The 17th Workshop on
First-Principles Computational Materials Physics

Unusual Thermoelectric Behaviors in Topological Insulator Nanostructures

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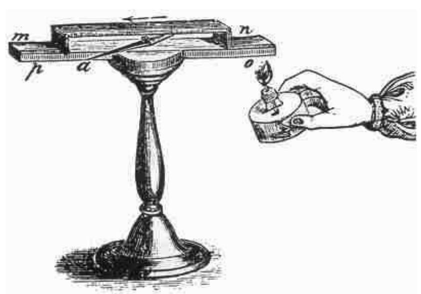
What is thermoelectricity?

- **Thermoelectricity**: The science and technology considering the conversion between the electrical energy and the thermal energy.

https://en.wikipedia.org/wiki/Thomas_Johann_Seebeck

Seebeck Effect (1821-3)
Using temperature difference to generate electrical power



http://www.thermoelectrics.caltech.edu/thermoelectrics/history.html

Instrument used by Seebeck to observe the deflection of a compass needle (a) due to a thermoelectric induced current

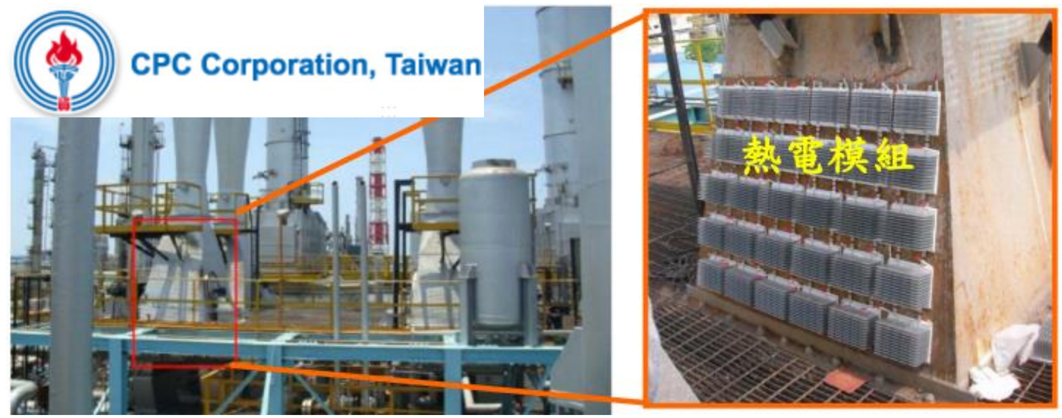
Peltier Effect (1834)
Using the electrical power to create temperature difference

https://en.wikipedia.org/wiki/Jean_Charles_Athanase_Peltier

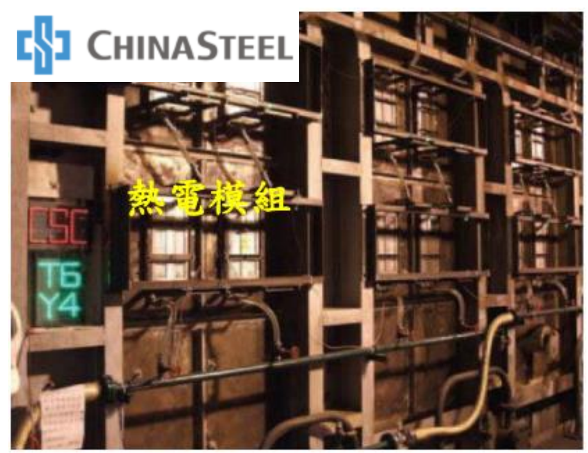
Applications of Thermoelectricity

- Thermoelectric generator
- Thermoelectric cooler

- Gas Company (CPC)
- Steel-making Company (CSC)
- Portable Devices
- Cooling Wine
- …



MATRIX
POWERWATCH



zT & Efficiency

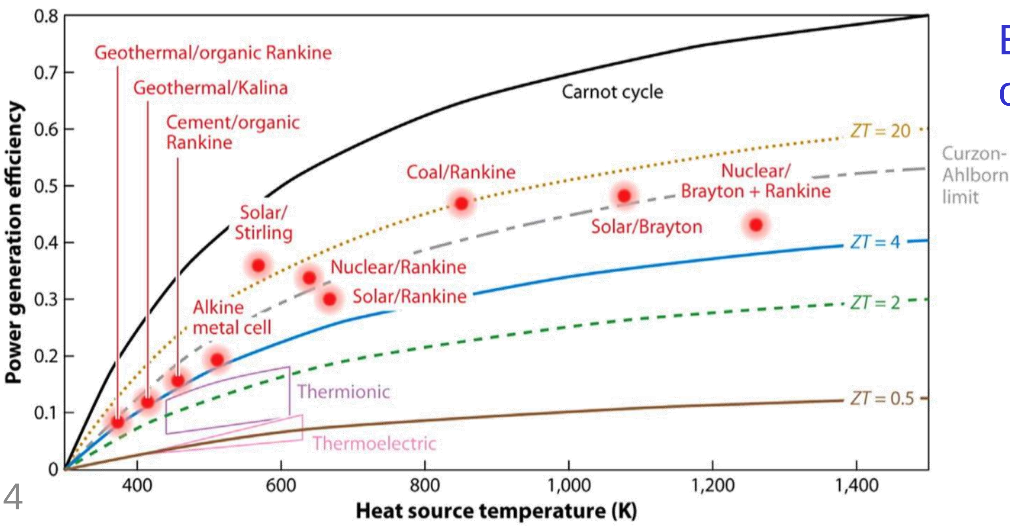
Figure of Merit (zT)

$$zT = \frac{\sigma S^2 T}{\kappa}$$

σ : Electrical Conductivity

$S = \frac{\Delta V}{\Delta T}$: Seebeck Coefficient

$\kappa = \kappa_e + \kappa_l$: Thermal Conductivity



Efficiency comparison between TEG and other energy-conversion technologies.

$$\eta = \frac{\Delta T}{T_h} \cdot \frac{\sqrt{1+z\bar{T}} - 1}{\sqrt{1+z\bar{T}} + T_c / T_h}$$

He, J. & Tritt, T. M. Advances in thermoelectric materials research: Looking back and moving forward. Science 357, 1369 (2017).

zT & Efficiency

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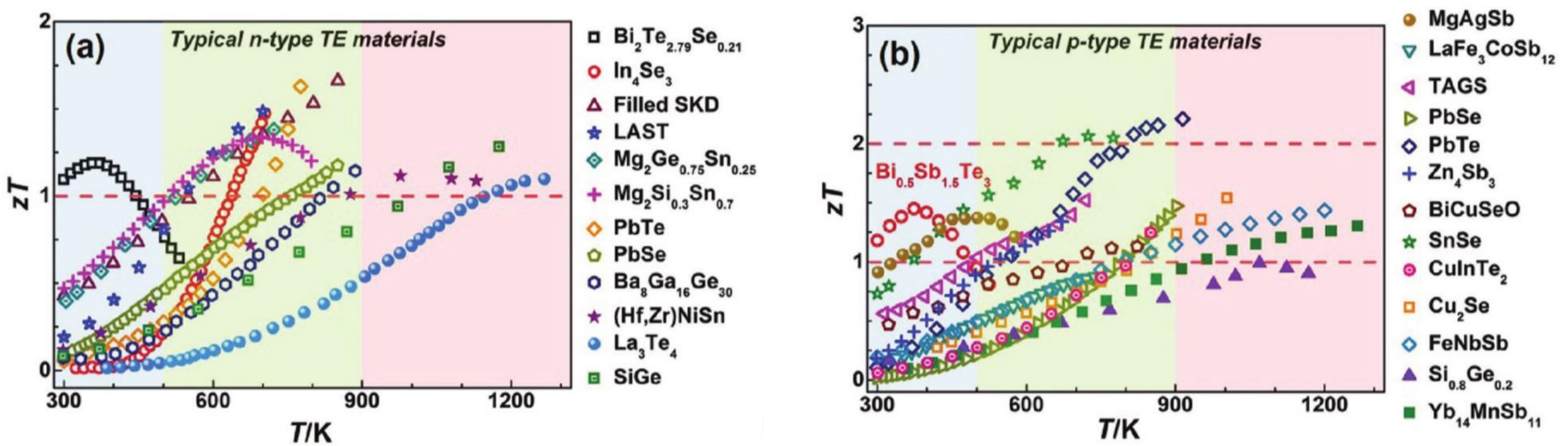


Zhu, T. *et al*. Compromise and Synergy in High-Efficiency Thermoelectric Materials. *Adv Mater* **29**, 1605884 (2017).

zT of Metals

Wiedemann -Franz Law

$$R_e = \frac{\sigma}{\kappa_e R_{WF}} \approx 1$$

$$R_{WF} = \frac{3e^2}{\pi^2 k_B^2 T}$$

zT of metals

$$zT \approx \frac{3}{\pi^2} R_e S_r^2 \approx 0.3 S_r^2$$

$$S_r = \frac{S}{k_B / e}$$ (Reduced Seebeck coefficient)

$$\frac{k_B}{e} = 86 \ (\mu V K^{-1})$$

Seebeck Coefficient of Metals

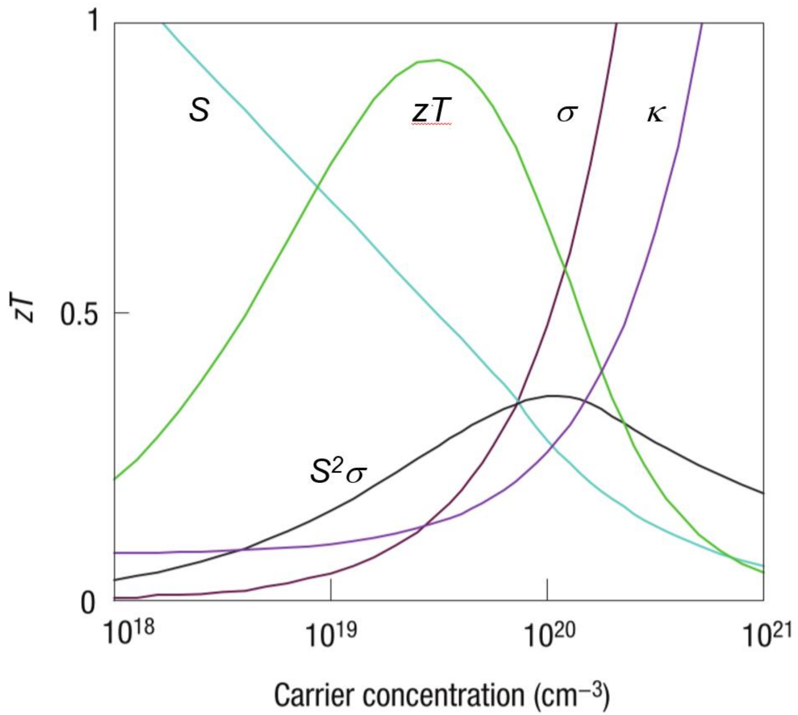
Material	S (uV/K)	S_r	$z_{cal}T$
Antimony	42	0.49	0.07
Nichrome	20	0.23	0.02
Molybdenum	5	0.06	>0.01
Cadmium, tungsten	2.5	0.03	>0.01
Gold, silver, copper	1.5	0.02	>0.01
Rhodium	1.0	0.01	>0.01

Material	S (uV/K)	S_r	$z_{cal}T$
Tantalum	-0.5	-0.01	>0.01
Lead	-1	-0.01	>0.01
Carbon	-2	-0.02	>0.01
Mercury	-4.4	-0.05	>0.01
Platinum	-5	-0.06	>0.01
Sodium	-7.0	-0.08	>0.01
Potassium	-14.0	-0.16	>0.01
Nickel	-20	-0.23	>0.01
Constantan	-40	-0.46	0.06
Bismuth	-77	0.89	0.24

https://en.wikipedia.org/wiki/Seebeck_coefficient

Trade-off between TE Parameters in Semiconductors

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



- There has to be a trade-off between the electrical conductivity and the magnitude of Seebeck coefficient.
- The zT can be enhanced by reducing the lattice thermal conductivity. This mostly achieved by introducing defects.
- However, defects could significantly impair the electrical conductivity deteriorating the TE performance.

Snyder, G. J. & Toberer, E. S. Complex thermoelectric materials. *Nat. Mater.* **7**, 105-114 (2008).

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Article

www.acsaem.org

Strongly Enhanced Thermoelectric Performance over a Wide Temperature Range in Topological Insulator Thin Films

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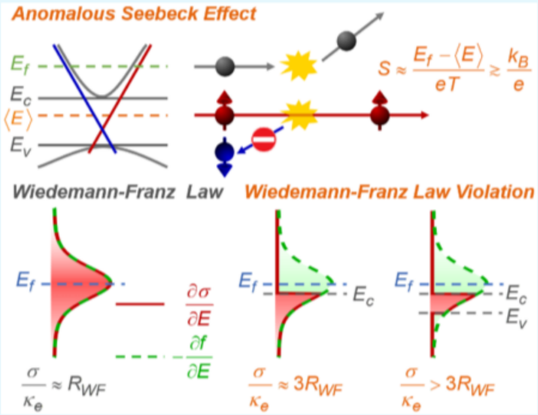
Supporting Information

ABSTRACT: Thermoelectric (TE) devices have been attracting increasing attention because of their ability to convert heat directly to electricity. To date, improving the TE figure of merit remains the key challenge. The advent of the topological insulator and the emerging nanotechnology open a new way to design high-performance TE devices. By combining first-principles calculations with Boltzmann transport theory, we demonstrate for epitaxial Bi_2Se_3 thin films with thickness slightly larger than six quintuple layers, the relaxation time of the in-gap topological surface states can reach hundreds of femtoseconds, which is 2 orders of magnitude larger than that of the bulk states. Such a strong relaxation time enhancement achieves an approximately 3 times larger electrical- to thermal-conductance ratio than the value predicted by the Wiedemann–Franz law. This condition also enhances the Seebeck coefficient, and consequently leads to the excellent TE figure of merit $zT \sim 2.1$ at room temperature with high TE efficiency over a wide temperature range. The TE performance can be further improved by introducing defects in the bulk-like middle layers of the thin film. The improvement is significant at room temperature and can be even better at a higher temperature. Similar strong enhancement of TE performance is expected in other topological insulator thin films.

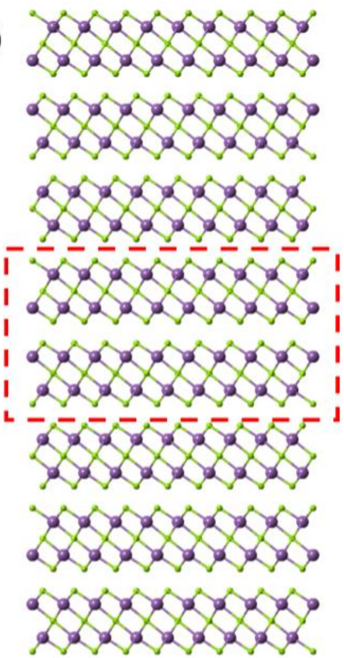


KEYWORDS: *thermoelectric, topological insulator, Bi_2Se_3, thin film, Wiedemann–Franz law violation, anomalous Seebeck effect*

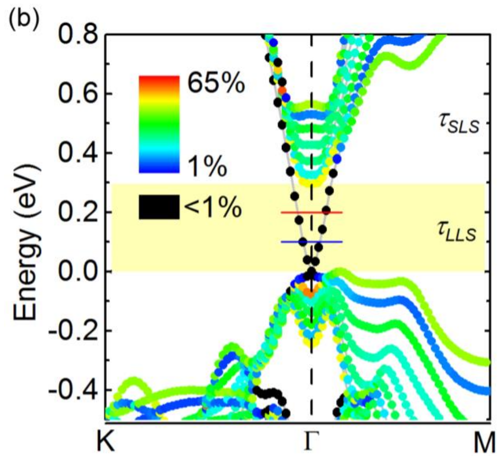
Topological-Insulator Thin Film

8QL-Bi_2Se_3

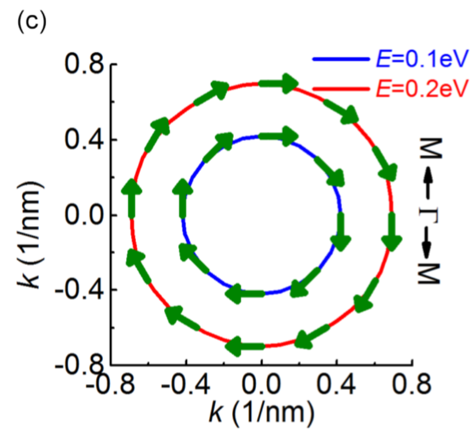
(a)



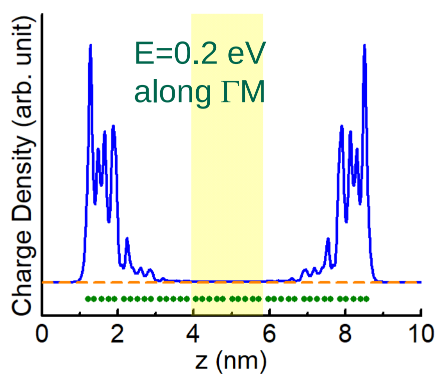
No bulks states in LLS region



Large-angle scattering is suppressed



Negligible Interaction between the TSSs at opposite side

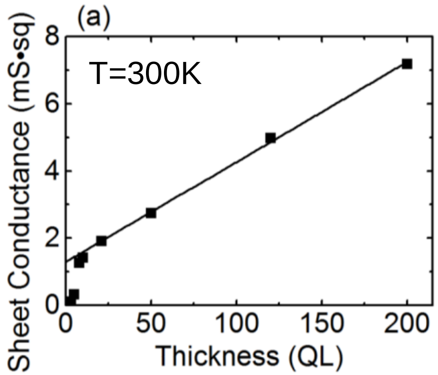


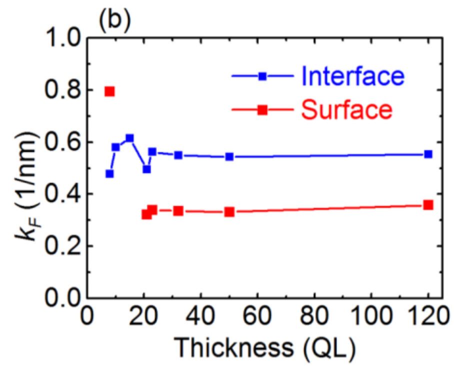
τ_{LLS} □ τ_{SLS}

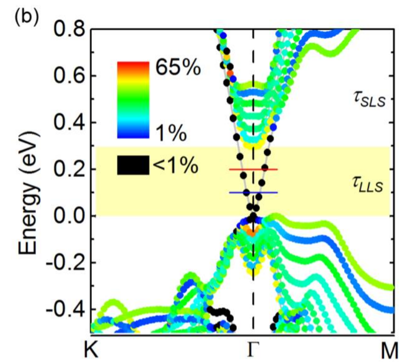
τ_{SLS} can be significant reduced without noticeable changing τ_{LLS} by introducing defect

Experimental Evidence of Large LLS Relaxation Time

Electrical conductance (exp.) + Fermi wave number (exp.) + Dispersion Relation (DFT)



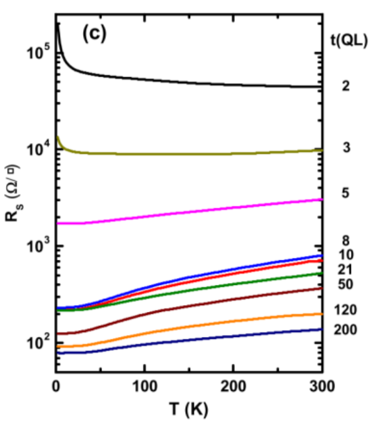




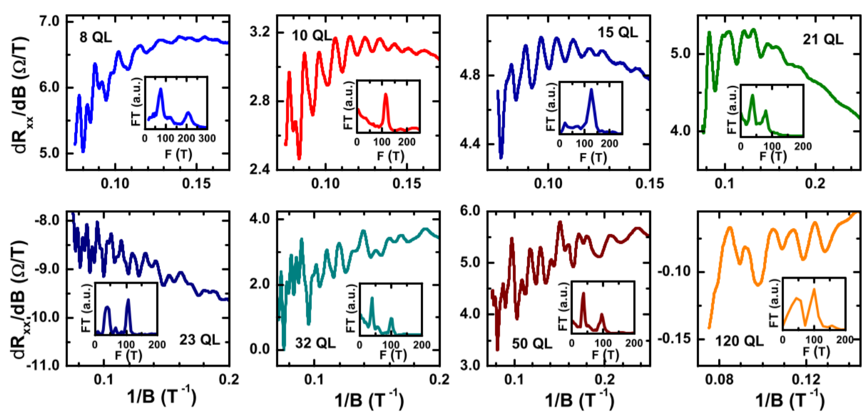
Cf.
BTE & Exp.

$\tau_{LLS} \approx 230$ fs

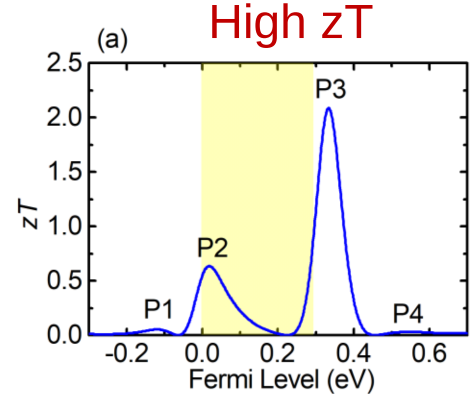
Sheet resistance



Spectra Shubnikov-de Haas Oscillation

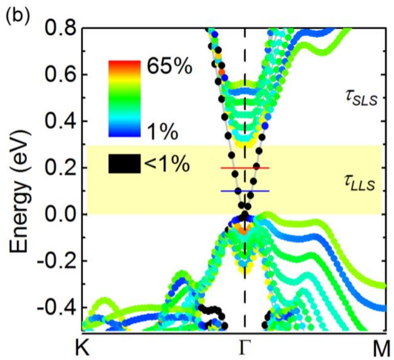


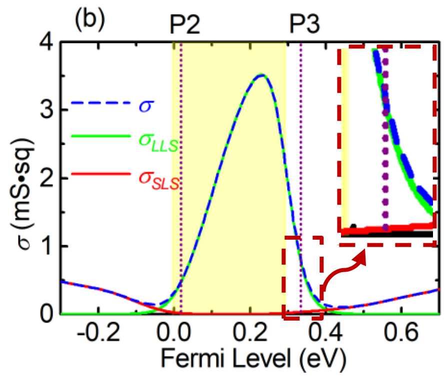
High zT



Taskin, A. A., Sasaki, S., Segawa, K. & Ando, Y. Manifestation of topological protection in transport properties of epitaxial Bi2Se3 thin films. Phys. Rev. Lett. 109, 066803 (2012).

Anomalous Seebeck Effect





TE transport in dual channels

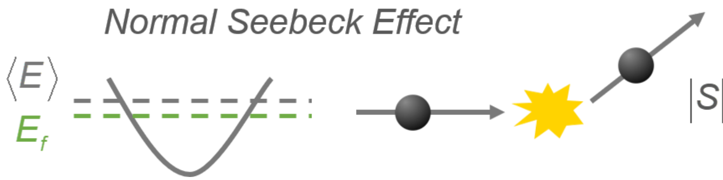
$$\sigma = \sigma_{LLS} + \sigma_{SLS}$$

$$S = \frac{\sigma_{LLS} S_{LLS} + \sigma_{SLS} S_{SLS}}{\sigma_{LLS} + \sigma_{SLS}}$$

$$S = \frac{E_F - \langle E \rangle}{eT}$$

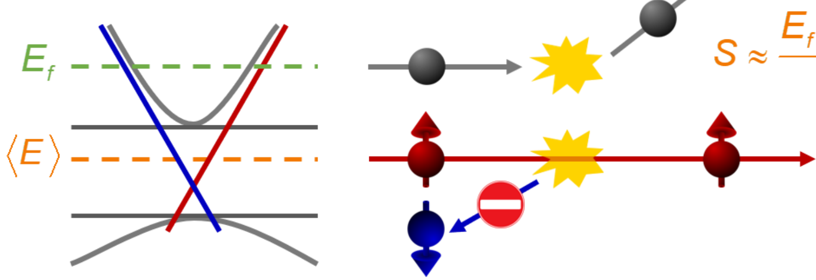
$$\langle E \rangle = \frac{\int E \sigma(E) dE}{\int \sigma(E) dE}$$

Normal Seebeck Effect

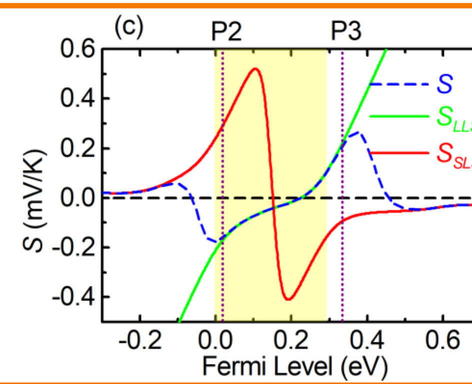


$$|S| \approx \left| \frac{E_f - \langle E \rangle}{eT} \right| \ll \frac{k_B}{e}$$

Anomalous Seebeck Effect



$$S \approx \frac{E_f - \langle E \rangle}{eT} \gtrsim \frac{k_B}{e}$$



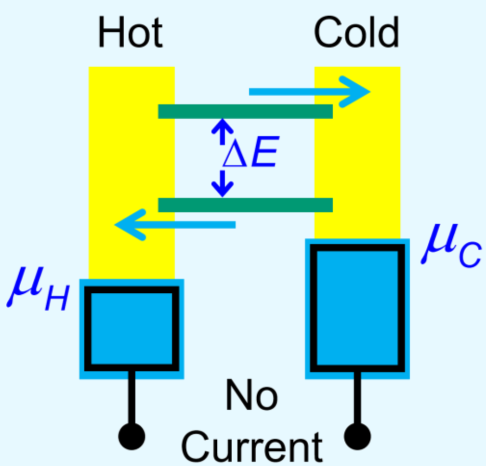
Insight of Wiedemann-Franz Law

Wiedemann-Franz Law

$$\frac{\sigma}{\kappa_e} = R_{WF} = \frac{3e^2}{\pi^2 k_B^2 T}$$

Indicating both charge and electronic heat currents are guided by the same scattering mechanisms

How electrons carry heat?



Datta, S. Lessons from Nanoelectronics: A New Perspective on Transport. (World Scientific Publishing Company, 2012).

Solution of BTE

$$\frac{\sigma}{\kappa_e} = \frac{\pi^2}{3\delta} \times R_{WF}$$

$$\delta = \left\langle \varepsilon^2 \right\rangle - \left\langle \varepsilon \right\rangle^2$$

$$\left\langle \varepsilon^n \right\rangle \equiv \int d\varepsilon \varepsilon^n \sigma_d(\varepsilon) / \int d\varepsilon \sigma_d(\varepsilon)$$

$$\sigma = \int d\varepsilon \sigma_d(\varepsilon), \quad \varepsilon = \frac{E}{k_B T}$$

$$\sigma_d(\varepsilon) = \left(-\frac{\partial f}{\partial \varepsilon}\right)\Sigma$$

Σ : Transport distribution function

δ is the reduced-energy variance of the differential conductivity;
It is the only factor determine the extent of Wiedemann-Franz law violation!

Violation of Wiedemann-Franz law

Solution of BTE

$$R_e = \frac{\sigma}{\kappa_e R_{WF}} = \frac{\pi^2}{3\delta}$$

$$R_{WF} = \frac{3e^2}{\pi^2 k_B^2 T}$$

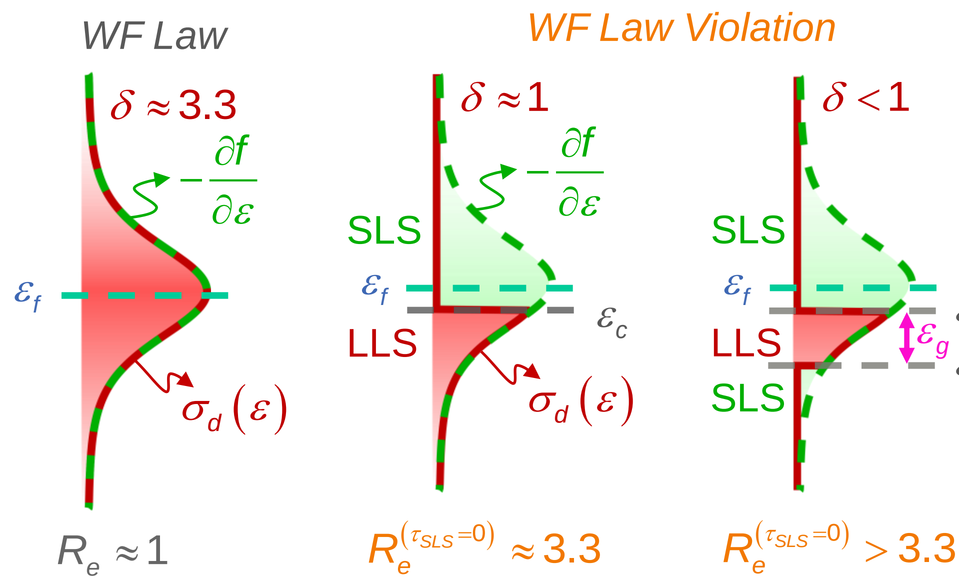
$$\varepsilon = \frac{E}{k_B T}$$

$$\delta = \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2$$

$$\langle \varepsilon^n \rangle \equiv \int d\varepsilon \varepsilon^n \sigma_d(\varepsilon) / \int d\varepsilon \sigma_d(\varepsilon)$$

$$\sigma_d(\varepsilon) = \left(-\frac{\partial f}{\partial \varepsilon} \right) \Sigma$$

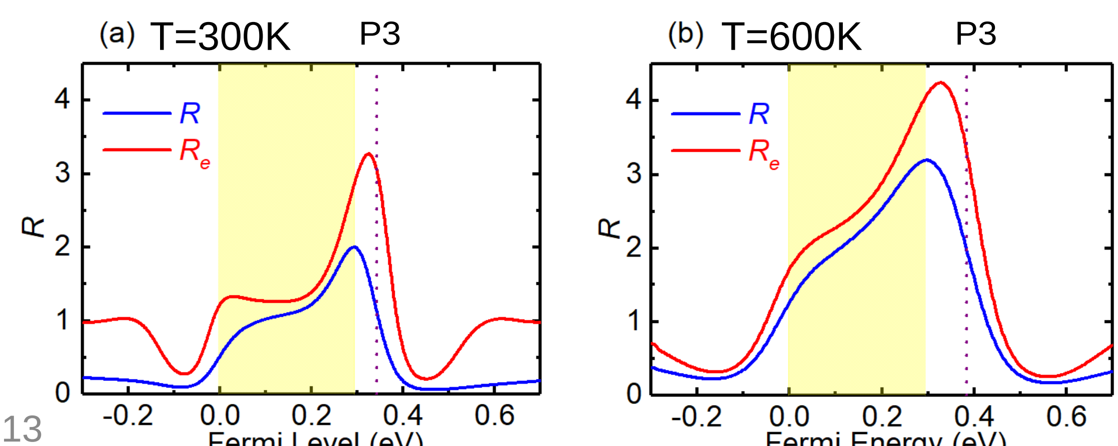
Σ : Transport distribution function



$$\varepsilon_g = \frac{E_g}{k_B T}$$

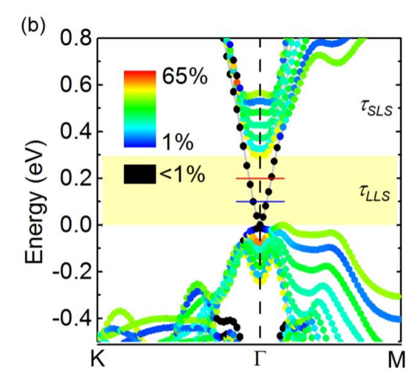
$$\varepsilon_f = \frac{E_f}{k_B T}$$

$$\varepsilon_{c,v} = \frac{E_{c,v}}{k_B T}$$

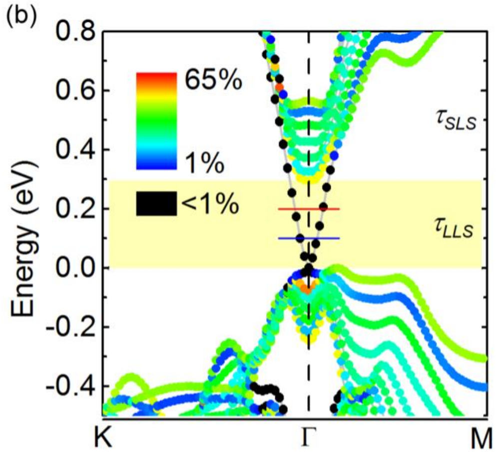


$$R = \frac{\sigma}{\kappa R_{WF}}$$

$$R_e = \frac{\sigma}{\kappa_e R_{WF}}$$



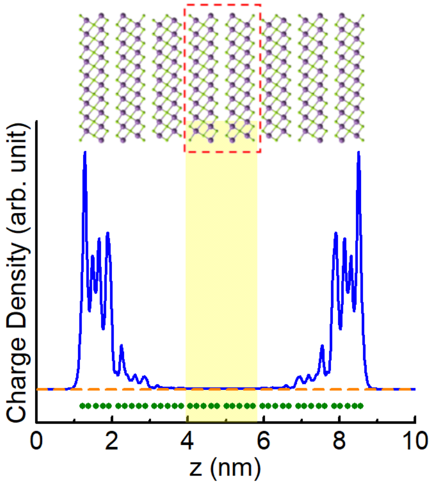
Enahance zT by Introducing Defects

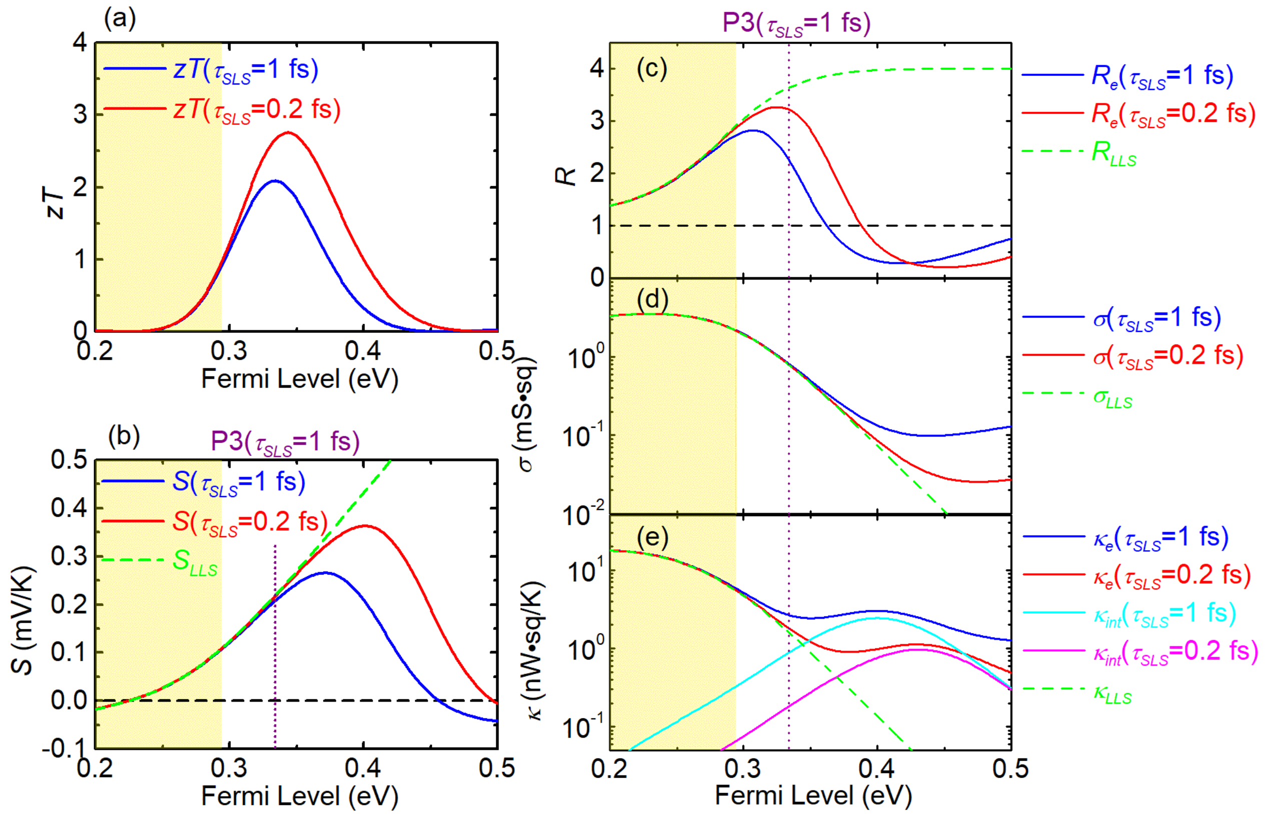


By introducing defect into the bulk like middle layers, we can significantly reduce the SLS relaxation time τ_{SLS} without noticeably deteriorating the LLS relaxation time τ_{LLS}.
This causes a further enhancement of the TE performance.

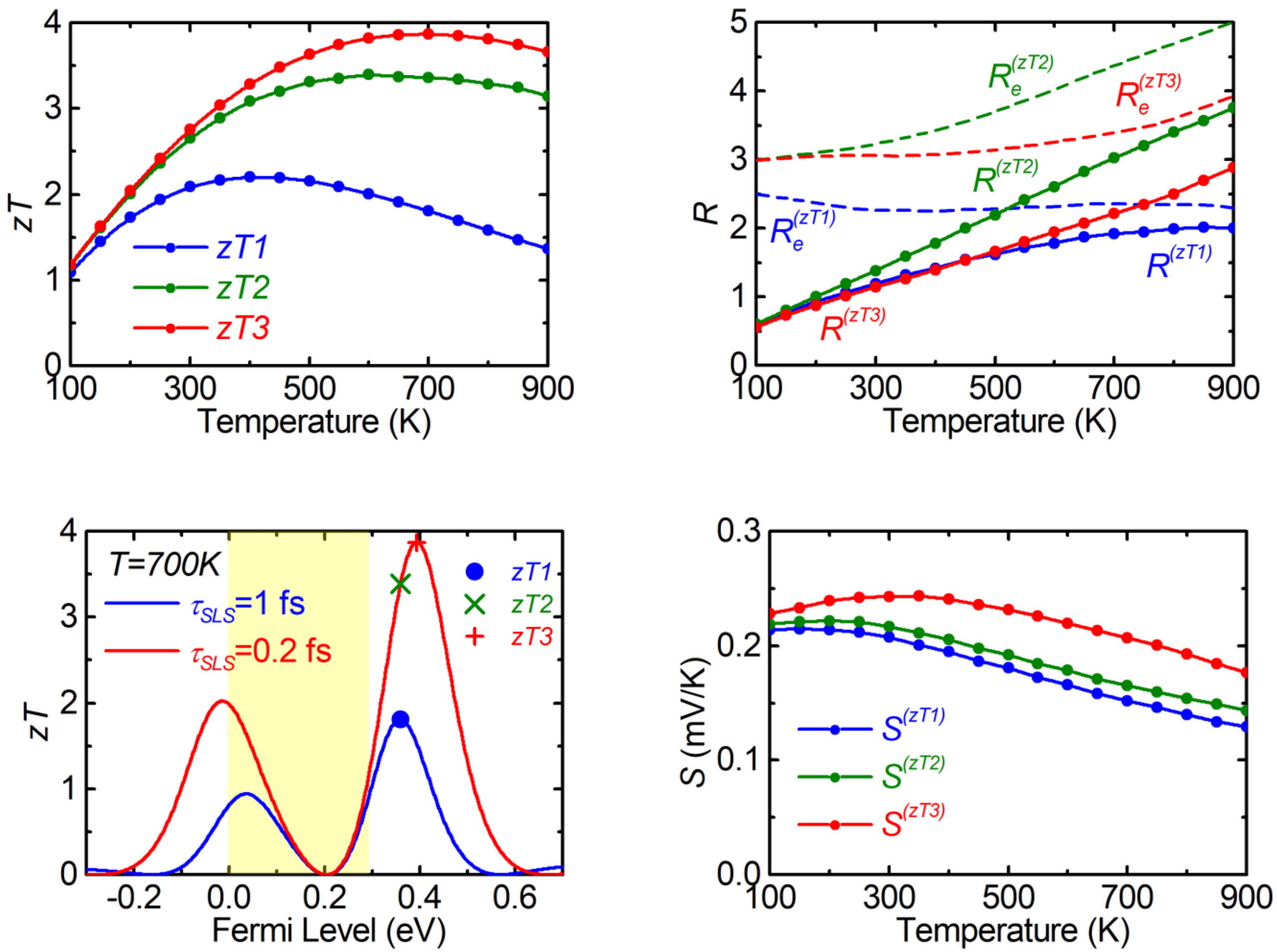
$$\sigma = \sigma_{LLS} + \sigma_{SLS}$$

$$\kappa_e = \kappa_{LLS} + \kappa_{SLS} + \kappa_{int}$$





Temperature-dependence of TE performance



Conclusions