

Transport

Current densities

Electrical $\vec{j}_{\text{elec}} = -e \int \vec{v}_{\vec{k}} D(\vec{k}) f(\vec{k}) d^3 k$

Particle $\vec{j}_n = \int \vec{v}_{\vec{k}} D(\vec{k}) f(\vec{k}) d^3 k$

Energy $\vec{j}_U = \int \vec{v}_{\vec{k}} E(\vec{k}) D(\vec{k}) f(\vec{k}) d^3 k.$

1st law: $dU = dQ - dW + \mu dN.$

Heat $\vec{j}_Q = \int \vec{v}_{\vec{k}} \left(E(\vec{k}) - \mu \right) D(\vec{k}) f(\vec{k}) d^3 k.$

Current densities

Electrical

$$\vec{j}_{\text{elec}} = -e \int \vec{v}_{\vec{k}} D(\vec{k}) f(\vec{k}) d^3 k$$

$$D(\vec{k}) = \frac{2}{(2\pi)^3} \longleftarrow \text{spin}$$

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

$f(\vec{k})$ Probability that state k is occupied.

Liouville's theorem

$f(\vec{r}, \vec{k}, t)$ Probability that state k is occupied at position r and time t .

Number of electrons:
$$N = \int d^3 r \int d^3 k f(\vec{r}, \vec{k}, t).$$

$$\frac{d}{dt} f(\vec{r}, \vec{k}, t) = 0.$$

If the probability of finding an electron at a particular position with a particular momentum decreases, the probability must increase somewhere else.

Boltzmann Equation

$$\frac{d}{dt} f(\vec{r}, \vec{k}, t) = 0.$$

$$\frac{d}{dt} f(\vec{r}, \vec{k}, t) = \frac{\partial f}{\partial x} \frac{dx}{dt} + \frac{\partial f}{\partial y} \frac{dy}{dt} + \frac{\partial f}{\partial z} \frac{dz}{dt} + \frac{\partial f}{\partial k_x} \frac{dk_x}{dt} + \frac{\partial f}{\partial k_y} \frac{dk_y}{dt} + \frac{\partial f}{\partial k_z} \frac{dk_z}{dt} + \frac{\partial f}{\partial t} = 0$$

$$\frac{d}{dt} f(\vec{r}, \vec{k}, t) = \frac{d\vec{r}}{dt} \cdot \nabla_{\vec{r}} f + \frac{d\vec{k}}{dt} \cdot \nabla_{\vec{k}} f + \frac{\partial f}{\partial t} = 0.$$

Crystal momentum $\vec{F}_{\text{ext}} = \hbar \frac{d\vec{k}}{dt}$

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

Collision term describes the transitions between k states.

Relaxation time approximation

$$\frac{\partial f}{\partial t} = -\frac{\vec{F}_{ext} \cdot \nabla_k f}{\hbar} - \vec{v} \cdot \nabla f + \left. \frac{\partial f}{\partial t} \right|_{collisions}$$

In the relaxation time approximation,

$$\left. \frac{\partial f}{\partial t} \right|_{collisions} = \frac{f_0(\vec{k}) - f(\vec{k})}{\tau(\vec{k})}$$

If the driving field is turned off, the collision term will drive the system back to equilibrium in time τ .

When $\nabla_k f = \nabla_r f = 0$ and the initial condition is $f = f_1$, the solution to the Boltzmann equation is,

$$f(t) = f_0 + f_1 e^{-t/\tau}$$

Boltzmann equation: relaxation time approx.

In the relaxation time approximation.

$$\frac{\partial f}{\partial t} = -\frac{\vec{F}_{ext} \cdot \nabla_k f}{\hbar} - \vec{v} \cdot \nabla f + \frac{f_0(\vec{k}) - f(\vec{k})}{\tau(\vec{k})}$$

in a stationary state $\frac{\partial f}{\partial t} = 0$

If the system is not far from equilibrium, $f \approx f_0$, and we can substitute f_0 for f on the right

$$f(\vec{k}) = f_0(\vec{k}) + \frac{\tau(\vec{k}) \vec{F}_{ext} \cdot \nabla_k f_0}{\hbar} + \tau(\vec{k}) \vec{v} \cdot \nabla f_0$$

$$f_0(\vec{k}) = \frac{1}{\exp\left(\frac{E(\vec{k}) - \mu}{k_B T}\right) + 1}$$

Boltzmann equation: relaxation time approx.

$$f(\vec{k}) \approx f_0(\vec{k}) + \frac{\tau(\vec{k}) \vec{F}_{ext} \cdot \nabla_k f_0}{\hbar} + \tau(\vec{k}) \vec{v} \cdot \nabla f_0$$

$$\nabla f_0 = \frac{\partial f_0}{\partial T} \nabla T + \frac{\partial f_0}{\partial \mu} \nabla \mu$$

$$f_0(\vec{k}) = \frac{1}{\exp\left(\frac{E(\vec{k}) - \mu}{k_B T}\right) + 1}$$

Temperature and
chemical potential can
depend on position

$$\vec{F}_{ext} = -e(\vec{E} + \vec{v} \times \vec{B})$$

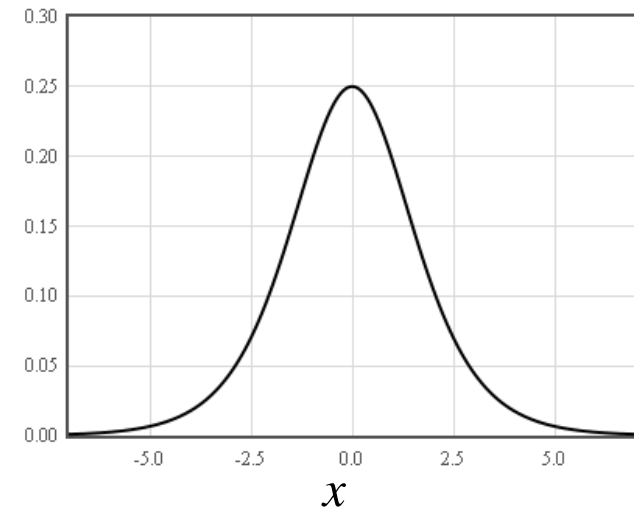
$$f(\vec{k}) \approx f_0(\vec{k}) + \frac{\tau(\vec{k}) (-e) (\vec{v} \times \vec{B} + \vec{E}) \cdot \nabla_k f_0}{\hbar} + \tau(\vec{k}) \vec{v} \cdot \left(\frac{\partial f_0}{\partial T} \nabla T + \frac{\partial f_0}{\partial \mu} \nabla \mu \right)$$

Temperature gradient

Concentration gradient

Boltzmann equation: relaxation time approx.

$$\frac{\partial f_0}{\partial \mu} = \frac{\frac{1}{k_B T} \exp\left(\frac{E(\vec{k}) - \mu}{k_B T}\right)}{\left(\exp\left(\frac{E(\vec{k}) - \mu}{k_B T}\right) + 1\right)^2} = -\frac{\partial f_0}{\partial E} \frac{\exp(x)}{(\exp(x) + 1)^2}$$



$$\begin{aligned} \nabla_k f_0 &= \frac{\frac{-1}{k_B T} \exp\left(\frac{E(\vec{k}) - \mu}{k_B T}\right)}{\left(\exp\left(\frac{E(\vec{k}) - \mu}{k_B T}\right) + 1\right)^2} \nabla_k E(\vec{k}) \\ &= \frac{\partial f_0}{\partial E} \nabla_k E(\vec{k}) \end{aligned}$$

$$\begin{aligned} \frac{\partial f_0}{\partial T} &= \frac{\frac{E(\vec{k}) - \mu}{k_B T^2} \exp\left(\frac{E(\vec{k}) - \mu}{k_B T}\right)}{\left(\exp\left(\frac{E(\vec{k}) - \mu}{k_B T}\right) + 1\right)^2} \\ &= -\frac{\partial f_0}{\partial E} \frac{E(\vec{k}) - \mu}{T} \end{aligned}$$

Only the states near the Fermi surface contribute.

Boltzmann equation: relaxation time approx.

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

$$\vec{j}_{elec} = -e \int \vec{v}(\vec{k}) D(\vec{k}) f(\vec{k}) d\vec{k}$$

The contribution of $f_0(k)$ is zero

density of states $D(\vec{k}) = \frac{2}{(2\pi)^3}$ ← spin

$$\vec{j}_{elec} = \frac{e}{4\pi^3} \int \vec{v}_{\vec{k}} \left(\tau(\vec{k}) \frac{\partial f_0}{\partial E} \left(-\frac{e}{\hbar} \left(\frac{\hbar \vec{k}}{m} \times \vec{B} + \vec{E} \right) \cdot \nabla_{\vec{k}} E(\vec{k}) + \frac{\hbar \vec{k}}{m} \cdot \left(\frac{E(\vec{k}) - \mu}{T} \nabla T + \nabla \mu \right) \right) \right) d^3k$$

Current densities

$$\vec{j}_{\text{elec}} = -e \int \vec{v}_{\vec{k}} D(\vec{k}) f(\vec{k}) d^3 k$$

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

$$\vec{j}_n = \int \vec{v}_{\vec{k}} D(\vec{k}) f(\vec{k}) d^3 k.$$

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

$$\vec{j}_U = \int \vec{v}_{\vec{k}} E(\vec{k}) D(\vec{k}) f(\vec{k}) d^3 k.$$

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

$$\vec{j}_Q = \int \vec{v}_{\vec{k}} (E(\vec{k}) - \mu) D(\vec{k}) f(\vec{k}) d^3 k$$

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

Electrochemical potential

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

The electrochemical potential $\tilde{\mu} = -e\phi + \mu$
is what a voltmeter measures

ϕ is the electrostatic potential
 μ is the chemical potential

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

Electrical conductivity

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

no temperature gradient or magnetic field

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

$$\begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \qquad \begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix} = e \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \begin{bmatrix} \frac{\partial \tilde{\mu}}{\partial x} \\ \frac{\partial \tilde{\mu}}{\partial y} \\ \frac{\partial \tilde{\mu}}{\partial z} \end{bmatrix}$$

Electrical conductivity

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

$$\begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix} = e \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \begin{bmatrix} \frac{\partial \tilde{\mu}}{\partial x} \\ \frac{\partial \tilde{\mu}}{\partial y} \\ \frac{\partial \tilde{\mu}}{\partial z} \end{bmatrix}$$

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

for cubic crystals:

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

Free-electron model: electrical conductivity

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m^*}, \quad \nabla_{\vec{k}} E(\vec{k}) = \frac{\hbar^2}{m^*} (k_x \hat{x} + k_y \hat{y} + k_z \hat{z})$$

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

assuming a single lifetime τ

$$\sigma = \frac{\hbar^2 e^2 \tau}{4\pi^3 m^{*2}} \int \frac{\partial f_0}{\partial \mu} k_z^2 d^3 k.$$

Free-electron model: electrical conductivity

$$\sigma = \frac{\hbar^2 e^2 \tau}{4\pi^3 m^{*2}} \int \frac{\partial f_0}{\partial \mu} k_z^2 d^3 k.$$

The differential volume is,

$$d^3 k = k^2 \sin \theta dk d\theta d\varphi \quad k_z = k \cos \theta,$$

$$\sigma = \frac{\hbar^2 e^2 \tau}{4\pi^3 m^{*2}} \int \frac{\partial f_0}{\partial \mu} k^4 \cos^2 \theta \sin \theta dk d\theta d\varphi.$$

The integral over φ contributes a factor of 2π .

$$\sigma = \frac{\hbar^2 e^2 \tau}{2\pi^2 m^{*2}} \int \frac{\partial f_0}{\partial \mu} k^4 \cos^2 \theta \sin \theta dk d\theta.$$

The integral over θ contributes a factor of $2/3$.

$$\sigma = \frac{\hbar^2 e^2 \tau}{3\pi^2 m^{*2}} \int \frac{\partial f_0}{\partial \mu} k^4 dk.$$

Free-electron model: electrical conductivity

$$\sigma = \frac{\hbar^2 e^2 \tau}{3\pi^2 m^{*2}} \int \frac{\partial f_0}{\partial \mu} k^4 dk.$$

The derivative of the Fermi function is,

$$\frac{\partial f_0}{\partial \mu} = \frac{\exp(x)}{k_B T (\exp(x) + 1)^2}$$

where

$$x = \frac{E - \mu}{k_B T} = \frac{\frac{\hbar^2}{2m^*} (k^2 - k_F^2)}{k_B T},$$

and $\mu = \hbar^2 k_F^2 / 2m^*$. Differentiating to find dk

$$dk = \frac{m^* k_B T}{\hbar^2 k} dx$$

The conductivity can be written as,

$$\sigma = \frac{e^2 \tau}{3\pi^2 m^*} \int \frac{\exp(x)}{(\exp(x) + 1)^2} k^3 dx.$$

Free-electron model: electrical conductivity

$$\sigma = \frac{e^2 \tau}{3\pi^2 m^*} \int \frac{\exp(x)}{(\exp(x) + 1)^2} k^3 dx.$$

k is approximately k_F and it can be pulled out of the integral.
The remaining integral over x evaluates to 1

$$\sigma = \frac{e^2 \tau k_F^3}{3\pi^2 m^*}.$$

For free electrons,

$$n = \frac{k_F^3}{3\pi^2}.$$

In terms of the electron density, the electrical conductivity is,

$$\sigma = \frac{ne^2 \tau}{m^*}.$$

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,

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

No magnetic field is applied. One end of the wire is grounded and 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,

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

Thermoelectric current

The electrons carry heat as well as charge.

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

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,

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

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

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

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,

$$\sigma = \frac{ne^2\tau}{m^*} \quad K = \frac{\pi^2\tau nk_B^2 T}{3m^*}.$$

The Lorentz number for free electrons is,

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

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.