Thermoelectric currents

Thermoelectric effects

$$f(\vec{k},\vec{r}) \approx f_0(\vec{k},\vec{r}) - \frac{\tau(\vec{k})}{\hbar}\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k})\cdot\left(\nabla_{\vec{r}}\tilde{\mu} + \frac{E(\vec{k})-\mu}{T}\nabla_{\vec{r}}T + \frac{e}{\hbar}\nabla_{\vec{k}}E(\vec{k})\times\vec{B}\right)$$

$$v(\vec{k}) = \frac{\nabla_{\vec{k}}E(\vec{k})}{\hbar}$$

Electrical current: $$\vec{j}_{elec} = \frac{-e}{4\pi^3}\int v(\vec{k})f(\vec{k})d^3k$$

Particle current: $$\vec{j}_n = \frac{1}{4\pi^3}\int v(\vec{k})f(\vec{k})d^3k$$

Energy current: $$\vec{j}_E = \frac{1}{4\pi^3}\int v(\vec{k})E(\vec{k})f(\vec{k})d^3k$$

Heat current: $$\vec{j}_Q = \frac{1}{4\pi^3}\int v(\vec{k})\left(E(\vec{k})-\mu\right)f(\vec{k})d^3k$$

Thermal conductivity

The electrons carry heat as well as charge.

$$\vec{j}_Q = -\frac{1}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\left(E(\vec{k})-\mu\right)\nabla_{\vec{k}}E(\vec{k})\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(\frac{E(\vec{k})-\mu}{T}\nabla_{\vec{r}}T\right)\right)d^3k.$$

Generally, the relationship between the thermal current density and the temperature gradient is described by the thermal conductivity matrix,

$$\begin{bmatrix} j_{Qx} \\ j_{Qy} \\ j_{Qz} \end{bmatrix} = -\begin{bmatrix} K_{xx} & K_{xy} & K_{xz} \\ K_{yx} & K_{yy} & K_{yz} \\ K_{zx} & K_{zy} & K_{zz} \end{bmatrix}\begin{bmatrix} \frac{\partial T}{\partial x} \\ \frac{\partial T}{\partial y} \\ \frac{\partial T}{\partial z} \end{bmatrix}.$$

The thermal conductivity matrix can be calculated from the dispersion relation as,

$$K_{ij} = \frac{1}{4\pi^3\hbar^2 T}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\left(E(\vec{k})-\mu\right)\nabla_{\vec{k}}E(\vec{k})\cdot\hat{e}_i\left(E(\vec{k})-\mu\right)\nabla_{\vec{k}}E(\vec{k})\cdot\hat{e}_j d^3k.$$

Here $\hat{e}_i$ are the unit vectors $i=[x,y,z]$. For cubic crystals the thermal conductivity is a constant,

$$K = \frac{1}{4\pi^3\hbar^2 T}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\left(\left(E(\vec{k})-\mu\right)\nabla_{\vec{k}}E(\vec{k})\cdot\hat{z}\right)^2 d^3k.$$

Thermal conductivity

For a free electron gas $E(\vec{k}) = \frac{\hbar^2 k^2}{2m^*}$

$$K = \frac{1}{4\pi^3\hbar^2 T}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\left(\left(E(\vec{k})-\mu\right)\nabla_{\vec{k}}E(\vec{k})\cdot\hat{z}\right)^2 d^3k.$$

(Similar calculation as before, See notes)

The electrical contribution to the thermal conductivity in the free electron model is,

$$K = \frac{\pi^2 \tau n k_B^2 T}{3m^*}.$$

Free-electron model: Wiedemann–Franz law

$$\frac{K}{\sigma} = LT.$$

Here K is the electrical component of the thermal conductivity, σ is the thermal conductivity, T is the absolute temperature, and L is the Lorentz number. For the free-electron model, the electrical and thermal conductivities are,

$$\sigma = \frac{ne^2\tau}{m^*} \qquad K = \frac{\pi^2 \tau n k_B^2 T}{3m^*}.$$

The Lorentz number for free electrons is,

$$L = \frac{\pi^2 k_B^2}{3e^2} = 2.44 \times 10^{-8}\,\mathrm{W}\,\Omega\,\mathrm{K}^{-2}.$$

Generally, both K and σ are matrices so when the crystal does not have a high symmetry, the general relationship between them would be described by a fourth-rank tensor.

Thermoelectric current

A temperature gradient can cause a current to flow along a wire. The electrons move from the hot side to the cold side. Both charge and energy are transported in this case. The general expression for the electric current density is,

$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k})\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(\nabla_{\vec{r}}\tilde{\mu} + \frac{E(\vec{k})-\mu}{T}\nabla_{\vec{r}}T\right)\right)d^3k.$$

One end of the wire is grounded an the other is attached to an ammeter which is then also grounded. There is no voltage drop across a perfect ammeter so the gradient of the electrochemical potential is zero. The thermoelectric current produced by this temperature gradient is,

$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k})\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(\frac{E(\vec{k})-\mu}{T}\nabla_{\vec{r}}T\right)\right)d^3k.$$

Thermoelectric current

$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k})\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(\frac{E(\vec{k})-\mu}{T}\nabla_{\vec{r}}T\right)\right)d^3k.$$

The relationship between the electrical current density and the temperature gradient can be written as a matrix,

$$\begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix} = \begin{bmatrix} \kappa_{xx} & \kappa_{xy} & \kappa_{xz} \\ \kappa_{yx} & \kappa_{yy} & \kappa_{yz} \\ \kappa_{zx} & \kappa_{zy} & \kappa_{zz} \end{bmatrix} \begin{bmatrix} \frac{\partial T}{\partial x} \\ \frac{\partial T}{\partial y} \\ \frac{\partial T}{\partial z} \end{bmatrix}.$$

The thermoelectric coefficients

$$\kappa_{ij} = \frac{e}{4\pi^3\hbar^2 T}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k})\cdot\hat{e}_i\left(E(\vec{k})-\mu\right)\nabla_{\vec{k}}E(\vec{k})\cdot\hat{e}_j d^3k.$$

Here $\hat{e}_i$ are the unit vectors $i = [x, y, z]$. For cubic crystals the thermal coefficient is a constant,

$$\kappa = \frac{e}{4\pi^3\hbar^2 T}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\left(E(\vec{k})-\mu\right)\left(\nabla_{\vec{k}}E(\vec{k})\cdot\hat{z}\right)^2 d^3k.$$

Thermoelectric current

For a free electron gas $E(\vec{k}) = \frac{\hbar^2 k^2}{2m^*}$

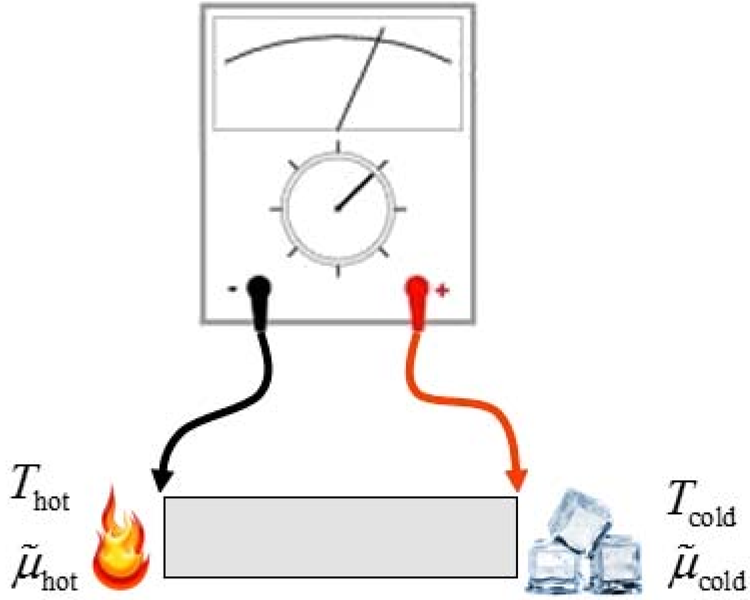
$$\kappa = \frac{e}{3\pi^2 T} \int_0^\infty \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \left(E(\vec{k}) - \mu \right) \left| \vec{v}_{\vec{k}} \right|^2 k^2 dk.$$

(Similar calculation as before, See notes)

$$\kappa = \frac{\ln(2) e k_B \tau n}{m^*}$$

Seebeck effect

$$\nabla_{\vec{r}}\tilde{\mu} = -eS\nabla_{\vec{r}}T$$



$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k})\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(\nabla_{\vec{r}}\tilde{\mu} + \frac{E(\vec{k})-\mu}{T}\nabla_{\vec{r}}T\right)\right)d^3k.$$

$$\vec{j}_{\text{elec}} = 0$$

Seebeck effect

$$\nabla_{\vec{r}}\tilde{\mu} = -eS\nabla_{\vec{r}}T$$

$$0 = \frac{e}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k})\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(\nabla_{\vec{r}}\tilde{\mu} + \frac{E(\vec{k})-\mu}{T}\nabla_{\vec{r}}T\right)\right)d^3k.$$

$$\begin{bmatrix} \frac{\partial\tilde{\mu}}{\partial x} \\ \frac{\partial\tilde{\mu}}{\partial y} \\ \frac{\partial\tilde{\mu}}{\partial z} \end{bmatrix} = -e\begin{bmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{zy} & S_{zz} \end{bmatrix}\begin{bmatrix} \frac{\partial T}{\partial x} \\ \frac{\partial T}{\partial y} \\ \frac{\partial T}{\partial z} \end{bmatrix}$$

$$0 = \frac{e}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k})\cdot\hat{e}_i\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(\begin{pmatrix} -eS_{xj} \\ -eS_{yj} \\ -eS_{zj} \end{pmatrix} + \frac{E(\vec{k})-\mu}{T}\right)\hat{e}_j\right)d^3k.$$

Solve by guessing S and integrating then iterating.

Seebeck effect

For cubic crystals, S is a constant

$$0 = \frac{e}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k})\cdot\hat{z}\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(-eS+\frac{E(\vec{k})-\mu}{T}\right)\hat{z}\right)d^3k.$$

S can be written as the ratio of two integrals

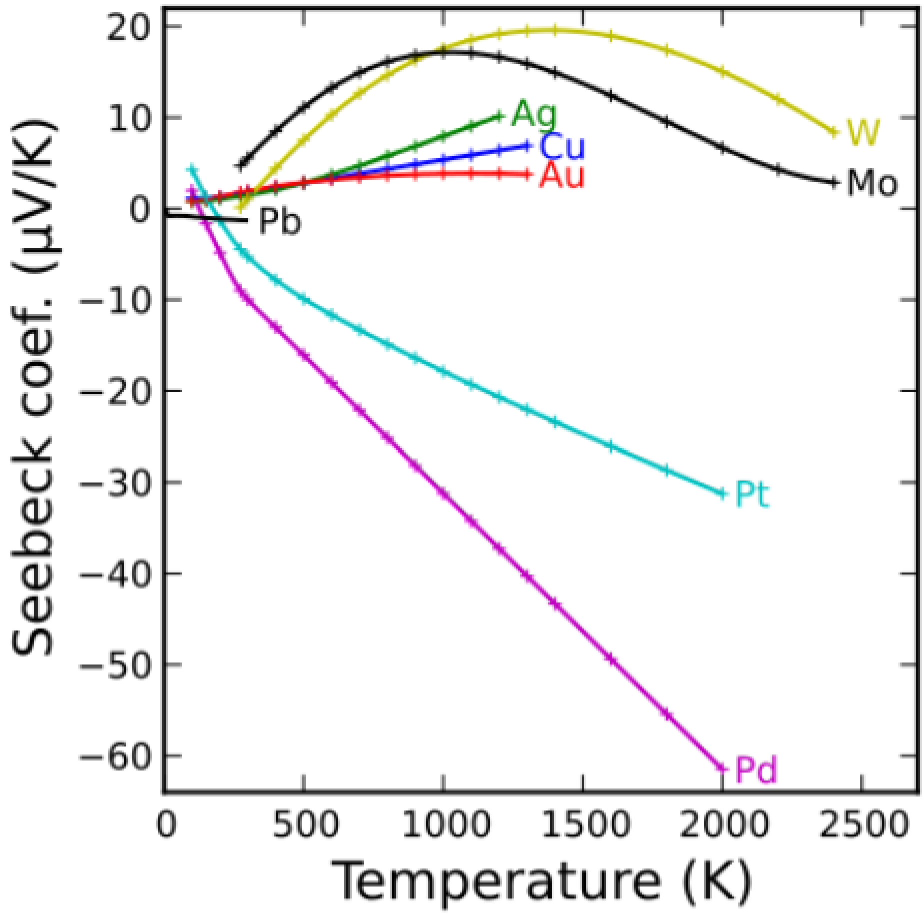
$$eS = -\frac{\overbrace{\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k})\cdot\hat{z}\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(\frac{E(\vec{k})-\mu}{T}\right)\hat{z}\right)d^3k}^{\kappa}}{\underbrace{\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k})\cdot\hat{z}\left(\nabla_{\vec{k}}E(\vec{k})\cdot\hat{z}\right)d^3k}_{\sigma}}.$$

$$\sigma S = -\kappa$$

For the free electron model

$$S = -\frac{\ln(2)k_B}{e} \approx -60\,\mu\mathrm{V/K}$$

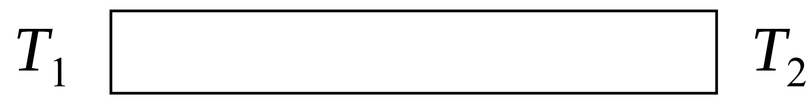
Seebeck effect



https://en.wikipedia.org/wiki/Seebeck_coefficient

For the free electron model: $$S = -\frac{\ln(2) k_B}{e} \approx -60\,\mu\mathrm{V/K}$$

Thermal conductivity again



Open boundary conditions

A heat current will also flow in this case. The expression for the heat current is,

$$\vec{j}_Q = -\frac{1}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\left(E(\vec{k})-\mu\right)\nabla_{\vec{k}}E(\vec{k})\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(\nabla_{\vec{r}}\tilde{\mu}+\frac{E(\vec{k})-\mu}{T}\nabla_{\vec{r}}T\right)\right)d^3k.$$

In this experiment, the electrochemical potential and the temperature gradient are related by $\nabla_{\vec{r}}\tilde{\mu} = -eS\nabla_{\vec{r}}T$ so this is inserted into the expression for the heat current.

$$\vec{j}_Q = -\frac{1}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\left(E(\vec{k})-\mu\right)\nabla_{\vec{k}}E(\vec{k})\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(-eS\nabla_{\vec{r}}T+\frac{E(\vec{k})-\mu}{T}\nabla_{\vec{r}}T\right)\right)d^3k$$

The thermal conductivity in this case is,

$$K_{ij} = -\frac{1}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\left(E(\vec{k})-\mu\right)\nabla_{\vec{k}}E(\vec{k})\cdot\hat{e}_i\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(-eS\hat{e}_j+\frac{E(\vec{k})-\mu}{T}\hat{e}_j\right)\right)d^3k$$

new term

Thermoelectric effects

Seebeck effect:
A thermal gradient causes a thermal current to flow. This results in a voltage which sends the low entropy charge carriers back to the hot end.

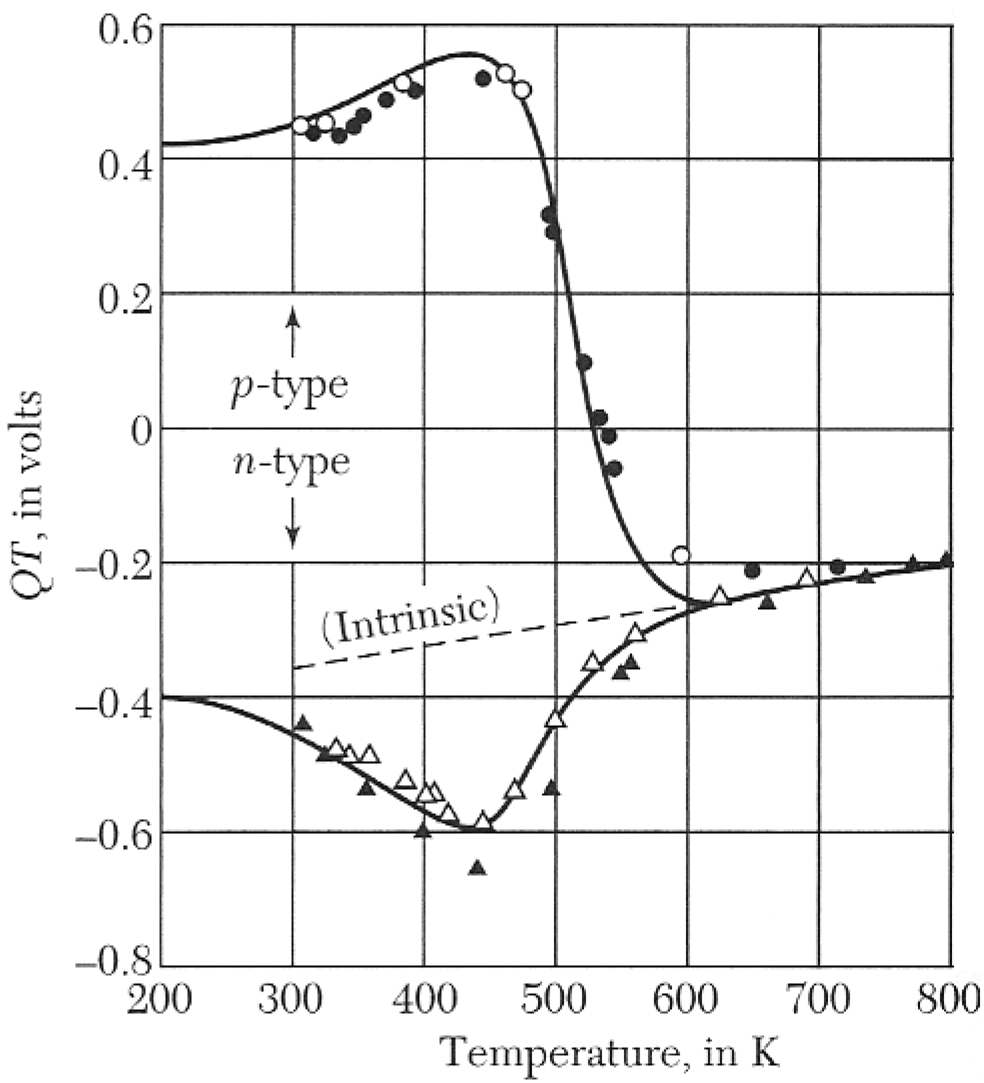
$$\nabla_{\vec{r}}\tilde{\mu} = -eS\nabla_{\vec{r}}T$$

S is the absolute thermal power (often also called *Q*). The sign of the voltage (electrochemical potential, electromotive force) is the same as the sign of the charge carriers.

The Seebeck effect can be used to make a thermometer. The gradient of the temperature is the same along both wires but the gradient in electrochemical potential differs.

Thermocouple

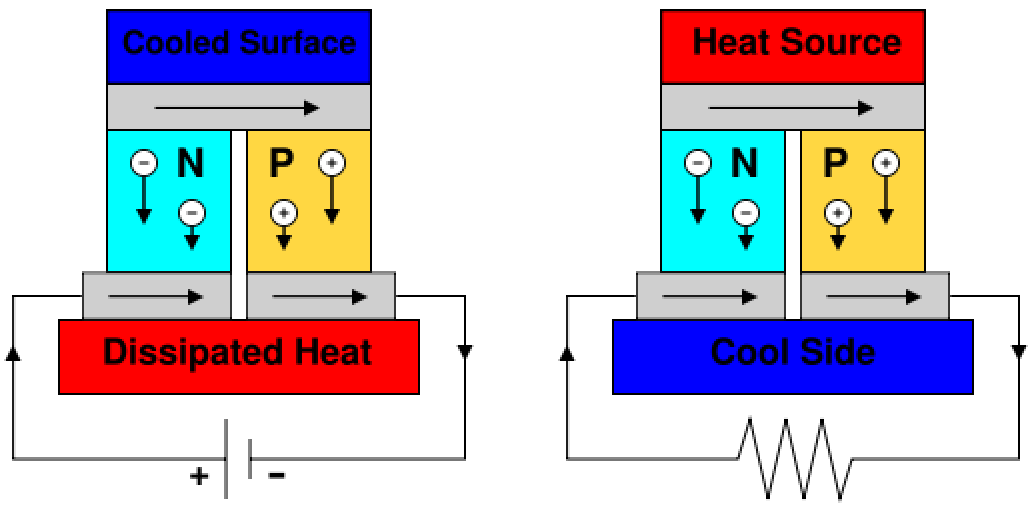
Thermoelectric effects



Intrinsic Q is negative because electrons have a higher mobility.

Thermoelectric effects

Peltier effect: driving a through a bimetallic junction causes heating or cooling.



Cooling takes place when the electrons make a transition from low entropy to high entropy at the junction.

Bismuth chalcogenides Bi_2Te_3 and Bi_2Se_3

http://en.wikipedia.org/wiki/Peltier_effect#Peltier_effect

Hall effect

$$f(\vec{k},\vec{r}) \approx f_0(\vec{k},\vec{r}) - \frac{\tau(\vec{k})}{\hbar}\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k}) \cdot \left(e\vec{E} + \nabla_{\vec{r}}\mu + \frac{E(\vec{k})-\mu}{T}\nabla_{\vec{r}}T + \frac{e}{\hbar}\nabla_{\vec{k}}E(\vec{k}) \times \vec{B} \right).$$

$$\nabla_{\vec{k}}E(\vec{k}) \cdot \left(\nabla_{\vec{k}}E(\vec{k}) \times \vec{B} \right) = 0$$

Need to go beyond the linear expansion in B.

$$R_{lmn} = \frac{E_l}{j_{em}B_n}$$

Nerst effect

Nerst effect: Apply a temperature gradient in a magnetic field and measure the voltage perpendicular to both the temperature gradient and the magnetic field.

$$N_{lmn} = \frac{E_l}{B_m \nabla T_n}$$

Ettingshausen effect: Apply a temperature gradient in a magnetic field and measure the current that flows perpendicular to both the temperature gradient and the magnetic field.

Annalen der Physik, vol. 265, pp. 343–347, 1886

http://dx.doi.org/10.1002/andp.18862651010

IX. *Ueber das Auftreten electromotorischer Kräfte in Metallplatten, welche von einem Wärmestrome durchflossen werden und sich im magnetischen Felde befinden;*

von A. v. Ettingshausen und stud. W. Nernst.

(Aus d. Anz. d. k. Acad. d. Wiss. in Wien, mitgetheilt von den Herren Verf.)

Bei Gelegenheit der Beobachtung des Hall'schen Phänomens im Wismuth wurden wir durch gewisse Unregelmässigkeiten veranlasst, folgenden Versuch anzustellen.

Eine rechteckige Wismuthplatte, etwa 5 cm lang, 4 cm breit, 2 mm dick, mit zwei an den längeren Seiten einander gegenüber liegenden Electroden versehen, ist in das Feld eines Electromagnets gebracht, sodass die Kraftlinien die Ebene der Platte senkrecht schneiden; dieselbe wird durch federnde Kupferbleche getragen, in welche sie an den kürzeren Seiten eingeklemmt ist, jedoch geschützt vor directer metallischer Berührung mit dem Kupfer durch zwischengelegte Glimmerblätter.

Boltzmann Group

Albert von Ettingshausen, Prof. at TU Graz.

Nernst was a student of Boltzmann and von Ettingshausen. He won the 1920 Nobel prize in Chemistry.

(Standing, from the left) Walther Nernst, Heinrich Streintz, Svante Arrhenius, Hiecke, (sitting, from the left) Aulinger, Albert von Ettingshausen, Ludwig Boltzmann, Ignacij Klemencic, Hausmanninger (1887).

Thermoelectric effects

$$f(\vec{k},\vec{r}) \approx f_0(\vec{k},\vec{r}) - \frac{\tau(\vec{k})}{\hbar}\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k}) \cdot \left(\nabla_{\vec{r}}\tilde{\mu} + \frac{E(\vec{k})-\mu}{T}\nabla_{\vec{r}}T + \frac{e}{\hbar}\nabla_{\vec{k}}E(\vec{k}) \times \vec{B}\right)$$

Electrical current: $\vec{j}_{elec} = \frac{-e}{4\pi^3}\int v(\vec{k})f(\vec{k})d^3k$

Particle current: $\vec{j}_n = \frac{1}{4\pi^3}\int v(\vec{k})f(\vec{k})d^3k$

Energy current: $\vec{j}_E = \frac{1}{4\pi^3}\int v(\vec{k})E(\vec{k})f(\vec{k})d^3k$

Heat current: $\vec{j}_Q = \frac{1}{4\pi^3}\int v(\vec{k})\left(E(\vec{k})-\mu\right)f(\vec{k})d^3k$

Thermoelectric effects

Electrical conductivity:	$\sigma_{mn} = \dfrac{j_{em}}{E_n}$	$\nabla T = 0, \vec{B} = 0$
Thermal conductivity:	$\kappa_{mn} = \dfrac{-j_{Qm}}{\nabla T_n}$	$\vec{B} = 0$
Peltier coefficient:	$\Pi_{mn} = \dfrac{j_{Qm}}{j_{en}}$	$\nabla T = 0, \vec{B} = 0$
Thermopower (Seebeck effect):	$S_{mn} = \dfrac{-\nabla \tilde{\mu}_m}{\nabla T_n}$	$\vec{j}_e = 0, \vec{B} = 0$
Hall effect:	$R_{lmn} = \dfrac{E_l}{j_{em} B_n}$	$\nabla T = 0, j_{el} = 0$
Nerst effect:	$N_{lmn} = \dfrac{E_l}{B_m \nabla T_n}$	$j_{elec} = 0$

Phonon transport

$\mu = 0$

$$\vec{j}_Q(\vec{r}) = \vec{j}_E(\vec{r}) = \sum_p \int D(\vec{k},p)E(\vec{k},p)\vec{v}_g(\vec{k},p)f(\vec{k},\vec{r},p)d^3k.$$

$$\frac{\partial f}{\partial t} = -\frac{1}{\hbar}\vec{F}_{\text{ext}} \cdot \nabla_{\vec{k}} f - \vec{v}_g \cdot \nabla_{\vec{r}} f + \left.\frac{\partial f}{\partial t}\right|_{collisions}$$

$$\frac{\partial f}{\partial t} + \vec{v}_g \cdot \nabla_{\vec{r}} f = \frac{f_{BE} - f}{\tau}$$

$$f(\vec{k},\vec{r},p) \approx f_{BE} - \frac{\tau}{\hbar}\,\frac{E\,\exp\left(\frac{E}{k_B T}\right)}{k_B T^2}\,f_{BE}^2 \nabla_{\vec{k}} E \cdot \nabla_{\vec{r}} T.$$

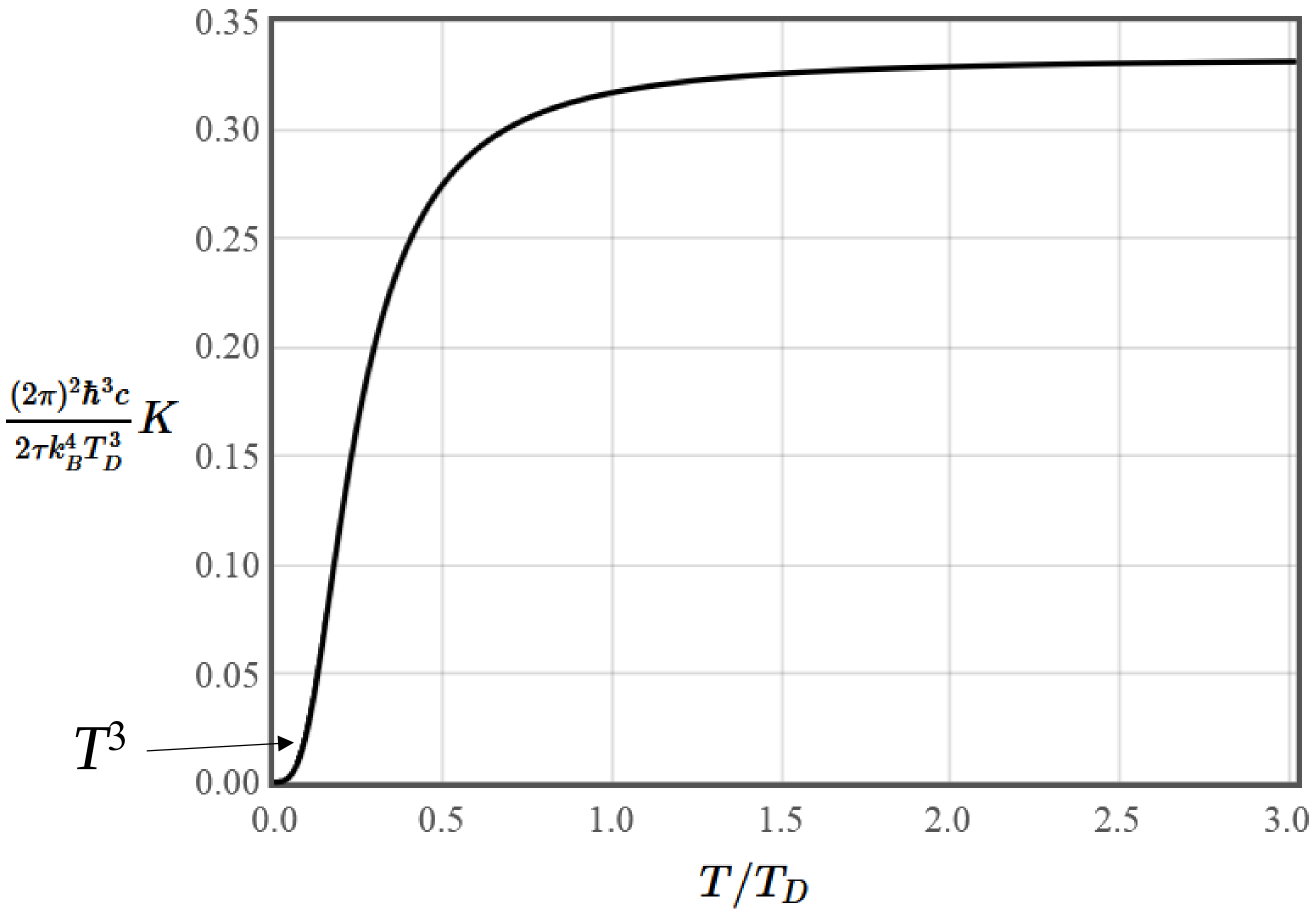
Phonon transport

$$\vec{j}_Q(\vec{r}) = -\sum_p \int \frac{\tau}{(2\pi)^3\hbar^2} \frac{E^2 \exp\left(\frac{E}{k_B T}\right)}{k_B T^2} f_{BE}^2 \nabla_{\vec{k}} E \cdot \nabla_{\vec{r}} T \nabla_{\vec{k}} E d^3 k.$$

$$\vec{j}_Q(\vec{r}) = -K\nabla T$$

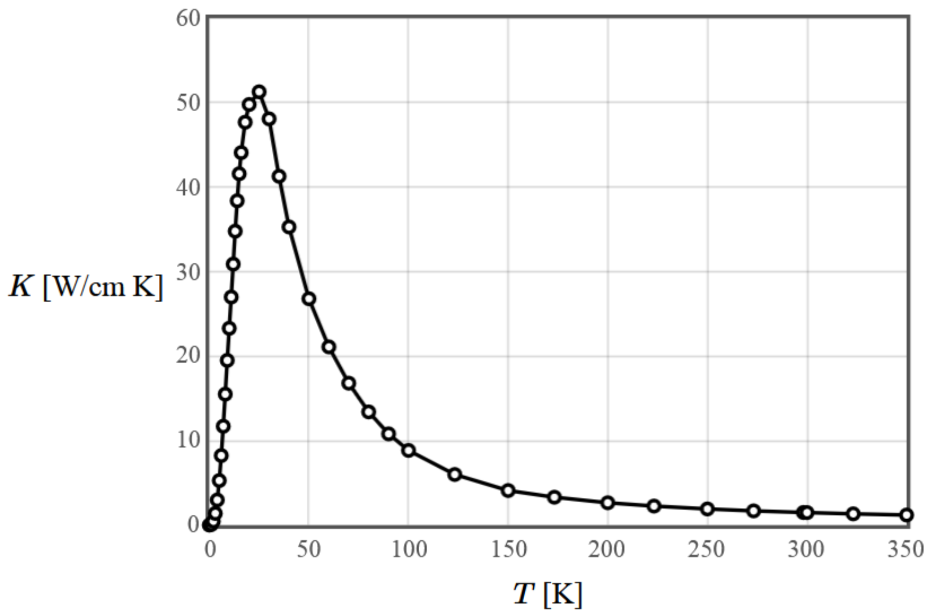
$$K_{ij} = \sum_p \int \frac{\tau}{(2\pi)^3\hbar^2} \frac{E^2 \exp\left(\frac{E}{k_B T}\right)}{k_B T^2} f_{BE}^2 \nabla_{\vec{k}} E \cdot \hat{e}_i \nabla_{\vec{k}} E \cdot \hat{e}_j d^3 k.$$

Linear acoustic branch, constant τ

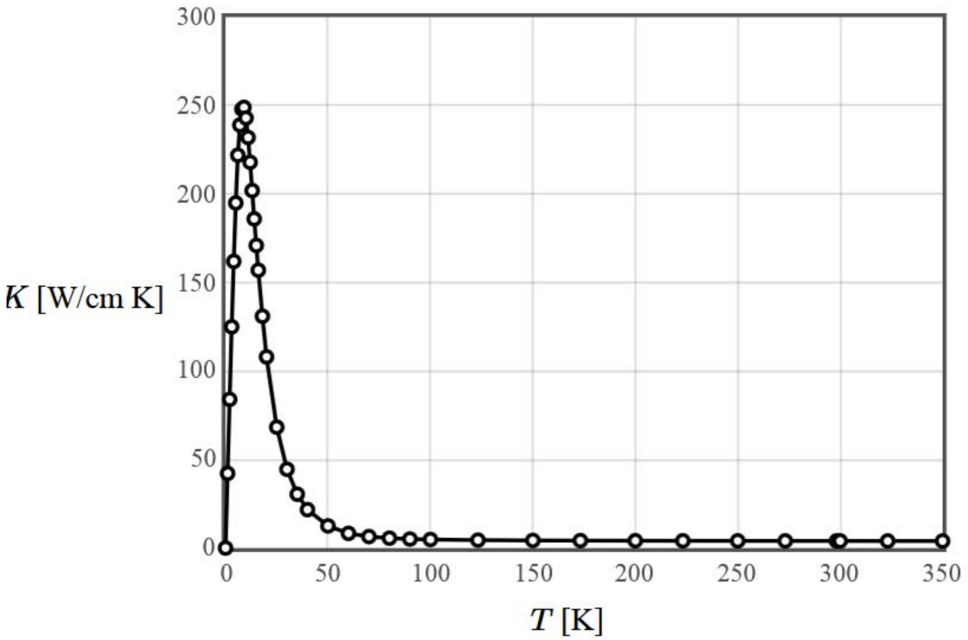


Optical branches don't contribute as much.

Thermal conductivity



The thermal conductivity of silicon.[1]



The thermal conductivity of copper.[1]