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Relation between the thermal and electrical conductivities of metals (Wiedemann-Franz Law)

It is an established fact that all good conductors of heat are also good conductors of electricity. Wiedemann and Franz expressed it in the form of a law known as Wiedemann-Franz law. The law states that the ratio of the thermal conductivity and electrical conductivity at a particular temperature is the same for all metals. Thus, if the thermal and electrical conductivities of a metal are k and σ then from this law

$$k/\sigma = \text{Constant}$$

But Lorentz showed that this ratio is ~~proportional~~ proportional to the absolute temperature.

$$\therefore k/\sigma T = \text{Constant}$$

According to Drude, there are a large number of free electrons in a metal which are in a state of random motion like a gas molecules. These free electrons are responsible for both the thermal and the electrical conduction in metals. These electrons, like gas molecules collide and are in equilibrium with the atoms of the metals. Hence the law of equilibrium of energy, they will have the same energy per degree of freedom as the atom inside the metal. The average drift of these electrons in any direction under the influence of a difference

of potential constitute the electric current, while the transfer of energy of random motion in any direction is thermal conduction.

Let us consider the conduction of electricity in a metallic wire across which a potential difference has been applied. Let this potential difference creates an electric field of intensity E along the wire. Then every free electrons in the wire is acted upon by a force Ee and possesses an acceleration Ee/m , where e is the charge and m is the mass of electrons. Let λ be the mean free path and \bar{c} the mean velocity of the electrons corresponding to the temperature T . The electron is accelerated between two collision, but loses its velocity on collision with the atom. Thus the velocity at the beginning of the path is zero, because, it is assumed that the electrons is at rest before the application of electric field.

The time taken by the electron per collision is $\frac{\lambda}{\bar{c}}$ and hence the velocity at the end of path = acceleration \times time

$$= \frac{Ee}{m} \times \frac{\lambda}{\bar{c}}$$

$$\therefore \text{Average drift velocity} = \frac{1}{2} \left(0 + \frac{Ee\lambda}{m\bar{c}} \right)$$

$$\text{or, } u = \frac{Ee\lambda}{2m\bar{c}}$$

If n be the number of free electrons per unit volume, the number of electrons crossing unit area of cross-section per second will be nu . Hence the total charge flowing per second per unit area is nue , which is the value of electric

Current by definition.

$$\therefore I = nue$$

$$I = ne \left(\frac{Ee\lambda}{2m\bar{c}} \right) = \frac{ne^2\lambda E}{2m\bar{c}}$$

Now the electrical conductivity is defined as the current flowing per unit area per second per unit electric field. Hence the electrical conductivity

$$\sigma = \frac{I}{E} = \frac{ne^2\lambda}{2m\bar{c}} \quad \text{--- (1)}$$

But from kinetic theory

$$\frac{1}{2} m\bar{c}^2 = \frac{3}{2} kT$$

$$\therefore m\bar{c} = \frac{3kT}{\bar{c}}$$

where k is Boltzmann constant

$$\therefore \sigma = \frac{ne^2\lambda\bar{c}}{6kT} \quad \text{--- (2)}$$

Now the thermal conductivity K for the electron-gas is given by

$$K = \frac{1}{3} mn\bar{c}\lambda C_v \quad \text{--- (3)}$$

where mc_v is the thermal capacity of a single travelling particle. The increase in its energy due to increase in temperature by dT is

$$d\bar{E} = mc_v dT$$

$$\therefore \frac{d\bar{E}}{dT} = mc_v \quad \text{--- (4)}$$

But if the electron is assumed to possess only the ~~thermal energy~~ translational energy and no rotational or internal energy, then by

equipartition law

$$\bar{E} = \frac{3}{2} kT$$

$$\therefore \frac{d\bar{E}}{dT} = \frac{3}{2} k \quad \text{--- (5)}$$

From equation (4) and (5), we get

$$(1) \quad mc_v = \frac{3}{2} k$$

putting this value in equation (3), we get

$$k = \frac{n\bar{c}_v k}{2} \quad \text{--- (6)}$$

Hence from equation (2) and (6), we get

$$\frac{k}{\sigma} = 3 \frac{k^2 T}{e^2}$$

$$\text{or, } \frac{k}{\sigma T} = 3 \left(\frac{k}{e} \right)^2$$

$$\therefore \frac{k}{\sigma T} = \text{Constant}$$

which is Wiedemann-Franz-Lorentz law.

This law holds good for a large number of metals between $+100^\circ\text{C}$ and -100°C . At low temperatures, the ratio $\frac{k}{\sigma}$ decreases and the value tends to zero at absolute zero. As the temperature of the metal decreases, the ~~increase~~ thermal and electrical conductivity of the metal increase. But the increase in the electrical conductivity is higher and its value tends to infinity at absolute zero. This corresponds to the superconducting state of the metal.