

Thermoelectricity: From Atoms to Systems

Week 5: Recent advances in thermoelectric materials and physics
Tutorial 5.1 [Homework solutions, problems 1-6](#)

By Je-Hyeong Bahk and Ali Shakouri
Electrical and Computer Engineering
Birck Nanotechnology Center
Purdue University

Prob. 1. Differential conductivity and $S - \sigma$ trade-off

Differential Conductivity (Transport Distribution Function)

$$\sigma_d(E) = e^2 \tau(E) v_x^2(E) \rho_{DOS}(E) \left(-\frac{\partial f_0(E)}{\partial E} \right)$$

$$ZT = \frac{S^2 \sigma}{\kappa_l + \kappa_e} T$$

$$\sigma = \sum \int \sigma_d(E) dE$$

$$S = \sum \left(\frac{k_B}{q} \right) \int \left[\frac{(E - E_F)}{k_B T} \right] \frac{\sigma_d(E)}{\sigma} dE$$

$$\kappa_e = \sum T \left(\frac{k_B}{q} \right)^2 \int \left[\frac{E - E_F}{k_B T} \right]^2 \sigma_d(E) dE - S^2 \sigma T$$

$\sum$: sum of bands

$\left\{ \begin{array}{l} q = -e \text{ (conduction band)} \\ q = +e \text{ (valence band)} \end{array} \right.$

Comparison with Landauer formalism in diffusive limit (see week 2 lectures)

$$\tau(E) v_x^2(E) \rho_{DOS}(E) = \frac{2L}{hA} M(E) T(E)$$

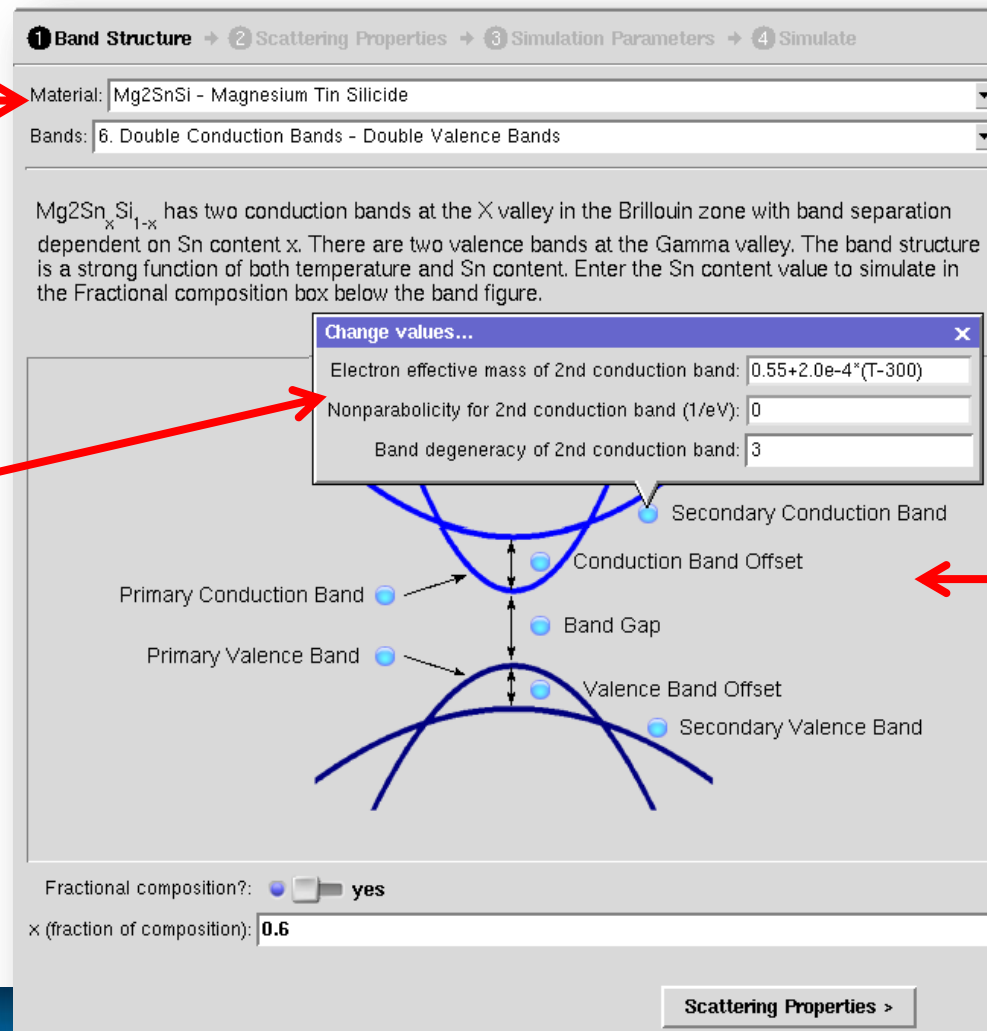
Prob. 1. Differential conductivity and $S - \sigma$ trade-off

The thermoelectric material properties simulation tool

<https://nanohub.org/tools/btesolver>

Built-in
materials
library

Band properties
as a function of
composition x and
temperature T



Customizable
band structure
(Max. 2 cond.
bands and 2 val.
Bands)

Convenient
graphical user
interface for
band structure
edits

Prob. 1. Differential conductivity and $S - \sigma$ trade-off

The thermoelectric material properties simulation tool

<https://nanohub.org/tools/btesolver>

Three scattering options:

1. Constant τ
2. Constant m.f.p.
3. Realistic E-dependent $\tau(E)$

Enable/disable specific scattering mechanisms

The screenshot displays the 'Scattering Properties' tab of the BTE solver tool. The interface includes a progress bar at the top with steps: 1 Band Structure, 2 Scattering Properties (active), 3 Simulation Parameters, and 4 Simulate. A dropdown menu for 'Scattering Options' is open, showing 'Energy-Dependent Scattering Time' as the selected option, with other options being 'Constant Scattering Time' and 'Constant Mean Free Path'. Below this, various material parameters are input, including 'Elastic modulus (N/m^2)' as 10.2e10 and 'Optical phonon energy (eV)' as .0314*(1-x)+0.0376*x. Several scattering mechanisms are listed with 'Enable' checkboxes: 'Acoustic phonon deformation potential scattering' (yes), 'Optical phonon deformation potential scattering' (no), 'Ionized impurity scattering' (yes), 'Defect vacancy deformation potential scattering' (no), 'Polar optical phonon scattering' (yes), and 'Alloy scattering' (yes). Some mechanisms have additional parameters, such as 'Ac. ph. deform. potential (eV)' as 5.92, 'Compensation ratio' as 1, 'r-factor (energy exponent)' as .49, and 'Alloy scattering potential' as 0.26+0.3*x. Navigation buttons at the bottom are '< Band Structure' and 'Simulation Parameters >'.

Prob. 1. Differential conductivity and $S - \sigma$ trade-off

1-1. In a single non-parabolic band (n-type $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$)

Select “n-InGaAlAs – n-type Indium Gallium Aluminum Arsenide”

The effective mass
and
nonparabolicity
are a function of
composition x

Enter “0” for x

Prob. 1. Differential conductivity and $S - \sigma$ trade-off

1-1. In a single non-parabolic band (n-type $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$)

2nd phase:

Select “Constant Scattering Time” option

1 Band Structure → 2 Scattering Properties → 3 Simulation Parameters → 4 Simulate

Scattering Options: Constant Scattering Time

Scattering Time (ps): 0.1

Enter “0.1” ps for scattering time.



3rd phase:

Select “Differential Conductivity Analysis” option

1 Band Structure → 2 Scattering Properties → 3 Simulation Parameters → 4 Simulate

Analysis type: Differential Conductivity Analysis

Options

Type of carrier concentration is Electron

Fermi level (eV): 0 relative to 1st Conduction Band Edge

Cut-Off energy level (eV): 0 relative to 1st Conduction Band Edge

Temperature (K): 300

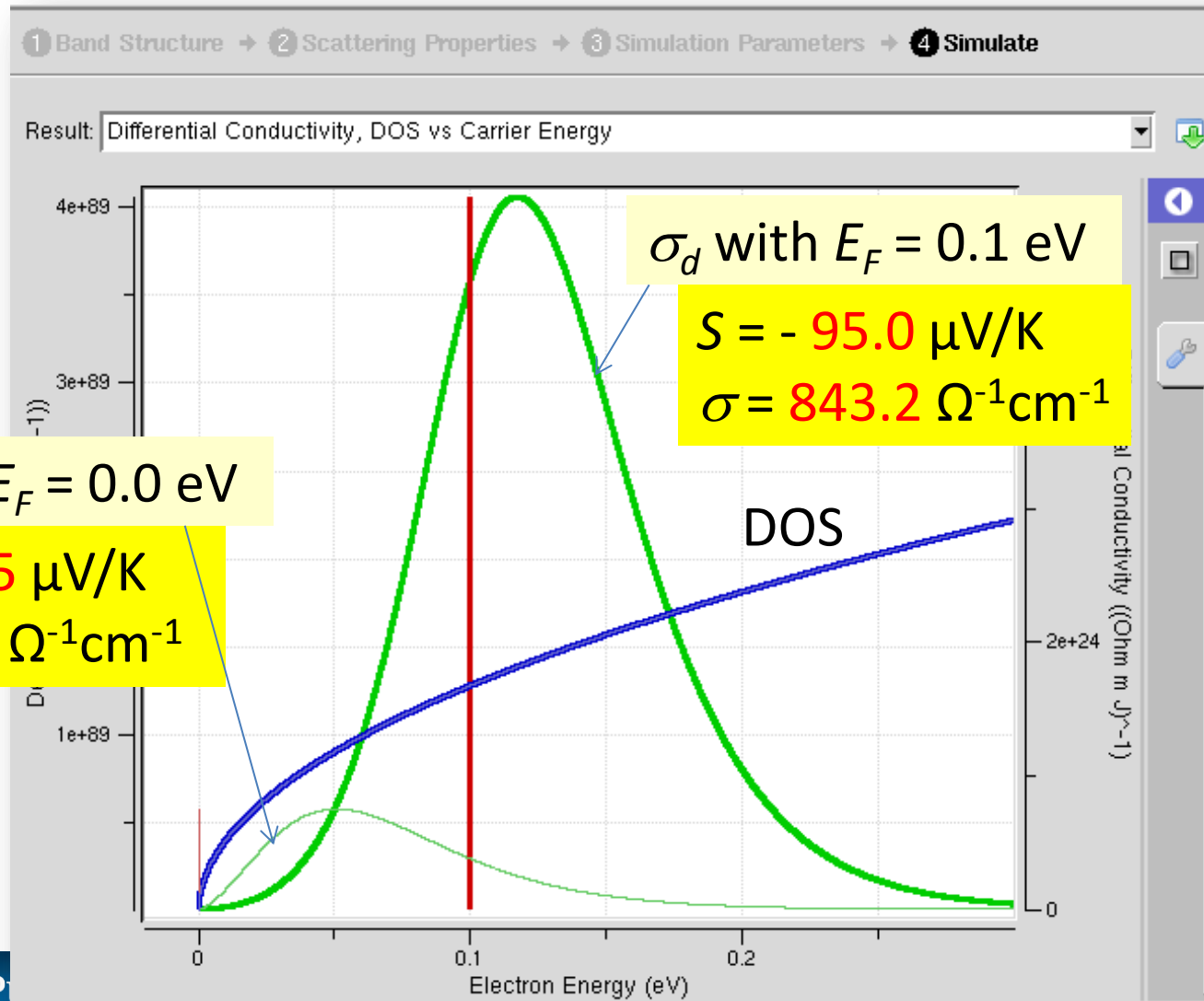
Lattice thermal conductivity (W/mK): 4

* Note: Lattice thermal conductivity can be a function of x (fractional composition) and T (temperature). For example, enter '5.0-0.03*(T-300)+0.2*(1-x)^2' without the quotation marks.

Enter values here

Prob. 1. Differential conductivity and $S - \sigma$ trade-off

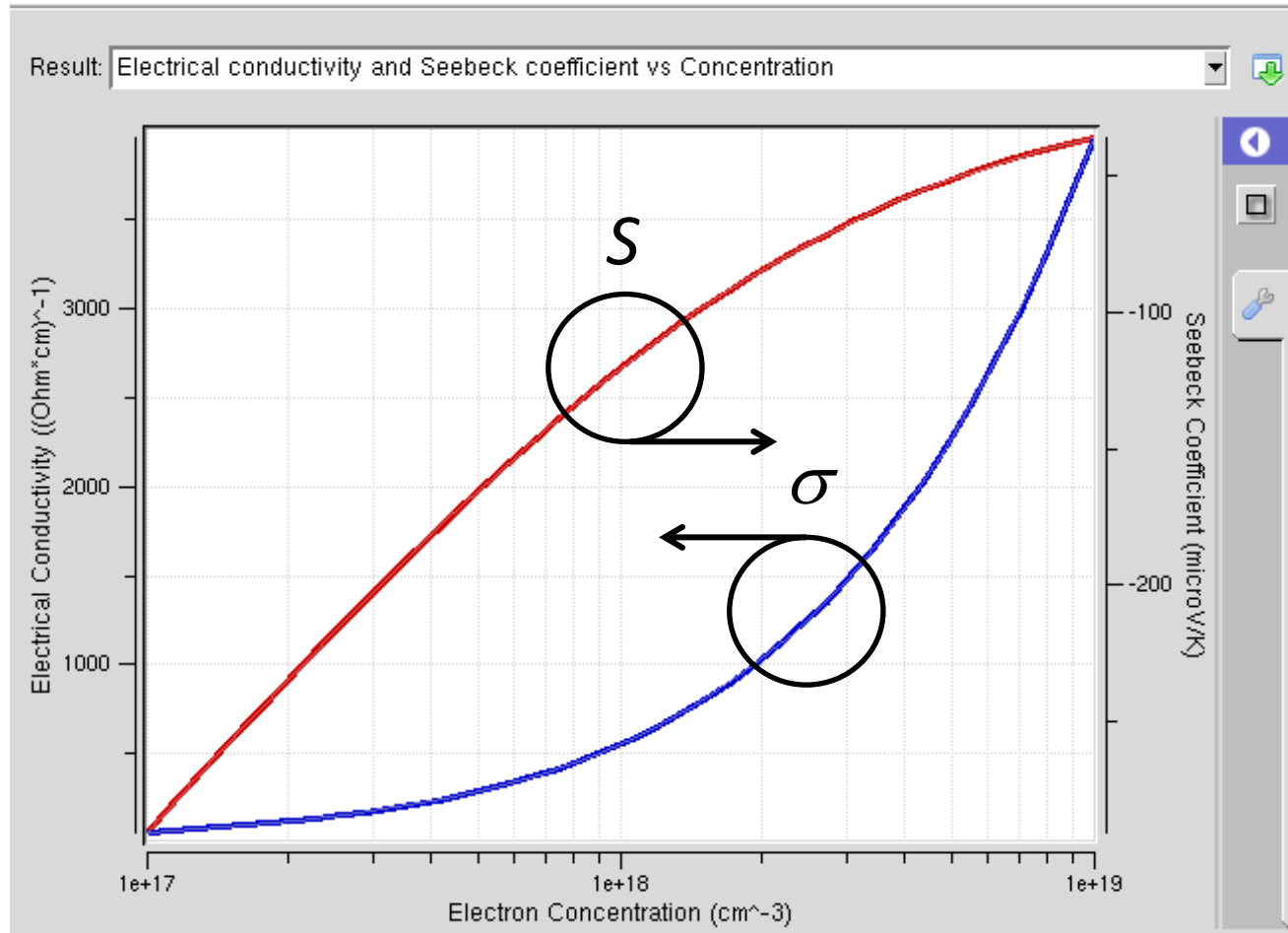
1-1 & 1-2. Differential conductivity vs. energy



Prob. 1. Differential conductivity and $S - \sigma$ trade-off

1-3 & 1-4. Seebeck coeff. and electrical cond. trade-off

Carrier concentration scan from $1e17$ to $1e19 \text{ cm}^{-3}$

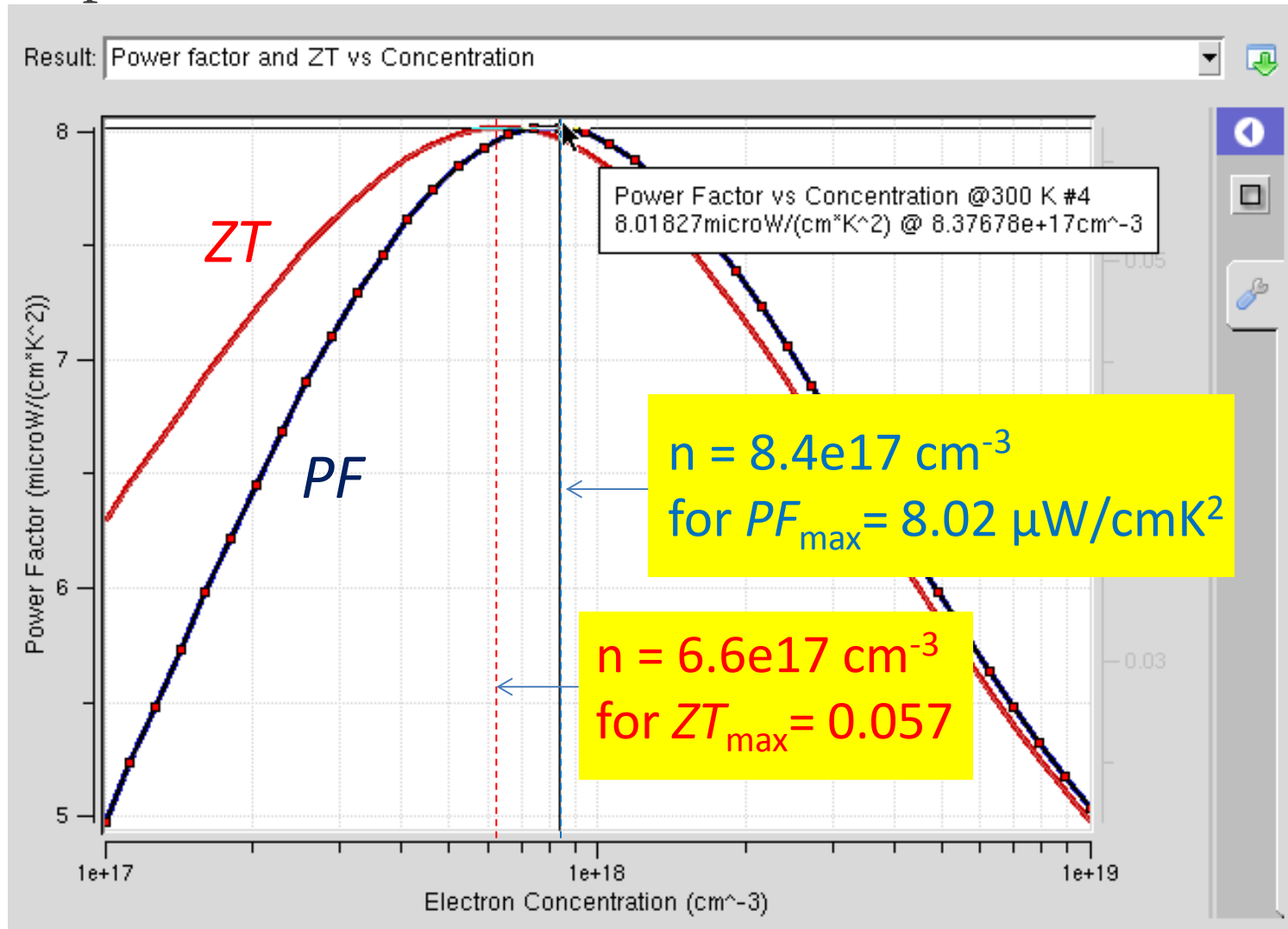


n-InGaAs
300 K
 $\tau = 0.1 \text{ ps}$

Prob. 1. Differential conductivity and $S - \sigma$ trade-off

1-3 & 1-4. Optimal carrier concentrations for PF and ZT

n-InGaAs
300 K
 $\tau = 0.1$ ps

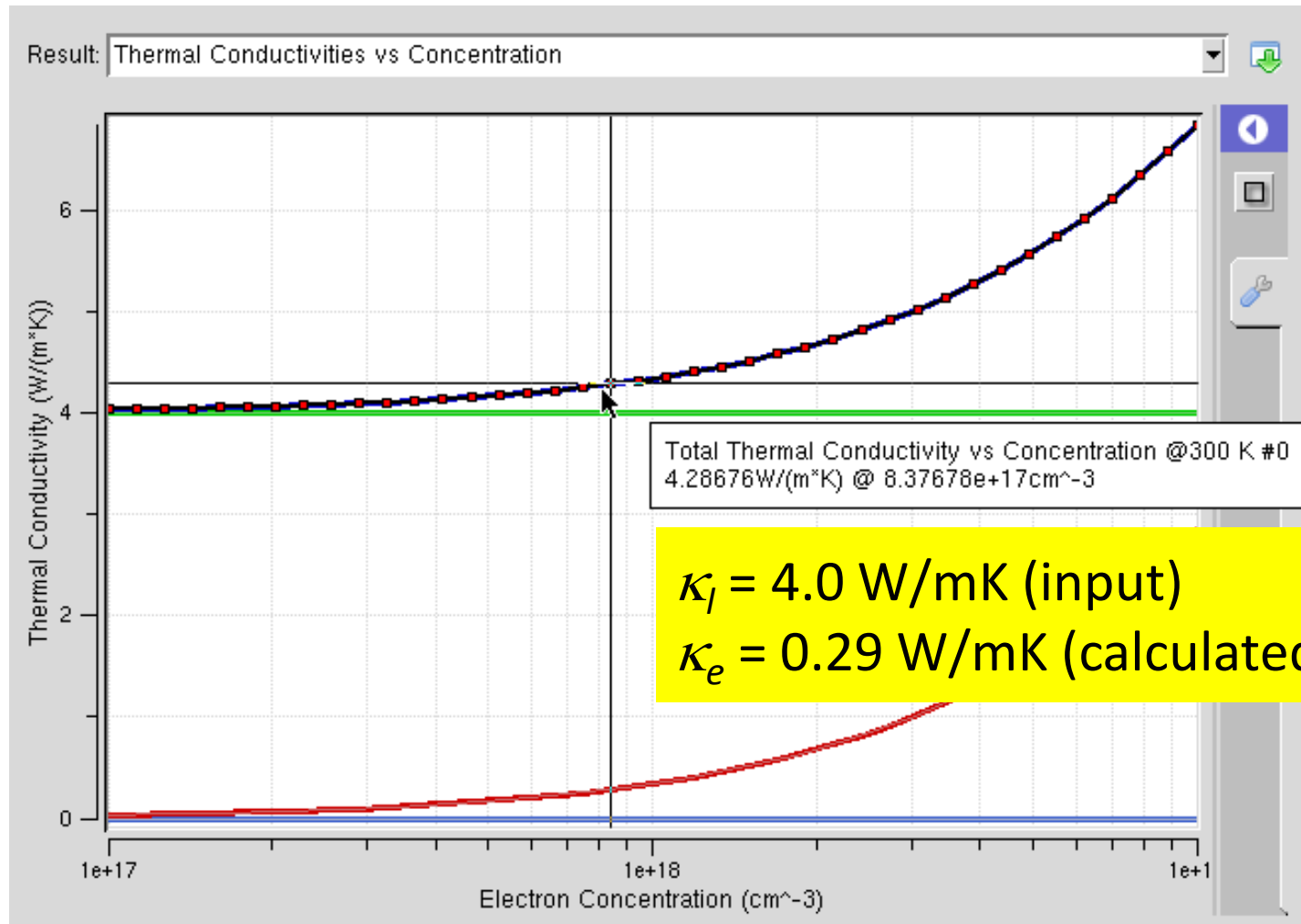


Prob. 1. Differential conductivity and $S - \sigma$ trade-off

1-3 & 1-4.
(cont'd)

Electronic thermal conductivity increases with carrier concentration

n-InGaAs
300 K
 $\tau = 0.1$ ps



Prob. 2. Influence of a secondary band

2-1

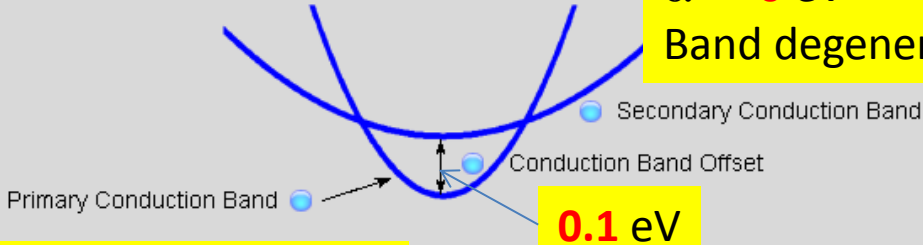
Add a secondary conduction band by choosing “double conduction bands” option

1 Band Structure → **2 Scattering Properties** → **3 Simulation Parameters** → **4 Simulate**

Material: n-InGaAlAs - n-type Indium Gallium Aluminum Arsenide

Bands: 4. Double Conduction Bands - No Valence Bands

Here we simulate n-type $(\text{In}_{0.53}\text{Ga}_{0.47}\text{As})_{1-x}(\text{In}_{0.52}\text{Al}_{0.48}\text{As})_x$ alloy. This III-V semiconductor alloy has the primary conduction band at the Gamma valley in the Brillouin zone. Although this material also has a valence band at the Gamma valley, we ignore the valence band in this simulation to focus only on electron transport. Enter the Al content x in the Fractional Composition box below the band figure.



Primary Conduction Band

Secondary Conduction Band

Conduction Band Offset

0.1 eV

$m^* = 0.041 m_0$
 $\alpha = 1.167 \text{ eV}^{-1}$
Band degeneracy = 1

$m^* = 0.1 m_0$
 $\alpha = 0 \text{ eV}^{-1}$
Band degeneracy = 1

Fractional composition?: ☒ yes

x (fraction of composition): 0

Scattering Properties >

Prob. 2. Influence of a secondary band

2-1

Double bands

$$S = -120.1 \mu\text{V/K}$$

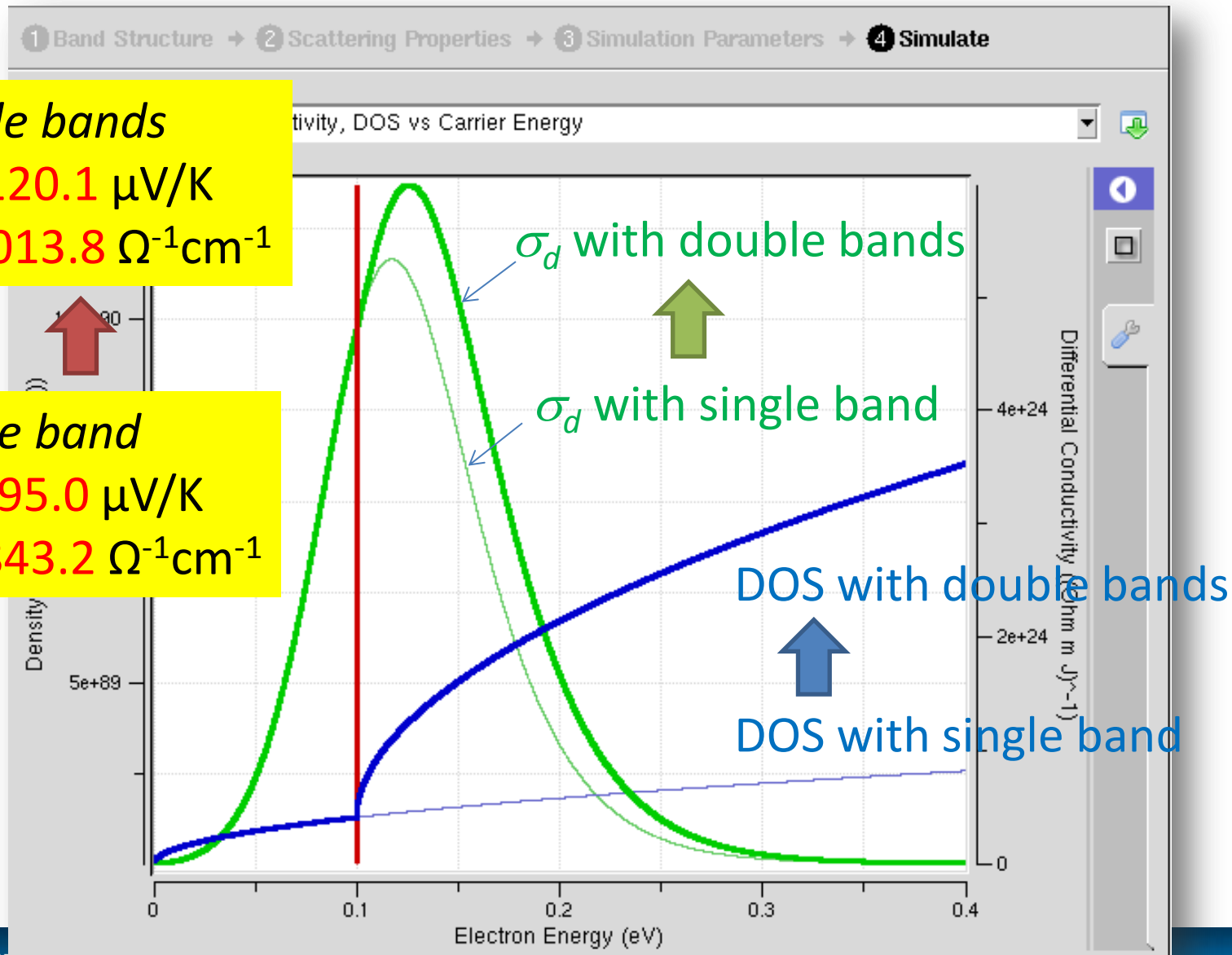
$$\sigma = 1013.8 \Omega^{-1}\text{cm}^{-1}$$

Single band

$$S = -95.0 \mu\text{V/K}$$

$$\sigma = 843.2 \Omega^{-1}\text{cm}^{-1}$$

300 K
 $\tau = 0.1 \text{ ps}$



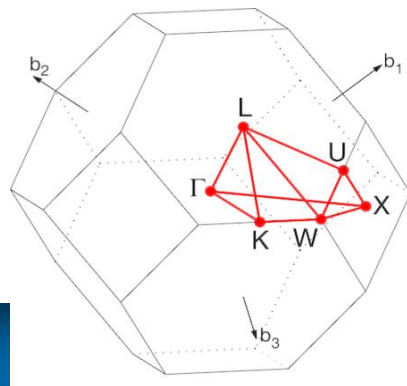
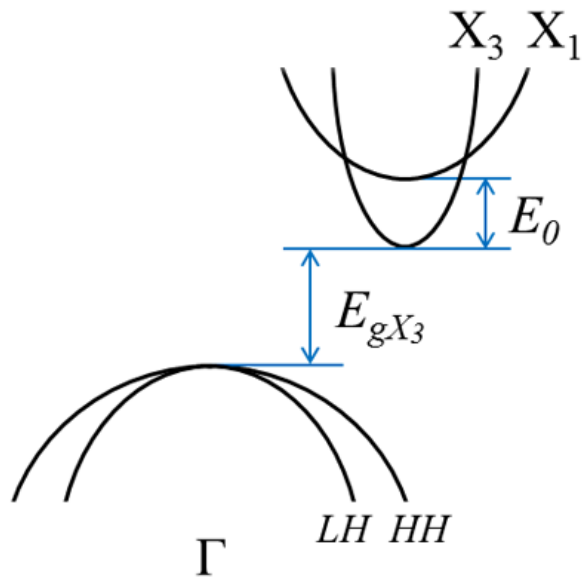
Prob. 2. Influence of a secondary band

2-2 Correct statement? Implication of band convergence effect

- a. The Seebeck coefficient decreased due to the existence of the secondary conduction band because of additional scattering.
- b. The Seebeck coefficient increased because the secondary band increased the differential conductivity above the Fermi level while the differential conductivity below the Fermi level remained the same, so that the degree of asymmetry of the differential conductivity around the Fermi level increased.
- c. The electrical conductivity decreased because the Seebeck coefficient increased by the influence of the secondary band and there are a trade-off between the Seebeck coefficient and the electrical conductivity.
- d. The electrical conductivity increased because the secondary band added more states within the Fermi window.

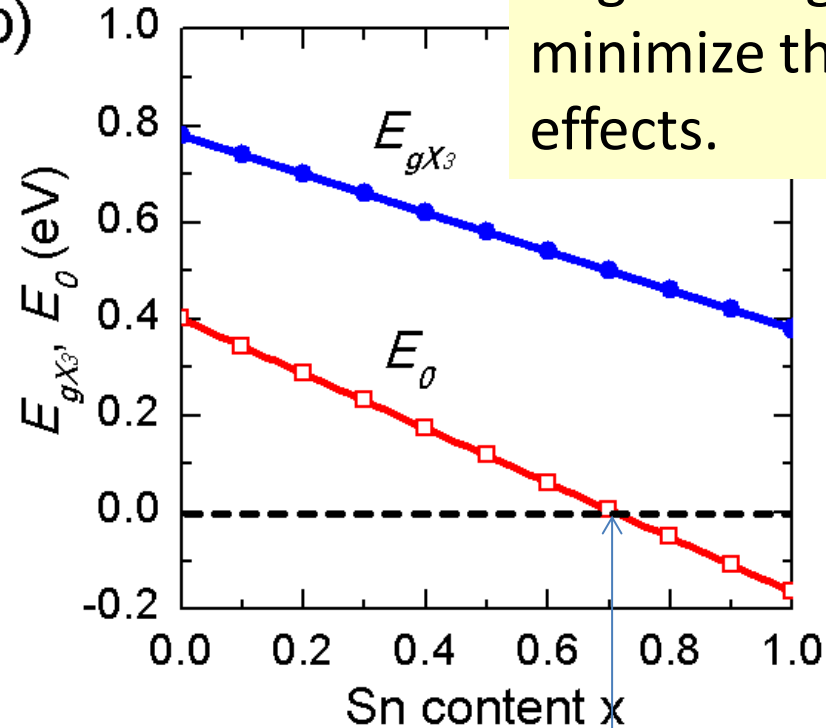
Prob. 3. $\text{Mg}_2\text{Sn}_x\text{Si}_{1-x}$ solid solution

(a)



< First Brillouin zone >

(b)

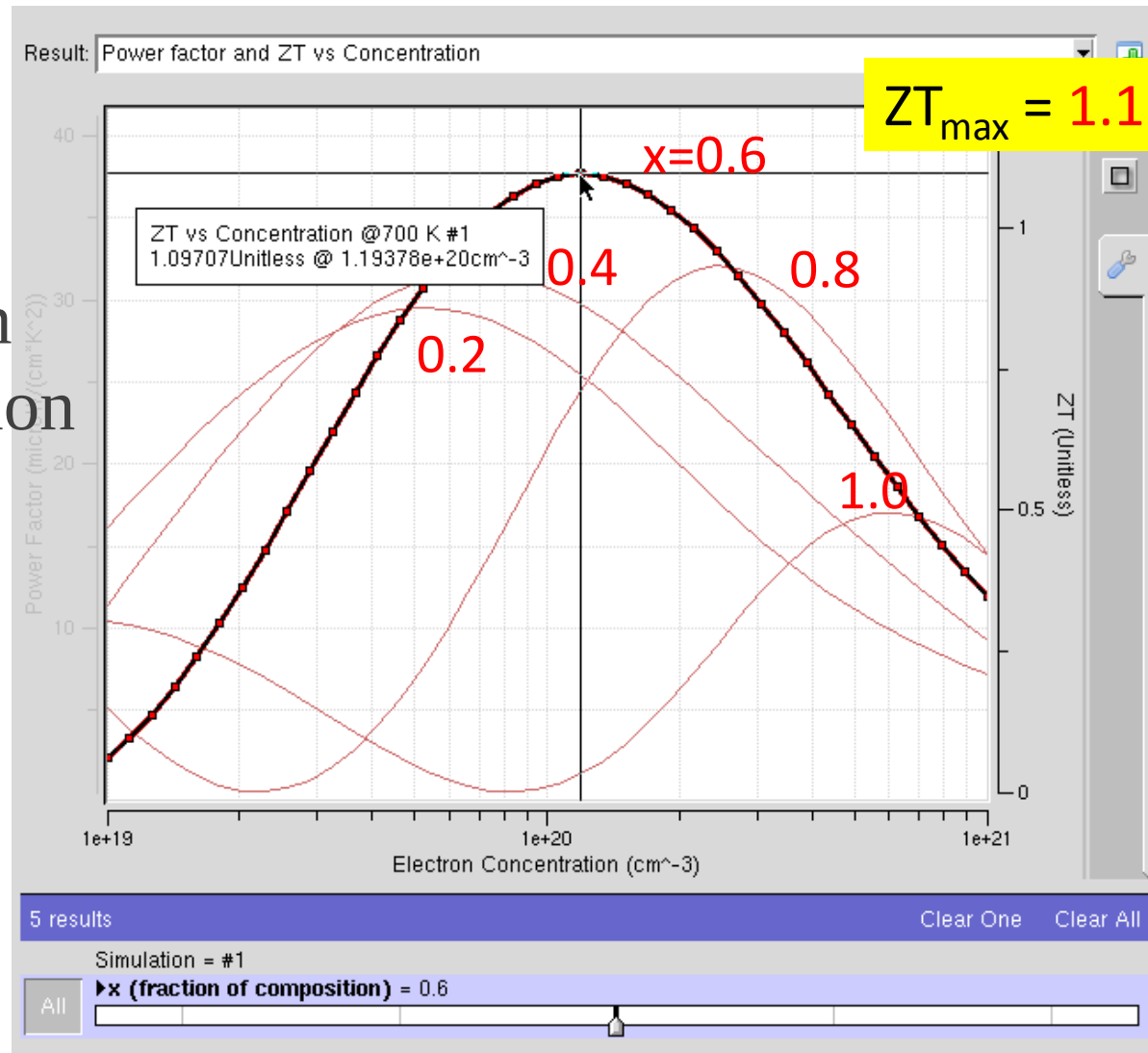


Band gap needs to be large enough to minimize the bipolar effects.

Convergence of the two conduction bands at X valley for $x=0.6 \sim 0.8$

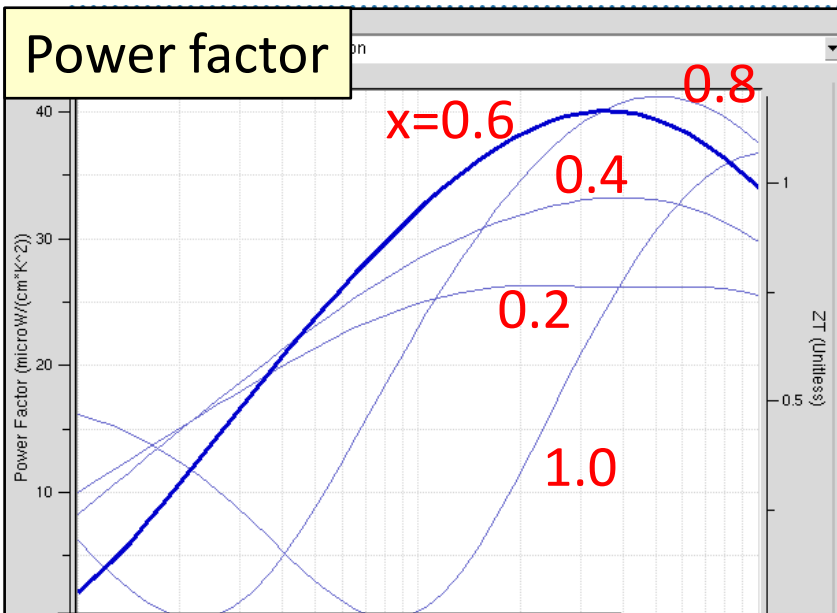
Prob. 3. $\text{Mg}_2\text{Sn}_x\text{Si}_{1-x}$ solid solution

3-1. Composition and carrier concentration co-optimization

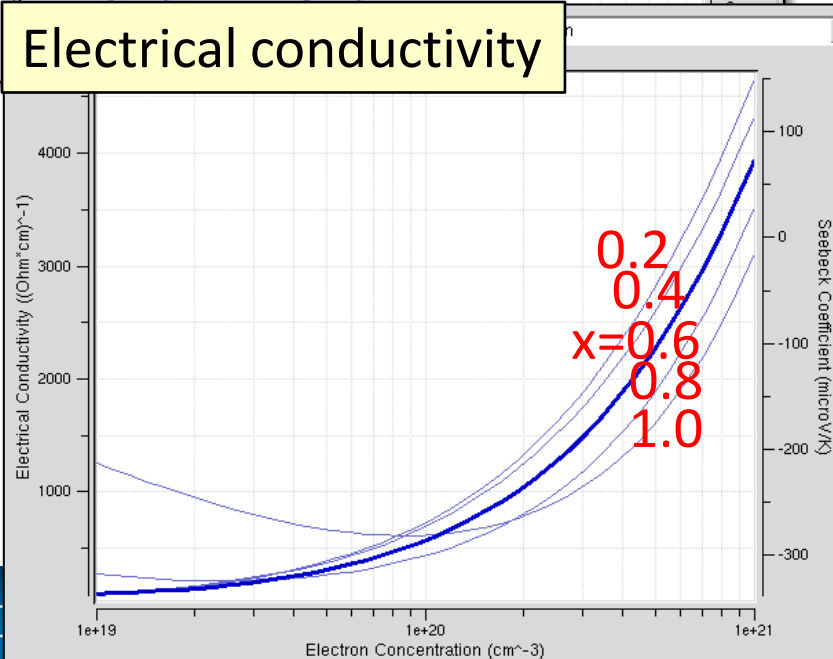


Prob. 3. $\text{Mg}_2\text{Sn}_x\text{Si}_{1-x}$ solid solution

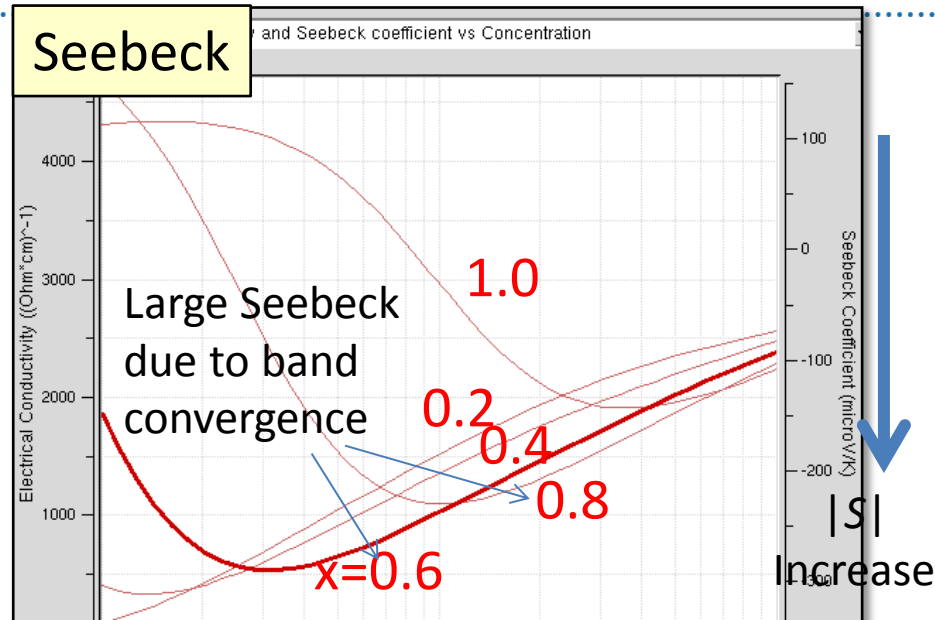
Power factor



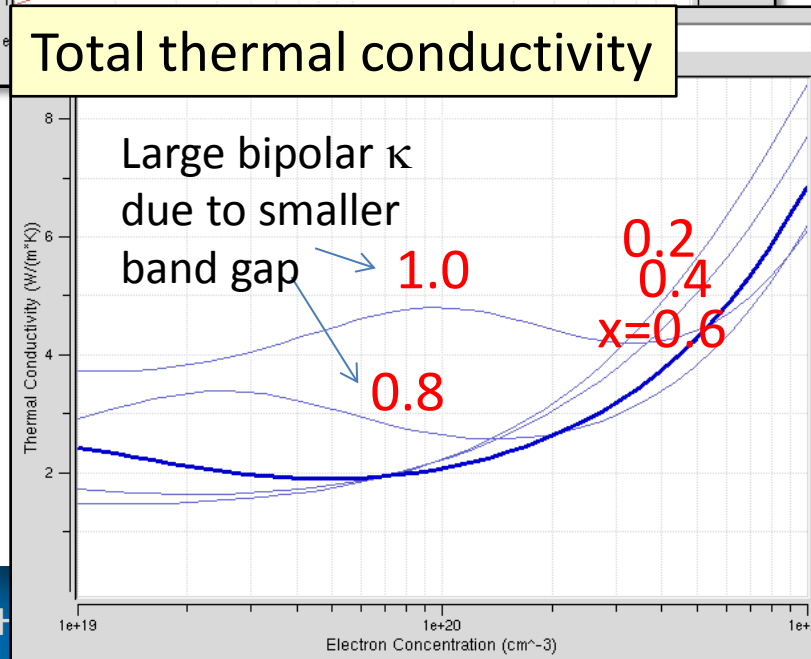
Electrical conductivity



Seebeck



Total thermal conductivity



Prob. 3. $\text{Mg}_2\text{Sn}_x\text{Si}_{1-x}$ solid solution (Sn content)

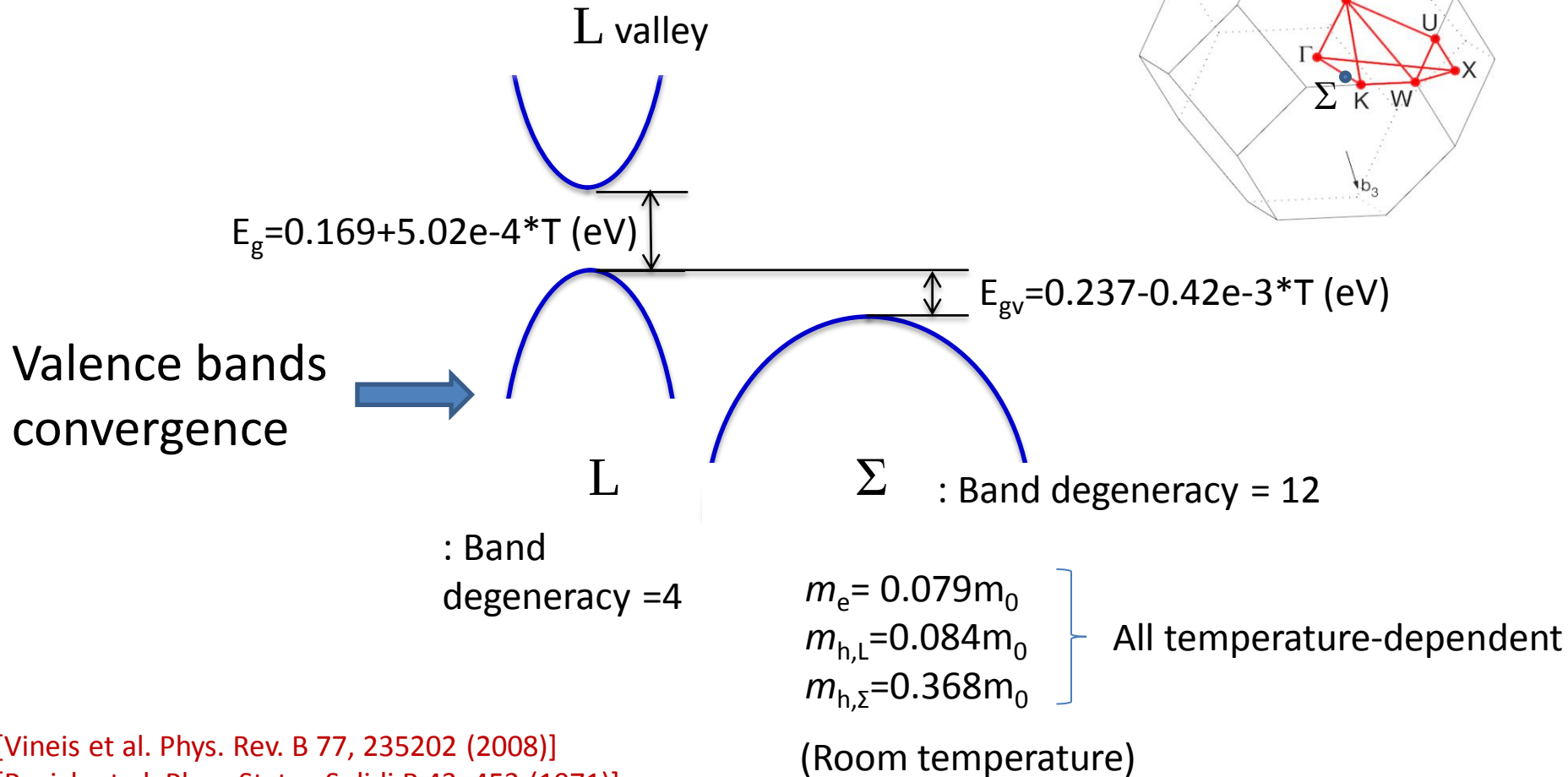
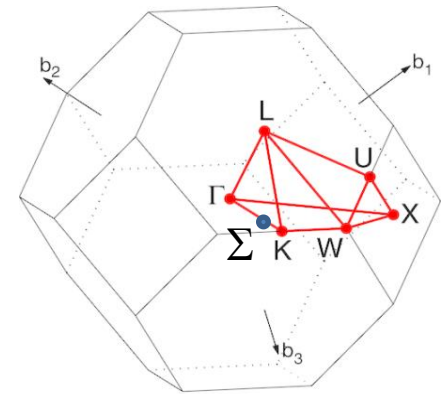
3-2. Band convergence and bipolar thermal conductivity

- a. Large Seebeck coefficients due to the larger separation of the two conduction bands
- b. Large Seebeck coefficients due to the convergence of the two conduction bands
- c. Large electrical conductivity due to the relatively lighter effective mass
- d. Large electrical conductivity due to the relatively heavier effective mass
- e. Smaller electronic thermal conductivity due to smaller lattice thermal conductivity
- f. Smaller electronic thermal conductivity due to the smaller bipolar electronic thermal conductivity with a larger band gap

Prob. 4. Doping optimization of p-type PbTe

Band structure of PbTe

< First Brillouin zone >



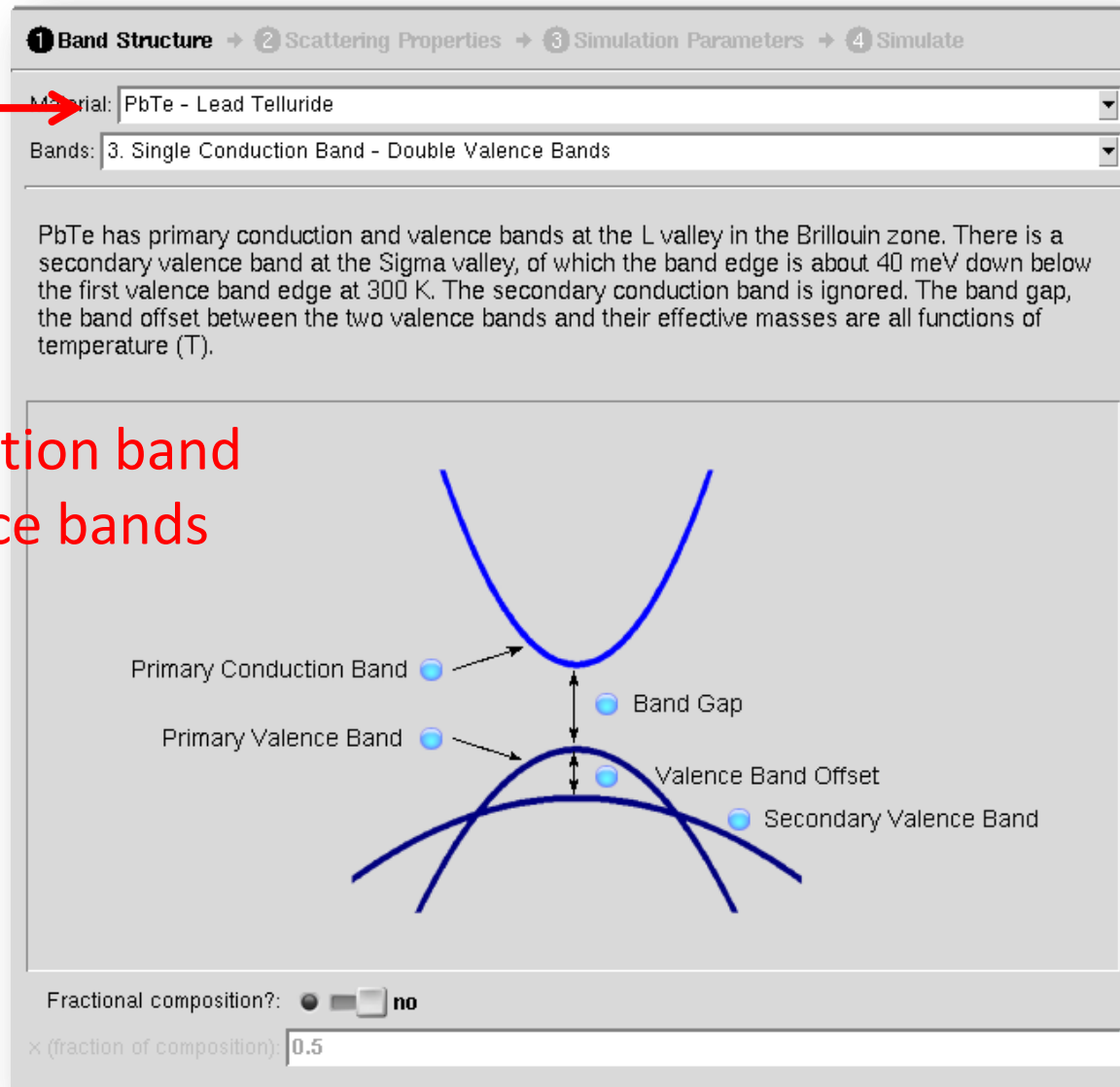
[Vineis et al. Phys. Rev. B 77, 235202 (2008)]

[Ravich et al. Phys. Status Solidi B 43, 453 (1971)]

Prob. 4. Doping optimization of p-type PbTe

PbTe material
selection

One conduction band
Two valence bands



Prob. 4. Doping optimization of p-type PbTe

Energy-dep.
scatterings

1 Band Structure → 2 Scattering Properties → 3 Simulation Parameters → 4 Simulate

Scattering Options: Energy-Dependent Scattering Time

Lattice constant (m): 6.46e-10 Static dielectric constant: 400
Mass density (kg/m³): 8.24e3 High freq. dielectric constant: 33
Elastic modulus (N/m²): 6.3e10 Optical phonon energy (eV): .0136

Acoustic phonon deformation potential scattering
Enable: ☒ yes
Ac. ph. deform. potential (eV): 18

Optical phonon deformation potential scattering
Enable: ☒ yes
Opt. ph. deform. potential (eV): 32

Ionized impurity scattering
Enable: ☒ yes
Compensation ratio: 1

Defect vacancy deformation potential scattering
Enable: ☐ no

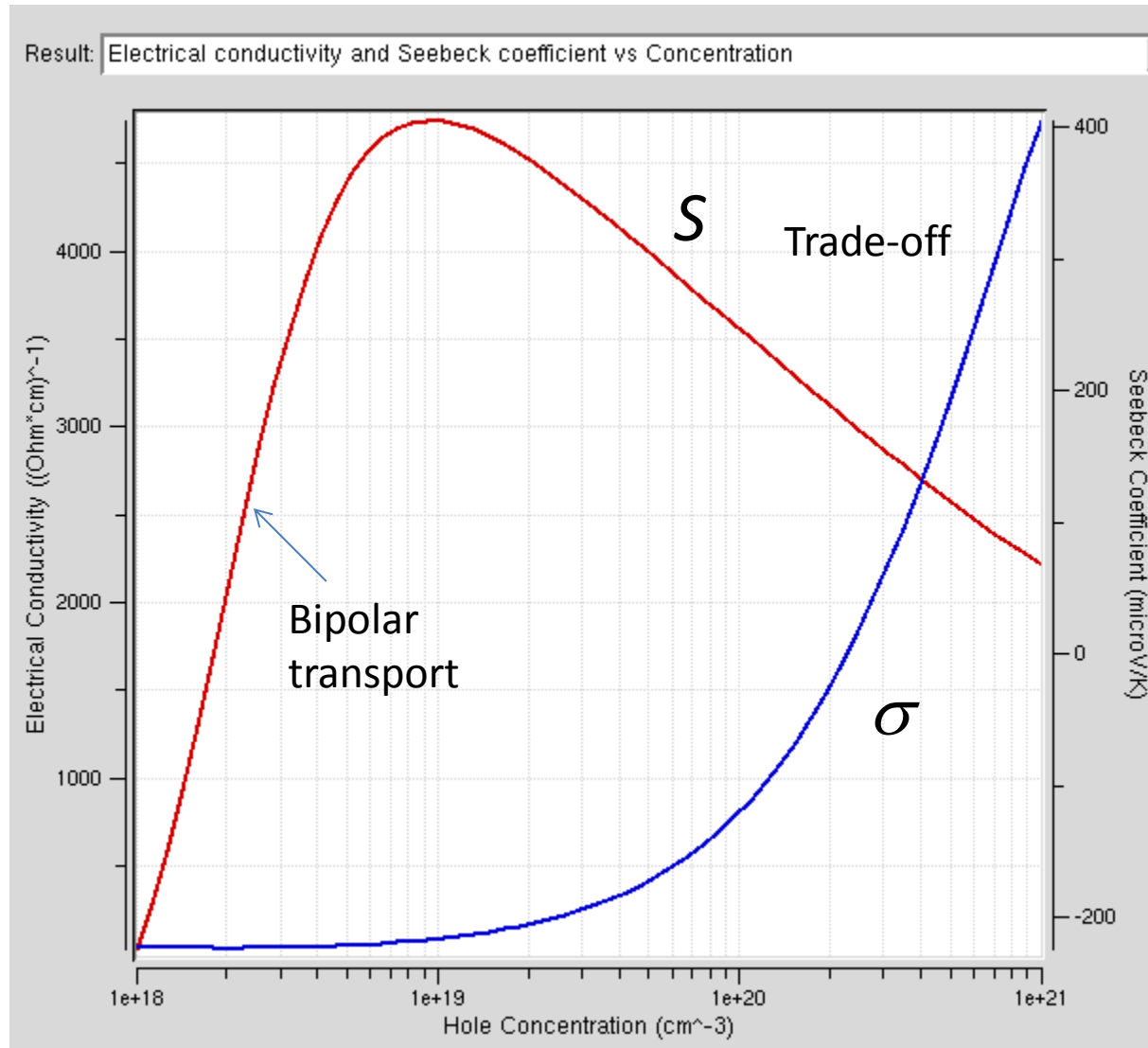
Polar optical phonon scattering
Enable: ☒ yes
r-factor (energy exponent): .427

Alloy scattering
Enable: ☐ no

1. Acoustic /optical phonon deformation potential scattering
2. Ionized impurity scattering
3. Polar optical phonon scattering

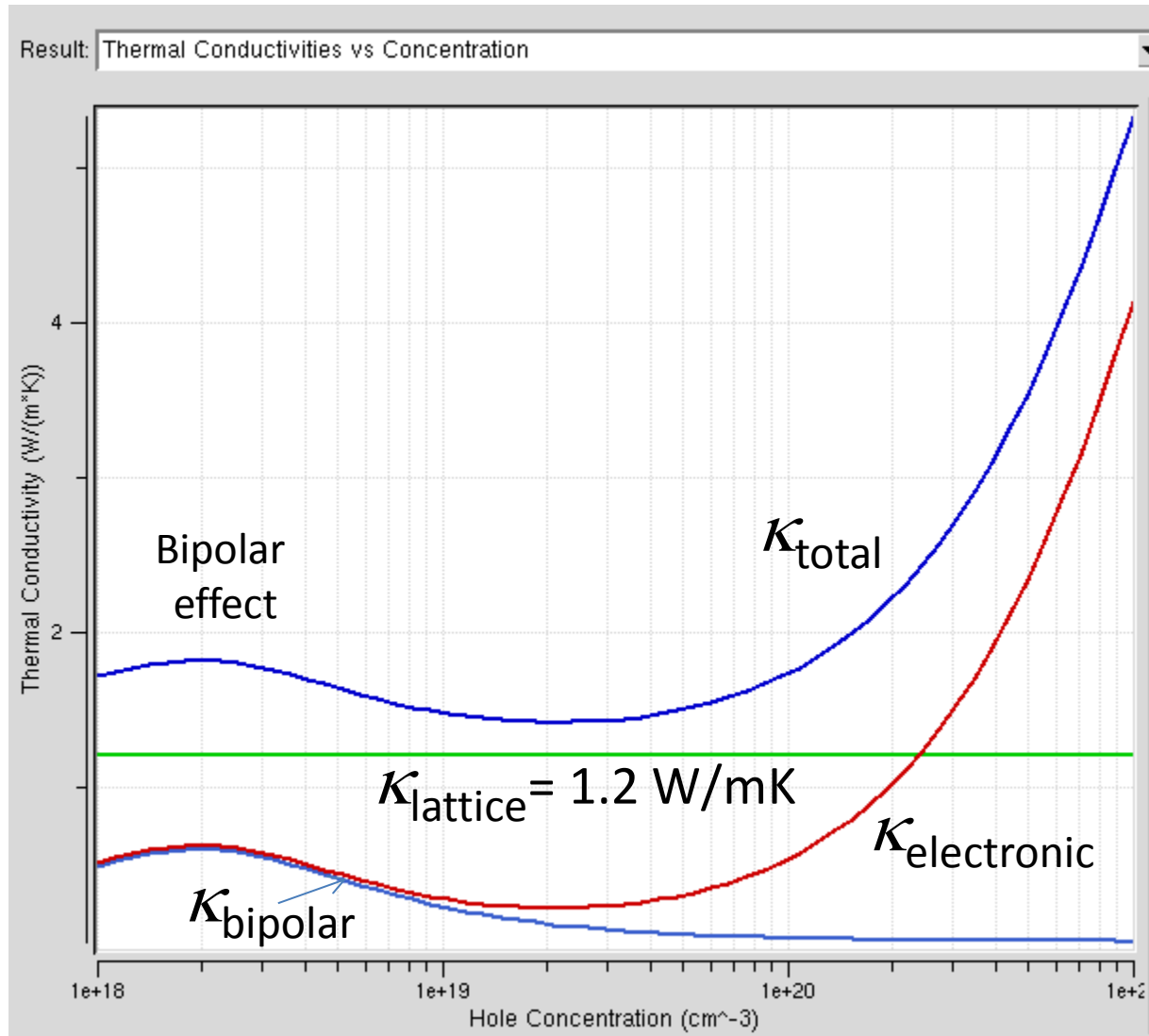
Prob. 4. Doping optimization of p-type PbTe

4-1.
p-PbTe
600 K



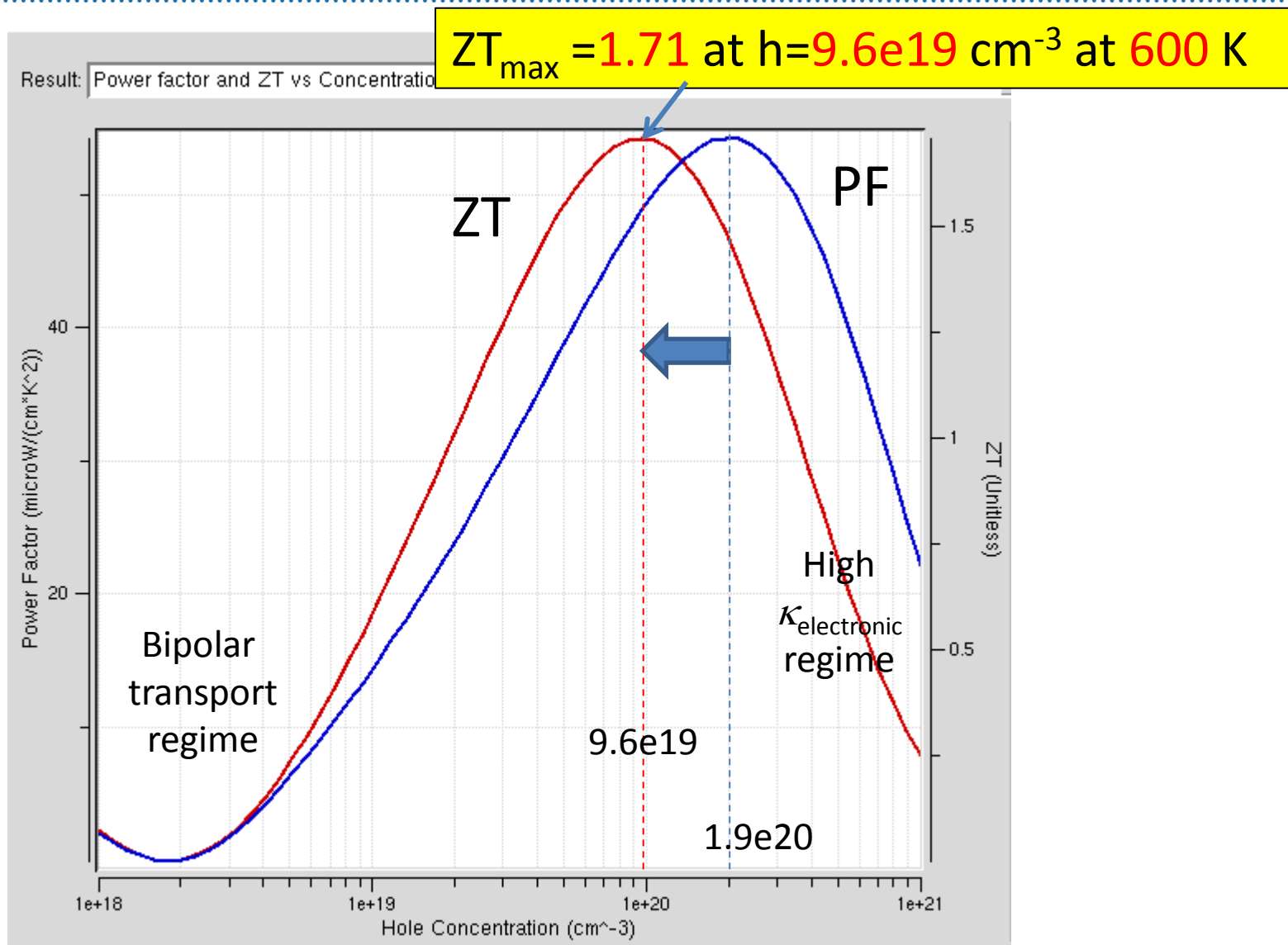
Prob. 4. Doping optimization of p-type PbTe

4-1.
p-PbTe
600 K



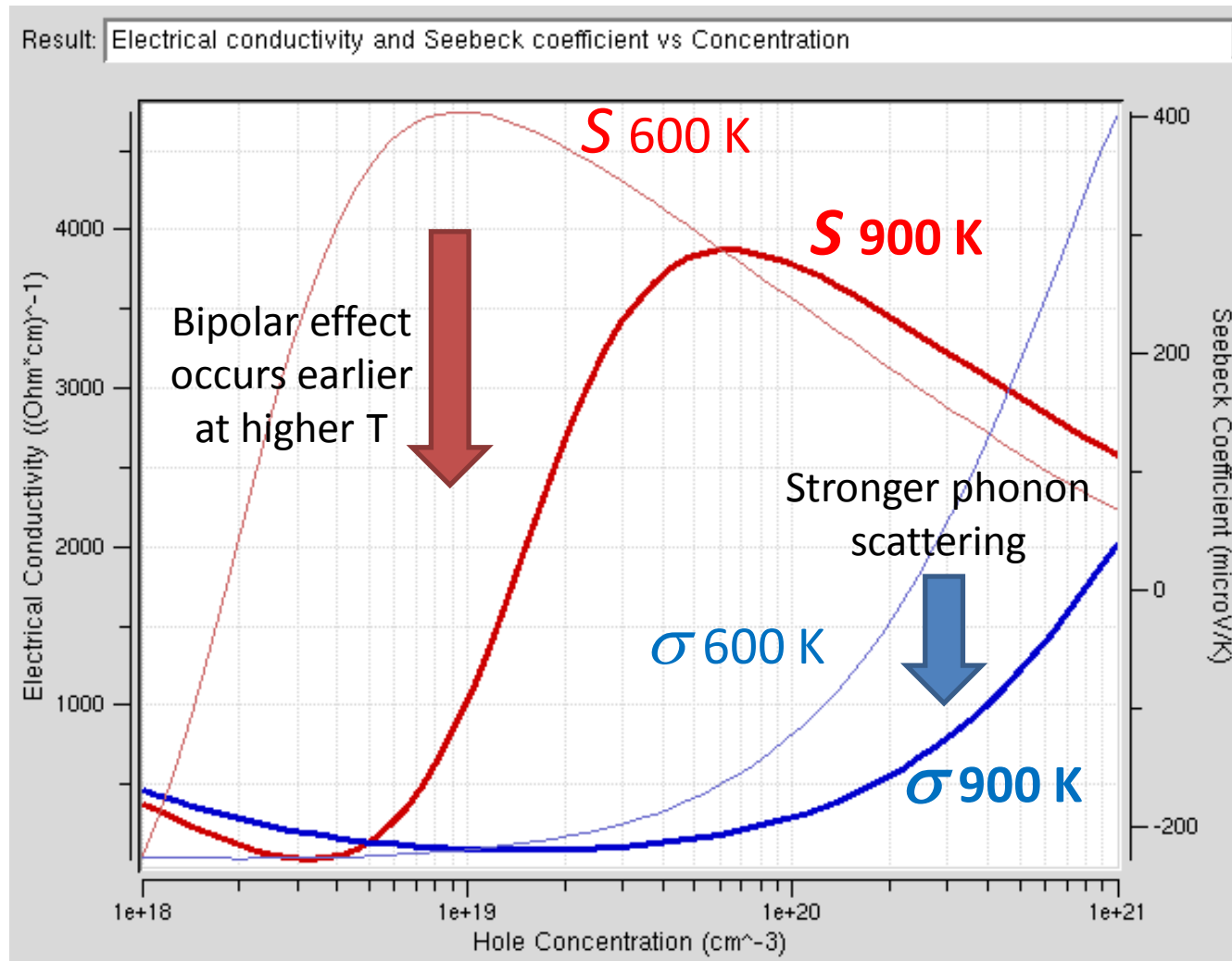
Prob. 4. Doping optimization of p-type PbTe

4-1.
p-PbTe
600 K



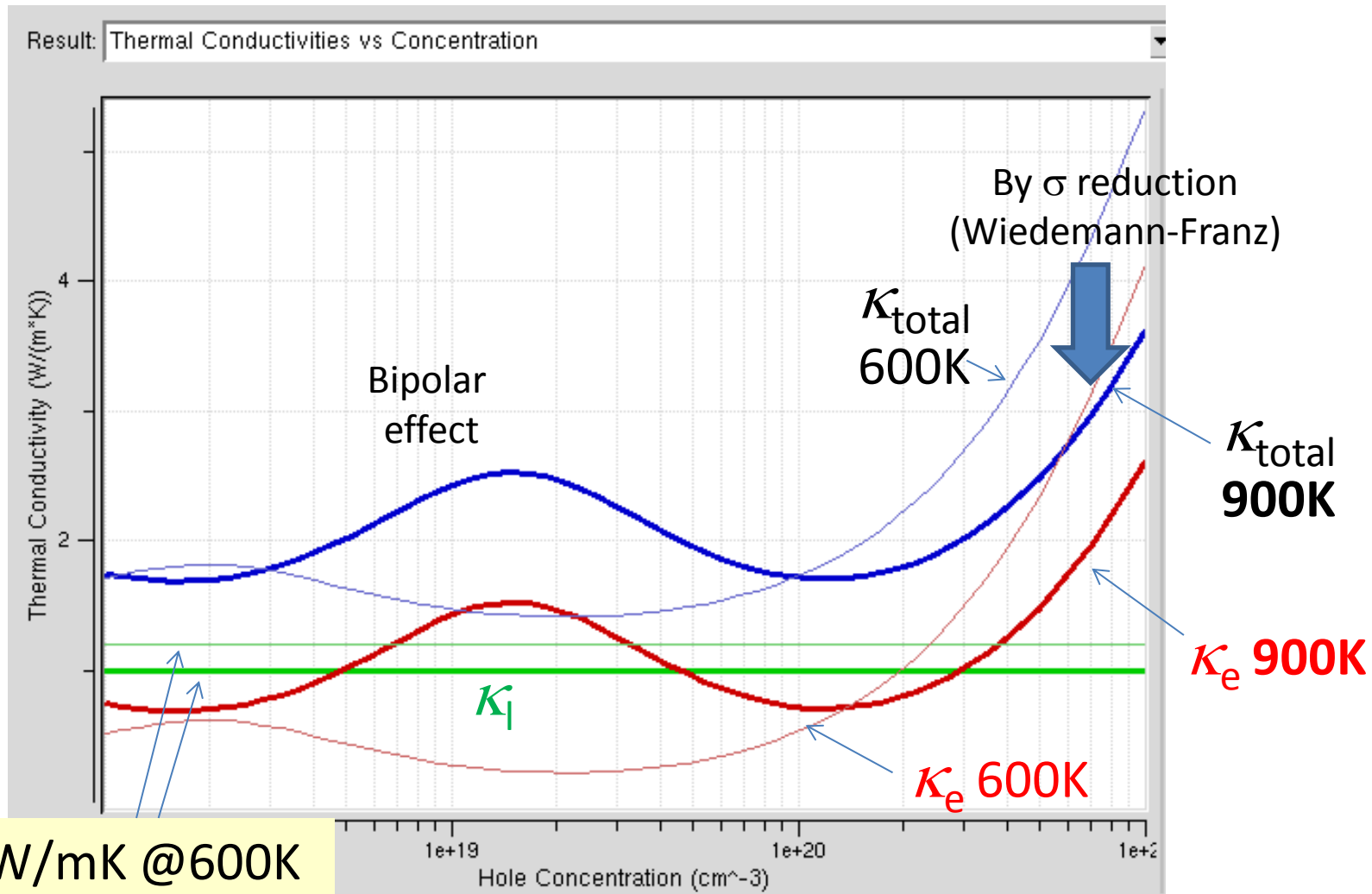
Prob. 4. Doping optimization of p-type PbTe

4-2.
p-PbTe
900 K



Prob. 4. Doping optimization of p-type PbTe

4-2.
p-PbTe
900 K

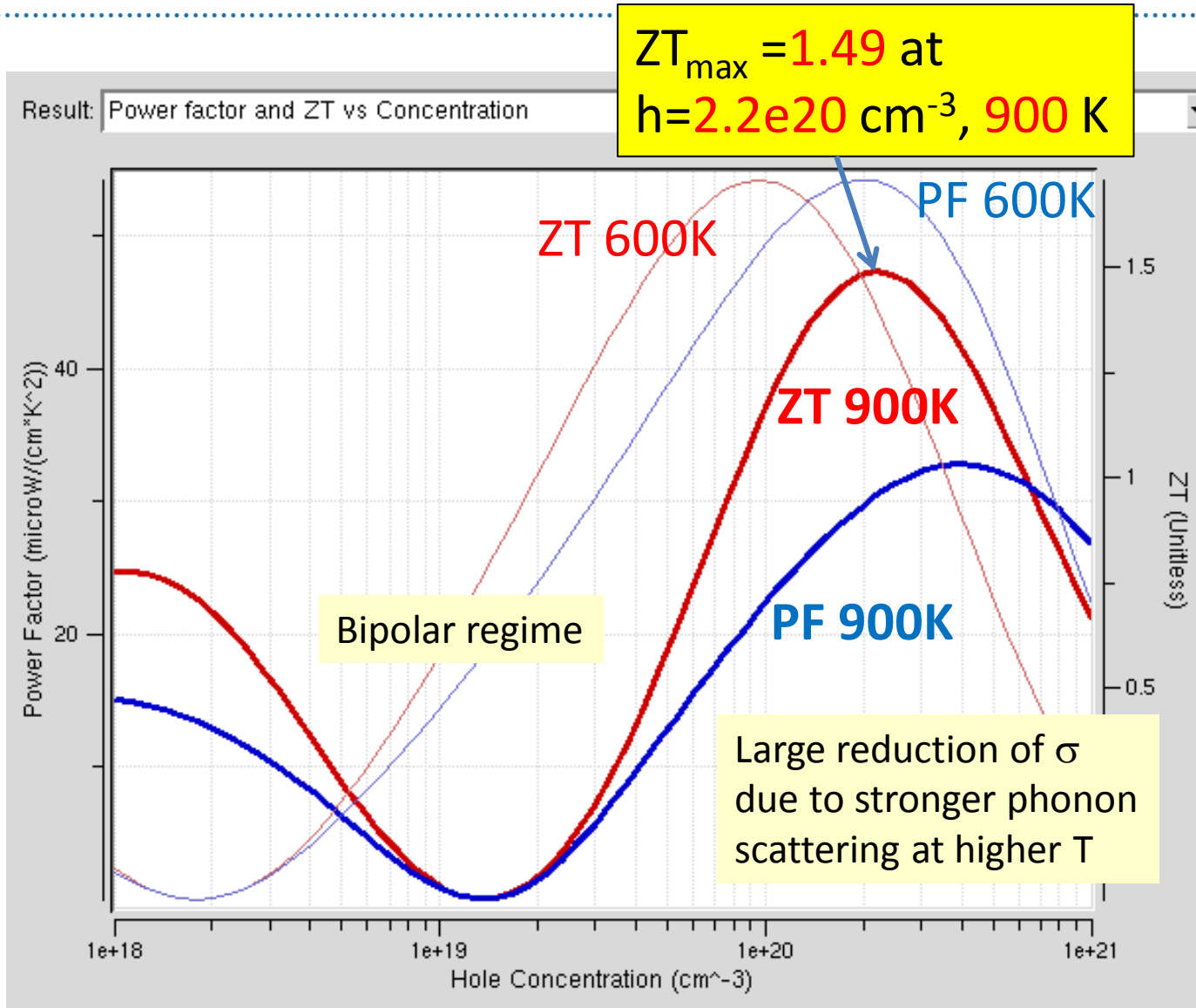


$$\kappa_l = 1.2 \text{ W/mK @ 600K}$$

$$\kappa_l = 1.0 \text{ W/mK @ 900K}$$

Prob. 4. Doping optimization of p-type PbTe

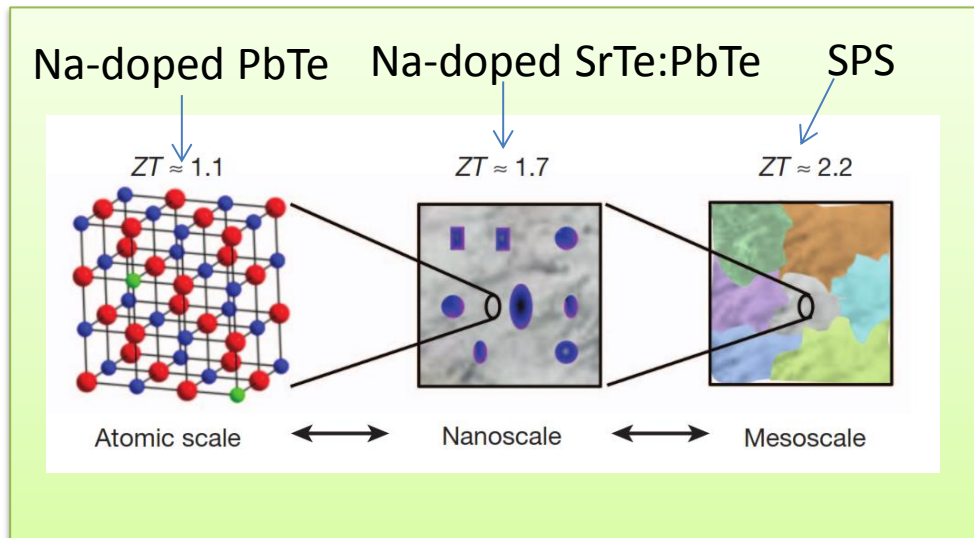
4-2.
p-PbTe
900 K



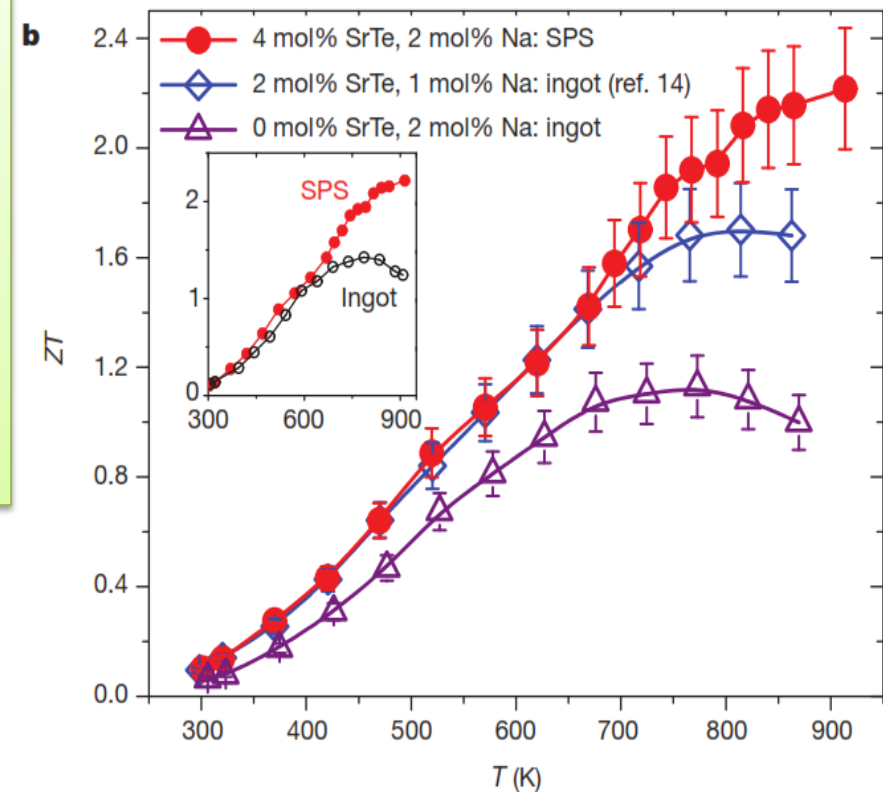
Prob. 5. Analysis of the recent Nature 2012 paper

[Biswas et al.(Kanatzidis group), *Nature* 489, 414 (2012)]

Spark-plasma-sintered Na(2%)-doped p-type PbTe:SrTe(4%)

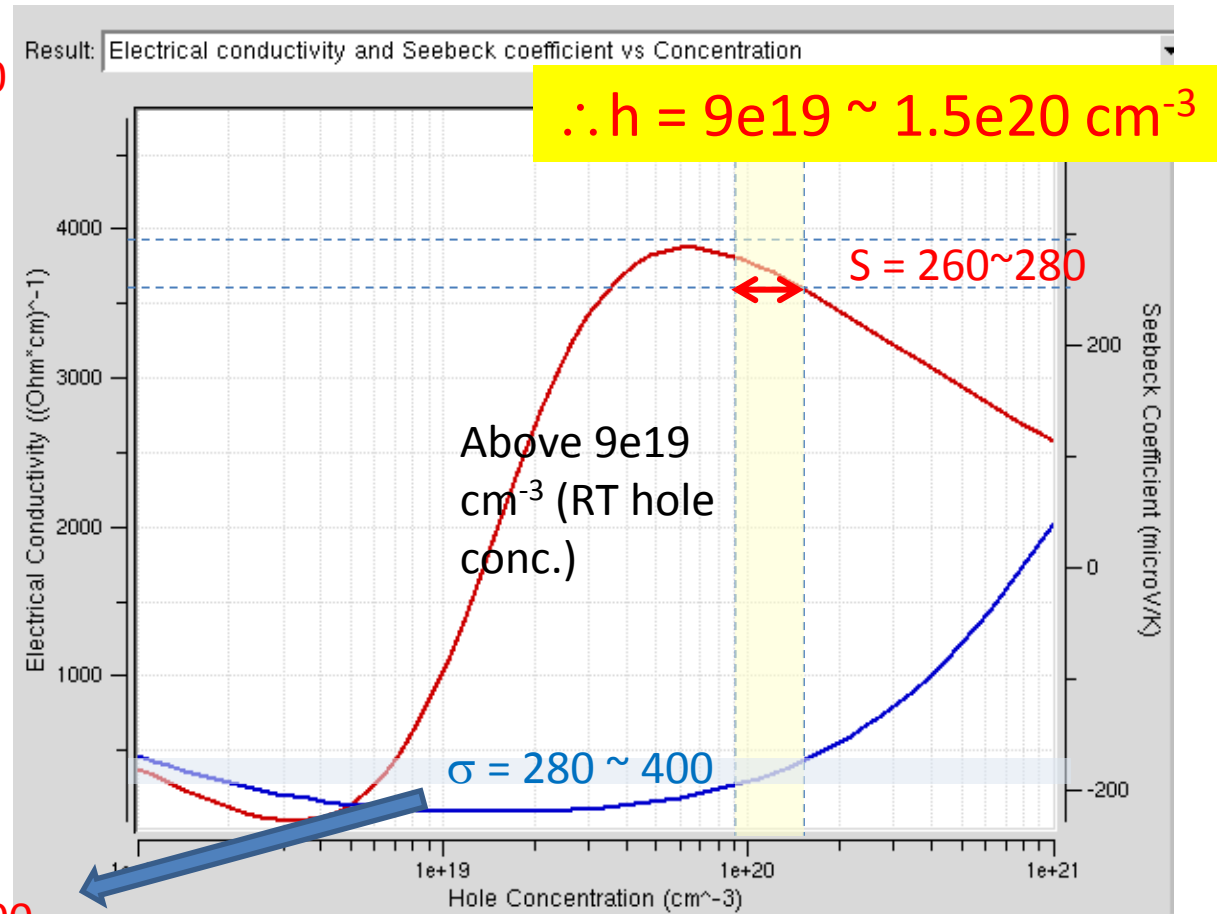
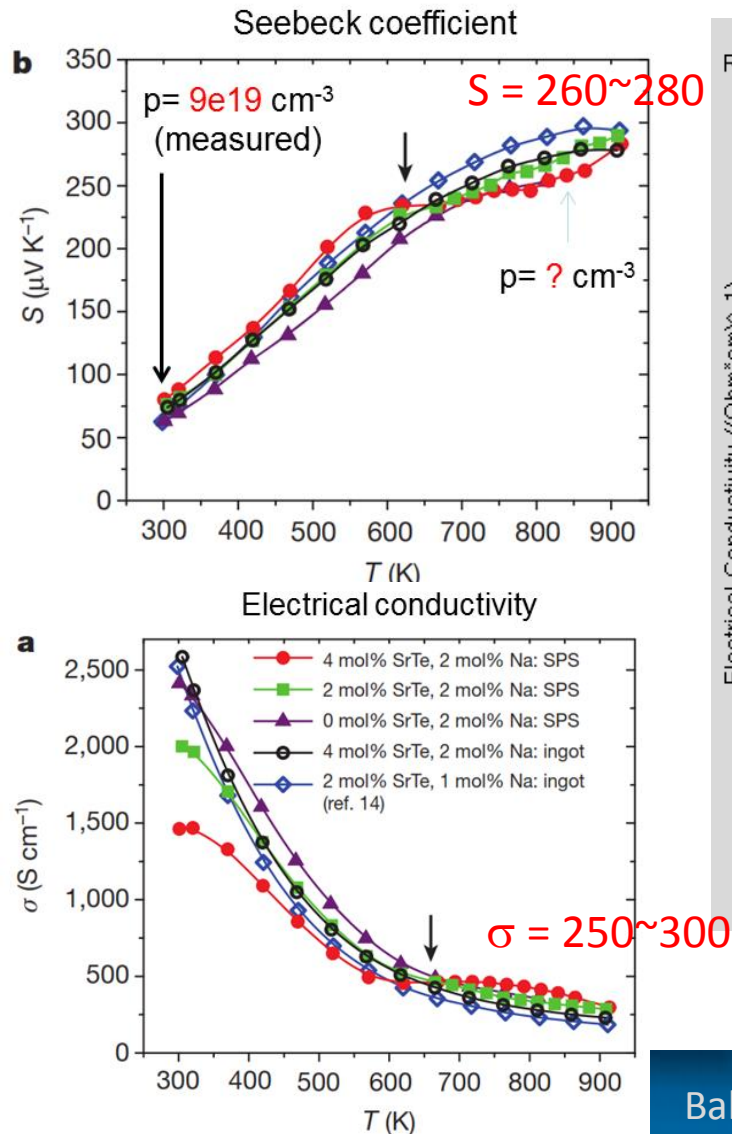


- All-scale hierarchical structures for thermal conductivity reduction.
- Electron transport near optimal.



Prob. 5. Analysis of the recent Nature 2012 paper

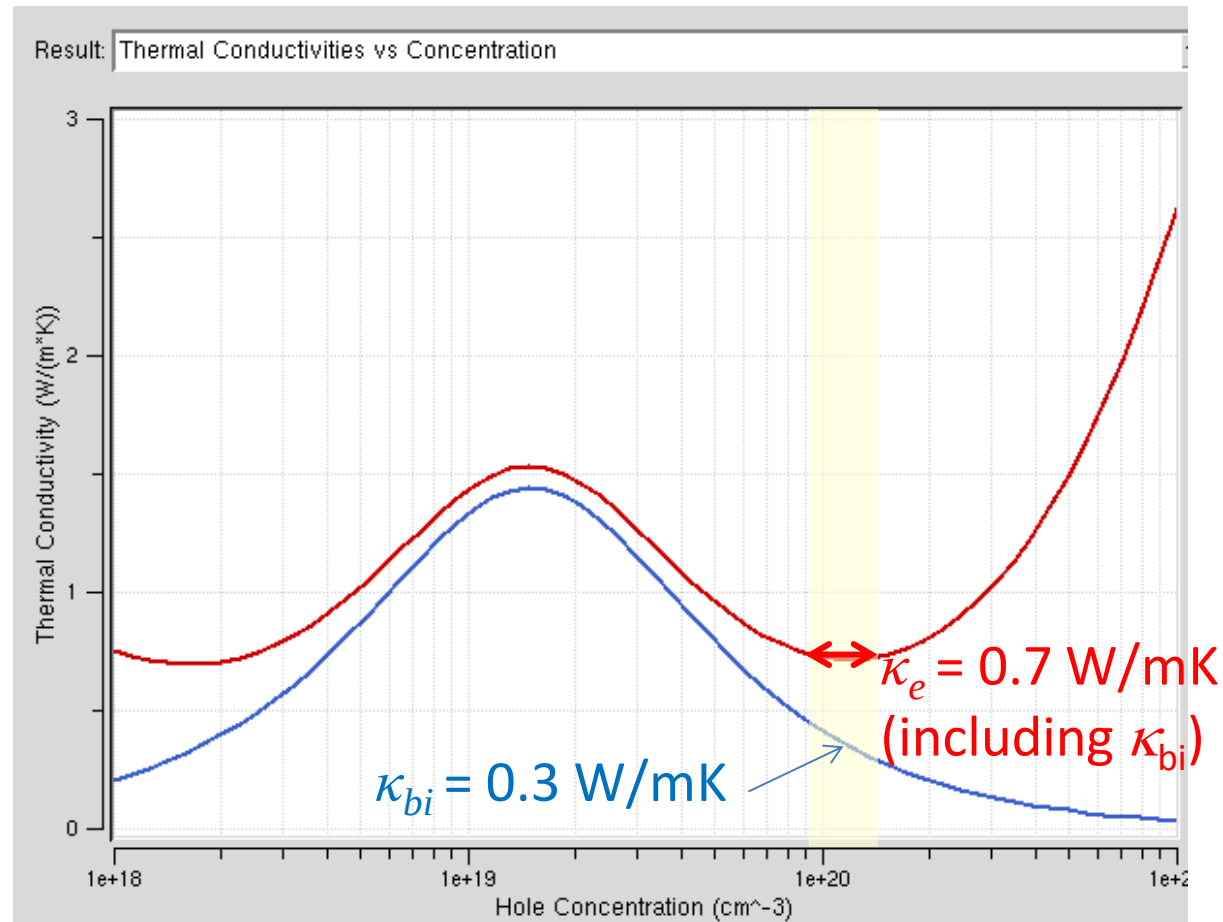
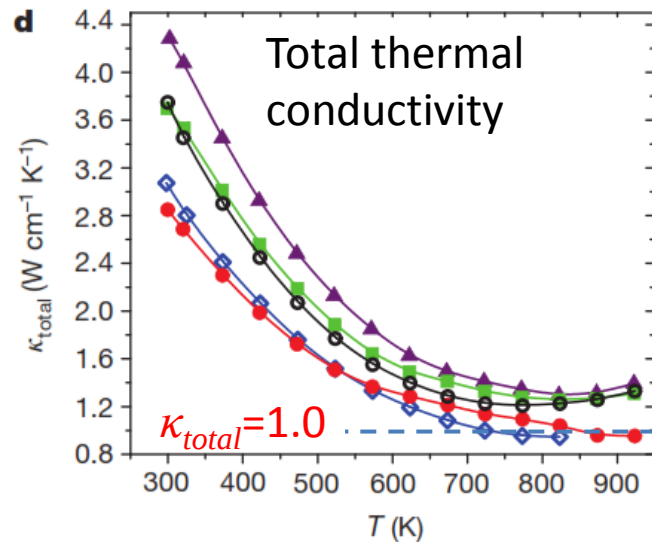
5-1 & 5-2. Hole concentration and σ at 900 K



Slightly reduced due to additional carrier scattering by nanostructures/grain boundaries

Prob. 5. Analysis of the recent Nature 2012 paper

5-3. Thermal conductivity at 900 K



$$\therefore \kappa_l = \kappa_{\text{total}} - \kappa_e = 1.0 - 0.7 = \mathbf{0.3 \text{ W/mK}}$$

Prob. 6. Carrier energy filtering in PbTe at 900 K

Differential Conductivity

$$\sigma_d(E) = e^2 \tau(E) v_x^2(E) \rho_{DOS}(E) \left(-\frac{\partial f_0(E)}{\partial E} \right)$$

Boltzmann transport with a cut-off energy

$$\sigma = \sum_i \int_{E_c}^{\infty} \sigma_d(E) dE$$

$$S = \sum_i \left(\frac{k_B}{q} \right) \int_{E_c}^{\infty} \left[\frac{(E - E_{F,i})}{k_B T} \right] \frac{\sigma_d(E)}{\sigma} dE$$

$$\kappa_e = T \left(\frac{k_B}{q} \right)^2 \sum_i \int_{E_c}^{\infty} \left[\frac{E - E_{F,i}}{k_B T} \right]^2 \sigma_d(E) dE - S^2 \sigma T$$

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_l + \kappa_{bi}}$$

: Electrical conductivity

: Seebeck coefficient

: Electronic thermal conductivity

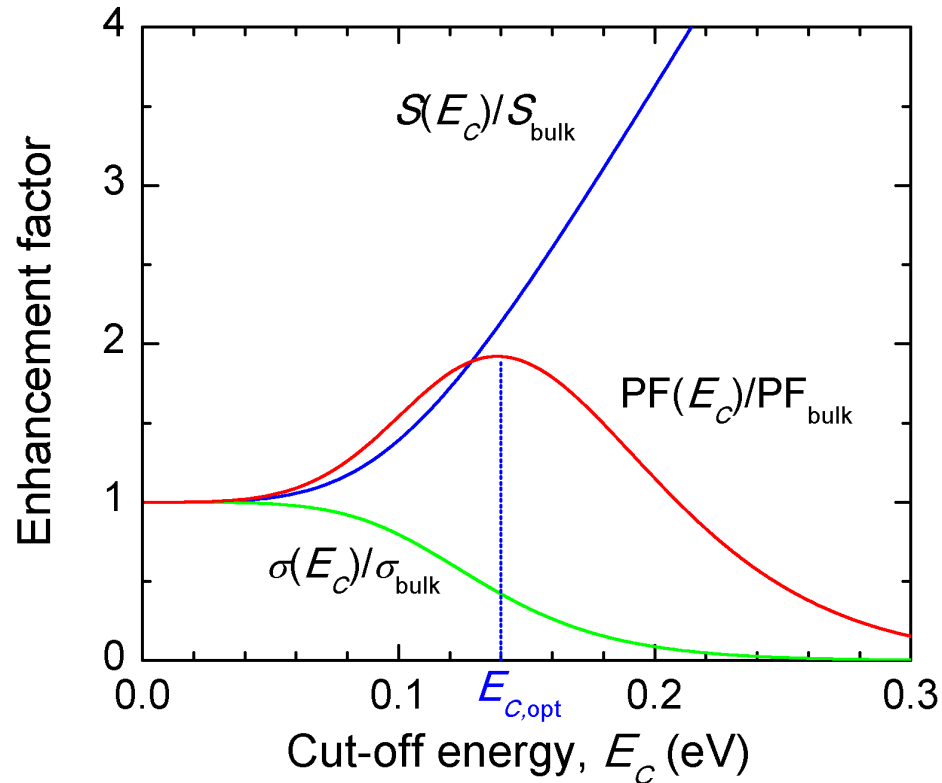
$\sum$: sum of bands

$\left\{ \begin{array}{l} q = -e \text{ (conduction band)} \\ q = +e \text{ (valence band)} \end{array} \right.$

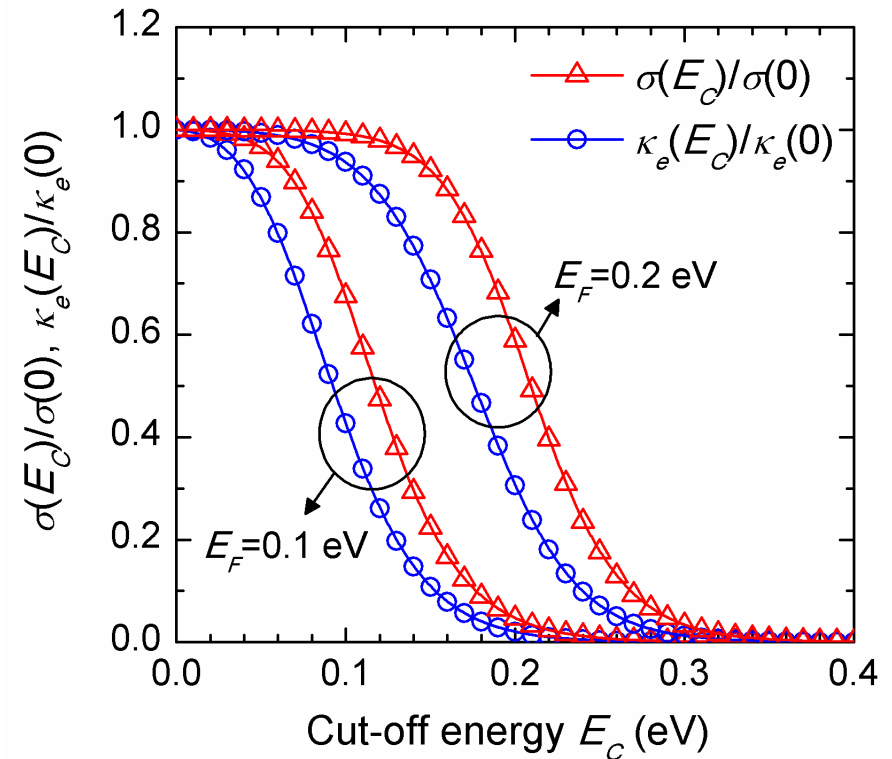
Prob. 6. Carrier energy filtering in PbTe at 900 K

J.-H. Bahk et al., *Phys. Rev. B* **87**, 075204 (2013)

Power factor enhancement



Electronic thermal conductivity reduction



300 K

$E_F=0.1$ eV (const.)

$r=0.5$

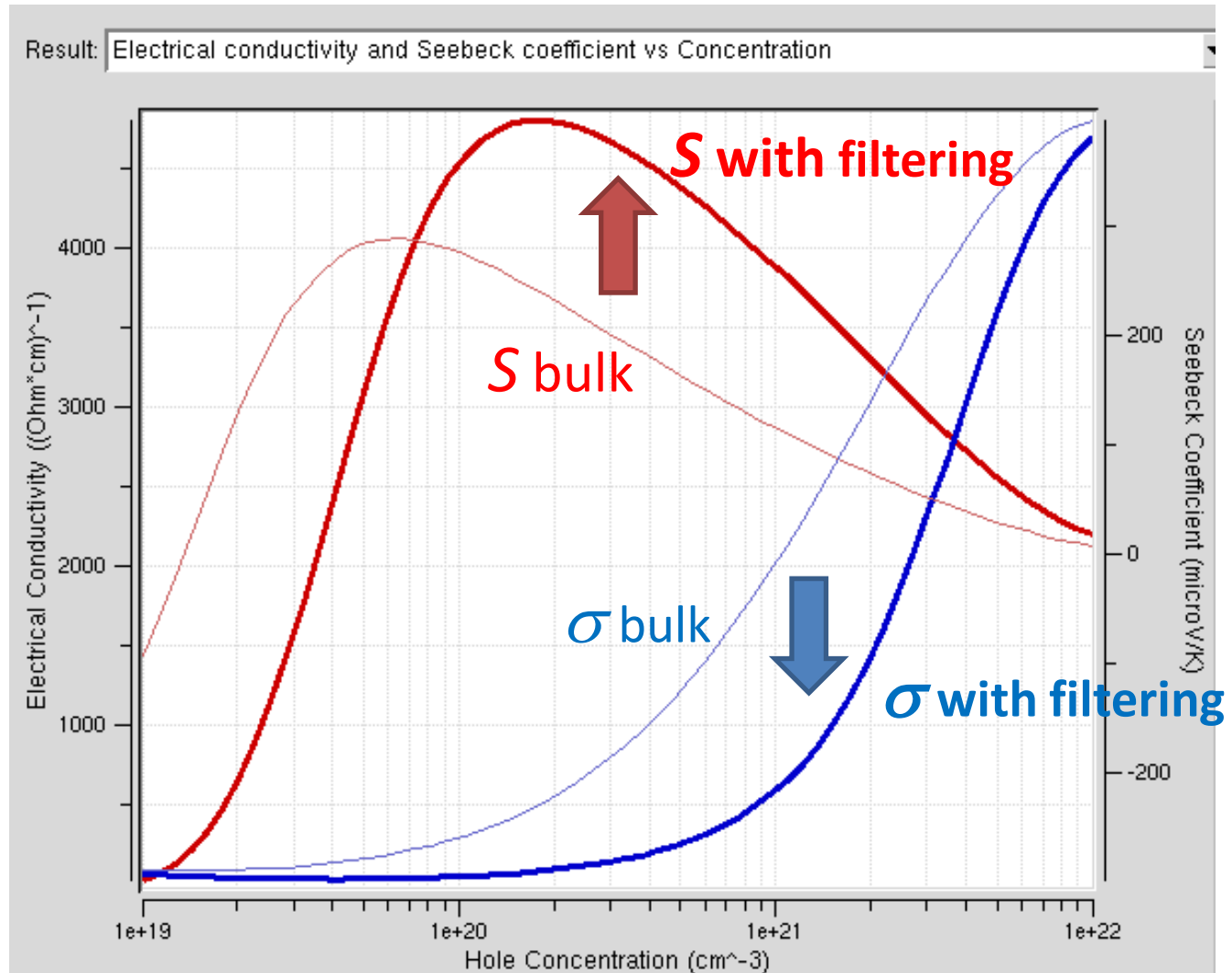
$$\kappa_e = L\sigma T$$

Prob. 6. Carrier energy filtering in PbTe at 900 K

p-type PbTe

900 K

$E_C = 0.1$ eV

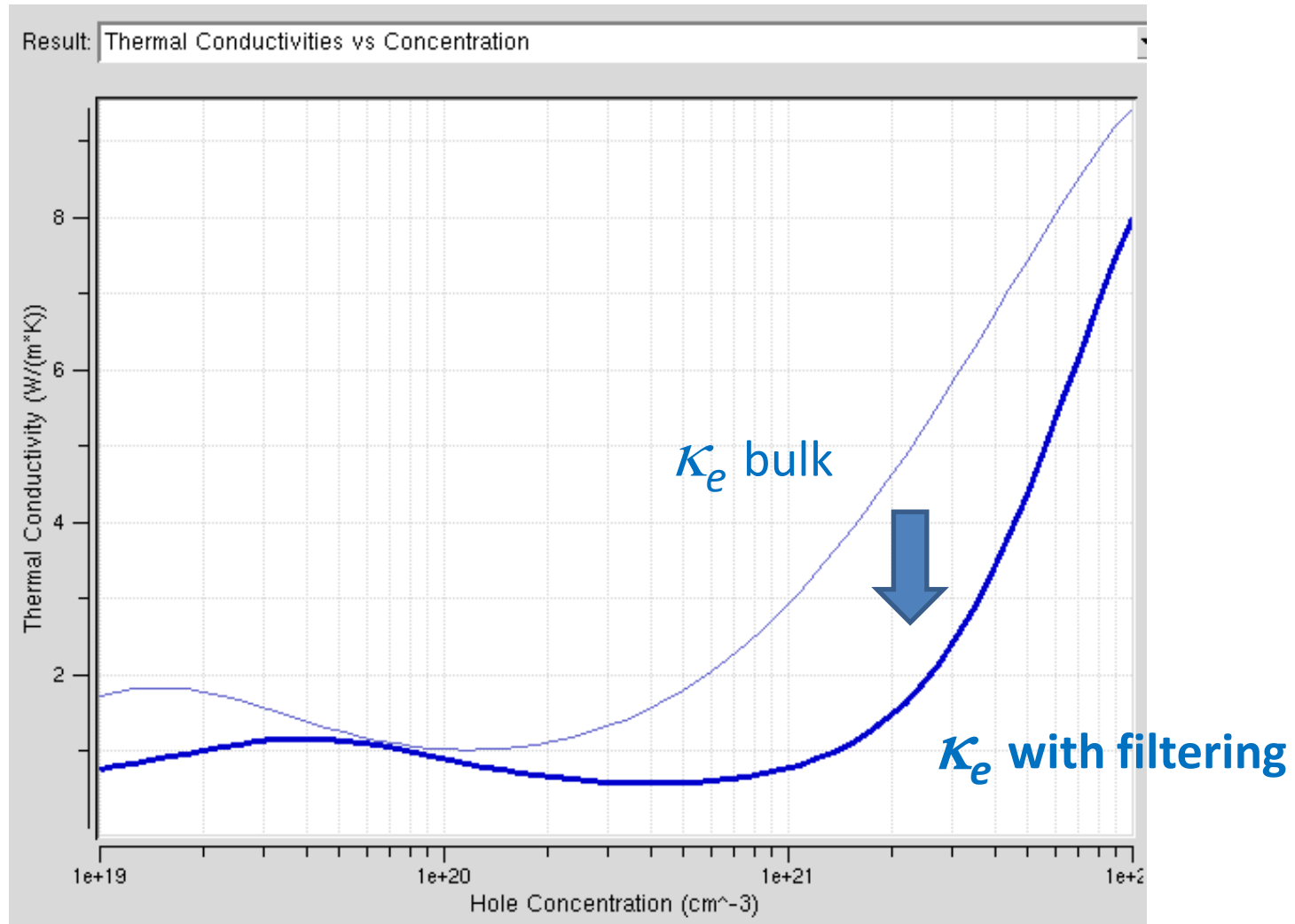


Prob. 6. Carrier energy filtering in PbTe at 900 K

p-type PbTe

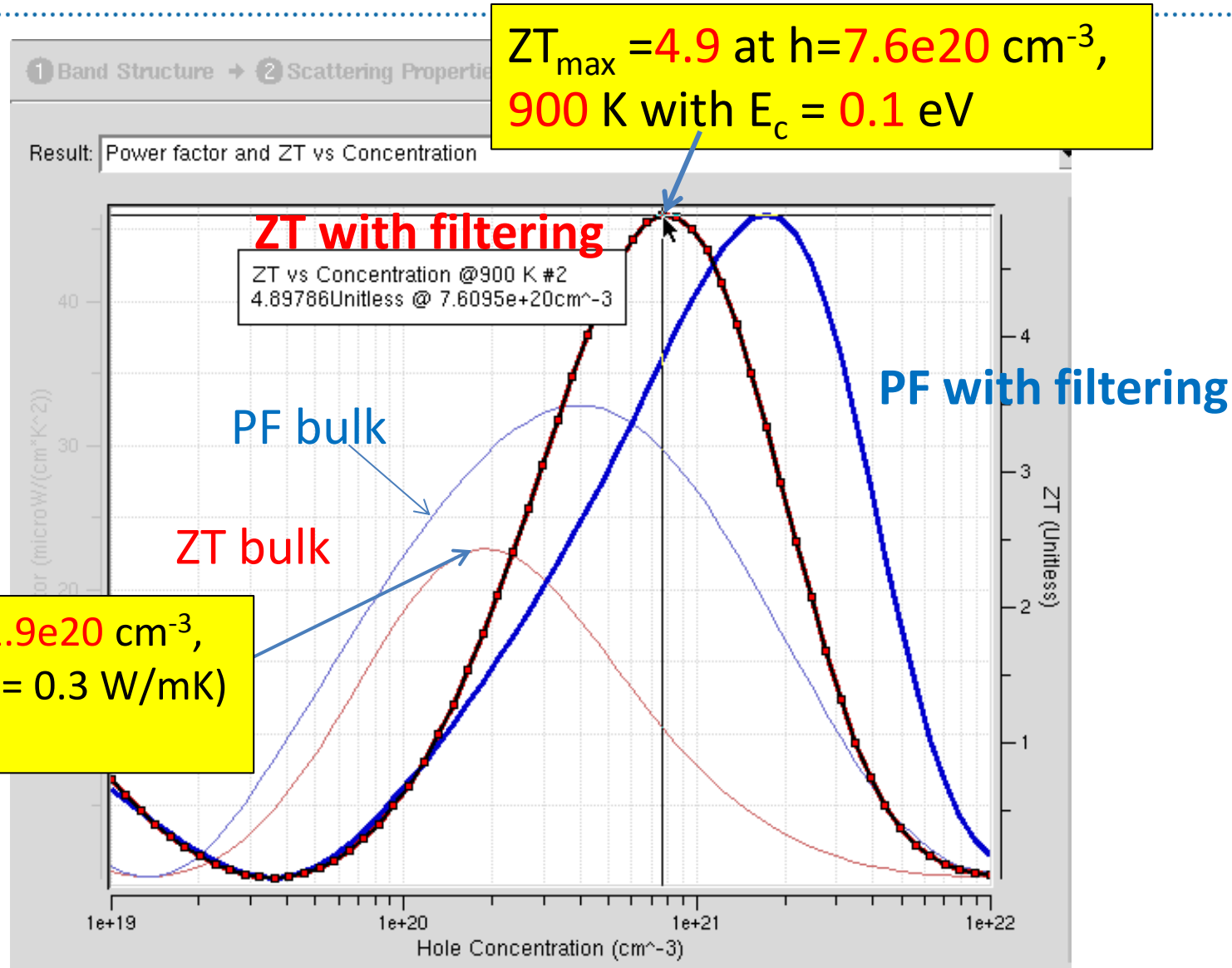
900 K

$E_C = 0.1$ eV



Prob. 6. Carrier energy filtering in PbTe at 900 K

p-type PbTe
900 K
 $E_c = 0.1$ eV



ZT_{max} = 2.4 at $h = 1.9 \times 10^{20} \text{ cm}^{-3}$, for bulk PbTe ($\kappa_l = 0.3$ W/mK) 900 K