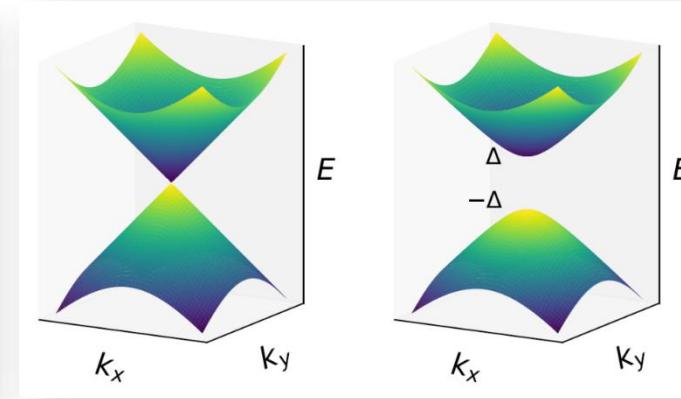
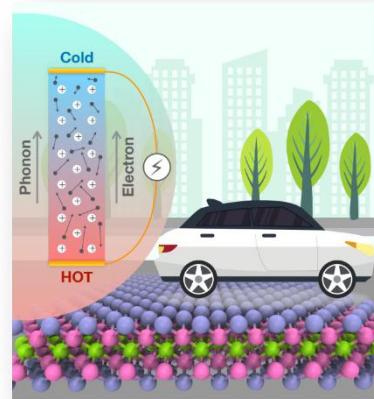


Kuliah “Teori Materi Kuantum Material” 20251105

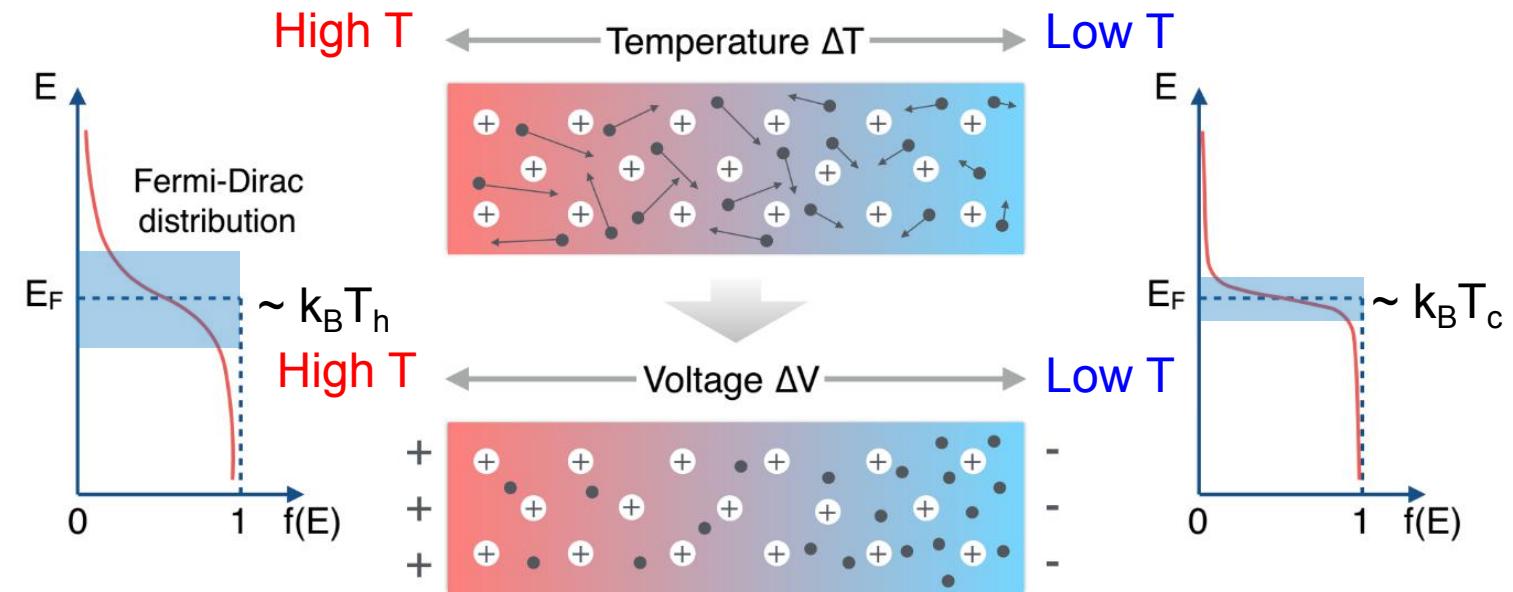
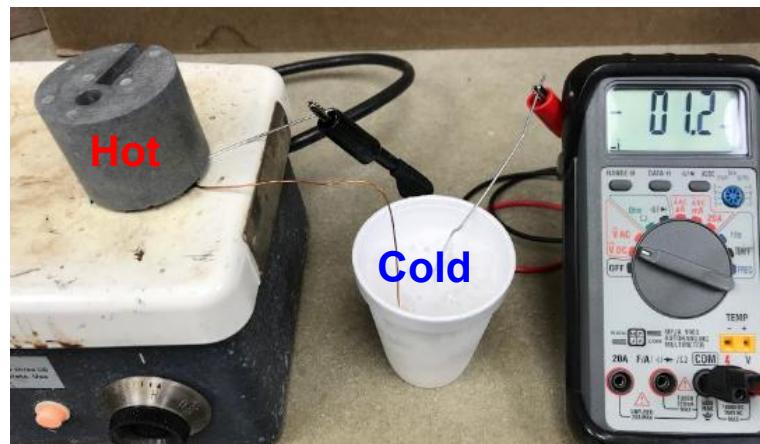
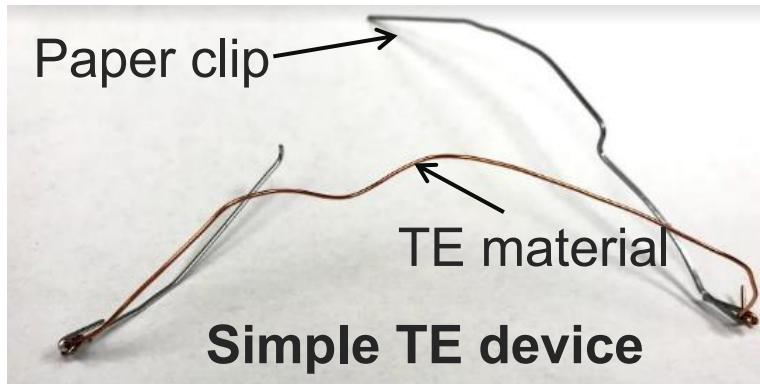
Designing High-Performance Thermoelectrics in Low-Dimensional Materials



Ahmad Ridwan Tresna Nugraha
Pusat Riset Fisika Kuantum, Badan Riset & Inovasi Nasional



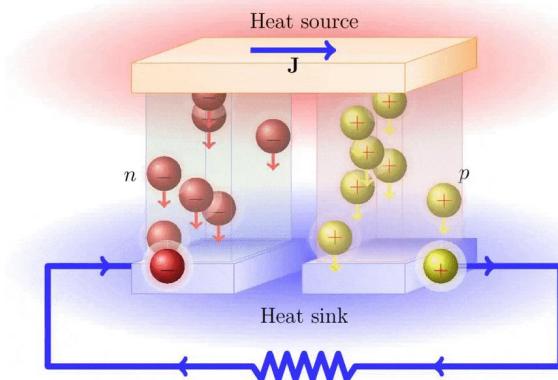
Thermoelectric (TE) / Seebeck's effect



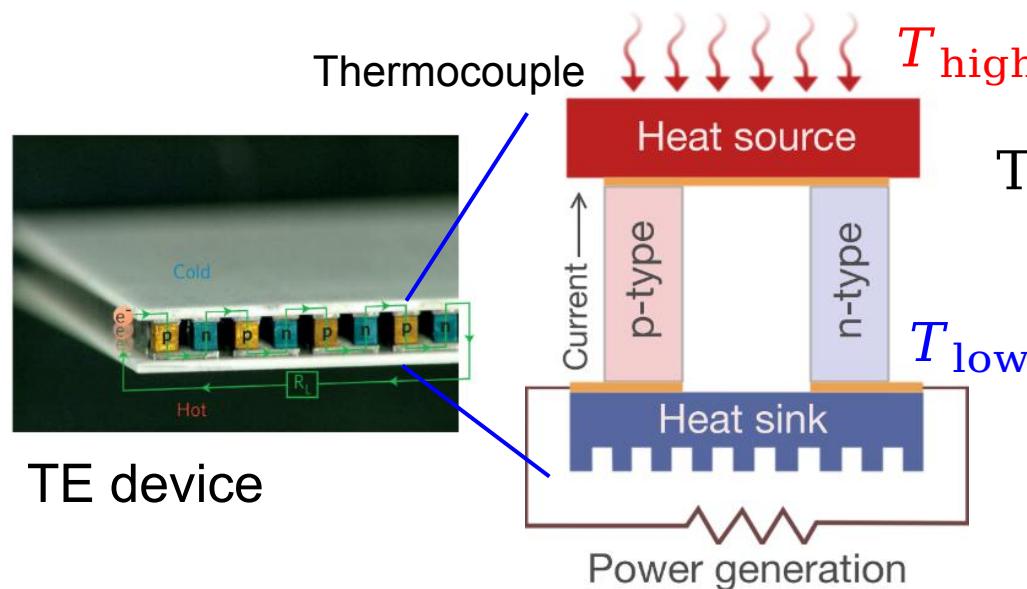
Seebeck's coefficient:

$$S = -\frac{\Delta V}{\Delta T} \quad [\text{V/K}]$$

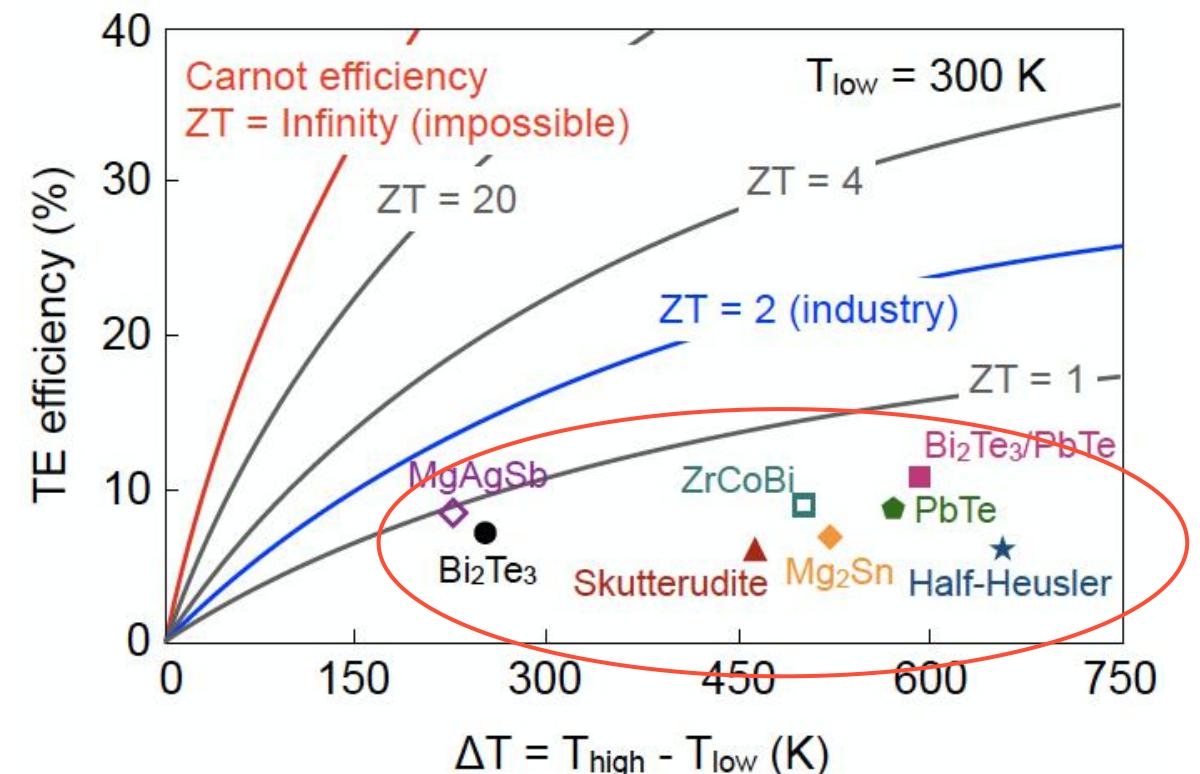
Heat → Electrical Energy: Useful for energy sustainability



Basic requirement of TE device



$$\text{TE efficiency} = \left(\frac{T_{\text{high}} - T_{\text{low}}}{T_{\text{high}}} \right) \left[\frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_{\text{high}}}{T_{\text{low}}}} \right]$$

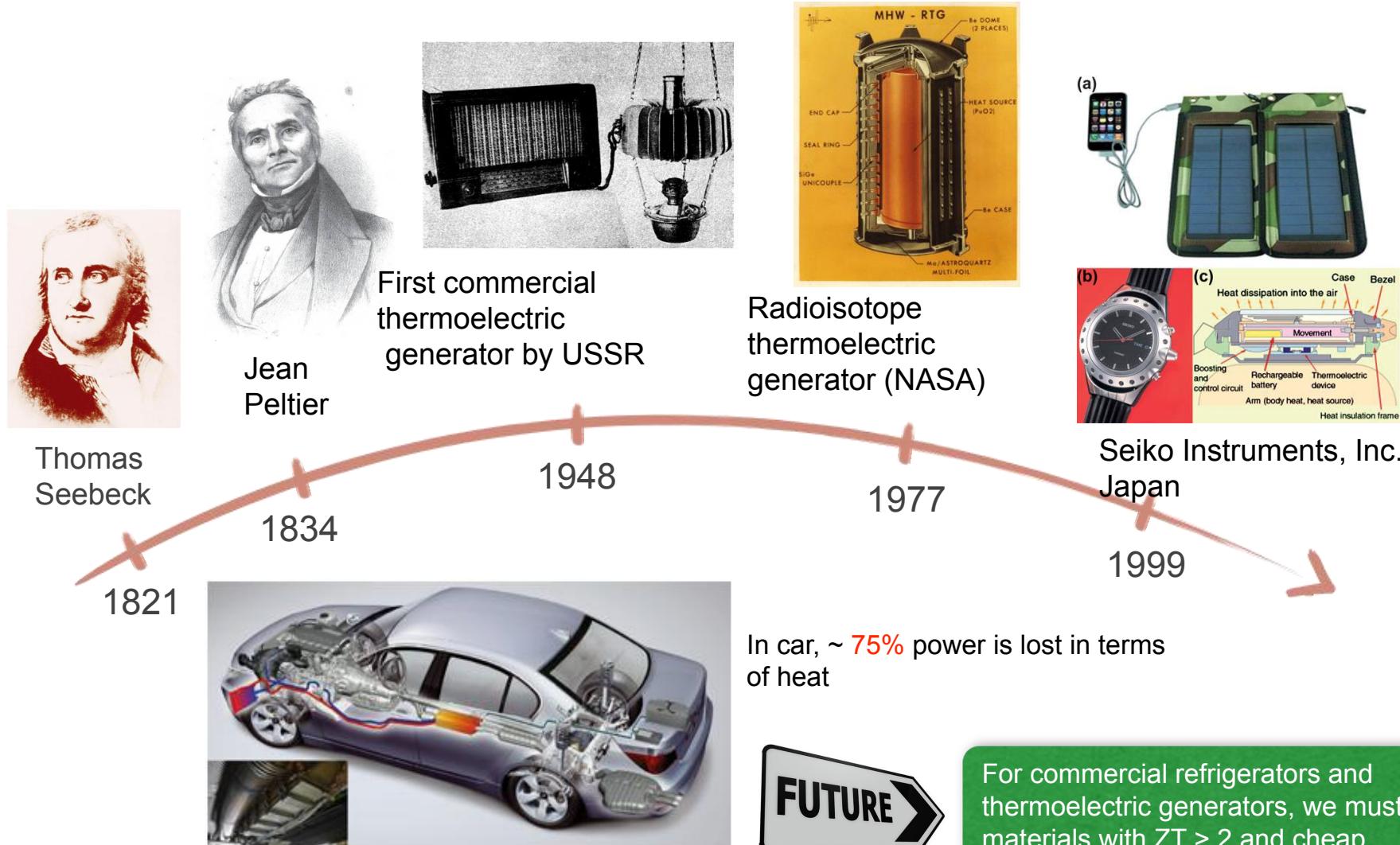


Power factor: S: Seebeck coefficient
 $\text{PF} = S^2 \sigma [\text{W/mK}^2]$
 σ : electrical conductivity
 κ : thermal conductivity

Figure of merit: $T = \frac{1}{2}(T_{\text{high}} + T_{\text{low}})$

$$ZT = \frac{S^2 \sigma}{K} T$$

History of thermoelectric power generation



For commercial refrigerators and thermoelectric generators, we must find materials with $ZT > 2$ and cheap.

Semiconductors for thermoelectrics

Semiconductor and insulator:

$$S \sim \frac{k_B}{e} \frac{E_g}{k_B T} \gg \frac{k_B}{e} \approx 87 \text{ } \mu\text{V/K}$$

Metal:

$$S \sim \frac{k_B}{e} \frac{k_B T}{E_F} \ll \frac{k_B}{e} \approx 87 \text{ } \mu\text{V/K}$$

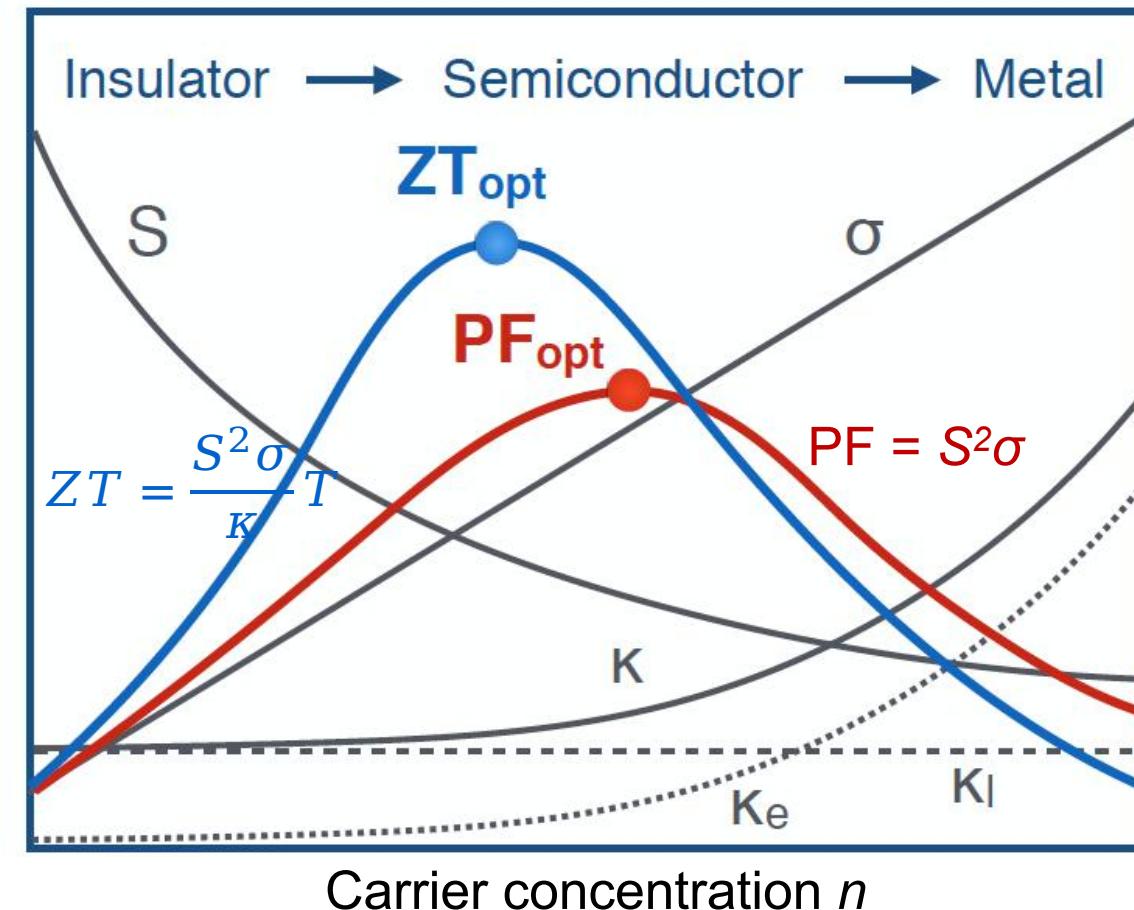
Drude model: $\sigma = n e \mu$

Thermal conductivity: $K = K_e + K_l$
 electron phonon

Wiedemann-Franz law:

$$K_e = L T \sigma$$

$L(n)$: Lorenz number



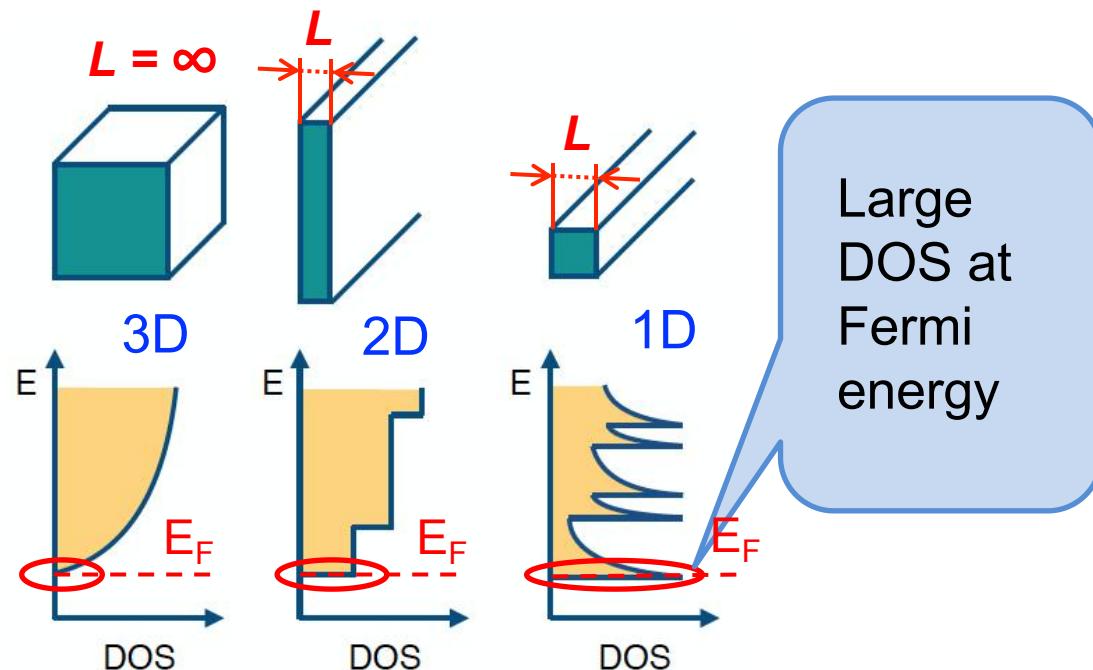
Semiconductors seem to be better TE materials than metals and insulators

Low-dimensional materials

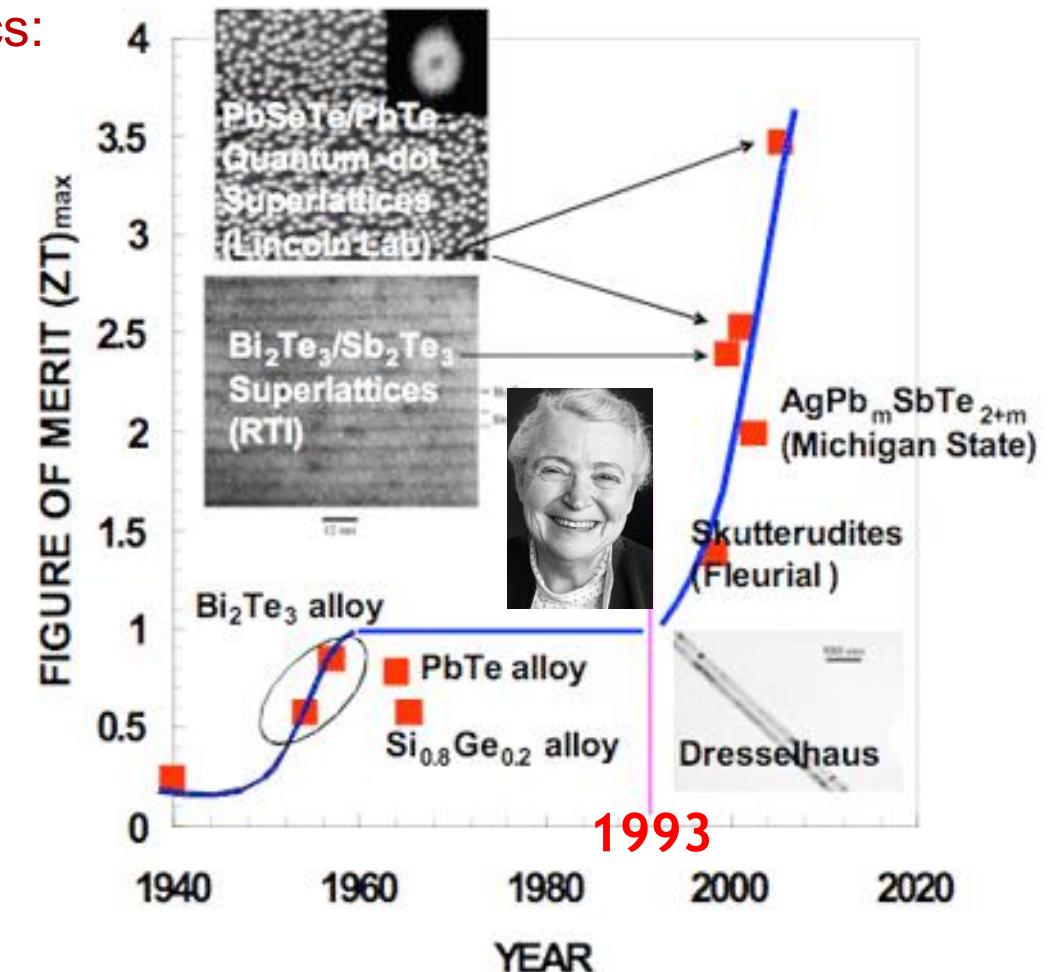
Hicks and Dresselhaus, PRB 47, 12727 (1993); PRB 47, 16631 (1993)

Using low-dimensional materials for thermoelectrics:

the idea from looking at DOS of CNTs



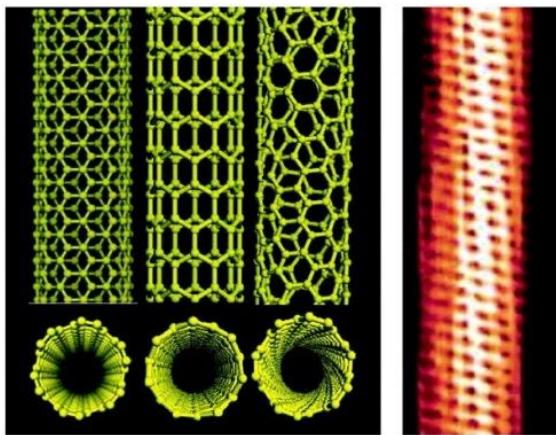
Confinement length L effect



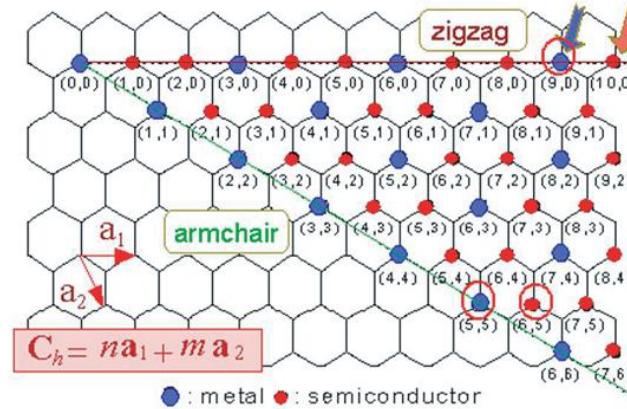
High thermoelectric performance in low-dimensional materials

Carbon nanotubes for thermoelectrics?

1D nanostructure

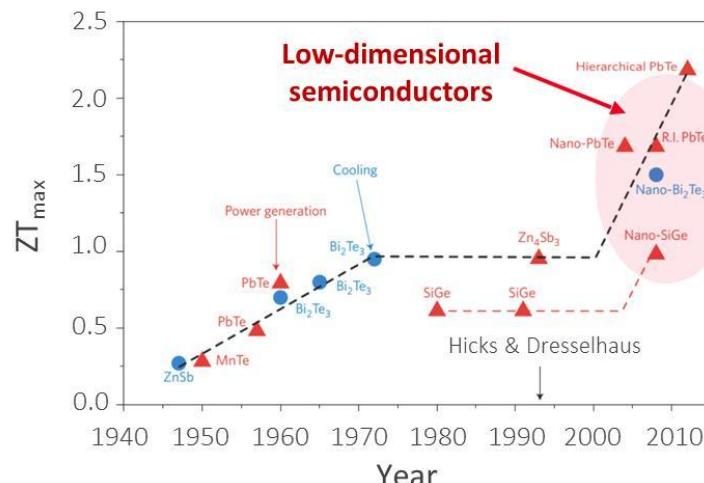


Semiconducting species (s-SWNTs)



R. H. Baughman et al., Science 3, 787-792 (2002)

R. Saito et al., Appl. Phys. Lett. 60, 2204 (1992)



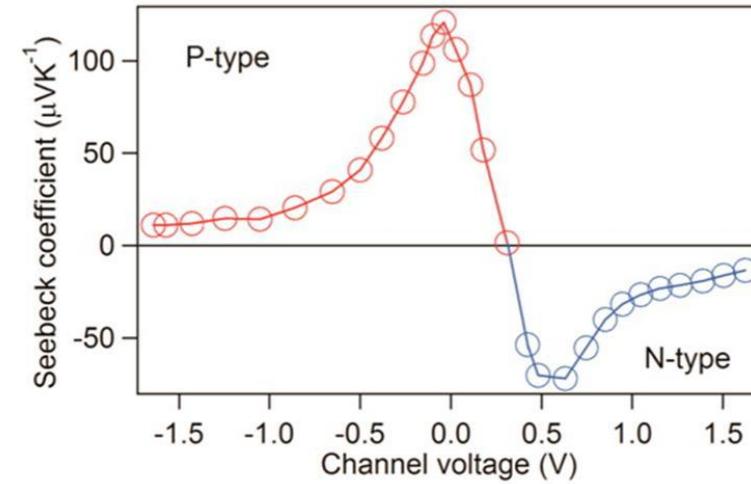
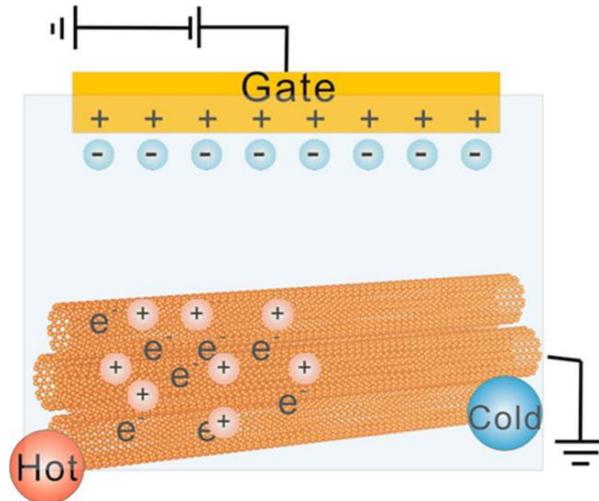
J. P. Heremans et al., Nat. Nanotechnol. 7, 471 (2013)
Hicks and Dresselhaus, Phys. Rev. B 47, 16631(R) (1993)

Figure of
Merit:

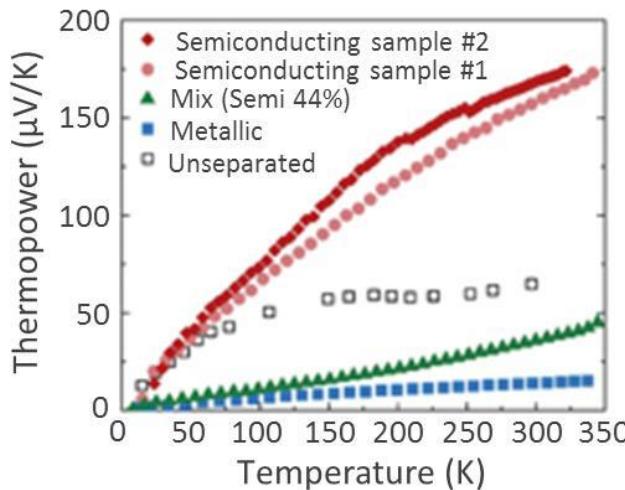
$$ZT = \frac{S^2 \sigma}{\kappa}$$

Larger thermopower $S \Rightarrow$ Higher ZT

Recent interests in semiconducting SWNTs



K. Yanagi et al., Nano Lett. 14, 6437–6442 (2014)



Y. Nakai et al., Appl. Phys. Express. 7, 025103 (2014)

Experiments on **s-SWNT bundles** seem to show large values of thermopower or Seebeck's coefficient (up to 200 $\mu\text{V}/\text{K}$)

What about purely separated one-chirality s-SWNT?

Evaluate thermopower of many s-SWNTs !

Formulation of Seebeck's coefficient

Multi-band model / Mott formula

► For **metals**

Seebeck's coefficient

$$S = -\frac{1}{|e|T} \frac{\int (\varepsilon - \mu) \sigma(\varepsilon) \frac{\partial f_0(\varepsilon)}{\partial \varepsilon} d\varepsilon}{\int \sigma(\varepsilon) \frac{\partial f_0(\varepsilon)}{\partial \varepsilon} d\varepsilon}$$

Electrical conductivity:

$$\sigma = \frac{i}{E} = \int -q^2 v \tau v \frac{\partial f_0}{\partial \varepsilon} g(\varepsilon) d\varepsilon$$

Mott formula:

$$S = -\frac{\pi^2}{3} \frac{k_B}{|e|} k_B T \left. \frac{d(\ln \sigma)}{d\varepsilon} \right|_{E_F}$$

We cannot use this for s-SWNTs!

H. J. Goldsmid, Intro. to Thermoelectricity (2009)

One-band model

► For **semiconductors**

Seebeck's coefficient:

$$S = -\frac{k_B}{q} \left(\eta - \frac{d}{2} - r - 1 \right)$$

Electrical conductivity:

$$\sigma = \frac{2q^2 \tau_0 (\frac{d}{2} + r) (k_B T)^{d/2} \Gamma(\frac{d}{2} + r)}{d L^{3-d} 2^{d/2-1} \pi^{d/2} \hbar^d \Gamma(\frac{d}{2})} (m^*)^{d/2-1} e^\eta$$

$\eta_{n,p} = \pm \eta_\mu - \frac{\eta_g}{2}$ $\eta_\mu = \mu/k_B T$: Reduced fermi level
 $\eta_g = E_g/k_B T$: Reduced band-gap

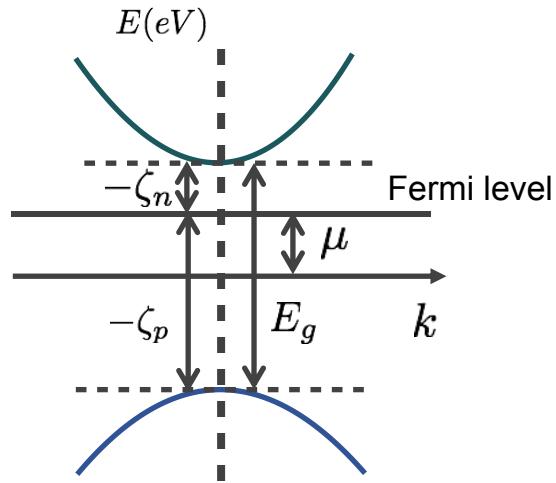
$d = 1, 2, 3$: Dimensions L : Confinement length

$\tau(\varepsilon) = \tau_0 (\varepsilon/k_B T)^r$: Relaxation time

Starting point for s-SWNTs!

Hung, Nugraha et al., Phys. Rev. B 92, 165426 (2015)

The two-band model



Seebeck's coefficient of s-SWNTs is a function of **chemical potential, band-gap, and temperature**.

Seebeck's coefficient

$$S = \frac{\sigma_n S_n + \sigma_p S_p}{\sigma_n + \sigma_p} \quad (\sigma_n, \sigma_p, S_n, S_p \text{ from one-band model})$$

$$S_{\text{CNT}} = \frac{k_B}{e} \left(\frac{\mu}{k_B T} - \frac{E_g}{2k_B T} - \frac{3}{2} + \frac{E_g/k_B T + 3}{e^{2\mu/k_B T} + 1} \right)$$

Optimized chemical potential:

$$\mu_{\text{opt}} = \frac{k_B T}{2} \ln \left(\frac{E_g}{k_B T} + 2 \pm \sqrt{\left(\frac{E_g}{k_B T} + 2 \right)^2 - 1} \right)$$

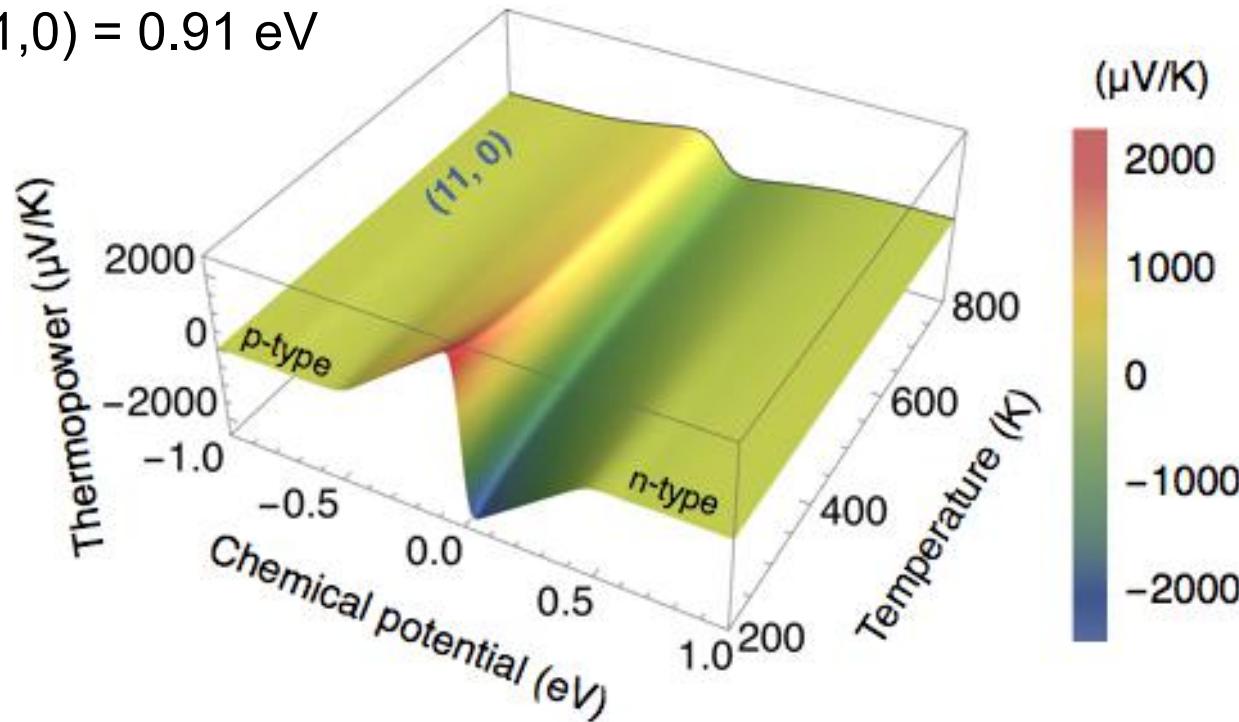
Optimized Seebeck's coefficient:

$$S_{\text{CNT}}^{\text{opt}} = S_{\text{CNT}}(\mu = \mu_{\text{opt}})$$

Seebeck's coefficient of (11,0) s-SWNT

$$S_{\text{CNT}} = \frac{k_B}{e} \left(\frac{\mu}{k_B T} - \frac{E_g}{2k_B T} - \frac{3}{2} + \frac{E_g/k_B T + 3}{e^{2\mu/k_B T} + 1} \right)$$

$$E_g (11,0) = 0.91 \text{ eV}$$

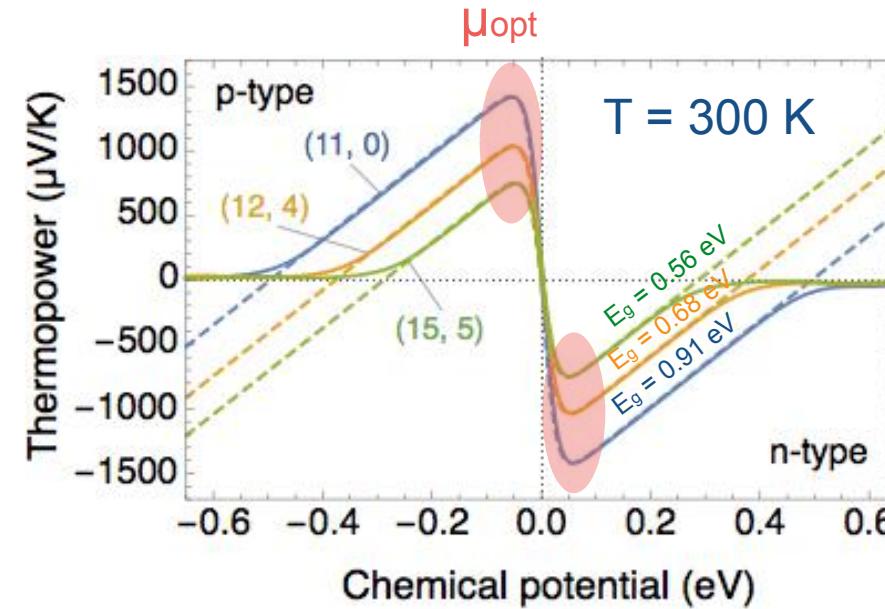
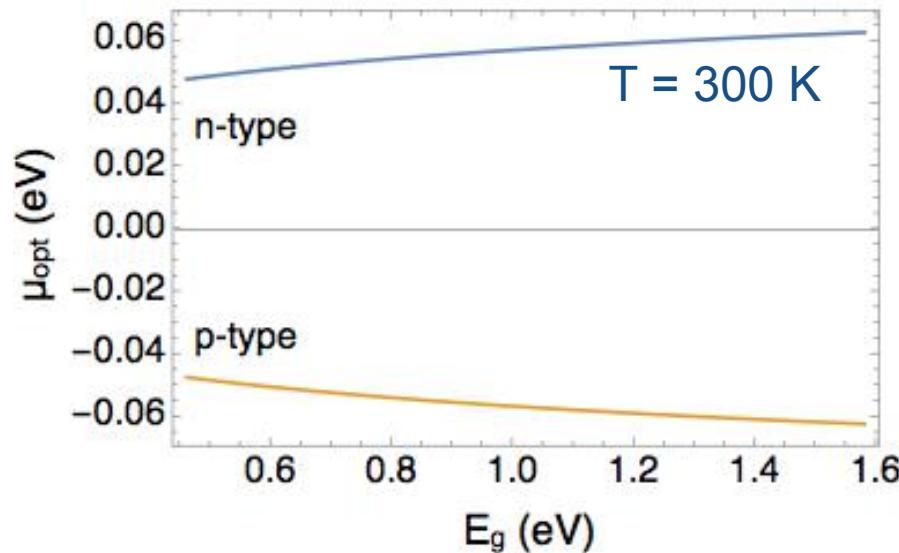


- Thermopower (Seebeck's coefficient) is optimized **near** $\mu \sim 0$
- Lower** temperature \Rightarrow **Higher** thermopower

Optimized chemical potential

$$\mu_{\text{opt}} = \frac{k_B T}{2} \ln \left(\frac{E_g}{k_B T} + 2 \pm \sqrt{\left(\frac{E_g}{k_B T} + 2 \right)^2 - 1} \right)$$

Let's check at $T = 300$ K

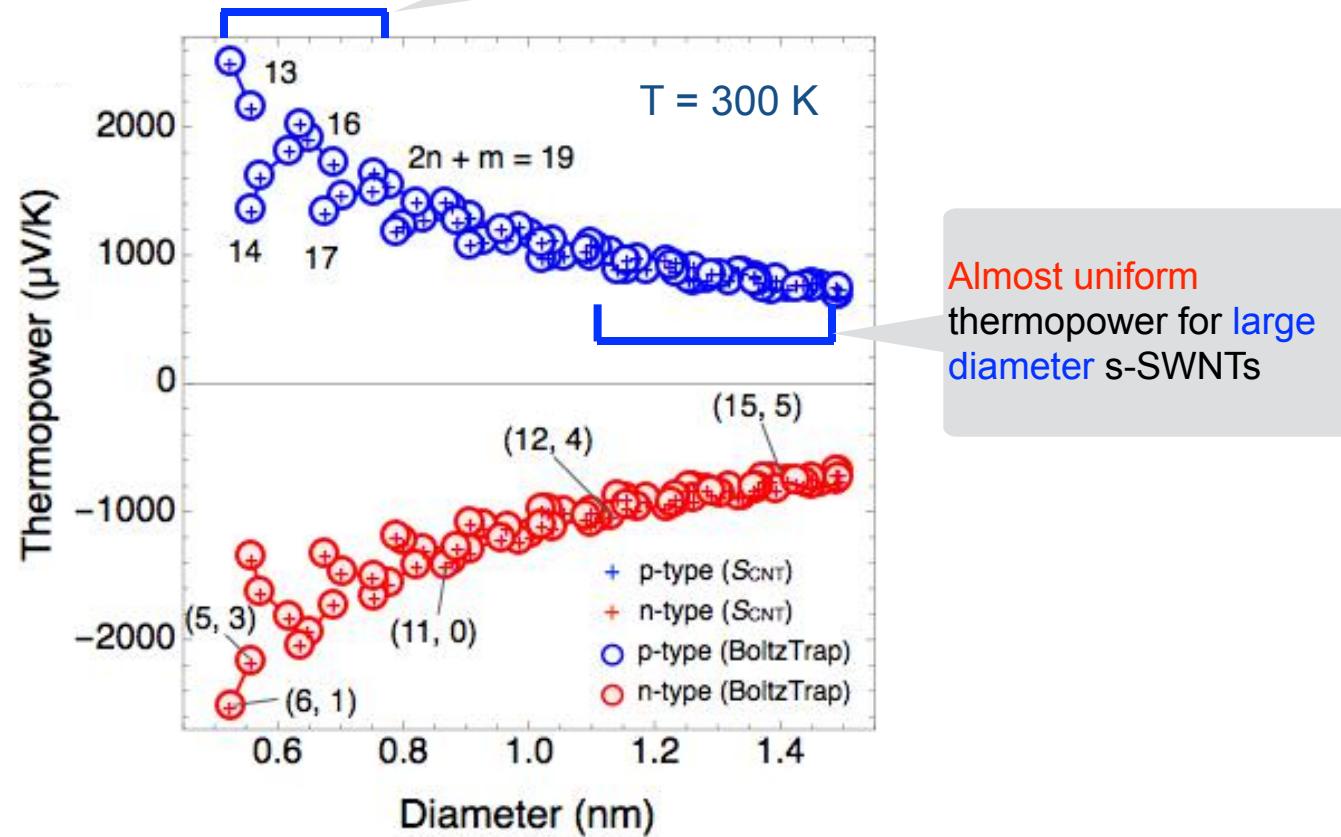


- Change in μ_{opt} is **only about 16 meV** although the change in E_g is as large as about 1.12 eV for all s-SWNTs.

“Thermal Kataura plot” of s-SWNTs

$$S_{\text{CNT}}^{\text{opt}} = S_{\text{CNT}}(\mu = \mu_{\text{opt}})$$

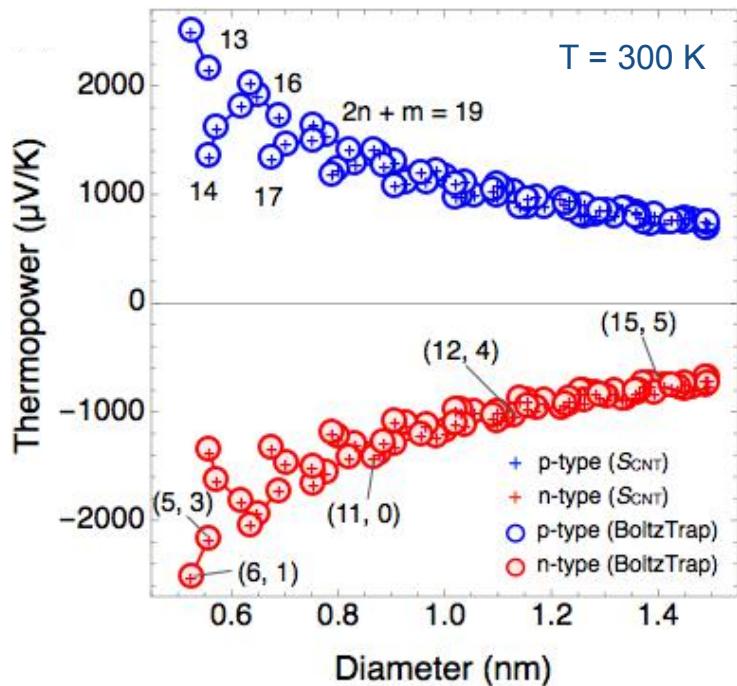
Higher thermopower for small diameter s-SWNTs, but please select chirality.



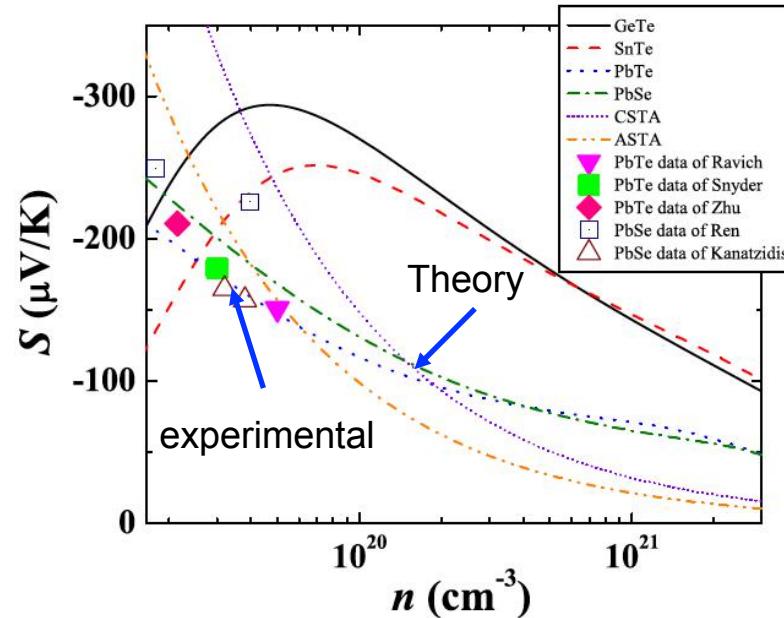
Almost uniform
thermopower for large
diameter s-SWNTs

- Analytical formula fits numerical results from BoltzTraP package (2-4% error)

Thermopower (Seebeck's coefficient) of s-SWNTs



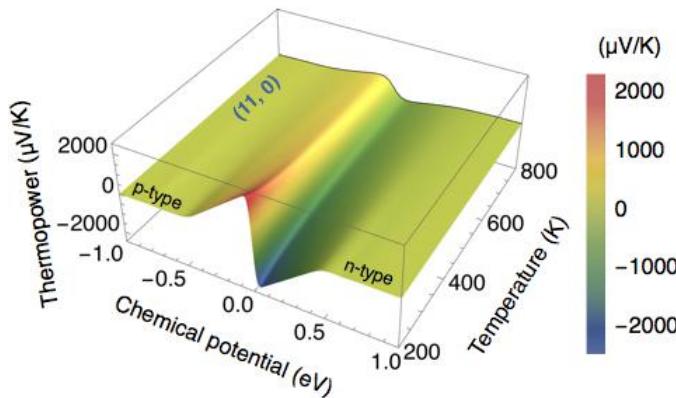
N. T. Hung et al., Phys. Rev. B 92, 165426 (2015)



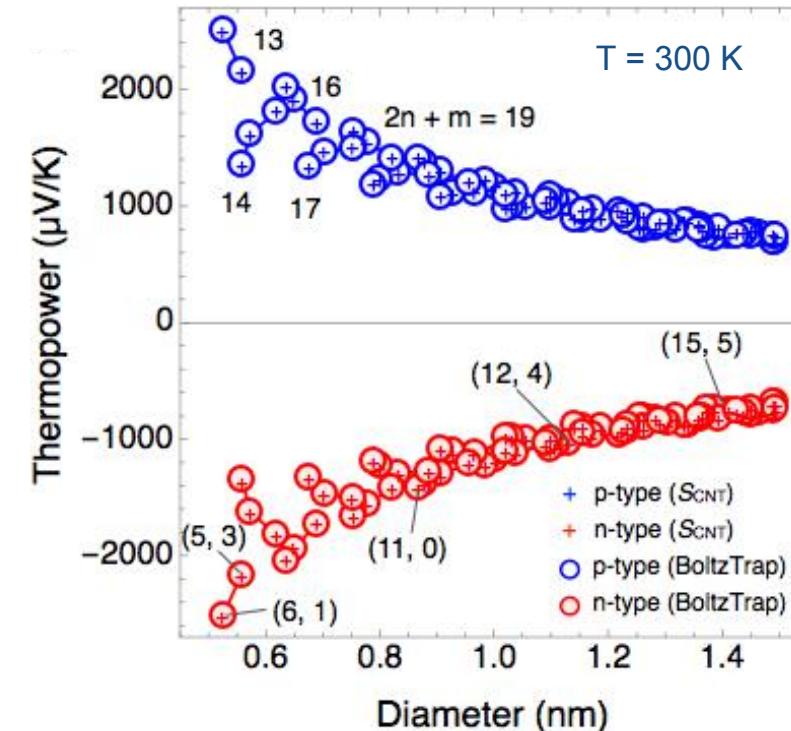
X. Chen et al., Scientific Reports 3, 3168 (2013)

- For (5, 3) and (6, 1) s-SWNTs, thermopower can reach more than $2000 \mu\text{V/K}$.
- Six to ten times larger than that found in commonly used thermoelectric materials!

Summary for SWNT's thermopower characteristics



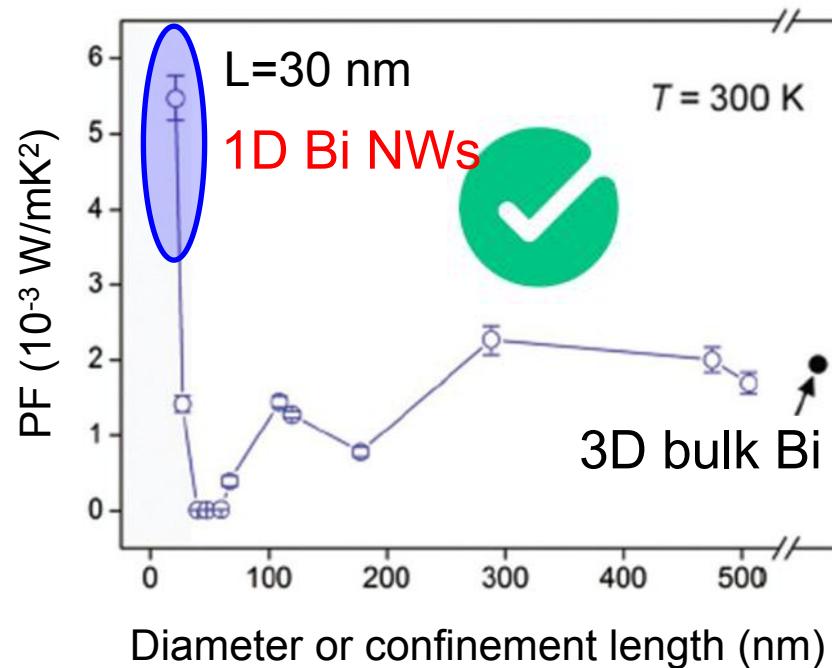
- **Analytical formula** useful to evaluate s-SWNT thermoelectric performance.
- **Optimized chemical potential** around ± 0.054 eV at $T = 300$ K for n-type and p-type of s-SWNTs, respectively.
- **Optimum thermopower** (n-type or p-type) can be larger than 2000 $\mu\text{V/K}$ at $T = 300$ K for (5, 3) and (6,1) s-SWNTs.



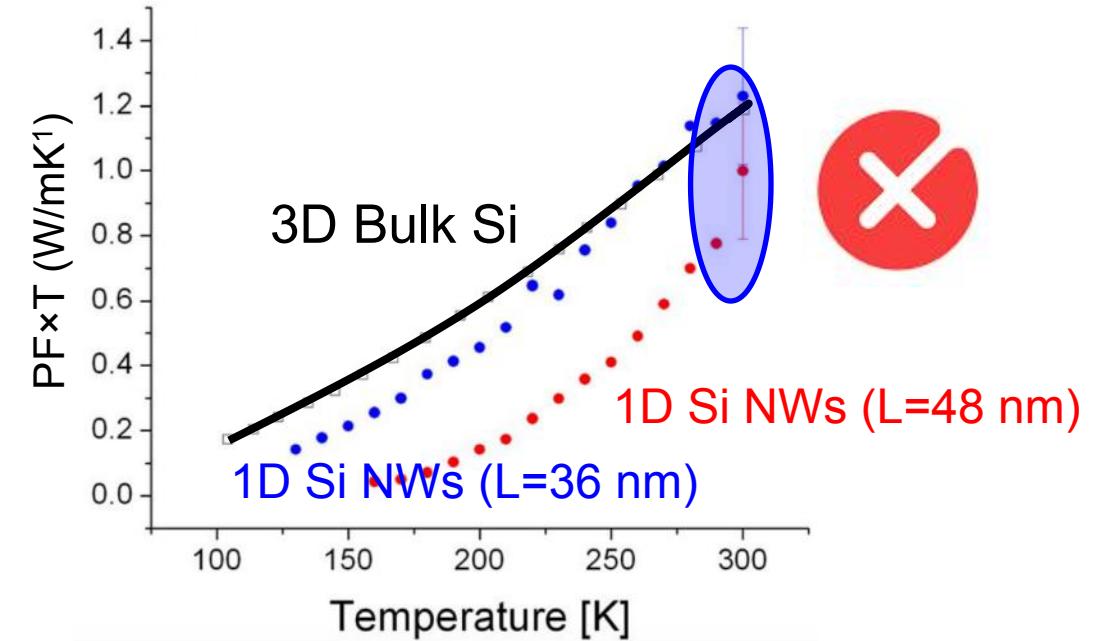
$$S_{\text{CNT}} = \frac{k_B}{e} \left(\frac{\mu}{k_B T} - \frac{E_g}{2k_B T} - \frac{3}{2} + \frac{E_g/k_B T + 3}{e^{2\mu/k_B T} + 1} \right)$$

Hung, Nugraha et al., Phys. Rev. B 92, 165426 (2015)

Paradox in low-dimensional materials?



J. Kim et al., Nanoscale 7, 5053 (2015)



A. I. Hochbaum et al., Nature 451, 163 (2008)

PF **increases** in Bi NWs but **does not increase** in Si NWs
by reducing confinement length: **Why?**

Formulas for calculating TE coefficients

within linearized Boltzmann transport formalism + relaxation time approximation

Electrical conductivity

$$\sigma = q^2 \mathcal{L}_0$$

Seebeck's coefficient

$$S = \frac{1}{qT} \frac{\mathcal{L}_1}{\mathcal{L}_0}$$

Thermal conductivity (electron)

$$\kappa_e = \frac{1}{T} \left(\mathcal{L}_2 - \frac{\mathcal{L}_1^2}{\mathcal{L}_0} \right)$$

Power factor

$$PF = S^2 \sigma = \frac{1}{T^2} \frac{\mathcal{L}_1^2}{\mathcal{L}_0}$$

Figure-of-merit

$$ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_l} T = \beta \frac{\mathcal{L}_1^2}{\mathcal{L}_0 \mathcal{L}_2 - \mathcal{L}_1^2}$$

$$\beta = 1 / (\kappa_p / \kappa_e + 1) \leq 1$$

TE kernel: $\mathcal{L}_i = \int T(E) I_i(E) dE \quad i = 0, 1, 2$
material-dependent

Transport distribution function

$$T(E) = v_x^2(E) \tau(E) \mathcal{D}(E)$$

Carrier velocity

Relaxation time

DOS

$$I_i(E) = (E - E_F)^i \left(-\frac{\partial f_0}{\partial E} \right)$$

/

Derivative of
the FD distribution
function

One-band model: Parabolic band

Transport distribution function

$$T(E) = v_x^2(E)\tau(E)\mathcal{D}(E)$$

$$\rightarrow T(E) = \frac{2CE}{md}$$

$$E = \frac{\hbar^2 \mathbf{k}^2}{2m} \rightarrow \text{Carrier velocity: } v(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial E(\mathbf{k})}{\partial \mathbf{k}} = \frac{\hbar \mathbf{k}}{m}$$

$$\text{Isotropic material with dimension d: } v_x^2(E) = \frac{v^2}{d} = \frac{\hbar^2 \mathbf{k}^2}{m^2 d} = \frac{2E}{md}$$

$$\text{Relaxation time: } \tau(E) = C\mathcal{D}(E)^{-1}$$

$$\rightarrow \mathcal{L}_i = \int T(E) I_i(E) dE \quad i = 0, 1, 2$$

$$I_i(E) = (E - E_F)^i \left(-\frac{\partial f_0}{\partial E} \right)$$

$$\text{PF} = \frac{1}{T^2} \frac{\mathcal{L}_1^2}{\mathcal{L}_0} = \frac{2Ck_B^3 T}{md} \frac{(2F_1 - \eta F_0)^2}{F_0}$$

$$ZT = \beta \frac{\mathcal{L}_1^2}{\mathcal{L}_0 \mathcal{L}_2 - \mathcal{L}_1^2} = \beta \frac{(2F_1 - \eta F_0)^2}{F_0(3F_2 - 4\eta F_1 + \eta^2 F_0) - (2F_1 - \eta F_0)^2}$$

$$\left. \begin{aligned} \mathcal{L}_0 &= \frac{2C}{md} (k_B T) F_0 \\ \mathcal{L}_1 &= \frac{2C}{md} (k_B T)^2 (2F_1 - \eta F_0) \\ \mathcal{L}_2 &= \frac{2C}{md} (k_B T)^3 (3F_2 - 4\eta F_1 + \eta^2 F_0) \end{aligned} \right.$$

Fermi-Dirac integral

$$F_j = \int \left(\frac{E}{k_B T} \right)^j f_0 d\left(\frac{E}{k_B T} \right)$$

Reduced chemical potential

$$\eta = E_F / k_B T$$

Some tricks to solve the integrals

$$\text{PF} = \frac{1}{T^2} \frac{\mathcal{L}_1^2}{\mathcal{L}_0} = \frac{2Ck_B^3 T}{md} \frac{(2F_1 - \eta F_0)^2}{F_0}$$

$$ZT = \beta \frac{\mathcal{L}_1^2}{\mathcal{L}_0 \mathcal{L}_2 - \mathcal{L}_1^2} = \beta \frac{(2F_1 - \eta F_0)^2}{F_0(3F_2 - 4\eta F_1 + \eta^2 F_0) - (2F_1 - \eta F_0)^2}$$

In case $\eta \leq 0$: $F_x \cong e^\eta \Gamma(x+1) \Gamma(1) = 1; \Gamma(2) = 1; \Gamma(3) = 2$

Fermi-Dirac integral Exponential × Gamma function



$$\text{PF} = \frac{2Ck_B^3 T}{md} (2 - \eta)^2 e^\eta$$

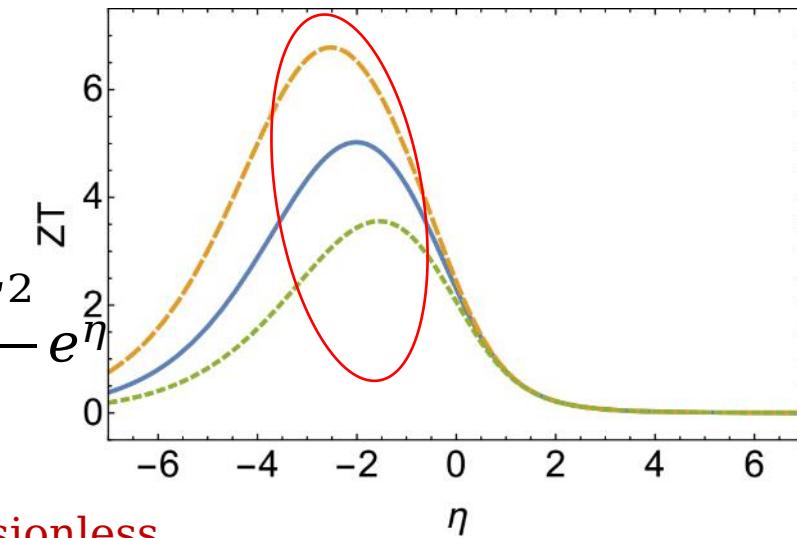
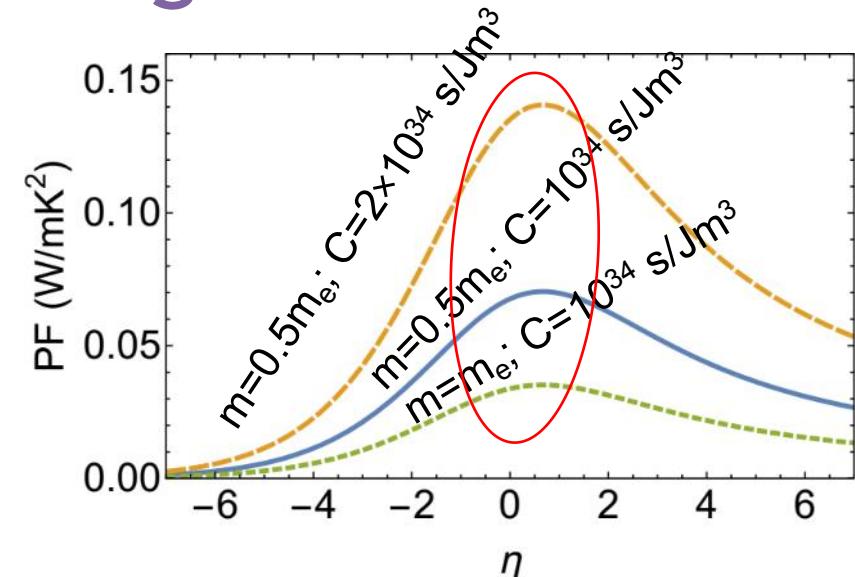
$$\frac{\frac{s}{Jm^3} \frac{J^3}{K^3} K}{kg} = \frac{s J^2 / kg}{m^3 K^2} = \frac{W}{mK^2}$$

$$ZT = \beta \frac{(2 - \eta)^2}{2}; \quad \beta = \frac{1}{\frac{K_L}{K_e} + 1}; \quad K_e = \frac{1}{T} \left(\mathcal{L}_2 - \frac{\mathcal{L}_1^2}{\mathcal{L}_0} \right) = \frac{4Ck_B^3 T^2}{md} e^{\frac{2}{\eta}}$$

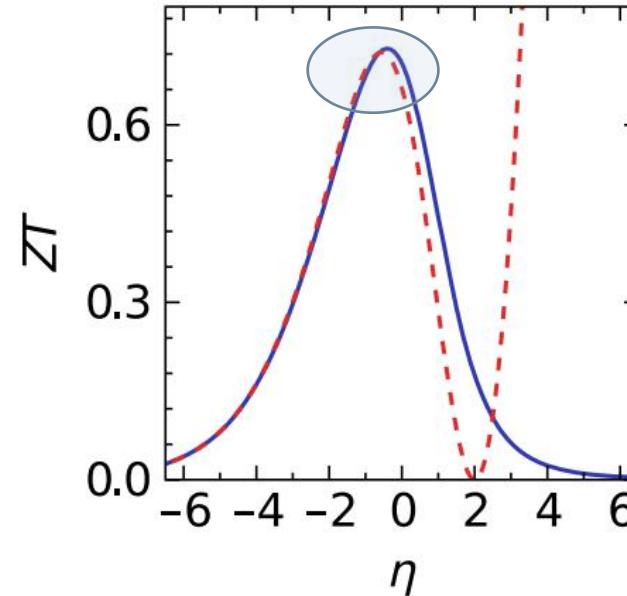
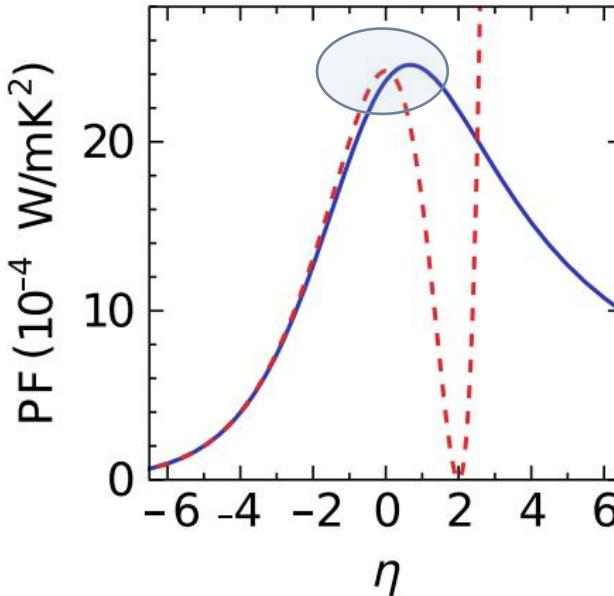


$$ZT = \frac{(2 - \eta)^2 e^\eta}{2(2/\alpha + e^\eta)} \quad \alpha = \frac{8Ck_B^3 T^2}{md K_L}$$

$$\frac{\frac{s}{Jm^3} \frac{J^3}{K^3} K^2}{kg \frac{W}{mK}} = \frac{s^2}{m^2 kg} J = \text{dimensionless}$$



Relationship between optimum PF and ZT



Full solution of FD integral: solid lines

$$\text{PF} = \frac{2Ck_B^3 T}{md} \frac{(2F_1 - \eta F_0)^2}{F_0}$$

$$ZT = \beta \frac{(2F_1 - \eta F_0)^2}{F_0(3F_2 - 4\eta F_1 + \eta^2 F_0) - (2F_1 - \eta F_0)^2}$$

Analytical approximation: dashed lines

$$\text{PF} = \frac{2Ck_B^3 T}{md} (2 - \eta)^2 e^\eta; \quad ZT = \frac{(2 - \eta)^2 e^\eta}{2(2/\alpha + e^\eta)}$$

Optimum PF: $\frac{d\text{PF}}{d\eta} = 0; \eta_{\text{PF}} = \rightarrow \text{PF}_{\text{opt}} = \frac{8Ck_B^3 T}{md}$

$$\alpha = \frac{8Ck_B^3 T^2}{md k_l}$$

Optimum ZT: $\frac{dZT}{d\eta} = 0; \eta_{ZT} = -W_0 \rightarrow ZT_{\text{opt}} = \frac{1}{2} W_0^2(\alpha) + W_0(\alpha)$

$$\alpha = (\text{PF}_{\text{opt}}/k_l)T$$

W_0 : Lambert W function

Where is the size effect?

$$\text{PF}_{\text{opt}} = \frac{\alpha_{K_l}}{T} = \frac{8C k_B^3 T}{md}$$



→ $\text{PF}_{\text{opt}} = \frac{16\tau_0 k_B^2}{md L^{3-d} \Gamma(d/2)} \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{d/2}$

Thermal de Broglie wavelength $\Lambda = \sqrt{2\pi\hbar^2/mk_B T}$

$$\text{PF}_{\text{opt}} = \frac{16\tau_0 k_B^2}{md \Gamma(d/2) L^3} \left(\frac{L}{\Lambda} \right)^d \propto \frac{1}{L^3} \left(\frac{L}{\Lambda} \right)^d$$

Our conjecture: $L < \Lambda$: Quantum system
 $L > \Lambda$: Classical system

Density of states:

$$\mathcal{D}(E) = \frac{(2m/\hbar^2)^{d/2} E^{d/2-1}}{L^{3-d} 2^{d-1} \pi^{d/2} \Gamma(d/2)}$$

e.g. 2D case ($d=2$) $\mathcal{D}(E) = \frac{2m}{L\hbar^2} [J^{-1}m^{-3}]$

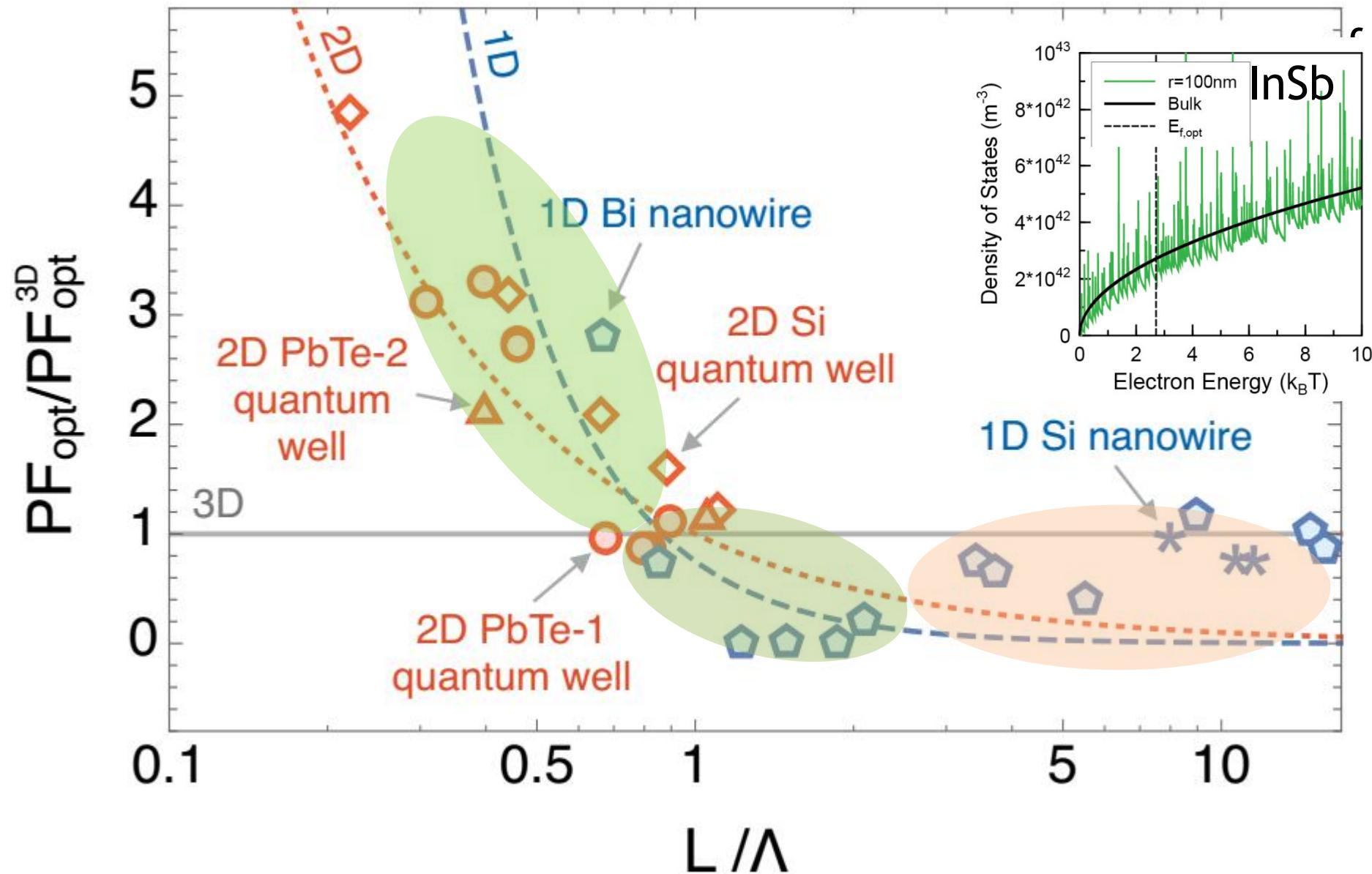
Relaxation times:

$$\tau(E) = \tau_0 \left(\frac{E}{k_B T} \right)^{1-d/2}$$

$$C = \tau(E) \mathcal{D}(E)$$

$$= \frac{2\tau_0}{L^{3-d} \Gamma(d/2) k_B T} \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{d/2} [W^{-1}m^{-3}]$$

Conditions for PF enhancement



Quantum size effect to improve TE performance

$$PF_{\text{opt}} \propto \frac{1}{L^{3-d}}$$

Hicks-Dresselhaus theory (1993)

$$PF_{\text{opt}} \propto \frac{1}{L^3} \left(\frac{L}{\Lambda}\right)^d$$

Our theory (2016)

$$\frac{PF_{\text{opt}}}{PF_{\text{opt}}^{3D}} \propto \left(\frac{L}{\Lambda}\right)^{d-3}$$

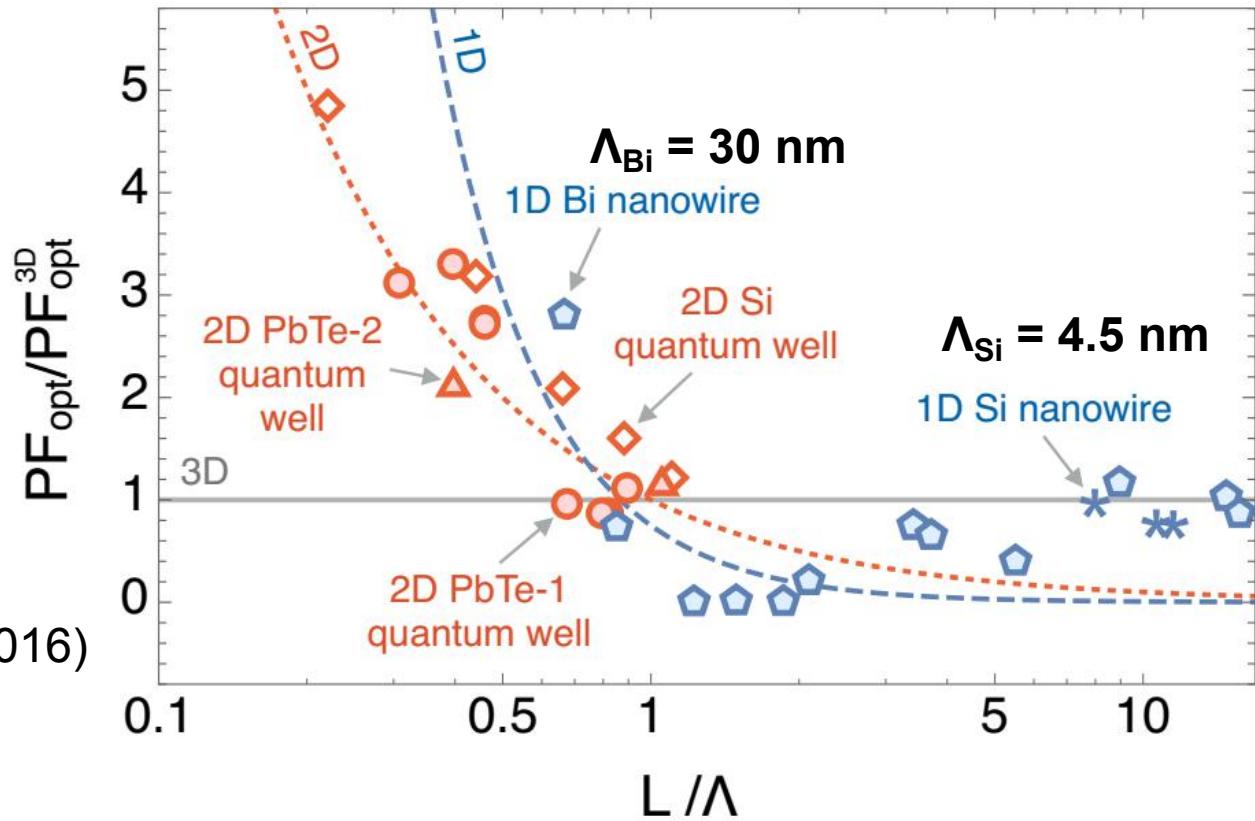
Enhancement factor

Hung, Nugraha, et al., Phys. Rev. Lett. 117, 036602 (2016)

Thermal de Broglie wavelength

$$\Lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \text{ [m]}$$

PF of any 2D or 1D material is enhanced when $L < \Lambda$



2D monolayer materials are promising ($L \sim 0.5 - 1 \text{ nm}$)

2D monolayer materials

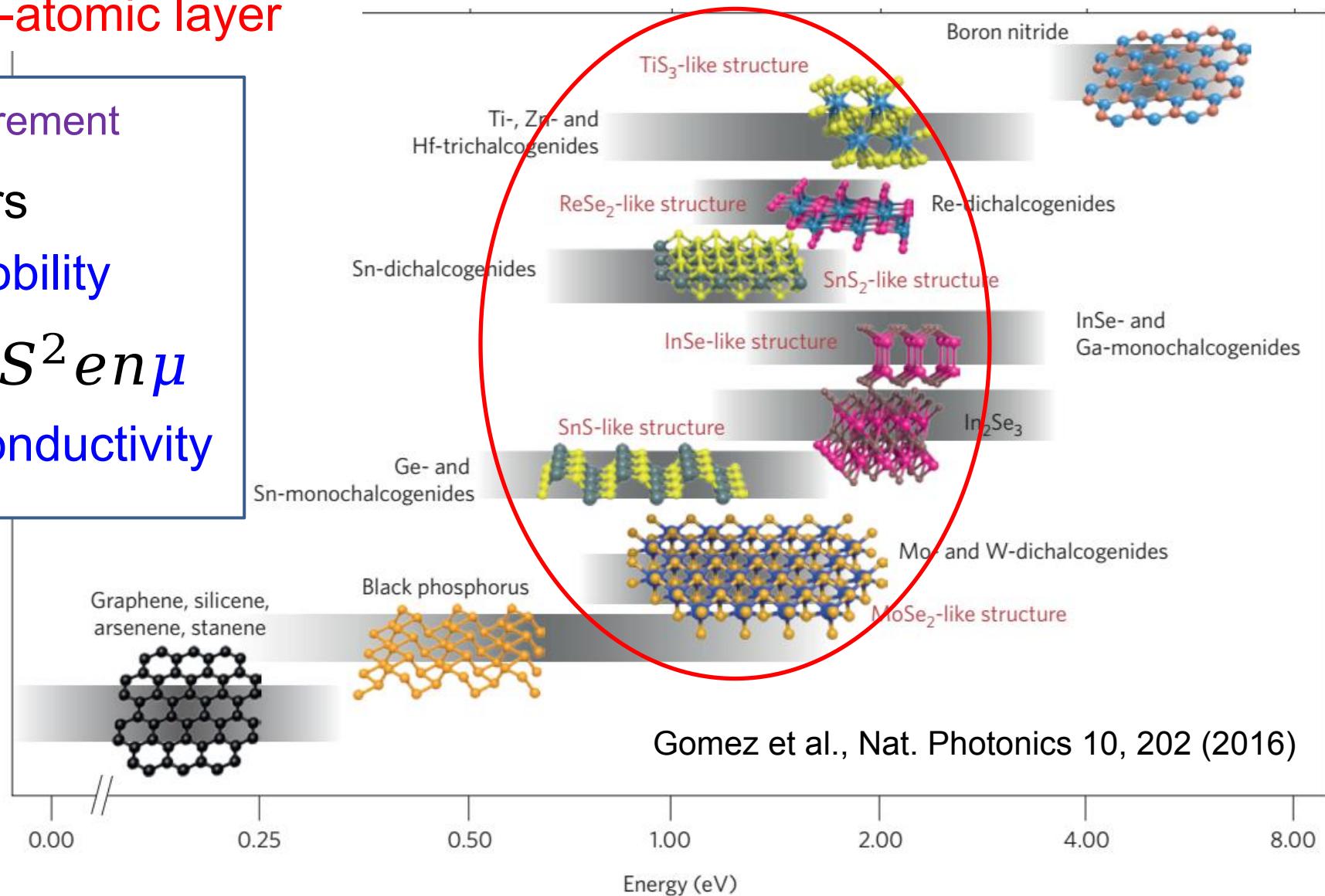
$L \sim$ thickness of 1-atomic layer

Reminder: TE requirement

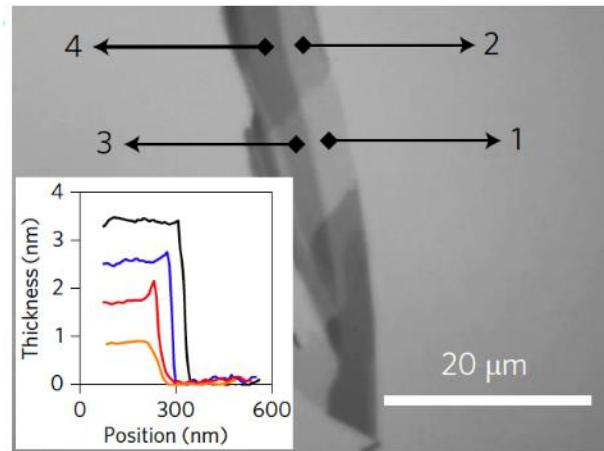
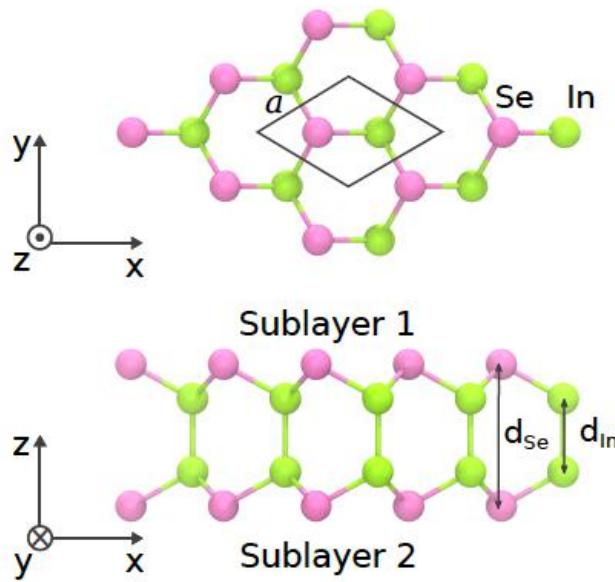
- Semiconductors
- High carrier mobility

$$PF = S^2\sigma = S^2en\mu$$

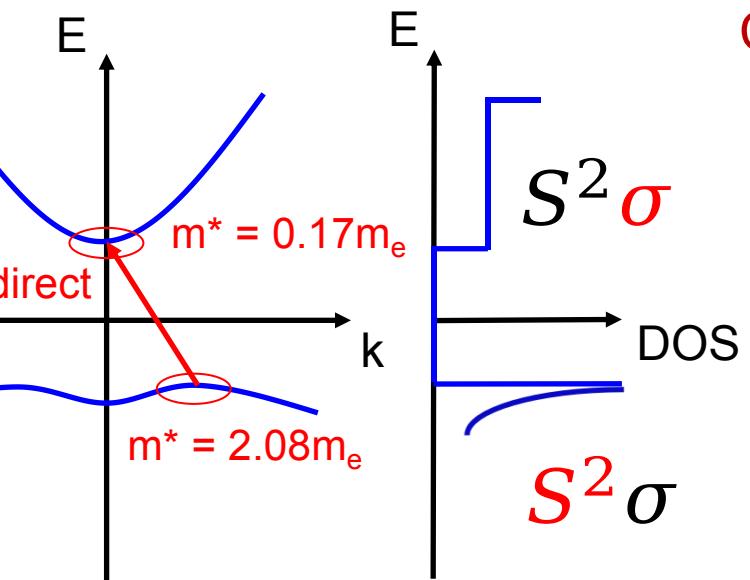
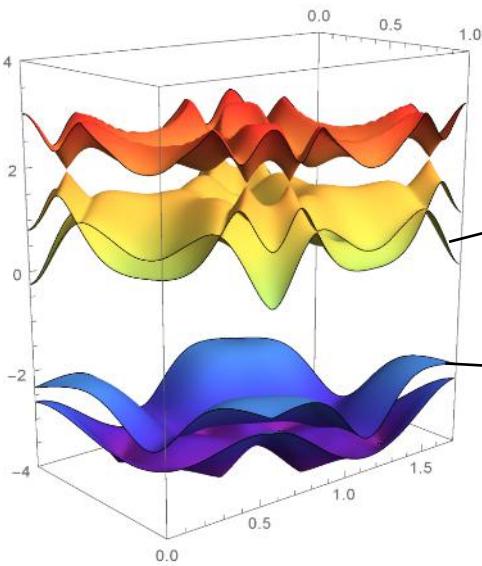
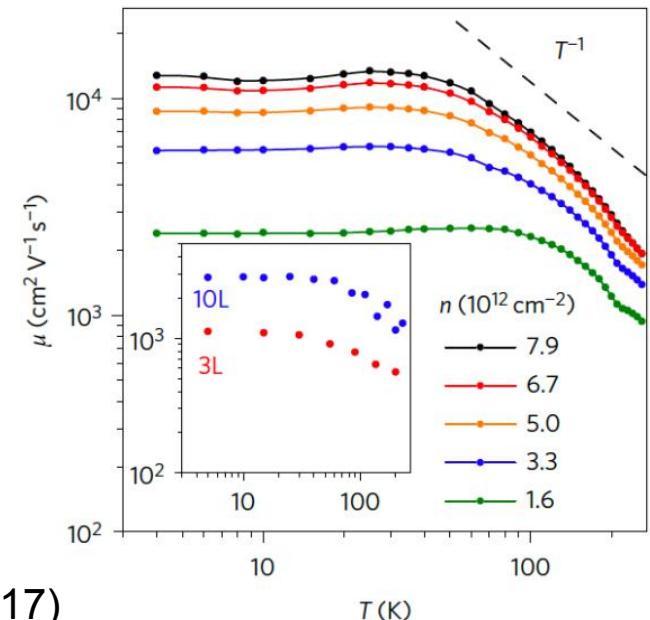
- Low thermal conductivity



Our first try: 2D InSe



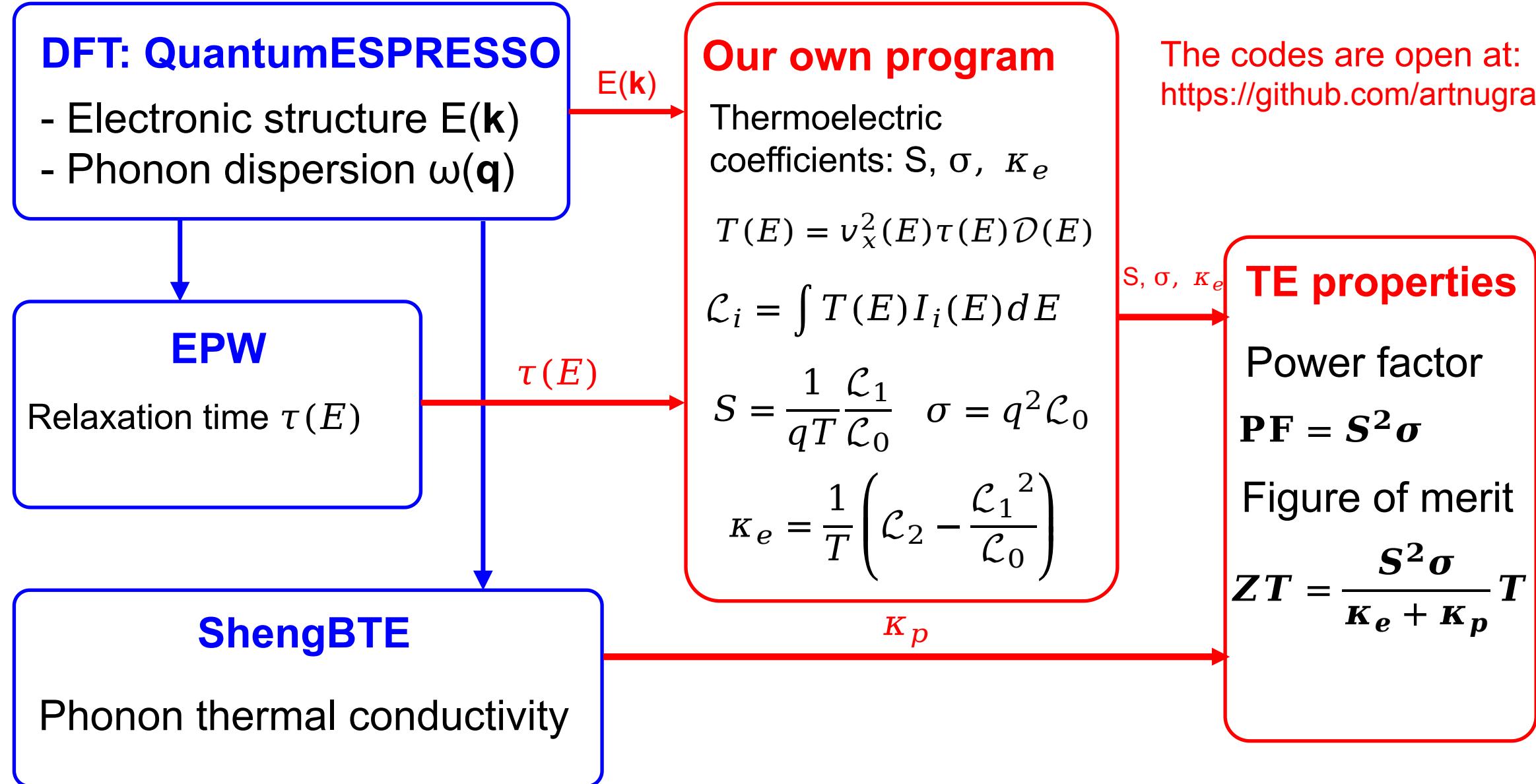
Bandurin et al., Nat. Nanotech. 12, 223 (2017)



Carrier mobility 2D InSe \sim Si at 300K

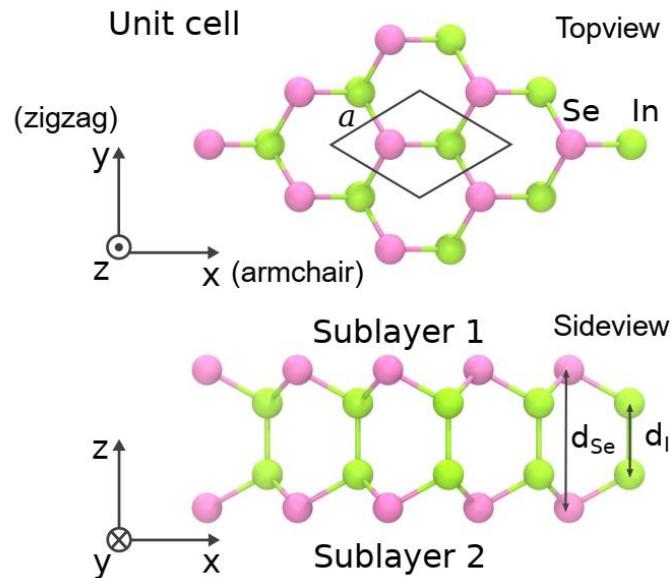
We expect that
both n-type and
p-type 2D InSe
have high PF

Numerical calculations for TE transport coefficients

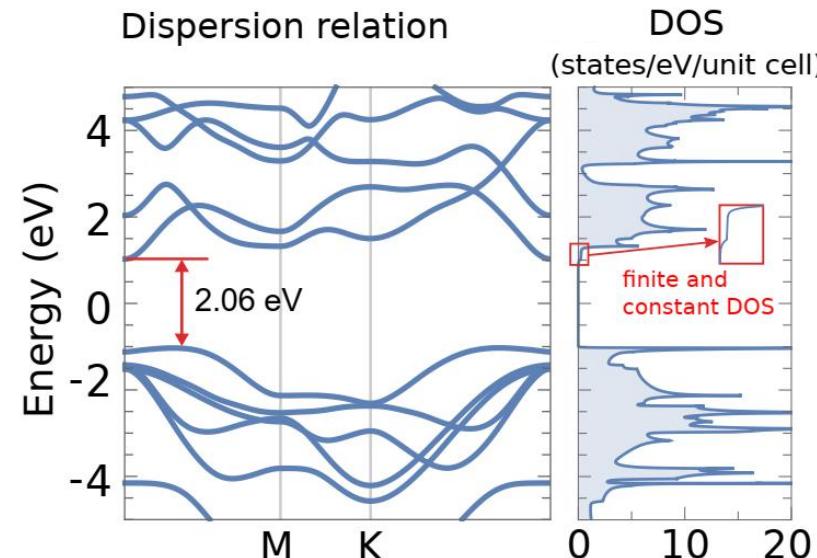


PF of monolayer InSe

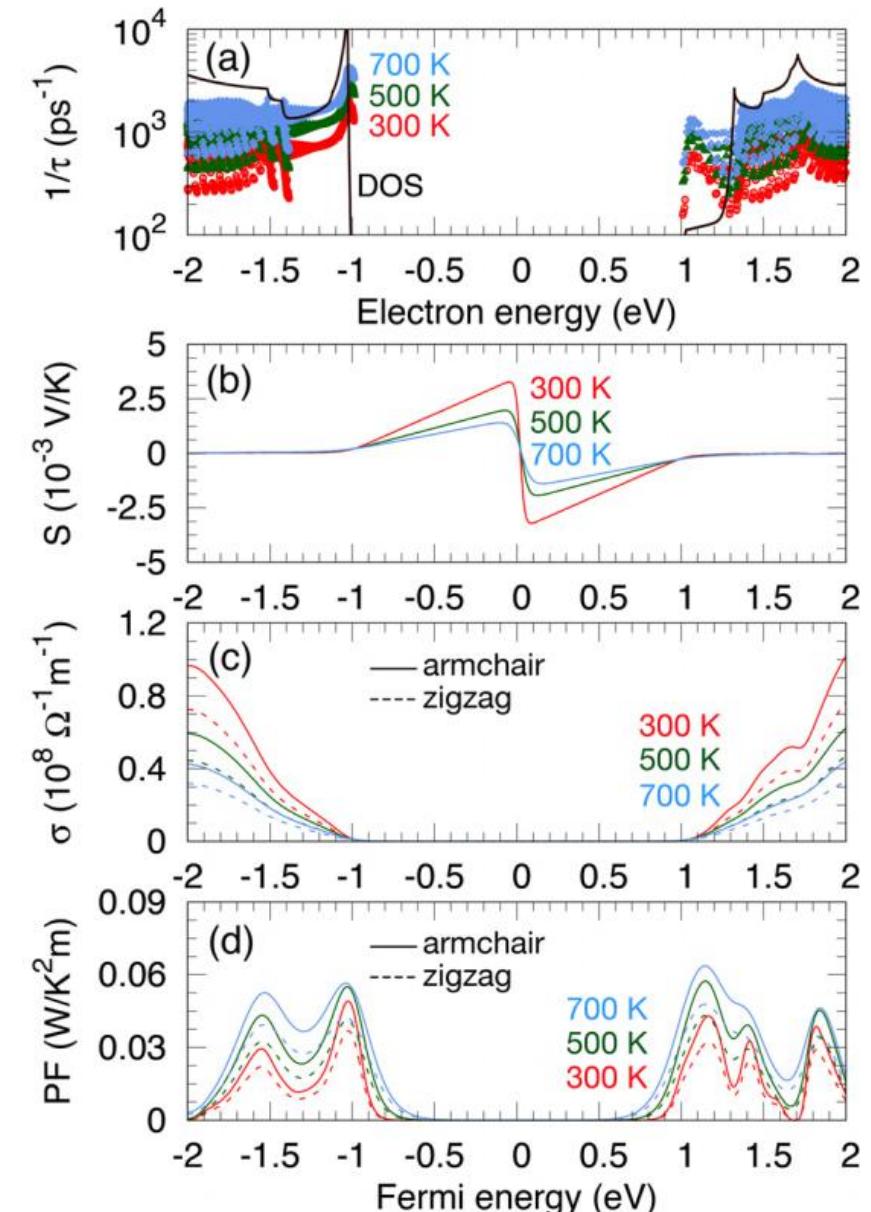
Hung, ♦Nugraha, Saito, Appl. Phys. Lett. 111, 092107 (2017)



PF $\sim 10 \times$ PF (bulk Bi₂Te₃)
ZT ~ 0.1 - 0.2



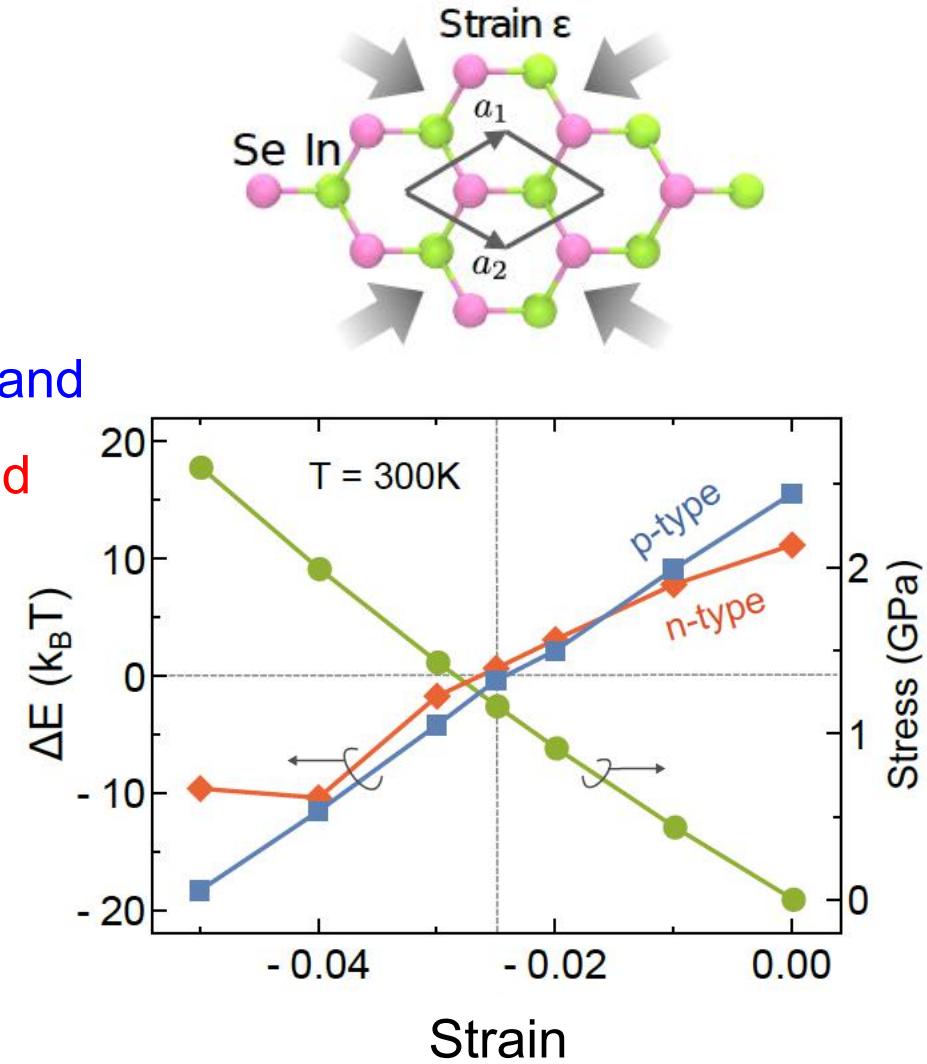
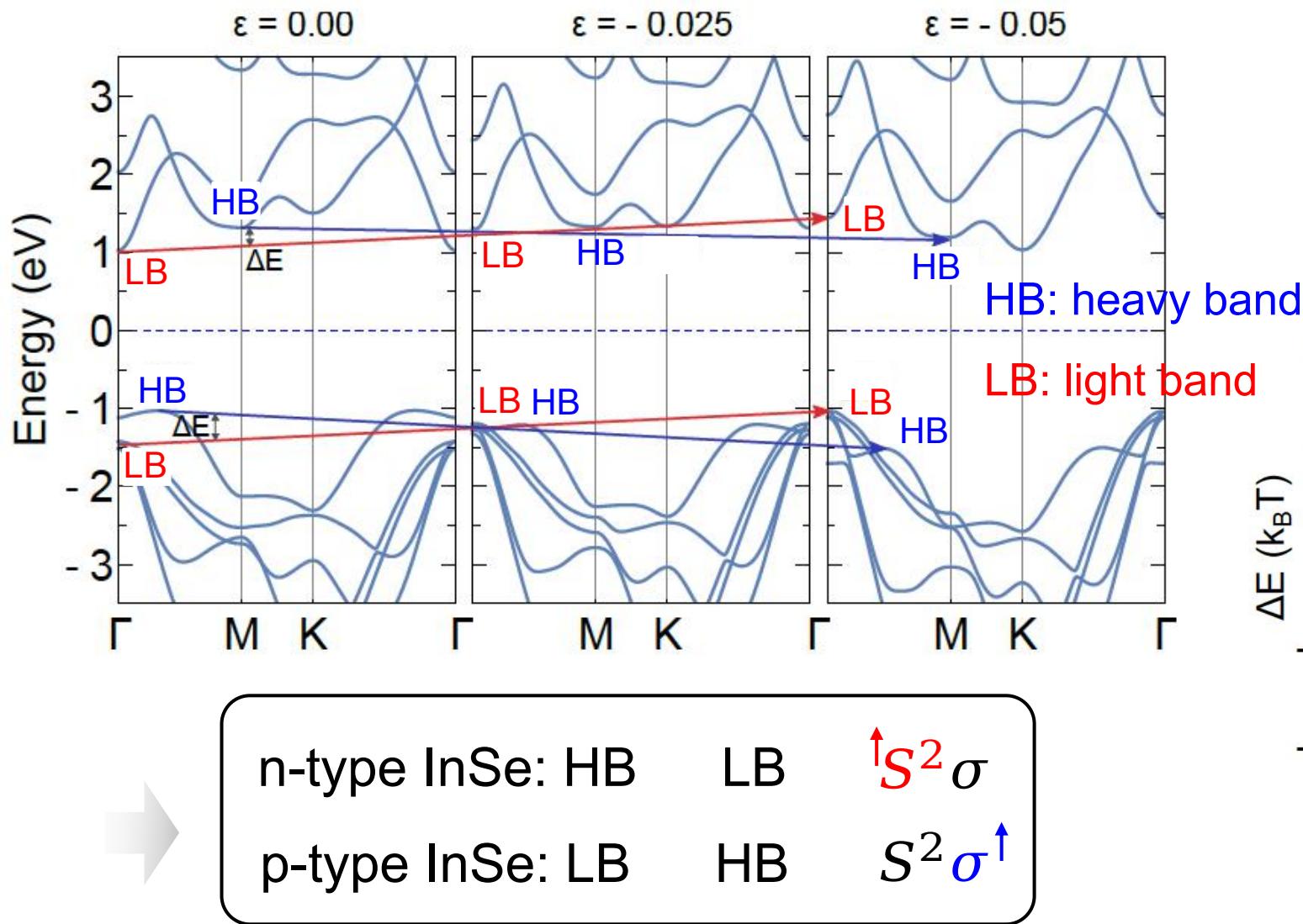
Anisotropic TE properties
TE armchair > TE zigzag



- Both n-type and p-type InSe have good PF
- ZT improvement is still needed

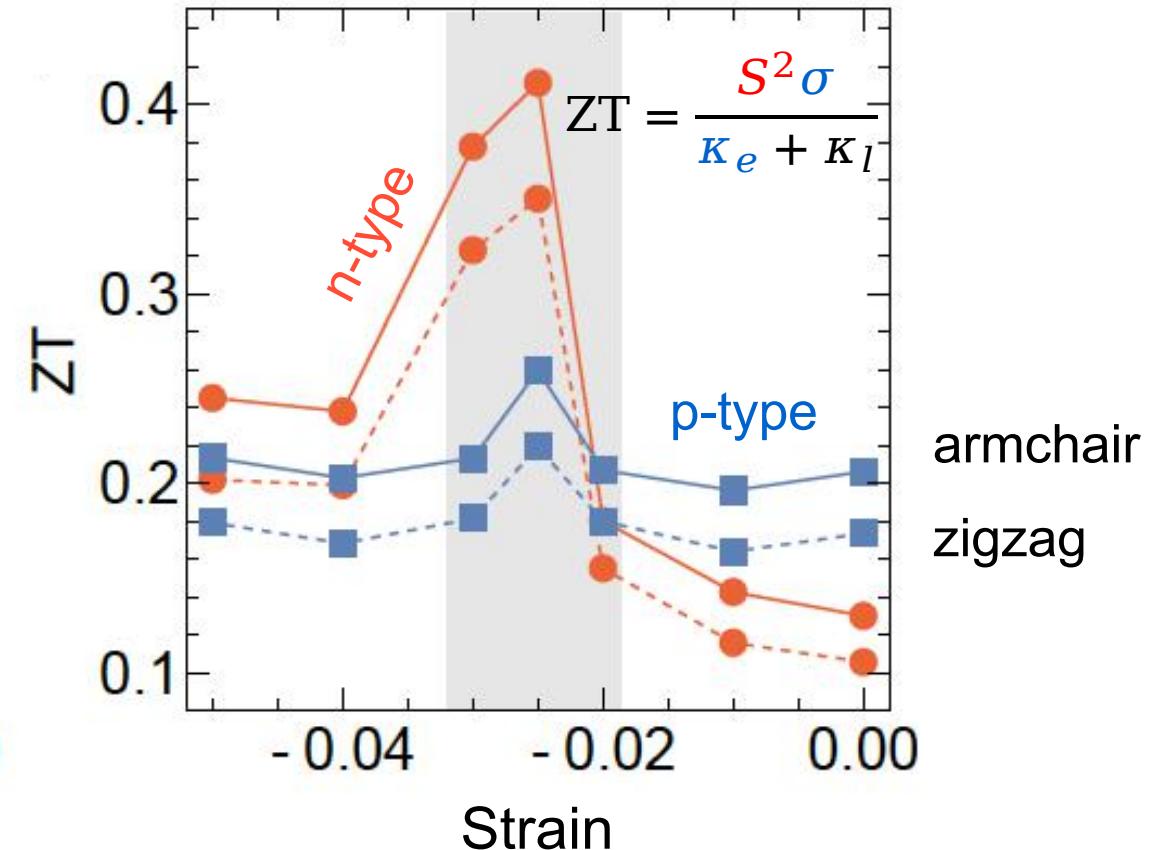
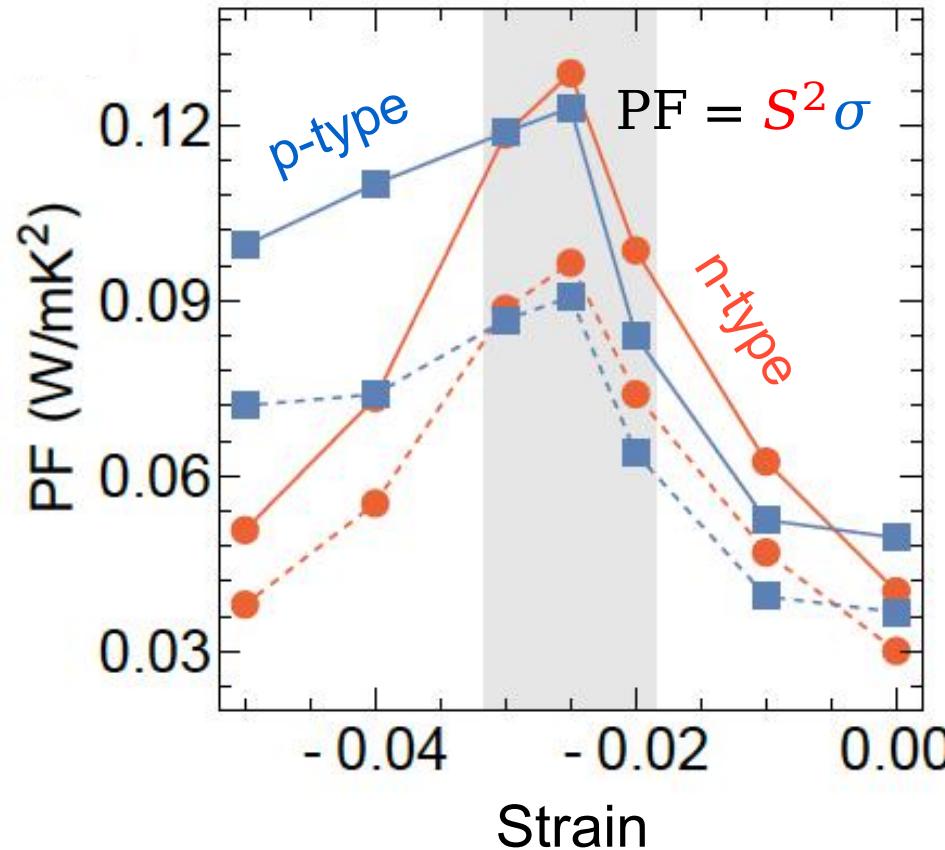
Band convergence in monolayer InSe

Hung, Nugraha, et al., J. Appl. Phys. 125, 082502 (2019)



PF and ZT of monolayer InSe with strain

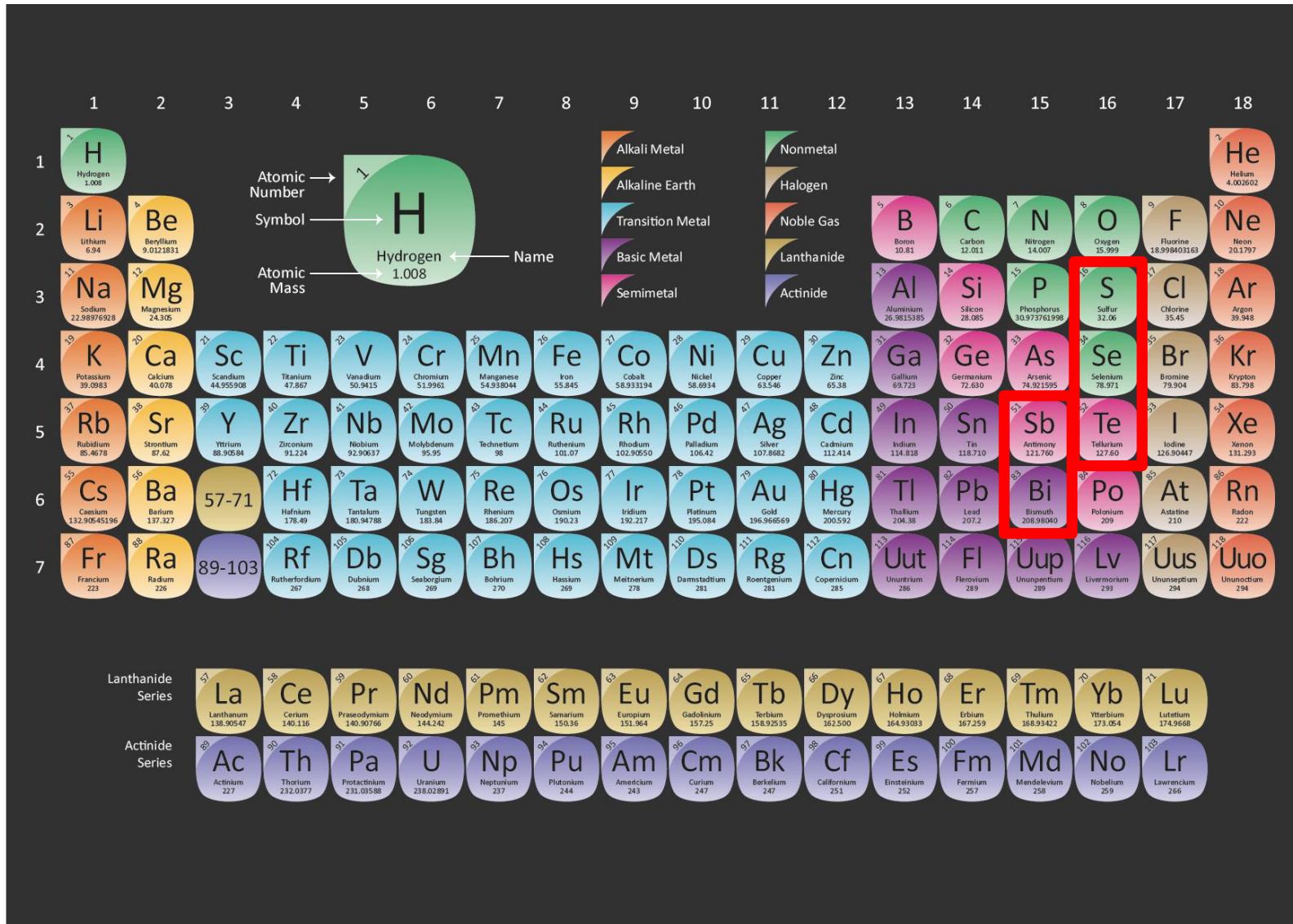
Hung, Nugraha, et al., J. Appl. Phys. 125, 082502 (2019)



- Both PF and ZT are enhanced by band convergence

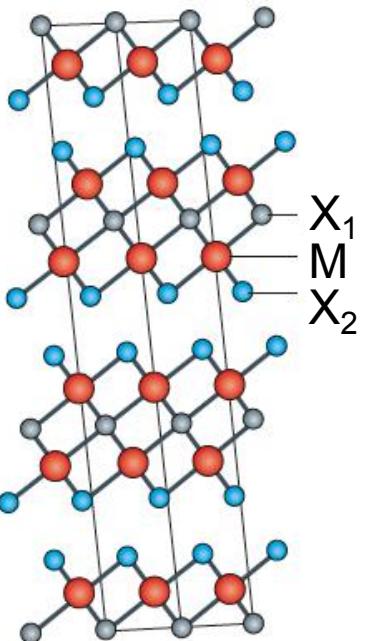
but ZT~0.4 is not really satisfying!

Going back to “old” TE materials

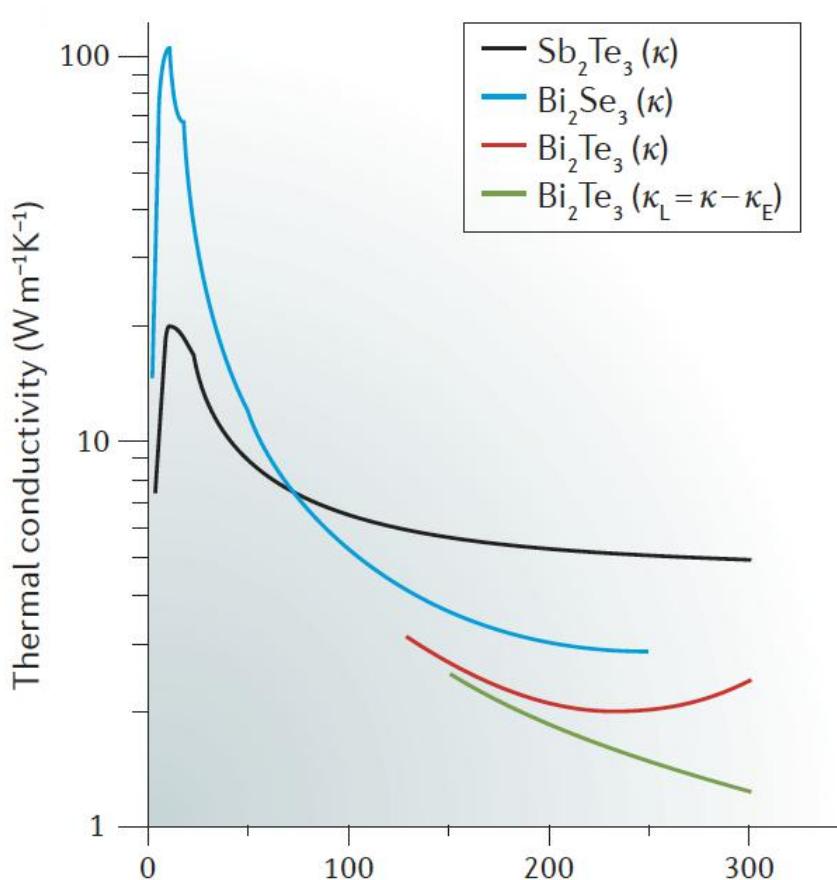


Tetradymites
 M_2X_3

M: Bi, Sb
X: Te, Se, S



Thermal conductivity of bulk tetradymite M_2X_3

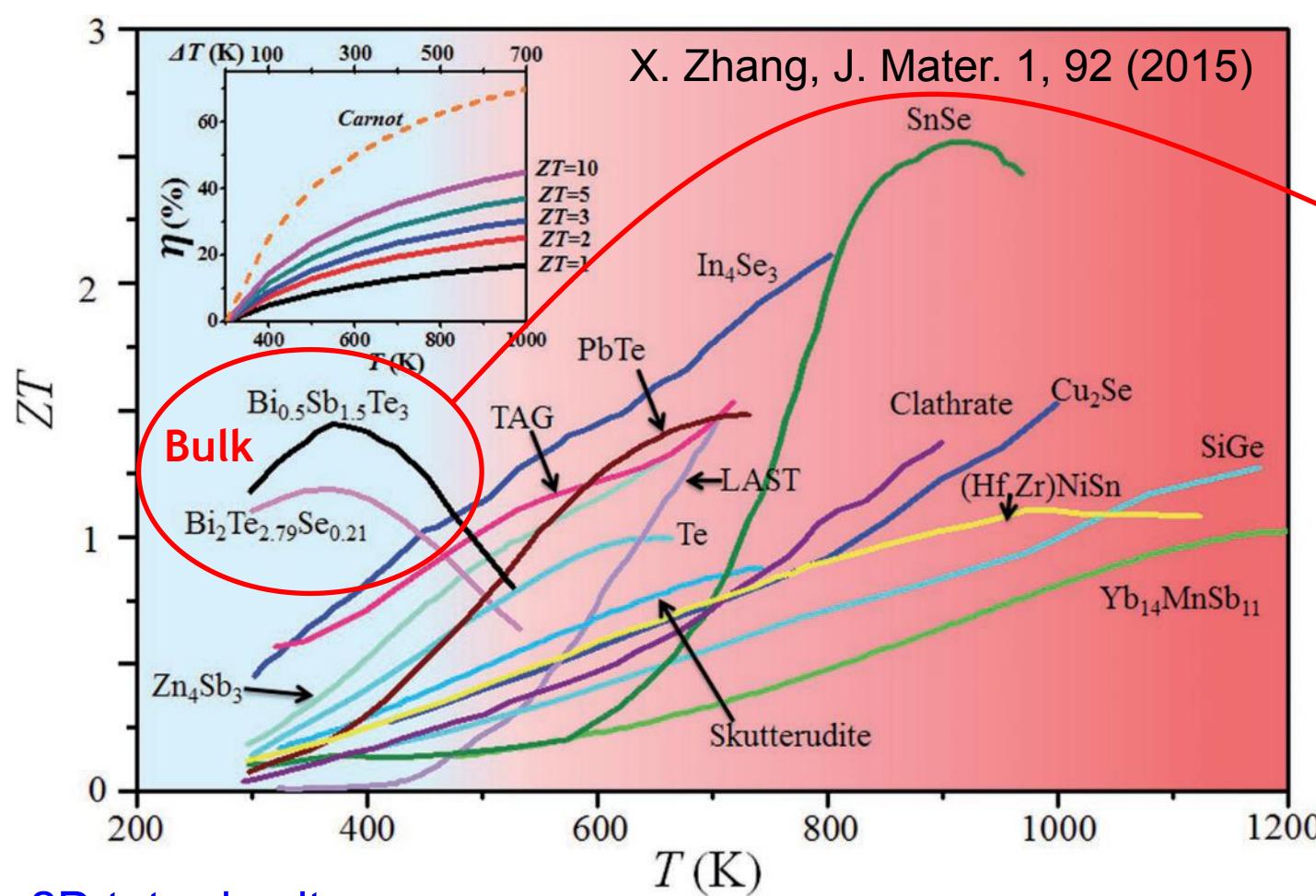


Heremans et al., Nat. Rev. Mat. 2, 1 (2017)

Thermal conductivity of $\text{Bi}_2X_3 < \text{Sb}_2X_3$

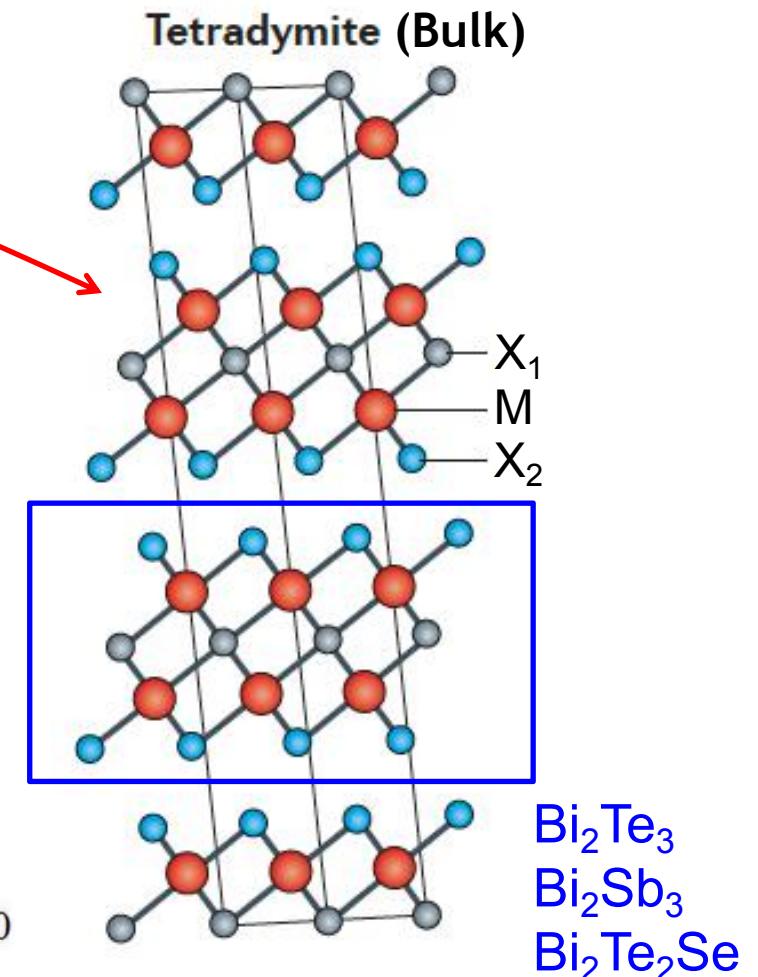
High ZT in Bi_2X_3

Our next try: 2D Bi_2X_3

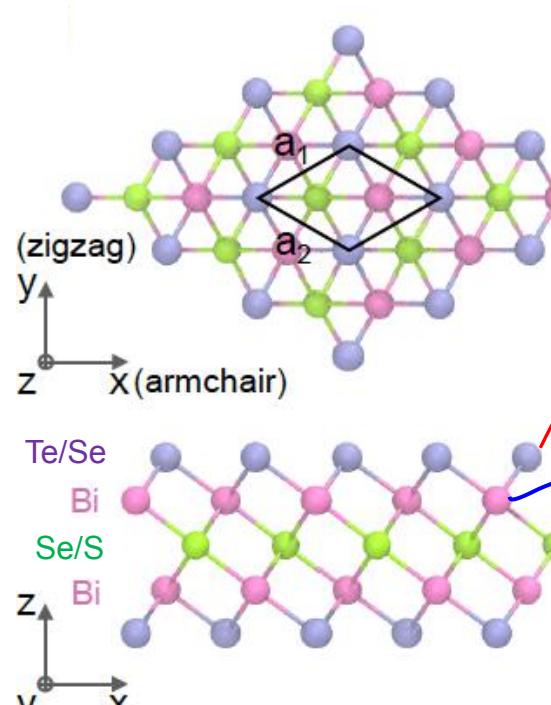


2D tetradymite:
semiconductor
+ heavy atoms

Can we get higher ZT for 2D tetradymite Bi_2X_3 ?

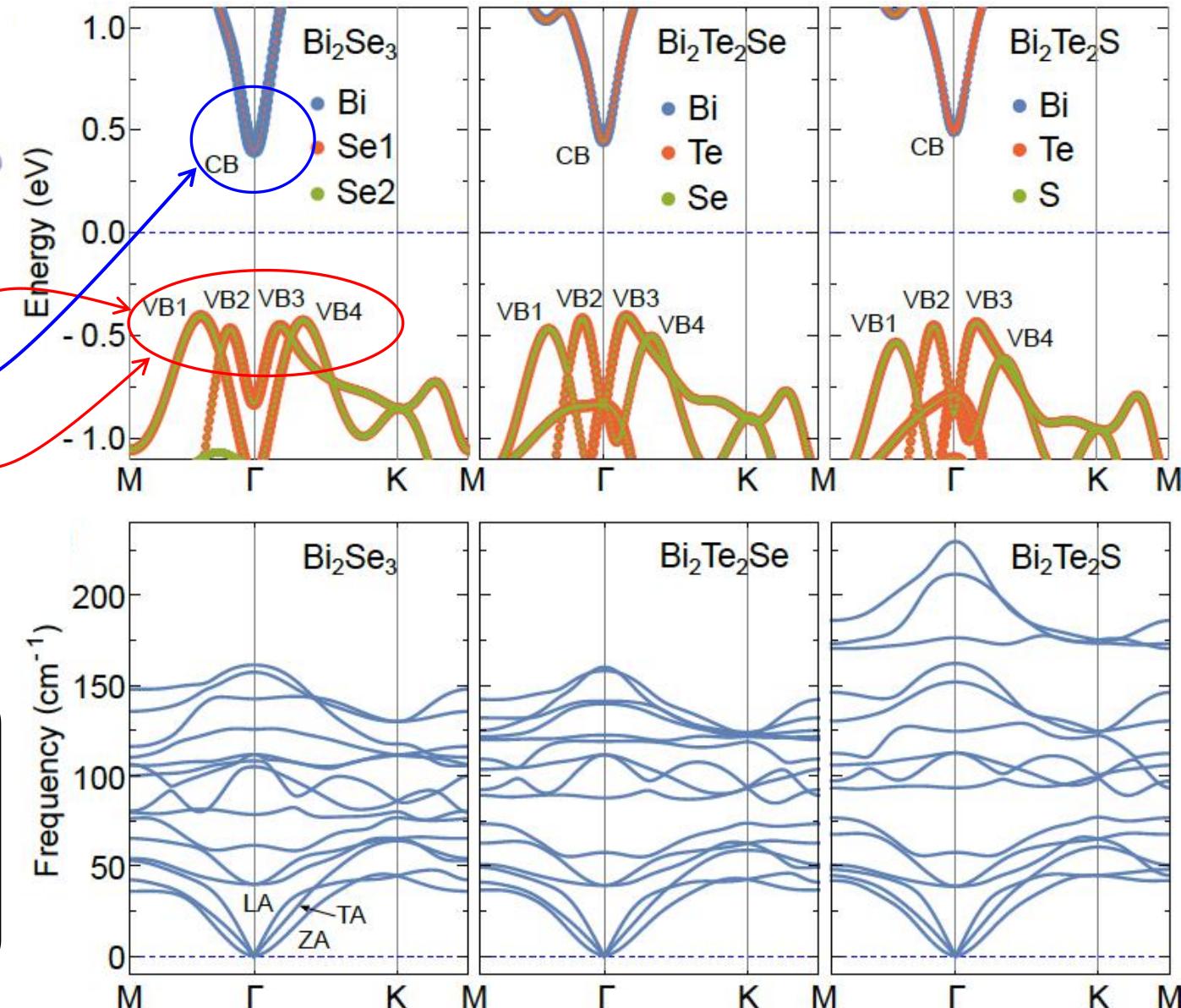


Electronic structure of 2D Bi_2X_3

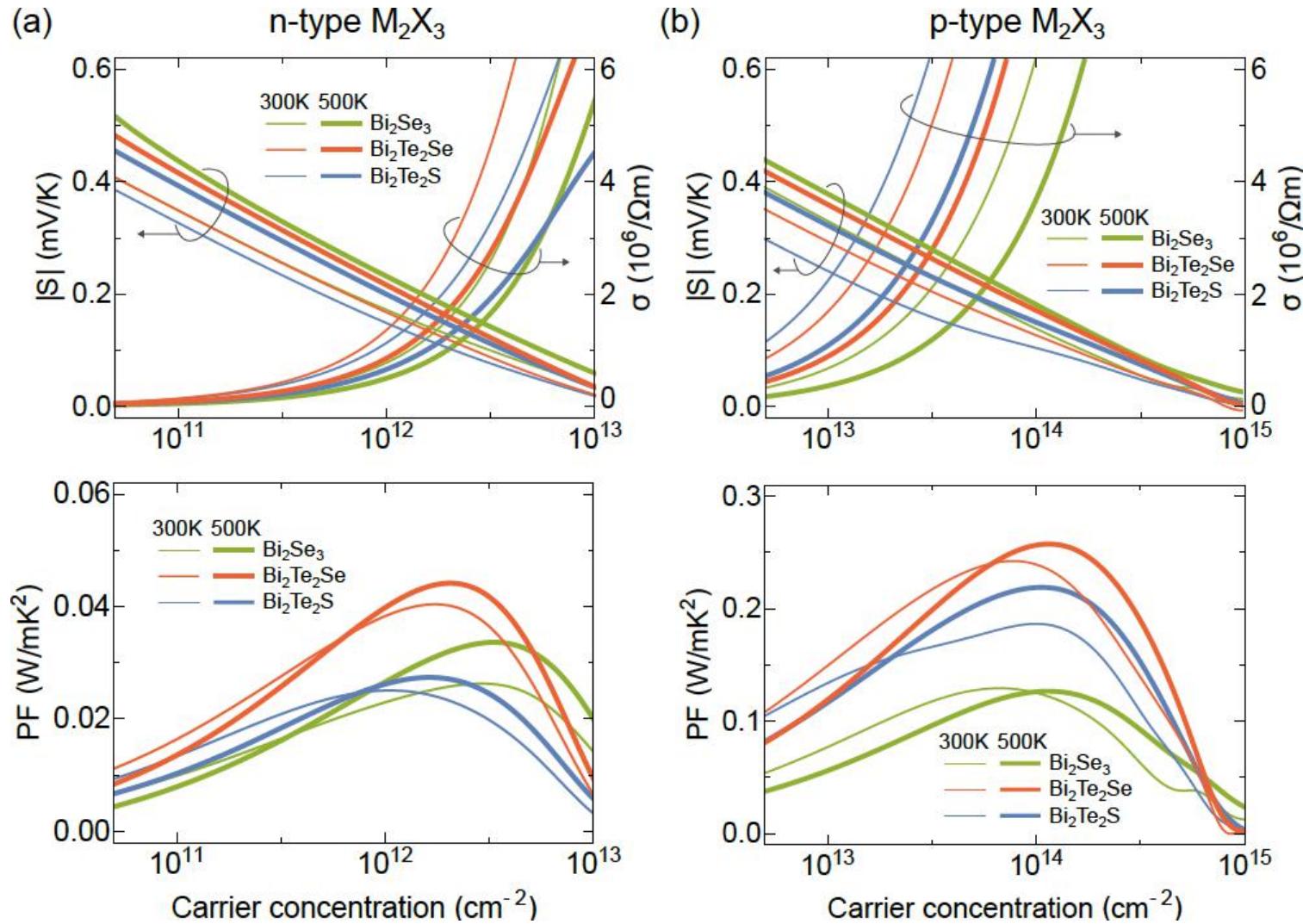


Single quintuple-layer

- Intrinsic band convergence in valence bands
- Low phonon frequency by heavy Bi atoms



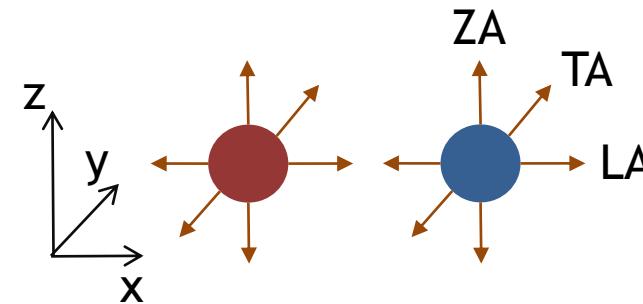
PF of 2D tetradymite Bi_2X_3



High PF for p-type Bi_2X_3 due to band convergence

Lattice thermal conductivity of 2D Bi₂X₃

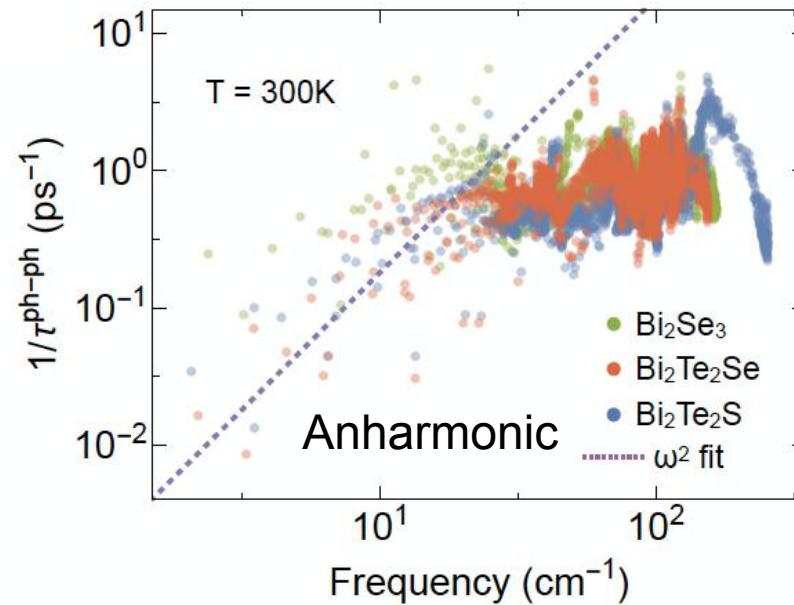
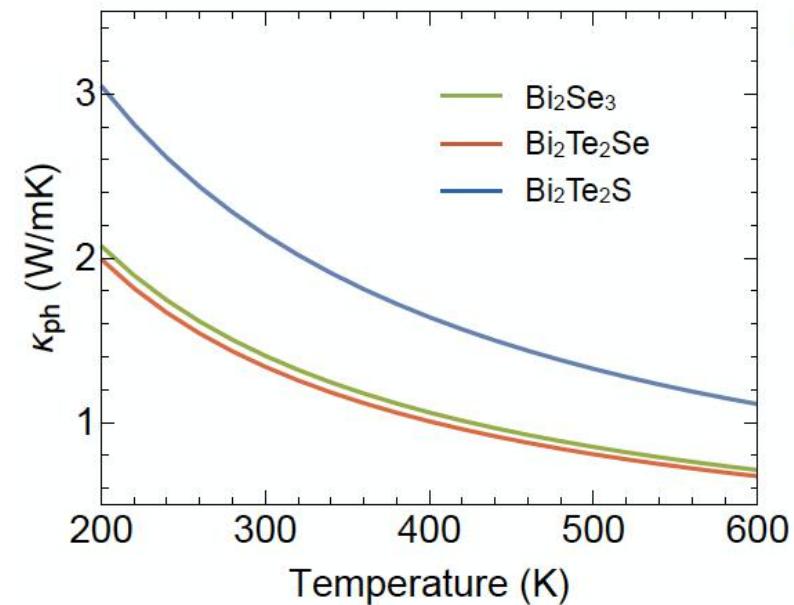
M2X3	v _{LA} (m/s)	v _{TA} (m/s)	v _{ZA} (m/s)
Bi ₂ Se ₃	444	268	78
Bi ₂ Te ₂ Se	454	267	94
Bi ₂ Te ₂ S	480	281	89



Phonon group velocity

$$\kappa_{\text{ph}} = \frac{1}{N_{\mathbf{q}} V} \sum_{\nu\mathbf{q}} \hbar \omega_{\nu\mathbf{q}} v_{\nu\mathbf{q}}^2 \tau_{\nu\mathbf{q}}^{\text{ph-ph}} \frac{\partial n_{\nu\mathbf{q}}}{\partial T}$$

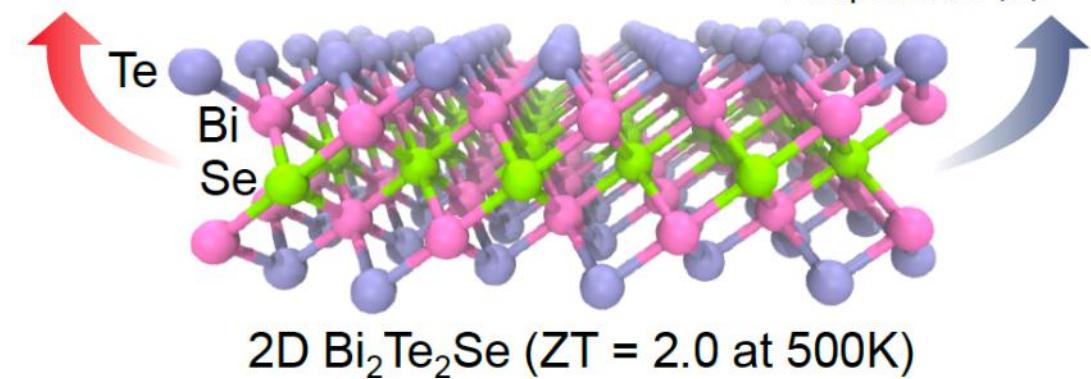
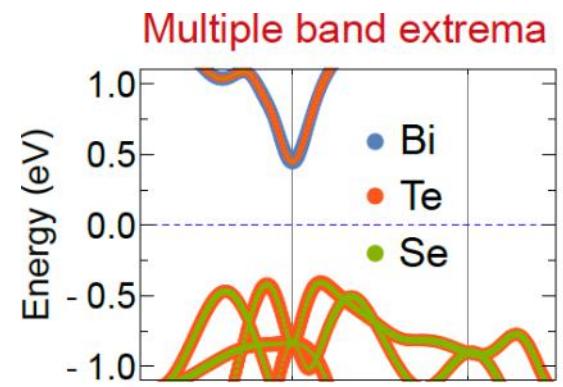
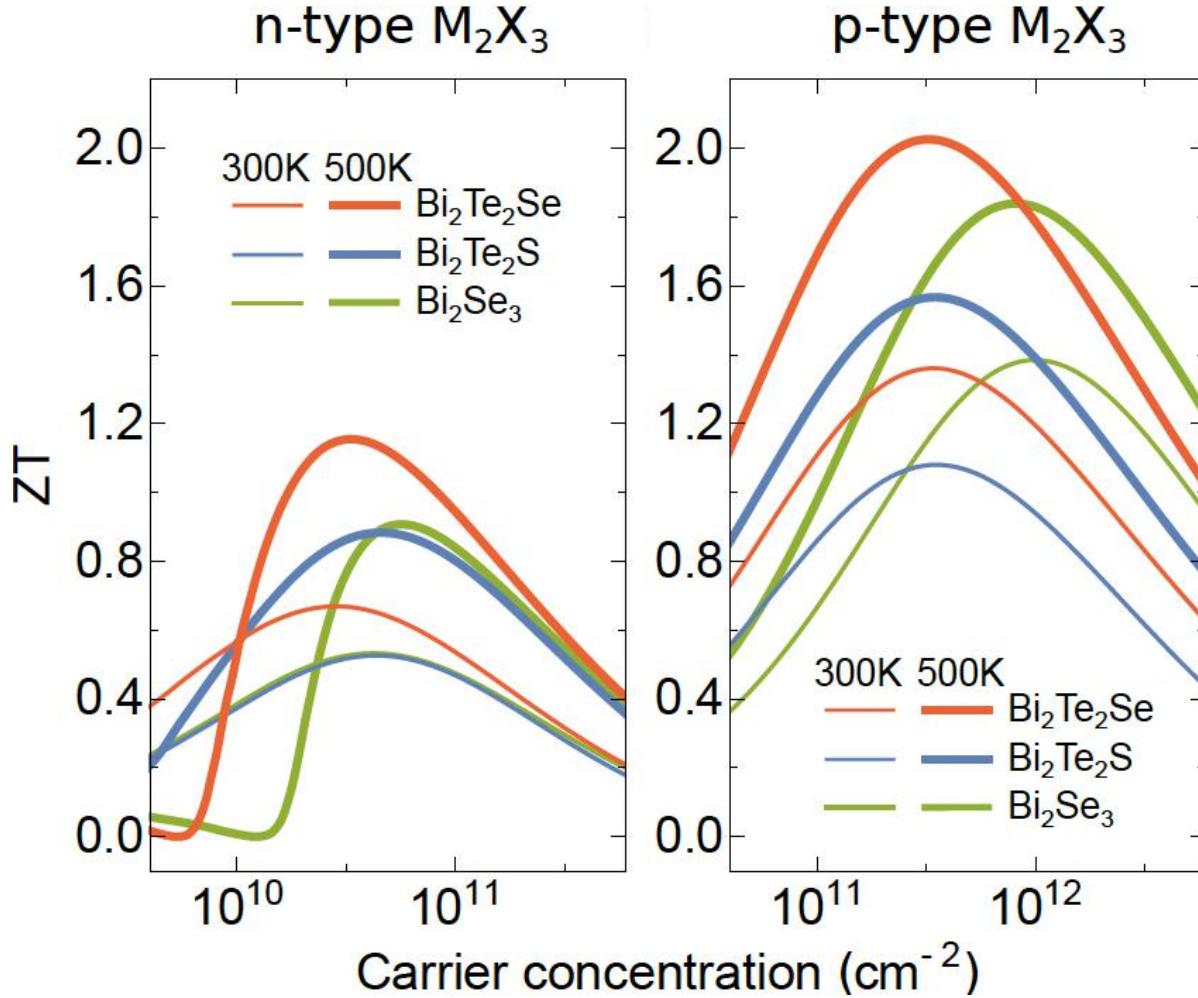
Phonon-phonon interaction



Heavy atomic masses + phonon anharmonicity
Low lattice thermal conductivity

ZT of 2D tetradymite M_2X_3

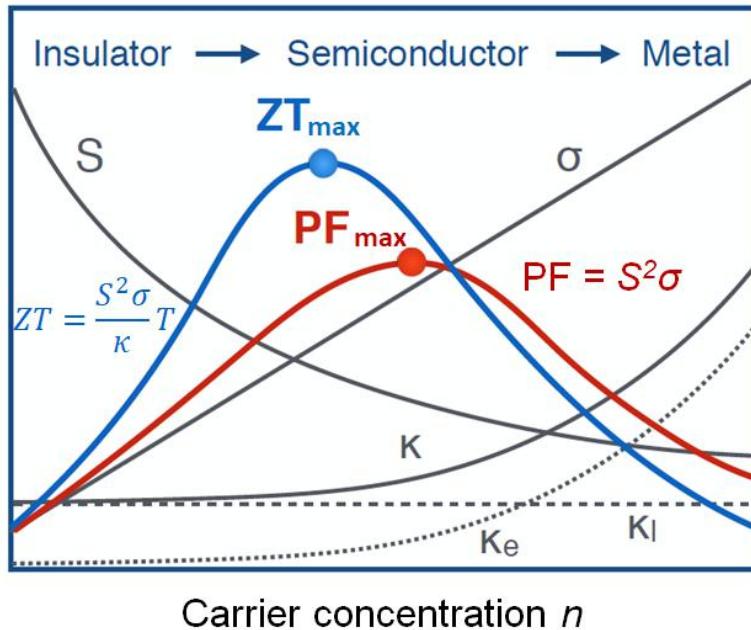
Hung, Nugraha, Saito, Nano Energy 58, 743 (2019)



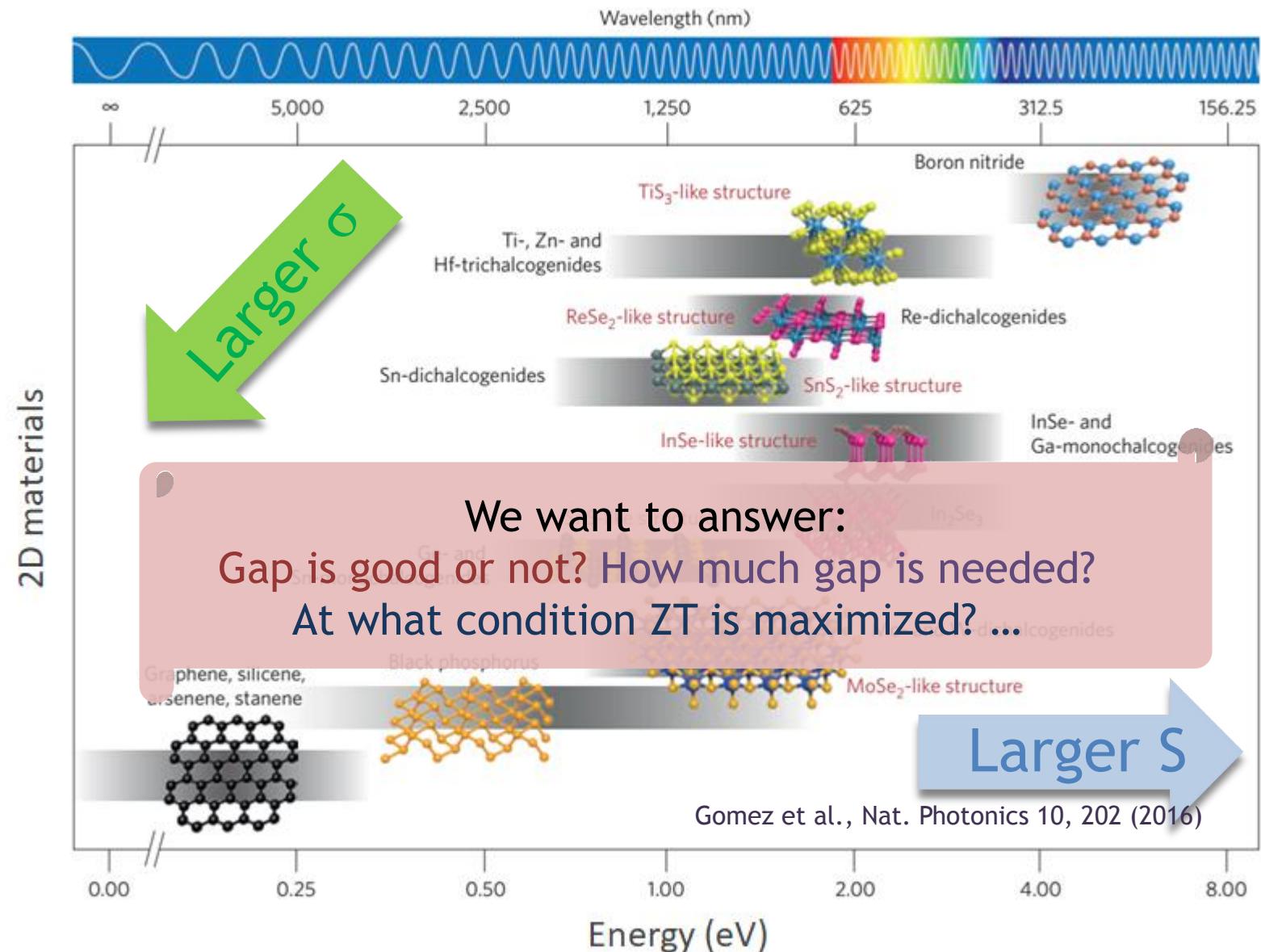
Can we achieve $ZT = 2$ for 2D tetradymite?

YES

Going back to the typical problem



This optimization problem
also occurs in 2D materials



Calculation methods

Thermoelectric (TE) kernel

$$\mathcal{L}_i = \int_{-\infty}^{\infty} \mathcal{T}(E)(E - \mu)^i \left(-\frac{\partial f}{\partial E} \right) dE \quad (i = 0, 1, 2)$$

$E(k)$: energy dispersion, μ : chemical potential, $f(E)$: Fermi-Dirac distribution

Transport distribution function (TDF)

$$\mathcal{T}(E) = v_x^2(E)\tau(E)\mathcal{D}(E) \quad \text{For isotropic materials: } v_x^2 = \frac{v_g^2}{d} \quad (d : \text{dimension})$$

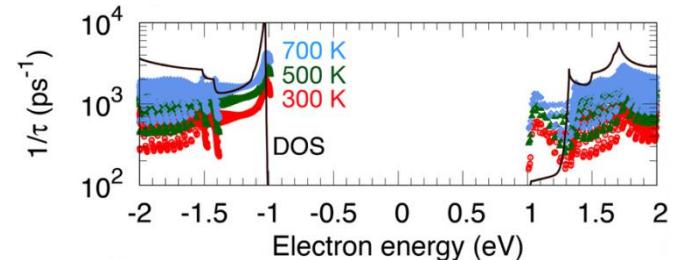
$v_x(E)$: one-dimensional carrier velocity, $\tau(E)$: relaxation time, $D(E)$: density of states

Approximation for relaxation time

$$\tau(E) = \frac{C}{\mathcal{D}(E)}$$

C : scattering coefficient
in units of $\text{W}^{-1}\text{m}^{-3}$

e.g., Appl. Phys. Lett. 092107 (2017)



Formulas for TE properties

Using the TE kernel:

$$\mathcal{L}_i = \int_{-\infty}^{\infty} \mathcal{T}(E)(E - \mu)^i \left(-\frac{\partial f}{\partial E} \right) dE \quad (i = 0, 1, 2)$$

We can calculate all TE properties for a given material:

Electrical conductivity

$$\sigma = q^2 \mathcal{L}_0$$

Seebeck's coefficient

$$S = \frac{1}{qT} \frac{\mathcal{L}_1}{\mathcal{L}_0}$$

Thermal conductivity
(electron part)

$$\kappa_e = \frac{1}{T} \left(\mathcal{L}_2 - \frac{(\mathcal{L}_1)^2}{\mathcal{L}_0} \right)$$

TE figure of merit: $ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_{\text{ph}}} T$

T : absolute temperature, κ_{ph} : lattice (phonon) thermal conductivity

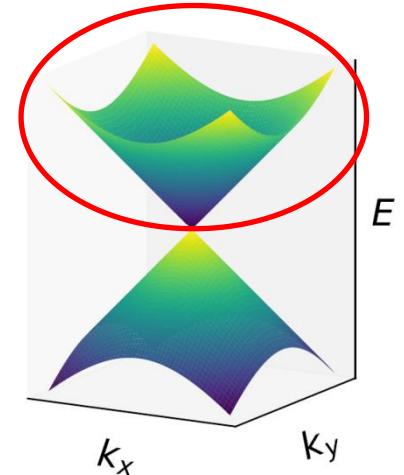
TE kernel for gapless 2D Dirac material

Energy dispersion: $E = \pm \hbar v_F |\mathbf{k}|$

Transport distribution function (TDF):

$$\mathcal{T}(E) = v_x^2(E)\tau(E)\mathcal{D}(E) = (v_F^2/d)C\mathcal{D}^{-1}\mathcal{D}$$

$$\mathcal{T}(E) = \frac{1}{2}v_F^2 C$$



Let's firstly focus on the conduction band with $E \in (0, \infty)$

$$\text{Calculation of TE kernel } \mathcal{L}_{i,c} = \int_0^\infty \mathcal{T}(E)(E - \mu)^i \left(-\frac{\partial f}{\partial E} \right) dE$$

$$\mathcal{L}_{i,c} = \mathcal{T} \int_0^\infty (E - \mu)^i \frac{1}{k_B T} \frac{e^{(E-\mu)/(k_B T)}}{\left(e^{(E-\mu)/(k_B T)} + 1\right)^2} dE$$

$$= \frac{1}{2}v_F^2 C (k_B T)^i \int_0^\infty (\varepsilon - \eta)^i \frac{e^{(\varepsilon-\eta)}}{\left(e^{(\varepsilon-\eta)} + 1\right)^2} d\varepsilon$$

$$\varepsilon = \frac{E}{k_B T}$$

$$\eta = \frac{\mu}{k_B T}$$

$$\mathcal{L}_{i,c} = \frac{1}{2}v_F^2 C (k_B T)^i \mathcal{F}_{i,c}(\eta) \quad \text{with} \quad \mathcal{F}_{i,c}(\eta) = \int_{-\eta}^\infty \frac{x^i e^x}{(e^x + 1)^2} dx \quad (x = \varepsilon - \eta)$$

Components of TE kernel

For the conduction band:

$$\mathcal{L}_{i,c} = \frac{1}{2}v_F^2 C(k_B T)^i \mathcal{F}_{i,c}(\eta) \quad \mathcal{F}_{i,c}(\eta) = \int_{-\eta}^{\infty} \frac{x^i e^x}{(e^x + 1)^2} dx$$

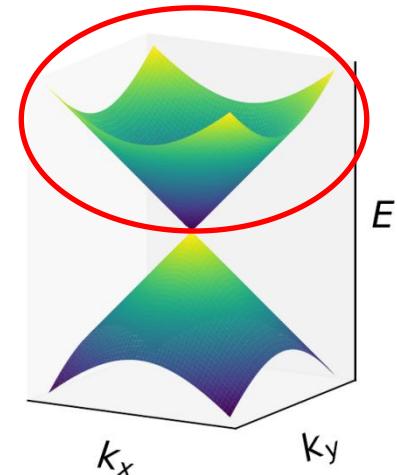
$$\mathcal{F}_{0,c}(\eta) = \frac{e^\eta}{e^\eta + 1}$$

$$\mathcal{F}_{1,c}(\eta) = \frac{\eta}{e^\eta + 1} + \ln(1 + e^{-\eta})$$

$$\mathcal{F}_{2,c}(\eta) = \frac{\pi^2}{3} - \frac{\eta^2}{e^\eta + 1} - 2\eta \ln(1 + e^{-\eta}) + 2\text{Li}_2(-e^{-\eta})$$

$$\text{Li}_k(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^k}$$

polylog function



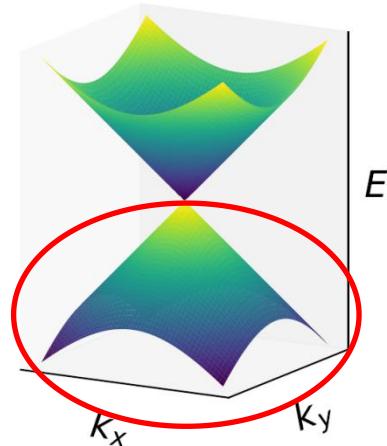
Similarly, for the valence band:

$$\mathcal{L}_{i,v} = \frac{1}{2}v_F^2 C(k_B T)^i \mathcal{F}_{i,v}(\eta) \quad \mathcal{F}_{i,v}(\eta) = \int_{-\infty}^{-\eta} \frac{x^i e^x}{(e^x + 1)^2} dx$$

$$\mathcal{F}_{0,v}(\eta) = \frac{1}{e^\eta + 1}$$

$$\mathcal{F}_{1,v}(\eta) = -\frac{\eta}{e^\eta + 1} - \ln(1 + e^{-\eta})$$

$$\mathcal{F}_{2,v}(\eta) = \frac{\eta^2}{e^\eta + 1} + 2\eta \ln(1 + e^{-\eta}) - 2\text{Li}_2(-e^{-\eta})$$



The two-band model

TE properties
due to conduction band:

$$\begin{aligned}\sigma_c &= q^2 \mathcal{L}_{0,c} \\ &= \frac{1}{2} e^2 v_F^2 C \mathcal{F}_{0,c}(\eta) \\ &= \sigma_0 \mathcal{F}_{0,c}(\eta)\end{aligned}$$

$$\begin{aligned}S_c &= \frac{1}{qT} \frac{\mathcal{L}_{1,c}}{\mathcal{L}_{0,c}} \\ &= -\frac{k_B}{e} \frac{\mathcal{F}_{1,c}(\eta)}{\mathcal{F}_{0,c}(\eta)} \\ &= -S_0 \frac{\mathcal{F}_{1,c}(\eta)}{\mathcal{F}_{0,c}(\eta)}\end{aligned}$$

$$\begin{aligned}\kappa_{e,c} &= \frac{1}{T} \left(\mathcal{L}_{2,c} - \frac{(\mathcal{L}_{1,c})^2}{\mathcal{L}_{0,c}} \right) \\ &= \frac{1}{2} v_F^2 C k_B^2 T \left(\mathcal{F}_{2,c}(\eta) - \frac{(\mathcal{F}_{1,c}(\eta))^2}{\mathcal{F}_{0,c}(\eta)} \right) \\ &= \kappa_0 \left(\mathcal{F}_{2,c}(\eta) - \frac{(\mathcal{F}_{1,c}(\eta))^2}{\mathcal{F}_{0,c}(\eta)} \right)\end{aligned}$$

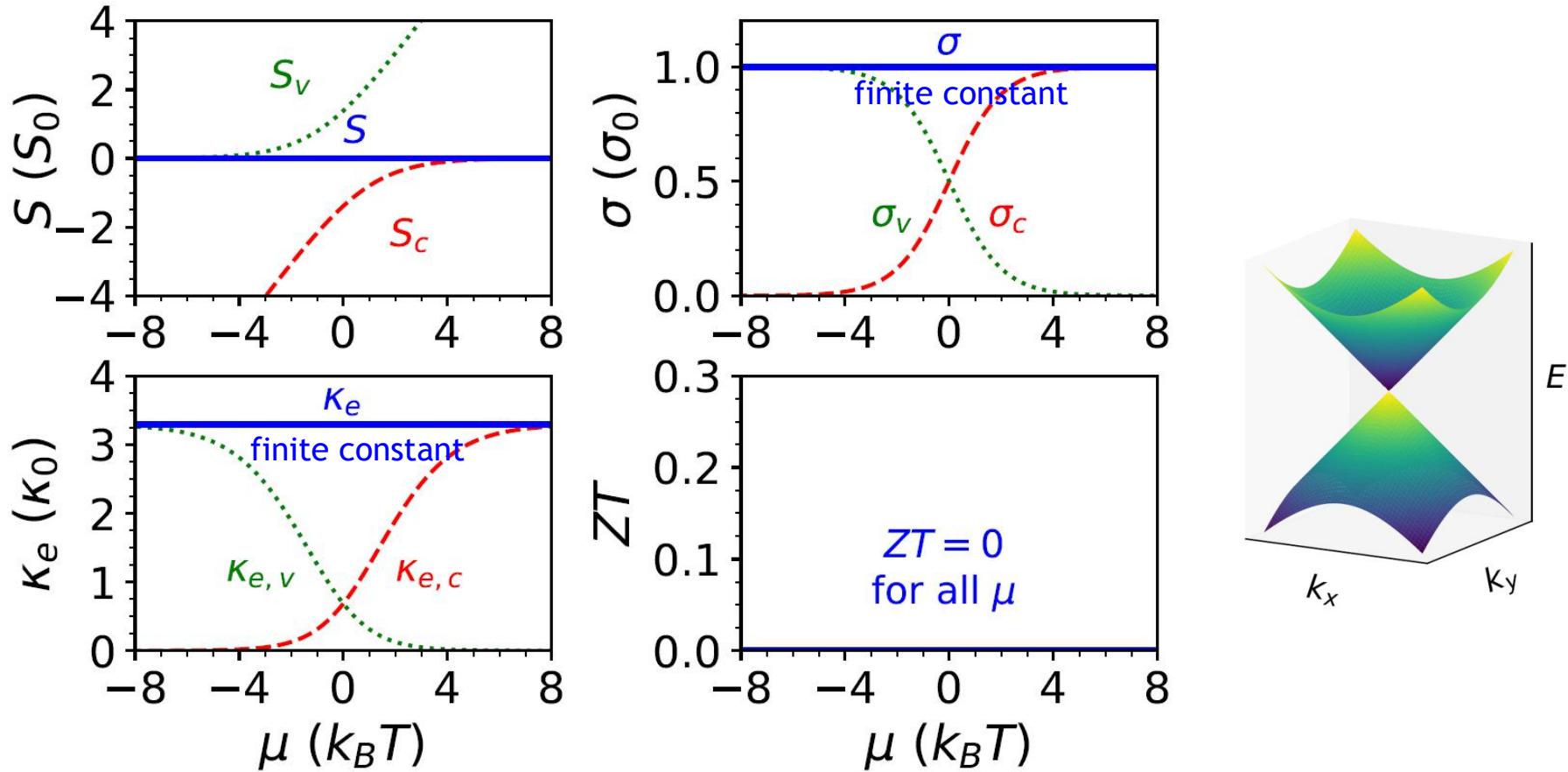
and for the valence band:

$$\begin{aligned}\sigma_v &= \sigma_0 \mathcal{F}_{0,v}(\eta) \\ S_v &= -S_0 \frac{\mathcal{F}_{1,v}(\eta)}{\mathcal{F}_{0,v}(\eta)} \\ \kappa_{e,v} &= \kappa_0 \left(\mathcal{F}_{2,v}(\eta) - \frac{(\mathcal{F}_{1,v}(\eta))^2}{\mathcal{F}_{0,v}(\eta)} \right)\end{aligned}$$

Total effect by the two bands:

$$\begin{aligned}\sigma &= \sigma_c + \sigma_v \\ S &= \frac{\sigma_c S_c + \sigma_v S_v}{\sigma_c + \sigma_v} \\ \kappa_e &= \frac{\sigma_c \sigma_v}{\sigma_c + \sigma_v} (S_c - S_v)^2 + (\kappa_{e,c} + \kappa_{e,v})\end{aligned}$$

TE properties: gapless 2D Dirac



$$S = 0 \text{ and thus } ZT = 0$$

Possible origin: assumption of relaxation time (DOS^{-1}) and symmetry in electron-hole TE kernel

Symmetry of TE kernel

$$\mathcal{F}_{0,c}(\eta) = \frac{e^\eta}{e^\eta + 1}$$

$$\mathcal{F}_{1,c}(\eta) = \frac{\eta}{e^\eta + 1} + \ln(1 + e^{-\eta})$$

$$\mathcal{F}_{2,c}(\eta) = \frac{\pi^2}{3} - \frac{\eta^2}{e^\eta + 1} - 2\eta \ln(1 + e^{-\eta}) + 2\text{Li}_2(-e^{-\eta})$$

$$\mathcal{F}_{0,v}(\eta) = \frac{1}{e^\eta + 1}$$

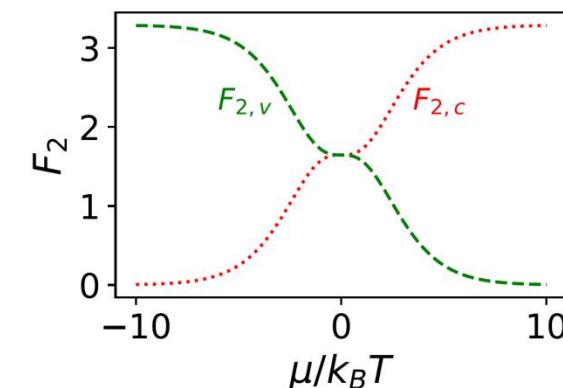
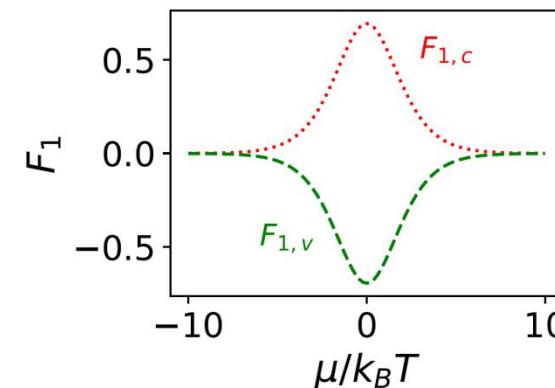
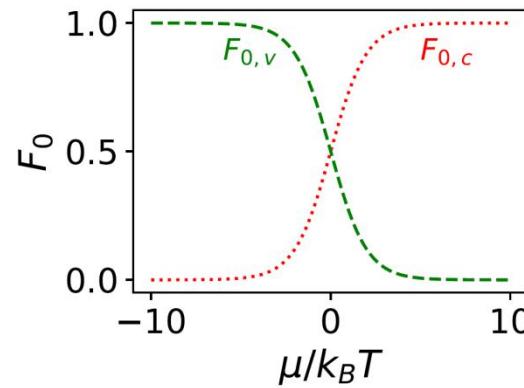
$$\mathcal{F}_{1,v}(\eta) = -\frac{\eta}{e^\eta + 1} - \ln(1 + e^{-\eta})$$

$$\mathcal{F}_{2,v}(\eta) = \frac{\eta^2}{e^\eta + 1} + 2x \ln(1 + e^{-\eta}) - 2\text{Li}_2(-e^{-\eta})$$

$$\mathcal{F}_{0,c}(\eta) = \mathcal{F}_{0,v}(-\eta)$$

$$\mathcal{F}_{1,c}(\eta) = -\mathcal{F}_{1,v}(\eta)$$

$$\mathcal{F}_{2,c}(\eta) = \mathcal{F}_{2,v}(-\eta)$$



Symmetry partially contributes to the vanishing Seebeck's coefficient

TE properties: gapped 2D Dirac

Energy dispersion $E = \pm \sqrt{(\hbar v_F |\mathbf{k}|)^2 + \Delta^2}$

$$\mathcal{T}(E) = \frac{1}{2} v_F^2 C \left(\frac{E^2 - \Delta^2}{E^2} \right)$$

TDF is now energy dependent!

TE kernel calculation for the conduction band:

$$\begin{aligned} \mathcal{L}_{i,c} &= \int_{\Delta}^{\infty} \frac{Cv_F^2(E^2 - \Delta^2)}{2E^2} (E - \mu)^i \frac{1}{k_B T} \frac{e^{(E-\mu)/(k_B T)}}{(e^{(E-\mu)/(k_B T)} + 1)^2} dE \\ &= \frac{Cv_F^2(k_B T)^i}{2} \int_{\tilde{\Delta}}^{\infty} \frac{(\varepsilon^2 - \tilde{\Delta}^2)}{\varepsilon^2} (\varepsilon - \eta)^i \frac{e^{(\varepsilon-\eta)}}{(e^{(\varepsilon-\eta)} + 1)^2} d\varepsilon \\ &= \frac{Cv_F^2(k_B T)^i}{2} \int_{\tilde{\Delta}-\eta}^{\infty} \left(1 - \frac{\tilde{\Delta}^2}{(x+\eta)^2} \right) \frac{x^i e^x}{(e^x + 1)^2} dx \quad (x = \varepsilon - \eta) \\ &= \frac{Cv_F^2(k_B T)^i}{2} \left(\mathcal{F}_{i,c}(\tilde{\Delta} - \eta) - \mathcal{G}_{i,c}(\eta, \tilde{\Delta}) \right) \end{aligned}$$

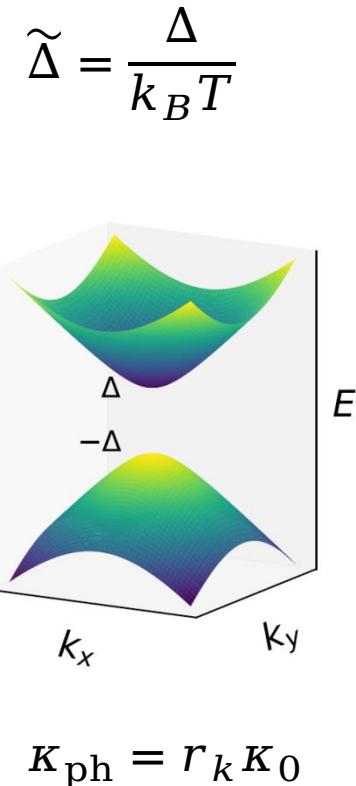
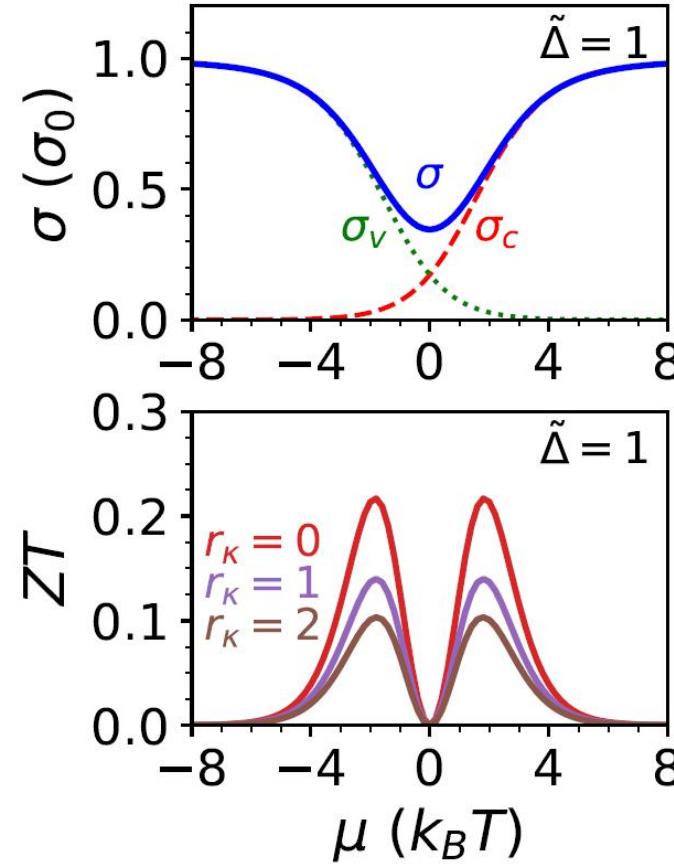
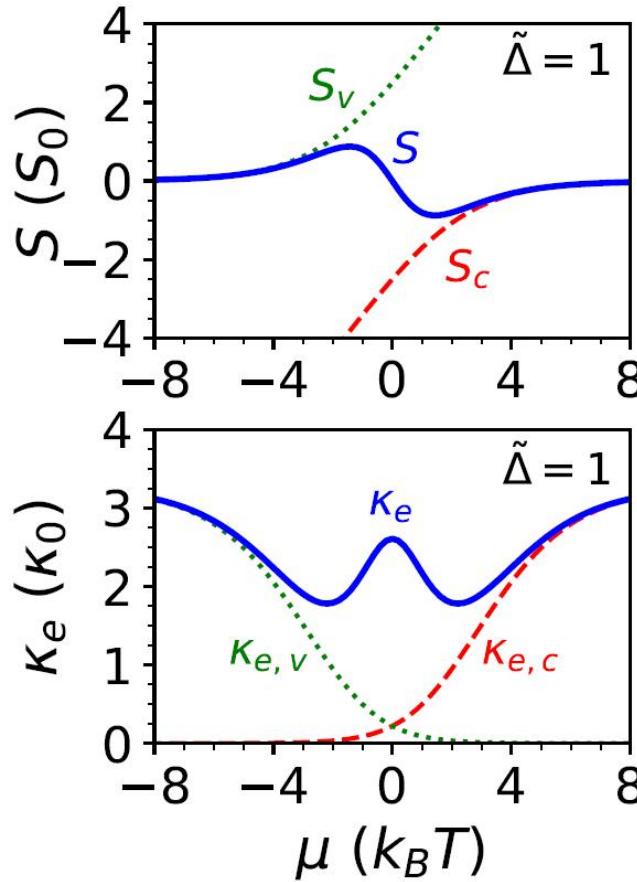
$$\mathcal{F}_{i,c}(x') = \int_{x'}^{\infty} \frac{x^i e^x}{(e^x + 1)^2} dx$$

$$\mathcal{G}_{i,c}(\eta, \tilde{\Delta}) = \int_{\tilde{\Delta}-\eta}^{\infty} \frac{\tilde{\Delta}^2}{(x+\eta)^2} \frac{x^i e^x}{(e^x + 1)^2} dx$$

Similar result for valence band:

$$\begin{aligned} \mathcal{L}_{i,v} &= \frac{Cv_F^2(k_B T)^i}{2} \left(\mathcal{F}_{i,v}(-\tilde{\Delta} - \eta) - \mathcal{G}_{i,v}(\eta, \tilde{\Delta}) \right) \\ &\quad \mathcal{G}_{i,v}(\eta, \tilde{\Delta}) = \int_{-\infty}^{-\tilde{\Delta}-\eta} \frac{\tilde{\Delta}^2}{(x+\eta)^2} \frac{x^i e^x}{(e^x + 1)^2} dx \end{aligned}$$

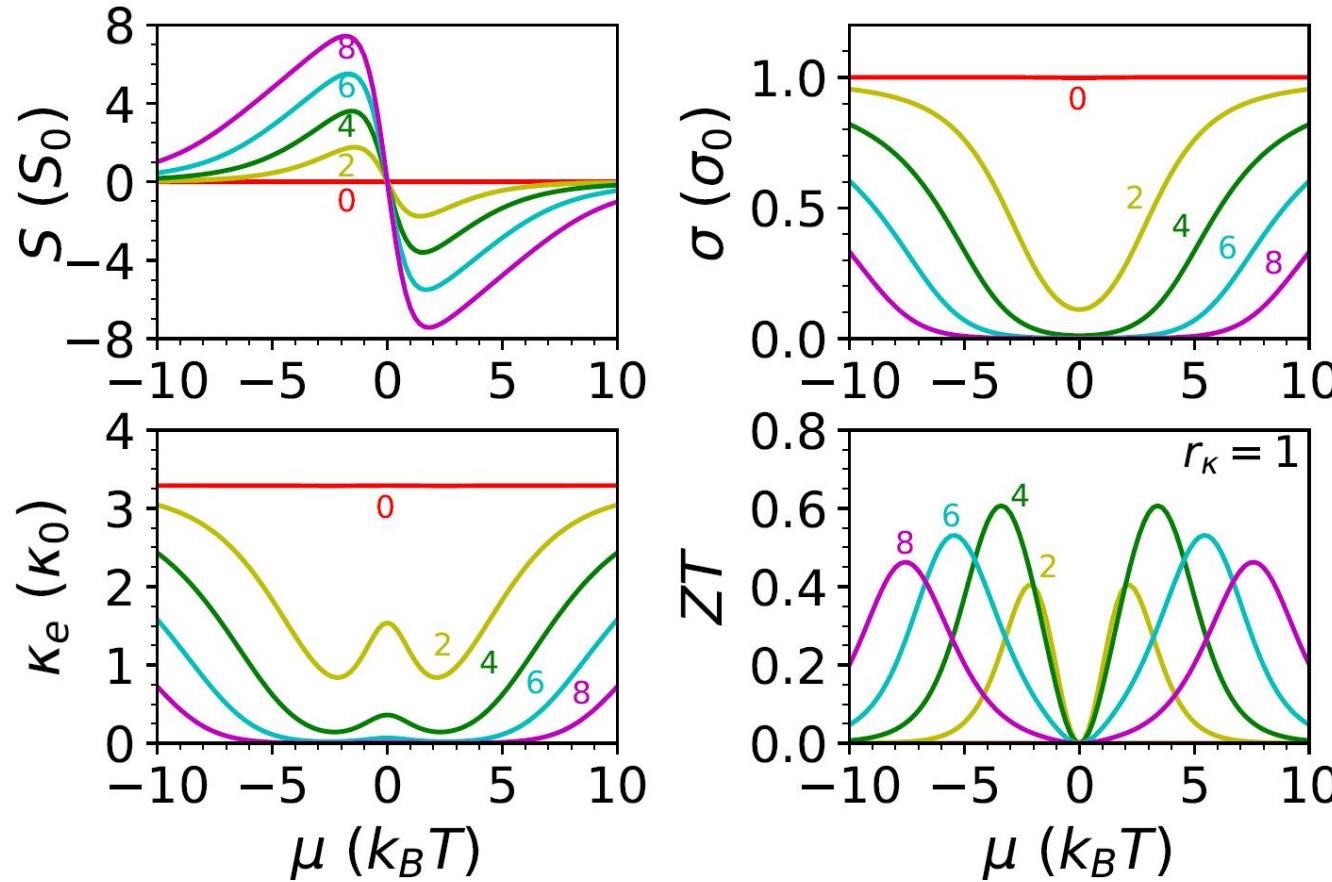
TE properties: gapped 2D Dirac



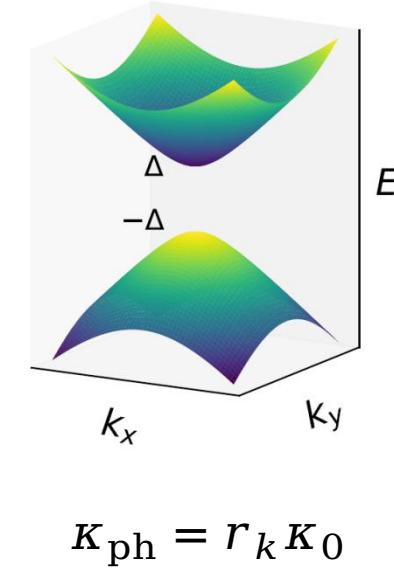
Opening gap might be beneficial for thermoelectric properties of 2D Dirac materials

Gap-dependent TE properties

Hasdeo, ♦Nugraha, et al., J. Appl. Phys. 126, 035109 (2019)



$$\tilde{\Delta} = \frac{\Delta}{k_B T}$$

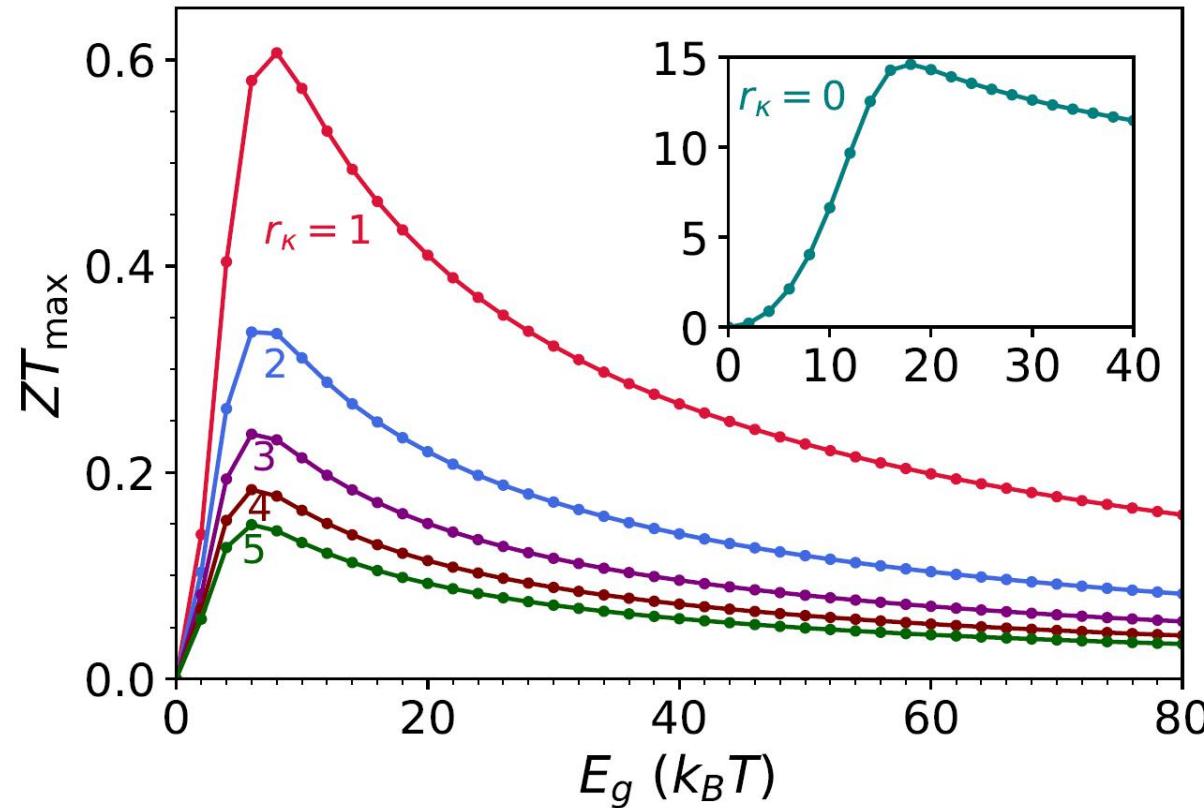


Increasing gap does not guarantee ZT to enhanced forever
Optimal gap?

Optimal band gap for ZT

Hasdeo, ◆Nugraha, et al., J. Appl. Phys. 126, 035109 (2019)

Take the max of ZT at a certain μ , then plot versus energy gap



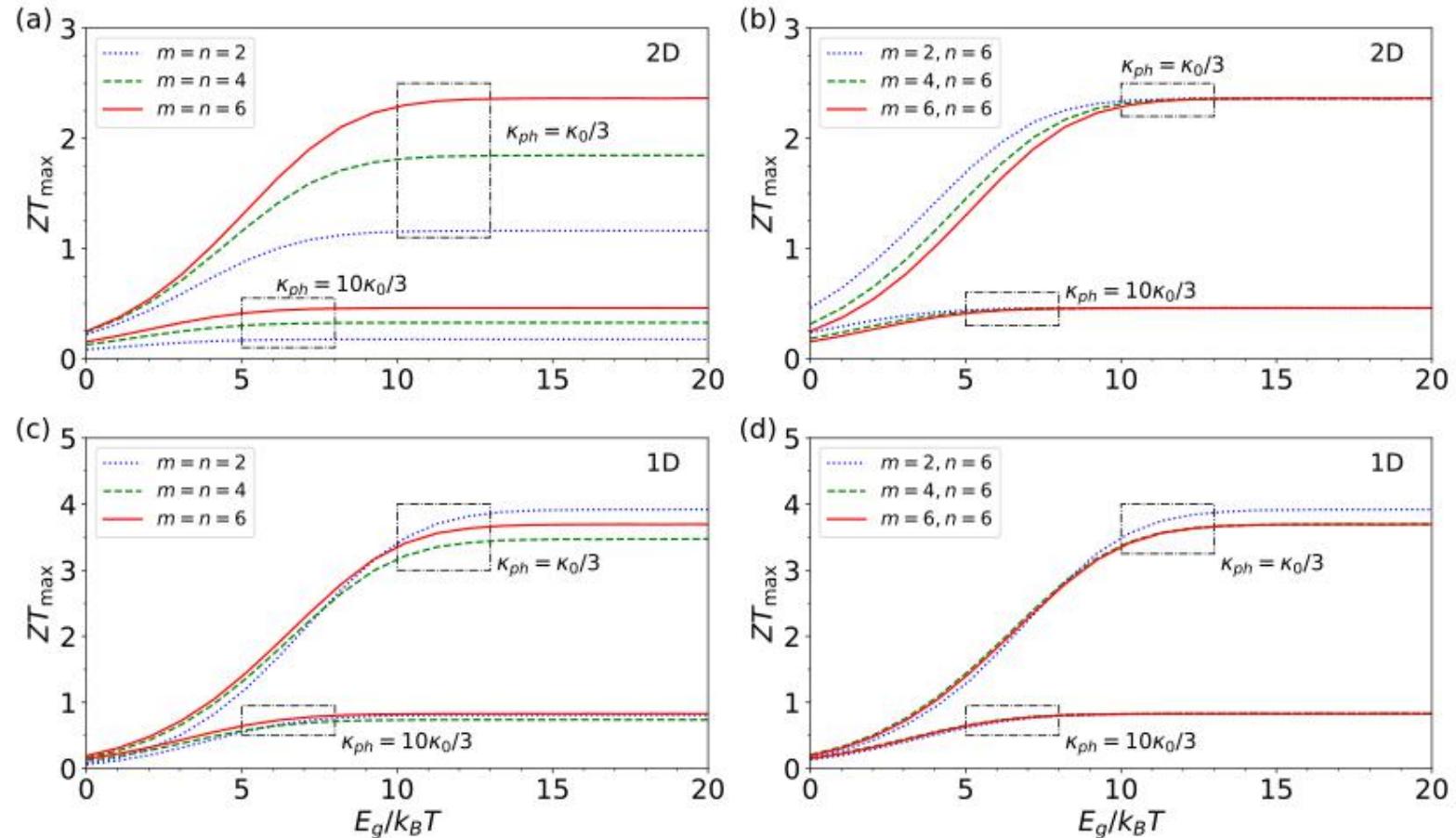
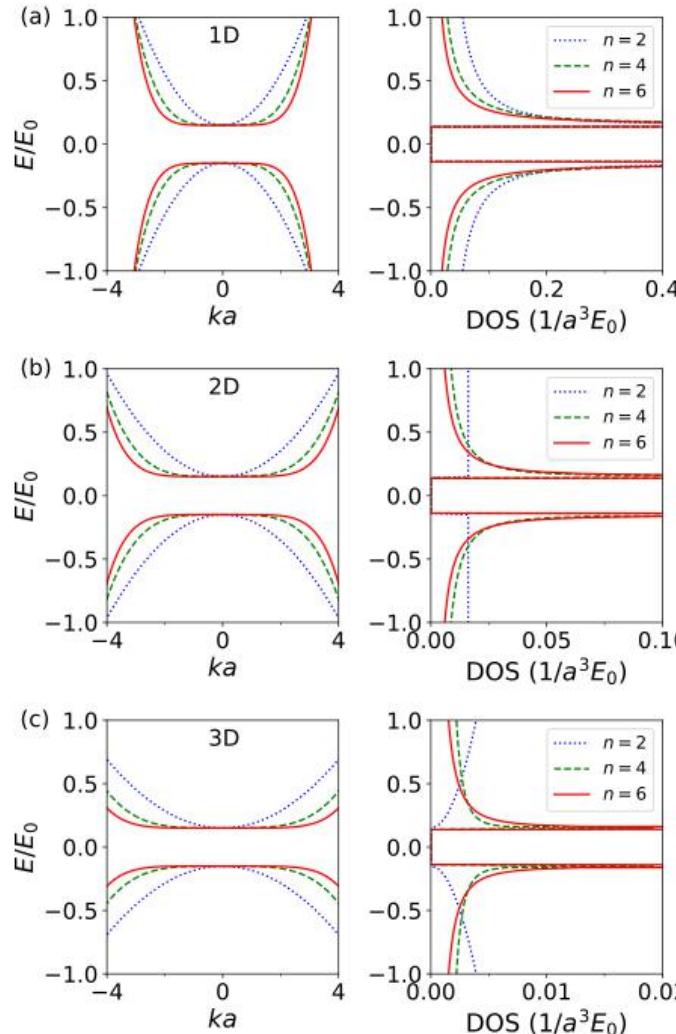
There exists optimal gap to maximize ZT:
only few k_BT (narrow gap): 6-18 k_BT

Further exploration with two-band models (1)

Semiconductors with various band shapes and curvatures

Adhidewata*, Nugraha*, et al., Mater. Today Commun. 31, 103737 (2022)

Darmawan, Suprayoga, AlShaikhi, Nugraha, Mater. Today Commun. 33, 104596 (2022)

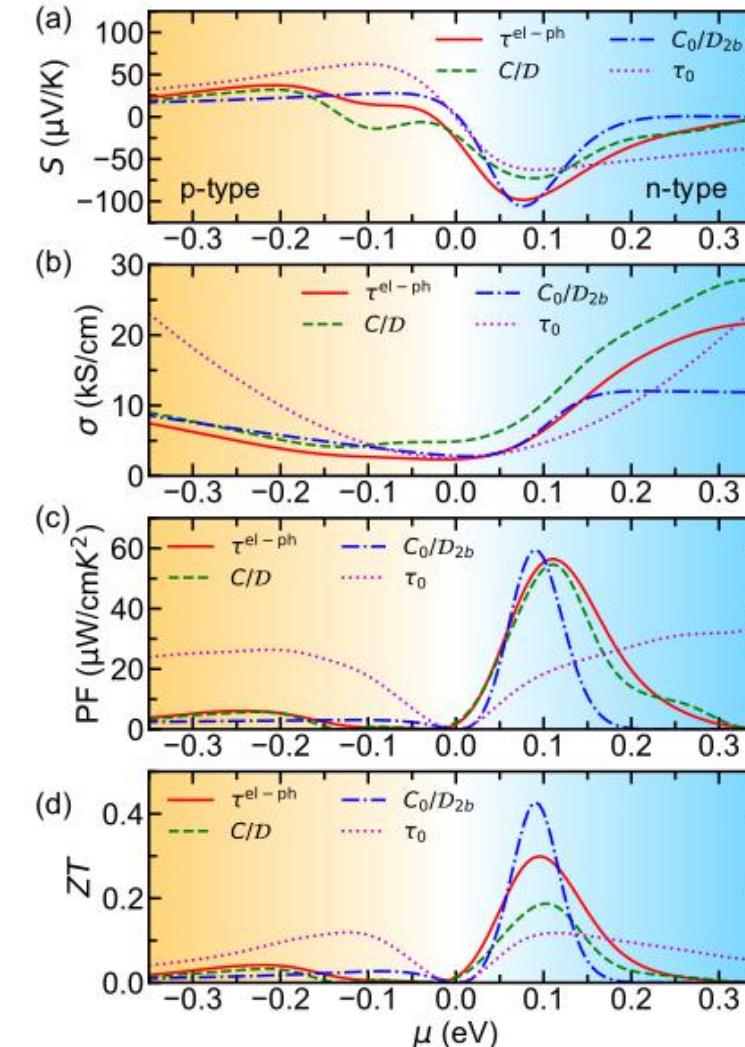
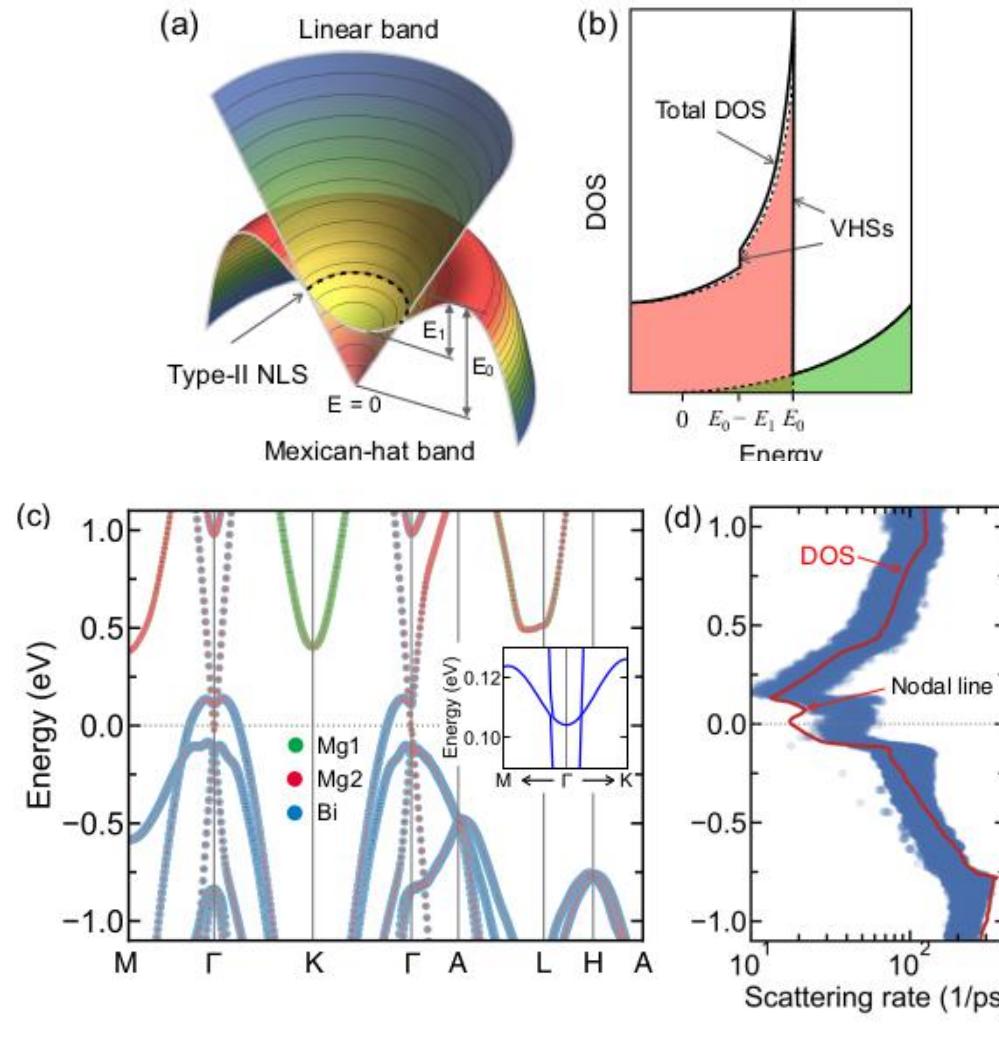


- Combining pudding-mold band shape, Dirac linear band
- Band gap effects (again there exists optimal gap), etc.

Further exploration with two-band models (2)

Enhanced Seebeck effects in a nodal line semimetal (type-II)

Hung, Adhidewata, Nugraha, Saito, Phys. Rev. B 105, 115142 (2022)



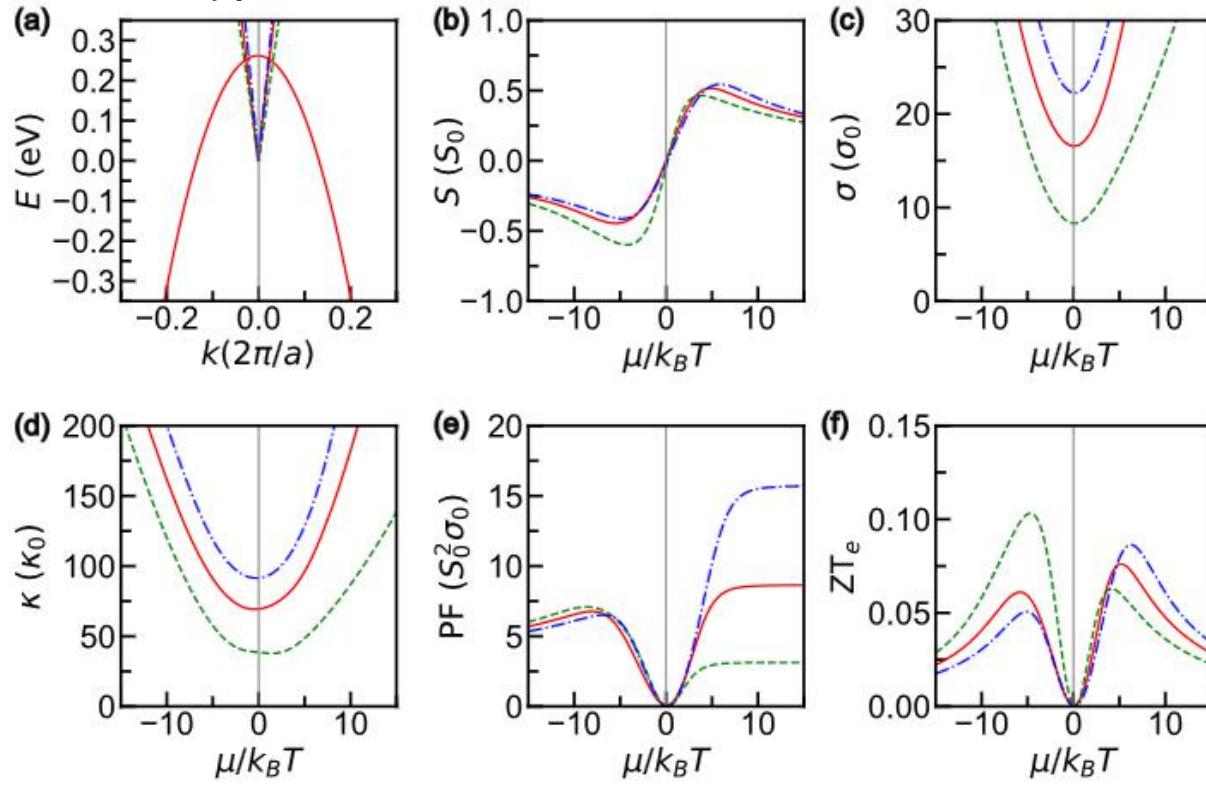
Mg₃Bi₂
type-II NLS
with $ZT \sim 0.4$
(exp. parameter)

Further exploration with two-band models (3)

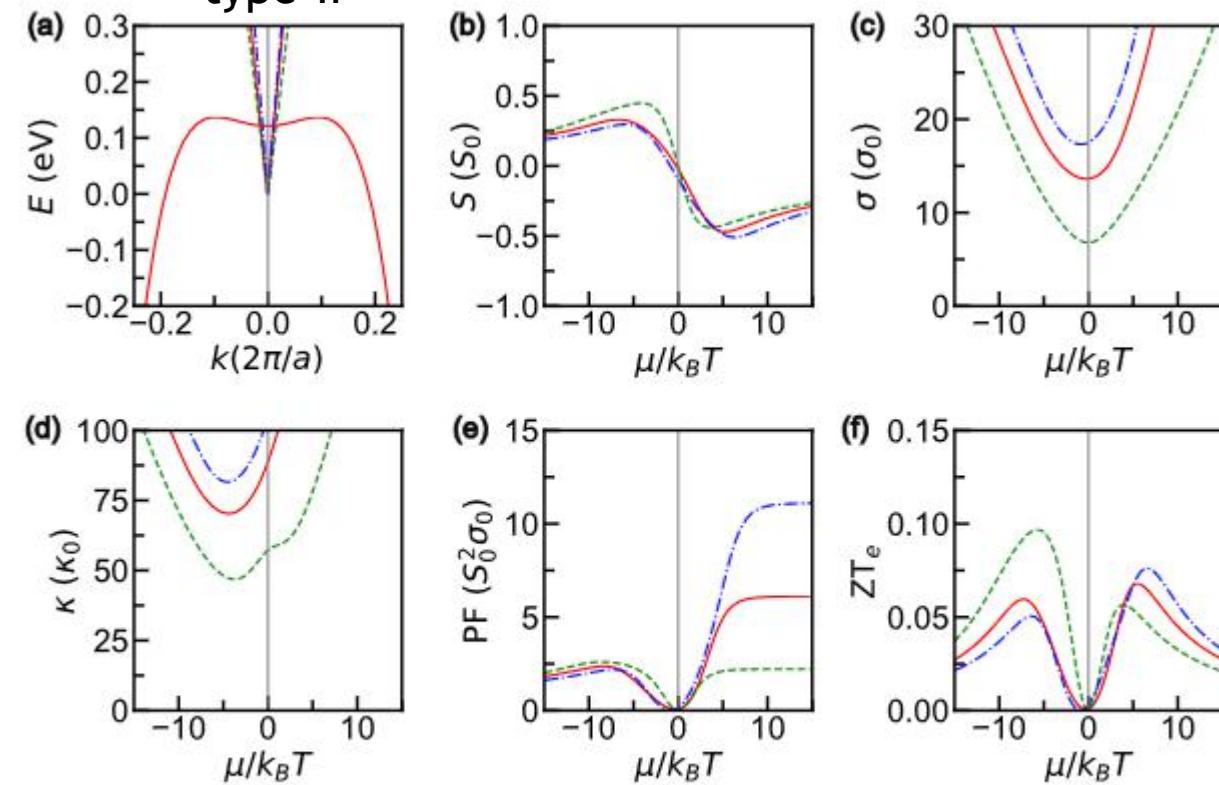
Questioning the importance of studying semimetals for thermoelectrics

Laksono, Majidi, Nugraha, in preparation (2024)

type-I



type-II



$m = 0.4m_0$ — $v_F = 1.89 \times 10^5$ m/s — $v_F = 5.17 \times 10^5$ m/s — $v_F = 1.03 \times 10^5$ m/s

$m = 0.4m_0$ — $v_F = 1.89 \times 10^5$ m/s — $v_F = 5.17 \times 10^5$ m/s — $v_F = 1.03 \times 10^5$ m/s

the most optimistic ZT value is just near 0.1 with full theoretical parameters

Summary and perspectives

Quantum size effect in low-dimensional materials:

$$\text{Enhancement factor: } \frac{\text{PF}_{\text{opt}}}{\text{PF}_{\text{opt}}^{\text{3D}}} \propto \left(\frac{L}{\Lambda}\right)^{d-3}$$

2D InSe with multi-valley convergence:

Highest PF at strain about – 0.025

2D Bi_2Se_3 with multi-valley convergence and low thermal conductivity

$ZT = 1.4 - 2.0$ at $300 - 500$ K

Gap-dependent ZT in 2D Dirac materials

Optimal band gap around $6-18$ $k_{\text{B}}\text{T}$

Two-band models help exploration of various materials

Band shape/curvature/gap effects

