BoltzTraP2

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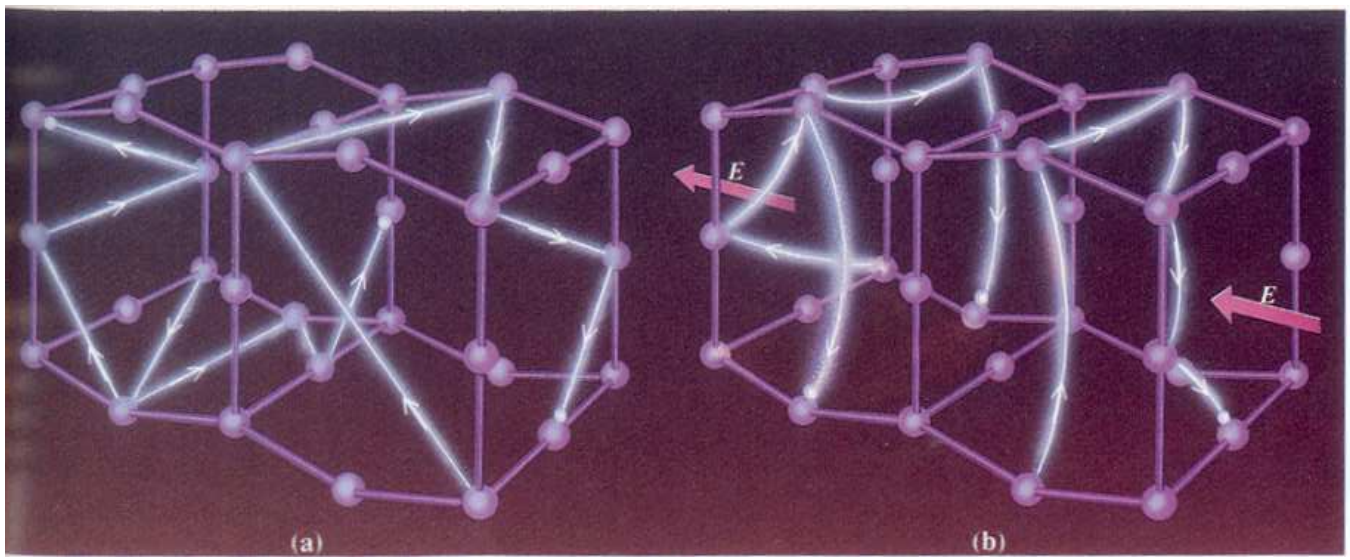
Overview

- 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: LiZnSb
  - Library: The parabolic band model
- Applications:
- Volumetric band alignment
- *p*-doped half-Heusler Compounds

Distribution function

Dilute gas of quasi particle described by the distribution function

$$f(\mathbf{r},\mathbf{p},t) = f(\mathbf{r} - \frac{\partial \mathbf{r}}{\partial t}dt, \mathbf{p} - \frac{\partial \mathbf{p}}{\partial t}dt, t - dt) + \left(\frac{\partial f}{\partial t}\right)_{scatt} dt$$

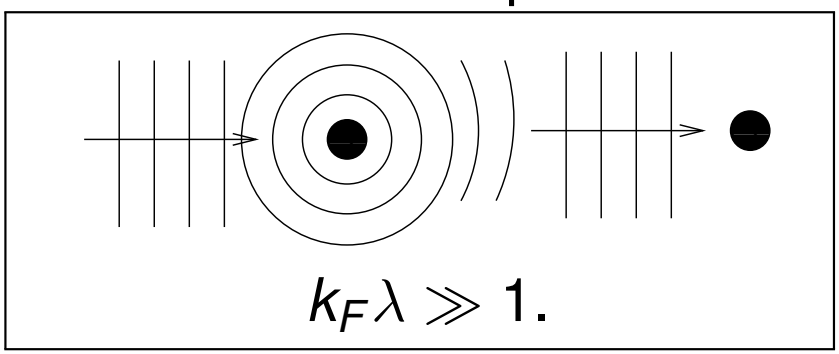


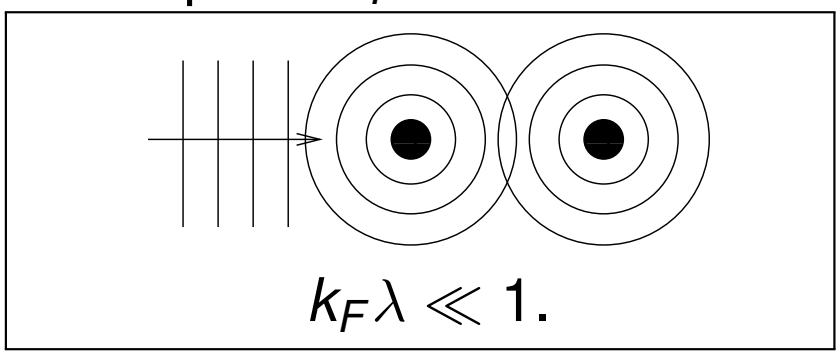
The Boltzmann equation

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. $k_F\lambda \ll 1$.



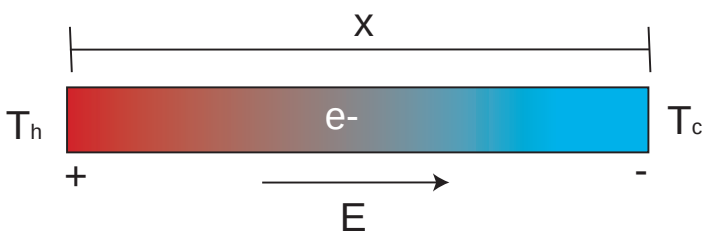


Boltzmann Equation

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

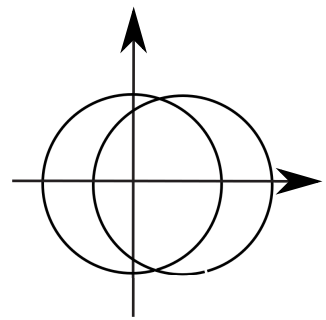
Diffusion:

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



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

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

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

The transport distribution

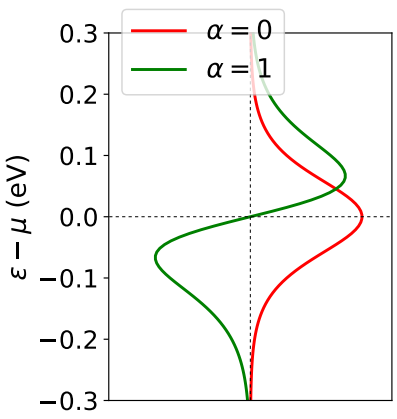
Introduce the transport distribution

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

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
$\nabla T = 0$:

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

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

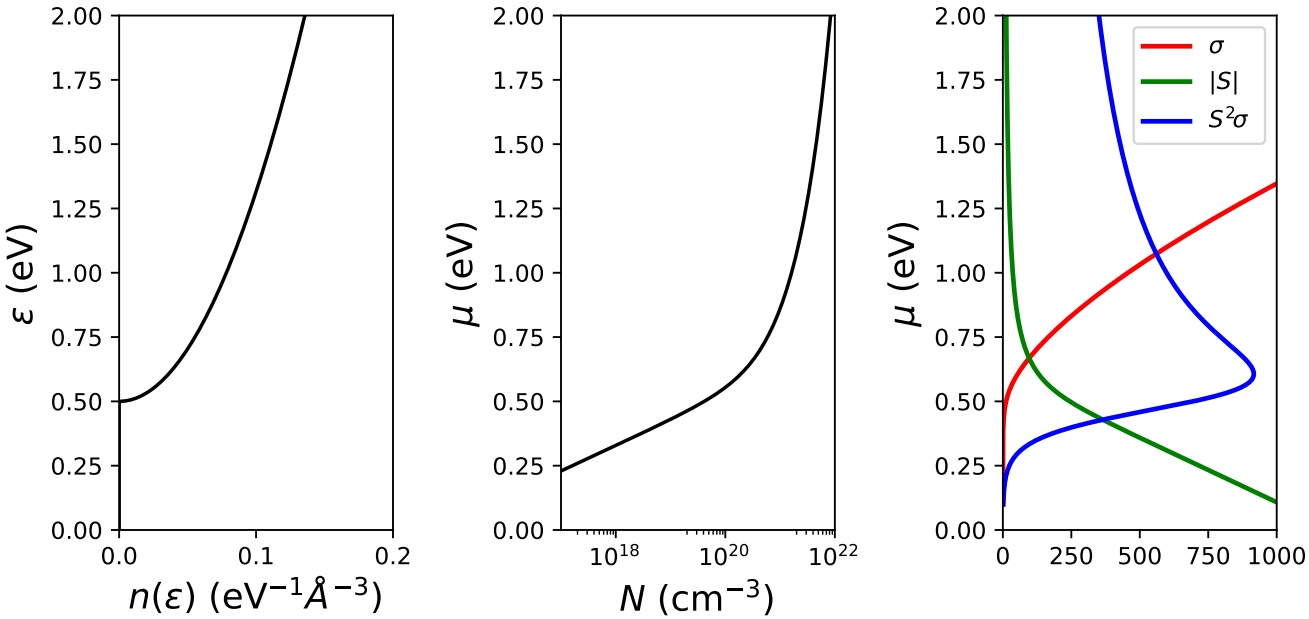
$j_e = 0$:

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

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

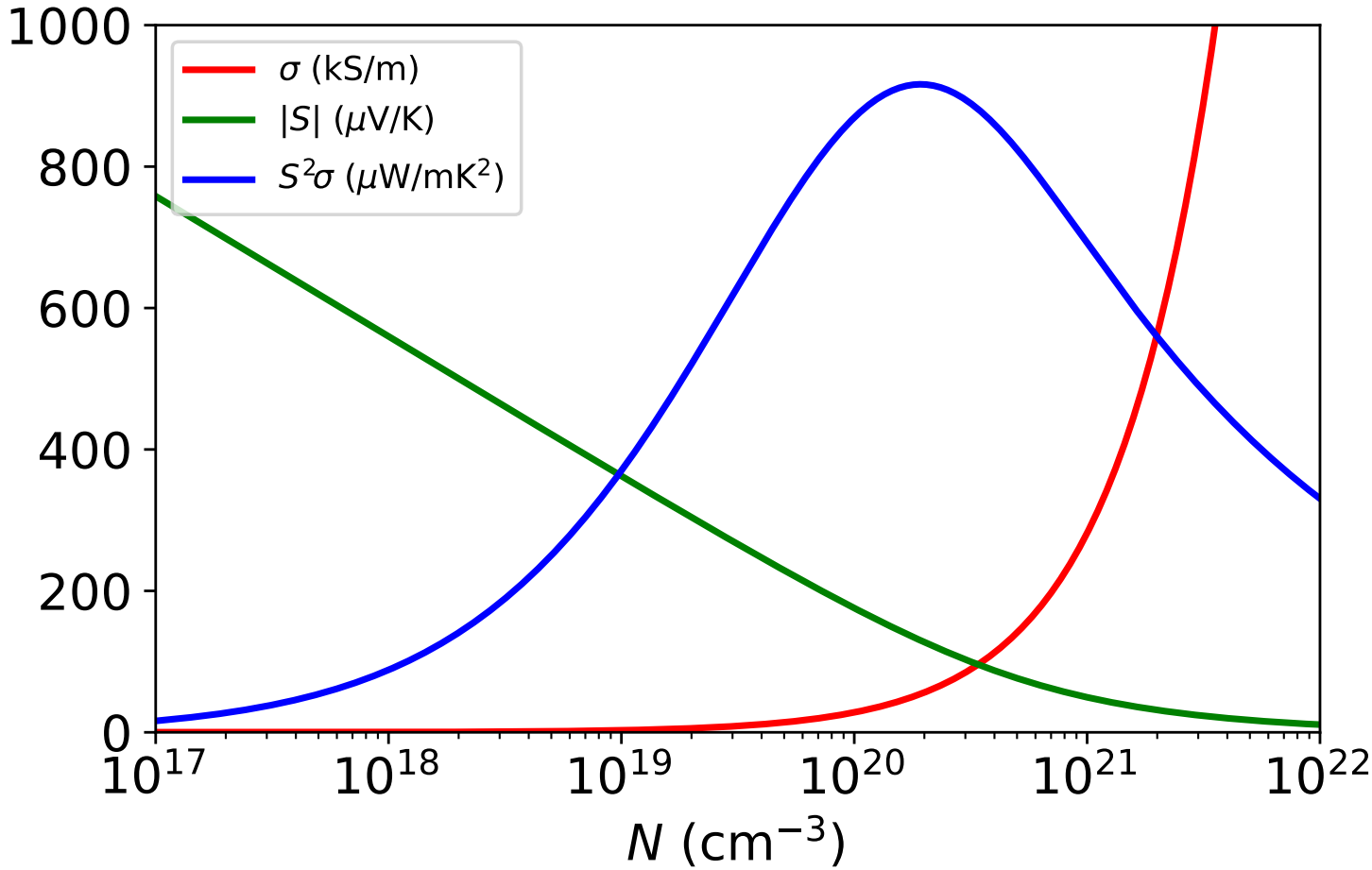
Homogeneous electron gas. DOS

$$\varepsilon(k) = \varepsilon_{\mathrm{CBM}} + \frac{\hbar^2 k^2}{2m^*}$$



$$n(\varepsilon) = \frac{m^{3/2}}{\pi^2\hbar^3}\sqrt{\frac{\varepsilon}{2}} \quad , \quad \sigma_{xx}(\varepsilon) = \frac{\sqrt{8m^*}}{\pi^2\hbar^3}\tau\varepsilon^{\frac{3}{2}}$$

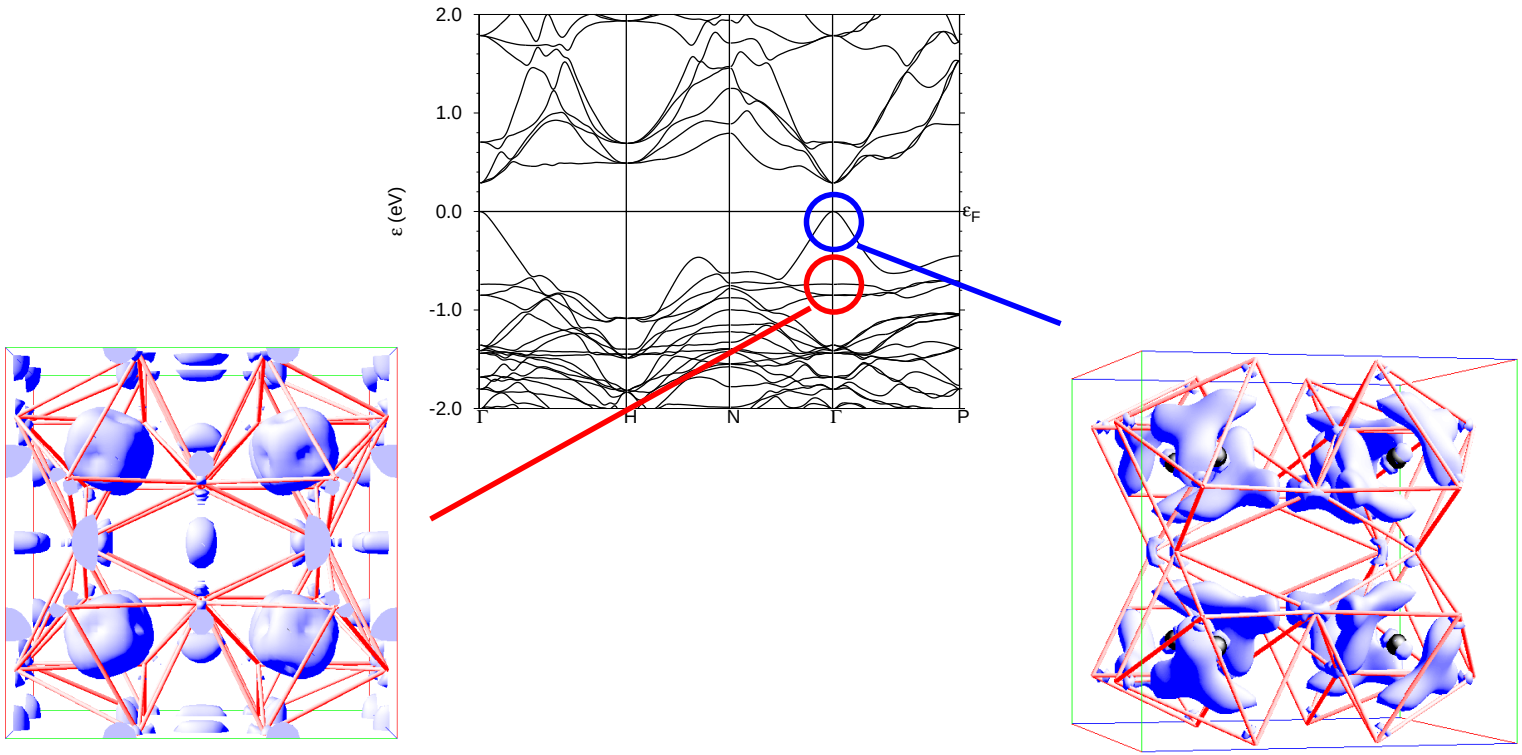
Carriers in parabollic band



- Peak in PF around 10^{20}-10^{21} cm^{-3}
- μ_e around band edge

Wave packet velocity

Velocity of a wave packet: $\mathbf{v}_{n\mathbf{k}} = \frac{1}{\hbar}\frac{\partial \varepsilon_{n\mathbf{k}}}{\partial \mathbf{k}}$



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

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

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

Calculated thermoelectric properties of La-filled skutterudites

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Code 6691, Naval Research Laboratory, Washington, DC 20375

I. I. Mazin
Code 6691, Naval Research Laboratory, Washington, DC 20375
and CSI, George Mason University, Fairfax, Virginia 22030

$$S(T)=\frac{e}{3T\sigma(T)}\int d\epsilon N(\epsilon)v^2(\epsilon)\epsilon\tau(\epsilon,T)\left(-\frac{\partial f(\epsilon)}{\partial\epsilon}\right)$$

$$=\frac{1}{3eT\sigma(T)}\int d\epsilon\sigma(\epsilon,T)\epsilon\left(-\frac{\partial f(\epsilon)}{\partial\epsilon}\right).$$

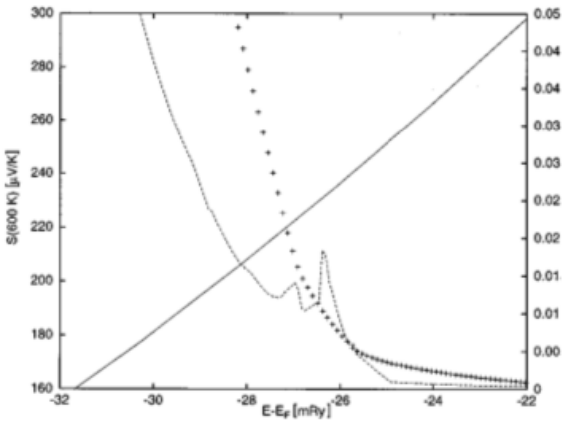
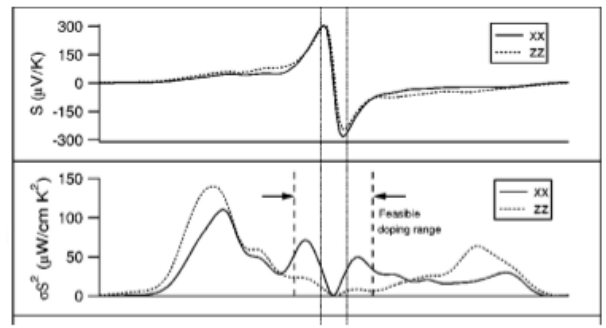


FIG. 2. Hole concentration (+), Hall number (dashed), and thermopower at 600 K (solid) as a function of the Fermi-level shift with

Transport coefficients from first-principles calculations

T. J. Scheidemantel,[1] C. Ambrosch-Draxl,[2] T. Thonhauser,[1] J. V. Badding,[3,4] and J. O. Sofo[1]

$$\vec{v}_{n,\vec{k}}=\frac{1}{m}\vec{p}_{n,\vec{k}}=\frac{1}{m}\langle\psi_{n,\vec{k}}|\vec{p}|\psi_{n,\vec{k}}\rangle$$

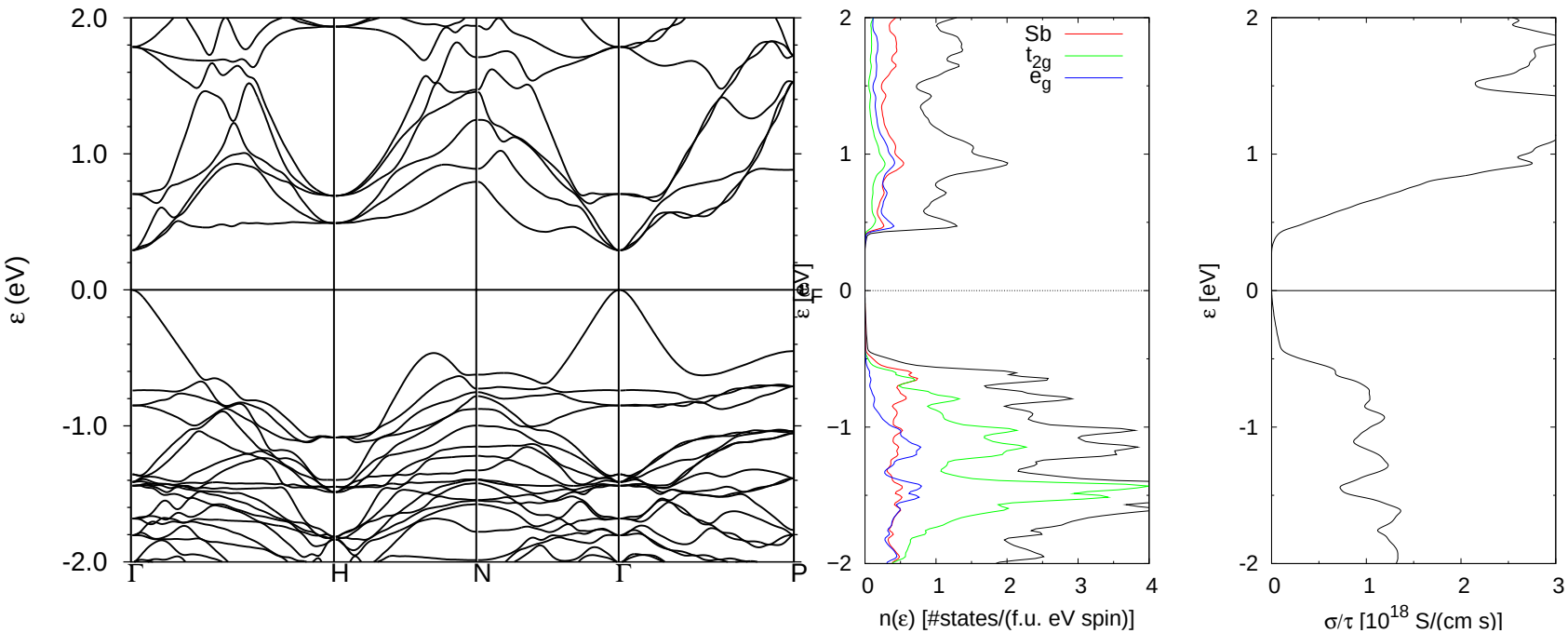


Transport distribution. $CoSb_3$

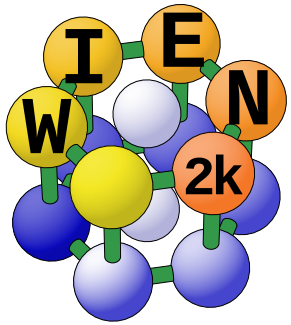
Transport distribution

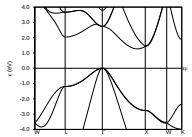
$$\sigma(\varepsilon) = \frac{1}{3}\sum_n \int v_{n\mathbf{k}} v_{n\mathbf{k}} \tau_{n\mathbf{k}} \delta(\varepsilon - \varepsilon_{n\mathbf{k}}) \frac{d\mathbf{k}}{8\pi^3}$$

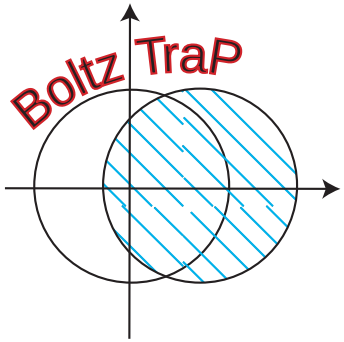
$CoSb_3$

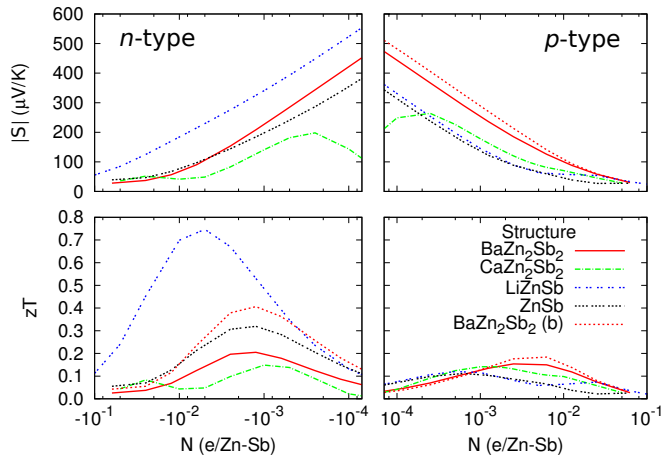


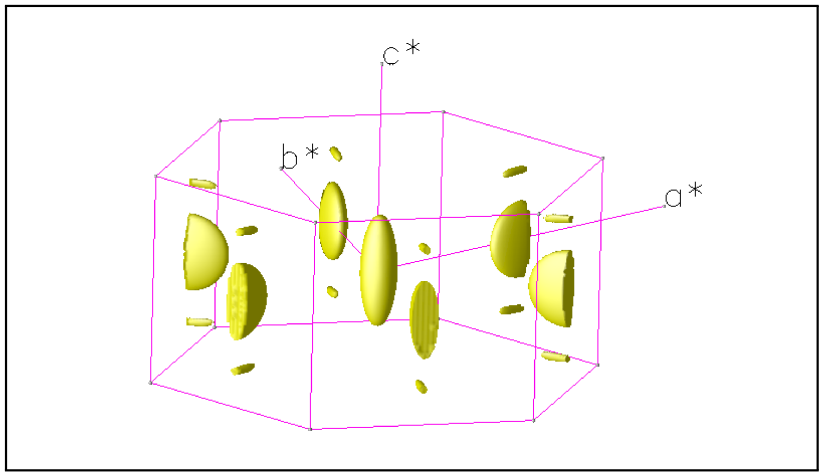
Automated search for new thermoelectrics











- 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)


FATBOY SLIM
I'M
#1
SO WHY
TRY HARDER
YOU'VE COME A LONG WAY, BABY
PARENTAL
GUIDANCE
EXPLICIT LYRICS

BoltzTraP2: A modern tool for modern workflows

Design goals:

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

Speed:

- New algoritmes
- Modularity, flexibility
- Readable code
- Standard formats

Two use cases:

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

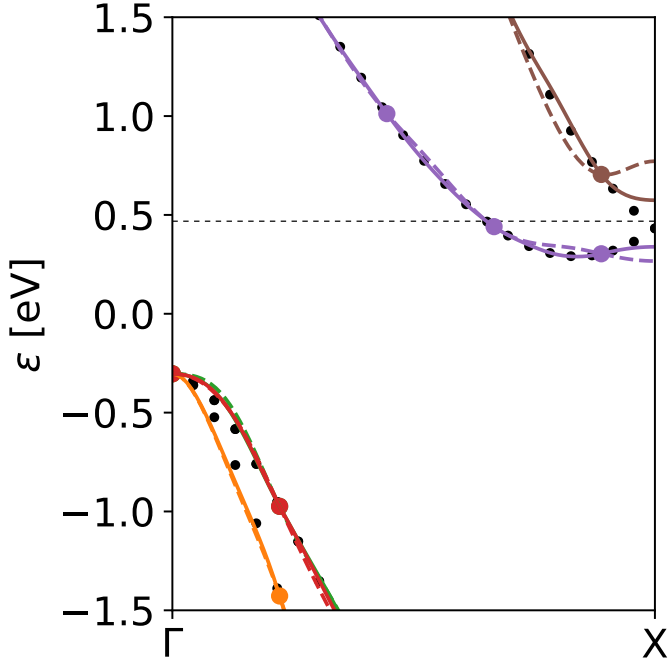
BoltzTraP2 interpolation

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

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

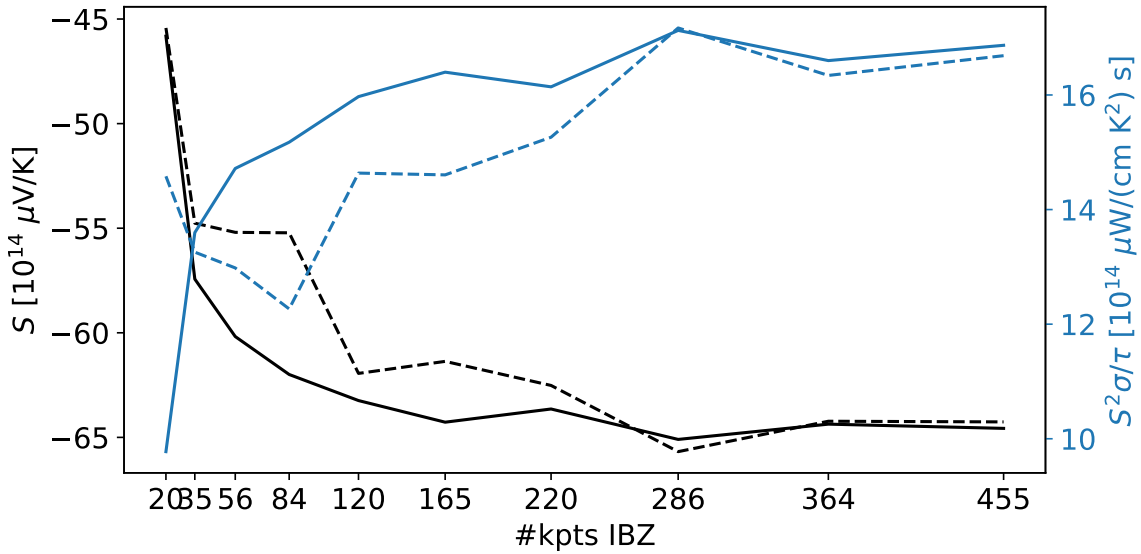
- Combine advantage of BoltzTraP (analytic bands) and Scheidemantel-Sofo approach (exact derivatives at calculated points)
- Potentially coarser k-mesh

Example: Silicon band structure



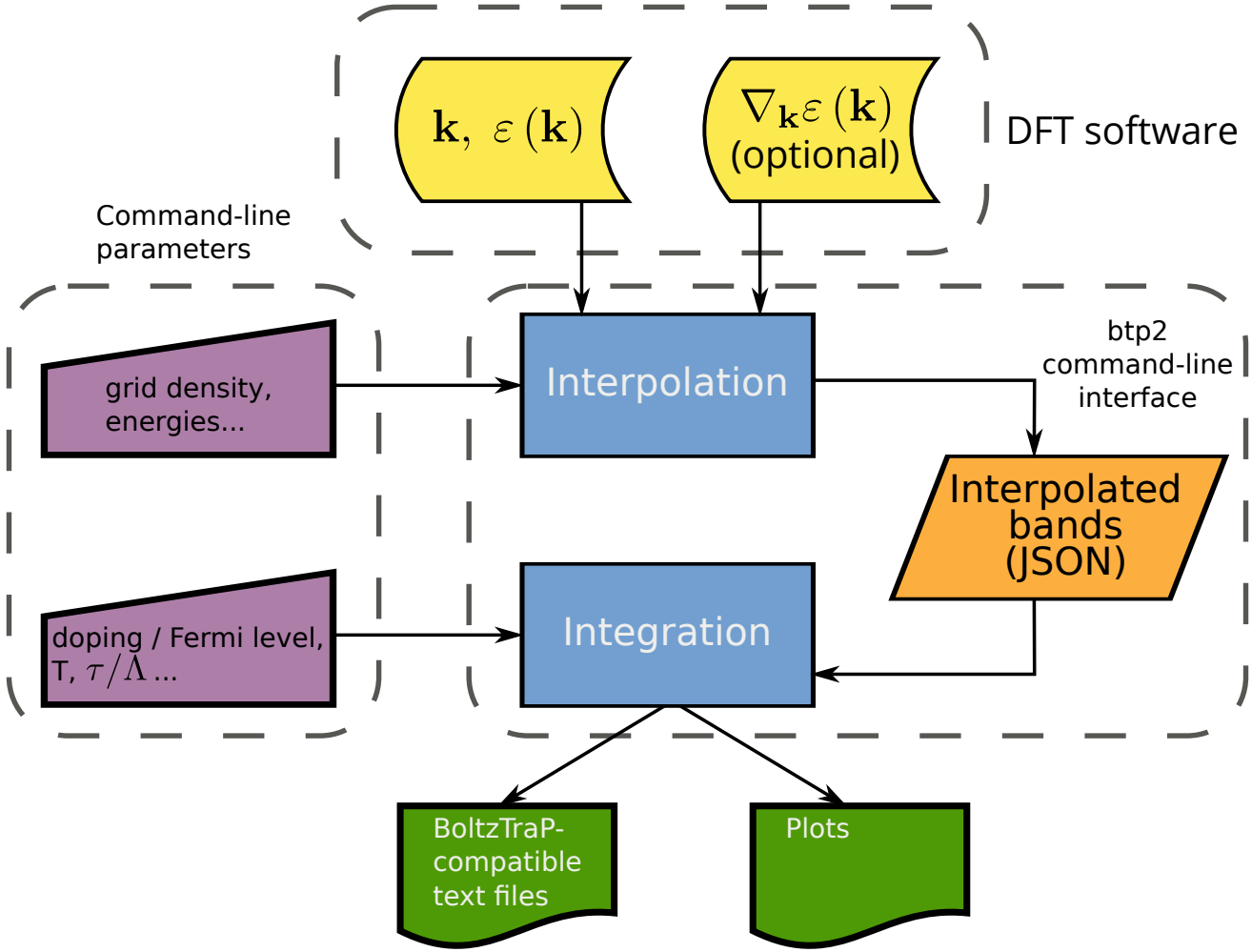
- CBM made up by degerate pocket along six-fold degenrate $\Gamma - X$ line
- Interpolated bands based on a coarse $9 \times 9 \times 9$ k-point mesh
- Modified Lagrangian forces the fit to reproduce the exact derivatives at the calculated points.
- Position and derivatives at the pocket are well reproduced

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

The BoltzTraP2 command-line workflow



Command Line Interface

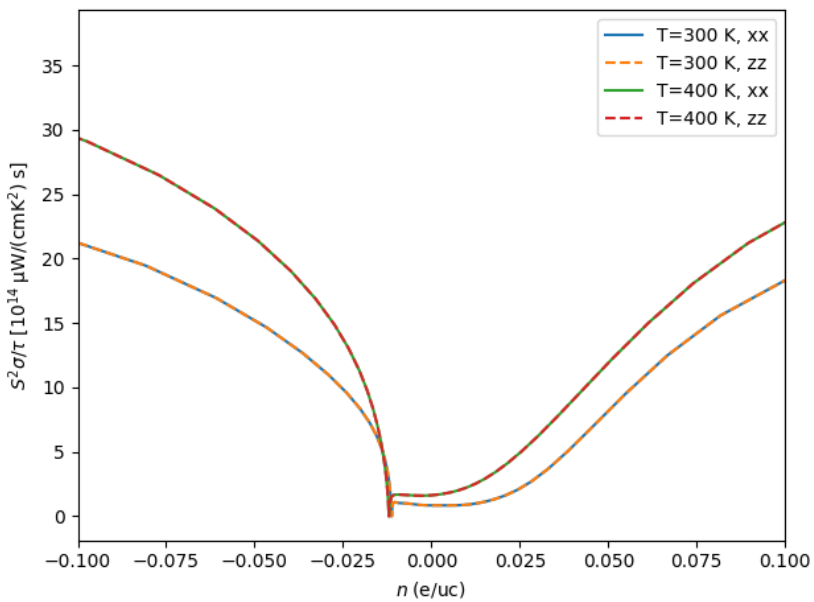
```
cp -r /area51/opt/boltztrap2/data/CoSb3 .
cd CoSb3
```

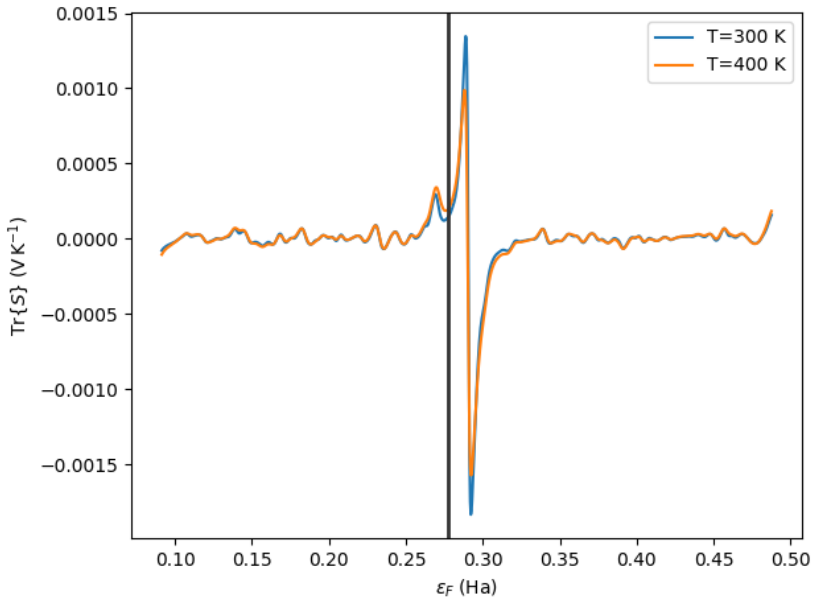
Fit the calculated eigenvalues in a window ± 0.2 Ha around the Fermi level. The interpolated *k*-mesh should be five times as dense as the original:

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

Integrate to get the transport properties

```
btp2 -vv integrate -b 1000 -t0 -T"300,500,100"
CoSb3.bt2
```





BoltzTraP2. Four steps to transport coefficients

1. Fit coefficients

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

2. Project transport distribution

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

3. Integrate to obtain transport coefficients

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

4. Convert to phenomenological transport coefficents (SI units)

$$\sigma = \mathcal{L}^{(0)} \quad , \quad S = \frac{1}{qT} \frac{\mathcal{L}^{(1)}}{\mathcal{L}^{(0)}} \quad , \quad \kappa_e = \frac{1}{q^2 T} \left(\frac{(\mathcal{L}^{(1)})^2}{\mathcal{L}^{(0)}} - \mathcal{L}^{(2)} \right)$$

Some highlights of BoltzTraP2

Flexibility

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

Portability

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

Speed

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

Documentation

- Fully documented code
- Several tutorials
- Accompanying article

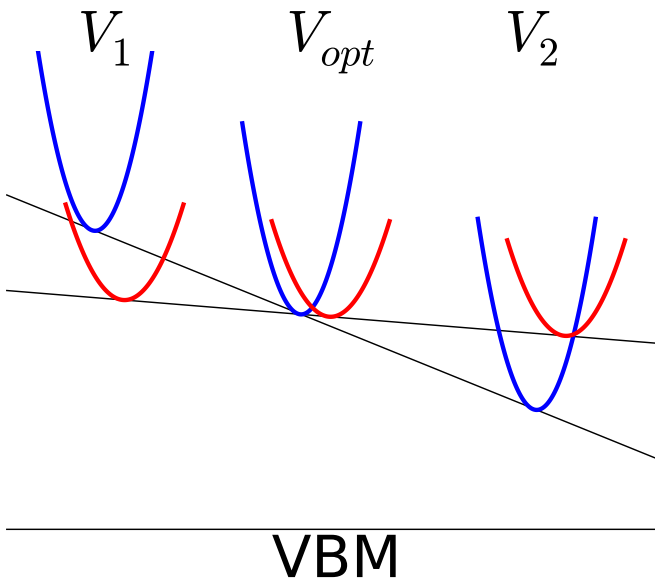
Sensible defaults

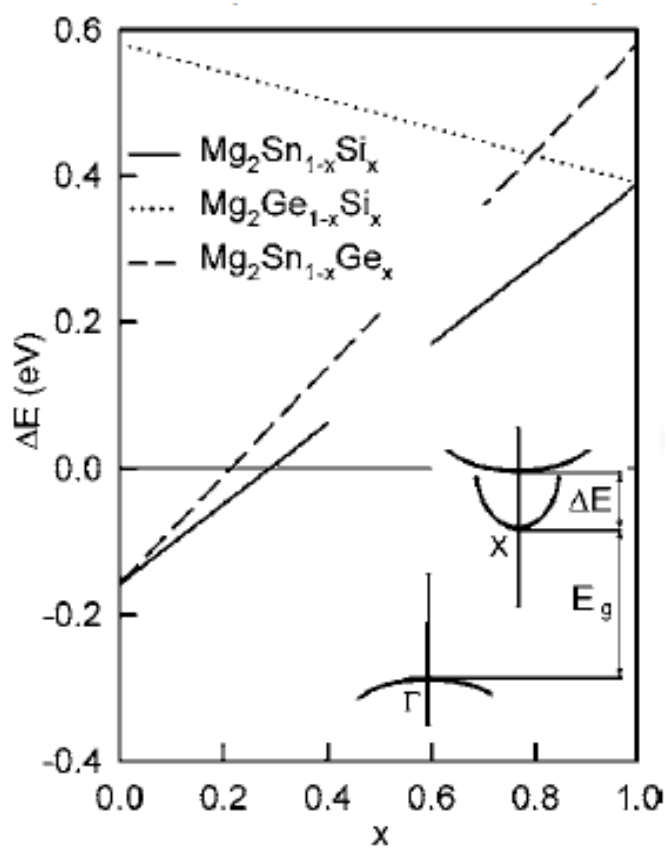
- Input source
- Grid density
- Number of bins in DOS (Freedman Diaconis)

Standard formats

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

Volumetric Band Alignment





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

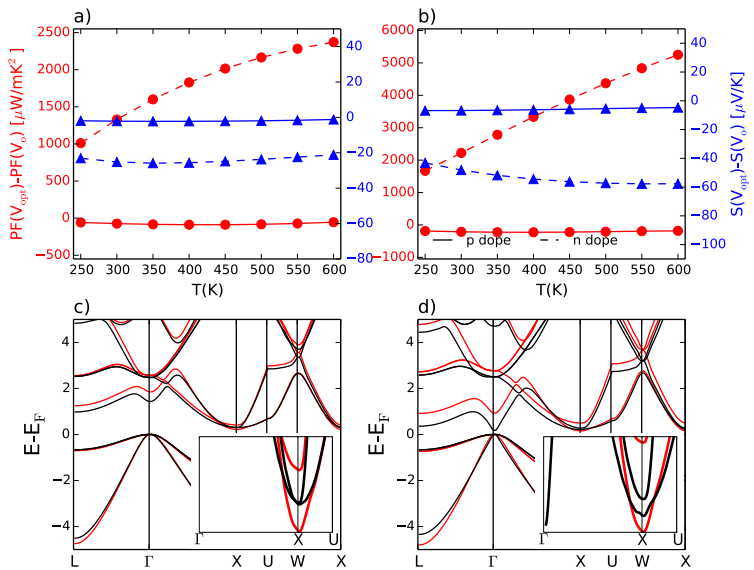
Optimize power factor by alignment of band edges

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

$Mg_2Si_xSn_{1-x}$

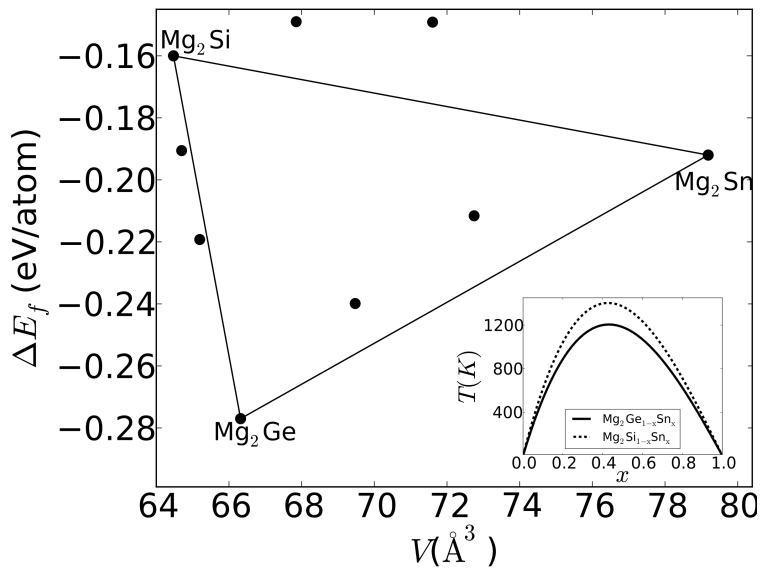
1. Band structure

Calculate volume dependence of S and σ/τ



2. Thermodynamics

Calculate mixing enthalpy (SQS)

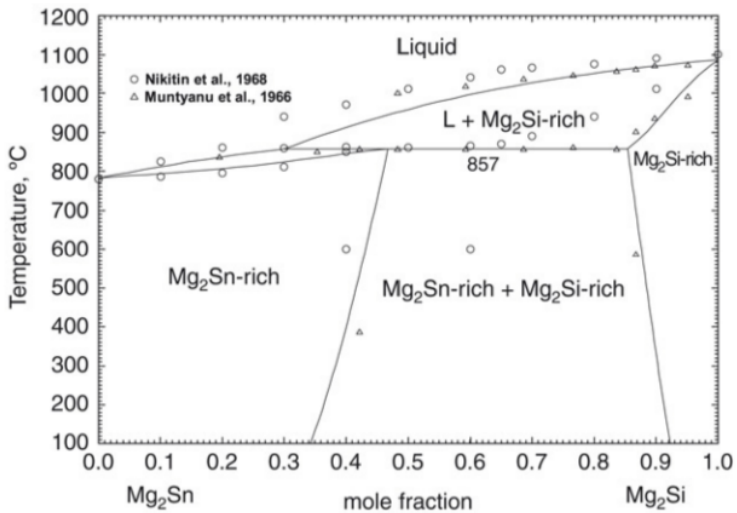


Bhattacharya, GKHM *Phys. Rev. B* 92, p085205 (2015)

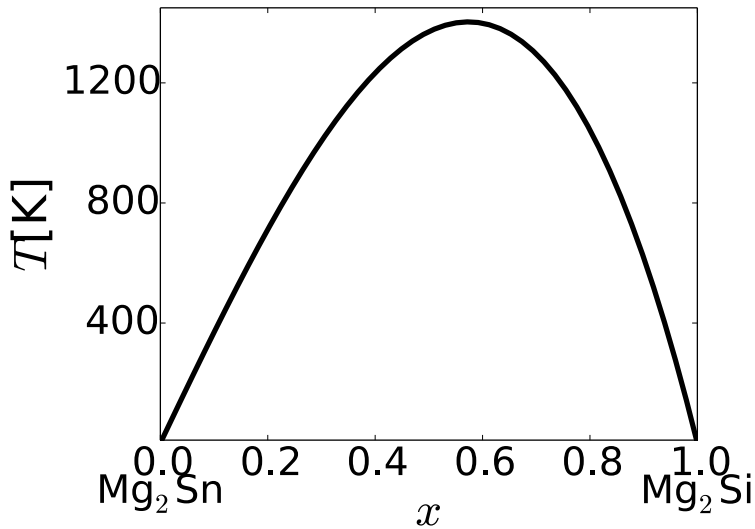
Phasediagram: Mg_2Sn-Si

$$\Delta E_{\mathrm{mix}}(x;\mathrm{AB}_n,\mathrm{AC}_n) = \Delta E_f(AB_{n-x}C_x) - \frac{x\Delta E_f(AC_n) + (n-x)\Delta E_f(AB_n)}{n}$$

$$\Delta G_{\mathrm{mix}}(x) = \Delta E_{\mathrm{mix}}(x) + \frac{RT}{n+1}\left[x\ln x + (1-x)\ln(1-x)\right]$$



Jung et al CALPHAD 31 p192 (2007)



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

VBA screening

Initial M-X combinations

3150

Thermodynamically stable structures

522

Good thermoelectrics ($zT > 0.4$)

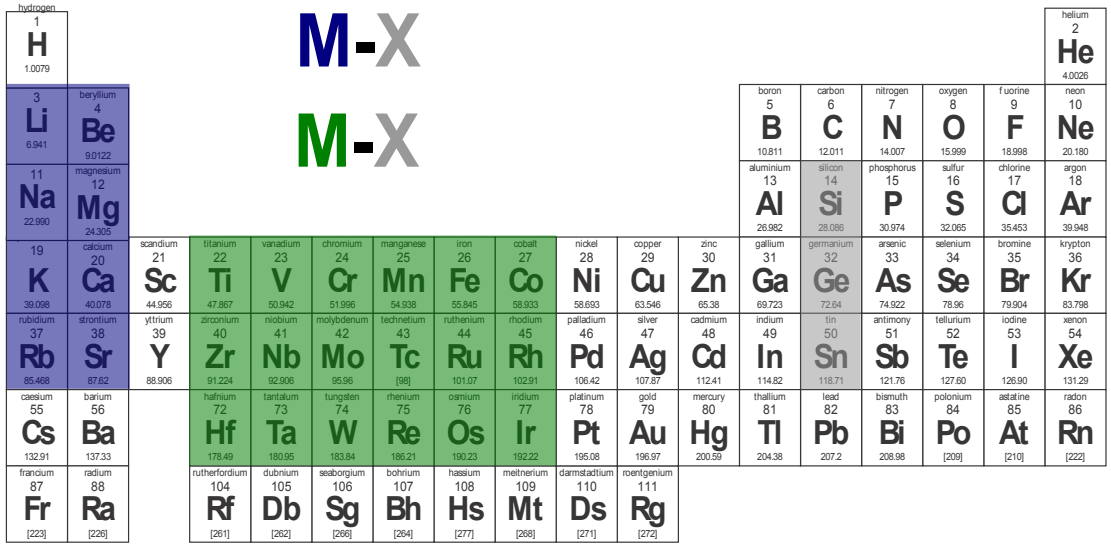
29

Candidates for VBA

8

Checks for alloy stability

4



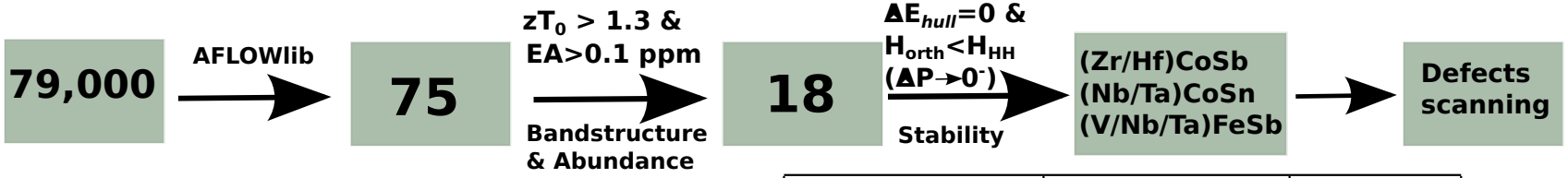
Bhattacharya, GKHM *Phys. Rev. B* 92, p085205 (2015)

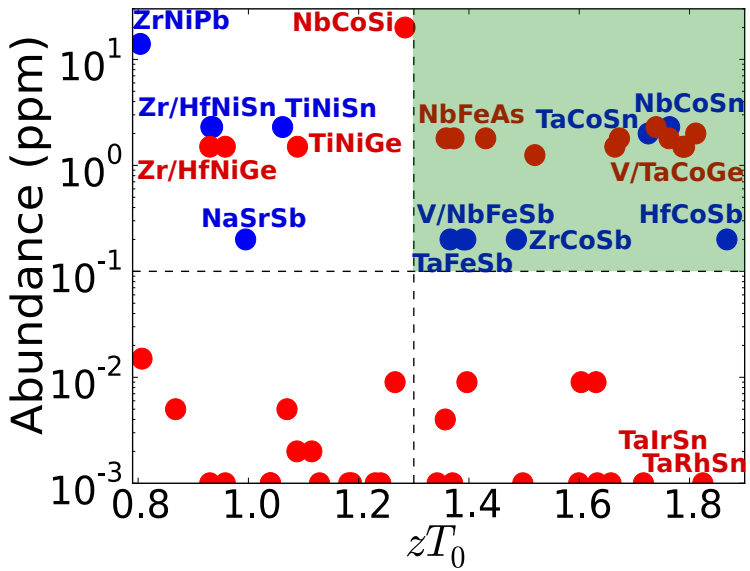
Alloy Thermodynamics

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)

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

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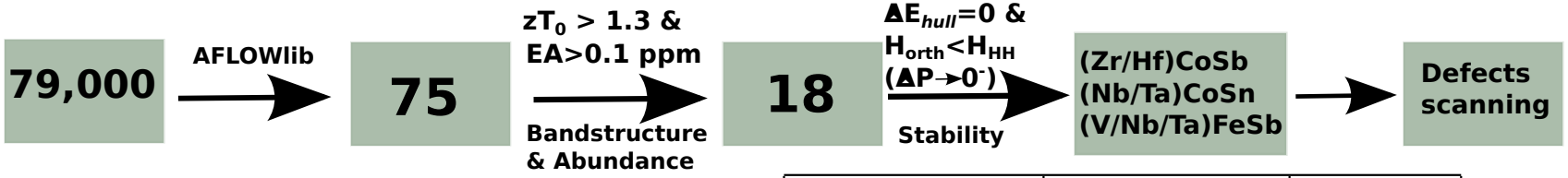
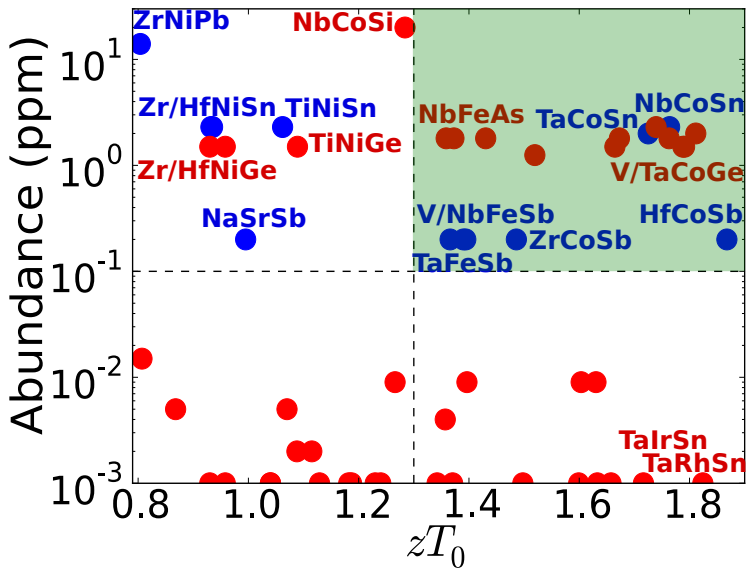
Screening. Band structure, abundance and stability.





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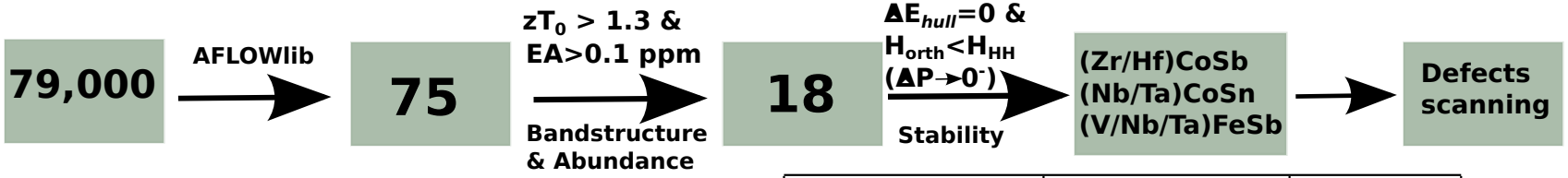

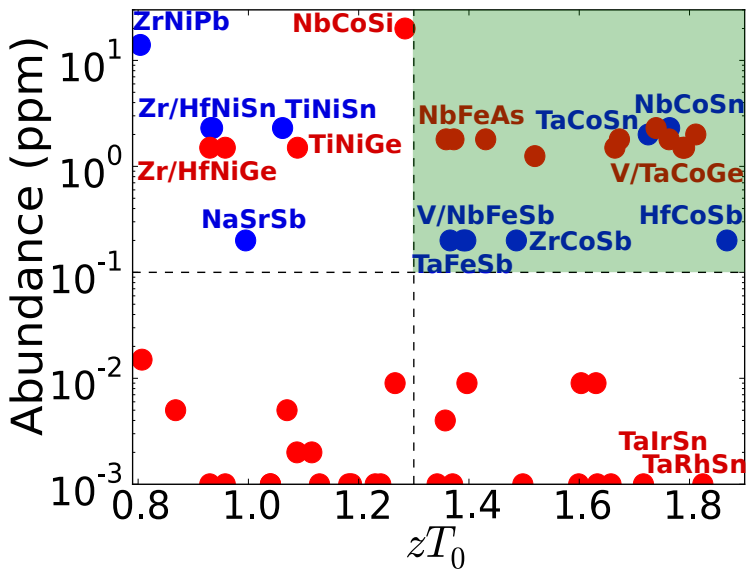

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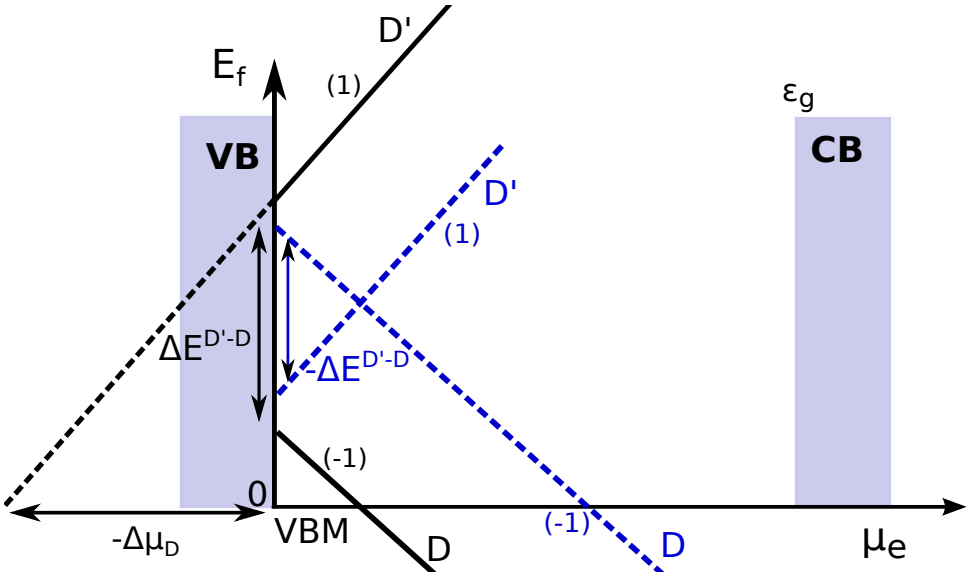
Intrinsic defects



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

No intrinsic doping limits

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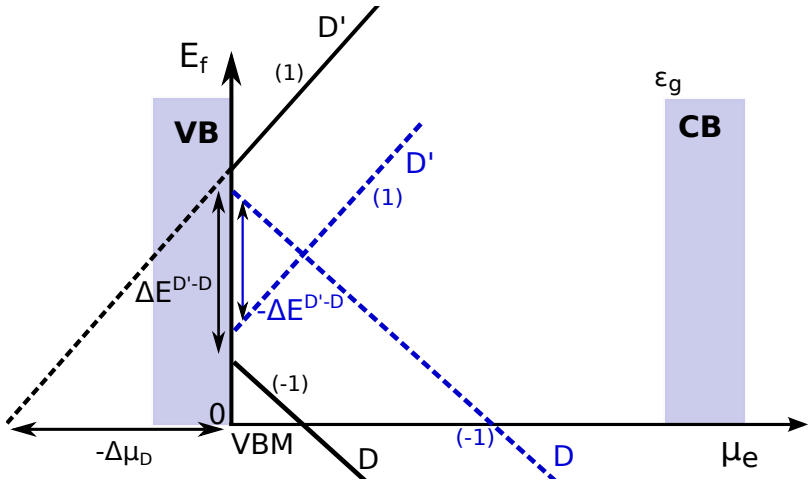
Extrinsic doping



	$E_f^D(\mu_{VB})$ (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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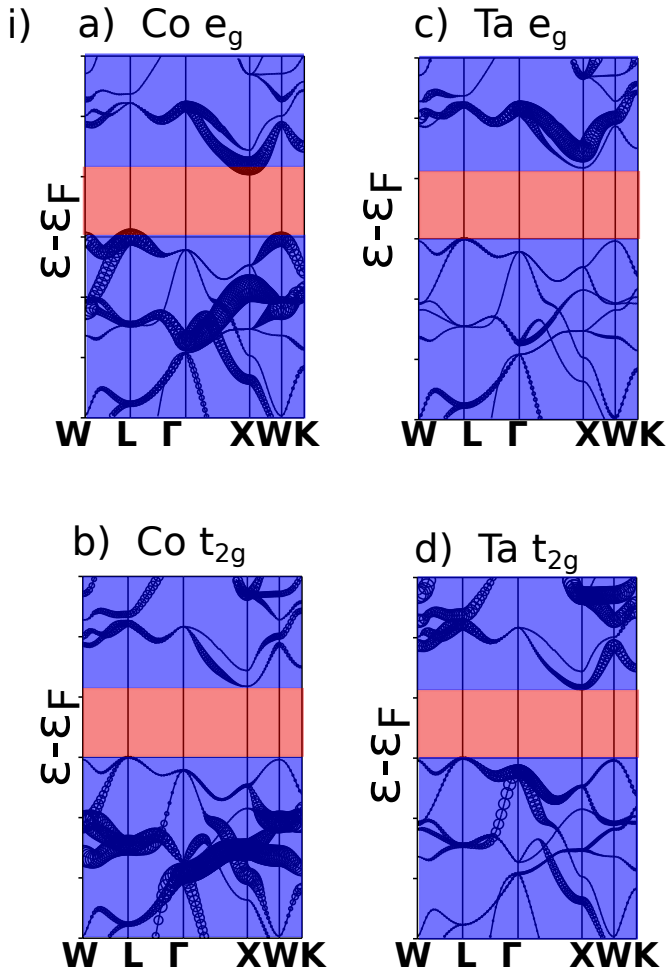
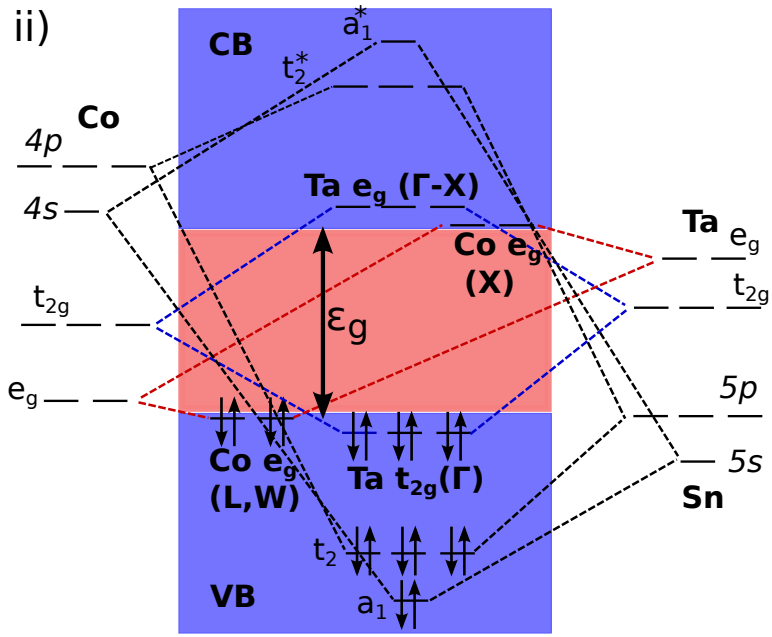
TE Heusler. Band structure.





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

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p-type HHC: (V/Nb)FeSb

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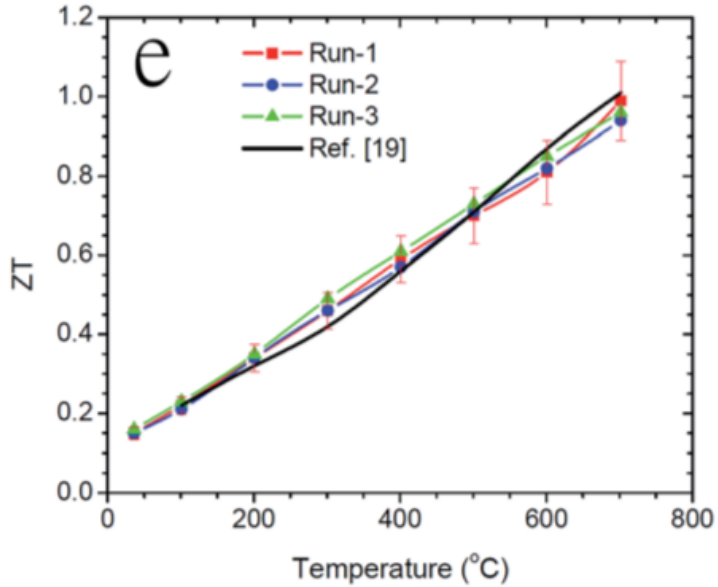
NbFeSb-based p-type half-Heuslers for power generation applications

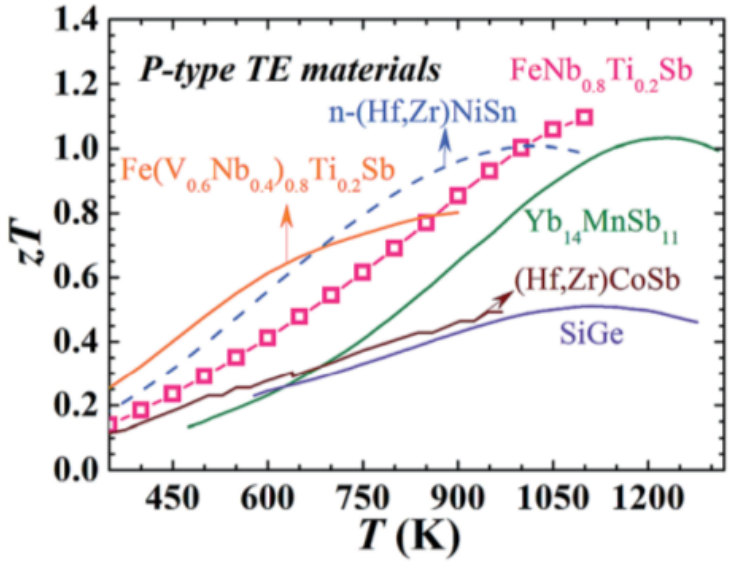
Giri Joshi,*[a] Ran He,[b] Michael Engber,[a] Georgy Samsonidze,[c] Tej Pantha,[a] Ekraj Dahal,[a] Keshab Dahal,[b] Jian Yang,[a] Yucheng Lan,[b] Boris Kozinsky[c] and Zhifeng Ren*[b]



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]



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Jesús Carrete

Matthieu Verstraete

Conclusion