Thermoelectric Effects

If we heat one end of a semiconductor, we add energy to that end. Both electrons and holes will then absorb some of the energy. Since they have more energy than the cooler end, both the electrons and holes will tend to move and carry the energy from the hotter end to the cooler end. At the cooler end, they will release their energy and then collect there until there is enough of them to have the electrical repulsion start to push them back to the hotter end. This should result in the electrons making the cooler end lower in voltage (since negative charges create negative voltage, and the holes making the cooler end higher in voltage (since positive charges create positive voltage). Let's now look at this in more detail.

Note on notations: in this section, the symbol μ is used both for the Fermi level (sometimes called the chemical potential) and the mobility. We will use a subscript on the μ to denote either electron or hole mobility, $\mu_{e/p}$, and we will not have a subscript on μ when using it as the Fermi level.

Mobility, $\mu_{e/p}$, is defined to be $\mu_{e/p} \equiv |v_{e/p}|/E$; so for electrons, which move opposite to the field ($v_e = -\mu_e E$). The **current density, $j_{q\text{-}elec}$**, with units of $(1/m^3)*(C)*(m/s) = \mathbf{A/m^2}$, is:

$$j_{q\text{-}elec} = n\,q\,v = n(-e)(-\mu_e E) = ne\mu_e E$$ for the electron. Recall $E = \Delta V/\Delta s$.

In the same way we can consider an **energy transport density, $j_{U\text{-}elec}$,** with units of $(1/m^3)(J)*(m/s) =$ **Watts/m²**, where the average energy per electron is

$\langle\varepsilon\rangle$ = average energy per electron = energy of conduction band above fermi energy level + kinetic energy
= $(\varepsilon_{conduction}-\mu) + (3/2)k_B T$.

(Note we relate the energy to the Fermi level, μ, because different materials in contact will adjust their levels so that their Fermi levels are the same; recall that the probability of a state being filled is ½ when ε=μ; if electrons in one material are on average in higher states than in another, then these electrons will tend to flow into the other material raising the number of electrons and so raising the potential energy until the fermi levels match.) Thus:

$$j_{U\text{-}elec} = n\langle\varepsilon\rangle v_e = n\{(\varepsilon_{conduction}-\mu) + (3/2)k_B T\}(-\mu_e)E$$ for the electron.

We now **define the Peltier coefficient**:

$$\Pi_e \equiv j_{U\text{-}e}/j_{q\text{-}e} = -[(\varepsilon_{conduction}-\mu) + (3/2)k_B T]/e$$ ($\Pi_e < 0$ for electron).

For the hole, we have:

$$j_{q\text{-}hole} = n\,q\,v = ne\mu_h E,$$ (since $v_h = +\mu_h E$) and

$$j_{U\text{-}hole} = n\langle\varepsilon\rangle v_h = n\langle\varepsilon\rangle\mu_h E,$$ where $\langle\varepsilon\rangle = (\mu - \varepsilon_{valence}) + (3/2)k_B T$

(with $\varepsilon_{valence}<\mu$ and $[\mu - \varepsilon_{valence}]$ being positive for the holes), so

$$\Pi_h \equiv j_{U\text{-}h}/j_{q\text{-}h} = +[(\mu - \varepsilon_{valence} + (3/2)k_B T]/e$$ ($\Pi_h > 0$ for hole).

If we put these two ideas together, we should get an electron and/or hole current if we have an energy flow (such as in thermal conduction). Thus, **if we heat one end of a semiconductor, an electric potential should exist and an electrical current should flow if we have a complete circuit**. Note that the Peltier coefficient has the units of $[Watt/m^2]/[Amp/m^2] = [J/s]/[C/s] =$ **volts**! [But also note that if the semiconductor is balanced between electrons and holes (as in an intrinsic semiconductor), then the total j_q is zero (adding a positive and a negative) while the j_U is not zero.] However, if we do not have an intrinsic semiconductor, we can determine whether the holes or electrons dominate by looking at the sign of the Peltier coefficient.

We can further define an **absolute thermoelectric power, Q**, for an open circuit electric field (**E**) created by a temperature gradient (∇T) [the symbol ∇ is the del operator, and gives the direction of maximum change and the amount of change in whatever it operates on] :

$\mathbf{E} = \mathbf{Q}\,\nabla T$ (units: [Volts/meter] = [units of Q] [Kelvins/meter]
thus Q has units of volts/Kelvin)

or: $\mathbf{Q} \equiv \mathbf{E}/\nabla T = E_x\, \Delta x/\Delta T$ (since $\nabla T = \Delta T/\Delta x$ where x is the direction of the temperature gradient)

or, since $E_x\, \Delta x = -\Delta V$ from definition of voltage, $\mathbf{Q} = -\Delta V/\Delta T$

so **Q** is the volts generated per temperature difference,

or, finally: $\mathbf{\Delta V = -Q\, \Delta T}$ where Q depends on the material.

Note that $\mathbf{\Pi}$ has the units of volts and depends on T (since j_U depends on T), and note that Q ΔT also has the units of volts. In fact, we can get the relation:

$$\mathbf{\Pi} = \mathbf{Q}\, T\ .$$

A rough and ready way to tell if a semiconductor is p type or n type is to heat one end and measure a voltage difference between the hot and cool end. If the hot end is higher in voltage, then the electrons must be carrying the heat to the cool end (and collecting there). Eventually (actually, very quickly) the electron concentration will build up and create a potential difference (more electrons means lower voltage at the cool end) that will force back some of the extra electrons, but these electrons will be at a lower temperature and so transport back less energy; thus the **net** heat transport will continue from hot to cool.

Note from above that if $\Pi<0$, then $Q<0$ (since $\mathbf{\Pi} = \mathbf{Q}\, T$) and ΔV and ΔT will have the same sign (since $\mathbf{Q} = -\Delta V/\Delta T$) and so the temperature gradient and the voltage gradient will both go in the same direction. This is what we have just argued for the electron. Conversely, if the cool end is higher in voltage, then the holes must be carrying the heat from the hot end to the cool end (and collecting there). This means that the voltage gradient and the temperature gradient are opposite in sign. This is consistent with $\Pi>0$ and $Q>0$.