Challenges and Recent Advances in Thermoelectricity

S. D. Mahanti

Michigan State University, USA

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Students

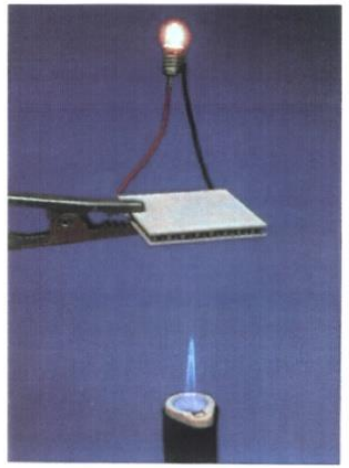
Dat Thanh Do. Hoang Khang, Salameh Ahmad
Daniel Bilc, Paul Larson

Postdocs, Faculty, Institutions

Mal-Soon Lee, Kanchana, David Singh, M. Kanatzidis,
IIT (Mumbai, India), NPL (Delhi, India)

Outline

- Thermoelectricity – a brief history
- Important ideas and developments
- Pre 1970
  Post 1970
- Recent advances and Major challenge



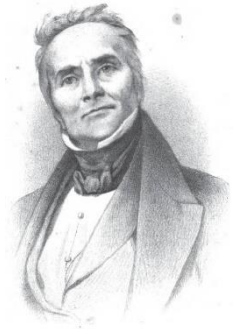
Electrical
Power Generation

Three Thermoelectric effects – the classical period



- In 1821-3 Thomas Johann Seebeck (German)

  The temperature difference produces an electric potential (voltage) - drives an electric current in a closed circuit- **Seebeck Effect**



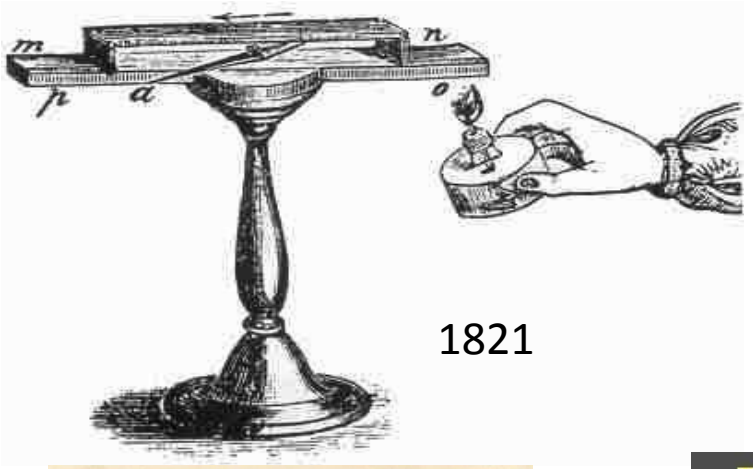
- In 1834, a watchmaker and part time physicist, Jean Charles Athanase Peltier (French)

  An electrical current would produce heating or cooling at the junction of two dissimilar metals – **Peltier Effect**

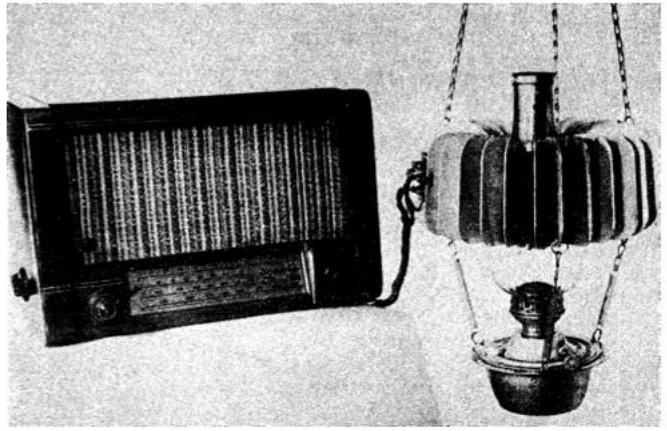


- In 1851, William Thomson (English man, later Lord Kelvin) explained the above two observations correctly and predicted a third thermoelectric effect, known as the **Thomson effect**, where heat is absorbed or produced when current flows in a material with a temperature gradient.

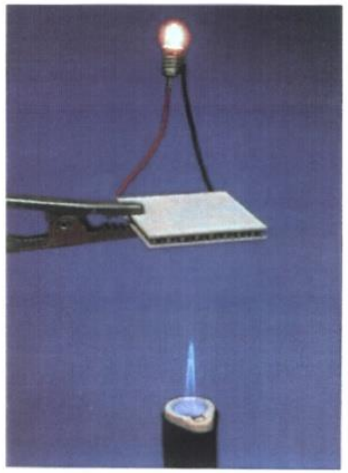
Why am I talking about such an old subject now?



1821

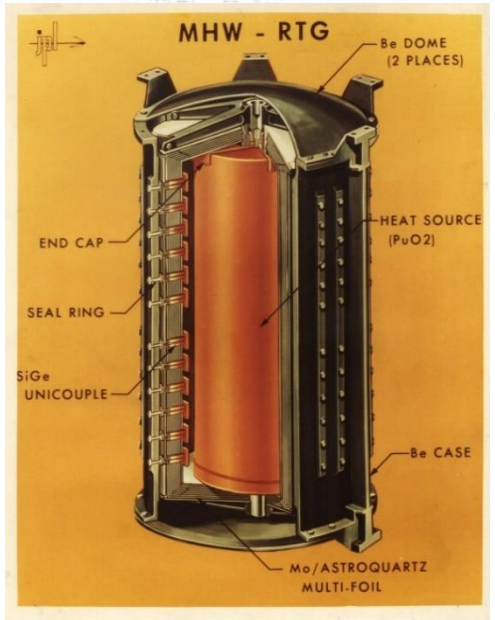


1940s

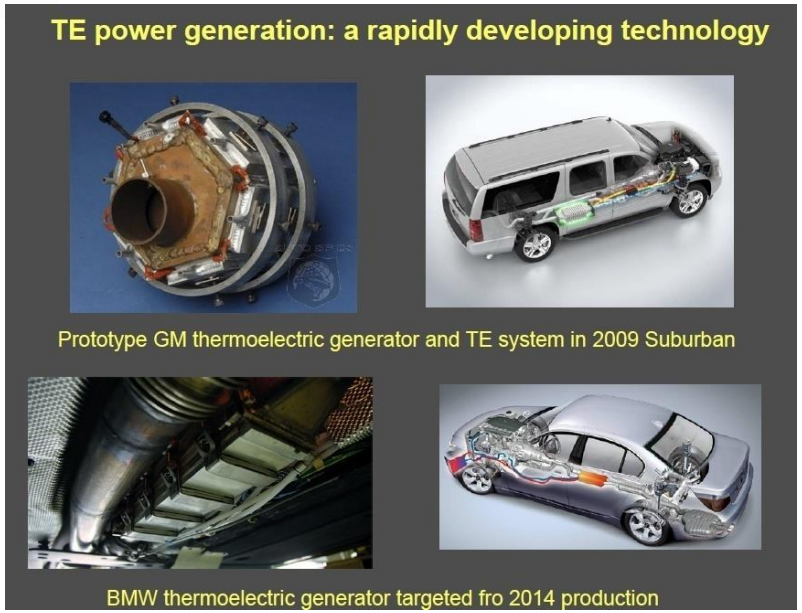


1950s

Electrical
Power Generation



1960s



2014

Almost 200 years!

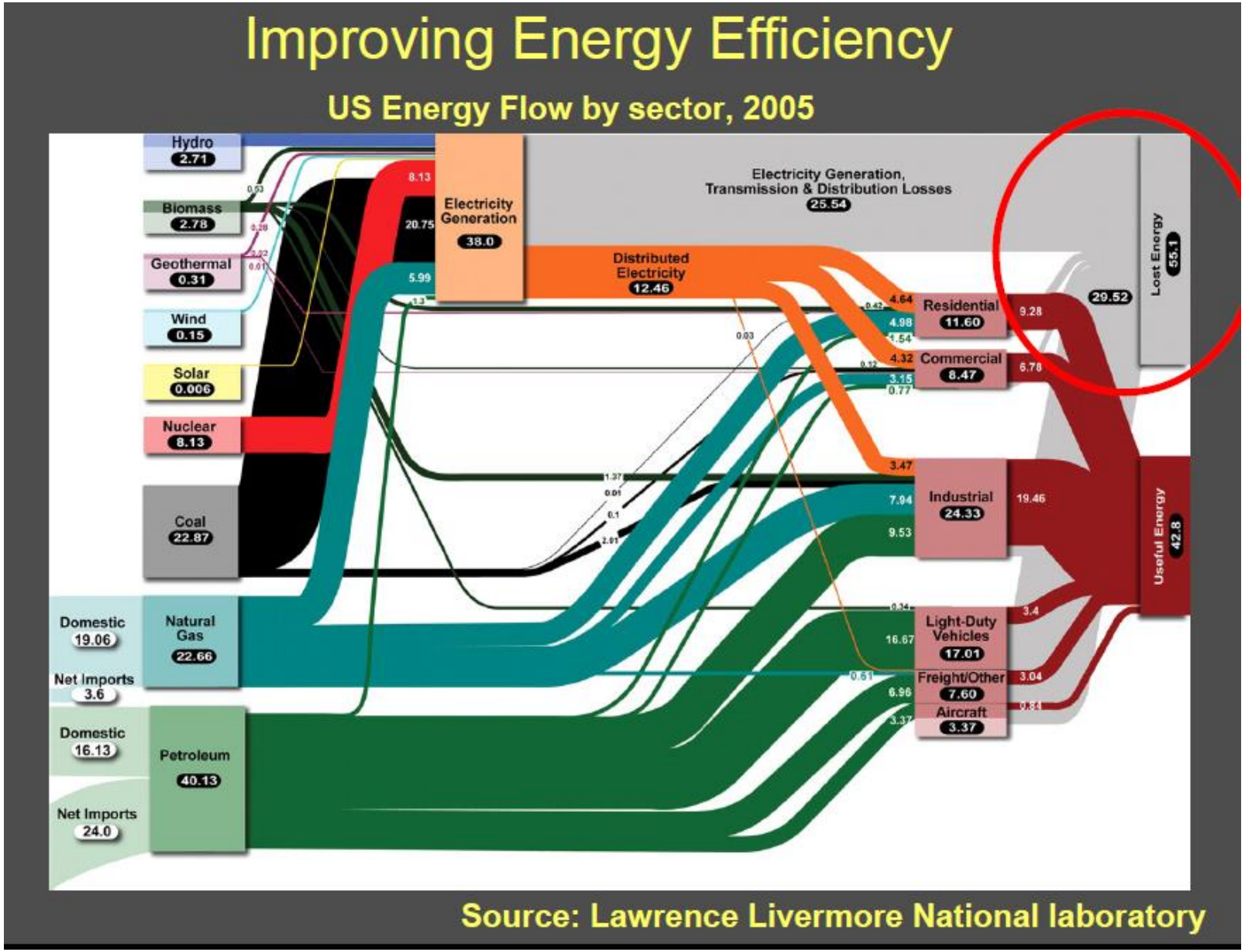
Experimental breakthroughs due to novel materials

Theoretical understanding and Prediction – Material genome

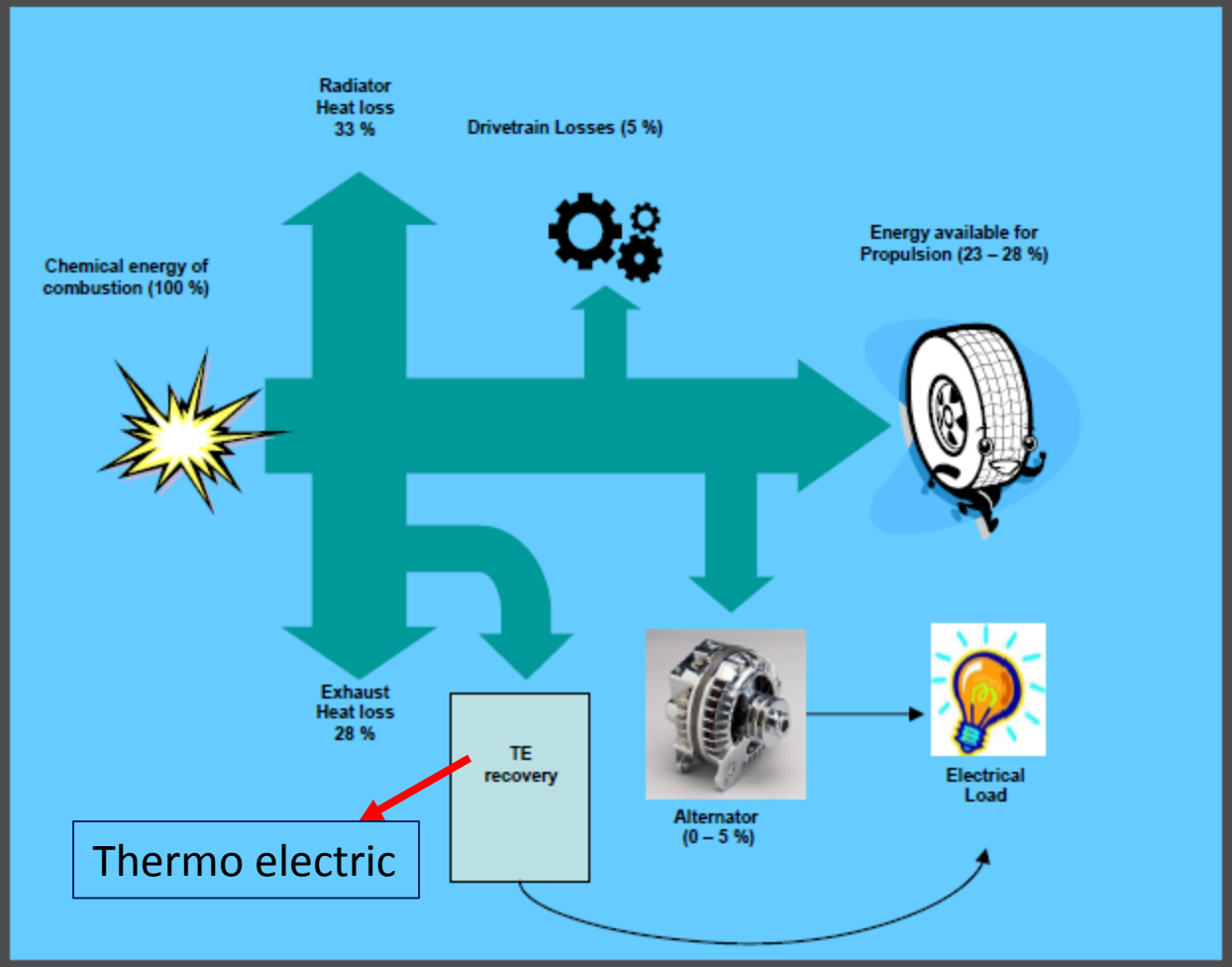
Energy Problem

Recovering electrical energy from waste heat

Active micro-cooling



A simple example: exhaust gas heat recovery



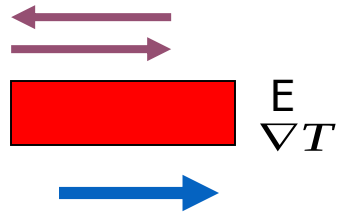
Waste heat recovery could increase fuel efficiency by > 5%!
(0.1 % increase = 100M gallons gasoline/yr)

Review some basic physics

- Electrical and Thermal Currents

$$J = \sigma[E - S\nabla T]$$

$$Q = [\sigma TS]E - \kappa\nabla T$$



J, Q Current and Heat Current density E: Electric Field :Temp gradient ∇T

σ: Electrical Conductivity κ: Thermal Conductivity S: Thermopower

Solid state system
Generates electric power from thermal gradient
OR
Does active cooling through electric current

- Cooling and Power generation
- Figure of Merit - Dimensionless $ZT = \sigma S^2 T / \kappa$
- Power Factor (PF) σS^2

Semiconductors with small band gap are the best TE
Need n-type and p-type

Narrowband gap semiconductors – good TE?

Ioffe, Goldsmid - Pre 1970



- Metals have large σ but small *S*
- Insulators have small σ but very large *S*
- Semiconductors are a good compromise
- Can be doped n and p type – tuning and optimizing

- Why narrow band gap SC?
- Maximum S is at a temperature T_{max}

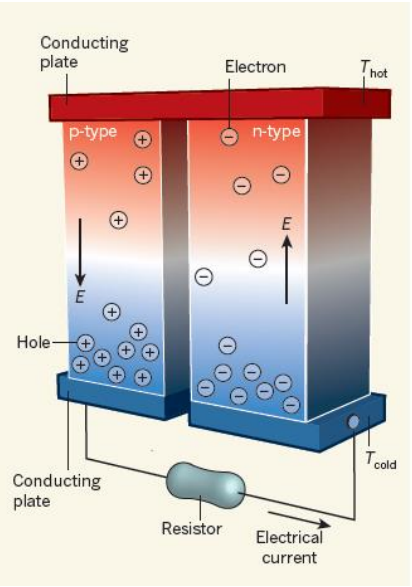
$k_B T_{max} \sim E_g / 10$

$T_{max} = 300K$

$E_g \sim 0.25$ eV

Bi_2Te_3





$$ZT = \sigma S^2 T / \kappa$$

ZT & Efficiency of TE Devices

η: Efficiency for power generation

$$ZT = \sigma S^2 T / \kappa$$

$$\eta = \frac{T_h - T_c}{T_h} \frac{\gamma - 1}{\gamma + T_c / T_h}$$

$$\gamma = (1 + ZT)^{1/2}$$

T_c : cold side temp
T_h: hot side temp

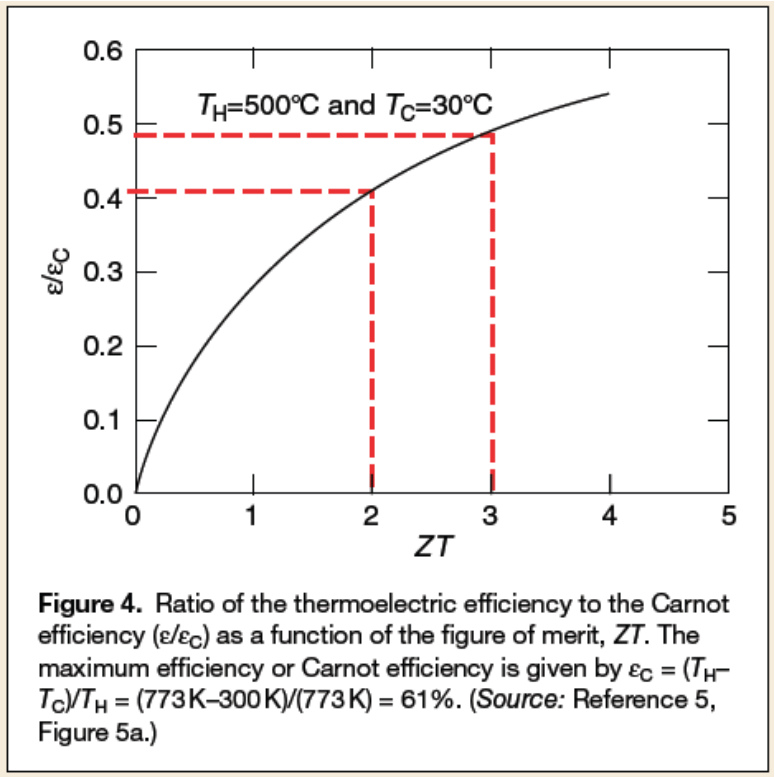
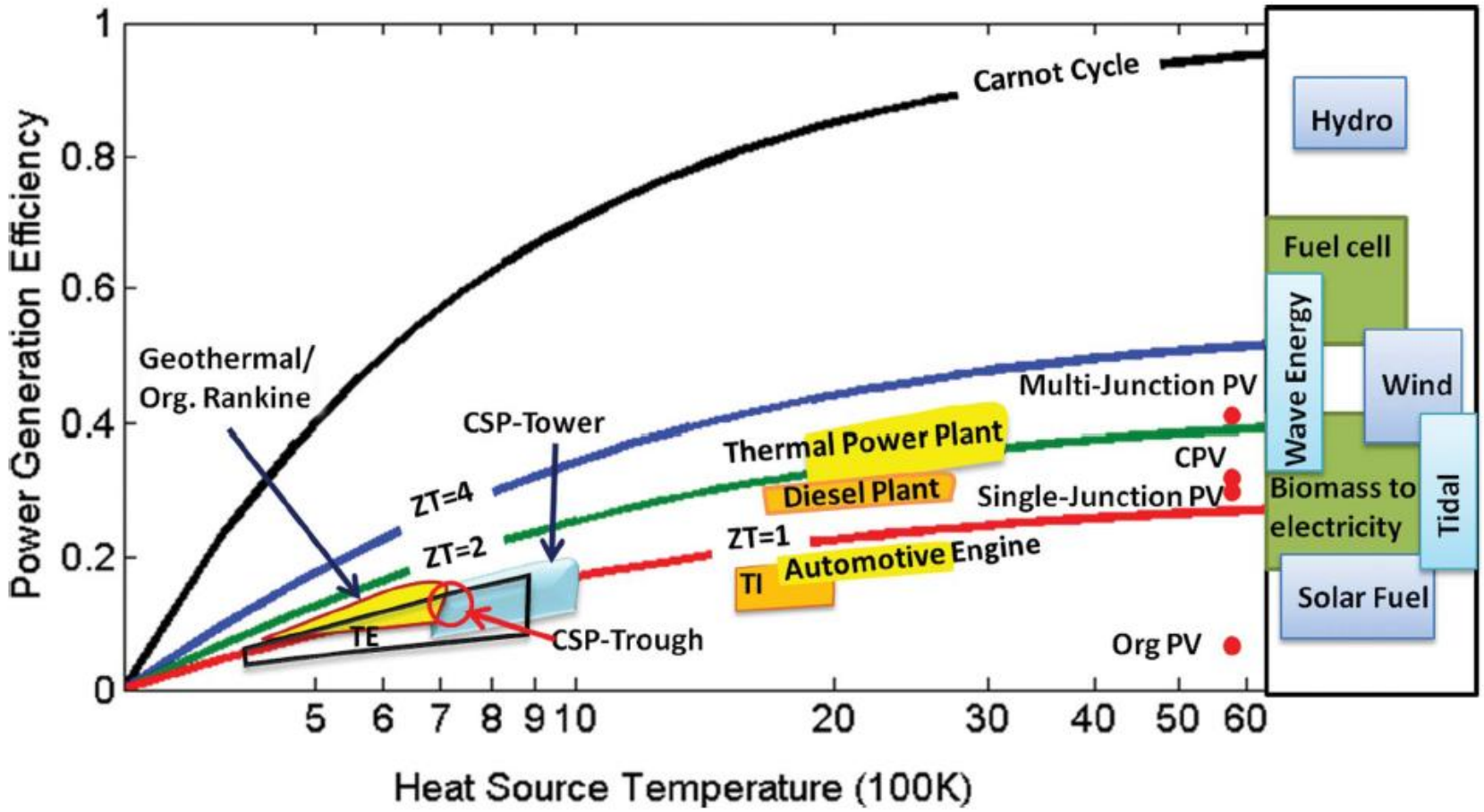


Figure 4. Ratio of the thermoelectric efficiency to the Carnot efficiency ($\varepsilon/\varepsilon_C$) as a function of the figure of merit, *ZT*. The maximum efficiency or Carnot efficiency is given by $\varepsilon_C = (T_H - T_C)/T_H = (773\,K - 300\,K)/(773\,K) = 61\%$. (*Source:* Reference 5, Figure 5a.)

INCREASE
ZT
When $\rightarrow \infty$
$\eta \rightarrow \eta_{Carnot}$

From: Zebarjadi et al. Energy and Environmental Science 5, 5147, 2012



Power generation efficiency vs temperature of the hot side. The cold side is at room temperature. PV: photo voltaic; CSP: concentrated solar power;
TE: thermo electric; TI: thermoionic

Strategies to increase & make $ZT > 1$

$$ZT = \sigma S^2 T / \kappa$$

For many years best ZT values were ≤ 1

Bi_2Te_3	T~300K
PbTe	T~600K
Si-Ge	T~1200K

Increase σ and S and Decrease κ

Easy said than done!

Conflicting (Contra-indicating) properties

- Increasing σ
- Decreases S (Pizarenko relation)
- Increases $\kappa = \kappa_{latt} + \kappa_{el}$

Three Important Ideas (Post 1970)

Reduce lattice thermal conductivity κ without affecting electron transport

Electron Crystal Phonon Glass (ECPG)

(Glenn Slack-1995)

Increase Power Factor σS^2 without increasing κ

Manipulate electronic density of states

Quantum Confinement in Nano-structures

(Hicks and Dresselhaus -1993)

Transport in a very narrow range of energy

(Ideal TE- Mahan Sofo – 1996)



Mildred Dresselhaus
MIT

Anisotropic system – Dimensional confinement

Assume a simple parabolic band model

Effective masses: $m_{xx}>m_{yy}>m_{zz}$

Transport direction is along the z-axis

$m_{xx}\sim m_{yy}\sim m_{zz}$ 3-dimensional

$m_{xx}>>m_{yy}\sim m_{zz}$ Quasi 2-dimensional

$m_{xx}\sim m_{yy}>>m_{zz}$ Quasi 1-dimensional

Hicks and Dresselhaus introduced B parameter

$$\boldsymbol{B = C(T)\left(m_{xx}m_{yy}m_{zz}\right)^{1/2}N\mu_{zz}/\kappa_{latt}}$$

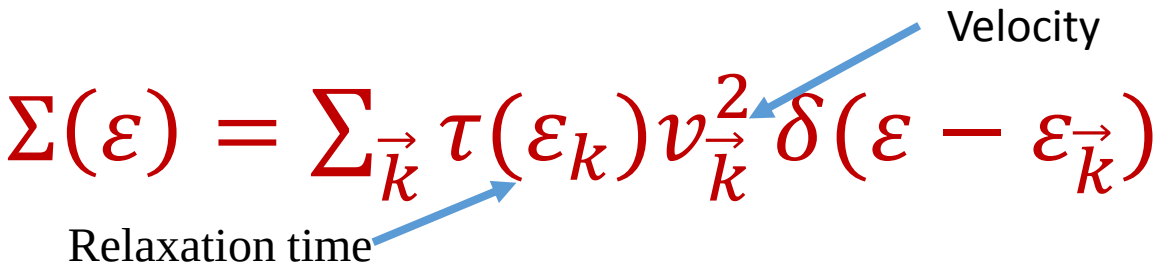
Transport mobility $\mu_{zz}= e\tau/m_{zz}$

- Decrease m_{zz}
  Increase m_{xx}, m_{yy}
  Quantum confinement-
  Diemsion reduction
- Increase band degeneracy N
- Manipulating Density of States
- Reduce κ_{latt} - phonon glass

ZT increases with B

Mahan and Sofo came up with a different idea

ZT is determined by a transport function



It is maximized when $\Sigma(\varepsilon)$ is nearly a delta function in energy
Transport takes place in a very narrow band – a
very different picture from the previous one – Ideal TE (ZT~∞)

Many follow up work question the validity of this idea

Resonant state near the Fermi energy still a viable picture

State of the art ZT values

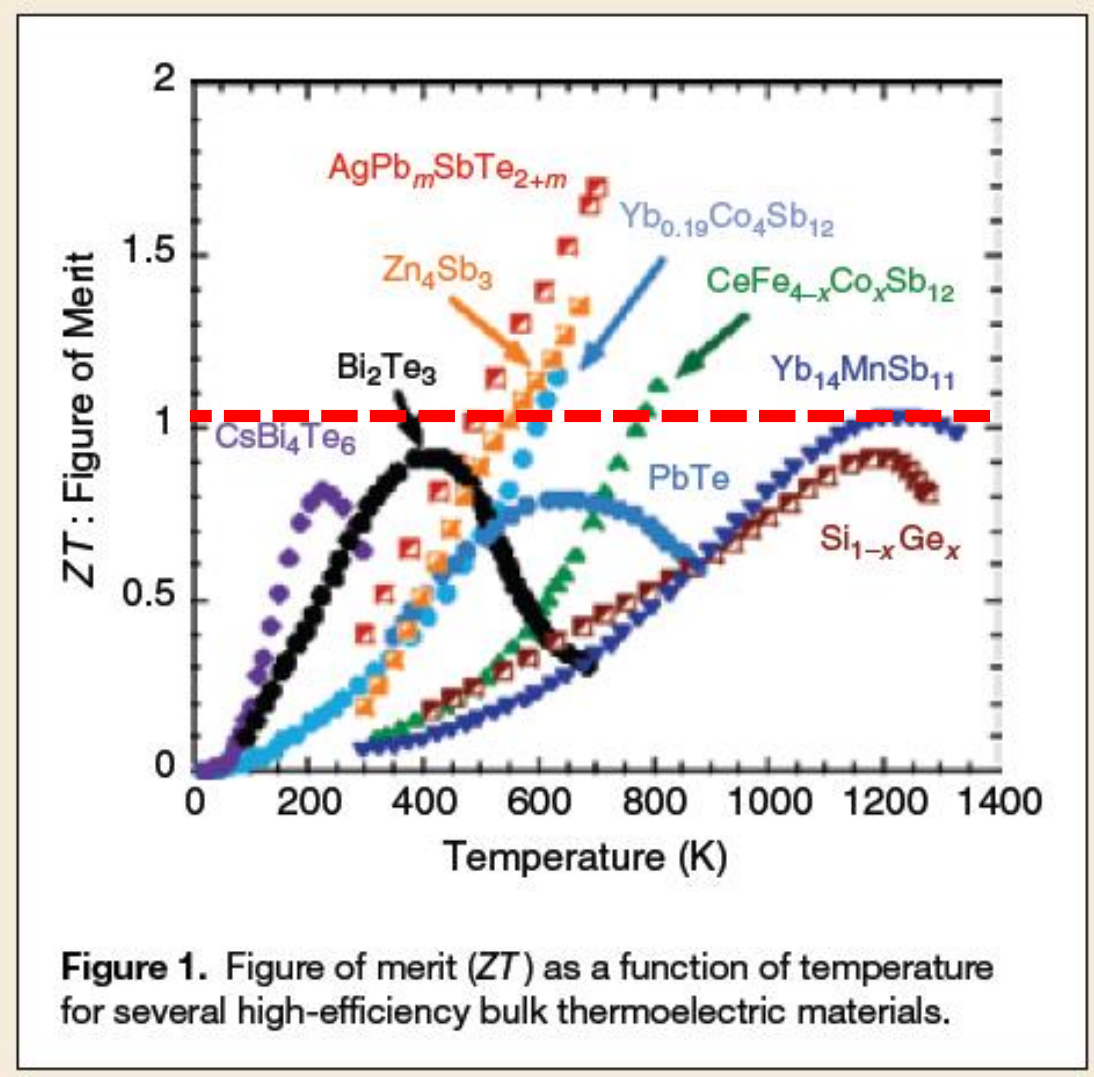


Figure 1. Figure of merit (*ZT*) as a function of temperature for several high-efficiency bulk thermoelectric materials.

Crossing the ZT=1 Barrier

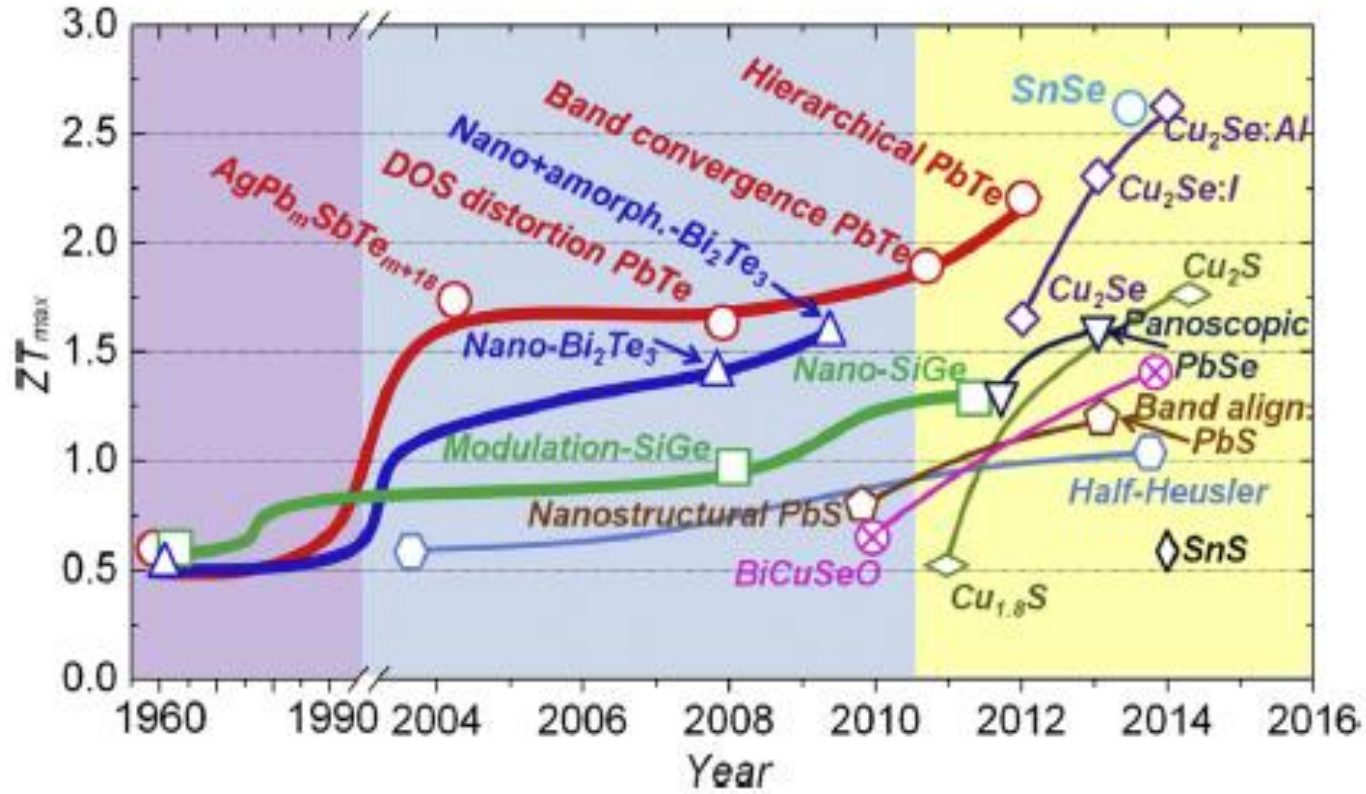


Fig. 2. ZT of the current bulk thermoelectric materials as a function of year: the left part indicates the three conventional thermoelectric systems with $ZT < 1.0$ before 1990s, Bi_2Te_3, PbTe and SiGe; the middle part elucidates that the ZTs were enhanced to about 1.7 by nanostructures ($AgPb_mSbTe_{m+2}$ [14], nano-Bi_2Te_3 [20], nano+amorphous-Bi_2Te_3 [21], nano-SiGe [22], nanostructural PbS [23]) and electronic structure engineering (Tl doped PbTe [24], $PbTe_{1-x}Se_x$ [15]), modulation doping (SiGe) [25,26]; the right part shows the high performance realized in hierarchical PbTe and promising thermoelectric materials developed recently and characterized by low-cost, earth-abundant, and low thermal conductivity, including panoscopic PbSe [27,28], band alignment PbS [29,30], BiCuSeO [31], Cu_2S systems [32,33], SnS [34,35], Cu_2Se systems [17,19,36,37], Half-Heusler [38,39], and SnSe [18]. Some materials show the ZTs > 2.0.

Discuss a few systems for illustrating these ideas

Phonon glass – Nano-structures and hierarchy

Resonant States

Dimension control

How do we lower thermal conductivity without lowering electrical conductivity?

LAST-m ($AgPb_mSbTe_{2+m}$)

K.F. Hsu et al, Science 303, 818 (2004)

m=∞, PbTe
m=0, $AgSbTe_2$

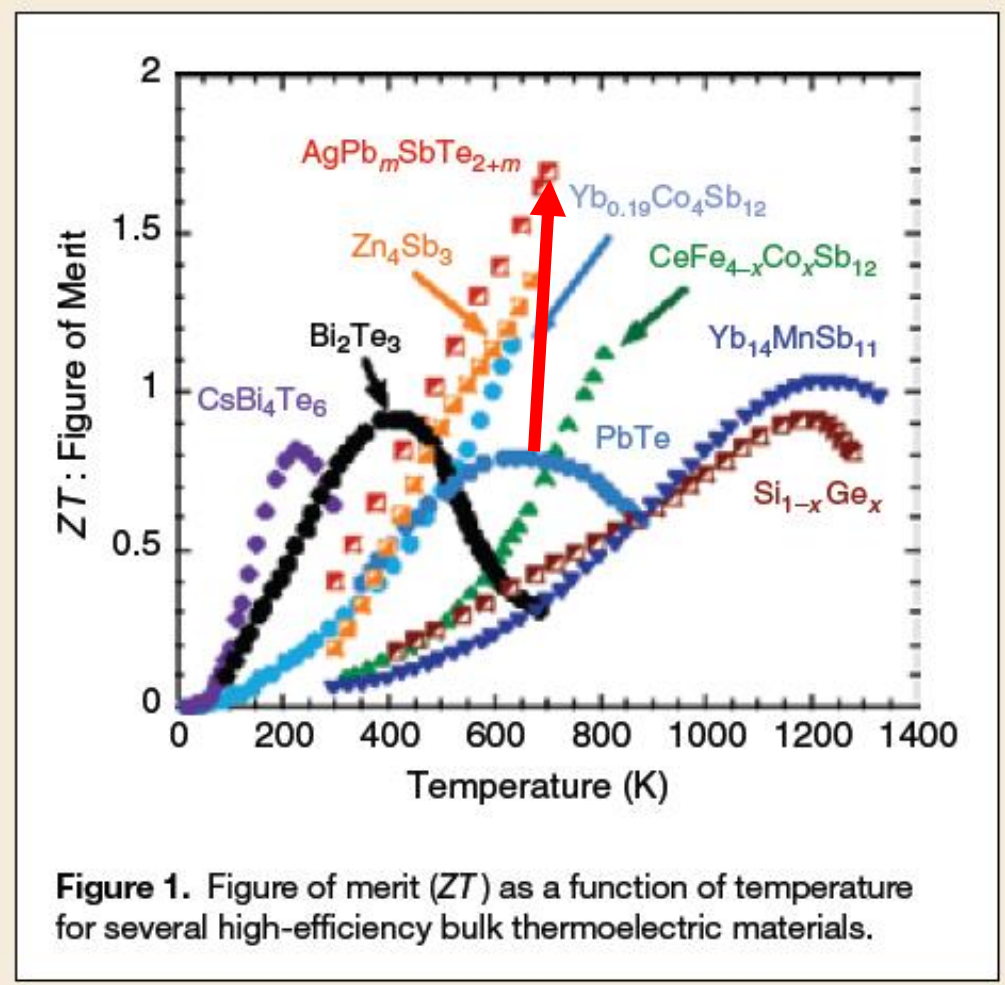
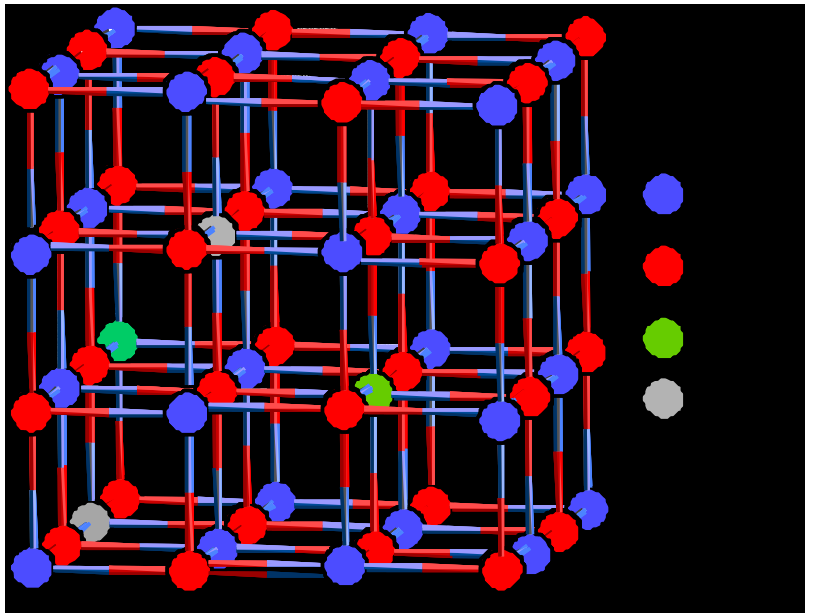


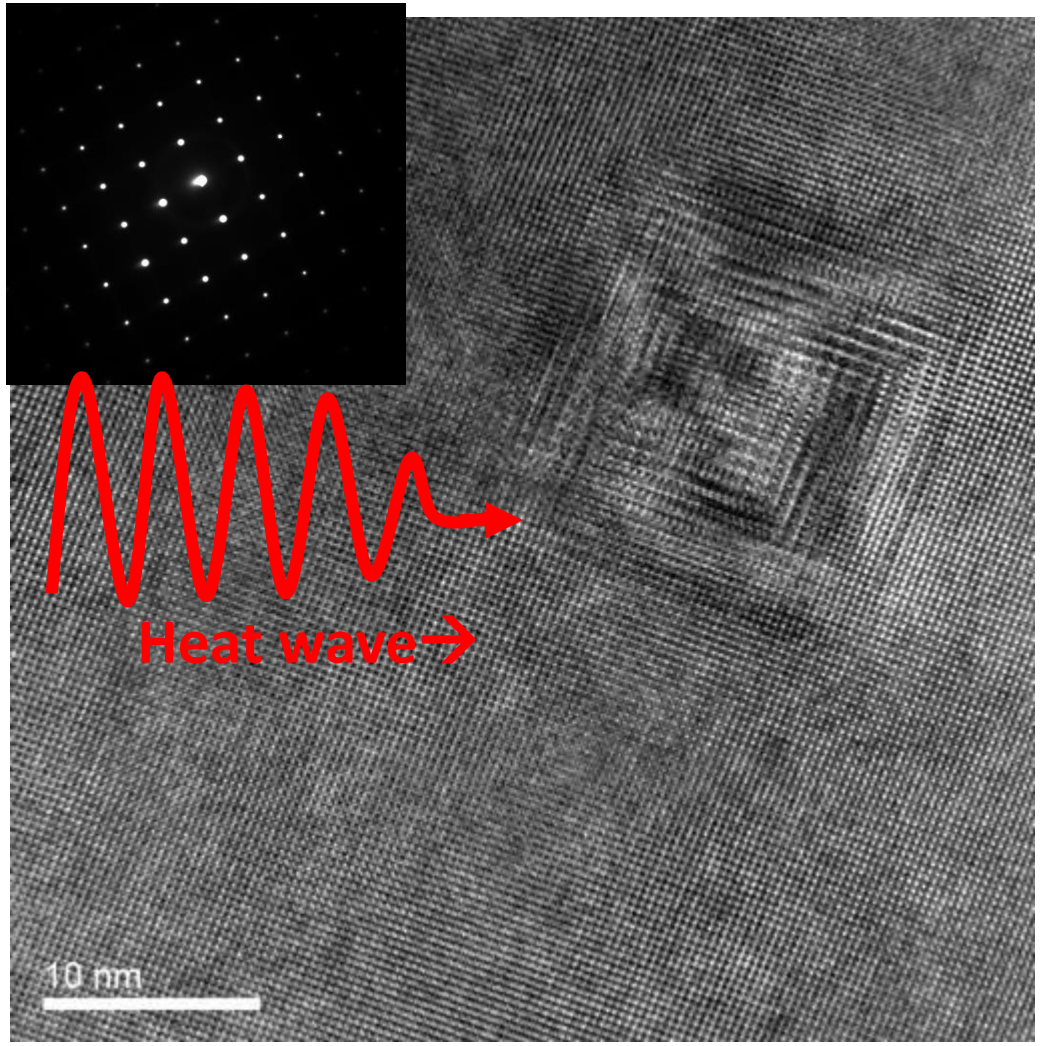
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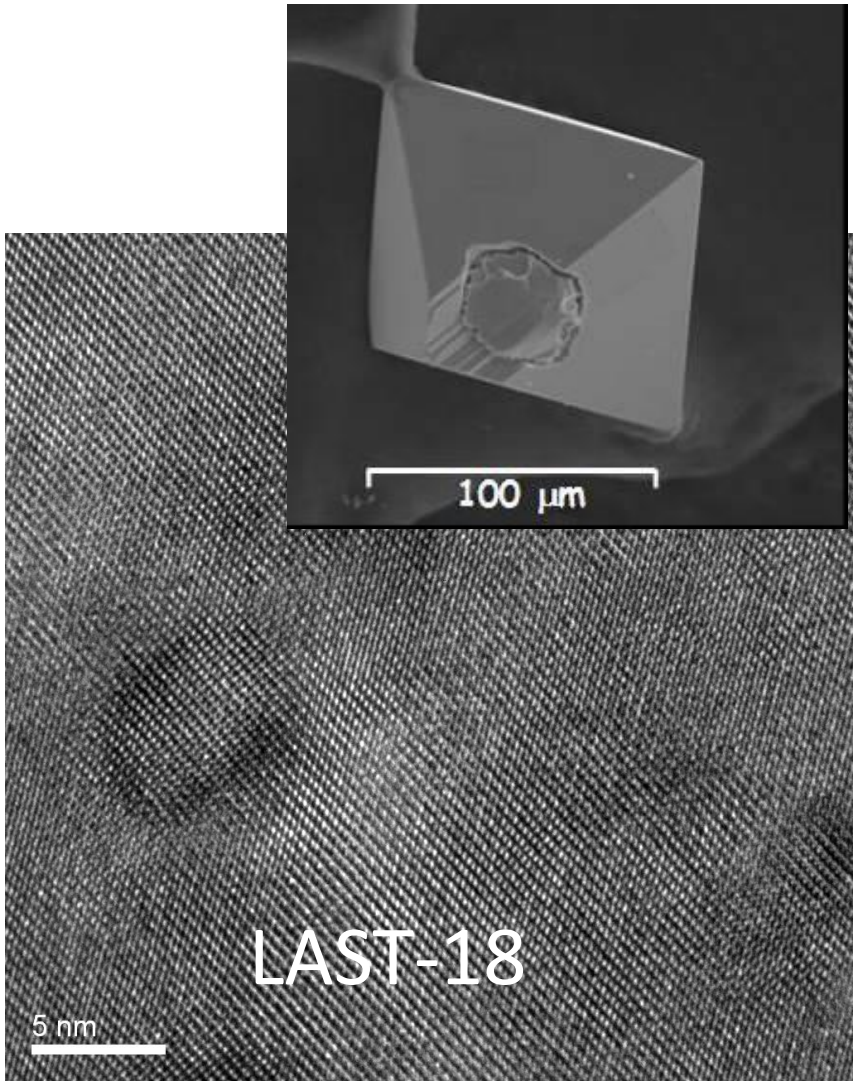


Blue: Pb; Red:Te; Green: Sb; Grey: Ag

What is the physics of large *ZT* ?
Resonant state or phonon glass

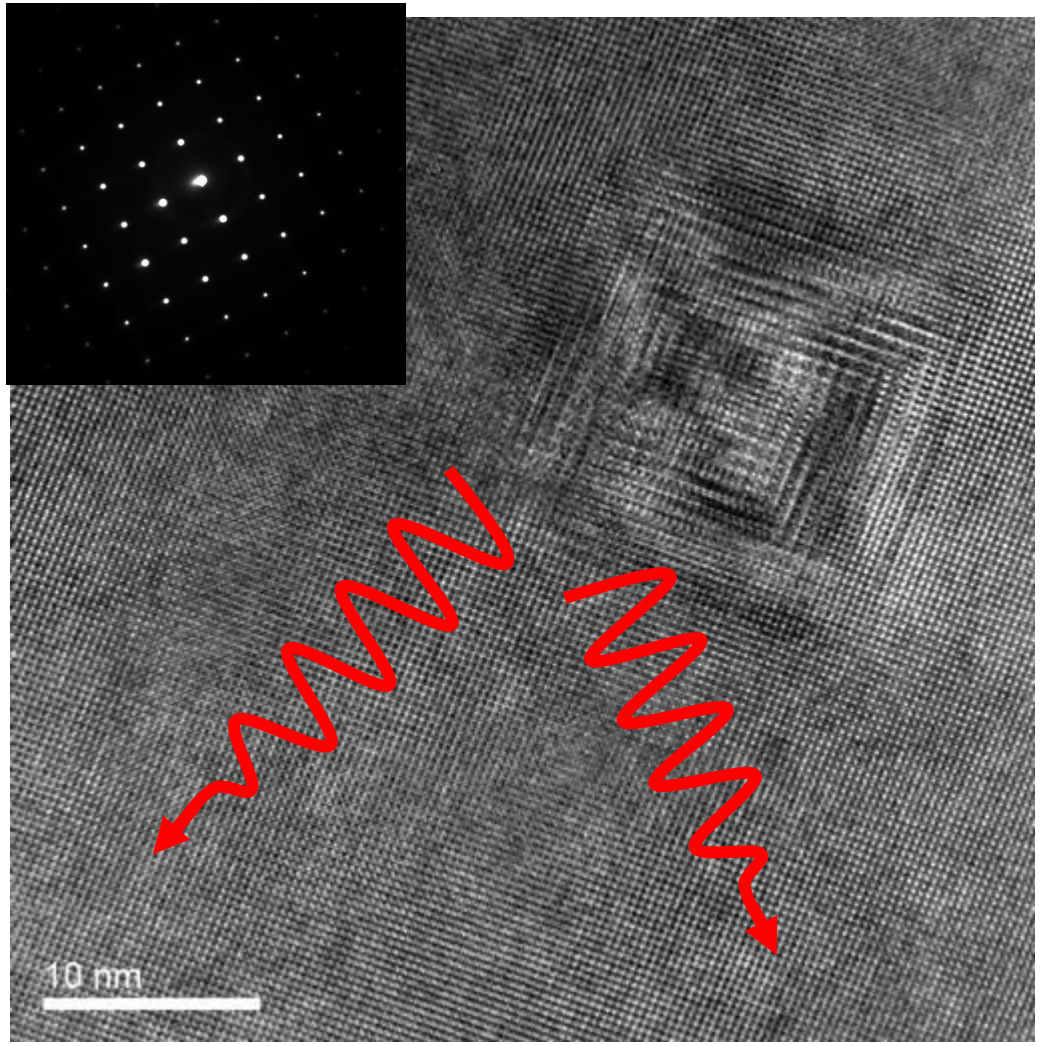
Endotaxy: Coherently embedded nanocrystals

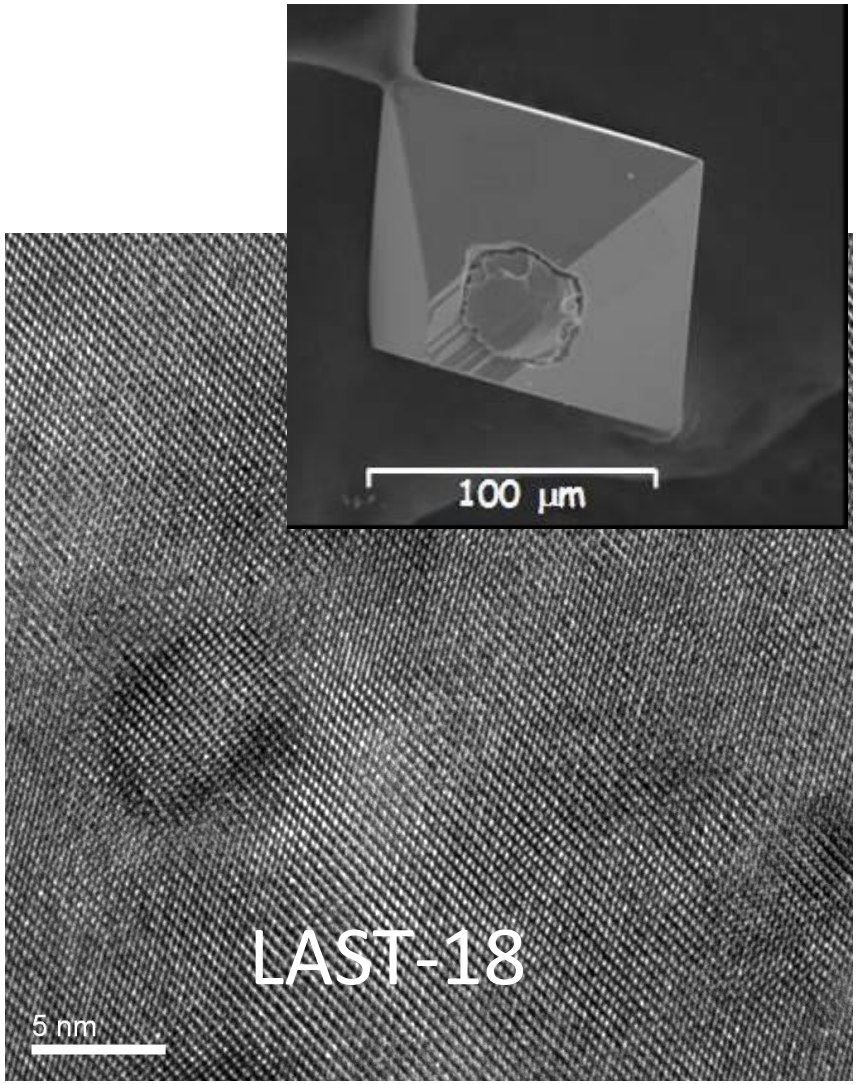




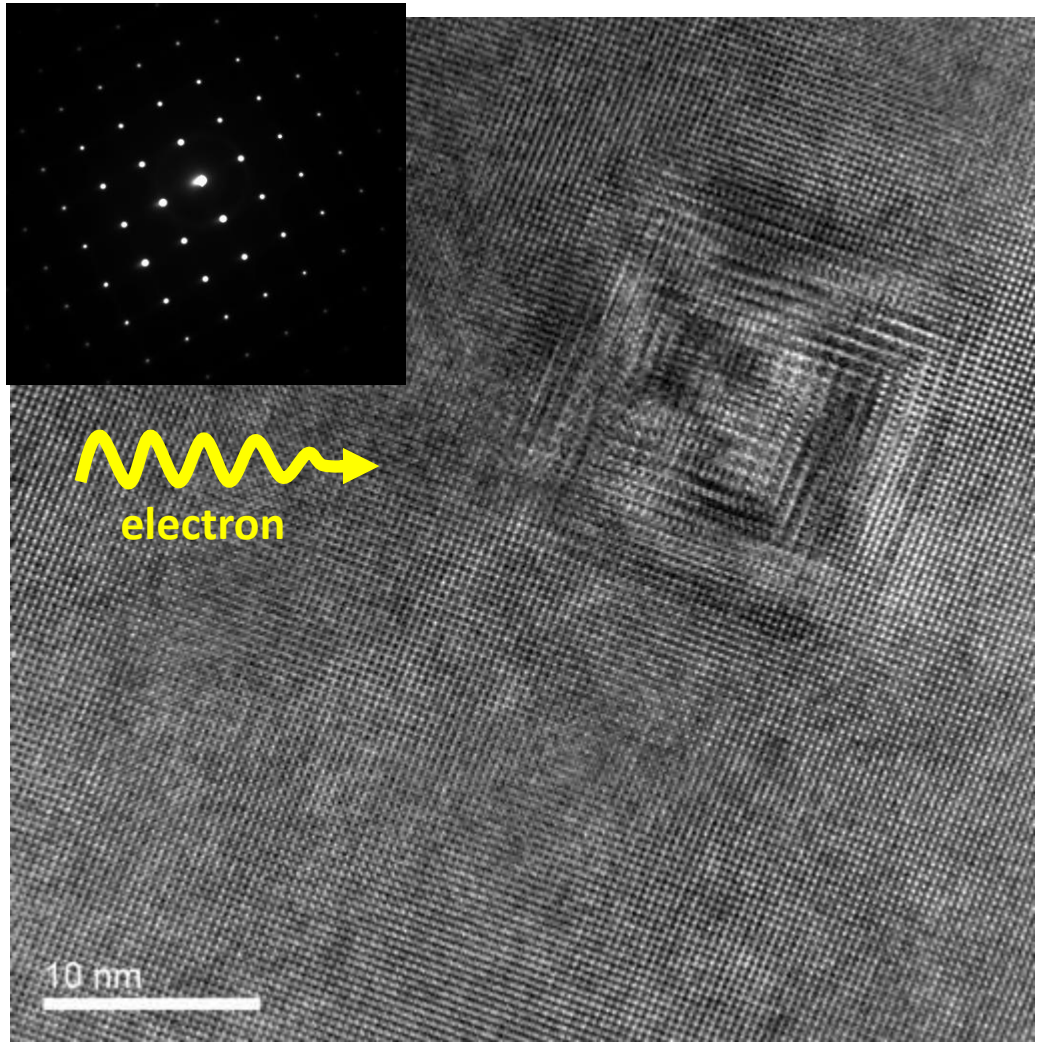
Kanatzidis group, MSU and Northwestern

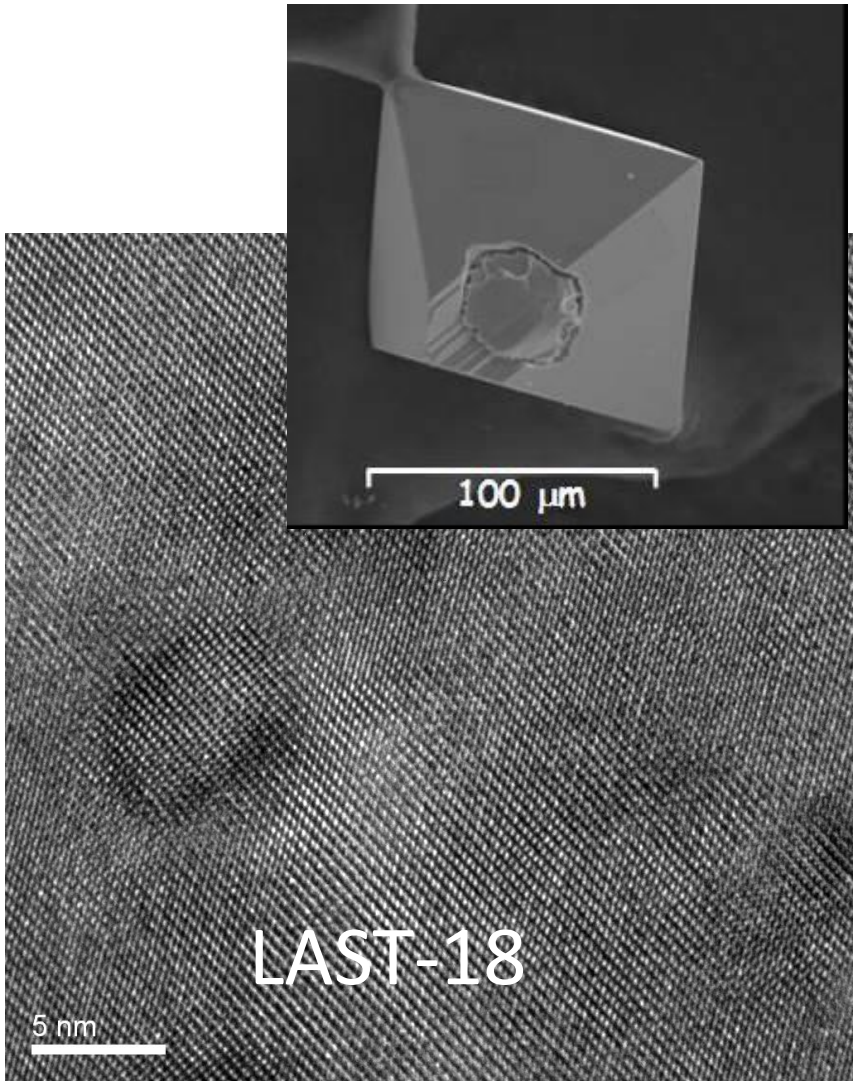
LAST-18 κ_{latt}=1.2 W/m-K at 300 K
PbTe κ_{latt}=2.2 W/m-K at 300 K



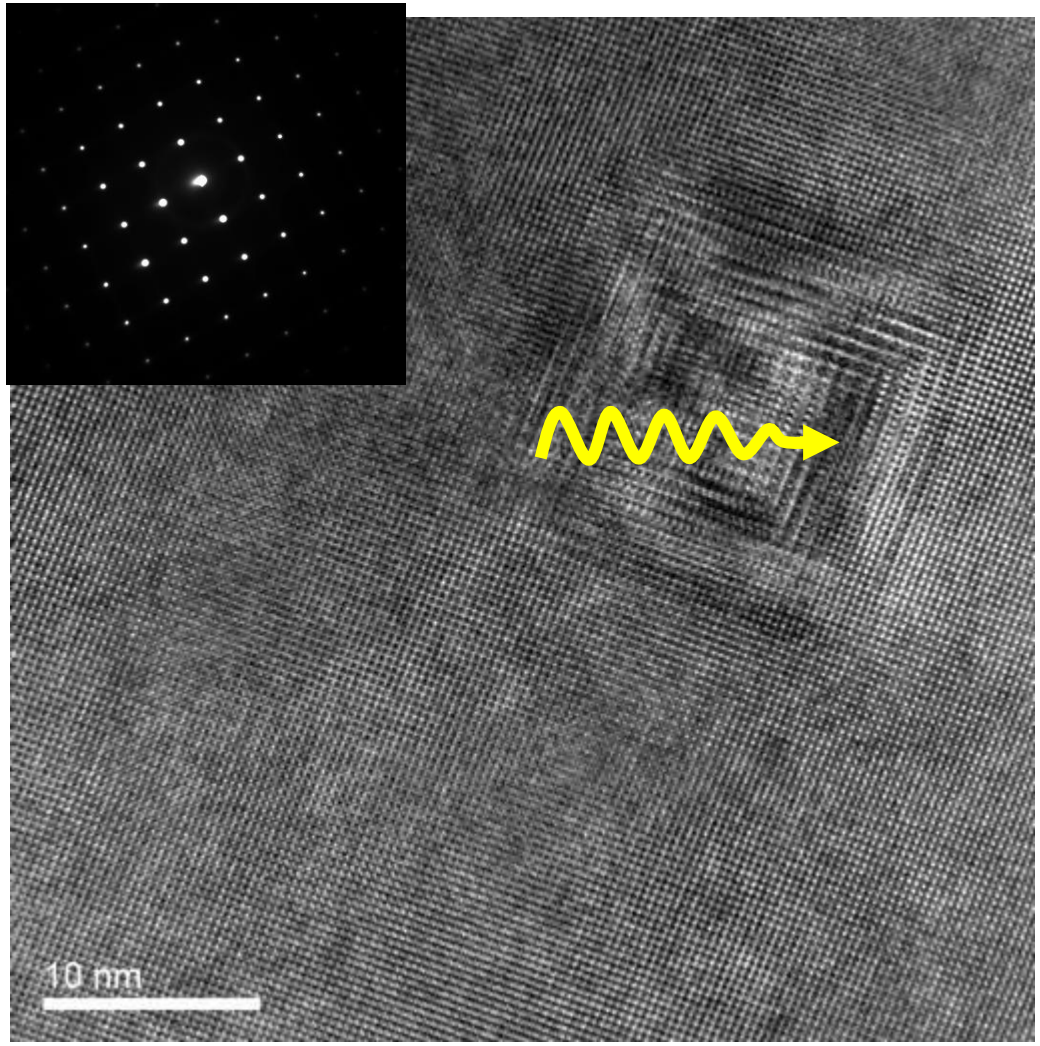


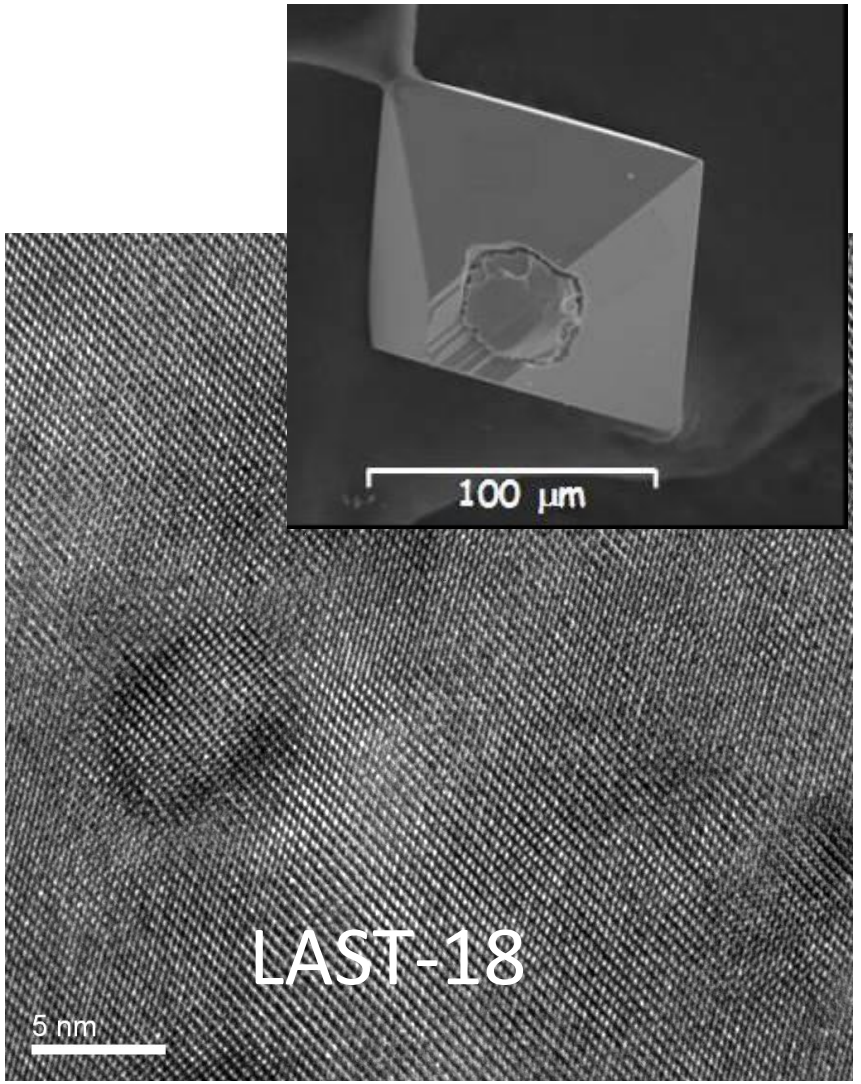
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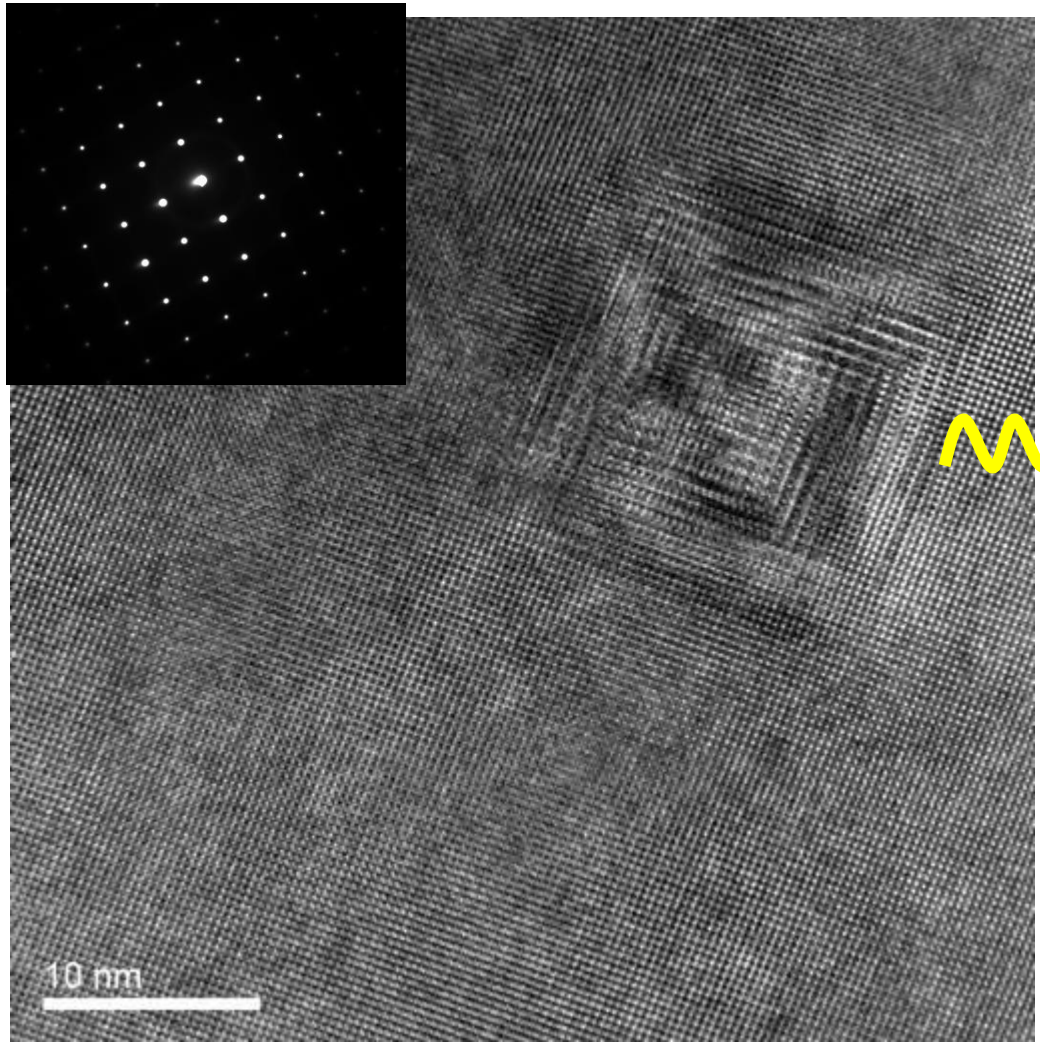
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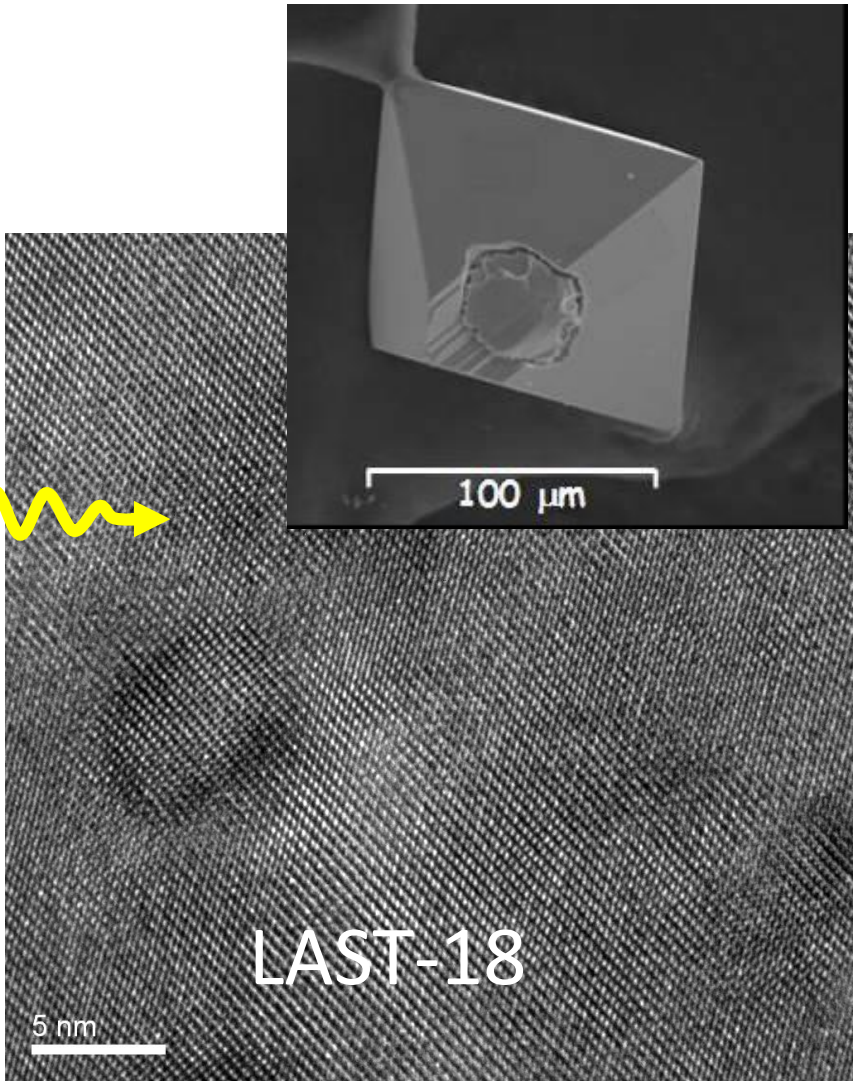




He, Dravid, Pcionek, Polychroniadis, Frangis

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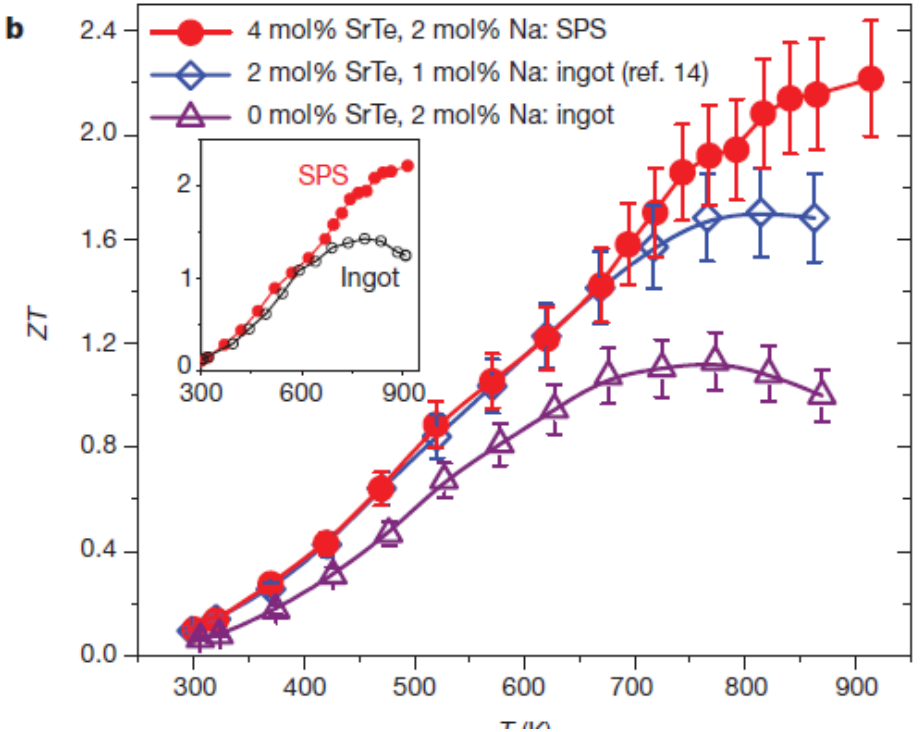


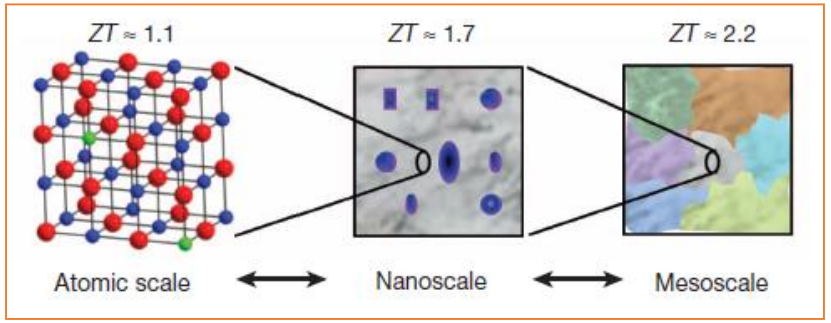
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He, Dravid, Pcionek, Polychroniadis, Frangis

PbTe-SrTe solid solution

Kanishka Biswas et al, Nature 489, 414 (2012)



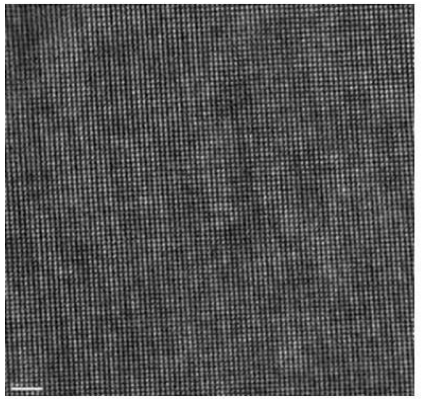


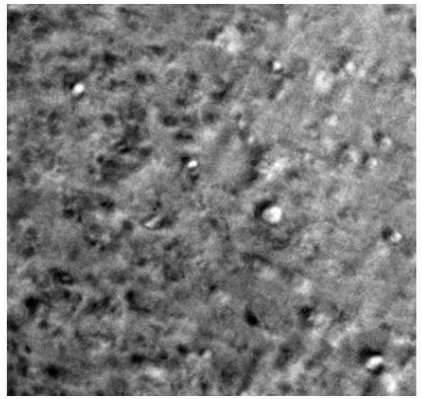
ZT>2

Bulk with embedded nano-structures at three length scales to scatter phonons efficiently

Importance of Band alignment

PbTe with SrTe inclusions





Pristine matrix

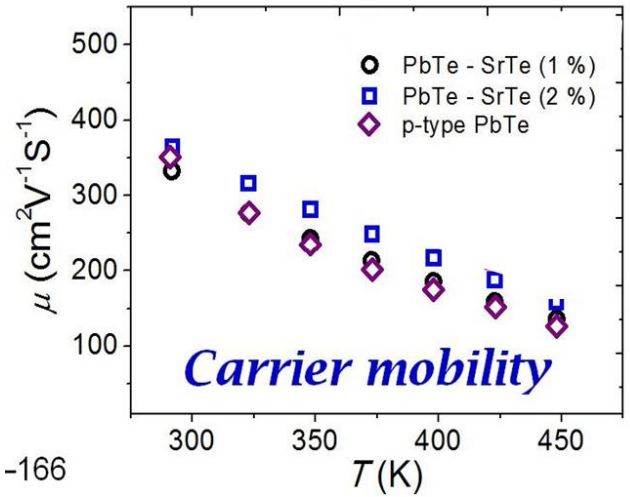
nanostructured

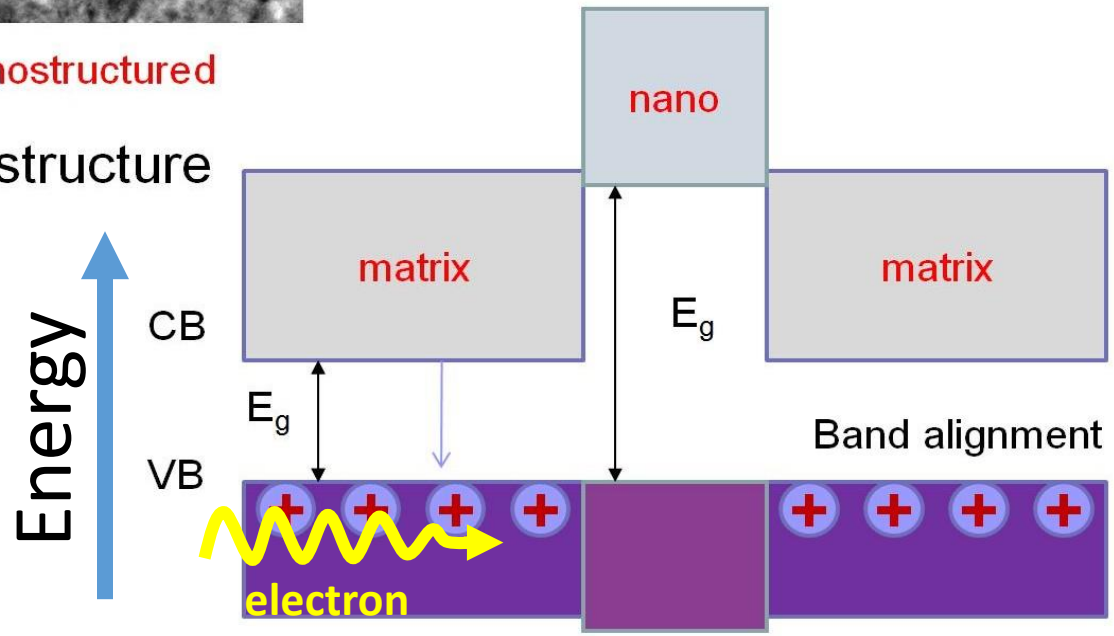
$K_{pristine} >> K_{nanostructure}$

Through band alignment

Comparable mobilities

$\mu_{pristine} \sim \mu_{nanostructure}$

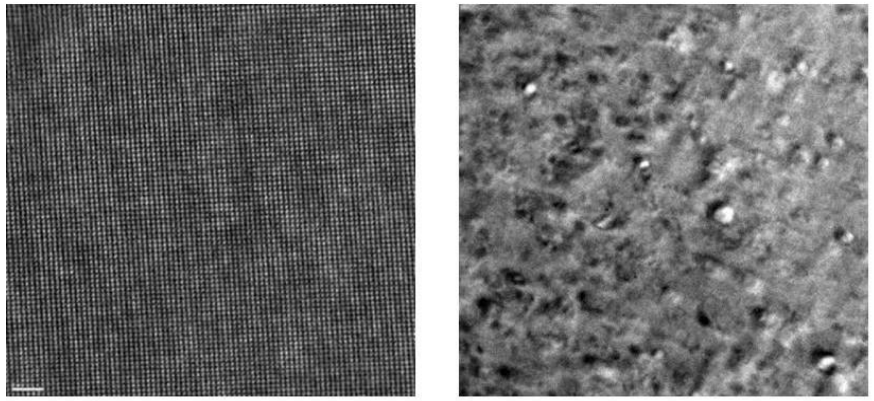




K. Biswas et al Nature Chemistry **2011**, 3, 160–166

PbTe with SrTe inclusions

Through band alignment



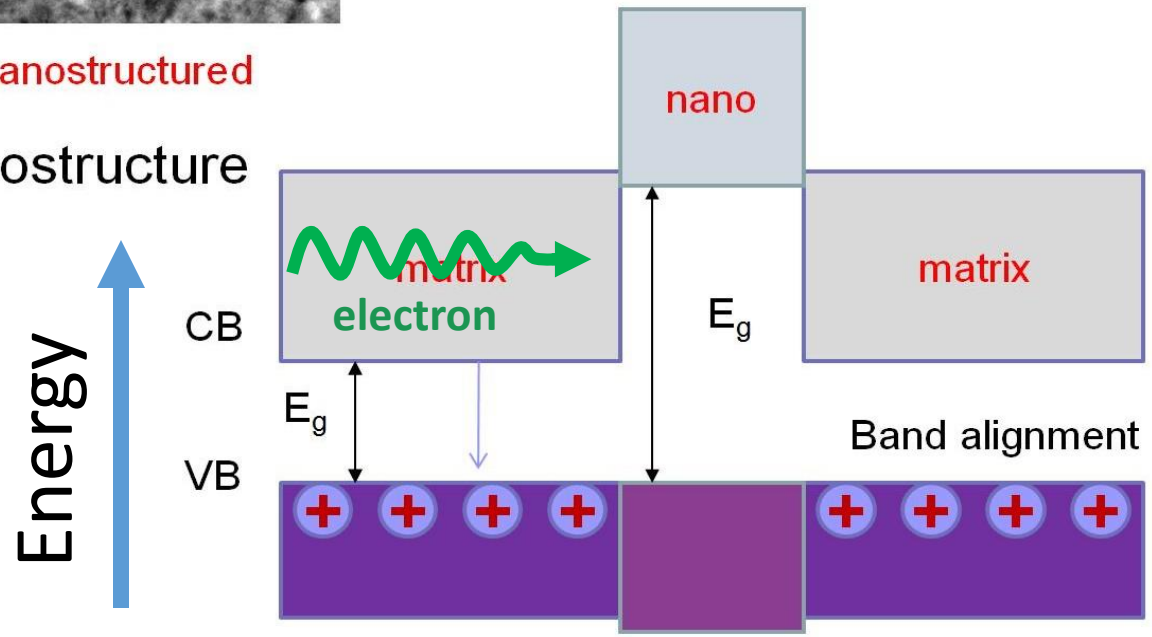
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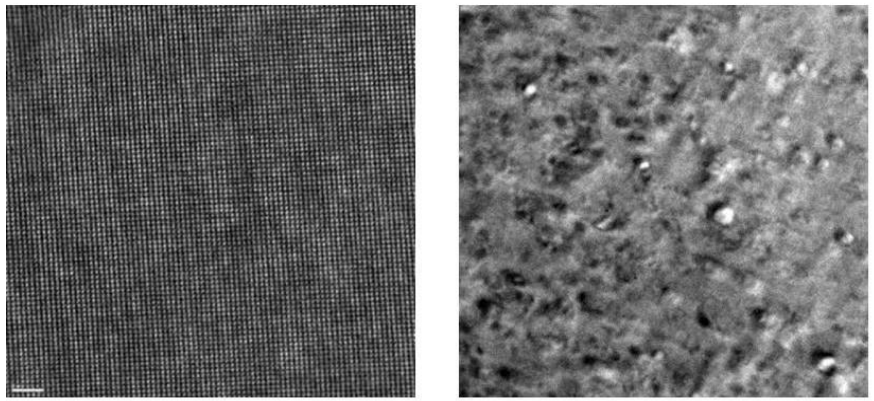
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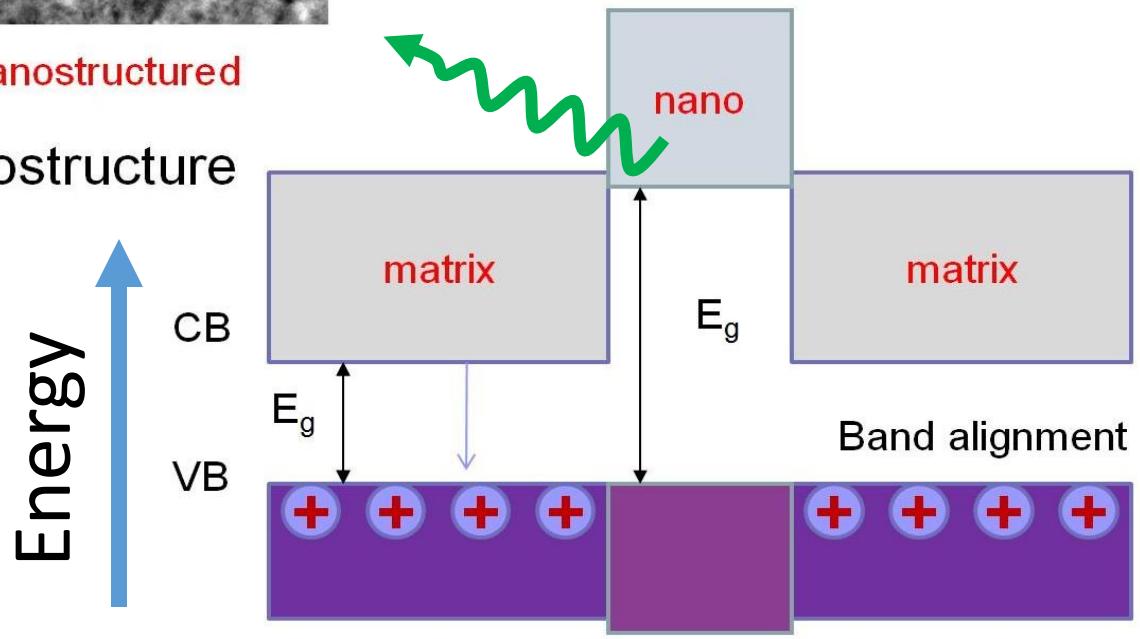
Pristine matrix

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Comparable mobilities

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K. Biswas et al Nature Chemistry **2011**, 3, 160–166

Enhancement of *ZT* by Distortion of the Electronic Density of States

Joseph P. Heremans et al, Science 321, 554 (2008)

Tl doped PbTe

S increases with dg(E)/dE

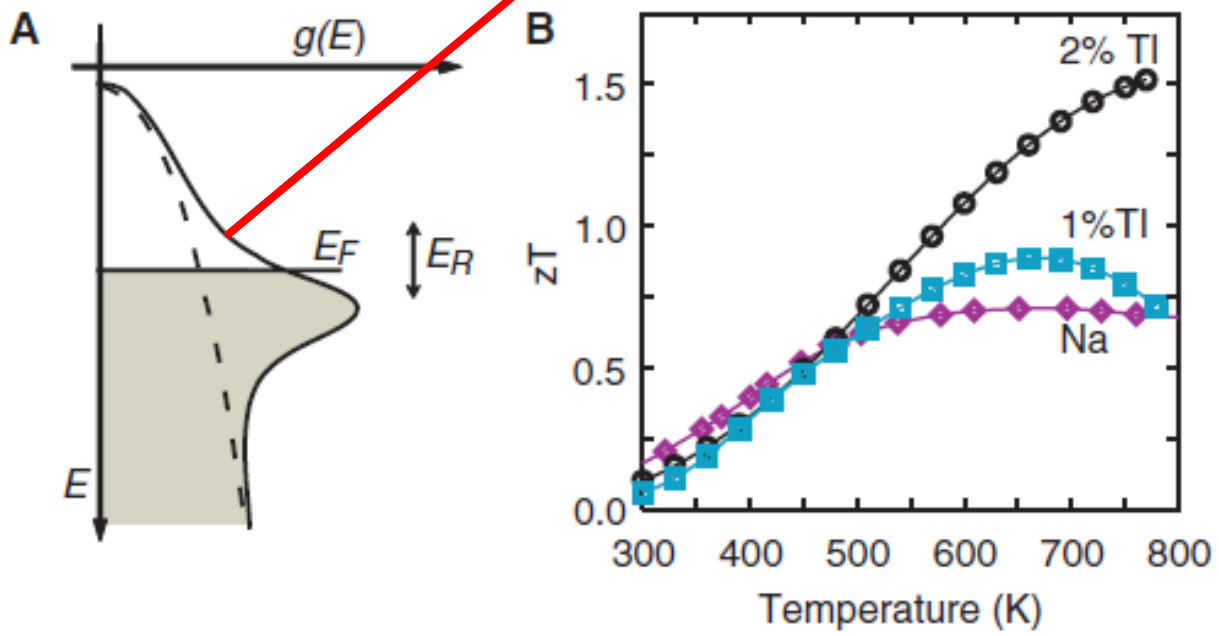


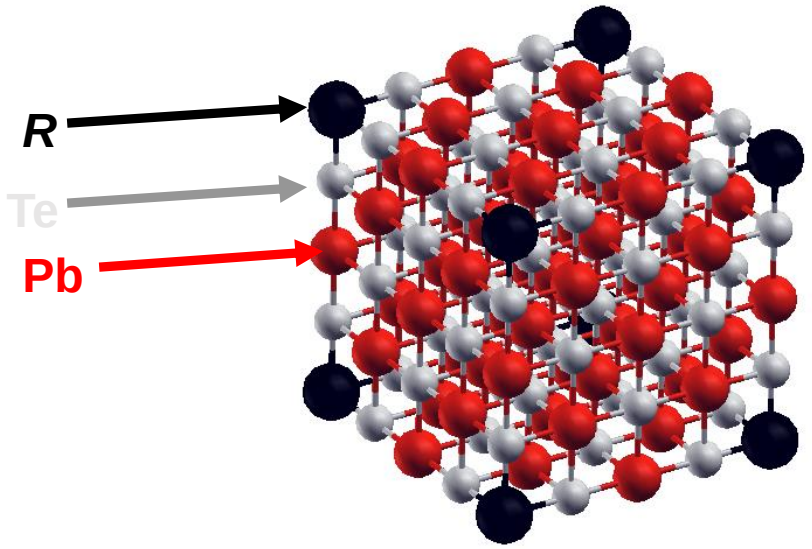
Fig. 1. (**A**) Schematic representation of the density of electron states of the valence band of pure PbTe (dashed line) contrasted to that of Tl-PbTe in which a Tl-related level increases the density of states. The figure of merit *zT* is optimized when the Fermi energy E_F of the holes in the band falls in the energy range E_R of the distortion. (**B**) The *zT* values for $Tl_{0.02}Pb_{0.98}Te$ (black squares) and $Tl_{0.01}Pb_{0.99}Te$ (blue circles) compared to that of a reference sample of Na-PbTe (purple diamonds).

Understanding and controlling defects – where theory can help?

Substitutional

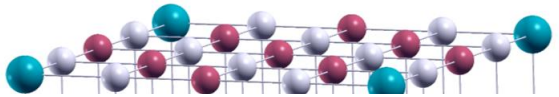
Quasi-periodic model
or Supercell model

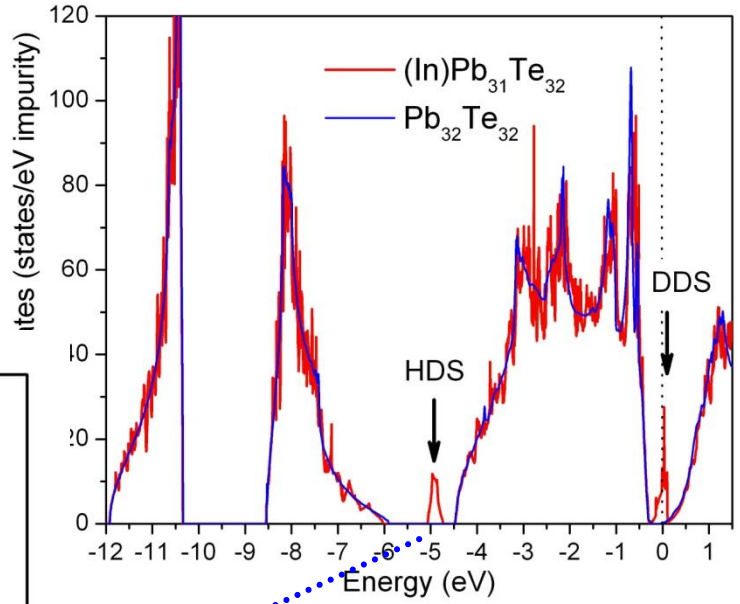
Unit cell for impurity in RPb$_{n-1}$Te$_n$ (n=32,108) where R is an impurity atom: R = Na, In, Tl

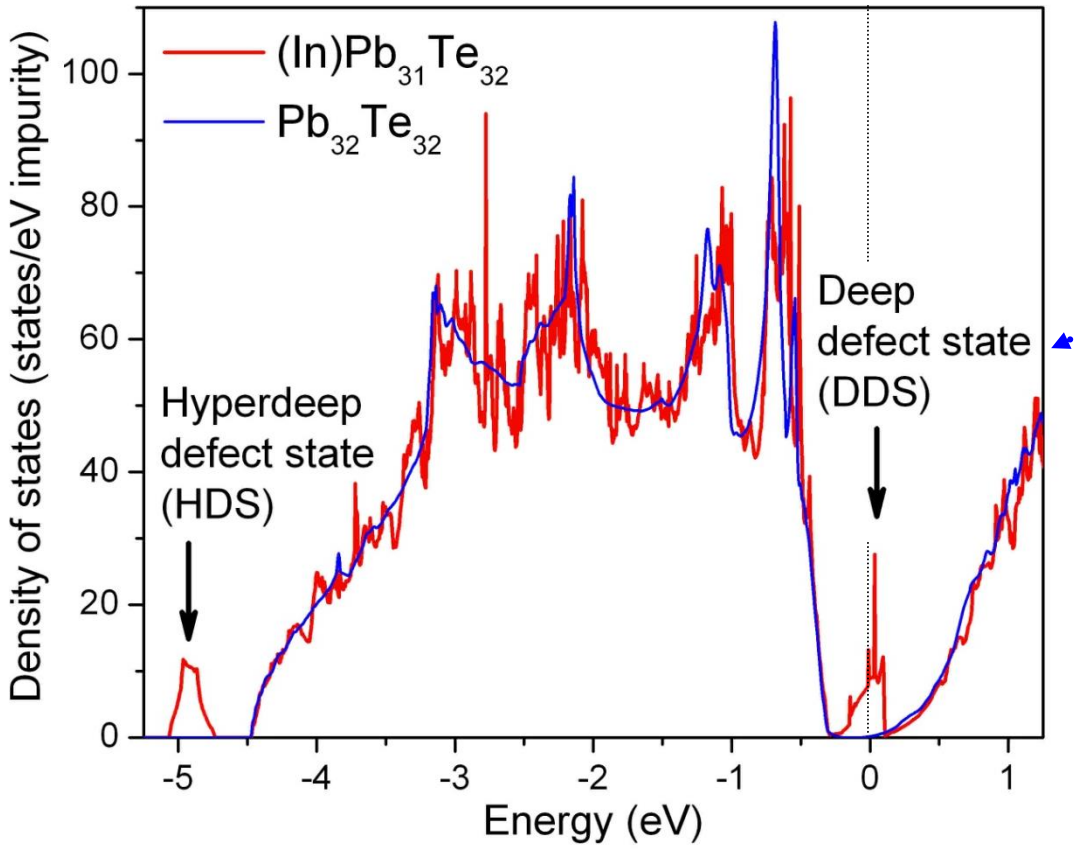


Ab initio electronic structure using
Density functional theory - GGA
All electron (WIEN2000)
PAW (VASP)

Ab initio calculations using density functional theory (DFT) and a supercell model (one Pb atom was replaced by a group III atom.)



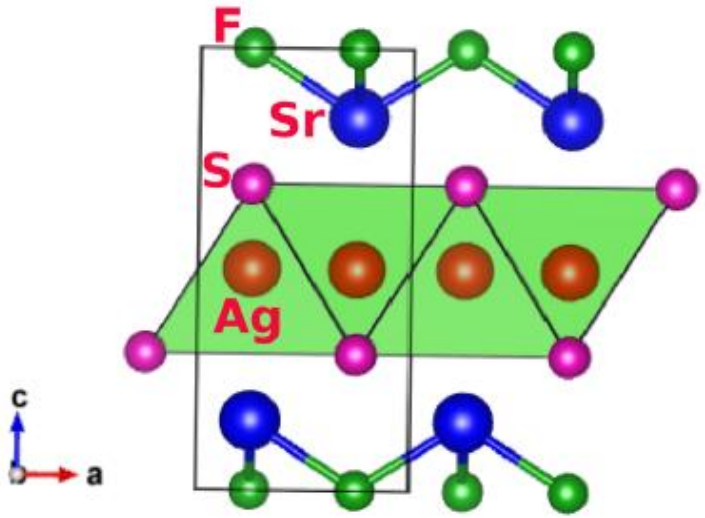


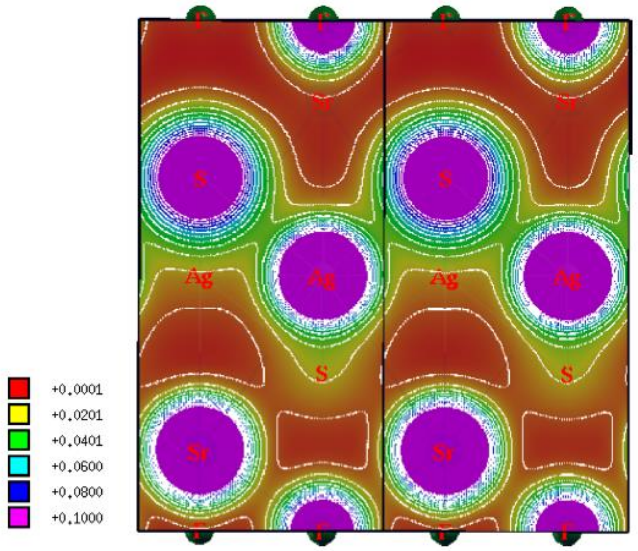


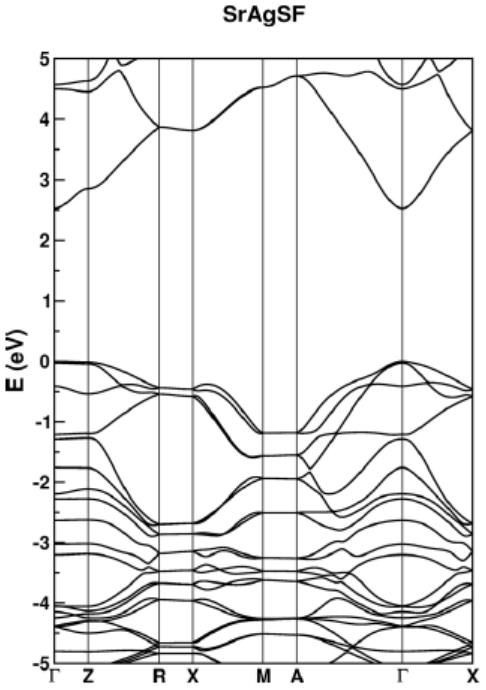
- HDS (DDS) can accommodate 2 electrons. HDS is filled; DDS is half-filled.
- HDS-DDS: ~5 eV → cast a doubt on the validity of the current accepted mixed-valence model assuming $2In^{2+} \rightarrow In^{1+} + In^{3+}$; **energetically, it is too costly to remove 2 electrons from HDS.**

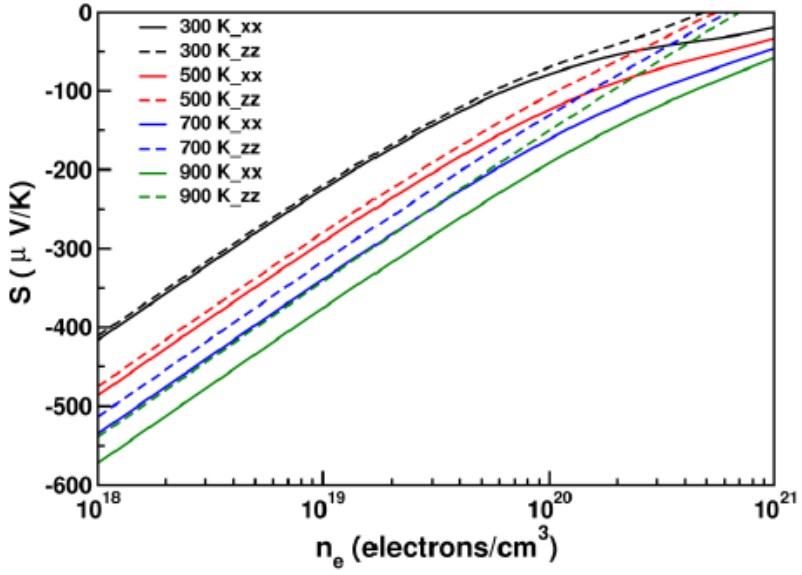
Ahmad,Mahanti,Hoang, PRL 2006
Ahmad et al Phys. Rev. B74 2006

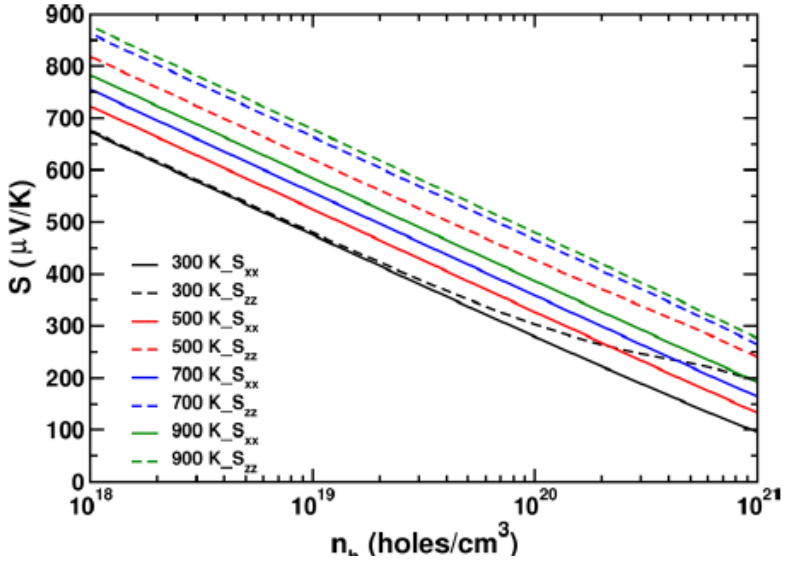
Quasi 2-dimensional system - potential confinement SrFAgS











PHYSICAL REVIEW B **92**, 045206 (2015)
Work in collaboration with IIT, Hyderabad and Hyderabad University and David Singh

BiOCuSe

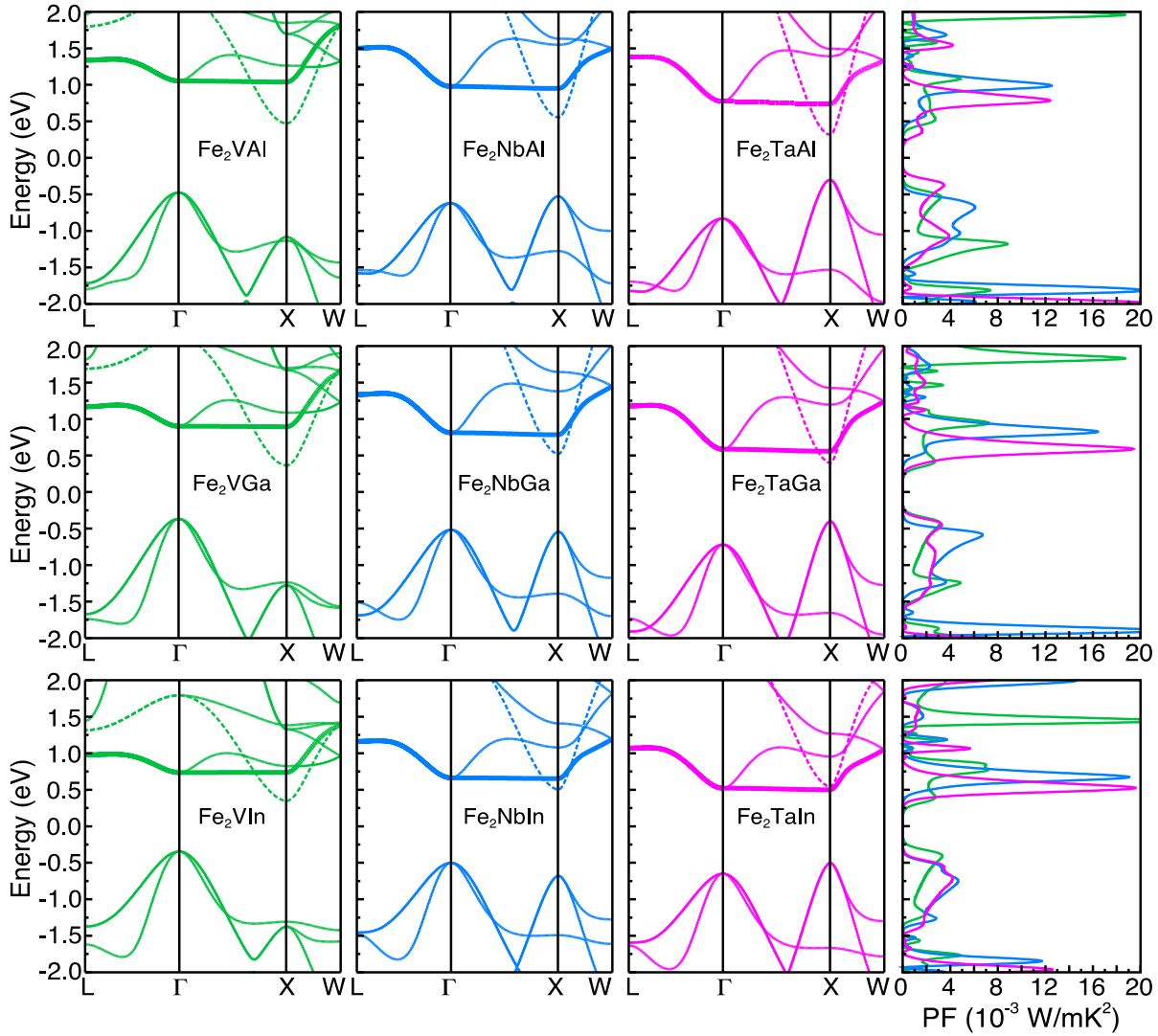
Can we combine dimensional confinement and resonant states?

Theoretical calculations using Density Functional based Methods

Resonant doping in BiCuSeO thermoelectrics from first principles,
J. Shen, H. Yu, Y. Pei, Y. J. Chen, *Mater. Chem. A* **2017,** *5* (3), 931-936.

Quasi 2-d Band structure engineering in Fe_2YZ

Bilc *et. al.*, *PRL* 114, 136601, 2015

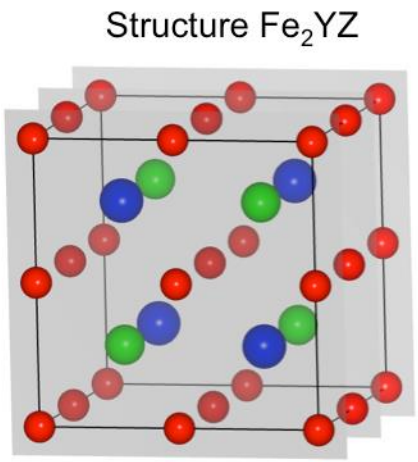


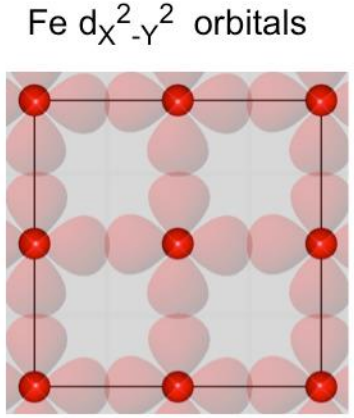
Anisotropic orbital overlap
d– orbitals

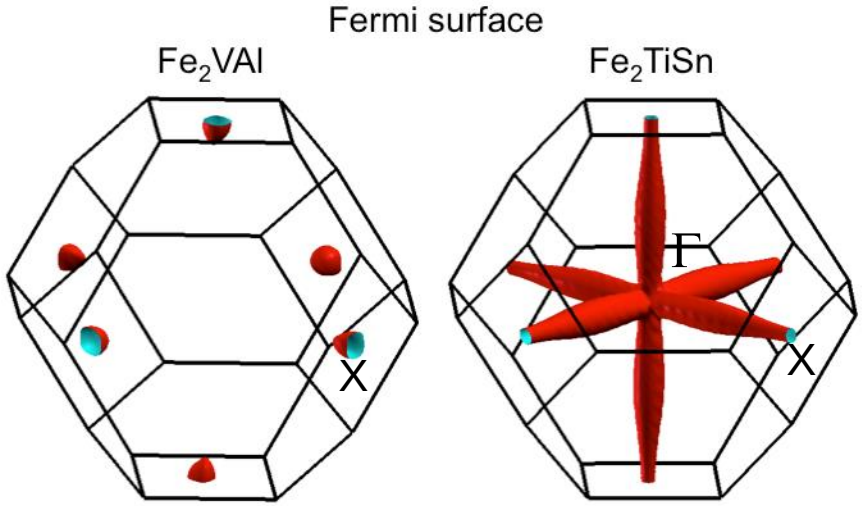
Flat bands near the Fermi energy

Low-dimensional charge transport

Cylindrical Fermi surfaces and low-d transport in Fe_2YZ full Heusler







⇒Low-D transport achieved through highly-directional Fe d e_g states

⇒Cylindrical Fermi surfaces – juxtaposition of many pockets along ΓX direction – maximization of and n

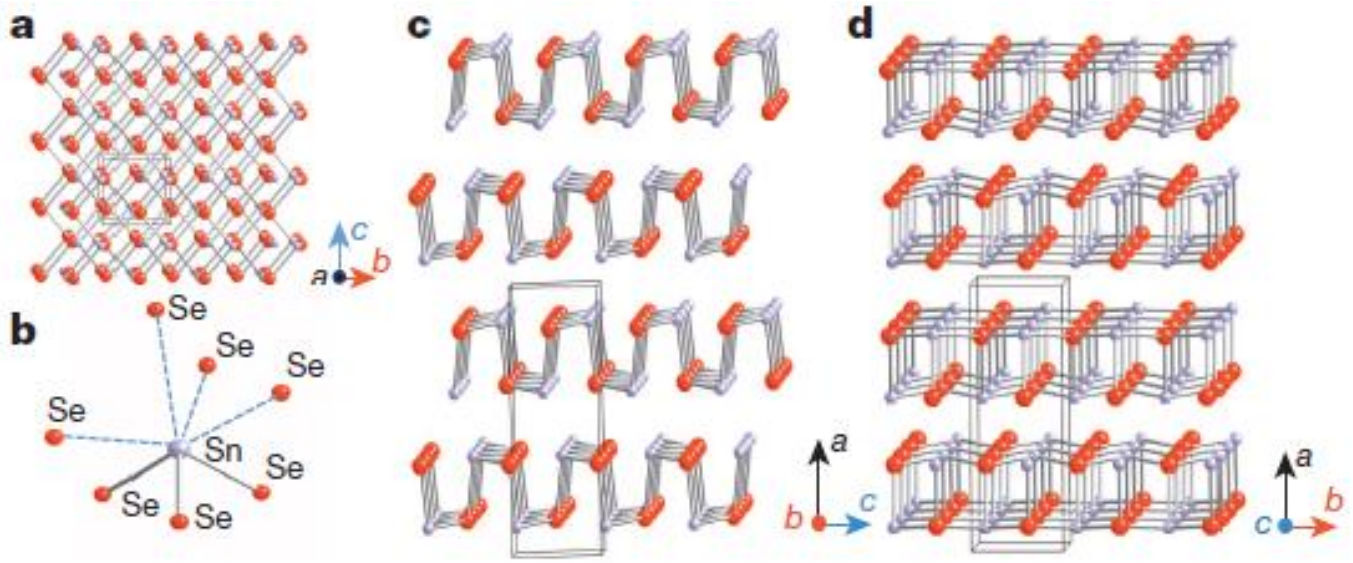
⇒Highly anisotropic effective masses:
$m_l \sim 90\ m_e$
$m_t \sim 0.2\ m_e$
$R = m_l/m_t \sim 450$

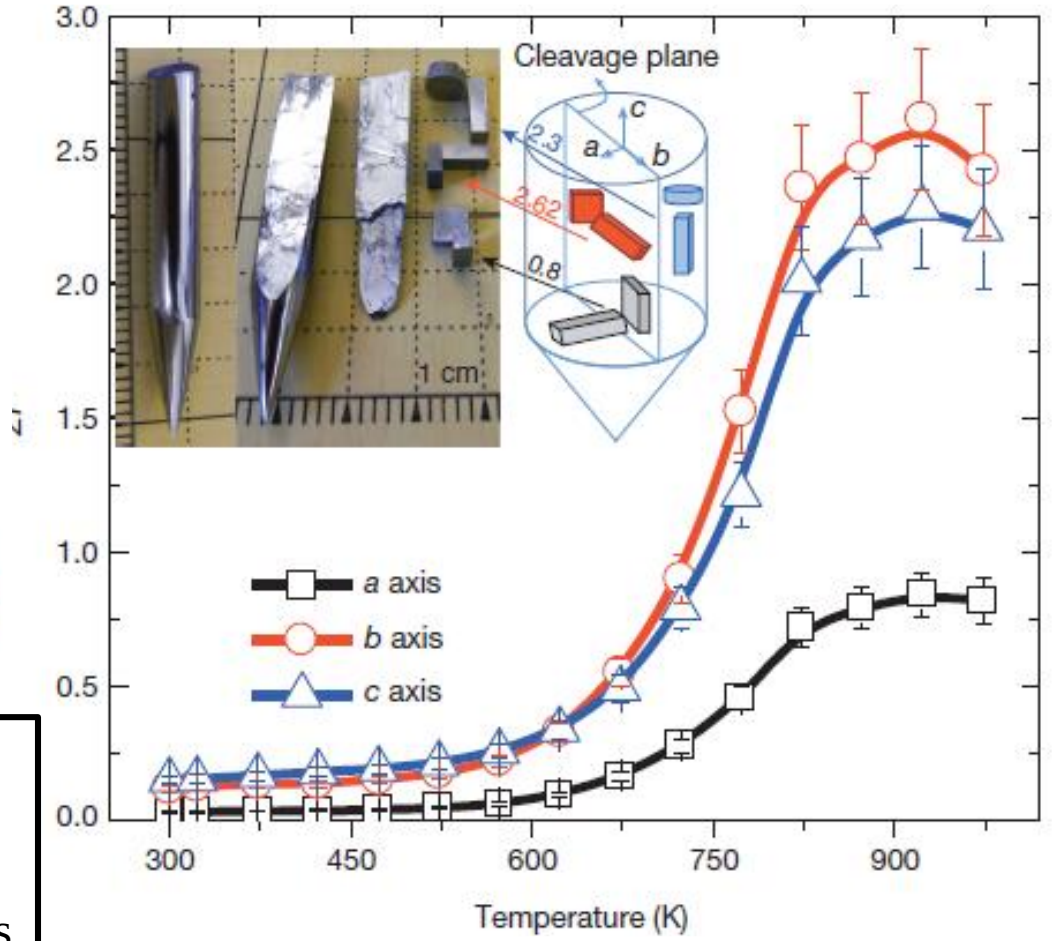
⇒**PF's 4-5 times larger than classical TE's**

Ultralow thermal conductivity and high ZT in SnSe

Zhao, Lo, Zhang, Sun, Tan, Uher, Wolverton, Dravid & Kanatzidis

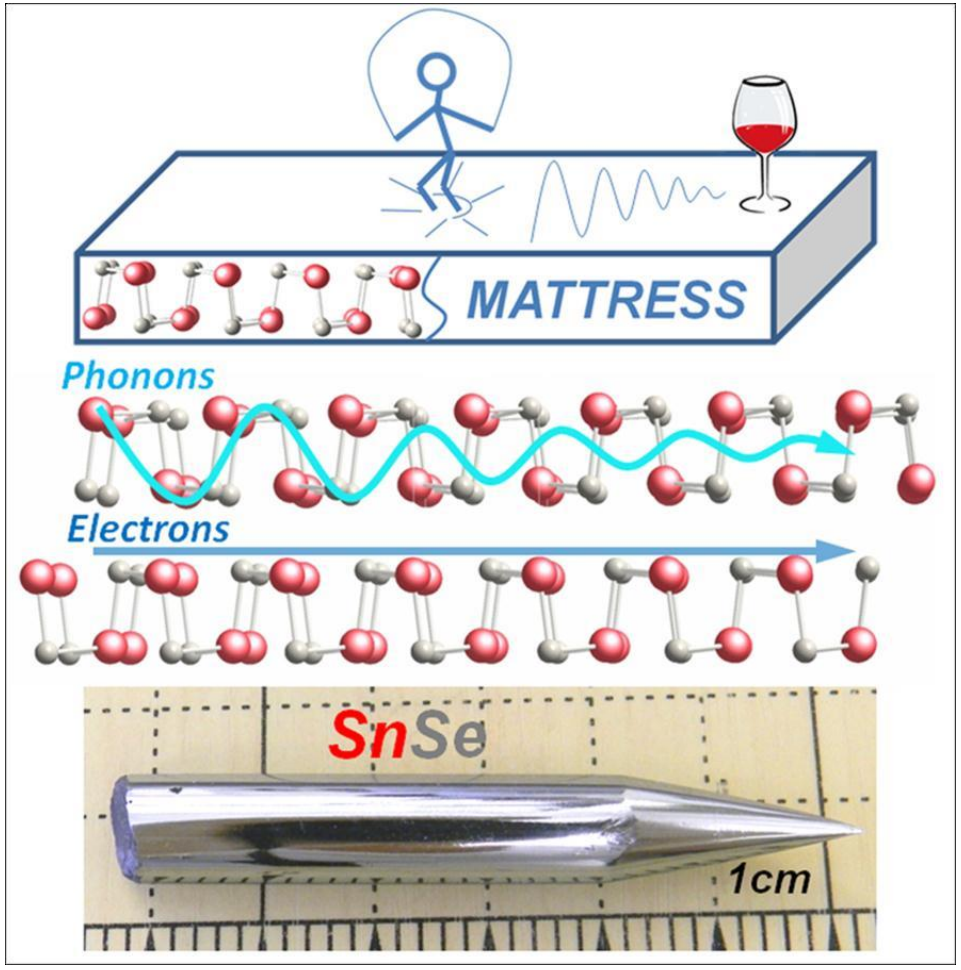
Nature 508, 373, 2014





- $SnSe_7$ polyhedral
- Sn Lone pair physics
- Large Gruneisen parameter
- Ultralow thermal conductivity

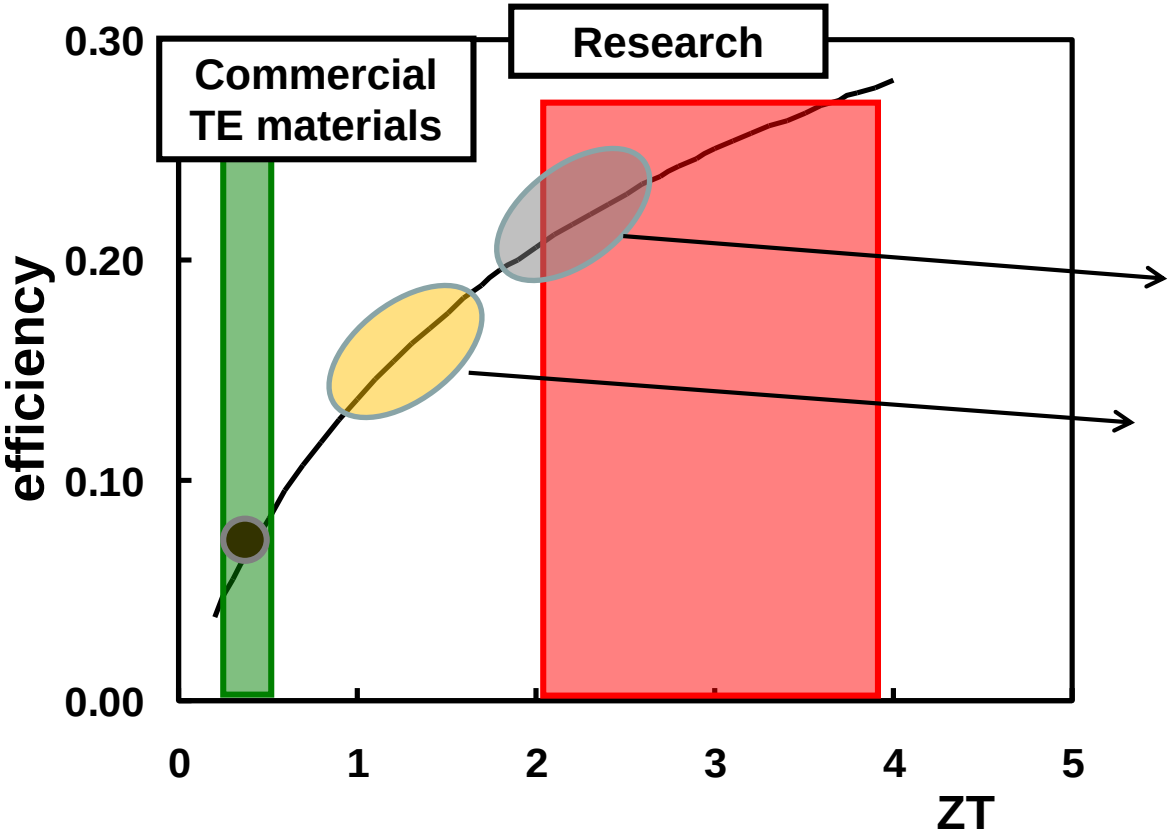
- Distorted NaCl structure
- Two-atom thick SnSe slabs
- Strong Sn-Se bonds along slab
- Weak Sn-Se bonds between slabs



Is it a perfect Electron Crystal – Phonon Glass?

Why was it waiting until nearly 800 K to show its great TE property?

Several new thermoelectrics with record performance



New materials from our EFRC:

best performing

earth abundant

We have reached the target of ZT ≥ 2 and will keep going!

MICHIGAN STATE UNIVERSITY
NORTHWESTERN UNIVERSITY
THE OHIO STATE UNIVERSITY
UCLA
WAYNE STATE UNIVERSITY
OAK RIDGE NATIONAL LABORATORY
[efrc] RMSSEC Revolutionary Materials for Solid State Energy Conversion

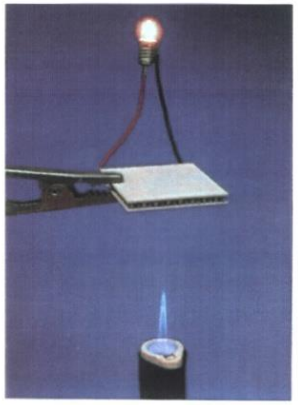
Important questions and challenges in Theory (Bulk)

- Pure systems
  - origin of band gaps in complex semiconductors
  - origin of unusually low thermal conductivity
- Nature of defect states
- Structure of nanostructures? How to model them?
  Electronic structure and transport in systems with embedded nano-structures?
- Electron-phonon, phonon-phonon interaction in complex anharmonic systems

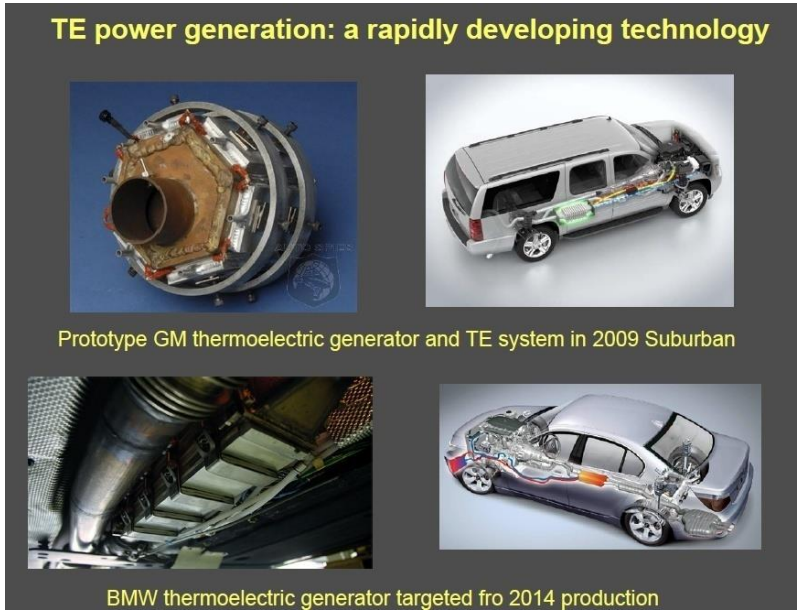
Some concluding thoughts

- Systems near structural instability or intrinsically anharmonic systems – low κ_{latt}
- Controlling and characterizing (quantitatively) nanostructure
- Understanding and modelling transport across interface – energy filtering

Thank you for your attention



Electrical
Power Generation



Special thanks to
Havilah Esther
Scientific Relations Manager