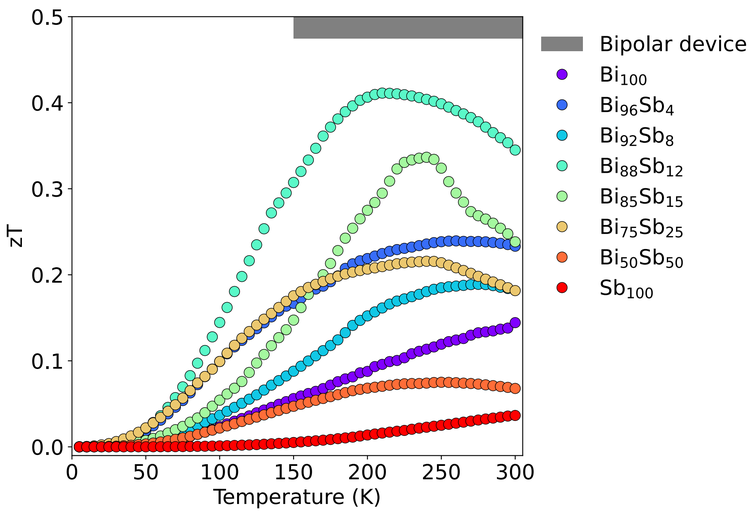
Bipolar transport in Bi-Sb semiconducting alloys

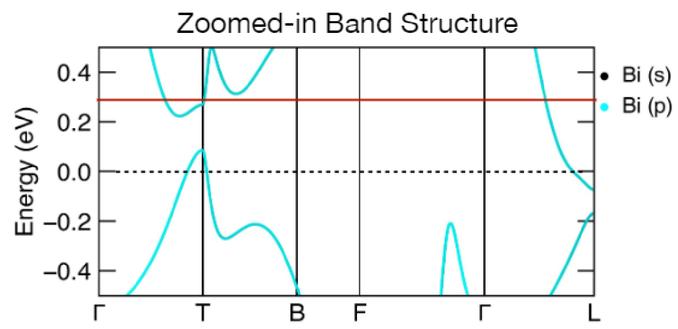
Rachel Orenstein[1], K. Ciesielski[1], J. Qu[2], L. C. Gomes[2,3], K Synoradzki[4], J. M. Adamczyk[1], S. Rogers[1], Elif Ertekin[2], E. S. Toberer[1]

[1] Physics Department, Colorado School of Mines, Golden, Colorado | [2] University of Illinois at Urbana-Champaign, Urbana, Illinois | [3] Instituto de Fisica Teorica, Sao Paulo State University (UNESP), Sao Paulo Brazil | [4] Institute of Molecular Physics, Polish Academy of Sciences, Poznan, Poland

Motivation and Background

- Bi-Sb semiconducting are known to be good thermoelectric (TE) materials for refrigeration, with a maximum zT of 0.4 at 210 K for alloy with Sb = 12 %
- Unusually, Bi-Sb alloy TE devices operate entirely in a bipolar transport regime, at temperatures above 150 K
- Prior models require significant approximations to minimize the number of free parameters.
- Further, prior models rarely leverage computational results to create simpler models with similar levels of accuracy
- Modeling this behavior will assist in optimization of thermoelectric performance

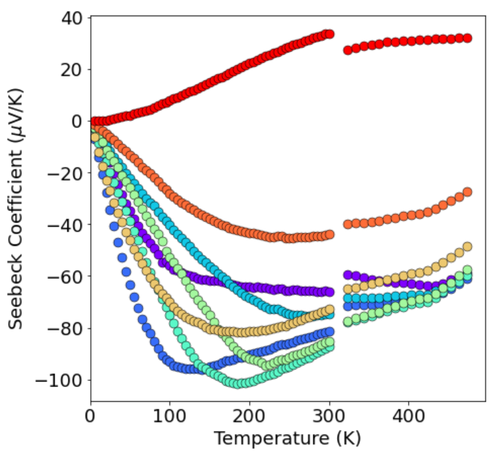




Band structure calculated by Jiaxing Qu using HSE and SOC

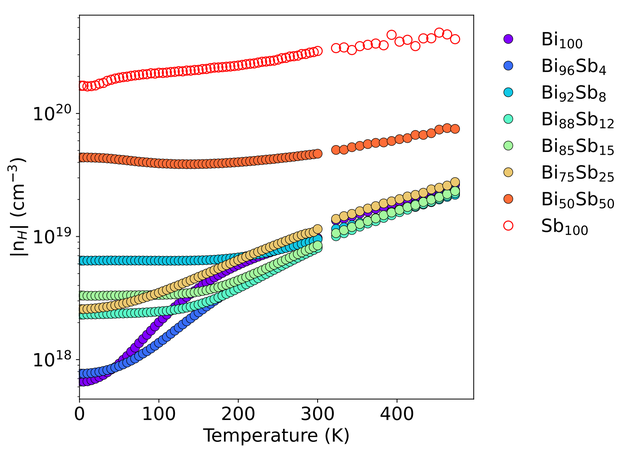
Bi begins as a semimetal as shown above, and transitions to a semiconductor as it is alloyed with greater percentages of Sb and the band gap opens

Low temperature properties



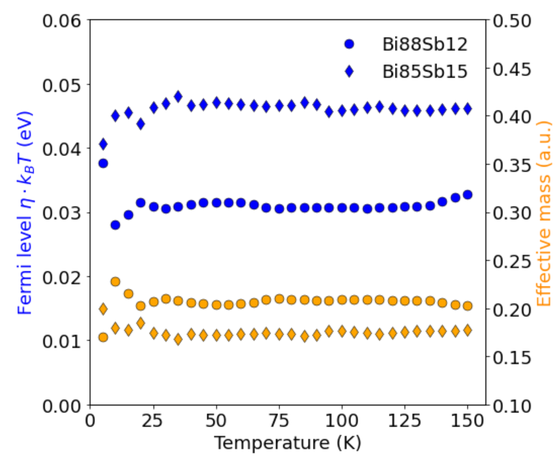
▲ At low temperatures, the Seebeck coefficient displays a linear trend, which is consistent with single-carrier Seebeck behavior

Bipolar transition occurs near 150 K for semiconducting Bi-Sb alloys



▲ Carrier concentration data shows that temperature independent behavior exists before 150 K, which corresponds to single-carrier behavior

Activation of carriers begins around the same bipolar transition temperature as seen in the Seebeck coefficient



◀ Using the single parabolic band (SPB) model, the Fermi level and electron effective mass is calculated for samples with percent Sb = 12 and 15 %

Both Fermi level and electron effective mass are independent of temperature, which is consistent with single carrier behavior compatible with the SPB model at low temperatures.

Bipolar model

Find fundamental transport coefficients

$\eta_{n,100\ K}$	Reduced Fermi level (100 K)
m_e^*	Electron effective mass
η_n, η_p	Reduced chemical potential
m_p^*	Hole effective mass
E_g	Band gap
τ_n, τ_p	Relaxation time

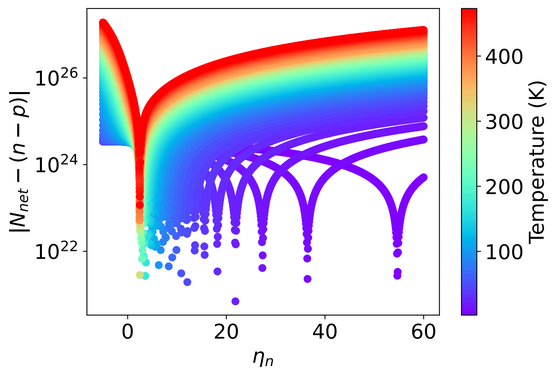
Assumption 1: Fully ionized defects by 100 K

Charge neutrality equation:

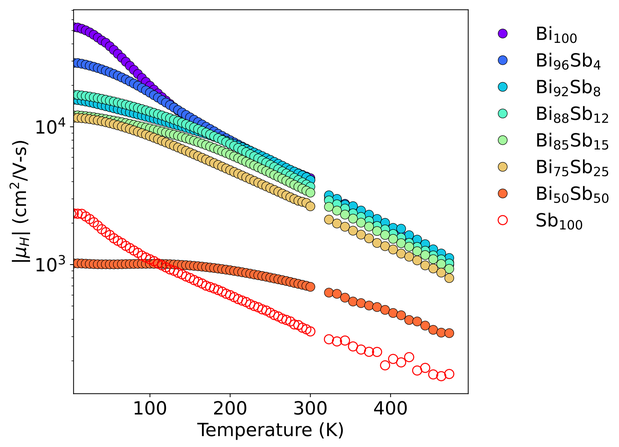
$$N_{net} = D^+ - A^- = n(\eta_n) - p(\eta_p)$$

N_{net} is constant in bipolar region → solve for η_n and η_p given:

$$N_{net}(100\ K) = n(\eta_n, T) - p(\eta_p, T)$$



Assumption 2: Temperature-independent scattering ratio

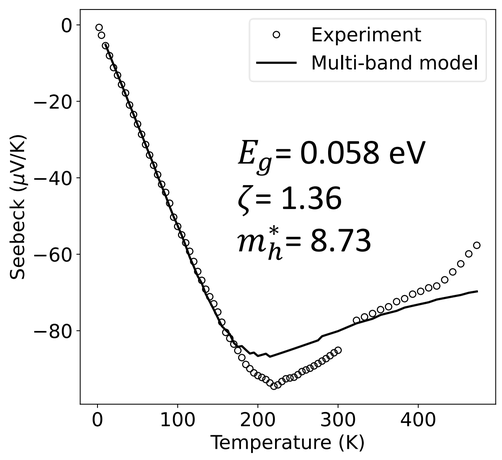


Hall mobility data shows that ionized impurity scattering dominates until 100K, while acoustic scattering dominates after 150 K. Therefore, the model uses a scattering coefficient *r* of -0.5.

$$\frac{\tau_p}{\tau_n} = \zeta \begin{cases} S = \dfrac{S_n n m_p^* + S_p p m_n^* \zeta}{n m_p^* + p m_n^* \zeta} \\ R_H = \dfrac{1}{e} \dfrac{p\zeta^2/{m_p^*}^2 - n/{m_n^*}^2}{\left(p\zeta^2/m_p^* - n/m_n^*\right)^2} \end{cases}$$

Using $\eta_{n,p}$ and m_e^*, above equations are fit to the experimental data with m_p^*, E_g, and ζ as fit parameters

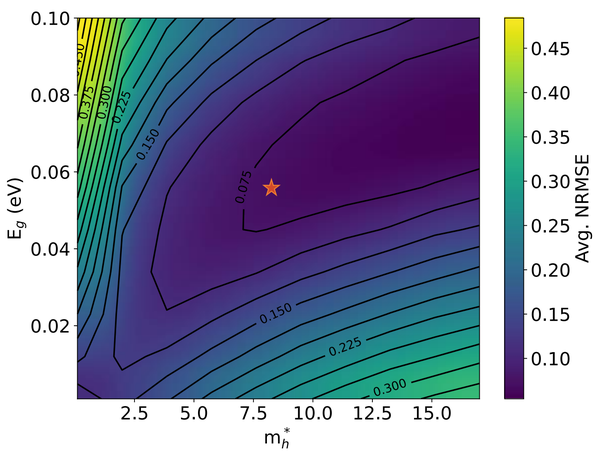
Bipolar model results

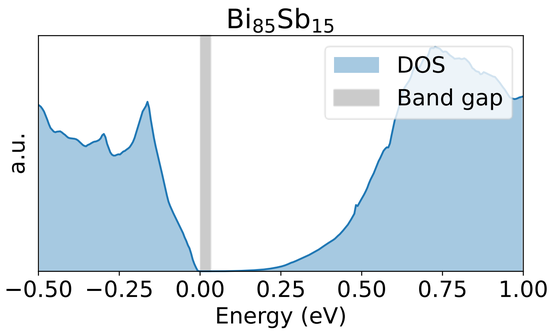


$$\sigma = \frac{e^2 n\, \tau_n}{m_n^*} + \frac{e^2 p \tau_n \zeta}{m_p^*}$$

Experimental conductivity and fundamental transport coefficients used to solve for τ_n, τ_p

Values of ζ are optimized for each E_g/m_h^* pair, and a goodness of fit is obtained by averaging the normalized root-mean-square-error for S and R_H





Alloy DOS calculated by Jiaxing Qu using a 20-atom SQS supercell

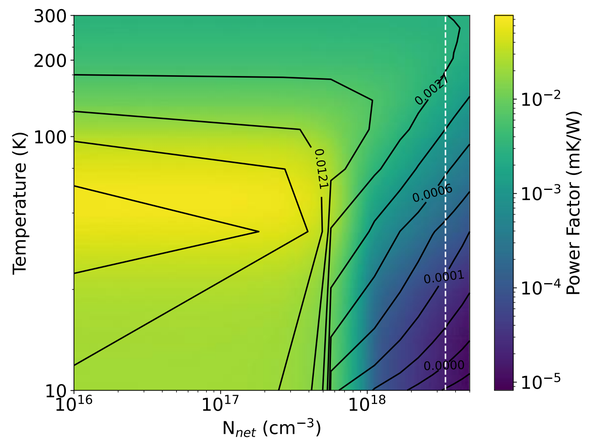
A ratio of effective masses is found from the ratio of DOS from 20meV into each band

This ratio, along with the electron effective mass value from the SPB model, is used to predict the hole effective mass.

The final band gap is predicted from the point of best fit corresponding to the predicted hole effective mass.

The final fits for Seebeck and Hall coefficient are pictured at far left

Outlook



Our multi-band model allows us to predict the optimal parameters for thermoelectric variables such as power factor, using variables such as temperature and net ionized defects

Model uses a unique assumption (ratio of τ's) and computational DFT results that allow us to minimize free parameters

Model is also generalizable to any system that shows a single carrier to bipolar transition

COLORADOSCHOOLOFMINES
EARTH ENERGY ENVIRONMENT