Crystal Structures and Crystallography

M V V K Srinivas Prasad
Assistant Professor
Dept. of Physics

Classification of matte

- Matter
  - GASES
  - LIQUIDS
  - SOLIDS
    - Amorphous
    - Qusicrystals
    - Crystals
      - Polycrystals
      - Single Crystals

- Based on atomic structure we can differentiate three types of arrangements

CLASSIFICATION OF SOLIDS BASED ON ATOMIC ARRANGEMENT

AMORPHOUS

~~Ordered~~
+
~~Periodic~~

QUASICRYSTALS

Ordered
+
~~Periodic~~

CRYSTALS

Ordered
+
Periodic

- The crystal exhibits a sharp melting point
- *"Crystal has a higher density"!!*

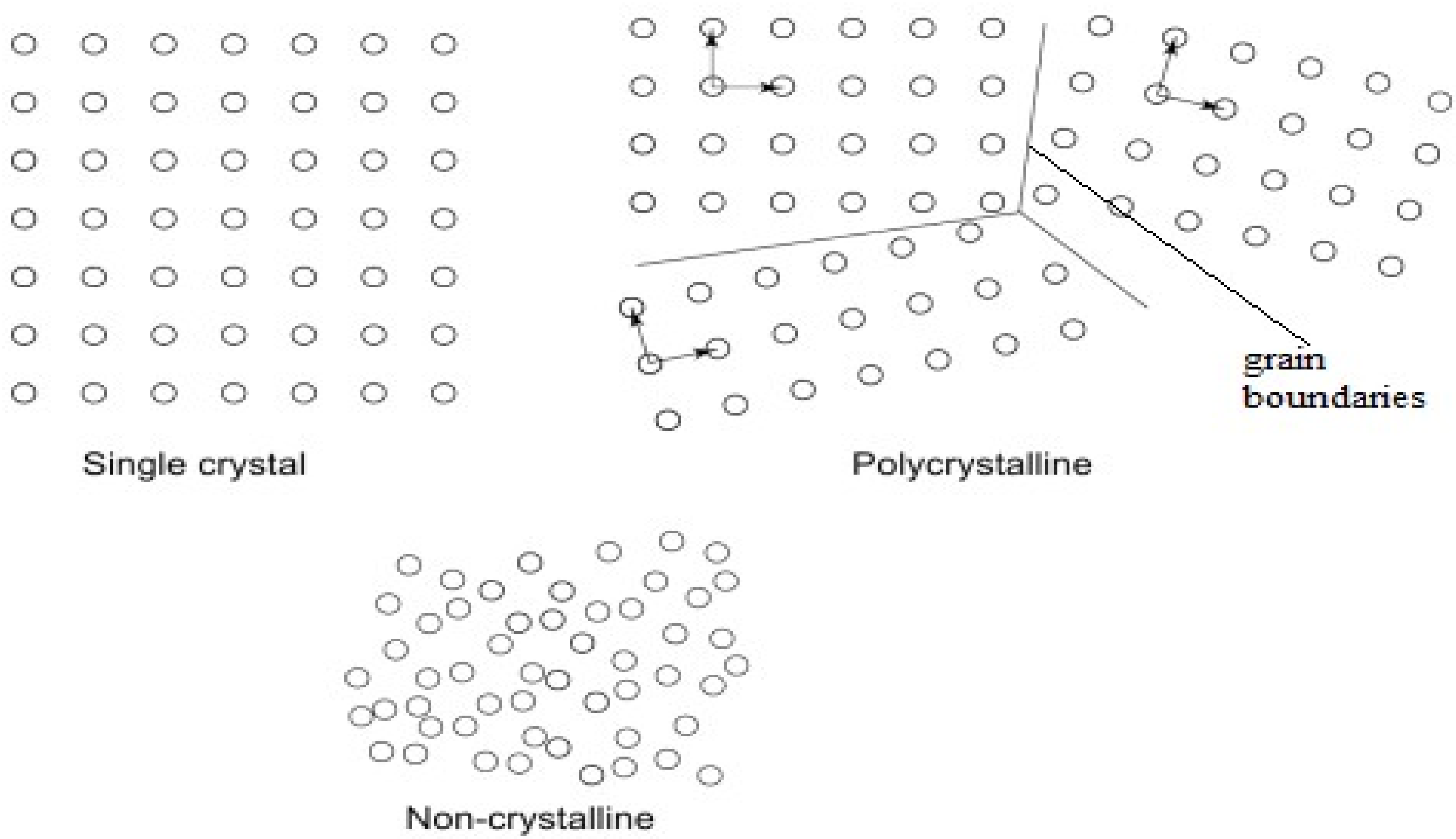
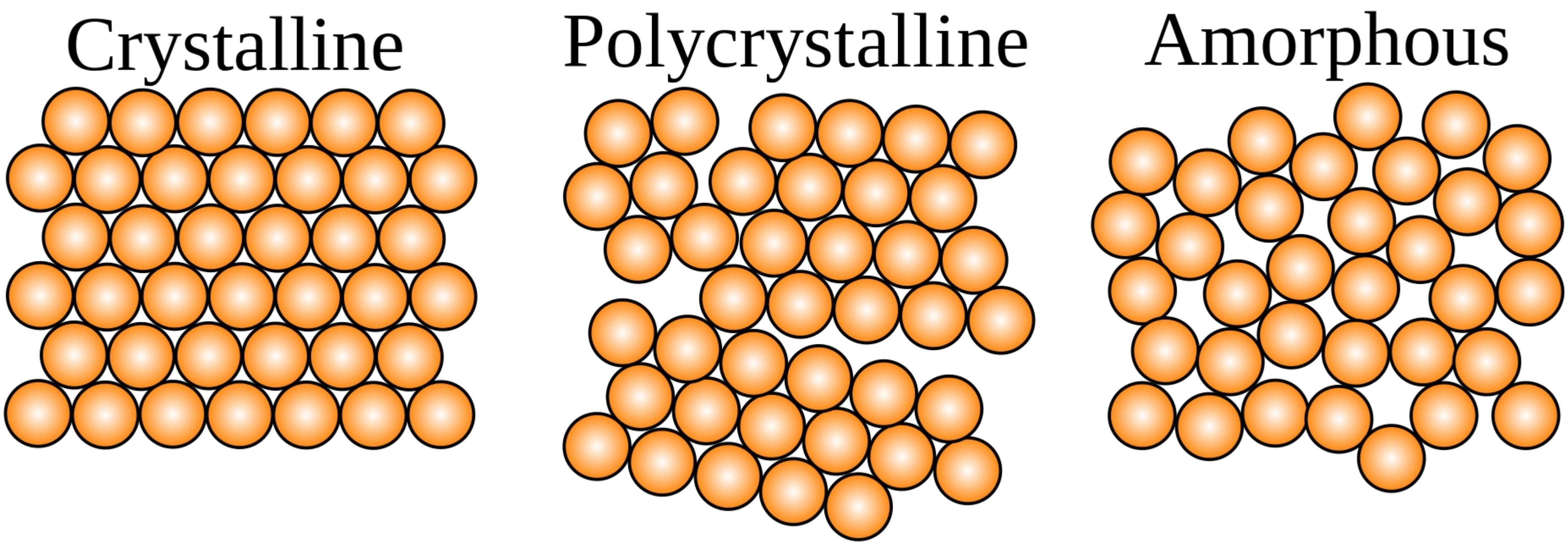
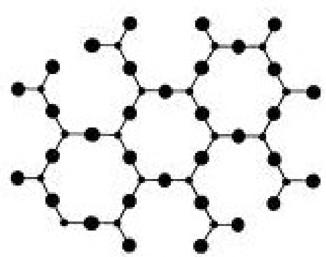


Fig. 1.1 *Two dimensional representation of single crystal, polycrystalline and non-crystalline materials*


Crystalline
Polycrystalline
Amorphous

Crystalline Solids

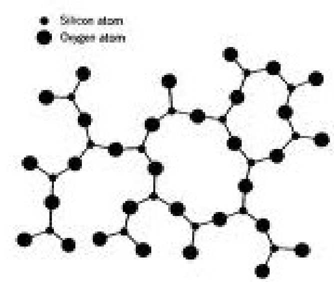
- Regular arrangement of atoms along the 3 D.
- Have long range order.
- Sharp melting point.
- They are anisotropic.
- They are most stable.
- They have a regular cut.
- They show all characteristic of solids.
- Ex: Diamond, NaCl, KCl, Copper, Iron, etc.



crystalline

Amorphous Solids

- No regular arrangement of atoms.
- Have short range order.
- No sharp melting point.
- They are isotropic.
- They are most unstable.
- They have irregular cut.
- They don’t show all characteristics of solids.
- Ex: Glasses, Plastic, Rubber.

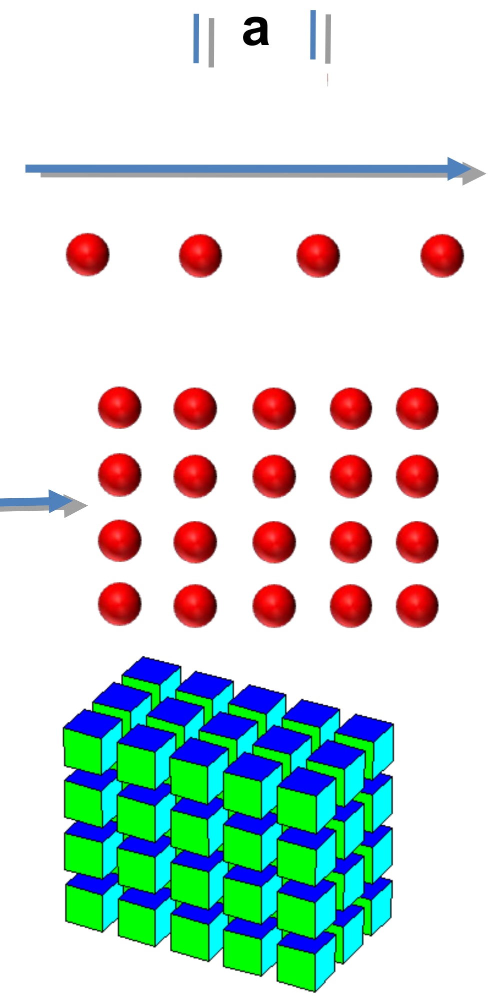


non-crystalline

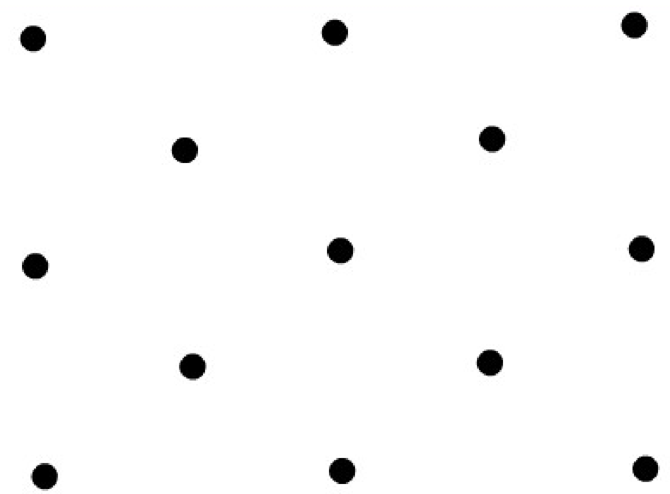
Basic Definitions

Lattice

- Linear Lattice
- Plane Lattice
- Space Lattice

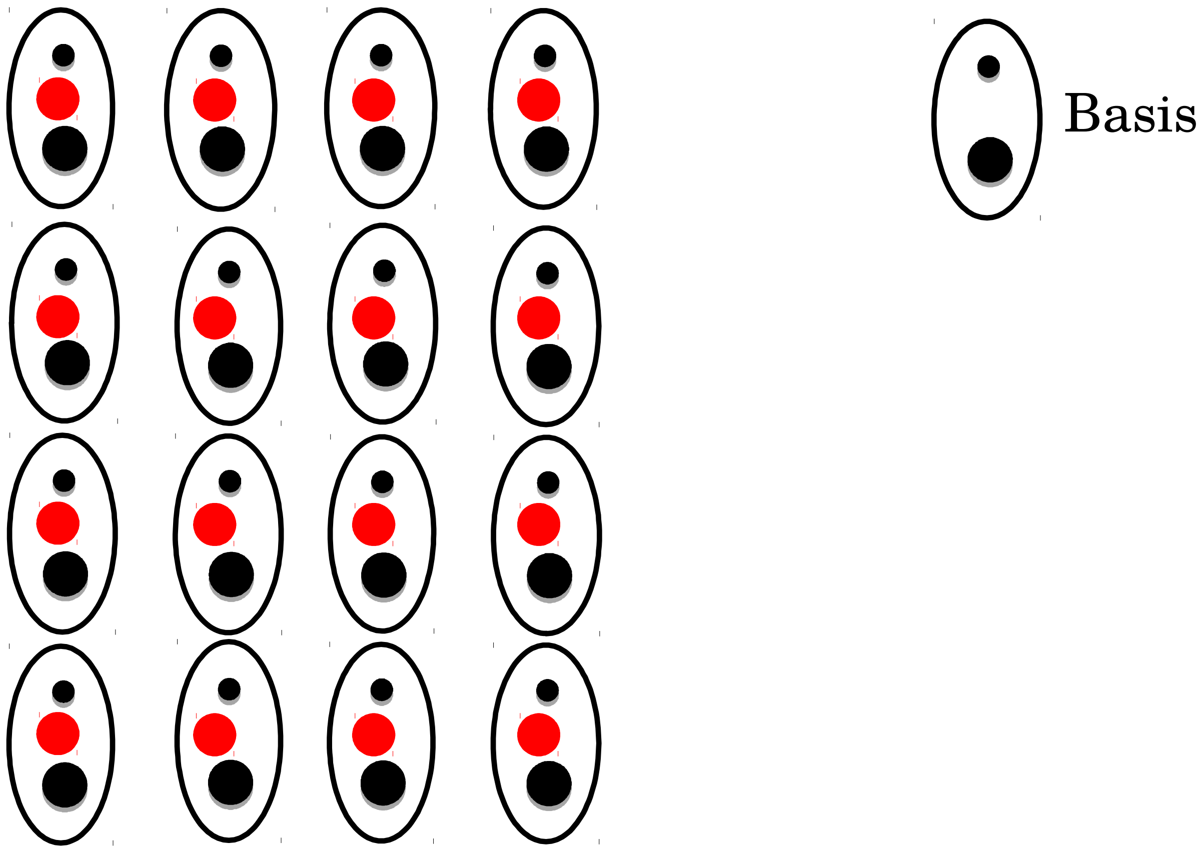


- **Crystal Lattice:** *An infinite array of imaginary points in which every point has environment as that of the other and hence one lattice point cannot be distinguished from the other.*
- **Space lattice:** *An infinite array of points in a three dimensional space such that every point has identical surrounding.*



Basis

A group of atoms (or ions) which when attached to every lattice points produces the crystal structure.

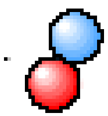


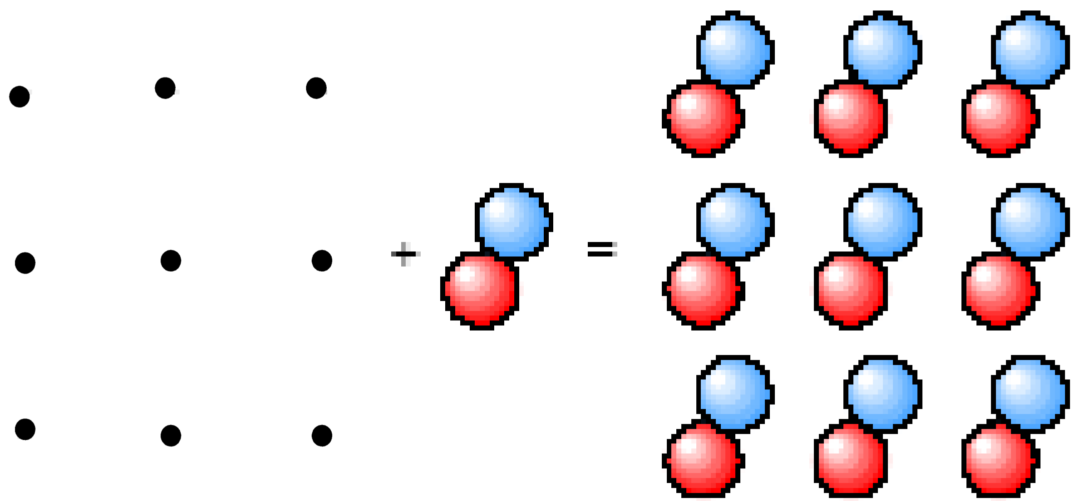
Lattice + Basis = Crystal structure

Crystal Structure

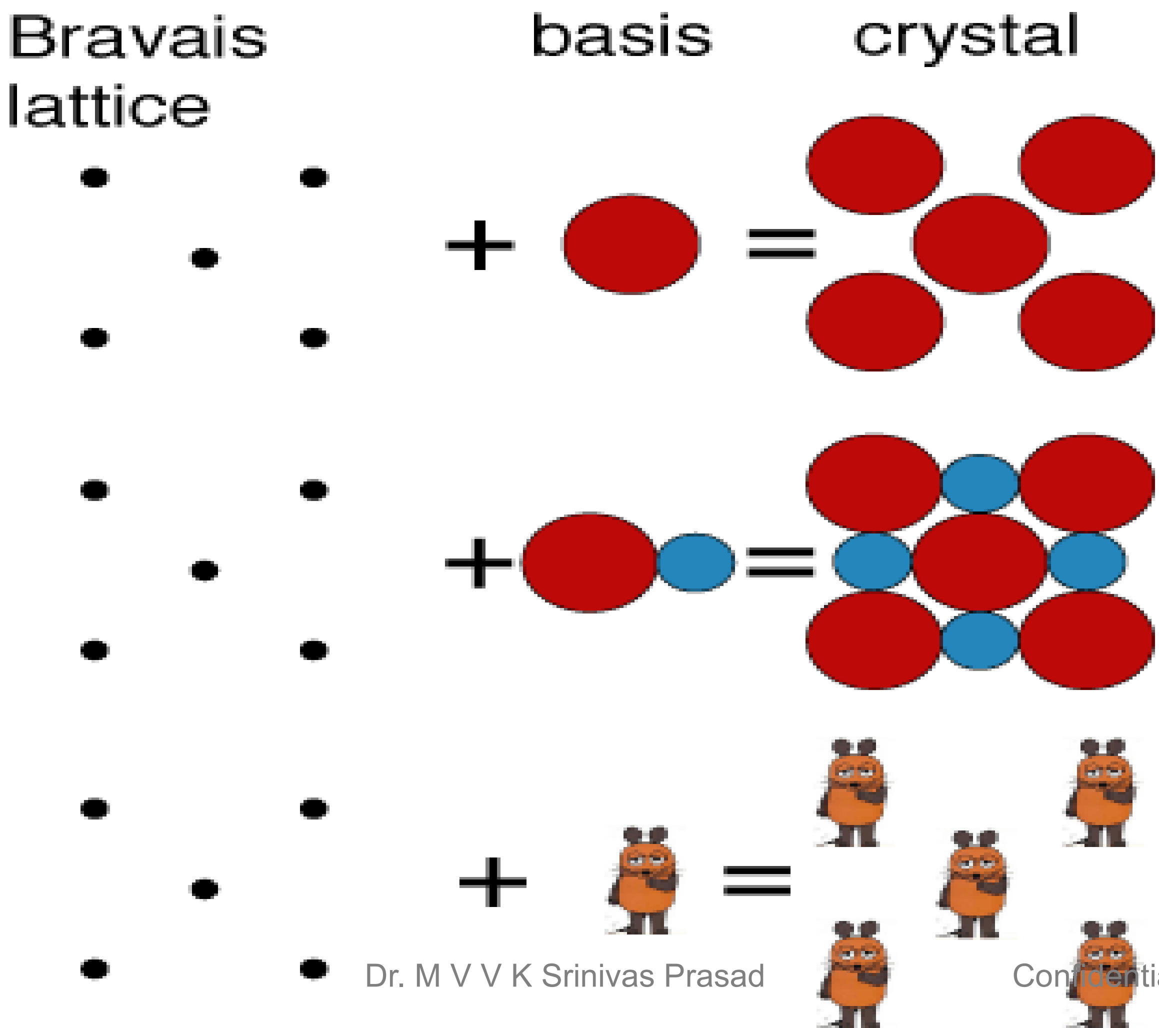
- *Crystal structure can be obtained by attaching atoms, groups of atoms or molecules which are called basis (motif) to the lattice sides of the lattice point.*

Crystal Structure = Crystal Lattice • + Basis



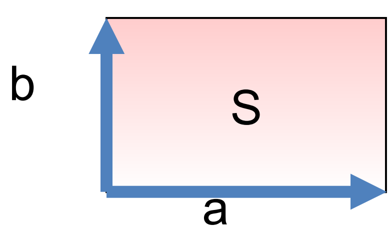


A two-dimensional Bravais lattice with different choices for the basis

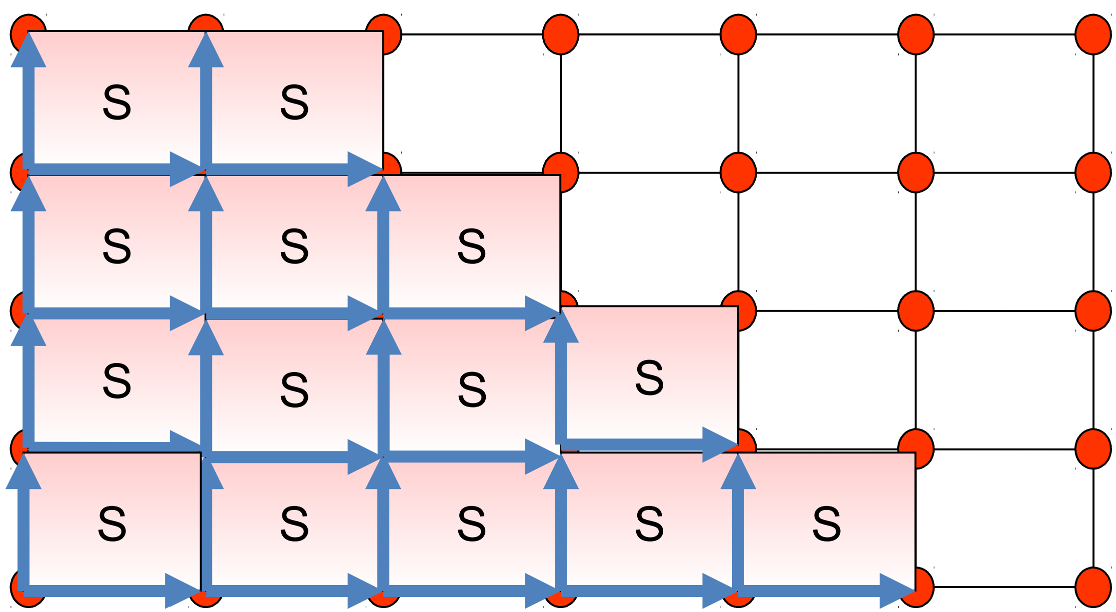


➢ **Unit Cell:** *The building block of the crystal which when translated along the three axes gives the actual crystal structure.*

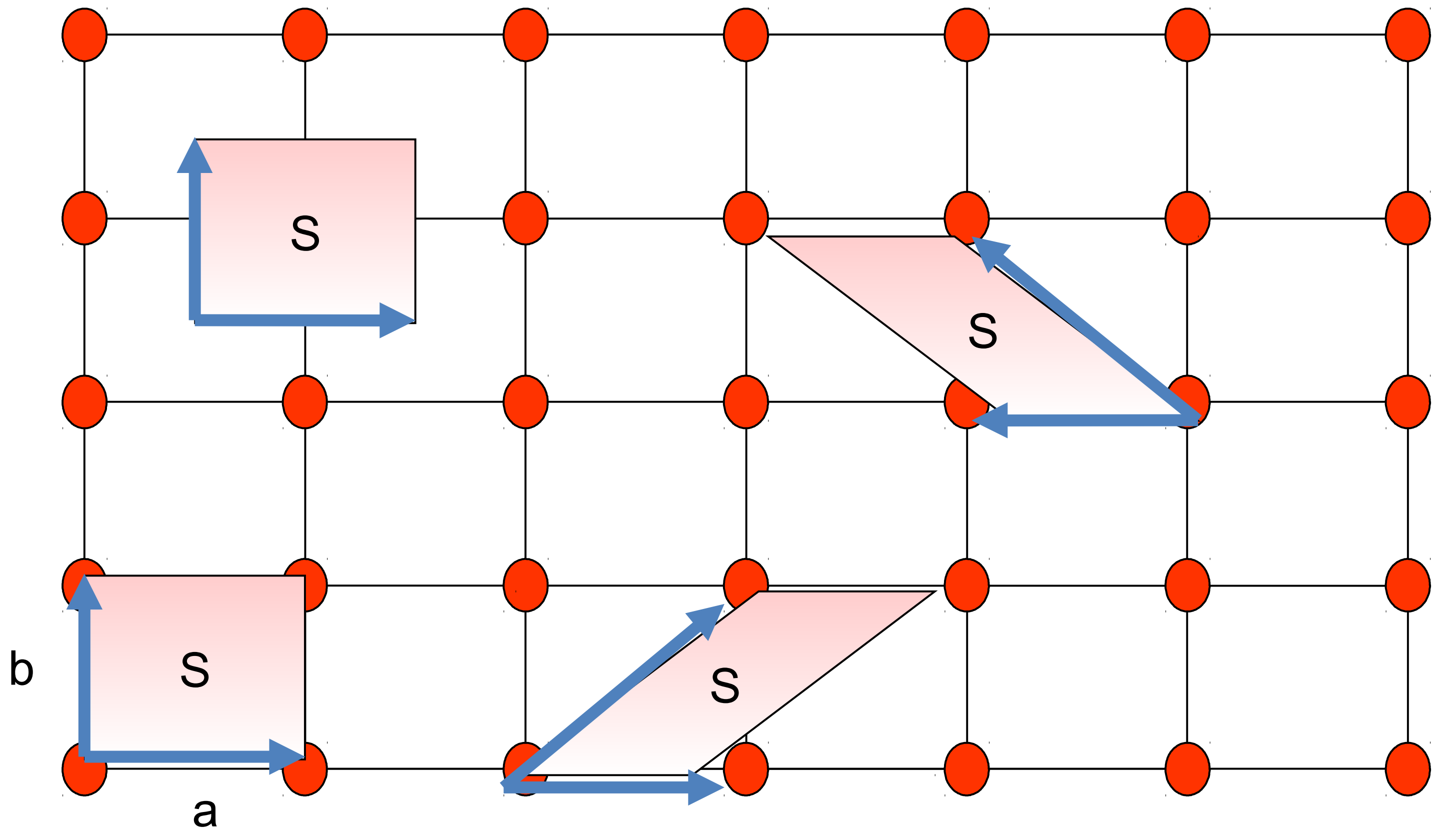
- *It should occupy a minimum volume.*
- *Smallest repeatable unit in a point lattice*
- *Choice of the Unit Cell is not unique*



Unit Cell

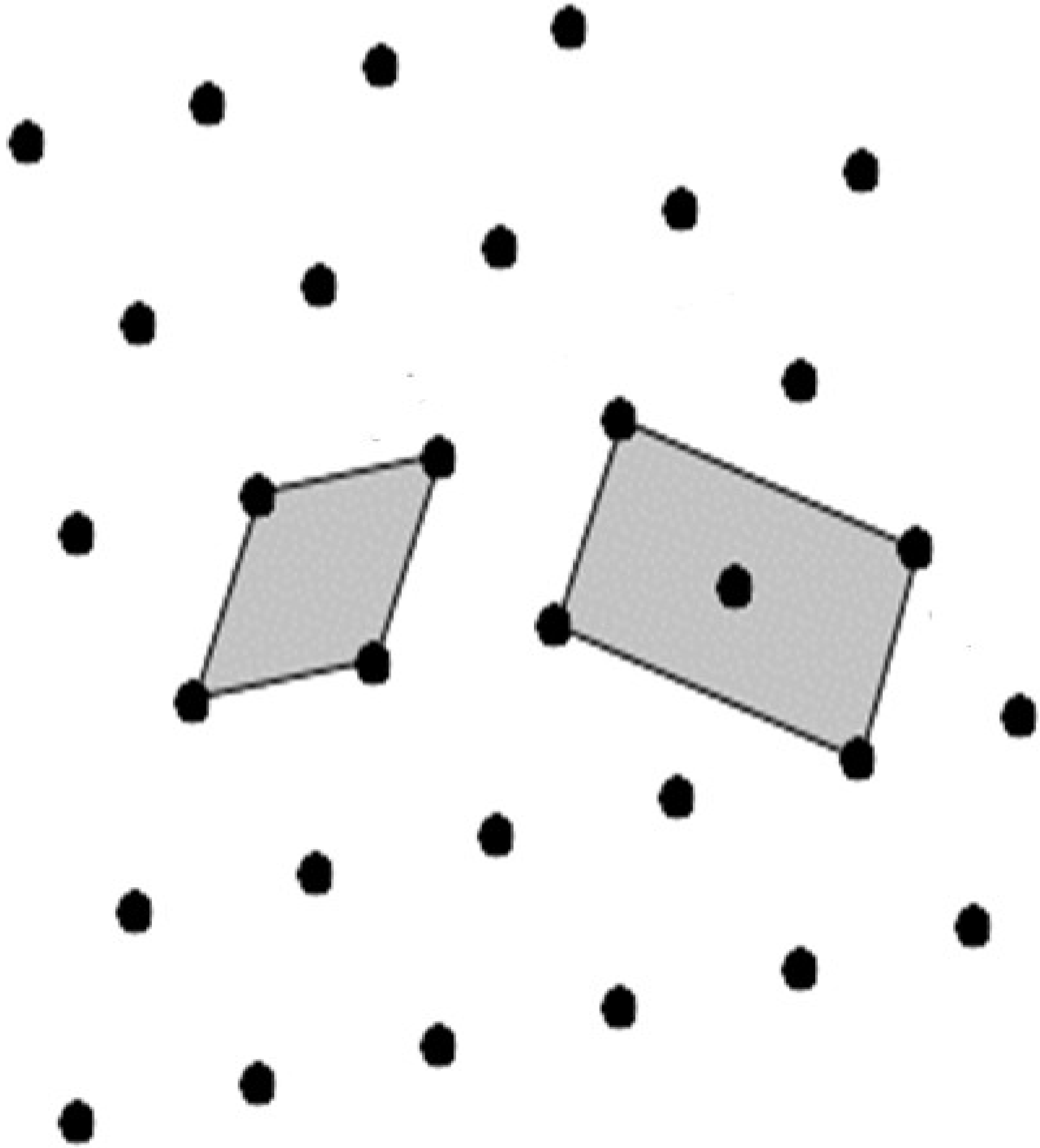


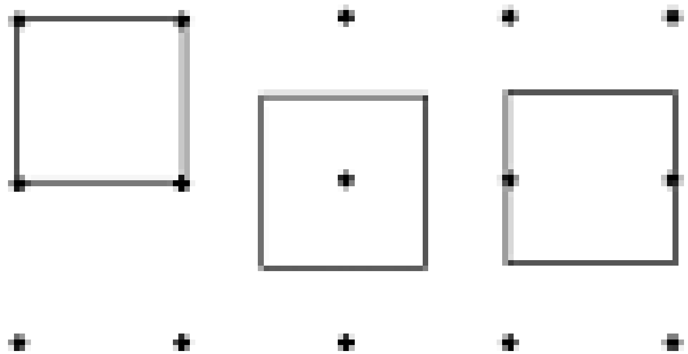
The choice of unit cell is not unique.



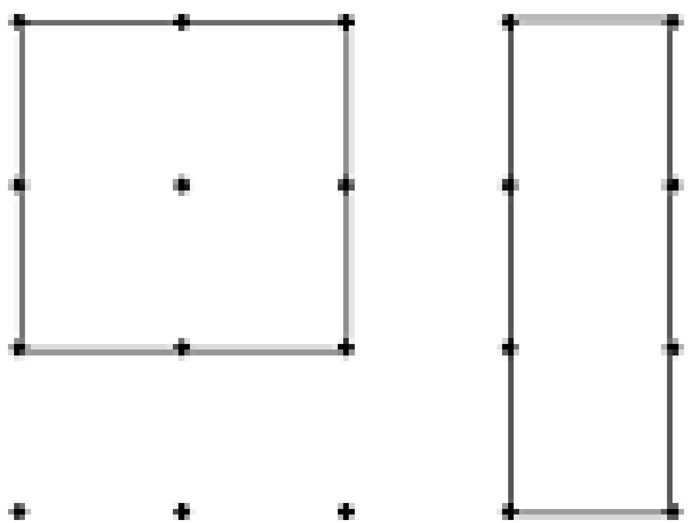
- **Primitive unit cells:** *Contains only one lattice point, in the unit cell. Example Simple Cubic (SC)*

- **Non-primitive unit cells:** *Contains more than one lattice point in the unit cell. Example Body Centered Cubic (BCC), Face Centered Cubic (FCC)*

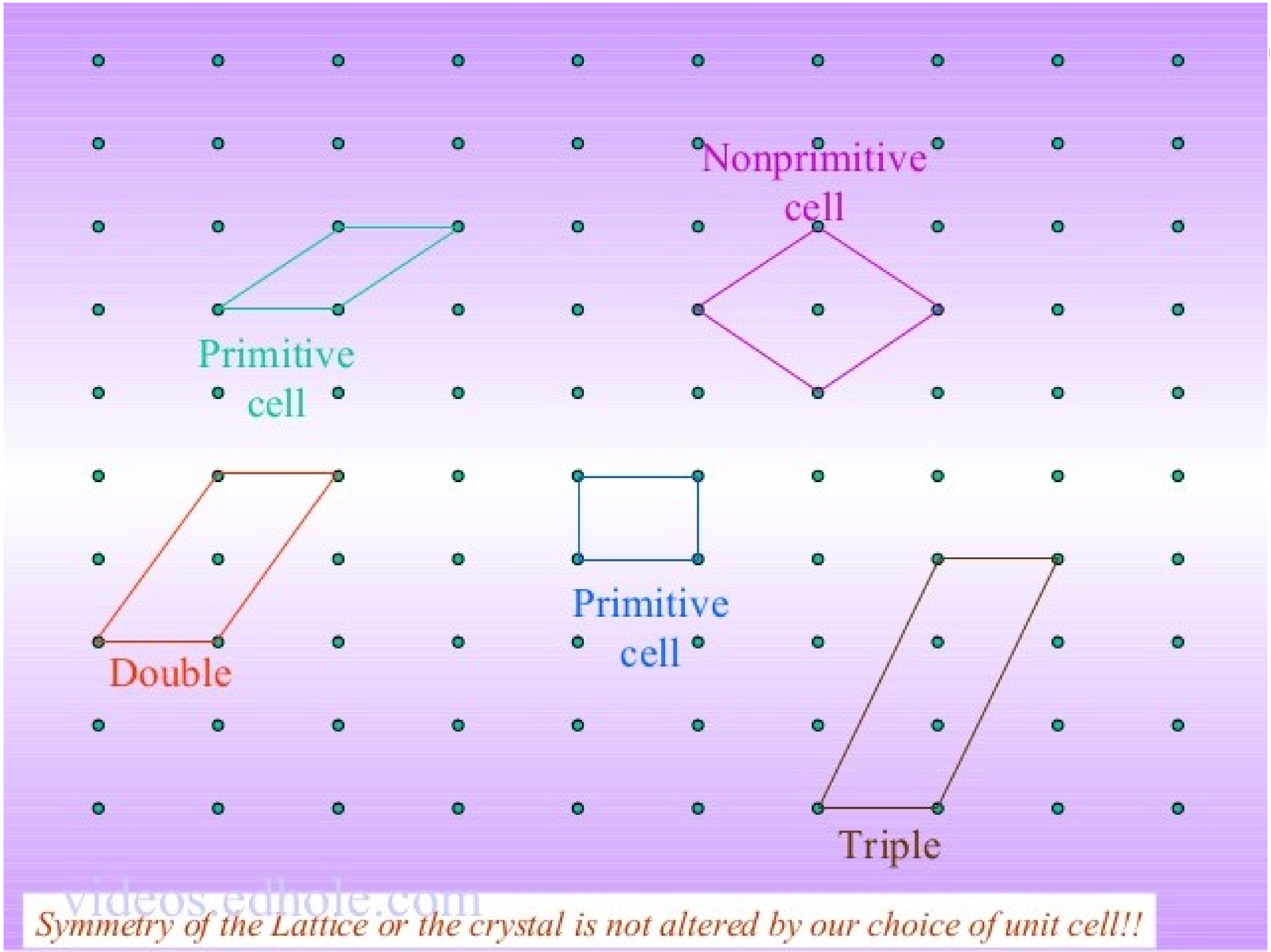


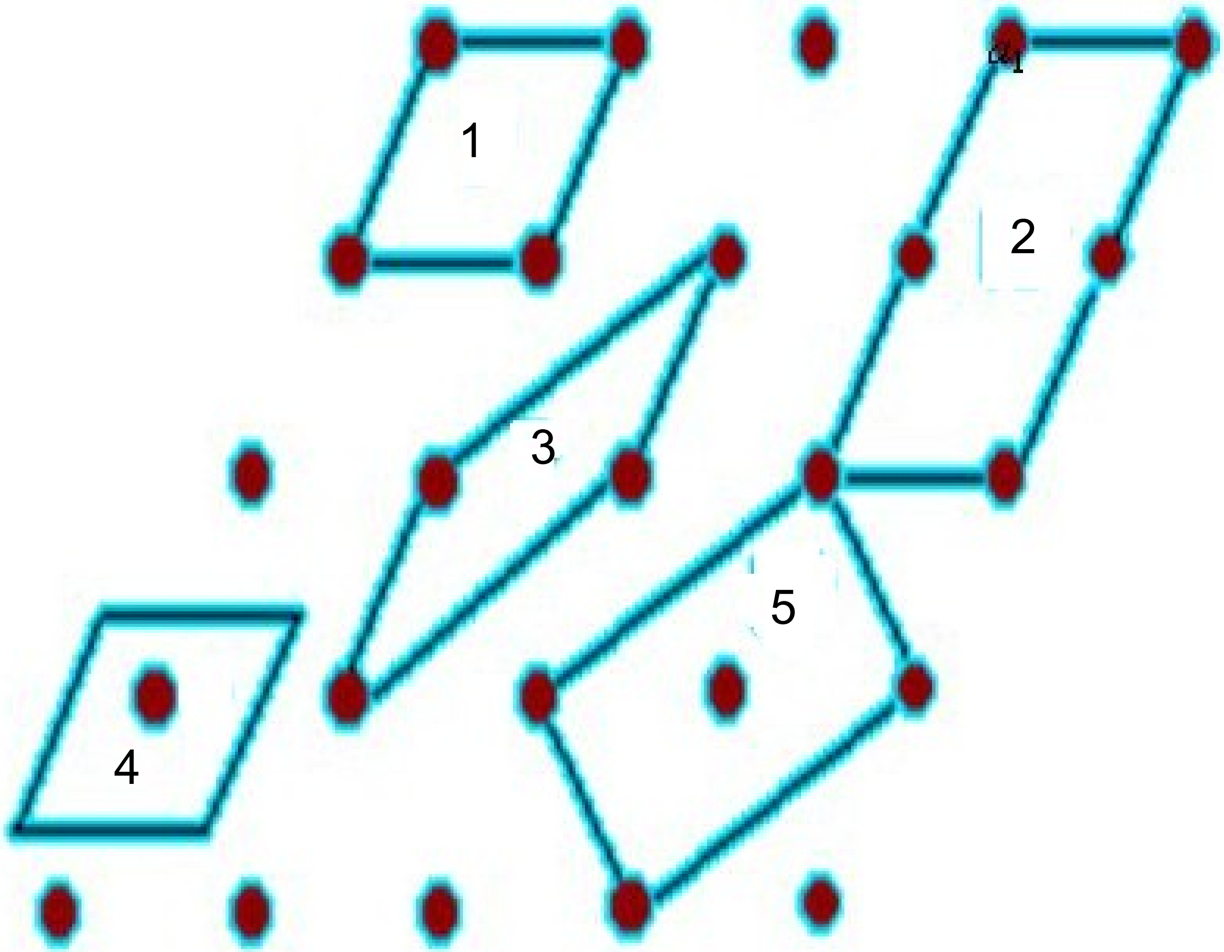


Primitive unit cells



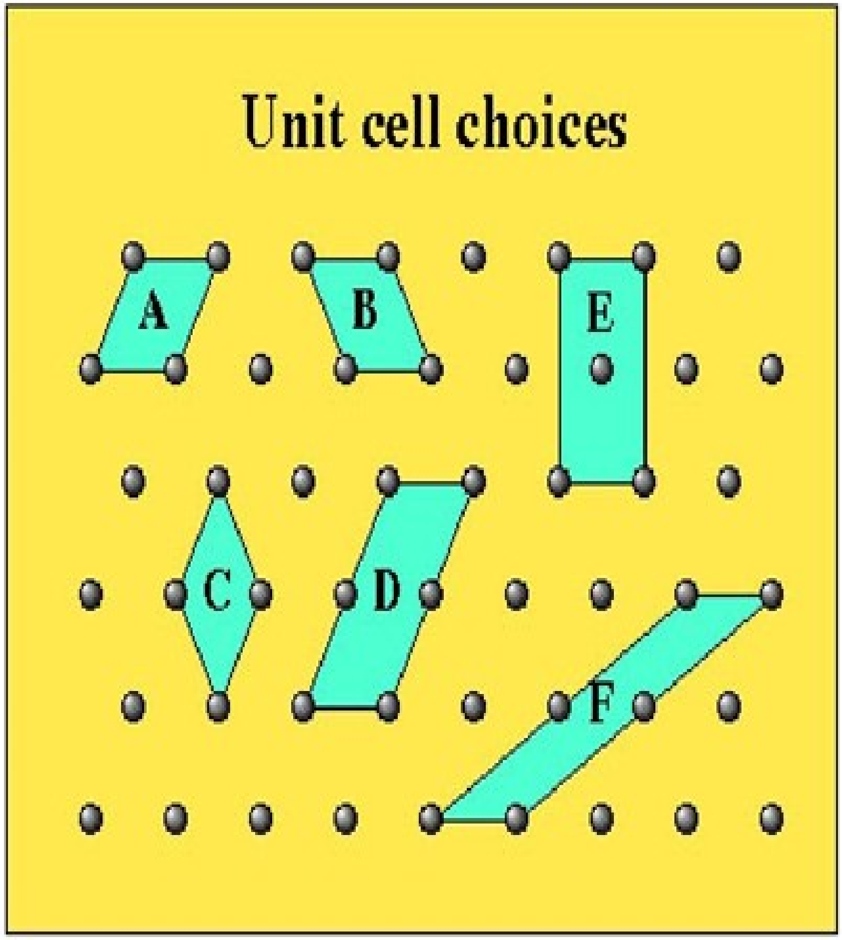
Non-primitive unit cells


Nonprimitive
cell
Primitive
cell
Double
Primitive
cell
Triple
videos.edhole.com
Symmetry of the Lattice or the crystal is not altered by our choice of unit cell!!

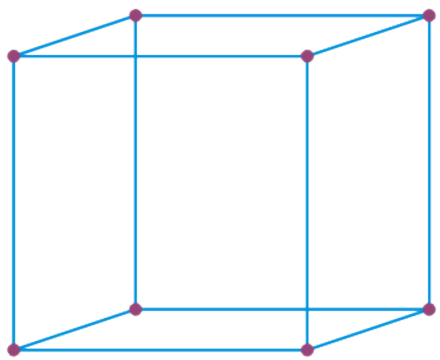

1
2
3
4
5

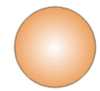
Choice of primitive cells

- Which unit cell is a good choice?
- A, B, and C are primitive unit cells. Why?
- D, E, and F are not. Why?
- Notice: the volumes of A, B, and C are the same. Also, the choice of origin is different, but it doesn't matter
- Also: There is only one lattice point in the primitive unit cells.



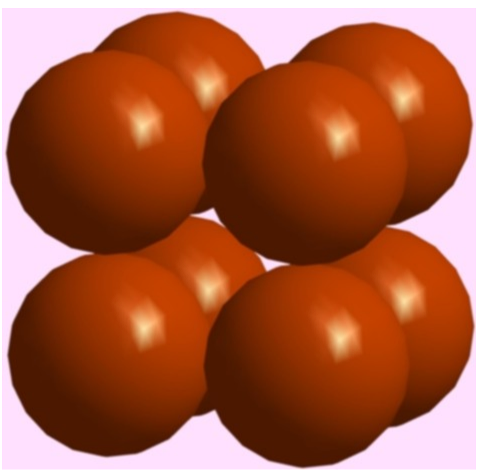
Simple Cubic (SC) Lattice + Sphere Motif





Unit cell of the SC lattice

Simple Cubic Crystal



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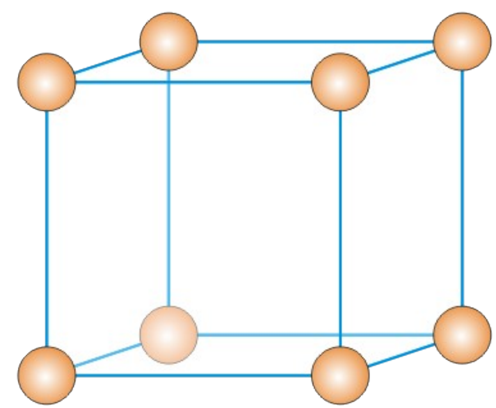
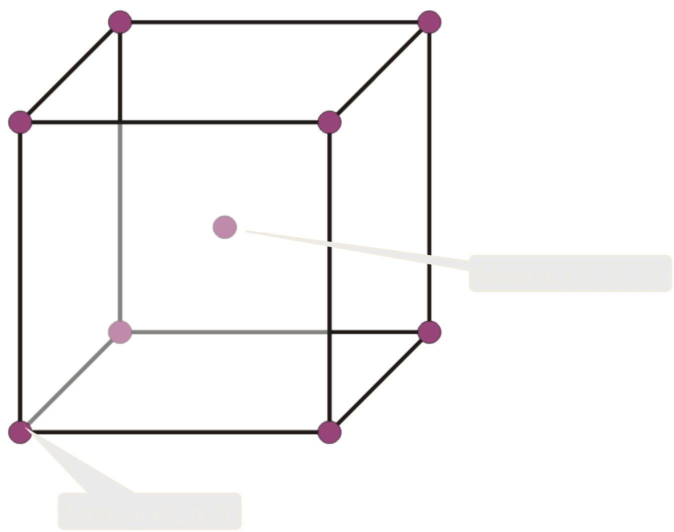
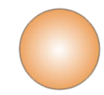


- If these spheres were *'spherical atoms'* then the atoms would be touching each other
- The kind of model shown is known as the *'Ball and Stick Model'*

Body Centred Cubic (BCC) Lattice + Sphere Motif

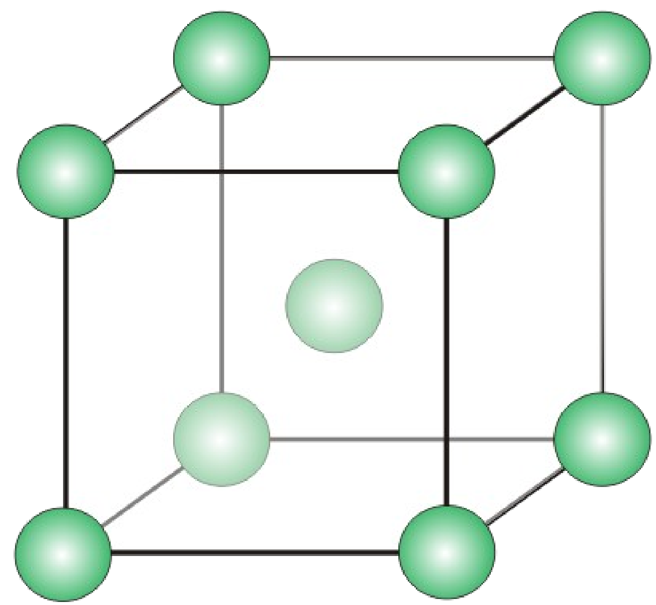


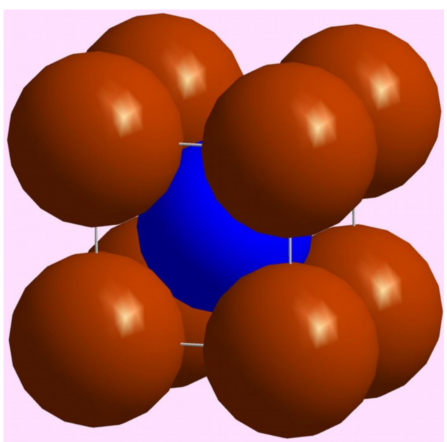


Unit cell of the BCC lattice

=

Body Centred Cubic Crystal





Space filling model

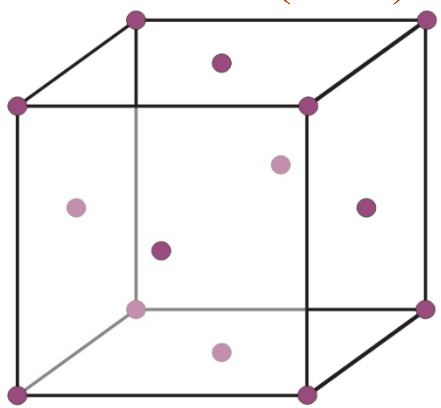
Central atom is coloured differently for better visibility

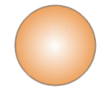
So when one usually talks about a BCC crystal what is meant is a BCC lattice decorated with a mono-atomic motif

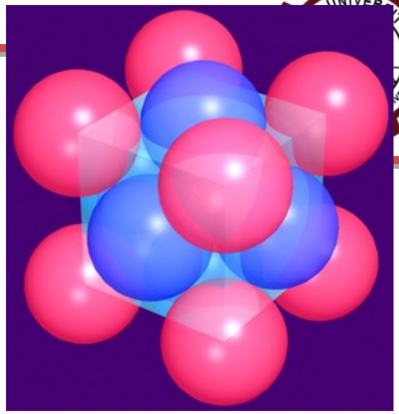
Note: BCC is a lattice and not a crystal

All atoms are identical- coloured differently for better visibility

Face Centred Cubic (FCC) Lattice + Sphere Motif





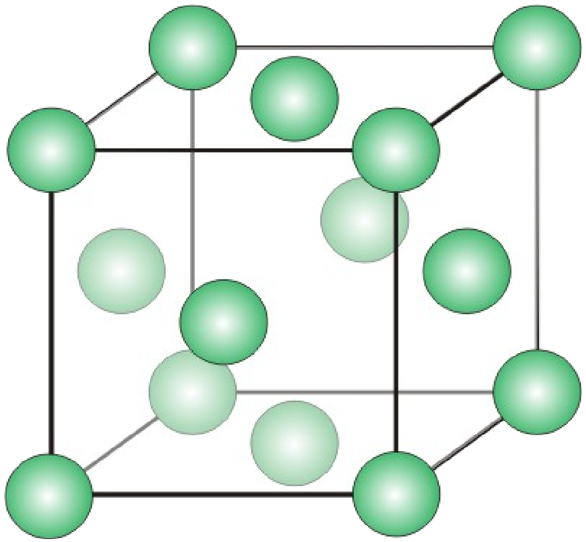


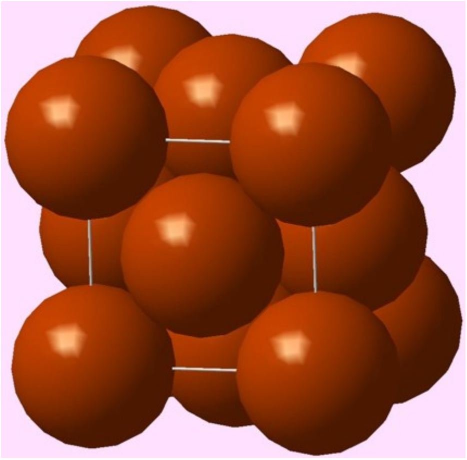
Unit cell of the FCC lattice

=

Cubic Close Packed Crystal

(Sometimes casually called the FCC crystal)





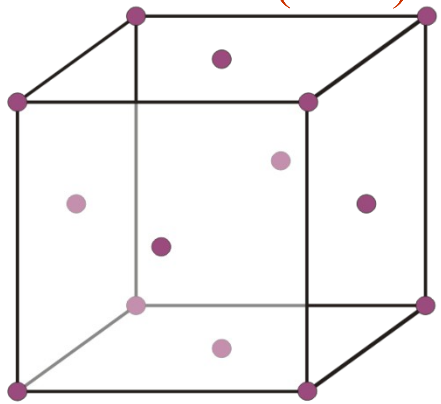
Space filling model

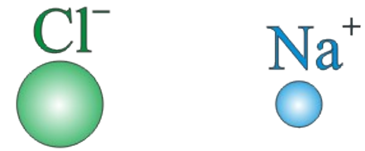
So when one talks about a FCC crystal what is meant is a FCC lattice decorated with a mono-atomic motif

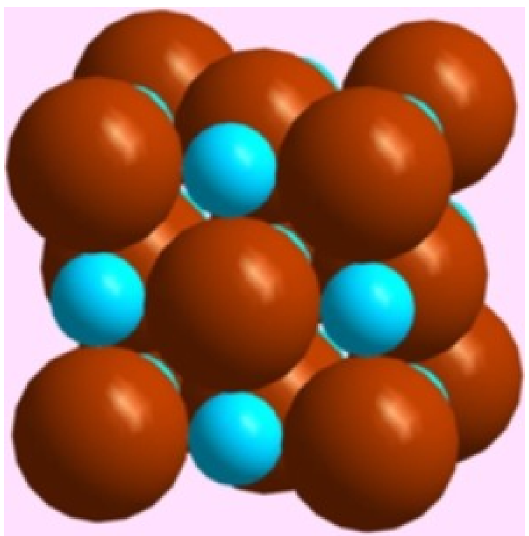
Note: FCC is a lattice and not a crystal

Video: FCC crystal

Face Centred Cubic (FCC) Lattice + Two Ion Motif







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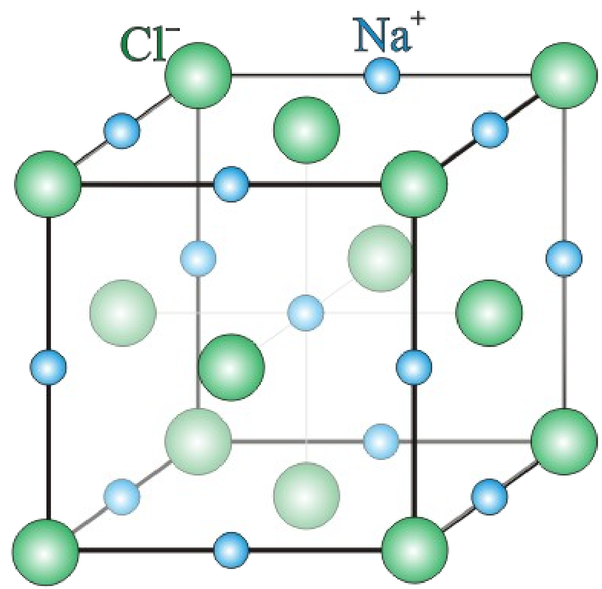
NaCl Crystal

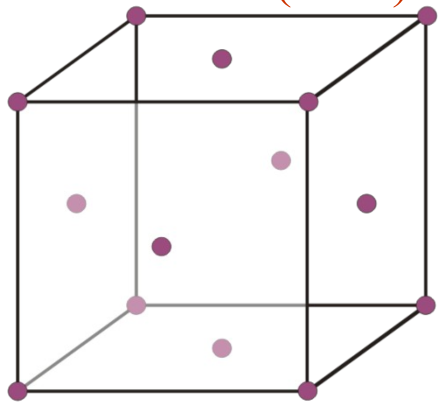


Note: This is not a close packed crystal

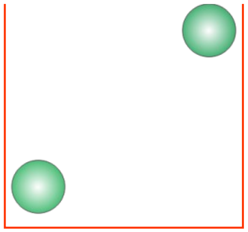
Has a packing fraction of ~0.67 *(using rigid sphere model)*

Note that the two ion motif leads to crystal which is not close packed- unlike the mono-atomic (sphere) packing case

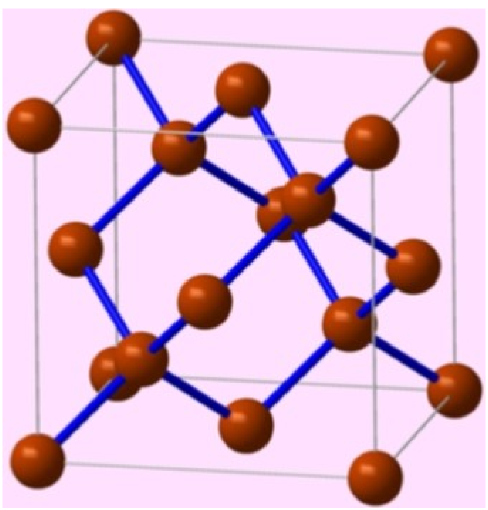
Face Centred Cubic (FCC) Lattice + Two Carbon atom Motif

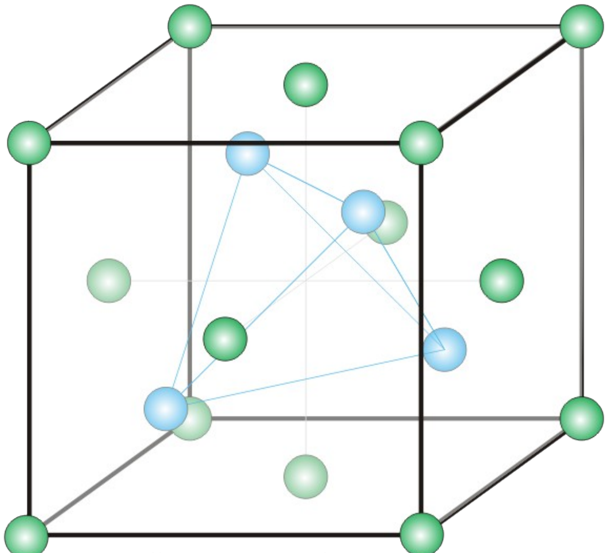


(0,0,0) & (¼, ¼, ¼)



= Diamond Cubic Crystal





All Atoms are Carbon
(coloured differently for better visibility)

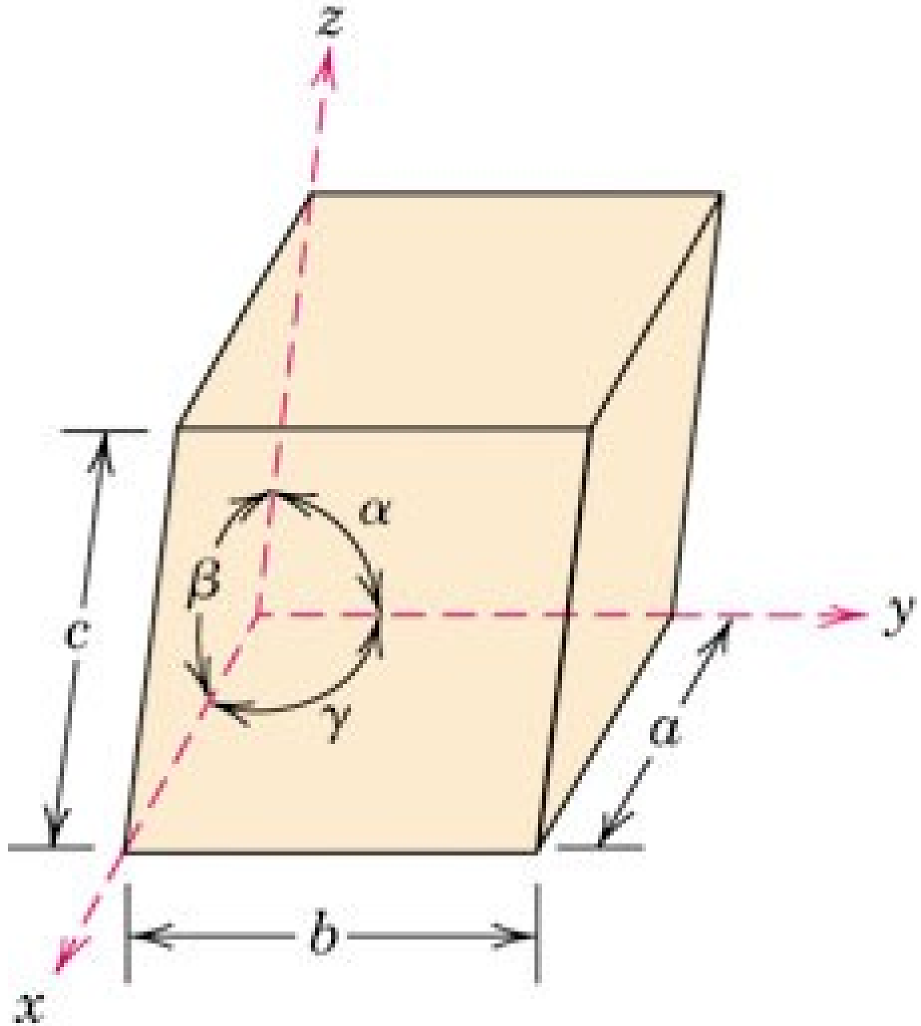
It requires a little thinking to convince yourself that the two atom motif actually sits at all lattice points!

Note: This is not a close packed crystal

There are no close packed directions in this crystal either!

Video: Diamond crystal

Crystallographic axes & Lattice parameters



Crystal systems

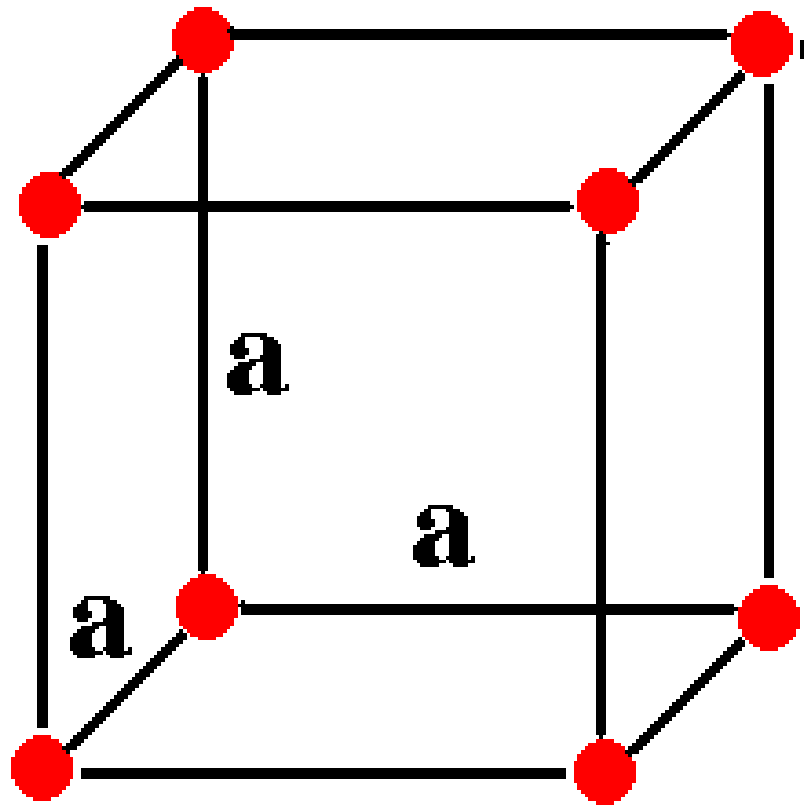
- Crystal systems
  - Cubic
  - Tetragonal
  - Orthorhombic
  - Monoclinic
  - Triclinic
  - Hexagonal
  - Trigonal (Rhombohedral)

http://www.materials.ac.uk/elearning/matter/Crystallography/3dCrystallography/7crystalsystems.html

1. Cubic Crystal System

Ex: Polonium

Other Cubic :Diamond, ZnS,Au,Cu,Ag,NaCl

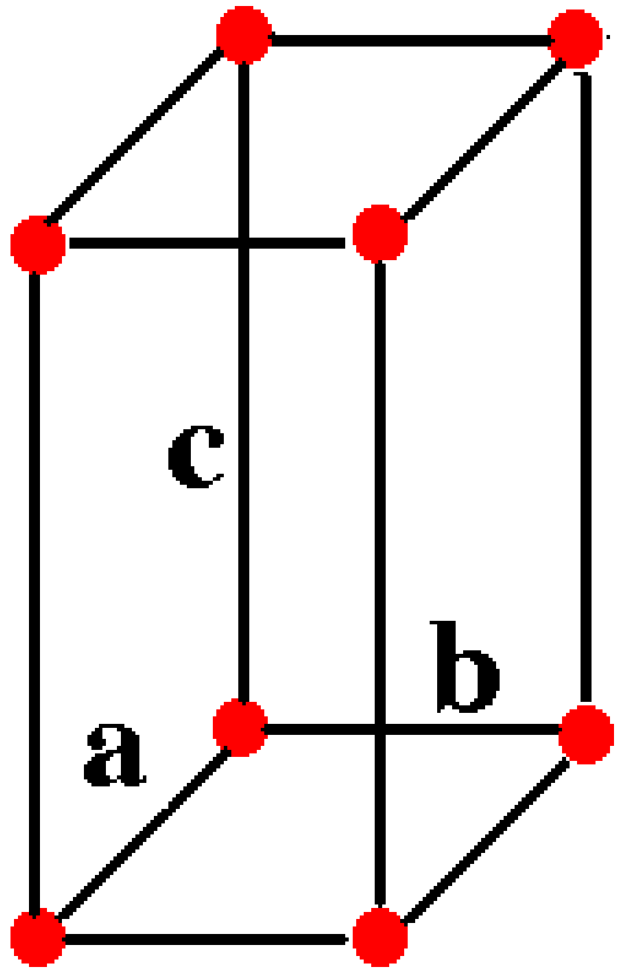


$$a = b = c$$

$$\alpha = \beta = \gamma = 90°$$

2.Tetragonal system

Ex: White Tin, SnO_4,TiO_2

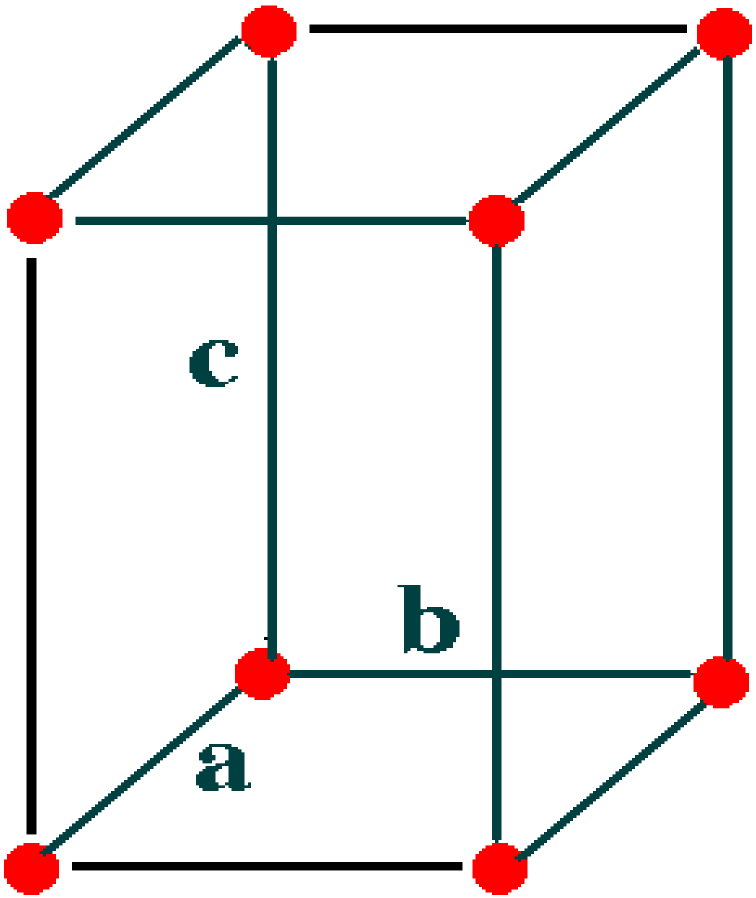


$a = b \neq c$

$\alpha = \beta = \gamma = 90°$

3. Orthorhombic system

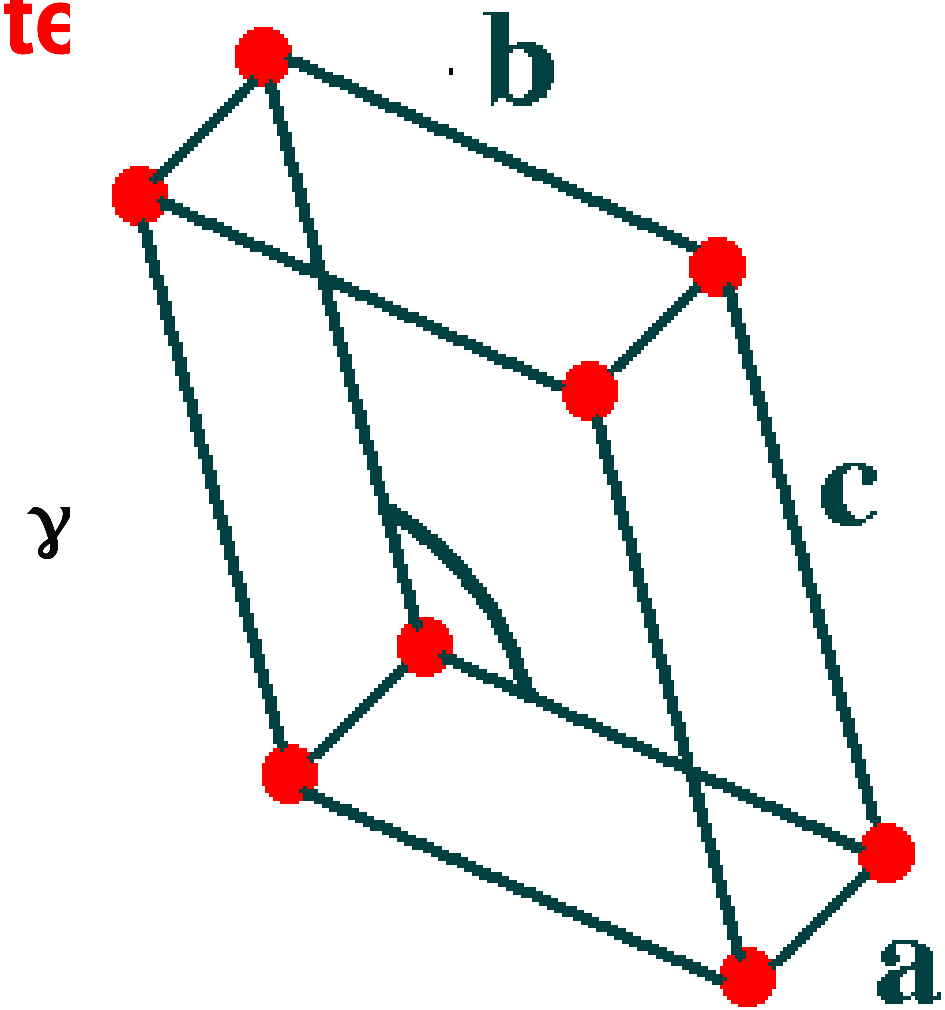
Ex: Mg_2SiO_4, $SnSO_4$, $KCl\ MgCl_2.H_2O$



$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

4. Monoclinic syste



Ex: Na_3AlF_6,$BaVO_4$

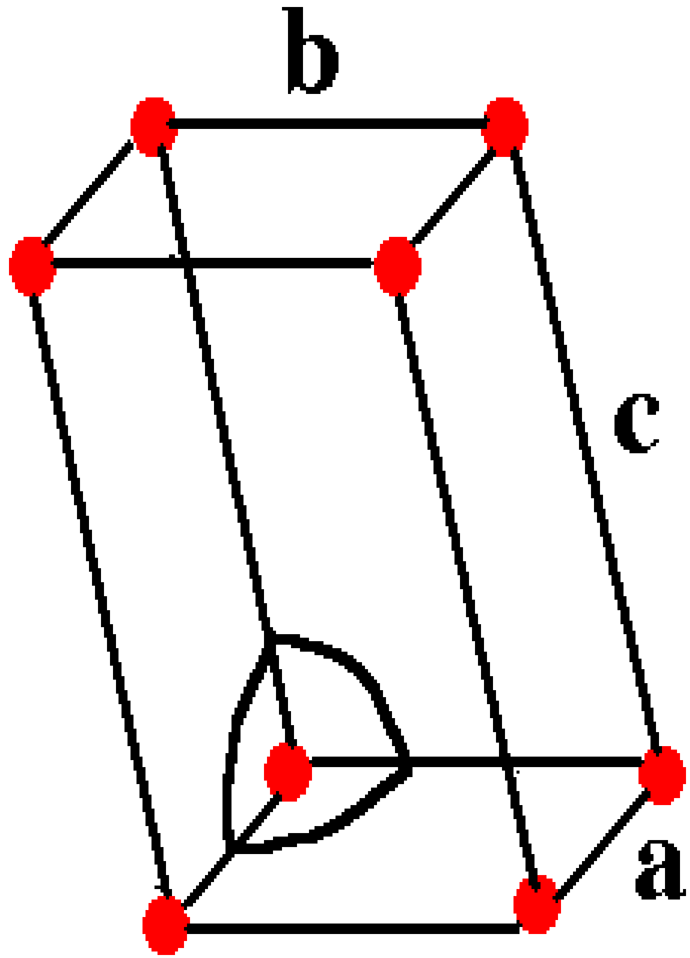
$Na_2B_4O_7.10\ H_2O$

$a \neq b \neq c$

$\alpha = \gamma = 90°, \beta \neq 90°$

5. Triclinic system

Ex: $K_2Cr_2O_7, H_3BO_3$

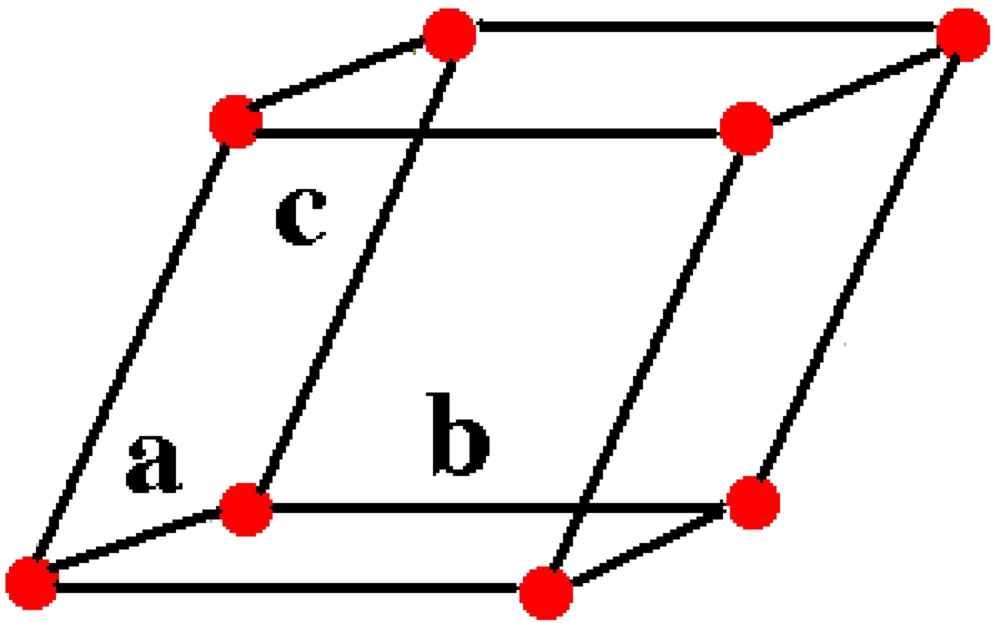


$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90°$

6. Rhombohedral (Trigonal) system

Ex: Calcite($CaCO_3$),
As, Sb, Bi ,

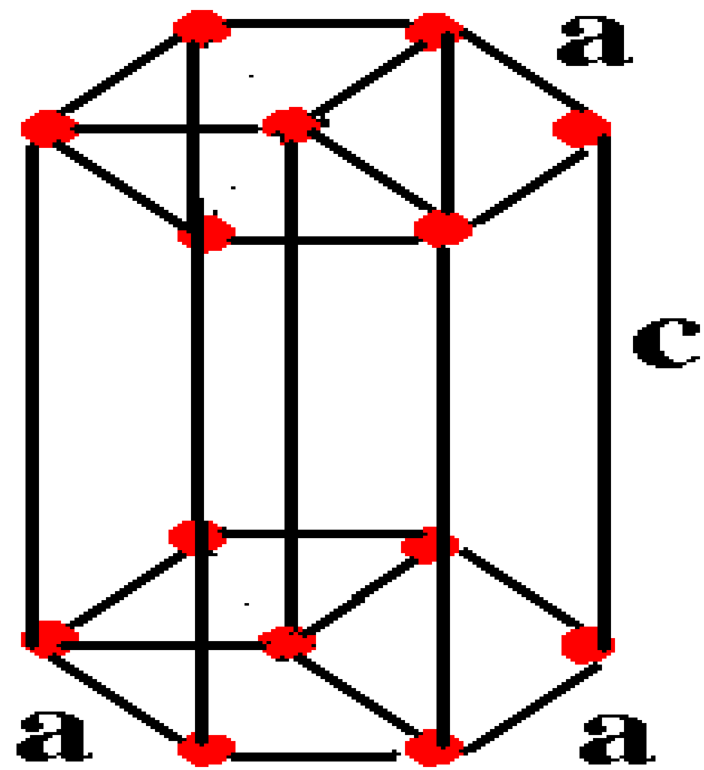


$$\boxed{a = b = c}$$

$$\boxed{\alpha = \beta = \gamma \neq 90^\circ}$$

7. Hexagonal system

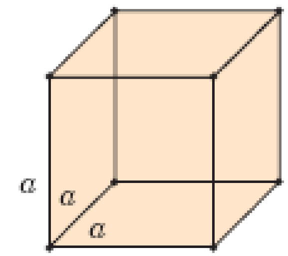
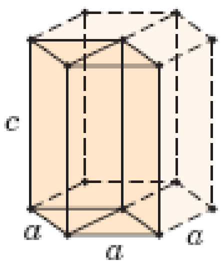
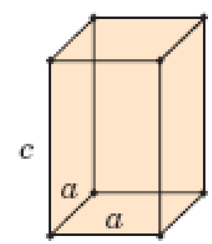
Ex: Quartz (SiO_2), AgI, ZnO



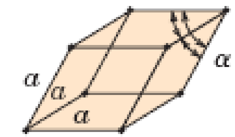
$a = b \neq c$

$\alpha = \beta = 90°, \gamma = 120°$

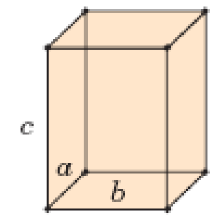
Table 3.2 Lattice Parameter Relationships and Figures Showing Unit Cell Geometries for the Seven Crystal Systems

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	

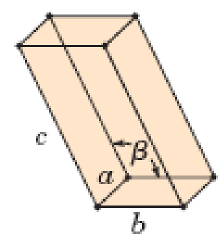
Rhombohedral (Trigonal) $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$



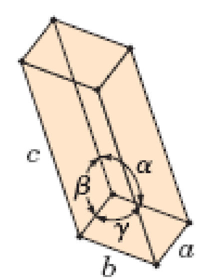
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$



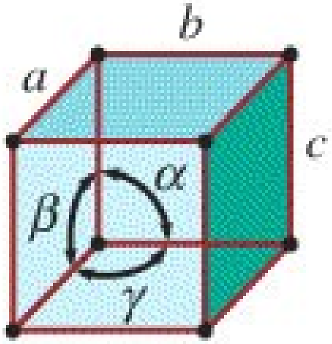
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$



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



Seven Types of Unit Cells

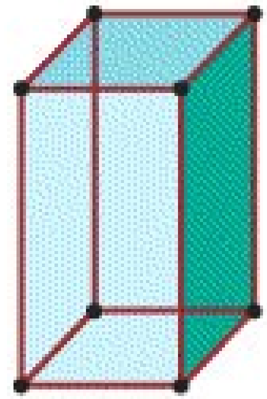


Simple cubic

$a = b = c$

$\alpha = \beta = \gamma = 90^\circ$

Nacl &CaF2

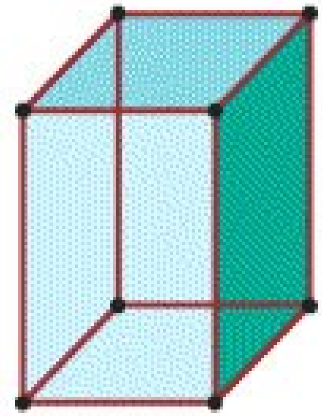


Tetragonal

$a = b \neq c$

$\alpha = \beta = \gamma = 90^\circ$

NiSO4 &SnO2

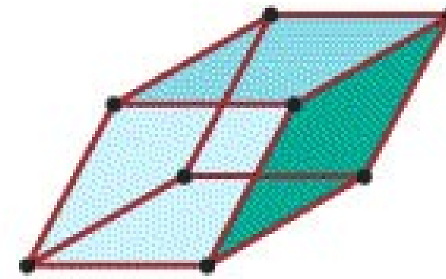


Orthorhombic

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90^\circ$

KNO3,BaSO4

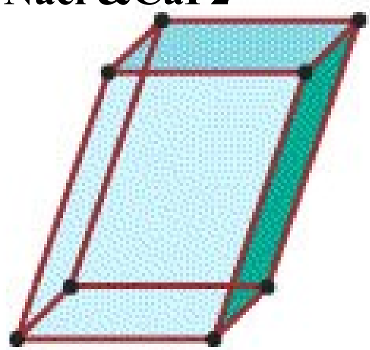


Rhombohedral

$a = b = c$

$\alpha = \beta = \gamma \neq 90^\circ$

Quartz,Calcite

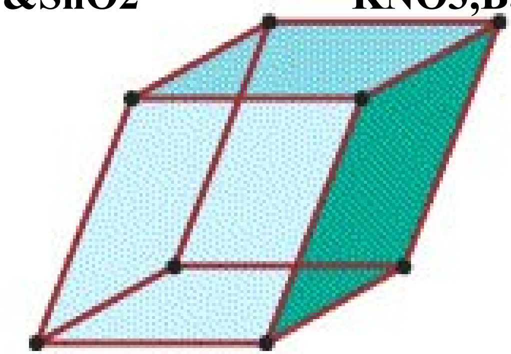


Monoclinic

$a \neq b \neq c$

$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$

Na2SO4,FeSO4

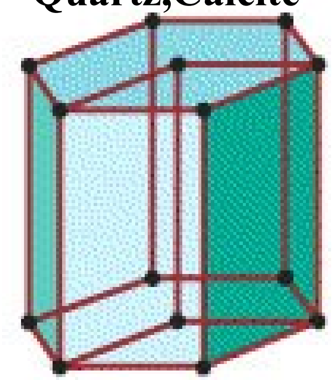


Triclinic

$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90^\circ$

CuSO4,K2Cr2O7



Hexagonal

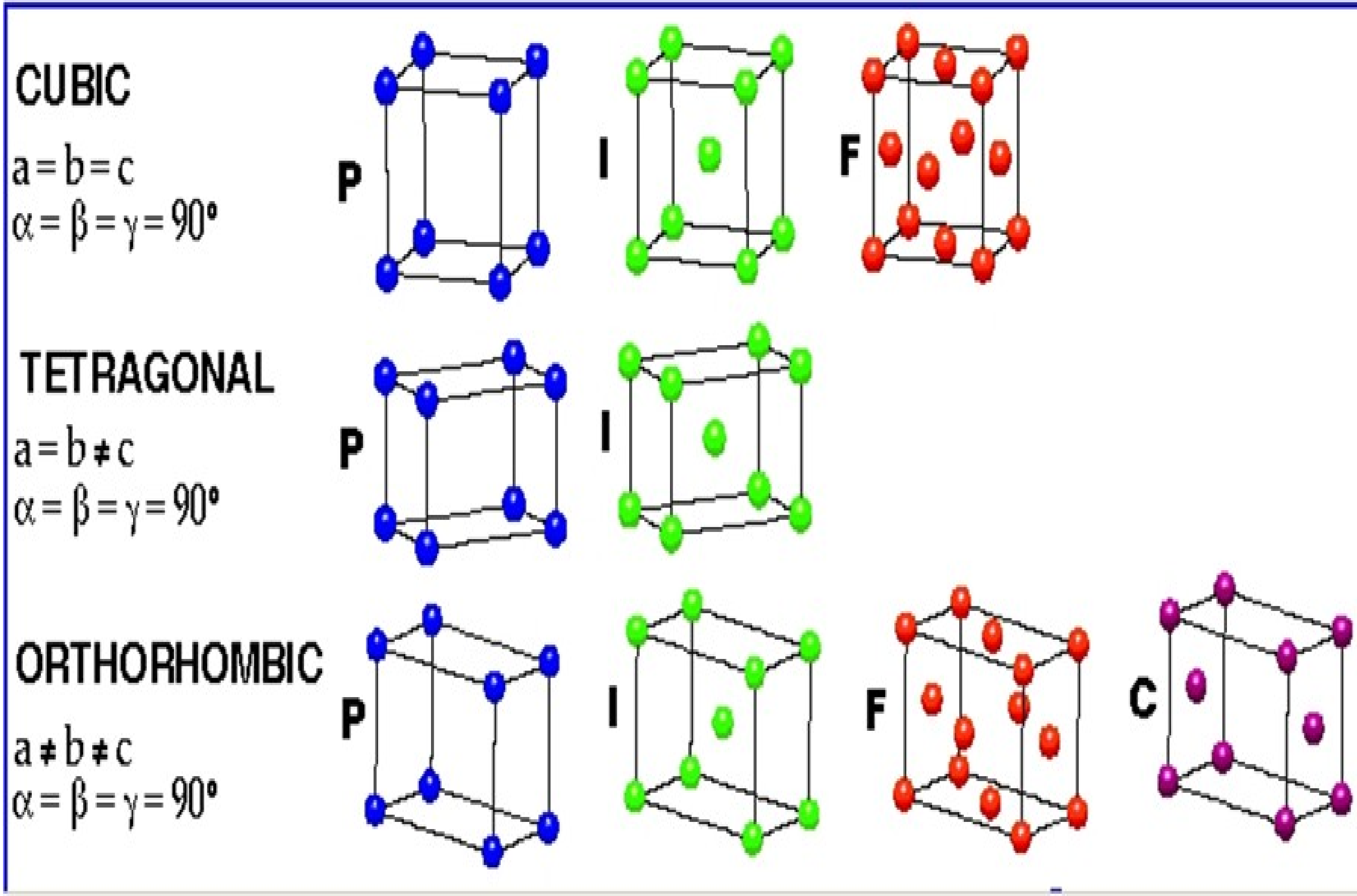
$a = b \neq c$

$\alpha = \beta = 90^\circ, \gamma = 120^\circ$

SiO2,AgI

Type	**Description**	**Symbol**
Primitive	Lattice points on corners only.	P
Body-Centered	Lattice points on corners as well as in the center of the unit cell body.	I
Face Centered	Lattice points on corners as well as in the centers of all faces.	F
Base Centered	Lattice points on corners as well as on the center of top & bottom face.	C

Summary: Fourteen Bravais Lattices in Three Dimensions


CUBIC
a = b = c
α = β = γ = 90°
P
I
F
TETRAGONAL
a = b ≠ c
α = β = γ = 90°
P
I
ORTHORHOMBIC
a ≠ b ≠ c
α = β = γ = 90°
P
I
F
C

Fourteen Bravais Lattices …

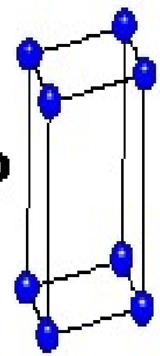
HEXAGONAL

$a = b \neq c$

$\alpha = \beta = 90°$

$\gamma = 120°$

P

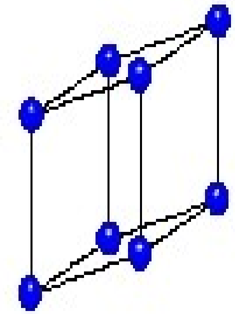


TRIGONAL

$a = b = c$

$\alpha = \beta = \gamma \neq 90°$

P



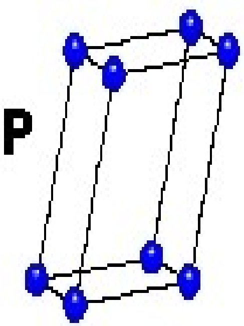
MONOCLINIC

$a \neq b \neq c$

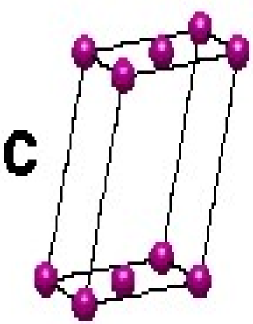
$\alpha = \gamma = 90°$

$\beta \neq 120°$

P



C

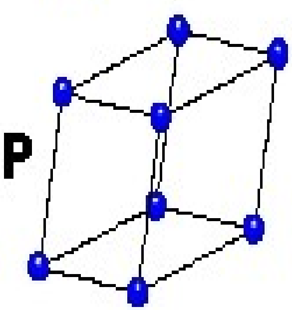


TRICLINIC

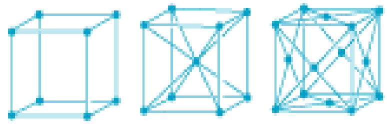
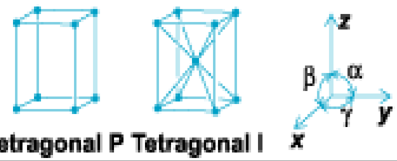
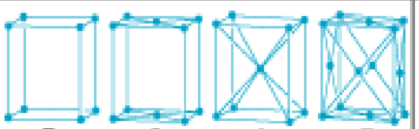
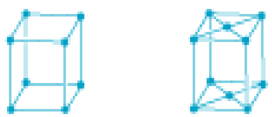
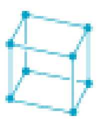
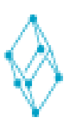
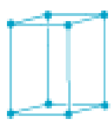
$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90°$

P



4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ **14 Bravais Lattices**

Bravais lattice cells	Axes and interaxial angles	Examples
 Cubic P Cubic I Cubic F	Three axes at right angles; all equal: $a = b = c$; $\alpha = \beta = \gamma = 90^\circ$	Copper (Cu), silver (Ag), sodium chloride (NaCl)
 Tetragonal P Tetragonal I	Three axes at right angles; two equal: $a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$	White tin (Sn), rutile (TiO_2), β-spodumene ($LiAlSi_2O_6$)
 P C I F Orthorhombic	Three axes at right angles; all unequal: $a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$	Gallium (Ga), perovskite ($CaTiO_3$)
 Monoclinic P Monoclinic C	Three axes, one pair not at right angles, of any lengths: $a \neq b \neq c$; $\alpha = \gamma = 90^\circ \neq \beta$	Gypsum ($CaSO_4 \cdot 2H_2O$)
 Triclinic P	Three axes not at right angles, of any lengths: $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90^\circ$	Potassium chromate (K_2CrO_7)
 Trigonal R (rhombohedral)	Rhombohedral: three axes equally inclined, not at right angles; all equal: $a = b = c$; $\alpha = \beta = \gamma \neq 90^\circ$	Calcite ($CaCO_3$), arsenic (As), bismuth (Bi)
 Trigonal and hexagonal C (or P)	Hexagonal: three equal axes coplanar at 120°, fourth axis at right angles to these: $a_1 = a_2 = a_3 \neq c$; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	Zinc (Zn), cadmium (Cd), quartz (SiO_2) [P]

14 Bravais lattices

Crystal system	Primitive (P)	Body centered (I)	Face centered (F)	Base centered (C)
Cubic	✓	✓	✓	✗
Tetragonal	✓	✓	✗	✗
Orthorhombic	✓	✓	✓	✓
Monoclinic	✓	✗	✗	✓
Triclinic	✓	✗	✗	✗
Rhombohedral	✓	✗	✗	✗
Hexagonal	✓	✗	✗	✗

[Click here for animation for 14 Bravais lattices]

Parameters Determining the Crystal Structure of the Materials

- **Number of atoms per unit cell or effective number of atoms**: *The total number of atoms present in a unit cell. Ex: SC: 1, BCC: 2, FCC: 3*

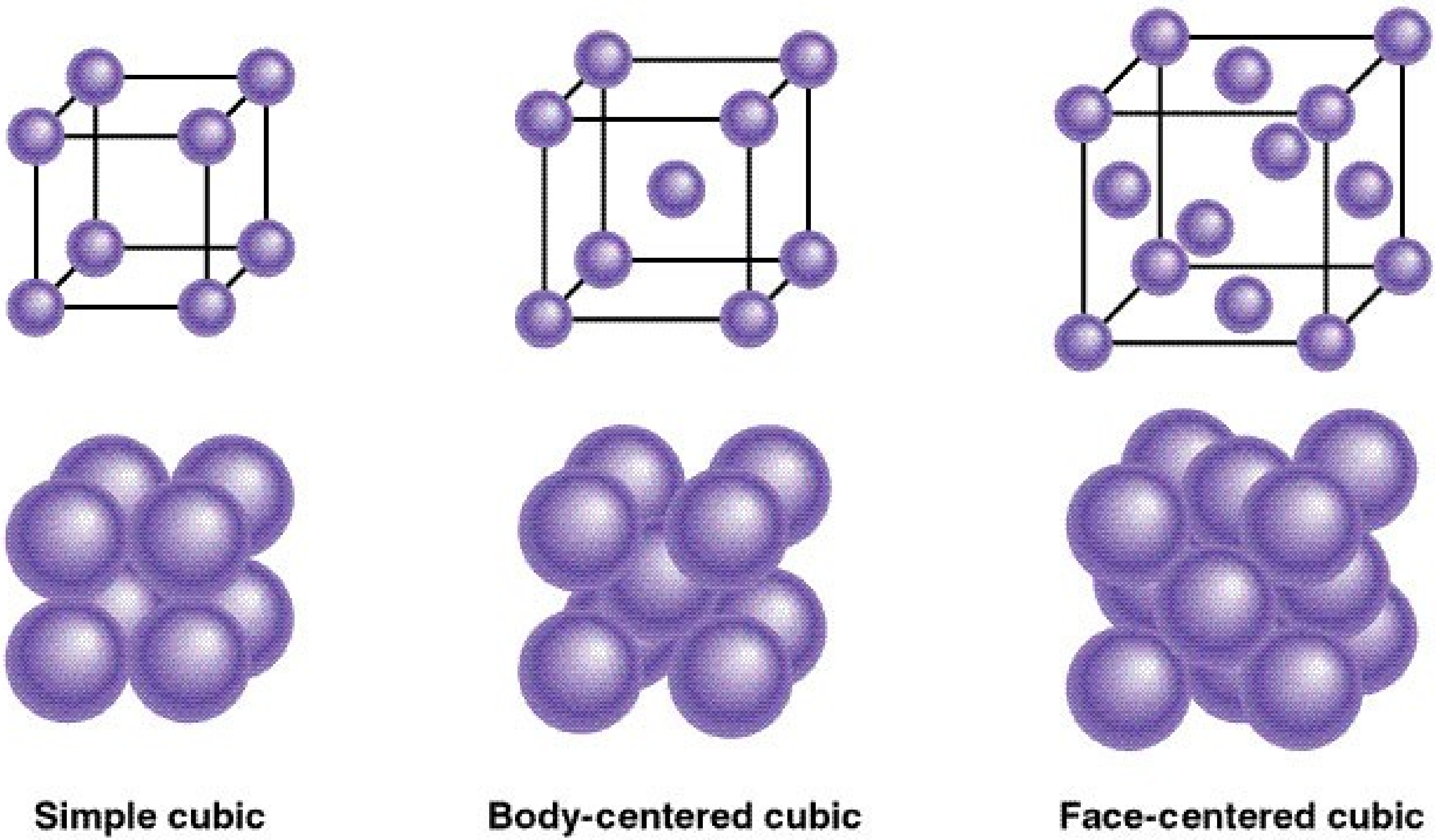
- **Atomic Radius**: *It is the half the distance between any two nearest neighbor atoms which have direct contact with each other.*

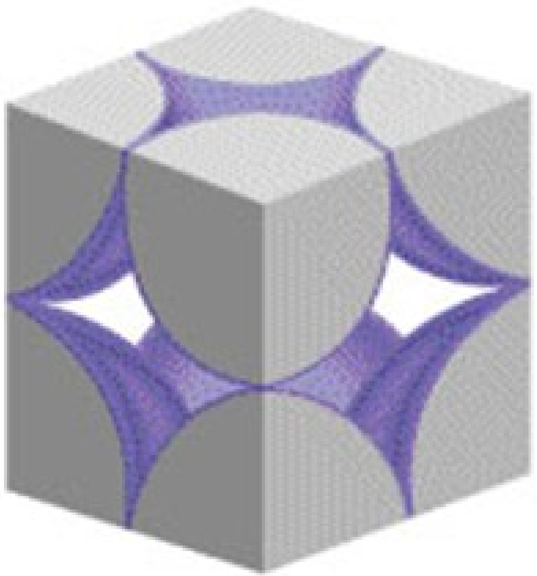
- **Coordination Number (N):** *It is the number of nearest neighboring and equidistance atoms to a particular atom.*

- **Atomic Packing Factor or Packing Fraction:** *It is the ratio of volume occupied by the atoms in a unit cell to the total volume of the unit cell.*

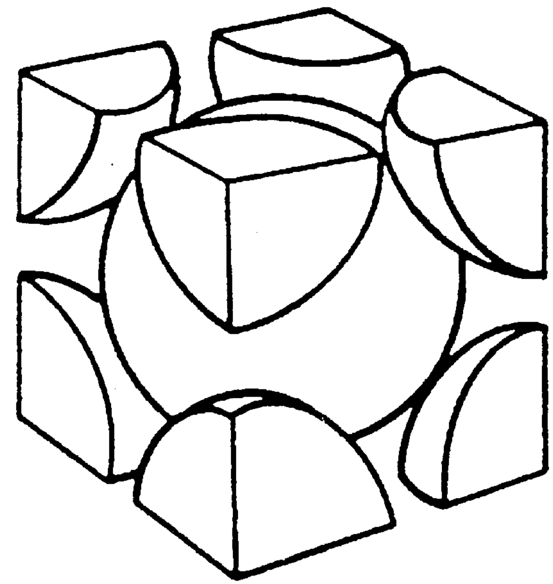
$$\text{Atomic Packing Factor (APF)} = \frac{\text{Volume occupied by the atoms in the unit cell}}{\text{Total Volume of the unit cell}}$$

Three Types of Cubic Cells

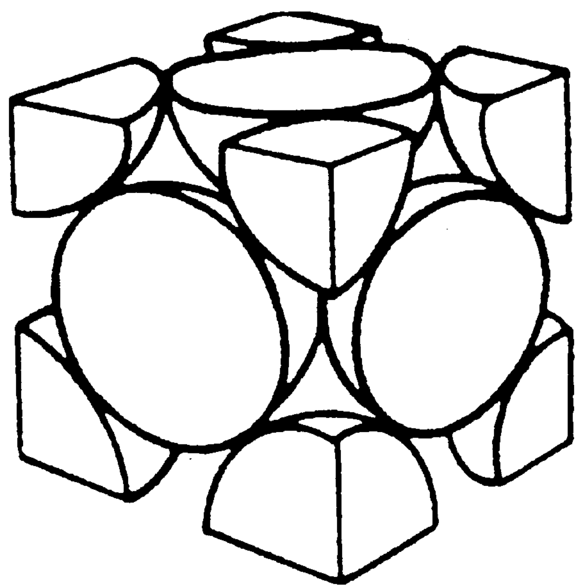




Simple Cubic
Or
Primitive



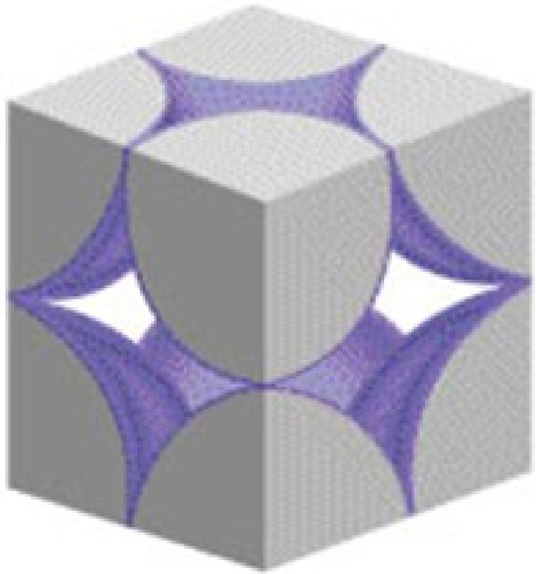
Body Centred Cubic
FCC



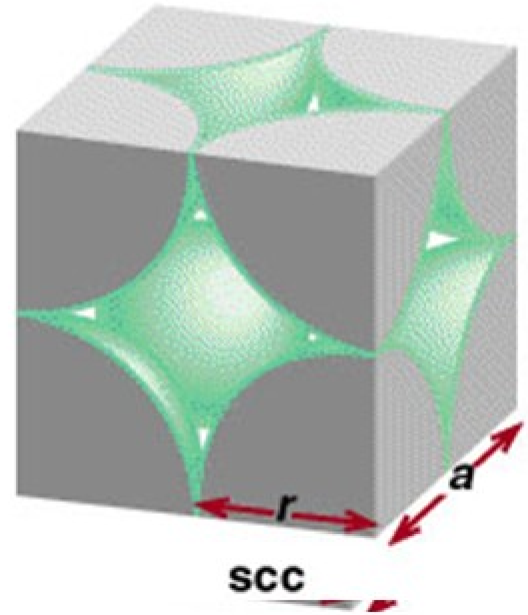
Face Centred Cubic
FCC

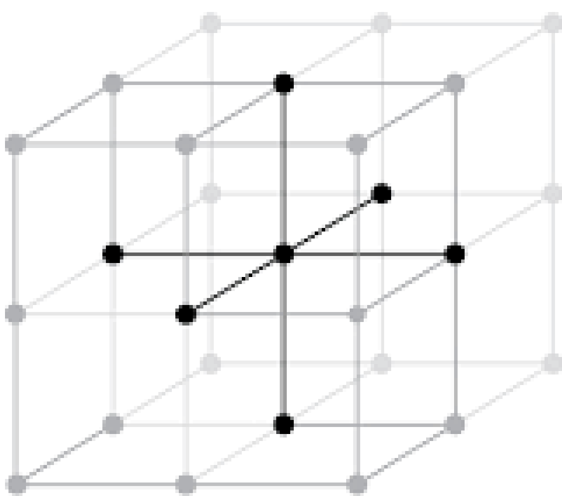
Simple Cubic or Primitive

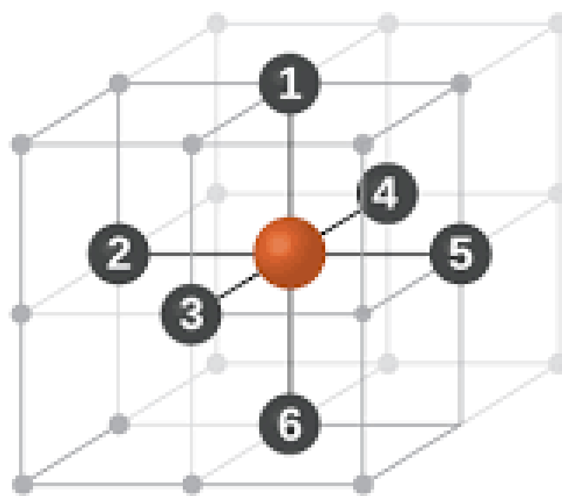
- It is a primitive cell.
- Atoms are present only at the corners of the unit cell.
- Corner atoms touch along the lattice constant.
- Number of atoms per unit cell is $Z = 1$.
- Atomic radius $a = 2r$ or $r = a/2$.
- Coordination Number or Number of nearest neighboring atoms $N = 6$.
- Packing Factor 52%.



$$n = 8 \times \frac{1}{8} = 1$$







$$r = a/2 \qquad Z = 1$$

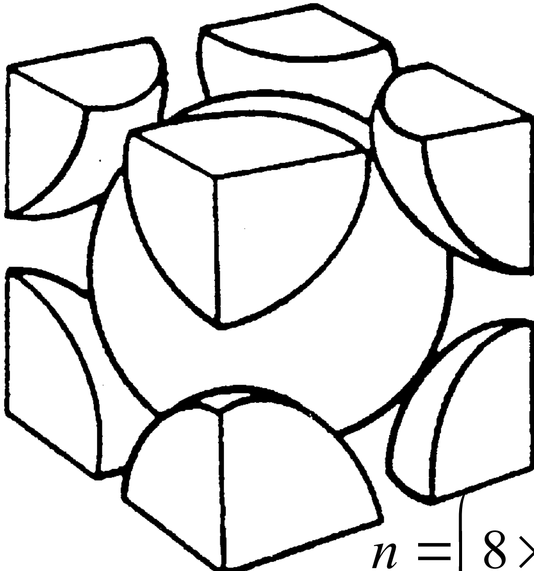
$$\mathrm{PF} = \frac{\frac{4}{3}\pi r^3}{a^3} \times Z$$

PF = 52%

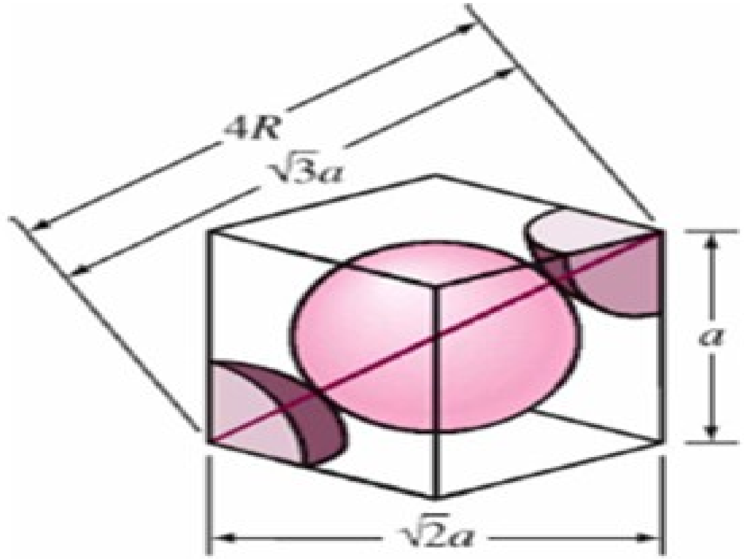
CN = 6

Body Centered Cubic (BCC)

- It is a non primitive cell.
- Atoms are present not only at the corners of the unit cell but also an atom at the center of the unit cell.
- Corner atoms touch along the body diagonal.
- Number of atoms per unit cell is Z = 2.
- Atomic radius $r = \frac{a\sqrt{3}}{4}$
- Coordination Number or Number of nearest neighboring atoms N = 8.
- Packing Factor 68%.



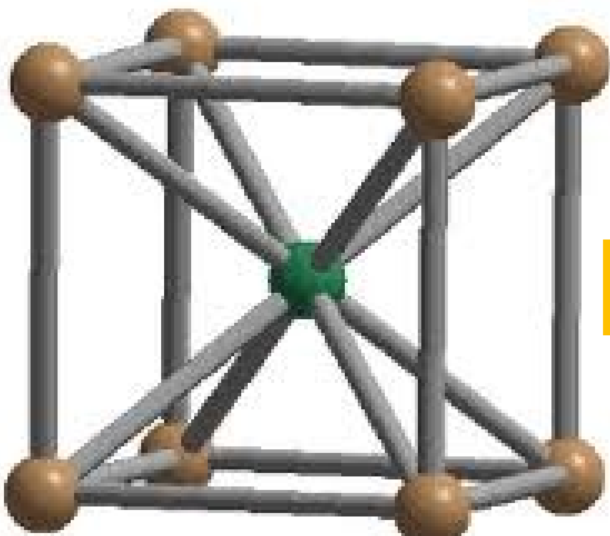
$$n = \left(8 \times \frac{1}{8}\right) + (1) = 2$$



$\sqrt{3}a = 4R$

bcc

$r = \sqrt{3}a / 4$ $\quad Z = 2$



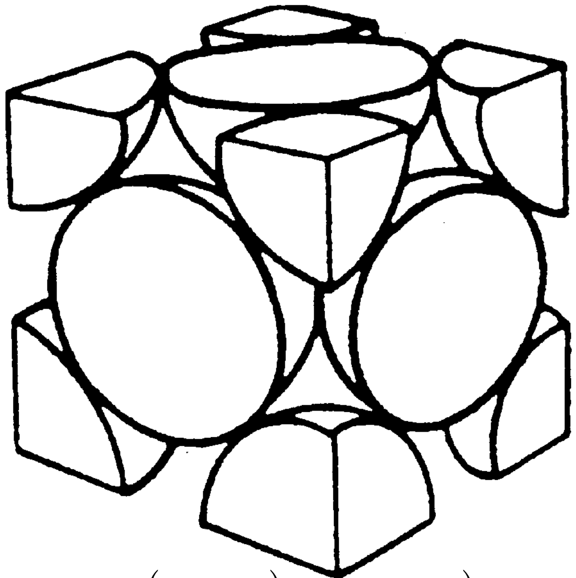
CN = 8

$$PF = \frac{\frac{4}{3}\pi r^3}{a^3} \times Z$$

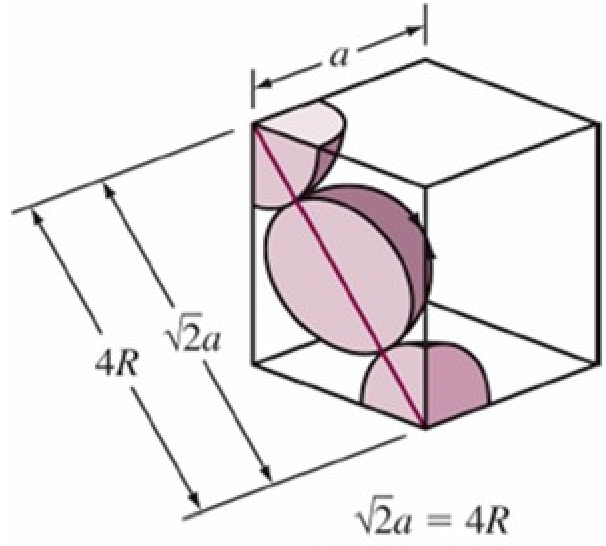
PF = 68%

Face Centered Cubic (FCC)

- It is a non primitive cell.
- Atoms are present not only at the corners of the unit cell but at the center of each face.
- Corner atoms touch along the face diagonal.
- Number of atoms per unit cell is Z = 4.
- Atomic radius $r = \frac{a\sqrt{2}}{4}$
- Coordination Number or Number of nearest neighboring atoms N = 12.
- Packing Factor 74%.

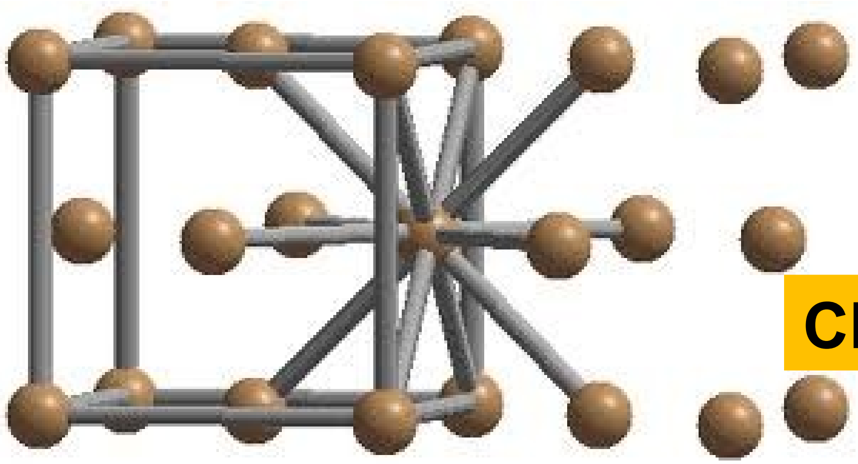


$$n = \left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$$



fcc

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



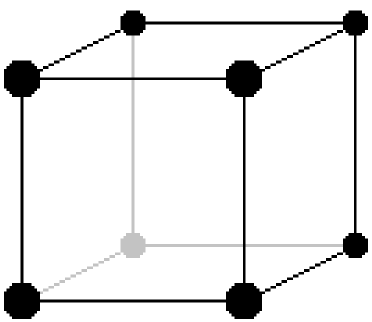
CN = 12

$$\mathrm{PF} = \frac{\frac{4}{3}\pi r^3}{a^3} \times \mathrm{Z}$$

PF = 74%

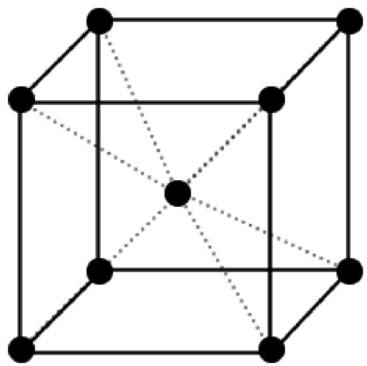
Number of Lattice points

Primitive (P)



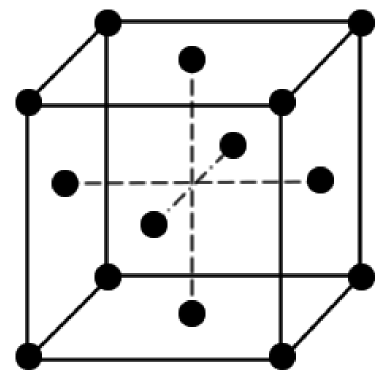
$$n = 8 \times \frac{1}{8} = 1$$

Body centered (I)



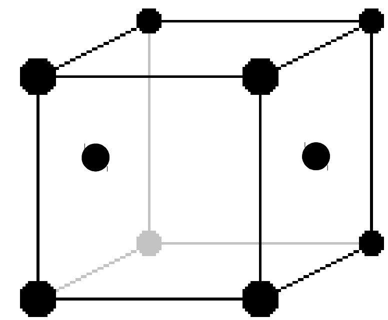
$$n = \left(8 \times \frac{1}{8}\right) + (1) = 2$$

Face centered (F)



$$n = \left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$$

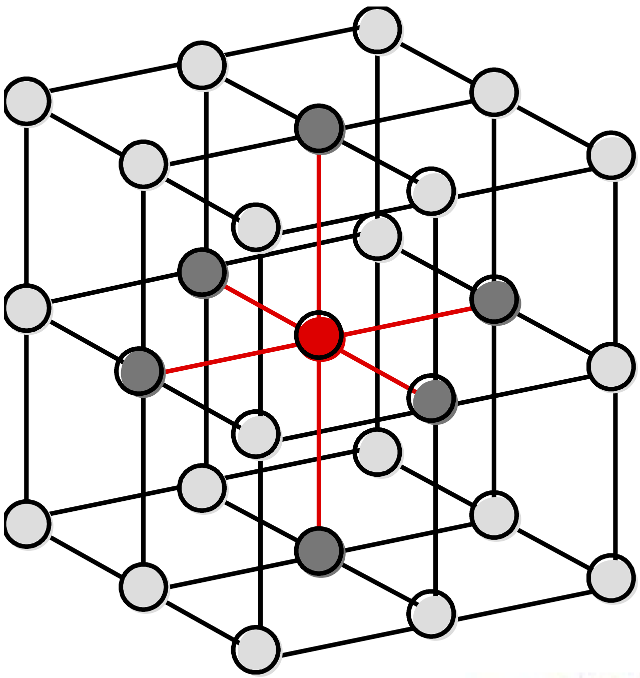
Base centered (C)

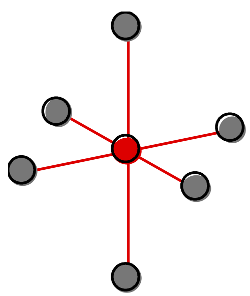


$$n = \left(8 \times \frac{1}{8}\right) + \left(2 \times \frac{1}{2}\right) = 2$$

Co-Ordination Number

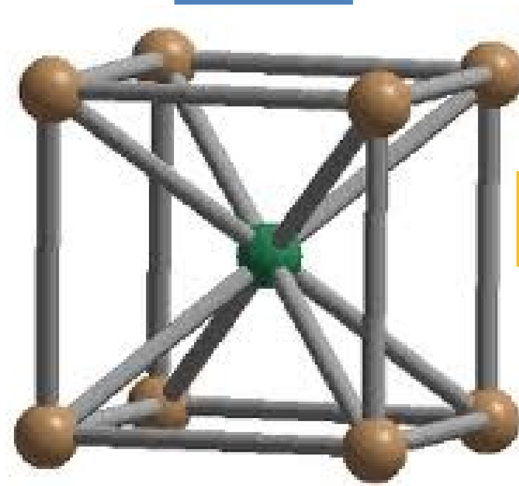
SC





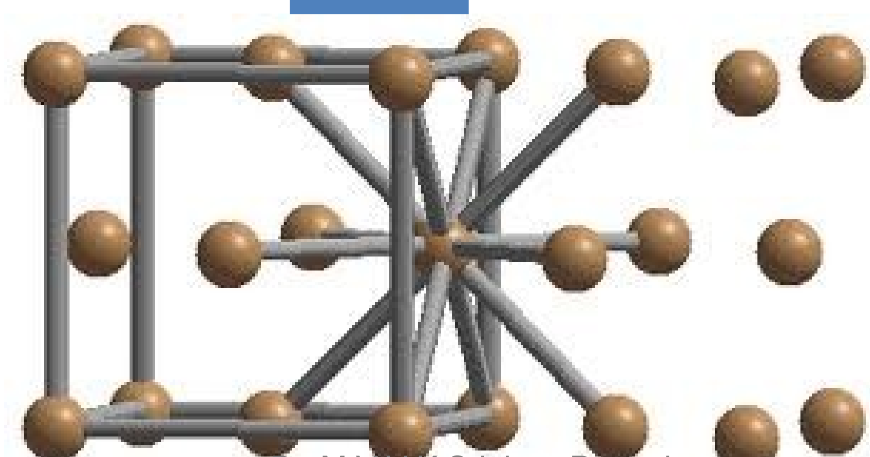
CN = 6

BCC



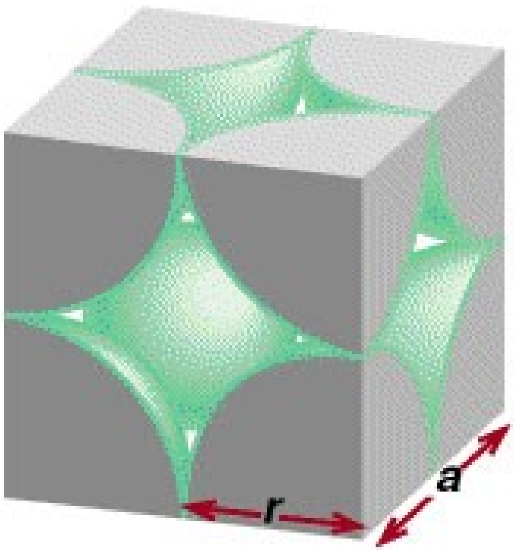
CN = 8

FCC



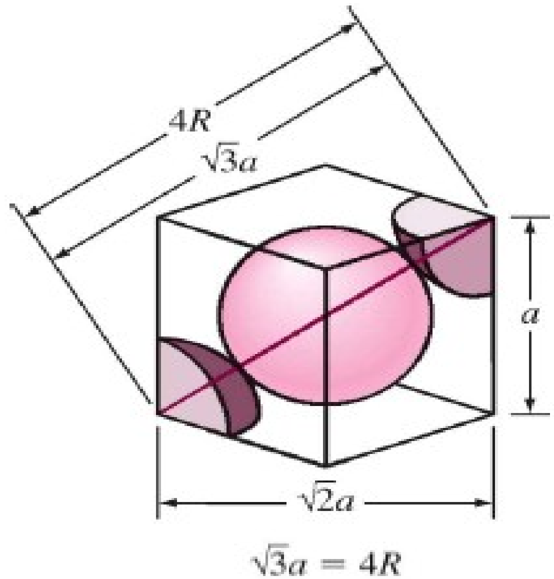
CN = 12

Relation between atomic radius and edge length



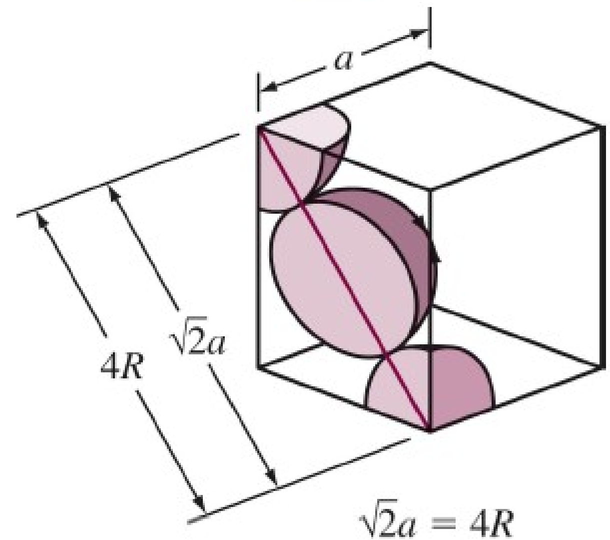
scc

$$a = 2r$$



bcc

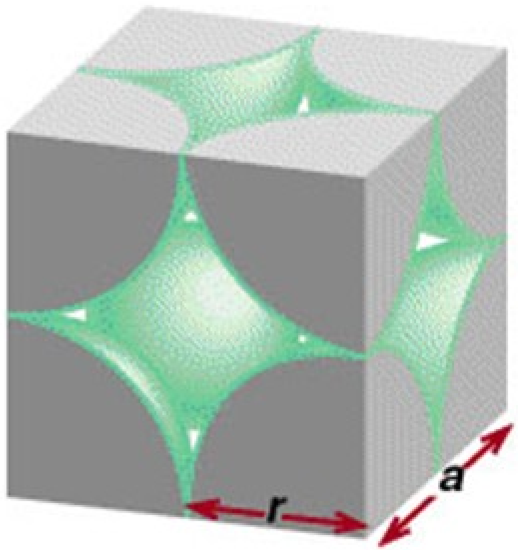
$$b^2 = a^2 + a^2$$
$$c^2 = a^2 + b^2$$
$$= 3a^2$$
$$c = \sqrt{3}a = 4r$$
$$a = \frac{4r}{\sqrt{3}}$$

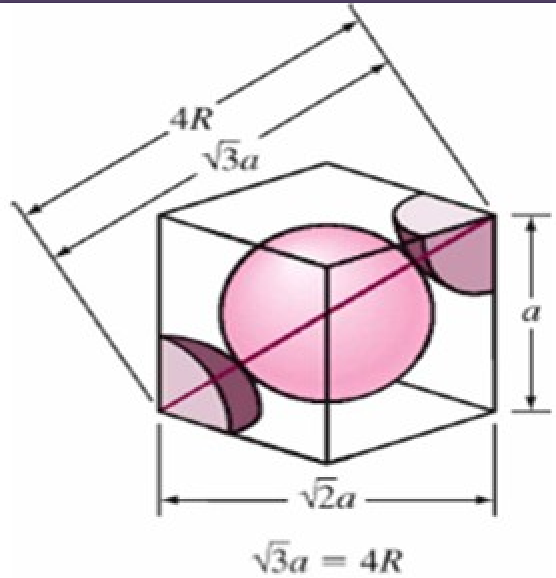


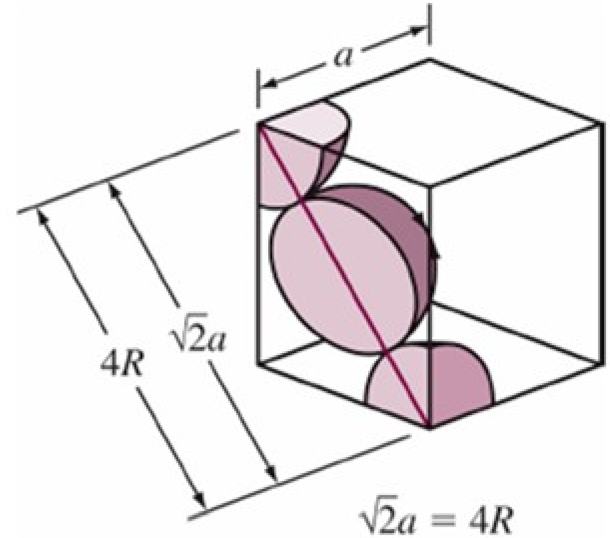
fcc

$$b = 4r$$
$$b^2 = a^2 + a^2$$
$$16r^2 = 2a^2$$
$$a = \sqrt{8}r$$

SC | B C C | F C C







SC: $r = a/2$ $Z = 1$

$$\mathrm{PF} = \frac{\frac{4}{3}\pi r^3}{a^3} \times Z$$

PF = 52%

BCC: $r = \sqrt{3}a/4$ $Z = 2$

$$\mathrm{PF} = \frac{\frac{4}{3}\pi r^3}{a^3} \times Z$$

PF = 68%

FCC: $r = a/2\sqrt{2}$ $Z = 4$

$$\mathrm{PF} = \frac{\frac{4}{3}\pi r^3}{a^3} \times Z$$

PF = 74%

COMPARISON OF CRYSTAL STRUCTURES

Crystal structure	coordination #	packing factor	close packed directions
Simple Cubic (SC)	6	0.52	cube edges
Body Centered Cubic (BCC)	8	0.68	body diagonal
Face Centered Cubic (FCC)	12	0.74	face diagonal
Hexagonal Close Pack (HCP)	12	0.74	hexagonal side

Density Computations

- Relation between lattice constant and Density

Lattice constant is “a”
Number of atoms per unit cell is “n”
Atomic weight of the substance is “A”
Density of the unit cell “ρ”
The Avagadro’s Number = N = 6.023 x 10^{23} atoms/ mole

$$\rho = \frac{nA}{V_C N_A}$$

$$Mass\ of\ each\ Molecule = \frac{A}{N}$$

$$Mass\ of\ n\ molecules = \frac{A}{N}\,n$$

$$Density\ of\ the\ unit\ cell\ \rho = \frac{Mass\ of\ an\ Unit\ cell}{Volume\ of\ the\ Unit\ cell}$$

$$Density\ of\ the\ unit\ cell\ \rho = \frac{nA}{Na^3} = \frac{nA}{NV_c}$$

Problems

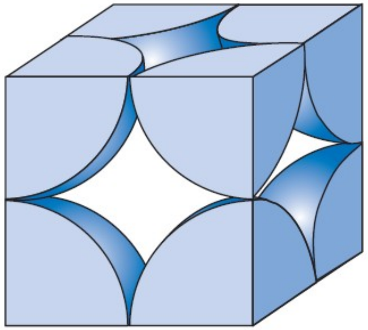
If the atomic radius of lead is 0.175 nm, calculate the volume of its unit cell in cubic meters

Molybdenum has a BCC crystal structure, an atomic radius of 0.1363 nm, and an atomic weight of 95.94 g/mol. Compute its density.

Calculate the radius of a palladium atom, given that Pd has an FCC crystal structure, a density of 12.0 g/cm^3, and an atomic weight of 106.4 g/mol.

Calculate the radius of a tantalum atom, given that Ta has a BCC crystal structure, a density of 16.6 g/cm^3, and an atomic weight of 180.9 g/mol.

Some hypothetical metal has the simple cubic crystal structure shown in Figure. If its atomic weight is 74.5 g/mol and the atomic radius is 0.145 nm, compute its density



Niobium has an atomic radius of 0.1430 nm and a density of 8.57 g/cm^3. Determine whether it has an FCC or BCC crystal structure, the atomic weight of Niobium is 92.91 g/mol.

The unit cell for uranium has orthorhombic symmetry, with *a*, *b*, and *c* lattice parameters of 0.286, 0.587, and 0.495 nm, respectively. If its density, atomic weight, and atomic radius are 19.05 g/cm^3, 238.03 g/mol, and 0.1385 nm, respectively, compute the atomic packing factor.

Determine the total void volume (cm^3 /mole) for gold (Au) at 27^{o}C; make the hard-sphere approximation in your calculation, and use data provided in the periodic table

Determine the atomic radius of Mo. Given that atomic weight is 95.94 g/mol and density of Mo is 10.2 g/cm^3.

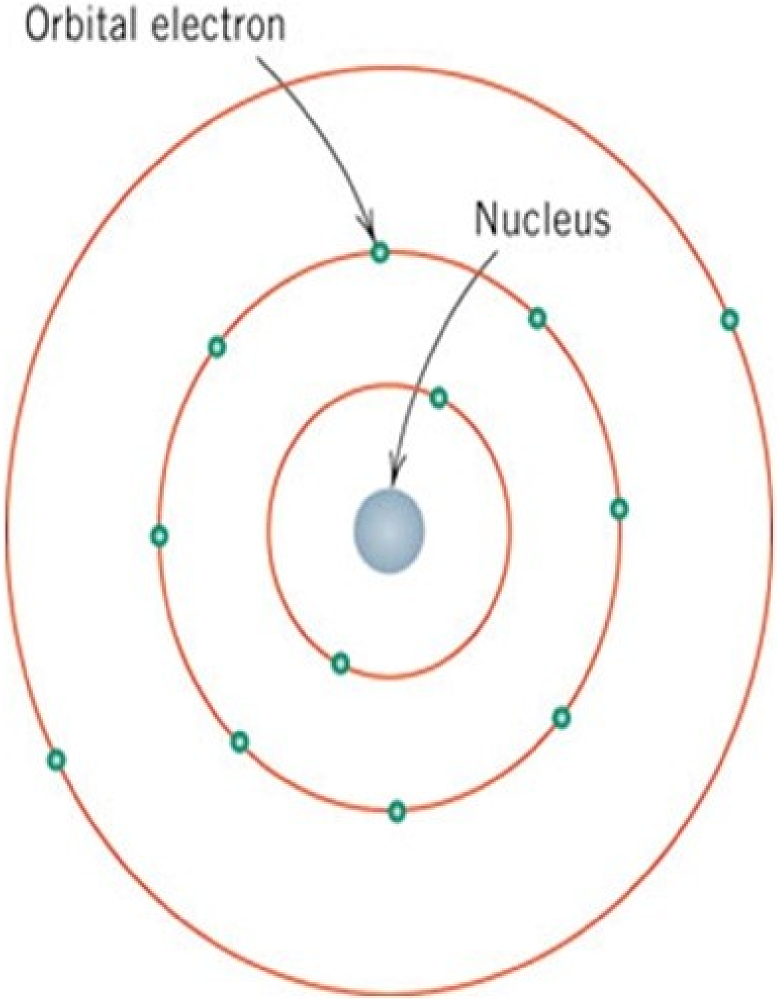
A metal is found to have BCC structure, a lattice constant of 3.31 Angstroms, and a density of 16.6 g/cm^3. Determine the atomic weight of the element

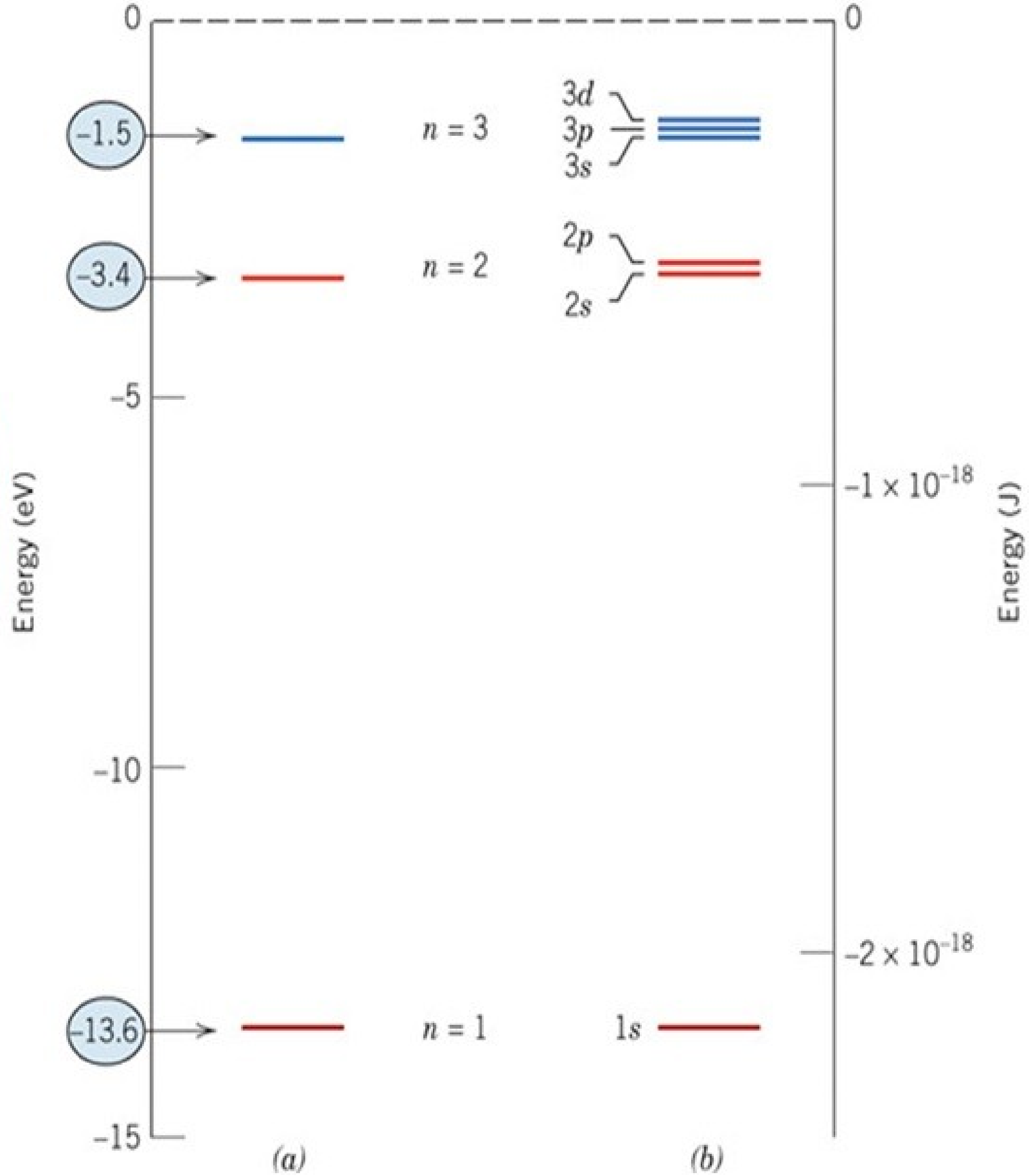
ENERGY BAND STRUCTURE

- *In most of solids conduction is by electrons.*
- *Conductivity "σ" depend on no. of electrons available for conduction.*
- *The no. of electrons available for conduction depends on*
  - *Arrangement of electrons states or levels with respect to energy.*
  - *The manner in which these states are occupied by electrons.*

Current carriers

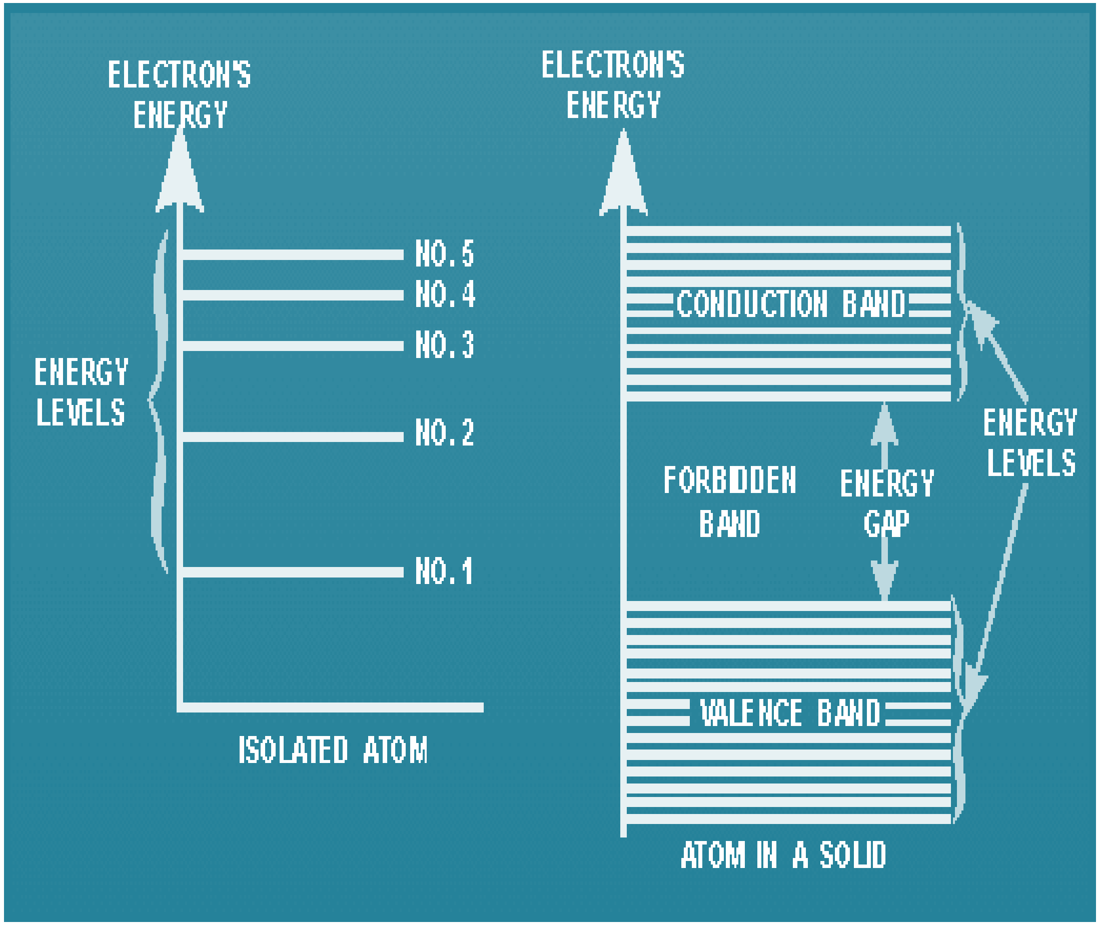
- *electrons in most solids*
- *ions can also carry (particularly in liquid solutions)*

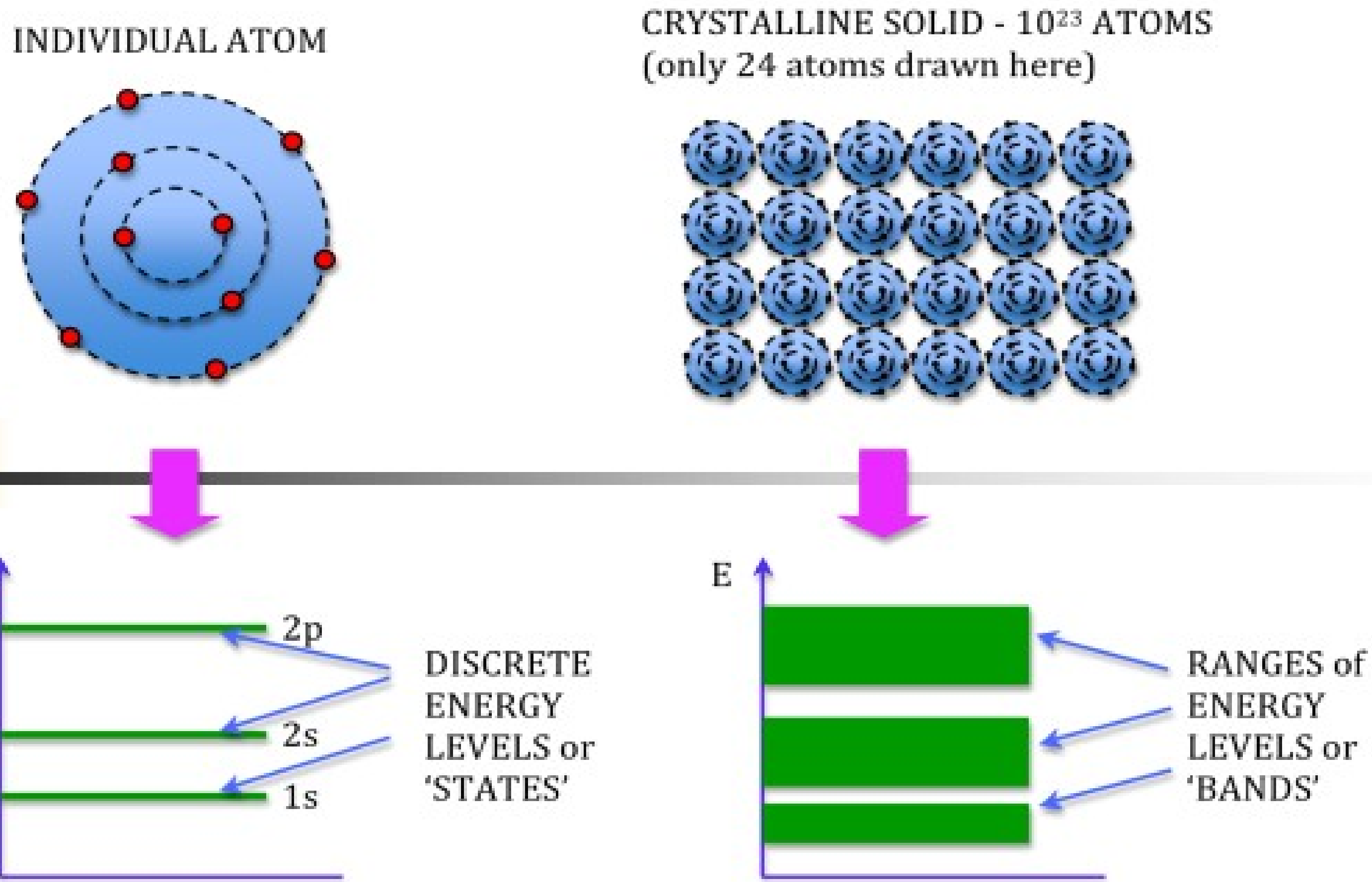

Orbital electron
Nucleus


0
-1.5
-3.4
-5
-10
-13.6
-15
Energy (eV)
n = 3
n = 2
n = 1
3d
3p
3s
2p
2s
1s
0
-1×10^{-18}
-2×10^{-18}
Energy (J)
(a)
(b)

Energy Band Structures in solids

- *The isolated atom has discrete energy levels, whereas the atom in a solid has* ***closely spaced energy levels*** *grouped into* ***ENERGY BANDS.***




INDIVIDUAL ATOM
CRYSTALLINE SOLID - 10²³ ATOMS
(only 24 atoms drawn here)
E
2p
2s
1s
DISCRETE
ENERGY
LEVELS or
'STATES'
E
RANGES of
ENERGY
LEVELS or
'BANDS'

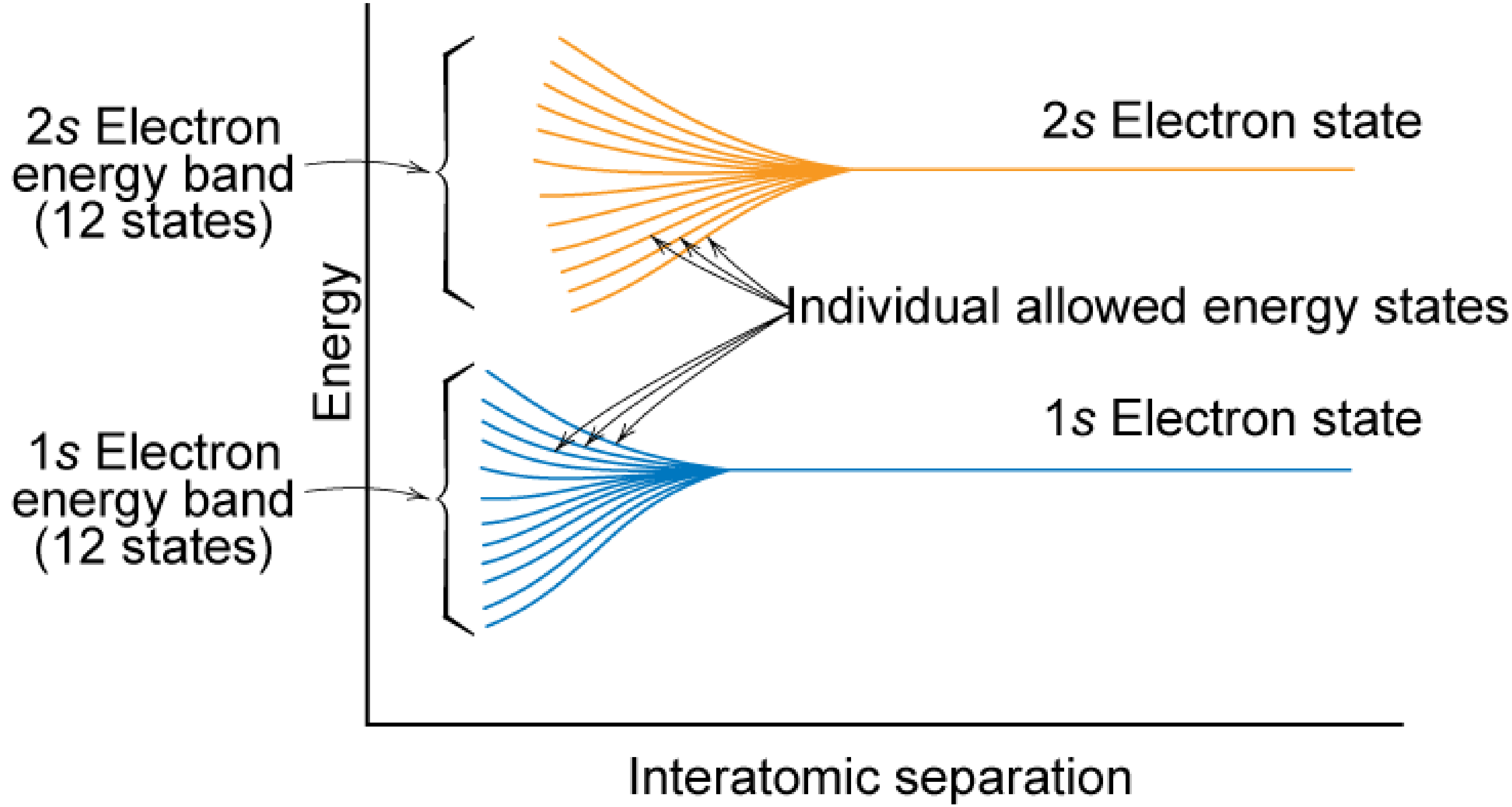
WHY ENERGY BANDS ARE FORMED?

- *Electrons of one atom are perturbed by the electrons and nuclei of the adjacent atoms.*

- *Results in splitting of atomic states into a series of closely spaced electron states to from what are called* ***ELECTRON ENERGY BAND.***

- *Extent of splitting depends on interatomic separation.*

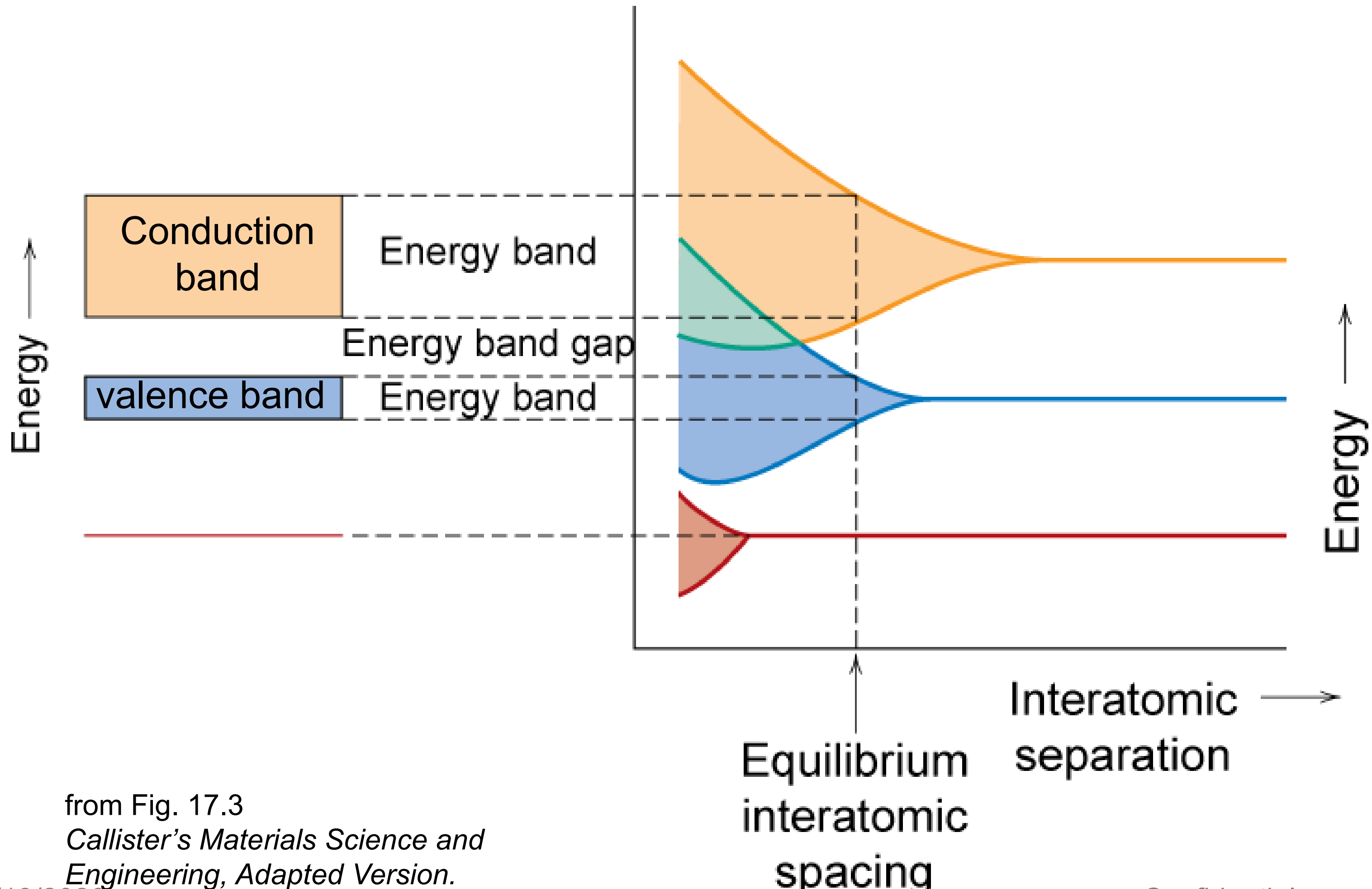
Electronic Band Structures



- *For 12 atoms, each of the 1s and 2s atomic states splits to form an electron energy band consisting of 12 states.*

Band Structure

- *Valence band – filled – highest occupied energy levels*
- *Conduction band – empty – lowest unoccupied energy levels*

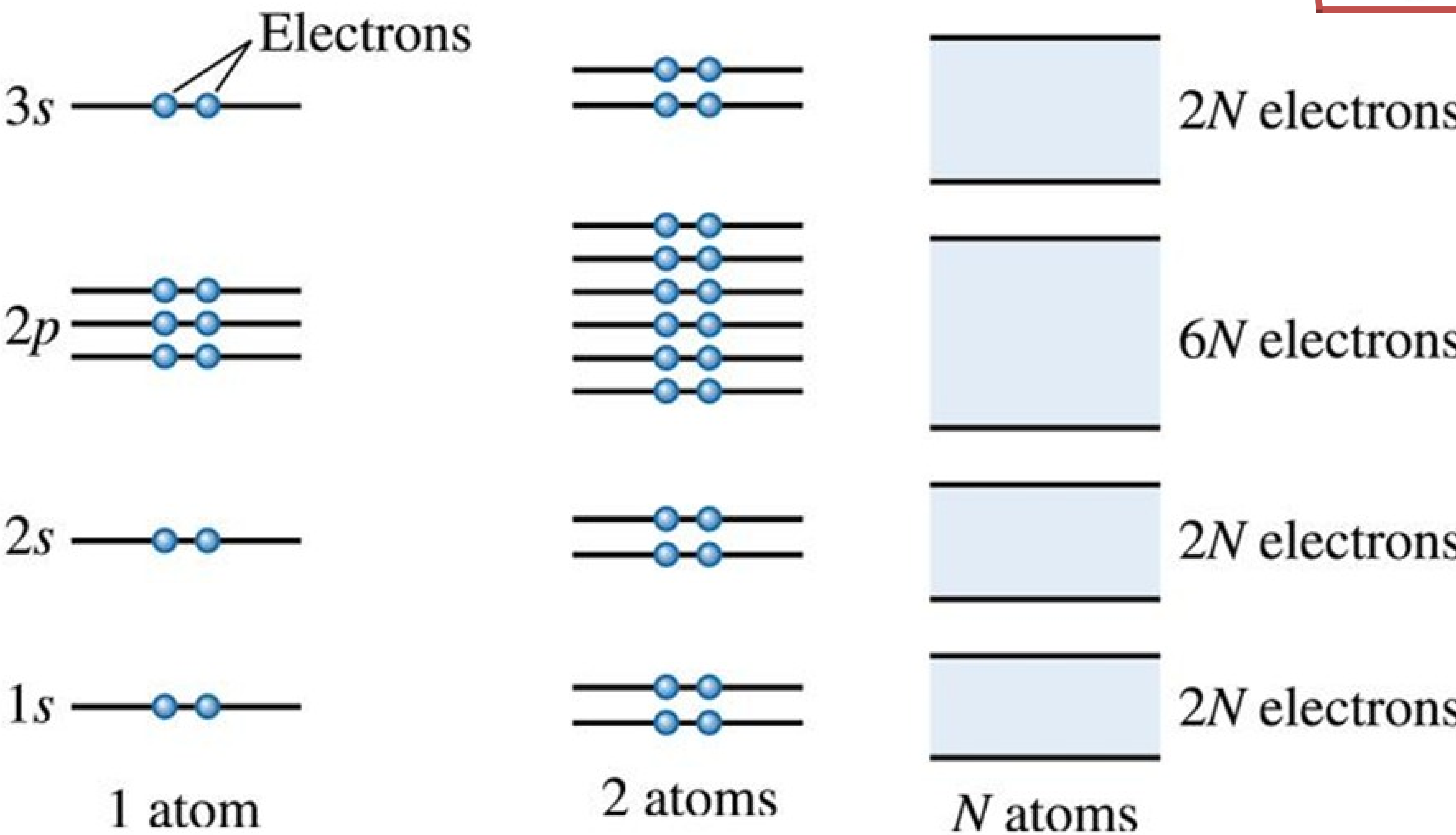


from Fig. 17.3
Callister's Materials Science and Engineering, Adapted Version.

- *With in each band the energy states are discrete.*

- *No. of states within each band will equal the total of all states contributed by the N atoms.*
  - *s band consists of N states & 2N electrons*
  - *p band consists of 3N states & 6N electrons*

- *Electrical properties of a solid depends on its electron band structure.*


Electrons
3s
2p
2s
1s
2N electrons
6N electrons
2N electrons
2N electrons
1 atom
2 atoms
N atoms

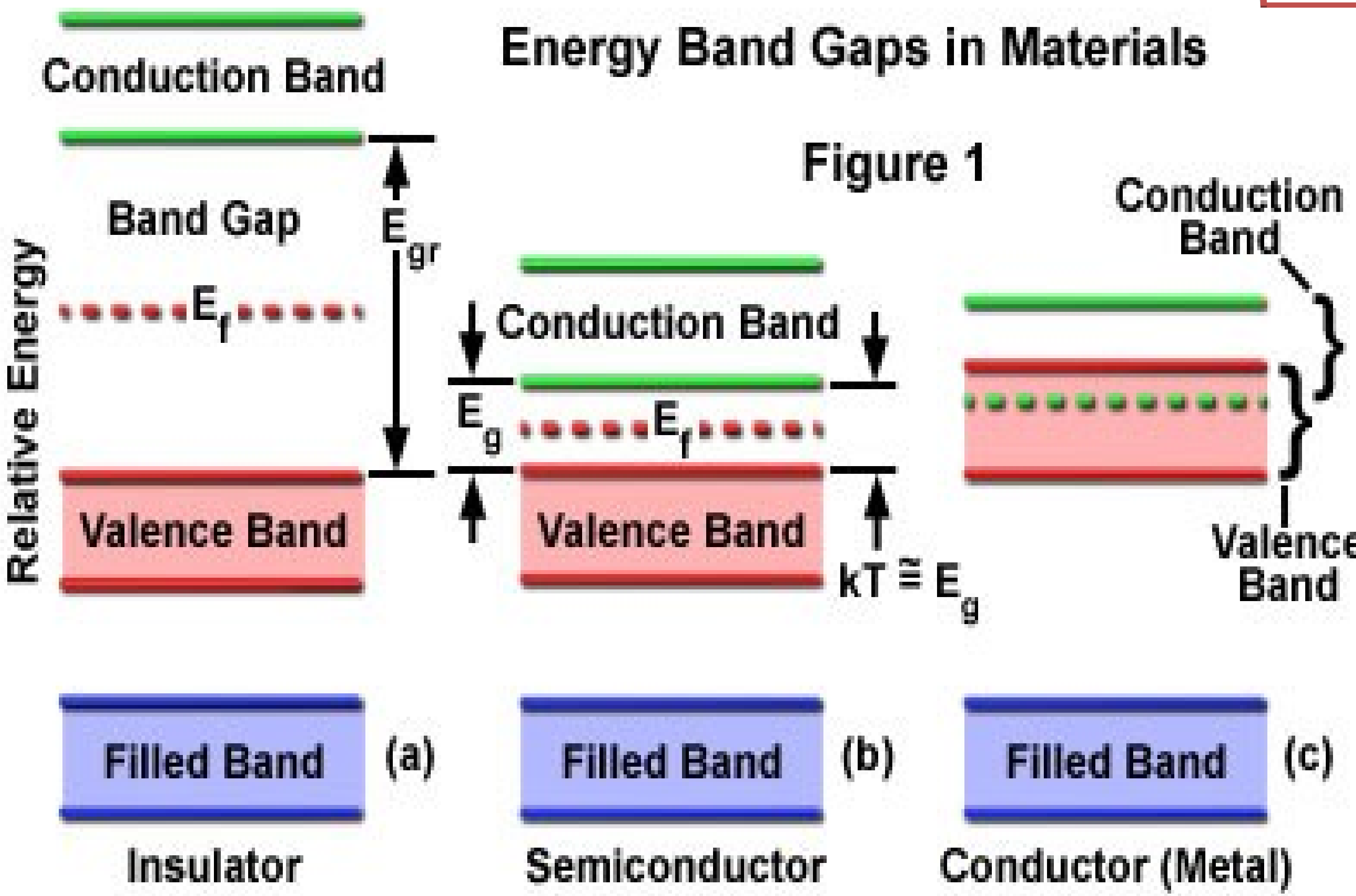
Electronic Band Structures

- Energy bands concept is particularly important in **classifying materials.**

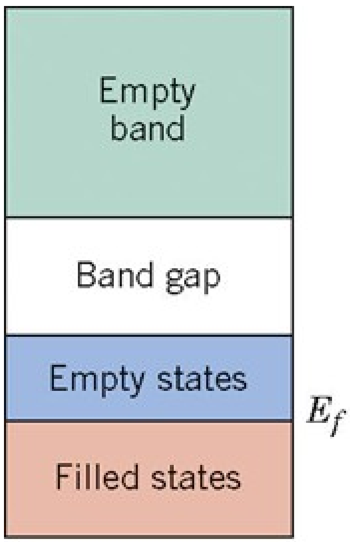
- An electron can exist in either of **two energy bands**, the conduction band or the valence band.

- All that is necessary to move an electron from the valence band to the conduction band so it can be used for **electric current**, is enough energy to carry the electron through the forbidden band.

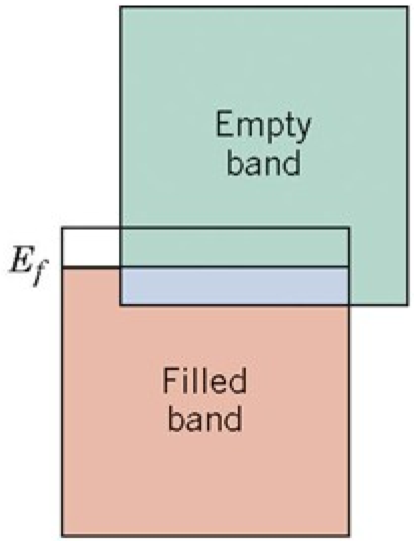
- The **width of the forbidden band or the separation** between the conduction and valence bands determines whether a substance is an insulator, semiconductor, or conductor.


Energy Band Gaps in Materials
Figure 1
Conduction Band
Band Gap
E
gr
E
f
Relative Energy
Valence Band
Filled Band
(a)
Insulator
Conduction Band
E
g
E
f
Valence Band
kT ≅ E
g
Filled Band
(b)
Semiconductor
Conduction
Band
Valence
Band
Filled Band
(c)
Conductor (Metal)

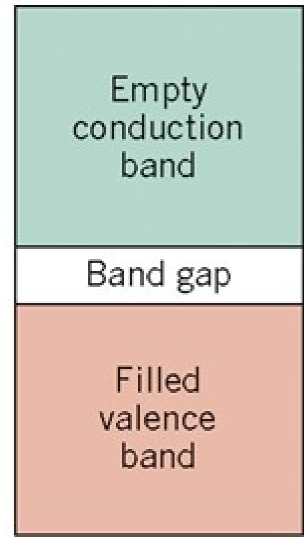
The energy corresponding to the highest filled state at 0 K is called the ***Fermi energy***



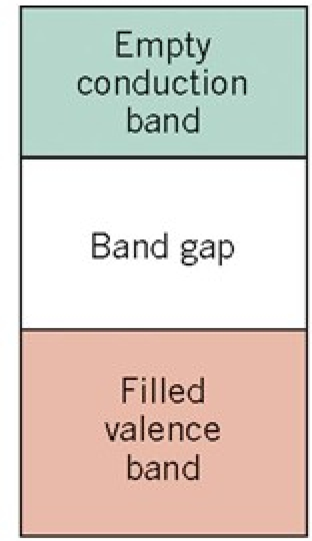
metals:
available and filled states in the same band (Cu, Au, Ag)



metals:
overlap between filled valence band and empty conduction band (Al, Mg)

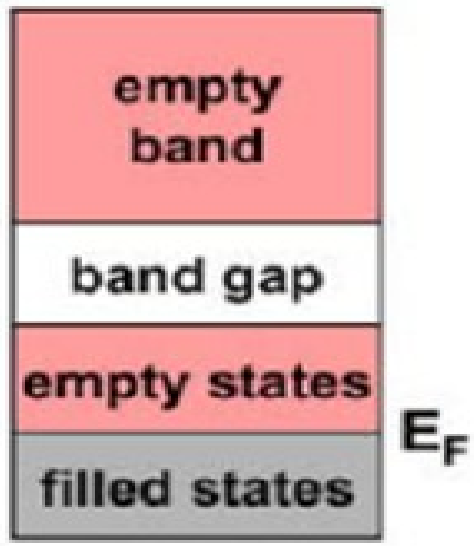


semiconductors:
filled valence band separated from empty conduction band by a narrow band gap (< 2 eV)



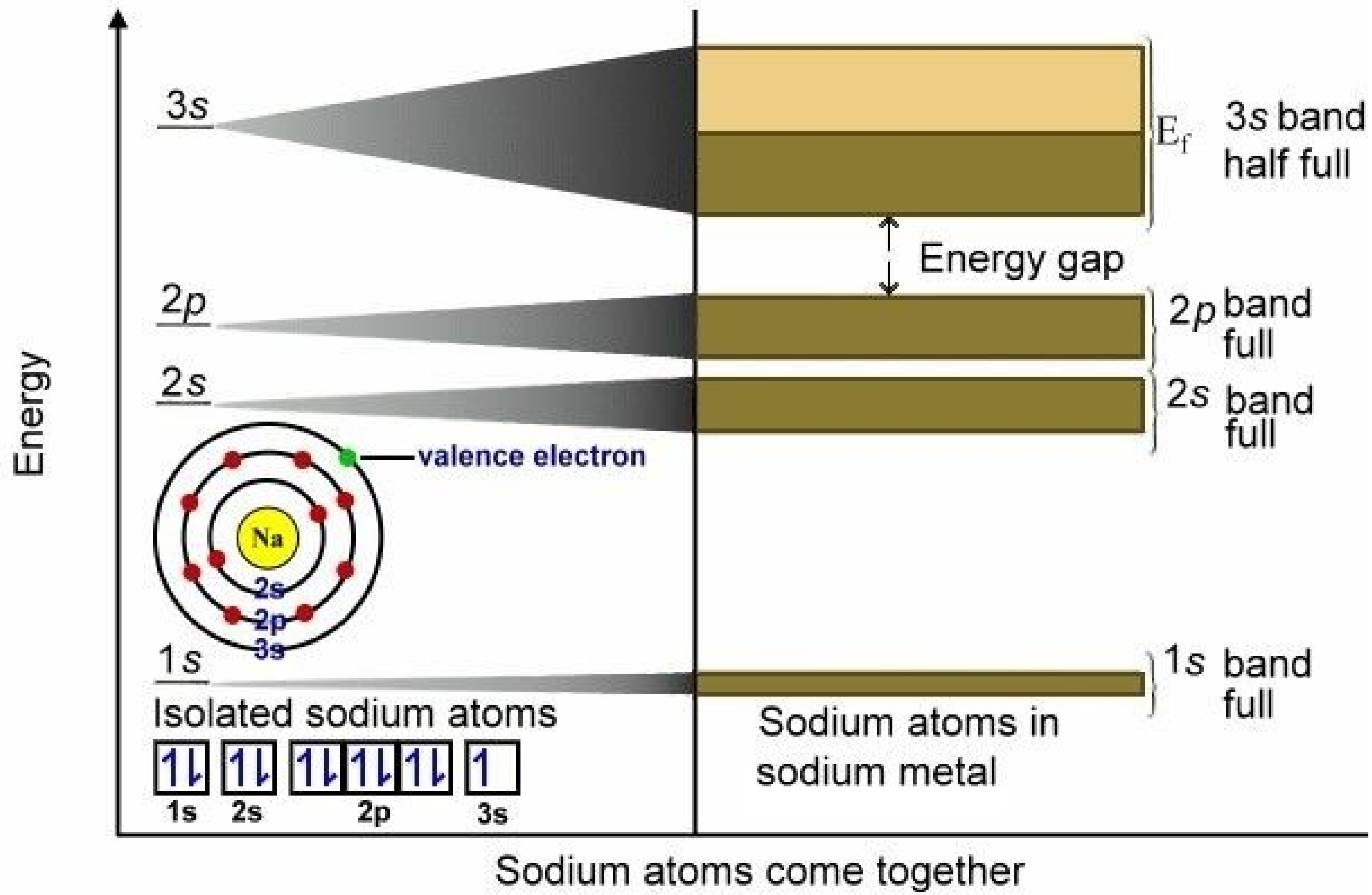
insulators:
filled valence band separated from empty conduction band by a large band gap (> 2 eV)

Conductors

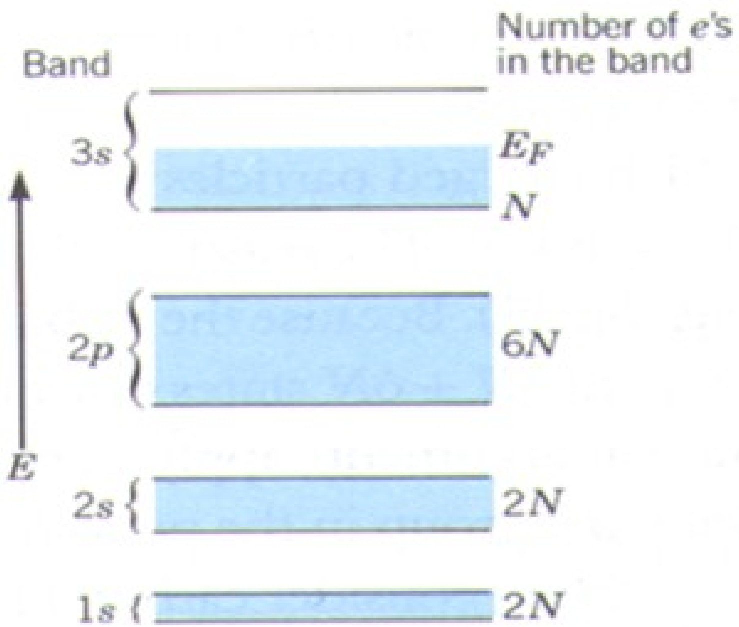


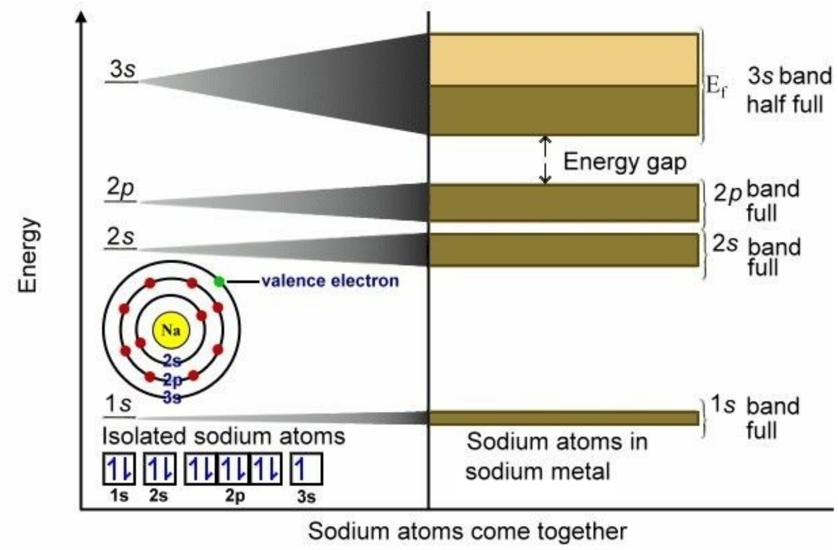
Cu-$3d^{10}$ $4s^{1}$- One 4s electron

metals:
available and filled states in the same band
(Cu, Au, Ag)

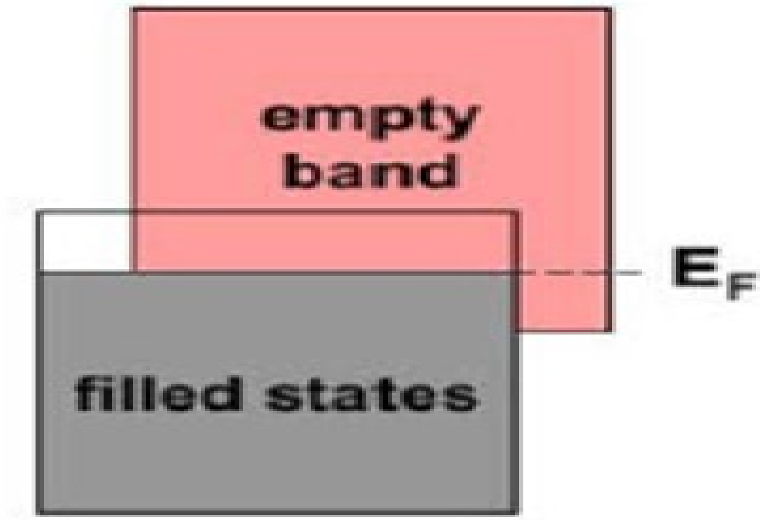


3s
2p
2s
1s
Energy
valence electron
Na
2s
2p
3s
E_f
3s band
half full
Energy gap
2p band
full
2s band
full
1s band
full
Isolated sodium atoms
1s
2s
2p
3s
Sodium atoms in
sodium metal
Sodium atoms come together


Band
Number of e's in the band
3s
E_F
N
2p
6N
E
2s
2N
1s
2N


Energy
3s
2p
2s
1s
3s band half full
E_f
Energy gap
2p band full
2s band full
1s band full
valence electron
Na
Isolated sodium atoms
1s 2s 2p 3s
Sodium atoms in sodium metal
Sodium atoms come together

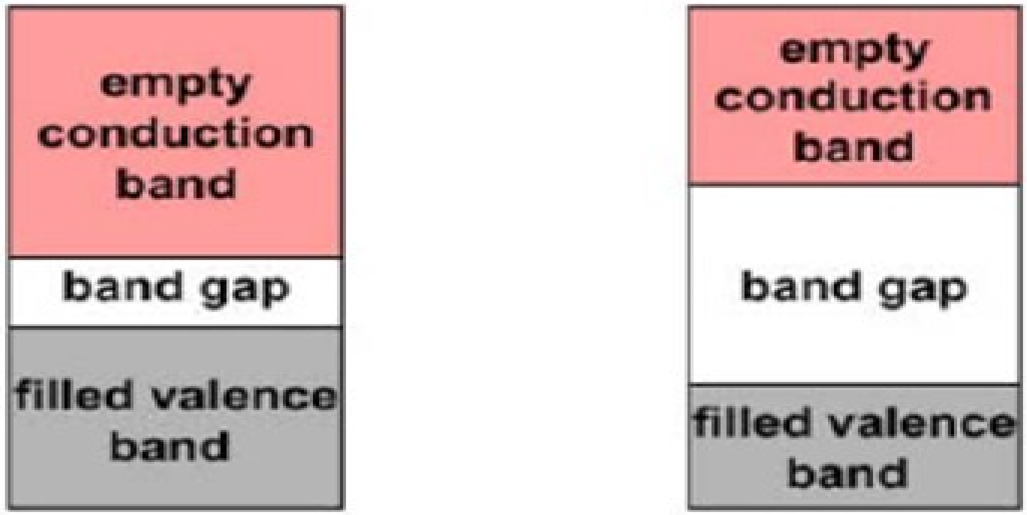
Conductors



Mg-12-Two 3*s* electrons

metals:
overlap between filled valence band and empty conduction band (Al, Mg)

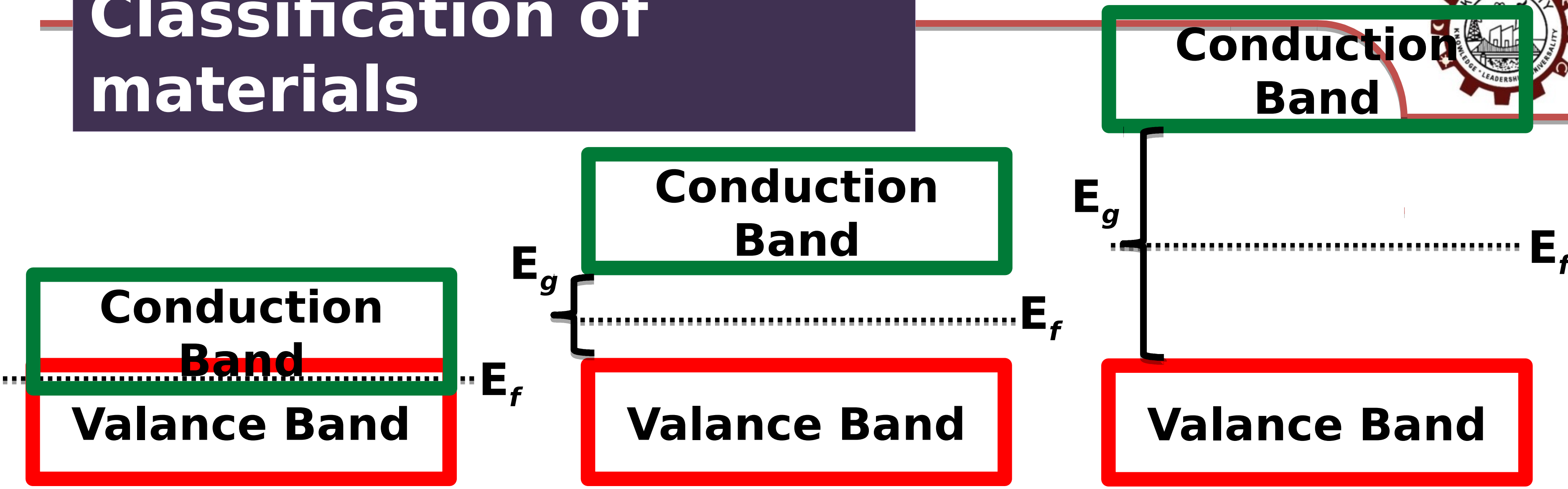
Semiconductors and Insulators



semiconductors: filled valence band separated from empty conduction band by a narrow band gap (< 2 eV)

insulators: filled valence band separated from empty conduction band by a large band gap (> 2 eV)

Classification of materials



Conductors

- Overlapping of bands
- Fermi energy level lies in valance band

Semiconductors

- Lower energy gap between the bands
- Fermi energy level lies at middle of the two bands

Insulators

- Large energy gap between the bands
- Fermi energy level lies at middle of the two bands

SEMICONDUCTORS

What is a Semiconductor?

- Low resistivity => “conductor”
- High resistivity => “insulator”
- Intermediate resistivity => “semiconductor”
  - conductivity lies between that of conductors and insulators

Semiconductors have a resistivity/ conductivity between that of conductors and insulators

Electrical properties are extremely sensitive to the presence of impurities.

INTRINIC SEMICONDUCTORS

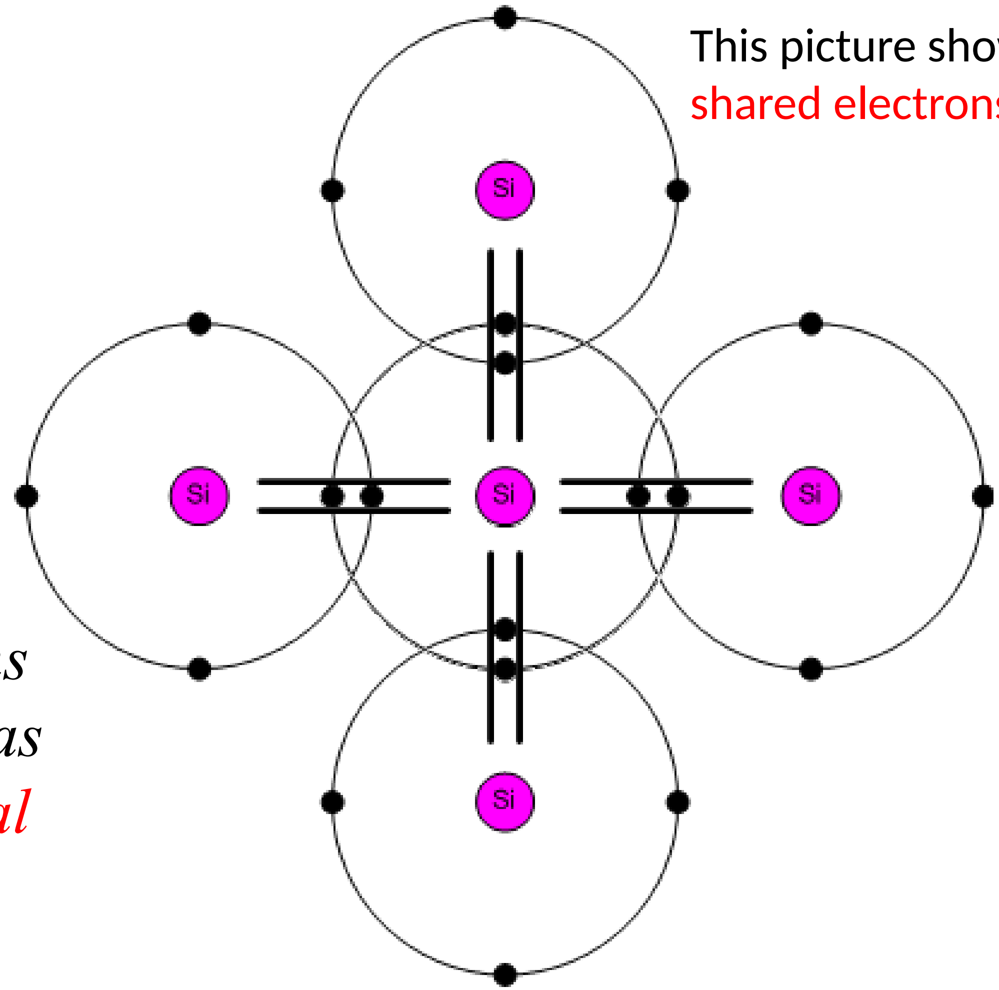
- Group IV A elements (C, Si, Ge, Sn, Pb, Fl)
- Compound semiconductors are formed between III A & V A group elements ex. GaAs, InSb.
- Elements of groups II B & IV A also display semiconducting nature ex. CdS, ZnTe.
- relatively narrow forbidden band gap, generally less than 2 eV.
- Si (1.1 eV) and Ge (0.7 eV) are widely used for device applications
- At 0 K, valence band is completely filled, conduction band is empty
- Equal carrier concentration (electron and hole) $n_i = n = p$
- The magnitude of hole mobility is always less than electron mobility for semiconductors
- Conductivity is given by $\sigma = ne\mu_e + pe\mu_h = nie(\mu_e + \mu_h)$

The Silicon, Si, Atom

Silicon has a valency of 4 i.e. 4 electrons in its outer shell

Each silicon atom shares its 4 outer electrons with 4 neighbouring atoms

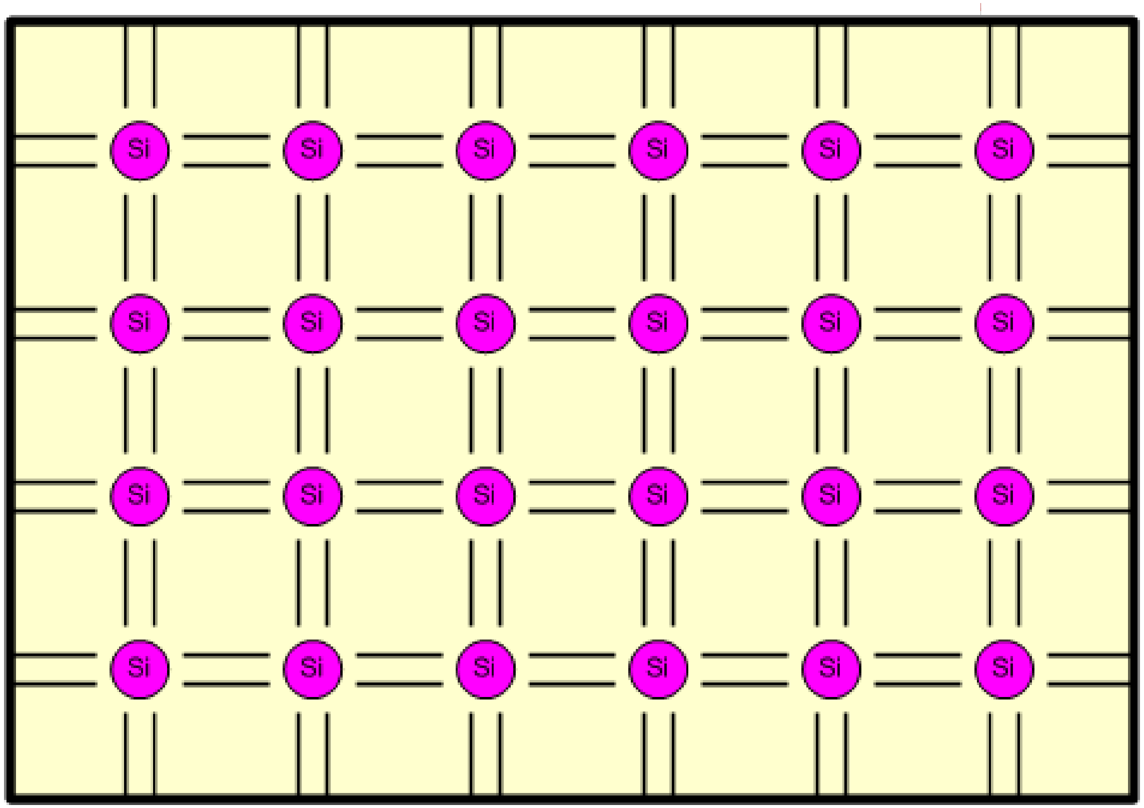
These shared electrons – bonds – are shown as horizontal and vertical lines between the atoms.



This picture shows the shared electrons

Silicon – the crystal lattice

If we extend this arrangement throughout a piece of silicon…



We have the crystal lattice of silicon

This is how silicon looks when it is 0K

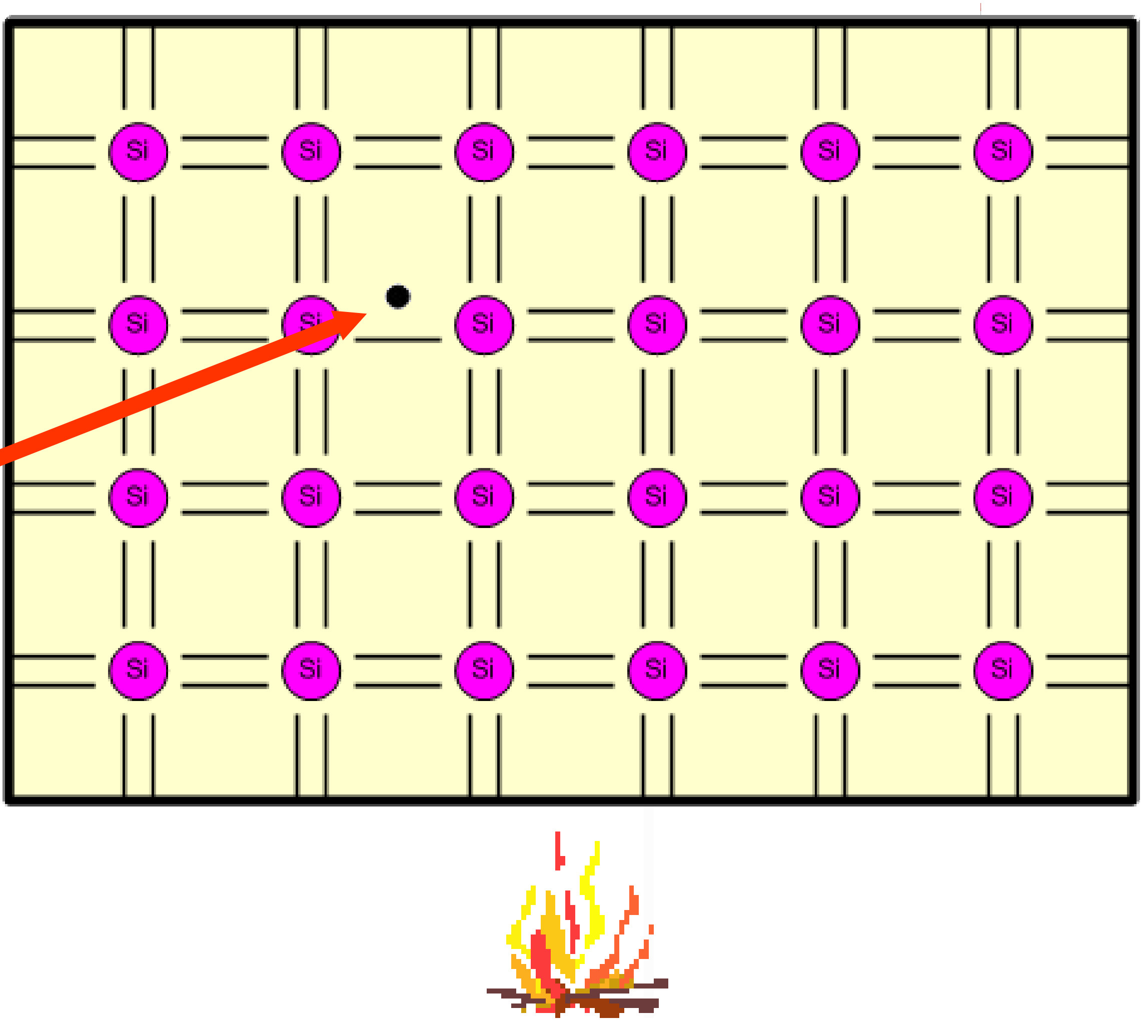
It has no free electrons – it cannot conduct electricity – therefore it behaves like an insulator

Electron Movement in Silicon

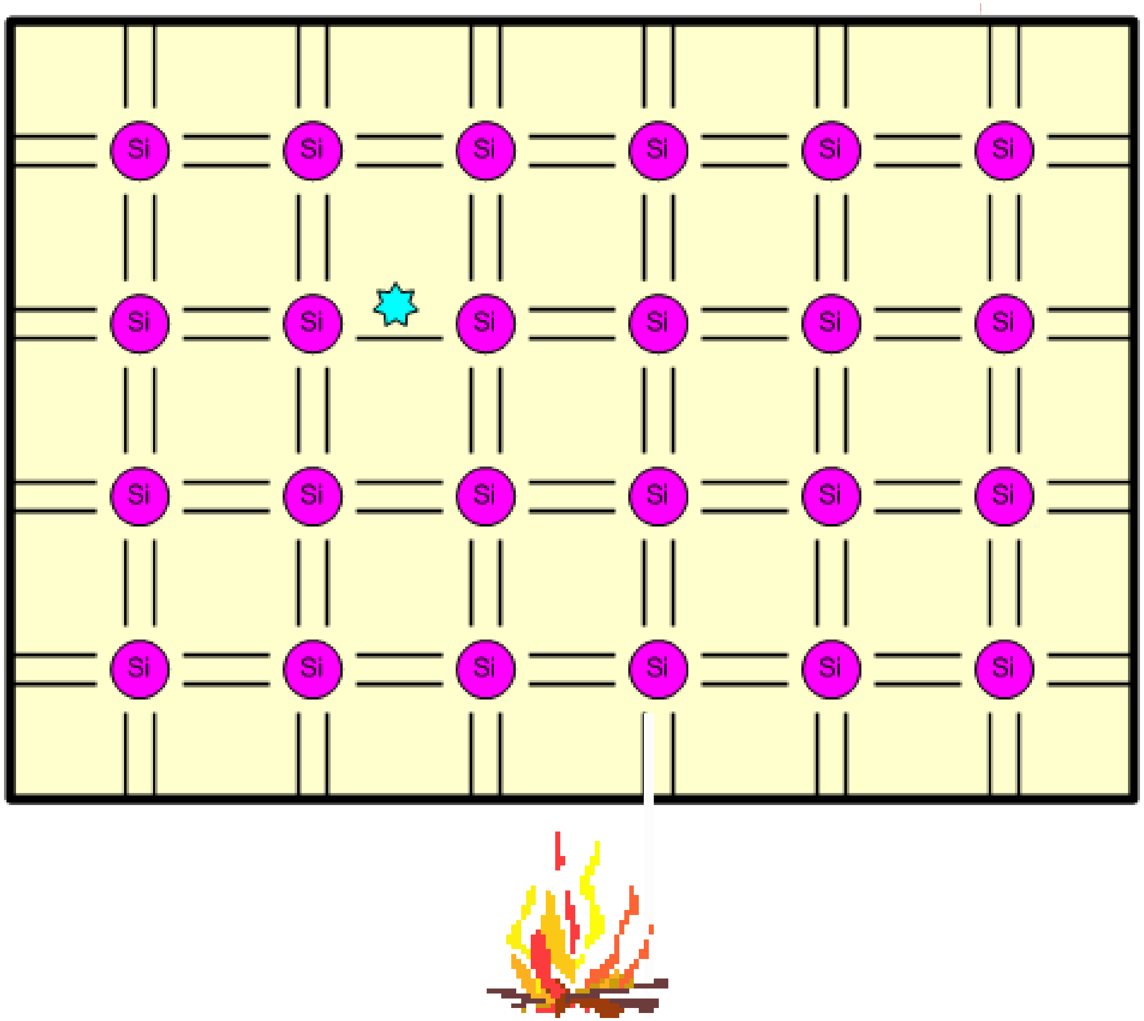
At room temperature

An electron may gain enough energy to break free of its bond…

It is then available for conduction and is free to travel throughout the material

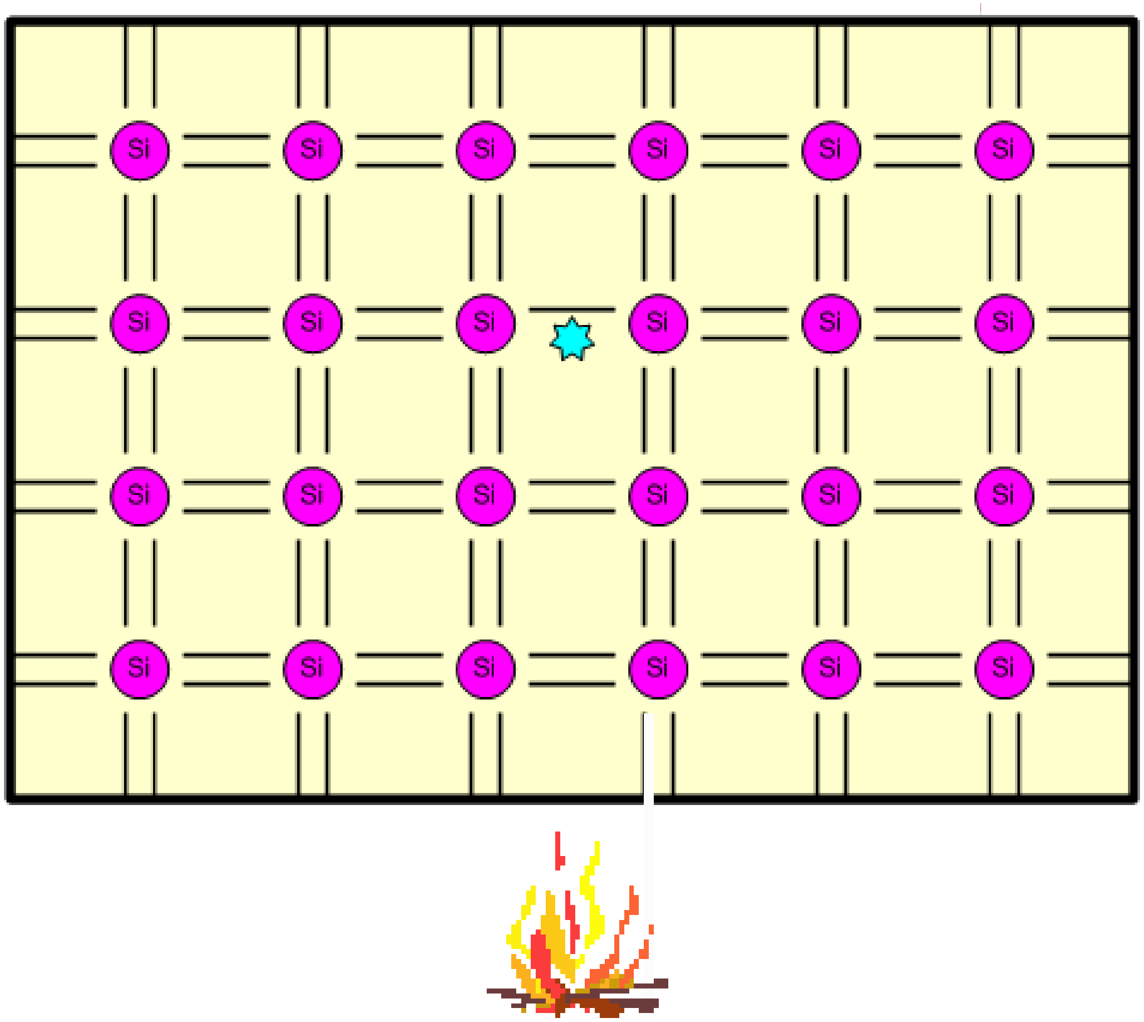


Hole Movement in Silicon



Hole Movement in Silicon

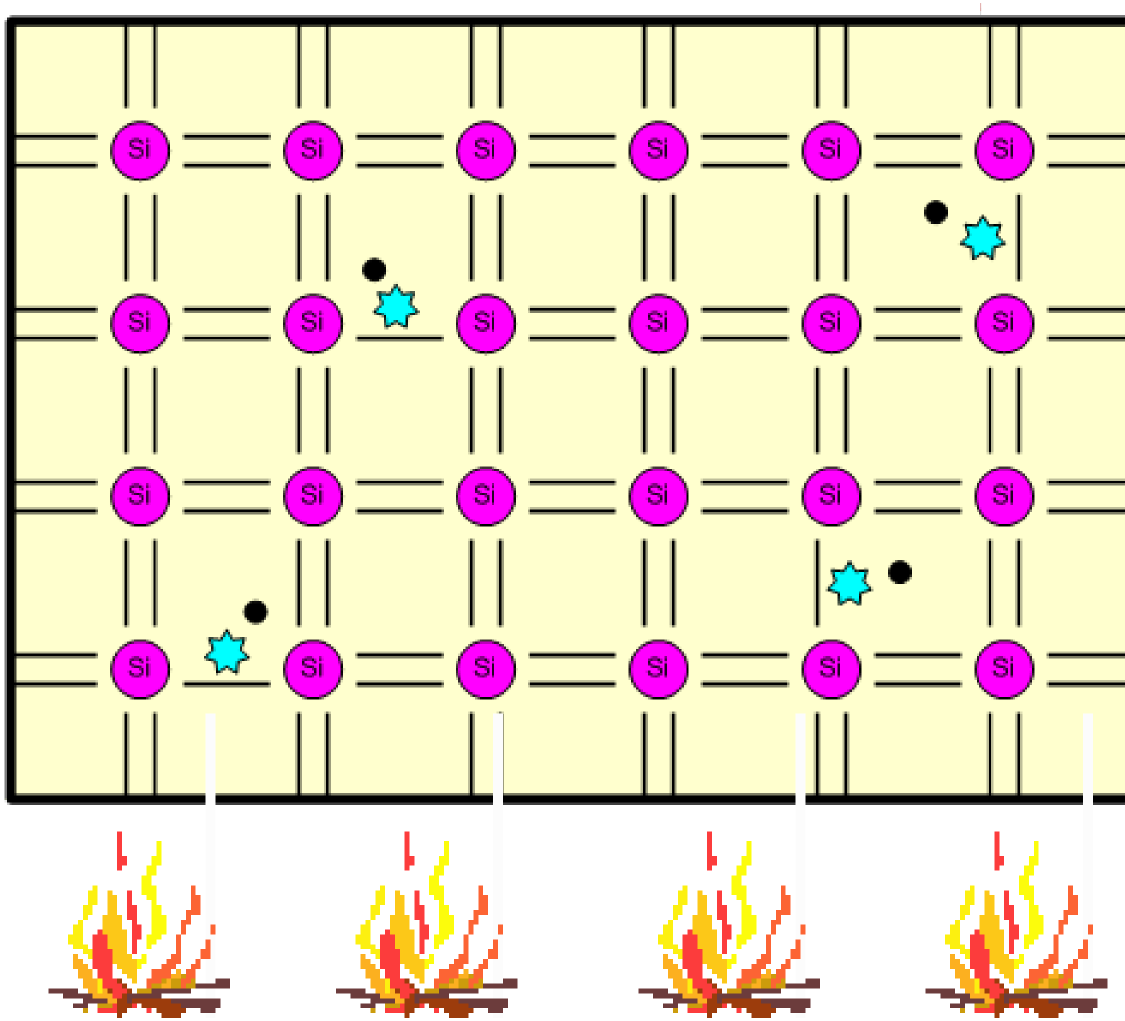
This hole can also move…



Heating Silicon

We have seen that, in silicon, heat releases electrons from their bonds…

This creates electron-hole pairs which are then available for conduction

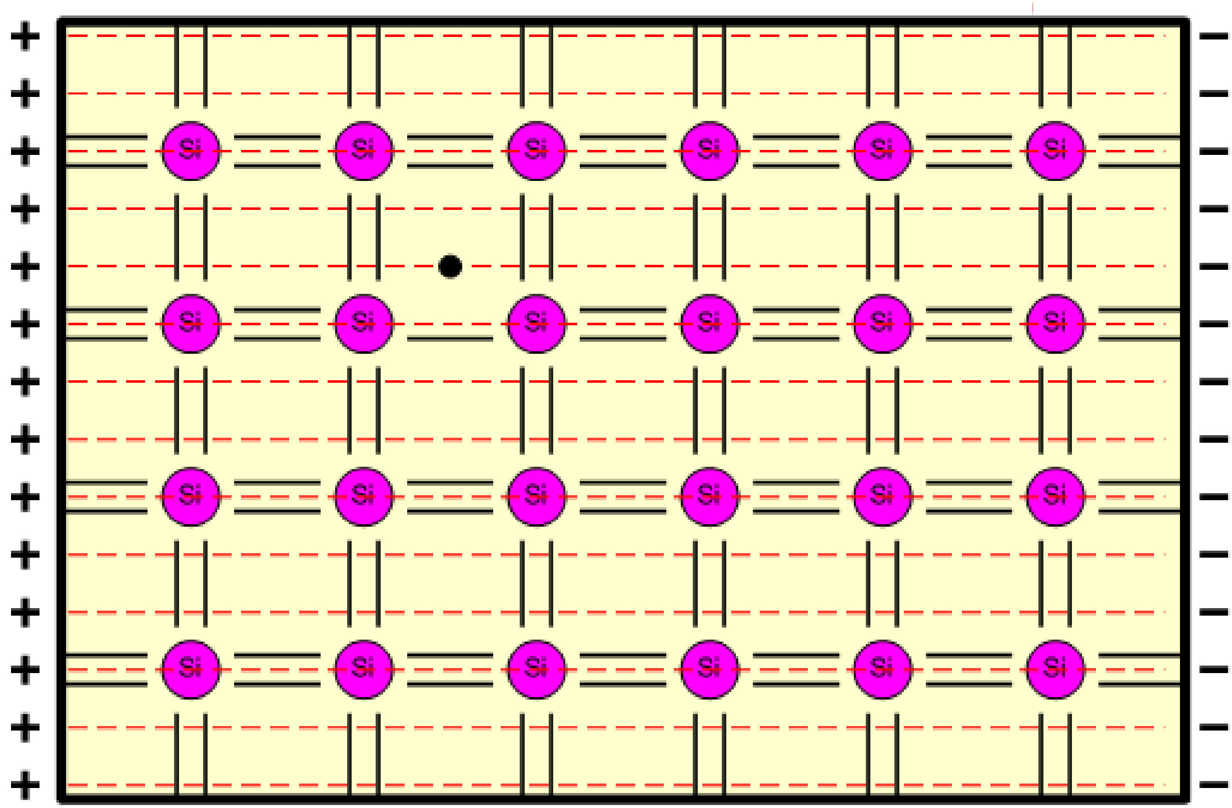


Intrinsic Conduction

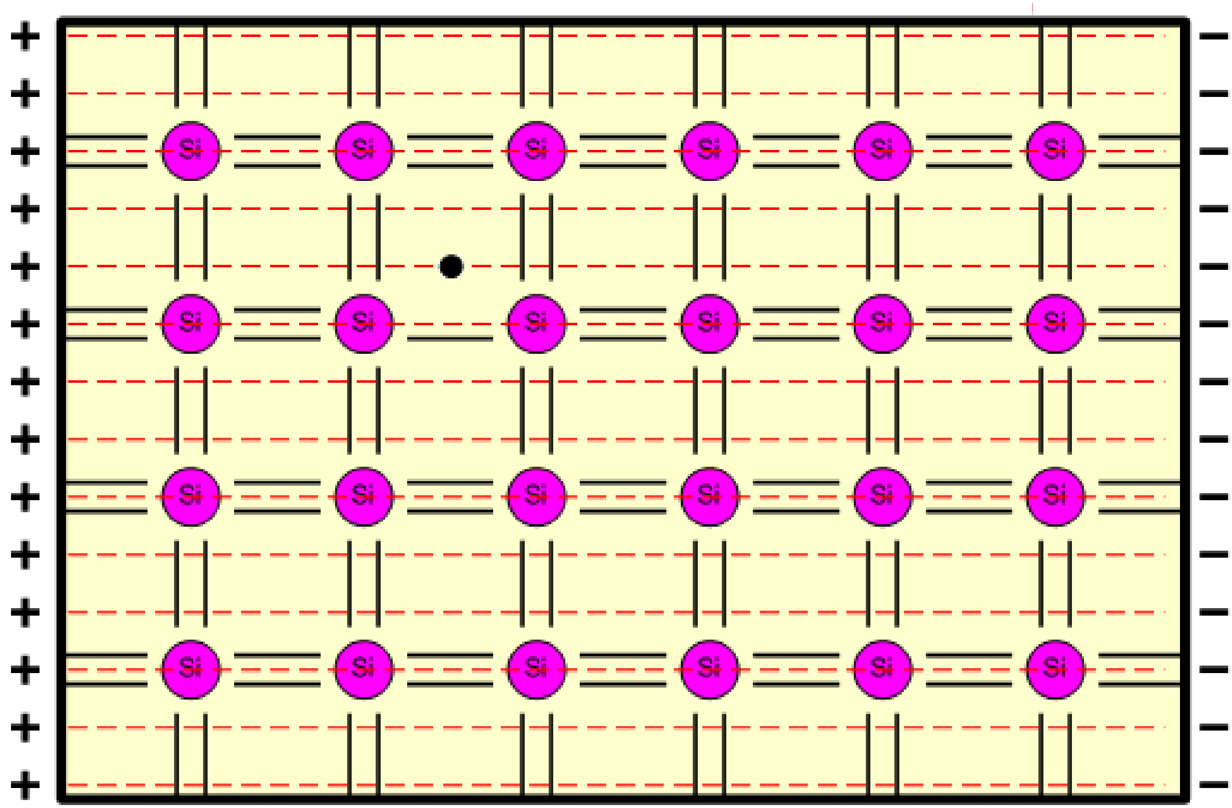
Take a piece of silicon…

And apply a potential difference across it…

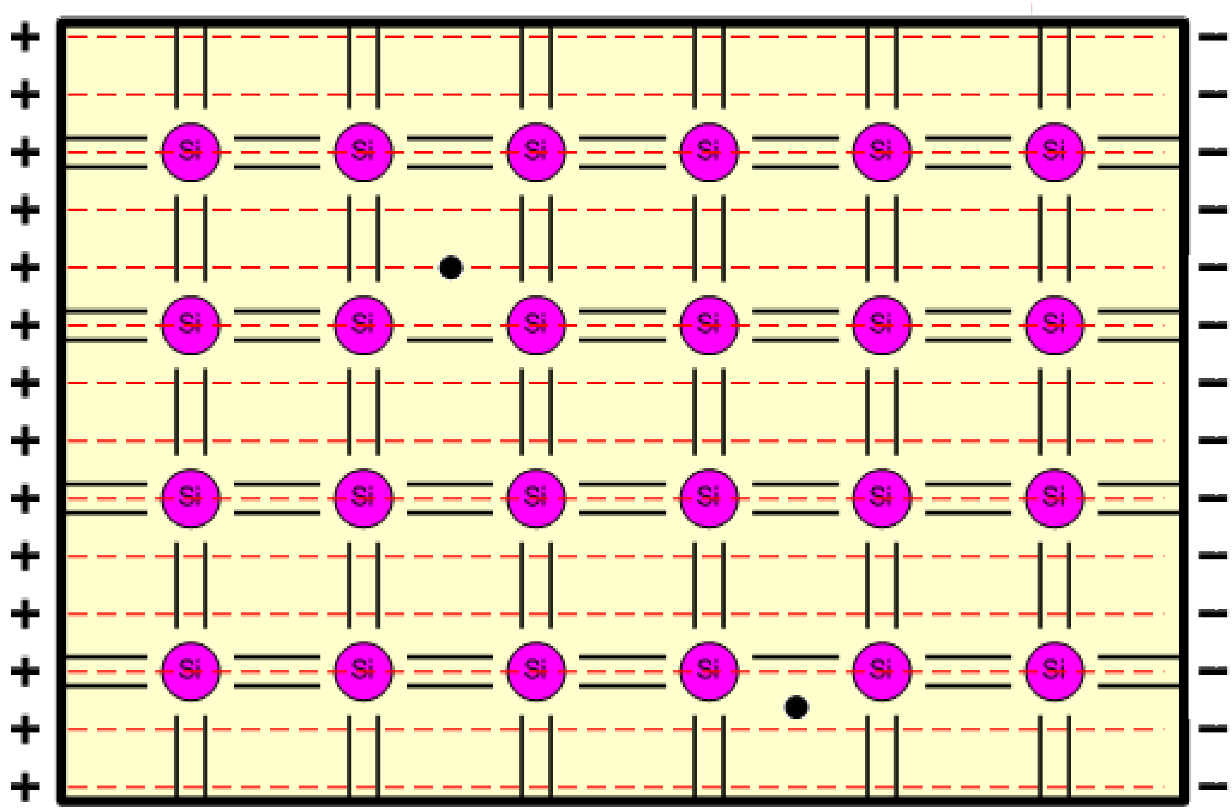
This sets up an electric field throughout the silicon – seen here as dashed lines



Intrinsic Conduction

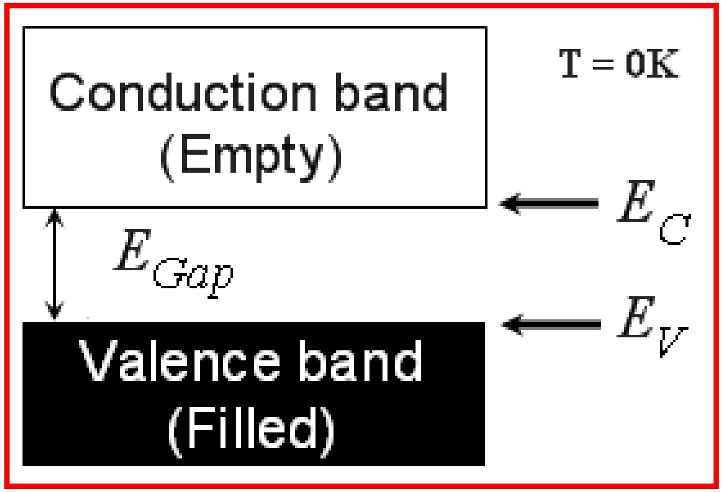


Intrinsic Conduction

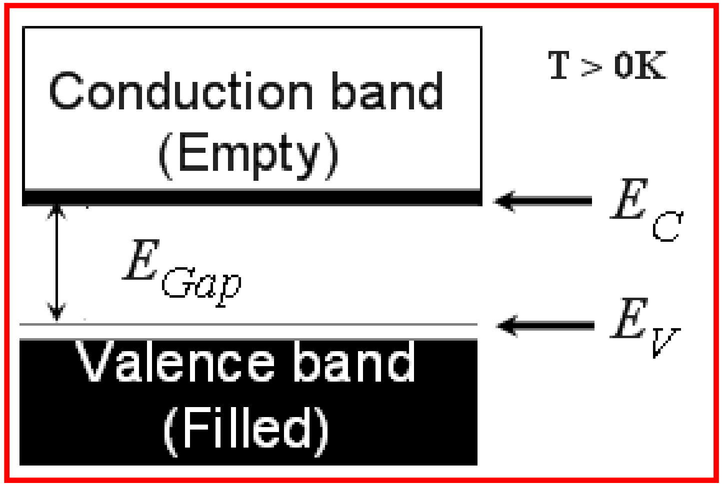


Intrinsic Semiconductors

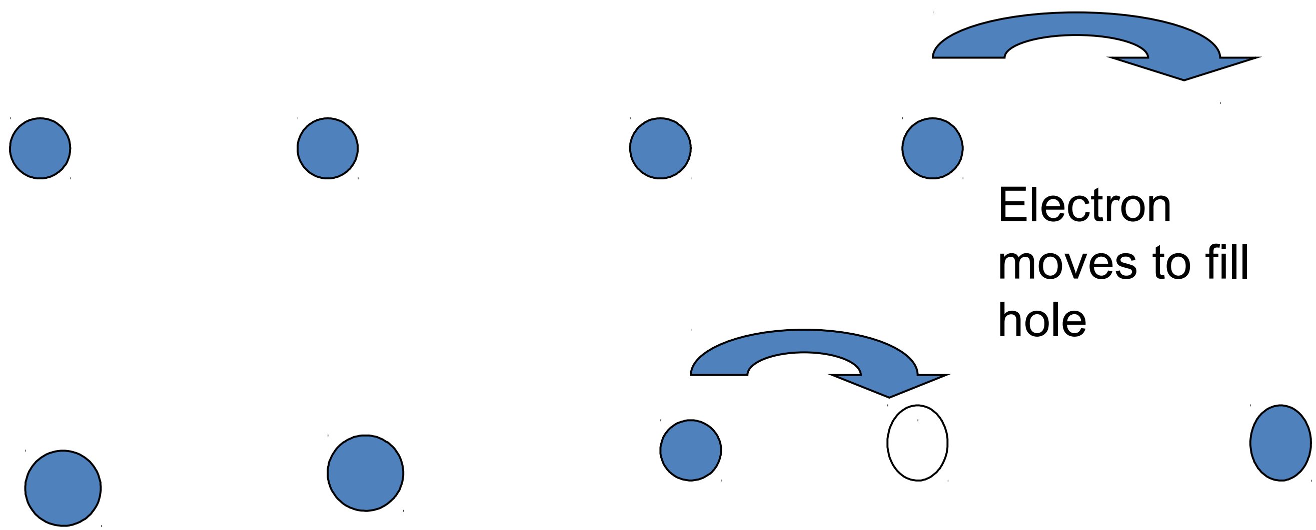
- *Consider nominally pure semiconductor at T = 0 K*
- *There is no electrons in the conduction band*



- *At T > 0 K a small fraction of electrons is thermally excited into the conduction band, "leaving" the same number of holes in the valence band*

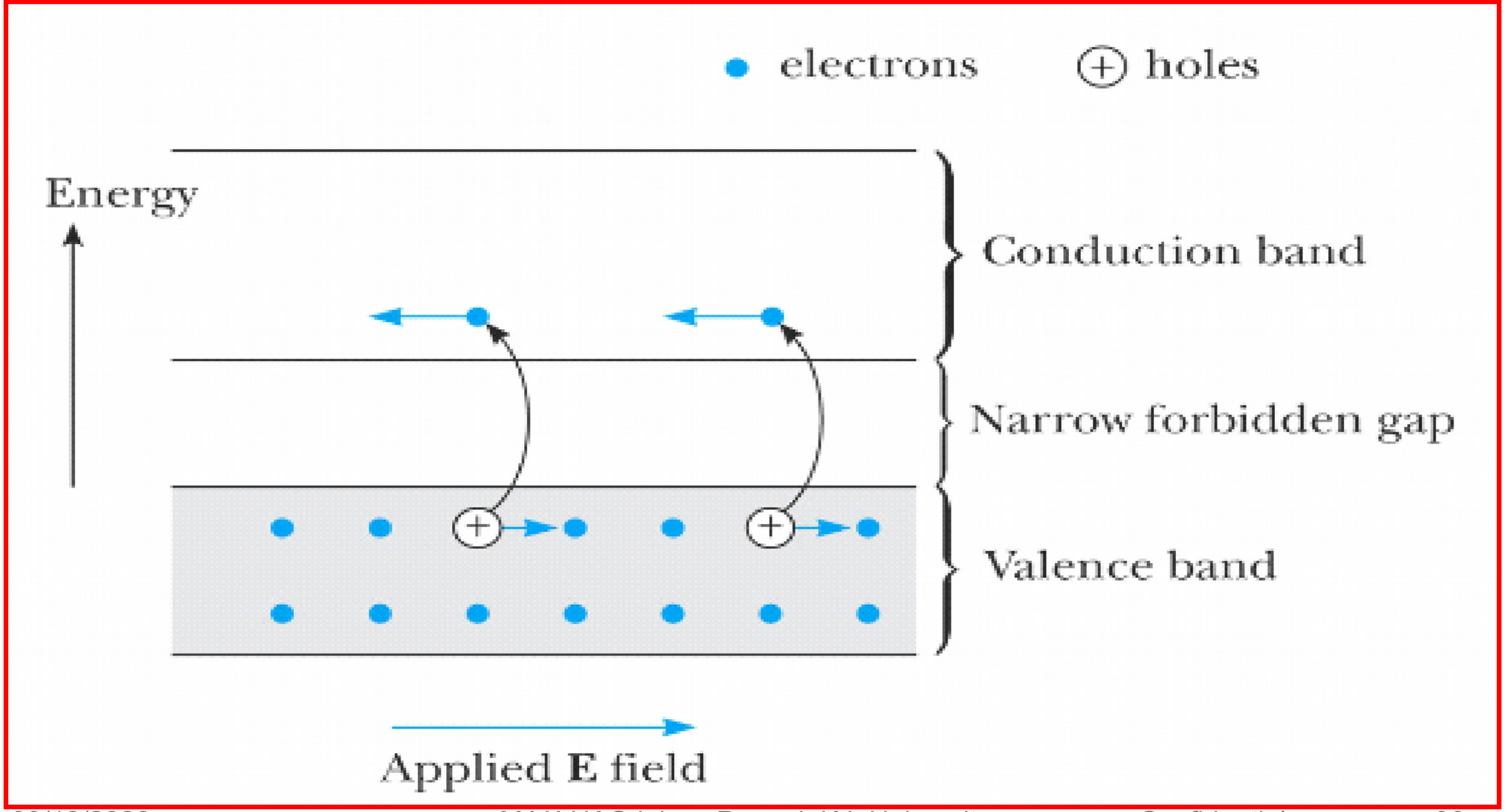


- *This hole is positive, and so can attract nearby electrons which then move out of their bond etc.*
- *Thus, as electrons move in one direction, holes effectively move in the other direction*

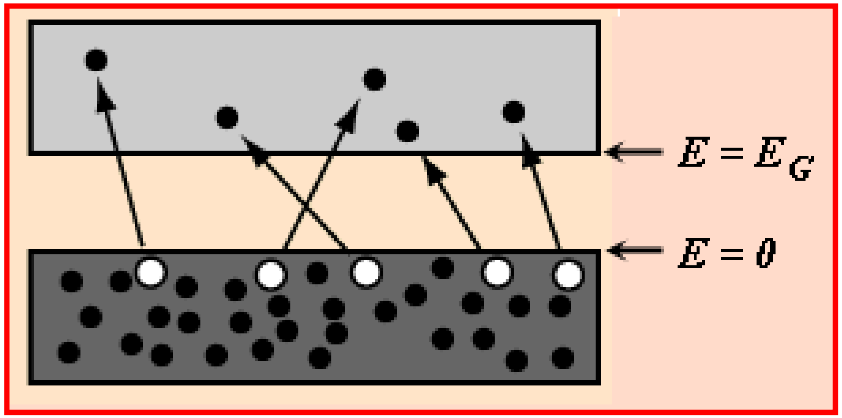


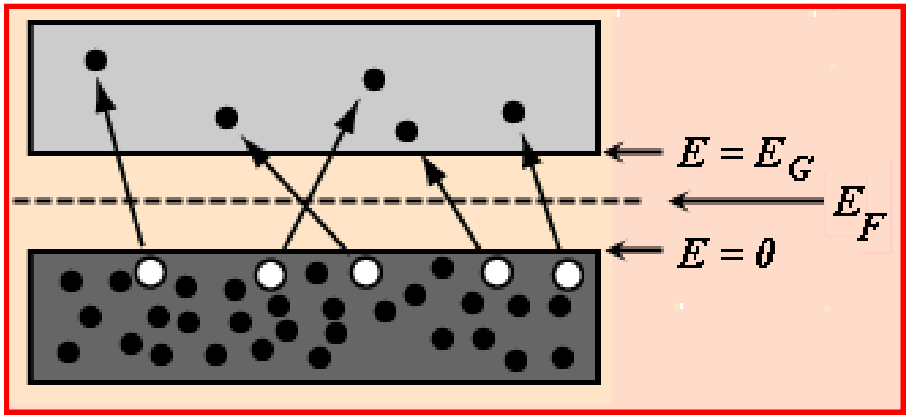
Intrinsic Semiconductors at T >0 K

- *Electrons and holes contribute to the current when a voltage is applied*

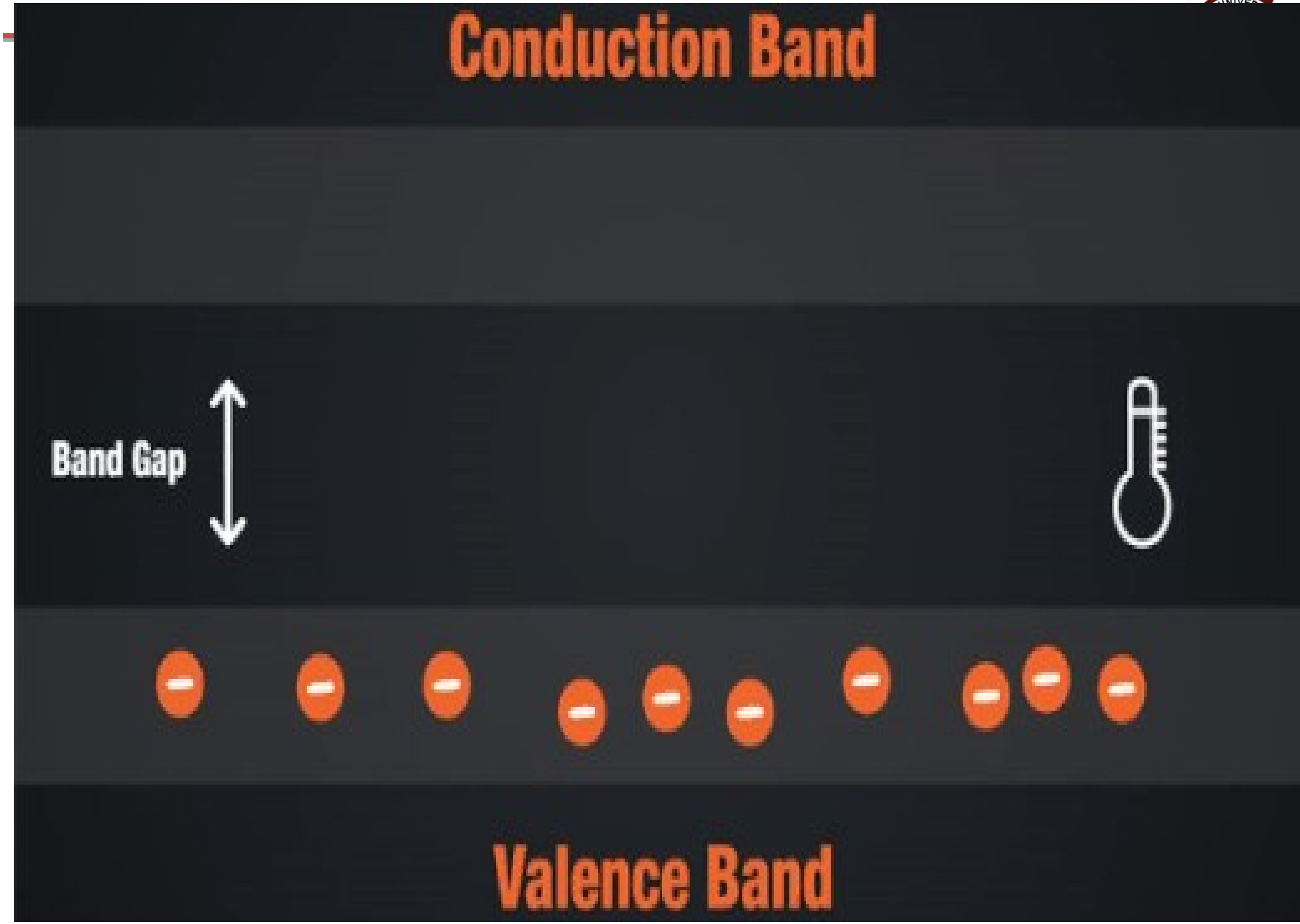


Carrier Concentrations at T >0 K



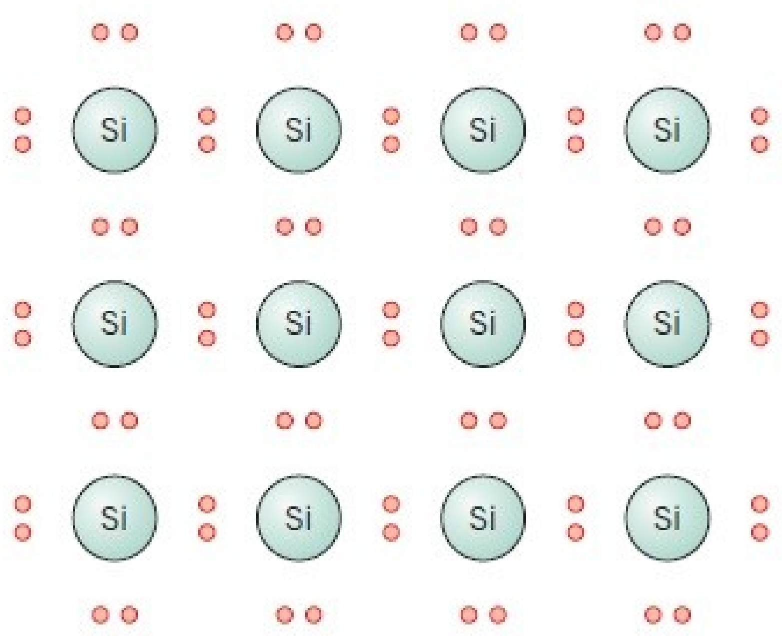


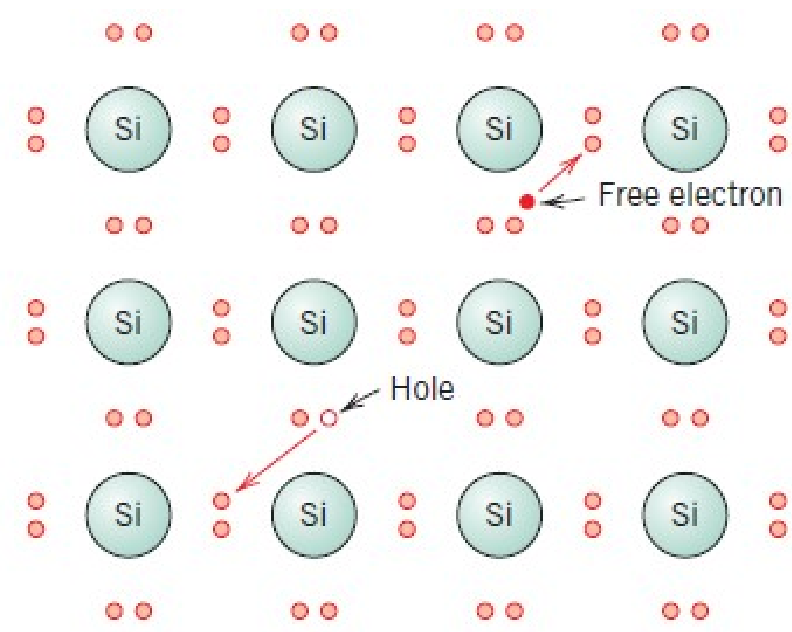
- *The number of electrons equals the number of holes,* $n_e = n_h$
- *The Fermi level lies in the middle of the band gap*
- $n_e = n_h$ *increase rapidly with temperature*


Conduction Band
Band Gap
Valence Band

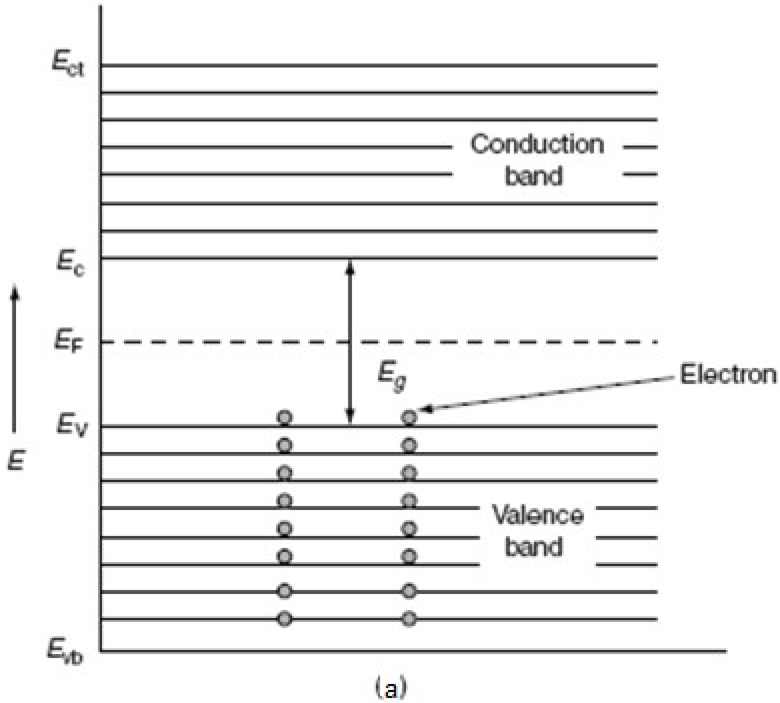
Electron bonding in intrinsic silicon

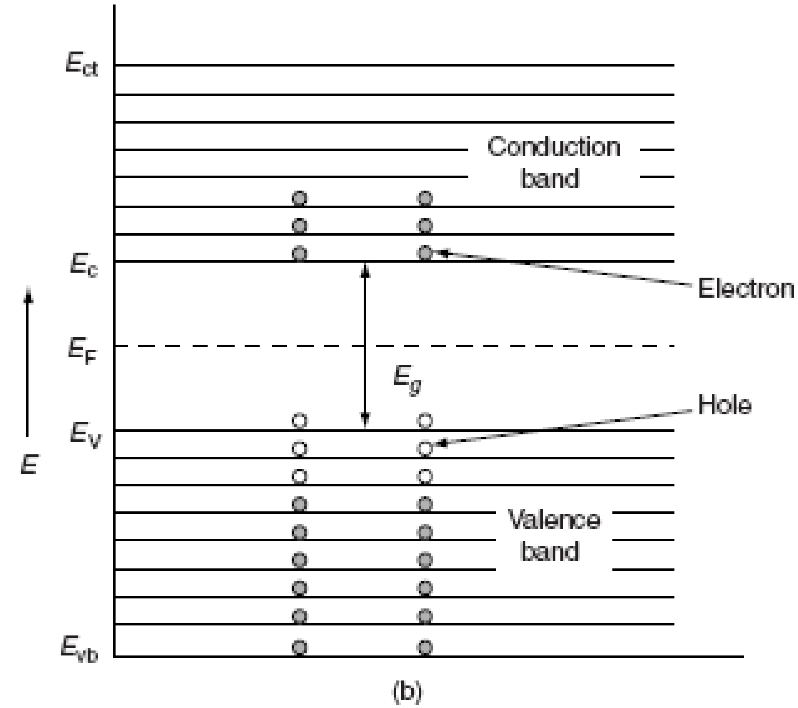
- ✓ Before excitation
- ✓ After excitation





Band diagram of intrinsic semiconductors

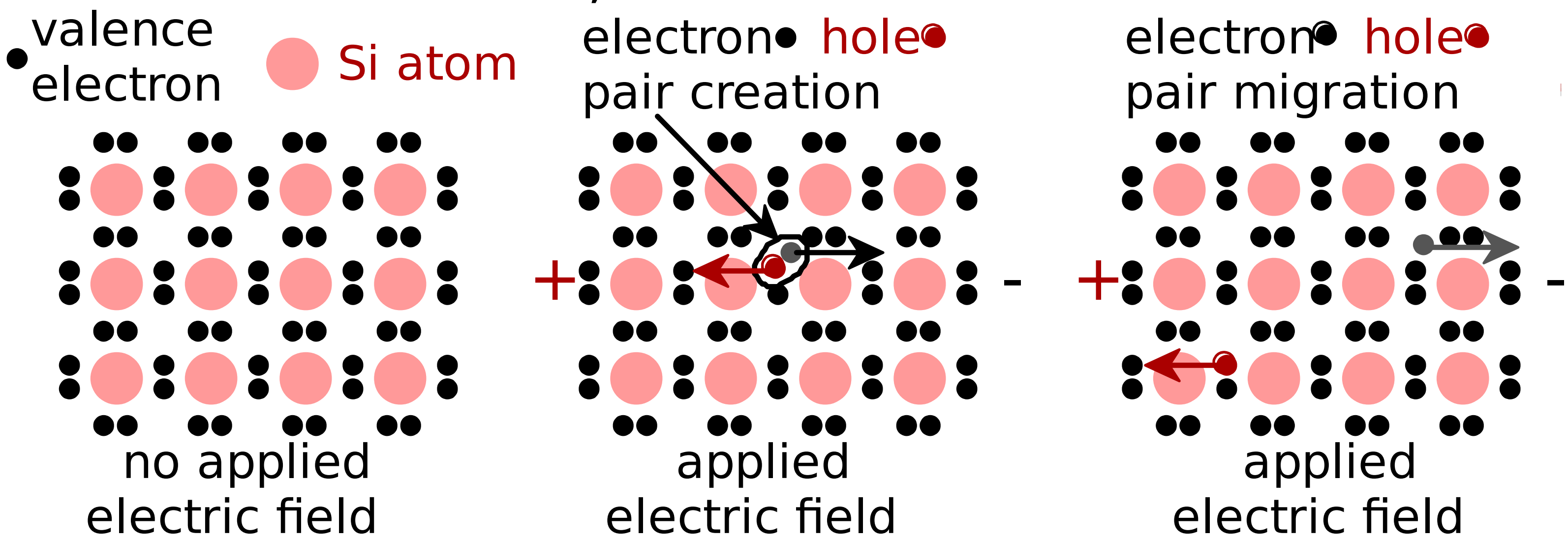




(a) Before Excitation **(b) After Excitation**

Electron and hole conductivity

- In a semiconductor, there can be electrons ***and*** holes:



- *Total Electrical Conductivity thus given by:*

\# holes/m^3

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

hole mobility

\# electrons/m^3

electron mobility

- *With intrinsic systems (**only**), for every free electron, there is also a free hole.*

$$\# \text{ electrons} = n = \# \text{ holes} = p = n_i$$

--true for pure Si, or Ge, etc.

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

μ_h *is ~20% of* μ_e

- *Holes don't move as easily (mobility of holes is always less than for electrons), but still there are so many that they will contribute at least an extra 10-20% to the intrinsic conductivity.*

Material	*Band Gap* (eV)	*Electrical Conductivity* $[(\Omega\text{-}m)^{-1}]$	*Electron Mobility* ($m^2/V\text{-}s$)	*Hole Mobility* ($m^2/V\text{-}s$)
		Elemental		
Si	1.11	4×10^{-4}	0.14	0.05
Ge	0.67	2.2	0.38	0.18
		III–V Compounds		
GaP	2.25	—	0.03	0.015
GaAs	1.42	10^{-6}	0.85	0.04
InSb	0.17	2×10^{4}	7.7	0.07
		II–VI Compounds		
CdS	2.40	—	0.03	—
ZnTe	2.26	—	0.03	0.01

EXTRINIC SEMICONDUCTORS

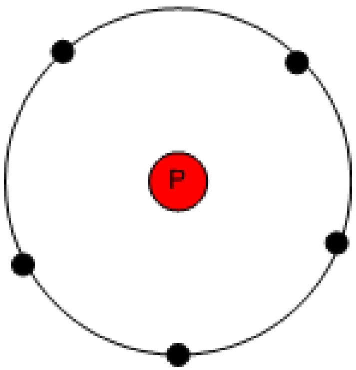
- *Prepared by adding (doping) impurities to intrinsic semiconductors*
- ***Doping** is the incorporation of [substitutional] impurities (trivalent or pentavalent) into a semiconductor according to our requirements*
- *In other words, impurities are introduced in a controlled manner*
- ***Electrical Properties of Semiconductors can be altered drastically by adding minute amounts of suitable impurities to the pure crystals***

Doping

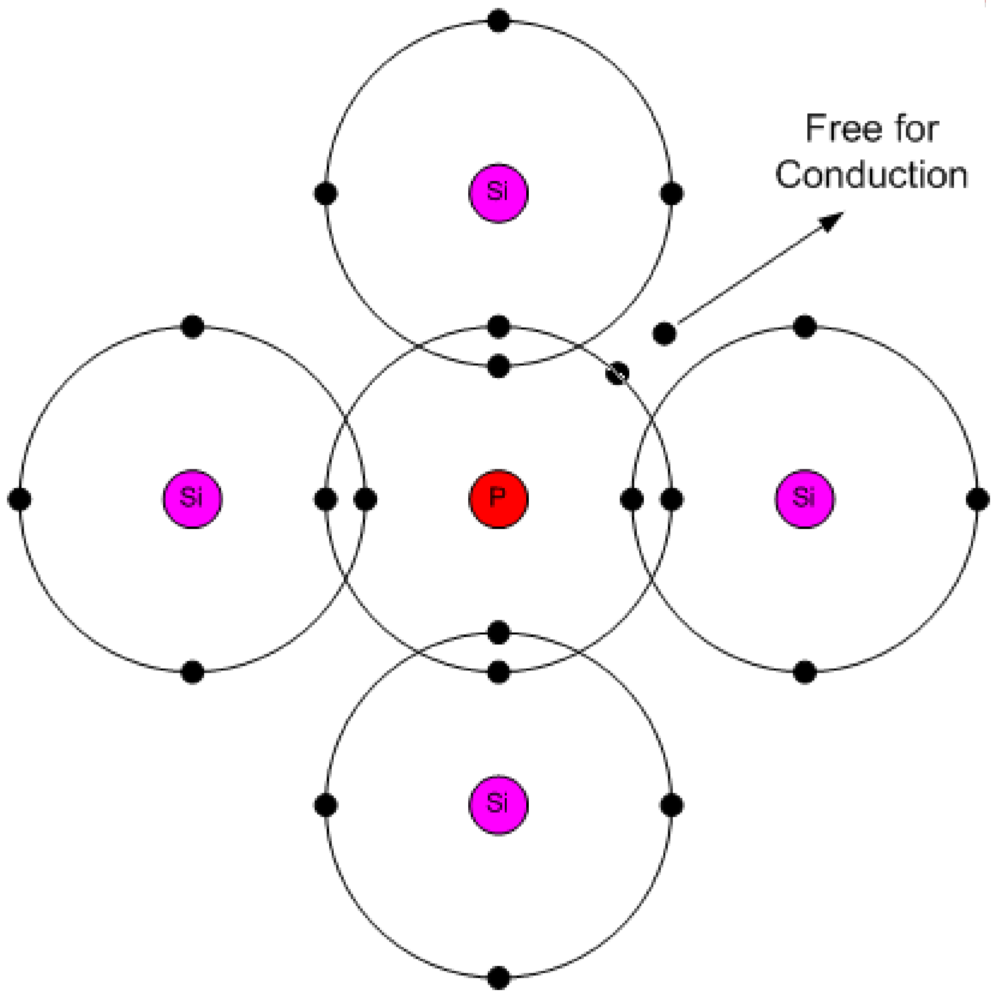
- *Pentavalent*
- *Group VA elements*
  - *Phosphorous*
  - *Arsenic*
  - *Antimony*
- *Trivalent*
- *Group III A elements*
  - *Boron*
  - *Gallium*
  - *Indium*

The Phosphorus Atom

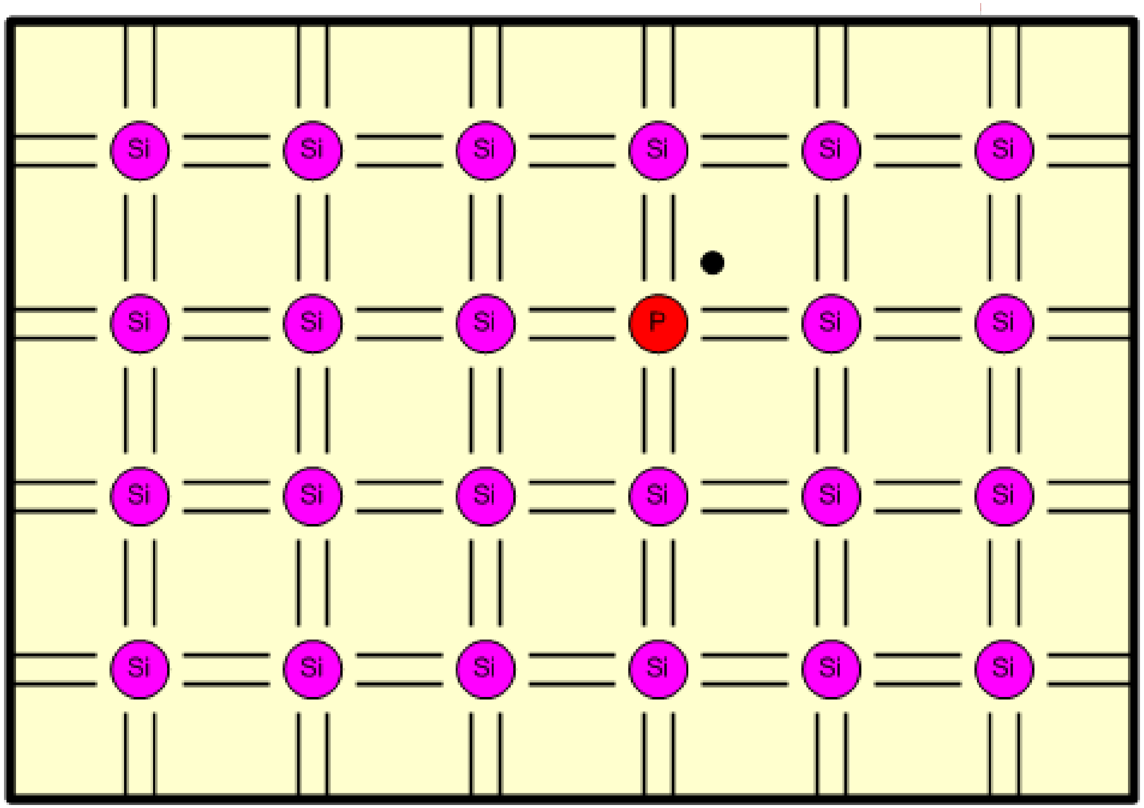
Phosphorus is *number 15 in the periodic table*



It has 15 protons and 15 electrons – 5 of these electrons are in its outer shell

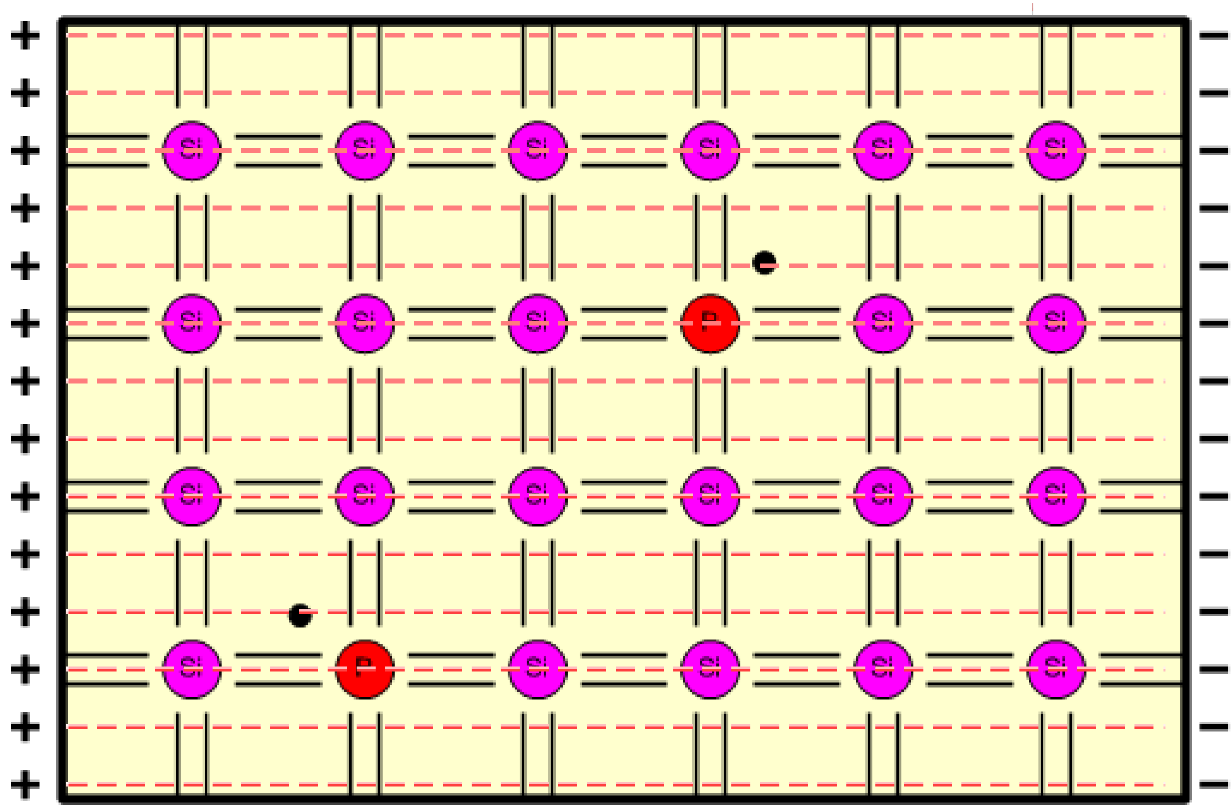


Doping – Making n-type Silicon



We now have an electron that is not bonded – it is thus free for conduction

Doping – Making n-type Silicon

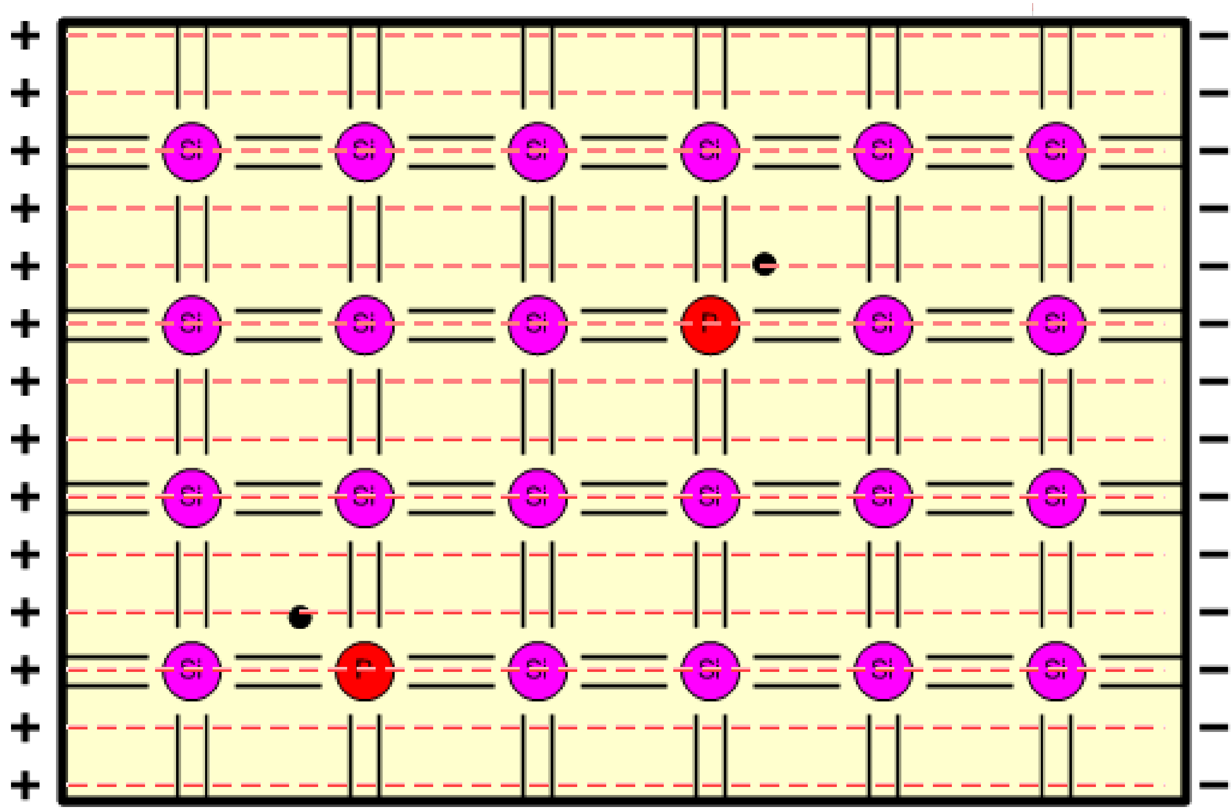


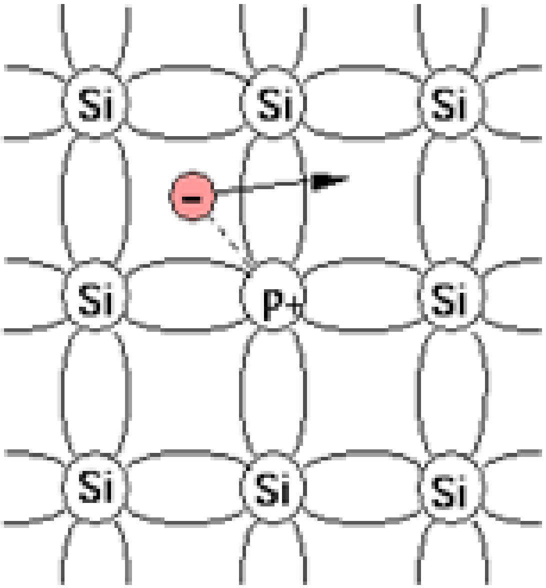
As more electrons are available for conduction we have increased the conductivity of the material

Phosphorus is called the dopant

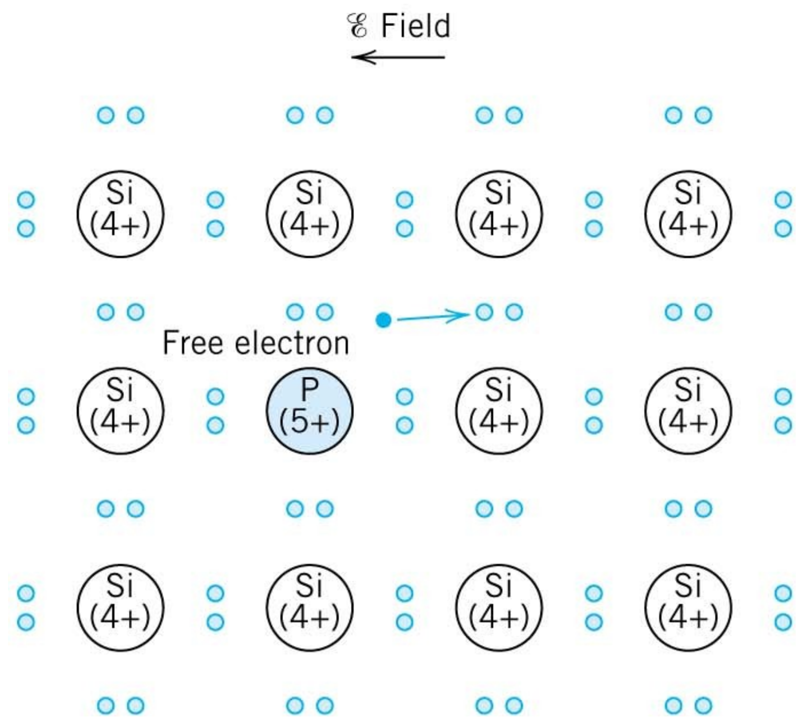
If we now apply a potential difference across the silicon…

Extrinsic Conduction – n-type Silicon





N-type (VA)
(donor)

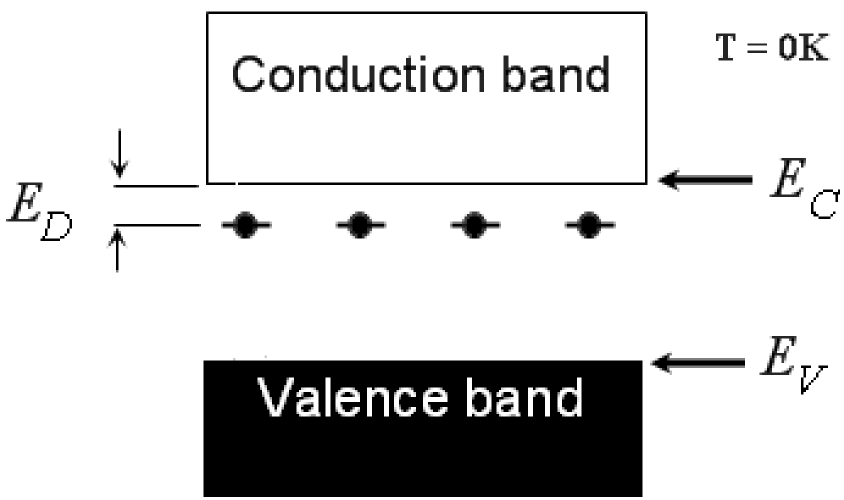


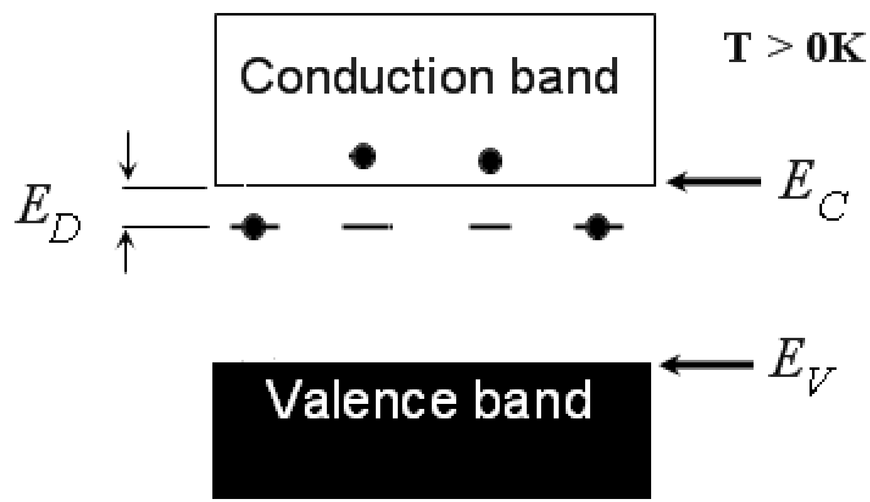
T = 0 K

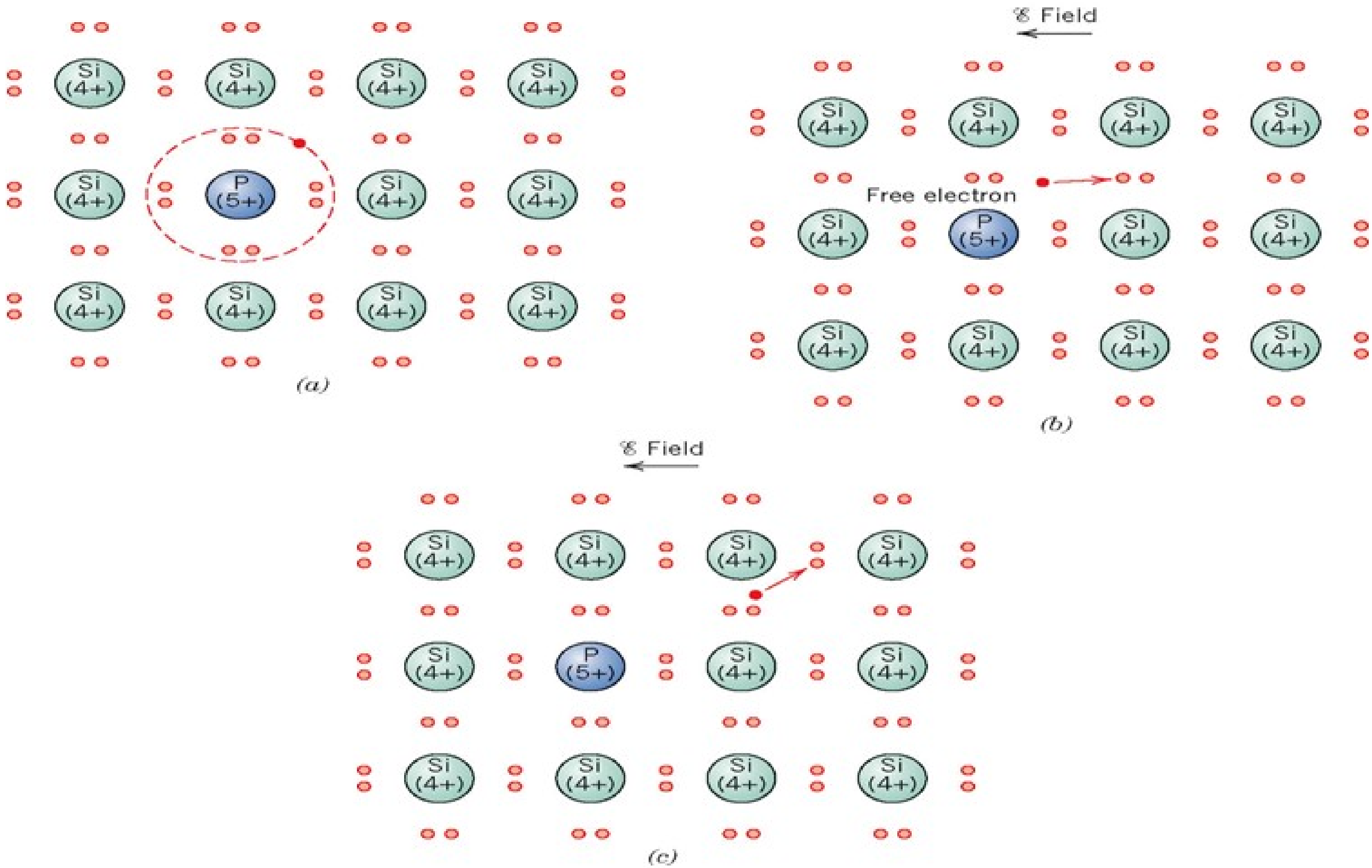
- Valence band is filled.
- Conduction band empty.
- Donar electrons are present in donar energy state.

T > 0 K

- Valence band is filled.
- Electrons from donar energy state jump in to conduction band.
- Conduction band contains donar electrons.

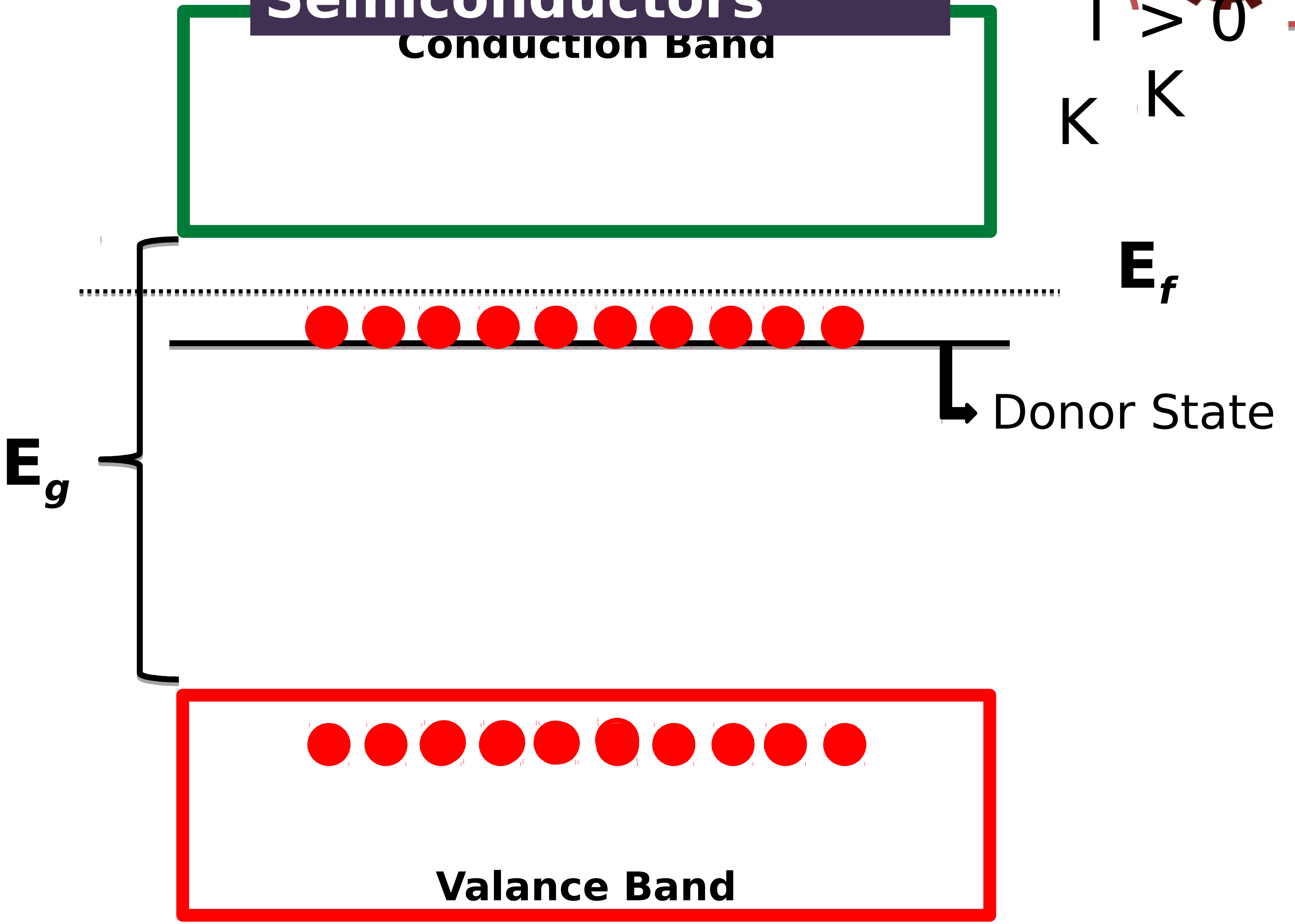






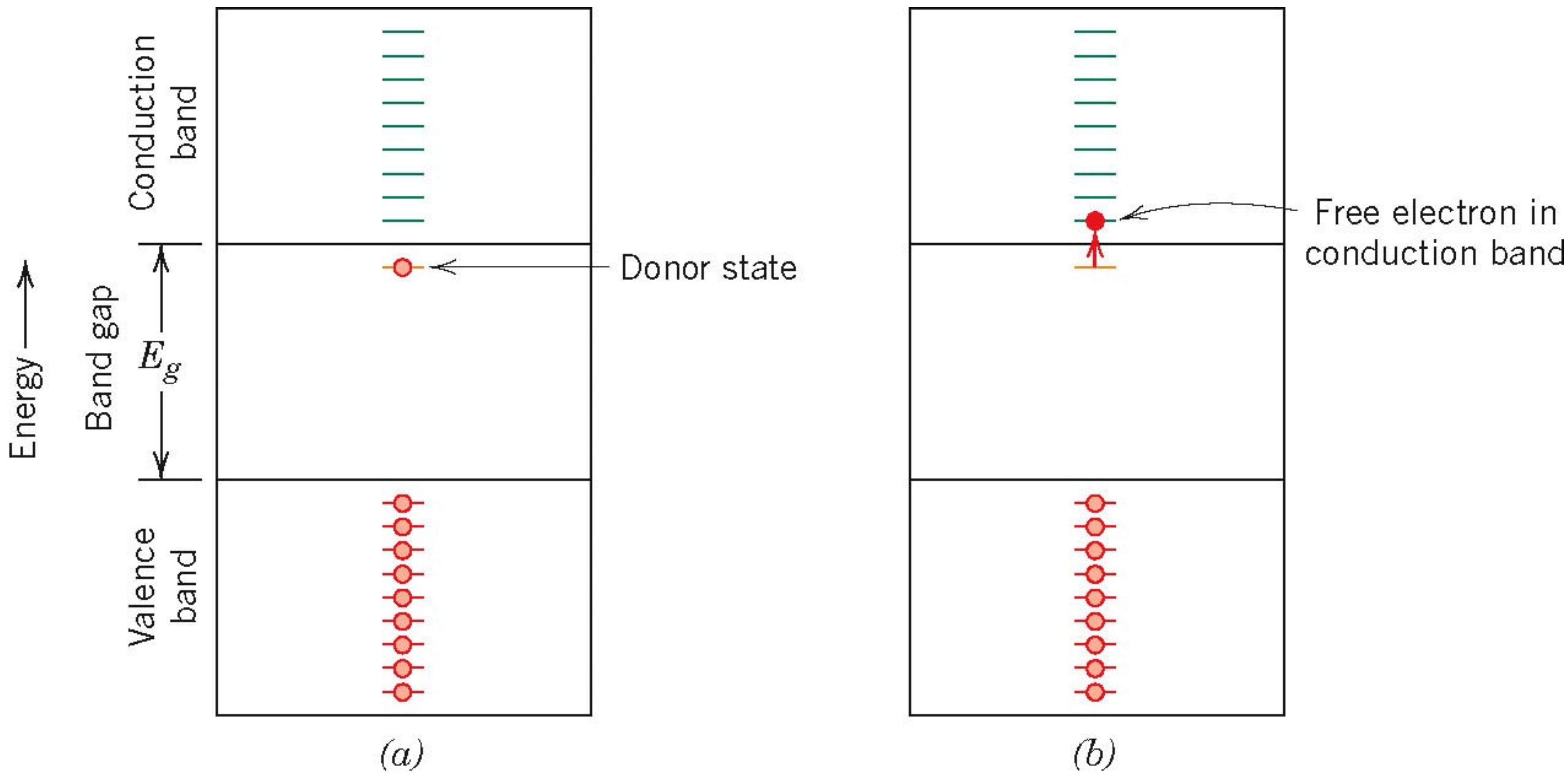
Si (4+)
P (5+)
(a)
ℰ Field
Free electron
(b)
ℰ Field
(c)

n - type Semiconductors



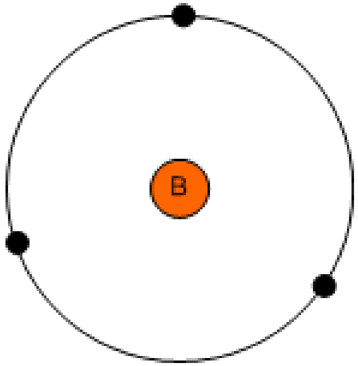
Donor electrons

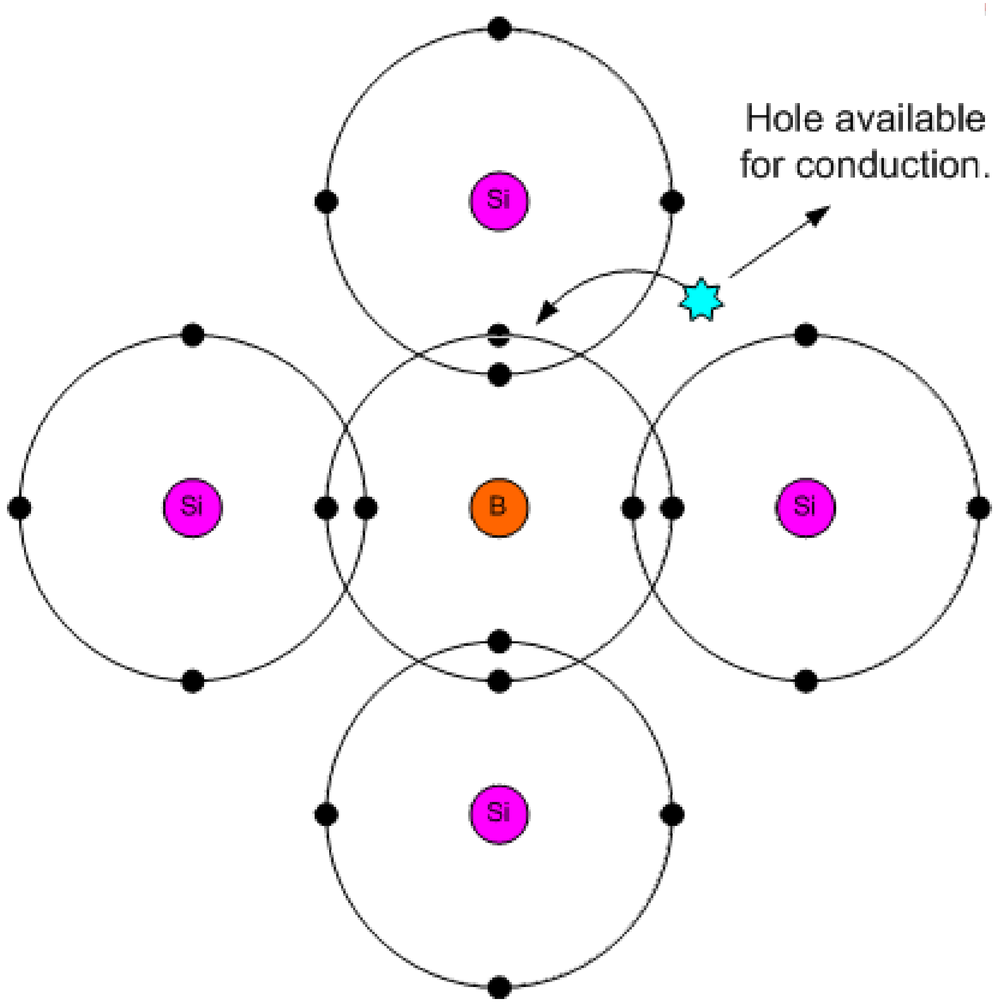
$$\sigma = n|e|\mu_e + p|e|\mu_h \approx n|e|\mu_e = N_d|e|\mu_e$$



The Boron Atom

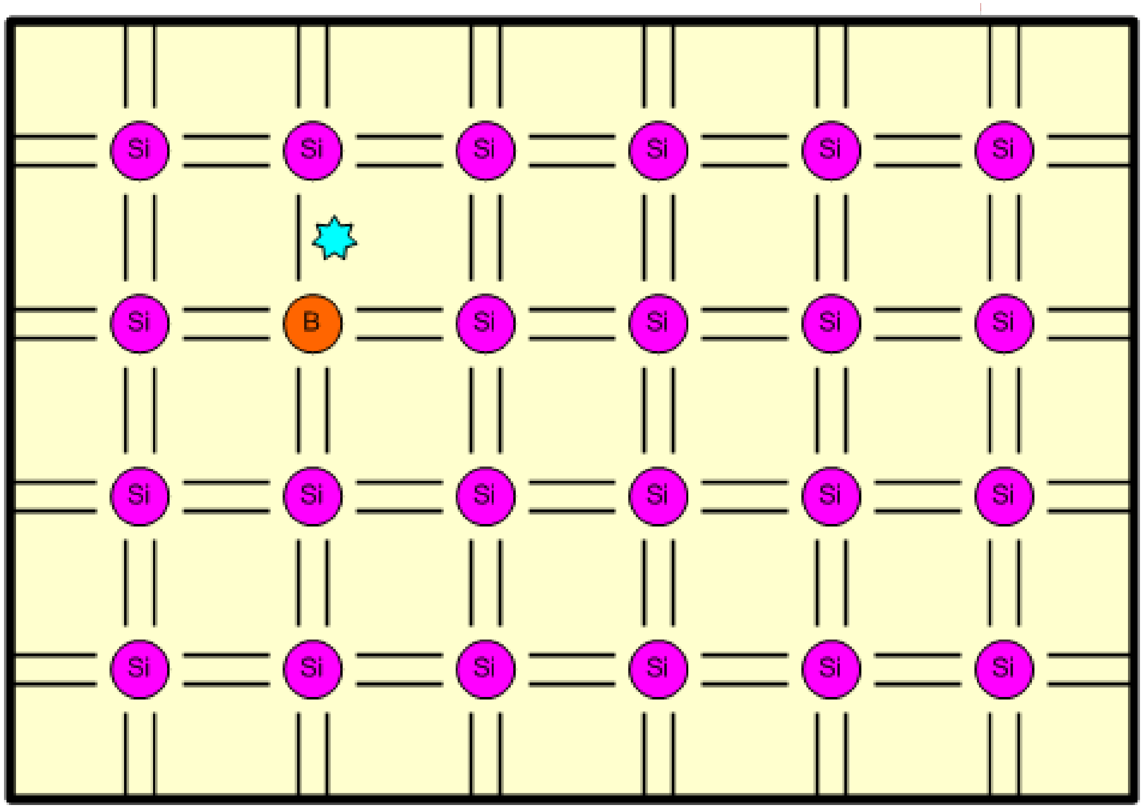
Boron is number 5 in the periodic table





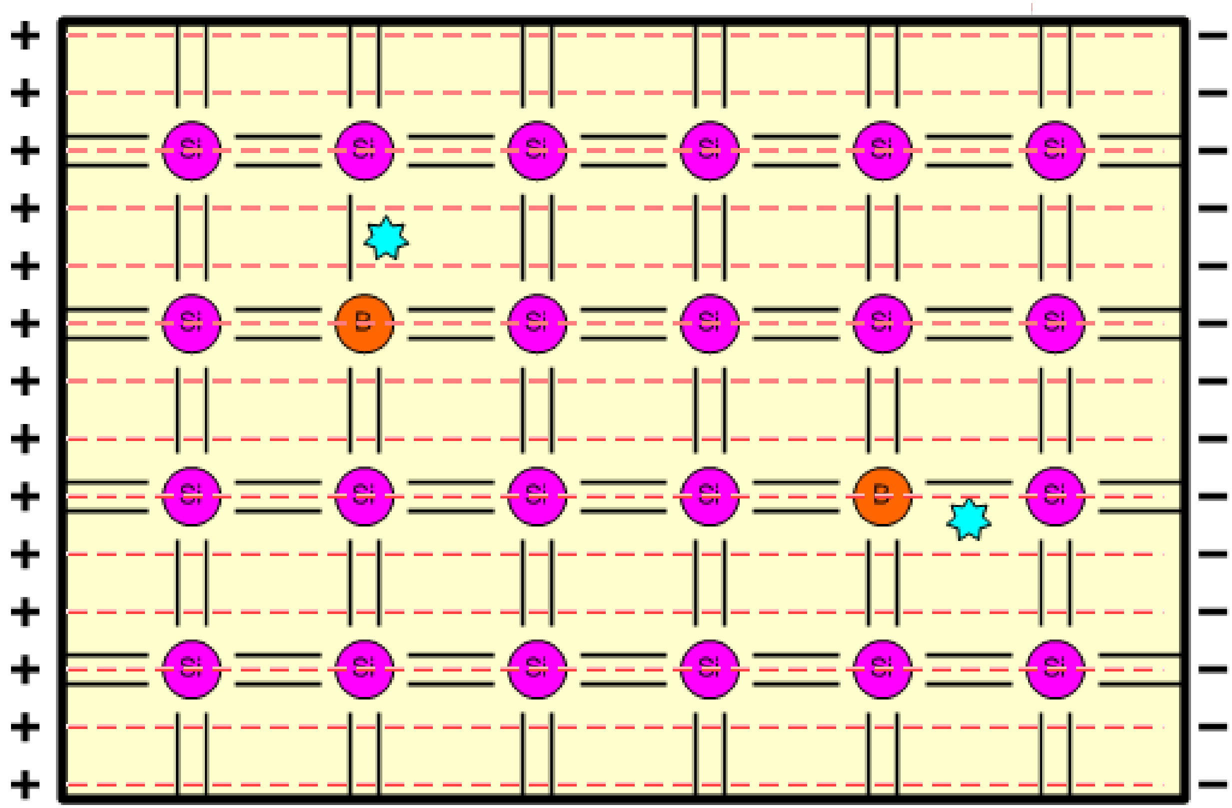
It has 5 protons and 5 electrons – 3 of these electrons are in its outer shell

Doping – Making p-type Silicon



Notice we have a hole in a bond – this hole is thus free for conduction

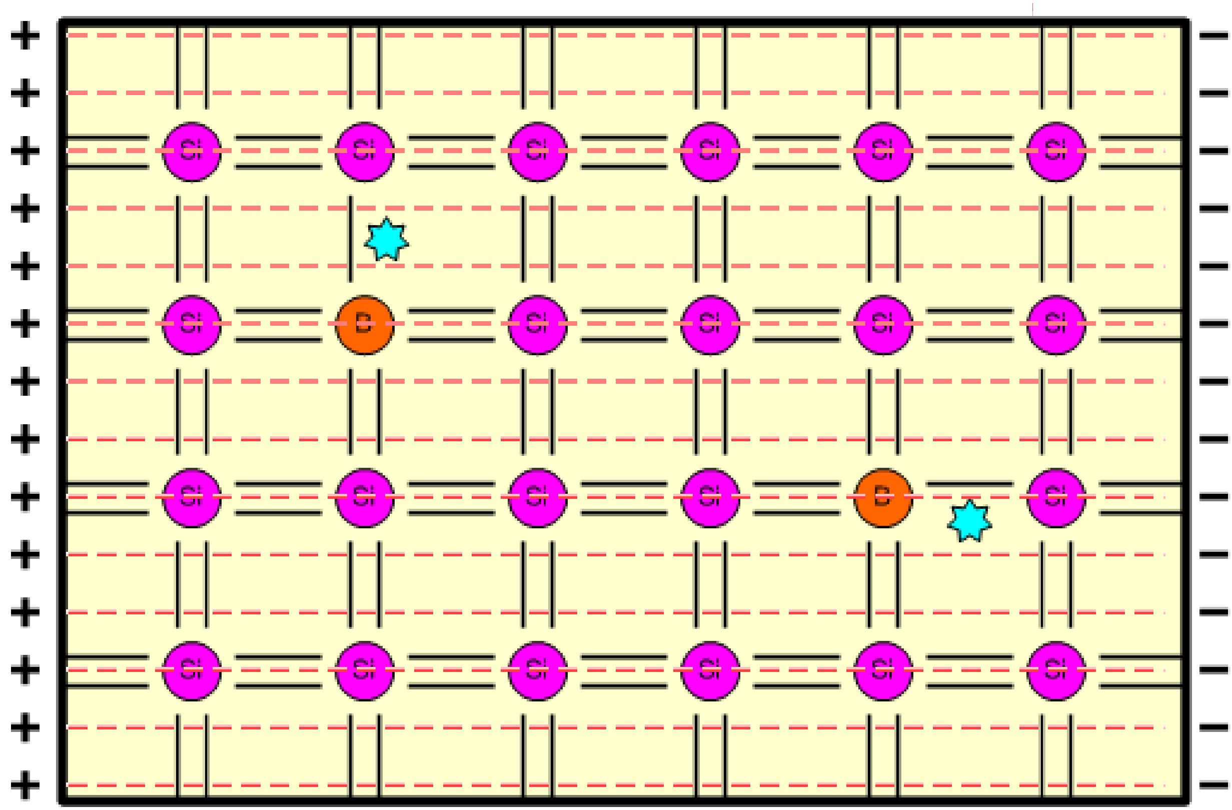
Doping – Making p-type Silicon

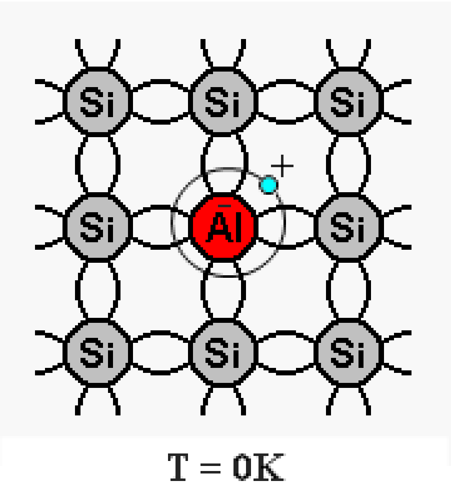


Boron is the dopant in this case

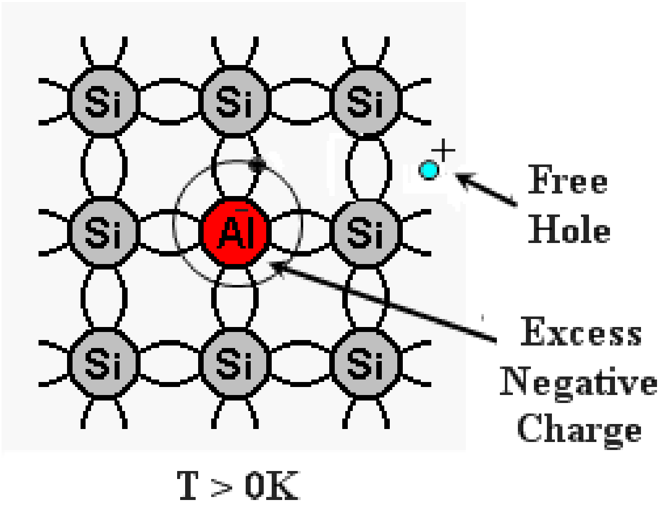
If we now apply a potential difference across the silicon…

Extrinsic Conduction – p-type silicon

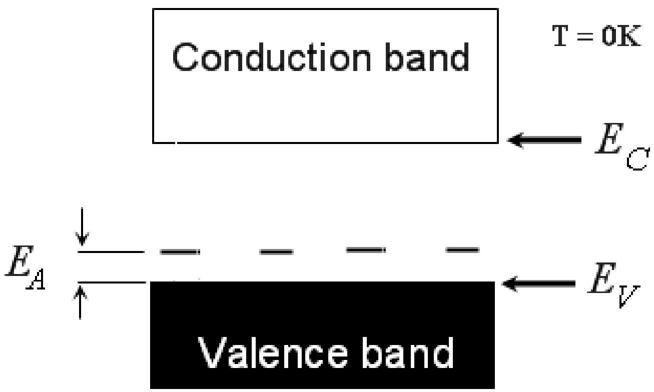




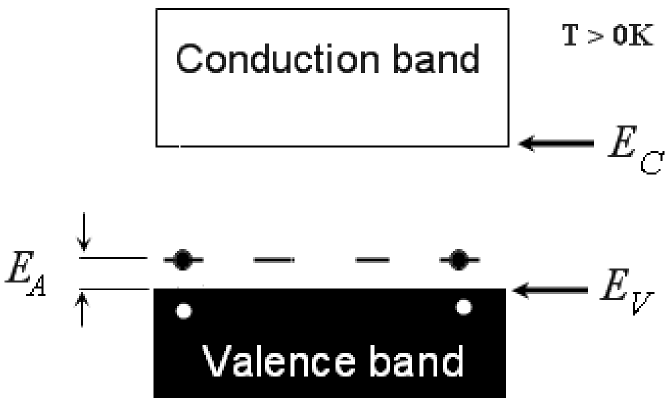
Si
Al
T = 0K



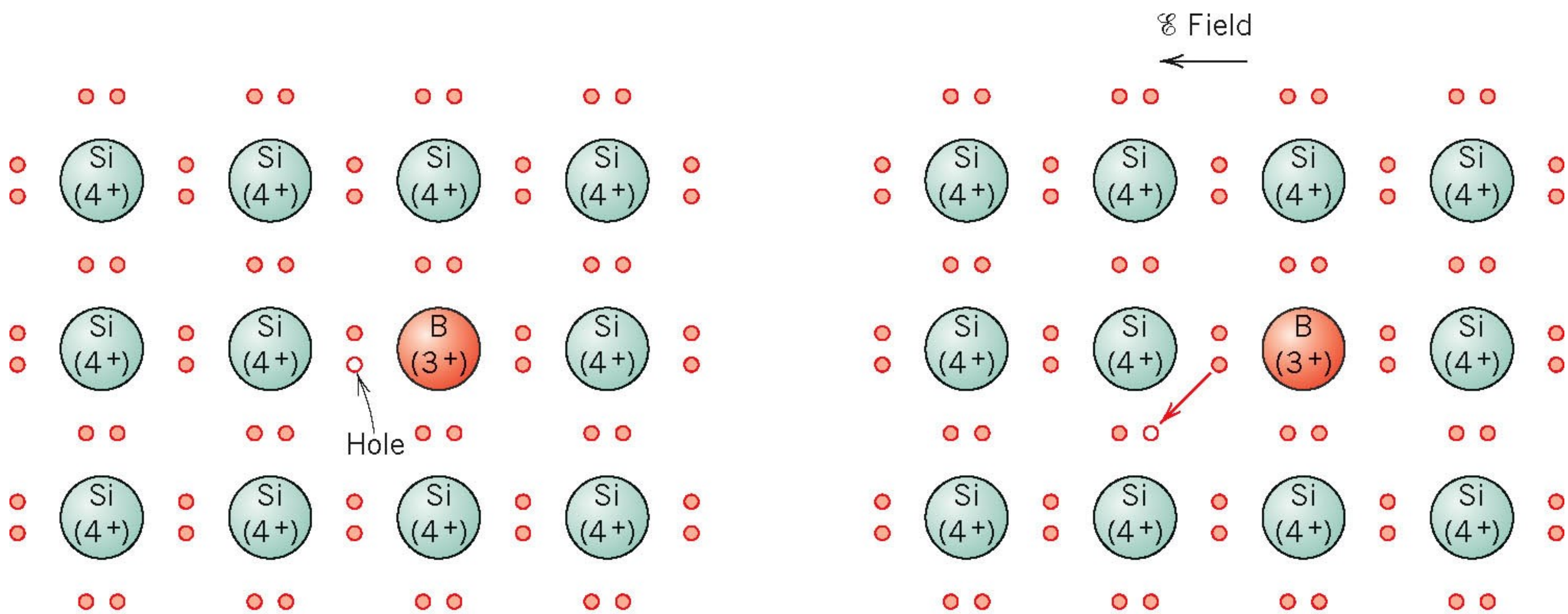
Si
Al
Free Hole
Excess Negative Charge
T > 0K



Conduction band
T = 0K
E_C
E_A
E_V
Valence band

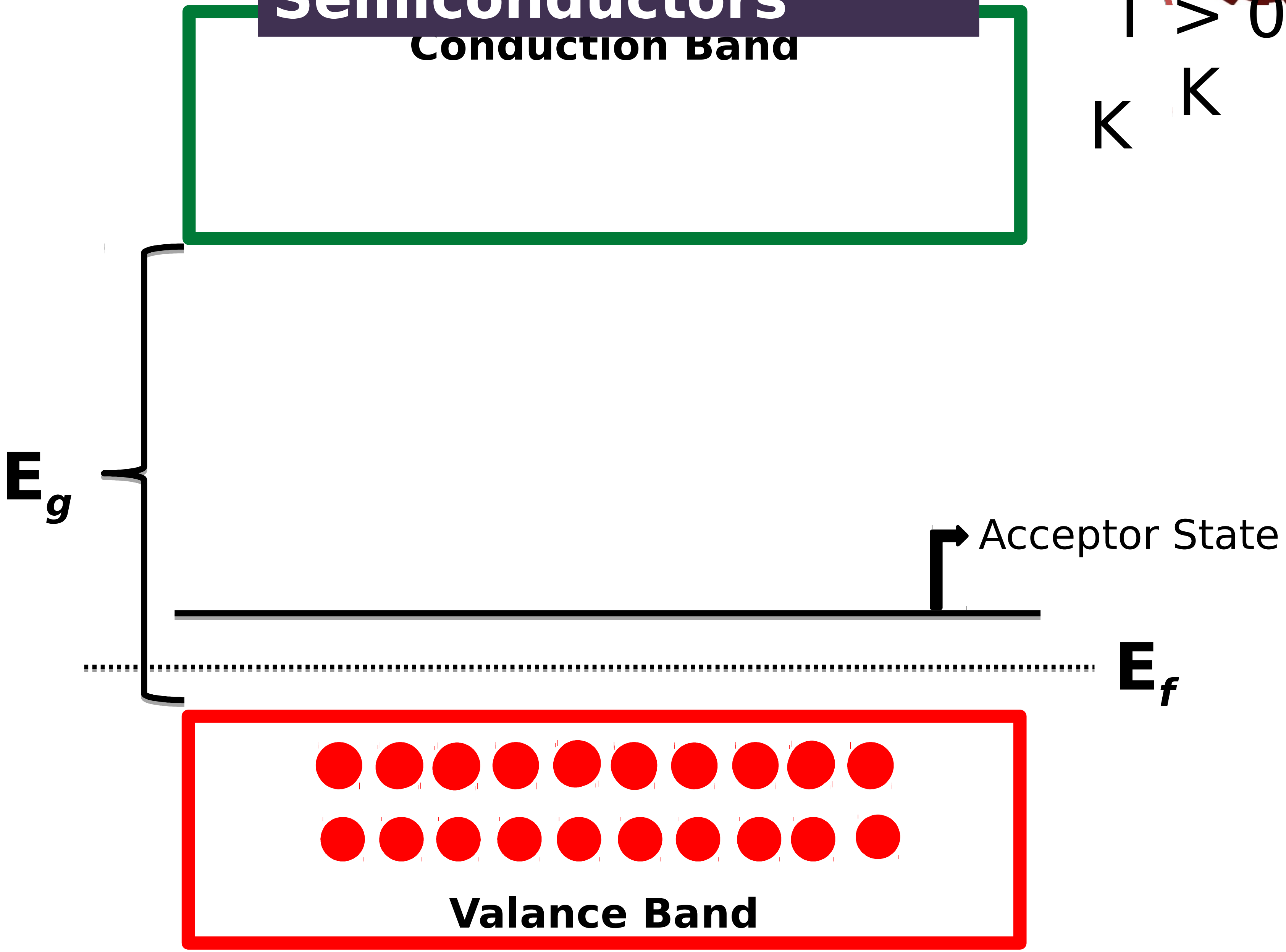


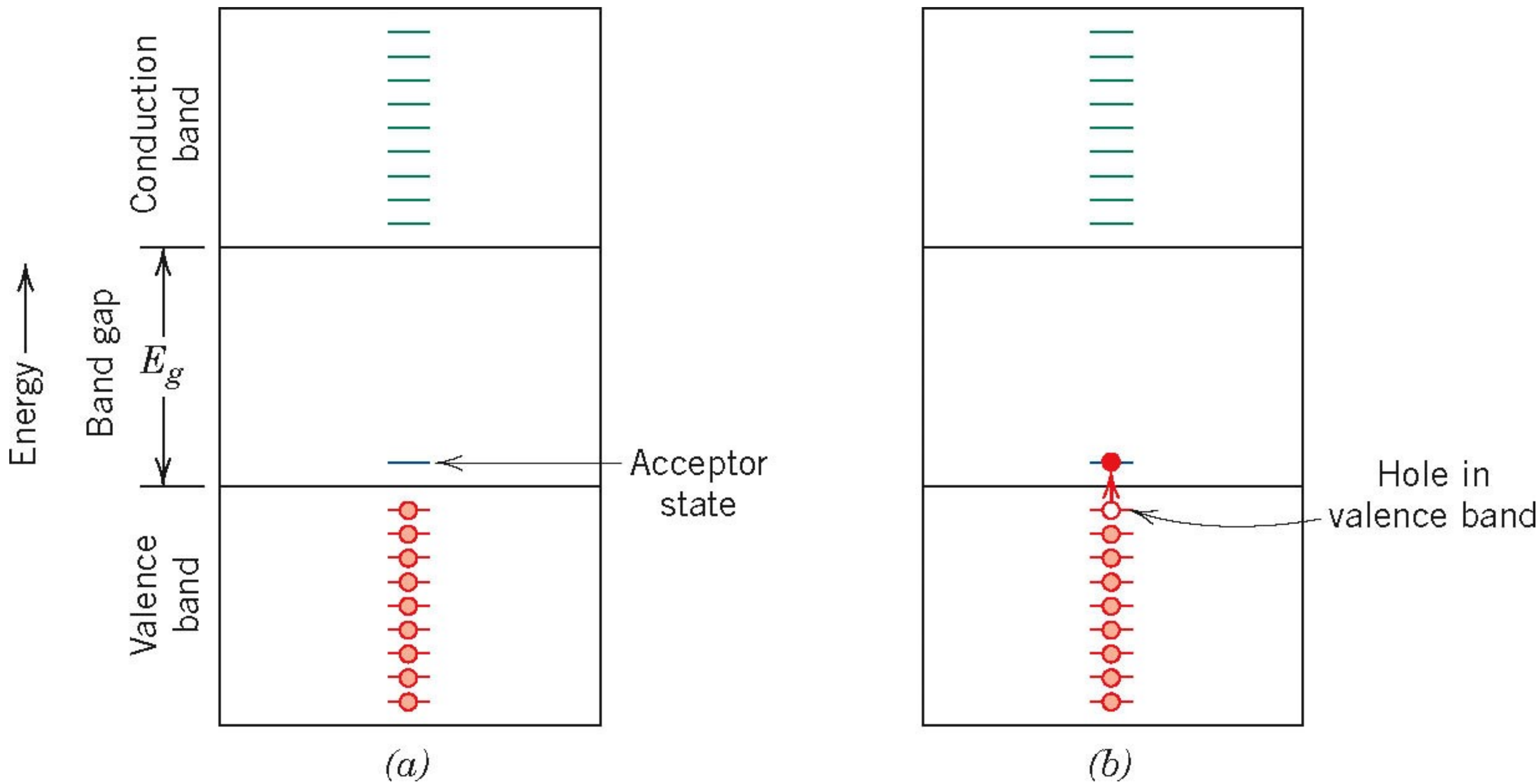
Conduction band
T > 0K
E_C
E_A
E_V
Valence band



(a) (b)

p - type Semiconductors

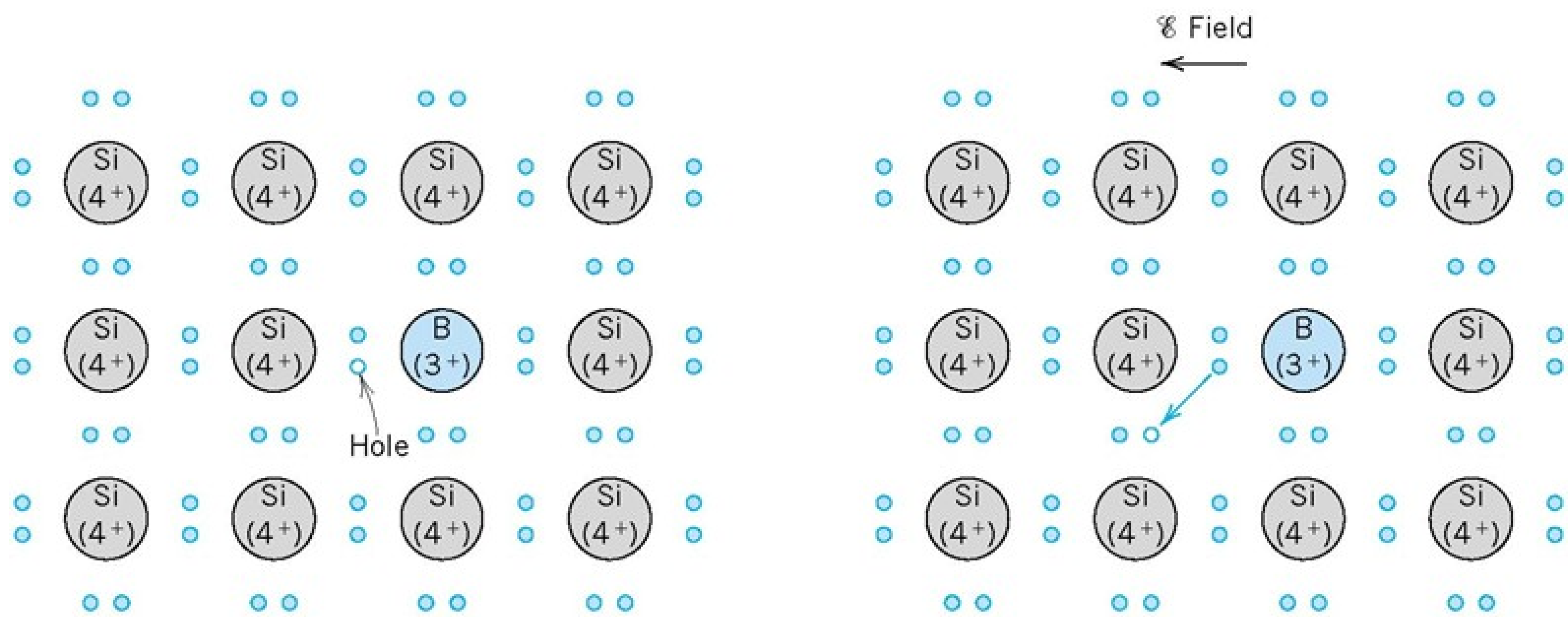



Conduction band
Energy
Band gap
E_g
Acceptor state
Valence band
(a)
Hole in valence band
(b)

Extrinsic conductivity—p type

- *Every acceptor generates excess mobile holes ($p=N_a$).*
- *Now holes totally outnumber electrons, so conductivity equation switches to p domination.*

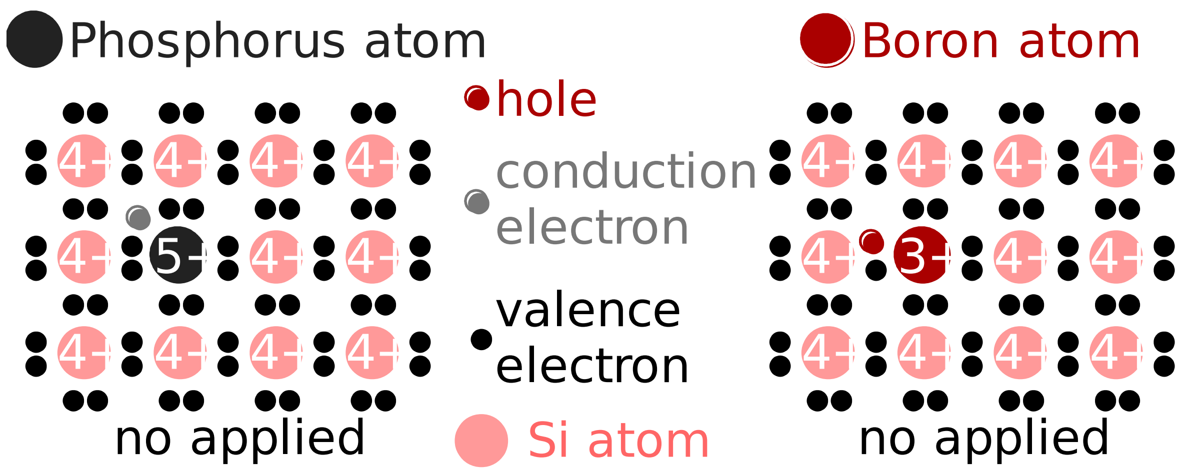
$$\sigma = n|e|\mu_e + p|e|\mu_h \approx p|e|\mu_h = N_a|e|\mu_h$$



(a) (b)

- **Intrinsic**:
  \# electrons = # holes (n = p) $\sigma \approx n_i|e|(\mu_e + \mu_h)$
  --case for pure Si
- **Extrinsic**: $\sigma = n|e|\mu_e + p|e|\mu_h$
  --n ≠ p
  --occurs when DOPANTS are added with a different
  \# valence electrons than the host (e.g., Si atoms)
- N-type Extrinsic: (n >> p) P-type Extrinsic: (p >> n)

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



no applied electric field

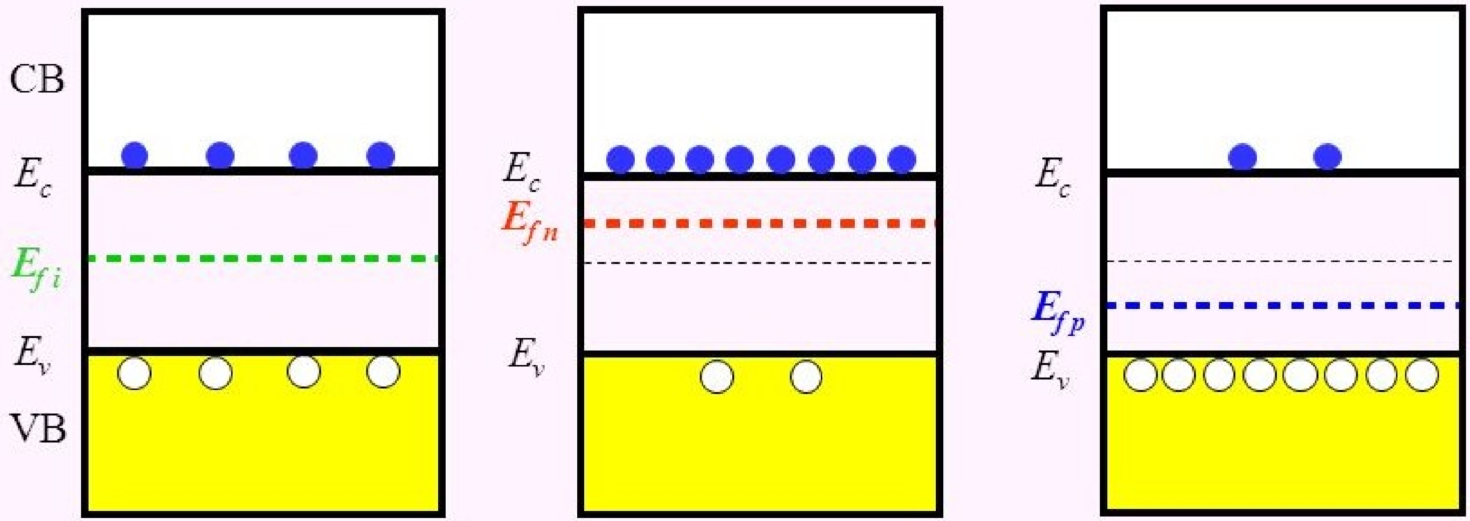
no applied electric field

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

$$n, p \geq n_i * 10^3$$

Intrinsic, n-Type, p-Type Semiconductors

- Energy band diagrams



(a) intrinsic (b) *n*-type (c) *p*-type

$$np = n_i^2$$

Note that donor and acceptor energy levels are not shown.

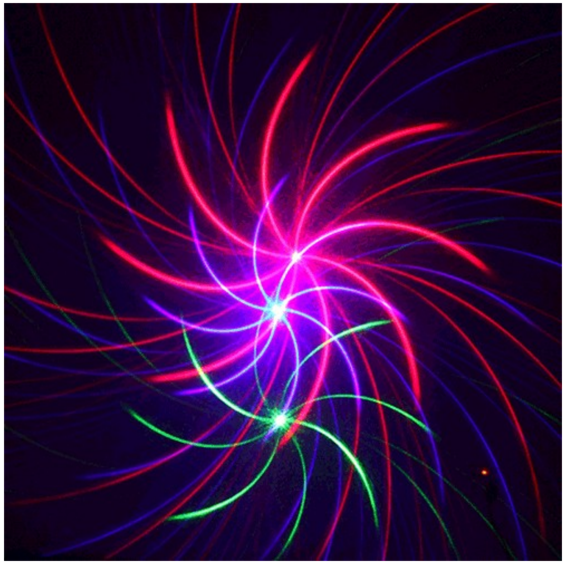
Conductivity and mobility of charge carriers in semi-conductors

- Intrinsic semiconductors:
- Equal carrier concentration (electron and hole)
- $n_i = n = p$
- The magnitude of hole mobility is always less than electron mobility for semiconductors
- Conductivity is given by
- $\sigma = ne\mu_e + pe\mu_h = n_i e(\mu_e + \mu_h)$

- Extrinsic semiconductors:
- Conductivity is mainly due to free electrons in n-type semiconductors
- $n >> p$
- $\sigma = ne\mu_e$
- Conductivity is mainly due to free holes in p-type semiconductors
- $p >> n$
- $\sigma = pe\mu_e$

LASER

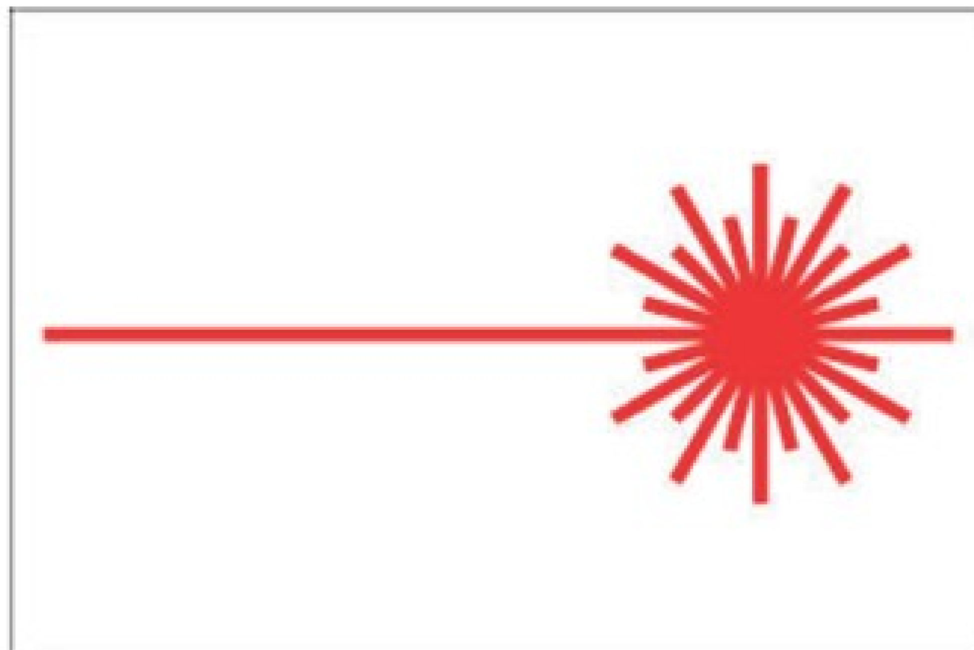
An Invention in Search of a Problem



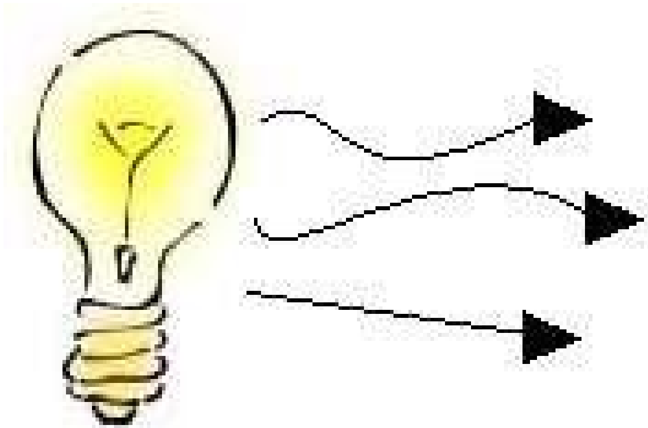
L.A.S.E.R

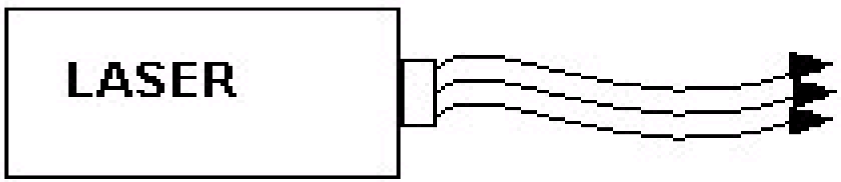
Definition

- Light
- Amplification
- Stimulation
- Emission
- Radiation.



Incandescent vs. Laser Light



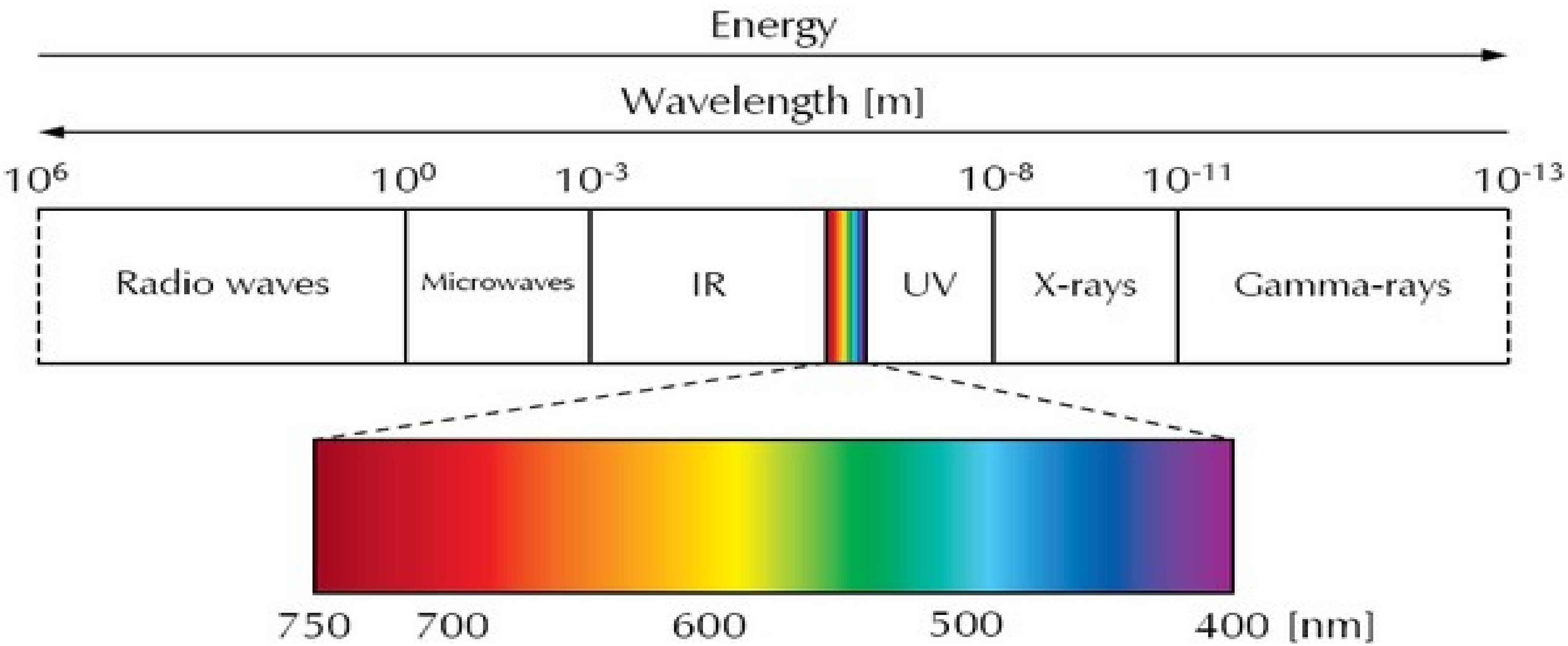


1. Many wavelengths
2. Multidirectional
3. Incoherent
4. Less Intensity

1. Monochromatic
2. Directional
3. Coherent
4. High Intensity

The combination of these Four properties makes laser light focus 100 times better than ordinary light

ELECTROMAGNETIC SPECTRUM



Lasers can operate in the ultraviolet, visible, and infrared.

Characteristics of LASERS

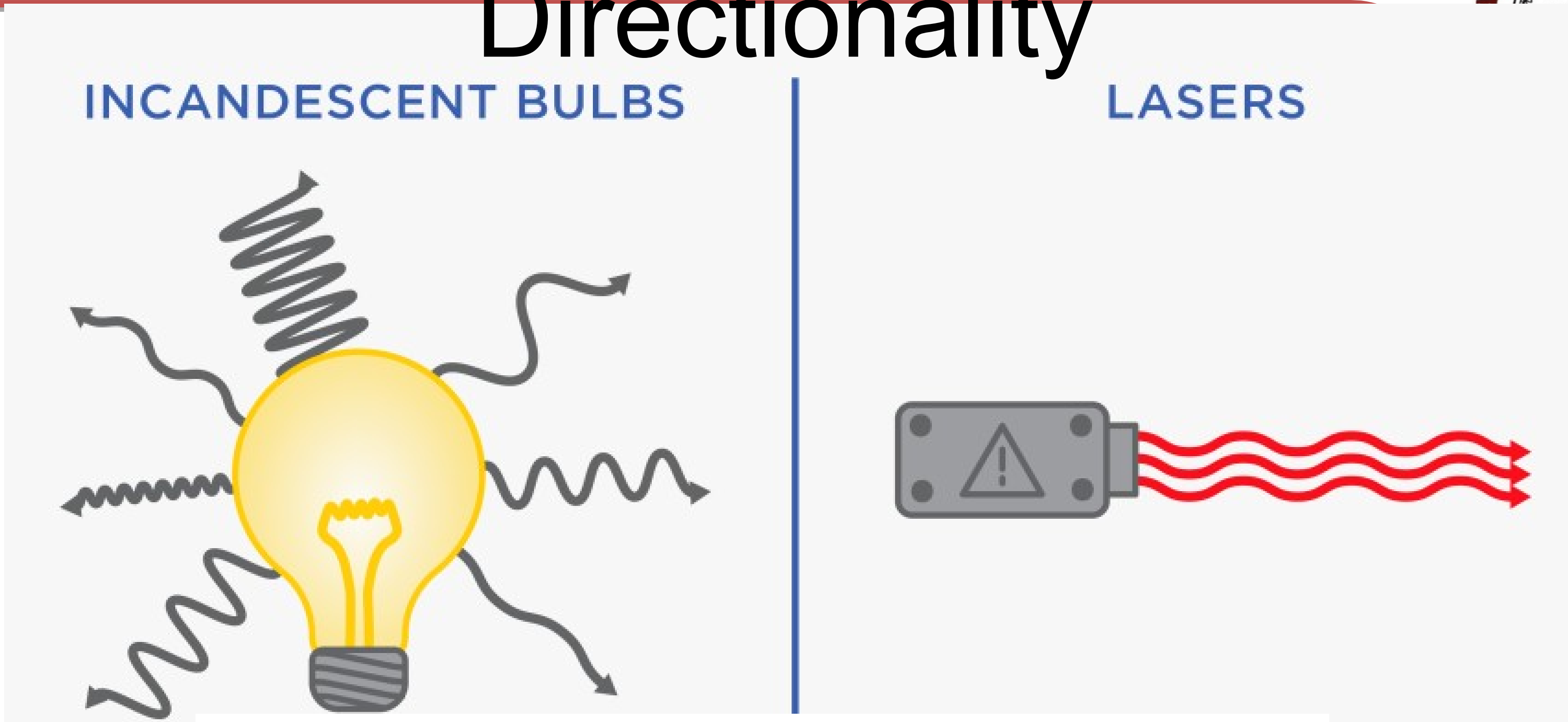
1) Directionality

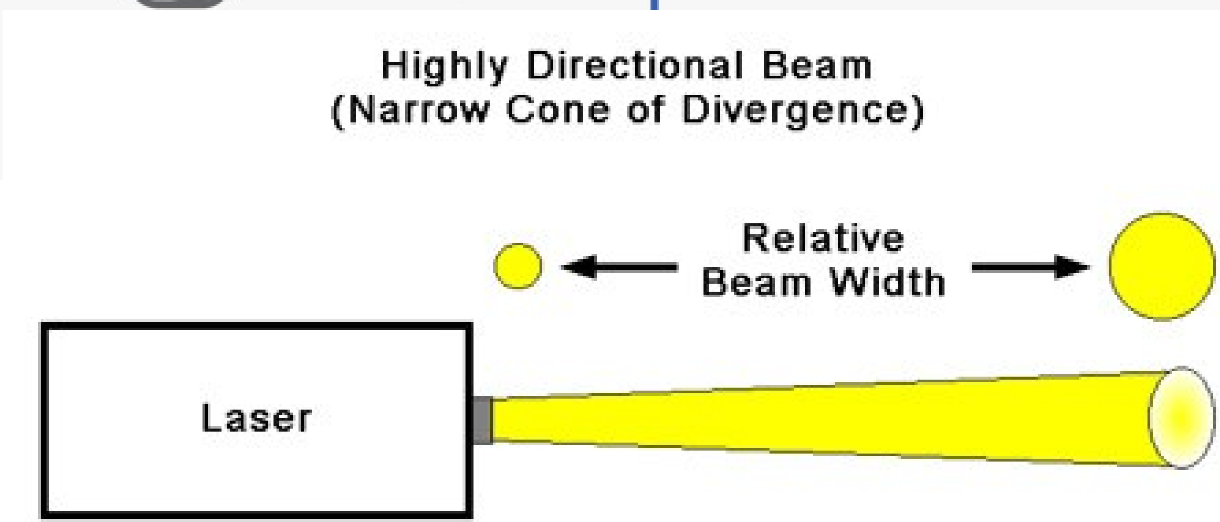
2) Monochromatic

3) Coherence

4) High Intensity

Directionality





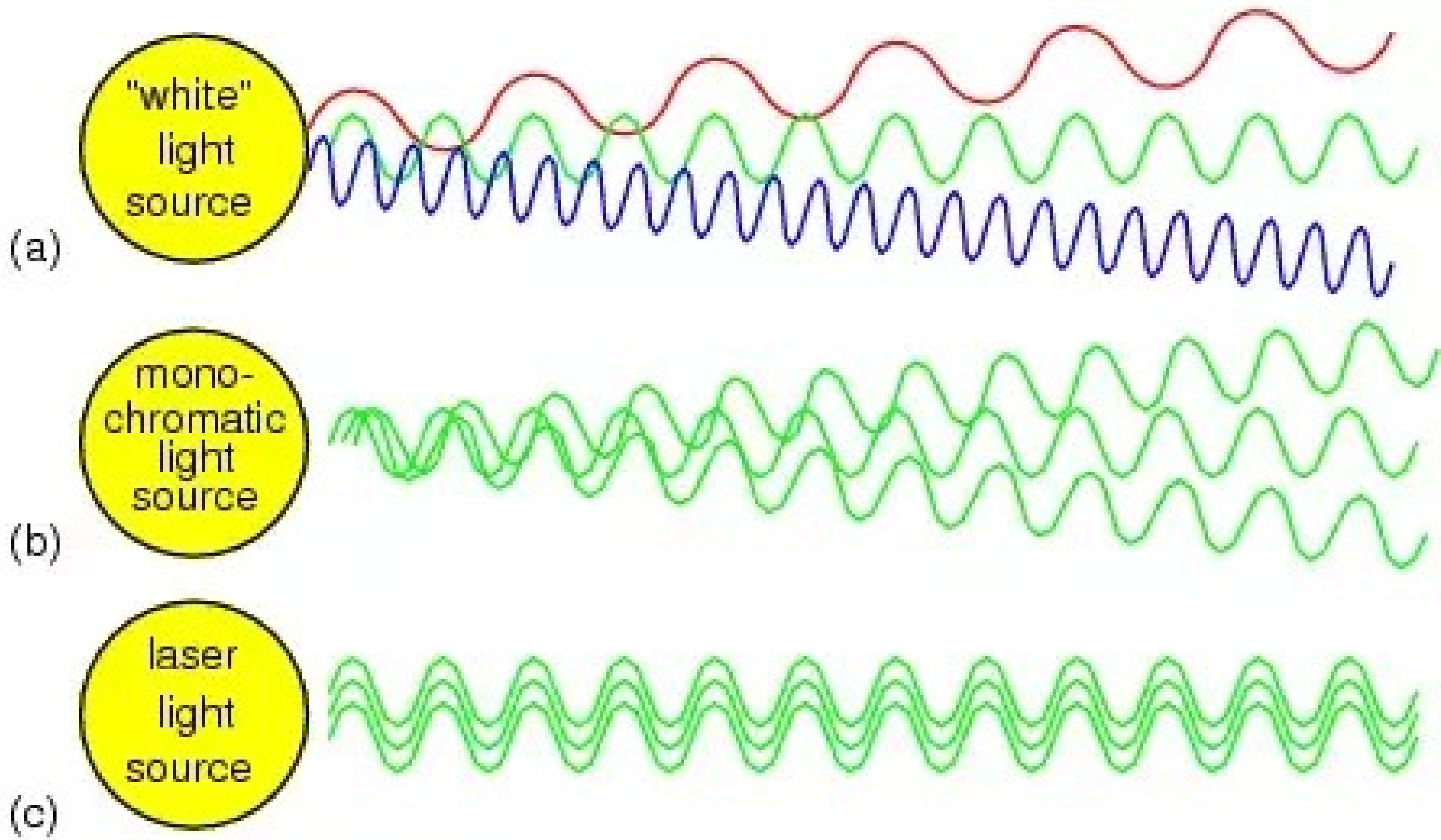
Directionality

- Laser light travels only in direction.
- Its angular spreading is very less.
- It is expressed in terms of DIVERGENCE.

$$\Delta\theta = \frac{r_1 - r_2}{D_2 - D_1}$$

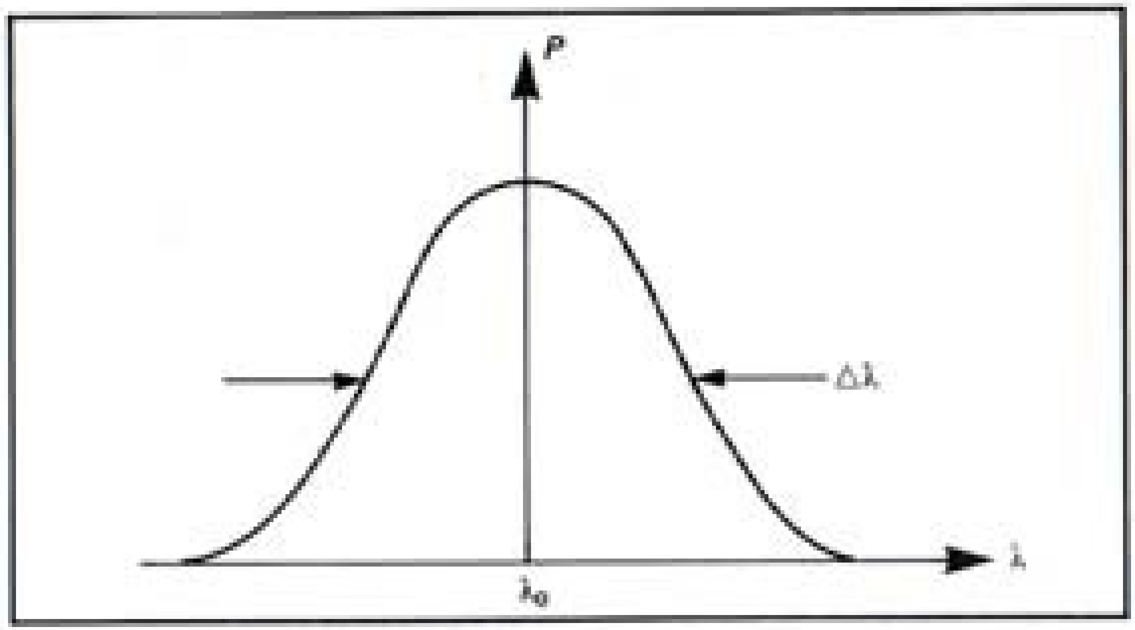
- Δθ = 0.01 milli radian for LASER.
- Δθ = 0.5 m for ordinary light.

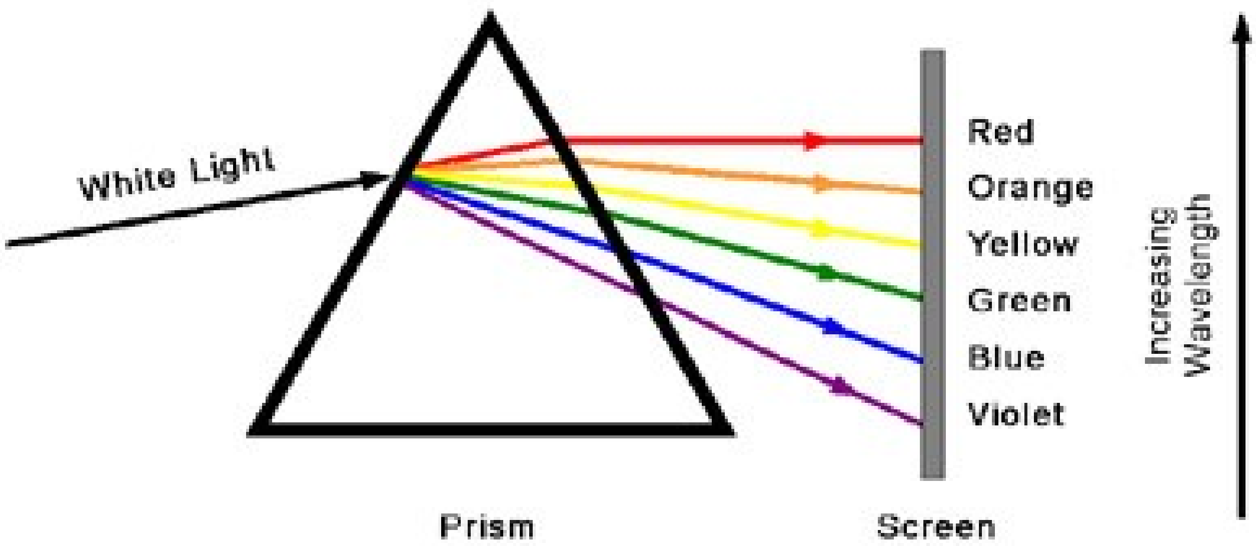
Monochromatic



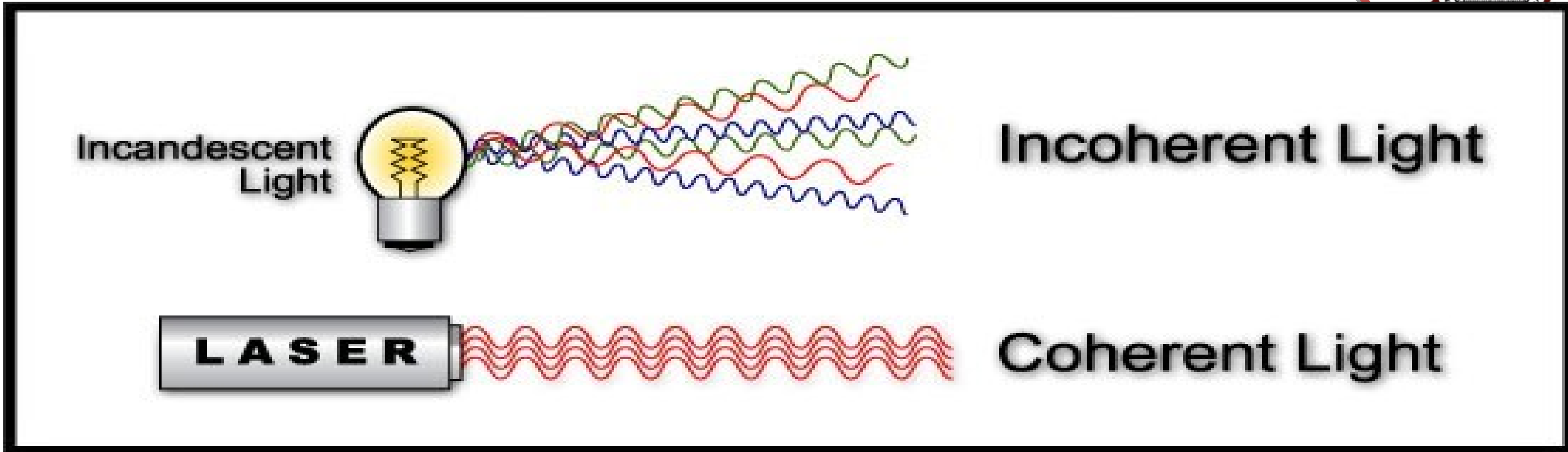
Monochromatic

- There is no perfect monochromatic light source in universe.
- For laser beam $\Delta\nu$ = 50Hz and ν = $5x10^{14}$Hz.
- non monochromacity = 10^{-13}
- For ordinary light it is 10^{-}

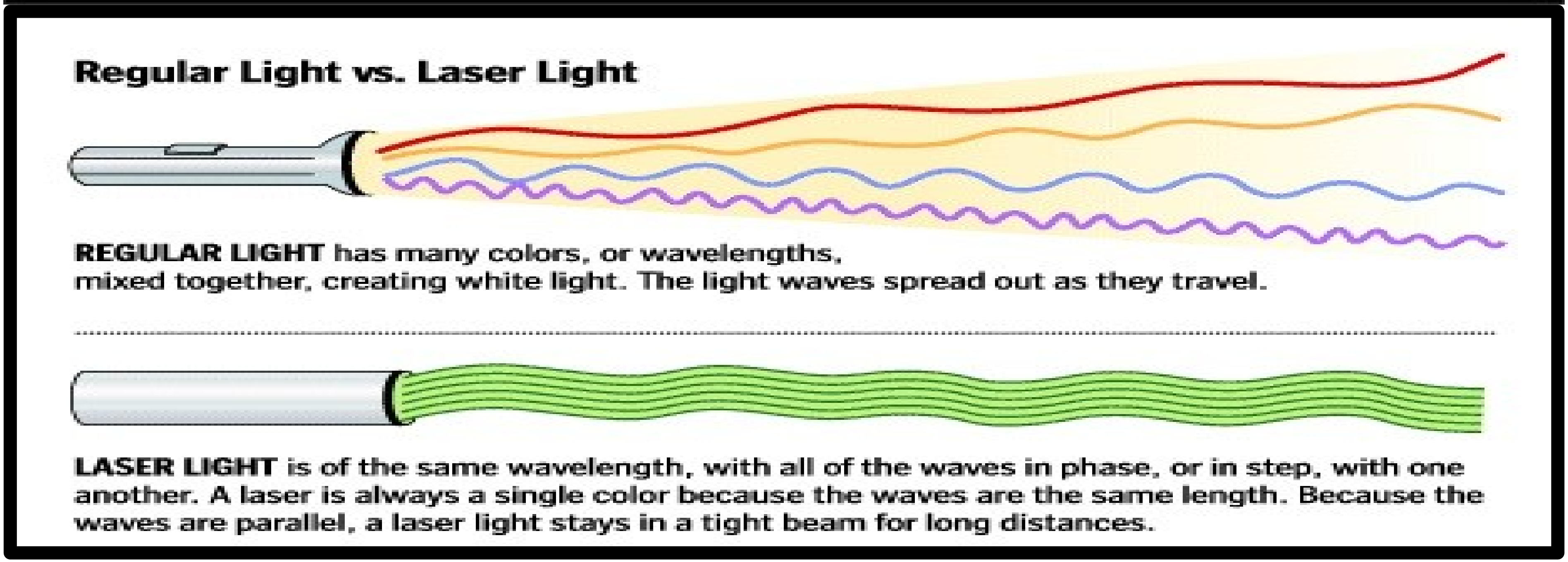

P
Δλ
λ
λ₀


White Light
Red
Orange
Yellow
Green
Blue
Violet
Increasing Wavelength
Prism
Screen

Coherence



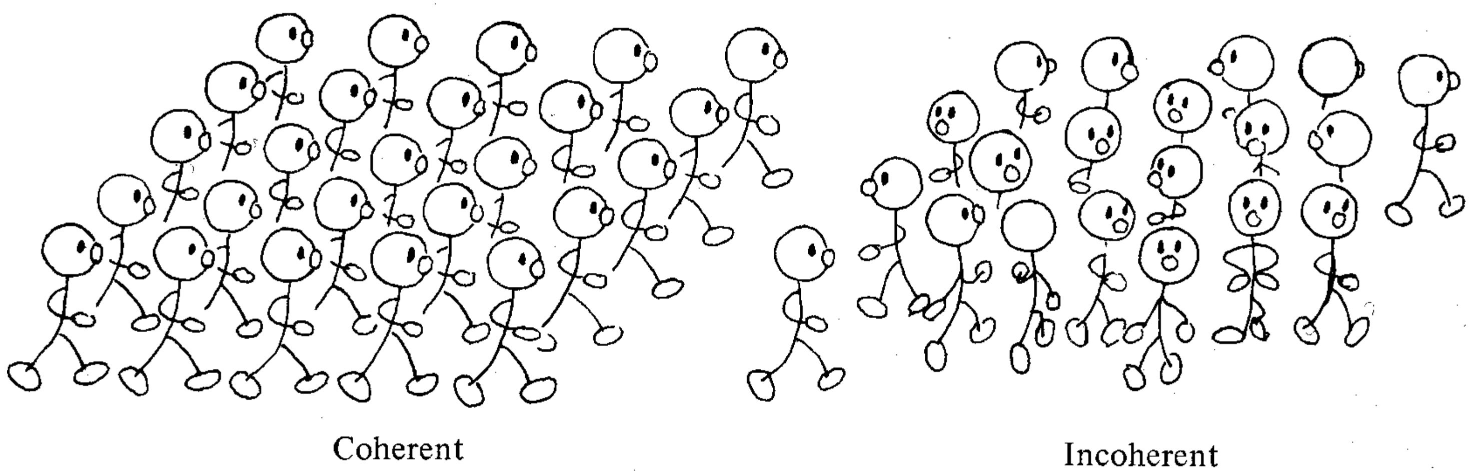
Incandescent Light
Incoherent Light
LASER
Coherent Light



Regular Light vs. Laser Light
REGULAR LIGHT has many colors, or wavelengths, mixed together, creating white light. The light waves spread out as they travel.
LASER LIGHT is of the same wavelength, with all of the waves in phase, or in step, with one another. A laser is always a single color because the waves are the same length. Because the waves are parallel, a laser light stays in a tight beam for long distances.

Coherence

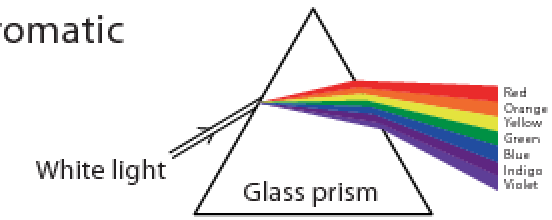
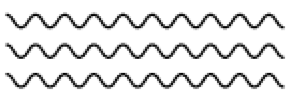
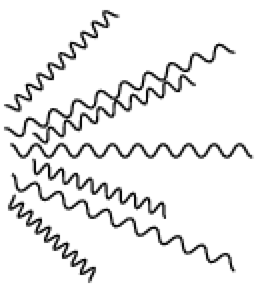
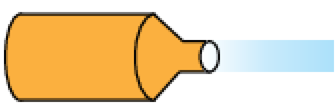
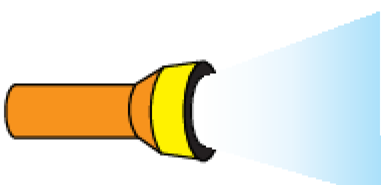
- All the emitted photons bear a constant phase relationship with each other in both time and phase.



High Intensity

- Very high intensity
- Since the whole energy is concentrated at a small region.
- 1m W He-Ne laser is 100 times more intense than the light that reaches earth from sun.
- No. of photons per sec per unit area is 10^{22} to 10^{34} in laser. $I=P/\lambda^2$

Comparison

Laser light	Non-laserlight (e.g. flashlight)
Monochromatic 	Polychromatic 
Coherent 	Incoherent 
Collimated 	Divergent 

Interaction of Light with matter

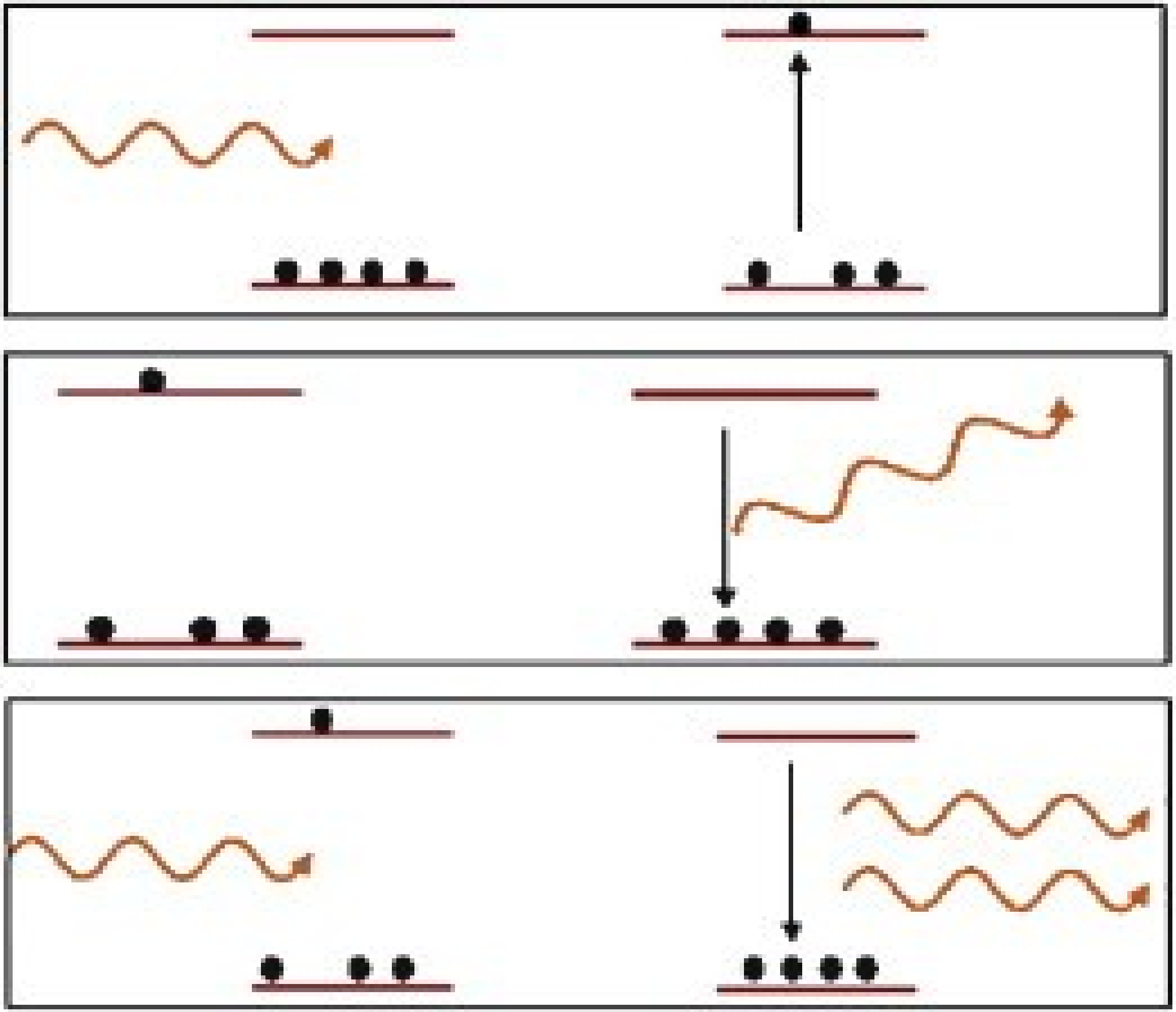
Absorption

Spontaneous Emission

Stimulated Emission

Population inversion

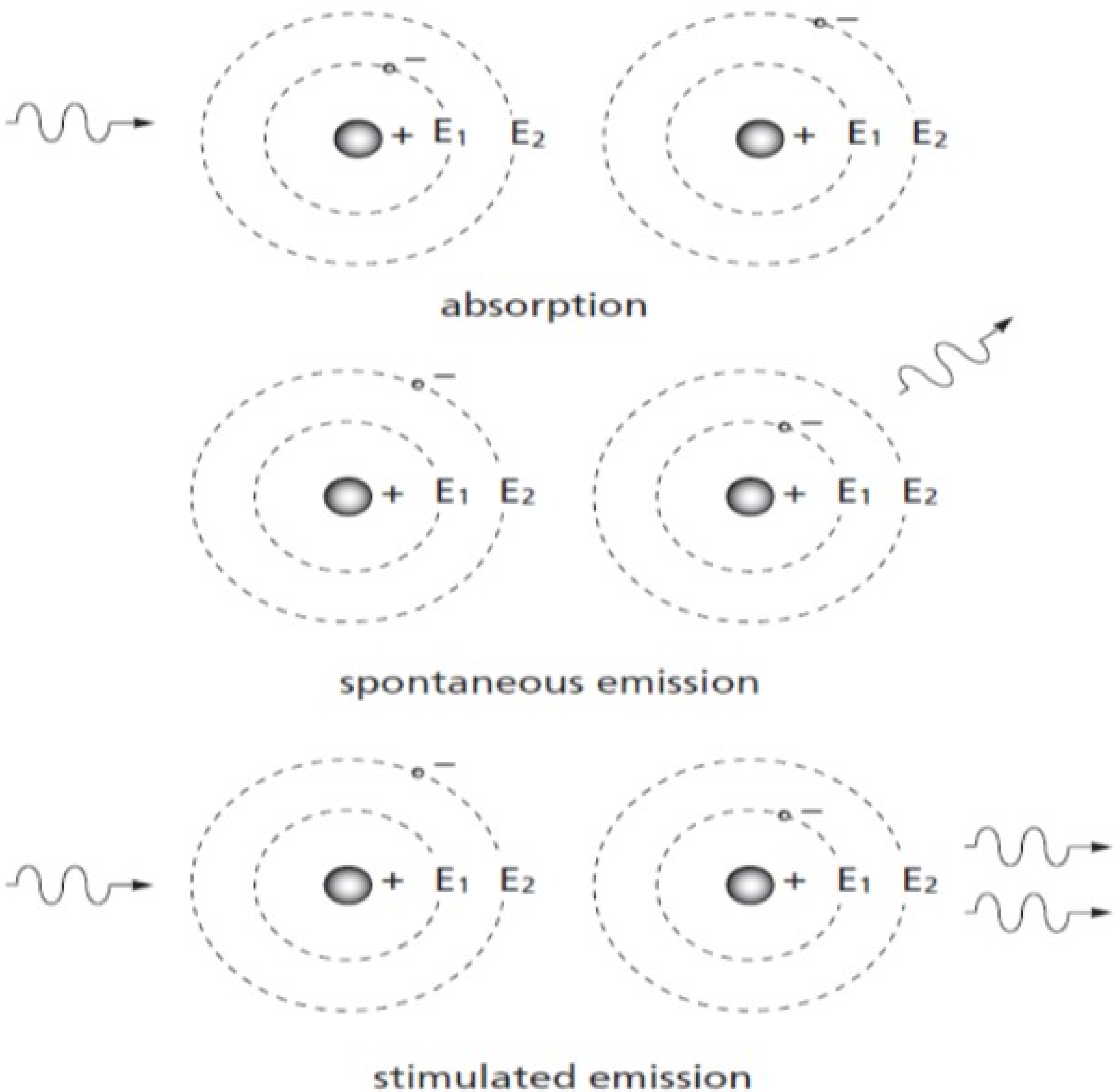
Absorption, Spontaneous, Stimulated Emission



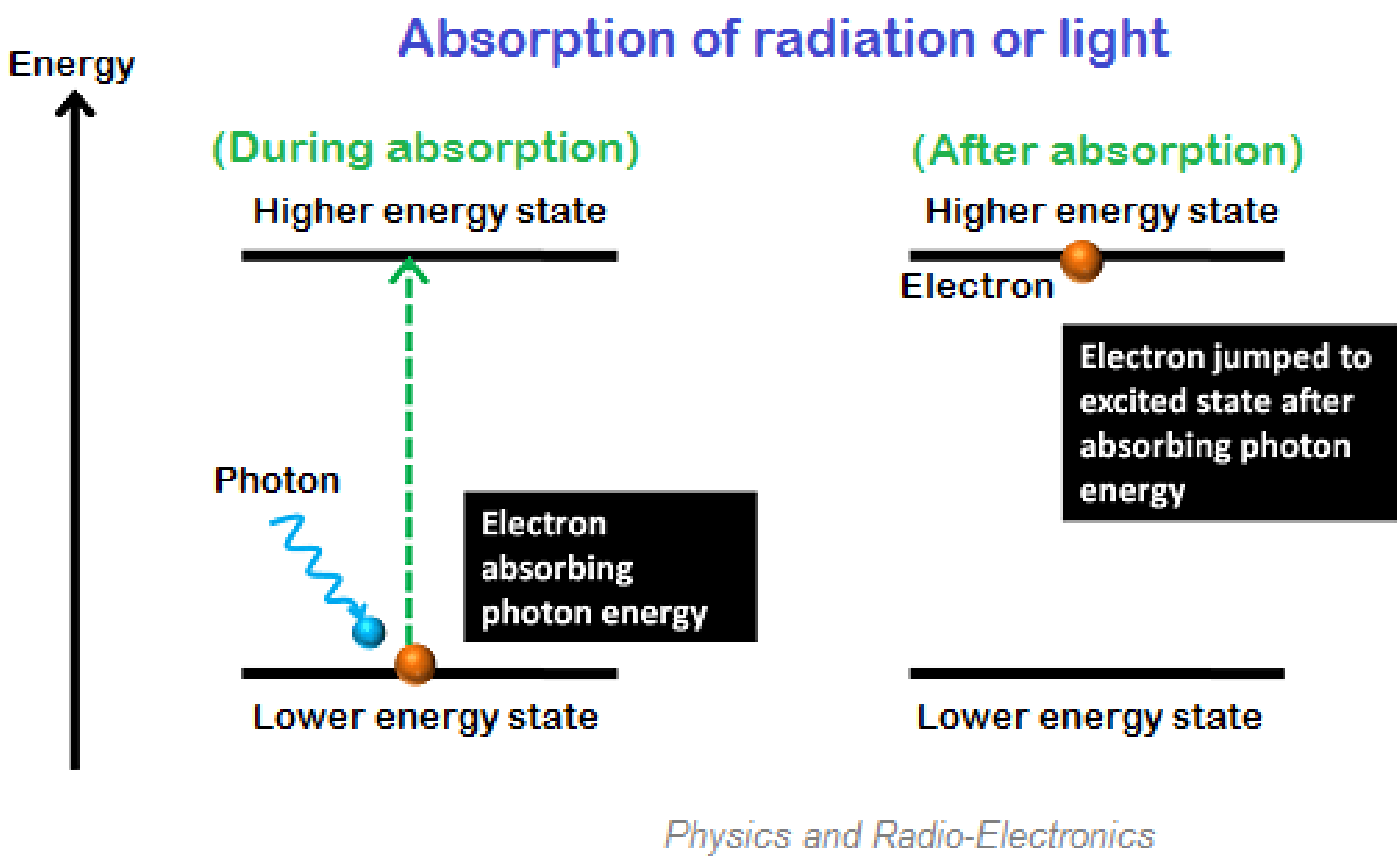
Absorption

Spontanous Emission

Stimulated Emission

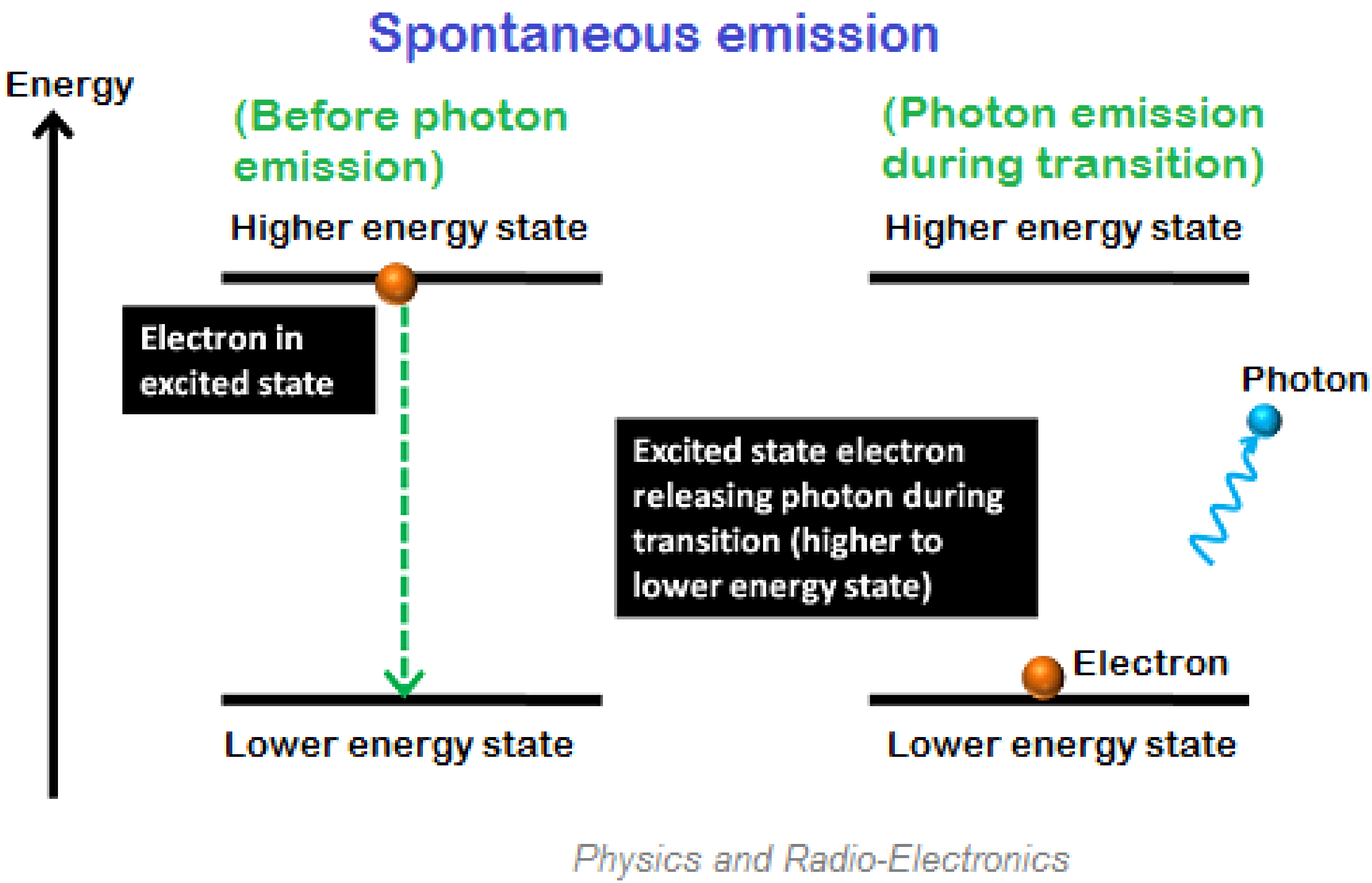

+ E1 E2
+ E1 E2
absorption
+ E1 E2
+ E1 E2
spontaneous emission
+ E1 E2
+ E1 E2
stimulated emission

Absorption

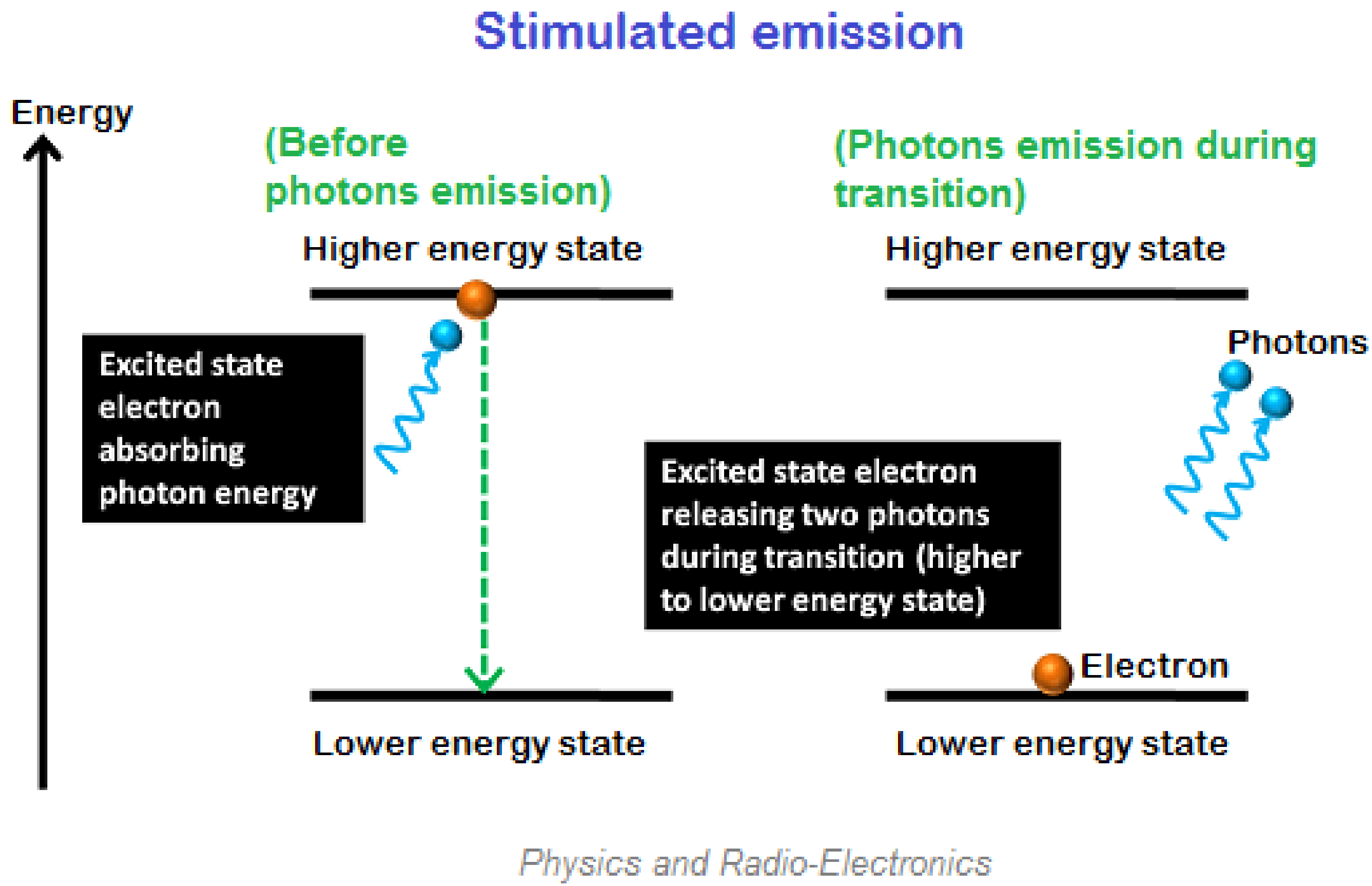


Absorption of radiation or light
Energy
(During absorption)
Higher energy state
Photon
Electron
absorbing
photon energy
Lower energy state
(After absorption)
Higher energy state
Electron
Electron jumped to
excited state after
absorbing photon
energy
Lower energy state
Physics and Radio-Electronics

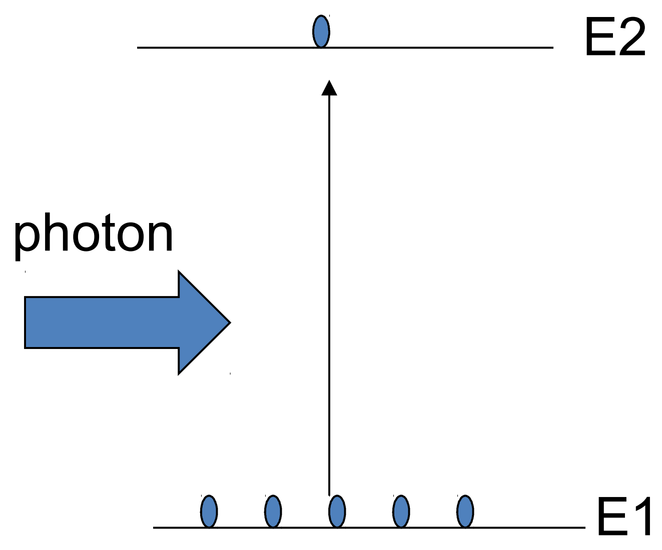
Spontaneous Emission



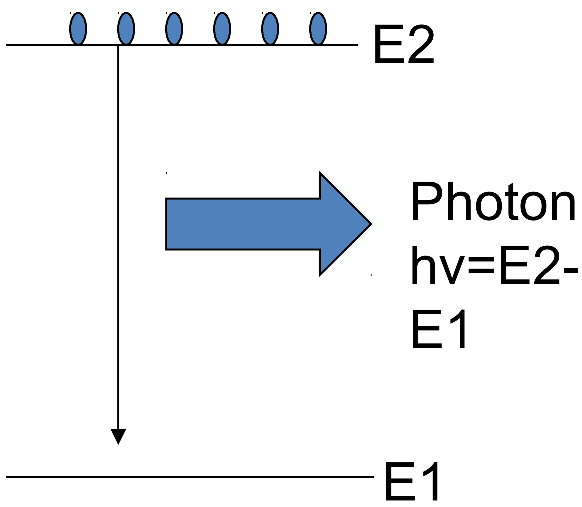
Stimulated Emission



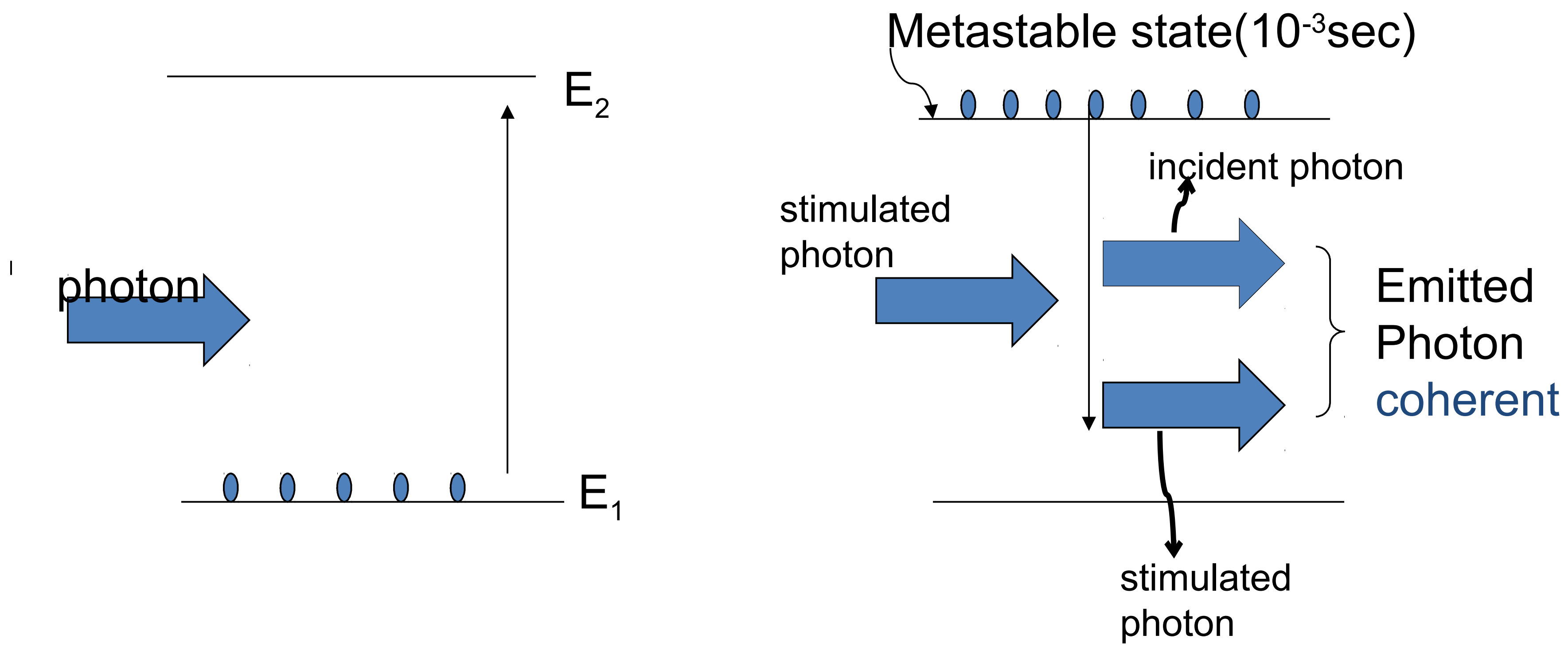
Stimulated Absorption



Spontaneous Emission



Stimulated Emission



Stimulated Emission

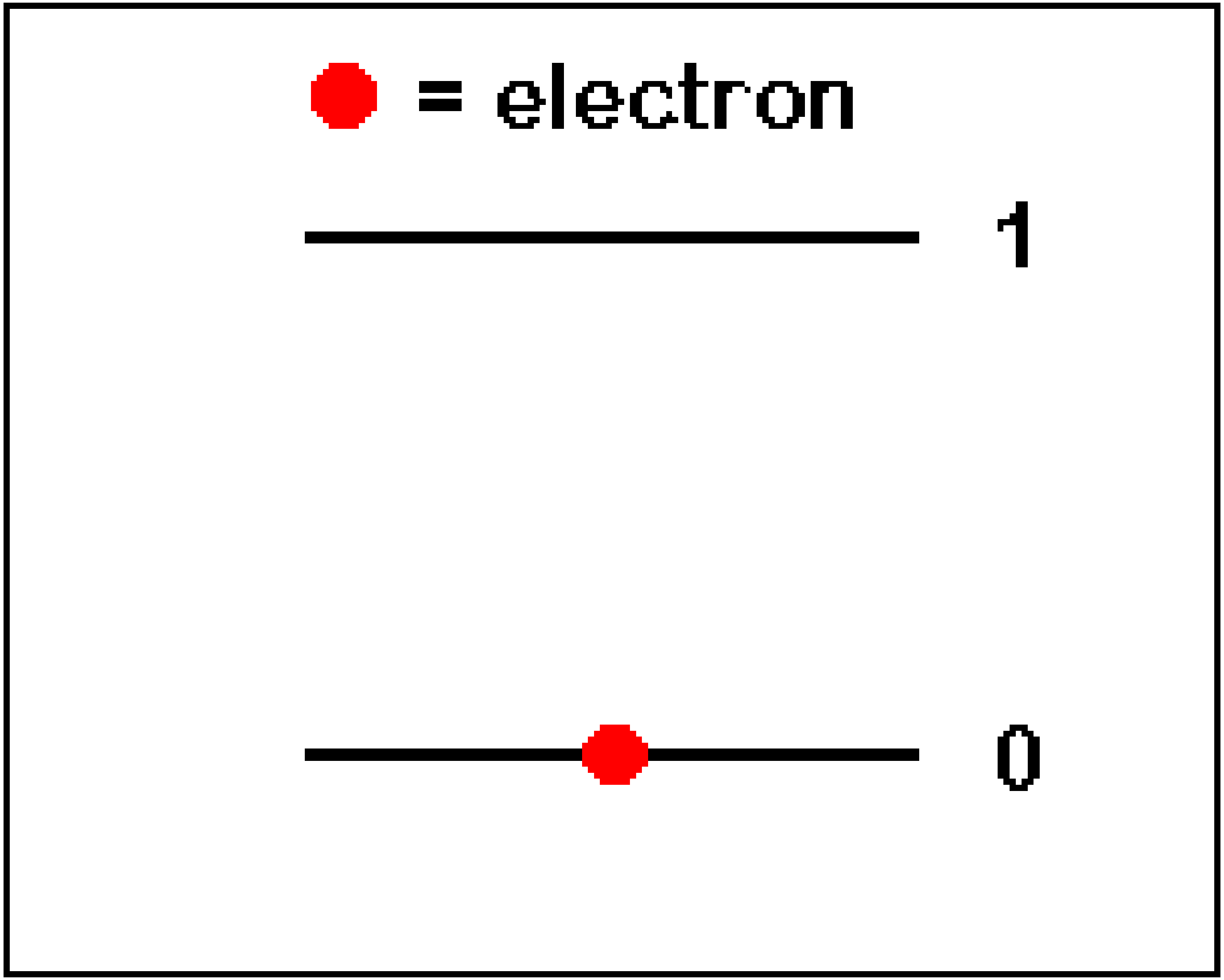
The stimulated photons have unique properties:

– **In phase** with the incident photon

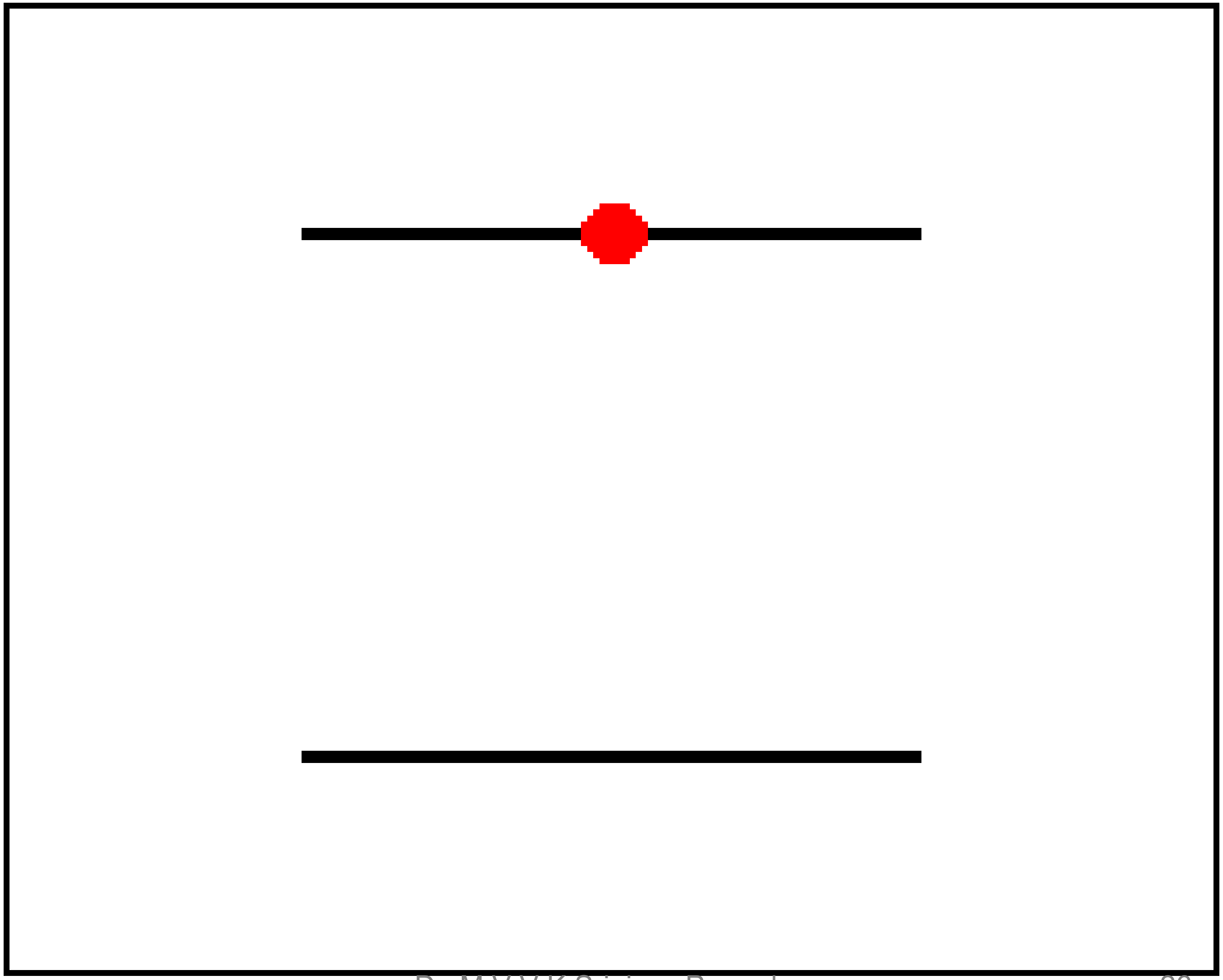
– **Same wavelength** as the incident photon

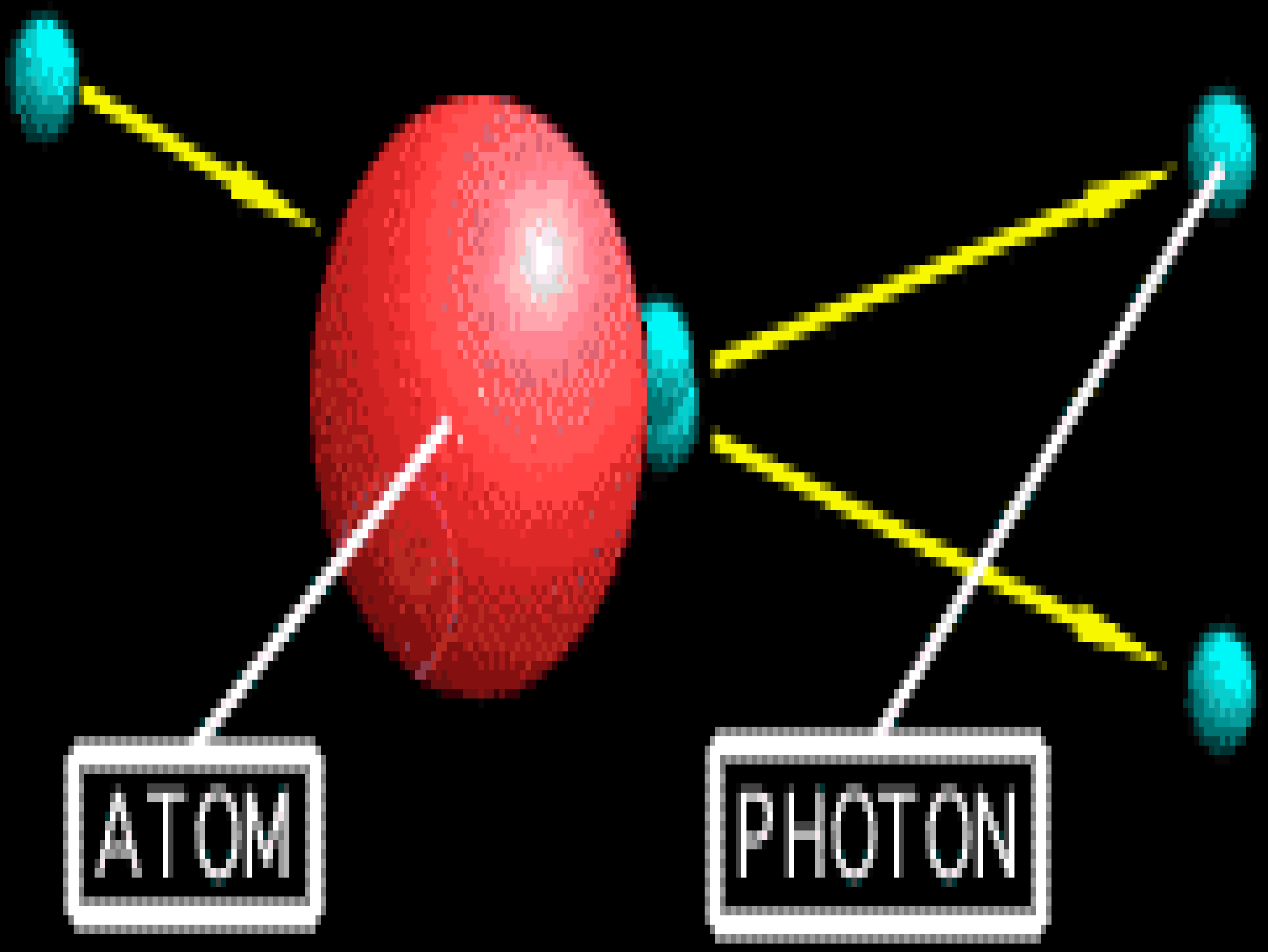
– Travel in **same direction** as incident photon

Absorption and Spontaneous Emission of Photons



Stimulated Emission of Photons in a Metastable State



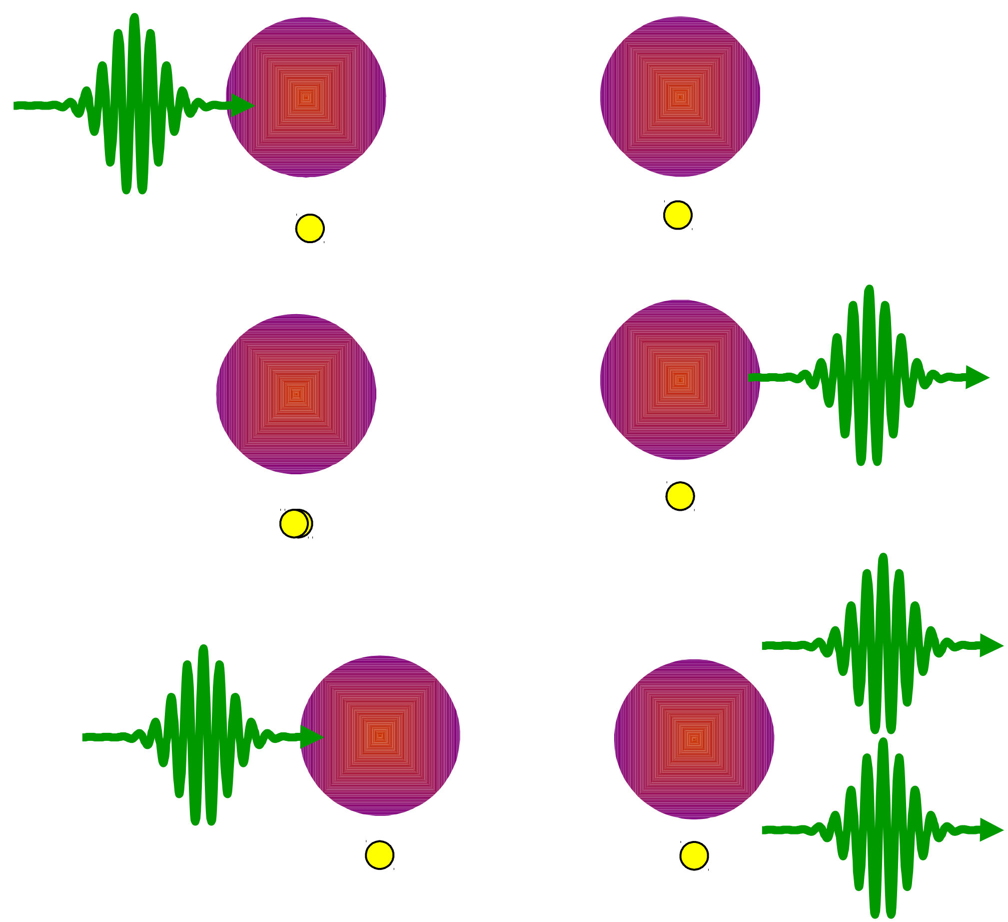

ATOM
PHOTON

Before After

Absorption

Spontaneous emission

Stimulated emission



Spontaneous Emission	Stimulated Emission
Takes place when excited atoms makes transitions to lower energy level voluntarily with out any external stimulation.	Takes place when a photon of energy of equal to hv stimulates an excited atom to make transition to lower energy level.
Polychromatic Radiation.	Monochromatic Radiation.
Less Intensity.	High Intensity.
Less directionality so more angular spread during propagation	High directionality so less angular spread during propagation.
Spatially and temporally incoherent radiation.	Spatially and temporally coherent radiation.

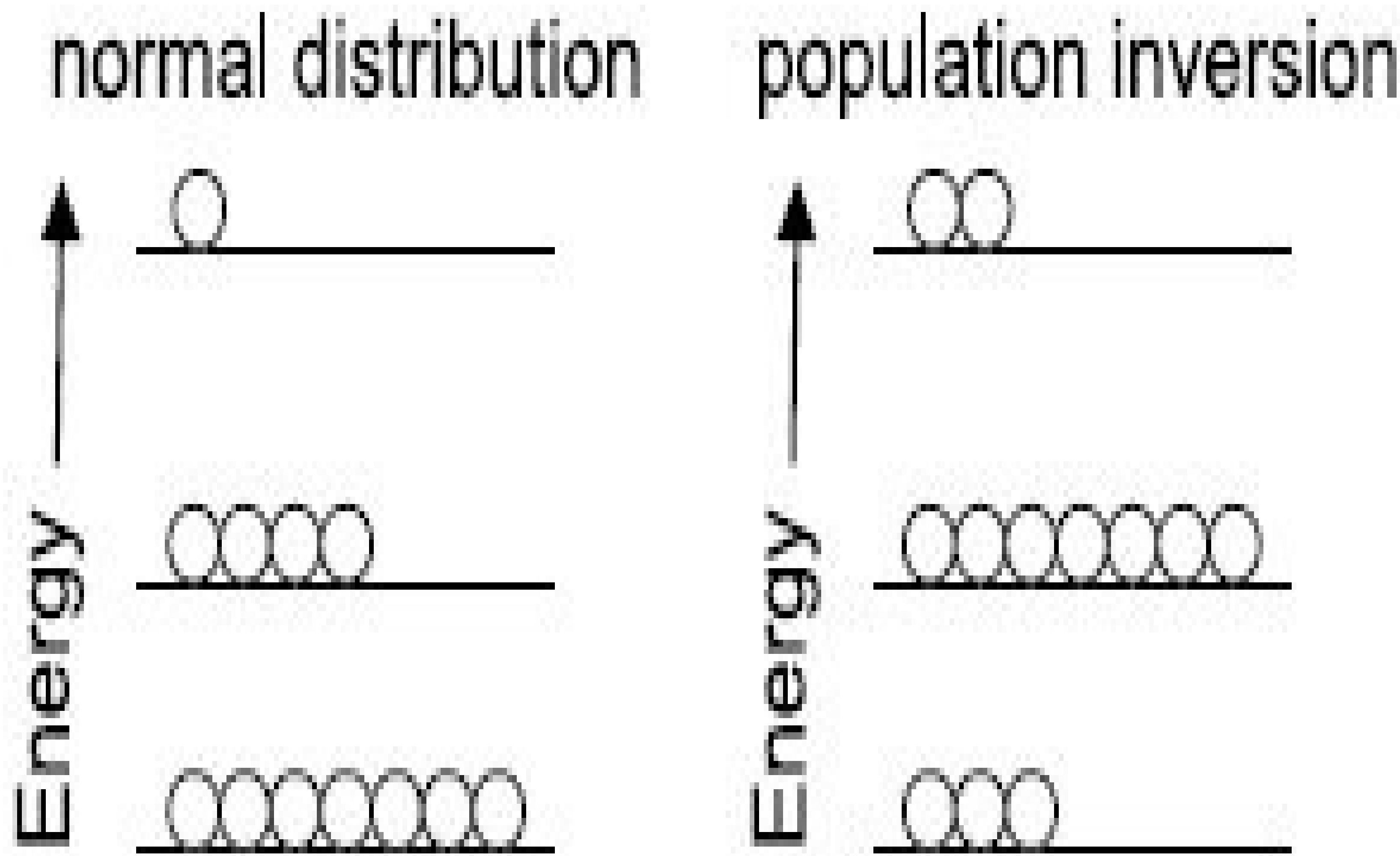
Population Inversion

- In thermal equilibrium no. of atoms in the ground state is very much greater than no. of atom in excited state.($N_1 > N_2$)

- **POPULATION INVERSION:**

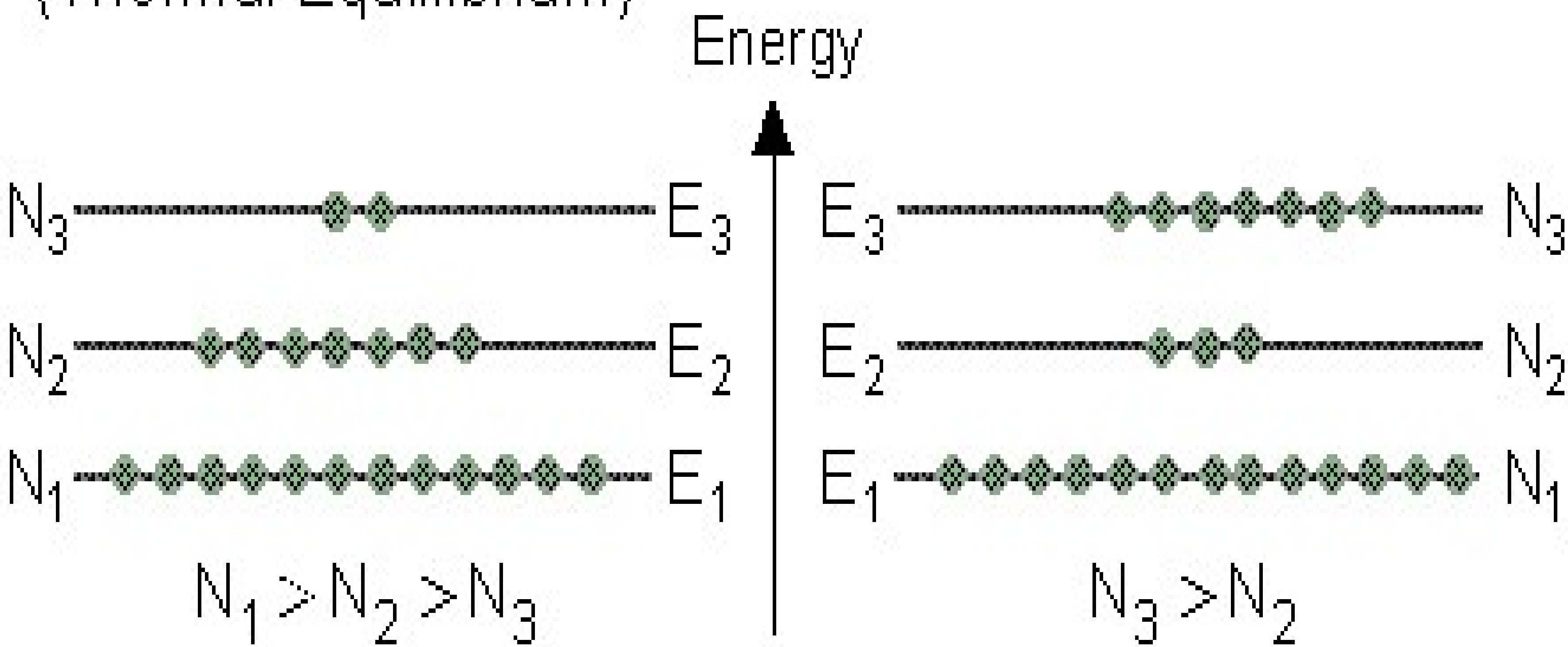
  It is the process of making no. atoms in the excited state greater than the no. of atoms in the lower energy state. i.e. the population is getting inverted. ($N_2 > N_1$).

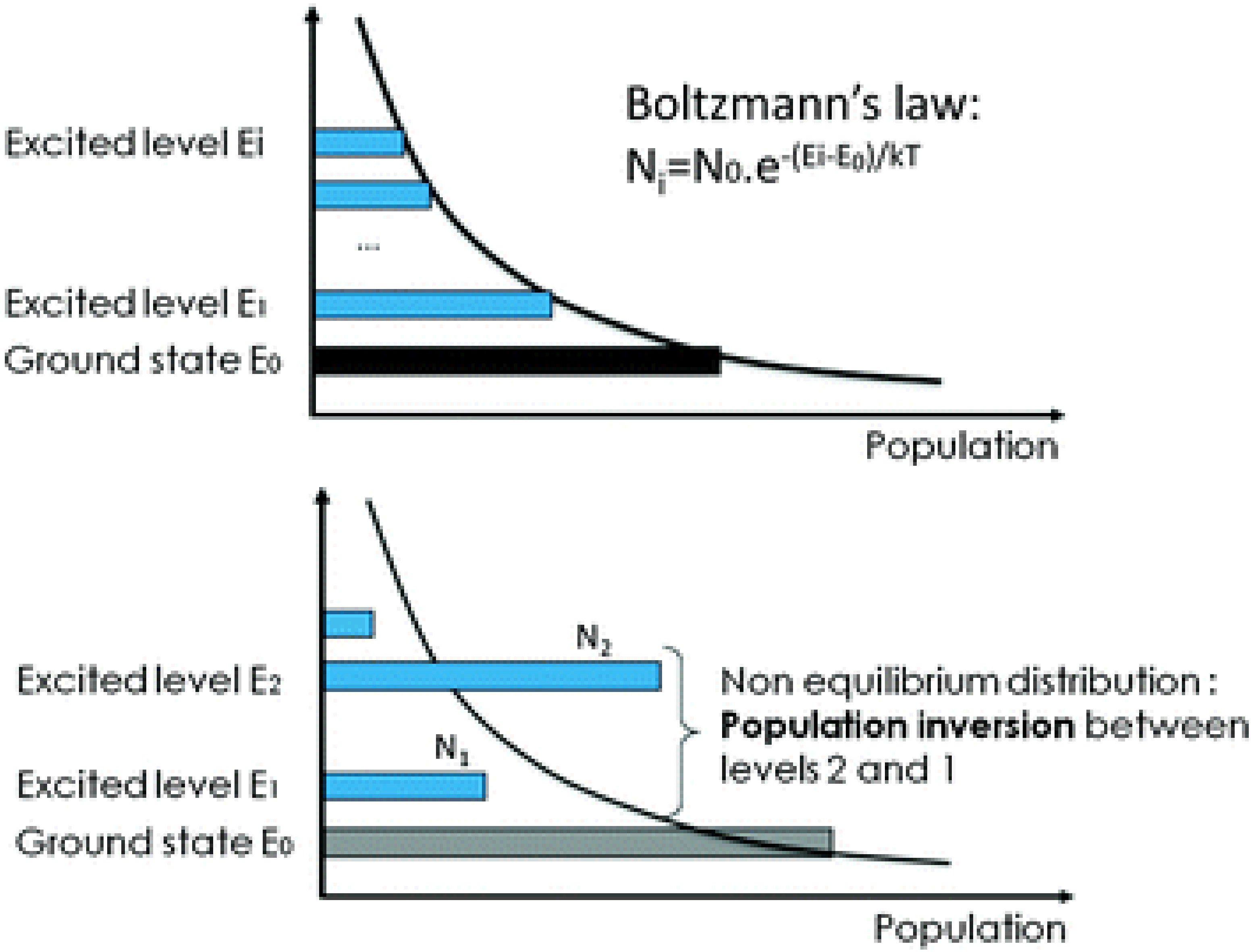
- Population inversion is achieved in **METASTABLE STATE** (lifetime of the order of 10^{-3} sec).


normal distribution
population inversion
Energy
Energy

a) Normal Population (Thermal Equillibrium)

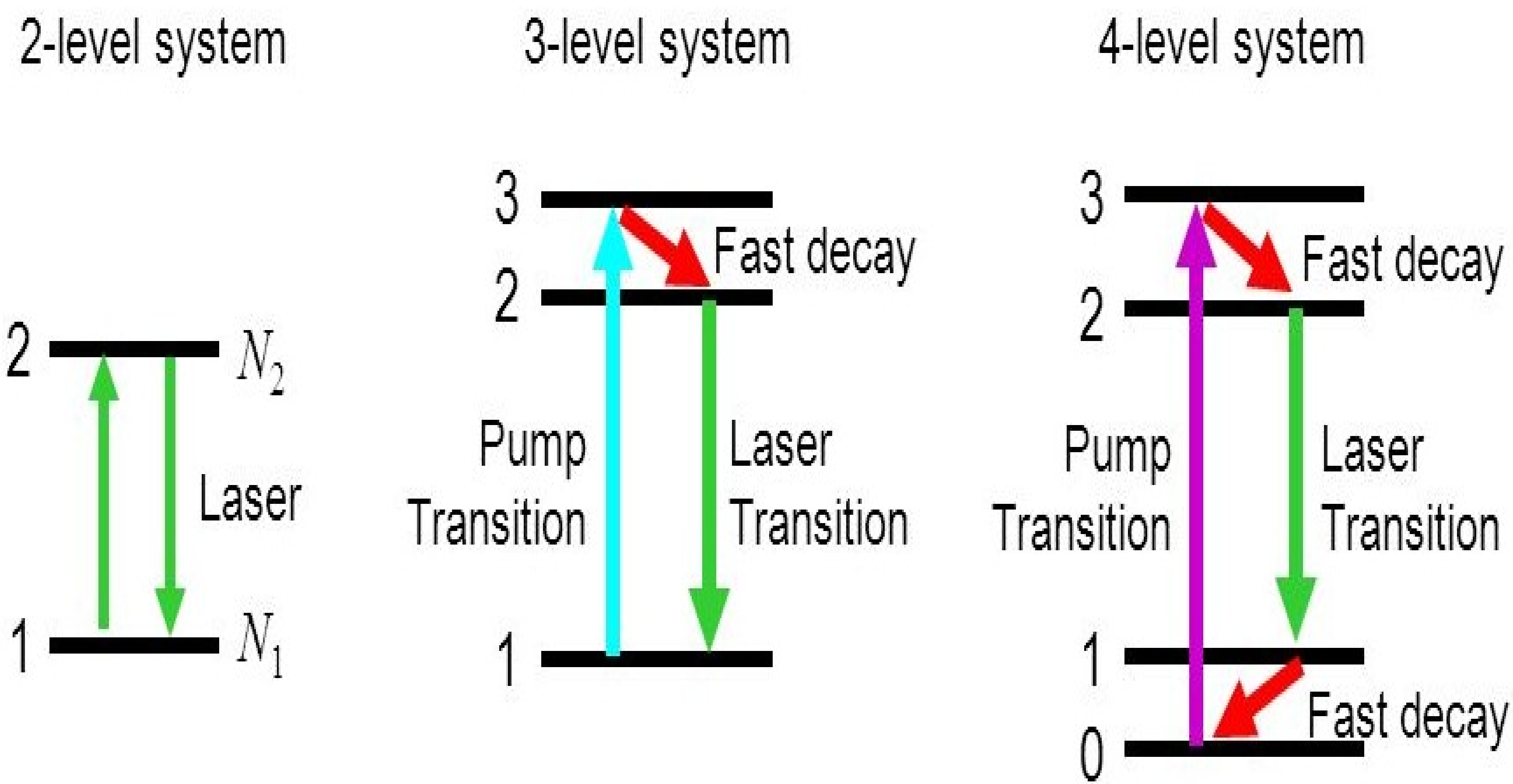
b) Population Inversion





Excited level Ei
Excited level E1
Ground state E0
Boltzmann's law:
$N_i = N_0 . e^{-(E_i - E_0)/kT}$
Population
N2
N1
Excited level E2
Excited level E1
Ground state E0
Non equilibrium distribution :
Population inversion between levels 2 and 1
Population

Obtaining Population Inversion



PUMPING

- The process of achieving population inversion is called Pumping i.e. sending the atoms from lower energy state to higher energy state.
- ***TYPES OF PUMPING :***

1. Optical pumping
2. Electrical pumping
3. X-ray pumping
4. Chemical pumping

Types of LASER's

a. **According to their sources:**
    1. Gas Lasers
    2. Crystal Lasers
    3. Semiconductors Lasers
    4. Liquid Lasers

b. **According to the nature of emission:**
    1. Continuous Wave
    2. Pulsed Laser

c. **According to their wavelength:**
    1. Visible Region
    2. Infrared Region
    3. Ultraviolet Region
    4. Microwave Region
    5. X-Ray Region

- **d. According to different levels**
- 1. 2-level laser
- 2. 3-level laser
- 3. 4-level laser
- **e. According to mode of pumping**
- 1. Optical
- 2. Chemical
- 3. Electric discharge
- 4. Electrical

Intro to lasers

BASIC LASER COMPONENTS

ACTIVE MEDIUM

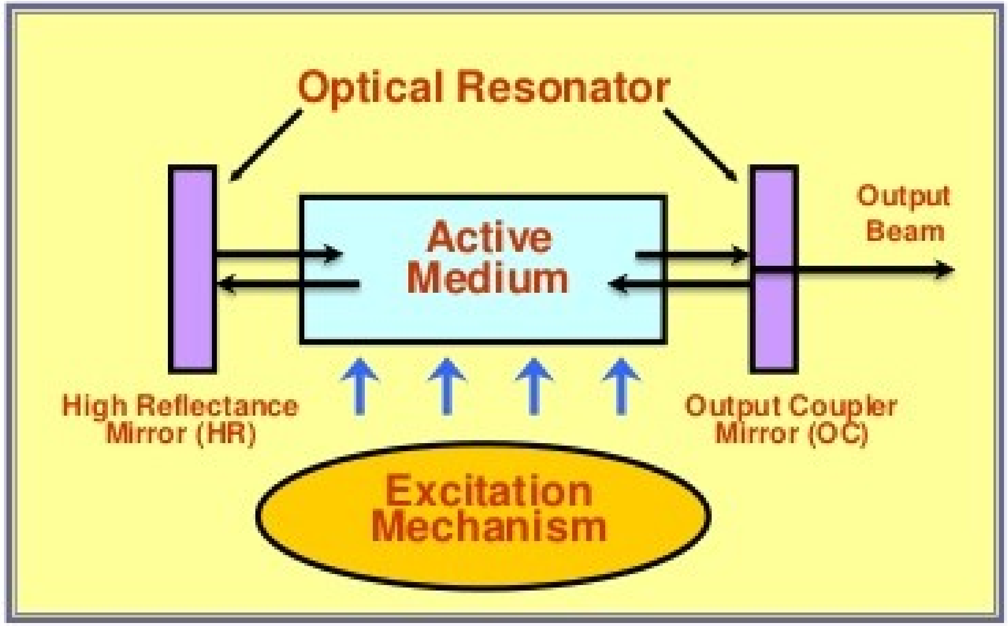
Solid (Crystal)
Gas
Semiconductor (Diode)
Liquid (Dye)

EXCITATION MECHANISM

Optical
Electrical
Chemical

OPTICAL RESONATOR

HR Mirror and
Output Coupler



The **Active Medium** contains atoms which can emit light by stimulated emission.

The **Excitation Mechanism** is a source of energy to excite the atoms to the proper energy state.

The **Optical Resonator** reflects the laser beam through the active medium for amplification.

Common Components of all Lasers

1. Active Medium:

The active medium may be solid crystals such as ruby or Nd:YAG, liquid dyes, gases like CO_2 or He:Ne, or semiconductors such as GaAs. Active mediums contain atoms whose electrons may be excited to a metastable energy level by an energy source.

2. Excitation Mechanism:

Excitation mechanisms pump energy into the active medium by one or more of three basic methods; optical, electrical or chemical.

3. Optical Resonator:

A part of a laser, consisting of two mirrors, one highly reflective (100% reflection) and one partly reflective (less than 100% reflection), placed on either side of a laser pump. Amplified light bounces back and forth between the mirrors, enhancing stimulated emission within the pump, eventually being emitted through the partly reflective mirror.

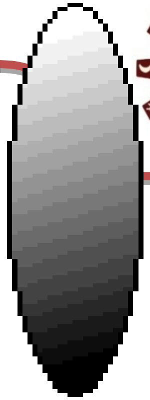
Why META STABLE State?

Metastable state is a higher energy state whose lifetime (10^{-3} sec) is more than an ordinary higher energy state (10^{-8} sec). In metastable state population inversion can be achieved. And when these atoms come back to the original ground level it emits laser beam.

Pump Source

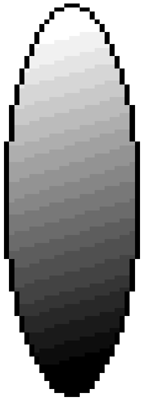
- It is a basic energy source for a laser.
- It excites atoms of laser medium to higher energy states.
- So that population inversion can take place & it is maintained with time.
- The excitation of atom occur directly or through atom or atom collision.
- There is various type of pump depending upon nature of medium.
  - Examples: electric discharges, flashlamps, arc lamps and chemical reactions.
- The type of pump source used depends on the gain medium.
  - A helium-neon (He:Ne) laser uses an electrical discharge in the helium-neon gas mixture.
  - Excimer lasers use a chemical reaction.

Optical Resonator

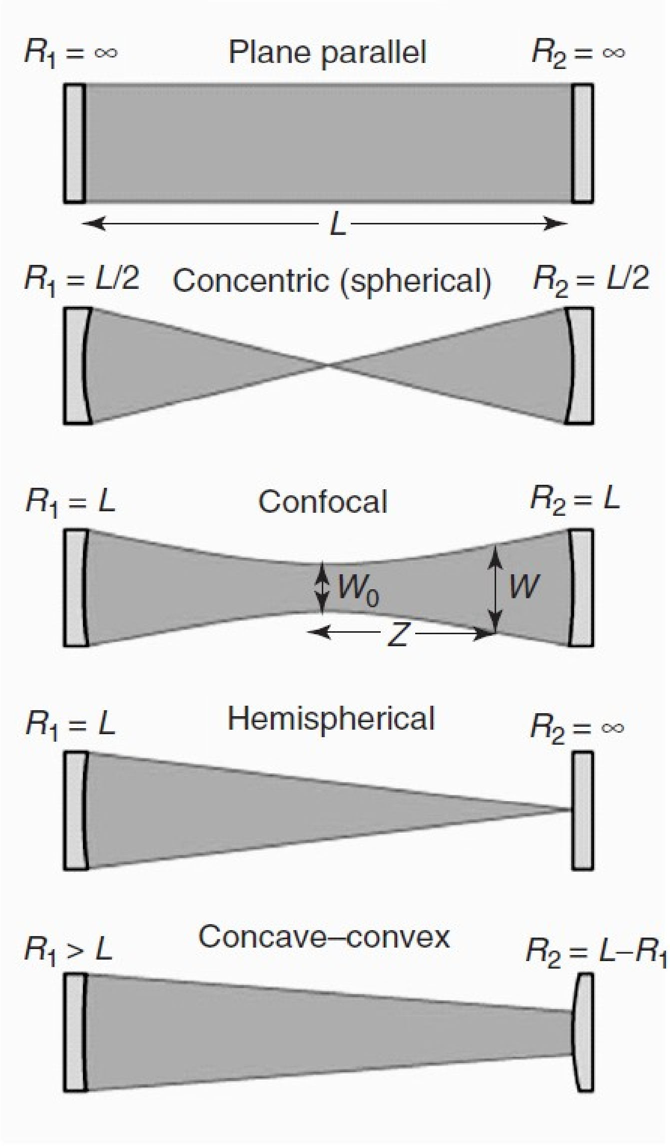


- It is an set up used to obtain amplification of stimulated photons, by oscillating them back & forth between two extreme limits. Consist of:

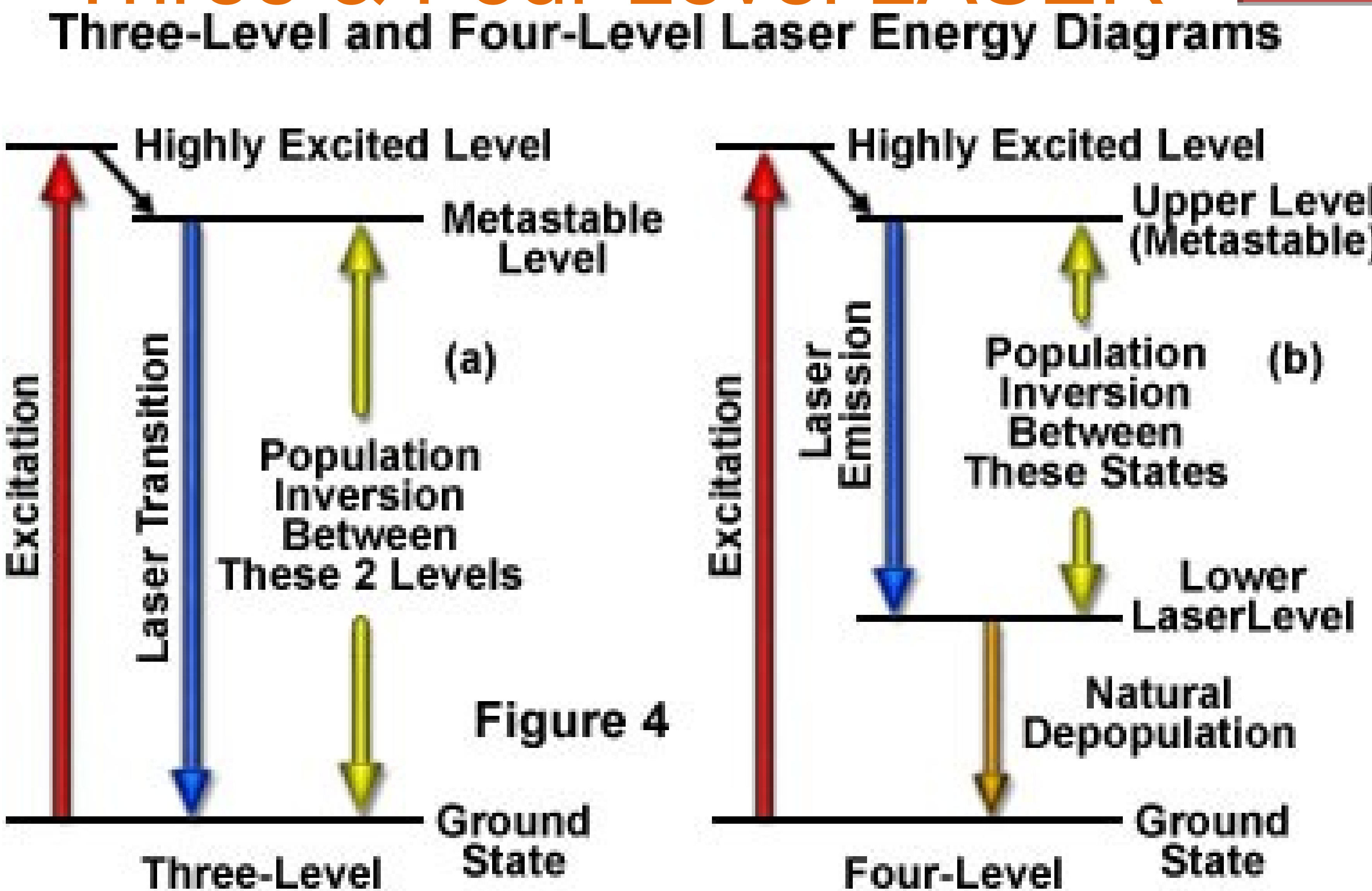
1. Two plane or concave mirrors placed co-axially.
2. One mirror is reflecting & other is partially reflecting.



Types of Resonator



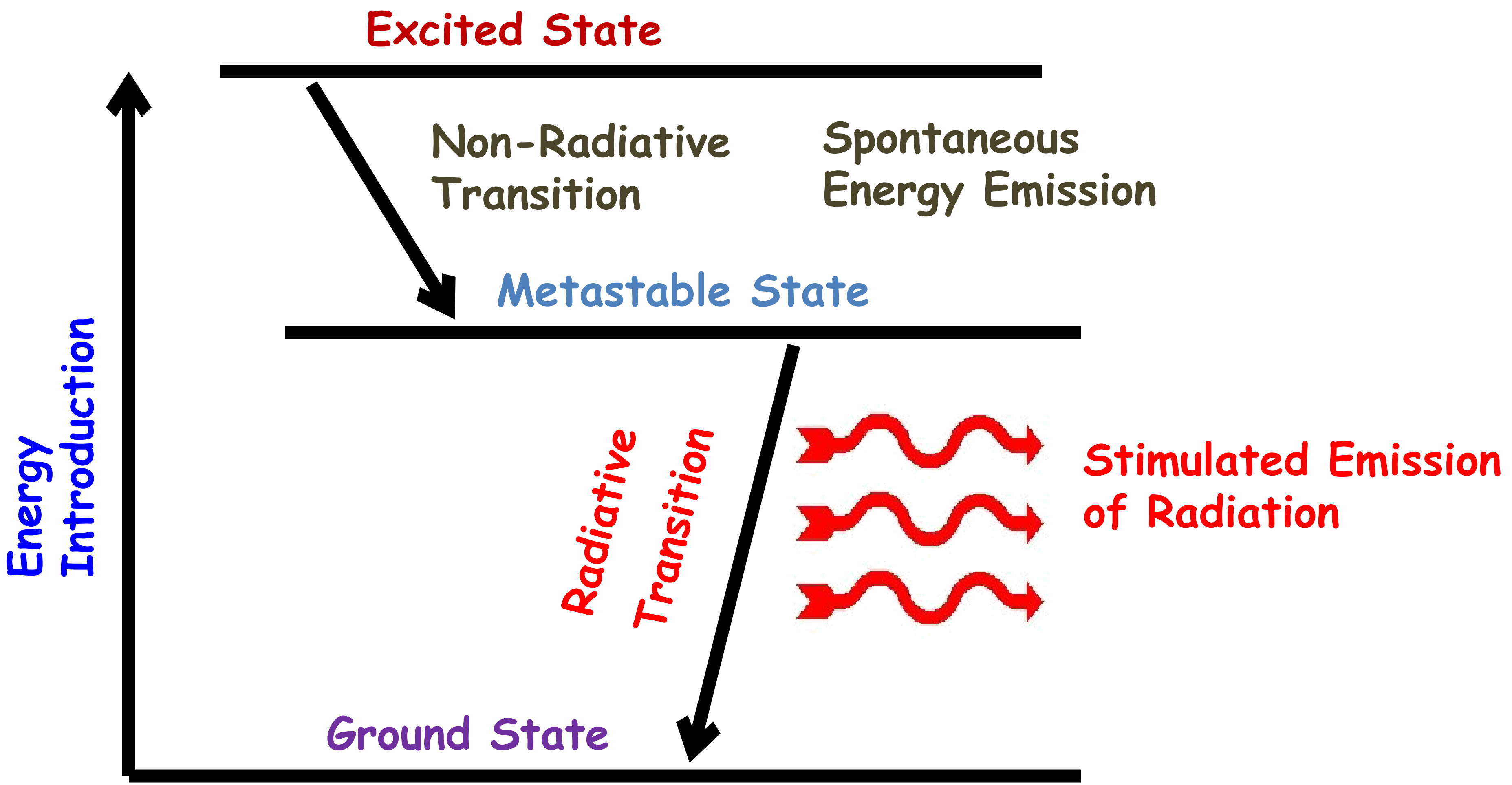
Three & Four Level LASER

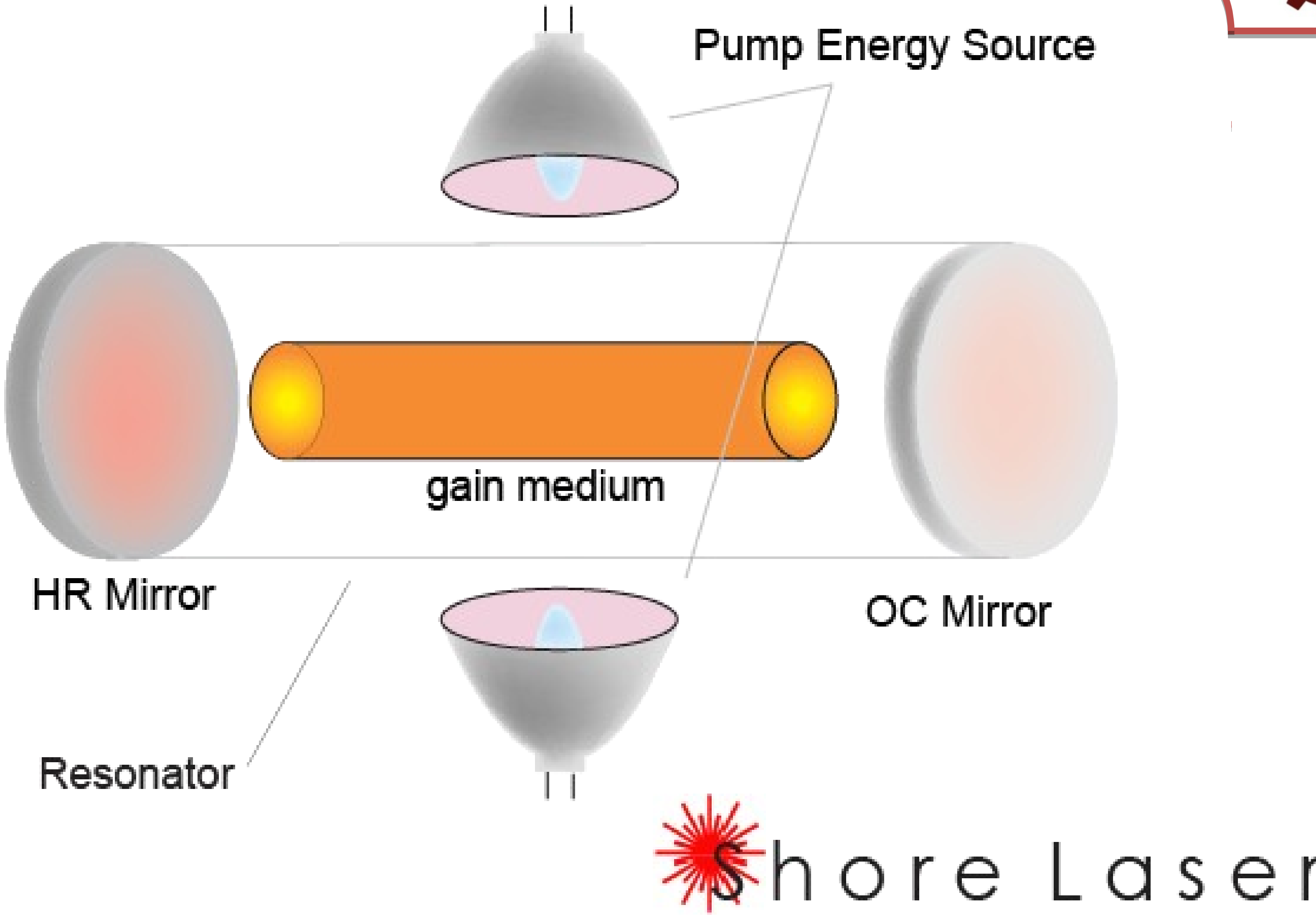


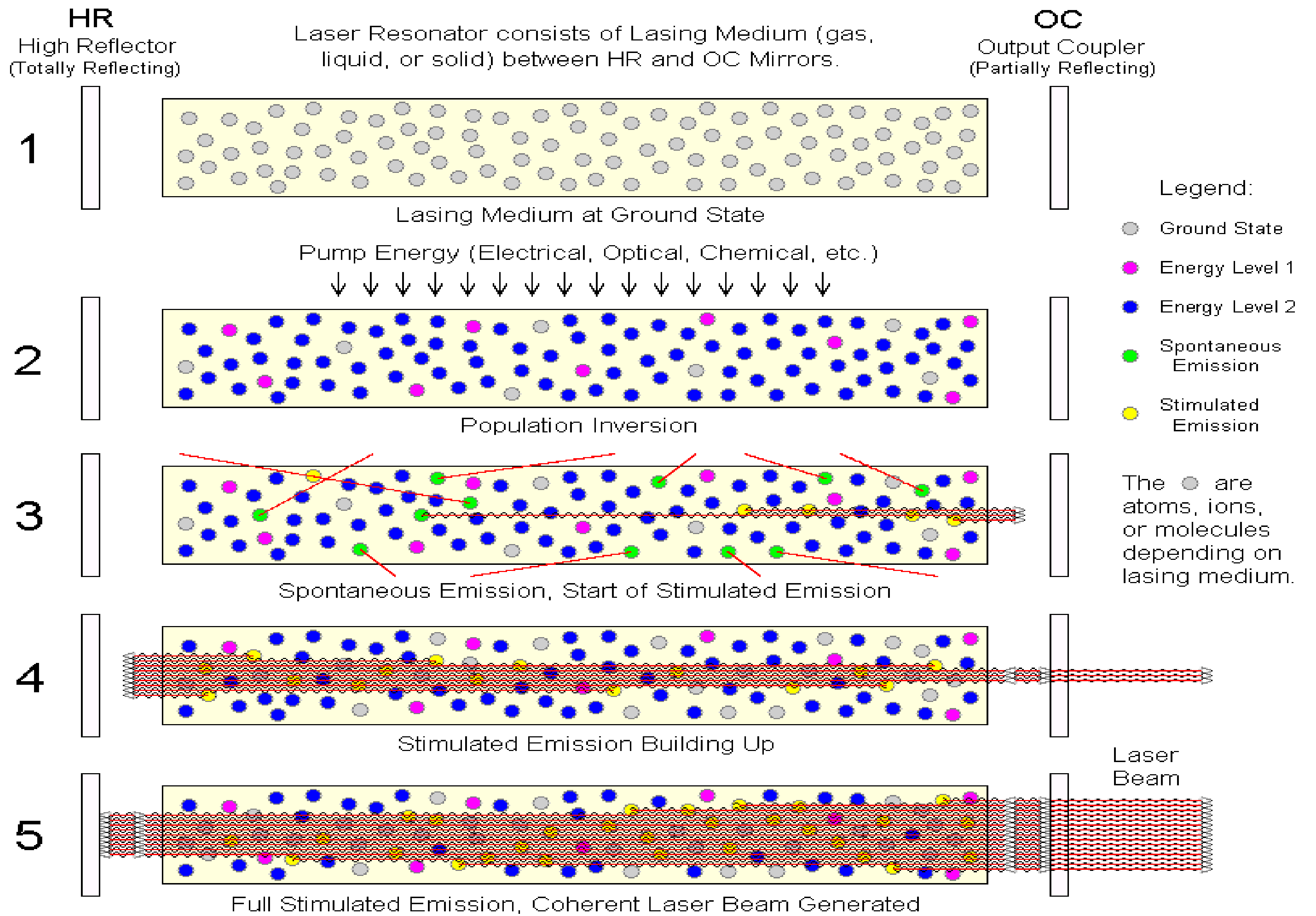
Lasing Action

1. Energy is applied to a medium raising electrons to an unstable energy level.
2. These atoms spontaneously decay to a relatively long-lived, lower energy, metastable state.
3. A population inversion is achieved when the majority of atoms have reached this metastable state.
4. Lasing action occurs when an electron spontaneously returns to its ground state and produces a photon.
5. If the energy from this photon is of the precise wavelength, it will stimulate the production of another photon of the same wavelength and resulting in a cascading effect.
6. The highly reflective mirror and partially reflective mirror continue the reaction by directing photons back through the medium along the long axis of the laser.
7. The partially reflective mirror allows the transmission of a small amount of coherent radiation that we observe as the “beam”.
8. Laser radiation will continue as long as energy is applied to the lasing medium.

Lasing Action Diagram



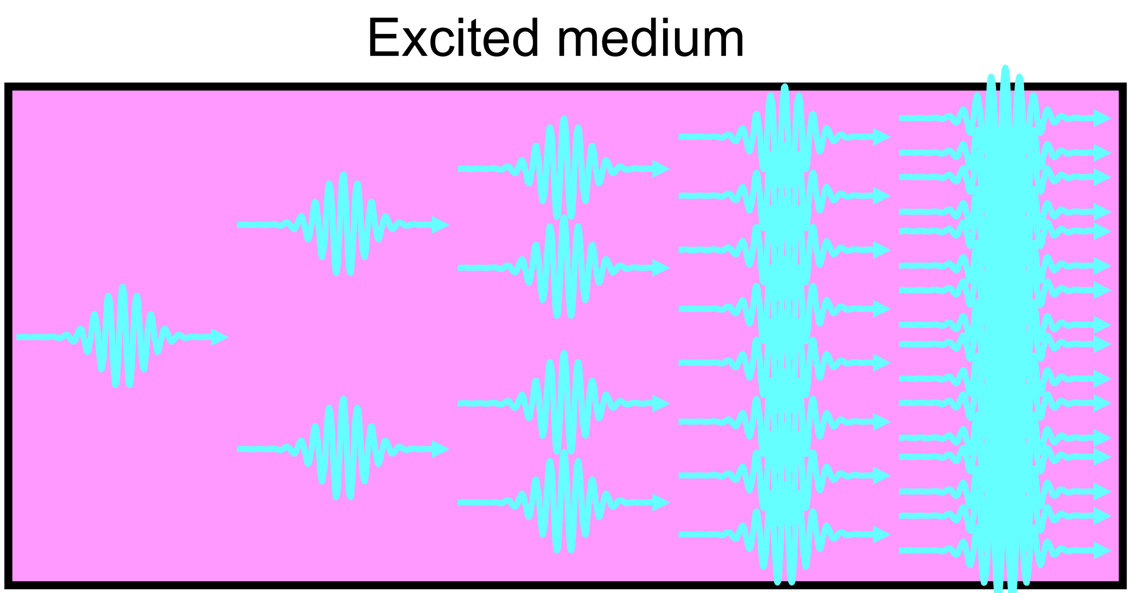

Pump Energy Source
gain medium
HR Mirror
OC Mirror
Resonator
Shore Laser



Basic Laser Operation

Stimulated emission can lead to a chain reaction and laser emission.

If a medium has many excited molecules, one photon can become many.



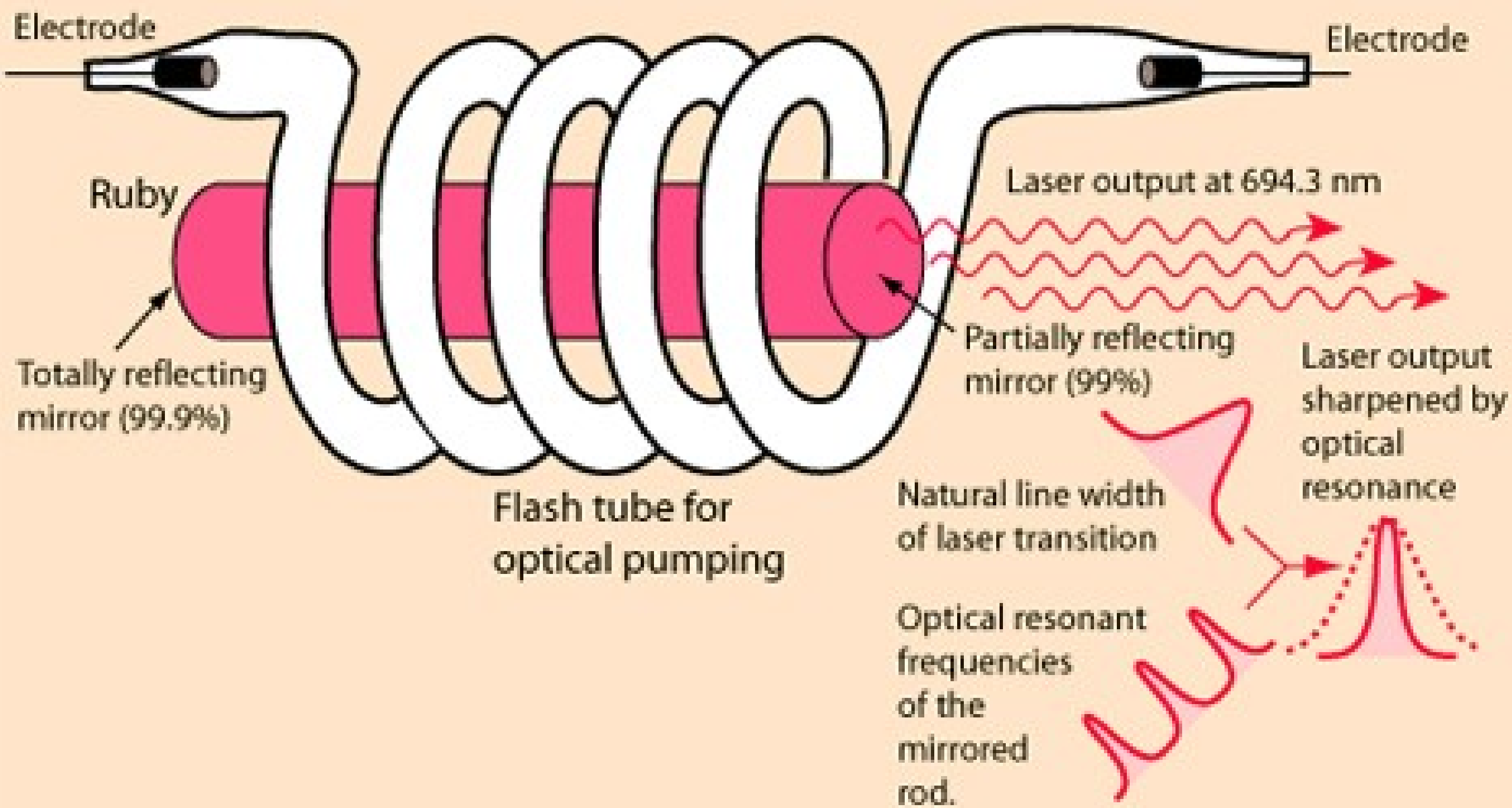
This is the essence of the laser. The factor by which an input beam is amplified by a medium is called the **gain** and is represented by G.

Ruby LASER

Basics of Ruby LASER

Type of laser	Solid State laser
Active medium	Ruby rod. It is a crystalline Al_2O_3 doped with Cr ions (0.5%), Cr ions being active centers.
Pumping method	Optical pumping, Xenon Helical Flash Lamp
Optical resonator	The two ends of the rod polished with silver.
Power output	$10^4 – 10^5$ watts.
Nature of output	Pulsed.
Characteristic wavelength	6943Å.

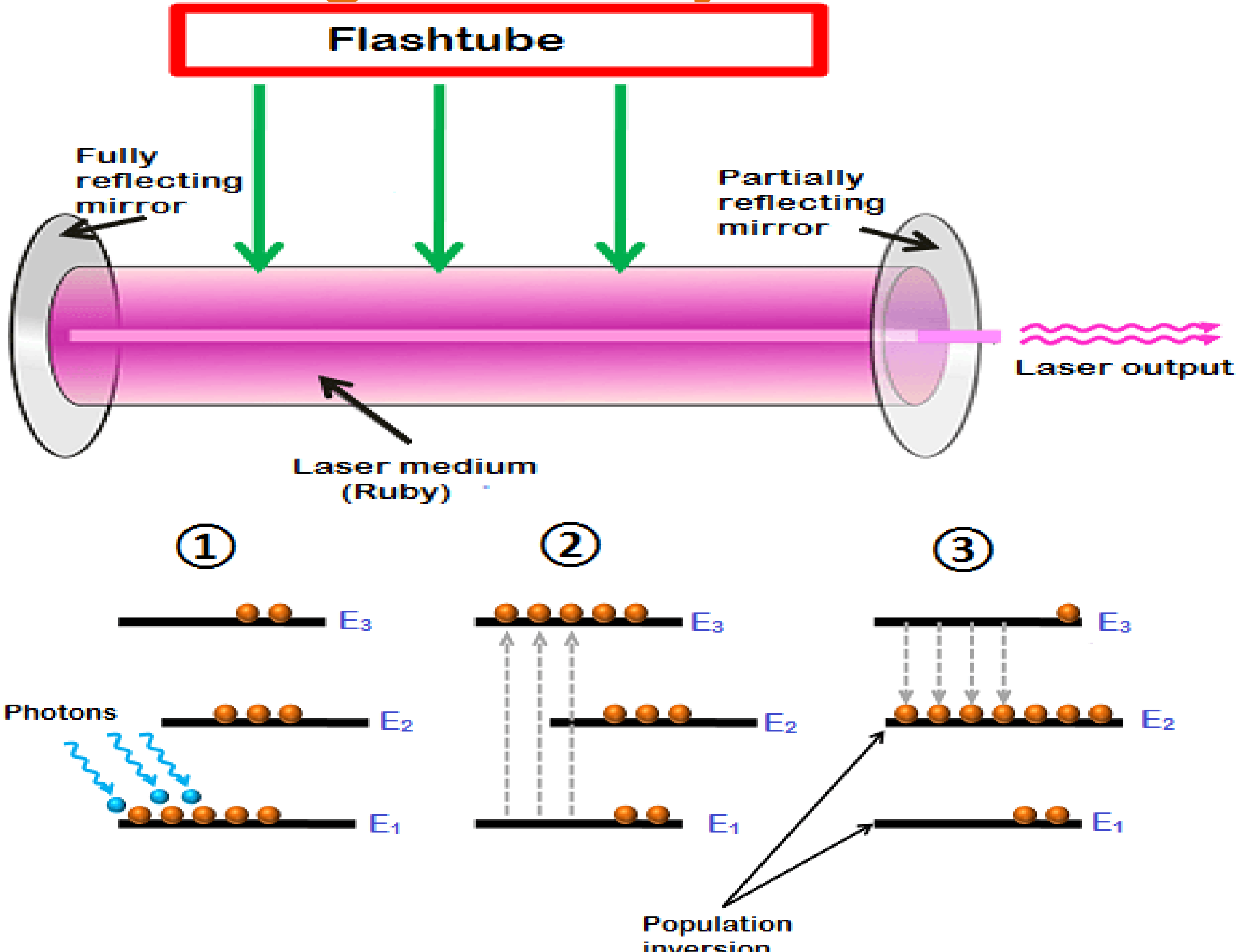
Ruby Laser and Flash Tube



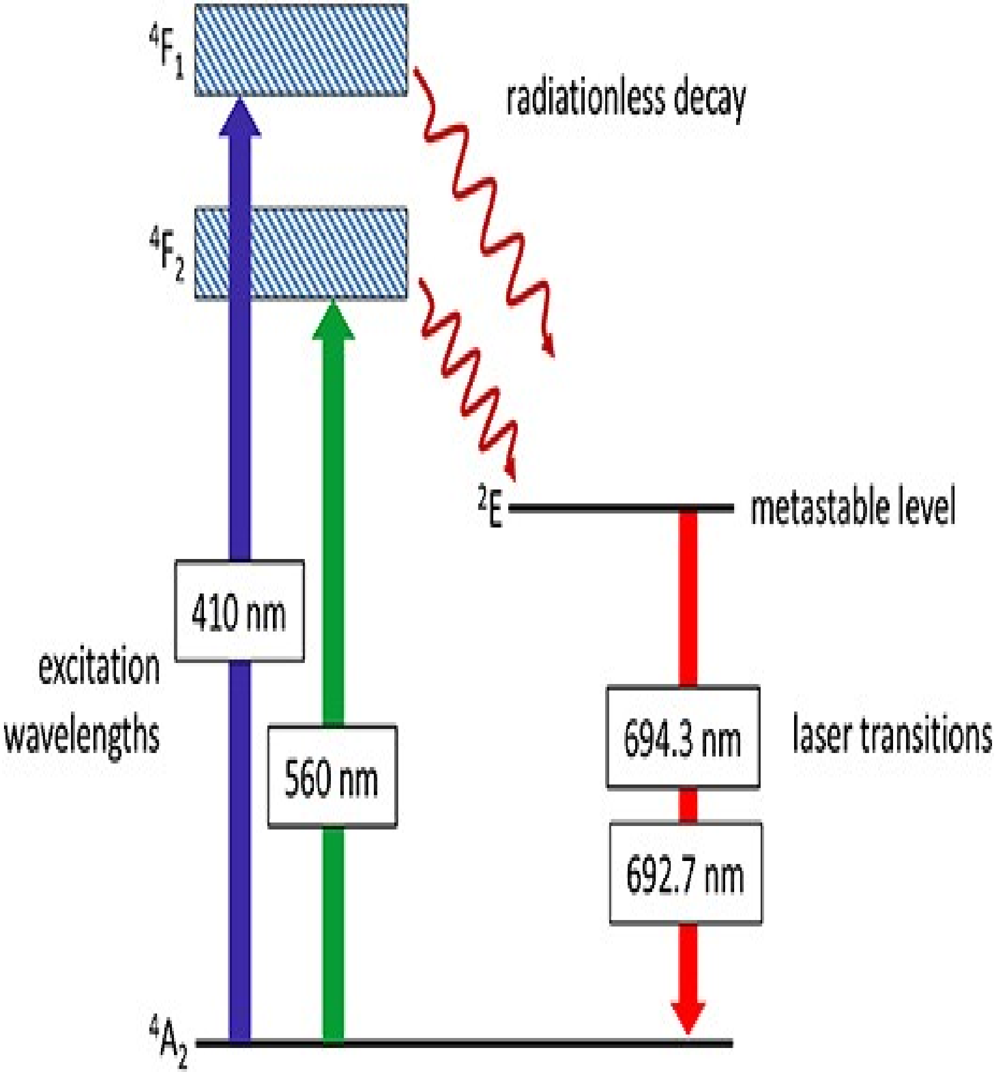
Construction of Ruby LASER

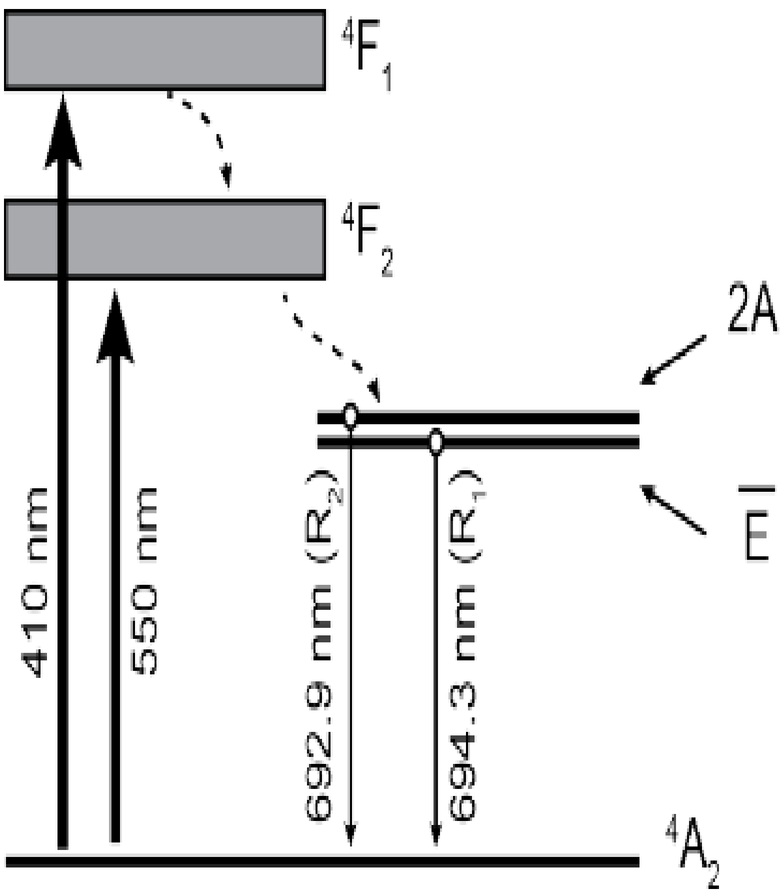
- Active Medium or Gain Medium or LASER Medium: Ruby Rod.
- Pump Source or Energy Source: Xenon Flash Lamp.
- Optical Resonator: Ruby Rod with one end 100% reflection and other 95% reflection.

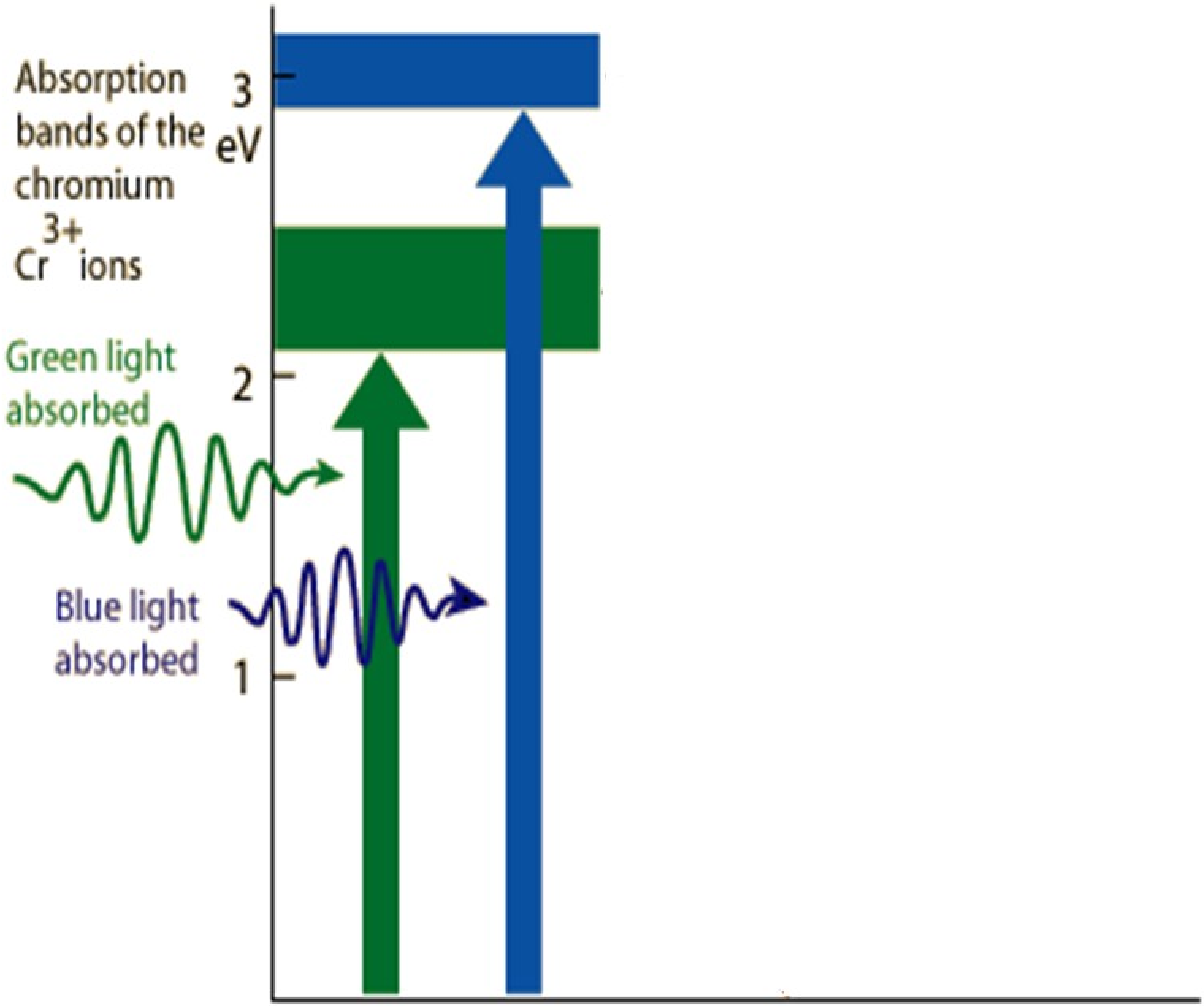
Working of Ruby LASER

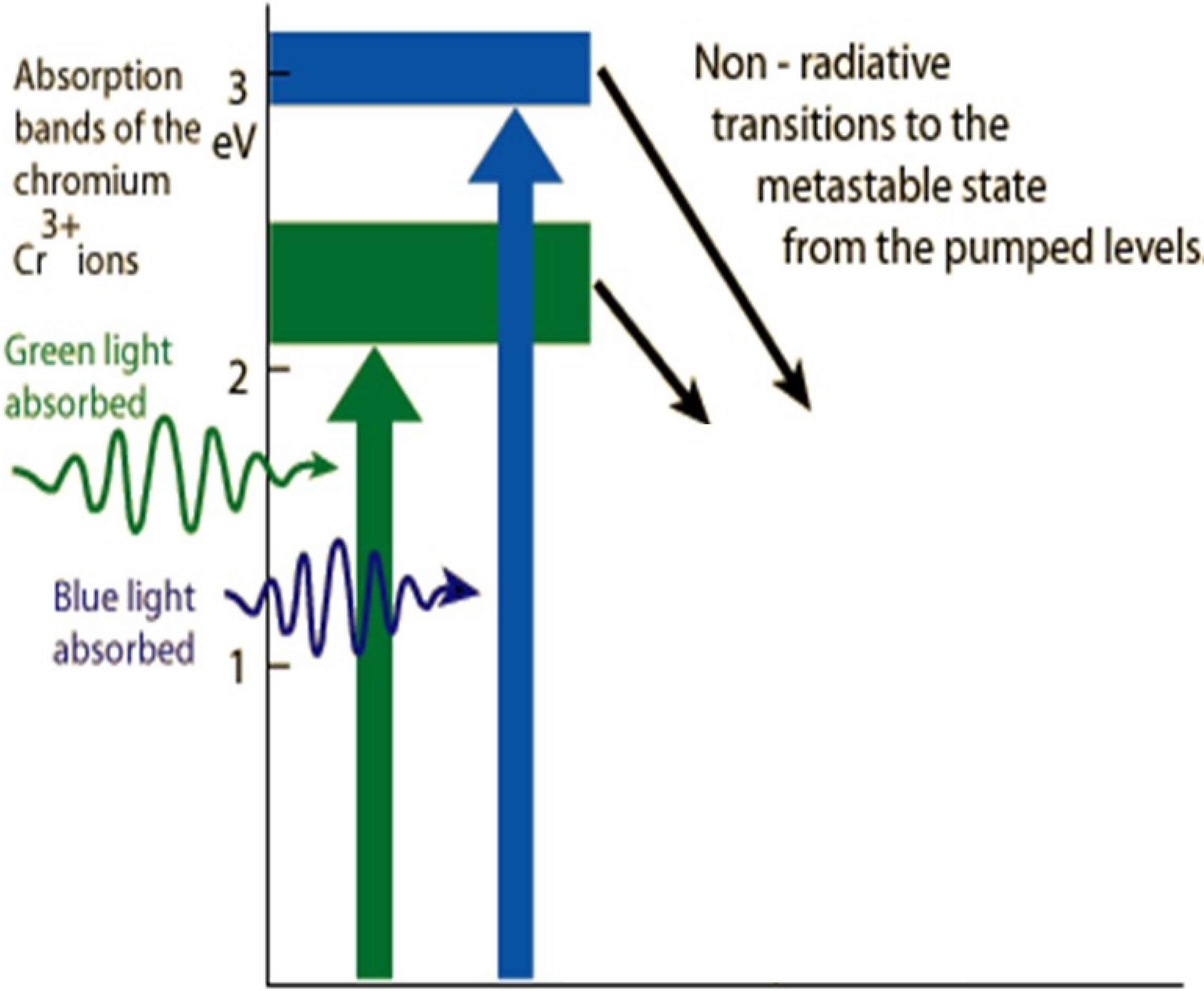


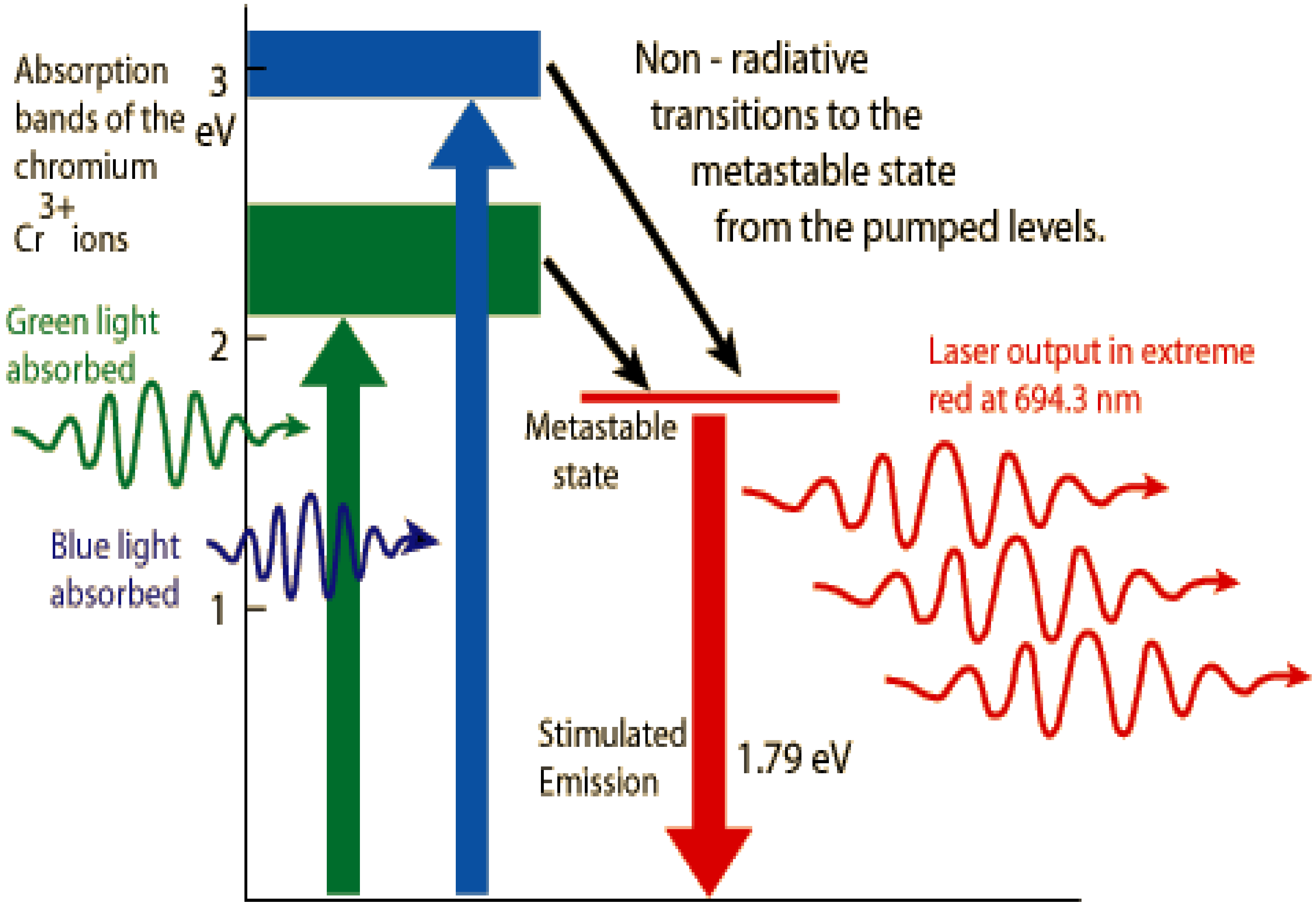
Energy Level Diagram






Absorption bands of the chromium Cr^{3+} ions
3
eV
2
1
Green light absorbed
Blue light absorbed


Absorption bands of the chromium Cr^{3+} ions
3
eV
2
1
Green light absorbed
Blue light absorbed
Non - radiative transitions to the metastable state from the pumped levels.


Absorption bands of the chromium Cr^{3+} ions
3
eV
2
1
Green light absorbed
Blue light absorbed
Non - radiative transitions to the metastable state from the pumped levels.
Metastable state
Laser output in extreme red at 694.3 nm
Stimulated Emission
1.79 eV

Applications

- Distance measurement using pulse echo technique.
- Used in atmospheric ranging, scattering studies and LIDAR measurement.
- Used for drilling high quality holes.
- In military used as target designators and range finders.
- Many non-destructive testing labs use ruby lasers to create holograms of large objects such as aircraft tires to look for weaknesses in the lining.
- Ruby lasers were used extensively in tattoo and hair removal

Advantages

- From the cost point of view, Ruby LASER is economical.
- Beam diameter of Ruby LASER is smaller than CO_2 gas LASER.
- outpower of Ruby LASER is not as less as He-Ne gas LASER.
- Since Ruby is in solid form, there is no chance of wasting material of active medium.

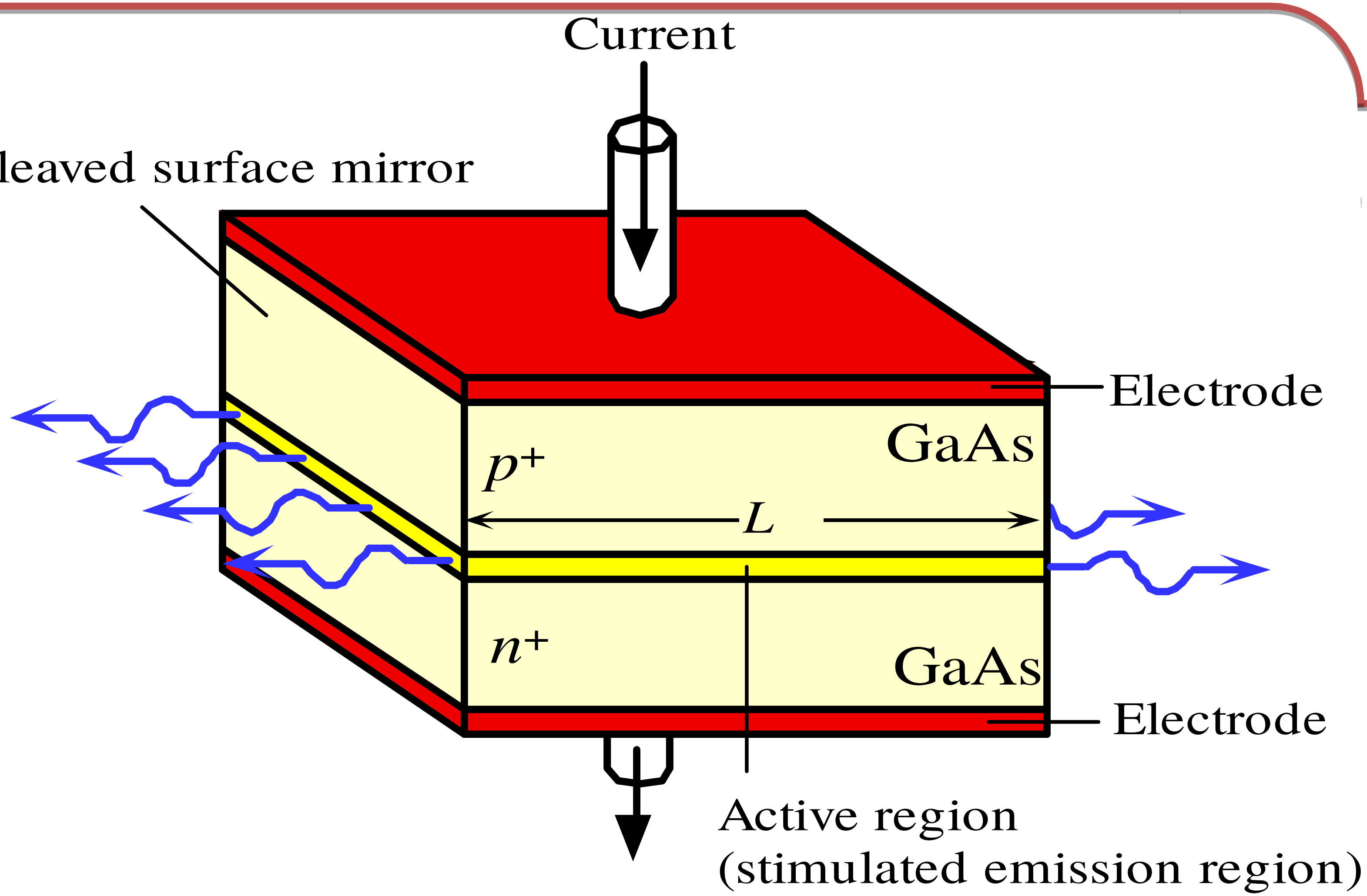
Drawbacks

- The laser requires high pumping power.
- The efficiency of ruby laser is very low.
- The laser output is not continuing but occurs in the form of pulses of microseconds duration.
- The defects due to crystalline imperfection are also present in this laser.

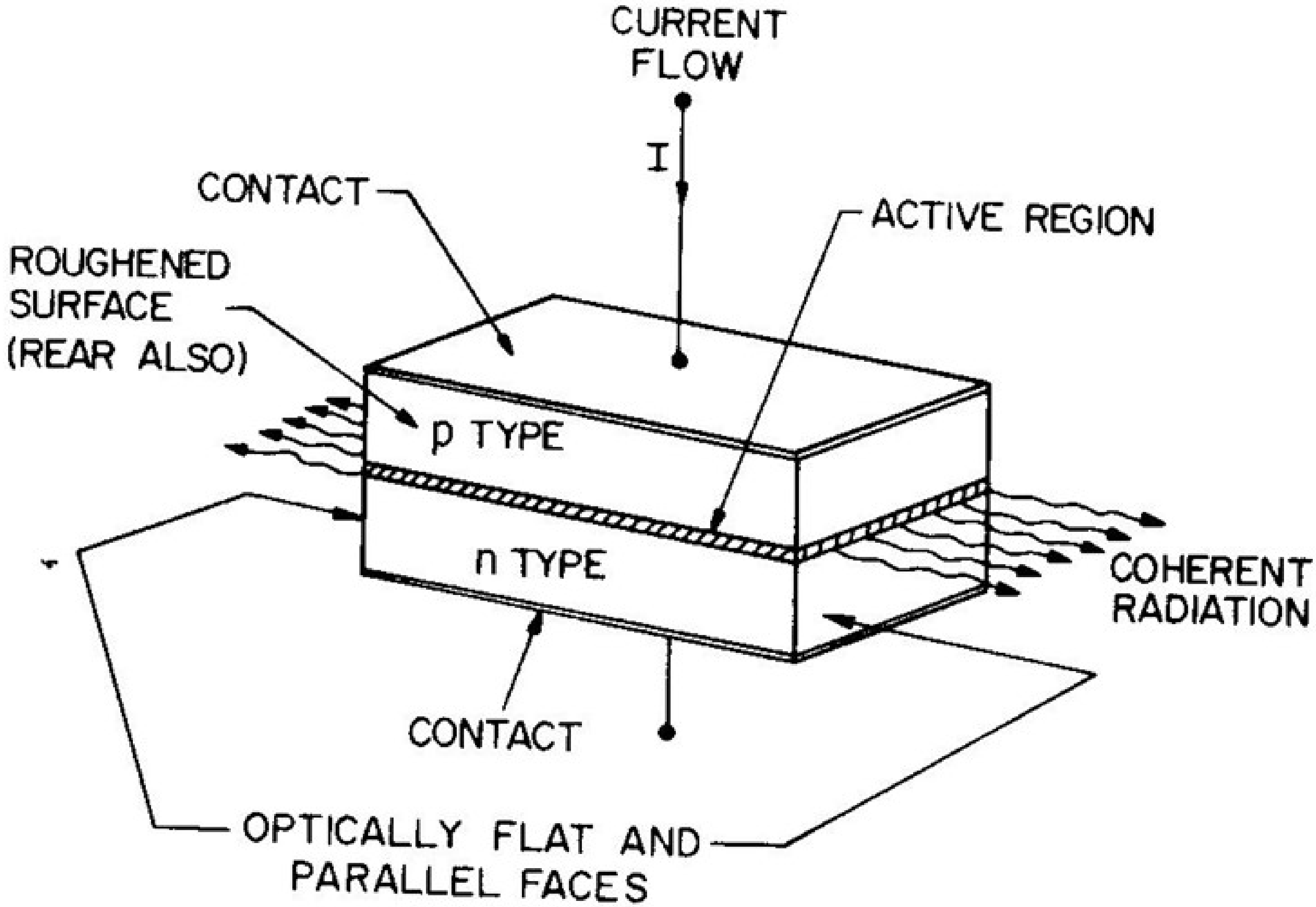
Semiconductor LASER

Basics of Semiconductor LASER

Type of laser	Semiconducting material
Active medium	p-n junction diode made up of GaAs
Pumping method	Direct pumping
Optical resonator	The polished front & back surfaces perpendicular to the plane of the junction
Power output	1 m W.
Nature of output	Continuous or pulsed
Characteristic wavelength	Any wavelength with in visible to IR depending on the material used.

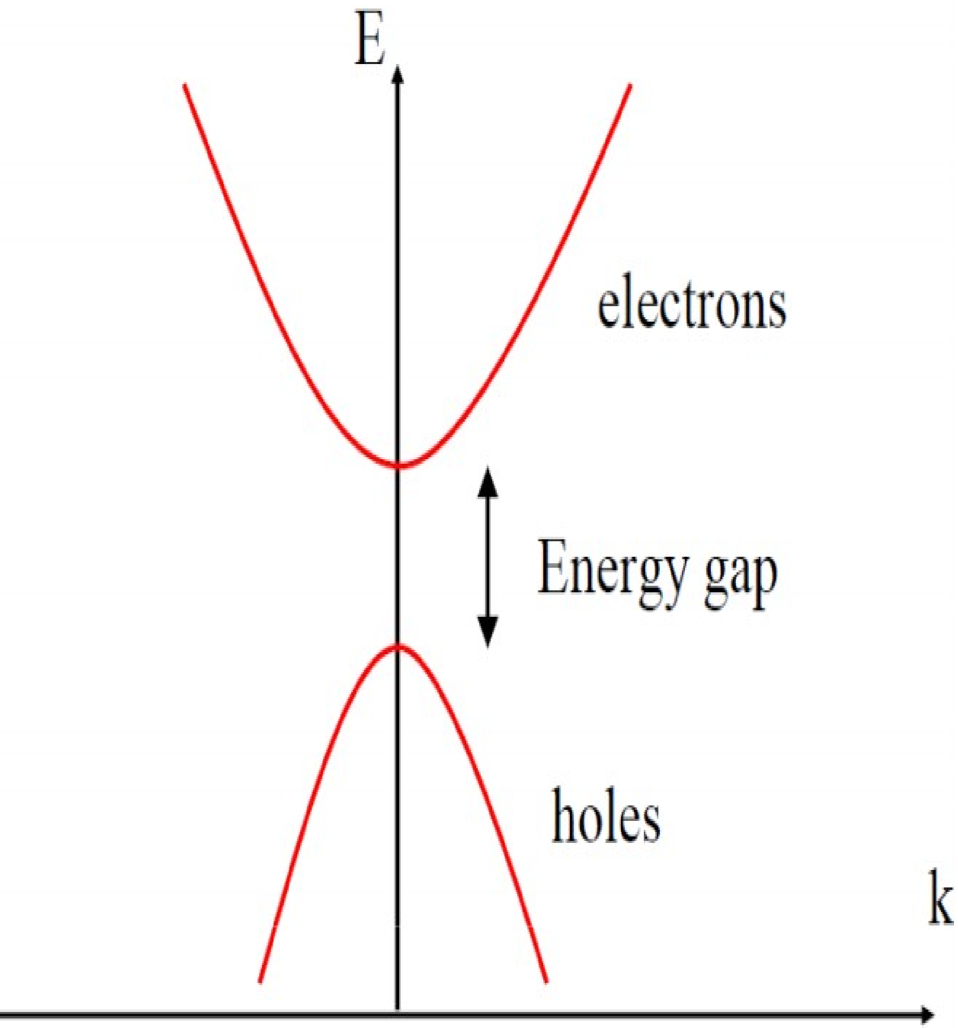


A schematic illustration of a GaAs homojunction laser diode. The cleaved surfaces act as reflecting mirrors.

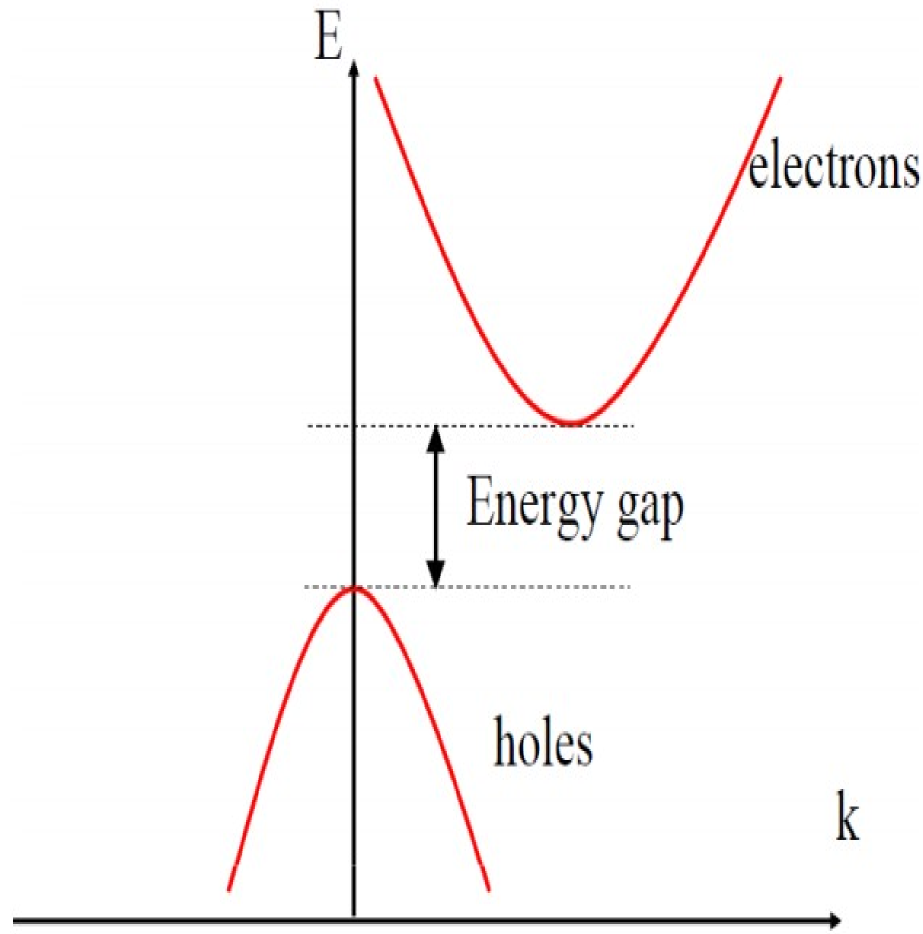

CURRENT
FLOW
I
CONTACT
ACTIVE REGION
ROUGHENED
SURFACE
(REAR ALSO)
p TYPE
n TYPE
COHERENT
RADIATION
CONTACT
OPTICALLY FLAT AND
PARALLEL FACES

Semiconductor Laser

- Like LED.
- Lasing action is possible in special type of semiconductors called DIRECT BANDGAP semiconductor.
- Recombination of hole & electron give energy in the for of EM radiation
- Lasers which use semiconductor as active medium, are based on a combination of elements in the III group (Al, Ga, In) and the V group (N, P, As, Sb) hence referred to as the III-V compounds.

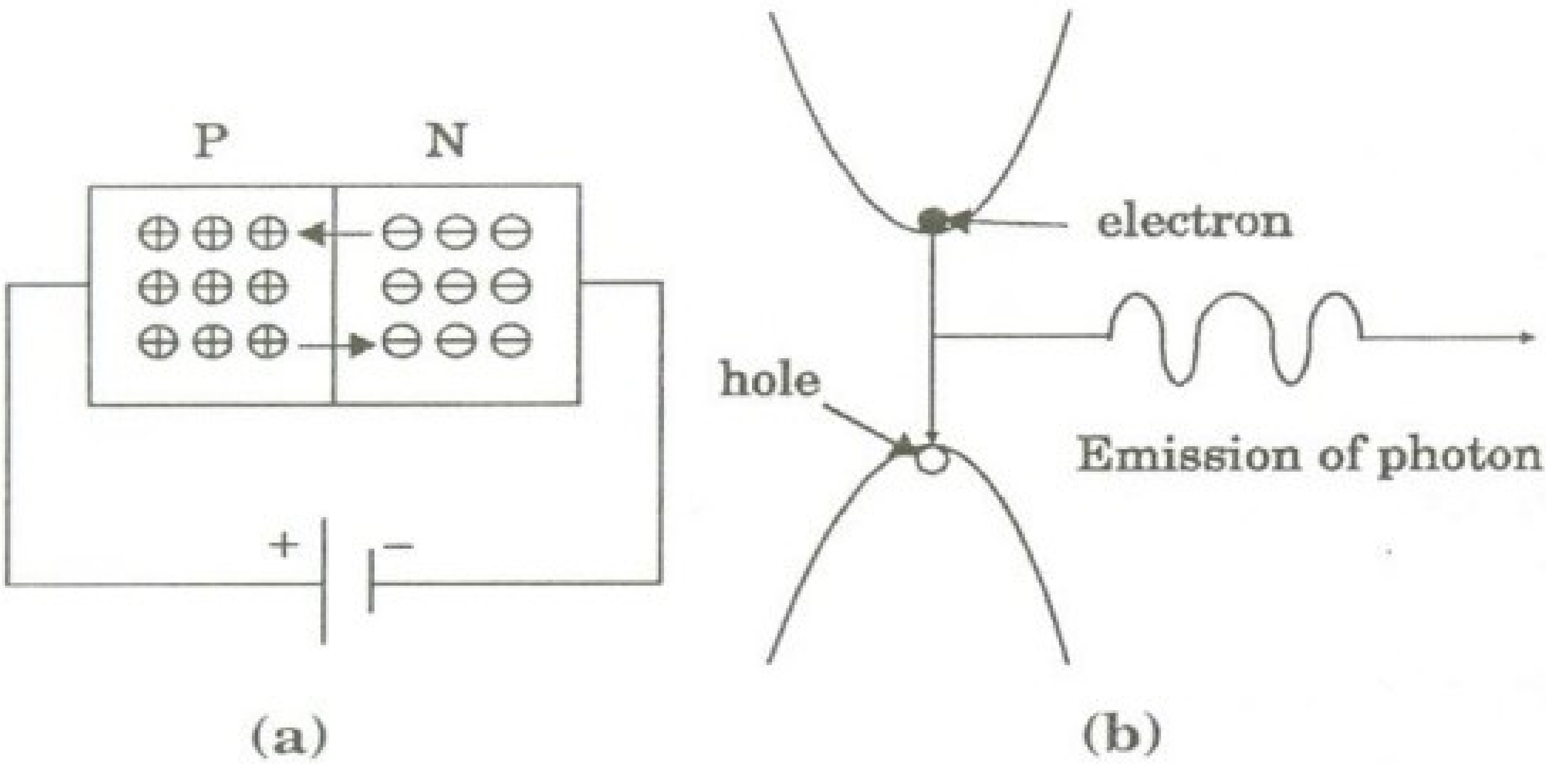


Direct bandgap semiconductors

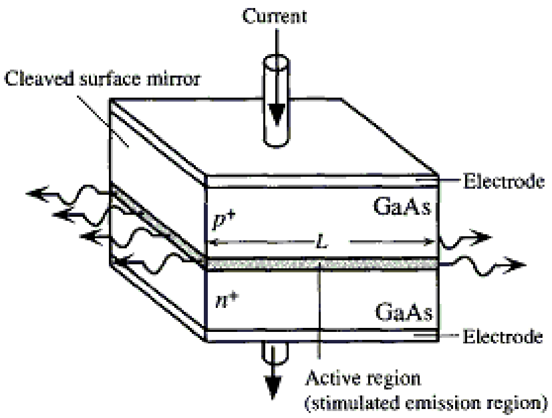


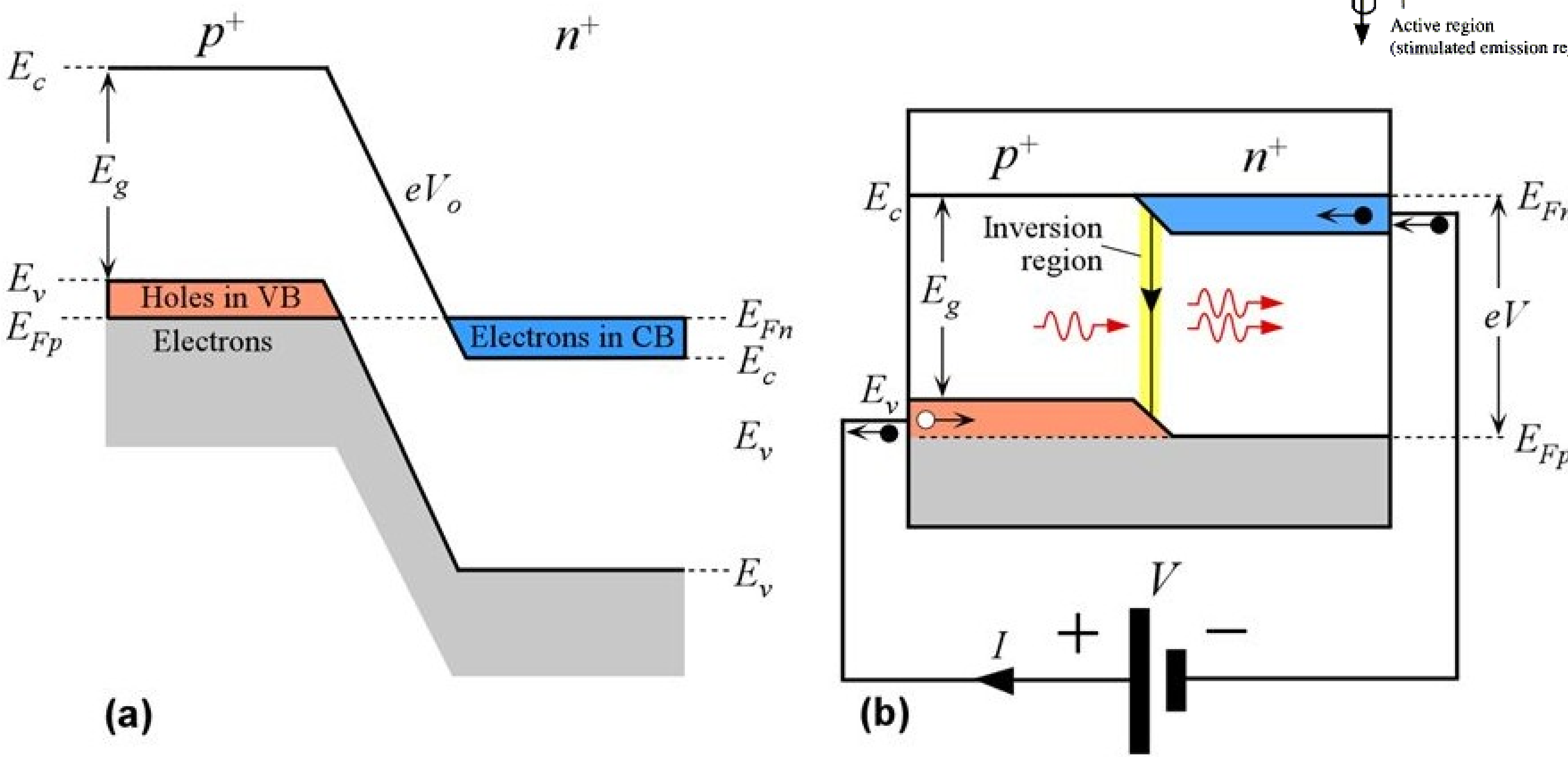
Indirect bandgap semiconductors

Working of Semiconductor LASER



Energy Level Diagram





(a) The energy band diagram of a degenerately doped *pn* with no bias. (b) Band diagram with a sufficiently large forward bias to cause population inversion and hence stimulated emission.

Applications

- It is widely used in fiber optic communication.
- It is used to heal the wounds by infrared radiation.
- It is also used as a pain killer.
- It is used in laser printers and CD writing and reading.

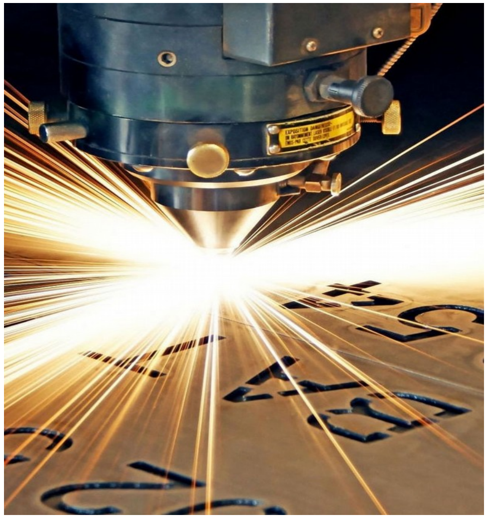
Advantages

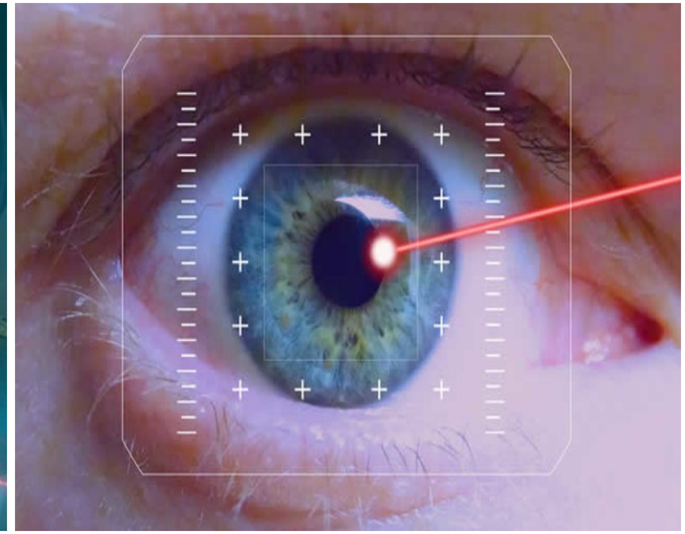
- It is very small in dimension. The arrangement is simple and compact.
- It exhibits high efficiency.
- Output can be controlled by controlling the junction current.
- It is operated with lesser power.
- It can give continuous and pulsed output.

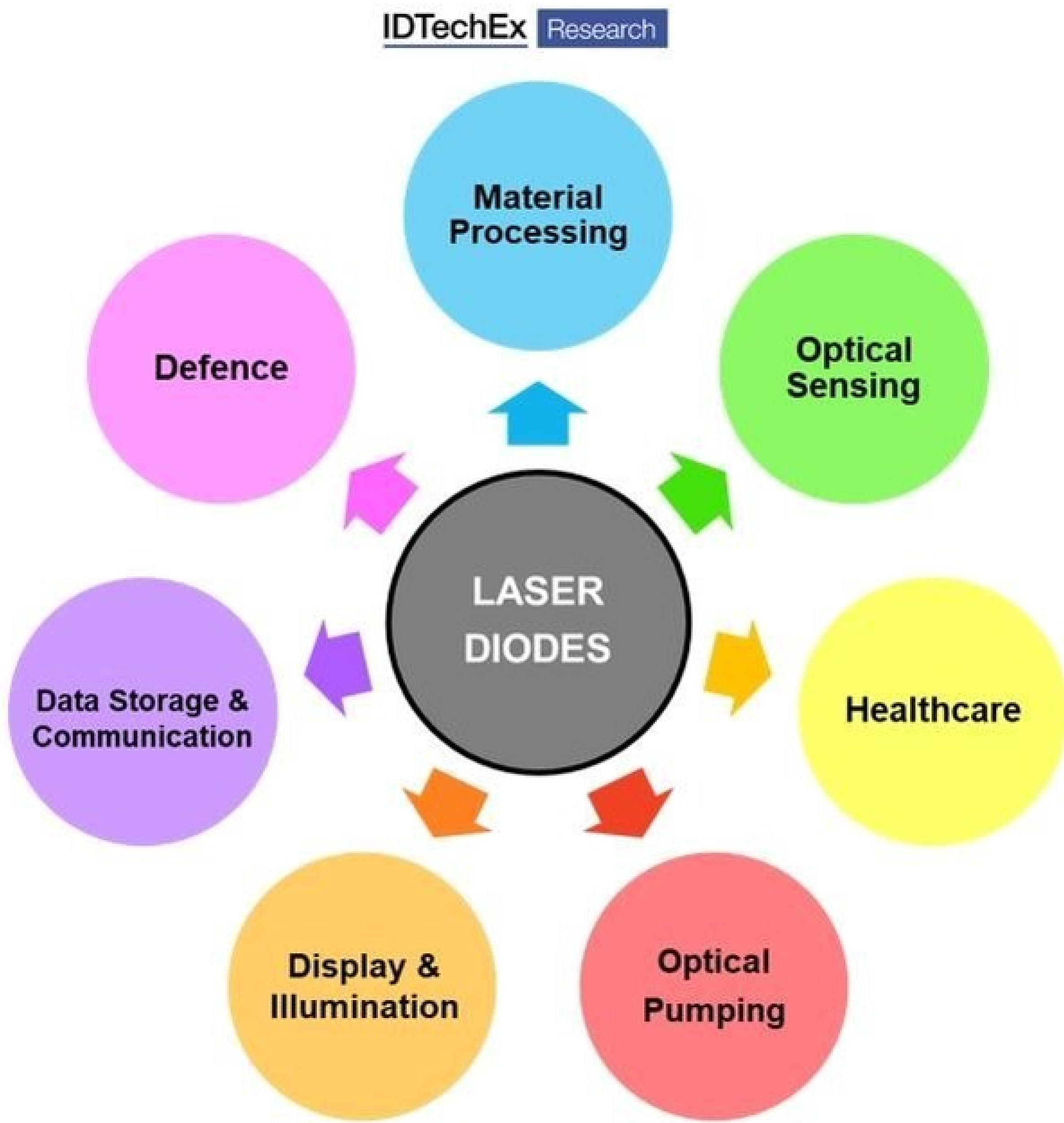
Drawbacks

- It is difficult to control the mode pattern and mode structure of laser.
- The output is usually from 5 degree to 15 degree i.e., laser beam has large divergence.
- The purity and monochromacity are power than other types of laser.
- Threshold current density is very large (400A/ mm^2).
- It has poor coherence and poor stability.

Wide ranging of laser applications






IDTechEx Research
Material Processing
Optical Sensing
Healthcare
Optical Pumping
Display & Illumination
Data Storage & Communication
Defence
LASER DIODES

LASERS

DEFENCE AND SECURITY
- Marking targets
- Guiding ammunitions
- Missiles
- Electro-optical counter measures
- Blinding troops

MEDICINE AND HEALTHCARE
- Bloodless surgery
- Kidney stone treatment
- Dermatology
- Ophthalmology
- Dentistry
- Neurology
- Tissue repairs
- Cosmetology

ENFORCEMENT AND SCIENTIFIC/ TECH RESEARCH
- Laser fingerprint detection
- Forensic science
- Spectroscopy
- Laser ablation
- Laser scattering microscopy
- Metrology

COMMERCIAL AND ENTERTAINMENT
- Laser printers
- Optical disks
- Barcode scanners
- Thermometers
- Laser pointers
- 3D holograms
- Laser light shows
- Decoration

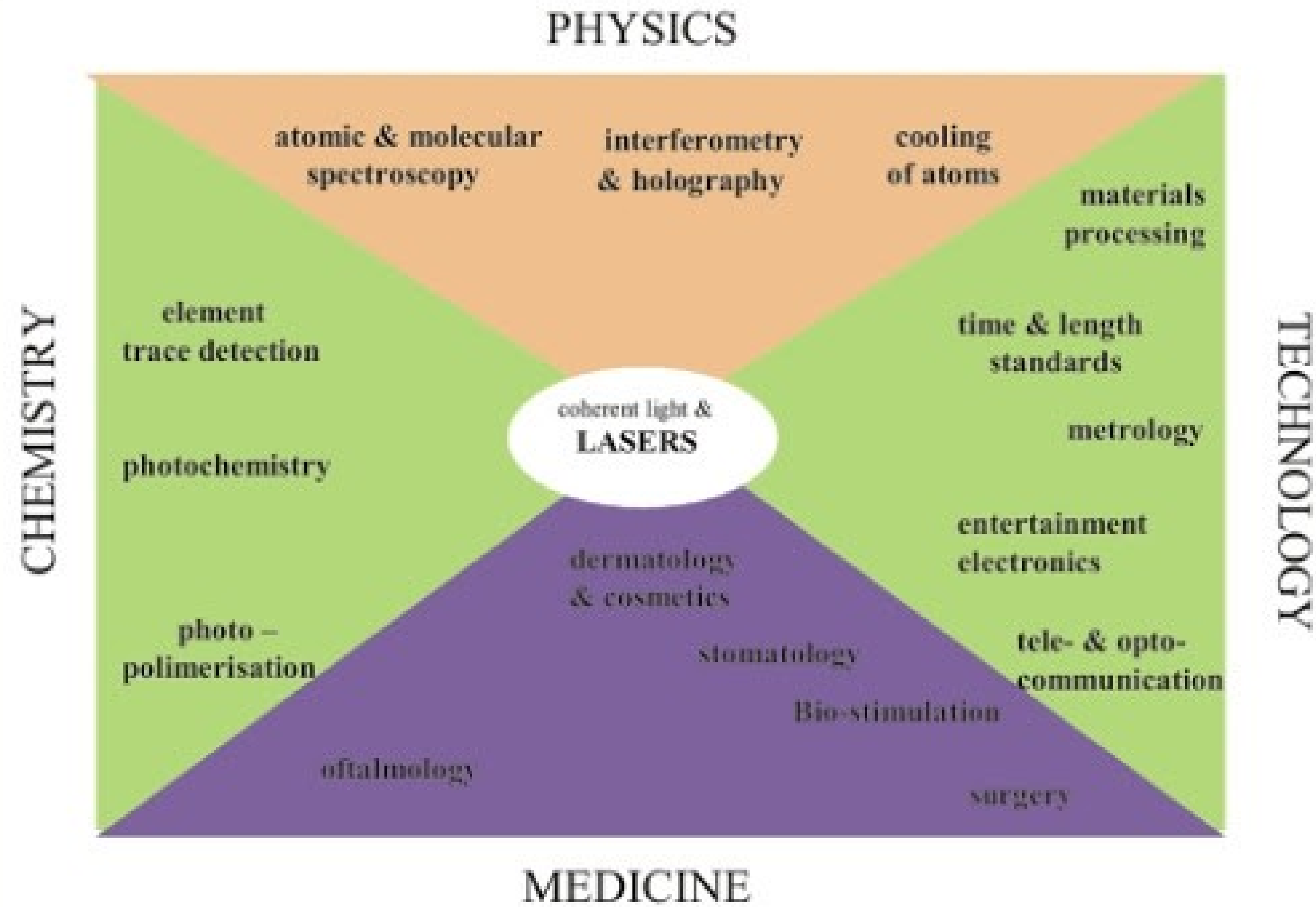
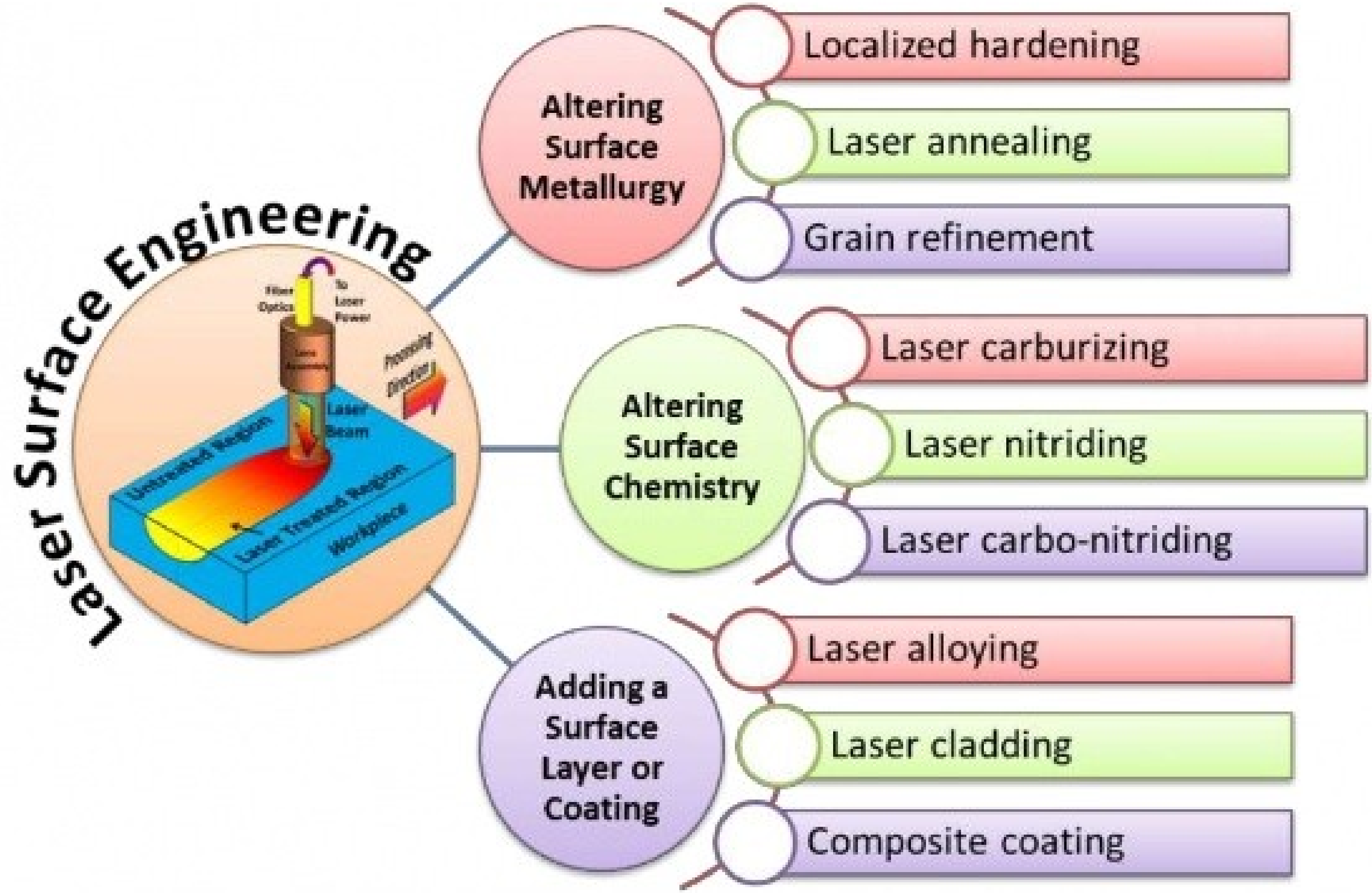


Fig. 1.1.6: Recent laser applications - an overview.

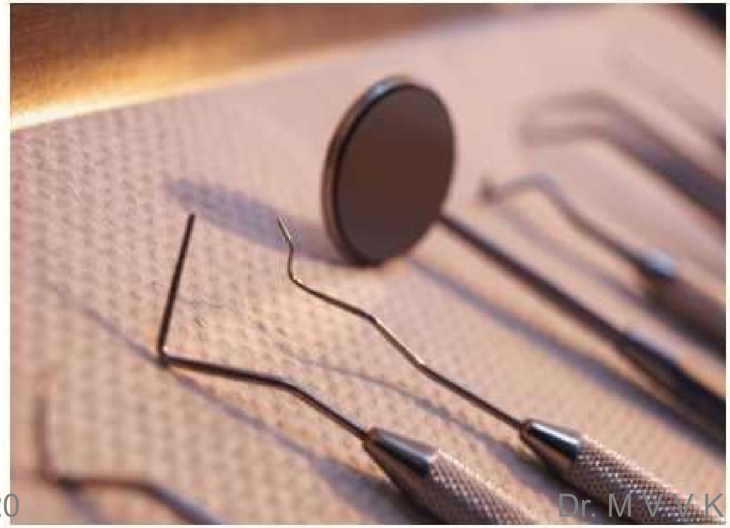
© Andreoni et al., in: "Handbook on the Use of Lasers in Conservation and Conservation Science", 2008.

Applications of lasers in surface engineering



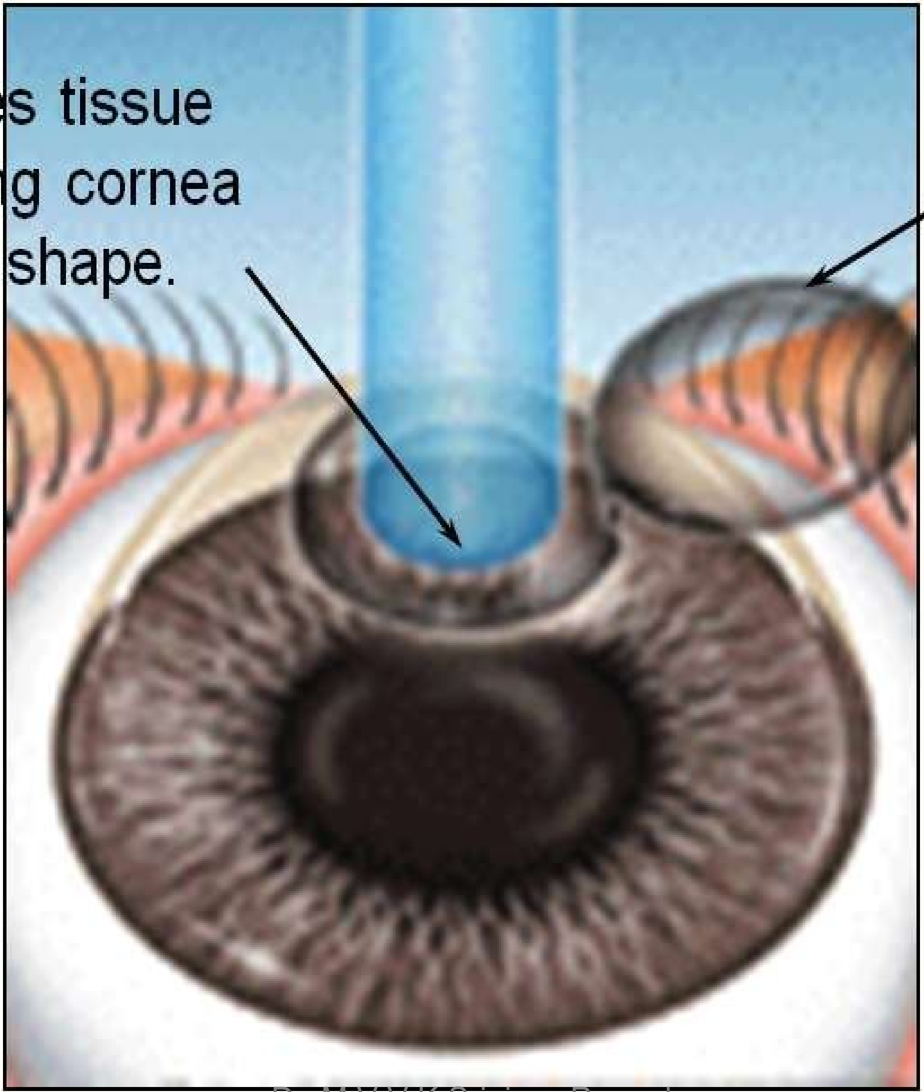
- Use for the treatment of detached retinas.
- Use in performing bloodless surgery
- Use for the treatment of human and animal cancers and skin tumors.

LASERS IN MEDICINE



Medical Applications

Laser Eye Surgery

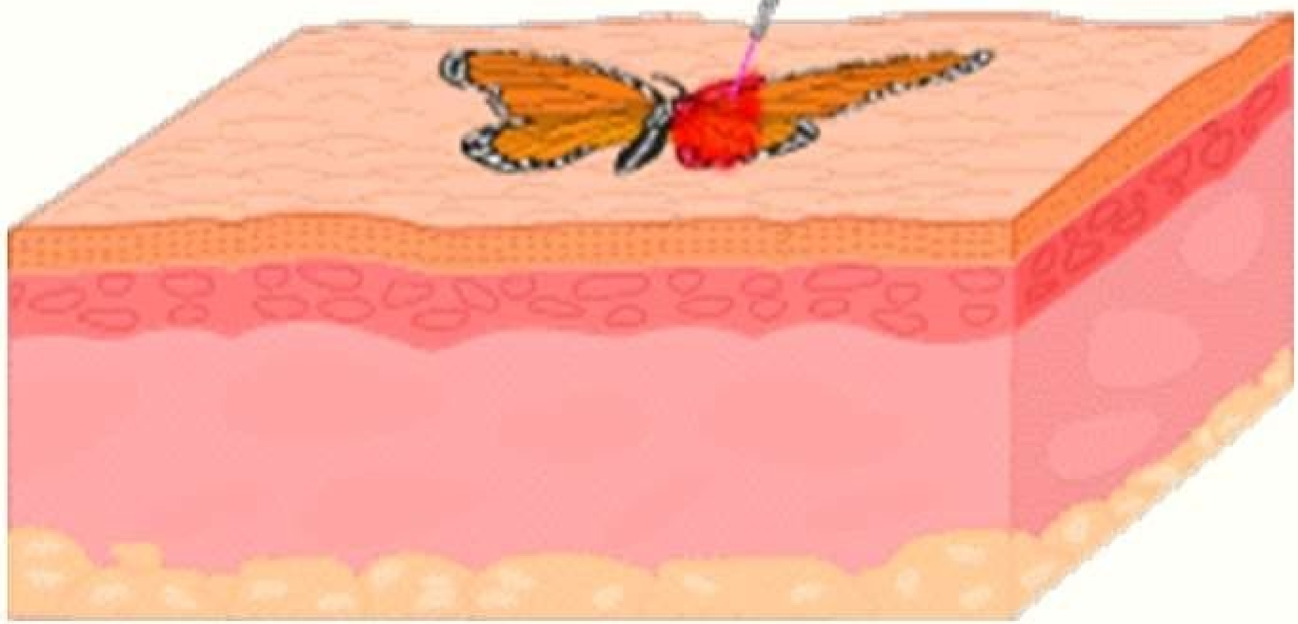


Laser in MRI (Magnetic Resonance Imaging)

Laser In Eye Treatment

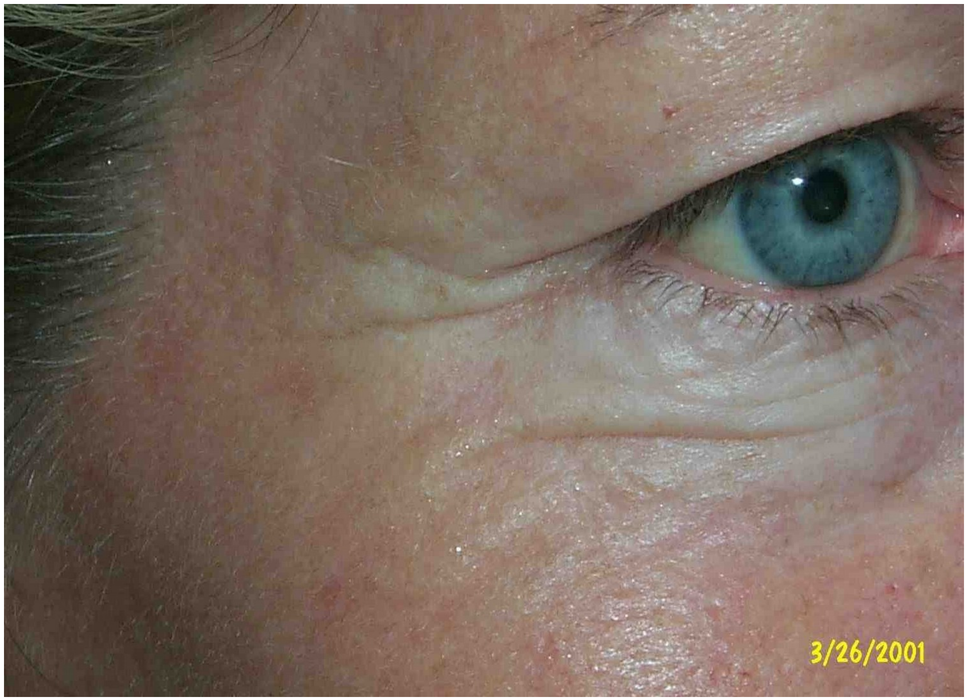
Laser Tattoo Removal

Tattoo can be removed with variety of lasers depending on the presence of inks in the tattoo



The laser beam breaks up the pigments in the tattoo into small particles. Then the body's immune system attacks and destroys them.

Laser skin rejuvenation



IR lasers are used to remove extremely thin layer of skin (<0.1 mm). In the absence of pigment in general, they take advantage of the presence of water in the skin to provide an ability to remove skin and body tissue.

Laser hair removal

selective absorption : absorbing component being melanin pigment in hair and follicle, it is best worked with a red light ruby laser. White hair can not be treated with any laser due to the lack of absorbing component.

Laser removal of port-wine stain

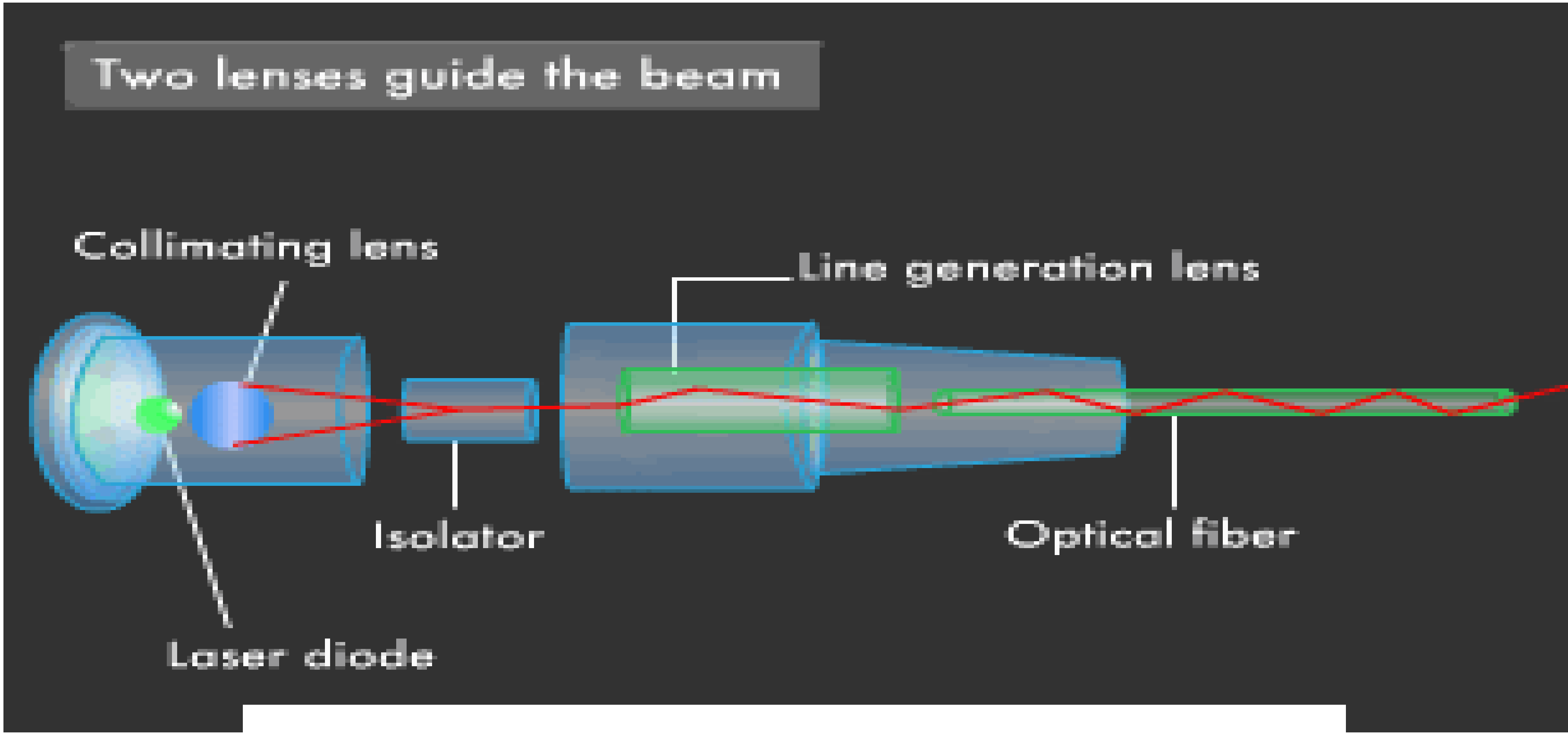
PORT-WINE STAINS can be treated with lasers. Excess blood vessels just under the outer layer of the skin (*left*) absorb yellow laser light, which destroys the red vessels (*right*). Because the beam is delivered in brief pulses, other tissue is undamaged.

Yellow laser is absorbed by the presence of hemoglobin in blood vessels.

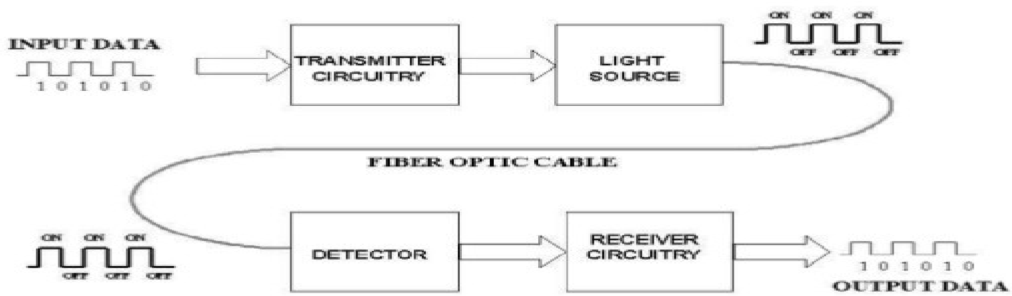
SURGICAL LASER SYSTEM :

Common lasers used in surgery include :

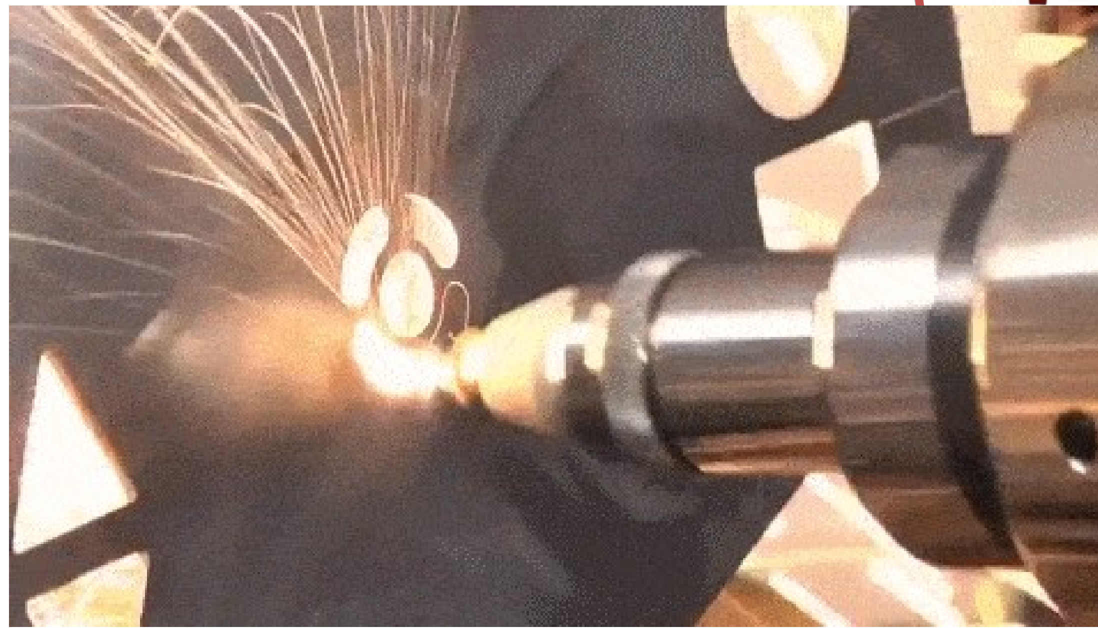
- CO2 laser	: 10600 nm	→	General surgery, Gynecology , ……
- Nd:YAG lasers	: 1064 nm	→	General surgery, …….
- Ho:YAG lasers	: 2100 nm	→	Urosurgery, Orthopedics,…..
- Diode lasers	: 810 nm	→	Vascular surgery, ENT surgery,…
- Dye laser	: 570 nm	→	Vascular surgery
- Excimer laser	: 193 nm	→	Ophthalmology

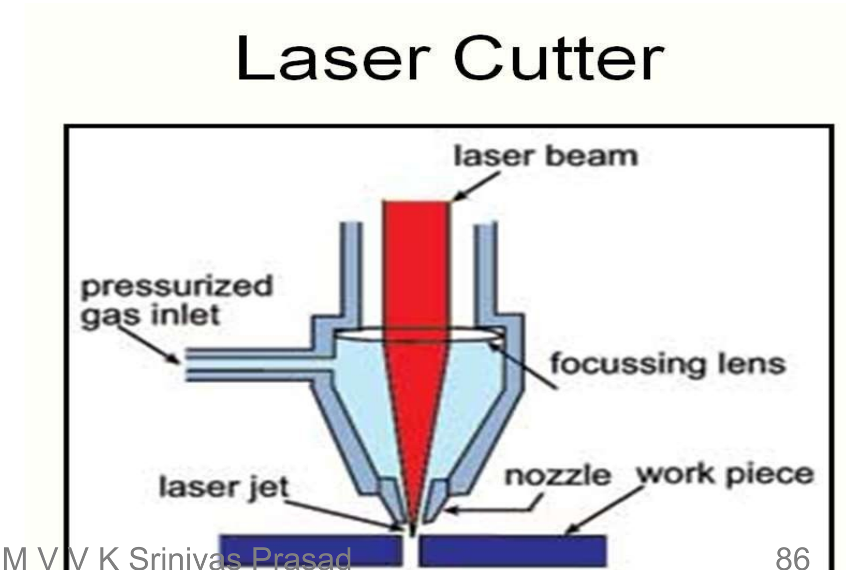


Optical fiber communication



LASERS in Welding and Cutting of metal

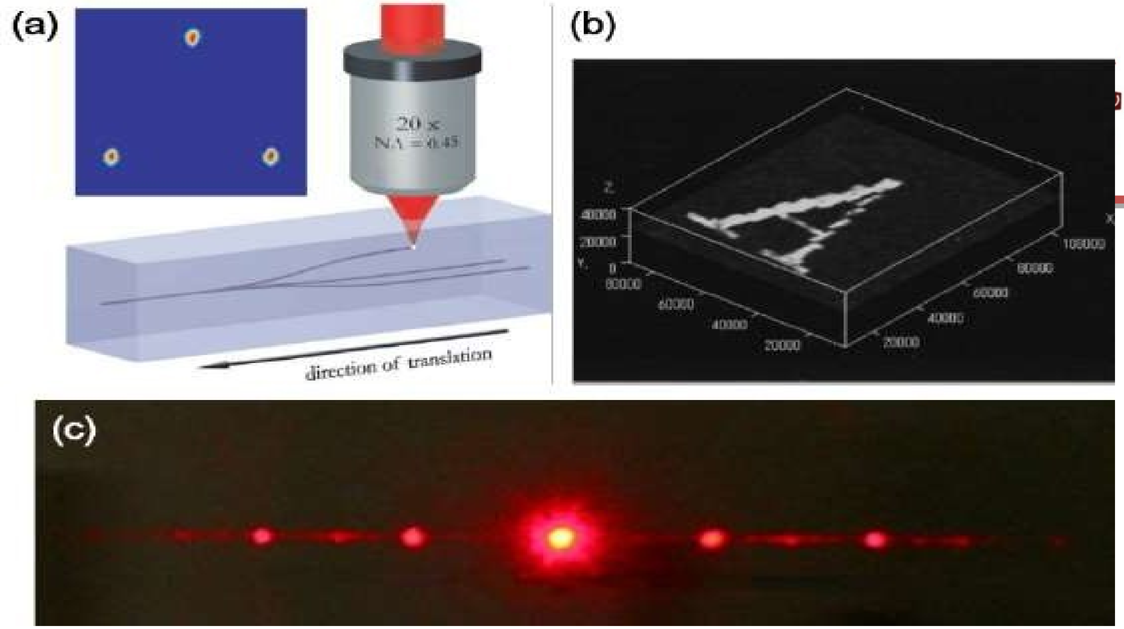




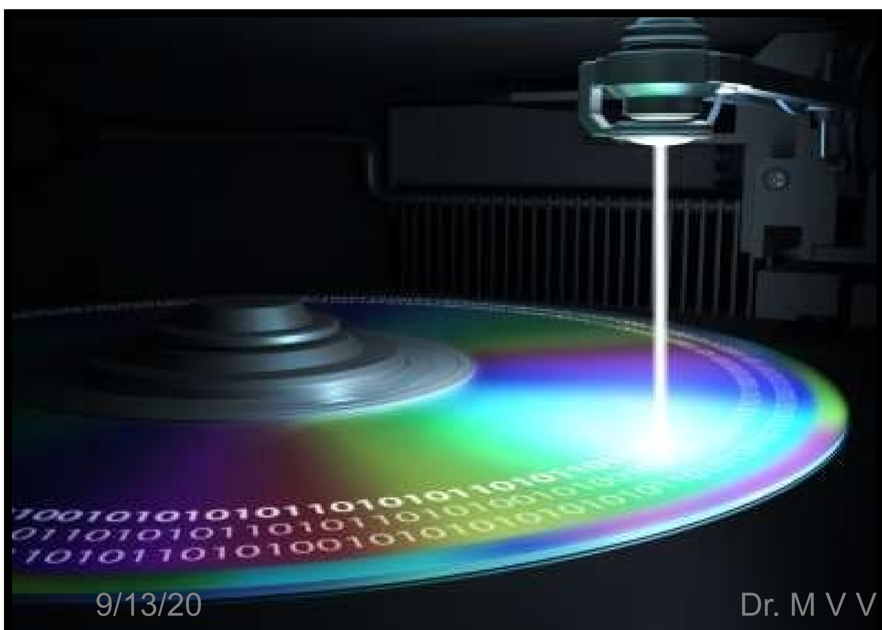
Laser in Garment Industry

CO2 laser engraving Designs

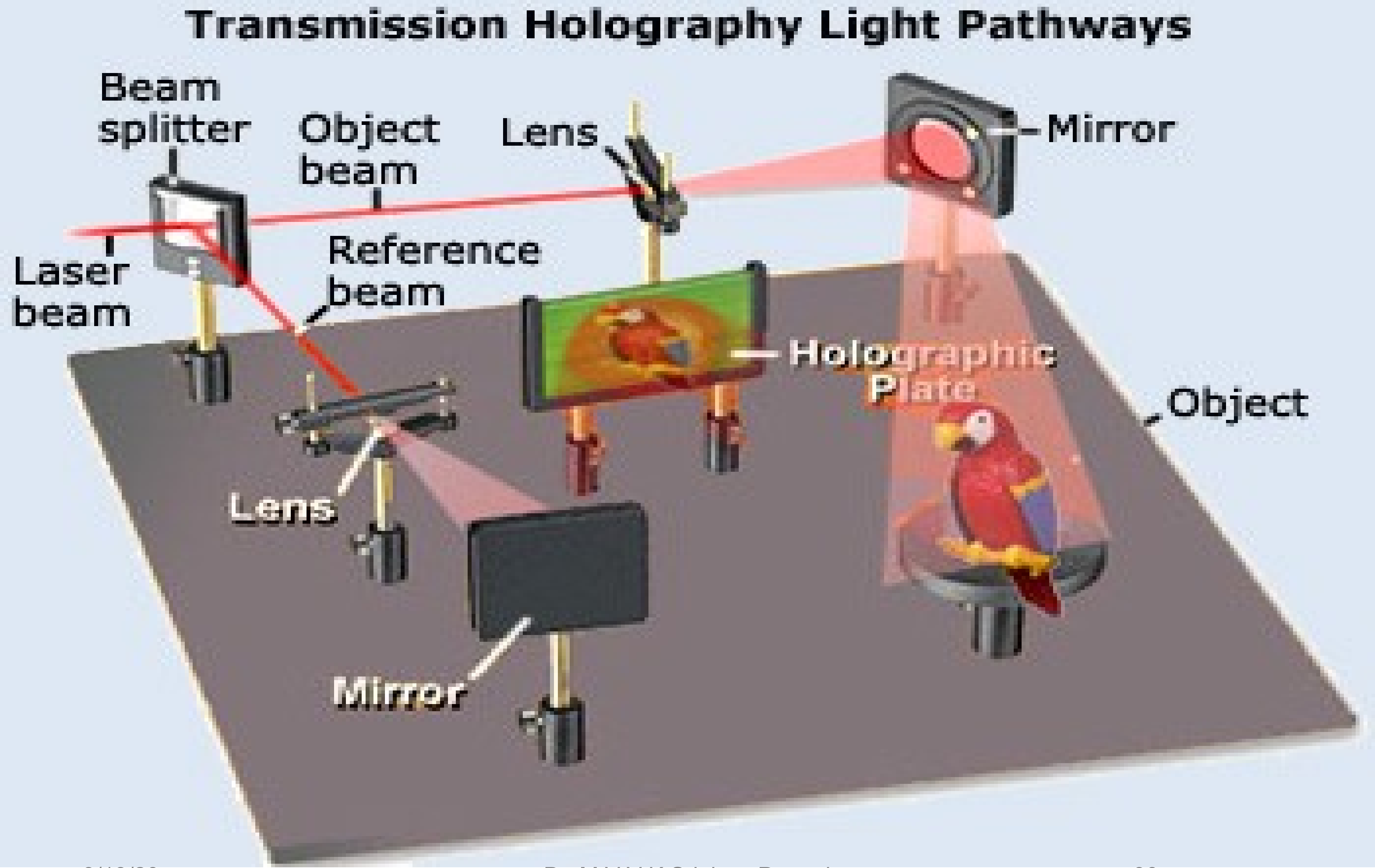
Laser Textile Stitching



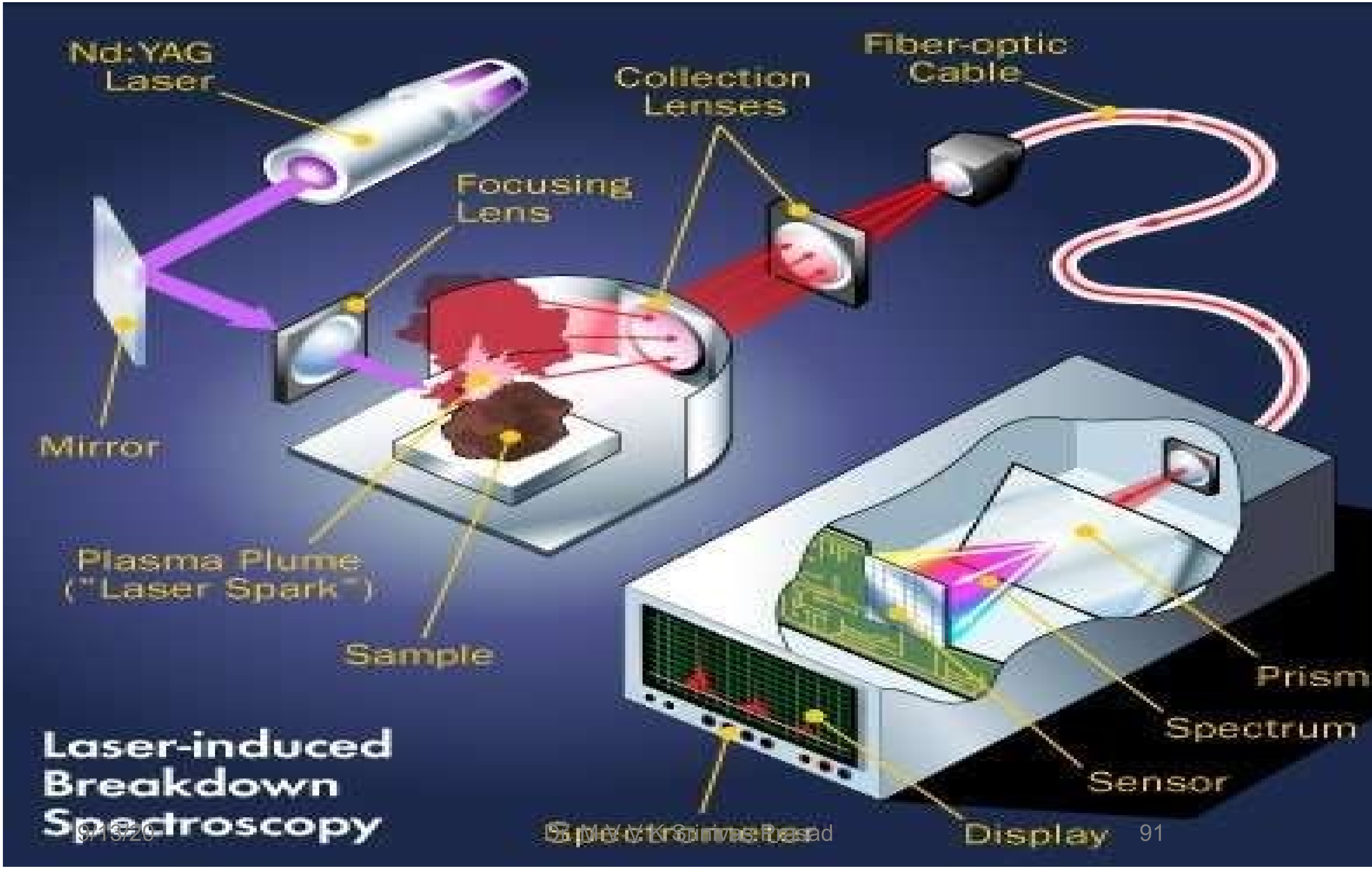
Laser in Data Storage



Laser In Holography

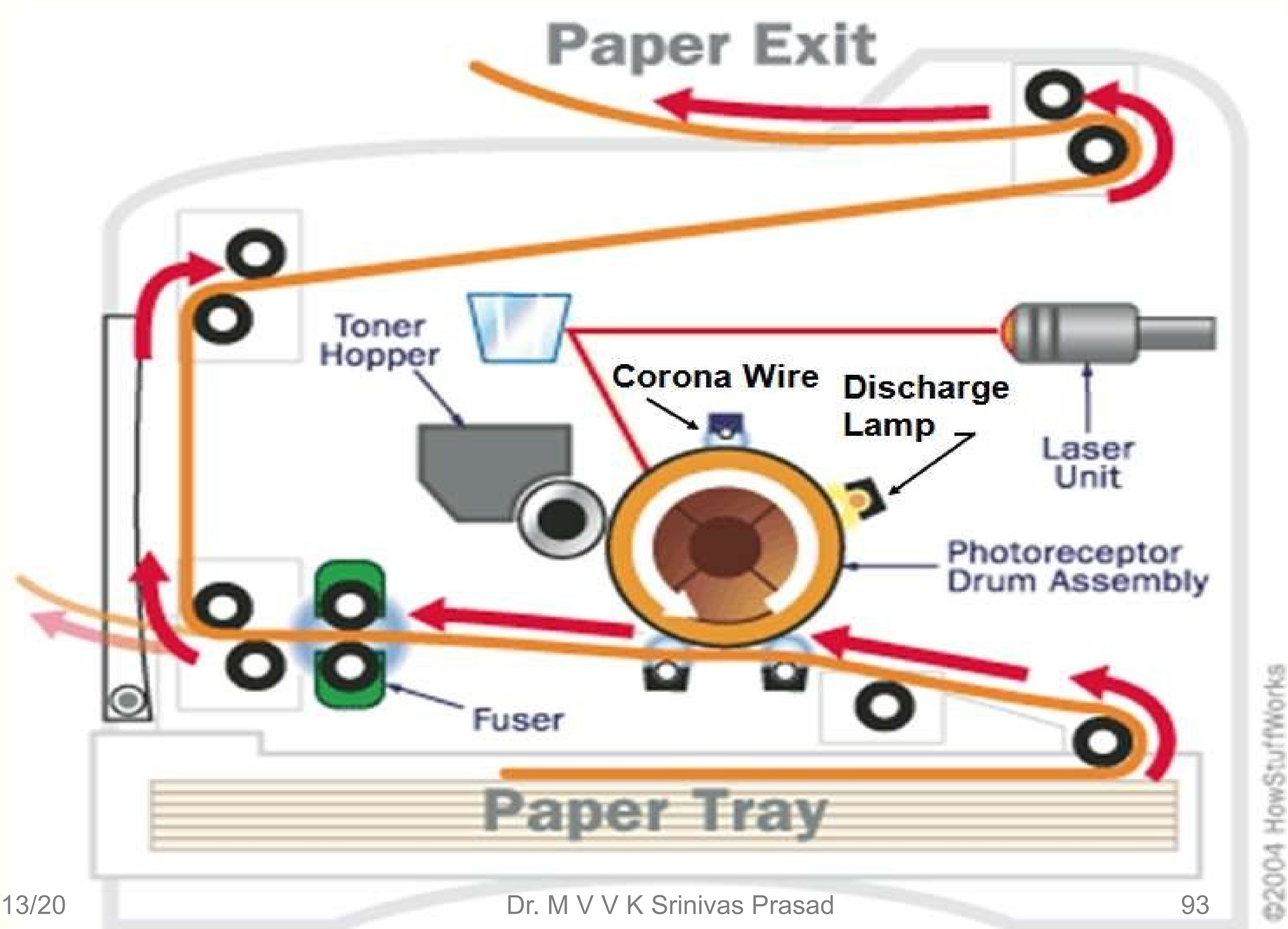


Laser In Spectroscopy



Laser In Barcode Scanning

Laser Printer



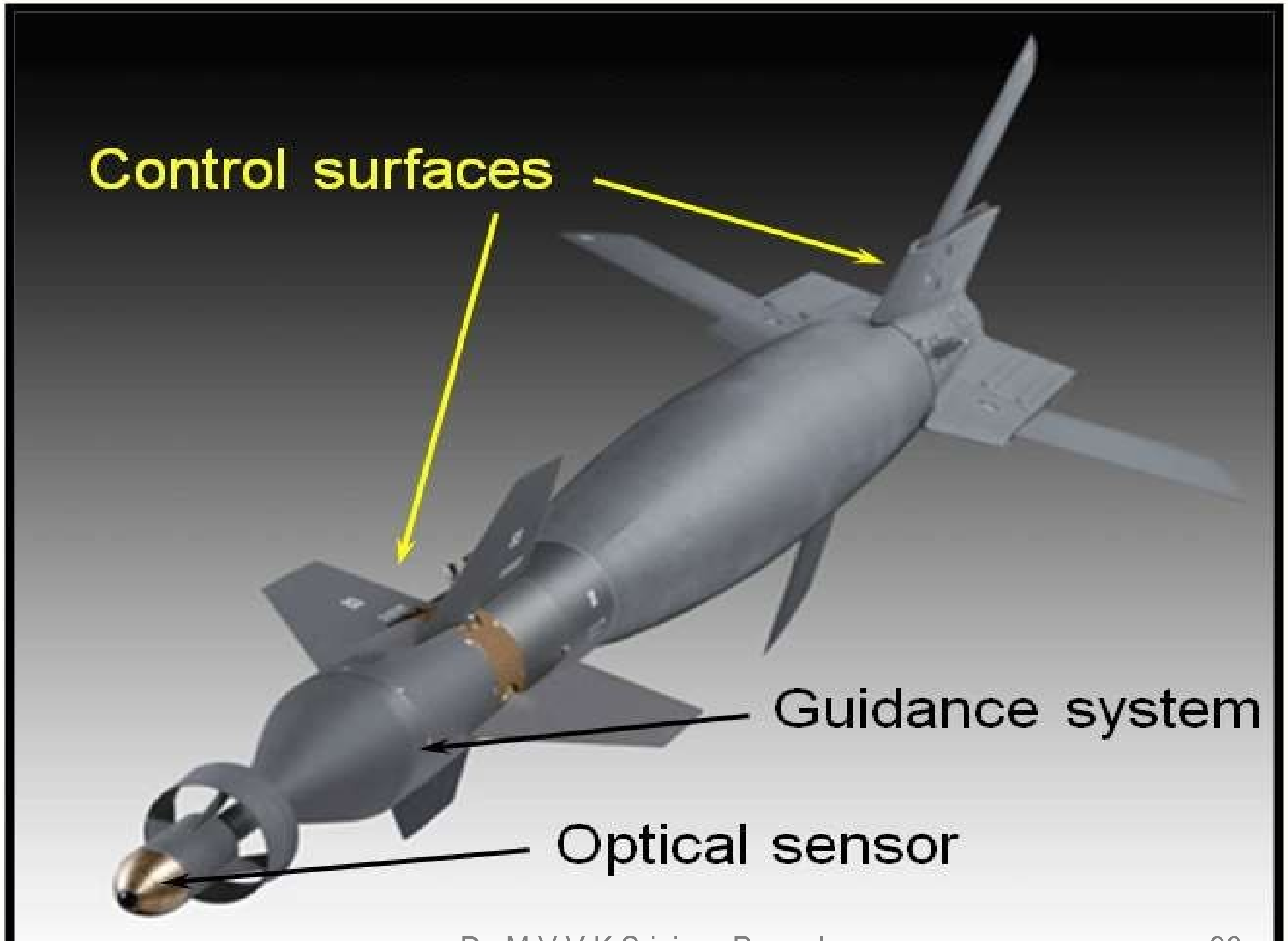
Laser Gun Sights

Laser Weapons

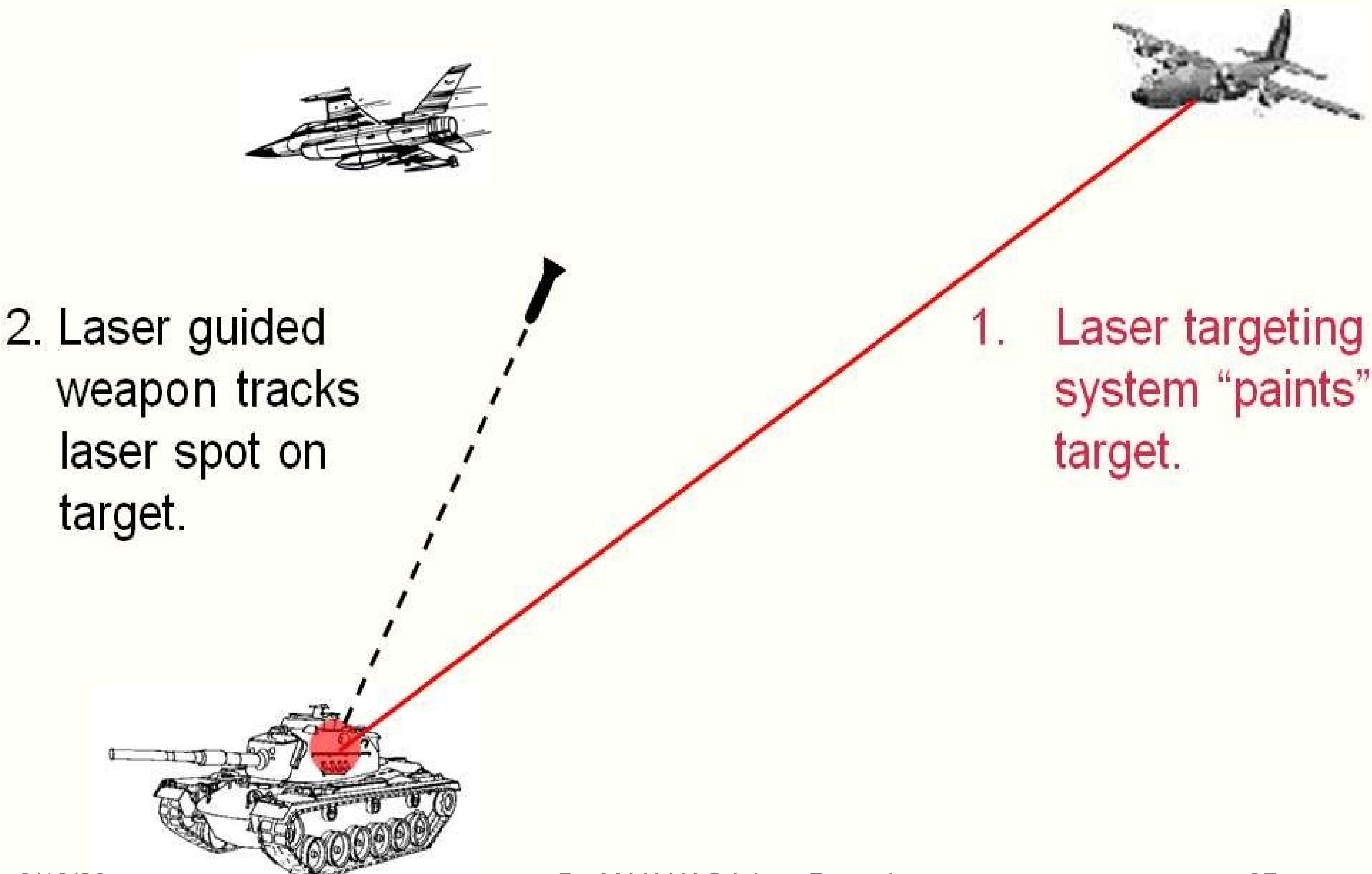
Laser Targeting System

Aircraft Mounted

Laser Guided Bomb
(“Smart” Bomb)



Laser Targeting



Laser Targeting System

Ground Based

Laser Guided Missile

Hellfire laser guided missiles mounted on a US Army Apache helicopter gunship.

Newer variation (Hellfire II) replaces laser guidance with radar guidance to penetrate smoke and cloud cover.