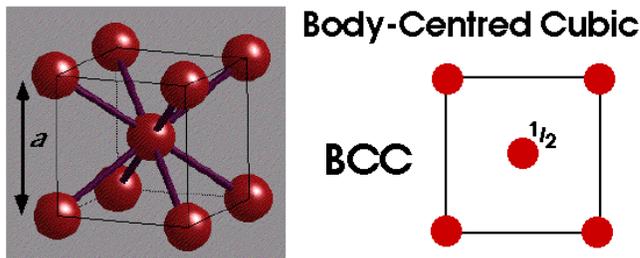


## Unit-III Metallic State

### Metallic bond

Metallic bonds are the force of attraction between valence electrons and the metal atoms. It is the sharing of many detached electrons between many positive ions, where the electrons act as "glue" giving the substance a definite structure. Metallic bonds causes many of the traits of metals, such as strength, malleability, ductility, luster, conduction of heat and electricity.

### Body Centred Cubic (BCC) Structure



At room temperatures, elements Li, Na, K, Rb, Ba, V, Cr and Fe have structures that can be described as body centre cubic (bcc) packing of spheres. The other two common ones are face centred cubic (fcc) and hexagonal closest (hcp) packing. This type of structure is shown by the diagram below. In a crystal structure, the arrangement extends over millions and millions of atoms, and the above diagram shows the unit cell, the smallest unit that, when repeatedly stacked together, will generate the entire structure.

Actually, the unit we draw is more than a unit cell. We use the centre of the atoms (or spheres) to represent the corners of the unit cell, and each of these atoms are shared by 8 unit cells. There is a whole atom located in the centre of the unit cell. Usually, the length of the cell edge is represented by  $a$ . The direction from a corner of a cube to the farthest corner is called body diagonal ( $bd$ ). The face diagonal ( $fd$ ) is a line drawn from one vertex to the opposite corner of the same face. If the edge is  $a$ , then we have:

$$\begin{aligned}fd^2 &= a^2 + a^2 = 2 a^2 \\bd^2 &= fd^2 + a^2 \\&= a^2 + a^2 + a^2 \\&= 3 a^2\end{aligned}$$

Atoms along the body diagonal ( $bd$ ) touch each other. Thus, the body diagonal has a length that is four times the radius of the atom,  $R$ .

$$bd = 4 R$$

The relationship between  $a$  and  $R$  can be worked out by the Pythagorean theorem:

$$\begin{aligned}(4 R)^2 &= 3 a^2 \\ \text{Thus,} \\ 4 R &= \text{sqrt}(3) a \\ \text{or} \\ a &= 4R/\text{sqrt}(3)\end{aligned}$$

Recognizing these relationships enable you to calculate parameters for this type of crystal. For example, one of the parameter is the packing fraction, the fraction of volume occupied by the spheres in the structure.

### **Cubic Close Packed (CCP) or Face Centred Cubic (FCC)**

These are two different names for the same lattice.

We can think of this cell as being made by inserting another atom into each face of the simple cubic lattice - hence the "face centred cubic" name. The reason for the various colors is to help point out how the cells stack in the solid. Remember that the atoms are all the same.

The unit cell is again shown expanded for visibility. Actually, the corner atoms touch the one in the center of the face. The name "close packed" refers to the packing efficiency of 74.05%. No other packing can exceed this efficiency (although there are others with the same packing efficiency). If we stack the cells into a lattice we notice that the atoms form diagonal layers - the reason for the colors is to make these stand out. Note that diagonal layers also form along our line of sight. Since these cut across the other layers, each layer will contain all three colors. A different and better way of looking at this structure focuses on those layers. We start with a hexagonal array of spheres (the blue "A" layer). Notice that this is a close-packed arrangement - there is no way to pack more spheres into a given area.

We then place a second close-packed layer (the gold "B" layer) atop the the first, so they nestle into the left-pointing holes in the first. *All spheres are actually the same atom, the colors are to help you keep track of the layers.* Notice that there are 2 separate choices for the second layer; in the animation below, we have arbitrarily chosen to cover the left-pointing holes. We *can* put them over either all the "left-pointing" interstices or all the "right-pointing" interstices.

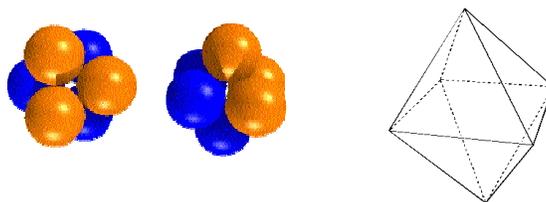
If we put them over the right-pointing interstices we generate a different layer, labeled the green or "C" layer. *Remember there are twice as many interstitial sites as spheres. (One left-pointing and one right-pointing).* We can continue to stack these layers in any order, providing that no 2 identical layers are adjacent. The cubic close packed structure can be constructed from the

A - B - C - A - B - C ..... sequence.

An alternate sequence might be B - A - C - B - A - C ...

The resulting structure is a 3-D analog of the hexagonal packing in a plane - it is the most efficient way to pack spheres. There are two types of interstitial sites in an fcc lattice. Let us consider a pair of layers - blue and gold. Remember, the gold atoms cover all the left-pointing interstices in the blue layer, and none of the right-pointing ones.

Under each gold atom is a small space surrounded by 4 atoms in a tetrahedral arrangement. This is a 4 - coordinate tetrahedral interstitial site. If we look at the right-pointing holes in the blue layer, we see that the gold layer does not nestle into them as it does the left-pointing ones. These cavities are surrounded by 6 atoms in octahedral geometry. This is a 6 - coordinate octahedral interstitial site.



Go back and look at the lattice again and locate the tetrahedral and octahedral interstitial sites.

Examples of fcc / ccp metals include nickel, silver, gold, copper, and aluminum.

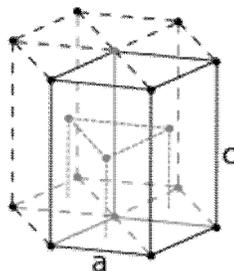
Another way of stacking these layers is to omit the "C" layers altogether - simply alternate "A" and "B". This is also a close-packed array, but the symmetry is different. It is called:

### Hexagonal Close Packed (HCP)

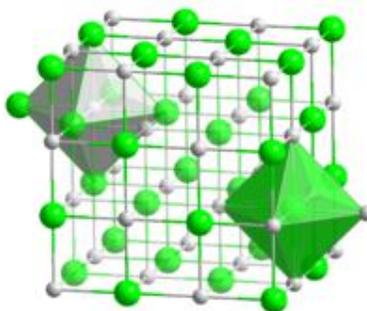
The hexagonal close packed structure can be made by piling layers in the

A - B - A - B - A - B ..... sequence.

An alternative sequence would be A - C - A - C - A ...



Rock-salt structure

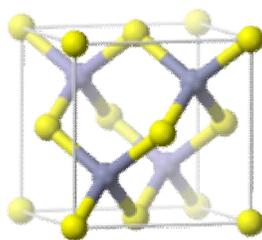


The space group of the rock-salt (NaCl) structure is called  $Fm\bar{3}m$ , or "225". The Strukturbericht designation is "B1". In the rock-salt or sodium chloride structure, each of the two atom types forms a separate face-centered cubic lattice, with the two lattices interpenetrating so as to form a 3D checkerboard pattern. Alternately, one could view this structure as a face-centered cubic structure with secondary atoms in its octahedral holes.

Examples of compounds with this structure include sodium chloride itself, along with almost all other alkali halides, and "many divalent metal oxides, sulfides, selenides, and tellurides". More generally, this structure is more likely to be formed if the cation is somewhat smaller than the anion. The coordination number of each atom in this structure is 6: each cation is coordinated to 6 anions at the vertices of an octahedron, and similarly, each anion is coordinated to 6 cations at the vertices of an octahedron.

The interatomic distance (distance between cation and anion, or half the unit cell length  $a$ ) in some rock-salt-structure crystals are: 2.3 Å ( $2.3 \times 10^{-10}$  m) for NaF, 2.8 Å for NaCl, and 3.2 Å for SnTe. Other compounds showing rock salt like structure are LiF, LiCl, LiBr, LiI, NaF, NaBr, NaI, KF, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsF, MgO, PbS, AgF, AgCl, AgBr and ScN.

### Zinblende structure



The space group of the Zinblende structure is called  $F43m$ , or 216. The Strukturbericht designation is "B3". The Zinblende structure (also written "zinc blende") is named after the mineral zinblende (sphalerite), one form of zinc sulfide ( $\beta$ -ZnS). As in the rock-salt structure, the two atom types form two interpenetrating face-centered cubic lattices. However, it differs from rock-salt structure in how the two lattices are positioned relative to one another. The zinblende structure has tetrahedral coordination: Each atom's nearest neighbors consist of four atoms of the opposite type, positioned like the four vertices of a regular tetrahedron. Altogether, the arrangement of atoms in zinblende structure is the same as diamond cubic structure, but with alternating types of atoms at the different lattice sites.

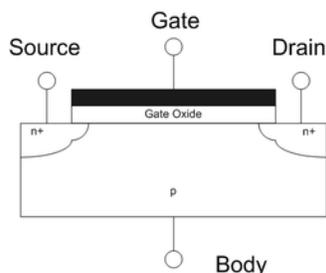
Examples of compounds with this structure include zinblende itself, lead(II) nitrate, many compound semiconductors (such as gallium arsenide and cadmium telluride), and a wide array of other binary compounds. Other compounds showing zinc blende-like structure are  $\alpha$ -AgI,  $\beta$ -BN, diamond, CuBr,  $\beta$ -CdS, BP and BAs.

### Example: Quartz

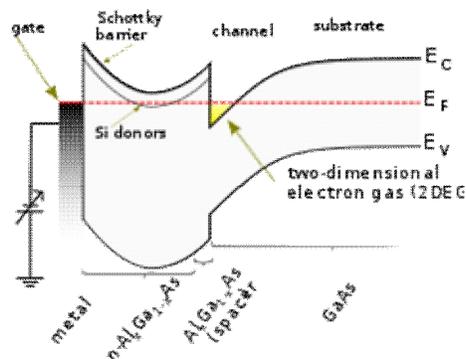
Quartz is a crystal that belongs to the hexagonal lattice system but exists in two polymorphs that are in two different crystal systems. The crystal structures of  $\alpha$ -quartz are described by two of the 18 space groups (152 and 154) associated with the trigonal crystal system, while the crystal structures of  $\beta$ -quartz are described by two of the 27 space groups (180 and 181) associated with the hexagonal crystal system.

### Electron gas

Electron gas is a scientific model in solid-state physics. It is an electron gas that is free to move in two dimensions, but tightly confined in the third. This tight confinement leads to quantized energy levels for motion in the third direction, which can then be ignored for most problems. Thus the electrons appear to be a 2D sheet embedded in a 3D world. The analogous construct of holes is called a two-dimensional hole gas (2DHG), and such systems have many useful and interesting properties



In MOSFETs, the 2DEG is only present when the transistor is in inversion mode, and is found directly beneath the gate oxide.



Band edge diagram of a basic HEMT. Conduction band edge  $E_C$  and Fermi level  $E_F$  determine the electron density in the 2DEG. Quantized levels form in the triangular well (yellow region) and optimally only one of them lies below  $E_F$ .

Most 2DEG are found in transistor-like structures made from semiconductors. The most commonly encountered 2DEG is the layer of electrons found in MOSFETs. When the transistor is in inversion mode, the electrons underneath the gate oxide are confined to the semiconductor-oxide interface, and thus occupy well defined energy levels. For thin-enough potential wells and temperatures not too high, only the lowest level is occupied (see the figure caption), and so the motion of the electrons perpendicular to the interface can be ignored. However, the electron is free to move parallel to the interface, and so is quasi-two-dimensional.

Other methods for engineering 2DEGs are high-electron-mobility-transistors (HEMTs) and rectangular quantum wells. HEMTs are field-effect transistors that utilize the heterojunction between two semiconducting materials to confine electrons to a triangular quantum well. Electrons confined to the heterojunction of HEMTs exhibit higher mobilities than those in MOSFETs, since the former device utilizes an intentionally undoped channel thereby mitigating the deleterious effect of ionized impurity scattering. Two closely spaced heterojunction interfaces may be used to confine electrons to a rectangular quantum well. Careful choice of the materials and alloy compositions allow control of the carrier densities within the 2DEG.

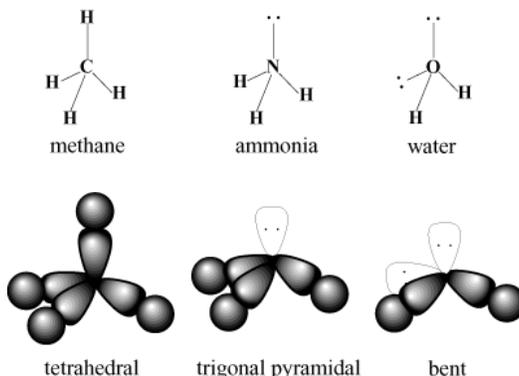
Electrons may also be confined to the surface of a material. For example, free electrons will float on the surface of liquid helium, and are free to move along the surface, but stick to the helium; some of the earliest work in 2DEGs was done using this system.<sup>[1]</sup> Besides liquid helium, there are also solid insulators (such as topological insulators) that support conductive surface electronic states.

Recently, atomically thin solid materials have been developed (graphene, as well as metal dichalcogenide such as molybdenum disulfide) where the electrons are confined to an extreme degree. The two-dimensional electron system in graphene can be tuned to either a 2DEG or 2DHG (2-D hole gas) by gating or chemical doping. This has been a topic of current research due to the versatile (some existing but mostly envisaged) applications of graphene.

A separate class of heterostructures that can host 2DEGs are oxides. Although both sides of the heterostructure are insulators, the 2DEG at the interface may arise even without doping (which is the usual approach in semiconductors). Typical example is a ZnO/ZnMgO heterostructure.<sup>[3]</sup> More examples can be found in a recent review<sup>[4]</sup> including a notable discovery of 2004, a 2DEG at the  $\text{LaAlO}_3/\text{SrTiO}_3$  interface<sup>[5]</sup> which becomes superconducting at low temperatures. The origin of this 2DEG is still unknown, but it may be similar to modulation doping in semiconductors, with electric-field-induced oxygen vacancies acting as the dopants.

## Pauling and Valence Bond Theory

Pauling's big contribution to chemistry was valence bond theory, which combined his knowledge of quantum mechanical theory with his knowledge of basic chemical facts, like bond lengths and bond strengths and shapes of molecules. Valence bond theory, like Lewis's bonding theory, provides a simple model that is useful for predicting and understanding the structures of molecules, especially for organic chemistry. Later Pauling applied his understanding of molecular shapes and bonding to a pretty good explanation of protein structures. Later still, he became famous for peace activism and promoting ascorbic acid (vitamin C) as a cure for colds and cancer.



*Examples of using valence bond theory to predict the structures of molecules.*

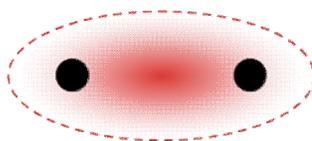
Valence bond theory is good for explaining the "ground state" properties of molecules, or the properties of molecules that only involve the lowest energy states. However, just like a hydrogen atom can be "excited" by light, moving the electron from  $n = 1$  to  $n = 2, 3, 4...$  states, molecules have excited states that can be very important for reactions, colors, etc. Valence bond theory is not good for anything involving excited states, so we will talk about Molecular Orbital Theory as our next big topic.

## Valence bond theory

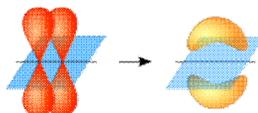
In chemistry, valence bond (VB) theory is one of two basic theories, along with molecular orbital (MO) theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed. In contrast, molecular orbital theory has orbitals that cover the whole molecule.

## Theory

According to this theory a covalent bond is formed between the two atoms by the overlap of half filled valence atomic orbitals of each atom containing one unpaired electron. A valence bond structure is similar to a Lewis structure, but where a single Lewis structure cannot be written, several valence bond structures are used. Each of these VB structures represents a specific Lewis structure. This combination of valence bond structures is the main point of resonance theory. Valence bond theory considers that the overlapping atomic orbitals of the participating atoms form a chemical bond. Because of the overlapping, it is most probable that electrons should be in the bond region. Valence bond theory views bonds as weakly coupled orbitals (small overlap). Valence bond theory is typically easier to employ in ground state molecules. The inner-shell orbitals and electrons remain essentially unchanged during the formation of bonds.



$\sigma$  bond between two atoms: localization of electron density



Two p-orbitals forming a  $\pi$ -bond.

The overlapping atomic orbitals can differ. The two types of overlapping orbitals are sigma and pi. Sigma bonds occur when the orbitals of two shared electrons overlap head-to-head. Pi bonds occur when two orbitals overlap when they are parallel. For example, a bond between two *s*-orbital electrons is a sigma bond, because two spheres are always coaxial. In terms of bond order, single bonds have one sigma bond, double bonds consist of one sigma bond and one pi bond, and triple bonds contain one sigma bond and two pi bonds. However, the atomic orbitals for bonding may be hybrids. Often, the bonding atomic orbitals have a character of several possible types of orbitals. The methods to get an atomic orbital with the proper character for the bonding is called hybridization.

### Applications of valence bond theory

An important aspect of the Valence Bond theory is the condition of maximum overlap, which leads to the formation of the strongest possible bonds. This theory is used to explain the covalent bond formation in many molecules.

For example, in the case of the  $F_2$  molecule, the F–F bond is formed by the overlap of  $p_z$  orbitals of the two F atoms, each containing an unpaired electron. Since the nature of the overlapping orbitals are different in  $H_2$  and  $F_2$  molecules, the bond strength and bond lengths differ between  $H_2$  and  $F_2$  molecules.

In an HF molecule the covalent bond is formed by the overlap of the  $1s$  orbital of H and the  $2p_z$  orbital of F, each containing an unpaired electron. Mutual sharing of electrons between H and F results in a covalent bond in HF.

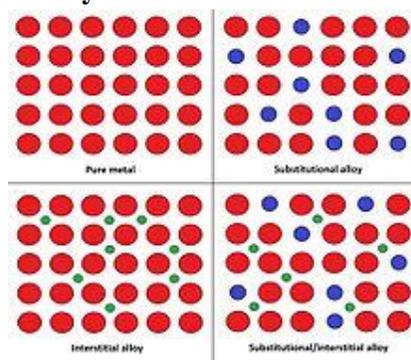
### Structure of Alloys

An alloy is a combination of metals or of a metal and another element. Alloys are defined by a metallic bonding character. An alloy may be a solid solution of metal elements or a mixture of metallic phases. Intermetallic compounds are alloys with a defined stoichiometry and crystal structure. Zintl phases are also sometimes considered alloys depending on bond types.

Alloys are used in a wide variety of applications. In some cases, a combination of metals may reduce the overall cost of the material while preserving important properties. In other cases, the combination of metals imparts synergistic properties to the constituent metal elements such as corrosion resistance or mechanical strength. Examples of alloys are steel, solder, brass, pewter, duralumin, bronze and amalgams. The alloy constituents are usually measured by mass percentage for practical applications, and in atomic fraction for basic science studies. Alloys are usually classified as substitutional or interstitial alloys, depending on the atomic arrangement that forms the alloy. They can be further classified as homogeneous or heterogeneous or intermetallic.

Bronze, an alloy of copper and tin, was the first alloy discovered, during the prehistoric period now known as the Bronze Age. It was harder than pure copper and originally used to make tools and weapons, but was later superseded by metals and alloys with better properties. In later times bronze has been used for ornaments, bells, statues, and bearings. Brass is an alloy made from copper and zinc. Unlike pure metals, most alloys do not have a single melting point, but a melting range during which the material is a mixture of solid and liquid phases. The temperature at which melting begins is called the solidus, and the temperature when melting is just complete is called the liquidus. For many alloys there is a particular alloy proportion (in some cases more than one), called either a eutectic mixture or a peritectic composition, which gives the alloy a unique and low melting point, and no liquid/solid slush transition.

### Substitutional and interstitial alloys



Different atomic mechanisms of alloy formation, showing pure metal, substitutional, interstitial, and a combination of the two.

When a molten metal is mixed with another substance, there are two mechanisms that can cause an alloy to form, called *atom exchange* and the *interstitial mechanism*. The relative size of each element in the mix plays a primary role in determining which mechanism will occur. When the atoms are relatively similar in size, the atom exchange method usually happens, where some of the atoms composing the metallic crystals are substituted with atoms of the other constituent. This is called a *substitutional alloy*. Examples of substitutional alloys include bronze and brass, in which some of the copper atoms are substituted with either tin or zinc atoms respectively. In the case of the interstitial mechanism, one atom is usually much smaller than the other and cannot successfully substitute for the other type of atom in the crystals of the base metal. Instead, the smaller atoms become trapped in the spaces between the atoms of the crystal matrix, called the *interstices*. This is referred to as an *interstitial alloy*. Steel is an example of an interstitial alloy, because the very small carbon atoms fit into interstices of the iron matrix. Stainless steel is an example of a combination of interstitial and substitutional alloys, because the carbon atoms fit into the interstices, but some of the iron atoms are substituted by nickel and chromium atoms.

Iron is usually found as iron ore on Earth, except for one deposit of native iron in Greenland, which was used by the Inuit people. Native copper, however, was found worldwide, along with silver, gold, and platinum, which were also used to make tools, jewelry, and other objects since Neolithic times. Copper was the hardest of these metals, and the most widely distributed. It became one of the most important metals to the ancients. Eventually, humans learned to smelt metals such as copper and tin from ore, and, around 2500 BC, began alloying the two metals to form bronze, which was much harder than its ingredients. Tin was rare, however, being found mostly in Great Britain. In the Middle East, people began alloying copper with zinc to form brass. Ancient civilizations took into account

the mixture and the various properties it produced, such as hardness, toughness and melting point, under various conditions of temperature and work hardening, developing much of the information contained in modern alloy phase diagrams.<sup>[13]</sup> For example, arrowheads from the Chinese Qin dynasty (around 200 BC) were often constructed with a hard bronze-head, but a softer bronze-tang, combining the alloys to prevent both dulling and breaking during use.<sup>[14]</sup>

### Hume-Rothery rules

The Hume-Rothery rules, named after William Hume-Rothery, are a set of basic rules that describe the conditions under which an element could dissolve in a metal, forming a solid solution. There are two sets of rules; one refers to substitutional solid solutions, and the other refers to interstitial solid solutions.

### Substitutional solid solution rules

For substitutional solid solutions, the Hume-Rothery rules are as follows:

- The atomic radius of the solute and solvent atoms must differ by no more than 15%:
- The crystal structures of solute and solvent must be similar.
- Complete solubility occurs when the solvent and solute have the same valency.<sup>[1]</sup> A metal of higher valency is more likely to dissolve in a metal with lower valency.
- The solute and solvent should have similar electronegativity. If the electronegativity difference is too great, the metals tend to form intermetallic compounds instead of solid solutions.

### Interstitial solid solution rules

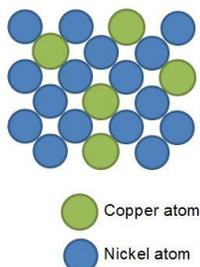
For interstitial solid solutions, the Hume-Rothery rules are:

- Solute atoms should have radius no larger than 59% of the radius of solvent atoms.
- The solute and solvent should have similar electronegativity.
- They should show a wide range of composition.

Solid solution strengthening is a type of alloying that can be used to improve the strength of a pure metal. The technique works by adding atoms of one element (the alloying element) to the crystalline lattice of another element (the base metal), forming a solid solution. The local nonuniformity in the lattice due to the alloying element makes plastic deformation more difficult by impeding dislocation motion. In contrast, alloying beyond the solubility limit can form a second phase, leading to strengthening via other mechanisms (e.g. the precipitation of intermetallic compounds).

### Solid Solutions

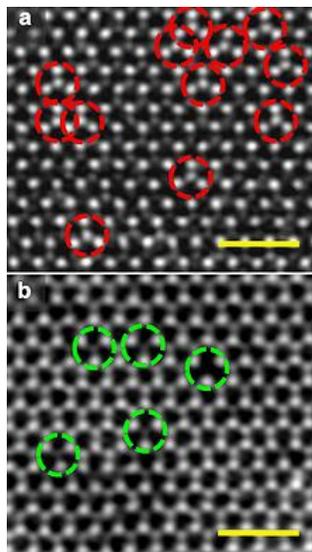
Just as two liquids can mix to form a liquid solution, two solids can mix to form a solid solution. For example, copper and nickel mix to form a solid solution. This means that the copper and nickel atoms completely mix with each other no matter how much copper or nickel there is. The image shows copper and nickel atoms in a solid solution.



*A plane of atoms in a solid solution of copper and nickel*

### Crystallographic defect

Crystalline solids exhibit a periodic crystal structure. The positions of atoms or molecules occur on repeating fixed distances, determined by the unit cell parameters. However, the arrangement of atoms or molecules in most crystalline materials is not perfect. The regular patterns are interrupted by crystallographic defects.

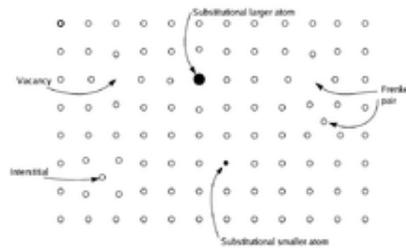


Electron microscopy of antisites (a, Mo substitutes for S) and vacancies (b, missing S atoms) in a monolayer of molybdenum disulfide. Scale bar: 1 nm.<sup>[1]</sup>

### Point defects

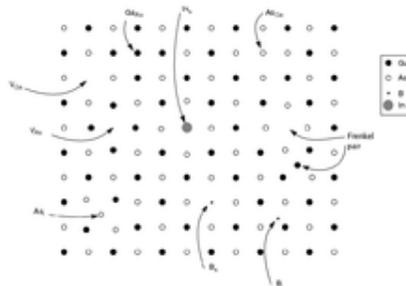
Point defects are defects that occur only at or around a single lattice point. They are not extended in space in any dimension. Strict limits for how small a point defect is are generally not defined explicitly. However, these defects typically involve at most a few extra or missing atoms. Larger defects in an ordered structure are usually considered dislocation loops. For historical reasons, many point defects, especially in ionic crystals, are called *centers*: for example a vacancy in many ionic solids is called a luminescence center, a color center, or F-center. These dislocations permit ionic transport through crystals leading to electrochemical reactions. These are frequently specified using Kröger–Vink Notation.

- Vacancy defects are lattice sites which would be occupied in a perfect crystal, but are vacant. If a neighboring atom moves to occupy the vacant site, the vacancy moves in the opposite direction to the site which used to be occupied by the moving atom. The stability of the surrounding crystal structure guarantees that the neighboring atoms will not simply collapse around the vacancy. In some materials, neighboring atoms actually move away from a vacancy, because they experience attraction from atoms in the surroundings. A vacancy (or pair of vacancies in an ionic solid) is sometimes called a Schottky defect.
- Interstitial defects are atoms that occupy a site in the crystal structure at which there is usually not an atom. They are generally high energy configurations. Small atoms in some crystals can occupy interstices without high energy, such as hydrogen in palladium.



Schematic illustration of some simple point defect types in a monatomic solid

- A nearby pair of a vacancy and an interstitial is often called a Frenkel defect or Frenkel pair. This is caused when an ion moves into an interstitial site and creates a vacancy.
- Due to fundamental limitations of material purification methods, materials are never 100% pure, which by definition induces defects in crystal structure. In the case of an impurity, the atom is often incorporated at a regular atomic site in the crystal structure. This is neither a vacant site nor is the atom on an interstitial site and it is called a *substitutional* defect. The atom is not supposed to be anywhere in the crystal, and is thus an impurity. In some cases where the radius of the substitutional atom (ion) is substantially smaller than that of the atom (ion) it is replacing, its equilibrium position can be shifted away from the lattice site. These types of substitutional defects are often referred to as off-center ions. There are two different types of substitutional defects: Isovalent substitution and aliovalent substitution. Isovalent substitution is where the ion that is substituting the original ion is of the same oxidation state as the ion it is replacing. Aliovalent substitution is where the ion that is substituting the original ion is of a different oxidation state than the ion it is replacing. Aliovalent substitutions change the overall charge within the ionic compound, but the ionic compound must be neutral. Therefore, a charge compensation mechanism is required. Hence either one of the metals is partially or fully oxidised or reduced, or ion vacancies are created.
- Antisite defects occur in an ordered alloy or compound when atoms of different type exchange positions. For example, some alloys have a regular structure in which every other atom is a different species; for illustration assume that type A atoms sit on the corners of a cubic lattice, and type B atoms sit in the center of the cubes. If one cube has an A atom at its center, the atom is on a site usually occupied by a B atom, and is thus an antisite defect. This is neither a vacancy nor an interstitial, nor an impurity.
- Topological defects are regions in a crystal where the normal chemical bonding environment is topologically different from the surroundings. For instance, in a perfect sheet of graphite (graphene) all atoms are in rings containing six atoms. If the sheet contains regions where the number of atoms in a ring is different from six, while the total number of atoms remains the same, a topological defect has formed. An example is the Stone Wales defect in nanotubes, which consists of two adjacent 5-membered and two 7-membered atom rings.



Schematic illustration of defects in a compound solid, using GaAs as an example.

- Also amorphous solids may contain defects. These are naturally somewhat hard to define, but sometimes their nature can be quite easily understood. For instance, in ideally bonded amorphous silica all Si atoms have 4 bonds to O atoms and all O atoms have 2 bonds to Si atom. Thus e.g. an O atom with only one Si bond (a dangling bond) can be considered a defect in silica. Moreover, defects can also be defined in amorphous solids based on empty or densely packed local atomic neighbourhoods, and the properties of such 'defects' can be shown to be similar to normal vacancies and interstitials in crystals.
- Complexes can form between different kinds of point defects. For example, if a vacancy encounters an impurity, the two may bind together if the impurity is too large for the lattice. Interstitials can form 'split interstitial' or 'dumbbell' structures where two atoms effectively share an atomic site, resulting in neither atom actually occupying the site.

### Line defects

Dislocations are linear defects, around which the atoms of the crystal lattice are misaligned. There are two basic types of dislocations, the *edge* dislocation and the *screw* dislocation. "Mixed" dislocations, combining aspects of both types, are also common.

### Planar defects

Grain boundaries occur where the crystallographic direction of the lattice abruptly changes. This usually occurs when two crystals begin growing separately and then meet.

- Antiphase boundaries occur in ordered alloys: in this case, the crystallographic direction remains the same, but each side of the boundary has an opposite phase: For example, if the ordering is usually ABABABAB (hexagonal close-packed crystal), an antiphase boundary takes the form of ABABBABA.
- Stacking faults occur in a number of crystal structures, but the common example is in close-packed structures. They are formed by a local deviation of the stacking sequence of layers in a crystal. An example would be the ABABCABAB stacking sequence.
- A twin boundary is a defect that introduces a plane of mirror symmetry in the ordering of a crystal. For example, in cubic close-packed crystals, the stacking sequence of a twin boundary would be ABCABCACBA.
- On planar of single crystals, steps between atomically flat terraces can also be regarded as planar defects. It has been shown that such defects and their geometry have significant influence on the adsorption of organic molecules<sup>[16]</sup>

### Bulk defects

- three-dimensional macroscopic or bulk defects, such as pores, cracks, or inclusions
- Voids — small regions where there are no atoms, and which can be thought of as clusters of vacancies
- Impurities can cluster together to form small regions of a different phase. These are often called precipitates.

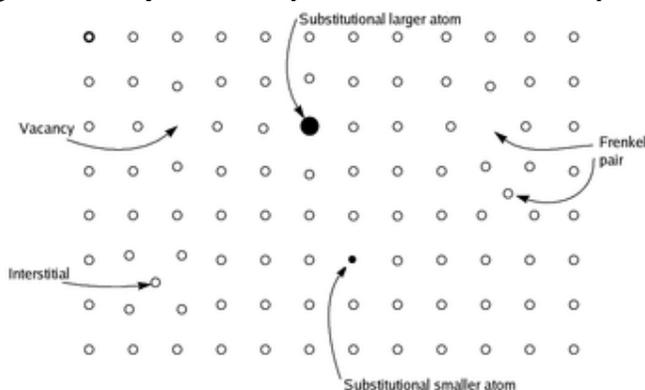
### Extrinsic defects

Various elemental analyses of diamond reveal a wide range of impurities.<sup>[9]</sup> They mostly originate, however, from inclusions of foreign materials in diamond, which could be nanometer-small and invisible in an optical microscope. Also, virtually any element can be

hammered into diamond by ion implantation. More essential are elements which can be introduced into the diamond lattice as isolated atoms (or small atomic clusters) during the diamond growth.

### Non-stoichiometric compound

Non-stoichiometric compounds are chemical compounds, almost always solid inorganic compounds, having elemental composition whose proportions cannot be represented by integers; most often, in such materials, some small percentage of atoms are missing or too many atoms are packed into an otherwise perfect lattice work.



Origin of title phenomena in crystallographic defects. Shown is a two-dimensional slice through a primitive cubic crystal system showing the regular square array of atoms on one face (open circles, o), and with these, places where atoms are missing from a regular site to create *vacancies*, displaced to an adjacent acceptable space to create a *Frenkel pair*, or substituted by a smaller or larger atom not usually seen (closed circles, •), in each case resulting in a material that is moved toward being measurably non-stoichiometric.

Contrary to earlier definitions, modern understanding of non-stoichiometric compounds view them as homogenous, and not mixtures of stoichiometric chemical compounds. Since the solids are overall electrically neutral, the defect is compensated by a change in the charge of other atoms in the solid, either by changing their oxidation state, or by replacing them with atoms of different elements with a different charge. Many metal oxides and sulfides have non-stoichiometric examples; for example, stoichiometric iron(II) oxide, which is rare, has the formula FeO, whereas the more common material is nonstoichiometric, with the formula Fe<sub>0.95</sub>O. The type of equilibrium defects in non-stoichiometric compounds can vary with attendant variation in bulk properties of the material. Non-stoichiometric compounds also exhibit special electrical or chemical properties because of the defects; for example, when atoms are missing, electrons can move through the solid more rapidly. Non-stoichiometric compounds have applications in ceramic and superconductive material and in electrochemical system designs.

Nonstoichiometry is pervasive for metal oxides, especially when the metal is not in its highest oxidation state. For example, although wüstite (ferrous oxide) has an ideal (stoichiometric) formula FeO, the actual stoichiometry is closer to Fe<sub>0.95</sub>O. The non-stoichiometry reflect the ease of oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> effectively replacing a small portion of Fe<sup>2+</sup> with two thirds their number of Fe<sup>3+</sup>. Thus for every three "missing" Fe<sup>2+</sup> ions, the crystal contains two Fe<sup>3+</sup> ions to balance the charge. The composition of a non-stoichiometric compound usually varies in a continuous manner over a narrow range. Thus, the formula for wüstite is written as Fe<sub>1-x</sub>O, where x is a small number (0.05 in the previous example) representing the deviation from the "ideal" formula. Nonstoichiometry is especially important in solid, three-dimensional polymers that can tolerate mistakes. To some extent, entropy drives all solids to be non-stoichiometric. But for practical purposes, the term

describes materials where the non-stoichiometry is measurable, usually at least 1% of the ideal composition.

The monosulfides of the transition metals are often nonstoichiometric. Best known perhaps is nominally iron(II) sulfide (the mineral pyrrhotite) with a composition  $\text{Fe}_{1-x}\text{S}$  ( $x = 0$  to 0.2). The rare stoichiometric FeS endmember is known as the mineral *troilite*. Pyrrhotite is remarkable in that it has numerous polytypes, i.e. crystalline forms differing in symmetry (monoclinic or hexagonal) and composition ( $\text{Fe}_7\text{S}_8$ ,  $\text{Fe}_9\text{S}_{10}$ ,  $\text{Fe}_{11}\text{S}_{12}$  and others). These materials are always iron-deficient owing to the presence of lattice defects, namely iron vacancies. Despite those defects, the composition is usually expressed as a ratio of large numbers and the crystals symmetry is relatively high. This means the iron vacancies are not randomly scattered over the crystal, but form certain regular configurations. Those vacancies strongly affect the magnetic properties of pyrrhotite: the magnetism increases with the concentration of vacancies and is absent for the stoichiometric FeS.

Palladium hydride is a nonstoichiometric material of the approximate composition  $\text{PdH}_x$  ( $0.02 < x < 0.58$ ). This solid conducts hydrogen by virtue of the mobility of the hydrogen atoms within the solid.

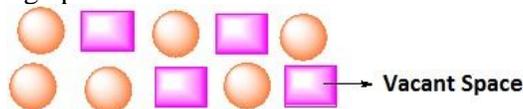
Tungsten oxides are sometimes difficult to determine if a material is non-stoichiometric or if the formula is best represented by large numbers. The oxides of tungsten illustrate this situation. Starting from the idealized material tungsten trioxide, one can generate a series of related materials that are slightly deficient in oxygen. These oxygen-deficient species can be described as  $\text{WO}_{3-x}$ , but in fact they are stoichiometric species with large unit cells with the formulas  $\text{W}_n\text{O}_{3n-2}$ , where  $n = 20, 24, 25, 40$ . Thus, the last species can be described with the stoichiometric formula  $\text{W}_{40}\text{O}_{118}$ , whereas the non-stoichiometric description  $\text{WO}_{2.95}$  implies a more random distribution of oxide vacancies.<sup>[citation needed]</sup>

### **Stoichiometric Defects**

- These ranges of point defects do not disturb the stoichiometry of the solid.
- They are also called *intrinsic* or thermodynamic defects.
- Non-ionic solids exhibit their defects as vacancy defects and interstitial defects.

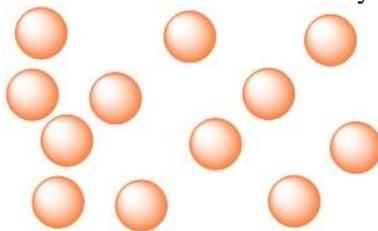
### ***Vacancy Defect:***

A crystal containing vacant lattice sites is said to have vacancy defect. This defect can also develop due to heating up of a substance.



### ***Interstitial Defect:***

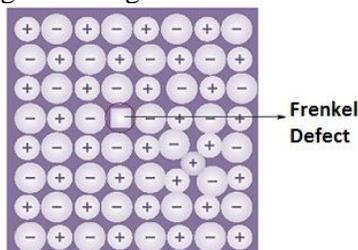
A crystal in which some constituent particles occupy an interstitial site, are said to have interstitial defect which increases the density of the substance.



Ionic solids exhibit their defects as Frenkel and Schottky defects.

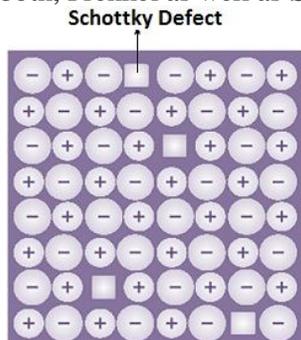
### Frenkel Defect:

- This defect is exhibited by the ionic substances due to the large difference in size of ions.
- The smaller ion (cation) is displaced from its normal site to an interstitial site which creates a vacancy defect at its original site and an interstitial defect at the new location.
- It is also called dislocation defect.
- It does not alter the density of the solid.
- For example, ZnS, AgCl, AgBr and AgI due to small size of  $Zn^{2+}$  and  $Ag^+$  ions.



### Schottky Defect:

- This defect in ionic solids is equivalent to the vacancy defect in non-ionic solids.
- In order to maintain electrical neutrality, the number of missing cations and anions are equal
- Schottky defect also decreases the density of the substance.
- This defect is shown by ionic substances in which the cation and anion are of almost similar sizes.
- In NaCl there are approximately  $10^6$  Schottky pairs per  $cm^3$  at room temperature. In  $1\ cm^3$  there are about  $10^{22}$  Thus, there is one Schottky defect per  $10^{16}$  ions.
- For example, NaCl, KCl, CsCl and AgBr.
- Out of these AgBr shows both, Frenkel as well as Schottky defects.



### Semi conductors

A semiconductor material has an electrical conductivity value falling between that of a metal, like copper, gold, etc. and an insulator, such as glass. Their resistance decreases as their temperature increases, which is behaviour opposite to that of a metal. Their conducting properties may be altered in useful ways by the deliberate, controlled introduction of impurities ("doping") into the crystal structure. Where two differently-doped regions exist in the same crystal, a semiconductor junction is created. The behavior of charge carriers which include electrons, ions and electron holes at these junctions is the basis of diodes, transistors and all modern electronics. Some examples of semiconductors are silicon, germanium, and gallium arsenide. After silicon, gallium arsenide is the second most

common semiconductor used in laser diodes, solar cells, microwave frequency integrated circuits, and others. Silicon is a critical element for fabricating most electronic circuits.

Semiconductor devices can display a range of useful properties such as passing current more easily in one direction than the other, showing variable resistance, and sensitivity to light or heat. Because the electrical properties of a semiconductor material can be modified by doping, or by the application of electrical fields or light, devices made from semiconductors can be used for amplification, switching, and energy conversion.

The conductivity of silicon is increased by adding a small amount of pentavalent (antimony, phosphorus, or arsenic) or trivalent (boron, gallium, indium) atoms (part in  $10^8$ ). This process is known as doping and resulting semiconductors are known as doped or extrinsic semiconductors. Apart from doping, the conductivity of a semiconductor can equally be improved by increasing its temperature. This is contrary to the behaviour of a metal in which conductivity decreases with increase in temperature.

The modern understanding of the properties of a semiconductor relies on quantum physics to explain the movement of charge carriers in a crystal lattice.<sup>[1]</sup> Doping greatly increases the number of charge carriers within the crystal. When a doped semiconductor contains mostly free holes it is called "p-type", and when it contains mostly free electrons it is known as "n-type". The semiconductor materials used in electronic devices are doped under precise conditions to control the concentration and regions of p- and n-type dopants. A single semiconductor crystal can have many p- and n-type regions; the p-n junctions between these regions are responsible for the useful electronic behavior.

Although some pure elements and many compounds display semiconductor properties, silicon, germanium, and compounds of gallium are the most widely used in electronic devices. Elements near the so-called "metalloid staircase", where the metalloids are located on the periodic table, are usually used as semiconductors.

### **Amorphous semiconductors**

Some materials, when rapidly cooled to a glassy amorphous state, have semiconducting properties. These include B, Si, Ge, Se, Te and there are multiple theories to explain them.

### **Intrinsic semiconductor**

An intrinsic (pure) semiconductor, also called an undoped semiconductor or i-type semiconductor, is a pure semiconductor without any significant dopant species present. The number of charge carriers is therefore determined by the properties of the material itself instead of the amount of impurities. In intrinsic semiconductors the number of excited electrons and the number of holes are equal:  $n = p$ . This may even be the case after doping the semiconductor, though only if it is doped with both donors and acceptors equally. In this case,  $n = p$  still holds, and the semiconductor remains intrinsic, though doped.

The electrical conductivity of intrinsic semiconductors can be due to crystallographic defects or electron excitation. In an intrinsic semiconductor the number of electrons in the conduction band is equal to the number of holes in the valence band. An example is  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$  at room temperature.

An indirect band gap intrinsic semiconductor is one in which the maximum energy of the valence band occurs at a different  $k$  ( $k$ -space wave vector) than the minimum energy of the conduction band. Examples include silicon and germanium. A direct band gap intrinsic semiconductor is one where the maximum energy of the valence band occurs at the same  $k$  as the minimum energy of the conduction band. Examples include gallium arsenide. A silicon crystal is different from an insulator because at any temperature above absolute zero, there is a non-zero probability that an electron in the lattice will be knocked loose from its position,

leaving behind an electron deficiency called a "hole". If a voltage is applied, then both the electron and the hole can contribute to a small current flow.

The conductivity of a semiconductor can be modeled in terms of the band theory of solids. The band model of a semiconductor suggests that at ordinary temperatures there is a finite possibility that electrons can reach the conduction band and contribute to electrical conduction. The term intrinsic here distinguishes between the properties of pure "intrinsic" silicon and the dramatically different properties of doped n-type or p-type semiconductors.

### **Extrinsic semiconductor**

An extrinsic semiconductor is one that has been *doped*; during manufacture of the semiconductor crystal a trace element or chemical called a doping agent has been incorporated chemically into the crystal, for the purpose of giving it different electrical properties than the pure semiconductor crystal, which is called an *intrinsic semiconductor*. In an extrinsic semiconductor it is these foreign dopant atoms in the crystal lattice that mainly provide the charge carriers which carry electric current through the crystal. The doping agents used are of two types, resulting in two types of extrinsic semiconductor. An *electron donor* dopant is an atom which, when incorporated in the crystal, releases a mobile conduction electron into the crystal lattice. An extrinsic semiconductor which has been doped with electron donor atoms is called an n-type semiconductor, because the majority of charge carriers in the crystal are negative electrons. An *electron acceptor* dopant is an atom which accepts an electron from the lattice, creating a vacancy where an electron should be called a *hole* which can move through the crystal like a positively charged particle. An extrinsic semiconductor which has been doped with electron acceptor atoms is called a p-type semiconductor, because the majority of charge carriers in the crystal are positive holes.

Doping is the key to the extraordinarily wide range of electrical behavior that semiconductors can exhibit, and extrinsic semiconductors are used to make semiconductor electronic devices such as diodes, transistors, integrated circuits, semiconductor lasers, LEDs, and photovoltaic cells. Sophisticated semiconductor fabrication processes like photolithography can implant different dopant elements in different regions of the same semiconductor crystal wafer, creating semiconductor devices on the wafer's surface. For example a common type of transistor, the n-p-n bipolar transistor, consists of an extrinsic semiconductor crystal with two regions of n-type semiconductor, separated by a region of p-type semiconductor, with metal contacts attached to each part.

### **N-type semiconductor**

An N-Type semiconductor is created by adding pentavalent impurities like phosphorus (P), arsenic (As), antimony (Sb), or bismuth (Bi). A pentavalent impurity is called a donor atom because it is ready to give a free electron to a semiconductor. The impurities are called dopants. The purpose of doing this is to make more charge carriers, or electron wires available in the material for conduction. In n-type semiconductors the number of electrons is more than the holes, so electrons are measured as majority charge carriers and holes are referred to as minority charge carriers.

Semiconductor materials like silicon and germanium have four electrons in their outer shell (valence shell). All the four electrons are used by the semiconductor atom in forming bonds with its neighbouring atoms, leaving a low number of electrons available for conduction. Pentavalent elements are those elements which have five electrons in their outer shell. When pentavalent impurities like phosphorus or arsenic are added into semiconductor, four electrons form bonds with the surrounding silicon atoms leaving one electron free. The resulting material has a large number of free electrons. Since electrons are negative charge carriers, the resultant material is called n-type (or negative type) semiconductor. The

pentavalent impurity that is added is called a 'dopant' and the process of addition is called 'doping' in simple the 8 electron is required to make a covalent bond and 1 electron remain in outer most shell which start acting as a free electron.

N-Type semiconductors are manufactured by doping 'intrinsic' or pure semiconductor material. The amount of impurity added is very small compared to the amount of semiconductor. The characteristics and nature of the resultant semiconductor can be controlled by controlling the quantity of the dopant.

### **P-type semiconductor**

A p-type semiconductor is a type of semiconductor. Ordinary semiconductors are made of materials that do not conduct (or carry) an electric current very well but are not highly resistant to doing so. They fall half way between conductors and insulators. An electric current occurs when electrons move through a material. In order to move, there must be an electron 'hole' in the material for the electron to move into. A p-type semiconductor has more holes than electrons. This allows the current to flow along the material from hole to hole but only in one direction.

Semiconductors are most often made from silicon. Silicon is an element with four electrons in its outer shell. To make a p-type semiconductor extra materials like boron or aluminium are added to the silicon. These materials have only three electrons in their outer shell. When the extra material replaces some of the silicon it leaves a 'hole' where the fourth electron would have been if the semiconductor was pure silicon.

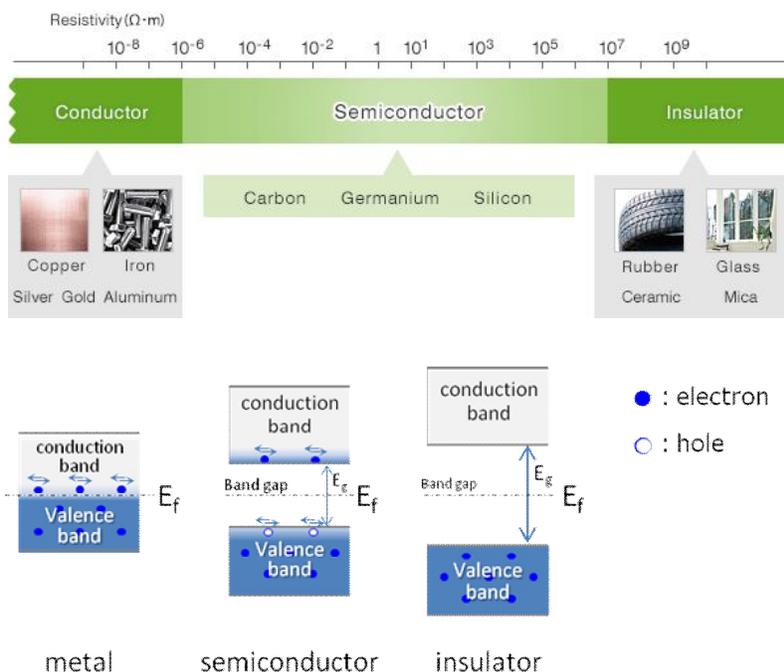
P-type semiconductors are made by doping the pure semiconductor material. The amount of impurity added is very small compared to the amount of semiconductor. The exact character of the semiconductor can be changed by varying the amount of 'dopant' that is added.

### **Properties of semiconductors**

The name "semiconductor" is widely known, but what are semiconductors? Semiconductors possess specific electrical properties. A substance that conducts electricity is called a conductor, and a substance that does not conduct electricity is called an insulator. Semiconductors are substances with properties somewhere between them. Electrical properties can be indicated by resistivity. Conductors such as gold, silver and copper have low resistance and conduct electricity easily.

Insulators such as rubber, glass and ceramics have high resistance and are difficult for electricity to pass through. Semiconductors have properties somewhere between these two. Their resistivity might change according to the temperature for example. At a low temperature, almost no electricity passes through them. But when the temperature rises, electricity passes through them easily.

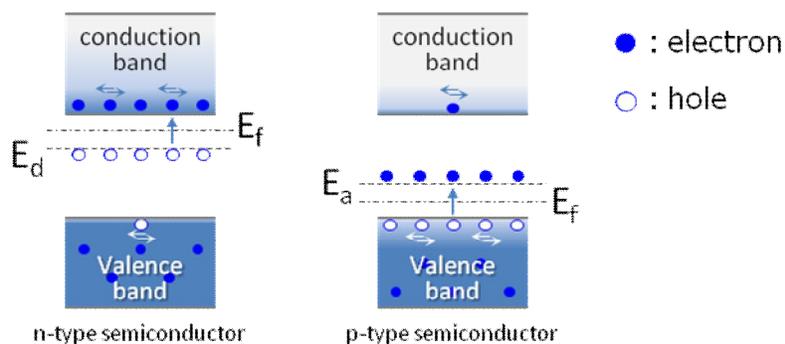
Semiconductors containing almost no impurities conduct almost no electricity. But when some elements are added to the semiconductors, electricity passes through them easily. Semiconductors comprising a single element are called elemental semiconductors, including the famous semiconductor material Silicon. On the other hand, semiconductors made up of two or more compounds are called compound semiconductors, and are used in semiconductor lasers, light-emitting diodes, etc.



In metals, the conduction band and the valence band come very close to each other and may even overlap, with the Fermi energy ( $E_f$ ) somewhere inside. This means that the metal always has electrons that can move freely and so can always carry current. Such electrons are known as free electrons. These free electrons are responsible for current that flows through a metal. In semiconductors and insulators, the valence band and conduction band are separated by a forbidden energy gap ( $E_g$ ) of sufficient width, and the Fermi energy ( $E_f$ ) is between the valence and conduction band. To get to the conduction band, the electron has to gain enough energy to jump the band gap. Once this is done, it can conduct.

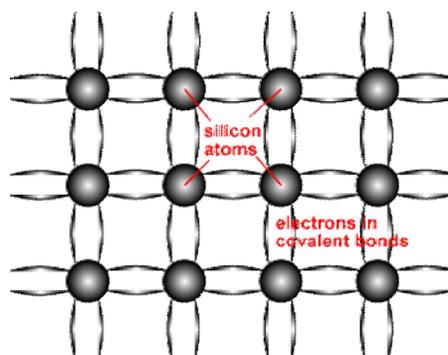
In semiconductors at room temperature, the band gap is smaller, there is enough thermal energy to allow electrons to jump the gap fairly easily and make the transitions in conduction band, given the semiconductor limited conductivity. At low temperature, no electron possesses sufficient energy to occupy the conduction band and thus no movement of charge is possible. At absolute zero, semiconductors are perfect insulators, The density of electrons in conduction band at room temperature is not as high as in metals, thus cannot conduct current as good as metal. The electrical conductivity of semiconductor is not as high as metal but also not as poor as electrical insulator. That is why, this type of material is called semiconductor - means half conductor.

The band gap for insulators is large so very few electrons can jump the gap. Therefore, current does not flow easily in insulators. The difference between insulators and semiconductors is the size of the band gap energy. In insulator where forbidden gap is very large and as a result the energy required by the electron to cross over to the conduction band is practically large enough. Insulators do not conduct electricity easily. That means the electrical conductivity of insulator is very poor. Semiconductor crystal used for IC etc. is high purity single crystal silicon of 99.9%, but when actually making a circuit, impurities are added to control the electrical properties. Depending on the added impurities, they become n-type and p-type semiconductors.



Pentavalent phosphorus (P) or arsenic (As) are added to high purity silicon for n-type semiconductors. These impurities are called donors. The energy level of the donor is located close to the conduction band, that is, the energy gap is small. Then, electrons at this energy level are easily excited to the conduction band and contribute to the conductivity. On the other hand, trivalent boron (B) etc. is added to p type semiconductor. This is called an acceptor. The energy level of the acceptor is close to the valence band. Since there are no electrons here, electrons in the valence band are excited here. As a result, holes are formed in the valence band, which contributes to the conductivity.

### Semiconductor Structure



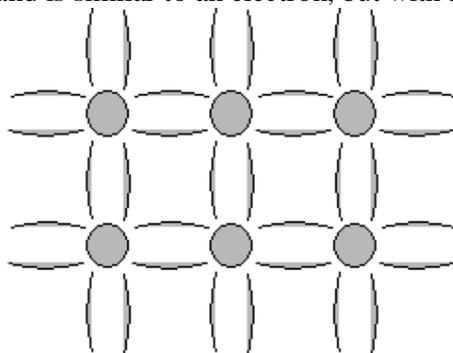
Schematic representation of covalent bonds in a silicon crystal lattice. Each line connecting the atoms represents an electron being shared between the two. Two electrons being shared are what form the covalent bond.

The atoms in a semiconductor are materials from either group IV of the periodic table, or from a combination of group III and group V (called III-V semiconductors), or of combinations from group II and group VI (called II-VI semiconductors). Silicon is the most commonly used semiconductor material as it forms the basis for integrated circuit (IC) chips and is the most mature technology and most solar cells are also silicon based. A full periodic table is given in the page Periodic Table. Several of the material properties of silicon are given in the page Silicon Material Parameters.

The bond structure of a semiconductor determines the material properties of a semiconductor. One key effect is limit the energy levels which the electrons can occupy and how they move about the crystal lattice. The electrons surrounding each atom in a semiconductor are part of a covalent bond. A covalent bond consists of two atoms "sharing" a single electron, such that each atom is surrounded by 8 electrons. The electrons in the covalent bond are held in place by this bond and hence they are localised to region surrounding the atom. Since they cannot move or change their energy, electrons in a bond are not considered "free" and cannot participate in current flow, absorption or other physical

processes of interest in solar cells. However, only at absolute zero are all electrons in a bonded arrangement. At elevated temperatures, the electron can gain enough energy to escape from its bond, and if this happens, the electron is free to move about the crystal lattice and participate in conduction. At room temperature, a semiconductor has enough free electrons to allow it to conduct current, while at, or close to absolute temperatures, a semiconductor behaves like an insulator.

The presence of the bond introduces two distinct energy states for the electrons. The lowest energy position for the electron is to be in its bound state. However, if the electron has enough thermal energy to break free of its bond, then it becomes free. The electron cannot attain energy values intermediate to these two levels; it is either at a low energy position in the bond, or it has gained enough energy to break free and therefore has a certain minimum energy. This minimum energy is called the "band gap" of a semiconductor. The number and energy of the free electrons is basic to the operation of electronic devices. The space left behind by the electrons allows a covalent bond to move from one electron to another, thus appearing to be a positive charge moving through the crystal lattice. This empty space is commonly called a "hole", and is similar to an electron, but with a positive charge.



Animation showing formation of "free" electrons and holes when an electron can escape its bond.

The most important parameters of a semiconductor material for solar cell operation are:

- the band gap;
- the number of free carriers available for conduction; and
- the "generation" and recombination of free carriers in response to light shining on the material.

### **Semiconductors & Electronics**

The movement towards environmentally friendly products, including 'green' cars and more efficient energy use, coupled with the growing use of mobile phones and personal communications, is driving demand for semiconductors and sophisticated electronics worldwide. Semiconductor manufacturers today need to be constantly developing new materials and technologies to meet these needs.

With their extremely high quality requirements, the semiconductor and electronics industries have used multivariate analysis for many years to develop models and monitor processes in real-time to improve product development, minimize waste and optimize output. This holds true within all aspects of the sector. For example, improved manufacturing process control can be achieved through first increasing process observability by using a combination of new instruments and cluster analysis. These techniques use acoustic waves to relay information about several physical parameters from within an injection mold. As these variables cannot be controlled individually, CAMO software is used to calculate their relationship to one another, and how that relates to the product.

## **Electronics and semiconductor manufacturing industry in India**

The Indian electronics industry is seeing growth encouraged both by government policies and incentives and by international investment. Its key and most resource-intensive segment, the semiconductor industry has substantial potential for growth since domestic demand is growing briskly. Semiconductors are required by a large number of industries, including telecommunications, information technology, industrial machinery and automation, medical electronics, automobile, engineering, power and solar photovoltaic, defense and aerospace, consumer electronics, and appliances. According to a NOVONOUS report, a steady and significant spurt in the semiconductor industry will increase the domestic market size fivefold during 2013-2020. As of 2015, however, the skill gap in Indian industry threatened progress, with 65 to 70 per cent of the market relying on imports.

### **Semiconductor industry**

With the newly heralded era of Internet of Things (IoT) dictating that the new generation of interconnected devices be capable of smart-computing, Indian semiconductor industry is set for a stable upsurge with bright prospects provided India's generic obstacles like redtape-ism, fund crunch and infrastructural deficits are adequately addressed. The fast growing electronics system design manufacturing ( ESDM ) industry in India has vibrant design capabilities with the number of units exceeding 120. As stated by the Department of Electronics and Information Technology (DeitY), approximately 2,000 chips are being designed in India every year with more than 200,000 engineers currently employed to work on various aspects of IC design and verification.