

A PRIMER IN THEORETICAL PHYSICS APPLY TO THERMOELECTRIC

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Abstract

A basic knowledge about theoretical physics is required to understand why a thermoelectric material is better than another. This article popularizes the key concepts required to calculate the transport properties in thermoelectric materials. Instead of starting with electrons and phonons we explain how to calculate the energy flux and the thermal conductivity in a gas of molecules. By doing so the subtractions of the distribution function at the non-thermodynamically at the equilibrium, which enter in the calculation of the Figure-of-Merit is introduced intelligibly. The Boltzmann's equation, which is used to calculate the Figure of Merit is derived by distinguishing the equilibrium state and the steady state. The profile of the ideal thermoelectric material is drawn up.

Introduction

The best encouragement to learn about theoretical physics is that good thermoelectric materials were rarely discovered by coincidence. In fact the values of effective masses, sound velocity, and Debye temperature give already a good indication about the potential of a material as thermoelectrics. In every respect, it is important to read the book of H.J. Goldsmid "Electronic refrigeration" to relate these material properties to the thermoelectric properties¹. This article sets one's heart on completing this book with a derivation of the energy flux, the thermal conductivity and the Boltzmann's equation. The transport properties and Figure of Merit are given as a function of scattering parameter, the Fermi-level, the effective mass, the Debye temperature and various

material constants assuming a parabolic band and one type of carrier. The maximization of the figure of merit is discussed.

Energy fluxes and thermal conductivity

Let us consider a gas molecule with a speed \vec{v} and a temperature $T + dT$ (Figure 1). After a time τ , this molecule experiences a collision. We refer to this time as the relaxation time. The molecule at the temperature $T + dT$ is not in thermodynamic equilibrium. The proportion of such a molecule is given by the distribution function $f(\vec{v}, T(\vec{r} - \vec{v}\tau))$ at the non-equilibrium. After the collision, the molecule is at the thermodynamic equilibrium and its temperature is T . The proportion of such a molecule is given by the distribution function $f_0(\vec{v}, T(\vec{r}))$ in the thermodynamic equilibrium. The distance between the position $\vec{r} - \vec{v}\tau$ and the position \vec{r} is the mean free path l . The mean free path is the distance traveled by a molecule without having experienced a collision. The mean free path is also the product of its speed with the relaxation time: $l = v \times \tau$. The molecule at the temperature $T + dT$ carries an energy $c(T + dT)$, where c is the heat capacity. The molecule at the temperature T carries the energy cT . Let us assume that the number of molecules per unit of volume is n . We are calculating now the fluxes of energy through an imaginary plane (vertical line in Figure 1). The energy flux is:

$$J_U = \frac{1}{3} \int_0^\infty n \times (f(\vec{v}, T(\vec{r} - \vec{v}\tau))(T + dT) - f_0(\vec{v}, T(\vec{r}))cT) \times v dv$$

Let assume, that the gradient of temperature is small ($T + dT \approx T$). In this case, the flux of energy becomes:

$$J_U = \frac{1}{3} \int_0^\infty n \times cT \times (f(\vec{v}, T(\vec{r} - \vec{v}\tau)) - f_0(\vec{v}, T(\vec{r}))) \times v dv \quad (\text{Eq. 1})$$

if n , cT and f were replaced in Eq. 1 by the density of state, the energy of an electron and the Fermi-Dirac distribution function respectively, and if the equation were evaluate in k-space with an additional electric field, the equation would give the

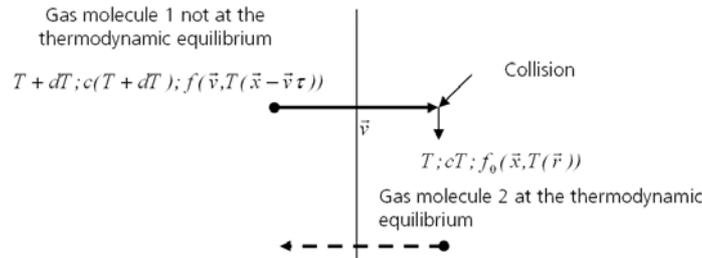


Figure 1: Depiction of the models used to calculate the energy flux of gas molecule subject to a temperature gradient.

Let approximate $f(\vec{v}, T)$ to $f_0(\vec{v}, T)$:

$$J_U = \frac{1}{3} \int_0^\infty n \times \frac{\partial f_0(v)}{\partial T} \times dT \times cT \times v dv$$

Let replace now cT through E and let multiply and divide the energy flux by the mean free path. The energy flux is then given by:

$$J_U = \frac{1}{3} \int_0^\infty n \times \frac{\partial f_0(v)}{\partial T} \times E \times \tau \times v^2 dv \frac{dT}{dx}$$

By using the definition of the thermal conductivity, $J_U = \lambda \times \Delta T / \Delta x$, the thermal conductivity of a gas of molecule is obtained :

$$\lambda = \frac{1}{3} \int_0^\infty n \times \frac{\partial f_0(v)}{\partial T} \times E \times \tau \times v^2 \times dv \quad (\text{Eq. 2})$$

This equation can be extended for the calculation of the thermal conductivity of a solid. In this case, the density should be replace by the number of vibration mode per unit of volume $g(\omega)$, the energy by $\hbar\omega$ and the distribution function f_0 by the mean excitation number $n = 1 / (e^{\hbar\omega/k_B T} - 1)$

By doing so we can obtained the equation 6.37 (page 108) of the book “thermal conduction in semiconductors” of C.M. Bhandari and D.M. Rowe.ⁱⁱ

energy flux of electron gas instead of the energy flux of a gas of molecules.

Let derive now the thermal conductivity of a gas by starting from the Eq.1. The problem is the calculation of the distribution function at the non thermodynamic equilibrium. This will be done with a Talor’s serie of $f(\vec{v}, T)$ in the neighborhood of T :

$$f(\vec{v}, T + dT) = f(\vec{v}, T) + \frac{\partial f(\vec{v}, T)}{\partial T}$$

The Boltzmann’s equation

We would like now calculate the difference of distribution function of the electrons when a force \vec{F} exerts its influence. The force \vec{F} results from an electric field. Let assume that we are in the steady state. The distribution function at the non-equilibrium is not a function of the time: $df/dt = 0$.

Since \vec{F} accelerate the electron, the distribution functions is also a function of the wave vector and the wave vector change between two collisions:

$$\vec{F} = \hbar \frac{\partial \vec{k}}{\partial \tau} \Leftrightarrow d\vec{k} = \frac{\vec{F}}{\hbar} d\tau$$

If the position and the time just after the collision (figure 1) is \vec{r} and $t + \varepsilon$, respectively, then at the time $t - \tau + \varepsilon$ ($\varepsilon \approx 0$), the position was $\vec{r} - \vec{v}\tau$. By integration of df/dt between $t - \tau + \varepsilon$ and $t + \tau + \varepsilon$, we obtain:

$$f(\vec{r}, \vec{k}) - f(\vec{r} - \vec{v}\tau, \vec{k} - \vec{F}d\tau/\hbar) = cst$$

The problem is to give the value of the constant. At the time t (prior to the collision), the distribution function is $f(\vec{r}, \vec{k})$. Just after this collision, at the time $t + \varepsilon$, the distribution function is

$f_0(\vec{r}, \vec{k})$. Between $t - \tau + \varepsilon$ and t , the electron did not experience any collision. As a consequence, we can say that the distribution function did not change in value during the time τ . The distribution function changes just between t and $t + \varepsilon$. Having this in mind, the constant can be calculated:

$$f(\vec{r}, \vec{k}) - f(\vec{r} - \vec{v}\tau, \vec{k} - \vec{F}d\tau/\hbar) = f(\vec{r}, \vec{k}) - f_0(\vec{r}, \vec{k})$$

If we are now developing $f(\vec{r} - \vec{v}\tau, \vec{k} - \vec{F}d\tau/\hbar)$ with a Taylor's series in the neighborhood of (\vec{r}, \vec{k}) , we get:

$$f(\vec{r} - \vec{v}\tau, \vec{k} - \vec{F}d\tau/\hbar) - f(\vec{r}, \vec{k}) = -\frac{\partial f(\vec{r}, \vec{k})}{\partial \vec{r}} \vec{v}\tau - \frac{\partial f(\vec{r}, \vec{k})}{\partial \vec{k}} \frac{\vec{F}}{\hbar} \tau = f(\vec{r}, \vec{k}) - f_0(\vec{r}, \vec{k})$$

And the Boltzmann's equation is:

$$\frac{\partial f(\vec{r}, \vec{k})}{\partial \vec{r}} \vec{v} + \frac{\partial f(\vec{r}, \vec{k})}{\partial \vec{k}} \frac{\vec{F}}{\hbar} = -\frac{f(\vec{r}, \vec{k}) - f_0(\vec{r}, \vec{k})}{\tau} \quad (\text{Eq. 3})$$

Transport properties

Thermodynamic identity $TdS = dU - \xi dN$ is very important to calculate the transport properties and often overlooked. S is the entropy, U the intern energy, ξ the chemical potential and dN is in fact the number of particles which experience a collision that bring the distribution function from $f(\vec{r}, \vec{k})$ to $f_0(\vec{r}, \vec{k})$. This thermodynamic identity can be written in term of fluxes (Chapter 13, N.W Aschcroft, N.D. Mermin, solid state physics, chapter 13, equation 13.40):ⁱⁱⁱ

$$T\vec{J}_S = \vec{J}_U - \xi\vec{J}_N \quad (\text{Eq. 4})$$

It can be shown that the thermodynamic identity is also used to derive the Fermi-Dirac distribution function in thermodynamic equilibrium.^{iv}

By using the (Eq. 4), the Boltzmann equation, and equations similar to (Eq. 2) but for the energy flux and the electric current, the transport properties are given by:

$$\sigma = \frac{e^2}{3\pi^2} \left(\lambda + \frac{3}{2} \right) \tau_0 \frac{2^{3/2} (k_B T)^{3/2+\lambda}}{\hbar^3} \frac{N_V m^{*3/2}}{m_I} F_{1/2+\lambda}$$

$$\alpha = \mp \frac{k_B}{e} \left[\zeta^* - \frac{(5/2 + \lambda) F_{3/2+\lambda}}{(3/2 + \lambda) F_{1/2+\lambda}} \right]$$

$$\lambda_e = \frac{\tau_0}{6\pi^2} \frac{2^{5/2} (k_B T)^{5/2+\lambda}}{\hbar^3} \frac{N_V m^{*3/2}}{m_I} k_B \times \left[\left(\frac{7}{2} + \lambda \right) F_{5/2+\lambda} - \frac{(5/2 + \lambda)^2 F_{3/2+\lambda}^2}{(3/2 + \lambda) F_{1/2+\lambda}} \right]$$

$$\mu = e \frac{2}{3} \left(\lambda + \frac{3}{2} \right) \tau_0 (k_B T)^{\lambda} m_I^{-1} \frac{F_{1/2+\lambda}}{F_{1/2}}$$

Where σ , α , λ_e and μ are the electrical conductivity, the Seebeck coefficient, the electronic part of the thermal conductivity and the mobility, respectively.

The figure of merit is given by:

$$ZT = \frac{\left(\frac{3}{2} + \lambda \right) \left[\frac{(5/2 + \lambda) F_{3/2+\lambda}}{(3/2 + \lambda) F_{1/2+\lambda}} - \zeta^* \right]^2 F_{1/2+\lambda}}{\frac{1}{B} + \left(\frac{7}{2} + \lambda \right) F_{5/2+\lambda} - \frac{(5/2 + \lambda)^2 F_{3/2+\lambda}^2}{(3/2 + \lambda) F_{1/2+\lambda}}}$$

where λ_L is lattice thermal conductivity.

The quality factor is given by:

$$B = \frac{1}{3\pi^2} \frac{2^{3/2}}{\hbar^3} (k_B T)^{5/2+\lambda} \tau_0 N_V \frac{m_N^{3/2}}{m_I} k_B \frac{1}{\lambda_L}$$

It was supposed that the relaxation time can be expressed as a simple power law of the form $\tau_0 E^\lambda$, where λ is the scattering parameter. m_I and m_N are the inertial and density of state effective mass in a multivalley (N_V valley) cubic crystal. F_r are the Fermi-Dirac integral.

We assume the lattice thermal conductivity be given by the minimal thermal conductivity of solid by the sake of simplicity:

$$\lambda_L \approx \lambda_{MIN} = \left(\frac{\pi}{6} \right)^{1/3} k_B n^{2/3} \sum_i v_i \left(\frac{T}{\theta_D} \right)^{2\theta_D/T} \int_0^{\theta_D/T} \frac{x^3 e^x}{(e^x - 1)^2} dx$$

Where θ_D is the Debye temperature, n is the number of atom per unit of volume and v is the sound velocity.

The Debye temperature is:

$$\theta_D = \frac{\hbar \omega_D}{k_B} = \frac{\hbar v k_D}{k_B} = \frac{\hbar v}{k_B} (6\pi^2 n)^{1/3}$$

The number of atom per unit of volume in λ_{MIN} can be replaced by a function of θ_D in order to obtain the post-factor P plotted in the figure 2: $P = T^2 \int_0^{\theta_D/T} \frac{x^3 e^x}{(e^x - 1)^2} dx$

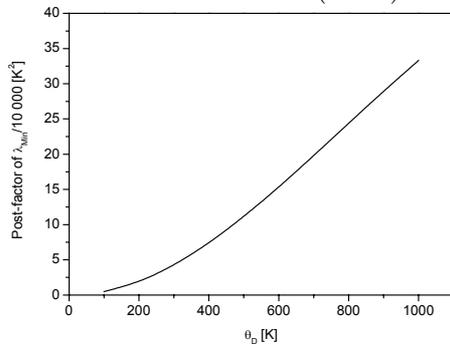


Figure 2: Post factor that enter in calculation

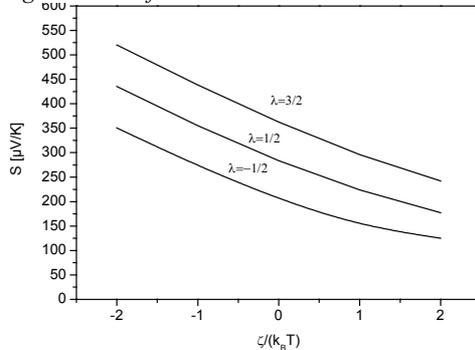


Figure 3: Thermopower for usual scattering parameter

Discussion

The Figure of Merit increases when the quality factor B increases. One way to increase B is to decrease the lattice thermal conductivity. It can be seen in the figure 1 that the thermal conductivity will decrease when the Debye temperature will decrease. Materials with low Debye temperature are material with few atoms per unit of volume i.e. with larger interatomic distance. The second way to increase the quality factor is to decrease the inertial mass.^v This can also be done by choosing a crystal structure with a large interatomic distance in the direction of the current flow. It may be apparent that the Quality Factor increases when the density of states effective m_N mass increase. But it is not so evident since the pre-factor τ_0 in the relaxation time may also be a function of m_N . In fact it can be shown than when the electron are scattered by acoustic phonon or in non-

polar semiconductor by optical phonon, the Quality Factor is not a function of m_N . On the other hand, there are scattering mechanisms (neutral and ionized impurities, acoustic phonon in non-centrosymmetrical crystal, optical phonon in polar-semiconductor) where higher m_N may be favorable.^{vi} It is more evident that multivalley semiconductor (N_V large) is favorable to get large figure of merit. The effect of the scattering parameter is like for the density of state effective mass not so evident. It is clear that larger scattering factor promote large Seebeck coefficient (figure 3). Nevertheless, it does not mean that the figure of merit will be always larger because of the factor $\tau_0(T)(k_B T)^{5/2+\lambda}$ in the Quality Factor. Since $k_B T$ is usually small (0.025 eV@300K). Smaller scattering factor promote large Quality factor. If it is possible to decrease very slightly the value of λ by $\delta\lambda$ for a given scattering mechanism without affecting τ_0 , a huge increase of the Quality Factor could be obtained. The increase would be about 10 ($\lambda = -0.5$, $\lambda - \delta\lambda = -0.55$) when the electrons are scattered by acoustic phonon at 300K: $(k_B T)^{5/2+\lambda-\delta\lambda} / (k_B T)^{5/2+\lambda} \cong 10$.

Conclusion

An engineering of the relaxation time may result in increase of Quality Factor by a factor 10.

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