

CHAPTER 5 FREE ELECTRON THEORY

Why mobile electrons appear in some solids and others?

When the interactions between electrons are considered this becomes a very difficult question to answer.

The common physical properties of metals;

- Great physical strength
- High density
- Good electrical and thermal conductivity, etc.

This chapter will calculate these common properties of metals using the assumption that conduction electrons exist and consist of all valence electrons from all the metals; thus metallic Na, Mg and Al will be assumed to have 1, 2 and 3 mobile electrons per atom respectively.

A simple theory of '**free electron model**' which works remarkably well will be described to explain these properties of metals.

Free Electron Theory

Many solids conduct electricity.

There are electrons that are not bound to atoms but are able to move through the whole crystal.

Conducting solids fall into two main classes; metals and semiconductors.

$\rho(RT)_{\text{metals}}$; $10^{-6} - 10^{-8} \Omega \cdot m$ and increases by the addition of small amounts of impurity. The resistivity normally decreases monotonically with decreasing temperature.

$\rho(RT)_{\text{semi-conductor}} < \rho(RT)_{\text{metal}}$ and can be reduced by the addition of small amounts of impurity.

Semiconductors tend to become insulators at low T.

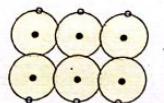
Why mobile electrons appear in some solids and not others?

□ According to free electron model (FEM), the valence electrons are responsible for the conduction of electricity, and for this reason these electrons are termed conduction electrons.

□ $\text{Na}^{11} \rightarrow \underbrace{1s^2 2s^2 2p^6}_{\text{Core electrons}} 3s^1 \leftarrow$ Valence electron (loosely bound)

□ This valence electron, which occupies the third atomic shell, is the electron which is responsible chemical properties of Na.

- When we bring Na atoms together to form a Na metal,

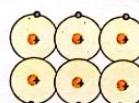


Na metal

- Na has a BCC structure and the distance between nearest neighbours is 3.7 \AA
 - The radius of the third shell in Na is 1.9 \AA
- Solid state of Na atoms overlap slightly. From this observation it follows that a valence electron is no longer attached to a particular ion, but belongs to both neighbouring ions at the same time.

- A valence electron really belongs to the whole crystal, since it can move readily from one ion to its neighbour, and then the neighbour's neighbour, and so on.

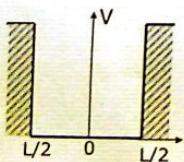
- This mobile electron becomes a conduction electron in a solid.



- The removal of the valence electrons leaves a positively charged ion.
- The charge density associated with the positive ion cores is spread uniformly throughout the metal so that the electrons move in a constant electrostatic potential. All the details of the crystal structure is lost when this assumption is made.

- According to FEM this potential is taken as zero and the repulsive force between conduction electrons are also ignored.

- Therefore, these conduction electrons can be considered as moving independently in a square well of finite depth and the edges of well corresponds to the edges of the sample.
- Consider a metal with a shape of cube with edge length of L ,
 - ψ and E can be found by solving Schrödinger equation



$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi \quad \text{Since, } V=0$$

- By means of periodic boundary conditions ψ 's are running waves.

$$\psi(x+L, y+L, z+L) = \psi(x, y, z)$$

- The solutions of Schrödinger equations are plane waves,

$$\psi(x, y, z) = \frac{1}{\sqrt{V}} e^{i\vec{k}\vec{r}} = \underbrace{\frac{1}{\sqrt{V}} e^{i(k_x x + k_y y + k_z z)}}_{\text{Normalization constant}}$$

- where V is the volume of the cube, $V=L^3$

$$Na = p\lambda \Rightarrow Na = p \frac{2\pi}{k} \quad \left(\text{where, } k = \frac{2\pi}{\lambda} \right) \Rightarrow k = \frac{2\pi}{Na} p = \frac{2\pi}{L} p$$

- So the wave vector must satisfy

$$k_x = \frac{2\pi}{L} p ; \quad k_y = \frac{2\pi}{L} q ; \quad k_z = \frac{2\pi}{L} r$$

where p, q, r taking any integer values; +ve, -ve or zero.

- The wave function $\Psi(x,y,z)$ corresponds to an energy of

$$E = \frac{\hbar^2 k^2}{2m} \quad E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

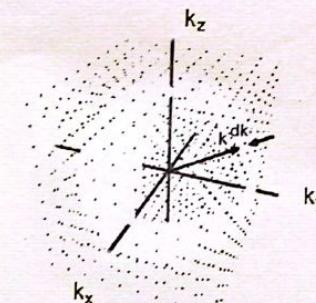
- the momentum of

$$p = \hbar(k_x, k_y, k_z)$$

- Energy is completely kinetic

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

- We know that the number of allowed k values inside a spherical shell of k -space of radius k of



$$g(k)dk = \frac{V k^2}{2\pi^2} dk,$$

- where $g(k)$ is the density of states per unit magnitude of k .

The number of allowed states per unit energy range?

- Each k state represents two possible electron states, one for spin up, the other is spin down.

$$g(E)dE = 2g(k)dk \rightarrow g(E) = 2g(k) \frac{dk}{dE}$$

$$E = \frac{\hbar^2 k^2}{2m} \quad \frac{dE}{dk} = \frac{\hbar^2 k}{m} \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

$$g(E) = \frac{V}{2\pi} \frac{2}{(\hbar^2)} \sqrt{\frac{2mE}{\hbar^2}} \frac{dk}{\frac{dE}{dk}} \rightarrow g(E) = \frac{V}{2\pi^2 \hbar^3} (2m)^{3/2} E^{1/2}$$

Ground state of the free electron gas

- Electrons are fermions ($s=\pm 1/2$) and obey Pauli exclusion principle; each state can accommodate only one electron.

- The lowest-energy state of N free electrons is therefore obtained by filling the N states of lowest energy.

- Thus all states are filled up to an energy E_F , **known as Fermi energy**, obtained by integrating density of states between 0 and E_F , should equal N. Hence

- Remember $g(E) = \frac{V}{2\pi^2\hbar^3} (2m)^{3/2} E^{1/2}$

$$N = \int_0^{E_F} g(E) dE = \int_0^{E_F} \frac{V}{2\pi^2\hbar^3} (2m)^{3/2} E^{1/2} dE = \frac{V}{3\pi^2\hbar^3} (2mE_F)^{3/2}$$

- Solve for E_F (Fermi energy);

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

- Typical values may be obtained by using monovalent potassium metal as an example; for potassium the atomic density and hence the valence electron density N/V is $1.402 \times 10^{28} \text{ m}^{-3}$ so that

$$E_F = 3.40 \times 10^{-19} \text{ J} = 2.12 \text{ eV}$$

$$k_F = 0.746 \text{ \AA}^{-1}$$

- Fermi (degeneracy) Temperature T_F by $E_F = k_B T_F$

$$T_F = \frac{E_F}{k_B} = 2.46 \times 10^4 \text{ K}$$

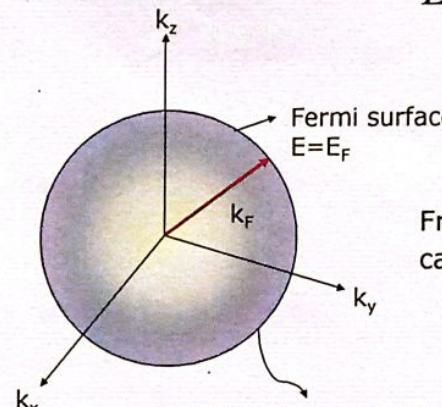
- The occupied states are inside the Fermi sphere in k-space shown below; radius is Fermi wave number k_F .

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

$$E_F = \frac{\hbar^2 k_F^2}{2m_e}$$

From **these** two equation k_F can be found as,

$$k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$



The surface of the Fermi sphere represent the boundary between occupied and unoccupied k states at absolute zero for the free electron gas.

- It is only at a temperature of this order that the particles in a classical gas can attain (gain) kinetic energies as high as E_F .

- Only at temperatures above T_F will the free electron gas behave like a classical gas.

- Fermi momentum $P_F = \hbar k_F$ $P_F = m_e V_F$

$$V_F = \frac{P_F}{m_e} = 0.86 \times 10^6 \text{ ms}^{-1}$$

- These are the momentum and the velocity values of the electrons at the states on the Fermi surface of the Fermi sphere.

- So, Fermi Sphere plays important role on the behaviour of metals.

Typical values of monovalent potassium metal:**Fermi-energy E_F :**

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} = 2.12 \text{ eV}$$

with the Fermi-wavevector k_F :

$$k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3} = 0.746 \text{ \AA}^{-1}$$

the Fermi-velocity v_F :

$$v_F = \frac{P_F}{m_e} = 0.86 \times 10^6 \text{ m s}^{-1}$$

the Fermi-temperature T_F :

$$T_F = \frac{E_F}{k_B} = 2.46 \times 10^4 \text{ K}$$

The Fermi wave vector: $k_F = (3\pi^2 n)^{1/3} \sim 1 \text{ \AA}^{-1}$ **The Fermi momentum:** $p_F = \hbar k_F \sim 10^{23} \text{ kg m/s}$ **The Fermi energy:** $\epsilon_F = \frac{\hbar^2 k_F^2}{2m} \sim 5 \text{ eV}$ **The Fermi velocity:** $v_F = \frac{p_F}{m} = \frac{\hbar}{m} k_F \sim 10^6 \text{ m/s}$ **The Fermi temperature:** $T_F = \frac{\epsilon_F}{k_B} \sim 10^4 \text{ K}$ **The free electron gas at finite temperature**

- At a temperature T the probability of occupation of an electron state of energy E is given by the Fermi distribution function

$$f_{FD} = \frac{1}{1 + e^{(E-E_F)/k_B T}}$$

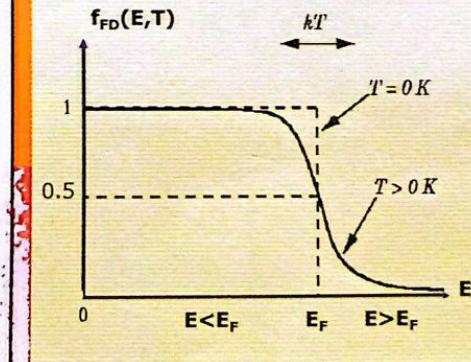
- Fermi distribution function determines the probability of finding an electron at the energy E .

Fermi Function at $T=0$ and at a finite temperature

$$f_{FD} = \frac{1}{1 + e^{(E-E_F)/k_B T}}$$

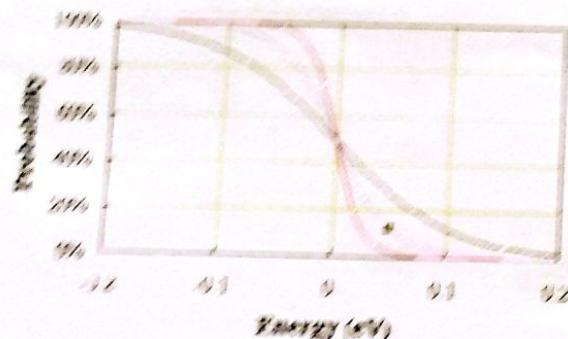
i. $f_{FD}=?$ At 0°K

$$f_{FD} = \frac{1}{1 + e^{(E-E_F)/k_B T}} = 1$$

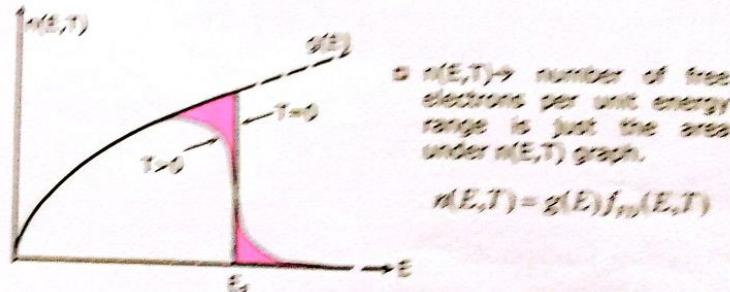


$$f_{FD} = \frac{1}{1 + e^{(E-E_F)/k_B T}} = 0$$

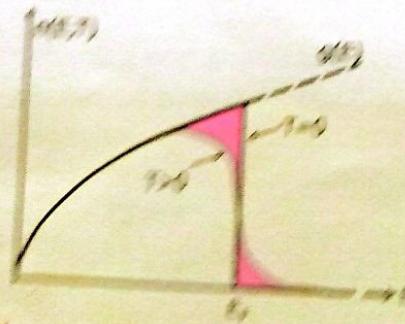
Fermi-Dirac distribution function at various temperatures,



- Number of electrons per unit energy range according to the free electron model?
- The shaded area shows the change in distribution between absolute zero and a finite temperature.

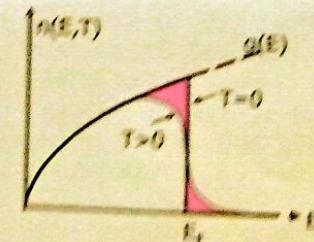


- Fermi-Dirac distribution function is a symmetric function; at finite temperatures, the same number of levels below E_F is emptied and same number of levels above E_F are filled by electrons.



Heat capacity of the free electron gas

- From the diagram of $n(E,T)$ the change in the distribution of electrons can be resembled into triangles of height $1/2g(E_F)$ and a base of $2k_bT$ so $1/2g(E_F)k_bT$ electrons increased their energy by k_bT .



- The difference in thermal energy from the value at $T=0^{\circ}\text{K}$

$$E(T) - E(0) \square \frac{1}{2} g(E_F)(k_b T)^2$$

- Differentiating with respect to T gives the heat capacity at constant volume,

$$C_v = \frac{\partial E}{\partial T} = g(E_F)k_B^2 T$$

$$N = \frac{2}{3} E_F g(E_F)$$

$$g(E_F) = \frac{3}{2} \frac{N}{E_F} = \frac{3N}{2k_B T_F}$$

$$C_v = g(E_F)k_B^2 T = \frac{3N}{2k_B T_F} k_B^2 T \rightarrow C_v = \frac{3}{2} N k_B \left(\frac{T}{T_F} \right)$$

Heat capacity of Free electron gas

Transport Properties of Conduction Electrons

- Fermi-Dirac distribution function describes the behaviour of electrons only at equilibrium.
- If there is an applied field (E or B) or a temperature gradient the transport coefficient of thermal and electrical conductivities must be considered.

Transport coefficients

σ , Electrical conductivity

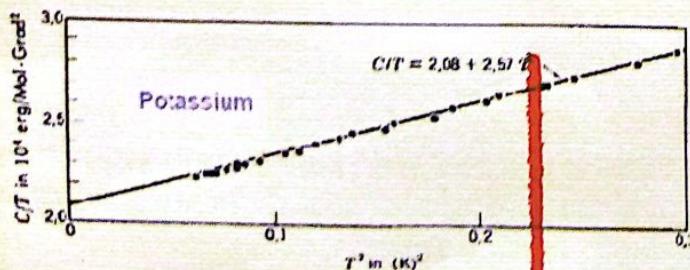
K, Thermal conductivity

- Total heat capacity at low temperatures

$$C = \gamma T + \beta T^3$$

Electronic Heat capacity Lattice Heat Capacity

- where γ and β are constants and they can be found drawing C_v/T as a function of T^2



- Equation of motion of an electron with an applied electric and magnetic field.

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

- This is just Newton's law for particles of mass m_e and charge (-e).
- The use of the classical equation of motion of a particle to describe the behaviour of electrons in plane wave states, which extend throughout the crystal. A particle-like entity can be obtained by superposing the plane wave states to form a wavepacket.

- The velocity of the wavepacket is the group velocity of the waves. Thus

$$\vec{v} = \frac{d\omega}{d\vec{k}} = \frac{1}{\hbar} \frac{dE}{d\vec{k}} = \frac{\hbar \vec{k}}{m_e} = \frac{\vec{p}}{m_e}$$

$$E = \hbar\omega = \frac{\hbar^2 k^2}{2m_e}$$

$$p = \hbar k$$

- So one can use equation of mdv/dt

$$m_e \left(\frac{d\vec{v}}{dt} + \frac{\vec{v}}{\tau} \right) = -e\vec{E} - e\vec{v} \times \vec{B} \quad (*)$$

τ = mean free time between collisions. An electron loses all its energy in time τ

- In the absence of a magnetic field, the applied E results a constant acceleration but this will not cause a continuous increase in current. Since electrons suffer collisions with

- phonons
- electrons

- The additional term $m_e \left(\frac{\vec{v}}{\tau} \right)$ cause the velocity v to decay exponentially with a time constant τ when the applied E is removed.

The Electrical Conductivity

- In the presence of DC field only, eq.(*) has the steady state solution

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

$\underbrace{}$ a constant of proportionality (mobility)

$$\mu_e = \frac{e\tau}{m_e}$$

Mobility for electron

- Mobility determines how fast the charge carriers move with an E .

- Electrical current density, J

$$J = n(-e)v \quad \vec{v} = -\frac{e\tau}{m_e} \vec{E} \quad n = \frac{N}{V}$$

- Where n is the electron density and v is drift velocity. Hence

$$\vec{J} = \frac{ne^2 \tau}{m_e} \vec{E} \quad \sigma = \frac{ne^2 \tau}{m_e}$$

Electrical conductivity

Ohm's law

$$\vec{J} = \sigma \vec{E}$$

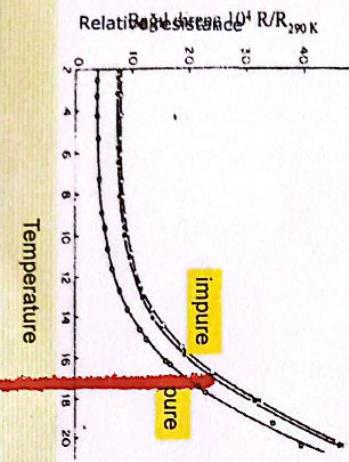
Electrical Resistivity and Resistance

$$\rho = \frac{1}{\sigma} \quad R = \frac{\rho L}{A}$$

Collisions

- In a perfect crystal; the collisions of electrons are with thermally excited lattice vibrations (scattering of an electron by a phonon).
- This electron-phonon scattering gives a temperature dependent $\tau_{ph}(T)$ collision time which tends to infinity as $T \rightarrow 0$.

- In real metal, the electrons also collide with impurity atoms, vacancies and other imperfections, this result in a finite scattering time τ_0 even at $T=0$.



Residual resistance ratio

Residual resistance ratio = room temp. resistivity / residual resistivity and it can be as high as 10^6 for highly purified single crystals.

Collision time

$$\sigma(RT)_{\text{ sodium}} = 2.0 \times 10^7 (\Omega - m)^{-1}$$

$$\sigma_{\text{residual, pure}} = 5.3 \times 10^{10} (\Omega - m)^{-1}$$

τ can be found by taking

$$m_e = m \quad \Rightarrow \quad \tau = \frac{m\sigma}{ne^2} \quad \square 2.6 \times 10^{-14} \text{ s} \quad \text{at RT}$$

$$n = 2.7 \times 10^{28} \text{ m}^{-3} \quad \square 7.0 \times 10^{-11} \text{ s} \quad \text{at } T=0$$

$$\text{Taking } v_F = 1.1 \times 10^6 \text{ m/s; and } l = v_F \tau \\ I(RT) = 29 \text{ nm} \\ I(T=0) = 77 \mu\text{m}$$

These mean free paths are much longer than the interatomic distances, confirming that the free electrons do not collide with the atoms themselves.

- The total scattering rate for a slightly imperfect crystal at finite temperature;

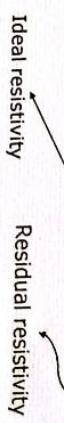
$$\frac{1}{\tau} = \frac{1}{\tau_{ph}(T)} + \frac{1}{\tau_0}$$

Due to phonon

Due to imperfections

$$\rho = \frac{m_e}{ne^2 \tau} = \frac{m_e}{ne^2 \tau_{ph}(T)} + \frac{m_e}{ne^2 \tau_0} = \rho_i(T) + \rho_0$$

This is known as Matthiesen's rule and illustrated in following figure for sodium specimen of different purity.



Thermal conductivity, K

Due to the heat transport by the conduction electrons

$$K_{\text{metals}} \square K_{\text{non-metals}}$$

Electrons coming from a hotter region of the metal carry more thermal energy than those from a cooler region, resulting in a net flow of heat. The thermal conductivity

$$K = \frac{1}{3} C_v v_F l \quad \text{where } C_v \text{ is the specific heat per unit volume}$$

v_F is the mean speed of electrons responsible for thermal conductivity since only electron states within about $k_B T$ of ε_F change their occupation as the temperature varies.

l is the mean free path; $l = v_F \tau$ and Fermi energy $\varepsilon_F = \frac{1}{2} m_e v_F^2$

$$K = \frac{1}{3} C_v v_F^2 \tau = \frac{1}{3} \frac{\pi^2}{2} \frac{N}{V} k_B \left(\frac{T}{T_F} \right) \frac{2}{m_e} \varepsilon_F \tau = \frac{\pi^2 n k_B^2 T \tau}{3 m_e} \quad \text{where } C_v = \frac{\pi^2}{2} N k_B \left(\frac{T}{T_F} \right)$$

Wiedemann-Franz law

$$\sigma = \frac{n e^2 \tau}{m_e}$$

$$K = \frac{\pi^2 n k_B^2 T \tau}{3 m_e}$$

The ratio of the electrical and thermal conductivities is independent of the electron gas parameters;

Lorentz number $\frac{K}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 = 2.45 \times 10^{-8} W \Omega K^{-2}$

$$L = \frac{K}{\sigma T} = 2.23 \times 10^{-8} W \Omega K^{-2} \quad \text{For copper at } 0^\circ C$$

**DEPARTMENT OF PHYSICS, UNIVERSITY OF LAGOS
SOLID STATE PHYSICS I: PHS 309 TUTORIALS 2017/2018 SESSION**

Q1. Powder diffraction patterns of three different monoatomic crystals A, B and C were taken. The following values for the Bragg angles, θ , are given in the following table:

| | A | B | C |
|--|-------|-------|-------|
| | 21.2° | 14.4° | 21.4° |
| | 24.6° | 20.5° | 36.6° |
| | 36.0° | 25.4° | 44.5° |
| | 43.7° | 29.8° | 57.5° |

- a) One of the crystals had bcc structure, and the others had a diamond and fcc structure. Determine the structure of each of the crystals A, B and C.
- b) What is the lattice constant in each case if the X-ray wavelength used was 1.54 Å?

Q2. The atomic planes orthogonal to the [111] direction in the ion crystal KCl consists of either only K⁺ or only Cl⁻. In this direction the velocity of long wavelength transversal phonons is 2450 m/s. KCl exhibits a strong absorption of infrared electromagnetic radiation, where an incident photon is absorbed due to the creation of a transversal phonon with the same energy. What kind of transverse phonon is it? Compute the frequency of the excited phonon. A one dimensional linear chain model can be used.

Q3. At temperatures where metallic materials are solid, we do not distinguish between the Fermi energy and the chemical potential and put them equal. However, there is a lattice mechanism leading to a temperature dependence of the Fermi energy for solid materials.
 a) What is this mechanism? Describe it. b) Determine the change in Fermi energy of Al, when the temperature is increased from 293 K to 373 K.

Q4. Draw to scale, in the reduced zone scheme, the two lowest energy bands in the [100] and [111] directions, for a divalent metal with a simple cubic lattice and lattice constant 4 Å. Use the free electron model (empty lattice approximation). Calculate the Fermi energy and mark it in the figure. Will the material still be metallic if a lattice potential with depth 0.8 eV is introduced?

Q5. At 300 K the conductivity of an undoped Ge sample is $0.256 (\Omega m)^{-1}$.

- a) Calculate the bandgap from the conductivity value and calculate also the chemical potential (effective masses and mobilities can be found in the Table) at 300 K.
- b) Ge is doped with 5 1021 B-atoms per m³. Which concentrations of electrons and holes are then obtained and what is the new conductivity at 300 K? Motivate any approximations you may do.
- c) Calculate the chemical potential at 300 K for the doped sample.

Q6. Diffraction of X-ray radiation ($\lambda=1.54 \text{ \AA}$) from the cubic metal Polonium was studied with the Debye-Scherrer method. The Bragg angles for the first and eighth reflex were $\theta=13.3^\circ$ and $\theta=43.8^\circ$, respectively. Determine the crystal structure, lattice parameter and density of Polonium from these data.

Q7. Crystalline iron has a sound velocity of 5160 m/s and a velocity of long-wave transversal vibrations of 3270 m/s. Assume that these values hold irrespective of direction in the crystal. Use a linear chain model for the lattice vibrations, with only nearest neighbour interactions.
 a) Calculate the maximum transverse and longitudinal vibration frequencies in the [111]-direction (at the P point) and sketch the dispersion relation.
 b) Calculate the Debye temperature of iron using the given data.

Q8. The specific heat of Zn has been measured at the following temperatures:

| T (K) | 1 | 2 | 3 | 4 | 6 |
|---------------|------|------|------|------|------|
| Cv (J/kmol K) | 0.72 | 1.83 | 3.80 | 7.19 | 18.9 |

Calculate the Debye temperature and the Fermi velocity from these data.

Q9. Copper is a monovalent metal. An electron is on the Fermi surface between Γ and L in the Brillouin zone. Determine the Fermi wave vector and Fermi energy. Which minimum photon energy is needed in order to excite the electron from the Fermi level to the next higher band? Assume free-electron bands and direct optical transitions.

Q10. A semiconductor has an intrinsic resistivity of $0.86 \Omega\text{m}$ and the mobilities of electrons and holes are equal and $0.25 \text{ m}_2/\text{Vs}$ at a temperature 300 K . Assume that the effective masses are equal to the electron mass. Calculate the band gap of the semiconductor.

b) The semiconductor becomes doped with an acceptor atom concentration of 10^{22} m^{-3} . The acceptor levels are situated 0.02 eV from the valence band. Calculate the chemical potential of the doped semiconductor.

Q11. The energy of a cubic primitive crystal structure is given by the expression:

$$E = \frac{\hbar^2}{2m} \left(k_x + \frac{2\pi}{a} \right)^2 \quad n = 0, \pm 1, \pm 2, \dots$$

(i) Calculate the origin (minimum value of k_x at zero energy, E) for $n = 0, \pm 1, \pm 2$ of the free electron parabola.

(ii) Determine the five energy eigenvalues for the cases, $\{k_x = \pi/a, n = 0\}; \{k_x = 0, \pi/a; n = 1\}; \{k_x = 0, \pi/a; n = 2\}$.

(iii) Sketch the free electron parabolas on composite energy- k_x axes for the cases, $n = 0, \pm 1, \pm 2$. [Let your k_x axis scale be integral multiple of π/a].

(iv) Slice and show the plots in (iii) above in a reduced zone scheme. Slice the figure further within the range $\{k_x = 0 : \pi/a\}$. Comment on the energy band diagram.

12. Given that;

| (E-E_F) eV | -0.4 | -0.3 | -0.2 | -0.1 | 0 | 0.1 | 0.2 | 0.3 | 0.4 |
|------------|------|------|------|------|---|-----|-----|-----|-----|
|------------|------|------|------|------|---|-----|-----|-----|-----|

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{KT}\right)}$$

- (i) Using the data set above, plot on composite axes the graphs of $f(E)$ against $(E-E_F) \text{ eV}$ at three temperatures 150K , 300K , and 600K . (ii) What are the implications of your graphs? (iii) Infer what the shape of the graph will be at absolute zero temperature.