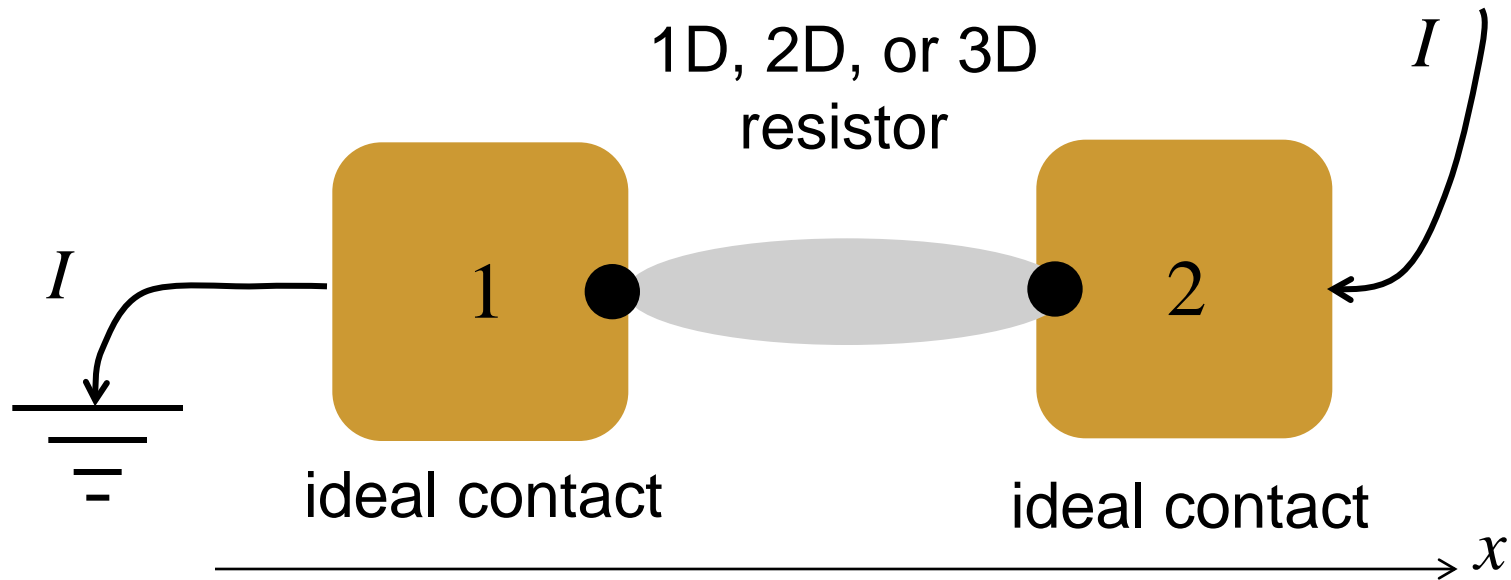


ECE-656: Fall 2011

**Lecture 9:
Thermoelectric Effects:
charge flow**

Professor Mark Lundstrom
Electrical and Computer Engineering
Purdue University, West Lafayette, IN USA

review



$$G = \frac{2q^2}{h} \int T(E) M(E) \left(-\frac{\partial f_0}{\partial E} \right) dE$$

$$G = \int G'(E) dE$$

$$G = \frac{2q^2}{h} \langle\langle T(E) \rangle\rangle \langle M(E) \rangle$$

$$G'(E) = \frac{2q^2}{h} T(E) M(E) \left(-\frac{\partial f_0}{\partial E} \right)$$

“differential conductance”

transport in the bulk (3D)

$$G = \frac{2q^2}{h} \int T(E) M(E) \left(-\frac{\partial f_0}{\partial E} \right) dE$$

$$G = \int G'(E) dE$$

$$G = \frac{2q^2}{h} \langle\langle T(E) \rangle\rangle \langle M(E) \rangle$$

$$G'(E) = \frac{2q^2}{h} T(E) M(E) \left(-\frac{\partial f_0}{\partial E} \right)$$

differential conductance

$$T(E) \rightarrow \lambda(E)/L$$

$$G = \sigma A/L$$

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

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

$$\sigma = \frac{2q^2}{h} \langle\langle \lambda(E) \rangle\rangle \left\langle \frac{M(E)}{A} \right\rangle$$

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

mathematical description of bulk transport

In Lecture 6 we saw that the electrical current in the bulk is:

$$J_{nx} = \sigma_n d(F_n/q)/dx \quad \sigma_n = \text{conductivity} = 1/\rho_n \quad (1/\Omega\text{-m})$$

Alternatively, we could write this equation in the inverted form as:

$$d(F_n/q)/dx = \rho_n J_{nx}$$

How do these equations change when there is a temperature gradient?

mathematical description

The answer is:

$$J_{nx} = \sigma_n \frac{d(F_n/q)}{dx} - S_n \sigma_n \frac{dT_L}{dx}$$

S_n is the Seebeck coefficient in V/K.

Alternatively, we can write this equation as:

$$\frac{d(F_n/q)}{dx} = \rho_n J_{nx} + S_n \frac{dT_L}{dx}$$

(inverted form of the equations)

in this lecture...

Our goal is to understand the physical origin of the **Seebeck coefficient** (which is also called the **thermopower**) and how it is mathematically related to the properties of the semiconductor.

outline

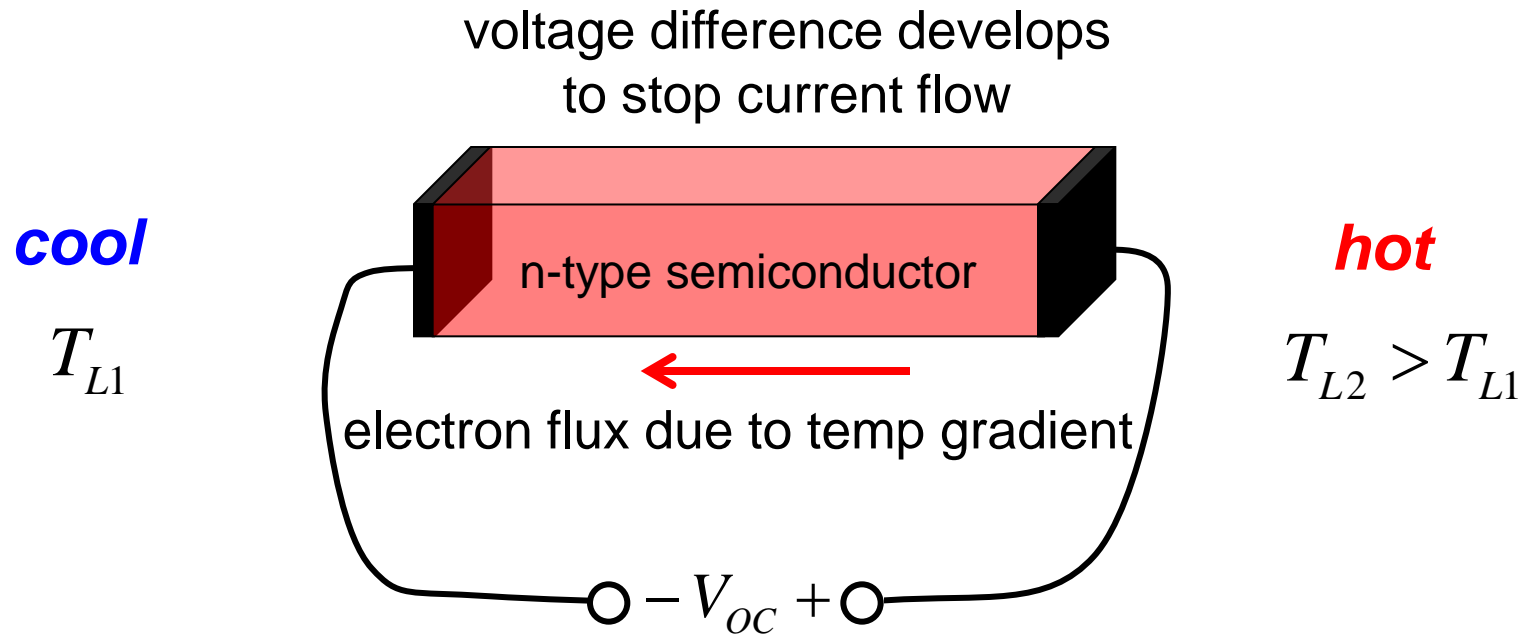
- 1) Introduction
- 2) Charge transport in a temperature gradient**
- 3) Mathematical formulation
- 4) Discussion
- 5) Summary

We will use an approach similar to that of Prof. Supriyo Datta,
Lessons from Nanoscience: A new approach to transport, World Scientific, 2011



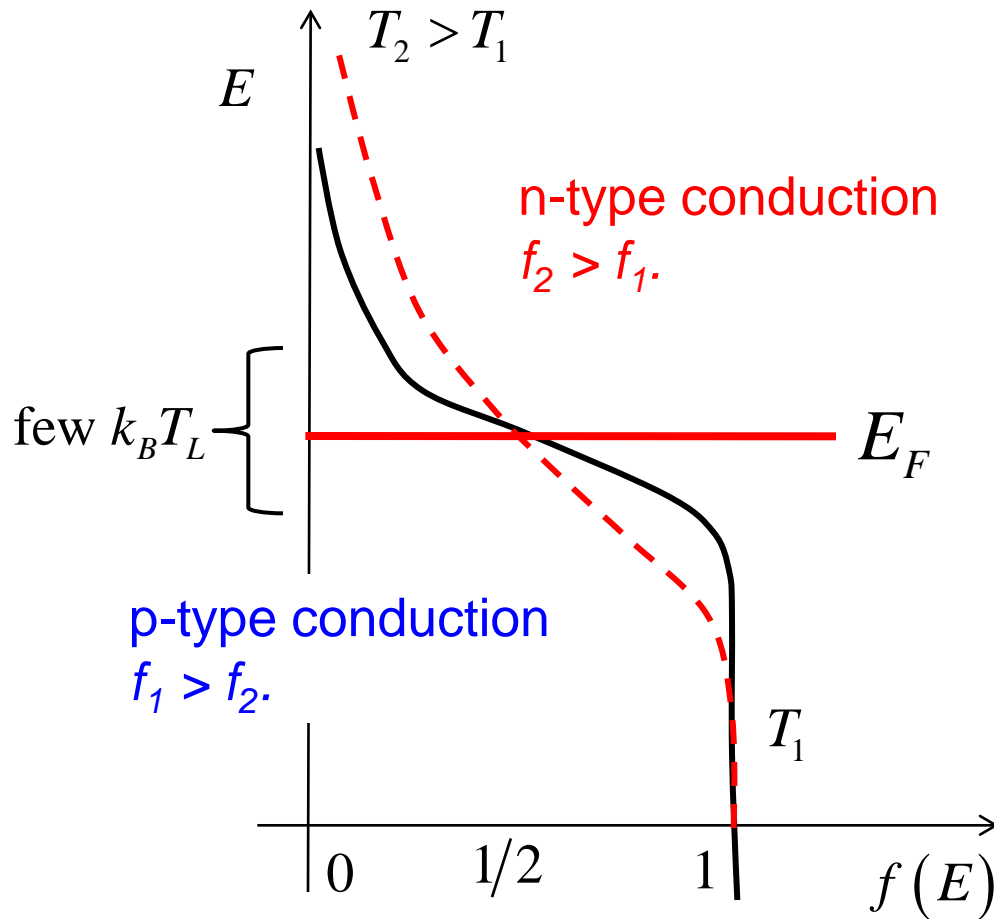
This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 3.0 United States License.
<http://creativecommons.org/licenses/by-nc-sa/3.0/us/>

temperature gradients and voltage



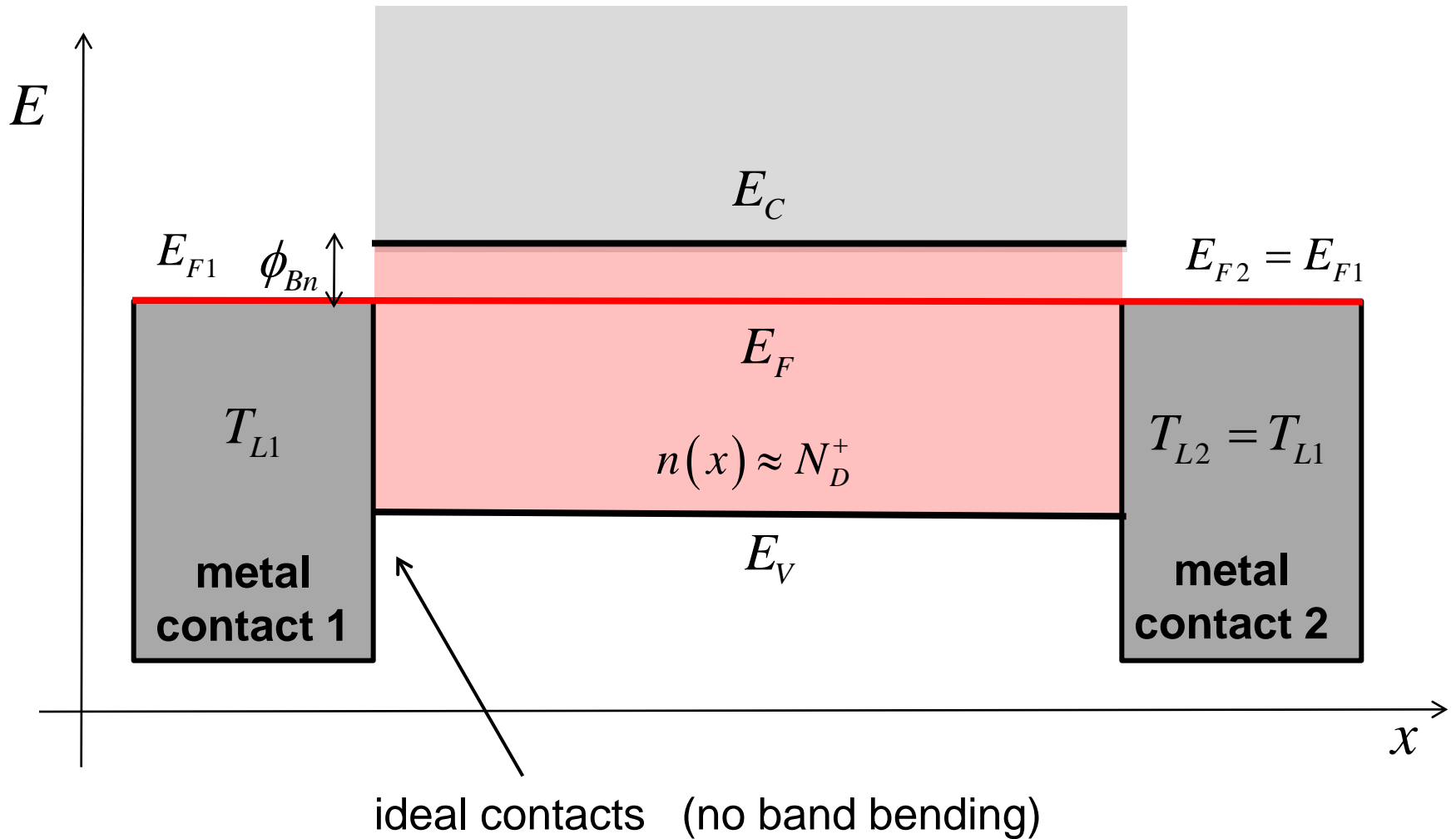
Temperature gradients give rise to an open circuit voltage, which is known as the Seebeck effect. We expect a **positive** voltage for an n-type semiconductor (and **negative** voltage for a p-type semiconductor.)

current is proportional to $(f_1 - f_2)$

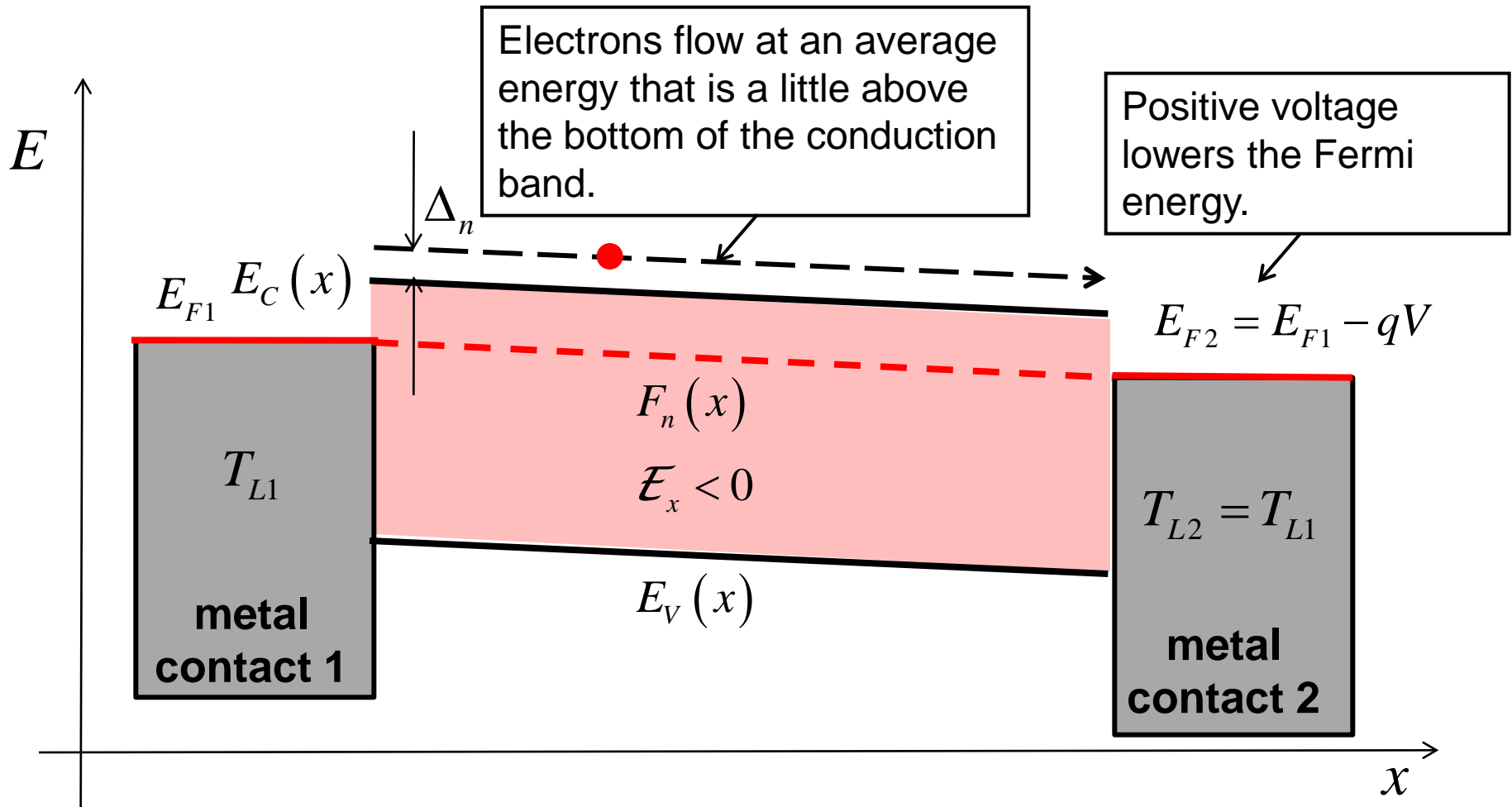


$$f(E) = \frac{1}{1 + e^{(E - E_F)/k_B T_L}}$$

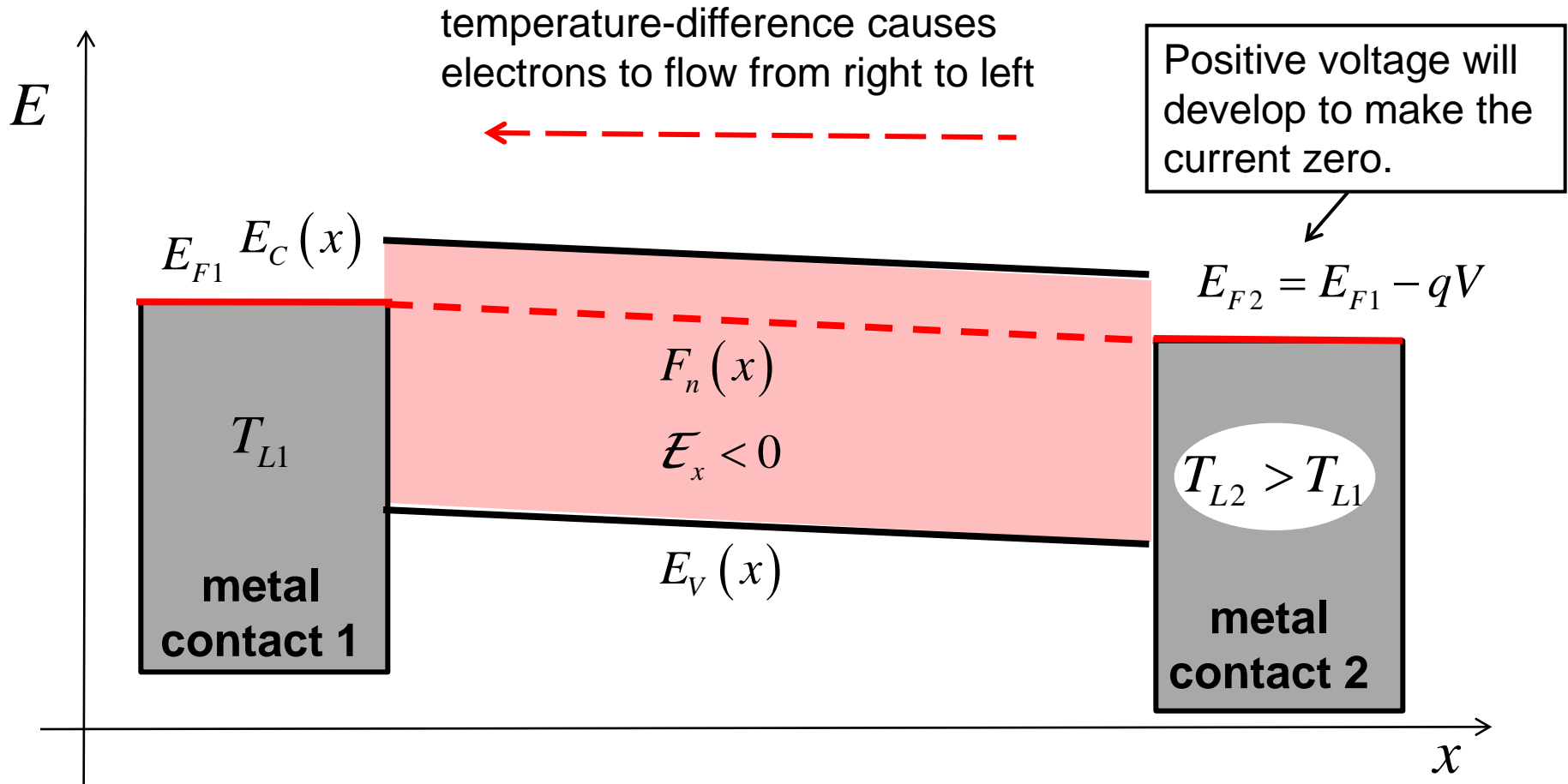
n-type semiconductor: equilibrium, $V = 0$



n-type semiconductor: isothermal, $V > 0$

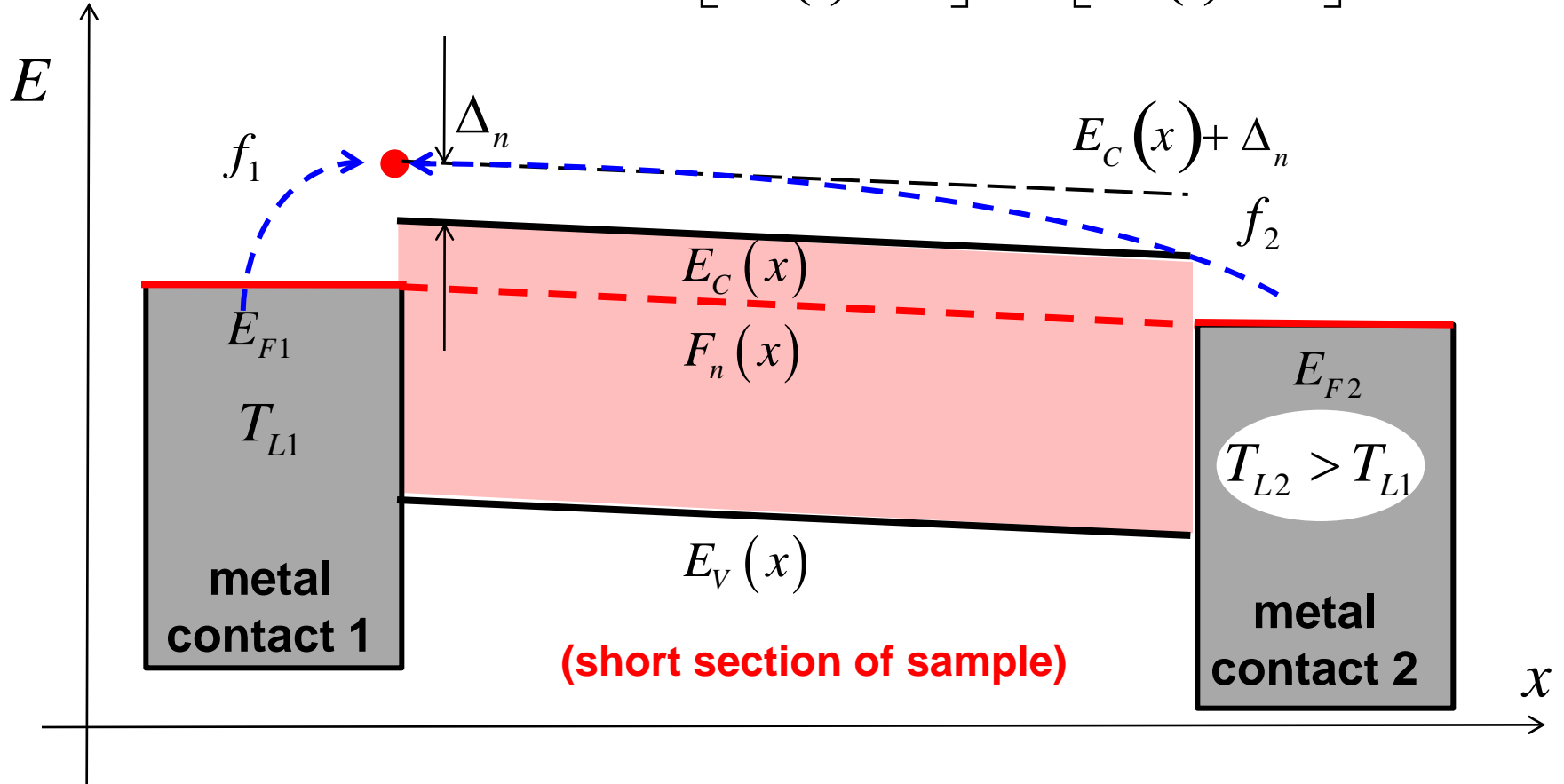


Seebeck effect



Seebeck effect (ii)

$$I = 0 \Rightarrow f_1 = f_2 \Rightarrow f_1 [E_C(0) + \Delta_n] = f_2 [E_C(0) + \Delta_n]$$



$$E_{F2} = E_{F1} - q\delta V$$

Seebeck coefficient

$$I = 0 \Rightarrow f_1 \left[E_C(0) + \Delta_n \right] = f_2 \left[E_C(0) + \Delta_n \right] \quad E_{F2} = E_{F1} - q\delta V$$

$$\frac{1}{1 + e^{(E_C + \Delta_n - E_{F1})/k_B T_{L1}}} = \frac{1}{1 + e^{(E_C + \Delta_n - E_{F1} + q\delta V)/k_B T_{L2}}}$$

$$\frac{(E_C + \Delta_n - E_{F1})}{k_B T_{L1}} = \frac{(E_C + \Delta_n - E_{F1} + q\delta V)}{k_B T_{L2}}$$

$$\delta V = \frac{E_C(0) + \Delta_n - E_{F1}}{qT_{L1}} \delta T_L = -S_n \delta T_L$$

$$\delta V = -S_n \delta T_L$$

$$S_n = - \frac{[E_C(0) + \Delta_n - E_{F1}]}{qT_{L1}}$$

$$S_n = - \frac{[E_J - E_{F1}]}{qT_{L1}}$$

(by convention, S is negative for *n*-type semiconductors.)

Seebeck coefficient: recap

$$V = RI - S\delta T_L$$

$$S = -\frac{(E_J - E_F)}{qT_L}$$

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

$$E_J = E_C + \Delta_n$$

$$\Delta_n = \frac{\int (E - E_C)\sigma'(E)dE}{\int \sigma'(E)dE}$$

$$I = GV + (SG)\delta T_L$$

S is proportional to the average energy of current flow (with respect to the Fermi level).

outline

- 1) Introduction
- 2) Charge transport in a temperature gradient
- 3) Mathematical formulation**
- 4) Discussion
- 5) Summary



This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 3.0 United States License.

<http://creativecommons.org/licenses/by-nc-sa/3.0/us/>

driving “forces” for transport

$$I = \frac{2q}{h} \int T(E) M(E) (f_1 - f_2) dE$$

Differences in occupation, f , produce current.

$$(f_1 - f_2) \approx -\frac{\partial f_1}{\partial E} \Delta E_F$$

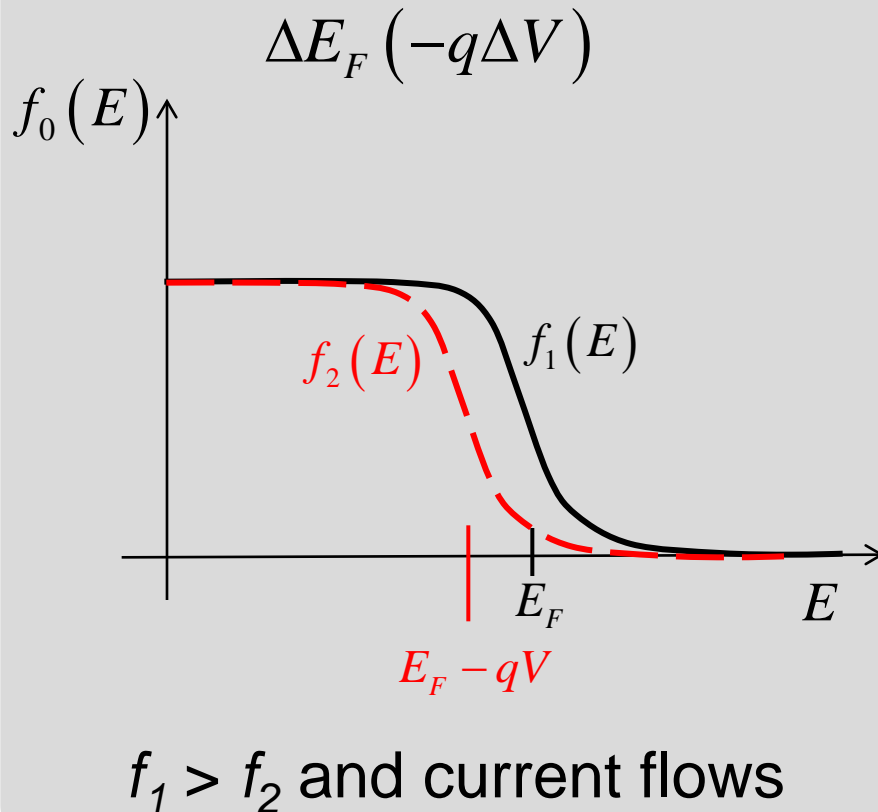
Assumes $T_{L1} = T_{L2}$.

but differences in temperature also produce differences in f and can, therefore, drive current (thermoelectric effects).

$$\Delta E_F = -q\Delta V = -q(V_2 - V_1)$$

$$\Delta T_L = T_{L2} - T_{L1}$$

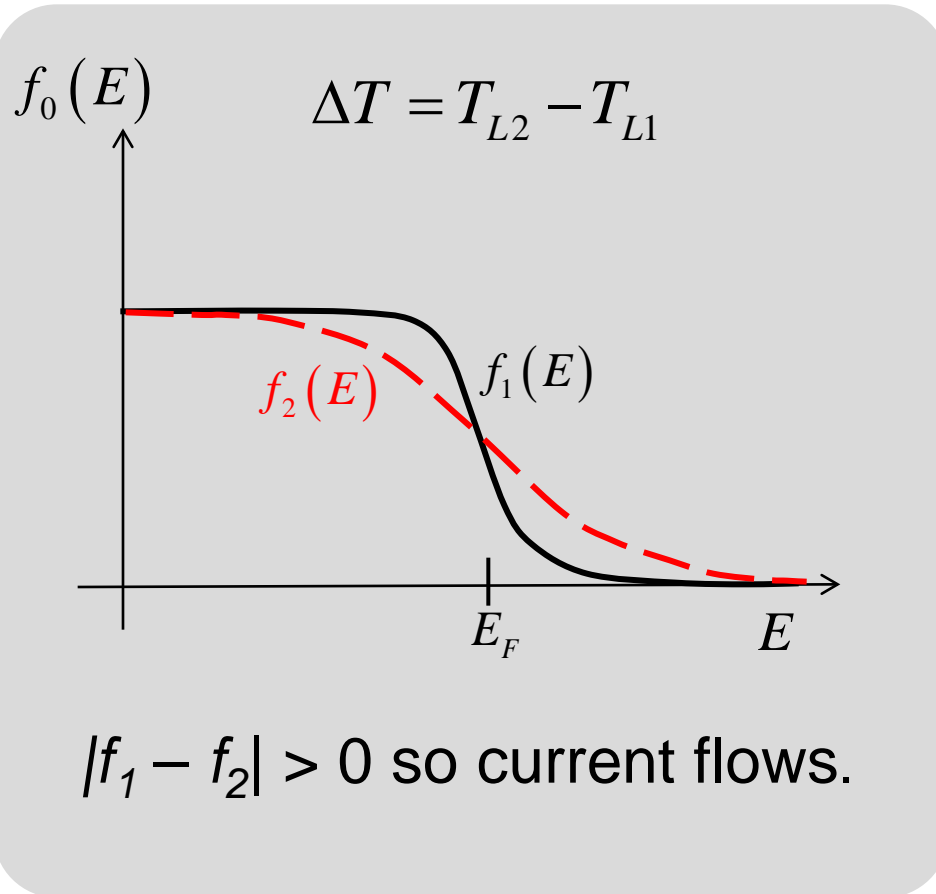
when $\otimes T = 0$, the driving force is: ΔE_F



$$(f_1 - f_2) \approx \left(-\frac{\partial f_0}{\partial E} \right) q\Delta V$$

$$(f_1 \approx f_2 \approx f_0)$$

driving force: differences in temperature



$$(f_1 - f_2) \approx f_1 - \left(f_1 + \frac{\partial f_1}{\partial T_L} \Delta T \right)$$

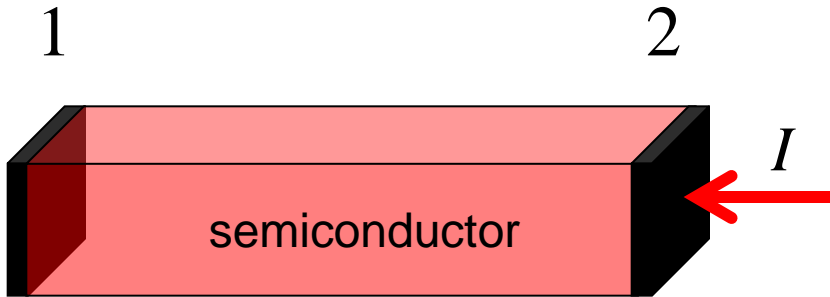
$$= -\frac{\partial f_1}{\partial T_L} \Delta T$$

$$\frac{\partial f_1}{\partial T_L} = -\frac{(E - E_F)}{T_L} \left(\frac{\partial f_0}{\partial E} \right)$$

$$(f_1 - f_2) \approx -\left(-\frac{\partial f_0}{\partial E} \right) \frac{(E - E_F)}{T_L} \Delta T$$

$$(f_1 \approx f_2 \approx f_0)$$

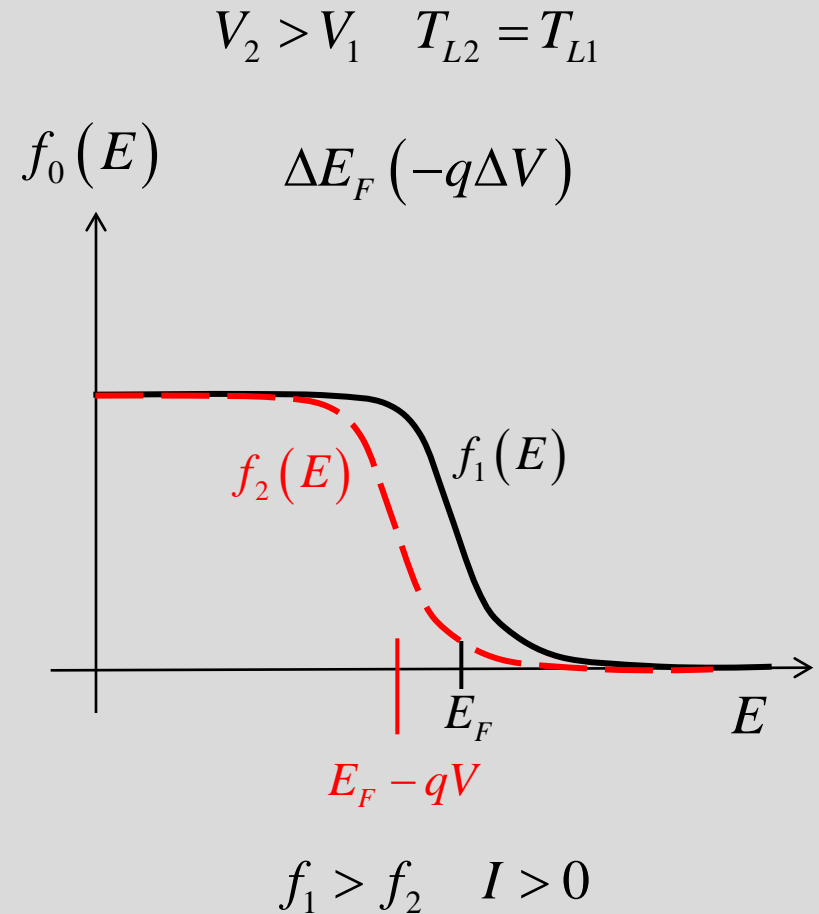
n-type vs. p-type...



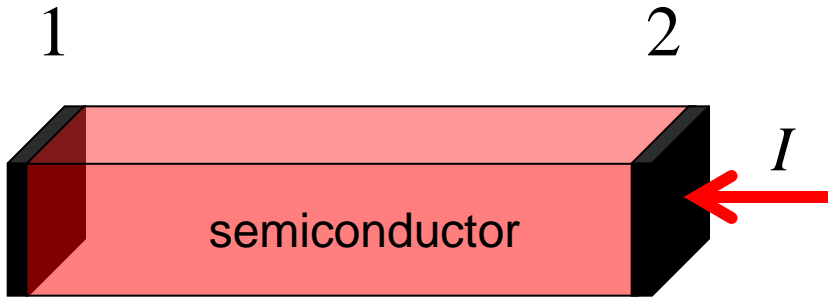
$$I = \frac{2q^2}{h} \int T(E) M(E) (f_1 - f_2) dE$$

The same answer for both n-type and p-type semiconductors!

This occurs because $f_1 > f_2$ for states above and below the Fermi energy.



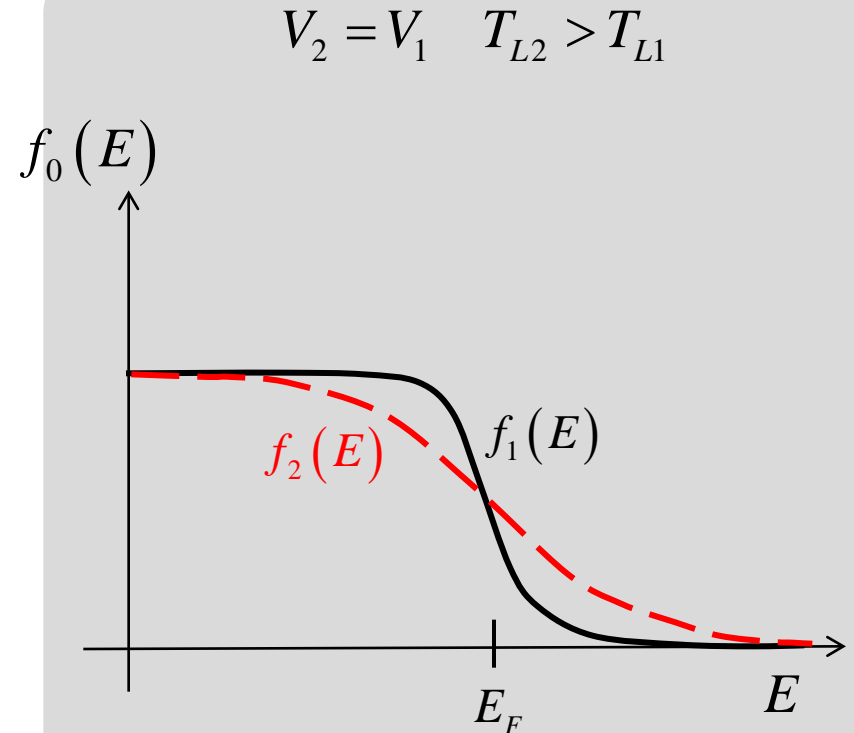
n-type vs. p-type (ii)...



$$I = \frac{2q}{h} \int T(E) M(E) (f_1 - f_2) dE$$

n-type: $I < 0$

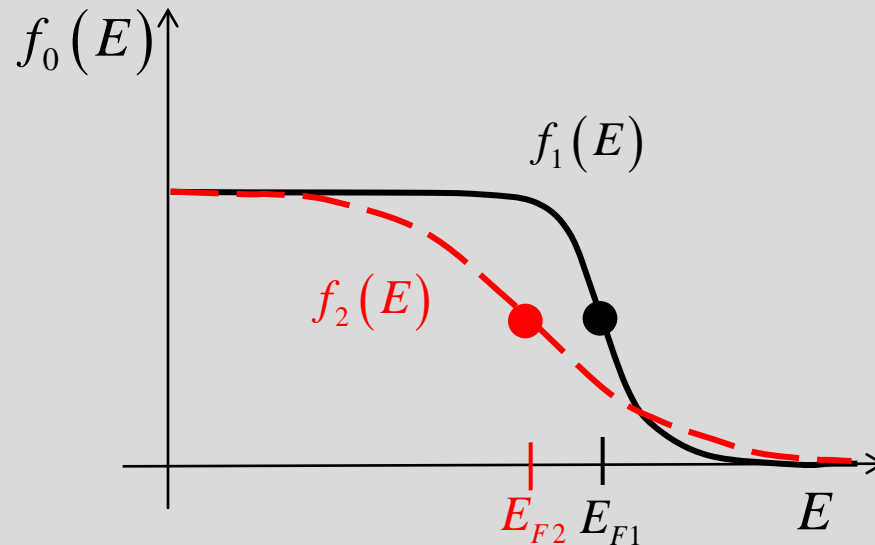
p-type: $I > 0$



n-type: $E > E_F : f_2 > f_1$

p-type: $E < E_F : f_1 > f_2$

finally: differences in **both** E_F and T



$$(f_1 - f_2) \approx \left(-\frac{\partial f_0}{\partial E} \right) q\Delta V - \left(-\frac{\partial f_0}{\partial E} \right) \frac{(E - E_F)}{T_L} \Delta T_L$$

the math...

$$I'(E) = \frac{2q}{h} T(E) M(E) (f_1 - f_2) \quad I = \int I'(E) dE$$

$$(f_1 - f_2) \approx \left(-\frac{\partial f_0}{\partial E} \right) q \Delta V - \left(-\frac{\partial f_0}{\partial E} \right) \frac{(E - E_F)}{T_L} \Delta T$$

$$I'(E) = G'(E) \Delta V + S'_T(E) \Delta T$$

S_T is related to the “Soret coefficient” for electro-thermal diffusion

the math...

$$I'(E) = G'(E)\Delta V + S'_T(E)\Delta T$$

$$S'_T(E) = -\frac{2q}{h}T(E)M(E)\left(-\frac{\partial f_0}{\partial E}\right)\frac{(E - E_F)}{T_L}$$

$$S'_T(E) = -G'(E)\frac{(E - E_F)}{qT_L}$$

$$S_T = \int S'_T(E)dE = -\int \frac{(E - E_F)}{qT_L}G'(E)dE$$

S_T is negative for n-type and positive for p-type.

re-cap

$$I = G\Delta V + S_T\Delta T$$

$$G = \frac{2q^2}{h} \int T(E)M(E) \left(-\frac{\partial f_0}{\partial E} \right) dE = \int G'(E) dE$$

$$S_T = - \int \frac{(E - E_F)}{qT_L} G'(E) dE = \int S_T(E) dE$$

Valid near equilibrium for 1D, 2D, or 3D and from ballistic to diffusive transport.

inverted form

$$\Delta V = \frac{1}{G} I - \frac{S_T}{G} \Delta T = RI - S\Delta T$$

$$S = \frac{S_T}{G} = -\frac{1}{qT_L} \frac{\int (E - E_F) G'(E) dE}{\int G'(E) dE} = -\frac{E_J - E_F}{qT_L}$$

$$E_J = E_C + \Delta_n \quad \Delta_n = \frac{\int (E - E_C) G'(E) dE}{\int G'(E) dE}$$

Valid near equilibrium for 1D, 2D, or 3D and from ballistic to diffusive transport.

outline

- 1) Introduction
- 2) Charge transport in a temperature gradient
- 3) Mathematical formulation
- 4) Discussion**
- 5) Summary



This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 3.0 United States License.

<http://creativecommons.org/licenses/by-nc-sa/3.0/us/>

current equation in the bulk

Develop a diffusive transport equation that describes bulk transport in the presence of gradients in the electrochemical potential **and** temperature.

$$J_{nx} = \sigma_n \frac{dF_n/q}{dx} \rightarrow ?$$

$$J_{nx} = \sigma_n \frac{dF_n/q}{dx} - S_T \frac{dT_L}{dx}$$

$$I = -I_x = G\Delta V + S_T\Delta T$$

$$I_x = J_{nx}A = -G\Delta V - S_T\Delta T$$

$$J_{nx} = -\frac{G}{A}\Delta V - \frac{S_T}{A}\Delta T$$

$$J_{nx} = -G\frac{L\Delta V}{A L} - S_T\frac{L\Delta T}{A L}$$

$$G = \sigma_n A/L$$

$$S_T = s_T A/L$$

$$\Delta V = -\Delta F_n/q$$

current equation in the bulk (ii)

$$J_{nx} = \sigma_n \frac{dF_n/q}{dx} - s_T \frac{dT_L}{dx}$$

$$s_T = s_T \frac{A}{L} \quad G = \sigma \frac{A}{L}$$

$$s_T = - \int \frac{(E - E_F)}{qT_L} \sigma'(E) dE$$

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

inverted form of the current equation

$$J_{nx} = \sigma_n \frac{dF_n/q}{dx} - S_T \frac{dT_L}{dx}$$

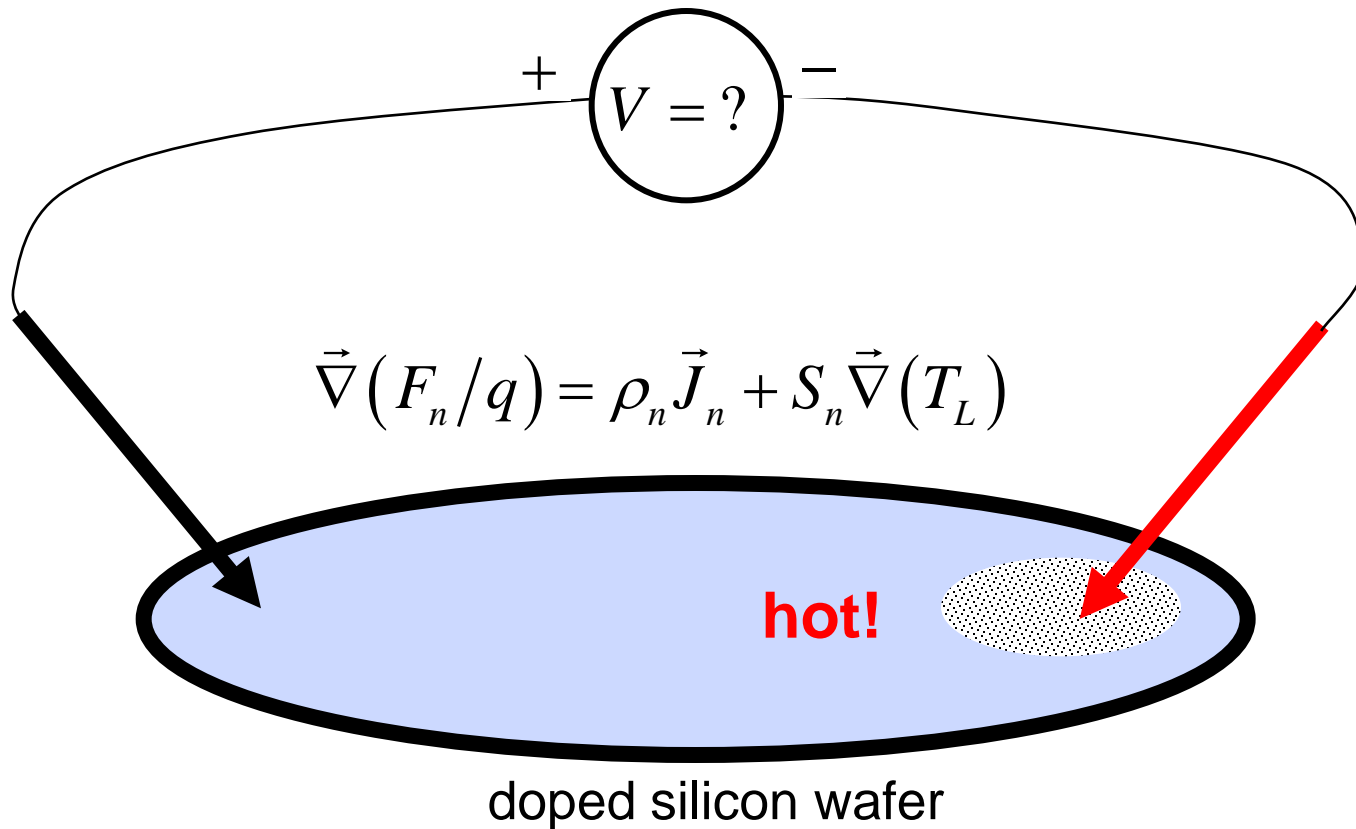
$$\frac{dF_n/q}{dx} = \rho_n J_{nx} + \rho_n S_T \frac{dT_L}{dx}$$

$$\frac{dF_n/q}{dx} = \rho_n J_{nx} + S_n \frac{dT_L}{dx}$$

$$S_n = \frac{S_T}{\sigma_n}$$

$$S_n = \left(-\frac{1}{qT_L} \right) \frac{\int (E - E_F) \sigma'(E) dE}{\int \sigma'(E) dE}$$

hot point probe



basic equation

$$\mathcal{E}_x = \rho_n J_{nx} + S_n \frac{dT_L}{dx}$$

(Uniform semiconductor assumed, so $d(F_n/q)/dx = \mathcal{E}_x$)

Two transport coefficients:

- 1) resistivity ($\Omega\text{-cm}$) = 1/conductivity (S/cm)
- 2) Seebeck coefficient (V/K)

Seebeck coefficient

$$S_n(T_L) = -\frac{1}{qT_L}(E_J - E_F)$$

$$S_n(T_L) = -\frac{1}{qT_L}(E_C + \Delta_n - E_F)$$

$$\Delta_n = \frac{\int (E - E_c) \sigma'_n(E) dE}{\int \sigma'_n(E) dE}$$

The parameter, Δ_n , depends on bandstructure and scattering.

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

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

$$\delta_n = \frac{E_J - E_C}{k_B T_L}$$

$$\delta_n \approx 2 \quad (3\text{D, non-degenerate})$$

Example: transport parameters of n-Ge

$$\rho_n \quad \Omega\text{-m}$$

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

$$\mathcal{E}_x = \rho_n J_{nx} + S_n \frac{dT_L}{dx} \quad \left(\frac{\text{V}}{\text{m}} \right)$$

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

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

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

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

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

TE transport parameters of n-Ge: resistivity

$$\rho_n \quad \Omega\text{-m}$$

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

$$\mathcal{E}_x = \rho_n J_{nx} + S_n \frac{dT_L}{dx} \quad \left(\frac{\text{V}}{\text{m}} \right)$$

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

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

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

$$\rho_n = 1/n_0 q \mu_n \approx 2 \text{ }\Omega\text{-cm}$$

TE transport parameters of n-Ge: Seebeck coeff.

$$\rho_n = 2\Omega\text{-m}$$

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



$$\mathcal{E}_x = \rho_n J_{nx} + S_n \frac{dT_L}{dx} \quad \left(\frac{\text{V}}{\text{m}} \right)$$

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

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

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

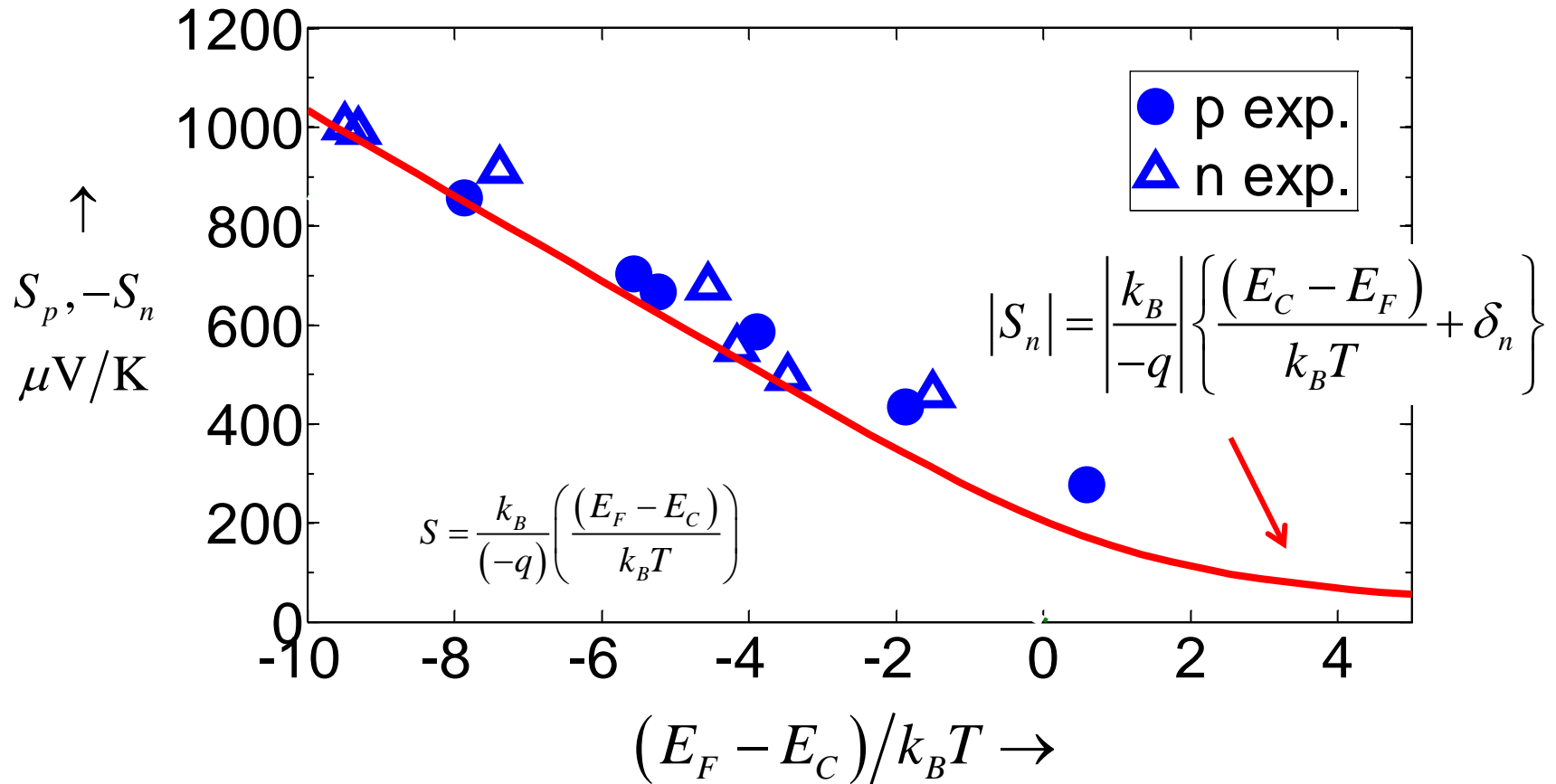
$$T_L = 300 \text{ K}$$

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

$$\delta_n \approx 2 \quad (\text{non-degenerate, 3D})$$

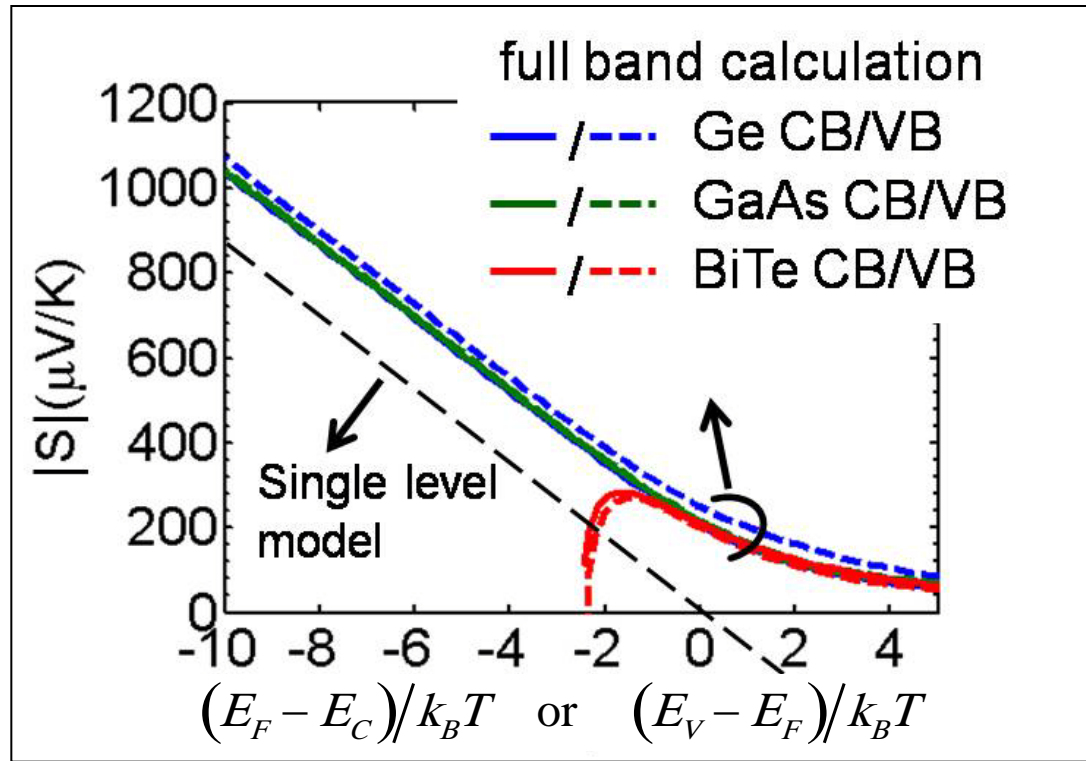
$$S_n = \left(\frac{k_B}{-q} \right) \left\{ \frac{(E_c - E_F)}{k_B T_L} + \delta_n \right\} \approx -970 \mu\text{V/K}$$

Seebeck coefficient of Ge



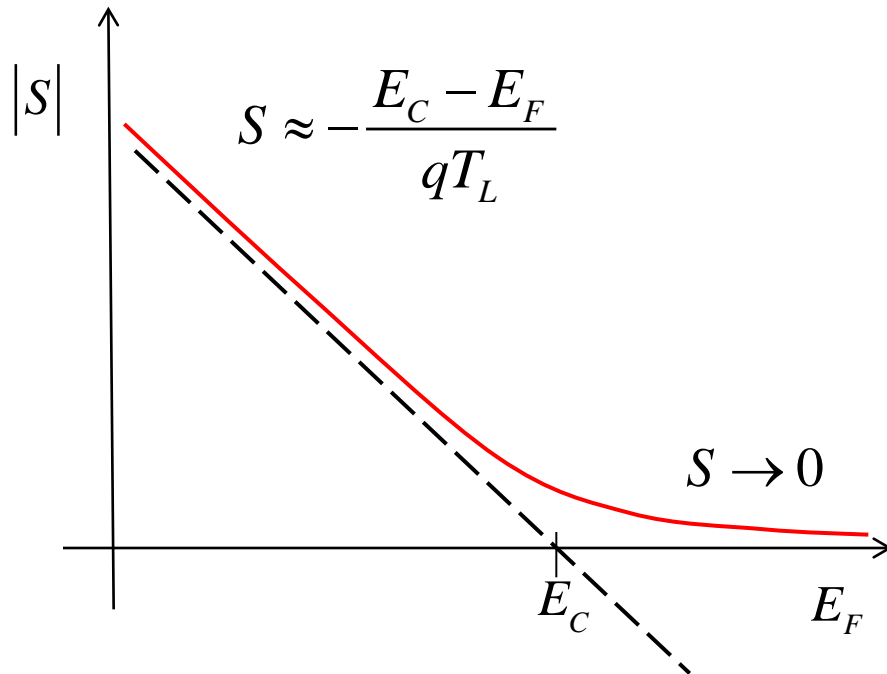
Exp. data: T.H. Geballe and G.W. Hull, "Seebeck Effect in Germanium," *Physical Review*, **94**, 1134, 1954.

“full band” Seebeck coefficient



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.

understanding Seebeck coefficients



$$S_n = -\frac{E_J - F_n}{qT_L}$$

- 1) $|S|$ is large for a non-degenerate semiconductor because the current carrying channels are way above (below) the Fermi level.
- 2) $|S|$ is small for a degenerate semiconductor (or metal) because the current flows near the Fermi energy.

outline

- 1) Introduction
- 2) Charge transport in a temperature gradient
- 3) Mathematical formulation
- 4) Discussion
- 5) **Summary**



This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 3.0 United States License.

<http://creativecommons.org/licenses/by-nc-sa/3.0/us/>

mathematical description

The answer is:

$$J_{nx} = \sigma_n \frac{d(F_n/q)}{dx} - S_n \sigma_n \frac{dT_L}{dx}$$

S_n is the Seebeck coefficient in V/K.

Alternatively, we can write this equation as:

$$\frac{d(F_n/q)}{dx} = \rho_n J_{nx} + S_n \frac{dT_L}{dx}$$

(inverted form of the equations)

transport parameters

$$\sigma_n = \int \sigma'_n(E) dE$$

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

$$S_n = \left(-\frac{1}{qT_L} \right) (E_J - E_F)$$

$$S_n = \left(-\frac{1}{qT_L} \right) \frac{\int (E - E_F) \sigma'_n(E) dE}{\int \sigma'_n(E) dE}$$

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

$$\delta_n = \frac{\int \frac{(E - E_C)}{k_B T_L} \sigma'_n(E) dE}{\int \sigma'_n(E) dE}$$

questions

- 1) Introduction
- 2) Charge transport in a temperature gradient
- 3) Mathematical formulation
- 4) Discussion
- 5) Summary

