Thermoelectricity:
From Atoms to Systems

Week 2: Thermoelectric Transport Parameters

Lecture 2.2: **TE Transport Coefficients**

By Mark Lundstrom
Professor of Electrical and Computer Engineering
Purdue University

coupled charge and heat currents

electrical current:

$$\mathcal{E}_x = \rho J_x + S\frac{dT}{dx}$$

heat current (electronic):

$$J_{Qx} = \pi J_x - \kappa_e \frac{dT}{dx}$$

heat current (lattice):

$$q_x = -\kappa_L\left(\frac{dT}{dx}\right)$$

$$\sigma'(E) = \frac{2q^2}{h}\lambda(E)\left(M(E)/A\right)\left(-\frac{\partial f_0}{\partial E}\right)$$

$$\sigma = \int_{-\infty}^{+\infty}\sigma'(E)dE \qquad \rho = 1/\sigma$$

$$S = -\frac{1}{q}\frac{\int_{-\infty}^{+\infty}(E-E_F)\sigma'(E)dE}{\int\sigma'(E)dE} = -\frac{E_J - E_F}{qT}$$

$$\pi = TS$$

$$\kappa_e = \kappa_0 - T\sigma S^2 \quad \kappa_0 = \frac{1}{q^2T}\int_{-\infty}^{+\infty}(E-E_F)^2\sigma'(E)dE$$

Lecture 2 topics

Goal: Develop an understanding and "feel" for:

1) Conductivity
2) Seebeck (and Peltier) coefficient
3) Thermal conductivity
4) Relations between the coefficients

1) conductivity (non-degenerate case)

$$\sigma_n = \int_{E_C}^{+\infty} \sigma'(E)\,dE \qquad \sigma'(E) = \frac{2q^2}{h}\lambda(E)\left(M(E)/A\right)\left(-\frac{\partial f_0}{\partial E}\right)$$

$$f_0 = \frac{1}{1+e^{(E-E_F)/k_BT}} \approx e^{(E_F-E_C)/k_BT} \qquad \lambda(E) = \lambda_0 \qquad M(E) = A\frac{m^*}{2\pi\hbar^2}(E-E_C)$$

(non-degenerate)

$$\sigma_n = n_0 q \mu_n \qquad \mu_n \equiv \sigma_n / n_0 q$$

$$n_0 = N_C e^{(E_F-E_C)/k_BT} \qquad N_C = \frac{1}{4}\left(\frac{2m^* k_B T}{\pi\hbar^2}\right)^{3/2}$$

$$\mu_n = \frac{\upsilon_T \lambda_0}{2k_BT/q} \qquad \upsilon_T = \sqrt{\frac{2k_BT}{\pi m^*}} \qquad D_n = \frac{\upsilon_T\lambda_0}{2}$$

conductivity (degenerate case)

$$\sigma = \int \sigma'(E)\,dE$$

$$\sigma'(E) = \frac{2q^2}{h}\lambda(E)\left(M(E)/A\right)\left(-\frac{\partial f_0}{\partial E}\right)$$

$$f_0 = \frac{1}{1+e^{(E-E_F)/k_BT}}$$

$$-\frac{\partial f_0}{\partial E} = \delta(E_F)$$

$$\sigma_n = \frac{2q^2}{h}\lambda(E_F)\left(M(E_F)/A\right)$$

Conductivity not directly proportional to n_0, but…

$$n_0 = \frac{\left(2m^*\right)^{3/2}}{3\pi^2\hbar^3}\left(E_F - E_C\right)^{3/2}$$

conductivity (general case)

$$\sigma_n = \int_{E_C}^{+\infty} \sigma'(E)\, dE \qquad \sigma'(E) = \frac{2q^2}{h}\lambda(E)\big(M(E)/A\big)\left(-\frac{\partial f_0}{\partial E}\right)$$

$$\sigma_n = \frac{2q^2}{h}\langle\langle\lambda\rangle\rangle\langle M/A\rangle$$

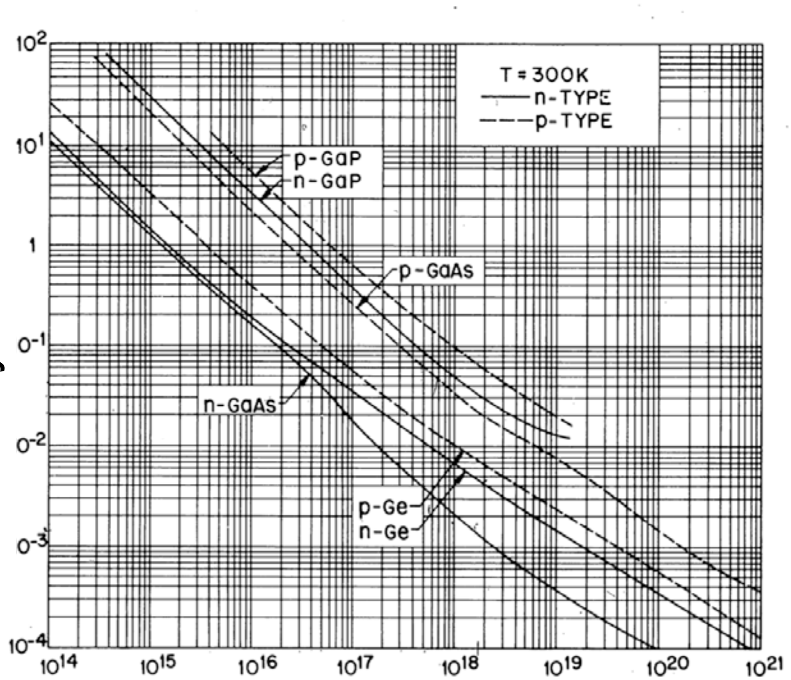
"quantum of conductance"

average mfp for backscattering

average number of channels in the Fermi window

measured conductivity

resistivity Ω - cm



impurity concentration cm^{-3}

S.M. Sze, *Physics of Semiconductor Devices*, 2nd Ed., p. 33, 1981.

By controlling the doping, we vary the carrier density over ~ 6-7 orders magnitude.

At the same time, the Fermi level varies.

carrier concentration and the Fermi level

$$n_0 = \int_{E_C}^{\infty} D(E - E_C) f_0(E)\, dE \quad \eta_F = (E_F - E_C)/k_B T$$

$$n_0 = N_C \mathcal{F}_{1/2}(\eta_F) \qquad N_C = \frac{1}{4}\left(\frac{2m^* k_B T}{\pi \hbar^2}\right)^{3/2}$$ parabolic energy bands

$$\eta_F << 0 \quad E_F << E_C \quad \mathcal{F}_{1/2}(\eta_F) \rightarrow e^{\eta_F} \quad n_0 = N_C e^{\eta_F} \text{ cm}^{-3}$$

(non-degenerate semiconductor)

For an introduction to Fermi-Dirac integrals, see:
"Notes on Fermi-Dirac Integrals," 3rd Ed., by R. Kim and M. Lundstrom
https://www.nanohub.org/resources/5475

location of the Fermi level

1) Doping determines the carrier concentration.

2) The carrier concentration determines the Fermi level.

$$n_0 = N_C \mathcal{F}_{1/2}(\eta_F) \rightarrow n_0 = N_C e^{\eta_F} \text{ m}^{-3} \qquad \eta_F = (E_F - E_C)/k_B T$$

3) The location of the Fermi level controls the conductivity.

4) The location of the Fermi level also determines the Seebeck coefficient.

2) Seebeck coefficient

$$S = -\frac{1}{qT}\frac{\int_{-\infty}^{+\infty}\left(E - E_F\right)\sigma'\left(E\right)dE}{\int \sigma'\left(E\right)dE}$$

$$S = -\frac{1}{qT}\left(E_J - E_F\right)$$

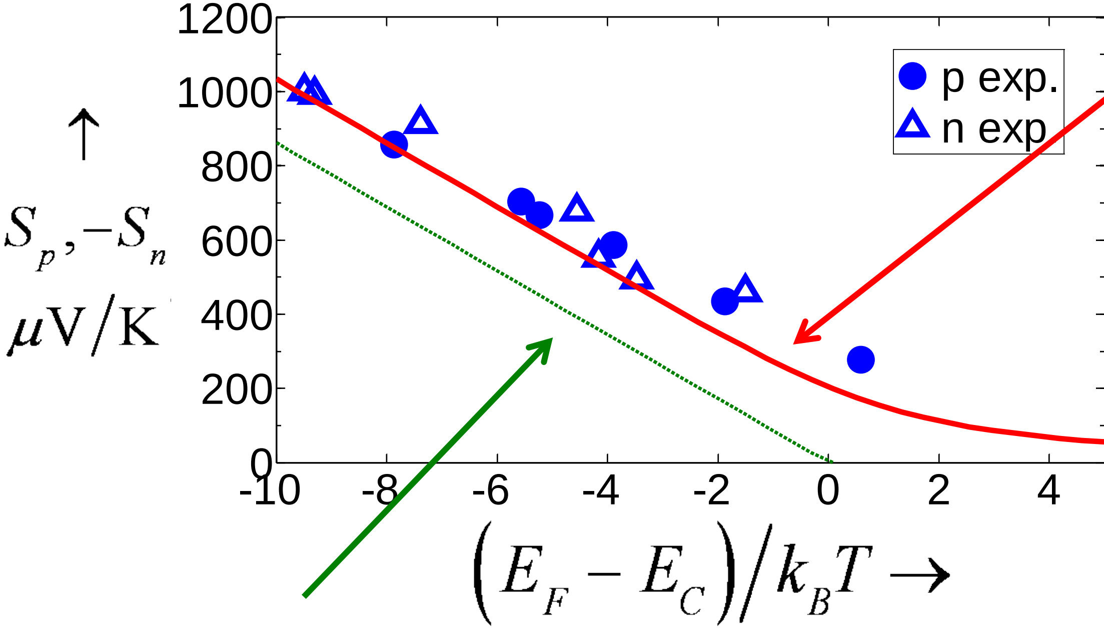
$$S = -\left(\frac{k_B}{q}\right)\left(\frac{E_J - E_F}{k_B T}\right)$$

$$\left(\frac{k_B}{q}\right) = 86\ \mu\mathrm{V/K}$$

S is negative for *n*-type semiconductors and positive for p-type semiconductors.

Seebeck coefficient of Ge

$$S_n = -\left(\frac{k_B}{q}\right)\left\{\frac{\left(E_J - E_F\right)}{k_B T}\right\}$$



$$S_n = -\left(\frac{k_B}{q}\right)\left(\frac{\left(E_C - E_F\right)}{k_B T}\right)$$

$$\left(\frac{k_B}{q}\right) = 86\ \mu\mathrm{V/K}$$

$$E_J - E_C \approx 2k_B T$$

$$\lambda(E) = \lambda_0$$

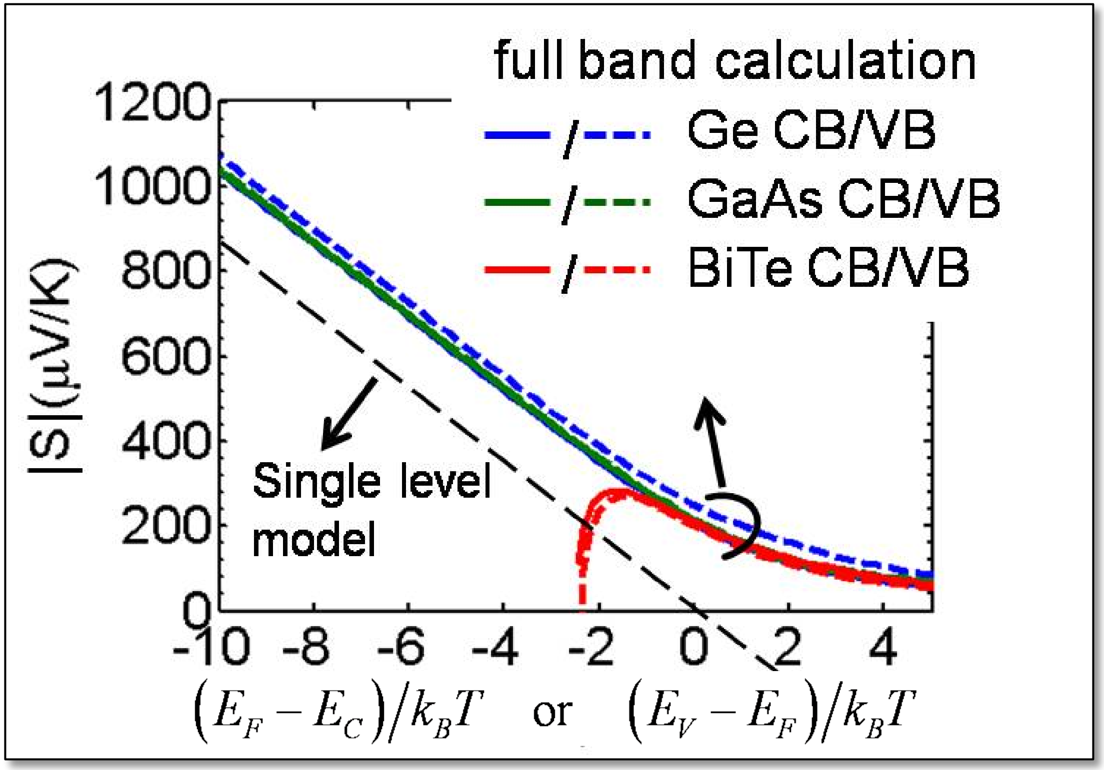
(3D, non-degenerate)

$E_J \rightarrow E_F$ (degenerate)

Exp. data: T.H. Geballe and G.W. Hull, “Seebeck Effect in Germanium,” *Physical Review*, **94**, 1134, 1954.

Seebeck coefficient of different materials

$$S_n = -\left(\frac{k_B}{q}\right)\left(\frac{E_J - E_F}{k_B T}\right)$$



Changwook Jeong, et al., "On Landauer vs. Boltzmann and Full Band vs. Effective Mass Evaluation of Thermoelectric Transport Coefficients," *J. Appl. Phys*., **107**, 023707, 2010.

3) electronic thermal conductivity

electrical current:

$$\mathcal{E}_x = \rho J_x + S\frac{dT}{dx}$$

heat current (electronic):

$$J_{Qx} = \pi J_x - \kappa_e \frac{dT}{dx}$$

heat current (lattice):

$$q_x = -\kappa_L \frac{dT}{dx}$$

1) conductivity (resistivity)

2) Seebeck coefficient (thermopower) and Peltier coefficient

3) Electronic thermal conductivity

electronic thermal conductivity

$$\mathcal{E}_x = \rho J_x + S\frac{dT}{dx}$$

$$J_{Qx} = \pi J_x - \kappa_e \frac{dT}{dx}$$

Kelvin relation

$$\pi = TS$$

(fundamental)

Onsager relations for coupled flows

We expect a relation between the electrical conductivity and the electronic thermal conductivity, but it is not fundamental; it depends material details.

electronic thermal conductivity

$$\kappa_0 = \int_{-\infty}^{+\infty} \frac{\left(E - E_F\right)^2}{q^2 T} \sigma'\left(E\right) dE \qquad \sigma'\left(E\right) = \frac{2q^2}{h} \lambda\left(E\right)\left(M\left(E\right)/A\right)\left(-\frac{\partial f_0}{\partial E}\right)$$

$$\kappa_e = \kappa_0 - T\sigma S^2$$

$$\kappa_0 = T\left(\frac{k_B}{q}\right)^2 \left\langle \left(\frac{E - E_F}{k_B T}\right)^2 \right\rangle \sigma \qquad S = \left(\frac{k_B}{q}\right)^2 \left\langle \left(\frac{E - E_F}{k_B T}\right) \right\rangle$$

$$\kappa_e = T\sigma\left(\frac{k_B}{q}\right)^2 \left\{ \left\langle \left(\frac{E - E_F}{k_B T}\right)^2 \right\rangle - \left\langle \left(\frac{E - E_F}{k_B T}\right) \right\rangle^2 \right\} = T\sigma \mathcal{L}$$

Wiedemann-Franz “Law”

electronic heat conductivity

$$\kappa_e = T\sigma\mathcal{L}$$

$\mathcal{L}$ is the "Lorenz number"

The Lorenz number depends on details of bandstructure, scattering, dimensionality, and degree of degeneracy, but for a constant mfp and parabolic energy bands, it is useful to remember:

$$\mathcal{L} \approx 2\left(\frac{k_B}{q}\right)^2$$

non-degenerate,
3D semiconductors

$$\mathcal{L} \approx \frac{\pi^2}{3}\left(\frac{k_B}{q}\right)^2$$

fully degenerate
e.g. 3D metals

basic TE equations with phonons

$$\mathcal{E}_x = \rho J_x + S\frac{dT}{dx}$$

$$J_{Qx} = \pi J_x - \left(\kappa_e + \kappa_L\right)\frac{dT}{dx}$$

Five transport coefficients:

1) Resistivity (Ω-cm) = 1/conductivity (S/cm)
2) Seebeck coefficient (V/K)
3) Peltier coefficient (W/A)
4) Electronic thermal conductivity (W/m-K)
5) Lattice thermal conductivity (W/m-K)

Note: "phonon drag" neglected.

lattice thermal conductivity

$$J_Q = \pi J_x - \kappa \frac{dT}{dx} \qquad \kappa = \kappa_e + \kappa_L$$

Both electrons and lattice vibrations carry heat – we have been discussing the electronic part.

In metals, heat conduction by electrons dominates: $\kappa_e >> \kappa_L$

In semiconductors, lattice vibrations dominate: $\kappa_L >> \kappa_e$

transport coefficients: recap

$\sigma = \frac{2q^2}{h} \langle M/A \rangle \langle\langle \lambda \rangle\rangle$	conductivity
$S = -\left(\frac{k_B}{q}\right)\left(\frac{E_J - E_F}{k_B T}\right)$	Seebeck coefficient or “thermopower”
$\pi = TS$	Peltier coefficient Kelvin relation
$\kappa_e = T\sigma\mathcal{L}$	electronic thermal conductivity W-F “law” - $\mathcal{L}$ is the “Lorenz number” $\mathcal{L} \approx (2-3)(k_B/q)^2$
κ_L	lattice thermal conductivity

example: TE transport parameters of n-Ge

ρ_n Ω-m

S_n V/K

π_n W/A = V

κ_e W/m-K

$$\mathcal{E}_x = \rho J_x + S\frac{dT}{dx} \quad \left(\frac{\text{V}}{\text{m}}\right)$$

$$J_Q = \pi J_x - \kappa\frac{dT}{dx} \quad \left(\text{W/m}^2\right)$$

$$N_D = 10^{15}\ \text{cm}^{-3}$$

$$T = 300\ \text{K}$$

$$\mu_n = 3200\ \text{cm}^2/\text{V-s}$$

$$n_0 = N_C e^{(E_F - E_c)/k_B T_L} \approx N_D$$

$$N_C = 1.04\times 10^{19}\quad \text{cm}^{-3}$$

$m^* = 0.12 m_0$ (conductivity effective mass)

example: mean-free-path of n-Ge

ρ Ω-m

S V/K

π W/A = V

κ_e W/m-K

$$\mathcal{E}_x = \rho J_x + S\frac{dT}{dx} \quad \left(\frac{\text{V}}{\text{m}}\right)$$

$$J_Q = \pi J_x - \kappa\frac{dT}{dx} \quad \left(\text{W/m}^2\right)$$

$$D_n = \frac{k_B T}{q}\mu_n = 83 \text{cm}^2/\text{s}$$

$$D_n = \frac{\upsilon_T \lambda_0}{2} \text{ cm}^2/\text{s}$$

$$\upsilon_T = \sqrt{\frac{2k_B T}{\pi m^*}} = 1.55\times 10^7 \text{ cm/s}$$

$$\lambda_0 = 107 \text{ nm}$$

TE transport parameters of n-Ge: resistivity

ρ	Ω-m
S	V/K
π	W/A = V
κ_e	W/m-K

$$\mathcal{E}_x = \rho J_x + S\frac{dT}{dx} \quad \left(\frac{\text{V}}{\text{m}}\right)$$

$$J_Q = \pi J_x - \kappa\frac{dT}{dx} \quad \left(\text{W/m}^2\right)$$

$$N_D = 10^{15}\ \text{cm}^{-3} \approx n_0$$

$$\mu_n = 3200\ \text{cm}^2/\text{V-s}$$

$$\sigma = n_0 q \mu_n \quad \text{S/cm}$$

$$\rho = 1/\left(n_0 q \mu_n\right) = 2\ \Omega\text{-cm}$$

TE transport parameters of n-Ge: Seebeck coeff.

$\rho = 2 \quad \Omega\text{-m}$

$S \quad \text{V/K}$

$\pi \quad \text{W/A} = \text{V}$

$\kappa \quad \text{W/m-K}$

$$\mathcal{E}_x = \rho J_x + S\frac{dT}{dx} \quad \left(\frac{\text{V}}{\text{m}}\right)$$

$$J_Q = \pi J_x - \kappa\frac{dT}{dx} \quad \left(\text{W/m}^2\right)$$

$$N_D = 10^{15}\ \text{cm}^{-3} \approx n_0$$

$$n_0 = N_C e^{(E_F - E_c)/k_B T_L}$$

$$N_C = 1.04 \times 10^{19} \quad \text{cm}^{-3}$$

$$T = 300\ \text{K}$$

$$(E_c - E_F)/k_B T \approx \ln(N_C/n_0) \approx 9.3$$

$\delta_n \approx 2$ (non-degenerate, 3D)

$$S = \left(\frac{k_B}{-q}\right)\left\{\frac{(E_c - E_F)}{k_B T} + \delta_n\right\} \approx -970\ \mu\text{V/K}$$

TE transport parameters of n-Ge: Peltier coeff.

$\rho = 2 \quad \Omega\text{-m}$

$S = -970 \text{ V/K}$

$\pi \quad \text{W/A} = \text{V}$

$\kappa_e \quad \text{W/m-K}$

$$\mathcal{E}_x = \rho J_x + S\frac{dT}{dx} \quad \left(\frac{\text{V}}{\text{m}}\right)$$

$$J_Q = \pi J_x - \kappa\frac{dT}{dx} \quad \left(\text{W/m}^2\right)$$

$$\pi = TS \approx -0.3 \text{ V}$$

TE transport parameters of n-Ge: Peltier coeff.

$\rho = 2 \quad \Omega\text{-m}$

$S = -970\ \mathrm{V/K}$

$\pi = -0.3\ \mathrm{W/A} = \mathrm{V}$

$\kappa_e \quad \mathrm{W/m\text{-}K}$

$$\mathcal{E}_x = \rho J_x + S\frac{dT}{dx} \quad \left(\frac{\mathrm{V}}{\mathrm{m}}\right)$$

$$J_Q = \pi J_x - \kappa\frac{dT}{dx} \quad \left(\mathrm{W/m^2}\right)$$

$\kappa_e = T\sigma\mathcal{L}$ (Lorenz number)

$\mathcal{L} \approx 2\left(k_B/q\right)^2$ (non-degenerate, 3D)

$\sigma = 1/\rho$

$$\kappa_e = 2.2\times 10^{-4} \quad \mathrm{W/m\text{-}K}$$

TE transport parameters of n-Ge:

$$\rho = 2 \quad \Omega\text{-m}$$

$$S = -970 \quad \text{V/K}$$

$$\pi = -0.3 \quad \text{W/A} = \text{V}$$

$$\kappa_e = 2.2 \times 10^{-4} \quad \text{W/m-K}$$

$$\mathcal{E}_x = \rho J_x + S\frac{dT}{dx} \quad \left(\frac{\text{V}}{\text{m}}\right)$$

$$J_Q = \pi J_x - \kappa \frac{dT}{dx} \quad \left(\text{W/m}^2\right)$$

All of these parameters depend on the temperature and carrier concentration (Fermi level).

Note also: $\kappa_L = 58\ \text{W/m-K} >> \kappa_e$

summary: basic equations with phonons

ρ resistivity Ω-m

S Seebeck coefficient V/K

π Peltier coefficient V

κ_e electronic thermal conductivity W/m-K

κ_L lattice thermal conductivity W/m-K

$$\mathcal{E}_x = \rho J_x + S\frac{dT}{dx}$$

$$J_{Qx} = \pi J_x - \left(\kappa_e + \kappa_L\right)\frac{dT}{dx}$$