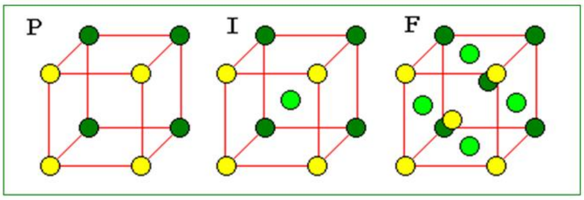
Solid state chemistry



INTRODUCTION

Three States of Matter:

- Solids
- Liquids
- Gases

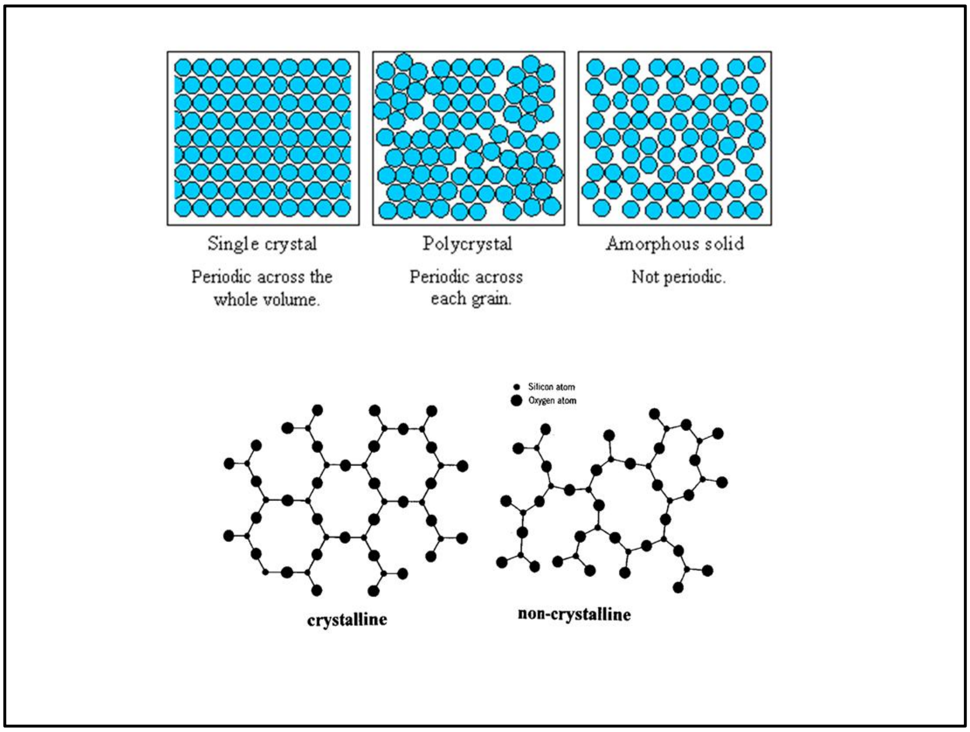
Solids:

The aggregates of atoms which preserve their volumes and shapes unless subjected to large external force are called solids".

There are two types of solids :

Amorphous (non-crystalline) and

Crystalline


Single crystal
Periodic across the whole volume.
Polycrystal
Periodic across each grain.
Amorphous solid
Not periodic.
Silicon atom
Oxygen atom
crystalline
non-crystalline

Difference Between Amorphous and Crystalline Solids

Amorphous

- Amorphous solids (means without form) are the solids which lacks the regular arrangement of atoms or molecules and hence they have a short range order or no order in their structure
- Do not have sharp melting point (because all bonds are not equally strong)
- Isotropic (Physical properties are same in different directions)
- Examples: glass, wax, plastics, etc.

Crystalline

- A crystalline solid is the one in which there is a regular repeating pattern in the structure, or in other words, there is long-range order
- Have sharp melting point (because all bond are equally strong)
- Anisotropic (Physical properties are different in different directions)
- Examples: diamond, table salt, ice, methanol, sodium chloride, etc.

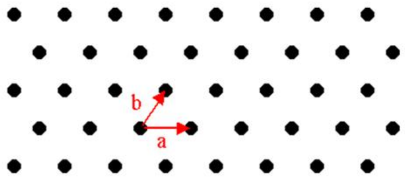
CRYSTAL LATTICES

A lattice is an infinite, regular array of points in space.

In the definition it should be noticed that no mention is made of atoms or any physical objects, just points in space - no more, no less. Hence we treat the lattice as a mathematical abstraction. Therefore, it is clear that there is no lattice inside the crystal. Even if we look the crystal through a powerful microscope we will not be able to see the lattice points, but rather atoms or groups of atoms. The lattice provides the 'recipe' that determines how the atomic or molecular units are to be repeated throughout the space to make the crystal structure.

Plane Lattice

Consider an array of points in such a way that the environment about any point is identical with the environment about any other point. Such an array of points in two dimensions is shown in Fig. and is called a **plane lattice**.



For constructing a two dimensional lattice, choose any two convenient axis such that the points lie at equal intervals *a* and *b* along these axis as shown in the Fig. There are generally 5 lattices in two dimensions: **Oblique, Square, Hexagonal, Rectangular and Centered Rectangular lattice**.

Space Lattice

If this array of points is extended to three dimensions then the array of points is called **space lattice**. For constructing the space lattice the points are arranged at equal intervals *c* in the third direction also. There are 14 space lattices in total, called **Bravais Lattice.**

Thus a lattice may also be defined as a parallel net like arrangement of points such that the environment about any point is identical with the environment about any other point.

Basis

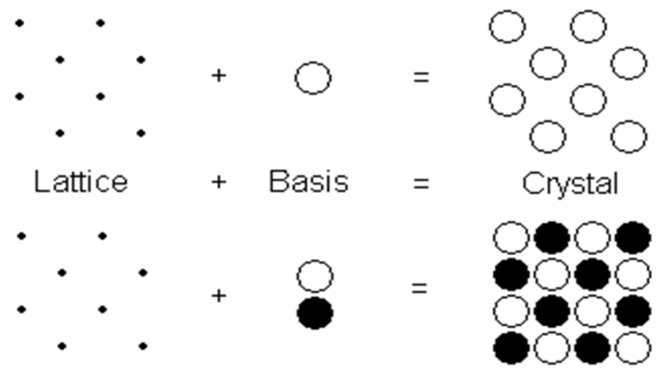
A basis is defined as an assembly of atoms, ions or molecules identical in composition, arrangement and orientation.

Basis consists of the simplest arrangement of atoms which is repeated at every point in the lattice to build up the crystal structure.

The number of atoms in a basis may be one as in case of many metals and inert gases, but could be as large as 1000 in many structures.

In ionic crystals, a basis is composed of two distinct types of ions. For example, Na^+ and Cl^- in a NaCl crystal.

When basis is attached identically to each lattice point, the actual crystal structure is formed as shown in the Fig.

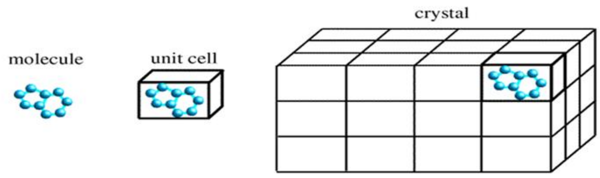


The relation can be written as

Lattice + Basis = Crystal Structure

UNIT CELL

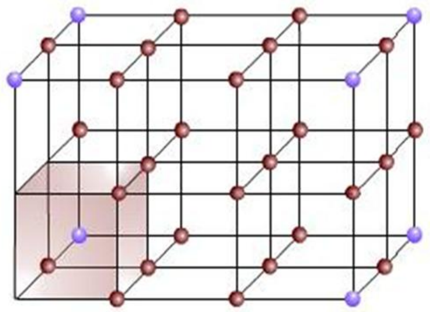
A unit cell is a region of space which when repeated by primitive translation vectors fills all space. Thus a unit cell is defined as **the smallest geometrical figure, the repetitions of which give the actual crystal structure.**



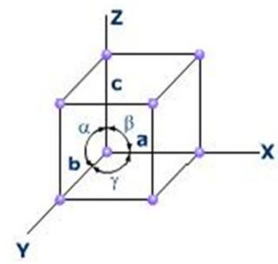
The choice of the unit cell is not unique. It can be constructed in a number of ways, but the unit cell should be chosen in such a way that it conveys all the symmetry of a crystal lattice, by having shortest possible size, which makes the mathematical calculations easy.

Each atom or molecule in a unit cell is considered as a lattice point. The distance between the two atoms or ions of the same type is the 'length of the unit cell'.

In general, a unit cell may be defined as the smallest volume of a solid from which the entire crystal may be constructed by translational repetitions in 3-dimension and which represent fully all the characteristics of a particular crystal. In Fig. a three dimensional unit cell is shown by the shaded portion.

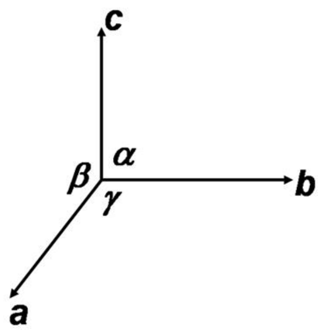


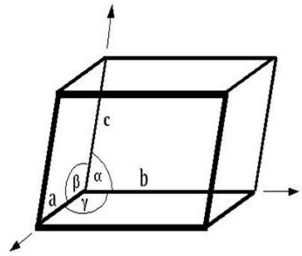
Representation of space lattice and unit cell



Representation of dimensions of a unit cell

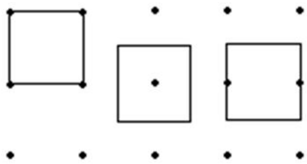
For a three dimensional case, the unit cell is a parallelopiped formed by basic vectors **a**, **b** and **c** as concurrent edges and the angles α, β and γ, between (**b**, **c**), (**c**, **a**), and (**a**, **b**) respectively as explained in the following Figures.





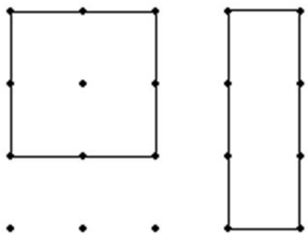
Lattice parameters
a, b, c
α, β, χ

Primitive and Non - primitive unit cell



Primitive unit cells

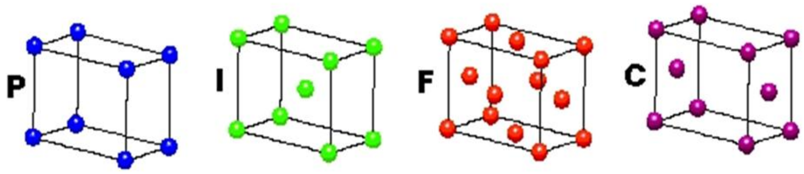
contain just one lattice point



Non-primitive unit cells

contain more than one lattice point

Type of unit cells



P	Simple
I	Body-centred
F	Face-centred
C	Base(side)-centred

CRYSTAL SYSTEMS AND BRAVAIS LATTICES

Crystals of different substances have similar shapes and hence the crystals are classified into the so called crystal systems depending upon their axial ratio and the interfacial angles α, β and γ. In three-dimension, there are 7 crystal systems. Bravais showed that throughout the seven crystal systems there are fourteen unique lattice types possible. These are known as **Bravais** or **space lattices**. These seven crystal systems with examples are :

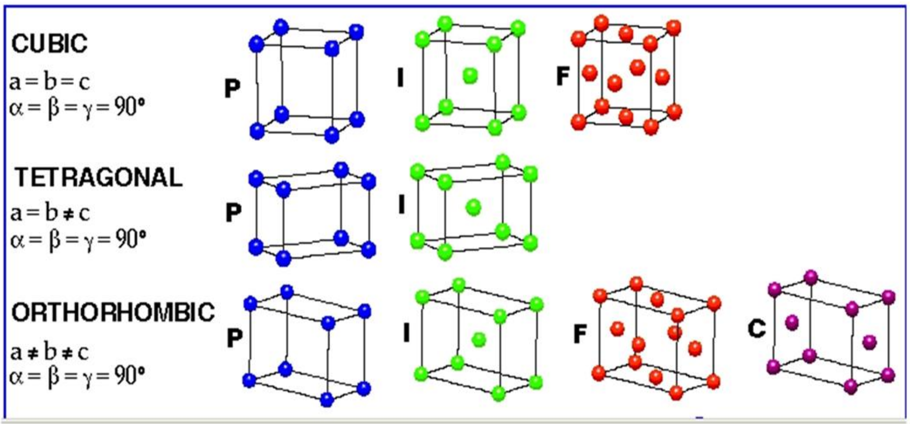
- Cubic(CsCl, NaCl, Cu)
- Tetragonal(SnO_2)
- Orthorhombic($PbSO_4$, $MgSO_4$)
- Monoclinic($FeSO_4$, $LiSO_4 \cdot H_2O$)
- Triclinic($FeSO_4 \cdot 5H_2O$, $K_2Cr_2O_7$)
- Trigonal (Rhombohedral)(Sb, As, $CaCO_3$)
- Hexagonal(Zn, Cd, Ni, As, SiO_2)

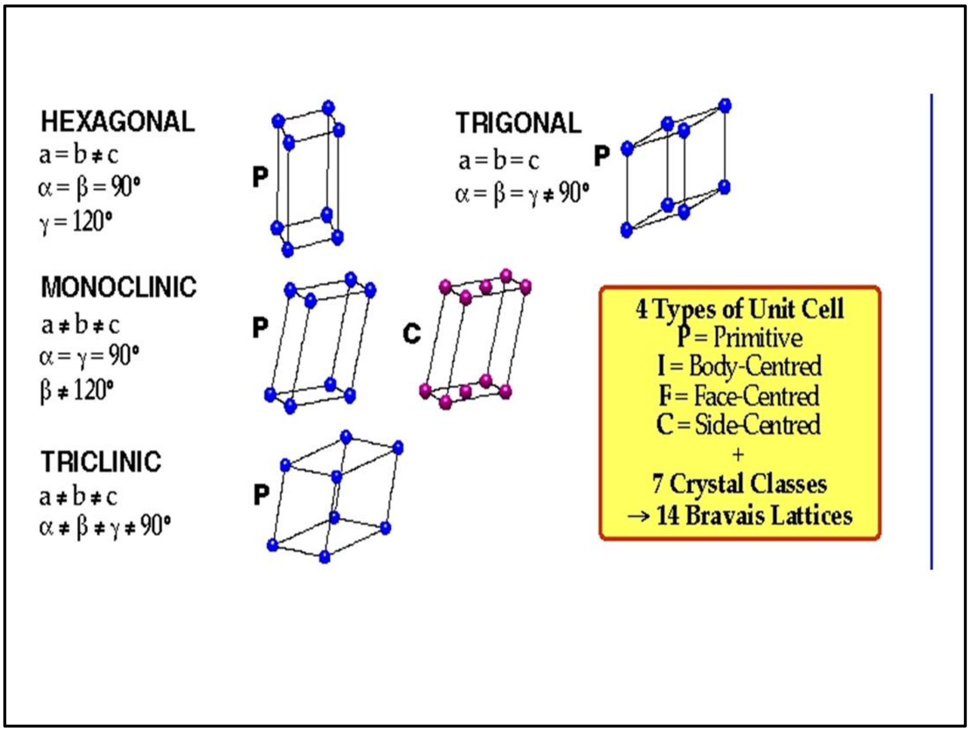
The characteristics features of these crystal systems and the corresponding Bravais lattices are as follows:

No.	Crystal class	Intercepts on Axes	Angles between Axes	Bravais space lattice
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^0$	Simple, body-centred, face-centred
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^0$	Simple, body-centred
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^0$	Simple, body-centred, face-centred, Base(side)-centred
4	Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^0$	Simple
5	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^0$, $\gamma = 120^0$	Simple
6	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^0 \neq \beta$	Simple, base-centred
7	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$	Simple

The 14 possible **BRAVAIS LATTICES**

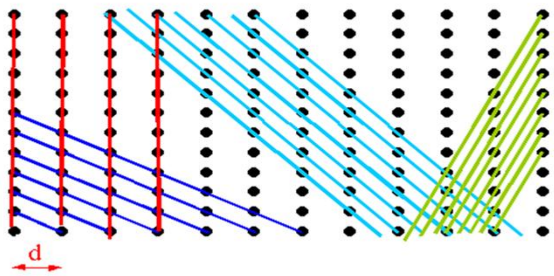
{note that spheres in this picture represent lattice points, <u>not</u> atoms!}




HEXAGONAL
a = b ≠ c
α = β = 90°
γ = 120°
P
TRIGONAL
a = b = c
α = β = γ ≠ 90°
P
MONOCLINIC
a ≠ b ≠ c
α = γ = 90°
β ≠ 120°
P
C
4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices
TRICLINIC
a ≠ b ≠ c
α ≠ β ≠ γ ≠ 90°
P

MILLER INDICES

The crystal structure may be regarded as made up of an aggregate of a set of parallel equidistant planes passing through at least one lattice point or a number of lattice points. These planes are known as **Lattice Planes**. For a given crystal, lattice planes can be chosen in different ways as shown in Fig.



In order to designate a lattice plane, British mineralogist William H. Miller, in 1839, developed a method by using three numbers (**h k l**) which are known as **Miller Indices.**

Miller Indices are the three smallest possible integers, which have the same ratio as the reciprocals of intercepts of the plane concerned on the three axis.

Miller indices are integer sets that were created to distinguish directions and planes in a lattice. They are used primarily in crystalline structures because they describe planes in relation to a larger lattice in relative terms, as opposed to absolute terms. An example of this is describing planes in a building, Miller indices would distinguish the floor from the walls, and north wall from west wall, however it would not distinguish the 4th floor from the 5th floor. This is useful in crystal lattices because the planes are the same in many directions(like floors in a tall building).

The Rule to Obtain Miller Indices

1. Set up coordinate axes along the edges of the unit cell and then note where the plane to be indexed intercepts the axes. Then divide each intercept value by the unit cell length along the respective coordinate axis. Record the resulting normalized intercept sent in the order x, y, z.
2. Invert the intercept values (i.e. 1/intercepts)
3. Using an appropriate multiplier, convert the 1/intercept set to the smallest possible set of whole numbers
4. Enclose the whole-number set in curvilinear bracket

- Important points:

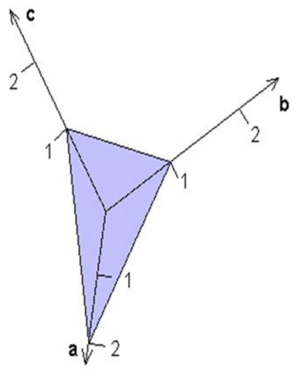
- Miller indices define the orientation of the plane within the unit cell

- If a set of planes is parallel to any of the axes, it would cut that axes at ∞, hence the Miller index along that direction is $1/\infty = 0$.

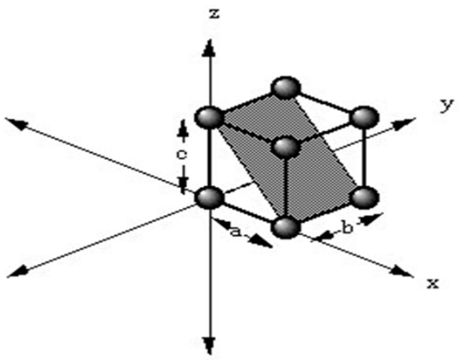
- If a plane to be indexed has an intercept along the negative portion of a coordinate axis, a minus sign is placed over the corresponding index.

- The Miller Index defines a *set of planes* parallel to one another (remember the unit cell is a subset of the "infinite" crystal), e.g., (002) planes are parallel to (001) planes, and so on.

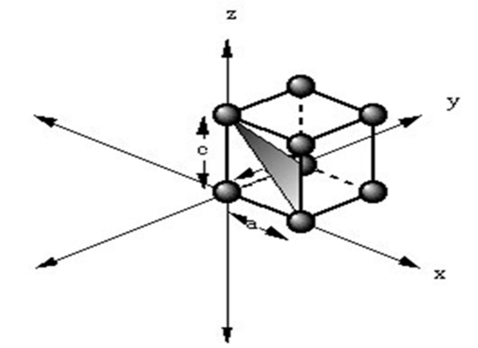
Let us take an example to find the Miller Indices of a given plane(see Fig.):



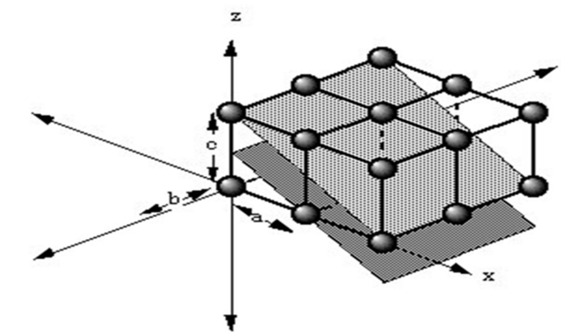
- Intercepts: 2a 1b 1c
- Dividing by unit translation vectors:
  2a/a 1b/b 1c/c = 2 1 1
- Taking the reciprocals: ½ 1/1 1/1
- Reducing to whole numbers: 1 2 2
- Miller indices: (122)



	a	b	c
intercept length	1	∞	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	1
Miller indice	(101)		

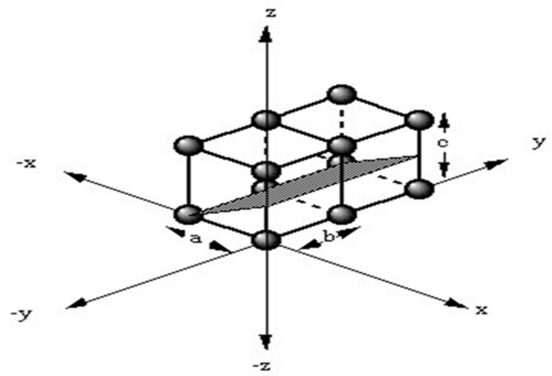


	a	b	c
intercept length	1	1	1
reciprocal	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$
cleared fraction	1	1	1
Miller indice	(111)		

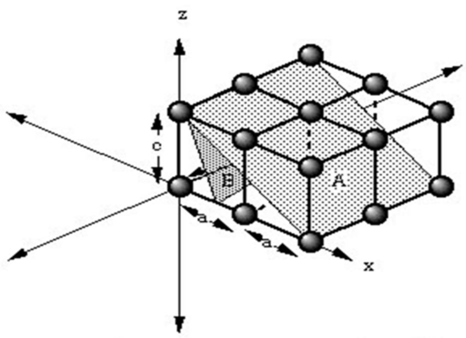


	a	b	c
intercept length	1	∞	1/2
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$
cleared fraction	1	0	2

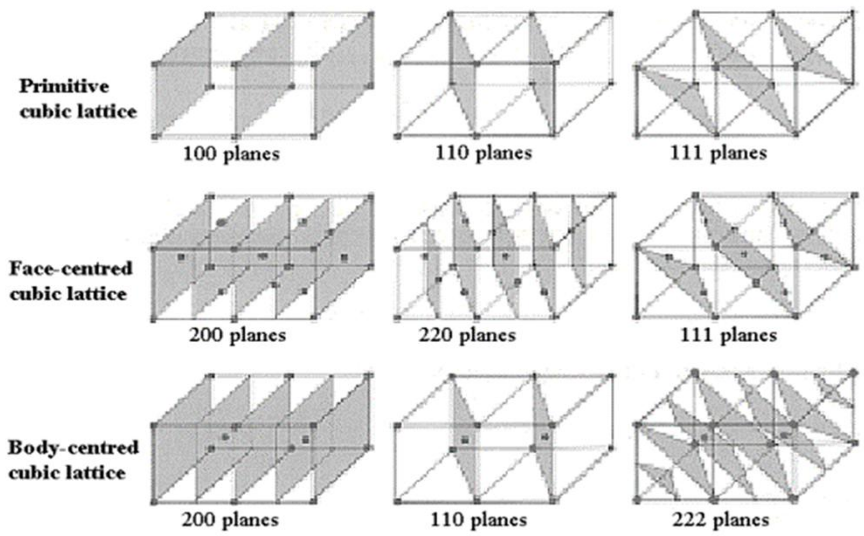
Miller indice (102)



	a	b	c
intercept length	-1	∞	$\frac{1}{2}$
reciprocal	$\frac{1}{-1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$
cleared fraction	-1	0	2
Miller indice	$(\bar{1}02)$		



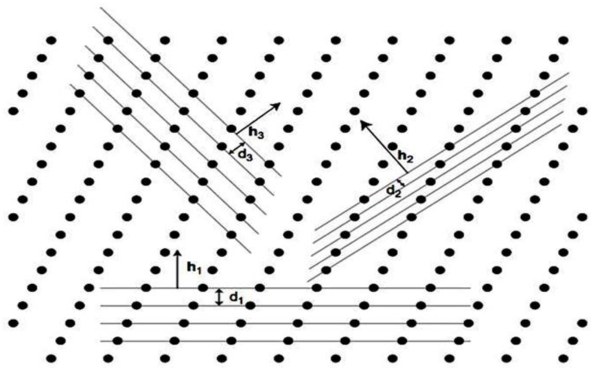
	plane A			plane B		
	a	b	c	a	b	c
intercept length	1	∞	$\frac{1}{2}$	$\frac{1}{2}$	∞	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$	$\frac{1}{1/2}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	2	2	0	1
Miller indice	(102)			(201)		



Miller indices for three types of cubic lattices.

INTERPLANER DISTANCE OR SPACING

Interplaner spacing is defined as the perpendicular distance d_{hkl} between corresponding planes. It is also perpendicular distance from the origin to the set of parallel planes (see Fig.)



$$d_{hkl}{}^2 = \frac{a^2}{h^2} + \frac{b^2}{k^2} + \frac{c^2}{l^2}$$

For a cubic lattice, *a* = *b* = *c*, therefore, we get

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Also, For a cubic lattice,

d_{100} = a, d_{110} = a/√2 and d_{111} = a/√3.

Physical Parameters for Crystal Structure

(i) Number of Atoms per Unit Cell

Number of atoms per unit cell determines how closely the solid is packed and is given by

$$N = N_c/8 + N_f/2 + N_i$$

here N_c is the number of corner atoms, N_f the number of face centred atoms and N_i the number of body centred atoms(see Fig.).

For SC crystal : In a SC crystal, there are 8 atoms only, each at one corner. Each atom is shared by 8 unit cells. Therefore, we have

$$N = N_c/8 = 8/8 = 1$$

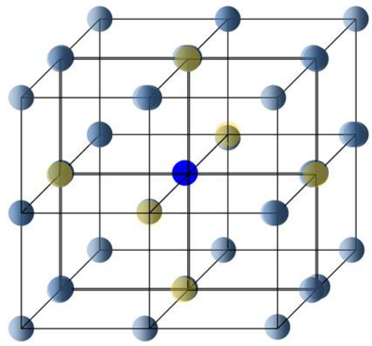
For BCC crystal : $N = N_c/8 + N_f/2 + N_i = 8/8 + 0 + 1 = 2$

For FCC crystal : $N = N_c/8 + N_f/2 + N_i = 8/8 + 6/2 + 0 = 4$

(ii) Coordination Number (CN)

In a crystal, the number of nearest neighbours of the same type and at equal distances from the given atom is called coordination number.

For SC : The corner atoms are the nearest neighbours of each other. Here CN = 6 (see Fig.) which is a group of 8 unit cell and atom at the centre has six corner atoms as its nearest neighbours).



For BCC : In this case all the corner atoms are at equal distances from the body centered atom.

Hence CN = 8.

For FCC : Here the nearest neighbours of any corner atom are the face centered atoms of the surrounding unit cells. Now for any corner atom there are 4 face centered atoms in each plane and there are three such planes. Therefore, CN = 12.

(iii) Atomic Radius and Nearest Neighbour Distance (NND)

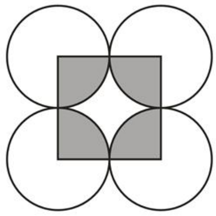
In a crystal the atoms are assumed to be spheres in contact. Now atomic radius is defined as half the distance between the nearest neighbours in a crystal of pure element, i.e., *the distance between the centres of neighbouring atoms.*

For SC : In a SC structure, corner atoms are the nearest neighbours and are in touch with each other. If the side of the unit cell is 'a' and 'r' be the radius , then

$$2r = a \quad \text{or} \quad r = a/2$$

Now Nearest Neighbour Distance(NND) is given by 2r

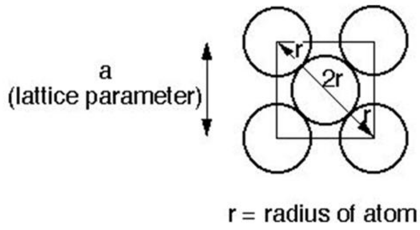
Therefore, NND = 2r = a

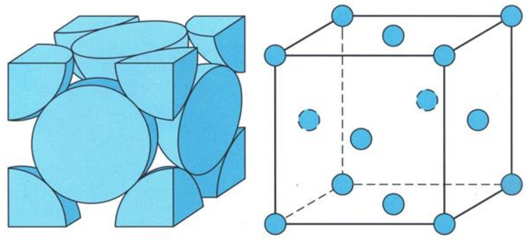


For FCC :

$r = \sqrt{2}\, a/4$

$NND = a/\sqrt{2}$



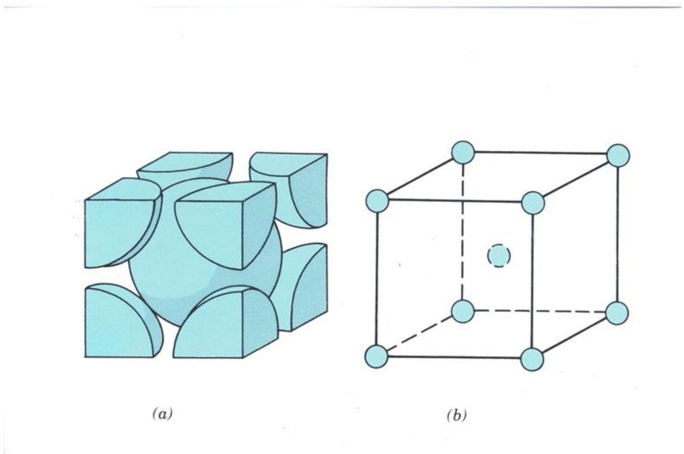


(a) *(b)*

For BCC :

$r = \sqrt{3}\, a/4$

$NND = \sqrt{3}\, a/2.$



(iv) Atomic Packing Fraction (or Factor) (APF)

It is defined as the ratio of the volume of the atoms occupying the unit cell to the volume of the unit cell. It is also called relative packing density.

APF = Volume occupied by the atoms in a unit cell / Volume of the unit cell.

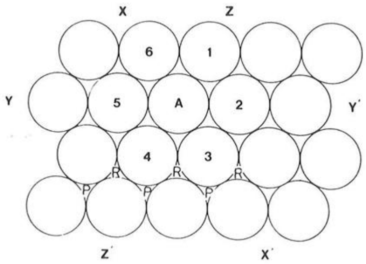
SC Crystal : No. of atoms/unit cell = 1
Volume of one atom = 4/3 πr^3
Side of the unit cell = a = 2r
Volume of the unit cell = a^3
APF = = = $\pi/6$ = 0.52 = 52%.

BCC Crystal : No. of atoms/unit cell = 2
Volume of two atoms = 2x4/3 πr^3
Side of the unit cell = a = $4r/\sqrt{3}$
Volume of the unit cell = a^3
APF = = = $\sqrt{3}\pi/8$ = 0.68 = 68%.

FCC Crystal : No. of atoms/unit cell = 4
Volume of four atoms = 4x4/3 πr^3
Side of the unit cell = a = $4r/\sqrt{2}$
Volume of the unit cell = a^3
APF = = = $\sqrt{2}\pi/6$ = 0.74 = 74%.

Closed Packed Structures

In a closed packed structure the constituent atoms are so arranged as to occupy minimum possible volume, reaching the maximum density.



Planar closed packed spheres

2-layers closed packed structure

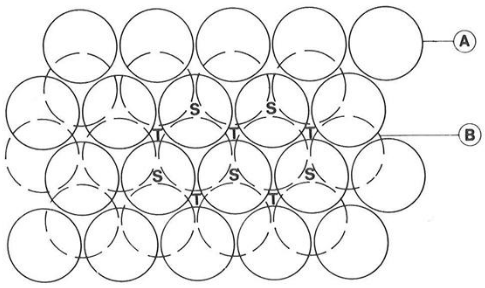
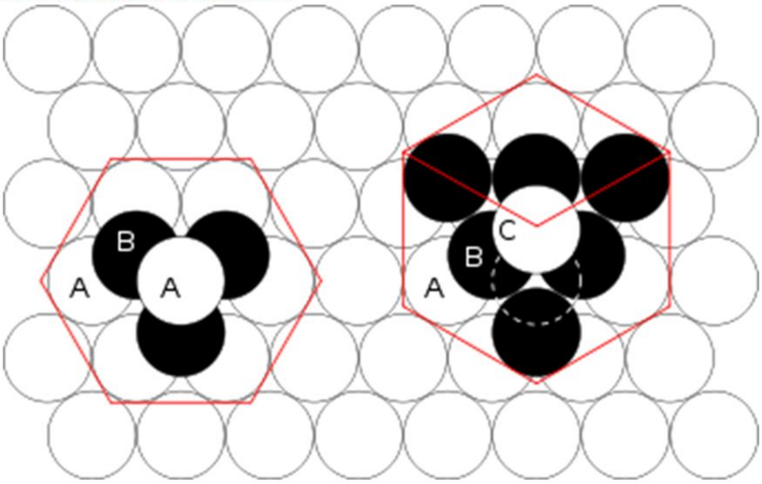


Fig. 1.13 Two close packed layers arranged in A and B positions. The B layer occupies the P positions shown in Fig. 1.12

Closed Packed Structures



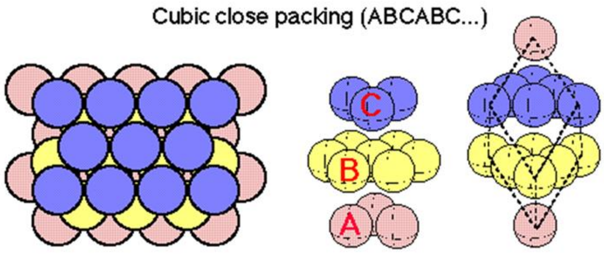
hcp

Hexagonal Closed Packed

ccp

Cubic Closed Packed

c.c.p. structure



(111) Of a FCC structure

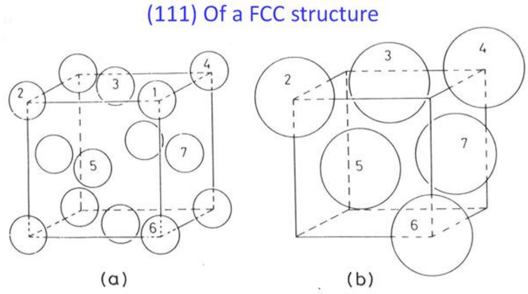
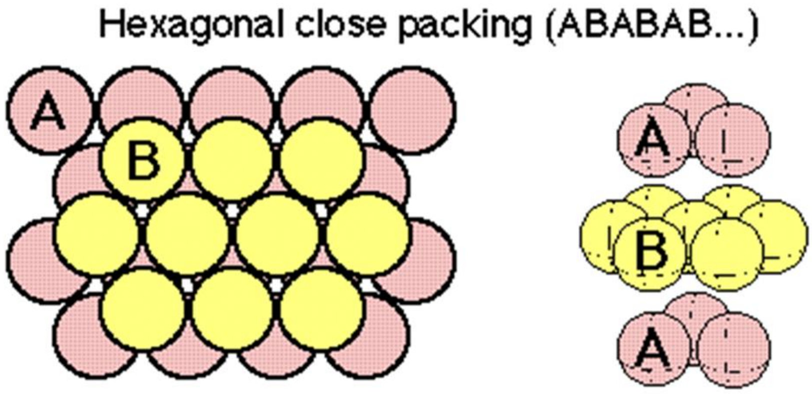
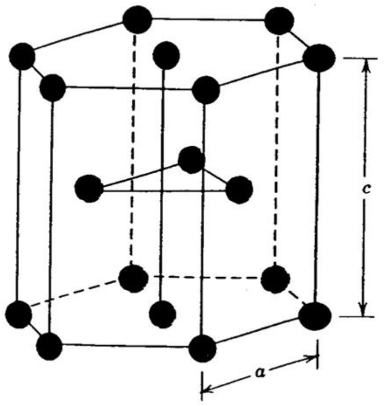


Fig. 1.16 Face centred cubic unit cell of a c.c.p. arrangement of spheres

h.c.p. structure



h.c.p. structure



$$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$$

Interstitial sites in Closed Packed Structures

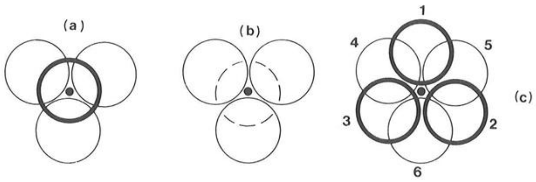


Fig. 1.18 Interstitial sites in a c.p. structure. Heavy circles are above and the dashed circles below the plane of the paper: (a) T_+ site, (b) T_- site (c) O site

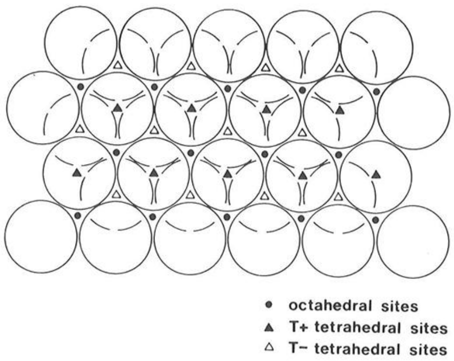


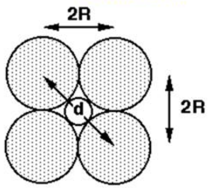
Fig. 1.19 Distribution of interstitial sites between two c.p. layers. Dashed circles are below the plane of the paper

Interstitial sites in Closed Packed Structures

Having determined what types of interstitial sites are available, we must now decide:

(a) Which sites are occupied by a given cation: this determined by the radius ratio (= r_{cation}/r_{anion})
(b) How many sites are occupied: this is determined by the stoichiometry.

For an octahedral site:



$$d = 2R_{anion} + 2r_{cation}$$

$$\text{also } d = \sqrt{[(2R_{anion})^2 + (2R_{anion})^2]}$$

$$\text{Therefore: } r_{cation}/r_{anion} = 0{\cdot}414$$

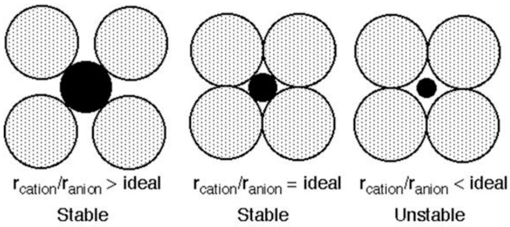
For a tetrahedral site, $r_{cation}/r_{anion} = 0.225$.

For these two values, the close packed structure of anions is maintained.

Interstitial sites in Closed Packed Structures

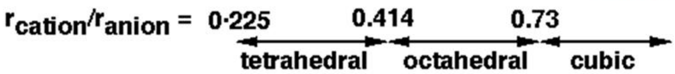
Stable Bonding Configurations in Ionic solids.

In reality an ideal fit of a cation into the close packed anion arrangement almost never occurs. Now consider what would be the consequence of placing a cation that is (a) larger than the ideal, (b) smaller than the ideal, into the cation sites.



For a stable coordination the bonded cation and anion must be in contact with each other.

If r_{cation}/r_{anion} becomes too big, the close packed structure of anions is converted into a simple cubic structure



Interstitial sites in Closed Packed Structures

Table 1.4 *Some close packed structures*

Anion arrangement	Interstitial sites T_+	T_-	Oct	Examples
c.c.p.	—	—	1	NaCl, rock salt
	1	—	—	ZnS, blende or sphalerite
	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{2}$	$MgAl_2O_4$, spinel
	—	—	$\frac{1}{2}$	$CdCl_2$
	1	—	—	$CuFeS_2$, chalcopyrite
	—	—	$\frac{1}{3}$	$CrCl_3$
	1	1	—	K_2O, antifluorite
h.c.p.	—	—	1	NiAs
	1	—	—	ZnS, wurtzite
	—	—	$\frac{1}{2}$	CdI_2
	—	—	$\frac{1}{2}$	TiO_2^*, rutile
	—	—	$\frac{2}{3}$	Al_2O_3, corundum
	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{2}$	Mg_2SiO_4, olivine
	1	—	—	β-Li_3PO_4
	$\frac{1}{2}$	$\frac{1}{2}$	—	γ-$Li_3PO_4^*$
c.c.p. 'BaO_3' layers	—	—	$\frac{1}{4}$	$BaTiO_3$, perovskite

*The h.c.p. oxide layers in rutile and γ-Li_3PO_4 are not planar but are buckled. The oxide ion arrangement in these may alternatively be described as tetragonal packed (t.p.).

Cubic structures

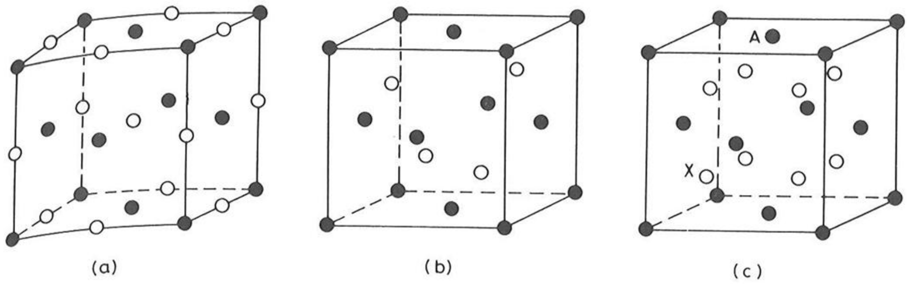
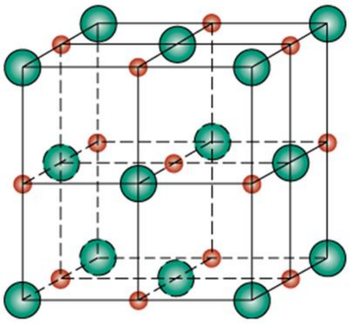


Fig. 1.24 Unit cell of (a) NaCl, (b) ZnS, sphalerite, and (c) Na_2O. Open circles are cations; closed circles anions

Rock salt: O sites occupied by cations; T_+, T_- empty
Zinc blende: T_+ (or T_-) sites occupied; O, T_- (or T_+) empty
Antifluorite: T_+, T_- occupied; O empty.

Rock salt structure



Na^+ r_{Na} = 0.102 nm

Cl^- r_{Cl} = 0.181 nm

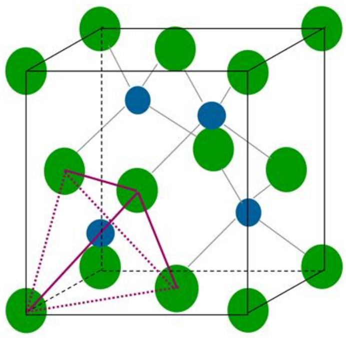
$r_{Na}/r_{Cl} = 0.564$

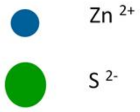
Octahedral sites preferred

Table 1.7 *Some compounds with the NaCl structure*

	a(Å)		a(Å)		a(Å)		a(Å)
MgO	4.213	MgS	5.200	LiF	4.0270	KF	5.347
CaO	4.8105	CaS	5.6948	LiCl	5.1396	KCl	6.2931
SrO	5.160	SrS	6.020	LiBr	5.5013	KBr	6.5966
BaO	5.539	BaS	6.386	LiI	6.00	KI	7.0655
TiO	4.177	αMnS	5.224	LiH	4.083	RbF	5.6516
MnO	4.445	MgSe	5.462	NaF	4.64	RbCl	6.5810
FeO	4.307	CaSe	5.924	NaCl	5.6402	RbBr	6.889
CoO	4.260	SrSe	6.246	NaBr	5.9772	RbI	7.342
NiO	4.1769	BaSe	6.600	NaI	6.473	AgF	4.92
CdO	4.6953	CaTe	6.356	NaH	4.890	AgCl	5.549
SnAs	5.7248	SrTe	6.660	ScN	4.44	AgBr	5.7745
TiC	4.3285	BaTe	7.00	TiN	4.240		
UC	4.955	LaN	5.30	UN	4.890		

Zinc blende structure





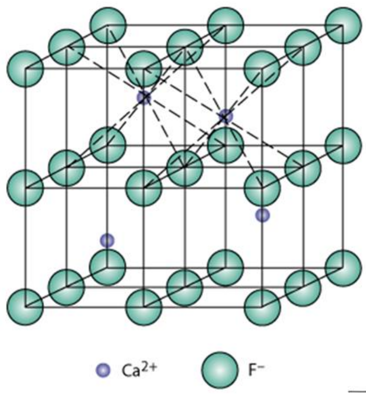
r_{Zn}/r_{S} = 0.074/0.184= 0.402

tetrahedral sites preferred

Table 1.8(a) *Some compounds with the zinc blende (sphalerite) structure (in ångstroms)*

CuF	4.255	BeS	4.8624	β-CdS	5.818	BN	3.616	GaP	5.448
CuCl	5.416	BeSe	5.07	CdSe	6.077	BP	4.538	GaAs	5.6534
γ-CuBr	5.6905	BeTe	5.54	CdTe	6.481	BAs	4.777	GaSb	6.095
γ-CuI	6.051	β-ZnS	5.4060	HgS	5.8517	AlP	5.451	InP	5.869
γ-AgI	6.495	ZnSe	5.667	HgSe	6.085	AlAs	5.662	InAs	6.058
β-MnS, red	5.600	ZnTe	6.1026	HgTe	6.453	AlSb	6.1347	InSb	6.4782
β-MnSe	5.88	β-SiC	4.358						

Fluorite and antifluorite



Fluorite structure

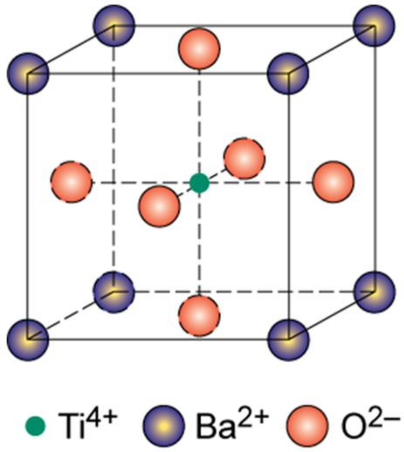
- Calcium Fluorite (CaF_2)
- Cations in cubic sites
- UO_2, ThO_2, ZrO_2, CeO_2
- Antifluorite structure – positions of cations and anions reversed

Fluorite structure				Antifluorite structure			
	a(Å)		a(Å)		a(Å)		a(Å)
CaF_2	5.4626	PbO_2	5.349	Li_2O	4.6114	K_2O	6.449
SrF_2	5.800	CeO_2	5.4110	Li_2S	5.710	K_2S	7.406
$SrCl_2$	6.9767	PrO_2	5.392	Li_2Se	6.002	K_2Se	7.692
BaF_2	6.2001	ThO_2	5.600	Li_2Te	6.517	K_2Te	8.168
$BaCl_2$	7.311	UO_2	5.372	Na_2O	5.55	Rb_2O	6.74
CdF_2	5.3895	NpO_2	5.4334	Na_2S	6.539	Rb_2S	7.65
HgF_2	5.5373	CmO_2	5.3598	Na_2Se	6.823		
EuF_2	5.836	PuO_2	5.386	Na_2Te	7.329		
β-PbF_2	5.940	AmO_2	5.376				

Perovskite ABO_3

- Perovskite structure

Ex: complex oxide
$BaTiO_3$



Perovskite ABO_3

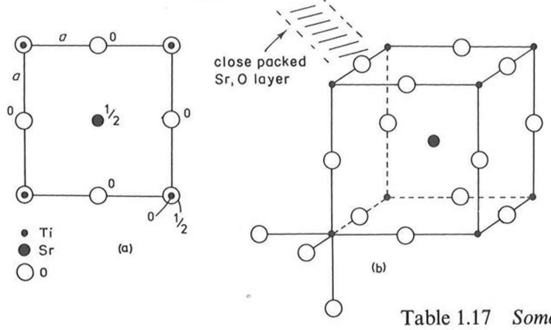
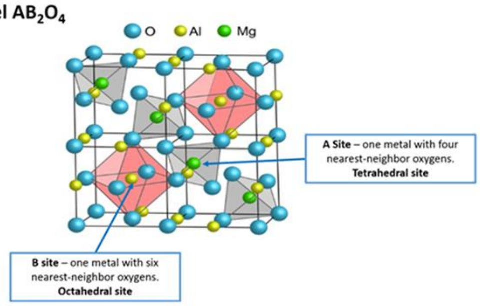


Table 1.17 *Some compounds with the perovskite structure*

Compound	a(Å)	Compound	a(Å)
$KNbO_3$	4.007	$SrTiO_3$	3.9051
$KTaO_3$	3.9885	$SrZrO_3$	4.101
KIO_3	4.410	$SrHfO_3$	4.069
$NaNbO_3$	3.915	$SrSnO_3$	4.0334
$NaWO_3$	3.8622	$SrThO_3$	
$LaCoO_3$	3.824	$CsCaF_3$	4.522
$LaCrO_3$	3.874	$CsCdBr_3$	5.33
$LaFeO_3$	3.920	$CsCdCl_3$	5.20
$LaGaO_3$	3.875	$CsHgBr_3$	5.77
$LaVO_3$	3.99	$CsHgCl_3$	5.44

Spinels

Spinel AB_2O_4



Normal

$$[A]^{tet}[B_2]^{oct}O_4$$

Inverse

$$[B]^{tet}[A, B]^{oct}O_4$$

Spinels

Normal

$$[A]^{tet}[B_2]^{oct}O_4$$

Inverse

$$[B]^{tet}[A,B]^{oct}O_4$$

Table 1.19(a) *Some compounds with the spinel structure*

Crystal	Type	a(Å)	Structure
$MgAl_2O_4$	2, 3	8.0800	Normal
$CoAl_2O_4$	2, 3	8.1068	Normal
$CuCr_2S_4$	2, 3	9.629	Normal
$CuCr_2Se_4$	2, 3	10.357	Normal
$CuCr_2Te_4$	2, 3	11.051	Normal
$MgTi_2O_4$	2, 3	8.474	Normal
Co_2GeO_4	2, 4	8.318	Normal
Fe_2GeO_4	2, 4	8.411	Normal
$MgFe_2O_4$	2, 3	8.389	Inverse
$NiFe_2O_4$	2, 3	8.3532	Inverse
$MgIn_2O_4$	2, 3	8.81	Inverse
$MgIn_2S_4$	2, 3	10.708	Inverse
Mg_2TiO_4	2, 4	8.44	Inverse
Zn_2SnO_4	2, 4	8.70	Inverse
Zn_2TiO_4	2, 4	8.467	Inverse
$LiAlTiO_4$	1, 3, 4	8.34	Li in 8a
$LiMnTiO_4$	1, 3, 4	8.30	Li in 8a
$LiZnSbO_4$	1, 2, 5	8.55	Li in 8a
$LiCoSbO_4$	1, 2, 5	8.56	Li in 8a

In order to explain the adoption of a particular cation distribution in a spinel structure, one must take into account the crystal field stabilization energies (CFSE) of the transition metals present. Some ions may have a distinct preference for the octahedral site depending on the d-electron count. If the A^{2+} ions have a strong preference for the octahedral site, they will displace half of the B^{3+} ions from the octahedral sites to tetrahedral sites. Similarly, if the B^{3+} ions have a low or zero octahedral site stabilization energy (OSSE), then they will occupy tetrahedral sites, leaving octahedral sites for the A^{2+} ions.

DEFECTS IN SOLIDS

No real crystal is perfect. Real crystals feature defects or irregularities in their ideal arrangements and it is these defects that critically determine many of the electrical and mechanical properties of real materials.

Ideally a perfect crystal is the one in which atoms are arranged in perfectly regular manner in all directions. The deviations of crystals from their perfect periodicity are called **defects** or **imperfections**.

These imperfections can be of different types such as:

point defects (zero–dimensional defects),

line defects (one–dimensional)

defects over a surface or a plane (two–dimensional) and volume defects (three–dimensional).

Point Defects

A point defect is a very localized imperfection in the regularity of a lattice and it does not spread over more than one or two lattice spacings. These defects are observed in metallic crystals (vacancies, substitutional impurity and interstitials) as well as in ionic crystals (Schottky and Frenkel) and are discussed here in brief.

Vacancies

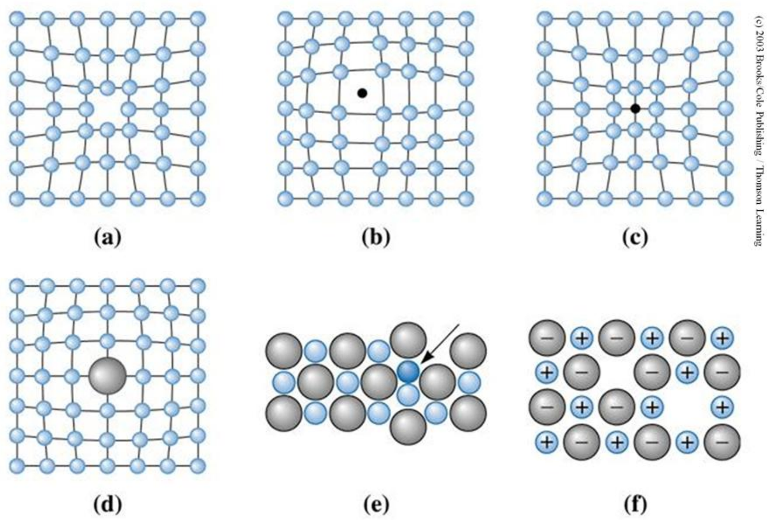
The absence of an atom or ion from a normally occupied site in a crystal is called a **vacancy** (see Fig.)

Substitutional Impurity

In this kind of defect, a **foreign atom** occupy a regular site in the crystal structure (see Fig.), i.e., .substitutional atom replaces the host atom from its position. For example, when a pure semiconductor crystal of Silicon or Germanium is doped with a trivalent or pentavalent impurity, we call it a substitutional impurity.

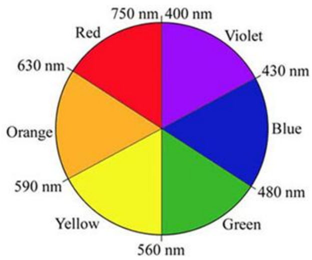
Interstitial Impurity

An **interstitial** is an atom or ion which can be inserted into the voids between the regularly occupied sites. In a closed packed arrangement of atoms the packing fraction is generally less than one. Therefore an extra atom, of smaller size than the parent atom, can enter the interstitial space without disturbing the regularly positioned atoms. Such an extra **impure** atom is called **interstitial impurity** while an extra atom in an interstitial position is called **self – interstitial atom**,as shown in Fig. If the size of the extra atom is not small then it will produce atomic distortion.

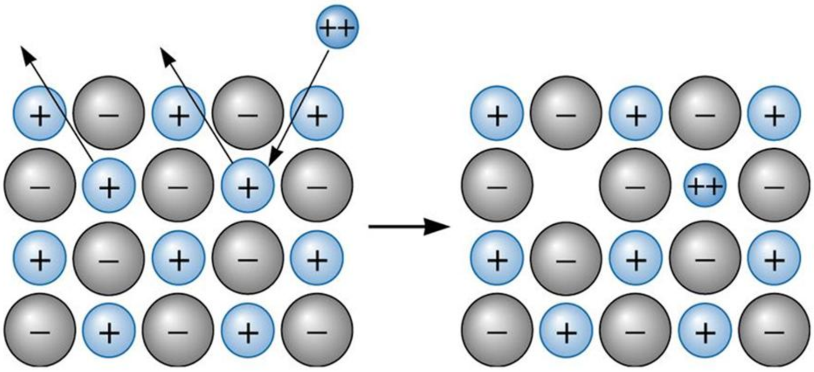

(a)
(b)
(c)
(d)
(e)
(f)
(c) 2003 Brooks/Cole Publishing / Thomson Learning

Emerald and **Ruby**:
Cr^{3+} impurities

Cr_2O_3: green

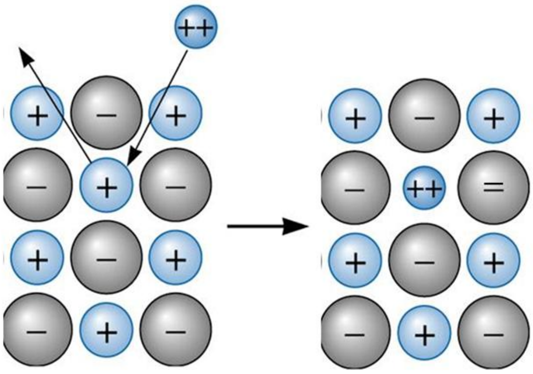


Charge compensation: vacancy formation



When a divalent cation replaces a monovalent cation, a second monovalent cation must also be removed, creating a vacancy.

Charge compensation: change in oxidation state



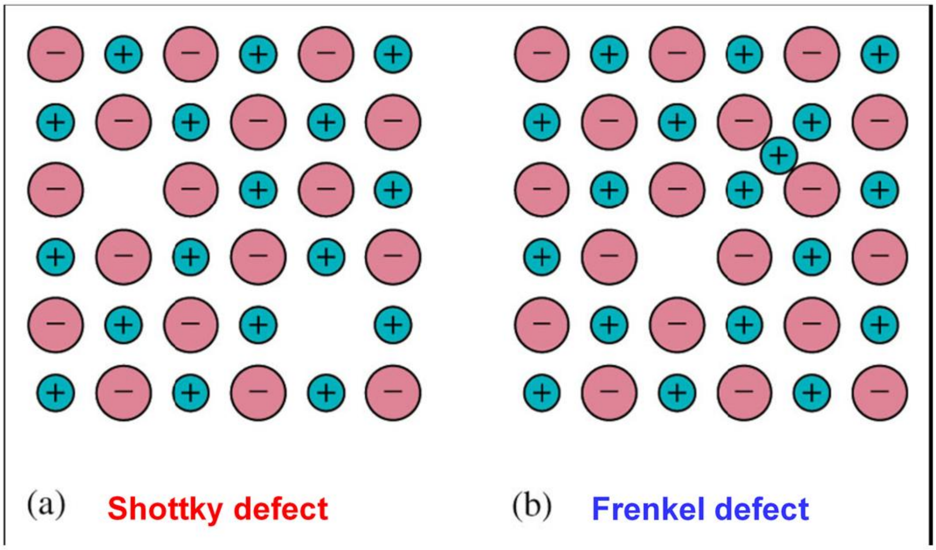
When a divalent cation replaces a monovalent cation, an anion must change its oxidation state.

Schottky Defect

In a metal, a vacancy is created if an atom is missing from its lattice position. In ionic crystals, a cation – anion pair will be missing from the respective lattice sites, as shown in Fig. Creation of such a pair, of one cation vacancy together with one anion vacancy, is called **Schottky defect**. Thus the interior of the ionic crystals remain electrically neutral.

Frenkel Defect

When an atom or ion leaves its normal position or site and is found to occupy another position in the interstice we get a Frenkel defect. Thus, in this case, two imperfections are created – an interstitial and a vacancy as shown in Fig. Normally anion leaves its parent site and occupy the interstitial space. These defects are dominant in open structures such as silver halides. Also a Frenkel defect does not affect the electrical neutrality of a crystal.


(a) Shottky defect
(b) Frenkel defect

Concentration of Schottky defects

$$n = Ne^{-E/2kT}$$

n = number of vacancy pairs
N = total number of sites
E = energy required to produce a pair of vacancies in the interior of a crystal

Concentration of Frenkel defects

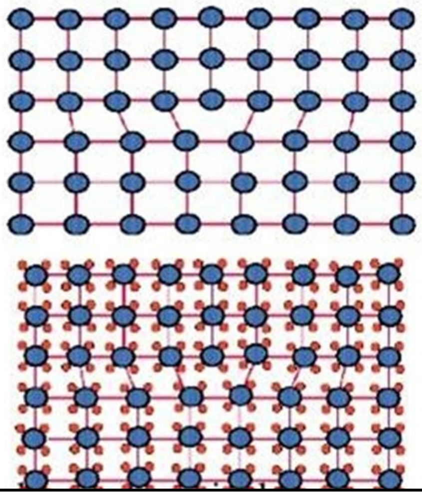
$$n = (N N_i)^{1/2} e^{-E_i/2kT}$$

n = number of vacancies = number of atoms in interstitial sites
N = total number of sites
N_i = number of interstitial positions in the crystal
E_i = energy required to produce a pair of vacancies in the interior of a crystal

Line Defects: Dislocations

Edge Dislocations

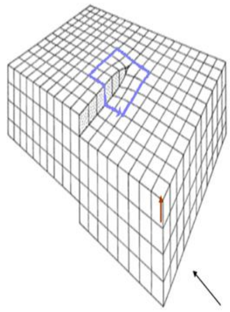
First elementary dislocation type: edge dislocations



Crystal defects/ Dislocations

Dislocation geometry

Second elementary dislocation type: screw dislocations

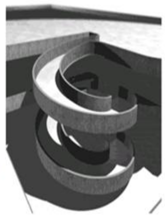


Edge dislocation:

Burgers vector perpendicular to dislocation line.

Screw dislocation:

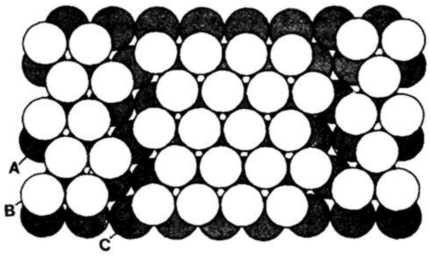
Burgers vector parallel to dislocation line.



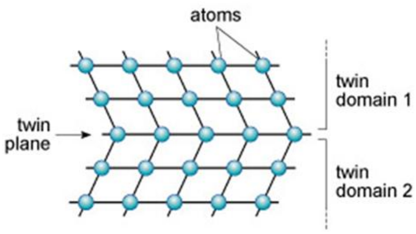
Looks like a parking ramp

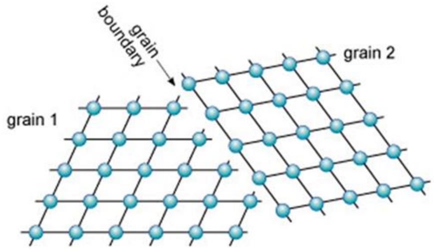
Stacking faults

Errors in crystals packing



Domains formation





Electronic properties of materials

Justify:

- Electron transport properties
- Optical properties

Metallic bond: LCAO model

Molecular orbital for N atoms:

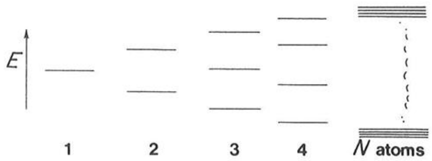


Fig. 2.16 Splitting of energy levels on molecular orbital theory

In the case of Na
(and other metals)

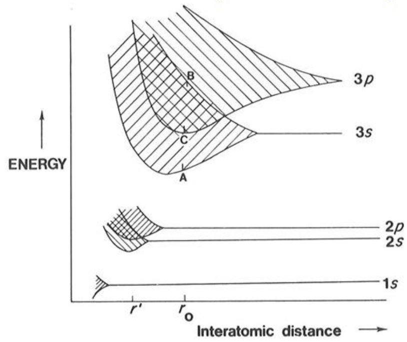


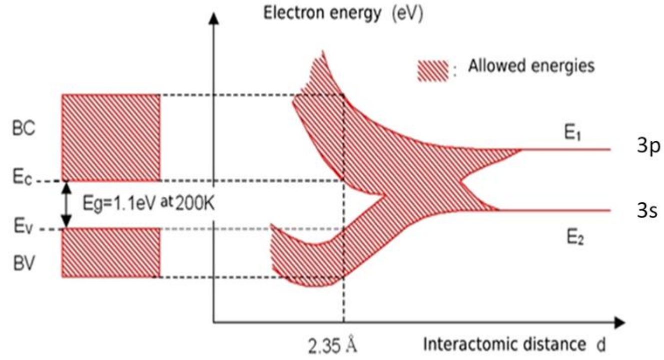
Fig. 2.17 Effect of interatomic spacing on atomic energy levels and bands for sodium, calculated using tight binding theory. Shaded areas represent bands of energy levels, formed by significant overlap of atomic orbitals on adjacent atoms

Metallic bond

Overlapping of the energy states deriving for higher occupied and lowest unoccupied atomic orbitals: electrons are allowed to spread around over all the atoms in the "molecule" (= crystal).

Metallic bond: LCAO model

In the case of Si:



Free Electron Model

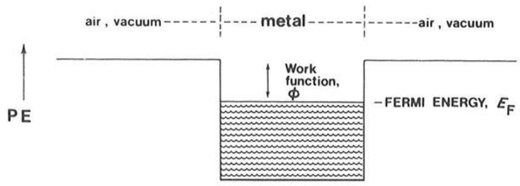


Fig. 2.18 Free electron theory of a metal; electrons in a potential well

In one dimension:

$$-\frac{h}{8\pi^2 m_e}\frac{d^2\Psi}{dx^2} = (\mathrm{E} - \mathrm{V})\Psi$$

$$V = 0;\ \Psi_{x=0} = 0; \Psi_{x=a}$$

$$E = \frac{n^2 h^2}{8 m_e a^2}$$

In 3D (crystal):

$$E = \frac{h^2}{8m_e}\left(\frac{n_a^2}{a^2} + \frac{n_b^2}{b^2} + \frac{n_c^2}{c^2}\right)$$

Many states with the same energy!!!!

Free Electron Model

Density of states

$$N_{(E)}dE = \frac{2(2m_e)^{3/2}VE^{1/2}}{\pi^2\hbar^3}dE$$

Fermi-Dirac "filling" function

$$f_{FD}(E) = \frac{1}{e^{\frac{(E-E_F)}{kT}}+1}$$

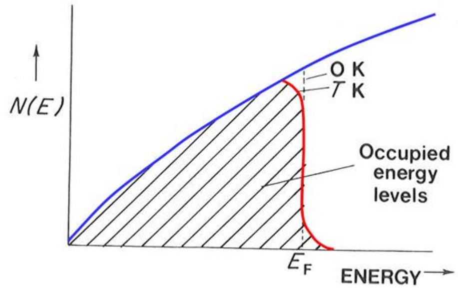


Fig. 2.19 Density of states plot on the free electron theory

E_F = Fermi Level
Energy of the highest occupied state at 0 K

Band structure model

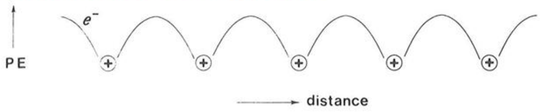


Fig. 2.20 Potential energy of electrons as a function of distance through a solid

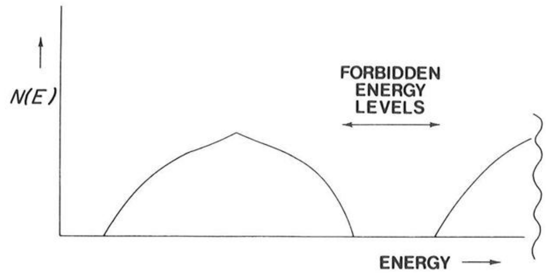


Fig. 2.21 Density of states on band theory

Electrical properties of a material depend on the filling of bands

Band structure model: metal

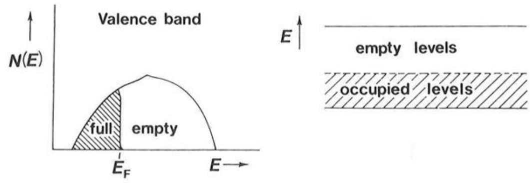


Fig. 2.22 Band structure of a metal

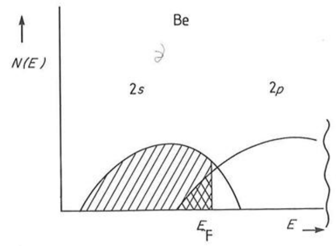


Fig. 2.23 Overlapping band structure of beryllium metal

Band structure model: insulator

$$\lambda\ (\text{nm}) = \frac{hc}{E\ (\text{eV})} = \frac{1240}{E\ (\text{eV})}$$

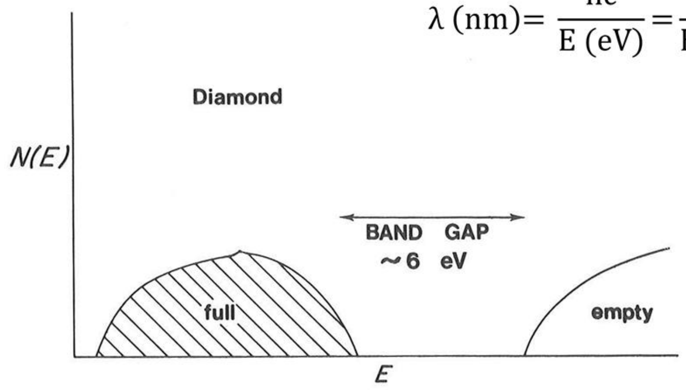
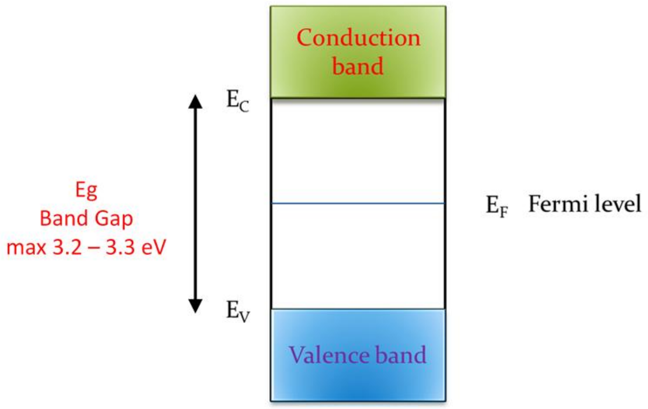


Fig. 2.24 Band structure of an insulator, carbon (diamond)

Intrinsic semiconductor



Extrinsic semiconductor

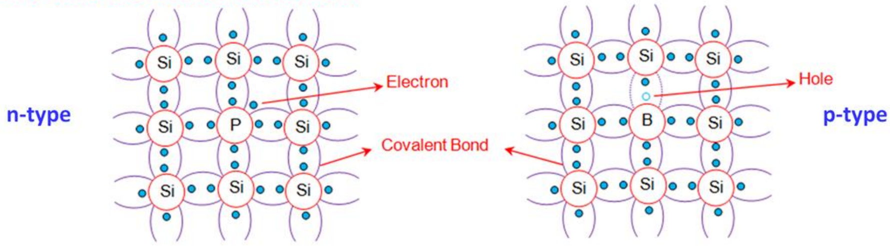
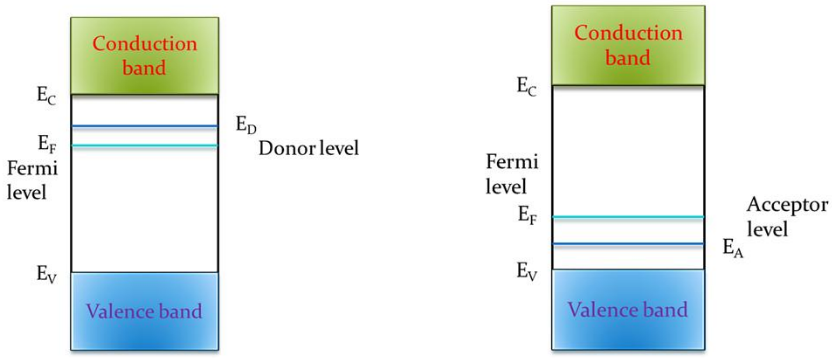
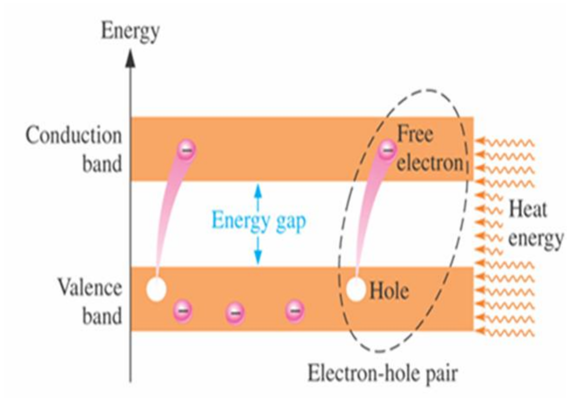


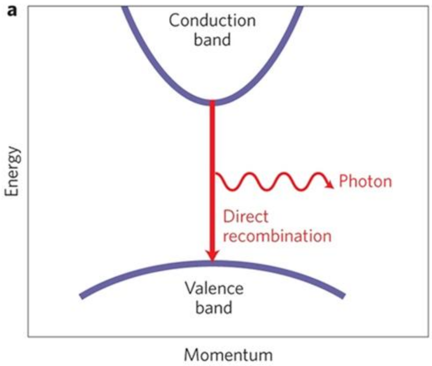
Figure 1 2-D Crystal Lattice of Silicon Doped with (a) Phosphorous (b) Boron



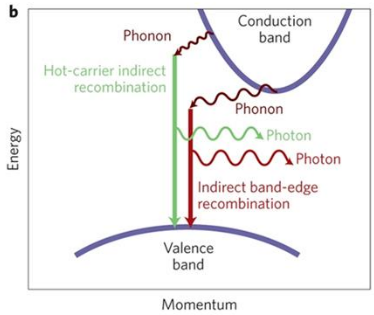
Electron-hole formation



Direct band gap



Indirect band gap

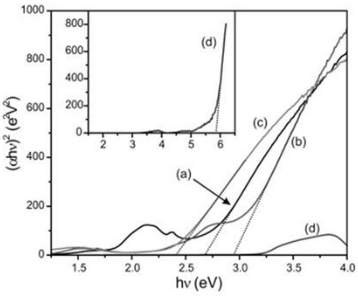


Tauc plot

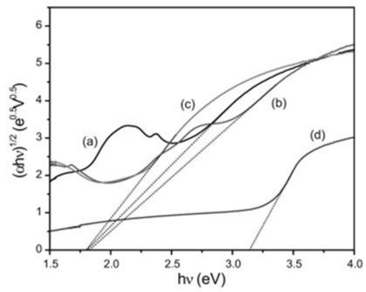
$$\alpha h\upsilon = A\left(h\upsilon - E_g\right)^n$$

n = 1/2 for direct allowed transitions
n = 2 for indirect allowed transitions

Direct



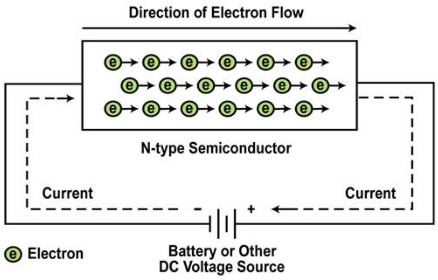
Indirect



	Material	Colour	Direct E_g (eV)	Indirect E_g (eV)
a	$CoWO_4$	Blue	2.68	1.80
b	$NiWO_4$	Ochre	2.95	1.82
c	$CuWO_4$	Brown-Green	2.41	1.78
d	$ZnWO_4$	White	5.85	3.14

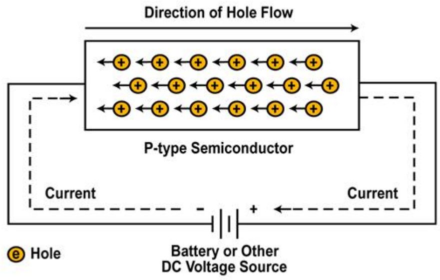
Current Flow in n-type Semiconductors

- The DC voltage source has a positive terminal that attracts the free electrons in the semiconductor and pulls them away from their atoms leaving the atoms charged positively.
- Electrons from the negative terminal of the supply enter the semiconductor material and are attracted by the positive charge of the atoms missing one of their electrons.
- Current (electrons) flows from the positive terminal to the negative terminal.

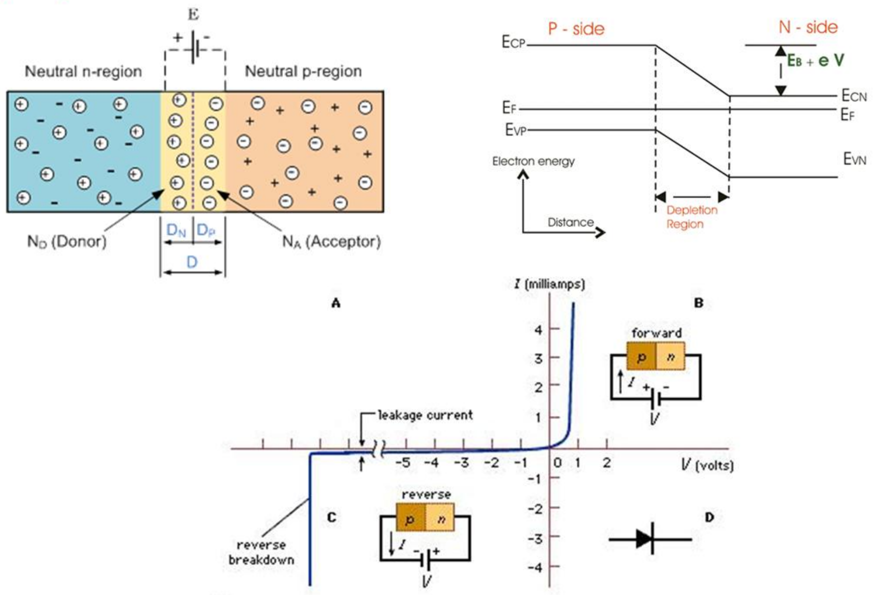


Current Flow in p-type Semiconductors

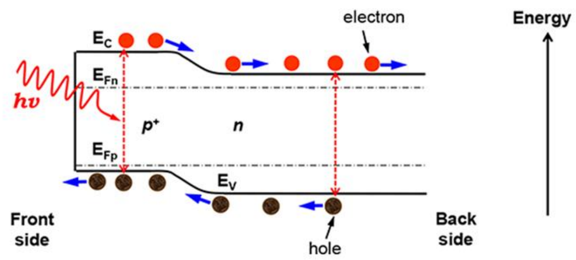
- Electrons from the negative supply terminal are attracted to the positive holes and fill them.
- The positive terminal of the supply pulls the electrons from the holes leaving the holes to attract more electrons.
- Current (electrons) flows from the negative terminal to the positive terminal.
- Inside the semiconductor current flow is actually by the movement of the holes from positive to negative.



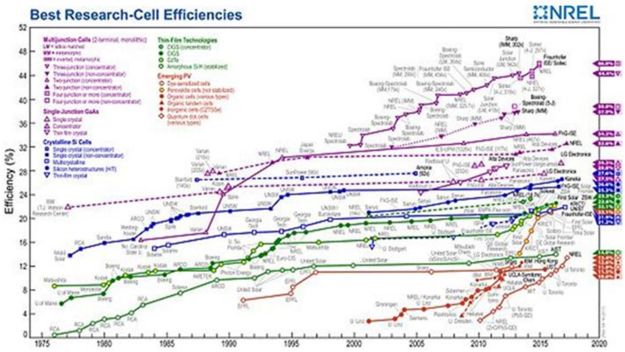
p-n junction


E
Neutral n-region
Neutral p-region
N_D (Donor)
N_A (Acceptor)
D_N
D_P
D
P - side
N - side
ECP
EB + e V
ECN
EF
EF
EVP
EVN
Electron energy
Distance
Depletion Region
I (milliamps)
A
B
C
D
forward
reverse
leakage current
reverse breakdown
V (volts)

Solar cells



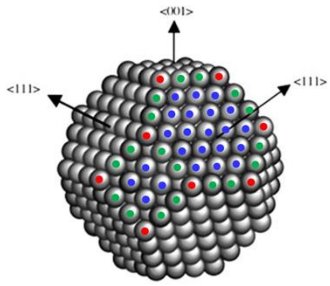
E_C
E_Fn
hν
p+
n
E_Fp
E_V
electron
hole
Front side
Back side
Energy



Best Research-Cell Efficiencies
NREL
Efficiency (%)
1975
1980
1985
1990
1995
2000
2005
2010
2015
2020

Surfaces

Represent the place in which the solid interacts with the environment.



Atoms on the surface have different chemical environment with respect to those in the bulk.

- Vertex
- Corner
- Facet

} Different coordination number

$$\textbf{Metal dispersion} = \frac{\text{Number of superficial atoms}}{\text{Total number of atoms}}$$

Surfaces

Surface energy $$\gamma = \frac{\partial G}{\partial A}$$ quantifies the disruption of intermolecular bonds that occur when a surface is created.

$$\Delta G_i = \sum_j \gamma_j O_j$$

represents the difference in energy between a real crystal composed of *i* molecules with a surface and a similar configuration of *i* molecules located inside an infinitely large crystal. This quantity is therefore the energy associated with the surface.

The equilibrium shape of the crystal will then be that which minimizes the value of ΔG_i.

Metal surfaces

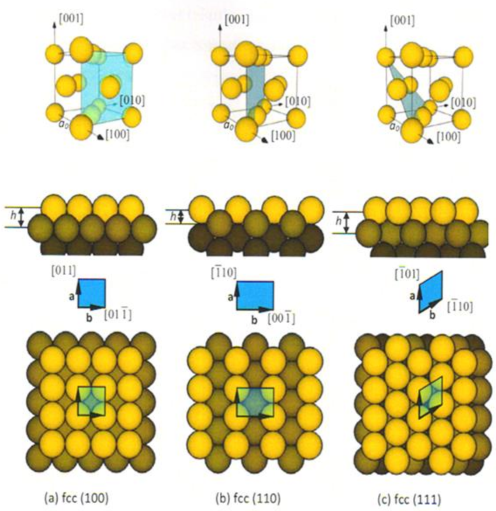


Figure 2-8 Unreconstructed surfaces of the face-centered cubic (fcc) crystal surfaces. a_0 is the lattice constant of the crystal. a and b are the unit-cell vectors. h is the distance between the first and the second layer. (a) fcc (100): $|\mathbf{a}|=|\mathbf{b}|=\frac{\sqrt{2}}{2}a_0$, and $h=\frac{1}{2}a_0$. To obtain the second layer, shift the first layer by $\frac{1}{2}\mathbf{a}+\frac{1}{2}\mathbf{b}$ in the plane, then $\frac{1}{2}a_0$ in the $[\bar{1}00]$ direction. (b) fcc (110): $|\mathbf{a}|=\frac{\sqrt{2}}{2}a_0$, $|\mathbf{b}|=a_0$, and $h=\frac{\sqrt{2}}{4}a_0$. To obtain the second layer, shift the first layer by $\frac{1}{2}\mathbf{a}+\frac{1}{2}\mathbf{b}$ in the plane, then $\frac{\sqrt{2}}{4}a_0$ in the $[\bar{1}\bar{1}0]$ direction. (c) fcc (111): $|\mathbf{a}|=|\mathbf{b}|=\frac{\sqrt{2}}{2}a_0$, and $h=\frac{\sqrt{3}}{3}a_0$. To obtain the second layer, shift the first layer by $\frac{1}{3}\mathbf{a}+\frac{1}{3}\mathbf{b}$ in the plane, then $\frac{\sqrt{3}}{3}a_0$ in the $[\bar{1}\bar{1}\bar{1}]$ direction.

Metal surfaces

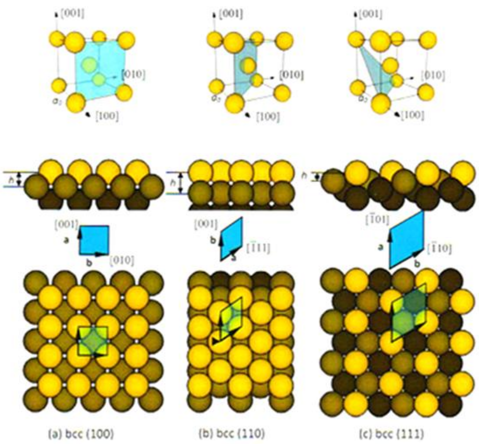
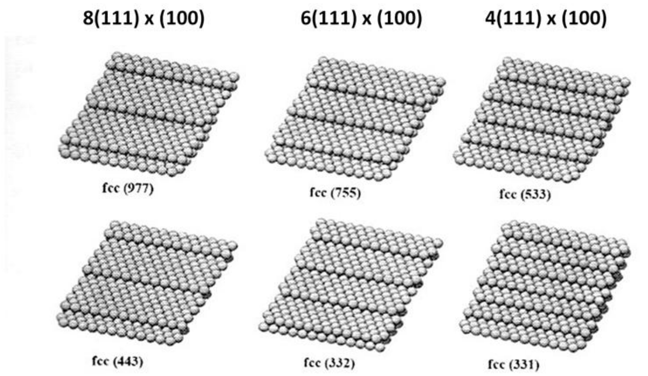


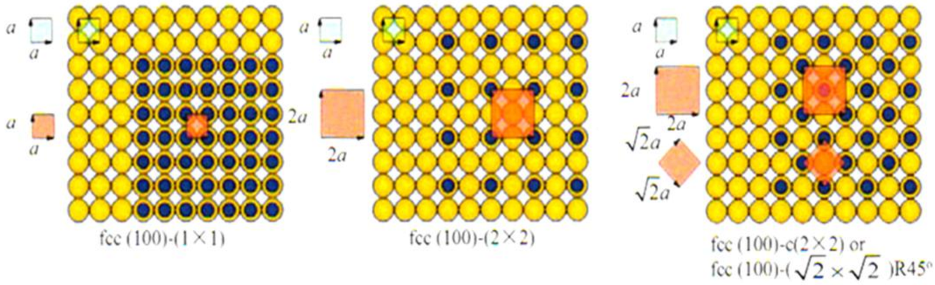
Figure 2-9 Unreconstructed surfaces of the body-centered cubic (bcc) crystal surfaces. a_0 is the lattice constant of the crystal. a and b are the unit-cell vectors. h is the distance between the first and the second layer. (a) bcc (100): $|\mathbf{a}|=|\mathbf{b}|=a_0$, and $h=\frac{1}{2}a_0$. To obtain the second layer, shift the first layer by $\frac{1}{2}\mathbf{a}+\frac{1}{2}\mathbf{b}$ in the plane, then $\frac{1}{2}a_0$ in the $[\bar{1}00]$ direction. (b) bcc (110): $|\mathbf{a}|=\frac{\sqrt{3}}{2}a_0$, $|\mathbf{b}|=a_0$, and $h=\frac{\sqrt{2}}{2}a_0$. To obtain the second layer, shift the first layer by $\frac{1}{2}\mathbf{b}$ in the plane, then $\frac{1}{2}a_0$ in the $[\bar{1}\bar{1}0]$ direction. (c) bcc (111): $|\mathbf{a}|=|\mathbf{b}|=\sqrt{2}a_0$, and $h=\frac{\sqrt{3}}{6}a_0$. To obtain the second layer, shift the first layer by $\frac{1}{3}\mathbf{a}+\frac{1}{3}\mathbf{b}$ in the plane, then $\frac{\sqrt{3}}{6}a_0$ in the $[\bar{1}\bar{1}\bar{1}]$ direction.

Metal surfaces – High-Miller-Index Stepped Surface



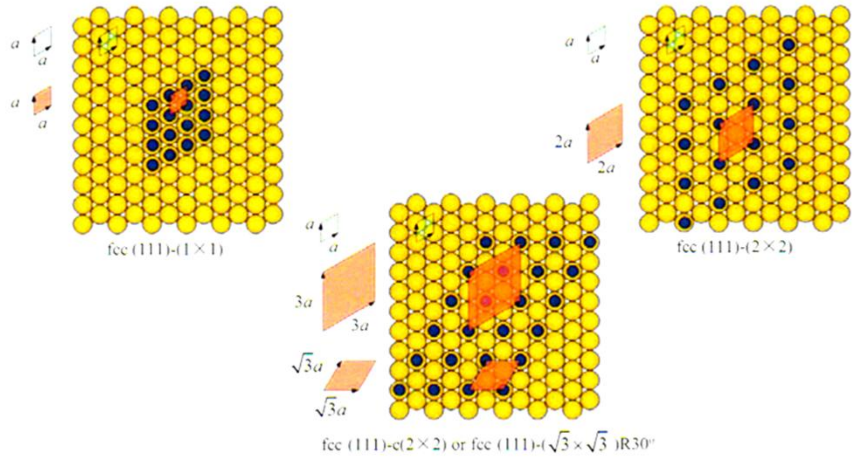
Metal surfaces - Superlattice

fcc (100) – (2x2)



Metal surfaces - Superlattice

fcc (111) – (2x2)

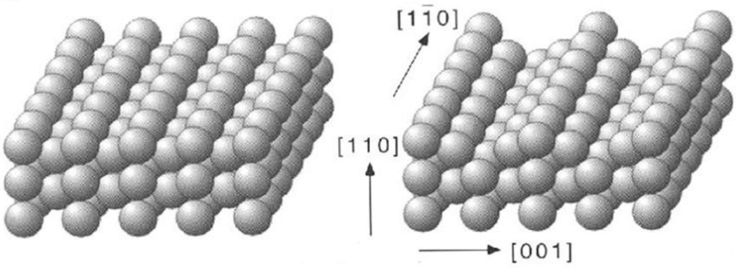


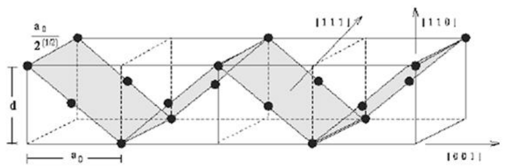
Metal surfaces - Superlattice

	Superlattice Unit Cell	
Substrate	Abbreviated Notation	Matrix Notation
fcc(100), bcc(100)	p(1 × 1)	$\begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}$
	c(2 × 2) = $(2\sqrt{2} \times \sqrt{2})$R45°	$\begin{vmatrix} 1 & -1 \\ 1 & 1 \end{vmatrix}$
	p(2 × 1)	$\begin{vmatrix} 2 & 0 \\ 0 & 1 \end{vmatrix}$
	p(1 × 2)	$\begin{vmatrix} 1 & 0 \\ 0 & 2 \end{vmatrix}$
	p(2 × 2)	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$
	$(2\sqrt{2} \times \sqrt{2})$R45°	$\begin{vmatrix} 2 & 2 \\ -1 & 1 \end{vmatrix}$
fcc(111)(60° between basis vectors)	p(2 × 1)	$\begin{vmatrix} 2 & 0 \\ 0 & 1 \end{vmatrix}$
	p(2 × 2)	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$
	$(\sqrt{3} \times \sqrt{3})$R30°	$\begin{vmatrix} 2 & 2 \\ -1 & 2 \end{vmatrix}$
fcc(110)	p(2 × 1)	$\begin{vmatrix} 2 & 0 \\ 0 & 1 \end{vmatrix}$
	p(3 × 1)	$\begin{vmatrix} 3 & 0 \\ 0 & 1 \end{vmatrix}$
	c(2 × 2)	$\begin{vmatrix} 1 & -1 \\ 1 & 1 \end{vmatrix}$
bcc(110)	p(2 × 1)	$\begin{vmatrix} 2 & 0 \\ 0 & 1 \end{vmatrix}$

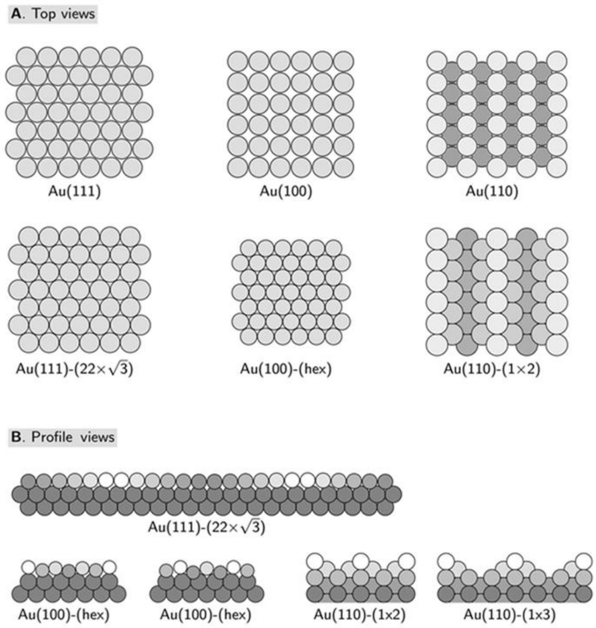
Metal surfaces - Reconstruction

Pd(110)



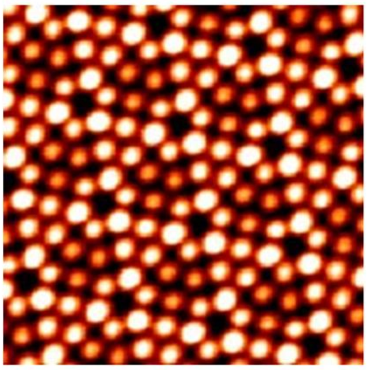


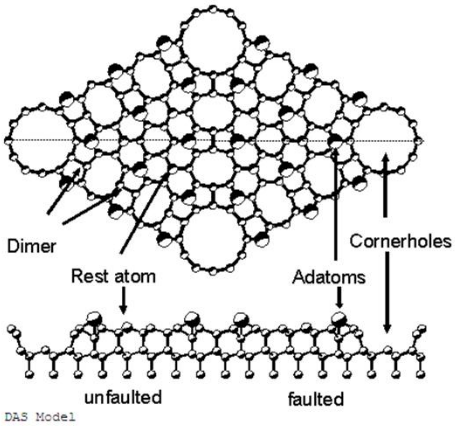
Metal surfaces - Reconstruction



Metal surfaces - Reconstruction

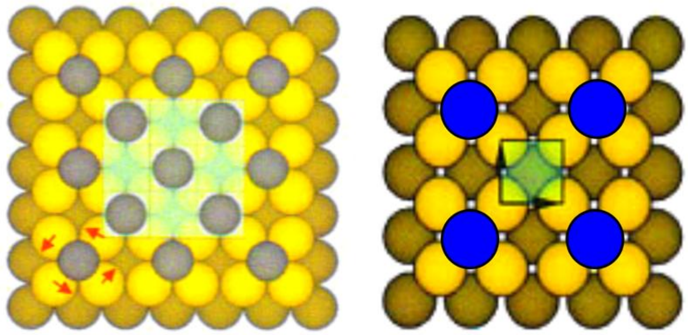
(7x7) Reconstruction of Si (111)





19 dangling bonds of (7x7) reconstructed surface
(12 adatom, 6 rest atom, 1 corner hole)

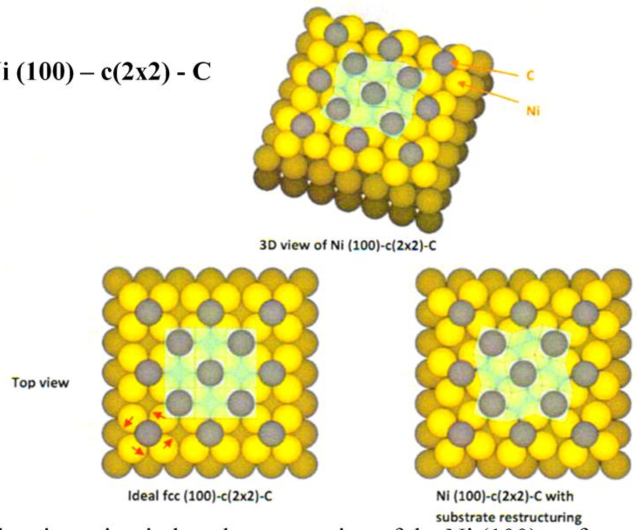
Coverage of adsorbate molecules



Definition of coverage: one monolayer corresponds to one adsorbate atom or molecules for each unit cell of the clean, unreconstructed substrate surface.
For example, the surface coverage of atom on fcc(100) is one-half a monolayer.

Metal surfaces – Adsorbate induced reconstructuring

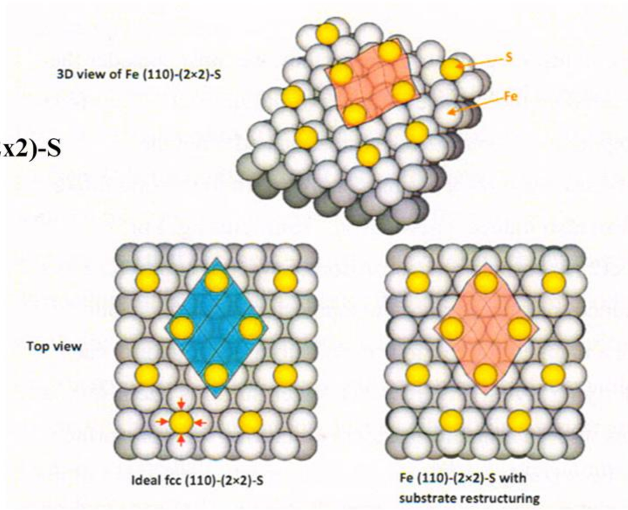
Ni (100) – c(2x2) - C



Carbon chemisorption induced restructuring of the Ni (100) surface.
Four Ni atoms surrounding each carbon atom rotate to form reconstructed substrate.

Metal surfaces – Adsorbate induced reconstructuring

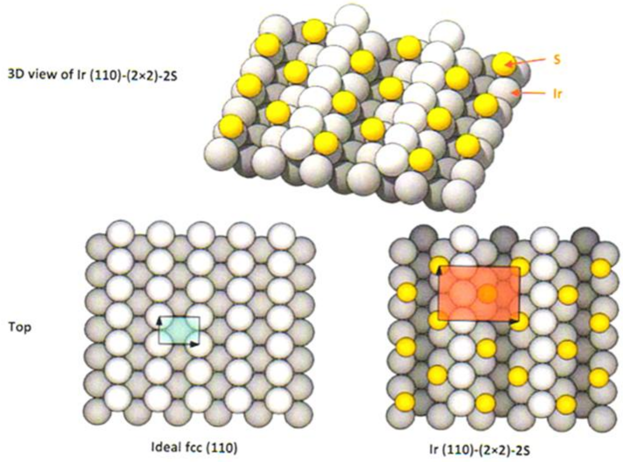
Fe (110) – (2x2)-S



S-Fe (110), Sulfur-chemisorption-induced restructuring of the Fe(110) surface.

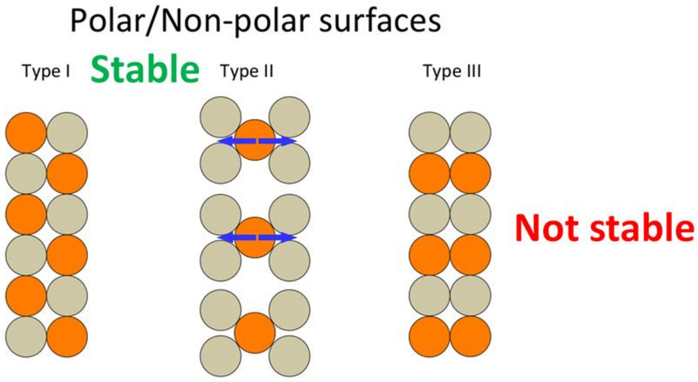
Metal surfaces – Adsorbate induced reconstructuring

Sulfur-chemisorption-induced restructuring of the Ir (110) surface



fcc(111) surface restructure more frequently upon chemisorption than do the closer-packed crystal faces.

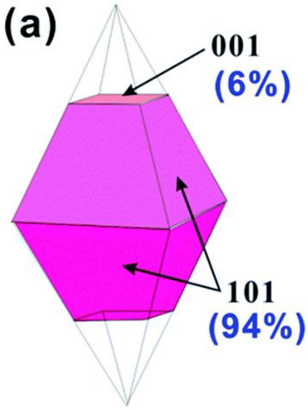
Ionic material surfaces

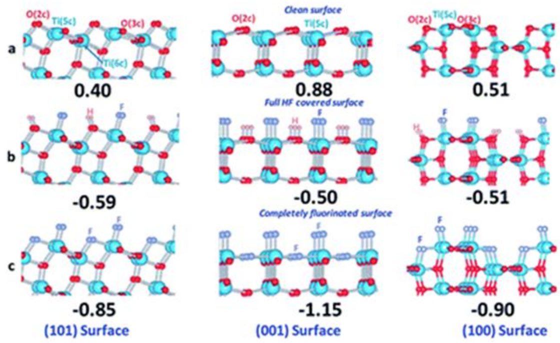


P W Tasker 1979 *J. Phys. C: Solid State Phys.* **12** 4977

Type 1 is neutral with equal numbers of anions and cations on each plane and type 2 is charged but there is no dipole moment perpendicular to the surface because of the symmetrical stacking sequence. Both these surfaces should have modest surface energies and may be stable with only limited relaxations of the ions in the surface region. The type 3 surface is charged and has a dipole moment in the repeat unit perpendicular to the surface. This surface can only be stabilised by substantial reconstruction.

Ionic material surfaces





Ionic material surfaces