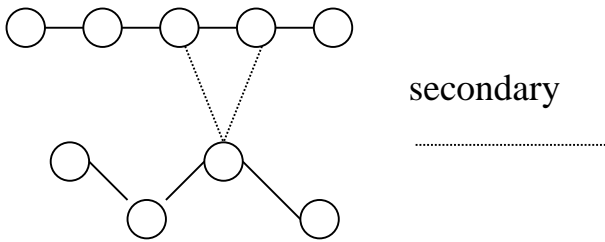
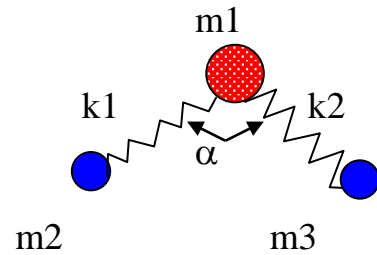
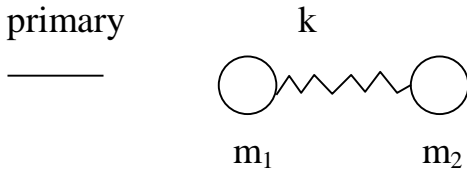


## Atomic bonding

primary



Primary bonds: Ionic, covalent, and metallic



Usually strong, stiff bonds  
High moduli, usually high melting point

Secondary bonds: Van der Waals and hydrogen bonds



Usually weaker

### IONIC bond:

Between strongly electropositive (metals) and strongly electronegative (nonmetals) elements

Electropositive  $\Rightarrow$  gives away electron(s)  $\Rightarrow$  becomes a positively charged Ion  $\rightarrow$  a cation

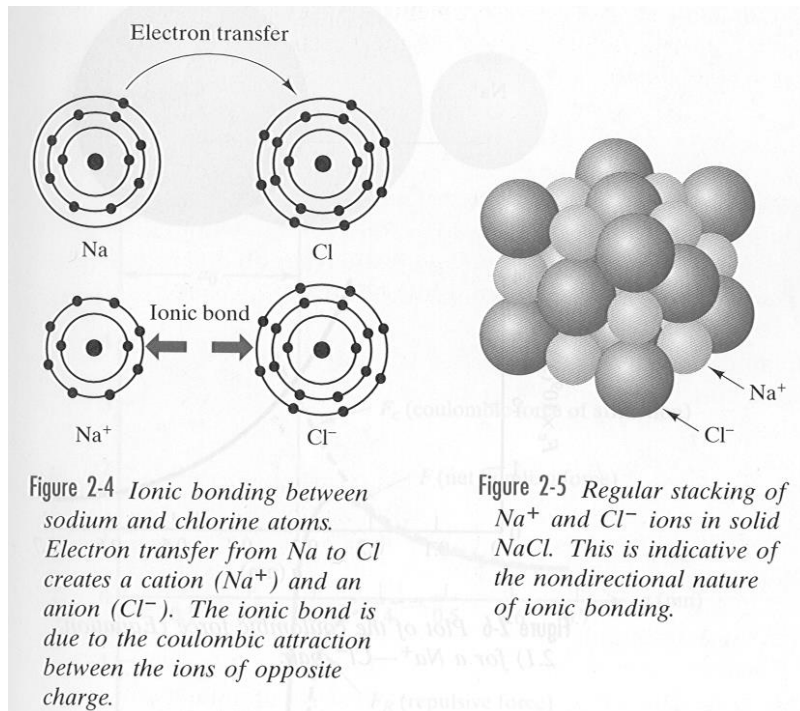
Electronegative  $\Rightarrow$  takes up electron(s)  $\rightarrow$  becomes negatively charged ion  $\rightarrow$  an anion

two opposing charges attack each other by electrostatic forces

both ions with filled “outer shells”

important property of the ionic bond:

electrostatic field of the electron clouds of the ions → spherically symmetric

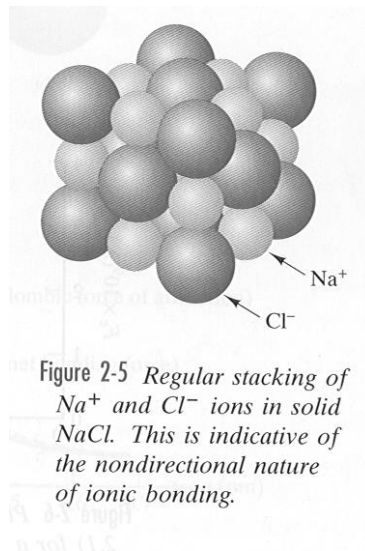


→ NO preferred directional character in the ionic bond

with the absence of directionality in the ionic bond

→ atomic arrangement in ionic solids:

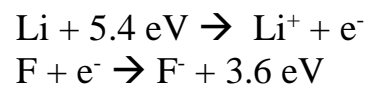
- i) atoms (ions) arrange themselves to provide local charge neutrality  
→ alternating (+) and (-) ions in a symmetrical arrangement
- ii) the packing fashion must be compatible with the different sizes of the ions.



Let's see what happens when we bring an electropositive and an electronegative atom together:

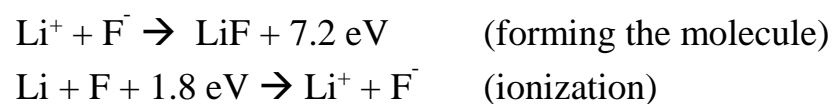
An example is Li and F

It takes about  $-5.4 \text{ eV}$  to create  $\text{Li}^+$  from Li (i.e. to ionize the neutral Li atom)  
 And when the F atom grabs an electron it gives out  $3.6 \text{ eV}$  (also the the fluorine atom is now ionized)



And then we can gain energy as we bring  $\text{F}^-$  and  $\text{Li}^+$  together from "infinity"

$$V = \int_{\infty}^{r_0} e^2/r^2 \text{ dr} \approx -e^2/r_0 = -7.2 \text{ eV}$$





By bringing Li and F together we lower the energy of the system and form a stable bond

As the (+) and (-) ions come together they do not collapse onto each other although there is an attractive force due to electrostatic attraction given by :

$$F = e^2 / (4\pi\epsilon_0 r^2)$$

$\epsilon_0$  - permittivity of  
free space

$$e^2 = |q^+| |q^-|$$

r - interatomic  
separation

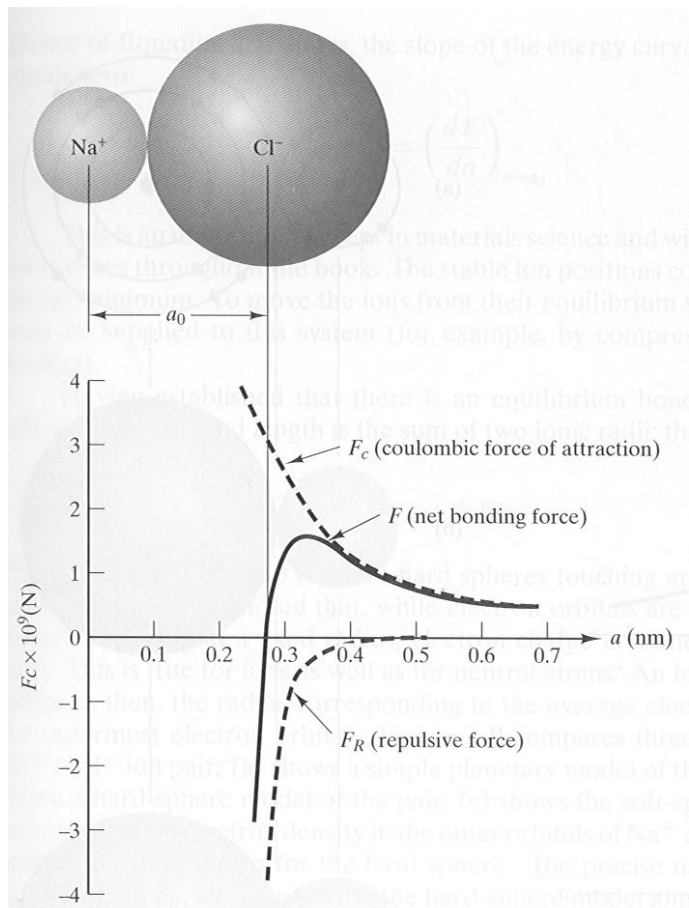
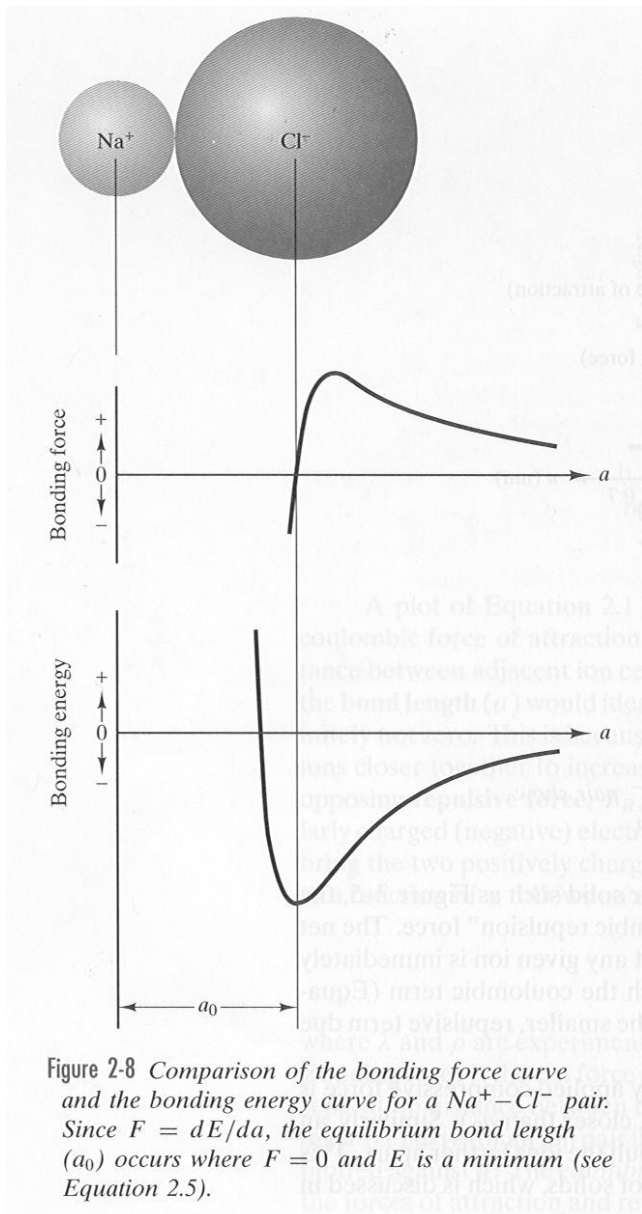


Figure 2-7 Net bonding force curve for a  $\text{Na}^+ - \text{Cl}^-$  pair showing an equilibrium bond length of  $a_0 = 0.28 \text{ nm}$ .

because as they come too close together the electron clouds start to overlap.....

the work done to bring these ions together from infinity is the total force integrated over  $r$

$$U = - \int_r^\infty F dr = -e^2 / (4\pi\epsilon_0 r)$$



Why don't collapse on to each other?

The overlap of the electron clouds from the two ions cause a very strong repulsion!!!

The total energy is given by contributions made by repulsive, attractive, and ionization forces.....

$$U_T = U_i - q^2/(4\pi\epsilon_0 r) + B/r^m$$

$m \sim 10$  for ionic bond

The repulsive contribution starts becoming dominant @ small  $r$ !!

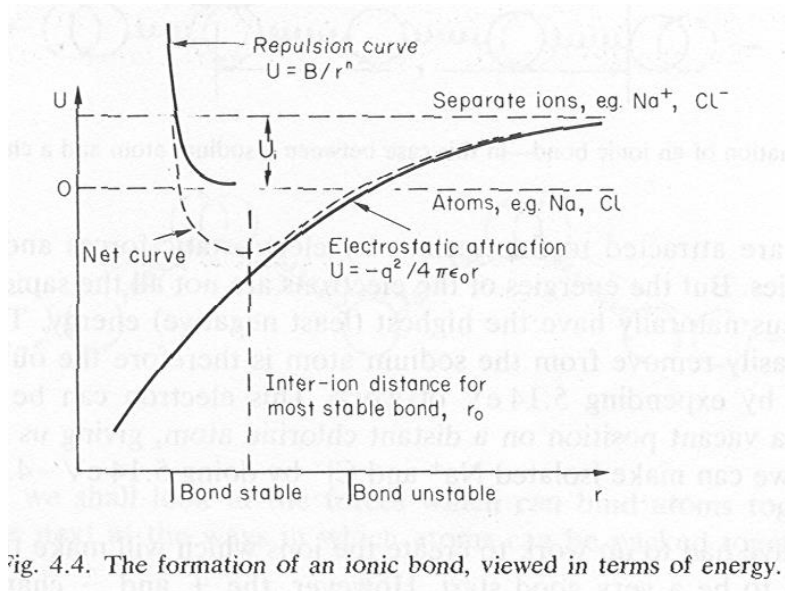


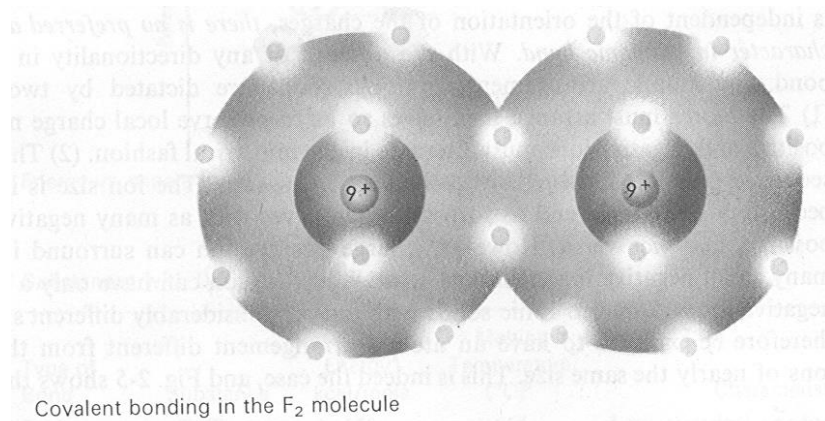
Fig. 4.4. The formation of an ionic bond, viewed in terms of energy.

- Ionic bond is → strong  
 → non-directional  
 → exist mainly in ceramic materials and minerals  
 → associated with high stiffness,  
 high melting point,  
 hard  
 brittle materials  
 poor electronic conductors  
 usually good thermal insulators  
 very good chemical resistance

## COVALENT Bond

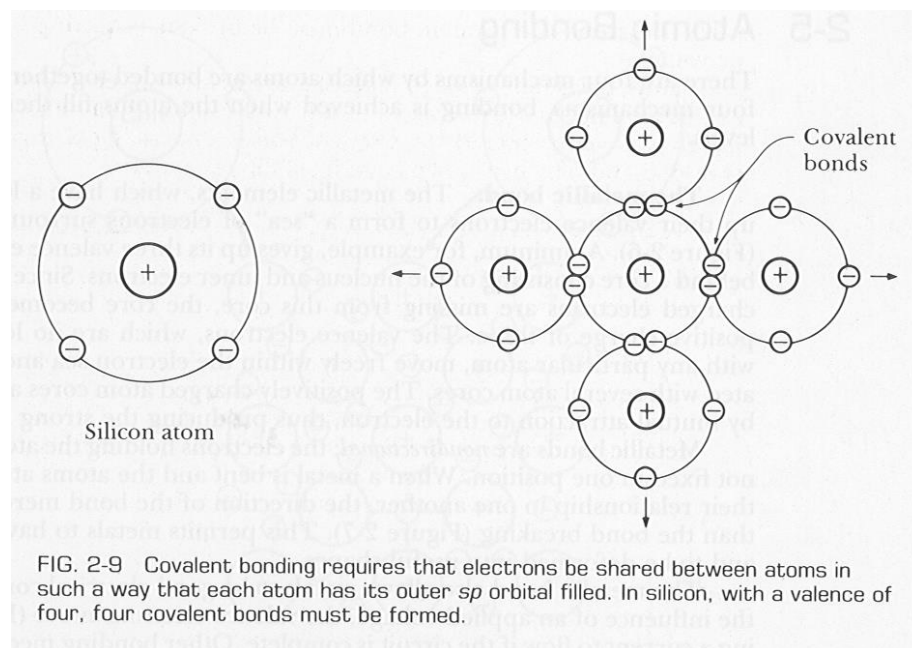
Forms by sharing outer **s** and **p** electrons,  
 mostly between atoms of elements near one another  
 in the periodic table

by sharing their electrons they both can have a complete outer electron shells of elements near one another in the periodic table.



By sharing their electrons they both can have complete outer electron shells.

Since the electrons are shared between the atoms forming the bond, covalent bond is extremely directional. In its purest forms it exists in diamond, silicon and germanium.



Covalent bond is usually associated with large moduli,  $E$  (high stiffness),  
poor ductility,  
poor electrical conductivity  
very high  $T_m$



many ceramics, polymers and even metals (high  $T_m$ , high  $E$ ) are partly bonded with covalent bonds.

The total energy diagram for this type of bond is also similar to the ionic bond with the exponents being different

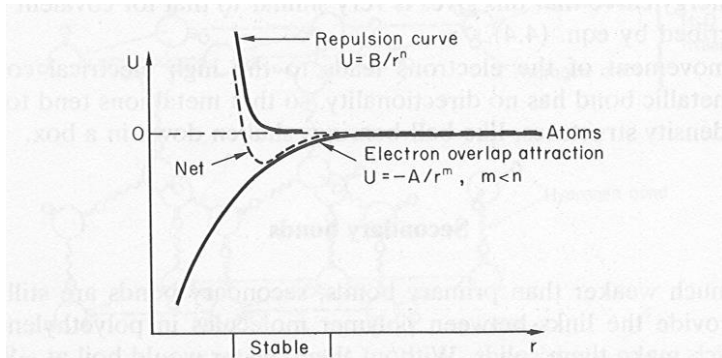


Fig. 4.6. The formation of a covalent bond, viewed in terms of energy.

$$(U_T)_{\text{covalent}} = -A/r^m + B/r^n \quad \text{where } m < n$$

strongly directional bonds with strong attractive and repulsive component in their total force curves  $\rightarrow$  very brittle materials.

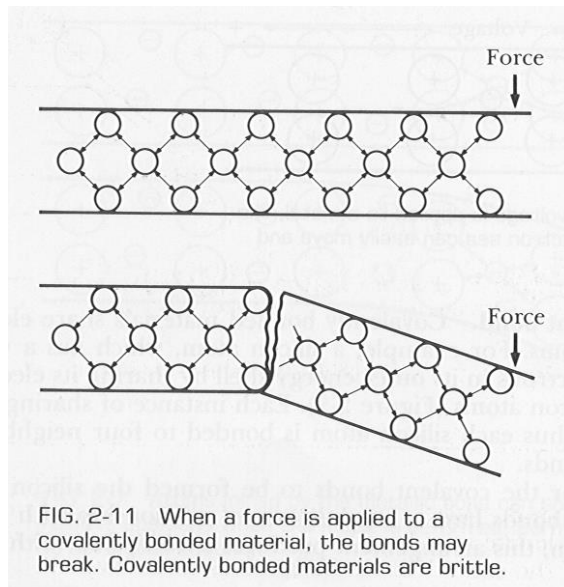


FIG. 2-11 When a force is applied to a covalently bonded material, the bonds may break. Covalently bonded materials are brittle.

# METALLIC BOND

Forms mostly among atoms with only few electrons in their outer s and p orbitals → mostly between metal atoms

Low valence metallic elements give up their valence electrons into the “soup” to form a “sea of electrons” surrounding the atomic cores ;

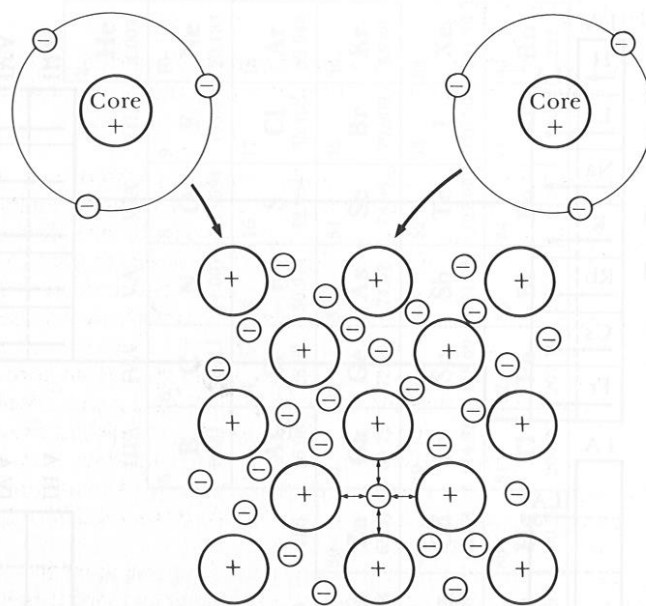


FIG. 2-6 The metallic bond forms when atoms give up their valence electrons, which then form an electron sea. The positively charged atom cores are bonded by mutual attraction to the negatively charged electrons.

once the valence electrons leave the atom, the core becomes effectively a positive ion. These (+) ions are held together by mutual attraction to the electrons between them.

Total potential energy of the metallic bond can be given by an equation similar to the one for covalent or ionic bond:

$$U_T = -A/r^m + B/r^n \quad \text{with } m < n$$

Metallic bond is somehow similar to ionic bond, but with ONE type of ionic core only.....

Metallic bond is non-directional, electrons are NOT fixed at one position thus , when a metal is bent, the atoms change their position to one another, and the direction of the bond is merely shifted

→→ metals have good ductility (easily deformable) , metals do NOT have strong primary directional bonds or any requirement for local charge neutrality → atoms slide over each other rather easily during deformation

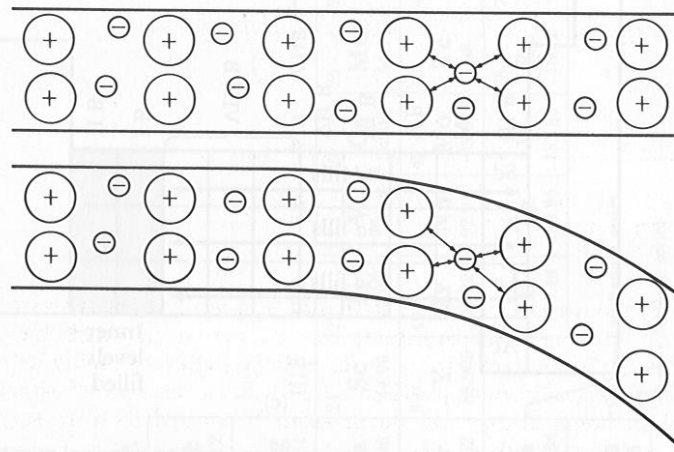


FIG. 2-7 Atoms joined by the metallic bond can shift their relative positions when the metal is deformed, permitting metals to have good ductility.

since there is no directionality in the metallic bond → metal ions tend to pack to give simple, highly dense structures, like ball bearings shaken down into a box.

The free electrons in the metals are responsible for good electrical conductivity and high thermal conductivity:

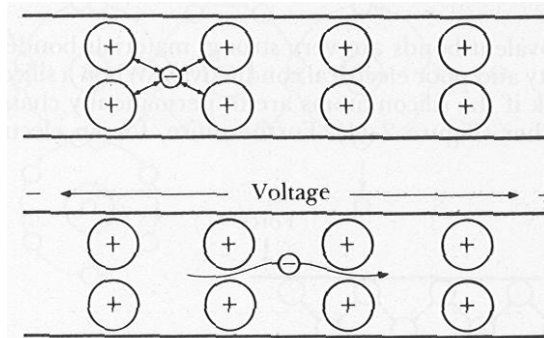


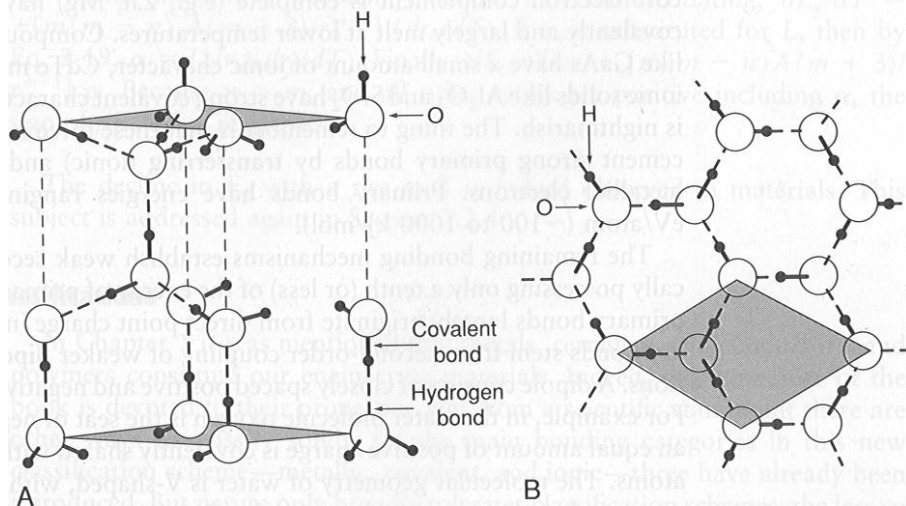
FIG. 2-8 When a voltage is applied to a metal, the electrons in the electron sea can easily move and carry a current.

Some metals with unfilled d or f orbitals do have covalent bonds which give them directionality in their properties and high melting points,  $T_m$ , like in Fe, W, Ti, Ta...

## SECONDARY BONDS

Van der Waals and hydrogen bonding

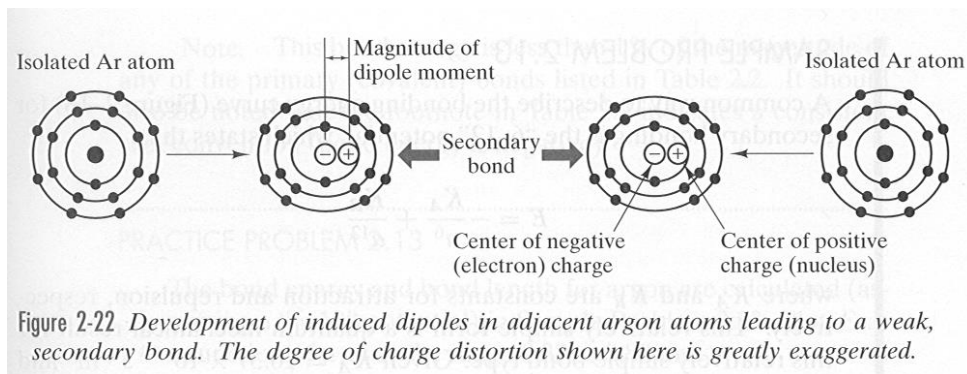
Typically 1/10 of the strength of primary bonds or less



Structure of ice shown in (A) side and (B) top views. (Also see Fig. 3-22D.) Intramolecular covalent bonds exist within the  $H_2O$  molecule. Intermolecular hydrogen bonds link  $H_2O$  molecules together. From K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*, Wiley, New York (1976).

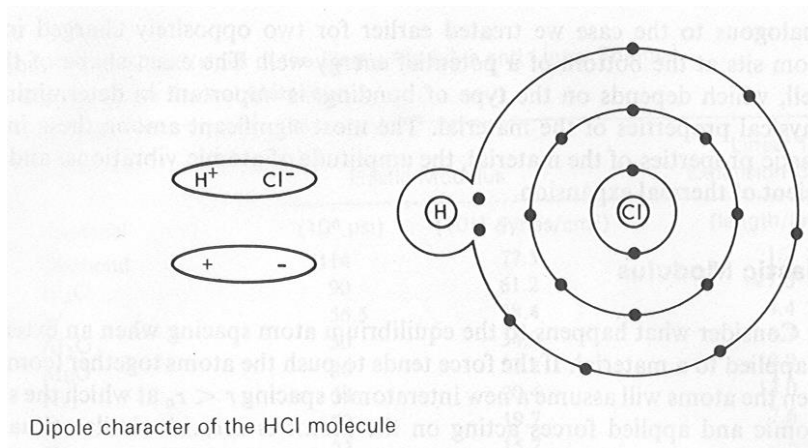
They usually co-exist with the primary bonds in materials or between materials:

Van der Waals bonding: due to fluctuating **dipoles**  
**dipole – dipole** interaction



energy  $U_T$  for the van der Waals bond (usually around 0.1 eV) :

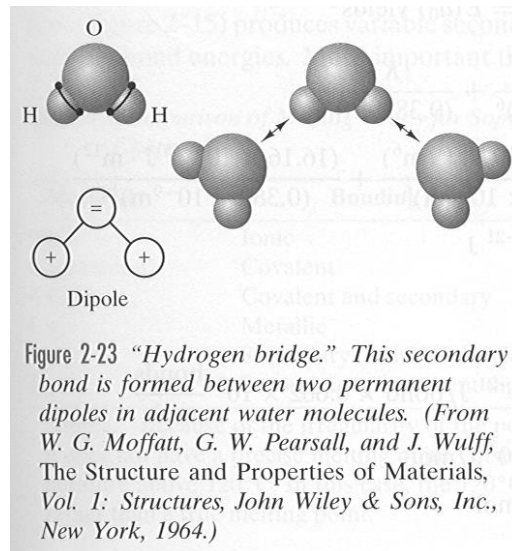
$$U_T = -A/r^n + B/r^m \quad \begin{matrix} n \cong 6 \\ m = 11-12 \end{matrix}$$



generally weak bonds, somehow non-directional due to fluctuating character

## Hydrogen Bond:

Hydrogen has only one e- → can only form one covalent bond with one anion, but then it is a mere cation (+) → it can act like a cation for another nearby anion → a weak attractive force is acting



Hydrogen bond are **also** operative between molecules containing permanent dipoles with hydrogen and strongly electronegative elements

*Examples are HCl, HF*

They are appreciably than primary bonds but are stronger than van der Waals bonds

Secondary bonds play a crucial role for life and aesthetic in coatings and paints

And other polymers and organic materials.....

## Bonds and properties of materials:

TABLE 2-2

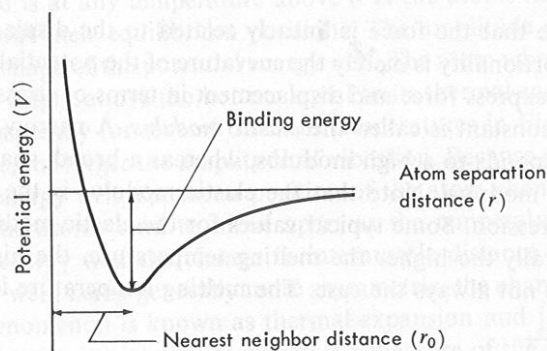
Examples of Substances with Different Types of Interatomic Bonds

Type of Bond	Substance	Bond Energy* kcal/mole	Melting Temperature (°C)	Characteristics
Ionic	CaCl	155	646	Low electrical conductivity; transparent; brittle; high melting temperature
	NaCl	183	801	
	LiF	240	870	
	CuF <sub>2</sub>	617	1360	
	Al <sub>2</sub> O <sub>3</sub>	3618	3500	
Covalent	Ge	75	958	Low electrical conductivity; very hard; very high melting temperature
	GaAs	≈75	1238	
	Si	84	1420	
	SiC	283	2600	
	Diamond	170	3550	
Metallic	Na	26	97.5	High electrical and thermal conductivity; easily deformable; opaque
	Al	74	660	
	Cu	81	1083	
	Fe	97	1535	
	W	201	3370	
Van der Waals	Ne	0.59	-248.7	Weak binding; low melting and boiling points; very compressible
	Ar	1.8	-189.4	
	CH <sub>4</sub>	2.4	-184	
	Kr	2.8	-157	
	Cl <sub>2</sub>	7.4	-103	
Hydrogen	HF	7	-92	Higher melting points than Van der Waals bonding; tendency to form groups of many molecules
	H <sub>2</sub> O	12	0	

\*The bond energy is the energy necessary to dissociate the solid into separated atoms, ions, or molecules, as appropriate.

## Binding Energy & Interatomic Spacing

Equilibrium nearest neighbor distance between two atoms (or ions) is where the energy of the system is at its minimum and there is no net force acting on the atoms (or ions).



Potential energy well for atoms in a solid

The shape of the energy well;

Depends on the type of bonding → determines several physical properties, like stiffness (Young's Modulus) coefficient of thermal expansion etc.

Interatomic Forces and Elastic (Young's) Modulus, E

@ equilibrium atoms (ions) are @ equilibrium distance,  $r_0$

if they are squizzed further together, i.e.  $r < r_0$ , there will be a repulsive restoring force

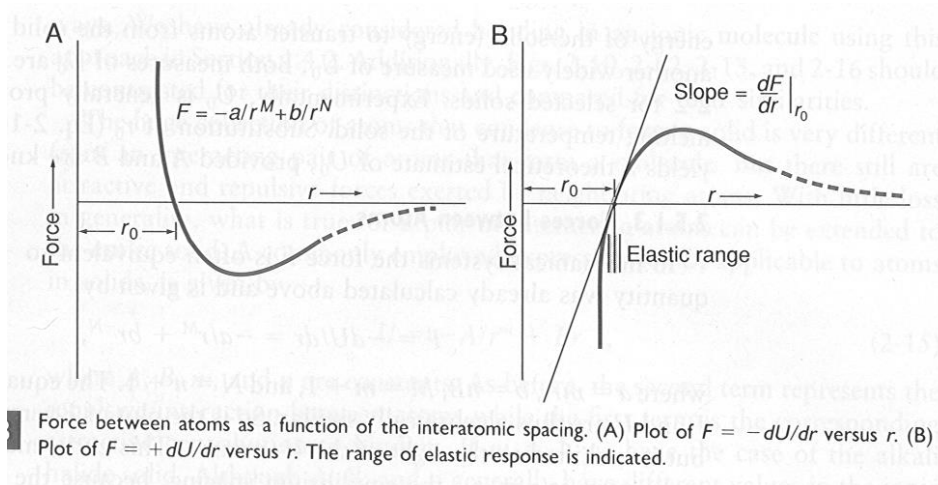
and

if they are pulled away from each other, i.e.  $r > r_0$  there will be a tensile restoring force....

The force between the atoms (ions) is :

$$F = -dU/dr$$

where U is the interatomic potential



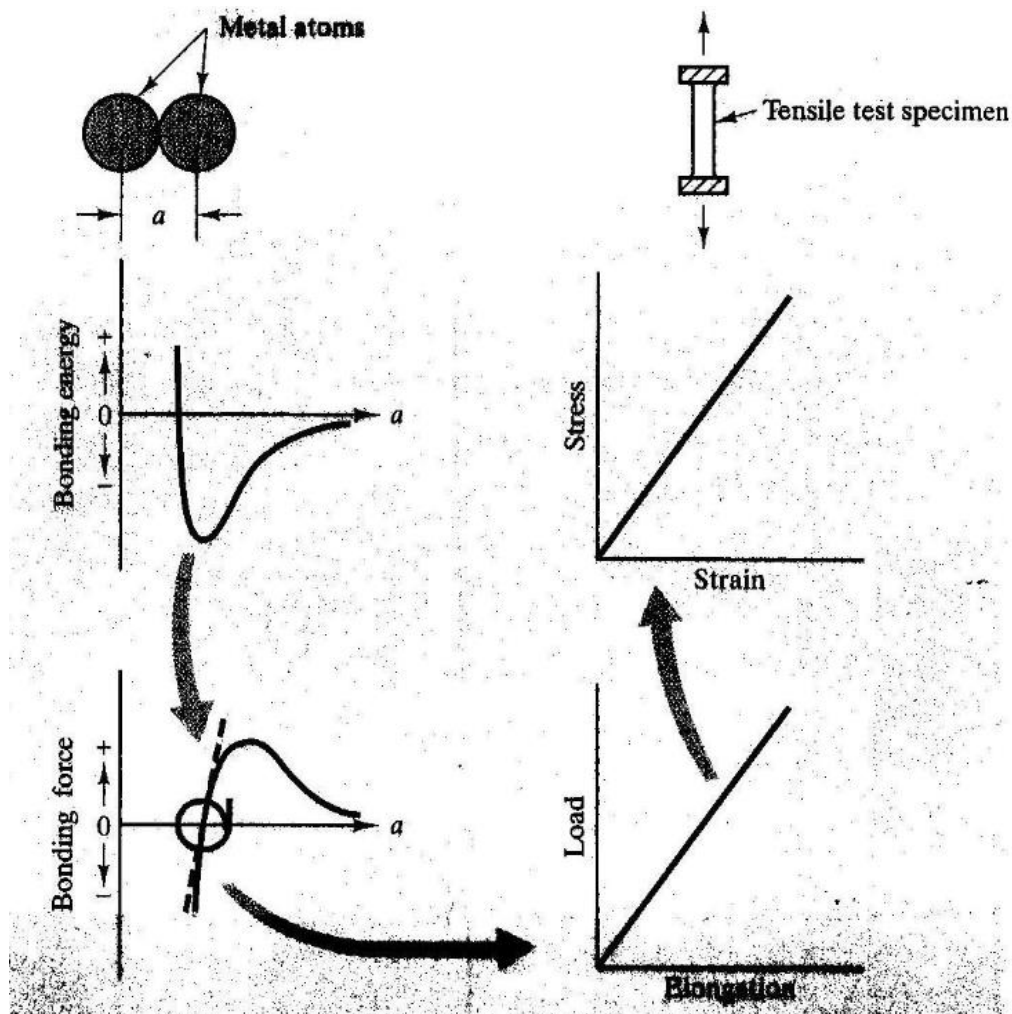


## Young's Modulus ( Elastic Modulus)

$$\rightarrow E = dF/dr$$

what does the above equation tell??

The stronger the curvature of the potential energy curve for the atomic bonds  $\rightarrow$  the higher the stiffness and the Young's Modulus of the material



The depth of the energy well  $\rightarrow$  binding energy

$\rightarrow$  melting temperature,  $T_m$

What about thermal expansion??

## ATOMIC ARRANGEMENT (in solids)

Depending partially on their bonding between them, atoms (ions) can be arranged in space with different degrees of **order**.....

In noble gases → complete lack of order (argon gas)

Bonds between the atoms in a molecule

or

directional bonds between nearest neighbour atoms

will force a **short range order** between atoms like in a water molecule

between oxygen and hydrogen atoms, or like in the silicon oxygen tetrahedra in **glass**

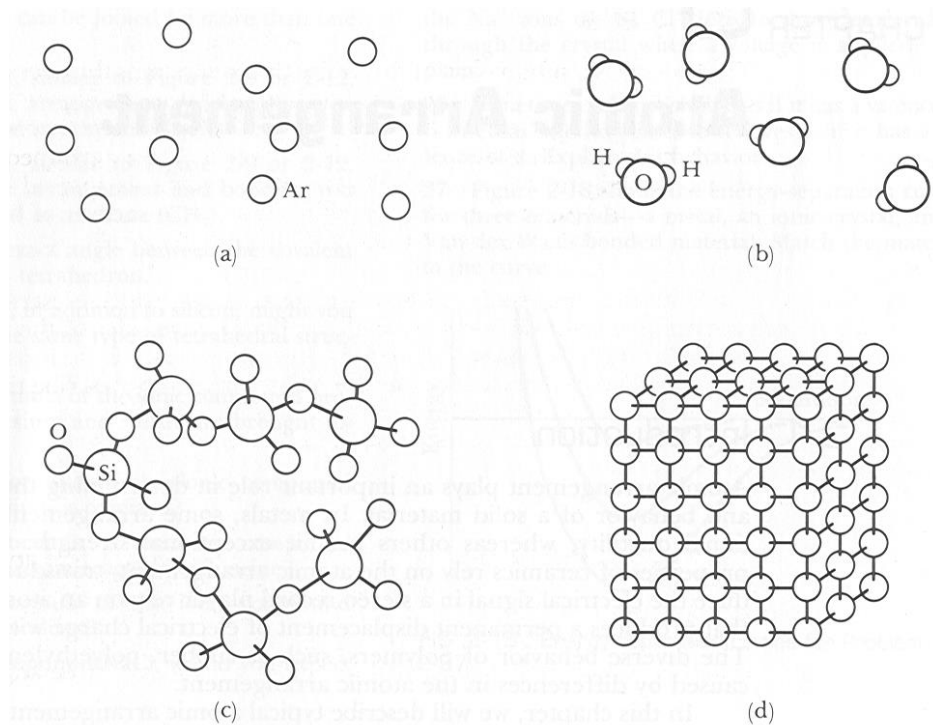


FIG. 3-1 The levels of atomic arrangement in materials. (a) Inert gases have no regular ordering of atoms. (b) and (c) Some materials, including steam and glass, have ordering only over a short distance. (d) Metals and many other solids have a regular ordering of atoms that extends throughout the material.

This short range order is typical of liquids or in the structure of so-called amorphous (amorph = lacking organization, or regular periodicity) materials.

The atomic arrangement in melts and amorphous solids are very similar. A major difference is their viscosities:

In amorphous solids the **disordered** structure is frozen in.

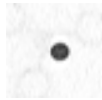
Crystalline solids exhibit “**long range order**” in the position and stacking sequence of atoms, molecules, or “**lattice points**”

In crystalline solids, each atom or molecule has identical surroundings in the crystal (except for the surface atoms)

**Crystal Lattice Concept:**

Crystalline structure → consists of regular array of “points” in 3 dimensional space

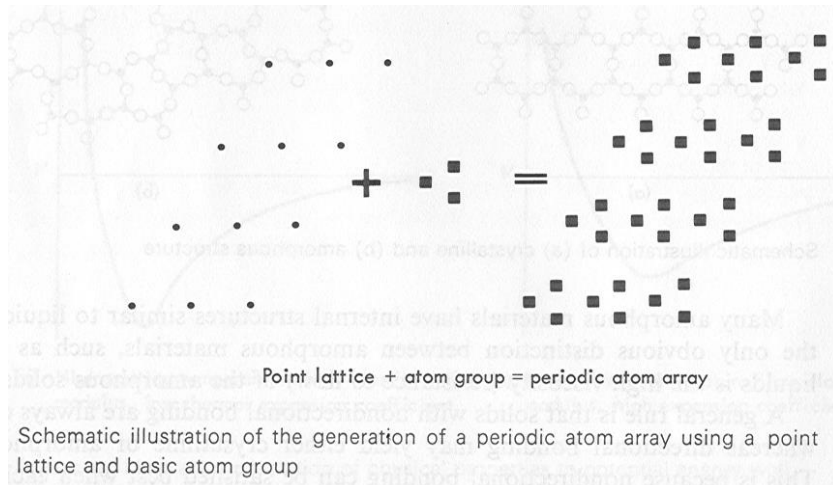
With each of the **lattice points**,



there may be *none, one or more atoms* associated

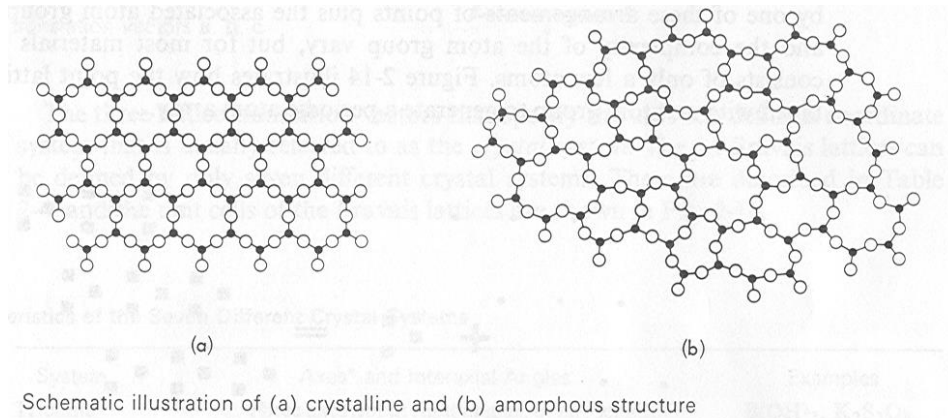


e.g. with each lattice point is one molecule of the above kind associated



**point lattice + atom group = periodic array of atoms**

crystalline and amorphous structure are built from exactly the same basic building blocks (short range order):



how many ways to pack atoms in regular self repeating units???

Fortunately, there are only limited number of ways that one can pack lattice points in 3-D space such that each point has identical surroundings. All the crystalline solids in the universe can be described by these 14 ways of packing lattice points in space. ( plus the local atoms group arrangement associated with each lattice point.) Most of the time we have one or few atoms associated with one lattice point.....BUT in a polymer this could be many atoms per lattice point!

The 14 different ways of packing → 14 **BRAVAIS** lattices distributed to 6 (or 7) **crystal systems**.....

Each **Bravais** lattice described by the smallest repeating unit :

## UNIT CELL

**Unit cell** is defined by the three lattice translation vectors,  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$ . The magnitude of  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$  are called “lattice parameters”.

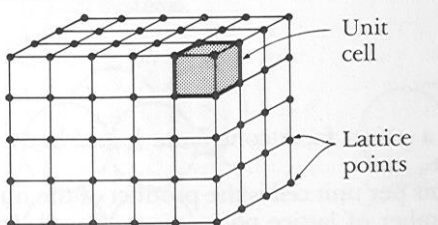
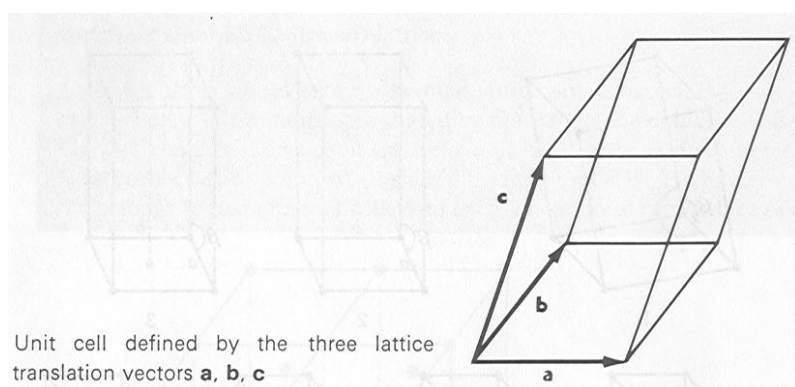
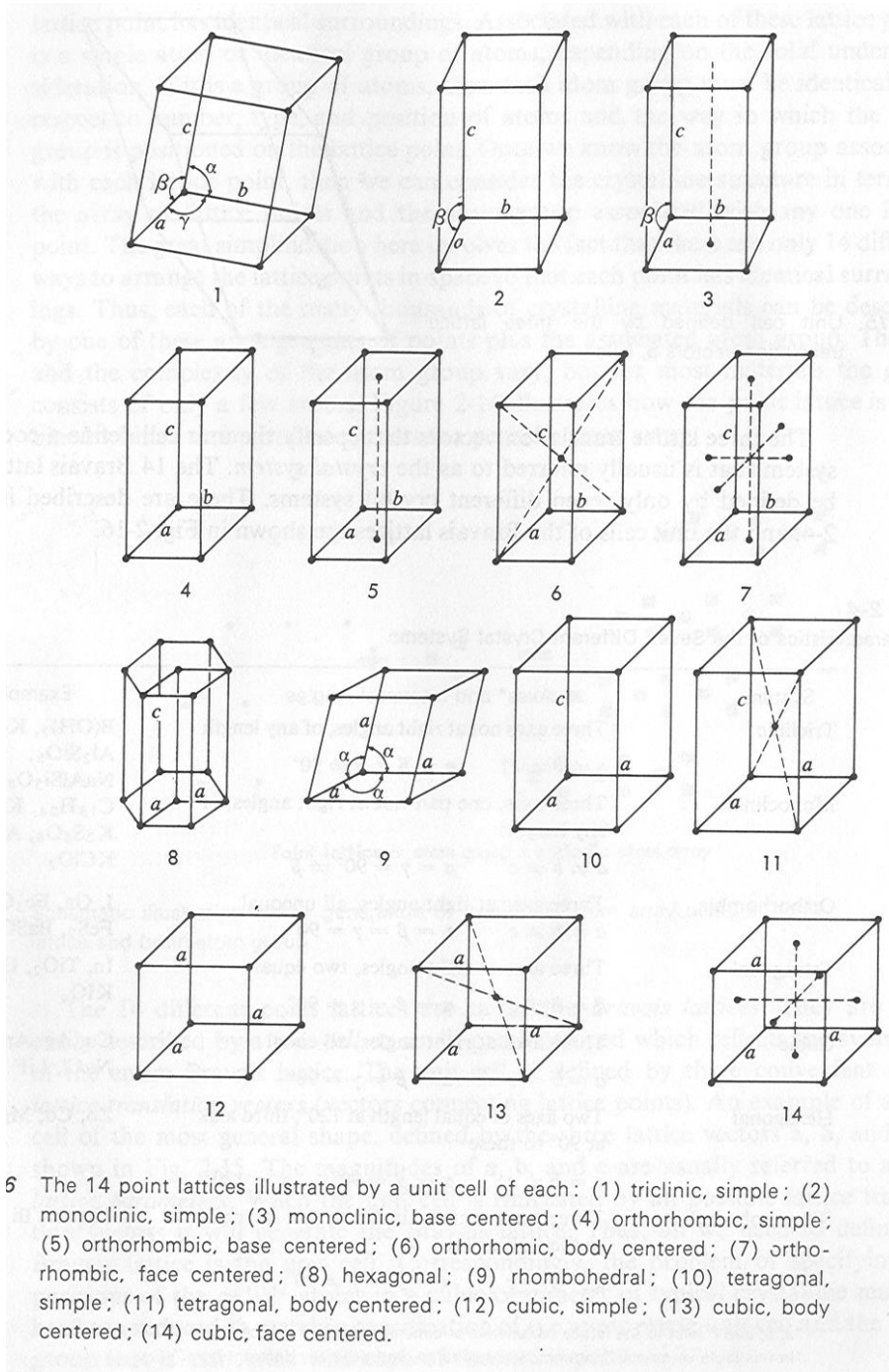


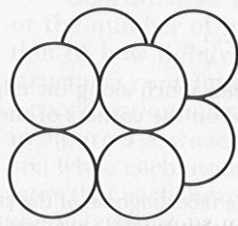
FIG. 3-2 A lattice is a periodic array of points that define space. The unit cell (heavy outline) is a subdivision of the lattice that still retains the characteristics of the lattice.



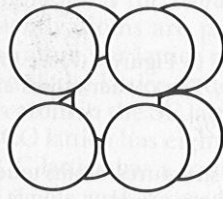
Depending on the ratio of  $a$ ,  $b$ , and  $c$  and the angle between them, each unit cell is assigned to one of the 6 (or 7) crystal system.



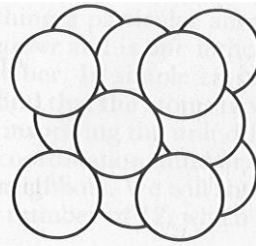
6 The 14 point lattices illustrated by a unit cell of each: (1) triclinic, simple; (2) monoclinic, simple; (3) monoclinic, base centered; (4) orthorhombic, simple; (5) orthorhombic, base centered; (6) orthorhombic, body centered; (7) orthorhombic, face centered; (8) hexagonal; (9) rhombohedral; (10) tetragonal, simple; (11) tetragonal, body centered; (12) cubic, simple; (13) cubic, body centered; (14) cubic, face centered.



Simple cubic



Body-centered cubic



Face-centered cubic

FIG. 3-5 The models for simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC) unit cells assuming only one atom per lattice point.

TABLE 2-4  
The Characteristics of the Seven Different Crystal Systems

System	Axes* and Interaxial Angles	Examples
Triclinic	Three axes not at right angles, of any length $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	$B(OH)_3$ , $K_2S_2O_8$ , $Al_2SiO_5$ , $NaAlSi_3O_8$
Monoclinic	Three axes, one pair not at right angles, of any lengths $a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	$C_{18}H_{24}$ , $KNO_2$ , $K_2S_4O_6$ , $As_4S_4$ , $KClO_3$
Orthorhombic	Three axes at right angles, all unequal $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	I, Ga, $Fe_3C$ , $FeS_2$ , $BaSO_4$
Tetragonal	Three axes at right angles, two equal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	In, $TiO_2$ , $C_4H_{10}O_4$ , $KIO_4$
Cubic	Three axes at right angles, all equal $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Cu, Ag, Ar, Si, Ni, NaCl, LiF
Hexagonal	Two axes of equal length at $120^\circ$ , third axis at $90^\circ$ to these $a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Zn, Cd, Mg, NiAs
Rhombohedral	Three axes equally inclined, not at right angles, all equal $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	Hg, Sb, Bi

\* $a$ ,  $b$ , and  $c$  refer to the lattice parameters or dimensions of the unit cell.

†In this table  $\neq$  means "not necessarily equal to, and generally different from."

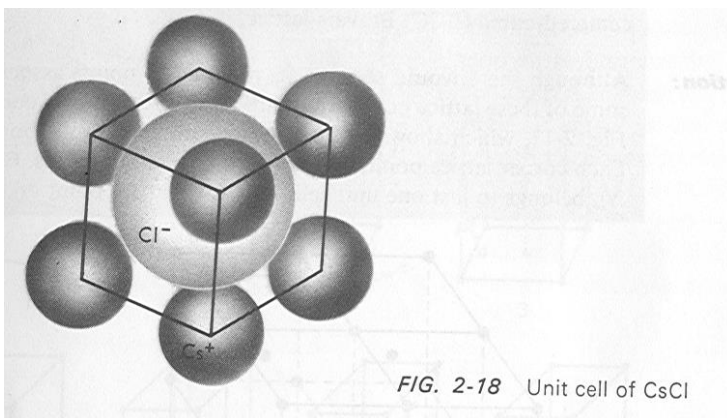
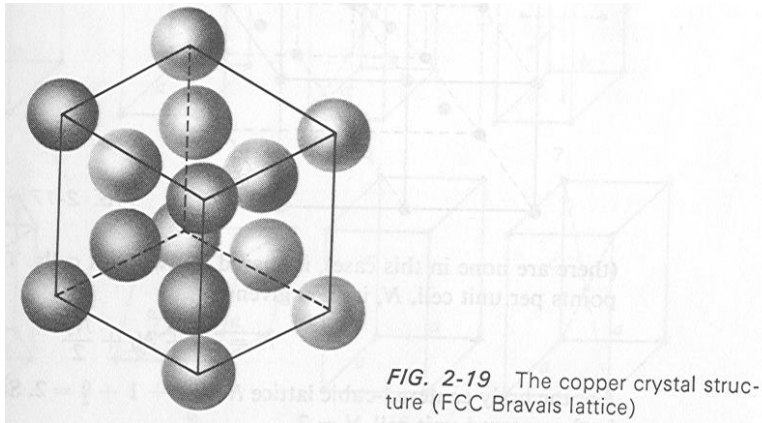


FIG. 2-18 Unit cell of CsCl



14 different ways of arranging atoms (ions), molecules in 3-D with long range order → 14 Bravais Lattices

**Lattice**: periodic arrangement of points in 3-D  
identical sites  
locations

Not all of these arrangements give the highest packing density of atoms (ions, molecules)

For example in metals:

FCC and HCP (hexagonal close packed) structures have the highest density of packing with 0.74

Metals with simple **metallic bond** → packed efficiently

**Directional bonds** → cause low packing density structures

(metals) theoretical (x-ray) density,  $\rho$  :

$$\rho = \left( \frac{\left( \frac{\text{atoms}}{\text{cell}} \right) \times (\text{atomic mass of atom})}{(\text{volume of unit cell}) \times (\text{Avogadro's number})} \right)$$

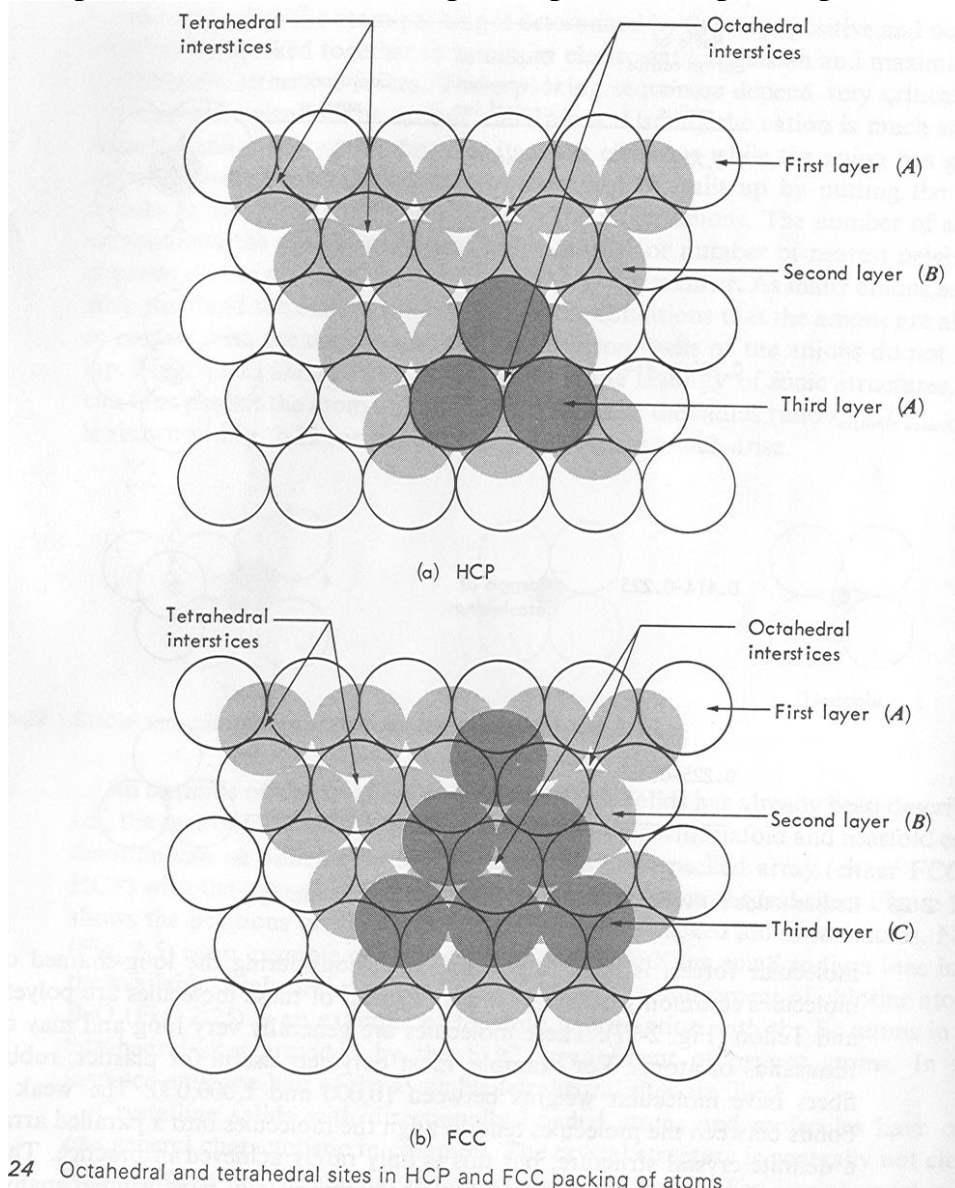
the two closed packed structures are very similar

the difference is in the sequence of stacking

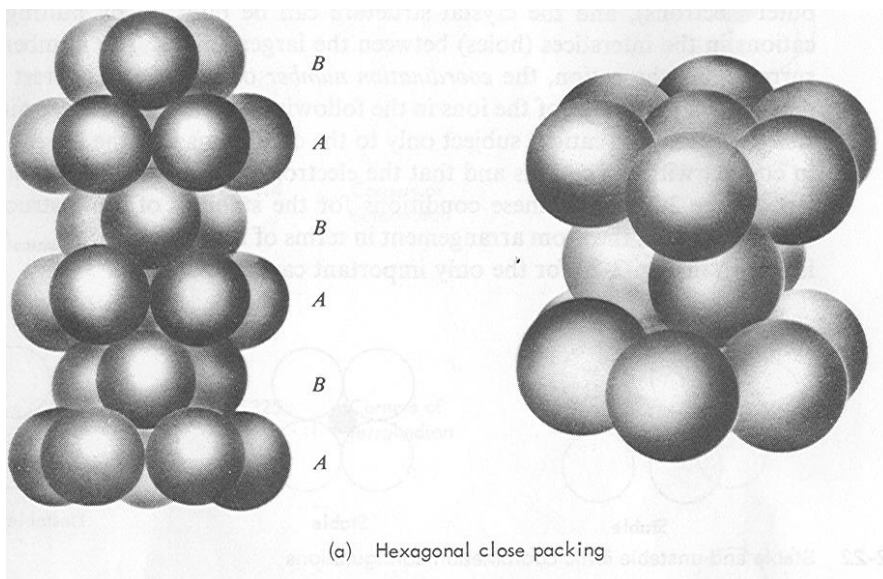
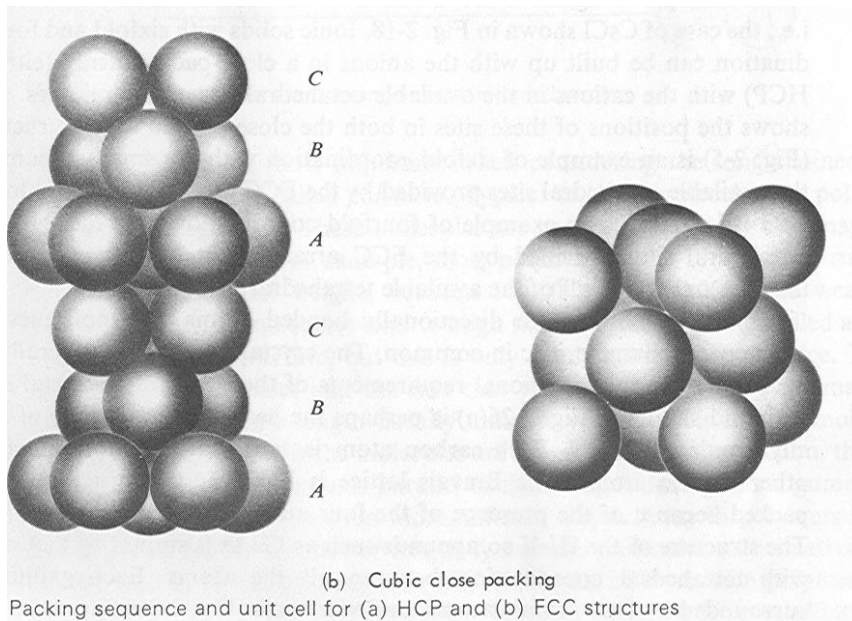
FCC:  $\rightarrow$  A B C A B C A B C A B C

HCP:  $\rightarrow$  A B A B A B A B A B

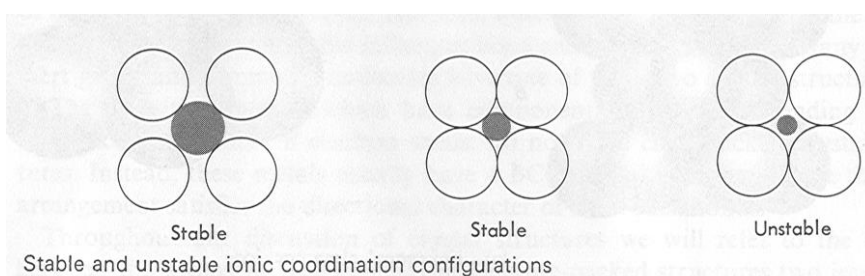
For spherical hard balls, both give highest solid packing ratio of 0.74



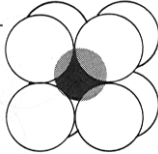
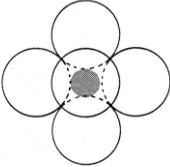
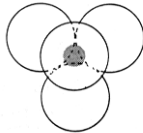





For identical balls packing → touching balls (typical of metals)  
 But for ions of different sizes more varieties are possible →  
**Stable** versus **unstable** packing for ionic materials



Like charges will repel each other if they start to overlap....  
 Depending on the size ratio of the ions making up the material a certain coordination of a small ion with large ions around it is stable... →

Ratio of cation radius to anion radius	Disposition of ions about central ion	Coordination number	
1-0.732	Corners of cube	8	
0.732-0.414	Corners of octahedron	6	
0.414-0.225	Corners of tetrahedron	4	
0.225-0.155	Corners of triangle	3	

Radius ratios for various atom arrangements in ionic bonding

“Rattling” small ion configuration → usually not “stable”  
 some “rules of thumb” :

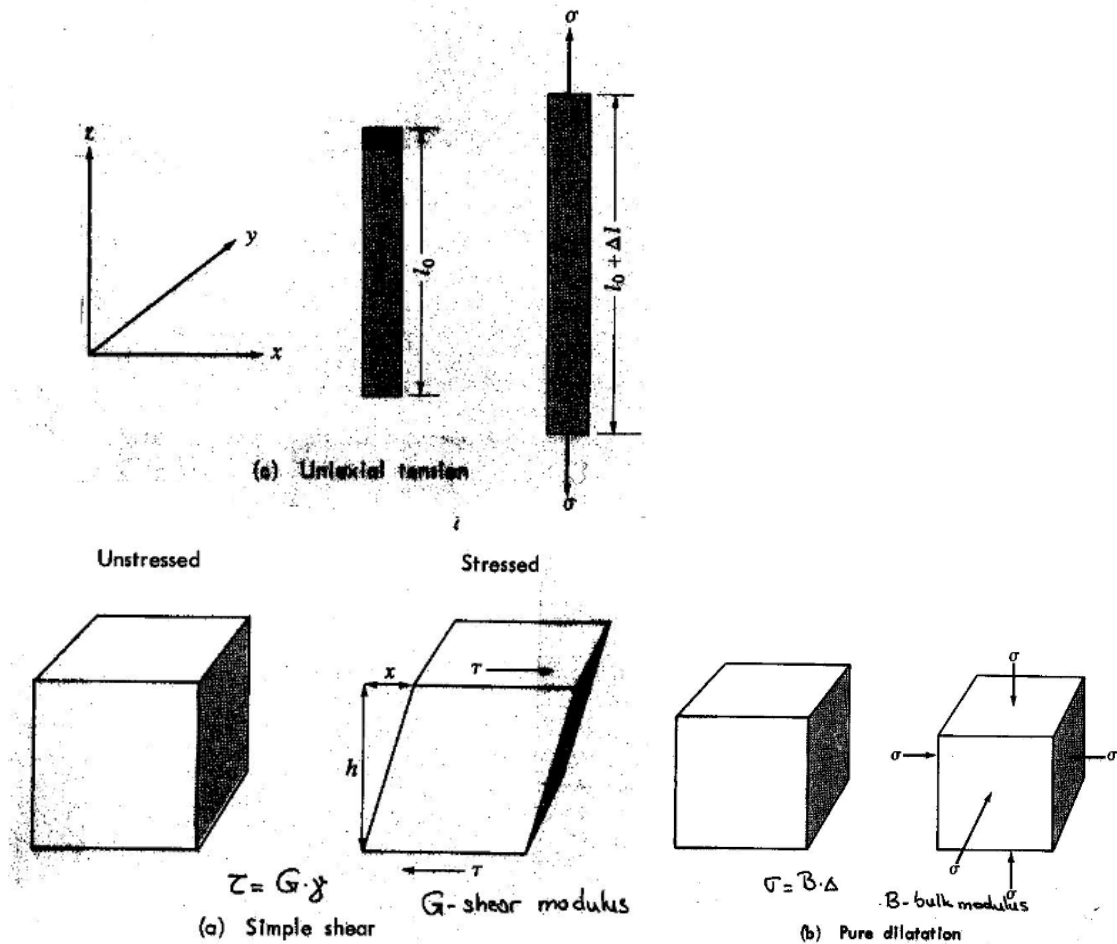
- as many anions as possible surrounding the cation
- anions always in contact with cations
- e<sup>-</sup> -shells of anions do NOT overlap

**Mechanical Properties** determines;

The response of the material to mechanical work (stress).

And the materials' response to different loading states

- ⇒ Elongation under tension
- ⇒ Shear under shear or twisting
- ⇒ Dilation under hydrostatic compression or tension



Load for deformation depends on the size of the specimen.

There is a need to normalize F w.r.t. the area over which it is applied;

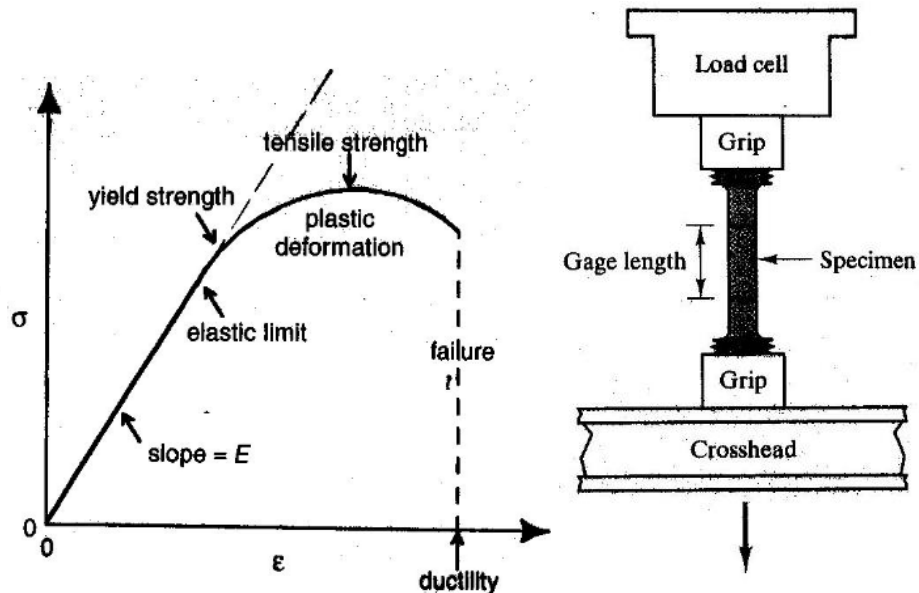
Stress ;  $\sigma = F/A_0$  where  $\sigma$  is engineering stress [Pa], F is load [N],  $A_0$  is initial area [ $m^2$ ] for the applied force.

Engineering strain,  $e = (l - l_0)/l_0$  (elongation) l-length under load,  $l_0$ -original length

Shear strain,  $\gamma = x/h$

Dilation strain ,  $\Delta = \Delta V/V_0$

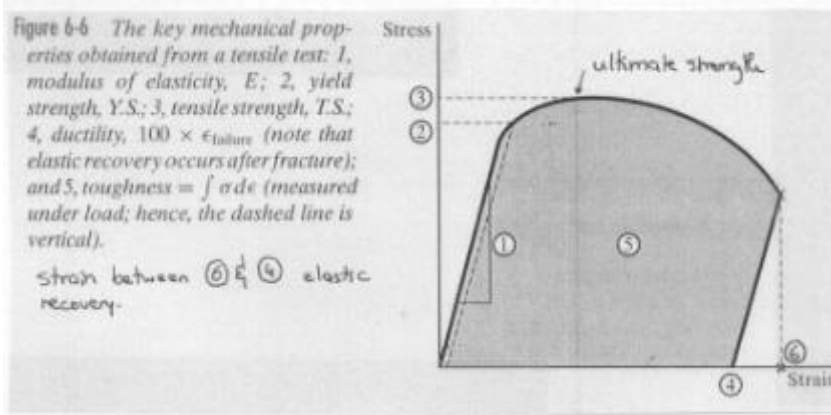
## Stress-Strain Curve under Tensile Loading



There are 2 important regimes; elastic and plastic deformations.

- (I) Elastic Deformation Range
  - a. Deformation is temporary and fully recovered when the load is removed.
  - b. Hook's Law applied; strain is proportional to stress;  
 $\sigma = E \cdot e$  where E is Elastic Modulus or Young's Modulus or Stiffness
- (II) Plastic Deformation Range
  - a. Deformation is permanent. Not recovered when the load is removed.

The two regimes are separated by "Yield Point" where the permanent deformation starts.



The region between Yield stress and UTS is very important for engineers. Why?

In this region the ductile material hardens as it is deformed further. Why?

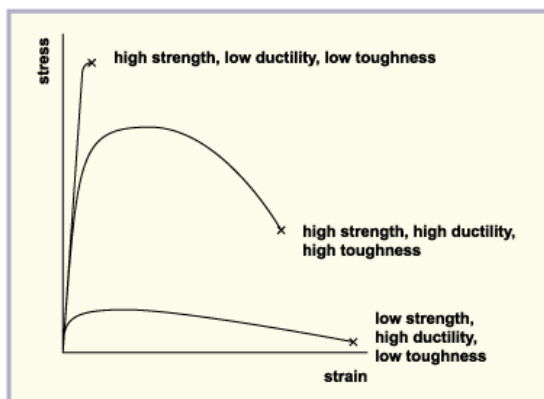
The stress required to have more elongation after UTS decreases. Why?

Poisson's Ratio:

$$\nu = -e_x/e_y = -e_y/e_z, \text{ generally } 0.25 < \nu < 0.35$$

Negative poisson's ratio is possible?

Different materials display different mechanical response under same tensile loading, depending on their bond character.

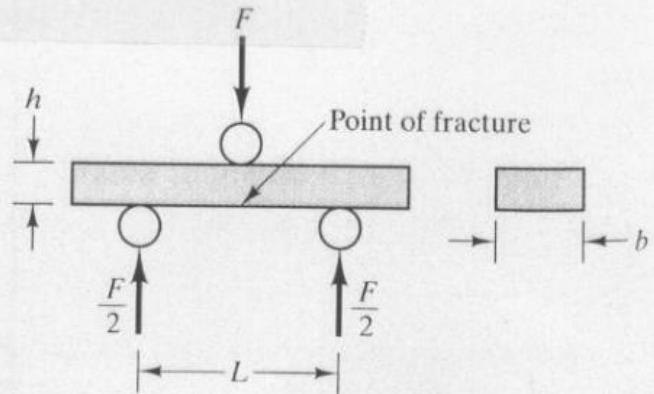


How is it for long chain polymers like elastomers?

Brittle materials are weak in tension, strong in compression!

Usually a flexural bending test is used to determine the mechanical properties.

Figure 6-14 The bending test that generates a modulus of rupture. This strength parameter is similar in magnitude to a tensile strength. Fracture occurs along the outermost sample edge, which is under a tensile load.



$$\text{Modulus of rupture} = \text{MOR} = \frac{3FL}{2bh^2}$$

Usually brittle material fails at the bottom outermost edge first, which is under tension. The top outermost edge is under compression.

Brittle materials are much stronger under compression than in tension. Why?

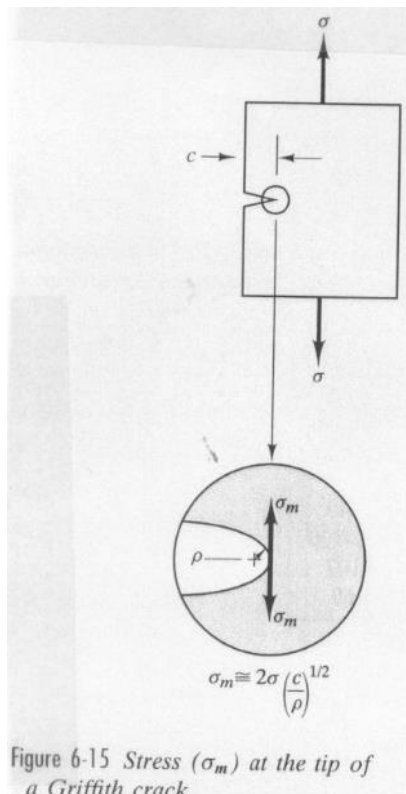
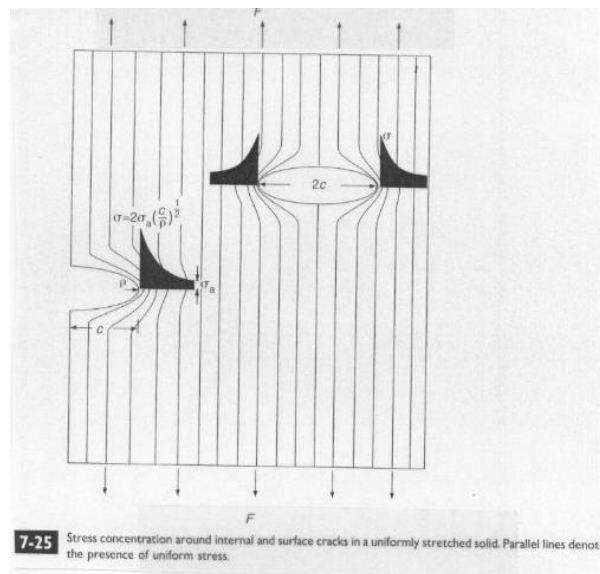


Figure 6-15 Stress ( $\sigma_m$ ) at the tip of a Griffith crack.

In brittle materials cracks are unavoidable  $\rightarrow$  material weak in tension. Compression tends to close Griffith cracks  $\rightarrow$  cracks are not effective in compression.

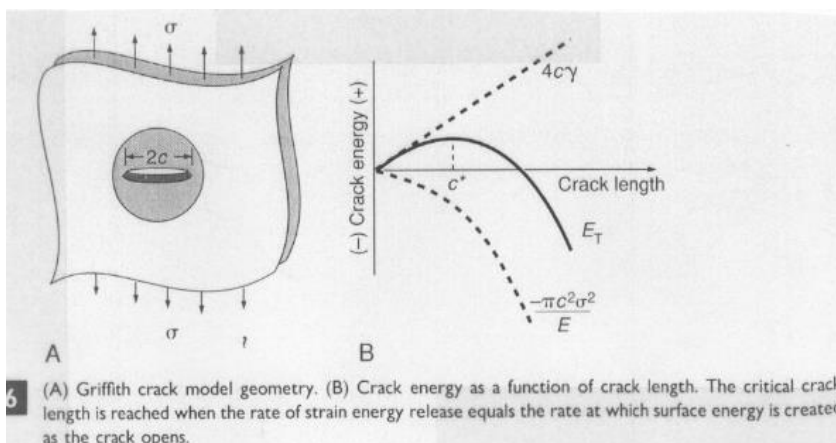
Pay attention to internal cracks.



Why whiskers or fibers are much stronger than bulk brittle materials?  
Fewer critical cracks that can grow!

Why cracks are not a problem in ductile materials?

### Crack Propagation



For an internal crack of length  $2c$ , the crack becomes critical when the gain in energy is releasing elastic strain energy around the crack under stress equals the surface energy required to create two new surfaces (elongation of crack)

- Energy released in a circular disc of unit thickness is  $2\pi c^2$

- Elastic strain energy per unit volume is  $\sigma^2/2E$

$$E_T = - \pi c^2 \sigma^2 / E + 4c\gamma \quad ; \gamma \text{ is surface energy per unit area}$$

when  $dE_T/dc=0$

$$\sigma_{\text{crit}} = (2E\gamma/\pi c)^{1/2}$$

$$K = \sigma(\pi c)^{1/2}$$