Matter & its Various states

•Have definite mass,

•Occupy space,

•Capable of resist forces

There are **three stable states** of a matter

•**Solid**-*having both definite volume and shape*

•**Liquid**-*having definite volume but not definite shape*

•**Gas**-*No definite shape and volume*

⟹ **In this subject we deal with solid state of a matter.**

Branch of Physics which deals with the arrangement of atoms or molecules in a matter is known as **Crystallography**.
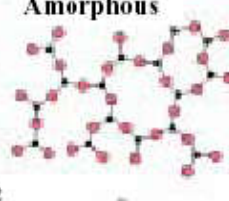
Types of solids

From the crystallographic point of view solids are found to be following types:-

Crystalline solids:-In crystalline solids atoms are stacked in a regular manner, forming a three-dimensional pattern which may be obtained by three dimensional repetition of a certain pattern unit.
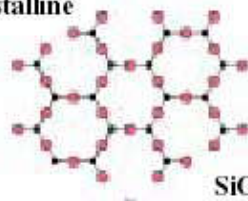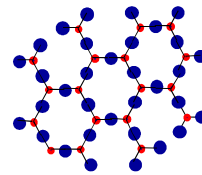

Crystalline   Amorphous

SiO_2

1

Materials and Packing

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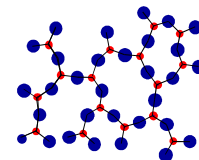

crystalline SiO_2

•**Si**   ●**Oxygen**

Noncrystalline materials...
• atoms have no periodic packing
• occurs for: -complex structures
   -rapid cooling

"Amorphous" = Noncrystalline

noncrystalline SiO_2

2

Single vs Polycrystals

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

E (diagonal) = 273 GPa

E (edge) = 125 GPa

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

200 μm
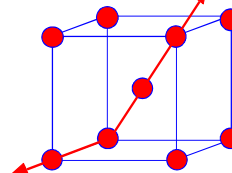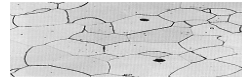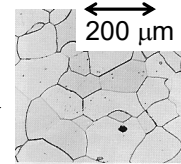
3

Polymorphism

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

iron system

liquid

titanium

- α, β-Ti

BCC   δ-Fe

1538ºC

1394ºC

FCC   γ-Fe

912ºC

carbon

- diamond, graphite   BCC   α-Fe

4

2
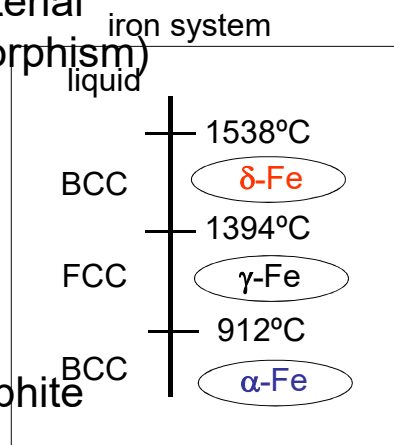
Single crystal: In a single crystal the periodicity of the pattern extends throughout a certain piece of material.

Polycrystalline solids: In polycrystalline materials the periodicity of structure is interrupted. It comprised of many small crystals or grains. The grains have different crystallographic orientation. There exists atomic mismatch within the where grains meet. These regions are called grain boundaries.
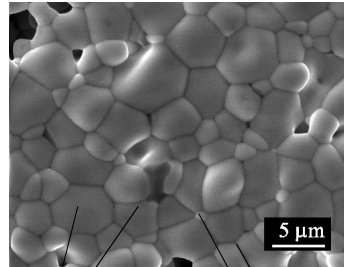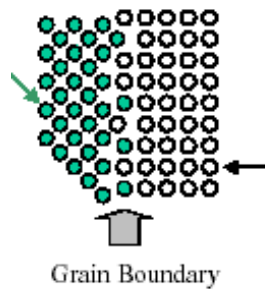
Grain Boundary

Grain

Grain boundaries

5 μm

Amorphous: Lacks of systematic arrangements of atoms. The size of the grains or crystals becomes comparable to the size of the pattern unit. In amorphous solid there is no long range order but may have some short range order.

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For most solid crystalline state is the natural state. The energy of the ordered atomic arrangement is lower than that of an irregular packing of atoms. However, when the atoms are not given an opportunity to arrange themselves properly , by inhibiting their mobility, amorphous material may be formed.

The solid state may corresponds to a supercooled liquid in which the molecular arrangement of the liquid state is frozen in, because of rapid cooling and a high viscosity of the liquid. Crystals may not have had time to grow and a glassy material results.

Upon annealing such a glassy substance may crystallize.

Liquid crystals: This type of crystal has only two or one dimensional regularity. Such substances actually flow and will rise in a capillary tube. Normal crystal exhibit flow only under influence of external forces. One of the example is ammonium oleate $C_{17}H_{33}COONH_{4..}$

Space Lattice and Basis

Bravais, in 1884 introduce the concept of the space lattice.

A space lattice is a mathematical concept and is defined as an infinite number of points in space with the property that the arrangements of the points about a given point is identical with that about any other point.

The points having above properties are known as lattice points.

6

3

Example: Consider a finite two dimensional square array of points. If we locate ourselves at any lattice point and look around in the plane of the paper, the scenery is the same irrespective of any lattice points.

Basis: The structure of all crystals is described in terms of a lattice with a group of atoms attached to each lattice point. The group is called basis; it is repeated in space to form the crystal structure.

A lattice is a mathematical abstraction: the crystal structure is formed only when a basis of atoms is attached identically to each lattice point. The logical relation is

Lattice + basis = Crystal Structure
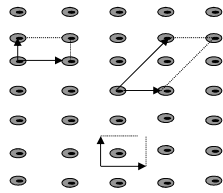
Unit Cell:
The unit cell is the smallest structural unit or building block that can describe the crystal structure. Repetition of the unit cell generate the entire crystal.

Adjacent figure shows various possible unit cell in 2D.

There are two types of unit cell: *Primitive* and *non-primitive cell*.

A primitive cell is a minimum-volume cell. One lattice point per primitive cell. Non-primitive cell contain more than one atom.
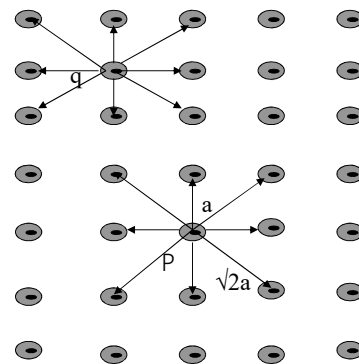
7

Lattice parameters of a unit cell

X, Y and Z are the three convenient crystal axes chosen arbitrarily and an unit cell is shown. These crystal axes may not essentially be the same with respect to orthogonal axes.

The intercepts **a**, **b** and **c** define the dimension of a unit cell and are known as its *primitives* or *characteristic intercepts* on the axes. The angles, α, β and γ, between the three axes are called *interfacial angles*. The primitives and interfacial angles constitute the lattice parameter of the unit cell
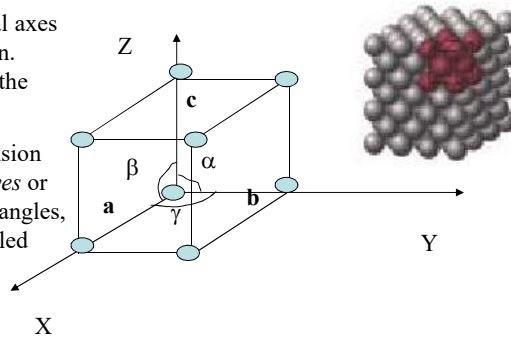
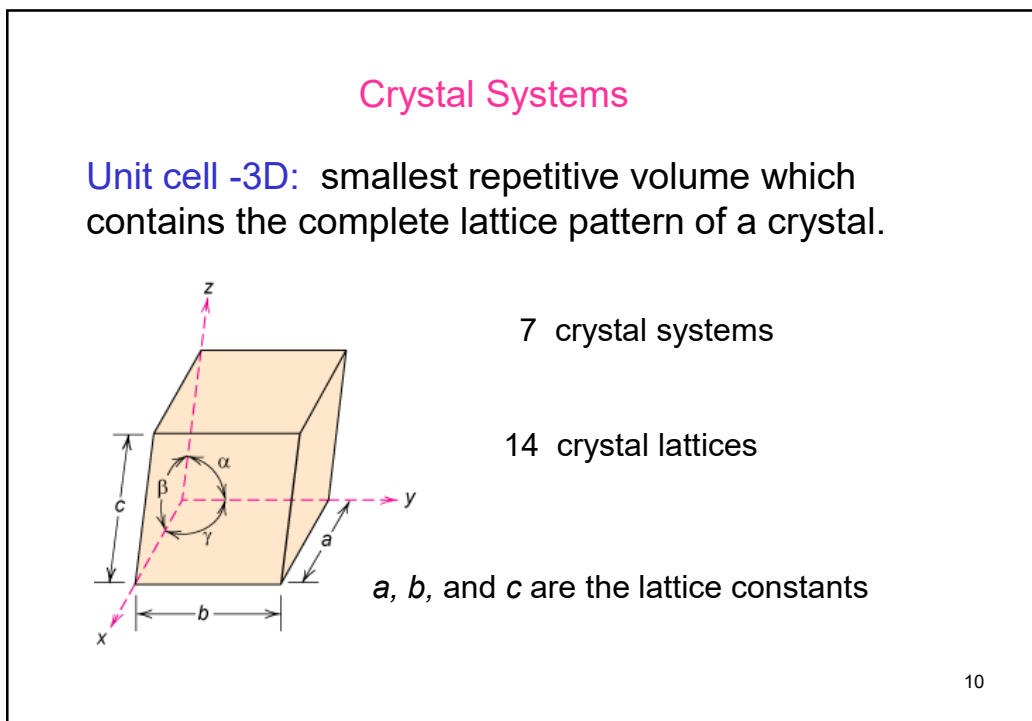## Two Dimensional Lattice Types

For two dimension (2D)lattices, the lattice parameters are **a** and **b** and angle between them ϕ.

There are five distinct types of lattices in 2D: *Oblique lattice* (there is no restriction in lattice parameters) and the *four special lattices* (there are four distinct types of restriction). Every distinct lattice type is known as *Bravais lattice*.

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(i) Oblique lattice
$|a| \neq |b|$; $\phi \neq 90°$

(ii) Square lattice
$|a| = |b|$; $\phi = 90°$

(iii) Rectangular lattice
$|a| \neq |b|$; $\phi = 90°$

(iv) Centered Rectangular lattice ;
axes are shown for both primitive
cell and for rectangular unit cell
$|a| \neq |b|$; $\phi = 90°$

(v) Hexagonal lattice
$|a| = |b|$; $\phi = 120°$

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Crystal Systems

Unit cell -3D: smallest repetitive volume which contains the complete lattice pattern of a crystal.

7 crystal systems

14 crystal lattices

a, b, and *c* are the lattice constants

10

5

Three Dimensional Lattice types

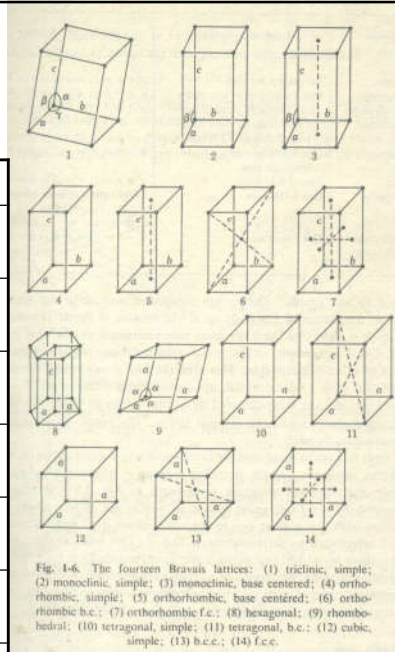In 3D, there are **fourteen** different lattice types (or Bravais Lattices); **one general** (no restriction in lattice parameters) and **13 special**. These 14 lattice types are conveniently grouped into **seven** crystal systems according to the seven types of unit cell.

Crystal System	No of lattices	Lattice parameters
Triclinic	1(Simple)	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2 (Simple, Base centered)	$a \neq b \neq c$ $\alpha = \beta = 90^\circ \neq \gamma$
Orthorhombic	4 (Simple, base centered, BCO, FCO)	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	2 (Simple, Body centered)	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Cubic	3 (simple, BCC, FCC)	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$
Trigonal or Rhombohedral	1 (simple)	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$
Hexagonal	1(simple)	$a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$

Fig. 1-6. The fourteen Bravais lattices: (1) triclinic, simple; (2) monoclinic, simple; (3) monoclinic, base centered; (4) orthorhombic, simple; (5) orthorhombic, base centered; (6) orthorhombic b.c.; (7) orthorhombic f.c.; (8) hexagonal; (9) rhombohedral; (10) tetragonal, simple; (11) tetragonal, b.c.; (12) cubic, simple; (13) b.c.c.; (14) f.c.c.
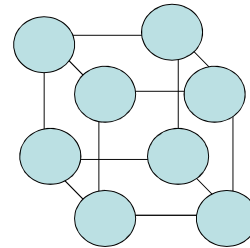
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Atomic Radius

To discuss the crystalline structure it is useful to consider atoms as being hard spheres with well defined radii. In this hard sphere model, the shortest distance between two like atoms is one diameter.

So, **atomic radius** can be defined as half of the distance between nearest neighbours in a crystal of a pure element.
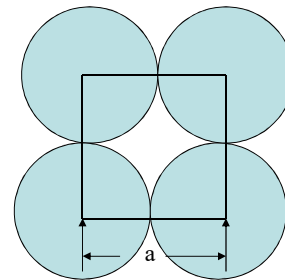
Simple Cubic crystal (SC)

It is obvious from the figure that 2 atomic radii make the lattice constant in this case.
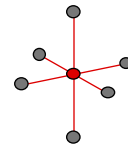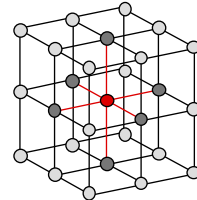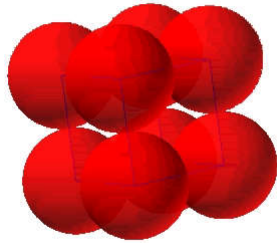
Therefore, 2r=a

And r=half of the lattice constant.

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Simple Cubic Structure (SC)

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

13

Body Centered Cubic Crystal (BCC)
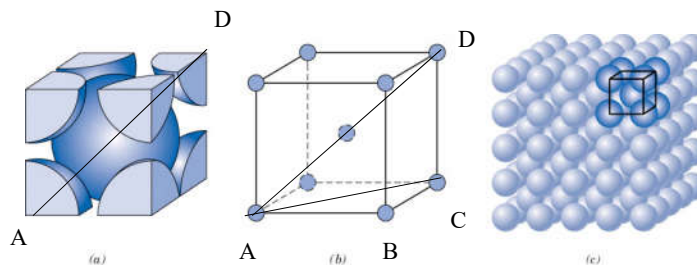
- Atoms touch each other along cube diagonals , Atoms at each corner and at center of cubic unit cell, --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing. Cr, α-Fe, Mo, Li, W, Ti, Ta have this crystal structure.

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{2}a,$$

$$AD = \sqrt{AC^2 + CD^2} = \sqrt{3}a$$

From the Figure we see that, the body diagonal, AD=four times the radius of a single atom.

Therefore,

$$Radius(r) = \frac{\sqrt{3}}{4}a$$

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Face Centered Cubic Crystal (FCC)

Atoms are located at each corner and the centre of the faces of unit cell. Atoms touch each other along face diagonals. --Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing. Cu, Al, Ag, Au, Ni, Pt, Pb, NaCl, Ca etc have this crystal structure
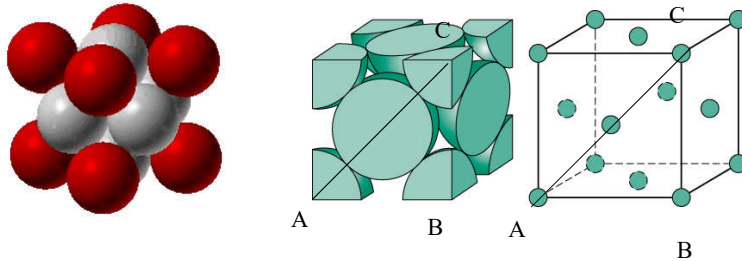
$$AC = \sqrt{AB^2 + BC^2} = \sqrt{2}a,$$

From the Figure we see that, the face diagonal, AC=four times the radius of a single atom.

Therefore, $Radius(r) = \dfrac{\sqrt{2}}{4}a$

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8
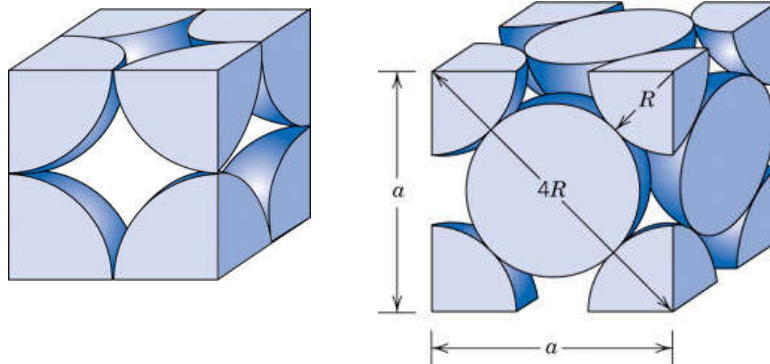
FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection

A sites
B sites
C sites
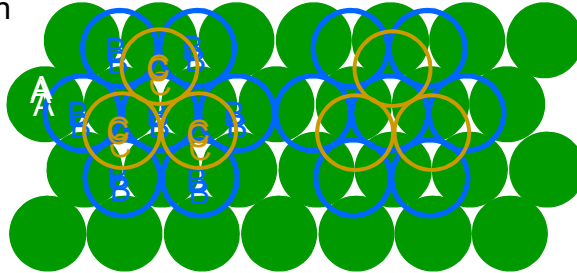
- FCC Unit Cell
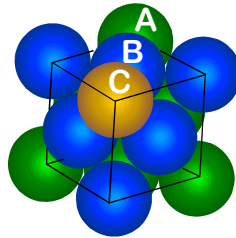
17

Number of Atoms per unit cell in various lattice types of Cubic crystal system
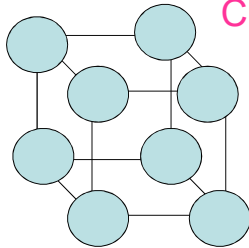
SC
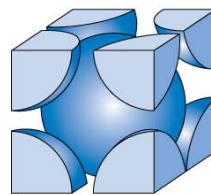
BCC
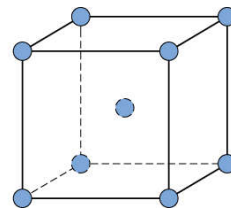
FCC

Each Corner atom is shared by eight surrounding unit cell. Therefore, share of each unit cell from each corner is 1/8.

For SC , number of atoms per unit cell (n) will be 1

For BCC, n=(1/8×8)+1=2

For FCC, n=(1/8×8)+(1/2×6)=4

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Density (Theoretical) Computations

Since the entire crystal can be generated by the repetition of the unit cell, **The density of the crystalline material, ρ= the density of the unit cell= (Atoms in the unit cell, n)× (mass of an atom, M)/(volume of the unit cell, V)**

$$Mass\ of\ an\ atom = \frac{Atomic\ Weight\ (M_A)}{Avogadro`s\ number\ (N_A)}$$

$$Mass\ of\ a\ unit\ cell = n \times \frac{M_A}{N_A} \qquad (i)$$

$$If\ the\ density\ is\ \rho, then\ mass\ of\ a\ unit\ cell\ is = \rho \times V \qquad (ii)$$

$$From\ (i)\ and\ (ii), we\ get$$

$$\rho = n \times \frac{M_A}{N_A} \times \frac{1}{V}$$

Atoms in the unit cell, n=1 (SC); 2 (BCC); 4(FCC); 6 (HCP)
The Volume of the cell, V=a³ (SC, BCC, FCC)

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Theoretical Density of Cr Metal
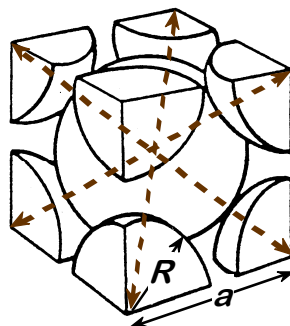
Cr is BCC) ,M_A = 52.00 g/mol , R = 0.125 nm, n = 2

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

$$\rho = \frac{\dfrac{atoms}{unit\ cell} \rightarrow 2 \quad 52.00 \leftarrow \dfrac{g}{mol}}{a^3 \quad 6.023 \times 10^{23}}$$

volume / unit cell

atoms / mol

$\rho_{theoretical}$ = 7.18 g/cm³

ρ_{actual} = 7.19 g/cm³

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Densities of Material Classes

In general
$\rho_{metals} > \rho_{ceramics} > \rho_{polymers}$

Why?

Metals have...
- close-packing (metallic bonding)
- often large atomic masses

Ceramics have...
- less dense packing
- often lighter elements

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

Composites have...
- intermediate values

Metals/Alloys — Platinum; Gold, W; Tantalum; Silver, Mo; Cu,Ni; Steels; Tin, Zinc; Titanium; Aluminum; Magnesium

Graphite/Ceramics/Semicond — Zirconia; Al oxide; Diamond; Si nitride; Glass -soda; Concrete; Silicon; Graphite

Polymers — PVC; PET; PC; HDPE, PS; PP, LDPE

Composites/fibers — Glass fibers; GFRE*; Carbon fibers; CFRE*; Aramid fibers; AFRE*; Wood

*GFRE, CFRE, & AFRE are Glass, Carbon, & Aramid Fiber-Reinforced Epoxy composites (values based on 60% volume fraction of aligned fibers in an epoxy matrix).

$\rho\,(g/cm^3)$ axis: 30, 20, 10, 5, 4, 3, 2, 1, 0.5, 0.4, 0.3

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Example

- **Example 1:** Consider α-Fe, which is body centered cubic. If the lattice constant is 0.287 nm, calculate its density. For Fe, M_A=55.85 g/mole. [7.86 g/cm^3]
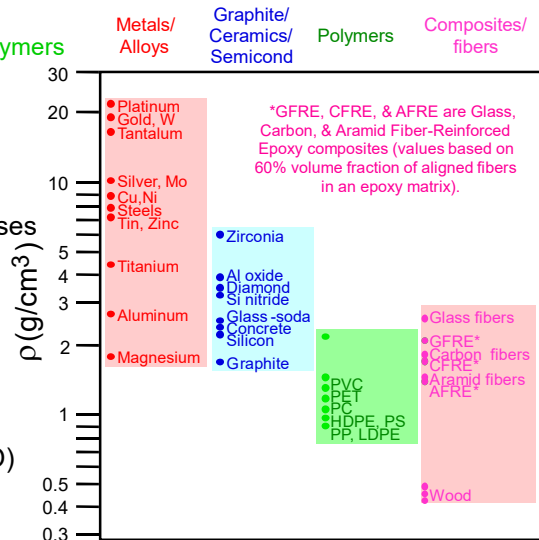
- **Example 2:** The Ag is FCC with lattice constant 0.4077 nm. Calculate the density of the Ag. The atomic weight of Ag is 108 g/mole. [10.6 g/cm^3]

- **Example 3:** Copper (Cu) has an FCC structure with an atom radius of 0.1278 nm. Calculate its density. The atomic weight of Cu is 63.5 g/mole. [8.93 g/cm^3]

- **Example 4:** Calcium is FCC with a density of 1.55 Mg/m^3 (1.55 g/cm^3). What is the volume per   unit cell. The atomic weight of Ca 40.08 g/mole.

- **Example 5:** Titanium is BCC at high temperature and its atomic radius is 0.145 nm. (a) How large is the edge of the unit cell? (b) Calculate the density. The atomic weight of Ti is 47.88 g/mole.

- **Example 6:** Niobium (Nb) is BCC with a density of 8.57 Mg/m^3. (a) Calculate the center to center distance between closest atoms. (b) What is the edge dimension of the unit cell? For Nb, M_A = 92.91 g/mole.

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Linear Density

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

[110]
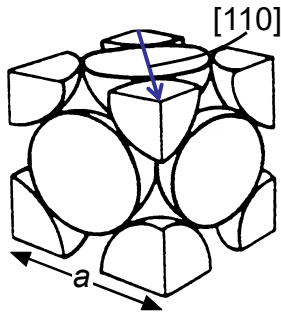
ex: linear density of Al in [110] direction

$a = 0.405$ nm

atoms

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

length

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Density of Packing or Packing Factor

- Packing factor is defined as the fraction of volume occupied by spherical atoms as compared to the total available volume of the structure.

$$PF = \frac{\text{Volume occupied by the atoms}}{\text{Available volume of the structure}}$$

$$= \frac{n \times \text{Volume of an atom}}{V_c}$$

$$= \frac{n \times 4/3\pi \times r^3}{\text{Available volume of the structure}}$$

n = number atoms per unit cell

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- In case of Simple Cubic atomic radius r=a/2

$$PF_{SC} = \frac{1 \times \frac{4}{3}\pi(a/2)^3}{a^3} = \frac{\pi}{6} = 0.52$$

•For BCC, Atomic radius r=√(3/4)a

$$PF_{BCC} = \frac{2 \times \frac{4}{3}\pi(\frac{\sqrt{3}}{4}a)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68$$

•For FCC, Atomic radius r=√(2/4)a

$$PF_{FCC} = \frac{4 \times (\frac{4}{3}\pi(\frac{\sqrt{2}}{4}a)^3}{a^3} = \frac{\sqrt{2}\pi}{6} = 0.74$$

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NaCl Crystal Structure

•It is often describe as two interpenetrating FCC lattices.

•Each atom has six nearest neighbour of opposite kind.

•LiH, MgO, MnO, NaCl, AgBr, PbS, KCl, KBr etc have this structure
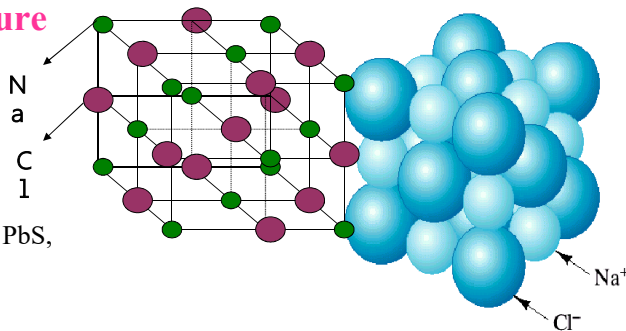
$a = 2r_{Cl} + 2r_{Na}$

$$PF = \frac{4\,(4\pi/3)r^3_{Cl} + 4\,(4\pi/3)r^3_{Na}}{(2r_{Cl}+2r_{Na})^3}$$

=0.67

r_{Cl}=0.187 nm; r_{Na}=0.097 nm
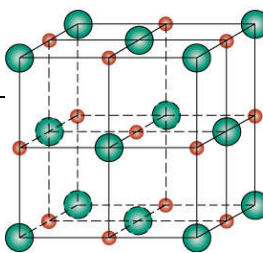
Crystal	a
LiH	4.08 Å
MgO	4.20
MnO	4.43
NaCl	5.63
AgBr	5.77
PbS	5.92
KCl	6.29
KBr	6.59

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CsCl Crystal Structure

The Cl^+ ions are located at the cells corner and the Cs^+ ions are located at center. However, this compound is not BCC, because the cell center possesses an ion different from that at the cell corners.

$a_{CsCl} = 2(r_{Cs} + R_{Cl})/\sqrt{3}$

C s C l

Crystal	a
BeCu	2.70 Å
AlNi	2.88
CuZn	2.94
CuPd	2.99
AgMg	3.28
LiHg	3.29
NH4Cl	3.87
TlBr	3.97
CsCl	4.11
TlI	4.20

Cs+

Cl−
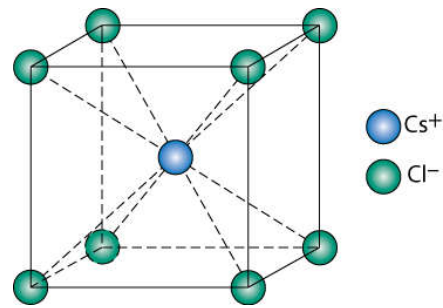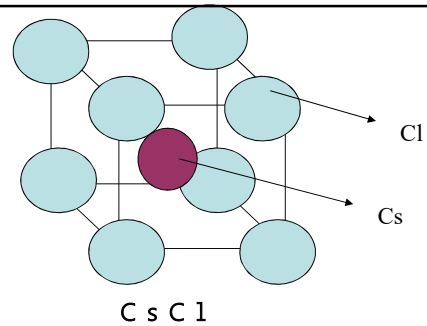
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Coordination number

By coordination number (CN), we meant the **number of nearest neighbours (NN)** of an atom has in the unit cell of any crystal system. It depends on the type of space lattices in the crystal system

S C

(i) SC Structure: Coordination number is six. NN of a corner atom is another corner atom. Therefore, there are 4 such atom in the same plane, one vertically above and one immediately below.

(ii) BCC Structure: CN is 8. NN neighbour of a body centred atom is corner atom. There are 8 such atom in a unit cell

(iii) FCC structure: CN is 12. NN of a face centred atom is corner atoms. There are 4 such atom in own plane, 4 above and 4 below.

B C C

F C C
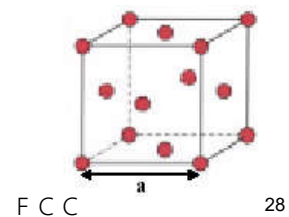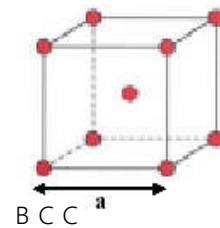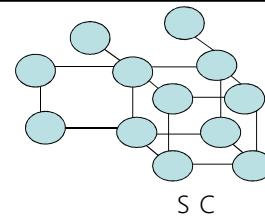
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Hexagonal Closed Packed Crystal Structure

Six atoms from regular hexagon, surrounding one atom in centre. Another plane is situated half way up unit cell (C-axis) with 3 additional atoms situated at interstices of hexagonal planes.

Cd, Mg and Zn have this crystal structure.

From the figure c=2 h

$OD=(AD^2-OA^2)^{1/2}$; AD=a, OA=2/3AE

$OA = 2/3ACsin 60 = 2/3(a)(\sqrt{3}/2) = a/\sqrt{3}$

Therefore, $OD=h=(\sqrt{2}/3)a$; So, $c=2(\sqrt{2}/3)a$;
$c/a=(\sqrt{8/3})=1.63$

CN=12 (Same as FCC); n=6

3 mid planes atoms shared by no other cells: 3

12 hexagonal corner atoms shared by 6 cells: $2\times1/6=2$

2 top and bottom plane centre atoms are shared by 2 cells: $2\times1/2=1$

PF=0.74

29
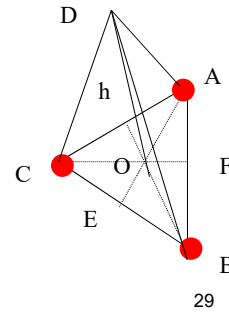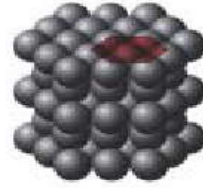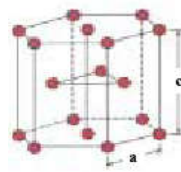
Hexagonal Close-Packed Structure (HCP)

• ABAB... Stacking Sequence

• 2D Projection

• 3D Projection

A sites

B sites

A sites

Top layer

Middle layer

Bottom layer

c

a

30

15
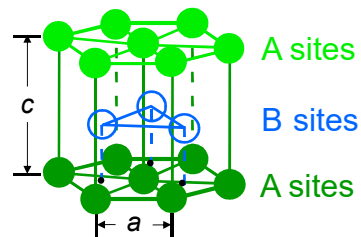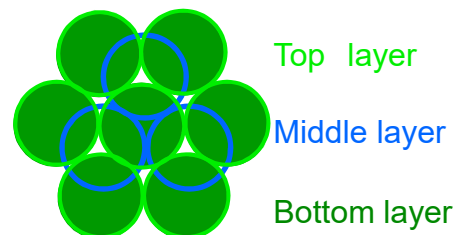
Crystal Planes

A crystal contains planes of atoms; these planes influence the properties and behaviour of a material. Thus it will be advantageous to identify various planes within the crystal.

Miller indices

A plane in the crystal is identified by the Miller indices. They are the **reciprocals** of the three intercepts that the plane makes with the axes. **Cleared of fractions** and of common multipliers.

To obtain Miller indices;

(i)   Find the intercepts on the crystal axes in terms of lattice constant.

(ii)   Take the reciprocals of these numbers

(iii)   Convert them to integers and the result is enclosed in parentheses, (hkl), without any comma.

Note that –ve intercept is handled readily with overbar.

(100)   (010)   (001)

31

Crystal Planes

(110)   (111)   (210)

(112)
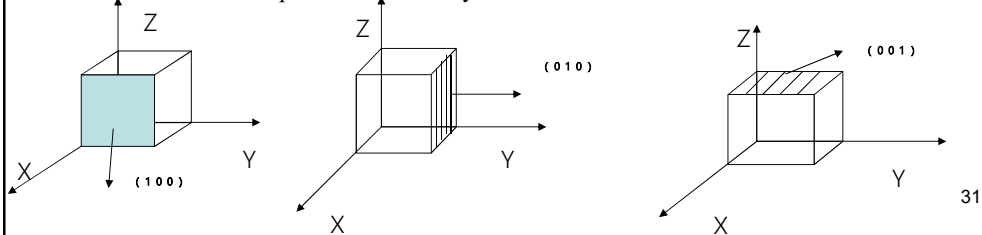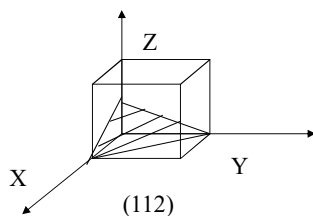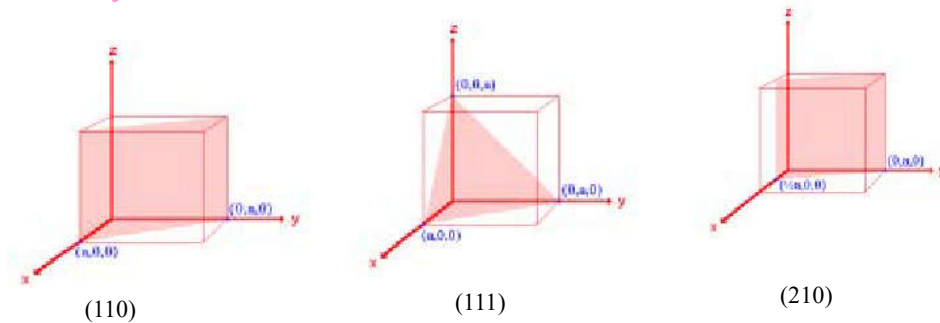
Families of Planes: Depending on the crystal system two or more planes may belong to the same family of planes. In the cubic crystal system

(100) (010) (001)

notation of the   –   ={100}; The collective

($\bar{1}$00) (010) (001)   family of planes is {hkl}

32

16

Crystal Directions

- Crystal directions are indexed simply as a ray extending from the origin through the locations with the lowest integer index. Crystal directions are denoted by [uvw].
- Thus [111] direction passes from 0,0,0 through 1,1,1. However, this direction also passes through ½. ½, ½ (and 2,2,2).

33

Crystallographic Planes

(a)

(001) Plane referenced to the origin at point O

Other equivalent (001) planes

(110) Plane referenced to the origin at point O

Other equivalent (110) planes

(b)

(111) Plane referenced to the origin at point O

Other equivalent (111) planes

(c)

34

17
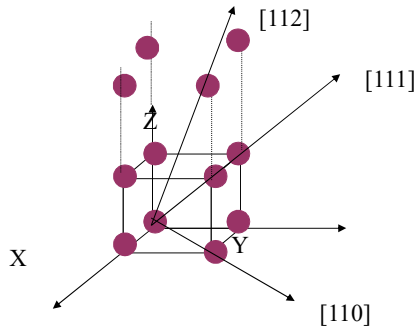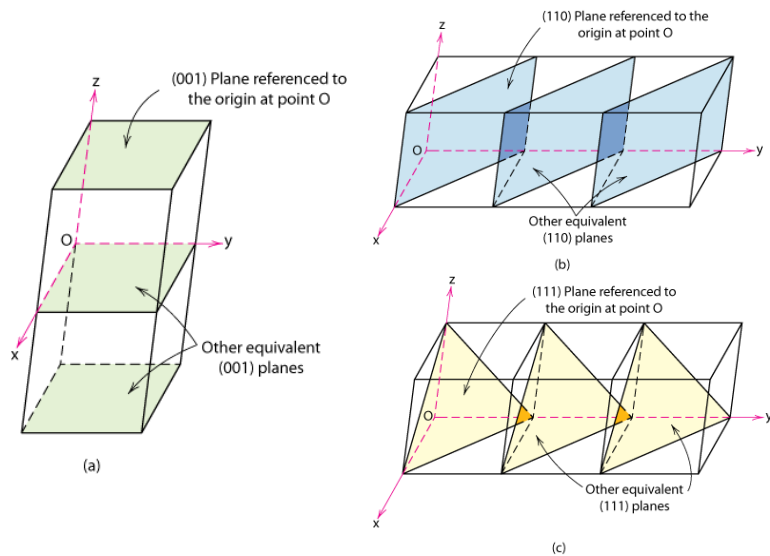
Crystallographic Planes

example		a	b	c
1.	Intercepts	1	1	∞
2.	Reciprocals	1/1	1/1	1/∞
		1	1	0
3.	Reduction	1	1	0
4.	Miller Indices	(110)		
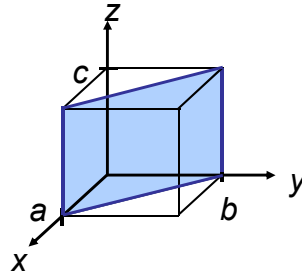
example		a	b	c
1.	Intercepts	1/2	∞	∞
2.	Reciprocals	1/½	1/∞	1/∞
		2	0	0
3.	Reduction	2	0	0
4.	Miller Indices	(100)		
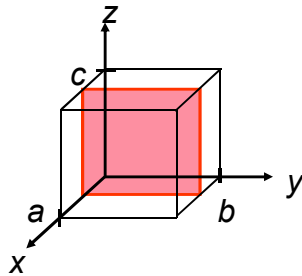
35

Crystallographic Planes

example		a	b	c
1.	Intercepts	1/2	1	3/4
2.	Reciprocals	1/½	1/1	1/¾
		2	1	4/3
3.	Reduction	6	3	4
4.	Miller Indices	(634)		
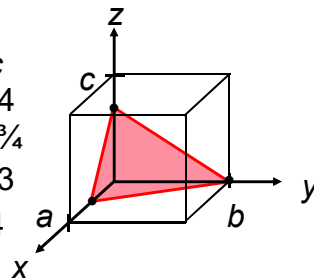
Family of Planes   {*hkl*}

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

36

18

Planar Density of (100) Iron

At T < 912°C iron has the BCC structure.

2D repeat unit

(100)

$$a = \frac{4\sqrt{3}}{3} R$$
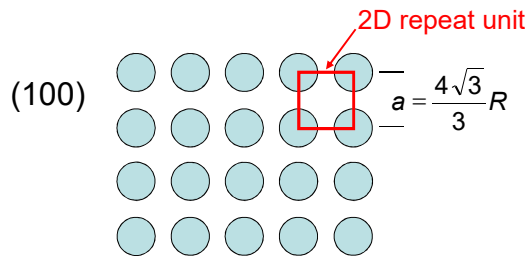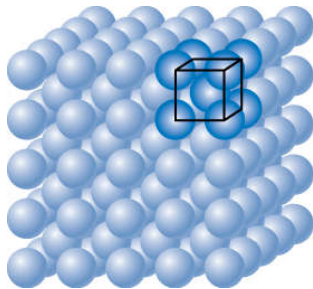
Radius of iron R = 0.1241 nm

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

37

Planar Density of (111) Iron

Solution (cont): (111) plane

1 atom in plane/ unit surface cell

$\sqrt{2}\ a$

○ atoms in plane
● atoms above plane
○ atoms below plane

2D repeat unit

$$h = \sqrt{\frac{3}{2}} a$$

$$\text{area} = \sqrt{2}\ ah = \sqrt{3}\ a^2 = \sqrt{3} \left(\frac{4\sqrt{3}}{3} R\right)^2 = \frac{16\sqrt{3}}{3} R^2$$
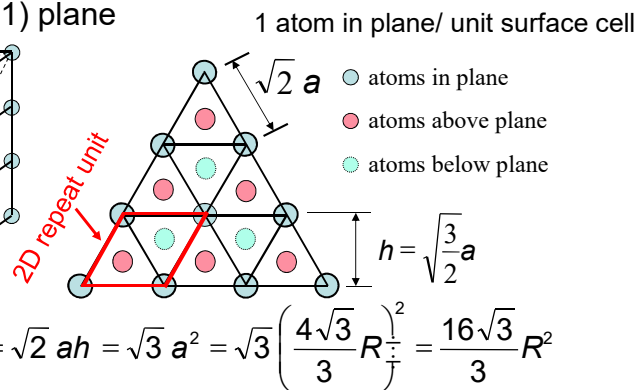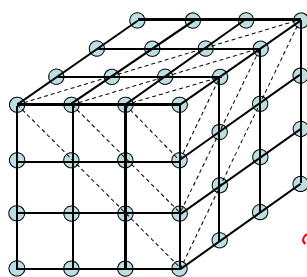
$$\text{Planar Density} = \frac{\dfrac{\text{atoms}}{\text{2D repeat unit}}}{\dfrac{\text{area}}{\text{2D repeat unit}}} = \frac{1}{\dfrac{16\sqrt{3}}{3} R^2} = 7.0 \frac{\text{atoms}}{\text{nm}^2} = 0.70 \times 10^{19} \frac{\text{atoms}}{\text{m}^2}$$

38

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X-Ray Diffraction

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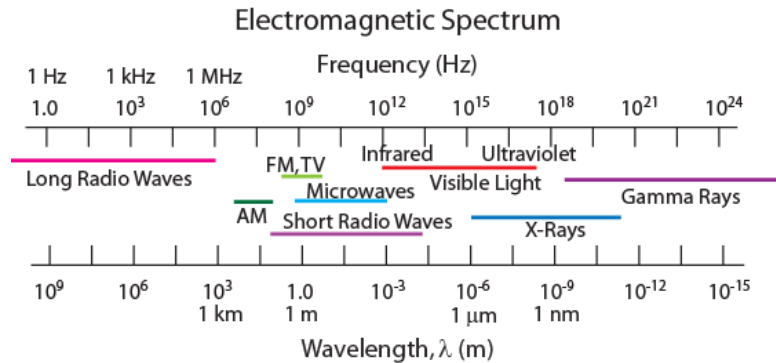
- Diffraction gratings must have spacings comparable to the wavelength of diffracted radiation.
- Can't resolve spacings $< \lambda$
- Spacing is the distance between parallel planes of atoms.

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Bragg`s Law of X-ray Diffraction

When X-ray encounters a crystalline material, they are diffracted by the plane of atoms (or ions) within the crystal. The diffraction angle denoted by the letter θ, depends on the wavelength of the X-ray and the interplanner distanced between the planes.
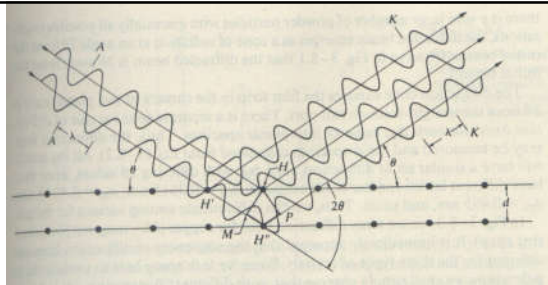
Consider the parallels planes of atoms in the adjacent figure from which X-rays are diffracted. The waves may be reflected from the atom H or H$^/$ and remain in phase at K. However, X-rays are reflected not only from the surface plane, but also from the adjacent subsurface plane. If these reflection are to remain in phase and be coherent, the distance MH$^{//}$P, which is the path difference between these two reflected waves, must be equal to one or more integer wavelength of the rays.

From the figure path

$$MH^{//}P = MH^{//} + PH^{//}$$
$$= d\sin\theta + d\sin\theta$$
$$= 2d\sin\theta$$

Therefore、

$$2d\ \sin\theta = n\lambda\ ;$$

This is known as Bragg`s Law of X-ray diffraction.

20
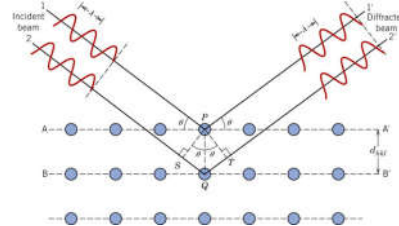
Typical X-ray diffraction pattern
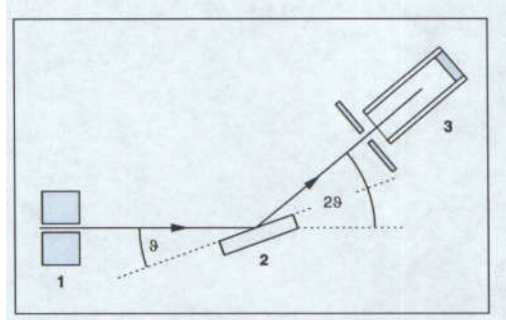
Fig: Schematic diagram for XRD machine
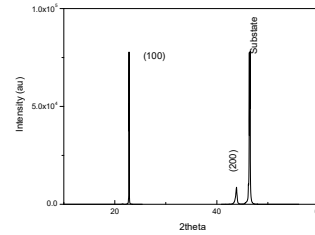
XRD pattern for Ba(Fe, Ta)$_{0.5}$O$_3$ Single crystal Film on (100) STO substrate
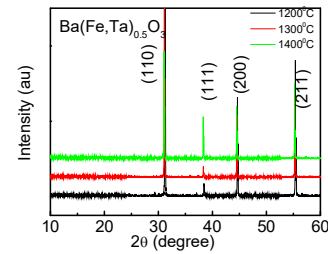
XRD Pattern for Ba(Fe, Ta)$_{0.5}$O$_3$ Polycrystalline samples

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X-Rays to Determine Crystal Structure

- Incoming X-rays diffract from crystal planes.

reflections must be in phase for a detectable signal

Adapted from Fig. 3.19, *Callister 7e*.

extra distance travelled by wave "2"

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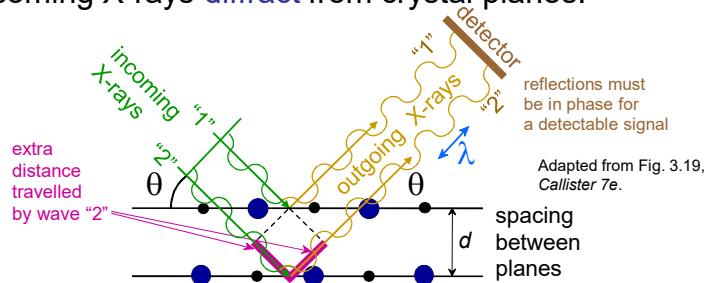
Measurement of critical angle, θ_c, allows computation of planar spacing, d.

X-ray intensity (from detector)

$$d = \frac{n\lambda}{2\sin\theta_c}$$

θ_c

42

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X-Ray Diffraction Pattern

Diffraction pattern for polycrystalline α-iron (BCC)
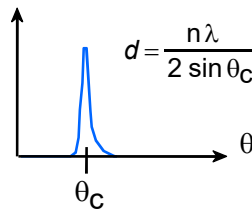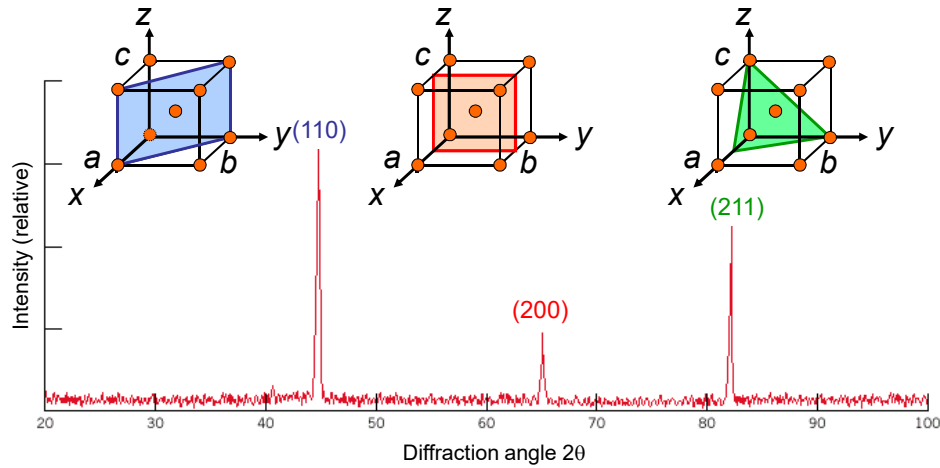
43

Relationship between interplaner distance and Miller indices
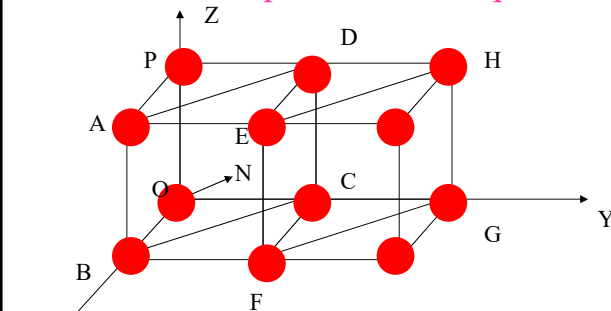
The Planes ABCD and EFGH have the same Miller indices. We Would like to find the distance between such parallel planes. From above figure we can find readily that the distance will be √2a/2. However we want to find a generalize relationship between (hkl) and the interplaner distance d.

The perpendicular distance form the origin (O) to the plane represents the interplaner distance d of this family of planes. Let the direction of cosines of ON be cosα`, cosβ` and cosγ`. The intercepts of the plane on the three axes are ;

OB=a/h; OC=b/k; OP=c/l

44

22

- $\cos\alpha` = d/OB = d/(a/h) = dh/a$
- $\cos\beta` = dk/b$
- $\cos\gamma` = dl/c$
- Now, $\cos^2\alpha` + \cos^2\beta + \cos^2\gamma` = 1$
- $d^2h^2/a^2 + d^2k^2/b^2 + d^2l^2/c^2 = 1$
- $d^2(h^2/a^2 + k^2/b^2 + l^2/c^2) = 1$
- $1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$
- For cubic crystal system, a=b=c
- Therefore, $\mathbf{1/d^2 = 1/a^2(h^2+k^2+l^2)}$

- **For (110) plane $d = a/\sqrt{2}$**

45

Problems

- 1. Lead (Pb) is FCC with atom radius 0.1750 nm. Calculate number of atoms per mm^2 on (100) planes. Ans: 8.2×10^{12} atoms/mm^2.
- 2. X-rays of unknown wavelength are diffracted 43.4° by copper (FCC), whose lattice constant a is 0.3615 nm. Separate determinations indicate that this diffraction line for copper is the first order (n=1) line for d_{111}. Ans: 0.1543
- 3. The same x-rays are used to analyze tungsten (bcc). What is the angle, 2θ, for the second-order (n=2) diffraction lines of the d_{010} spacings? 58.4°
- 4. The lattice constant for a unit cell of lead is 0.4950 nm. (a) What is d_{220} ? (b) What is d_{111}? (c) What is d_{200}?
- 5. A NaCl crystal is used to measure the wavelength λ of some x-rays. The diffraction angle 2θ is 27°30$^/$ for the d_{111} spacing of the chloride ions. (a) What is the wavelength? (the lattice constant is 0.563 nm) (b) What would have been the value of 2θ if λ has been 0.058 nm?
- 6. A plane intercepts the crystal axes at a=1, b=2 and c=1. What are the Miller indices?
- 7. KCl is a face centered cubic crystal having a density of 1.98 g/cm^3. If its molecular weight is 74.6, calculate (a) the distance from one atom to the next atom of same kind and (ii) the distance between adjacent atoms. Ans= 0.63 nm and 0.315 nm.

46

Defects in Solid

- *"Crystals are like people, it is the defects in them which tend to make them interesting!"* - Colin Humphreys.

Defects in Solids

Any deviation in a crystal from a perfect periodic lattice or structure is known as crystal defects. Therefore, Crystal defects is an imperfection.

- **Point defects**

atoms missing or in irregular places in the lattice

vacancies (Schottky defect)

interstitials (Frenkel defect)

impurities,

Dislocations （Line defect)

Groups of atoms in irregular positions

edge and screw dilocations

Grain boundaries (Plane defect)

the interfaces between homogeneous regions of the material

grain boundaries,

external surfaces

Pores, Cracks

Atomic vibrations

1

Real crystals are never perfect, there are always defects

- According to thermodynamics, the equilibrium of a solid at a temperature, *T*, is determined by the minimum value of the free energy, *F=U-TS*, where *U* is the internal energy, *S* is the entropy of the system. We shall see below that to satisfy above condition, a piece of crystal needs certain amount of disorder in the lattice at all temperatures *T>0K*.

- Consider a perfect crystal, If we would like to create certain number of vacant lattice sites (Simplest defect), it needs to supply some energy in the crystal, i.e internal energy, *U*, increases, consequently *F* increases, which is thermodynamically unfavourable.

- On the other hand, creation of vacancies increases the disorder in the crystal and thus increase the configurational entropy from zero to certain value depending on the number of vacancies, *n*.

- This increase in entropy will decrease the free energy, *F*, of the crystal and is thus favourable thermodynamically.

- As a result of the competition of the energy and entropy the stable configuration is one in which a certain fraction of lattice sites is unoccupied.

2

Crystal defects
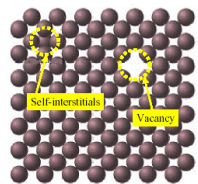
If n increases, then U increases=>F increases, Unfavourable

If n increase, then S increases=> F decreases, Favourable

Certain number of defect will remain in the crystal

Fig: Schematic representation of the energy and the entropy as a function of n/N

point defects

interstitial   vacancy   impurities

Vacancy: A lattice position that is vacant, because the atom is missing=>**Schottky defect**

Interstitial: An atom that occupies a place outside the normal lattice position. It may be the same type of an atom as the others (Self interstitial) or an impurity interstial atom.=>**Frenkel defect**

3

Point Defects

- Vacancies:
  -vacant atomic sites in a structure.

distortion of planes
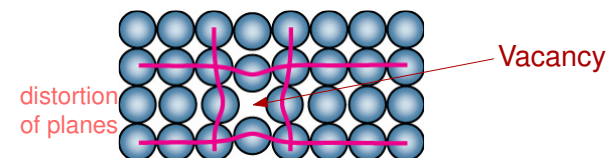
Vacancy

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

distortion of planes

self-interstitial
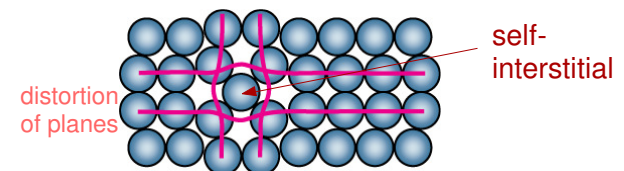
4

Schottky defects

Missing of atoms or ions from its regular lattice sites is known as vacancy or Schottky defect.

We create a Schottky defect in a perfect crystal by transferring an atom from a lattice site in the interior to a lattice site on the surface of the crystal. In thermal equilibrium a certain number of lattice vacancies are always present in an otherwise perfect crystal, because the entropy is increased by the presence of disorder in the structure .

The probability that a given lattice site is vacant is proportional to the Boltzmann factor for thermal equilibrium; $p = exp\,(-E_v/k_BT)$, where E_v is the energy required to create to take an atom from a lattice site inside the crystal to a lattice site on the surface.

If there are N atoms, the equilibrium number n of vacancies is given by the Boltzmann factor

$$\frac{n}{N-n} = \exp(-E_v / k_B T)$$

If $n \ll N$, then $n/N = exp\,(-E_v/k_BT)$

Problem: Suppose E_v is 1 eV. Calculate n/N at 727°C.

5

Estimating Vacancy Concentration

- Find the equilibrium number of vacancies in 1 m^3 of Cu at 1000°C.
- Given:

ρ = 8.4 g/cm^3 $M_{A Cu}$ = 63.5 g/mol

E_v = 0.9 eV/atom N_A = 6.02 x 10^{23} atoms/mol

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

0.9 eV/atom

1273K

8.62 x 10^{-5} eV/atom-K

For 1 m^3, $N = \rho \times \dfrac{N_A}{M_A} \times$ 1 m^3 = 8.0 x 10^{28} sites

- Answer:

n = (2.7 x 10^{-4})(8.0 x 10^{28}) sites = 2.2 x 10^{25} vacancies

6

Schottky defects in ionic crystal

In ionic crystal it is usually favorable energetically to form roughly equal numbers of positive and negative ion vacancies. The formation of pairs of vacancies keeps the crystal electrostatically neutral on a local scale. From statistical calculation we obtain
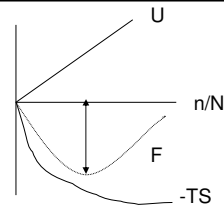
$n \approx N\, exp(-E_p/2k_BT)$ for the number of pairs, where E_p is the energy of formation of a pair vacancy.

Schottky defect
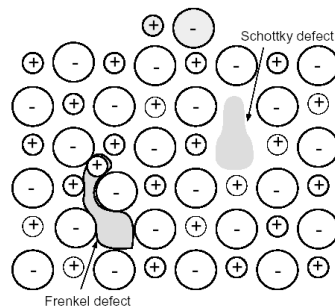
Frenkel defect

Figure 4   Point defects in ionic solids.

7

Frenkel Defect

If an atom is transferred from a lattice site to an interstitial position, a position not normally occupied by an atom.

If the number n of Frenkel defects is much smaller than the number of lattice sites N and the number of interstitials N`, the result is

$n \approx (NN`)^{1/2}\, exp\,(-E_I/2k_BT)$, where E_I is the energy necessary to remove an atom from a lattice site to an interstitial position.

Problems:

1. Suppose that the energy required to remove a sodium atom from the inside of a sodium crystal to the boundary is 1 eV. Calculate the concentration of Schottky vacancies at room temperature (27°C)

2. The average energy required to create a Frenkel defect in an ionic crystal, $A^{2+}B^{2-}$, is 1.4 eV. Calculate the ratio of frenkel defects at 27°C and 527°C in 1 g crystal. 1.316×10^{-6}.

3. The experimental density of a single crystal Al is 2.697 g/cm^3. The lattice constant is 0.4049 nm. If the discrepancy between calculated value and the experimental value of the density is a result of vacancies, (a) what fraction of atom is absent? (b) how many vacancies are there per cm^3?

4. Calculate the atomic percentages of interstitials and vacancies at the melting point in Cu (1356 K). The formation for these defects in Cu are, 4.5 eV and 1.5 eV, respectively. Repeat the calculations at Room temperatures (300K)

8

Line Defects

Dislocations:
- are line defects,
- slip between crystal planes result when dislocations move,
- produce permanent (plastic) deformation.
- A dislocation is a linear or one-dimensional defect around which some of the atoms are misaligned.

Schematic of Zinc (HCP):

- before deformation
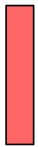
- after tensile elongation

slip steps
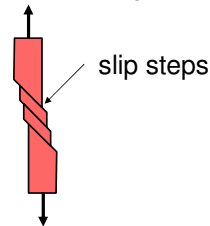
Dislocation

- **Dislocation moves along slip plane in slip direction perpendicular to dislocation line**
- **Slip direction same direction as Burgers vector**

Direction of motion

τ

Edge dislocation

Direction of motion

τ
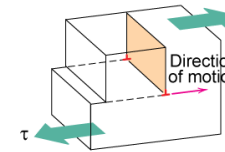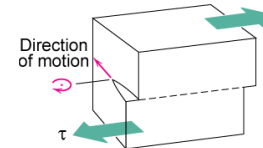
Screw dislocation

Imperfections in Solids

- Linear Defects (Dislocations)
  - Are one-dimensional defects around which atoms are misaligned
- Edge dislocation:
  - extra half-plane of atoms inserted in a crystal structure
  - **b** $\perp$ to dislocation line
- Screw dislocation:
  - spiral planar ramp resulting from shear deformation
  - **b** $\parallel$ to dislocation line

The magnitude and direction of the lattice distortion associated with a dislocation is expressed in terms of a **Burgers vector,** denoted by a **b.**

Burger's vector, **b**: measure of lattice distortion

Edge Dislocation

An extra portion of a plane of atoms, or half-plane, the edge of which terminates within the crystal. This is termed an edge dislocation; it is a linear defect that centers on the line that is defined along the end of the extra half-plane of atoms.

This is sometimes termed the dislocation line, which, for the edge dislocation in is perpendicular to the plane of the page. Within the region around the dislocation line there is some localized lattice distortion. The atoms above the dislocation line are squeezed together, and those below are pulled apart; this is reflected in the slight curvature for the vertical planes of atoms as they bend around this extra half-plane.

The magnitude of this distortion decreases with distance away from the dislocation line; at positions far removed, the crystal lattice is virtually perfect. Sometimes the edge dislocation is represented by the symbol which also indicates the position of the dislocation line. An edge dislocation may also be formed by an extra half-plane of atoms that is included in the bottom portion of the crystal.

Burgers vector

b

Edge dislocation line
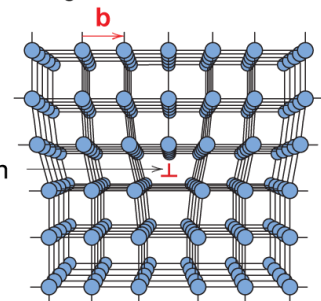
Screw dislocation, may be thought of as being formed by a shear stress that is applied to produce the distortion shown in **Figure a**: the upper front region of the crystal is shifted one atomic distance to the right relative to the bottom portion. The atomic distortion associated with a screw dislocation is also linear and along a dislocation line, line AB in **Figure b**. The screw dislocation derives its name from the spiral or helical path or ramp that is traced around the dislocation line by the atomic planes of atoms.
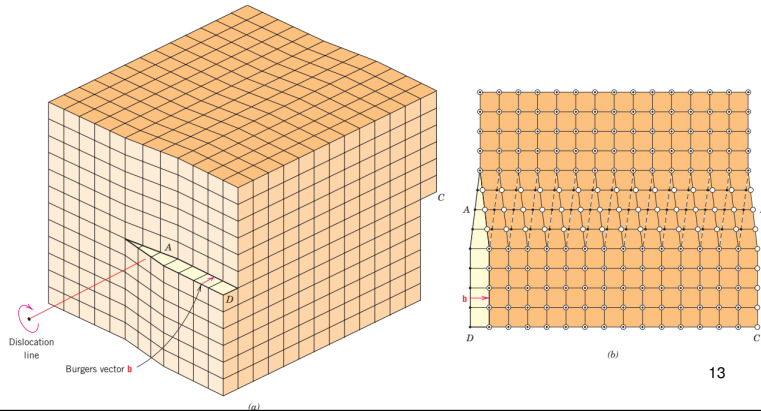
13

Planar Defects in Solids

These imperfections include (i) external surfaces, (ii) grain boundaries, (iii) phase boundaries, (iv) twin boundaries, and (v) stacking faults.

External Surfaces

One of the most obvious boundaries is the external surface, along which the crystal structure terminates. Surface atoms are not bonded to the maximum number of nearest neighbors, and are therefore in a higher energy state than the atoms at interior positions.

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Grain Boundary

Another interfacial defect, the grain boundary, was introduced earlier, as the boundary separating two small grains or crystals having different crystallographic orientations in polycrystalline materials. A grain boundary is represented schematically from an atomic perspective in Figure below. Within the boundary region, which is probably just several atom distances wide, there is some atomic mismatch in a transition from the crystalline orientation of one grain to that of an adjacent one.
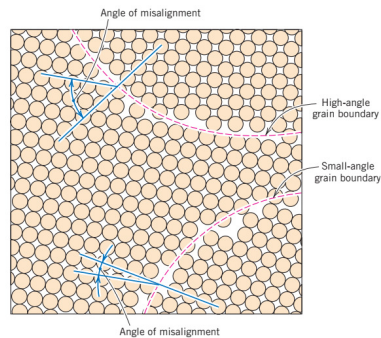
15

Phase Boundaries

Phase boundaries exist in multiphase materials, wherein a different phase exists on each side of the boundary; furthermore, each of the constituent phases has its own distinctive physical and/or chemical characteristics. Phase boundaries play an important role in determining the mechanical characteristics of some multiphase metal alloys.

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Twin Boundaries

A *twin boundary* is a special type of grain boundary across which there is a specific mirror lattice symmetry; that is, atoms on one side of the boundary are located in mirror-image positions of the atoms on the other side

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

Twin plane (boundary)
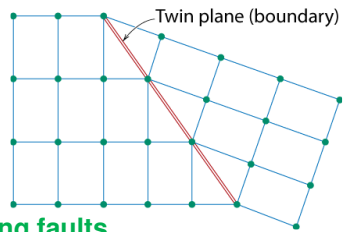
- **Stacking faults**
  - For FCC metals an error in ABCABC packing sequence
  - Ex: ABCABABC

17

Bonds in Solid

• **Interatomic bonds exist in all solids**

• **Reduction of energy**

• The repulsion between atoms, when they are bought close together, is related to the Pauli principle: When the electronic clouds surrounding the atoms starts to overlap, the energy of the system increases abruptly.

• The attractive part, dominating at large distances, depends on particular type of bonding.

$E_{rep} = b/r^n$

$E_{total} = E_{attr} + E_{rep}$

E_{coul}

(+)

cation   Anion

0

"Bond Energy"

$E_{attr} = -e^2/4\pi\varepsilon_0 r$

E_0

r_0

(-)

equilibrium distance of separation (r_0) at Energy minimum (Bond energy)

Fig. 1: Energy of ionic bonding

1

Type of Bonds

Bonds provide strength and related electrical and thermal properties. For example, strong bonds lead to **high melting temperatures**, **high moduli of elasticity**, **shorter interatomic distances**, and lower **thermal-expansion coefficients**, as well as contributing to greater **hardness** and **strength.**

♦ **Primary bonds:** electron (e^-) are transferred or shared, Strong bonds(100-1000KJ/mole or 1-10 eV/atom)

♣ Ionic bond: Strong Coulomb interaction among negative atoms (have an extra electron) and positive atoms (lost an electron). Example NaCl

♣ Covalent bond: Electrons are shared between the molecules, to saturate the valency. Example: F or Cl molecules

♣ Metallic bond: The atoms are ionized, losing some electrons from the valence band. Those electrons form a electron sea, which binds the charged nuclei in place.

♦ **Secondary bonds:** No e^- transferred or shared, Interaction of atomic/molecular dipoles, Weak bonds(<100 KJ/Mole or 1 eV/ atom)

♣ Permanent dipole bonds (Polar molecules- H_2O)

♣ Polar molecule induced dipole bonds (A polar molecule induce a dipole in a nearby non-polar molecules)

♣ Hydrogen bond

2

Ionic Bond

Formation of ionic bond:
1. Mutual ionization occurs by electron transfer
   • **Ion** = charged atom   • **Anion** = negatively charged atom
   • **Cation** = positively charged atom
2. Ions are attracted by strong coulombic interaction
   • Oppositely charged atoms attract
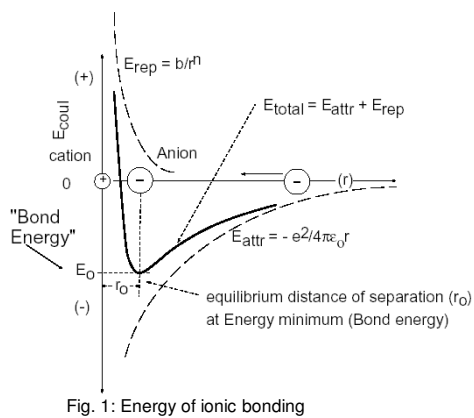   • An ionic bond is non-directional (ions may be attracted to one another in any direction
   Example: NaCl
   Na has 11 electrons, 1 more than needed for a full outer shell (Neon)
   Cl has 17 electron, 1 less than needed for a full outer shell (Argon)
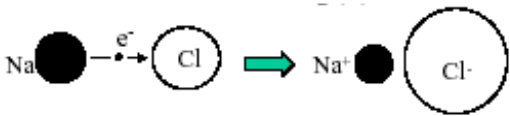
   • Electron transfer reduces the energy of the system of atoms, that is, electron transfer is energetically favorable
   • Note relative sizes of ions: Na shrinks and Cl expands

3

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ionic crystals (contd.)

low ionization energy atoms (e.g. alkalis: Li, Na)
combined with high electron affinity atoms (e.g. halogens: F, Cl)

an alkali atoms transfer one or more electrons to a halogen atom

sodium contributes electron, leaving it with a closed shell

$Na\bullet + \bullet Cl \longrightarrow Na^+ + Cl^-$

forming ionic bond

chlorine gains electron, leaving it with a closed shell

$\bullet Mg\bullet + O \longrightarrow Mg^{2+} + O^{2-}$

forming ionic bond

$\bullet Ca\bullet + \bullet Cl + Cl \bullet \longrightarrow Ca^{2+} + Cl^- + Cl^-$

4
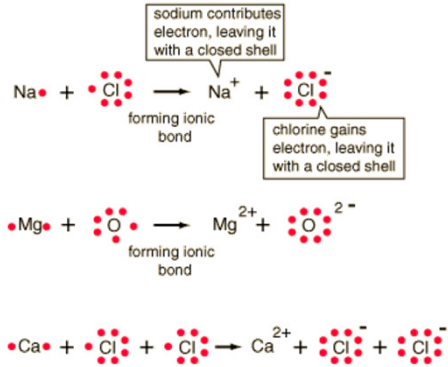
Covalent Bond

In covalent bonding, electrons are shared between the molecules, to saturate the valency. The simplest example is the H2 molecule, where the electrons spend more time in between the nuclei than outside, thus producing bonding.

Formation of covalent bonds:

- Cooperative sharing of valence electrons
- Can be described by orbital overlap
- Covalent bonds are HIGHLY directional
- Bonds - in the direction of the greatest orbital overlap
- Covalent bond model: an atom can covalently bond with at most 8-N', N' = number of valence electrons

Example: Cl_2 molecule. $Z_{Cl} = 17$ ($1S^2 2S^2 2P^6 3S^2 3P^5$)

- N' = 7, 8 - N' = 1 → can form only one covalent bond
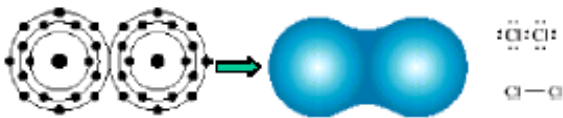
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covalent bond (Contd.)

two or more atoms share electrons to reach noble gas configuration for each atom

often atoms with similar ionization energies (→diatomic molecules)
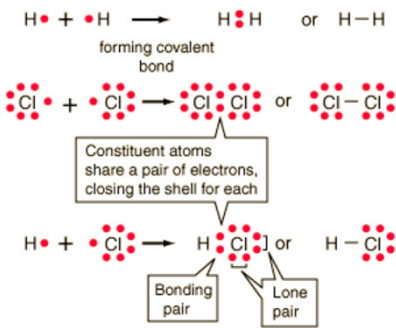
6

covalent crystals (Contd.)

- only few solids are covalently bound (diamond, Si, Ge, SiC)
- covalent bond stronger than ionic
  - hardest materials
  - high melting points
  - insoluble
- all covalent crystals have tetrahedral (diamond) structure
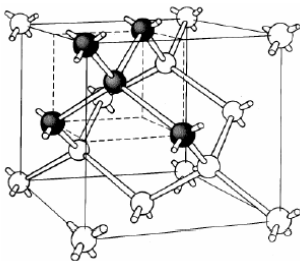
7

Cohesive energy of an Ionic crystal

The cohesive energy of an ionic crystal is the energy that would be liberated by the formation of the crystal from individual neutral atoms.

Consider NaCl crystal (Adjacent fig.)

The principle contribution to the cohesive energy of an ionic crystal is the electrostatic P.E., $V_{Coulomb}$ of the ions. Let us consider an Na^+ ion in NaCl.

Its nearest neighbors are 6 Cl^- ions, each one the distance r away. The P.E. of the Na^+ ion due to these 6 Cl^- ions is

$$V_1 = -\frac{6e^2}{4\pi\varepsilon_0 r}$$

The next nearest neighbours are 12 Na^+ ions, each one the distance √2 r away.

The P.E. of the Na^+ ion due to the 12 Na^+ ions is

$$V_2 = +\frac{12e^2}{4\pi\varepsilon_0 \sqrt{2}r}$$
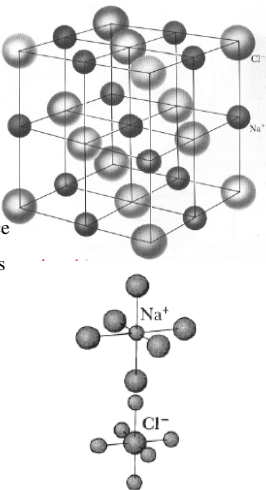
8

Total coulomb potential will be

$$V_{coulomb} = -\frac{e^2}{4\pi\varepsilon_0 r}(6 - \frac{12}{\sqrt{2}} + ...) = -\alpha\frac{e^2}{4\pi\varepsilon_0 r}$$

The quantity α is called the Madelung constant of the crystal, and it has same value for all crystals of same kind, and the value is 1.748 for *NaCl* crystal structure.

The P. E. contribution of the repulsive forces due to the action of the exclusion principle can be expressed in the form,

$$V_{repulsive} = \frac{B}{r^n}$$

The Total P. E. *V* of each ion due to its interactions with all the other ions is therefore,

$$V = V_{Coulomb} + V_{repulsive} = -\frac{\alpha}{4\pi\varepsilon_0 r} + \frac{B}{r^n}$$

At the equilibrium separation r_0 of the ions, *V* is a minimum by definition, and so *(dV/dr)=0* when $r=r_0$.

9

$$(\frac{dV}{dr})_{r=r_0} = \frac{\alpha e^2}{4\pi\varepsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}} = 0$$

$$or, \quad \frac{\alpha e^2}{4\pi\varepsilon_0 r_0^2} = \frac{nB}{r_0^{n+1}}; or, \quad B = \frac{\alpha e^2}{4\pi\varepsilon_0 n}r_0^{n-1}$$

So, the P. E. is

$$V = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0}(1 - \frac{1}{n})$$

Na (atom)+5.14 eV (ionization energy)→Na$^+$ + e$^-$

e$^-$ +Cl (atom) → Cl$^-$ + 3.61 eV (electron affinity)

The electron transfer energy is the difference between +5.14eV ionization energy of the *Na* and the -3.61 eV electron affinity of *Cl,* or +1.53 eV

Therefore the total energy, per molecule unit of *NaCl* of a crystal is **$V + 1.53\ eV$** lower than the energy of separated neutral atoms

$$E_{cohesive} = -\frac{1}{2}\frac{\alpha e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right) + \frac{1}{2}E_{electron\ transfer}$$

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Problem 1: Calculate Cohesive energy of *NaCl* Crystal if the equilibrium distance of *Na* and *Cl* ions is 0.281 nm, α=1.748 and n=9.

Sol^n: V= -1.27 × 10^{-18} joule

          = - 7.97 eV

$E_{cohesive}$= V + 1.53 eV = -7.97 eV + 1.53 eV = - 6.44 eV/molecule = - 3.22 eV/atom

Problem 2: The ionization energy of the potassium is *4.34 eV* and the electron affinity of Chlorine is *3.61 eV*. The Madelung constant for the *KCl* structure is *1.748* and the distance between ions of opposite sign is *0.314 nm*. If *n=9* calculate cohesive energy for *KCl* crystal.

Problem 3: The covalent bonding energy of C-C is 370 KJ/Mole. What wavelength of light will break C-C bond.

Hints: Energy per bond is equal to 370×10^3/6.023×10^{23}

To break this bond, supplied light energy must be equal to hv

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Metallic Bond

Metals are characterize by high electrical conductivity, and a large number of electrons in a metal are free to move about, usually one or two per atom. The electrons available to move about are called conduction electrons. The valence electrons of the atom becomes the conduction electrons of the metal.

Valence electrons are detached from atoms, and spread in an 'electron sea' that "glues" the ions together.

- **A metallic bond is non-directional (bonds form in any direction) → atoms pack closely**

Electron cloud from valence electron

ion core
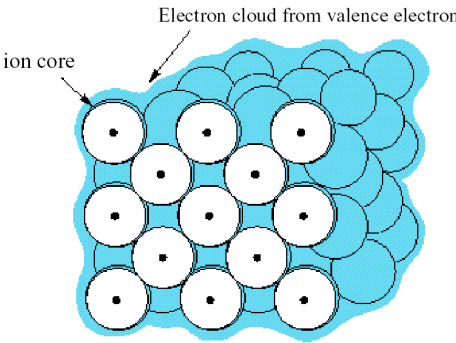
12

Secondary Bonding

Secondary bonding results from interaction of atomic or molecular dipoles and is weak, ~0.1 eV/atom or ~10 kJ/mol.

  - van der Waals bonding

Permanent dipole moments exist in some molecules (called **polar molecules**) due to the asymmetrical arrangement of positively and negatively regions (HCl, H_2O). Bonds between adjacent polar molecules – **permanent dipole bonds** – are strongest among secondary bonds.

Polar molecules can *induce* dipoles in adjacent non-polar molecules and bond is formed due to the attraction between the permanent and induced dipoles.

Even in electrically symmetric molecules/atoms an electric dipole can be created by fluctuations of electron density distribution. Fluctuating electric field in one atom A is felt by the electrons of an adjacent atom, and induce a dipole momentum in this atom. This bond due to fluctuating induced dipoles is the weakest (inert gases, H_2, Cl_2).

Example: hydrogen bond in water. The H end of the molecule is positively charged and can bond to the negative side of another H_2O molecule (the O side of the H_2O dipole)

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"Hydrogen bond" – secondary bond formed between two **permanent dipoles** in adjacent water molecules.

Table 2.3 Bonding Energies and Melting Temperatures for Various Substances

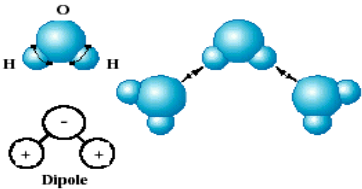| Bonding Type	Substance	Bonding Energy kJ/mol (kcal/mol)	eV/Atom, Ion, Molecule	Melting Temperature (°C)
Ionic	NaCl	640 (153)	3.3	801
	MgO	1000 (239)	5.2	2800
Covalent	Si	450 (108)	4.7	1410
	C (diamond)	713 (170)	7.4	>3550
Metallic	Hg	68 (16)	0.7	−39
	Al	324 (77)	3.4	660
	Fe	406 (97)	4.2	1538
	W	849 (203)	8.8	3410
van der Waals	Ar	7.7 (1.8)	0.08	−189
	Cl₂	31 (7.4)	0.32	−101
Hydrogen	NH₃	35 (8.4)	0.36	−78
	H₂O	51 (12.2)	0.52	0

14

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van der Waals Forces

All atoms and molecules- even inert gas atoms such as those of helium and Argon- exhibit weak, short-range attractions for one another due to van der Waals forces. These forces are responsible for the condensation of gases into liquids and the freezing of liquids into solids despite the absence of ionic, covalent or metallic bonding mechanisms

As we know that polar molecules possess permanent electric dipole moments. Such molecules tend to align themselves so that ends of opposite sign are adjacent, and in this orientation the molecules strongly attract each other.

A polar molecule is also able to attract molecules which do not normally have a permanent dipole moments. The electric field of polar molecule causes a separation of charge in the other molecule, with the induced moment the same in direction as that of the polar molecule
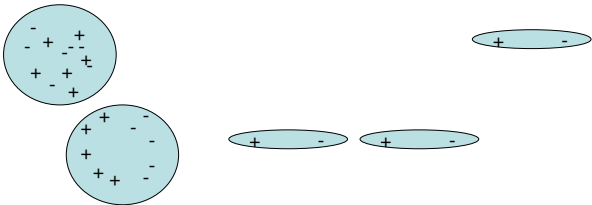
15

The electric field E a distance r from a dipole of moment P is given by

 dipole moment $\vec{p}$ $\vec{E} = \dfrac{1}{4\pi\varepsilon_0}[\dfrac{\vec{P}}{r^3} - \dfrac{3(\vec{P}.\vec{r})}{r^5}\hat{r}]$

$p . r = prcos\theta$, where θ is the angle between p and r. The field E induces in the other, normally non polar molecule an electric dipole moment $P`$ proportional to E in magnitude and in the same direction. Hence  $P` = \alpha E$, where α is a constant called the polarizibility of the molecule. The energy of the induced dipole in the electric field E is

$$V = -\vec{p}`.\vec{E} = -\frac{\alpha}{(4\pi\varepsilon_0)^2}(\frac{p^2}{r^6} - \frac{3p^2}{r^6}\cos^2\theta - \frac{3p^2}{r^6}\cos^2\theta + \frac{9p^2}{r^6}\cos^2\theta = -\frac{\alpha}{(4\pi\varepsilon_0)^2}(1+3\cos^2\theta)\frac{p^2}{r^6}$$

The force is equal to $-dV/dr$, and is proportional to $1/r^{-7}$, which means that it drops rapidly with increasing separation.

Problem: If the distance between molecule is double of its original value. What would be the ratio of the forces between two molecules? (Ans. 0.8 % of its original value)
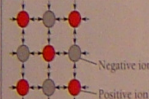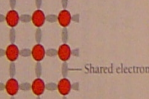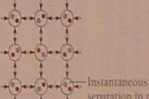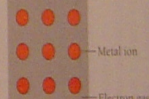
Examples of bonding in Materials:
Metals: Metallic; **Ceramics:** Ionic / Covalent; **Polymers:** Covalent and Secondary
Semiconductors: Covalent or Covalent / Ionic

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bonding in crystalline solids

TABLE 10.1 Types of Crystalline Solids. The cohesive energy is the work needed to remove an atom (or molecule) from the crystal and so indicates the strength of the bonds holding it in place.

Type	Ionic	Covalent	Molecular	Metallic
Lattice	Negative ion / Positive ion	Shared electrons	Instantaneous charge separation in molecule	Metal ion / Electron gas
Bond	Electric attraction	Shared electrons	Van der Waals forces	Electron gas
Properties	Hard; high melting points; may be soluble in polar liquids such as water; electrical insulators (but conductors in solution)	Very hard; high melting points; insoluble in nearly all liquids; semiconductors (except diamond, which is an insulator)	Soft; low melting and boiling points; soluble in covalent liquids; electrical insulators	Ductile; metallic luster; high electrical and thermal conductivity
Example	Sodium chloride, NaCl $E_{cohesive} = 3.28$ eV/atom	Diamond, C $E_{cohesive} = 7.4$ eV/atom	Methane, CH_4 $E_{cohesive} = 0.1$ eV/molecule	Sodium, Na $E_{cohesive} = 1.1$ eV/atom

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Energy Band Structures in Solids

In an isolated atom electrons occupy well defined energy states. **When atoms come together** to form a solid, their valence electrons interact with each other and with nuclei due to Coulomb forces. In addition, two specific quantum mechanical effects happen. First, by *Heisenberg's uncertainty principle*, constraining the electrons to a small volume raises their energy. The second effect, due to the *Pauli exclusion principle*, limits the number of electrons that can have the same energy.

As a result of these effects, the valence electrons of atoms form wide **electron energy bands** when they form a solid. The bands are separated by **gaps**, where electrons cannot exist.

Charge Carriers

- **Two charge carrying mechanisms**

  - **Electron – negative charge**
  - **Hole – equal & opposite positive charge**
  - **Move at different speeds - drift velocity**

Higher temp. promotes more electrons into the conduction band

$\therefore$ $\sigma\uparrow$ as $T\uparrow$

Electrons scattered by impurities, grain boundaries, etc.

4

Energy Band Structures and Conductivity

- **Fermi Energy** (EF) - highest filled state at 0 K
- **Conduction band** - a partially filled or empty energy band
- **Valence band** – the highest partially or completely filled band

In semiconductors and insulators, the valence band is filled, and no more electrons can be added (Pauli's principle).

Electrical conduction requires that electrons be able to gain energy in an electric field. This is not possible in these materials because that would imply that the electrons are promoted into the forbidden band gap.

2

Energy Band Structures and Conductivity (semiconductors and insulators)

- In semiconductors and insulators, electrons have to jump across the band gap into conduction band to find conducting states above E_f
- The energy needed for the jump may come from heat, or from irradiation at sufficiently small wavelength.
- The difference between semiconductors and insulators is that in semiconductors electrons can reach the conduction band at ordinary temperatures, where in insulators they cannot.
- The probability that an electron reaches the conduction band is about $\exp(-E_g/2k_BT)$, where E_g is the band gap. If this probability is $< 10^{-24}$ one would not find a single electron in the conduction band in a solid of 1 cm^3. This requires $E_g/2k_BT > 55$. At room temperature, $2k_BT = 0.05$ eV $\rightarrow E_g > 2.8$eV corresponds to an insulator.
- An electron promoted into the conduction band leaves a **hole** (positive charge) in the valence band, that can also participate in conduction. Holes exist in metals as well, but are more important in semiconductors and insulators.

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Energy States: Insulators & Semiconductors

- Insulators:
  -- Higher energy states not accessible due to gap (> 2 eV).

- Semiconductors:
  -- Higher energy states separated by smaller gap (< 2 eV).

3

Energy Band Structures and Conductivity (metals)

In **metals**, highest occupied band is partially filled or bands overlap.

Conduction occurs by promoting electrons into conducting states, that starts right above the Fermi level. The conducting states are separated from the valence band by an infinitesimal amount.

Energy provided by an electric field is sufficient to excite many electrons into conducting states. → High conductivity.

6

1

Energy Band Structures and Bonding
### (metals, semiconductors, insulators)

Relation to atomic bonding:

☼ **Insulators** – valence electrons are tightly bound to (or shared with) the individual atoms – strongest ionic (partially covalent) bonding.

☼ **Semiconductors** - mostly covalent bonding somewhat weaker bonding.

☼ **Metals** – valence electrons form an "electron gas" that are not bound to any particular ion.

7

Conduction in Terms of Electron and Hole Migration
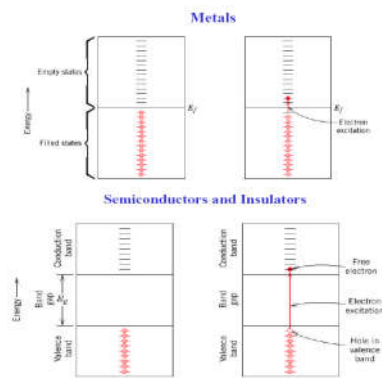
• Concept of electrons and holes:
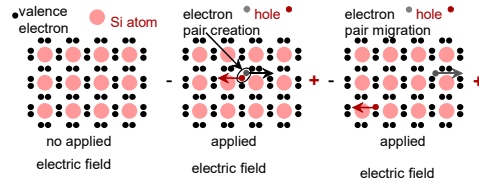
• Electrical Conductivity given by:

$$\sigma = n|e|\mu_e + p|e|\mu_h$$

electrons/m^3 electron mobility   # holes/m^3 hole mobility
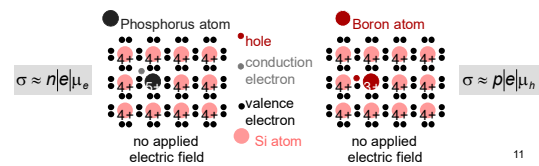
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Energy Band Structures and Conductivity

8

Intrinsic vs Extrinsic Conduction

• Intrinsic:
Number of electrons = Number of holes ($n = p$)
  --case for pure Si

• Extrinsic:
  --$n \neq p$
  --occurs when impurities are added with a different number of valence electrons than the host (e.g., Si atoms)

• *n*-type Extrinsic: ($n >> p$)   • *p*-type Extrinsic: ($p >> n$)

$\sigma \approx n|e|\mu_e$ $\sigma \approx p|e|\mu_h$

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Semiconductors

• **Intrinsic semiconductors** – A Semiconductor in its pure form; electrical conductivity is defined by the electronic structure of pure material.
• **Extrinsic semiconductors** – A semiconductor with added impurities; electrical conductivity is defined by impurity atoms.

Intrinsic semiconductors

Since both electrons and holes conduct the conductivity of an intrinsic semiconductor is

$$\sigma = n|e|\mu_e + p|e|\mu_h$$

where p is the hole concentration and μ_h the hole mobility.
Electrons are more mobile than holes, $\mu_e > \mu_h$

In an intrinsic semiconductor, a hole is produced by the promotion of each electron to the conduction band. Therefore, **n = p** and

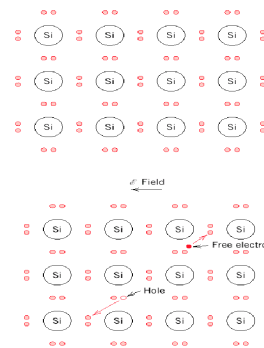$$\sigma = n|e|(\mu_e + \mu_h) = p|e|(\mu_e + \mu_h)$$

(only for intrinsic semiconductors)

n (and p) increase exponentially with temperature, whereas μ_e and μ_h decrease (about linearly) with temperature.
⇒ **The conductivity of intrinsic semiconductors is increasing with temperature (different from metals!)**

9

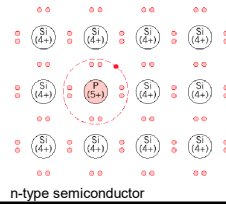## Intrinsic semiconductors

12

2

Extrinsic semiconductors

Si is considered to be extrinsic at room T if impurity concentration is one atom per 10^{12} (remember our estimation of the number of electrons promoted to the conduction band by thermal fluctuations at 300 K)

Unlike intrinsic semiconductors, an extrinsic semiconductor may have different concentrations of holes and electrons. It is called **p-type** if p > n and **n-type** if n > p.

One can engineer conductivity of extrinsic semiconductors by controlled addition of impurity atoms – **doping** (addition of a very small concentration of impurity atoms). Two common methods of doping are diffusion and ion implantation.
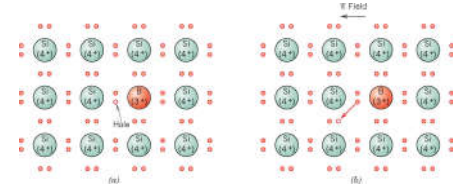

n-type semiconductor

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p-type extrinsic semiconductors

- Excess holes are produced by substitutional impurities that have fewer valence electrons per atom than the matrix.
- A bond with the neighbors is incomplete and can be viewed as a **hole** weakly bound to the impurity atom.
- Elements in columns III of the periodic table (B, Al, Ga) are donors for semiconductors in the IV column, Si and Ge.
- Impurities of this type are called **acceptors**, $N_A = N_{Boron} \sim p$
- The energy state that corresponds to the hole (**acceptor state**) is close to the top of the valence band. An electron may easily hop from the valence band to complete the bond leaving a hole behind. Conduction occurs mainly by the holes (thus p-type).

$$\sigma \sim p|e|\mu_p \sim N_A |e|\mu_p$$
(for extrinsic p-type semiconductors)

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n-type extrinsic semiconductors

Excess electron carriers are produced by substitutional impurities that have more valence electron per atom than the semiconductor matrix

Example: phosphorus (or As, Sb etc.) with 5 valence electrons, is an electron donor in Si since only 4 electrons are used to bond to the Si lattice when it substitutes for a Si atom. Fifth outer electron of P atom is weakly bound in a **donor state** (~ 0.01 eV) and can be easily promoted to the conduction band.

Impurities which produce extra conduction electrons are called **donors**, $N_D = N_{Phosphorus} \sim n$

Elements in columns V and VI of the periodic table are donors for semiconductors in the IV column, Si and Ge.
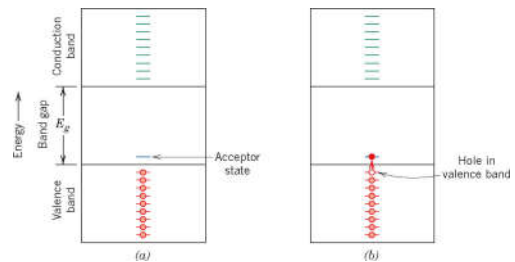
The hole created in donor state is far from the valence band and is immobile. Conduction occurs mainly by the donated electrons (thus n-type).

$$\sigma \sim n|e|\mu_e \sim N_D |e|\mu_e$$
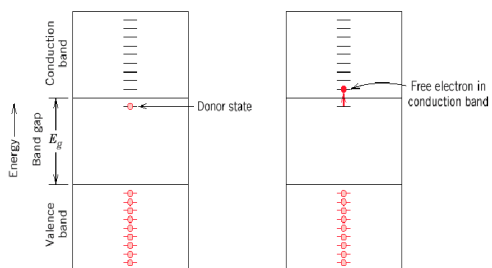(for extrinsic n-type semiconductors)

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Band diagram for p-type semiconductors

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Band diagram for n-type semiconductors

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Conductivity: Comparison

- Room T values $(\text{Ohm-m})^{-1} = (\Omega \cdot \text{m})^{-1}$

METALS	conductors	CERAMICS	
Silver	6.8×10^{7}	Soda-lime glass	10^{-10}-10^{-11}
Copper	6.0×10^{7}	Concrete	10^{-9}
Iron	1.0×10^{7}	Aluminum oxide	$<10^{-13}$

| SEMICONDUCTORS		POLYMERS	
Silicon	4×10^{-4}	Polystyrene	$<10^{-14}$
Germanium	2×10^{0}	Polyethylene	10^{-15}-10^{-17}
GaAs	10^{-6}		

semiconductors   insulators

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p-n Rectifying Junction

- Allows flow of electrons in one direction only (e.g., useful to convert alternating current to direct current.
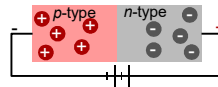- Processing: diffuse P into one side of a B-doped crystal.
- Results:

--No applied potential: no net current flow.

--Forward bias: carrier flow through *p*-type and *n*-type regions; holes and electrons recombine at *p-n* junction; current flows.
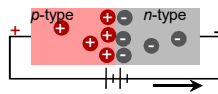
--Reverse bias: carrier flow away from *p-n* junction; carrier conc. greatly reduced at junction; little current flow.

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EXERCISE

1. A solid is found to have an energy band gap (E_g) of 3 eV. What is the likely color of this solid in transmitted sunlight?

2. An optically transparent solid appears green in transmitted sunlight. What do you expect the band gap (E_g) of this solid to be (in eV)?

3. What is the radiation of longest wavelength which is still capable of being transmitted through: (a) Si with Eg = 1.1 eV (b) Ge with Eg = 0.7 eV, and (c) the compound GaAs with Eg = 1.43 eV?

4. The energy gap (E_g) in zinc oxide (ZnO) is 3.2 eV. (a) Is this material transparent to visible radiation? (b) Do you expect this material to be a conductor at room temperature? (Give the reasons for your answer.)

5. A crystal of germanium (Eg = 0.7 eV) is found to be n-type with 5 x 10^{18} mobile charge carriers/cm^3 (at room temperature). (a) Draw a schematic energy band diagram that reflects the indicated properties. (b) Do you expect this crystal to be transparent or opaque to radiation of ν = 1 x 1015 s.1?

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