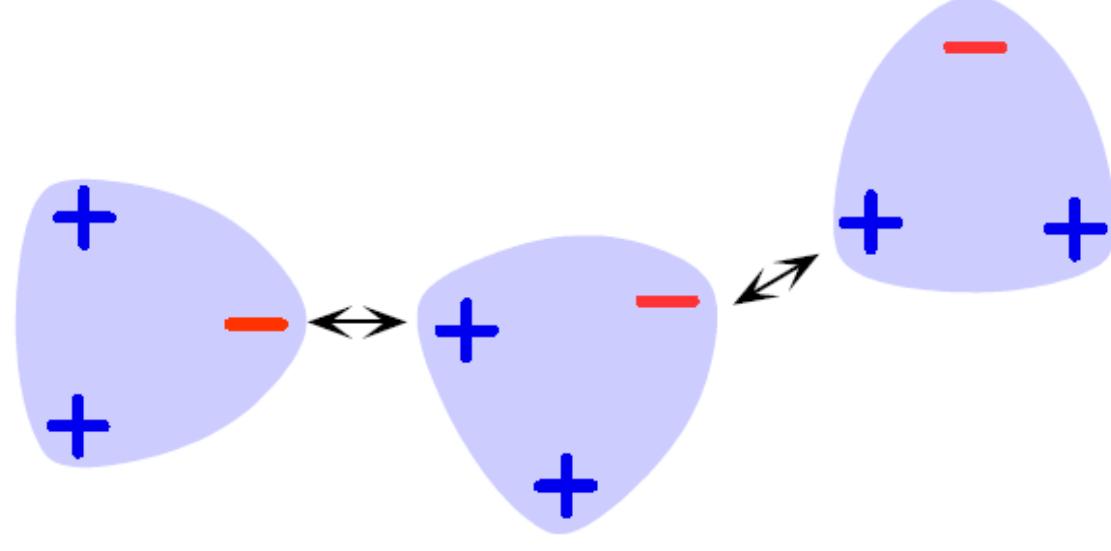


(c)

- (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.



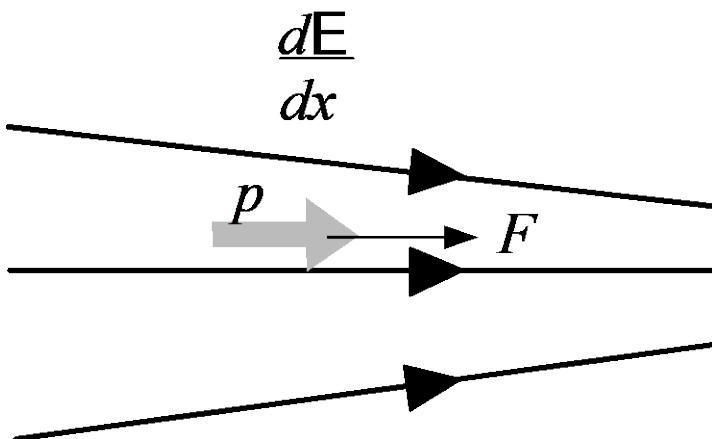
(a)



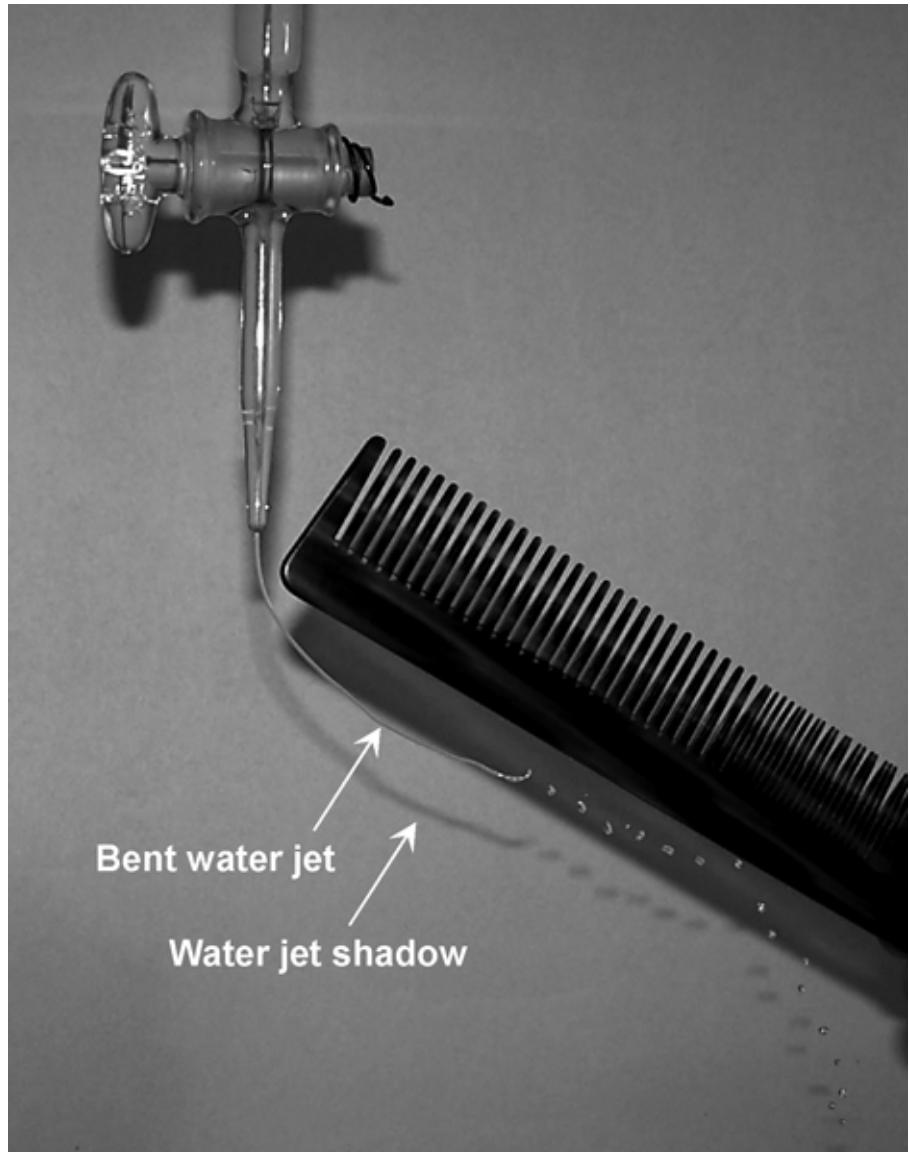
(b)

The origin of van der Walls bonding between water molecules.

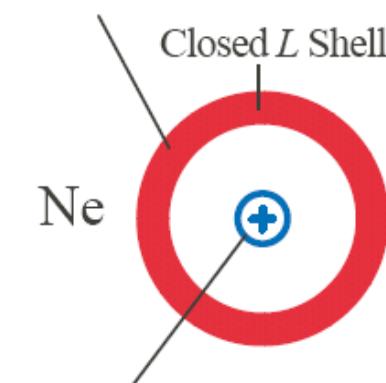
- (a) The H<sub>2</sub>O molecule is polar and has a net permanent dipole moment
- (b) Attractions between the various dipole moments in water gives rise to van der Walls bonding



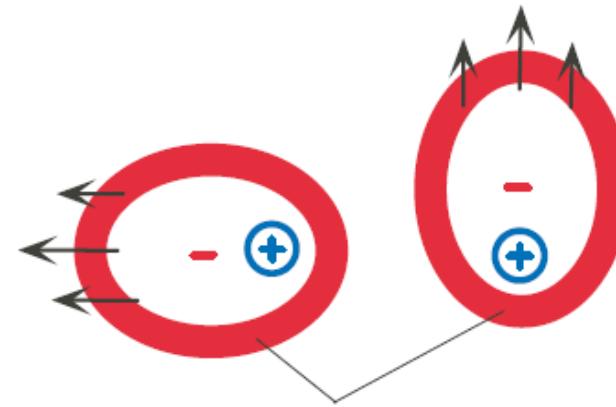
A dipole moment in a nonuniform field experiences a net force  $F$  that depends on the dipole moment  $p$  and the field gradient  $dE/dx$ . When a charged comb (by combing hair) is brought close to a water jet, the field from the comb attracts the polarized water molecules toward higher fields.  
[See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



Time averaged electron (negative charge) distribution

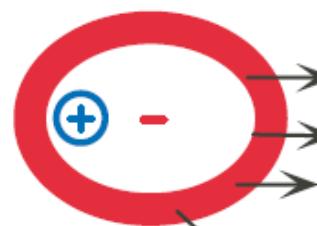


Ionic core  
(Nucleus + *K*-shell)



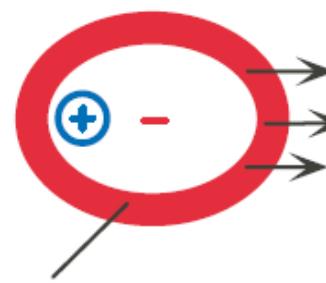
Instantaneous electron (negative charge) distribution fluctuates about the nucleus.

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 <sup>-3</sup> )	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 <sub>2</sub> 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

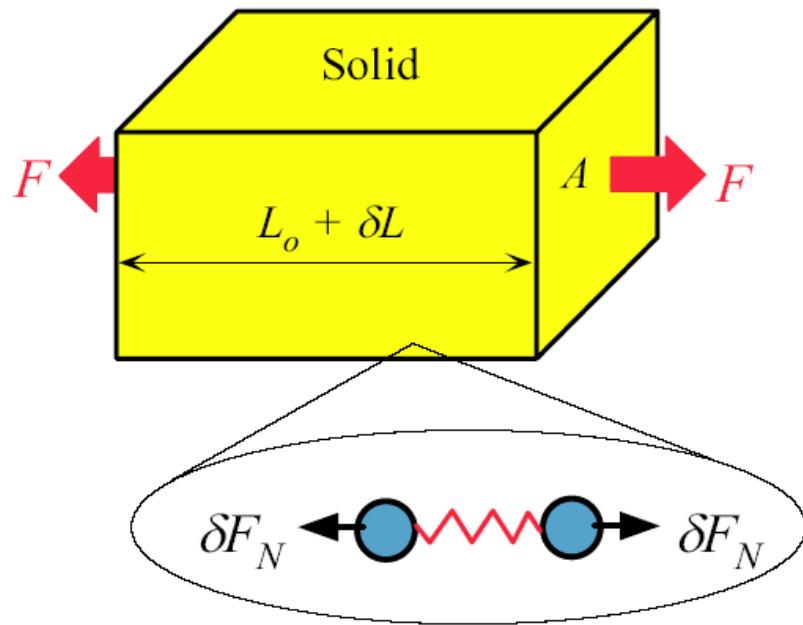
$$\sigma = Y\epsilon$$

$\sigma$  = applied stress (force per unit area),  $Y$  = elastic modulus,  $\epsilon$  = elastic strain (fractional increase in the length of the solid)

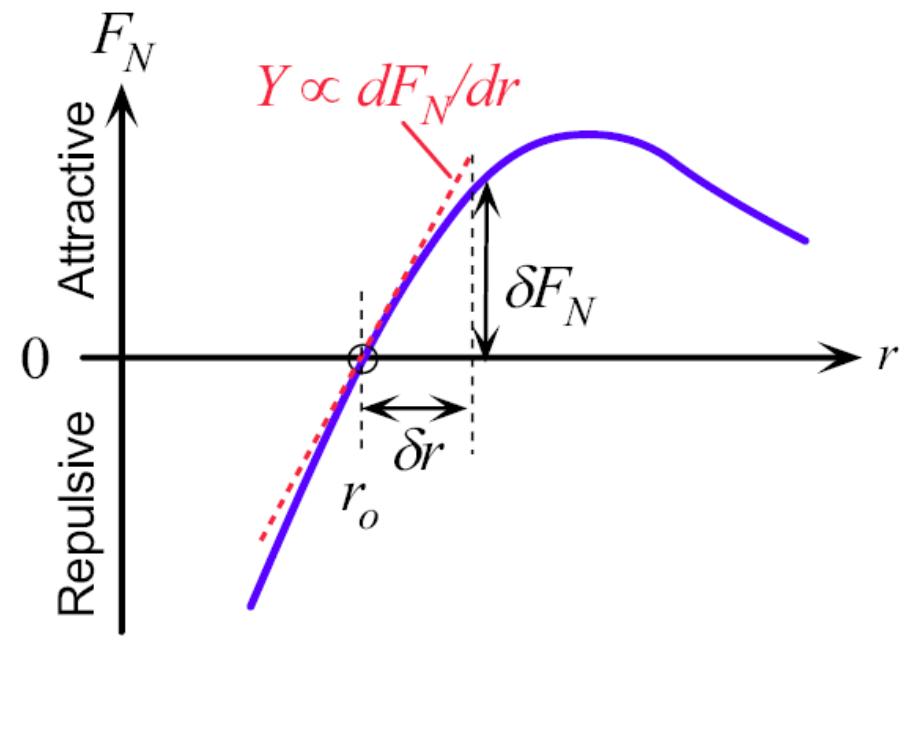
## Elastic Modulus and Bonding

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

$Y$  = 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  $\delta L$ . The force is divided amongst chains of atoms that make the solid. Each chain carries a force  $\delta F_N$ .

(b) In equilibrium, the applied force is balanced by the net force  $\delta F_N$  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

$E_{\text{bond}}$  = 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

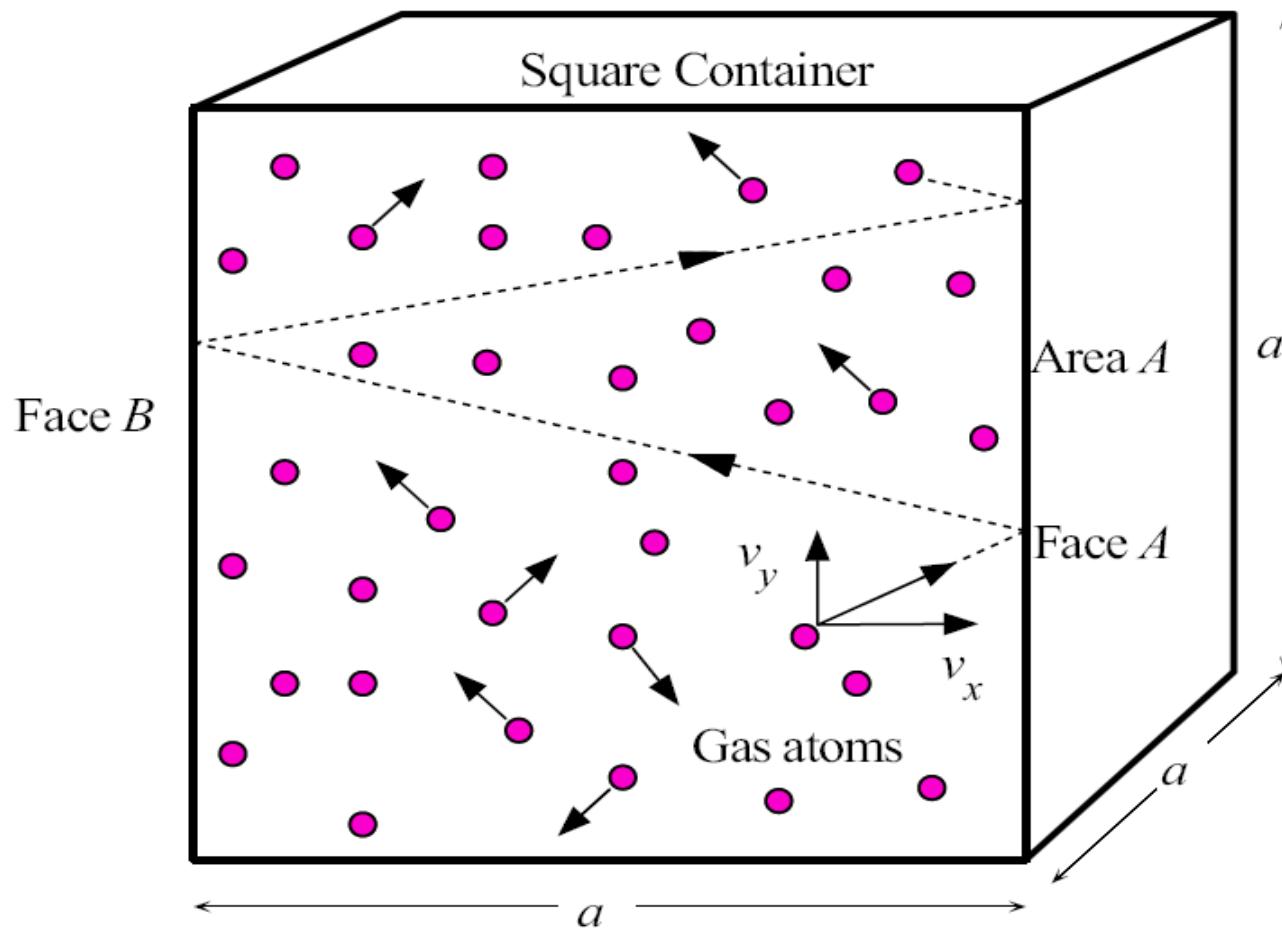
$$PV = (N/N_A)RT$$

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

## Change in Momentum of a Molecule

$$\Delta p = 2mv_x$$

$\Delta p$  = 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,  $\Delta p$  = change in momentum,  $\Delta t$  = 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,  $\rho$  = 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

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

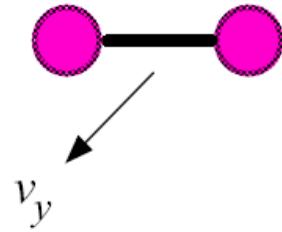
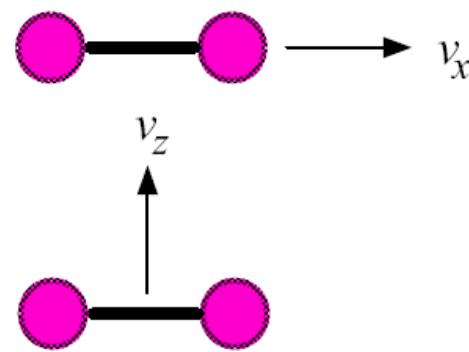
$U$  = total internal energy per mole,  $N_A$  = Avogadro's number,  $m$  = mass of the gas molecule,  $k$  = Boltzmann constant,  $T$  = temperature

## Molar Heat Capacity at Constant Volume

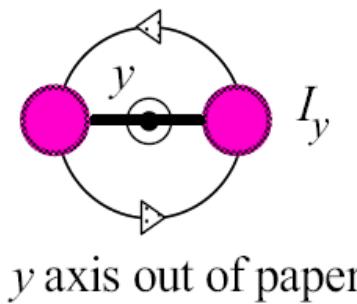
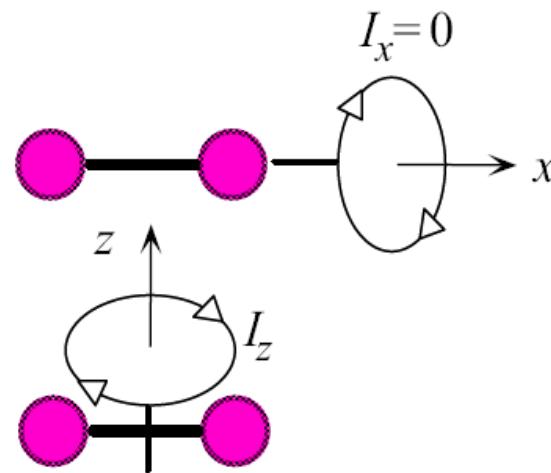
$$C_m = \frac{dU}{dT} = \frac{3}{2} N_A k = \frac{3}{2} R$$

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

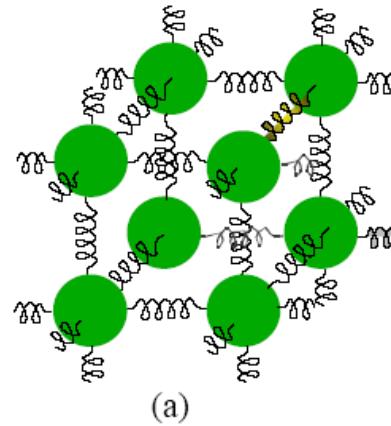
## TRANSLATIONAL MOTION



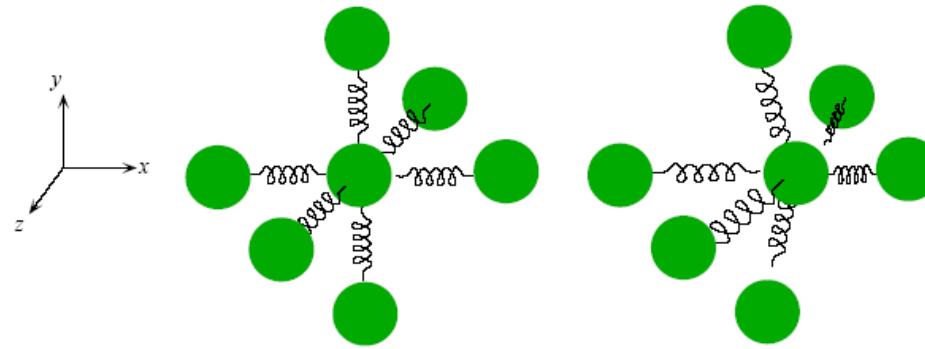
## ROTATIONAL MOTION



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

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

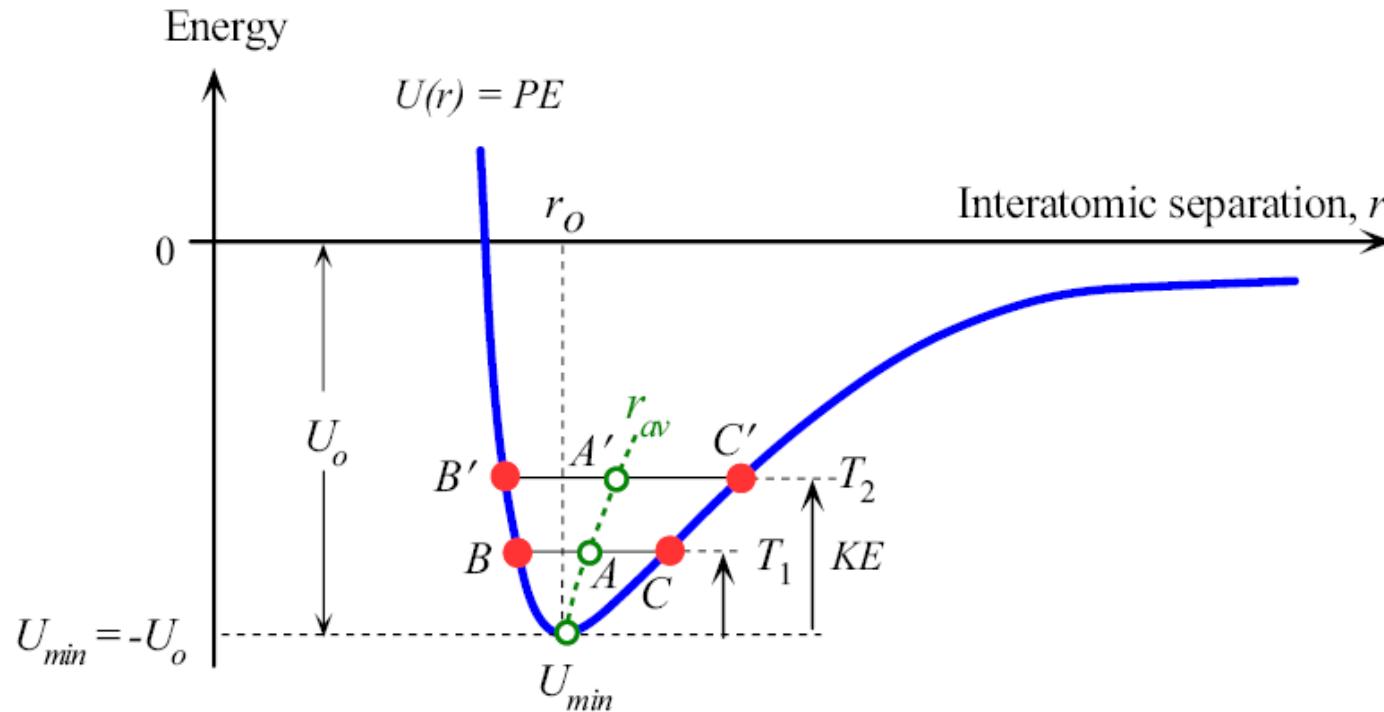
$U$  = total internal energy per mole,  $N_A$  = Avogadro's number,  $R$  = gas constant,  $k$  = Boltzmann constant,  $T$  = temperature

## Dulong-Petit Rule

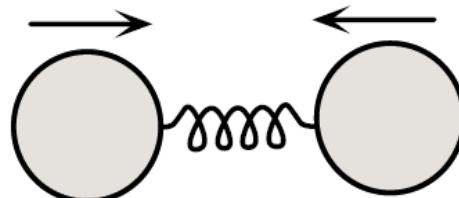
$$C_m = \frac{dU}{dT} = 3R = 25 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

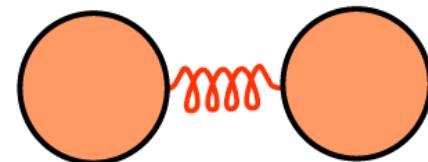
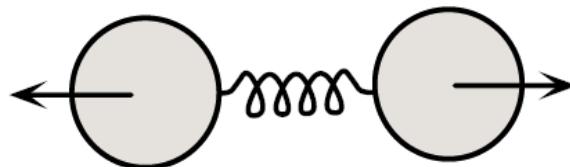
# Thermal Expansion



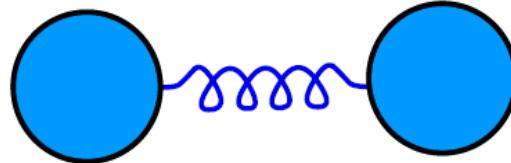
The potential energy PE curve has a minimum when the atoms in the solid attain the interatomic separation  $r = r_0$ . Due to thermal energy, the atoms will be vibrating and will have vibrational kinetic energy. At  $T = T_1$ , the atoms will be vibrating in such a way that the bond will be stretched 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

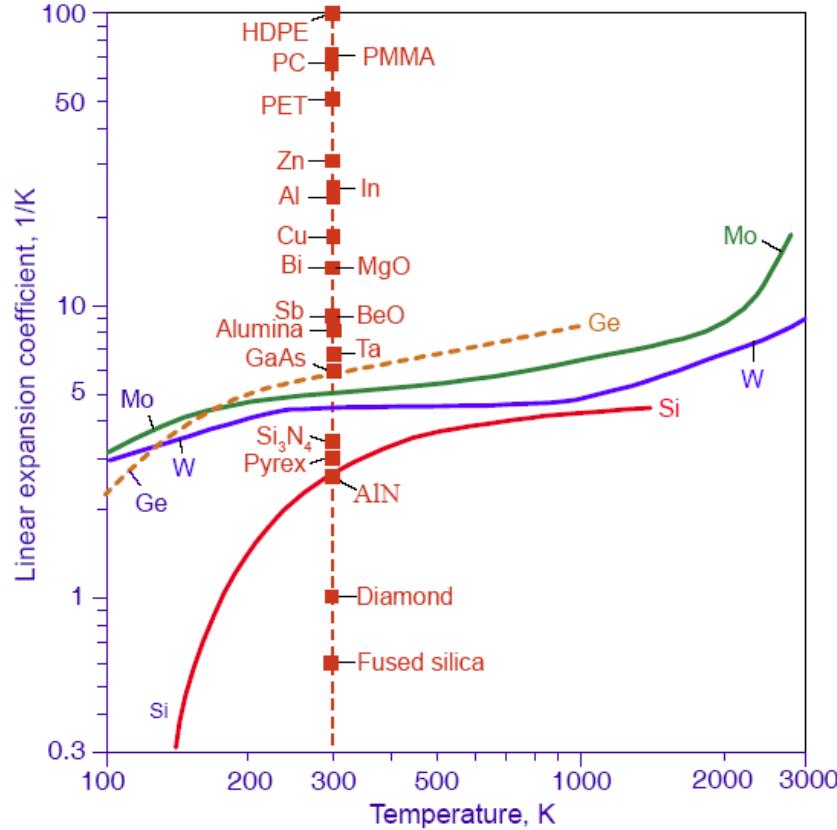
$$\lambda = \frac{1}{L_o} \cdot \frac{\delta L}{\delta T}$$

$\lambda$  = thermal coefficient of linear expansion or thermal expansion coefficient,  $L_o$  = original length,  $L$  = length at temperature  $T$

## Thermal Expansion

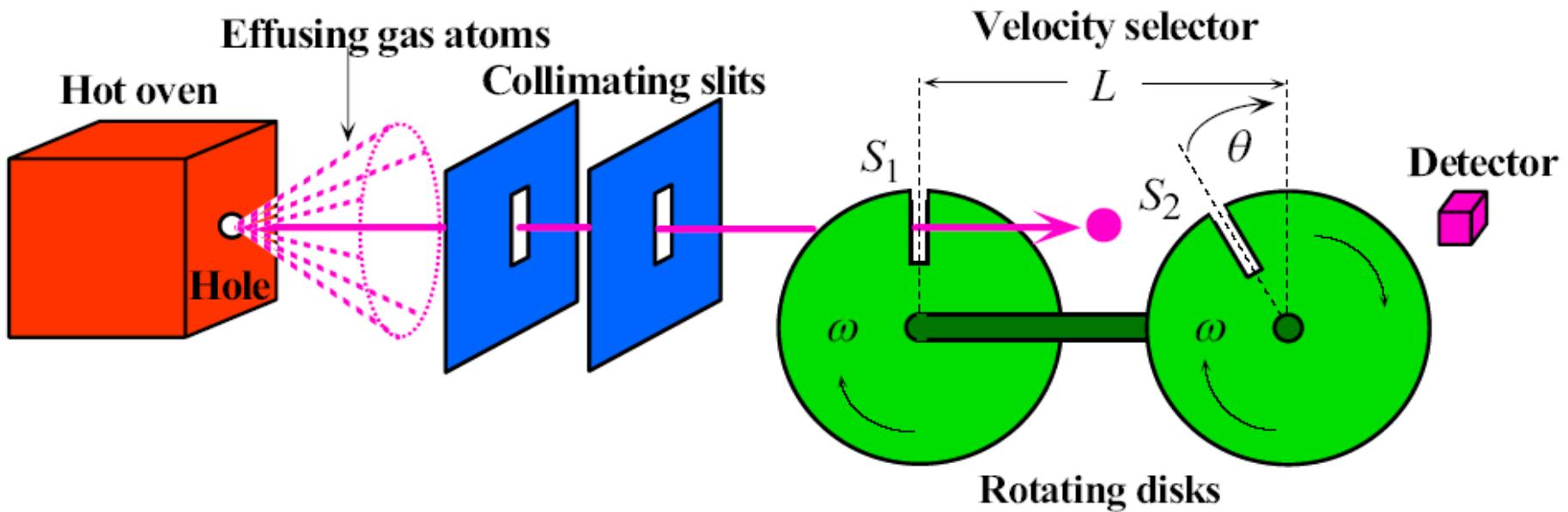
$$L = L_o[1 + \lambda(T - T_o)]$$

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



Dependence of the linear thermal expansion coefficient  $\lambda$  ( $K^{-1}$ ) 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.

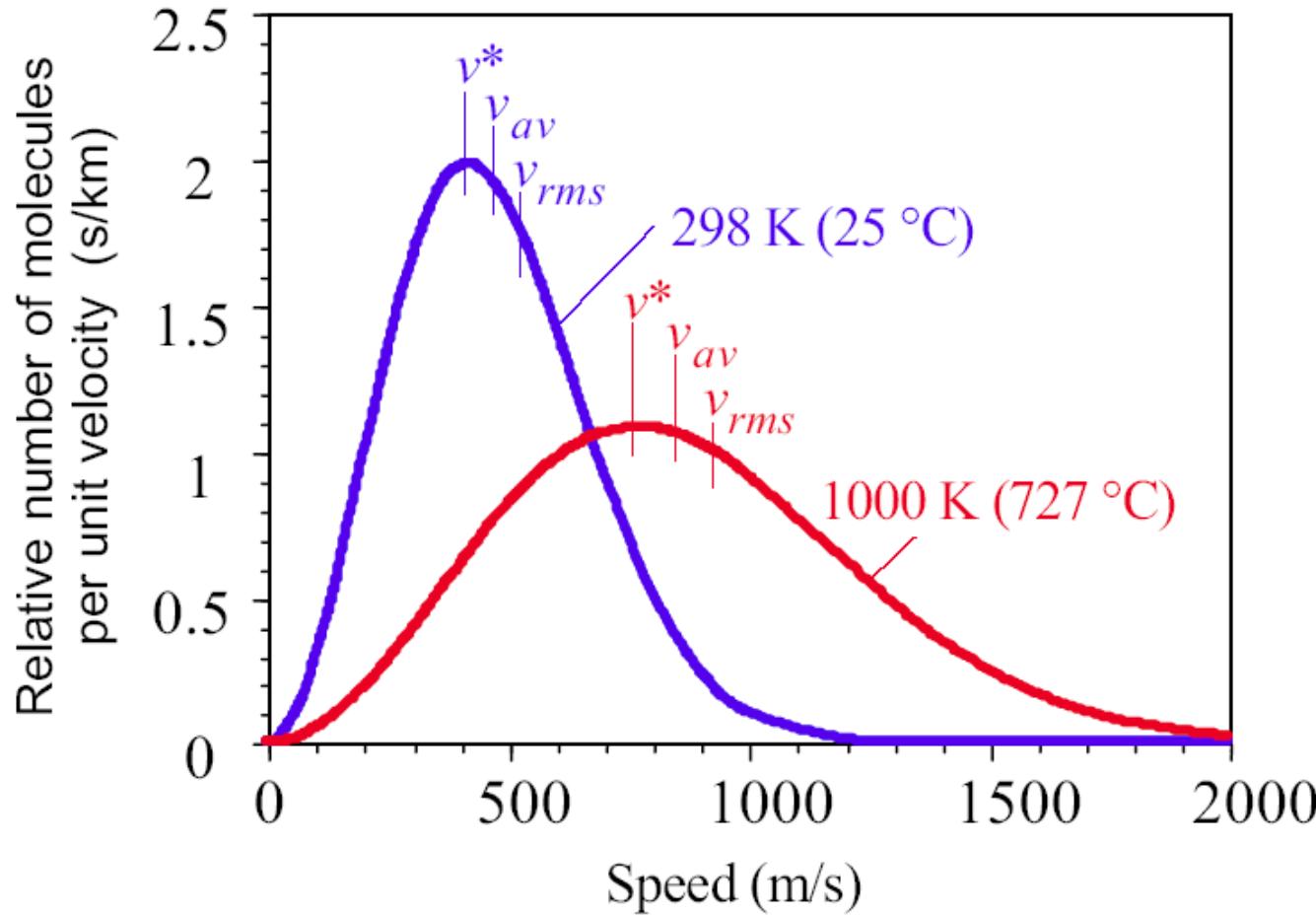


Schematic diagram of a stern type experiment for determining the distribution of molecular velocities

# 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

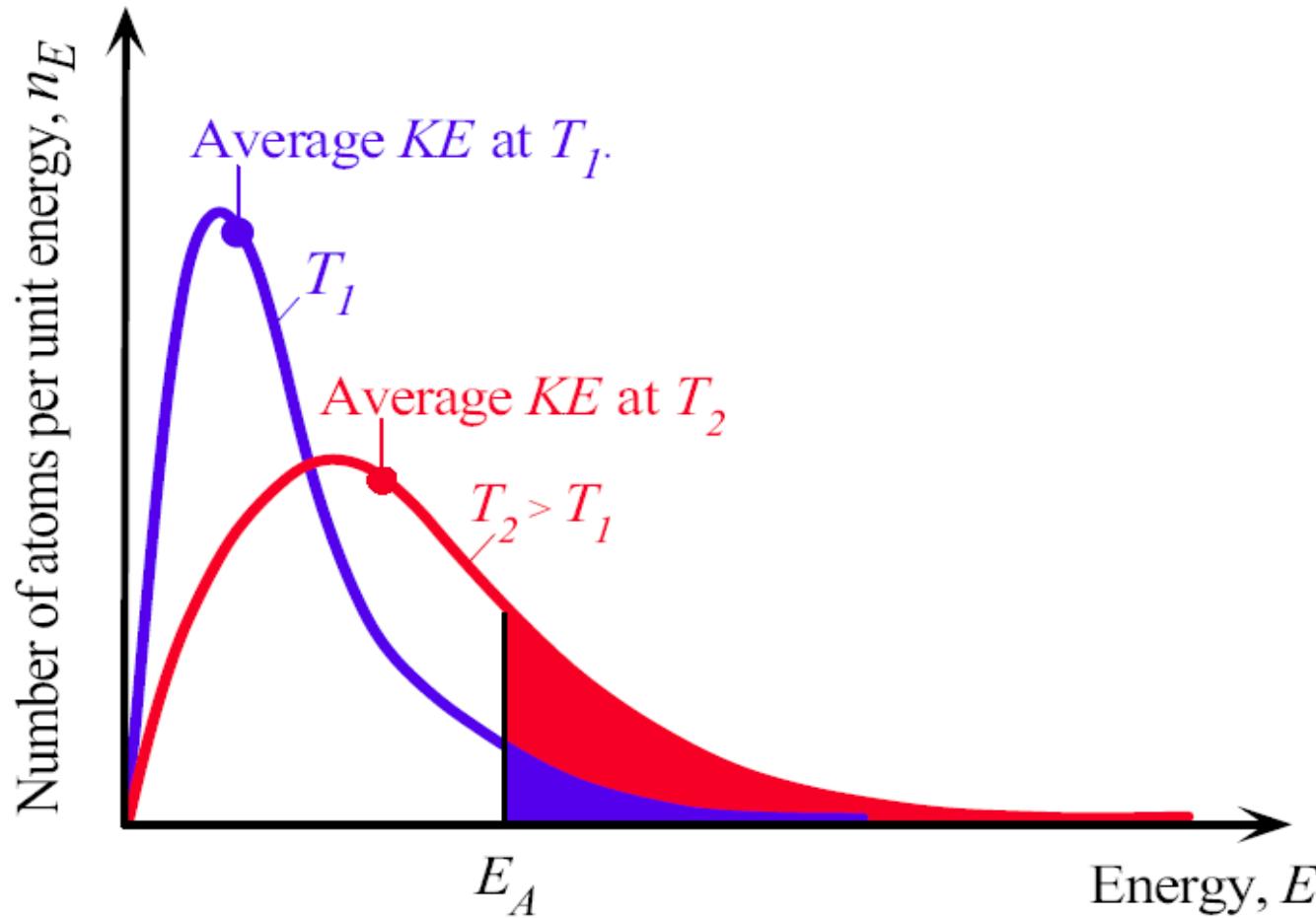


Maxwell Boltzmann distribution of molecular speeds in nitrogen gas at two temperatures. The ordinate is  $dN/(Ndv)$ , the fractional number of molecules per unit speed interval in  $(\text{km}/\text{s})^{-1}$ .

# 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.

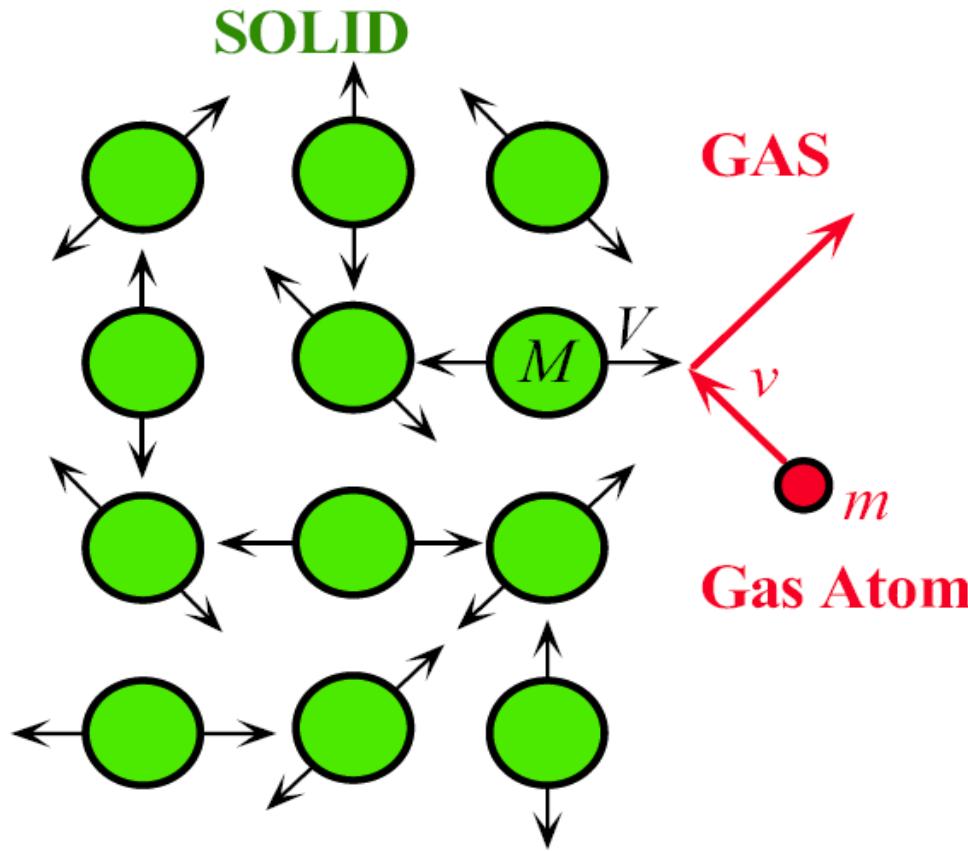


Energy distribution of gas molecules at two different temperatures. The number of molecules that have energies greater than  $E_A$  is the shaded area. This area depends strongly on the temperature as  $\exp(-E_A/kT)$

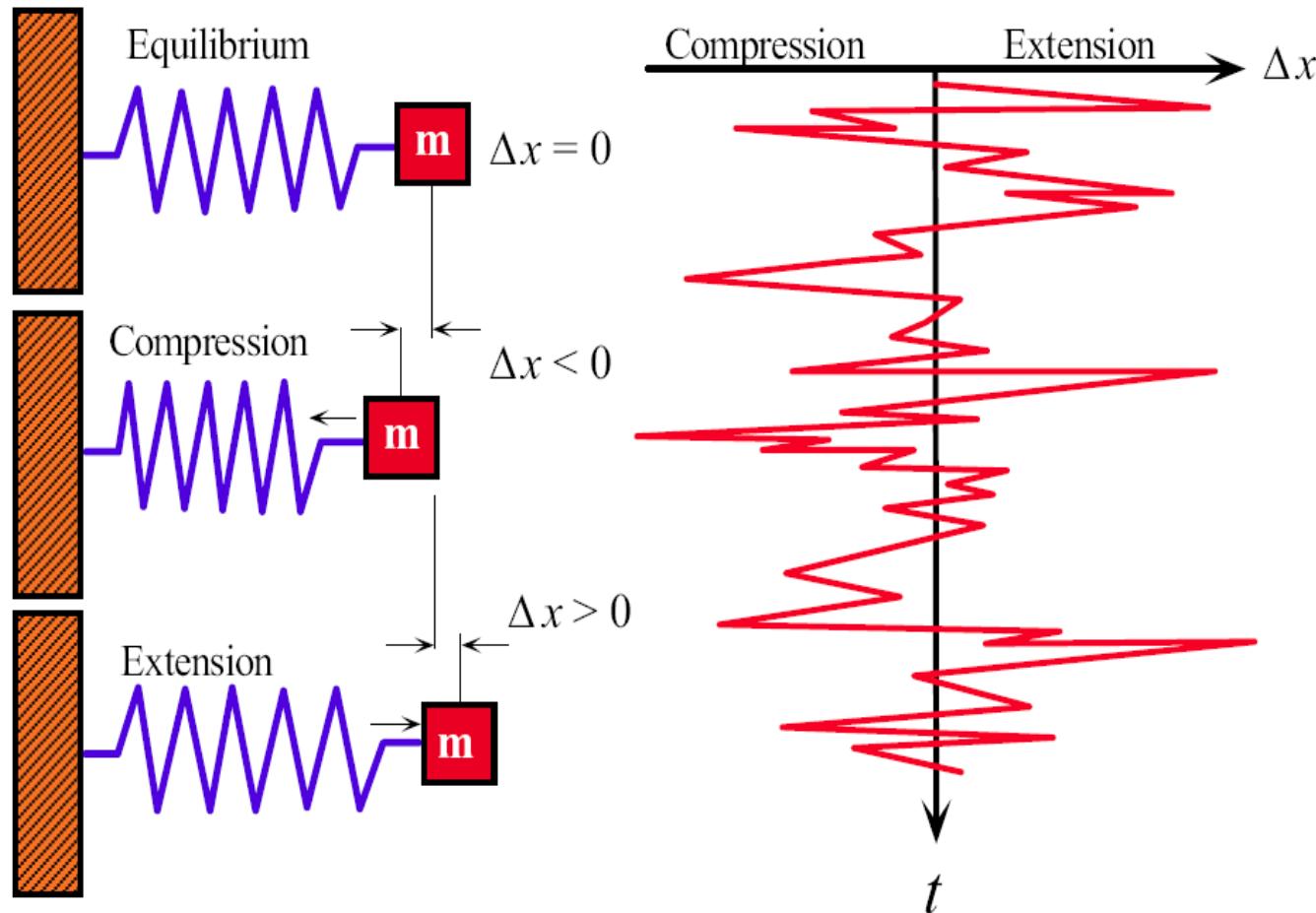
# Boltzmann Energy Distribution

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

$n_E$  = 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.

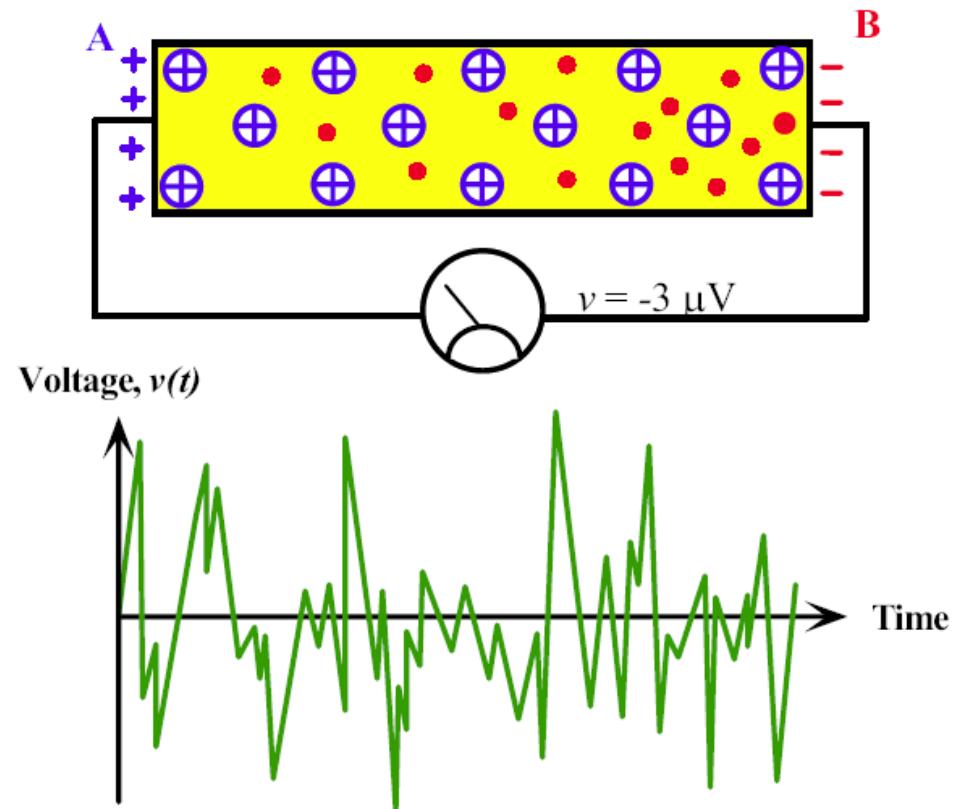
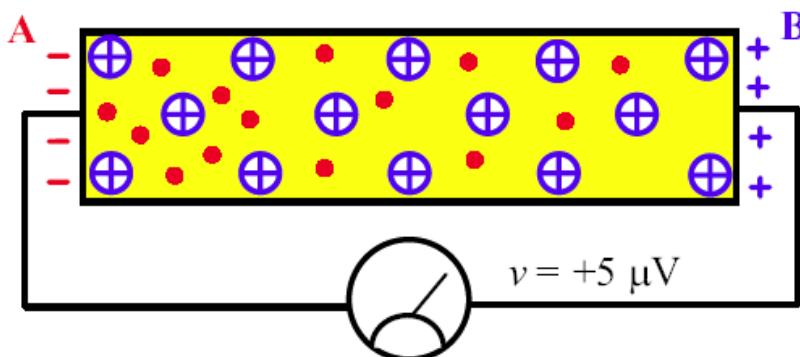
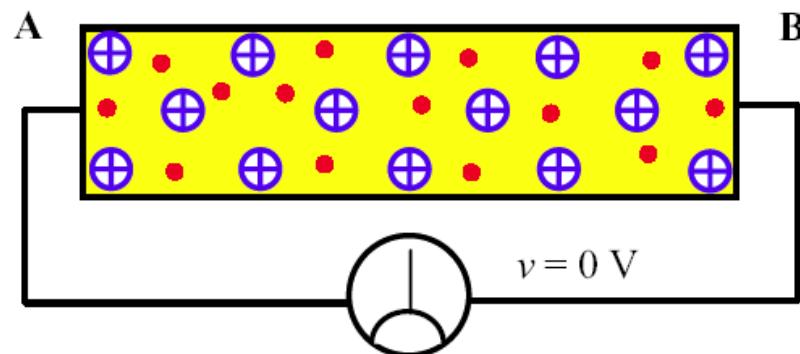


Fluctuations of a mass attached to a spring due to random bombardment of air molecules.

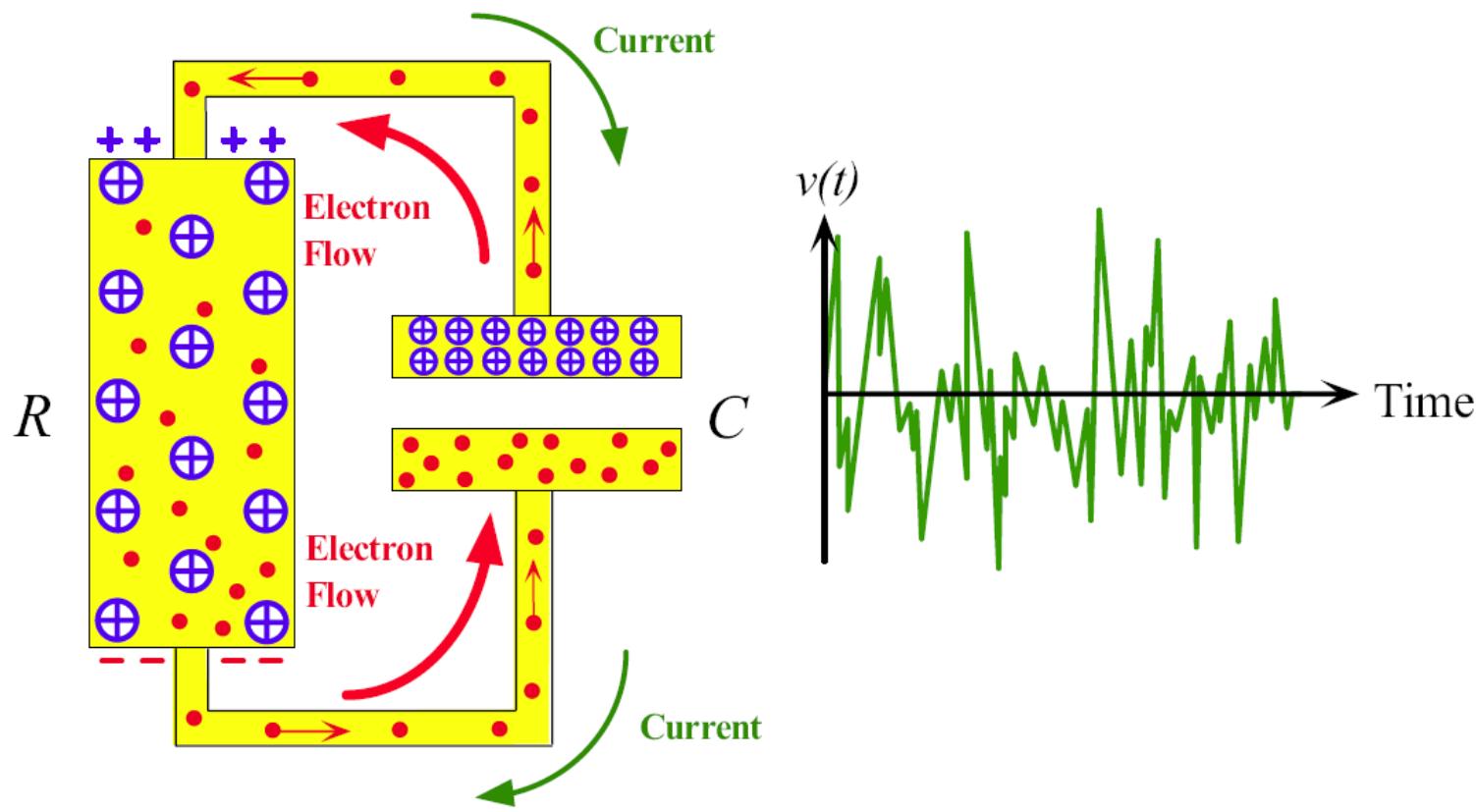
# Root Mean Square Fluctuations of a Body Attached to a Spring of Stiffness $K$

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

$K$  = 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.

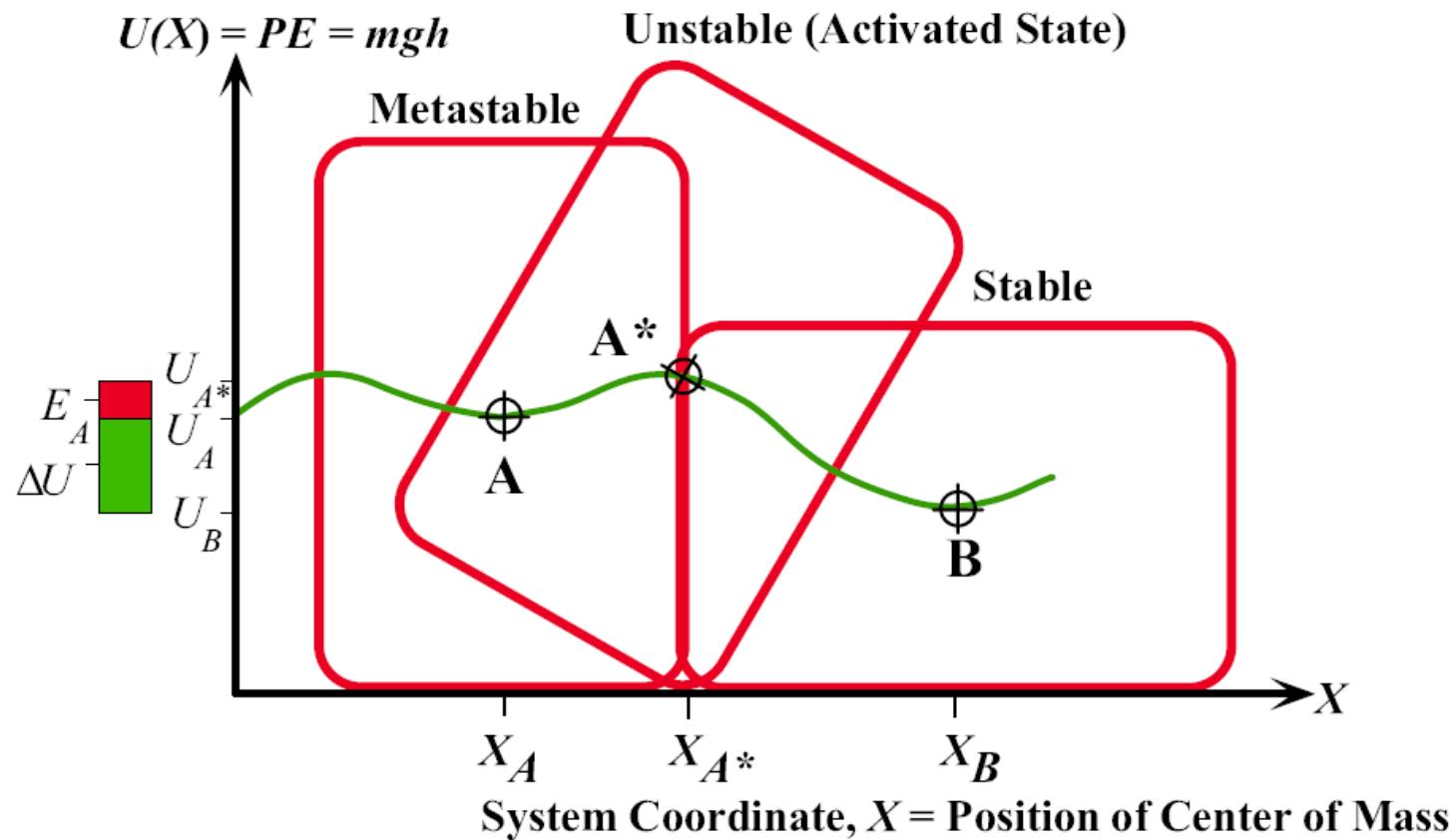


Charging and discharging of a capacitor by a conductor due to the random thermal motions of the conduction electrons.

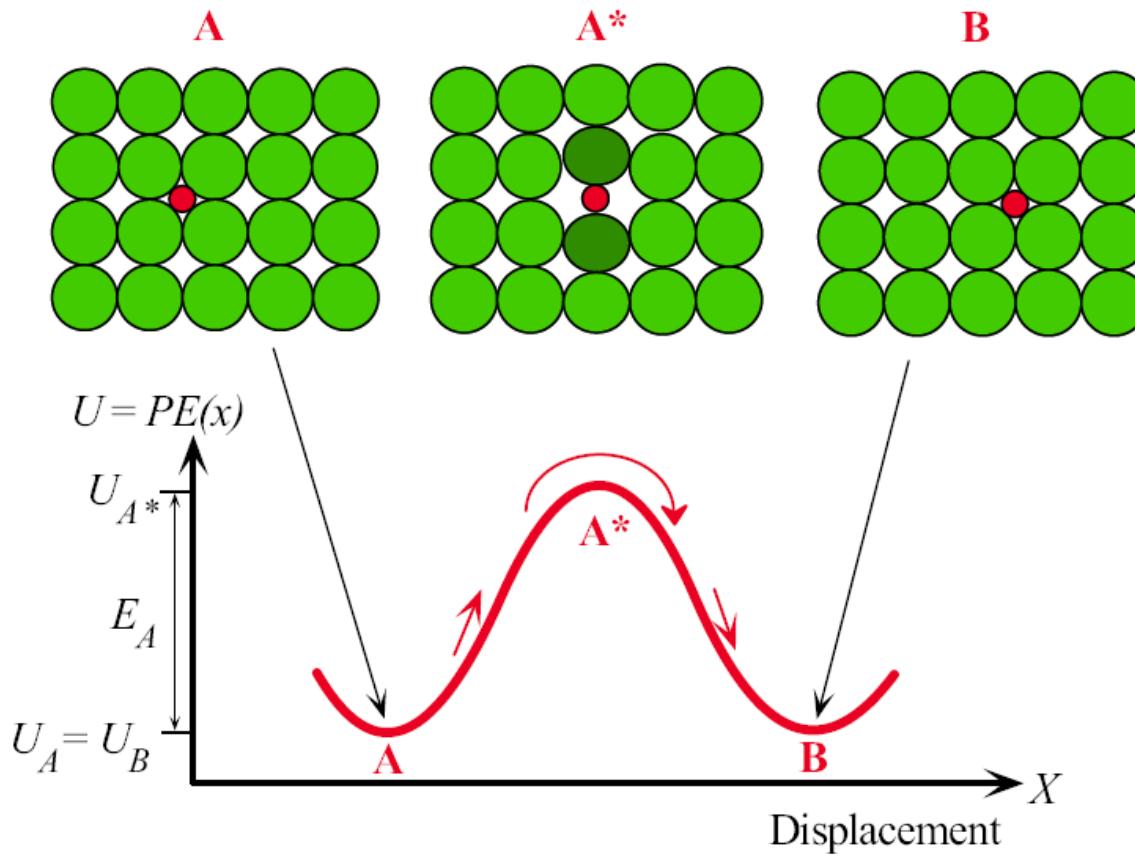
# Root Mean Square Noise Voltage Across a Resistance

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

$R$  = resistance,  $B$  = bandwidth of the electrical system in which noise is being measured,  $v_{\text{rms}}$  = 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  $A$ .



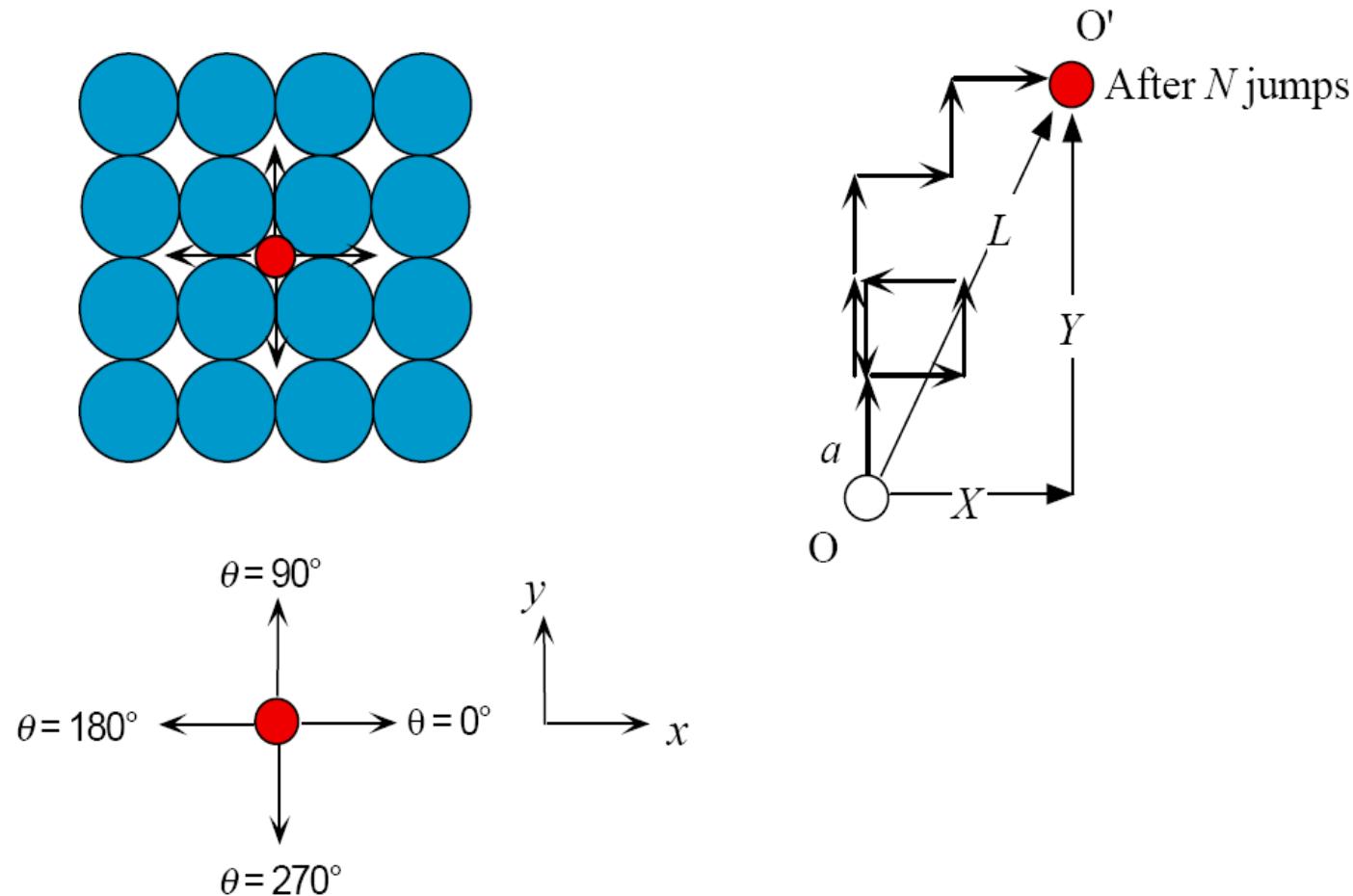
Diffusion of an interstitial impurity atom in a crystal from one void to a neighboring void. The impurity atom at position A must possess an energy  $E_A$  to push the host atoms away and move into the neighboring void at B.

# Rate for a Thermally Activated Process

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

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

$\vartheta$  = 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

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

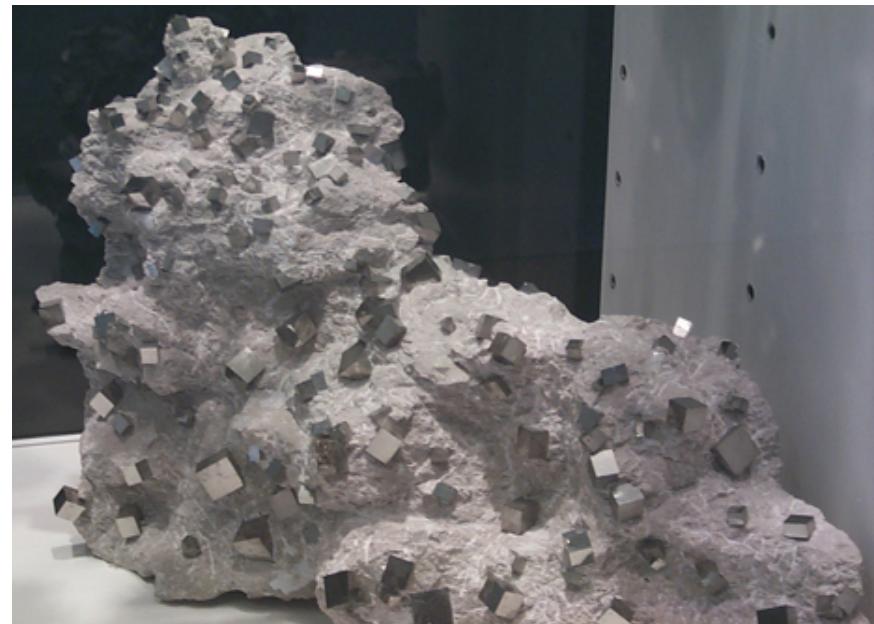
$L$  = “distance” diffused after time  $t$ ,  $a$  = closest void to void separation (jump distance),  $\vartheta$  = frequency of jumps,  $t$  = time,  $D$  = diffusion coefficient

## 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

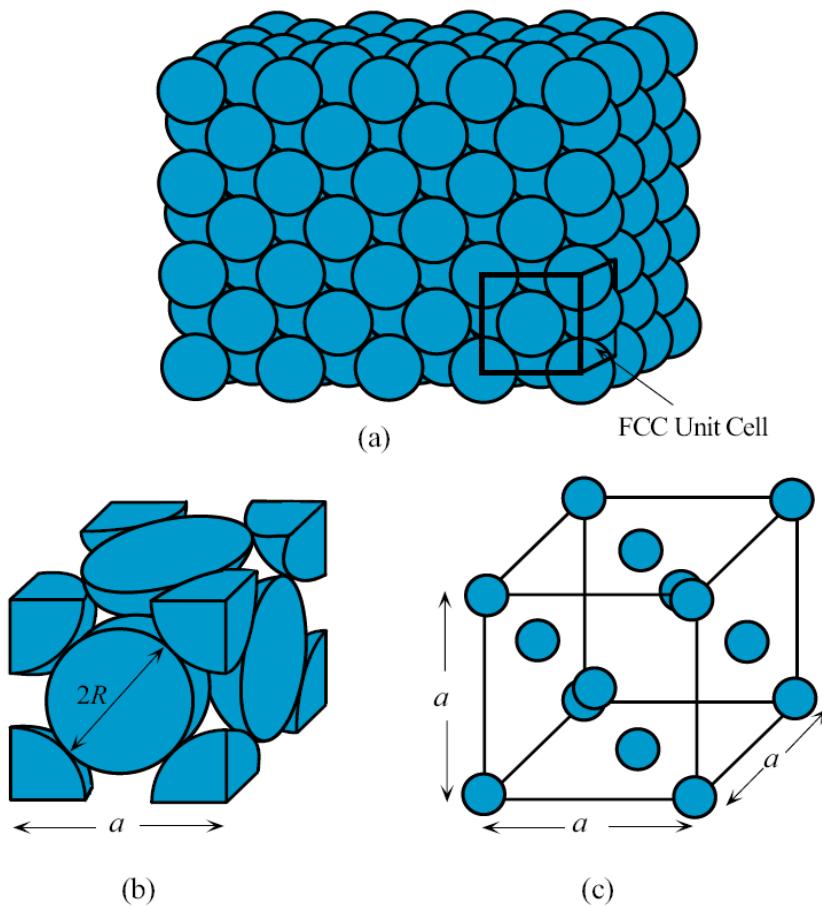


Cubic  $\text{FeS}_2$ , iron sulfide, or pyrite, crystals. The crystals look brass-like yellow ("fool's gold").

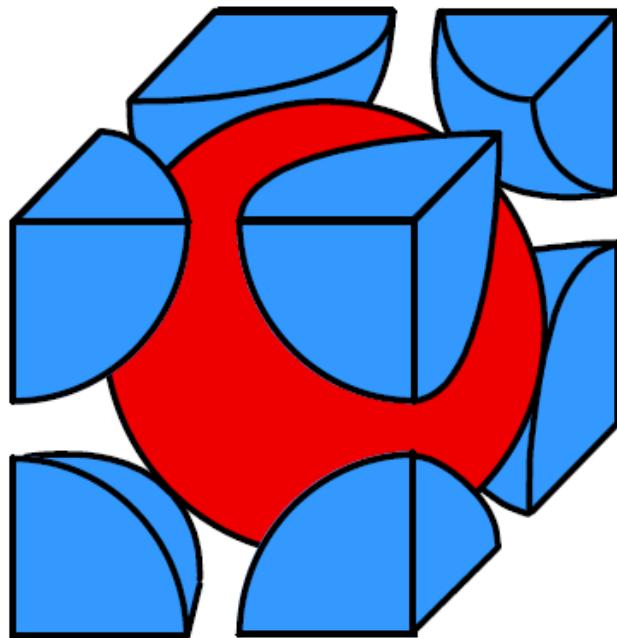
|SOURCE: Photo by SOK

Galena is lead sulfide,  $\text{PbS}$ , and has a cubic crystal structure

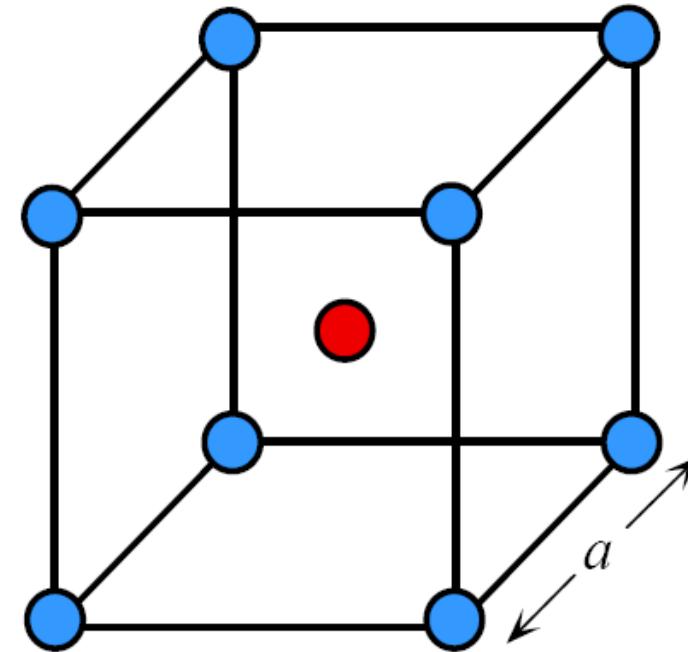
|SOURCE: Photo by SOK



- (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,  $\gamma$ -Fe ( $>912$  °C), Ni, Pd, Pt, Rh.



a

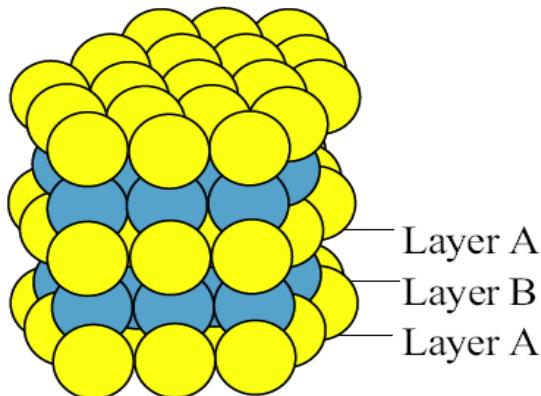


b

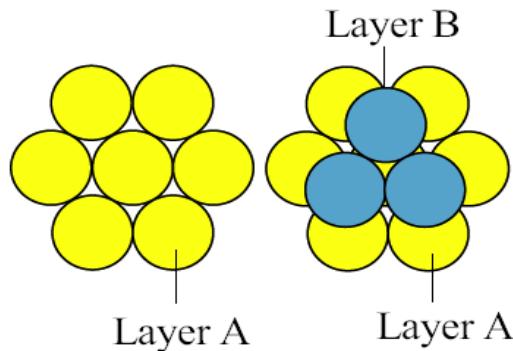
Example: Alkali metals (Li, Na, K, Rb), Cr, Mo, W, Mn,  $\alpha$ -Fe ( $< 912$  °C),  $\beta$ -Ti ( $> 882$  °C)

Body centered cubic crystal (BCC) crystal structure.

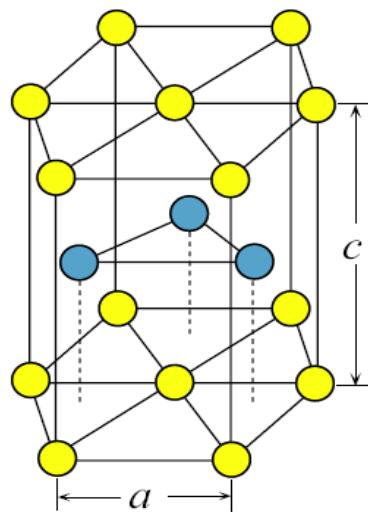
- (a) A BCC unit cell with closely packed hard spheres representing the Fe atoms.
- (b) A reduced-sphere unit cell.



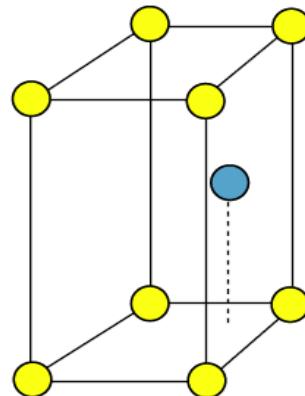
(a)



(b)



(c)



(d)

The Hexagonal Close Packed (HCP) Crystal Structure.

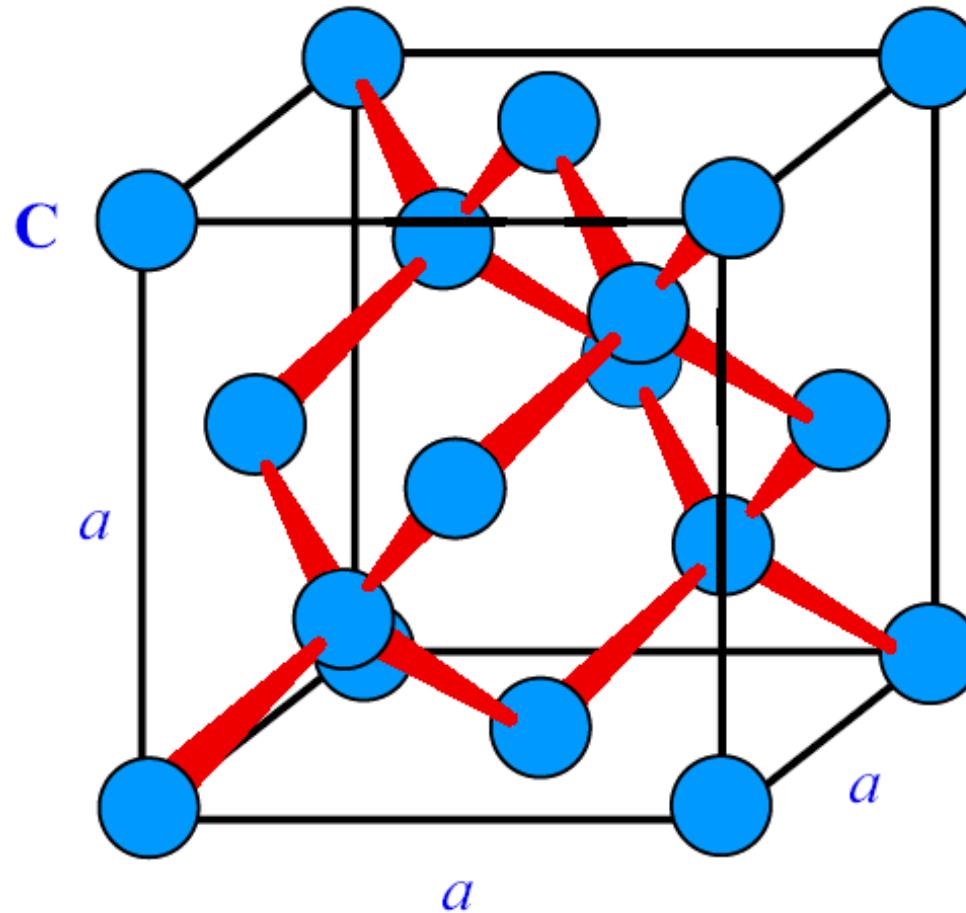
**(a)** The Hexagonal Close Packed (HCP) Structure. A collection of many Zn atoms. Color difference distinguishes layers (stacks).

**(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,  $\alpha$ -Ti ( $< 882^\circ\text{C}$ ), Cr, Co, Zn, Zr, Cd



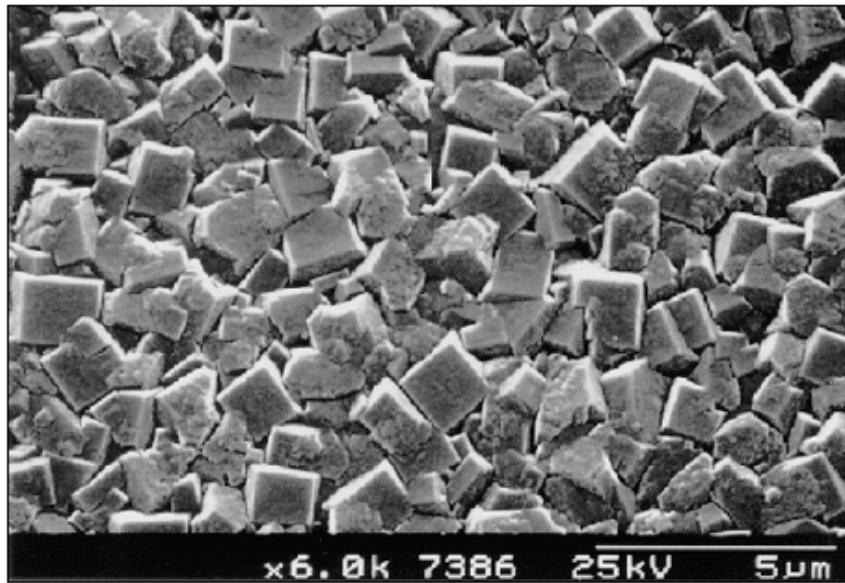
The diamond unit cell is cubic. The cell has eight atoms. Grey Sn ( $\alpha$ -Sn) and the Elemental semiconductors Ge and Si have this crystal structure.

# Silicon

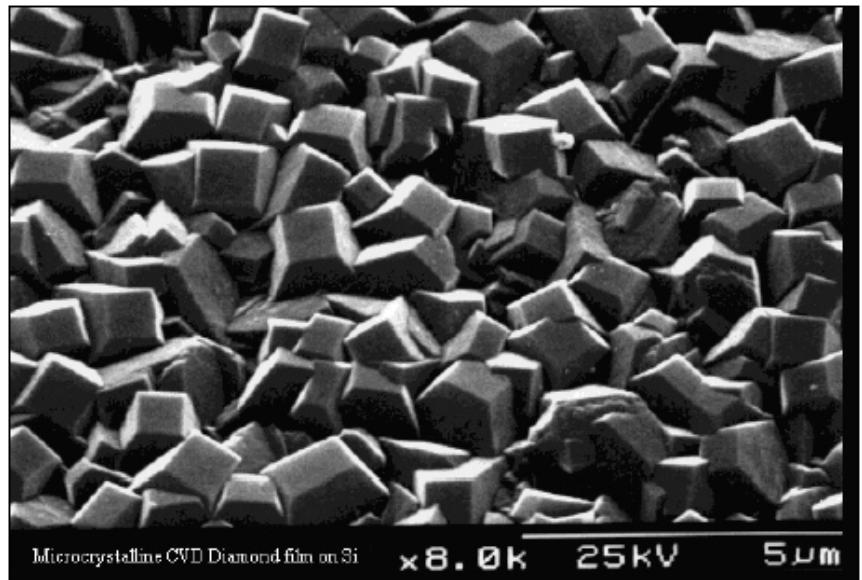


A silicon ingot is a single crystal of Si. Within the bulk of the crystal, the atoms are arranged on a well-defined periodical lattice. The crystal structure is that of **diamond**.

|Courtesy of MEMC, Electronic Materials Inc.



x6.0k 7386 25kV 5 $\mu$ m

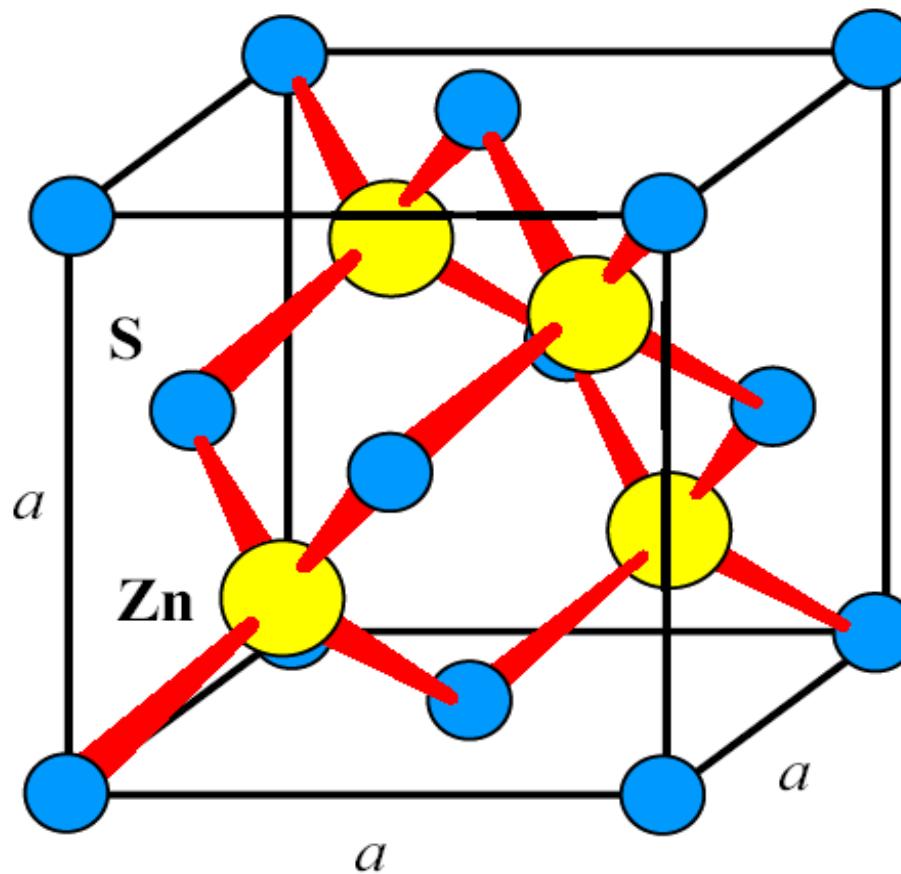


Microcrystalline CVD Diamond film on Si x8.0k 25kV 5 $\mu$ m

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

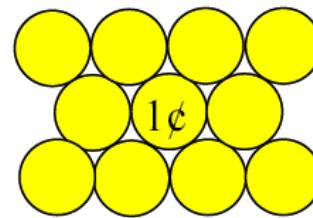
Left: A polycrystalline diamond film on the (100) surface of a single crystal silicon wafer. The film thickness is 6 microns and the SEM magnification is 6000.

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

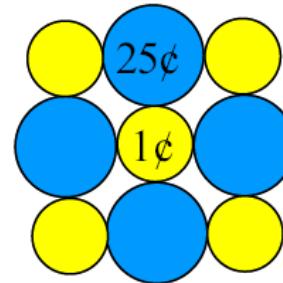


The Zinc blende (ZnS) cubic crystal structure. Many important compound crystal Structures have the zinc blende structure. Examples: AlAs, GaAs, Gap, GaSb, InAs, InP, InSb, ZnS, ZnTe.

Ratio of radii = 1

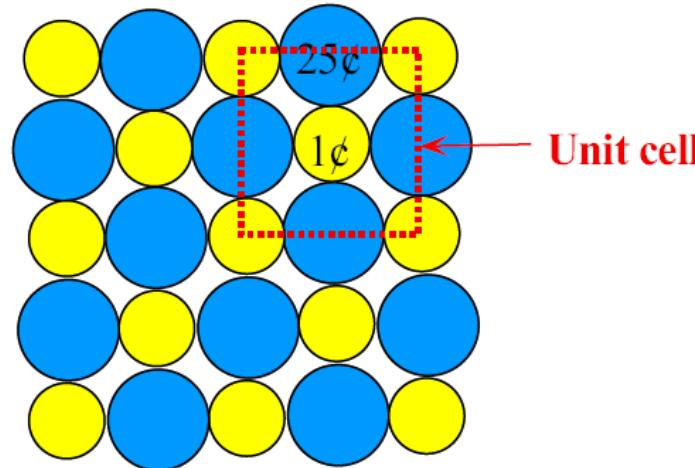


Ratio of radii = 0.75



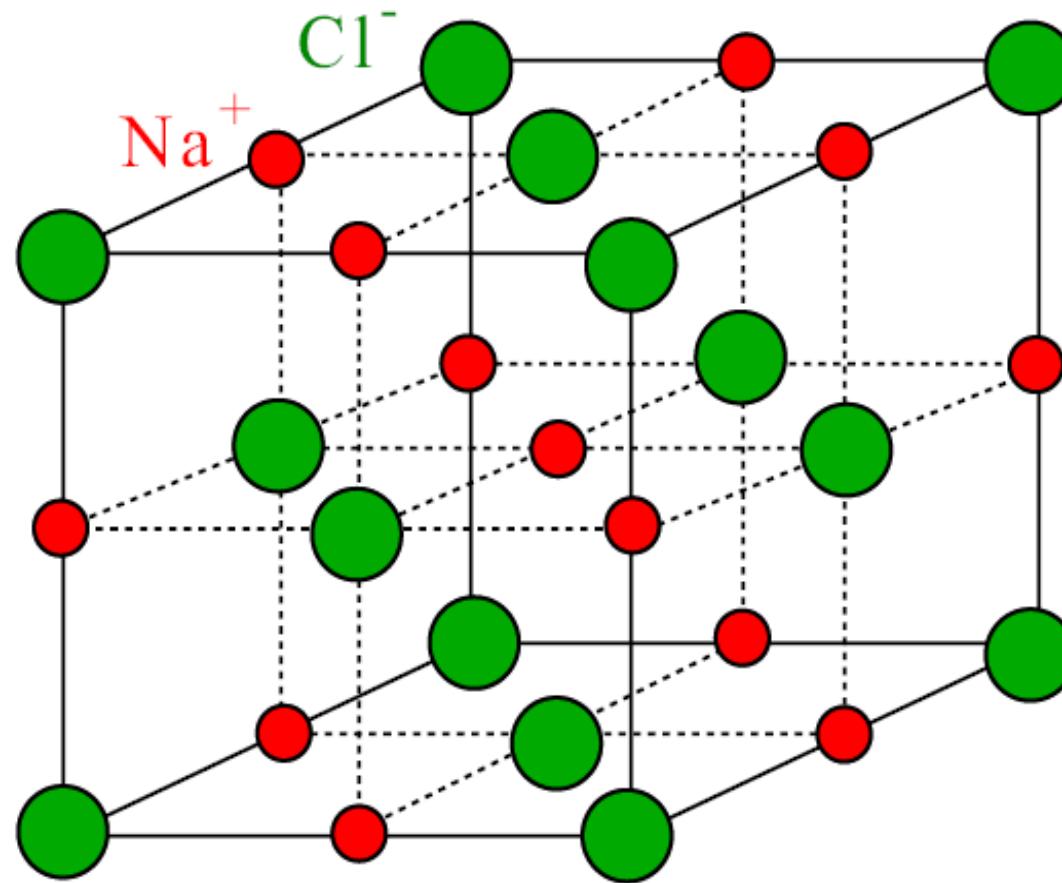
Nearest neighbors = 6

Nearest neighbors = 4



A two-dimensional crystal of pennies and quarters

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

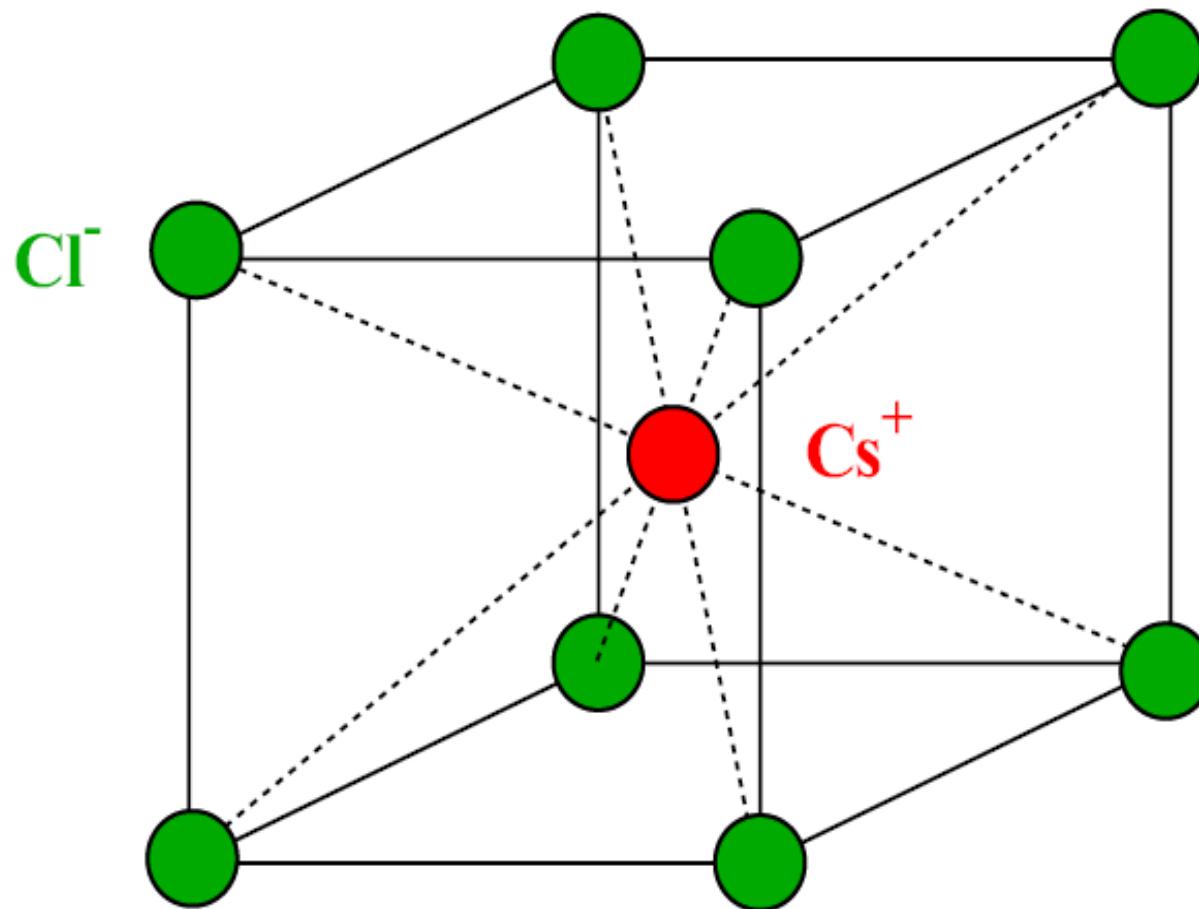


A possible reduced sphere unit cell for the NaCl (rock salt) crystal. An alternative Unit cell may have  $\text{Na}^+$  and  $\text{Cl}^-$  interchanged. Examples: AgCl, CaO, CsF, LiF, LiCl, NaF, NaCl, KF, KCl, MgO.

# NaCl or halite crystals are transparent



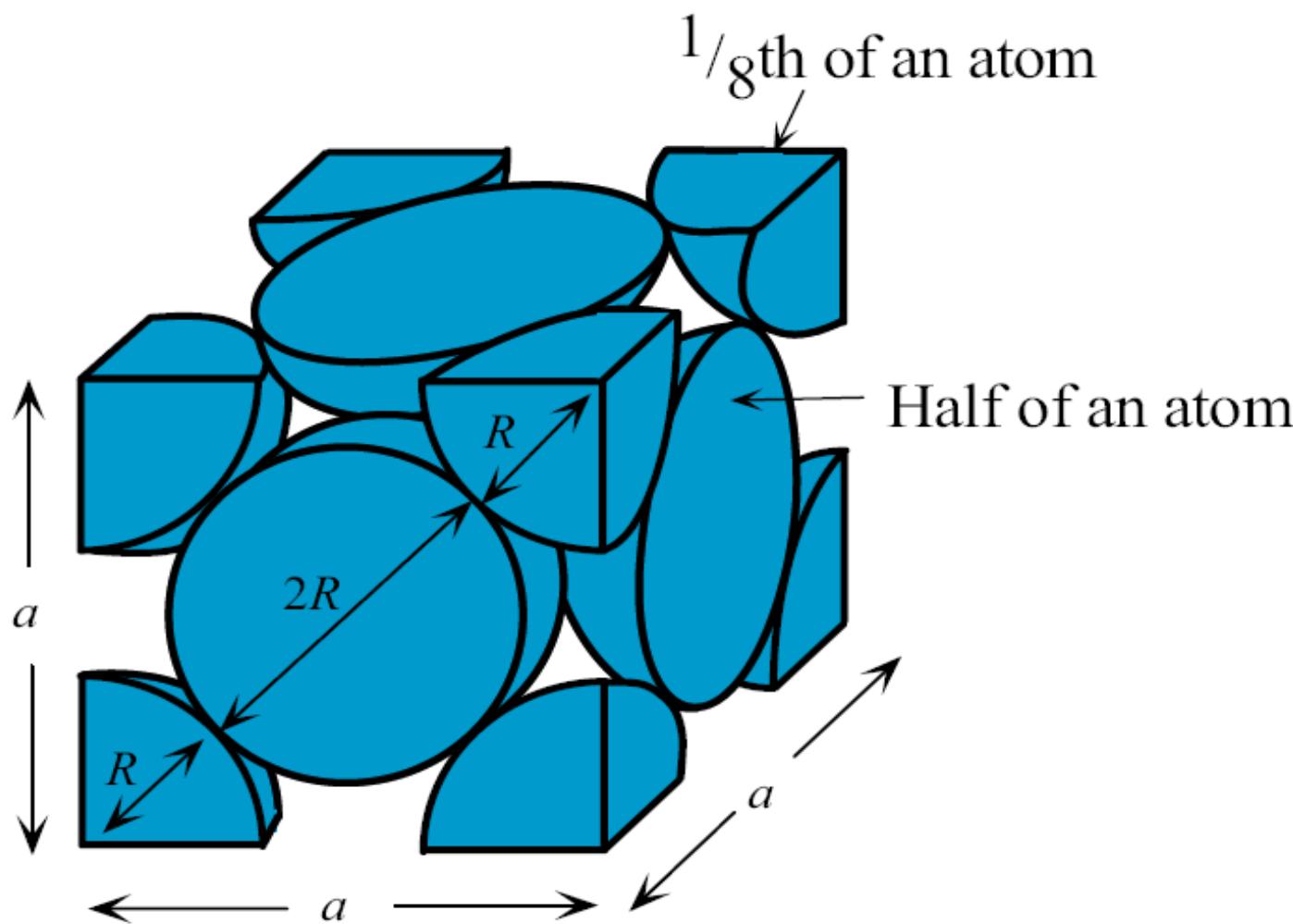
|SOURCE: Photo by SOK



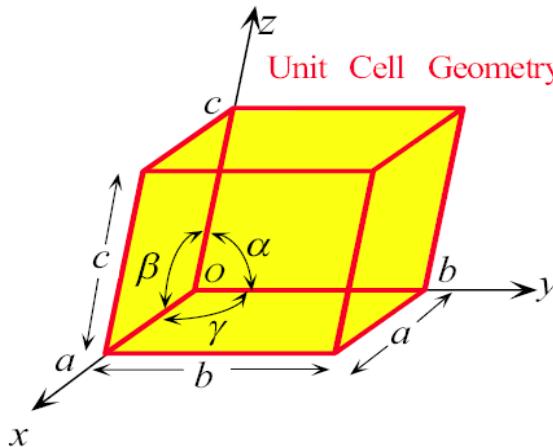
A possible reduced sphere unit cell for the CsCl crystal. An alternative unit cell may have  $\text{Cs}^+$  and  $\text{Cl}^-$  interchanged. Examples:  $\text{CsCl}$ ,  $\text{CsBr}$ ,  $\text{CsI}$ ,  $\text{TlCl}$ ,  $\text{TlBr}$ ,  $\text{TlI}$ .

**Table 1.3** Properties of some important crystal structures

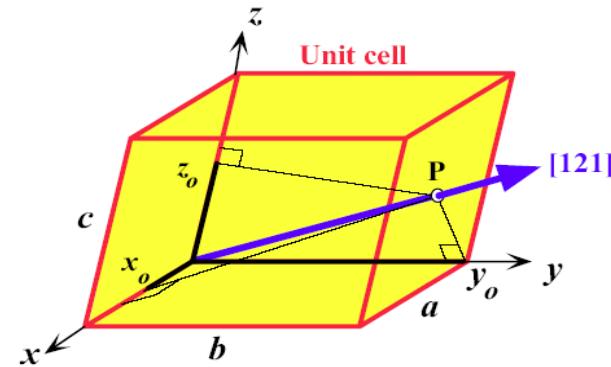
Crystal Structure	$a$ and $R$ ( $R$ is the Radius of the Atom)	Coordination Number (CN)	Number of Atoms per Unit Cell	Atomic Packing Factor	Examples
Simple cubic	$a = 2R$	6	1	0.52	No metals (Except Po)
BCC	$a = \frac{4R}{\sqrt{3}}$	8	2	0.68	Many metals: $\alpha$ -Fe, Cr, Mo, W
FCC	$a = \frac{4R}{\sqrt{2}}$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



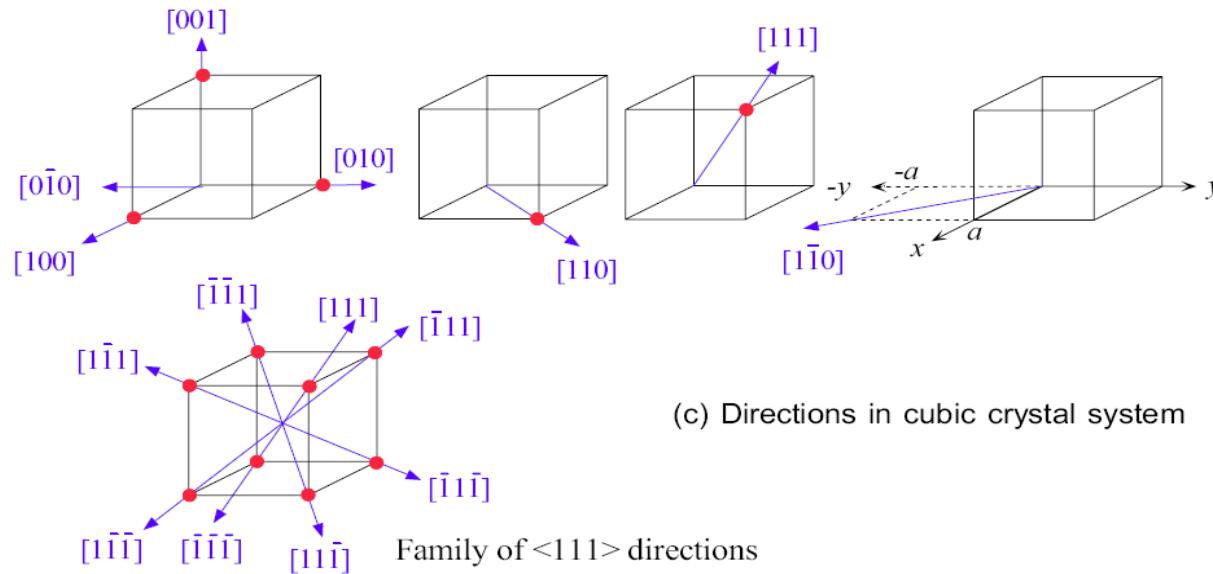
The FCC unit cell. The atomic radius is  $R$  and the lattice parameter is  $a$



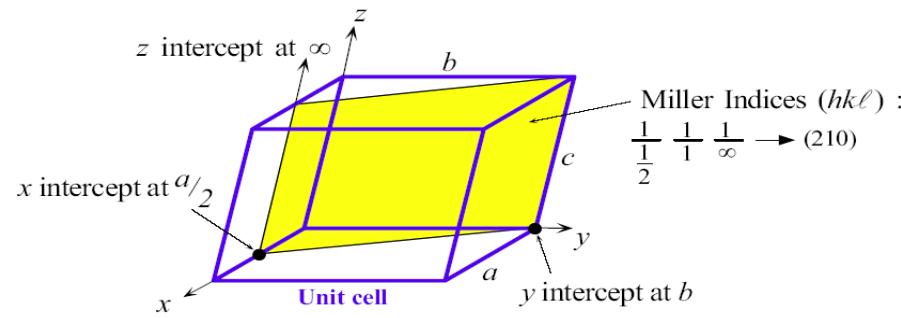
(a) A parallelepiped is chosen to describe geometry of a unit cell. We line the  $x$ ,  $y$  and  $z$  axes with the edges of the parallelepiped taking lower-left rear corner as the origin



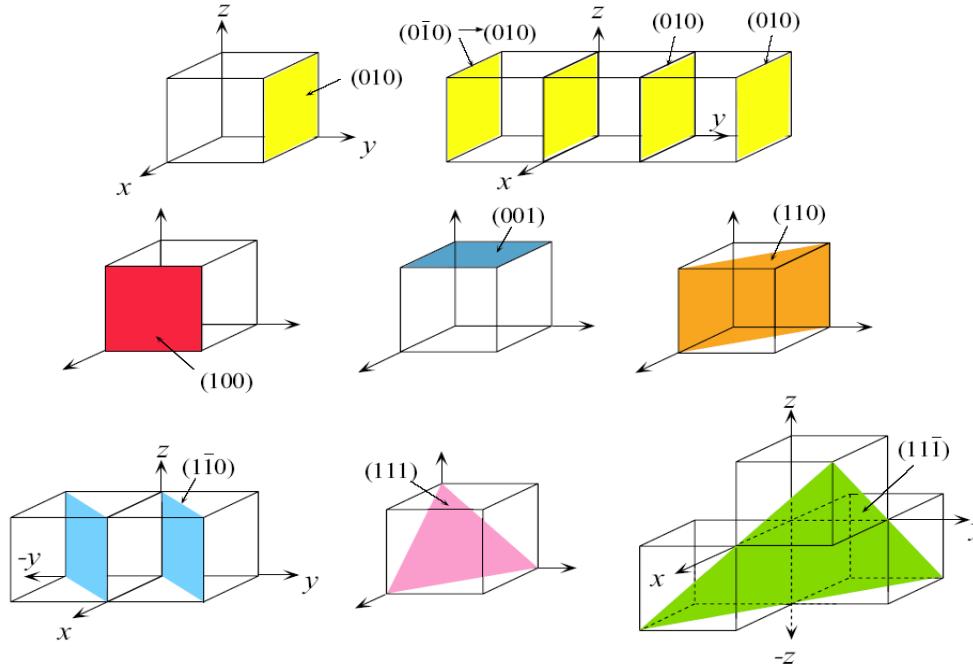
(b) Identification of a direction in a crystal



(c) Directions in cubic crystal system

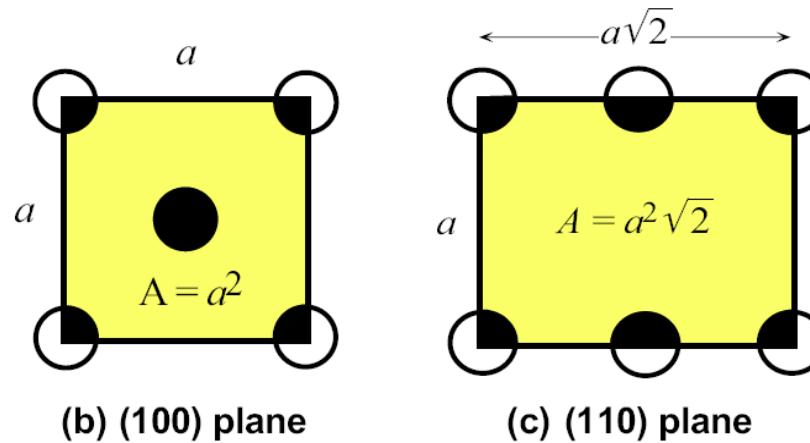
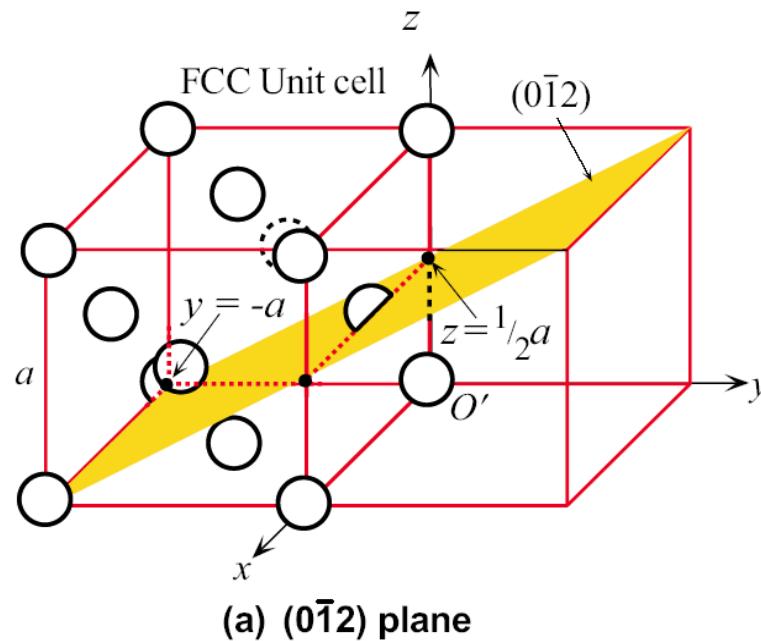


(a) Identification of a plane in a crystal

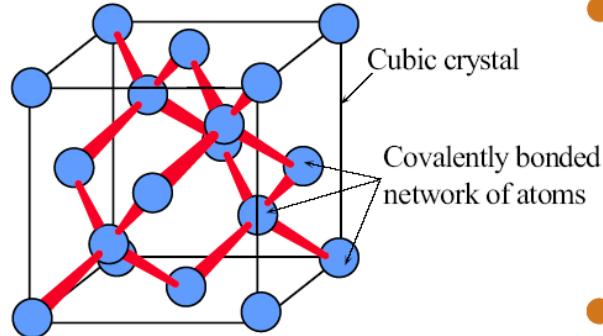


(b) Various planes in the cubic lattice

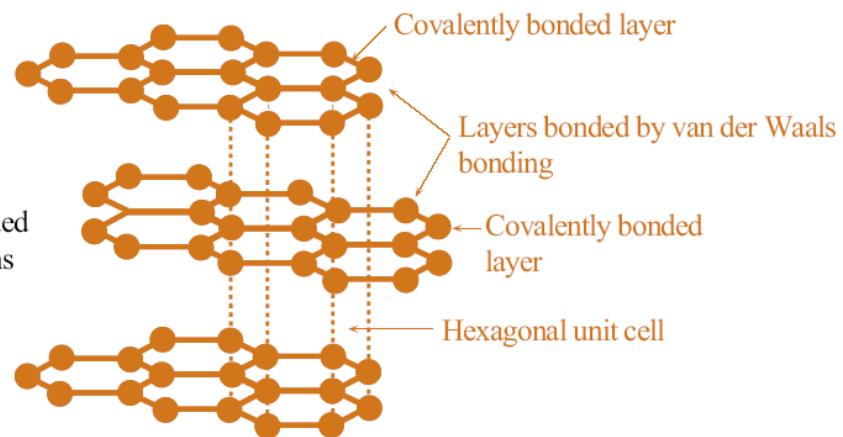
Labeling of crystal planes and typical examples in the cubic lattice



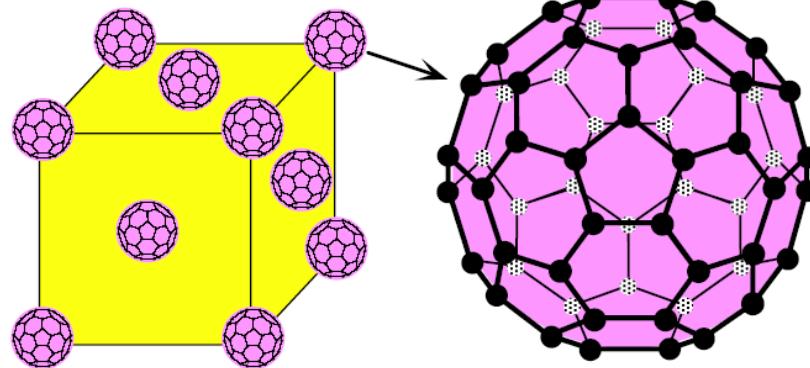
The (012) plane and planar concentrations in an FCC crystal.



(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

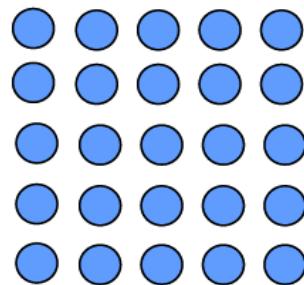
$E_v$  = vacancy formation energy

$k$  = Boltzmann constant

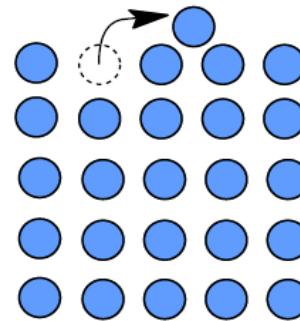
$T$  = temperature (K)

**Table 1.4** Crystalline allotropes of carbon ( $\rho$  is the density and  $Y$  is the elastic modulus or Young's modulus)

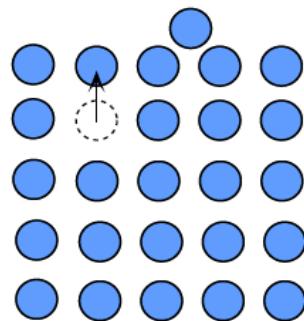
	<b>Graphite</b>	<b>Diamond</b>	<b>Buckminsterfullerene Crystal</b>
<b>Structure</b>	Covalent bonding within layers. Van der Waals bonding between layers. Hexagonal unit cell.	Covalently bonded network. Diamond crystal structure.	Covalently bonded $C_{60}$ spheroidal molecules held in an FCC crystal structure by van der Waals bonding.
<b>Electrical and thermal properties</b>	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.
<b>Mechanical properties</b>	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. $Y \approx 18 \text{ GPa}$ $\rho = 1.65 \text{ g cm}^{-3}$
<b>Comment</b>	Stable allotrope at atmospheric pressure	High-pressure allotrope.	Laboratory synthesized. Occurs in the soot of partial combustion.
<b>Uses, potential uses</b>	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.



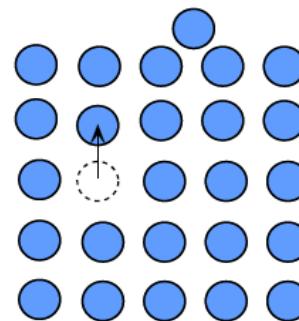
(a) Perfect crystal without vacancies



(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.

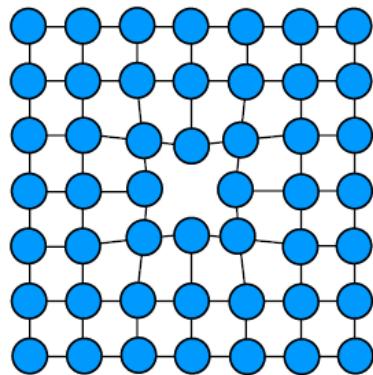


(c) An atom in the bulk diffuses to fill the vacancy thereby displacing the vacancy towards the bulk.

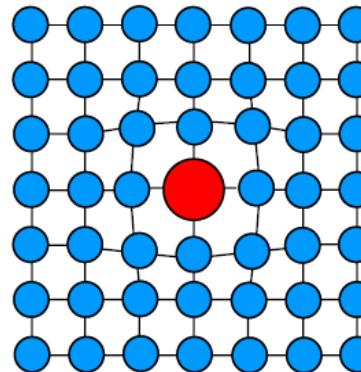


(d) Atomic diffusions cause the vacancy to diffuse into the bulk.

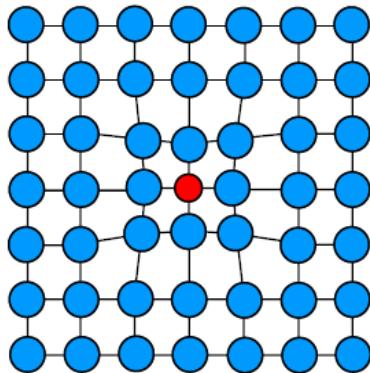
Generation of a vacancy by the diffusion of atom to the surface and the subsequent diffusion of the vacancy into the bulk.



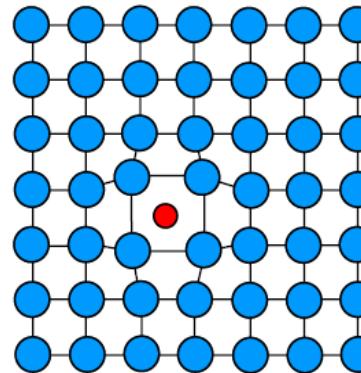
(a) A vacancy in the crystal.



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

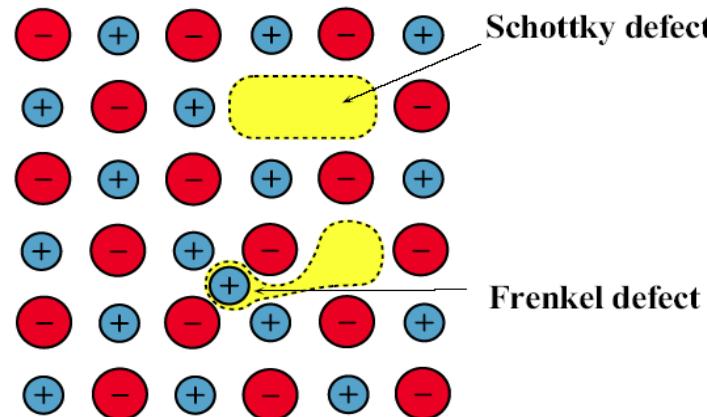


(c) A substitutional impurity in the crystal. The impurity atom is smaller than the host atom.

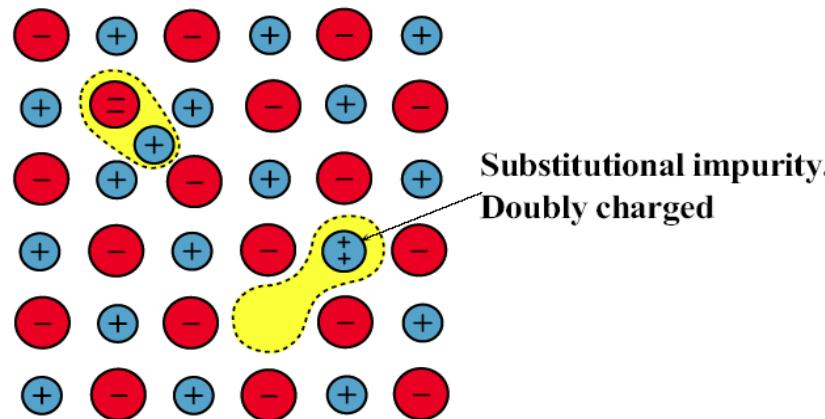


(d) An interstitial impurity in the crystal. It occupies an empty space between host atoms.

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

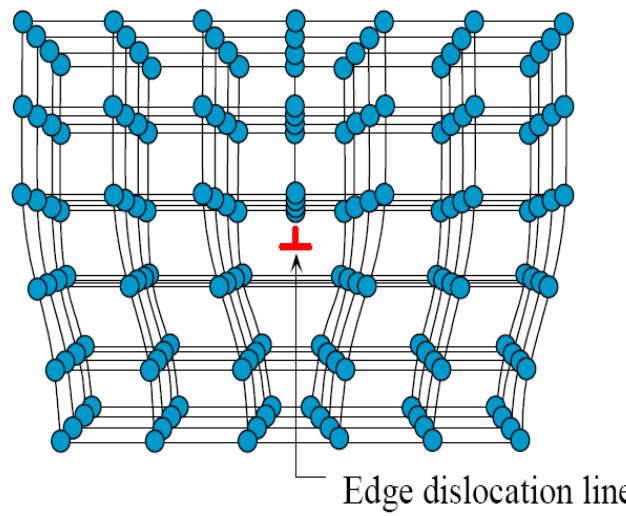


(a) Schottky and Frenkel defects in an ionic crystal.

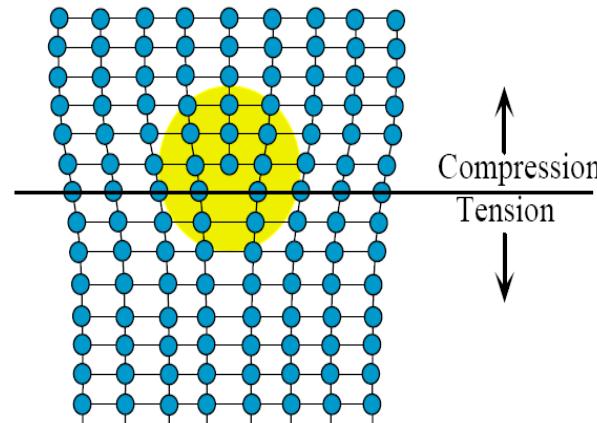


(b) Two possible imperfections caused by ionized substitutional impurity atoms in an ionic crystal.

Point defects in ionic crystals

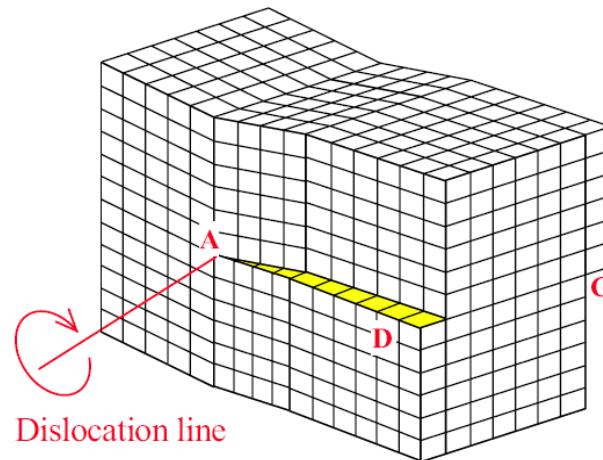


(a) Dislocation is a line defect. The dislocation shown runs into the paper.

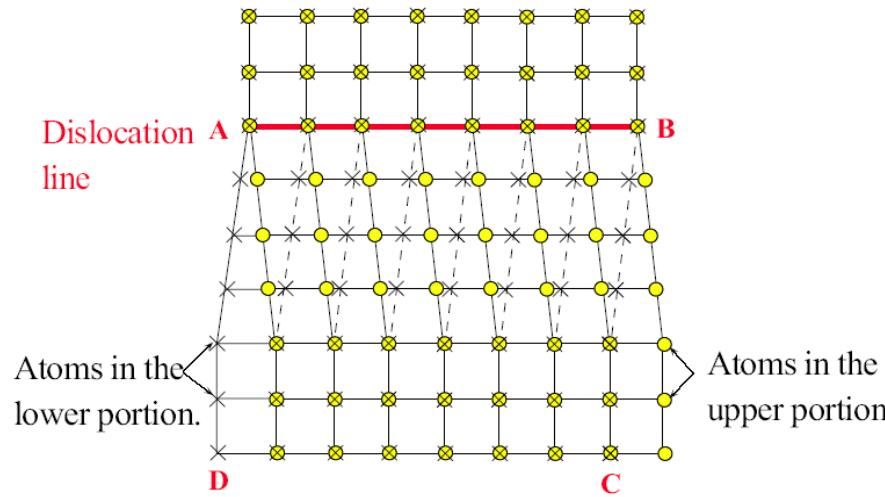


(b) Around the dislocation there is a strain field as the atomic bonds have been compressed above and stretched below the dislocation line

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

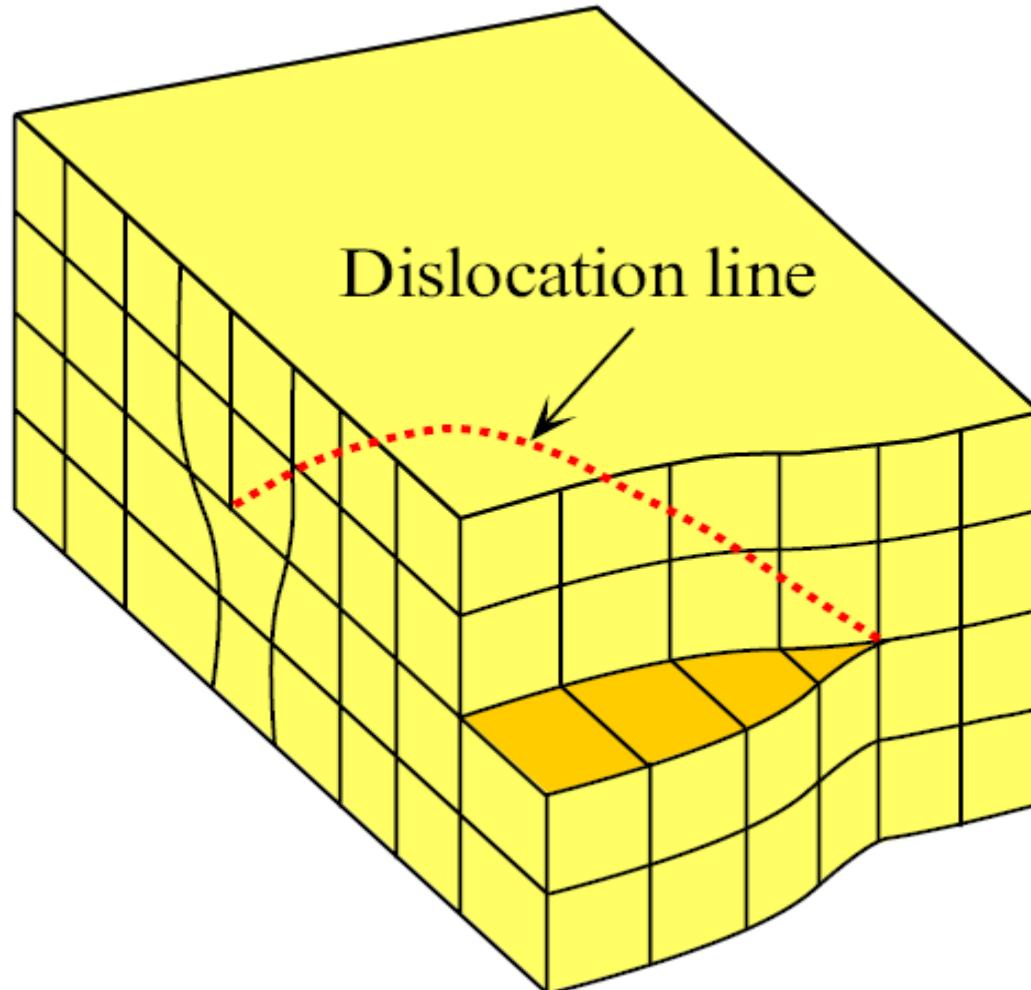


(a) A screw dislocation in a crystal.

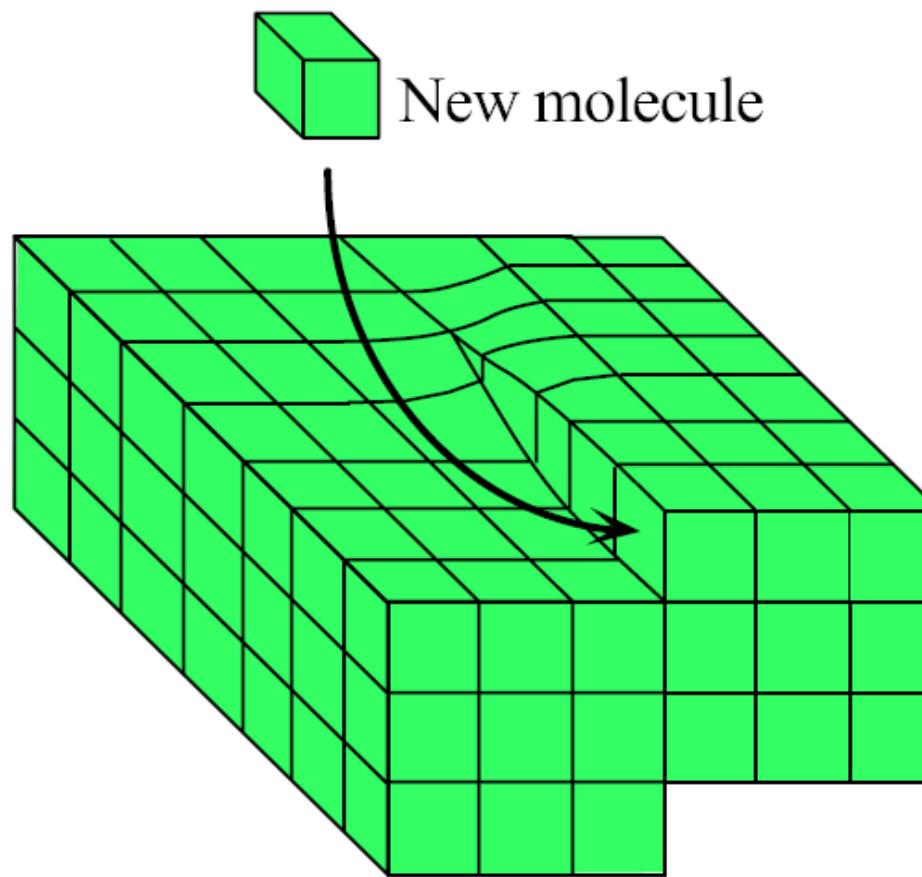


(b) The screw dislocation in (a) as viewed from above.

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

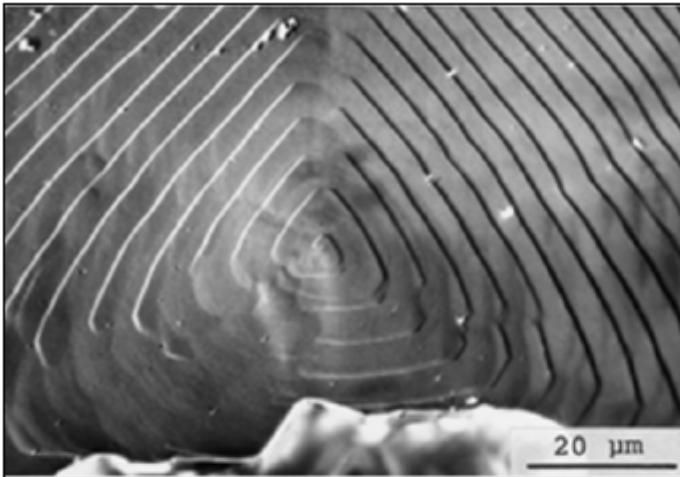


Screw dislocation aids crystal growth because the newly arriving atom can attach to two or three atoms instead of one atom and thereby form more bonds.



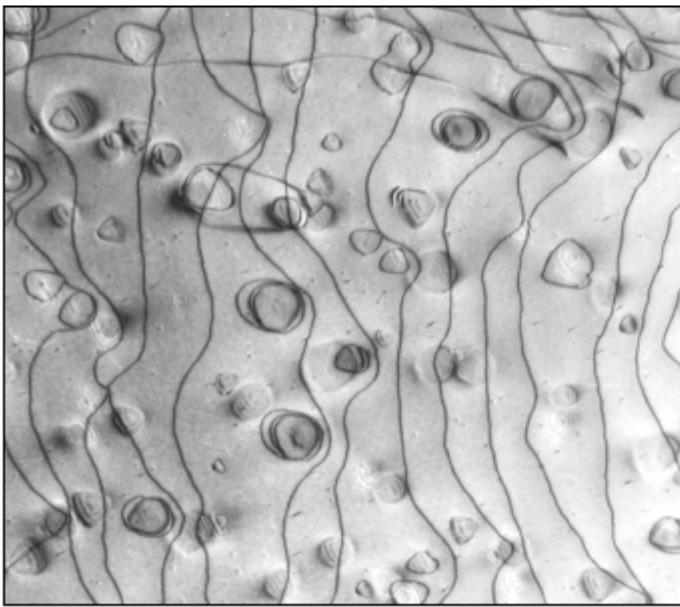
Growth spiral on the surface of a polypropylene crystal due to screw dislocation aided crystal growth.

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



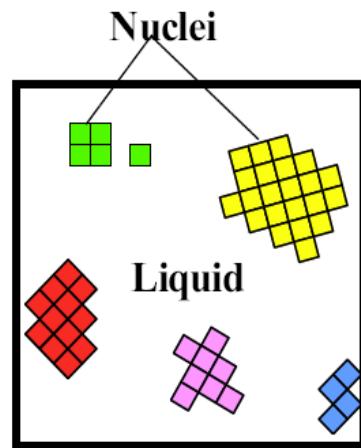
The photograph of the surface of a synthetic diamond grown on the (111) surface of natural diamond from sodium carbonate solvent at 5.5 GPa and 1600 °C.

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

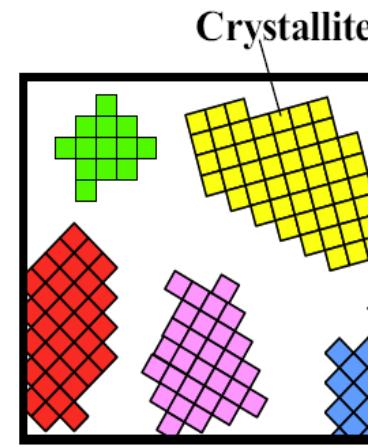


Dislocations can be seen by examining a thin slice of the sample under a transmission electron microscope (TEM). They appear as dark lines and loops as shown here in a Ni-Si alloy single crystal. The loop dislocations are around Ni<sub>3</sub>Si particles inside the crystal. The sample had been mechanically deformed, which generates dislocations.

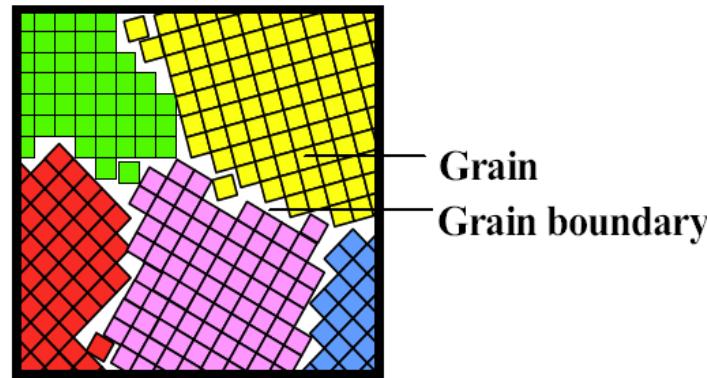
SOURCE: Courtesy of Professor John Humphreys, UMIST, England. (J. Humphreys and V. Ramaswamy in *High Voltage Electron Microscopy*, ed. P. R. Swann. C. J. Humphreys and M. J. Goringe, New York: Academic Press, 1974, p. 26.)



(a)

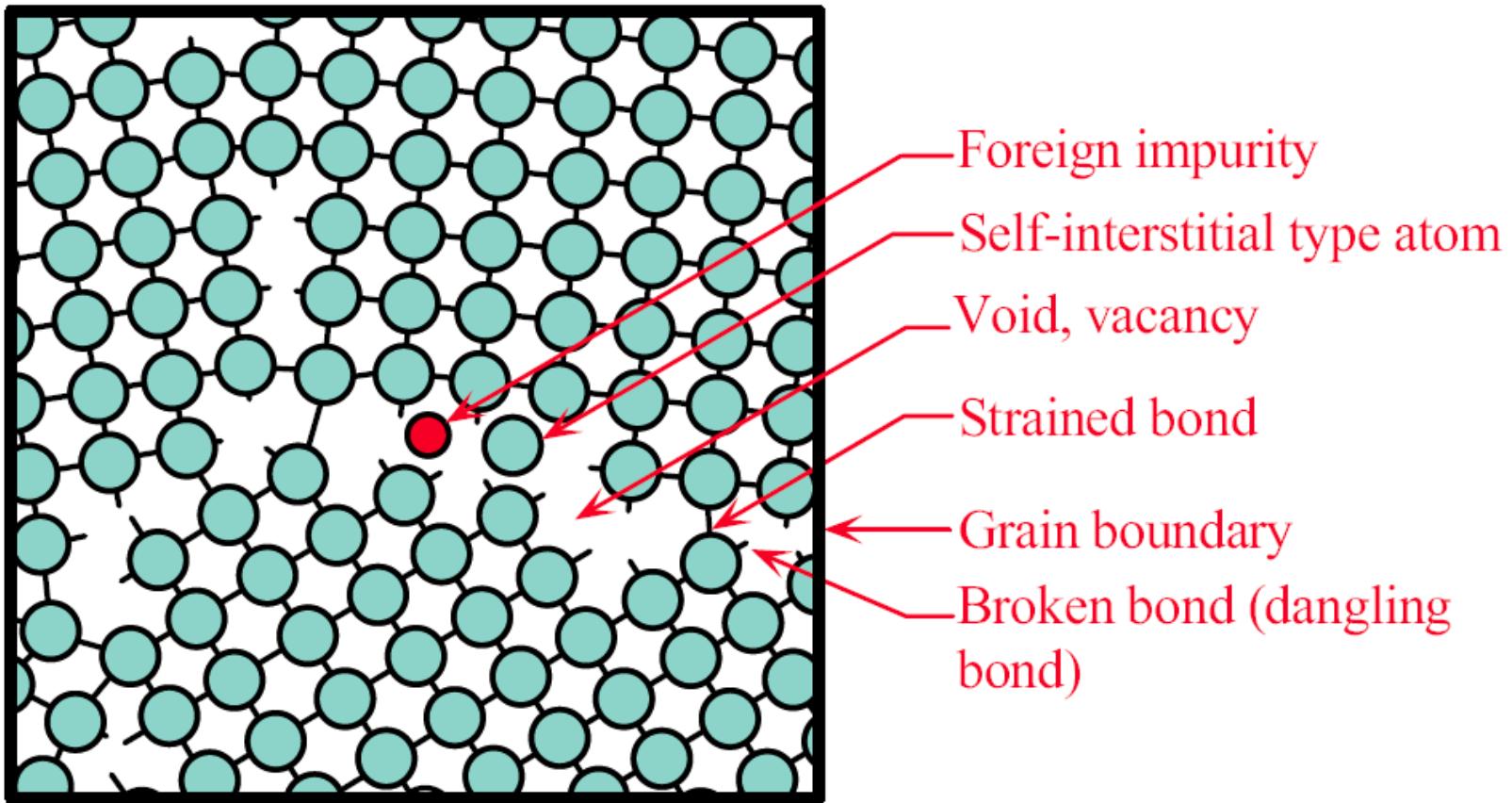


(b)

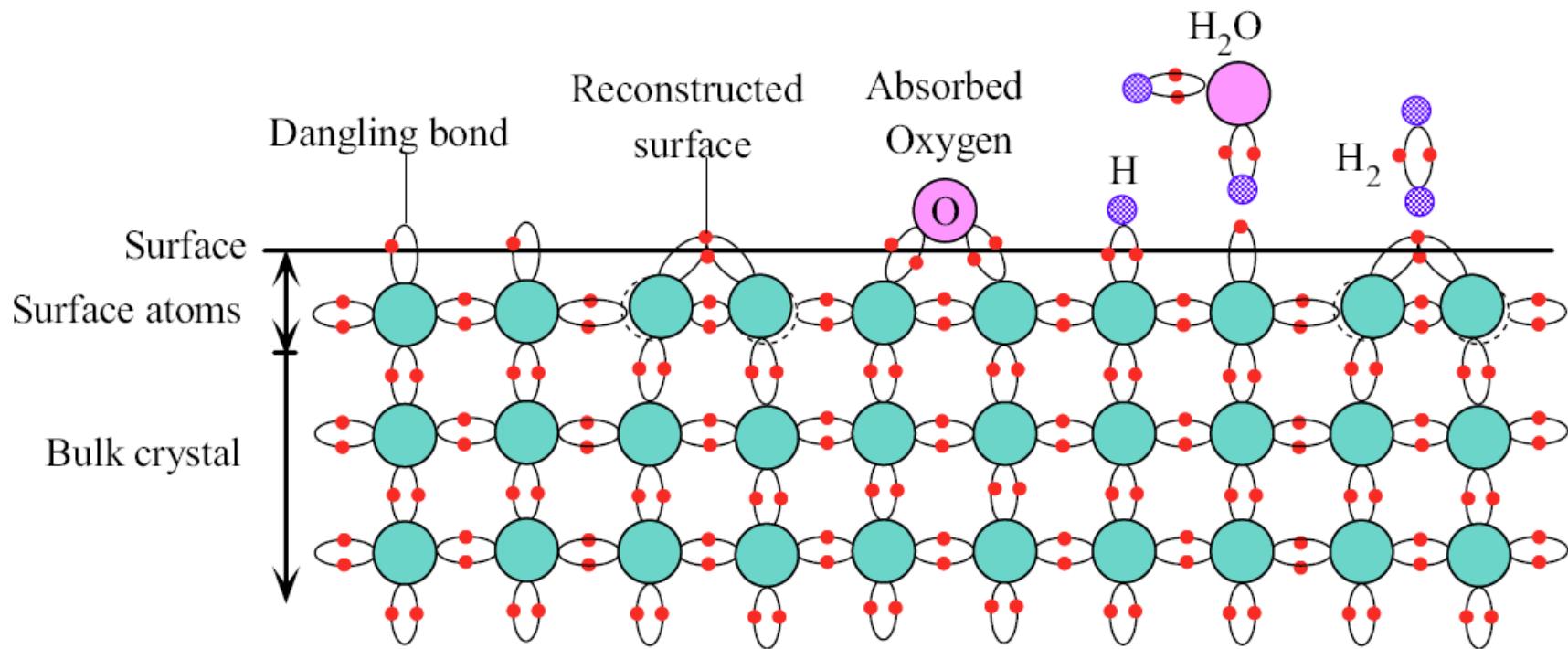


(c)

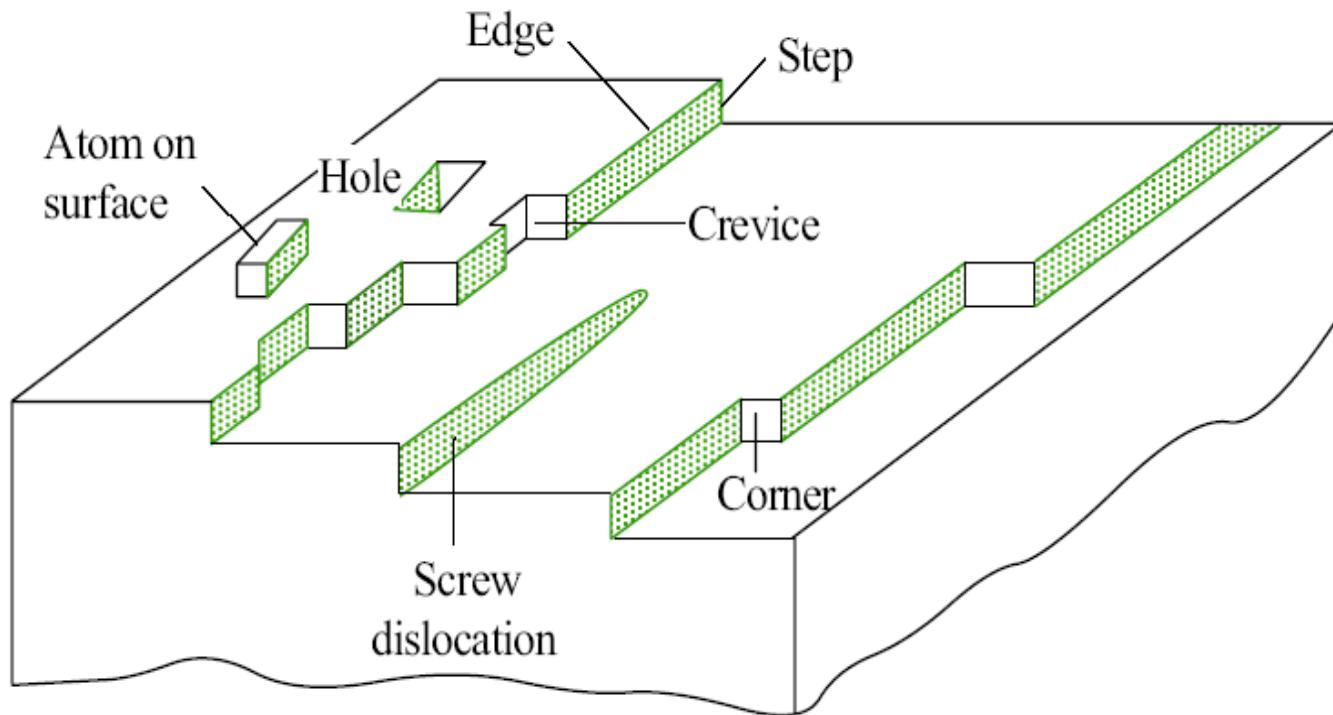
Solidification of a polycrystalline solid from the melt. (a) Nucleation. (b) Growth. (c) The solidified polycrystalline solid. For simplicity cubes represent atoms.



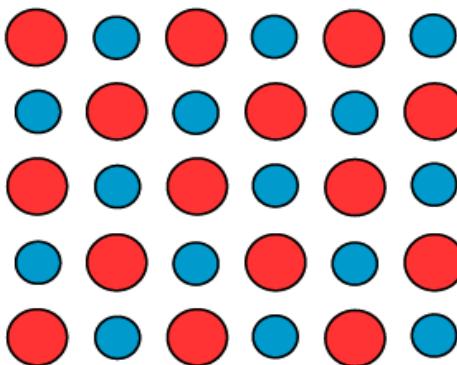
The grain boundaries have broken bonds, voids, vacancies, strained bonds and “interstitial” type atoms. The structure of the grain boundary is disordered and the atoms in the grain boundaries have higher energies than those within the grains.



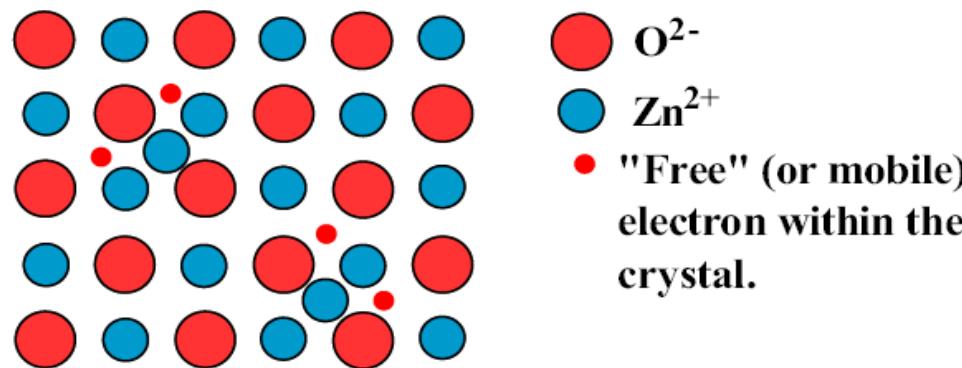
At the surface of a hypothetical two dimensional crystal, the atoms cannot fulfill their bonding requirements and therefore have broken, or dangling, bonds. Some of the surface atoms bond with each other; the surface becomes reconstructed. The surface can have physisorbed and chemisorbed atoms.



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

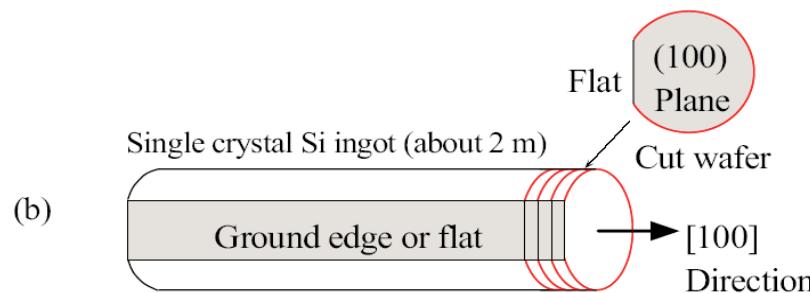
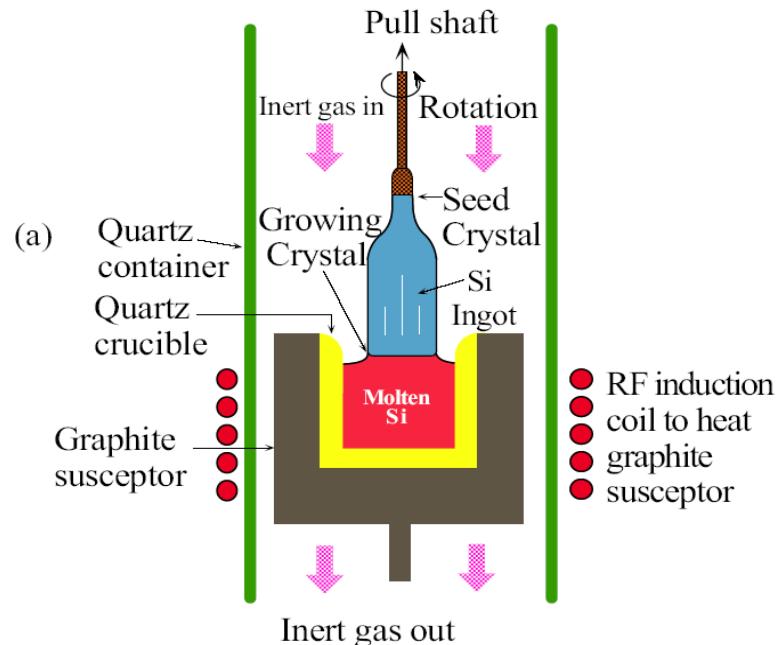


(a) Stoichiometric ZnO crystal with equal number of anions and cations and no free electrons.

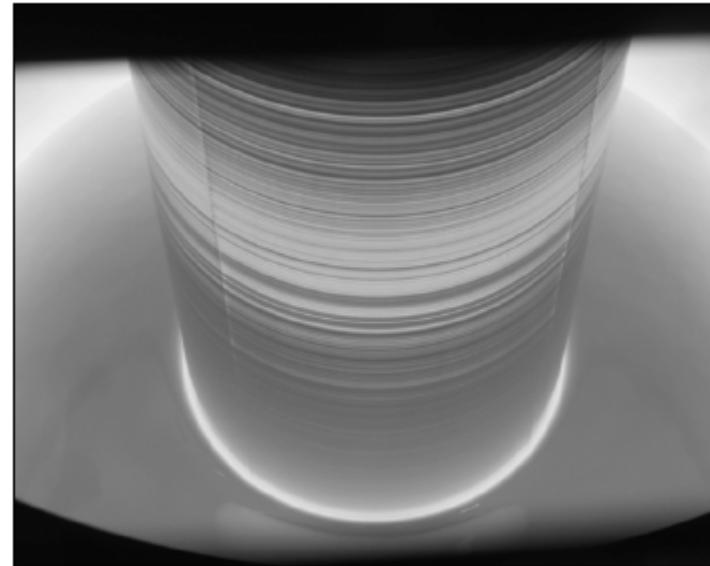
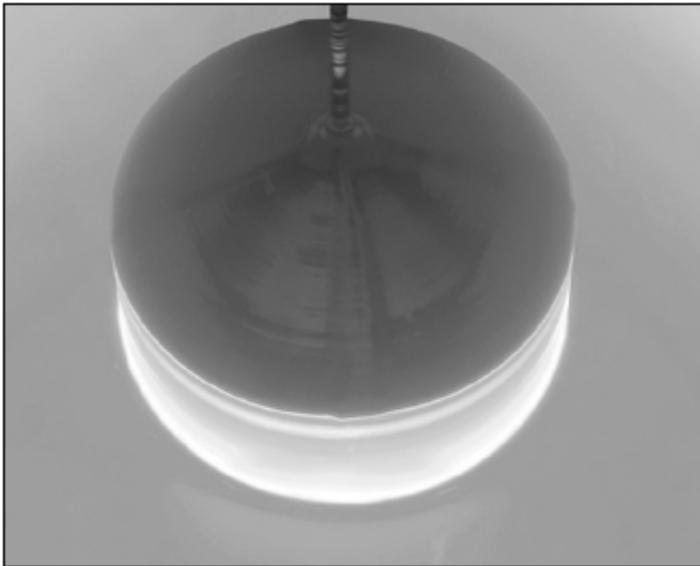


(b) Non-Stoichiometric ZnO crystal with excess Zn in interstitial sites as Zn<sup>2+</sup> cations.

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.

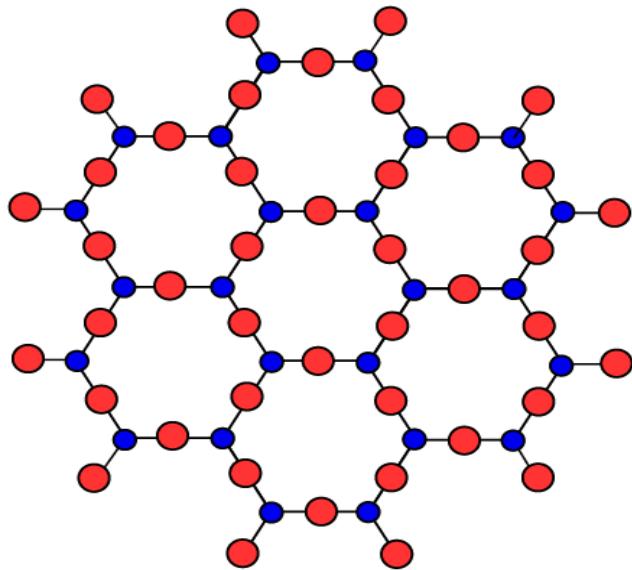


Left: Silicon crystal ingots grown by the  
Czochralski crystal drawers in the background  
|Courtesy of MEMC, Electronic Materials Inc.

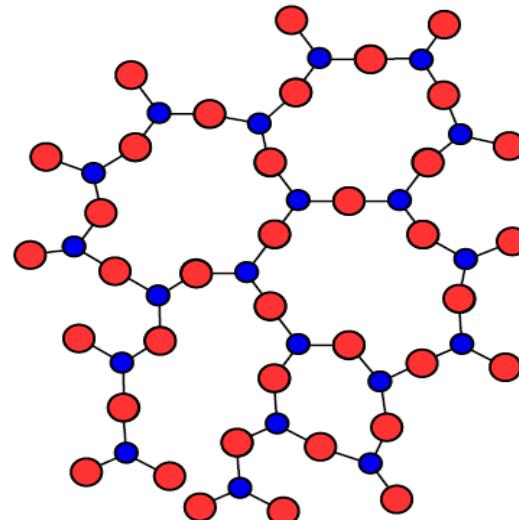


Right: 200 mm and 300 mm Si  
|Courtesy of MEMC, Electronic Materials  
Inc.

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

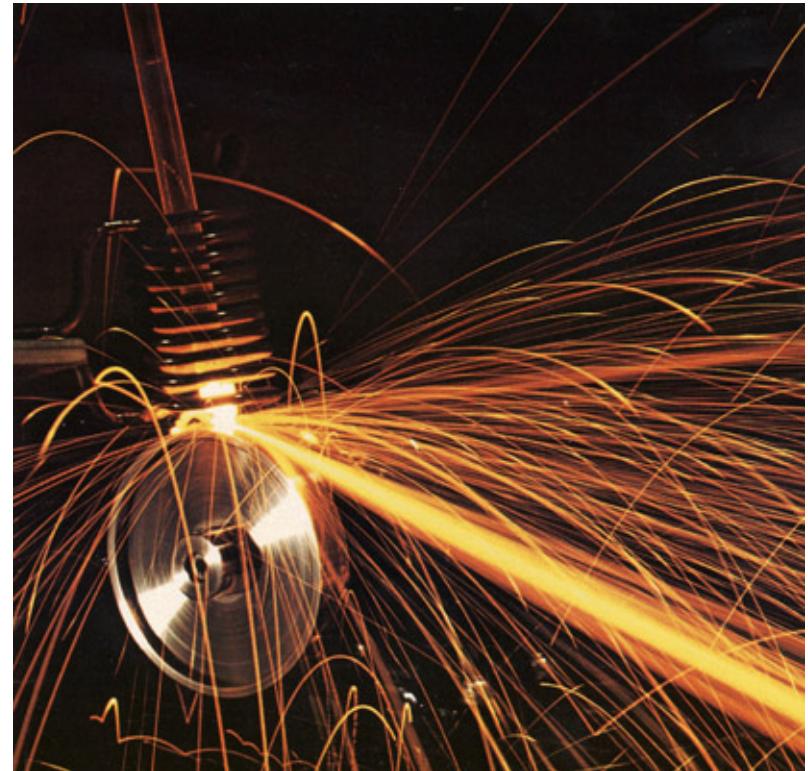
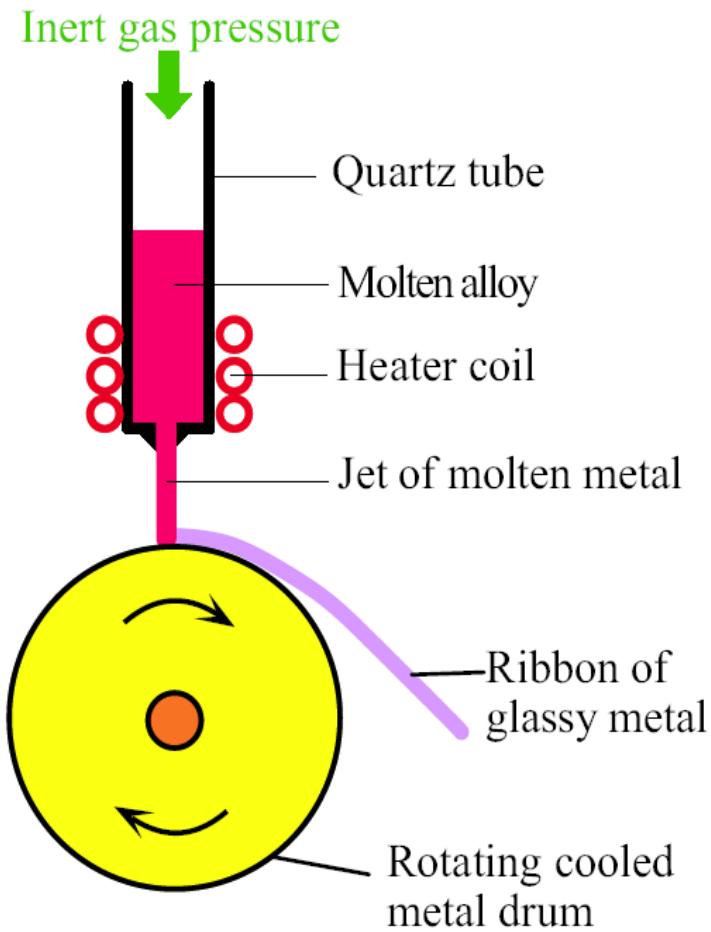


(a) A crystalline solid reminiscent to  
crystalline  $\text{SiO}_2$ . (Density =  $2.6 \text{ g cm}^{-3}$ )



(b) An amorphous solid reminiscent  
to vitreous silica ( $\text{SiO}_2$ ) cooled from  
the melt (Density =  $2.2 \text{ g cm}^{-3}$ )

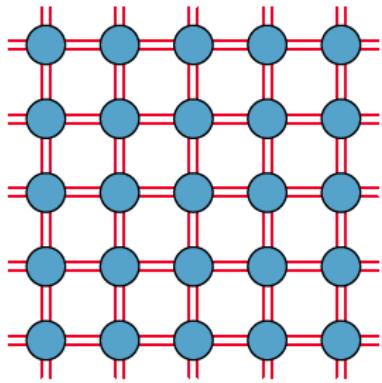
Crystalline and amorphous structures illustrated schematically in two dimensions



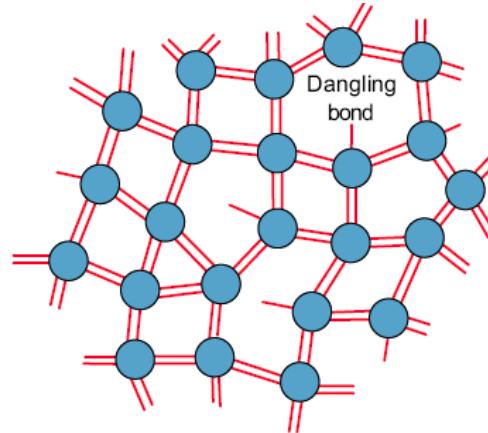
Melt spinning involves squirting a jet of molten metal onto a rotating cool metal drum. The molten jet is instantly solidified into a glassy metal ribbon which is a few microns in thickness. The process produces roughly 1 to 2 kilometers of ribbon per minute.

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

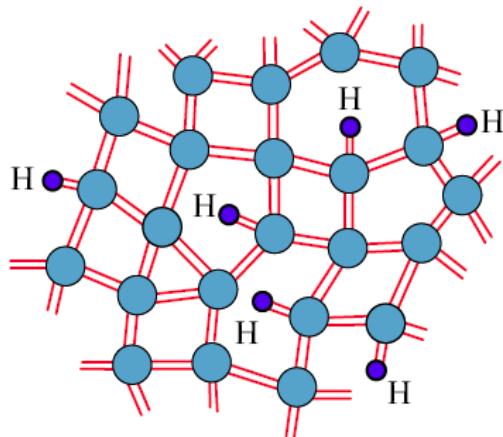
It is possible to rapidly quench a molten metallic alloy, thereby bypassing crystallization, and forming a glassy metal commonly called a metallic glass. The process is called *melt spinning*.



(a) Two dimensional schematic representation of a silicon crystal

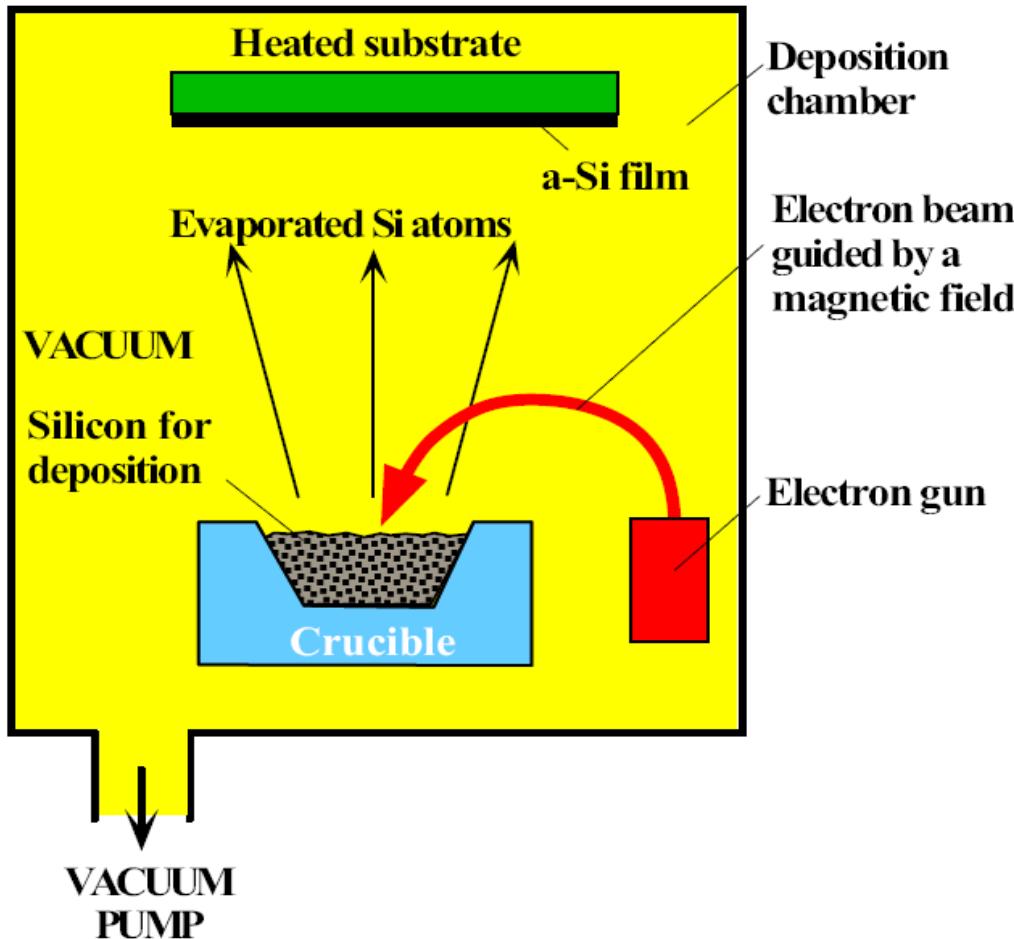


(b) Two dimensional schematic representation of the structure of amorphous silicon. The structure has voids and dangling bonds and there is no long range order.

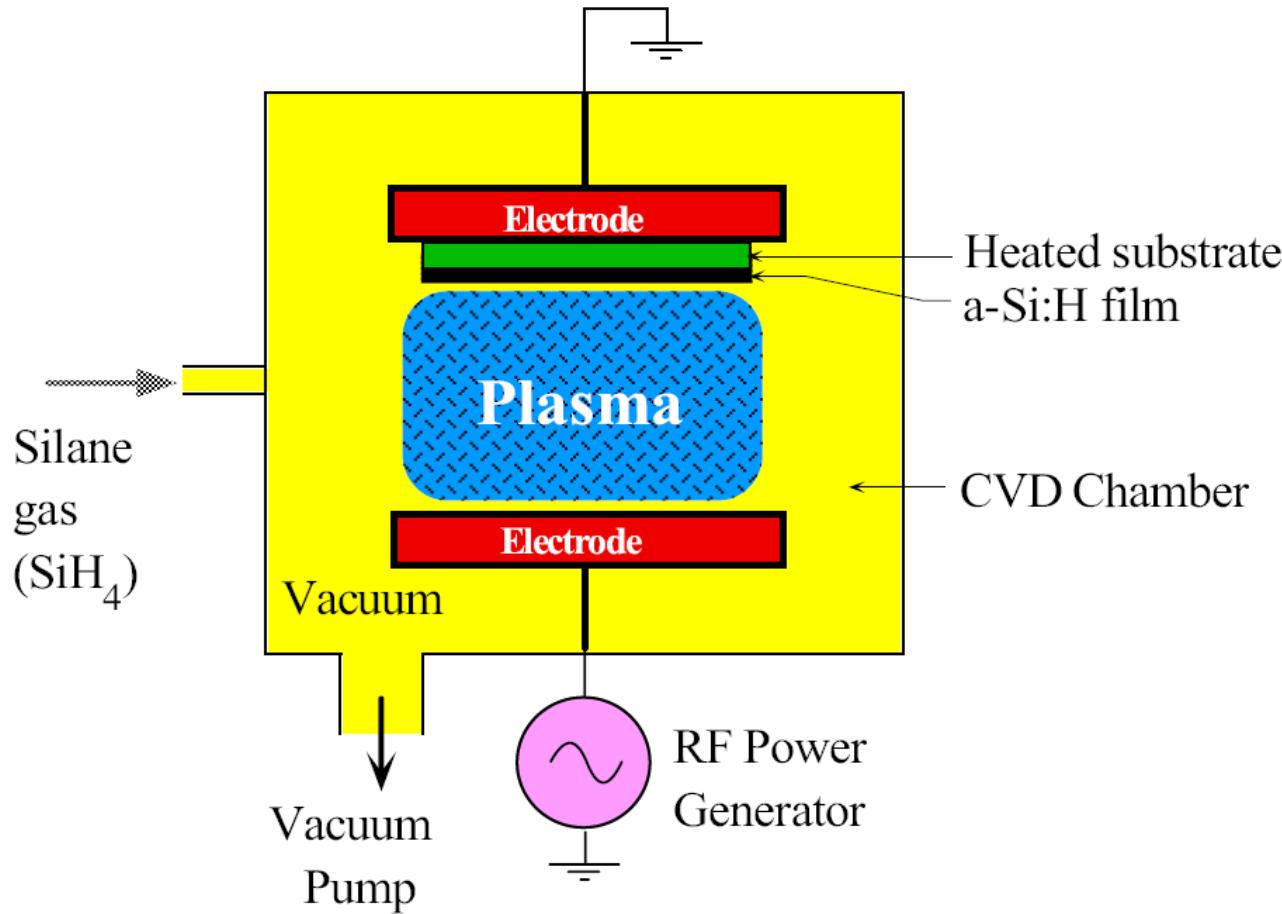


(c) Two dimensional schematic representation of the structure of hydrogenated amorphous silicon. The number of hydrogen atoms shown is exaggerated.

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.



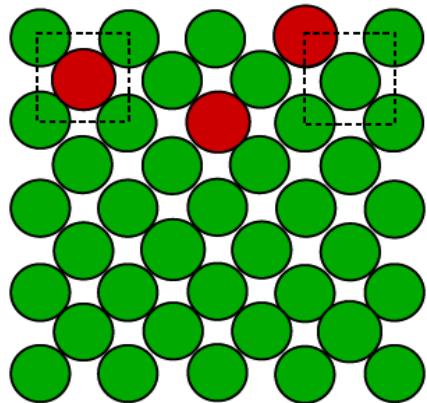
Amorphous silicon, a-Si, can be prepared by an electron beam evaporation of silicon. Silicon has a high melting temperature so that an energetic electron beam is used to melt the crystal in the crucible locally and thereby vaporize Si atoms. Si atoms condense on a substrate placed above the crucible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



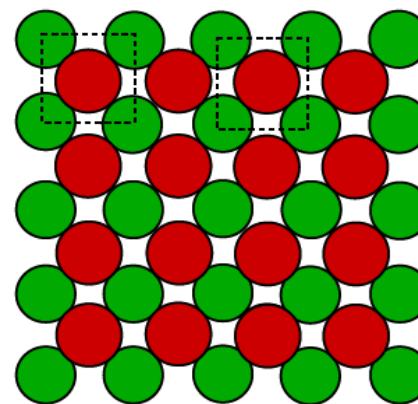
Hydrogenated amorphous silicon, a-Si:H, is generally prepared by the decomposition of silane molecules in a radio frequency (RF) plasma discharge. Si and H atoms condense on a substrate to form a film of a-Si:H

**Table 1.5** Crystalline and amorphous silicon

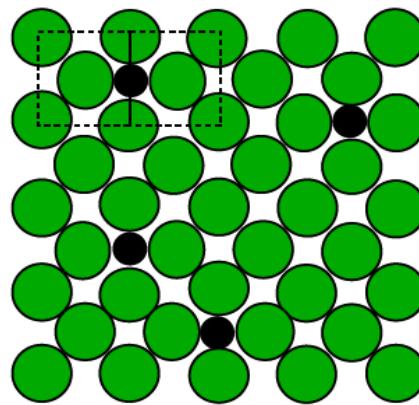
	<b>Crystalline Si (c-Si)</b>	<b>Amorphous Si (a-Si)</b>	<b>Hydrogenated a-Si (a-Si:H)</b>
Structure	Diamond cubic.	Short-range order only. On average, each Si covalently bonds with four Si atoms. Has microvoids and dangling bonds.	Short-range order only. Structure typically contains 10% H. Hydrogen atoms 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 ( $\text{g cm}^{-3}$ )	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)

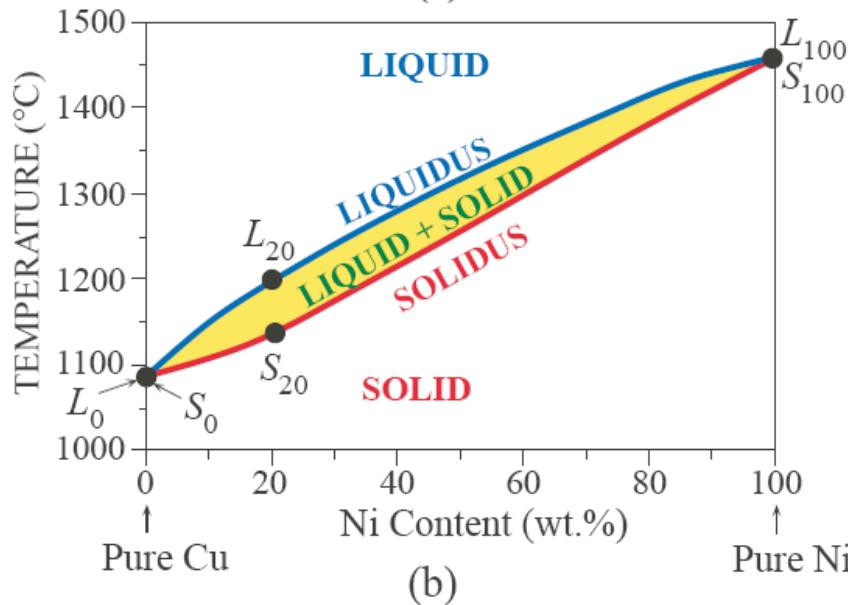
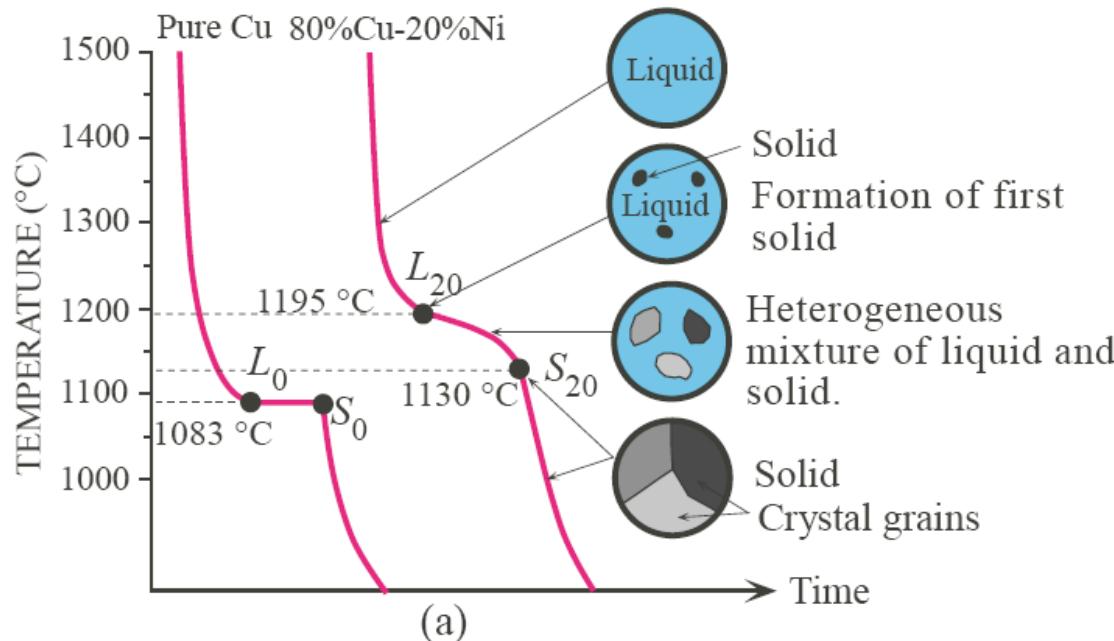


(b) Ordered Substitutional Solid Solution. Example: Cu-Zn alloy of composition 50%Cu-50%Zn. ( $\{110\}$  planes).



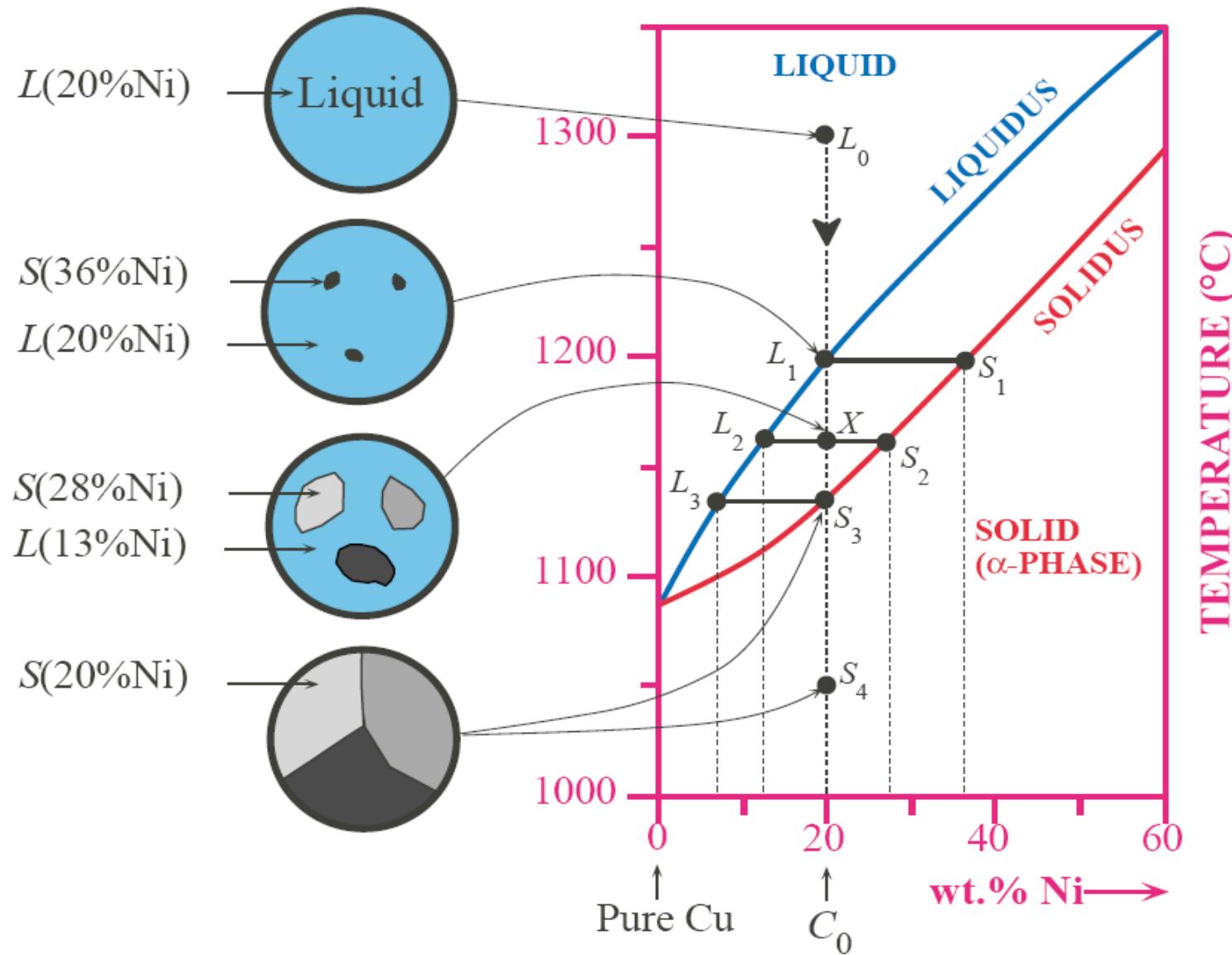
(c) Interstitial Solid Solution. Example: Small number of C atoms in FCC Fe (austenite). ( $\{100\}$  planes)

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



Solidification of an isomorphous alloy such as Cu-Ni.

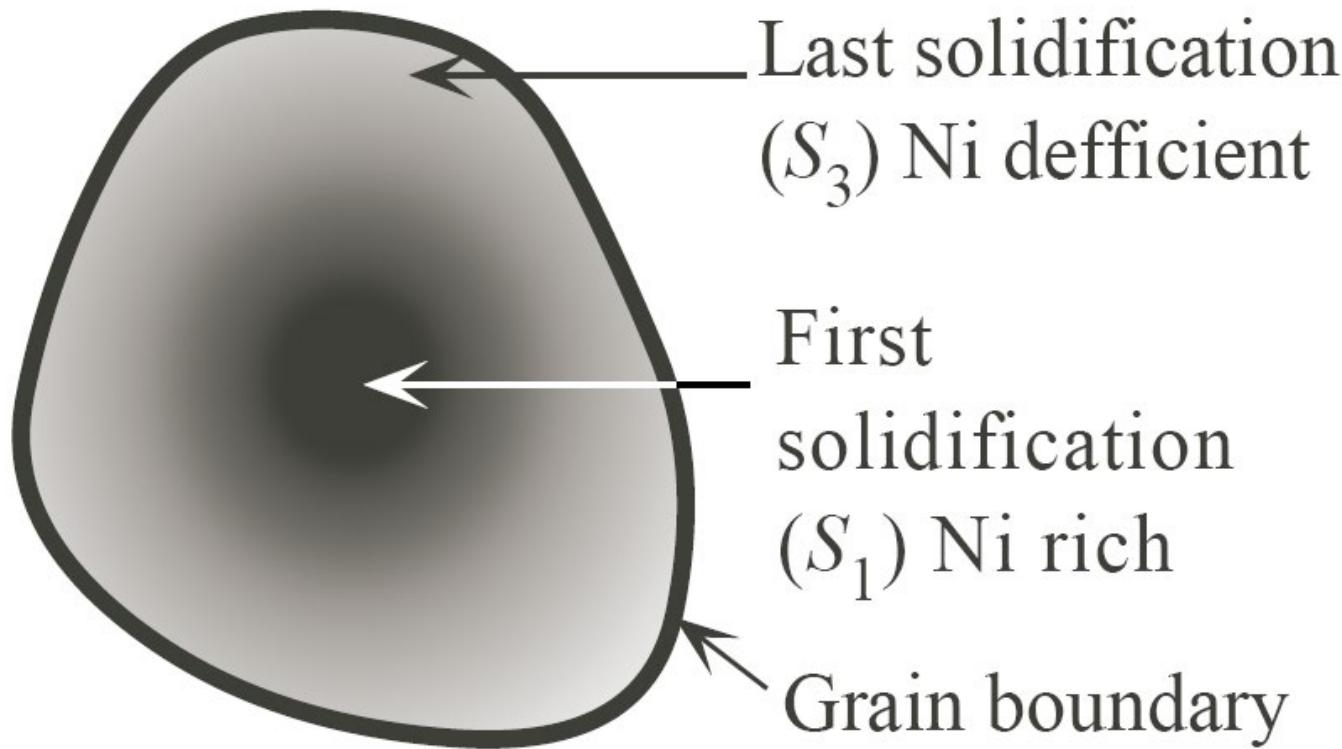
- (a) Typical cooling curves
- (b) The phase diagram marking the regions of existence for the phases



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%

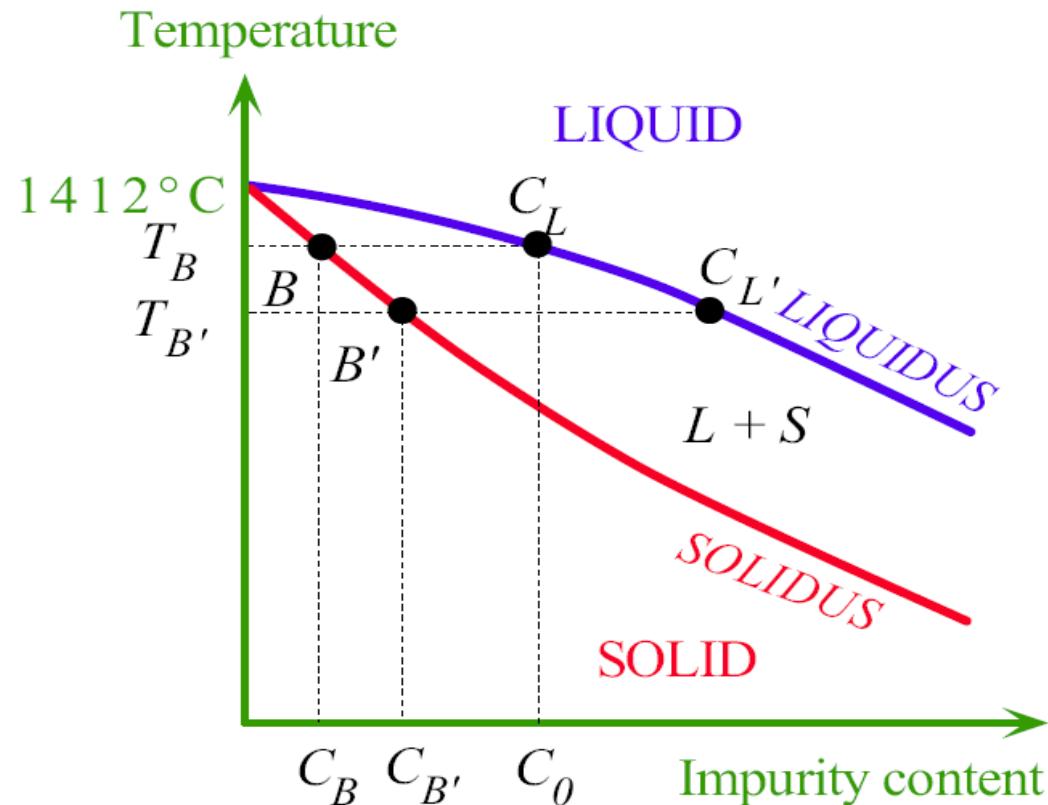


Segregation in a grain due to rapid cooling (nonequilibrium cooling)

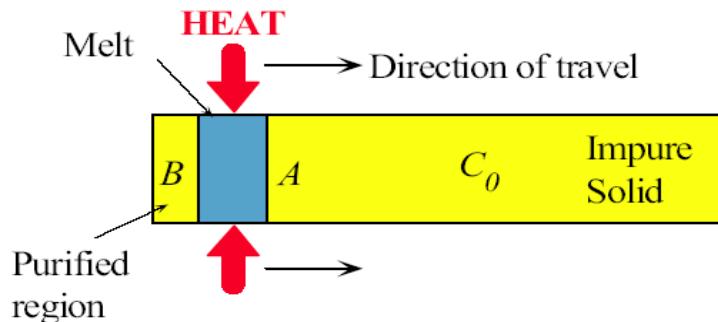
## Lever Rule

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

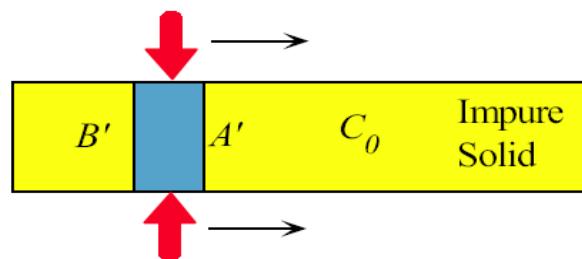
$W_L$  = the weight fraction of the liquid phase,  $W_S$  = the weight fraction of the solid phase,  $C_S$  = composition of the solid phase,  $C_L$  = composition of the liquid phase,  $C_O$  = overall composition.



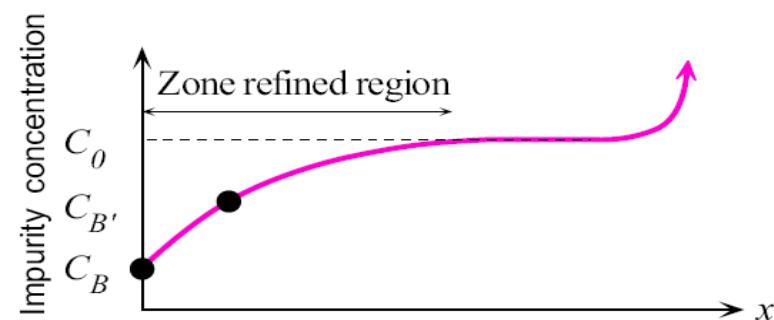
The phase diagram of Si with impurities near the low-concentration region



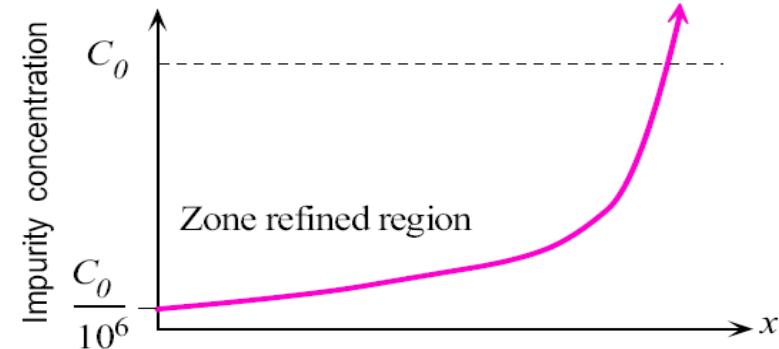
(a) Heat is applied locally starting at one end. The impurity concentration in the refrozen solid at  $B$  is  $C_B < C_0$ . The impurity concentration in the melt is  $C_{L'} > C_0$ .



(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  $C_{L'}$ .

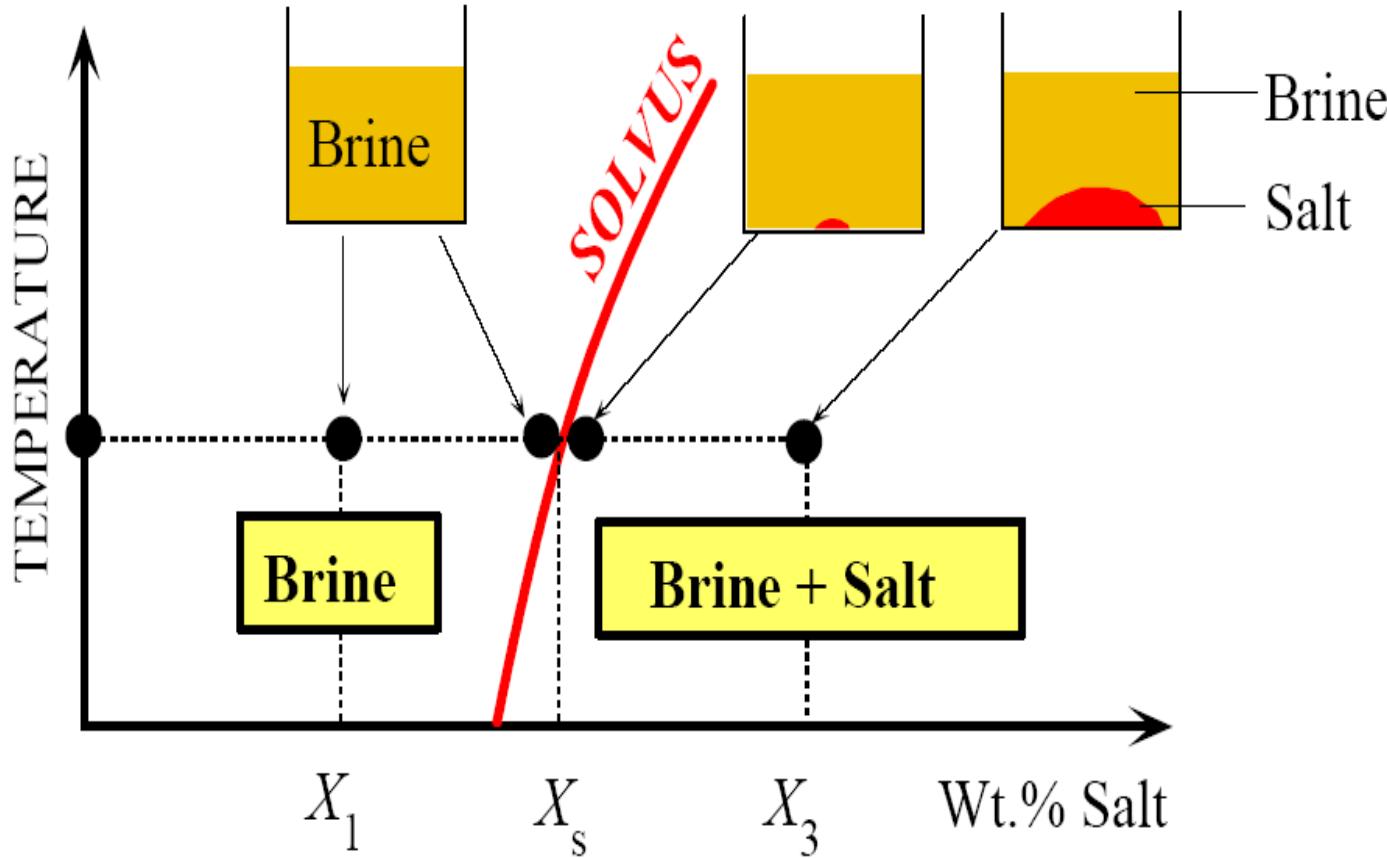


(c) The impurity concentration profile in the refrozen solid after one pass.



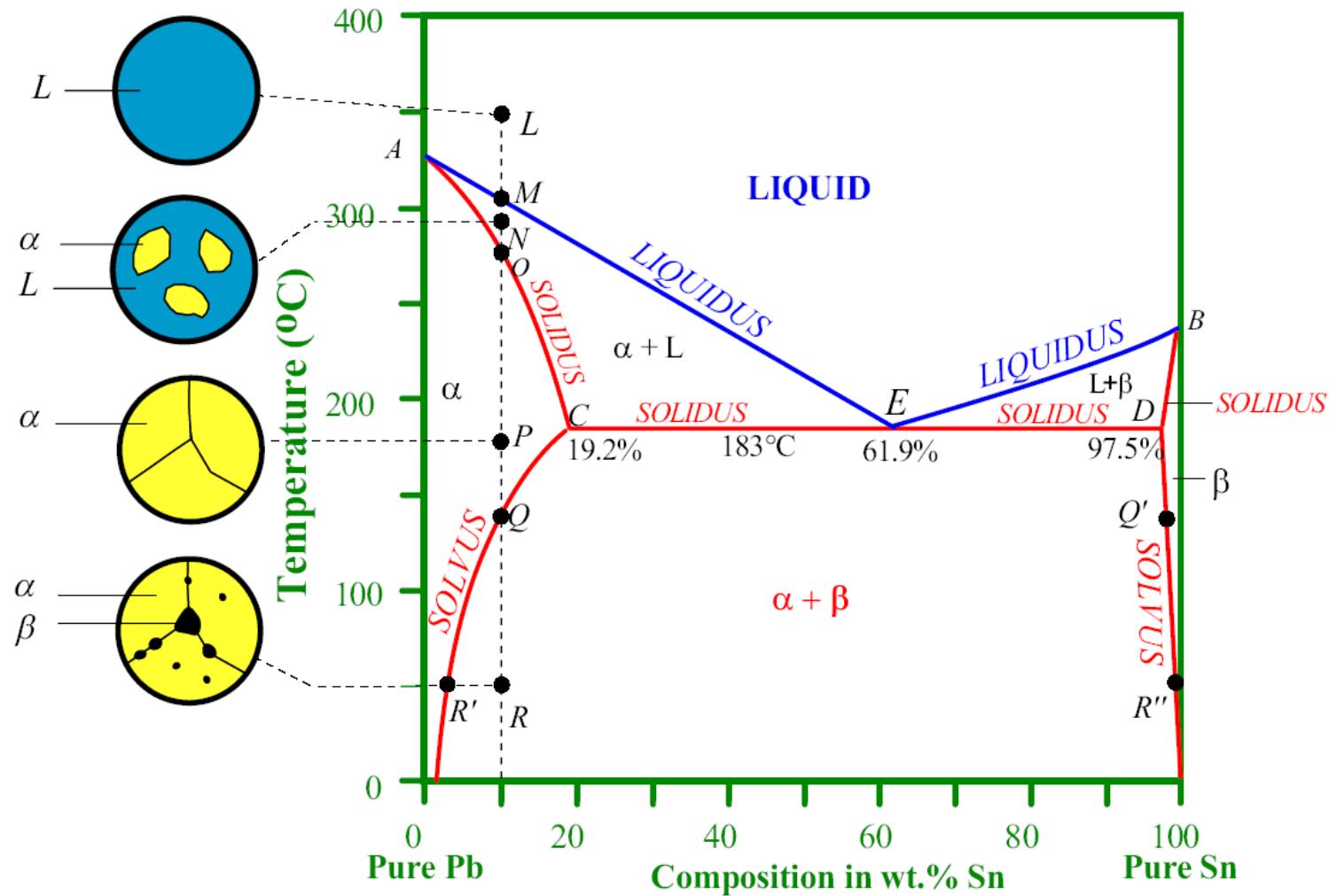
(d) Typical impurity concentration profile after many passes.

The principle of zone refining

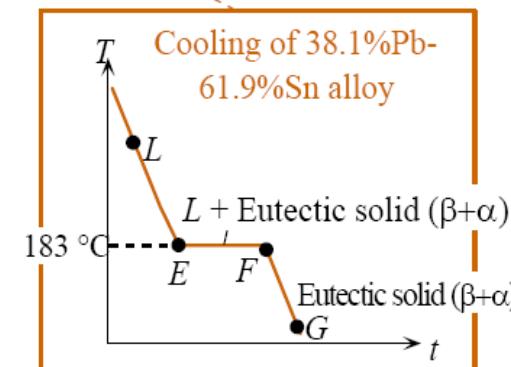
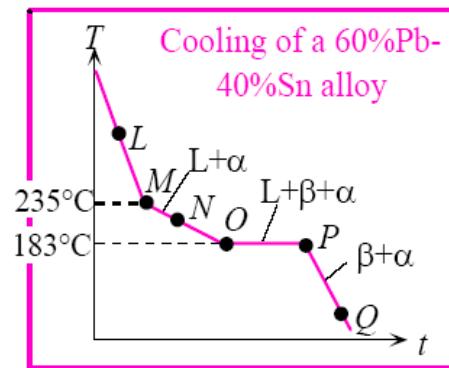
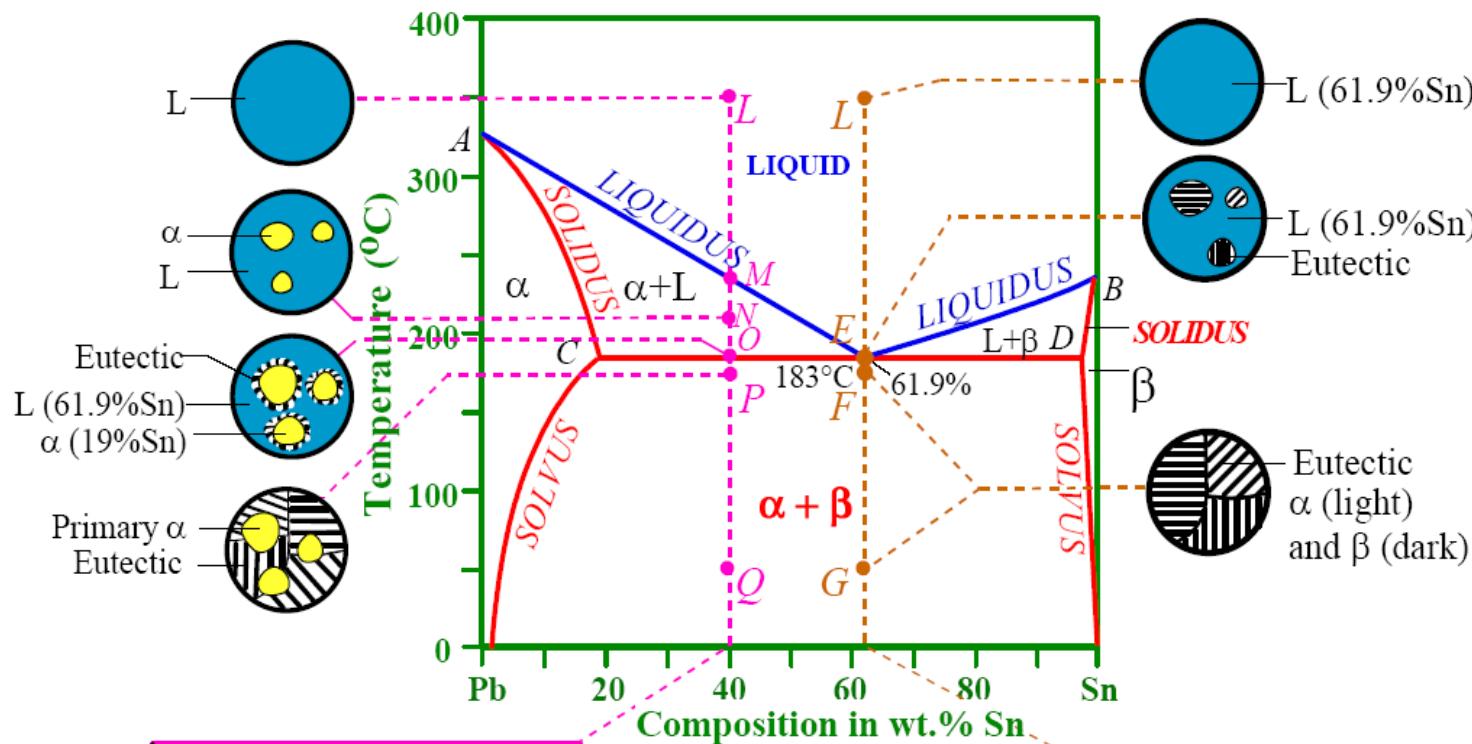


We can only dissolve so much salt in brine (solution of salt in water).

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).

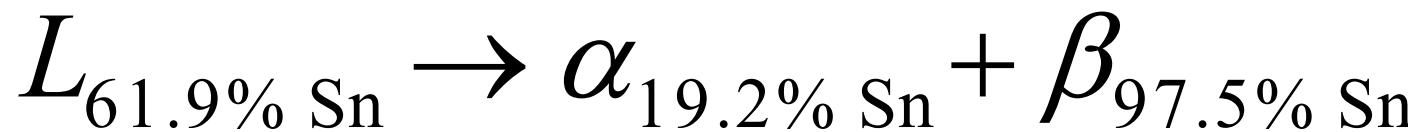


The alloy with the eutectic composition cools like a pure element exhibiting a single solidification temperature at 183°C. The solid has the special eutectic structure. The alloy with the composition 60%Pb-40%Sn when solidified is a mixture of primary  $\alpha$  and eutectic solid.

**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 ( $\alpha$ -phase) nucleates in the liquid.
	$\alpha$	15% Sn	0	
210	$L$	50% Sn	68.7	Mixture of liquid and $\alpha$ phases. More solid forms. Compositions change.
	$\alpha$	18% Sn	31.3	
183.5	$L$	61.9% Sn	48.7	Liquid has the eutectic composition.
	$\alpha$	19.2% Sn	51.3	
182.5	$\alpha$	19.2% Sn	73.4	Eutectic ( $\alpha$ and $\beta$ phases) and primary $\alpha$ -phase.
	$\beta$	97.5% Sn	26.6	

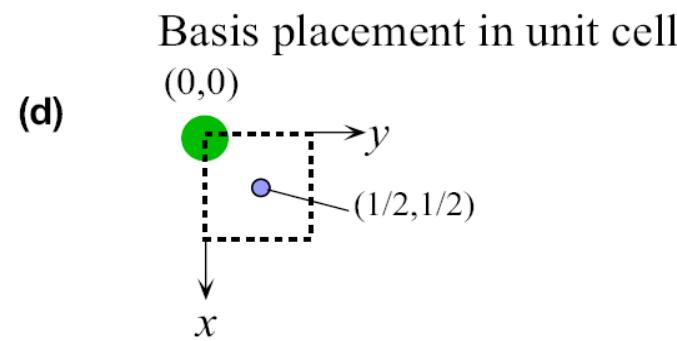
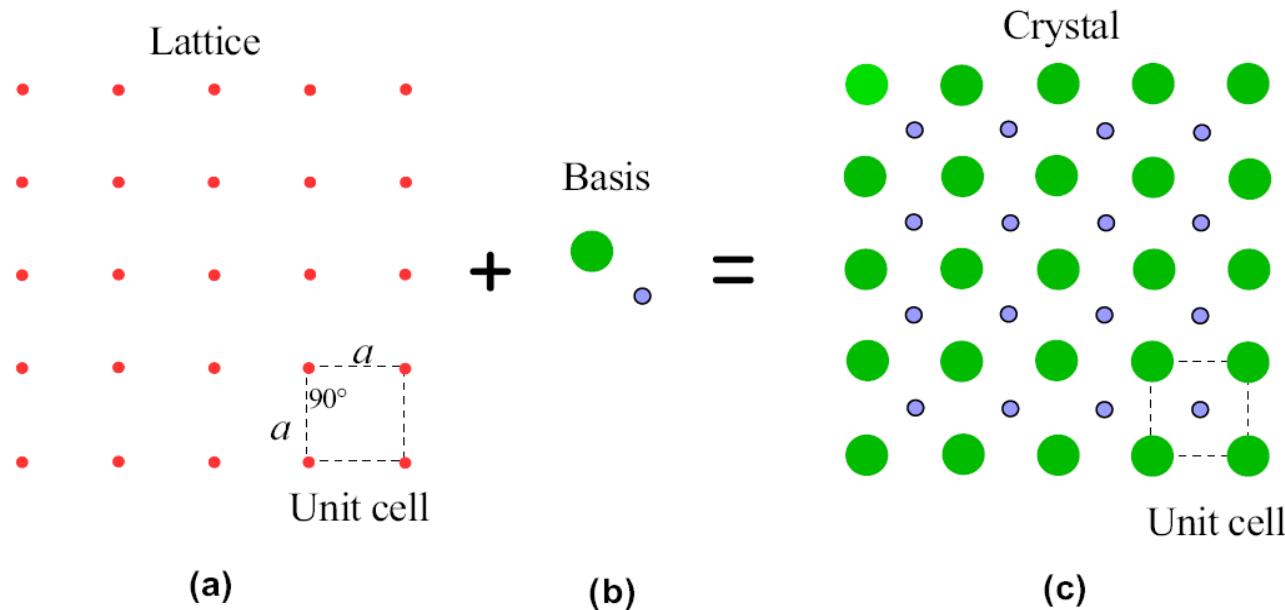
# Eutectic Transformation



$L$  = liquid phase

$\alpha$  = Pb-rich solid phase of PbSn

$\beta$  = Sn-rich solid phase of PbSn

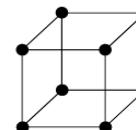


- (a) A simple square lattice. The unit cell is a square with a side  $a$ .
- (b) Basis has two atoms.
- (c) Crystal = Lattice + Basis. The unit cell is a simple square with two atoms.
- (d) Placement of basis atoms in the crystal unit cell.

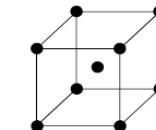
## CUBIC SYSTEM

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

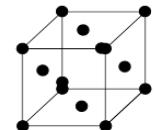
Many metals, Al, Cu, Fe, Pb. Many ceramics and semiconductors, NaCl, CsCl, LiF, Si, GaAs



Simple cubic



Body centered cubic

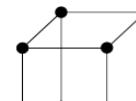


Face centered cubic

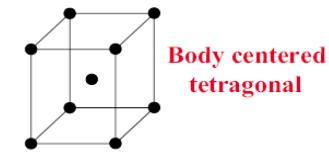
## TETRAGONAL SYSTEM

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

In, Sn, Barium Titanate,  $\text{TiO}_2$



Simple tetragonal

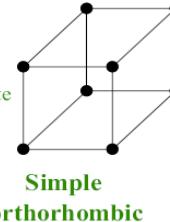


Body centered tetragonal

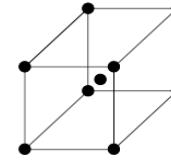
## ORTORHOMBIC SYSTEM

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

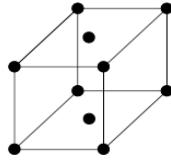
S, U, Pt, Ga (<30°C), Iodine, Cementite ( $\text{Fe}_3\text{C}$ ), Sodium Sulfate



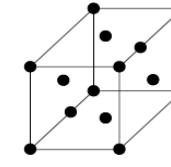
Simple orthorhombic



Body centered orthorhombic



Base centered orthorhombic

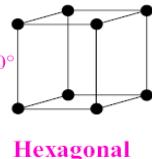


Face centered orthorhombic

## 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)

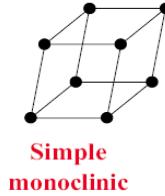


Rhombohedral

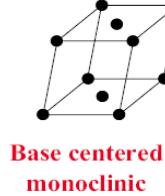
## MONOCLINIC SYSTEM

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

$\alpha$ -Selenium, Phosphorus, Lithium Sulfate, Tin Fluoride



Simple monoclinic

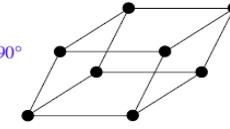


Base centered monoclinic

## TRICLINIC SYSTEM

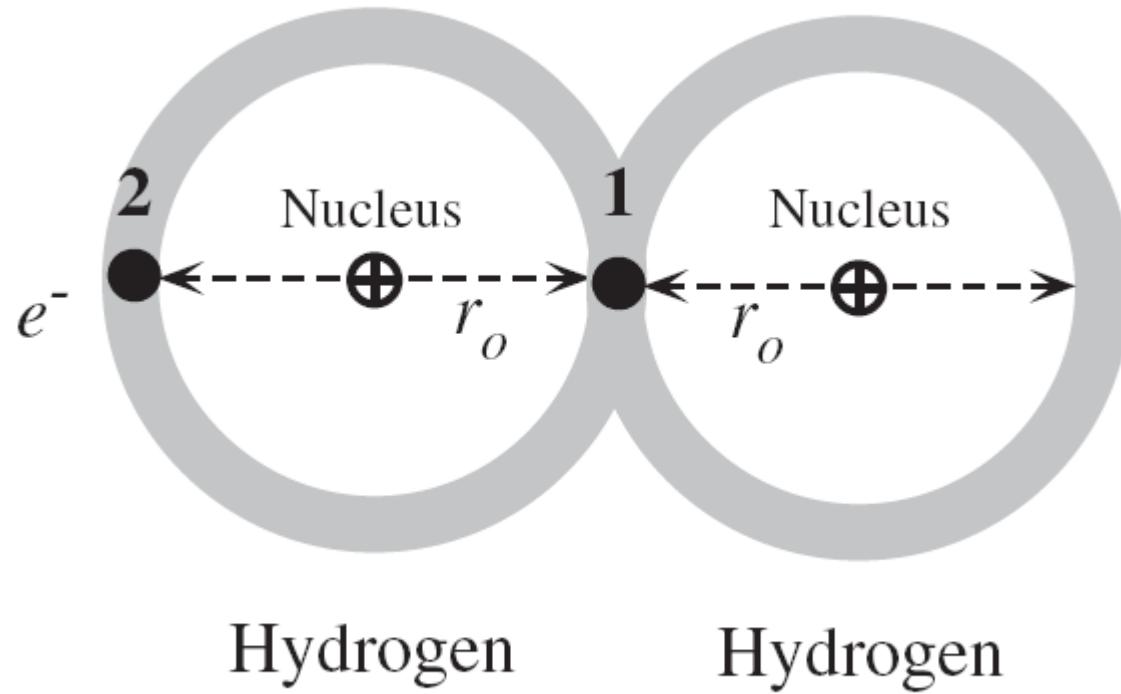
$$a \neq b \neq c \quad \alpha \neq \beta \neq \gamma \neq 90^\circ$$

Potassium dicromate

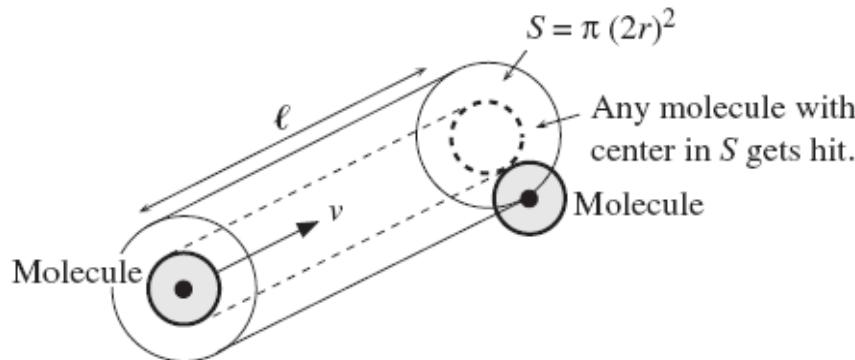


Triclinic

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



A simplified view of the covalent bond in  $\text{H}_2$ . A snapshot at one instant.

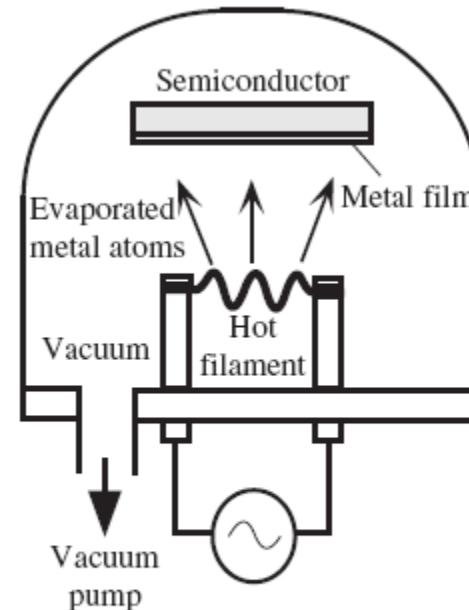


(a) A molecule moving with a velocity  $v$  travels a mean distance  $\ell$  between collisions. Since the collision cross-sectional area is  $S$ , in the volume  $S\ell$  there must be at least one molecule. Consequently,  $n(S\ell) = 1$ .

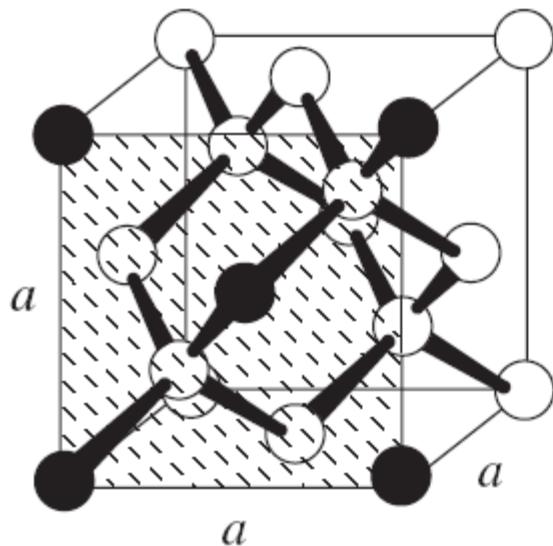


Walter Houser Brattain (1902–1987), experimenting with metal contacts on copper oxide (1935) at Bell Telephone Labs. A vacuum evaporation chamber is used to deposit the metal electrode.

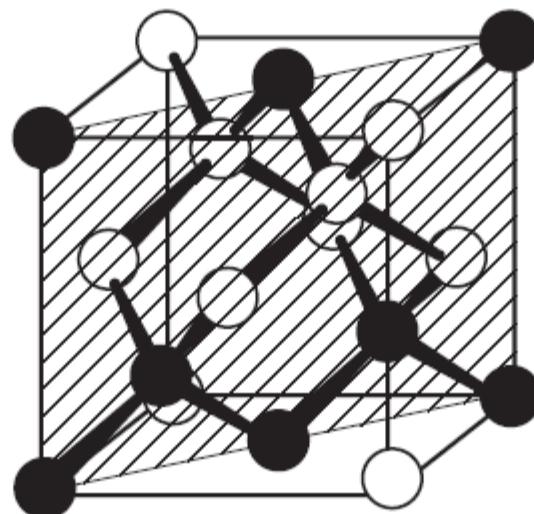
| SOURCE: Bell Telephone Laboratories, courtesy AIP Emilio Segrè Visual Archives.



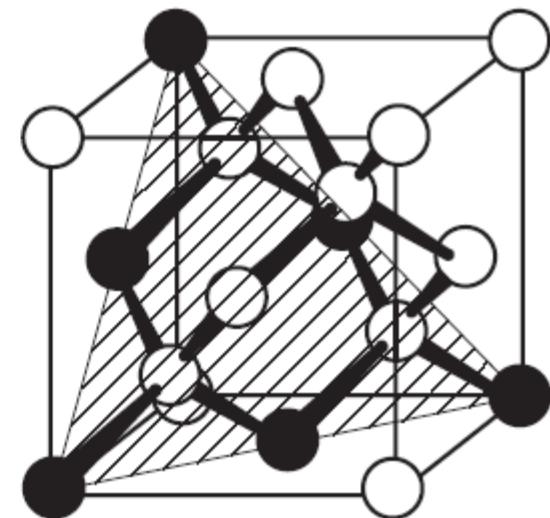
(b) Vacuum deposition of metal electrodes by thermal evaporation.



(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.