

Transport Properties Derivations of the Thermoelectric Material in a Weak Magnetic Field

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I. FIGURE OF MERIT & QUALITY FACTOR

According to Stephen Kang(cite), the Figure of Merit characterizes the materials performance by assembling the coefficients that represents the electrons behavior in semiconductor thermoelectric material.

$$zT = \frac{TS^2\sigma}{\kappa} \quad (1)$$

$$\kappa = \kappa_B + \kappa_L + L\sigma T, \quad (2)$$

which S is the Seebeck coefficient, T is the temperature, σ is the conductivity, L is the Lorenz number and κ is the thermal conductivity, which can be decompose to lattice thermal conductivity κ_L , bipolar thermal conductivity κ_B , and electronic thermal conductivity $\kappa_e = L\sigma T$.

Usually, this formula works for considering only dissipative current, whereas the presenting of magnetic field will generate non-dissipative current and causing transverse transport properties. The, transverse zT tensor should be computed as:

$$zT = \frac{TS^2}{\rho\kappa} \quad (3)$$

Since the dependency on the density of electrons η of coefficients S , L , and σ , zT can be optimized at specific value of η , and the optimized zT is the best performance of such material.

However, the best performance can be evaluated before the optimization process by extract the quality factor B from zT :

$$zT(\eta, B) = \frac{S(\eta)^2}{\left(\frac{k_B}{e}\right)^2 \frac{1}{B} \frac{1}{sF_{s-1}(\eta)} + L(\eta)}$$

$$B = \left(\frac{k_B}{e}\right)^2 \frac{\sigma_{E_0}}{\kappa_L} T,$$

which $\sigma = \sigma_{E_0} sF_{s-1}(\eta)$ shows the conductivity can be written as a separable form between the integral over energy of the electron and the grouping of parameters that varies between different materials. The dimensionless quality factor B further group the σ_{E_0} into other property parameters together that represents the intrinsic potential of material thermoelectric performances that independent of the extrinsic manipulation of the environment or η .

The concise form of $zT(\eta, B)$ works of the absents of fields. When there is an magnetic field, the value of S and L will have the field dependencies, so extracting the quality factor B will be more complicated. The following sections of the paper will shows the new form of B under the presents of magnetic field with some approximations.

II. ELECTRON TRANSPORT FUNCTION UNDER MAGNETIC FIELD

Under the influence of fields, S , σ , and L become tensors, and these transport properties is obtained from the Boltzmann Transport Function in semi-classical approximation, since the electron in the semi-conductor context are mainly focused on their behavior near the edge of their energy band.

With that being said, there is some assumptions should be made prior to find the transport properties.

1. We only assume there is one type of carriers, which is electron, and that means there is only single parabolic band. Near the band edge, the dispersion relation can be assumed as parabolic using the *Effective Mass Model*(cite) assuming:

$$\epsilon_k = \frac{\hbar^2 k^2}{m^*} \quad \text{and} \quad v_k = \frac{2\epsilon_k}{m^*} \quad (4)$$

2. For the convenience of the calculation, the energy at the band edge is equal to 0, since electron transport depends on the relative position of the Fermi level to the band edge. Thus, the band energies ϵ_t can be shifted a constant value to 0.

$$\frac{\epsilon_k - \epsilon_t}{k_B T} = \frac{\epsilon_k}{k_B T}$$

3. The electron transport property is measured from non-equilibrium distribution of electron happened within the relaxation time τ , known as the *Relaxation Time Approximation*

$$\frac{\partial f_{neq}}{\partial t} = -\frac{f_{neq} - f_{eq}}{\tau} = -\frac{f_{\Delta}}{\tau}$$

4. The chemical potential is uniform: $\nabla_{\mathbf{r}}\mu_{\mathbf{r}} = 0$

With the non-equilibrium shift from the Fermi distribution, the current density \mathbf{J} and the thermal current \mathbf{U} can be calculated from:

$$\mathbf{J} = q \int_{BZ} v_k f_{\Delta}$$

$$\mathbf{U} = \int_{BZ} v_k (\epsilon_k - \epsilon_F) f_{\Delta}.$$

Plugging f_{Δ} in the above equations can get the general

form of these current can get the necessary information to calculate the transport properties.

To characterize the the transport properties, simplify the external field influences can lead to succinct information. Thus, as most other tasks that looking for influences from electromagnetic fields, we choose to focus on the magnetic field $\mathbf{B} = B_z$ and the electric field that perpendicular to it $\mathbf{E} = E_x + E_y$, of which has the temperature gradient perpendicular to, $\nabla T = \partial_x T + \partial_y T$. Then, the simplified \mathbf{J} and \mathbf{U} in x-y direction will become:

$$J_x = \int_{BZ} \frac{d^3 p}{(2\pi)^3} \frac{v^2}{3} \frac{2q^2 \tau}{1 + (\omega_c \tau)^2} [E_x + (\omega_c \tau) E_y] \left(-\frac{\partial f_{eq}}{\partial \epsilon_k} \right) - \int_{BZ} \frac{d^3 p}{(2\pi)^3} \frac{v^2}{3} \frac{2q^2 \tau \epsilon_k}{1 + (\omega_c \tau)^2} \left[\frac{\partial T}{\partial x} + (\omega_c \tau) \frac{\partial T}{\partial y} \right] \left(-\frac{\partial f_{eq}}{\partial \epsilon_k} \right)$$

$$J_y = \int_{BZ} \frac{d^3 p}{(2\pi)^3} \frac{v^2}{3} \frac{2q^2 \tau}{1 + (\omega_c \tau)^2} [-(\omega_c \tau) E_x + E_y] \left(-\frac{\partial f_{eq}}{\partial \epsilon_k} \right) - \int_{BZ} \frac{d^3 p}{(2\pi)^3} \frac{v^2}{3} \frac{2q^2 \tau \epsilon_k}{1 + (\omega_c \tau)^2} \left[-(\omega_c \tau) \frac{\partial T}{\partial x} + \frac{\partial T}{\partial y} \right] \left(-\frac{\partial f_{eq}}{\partial \epsilon_k} \right)$$

$$U_x = \int_{BZ} \frac{d^3 p}{(2\pi)^3} \frac{v^2}{3} \frac{2q^2 \tau (\epsilon_k - \epsilon_F)}{1 + (\omega_c \tau)^2} [E_x + (\omega_c \tau) E_y] \left(-\frac{\partial f_{eq}}{\partial \epsilon_k} \right) - \int_{BZ} \frac{d^3 p}{(2\pi)^3} \frac{v^2}{3} \frac{2q^2 \tau \epsilon_k (\epsilon_k - \epsilon_F)}{1 + (\omega_c \tau)^2} \left[\frac{\partial T}{\partial x} + (\omega_c \tau) \frac{\partial T}{\partial y} \right] \left(-\frac{\partial f_{eq}}{\partial \epsilon_k} \right)$$

$$U_y = \int_{BZ} \frac{d^3 p}{(2\pi)^3} \frac{v^2}{3} \frac{2q^2 \tau (\epsilon_k - \epsilon_F)}{1 + (\omega_c \tau)^2} [-(\omega_c \tau) E_x + E_y] \left(-\frac{\partial f_{eq}}{\partial \epsilon_k} \right) - \int_{BZ} \frac{d^3 p}{(2\pi)^3} \frac{v^2}{3} \frac{2q^2 \tau \epsilon_k (\epsilon_k - \epsilon_F)}{1 + (\omega_c \tau)^2} \left[-(\omega_c \tau) \frac{\partial T}{\partial x} + \frac{\partial T}{\partial y} \right] \left(-\frac{\partial f_{eq}}{\partial \epsilon_k} \right),$$

since the electron that propagate in z direction will not be affected by either the electric and magnetic field and the isotropic case of the velocity will only be on the diagonal of the velocity matrix and appears to become $v_x^2 = v_y^2 = v_z^2 = v^2/3$. To view this function set concisely, the \mathbf{J} and \mathbf{U} can be written in the tensor form:

$$\mathbf{J} = \begin{pmatrix} K_0 & -H_0 \\ H_0 & K_0 \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix} + \frac{1}{qT} \begin{pmatrix} K_1 & -H_1 \\ H_1 & K_1 \end{pmatrix} \begin{pmatrix} \partial_x T \\ \partial_y T \end{pmatrix} \quad (5)$$

$$\mathbf{U} = -\frac{1}{q} \begin{pmatrix} K_1 & -H_1 \\ H_1 & K_1 \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix} - \frac{1}{q^2 T} \begin{pmatrix} K_2 & -H_2 \\ H_2 & K_2 \end{pmatrix} \begin{pmatrix} \partial_x T \\ \partial_y T \end{pmatrix} \quad (6)$$

The tensor element is the modified form of Fermi integral:

$$K_m = \int g(\epsilon_k) \left(-\frac{\partial f_0}{\partial \epsilon_k} \right) \frac{v^2}{3} \frac{\tau}{1 + \tau^2 \omega_c^2} (\epsilon_k - \mu)^m d\epsilon_k \quad (7)$$

$$H_m = \int g(\epsilon_k) \left(-\frac{\partial f_0}{\partial \epsilon_k} \right) \frac{v^2}{3} \frac{\tau^2 \omega_c}{1 + \tau^2 \omega_c^2} (\epsilon_k - \mu)^m d\epsilon_k, \quad (8)$$

Additionally, the scattering rate τ is dependent on the energy and the magnetic field, which will results in different form as we made further approximations. The scattering rate, which is the inverse of relaxation time, is calculated from the electron-phonon interaction. In quantum field theory, the electromagnetic field is quantized and its annihilation and creation operators has

the bosonic communication relationship, so does that of the phonon quasi-particles. Thus, the interaction between the field and the phonon can be ignored, which aligns with the Born-Oppenheimer approximation, and the one left is the interaction between the field and electron. By using the landau quantization of electron in magnetic field, the relaxation time has the following expression:

$$\frac{1}{\tau} = \frac{\pi}{\hbar} \frac{E_1^2 k_B T}{\rho s^2} \left(\frac{1}{2\pi} \right)^2 \hbar \omega_c \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sum_{n=0}^{max} [\epsilon - \hbar \omega_c (n + \frac{1}{2})]^{-\frac{1}{2}}, \quad (9)$$

which the scattering rate is due to the acoustic phonon scattering, since we are considering the relatively higher temperature, which result in many phonon in the system and this type of scattering dominates. As for higher temperature, the value of $\hbar \omega_c$ is smaller than $k_B T$, so the above expression can be treated as an Riemann Integral:

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} \frac{E_1^2 k_B T}{\rho s^2} \left(\frac{1}{2\pi} \right)^2 \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_{\hbar \omega_c = x \approx 0}^{\epsilon} (\epsilon - x)^{-\frac{1}{2}} dx \quad (10)$$

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} \frac{E_1^2 k_B T}{\rho s^2} \left(\frac{1}{2\pi} \right)^2 \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \epsilon^{1/2} \quad (11)$$

Thus, in our model, we focus on the relaxation time has the following expression, which $\tau = \tau_0 (\frac{\epsilon}{k_B T})^{-\frac{1}{2}}$. So

the Integrals becomes:

$$\begin{aligned}
K_m &= PF_1' \int_0^\infty \epsilon \frac{\partial f}{\partial \epsilon} \frac{(\epsilon - \mu)^m}{1. + PF_2' \epsilon^{-1}} d\epsilon \\
H_m &= PF_1' PF_2'^{1/2} \int_0^\infty \epsilon^{1/2} \frac{\partial f}{\partial \epsilon} \frac{(\epsilon - \mu)^m}{1. + PF_2' \epsilon^{-1}} d\epsilon \\
PF_1' &= \frac{\tau_0 2\sqrt{2} NV m^{1/2}}{3\pi^2 \hbar^3 (k_B T)^r} \\
PF_2' &= \left(\frac{eH\tau_0}{m(k_B T)^r} \right)^2
\end{aligned}$$

III. TRANSPORT PROPERTIES

Seebeck Coefficient

Now it is available to find the transport properties based on \mathbf{J} and \mathbf{U} by setting the $\mathbf{J} = 0$.

$$0 = \mathbf{J} = \sigma \mathbf{S} \nabla T + \sigma \mathbf{E} \quad (12)$$

$$= \sigma \mathbf{S} \nabla T - \sigma \nabla V \quad (13)$$

$$\mathbf{U}|_{\mathbf{J}=0} = T \sigma \mathbf{S} \mathbf{E} - \kappa_0 \nabla T \quad (14)$$

$$= -(\mathbf{L} \sigma T) \nabla T \quad (15)$$

Plugging the Equation5 into Equation12, the Seebeck coefficient can be written in the matrix form.

$$\begin{pmatrix} K_0 & -H_0 \\ H_0 & K_0 \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix} = \frac{1}{qT} \begin{pmatrix} K_1 & -H_1 \\ H_1 & K_1 \end{pmatrix} \begin{pmatrix} \partial_x T \\ \partial_y T \end{pmatrix} \quad (16)$$

$$\begin{bmatrix} E_x \\ E_y \end{bmatrix} = \begin{bmatrix} S_{xx} & S_{xy} \\ S_{yx} & S_{yy} \end{bmatrix} \begin{bmatrix} \partial_x T \\ \partial_y T \end{bmatrix} \quad (17)$$

$$\begin{bmatrix} S_{xx} & S_{xy} \\ S_{yx} & S_{yy} \end{bmatrix} = \frac{1}{qT} \begin{bmatrix} K_0 & -H_0 \\ H_0 & K_0 \end{bmatrix}^{-1} \begin{bmatrix} K_1 & -H_1 \\ H_1 & K_1 \end{bmatrix} \quad (18)$$

Lorenz Number

From the relationship between Seebeck coefficient and the electric field in Equation17 and plugging into Equation15, the following relationship can be found:

$$\mathbf{L} \sigma T = \kappa_0 - T \mathbf{S}^2 \sigma,$$

which make \mathbf{U} a new form in which can extract $\mathbf{L} \sigma T$ from.

$$\mathbf{U} = - \left(\frac{1}{q} \begin{pmatrix} K_1 & -H_1 \\ H_1 & K_1 \end{pmatrix} \begin{bmatrix} S_{xx} & S_{xy} \\ S_{yx} & S_{yy} \end{bmatrix} + \frac{1}{q^2 T} \begin{pmatrix} K_2 & -H_2 \\ H_2 & K_2 \end{pmatrix} \right) \begin{bmatrix} \partial_x T \\ \partial_y T \end{bmatrix}$$

With the above expression, expression of \mathcal{L} can be found in the similar way as getting \mathcal{S} in Equation18.

However, it is less important to get the expression for \mathcal{L} since $\mathbf{L} \sigma T$ can be directly treated as a group when figure of merit is the ultimate goal as described in Equation2, whereas the similar argument does not really applied to the route for getting \mathcal{S} . The reason is \mathcal{S} is necessary for expressing the $\mathbf{L} \sigma T$ by plugging it in, even though $T \mathbf{S}^2 \sigma$, which is the numerator of zT, is extracted from $\mathbf{L} \sigma T$.

The full expression for $\mathbf{L} \sigma T$ is

$$\begin{aligned}
\mathbf{L} \sigma T &= \\
\frac{1}{q^2 T} &\left(\begin{bmatrix} K_2 & -H_2 \\ H_2 & K_2 \end{bmatrix} - \begin{bmatrix} K_1 & -H_1 \\ H_1 & K_1 \end{bmatrix} \begin{bmatrix} K_0 & -H_0 \\ H_0 & K_0 \end{bmatrix}^{-1} \begin{bmatrix} K_1 & -H_1 \\ H_1 & K_1 \end{bmatrix} \right), \quad (19)
\end{aligned}$$

and

$$T \sigma \mathbf{S}^2 = \frac{1}{q^2 T} \begin{bmatrix} K_1 & -H_1 \\ H_1 & K_1 \end{bmatrix} \begin{bmatrix} K_0 & -H_0 \\ H_0 & K_0 \end{bmatrix}^{-1} \begin{bmatrix} K_1 & -H_1 \\ H_1 & K_1 \end{bmatrix}. \quad (20)$$

Combined Equation20 and 19, the figure of merit from Equation1 can be expressed in the matrix form. One of the advantage to calculate zT by grouping $T \mathbf{S}^2 \sigma$ and $\mathbf{L} \sigma T$ is circumventing the problem of order of matrix multiplication, which often rises when matrices do not commute with the others.

$$zT = \frac{\frac{1}{q^2 T} \begin{bmatrix} K_0 & -H_0 \\ H_0 & K_0 \end{bmatrix}^{-1} \begin{bmatrix} K_1 & -H_1 \\ H_1 & K_1 \end{bmatrix} \begin{bmatrix} K_0 & -H_0 \\ H_0 & K_0 \end{bmatrix}^{-1} \begin{bmatrix} K_1 & -H_1 \\ H_1 & K_1 \end{bmatrix}}{\begin{bmatrix} K_0 & -H_0 \\ H_0 & K_0 \end{bmatrix}^{-1} \kappa_L + \frac{1}{q^2 T} \begin{bmatrix} K_0 & -H_0 \\ H_0 & K_0 \end{bmatrix}^{-1} \left(\begin{bmatrix} K_2 & -H_2 \\ H_2 & K_2 \end{bmatrix} - \begin{bmatrix} K_1 & -H_1 \\ H_1 & K_1 \end{bmatrix} \begin{bmatrix} K_0 & -H_0 \\ H_0 & K_0 \end{bmatrix}^{-1} \begin{bmatrix} K_1 & -H_1 \\ H_1 & K_1 \end{bmatrix} \right)} \quad (21)$$

note that the ρ tensor in the denominator and numerator cannot be simply canceled, and it can only be writ-

ten as the form above.

The Figure1 shows the zT dependence on the doping

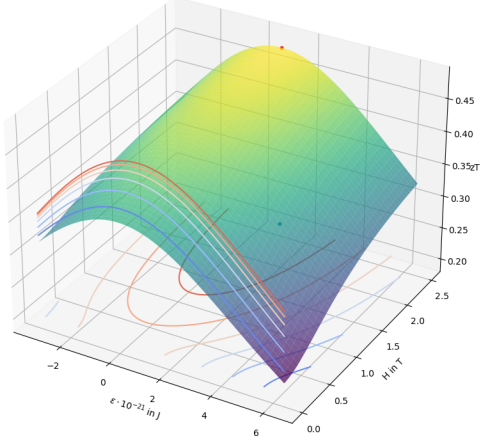


Figure 1. The 3D surface plot of zT dependence on magnetic field and fermi energy, which choosing arbitrary material property constant. The contour plot at the $zT = 0.2$ and $H = 0$ positions show the projection of zT . The scattered points show where the zT max at the surface plot and the projection contour plot.

energy (fermi energy ϵ_f) and the magnetic field. From the Figure1, we can infer that there is a maximum zT value by shifting the ϵ_f , and the zT value should increase monotonically with the external magnetic field H , so that the curves that zT vs ϵ_f do not intersect with other zT vs ϵ_f curve when the external field H is modified, which will be useful when we made approximations.