PYL102 Course

Lectures-1&2 on 09/11-08-2021

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PYL102:

Principles of Electronic Materials

- Details of Course content…….
- Details of examination and evaluation policy…
- Behavior of electrons in metals…..free electron model……..
- Conductivity in metals….

Course details

Course: PYL102 (Principles of Electronic Materials), 3-0-0, first semester, 2021-2022

Pre-requisites: PYL101

[Program Linked Course: Not available to B.Tech. (Engineering Physics) students]

Part I: Basics of electronic materials and Magnetism:

Free electron model, Conductivity in metals and Concepts of Fermi level, Energy bands in solids (Kronig-Penney model), Bloch's theorem, Classification of electronic materials: metals, semiconductors and insulators. Effective mass and holes, Concept of phonons, Thermoelectricity, Magnetism in materials – types of interactions, Magnetic susceptibility, Curie and Neel temperatures; Domains, Magnetic anisotropies, Spin-orbit interaction.

Part II: Semiconductors and Dielectrics:

Intrinsic, extrinsic and degenerate semiconductors, Fermi level variation by carrier concentration and temperature, Metal-semiconductor junction, p-n junction, Diffusion and drift transport, carrier life time and diffusion length; Direct and indirect band gaps, optical transitions, photon absorption, Exciton, photovoltaic effect, Dielectrics and electrical polarization, Depolarization field, Clausius- Mossotti relation; Drude model, Electronic polarization and its mechanisms, Dielectric breakdown; Piezoelectricity, Pyroelectricity and Ferroelectricity

Some of the reference books:

1. Safa O. Kasap, Principles of Electronic Materials and Devices, McGraw-Hill Education, 2005
2. N. W. Ashcroft, N. D. Mermin, Solid State Physics, 2nd Ed., Holt Rinehart & Winston; 2002
3. B. D. Cullity (Author), C. D. Graham, Introduction to Magnetic Materials; 2nd Edition, 2008
4. C. Kittel, Introduction to Solid State Physics
5. Nicola Spaldin, Magnetic materials: fundamentals and device applications
6. Rolf E. Hummel, Electronic Properties of Materials, Springer Science & Business Media
7. Semiconductor materials by B. G. Yacobi
8. Physics of Semiconductor Devices by J.-P. Colinge, C.A. Colinge.
9. Dielectric Materials for Electrical Engineering by Juan Martinez-Vega

General Instructions, Examinations, Evaluation policies, etc.:

- All the classes will be conducted through online mode on Microsoft Teams.
- Total marks = 100, [Mid-Sem exam (1.5 hr), home assignment/Quiz/surprise quiz, and Major exam (2 hr): each of maximum marks 35, 20 and 45, respectively].
- 45 marks in Major exam: ~80% (after Mid-Sem Exam), ~20% (before Mid-Sem exam)
- 'A' grade will be awarded only if your overall performance is above 80%.
- For minimum valid pass grade 'D', you have to score at least 30% overall marks.
- As per the institute's rule, 100% attendance is required.
- If aggregate attendance < 75% (60%), grade will be lowered by one (two).
- If attendance < 50%, no re-minor/re-major.
- For audit pass grade, attendance ≥75% and passing marks as per the institute norms.
- If you are late in the class by >5 mins, your attendance will be marked as ABSENT.
- Any change in the marks distribution or exam time will be intimated well in time.

Free electron model/theory of metals:

A free electron model is the simplest way to represent the electronic structure of metals.

Although the free electron model is a great oversimplification of the reality, surprisingly in many cases it works pretty well, so that it is able to describe many important properties of metals.

According to this model, the loosely bound valence electrons of the constituent atoms of the crystal become conduction electrons and travel freely throughout the crystal.

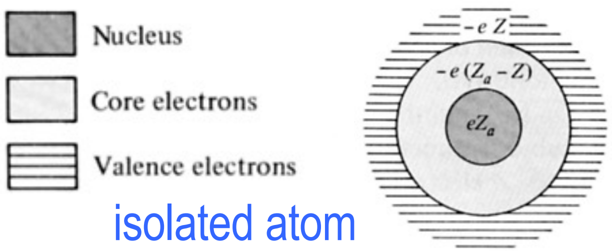
Paul Drude,
Uni. of Leipzig
(1863 – 1906)

Classical approach (Drude's classical theory in 1900)

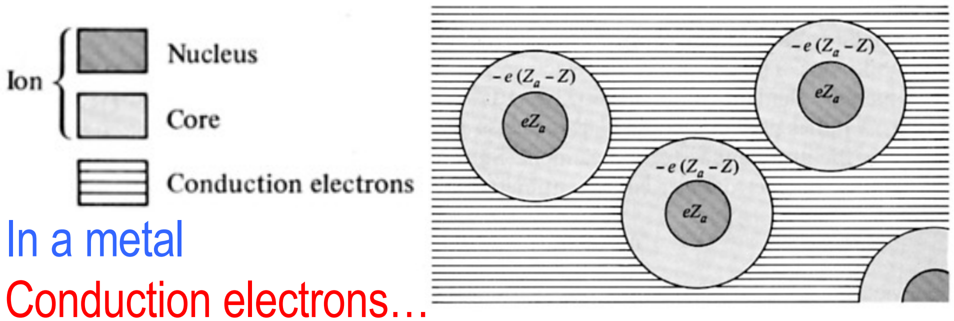
Some of the crucial discoveries that paved the way for the Drude model include….

- Ohm's law, 1827
- Joule heating of metals, 1841
- Equipartition theorem, 1845
- Discovery of the electron, by J. J. Thomson, in 1897

Drude treated the (free) electrons as a <u>classical ideal gas,</u> but the electrons should collide with the stationary ions, and neglected e^- - e^- collision…..



isolated atom



In a metal

Conduction electrons…

Drude's classical theory:

Each of the atoms a metal is composed of has lost one or more of its valence electrons and so has become a positively charges ion. It was assumed that free electrons will obey kinetic theory of gases…

This means, electrons move freely inside the metal, except for collisions with 'ions'….

Between elastic collisions, electrons move in a straight line with fixed velocity

Free electrons move in random direction, and the collisions with scattering centres are instantaneous...

that abruptly alter the velocity of an electron…

The motion of these free electrons obeys classical Maxwell-Boltzmann (M-B) velocity distribution law….

– Independent electron approximation:

neglect interaction between electrons…

– Free electron approximation:

neglect interaction between electrons and ions…

i.e., neglected electrostatic interactions between electrons or the electrons and ions….

Imagine if there are no collisions of electrons and if we apply a fixed electric field E, then electrons will experience a force of (qE), where q is the charge of an electron.

We can write equation of motion: $m(dv/dt)=qE$, where m is the mass of electron and v is the velocity experienced which is also a function of time t.

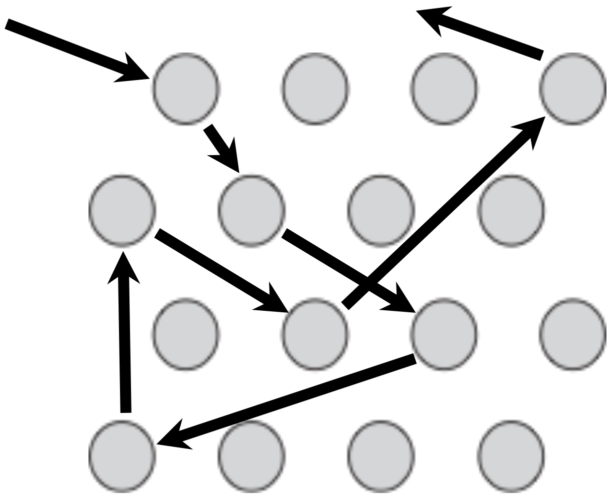
Drude's classical theory:

Flaw in above equation!!
Here q, m, and E are fixed quantities, So (dv/dt) is a constant. That implies as t passes v keep on increasing.→ No steady state contrary to what we observe in real life

So, it is necessary to include some form of general resistance preventing the indefinite acceleration of the momentum of electrons → Next assumption for rescue

The assumption is that through collisions with ions, e^- immediately achieve thermal equilibrium with the lattice……..

Its speed is related to T, the 'local' temperature (assuming that a temperature can be assigned to a region within the metal)……. Here, the kinetic energy is a measure of T……



From classical equipartition of energy, we can write

$$\frac{1}{2}mv_t^2 = \frac{3}{2}k_B T$$

average rms speed

$$v_t = \sqrt{\frac{3k_B T}{m}}$$

So, at room temperature

$$v_t \approx 10^5 \mathrm{ms}^{-1}$$

Drude's classical theory:

As discussed before, electrons move freely in between the collisions, and random motion through the metal….

The mean length of this free movement is called the mean free path λ.

If we know the value of the density of the ions, we can estimate the mean free path value of electrons, which is normally 1nm….

Now let's find the probability of a given electron undergoing a collision in an infinitesimal interval dt, that is given by dt/τ.

τ is a system parameter called 'relaxation time' or 'mean free time' and plays a fundamental role in the theory of metallic conductions

Relaxation time: time between two successive collisions, i.e. average time between scattering events…

How to find the relaxation time τ?

Let's take the mean free path:

$$\lambda = \tau v_t \quad \Longrightarrow \quad \left\{ \begin{array}{l} \lambda \approx 1\mathrm{nm} \\ v_t \approx 10^5 \mathrm{ms}^{-1} \\ \tau \approx 1 \times 10^{-14}\ \mathrm{s} \end{array} \right.$$

τ for selected elements:

DRUDE RELAXATION TIMES IN UNITS OF 10^{-14} SECOND

ELEMENT	77 K	273 K	373 K
Li	7.3	0.88	0.61
Na	17	3.2	
K	18	4.1	
Rb	14	2.8	
Cs	8.6	2.1	
Cu	21	2.7	1.9
Ag	20	4.0	2.8
Au	12	3.0	2.1
Be		0.51	0.27
Mg	6.7	1.1	0.74
Ca		2.2	1.5
Sr	1.4	0.44	
Ba	0.66	0.19	
Nb	2.1	0.42	0.33
Fe	3.2	0.24	0.14
Zn	2.4	0.49	0.34
Cd	2.4	0.56	
Hg	0.71		
Al	6.5	0.80	0.55
Ga	0.84	0.17	
In	1.7	0.38	0.25
Tl	0.91	0.22	0.15
Sn	1.1	0.23	0.15
Pb	0.57	0.14	0.099
Bi	0.072	0.023	0.016
Sb	0.27	0.055	0.036

As we discussed before,

$\lambda = v_t \tau$
where v_t is the average electronic speed

Which is of the order of 10^5 m/s @RT

λ is of 1 to 10 Å at that time…

Interestingly, this distance is comparable to the interatomic spacing…

This is consistent with Drude's original idea that collisions happen when the electron hit the large heavy ions…

However, later we will see that estimate of v_t is not quite correct…

and so on….

How to find conduction electron density:

A gas of conduction electrons of mass m, which move against a background of heavy immobile ions…

Electron density $n = 0.6022 \times 10^{24} \frac{Z\rho_m}{A}$

0.6022×10^{24} Avogadro's number

ρ_m Mass density in g/cm³

A Atomic mass in g/mole

Z Number of electron each atom contribute

$\frac{1}{n}$: volume per electron

$r_s / a_0 \sim 2-3$ in typical metal

Bohr radius

Also, 3-6 in alkali metals

It can be about 10 in some metallic systems…

Alternative measure of r_s

measure of electronic density..

which is defined as the radius of a sphere whose volume is equal to the volume/conduction electron

$$\frac{V}{N} = \frac{1}{n} = \frac{4}{3}\pi r_s^3$$

$$r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$$

Conduction electron density:

mostly @ RT

These densities are typically a thousand times > than those of a classical gas at normal temperature and pressure.

ELEMENT	Z	$n\ (10^{22}/cm^3)$	$r_s(Å)$	r_s/a_0
Li (78 K)	1	4.70	1.72	3.25
Na (5 K)	1	2.65	2.08	3.93
K (5 K)	1	1.40	2.57	4.86
Rb (5 K)	1	1.15	2.75	5.20
Cs (5 K)	1	0.91	2.98	5.62
Cu	1	8.47	1.41	2.67
Ag	1	5.86	1.60	3.02
Au	1	5.90	1.59	3.01
Be	2	24.7	0.99	1.87
Mg	2	8.61	1.41	2.66
Ca	2	4.61	1.73	3.27
Sr	2	3.55	1.89	3.57
Ba	2	3.15	1.96	3.71
Nb	1	5.56	1.63	3.07
Fe	2	17.0	1.12	2.12
Mn (α)	2	16.5	1.13	2.14
Zn	2	13.2	1.22	2.30
Cd	2	9.27	1.37	2.59
Hg (78 K)	2	8.65	1.40	2.65
Al	3	18.1	1.10	2.07
Ga	3	15.4	1.16	2.19
In	3	11.5	1.27	2.41
Tl	3	10.5	1.31	2.48
Sn	4	14.8	1.17	2.22
Pb	4	13.2	1.22	2.30
Bi	5	14.1	1.19	2.25
Sb	5	16.5	1.13	2.14

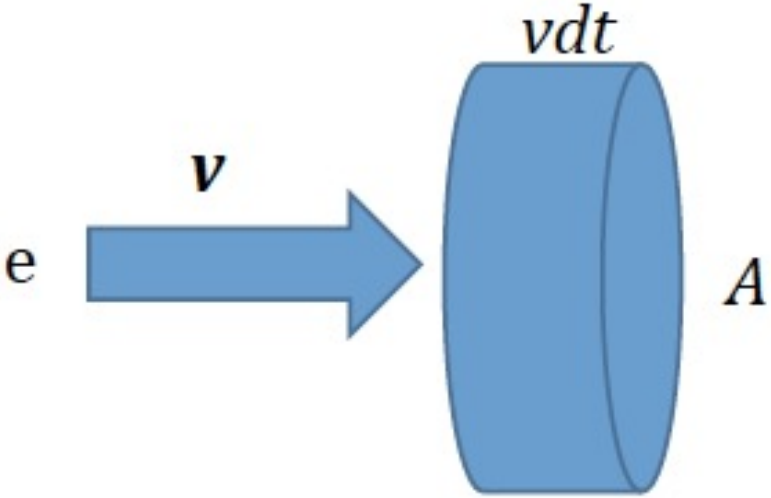
DC electrical conductivity of a metal:

As we know from EM, current density can be written as $\vec{j} = \sigma \vec{E}$

This is familiar Ohm's law.

a vector parallel to the flow of charge….

its magnitude is the amount of charge/time crossing a unit area perpendicular to the flow…



If n electrons/volume, all move with velocity v…

In a time dt, the electrons will move by a distance $v$dt

This means, n($v$dt)A electrons will cross an area A, perpendicular to the direction of flow….

Charge crossing A in time dt, is (–e)n($v$dt)A…..

$$j = \frac{-nevAdt}{Adt} = -nev$$

$$\vec{j} = -ne\vec{v}$$

$\vec{v}$ the average electronic velocity

DC electrical conductivity of a metal:

Now, let's calculate the DC electrical Conductivity from Drude model:

At any point in a metal, e^-s are always moving in a variety of directions with a variety of thermal energies…

It is important to note that when E = 0, v = 0 and that means j = 0

i.e. random orientations, no net flow of charge

However, when E ≠ 0, $v \neq 0$ and that means j ≠ 0……

Now the question is how to find j when E ≠ 0…??

First consider a typical e^- at t = 0.

Now, let *t* be the time after its last collision.

Its velocity at t = 0 will be its velocity $\mathbf{v}_0$ immediately after that collision

plus additional velocity acquired after collision in time t is $-eEt/m$……..

DC electrical conductivity of a metal:

How can we understand this in simple way?

Let's say, when an electric field E is applied. The equation of motion is: $m_e \frac{d\mathbf{v}}{dt} = -e\mathcal{E}$,

This gives us $\mathbf{v}(t) = \frac{-e\mathcal{E}t}{m_e}$,

Now, If we assume that the drift motion is destroyed in a collision with the ions and that on average the time for a collision-free drift is τ, the average drift velocity is

$$\bar{\mathbf{v}} = \frac{-e\mathcal{E}\tau}{m_e}.$$

For an electric field of ≈ 10 V m^{-1}, we get a drift velocity of $|\mathbf{v}| = 10^{-2}$ m s^{-1}

To calculate the conductivity, we need to consider an area A perpendicular to the electric field. The charge passing through the area per unit time is $-en|\bar{\mathbf{v}}|A$.

As we know, the current density is given by:

$$\mathbf{j} = -en\bar{\mathbf{v}}, \Rightarrow \mathbf{j} = \boxed{\frac{ne^2\tau}{m_e}}\mathcal{E} = \sigma\mathcal{E} = \frac{\mathcal{E}}{\rho},$$

Conductivity

called resistivity, which is reciprocal to the conductivity

PYL102 Course
Lecture-3 on 12-08-2021

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PYL102:
Principles of Electronic Materials

- Conductivity in metals.........
- Problems with free electron model...
- Quantum free electron model........
- Fermi level....

DC electrical conductivity of a metal:

Here, we assume that an e^- emerges from a collision in a random direction…

This means there will be no contribution from v_0 (i.e., $\langle v_0 \rangle = 0$) to the average electronic velocity v_{avg}…

In this case, v_{avg} is entirely given by the average of $-eEt/m$…

where the average of t is the relaxation time τ

Therefore, $$\boldsymbol{v}_{avg} = -e\frac{\boldsymbol{E}\bar{t}}{m} = -e\frac{\boldsymbol{E}\tau}{m}$$

$$\boxed{\mathbf{j} = \frac{ne^2\tau}{m_e}\mathbf{E}} \quad \Rightarrow \quad \mathbf{j} = \sigma\mathbf{E}; \quad \sigma = \frac{ne^2\tau}{m}$$

DC electrical conductivity of a metal:

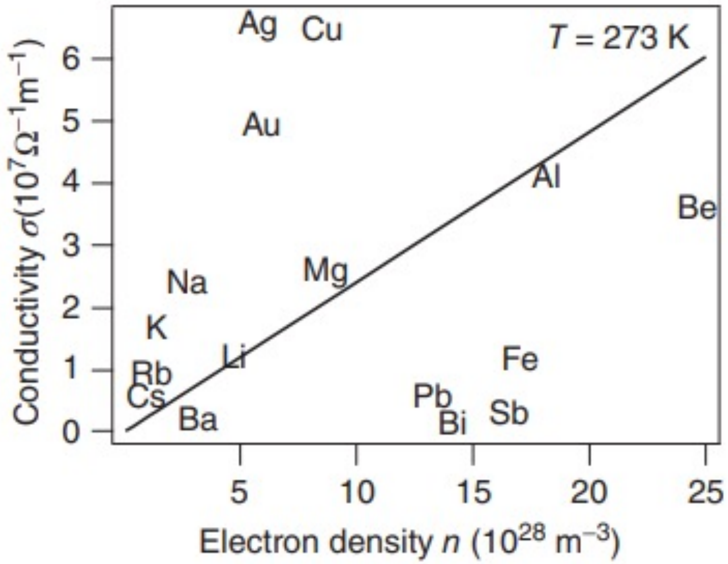
However, the relaxation time τ is unknown… we can write τ as,

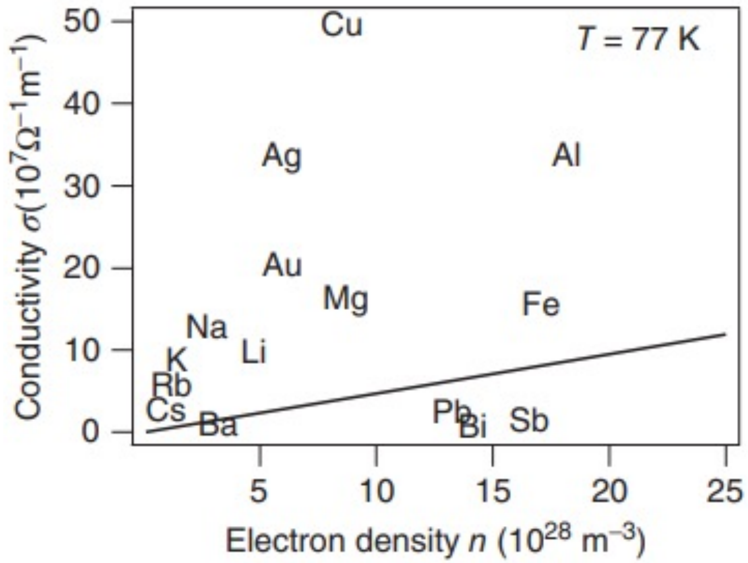
$$\tau = \frac{m}{\rho n e^2}$$

here, the resistivity is in uΩ/cm

ELECTRICAL RESISTIVITIES OF SELECTED ELEMENTS

ELEMENT	77 K	273 K	373 K
Li	1.04	8.55	12.4
Na	0.8	4.2	Melted
K	1.38	6.1	Melted
Rb	2.2	11.0	Melted
Cs	4.5	18.8	Melted
Cu	0.2	1.56	2.24
Ag	0.3	1.51	2.13
Au	0.5	2.04	2.84
Be		2.8	5.3
Mg	0.62	3.9	5.6
Ca		3.43	5.0
Sr	7	23	
Ba	17	60	
Nb	3.0	15.2	19.2
Fe	0.66	8.9	14.7
Zn	1.1	5.5	7.8
Cd	1.6	6.8	
Hg	5.8	Melted	Melted
Al	0.3	2.45	3.55
Ga	2.75	13.6	Melted
In	1.8	8.0	12.1
Tl	3.7	15	22.8
Sn	2.1	10.6	15.8
Pb	4.7	19.0	27.0
Bi	35	107	156
Sb	8	39	59





Problems with free electron classical theory:

Despite its limitations, Drude's model predicts correctly that metals which can conduct heat well are also good electrical conductors…

It also predicts that the current in a metal obeys Ohm's law: $V = IR$

However, Drude's model produces a value for the heat capacity that is much larger than the true value. This is because the electrons are assumed to be an ideal gas, so the distribution of their kinetic energies was assumed to behave like M-B distribution.

According to the classical gas model, the average thermal energy of each electron is $\langle E \rangle = 3k_BT/2$, and if this is multiplied by the number of free electrons per unit volume of a mole of the substance under consideration, a molar heat capacity is produced.

The value of this is, however, a factor of 100 higher than experimentally measured values for molar specific heat. In reality, the heat capacity is due to the thermal vibrations of the lattice ions, and the free electrons make almost no contribution.

Also, according to Drude's classical theory, resistivity of a metal is proportional to the square root of temperature. However, experiments show that above the Debye temperature, resistivity varies linearly with temperature,

So to get nearer to the actual situation that occurs in solids, quantum theory needs to be taken into account…Sommerfeld model.

Quantum free electron theory: Sommerfeld…

Fundamental difference between the free electron gas and ordinary gas of molecules:

1) electrons are charged particles ⇒ to maintain the charge neutrality of the whole crystal, we need to include positive ions.
This is done within the jelly model: the positive charge of ions is smeared out uniformly throughout the crystal - charge neutrality is maintained, no field on the electrons exerted

2) Free electron gas must satisfy the Pauli exclusion principle, which leads to important consequences. So we need to include quantum phenomenon/model…..

This model is quite similar to Drude's model in that it still treats the conduction electrons as if they were the molecules of a gas that are free to move through the crystal.

However, it takes quantum theory into account and so considers the electrons to be fermions. In this case the electrons are then subject to Pauli's exclusion principle.

This prevents any two electrons from having exactly the same quantum state….

The free electron gas in this model is not confused with the free electron gas in Drude's model, it is known as the free electron Fermi gas, which is often called "Fermi gas".

In this case, electrons rarely scattered by each other…and also electrons in a Fermi gas do not collide with the +ve ions in the lattice when they are in their correct positions.

Quantum free electron theory:...

Assumptions now:

1. The free electrons in a metal can have only discrete energy values. Thus the energies are quantized.

2. The electrons obey Pauli's Exclusion Principle, which states that there cannot be more than two electrons in any energy level.

3. The distribution of electrons in various energy levels obey the Fermi-Dirac quantum statistics.

4. Free electrons have the same potential energy everywhere within the metal, because the potential due to ionic cores is uniform throughout the metal.

5. The force of attraction between electrons & lattice ions and the force of repulsion between electrons can be neglected.

6. Electrons are treated as wave-like particles.

As we know that for a metal containing N atoms, there will be N number of energy levels in each band.
According to Pauli's exclusion principle, each energy level can accommodate a maximum of two electrons, one with spin up (+½) and the other with spin down (-½).

Fermi level:

A Fermi System is concept in quantum mechanics where a system containing charged particles don't interact (collide.)

At absolute zero temperature, two electrons with opposite spins will occupy the lowest available energy level. The next two electrons with opposite spins will occupy the next energy level and so on.

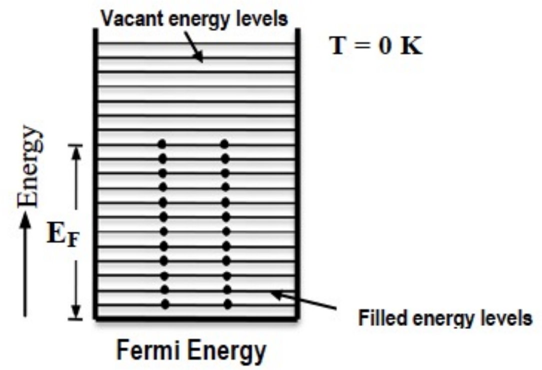
Thus, the top most energy level occupied by electrons at absolute zero temperature is called **Fermi-energy level**. This concept comes from Fermi-Dirac statistics.
The energy corresponding to that energy level is called **Fermi-energy**.

The energy of the highest occupied level at zero degree absolute is called Fermi energy, and the energy level is referred to as the Fermi level.
The Fermi energy/level is denoted as $\mathbf{E_F}$.

All energy levels below Fermi level are completely filled and above which all energy levels are completely empty.

At temperatures above absolute zero, the electrons get thermally excited and move up to higher energy levels.

As a result there will be many vacant energy levels below as well as above Fermi energy level.



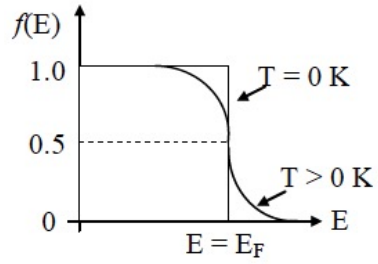
Fermi level:

Under thermal equilibrium, the distribution of electrons among various energy levels is given by statistical function *f*(E).

The function ***f*(E)** is called **Fermi-factor** and this gives the probability of occupation of a given energy level under thermal equilibrium.

The expression for *f*(E) is given by

$$f(E) = \frac{1}{\exp((E - E_F)/kT) + 1}$$



Variation of *f*(E) with E

Where ***f*(E)** is called Fermi-Dirac distribution function or Fermi factor, $\mathbf{E_F}$ is the Fermi energy, **k** is the Boltzmann constant and **T** is the temperature of metal under thermal equilibrium.

1. The Fermi-Dirac distribution function *f*(E) is used to calculate the probability of an electron occupying a certain energy level.

2. The distribution of electrons among the different energy levels as a function of temperature is known as Fermi-Dirac distribution function.

The Fermi level of a body is a thermodynamic quantity, and the thermodynamic work required to add one electron to the body (not counting the work required to remove the electron from wherever it came from).

Core and valence electrons:

The most highly conducting metals are formed from atoms with partially filled atomic orbitals.

e.g. Li, Na, and K etc, which have the electronic structure

Li $1s^2 2s^1$ **Na** $1s^2 2s^2 2p^6 3s^1$ **K** $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

The best insulators are formed from atoms with closed shells

e.g. Solid inert gases which have the electronic structure

He $1s^2$ **Ne** $1s^2 2s^2 2p^6$ **Ar** $1s^2 2s^2 2p^6 3s^2 3p^6$

In a simple picture we distinguish between CORE electrons, which are tightly bound to the nuclei, and VALENCE electrons that move freely through the metals.

Isolated atoms have precise allowed energy levels.

In solids the electron states of tightly bound (high binding energy) electrons are very similar to those of the isolated atoms.

Lower binding electron become bands of allowed states..