# Renewable Approaches to Distributed Energy Storage

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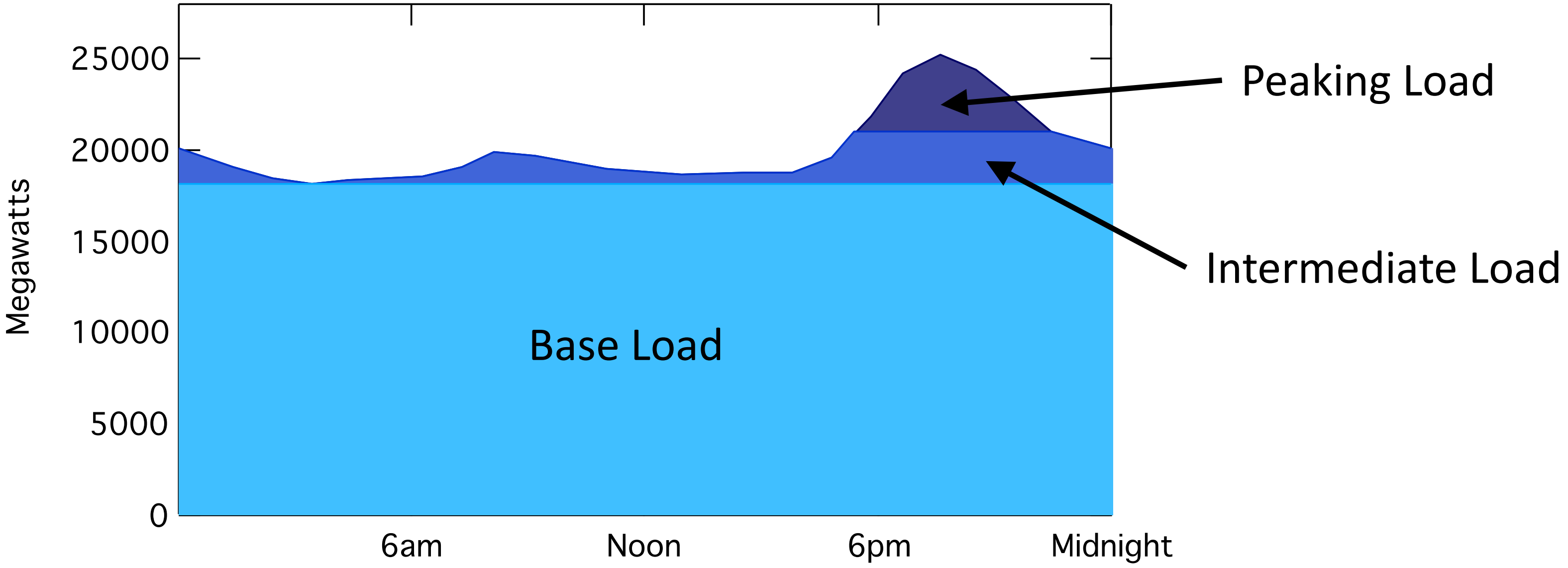
# 30 minute goals

- Appreciate **grid complexities & need for storage**
- Storage approaches & identify **primary approaches** to distributed storage
- Define challenges & opportunities within t**hermal energy storage**
- Consider role of **thermoelectrics materials** and material design strategies
- Thermoelectric search strategies

# Today: Storage, the electric grid, and its components

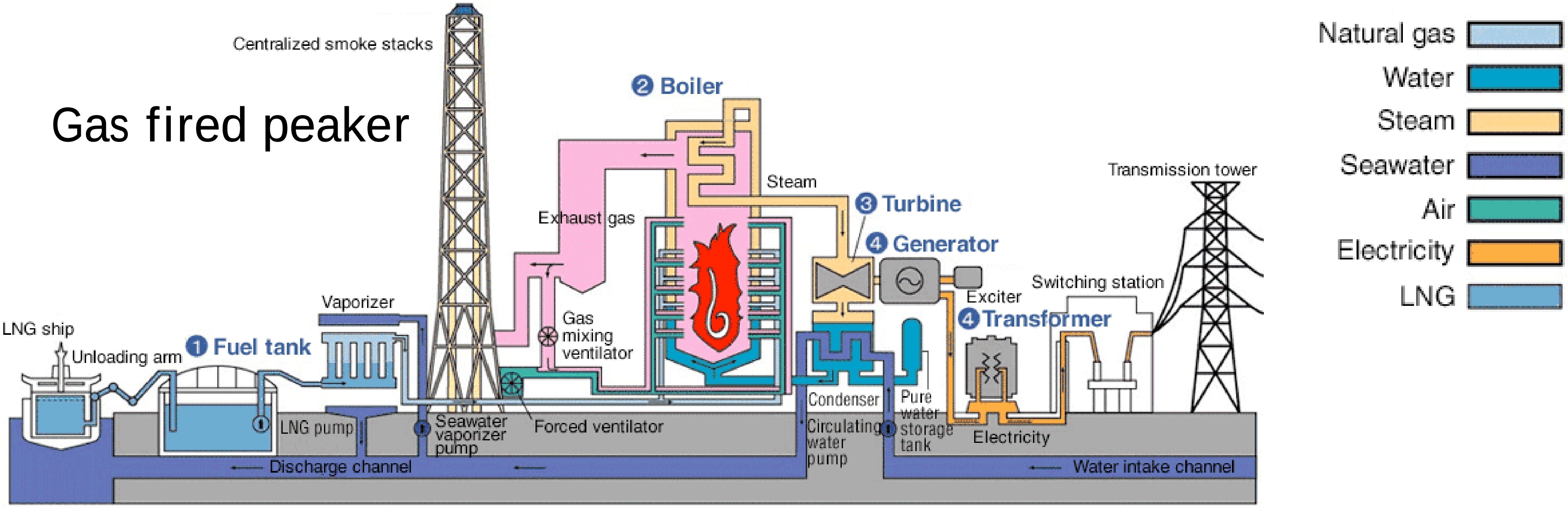
- Current electric grid has **virtually no built-in storage** capacity
- Plants are ramped on and off based on current demand



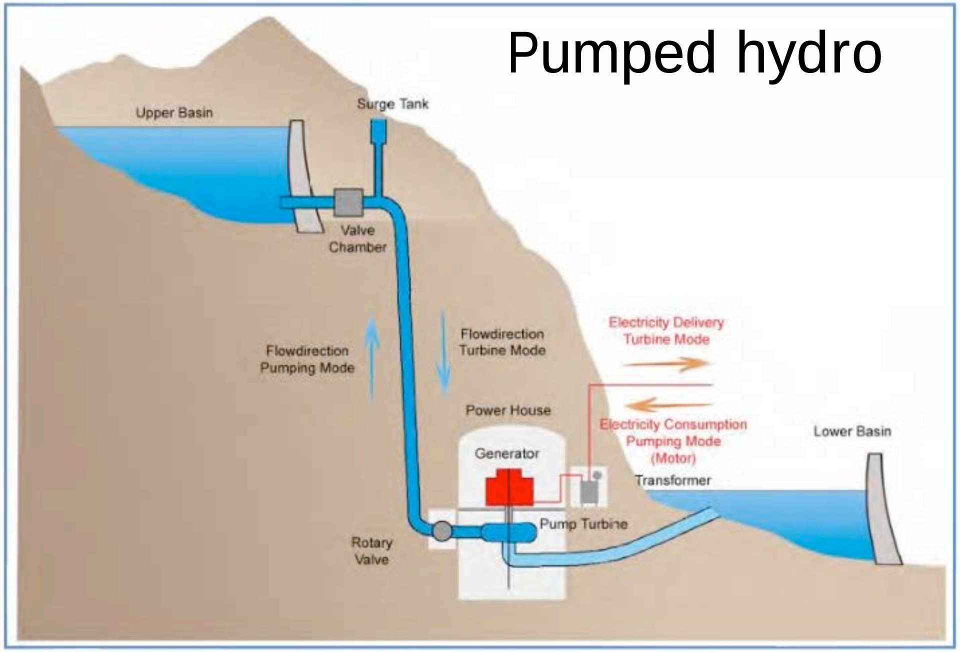
- Current demand: Large ***base load*** with hourly fluctuations due to lifestyle patterns

# Addressing fluctuations: Peaking sources today

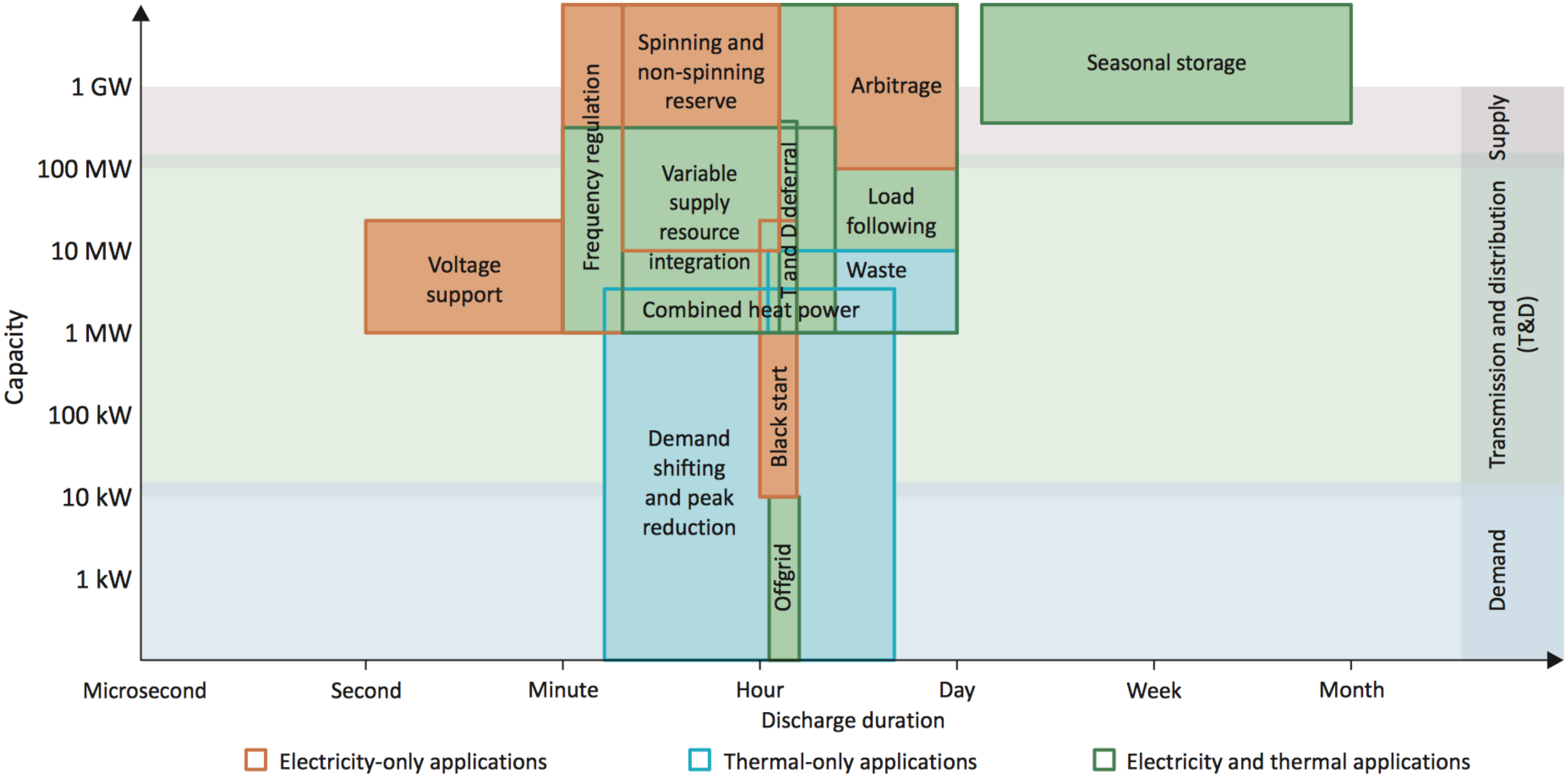
Gas fired peaker



Pumped hydro

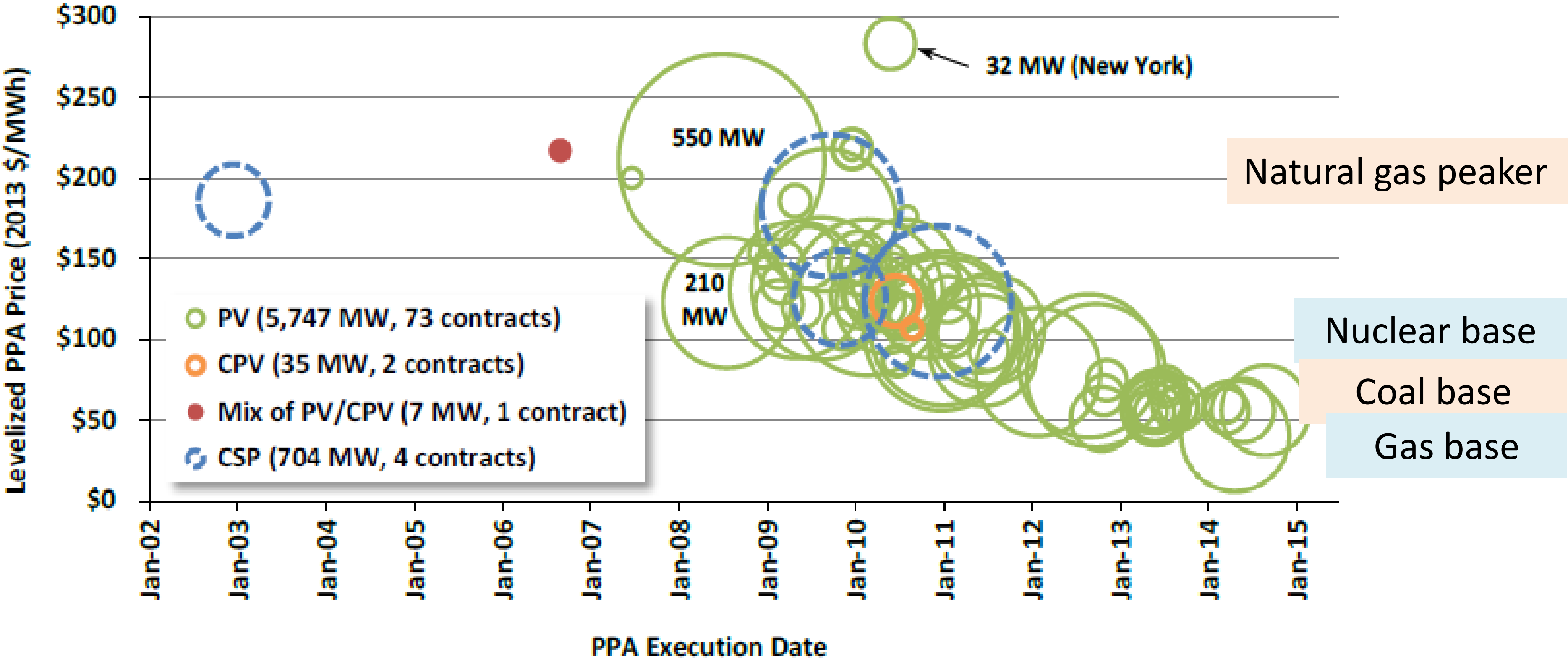


# Figure 1: Power requirement versus discharge duration for some applications in today's energy system



Sources: modified from IEA (2014), Energy Technology Perspectives, OECD/IEA, Paris, France. Battke, B., T.S. Schmidt, D. Grosspietsch and V.H. Hoffmann (2013), "A review and probabilistic model of lifecycle costs of stationary batteries in multiple applications", *Renewable and Sustainable Energy Reviews* Vol. 25, pp. 240-250. EPRI (Electric Power Research Institute) (2010), "Electrical Energy Storage Technology Options", Report, EPRI, Palo Alto, CA, United States. Sandia National Laboratories (2010), *Energy Storage for the Electricity Grid: Benefits and Market Potential Assessment Guide, A Study for the DOE Energy Storage Systems*, Albuquerque, NM and Livermore, CA, United States. IEA-ETSAP (Energy Technology Systems Analysis Programme) and IRENA (2013), "Thermal Energy Storage", Technology Brief E17, Bonn, Germany.

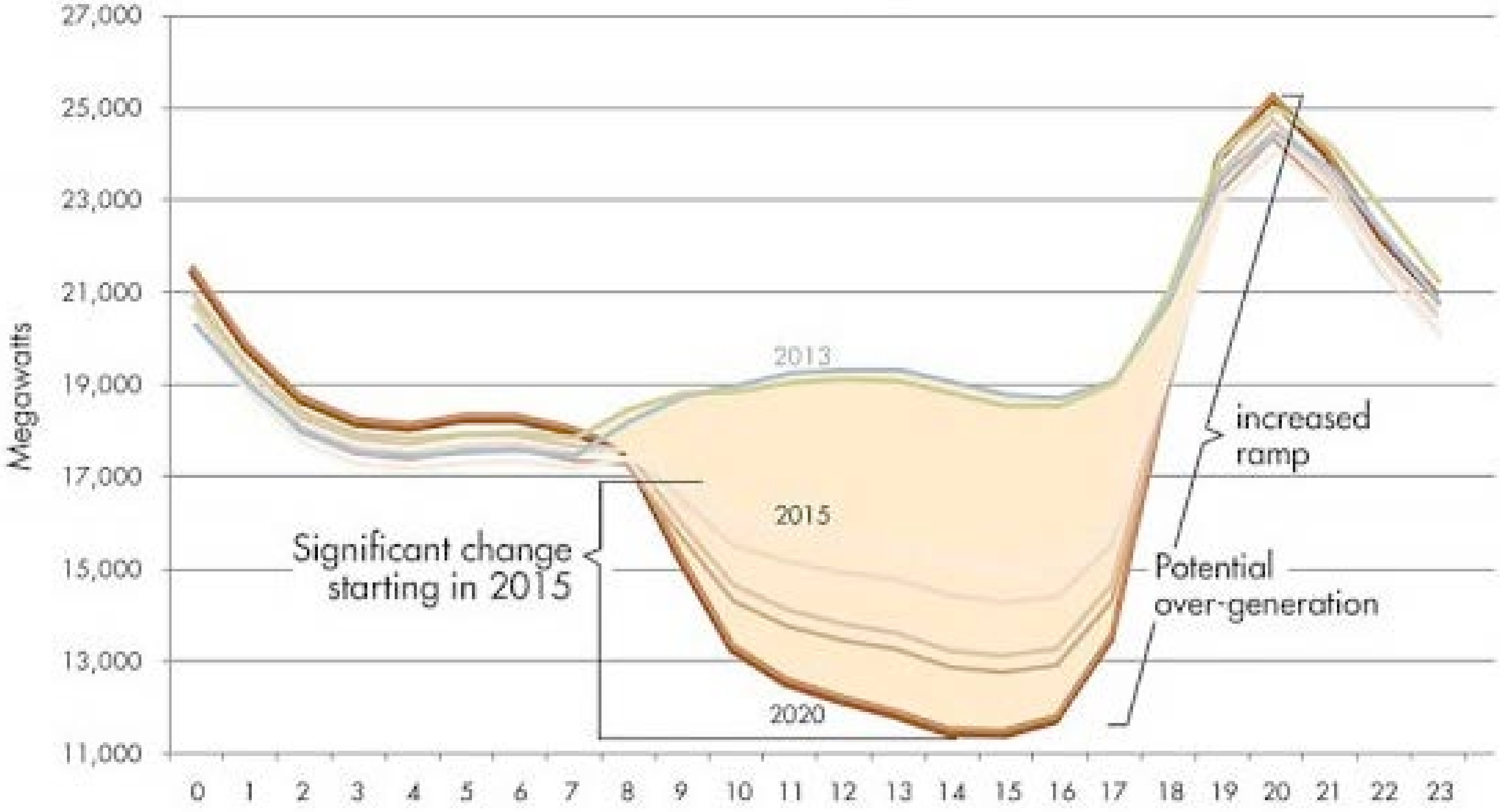
# Grid is changing due to falling price of solar electricity



- Factor of **4** drop in installed PV price in last **5** years
- PV now at grid **parity** w/ non-renewable sources
- 50% of new grid installations are PV!

# Challenge of PV and increased grid penetration

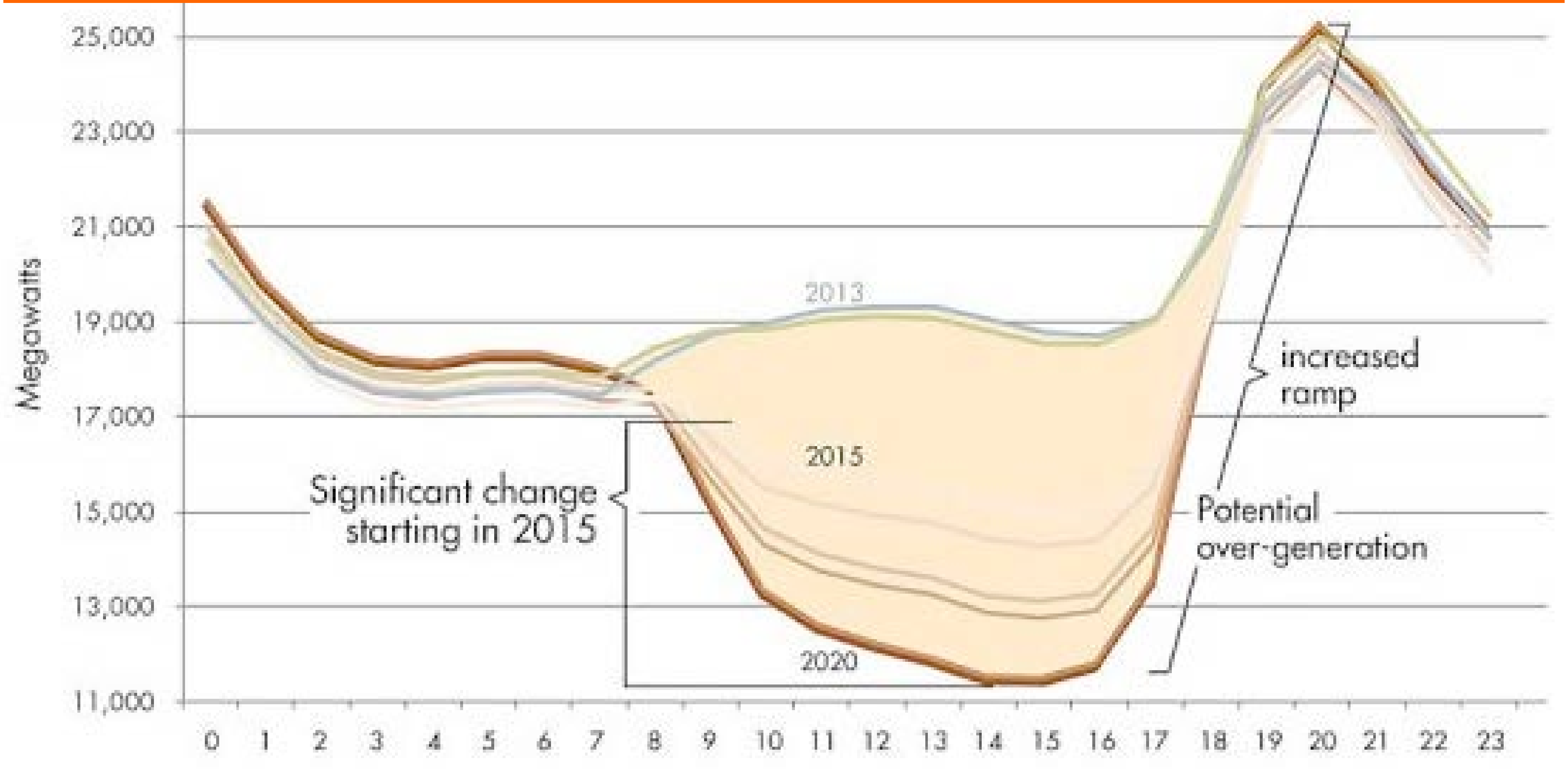
- Photovoltaics are considered a ***variable*** source and when penetration is large, can lead to over-generation
- Base load plants do not want to be throttled down



# Need renewable sources of electricity at night

- ***Dispatchable*** renewable sources needed to smooth out renewable, variable production curve
- Will ultimately lead to reduced carbon-derived base load

**If we don't solve the storage problem, PV's impact will be limited**



# A renewable grid

Daytime electricity from PV

Carbon neutral route to address nighttime electricity demand

?

Need to ***time-shift*** solar energy into periods where sun is ‘off’

**Unclear** what renewable storage technology will emerge with sufficiently low $/kWh to compete with natural gas peaking plants

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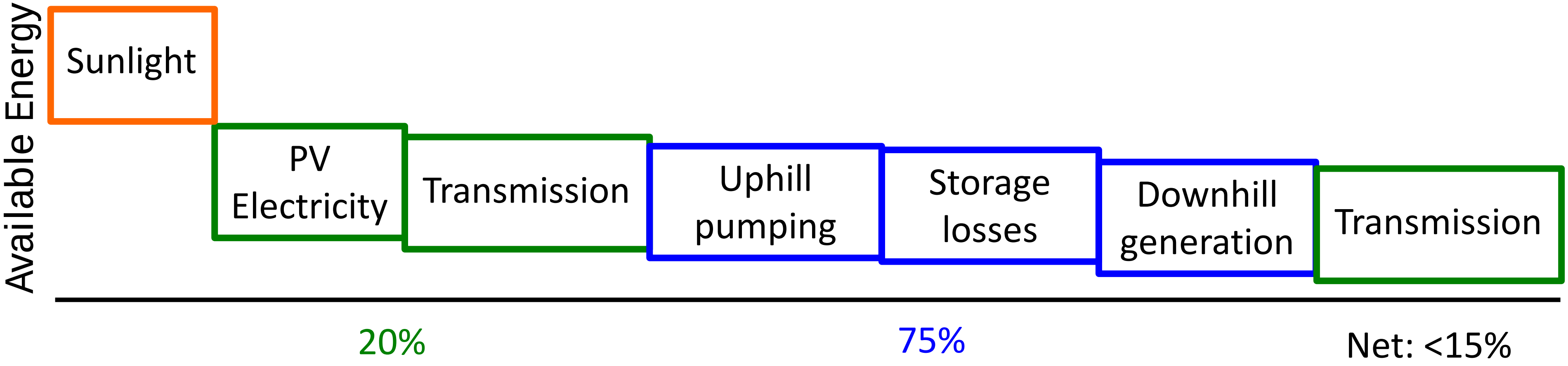
# Carbon-neutral storage approaches

* wind, PV

| Internal energy: | Example: | Renewable Source: |
|---|---|---|
| Gravity | Pumped hydro | Indirect solar* |

“Indirect source” example:

99% of bulk storage capacity worldwide



Pro:
Separate optics from storage

Con:
Additional energy conversion steps lead to reduced overall efficiency

# Carbon-neutral storage approaches

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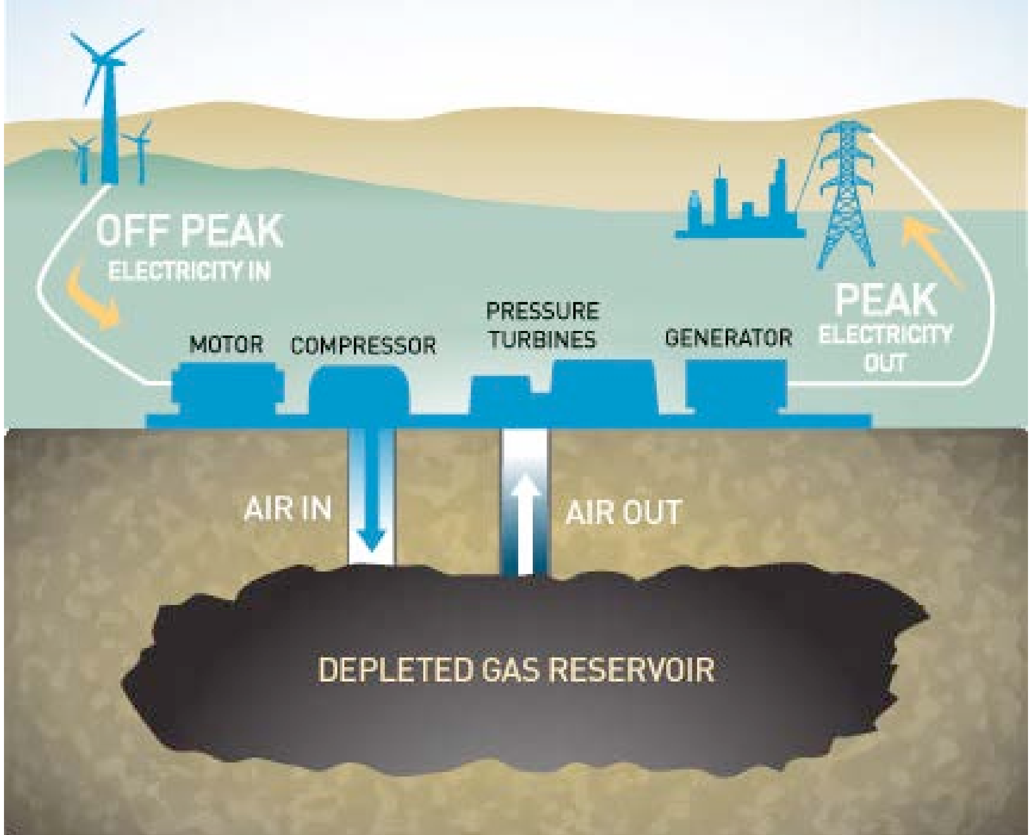

Gas Storage Location:
Caverns, potentially depleted gas reservoirs (PG&E, ongoing)

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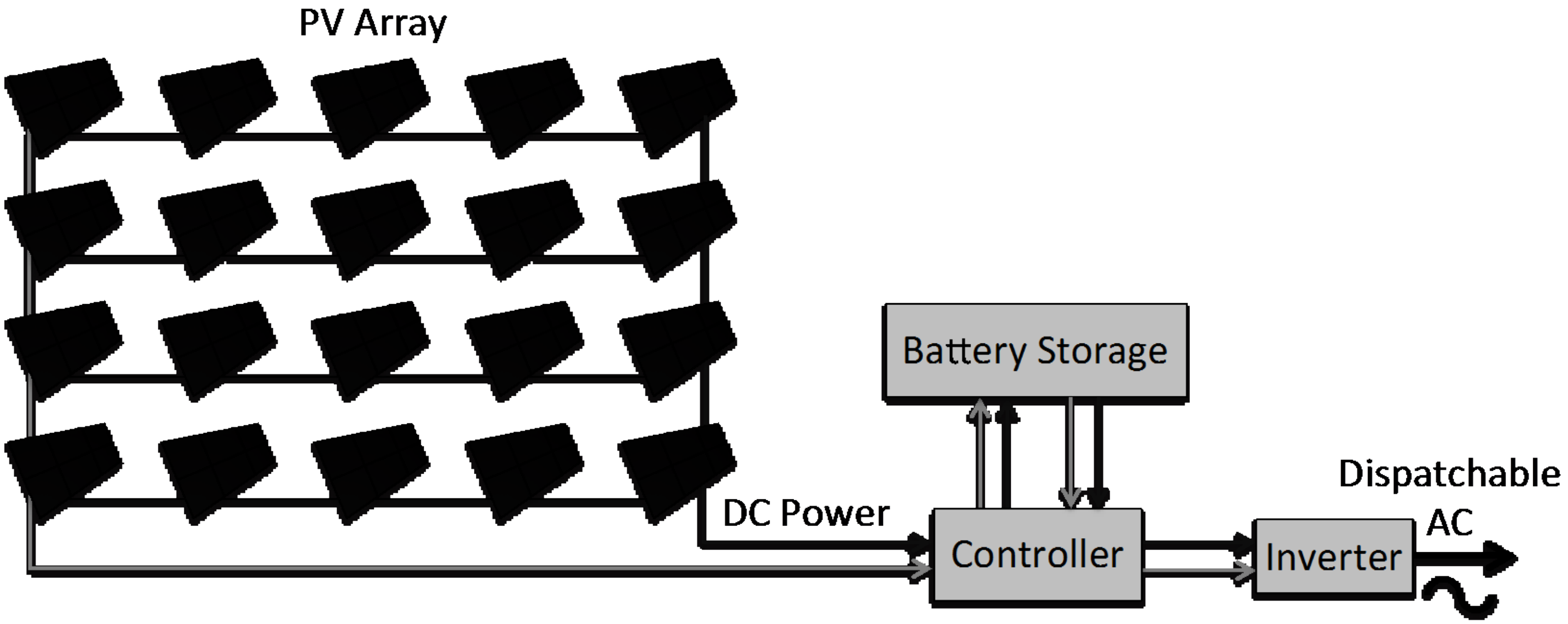

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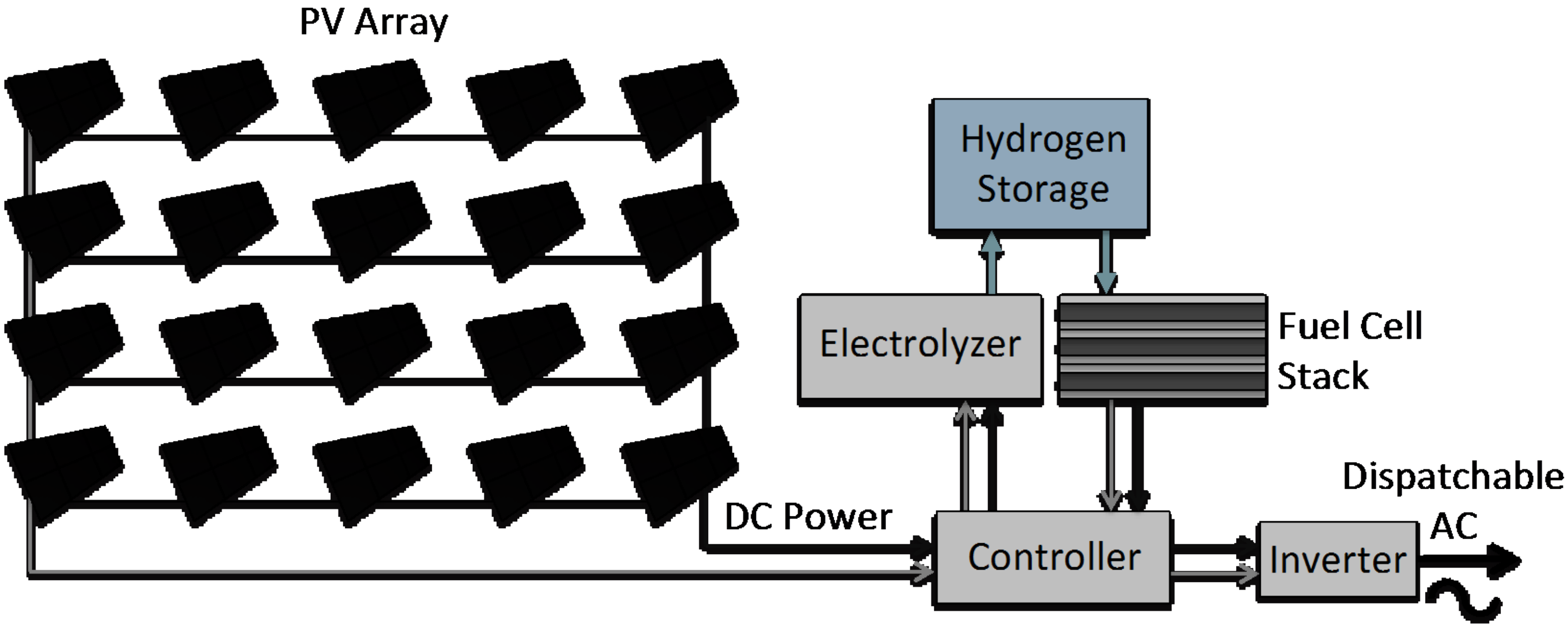

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| Kinetic | Flywheels | Indirect solar |
| Chemical | Solar biofuels, thermochemical | Direct abs. |

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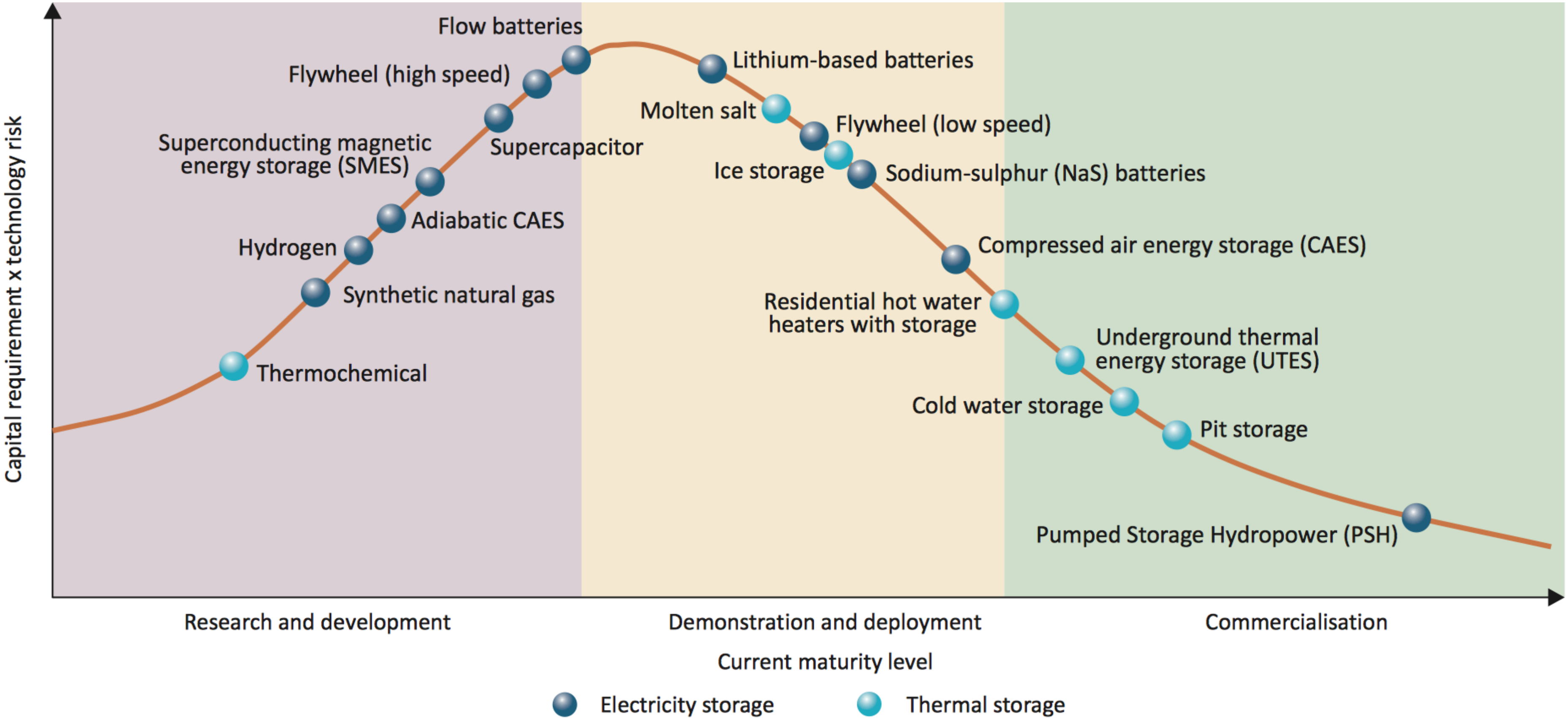
| Temperature | Heat engines, refrigeration | Direct or indirect |

## Figure 3: Maturity of energy storage technologies



Source: Decourt, B. and R. Debarre (2013), “Electricity storage”, *Factbook*, Schlumberger Business Consulting Energy Institute, Paris, France and Paksoy, H. (2013), “Thermal Energy Storage Today” presented at the IEA Energy Storage Technology Roadmap Stakeholder Engagement Workshop, Paris, France, 14 February.

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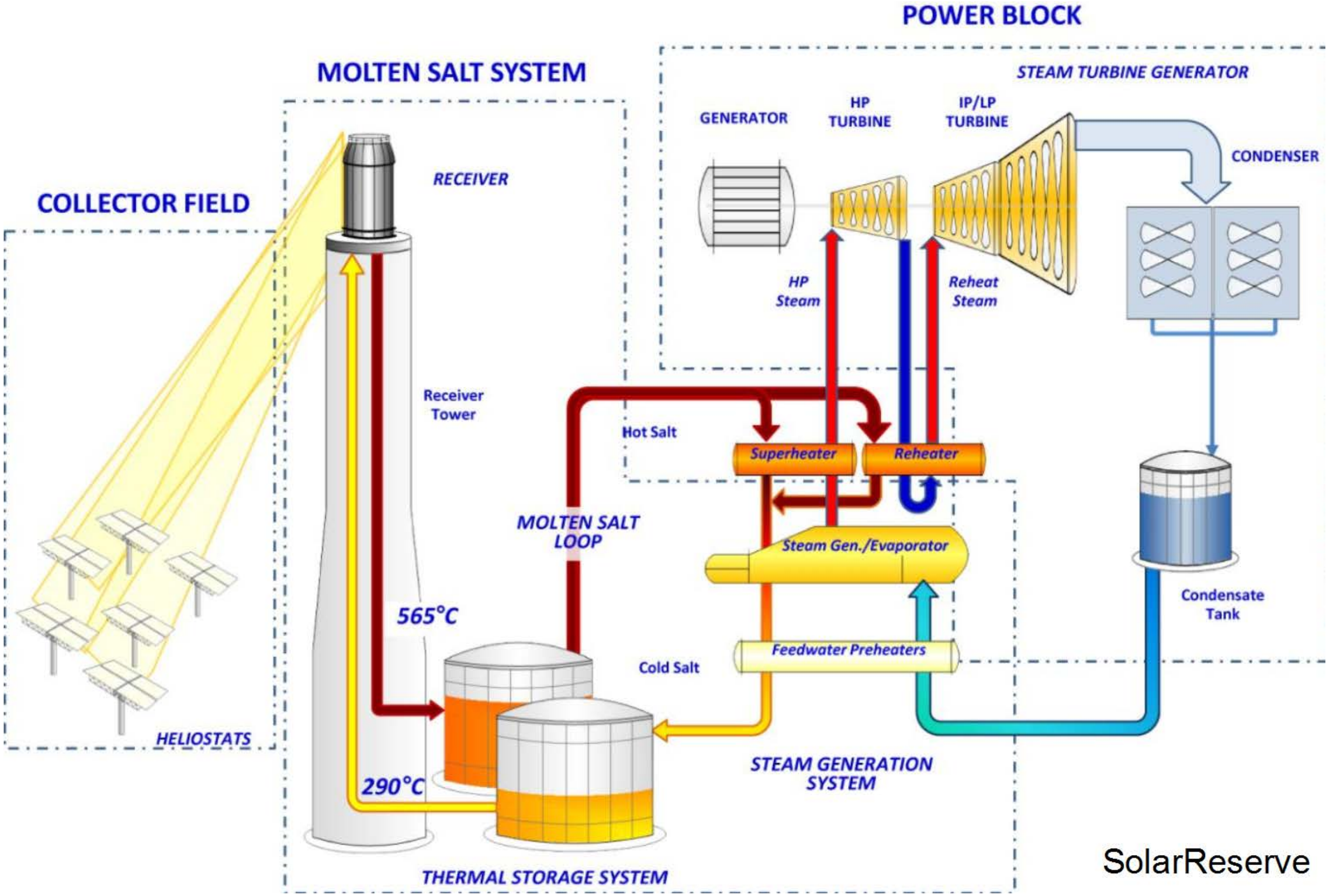
To centralize or distribute?

# Why centralized storage technologies?

Storage involving mechanical turbines & generators typically must be **large** (MW-scale) to achieve high **efficiencies** due to **power block scaling issues** & costs which do not scale **linearly** w/ size



SolarReserve

# Why distributed storage technologies?

- Smaller construction costs enable greater iteration rate (faster learning curve)
- Grid security
- Transmission losses & less disruptive to existing grid
- Co-generation opportunities for enhanced efficiency
- Technology can still be centralized (modularity) if desired

# Distributed storage approaches

Distributed storage requires

- efficiency at small scales
- simplicity
- low operation/maintenance costs
- safety
- silence
- small footprint

Today's focus

| Internal energy: | Example: |
|---|---|
| Gravity | Pumped hydro |
| Pressure | Compressed air |
| Electrochemical | Electrolyzers, **batteries** |
| Electromagnetic | Superconducting coils |
| Kinetic | Flywheels |
| Chemical | Solar biofuels, thermochemical |
| Temperature | **Heat engines, refrigeration** |

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# Indirect storage: Thermal storage through refrigeration

Assume smart metering implemented
(variable electricity cost):

Electricity production approaching overcapacity

Refrigerator solidifies phase change material (PCM)

Air conditioning transitions PCM back to liquid

Could be implemented today w/ traditional compression refrigeration

In future: Peltier (thermoelectric) coolers

# Direct storage: Can we shrink concentrated solar thermal?

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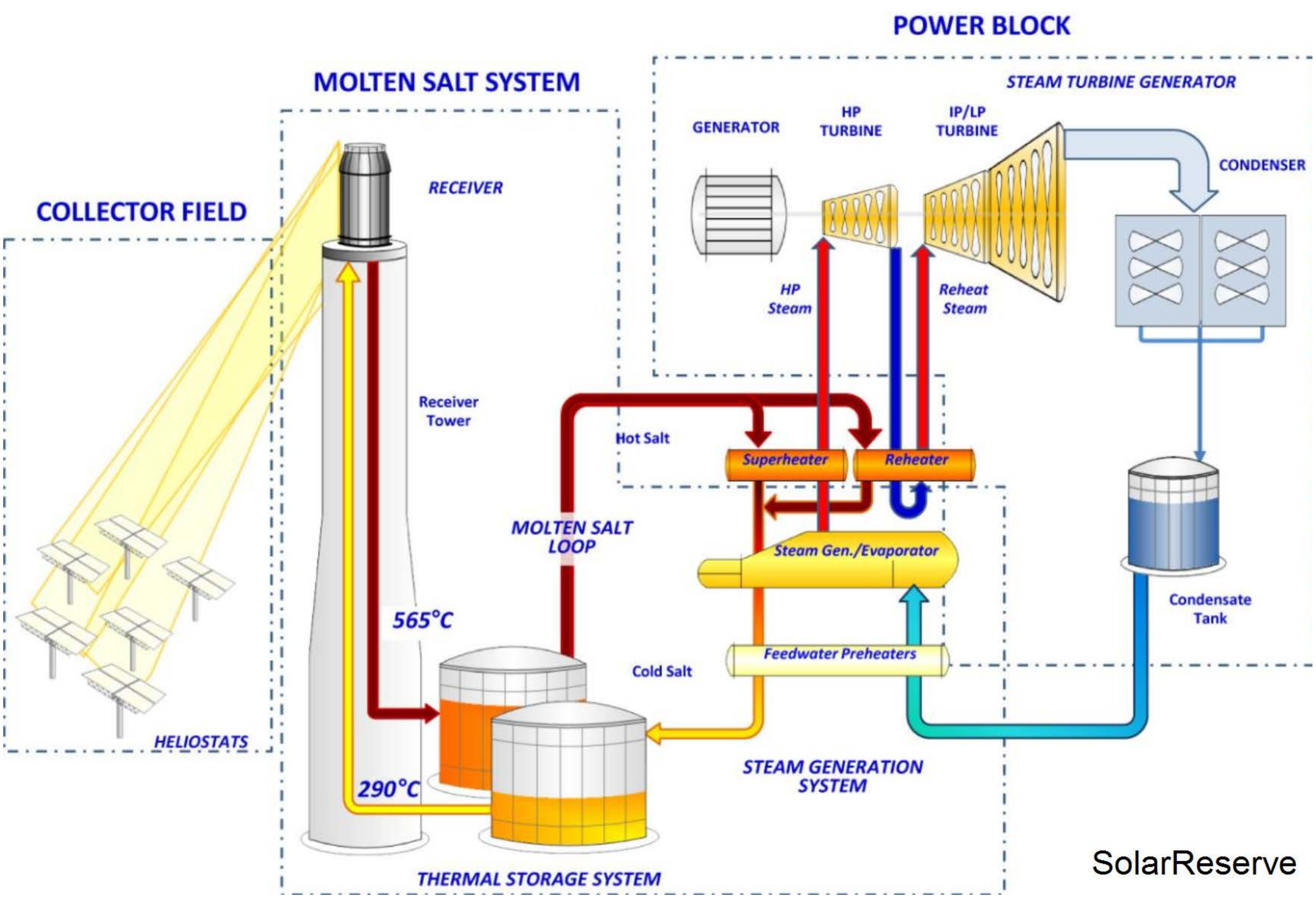
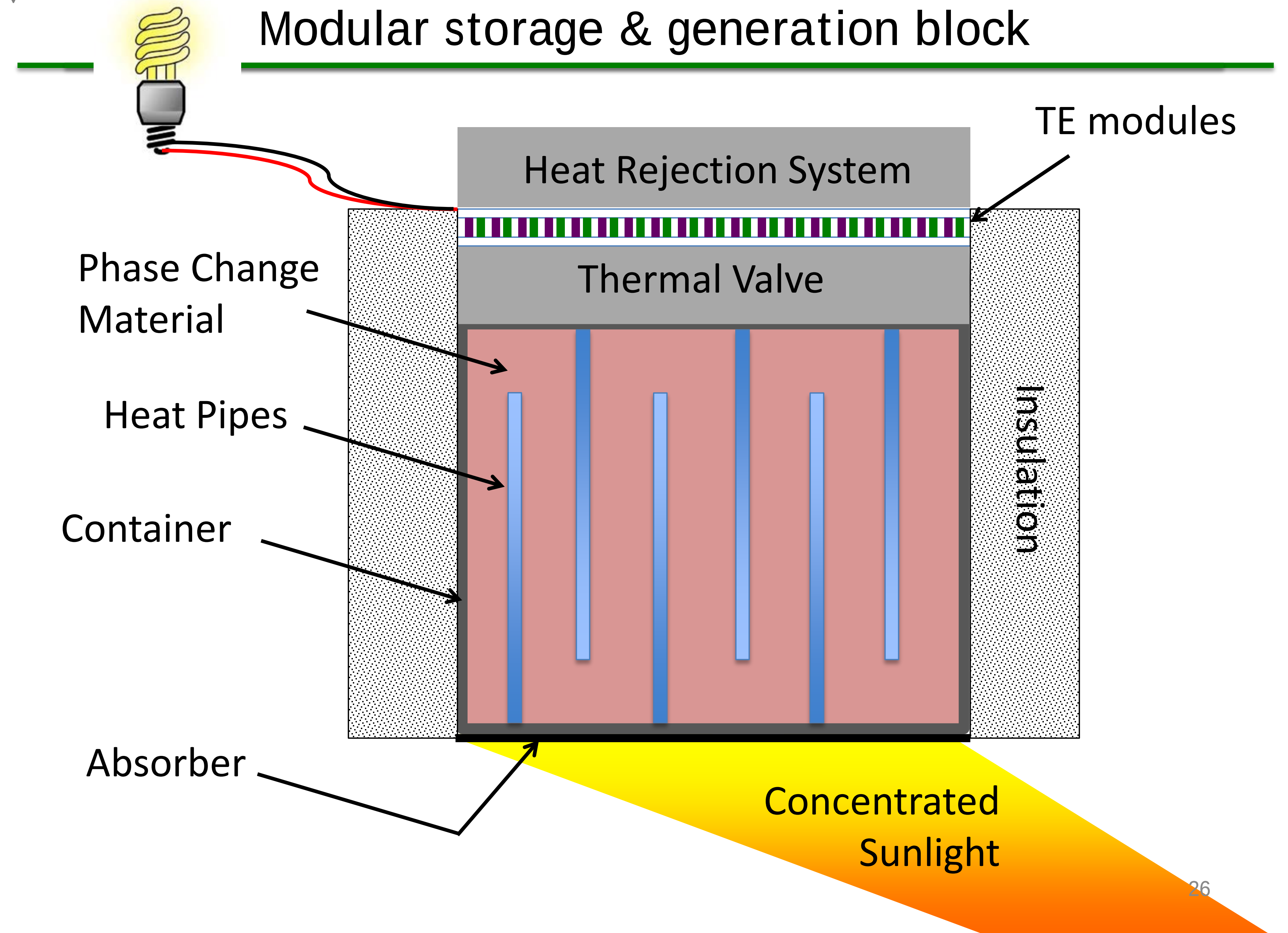


SolarReserve

# Modular storage & generation block



# Direct storage: Can we shrink concentrated solar thermal?

| Need to satisfy: | |
|---|---|
| efficiency at small scales<br>silence | Turbine → Solid state thermoelectric generator |
| simplicity<br>low operation/maintenance costs | Pumped working fluid → “static” system, minimal moving parts |
| safety | Non-flammable working fluid |
| small footprint | Sensible heat storage → Phase change material with high latent heat |
| dispatchability | Pumped working fluid → “thermal valve” |

arpa·e

**S**olar **T**hermo**e**lectricity vi**a** **A**dvanced **L**atent Heat **S**torage (**STEALS**)

# Thermoelectric generators

Overall system design driven largely by thermoelectric generators

- Efficiency driven by Carnot and material terms:

$$\eta = \eta_{Carnot}\,\eta_{Materials}$$

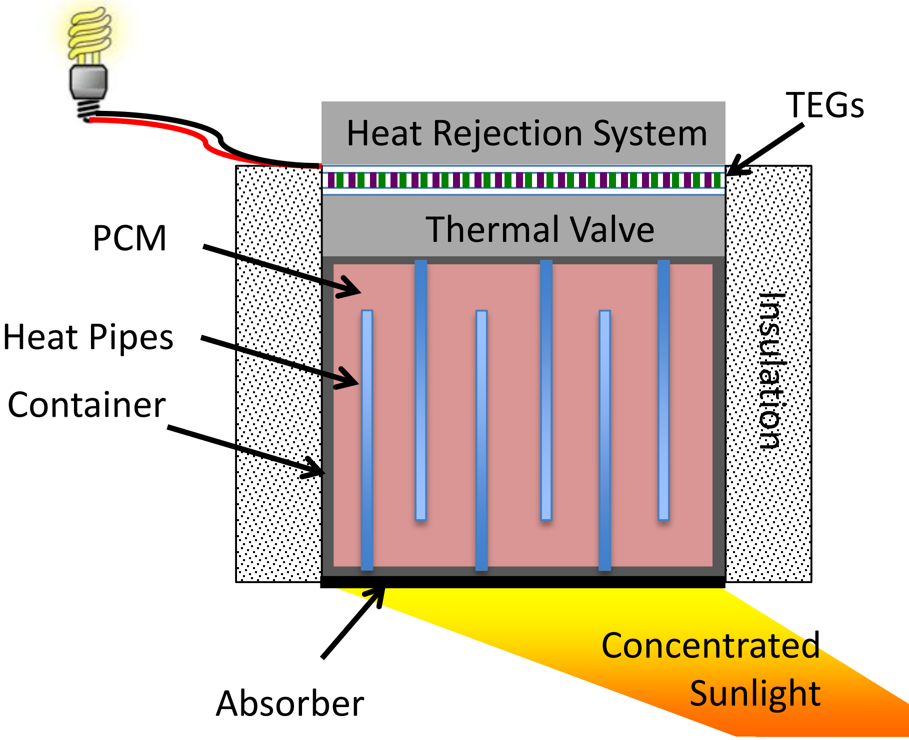
$$\eta_{Carnot} = \frac{T_{hot} - T_{cold}}{T_{hot}}$$

- Maximize $T_{hot}$ for efficiency
- However, $T_{hot}$ impacts radiation, material selection & corrosion

Compromise:

~600C (steel rather than exotic alloys)

Still good efficiencies



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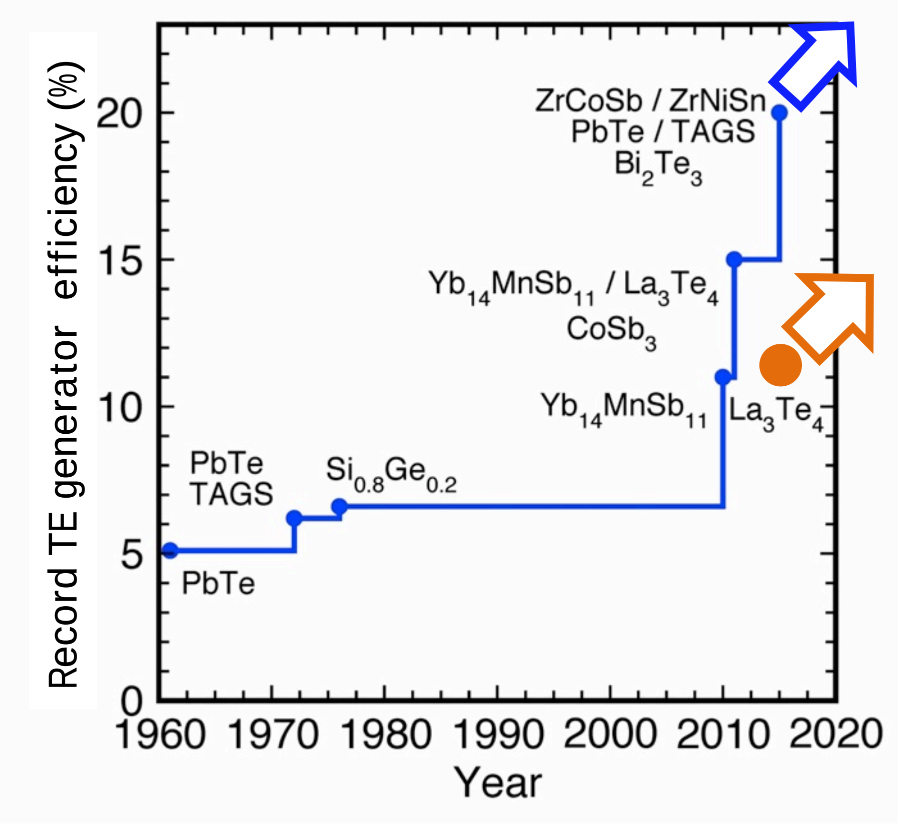


● Industry development

# Phase change material (PCM)

Storage capacity: Aluminum example

Specific heat: 0.9 J/gK

Heat of fusion: 400 J/g

Initially, it would appear that with a storage temperature of 600C, specific heat stores more energy.

Energy vs exergy – ability to do work w/ stored energy

Carnot efficiency

-> 0% as T storage approaches T ambient

# Phase change material (PCM)

Latent heat storage at 600C:

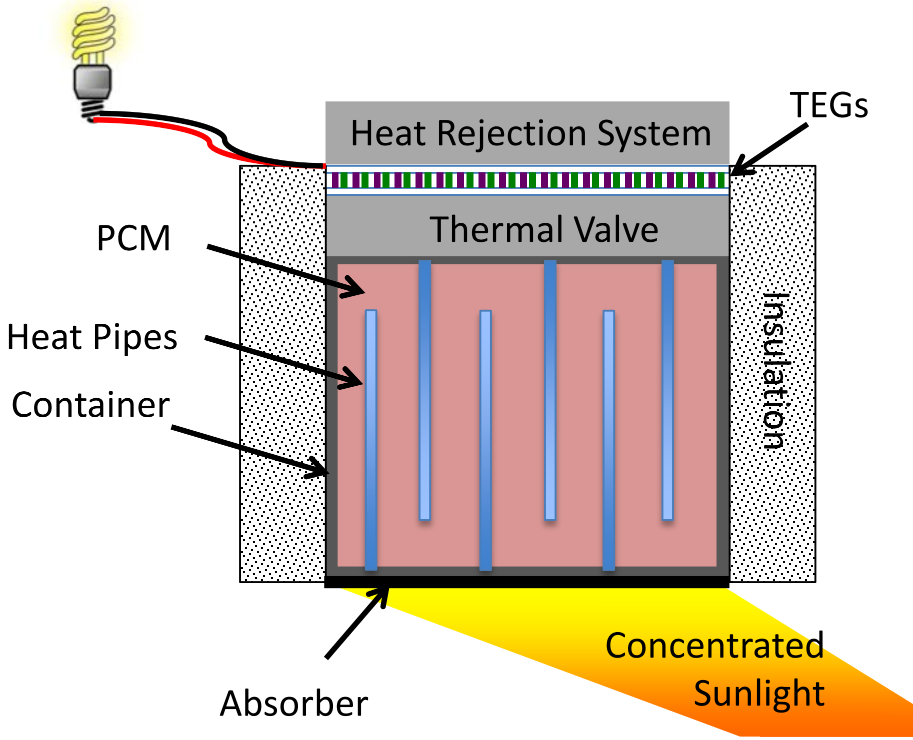
**Molten salts** (e.g. $CaCl_2/KCl$ eutectic)

- Economically viable corrosion solutions exist
- Low thermal conductivity

**Metals** (e.g. aluminum-silicon eutectic)

- High thermal conductivity
- Economically viable corrosion solutions unknown

30 year lifetimes….?



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# Motivation – Electrical energy production

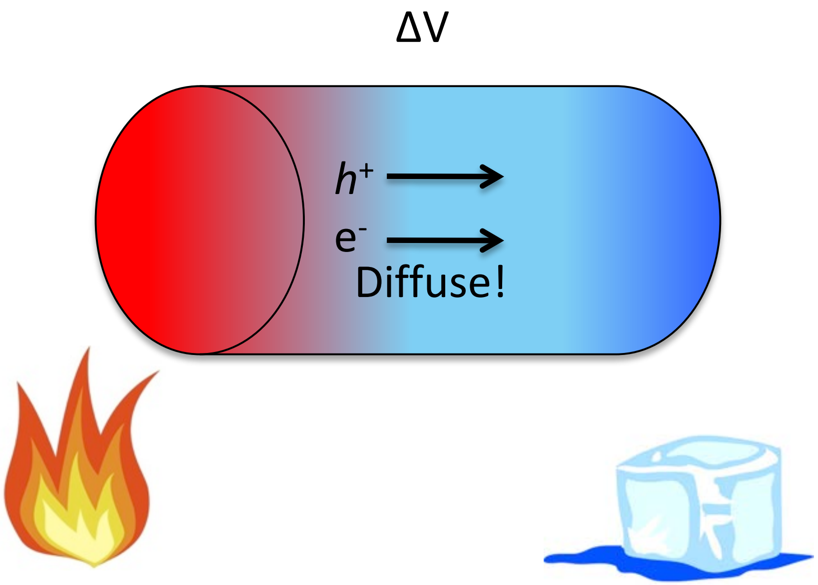
Thermoelectric materials directly convert the flow of heat into electrical power

Seebeck effect

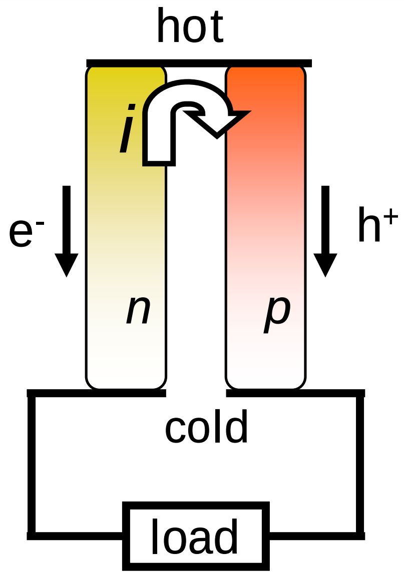
Known since 1821

$$\alpha = \frac{\Delta V}{\Delta T}$$

$$\frac{\text{Voltage}}{\text{Temperature gradient}}$$



# Material efficiency: Transport



Efficiency: Want maximum power for a given transfer of heat (heat is our fuel)

Two sources of loss:

- electrical resistance -> $P=V^2/R$
- thermal shorting

$$\text{Figure of merit (z)} = \frac{\text{Seebeck coefficient}^2}{\text{electrical resistivity} \quad \text{thermal conductivity}}$$

↓

$$\boxed{zT = \frac{\alpha^2 T}{\rho\kappa}}$$

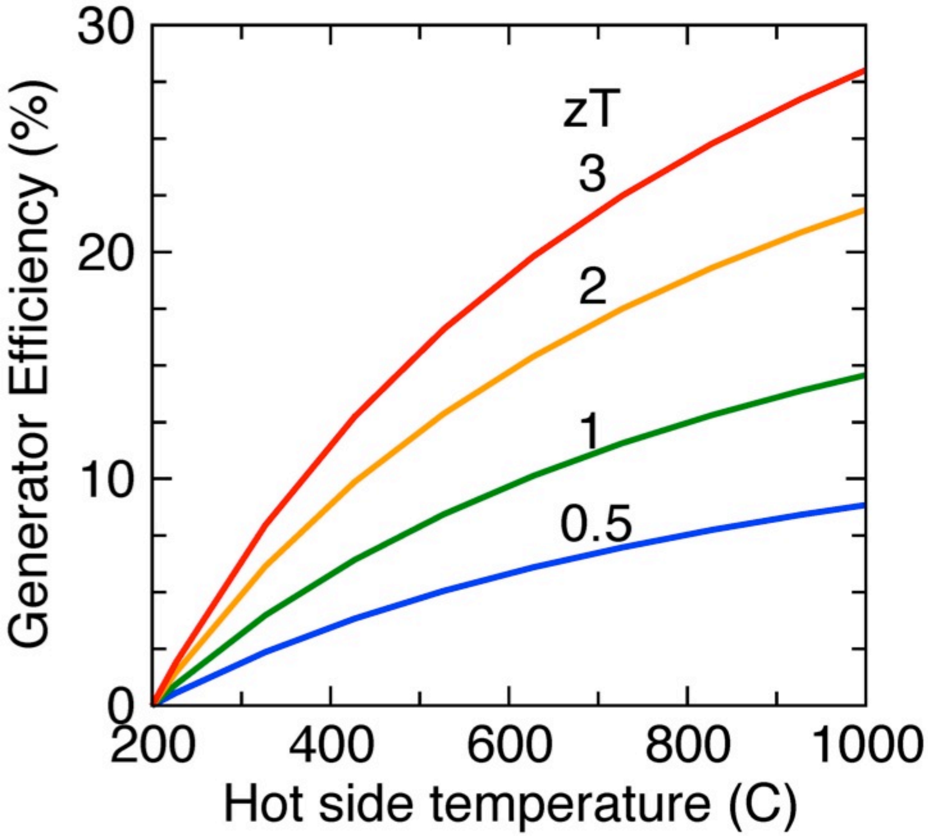
Avoid parasitic heat loss.

All heat transferred should be creating current.

# Thermoelectrics and generator efficiency

Thermoelectric figure of merit: ***zT***

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



$\alpha$ – Seebeck coef.
$\sigma$ – electrical conductivity
$\kappa$ – thermal conductivity

Generators based on materials with average zT >2 would be **transformative**!

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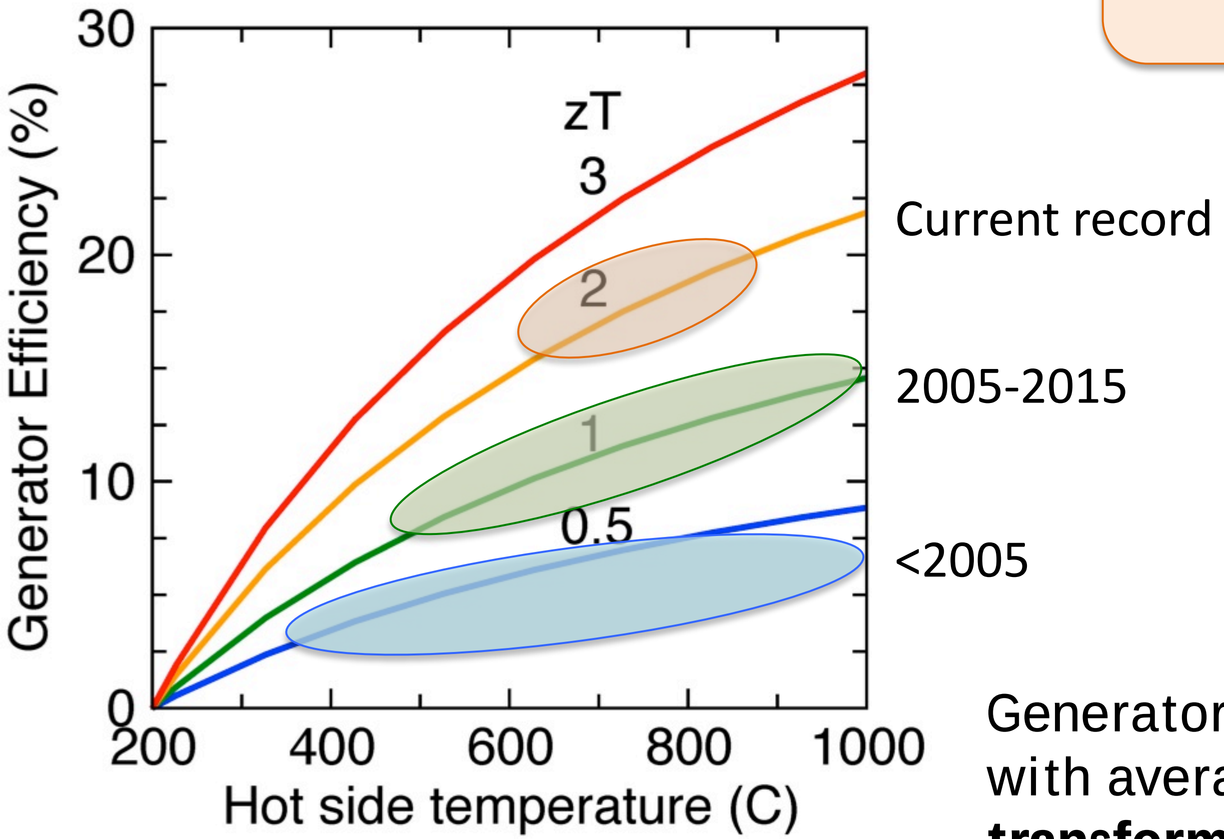

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How do we design materials with desired transport properties?

# Thermoelectrics and generator efficiency

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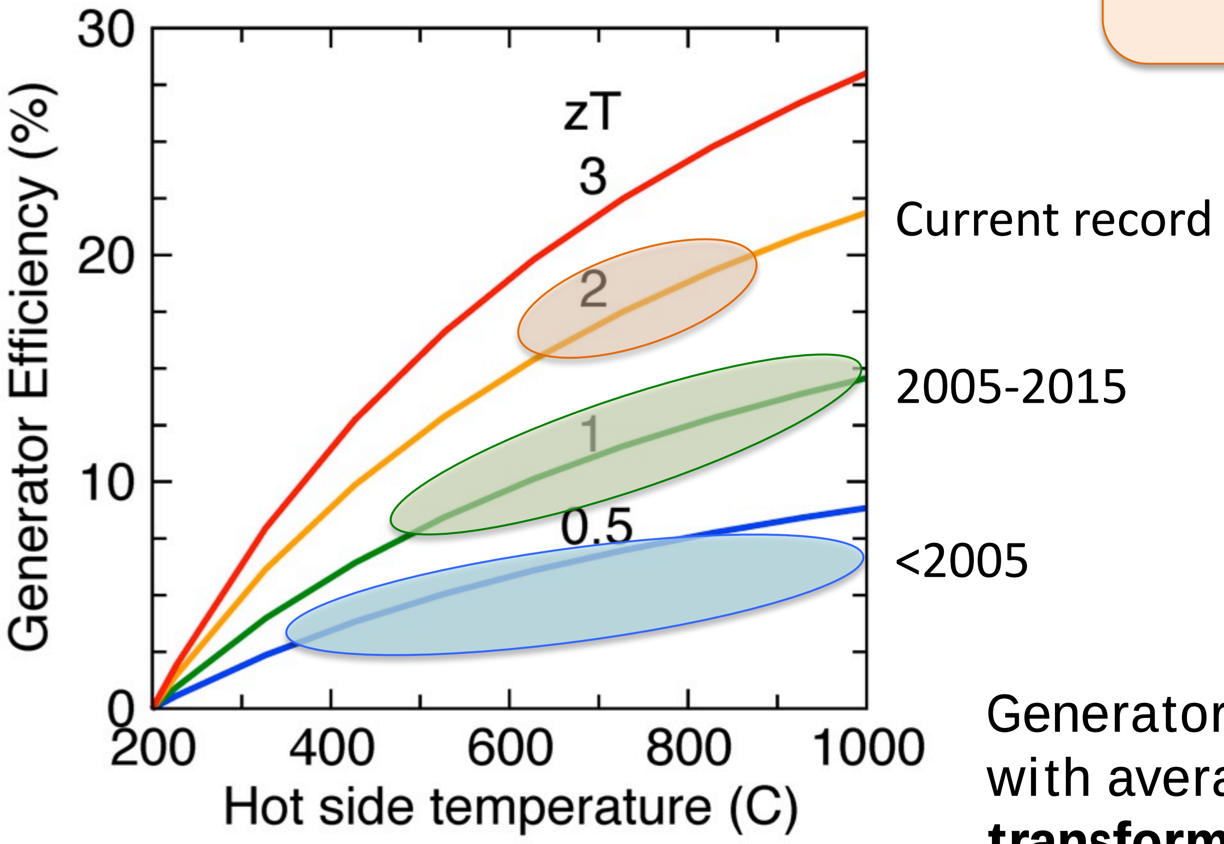


Generators based on materials with average zT >2 would be **transformative**!

How do we design materials with desired transport properties?

# Controlling transport – Landauer approach

Electrical conductivity & “*transport function*” (isotropic assumption)

$$\sigma = e^2 \int dE \left( -\frac{\partial f(E)}{\partial E} \right) \Sigma \qquad \Sigma = v^2 \, \tau_e \, g$$

How many (*g*), how fast (*v*) & how long ($\tau$)?

Weighed by partial state occupation (-*df/dE*)

| | |
|---|---|
| $E$ | Energy |
| $\Sigma$ | Transport function |
| $g(E)$ | density of states |
| $f(E)$ | Fermi distribution |
| $\tau_e$ | carrier relaxation time |
| $v$ | Group velocity |

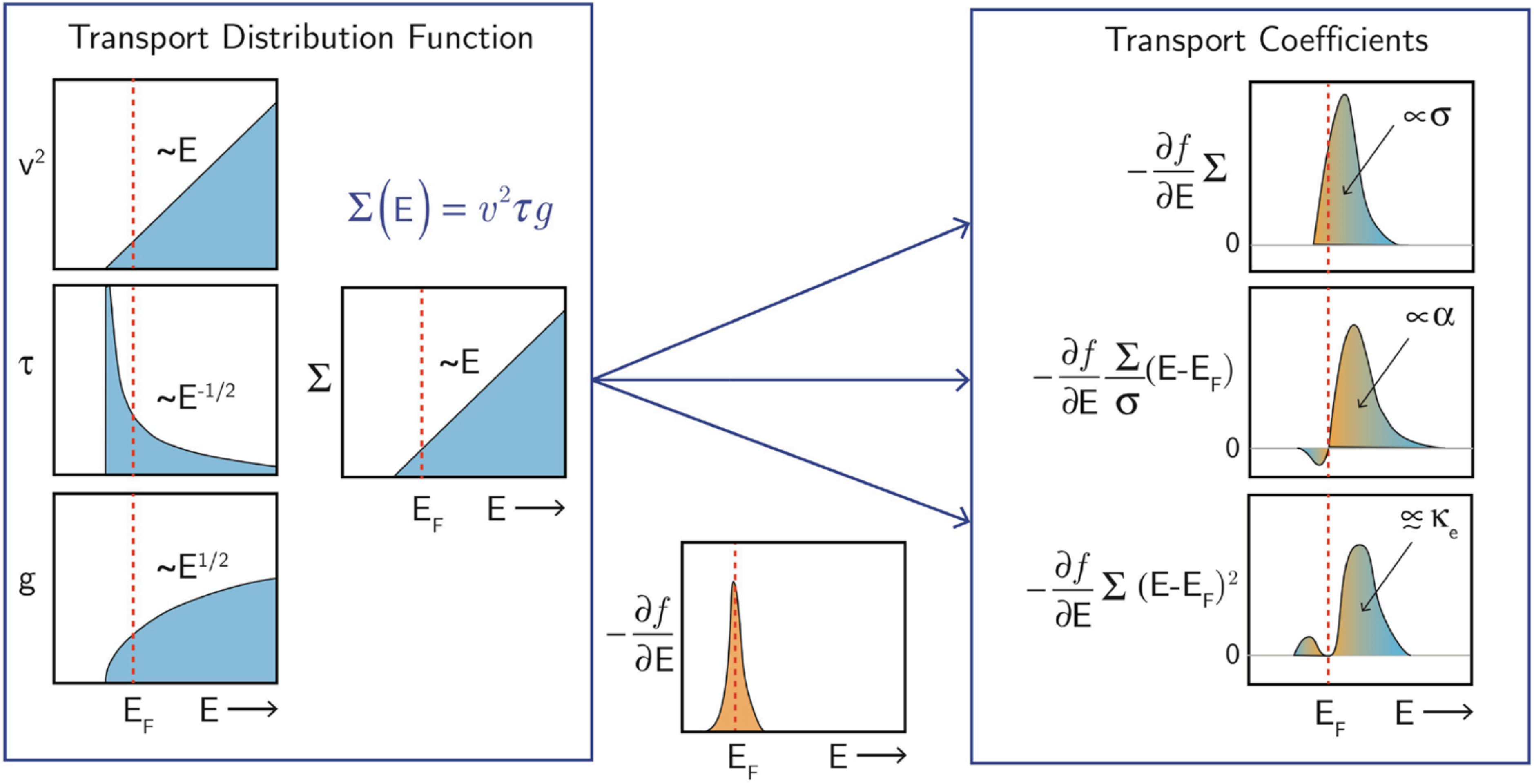
Even in simplest form, material design in **reciprocal space** and charge carrier and phonon **scattering**

Chemical intuition lacking….

# Controlling transport – Landauer approach

Electrical conductivity:

$$\Sigma = v^2 \tau_e g \qquad \sigma = e^2 \int dE \left( -\frac{\partial f(E)}{\partial E} \right) \Sigma$$

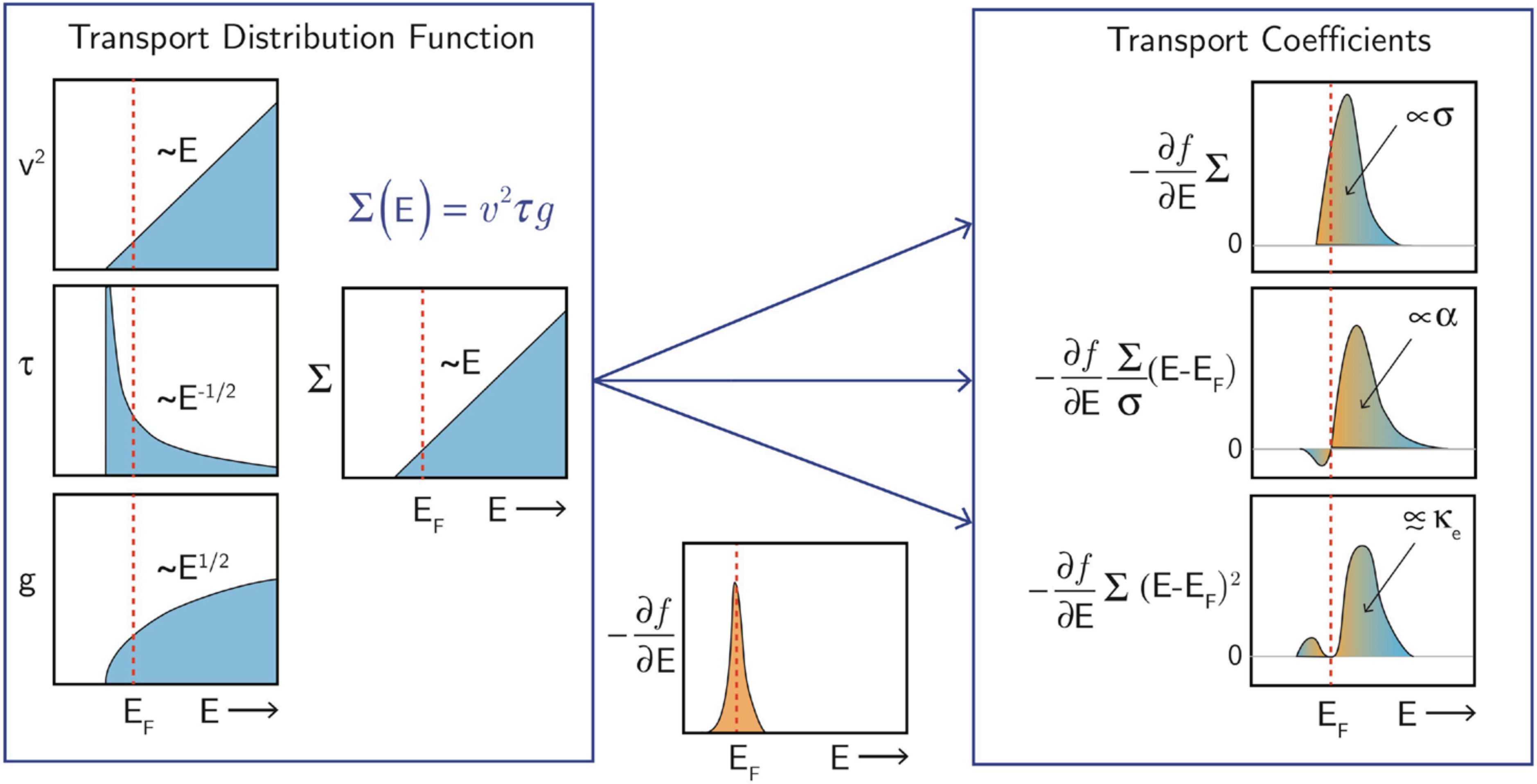


# Controlling transport – Landauer approach

$$\Sigma = v^2 \tau_e g$$

Seebeck coefficient is similar:

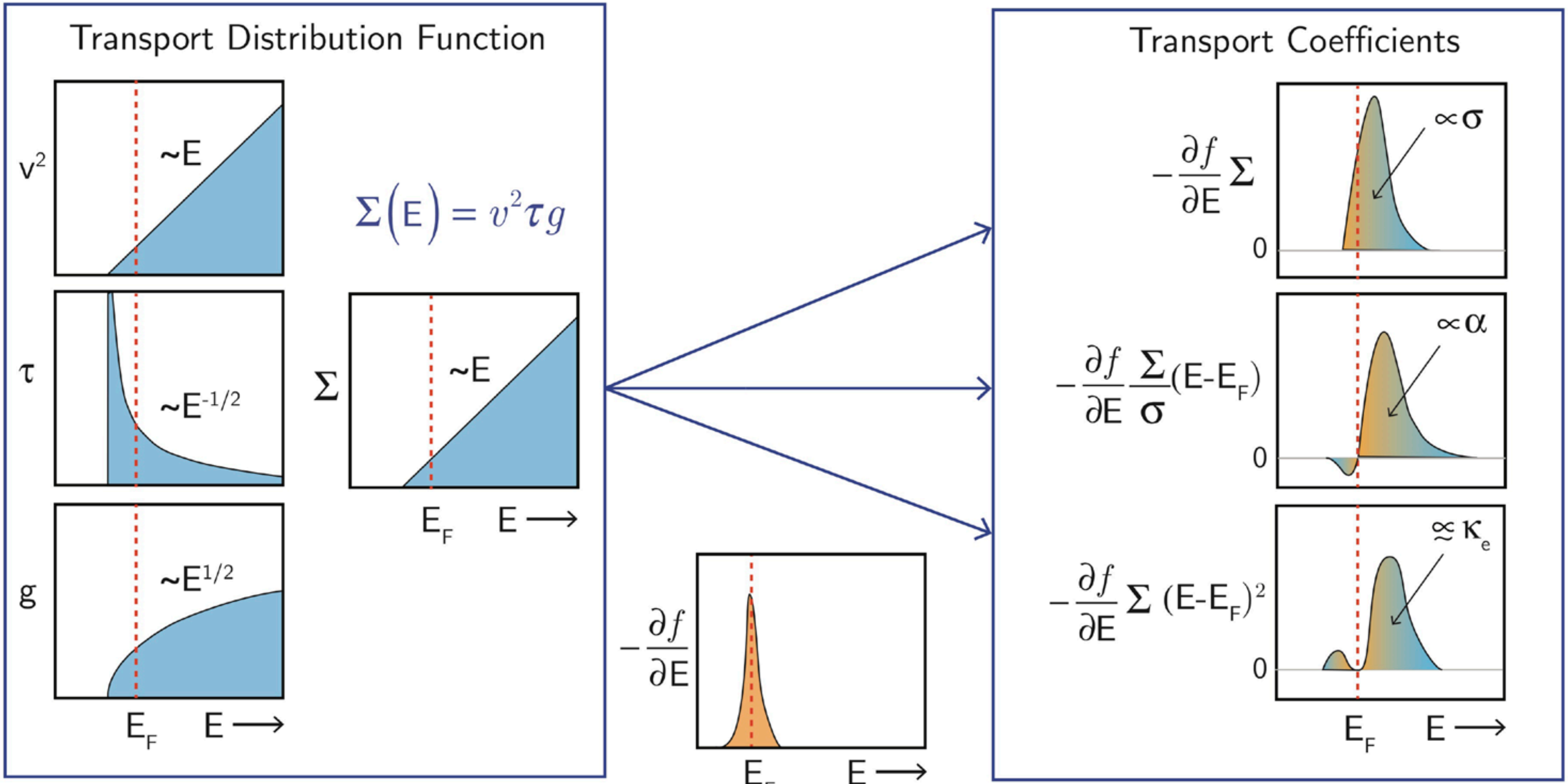
$$\alpha = \frac{e}{\sigma T} \int dE \left( -\frac{df}{dE} \right) \Sigma \left( E - E_F \right)$$



# Insight from Landauer approach

Seek to maximize both $\Sigma$'s magnitude and asymmetry (about $E_F$)

*Conductivity* *Seebeck coef*



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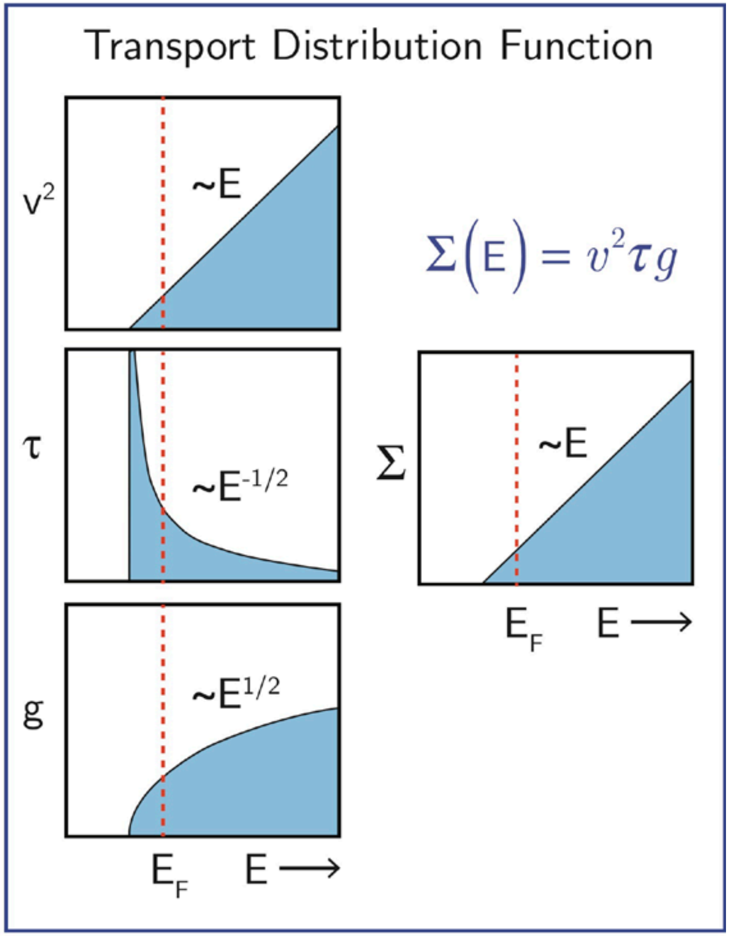
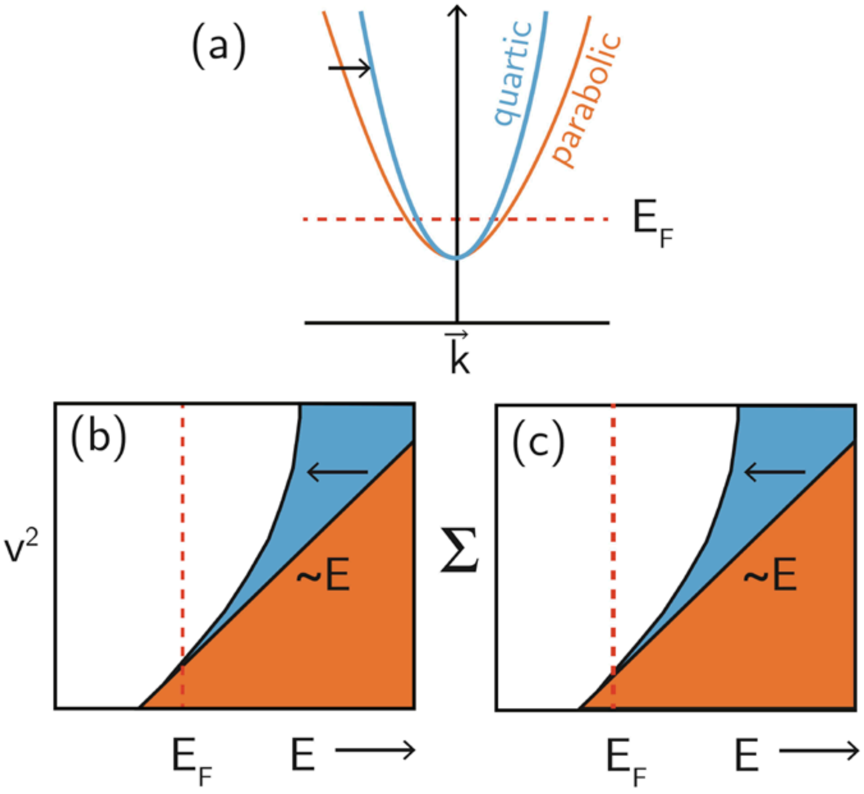


**Non-parabolic bands** (to date, largely detrimental)



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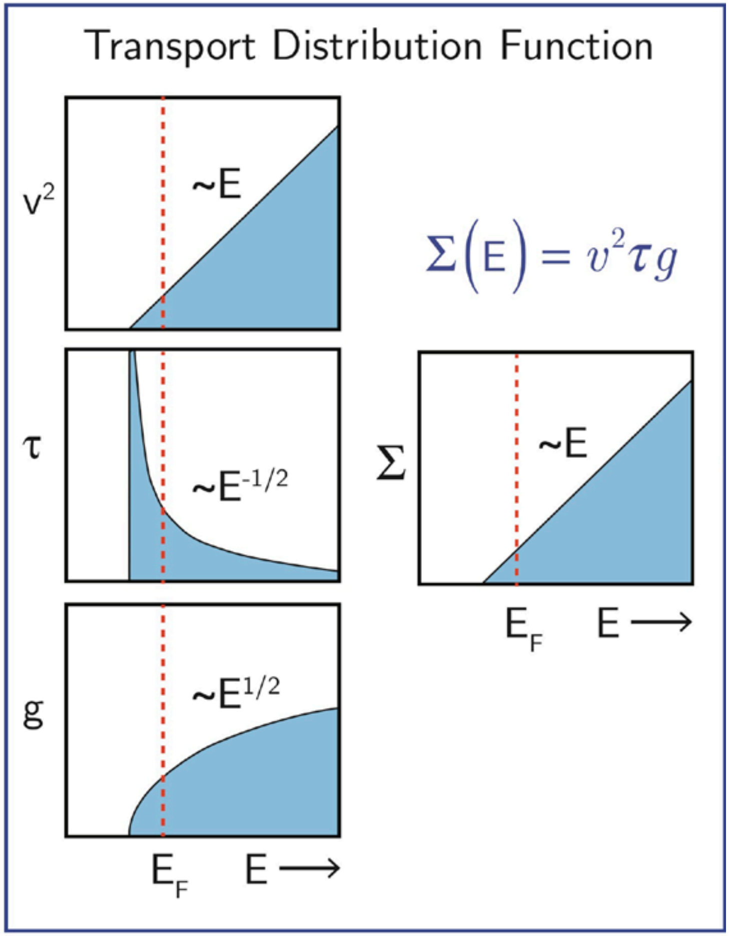
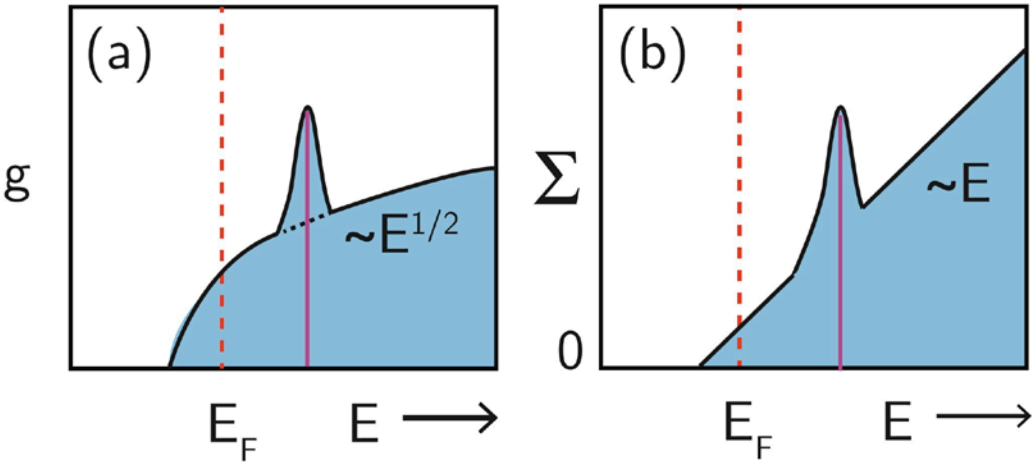
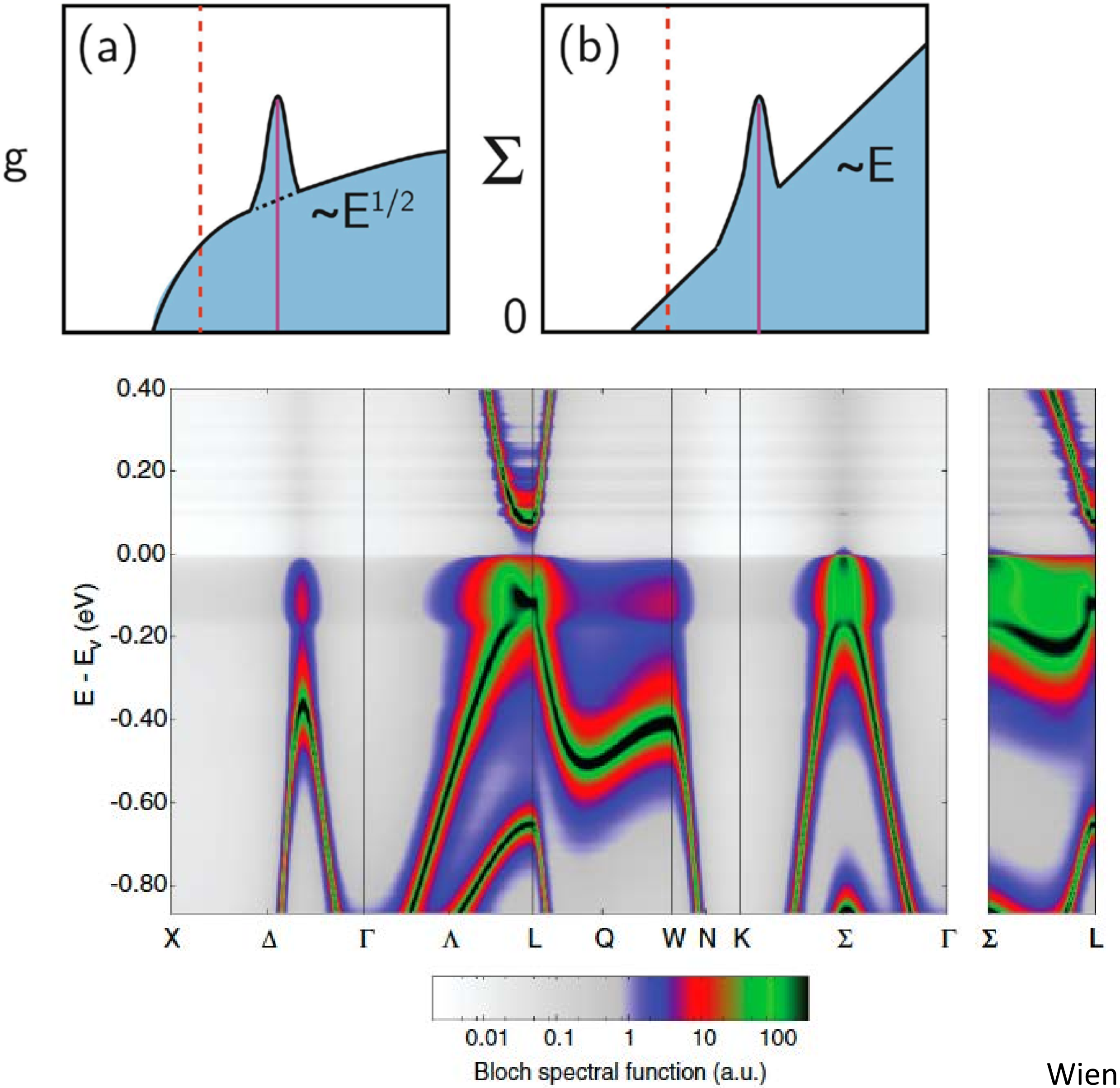


**Resonant states:**
Alloying to *insert* electronic states at specific energies (e.g. Tl-PbTe)



# Resonant states (e.g. Tl-PbTe)



Bloch spectral function for states near band edge

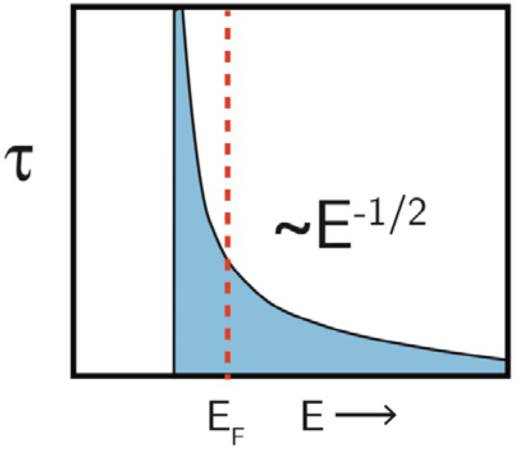
Tl resonant states

Pro: Enhanced g near band edge

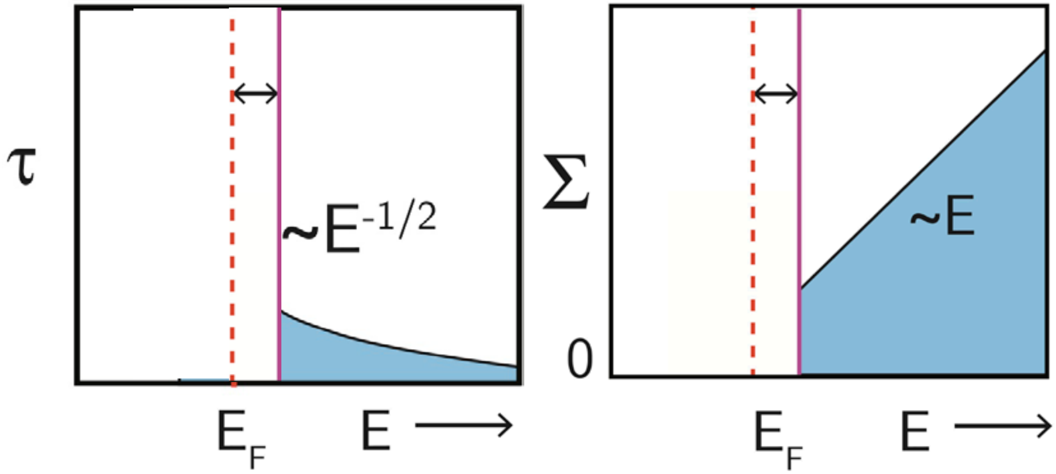
Con: Decrease in mobility due to increased scattering

Wiendlocha DOI: 10.1103/PhysRevB.88.205205

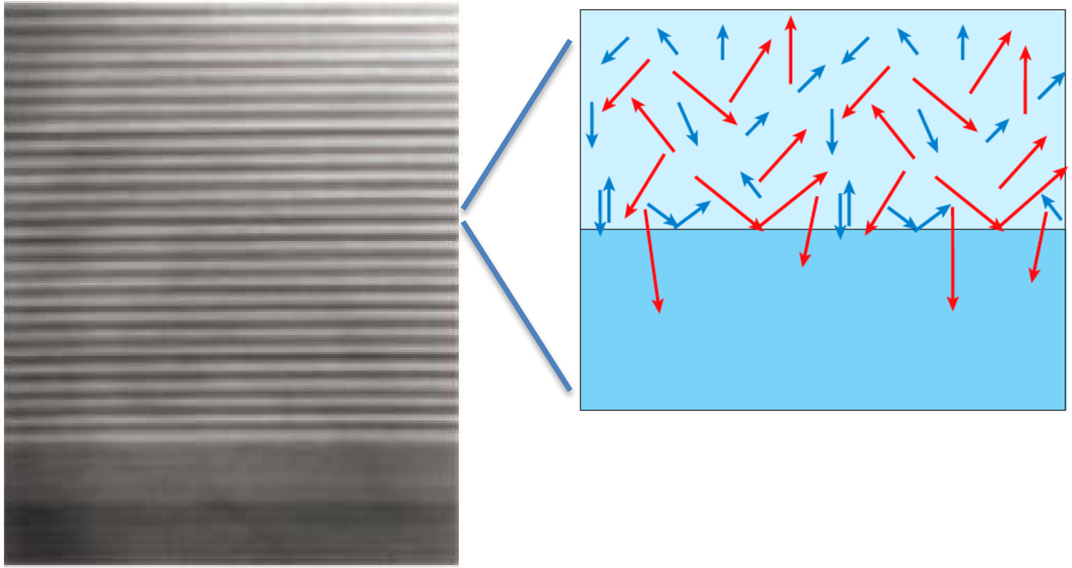
# Electron filtering to enhance Σ asymmetry



**Electron filtering**



Superlattice limits mobility of low energy electrons due to quantum well formation

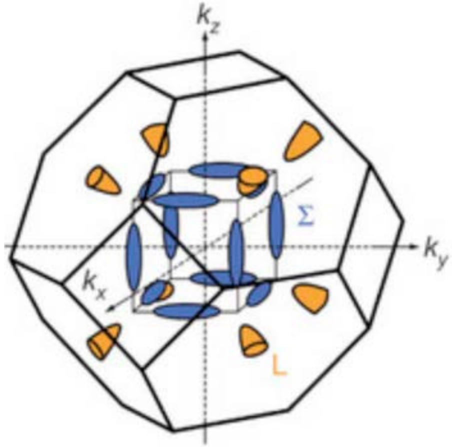


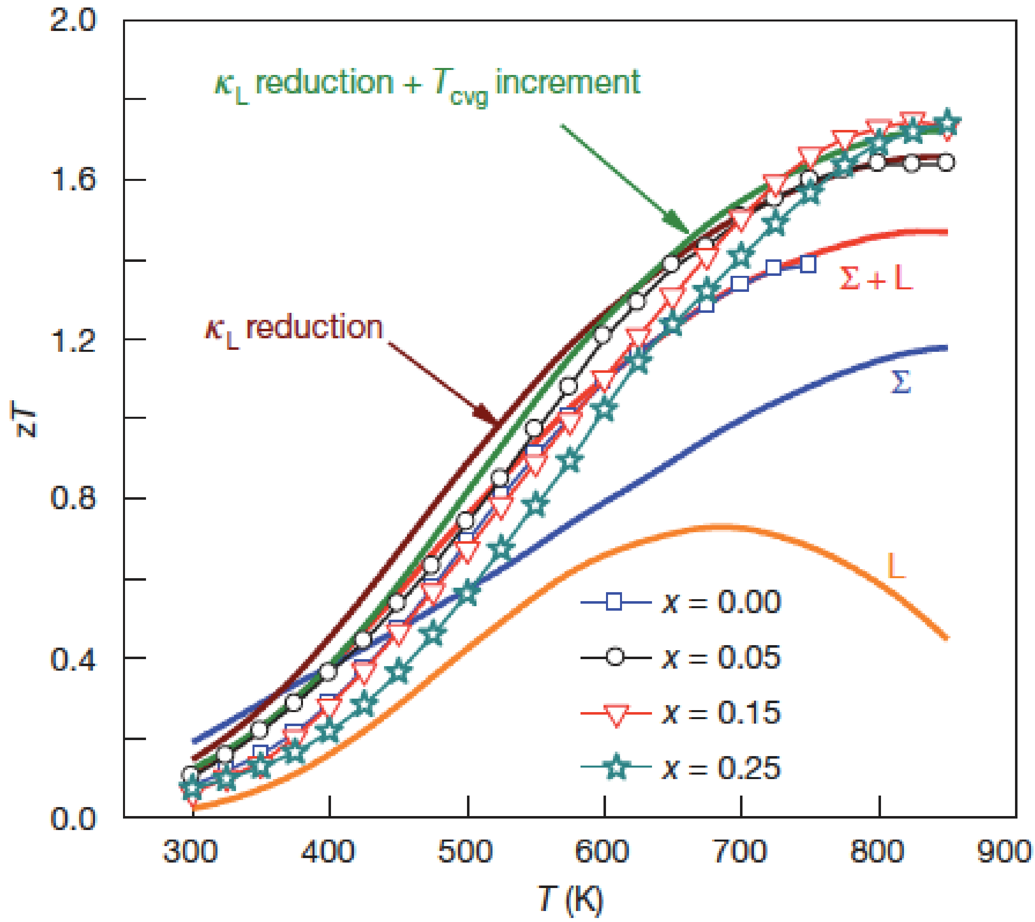
# Increasing Σ through band degeneracy

Symmetry leads to multiple band extrema

Increase *g* without decreasing *v*

May decrease **τ** due to inter-valley scattering





Pei Nature 2011

arXiv:1404.1807v3

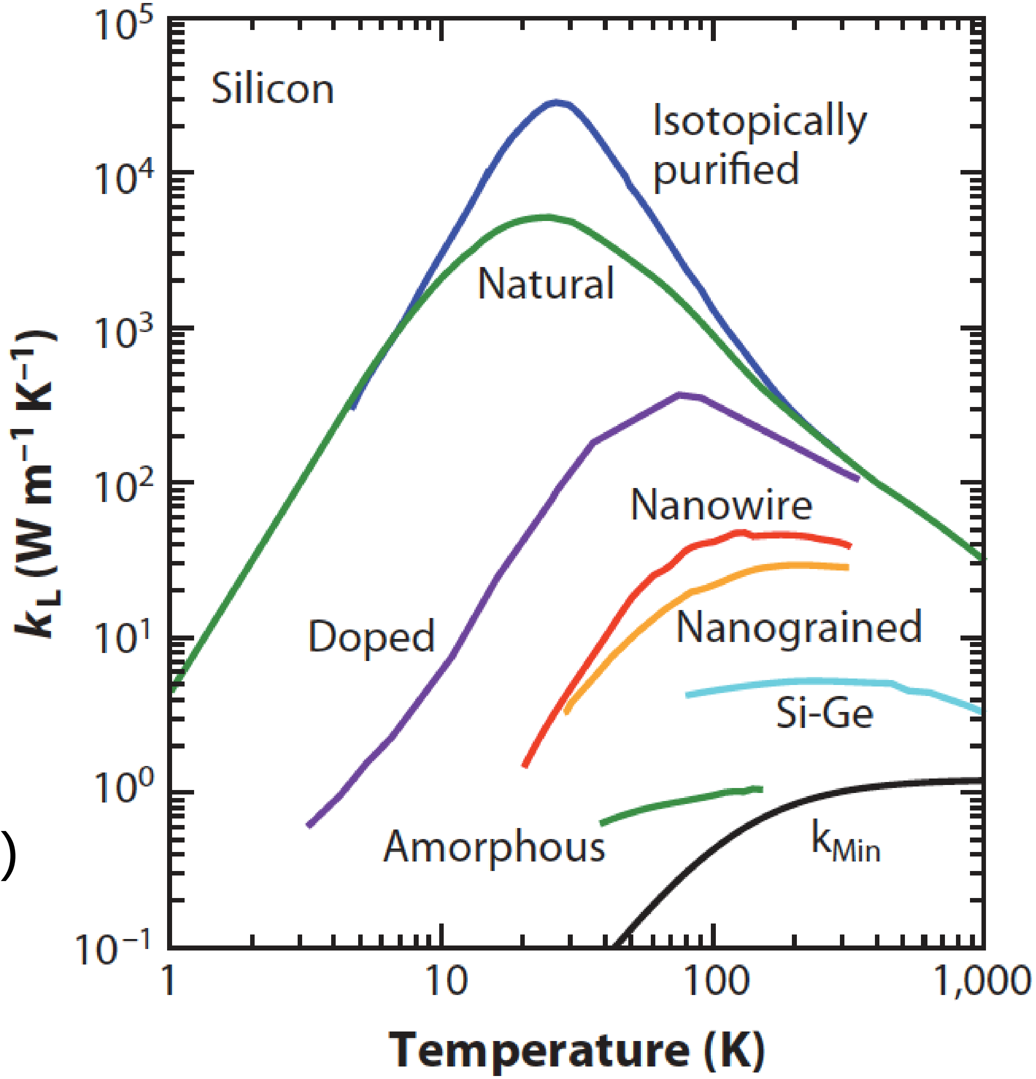
# Thermal conductivity – Debye Callaway Approach

$$\kappa_L = \frac{1}{3}\int d\omega\, C\, v_g^2\, \tau$$

| | |
|---|---|
| $C$ | Heat capacity |
| $v$ | Group velocity |
| $\tau$ | phonon relaxation time |

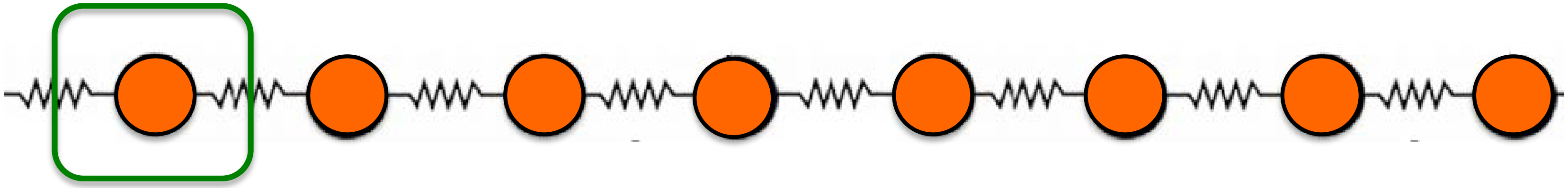
Low lattice thermal conductivity (phonon transport) achieved by:

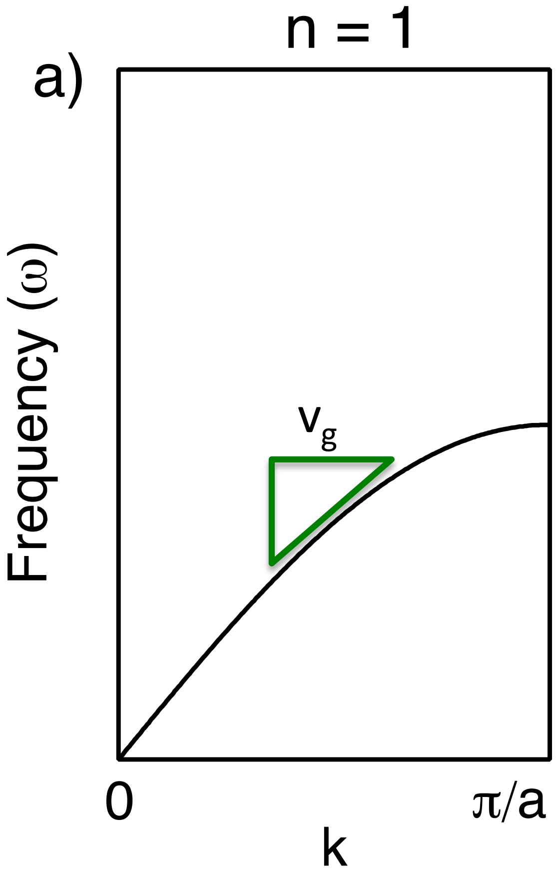
- reducing the group velocity (v)
- inducing scattering sources



Baranowski ARMR 2012

# Structural complexity and low thermal conductivity

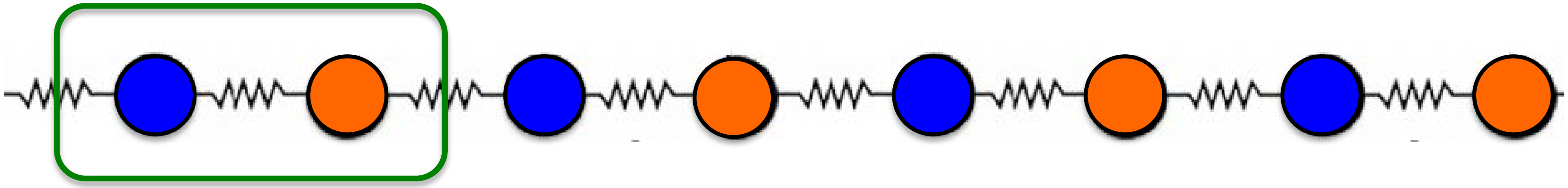


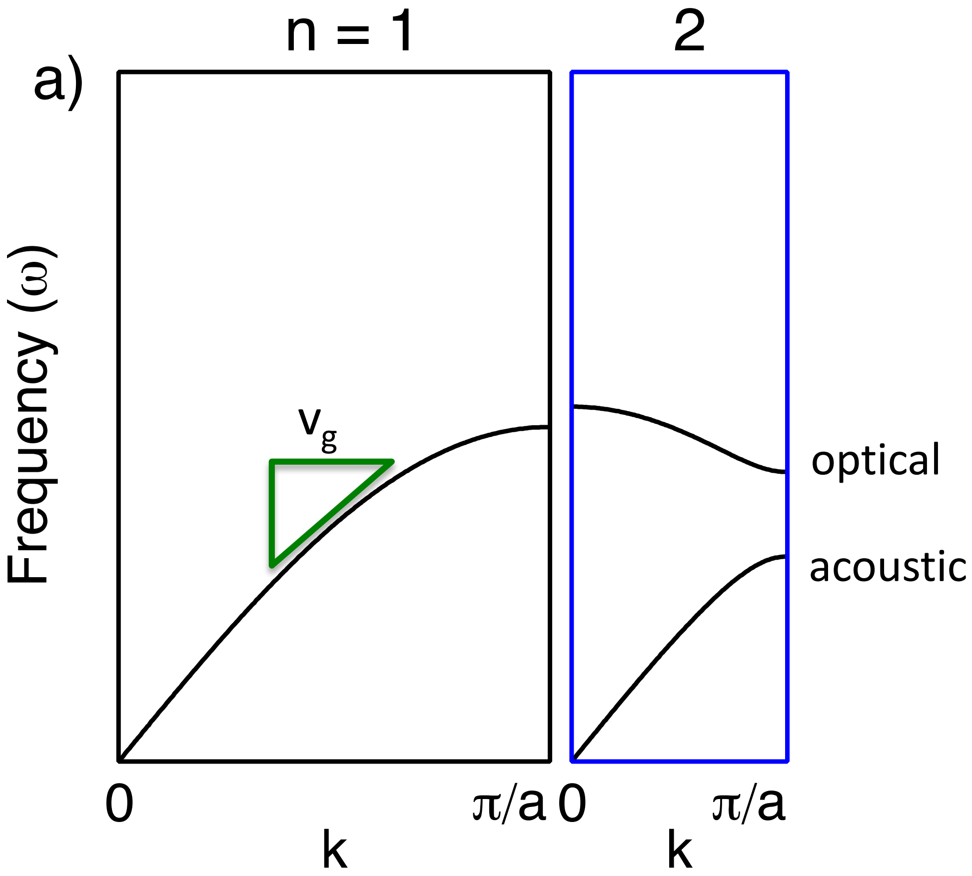


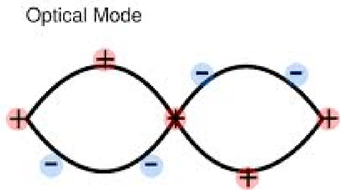
Group velocity: $v_g = d\omega/dk$

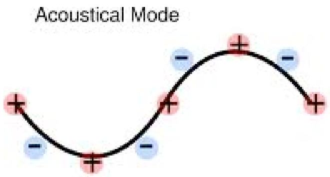
Roufosse & Klemens *PRB* 1973
Toberer, Zevalkink, Snyder, J. Mater. Chem 2011

# Structural complexity and low thermal conductivity









Roufosse & Klemens *PRB* 1973
Toberer, Zevalkink, Snyder,
J. Mater. Chem 2011

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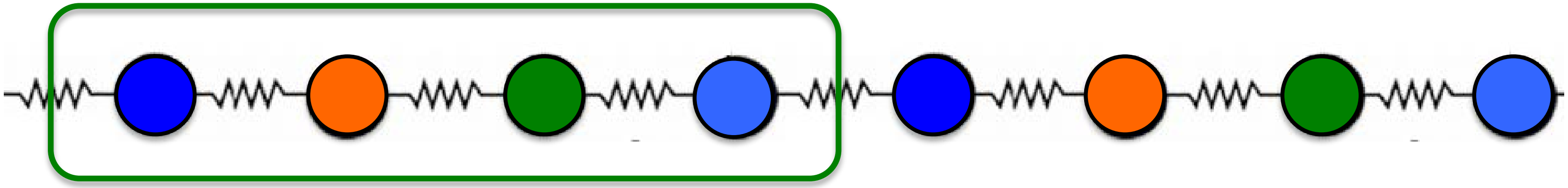

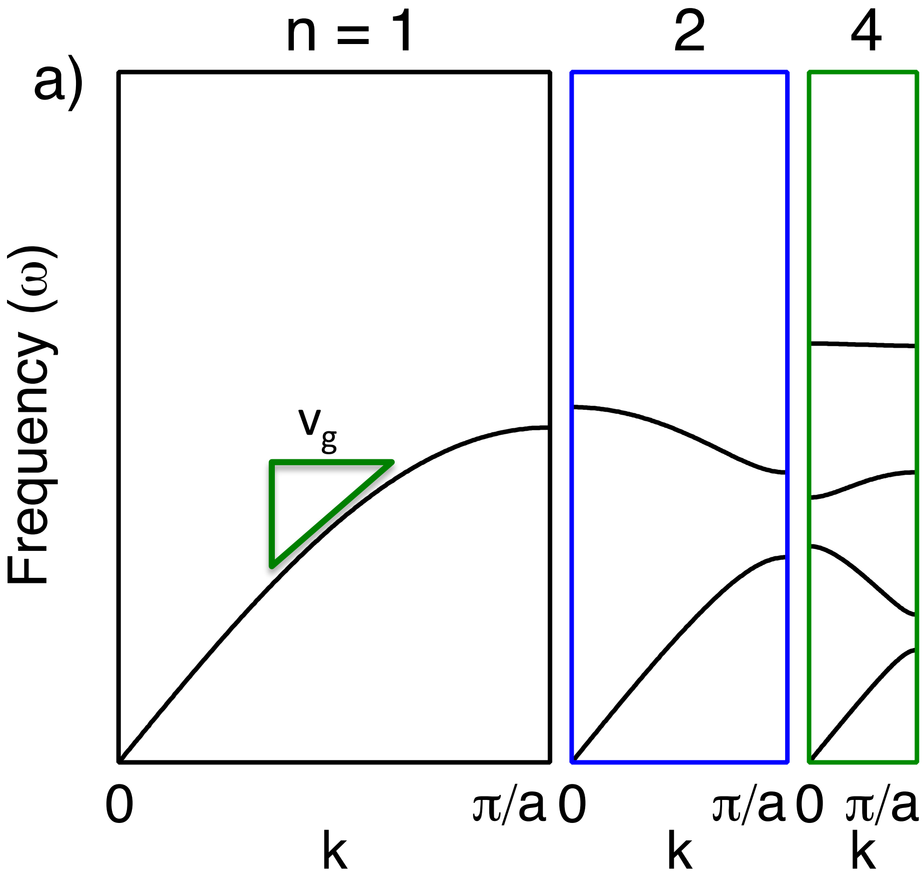

Roufosse & Klemens *PRB* 1973
Toberer, Zevalkink, Snyder, J. Mater. Chem 2011

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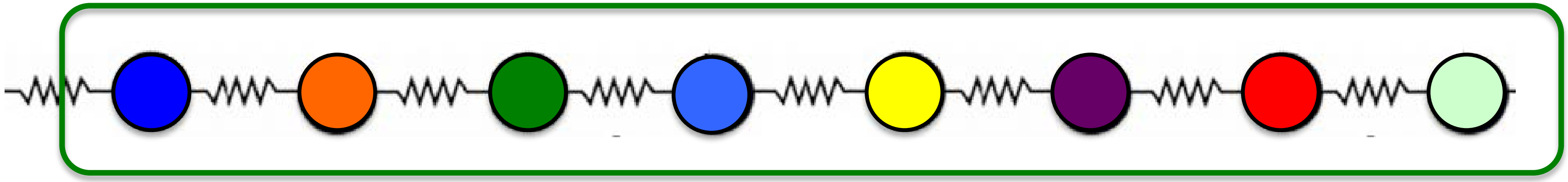
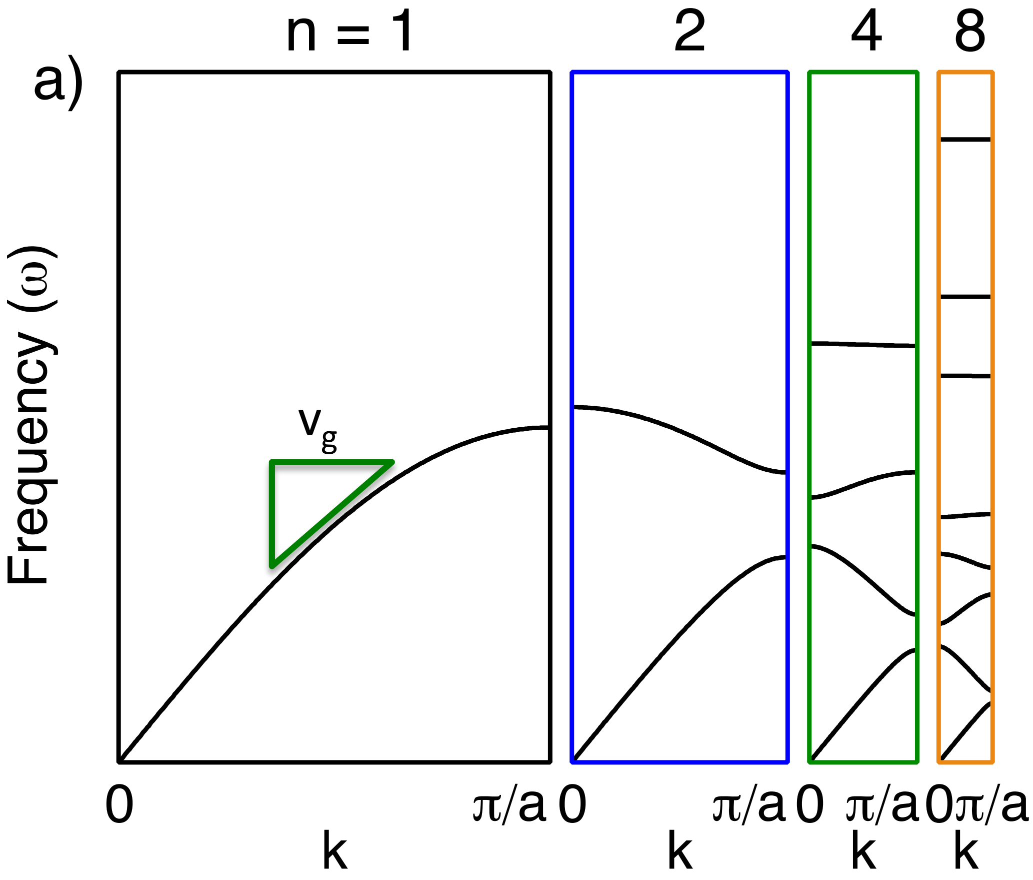
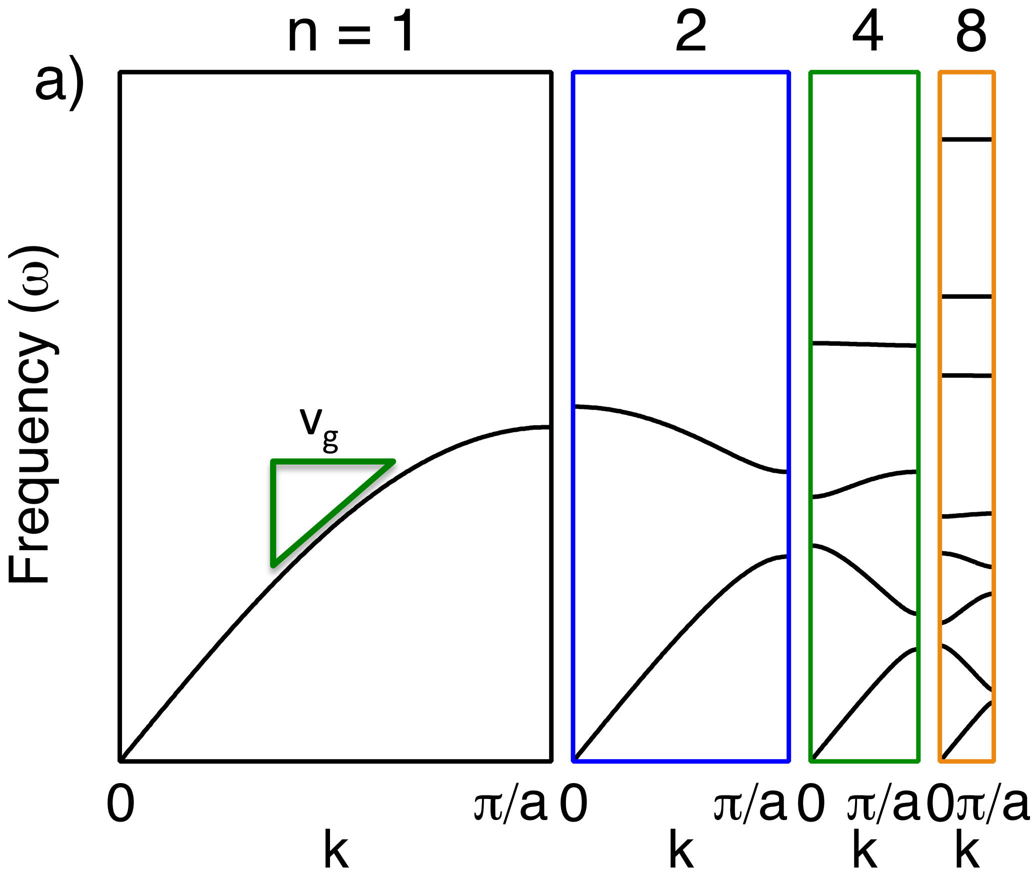




Roufosse & Klemens *PRB* 1973
Toberer, Zevalkink, Snyder, J. Mater. Chem 2011

# Structural complexity and low thermal conductivity



Theory:

$\kappa_L$ proportional to $n^{-2/3}$

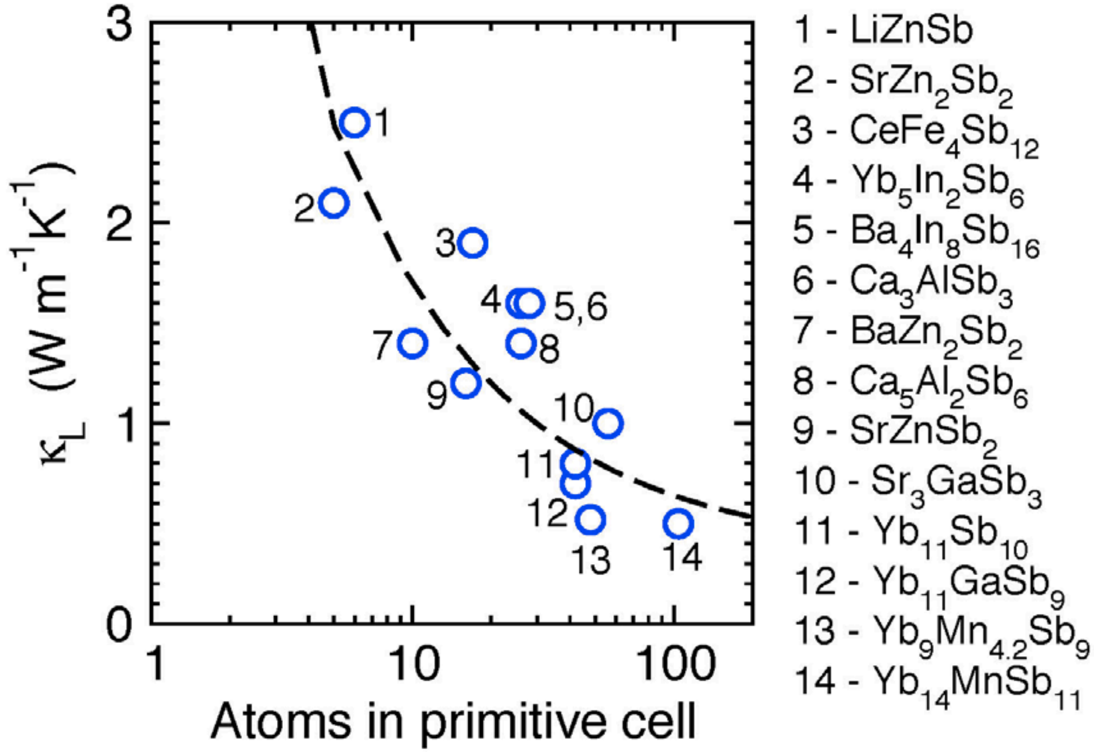
n: # atoms primitive cell

Expectation that *structurally complex* crystalline materials will have incredibly low thermal conductivity.

Roufosse & Klemens *PRB* 1973
Toberer, Zevalkink, Snyder, J. Mater. Chem 2011

# Experimental validation

Structural complexity proves to be a good predictor of $\kappa_L$ for similar compounds (e.g. antimonides)!



Roufosse & Klemens *PRB* 1973
Toberer, Zevalkink, Snyder,
J. Mater. Chem 2011

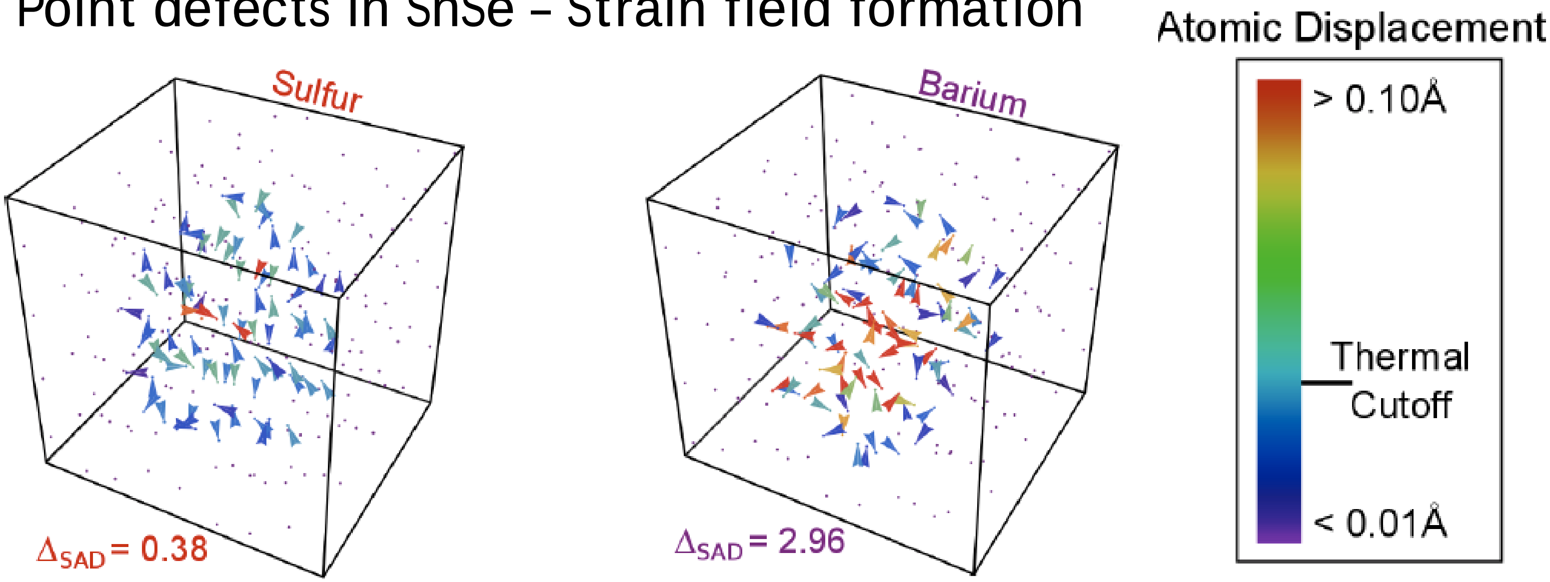
# Beyond low group velocity: Phonon scattering

Primary sources of phonon scattering?

- Other phonons - Unklapp (phonon-phonon) scattering
- Point defects (mass disorder, strain fields)
- Extended defects and nanostructures

Opportunities both *within* and *beyond* the unit cell to design materials with strong phonon scattering

Point defects in SnSe – Strain field formation

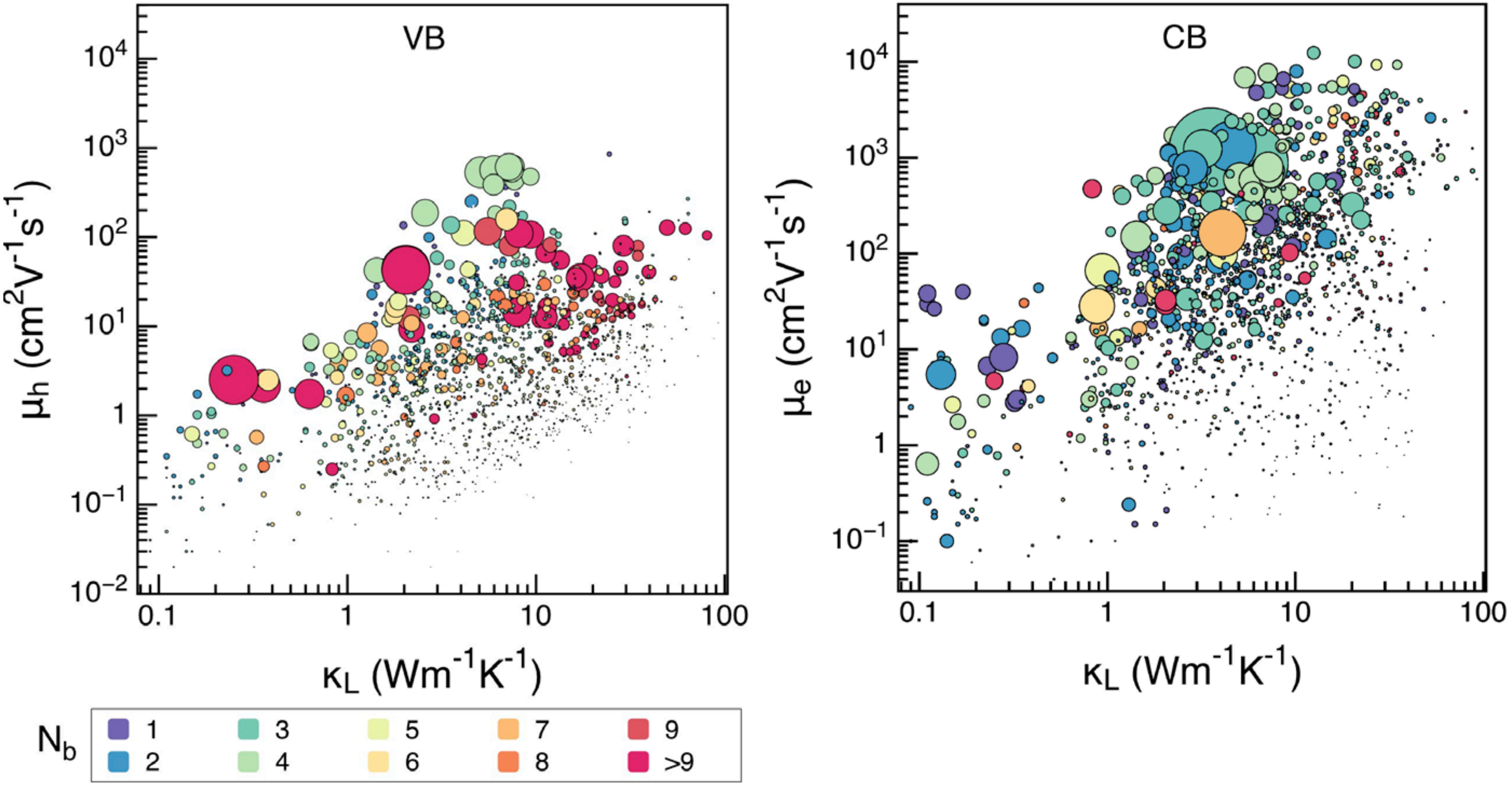


# 30 minute goals

- Appreciate **grid complexities & need for storage**
- Storage approaches & identify **primary approaches** to distributed storage
- Define challenges & opportunities within t**hermal energy storage**
- Consider role of **thermoelectrics materials** and material design strategies
- Thermoelectric search strategies

# New search methodologies needed!

Computationally driven search approaches

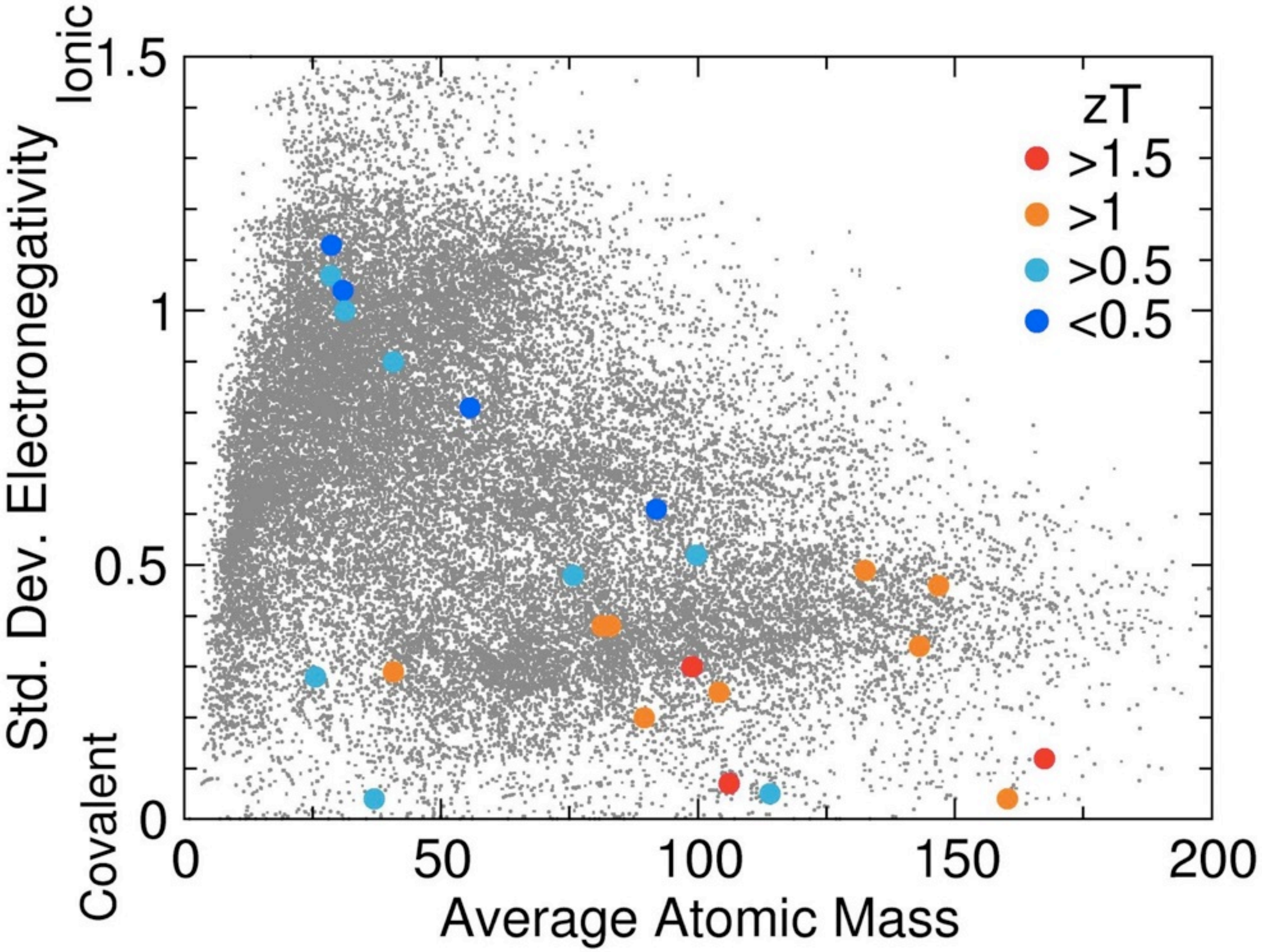


# Known non-intermetallic compounds and TE materials

~50,000 unique crystalline compounds (excluding intermetallics) within the Inorganic Crystal Structure Database (ICSD)

*Only a small fraction have been considered for TE performance!*

:

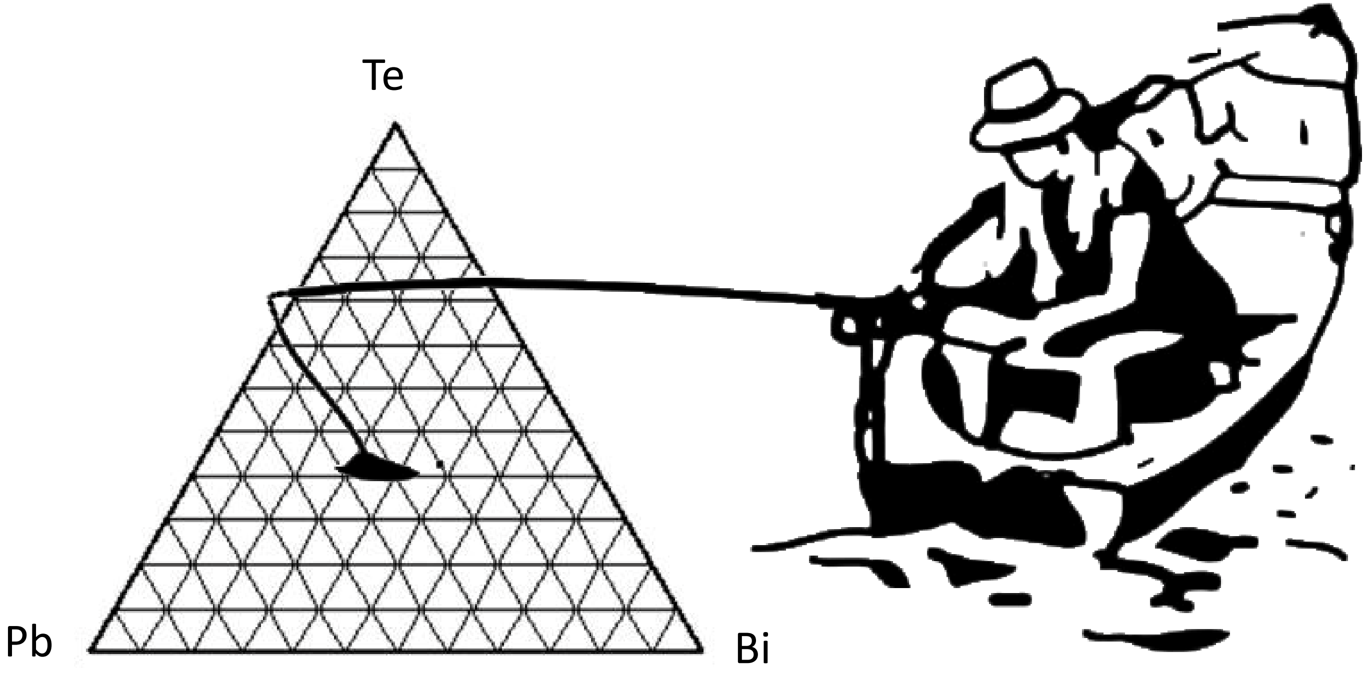


Yan et al EES 2015

# **Current approach:** Serendipity & intuition

… also known as …

*fishing*

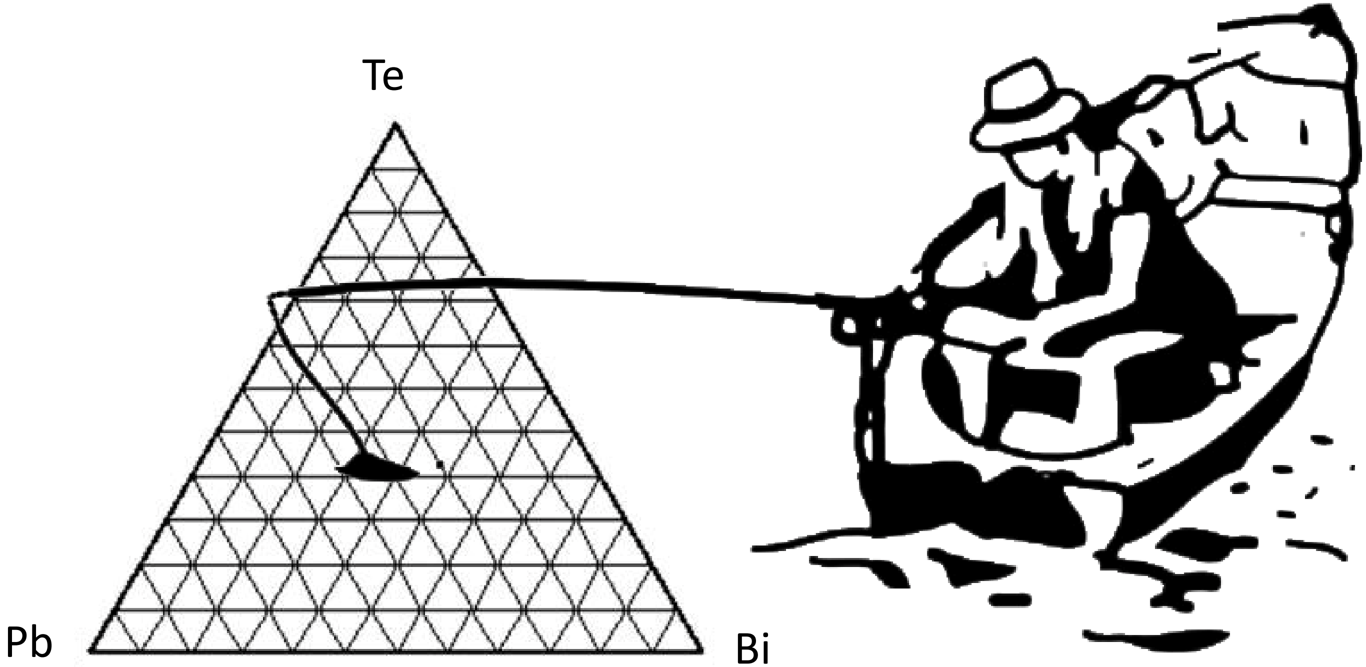


However, TE design is a **reciprocal (momentum) space** problem.
Minimal intuition for reciprocal space……

# **Current approach:** Serendipity & intuition

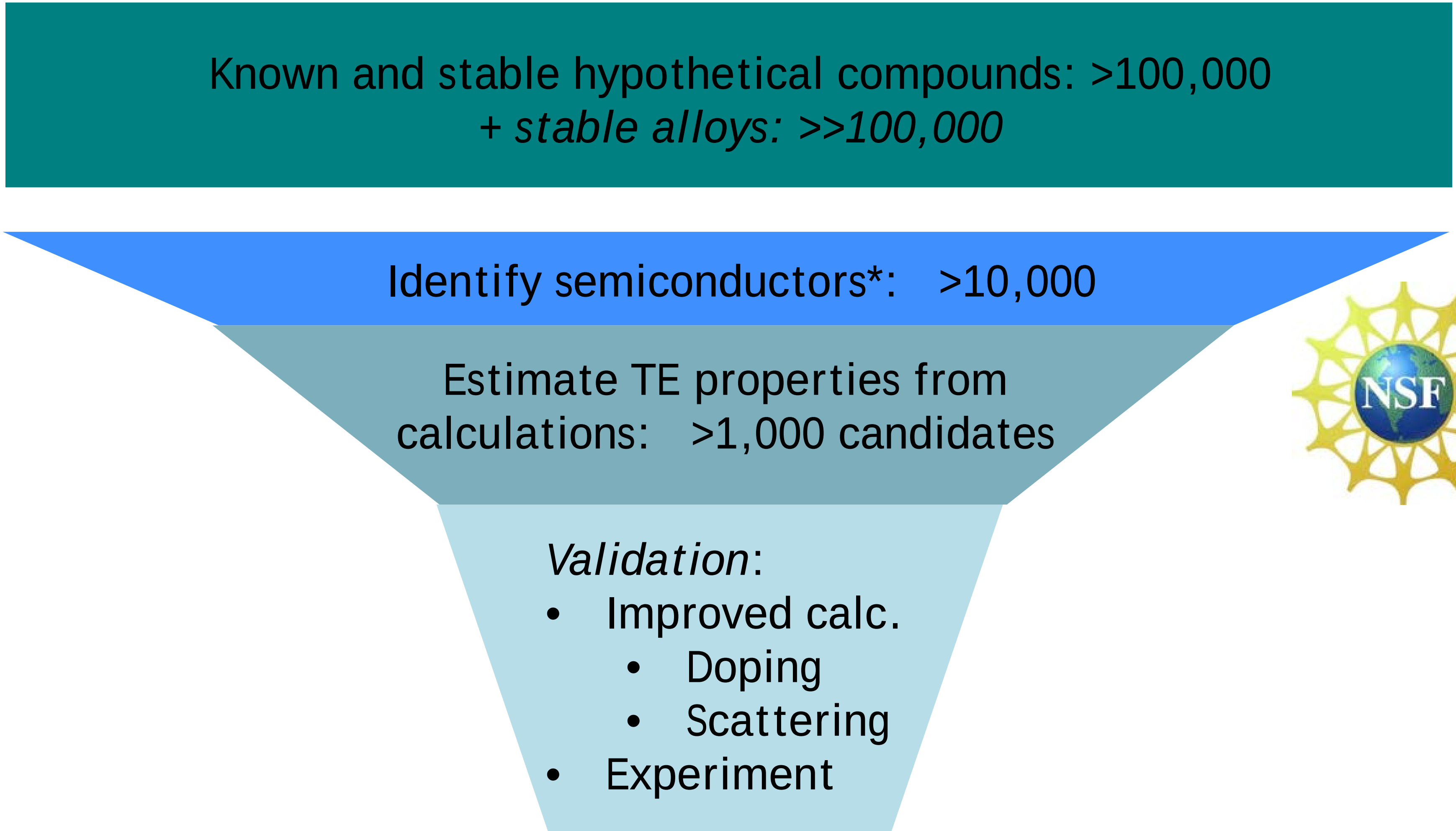
… also known as …

*fishing*



**Grand Challenge:** New paradigms for material ***discovery & design*** needed!

# Discovery methodology



Known and stable hypothetical compounds: >100,000
+ *stable alloys: >>100,000*

Identify semiconductors*: >10,000

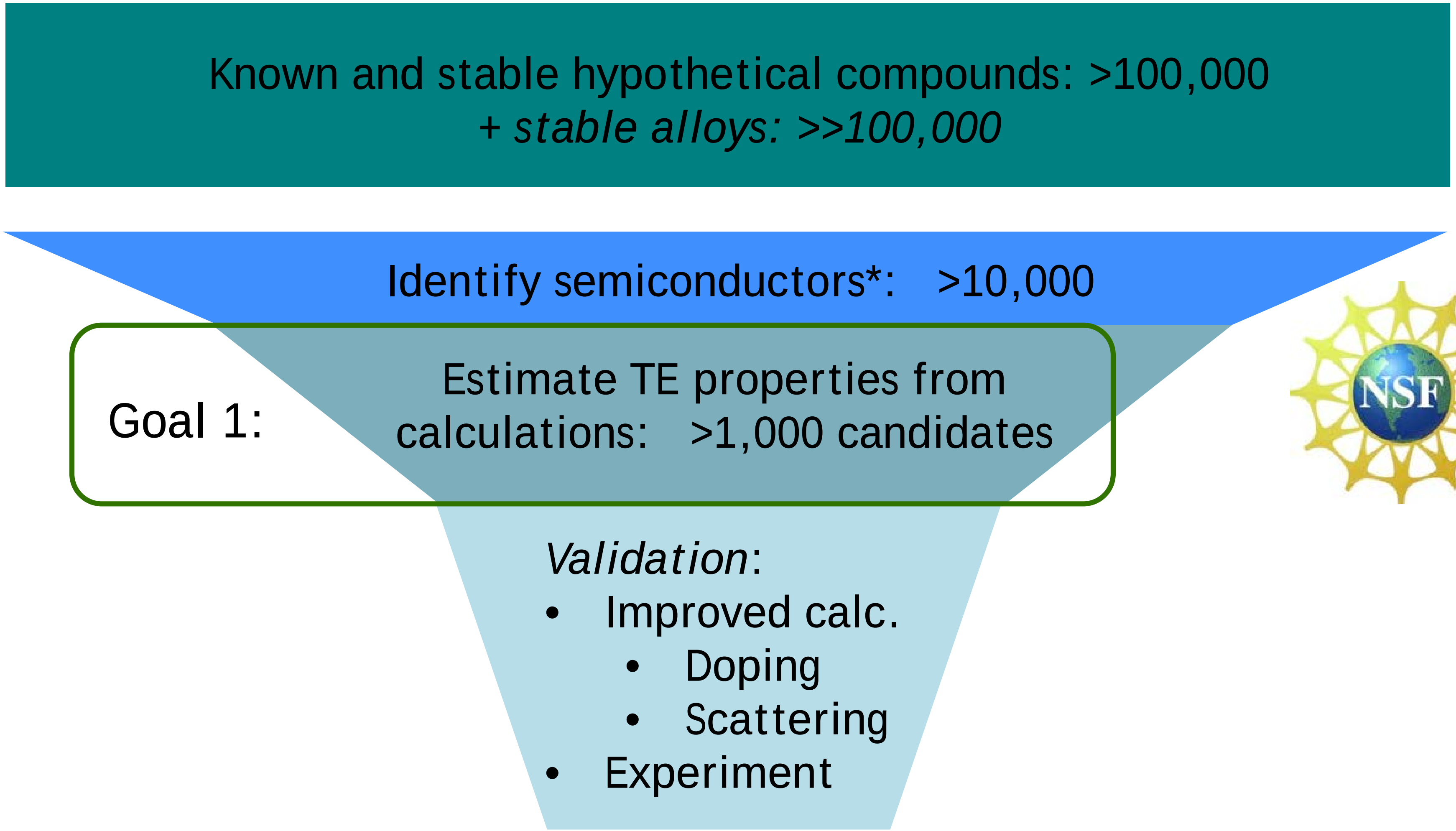
Estimate TE properties from calculations: >1,000 candidates

*Validation*:

- Improved calc.
  - Doping
  - Scattering
- Experiment

* Building off of NREL's Center for Inverse Design codes for photovoltaics

# Discovery methodology



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Identify semiconductors*: >10,000

Goal 1:

Estimate TE properties from calculations: >1,000 candidates

*Validation*:

- Improved calc.
  - Doping
  - Scattering
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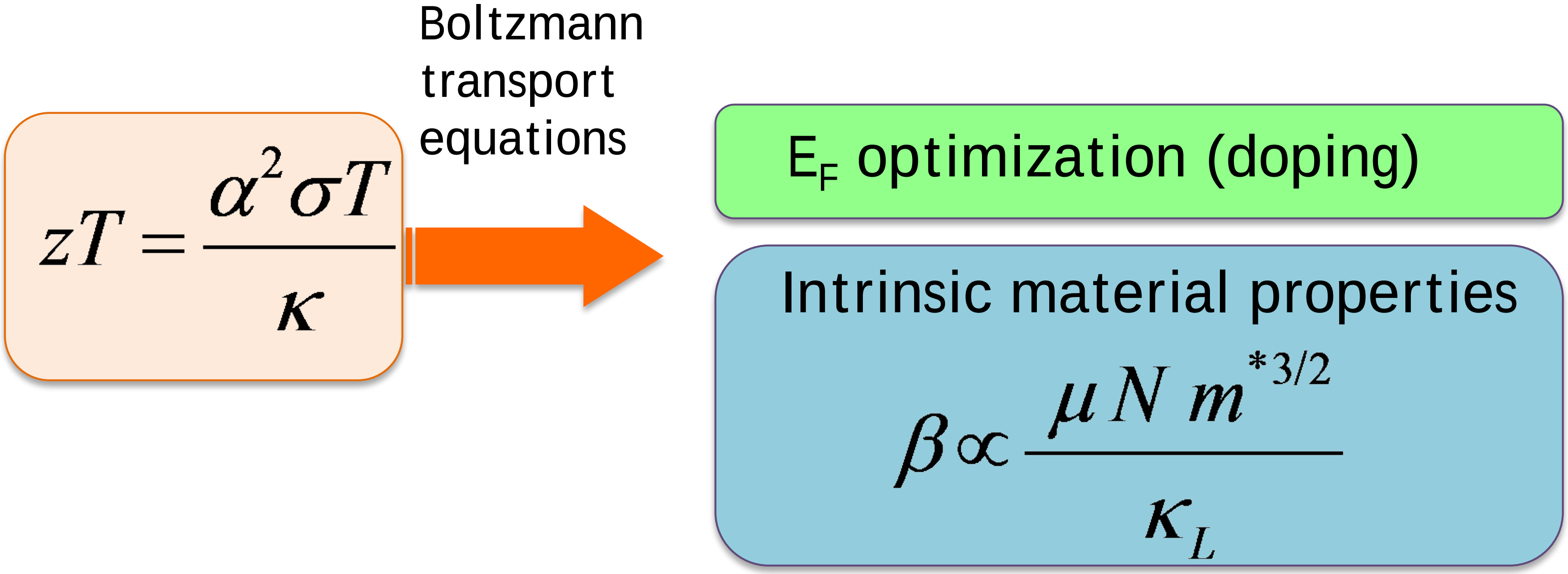
* Building off of NREL's Center for Inverse Design codes for photovoltaics

# Framing the problem: Alternative metrics



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

Boltzmann transport equations

$E_F$ optimization (doping)

Intrinsic material properties

$$\beta \propto \frac{\mu N m^{*3/2}}{\kappa_L}$$

$\mu$ – mobility
$N$ – number of band minima/maxima
$m^*$ - band effective mass
$\kappa_L$ – lattice thermal conductivity

Separating out doping enables improved
structure-property database development and data mining

Goldsmid & Douglas, Brit. J. Appl. Phys, 1954
Chasmar & Stratton J. Electron. Control, 1959.

# Alternative metric for material discovery

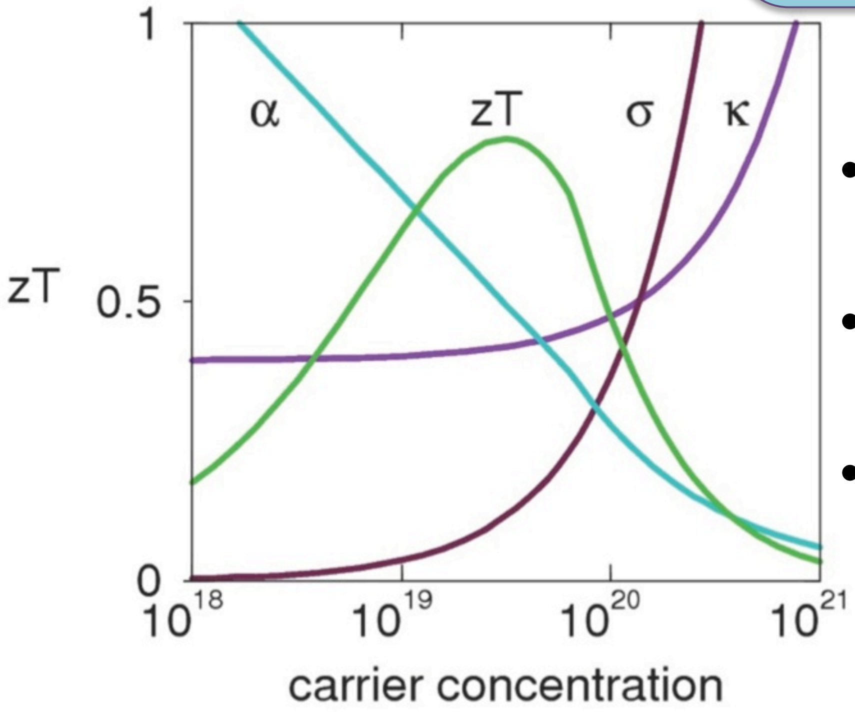
$$zT = \frac{\alpha^2 \sigma T}{\kappa}$$

Boltzmann transport equations

$E_F$ optimization (doping)

Intrinsic material properties

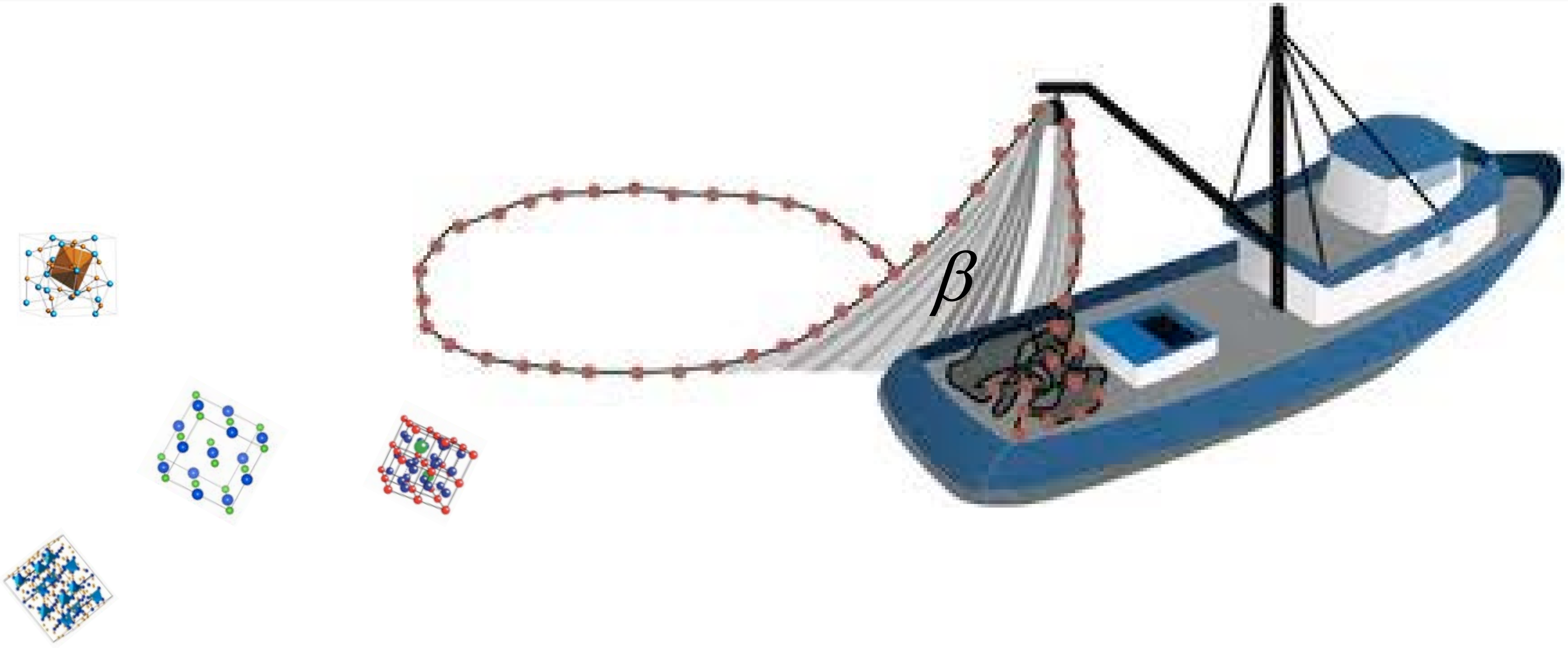
$$\beta \propto \frac{\mu N m^{*3/2}}{\kappa_L}$$



- High $\beta$ is a necessary but insufficient criteria for high zT.
- Potentially easier to search for $\beta$ than for "dopability"
- $\beta$ doesn't solve the problem of **scattering**

Snyder & Toberer Nature Mat. 2008

# Applying $\beta$ to high throughput calculations



$$\beta \propto \frac{\overset{\downarrow}{\mu}\,\overset{\downarrow}{N}\,\overset{\downarrow}{m}^{*3/2}}{\underset{\uparrow}{\kappa_L}}$$

**Ground state:**

Electronic band structure (*k*) 🟢

Phonon band structure (*q*) 🟠

**Coupling:**

Electron scattering rates (*k* + *q*) 🔴

Phonon scattering rates ($q_1$+$q_2$) 🔴

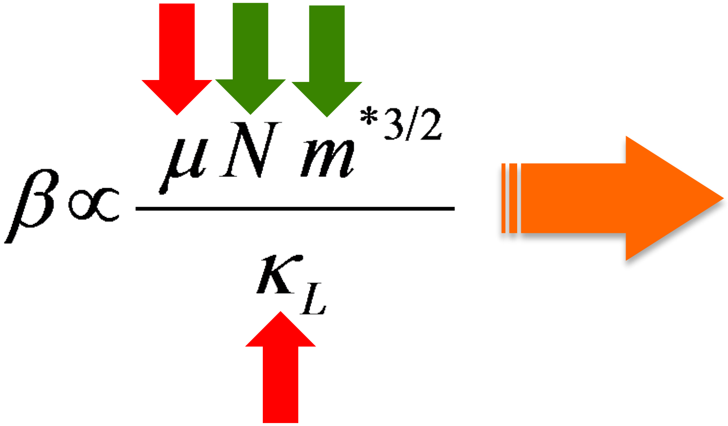
# Applying $\beta$ to high throughput calculations

**Goal:** Develop **semi-empirical models** for mobility ($\mu$) and $\kappa_L$ which correlate **ground-state** DFT calculations & structural data (.cif file) with experimental measurements.

Source experimental data:

- Known thermoelectric materials
- Classic III-V and II-VI semiconductors
- Oxides

Too little experimental data for machine learning, use theory driven models instead.



$$\beta \propto \frac{\mu N m^{*3/2}}{\kappa_L}$$

**Ground state:**

Electronic band structure (*k*) 🟢

Phonon band structure (*q*) 🟠

**Coupling:**

Electron scattering rates (*k* + *q*) 🔴

Phonon scattering rates ($q_1$+$q_2$) 🔴

# Semi-empirical approach to lattice thermal conductivity

Can we down-select materials *without* knowledge of anharmonicity or $v_g(k)$?

$$\kappa_L \propto C\, v_g^2\, \tau$$

$$\downarrow \qquad \downarrow \qquad \downarrow$$

$$\kappa_L \sim \frac{1}{n^x}\;\frac{B^x}{d^x}\;B^{x^*}$$

$C$ – optical modes have extremely low velocity, effectively decreasing available heat capacity

$v$ – acoustic branch carries heat, using low frequency approximation - speed of sound $v_s$

$\tau$ - Expectation that stiffer lattices have lower phonon-phonon coupling

*n* = number of atoms in primitive cell
*B* = bulk modulus
*d* = density

* - plus small optical phonon term

Yan et al EES 2015

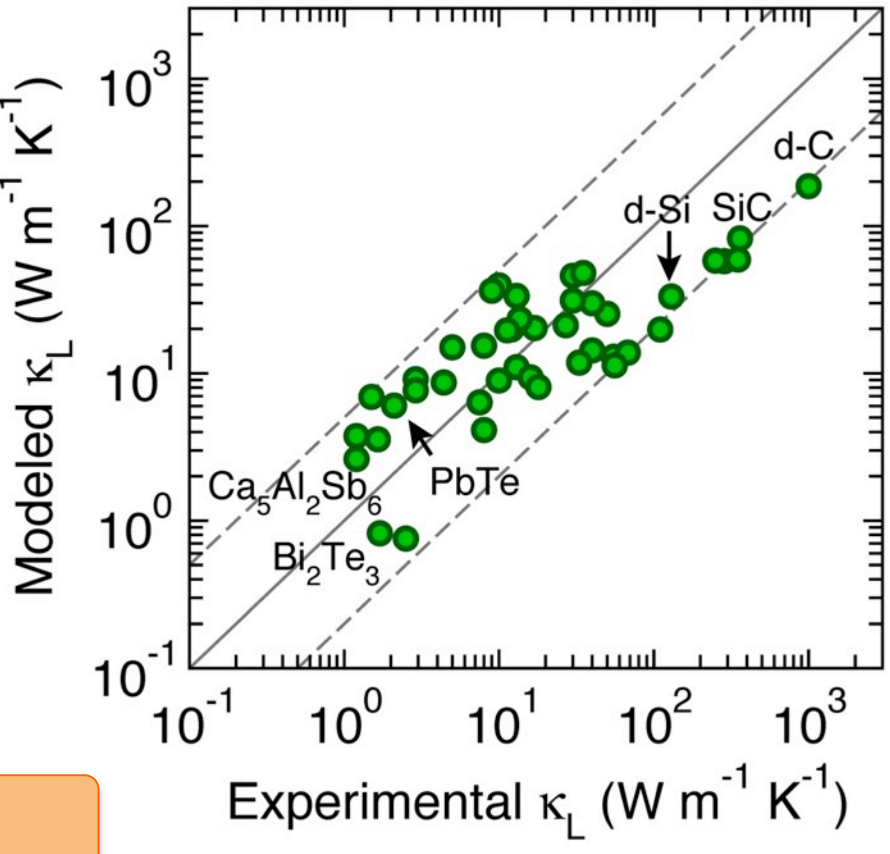
# Semi-empirical approach to lattice thermal conductivity

$$\begin{array}{lccc} \kappa_L \propto & C & v_g^2 & \tau \\ & \downarrow & \downarrow & \downarrow \\ \kappa_L \sim & \dfrac{1}{n^x} & \dfrac{B^x}{d^x} & B^x \end{array}$$

+ minimum term for optical modes

Calculate via:

- DFT bulk modulus (*B*)
- known mass density (*d*)
- # atoms in primitive cell (*n*)



Trying not to over fit the data!!
Similar approach applied to mobility

Yan et al EES 2015

# Development of high throughput descriptors for $\beta$

$$\beta \propto \frac{\mu N m^{*3/2}}{\kappa_L}$$

$$\beta_{SE} \approx \frac{n^a d^b N^c}{m_b^{*d} B^e}$$

From .cif:

$n$ – number of atoms in primitive cell

$d$ – density

From DFT:

$N$ – band degeneracy

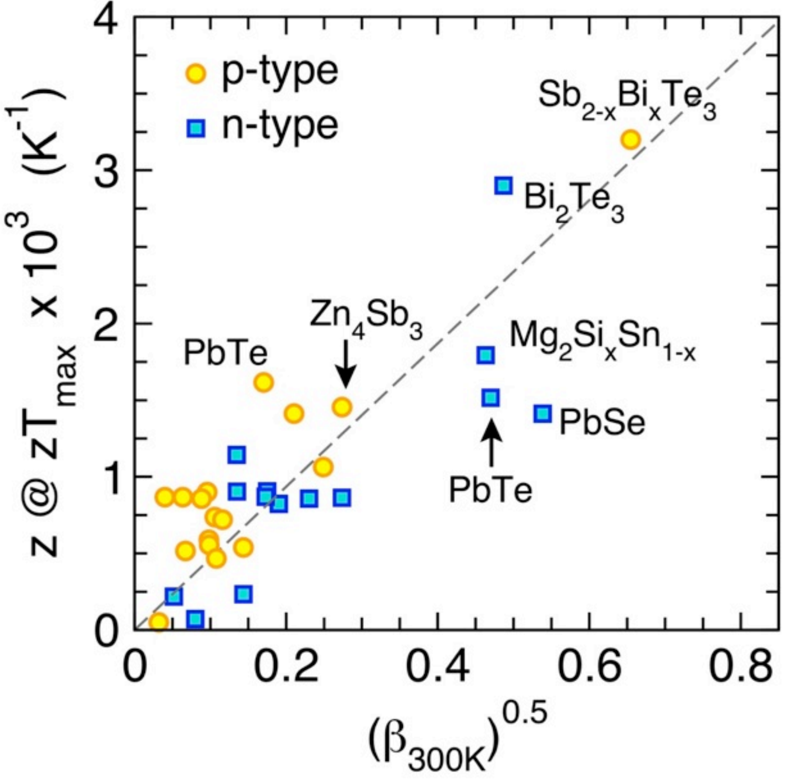
$m^*_b$ – band effective mass

$B$ – bulk modulus

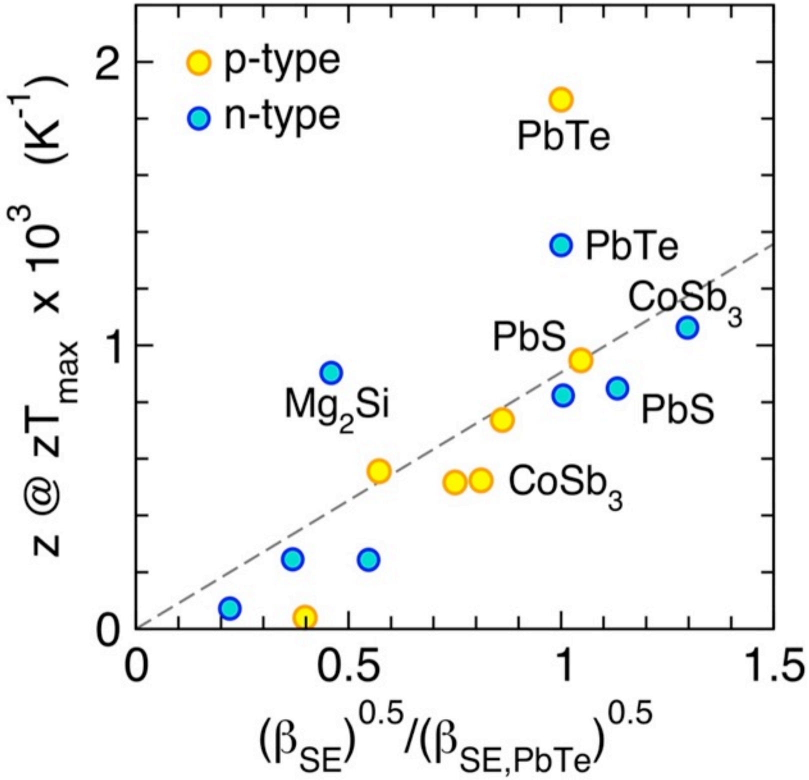
Yan et al EES 2015

# Comparison between $\beta_{\text{exp}}$ and $\beta_{\text{SE}}$

Experimental



Semi-empirical



- Semi-empirical $\beta$ as accurate as experimental in predicting TE performance
- $Mg_2Si$ and p-PbTe underestimated due to doping (Bi) and T-dependent effects

Yan et al EES 2015

# Trial high-throughput calculations – ICSD source

**Compounds:** (~2,000 unique structures from ICSD & 10 TE materials)

- Stoichiometric
- No H, O
- No more than 10 atoms in primitive cell
- No row 7, La, Ac, Noble gases

**DFT Calculations:**

- ~4000 k-points
- Magnetic systems – compared non-magnetic, ferromagnetic and antiferromagnetic configurations and chose lowest energy spin configuration

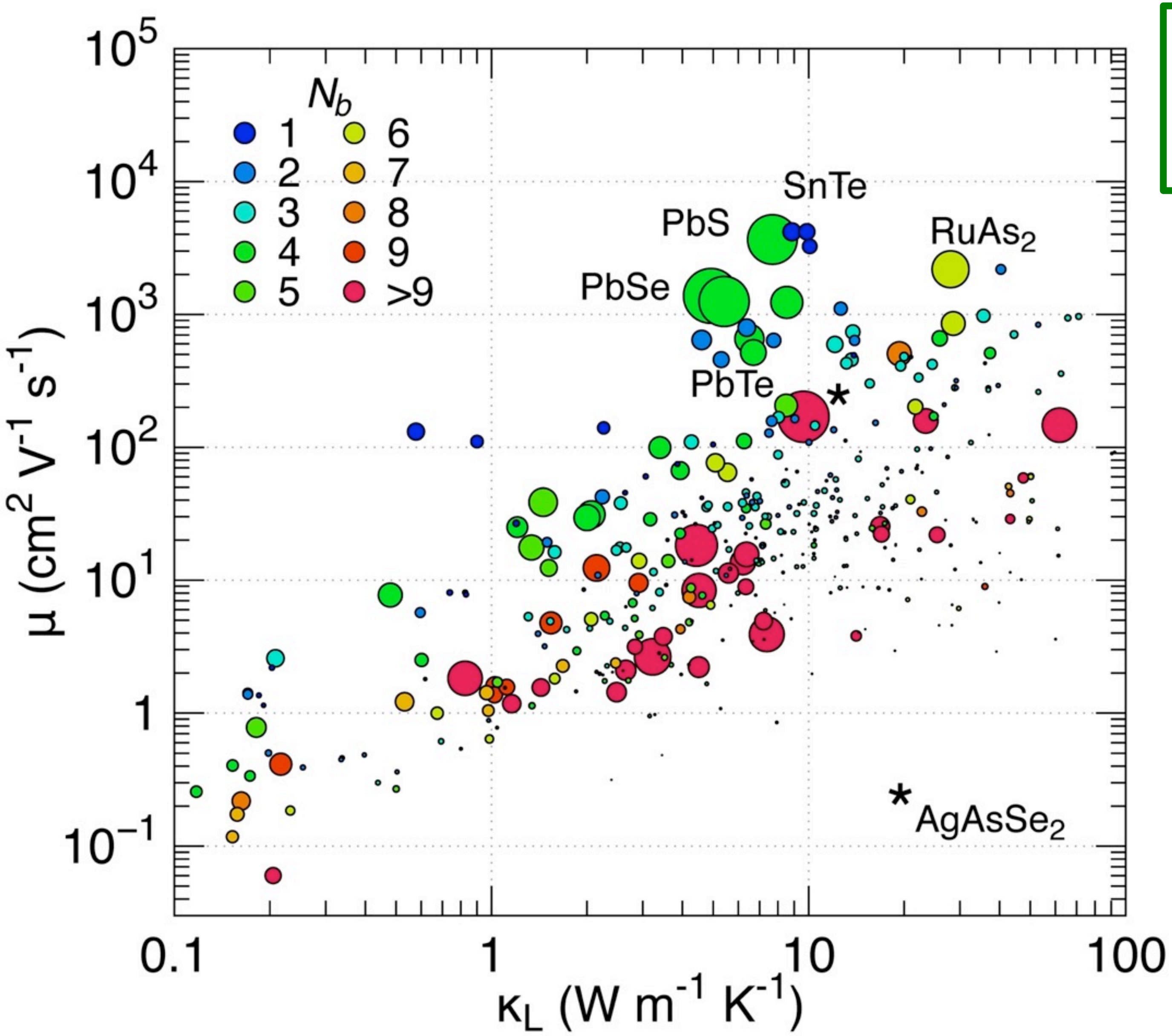
**Yield:**

~600 semiconductors

Downselected remaining semiconductors to $E_g$ <2 eV:

~450 compounds remain

# Trial high-throughput calculations – valence band



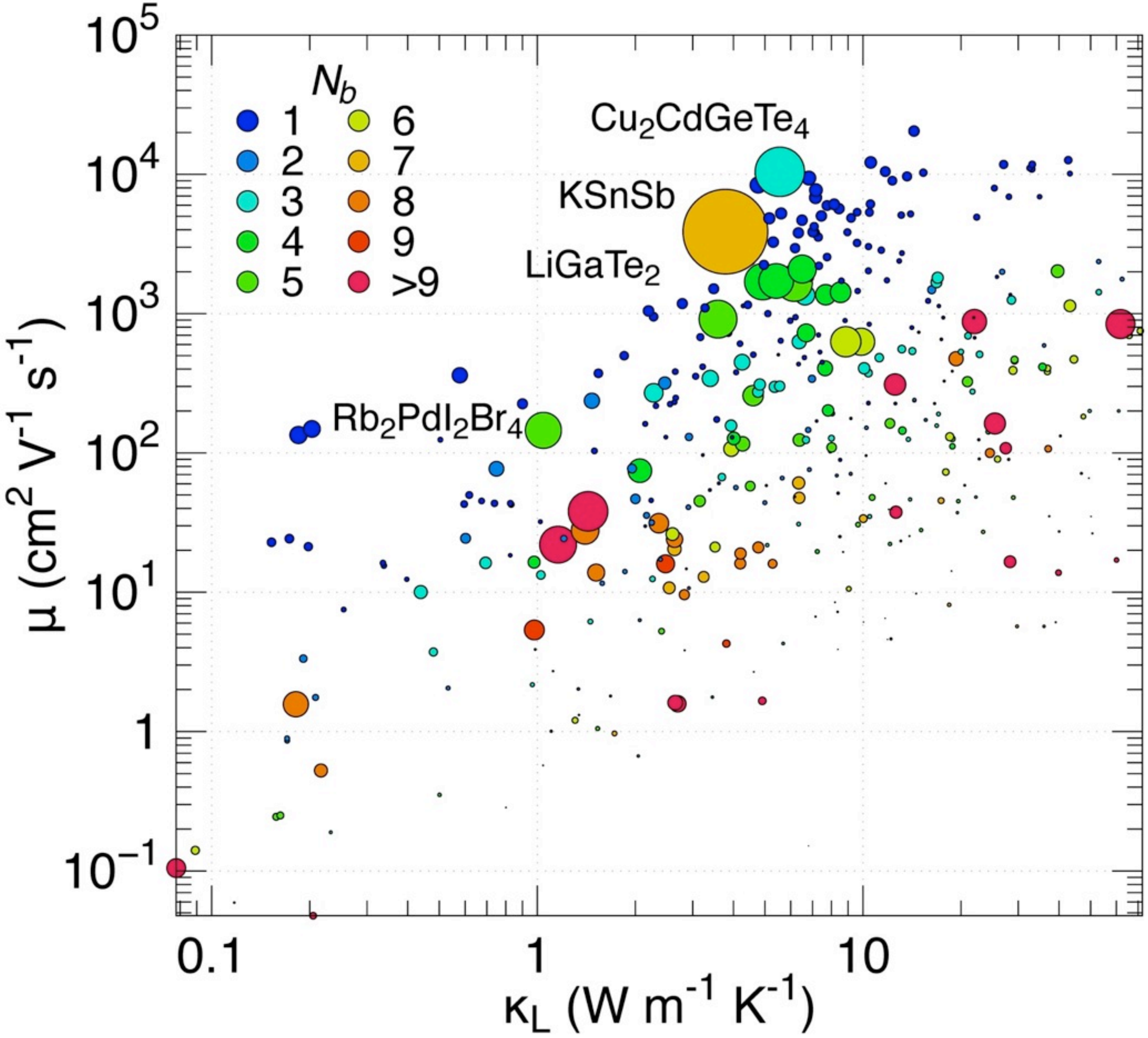
$$\beta_{SE} \propto \frac{\mu N m^{*3/2}}{\kappa_L}$$

Bubble area indicates $\beta_{SE}$

$Bi_2Te_3$, PbTe, PbSe PbS all in top 4% of down-selected compounds

Yan et al EES 2015

# Trial high-throughput calculations – conduction band



$$\beta_{SE} \propto \frac{\mu N m^{*3/2}}{\kappa_L}$$

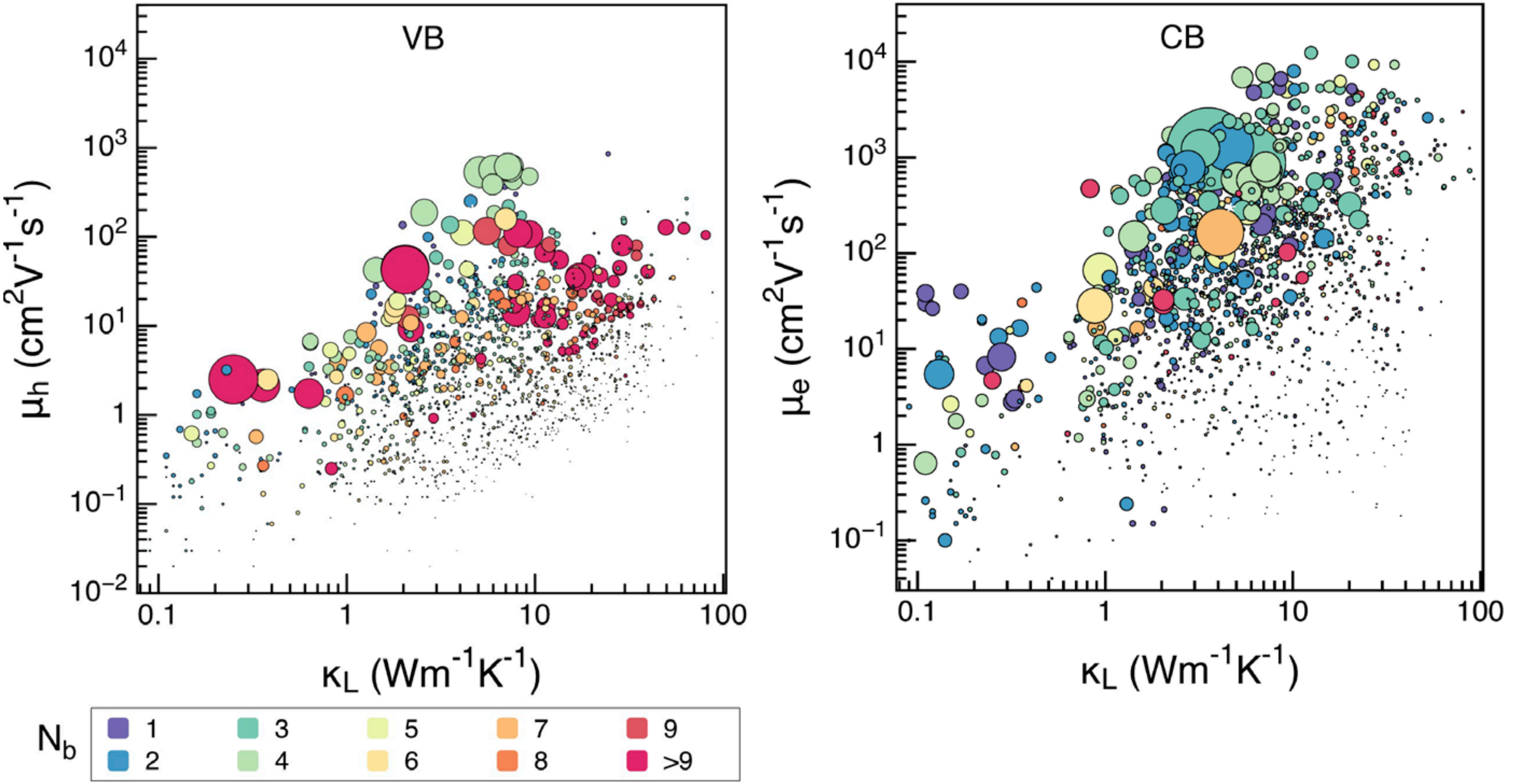
Bubble area indicates $\beta_{SE}$

Yan et al EES 2015

# Expanding the search – 1,600 semiconductors

Atom count: up to 30 in primitive cell

Pnictides, oxides, chalcogenides



# Thermoelectric material design: Looking forward

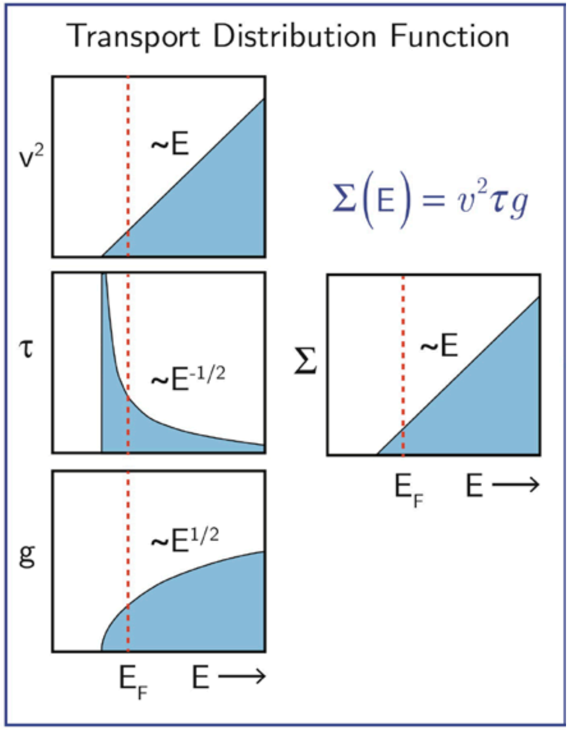
Things get even neater in:

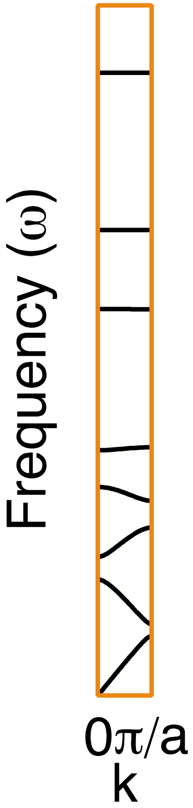
- Anisotropic materials
- Correlated systems

Not discussed:

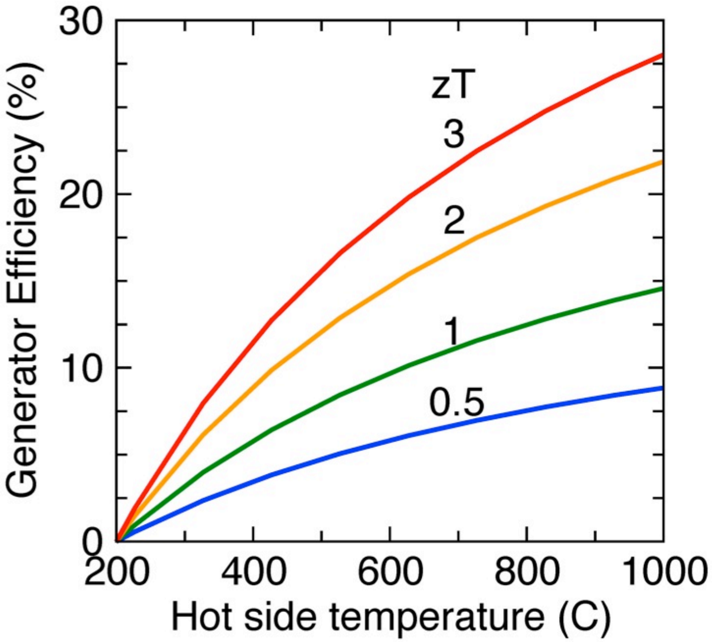
- Solid state refrigeration (Peltier cooling)

Beginning to design charge & phonon transport:





A solid state heat engine with >25% efficiency would ***transform*** energy storage.



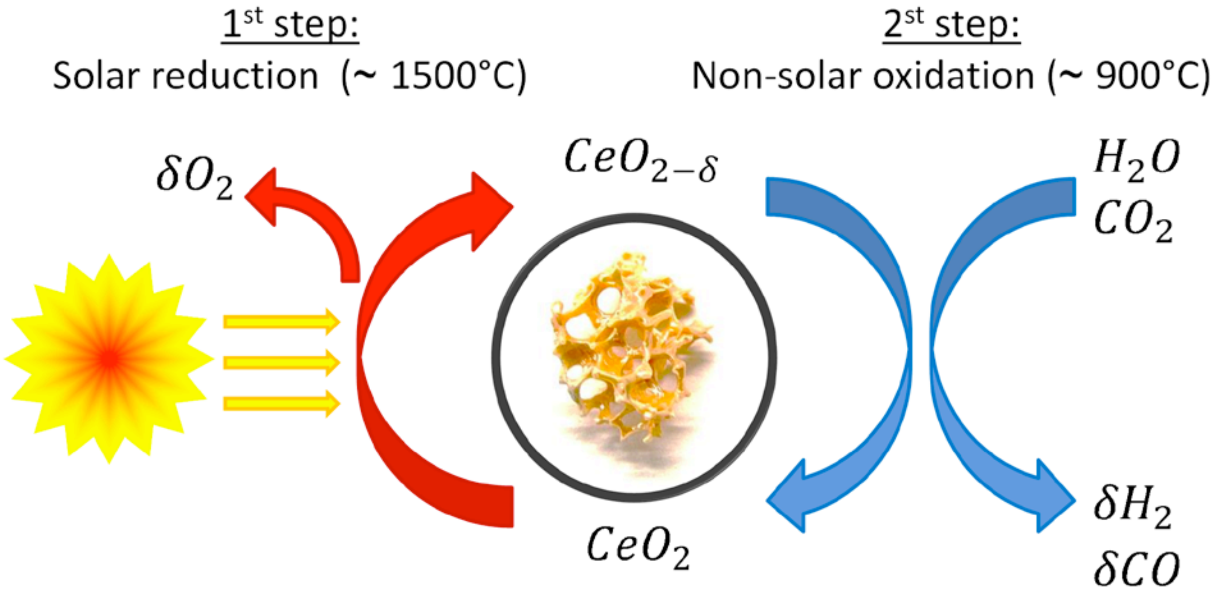
# Carbon-neutral storage approaches

* wind, PV

Internal energy:

Example:

Renewable Source:



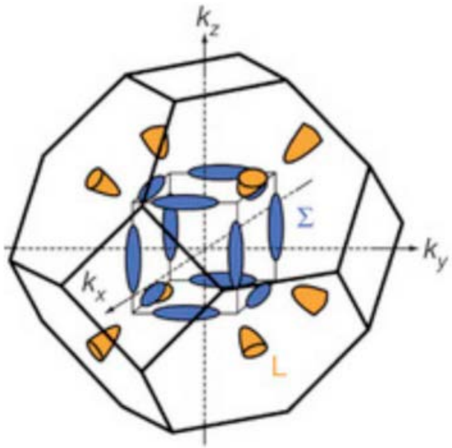
Syn gas?

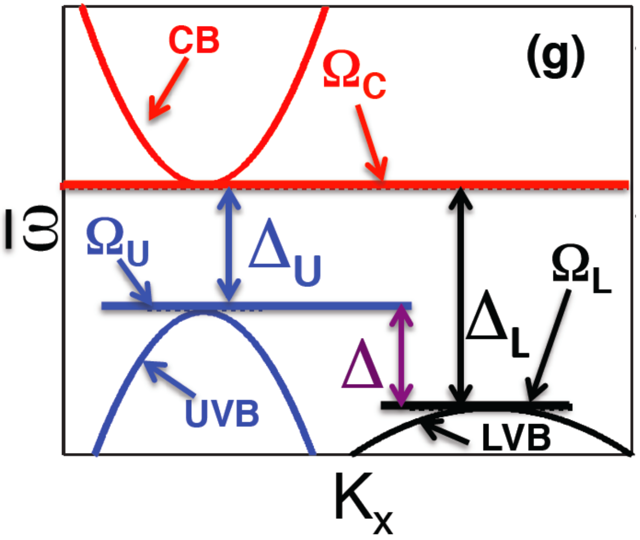
Chemical

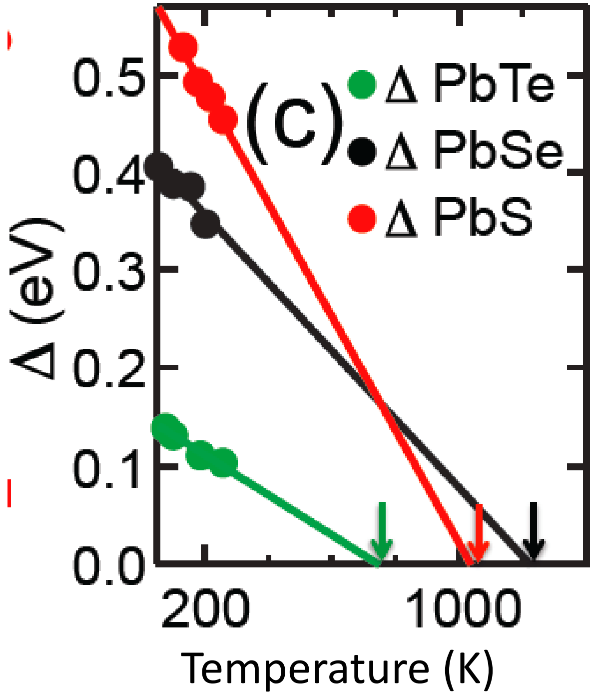
Solar biofuels, thermochemical

Direct abs.

# Example of Band Degeneracy: p-type PbTe







arXiv:1404.1807v3