http://en.wikipedia.org/wiki/Bravais_lattice

Introduction to Solid State

Crystalline vs. non-crystalline solids:

Lattice

Unit cell

No. of spheres in a unit cell :

Bravais lattices

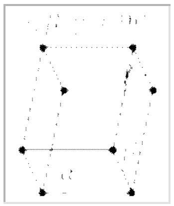
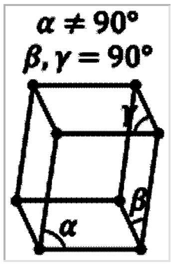
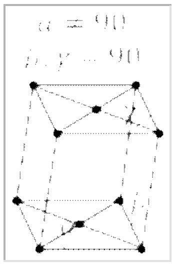
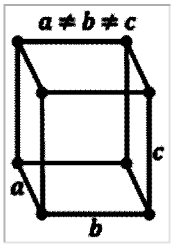
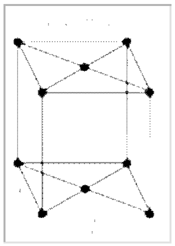
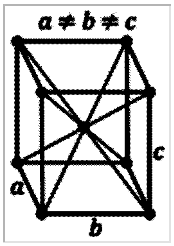
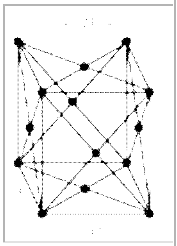
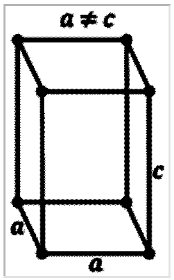
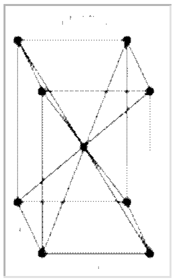
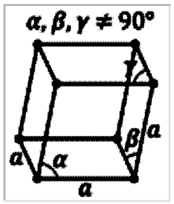
In geometry and crystallography, a **Bravais lattice**, named after Auguste Bravais, is an infinite set of points generated by a set of discrete translation operations. A crystal is made up of one or more atoms (the *basis*) which is repeated at each lattice point. The crystal then looks the same when viewed from any of the lattice points. In all, there are 14 possible Bravais lattices that fill three-dimensional space. Related to Bravais lattices are Crystallographic point groups of which there are 32 and Space groups of which there are 230.Development of the Bravais lattices

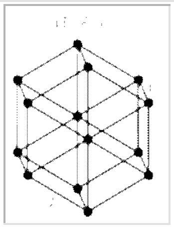
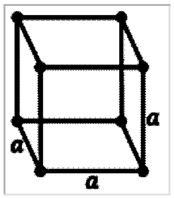
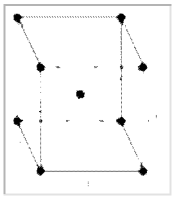
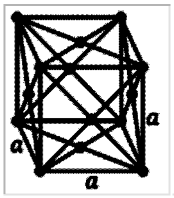
The 14 Bravais lattices are arrived at by combining one of the seven crystal systems (or axial systems) with one of the lattice centerings.

The lattice centerings are:

- Primitive centering (P): lattice points on the cell corners only
- Body centered (I): one additional lattice point at the center of the cell
- Face centered (F): one additional lattice point at center of each of the faces of the cell
- Centered on a single face (A, B or C centering): one additional lattice point at the center of one of the cell faces.

Not all combinations of the crystal systems and lattice centerings are needed to describe the possible lattices. There are in total 7 × 6 = 42 combinations, but it can be shown that several of these are in fact equivalent to each other. For example, the monoclinic I lattice can be described by a monoclinic C lattice by different choice of crystal axes. Similarly, all A- or B-centered lattices can be described either by a C- or P-centering. This reduces the number of combinations to 14 conventional Bravais lattices, shown in the table below.

Crystal system	Bravais lattices			
triclinic	P			
				
monoclinic	P	C		
				
orthorhombic	P	C	I	F
				
tetragonal	P	I		
				
rhombohedral (trigonal)	P			
				
hexagonal	P			

			
	P	I	F
cubic			

The volume of the unit cell can be calculated by evaluating $\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$ where $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ are the lattice vectors. The volumes of the Bravais lattices are given below:

http://en.wikipedia.org/wiki/Close-packing

Close-packing

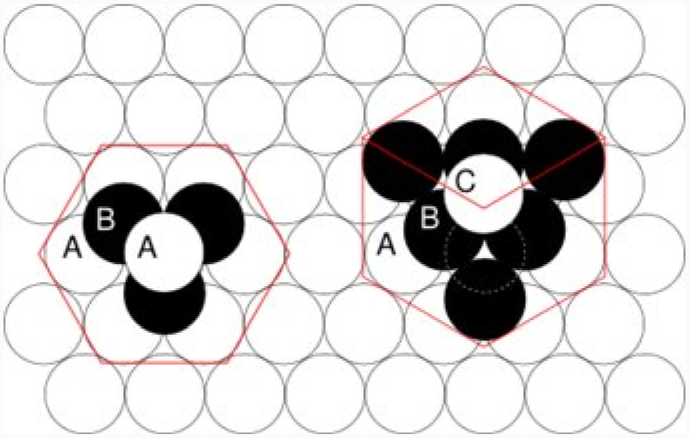


Fig. 1 Shown above are the HCP lattice (left) and the FCC lattice (right). Note that the two groups shown here are not *unit cells* that are capable of tessellating in 3D space. These groups do however, readily illustrate the difference between the two lattices.

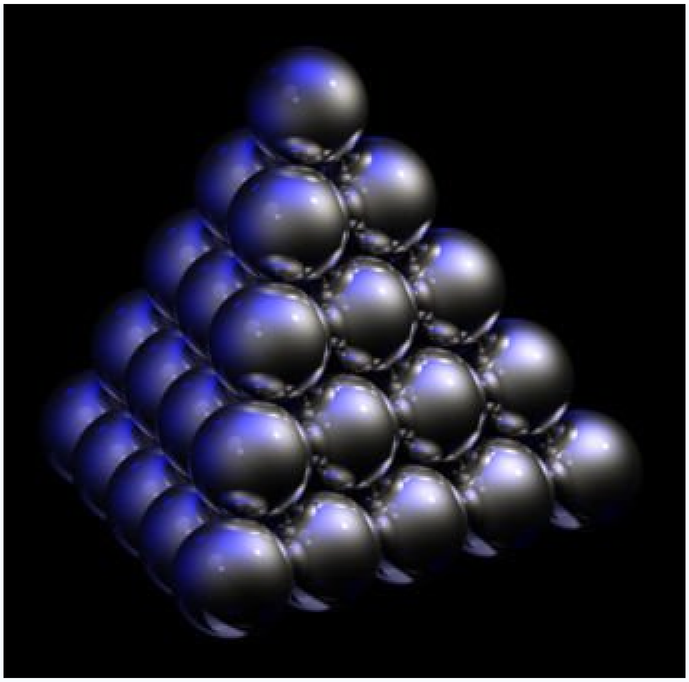


Fig. 2 Thomas Harriot in ca. 1585 first pondered the mathematics of the *cannonball arrangement* or *cannonball stack,* which has an FCC lattice. Note how the two balls facing the viewer in the second tier from the top contact the same ball in the tier below. This does not occur in an HCP lattice (the left organization in *Fig. 1* above, and *Fig. 4* below).

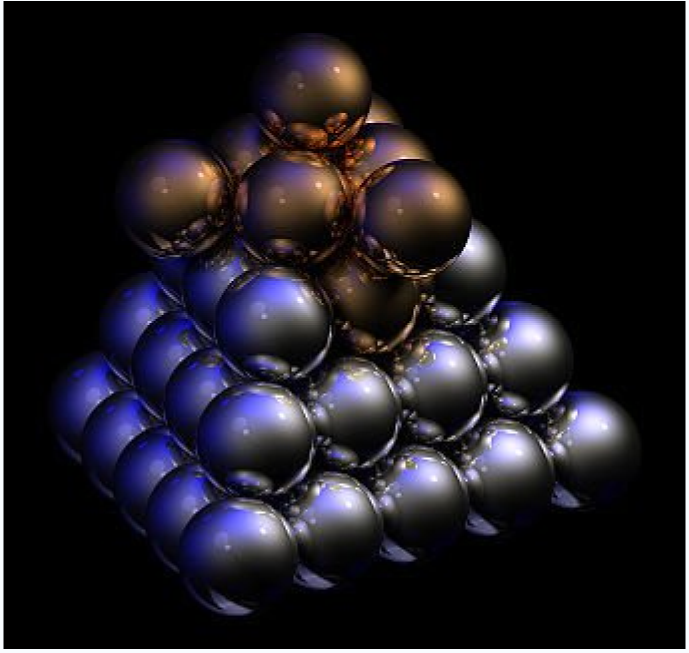


Fig. 3 Shown here is a modified form of the cannonball stack wherein three extra spheres have been added to show all eight spheres in the top three tiers of the FCC lattice diagramed in *Fig. 1*.

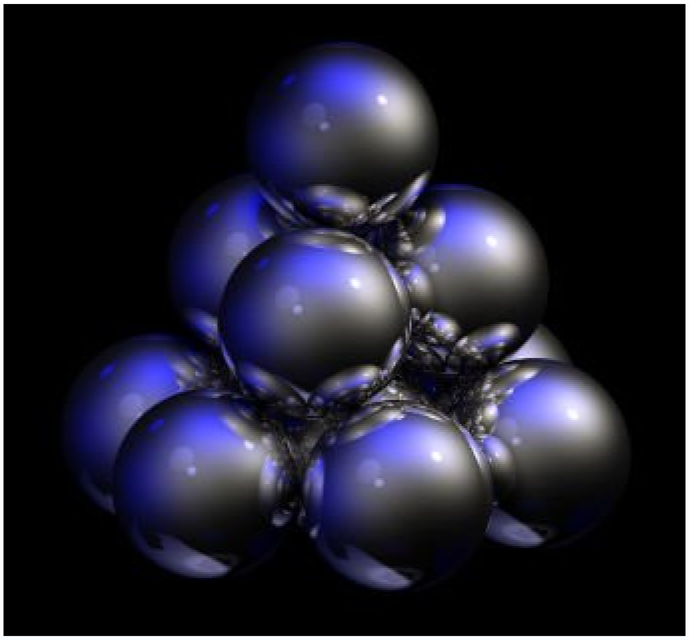


Fig. 4 Shown here are all eleven spheres of the HCP lattice illustrated in *Fig. 1*. The difference between this stack and the top three tiers of the cannonball stack all occurs in the bottom tier, which is rotated half the pitch diameter of a sphere (60°). Note how the two balls facing the viewer in the second tier from the top do not contact the same ball in the tier below.

Close-packing of spheres is the arranging of an infinite lattice of spheres so that they take up the greatest possible fraction of an infinite 3-dimensional space. Carl Friedrich Gauss proved that the highest average density that can be achieved by a regular lattice arrangement is $\frac{\pi}{3\sqrt{2}} \simeq 0.74048$. The Kepler conjecture states that this is the highest density that can be achieved by any arrangement of spheres, either regular or irregular.

There are two regular lattices that achieve this highest average density. They are called face-centered cubic (FCC) and hexagonal close-packed (HCP), based on their symmetry. Both are based upon sheets of spheres arranged at the vertices of a triangular tiling; they differ in how the sheets are stacked upon one another. In both arrangements each sphere has twelve neighbors. For every sphere there is one gap surrounded by six spheres (octahedral) and two smaller gaps surrounded by four spheres (tetrahedral).

Relative to a reference layer with positioning A, two more positionings B and C are possible. Every sequence of A, B, and C without immediate repetition of the same one is possible and gives an equally dense packing for spheres of a given radius.

The most regular ones are:

- HCP = ABABABA
- FCC = ABCABCA

Many crystal structures are based on a close-packing of atoms, or of large ions with smaller ions filling the spaces between them. The cubic and hexagonal arrangements are very close to one another in energy, and it may be difficult to predict which form will be preferred from first principles.

The coordination number of HCP and FCC is 12 and its atomic packing factor (APF) is the number mentioned above, 0.74.

Atomic packing factors and examples

The cubic crystal system is one of the most common crystal systems found in elemental metals, and naturally occurring crystals and minerals. One very useful way to analyse a crystal is to consider the atomic packing factor. In this approach, the amount of space which is filled by the atoms is calculated under the assumption that they are spherical.

Consider the simple cubic, then:

$APF = 8X(1/8)(4/3)(r^3)\pi \;/\; (2r)^3 = 0.52$

Examples:

1) Calculate APF for each of the following unit cells: FCC ,. BCC

2) Which of the following structures is a closest packed arrangement: FCC , BCC , Simple cubic,

*** Single-element lattices*

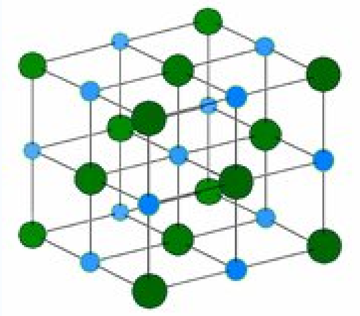
Assuming one atom per lattice point, the atomic packing factor of the **simple cubic system is only 0.524**. Due to its low density, this is **a high energy structure and is rare in nature, but is found in Polonium** [1].

Similarly, the **body centered structure** has **APF of 0.680**. The higher density makes this a low energy structure which is fairly common in nature. Examples include iron, chromium, and tungsten.

Finally, the face centered cubic crystals have a density of 0.741, a ratio that it shares with several other systems, **including hexagonal close packed**

This is the most tightly packed crystal possible with spherical atoms. Due to its low energy, **FCC is extremely common, examples include lead (for example in lead(II) nitrate), aluminum, copper, and gold**.

** *Multi-element compounds*



The Sodium Chloride Crystal Structure of type fcc. Each atom has six nearest neighbors, with octahedral geometry. The arrangement of the atoms of each type is known as *cubic close packed* (ccp).
Light blue = Na^+ (Sodium ion)
Dark green = $Cl^−$ (Chloride ion)

When the compound is formed of two elements whose ions are of roughly the same size, they have what is called the **interpenetrating simple cubic** structure, where two atoms of a different type have individual simple cubic crystals. However, the unit cell consists of the atom of one being in the middle of the 8 vertices, structurally resembling body centered cubic. The most common example is caesium chloride CsCl.

However, if the cation is slightly smaller than the anion (a cation/anion radius ratio of 0.414 to 0.732), the crystal forms a different structure, **interpenetrating FCC**. When drawn separately, both atoms are arranged in an FCC structure. The unit cell for this is shown to the left.

Tetrahedral and octahedral sites:

Between two layers of ccp structures, there exist Td and Oh sites.

Radius ratio and structure:

Example	R^+/r^- ideal	. R^+/r^- actual	C.N	Site	Example
No ccp	0.73	0.93	8		CsCl
CCP	0.41	0.53	6	Oh	NaCl
CCP	0.225	0.402	4	Td	ZnS

Exercise: Use simple geometry to prove the conclusions shown in the above Table.

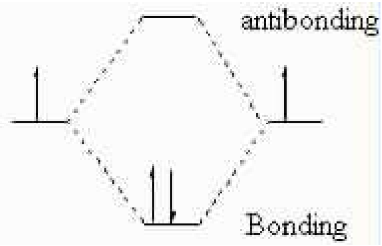
http://www.chembio.uoguelph.ca/educmat/chm729/band/concept.htm

Band Theory

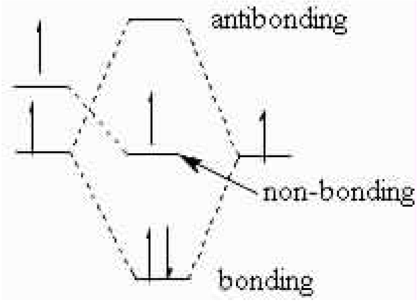
When solids made of an infinite number of atoms are formed, it is a common misconception to consider each atom individually. Rather, we must consider the structure of the solid as a whole. This provides the basis for the description of metals and other types of solids to account for their unique chemical and physical properties.

To fully understand the properties,it is essential to start with molecular orbital theory. In the basic theory, it was assumed that if atoms were brought together, they would form bonding, non-bonding and antibonding orbitals of different energies. These molecular orbitals are described by wave functions. The most important point to come out of the theory is that for N atomic orbitals in a molecule, N molecular orbitals must be the outcome.

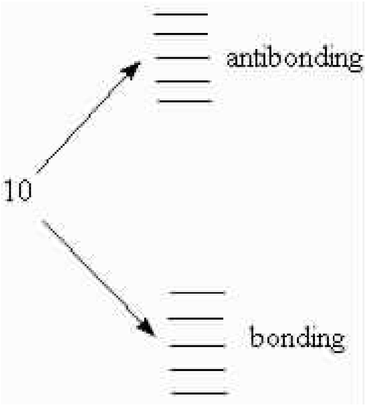
For example, consider a molecule with two atomic orbitals. The result must be that two molecular orbitals will be formed from these atomic orbitals: one bonding and one antibonding, separated by a certain energy.



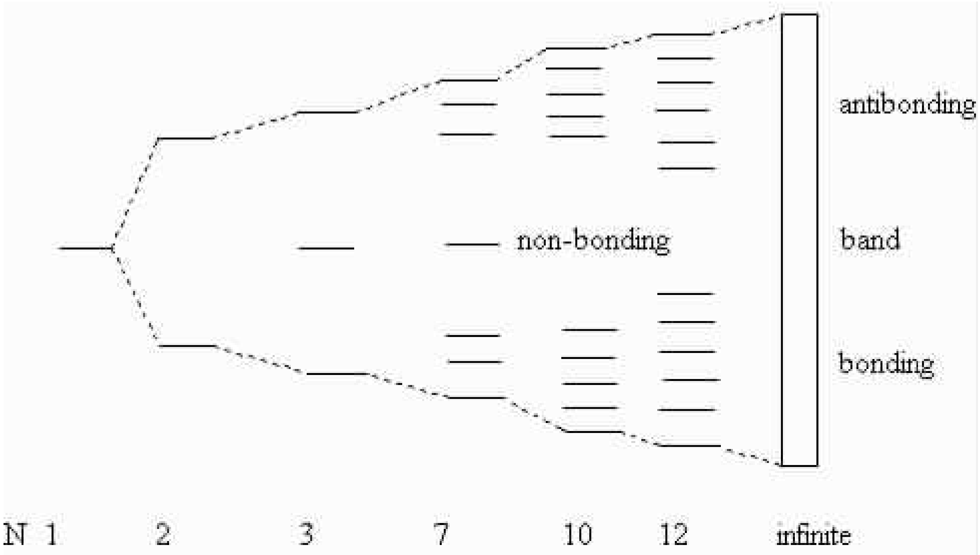
If this is expanded to a molecule with three atoms, assuming 1 atomic orbital for each, then the result must be that 3 molecular orbitals will be formed: one bonding, one non-bonding and one anti-bonding.



Now , let's take it to 10 atoms. This will produce 10 molecular orbitals: 5 bonding and 5 anti-bonding. Now lets take a close look at the separation between each set of orbitals. As the number of molecular orbitals inceases, the energy difference between the lowest bonding and the higherst antibondig increases, while the space between each individual orbital decreases. As the number of molecular orbitals increses with the number of atoms in a molecule, it will the observed that the spaciung between the lowest bonding and highest antibonding orbital will reach a maximum.

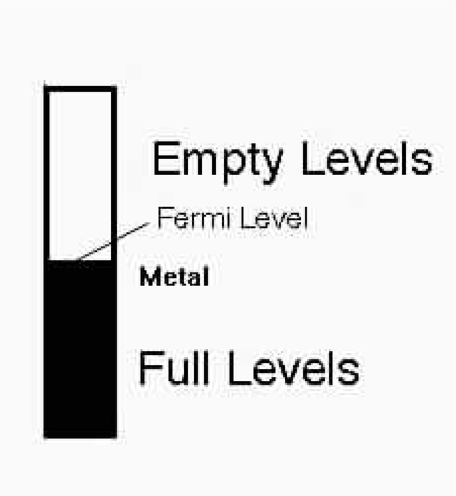


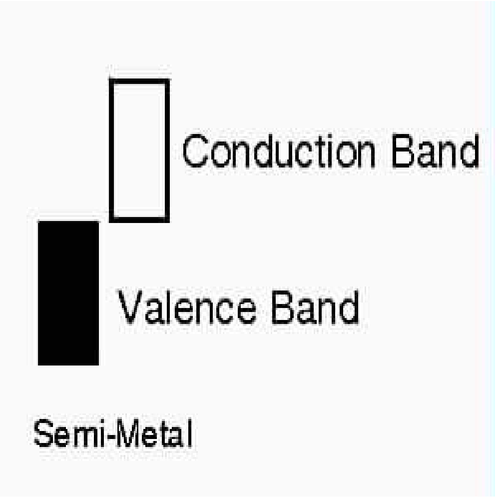
Now consider a metal with an infinite number of atoms. This will form an infinite number of molecular orbitals so close together they blur into one another forming a band. This whole process is shown below.



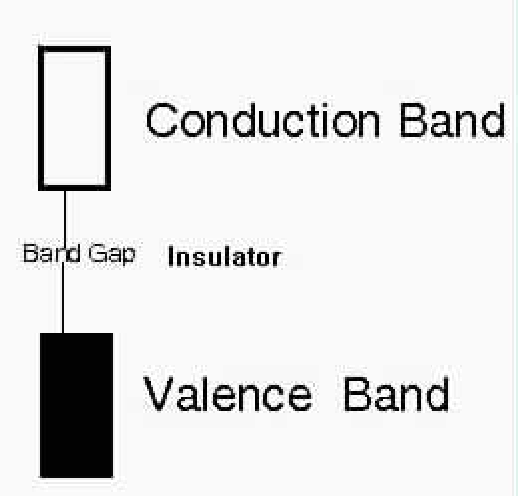
In the above image, the origin fo the band becomes quite clear because as the number of molecular orbitals incerases, they bonding and antibonding orbitals get closer together filling in the middle. This results in the band seen on the right hand side. It becomes quite clear that the molecular orbitals become blurred and hence mix with each other, which creates the delocalised cloud of electrons that metals are said to posses.

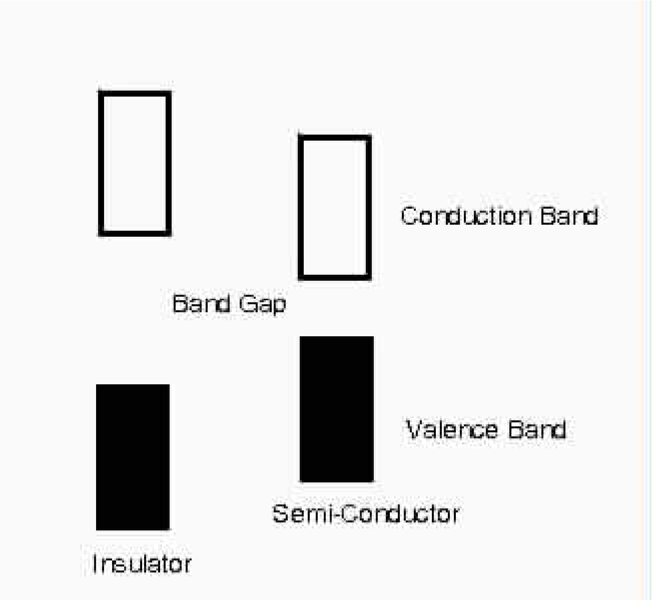
By describing the molecular orbitals of certain materials as bands, it becomes much ٮeasier to understand the properties of metals and semi-metals. Other materials like insulators and semi-conductors will be discussed and concepts such as the valence band, conduction band and the Fermi Level will be defined using the band theory

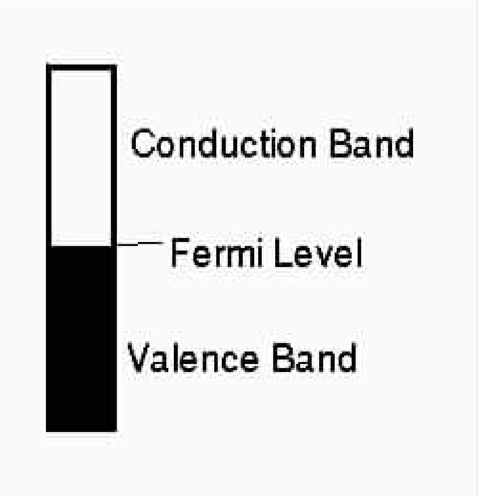




Semi-metal (graphite)


Conduction Band
Band Gap
Insulator
Valence Band


Conduction Band
Band Gap
Valence Band
Semi-Conductor
Insulator



http://en.wikipedia.org/wiki/Semiconductor

Semiconductors

A **semiconductor** is a solid whose electrical conductivity is in between that of a metal and that of an insulator, and can be controlled over a wide range, either permanently or dynamically.[1] Semiconductors are tremendously important technologically and economically. Silicon is the most commercially important semiconductor, though dozens of others are important as well.

Semiconductor devices, electronic components made of semiconductor materials, are essential in modern electrical devices, from computers to cellular phones to digital audio players.

Overview

Semiconductors are very similar to insulators. The two categories of solids differ primarily in that insulators have larger band gaps — energies that electrons must acquire to be free to flow. In semiconductors at room temperature, just as in insulators, very few electrons gain enough thermal energy to leap the band gap, which is necessary for conduction. For this reason, pure semiconductors and insulators, in the absence of applied fields, have roughly similar electrical properties. The smaller bandgaps of semiconductors, however, allow for many other means besides temperature to control their electrical properties.

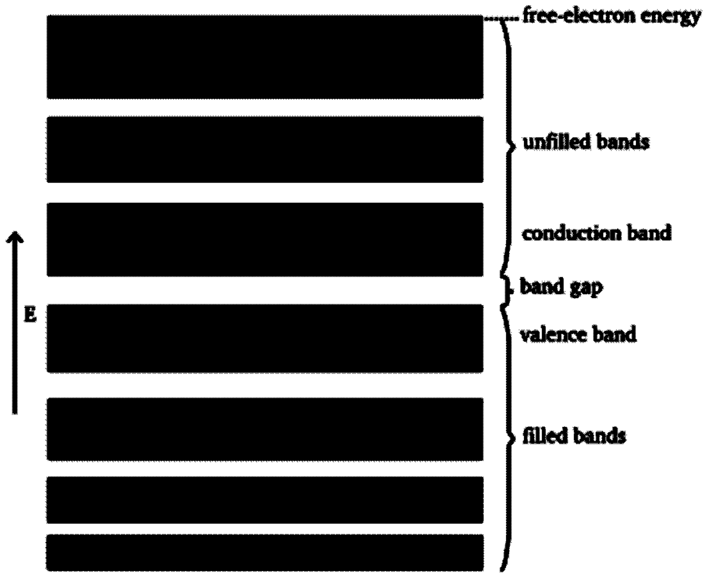
Semiconductors' intrinsic electrical properties are very often permanently modified by introducing impurities, in a process known as doping. Usually it is reasonable to approximate that each impurity atom adds one electron or one "hole" (a concept to be discussed later) that may flow freely. Upon the addition of a sufficiently large proportion of dopants, semiconductors conduct electricity nearly as well as metals. Depending on kind of the impurity, a region of semiconductor can have more electrons or holes, and then it is called N-type or P-type semiconductor, respectively. Junctions between regions of N- and P-type semiconductors have built-in electric fields, which cause electrons and holes to escape from them, and are critical to semiconductor device operation. Also, a density difference of impurities produces in the region small electric field which is used to accelerate non-equilibrium electrons or holes in it.

In addition to permanent modification through doping, the electrical properties of semiconductors are often dynamically modified by applying electric fields. The ability to control conductivity in small and well-defined regions of semiconductor material, both statically through doping and dynamically through the application of electric fields, has led to the development of a broad range of semiconductor devices, like transistors. Semiconductor devices with dynamically controlled conductivity are the building blocks of integrated circuits, like the microprocessor. These "active" semiconductor devices are combined with simpler passive components, such as semiconductor capacitors and resistors, to produce a variety of electronic devices.

In certain semiconductors, when electrons fall from the conduction band to the valence band (the energy levels above and below the band gap), they often emit light. This photoemission process underlies the light-emitting diode (LED) and the semiconductor laser, both of which are very important commercially. Conversely, semiconductor absorption of light in photodetectors excites electrons from the valence band to the conduction band, facilitating reception of fiber optic communications, and providing the basis for energy from solar cells.

Semiconductors may be elemental materials such as silicon and germanium, or compound semiconductors such as gallium arsenide and indium phosphide, or alloys such as silicon germanium or aluminium gallium arsenide.

Band structure



Band structure of a semiconductor showing a full valence band and an empty conduction band.

Like other solids, the electrons in semiconductors can have energies only within certain bands between the energy of the ground state, corresponding to electrons tightly bound to the atomic nuclei of the material, and the free electron energy, which is the energy required for an electron to escape entirely from the material. The energy bands each correspond to a large number of discrete quantum states of the electrons, and most of the states with low energy are full, up to a particular band called the *valence band*. Semiconductors and insulators are distinguished from metals because the valence band in the former materials is very nearly full under normal conditions.

The ease with which electrons in a semiconductor can be excited from the valence band to the conduction band depends on the band gap between the bands, and it is the size of this energy bandgap that serves as an arbitrary dividing line (roughly 4 eV) between semiconductors and insulators.

The electrons must move between states to conduct electric current, and so due to the Pauli exclusion principle full bands do not contribute to the electrical conductivity. However, as the temperature of a semiconductor rises above absolute zero, the states of the electrons are increasingly randomized, or smeared out, and some electrons are likely to be found in states of the *conduction band*, which is the band immediately above the valence band. The current-carrying electrons in the conduction band are known as "free electrons", although they are often simply called "electrons" if context allows this usage to be clear.

Electrons excited to the conduction band also leave behind electron holes, or unoccupied states in the valence band. Both the conduction band electrons and the valence band holes contribute to electrical conductivity. The holes themselves don't actually move, but a neighbouring electron can move to fill the hole, leaving a hole at the place it has just come from, and in this way the holes appear to move, and the holes behave as if they were actual positively charged particles.

One covalent bond between neighboring atoms in the solid is ten times stronger than the binding of the single electron to the atom, so freeing the electron does not imply to destroy the crystal structure.

The notion of holes, which was introduced for semiconductors, can also be applied to metals, where the Fermi level lies *within* the conduction band. With most metals the Hall effect reveals electrons to be the charge carriers, but some metals have a mostly filled conduction band, and the Hall effect reveals positive charge carriers, which are not the ion-cores, but holes. Contrast this to some conductors like solutions of salts, or plasma. In the case of a metal, only a small amount of energy is needed for the electrons to find other unoccupied states to move into, and hence for current to flow. Sometimes even in this case it may be said that a hole was left behind, to explain why the electron does not fall back to lower energies: It cannot find a hole. In the end in both materials electron-phonon scattering and defects are the dominant causes for resistance.

The energy distribution of the electrons determines which of the states are filled and which are empty. This distribution is described by Fermi-Dirac statistics. The distribution is characterized by the temperature of the electrons, and the *Fermi energy* or *Fermi level*. Under absolute zero conditions the Fermi energy can be thought of as the energy up to which available electron states are occupied. At higher temperatures, the Fermi energy is the energy at which the probability of a state being occupied has fallen to 0.5.

The dependence of the electron energy distribution on temperature also explains why the conductivity of a semiconductor has a strong temperature dependency, as a semiconductor operating at lower temperatures will have fewer available free electrons and holes able to do the work.

Carrier generation and recombination

When ionizing radiation strikes a semiconductor, it may excite an electron out of its energy level and consequently leave a hole. This process is known as *electron–hole pair generation*. Electron-hole pairs are constantly generated from thermal energy as well, in the absence of any external energy source.

Electron-hole pairs are also apt to recombine. Conservation of energy demands that these recombination events, in which an electron loses an amount of energy larger than the band gap, be accompanied by the emission of thermal energy (in the form of phonons) or radiation (in the form of photons).

In the steady state, the generation and recombination of electron–hole pairs are in equipoise. The number of electron-hole pairs in the steady state at a given temperature is determined by quantum statistical mechanics. The precise quantum mechanical mechanisms of generation and recombination are governed by conservation of energy and conservation of momentum.

As probability that electrons and holes meet together is proportional to the product of their amounts, the product is in steady state nearly constant at a given temperature, providing that there is no significant electric field (which might "flush" carriers of both types, or move them from neighbour regions containing more of them to meet together) or externally driven pair generation. The product is a function of the temperature, as the probability of getting enough thermal energy to produce a pair increases with temperature, being approximately 1/exp(band gap / kT), where k is Boltzmann's constant and T is absolute temperature.

The probability of meeting is increased by carrier traps – impurities or dislocations which can trap an electron or hole and hold it until a pair is completed. Such carrier traps are sometimes purposely added to reduce the time needed to reach the steady state.

Doping

The property of semiconductors that makes them most useful for constructing electronic devices is that their conductivity may easily be modified by introducing impurities into their crystal lattice. The process of adding controlled impurities to a semiconductor is known as *doping*. The amount of impurity, or dopant, added to an *intrinsic* (pure) semiconductor varies its level of conductivity. Doped semiconductors are often referred to as *extrinsic*.

Dopants

The materials chosen as suitable dopants depend on the atomic properties of both the dopant and the material to be doped. In general, dopants that produce the desired controlled changes are classified as either electron acceptors or donors. A donor atom that activates (that is, becomes incorporated into the crystal lattice) donates weakly-bound valence electrons to the material, creating excess negative charge carriers. These weakly-bound electrons can move about in the crystal lattice relatively freely and can facilitate conduction in the presence of an electric field. (The donor atoms introduce some states under, but very close to the conduction band edge. Electrons at these states can be easily excited to conduction band, becoming free electrons, at room temperature.) Conversely, an activated acceptor produces a hole. Semiconductors doped with donor impurities are called *n-type*, while those doped with acceptor impurities are known as *p-type*. The n and p type designations indicate which charge carrier acts as the material's majority carrier. The opposite carrier is called the minority carrier, which exists due to thermal excitation at a much lower concentration compared to the majority carrier.

For example, the pure semiconductor silicon has four valence electrons. In silicon, the most common dopants are IUPAC group 13 (commonly known as *group III*) and group 15 (commonly known as *group V*) elements. Group 13 elements all contain three valence electrons, causing them to function as acceptors when used to dope silicon. Group 15 elements have five valence electrons, which allows them to act as a donor. Therefore, a silicon crystal doped with boron creates a p-type semiconductor whereas one doped with phosphorus results in an n-type material.

Carrier concentration

The concentration of dopant introduced to an intrinsic semiconductor determines its concentration and indirectly affects many of its electrical properties. The most important factor that doping directly affects is the material's carrier concentration. In an intrinsic semiconductor under thermal equilibrium, the concentration of electrons and holes is equivalent. That is,

$$n = p = n_i$$

Where n is the concentration of conducting electrons, p is the electron hole concentration, and n_i is the material's intrinsic carrier concentration. Intrinsic carrier concentration varies between materials and is dependent on temperature. Silicon's n_i, for example, is roughly 1×10^{10} cm^{-3} at 300 kelvins (room temperature).

In general, an increase in doping concentration affords an increase in conductivity due to the higher concentration of carriers available for conduction. Degenerately (very highly) doped semiconductors have conductivity levels comparable to metals and are often used in modern integrated circuits as a replacement for metal. Often superscript plus and minus symbols are used to denote relative doping concentration in semiconductors. For example, n^{+} denotes an n-type semiconductor with a high, often degenerate, doping concentration. Similarly, p^{-} would indicate a very lightly doped p-type material. It is useful to note that even degenerate levels of doping imply low concentrations of impurities with respect to the base semiconductor. In crystalline intrinsic silicon, there are approximately 5×10^{22} atoms/cm³. Doping concentration for silicon semiconductors may range anywhere from 10^{13} cm^{-3} to 10^{18} cm^{-3}. Doping concentration above about 10^{18} cm^{-3} is considered degenerate at room temperature. Degenerately doped silicon contains a proportion of impurity to silicon in the order of parts per thousand. This proportion may be reduced to parts per billion in very lightly doped silicon. Typical concentration values fall somewhere in this range and are tailored to produce the desired properties in the device that the semiconductor is intended for.

Effect on band structure

Band diagram of a $p^{+}n$ junction. The band bending is a result of the positioning of the Fermi levels in the p^{+} and n sides.

Doping a semiconductor crystal introduces allowed energy states within the band gap but very close to the energy band that corresponds with the dopant type. In other words, donor impurities create states near the conduction band while acceptors create states near the valence band. The gap between these energy states and the nearest energy band is usually referred to as dopant-site bonding energy or E_B and is relatively small. For example, the E_B for boron in silicon bulk is 0.045 eV, compared with silicon's band gap of about 1.12 eV. Because E_B is so small, it takes little energy to ionize the dopant atoms and create free carriers in the conduction or valence bands. Usually the thermal energy available at room temperature is sufficient to ionize most of the dopant.

Dopants also have the important effect of shifting the material's Fermi level towards the energy band that corresponds with the dopant with the greatest concentration. Since the Fermi level must remain constant in a system in thermodynamic equilibrium, stacking layers of materials with different properties leads to many useful electrical properties. For example, the p-n junction's properties are due to the energy band bending that happens as a result of lining up the Fermi levels in contacting regions of p-type and n-type material.

This effect is shown in a *band diagram*. The band diagram typically indicates the variation in the valence band and conduction band edges versus some spatial dimension, often denoted x. The Fermi energy is also usually indicated in the diagram. Sometimes the *intrinsic Fermi energy*, E_i, which is the Fermi level in the absence of doping, is shown. These diagrams are useful in explaining the operation of many kinds of semiconductor devices.

Preparation of semiconductor materials

Semiconductors with predictable, reliable electronic properties are necessary for mass production. The level of chemical purity needed is extremely high because the presence of impurities even in very small proportions can have large effects on the properties of the material. A high degree of crystalline perfection is also required, since faults in crystal structure (such as dislocations, twins, and stacking faults) interfere with the semiconducting properties of the material. Crystalline faults are a major cause of defective semiconductor devices. The larger the crystal, the more difficult it is to achieve the necessary perfection. Current mass production processes use crystal ingots between four and twelve inches (300 mm) in diameter which are grown as cylinders and sliced into wafers.

Because of the required level of chemical purity and the perfection of the crystal structure which are needed to make semiconductor devices, special methods have been developed to produce the initial semiconductor material. A technique for achieving high purity includes growing the crystal using the Czochralski process. An additional step that can be used to further increase purity is known as zone refining. In zone refining, part of a solid crystal is melted. The impurities tend to concentrate in the melted region, while the desired material recrystalizes leaving the solid material more pure and with fewer crystalline faults.

In manufacturing semiconductor devices involving heterojunctions between different semiconductor materials, the lattice constant, which is the length of the repeating element of the crystal structure, is important for determining the compatibility of materials.

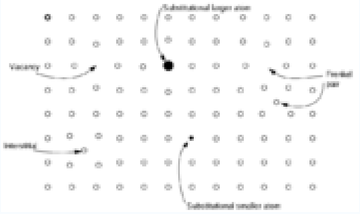
Crystal Imperfections:

Important as order is.

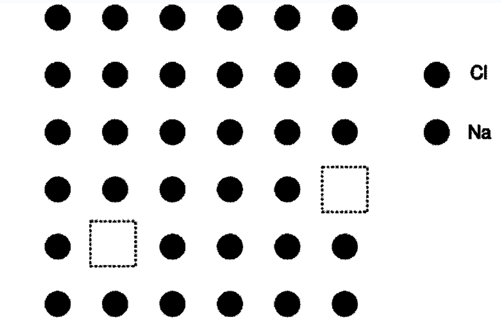
Imperfections reflect entropy

I. Point Defects:

a) Frenkel defects: Creation of a vacancy by removal to an interstitial position.
b) B) Schottky defects: In ionic crystals, vacancy formation occurs in such a way to maintain electrical neutrality.



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



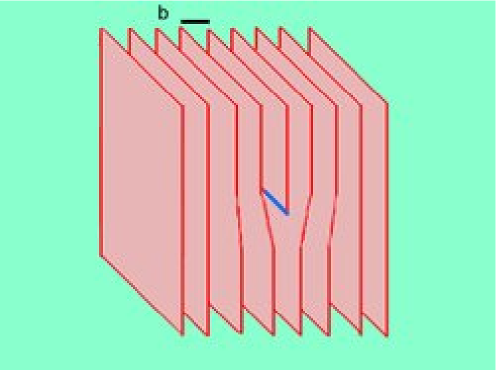
Schematic Schottky defects.

II. Line Defects (Dislocations):

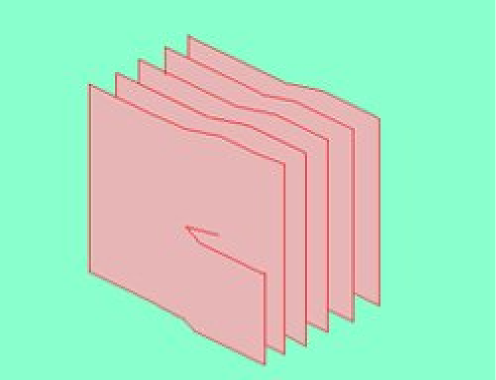
Occur during crystal growth. Two types:

a) Screw-Dislocation
b) Edge-Dislocation

Figures here



Edge-Dislocation



Screw Dislocation

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