

Yonsei University Graduate Class

Energy Materials: Design, Discovery and Data Design Principles for Energy Technologies

Prof. Aron Walsh

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Imperial College London



<https://wmd-group.github.io>



@lonepair

Figure of Merit

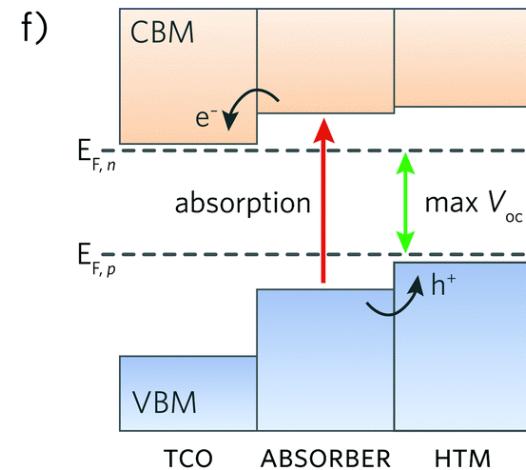
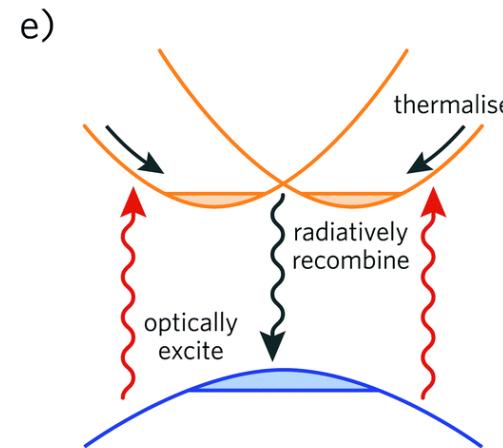
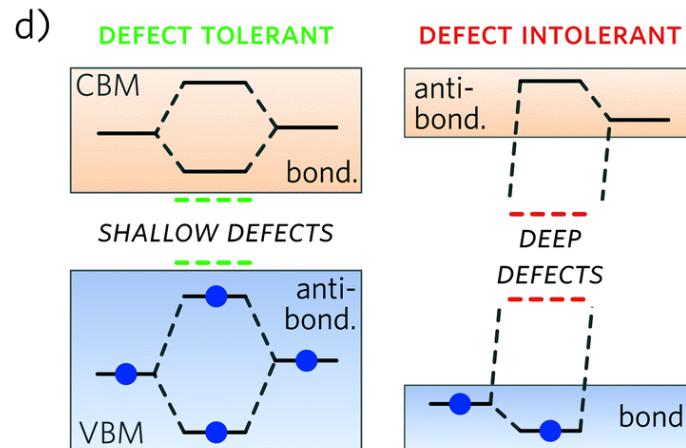
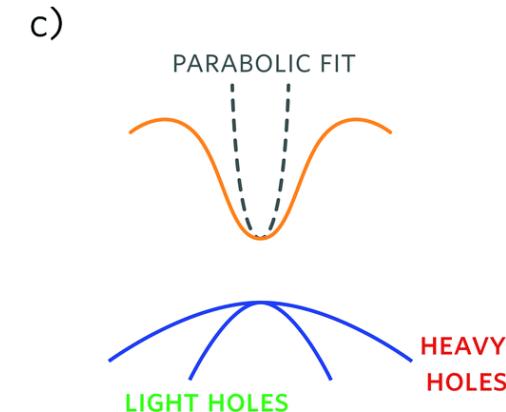
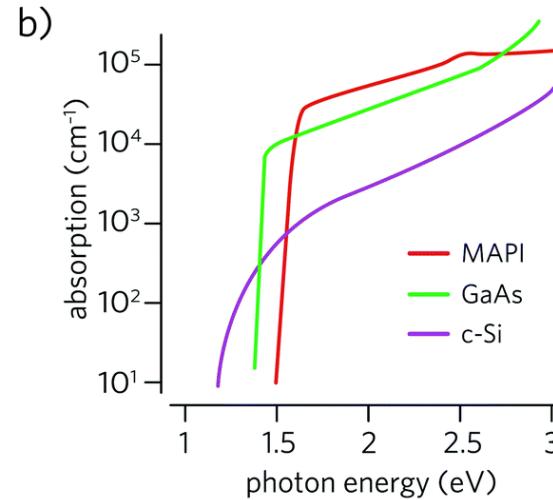
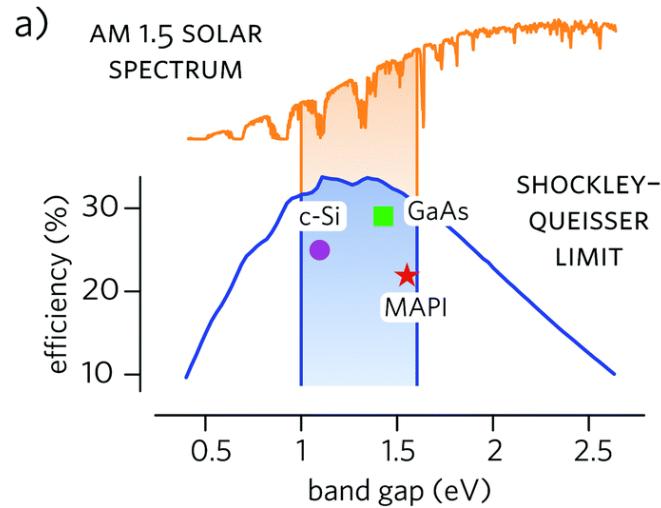
Definition of a practical and meaningful figure of merit is essential for high-throughput screening or materials design procedures

Performance = f (Descriptors)

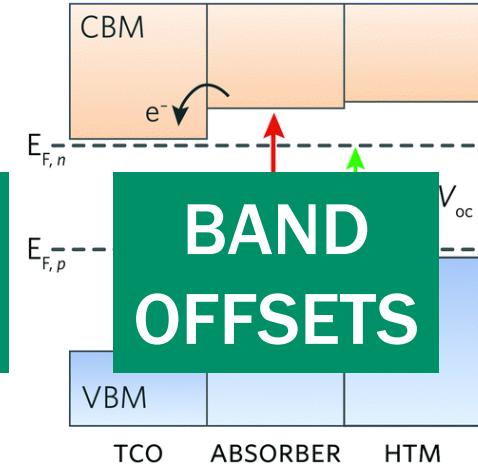
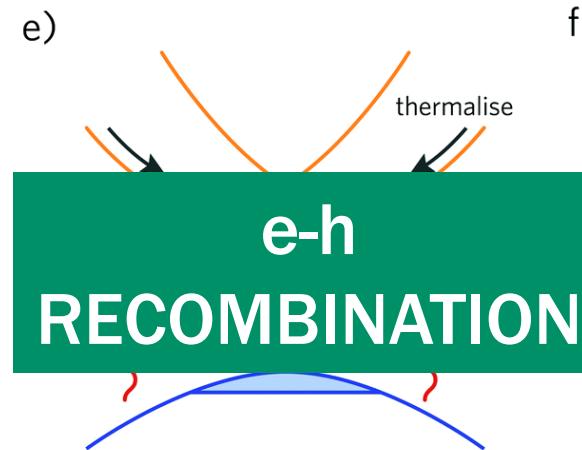
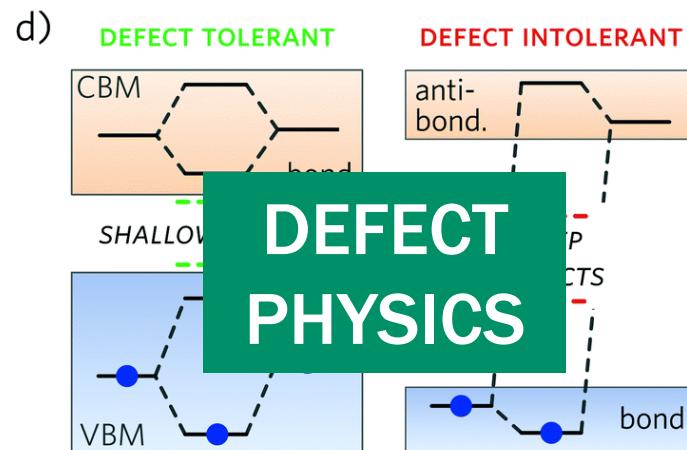
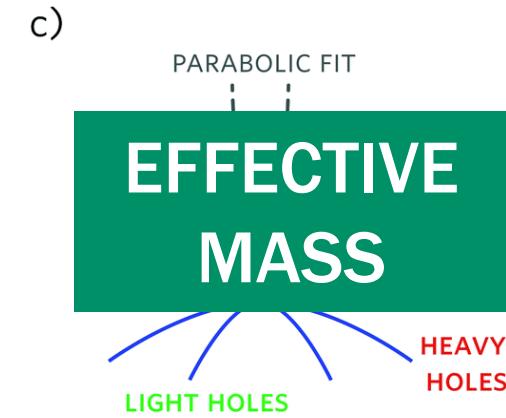
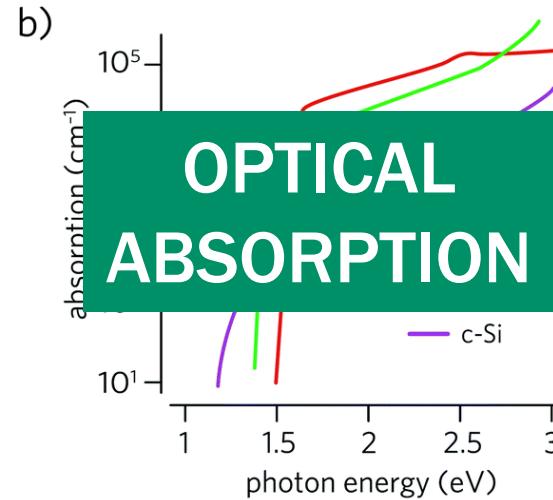
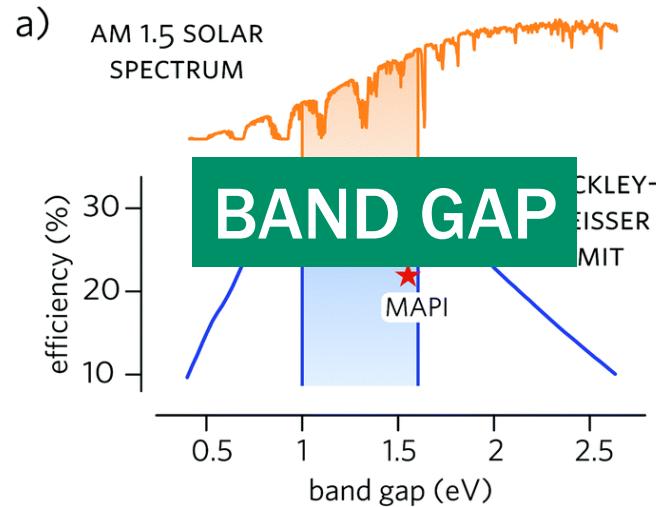
An Ideal Photovoltaic Absorber

- Low-cost and non-toxic elements
- Direct optical bandgap (1.0 – 1.5 eV)
- Easy to deposit and scale-up production
- Semiconductor with low carrier concentrations
- Tolerant to impurities and microstructure
- Chemically stable at interfaces
- Workfunction matched to standard contacts
- Lattice matched to wide-gap absorbers (e.g. ZnSe) for low cost multi-junction devices

Performance Descriptors



Performance Descriptors

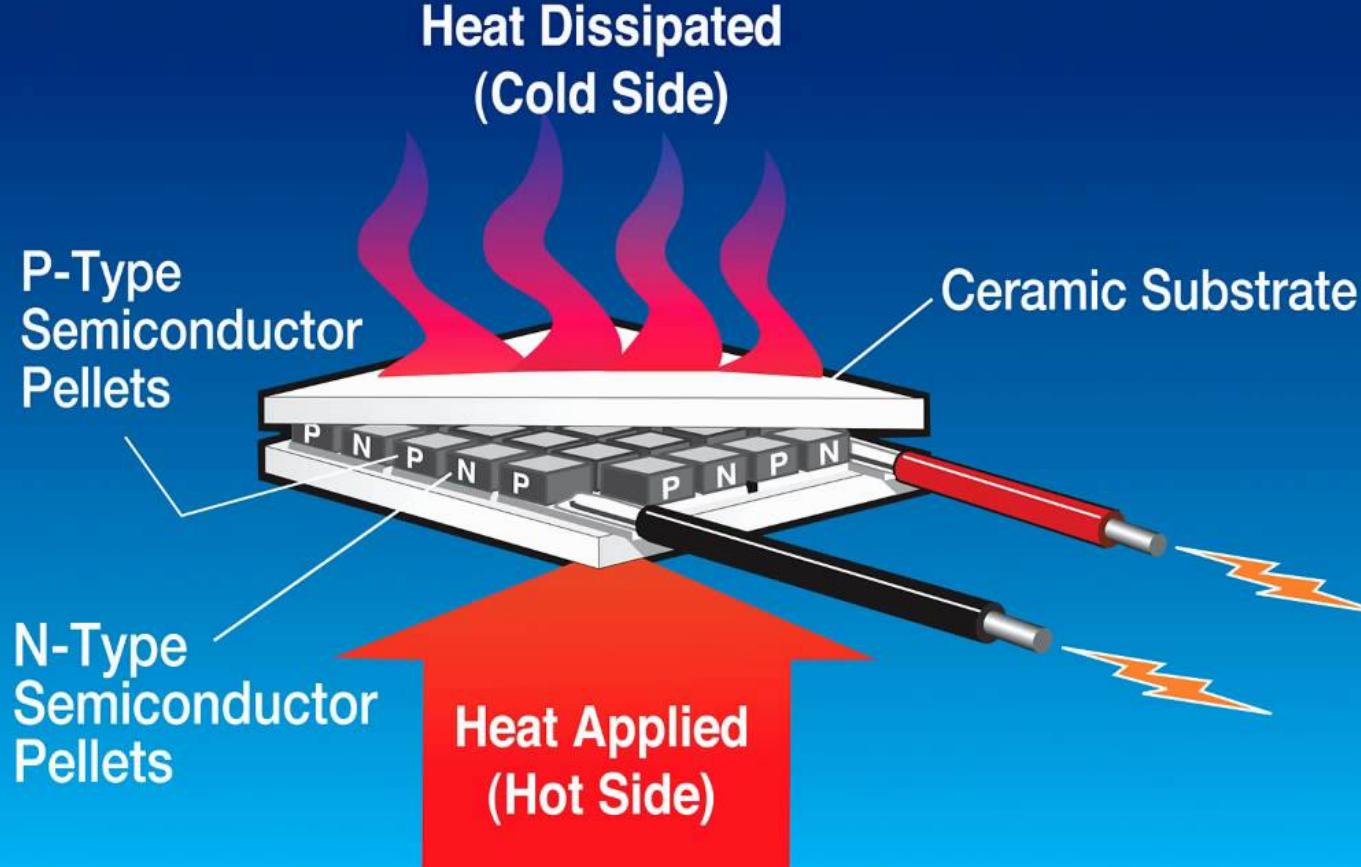


Case Study: Thermoelectrics

A. Materials and Devices

B. New Directions

Solid-State Heating and Cooling

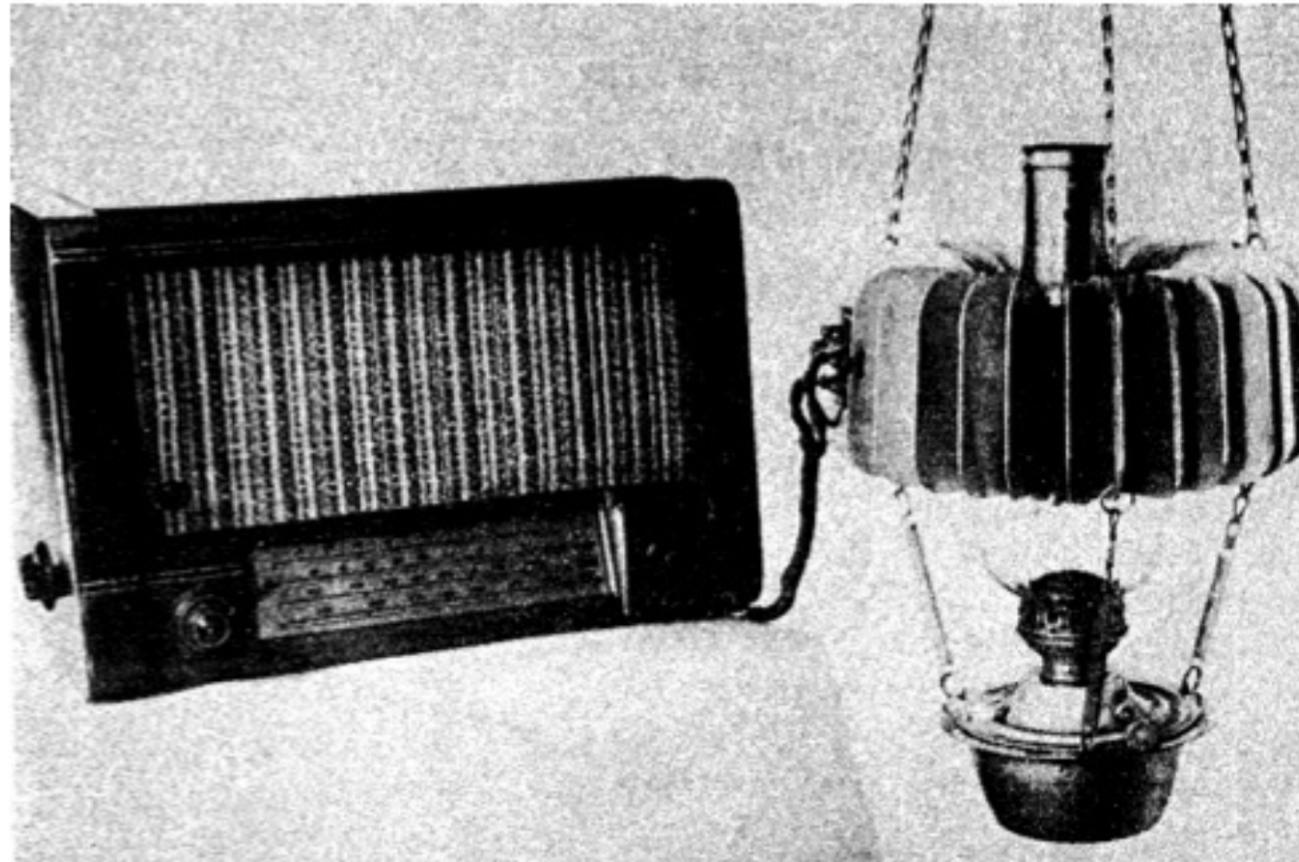


<https://www.youtube.com/watch?v=YhynSkFIJOs>

Class Question

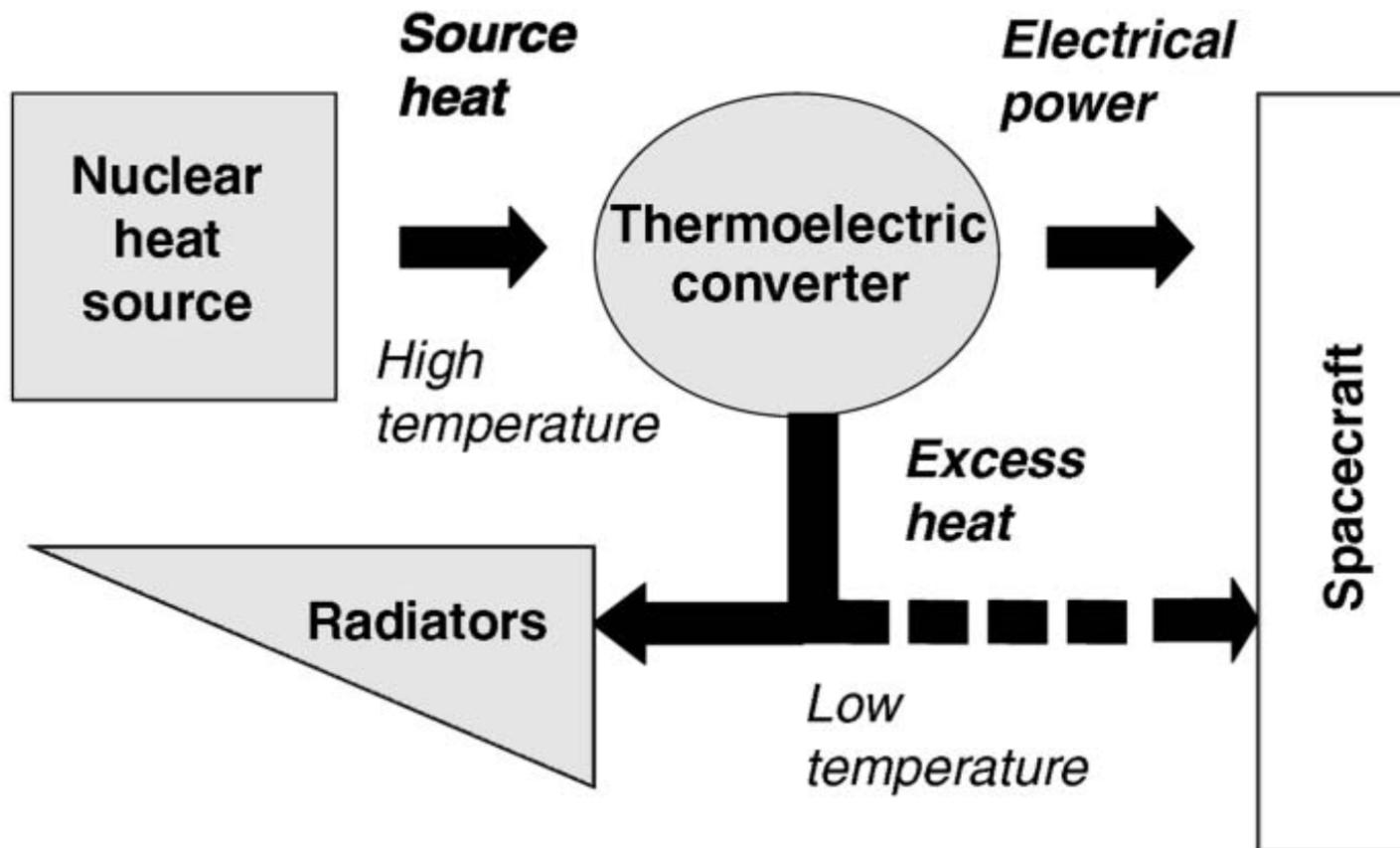
Where could thermoelectric devices be useful?

Portable Radio

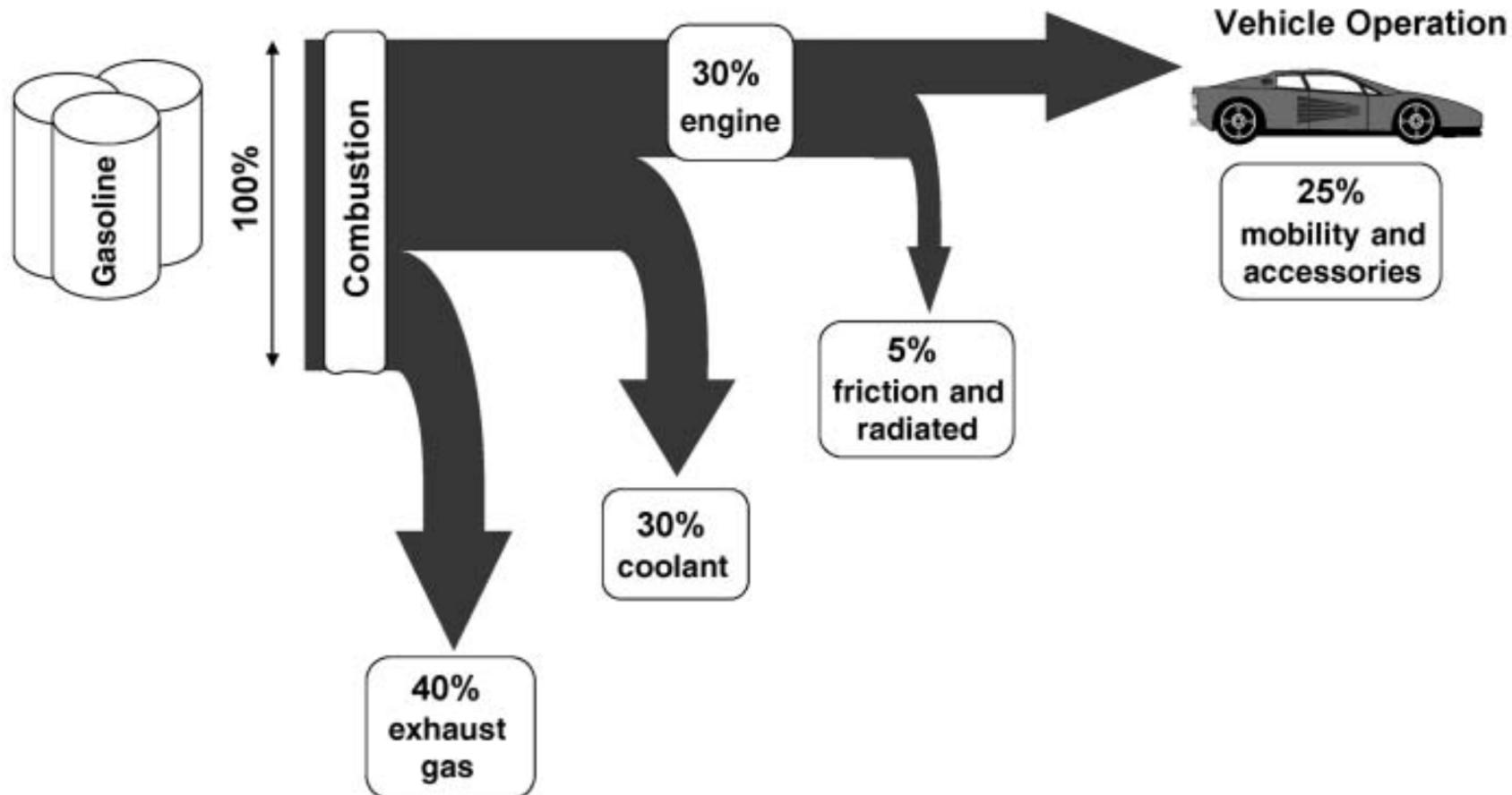


ZnSb
(1948, USSR)

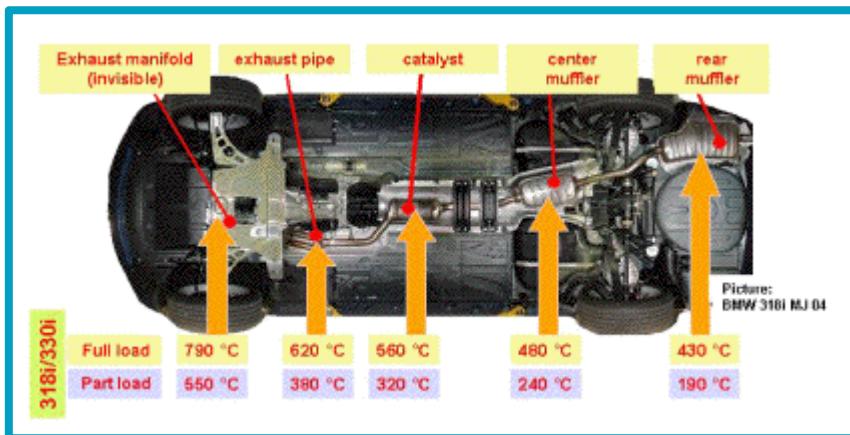
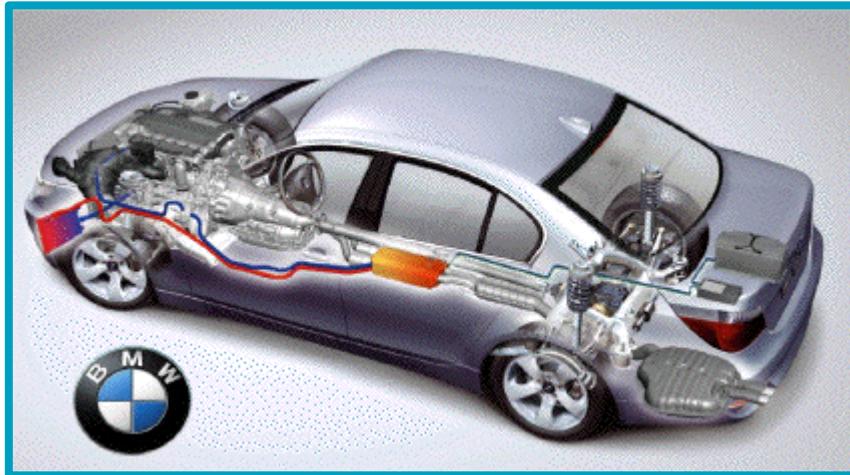
Power in Space



Waste Heat Recovery



Waste Heat Recovery



- 75% of energy produced in combustion cycle is lost to heat.
- Exhaust temperatures reach 300 – 500 °C depending on load.
- Thermoelectrics could improve fuel economy by 10%.

1834: Peltier Effect

Nouvelles Expériences sur la Caloricité des courans électriques;

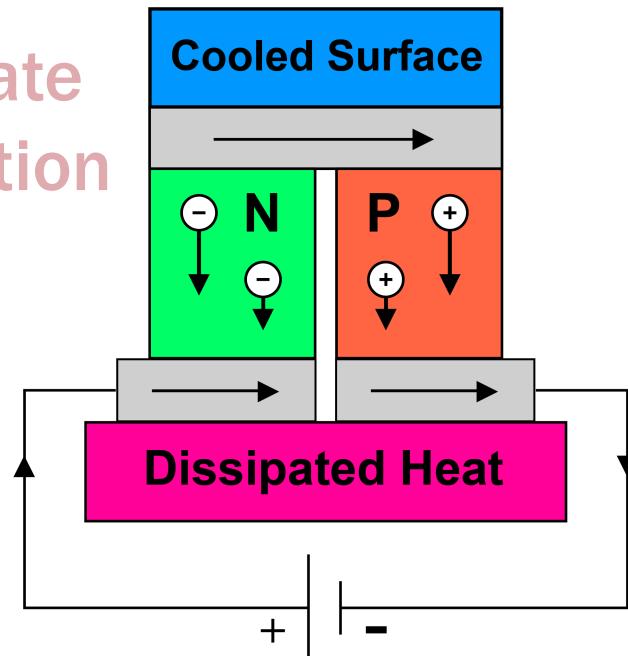
PAR M. PELETIER.

Les effets calorifiques que produit un courant électrique n'ont jamais été mesurés avec des instrumens assez sensibles pour qu'on pût apprécier la variété de phénomènes qui l'accompagne lorsqu'il n'a qu'une très faible intensité. Avec les moyens d'investigations dont on a fait usage jusqu'ici, il a toujours fallu employer un courant énergique dont le résultat a été une constante élévation de température; aussi n'est-ce que sous ce rapport

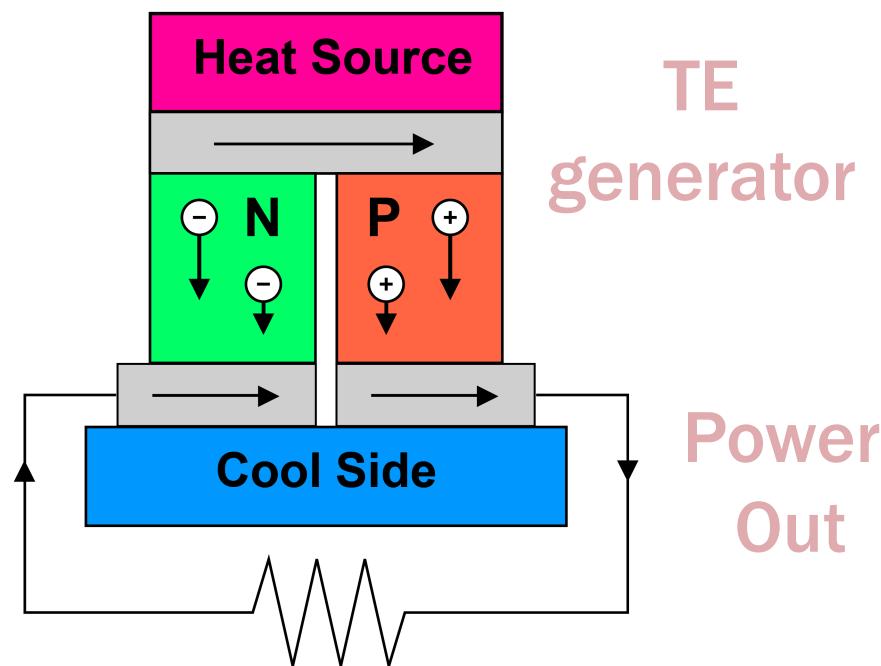
Thermoelectric Circuits

Peltier Cooling: Thermoelectric heat pumps that produce a temperature gradient proportional to an applied current

Solid-state
refrigeration



Power
In



TE
generator

Power
Out

1954: Bi₂Te₃, PbTe, HgTe

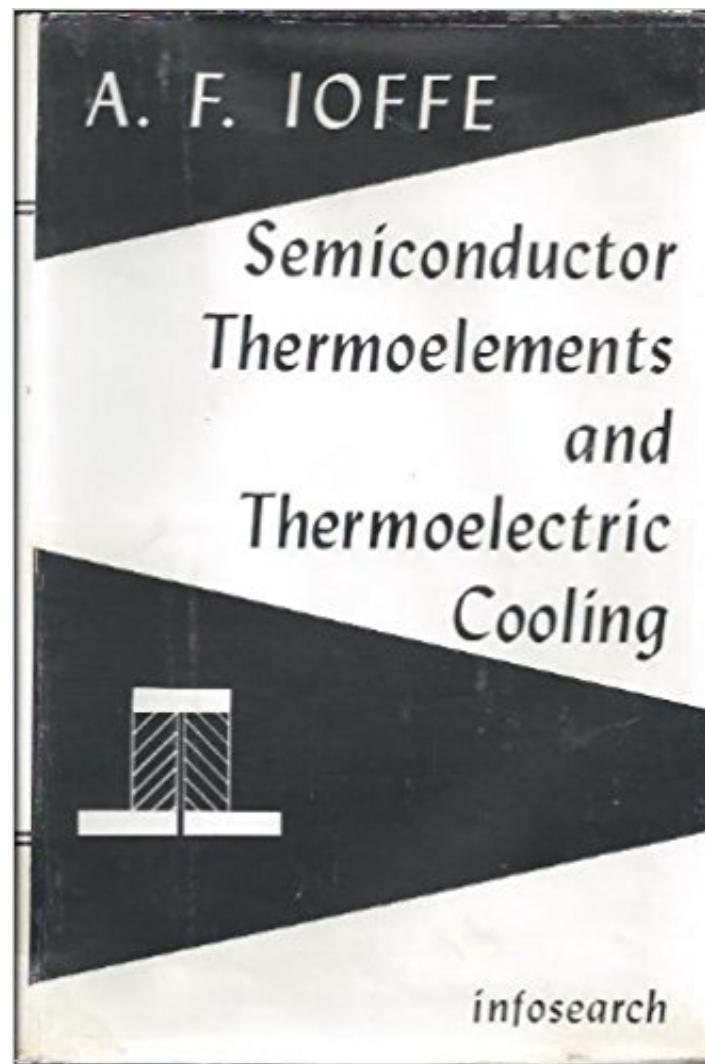
The use of semiconductors in thermoelectric refrigeration

By H. J. GOLDSMID, B.Sc., and R. W. DOUGLAS, B.Sc., F.S.G T., F Inst.P., Research Laboratories,
The General Electric Co. Ltd , Wembley, Middlesex

[*Paper received 6 July, 1954*]

In the past the possibility of thermoelectric refrigeration has been considered, but all attempts to produce a practical refrigerator have failed owing to lack of suitable thermocouple materials. In this paper it is proposed that semiconductors should be used and the factors governing their selection are discussed. It is concluded that the semiconductors should be chosen with high mean atomic weights and that they should be prepared with thermoelectric powers lying between 200 and 300 $\mu\text{V. } ^\circ\text{C}^{-1}$. Preliminary experiments have led to the production of a thermocouple consisting of bismuth telluride, Bi₂Te₃, and bismuth, capable of maintaining 26° C of cooling

1956: Thermoelectric Figure of Merit



Thermoelectric Figure of Merit

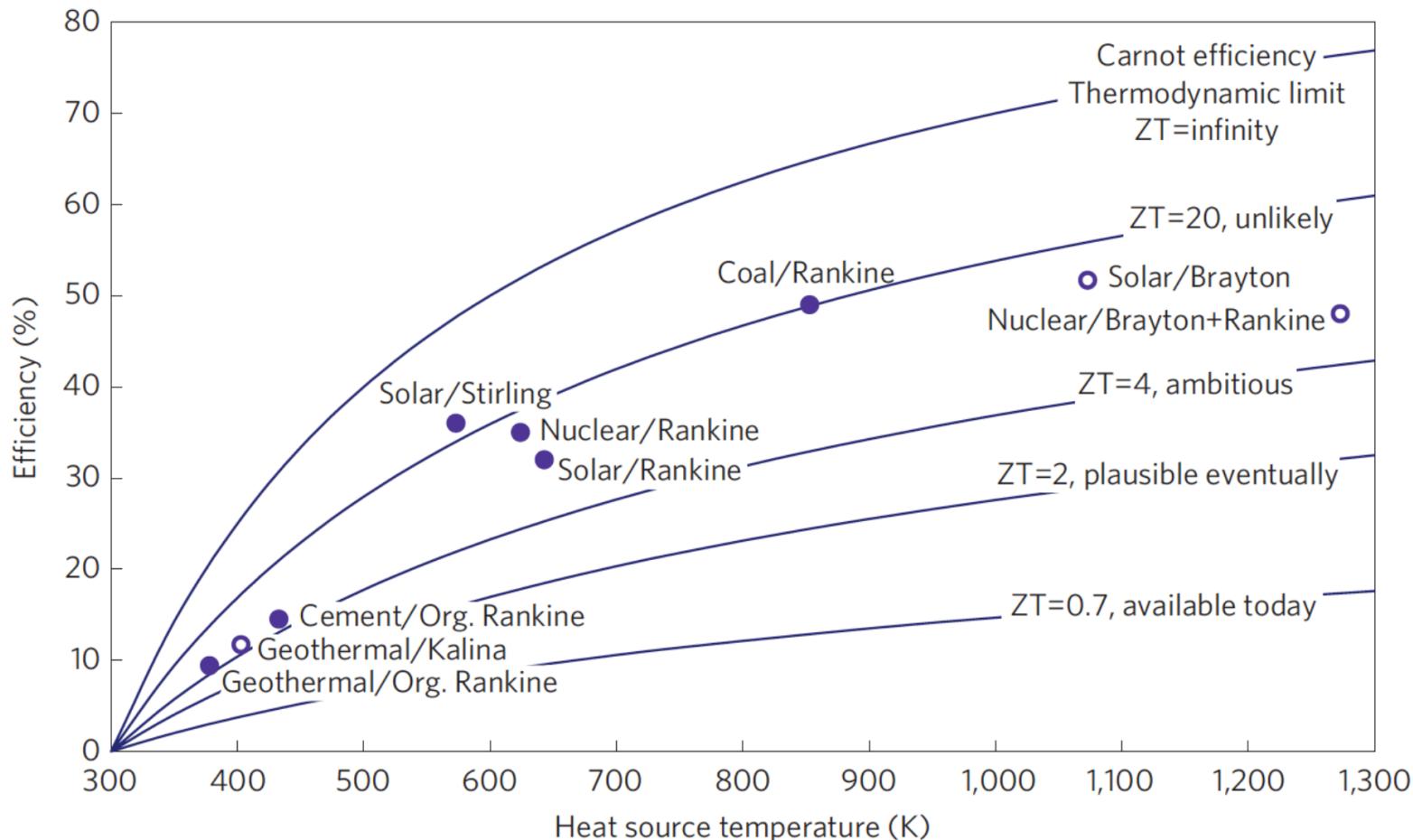
Seebeck coefficient, $\alpha = -\frac{\Delta V}{\Delta T}$
Units: VK^{-1}

Electrical conductivity
Units: Sm^{-1}

$$ZT = \frac{\alpha^2 \sigma T}{\kappa_{latt} + \kappa_{el}}$$

Lattice and electronic
thermal conductivity
Units: $Wm^{-1}K^{-1}$

ZT and Thermodynamic Efficiency



Electrical Conductivity

Requires high carrier concentration and
high mobility (small carrier effective mass)

$$\sigma = ne\mu$$

Carrier mobility
Units: cm/Vsec
 $(\mu = \frac{e\tau}{m^*})$

Carrier concentration
Units: cm⁻³

Seebeck Coefficient

Related to entropy per carrier: maximum at low carrier concentrations and high density of states (large carrier effective mass)

$$\alpha = \frac{8\pi k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{\frac{2}{3}}$$

Carrier effective mass

Units: m_e

Lattice Thermal Conductivity

Heat conduction by lattice vibrations
(low energy phonon modes)

$$\kappa_{\text{latt}} = \int_q C_V v \Lambda$$

Phonon modes

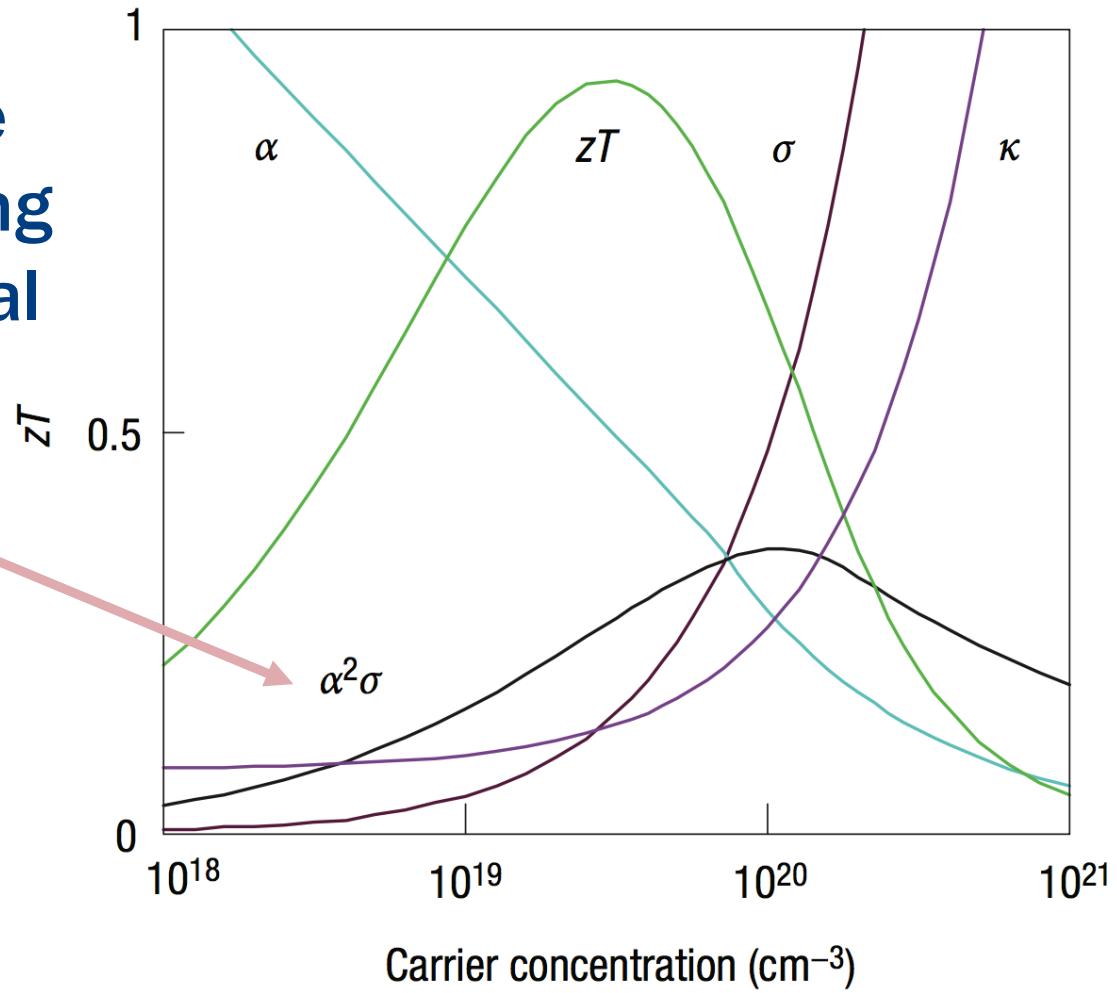
Heat capacity
Group velocity
Mean free path

The diagram shows the equation for lattice thermal conductivity, $\kappa_{\text{latt}} = \int_q C_V v \Lambda$. Three green arrows point from labels to specific terms: one arrow points from 'Phonon modes' to the 'q' in the integral, another points from 'Heat capacity' to C_V , and a third points from 'Group velocity' and 'Mean free path' to $v \Lambda$.

Balance of Competing Effects

Accessible range
restricted by doping
limits of a material

“Power Factor”

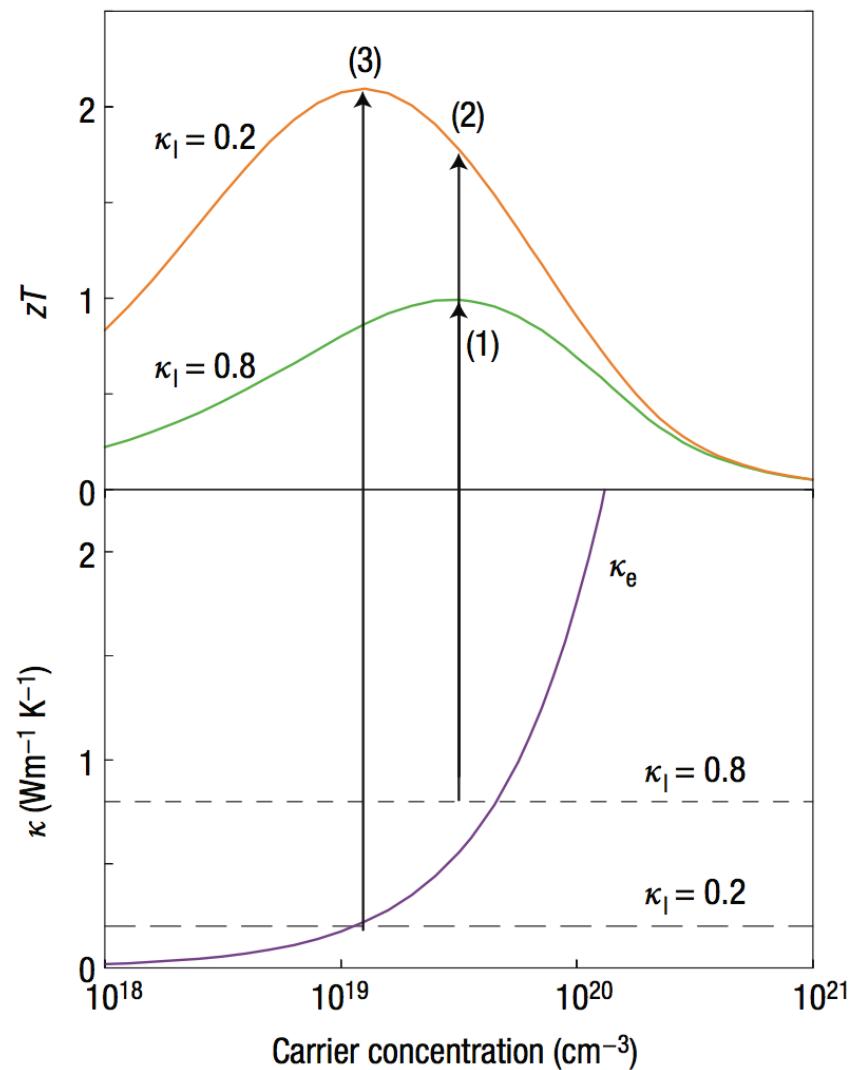


Minimise Lattice Thermal Conductivity

Avoid heat transfer:

- (i) Phonons (lattice term)
- (ii) Electron Transport
- (iii) Ion Transport

Optimal value: $< 1 \text{ Wm}^{-1}\text{K}^{-1}$



Minimise Lattice Thermal Conductivity

J. Phys. Chem. Solids Pergamon Press 1970. Vol. 31, pp. 19–40. Printed in Great Britain.

LATTICE THERMAL CONDUCTIVITY OF SEMI-CONDUCTORS: A CHEMICAL BOND APPROACH

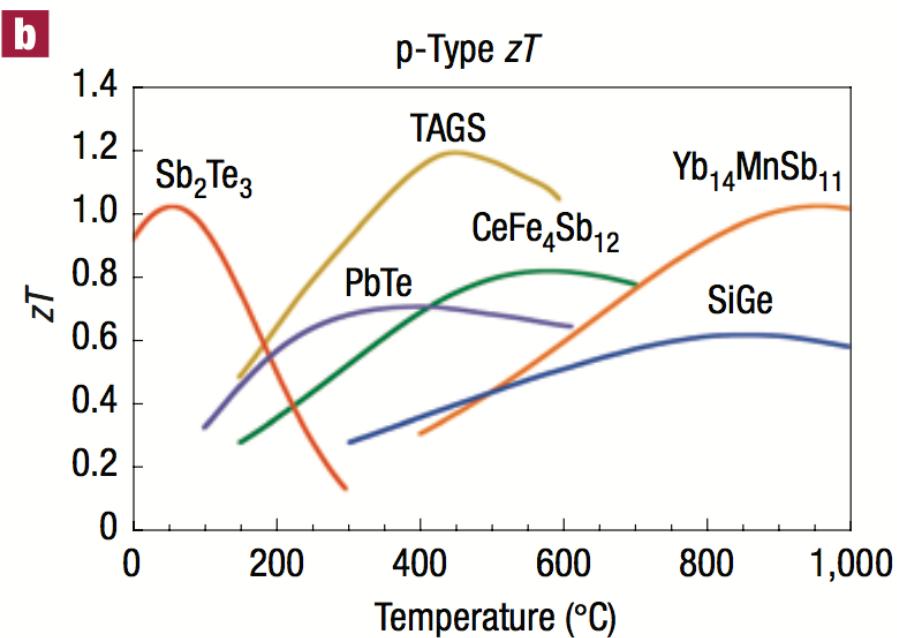
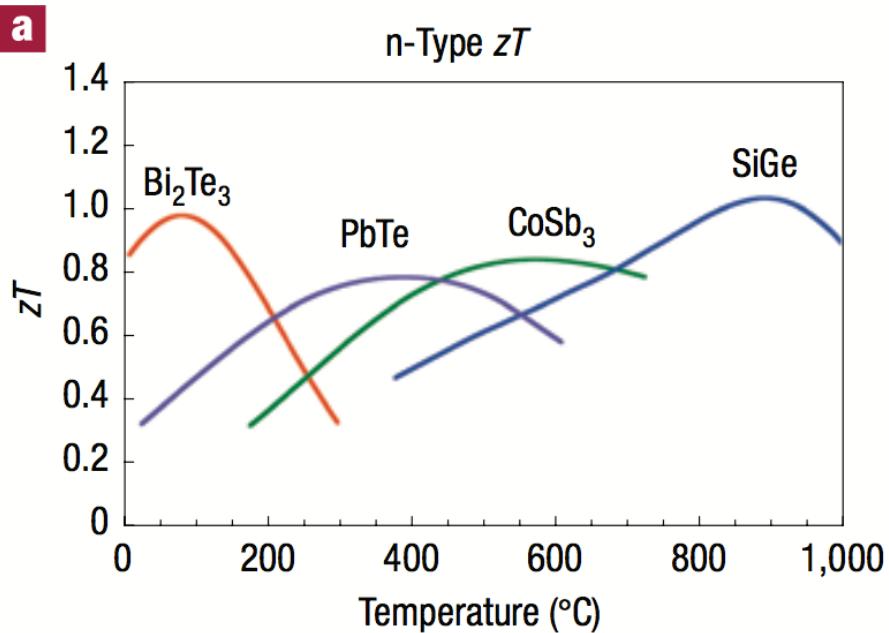
D. P. SPITZER

American Cyanamid Company, Stamford, Conn. 06904, U.S.A.

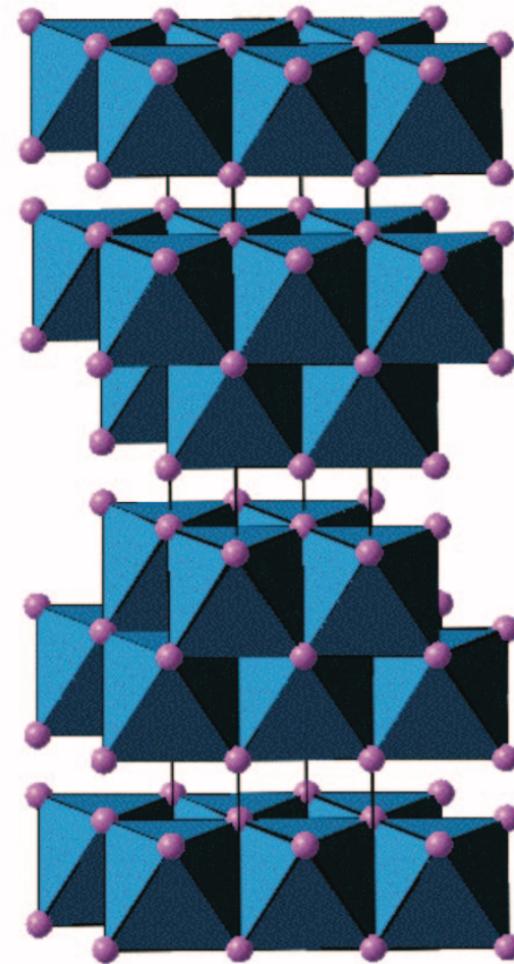
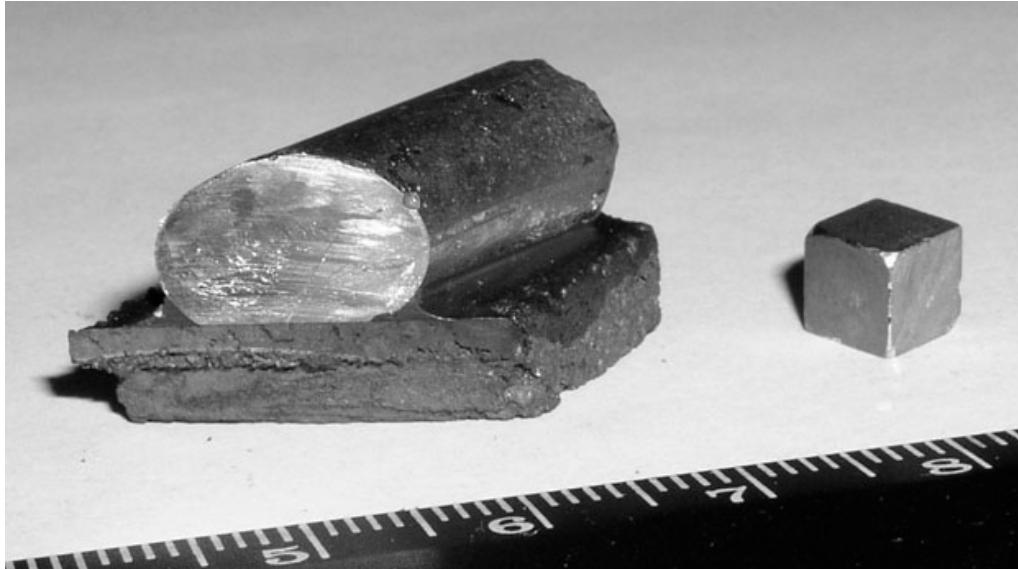
(Received 16 April 1969; in revised form 2 July 1969)

Abstract—Lattice thermal conductivity data at room temperature are compiled for more than 200 semiconductors. The data for over seventy semiconductors were obtained at our laboratory and are previously unpublished. It is found that lattice thermal conductivity may be correlated rather reliably with crystal structure. In general, increasing coordination of the ions is associated with decreasing thermal conductivity. Low thermal conductivity may also be caused by cation or anion vacancies. Only compounds which have predominantly tetrahedral bonding have thermal conductivities greater than 100 mW/cm·°C. All tetrahedrally-bonded compounds tend to have relatively high thermal conductivity, regardless of the complexity of their structure. At the other extreme, many compounds with higher coordination and partially-filled lattice sites have thermal conductivities below 10 mW/cm·°C. A majority of semiconductors have intermediate structures, and thermal conductivities within the range of values mentioned. Using these correlations, an unknown thermal conductivity can generally be estimated to within a factor of 2.

State of the Art (2008)



Prototype: Bi_2Te_3



[Thermoelectric Themed Issue] MRS Bulletin 31 (2006)

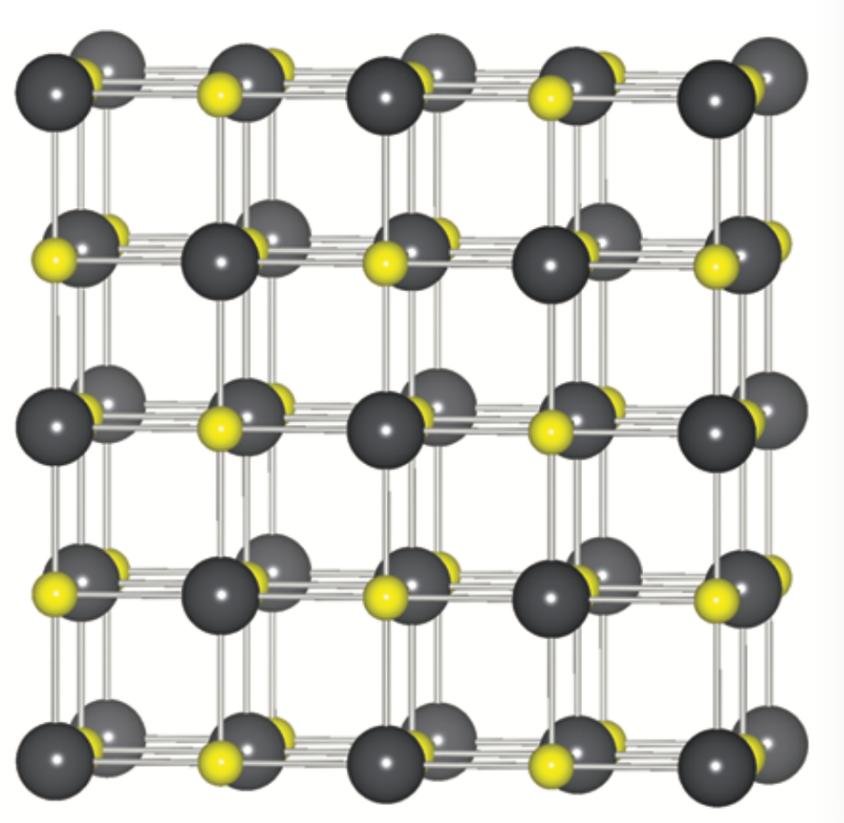
Prototype: Bi_2Te_3

Property	Value ($T = 300\text{K}$)
E_g	0.15 eV
m_p	0.1 / 0.3 m_e
ϵ_∞	85 / 50
ϵ_0	290 / 75
κ	$\sim 2 \text{ W/mK}$
μ	$> 1000 \text{ cm}^2/\text{Vs}$

Prototype: Bi_2Te_3

- Usually non-stoichiometric and naturally p-type
 - With specific growth techniques, n-type materials can be made (excess Te or I-doped)
- Thermal conductivity of $2 \text{ Wm}^{-1}\text{K}^{-1}$, which can be reduced by alloying (Sb,Bi or Se,Te) to enhance ZT to ~ 1 at room temperature
 - Example of a topological insulator

Prototype: PbTe



Prototype: PbTe

Property	Value ($T = 300K$)
E_g	0.31 eV
m_p	0.02 / 0.3 m_e
ϵ_∞	33
ϵ_0	414
κ	$\sim 2 \text{ W/mK}$
μ	$> 1500 \text{ cm}^2/\text{Vs}$

Prototype: PbTe

- Can be donor or acceptor doped to achieve p-type and n-type samples
 - Similar to Bi_2Te_3 , alloying can enhance performance (e.g. SnTe/PbTe mixtures)
 - Local structure is controversial: dynamic symmetry breaking with rocksalt on average

Case Study: Thermoelectrics

A. Materials and Devices

B. New Directions

An Ideal Thermoelectric Material

Metals are generally poor, while the best performance is achieved with low band gap semiconductors ($E_g \sim 10k_B T \sim 0.25$ eV)

- Low transport effective mass (conductivity)
- High electronic density of states (Seebeck)
- High carrier mobility (conductivity)
- Low lattice thermal conductivity (phonons)
- Tunable carrier concentrations (dopable)



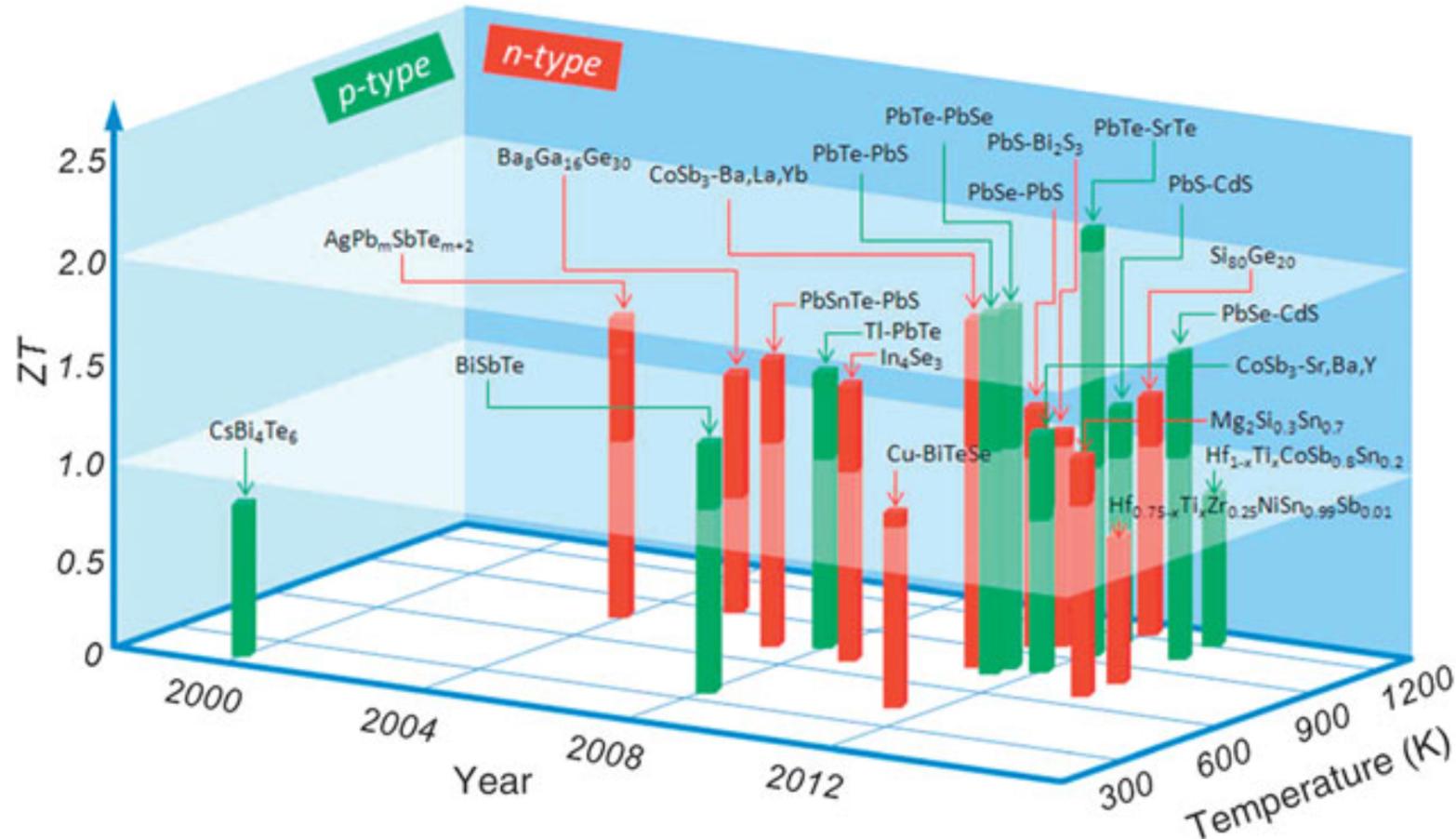
Design Principles

- **Phonon glass electron crystal** – proposed by G. A. Slack (1995) in CRC Thermoelectric Handbook
- **Rattling lattice** – reduced thermal conductivity with loosely bound atoms or molecules in open framework structures (e.g. clathrates). CoSb_3 -based skutterites with $ZT \sim 1.5$ above $T = 600$ K
- **Size variation** – light and heavy elements in the same structure to increase phonon scattering and minimise thermal conductivity, e.g. $\text{Cu}_2\text{ZnGeSe}_4$

Design Principles

- **Complex structures** – go beyond binary inorganic tetrahedral semiconductors, e.g. CsBi_4Te_6 has $ZT = 0.8$ at 225 K (40% better than Bi_2Te_3 related)
- **Nanosizing** – nanostructures can restrict thermal transport (enhancements seen for PbTe)

Recent Progress



Recent Champion: SnSe

LETTER

doi:10.1038/nature13184

Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals

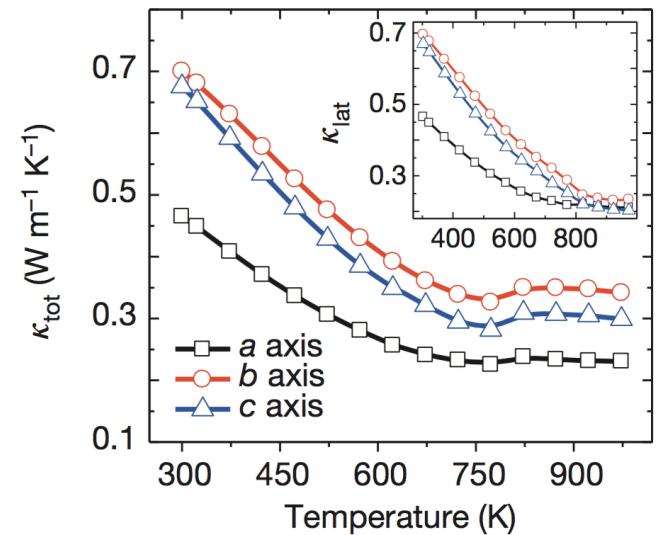
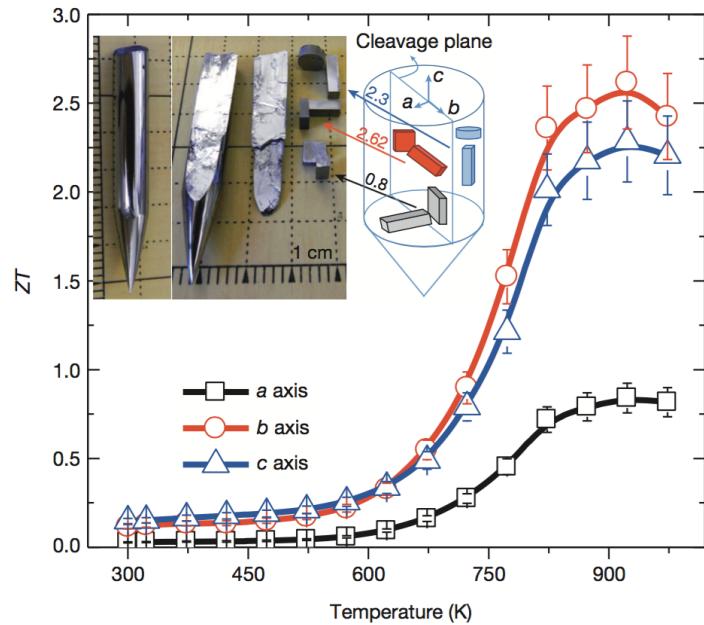
Li-Dong Zhao¹, Shih-Han Lo², Yongsheng Zhang², Hui Sun³, Gangjian Tan¹, Ctirad Uher³, C. Wolverton², Vinayak P. Dravid² & Mercouri G. Kanatzidis¹

The thermoelectric effect enables direct and reversible conversion between thermal and electrical energy, and provides a viable route for power generation from waste heat. The efficiency of thermoelectric materials is dictated by the dimensionless figure of merit, ZT (where Z is the figure of merit and T is absolute temperature), which governs the Carnot efficiency for heat conversion. Enhancements above the generally high threshold value of 2.5 have important implications for commercial deployment^{1,2}, especially for compounds free of Pb and Te. Here we report an unprecedented ZT of 2.6 ± 0.3 at 923 K, realized in SnSe single crystals measured along the b axis of the room-temperature orthorhombic unit cell. This material also shows a high ZT of 2.3 ± 0.3 along the c axis but a significantly reduced ZT of 0.8 ± 0.2 along the a axis. We attribute the remarkably high ZT along the b axis to the intrinsically ultralow lattice thermal conductivity in SnSe. The layered structure of SnSe derives from a distorted rock-salt structure, and features anomalously high Grüneisen parameters, which reflect the anharmonic and anisotropic bonding. We attribute the exceptionally low lattice thermal conductivity ($0.23 \pm 0.03 \text{ W m}^{-1} \text{ K}^{-1}$ at 973 K) in SnSe to the anharmonicity. These findings highlight alternative strategies to nanostructuring for achieving high thermoelectric performance.

power factor (along the b axis), but, even more surprisingly, we observe that the thermal conductivity of SnSe is intrinsically ultralow ($<0.25 \text{ W m}^{-1} \text{ K}^{-1}$ at >800 K), resulting in $ZT = 2.62$ at 923 K along the b axis and 2.3 along the c axis; these represent the highest ZT values reported so far for any thermoelectric system. Along the a direction, however, ZT is significantly lower, ~ 0.8 . Here, it should be noted that SnSe along the b axis shows a room-temperature $ZT = 0.12$, which is comparable to the room-temperature value of 0.15 reported earlier¹⁹. SnSe, however, reveals high ZT values near and above the transition temperature of 750 K at which the structure converts from $Pnma$ to $Cmcm$ ^{20–22}. Such ultrahigh ZT along two principal directions and the observed crystallographic and ZT anisotropy prompted us to investigate the scientific underpinning of these intriguing results.

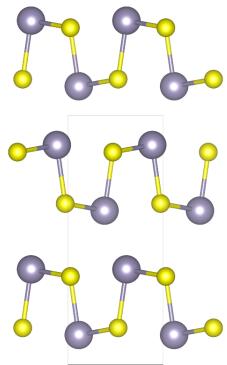
SnSe adopts a layered orthorhombic crystal structure at room temperature, which can be derived from a three-dimensional distortion of the NaCl structure. The perspective views of the room-temperature SnSe crystal structure along the a , b and c axial directions are shown in Fig. 1a–d. There are two-atom-thick SnSe slabs (along the b – c plane) with strong Sn–Se bonding within the plane of the slabs, which are then linked with weaker Sn–Se bonding along the a direction²⁰. The structure contains highly distorted SnSe₇ coordination polyhedra, which have

Recent Champion: SnSe

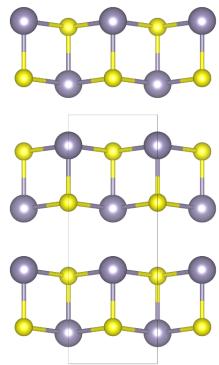


Thermal conductivity

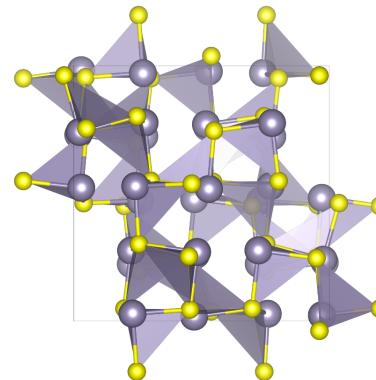
Tin Sulfides and Selenides



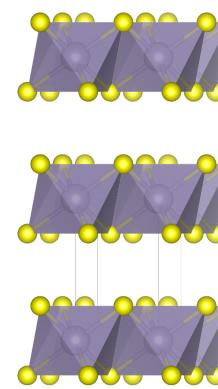
SnS (*Pnma*)



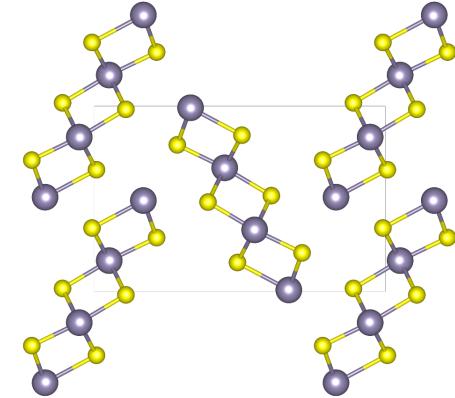
SnS (*Cmcm*)



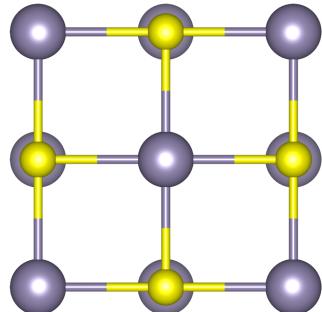
SnS (π -cubic)



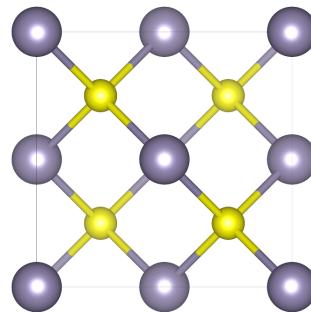
SnS₂



Sn₂S₃



SnS (Rocksalt)



SnS (Zincblende)

SnSe

Property	Value ($T = 300K$)
E_g	0.9 eV
m_p	$0.15 / 0.5 m_e$
ϵ_∞	13 / 17 / 16
ϵ_0	45 / 62 / 42
κ	< 1 W/mK
μ	> 7000 cm ² /Vs

SnSe: Anharmonic Vibrations

nature
physics

ARTICLES

PUBLISHED ONLINE: 19 OCTOBER 2015 | DOI: 10.1038/NPHYS3492

Orbitally driven giant phonon anharmonicity in SnSe

C. W. Li^{1†}, J. Hong^{1†}, A. F. May¹, D. Bansal¹, S. Chi², T. Hong², G. Ehlers² and O. Delaire^{1*}

Understanding elementary excitations and their couplings in condensed matter systems is critical for developing better energy-conversion devices. In thermoelectric materials, the heat-to-electricity conversion efficiency is directly improved by suppressing the propagation of phonon quasiparticles responsible for macroscopic thermal transport. The current record material for thermoelectric conversion efficiency, SnSe, has an ultralow thermal conductivity, but the mechanism behind the strong phonon scattering remains largely unknown. From inelastic neutron scattering measurements and first-principles simulations, we mapped the four-dimensional phonon dispersion surfaces of SnSe, and found the origin of the ionic-potential anharmonicity responsible for the unique properties of SnSe. We show that the giant phonon scattering arises from an unstable electronic structure, with orbital interactions leading to a ferroelectric-like lattice instability. The present results provide a microscopic picture connecting electronic structure and phonon anharmonicity in SnSe, and offers new insights on how electron-phonon and phonon-phonon interactions may lead to the realization of ultralow thermal conductivity.

SnSe: Anharmonic Vibrations

PRL 117, 075502 (2016)

PHYSICAL REVIEW LETTERS

week ending
12 AUGUST 2016

Anharmonicity in the High-Temperature *Cmcm* Phase of SnSe: Soft Modes and Three-Phonon Interactions

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Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom

Chang-Eun Kim and Aloysius Soon

Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea

John Buckeridge, Alexey A. Sokol, and C. Richard A. Catlow

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20 Gordon Street, London WC1H 0AJ, United Kingdom*

Atsushi Togo and Isao Tanaka

Elements Strategy Initiative for Structural Materials, Kyoto University, Kyoto Prefecture 606-8501, Japan

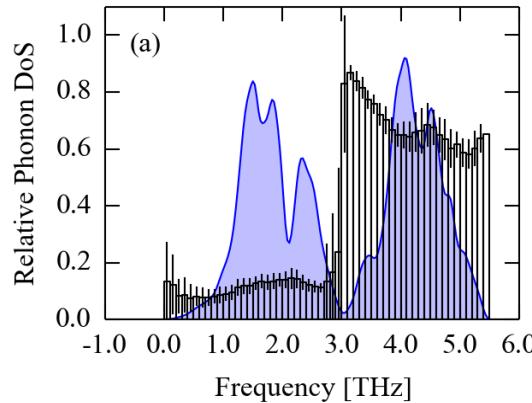
(Received 13 January 2016; published 10 August 2016)

The layered semiconductor SnSe is one of the highest-performing thermoelectric materials known. We demonstrate, through a first-principles lattice-dynamics study, that the high-temperature *Cmcm* phase is a dynamic average over lower-symmetry minima separated by very small energetic barriers. Compared to the low-temperature *Pnma* phase, the *Cmcm* phase displays a phonon softening and enhanced three-phonon scattering, leading to an anharmonic damping of the low-frequency modes and hence the thermal transport. We develop a renormalization scheme to quantify the effect of the soft modes on the calculated properties, and confirm that the anharmonicity is an inherent feature of the *Cmcm* phase. These results suggest a design concept for thermal insulators and thermoelectric materials, based on displacive instabilities, and highlight the power of lattice-dynamics calculations for materials characterization.

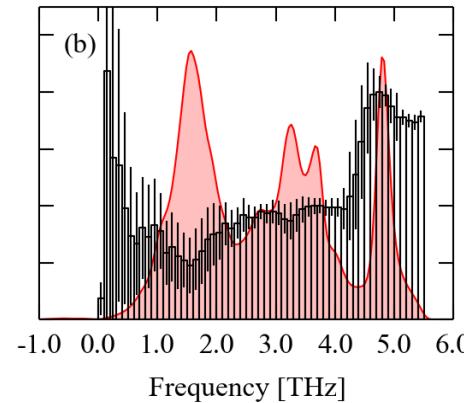
SnSe: Anharmonic Vibrations

High T soft phonons enhance anharmonicity

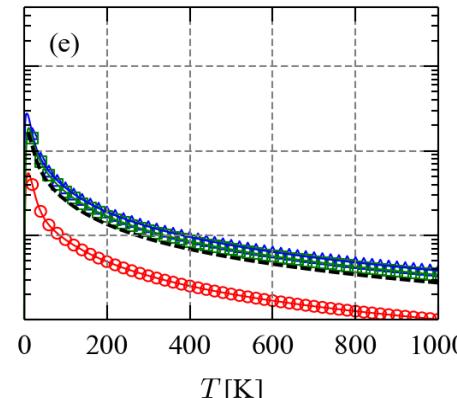
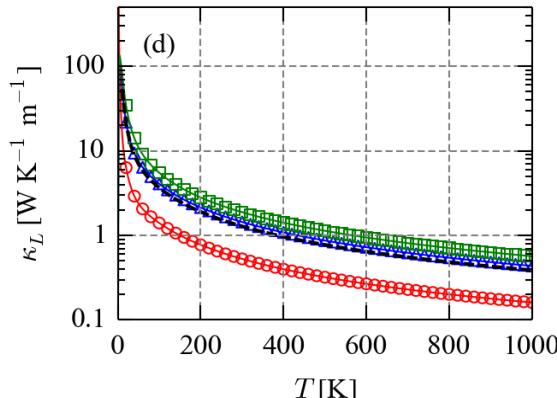
Pnma



Cmcm

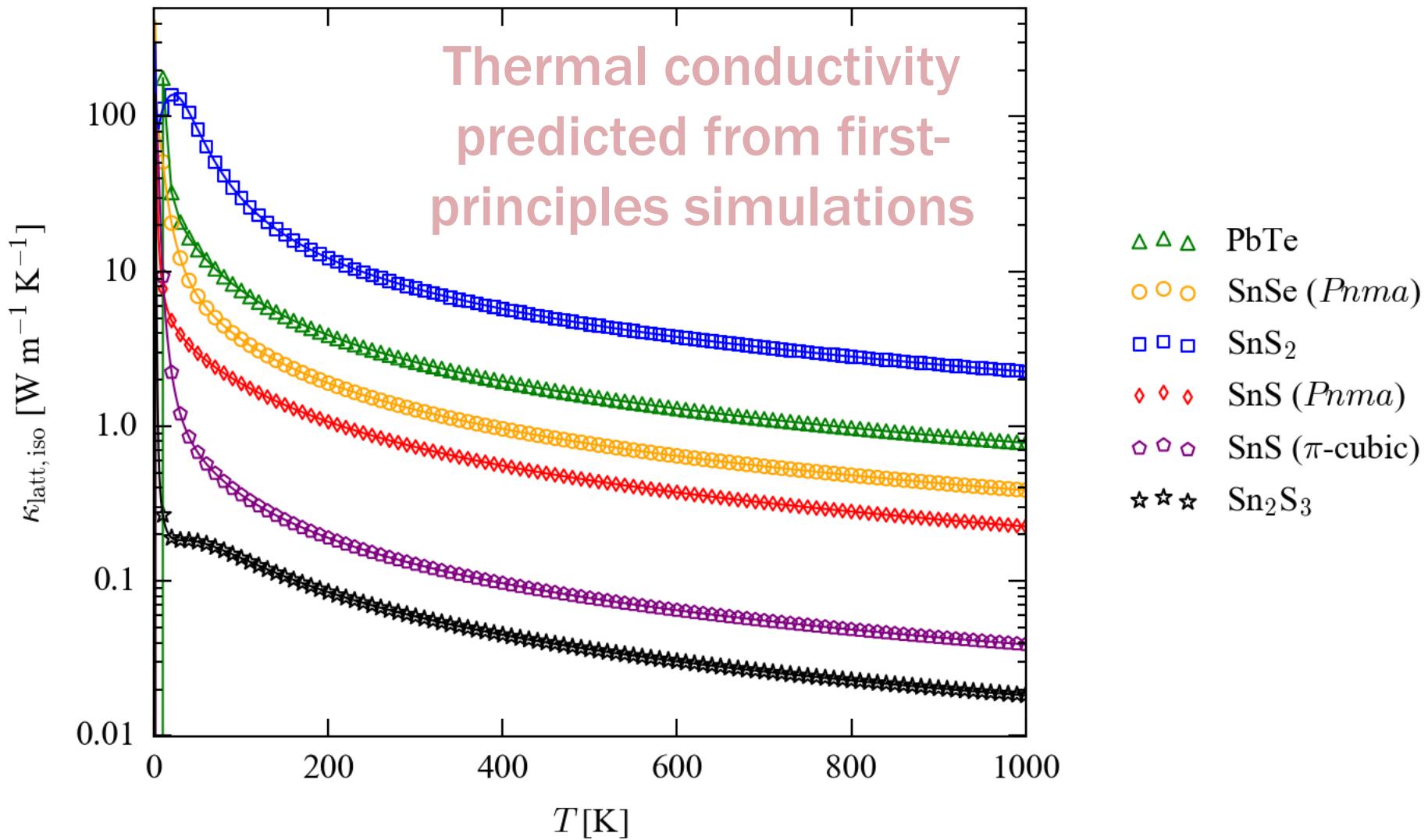


Phonon
interaction
strength



Lattice
thermal
conductivity

From Selenides to Sulfides



Summary – Key Points

- Origins and applications of thermoelectric effect
- How properties defining ZT figure of merit can be controlled
- A well-defined figure of merit can focus research effort and aid in discovery and design of new materials