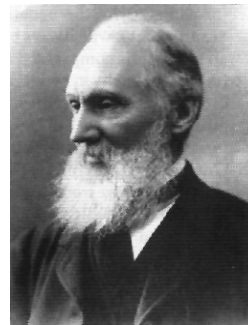


# THERMOELECTRIC EFFECTS IN METALS: THERMOCOUPLES

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"I often say that when you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind."



*Lord Kelvin*  
(1824-1907; William Thomson)  
From Lecture to the  
Institution of Civil Engineers, 3 May 1883

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**Seebeck effect:** A temperature difference between two points in a conductor or semiconductor results in a voltage difference between these two points. Stated differently, a temperature gradient in a conductor or a semiconductor gives rise to a built-in electric field. This phenomenon is called the Seebeck effect or the thermoelectric effect. The Seebeck coefficient gauges the magnitude of this effect. The thermoelectric voltage developed per unit temperature difference in a conductor is called the Seebeck coefficient. Only the net Seebeck voltage difference between different metals can be measured. The principle of the thermocouple is based on the Seebeck effect.

## 1. The Seebeck Effect and Normal Metals

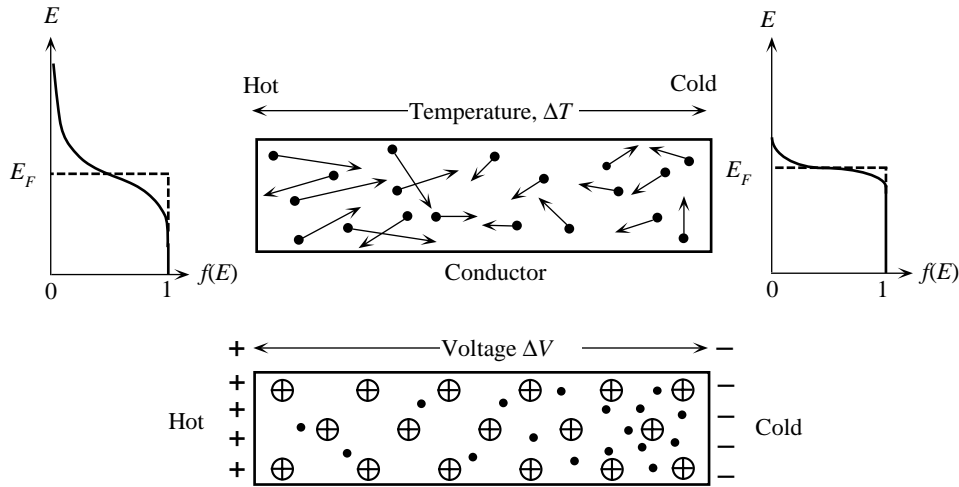
Consider an aluminum rod that is heated at one end and cooled at the other end as depicted in Figure 1. The electrons in the hot region are more energetic and therefore have greater velocities than those in the cold region<sup>1</sup>. Consequently there is a net diffusion of electrons from the hot end toward the cold end which leaves behind exposed positive metal ions in the hot region and accumulates electrons in the cold region. This situation prevails until the electric field developed between the positive ions in the hot region and the excess electrons in the cold region prevents further electron motion from the hot to cold end. A voltage is therefore developed between the hot and cold ends with the hot end at positive potential. The potential

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<sup>1</sup>The conduction electrons around the Fermi energy have a mean speed that only has a small temperature dependence. This small change in the mean speed with temperature is, nonetheless, important in understanding the thermoelectric effect.

difference  $\Delta V$  across a piece of metal due to a temperature difference  $\Delta T$  is called the Seebeck effect<sup>2</sup>. To gauge the magnitude of this effect we introduce a special coefficient which is defined as the potential difference developed per unit temperature difference, *i.e.*

$$S = \frac{dV}{dT} \quad \text{Seebeck coefficient} \quad (1)$$



The Seebeck effect. A temperature gradient along a conductor gives rise to a potential difference.

**Figure 1**

By convention, the sign of  $S$  represents the potential of the cold side with respect to the hot side. If electrons diffuse from hot to cold end, then the cold side is negative with respect to the hot side and the Seebeck coefficient is negative. In a  $p$ -type semiconductor, on the other hand, holes would diffuse from the hot to the cold end. The cold side would be positive with respect to the hot side which would make  $S$  a positive quantity.

The coefficient  $S$  is widely referred to as the thermoelectric power even though this term is certainly misleading as it refers to a voltage difference rather than power. The term, however, has stuck and we have to learn the misnomer. An alternative recent and more appropriate term is the Seebeck coefficient.  $S$  is a material property that depends on temperature;  $S = S(T)$ . It is tabulated for many materials as a function of temperature. Given the Seebeck coefficient  $S(T)$  for a material, the voltage difference between two points where temperatures are  $T_o$  and  $T$ , from Equation (1), is given by

$$\Delta V = \int_{T_o}^T SdT \quad (2)$$

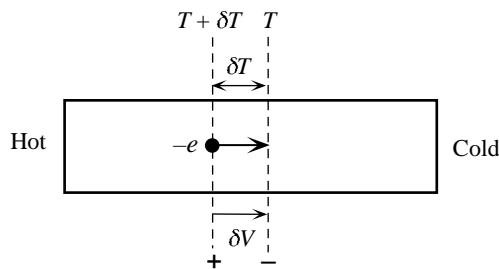
The voltage difference in Equation (2) above is for the cold end with respect to hot as in the convention for  $S$ .

The average energy  $E_{av}$  per electron in a metal in which the density of states  $g(E) \propto E^{1/2}$  is given by (see, for example, Ch. 4 in *Principles of Electronic Materials and Devices*, McGraw-Hill),

<sup>2</sup>Thomas Seebeck observed the thermoelectric effect in 1821 using two different metals as in the thermocouple which is the only way to observe the phenomenon. It was Thompson (Lord Kelvin) who explained the observed effect.

$$E_{av}(T) = \frac{3}{5} E_{FO} \left[ 1 + \frac{5\pi^2}{12} \left( \frac{kT}{E_{FO}} \right)^2 \right] \quad (3)$$

where  $E_{FO}$  is the Fermi energy at 0 K. It is clear from Equation (3) that the Fermi-Dirac distribution actually extends to much higher energies when the temperature is raised, as depicted in Figure 1, so that the average energy per electron, as determined by Equation (3), is actually greater in the hot end. Consequently the more energetic electrons in the hot end diffuse toward the cold region until a potential difference  $\Delta V$  is built up which prevents further diffusion. We should also note that the average energy per electron as determined by Equation (3) also depends on the material by virtue of  $E_{FO}$ .



Consider a small length  $\delta x$  over which the temperature difference is  $\delta T$  and voltage difference is  $\delta V$ . Suppose that one electron diffuses from hot to cold region across this potential difference.

Figure 2

Table 1

Seebeck coefficients of selected metals (from various sources).

Metal	$S$ at 0 °C ( $\mu\text{V K}^{-1}$ )	$S$ at 27 °C ( $\mu\text{V K}^{-1}$ )	$E_F$ (eV)	$x$
Na		-5	3.1	2.2
K		-12.5	2.0	3.8
Al	-1.6	-1.8	11.6	2.78
Mg	-1.3		7.1	1.38
Pb	-1.15	-1.3		
Pd	-9.00	-9.99		
Pt	-4.45	-5.28		
Mo	+4.71	+5.57		
Li	+14		4.7	-9.7
Cu	+1.70	+1.84	7.0	-1.79
Ag	+1.38	+1.51	5.5	-1.14
Au	+1.79	+1.94	5.5	-1.48
Zn			9.4	

Suppose that a small temperature difference of  $\delta T$  results in a voltage difference  $\delta V$  between the accumulated electrons and exposed positive metal ions as depicted in Figure 2. Suppose that one electron manages to diffuse from the hot region to the cold region. It has to do work against the potential difference  $\delta V$  which is  $-e\delta V$ . This work done against  $\delta V$  decreases the average energy of the electron by  $\delta E_{av}$  from  $E_{av}(\text{hot})$  to  $E_{av}(\text{cold})$ :

$$-e\delta V = E_{av}(T + \delta T) - E_{av}(T)$$

Substituting for  $E_{av}(T)$  from Equation (3) and expanding  $(T + \delta T)$  and neglecting  $\delta T^2$  term we obtain,

$$-e\delta V \approx \frac{\pi^2 k^2 T \delta T}{2E_{FO}}$$

Since  $S = \delta V / \delta T$ , the Seebeck coefficient is given by

$$S \approx -\frac{\pi^2 k^2 T}{2eE_{FO}} \quad \text{Seebeck coefficient metals} \quad (4)$$

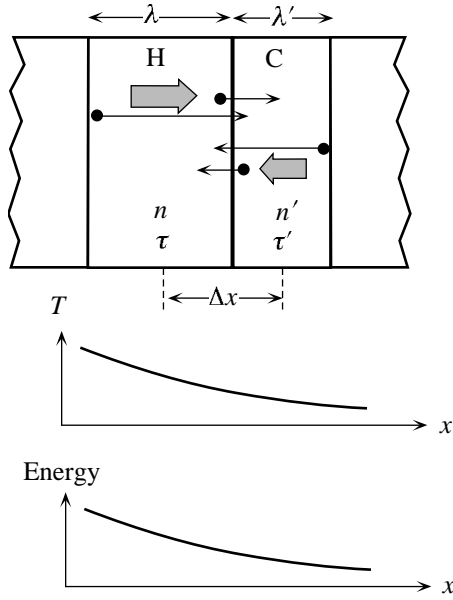
For example, for Al,  $E_{FO} = 11.6$  eV so that at  $T = 300$  K ( $27^\circ\text{C}$ ), Equation (4) predicts  $-0.94 \mu\text{V K}^{-1}$  which is of the order of the experimentally inferred value of about  $-1.8 \mu\text{V K}^{-1}$ . Table 1 summarizes some typical experimental values for the Seebeck coefficient of a selection of metals where it is apparent that the values are in the microvolt per Kelvin range. It is also startlingly apparent that there are metals with positive Seebeck coefficients such as copper. This means that electrons migrate from cold to hot end of a copper bar.

It should be emphasized that the above explanation is based on assuming that the conduction electrons in the metal behave as if they were “free”. This means that the density of states  $\mathcal{G}(E) \propto E^{1/2}$  up to and beyond the Fermi energy. It also means that the electron energy  $E = KE = \frac{1}{2}m_e^*v^2$  and that the effective electron mass  $m_e^*$  is constant; energy independent. Further, electrons with higher energy have greater mean speeds and longer mean free paths so that they diffuse from the hot to cold region. These assumptions only apply to what are called normal metals (*e.g.* Na, K, Al etc.).

## 2. The Sign of the Seebeck Coefficient and Scattering in Metals

The diffusion of electrons from the hot to cold region assumes that the electrons in the hot region have higher speeds as in the “free electron theory of metals”; the conduction electrons are taken to be free within the metal. This means that the mean speed  $v$  and the mean free path (MFP)  $\lambda$  increase with the electron energy.

In reality, however, we have to consider the interactions of the conduction electrons with the metal ions and the lattice vibrations and thus on how the conduction electrons are scattered. Except for certain metals, the free electron theory is unable to account for the sign of the thermoelectric effect. We can understand the importance of scattering from a classical argument as follows.



Consider two neighboring regions H and C with widths corresponding to the mean free paths  $\lambda$  and  $\lambda'$  in H and C. Half the electrons in H would be moving in  $+x$  direction and the other half in  $-x$  direction. Half of the electrons in H therefore cross into C, and half in C cross into H.

**Figure 3**

Consider two neighboring relatively hot and cold regions, H and C, in a conductor at one instant as shown in Figure 3. The electron concentrations in H and C are  $n$  and  $n'$ . The width of the H region is  $\lambda$ , the mean free path (MFP) along  $x$  in H and that of C is  $\lambda'$ , the MFP along  $x$  in C. Electrons in H moving towards the interface and, within a distance  $\lambda$ , cross the interface into C. Only half of these would be moving towards C so that the number of electrons that cross into C is  $1/2(n\lambda)$ ; assume that the cross sectional area is unity. If  $\tau$  is the mean scattering time then the electron flux (number of electrons flowing per unit area per unit time) from H to C is  $1/2(n\lambda)/\tau$ . There is a similar electron flux from C to H so that the net flux from H to C is

$$\Gamma = \frac{n\lambda}{2\tau} - \frac{n'\lambda'}{2\tau'} \quad (5)$$

We can write  $n' \approx n + (dn/dx)\Delta x$ ,  $\lambda' \approx \lambda + (d\lambda/dx)\Delta x$ , and  $\tau' \approx \tau + (d\tau/dx)\Delta x$ . Taking  $\Delta x = (\lambda + \lambda')/2 \approx \lambda$ , then Equation (5) becomes,

$$\Gamma \approx -\frac{\lambda^2}{2\tau} \left( \frac{\partial n}{\partial x} \right) - \frac{n\lambda}{2\tau} \left( \frac{\partial \lambda}{\partial x} \right) + \frac{n\lambda^2}{2\tau^2} \left( \frac{\partial \tau}{\partial x} \right) \quad (6a)$$

or

$$\Gamma \approx -\frac{\lambda^2}{2\tau} \left( \frac{\partial n}{\partial x} \right) - \frac{n\lambda}{2\tau} \left( \frac{\partial \lambda}{\partial x} \right) + \frac{n\lambda^2}{2\tau} \left( \frac{\partial \ln \tau}{\partial x} \right) \quad (6b)$$

It is clear that the net electron migration, whether from hot to cold, or cold to hot, is determined by the energy dependence of the electron concentration  $n$ , MFP  $\lambda$  and the mean scattering time  $\tau$ . For example, if the MFP increases strongly with energy,  $\partial\lambda/\partial E$  and hence  $\partial\lambda/\partial x$  will be negative. This will make  $\Gamma$  in Equation (6b) positive ( $+x$  direction) so that electron diffusion will be from hot to cold and the thermoelectric power will be negative. In those metals in which  $\lambda$  decreases strongly with the energy, electrons migrate from cold to hot and the thermoelectric power is positive. These conclusions apply primarily to metals.

By including the energy dependence of the scattering processes, Mott and Jones have derived the following expression for the Seebeck coefficient,

$$S \approx -\frac{\pi^2 k^2 T}{3eE_{FO}} x \quad \text{Mott-Jones thermoelectric power} \quad (7)$$

where  $x$  is a numerical constant that depends on the energy dependences of various charge transport parameters; a few examples for  $x$  are given in Table 1. These  $x$  values allow Equation (7) to agree with the experimental Seebeck coefficients at 273 K given  $E_{FO}$ .

Equation (7) does not apply to metals in which electrons can be scattered from one transport band to another transport band as in transition metals. In transition metals (e.g. Ni)  $s$  and  $d$  bands overlap and indeed the  $d$ -band may even be substantially full. The electrons in these two bands have different effective masses and different mean free paths with different energy dependences.

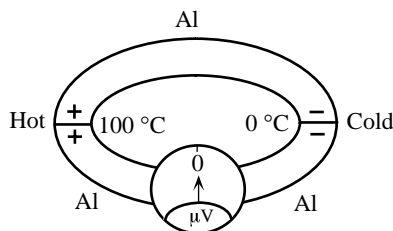
### 3. The Thermocouple

Consider an aluminum rod heated at one end and cooled at the other end. Suppose that we try to measure the voltage difference  $\Delta V$  across the aluminum rod by using aluminum connecting wires to a voltmeter as indicated in Figure 4. The same temperature difference, however, now also exists across the aluminum connecting wires and therefore an identical voltage also develops across the connecting wires, opposing that across the aluminum rod. Consequently no net voltage will be registered by the voltmeter. It is, however, possible to read a net voltage difference, if the connecting wires are of different material, i.e. have a different Seebeck coefficient than that of aluminum, so that across this material the thermoelectric voltage is different than that across the aluminum rod as in Figure 5.

The Seebeck effect is fruitfully utilized in the thermocouple (TC), shown in Figure 5, which 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 its Seebeck coefficient so that the potential difference between the two wires will depend on  $S_A - S_B$ . The emf between the two wires,  $V_{AB} = \Delta V_A - \Delta V_B$ , by virtue of Equation (2), is then given by

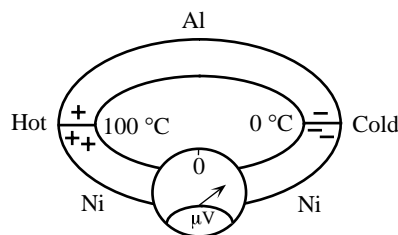
$$V_{AB} = \int_{T_0}^T (S_A - S_B) dT = \int_{T_0}^T S_{AB} dT \quad (8)$$

where  $S_{AB} = S_A - S_B$  is defined as the thermoelectric power for the thermocouple pair A-B. For the chromel-alumel (K-type) TC, for example,  $S_{AB} \approx 40 \mu\text{V K}^{-1}$  at 300 K.



If Al wires are used to measure the Seebeck voltage across the Al rod, then the net emf is zero.

Figure 4



The Al and Ni have different Seebeck coefficients. There is therefore a net emf in the Al-Ni circuit between the hot and cold ends that can be measured.

Figure 5

The output voltage from a TC pair obviously depends on the two metals used. Instead of tabulating the emf from all possible pairs of materials in the world, which is an impossible task, engineers have tabulated the emfs available when a given material is used with a reference metal which is chosen to be platinum. The reference junction is kept at 0 °C (273.16 K) which corresponds to a mixture of ice and water. Some typical materials are listed in Table 2 to compare their emfs.

By using the expression for the Seebeck coefficient, Equation (7), in Equation (8) we can readily show, through simple mathematics, that the integration leads to the familiar thermocouple equation,

$$V_{AB} = a\Delta T + b(\Delta T)^2 \qquad \text{Thermocouple Equation} \qquad (9)$$

where  $a$  and  $b$  are the thermocouple coefficients and  $\Delta T = T - T_0$  is the temperature with respect to the reference temperature,  $T_0$  (273.16 K). The inference to engineers from Equation (9) is that the emf output from the thermocouple wire does not depend linearly on the temperature difference,  $\Delta T$ , and consequently we have to use a look-up table either ourselves or on the computer memory to convert the emf to the temperature difference.

Figure 5 shows the emf output vs. temperature for various thermocouples where it should be immediately obvious that the voltages are small, typically few tens of a microvolt per degree temperature difference. At 0 °C, by definition, the TC emf is zero. The K-type thermocouple, the chromel-alumel pair, is a widely employed general purpose thermocouple sensor up to ~1200 °C.

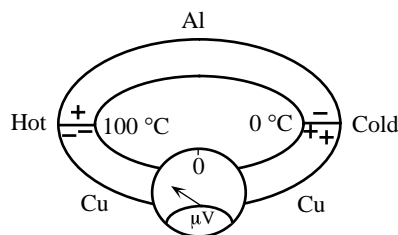
**Table 2**

Thermoelectric emf for metals at 100 and 200 °C with respect to Pt and the reference junction at 0 °C.

<b>MATERIAL</b>	<b>EMF, mV</b>	<b>EMF, mV</b>
<b>Elements</b>	<b>At 100 °C</b>	<b>At 200 °C</b>
Copper, Cu	0.76	1.83
Gold, Au	0.78	1.84
Aluminum, Al	0.42	1.06
Molybdenum	1.45	3.19
Nickel, Ni	-1.48	-3.10
Palladium, Pd	-0.57	-1.23
Platinum, Pt	0	0
Silver, Ag	0.74	1.77
Tungsten, W	1.12	2.62
<b>Thermocouple Materials</b>		
Alumel	-1.29	-2.17
Chromel	2.81	5.96
Constantan	-3.51	-7.45
Copper, Cu	0.76	1.83
Iron, Fe	1.89	3.54
90%Pt-10%Rh (Platinum-Rhodium)	0.643	1.44

**3.1. Example 1: The thermocouple EMF**

Consider a thermocouple pair from Al and Cu which have Fermi energies and  $x$  in Table 1. Estimate the emf available from this thermocouple if one junction is held at 0 °C and the other at 100 °C? Which end is positive?



The Al-Cu thermocouple. The cold end is maintained at 0 °C which is the reference temperature. The other junction is used to sense the temperature. In this example it is heated to 100 °C.

**Figure 6**

**Solution**

We essentially have the arrangement shown in Figure 6. For each metal there will be a voltage across it given by integrating the Seebeck coefficient. From the Mott-Jones equation,



$$\Delta V = \int_{T_0}^T SdT = \int_{T_0}^T -\frac{x\pi^2k^2T}{3eE_{FO}}dT = -\frac{x\pi^2k^2}{6eE_{FO}}(T^2 - T_0^2)$$

The emf ( $V_{AB}$ ) available is the difference in  $\Delta V$  for the two metals so that

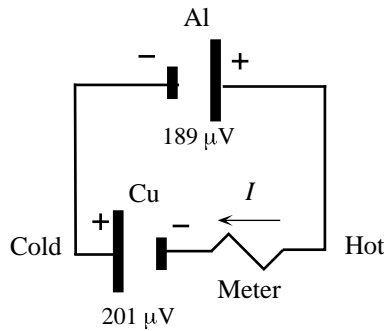
$$V_{AB} = \Delta V_A - \Delta V_B = -\frac{\pi^2k^2}{6e} \left[ \frac{x_A}{E_{FAO}} - \frac{x_B}{E_{FBO}} \right] (T^2 - T_0^2) \quad (10)$$

where in this example  $T = 373$  K and  $T_0 = 273$  K.

For Al (A),  $E_{FAO} = 11.6$  eV,  $x_A = 2.78$ , and for copper (B),  $E_{FBO} = 7.01$  eV,  $x_B = -1.79$ . Thus,

$$V_{AB} = -189.3 \mu\text{V} - 201.14 \mu\text{V} = -390.4 \mu\text{V}$$

To find which end is positive, we put in the resistance of the voltmeter and replace each metal by its emf,  $\Delta V_{Cu}$  and  $\Delta V_{Al}$  and determine the direction of current flow as in Figure 7. For the particular circuit shown, positive end is at the hot side.



The polarity of the measured voltage in terms of hot side being positive or negative depends where the voltmeter is inserted.

**Figure 7**

Thermocouple EMF calculations that closely represent experimental observations require thermocouple voltages for various metals listed against some reference metal. The reference is usually Pt with the reference junction at 0 °C. From Table 2 we can read Al-Pt and Cu-Pt emfs as  $V_{Al-Pt} = 0.42$  mV and  $V_{Cu-Pt} = 0.76$  mV at 100 °C with the experimental error being around  $\pm 0.01$  mV, so that for the Al-Cu pair,

$$V_{Al-Cu} = V_{Al-Pt} - V_{Cu-Pt} = 0.42 \text{ mV} - 0.76 \text{ mV} = -0.34 \text{ mV or } -340 \mu\text{V}$$

There is a reasonable agreement with the calculation using the Mott-Jones equation.

### 3.2. Example 2: The thermocouple equation

We know that we can only measure differences between thermoelectric powers of materials as in the thermocouple since the thermally induced voltages cancel when both metals are the same. When two different metals, A and B, are connected to make a thermocouple as in Figure 6, then the net emf is the voltage difference between the two elements from Equation (10).

$$V_{AB} = \Delta V_A - \Delta V_B = -\frac{\pi^2k^2}{6e} \left[ \frac{x_A}{E_{FAO}} - \frac{x_B}{E_{FBO}} \right] (T^2 - T_0^2)$$

*i.e.* 
$$V_{AB} = C(T^2 - T_0^2)$$

where  $C$  is a constant that is independent of  $T$  but dependent on the material properties ( $x$ ,  $E_{FO}$  for the metals).

We can now expand  $V_{AB}$  about  $T_0$  by using Taylor's expansion for a function  $f(T)$ ,

$$f(T) \approx f(T_0) + \Delta T(df/dT)_0 + 1/2(\Delta T)^2(d^2f/dT^2)_0$$

where  $F = V_{AB}$  and  $\Delta T = T - T_0$  and the derivatives are evaluated at  $T_0$ . The result is the thermocouple equation:

$$V_{AB}(T) = a(\Delta T) + b(\Delta T)^2$$

where the coefficients  $a$  and  $b$  are  $2CT_0$  and  $C$  respectively.

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## NOTATION

C	cold
$e$	electronic charge (magnitude only)
$E$	energy of an electron
$E_{av}$	average electron energy (depends on the density of states)
$E_F$	Fermi energy
$E_{FO}$	Fermi energy at 0 K
EMF	emf, electromotive force (open circuit voltage)
$F(T)$	function of temperature
$g(E)$	density of states
H	hot
$k$	Boltzmann's constant
$m_e$	mass of the electron (in free space)
$m_e^*$	effective mass of the electron in a crystal
MFP	mean free path
$n$	concentration of conduction electrons (number of conduction electrons per unit volume)
$S$	Seebeck coefficient; thermoelectric power
$S_{AB}$	$S_A - S_B$
$T$	temperature (absolute temperature)
TC	thermocouple
$u$	mean speed of electrons
$V$	voltage
$V_{AB}$	EMF from a thermocouple A-B
$v$	mean speed, velocity
$x$	a numerical factor in the Mott-Jones thermoelectric power equation that represents the effect of the energy dependence of electron scattering in metals
$\Delta$	change, difference
$\delta$	a very small change
$\Gamma$	particle flux, number of particles crossing per unit area per unit time
$\lambda$	mean free path along $x$
$\tau$	mean scattering time of conduction electrons

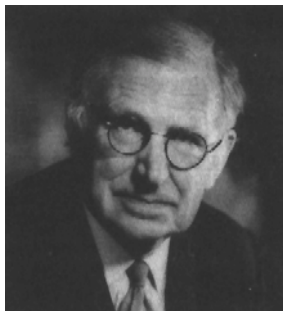
## USEFUL DEFINITIONS

**Fermi energy** ( $E_F$ ) or level may be defined in several equivalent ways. Fermi level is the energy level corresponding to the energy required to remove an electron from the semiconductor; there need not be any actual electrons at this energy level. The energy needed to remove an electron defines the work function  $\Phi$ . We can define the Fermi level to be  $\Phi$  below the vacuum level.  $E_F$  can also be defined as that energy value below which all states are full and above which all states are empty at absolute zero of temperature.  $E_F$  can also be defined through a difference. A difference in the Fermi energy,  $\Delta E_F$ , in a system is the external electrical work done per electron either on the system or by the system just as electrical work done when a charge  $e$  moves through a electrostatic potential energy ( $PE$ ) difference is  $e\Delta V$ . It can be viewed as a fundamental material property. In more advanced texts it is referred to as the chemical potential of the semiconductor.

**Mean free path** is the mean distance traversed by an electron between scattering events. If  $\tau$  is the mean free time between scattering events, and  $v$  is the mean speed of the electron, then the mean free path,  $\lambda = v\tau$ .

**Mean free time** is the average time it takes to scatter a conduction electron. If  $t_i$  is the free time between collisions (between scattering events) for an electron labeled as  $i$ , then  $\tau = \overline{t_i}$  averaged over all the electrons. The drift mobility is related to the mean free time by  $\mu_d = e\tau / m_e$ . The reciprocal of the mean free time is the mean probability per unit time that a conduction electron will be scattered, or, put differently, the mean frequency of scattering events.

**Semiconductor** is a nonmetallic element (*e.g.* Si or Ge) that contains both electrons and holes as charge carriers in contrast to an enormous number of electrons only as in metals. A hole is essentially a "half-broken" covalent bond which has a missing electron and therefore behaves effectively as if positively charged. Under the action of an applied field, the hole can move by accepting an electron from a neighboring bond, thereby passing on the "hole". Electron and hole concentrations in a semiconductor are generally many orders of magnitude less than those in metals, thus leading to much smaller conductivities.



Sir Nevill Mott (1905-1996)

"At a personal level, I always found Sir Nevill to possess the typical helpful and pleasant personality that people with his outstanding intellect so often exhibit."

*Professor Joe Marshall*  
University of Wales at Swansea,  
September 1996

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