Notes on Bipolar Thermal Conductivity

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1. Electronic thermal conductivity

Basic equations:

$$\sigma = \int_{-\infty}^{+\infty} \sigma'(E)\,dE = \sigma_n + \sigma_p \tag{1a}$$

$$S = -\frac{1}{qT}\frac{\int_{-\infty}^{+\infty}(E-E_F)\sigma'(E)\,dE}{\int_{-\infty}^{+\infty}\sigma'(E)\,dE} \tag{1b}$$

$$S_T = -\frac{1}{qT}\int_{-\infty}^{+\infty}(E-E_F)\sigma'(E)\,dE = S_{Tn} + S_{Tp} \tag{1c}$$

$$\kappa_0 = \frac{1}{q^2T}\int_{-\infty}^{+\infty}(E-E_F)^2\sigma'(E)\,dE = \kappa_{0n} + \kappa_{0p} \tag{1d}$$

$$\kappa_e = \kappa_0 - T\sigma S^2 \,. \tag{1e}$$

The quantities, σ, S_T, and κ_0 add; if we have two bands, we just add the contribution from each band. The quantities, S and κ_e do not add. It is easy to show that

$$S = \frac{\sigma_n S_n + \sigma_p S_p}{\sigma_n + \sigma_p}\,. \tag{2}$$

From (1e) we find:

$$\kappa_e = \kappa_{0n} + \kappa_{0p} - T\left(\sigma_n + \sigma_p\right)\left[\frac{\sigma_n S_n + \sigma_p S_p}{\sigma_n + \sigma_p}\right]^2. \tag{3}$$

Now write this as

$$\begin{aligned}\kappa_e &= \left(\kappa_{0n} - T\sigma_n S_n\right) + \left(\kappa_{0p} - T\sigma_p S_p\right) \\ &\quad + \frac{T}{\left(\sigma_n + \sigma_p\right)}\left[-\left(\sigma_n S_n + \sigma_p S_p\right)^2 + \left(\sigma_n + \sigma_p\right)\sigma_n S_n + \left(\sigma_n + \sigma_p\right)\sigma_p S_p\right].\end{aligned} \tag{4}$$

The electronic thermal conductivity for the conduction band alone is

$$\kappa_e = \kappa_{0n} - T\sigma_n S_n, \tag{5a}$$

and for the valence band alone,

$$\kappa_p = \kappa_{0p} - T\sigma_p S_p, \tag{5b}$$

Using (5a) and (5b) in (4):

$$\begin{aligned}\kappa_e &= \kappa_{en} + \kappa_{ep} + \frac{T}{\left(\sigma_n + \sigma_p\right)} \times \\ &\left[-\left(\sigma_n S_n + \sigma_p S_p\right)^2 + \left(\sigma_n + \sigma_p\right)\sigma_n S_n^2 + \left(\sigma_n + \sigma_p\right)\sigma_p S_p^2\right]\end{aligned} \tag{6}$$

$$\begin{aligned}\kappa_e &= \kappa_{en} + \kappa_{ep} + \frac{T}{\left(\sigma_n + \sigma_p\right)} \times \\ &\left[-\sigma_n^2 S_n^2 - \sigma_p^2 S_p^2 - 2\sigma_n \sigma_p S_n S_p + \sigma_n^2 S_n^2 + \sigma_p \sigma_n S_n^2 + \sigma_p^2 S_p^2 + \sigma_n \sigma_p S_p^2\right]\end{aligned}$$

$$\kappa_e = \kappa_{en} + \kappa_{ep} + \frac{T}{\left(\sigma_n + \sigma_p\right)} \times \left[-2\sigma_n \sigma_p S_n S_p + \sigma_p \sigma_n S_n^2 + \sigma_n \sigma_p S_p^2\right]$$

$$\kappa_e = \kappa_{en} + \kappa_{ep} + T\frac{\sigma_n \sigma_p}{\left(\sigma_n + \sigma_p\right)} \times \left[-2S_n S_p + S_n^2 + S_p^2 \right]$$

$$\boxed{\kappa_e = \kappa_{en} + \kappa_{ep} + T\frac{\sigma_n \sigma_p}{\left(\sigma_n + \sigma_p\right)} \left(S_p - S_n\right)^2}. \tag{7}$$

This is our answer. The electronic thermal conductivity consists of a contribution due to the conduction band alone, another contribution due to the valence band alone, and a bipolar contribution. It is easy to see that the bipolar contribution is important only when $\sigma_n \approx \sigma_p$.

2. Lorenz Number

The Lorenz number we get including bipolar conduction is:

$$\mathcal{L} = \frac{\kappa_e}{\sigma T} \tag{8}$$

$$\boxed{\mathcal{L} = \frac{\kappa_{en}}{\sigma_n T} \frac{\sigma_n}{\left(\sigma_n + \sigma_p\right)} + \frac{\kappa_{ep}}{\sigma_p T} \frac{\sigma_p}{\left(\sigma_n + \sigma_p\right)} + \sigma_n \sigma_p \left(\frac{S_p - S_n}{\sigma_n + \sigma_p} \right)^2}$$

The first two terms in (8) are easy to understand – they represent the weighted contributions from each of the two bands. The third term requires some discussion.

To estimate the magnitude of the bipolar contributions, assume that $\sigma_n \approx \sigma_p$, then

$$\mathcal{L} = \frac{\kappa_{en}}{2\sigma_n T} + \frac{\kappa_{ep}}{2\sigma_p T} + \frac{\left(S_p - S_n\right)^2}{4}$$

We also know that at mid-gap:

$$S_p \approx -S_n = S \approx \frac{E_G}{2qT} .$$

The normalized Lorenz number is

$$\mathcal{L}' = \frac{\mathcal{L}}{\left(k_B/q\right)^2} = \frac{\kappa_{en}}{2\sigma_n T \left(k_B/q\right)^2} + \frac{\kappa_{ep}}{2\sigma_p T \left(k_B/q\right)^2} + \left(\frac{E_G}{2k_B T} \right)^2$$

So the bipolar contribution to the normalized Lorenz number is

$$\mathcal{L}'_{bipolar} = \left(\frac{E_G}{2k_B T} \right)^2 . \qquad (9)$$

3. Physical picture of bipolar thermal conduction

$$J = \sigma \frac{dE_F}{dx} - \sigma S \frac{dT}{dx} \qquad (10)$$

$$J_Q = T\sigma S \frac{dE_F}{dx} - \kappa_0 \frac{dT}{dx} \qquad (11)$$

Case 1: Holes only.
Under open-circuit conditions:

$$J_p = \sigma_p \frac{dE_F}{dx} - \sigma_p S_p \frac{dT}{dx} = 0 \qquad (12)$$

$$\frac{dE_F}{dx} = S_p \frac{dT}{dx} \qquad (13)$$

Insert (13) in (11)

$$J_Q = T\sigma_p S_p^2 \frac{dT}{dx} - \kappa_0 \frac{dT}{dx} = \left[T\sigma_p S_p^2 - \kappa_0 \right] \frac{dT}{dx}$$

$$J_Q = -\left[\kappa_0 - T\sigma_p S_p^2 \right] \frac{dT}{dx} = -\kappa_e \frac{dT}{dx} . \qquad (14)$$

The physical picture is shown in Fig. 1 below. The electrical current is zero, but the heat current is not zero. Hotter holes move to the left, and cooler holes move to the right.

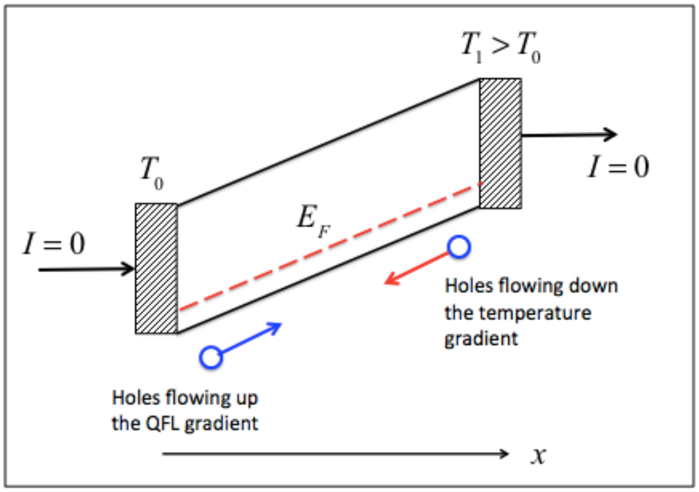

Fig. 1. Illustration of hole current flow under electrically open circuit conditions with a temperature gradient applied. Hole diffusion down the temperature gradient and up the QFL gradient precisely balance electrically but not thermally.

Now consider what happens when there are **both** electrons and holes. From (10):

$$J_p + J_n = \left(\sigma_p + \sigma_n\right)\frac{dE_F}{dx} - \left(\sigma_p S_p + \sigma_n S_n\right)\frac{dT}{dx} = 0 \tag{15}$$

$$\frac{dE_F}{dx} = \left(\frac{\sigma_p S_p + \sigma_n S_n}{\sigma_p + \sigma_n}\right)\frac{dT}{dx} \tag{16}$$

This gradient of the QFL drives **both** the hole and electron currents, and it depends on both the hole and electron conductivities. Compare (16) to (13). Since S_n is negative, the numerator of (6) is reduced, and the denominator is also larger, so the gradient of the QFL is reduced. Accordingly, the first term on the RHS of (12) is reduced, so now $J_p \neq 0$; $J_p < 0$. There is a net hole current to the left. What direction is the electron current?

For the electron current, we begin with (10) for the conduction band:

$$J_n = \sigma_n \frac{dE_F}{dx} - \sigma_n S_n \frac{dT}{dx} \tag{17}$$

Now use (16) in (17):

$$J_n = \sigma_n \left\{\left(\frac{\sigma_p S_p + \sigma_n S_n}{\sigma_p + \sigma_n}\right)\frac{dT}{dx}\right\} - \sigma_n S_n \frac{dT}{dx} \tag{18}$$

The electron current depends on the hole conductivity and hole Soret coefficient, because they determine the gradient of the QFL. From (18)

$$J_n = \left(\frac{\sigma_n \sigma_p S_p}{\sigma_p + \sigma_n}\right)\frac{dT}{dx} + \left(\frac{\sigma_n^2 S_n}{\sigma_p + \sigma_n}\right)\frac{dT}{dx} - \left(\frac{\sigma_p \sigma_n S_n}{\sigma_p + \sigma_n}\right)\frac{dT}{dx} - \left(\frac{\sigma_n^2 S_n}{\sigma_p + \sigma_n}\right)\frac{dT}{dx}$$

$$J_n = \frac{\sigma_n \sigma_p}{\sigma_p + \sigma_n}\left(S_p - S_n\right) > 0 \tag{19}$$

The electron current is positive; electrons flow to the left. Now use (16) in (12) to examine the hole current.

$$J_p = \sigma_p \left\{ \left(\frac{\sigma_p S_p + \sigma_n S_n}{\sigma_p + \sigma_n} \right) \frac{dT}{dx} \right\} - \sigma_p S_p \frac{dT}{dx}$$

$$J_p = -\frac{\sigma_n \sigma_p}{\sigma_p + \sigma_n}\left(S_p - S_n\right)\frac{dT}{dx} = -J_n \tag{20}$$

The hole current is negative; holes also flow to the left.

The physical picture is shown below – both electrons and holes flow to the left and recombine at the contact, but the currents are in opposite directions, so they cancel.

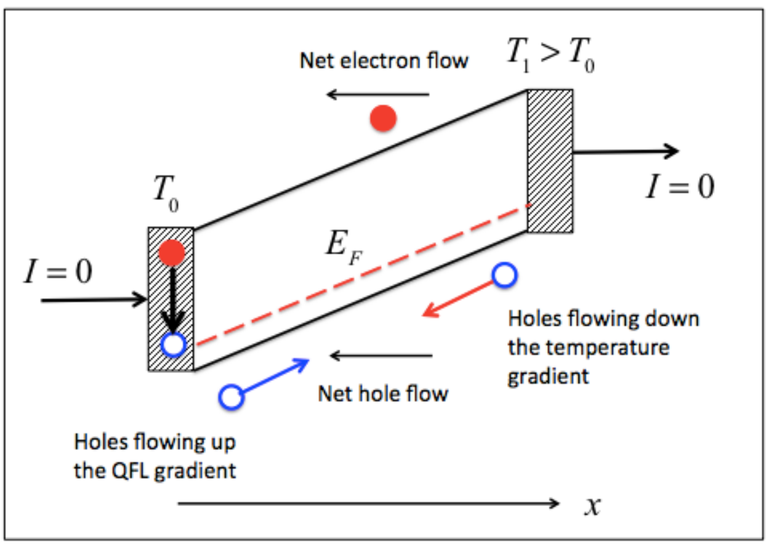

Fig. 2 Illustration of hole and electron current flow under electrically open circuit conditions with a temperature gradient applied. Minority carriers have lowered the QFL gradients so that hole diffusion down the temperature gradient and up the QFL gradient no longer precisely balance electrically. Holes flow to the left contact at precisely the same rate at which electrons flow to the left contact. In the contact, electrons and holes recombine, giving up an energy a little larger than the band gap. This process constitutes the bipolar heat conduction.

Discussion:

We are most interested in extrinsic samples doped to operate at maximum zT. Consider an extrinsic, p-type sample: $\sigma_p >> \sigma_n$. Equation (20) becomes

$$J_p = -\sigma_n \left(S_p - S_n \right) \frac{dT}{dx} = -J_n . \tag{21}$$

The minority carrier conductivity controls both currents. When $\sigma_n \to 0$, $J_p \to 0$, as considered in Case 1.

The physics of bipolar heat conduction was illustrated in Fig. 2. How can we understand this better? Recall the electronic thermal conductivity from (7):

$$\kappa_e = \kappa_{en} + \kappa_{ep} + T \frac{\sigma_n \sigma_p}{\left(\sigma_n + \sigma_p \right)} \left(S_p - S_n \right)^2 . \tag{22}$$

The heat carried by the bipolar component is

$$J_Q^{bip} = -\kappa_{bip} \frac{dT}{dx} = -T \frac{\sigma_n \sigma_p}{\left(\sigma_n + \sigma_p \right)} \left(S_p - S_n \right)^2 \frac{dT}{dx} . \tag{23}$$

How does this relate to the electrical current?

From (20), we find

$$J_p = -\frac{\sigma_n \sigma_p}{\sigma_p + \sigma_n} \left(S_p - S_n \right) \frac{dT}{dx} , \tag{24}$$

which can be used in (13) to write

$$\frac{J_Q^{bip}}{J_p} = T \left(S_p - S_n \right), \tag{25}$$

which has a nice physical interpretation as discussed below.

Recall that the Seebeck coefficient is related to the average energy at which current flows, E_J, with respect to the Fermi level:

$$S = -\frac{E_J - E_F}{qT} . \tag{26}$$

For the conduction band,

$$S_n = -\frac{E_C + \Delta_n - E_F}{qT} . \tag{27a}$$

and for the valence band,

$$S_p = -\frac{E_V - \Delta_p - E_F}{qT} . \tag{27b}$$

Here, Δ_n is how far above the bottom of the conduction band current flows ($\Delta_n = 2k_BT$ for a non-degenerate semiconductor, and Δ_p is how far below the top of the valence band current flows.) Using (27a) and (27b) in (25), we find

$$\frac{J_Q^{bip}}{J_p} = \frac{\left(E_G + \Delta_n + \Delta_p\right)}{q} \tag{28}$$

or

$$J_Q^{bip} = \left(E_G + \Delta_n + \Delta_p\right)\left(J_p/q\right) \tag{29}$$

The physical interpretation is that the flux of electrons and holes to the contact ($J_n/q = -J_p/q$) times the energy given up when they recombine (slightly larger than the bandgap) represents bipolar heat flow.

References

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