BoltzTraP2

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Overview

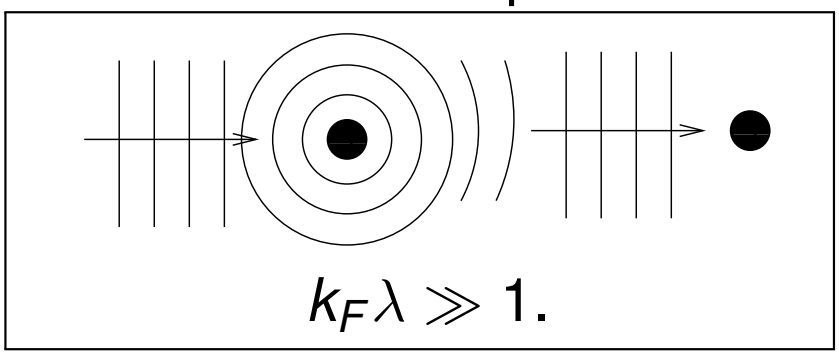
- The Boltzmann transport equations
- BoltzTraP (Smoothed Fourier band interpolation)
- BoltzTraP2. A modern tool for modern workflows
  - Algorithm
  - Including the momentum matrix elements
  - Command-line interface and Python3 library: CoSb3
- Applications:
  - Volumetric band alignment
  - *p*-doped half-Heusler Compounds

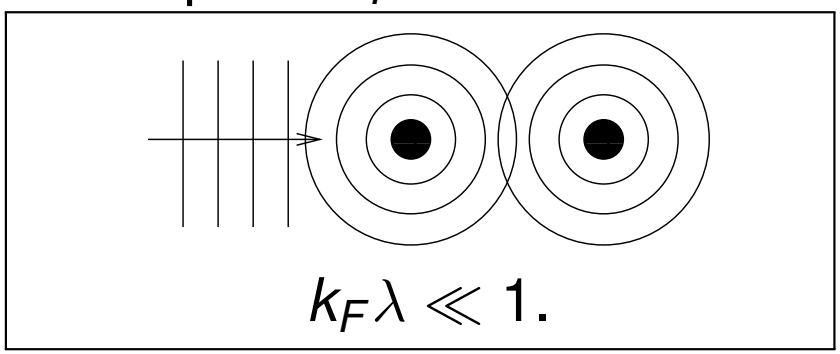
The Boltzmann equation

The *steady state* distribution f is constant in time

$$\left(\frac{\partial f}{\partial t}\right)_{\text{diff}} + \left(\frac{\partial f}{\partial t}\right)_{\text{field}} + \left(\frac{\partial f}{\partial t}\right)_{\text{scatt}} = 0$$

Assumption:
k should be a good quantum number. i.e. wavelength of electron small compared to mean free path. $k_F\lambda \ll 1$.



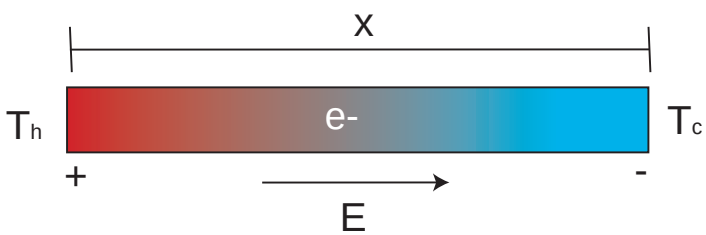


Boltzmann Equation

$$\left(\frac{\partial f}{\partial t}\right)_{\text{diff}} + \left(\frac{\partial f}{\partial t}\right)_{\text{field}} + \left(\frac{\partial f}{\partial t}\right)_{\text{scatt}} = 0$$

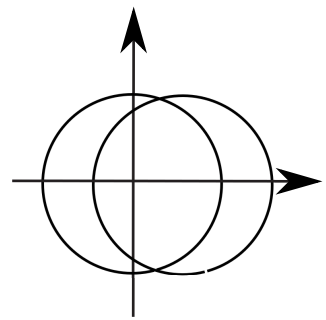
Diffusion:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{diff}} = \frac{\partial f}{\partial T}\nabla T\mathbf{v}$$



Field:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{field}} = -\frac{\partial f}{\partial \varepsilon}\mathbf{v}q\mathbf{E}$$



$$\mathbf{v}\left(-\frac{\partial f}{\partial \varepsilon}\right)\left(-\frac{\varepsilon-\mu}{T}\nabla T + q\mathbf{E}\right) = -\left(\frac{\partial f}{\partial t}\right)_{\text{scatt}}$$

Relaxation time approximation

Phenomological assumption: Exponential decay of deviation from equilibrium with τ as the relaxation time.

$$\left(\frac{\partial f}{\partial t}\right)_{scatt} = -\frac{f - f^{(0)}}{\tau}$$

thereby

$$j_e = \sum_n \int q v_{n\mathbf{k}} v_{n\mathbf{k}} \tau_{n\mathbf{k}} \left(-\frac{\partial f^{(0)}}{\partial \varepsilon}\right) \left(-\frac{\varepsilon - \mu}{T} \nabla T + q\mathbf{E}\right) \frac{\mathrm{d}\mathbf{k}}{8\pi^3}$$

$$j_Q = \sum_n \int (\varepsilon - \mu) v_{n\mathbf{k}} v_{n\mathbf{k}} \tau_{n\mathbf{k}} \tau_{\mathbf{k}} \left(-\frac{\partial f^{(0)}}{\partial \varepsilon}\right) \left(-\frac{\varepsilon - \mu}{T} \nabla T + q\mathbf{E}\right) \frac{\mathrm{d}\mathbf{k}}{8\pi^3}$$

The transport distribution

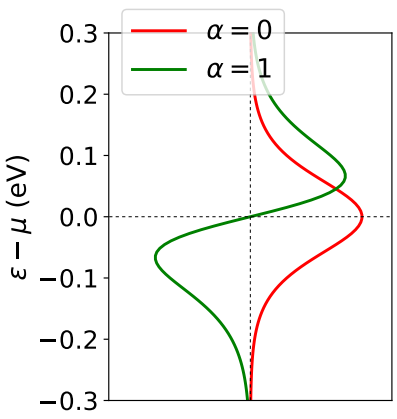
Introduce the transport distribution

$$\sigma(\varepsilon) = \sum_n \int v_{n\mathbf{k}} v_{n\mathbf{k}} \tau_{n\mathbf{k}} \delta(\varepsilon - \varepsilon_{n\mathbf{k}}) \frac{\mathrm{d}\mathbf{k}}{8\pi^3}$$

The generalized transport coefficients are moments of the transport distribution

$$\mathcal{L}^{(\alpha)}(T,\mu) = q^2 \int \sigma(\varepsilon)(\varepsilon-\mu)^\alpha \left(-\frac{\partial f}{\partial \varepsilon}\right) \mathrm{d}\varepsilon$$

$$-(\varepsilon-\mu)^\alpha \frac{\partial f}{\partial \varepsilon}$$



$$j_e = \mathcal{L}^{(0)}\mathbf{E} + \frac{\mathcal{L}^{(1)}}{qT}(-\nabla T)$$

$$j_Q = \frac{\mathcal{L}^{(1)}}{q}\mathbf{E} + \frac{\mathcal{L}^{(2)}}{q^2 T}(-\nabla T)$$

Phenomenological transport coefficients

Identify two kinds of experimental situations

$\nabla \mathbf{T} = \mathbf{0}$:

$$j_e = \mathcal{L}^{(0)} E \quad \Rightarrow \quad \sigma = \mathcal{L}^{(0)}$$

$$j_Q = \frac{\mathcal{L}^{(1)}}{q} \mathbf{E} = \frac{\mathcal{L}^{(1)}}{q\mathcal{L}^{(0)}} j_e \quad \Rightarrow \quad \Pi = \frac{\mathcal{L}^{(1)}}{q\mathcal{L}^{(0)}}$$

$\mathbf{j_e} = \mathbf{0}$:

$$\mathcal{L}^{(0)} E = \frac{\mathcal{L}^{(1)}}{qT} \nabla T \Rightarrow \quad S = \frac{1}{qT} \frac{\mathcal{L}^{(1)}}{\mathcal{L}^{(0)}}$$

$$j_q = \frac{1}{q^2 T} \left(\frac{(\mathcal{L}^{(1)})^2}{\mathcal{L}^{(0)}} - \mathcal{L}^{(2)} \right) \nabla T \Rightarrow \quad \kappa_e = \frac{1}{q^2 T} \left(\frac{(\mathcal{L}^{(1)})^2}{\mathcal{L}^{(0)}} - \mathcal{L}^{(2)} \right)$$

Harvesting of waste heat

- The thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice-versa
- Approximately 70% of energy is lost as waste heat when burning fossil fuels for power generation

Figure of merit

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

Electronic power factor

$$PF = S^2 \sigma$$

Shankland-Pickett algorithm

Constrained optimization procedure: Minimize roughness function with respect to the Fourier coefficients while exactly reproducing calculated eigenvalues.

$$\tilde{\varepsilon}_{\mathbf{k}} = \sum_{\Lambda} c_{\Lambda} \sum_{R \in \Lambda} \exp(i\mathbf{k} \cdot \mathbf{R})$$

Minimize the Lagrangian

$$I = \frac{1}{2} \sum c_{\Lambda} \rho_{\Lambda} + \sum_{\mathbf{k}} \lambda_{\mathbf{k}} \left(\varepsilon_{\mathbf{k}} - \tilde{\varepsilon}_{\mathbf{k}} \right)$$

Euwema, Shankland et al, Phys. Rev. 178 (1969) 1419–1423
Shankland, Int. J. Quantum Chem. 5 (1971) 497–500.

Roughness function

$$\rho = \left(\tilde{\varepsilon}_{\mathbf{k}} - \varepsilon_0 + C_1 \nabla^2 \tilde{\varepsilon}_{\mathbf{k}} \right)^2$$

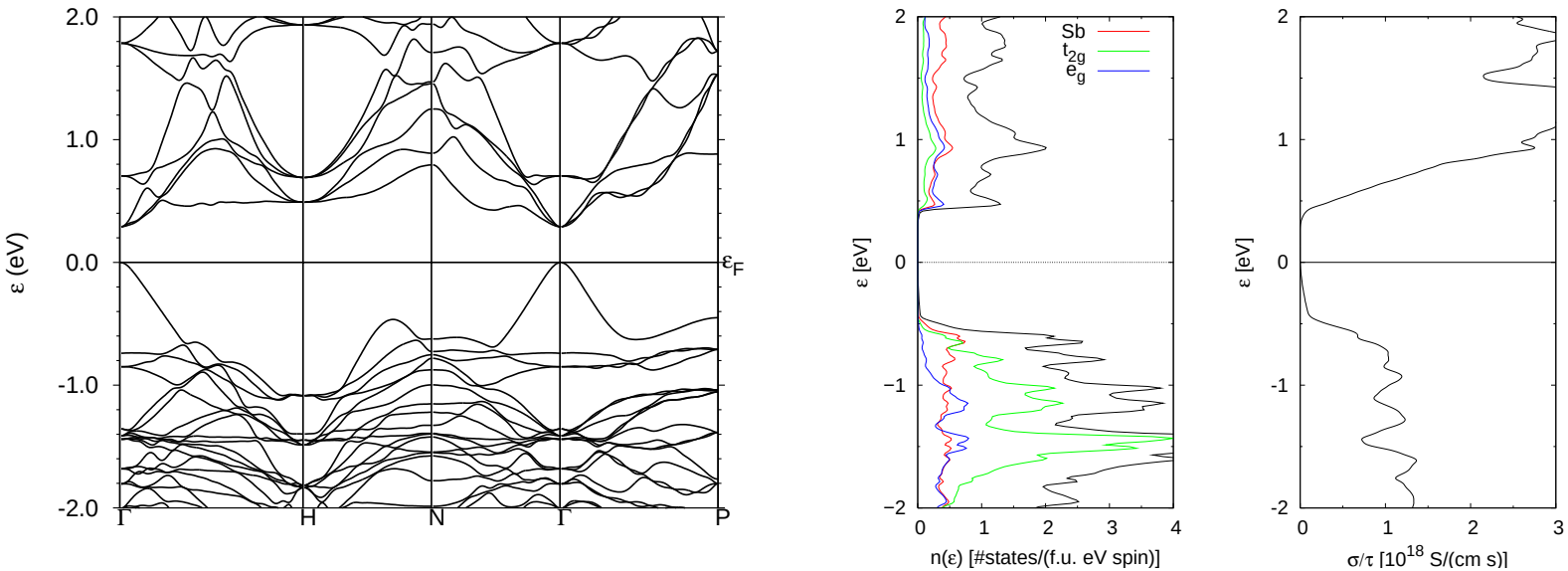
Pickett et al. Phys. Rev. B 38 (1988) 2721–2726.

Transport distribution. $CoSb_3$

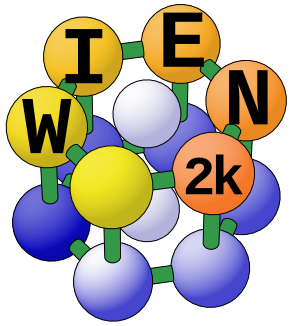
Transport distribution

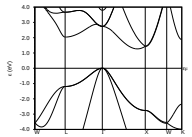
$$\sigma(\varepsilon) = \frac{1}{3}\sum_n \int v_{n\mathbf{k}} v_{n\mathbf{k}} \tau_{n\mathbf{k}} \delta(\varepsilon - \varepsilon_{n\mathbf{k}}) \frac{d\mathbf{k}}{8\pi^3}$$

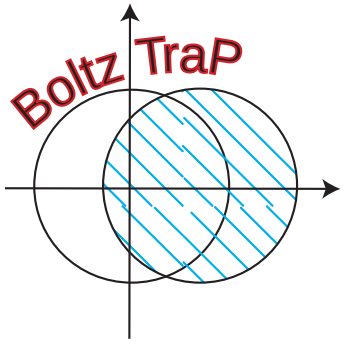
$CoSb_3$

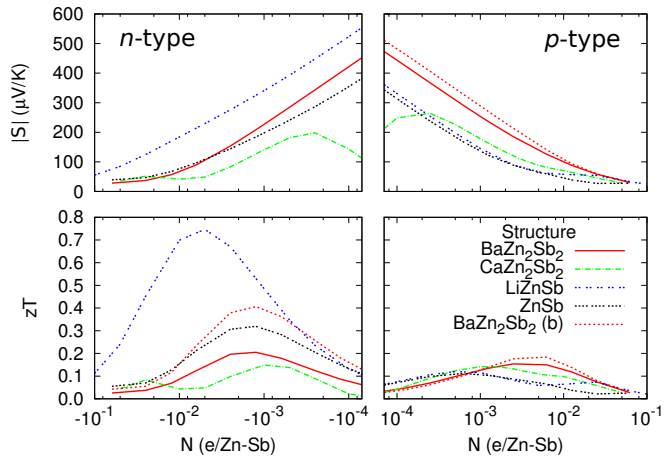


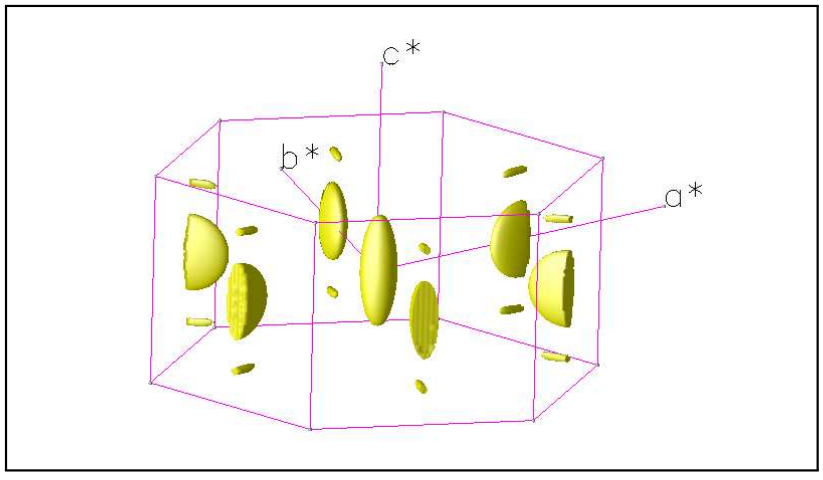
Automated search for new thermoelectrics











- BoltzTrap:
  - All crystal structures
  - Full tensors quantities
  - Numerically efficient and stable

GKHM *JACS* **128** p12140 (2006)
GKHM, Singh, *Comput. Phys. Commun.* **175**, p67 (2006)
Bjerg, GKHM, Iversen, *Chem. Mat.* **23** p3907 (2011)

BoltzTraP2: A modern tool for modern workflows.

Boltz
TraP2

Design goals:

- All useful features from BoltzTraP
- Easy installation, portability
  `pip3 install BoltzTraP2`
- Command-line interface
  (no config files)

Speed:

- New algoritmes
- Modularity, flexibility
- Standard formats

Two use cases:

1. *I want to estimate the Onsager thermoelectric coefficients from my DFT results*
   $\Rightarrow$ **BoltzTraP2 as a stand-alone tool**
2. *I need interpolated bands as inputs to my own algorithm*
   $\Rightarrow$ **BoltzTraP2 as a Python module**

boltztrap.org
Madsen, Carrete, Verstraete *Comp. Phys. Comm* 231 p140 **2018**

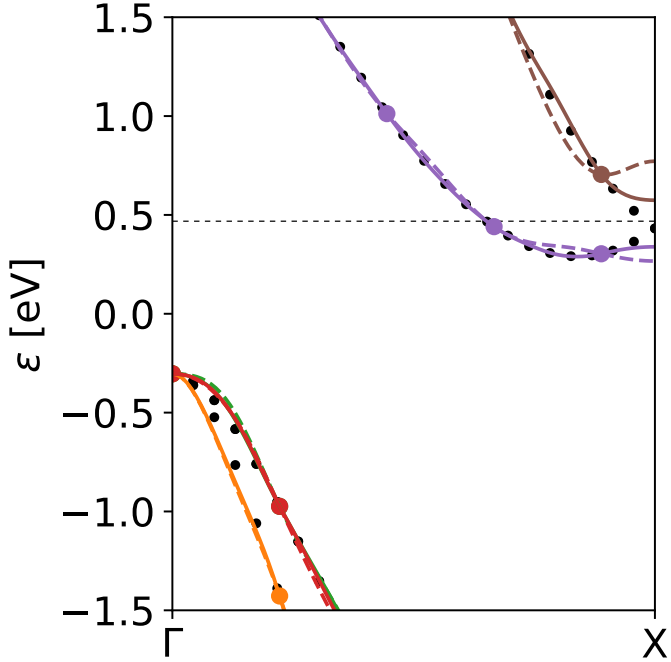
BoltzTraP2 interpolation

Minimize roughness function with respect to the Fourier coefficients while exactly reproducing calculated eigenvalues *and derivatives*

$$l = \frac{1}{2}\sum c_\Lambda \rho_\Lambda + \sum_{\mathbf{k}} \lambda_{\mathbf{k}} \left(\varepsilon_{\mathbf{k}} - \tilde{\varepsilon}_{\mathbf{k}} \right) + \sum_{\mathbf{k}} \lambda'_{\mathbf{k}} \left(\nabla \varepsilon_{\mathbf{k}} - \nabla \tilde{\varepsilon}_{\mathbf{k}} \right)$$

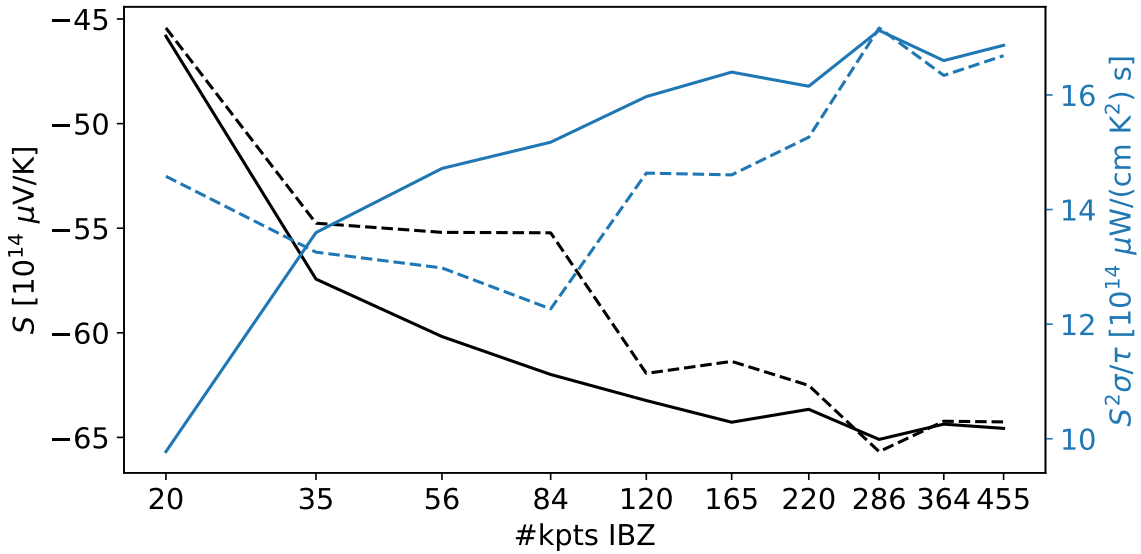
- Combine advantage of BoltzTraP (analytic bands) and Scheidemantel-Sofo approach (exact derivatives at calculated points)
- Potentially coarser *k*-mesh in ab-initio calculation

Example: Silicon band structure



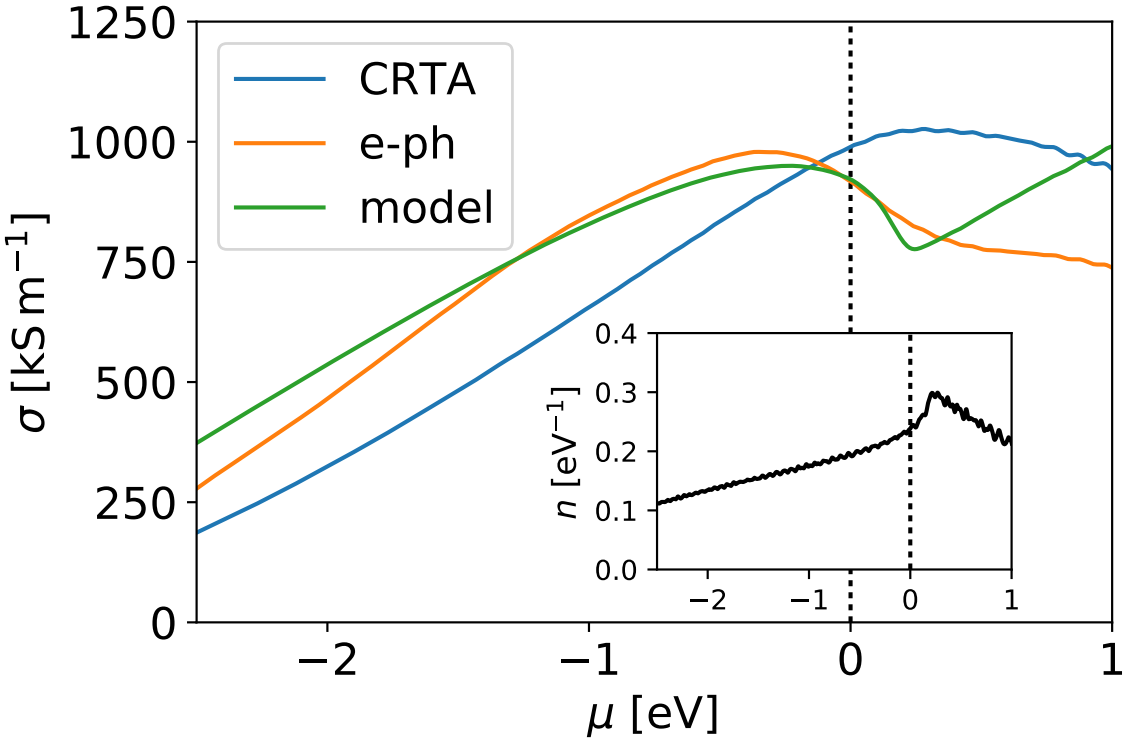
- CBM made up by degerate pocket along six-fold degenrate $\Gamma - X$ line
- Interpolated bands based on a coarse $9 \times 9 \times 9$ k-point mesh
- Modified Lagrangian forces the fit to reproduce the exact derivatives at the calculated points.
- Position and derivatives at the pocket are well reproduced

Example: Silicon transport



- Seebeck coefficient and thermoelectric power factor calculated at a chemical potential close to the CBM using the CRTA
- The results obtained by the modified Lagragian show both a faster and more systematic convergence towards the converged values
- Convergence reached at about half the number of k-points

Example: Band and momentum dependent relaxation times



- Including band and momentum dependent relaxation times changes the slope of the transport distribution (and thereby the Seebeck coefficient)

Madsen, Carrete, Verstraete *Comp. Phys. Comm* 231 p140 **2018**
$\tau_{b\mathbf{k}}$ from Xu, Verstraete, *Phys. Rev. Lett.* 112 p196603 **2014**

Some highlights of BoltzTraP2

Flexibility

- Usable as a Python module
- Extensible scattering models
- Automatic detection of space group

Speed

- Highly vectorized Python
- Symmetry module in C++
- fftw

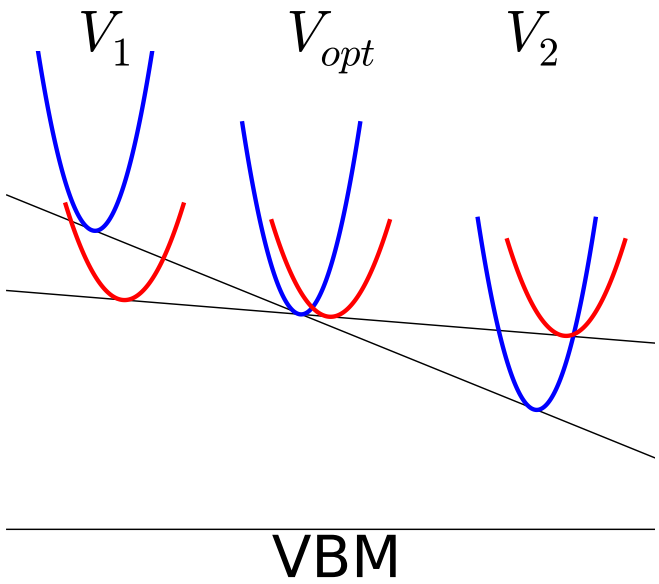
Portability

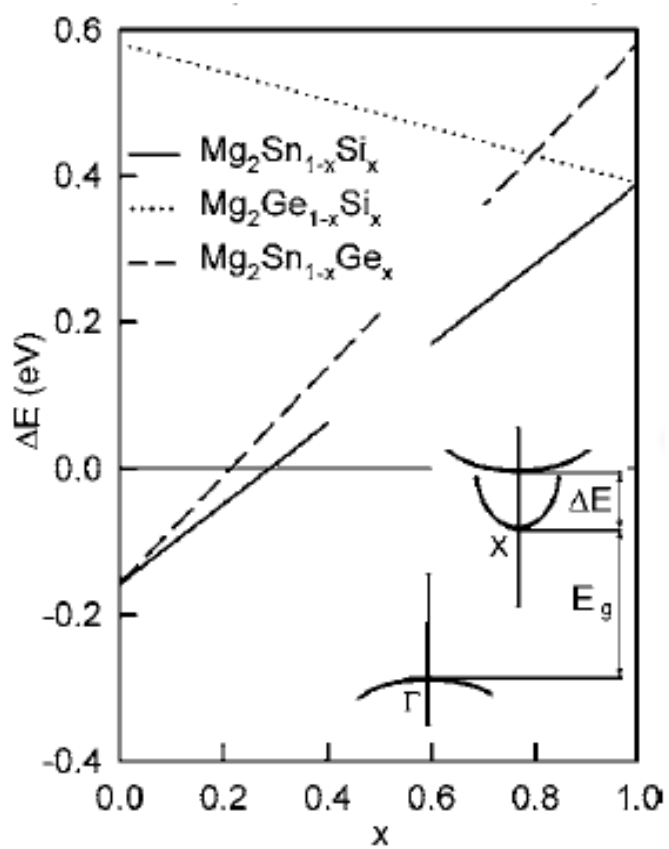
- Standard Python setup toolchain
- Detection of compilers and libraries
- Adherence to C++11

Standard formats

- JSON: Human readable & parsers for every language
- Final output as text

Volumetric Band Alignment





Zaitsev et al. *PRB* 74 p045207 (2006)

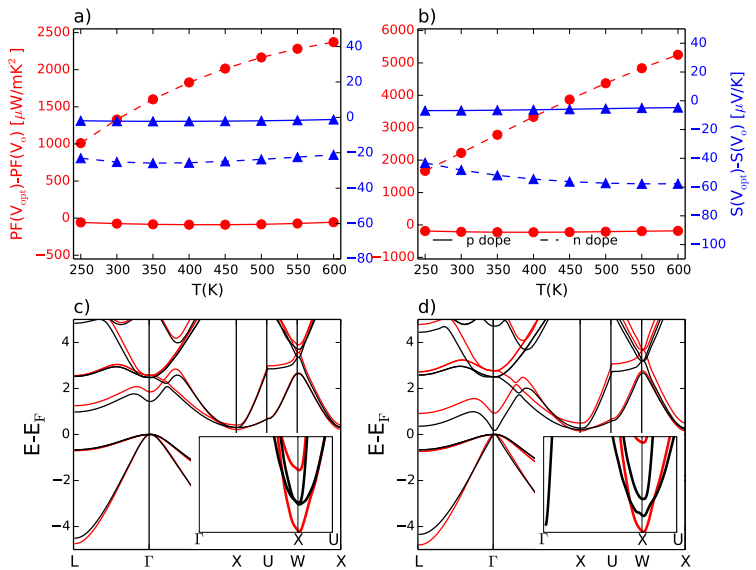
Optimize power factor by alignment of band edges

$$S^2\sigma = \frac{1}{q^2 T^2} \frac{\left(\mathcal{L}^{(1)} + \mathcal{L}^{(1)}\right)^2}{\mathcal{L}^{(0)} + \mathcal{L}^{(0)}}$$

$Mg_2Si_xSn_{1-x}$

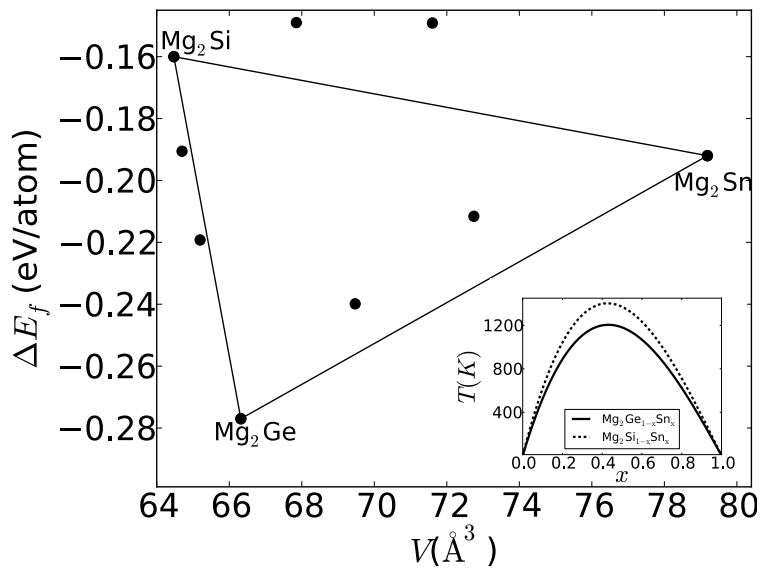
1. Band structure

Calculate volume dependence of S and σ/τ



2. Thermodynamics

Calculate mixing enthalpy (SQS)



Bhattacharya, GKHM *Phys. Rev. B* 92, p085205 (2015)

VBA screening

Initial M-X combinations

3150

Thermodynamically stable structures

522

Good thermoelectrics ($zT > 0.4$)

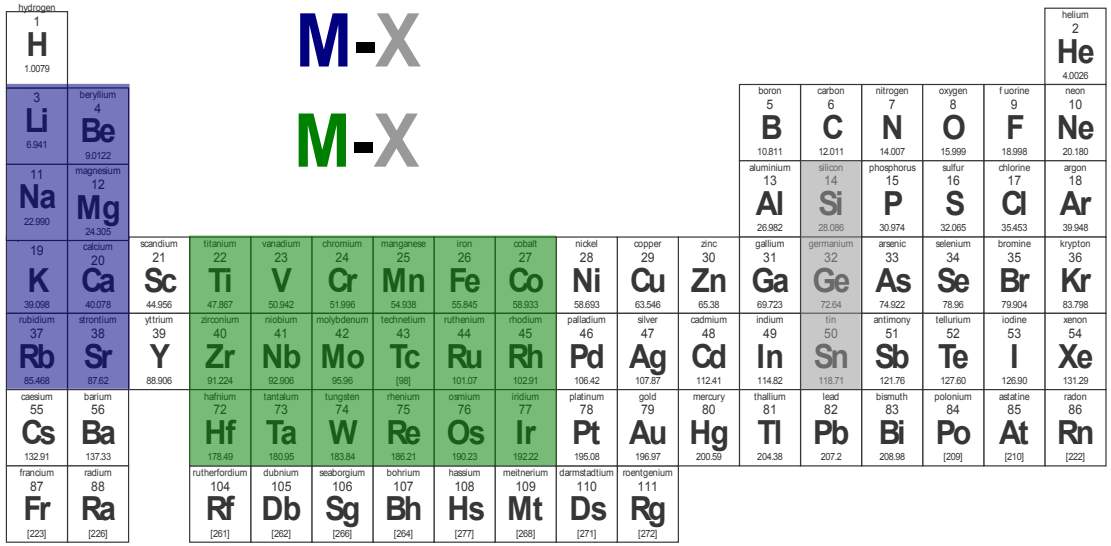
29

Candidates for VBA

8

Checks for alloy stability

4



Bhattacharya, GKHM *Phys. Rev. B* 92, p085205 (2015)

Alloy Thermodynamics

Compound	ΔE_{h} [$\Delta E_{\mathrm{h}}^{\mathrm{Sn}}$] (meV/atom)	V_{opt} (%)	x_{alloy}	$\Delta E_{\mathrm{mix}}(0.25)$ (kJ/mol)	x (800 K)
$Mg_2Si_{1-x}Sn_x$	0[0]	2.0	0.09	1.997	0.171
$Ca_2Si_{1-x}Sn_x$	0[0]	5.0	0.30	0.013	all
$Ca_9Ge_{5-x}Sn_x$	37.4[17.9]	6.1	0.28	4.495	0.019
$\beta-MoSi_{2-x}Sn_x$	27.3[180.8]	3.0	0.07	30.980	0.008
o-$Fe_2Ge_{3-x}Sn_x$	0.1[22.5]	3.0	0.10	32.746	0.004

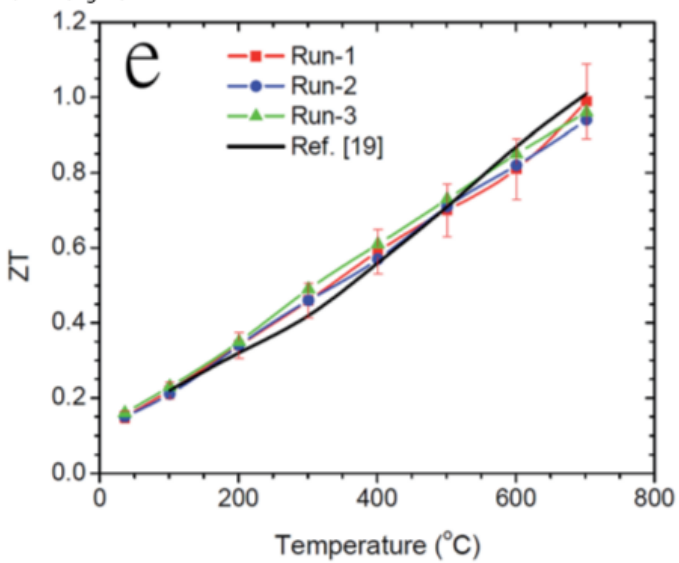
Bhattacharya, GKHM *Phys. Rev. B* 92, p085205 (2015)

p-type HHC: (V/Nb)FeSb

Cite this: *Energy Environ. Sci.*, 2014, 7, 4070

NbFeSb-based p-type half-Heuslers for power generation applications

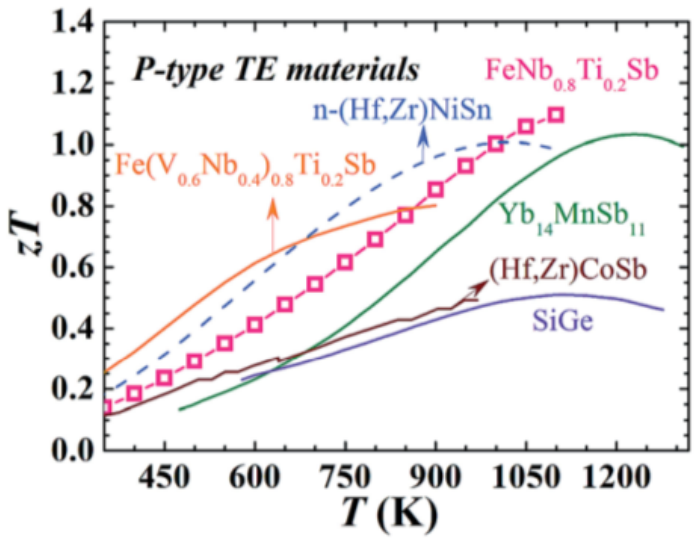
Giri Joshi,*[a] Ran He,[b] Michael Engber,[a] Georgy Samsonidze,[c] Tej Pantha,[a] Ekraj Dahal,[a] Keshab Dahal,[b] Jian Yang,[a] Yucheng Lan,[b] Boris Kozinsky[c] and Zhifeng Ren*[b]



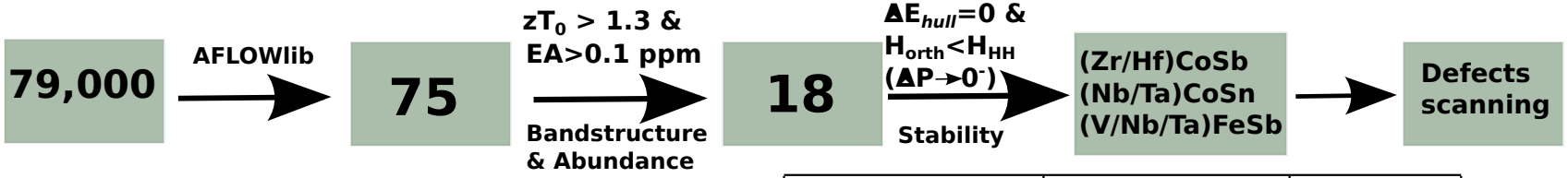
Cite this: *Energy Environ. Sci.*, 2015, 8, 216

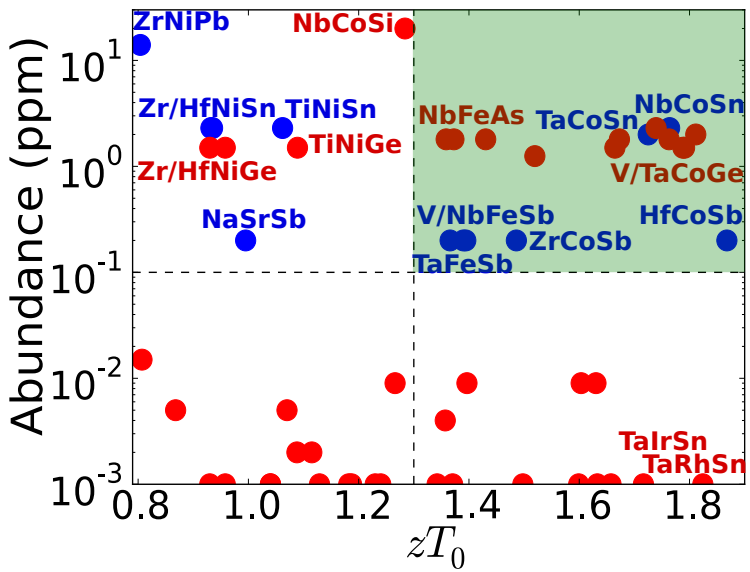
Band engineering of high performance p-type FeNbSb based half-Heusler thermoelectric materials for figure of merit $zT > 1$†

Chenguang Fu,[a] Tiejun Zhu,*[ab] Yintu Liu,[a] Hanhui Xie[a] and Xinbing Zhao[ab]



Screening. Band structure, abundance and stability.

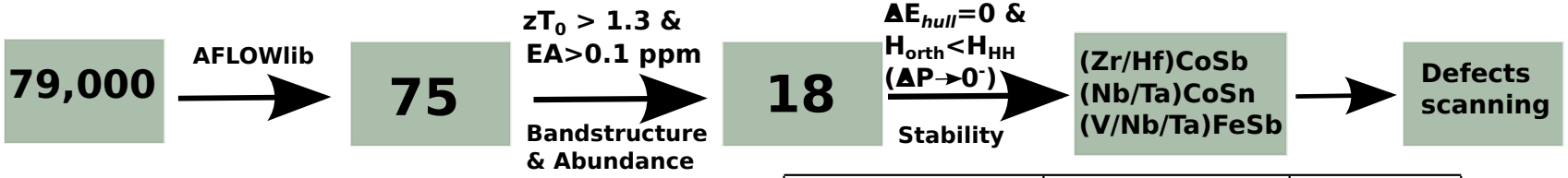


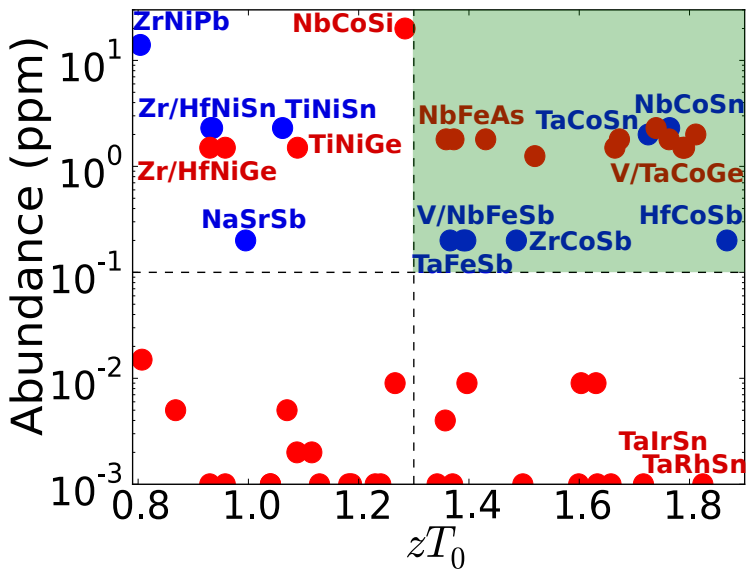


Compound	ΔE_{hull} meV/atom	orth phase
TaFeAs	33.03	yes
TaFeSb	0.00	no
NbFeAs	125.81	yes
NbFeSb	0.00	no
VFeSb	0.00	no
ZrCoAs	0.00	yes
ZrCoSb	0.00	no
WFeGe	64.34	no
NbCoGe	0.00	yes
HfCoAs	0.00	yes
TaCoSn	0.00	no
VCoSn	90.77	no
TiCoAs	0.00	yes
NbCoSn	0.00	no
TaCoGe	0.00	yes
VCoGe	0.00	yes
TaCoSi	91.47	yes
HfCoSb	0.00	no

Bhattacharya, GKHM *J. Mater. Chem. C*, **4**, p11261 (2016)

Screening. Band structure, abundance and stability.





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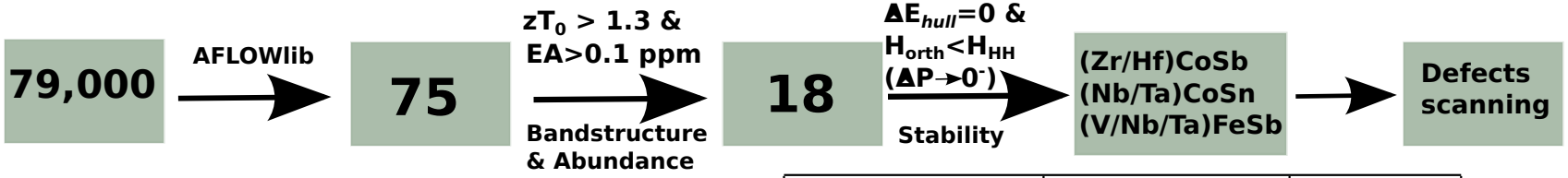

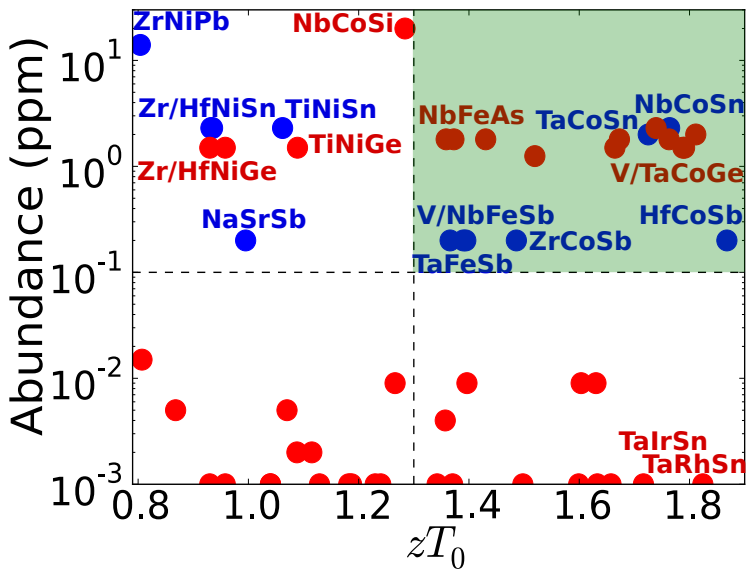

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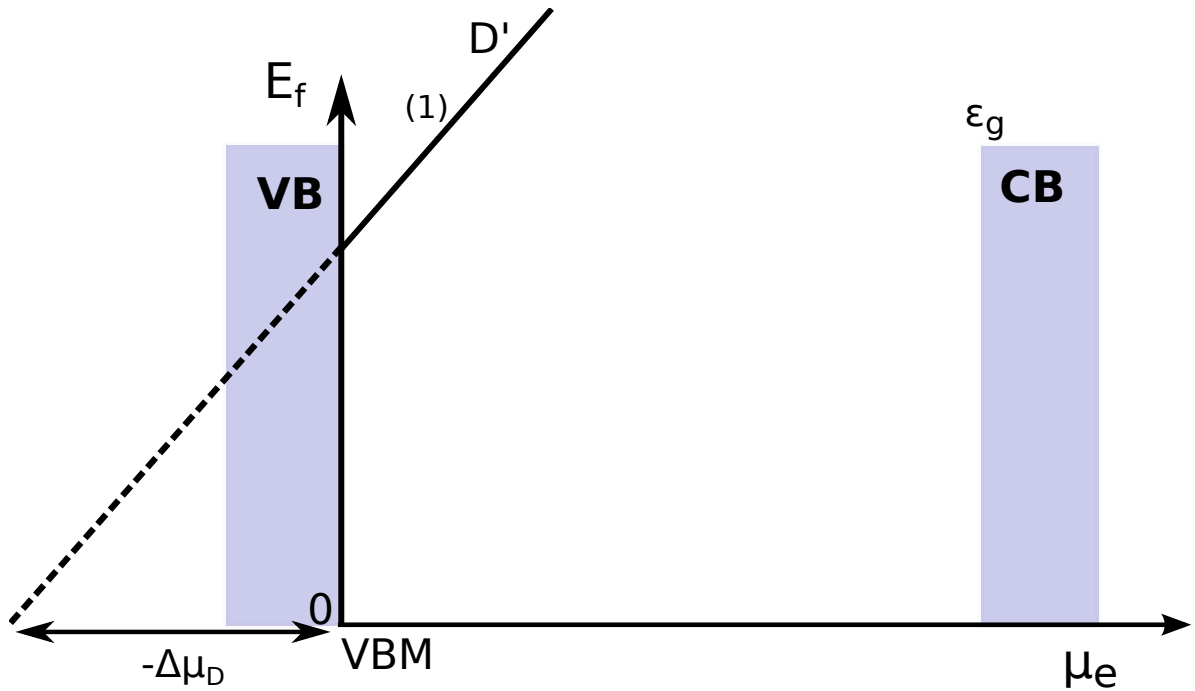
Bhattacharya, GKHM *J. Mater. Chem. C*, **4**, p11261 (2016)

Intrinsic defects

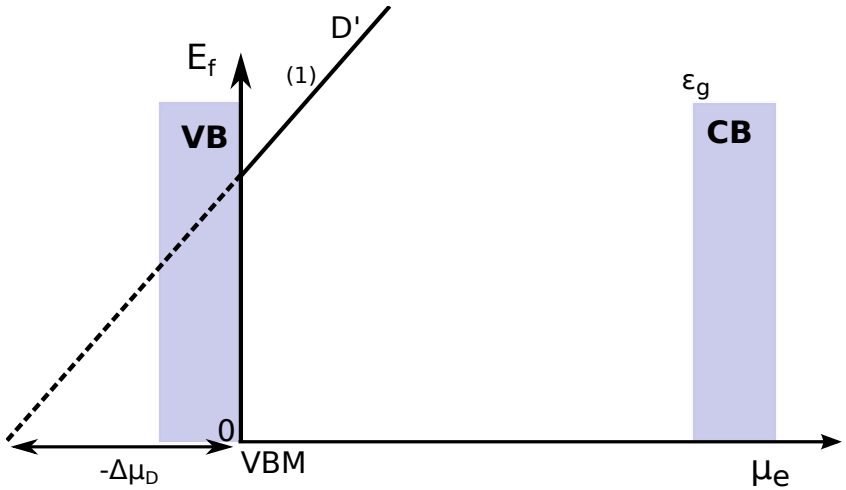


	$\Delta\mu_{D'}$ (eV)	$D'^{(q)}$		$\Delta\mu_{D'}$ (eV)	$D'^{(q)}$		$\Delta\mu_{D'}$ (eV)	$D'^{(q)}$
NbCoSn	-0.27	$Co_{Int}^{(3)}$	VFeSb	-0.18	$Fe_{Int}^{(2)}$	ZrCoSb	-0.51	$Sb_{Zr}^{(1)}$
TaCoSn	-0.26	$Co_{Int}^{(2)}$	NbFeSb	-0.60	$Fe_{Int}^{(2)}$	HfCoSb	-0.37	$Co_{Int}^{(2)}$

No intrinsic doping limits

Bhattacharya, GKHM *J. Mater. Chem. C*, **4**, p11261 (2016)

Extrinsic doping



	$E_f^D(\mu_{VB})$ (eV)	$D^{(q)}$	$\Delta E^{D'-D}$ (eV)	$D'^{(q)}$
NbFeSb	-0.01	$Hf_{Nb}^{(-1)}$	1.20	$Fe_{Int}^{(2)}$
	0.09	$Ti_{Nb}^{(-1)}$	1.10	$Fe_{Int}^{(2)}$
	0.21	$Mn_{Fe}^{(-1)}$	0.72	$Vac_{Fe}^{(2)}$
	0.41	$Zr_{Nb}^{(-1)}$	0.78	$Fe_{Int}^{(2)}$
	0.55	$Sn_{Sb}^{(-1)}$	0.70	$Fe_{Int}^{(2)}$
ZrCoSb	0.17	$Sc_{Zr}^{(-1)}$	0.60	$Sb_{Zr}^{(1)}$
	0.61	$Sn_{Sb}^{(-1)}$	0.35	$Vac_{Co}^{(1)}$
	0.61	$Fe_{Co}^{(-1)}$	-0.48	$Vac_{Co}^{(1)}$
NbCoSn	0.32	$Hf_{Nb}^{(-1)}$	0.50	$Co_{Int}^{(3)}$
	0.62	$Fe_{Co}^{(-1)}$	-0.15	$Fe_{Int}^{(2)}$
	0.68	$Ti_{Nb}^{(-1)}$	0.14	$Co_{Int}^{(3)}$
	0.72	$Zr_{Nb}^{(-1)}$	0.10	$Co_{Int}^{(3)}$
TaCoSn	0.44	$Hf_{Ta}^{(-1)}$	0.33	$Co_{Int}^{(2)}$
	0.87	$Fe_{Co}^{(-1)}$	-0.10	$Fe_{Int}^{(2)}$

- Known carrier inducing defects reproduced in NbFeSb and ZrCoSb
- A new system with favorable extrinsic dopants identified

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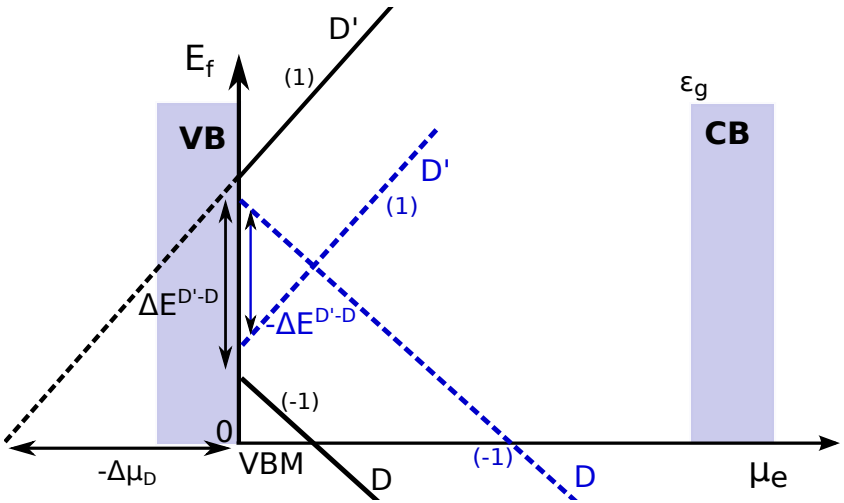
Extrinsic doping



	$E_f^{\mathrm{D}}(\mu_{\mathrm{VB}})$ (eV)	$\mathrm{D}^{(q)}$	$\Delta E^{\mathrm{D}'-\mathrm{D}}$ (eV)	$\mathrm{D}'^{(q)}$
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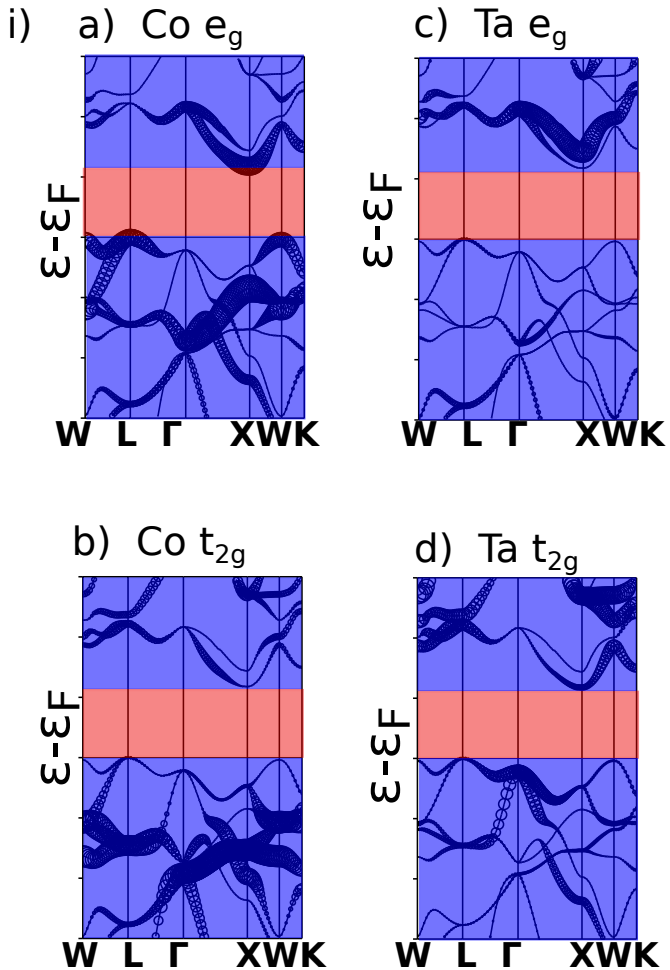
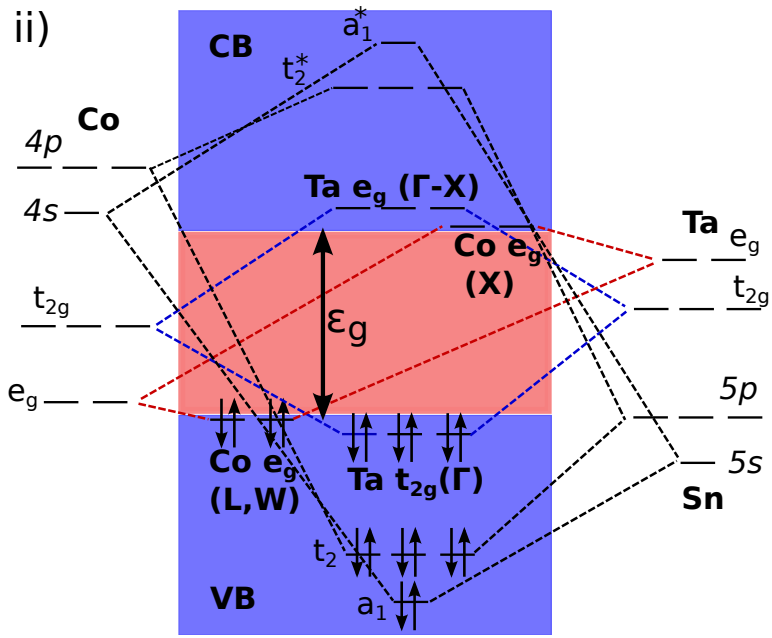
TE Heusler. Band structure.





- Alignment of pockets at *L* and *W* (and Γ)

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Installing Anaconda and BoltzTraP2

```
ssh -X wienXXX@psiXX.theochem.tuwien.ac.at
wget https://repo.anaconda.com/archive/Anaconda3-2019.07-Linux-x86_64.sh
chmod u+x Anaconda3-2019.07-Linux-x86_64.sh
bash
./Anaconda3-2019.07-Linux-x86_64.sh
# Complete the installation procedure and init
# Log out of and log into the machine.
conda config --set auto_activate_base false
conda install cmake git vtk pytest
pip install pyfftw
pip install boltztrap2
# Now, to download the example data:
git clone https://gitlab.com/sousaw/BoltzTraP2.git
tar -xvf BoltzTraP2/data.tar.xz
```

Command Line Interface

Make working directory and copy data. Activate Conda if you have switched the autoconfig off.
Fit the calculated eigenvalues. The interpolated k-mesh should be five times as dense as the original:

```
btp2 interpolate .  -m 5 -o CoSb3.bt2
```

Integrate to get the transport properties

```
btp2 integrate CoSb3.bt2 50:500:50
```

Plot the results

```
btp2 plot -c '["xx"]' CoSb3.btj S
```

Read the wiki

Acknowledgements

Sandip Bhattacharya

Jesús Carrete

Matthieu Verstraete