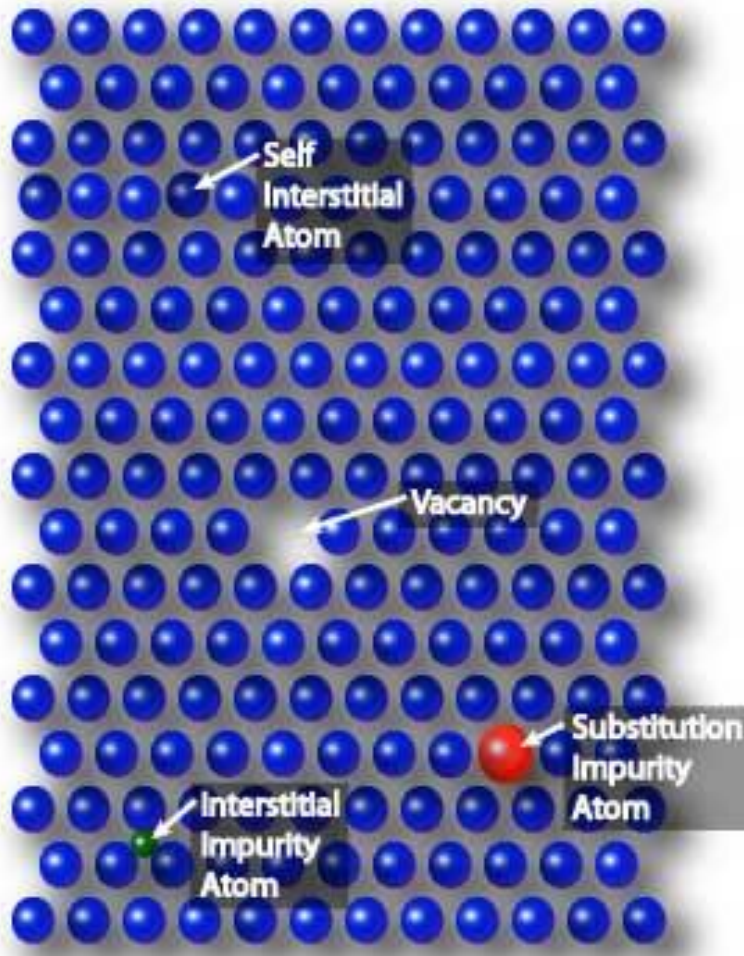


Defects in solids

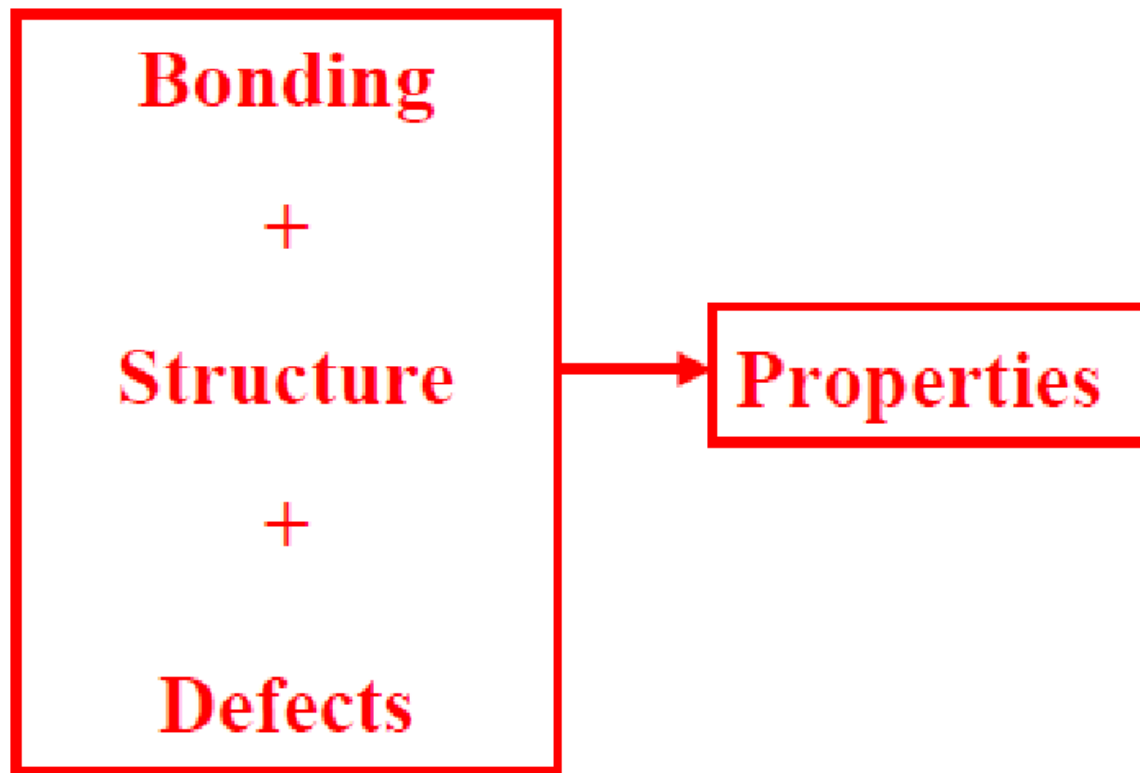


“Solids are like people -
imperfect!”

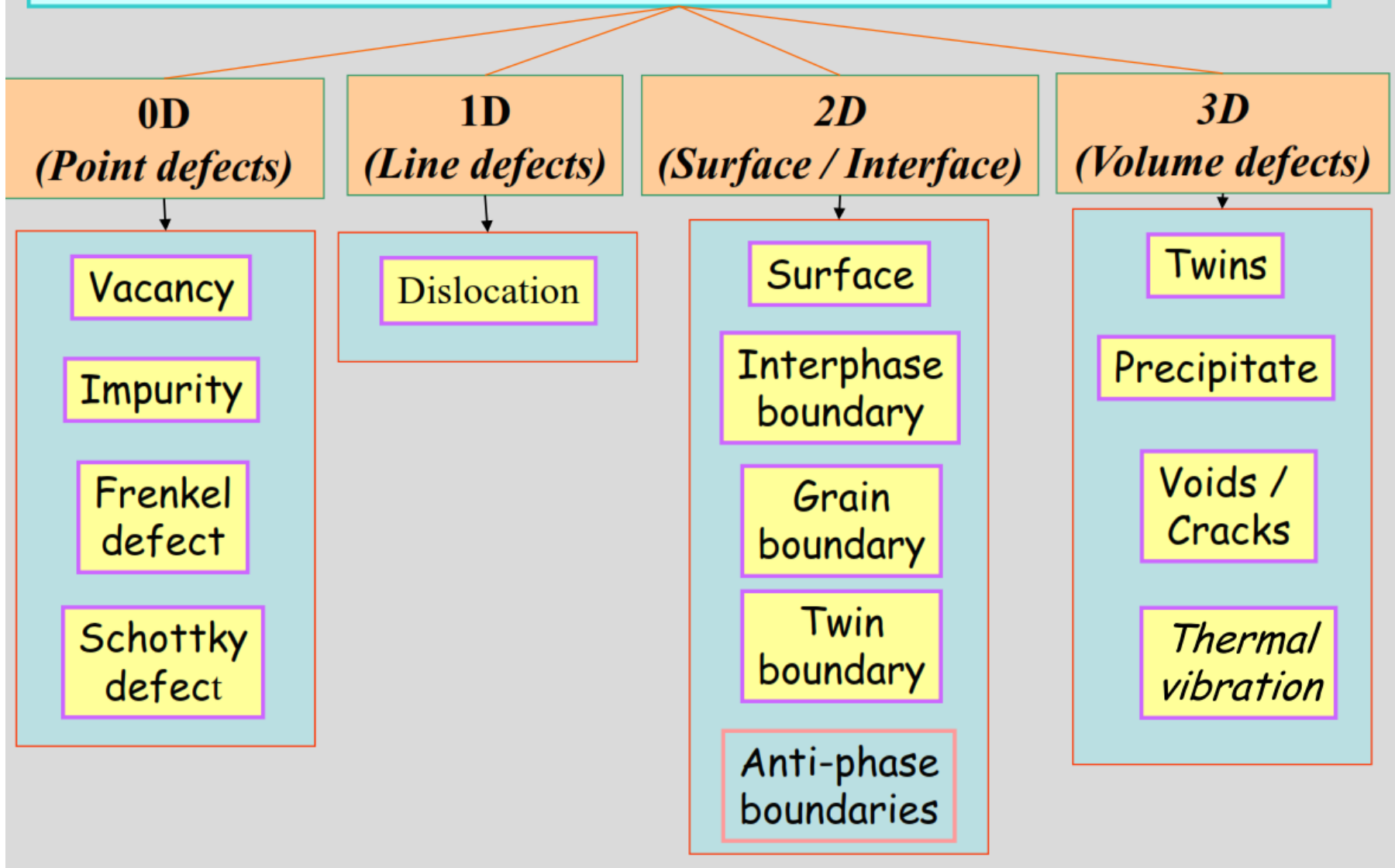
It's the defects that make
them unique & interesting”
(J. Corish)

A perfect crystal, with every atom of the same type in the correct position, does not exist.

**Defects have a profound impact on the macroscopic
properties of materials**



CLASSIFICATION OF DEFECTS BASED ON DIMENSIONALITY



- **Point defects** are where an atom is missing or is in an irregular place in the lattice structure.
- **Point defects include:**
 1. Self interstitial atoms
 2. Interstitial impurity atoms
 3. Substitutional impurity atoms
 4. Vacancies
- **Self interstitial atom :**

A self interstitial atom is an extra atom that has crowded its way into an interstitial void in the crystal structure. Self interstitial atoms occur only in low concentrations in metals because they distort and highly stress the tightly packed lattice structure.
- **Interstitial impurity atoms:**

Interstitial impurity atoms are much smaller than the atoms in the bulk matrix. Interstitial impurity atoms fit into the open space between the bulk atoms of the lattice structure.

An example of interstitial impurity atoms is the carbon atoms that are added to iron to make steel. Carbon atoms, with a radius of 0.071 nm, fit nicely in the open spaces between the larger (0.124 nm) iron atoms.

Substitutional impurity atom :

A substitutional impurity atom is an atom of a different type than the bulk atoms, which has replaced one of the bulk atoms in the lattice. Substitutional impurity atoms are usually close in size (within approximately 15%) to the bulk atom.

An example of substitutional impurity atoms is the zinc atoms in brass. In brass, zinc atoms with a radius of 0.133 nm have replaced some of the copper atoms, which have a radius of 0.128 nm

Vacancies:

Vacancies are empty spaces where an atom should be, but is missing. They are common, especially at high temperatures when atoms are frequently and randomly change their positions leaving behind empty lattice sites.

In most cases diffusion (mass transport by atomic motion) can only occur because of vacancies.

Vacancy defects are of two types

◆ Schottky defect

- A pair of oppositely charged ion vacancies

◆ Frenkel defect

- A vacancy-interstitialcy combination

Schottky Defect

If in an ionic crystal of the type $A^+ B^-$, equal number of cations and anions are missing from their lattice. It is called Schottky defect.

- This type of defect is shown by highly ionic compounds which have
 - High Co – ordination number and
 - Small difference in the sizes of cations and anions
 - A few examples of ionic compounds exhibiting Schottky defect are NaCl, KCl, KBr and CsCl.

Consequences of Schottky Defect:

- As the number of ions decreases as a result of this defect, the mass decreases whereas the volume remains the same. Hence density of the solid decreases
- The crystal begins to conduct electricity to a small extent by ionic mechanism
- The presence of too many voids lowers lattice energy and the stability of the crystal

■ Frenkel Defect

If an ion is missing from its correct lattice sites (causing a vacancy or a hole) and occupies an interstitial site, electrical neutrality as well as stoichiometry of the compounds are maintained.

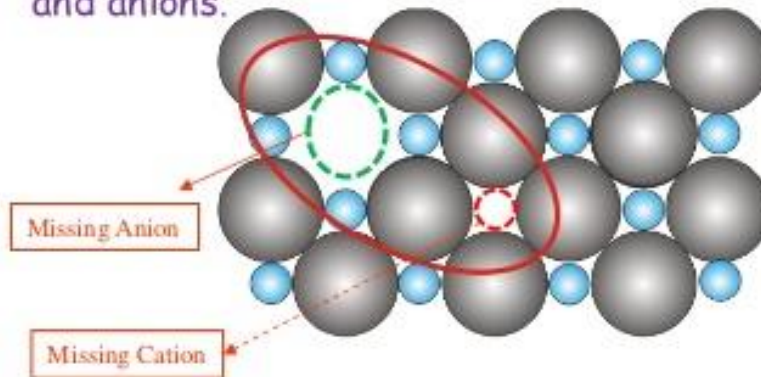
This type of defect is called Frenkel defect. Since cations are usually smaller it is more common to find the cations occupying interstitial sites.

- This type of defect is present in ionic compounds which have
 - Low co ordinations number
 - Larger difference in size of cation and anions
 - Compounds having highly polarising cation and easily polarisable anion. A few examples of ionic compounds exhibiting this defect are AgCl, AgBr, AgI, ZnS etc.
- Consequences of Frenkel defect
 - As no ions are missing from the crystal lattice as a whole, therefore density of the solid remains the same
 - The closeness of like charges tends to increases the dielectric constant of the crystal
 - The crystal conducts electricity to a small extent by ionic mechanism

Schottky defect and Frenkel defect

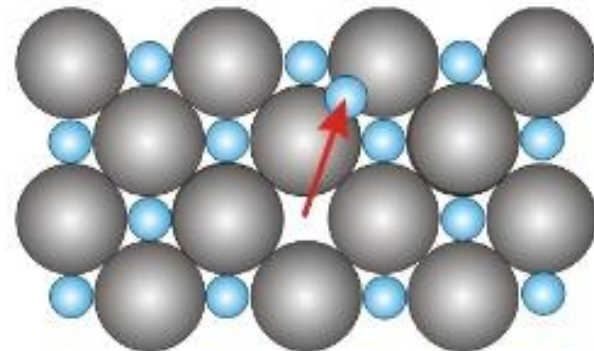
Schottky Defect:

- ❖ Forms when oppositely charged ions leave their lattice sites, creating vacancies.
- ❖ These vacancies are formed in stoichiometric units, to maintain an overall neutral charge in the ionic solid.
- ❖ Density of the solid crystal is less than normal
- ❖ Occurs only when there is small difference in size between cations and anions.



Frenkel Defect:

- ❖ Smaller ion (usually the cation) is displaced from its lattice position to an interstitial site.
- ❖ Creates a **vacancy defect** at its original site and an **interstitial defect** at its new location.
- ❖ Does not change the density of the solid.
- ❖ Shown in ionic solids with large size difference between the anion and cation.



Defects contd.....

- **Colour Centers:**
- **F-center:** Anion missing from its site, where an electron is trapped. The electron behave as 'trapped in a potential well' and has quantised energy levels. Electron absorb at specific wavelength from visible light causing colouration of crystals. Ex: 1. Yellow colour of NaCl when heated in Na vapour, 2. Lilac colour for KCl when heated in Na vapour
- **F'-center:** 2 electron in anion vacancy,
- **F_A center:** A foreign cation in the neighbourhood of F-centre
- **M-Center:** 2 F-centres in the neighbourhood
- **R-Center:** 3 adjacent F-centres in 111 plane.
- **Hopping semiconductor:** When NiO is heated to 1000 °C some Ni²⁺ get oxidized to Ni³⁺. Electron 'hop' from one Ni²⁺ to Ni³⁺ site causing semiconducting behaviour. $\text{Ni}_{1-3x}^{2+}\text{Ni}_{2x}^{3+}\text{V}_x\text{O}$
- Also achieved when NiO is heated in the presence of Li₂O:
Composition: $\text{Li}_x\text{Ni}_{1-2x}^{2+}\text{Ni}_x^{3+}\text{O}$

Electronic Materials

- The goal of electronic materials is to generate and control the flow of an electrical current.
- Electronic materials include:
 1. Conductors: have low resistance which allows electrical current flow
 2. Insulators: have high resistance which suppresses electrical current flow
 3. Semiconductors: can allow or suppress electrical current flow

Conductors

- Good conductors have low resistance so electrons flow through them with ease.
- **Best** element conductors include:
 - Copper, silver, gold, aluminum, & nickel
- Alloys are also good conductors:
 - Brass & steel
- Good conductors can also be liquid:
 - Salt water

Insulators

- Insulators have a high resistance so current does not flow in them.
- Good insulators include:
 - Glass, ceramic, plastics, & wood
- Most insulators are compounds of several elements.
- The atoms are tightly bound to one another so electrons are difficult to strip away for current flow.

Semiconductors

- Semiconductors are materials that essentially can be conditioned to act as good conductors, or good insulators, or any thing in between.
- Common elements such as **carbon**, **silicon** , and **germanium** are semiconductors.
- Silicon is the best and most widely used semiconductor.

SEMICONDUCTOR MATERIALS : Si, Ge, GaAs

- ◉ Germanium, Silicon and GaAs
- ◉ Semiconductors are special class of elements having a conductivity between insulator and conductor
- ◉ Classes of semiconductor material:
 - Single crystal: Germanium and Silicon
 - Compound : cadmium sulphide (CdS), Gallium arsenide (GaAs), Gallium Nitride (GaN), Gallium arsenide phosphide (GaAsP).
- ◉ After the discovery of diode in 1939 and the transistor in 1947 the Germanium is commonly used material.
- ◉ As Germanium available in pure form due to its refinery process and available in large quantity.

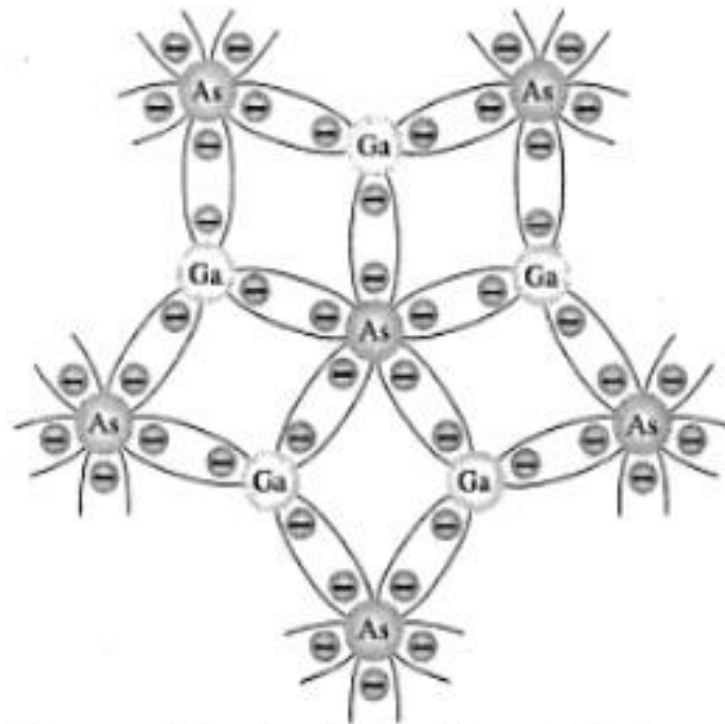


Figure. Covalent bonding of GaAs atom

- The figure show the covalent bonding between two different atom
- Gallium is having 3 valence electrons and Arsenide is having 5 valence electrons
- Which will result in stronger bonding between two atoms.

Semiconductors can be Insulators

- If the material is pure semiconductor material like silicon, the crystal lattice structure forms an excellent insulator since all the atoms are bound to one another and are not free for current flow.
- Good insulating semiconductor material is referred to as intrinsic.
- Since the outer valence electrons of each atom are tightly bound together with one another, the electrons are difficult to dislodge for current flow.
- Silicon in this form is a great insulator.
- Semiconductor material is often used as an insulator.

EXTRINSIC MATERIAL

- ⦿ extrinsic material is obtained by doping process
- ⦿ Adding impurities in semiconductor material is called as **Doping**.
- ⦿ Impurities are added to obtain change in the covalent bonding of semiconductor material for obtaining better electrical properties .
- ⦿ there are two types of extrinsic material : n-type and p-type material.

⦿ N-type material

- ⦿ When **pentavalent** impurities are added to silicon base material then the **N-type material** is obtained. Like **Antimony** ,**Arsenic** and **Phosphorous**.
- ⦿ Pentavalent stands for atoms are having 5 valence electrons i.e 5 electrons in the outermost orbit.

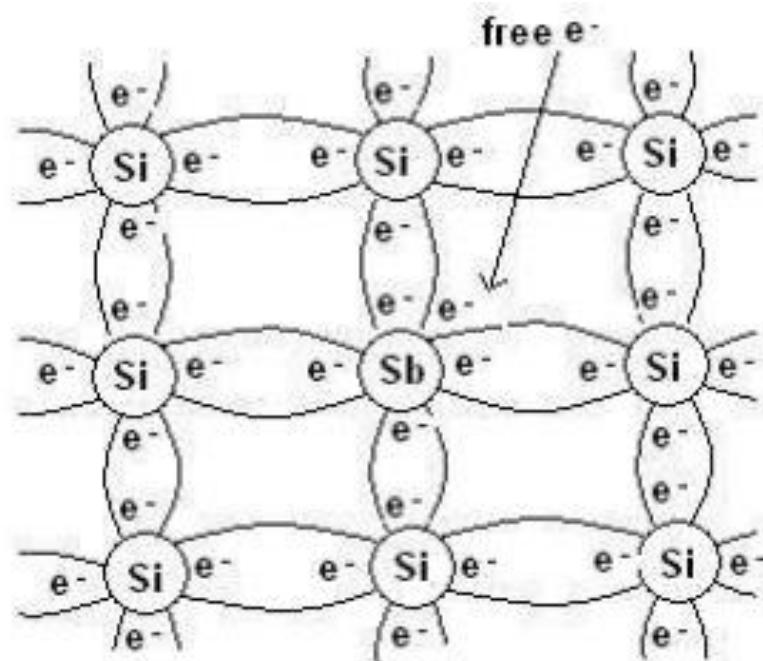


Figure. Antimony impurity in N-type material

- ⊙ As silicon is having 4 valence electrons and antimony is having 5 valence electrons.
- ⊙ when we doped antimony atom in silicon atom the 4 valence electrons are get with 4 valence electrons' of silicon and 1 electron remains free at each doping level so called “donor atom”
- ⊙ Normally doping is done at 1 part per million . i.e 1 atom of antimony with 1 million atom of silicon which results in 100000:1 carrier concentration

⦿ P-type material

- ⦿ The p-type material is formed by doping pure silicon atom with impurities having 3 valence electrons (Trivalent impurities)
- ⦿ **Boron**, **Gallium** and **Indium** are trivalent impurities .

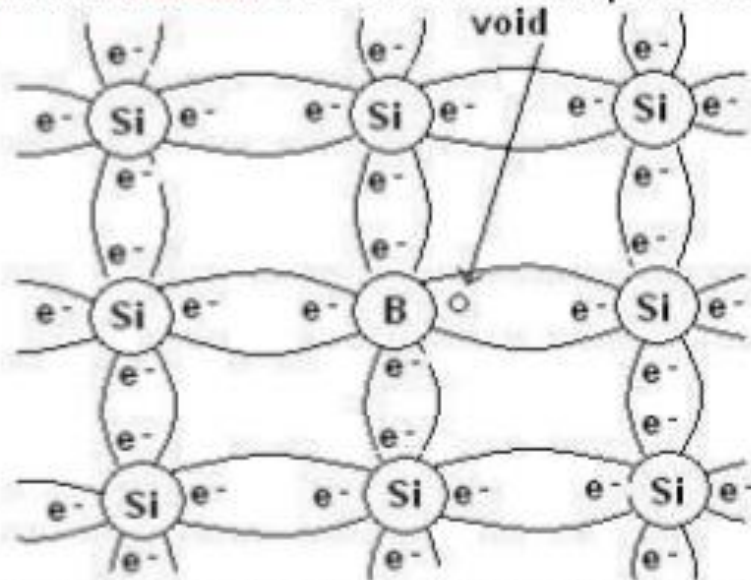
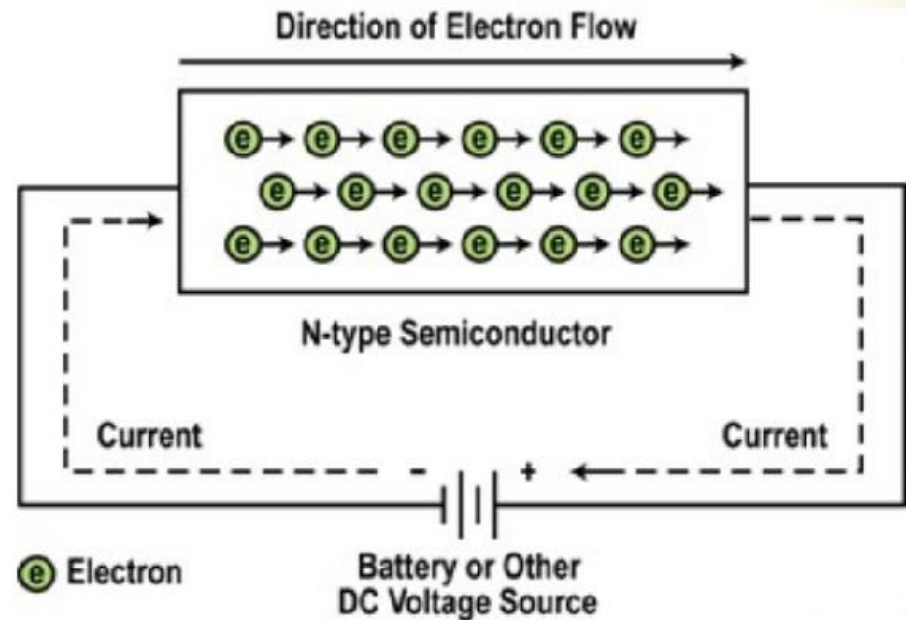


Figure. Boron impurity in P-type material

- ⦿ Boron is having 3 valence electrons and silicon is having 4 valence electrons hence the insufficient number of electrons are there complete covalent bond
- ⦿ Since resulting vacancy will readily **accept** a free electrons.

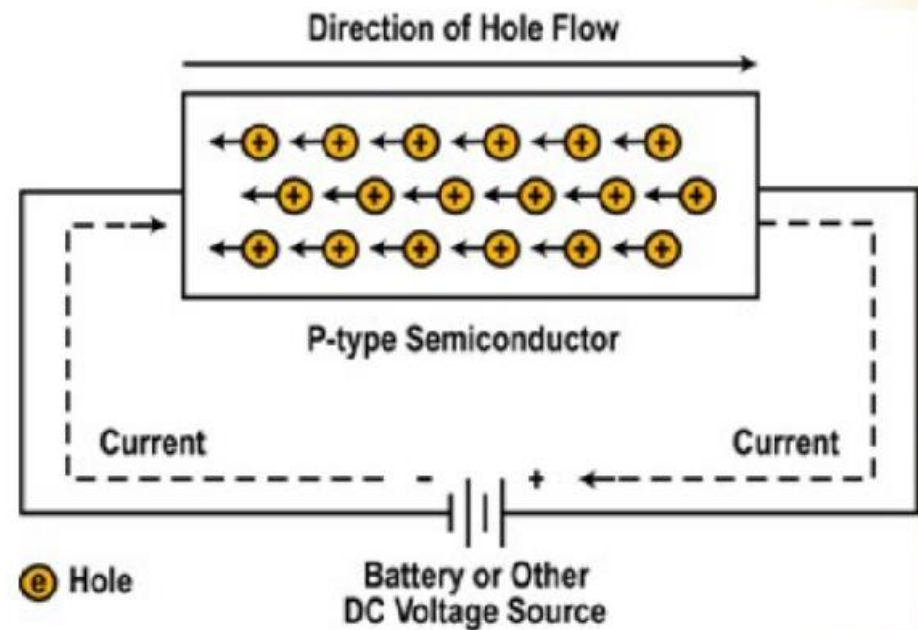
Current Flow in N-type Semiconductors

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



Current Flow in P-type Semiconductors

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



In Summary

- In its pure state, semiconductor material is an excellent insulator.
- The commonly used semiconductor material is silicon.
- Semiconductor materials can be doped with other atoms to add or subtract electrons.
- An N-type semiconductor material has extra electrons.
- A P-type semiconductor material has a shortage of electrons with vacancies called holes.
- The heavier the doping, the greater the conductivity or the lower the resistance.
- By controlling the doping of silicon the semiconductor material can be made as conductive as desired.

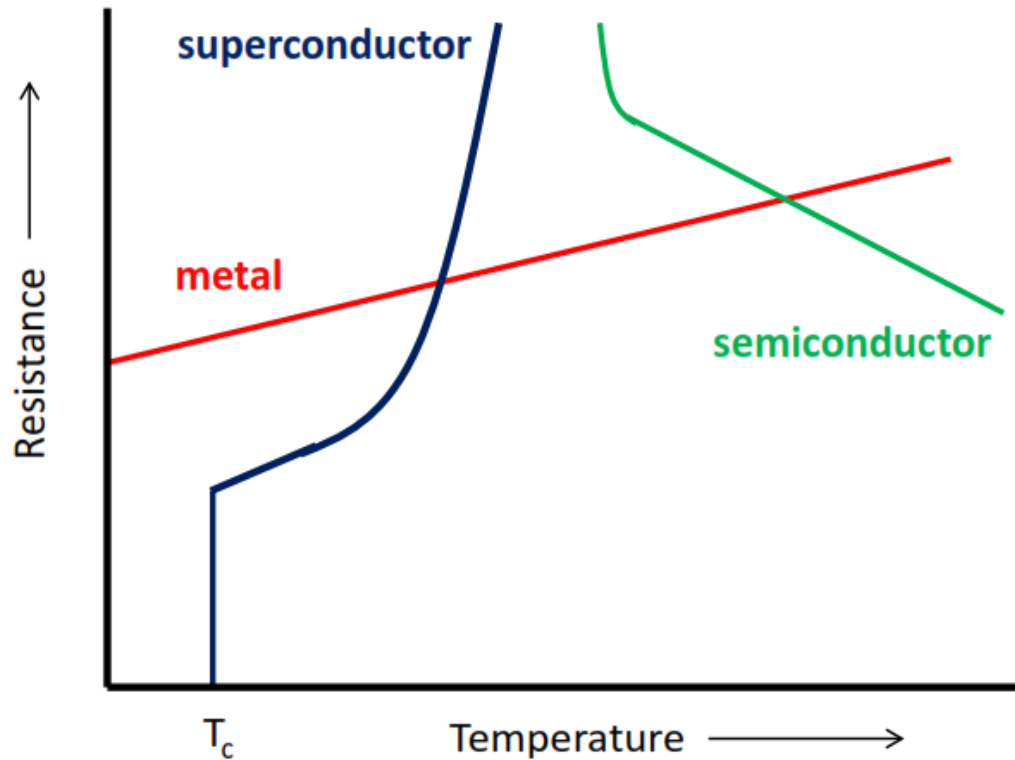
Superconductors

Definition of Superconductor:

- An element, inter-metallic alloy, or compound that will conduct electricity without resistance below a certain temperature, magnetic field, and applied current.
- A material that exhibits zero electrical resistance when cooled below its **critical temperature** (T_c).
 - This transition to zero resistance is immediate upon reach T_c
 - Because superconductors have zero resistance, current can be maintained in superconducting rings indefinitely
- “High Critical Temperature Superconductors” ($T_c > 77\text{K}$) are of particular interest because the low cost refrigerant $\text{N}_2(\text{L})$ can be used to maintain the superconducting state.

Effects of Temperature on Electrical Resistance

High resistance = poor current = poor conductivity

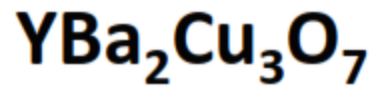


T_c :

This is the critical temperature at which the resistivity of a superconductor goes to zero. Above this temperature the material is non-superconducting, while below it, the material becomes superconducting.

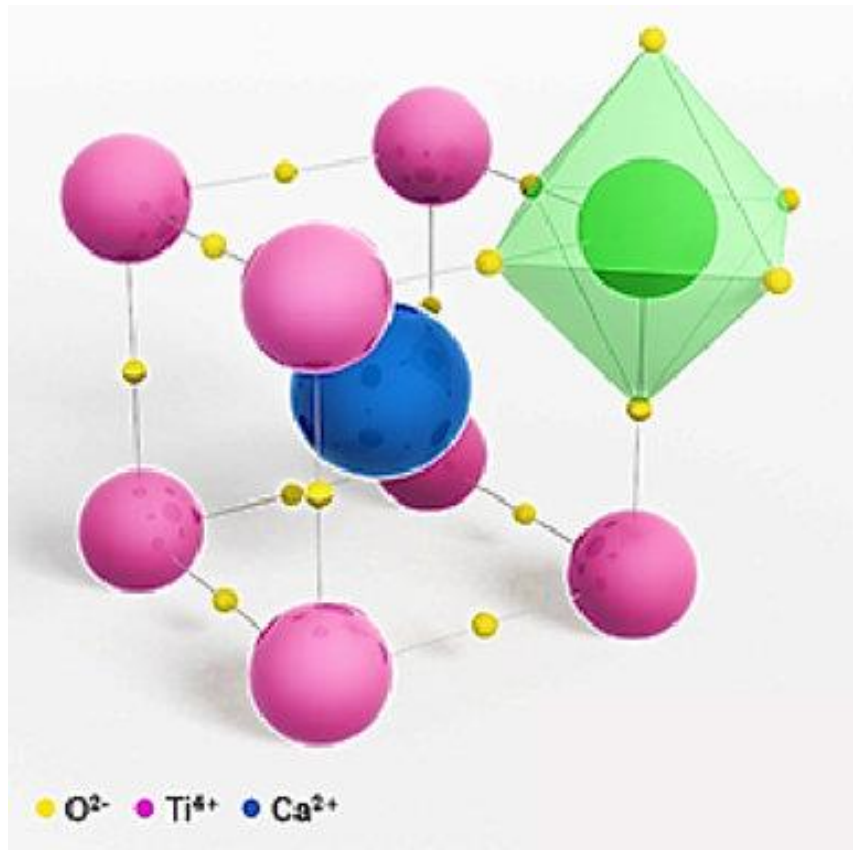
A Brief History of Superconductors

- In 1911 superconductivity was first observed in mercury by Dutch physicist Heike Kamerlingh Onnes of Leiden University. When he cooled it to the temperature of liquid helium, 4 degrees Kelvin, its resistance suddenly disappeared! In 1933 Walter Meissner and Robert Ochsenfeld discovered that a superconducting material will repel a magnetic field. This phenomenon is known as perfect diamagnetism and is often referred to as the Meissner effect.
- Since then major developments have been made in both the discovery of higher temperature superconductors as well as progress in the theory of superconductivity. In 1957 the 1st major advancement in the theory was made by American physicists John Bardeen, Leon Cooper, and John Schrieffer. Their *Theories of Superconductivity* became known as the BCS theory - abbreviated for the first letter of each man's last name - and won them a Nobel prize in 1972. BCS theory explained superconductivity at temperatures close to absolute zero for elements and simple alloys. However, at higher temperatures and with different superconductor systems, the BCS theory has become inadequate to fully explain how superconductivity is occurring.
- In 1962 Brian D. Josephson, a graduate student at Cambridge University, predicted that electrical current would flow between 2 superconducting materials - even when they are separated by a non-superconductor or insulator! His prediction that superconductors would exhibit this quantum effect on a macro scale was later confirmed and won him a share of the 1973 Nobel Prize in Physics. This tunneling phenomenon is today known as the "Josephson effect" and has been applied to electronic devices such as the SQUID (Superconducting Quantum Interference Device), an instrument capable of detecting even the weakest magnetic fields. More recently scientists have made improvements in the area of predicting and engineering new types of superconductors. In the 80's carbon based superconductors as well as ceramic superconductors were developed. These superconductors have fantastic magnetic properties as well as high critical temperatures, but their mechanical properties are poor.



- Type II Superconductor
 - Made from an alloy, as opposed to a pure metal
- Superconductivity is observed at $T \geq 92 \text{ K}$
- Structure is that of a “defect perovskite”
 - Similar to the standard perovskite structure (ABO_3) but some atoms are missing
 - Copper ions occupy the A sites
 - Both Ba^{2+} and Y^{3+} occupy the B sites
 - The ratio is not 1:1:3 because some oxygen atoms are missing
 - Coordination numbers of 8 for Y, 10 for Ba, and either 4 or 5 for Cu
 - Orthorhombic

Metal Oxides: Perovskites (CaTiO_3)



Lattice: Primitive Cubic

1 CaTiO_3 per unit cell

A-Cell Motif:

Ti at $(0, 0, 0)$; **Ca** at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$; 3 **O** at $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, $(0, 0, \frac{1}{2})$

Ca 12-coordinate by **O** (cuboctahedral)

Ti 6-coordinate by **O** (octahedral)

O distorted octahedral ($4 \times \text{Ca} + 2 \times \text{Ti}$)

TiO₆ octahedra share only vertices

CaO₁₂ cuboctahedra share faces

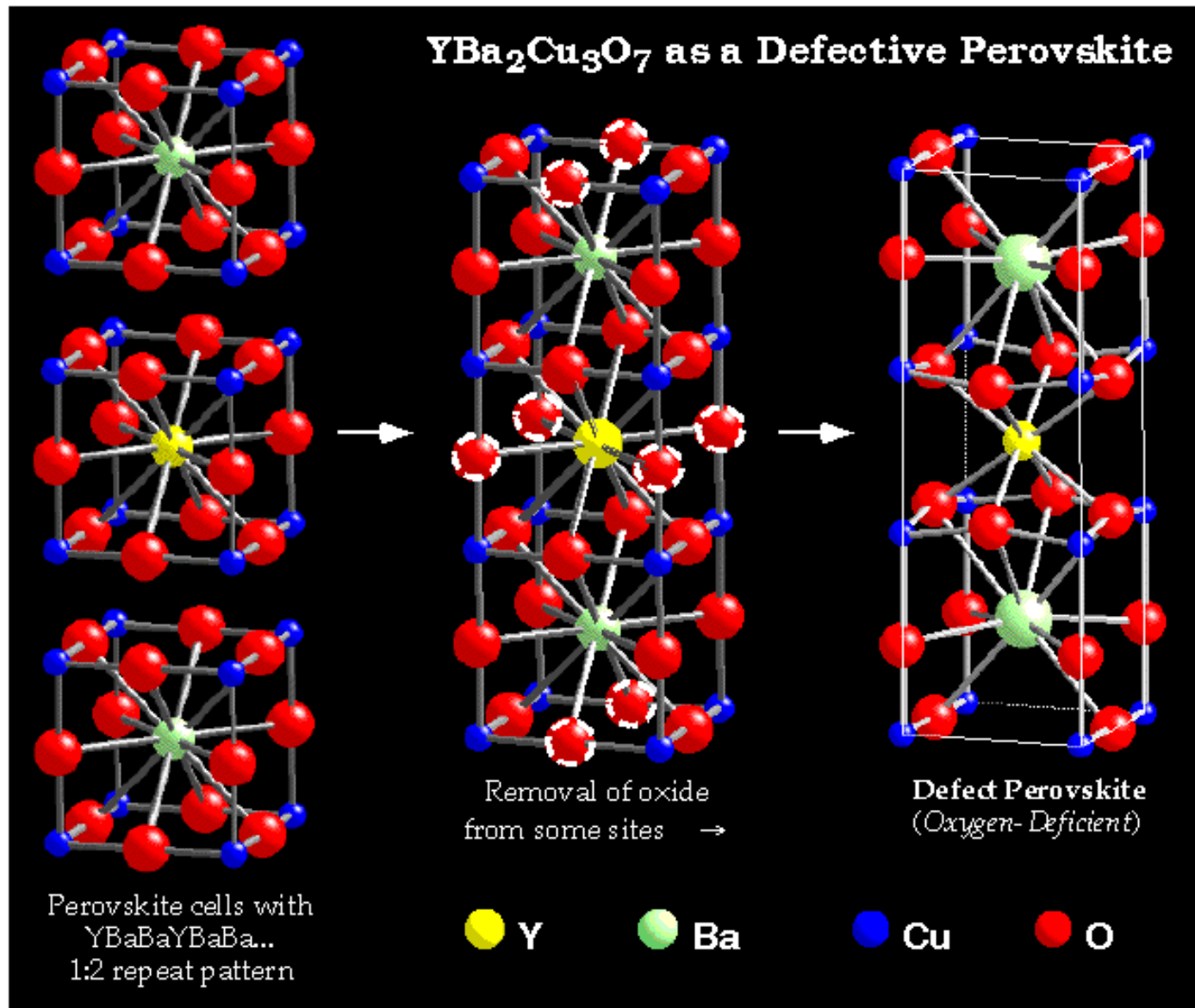
Ca fills the vacant ccp site in ReO_3 , \rightarrow

a **CaO_3 ccp arrangement** with $\frac{1}{4}$ of **octahedral holes** (those defined by $6 \times \text{O}$) **filled by Ti**

Examples: NaNbO_3 , BaTiO_3 , CaZrO_3 , YAlO_3 , KMgF_3

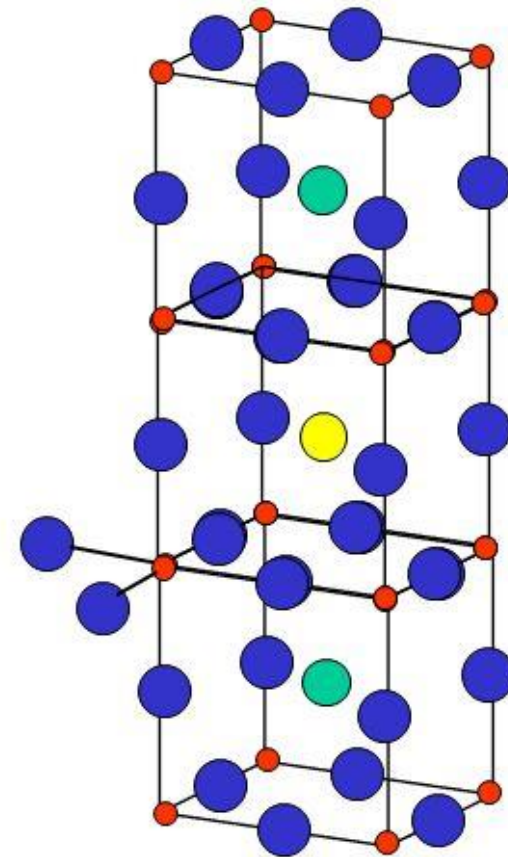
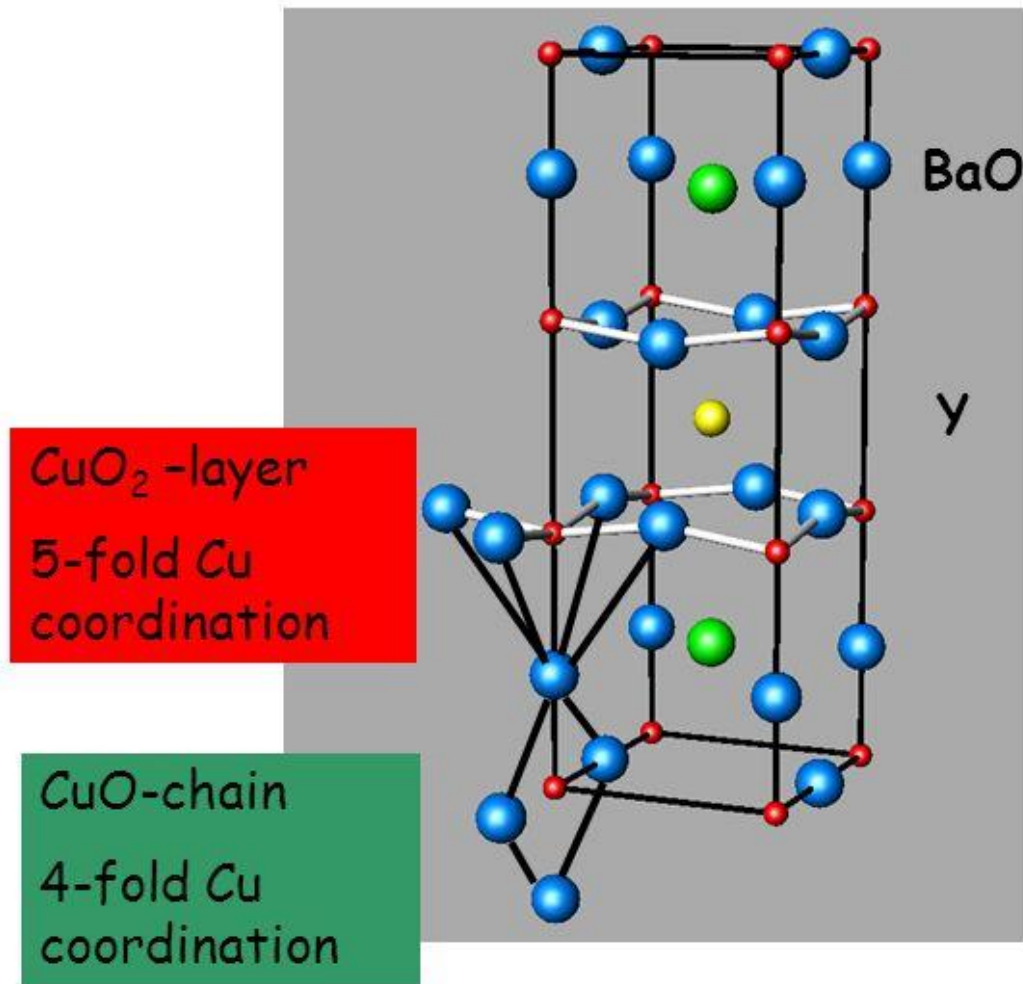
Many undergo small distortions: e.g. BaTiO_3 is *ferroelectric*

$\text{YBa}_2\text{Cu}_3\text{O}_7$ - the 1:2:3 Superconductor



Oxygen-Deficient Perovskite $T_c > 77 \text{ K}$

High Temperature Superconductor: $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$



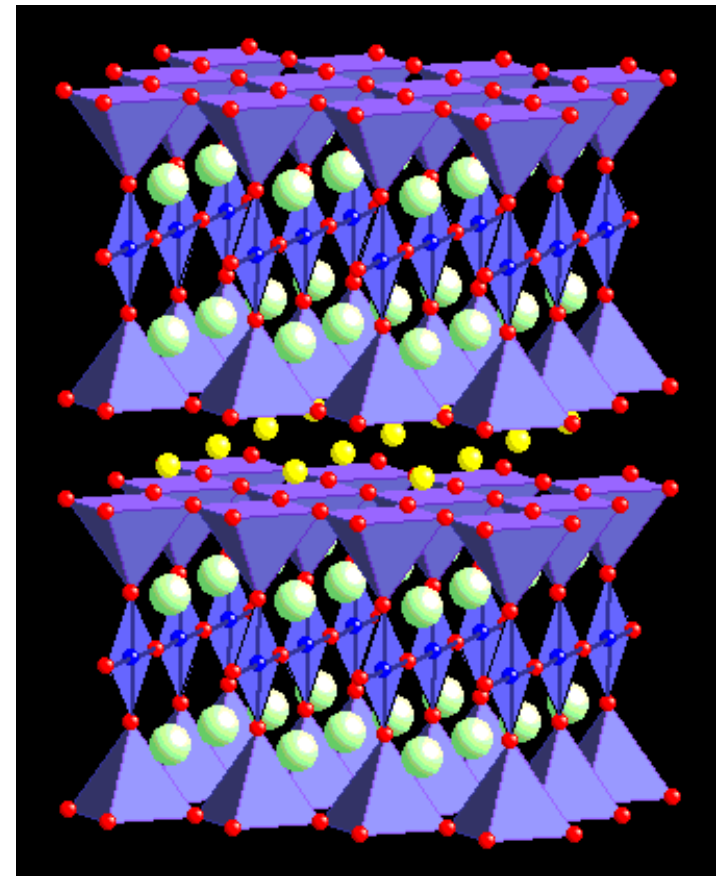
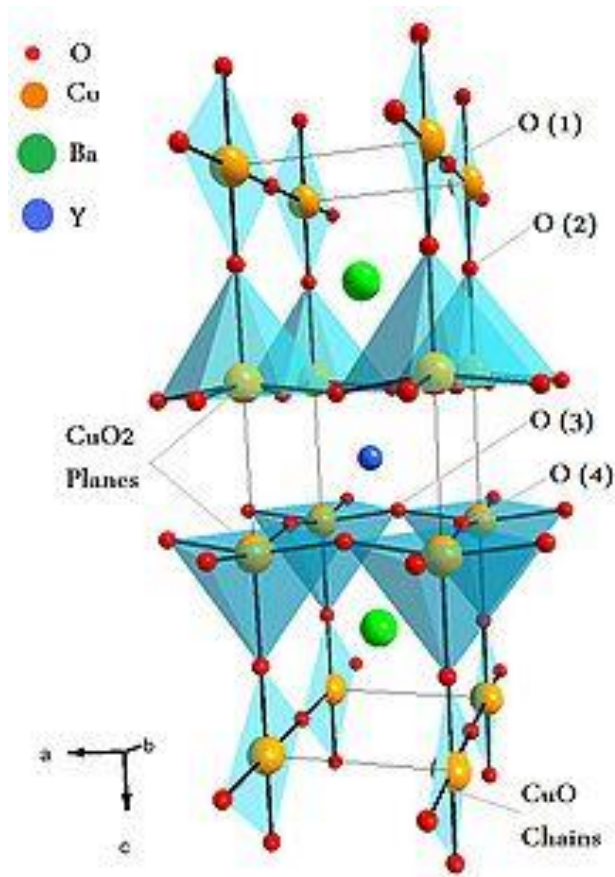
Perovskite
" $\text{YBa}_2\text{Cu}_3\text{O}_9$ "

$\text{YBa}_2\text{Cu}_3\text{O}_7$ - the 1:2:3 Superconductor

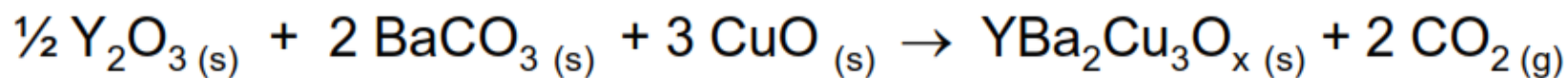
Two types of copper sites

Layers of CuO_5 square pyramids

Chains of vertex-linked CuO_4 squares



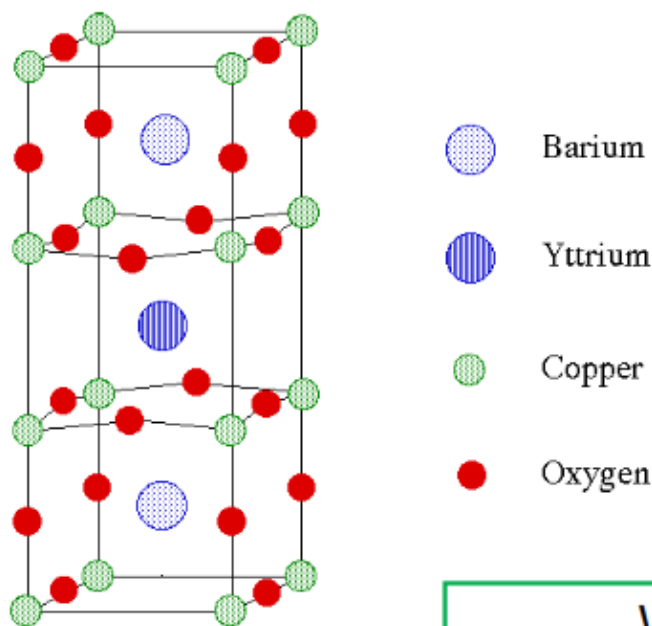
Stoichiometry of $\text{YBa}_2\text{Cu}_3\text{O}_x$: Determining x



What value of 'x' is expected from stoichiometry? 6.5

Desired for superconductivity? 7

Unit cells of $\text{YBa}_2\text{Cu}_3\text{O}_x$ and CaTiO_3



What would CaTiO_3 (Perovskite) look like?

Applications

- Particle Accelerators
- Generators
- Transportation
- Power Transmission
- Electric Motors
- Military
- Computing
- Medical