Joseph Henry Project – Thermoelectric Battery

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1. Introduction

Seebeck discovered that heating junction of loop composed of dissimilar metals can deflect a compass in the middle in 1821. Although he did not really notice a voltage hence current was actually generated, the phenomenon is named after him – the Seebeck Effect.

Joseph Henry was the first one who predicted the production of sparks by thermoelectricity with connection to ribbon coil. In his lecture on Natural Philosophy in College of New Jersey, he demonstrated the production of sparks with the use of a thermoelectric battery. The battery was kept as an artifact left in Physics Department of Princeton University. From the description in student notebook in his course, the thermoelectric battery is heated from above by a hot iron and cooled from below by freezing mixture to produce a spark.

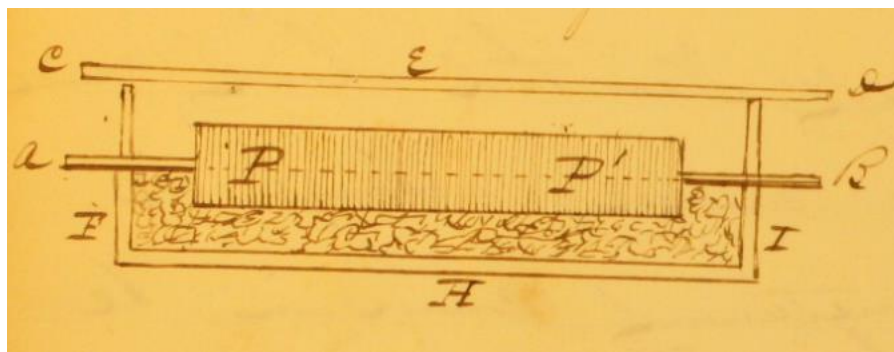*Figure 1 Thermoelectric battery of Joseph Henry*

Figure 2 Student Notebook by Daniel Ayres Jr.

The thermoelectric battery is made of 25 pairs of bismuth and antimony plates connected in a zig-zag manner with paper intervening each pair.

A study to understand the situation when Joseph Henry did the experiment is done. For example, we want to know what was the voltage created and what coil is needed for production of a spark. The study began with theoretical deduction, free electron gas theory is again verified to be bad theory to explain the seebeck effect. The method to arrive at the Mott Expression of thermopower by Boltzmann Transport Equation is reviewed as well. Study with nearly free electron and semiclassical transport theory would be time-consuming. Collection of experimental data is therefore carried out to deduce the seebeck voltage produced at that time.

2. Experimental Determination

The artifact should not be harmed with extreme temperature for historical purposes. Therefore, relevant data regarding the of study on seebeck coefficients of bismuth and antimony are collected from reliable sources. A uniform temperature gradient is assumed so that the seebeck coefficient at certain temperature difference is determined by an average (integration of seebeck coefficient over temperature).

Data are collected from papers cautiously and a fitting equation was created for each data set. The data from G.A. Saunders and O. Oktu (1967) showed clear experimental measurement regarding thermopower of antimony. The data are reproduced for analysis as below.
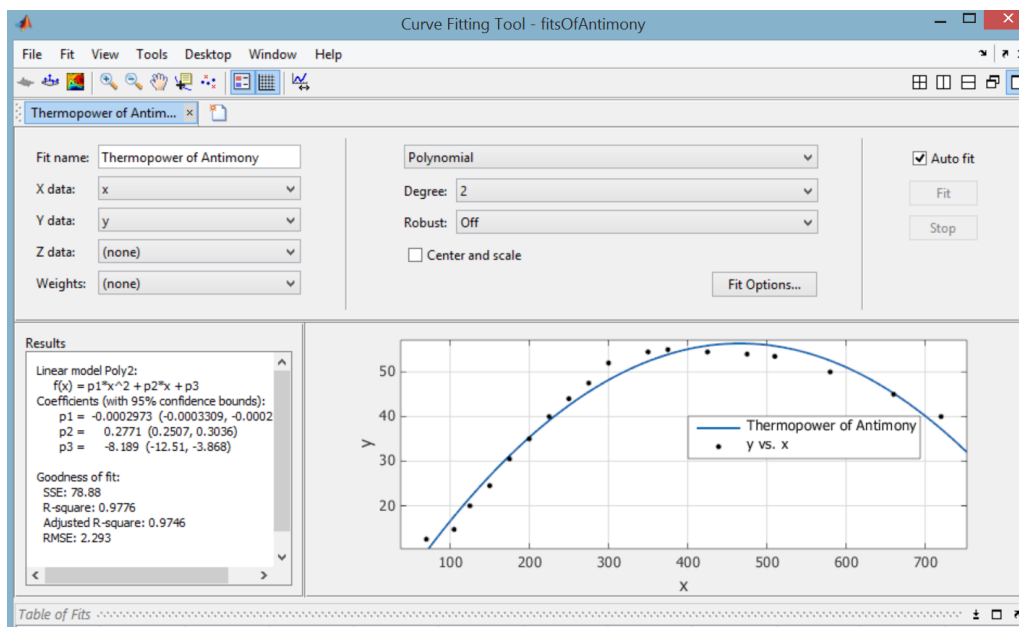

Figure 3 Curve Fitting of Antimony Data (y: Thermopower uV/K, x: Temperature K)
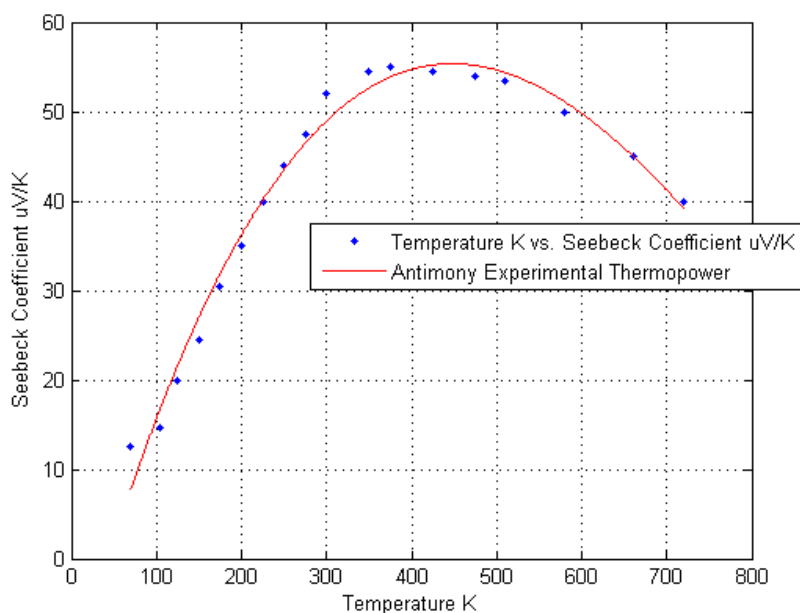
Figure 4 Curve Fitting of Antimony with labels

For Bismuth, since the absolute thermopower (reference to platinum) is not available. However, The data for bismuth thermopower relative to copper and absolute thermopower of copper were found. So The difference between the two was used to compute the absolute thermopower of bismuth.
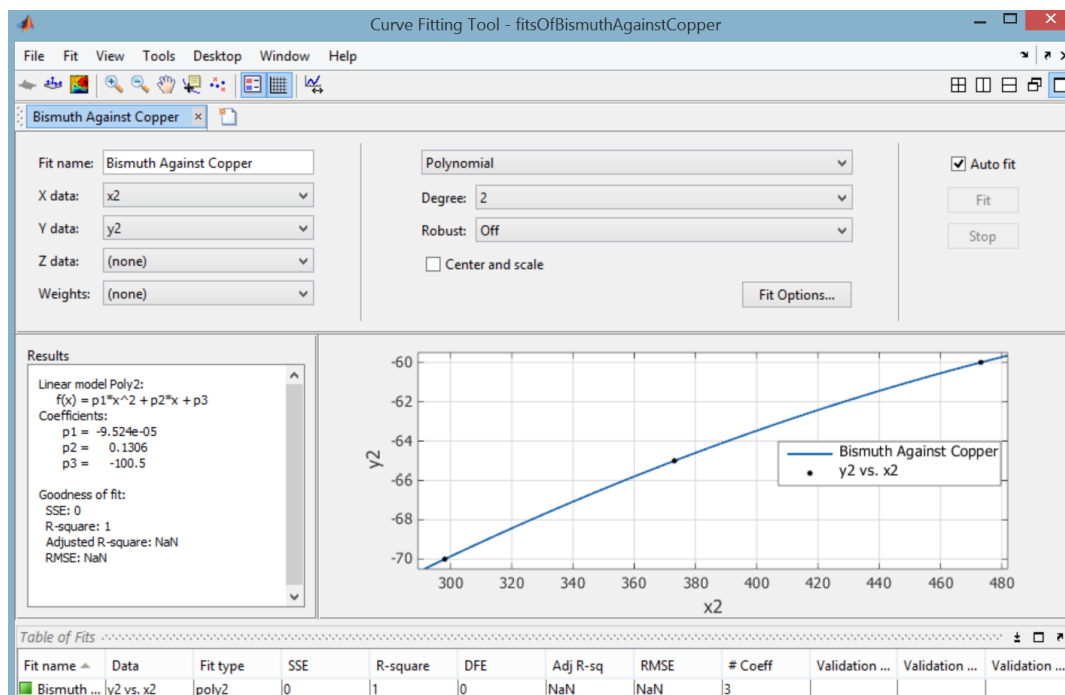

Figure 5 Curve Fitting of Bismuth Data (copper as reference, y: Thermopower uV/K, x: Temperature K)
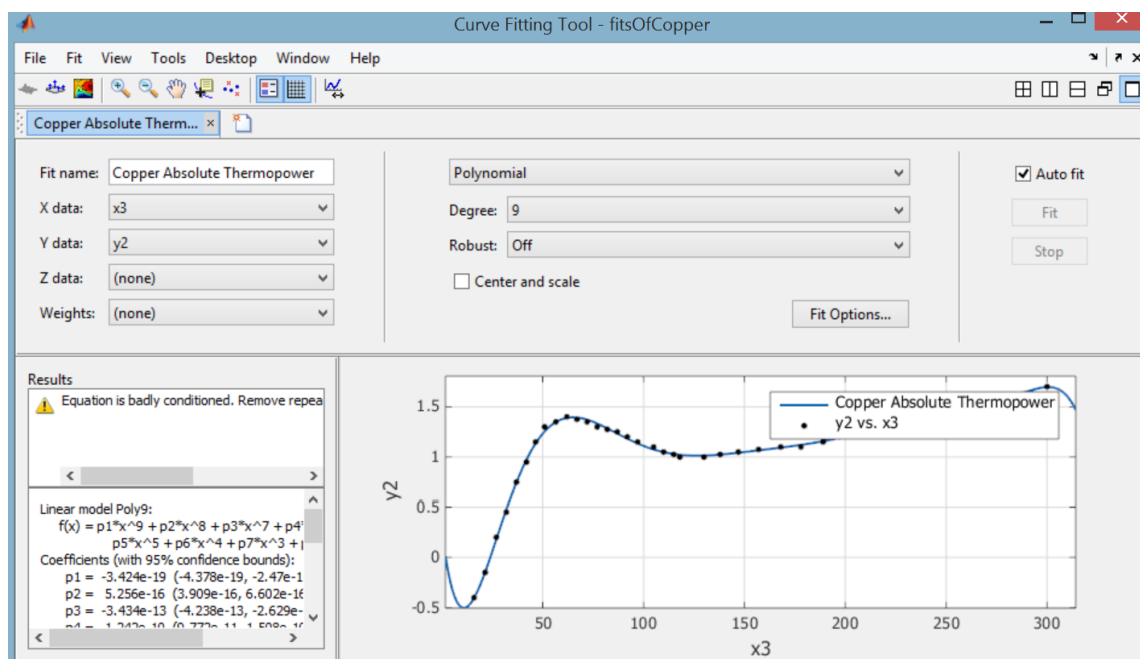
Figure 6 Fitting of Copper Data (, y: Thermopower uV/K, x: Temperature K)

Fitting equations were created for each curve. The difference between the fitting equations on figure 5 and figure 6 was used to model the absolute thermopower. The computation made on matlab explains it.

Figure 7 Computation for Seebeck Voltage created for connecting 25 pairs of bismuth and antimony

Reference for this section:
The Seebeck Coefficient of Bismuth Single Crystals, B.S. Chandrasekhar (1959)
Seebeck effect in heavy rare earth single crystals, P40, Larry Robert Sill (1964)
The Seebeck Coefficient and the Fermi Surface of Antimony Single Crystals, G.A. Saunders and O. Oktu (1967)

3. Free Electron Gas Model

This model includes both free electron assumption and independent electron assumption. That means we assume no electron-ion and electron-electron interactions. With this simple model, the relationship between seebeck effect and temperature is sought.

3.1 Drude Theory

In 1900, Paul Drude applied the Boltzmann's kinetic theory of free gases to study the motion within a metal. There are three main assumptions regarding the Drude Theory.

1. Electrons have a scattering time τ. The probability of scattering within a time interval dt is dt/τ.
2. Electron returns to momentum $\mathbf{p} = 0$ after scattering ($\mathbf{p}$ as a vector so on average, it vanishes)
3. In between scattering events, the electrons are subjected to Lorentz force.

So the expectation of $\mathbf{p}$ after dt can be written as:

$$< \boldsymbol{p}(t + dt) > = \left(1 - \frac{dt}{\tau}\right)(\boldsymbol{p}(t) + \boldsymbol{F}dt) + \boldsymbol{0}dt$$

$\mathbf{F}$ is the Lorentz force which is $-e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$. $(1-dt/\tau)$ is the probability that the electron is not scattered so that the resultant momentum changed by the Lorentz Force. If the electron is scattered (with probability dt/τ), the resultant momentum is $\mathbf{0}$ (with assumption 2). The term with dt^2 is dropped and therefore we have,

$$\frac{d\boldsymbol{p}}{dt} = \boldsymbol{F} - \frac{\boldsymbol{p}}{\tau}$$

which is a first order differential equation with respect to $\mathbf{p}$, so we expect

$$\boldsymbol{p} = \boldsymbol{A}e^{-t/\tau}$$

where $\mathbf{A}$ is some initial value for momentum.

Under only the influence of electric field, current density can be expressed as

$$\boldsymbol{j} = -en\boldsymbol{v}$$

with e as charge of carrier, n as the charge density per unit volume of solid and $\mathbf{v}$ as the drift velocity of electron. At steady state, dp/dt is zero, so we have

$$\boldsymbol{F} = -e\boldsymbol{E} = \frac{\boldsymbol{p}}{\tau} = \frac{m\boldsymbol{v}}{\tau}$$

$$\boldsymbol{v} = -\frac{e\boldsymbol{E}\tau}{m}$$

$$\boldsymbol{j} = -\frac{e^2 n\tau}{m}\boldsymbol{E}$$

with conductivity $\sigma = -e^2 n\tau/m$.

Because electrons move only due to electric field according to Drude Model (neglected chemical potential, charge concentration), voltage difference along the metal is the electrical potential. Seebeck Coefficient is defined as the electric field created caused by temperature gradient.

$$E = Q\nabla T$$

where Q is the thermopower / Seebeck Coefficient.

Consider a one-dimensional model of metal bar. The mean electronic velocity at a point x due to the temperature gradient is

$$vq = \frac{1}{2}[v(x - v\tau) - v(x + v\tau)] = -\tau v \frac{dv}{dx} = -\tau \frac{d(\frac{v^2}{2})}{dx}$$

Generalizing to 3D we have:

$$ve = -\frac{\tau}{6}\frac{d(v^2)}{dx} = -\frac{\tau}{6}\frac{d(v^2)}{dT}\nabla T$$

For equilibrium under no current flowing, vq + ve = 0:

$$Q = -\left(\frac{1}{3e}\right)\frac{d}{dT}\left(\frac{mv^2}{2}\right) = -\frac{c_v}{3ne}$$

where c is the heat capacity for the electron gases. Classically, c is 3nk/2 where k is the Boltzmann Constant. So the value of Q:

$$Q = -\frac{k}{2e}, which\ is\ a\ constant$$

The Drude model makes no sense in explaining the seebeck effect as it is saying that the thermopower is a universal constant for any materials.

Reference of this section:
Solid States Physics, Ashcroft/Mermin, Chapter 1
The Oxford Solid State Basics, Steven H. Simon, Chapter 3

3.2 Sommerfeld Theory
Sommerfeld incorporated the Fermi Statistics into the Drude's Theory of metal.

Since we consider free electron gas, the Hamiltonian only needs not to include the potential part (which is one of the reason the Sommerfeld model does not explain well since electrons in lattice experience periodic potential). The time-independent Schrodinger Equation is:

$$-\frac{h^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(r) = \varepsilon\psi(r)$$

with periodic boundary condition,

$$\psi(x, y, z + Lz) = \psi(x, y, z)$$

$$\psi(x, y + Ly, z) = \psi(x, y, z)$$

$$\psi(x + Lx, y, z) = \psi(x, y, z)$$

where L's are the dimensions of solid.

The periodic boundary condition gives the quantum confinement of the system. That makes k, the wave vector, to be $2\pi n/L$, where n is integer for the 3 dimensions. Volume of one cell in the k-space is $8\pi^3/L$. So the k-space density is $V/8\pi^3$ where V is the volume of solid.

The Fermi Function tells us the probability of a state at certain energy being occupied by fermions (electrons).

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/kT} + 1}$$

Because of having 2-spin in one state, so the number of electrons is

$$N = 2 \int_0^\infty \frac{V}{8\pi^3} f(\varepsilon(\boldsymbol{k})) \, d\boldsymbol{k}$$

So the electron density per unit volume

$$n = \int_0^\infty \frac{f(\varepsilon(\boldsymbol{k}))}{4\pi^3} \, d\boldsymbol{k}$$

And the energy density is

$$u = \int_0^\infty \frac{f(\varepsilon(\boldsymbol{k}))}{4\pi^3} \varepsilon(\boldsymbol{k}) \, d\boldsymbol{k}$$

For free electrons, the energy is simply related to its momentum by

$$\varepsilon(\boldsymbol{k}) = \frac{\hbar^2 k^2}{2m}$$

And for large k, the volume in k-space forms a sphere, so we can rearrange the integrals in this way

$$n = \int_0^\infty \frac{f(\varepsilon(\boldsymbol{k}))}{4\pi^3} \, d\boldsymbol{k} = \int_0^\infty \frac{k^2 dk f(\varepsilon(\boldsymbol{k}))}{\pi^2} = \int_0^\infty d\varepsilon g(\varepsilon) f(\varepsilon(\boldsymbol{k}))$$

$$u = \int_0^\infty d\varepsilon g(\varepsilon) \varepsilon f(\varepsilon(\boldsymbol{k}))$$

where g(ε) is the density of states per unit volume per small interval of energy.

$$g(\varepsilon) = \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2m\varepsilon}{\hbar^2}}$$

Evaluating the integral for electron density yields

$$\mu = \varepsilon_F - \frac{\frac{\pi^2}{6}(k_B T)^2 g(\varepsilon_F)}{g'(\varepsilon_F)} = \varepsilon_F \left(1 - \frac{1}{3}\left(\frac{\pi k_B T}{2\varepsilon_F}\right)^2\right)$$

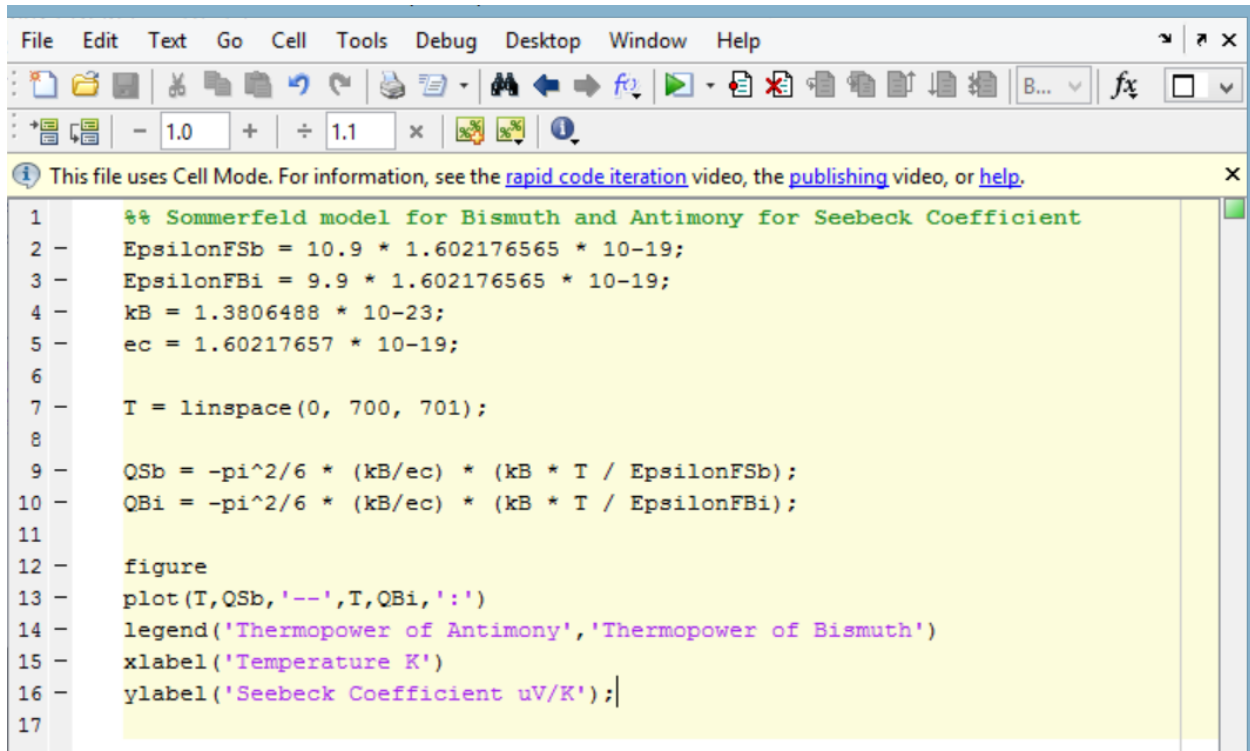And by differentiating the integral for energy density we get the specific heat of the electron gas

$$c_v = \left(\frac{\partial u}{\partial T}\right)_n = \frac{\pi^2}{3} k_B^2 T g(\varepsilon_F) = \frac{\pi^2}{2}\left(\frac{k_B T}{\varepsilon_F}\right) n k_B$$

Using this equation of specific heat for the thermopower Q considered in the Drude Model, we have

$$Q = -\frac{c_v}{3ne} = -\frac{\frac{\pi^2}{2}\left(\frac{k_B T}{\varepsilon_F}\right) n k_B}{3ne} = -\frac{\pi^2}{6}\left(\frac{k_B T}{\varepsilon_F}\right)\left(\frac{k_B}{e}\right)$$

Since the thermopower is temperature dependent now, the writer of this report applied the Sommerfeld theory to bismuth and antimony and compared the results with the experimental data in Section 2 of this report. It was found that free electron gas theory works badly for Seebeck Effect prediction.

The fermi energies ε_F of bismuth and antimony are 9.90 eV and 10.9 eV respectively. So the computation is simple to compute from the equation of Q above

```
%% Sommerfeld model for Bismuth and Antimony for Seebeck Coefficient
EpsilonFSb = 10.9 * 1.602176565 * 10-19;
EpsilonFBi = 9.9 * 1.602176565 * 10-19;
kB = 1.3806488 * 10-23;
ec = 1.60217657 * 10-19;

T = linspace(0, 700, 701);

QSb = -pi^2/6 * (kB/ec) * (kB * T / EpsilonFSb);
QBi = -pi^2/6 * (kB/ec) * (kB * T / EpsilonFBi);

figure
plot(T,QSb,'--',T,QBi,':')
legend('Thermopower of Antimony','Thermopower of Bismuth')
xlabel('Temperature K')
ylabel('Seebeck Coefficient uV/K');
```

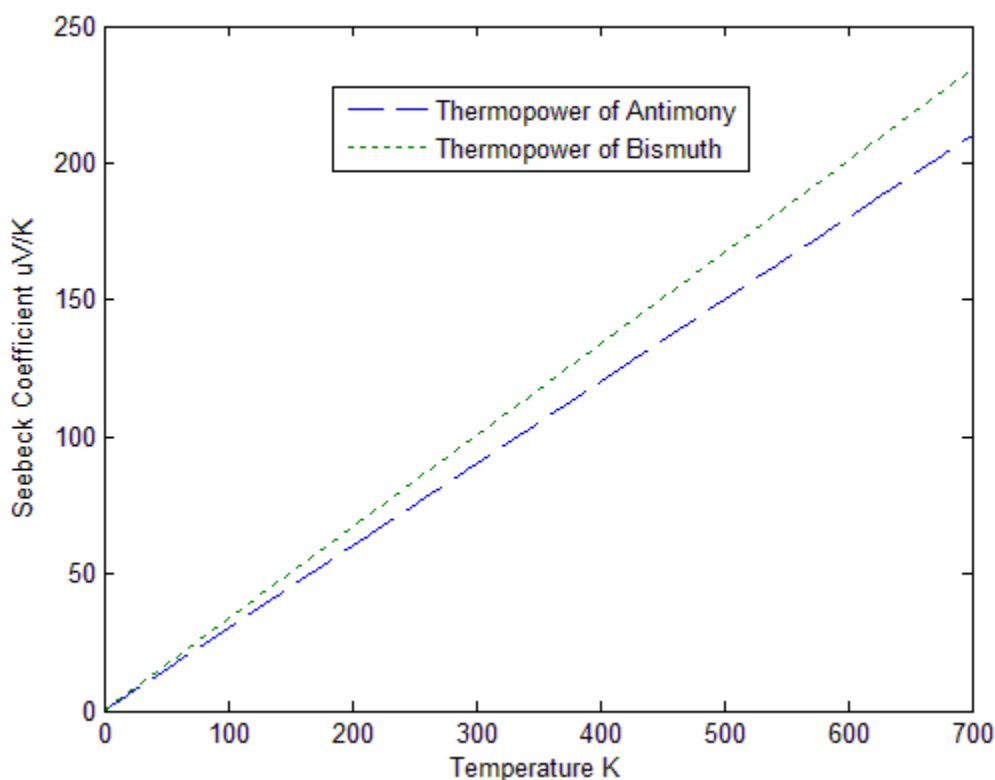*Figure 8 Computation of thermopower of Bismuth and Antimony*

Figure 9 Sommerfeld Theory prediction on thermopower of bismuth and antimony

The Sommerfeld model predicts a linear relationship between thermopower and temperature, which is not what we observed (see figure 4 and 6). Only fermi energies of metals affect the thermopowers. And this theory does not explain positivity of antimony thermopower.

Reference of this section:
Solid States Physics, Ashcroft/Mermin, Chapter 2
The Oxford Solid State Basics, Steven H. Simon, Chapter 4

4. Semi-Classical Transport Theory

The semi-classical transport theory, which is derived from Boltzmann Equation, is credible for predicting thermoelectric parameters and the theoretical derived result matches the Law of Widedemann and Franz. The derivation for the seebeck coefficient from semi-classical transport can be referenced to a passage named: *Charge and Heat Transport Properties of Electrons*. Here we extracted the part related to Seebeck Effect.

Consider an electron under a small electric field, temperature gradient, and concentration gradient along the conductor. Consider an infinitesimal point at Z. At this point, the distribution function of electrons is *f*, and the number of electrons with an energy between *E* and *E+dE* is *fD(E)dE* (where D(E) is the density of states per unit of energy, so *D(E)dE* gives the number of states within the small energy range). Since the electric field, temperature gradient and concentration gradient are small, these electrons will have almost the same probability to move toward any direction. Also because the solid angle of a sphere is 4π, the probability for an electron to move in the (*θ, φ*)

direction within a solid angle dΩ (= $\sin\theta d\theta d\phi$) will be dΩ/4π. A charge q (= -e for electrons and +e for holes) moving in the (θ, ϕ) direction within a solid angle dΩ causes a charge flux of $qv\cos\theta$ and energy flux $Ev\cos\theta$ along the conduction, where θ is defined as the angle between the velocity vector and along the conduction. Hence, the charge flux and energy flux in the Z direction carried by all electrons moving toward the entire sphere surrounding the point are respectively

$$J_z = \int_{4\pi} \frac{d\Omega}{4\pi} \int_{E=0}^{\infty} (fD(E))(qv\cos\theta)dE = \int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \int_{\theta=0}^{\pi} \sin\theta\cos\theta d\theta \int_{E=0}^{\infty} fD(E)qvdE \qquad (1a)$$

$$J_{E_z} = \int_{4\pi} \frac{d\Omega}{4\pi} \int_{E=0}^{\infty} (fD(E))(Ev\cos\theta)dE = \int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \int_{\theta=0}^{\pi} \sin\theta\cos\theta d\theta \int_{E=0}^{\infty} fD(E)EvdE \qquad (1b)$$

With the relaxation-time approximation, the Boltzmann Transport Equation for electrons take the following form:

$$\frac{\partial f}{\partial t} + \vec{v}\bullet\nabla f + q\vec{E}\bullet\frac{\partial f}{\partial \vec{p}} = \frac{f_0 - f}{\tau} \qquad (2)$$

where $q=-e$ for electrons and $+e$ for holes. For the steady state case with small temperature/concentration gradient and electric field only, the variation of the distribution function in time is much smaller than that in space, or $\frac{\partial f}{\partial t} << \vec{v}\bullet\nabla f$, so that we can assume $\frac{\partial f}{\partial t}$ ~0. The temperature gradient and electric field is small so that the deviation from equilibrium distribution f_0 is small, i.e. $f_0 - f << f_0$, so we have $\nabla f \approx \nabla f_0$, and $\frac{\partial f}{\partial \vec{p}} \approx \frac{\partial f_0}{\partial \vec{p}} = \frac{\partial f_0}{\partial E}\frac{dE}{d\vec{p}} = \vec{v}\frac{\partial f_0}{\partial E}$. With these assumptions, eqn. 2 becomes

$$\vec{v}\bullet[\nabla f_0 + q\vec{E}\frac{\partial f_0}{\partial E}] = \frac{f_0 - f}{\tau} \qquad (3)$$

The equilibrium distribution of electrons is the Fermi-Dirac distribution

$$f_0(\vec{k}) = \frac{1}{\exp(\frac{E(\vec{k}) - \mu}{k_B T}) + 1} = \frac{1}{\exp(\eta) + 1}; \ \eta \equiv \frac{E - \mu}{k_B T} \qquad (4)$$

where μ is the chemical potential that depends strongly on carrier concentration and *weakly on temperature* (See section 4.2 for the Sommerfeld theory) temperature. Both E and μ are measured from the *band edge* (e.g. E_C, for the bottom of conduction bands). This reference system essentially sets $E_C = 0$ at different locations although the absolute value of $\underline{E_C}$ measured from a global reference varies at different location as shown in Fig. 6.9b in Chen ($\mu = E_F$ in Chen, (*Nanoscale Energy Transport and Conversion: A Parallel Treatment of Electrons, Molecules, Phonons, and Photons*). In this reference system corresponding to Fig. 6.9b in Chen, the same quantum state $\vec{k}$ = (k_x, k_y, k_z) has the same energy $E(\vec{k}) = E(\vec{k}) - E_C = \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m}$ at different locations.

Hence this reference system yields the gradient $\nabla E(\vec{k}) = 0$ (the writer of this report interprets it as constant band structure), simplifying the following derivation. If we use a global reference level as our zero energy reference point as in Fig. 6.9a in Chen, the same quantum state $\vec{k} = (k_x, k_y, k_z)$ has different energy $E(\vec{k}) = \dfrac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m} + E_C$ because E_C changes with locations. In this case, $\nabla E(\vec{k}) = \nabla E_C \neq 0$, making the following derivation somewhat inconvenient. However, both reference systems will yield the same result.

From eq. 4,

$$\frac{\partial f_0}{\partial E} = \frac{df_0}{d\eta}\frac{\partial \eta}{\partial E} = \frac{df_0}{d\eta}\frac{1}{k_B T} \quad \rightarrow \quad \frac{df_0}{d\eta} = k_B T \frac{\partial f_0}{\partial E} \tag{5}$$

From eq. 5,

$$\nabla f_0 = \frac{df_0}{d\eta}\nabla \eta = k_B T \frac{\partial f_0}{\partial E}\nabla \eta \tag{6}$$

Also because $\nabla E(\vec{k}) = 0$ for the reference system that we are using, from (4)

$$\nabla \eta = \frac{1}{k_B T}(\nabla E(\vec{k}) - \nabla \mu) - \frac{E - \mu}{k_B T^2}\nabla T = -\frac{1}{k_B T}\nabla \mu - \frac{E - \mu}{k_B T^2}\nabla T \tag{7}$$

From eqs. 6-7,

$$\nabla f_0 = -\frac{\partial f_0}{\partial E}(\nabla \mu + \frac{E - \mu}{T}\nabla T) \tag{8}$$

Combine eqs. 3 and 8, we obtain

$$\vec{v} \bullet [-\nabla \mu - \frac{E - \mu}{T}\nabla T + q\vec{E}]\frac{\partial f_0}{\partial E} = \frac{f_0 - f}{\tau} \tag{9}$$

Note that

$$\vec{E} = -\nabla \varphi_e \tag{10}$$

where φ_e is the electrostatic potential (also called electrical potential, which is the potential energy per unit of charge associated with a time-invariant electric field $\vec{E}$);

From eqns. 9-10, we obtain

$$\vec{v} \bullet [-\nabla \mu - \frac{E - \mu}{T}\nabla T - q\nabla \varphi_e]\frac{\partial f_0}{\partial E} = \frac{f_0 - f}{\tau} \tag{11}$$

From eqn. 11, we obtain

$$f = f_0 - \tau \vec{v} \bullet [-\nabla \Phi - \frac{E - \mu}{T} \nabla T] \frac{\partial f_0}{\partial E} \tag{12}$$

where $\Phi = \mu + q\varphi_e$, is the <u>electrochemical potential that combines the chemical potential and electrostatic potential energy (two reasons to flow of carriers, diffusion current is the part that caused by chemical potential)</u>. Electrochemical potential is the (total) driving force for current flow, which can be caused by the gradient in either chemical potential (e.g. due to the gradient in carrier concentration) or the gradient in electrostatic potential (i.e. electric field). <u>When you measure voltage ΔV across a solid using a voltmeter, you actually measured the electrochemical potential difference $\Delta \Phi$ per unit charge between the two ends of the solid</u>, i.e. $\Delta V = \Delta \Phi / q$. If there is no temperature gradient or concentration gradient in the solid, the measured voltage equals $\Delta \varphi_e$.

In the current case all the gradients and $\vec{E}$ are in the Z direction, so from eq. 12,

$$f = f_0 - \tau v \cos \theta [-\frac{d\mu}{dZ} - \frac{E - \mu}{T} \frac{dT}{dZ} + qE_z] \frac{\partial f_0}{\partial E} = f_0 - \tau v \cos \theta [-\frac{d\Phi}{dZ} - \frac{E - \mu}{T} \frac{dT}{dZ}] \frac{\partial f_0}{\partial E} \tag{13}$$

Combine eqns. 1 and 13, we obtain the charge flux and energy flux respectively

$$J_Z = \int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \int_{\theta=0}^{\pi} \sin \theta \cos \theta d\theta \int_{E=0}^{\infty} f_0 D(E) q v dE$$

$$+ \int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \int_{\theta=0}^{\pi} \sin \theta \cos^2 \theta d\theta \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) q v^2 \tau (\frac{d\mu}{dZ} + \frac{E - \mu}{T} \frac{dT}{dZ} - qE_z) dE \tag{14a}$$

and

$$J_{E_Z} = \int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \int_{\theta=0}^{\pi} \sin \theta \cos \theta d\theta \int_{E=0}^{\infty} f_0 D(E) E v dE$$

$$+ \int_{\phi=0}^{2\pi} \frac{1}{4\pi} d\phi \int_{\theta=0}^{\pi} \sin \theta \cos^2 \theta d\theta \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E v^2 \tau (\frac{d\mu}{dZ} + \frac{E - \mu}{T} \frac{dT}{dZ} - qE_z) dE \tag{14b}$$

Note that the first term in the right hand of eqn. 14 side is zero and the second term yields

$$J_Z = \frac{1}{3} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) q v^2 \tau (\frac{d\mu}{dZ} + \frac{E - \mu}{T} \frac{dT}{dZ} - qE_z) dE \tag{15a}$$

$$J_{E_Z} = \frac{1}{3} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E v^2 \tau (\frac{d\mu}{dZ} + \frac{E - \mu}{T} \frac{dT}{dZ} - qE_z) dE \tag{15b}$$

Note that

$$E = \frac{1}{2} m v^2 \tag{16}$$

Use eqn. 16 to eliminate v in eq. 15, we obtain

$$J_z = \frac{2q}{3m}\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E\tau(\frac{d\mu}{dZ}+\frac{E-\mu}{T}\frac{dT}{dZ}-qE_z)dE$$

$$= \frac{2q}{3m}\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E\tau(\frac{d\Phi}{dZ}+\frac{E-\mu}{T}\frac{dT}{dZ})dE$$

(17a)

$$J_{E_z} = \frac{2}{3m}\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E^2\tau(\frac{d\mu}{dZ}+\frac{E-\mu}{T}\frac{dT}{dZ}-qE_z)dE$$ (17b)

The energy flux from Eq. 17b can be broken up into two terms as following

$$J_{E_z} = \frac{2}{3m}\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E^2\tau(\frac{d\mu}{dZ}+\frac{E-\mu}{T}\frac{dT}{dZ}-qE_z)dE$$

$$= \frac{2}{3m}\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E(E-\mu)\tau(\frac{d\mu}{dZ}+\frac{E-\mu}{T}\frac{dT}{dZ}-qE_z)dE$$

$$+ \mu\frac{2}{3m}\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E\tau(\frac{d\mu}{dZ}+\frac{E-\mu}{T}\frac{dT}{dZ}-qE_z)dE$$ (18)

$$= \frac{2}{3m}\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E(E-\mu)\tau(\frac{d\mu}{dZ}+\frac{E-\mu}{T}\frac{dT}{dZ}-qE_z)dE + \frac{\mu J_z}{q}$$

$$= \frac{2}{3m}\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E(E-\mu)\tau(\frac{d\Phi}{dZ}+\frac{E-\mu}{T}\frac{dT}{dZ})dE + \frac{\mu J_z}{q}$$

where J_z is the current density or charge flux given by eq. 17a. At temperature $T = 0$ K, the first term in the right hand side of eq. 18 is zero, so that the energy flux at $T = 0$ K is

$$J_{E_z}(T=0K) = \frac{\mu J_z}{q}$$ (19)

Because electrons don't carry any thermal energy at $T = 0$ K, the thermal energy flux or heat flux carried by the electrons at $T \neq 0$ is

$$J_{q_z}(T) = J_{E_z}(T) - J_{E_z}(T=0)$$

$$= \frac{2}{3m}\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E(E-\mu)\tau(\frac{d\Phi}{dZ}+\frac{E-\mu}{T}\frac{dT}{dZ})dE$$ (20)

Equations 17a and 20 can be rearranged as

$$J_z = L_{11}(-\frac{1}{q}\frac{d\Phi}{dZ})+L_{12}(-\frac{dT}{dZ})$$ (21a)

$$J_{q_z} = L_{21}(-\frac{1}{q}\frac{d\Phi}{dZ})+L_{22}(-\frac{dT}{dZ})$$ (21b)

where

$$L_{11} = -\frac{2q^2}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E \tau dE \tag{22a}$$

$$L_{12} = -\frac{2q}{3mT} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E (E - \mu) \tau dE \tag{22b}$$

$$L_{21} = -\frac{2q}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E (E - \mu) \tau dE = TL_{12} \tag{22c}$$

$$L_{22} = -\frac{2}{3mT} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E (E - \mu)^2 \tau dE \tag{22d}$$

Writer of this report remarks that this is the Onsager Relation (Coupled Current Equation).

Electrical conductivity:

In the case of zero temperature gradient and zero chemical potential, $\frac{dT}{dZ} = 0$ and $\frac{d\mu}{dZ} = 0$, eqn. 21a becomes

$$J_z = L_{11}(-\frac{1}{q}\frac{d\Phi}{dZ}) = L_{11}(-\frac{1}{q}\frac{d\mu}{dZ} + E_z) = L_{11}E_z \tag{23}$$

The electrical conductivity is defined as

$$\sigma \equiv \frac{J_z}{E_z} = L_{11} = -\frac{2q^2}{3m} \int_{E=0}^{\infty} \frac{\partial f_0}{\partial E} D(E) E \tau dE \tag{24}$$

Equation 24 will be simplified further in the following section on Wiedemann-Franz law.

Seebeck Coefficient:

In the case of non-zero temperature gradient along the Z direction (along the conductor), a thermoelectric voltage can be measured between the two ends of the solid with an open loop electrometer, i.e. $J_Z = 0$ (Seebeck voltage is measured when there is not electrical flow). Hence from eq. 21a we obtain

$$J_z = L_{11}(-\frac{1}{q}\frac{d\Phi}{dZ}) + L_{12}(-\frac{dT}{dZ}) = 0 \tag{25}$$

Therefore

$$\frac{\left(\dfrac{d\Phi}{dZ}\right)}{\left(\dfrac{dT}{dZ}\right)} = -\frac{qL_{12}}{L_{11}} \tag{26}$$

As discussed above, the voltage that the electrometer measure between the two ends of the solid is $\Delta V = \Delta\Phi / q$. Similarly, $dV = d\Phi / q$. The Seebeck coefficient is defined as the ratio between the voltage gradient and the temperature gradient for an open loop configuration with zero net current flow

$$S = -\frac{\left(\dfrac{dV}{dZ}\right)}{\left(\dfrac{dT}{dZ}\right)} = -\frac{1}{q}\frac{\left(\dfrac{d\Phi}{dZ}\right)}{\left(\dfrac{dT}{dZ}\right)} = \frac{L_{12}}{L_{11}} = \frac{1}{qT}\left(\frac{\displaystyle\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E(E-\mu)\tau dE}{\displaystyle\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E\tau dE}\right)$$

$$= -\frac{1}{qT}\left(\mu - \frac{\displaystyle\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E^2\tau dE}{\displaystyle\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E\tau dE}\right)$$

(27)

Combine eq. 27, 24, and 21 a, we can write $J_z = \sigma(-\frac{1}{q}\frac{d\Phi}{dZ}) + \sigma S(-\frac{dT}{dZ})$

The scattering mean free time depends on the energy, and we can assume

$$\tau = \tau_0 E^r$$

(28)

where τ_0 is a constant independent of E.

When E is measured from the band edge for either electrons or holes, the density of states

$$D(E) = \frac{(2m)^{3/2}}{2\pi^2\hbar^3}E^{1/2}$$

(29)

Combine eqns. 27 & 29

$$S = -\frac{1}{qT}\left(\mu - \frac{\displaystyle\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E^2\tau dE}{\displaystyle\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}D(E)E\tau dE}\right) = -\frac{1}{qT}\left(\mu - \frac{\displaystyle\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}E^{2+r+1/2}dE}{\displaystyle\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}E^{1+r+1/2}dE}\right)$$

(30)

The integrals in Eq. 30 can be simplified using the product rule

$$\int_{E=0}^{\infty}\frac{\partial f_0}{\partial E}E^s dE = f_0 E^s\Big|_0^{\infty} - s\int_{E=0}^{\infty}f_0 E^{s-1}dE = -s\int_{E=0}^{\infty}f_0 E^{s-1}dE$$

(31)

Using eq. 31 to reduce eq. 30 to

$$S = -\frac{1}{qT}\left(\mu - \frac{(r+5/2)\int\limits_{E=0}^{\infty} f_0 E^{r+3/2}dE}{(r+3/2)\int\limits_{E=0}^{\infty} f_0 E^{r+1/2}dE}\right) \tag{32}$$

The two integrals in eq. 32 can be simplified with the reduced energy $\zeta = E/k_{BT}$

$$\int\limits_{E=0}^{\infty} f_0(E,\mu)E^n dE = (k_B T)^{n+1}\int\limits_{0}^{\infty} f_0(\zeta,\eta)\zeta^n d\zeta = (k_B T)^{n+1}F_n(\eta); \quad \eta = \mu/k_B T \tag{33}$$

where the Fermi-Dirac integral is defined as

$$F_n(\eta) = \int\limits_{0}^{\infty} f_0(\zeta,\eta)\zeta^n d\zeta \tag{34}$$

Use Eq. 33 to reduce eq. 32 to

$$S = -\frac{1}{qT}\left(\mu - k_B T \frac{\left(r+\frac{5}{2}\right)F_{r+3/2}(\eta)}{\left(r+\frac{3}{2}\right)F_{r+1/2}(\eta)}\right) = -\frac{k_B}{q}\left(\eta - \frac{\left(r+\frac{5}{2}\right)F_{r+3/2}(\eta)}{\left(r+\frac{3}{2}\right)F_{r+1/2}(\eta)}\right) \tag{35}$$

Seebeck coefficient for metals:

For metals with $\eta = \mu/k_B T \gg 0$, the Fermi-Dirac integral can be expressed in the form of a rapidly converging series

$$\begin{aligned}
F_n(\eta) &= \int\limits_{0}^{\infty} f_0 \zeta^n d\zeta = -\frac{1}{n+1}\int\limits_{0}^{\infty} \frac{\partial f_0}{\partial \zeta}\zeta^{n+1}d\zeta \\
&= -\frac{1}{n+1}\int\limits_{0}^{\infty} \frac{\partial f_0}{\partial \zeta}\left(\eta^{n+1} + \sum_{m=1}^{\infty} \frac{d^m(\zeta^{n+1})}{d\zeta^m}\bigg|_{\zeta=\eta} \frac{(\zeta-\eta)^m}{m!}\right)d\zeta \\
&= -\frac{1}{n+1}\int\limits_{0}^{\infty} \frac{\partial f_0}{\partial \zeta}\left(\eta^{n+1} + (n+1)\eta^n(\zeta-\eta) + (n+1)n\eta^{n-1}\frac{(\zeta-\eta)^2}{2} + ...\right)d\zeta \\
&= \frac{\eta^{n+1}}{n+1} + n\eta^{n-1}\frac{\pi^2}{6} + ...
\end{aligned} \tag{36}$$

If we use only the first two terms of eq. 36 to express the two Fermi-Dirac integrals in eq. 35, we obtain the following ($q = -e$ for electrons in metals)

$$S = -\frac{k_B}{q}\left(\eta - \frac{\left(r+\frac{5}{2}\right)F_{r+3/2}(\eta)}{\left(r+\frac{3}{2}\right)F_{r+1/2}(\eta)}\right) = \frac{k_B}{e}\left(\frac{\eta\left(r+\frac{3}{2}\right)F_{r+1/2}(\eta) - \left(r+\frac{5}{2}\right)F_{r+3/2}(\eta)}{\left(r+\frac{3}{2}\right)F_{r+1/2}(\eta)}\right)$$

$$= \frac{k_B}{e}\left(\frac{\eta\left(r+\frac{3}{2}\right)\left(\frac{\eta^{r+3/2}}{r+\frac{3}{2}} + \left(r+\frac{1}{2}\right)\eta^{r-1/2}\frac{\pi^2}{6}\right) - \left(r+\frac{5}{2}\right)\left(\frac{\eta^{r+5/2}}{r+\frac{5}{2}} + \left(r+\frac{3}{2}\right)\eta^{r+1/2}\frac{\pi^2}{6}\right)}{\left(r+\frac{3}{2}\right)\frac{\eta^{r+3/2}}{r+\frac{3}{2}}}\right) \quad (37)$$

$$= -\frac{\pi^2 k_B}{3e}\left(\frac{k_B T}{\mu}\right)\left(\frac{3}{2} + r\right)$$

Note that this is the Mott Expression for seebeck coefficient of metals.

This value can be either positive or negative depending on r, or how the scattering rate depends on electron energy. We can ignore the weak temperature dependence of μ and assume $\mu = E_F$, the Fermi level that is the highest energy occupied by electrons at 0 K in a metal.

To apply the theory of semiclassical transport, the band structure of bismuth and antimony need to be obtained. Scattering data (form factor) and crystal structure need to be understood in advance to that. The writer of this report will put it in another document for detailed analysis

Reference of this section:
Charge and Heat Transport Properties of Electrons, Li Shi, University of Texas at Austin