THERMOELECTRIC PHENOMENA

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ABSTRACT

Potential usefulness of thermoelectric (TE) effects is hard to overestimate—while at the present time the uses of those effects are limited to niche applications. Possibly because of this situation, coverage of TE effects, TE materials and TE devices in instruction in Materials Science and Engineering is largely perfunctory and limited to discussions of thermocouples. We begin a series of review articles to remedy this situation. In the present article we discuss the Seebeck effect, the Peltier effect, and the role of these effects in semiconductor materials and in the electronics industry. The Seebeck effect allows creation of a voltage on the basis of the temperature difference. The twin Peltier effect allows cooling or heating when two materials are connected to an electric current. Potential consequences of these phenomena are staggering. If a dramatic improvement in thermoelectric cooling device efficiency were achieved, the resulting elimination of liquid coolants in refrigerators would stop one contribution to both global warming and destruction of the Earth's ozone layer.

Keywords: Seebeck effect, Peltier effect, semiconductors, thermoelectric materials, thermoelectric devices, electronics industry, solid state cooling, energy generation, ozone layer, global warming, thermocouples

1. INTRODUCTION

We describe here general thermoelectric (TE) material properties and laboratory setups to measure some of these properties. TE materials such as alloys of Bi2Te3 are used to fabricate TE devices and assemblies that are utilized in a wide range of industries including biomedical, automotive, military, telecommunications, and consumer products. Due to intrinsic TE material properties, the TE devices create a temperature difference when a current flows through the device, while a voltage is produced when a different temperature is applied to each side of the device. TE devices can therefore be used to heat or cool objects or else to produce electricity from heat sources.
In spite of the importance of the TE phenomena, materials and devices, instruction in Materials Science and Engineering (MSE) has almost ignored this area. The present article is, therefore, the first in a series aimed at rectification of this situation. The exception is discussions of thermocouples, but such discussions are not consistently well connected to the phenomenon of thermoelectricity. Kinds of materials exhibiting the TE effect, heating and cooling with TE devices, and power generation with TE devices will be the subjects of three subsequent articles.

2. BASIC THERMOELECTRIC PROPERTIES

Goldsmid in his pioneer text on thermoelectricity 1, Nolas, Sharp and Goldsmid in a later edition 2 and electronic materials texts such as Schröder’s 3 or Kasap’s 4 provide an excellent foundation in thermoelectric theory. The important thermoelectric (TE) effects and the equations describing those effects are discussed here.

There are at least two thermoelectric effects. First, in 1821 the Estonian-German physicist Thomas Johann Seebeck discovered in the city now called Tallinn an effect later named after him. Namely, a temperature difference ΔT between two dissimilar electrical conductors in contact with each other produces a voltage V. We now know this applies also to semiconductors. The magnitude of the effect is represented by the Seebeck parameter, S:

\[ S = \frac{V}{\Delta T} \]  

(1)

Thermocouples constitute a widely used application of the Seebeck effect. The voltage V is measured, and the dependence of V on T for a given composition is known. A reference temperature is determined such as 0°C (ice + liquid water), and a readout for instance in degrees Celsius is provided. Needless to say, such a temperature meter requires no external energy.

Thirteen years later, in 1834 a French physicist Jean Charles Athanase Peltier discovered a twin effect. Again, we have two conductors or semiconductors. In this case there is a battery connected to the two materials. The result is the cooling of one junction and the heating of the other. Calling the two materials a and b, giving the symbol Q to heat either absorbed or released, we have

\[ Q = (\Pi_a - \Pi_b) I \]  

(2)

Here, I is the electric current flowing from a to b. Eq. (2) serves also as the definition of the Peltier parameter Π, also called the Peltier coefficient.

We have said above that there are at least two TE effects. There is also Joule heating, named after James Prescott Joule (British physicist and brewer) where heat is generated when a current passes through a resistive material. In this case there are two reasons for confusion. First, some people claim that Joule heating cannot be classified as a TE effect. The reason is that the Seebeck effect and the Peltier effect are in principle thermodynamically reversible—while the Joule heating is not. Further, there is also the Thomson effect, also reversible and originating from the temperature dependence of the Seebeck coefficient. William Thomson (the original name of Lord Kelvin) derived from the principles of thermodynamics the relationship between the Seebeck parameter S and the Peltier parameter Π, namely

\[ \Pi = ST \]  

(3)

In the following, we discuss each of these effects in some detail. Before further discussion of TE effects, however, we need to discuss the band theory of conductivity.

3. BAND THEORY OF CONDUCTIVITY

Consider a plot of energy values of electrons. By definition, those energies take discrete values. However, given that so many of those values exist, we simplify the situation by assuming that the energies form continuous bands. For our purposes this simplification is
good enough and conclusions drawn will be valid. In Figure 1 we use the electron energy $E$ as the vertical coordinate to show the behavior of main classes of materials.

To understand Figure 1, we need to invoke the concept of the Fermi level $E_F$, named after the Italian physicist Enrico Fermi. There have been a number of articles in this Journal dealing with electronic properties of materials, but we need the definition to explain Figure 1 well. $E_F$ is the thermodynamic work required to add one electron to the material; the work required to move the electron from its point of origin in free space to the vicinity of the material sample is not taken into account. The Fermi energy $E_F$ is also a cutoff energy; that is, at $T = 0$ K, the occupation probability at energy $E$, called $p(E)$, is equal to unity for $E < E_F$, while $p(E) = 0$ for $E > E_F$ and $p(E_F) = \frac{1}{2}$.

We see in Figure 1 that in metals the non-conducting and the conducting states form a single band. Therefore, even a minute amount of energy can move an electron to a higher energy state—which is the requirement for conduction. In semimetals there is also the continuity, but there is a lower concentration of electrons near $E_F$. Now we need to consider that charge carriers can be either electrons or holes (locations where electrons can be considered as missing). In semiconductors, there is a band gap, a range of energy values that are forbidden. To bring an electron from the lower band called the valence band across the band gap to the conduction band requires energy. In a pure or intrinsic semiconductor, the band gap is symmetric with respect to $E_F$. Doping, which is the addition of foreign atoms to a semiconductor material, can increase significantly the number of charge carriers by shifting $E_F$ near one band or the other. If the dopant adds holes, then we have a $p$-type semiconductor. If the dopant adds electrons, then we have an $n$-type semiconductor. Finally, we have insulators, with a large energy gap and for which doping generally is ineffective in providing a useful electrical conductivity. Supplying much energy (temperature) to force the electrons to conduct can result in thermal degradation (aka burning). We are now ready to consider the thermoelectric effects in some detail.

4. SEEBECK EFFECT

If a single conducting rod is heated on one end and cooled on the other, the electrons on the hot end are more energetic and have greater
velocities than electrons on the cold end. Therefore, the electrons on the hot end diffuse to the cold end until the developing electric field prevents further diffusion. The diffusion of electrons gives the conducting rod an increased negative electron concentration at the cold end, leaving some uncompensated positive ions at the hot end. A voltage potential difference, therefore, results with the hot end at a positive potential due to lower electron density. We have seen the Seebeck parameter $S$, a bulk property, defined by Eq. (1). By convention, if electrons accumulate at the cold end, $S$ is negative, and, conversely, if electrons accumulate at the hot end, $S$ is positive.

The original work of Thomas Seebeck in 1821 involved two metals joined as a thermocouple. The Seebeck parameter is also known as the Seebeck coefficient or else as the thermal EMF (electromotive force) coefficient. The more accurate symbol $S_{a,b}$ includes naming the materials $a$ and $b$. By convention, voltage is positive if the electromotive force drives a current across the circuit clockwise. As already mentioned, the Seebeck effect is used in thermocouples in making temperature measurements, as well as in the TE material and device applications. The effect can be used to turn a heat source into electrical power using a TE generator (TEG) device. Since the Seebeck coefficient is a bulk property, $S_{a,b}$ can be represented as $S_a - S_b$, the difference between the absolute Seebeck coefficients for the two conductors.

We now recall Ohm’s Law (honoring Georg Simon Ohm):

$$V = IR$$

(4)

Here, $I$ is the current as before while the resistance $R$ is

$$R = \rho L/A$$

(5)

The resistance $R$ is an extensive property, while the resistivity $\rho$ is an intensive property; $L$ is the length, and $A$ the cross-sectional area of the material.

The Seebeck coefficient can be measured for a normal conductor coupled with a superconductor—by assigning zero to the superconductor. This has been done for the metal lead (Pb) and the superconductor Nb$_3$Sn over a range of useful temperatures. Other metals can then more easily be measured against Pb. Tables of Seebeck coefficients for many conductors are readily available.

One can consider the Seebeck effect and the parameter $S$ in terms of entropy. From Equations 2 and 3, one can see that $S$ is related to the entropy to charge ratio of the carriers. (This is why it is a reasonable convention to use $S = 0$ for a superconductor—the charge carriers are in a ground state.) We need to remember at all times that entropy $= k_b \ln \Omega$, where $k_b$ is the Boltzmann constant and $\Omega$ is the number of possible energy states of the system. These changes in entropy are of two kinds. First, charge carriers (such as thermally excited electrons) are distributed among their thermally accessible states; they are in equilibrium with the lattice. Second, we have scattering and energy dissipation during movement of the carriers. The distribution of available energy states and the dependence of carrier mobility on energy combine to determine the Seebeck coefficient.

Finally, we mention the Nernst effect, also called the Nernst-Ettingshausen effect (thus honoring both Walther Nernst and Albert von Ettingshausen, the former was a student of the latter). An electricity conductor is subjected to a magnetic field and simultaneously to a temperature gradient, perpendicular to each other. The result is an electric field perpendicular (normal) to both. The reverse process is known as the Ettingshausen effect, or else as the second Nernst-Ettingshausen effect. One applies a current along an axis, say the y-axis, and a perpendicular magnetic field along the z-axis. As a result, a temperature gradient appears along the x-axis. We have accumulation of electrons on one side of the sample, therefore the number of electron collisions increases and a higher temperature appears on that side.
5. PELTIER EFFECT AND SCHOTTKY JUNCTIONS

As said in Section 1, when a direct current (DC) passes between the junctions of two different materials, there is a heating or cooling effect depending on the direction of the current flow. This is the Peltier effect, quantitatively characterized by Eq. (2). When two dissimilar materials are in contact and a DC current is passed through the junction, heat is absorbed or released depending on the direction of the current flow. We reiterate that both the Seebeck and the Peltier effects are bulk effects and not merely interfacial ones. Typical metals such as nickel used as diffusion barriers in TE devices form ohmic contacts with Bi$_2$Te$_3$ alloys. Ohmic means that Ohm's law, our Eq. (4), is obeyed. To understand the Peltier effect better, we need to use the band structure theory of materials explained in Section 3.

We now need to define the term *work function*, which is the minimum thermodynamic work needed to move an electron from inside of a solid to a point in vacuum immediately outside the surface of that solid. Figure 2 is patterned after an example by Kasap. It illustrates the mechanism of electronic heat exchange for a generic metal with a low work function to n-type semiconductor (ohmic junction) as a function of current I. $E_{Fm}$ is the metal Fermi level, $E_{Fn}$ is the n-type semiconductor Fermi level, $E_C$ is the conduction band edge (top) energy and $E_V$ is the valence band edge energy.

For the case of heat absorption, electrons near the Fermi level in the metal flow with the current into the conduction band of the semiconductor. When they reach the end of

![Figure 2. Peltier effect in a metal to semiconductor ohmic contact. Note that the assumption of the ohmic contact is an idealization.](image-url)
the conduction band, their energy can be considered equal to $E_C$ plus the average kinetic energy $(3/2)k_BT$. Actually, this is an approximation—in reality, the average kinetic energy that is pertinent depends on the energy dependence of the carrier mobility. There is an increase in the average total energy of the electrons so they must absorb heat from the environment through lattice vibrations to gain this energy. The total energy $E_i$ of the electron is given by the sum of the potential energy $E_p$ plus the kinetic energy $E_k$, namely

$$E_i = E_p + E_k = E_C + 3k_BT/2 \quad (6)$$

Recall now Eq. (2). Below we present a more detailed analysis—which can be omitted in basic courses of MSE. Considering the actual power absorbed by the charge carriers at a junction, $Q_{abs}$, it is not necessary to take into account the effects of the Joule heating discussed at the end of Section 2. We then find that $Q_{abs}$ is proportional to $I/q$, where $q$ is the electron charge of $1.60218 \times 10^{-19}$ Coulomb. The actual relation is

$$Q_{abs} = [E_C + 3k_BT/2 - E_{Fm}] (I/q) \quad (7)$$

We now use Eqs. (2), (3) and (7) to obtain

$$S = \Pi/T = 1/(Tq) [E_C - E_{Fm} + 2k_BT] \quad (8)$$

When electrons travel from the semiconductor into the metal, there is another exchange of energy. However, now the electrons must lose energy equivalent to $(E_C - E_{Fm})$ since $E_C$ is at a higher energy than the Fermi level and the energy is released to the lattice (and eventually to the environment). This is also illustrated in Figure 2; we see the Peltier effect at the hot side of an n-type TE element where heat is released.

We shall now consider Schottky junctions, so named after the German physicist Walter H. Schottky. The Schottky barrier is a potential energy barrier at the junction between a semiconductor and a metal, characterized by the barrier height $\phi_b$, namely

$$\phi_b = E_C - E_F \quad (9)$$

Schottky barriers have rectifying characteristics, so they can be used as diodes. A diode is a two-terminal electronic component with very low resistance to current in one direction and very high (in the limit infinite) electrical resistance in the other direction. However, the Schottky barriers are not formed automatically; if current is conducted in both directions without rectification, we have an ohmic contact (possibly the barrier exists but is so low that it produces no effects.

![Figure 3. Energy band diagram for a metal and n-type semiconductor before contact; $\phi_m > \phi_n$.](image-url)
Recall that the work function is the minimum thermodynamic work needed to move an electron from inside of a solid to a point in vacuum immediately outside the surface of that solid. We consider the work function for a metal $\phi_m$, for the n-type semiconductor $\phi_n$, and for the p-type semiconductor $\phi_p$. If we have $\phi_m > \phi_n$, or else $\phi_m < \phi_p$, a Schottky junction is formed. The former case is illustrated in Figure 3 before contact occurs. Here $\chi_n$ is the electron affinity, which is the amount of energy released when an electron is added to a neutral atom or molecule in the gaseous state so as to form a negative ion.

When the metal and the n-type semiconductor from Figure 3 are brought into contact, the semiconductor electrons in the conduction band are initially at a higher energy level than the metal electrons at the metal Fermi level. The semiconductor electrons therefore cross the interface and reside at the metal surface until electron energies are brought into equilibrium and the two Fermi levels are essentially equal.

The electrons stay near the metal surface and leave a region depleted of electrons in the semiconductor. This results in a concentration of positive charges from the ion cores in the semiconductor depletion region. Figure 4 is also patterned after an example by Kasap and shows the metal and n-type semiconductor after making contact. We see in the figure the Schottky barrier $\phi_{bn}$ defined graphically, the built-in or contact potential $V_0$, the built-in electric field $E_0$, and the depletion width $D$. From Figure 4 one can derive the so-called Schottky-Mott relation (honoring Sir Nevill F. Mott)

$$\phi_{bn} = \phi_m - \chi_n$$ (10)

Note that the experimental value for $\phi_{bn}$ is typically 0.5 eV higher than the calculated value from Eq. (10) due to interfacial effects. Moreover

$$qV_0 = \phi_m - \phi_n$$ (11)

Eq. (11) also neglects the interfacial effects. To consider those effects, let us look at Figure 4:

![Figure 4. Energy band diagram for an unbiased metal and n-type semiconductor after contact; $\phi_m > \phi_n$ which results in a Schottky contact.](image-url)
It is interesting to note that the band bending shown in Figure 4 is the result of the lower concentration of electrons in the depletion region. Since the concentration of electrons has decreased, the difference between the conduction band edge and Fermi level ($E_C - E_{Fn}$) must increase to accommodate the relationship for the concentration of electrons $n_e$ in an n-type semiconductor. We define $N_c$ as the effective density of states for electrons in the conduction band; then

$$n_e = N_c \exp\left[-\frac{(E_C - E_{Fn})}{(k_bT)}\right]$$  \hspace{1cm} (12)

Eq. (12) also helps to explain the existence of the built-in electric field $E_0$ since there is a non-uniform distribution of carriers and hence positive charges across the depletion region. $E_0$ is at a maximum at the metal to semiconductor interface since this is the greatest concentration of positive charge in the depletion region.

Consider now the so-called forward bias situation displayed in Figure 5 where an external voltage is applied.

In Figure 5, the voltage $V$ is applied such that current flow $I$ is from the metal through the depletion region and into the n-type semiconductor. The built-in potential, or contact potential, $V_0$ is lowered by the magnitude of the applied voltage, i.e. $(V_0 - V)$. The semiconductor energy band outside the depletion region is raised with respect to the metal and the barrier height $\phi_{bn}$ is unchanged. Electrons at $E_C$ can easily overcome the potential energy (PE) barrier of $q(V_0 - V)$ with the available thermal energy. As the electrons move from the semiconductor conduction band $E_C$ to the Fermi level $E_{Fm}$, they lose energy equivalent to $\phi_{bn}$ in crossing the Schottky barrier. The total energy loss, however, is lower by $q(V_0 - V)$ since this energy is absorbed to cross the PE barrier. The rate of heat release is, therefore given by:

$$Q_{rel} = \frac{1}{q}[(E_c - q(V_0 - V) + 3k_bT/2 - E_{Fm})]$$  \hspace{1cm} (13)

![Diagram of Forward biased Schottky junction for a metal and n-type semiconductor; heat is released.](image-url)
Here, as before, $Iq$ is the rate of electron flow through the junction. Again, heat loss is primarily through crystal lattice interactions. The Peltier parameter $\Pi$ is

$$\Pi = \frac{Q_{rel}}{I} = \frac{1}{q} [E_c - q(V_0 - V) + 3k_bT/2 - E_{Fn}]$$

(14)

$\Pi$ is also lowered by $q(V_0 - V)$ relative to the ohmic contact; the forward bias Schottky junction will exhibit less efficient thermoelectric cooling/heating than the ohmic contact junction. For very large fields, e.g. $E > 10^7 \text{ V cm}^{-1}$, the band may bend to give a narrow PE barrier that allows field-assisted thermionic emission, i.e. electrons to tunnel through the barrier.

In turn, we now consider the so-called reverse bias case; see Figure 6.

In Figure 6, the current flow is from the n-type semiconductor into the metal and the corresponding electron movement is from the metal into the n-type semiconductor. The applied voltage or reverse bias does not oppose the built-in voltage $eV_0$ and the contact potential therefore increases by the applied voltage, i.e. $q(V_0 + V)$. The electrons are therefore faced with an increased contact potential and cannot easily overcome this barrier. There is virtually no flow of electrons in the reverse bias condition, the Schottky barrier is rectifying, and the electrons flow in only one direction.

Also in the situation presented in Figure 6 the heat gain will be primarily through carrier-lattice interactions, and the rate is given by Eq. (15). The Peltier parameter in Eq. (16) is lower than the ohmic contact case by $q(V_0 + V)$; the flow of electrons is greatly reduced. We have

$$Q_{abs} = [E_c - q(V_0 + V) + 3k_bT/2 - E_{Fn}] (I/q)$$

(15)

$$\Pi = \frac{Q_{rel}}{I} = \frac{1}{q} [E_c - q(V_0 + V) + 3k_bT/2 - E_{Fn}]$$

(16)

Figure 6. Reverse biased Schottky junction for metal and n-type semiconductor; heat would be absorbed if there were electron flow.
We show in Figure 7 the semi-log plot of the saturation current $J_s$ as a function of the barrier height $\phi_{bn}$. The Figure illustrates the dramatic impact of the barrier height on the current. The higher magnitude barrier height is indicative of more Schottky or rectifying character.

![Figure 7. Semi-log plot of the saturation current $J_s$ as a function of the barrier height $\phi_{bn}$ for $B_e = 10$ A K$^{-2}$ cm$^{-2}$ and $T = 300$ K. Here $B_e$ is the so-called emission constant, also known as the Richardson constant, a parameter related to the emission current density.](image)

There also can be Schottky junctions between $p$- and $n$-semiconductors. An example is shown in Figure 8. By doping, one can create an interface even inside of a single crystal. Growing a crystal doped with one kind of dopant on a substrate where another type of dopant was used is called epitaxy—another option of creating the situation depicted in Figure 8.

![Figure 8. A junction between $p$- and $n$-type semiconductors.](image)

6. THOMSON EFFECT

The Thomson effect is defined separately for the conductors in the thermocouple. The Thomson coefficient $\tau$ is defined as a function of the rate of heating per unit length, $dQ/dx$, the current $I$, and the temperature gradient $dT/dx$:

$$\tau = \frac{(1/I)(dQ/dx)}{(dT/dx)}$$

We also have

$$\tau_a - \tau_b = T_a(dS_{a,b}/dT)$$

We recall at this point Eq. (3): it relates the rate of Peltier cooling (or heating) to the Seebeck coefficient, which is relatively easy to measure.

As noted in Section 2, the Thomson effect is reversible. As also noted there, irreversible Joule heating is also observed. Passage of electric current through a conductor produces heat which is proportional to the square of the current $I^2$. Sometimes the name resistive heating is also used for the Joule heating. Actually, it is the work of Joule on this effect that is recognized by the name of joule and the symbol $J$ for the basic unit of energy in the international system of units (SI = Système International). Recall also that power $W$ (watt) is defined as the rate of energy dissipation in Joules per second.

7. THERMAL CONDUCTIVITY AND THE FIGURE OF MERIT

The irreversible Joule heating and thermal conduction effects oppose the reversible thermoelectric effects. A good thermoelectric material will have a high Seebeck and Peltier coefficient and low electrical resistivity and strong scattering by electrons and holes, making such a device hardly usable. Desai and Kapral in their comprehensive book stress the fact that interfaces have strong effects on properties of multiphase systems. We seem to have here an example par excellence of their statement.
also low thermal conductivity. One uses in industry a so-called Figure of Merit Z, or the dimensionless Figure of Merit ZT:

\[ ZT = \frac{S^2 T}{\rho \kappa} \]  

(19)

Here \( \rho \) is the electrical resistivity as before while \( \kappa \) is the thermal conductivity. Plots of \( ZT \) vs. \( T \) are used for material choices for both cooling (heating) and power generation.

We have discussed in this paper the thermoelectric phenomena. In the second article in this series we shall discuss the respective materials. In fact, some of us have done work on service performance of bismuth telluride \(^{18}\), but more such materials are in use.

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