Thermoelectricity: From Atoms to Systems

Week 5: Recent advances in thermoelectric materials and physics
Tutorial 5.1 Homework solutions, problems 1-6

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

Differential Conductivity (Transport Distribution Function)

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

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

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

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

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

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

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

$\sum$: sum of bands

$q = -e$ (conduction band)

$q = +e$ (valence band)

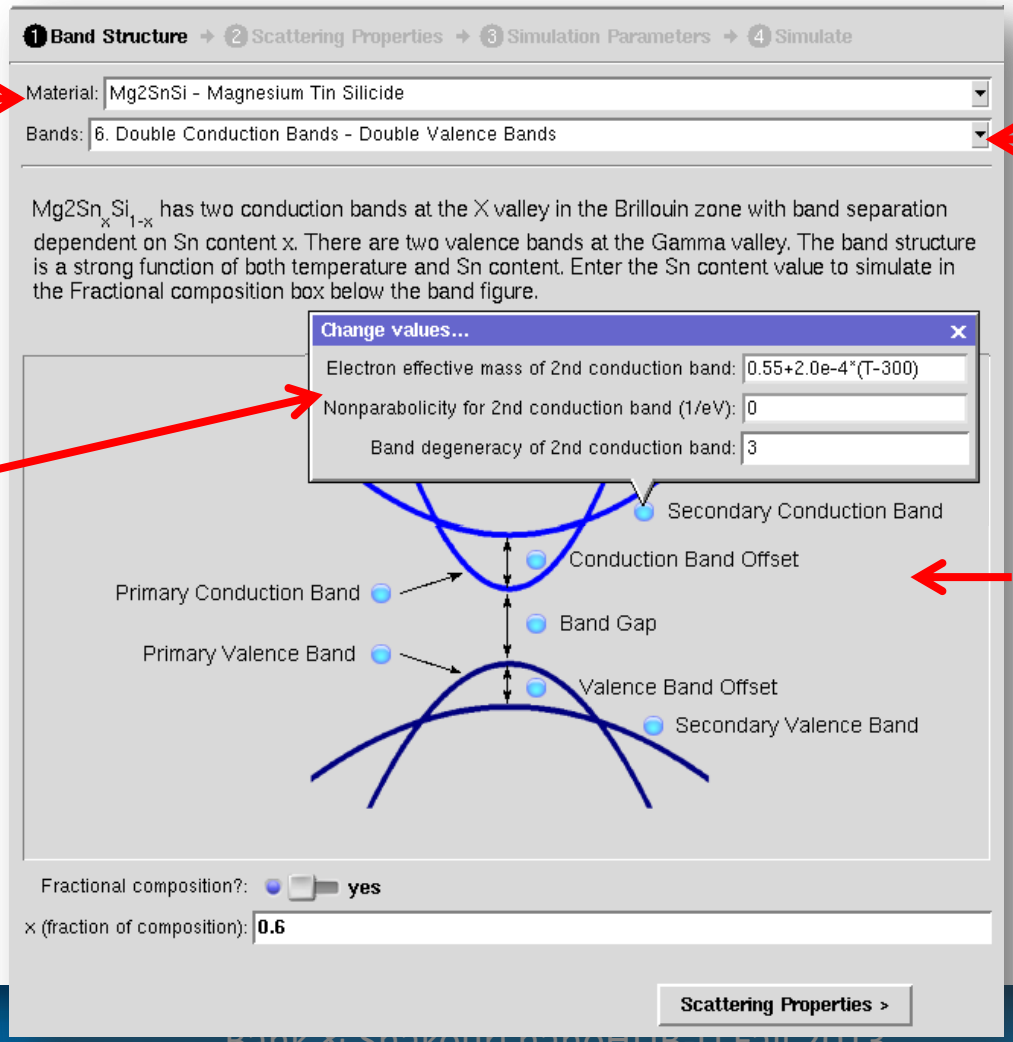
Prob. 1. Differential conductivity and $S - \sigma$ trade-off

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

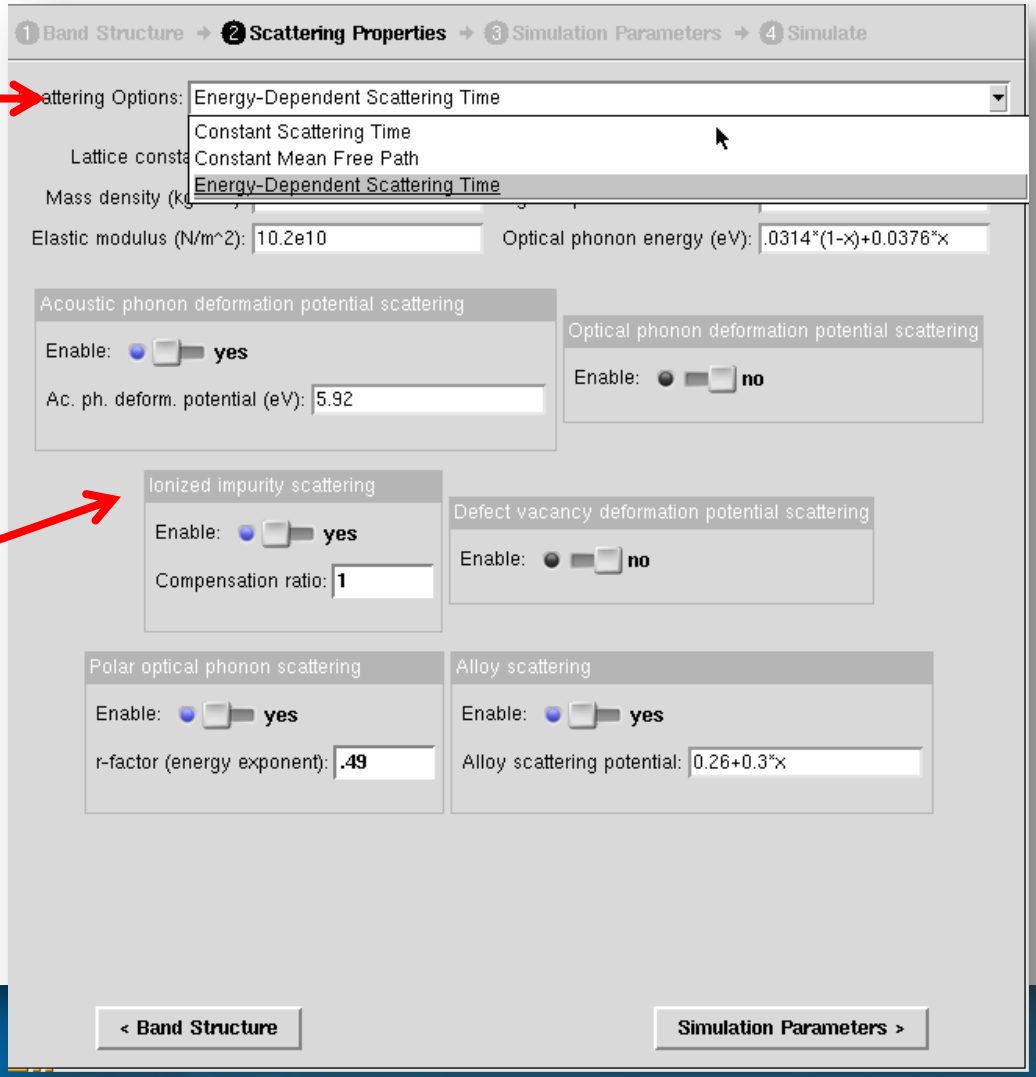
The thermoelectric material properties simulation tool

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

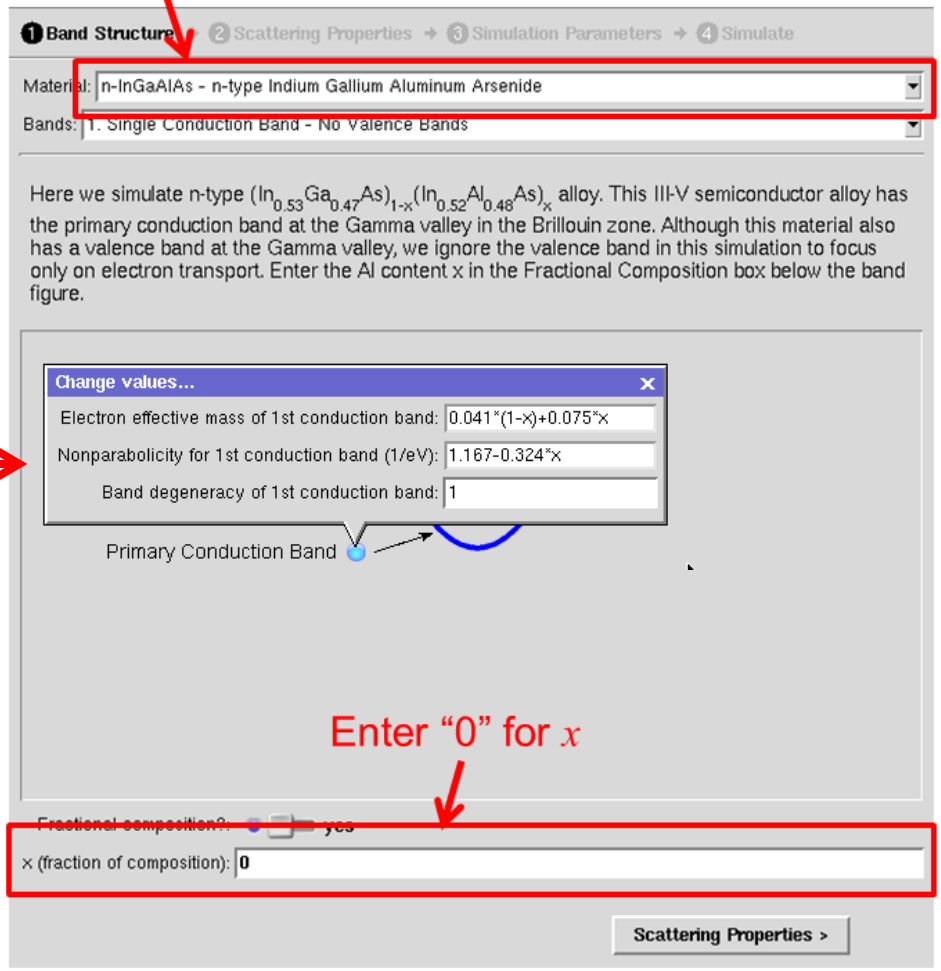


Prob. 1. Differential conductivity and $S - \sigma$ trade-off

1-1. In a single non-parabolic band (n-type $In_{0.53}Ga_{0.47}As$)

Select "n-InGaAlAs – n-type Indium Gallium Aluminum Arsenide"

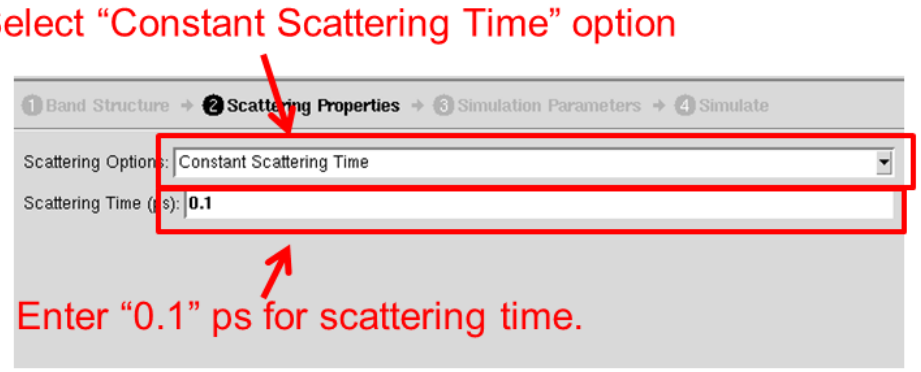
The effective mass and nonparabolicity are a function of composition x



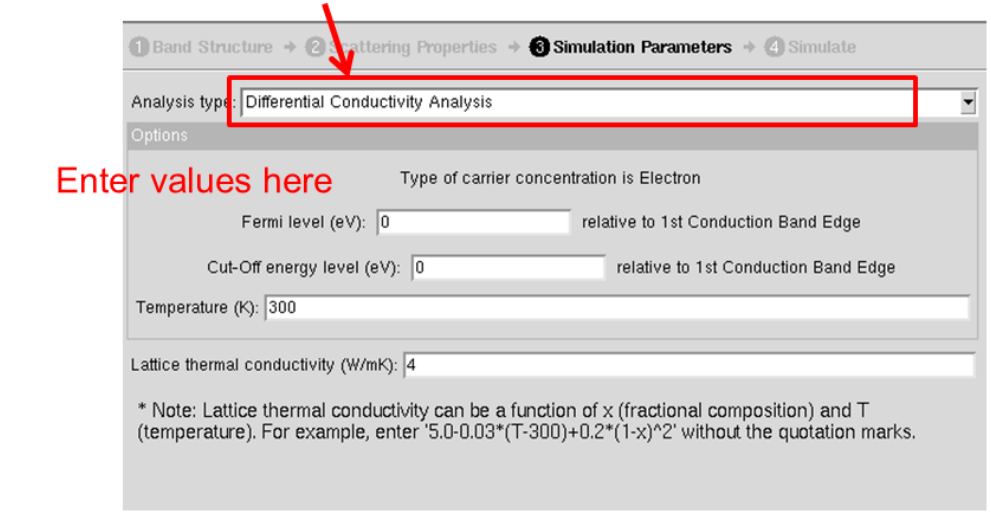
Prob. 1. Differential conductivity and $S - \sigma$ trade-off

1-1. In a single non-parabolic band (n-type $In_{0.53}Ga_{0.47}As$)

2nd phase:

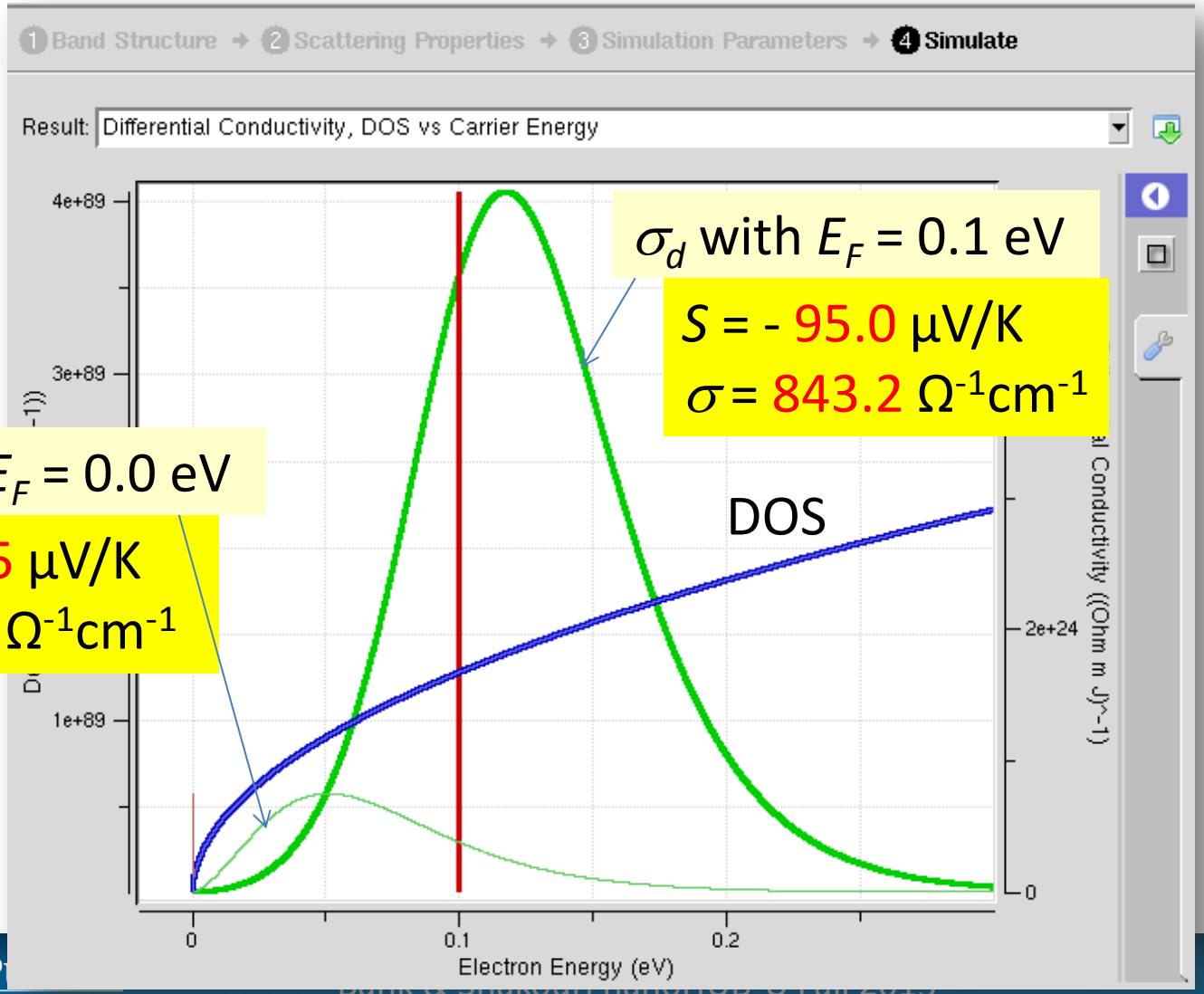


3rd phase:



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

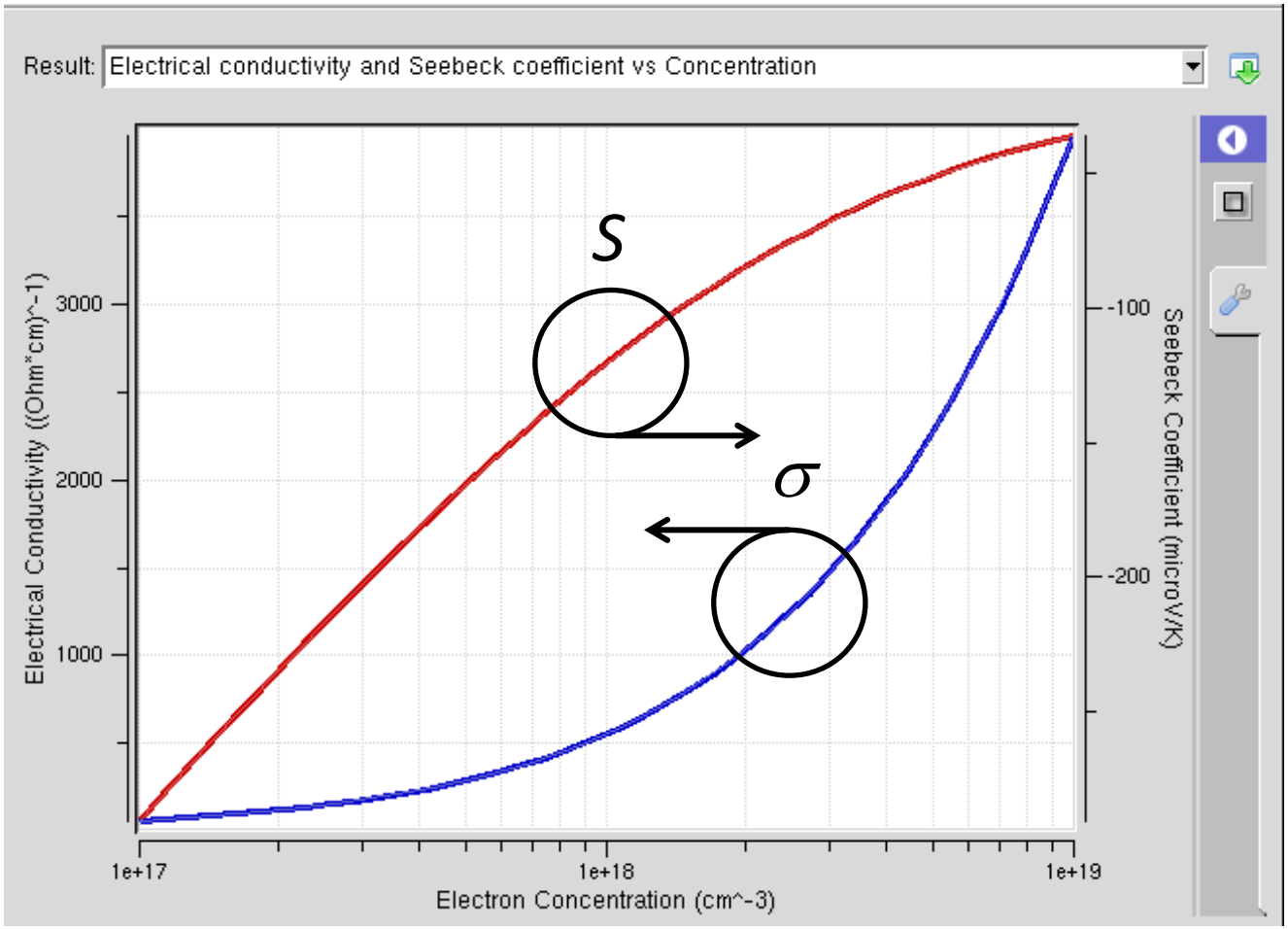
1-1 & 1-2. Differential conductivity vs. energy



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 cm^{-3}

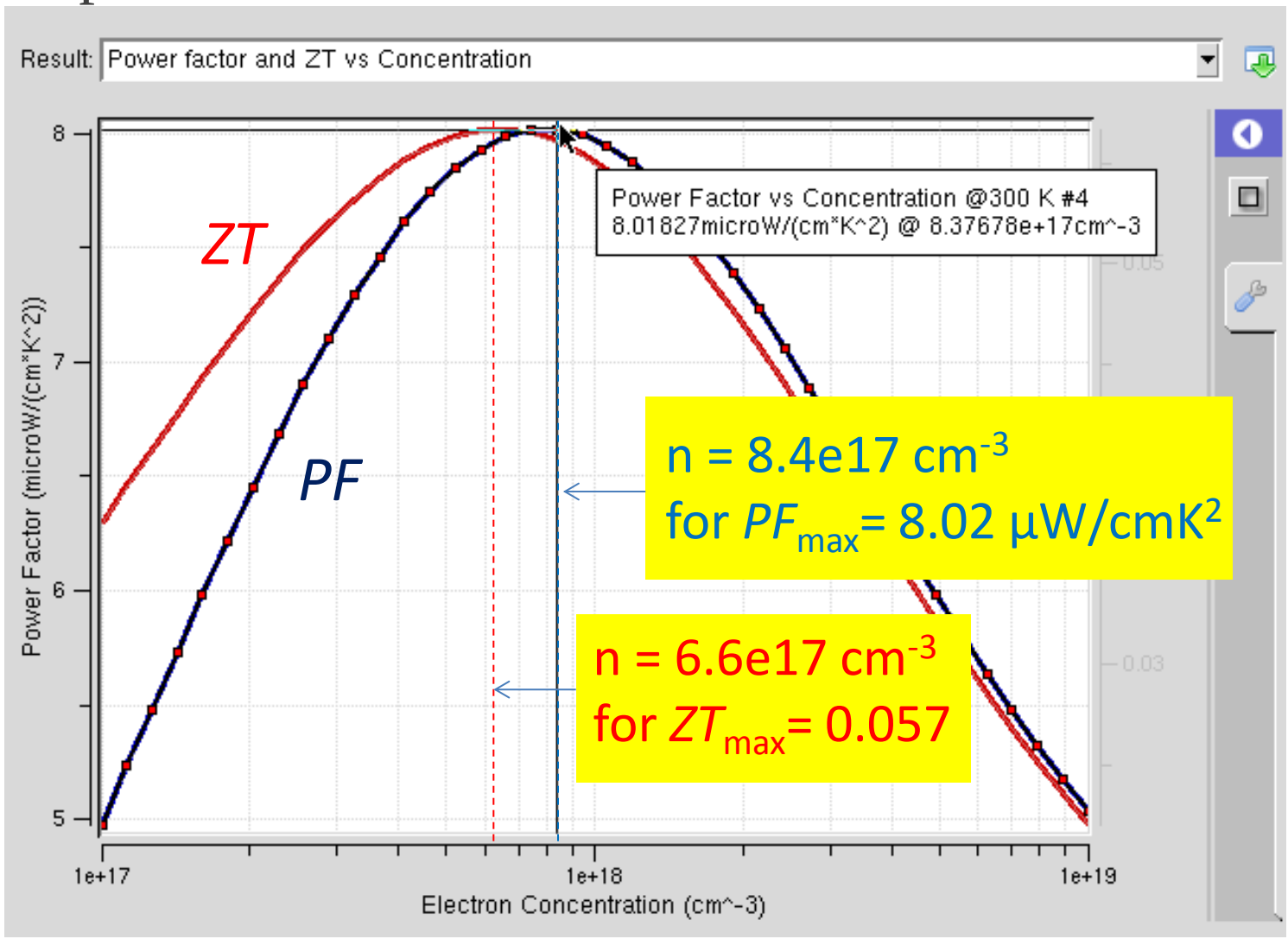


n-InGaAs
300 K
τ = 0.1 ps

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

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

n-InGaAs
300 K
τ = 0.1 ps

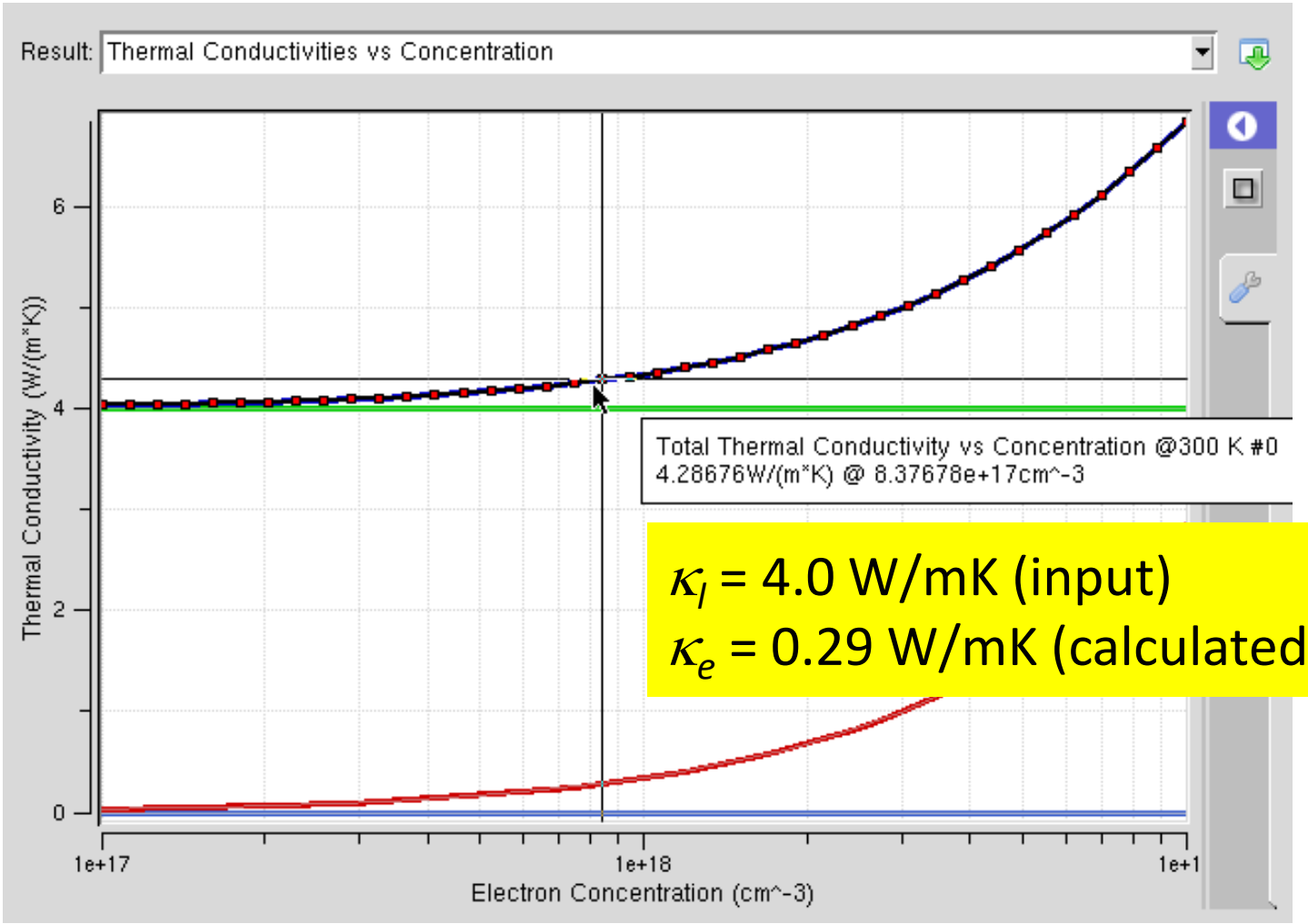


Prob. 1. Differential conductivity and $S - \sigma$ trade-off

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

Electronic thermal conductivity increases with carrier concentration

n-InGaAs
300 K
τ = 0.1 ps

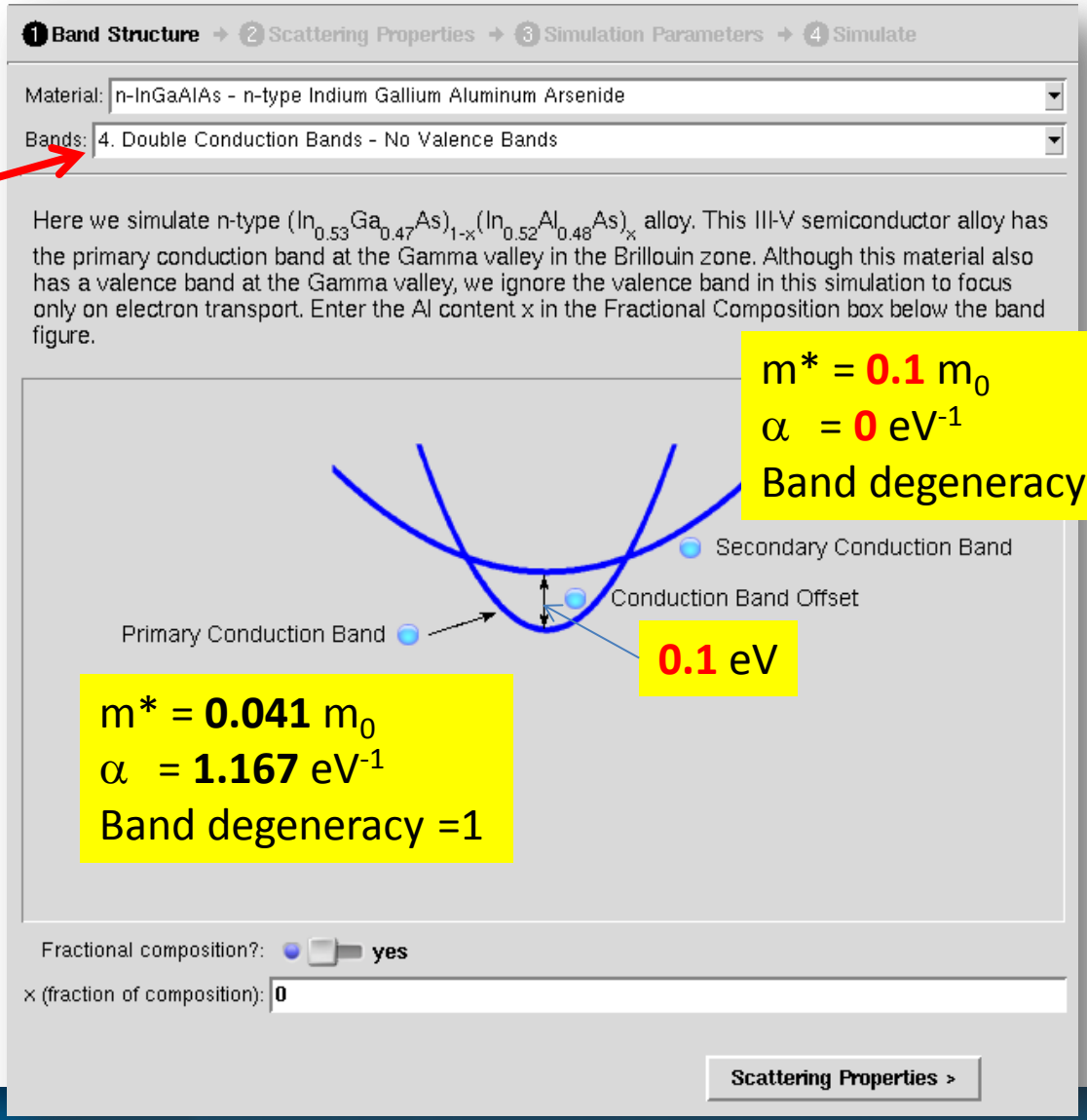


κ_l = 4.0 W/mK (input)
κ_e = 0.29 W/mK (calculated)

Prob. 2. Influence of a secondary band

2-1

Add a secondary conduction band by choosing "double conduction bands" option



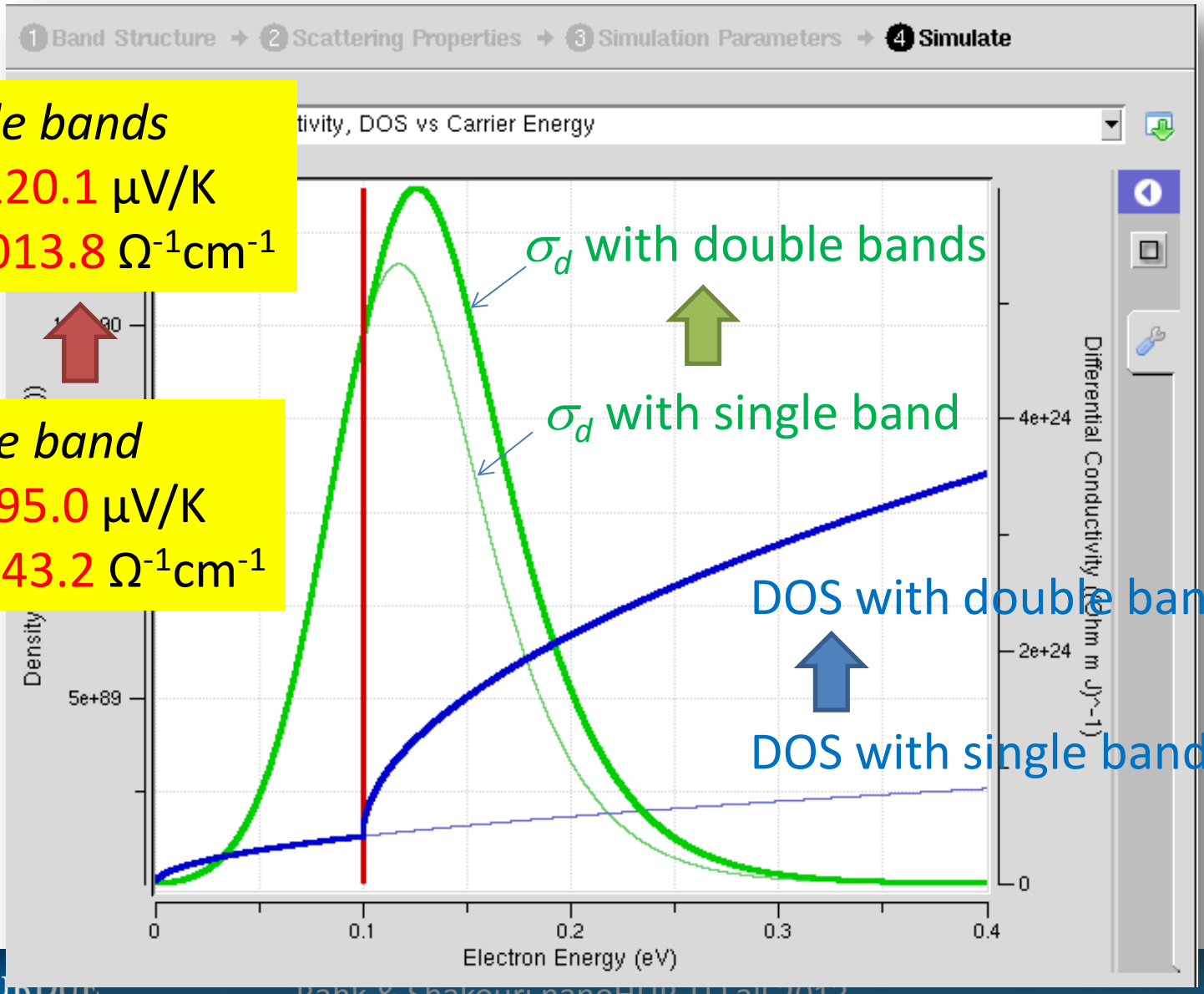
Prob. 2. Influence of a secondary band

2-1

Double bands
S = - 120.1 μV/K
σ = 1013.8 $\Omega^{-1}cm^{-1}$

Single band
S = - 95.0 μV/K
σ = 843.2 $\Omega^{-1}cm^{-1}$

300 K
τ = 0.1 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.

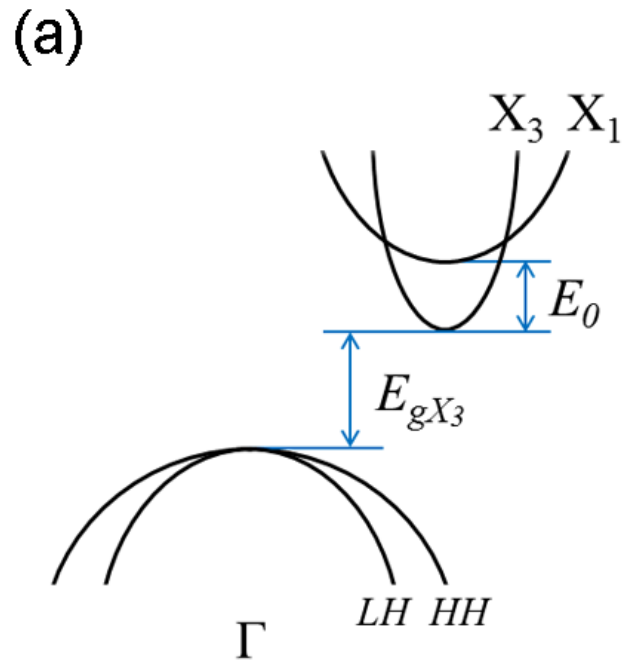
b. The Seebeck coefficient increased because the secondary band increased the differential conductivity above the Fermi level while the differential conductivity below the Fermi level remained the same, so that the degree of asymmetry of the differential conductivity around the Fermi level increased.

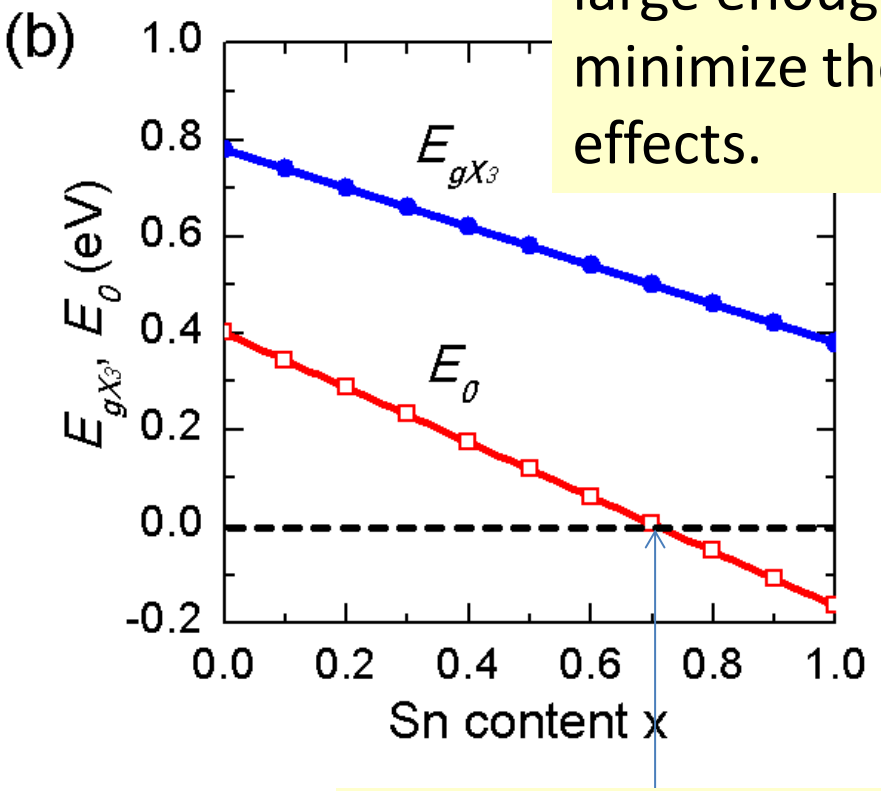
c. The electrical conductivity decreased because the Seebeck coefficient increased by the influence of the secondary band and there are a trade-off between the Seebeck coefficient and the electrical conductivity.

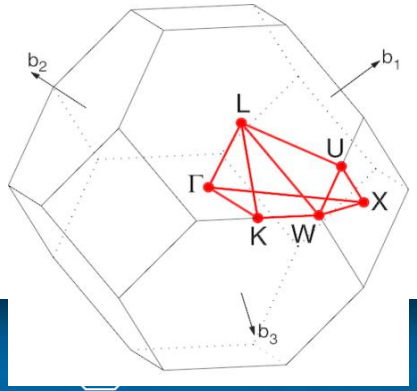
d. The electrical conductivity increased because the secondary band added more states within the Fermi window.

Prob. 3. $Mg_2Sn_xSi_{1-x}$ solid solution

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





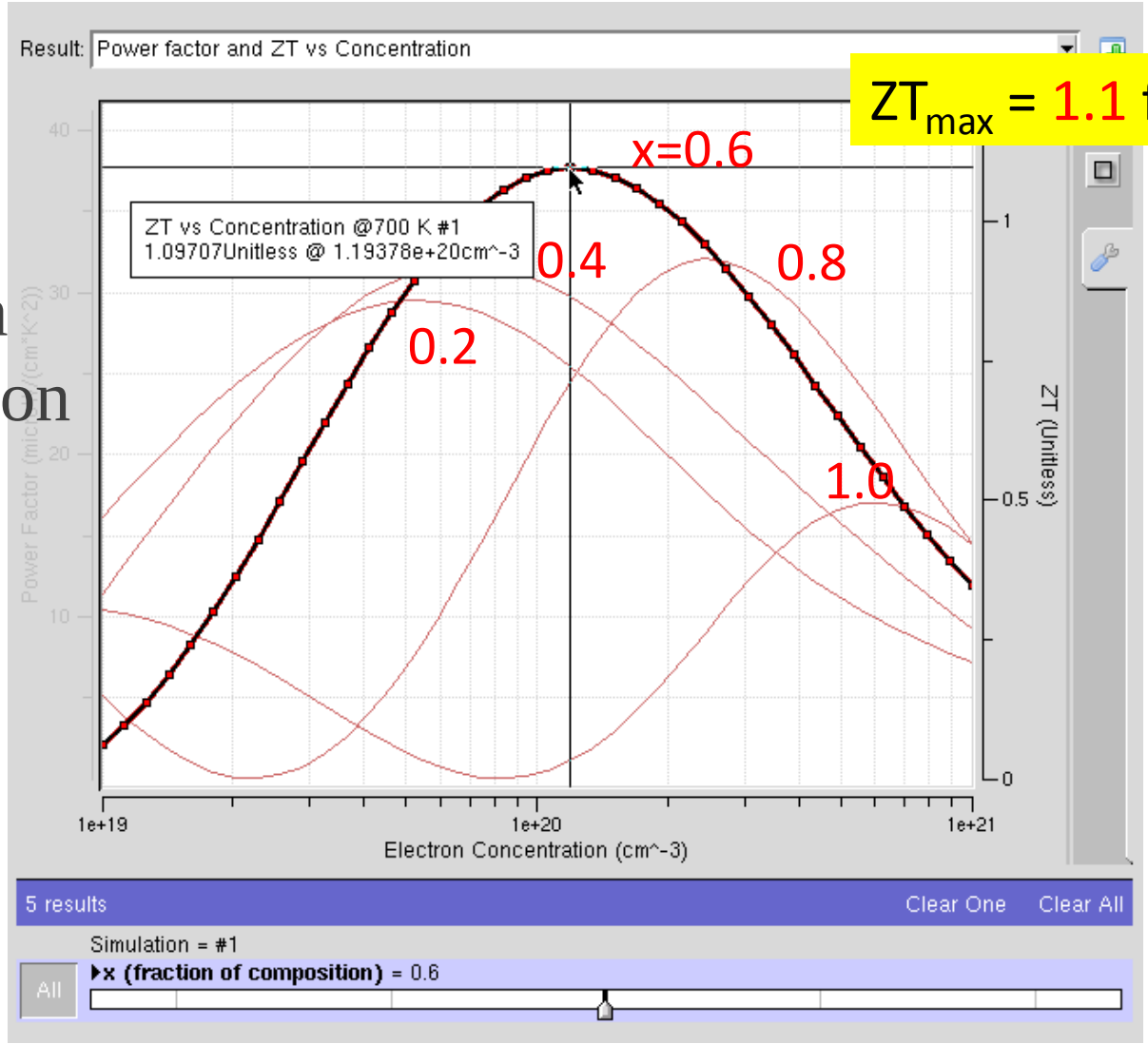


< First Brillouin zone >

Convergence of the two conduction bands at X valley for x=0.6~0.8

Prob. 3. $Mg_2Sn_xSi_{1-x}$ solid solution

3-1. Composition and carrier concentration co-optimization

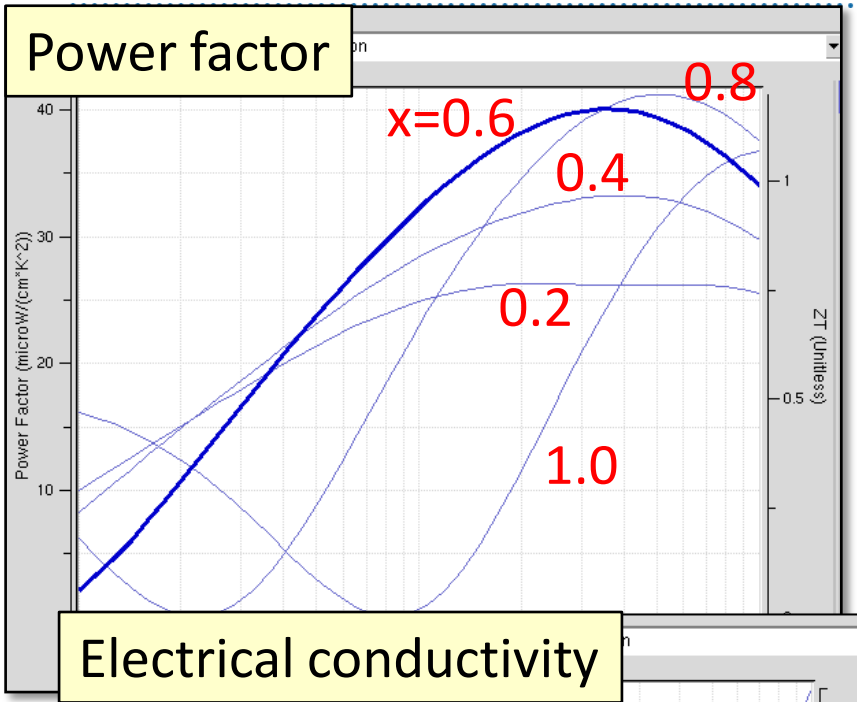


ZT_{max} = 1.1 for x=0.6

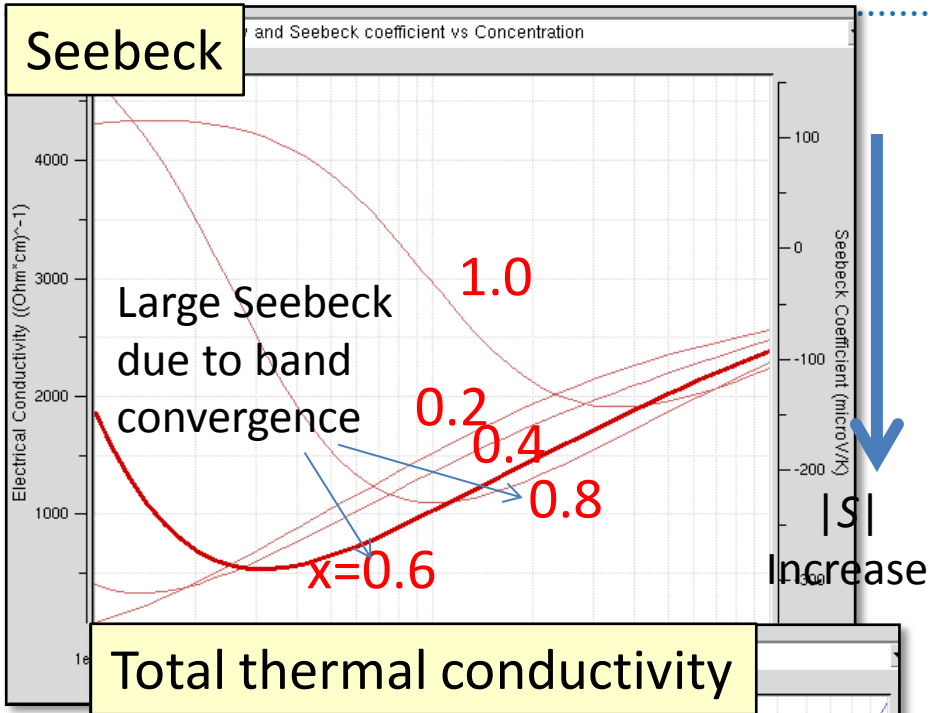
700 K

Prob. 3. $Mg_2Sn_xSi_{1-x}$ solid solution

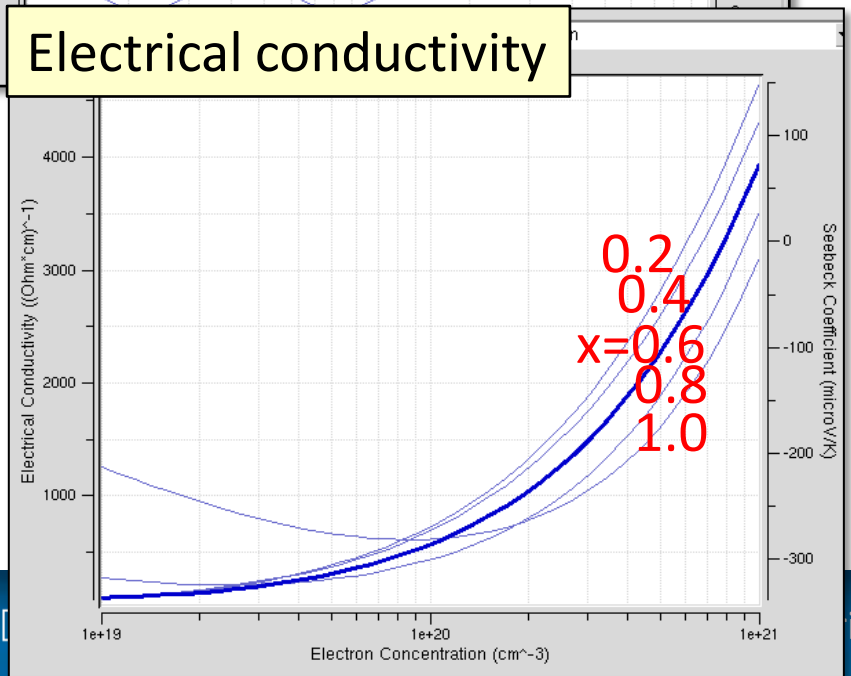
Power factor



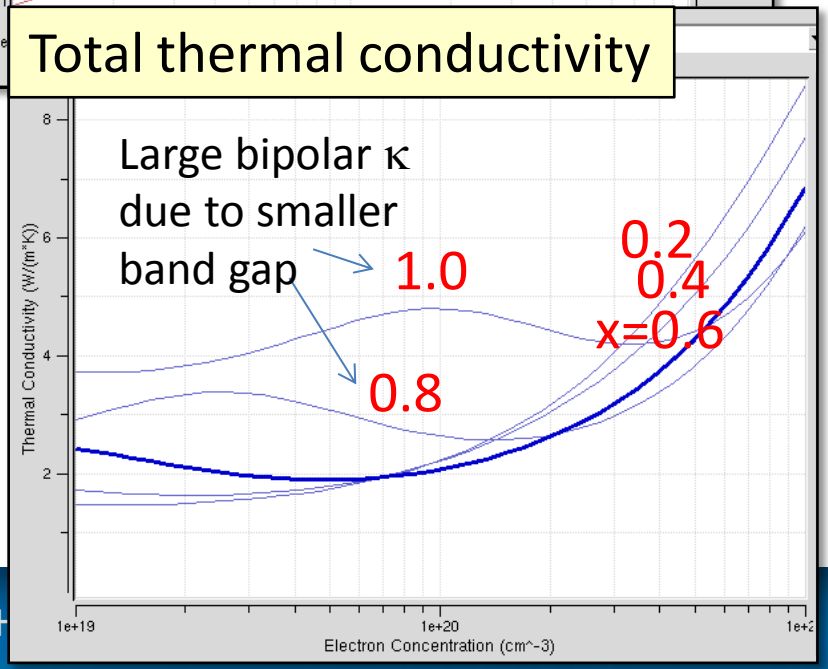
Seebeck



Electrical conductivity



Total thermal conductivity



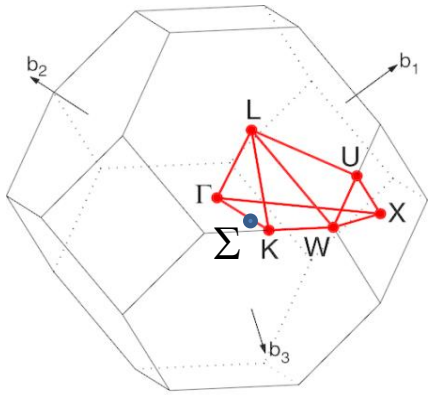
Prob. 3. $Mg_2Sn_xSi_{1-x}$ solid solution (Sn content)

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

< First Brillouin zone >



Band structure of PbTe

L valley

E_g=0.169+5.02e-4*T (eV)

E_{gv}=0.237-0.42e-3*T (eV)

Valence bands convergence

L : Band degeneracy =4

Σ : Band degeneracy = 12

m_e= 0.079m_0
$m_{h,L}$=0.084m_0
$m_{h,\Sigma}$=0.368m_0

All temperature-dependent

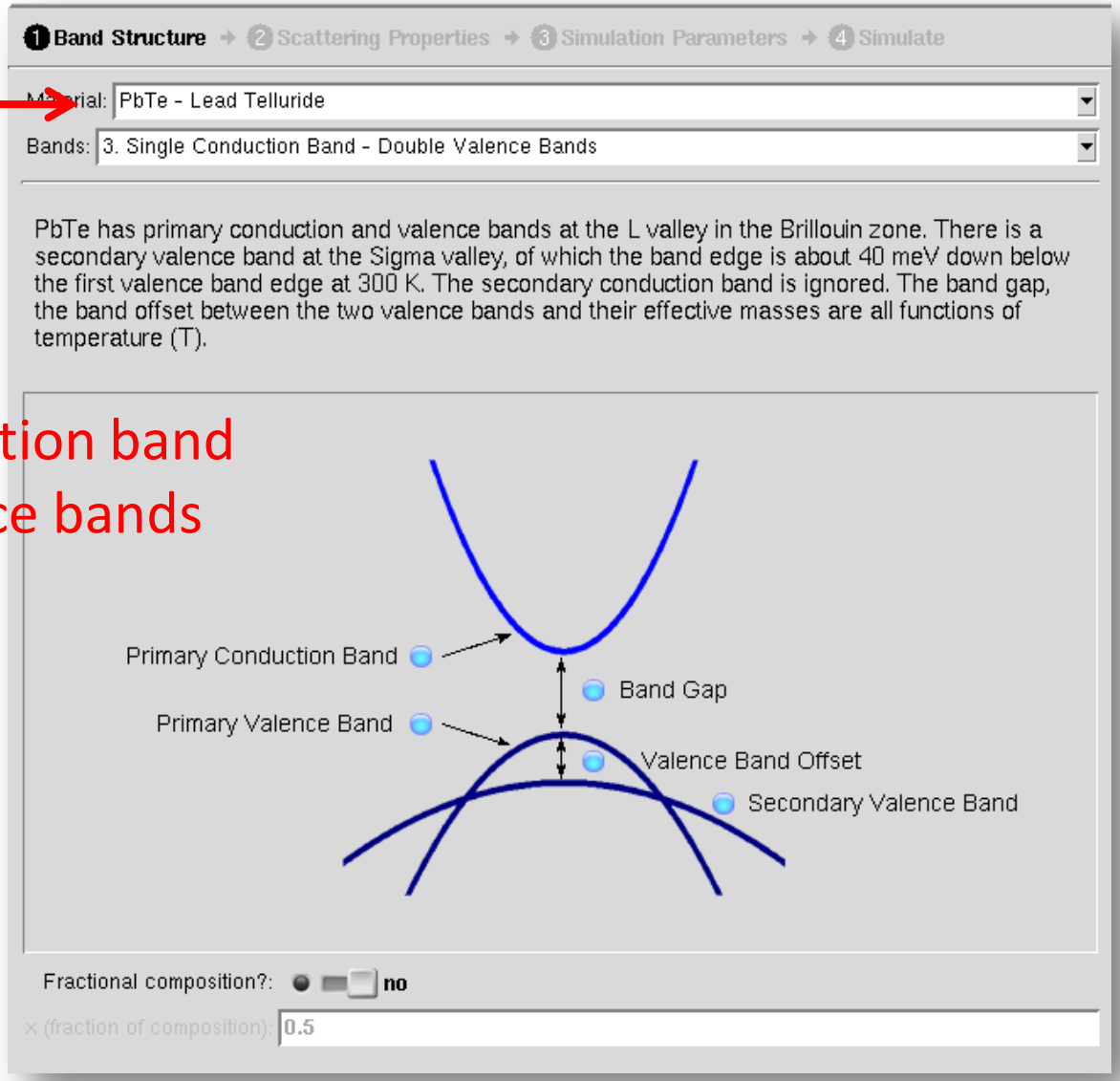
(Room temperature)

[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

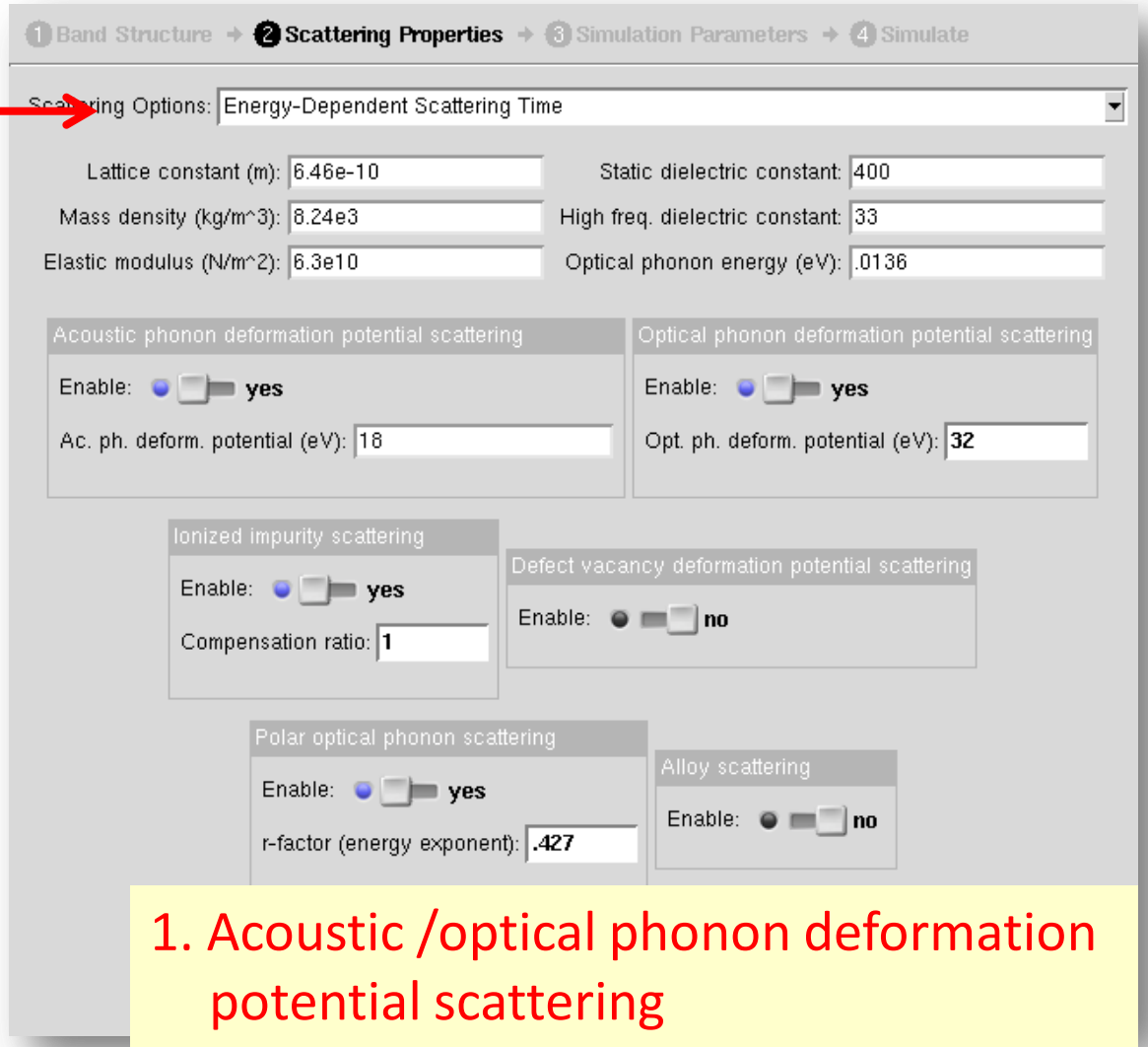
PbTe material selection

One conduction band
Two valence bands



Prob. 4. Doping optimization of p-type PbTe

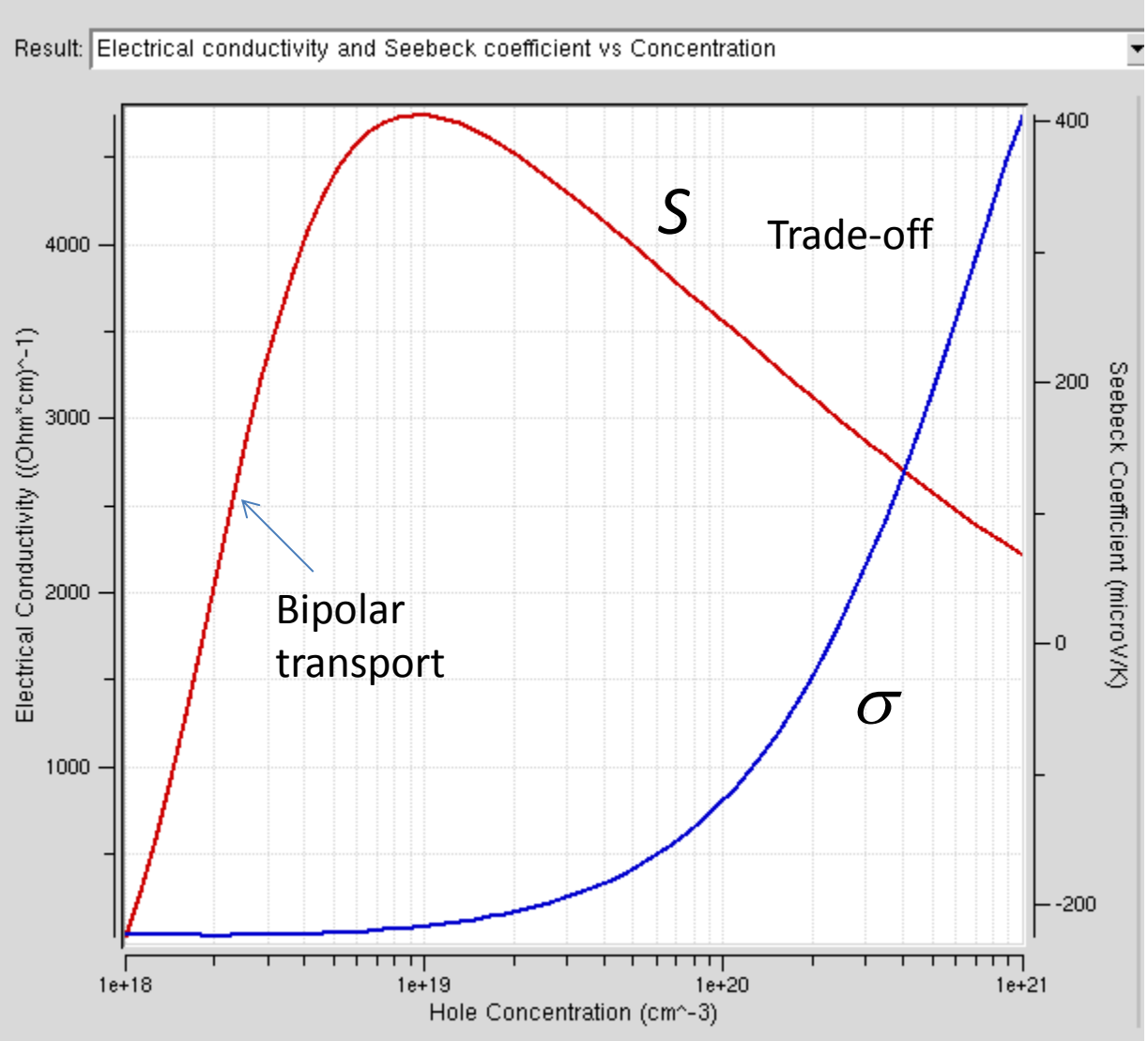
Energy-dep. scatterings



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

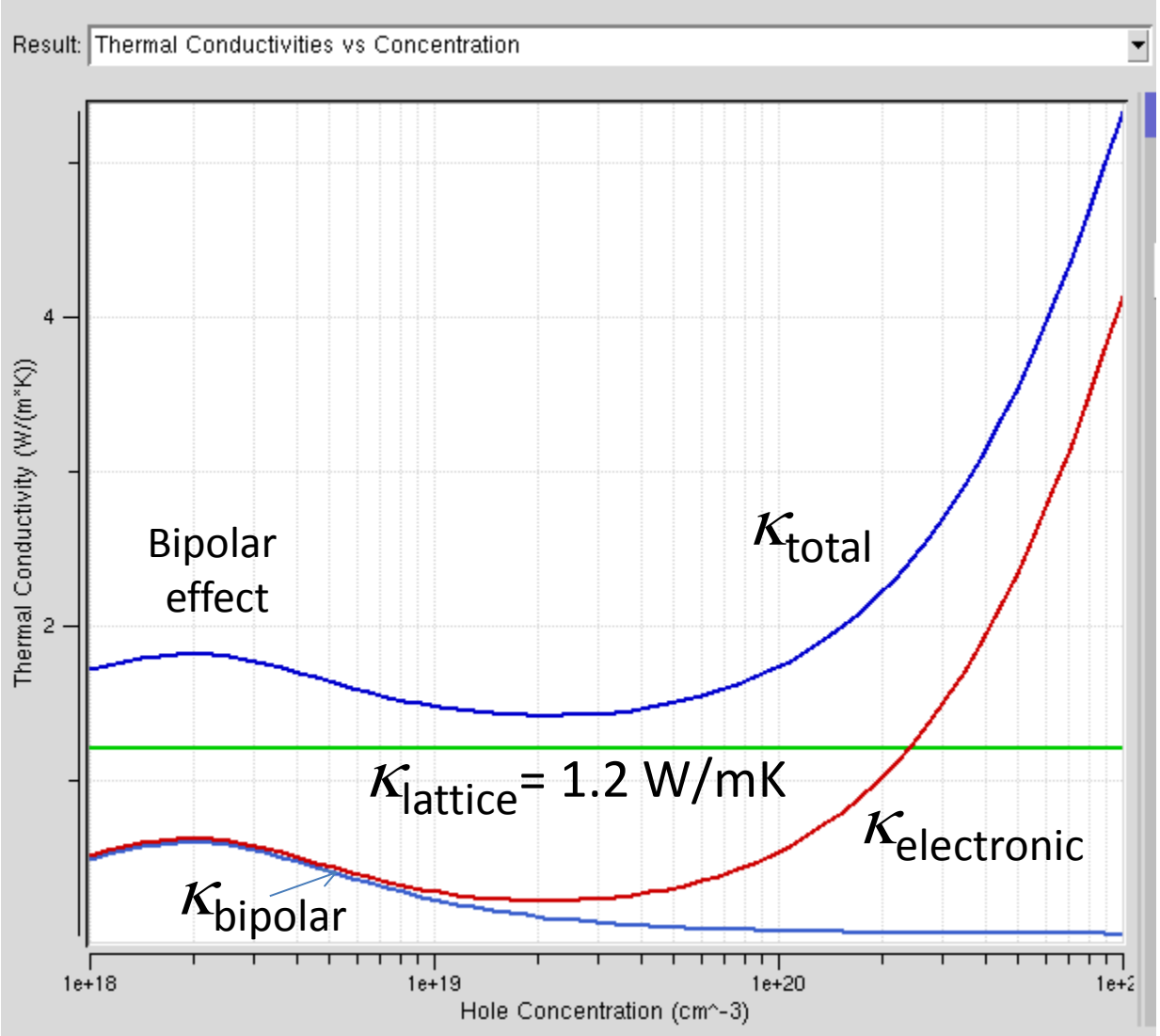
Prob. 4. Doping optimization of p-type PbTe

4-1.
p-PbTe
600 K



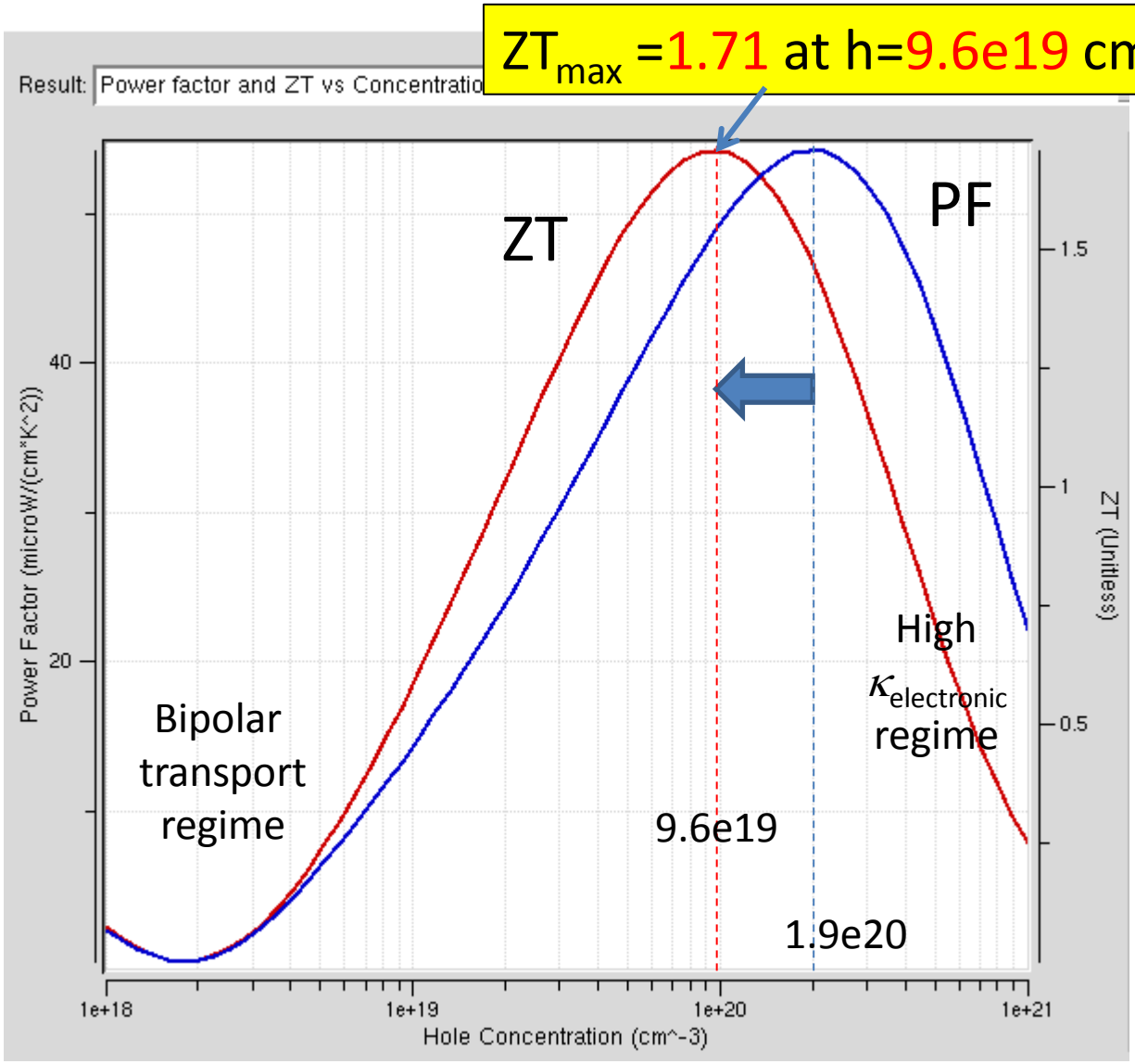
Prob. 4. Doping optimization of p-type PbTe

4-1.
p-PbTe
600 K



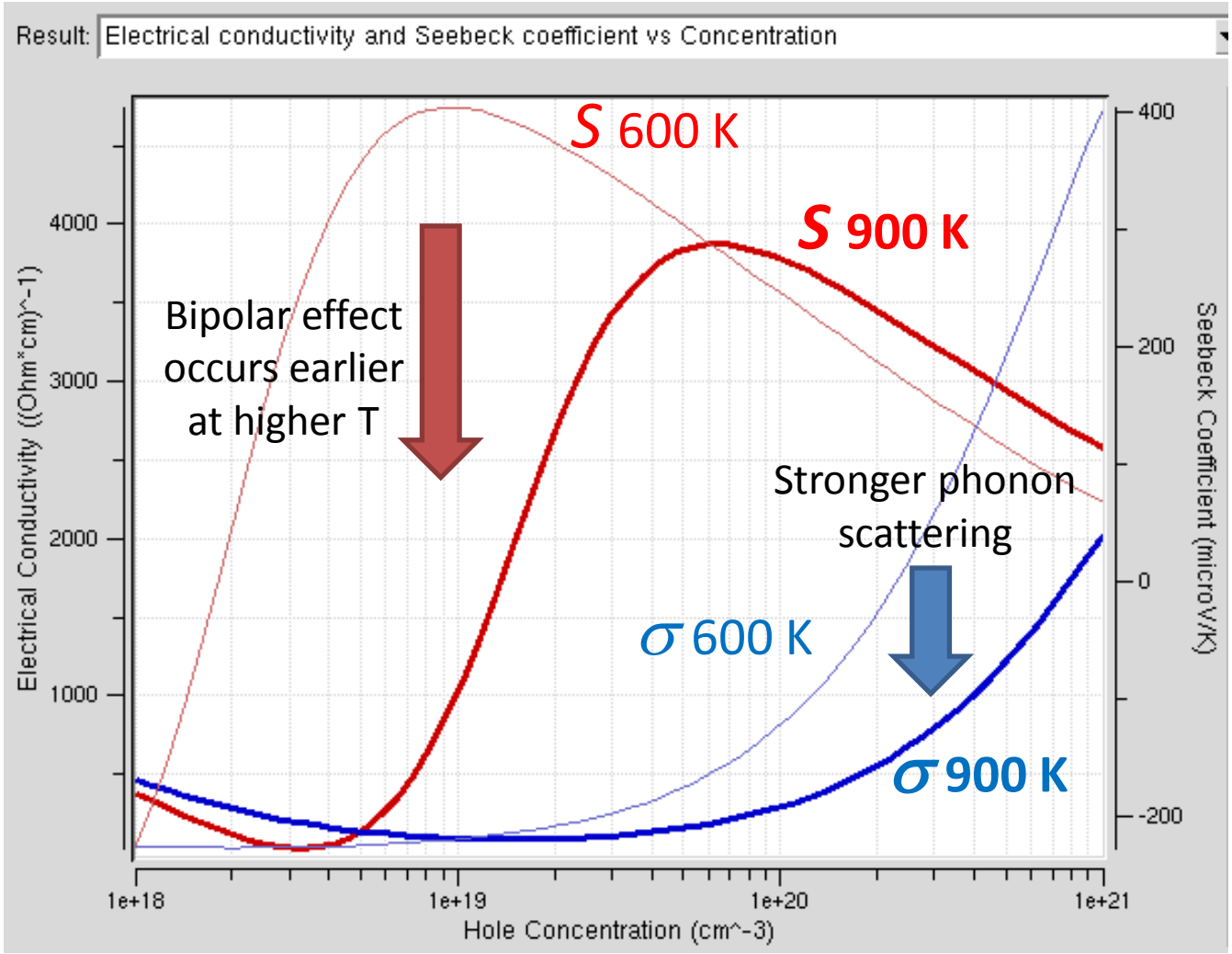
Prob. 4. Doping optimization of p-type PbTe

4-1.
p-PbTe
600 K



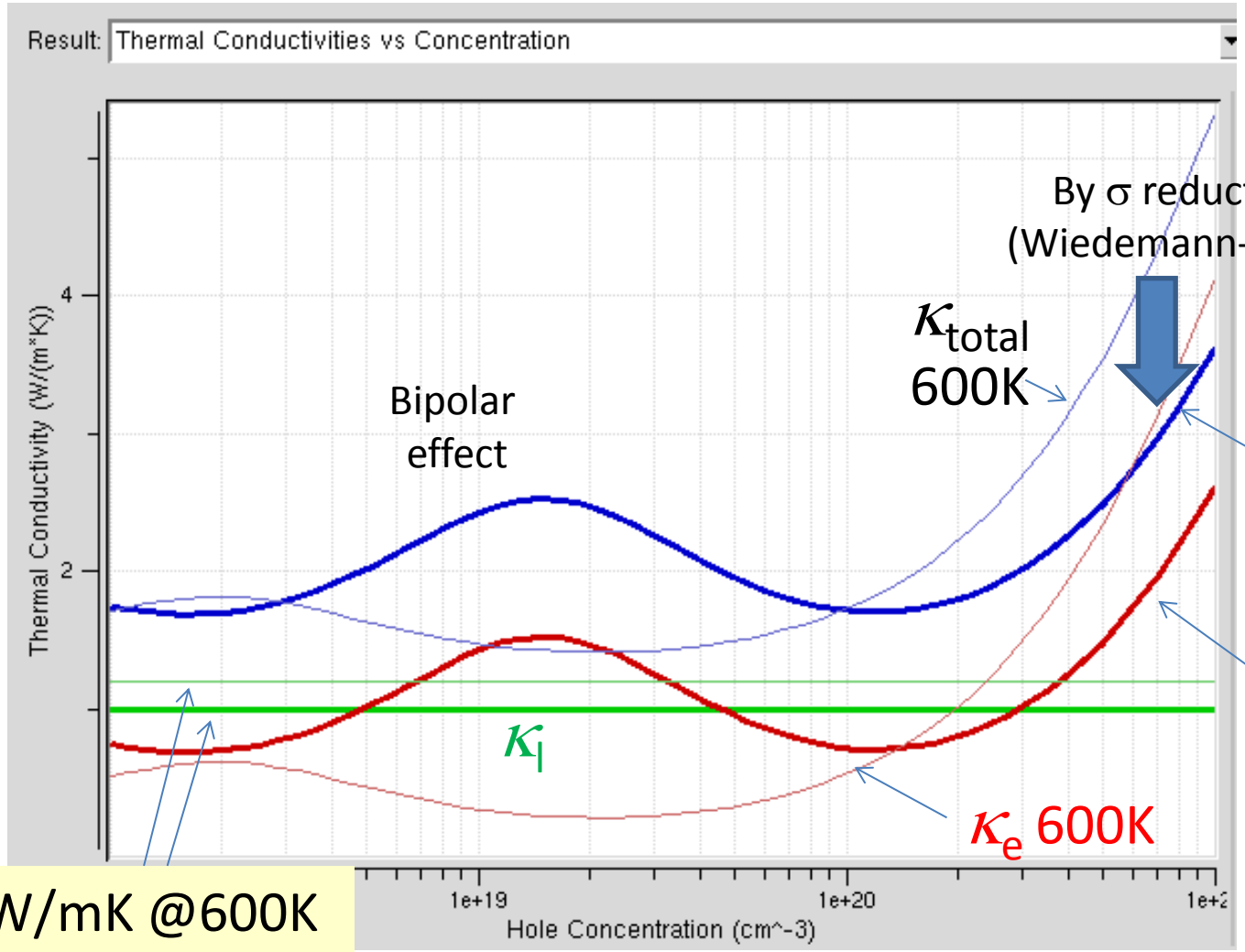
Prob. 4. Doping optimization of p-type PbTe

4-2.
p-PbTe
900 K



Prob. 4. Doping optimization of p-type PbTe

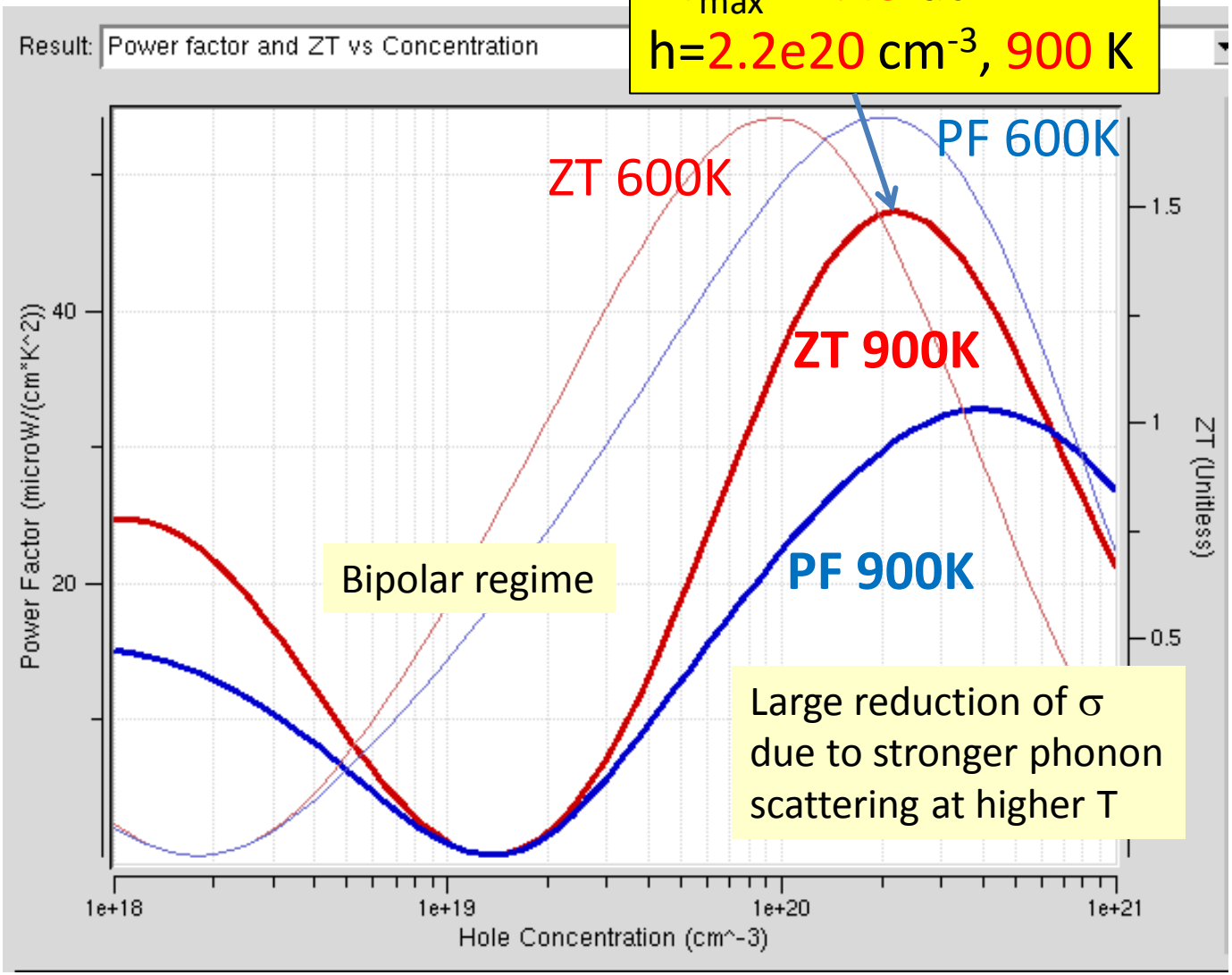
4-2.
p-PbTe
900 K



κ_l= 1.2 W/mK @600K
κ_l= 1.0 W/mK @ 900K

Prob. 4. Doping optimization of p-type PbTe

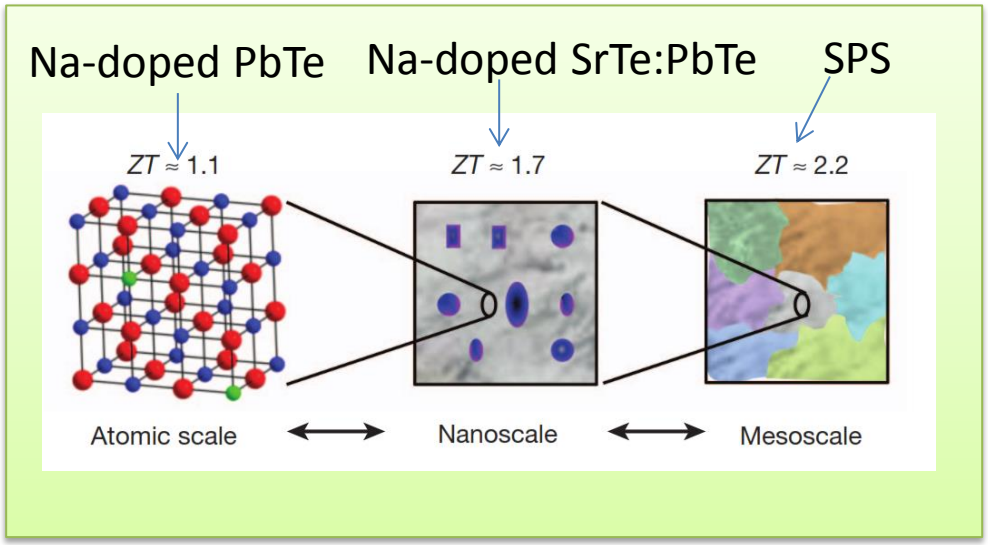
4-2.
p-PbTe
900 K

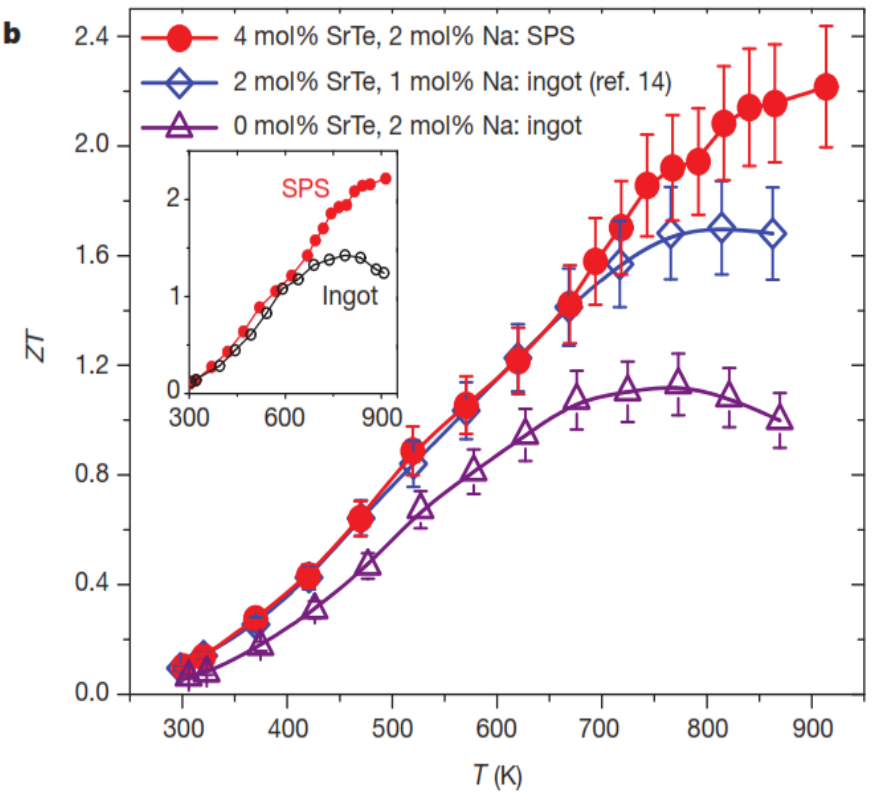


Prob. 5. Analysis of the recent Nature 2012 paper

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

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

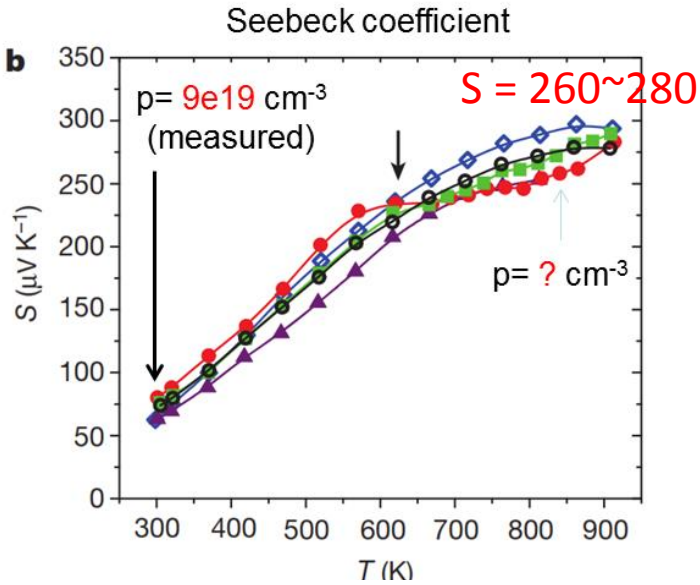


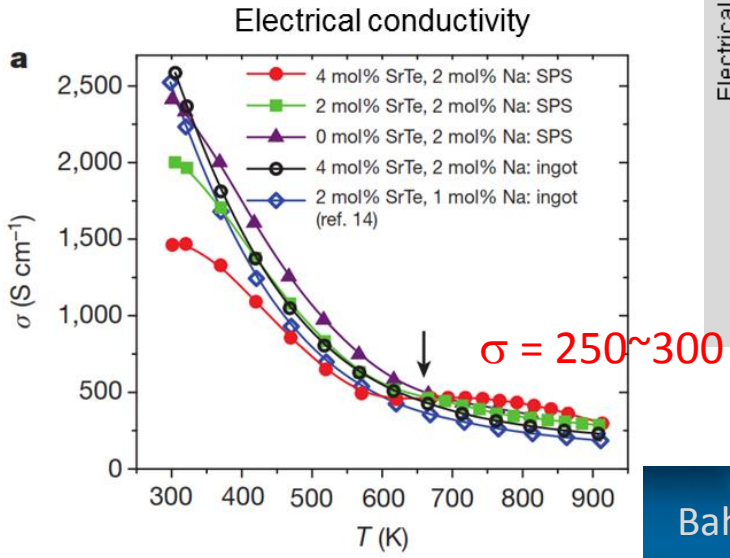


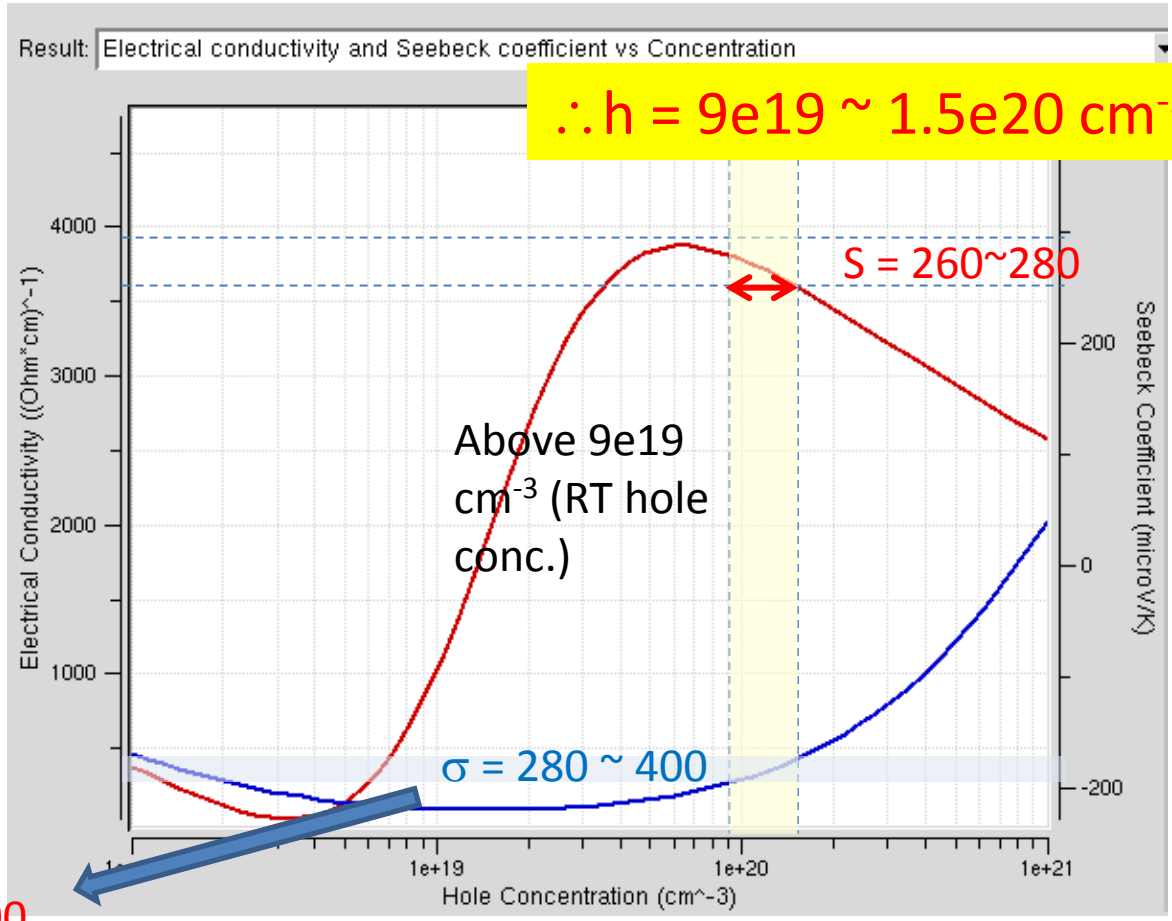
- All-scale hierarchical structures for thermal conductivity reduction.
- Electron transport near optimal.

Prob. 5. Analysis of the recent Nature 2012 paper

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



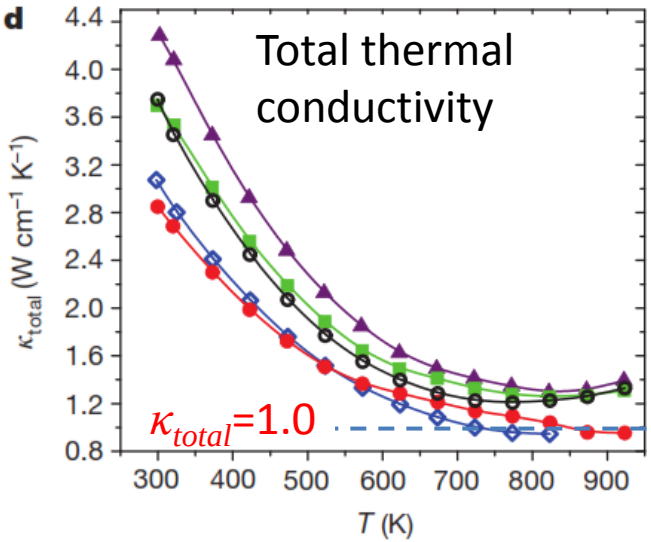


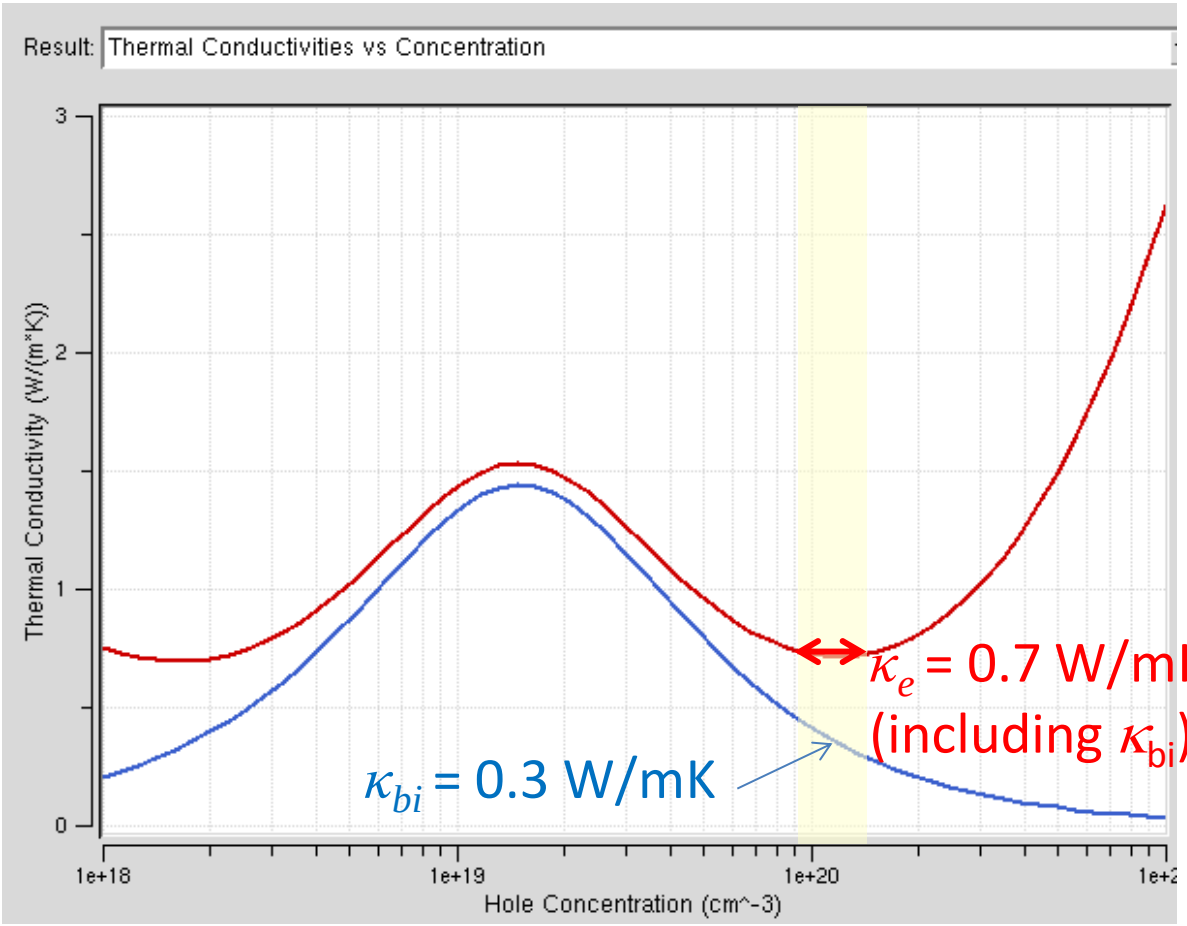


Slightly reduced due to additional carrier scattering by nanostructures/grain boundaries

Prob. 5. Analysis of the recent Nature 2012 paper

5-3. Thermal conductivity at 900 K





$\therefore \kappa_l = \kappa_{total} - \kappa_e$ = 1.0 - 0.7 = **0.3** 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

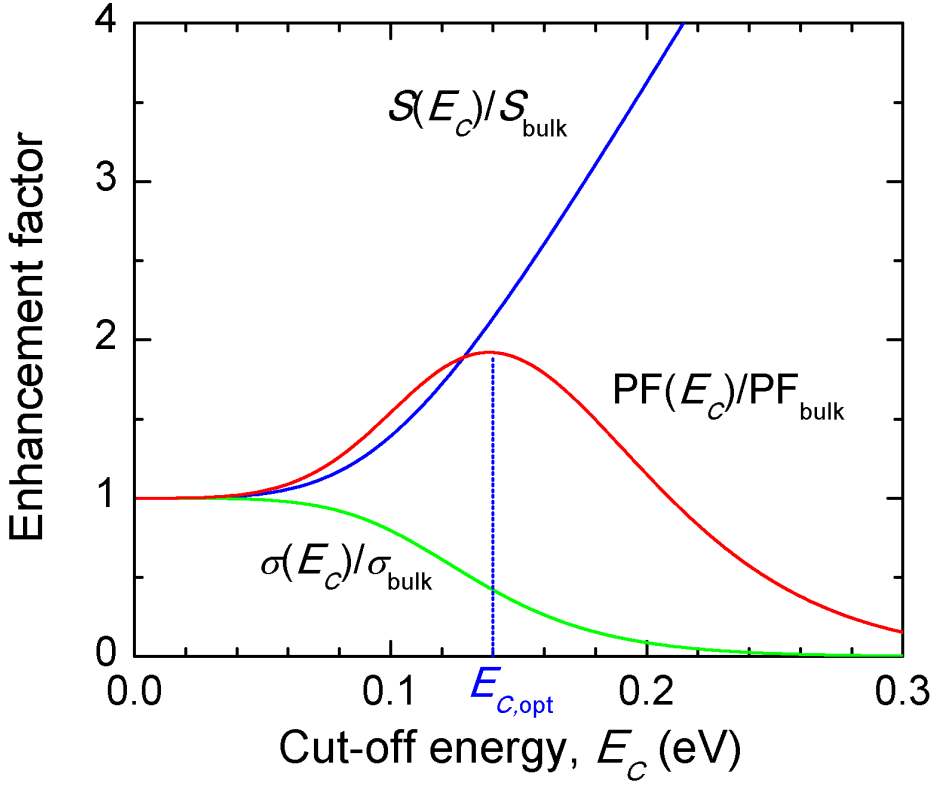
$q = -e$ (conduction band)

$q = +e$ (valence band)

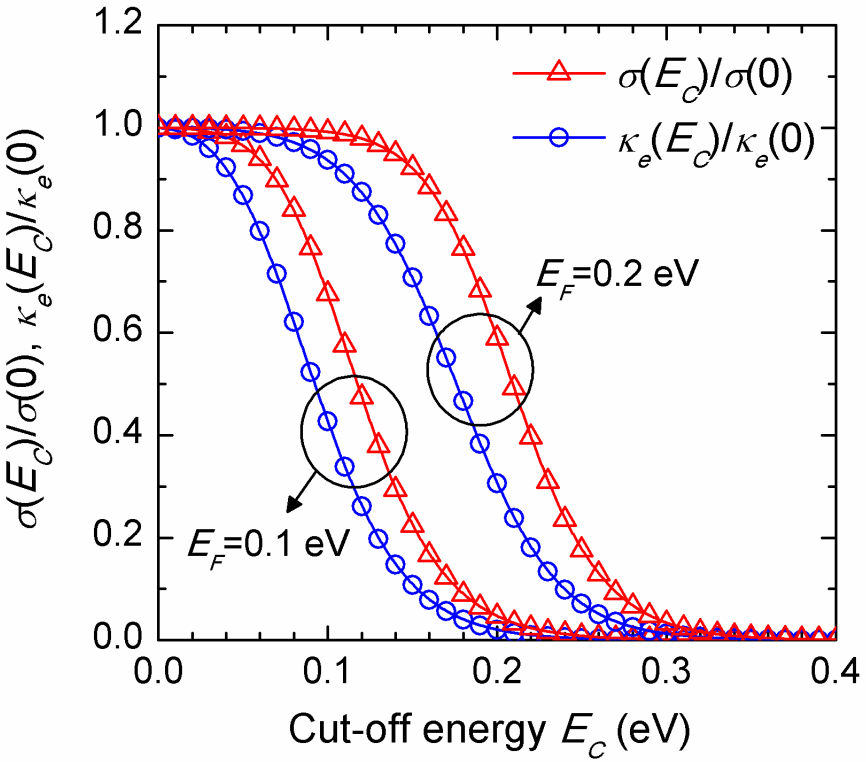
Prob. 6. Carrier energy filtering in PbTe at 900 K

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

Power factor enhancement



Electronic thermal conductivity reduction

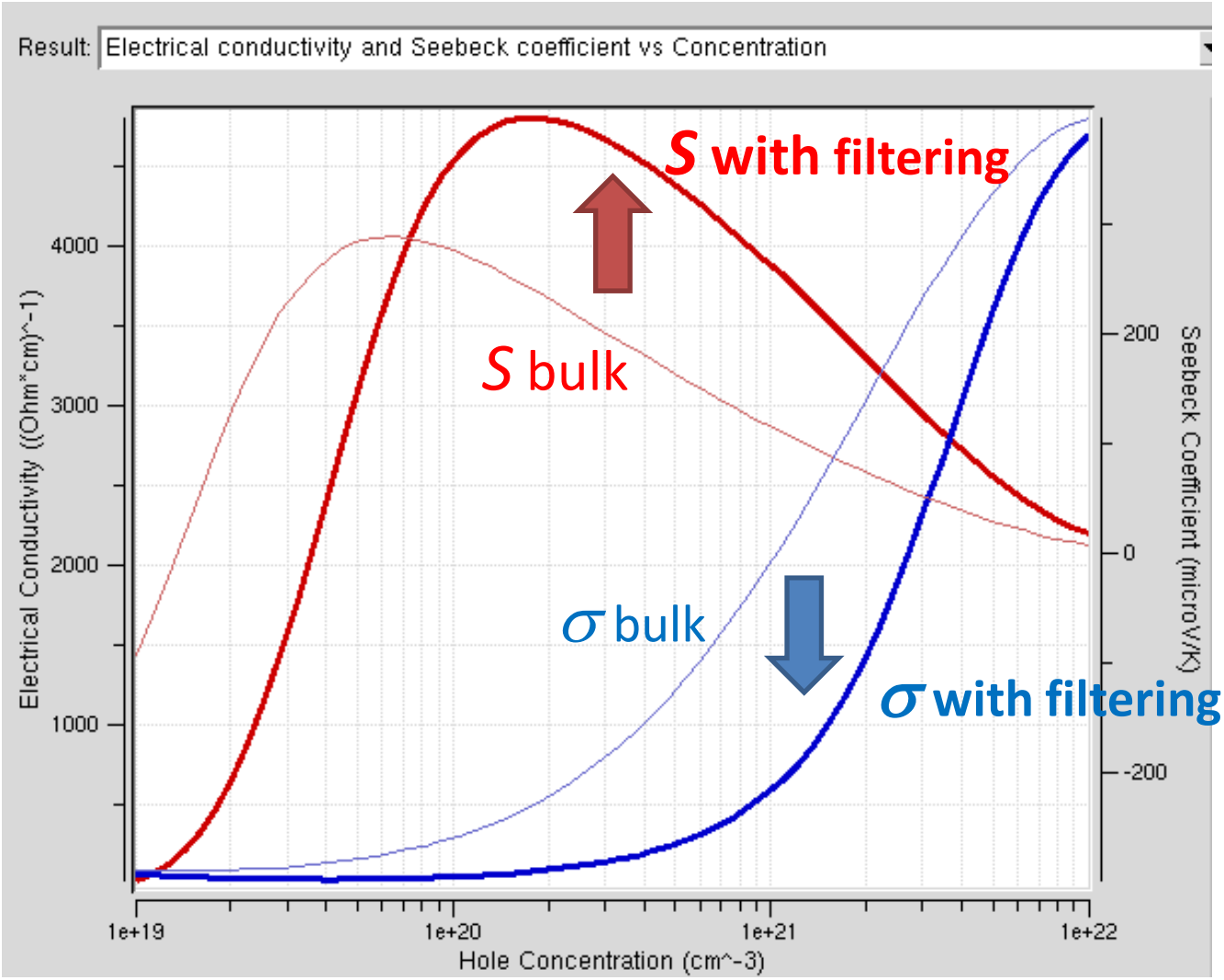


300 K
E_F=0.1 eV (const.)
r=0.5

$$\kappa_e = L\sigma T$$

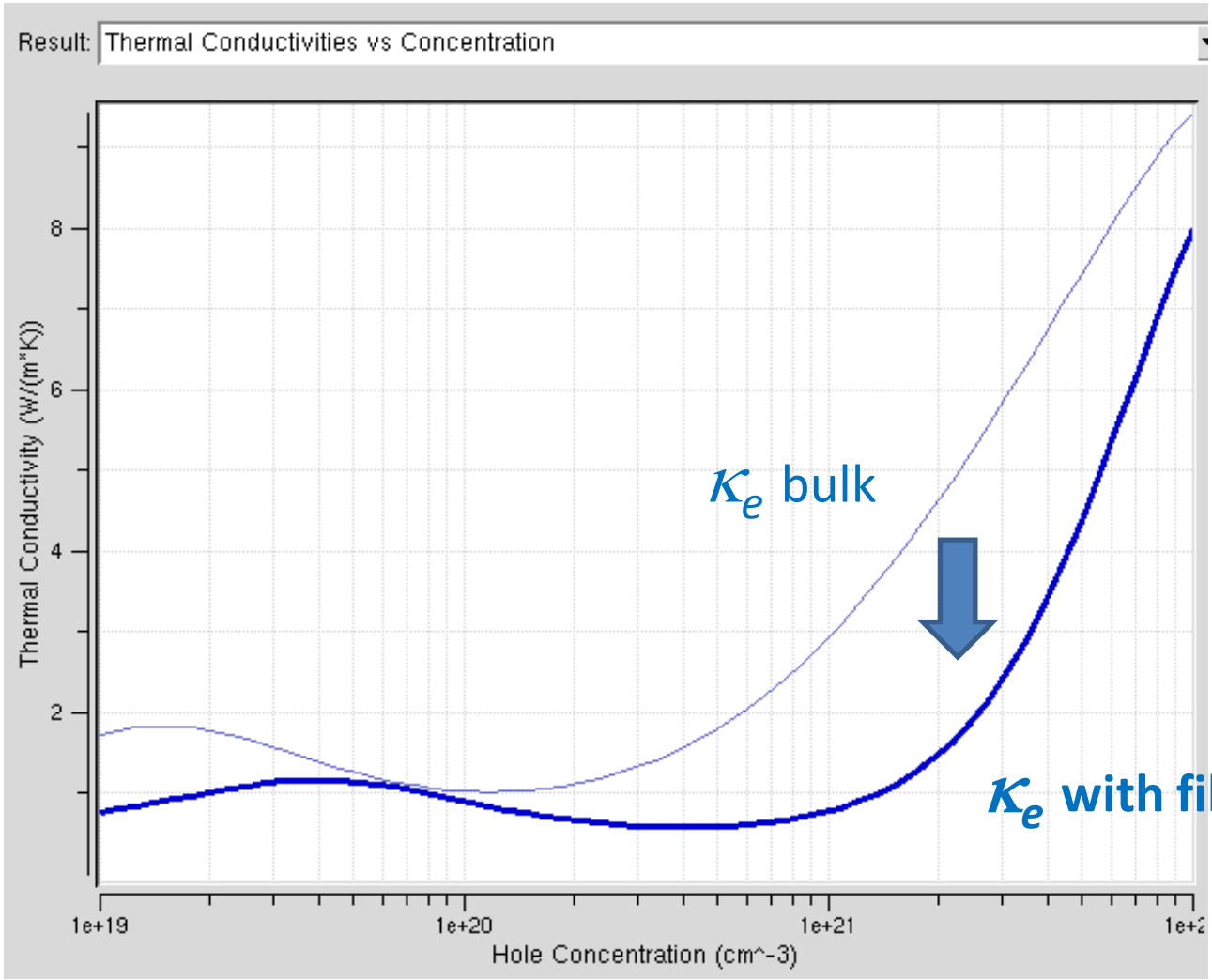
Prob. 6. Carrier energy filtering in PbTe at 900 K

p-type PbTe
900 K
E_C = 0.1 eV



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

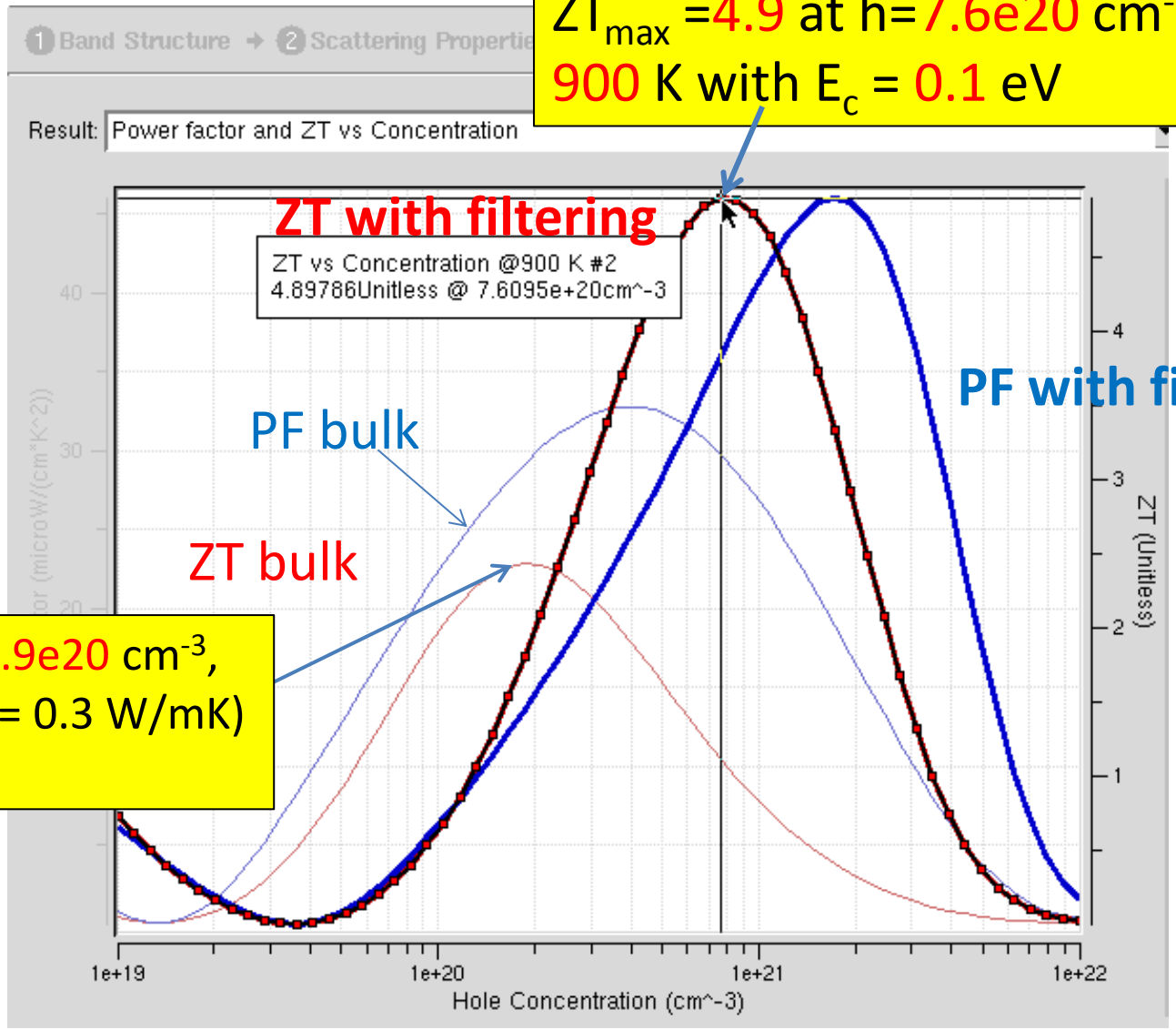
p-type PbTe
900 K
E_C = 0.1 eV



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

p-type PbTe
900 K
E_C = 0.1 eV

ZT_{max} =4.9 at h=7.6e20 cm^{-3},
900 K with E_c = 0.1 eV



ZT_{max} =2.4 at h=1.9e20 cm^{-3},
for bulk PbTe (κ_l = 0.3 W/mK)
900 K