Band convergence of half-Heuslers for a high thermoelectric power factor

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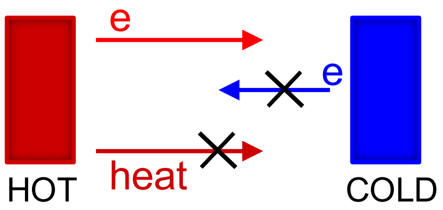
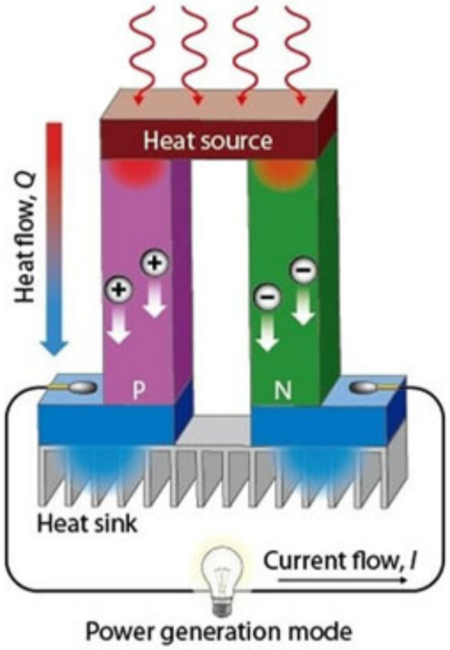
WARWICK

Thermoelectricity -basics

Direct conversion of temperature differences to electric voltage and vice versa.

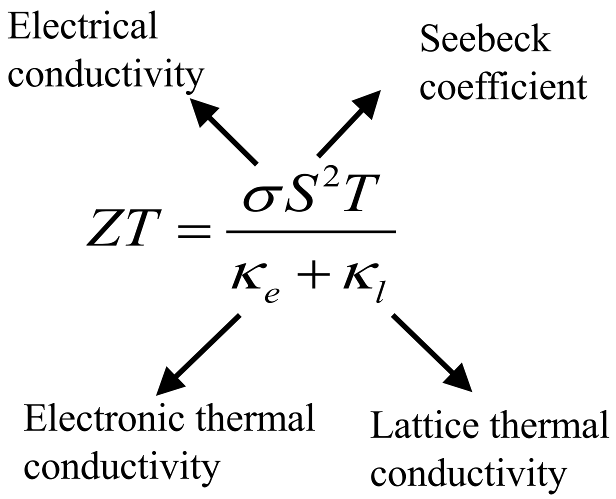




$$S \propto n^{-\frac{2}{3}}$$

$$\sigma, \kappa_e \propto n$$

Thermoelectric figure of merit



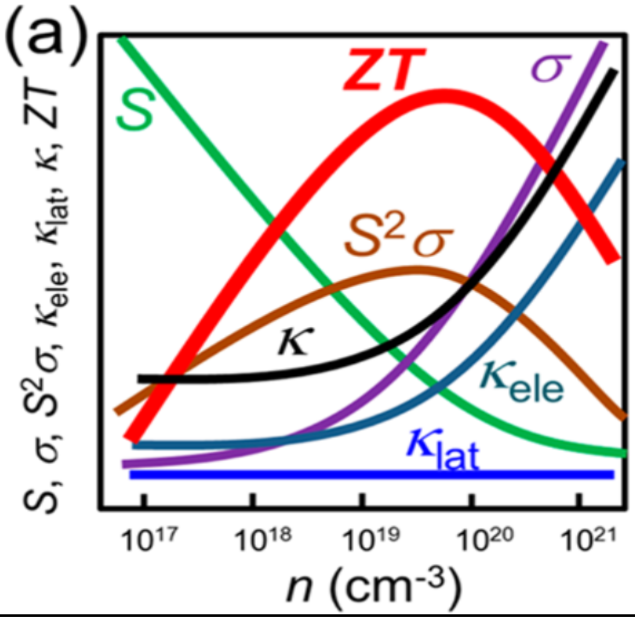
Electrical conductivity

Seebeck coefficient

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

Electronic thermal conductivity

Lattice thermal conductivity



Methods of improving ZT

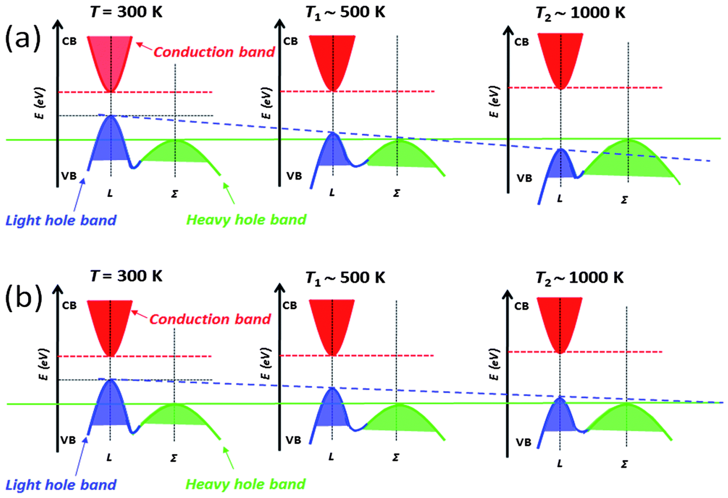
Increase the power factor (σS^2)

- ➢ Bandstructure engineering
  - -Band aligning
  - -Modify band masses
  - -Resonant doping

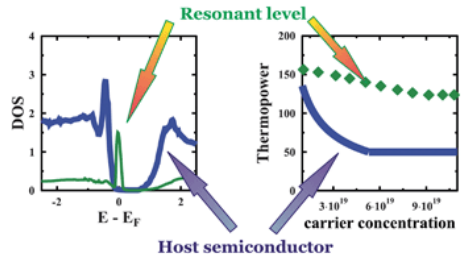
Reducing the thermal conductivity ($\kappa_e + \kappa_l$)

- ➢ Hierarchical architectures
- ➢ Phonon engineering

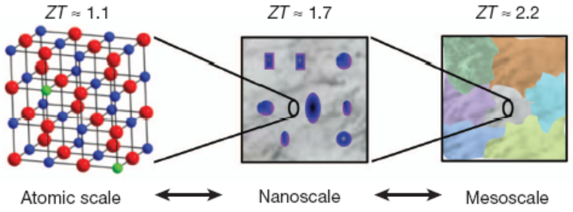
$$ZT = \frac{\sigma S^2 T}{\kappa_e + \kappa_l}$$



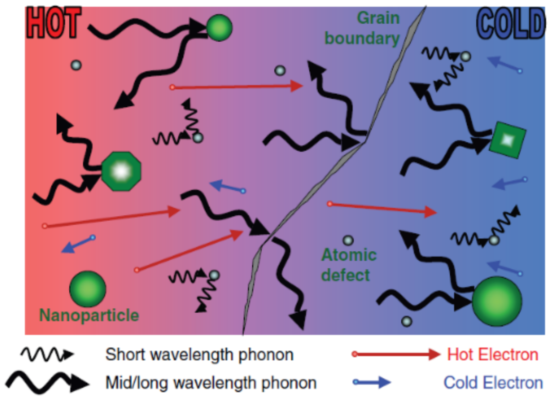
Li-Dong *et* al, ***Energy Environ. Sci.***, 2014



Poehler *et* al, ***Energy Environ. Sci.***, 2012



Biswas *et* al, ***Nature***, 2012.
(p-type PbTe)



Vineis, ***Adv. Mat.***, 2010

Outline

- Band convergence
  - Introduction to transport equations
  - Scattering mechanisms : parabolic band approximation

- Introduction to half-Heuslers

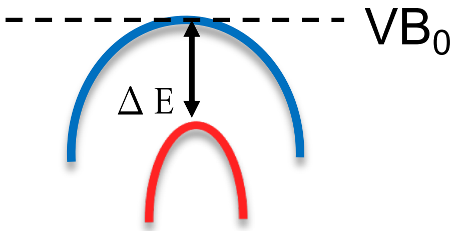
- Modeling half-Heuslers : non parabolic band approximation
  - Non parabolic band approximation
  - Band aligning – NbCoSn,TiCoSb

- Aligning bands of half-Heuslers with strain
  - NbCoSn
  - TiCoSb
  - ZrCoSb

- Conclusions

Band aligning

- Increases number of carrier available for transport.
- Also increase the scattering.
- Depends on the nature of the bands.



Power Factor = σS^2

Conductivity

$$\sigma(T, E_F) = \frac{1}{V} \int \Xi(E) \left(-\frac{\partial}{\partial E} f\ (E, E_F, T) \right) dE$$

Seebeck coefficient

$$S(T, E_F) = \frac{1}{eTV\ \sigma(T, E_F)} \int \Xi_{\alpha\beta}(E)(E - E_F) \left(-\frac{\partial}{\partial E} f\ (E, E_F, T) \right) dE$$

Transport distribution function

$$\Xi(E) = \sum_i e^2 \tau_i(E)\ {v_i}^2(E)\ \mathrm{DOS}_i\ (E)$$

Scattering mechanisms

- Constant rate of scattering (most commonly used)

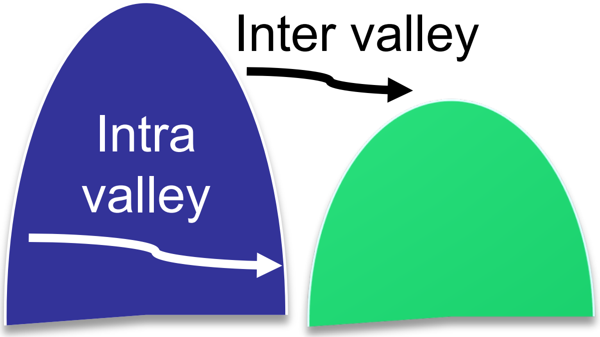
$$\tau(E) = \text{Constant}$$

$$\Xi_{\alpha\beta}(E) \propto \sum_i m_i^{\frac{1}{2}} E^{\frac{3}{2}}$$

- Scattering $\propto$ DOS_i (Intra-valley scattering)

$$\tau(E)_i \propto \frac{1}{\mathrm{DOS}_i(E)}$$

$$\Xi_{\alpha\beta}(E) \propto \sum_i \frac{E}{m_i}$$



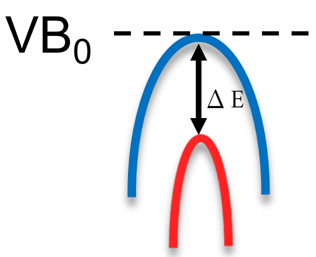
- Scattering $\propto$ $\sum \mathrm{DOS}_i$ (Inter- and intra-valley scattering)

$$\tau(E) = \frac{1}{\sum \mathrm{DOS}_i(E)} \qquad \Xi_{\alpha\beta}(E) \propto \frac{\sum_i \; m_i^{\frac{1}{2}} E^{\frac{3}{2}}}{\sum_i m_i^{\frac{3}{2}} E^{\frac{1}{2}}}$$

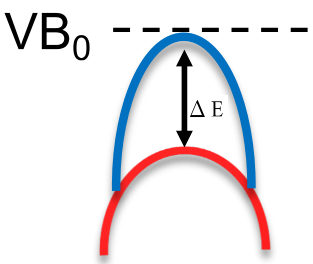
Case study: Constant scattering rate

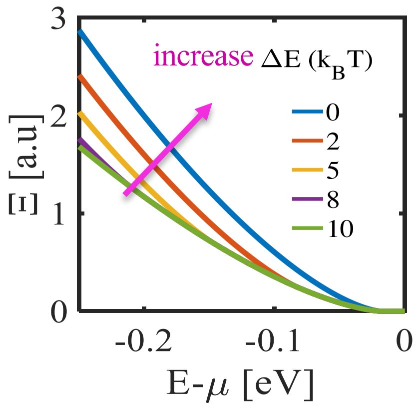
$$\Xi_{\alpha\beta}(E) \propto \sum_i m_i^{\frac{1}{2}}\, E^{\frac{3}{2}}$$

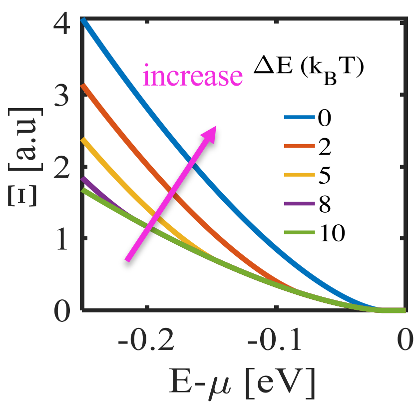
m_1=1, m_2 = 0.5



m_1=1, m_2 = 2

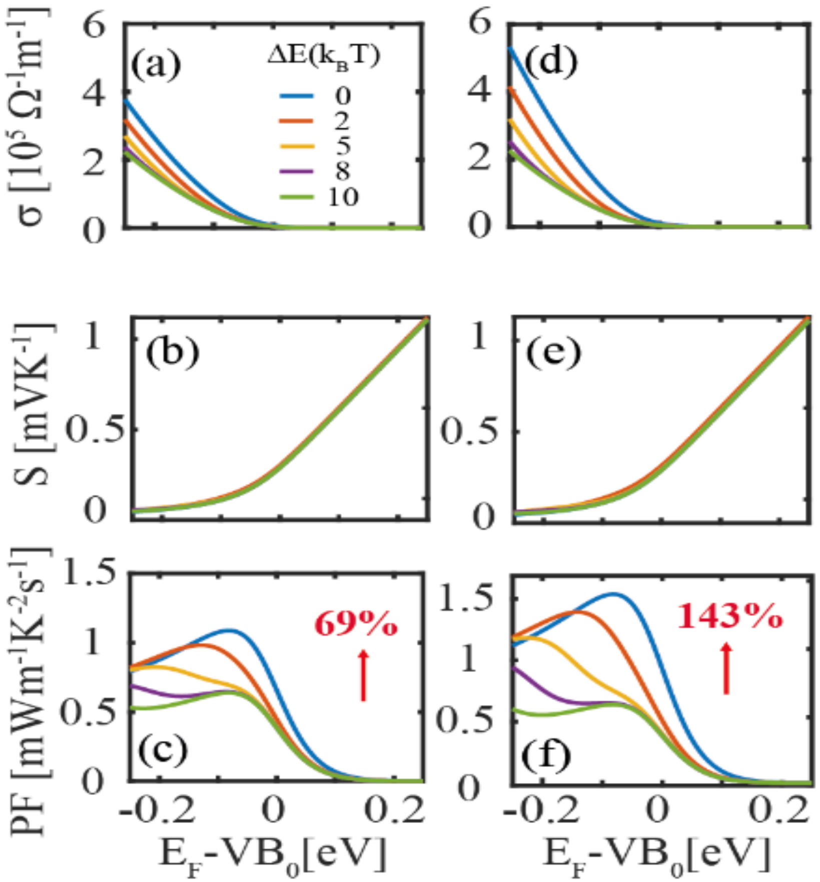






Aligning any band will improve the transport distribution.

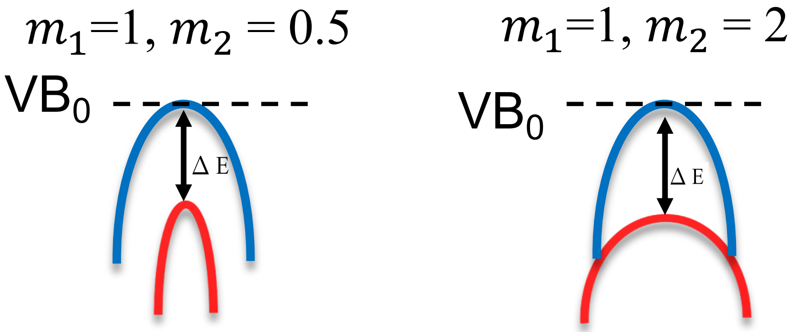
m_1=1, m_2 = 0.5 m_1=1, m_2 = 2

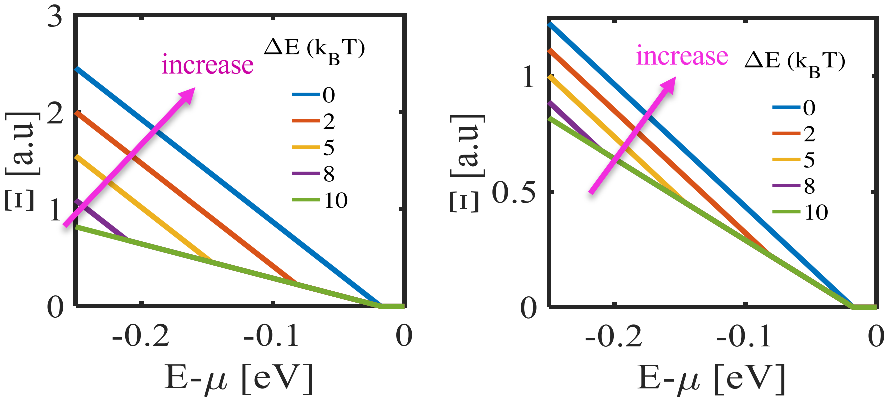


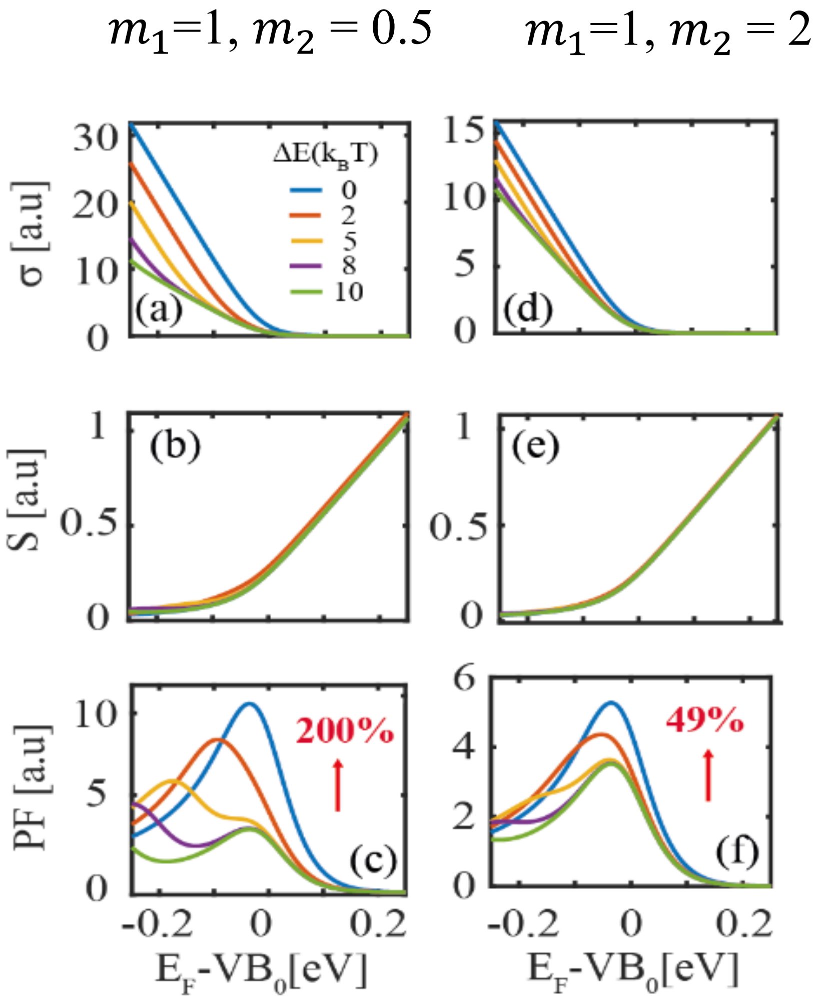
Heavier masses results in a larger transport distribution, larger conductivity and a better PF.

Case study: Scattering $\propto$ DOS$_i$ (Intra-valley scattering only)

$$\boxed{\Xi_{\alpha\beta}(E) \propto \sum_i \frac{E}{m_i}}$$







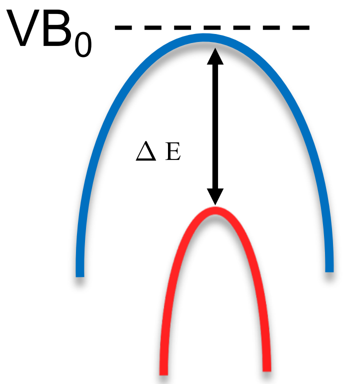
Aligning any band will improve the transport distribution.

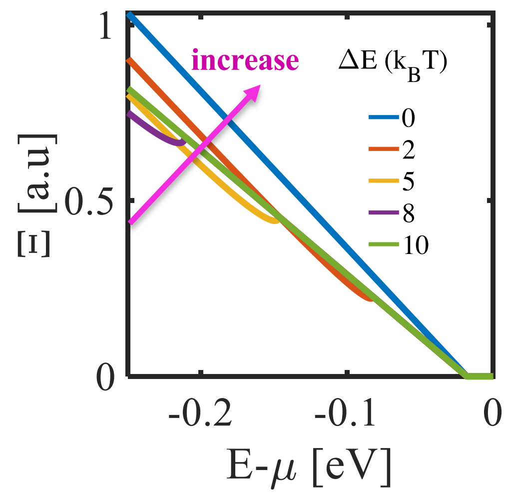
Lighter masses results in a a larger transport distribution, larger conductivity and a better PF.

Case study: Scattering ∝ $\sum \mathrm{DOS}_i$ (Inter- and intra-valley scattering)

$$\Xi_{\alpha\beta}(E) \propto \frac{\sum_i \; m_i^{\frac{1}{2}}\, E^{\frac{3}{2}}}{\sum_i m_i^{\frac{3}{2}}\, E^{\frac{1}{2}}}$$

m_1=1, $m_2 = 0.5$



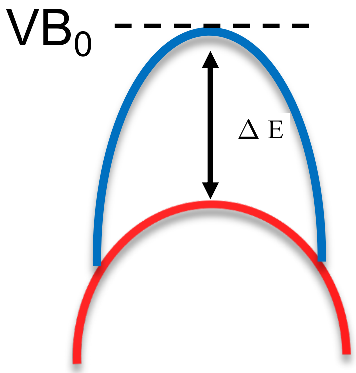


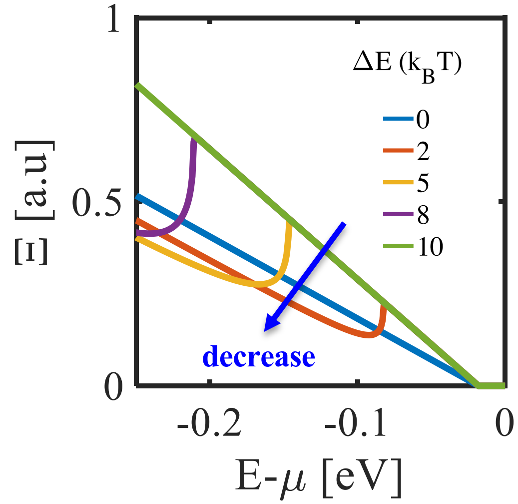
Aligning any band will NOT improve the transport distribution

In the case of 2 bands,

$$\mathbf{m_1 > m_2}$$

m_1=1, $m_2 = 2$

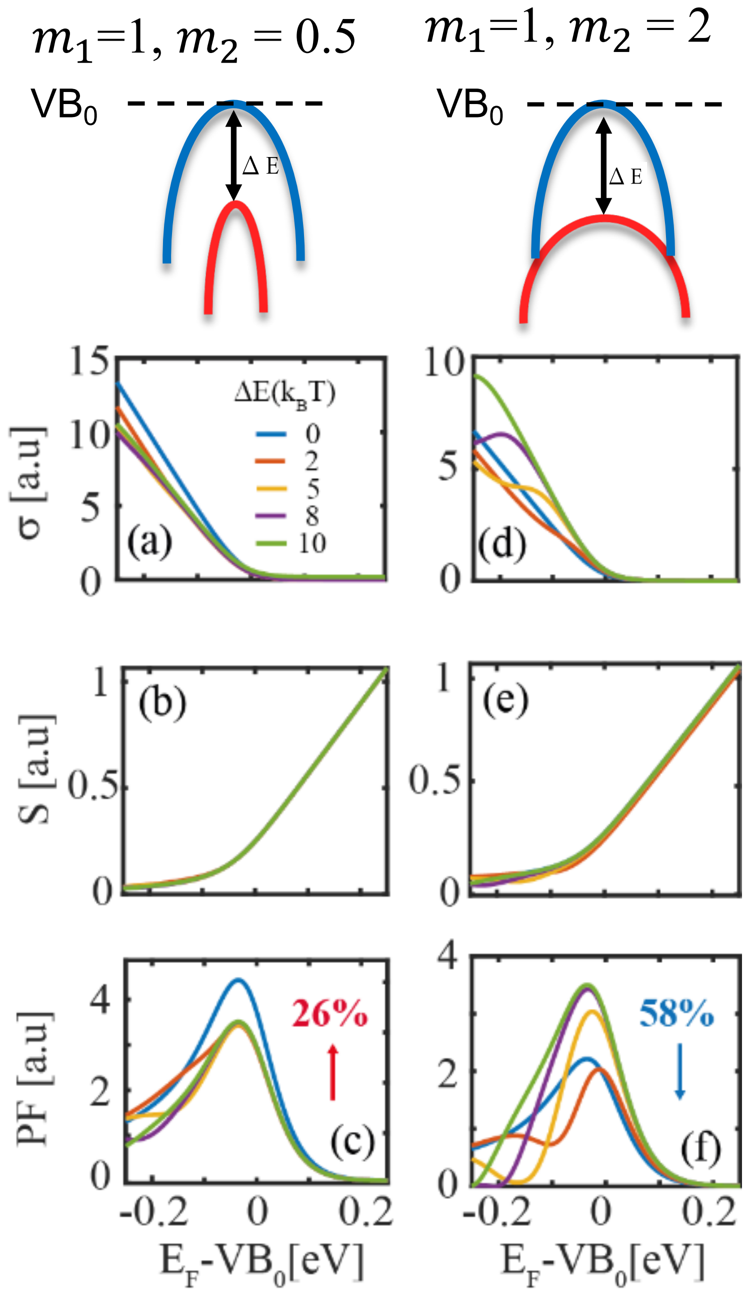




In the case of 3 bands,

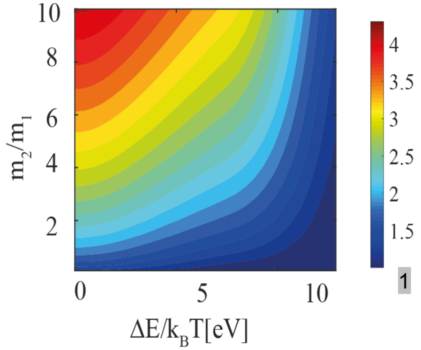
$$\mathbf{m_1 > \frac{m_2^{\frac{3}{2}} + m_3^{\frac{3}{2}}}{m_2^{\frac{1}{2}} + m_3^{\frac{1}{2}}}}$$

Case study: Scattering $\propto \sum \mathrm{DOS}_i$ (Inter- and intra-valley scattering)



Summary of conditions

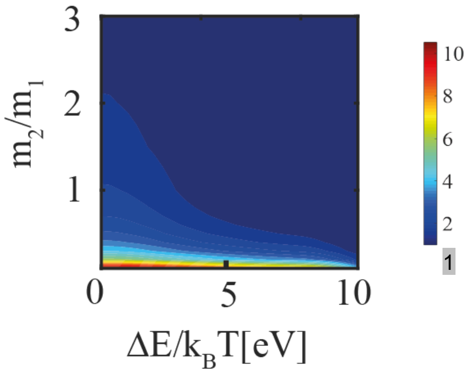
Constant scattering



Under a constant scattering rate

- Any band will improve the powerfactor.
- Improvement is better with heavier masses.

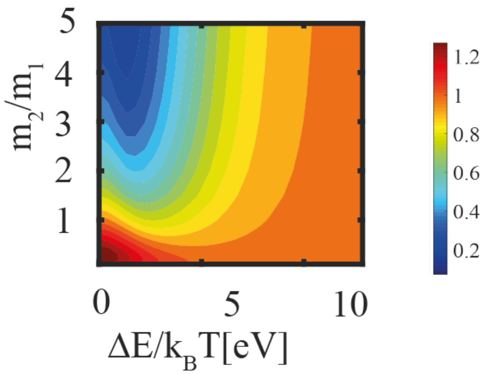
Intra-valley scattering only



When Scattering $\propto$ DOS$_i$ (Intra-valley scattering only)

- Any band will improve the powerfactor.
- Improvement is better with lighter masses.

Inter- and intra-valley scattering



When Scattering $\propto$ DOS$_i$ (Intra- and inter- valley scattering)

- Only specific masses improve the powerfactor.
- In the case 2 bands, aligning mass has to be lighter than the existing one.

Outline

- Band convergence
  - Introduction to transport equations
  - Scattering mechanisms : parabolic band approximation

- Introduction to half-Heuslers

- Modeling half-Heuslers : non parabolic band approximation
  - Non parabolic band approximation
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- Aligning bands of half-Heuslers with strain
  - NbCoSn
  - TiCoSb
  - ZrCoSb

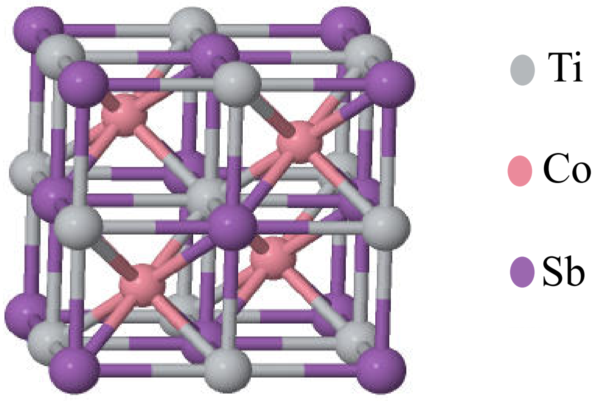
- Conclusions

Why half-Heuslers?

Relatively high thermoelectric performance combined with

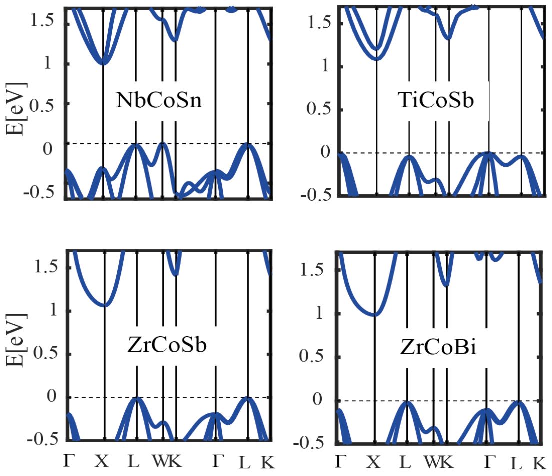
- relatively inexpensive elemental composition
- robust mechanical properties.
- high temperature stability

- XYZ form, where X and Y are transition metals and Z is in the p-block.
- Many combinations of X,Y and Z



TiCoSb Unit cell

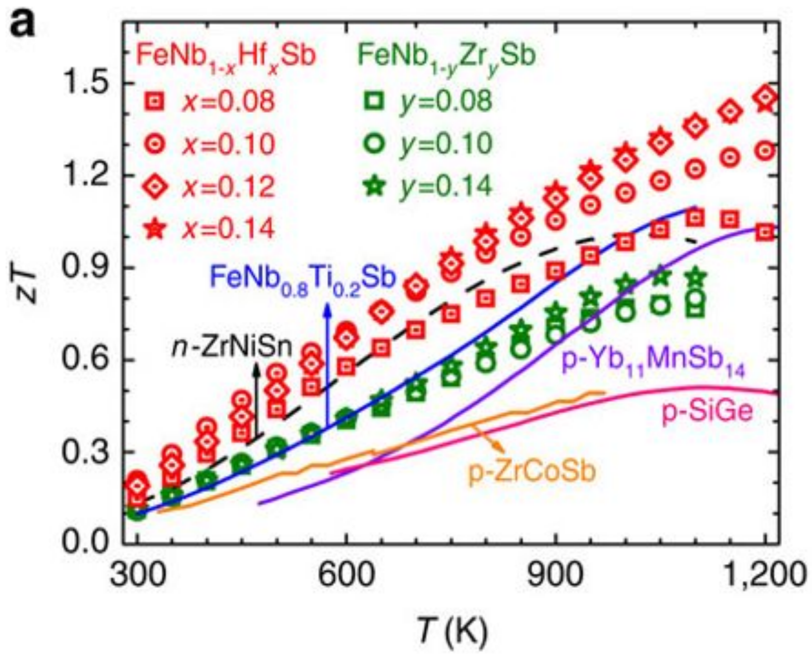
- Complex band structure offering a high band degeneracy, multiple valleys contributing to conduction



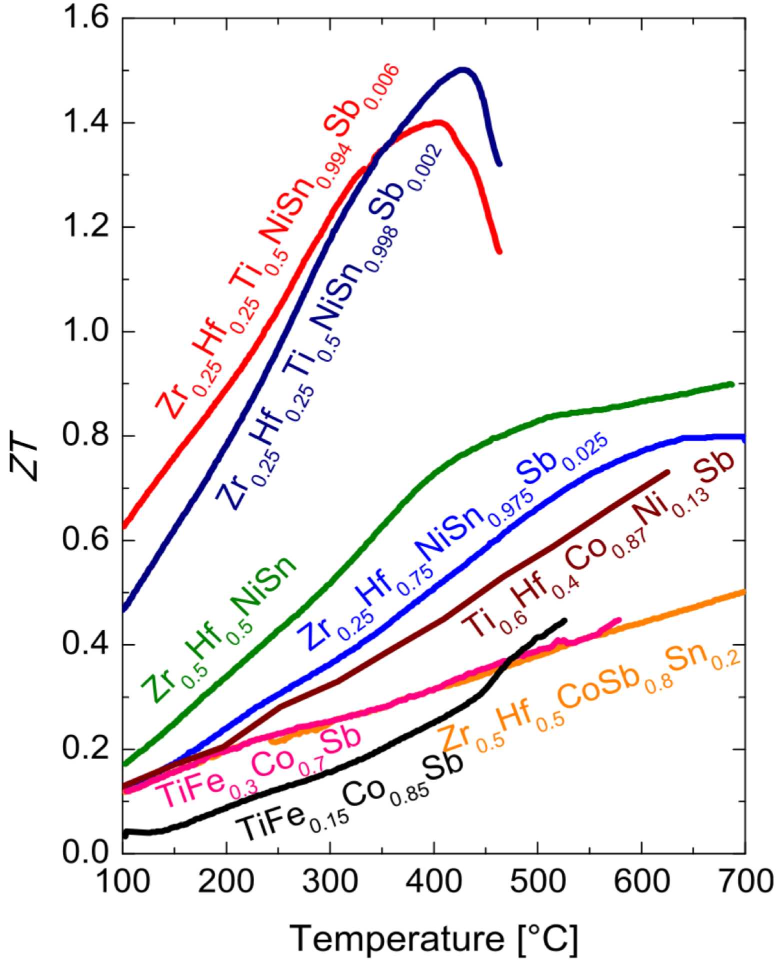
Half –Heuslers : Current state of research

Much work focuses on the reduction of the thermal conductivity

- nanocomposites
- grain size
- point defects
- alloying for large mass contrast

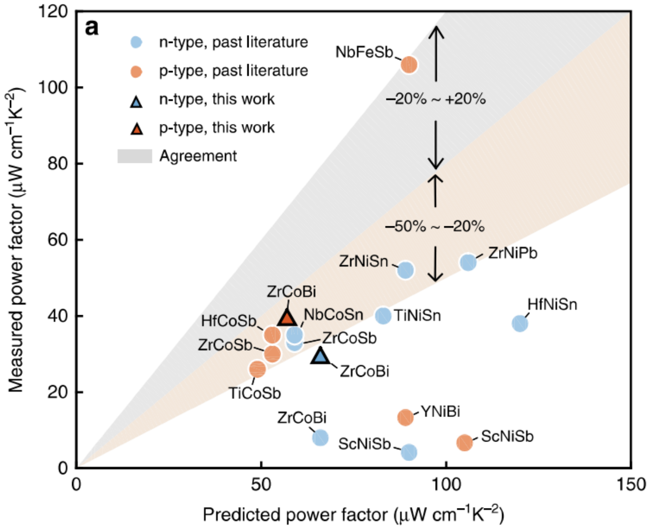


Fu et.al, *Nature Comm.* (2015).



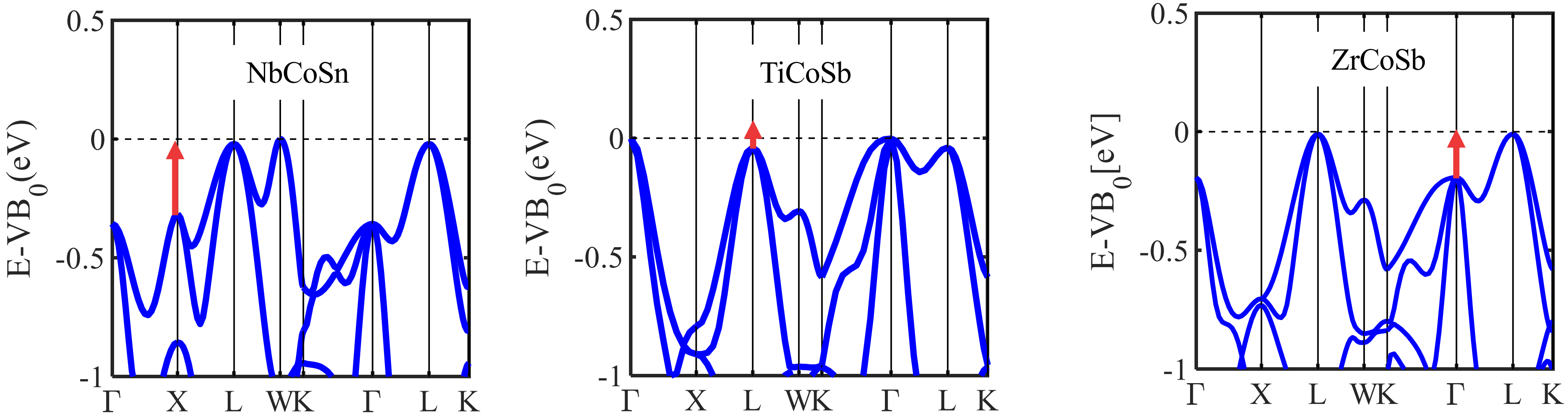
Graf et.al, *Prog. Solid State Chem.* (2011).

Co based half-Heuslers :TiCoSb, NbCoSn, ZrCoSb



Band aligning techniques

- **Strain**
- **Alloying**
- **Second phasing**



Potential for improving power factor through band aligning

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- Scattering mechanisms : parabolic band approximation
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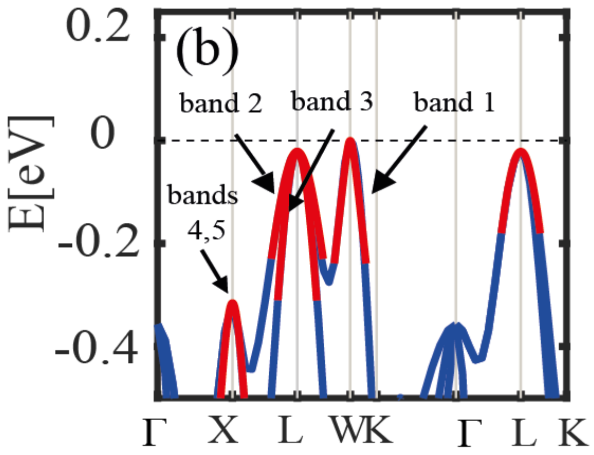
Non parabolic band approximation



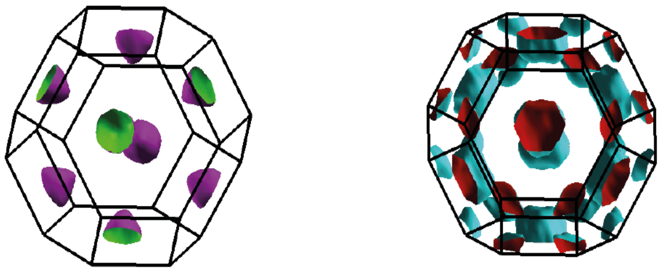
Bandstructure of of NbCoSn

$$E(1+\alpha E) = \frac{\hbar^2 k^2}{2m}$$

$$v = \sqrt{\frac{2E(1+\alpha E) - E0}{m}}\ \frac{1}{(1+2\alpha E)}$$

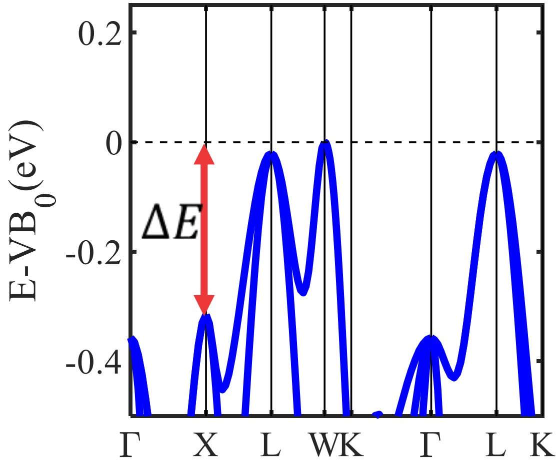
$$DOS = \frac{m^{\frac{3}{2}}}{\pi^2 \hbar^3} N \sqrt{2E(1+\alpha E)}\ (1+2\alpha E)$$

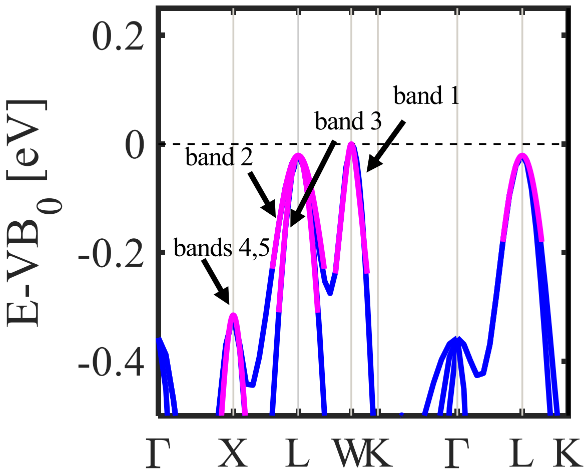
$$\boxed{\Xi(E) = \sum_i e^2 \tau_i(E)\, {v_i}^2(E)\, \mathrm{DOS}_i\,(E)}$$



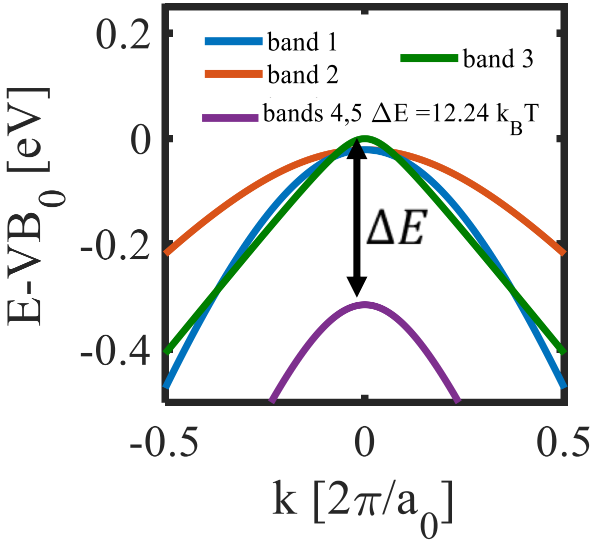
Fermi surface below 0.1eV of valance band edge of NbCoSn

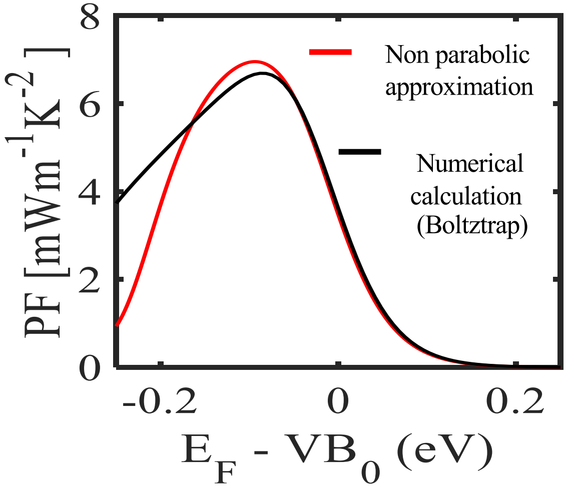
NbCoSn :Non parabolic band approximation (NPBA)



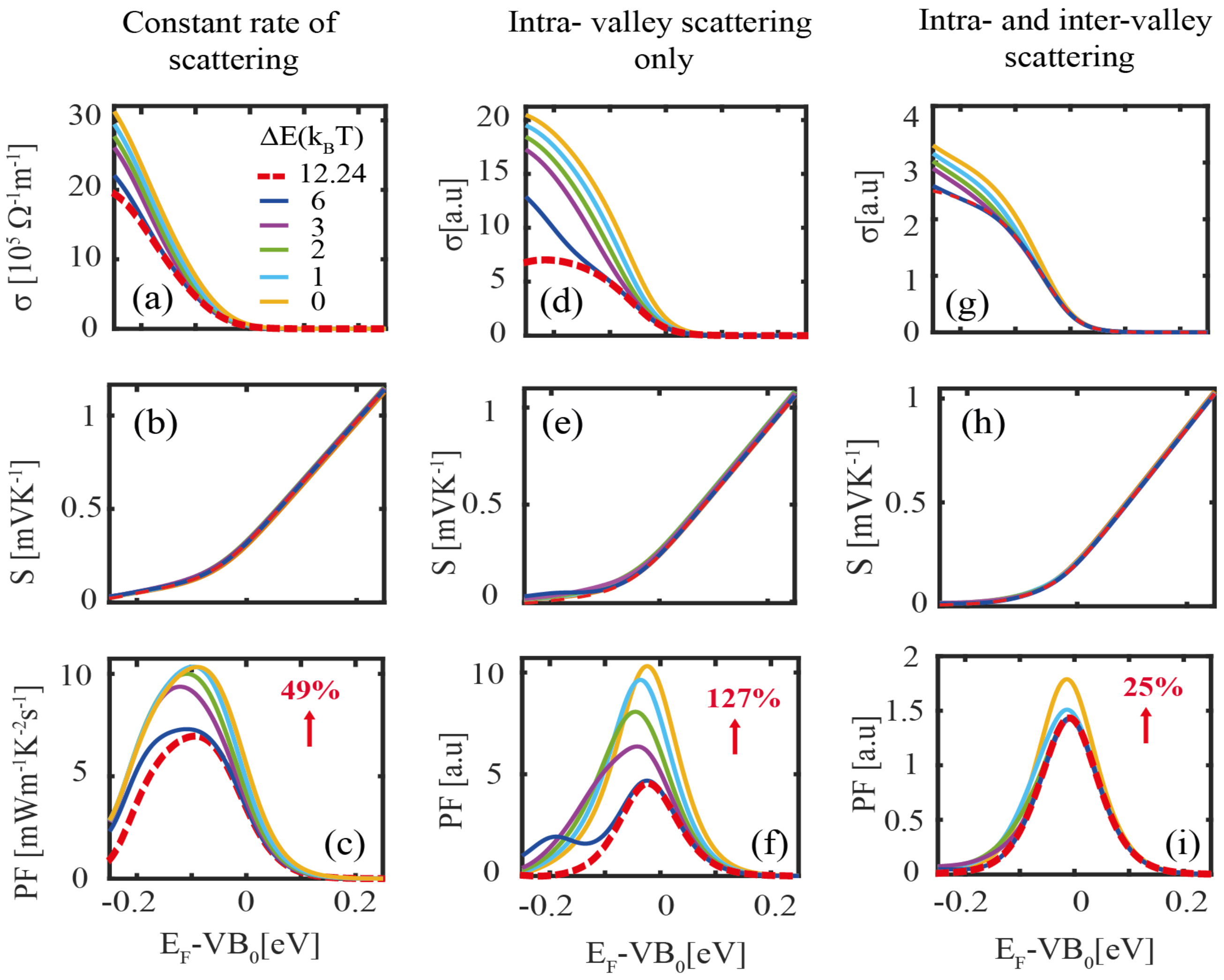


- Align valleys at X point with valence band edge
- 2 bands with similar masses





NbCoSn – Aligning X valley

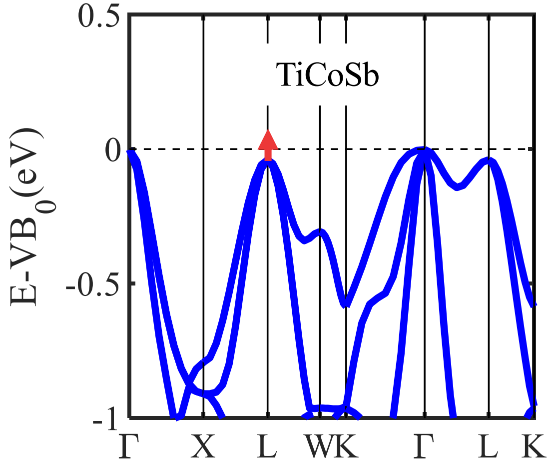


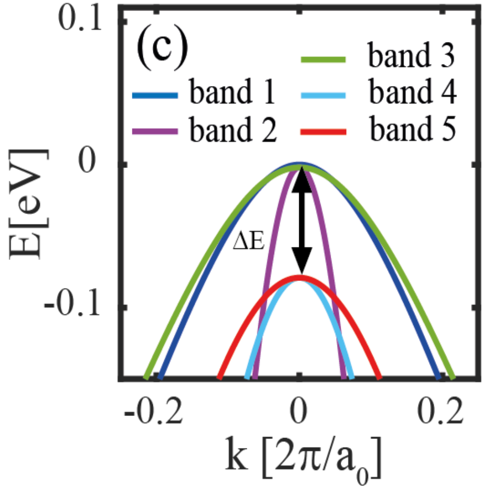
Constant rate of scattering

Intra- valley scattering only

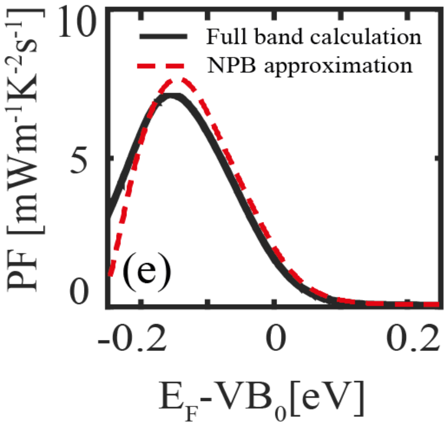
Intra- and inter-valley scattering

TiCoSb – Aligning L valley



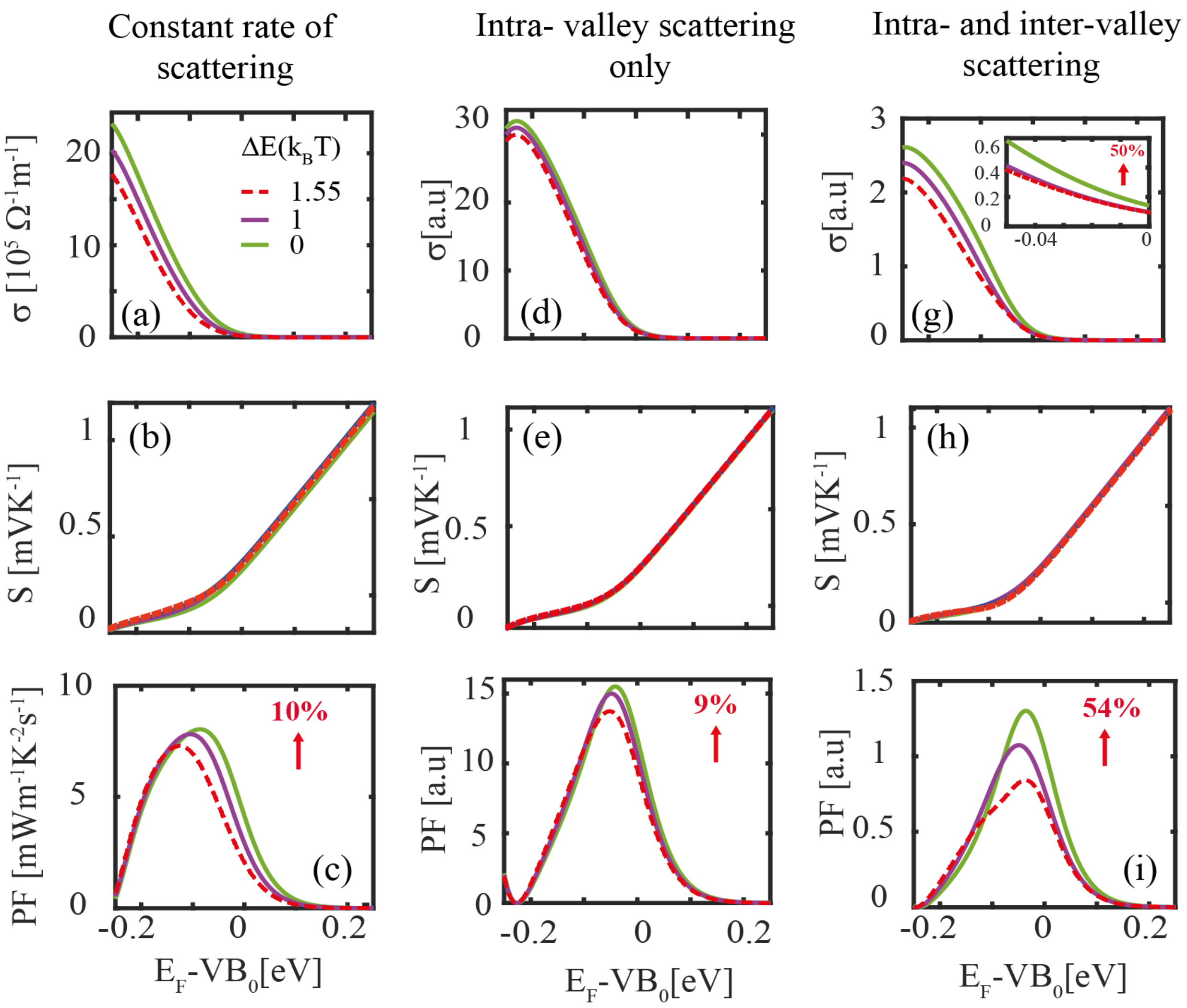


Aligning 2 bands with two different masses.



Reasonable match between NPBA and full band coalculations.

TiCoSb – Aligning L valley


Constant rate of scattering

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Intra- and inter-valley scattering

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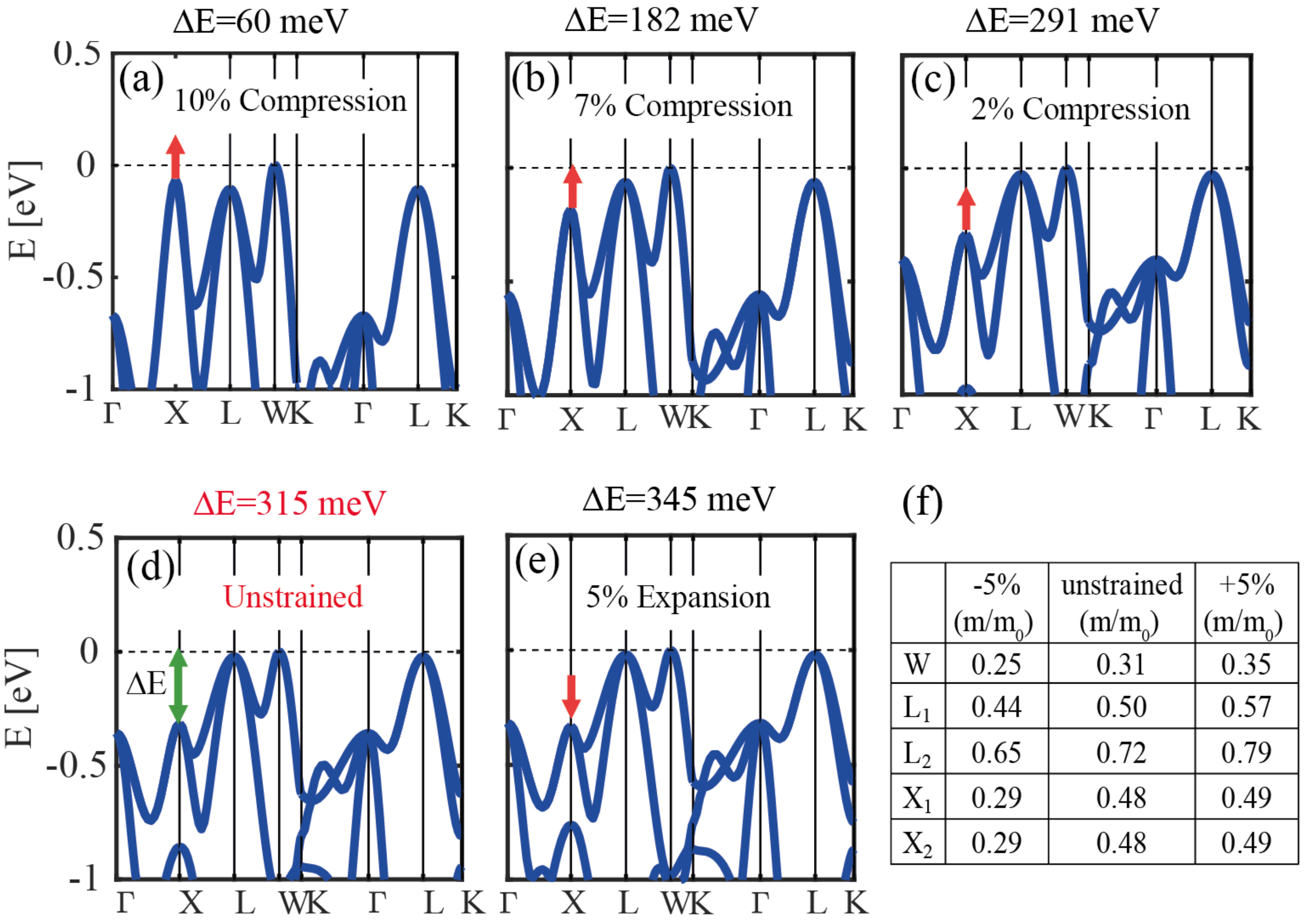
  - ZrCoSb

- Conclusions

NbCoSn bandstructure with strain



(f)

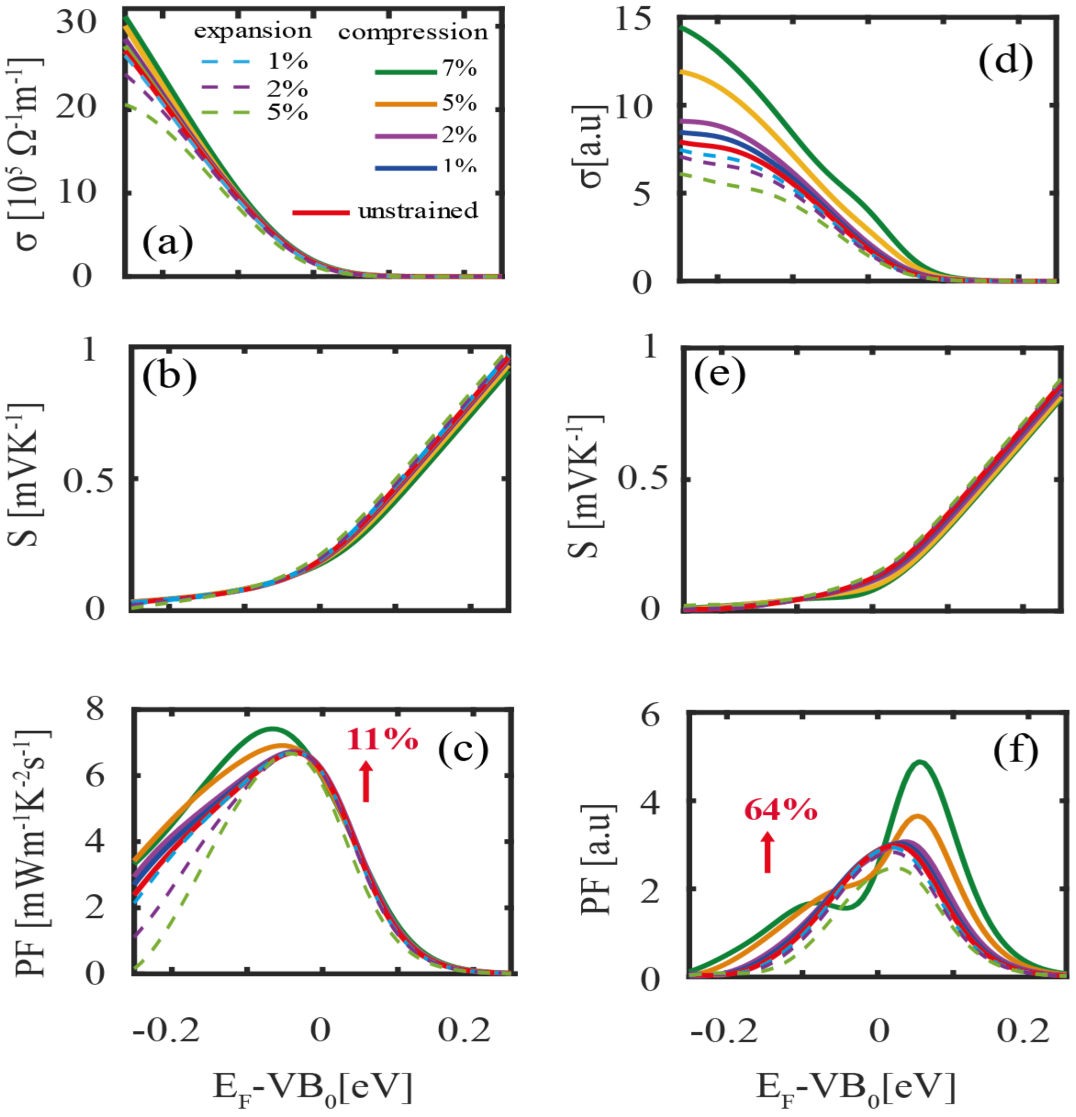
	-5% (m/m_0)	unstrained (m/m_0)	+5% (m/m_0)
W	0.25	0.31	0.35
L_1	0.44	0.50	0.57
L_2	0.65	0.72	0.79
X_1	0.29	0.48	0.49
X_2	0.29	0.48	0.49

Compression can align the bands at the X point.
Masses reduce with compression.

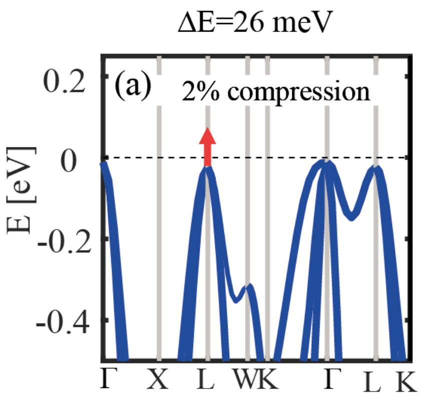
NbCoSn thermoelectric performance with strain

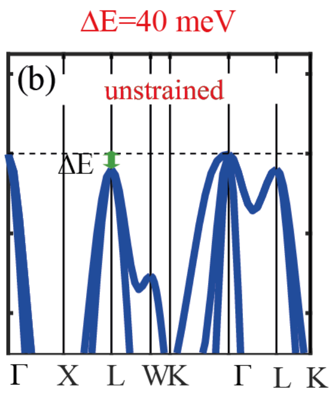
Constant rate of scattering

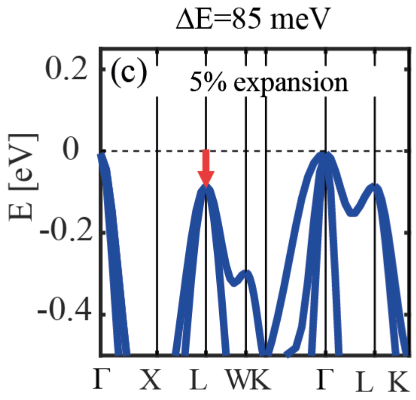
Intra- and inter-valley scattering



TiCoSb – Strain bandstructure





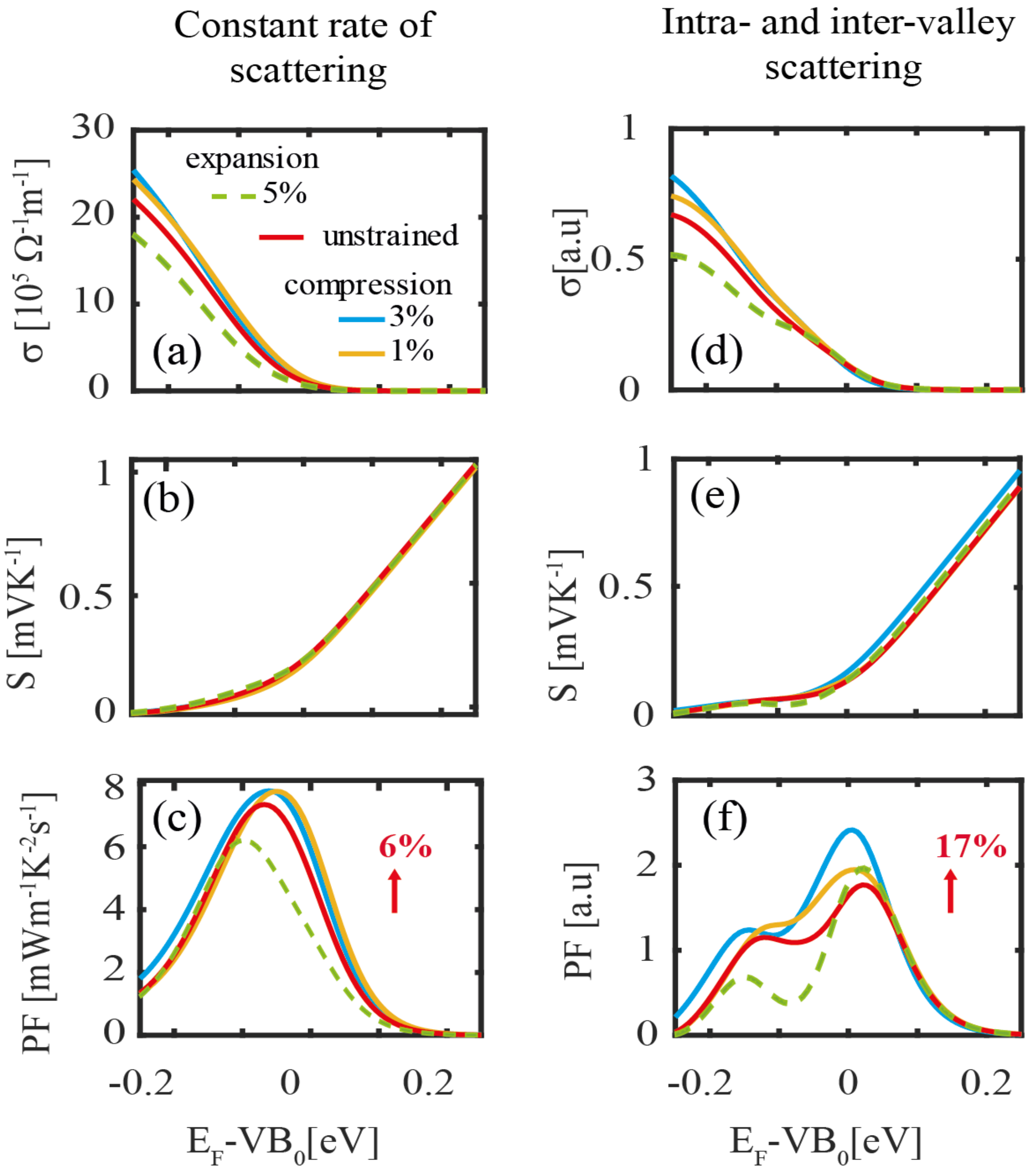


(d)

	-5% (m/m_0)	unstrained (m/m_0)	+5% (m/m_0)
Γ_1	0.30	0.30	0.31
Γ_2	0.44	0.50	0.51
Γ_3	0.44	0.50	0.51
L_1	0.44	0.53	0.58
L_2	0.71	0.93	1.06

Compression can align the bands at the L point.
Masses reduce with compression.

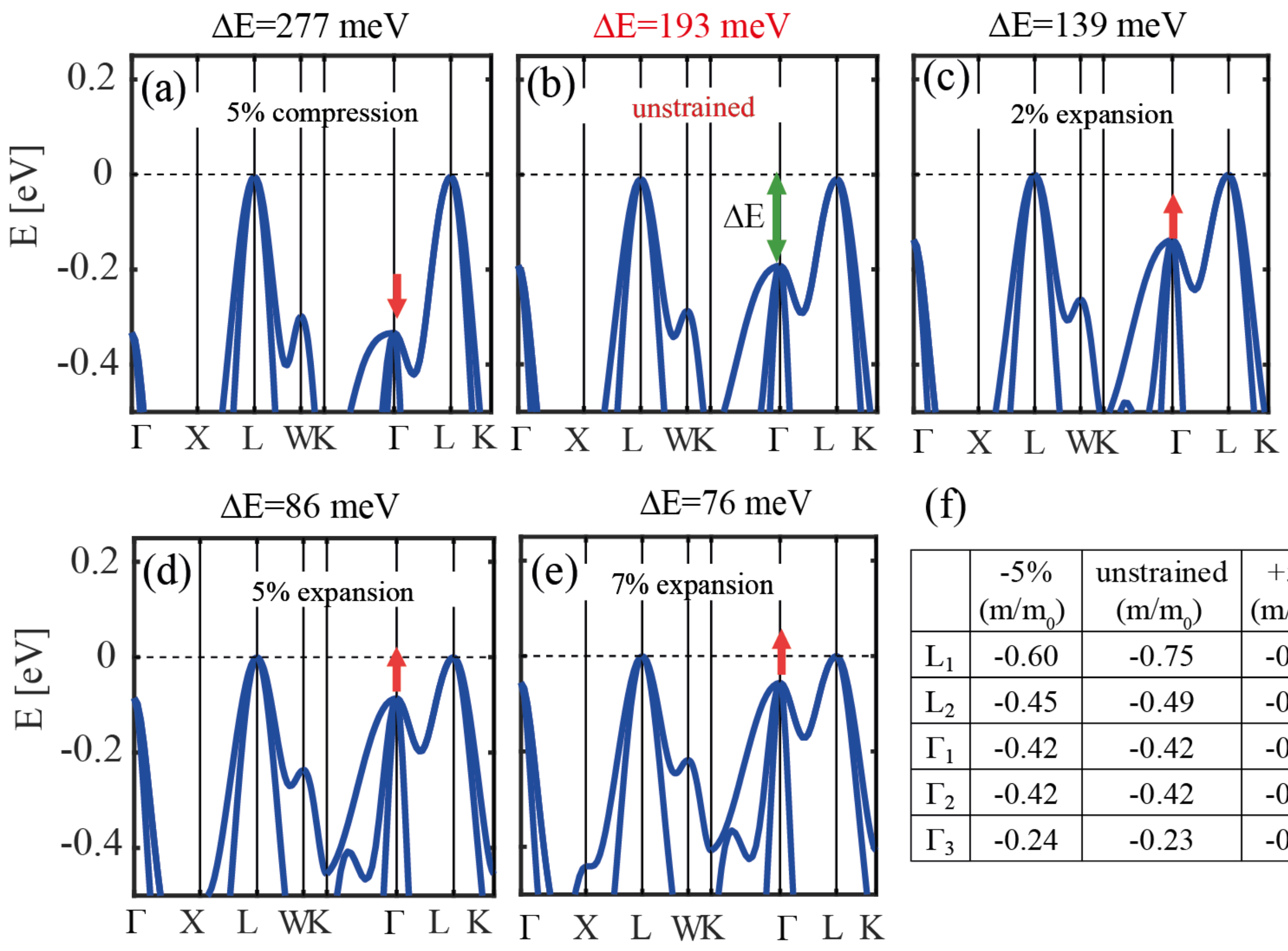
TiCoSb thermoelectric performance with strain



Constant rate of scattering

Intra- and inter-valley scattering

ZrCoSb – Strain bandstructure

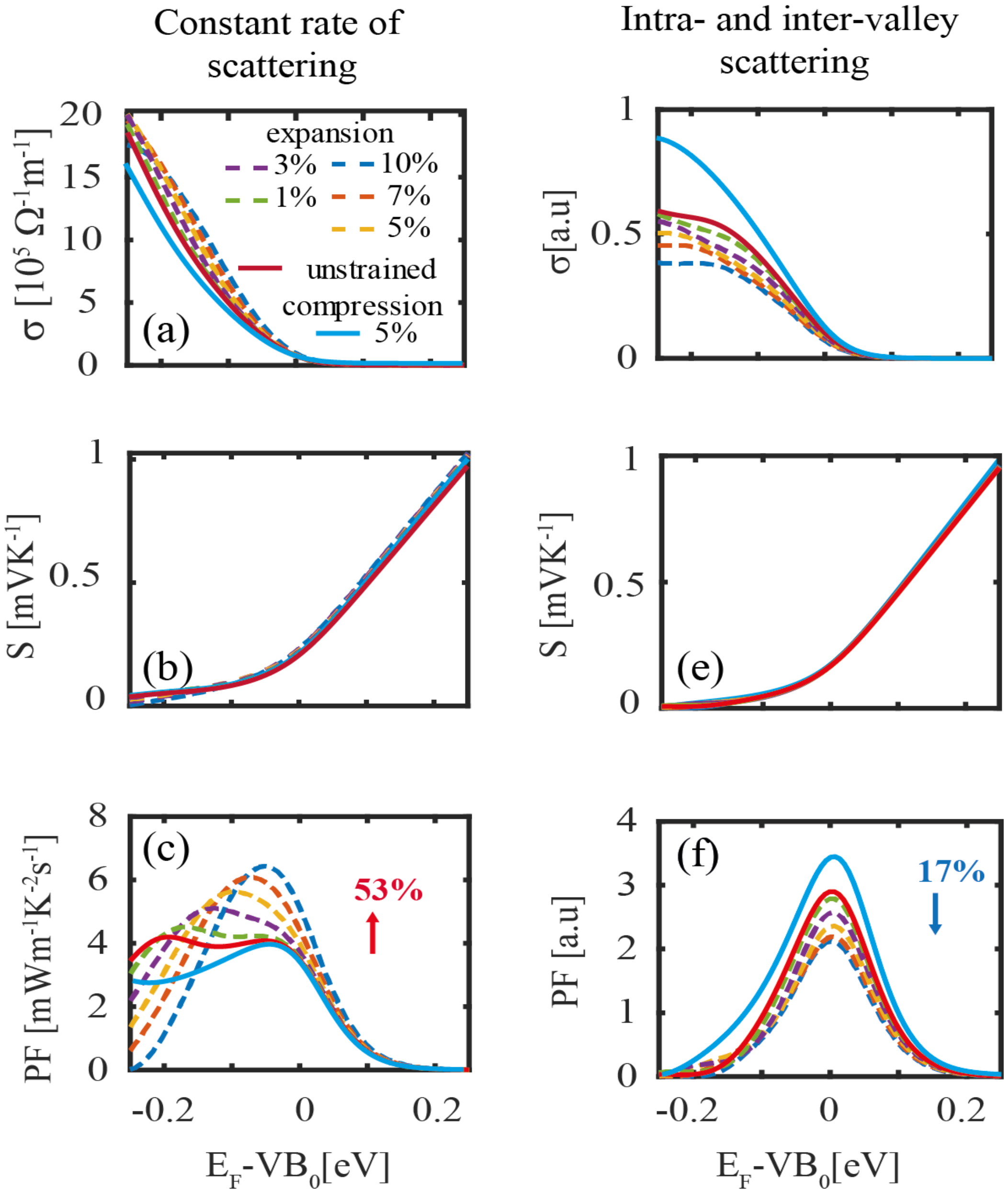


(f)

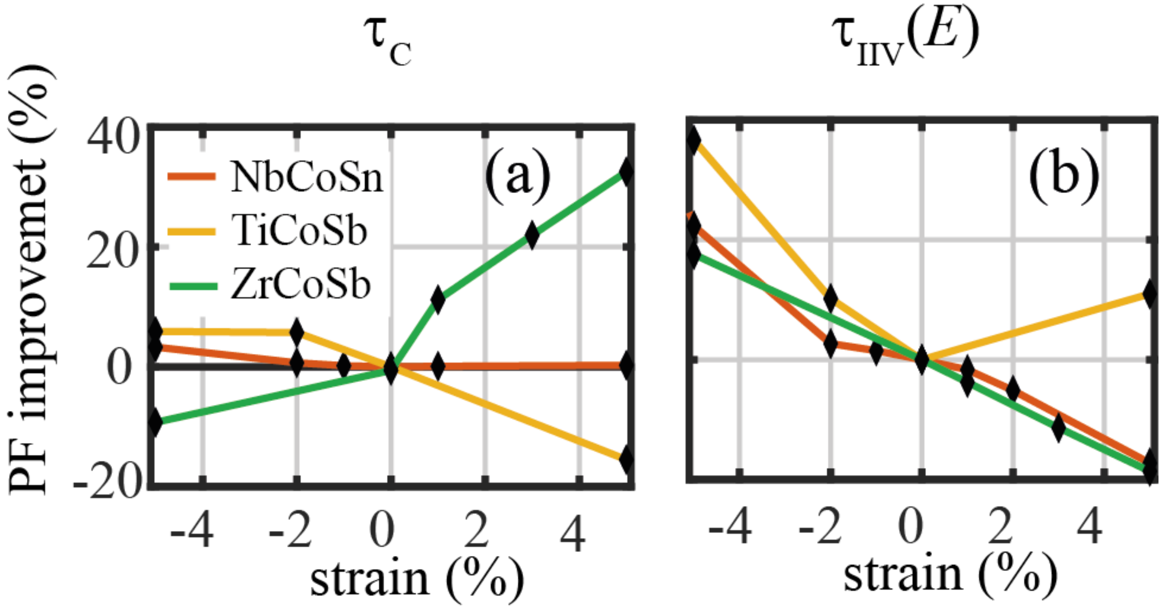
	-5% (m/m_0)	unstrained (m/m_0)	+5% (m/m_0)
L_1	-0.60	-0.75	-0.84
L_2	-0.45	-0.49	-0.54
Γ_1	-0.42	-0.42	-0.41
Γ_2	-0.42	-0.42	-0.41
Γ_3	-0.24	-0.23	-0.21

Expansion can align the bands at the Γ point.
Masses increase with expansion.

ZrCoSb thermoelectric performance with strain



Summary of strain analysis



Outline

- Band convergence
    - Introduction to transport equations
    - Scattering mechanisms : parabolic band approximation

- Modeling half-Heuslers : non parabolic band approximation
    - Non parabolic band approximation
    - Band aligning – NbCoSn, TiCoSb

- Aligning bands of half-Heuslers with strain
    - NbCoSn
    - TiCoSb
    - ZrCoSb

- Conclusions

Conclusion

- Band aligning outcome depend on the electron scattering rate
  - Constant : any band will improve PF, higher masses are better
  - Intra-valley only : any band will improve the PF, lower masses are better.
  - Intra and inter-valley: only certain masses will improve PF
- Non parabolic approximation can model NbCoSn ,TiCoSb
- Strain can be used for aligning bands in NbCoSn ,TiCoSb and ZrCoSb.

Future work

- Other complex crystalline structure material
- Multi-phase material
- Material screening using machine learning techniques
- Study larger systems MC,MD and NEGF codes.

Thank you!