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Theories of Metals and their Limitations

4.1 INTRODUCTION

KEY WORDS

polytetrafluoro ethylene (PTFE), valance electrons, free electrons, electron gas, zig-zag motion, drift velocity, Drude-Lorentz, non-interacting particles, root mean square velocity, Boltzmann constant, unidirectional motion, memory of momentum, thermal velocity, drift velocity, mobility of charge, current density, lattice scattering, random velocity, mean free path, molar electronic specific heat, lattice positions, computation of mean free path, Fermi-Dirac statistics, thermal conductivity, Wiedemann-Franz law, Fermions, Fermi function, electrical resistivity, Lorentz number, octant, discrete energy levels, Pauli's exclusion principle, mean energy of electron, trivalent metal, occupied and unoccupied levels, probability occupation, Fermi temperature, Fermi velocity, heat capacity of electrons, lattice contribution, electronic contribution, thermal equilibrium, Fermi surface, zero momentum, Fermi sphere, effective mass of electron, Debye temperature, Bloch-Gruneisen law, superconductors, Matthiessen's rule, Wiedemann-Franz law, Lorentz number, Sommerfeld, Richardson-Dushman, thermionic emission, Fermi surface, anomalous expansion of water, the coefficient of expansion, periodic lattice, Kronig-Penney model, Sommerfeld quantum theory, periodicity character, Schrödinger equation, Bloch, forbidden energy, potential barrier strength, points of discontinuity, (E–k) curve, Brillouin zones, effective mass, gauge factor, Bridgeman constant, Electrical strainometer, nichrome, Wheatstone's bridge, electrical engineering materials, low resistivity materials, temperature coefficient of resistance, ductility, high resistivity materials, heating elements, resistance thermometers, precision resistors, high frequency conduction.

4.1 INTRODUCTION

Metals are to be considered as an important class of solids on account of their favourable electrical, thermal and mechanical properties at normal temperature and pressure. The other interesting point is the electrical resistivities of materials at room temperature vary over a wide range of values than any physical property—from 1.5×10^{-8} Ω m for silver to about 10^{16} Ω m for *polytetrafluoro ethylene* (PTFE). This range over 24 orders of magnitude may be compared with the ratio of the earth's orbit (1.5×10^{11} m) to the Bohr radius of hydrogen atom (5×10^{-11} m). Because of the special features of metals, it has to be assumed that the outer electrons (valance electrons) of atoms of metals are free to move randomly, just as the molecules of a gas. These electrons are called '*free electrons*', and their aggregate in a given metal is called an '*electron gas*'. These electrons are free to move throughout the lattice and do not belong to any particular atom. For a monovalent metal, the number of free electrons in a given volume is equal to the number of atoms in the same volume. In the absence of an electric field, the random velocity due to the *zig-zag motion* is determined by the absolute temperature with zero *drift velocity* in a particular direction.

Q 4.1 Discuss classical free electron theory of metals and obtain the expression for electrical conductivity.

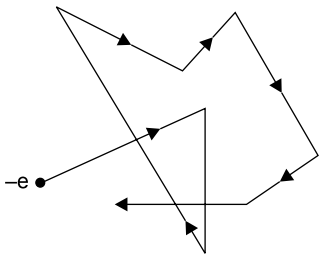
***Answer*:** The free electron theory of metals using classical laws was developed by *Drude* and *Lorentz* in the beginning of the last century where the valance electrons in metals were regarded as the non-interacting particles of an ideal gas. The only difference is that electrons are charged. If we assume that the kinetic theory of gases can be applied to the free-electron gas, then the *root mean square velocity* of the electron is

$$\boxed{\bar{c} = \sqrt{\frac{3k_B T}{m}}} \qquad \text{(Q 4.1.1)}$$

where k_B is *Boltzmann's constant* and T is absolute temperature. Refer Fig. Q. 4.1.1(a).

Thus $\bar{c} \propto \sqrt{T}$

Let us now sound the system with an external electric field. i.e., the given copper rod of uniform cross-section (say 1 sq. m) is subjected to a field of strength E applied in the direction as shown in Fig. Q 4.1.1(b). The possessive nature of the electrons is now suppressed. The random motion is discouraged and the charged electrons prefer to have a *unidirectional motion* in a direction opposite to the direction of the applied electric field as sketched in Fig. Q 4.1.1(c).



(a)

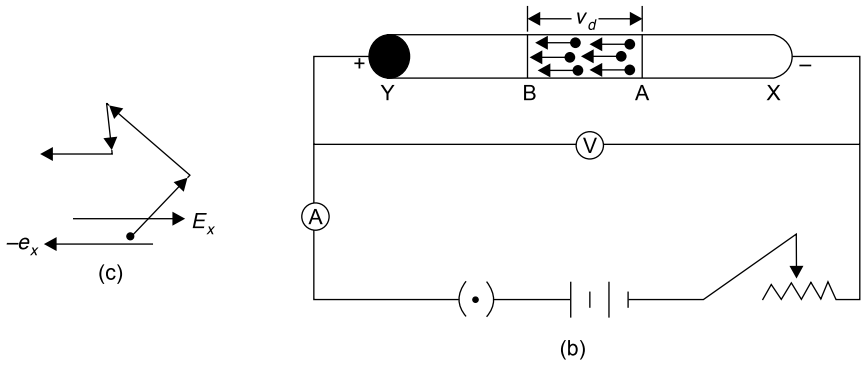


Fig. Q 4.1.1 *(a) zig-zag motion (b) Drift in a field*

Now it appears reasonable to expect that the free electrons will bump into a cation of the lattice from time to time. Let the average time between such collisions be τ sec. Immediately after a collision we further suppose that the velocity of the electron averages to zero; that is to say, the electron has no *memory* of the momentum acquired from the field and that its *thermal velocity* averages to zero. In a time τ sec the electron will attain a velocity given by:

$$v_d = a\tau$$

Here v_d is called *drift velocity* and the magnitude of $a = \dfrac{eE}{m}$

Thus

$$\boxed{v_d = -\frac{eE\tau}{m}} \qquad \text{(Q 4.1.2)}$$

Usually the term $\dfrac{e\tau}{m}$ is replaced by μ called the *mobility* of charge carriers, or defined as the *drift velocity in unit field*

Thus

$$\boxed{v_d = -\mu E} \qquad \text{(Q 4.1.3)}$$

If n is the density of electron and $-e$ is the charge of the electron, then charge flowing through unit area for one sec (or the *current density*) J_x (in A/m^2) is

$$J_x = -n\, e\, v_d$$

Substituting for v_d from Eqn. (Q 4.1.2), we get,

$$\boxed{J_x = \frac{ne^2 E\tau}{m}} \qquad \text{(Q 4.1.4)}$$

Thus the *electric conductivity*, $\sigma = \dfrac{1}{\rho}$ is:

$$\frac{J_x}{E} = \frac{ne^2\tau}{m}$$

i.e., $$\sigma = \frac{ne^2\tau}{m}; \text{ or } \rho = \frac{m}{ne^2\tau}$$

Also $$\boxed{\sigma = \text{ne}\mu \text{ and } \rho = \frac{1}{ne\mu}} \qquad \text{(Q 4.1.5)}$$

In a metal, when temperature increases, n remains constant, but μ decreases as *lattice scattering* increases and therefore conductivity decreases.

Q 4.2 Discuss with a simple theory, the temperature dependence of the electrical resistivity of a metal (say copper).

***Answer*:** Let us consider a copper rod of uniform cross-section a sq. m and length l (say 1 m) and totally free from the influence of the external electric field. The free electrons have now the liberty of receiving thermal energy (of the order k_BT) from the atmosphere in all possible directions. The result is the *zig-zag motion* for the electrons and will be in thermal equilibrium. The *kinetic energy* associated with the electron is:

$$\boxed{\frac{1}{2}m\bar{c}^2 = \frac{3}{2}k_BT} \qquad \text{(Q 4.2.1)}$$

When an electric field is applied, the electron will acquire a *drift velocity* and the resulting acceleration is, $a = \frac{eE}{m}$. The *drift velocity* is small compared to the *random velocity*, $\bar{c}$. Further the drift velocity is not retained after a collision with an atom because of the relatively large mass of the atom. Hence just after a collision the drift velocity is reduced to zero. If the *mean free path* is λ, then the time that elapses before the next collision takes place is $\frac{\lambda}{\bar{c}}$. Hence the drift velocity acquired just before the next collision takes place is,

$$u = \text{acceleration} \times \text{time interval} = \frac{eE}{m}\left(\frac{\lambda}{\bar{c}}\right)$$

The *average drift velocity* is:

$$\boxed{\frac{u}{2} = \frac{eE\lambda}{2m\bar{c}} = v_{ad}} \qquad \text{(Q 4.2.2)}$$

If n is the number of electrons per unit volume and hence the current flowing through unit area for unit time is

$$J_x = \frac{neu}{2} = \frac{ne^2E\lambda}{2m\bar{c}} \text{ where } \bar{c} = \sqrt{\frac{3k_BT}{m}}$$

or
$$\sigma = \frac{J_x}{E} = \frac{ne^2\lambda}{2m\bar{c}} = \frac{ne^2\lambda}{\sqrt{12mk_BT}}$$

$$\boxed{\rho = \frac{\sqrt{12mk_BT}}{ne^2\lambda}} \qquad \text{(Q 4.2.3)}$$

It was assumed by Drude and Lorentz that λ is independent of temperature and that it is of the order of interatomic distance. Also $\rho \propto \sqrt{T}$. This means that the specific resistance of an electric conductor is directly proportional to the square root of the absolute temperature. This is not in agreement with the experimental observation that $\rho \propto T$.

Q 4.3 Outline the important drawbacks of the classical free electron theory of metals bringing out the bad assumptions made while explaining them.

Answer*:** (i) ***Molar electronic specific heat

In many solids the most important types of internal energy are (a) the vibrational energy of the atoms about their mean *lattice positions* and (b) the kinetic energy of the free electrons. The kinetic energy with one kmol of a monovalent metal is:

$$U = \frac{1}{2}m\bar{c}^2 N_A = \frac{mN_A}{2}\left(3k_BT/m\right) = \frac{3}{2}R_uT$$

The molar electronic specific heat is:

$$\boxed{C_{ve} = \frac{dU}{dT} = 1.5R_u = 12.5 \times 10^3 \text{ J/kmol/K}} \qquad \text{(Q 4.3.1)}$$

This value of 1.5 R_u is about hundred times greater than the experimentally predicated value. Our assumption that all the free electrons make contribution to the specific heat may be wrong and hence to be corrected.

(ii) ***Computation of mean free path***

The microscopic relation for the resistivity of a metal is:

$$\rho = \frac{m}{ne^2\tau}; \text{ or } \tau = \frac{m}{ne^2\rho}$$

For copper, $n = 8.5 \times 10^{28}/\text{m}^3$ and $\rho = 1.69 \times 10^{-8}\ \Omega\,\text{m}$

Thus

$$\tau = \frac{9.1 \times 10^{-31}}{8.5 \times 10^{28} \times \left(1.6 \times 10^{-19}\right)^2 \times 1.69 \times 10^{-8}} = 2.47 \times 10^{-14} \text{ sec}$$

$$\lambda = \tau\bar{c} = 2.47 \times 10^{-14} \times 1.154 \times 10^5 = 2.85 \times 10^{-9} \text{ metre}$$

$$\boxed{\lambda = 2.85 \text{ nm}} \qquad \text{(Q 4.3.2)}$$

The experimentally found value for λ is about ten times greater than this value of 2.85 nm. Probably the application of Fermi-Dirac statistics (instead of classical statistics) to the free electrons in metals may help us to explain the difference in the values of λ.

Q 4.4 Obtain the expression for the thermal conductivity of a metal in terms of well known microscopic parameters. Get Wiedemann-Franz law and Lorentz number.

***Answer*:** The following figure shows the view of a copper rod of an appreciable length in the steady state with a cross-section 1 sq. m.

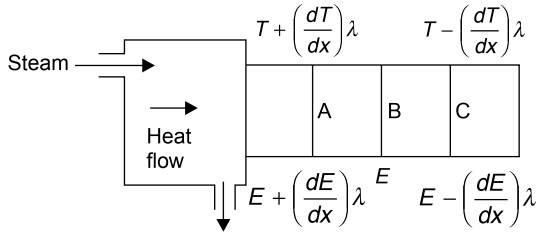


Fig. Q 4.4.1 *Flow of heat through a copper rod at the steady state*

The excess of energy carried by an electron from A to B is $\left[\frac{dE}{dx}\right]\lambda$. Hence the excess of energy transported by the process of conduction through unit area in unit time at the middle layer B is $\frac{n\bar{c}\,\lambda}{6}\left[\frac{dE}{dx}\right]$.

Similarly the deficit of energy transported through B in the opposite direction is $\frac{1}{6}n\bar{c}\,\lambda\left[\frac{dE}{dx}\right]$ assuming $\frac{1}{6}n\bar{c}$ is the number of free electrons flowing in a given direction through unit area in unit time.

Thus the net energy transported through unit area in unit time from A to B is:

$$\frac{1}{6}n\bar{c}\,\lambda\left[\frac{dE}{dx}\right] - \left\{-\frac{1}{6}n\bar{c}\,\lambda\left[\frac{dE}{dx}\right]\right\} = \frac{n\bar{c}\,\lambda}{3}\left(\frac{dE}{dT}\right)\left(\frac{dT}{dx}\right)$$

i.e.,

$$\boxed{\sigma_T\left(\frac{dT}{dx}\right) = \frac{n\bar{c}\,\lambda}{3}\left[C_v\right]_{el}\left(\frac{dT}{dx}\right)} \qquad \text{(Q 4.4.1)}$$

Knowing $\left[\frac{dE}{dT}\right] = [C_v]_{el} = \frac{3}{2}k_B$ (with respect to one electron) and $\bar{c} = \sqrt{\frac{3k_BT}{m}}$ and equating the above value with the general expression for *thermal conductivity*, one gets

$$\sigma_T\left[\frac{dT}{dx}\right] = \frac{n\lambda}{3}\left[\frac{3k_B}{2}\right]\left[\sqrt{\frac{3k_BT}{m}}\right]\left(\frac{dT}{dx}\right)$$

or

$$\boxed{\sigma_T = \left(\frac{n\lambda k_B}{2}\right)\sqrt{\frac{3k_BT}{m}}} \qquad \text{(Q 4.4.2)}$$

The general expression for electrical conductivity is:

$$\sigma = \frac{ne^2\lambda}{\sqrt{12mk_BT}}$$

i.e.,

$$\boxed{\frac{\sigma_T}{\sigma} = 3\left(\frac{k_B}{e}\right)^2 T} \qquad \text{(Q 4.4.3)}$$

This is known as *Wiedemann–Franz* law and the multiplying constant $3\left(\frac{k_B}{e}\right)^2$ is called *Lorentz number* (L).

***Example*:** For copper at 20°C, the thermal conductivity and electrical resistivity are respectively 386 W $m^{-1}K^{-1}$ and 1.7×10^{-8} Ω m. Computation of Lorentz number is done as follows:

$$L = \frac{\sigma_T}{\sigma \times T} = \frac{\sigma_T\rho}{T} = \frac{386 \times 1.7 \times 10^{-8}}{293} = 2.26 \times 10^{-8}$$

$$\boxed{L = 2.26 \times 10^{-8}\, W\Omega\, K^{-2}} \qquad \text{(Q 4.4.4)}$$

This value of L does not match with the one calculated using the RHS of Eqn. (Q 4.4.3). This is another failure of classical theory.

Q 4.5 Get the standard expression for the density of energy states using Fermi-Dirac statistics.

***Answer*:** Some of the results of wave mechanics discussed earlier combined with *Fermi-Dirac statistics* may help us to over come the difficulties arised in the classical treatment of free electron theory of metals. In order to account for the unexpectedly low specific heat compared with the one predicted by classical theory and also the unacceptable values of mean free path of electrons and *Lorentz–number*, it was assumed that the free electrons obey Fermi–Dirac statistics and not the classical one. Such particles are then called *Fermions*.

If $N(E)$ is the number of electrons in a system that have energy E, and $Z(E)$ is the number of energy states have energy E, then the number of electrons having energy values lying between E and $E + dE$ or in the energy interval dE is: