

Sommerfeld's free electron theory of metals

Sommerfeld modified the free electron model by taking into account the Quantum Theory and Pauli Exclusion principle. Main assumptions of Sommerfeld are:

1. The free electrons are the valence electrons of the composing atoms. Thus the alkali metals are assumed to contain one free electron per atom while aluminium has three free electrons per atom.
2. A valence electron in metal finds itself in the field of all ions and that of all other electrons. In this model, the mutual repulsion between electrons is neglected and the potential field representing the attractive interaction of ions is assumed to be completely uniform everywhere inside the solid.

3. Since the electron emission can not be observed at room temperature, the potential energy of an electron at rest inside the metal is assumed to be lower than that of an electron outside the metal.

Thus the potential energy for an electron is periodic. The free electrons find themselves in the potential which is constant everywhere inside the metal but the potential outside the metal is very high which restrains the conduction electrons to remain inside the metal at room temperature.

Thus the metal surfaces are the sites of sharp potential barrier of height E_s .

This Fig 1. represents the physical model for metal where the interior is represented as consisting of a gas of electron confined by potential barrier within a certain region of space called a potential energy box of depth E_s .

Thus E_s represents the energy difference between an electron at rest inside the metal and one at rest in vacuum (i.e., on the surfaces). At $T = 0$ all energy levels upto E_F are filled while all higher ones are empty. Thus work function of metal $\phi = E_s - E_F$

E_F is called Fermi energy. It is defined as the maximum kinetic energy that a free electron can have at the absolute zero of temperature.

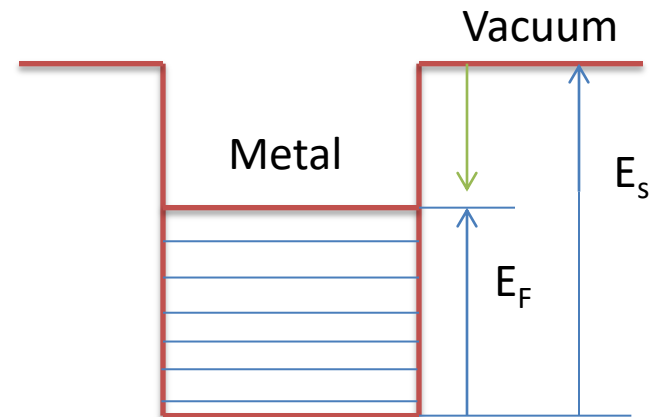


Fig 1.

4. The free electron gas in a solid does not obey the classical Maxwell Boltzmann statistical law. The distribution of energy in an electron gas obeys the Fermi-Dirac quantum statistics.

5. In a metal, the energy levels are filled in accordance with Pauli's exclusion principle according to which an energy level can accommodate at the most two electrons, one with spin up and other with spin down. Thus in filling the energy levels, two electrons in the metal have been accommodated.

Introduction to periodic potential & Kronig-Penny model (Qualitative)

The free electron theory was able to explain successfully many different phenomena such as the electrical conductivity, electron emission, electron paramagnetism etc.

However there are other electronic properties which could not be explained by free electron model. For example, the model fails to explain why some solids are conductors, some are semiconductors while some are insulators.

These and many other phenomena can be satisfactorily explained by the band theory of solids.

The simplest quantum mechanical view of the potential experienced by an electron in passing through the crystal is one which is perfectly periodic as shown in Fig 2.

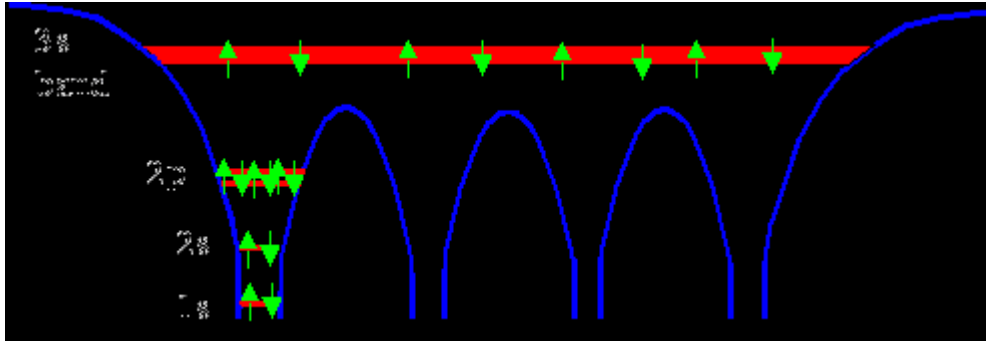


Fig 2.

The distribution of potential between the nuclei is a series of humps and increases at the boundary of the solid. The periodicity of the potential is the result of Coulomb interaction between the moving electron and the periodic charge distribution arising from the positive ions situated on the lattice sites. Thus the periodicity of the potential is equal to the periodicity of the lattice.

The solution of Schrodinger wave equation for the single electron in this one dimensional periodic crystal potential provides the set of one electron states which the electron may occupy.

The problem is simplified by replacing the periodic potential with rectangular barriers as shown in Fig 3. This is so called Kronig - Penny Model.

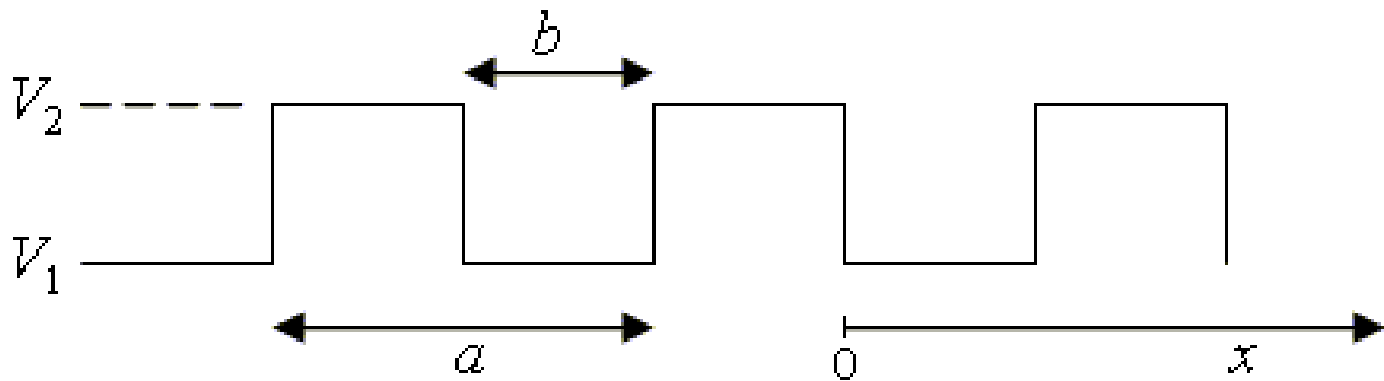


Fig 3.

The Schrödinger equations corresponding to the two regions are

$$d^2\psi/dx^2 + 2m/\hbar^2 E\psi = 0 \text{ [for } 0 < x < a],$$

$$d^2\psi/dx^2 + 2m/\hbar^2 (E - V_0)\psi = 0 \text{ [for } -b < x < 0]. \quad \dots(1)$$

The effect of the periodic potential on the wave function is to change the wave function of the electron $\exp(i\mathbf{K}x)$ to

$$\psi(x) = \exp(i\mathbf{K}x) U_{\mathbf{K}}(x).$$

$$K = \frac{\sqrt{2m(E - V(x))}}{\hbar} \quad \dots(2)$$

The modulating amplitude $u(x)$ almost unity at the center of the well and appreciably different from unity near the boundary of each well. Thus $u(x)$ repeats from the lattice to lattice and satisfies the condition

$$U(x)=u(x+a) \quad \dots(3)$$

where a is the lattice spacing. Eqs. (2) and (3) together are known as Bloch's theorem which is a mathematical statement regarding the form of one electron wave functions for a perfectly periodic potential.

Using Bloch's theorem and periodic boundary conditions for continuity of a wave function and its derivative, we get the condition for the solution of the wave equation to exist in the form

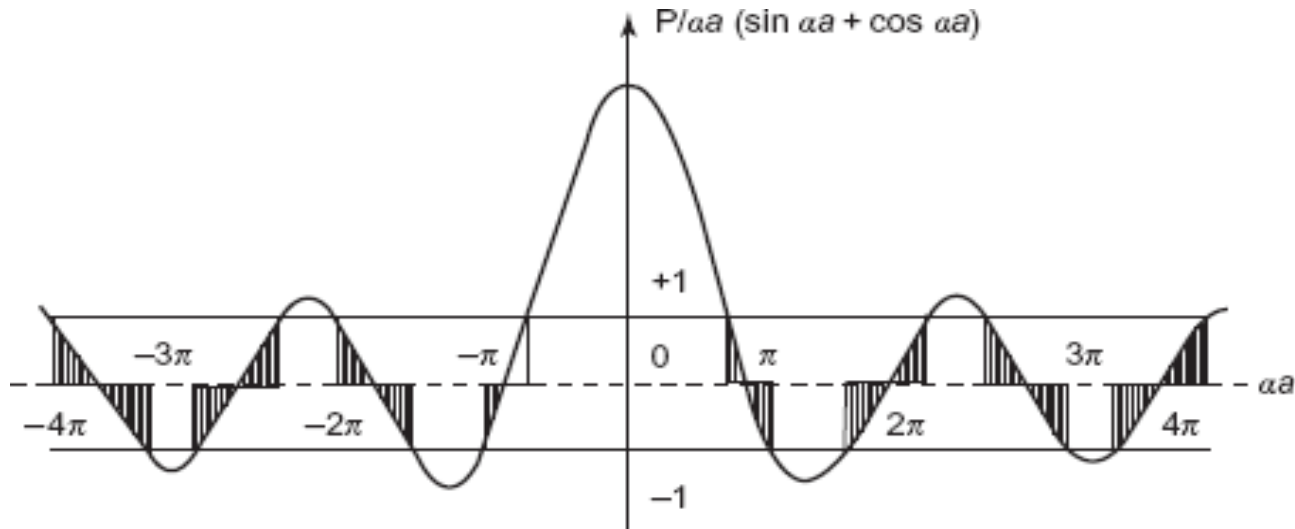
$$\cos Ka = P \sin \alpha a / \alpha a + \cos \alpha a \quad \dots(4)$$

where P and α are constants given by

$$P = \frac{mV_0ba}{\hbar^2} \quad \text{and} \quad \alpha = \frac{\sqrt{2mE}}{\hbar}$$

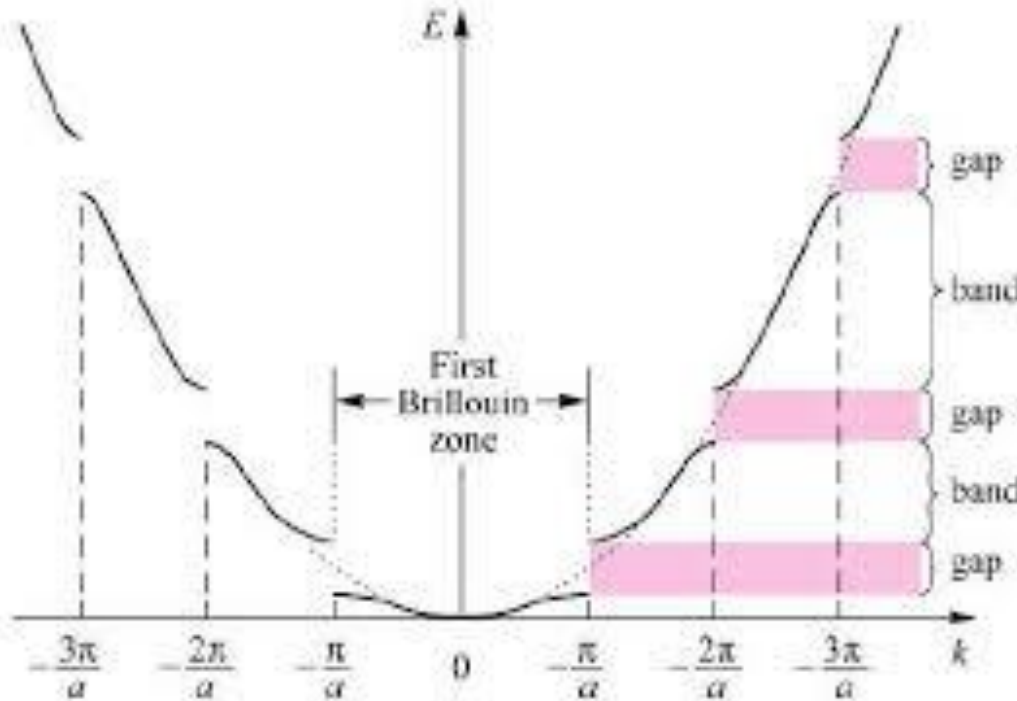
The allowed energy levels of an electron in a periodic potential can be obtained by the following interpretations:

Interpretation of the right hand side of equation:



1. There are allowed energy bands and forbidden energy regions.
2. As we go higher in energy, the energy bands become broader and the forbidden bands become narrower.

Interpretation of the left hand side of equation:



If we plot a curve showing the energy

$$E = \frac{K^2 \hbar^2}{2m}$$

As a function of $K\alpha$, then a dashed line parabola shown in Fig obtained. Discontinuities in the E versus $K\alpha$ occur for $\cos K\alpha = \pm 1$, when $K\alpha = \pm n\pi$ where $n=0,1,2,\dots$

The heavy lines in Fig show the plot of allowed energy values E versus $K\alpha$. When these allowed values are projected to the right, allowed bands are obtained. Between allowed bands there are forbidden bands shown in Fig.

The Band Theory of Solids

In case of a single isolated atom, there are discrete energy levels, 1s, 2s, 2p, 3s, ... that can be occupied by the electrons of atom, as shown in Fig 1. All the atoms of a solid, if assumed isolated from one another, can have completely identical electronic schemes of their energy levels. Then the electrons fill the levels in each atom independently.

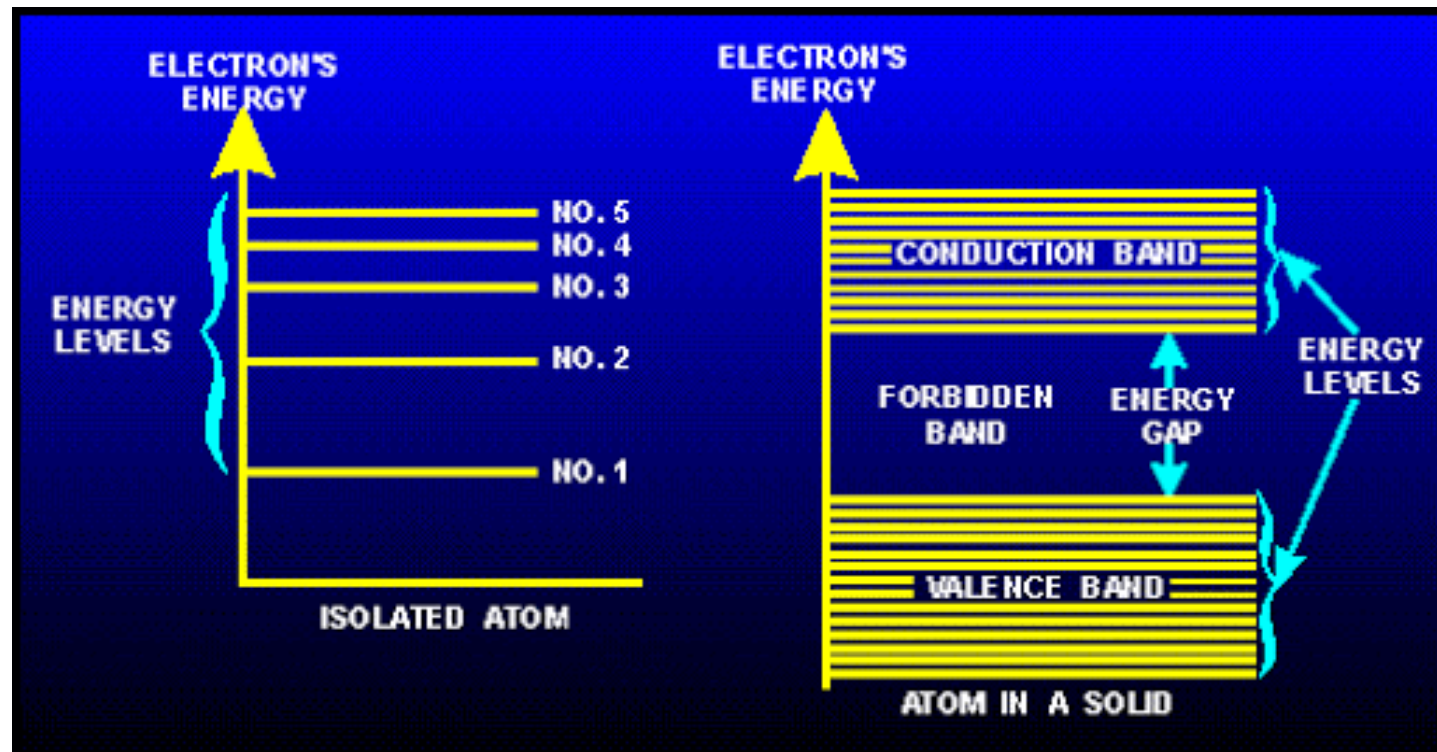


Fig 1.

As isolated atoms are brought together to form a solid, various interactions occur between neighboring atoms.

As a result of this interaction, the higher energy levels are considerably affected, i.e., the energy level of outer shells are slightly altered without violating Pauli's exclusion principle.

There will be splitting of single energy level of an isolated atom into a large no. of energy levels.

Since in a solid, many atom ($N = 10^{23}$ atoms/cm³) brought together, the separation between N sub-levels is very small.

For example, if there are 50 atoms in a piece of solid material, then there will be 50 levels of slightly different energies, i.e., 50 energy level diagrams would be superimposed on each other. Consequently, the split energy levels are almost continuous and are said to form an energy band.

Now, the energy band in a solid correspond to the energy levels in an atom.

As electron in a solid can have only those discrete energies that lie within these energy bands. These bands are, therefore, called allowed energy bands.

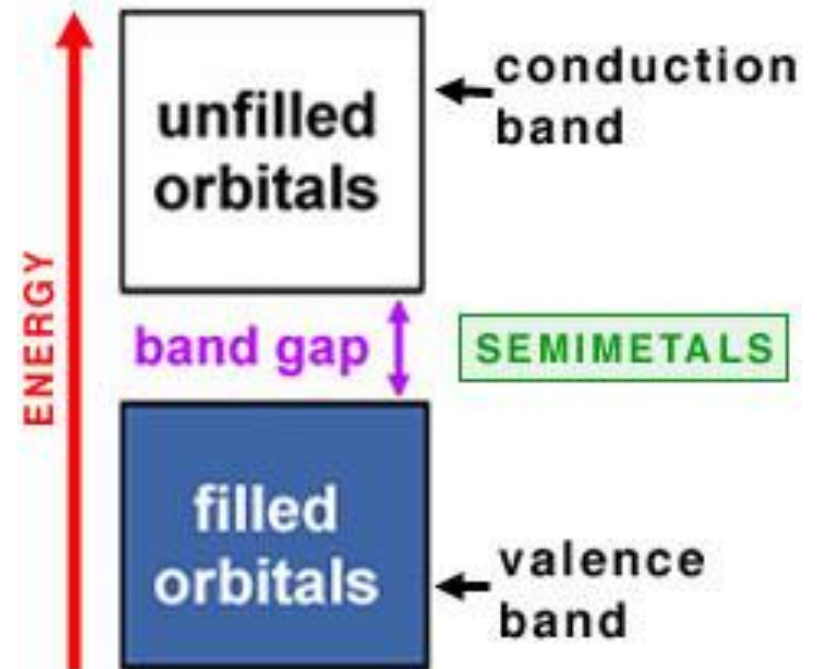
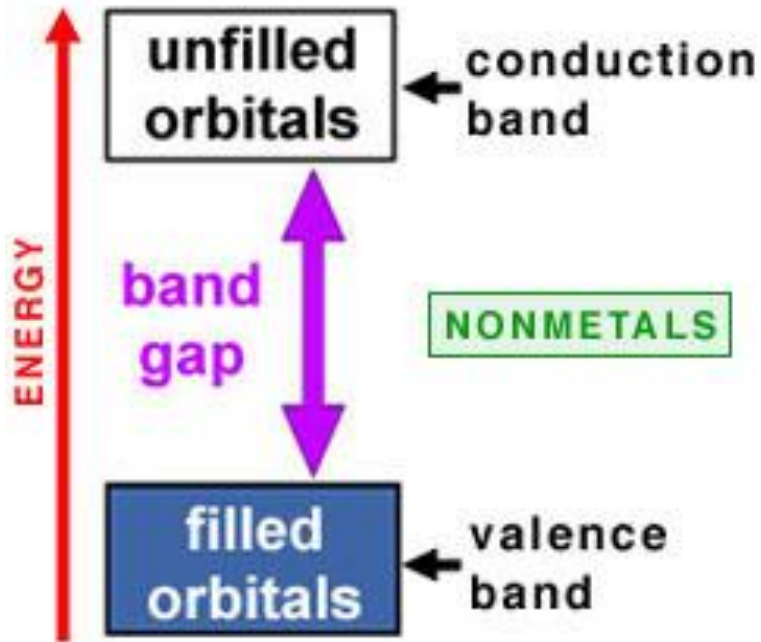
These allowed energy bands, in general, separated by some gaps which have no allowed energy levels. These gaps are known as forbidden energy bands.

Energy bands occupied by the valence electrons is called valence bands and obviously, the highest occupied band.

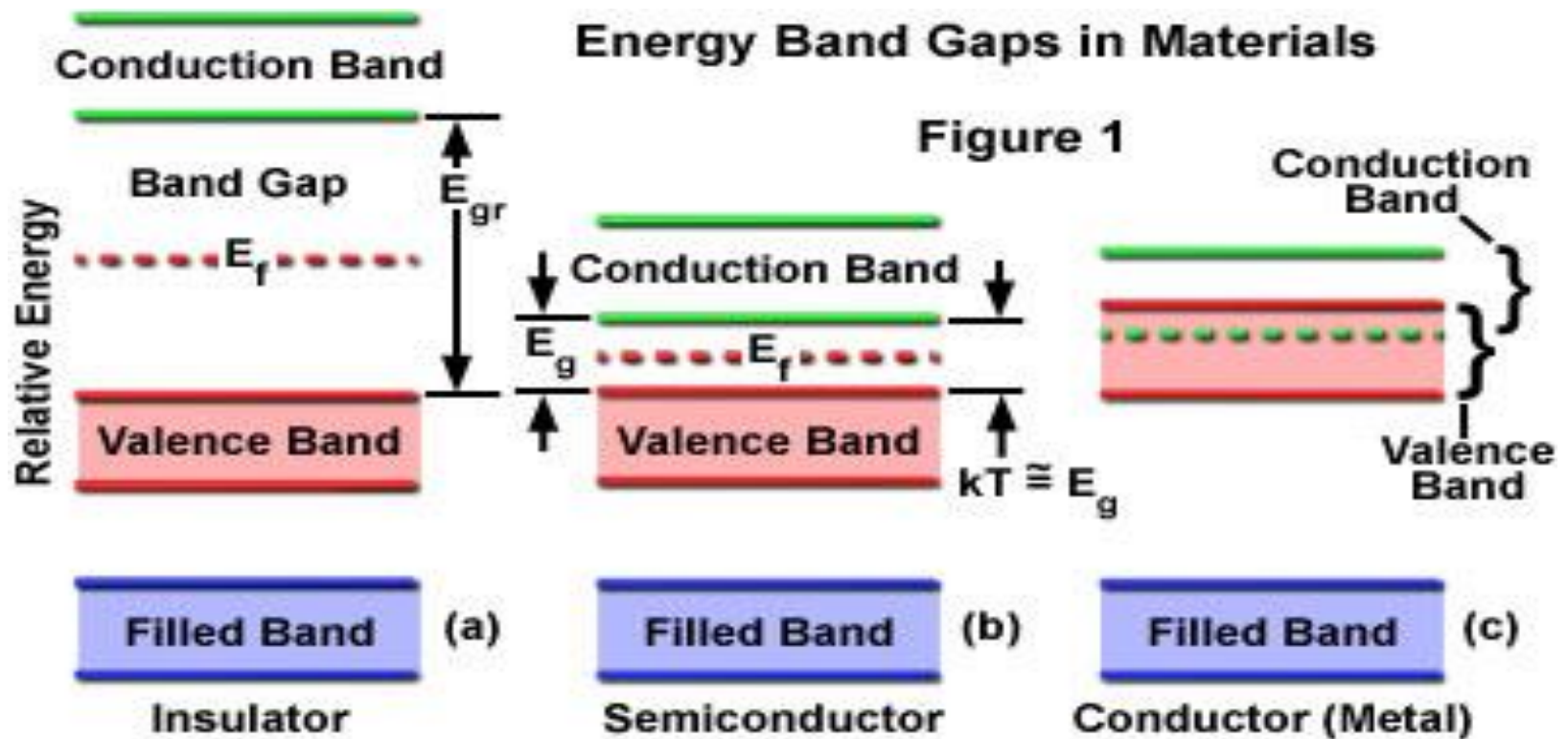
Electrons which have left the valence band are called conduction electrons and are only weakly bound to the nucleus. The bands occupied by these electrons is called the conduction bands.

Thus the band beyond forbidden band is called conduction band, into which, when the electron pass, they can move freely.

Bands and Gaps



Conductors, Insulators and Semiconductors



According to band theory, the electrons in a solid can possess bands of energies called allowed bands of energies and these electrons may not possess some other bands of energies called forbidden bands of energies.

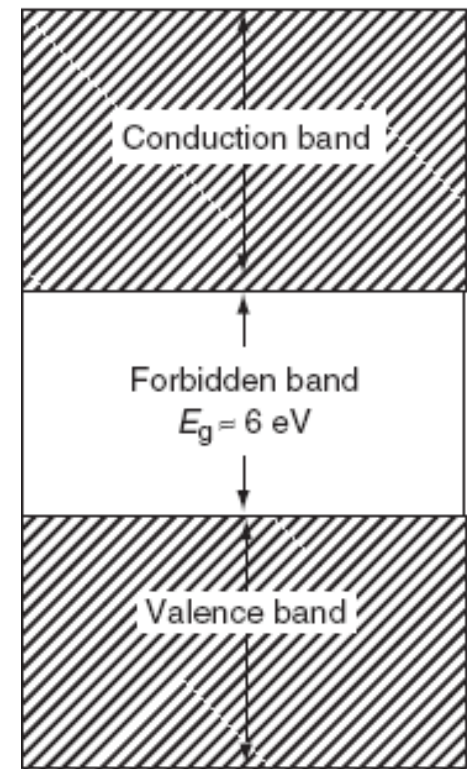
The allowed bands of energies and forbidden bands of energies are present alternatively one after another for the electrons of a solid.

The top-most band is called Conduction band and the next band below Conduction band is valance band. These two bands are separated by forbidden band.

1. Insulator: The valence band of those materials remains full of electrons.

The conduction band of those materials remains empty. The forbidden energy gap between the conduction band and the valence band is widest.

The difference is more than 4 eV. Crossing the forbidden energy gap from valence band to conduction band require large amount of energy. Mica, glass, eboniote etc are the examples of insulators.

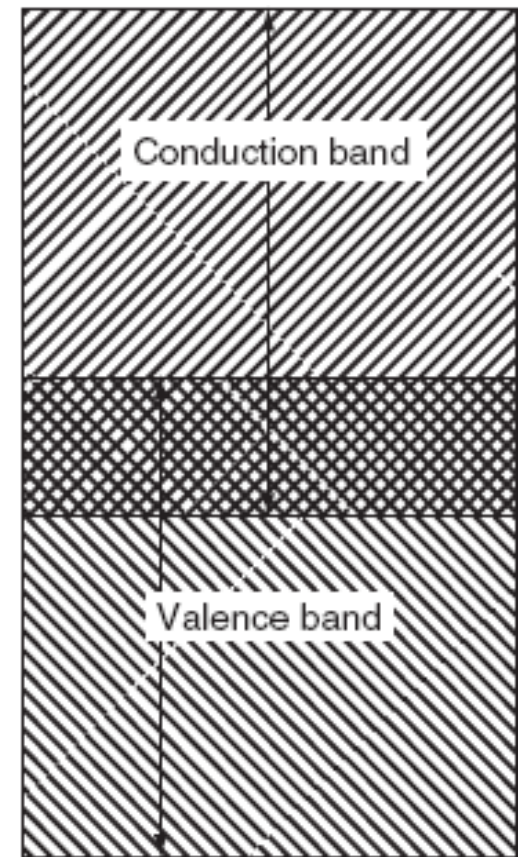


(a)

2. Conductors: The valence band and the conduction band overlap each other. There is no forbidden energy gap here so $E_g=0$. At absolute zero temperature large number of electrons remains in the conduction band.

The resistance of conductor is very low; large number charge carriers are available here.

So, the electricity can pass easily through the conductors. Aluminum, Silver, etc are good conductors.



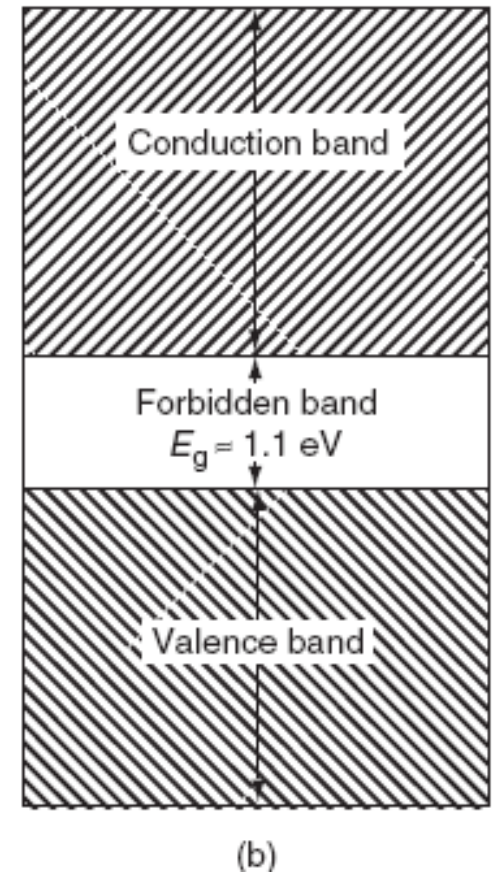
(c)

3. Semiconductors: A semiconductor remains partially full valence band and partially full conduction band at the room temperature. The energy gap is narrower.

The conduction band remains full empty of a semiconductor where the valence band remains full of electrons at absolute zero temperature.

The value of $E_g = 1.1\text{eV}$ for silicon crystal and $E_g = 0.7\text{eV}$ for germanium. It can easily overcome due to thermal agitation or light.

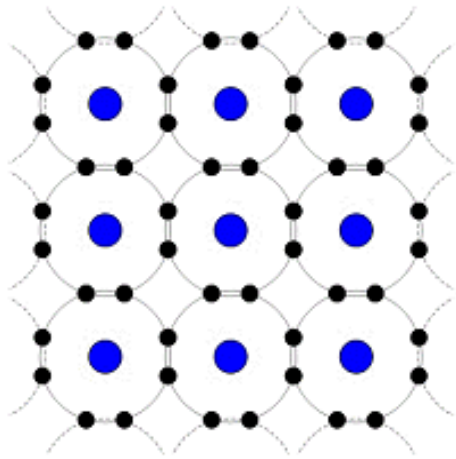
So, silicon and germanium are insulators at absolute zero temperature. On the other hand with the increasing of temperature the electrical conductivity of semiconductors increase.



Doped Semiconductors

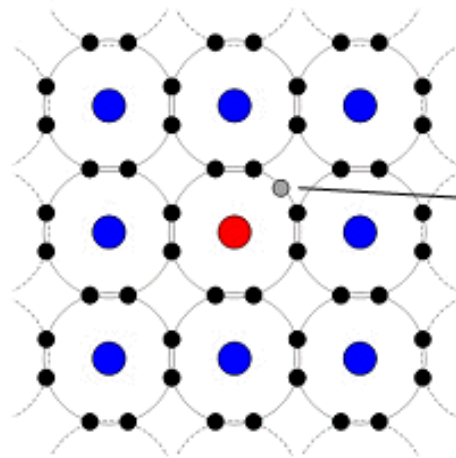
Pure Silicon

● Silicon nuclei



N-Type Silicon

● Phosphorous nucleus

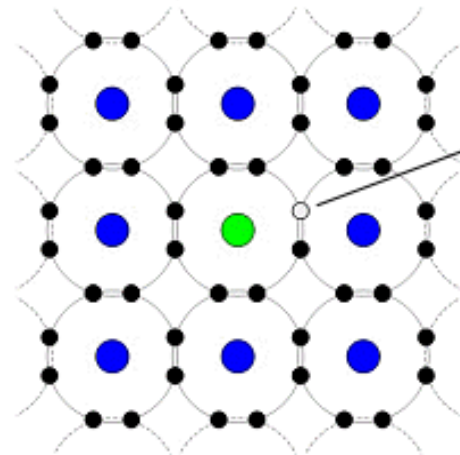


The phosphorous atom creates an extra electron.



P-Type Silicon

● Boron nucleus



The boron atom creates a hole. ○

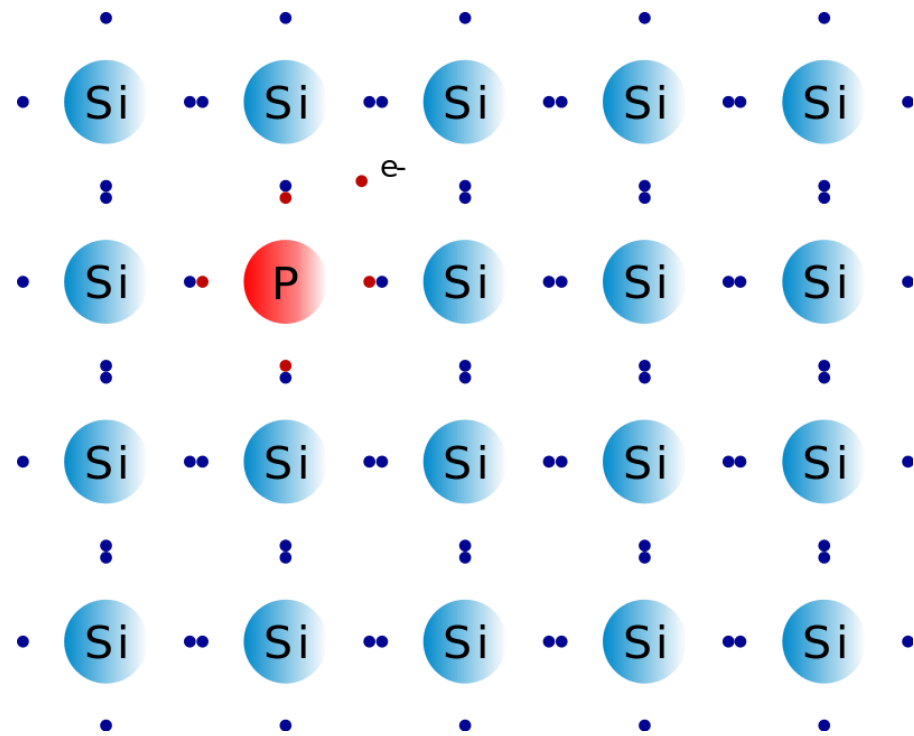
Doping is the process of adding impurities to intrinsic semiconductors to alter their properties. Normally Trivalent and Pentavalent elements are used to dope Silicon and Germanium. When an intrinsic semiconductor is doped with Trivalent impurity it becomes a P-Type semiconductor.

The P stands for Positive, which means the semiconductor is rich in holes or Positive charged ions. When we dope intrinsic material with Pentavalent impurities we get N-Type semiconductor, where N stands for Negative. N-type semiconductors have Negative charged ions or in other words have excess electrons in it.

Atoms follow a rule called Octet Rule. According to Octet-rule atoms are stable when there are eight electrons in their valence shell. If not, atoms readily accept or share neighboring atoms to achieve eight electrons in their valence shell.

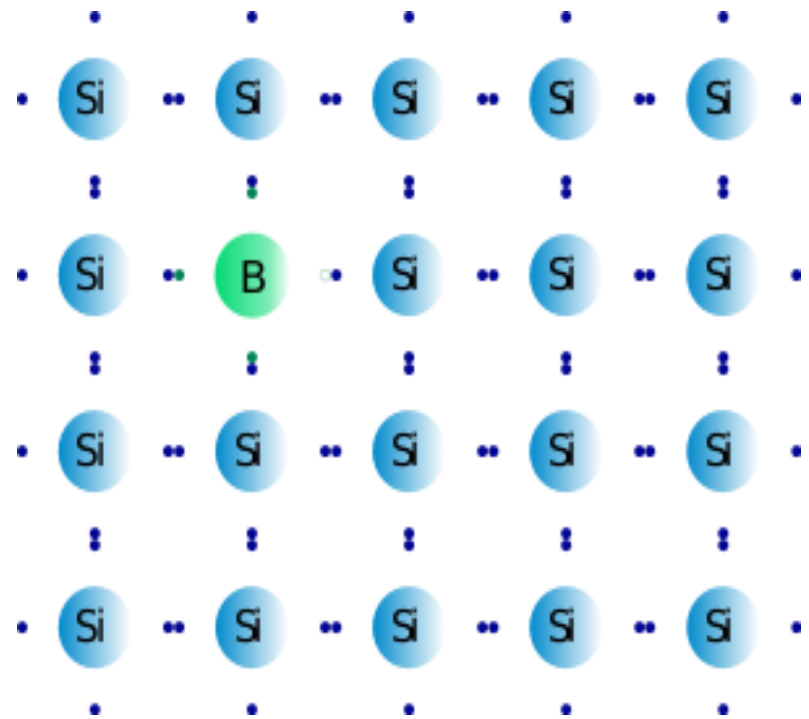
In the silicon lattice, each silicon atom is surrounded by four silicon atoms. Each silicon atom shares one of its electron in the valence shell to its neighboring silicon atom to satisfy the octet-rule. A schematic diagram of an intrinsic semiconductor is shown in image right (Figure : Intrinsic Silicon Lattice).

We have doped the silicon lattice with Phosphorous, a pentavalent element. Now pentavalent element has five electrons, so it shares an electron with each of the four neighbouring silicon atoms, hence four electrons are tied up with the silicon atoms in the lattice. This leaves an extra electron.



This excess electron is free to move and is responsible for conduction. Hence N-type (Negative Type) extrinsic semiconductor (silicon in this case) is made by doping the semiconductor with pentavalent element.

To create a P-type semiconductor, all we must do is to dope in a trivalent element into the lattice. A trivalent element has three electrons in its valence shell. It shares three electrons with three neighboring silicon atoms in the lattice, the fourth silicon atom demands an electron but the trivalent atom has no more electron to share.



This creates a void in lattice which we call it has hole. Since the electron is deficient, the hole readily accepts an electron, this makes it a P-type (Positive type) extrinsic semiconductor.

Photoconductivity

Photoconductivity is an optical and electrical phenomenon in which a material becomes more electrically conductive due to the absorption of electromagnetic radiation such as visible light, ultraviolet light, infrared light, or gamma radiation.

When light is absorbed by a material such as a semiconductor, the number of free electrons and electron holes increases and raises its electrical conductivity.

To cause excitation, the light that strikes the semiconductor must have enough energy to raise electrons across the band gap, or to excite the impurities within the band gap.

When a bias voltage and a load resistor are used in series with the semiconductor, a voltage drop across the load resistors can be measured when the change in electrical conductivity of the material varies the current through the circuit.

Classic examples of photoconductive materials include :

- ❑ the conductive polymer polyvinylcarbazole, used extensively in photocopying (xerography);
- ❑ lead sulfide, used in infrared detection applications, such as the U.S. Sidewinder and Soviet (now Russian) Atoll heat-seeking missiles;
- ❑ selenium, employed in early television and xerography.

Applications

When a photoconductive material is connected as part of a circuit, it functions as a resistor whose resistance depends on the light intensity. In this context, the material is called a photoresistor (also called *light-dependent resistor* or *photoconductor*). The most common application of photoresistors is as photodetectors, i.e. devices that measure light intensity. Photoresistors are not the *only* type of photodetector—other types include charge-coupled devices (CCDs), photodiodes and phototransistors—but they are among the most common. Some photodetector applications in which photoresistors are often used include camera light meters, street lights, clock radios, infrared detectors, nanophotonic systems and low-dimensional photo-sensors devices

Negative photoconductivity

Some materials exhibit deterioration in photoconductivity upon exposure to illumination. One prominent example is hydrogenated amorphous silicon (a-Si:H) in which a metastable reduction in photoconductivity is observable.

Other materials that were reported to exhibit negative photoconductivity include molybdenum disulfide, graphene, indium arsenide nanowire, and metal nanoparticles.

Magnetic photoconductivity

In 2016 it was demonstrated that in some photoconductive material a magnetic order can exist.

One prominent example is $\text{CH}_3\text{NH}_3(\text{Mn:Pb})\text{I}_3$. In this material a light induced magnetization melting was also demonstrated thus could be used in magneto optical devices and data storage.

Photoconductive Cell

Photoconductive cell is a two terminal semiconductor device. Its resistance will vary (linearly) with the intensity of the incident light. It is frequently known a **photo-resistive device**.

The photoconductive materials most frequently used include cadmium sulphide (CdS) and Cadmium selenide (CdSe). Both materials reasonably rather slowly to changes in light intensity. The spectral response time of CdS units is about 100 ms and 10 ms for CdSe cells.

Another important unlikeness between the two materials is their temperature sensitivity.

There is large change response of a cadmium sulphide in applications where the resistance of a cadmium selenide cell with changes in ambient temperature.

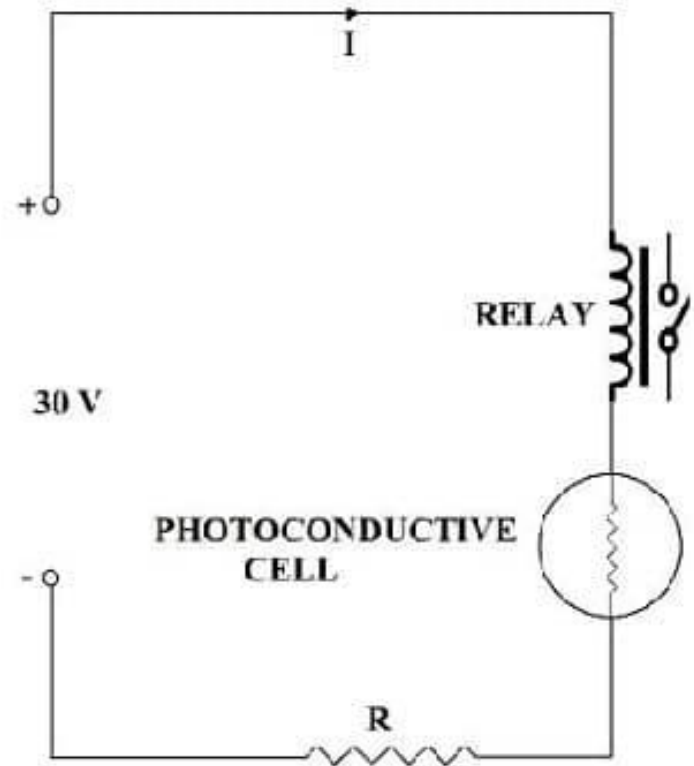
But the resistance of cadmium sulphide remains relatively stable. The spectral response of a cadmium sulphide cell closely matches that of the human eye. That is why the cell is therefore often finds applications where human vision is a factor. For example street light control or automatic iris control for cameras.

The main elements of a photo-resistive device are **ceramic substrate, a layer of photoconductive material, metallic electrodes** to connect the device into a circuit and a **moisture resistant enclosure**.

Applications of Photoconductive Cell

The photoconductive cell used for relay control. When the cell is lit up. Then its resistance is less and the relay current is at its maximum.

When the cell is dark, its high resistance reduces the current down to a level too low to energize the relay. Resistance R is to limit the relay current to desired level when the resistance of the cell is low.



Drawbacks

Temperature variations cause substantial variations in resistance for a particular light intensity.

Therefore such cell is unsuitable for analog applications. Such cells find wide use in industrial and laboratory control applications.

Photovoltaic Cell

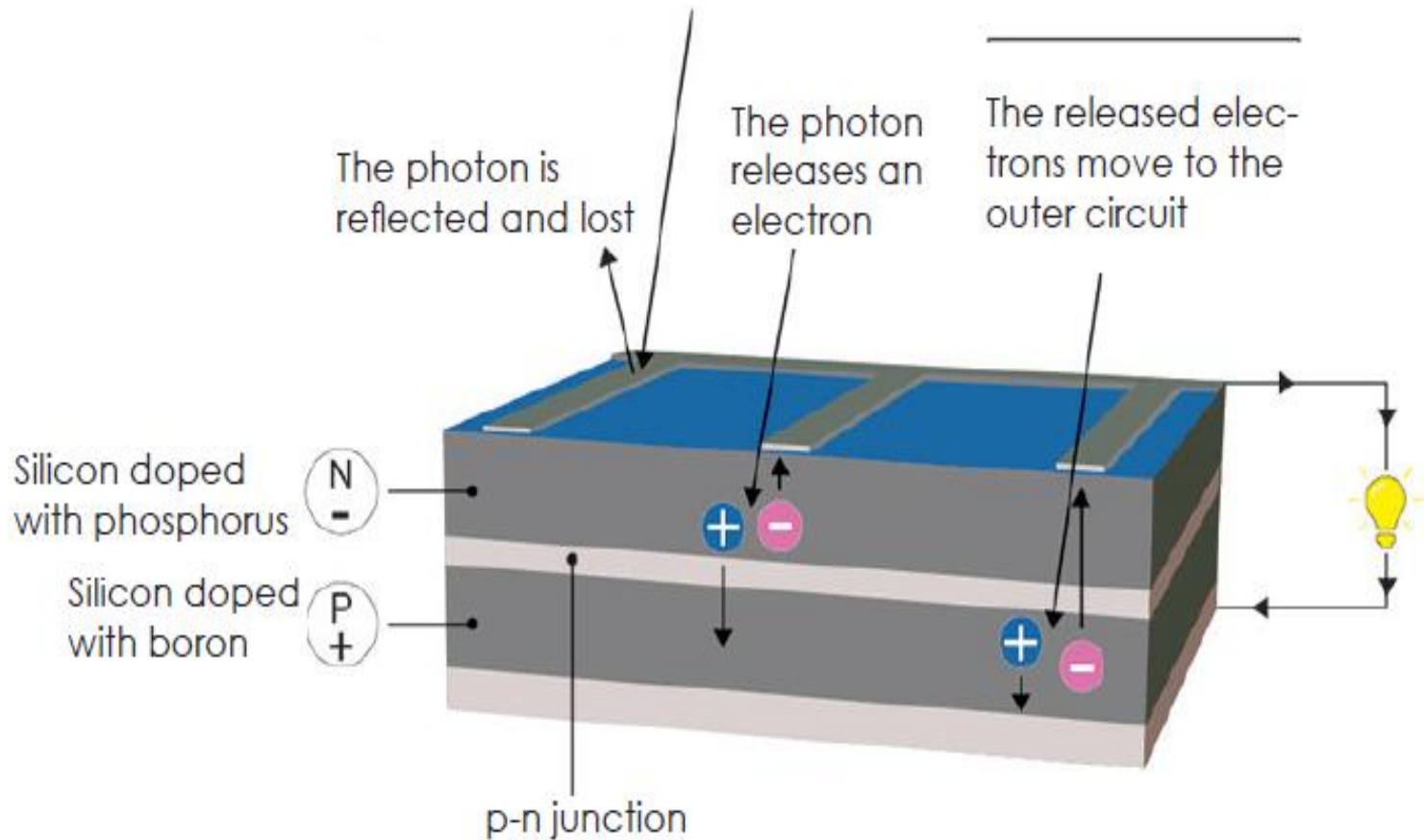
A photovoltaic (PV) cell, also known as a solar cell, is an electronic component that generates electricity when exposed to photons, or particles of light.

This conversion is called the photovoltaic effect, which was discovered in 1839 by French physicist Edmond Becquerel.

It was not until the 1960s that photovoltaic cells found their first practical application in satellite technology.

Solar panels, which are made up of PV cell modules, began arriving on rooftops at the end of the 1980s.

HOW A PHOTOVOLTAIC CELL WORKS



How a Photovoltaic Cell Works

A photovoltaic cell is made of semiconductor materials that absorb the photons emitted by the sun and generate a flow of electrons.

Photons are elementary particles that carry solar radiation at a speed of 300,000 kilometers per second. In the 1920s, Albert Einstein referred to them as “grains of light”.

When the photons strike a semiconductor material like silicon, they release the electrons from its atoms, leaving behind a vacant space.

The stray electrons move around randomly looking for another “hole” to fill.

To produce an electric current, however, the electrons need to flow in the same direction.

This is achieved using two types of silicon. The silicon layer that is exposed to the sun is doped with atoms of phosphorus, which has one more electron than silicon, while the other side is doped with atoms of boron, which has one less electron.

The resulting sandwich works much like a battery: the layer that has surplus electrons becomes the negative terminal (n) and the side that has a deficit of electrons becomes the positive terminal (p).

An electric field is created at the junction between the two layers.

When the electrons are excited by the photons, they are swept to the n-side by an electric field, while the holes drift to the p-side.

The electrons and holes are directed to the electrical contacts applied to both sides before flowing to the external circuit in the form of electrical energy.

This produces direct current. An anti-reflective coating is added to the top of the cell to minimize photon loss due to surface reflection.

Photovoltaic Cell Efficiency

Efficiency is the ratio of electrical power produced by the cell to the amount of sunlight it receives.

To measure efficiency, the cells are combined into modules, which are in turn assembled into arrays.

The resulting panels are then placed in front of a solar simulator that mimics ideal sunlight conditions: 1,000 watts (W) of light per cubic meter at an ambient temperature of 25°C.

The electrical power produced by the system, or peak power, is a percentage of the incoming solar energy.

If a panel measuring one square meter generates 200 W of electrical power, it has an efficiency of 20%.

The maximum theoretical efficiency of a PV cell is around 33%. This is referred to as the Shockley-Queisser limit.

In real life, the amount of electricity produced by a cell, known as its output, is based on its efficiency, the average annual sunshine of the surrounding area and the type of installation.

Incident solar radiation varies significantly, measuring 1 megawatt-hour per square meter per year (MWh/sq.m/y) in the Paris area versus roughly 1.7 MWh/sq.m/y in southern France and nearly 3 MWh/sq.m/y in the Sahara Desert.

This means that a solar panel with a 15% efficiency rating will generate 150 kWh/sq.m/y in Paris and 450 kWh/sq.m/y in the Sahara.

Different Types of Photovoltaic Cells

- ☐ Crystalline Silicon Cells
- ☐ Thin-Film Cells
- ☐ Organic Cells
- ☐ Perovskites

Superconductivity

Superconductivity is the set of physical properties observed in certain materials, wherein electrical resistance vanishes and from which magnetic flux fields are expelled.

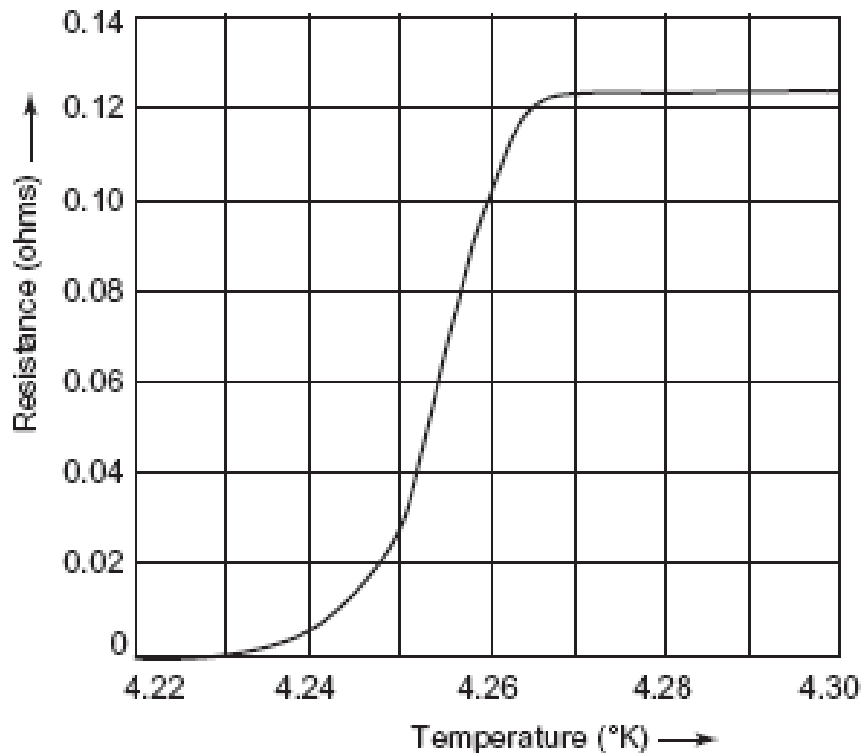


Figure 1 Temperature dependence of the resistance of Hg. First experiment on superconductivity

superconductor has a characteristic critical temperature below which the resistance drops abruptly to zero. An electric current through a loop of superconducting wire can persist indefinitely with no power source

Meissner effect

In Figure 2(a1), the specimen is a spherical ball of lead in the normal state, that is, $T > T_c$ and a finite value of magnetic field ($H \neq 0$) has been applied. Magnetic lines of force pass through the inside and outside of the ball. In Figure 2(a2), the ball has been cooled below T_c (i.e. in the superconducting state), the magnetic lines of force have been expelled from the body of the sample, that is ($H = 0$).

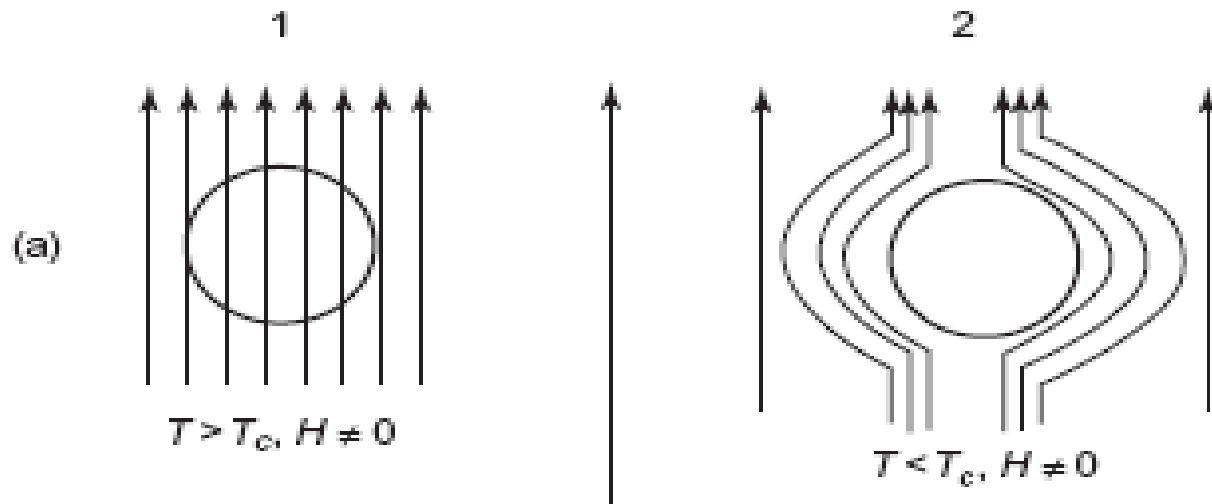
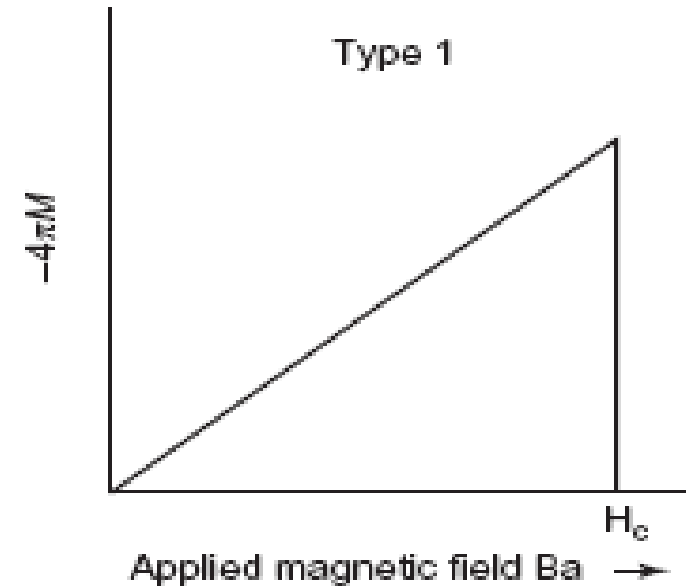


Figure 2

Type 1 and Type 2 Superconductors

In Type 1 superconductors, the flux is totally ejected out and is a case of complete Meissner effect.

The superconductor comes into normal state after the application of H_c , which is a small field of the order of a few hundred gauss, and such materials cannot be put to any technical use. Pure elements generally belong to Type 1 and are known as the soft superconductors.



In Type 2 superconductors, the flux starts being ejected out after the field H_{c1} and is completely ejected out at the field H_{c2} , after which the superconductor comes into normal state. The difference between H_{c1} and H_{c2} is big, sometimes ≈ 100 times greater than H_{c1} . H_{c2} can be as high as ≈ 200 kG. In building powerful magnets and for all other practical purposes, Type 2 superconductors are used.

They are known as hard superconductors and are generally alloys or transition metals, whose normal state resistivities are quite high or the mean free path of electrons " l " is small. In the region between H_{c1} and H_{c2} the superconductor is threaded by flux lines and is said to be in the vortex state.

