

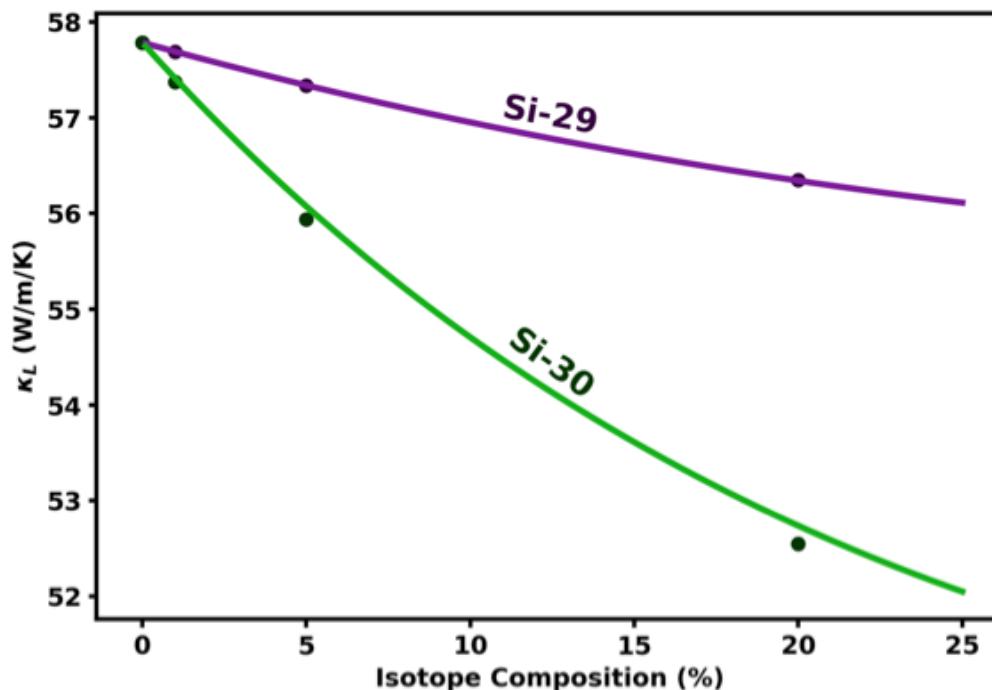
Revisiting Analytical Models of Phonon-Point Defect Scattering

Ramya Gurunathan

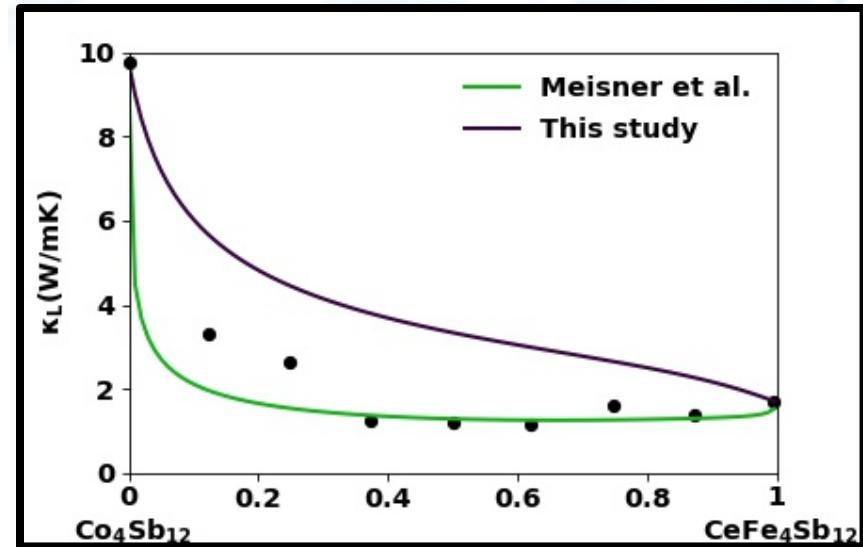
Snyder Group @ Northwestern University

11/8/2018 DMREF Meeting

Closed Form Solutions for Point Defect Scattering are Surprisingly Predictive..



Points: Calculated using DFT supercell calculations, T-matrix scattering theory, full solution of the BTE
Lines: Calculated using Klemens/Callaway model



Discrepancies over model inputs can lead to incomplete conclusions over the dominant scattering mechanisms in a system

G. P. Meisner et al. *Phys. Rev. Lett.*, **80**, 3551–3554 (1998)

The Klemens/Callaway Model

$$\tau^{-1} = \tau_{PD}^{-1} + \tau_U^{-1}$$

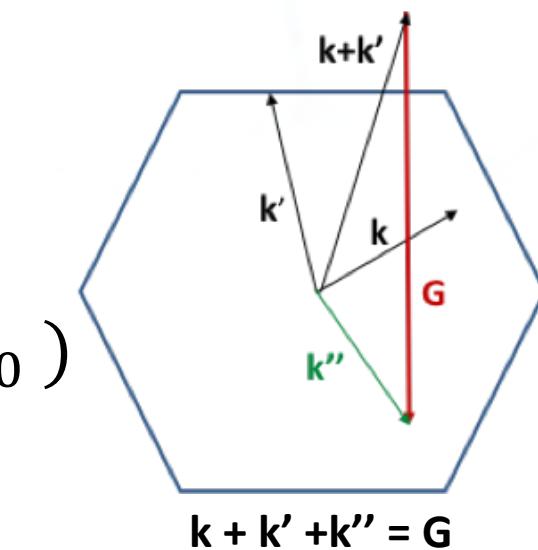
$$\tau_{PD}^{-1} = A\omega^4$$

$$\tau_U^{-1} = B(T)\omega^2$$

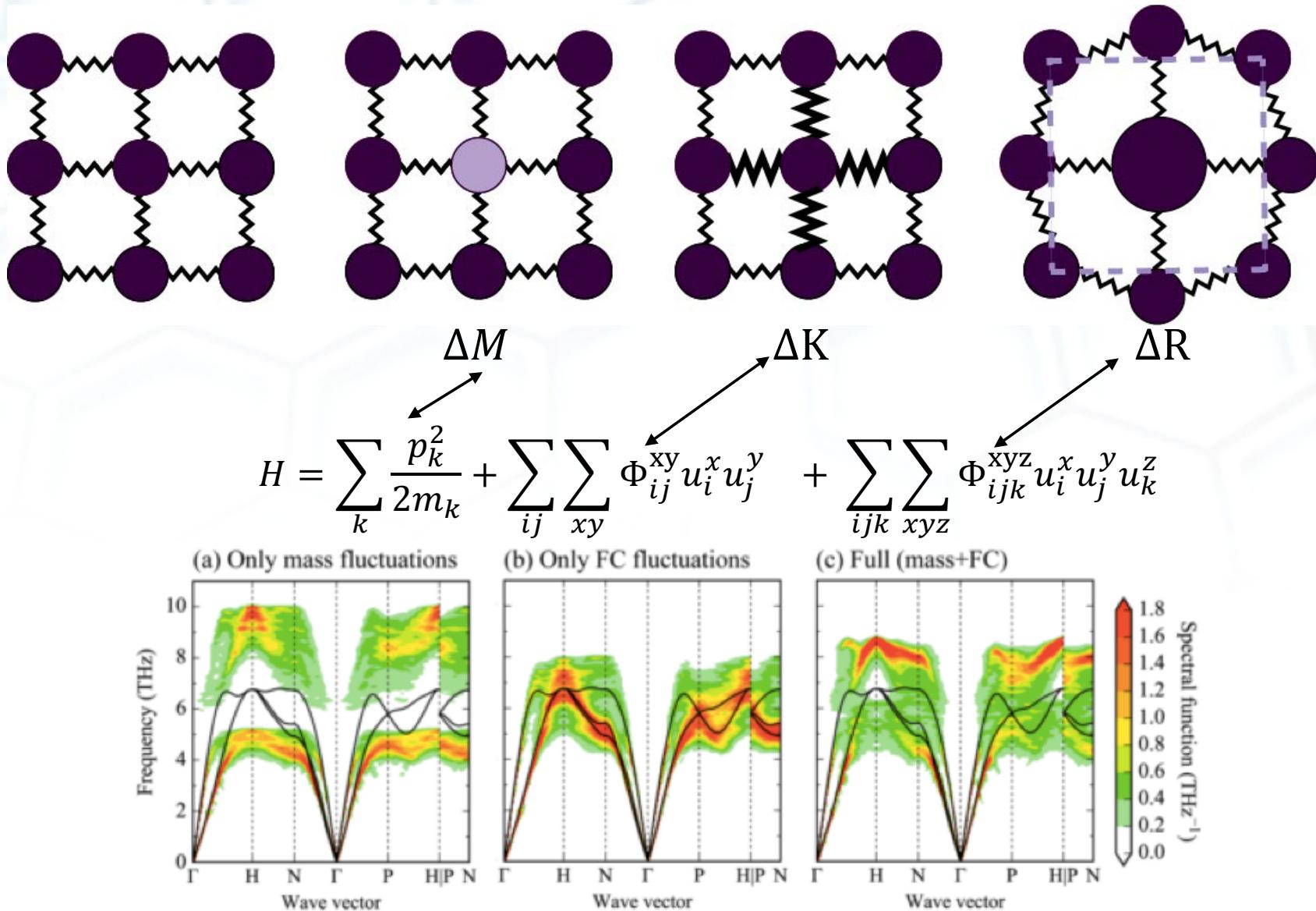
$$\Gamma = f_i \left[\left(\frac{\Delta M}{M} \right)^2 + \dots \right], V_0$$

$$\kappa_L = \frac{1}{3} \int_0^{\omega_{max}} C(\omega) v_g^2(\omega) \tau(\omega) d\omega$$

$$\kappa_L = \frac{\arctan(u)}{u} \quad u = f(\Gamma, V_0, \kappa_0)$$



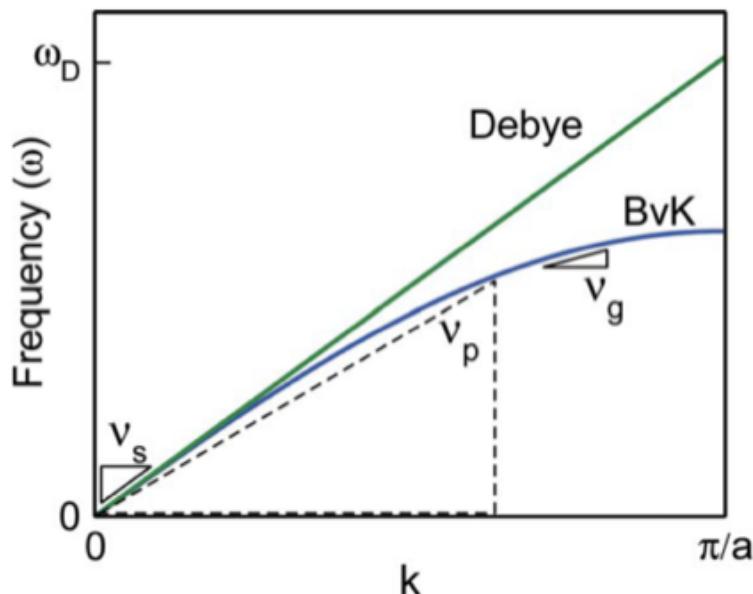
Point Defect Perturbation



F. Körmann, Y. Ikeda, B. Grabowski, and M. H. F. Sluiter, *npj Comput. Mater.*, (3), 36, 2017.

Stated Assumptions of the Model

Debye Model Dispersion



$$v_g = v_p = v_s$$

1 Atom Per U.C.



Monatomic Lattice Approximation (MLA):

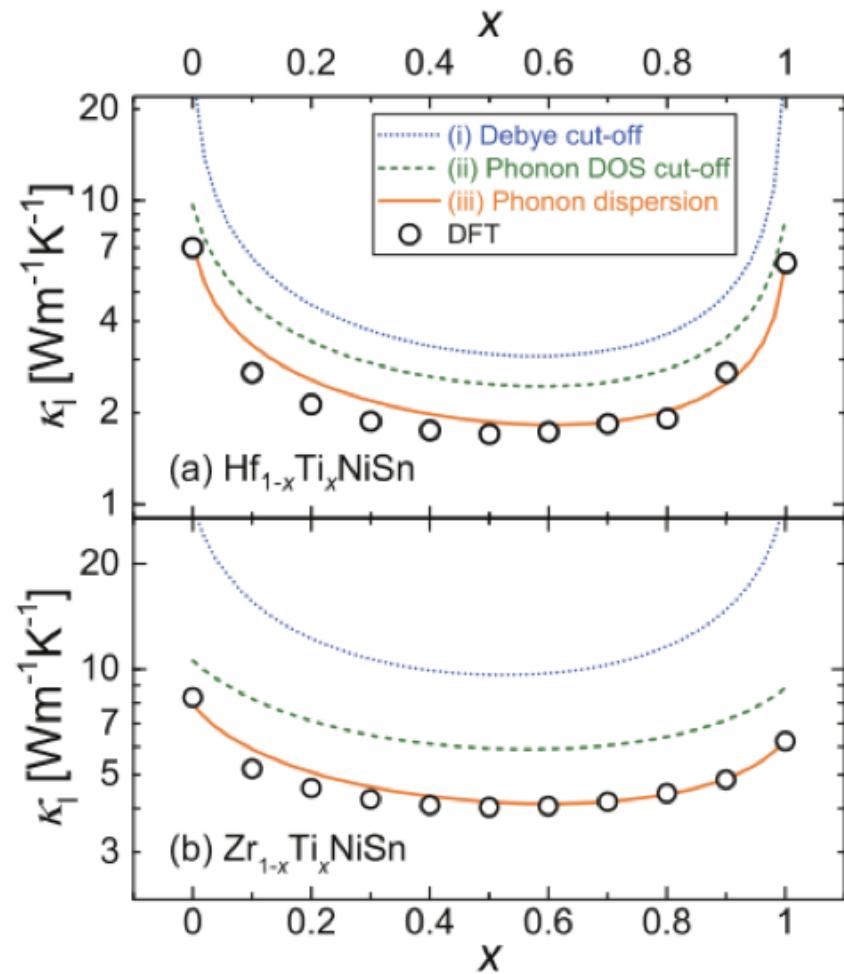
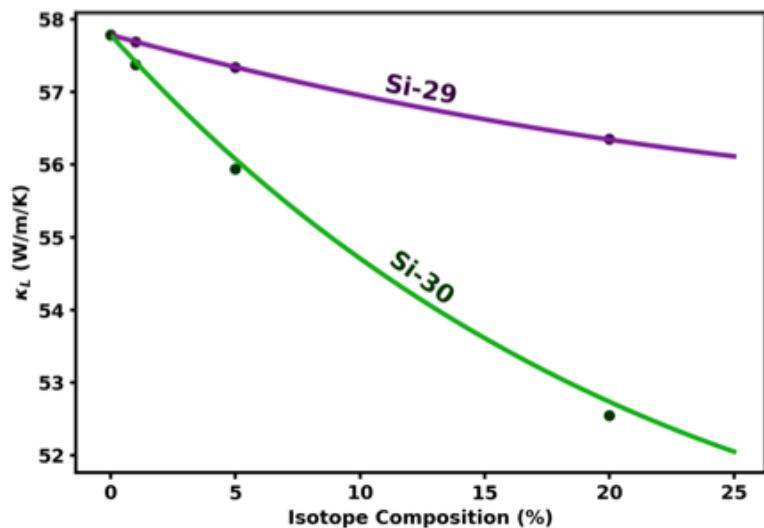
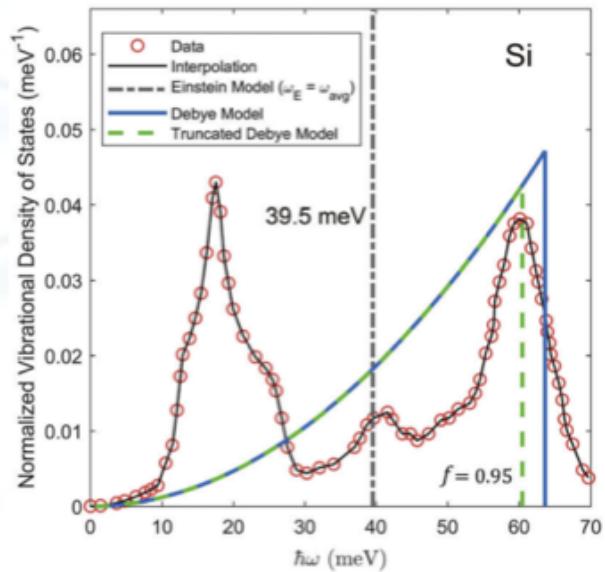


Virtual Crystal Approximation (VCA):



E. S. Toberer, et al., *J. Mater. Chem.*, **21**, 15843–15852 (2011).

Dispersion Dependence



M. Schrade and T. G. Finstad, *Phys. Status Solidi*, 1800208, 1–6, 2018.

M. T. Agne, R. Hanus, and G. J. Snyder, *Energy Environ. Sci.*, **11** (13) 609–616, 2018.

Dispersion Dependence

Fermi's Golden Rule:

$$W_{i,f} = \frac{2\pi}{\hbar^2} \langle i | H' | f \rangle^2 \delta(\Delta\omega)$$

Form of the Perturbation: $\langle i | H' | f \rangle = C_3(k, k', k'') a(k) a^*(k') a^*(k'')$

$$\underbrace{\frac{\Delta M}{M}}_{\gamma}$$

Express real space
perturbations in Fourier
components:

$$\Delta \tilde{M}(\mathbf{Q}) = \frac{1}{S} \sum_{\mathbf{R}} \Delta M(\mathbf{R}) e^{i\mathbf{QR}}$$

Integrate W over all
possible final states:

$$\tau^{-1} = \sum_{\mathbf{b}} \frac{V}{(2\pi)^3} \int W_{i,f} d^3 \mathbf{k}'$$

Dispersion Dependence

Umklapp:

$$\tau^{-1} = \frac{4\pi a\gamma^2 T k_B}{M} \frac{\omega^2}{v_p^2(k)v_g(k'')}$$

$$g(\omega) = \frac{3\omega^2}{2\pi^2 v_p^2(\omega)v_g(\omega)}$$

Point Defect:

$$\tau^{-1} = \frac{\Omega_0}{4\pi} f_i \left(\frac{\Delta M}{M} \right)^2 \frac{\omega^4}{v_p^2(\omega)v_g(\omega)}$$

$$C_v(\omega) = \frac{3k_B \omega^2}{2\pi^2 v_p^2(\omega)v_g(\omega)}$$

Dispersion Dependence

Umklapp:

$$\tau^{-1} = \frac{4\pi a\gamma^2 T k_B}{M} \frac{\omega^2}{v_p^2(k)v_g(k'')}$$

$$g(\omega) = \frac{3\omega^2}{2\pi^2 v_p^2(\omega)v_g(\omega)}$$

Point Defect:

$$\tau^{-1} = \frac{\pi\Omega_0}{6} f_i \left(\frac{\Delta M}{M} \right)^2 g(\omega) \omega^2$$

$$\kappa = \frac{k_B}{2\pi^2 b} \int_0^{\omega_D} v_g^2(\omega) \frac{1}{1 + a\omega^2/b} d\omega$$

$$C_v(\omega) = k_B g(\omega)$$

$$\kappa = \frac{k_B}{2\pi^2 b} \langle v_g^2 \rangle_{avg} \int_0^{\omega_D} \frac{1}{1 + a\omega^2/b} d\omega$$

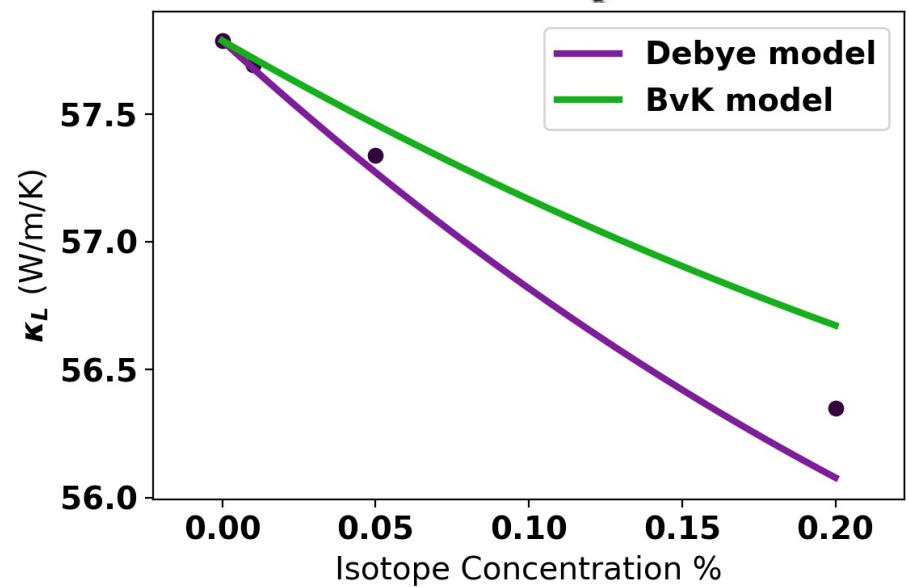
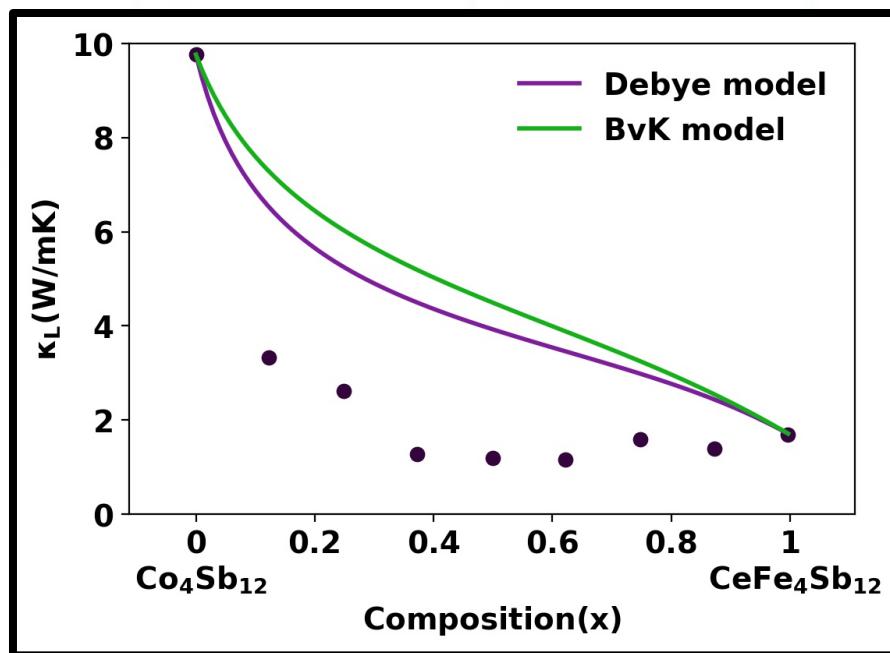
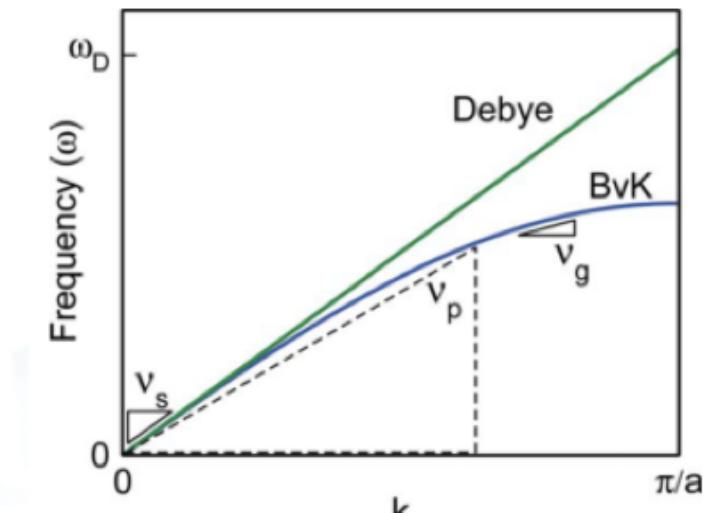
Quantity of interest: κ/κ_0

Dispersion Dependence

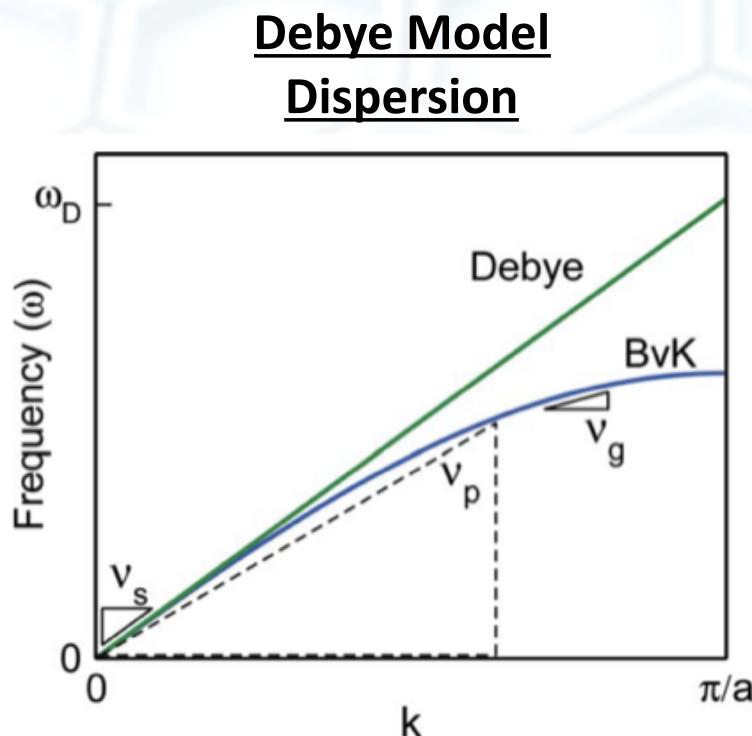
$$\omega(k) = v_s \left(\frac{2}{\pi} \right) k_{max} \sin \left(\frac{\pi}{2} \frac{k}{k_{max}} \right)$$

$$v_g(k) = \frac{d\omega}{dk}, v_p(k) = \frac{\omega}{k}$$

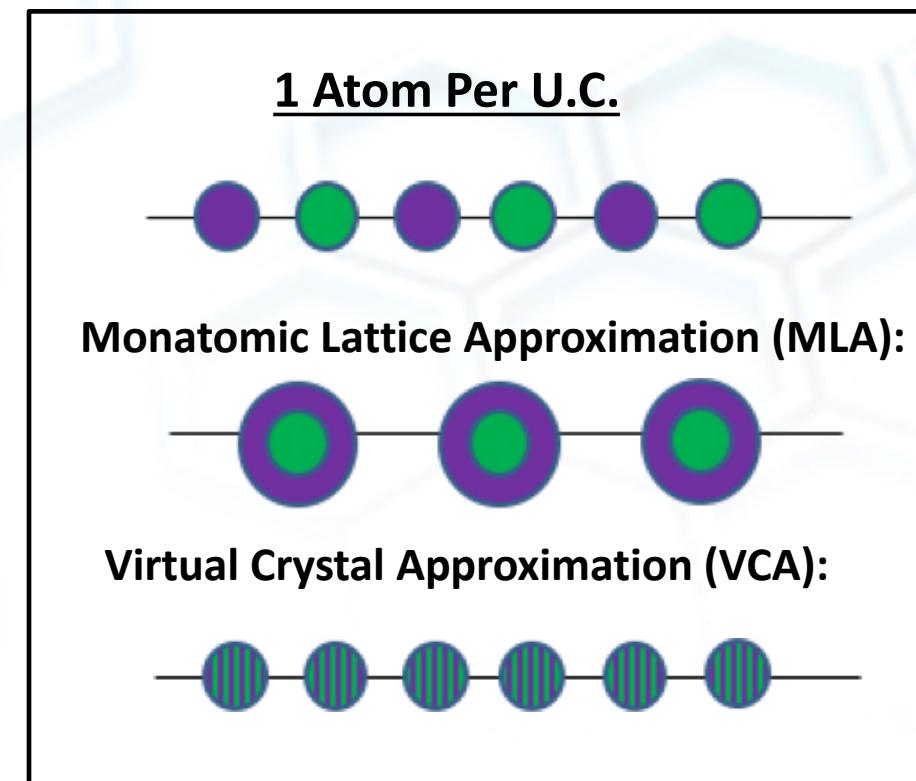
$$\frac{\kappa}{\kappa_0} = \frac{1}{\int_0^{k_m} v_g^3(k) dk} \int_0^{k_m} v_g^3(k) \left(\frac{1}{1 + \frac{a(\omega^2(k))}{b}} \right) dk$$



Stated Assumptions of the Model



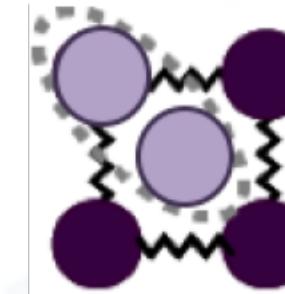
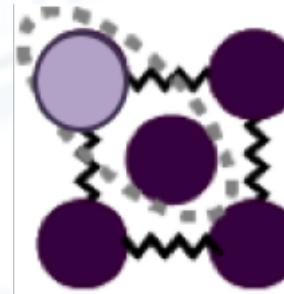
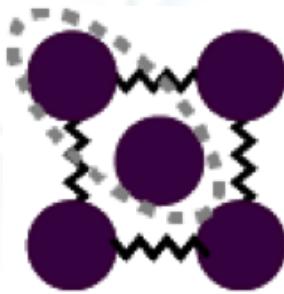
$$v_g = v_p = v_s$$



E. S. Toberer, et al., *J. Mater. Chem.*, **21**, 15843–15852 (2011).

MLA: Per Primitive Unit Cell

The various primitive unit cells in the lattice are your “microstates”

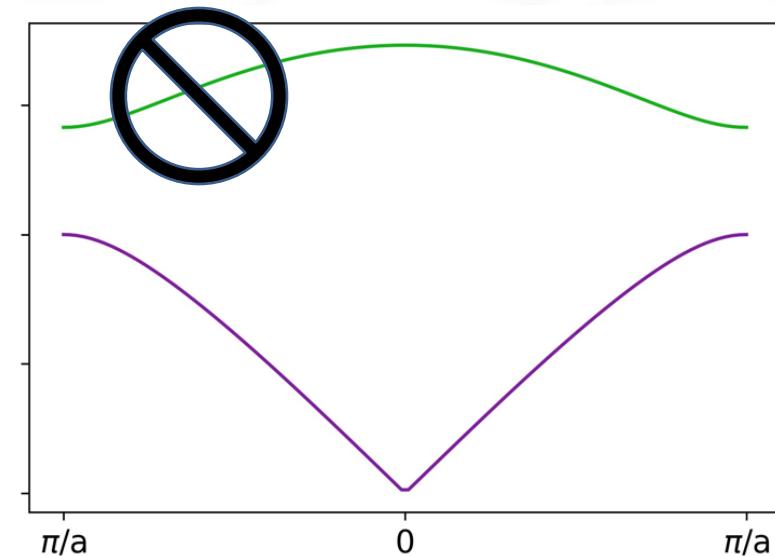


$$\Gamma_{\text{micro}} = \left(\frac{\Delta M_{uc}}{\overline{M}_{uc}} \right)^2$$

$$P_{\text{micro}} = \binom{n}{k} f_i^k (1 - f_i)^{n-k} (\dots)$$

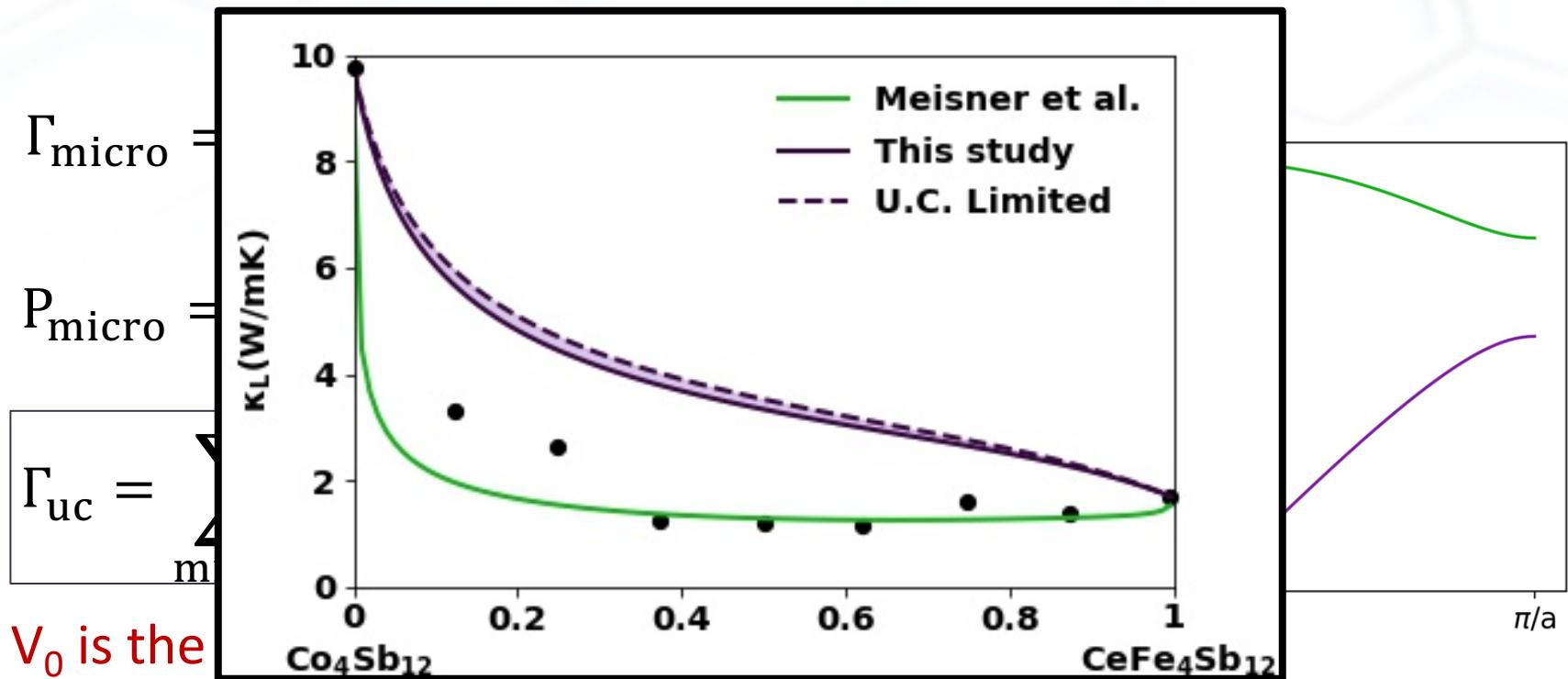
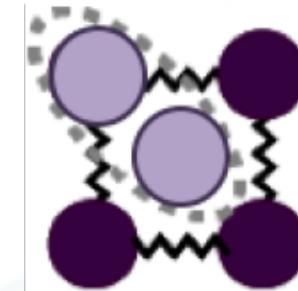
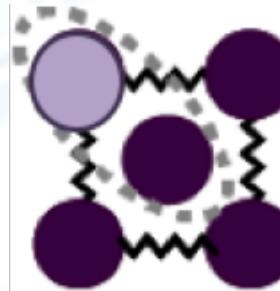
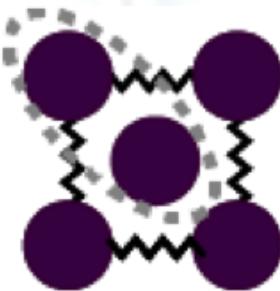
$$\boxed{\Gamma_{uc} = \sum_{\text{micro}} P_{\text{micro}} \Gamma_{\text{micro}}}$$

V_0 is the primitive unit cell volume



MLA: Per Primitive Unit Cell

The various primitive unit cells in the lattice are your “microstates”



V_0 is the

VCA: Per Atomic Site

Every atom has the **averaged** atomic volume and mass of the lattice

For the example compound: $A_xB_yC_z$

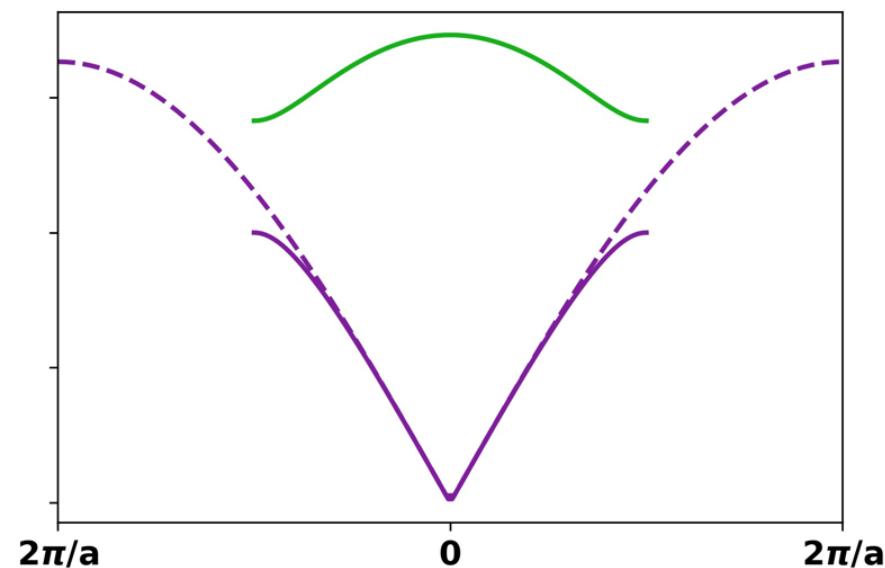
$$(\Delta m)^2 = \frac{x(\Delta m)_A^2 + y(\Delta m)_B^2 + z(\Delta m)_C^2}{x + y + z}$$

$$\Delta m = m_i - \overline{m}_A \quad \Gamma = f_i \left(\frac{\Delta M}{M} \right)^2$$

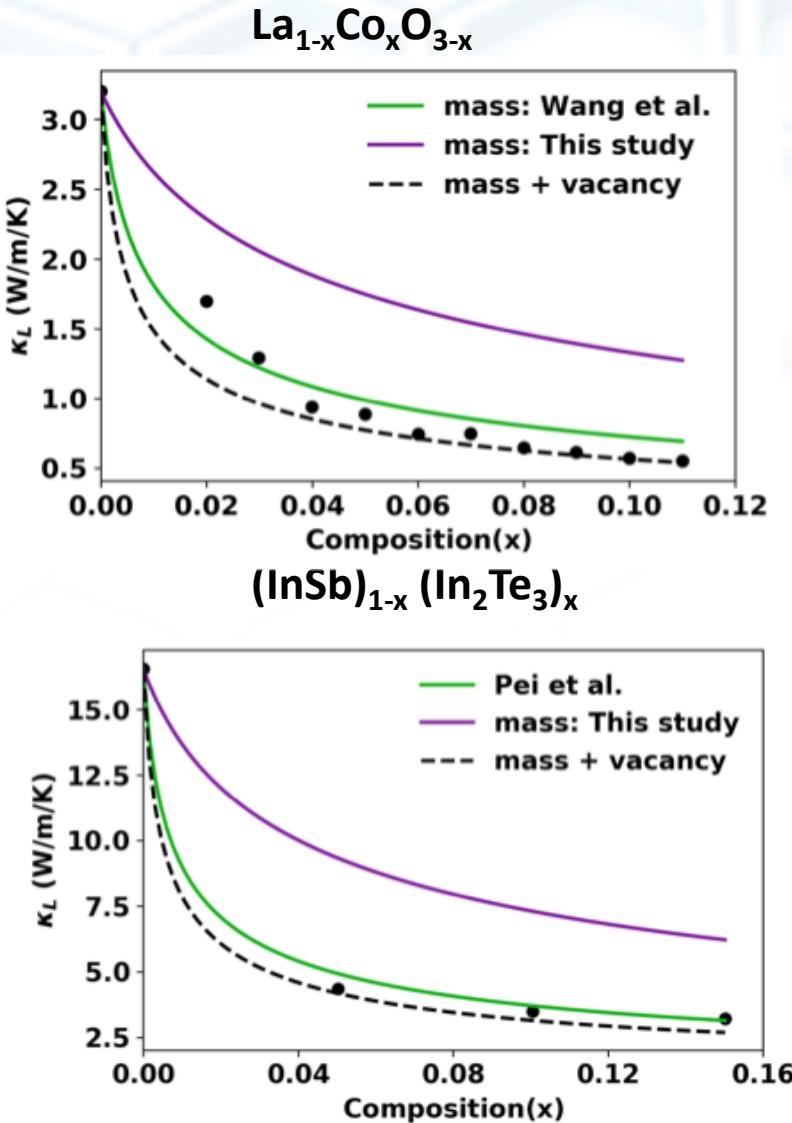
$$\Gamma_{atom} = \frac{x}{x + y + z} \left(\frac{\overline{m}_A}{\overline{m}} \right)^2 \Gamma_A + \frac{y}{x + y + z} \left(\frac{\overline{m}_B}{\overline{m}} \right)^2 \Gamma_B + \frac{z}{x + y + z} \left(\frac{\overline{m}_C}{\overline{m}} \right)^2 \Gamma_C$$

$$\Gamma_A = \sum_i f_i \left(1 - \frac{m_i}{\overline{m}_A} \right)^2$$

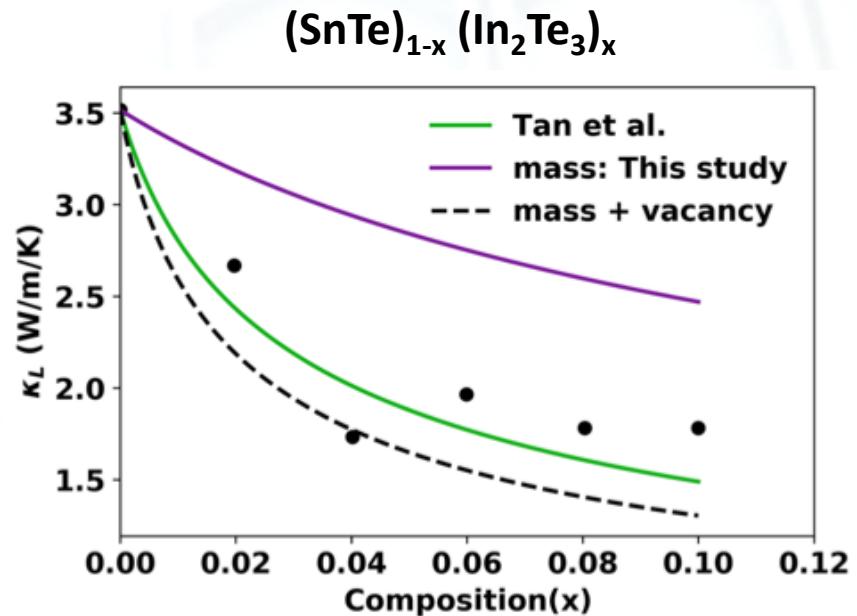
V_0 is the atomic volume



Simple and Effective Treatment of Vacancies

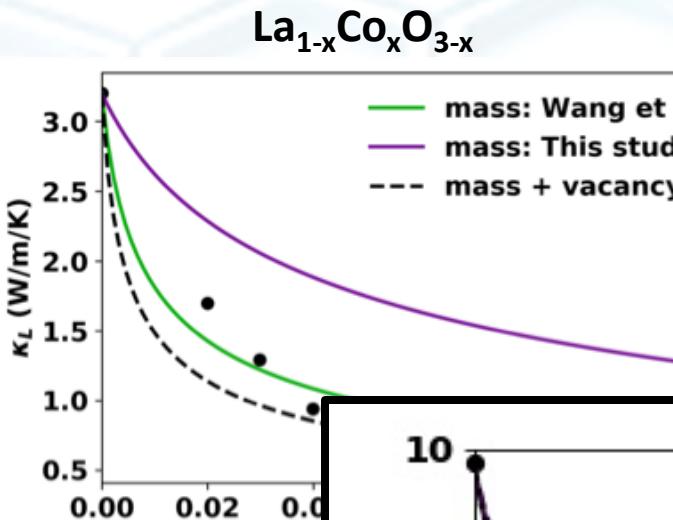


$$\Gamma = f_v \left(- \left(\frac{M_a}{\bar{M}} \right) - 2 \right)^2$$

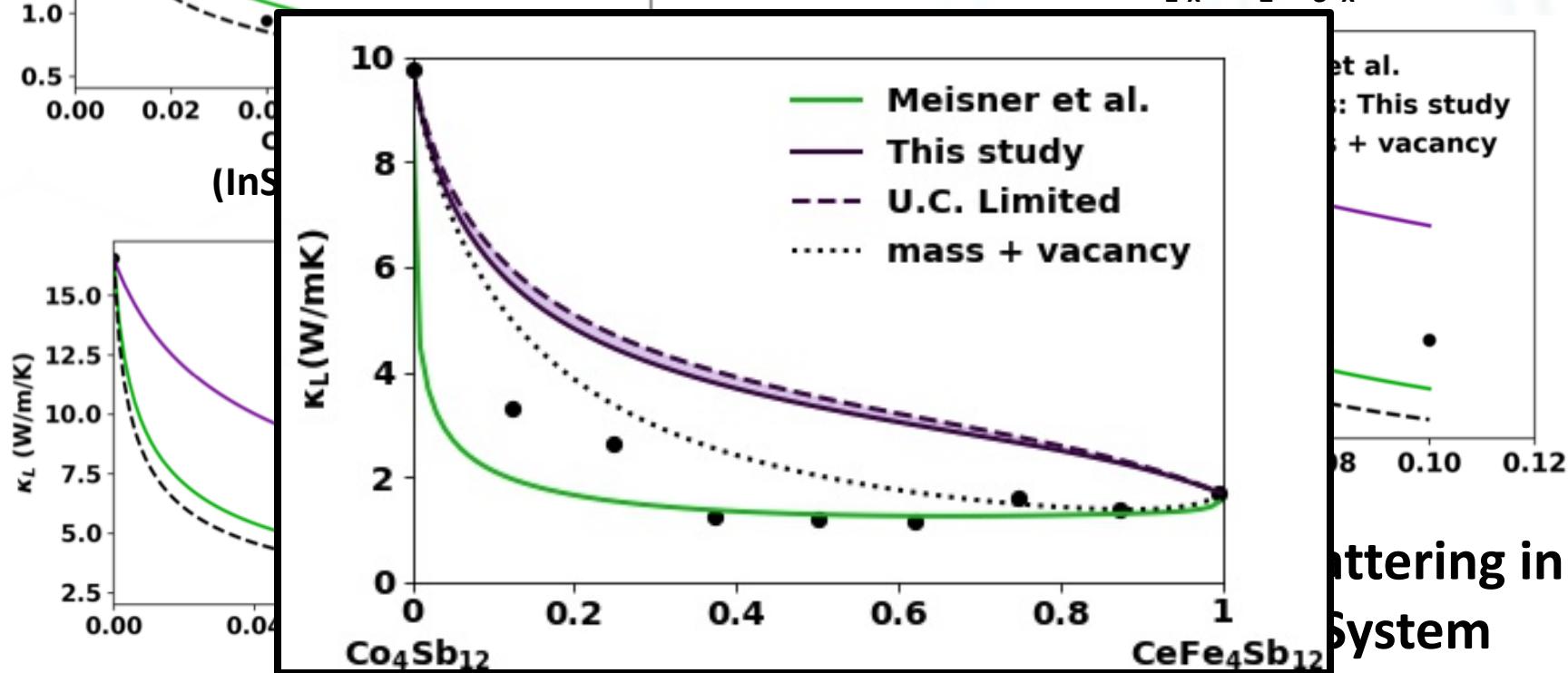


Coming soon: Vacancy scattering in the
 $\text{TiCoSb} \cdots \text{Ti}_{0.9}\text{NiSb}$ System

Simple and Effective Treatment of Vacancies



$$\Gamma = f_v \left(- \left(\frac{M_a}{\bar{M}} \right) - 2 \right)^2$$

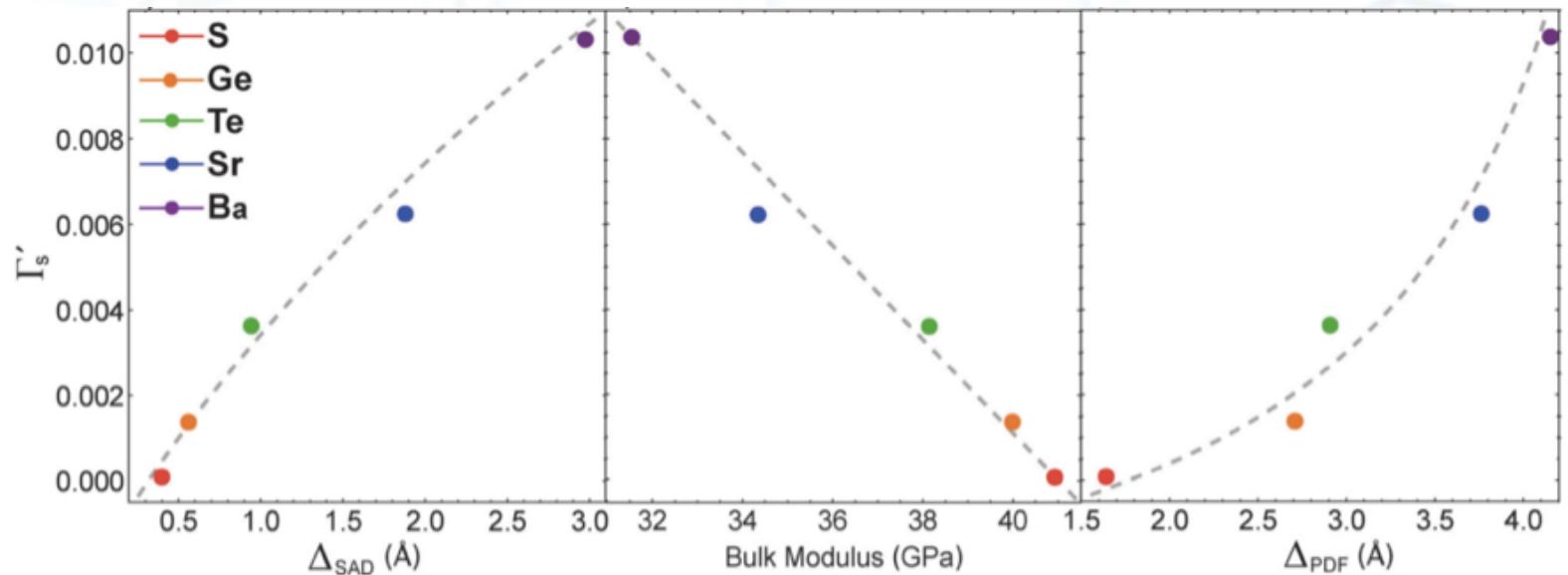


Scattering in the
System

Features for Point Defect Scattering

Mass fluctuation: $\left(\frac{\Delta M}{M}\right)^2$

Force constant fluctuation:



Check: Correlation between defect formation energy and defect scattering strength

$$E^f[X^q] = E_{\text{tot}}[X^q] - E_{\text{tot}}[\text{bulk}] - \sum_i \mu_i n_i + qE_F + E_{\text{corr}}$$

B. R. Ortiz, et al. *PCCP*, **17**, 19410–19423 (2015).

Takeaways:

Important Points for the Klemens/Callaway Model:

- Historical discrepancy over defining inputs on a “per atom” or “per unit cell” basis. Either is valid as long as the “accounting” is consistent.
- In practice, in dispersion relation sensitivity of the model appears to be lifted.
- A simple treatment of vacancy scattering with a “-2” term for broken bonds seems robust

Further Exploration:

- Impact of “associated defects” and “defect clusters”

Potential Action Items for DMREF?

See if features describing “lattice perturbation” introduced by dopants are relevant to defects database.

Extra Slides

Unpacking the Dispersion Comparison

