

PYL102 Lecture Notes

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Chapter 1

Electron Band Theory

1.1 Free Electron Model/Theory of metals

- Simplest way to represent electronic structure of metals.
- Oversimplification but works surprisingly well.

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.

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

1.2 Drude's classical theory

1.2.1 Axioms

Each of the atoms, a metal is composed of, has lost one or more of its valence electrons and so has become a positively charged 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 electrostatic interactions between electrons and ions

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:

$$m \frac{dv}{dt} = qE$$

where m is the mass of electron and v is the velocity experienced which is also a function of time t . Flaw in above equation!! Here q, m and E are fixed quantities, So $\frac{dv}{dt}$ is 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.

1.2.2 RMS Velocity

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:

$$\frac{1}{2}mv_t^2 = \frac{3}{2}k_bT$$

Average rms speed

$$v_t = \sqrt{\frac{3k_bT}{m}}$$

So, at room temperature:

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

1.2.3 Mean free path λ

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 $\lambda \approx 1nm$.

1.2.4 Relaxation Time τ

Time between two successive collisions, i.e. average time between scattering events.

$$\lambda = \tau v_t$$

$$\lambda \approx 1nm$$

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

$$\tau \approx 10^{-14}s$$

1.2.5 Conduction electron density

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

$$n = \frac{N_a Z \rho_m}{A}$$

Where, N_a is Avogadro's Number, Z is the number of electrons each atom contributes, ρ_m is Mass density (g/cc), A is Atomic mass (g/mole).

$\frac{1}{n}$ is Volume per electron. r_s is defined as the radius of a sphere whose volume is equal to the volume/conduction electron.

$$\begin{aligned}\frac{V}{N} &= \frac{1}{n} = \frac{4}{3}\pi r_s^3 \\ r_s &= \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}} \\ \frac{r_s}{a_0} &\sim 2-3\end{aligned}$$

where a_0 is Bohr radius.

1.2.6 DC electrical conductivity of a metal-1

Current density can be written as $\vec{j} = \sigma \vec{E}$. (Ohm's Law). It is a vector parallel to the flow of charge. Its magnitude is the amount of charge/time crossing a unit area perpendicular to the flow. Consider n electrons per volume, moving with velocity v . Charge crossing area A in time dt is $(-e)nv dt A$. Thus, $j = \frac{(-e)nv(dt)A}{A}$, and we have

$$\vec{j} = (-e)n\vec{v}$$

1.2.7 DC electrical conductivity of a metal-2 (Using Drude's model)

First consider a typical electron at $t = 0$. Now, let t be the time after its last collision. When an electric field E is applied, the equation of motion is

$$m_e \frac{d\vec{v}}{dt} = -e\vec{E}$$

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

$$\bar{v} = \frac{-eE\tau}{m_e}$$

For $|E| \approx 10V m^{-1}$, $|\mathbf{v}| = 10^{-2}ms^{-1}$.

$\vec{j} = (-e)n\vec{v}$ and $\bar{v} = \frac{-eE\tau}{m_e}$ gives us:

$$\begin{aligned}j &= \frac{ne^2\tau}{m_e}E \\ j &= \sigma E \\ \sigma &= \frac{ne^2\tau}{m_e}\end{aligned}$$

This establishes the linear dependence of \mathbf{j} on \mathbf{E} and gives an estimate of the conductivity σ in terms of quantities that are all known except for the relaxation time τ . We may therefore use the above equation and the observed resistivities to estimate the size of the relaxation time:

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

If ρ_μ is the resistivity in microhm centimeters, then a convenient way of expressing the relaxation time is

$$\tau = \left(\frac{0.22}{\rho_\mu}\right) \left(\frac{r_s}{a_0}\right)^3 \times 10^{-14} sec.$$

At any time t the average electronic velocity \mathbf{v} is just $\mathbf{p}(t)/m$, where \mathbf{p} is the total momentum per electron. Hence, the current density is

$$\mathbf{j} = -\frac{ne\mathbf{p}(t)}{m}.$$

If it experiences no collision, however, it simply evolves under the influence of the force $\mathbf{f}(t)$ (due to spatially uniform electric or/and magnetic fields), then the equation for change in $\mathbf{p}(t)$ comes out to be:

$$\frac{d\mathbf{p}(t)}{dt} = -\frac{\mathbf{p}(t)}{\tau} + \mathbf{f}(t).$$

This simply states that the effect of individual electron collisions is to introduce a frictional damping term into the equation of motion for the momentum per electron.

1.2.8 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 $\langle E \rangle = \frac{3}{2}k_bT$, 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.

Chapter 2

Quantum free electron theory: Sommerfield

2.1 Background

Difference between the free electron gas and ordinary gas molecules:

1. Electrons are charged particles. So, 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.

2.1.1 Assumptions

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 and 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 $\frac{+1}{2}$ and the other with spin down $\frac{-1}{2}$.

2.1.2 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 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.

2.1.3 Fermi Factor $f(E)$

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.

$$f(E) = \frac{1}{e^{\frac{E-E_f}{kT}} + 1}$$

Where $f(E)$ is called Fermi-Dirac distribution function or Fermi factor, 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).

2.2 Electrons in Periodic Potential

2.2.1 Free Electron Theory

In free electron theory, the conduction electrons are described by free electron wave functions, and these have certain allowed values of wave vector k that are analogous to the quantum numbers n , l , and m that describe the permitted states of an electron in an atom. In fact, the energy of a free electron in a metal is related to its wave vector, k , by

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

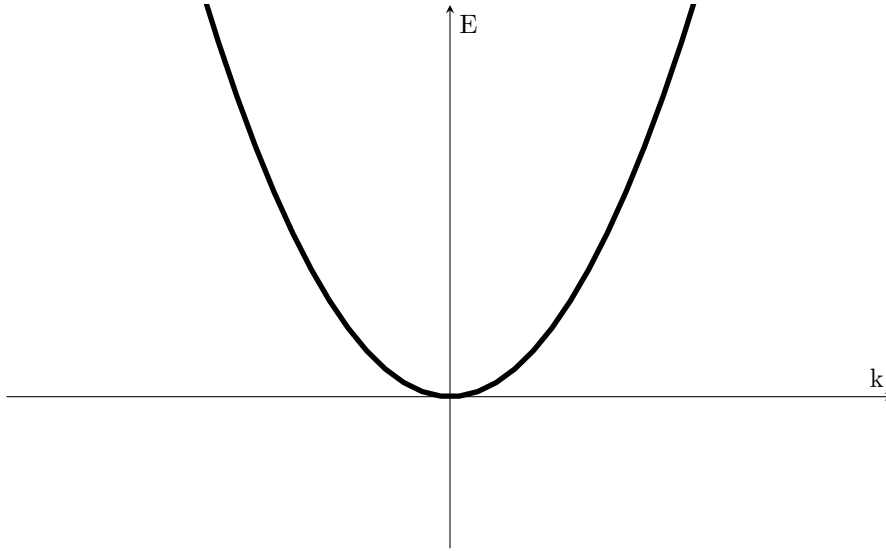
Since the energy of a free electron is entirely energy due to its motion—in other words, due to its kinetic energy, so we can write as below:

$$\frac{1}{2}mv^2 = \frac{\hbar^2 k^2}{2m}$$

which can be written as:

$$mv = \hbar k$$

k is often referred to as the “quasi-momentum”. This is because although it gives an indication of the momentum—and hence the velocity of a totally free conduction electron, but we will see in the next sections, it does not always do so for conduction electrons influenced by the lattice ions.



This is the $E - k$ relationship for a totally free electron, which does not interact with the crystal lattice but behaves as though it is a particle in a quantum gas.

After Pauli’s free electron theory, we can give a good explanation of many of the properties of metals, including their thermal and electrical conductivities.

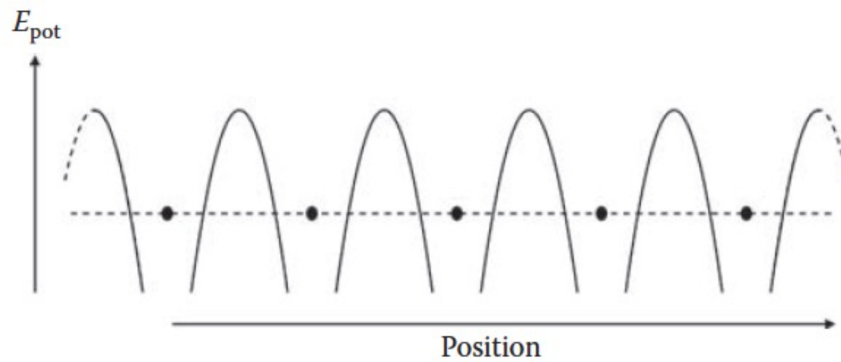
But it still fails to explain why some materials are conductors, some semiconductors, and some insulators, and cannot account for the electron mean free path being around a hundred or more atomic spacings.

A better way to understand these topics is to view solids in terms of energy bands instead, and as we will see, there are two totally different ways of considering how energy bands come about.

2.2.2 Extension to Pauli’s Quantum Free Electron Model

This model takes into account the effect that the ions in the lattice have on the sea of electrons. In Pauli’s model, the conduction electrons are assumed to have a uniform potential energy because the positive charge of the lattice ions is effectively spread out across the whole of the specimen of metal being considered. In fact, the potential energy of electrons within a metal was actually taken to be zero for simplicity, while the potential energy outside the metal is assumed to be infinite so that the electrons are confined within the metal.

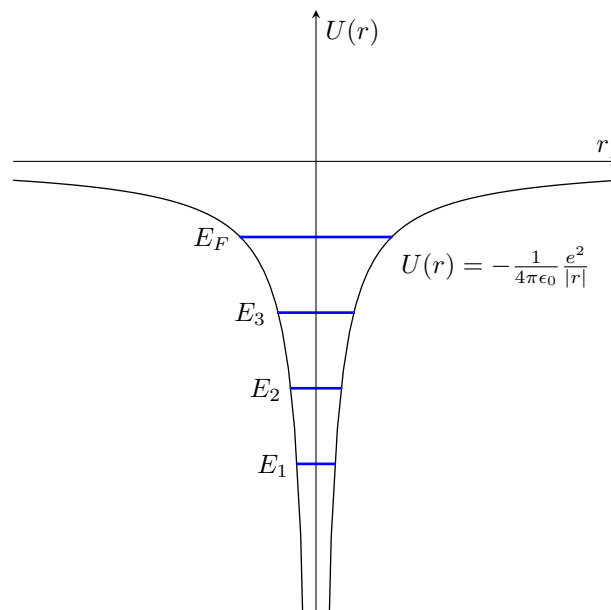
However, the potential energy of the electrons is like that shown below:



Once the interaction of the conduction electrons with the positively charged lattice ions is considered. As the above diagram shows, the potential energy of an electron is lower than its average value when that electron is near a positive ion, and is at its highest when the electron is exactly in between two ions.

Electrons motion in a crystal will now be considered from a quantum mechanical point of view based on Schrödinger equation. The crystal may be viewed as a periodic arrangement of atoms, i.e., positively-charged ion cores comprising the positively charged nuclei and non-valence electrons that may be assumed stationary in the lattice points.

The potential energy of a valence electron in a single isolated atom is shown:



If several of these atoms are placed in close proximity and equidistant from each other, the potential functions of neighboring atoms overlap so that the net potential function will look like the potential function as shown:

img;

2.3 Bloch's Theorem and Kronig-Penney Model

2.3.1 Kronig-Penney Simplification of 1-D Potential

We can simplify the potential function by using the potential function shape (referred to as *Kronig-Penny* Model).

img

In the Kronig-Penney model, a single electron is considered which moves in a one dimensional crystal of certain length L . Potential energy is periodic array of square wells with period $(a + b)$. Now we can write the time-independent Schrödinger equation for the motion of the electron in the one-dimensional periodic potential takes the form

$$H\Psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\Psi = E\Psi,$$

which can also be written as:

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\Psi = 0$$

It is of course implicit in the equation above that the time-dependent component of the wave-function is of the form:

$$e^{-i\frac{E}{\hbar}t}$$

where E is Total Energy.

Now, we can write the Schrödinger equation in both the regions:

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\Psi_I}{dx^2} &= E\Psi_I, \text{ for } 0 < x < a \\ -\frac{\hbar^2}{2m}\frac{d^2\Psi_{II}}{dx^2} + V_0\Psi_{II} &= E\Psi_{II}, \text{ for } -b < x < 0 \end{aligned}$$

2.3.2 Bloch Theorem

To obtain the solution to the Schrödinger equation, we utilize a mathematical theorem by Bloch. Bloch's theorem: The eigenstates Ψ of the one e- Hamiltonian

$$H = -\frac{\hbar^2\nabla^2}{2m} + V(r) \text{ where } V(r + R) = V(r) \text{ for all } R \text{ in Bravais Lattice}$$

$$\Psi(x) = u(x)e^{ikx}$$

- Wave function which satisfies Schrödinger equation for perfect periodicity of lattice
- Due to periodicity of the potential the wavefunction is also periodic
- Bloch function is a function which is a product of plane wave and a function which contains periodicity of lattice vector.
- The function $u(x)$ is called Bloch function and it is periodic with the same periodicity as that of the potential function.

2.3.3 Solution using Kronig-Penney Model

Now let's first consider:

$$\alpha^2 = \frac{2mE}{\hbar^2} \text{ and } \beta^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

Using the Bloch's function from the previous section,

$$\Psi(x) = u(x)e^{ikx}$$

Substituting it in the Schrödinger equation and solving, we get the solutions as:

$$u_I = Ae^{i(\alpha-k)x} + Be^{-(\alpha+k)x}, \text{ for } x \in (0, a)$$

$$u_{II} = Ce^{(\beta-ik)x} + Be^{-(\beta+ik)x}, \text{ for } x \in (-b, 0)$$

Now we apply the boundary conditions. Requirements of continuity:

$$u_I(0) = u_{II}(0)$$

$$\left. \frac{du_I}{dx} \right|_{x=0} = \left. \frac{du_{II}}{dx} \right|_{x=0}$$

Requirements of Periodicity:

$$u_I(a) = u_{II}(-b)$$

$$\left. \frac{du_I}{dx} \right|_{x=a} = \left. \frac{du_{II}}{dx} \right|_{x=-b}$$

On applying these boundary conditions and putting the determinant of A, B, C, D to be zero, we get:

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh(\beta b) \sin \alpha a + \cosh(\beta b) \cos \alpha a = \cos k(a+b)$$

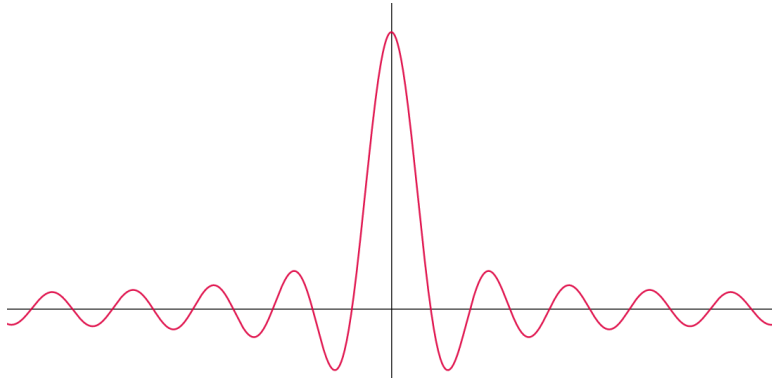
We make the further assumption that the potential barrier is a delta function, i.e. as $V_0 \rightarrow \infty$, $b \rightarrow 0$ and $V_0 \cdot b \neq 0$. Under this assumption, the above equation transforms to,

$$\frac{mV_0b}{\hbar^2\alpha} \sin \alpha a + \cos \alpha a = \cos ka$$

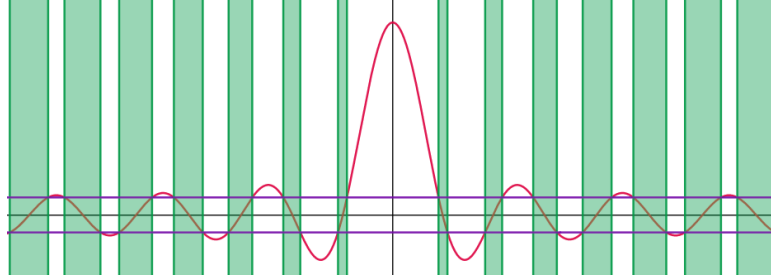
Take $P = \frac{mV_0ab}{\hbar^2}$ and rewrite the above as,

$$\boxed{\frac{P \sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka}$$

Now we can graph this with α as the x axis and the LHS as the y axis.

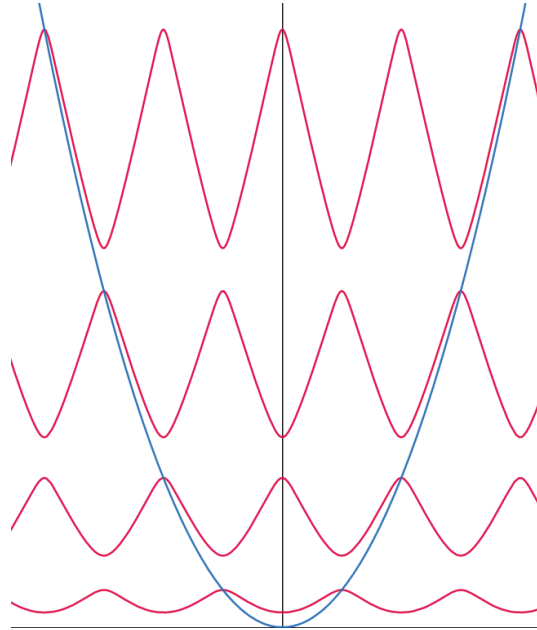


Now, notice that the RHS of the above expression lies between -1 and 1 , so not all values of αa (energy) are allowed in the LHS, as illustrated in the graph below. This gives a relation between energy (through α) and the wave vector k for a simple potential described by a finite product $V_0.b$.



We can write α proportional to \sqrt{E} and make a graph with respect to k of the following equation:

$$\frac{P \sin(c_1 \sqrt{E})}{c_1 \sqrt{E}} + \cos(c_1 \sqrt{E}) = \cos(c_2 k)$$



Here the blue line represents $c_1 \sqrt{E} = c_2 k$. This compares the energies obtained by the K-P model with the free electron model. The gaps in the K-P model are the forbidden energy bands.

2.4 Energy Bands in Solids

Now let us consider the graph of the LHS of the boxed equation plotted against αa above for any arbitrary value of P . Remember that since the RHS lies between -1 and 1 , therefore solution to the equation can exist only in those regions (we call these **allowed energy bands**), and wherever the value exceeds these limits, no solution exists and we say these are **forbidden energy gaps** or simply band gaps.

2.4.1 Conclusions from Kronig-Penney Model

We make the following conclusions from the KP model:

1. Electrons that move in a periodically varying potential field can only occupy certain allowed energy zones
2. Energies outside of these allowed zones or “bands” are prohibited.
3. When we increase the value of energy, i.e. the value of αa increases, the amplitude of the graph decreases and so the size of the forbidden bands become narrower.

2.4.2 Effect of P on Energy Spectrum

The effect of P ($= \frac{mV_0ab}{\hbar^2}$) on the energy spectrum can be summarized in the following cases:

1. **Case 1:** When the “potential barrier strength” V_0b is large, P is also large and the curve proceeds more steeply. The allowed bands are narrow. Note that, if the potential barrier strength, and therefore P , is small, the allowed bands become wider.
2. **Case 2:** When P goes to zero, i.e. when potential barrier strength approaches zero, we have:

$$\cos \alpha a = \cos ka$$

Therefore, $\alpha = k$ and $E = \frac{\hbar^2 k^2}{2m}$ which is exactly like the case of the free electron model.

3. **Case 3:** If $V_0 \rightarrow \infty$ then $P \rightarrow \infty$ However, because the LHS of equation has to stay within the limits ± 1 , i.e., it has to remain finite, it follows that:

$$\frac{\sin \alpha a}{\alpha a} \rightarrow 0 \implies \alpha a = n\pi$$

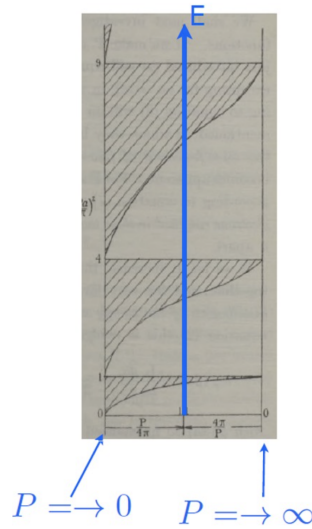
Thus, we may write,

$$\alpha^2 = \frac{n^2 \pi^2}{a^2} \text{ for } n = 1, 2, 3, \dots$$

Since we know $E = \frac{\alpha^2 \hbar^2}{2m}$, we finally get,

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

If we draw the energy spectrum for such a bound electron in a solid, for $P \neq 0$ we would notice that width of the allowed bands decreases with increasing P (as explained in Case 1).



2.4.3 Dispersion Relations

If we consider the plot between E and k , notice that there are discontinuities in the graph which occur at

$$k = \frac{n\pi}{a}$$

These represent the boundaries of the Brillouin Zones. Energy ranges between the allowed energy bands which are not accessible to the electrons, due to the interaction of the conduction electrons with the periodic potential of the lattice, V . This energy range is called energy gap.

2.5 Origin of Band Formation in Solids

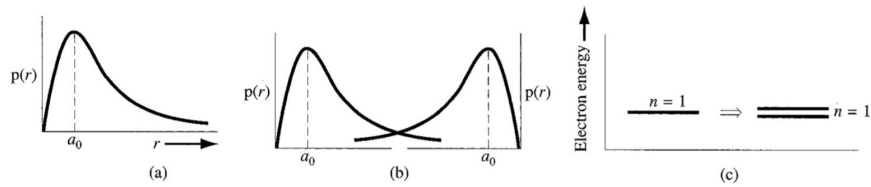
2.5.1 Tight Binding Model

The tight-binding model reveals what happens when a very large number of atoms, initially at an infinite distance apart come closer together to form a solid. As the atoms approach one another to form the solid, the wave functions of their electrons start to overlap. The interactions between the electrons cause the discrete energy levels of each of the isolated atoms to split into a huge number of energy levels forming a **band** of levels.

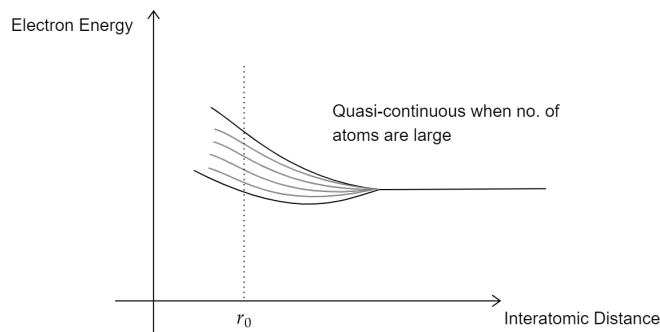
This prevents the Pauli exclusion principle from being violated, as while two atoms can have their electrons in exactly the same levels as one another if they are isolated, this cannot occur with the atoms side by side in a solid. So, the split levels created when a solid is formed get round this problem by providing enough separate states to accommodate all the electrons in the solid with the same quantum numbers. These energy levels are in fact so close together within the bands that they can be considered to be a *continuum of levels* rather than a collection of discrete energy levels.

Hydrogen Atom

When the wave function of the electrons of the two different atoms begin to overlap considerably, the energy levels corresponding to those wave functions split into two. When two hydrogen atoms are brought close enough

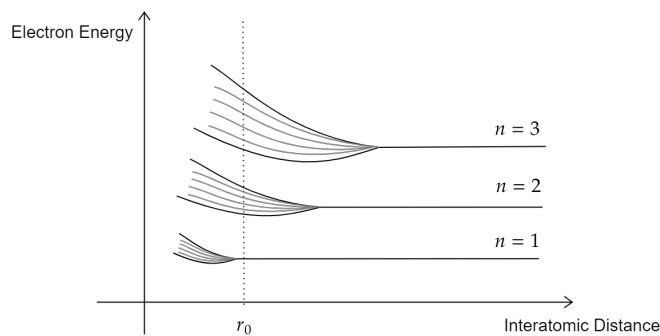


for the wave functions of $n=1$ electrons to start interacting, the $n=1$ state splits into two different energies, in accordance with Pauli's exclusion principle. Note here, r_0 is the equilibrium interatomic distance.



Many Electron Atoms

In an atom containing many more electrons, note that the states in the outmost shells split first. Depending on the value of r_0 , the lower states may or may not split.



The wave functions of the outermost electron shells that overlap more than those of the electrons closest to the nucleus. The width of the band depends on the degree of overlap of electrons of adjacent atoms and is largest for the outermost atomic electrons. In fact the outermost electrons can take part in conduction because the overlap of the outermost e^- wave functions is so great that it actually extends throughout the whole solid.

Chapter 3

Band Theory - Metals, Insulators, Semiconductors

3.1 Introduction

Electrons can have any of the values of energy contained within the energy bands. This means they can move about within the energy bands, as in a band, there are empty levels nearby that electrons can move into. This is important to explain the difference between conductors, insulators, and semiconductors, as each different type of solid has a different band structure. Some definitions:

1. **Valence Band:** The topmost fully filled band at 0 K.
2. **Conduction Band:** The next higher energy band. It may be empty or partially filled.
3. **Forbidden Gap:** The energy difference between the bottom of the Conduction Band (CB) and the top of the Valence Band (VB).

When sufficient energy is supplied, in the form of thermal energy, or electric field, electrons jump from the VB to the CB by overcoming the band gap and thus resulting in the flow of current.¹

3.2 Classification

Note that electrical conduction will occur if the highest occupied energy band is partially filled. So, we can classify the materials based on the type of band structure they possess, into **conductors**, **semiconductors**, and **insulators**.

3.2.1 Metals

In metals, as the levels are closely spaced to each other in energy and there is an overlap between the bands, generally the energy provided by the electric field or temperature is sufficient to stimulate an electrons to any empty states. Resistivity of metals typically increases linearly with temperature, according to the relation:

$$\rho = \rho_0 + \alpha T$$

¹Note that only those electrons in the materials that are close to Fermi level participate in the conduction of electricity and heat. This is because electrons just below the Fermi level gain enough thermal energy to occupy the states that are available to them. Electrons in lower energy levels do not have vacant energy states nearby to occupy.

Here, ρ_0 and α are constants depending on the material. Note that at lower temperatures the relation is not quite linear due to impurities in the solid.

3.2.2 Insulators

Insulators are the materials which don't allow the flow of electrons through them, since electrons must be promoted across the energy gap to conduct, but the energy gap is large in these materials ($> 4eV$). These possess very high resistivity, breakdown voltage, and air permeability. Even though many energy levels may be lying in proximity, overlap is not possible as they are full.

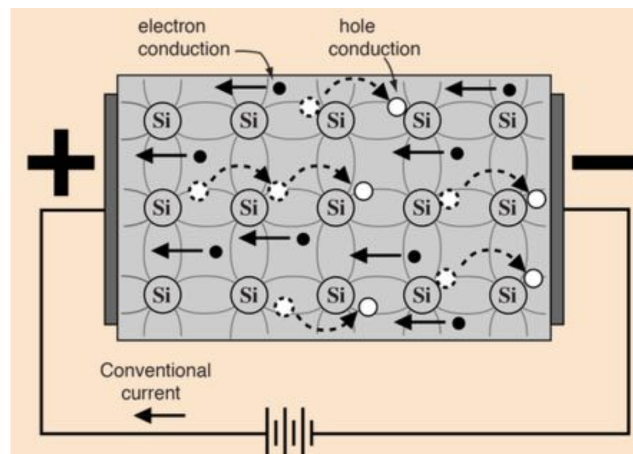
At $T = 0\text{ K}$, lower valence band is filled with electrons and upper conduction band is empty, leading to zero conductivity. Even at $T > 0\text{ K}$, electrons are **not** thermally "excited" from valence to conduction band, leading to zero conductivity.

3.2.3 Semi-Conductors

A finite but small band gap ($< 3eV$) exists. At $0K$ the conductivity is zero because all states in the VB are filled and all states in the CB are vacant. As the temperature is increased, there is a finite probability that an electron is thermally excited from the VB to the CB, where they become mobile. Such carriers are called "intrinsic."

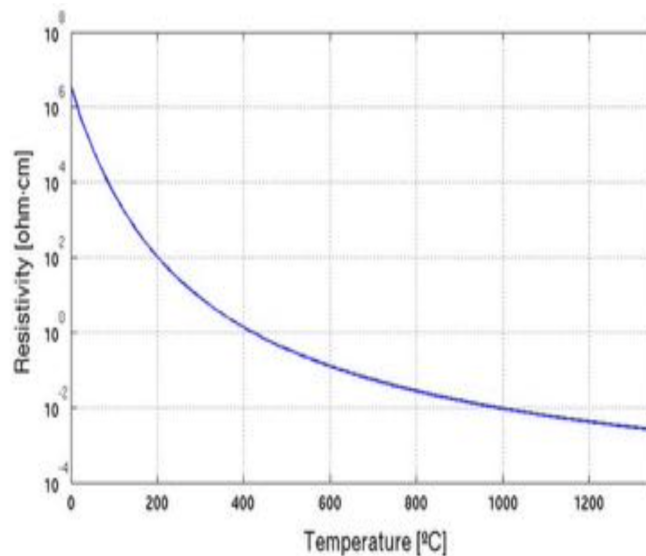
Hole

Hole: When an electron is excited to CB from a VB it leaves behind an unoccupied state known as hole. Holes are therefore absence/deficiency of an electron. Hole is a positively charged carrier and has a charge equal to that of an electron but with an opposite polarity. Holes also participate in total conduction. Holes in a semiconductor can move in crystal lattice like electrons and play an important role in conduction.



3.3 Conduction in Semiconductors

Movement of the holes will be due to the jumping of neighboring electrons into the holes. Holes will move in opposite directions to the electrons and contribute positively to the current as they possess a positive charge.



Resistivity behavior of intrinsic silicon material with the temperature.

Holes have effective mass higher compared to their electron counterparts meaning that they are *less mobile* compared to electrons. In an intrinsic semiconductor, the number of free electrons equals the number of holes. As the temperature is increased the number of free electrons in the conduction band and holes in valance band increases. Number of free charge carriers at a fixed temperature also depends on the energy gap of the semiconductor. For large gap materials number of free electron and holes will lower compared to the material with small band gap at fixed temperature. Light can also generate free electrons and holes in a semiconductor. Optical: The energy of the photons $h\nu$ must equal or exceed the energy gap of the semiconductor E_g . If $h\nu > E_g$, a photon can be absorbed, creating a free electron and leaving behind a hole.

3.3.1 Direct and indirect band gap semiconductors

- In the direct band gap semiconductors, the lowest point of the conduction band occurs at the same value of k as the highest point of the valence band.
- In indirect band gap semiconductors, the lowest of the conduction band and highest point of the valance band both exist at different values of k .
- The indirect transition involves both a *photon* and a *phonon* because the band edges of the conduction and valence bands are widely separated in k space.

3.3.2 Increasing Conductivity by doping

An impurity, or element like arsenic, has 5 valence electrons. Adding arsenic (doping) will allow four of the arsenic valence electrons to bond with the neighboring silicon atoms. The one electron left over for each arsenic atom becomes available to conduct current flow.

Chapter 4

Effective Mass

If an electron is travelling through a vacuum and being accelerated by an electric field, its motion can be described by Newton's laws of motion. Newton's laws can also describe the motion of a free electron that is being accelerated within a crystal by the electric field produced by an applied voltage.

When an electric field E_x is applied to a metal, an electron near the Fermi level can gain energy from the field and move to higher energy levels.¹

4.1 Effective Mass

However, as the electrons are interacting with different potentials as they make their way through the lattice, in order for the simple Newtonian physics to work, the normal mass of the electron, m_e , must be replaced by the effective mass, m_e^* .² When the same force F_{ext} , is applied to the electron inside a crystal, the acceleration of the electron will be different, because it will also experience internal forces, its acceleration in the crystal will be

$$a_{cryst}^{\rightarrow} = \frac{F_{ext}^{\rightarrow} + F_{int}^{\rightarrow}}{m_e}$$

where F_{int} is the sum of all the internal forces acting on the electron.³

It has been found that when the electron is in a band that is not full, we can use the equation

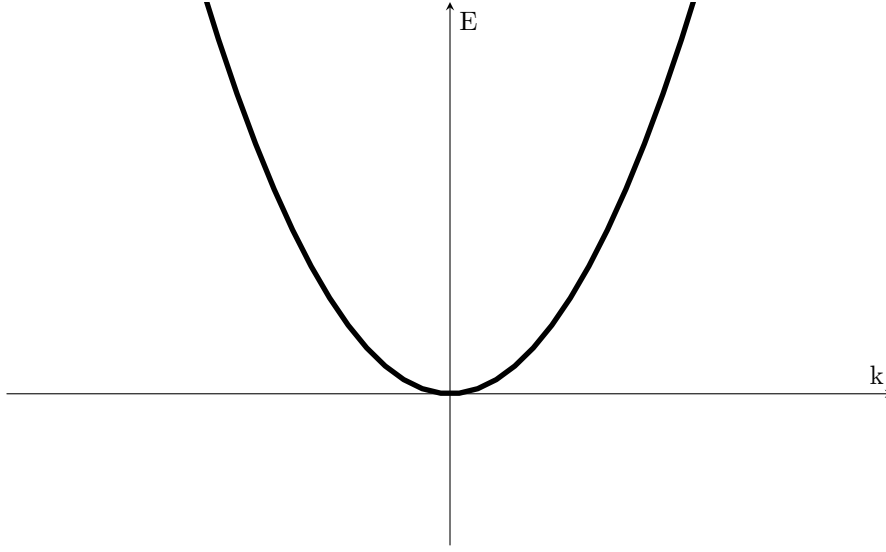
$$a_{cryst}^{\rightarrow} = \frac{F_{ext}^{\rightarrow}}{m_e^*}$$

¹The external force $F_{ext} = eE_x$ is in the x direction, and it drives the electron along x . The acceleration of the electron is still given by $a = \frac{F_{ext}}{m_e}$, where m_e is the mass of the electron in vacuum.

²An electron in a periodic potential is accelerated relative to the lattice in an applied electric or magnetic field as if its mass is equal to what is called an effective mass. There are crystals in which the effective mass of the carriers is much larger or much smaller than m_e .

³To the outside agent applying the force F_{ext} the electron will appear to be exhibiting a different inertial mass, since its acceleration will be different.

4.2 Relation with Wavevector-Energy Graphs



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

$$\frac{dE}{dk} = \text{Slope}$$

$$\frac{d^2E}{dk^2} = \text{Rate of change of Slope}$$

So, the mass of electron is inversely proportional to the curvature of band structure (rate of change of slope). We shall now attempt to find an expression for the effective mass.

$$v_g = \frac{d\omega}{dk} = \frac{d(2\pi\nu)}{dk} = \frac{d\frac{2\pi E}{h}}{dk} = \frac{1}{h} \frac{dE}{dk}$$

Where, ω is the angular frequency and $k = \frac{2\pi}{\lambda}$ is the wave number. We can write acceleration as:

$$a = \frac{dv_g}{dt} = \frac{1}{h} \frac{d^2E}{dk^2} \frac{dk}{dt}$$

As we know $p = \hbar k$,

$$\frac{dp}{dt} = \hbar \frac{dk}{dt}$$

By combining the above equations, we get:

$$a = \frac{1}{\hbar^2} \frac{d^2E}{dk^2} \frac{dp}{dt} = \frac{1}{\hbar^2} \frac{d^2E}{dk^2} \frac{dmv}{dt} = \frac{1}{\hbar^2} \frac{d^2E}{dk^2} F$$

Where $F = m_e^* a$. So, we get:

$$m_e^* = \hbar^2 \left(\frac{d^2E}{dk^2} \right)^{-1}$$

So, we can get the following information from the band diagrams:

- Allowed and forbidden bands. Identification of the gap energy
- Slope of the bands – group velocity $v_g = \frac{1}{\hbar} \frac{dE}{dk}$
- Curvature of bands – effective mass

Note that $\frac{d^2E}{dk^2}$ can be positive, negative or zero.

$$m_e^* \Rightarrow \begin{cases} \text{electron} & \text{when } \frac{d^2E}{dk^2} > 0 \\ \text{hole} & \text{when } \frac{d^2E}{dk^2} < 0 \\ \text{Immovable particle} & \text{when } \frac{d^2E}{dk^2} = 0 \end{cases}$$

Chapter 5

Thermoelectricity

5.1 Phonons

Atoms never sit completely still. They always have some motion about their lattice point.¹ So although diffraction reveals the positions of the atoms in a crystal, it only in fact reveals the positions of the atoms at the instant they reflect the radiation being used in the diffraction experiment. An instant later, their positions will have changed. However, this change in position is incredibly small, so it makes no difference to identifying a structure by diffraction.²

In particular the *thermal properties of solids are entirely due to atomic motion*.³

5.1.1 Zero-point energy

Since atoms in solids do not remain still at their lattice positions, they need some form of energy in order to be able to move. This energy is either heat energy or mechanical energy. The hotter a solid is, the more the atoms vibrate about their positions in the lattice.

Although atoms move much less at low temperatures than at high temperatures, they still move even at absolute zero. This movement is known as zero-point motion, and the kinetic energy possessed by atoms with zero-point motion is termed “**zero-point energy**”.

5.1.2 What are Phonons?

If an atom is considered individually, its motion about its own lattice point can be simplified as *simple harmonic motion (SHM)*. However, atoms cannot vibrate independently of each other because they are connected together by bonds. So any vibration in one atom gets passed on to its neighbours, which in turn pass the vibration on to their neighbours, and so on, and thus producing a vibratory wave that passes through the solid.

There are two ways in which an elastic wave:

- Longitudinal Waves
- Latitudinal Waves

¹In fact if they did not, they would violate Heisenberg’s uncertainty principle, which states that if the position of a particle is known exactly, its momentum cannot be known as well, and vice versa.

²Although the structure of a particular crystal may look the same when different diffraction patterns from it are analysed, there are other properties of crystals that are affected much more by the motion of the atoms about their lattice positions.

³Also, the electrical properties of solids are influenced by the vibrations of their atoms.

In the same way that light can be regarded as either a wave or a stream of particles known as photons, *vibrations in solids can be thought of either as waves or particles known as **phonons***. Phonons are quantized lattice waves; these are quasi-particles associated to the lattice vibration. Phonons are characterized by a frequency ω and a wavevector k with a dispersion relation, basically phonons are bosons, described by symmetric wavefunction. As with other quantum mechanical particles, phonons can only have certain values of energy. A phonon vibrating at a frequency ω can only have values of energy that are $\hbar\omega$ apart from one another.

A region of a solid containing larger amplitude atomic vibrations than another area can be said to contain more phonons. Equally, if a solid is considered as a whole, the greater the atomic vibrations are throughout the solid, the more phonons are said to be in the solid.

Properties of Phonons

The particle nature of phonons means they can be considered to “move” through solids, and many properties of solids that are affected by temperature can be explained in terms of phonons being scattered. This scattering can either be by point defects or dislocations, by one another, or by the surface of the solid. In each case there will be a mean free path which represents how far a phonon travels on average before being scattered.

Phonons have a wavelength associated with them, that depends on the temperature of the solid and the extent to which phonons are scattered by lattice defects depends on this wavelength. There is actually a range of phonon wavelengths at all temperatures, but on average *the phonon wavelength is longer at low temperatures and shorter at high temperatures*.⁴ This means that at low temperatures, the phonon wavelength is much larger than any point defect, so the defect is unable to scatter the wave. Therefore, the amount of scattering is much less at low temperatures than that at higher temperatures, where the phonon wavelength is of a comparable size to that of the defects. As higher temperatures mean a larger amount of movement of the atoms, and the larger the amplitude of any two waves the greater the chance of them interacting, the scattering of phonons by one another is also greater at higher temperatures.⁵

5.2 Seebeck Effect

The word thermoelectric means the production of the electricity by the means of the temperature difference.

5.2.1 Definition

Creation of thermal emf (electromotive force) by temperature gradient

In 1820-21, German physicist discovered that when two dissimilar metals, *Cu* and *Bi* are joined at the ends to form a loop, a voltage is developed in the circuit if the two junctions are kept at different temperatures. The pair of metals forming the circuit is called a **thermocouple**. As energy flows from the higher energy to the lower energy, the heat will flow from the hot surface to the cold surface. The conduction of the heat inside the material can be transferred by the various routes:

- Phonons
- Ionic conductors: ions
- Mobile carriers: electrons and holes

⁴In fact as a very rough guide, the dominant phonon wavelength can be considered to be in the order of a few hundred atomic spacings just above absolute zero, while at room temperature and above it is around twice the value of the lattice parameter, a .

⁵the internal energy U of the solid can be written as $U = E_{static} + E_{vib}$, where E_{static} is the electronic ground state energy with a fixed lattice (on which we have focused so far) and E_{vib} is the additional energy due to lattice motion. In general (and we will substantiate this below), $E_{static} \gg E_{vib}$ and thus many properties are correctly obtained, even when simply neglecting E_{vib} .

Electrons at the hot end being more energetic, have higher velocities than the electrons in the cold end. Net diffusion of the electrons from the hot end to the cold end. Positive ions at the hot end and the electrons accumulates at the cold end. This situation prevails until the electric field developed between the positive ions in the hot region and electrons in the cold end prevent the electronic motion at both ends. A voltage is developed between both the ends, with the hot end at the positive potential. *The potential difference ΔV across the piece of metal as a result of the temperature difference ΔT is called the **Seebeck Effect**.* The magnitude of Seebeck effect is defined by the coefficient S (*Seebeck Coefficient or Thermoelectric Power*).

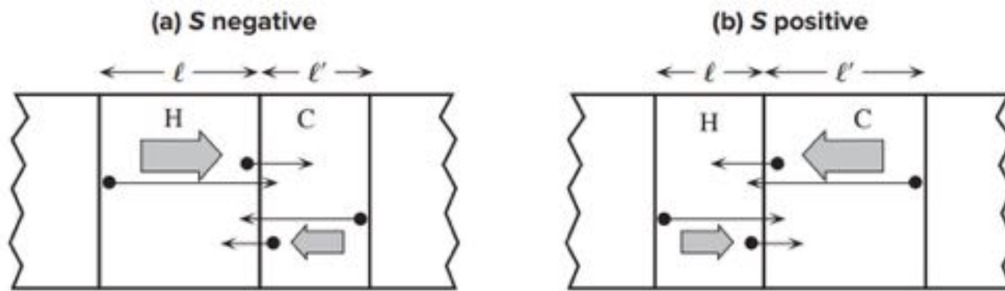
$$S = \frac{\Delta V}{\Delta T}$$

By convention, the sign of S represents the potential of the cold side with respect to the hot side. If electrons diffuse from the hot end to the cold end, then the cold side is negative with respect to the hot side and $S < 0$ (as for aluminum). But, for Copper, $S > 0$.

5.2.2 Explaining Seebeck Effect

Factors affecting Seebeck effect

Consider a hot region H and cold region C with the widths proportional to the mean free path lengths l and l' in the hot and cold regions. The electron concentration n in the hot and cold regions is roughly the same. Half



of the electrons move in the $+x$ direction and other half move in the $-x$ direction. Half of the electrons in H therefore cross into C , and half in C cross into H . Number of electrons travelling from H to C is $\frac{1}{2}nl$ and the no. of electrons travelling from C to H is $\frac{1}{2}nl'$. So, net diffusion from H to $C \propto \frac{1}{2}n(l - l')$.

For $l > l'$, scattering of electrons is such that l increases strongly with the electron energy. Then electrons in H , which are more energetic, have a longer mean free path. The net migration is from the hot region to the cold region and $S < 0$. For metals such as Cu , l decreases strongly with the energy, electrons in the cold region have a longer mean free path, $l' > l$. The net migration of the electrons is from the cold region to the hot region and $S > 0$.

Causes of Seebeck Effect

Seebeck effect arises from the diffusion of the electrons via different scattering processes along with a temperature gradient, called as electron diffusion contribution. The other driving force is the thermal vibrations that setup the lattice waves which travel inside the crystal, called as phonons.

Lattice waves will flow from the hot to the cold region, will collide with the electron, scatter them and push them along the temperature gradient. Collision of the phonons with the electrons drags them along with the phonons and creates potential difference, this contribution is called as *phonon drag contribution*.

5.2.3 Seebeck Coefficient

S is a function of temperature.

$$\Delta V = \int_{T_0}^T S \, dT$$

Around and above room temperature, the magnitude of S increases almost linearly with the temperature. For pure metal Al, S arises from the diffusion of the electrons and phonon drag.

$$S \approx aT + \frac{b}{T}$$

5.2.4 Thermocouple

Thermocouple uses two different metals with one junction maintained at a reference temperature T_0 and the other used to sense the temperature T . The voltage across each metal element depends on the Seebeck Coefficient. The potential difference between the two wires will depend on the $S_A - S_B$. The electromotive force between the two wires is given as:

$$V_{AB} = \Delta V_A - \Delta V_B$$
$$V_{AB} = \int_{T_0}^T (S_A - S_B) \, dT = \int_{T_0}^T S_{AB} \, dT$$

Here $S_A - S_B$ is defined as the **thermoelectric power** for the thermocouple pair $A-B$. S_{AB} also represents the **sensitivity** of the thermocouple.

5.3 Uses and Applications

- **Refrigeration:** Driving current through the same solid results in heating in one contact and cooling in another.
- **Power generation:** Temperature difference across a solid produces thermally generated emf which can drive current through a load
- TEs could play a big role in waste heat recovery.
 - Cooling in small size applications.
 - Improving Efficiency
- TE modules in cooking stoves and solar thermal systems.
- Many groups are looking at polymer TEs even though efficiency is lower than traditional semiconductors, paralleling work in solar cell community

Chapter 6

Magnetism in Materials

6.1 What causes Magnetism in materials?

All magnetic moments are produced by the angular momentum of electrons in the atoms of solids, and there are two types of angular momentum for electrons in atoms:

- *orbital*: Electrons revolving around nucleus
- *spin*: electrons spinning about their own axis

Both can be considered as tiny current loops. For macroscopic purposes, these current loops are so small that we generally consider them as magnetic dipoles. In general, these magnet dipoles cancel each other due to random orientations of the atoms. when a magnetic field is applied, a net alignment of these magnetic dipoles occurs, and the medium becomes magnetically polarized, or magnetized Unlike electric polarization, which is almost always in the same direction as E , some materials acquire a magnetization maybe parallel or anti-parallel to B :

- *Paramagnets*: Magnetization is parallel to B .
- *Diamagnets*: Magnetization is opposite (anti-parallel) to B .
- *Ferromagnets*: Retain their magnetization even after the external field has been removed. The magnetization is not determined by the present field but by the whole magnetic “history” of the object.

6.2 Forces and Torques on Magnetic Dipoles

6.2.1 Magnetic Dipole

There is no net force on a magnetic dipole but it experiences a torque

$$\boldsymbol{\tau} = \mathbf{m} \times \mathbf{B}$$

The torque is again in such a direction as to line the dipole up parallel to the field. This is a universal phenomena since every electron constitute a magnetic dipole.

6.2.2 Effect of B on Atomic Orbits

For simplicity, let's assume that the electrons orbit in a circle of radius R around the nucleus. We consider the consequent current to be a steady current as the period of motion is too small, so the steady current.

$$\begin{aligned} I &= \frac{-e}{T} \\ &= -\frac{ev}{2\pi R} \end{aligned} \quad (6.1)$$

The orbital dipole moment $I\pi R^2$:

$$\mathbf{m} = -\frac{1}{2}evR\hat{\mathbf{z}} \quad (6.2)$$

Normally, it's a lot harder to tilt the entire orbit than it is the spin, so the orbital contribution to paramagnetism is small. There is, however, a more significant effect on the orbital motion. The electron speeds up or slows down, depending on the orientation of B . The centripetal acceleration is ordinarily sustained by electrical forces alone:

$$\frac{1}{4\pi\epsilon_0} \frac{e^2}{R^2} = m_e \frac{v_0^2}{R} \quad (6.3)$$

For B perpendicular to the plane of orbit,

$$\frac{1}{4\pi\epsilon_0} \frac{e^2}{R'^2} + evB = m_e \frac{v^2}{R'} \quad (6.4)$$

When $\Delta R = 0, v > v_0$,

$$\begin{aligned} evB &= \frac{m_e}{R} v^2 - v_0^2 \\ &= \frac{m_e}{R} (v - v_0)(v + v_0) \end{aligned} \quad (6.5)$$

Assuming $\Delta v \approx 0$,

$$\Delta v = \frac{eRB}{2m_e} \quad (6.6)$$

$\Delta v \Rightarrow \Delta \mathbf{m}$. So,

$$\begin{aligned} \Delta \mathbf{m} &= -\frac{1}{2}e(\Delta v)R\hat{\mathbf{z}} \\ &= -\frac{e^2 R^2}{4m_e} \mathbf{B} \end{aligned} \quad (6.7)$$

The change in \mathbf{m} is opposite to the direction of \mathbf{B} .

6.3 Materials in magnetic field

Ordinarily, the electron orbits are randomly oriented, and the orbital dipole moments cancel out. But in the presence of a magnetic field, each atom picks up a little "extra" dipole moment, and these increments are all antiparallel to the field. This is the mechanism responsible for *diamagnetism*. With the application of a magnetic field, magnetic moments in a material tend to align and thus increase the magnitude of the field strength. Depending on the existence and alignment of magnetic moments with or without application of magnetic field, broadly speaking, five types of magnetism can be defined:

- Diamagnetism

- Paramagnetism
- Ferromagnetism
- Ferrimagnetism
- Antiferromagnetism

Being a moving charge, electrons produce a small magnetic field having a magnetic moment along the axis of rotation. The spin of electrons also produces a magnetic moment along the spin axis. Magnetism in a material arises due to alignment of magnetic moments.

6.3.1 Magnetic Susceptibility

Magnetic Flux Density B in an external Magnetic field H is given by:

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$$

where μ_0 is vacuum permeability and M is the magnetization given by:

$$\mathbf{M} = \chi \mathbf{H}$$

where χ and can be expressed in terms of volume, atomic or molar susceptibility. Therefore, we can write:

$$\mathbf{B} = \mu_0(1 + \chi)\mathbf{H}$$

The magnetic properties of a material are characterized not only by the magnitude and sign of M but also the way in which M varies with H .

Diamagnetism and paramagnetism are usually referred to as non-magnetic, whereas those which are referred to as magnetic are actually ferromagnetic. Anti-ferromagnetism is observed in pure elements at Room Temperature. Finally, ferri-magnetic, not observed in pure element, but can only be found in compounds, such as the mixed oxides, known as ferrites.

6.3.2 Diamagnetism

In a diamagnetic material the atoms have no net magnetic moment when there is no applied field. Diamagnetism is a weak form of magnetism which arises only when an external field is applied. It arises due to change in the orbital motion of electrons on application of a magnetic field. There are no magnetic dipoles in the absence of a magnetic field and when a magnetic field is applied the dipole moments are aligned opposite to the field direction.

$\chi < 0$, χ is independent of temperature.

When an atom is placed in a magnetic field, due to the presence of Lorentz force, the speed of the electron changes. This change in orbital speed of the electrons, leads to change in the magnetic moment. Lenz's law tells us that the currents are induced in the direction which opposes the applied field, so the induced magnetic moments are directed opposite to the applied field.

The magnetic susceptibility, $\chi_m = \mu_r - 1 < 0$ i.e., B in a diamagnetic material is less than that of vacuum.

Examples: metals Au, Cu, Hg ; non-metallic elements B, Si, P, S ; many ions Na^+, Cl^- and their salts; diatomic molecules H_2, N_2, H_2O , most organic compounds. Monoatomic rare gases He, Ne , etc., which have closed-shell electronic structures and gases such as H_2, N_2 , etc., as the molecule formation usually leads to filled electron shells and no net magnetic moment per molecule, same argument explains the diamagnetism of ionic solids like $NaCl$, and covalent elements like C (diamond), Si , and Ge .¹

¹Ions like Na^+ and Cl^- have closed shells and are both diamagnetic, as it leads to closed shells. Element like Si have Covalent bonding by the sharing of electrons, also leads to closed shells hence are diamagnetic. Not all gases are diamagnetic, nor are all ionic or covalent solids.

6.3.3 Paramagnetism

Paramagnetism is a magnetic property present in materials with a non-zero magnetic moment, due to unpaired electrons and hence magnetic moments exist without any external magnetic field. However, the magnetic moments are randomly aligned and hence no net magnetization without any external field. When a magnetic field is applied all the dipole moments are aligned in the direction of the field. Only extremely weak interactions exist between neighboring atoms in paramagnetic materials, and they assumed to act independently of one another. χ is small but positive, i.e., B in a paramagnetic material is slightly greater than that of vacuum. Examples of Metals Al ; diatomic gases, O_2 , NO ; ions of transition metals and rare earth metals, and their salts; rare earth oxides.

6.3.4 Ferromagnetism

Certain materials like Fe, Co, Ni possess permanent magnetic moments in the absence of an external magnetic field, due to unpaired electrons in partially filled electron orbitals. This is known as ferromagnetism. Unlike paramagnetic materials, neighboring atomic moments in a ferromagnetic material exhibit very strong interactions (produced by electronic exchange forces) couples neighboring atomic magnetic moments and result in a parallel alignment of atomic moments and therefore, in a large net positive magnetization. The long-range ordering present in ferromagnetic materials is a result of this exchange interaction. They exhibit a spontaneous magnetization even in the absence of an applied field which gives rise to the characteristic hysteretic behavior of ferromagnetic materials. The applied field is not creating the magnetisation, it is rearranging the spontaneous magnetisation which is already in the sample.

Domain

FM materials exhibit a long-range ordering phenomenon at the atomic level which causes the unpaired e- spins to align in the same direction in a region called a domain. Ferromagnetic material consists of small macroscopic regions (called domains), which are already spontaneously magnetized.²

²Pierre Weiss (1907)