# Energy Bands in Solids

Formation of Bands in Solids

The formation of energy bands in solids arises from the overlap of atomic orbitals when atoms come together to form a solid. Here's how it occurs:
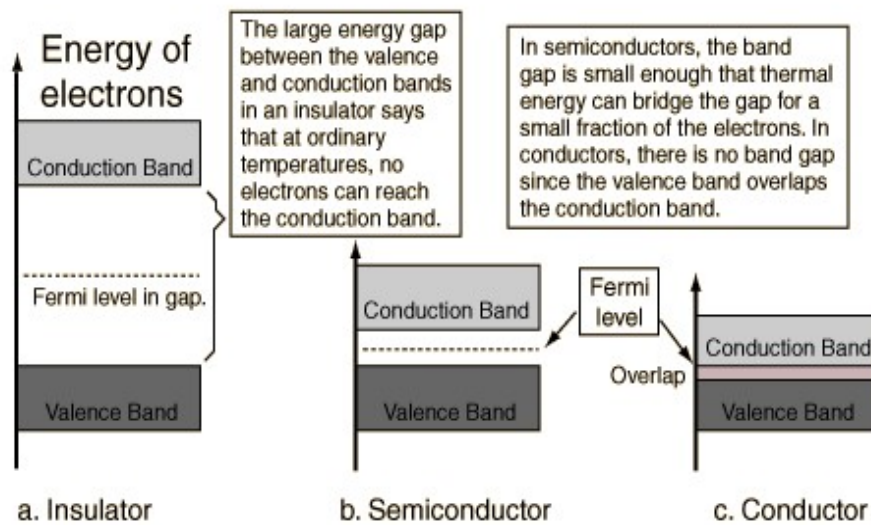
1. **Atomic Orbitals**: In isolated atoms, electrons occupy discrete energy levels corresponding to their atomic orbitals.

2. **Close Packing**: When atoms are brought close together, their atomic orbitals begin to overlap. This overlap causes the discrete energy levels to split into many closely spaced energy levels.

3. **Band Formation**: As the number of atoms increases, the energy levels form continuous bands:

   o   The overlapping atomic orbitals combine to create a range of energy levels.

   o   Each energy band can accommodate a certain number of electrons, determined by the Pauli exclusion principle.
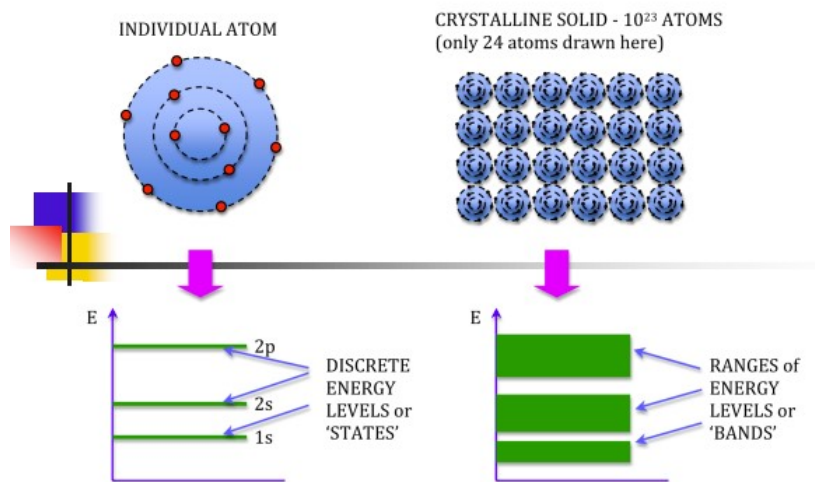
4. **Valence and Conduction Bands**:

The lower energy band formed from the bonding orbitals is called the valence band, while the higher energy band, consisting of the antibonding orbitals, is known as the conduction band.

The presence of a band gap between these two bands arises due to the energy difference between the filled (valence) and empty (conduction) states.

Energy of electrons

Conduction Band

Fermi level in gap.

Valence Band

a. Insulator

The large energy gap between the valence and conduction bands in an insulator says that at ordinary temperatures, no electrons can reach the conduction band.

Conduction Band

Valence Band

b. Semiconductor

In semiconductors, the band gap is small enough that thermal energy can bridge the gap for a small fraction of the electrons. In conductors, there is no band gap since the valence band overlaps the conduction band.

Fermi level

Overlap

Conduction Band

Valence Band

c. Conductor

Consider a neutral sodium atom, the ground state configuration of isolated Na atom is $1s^2 2s^2 2p^6 3s^1$. $1s^2 2s^2 2p^6$ is completely filled while $3s^1$ is half filled, each occupying a specific energy level as indicated in fig. The energy levels of sodium become bands when the atoms lie close together. For large atomic distances, the interactions between atoms are negligible and the energy levels remain un-splitted. With the decrease in interatomic distance, 3s level splits into bands and with further decrease in distance, 2p level also starts to split. 1s and 2s levels does not split at all. If there are N atoms in a solid, there are N allowed states in each band. Each state can be occupied by a maximum of two electrons with opposite spin. Thus, each band can be occupied by 2N electrons. In figure, r_o represents the spacing between atoms in solid sodium. When the atoms are part of a solid, they interact with each other, and the electrons have slightly different energies.
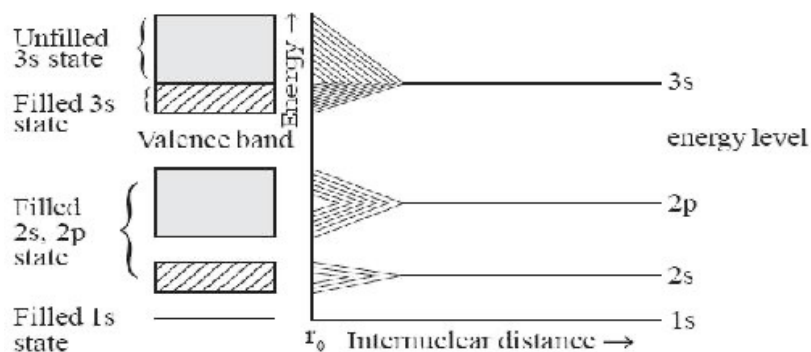

Fig: energy level diagram of sodium

Conduction Band, Valence Band, and Forbidden Energy Gap in Solids

1. Valence Band:

- The valence band is the energy band that contains the electrons responsible for chemical bonding and electrical conductivity in solids. It is filled with electrons that are involved in bonding between atoms.

- The top of the valence band is the highest energy level that is occupied by electrons at absolute zero temperature.

2. Conduction Band:

- The conduction band is the energy band above the valence band. It contains the energy levels that electrons can occupy when they gain enough energy to break free from the bonds holding them in the valence band.

- Electrons in the conduction band are free to move throughout the material, contributing to electrical conductivity.

3. Forbidden Energy Gap (Band Gap):

- The forbidden energy gap (or band gap) is the energy difference between the valence band and the conduction band. It represents the energy required for an electron to transition from the valence band to the conduction band.

- The size of the band gap determines the electrical and optical properties of a material:

  - **Conductors**: No band gap, as the conduction and valence bands overlap (e.g., metals).

  - **Semiconductors**: Small band gap (typically less than 3 eV), allowing for some electron excitation at room temperature (e.g., silicon).

  - **Insulators**: Large band gap (greater than 3 eV), making it difficult for electrons to jump from the valence band to the conduction band (e.g., glass).

Classification of Metals, Semiconductors, and Insulators

We can classify the materials into 3 categories, based on the band gap between the conduction and valence band

Metal- If the conduction and valence bands overlap, electrons are free to roam inside material due to the overlapping of the valence and conduction bands. Electrons don't need extra energy to jump in the conduction band.

Semiconductor- If there exists some energy difference (< 3 eV) between the valence and conduction band, in that case, electrons need to excitation energy (< 3 eV) to be in a state of free conduction (i.e. to jump into the conduction band).

Insulators- If there exists a large energy difference between the valence and conduction band (> 3eV), materials are called insulators. Electrons need very large energy to be in the state of free roaming through materials.

The energy difference between valence and conduction bands is always measured from the valence band maxima to the conduction band minima.
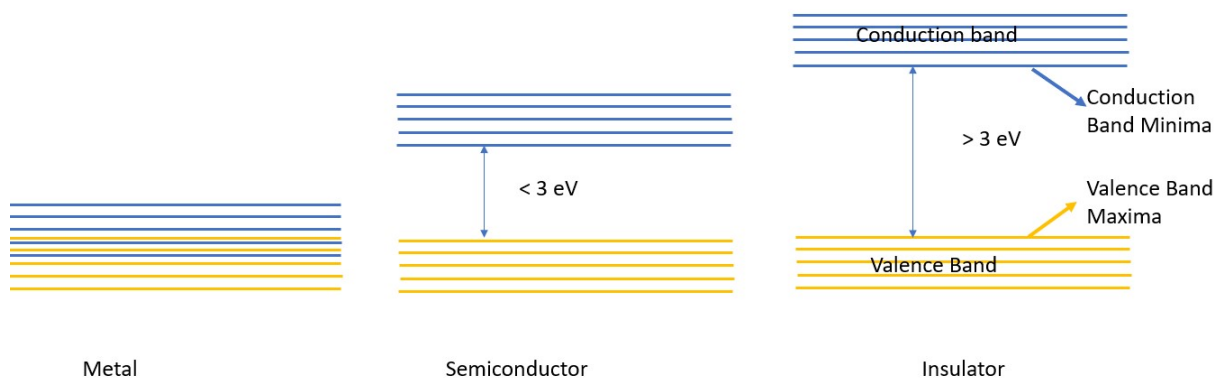

Figure – Classification of metal, semiconductor, and insulators based on the energy difference between valence and conduction bands.

Fermi Dirac Distribution Function

- **Fermi Dirac Distribution Function Definition**: The Fermi Dirac distribution function describes the probability that a fermion, such as an electron, will occupy a particular energy level at a given temperature.

- **Material Conductivity**: This function is essential in electronics for understanding how many free electrons are available to conduct electricity in a material

- **Energy Band Theory**: The distribution function ties into energy band theory, helping to explain the concentration of electrons in the conduction band.

- **Temperature Effects**: The Fermi-Dirac distribution function shows how electron energy states change with temperature, affecting the material's conductive properties.

Fermi Dirac Distribution Expression

Mathematically the probability of finding an electron in the energy state E at the temperature T is expressed as

$$f(E) = \frac{1}{1 + e^{\left(\frac{E - E_f}{K_B T}\right)}} \quad \ldots\ldots (1)$$
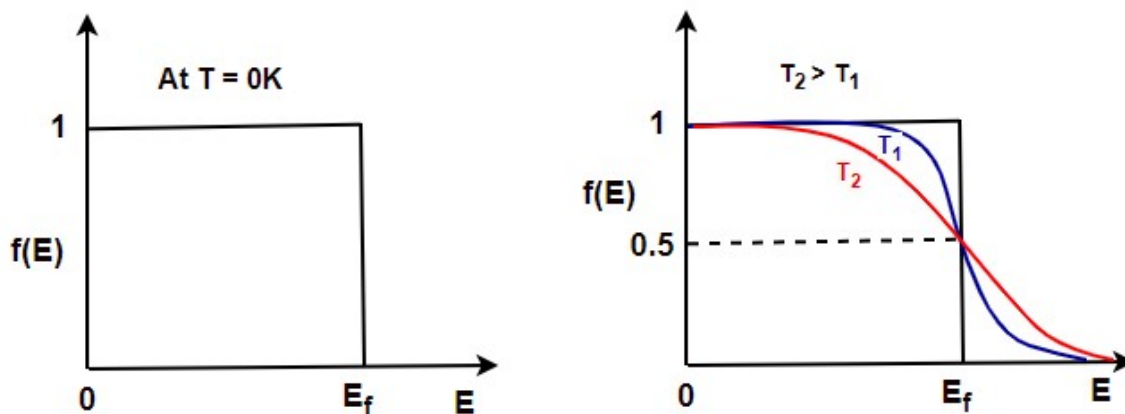
Where,

$K_B = 1.38 \times 10^{-23} JK^{-1}$ is the Boltzmann constant
T is the absolute temperature
E_f is the Fermi level or the Fermi energy

Lets discuss the following cases to understand the significance of Fermi Dirac function.
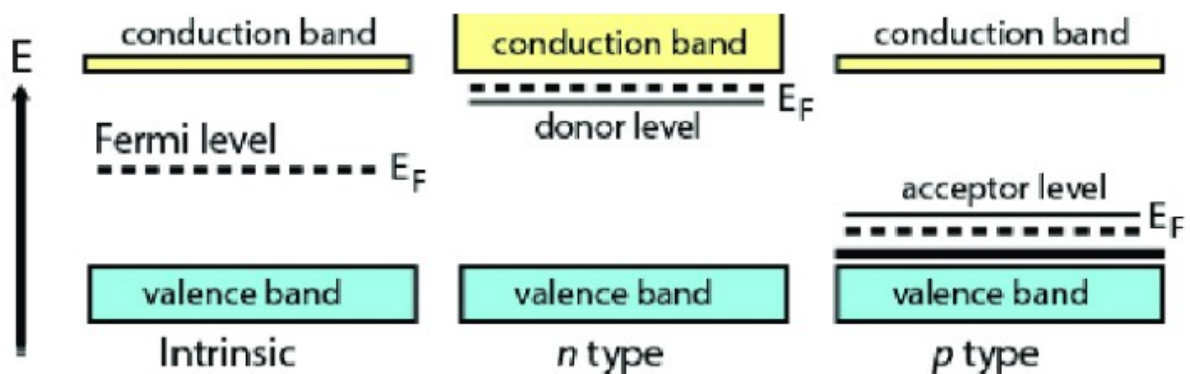
At temperature T = 0 K,

$$f(E) = \begin{cases} 1; & \text{if } E < E_f \\ 0; & \text{if } E > E_f \end{cases}$$

This means at 0 kelvin all the energy states below the Fermi energy are occupied and all energy state above E_f are unoccupied. At 0 kelvin f(E) is just a delta function. Also at any temperature T, for $E = E_f$; f(E) = 1/2.

if we increase the temperature some of the states above E_f will get populated. If we further increase the temperature (T_2), f(E) will increase. However, irrespective of temperature, probability at Fermi energy E_f will always be half.

Fermi Level

The highest energy level that an electron can occupy at the absolute zero temperature is known as the Fermi Level. The Fermi level lies between the valence band and conduction band for intrinsic semiconductor because at absolute zero temperature, the electrons are all in the lowest energy state.

Superconductors

The phenomenon of superconductivity was discovered by Kammerlingh Onnes in 1911 when he measures the resistivity of pure mercury drops at low temperature. He observed that electrical resistivity of pure mercury drops to zero at temperature about 4.2K. Kammerlingh Onnes recognize this a new phenomenon in which mercury has passes into a new state called as superconductivity.

When a substance loss its electrical resistance i.e. a current can continue through it without changing its value, the phenomenon is known as superconductivity.

Or

When electrical resistance of a substance drops suddenly to zero when it is cooled below a certain temperature, the phenomenon is known as superconductivity. The substance showing this property known as superconductors.

Example: Mercury, silver, lead, gallium, iridium etc.

Temperature dependence of resistivity in superconductors

Metals are good conductors of electricity as they have plenty of free electrons, however they offer resistance to the flow of charges. Even at 0K, the metals offer some resistance called residual resistance (Fig1).


Fig. (1) Variation of resistivity of a metal with temperature.
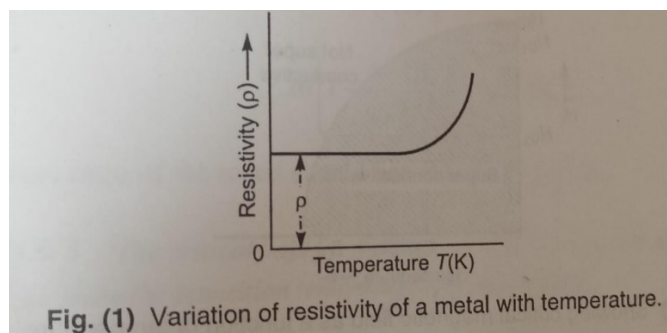
On contary, the resistance of superconductors in non-superconducting state decreases with decrease as in case of normal metal. But at a particular temperature Tc, the resistivity abruptly drops to zero. **The temperature at which a normal material turn into superconductor is known as critical temperature.**

Fig. (2) Dependence of resistivity on temperature
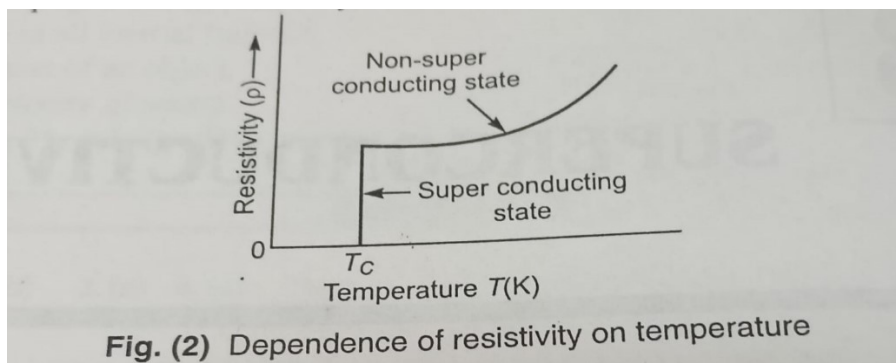
Effect of External Field

In 1913 Kammerlingh Onnes observed that superconductivity is destroyed if a sufficient strong magnetic field is applied. The superconducting material restores its normal resistance when a strong magnetic field is applied. The minimum magnetic field which is necessary to regain the normal resistivity is called **critical field (H_c)**. If the applied magnetic field exceeds the critical value $H_C(0)$, the superconducting state is destroyed. The variation of H_C w.r.t. T is shown in figure.

Variation In Critical Magnetic
Field with The Temparature
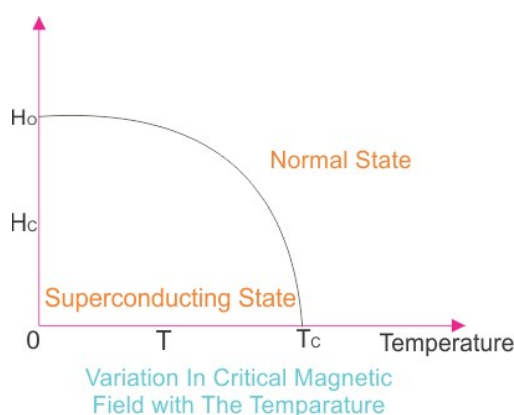
The dependence of critical field upon the temperature is given by

$$H_C(T) = H_C(0)\left[1 - \frac{T^2}{T_C^2}\right]$$

$H_c(T)$ is critical field at T temperature,

$H_c(0)$ is critical field at absolute zero (0K) temperature,

T_c is critical temperature or transition temperature

Isotopic effect

In superconducting materials, the transition temperature varies with the average isotopic mass of their constituents. The variation is found to be in general form

$$T_C \propto M^{-\alpha}$$

Or $T_C M^{-\alpha} = \text{constant}$

Where α is the isotopic effect coefficient and is defined as

$$\alpha = \frac{\partial \ln T_C}{\partial \ln M}$$

The value of α is approximately 0.5. For example, the average mass varies from 199.5 to 203.4 atomic mass units and accordingly the transition temperature varies from 4.185K to 4.146K.

Meissner Effect

When a material transitions from the normal to the superconducting state, it actively expels magnetic fields from its interior—a phenomenon known as the Meissner effect. This exclusion of magnetic fields is fundamentally different from the perfect diamagnetism that would arise solely due to zero electrical resistance.

In a perfect conductor (with zero resistance), an imposed magnetic field would generate persistent current loops to cancel the applied field, as dictated by Lenz's law. However, if the material initially possessed a steady magnetic field before being cooled below its superconducting transition temperature, the field would remain unchanged because no electromotive force (EMF) would be induced (per Faraday's law) to drive currents. This suggests that the Meissner effect is a unique and active property of superconductors, separate from their zero-resistance behaviour.

In Type II superconductors, the Meissner effect can exist in a mixed state, where magnetic flux partially penetrates the material in quantized vortices while the rest of the superconductor remains flux-free.

One theoretical explanation for the Meissner effect is provided by the London equations. These equations demonstrate that the magnetic field inside a superconductor decay exponentially over a characteristic distance, known as the London penetration depth, typically ranging between 20 and 40 nm. The London penetration depth is a critical parameter for understanding how magnetic fields behave near the surface of superconductors.
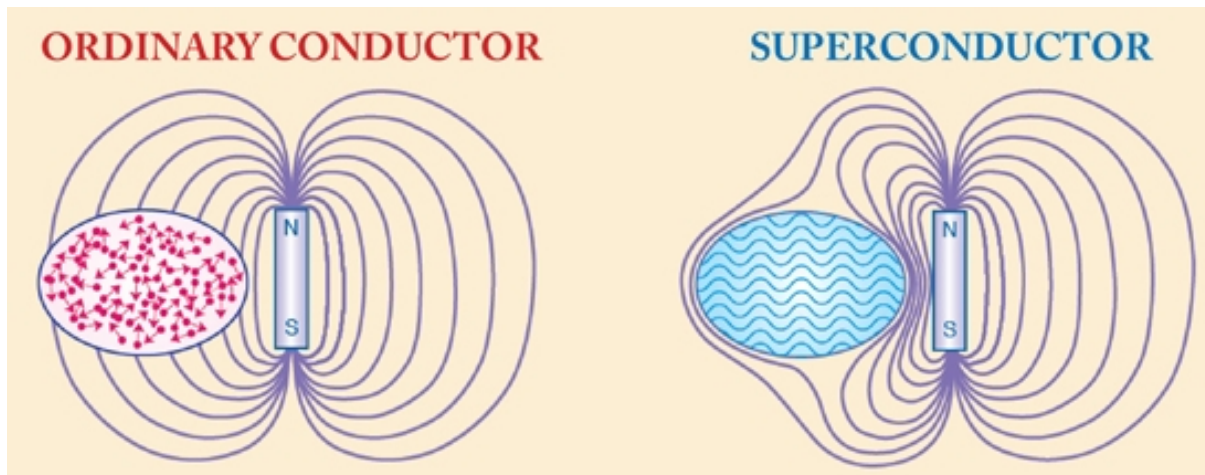

Figure: Illustration of ordinary and superconductor inside magnetic field.
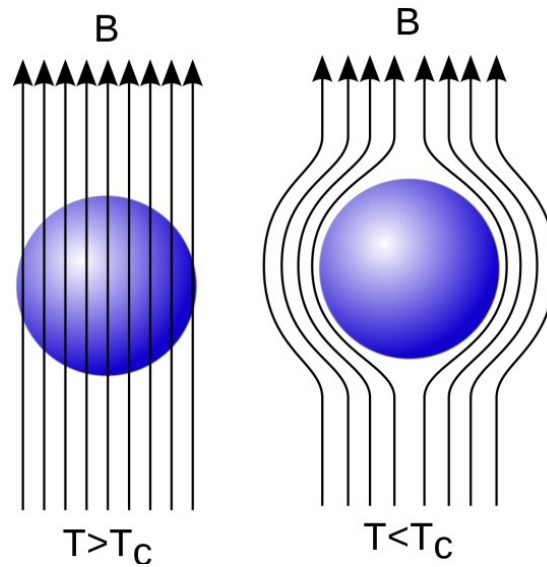
Figure: Behaviour of superconductor in applied magnetic field at $T > T_c$ and $T < T_c$.

Type – I and Type – II Superconductors

Superconductors are materials that exhibit the phenomenon of superconductivity when they are cooled below a critical temperature. They are the materials that obey the Meissner effect. These materials possess zero electrical resistance, exhibit perfect diamagnetism, and have high critical current density. Broadly, there are two categories of Superconductor namely, Type-I Superconductor and Type-II Superconductor. These types of Superconductors have their own advantages and disadvantages. There are various applications of Superconductors which include power transmission, Magnetic Resonance Imaging (MRI), Maglev Trains, Superconducting Magnets, Quantum Computing, etc.

Type-I Superconductors

Type-I Superconductors are materials that show superconductivity at temperatures below a critical temperature. They exhibit perfect diamagnetism and conductivity. Heike Kamerlingh Onnes, a Dutch physicist first observed the phenomenon of superconductivity in 1911 in mercury. They are materials that show superconductivity at relatively low temperatures. Their transition temperatures are below 30K and are generally referred to as low-temperature superconductors. They generally consist of pure metals. They perfectly obey the Meissner effect. There is no effect of slight impurity on the superconductivity of

type-I superconductors. They are used in various range of applications, like magnets, transformers, and medical imaging. Examples: Hg, Pb, Zn, etc.
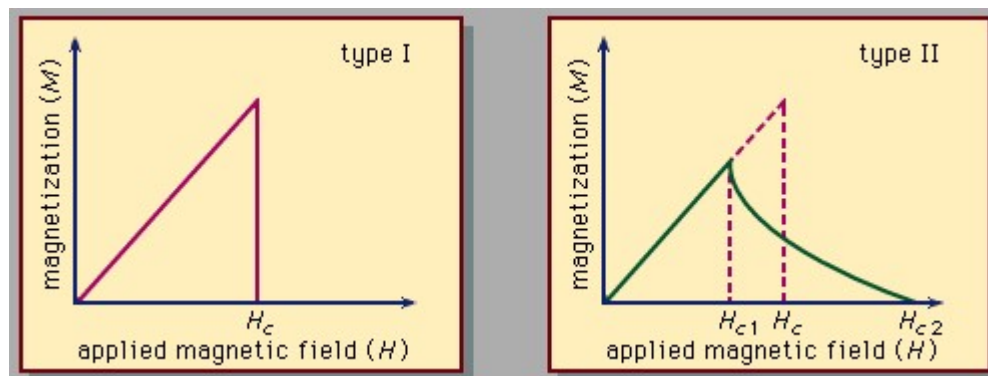
Type-II Superconductors

Type II are the materials which show superconductivity at temperatures above a critical temperature. They don't exhibit perfect diamagnetism. American physicists John Bardeen, Leon Cooper, and John Schrieffer first observed the phenomenon of superconductivity in 1957 in niobium-germanium. They are materials which have relatively weaker magnetic fields than Type-I superconductors. They are generally referred to as High temperature superconductors. They consist of alloys and complex oxides of ceramics. They partly obey the Meissner effect. There is a great effect of slight impurity on superconductivity of type-II superconductors. Examples: NbTi, Nb3Sn, etc.

Comparison of Type - I and Type - II Superconductors

Type - I	Type - II
Type - I Superconductors exhibit single critical magnetic field.	Type - II Superconductors contains two critical magnetic fields.
Type - I Superconductors are completely diamagnetic.	Type - II Superconductors are not completely diamagnetic.
Type - I Superconductors are also referred to as Low-temperature Superconductors.	Type - II Superconductors are also referred to as High-temperature Superconductors.
The temperature typically ranges from 0K to 10K.	The temperature is typically greater than 10K.
Type - I Superconductors typically have a Low critical magnetic field which ranges from 0.0000049 to 1T.	Type - II Superconductors typically have a High critical magnetic field which is typically greater than 1T.
Type - I Superconductors perfectly obey the Meissner effect.	Type - II Superconductors partly obey the Meissner effect.
Type - I Superconductors is also termed as soft superconductors.	Type - II Superconductors are also termed hard superconductors.
In Type - I Superconductors there is not existence of mixed state.	In Type - II Superconductors there is existence of mixed state.
There is no effect of slight impurity on superconductivity of type - I superconductors.	There is great effect of slight impurity on superconductivity of type - II superconductors.
Type - I Superconductors generally consist of pure metals.	Type - II Superconductors consist of alloys and complex oxides of ceramics.
For Type-I superconductors, the transition from a superconducting state to a normal state happens very quickly and sharply due to the external magnetic field.	For Type-II superconductors, the transition from a superconducting state to a normal state due to the external magnetic field is gradually but not sharp and abrupt .
Examples: Hg, Pb, Zn, etc.	Examples: NbTi, Nb3Sn, etc.

High-temperature superconductors (HTS)

High-temperature superconductors are materials that can conduct electricity with little to no resistance loss at warmer temperatures than conventional superconductors:

Temperature

HTS materials have a critical temperature above 77 K, the boiling point of liquid nitrogen. This is much warmer than conventional superconductors, which operate at temperatures close to absolute zero (-460°F).

Efficiency

HTS materials are 100% efficient, meaning that current passes through them with zero energy loss.

Magnetic fields

HTS materials can perform in magnetic fields that are more than twice as strong as those of low-temperature superconductors.

Coolants

HTS materials can be cooled using liquid nitrogen, which has a temperature of -196°C.

HTS materials have many potential applications, including:

Power grids

HTS materials can be used to replace high-voltage cables with medium-voltage cables, saving space and reducing losses.

Rotating electromechanical machines

HTS materials can be used to replace copper coils in motors, generators, and synchronous condensers.

Magnetic energy storage

HTS materials can be used to store energy nearly indefinitely, and release bursts of power almost instantaneously.