Transport: BoltzTraP2

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Overview

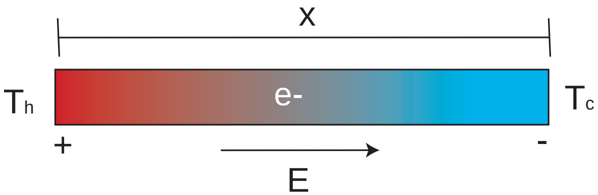
- The Boltzmann transport equation
- BoltzTraP2
- The discovery of CoSbS as a thermoelectric material

Linearized Boltzmann transport equation

Steady-state:

$$-\underbrace{\frac{\partial f}{\partial \boldsymbol{r}}\mathbf{v}}_{\text{Diffusion}} - \underbrace{\frac{\partial f}{\partial \mathbf{p}}m\mathbf{a}}_{\text{Field}} + \left(\frac{\partial f}{\partial t}\right)_{\text{scatt}} = 0$$

Electrons and holes:



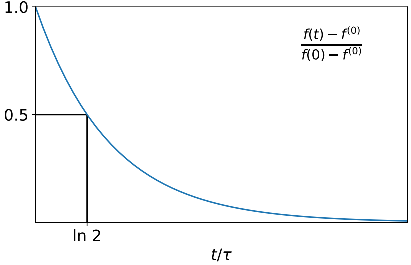
$$\mathbf{v}\left(-\frac{\partial f}{\partial \varepsilon}\right)\left(-\frac{\varepsilon-\mu}{T}\nabla T + q\mathbf{E}\right) + \left(\frac{\partial f}{\partial t}\right)_{\text{scatt}} = 0$$

The relaxation time approximation

$$\mathbf{v}\left(-\frac{\partial f}{\partial \varepsilon}\right)\left(-\frac{\varepsilon-\mu}{T}\nabla T + q\mathbb{E}\right) + \left(\frac{\partial f}{\partial t}\right)_{\mathrm{scatt}} = 0$$

Phenomological assumption: Exponential decay of deviation from equilibrium

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



Current density

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

The transport distribution and coefficients

Introduce the transport distribution

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

$$j_e = \int q\sigma(\varepsilon)\left(-\frac{\partial f}{\partial \varepsilon}\right)\left(-\frac{\varepsilon - \mu}{T}\nabla T + q\mathbf{E}\right)\mathrm{d}\varepsilon$$

Introduce generalized transport coefficients in terms moments of the transport distribution

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

The current in terms of the transport coefficients

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

Phenomenological transport coefficients

$$j_e = \mathcal{L}^{(0)}\mathbf{E} + \frac{\mathcal{L}^{(1)}}{qT}(-\nabla T) \quad , \quad j_Q = \frac{\mathcal{L}^{(1)}}{q}\mathbf{E} + \frac{\mathcal{L}^{(2)}}{q^2 T}(-\nabla T)$$

Identify two kinds of experimental situations

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

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

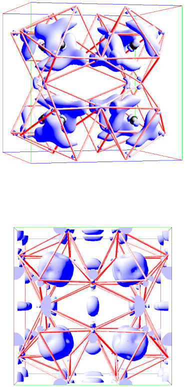
$\mathbf{j_e} = \mathbf{0}$:

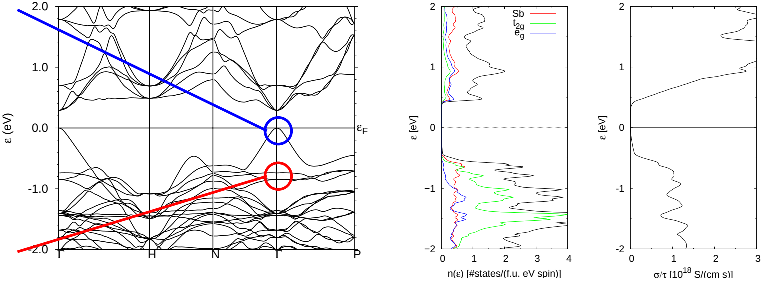
$$\mathcal{L}^{(0)} E = \frac{\mathcal{L}^{(1)}}{qT}\nabla T \Rightarrow \quad S = \frac{1}{qT}\frac{\mathcal{L}^{(1)}}{\mathcal{L}^{(0)}}$$

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

Transport distribution. $CoSb_3$

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

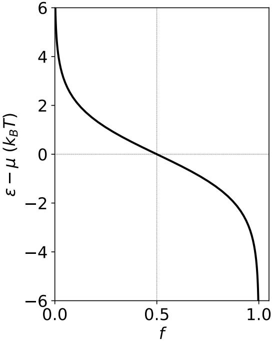




$$\sigma(\varepsilon) = \frac{1}{3}\sum_n \int v_{n\boldsymbol{k}} v_{n\boldsymbol{k}} \tau_{n\mathbf{k}} \delta(\varepsilon - \varepsilon_{n\mathbf{k}}) \frac{\mathrm{d}\boldsymbol{k}}{8\pi^3}$$

Dirac-Fermi distribution

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1}$$



$T = 0$:

$$f = \begin{cases} 1 & \text{, if } \varepsilon < \mu \\ \frac{1}{2} & \text{, if } \varepsilon = \mu \\ 0 & \text{, if } \varepsilon > \mu \end{cases} \quad , \quad \mu = \varepsilon_F$$

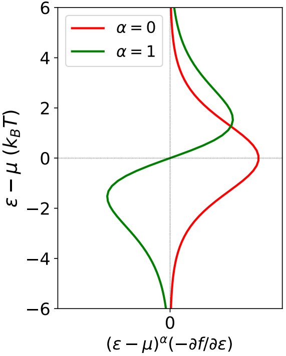
- Smoother transition, width of a few $k_\mathrm{B} T$
- Value at μ always $\frac{1}{2}$

Transport coefficients. The Fermi distribution.

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

$$\alpha = 0 : -\frac{\partial f}{\partial \varepsilon}$$

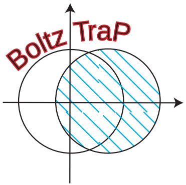
$$\alpha = 1 : (\varepsilon-\mu)\left(-\frac{\partial f}{\partial \varepsilon}\right)$$



- Influence of temperature and doping controlled through $(\varepsilon-\mu)^\alpha \partial f/\partial\varepsilon$ in a rigid band approximation
- $S \propto \mathcal{L}^{(1)}/\mathcal{L}^{(0)}$ is independent of τ in a constant relaxation time approximation and related to slope of $\sigma(\varepsilon)$ at Fermi level.
- Gap size strongly influences temperature profile

Program: BoltzTraP

1. Smoothed Fourier expansion of band energies
2. Transport distribution, $\sigma(\varepsilon) = \frac{1}{N} \sum \sigma_{n\mathbf{k}} \delta(\varepsilon - \varepsilon_{n\mathbf{k}})$
3. Rigid band approach, $\mathcal{L}^{(\alpha)}(\mu; T) = q^2 \int \sigma(\varepsilon)(\varepsilon - \mu)^{\alpha} \left(-\frac{\partial f_{T\mu}(\varepsilon)}{\partial \varepsilon} \right) d\varepsilon$



GKHM, Singh, *Comput. Phys. Commun.* 175 (2006) p67

- All crystal structures
- Full tensors quantities
- Conductivity, Seebeck and Hall tensors and Lorentz number.

Shankland-Pickett algorithm

Fourier sum

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

Minimize roughness function with respect to the Fourier coefficients while exactly reproducing calculated eigenvalues.

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

Shankland, *Int. J. Quantum Chem.* 5 (1971) 497–500.

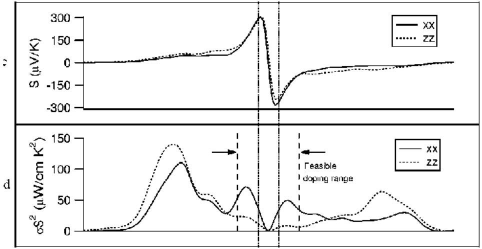
Roughness function

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

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

Testing BoltzTraP. Bi_2Te_3

Scheidemantel, Sofo:

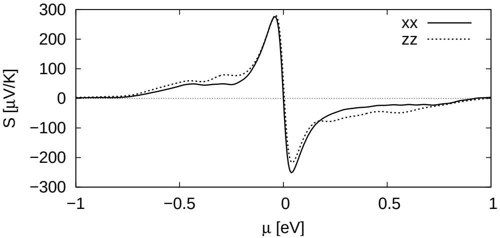


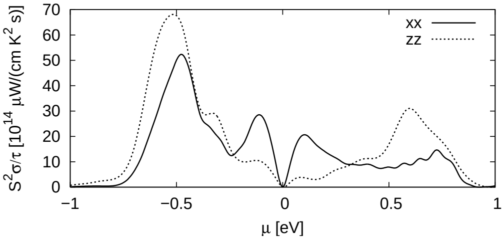
Scheidemantel, Ambrosch-Draxl, Thonhauser, Badding, Sofo *Phys. Rev. B* 68 (2003) p125210

Calculate group velocities from momentum matrix elements.

$$\mathbf{v}_{n\boldsymbol{k}} = \frac{\langle \psi_{n\boldsymbol{k}} | \hat{\mathbf{p}} | \psi_{n\boldsymbol{k}} \rangle}{m_e}$$

BoltzTraP:





GKHM, Singh, *Comput. Phys. Commun.* 175 (2006) p67

BoltzTraP2: A modern tool for modern workflows.

Design goals:

- Python
- Easy installation, portability
  `pip3 install BoltzTraP2`
- Command-line interface
- New algoritmes
- Modularity, flexibility
- Standard formats
- All useful features from BoltzTraP

Two use cases:

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

BoltzTraP2 interpolation scheme

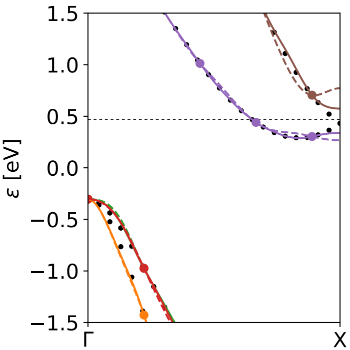
Minimize roughness function while exactly reproducing calculated eigenvalues *and derivatives*

$$\mathcal{L} = \frac{1}{2}\sum c_{\Lambda}\rho_{\Lambda} + \sum_{\boldsymbol{k}}\left[\lambda_{\boldsymbol{k}}\left(\varepsilon_{\boldsymbol{k}} - \tilde{\varepsilon}_{\boldsymbol{k}}\right) + \sum_{\alpha}\lambda'_{\alpha\boldsymbol{k}}\nabla_{\alpha}\left(\varepsilon_{\boldsymbol{k}} - \tilde{\varepsilon}_{\boldsymbol{k}}\right)\right]$$

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

Madsen, Carrete, Verstraete *Comp. Phys. Comm* 231 (2018) p140

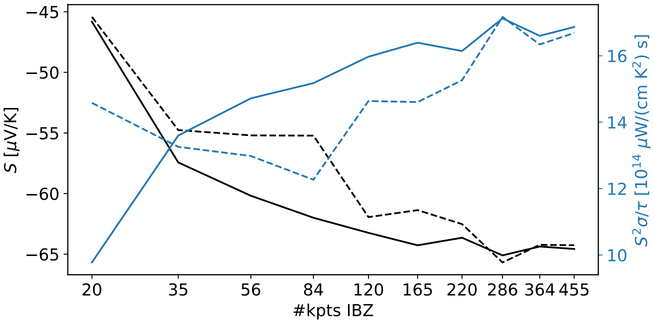
Example: Silicon band structure



- CBM made up by pockets along six-fold degenerate $\Gamma - X$ line
- Interpolated bands based on a coarse $9 \times 9 \times 9$ k-point mesh
- Modified $\mathcal{L}$ forces fit to reproduce the calculated derivatives
- Position and derivatives at the pocket are well reproduced

Madsen, Carrete, Verstraete *Comp. Phys. Comm* 231 (2018) p140

Example: Silicon transport

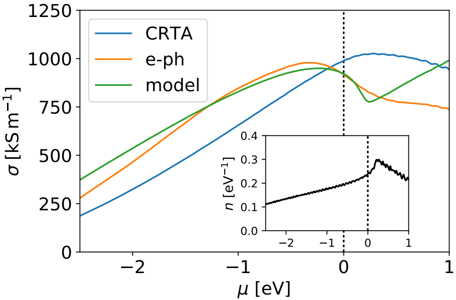


- Seebeck coefficient and thermoelectric power factor calculated at a chemical potential close to the CBM using the CRTA
- The results obtained by the modified Lagragian show both a faster and more systematic convergence towards the converged values
- Convergence reached at about half the number of $\boldsymbol{k}$-points

Madsen, Carrete, Verstraete *Comp. Phys. Comm* 231 (2018) p140

BCC-Li: Band and momentum dependent relaxation times

Interpolate calculated $\tau_{n\mathbf{k}}$ onto same mesh as $\mathbf{v}_{n\mathbf{k}}$ and evaluate $\mathbf{v}_{n\mathbf{k}}\mathbf{v}_{n\mathbf{k}}\tau_{n\mathbf{k}}$

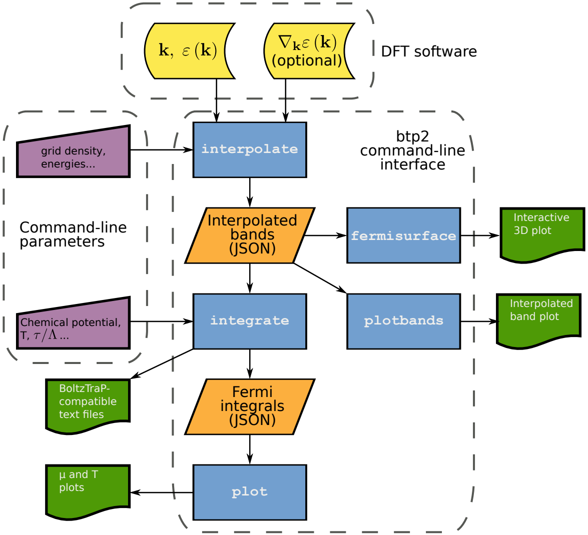


- Including $\tau_{n\mathbf{k}}$ changes the slope of the transport distribution (and thereby sign of Seebeck coefficient)
- Simple $\tau^{-1}(\varepsilon) = cn(\varepsilon)$ model reproduces result

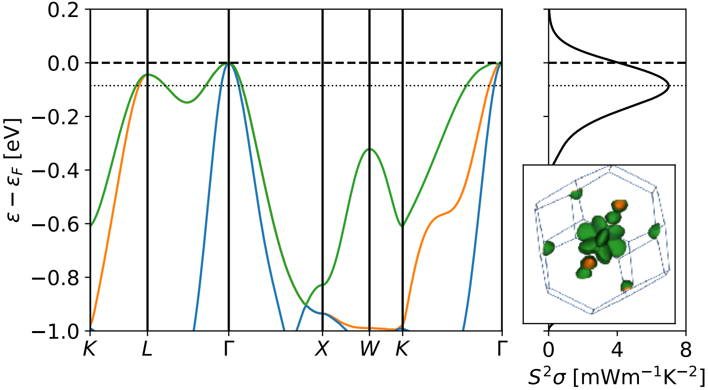
Madsen, Carrete, Verstraete *Comp. Phys. Comm* 231 (2018) p140

$\tau_{n\mathbf{k}}$ from: Xu, Verstraete, *Phys. Rev. Lett.* 112 (2014) p196603. Review: Poncé, Giustino *Rep. Prog. Phys.* 83 (2020) 036501

The BoltzTraP2 command-line workflow



Example: TiCoSb band structure analysis



- Isoenergy surfaces of band structures
- Fermi surface in a metal

Blaha et. al. *J. Chem. Phys.* 152 (2020) 074101

Some highlights of BoltzTraP2

Flexibility

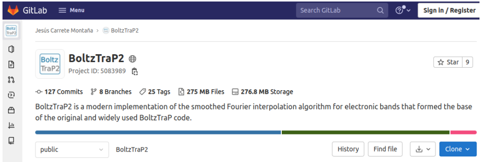
- Usable as a Python module
- Extensible scattering models
- Automatic detection of space group

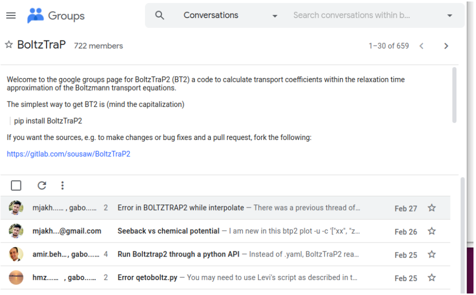
Speed

- Highly vectorized Python
- Symmetry module in C++

Portability

- Standard Python setup toolchain
- Detection of compilers and libraries
- JSON: Human readable & parsers for every language
- Final output as text





www.boltztrap.org

- 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

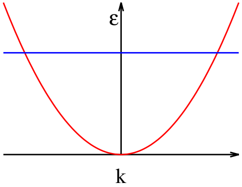
$$PF = S^2 \sigma$$

Band structures for a high powerfactor

Transport distribution: $\sigma(\varepsilon) = \langle v^2 \rangle n(\varepsilon)$

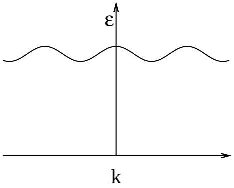
Disperse

$n(\varepsilon)$	-
$\langle v^2 \rangle$	+



Flat bands

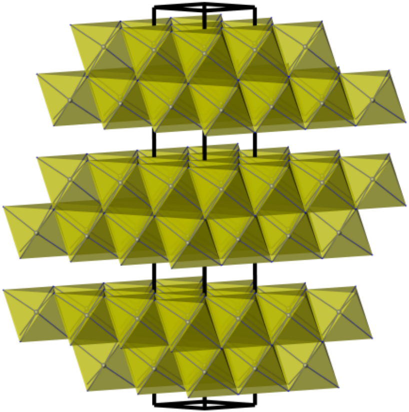
$n(\varepsilon)$	+
$\langle v^2 \rangle$	-

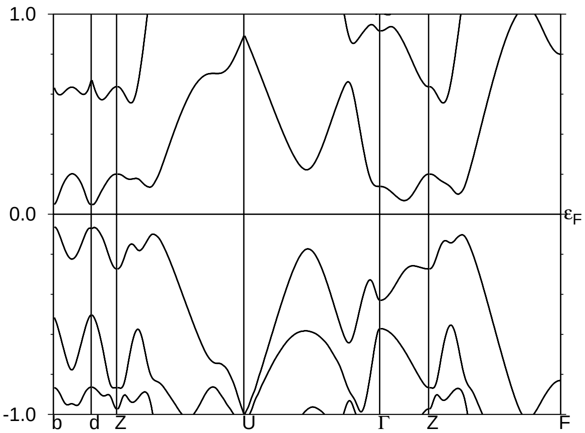


Pockets

$n(\varepsilon)$	+
$\langle v^2 \rangle$	+

Bi_2Te_3 band structure





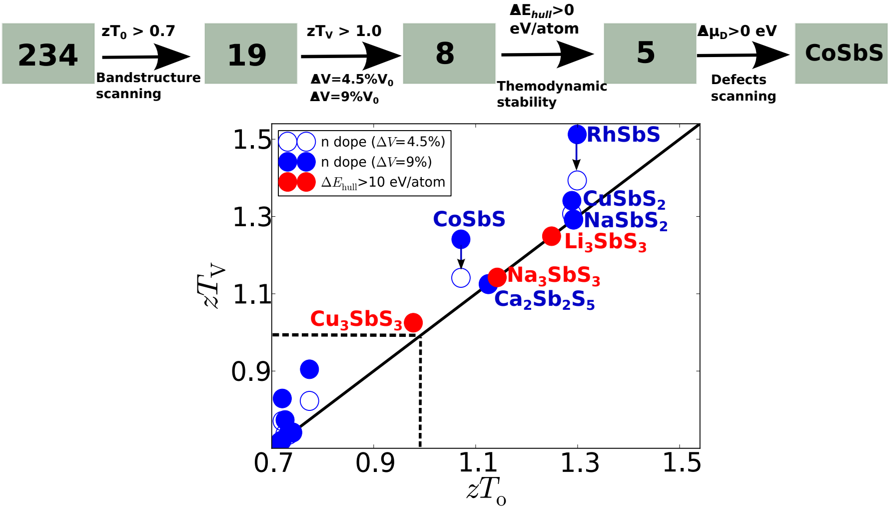
- Narrow band gap
- Multiple pockets at Fermi level

Automated search strategy

- Goal: Low-cost high-performance thermoelectric
- Computationally screen transport properties of innocuos, abundant sulfides
- Calculate bulk energy of competing phases
- Screen intrinsic defects, vacancies, antisites and interstitials, for potential doping limits
- Screen potential extrinsic potential defects, if no doping limits

Find ternary ***n***-type sulfide to be used with ***p***-type tetrahedrites

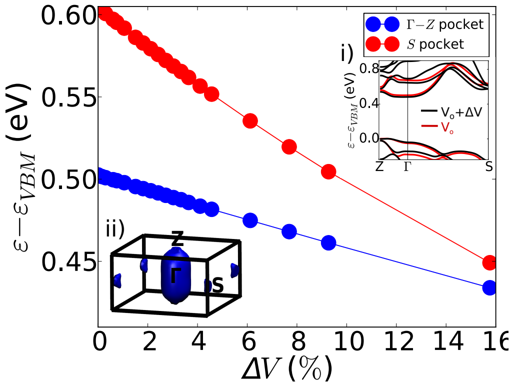
Ternary Stanide and Antimonide-Sulfides

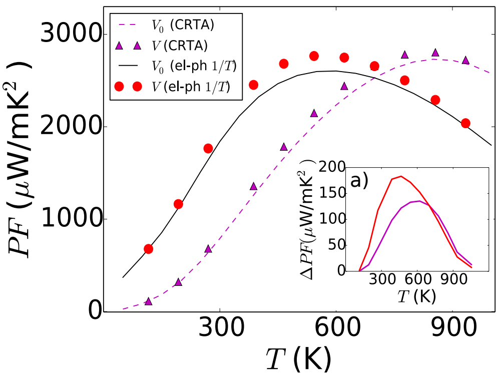


Therm. exp. 2 – 4% at 600 K

Bhattacharya et al. *J. Mater. Chem. A* 4, p11086 (2016)

VBA in CoSbS





- Alignment of band will increase with temperature
- Use simple linear thermal expansion model to account for volume change
- Gap closes and scattering increases with temperature

Bhattacharya et al. *J. Mater. Chem. A* 4, p11086 (2016)