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The effect of extended strain fields on point defect scattering

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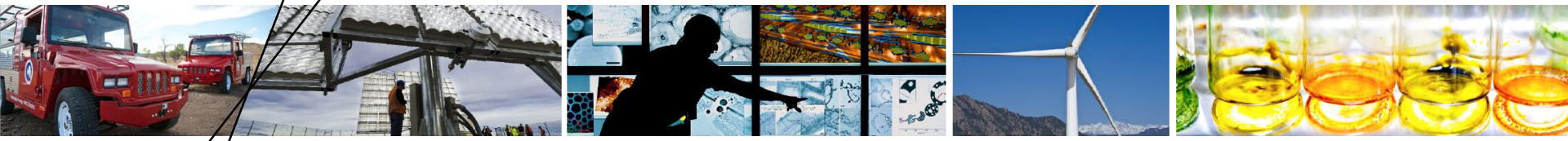
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Extended Strain Fields and Point-Defect Phonon Scattering



Brenden Ortiz, Haowei Peng, Armando Lopez, Phillip Parilla, Stephan Lany, Eric Toberer

Colorado School of Mines, Golden, CO

National Renewable Energy Laboratory, Golden, CO

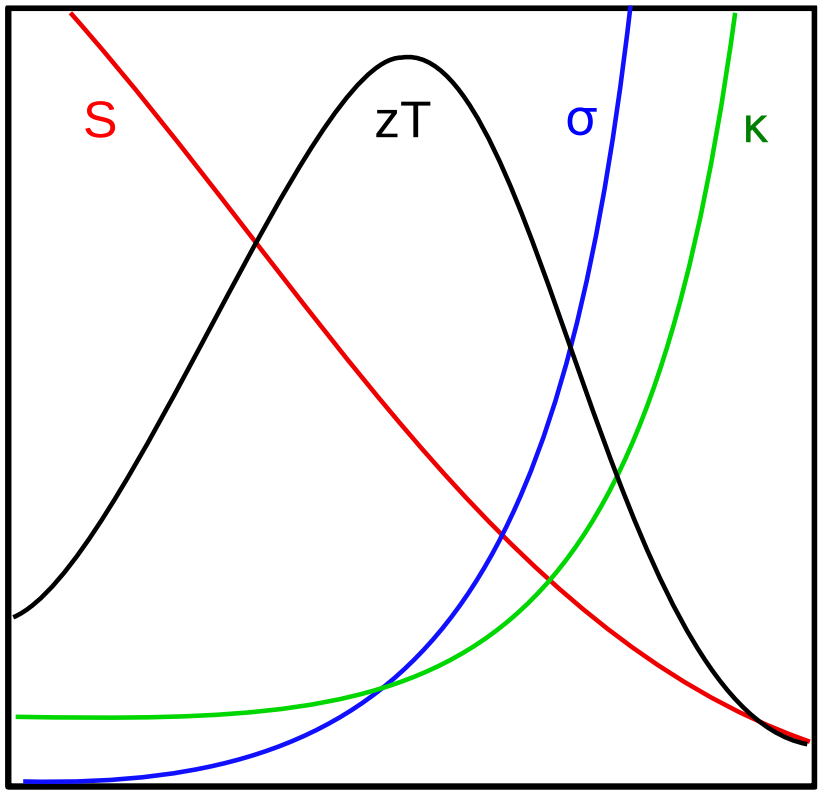
ECI Non-Stoichiometric Compounds (Santa Fe 2016)

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Thermoelectrics as an Optimization Problem

$$zT(\kappa, S, \sigma, T) = \frac{S^2\sigma}{\kappa}T$$

$$zT = zT(\eta, m^*, \tau, E_g, \ldots)$$



+

Each transport phenomenon **also** has T dependence

Thermoelectrics as an Optimization Problem

$$zT(\kappa, S, \sigma, T) = \frac{S^2\sigma}{\kappa}T$$

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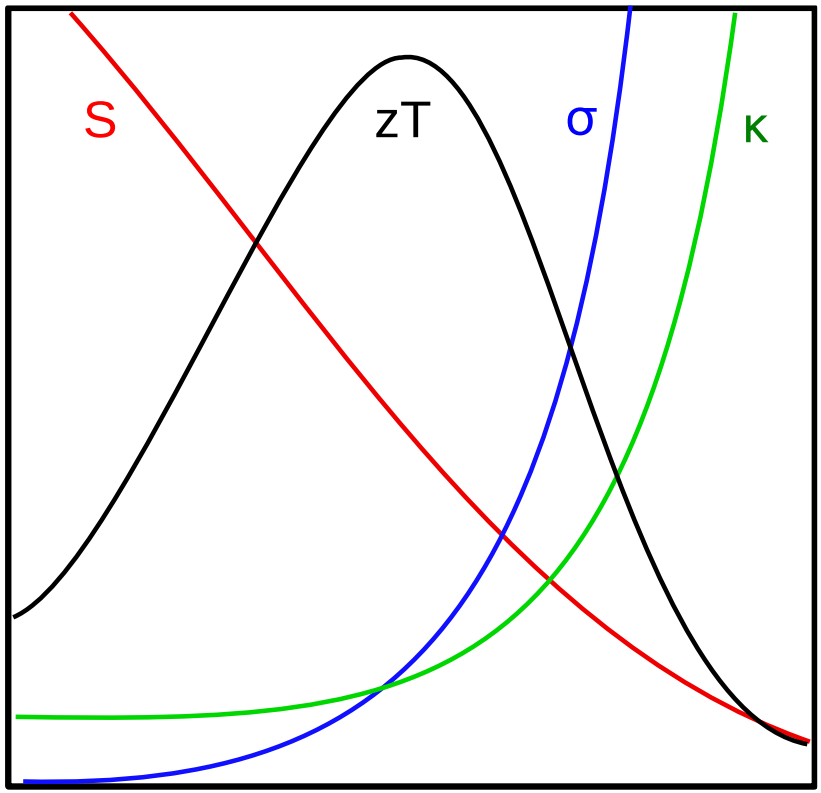
The thermal conductivity, **κ**, is commonly targeted for optimization.



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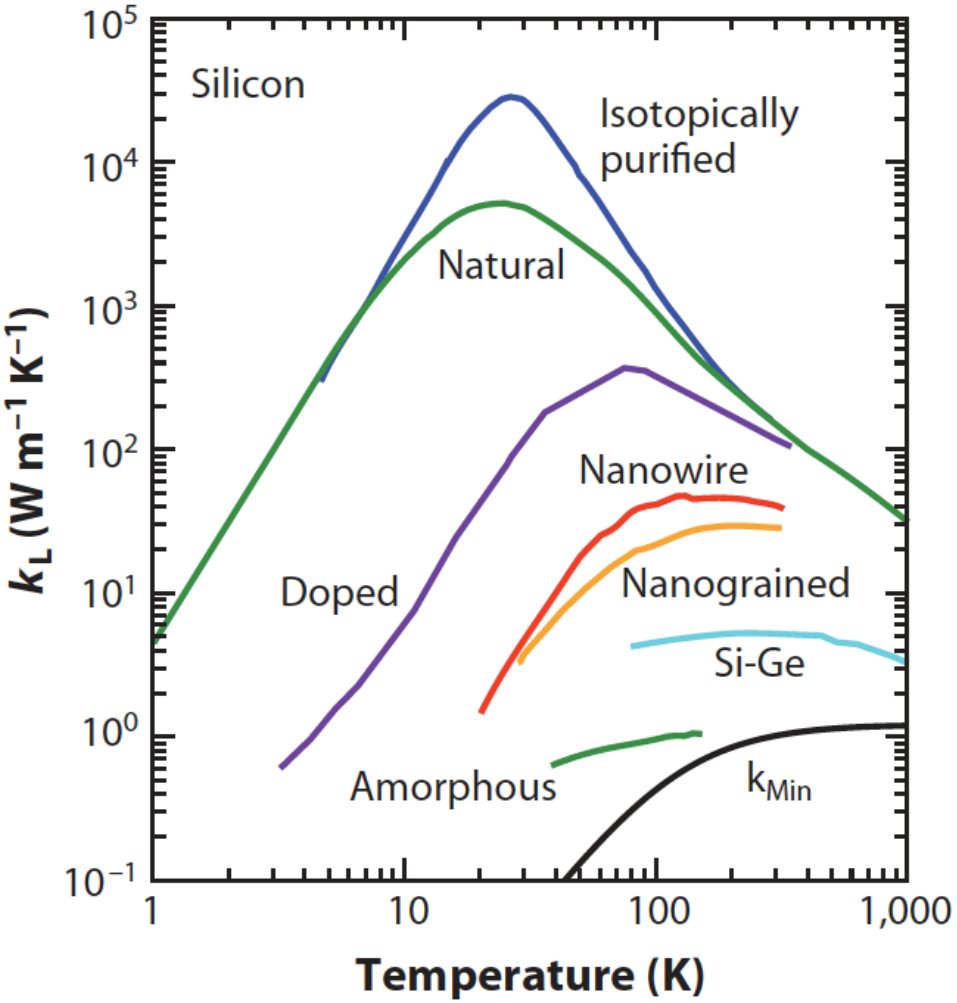

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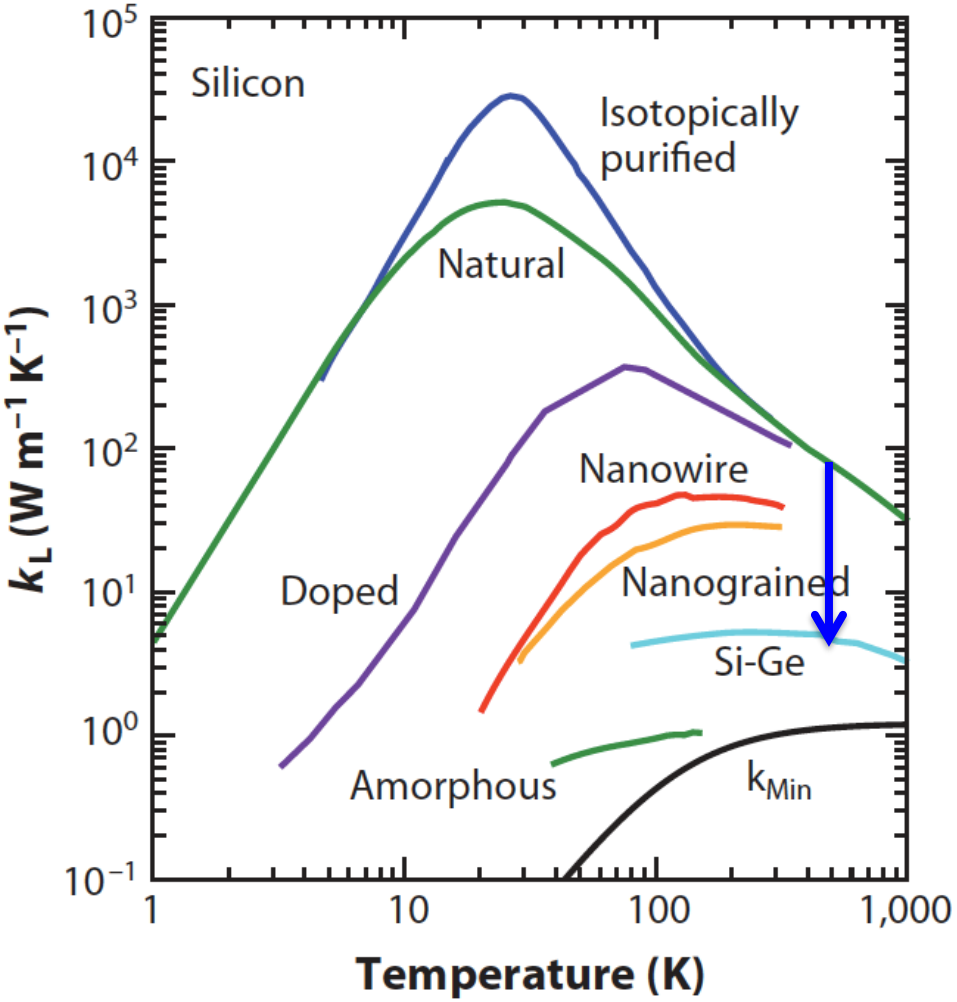

Thermoelectrics as an Optimization Problem

$$zT(\kappa, S, \sigma, T) = \frac{S^2\sigma}{\kappa}T$$

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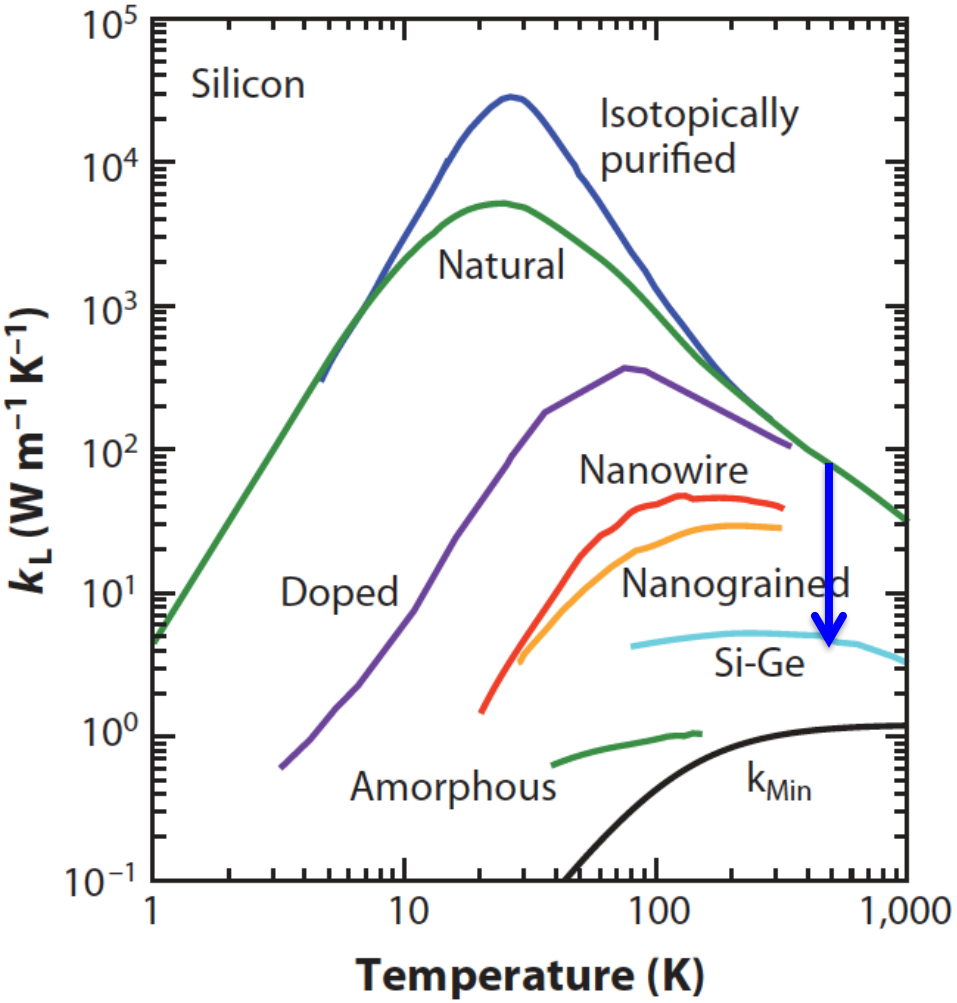
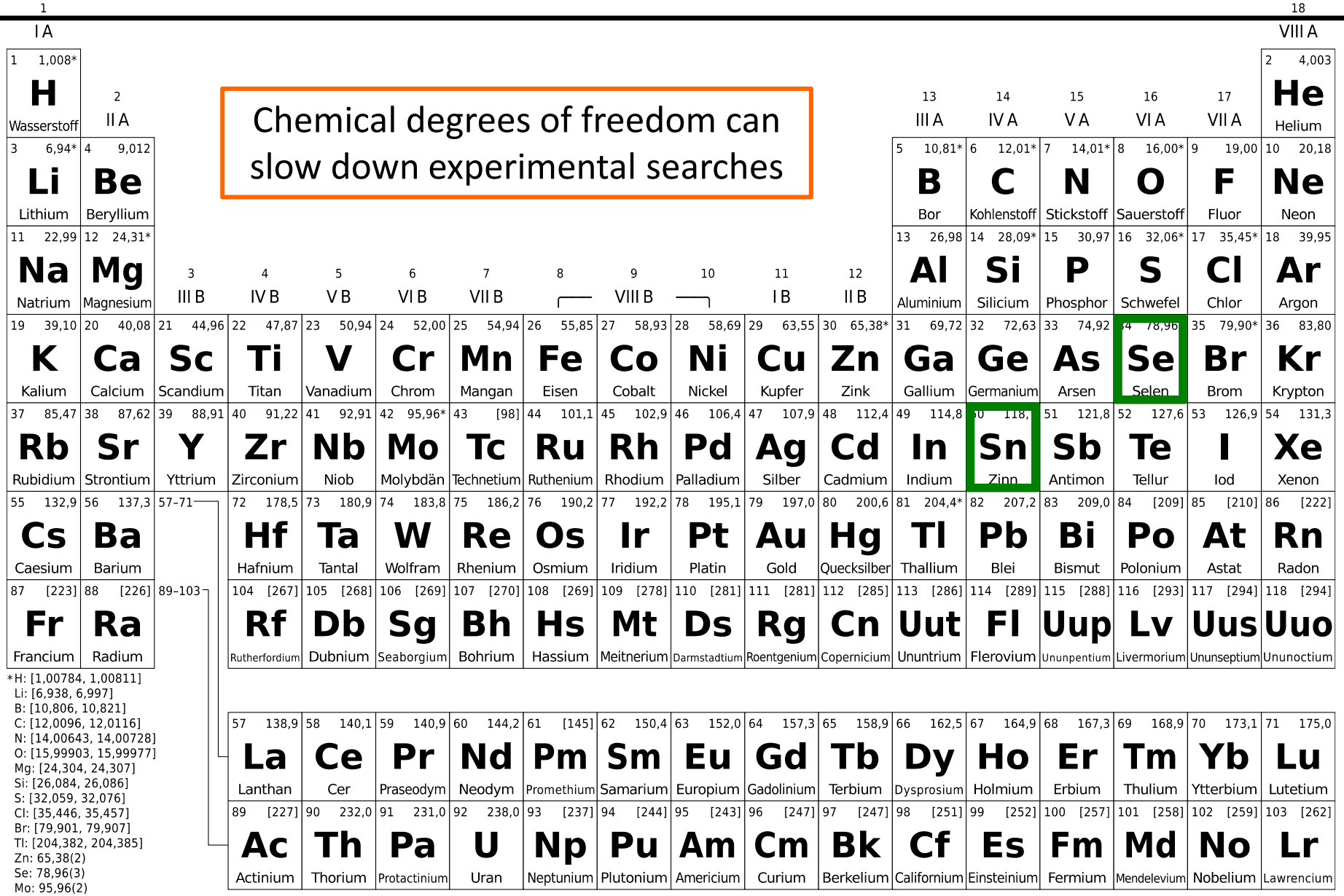
Alloys as a source of point defect scattering

Mass contrast simple, but role of **strain field** not obvious in **complex crystals**



Thermoelectrics as an Optimization Problem

Chemical degrees of freedom can slow down experimental searches



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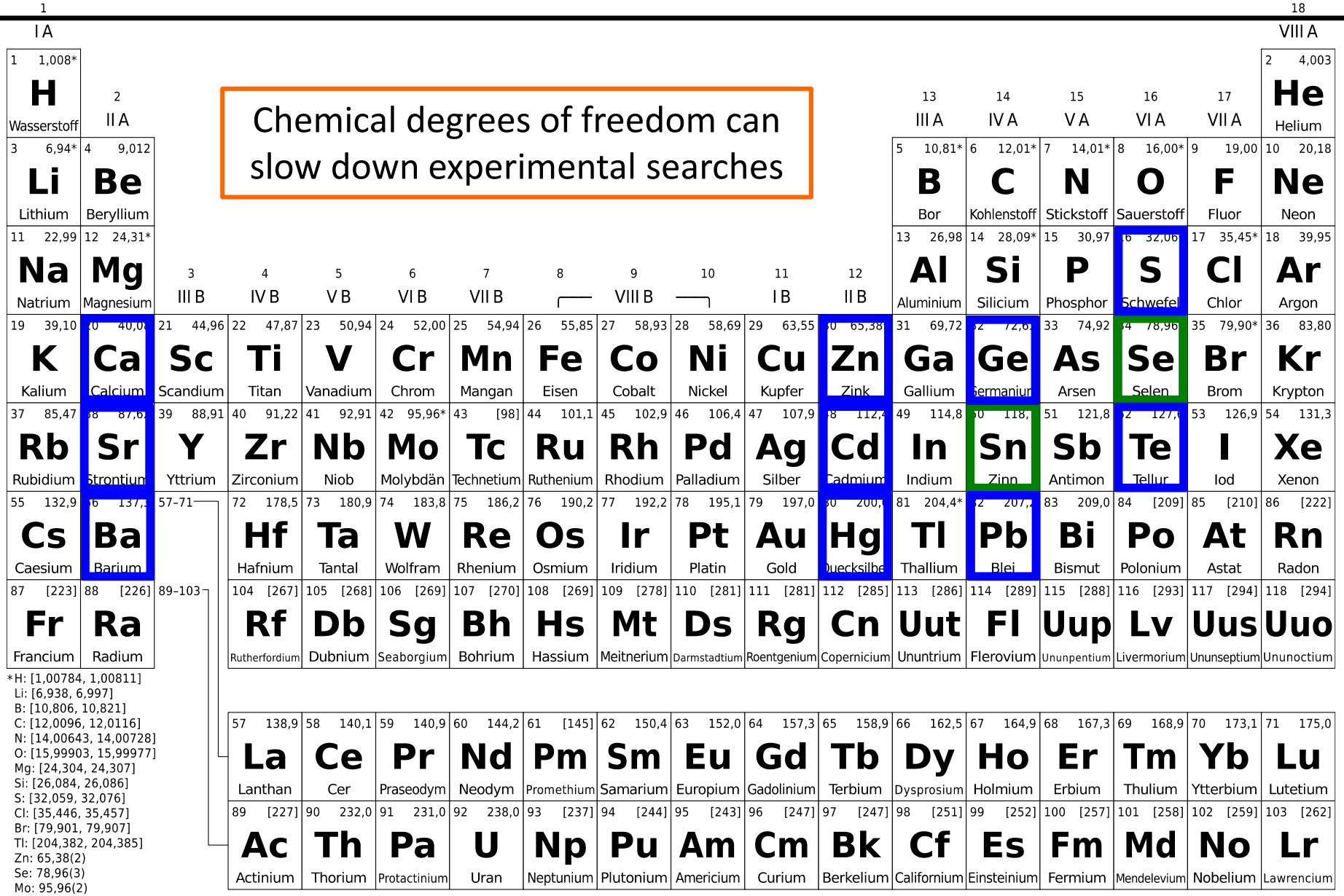
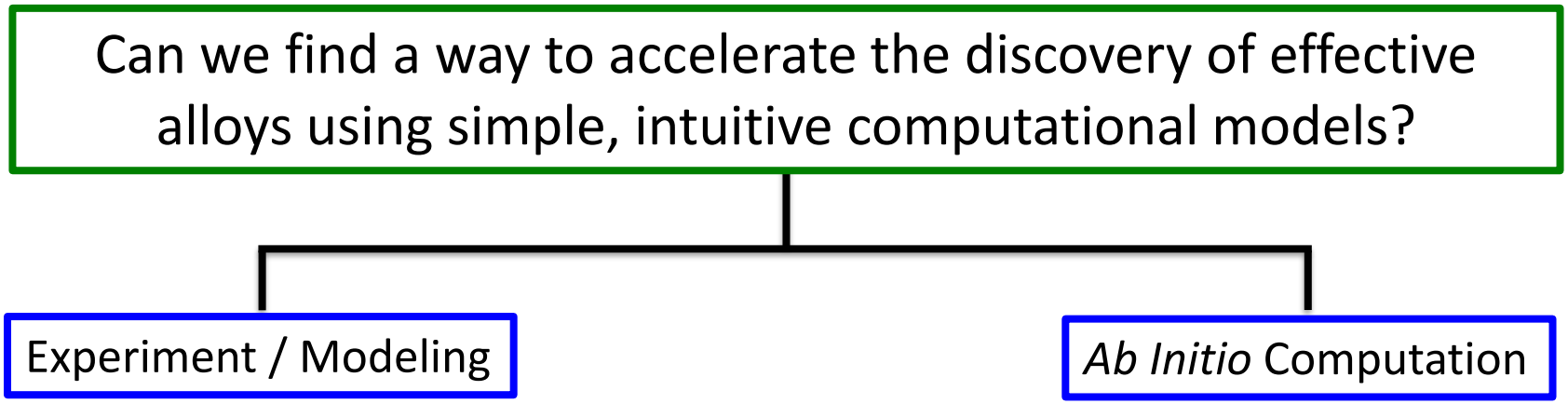


Mission Statement

Can we find a way to accelerate the discovery of effective alloys using simple, intuitive computational models?

Mission Statement



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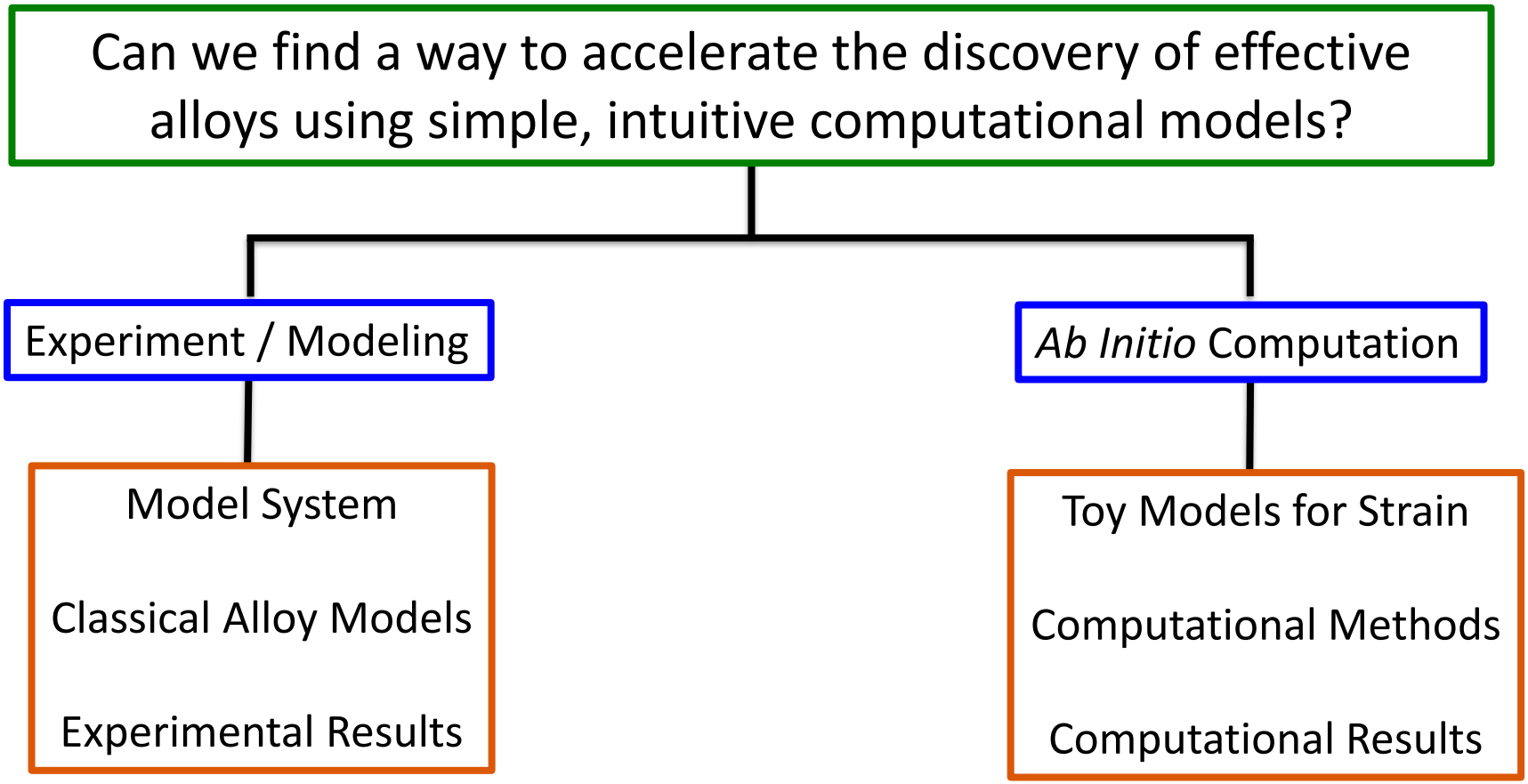

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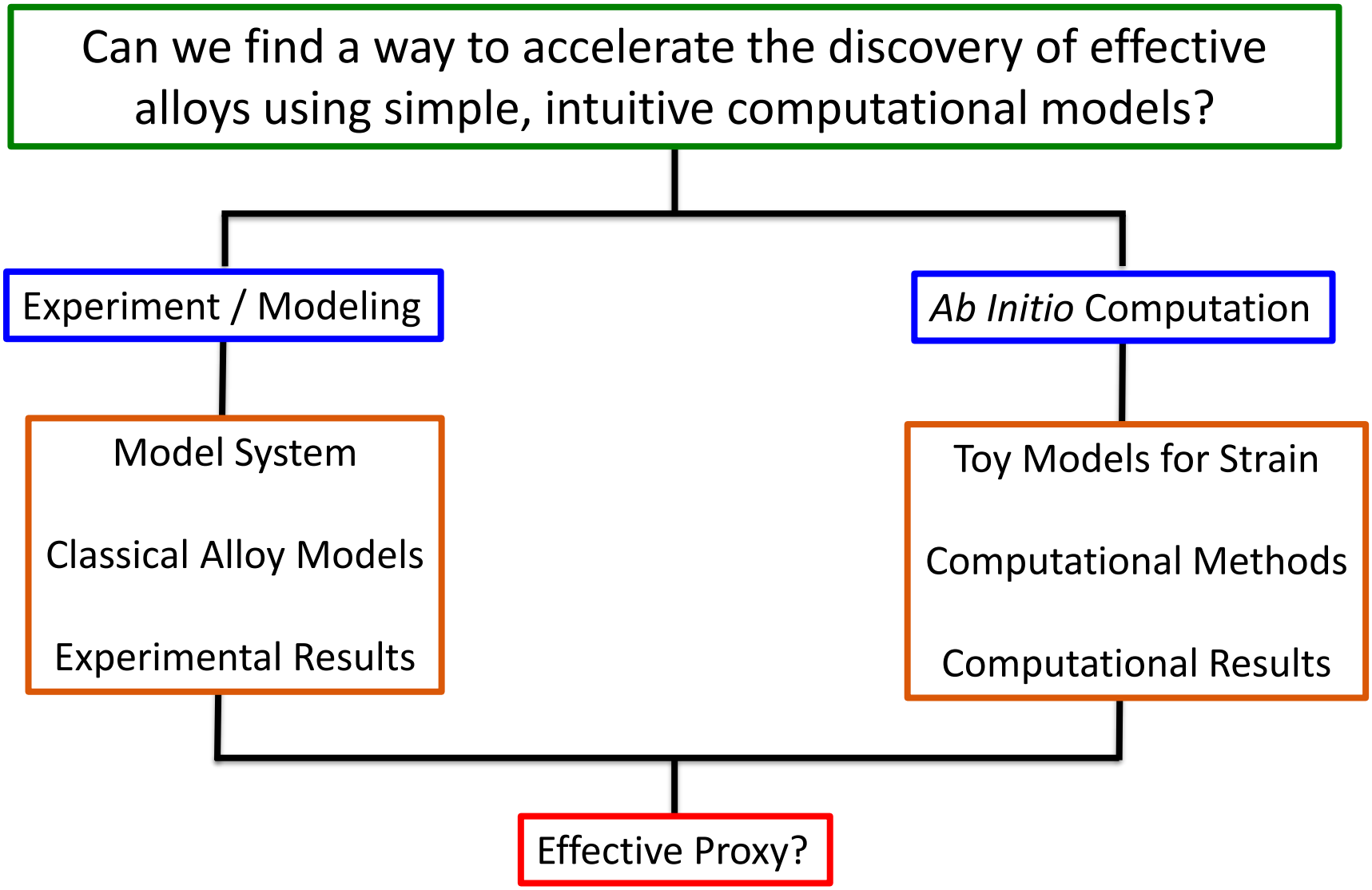
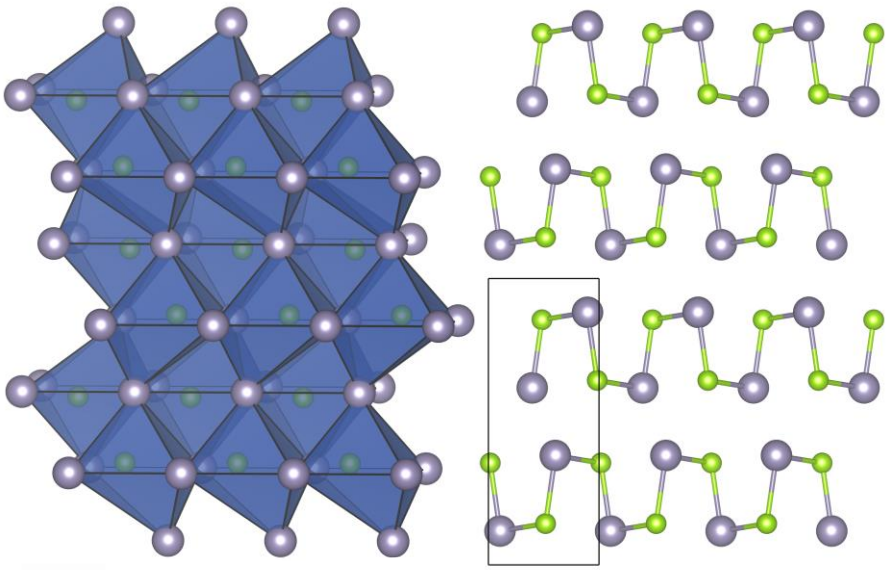


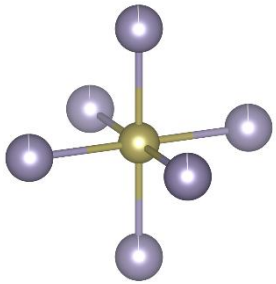
Experiment – Model System

SnSe (Pnma) + one of Sr, Ba, S, Se, Te
(e.g. $Sn_{1-x}Ba_xSe$)

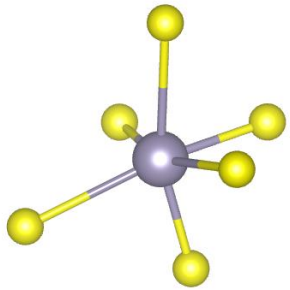


Distorted-rock salt structure
+
Rock-salt and non rock-salt endpoints

BaSe, SrSe, SnTe: Rock-salt



SnS, GeSe: Layered Pnma (distorted-RS)



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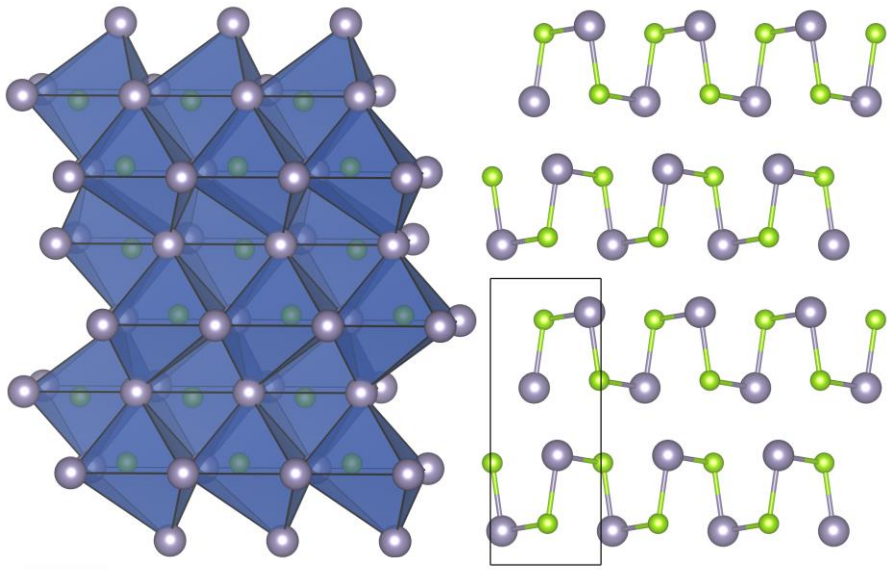

Synthesis (e.g SnSe + $SnSe_2$ + Ba)
+
Ball-milling and inductive hot-pressing

Experiment – Model System

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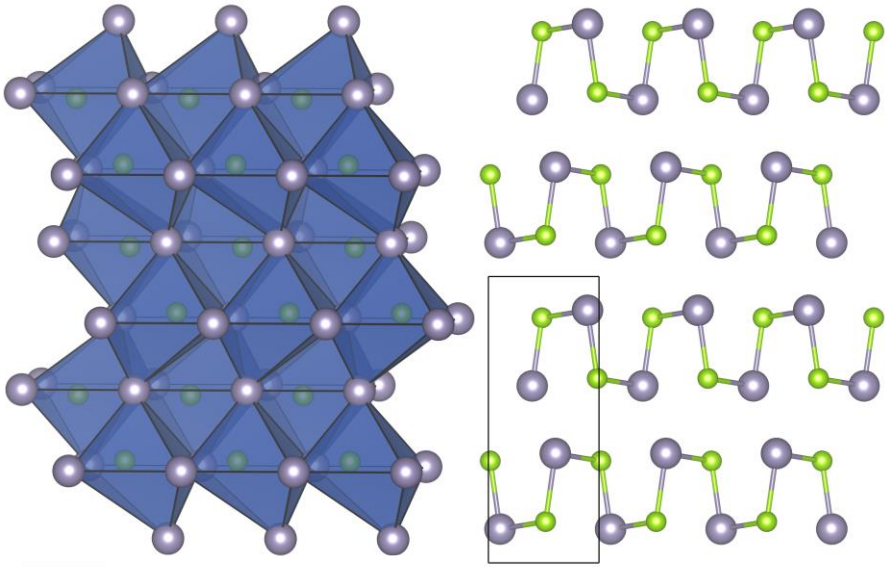
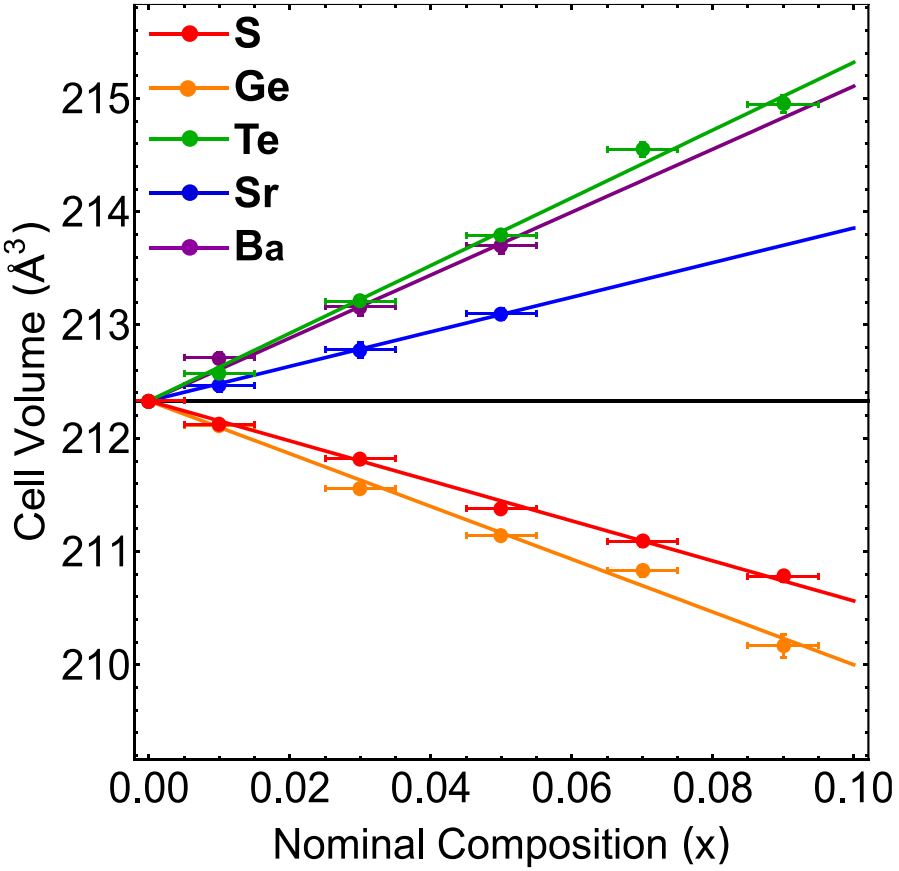
(e.g. $Sn_{1-x}Ba_xSe$)



X-ray Diffraction, Rietveld Refinement
+
Vegard's Law



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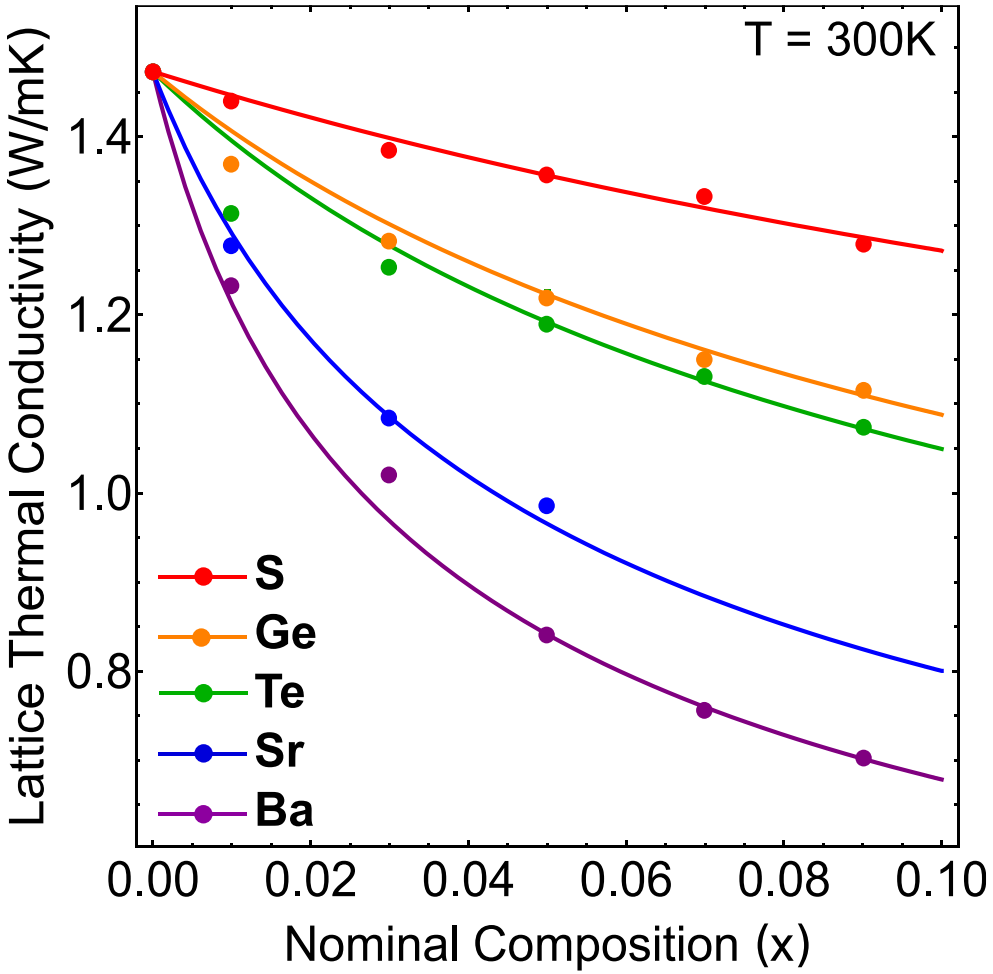

Note large spread in the thermal conductivity w/alloying species.

Depressions range from slight (e.g. Sulfur) to severe (e.g. Ba)

Need to model to understand role of chemistry on scattering.

Abeles Model for Alloy Scattering [1]

[1] B. Abeles, Phys. Rev., 1963, 131, 1906–1911.

Experiment – Transport and Modeling

Abeles model for composition dependent thermal conductivity

Thermal Conductivity of Alloy (κ_{alloy}) …

$$\kappa_{\text{alloy}} = \kappa_0 \left(\frac{\tan^{-1}(u)}{u} \right)$$

Experiment – Transport and Modeling

Abeles model for composition dependent thermal conductivity

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Disorder Scaling Parameter (u) …

$$u = \left(\frac{\pi^2 \Theta \Omega}{h v_s^2} \kappa_0 \Gamma_{\text{tot}} \right)^{1/2}$$

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Net Scattering Factor (Γ_{tot}) …

$$\Gamma'_{\text{tot}} = \Gamma'_{\text{m}} + \Gamma'_{\text{s}}$$

Experiment – Transport and Modeling

$$\Gamma'_{tot} = \Gamma'_m + \Gamma'_s \begin{cases} \Gamma'_m = x(1-x)\dfrac{a}{a+b}\left(\dfrac{\Delta M_{Sn,X}}{M_{Sn,X}}\right)^2 \\ \Gamma'_s = x(1-x)\varepsilon\dfrac{a}{a+b}\left(\dfrac{\Delta r_{Sn,X}}{r_{Sn,X}}\right)^2 \end{cases}$$

Experiment – Transport and Modeling

Mass Contrast

$$\Gamma'_{tot} = \Gamma'_m + \Gamma'_s \begin{cases} \Gamma'_m = x(1-x)\dfrac{a}{a+b}\left(\dfrac{\Delta M_{Sn,X}}{M_{Sn,X}}\right)^2 \\ \Gamma'_s = x(1-x)\varepsilon\dfrac{a}{a+b}\left(\dfrac{\Delta r_{Sn,X}}{r_{Sn,X}}\right)^2 \end{cases}$$

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Radii Contrast

Experiment – Transport and Modeling

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Free parameter

Radii Contrast

Experiment – Transport and Modeling

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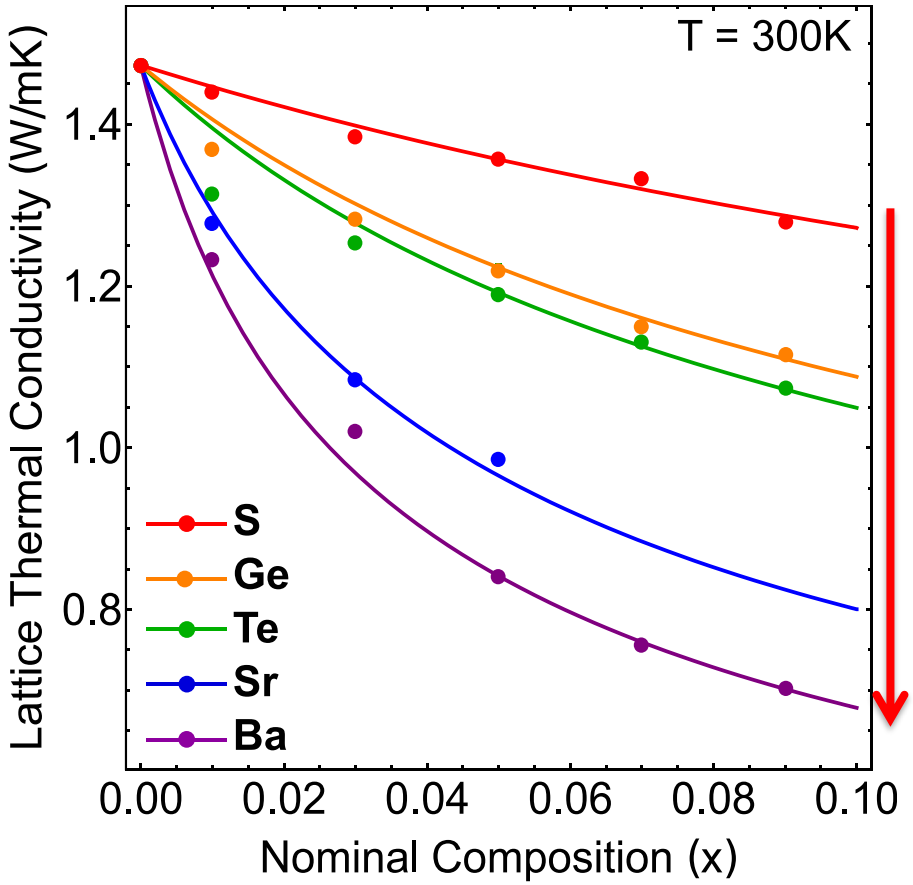
Free parameter

Radii Contrast

$$\kappa_{alloy}\left(\kappa_0, \nu_s, x, \varepsilon, r_\alpha \ldots, m_\alpha \ldots\right)$$

Experimental Summary

$$\kappa_{\text{alloy}}\left(\kappa_0, v_s, x, \varepsilon, r_\alpha \ldots, m_\alpha \ldots\right)$$



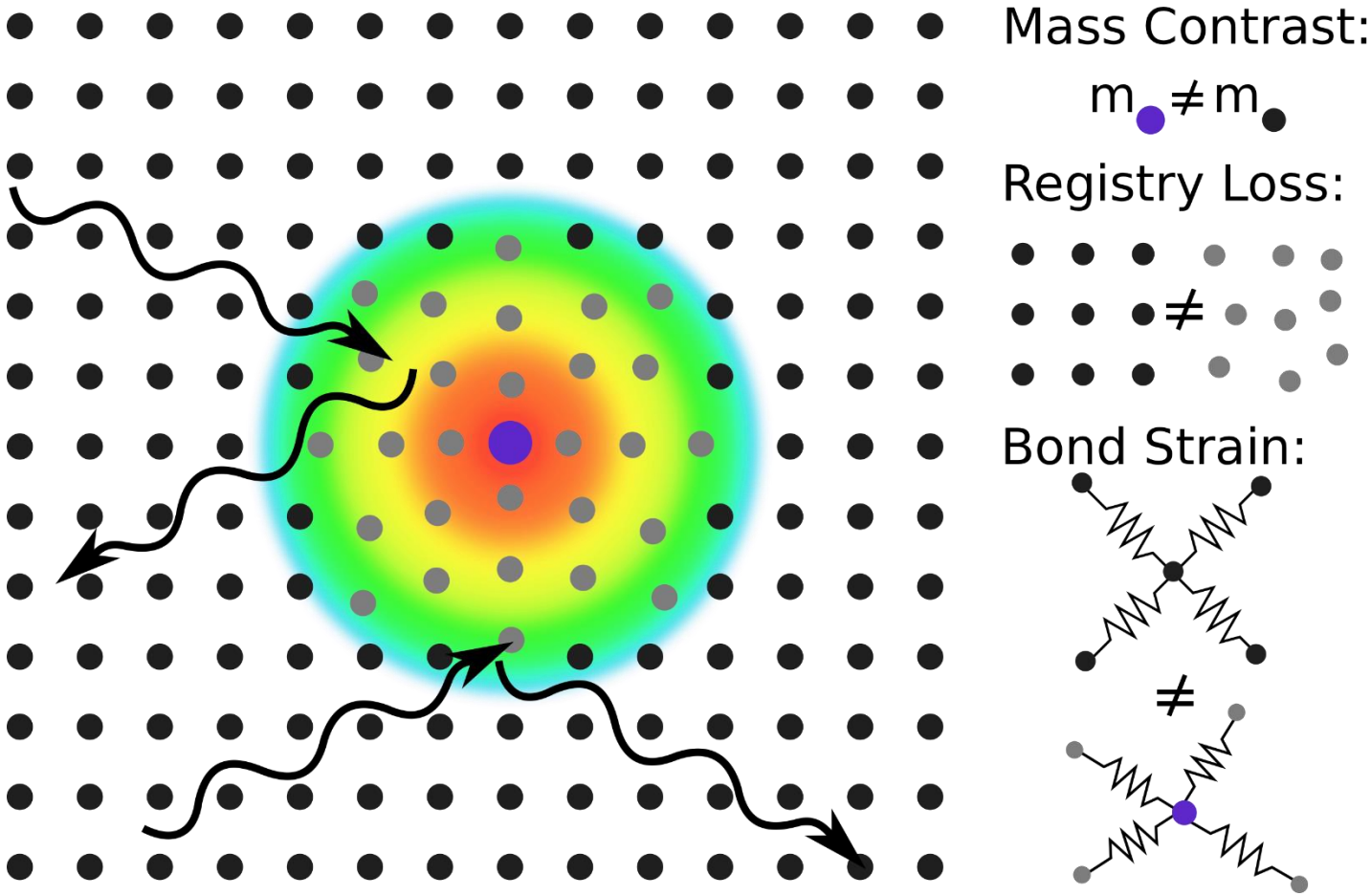
Increasing Strain Contribution

+

Decreasing Thermal Conductivity

Alloy	Γ_s/Γ_m	Γ_s'
S	0	0
Ge	1.73	0.0063
Te	1.99	0.0168
Sr	17.8	0.0297
Ba	85.0	0.0491

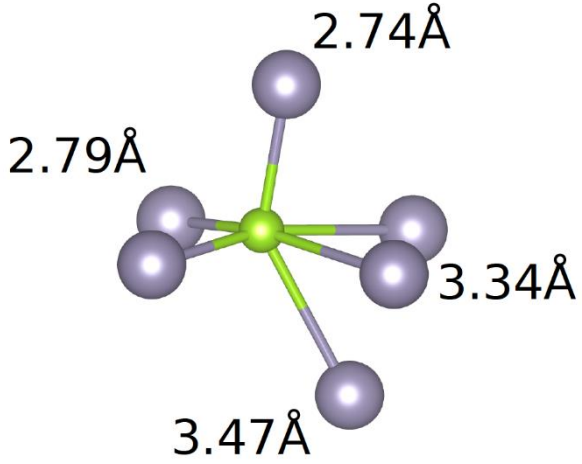
Computational Toy Models



Computational Methods

Approach 1: Pair-Distribution Function (Supercell)

32-atom special quasi-random structures (SQS) to mimic 25% alloy PDF's



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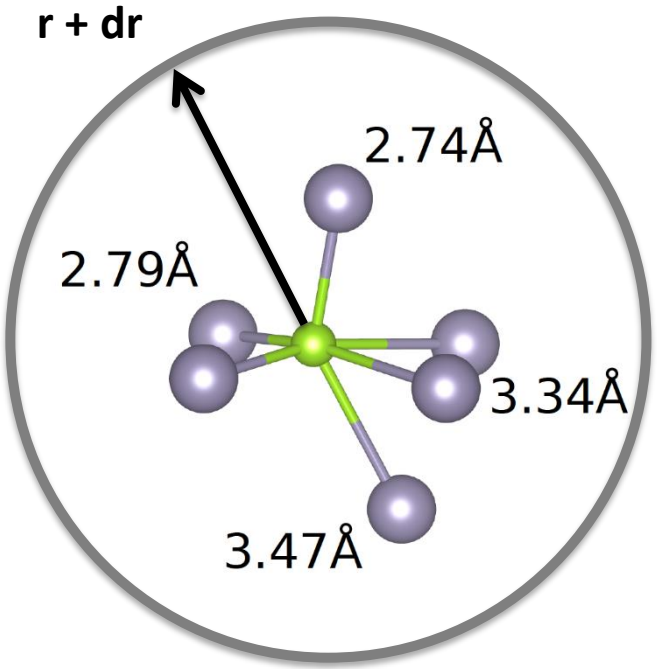

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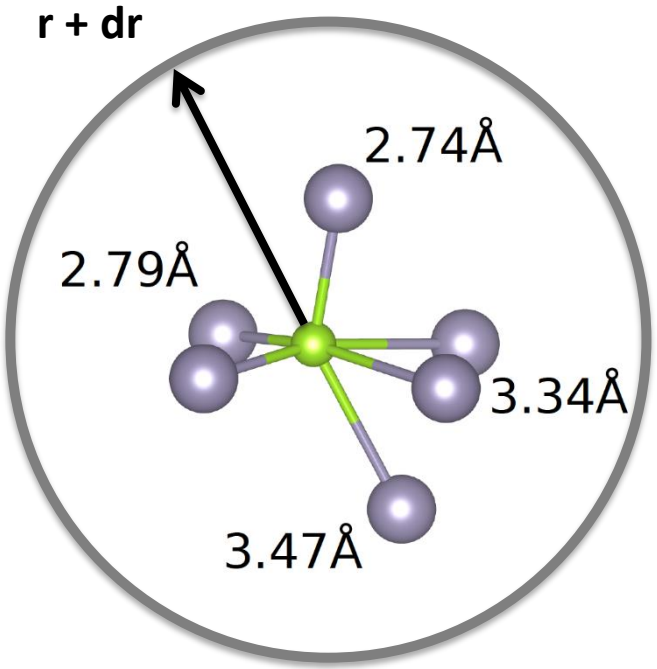
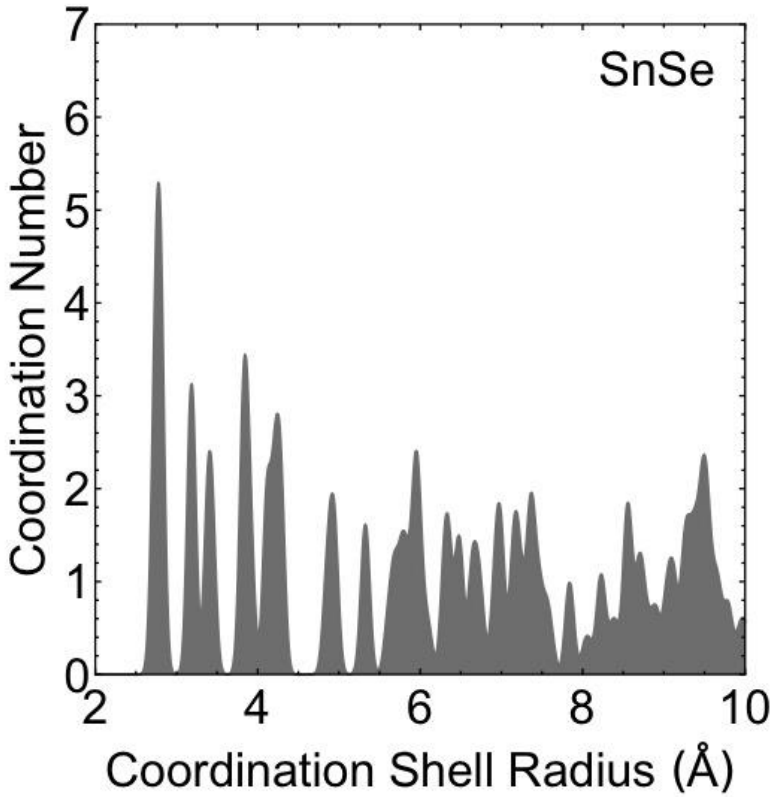
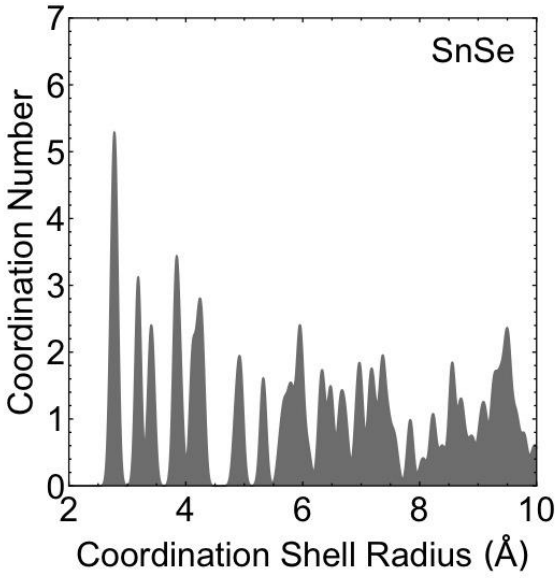
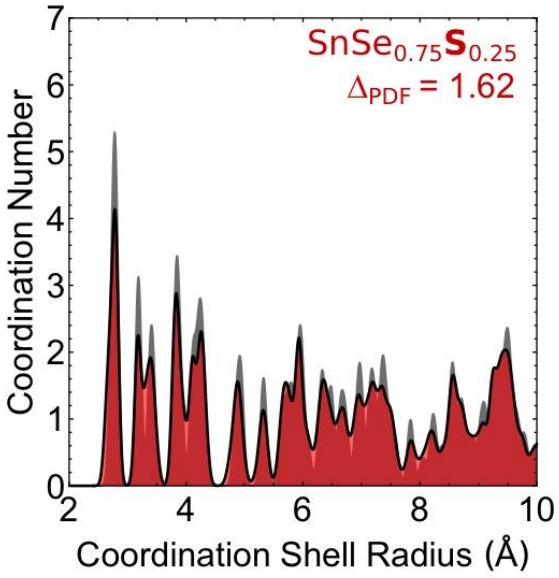
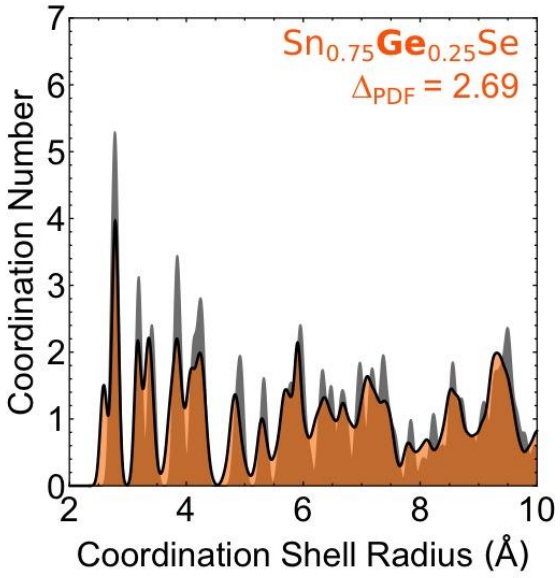


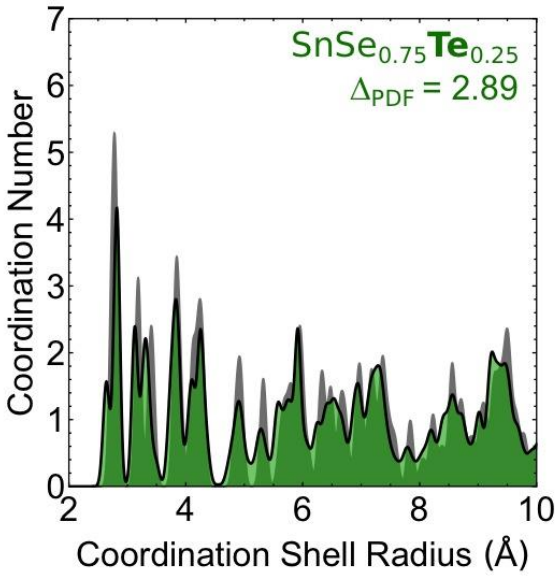


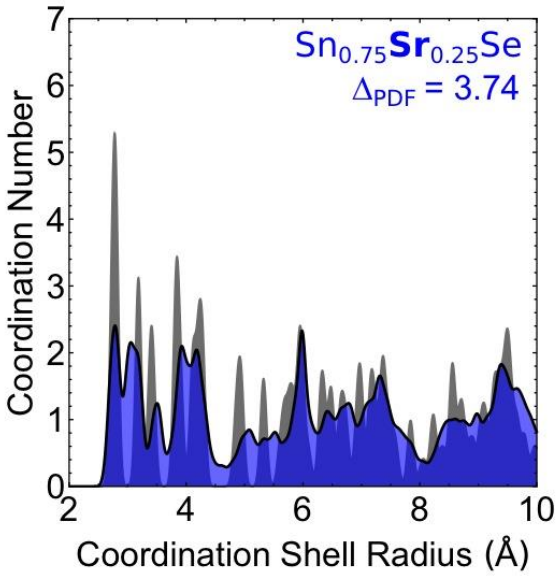
Computational Methods – Pair Distribution Fn

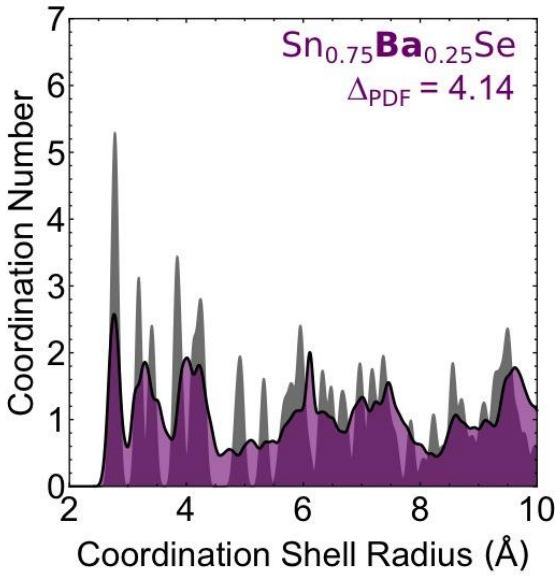






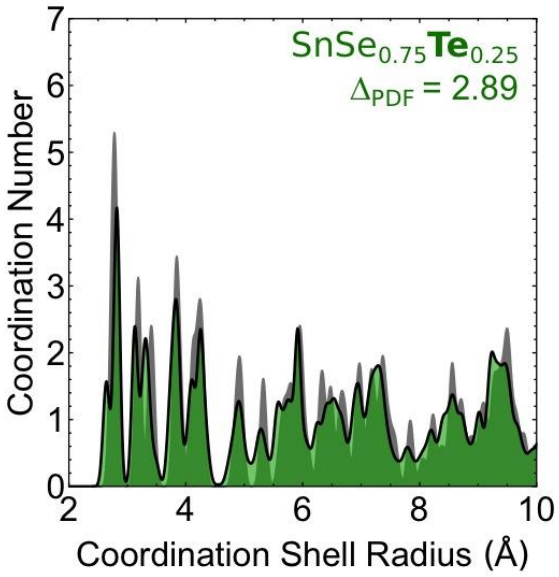


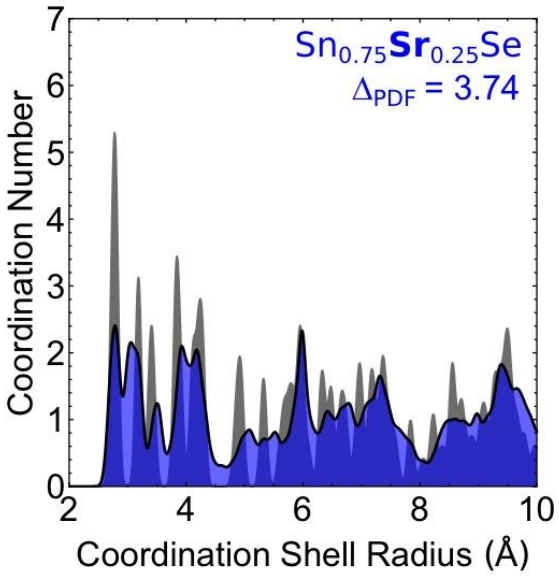


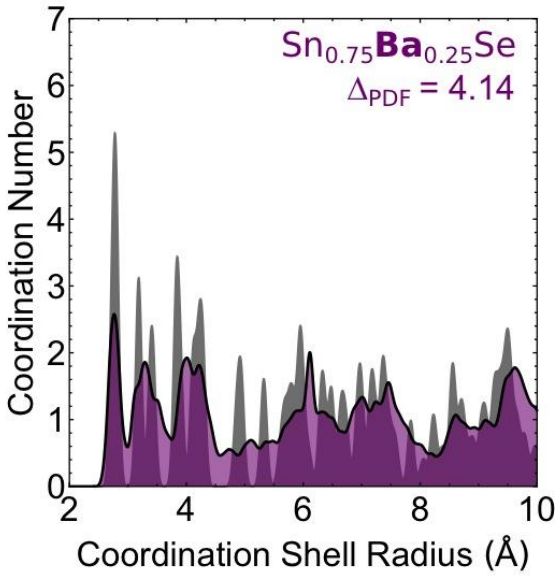


Computational Methods – Pair Distribution Fn

$$\Delta_{PDF} = \int_0^{r_{max}} |PDF_{SnSe}(r) - PDF_{Alloy}(r)|\, dr$$







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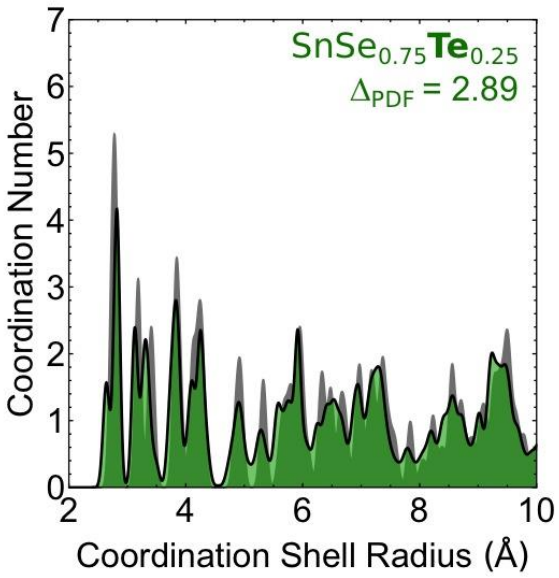
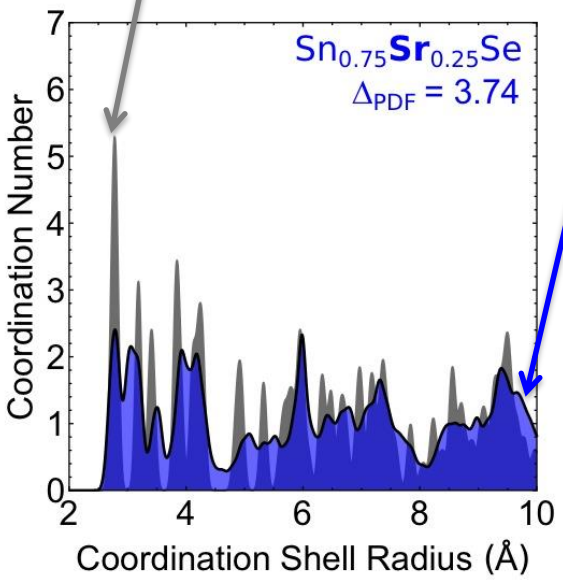
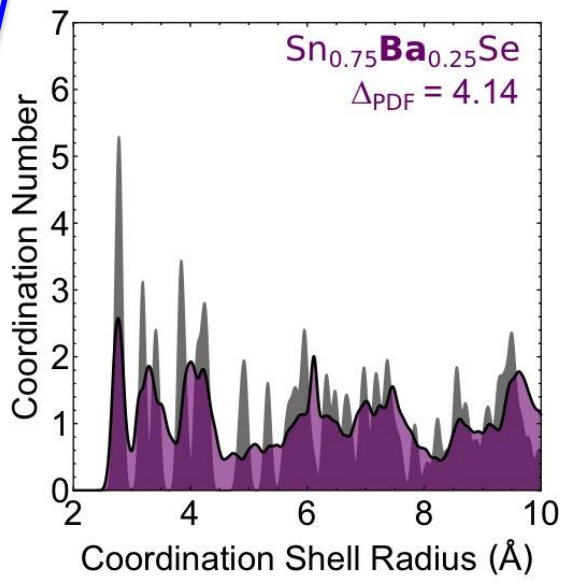


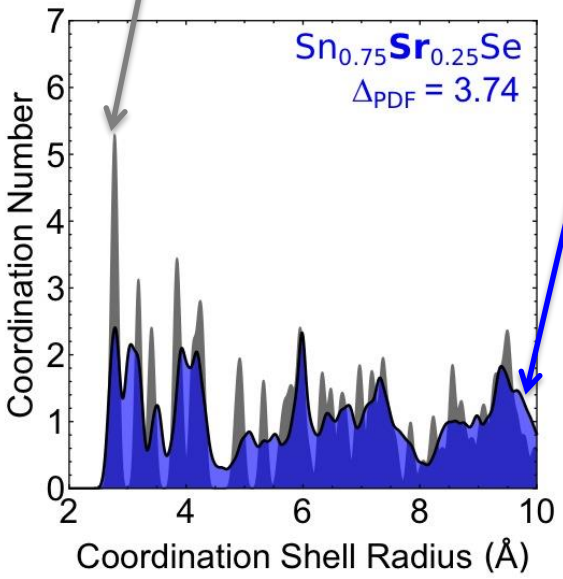


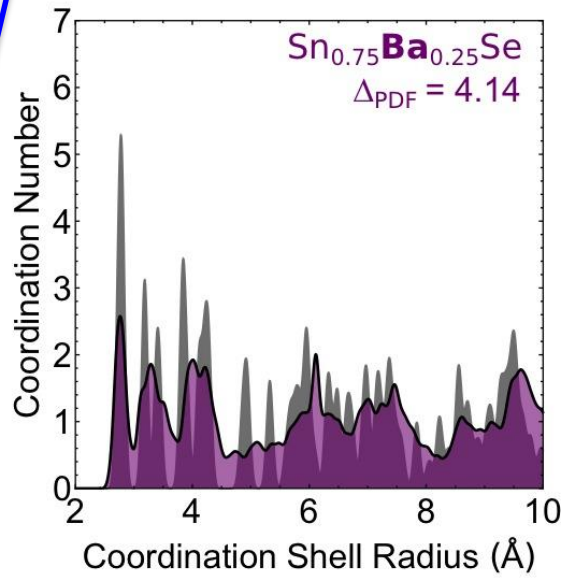


Computational Methods – Pair Distribution Fn

$$\Delta_{PDF} = \int_0^{r_{max}} \left| PDF_{SnSe}(r) - PDF_{Alloy}(r) \right| dr$$

Alloy	Δ_{PDF} (Å)
SnSe	0
S	1.62
Ge	2.69
Te	2.89
Sr	3.74
Ba	4.14

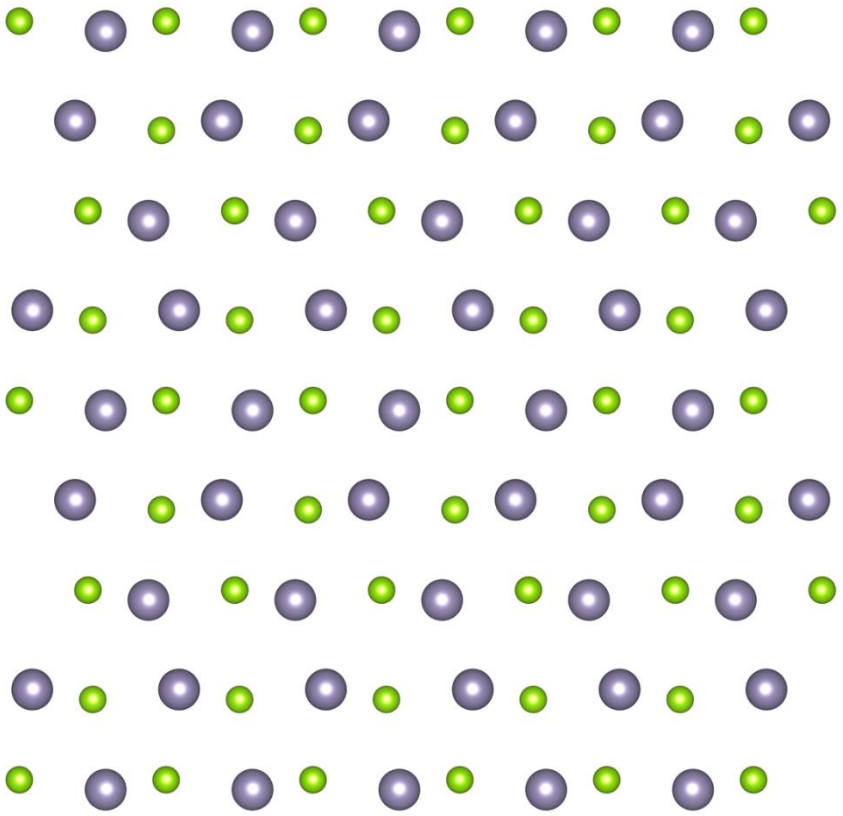




Computational Methods

Approach 2: Single Atom Distortion (Supercell)

256-atom supercell with singular atom replaced by alloying species



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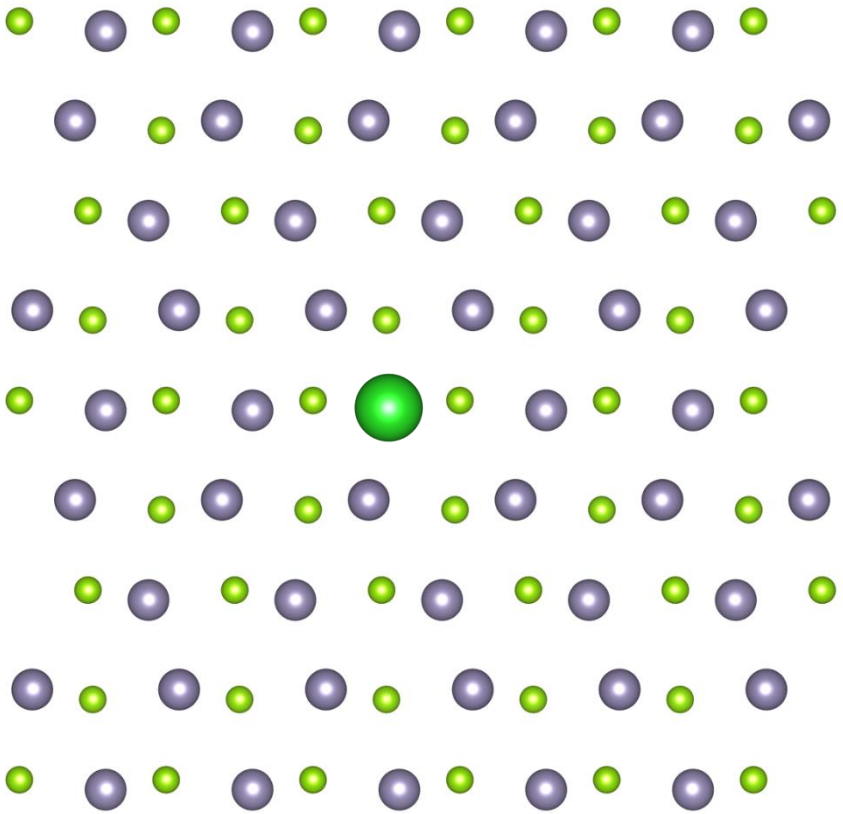

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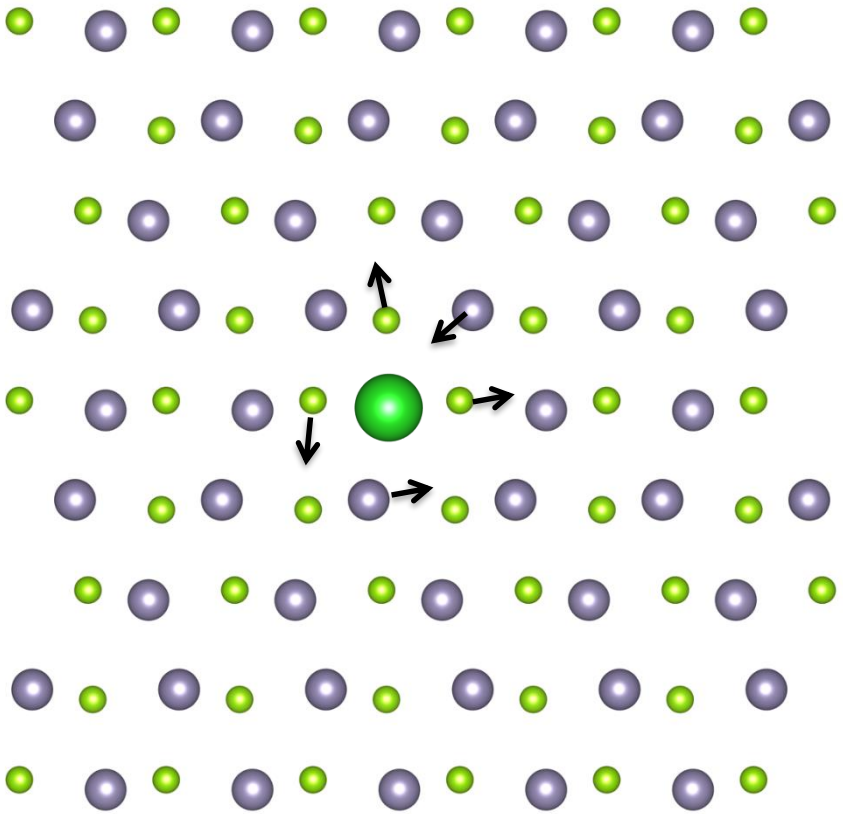

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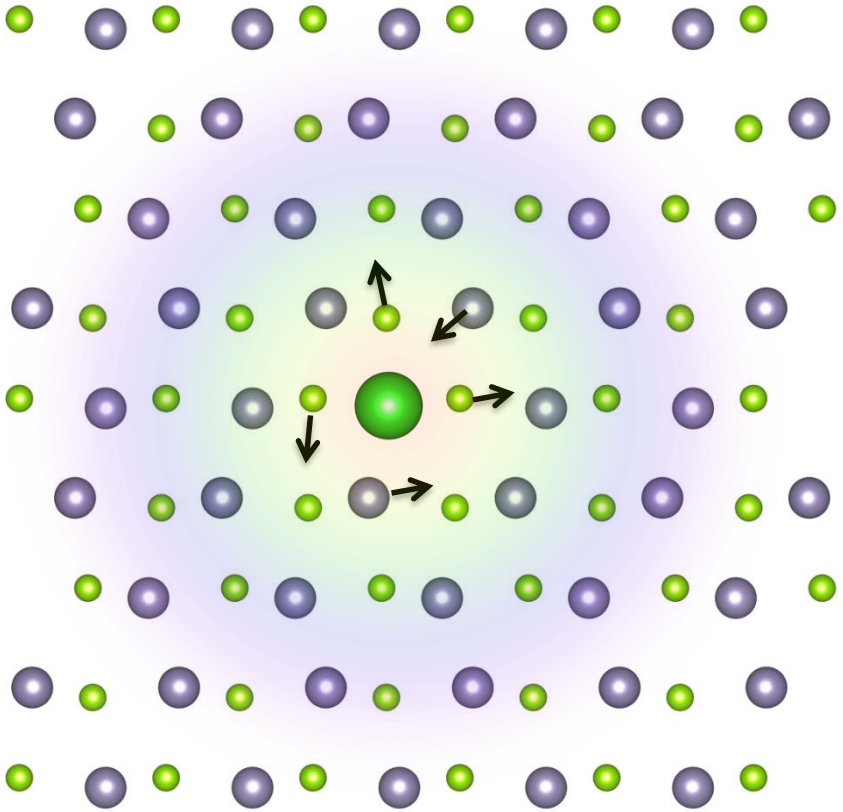

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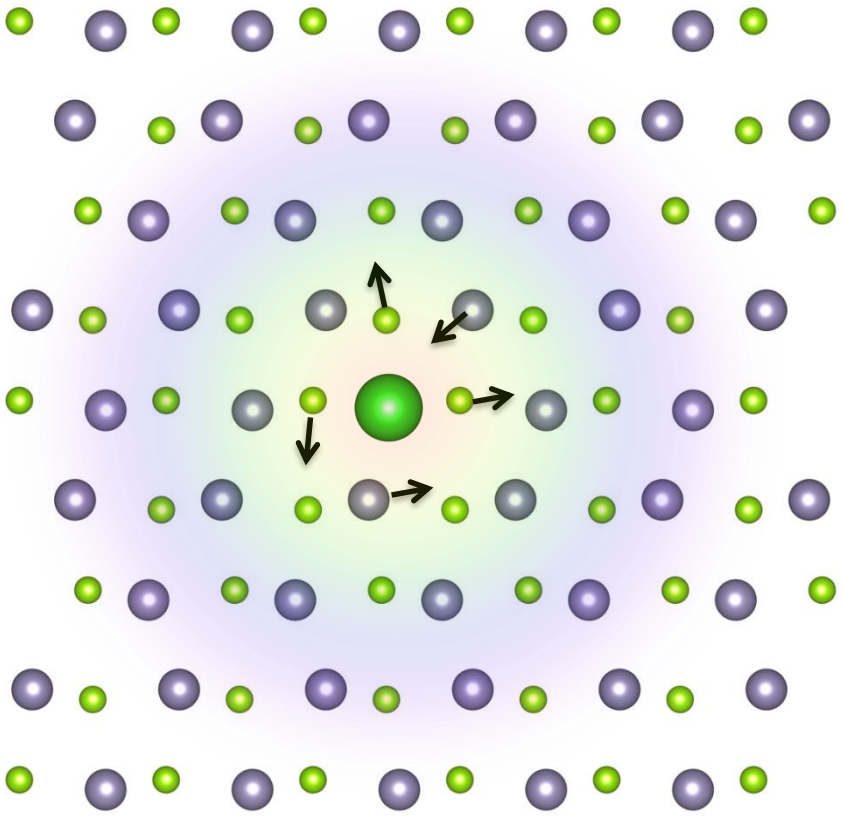


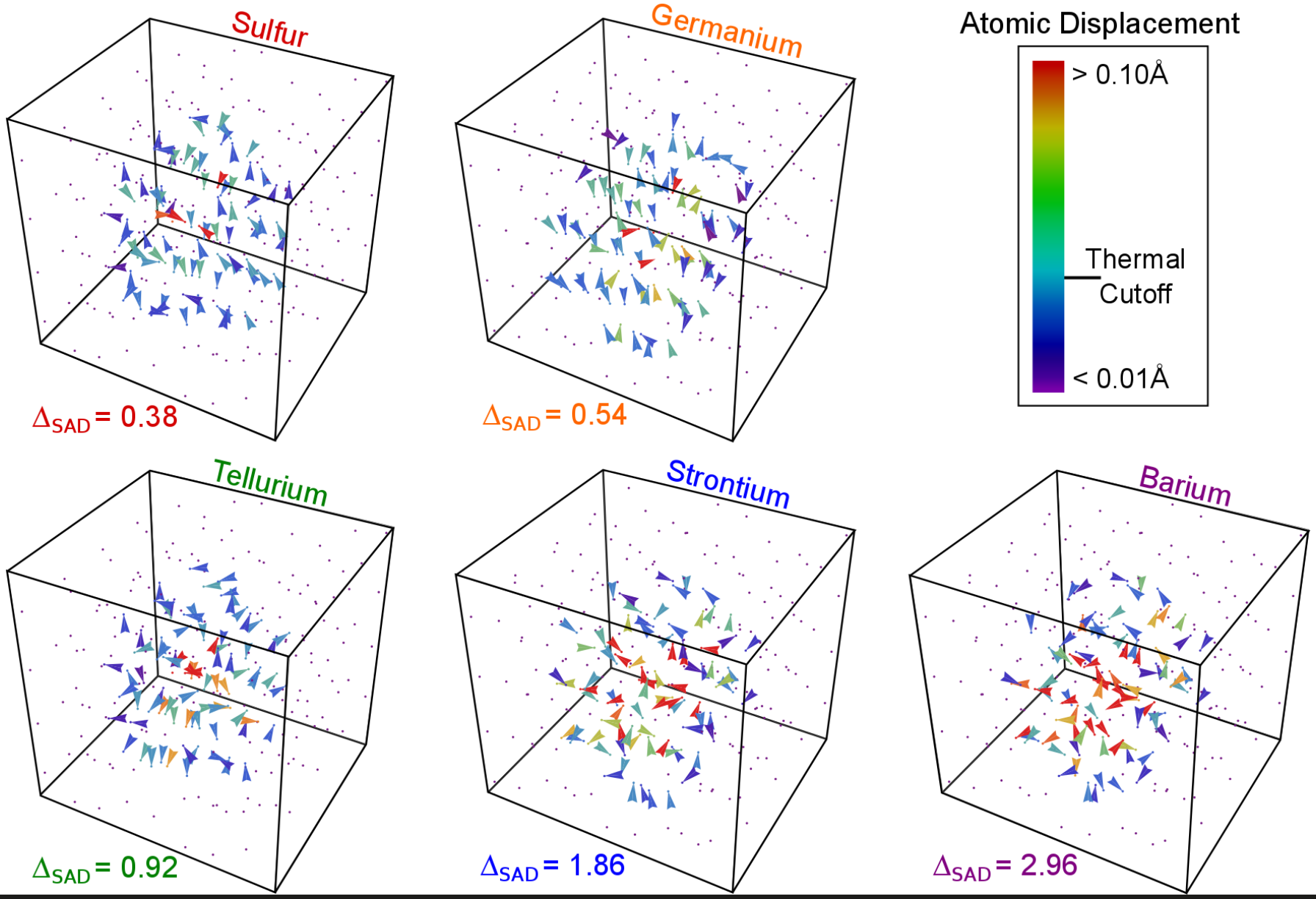
Change in local coordination around species…

How far from source atom does it extend?

How large of a distortion?

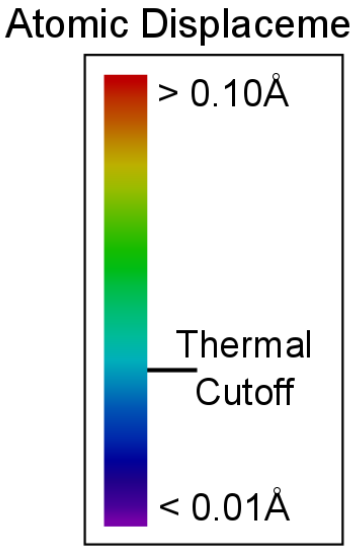
Relation with chemistry?

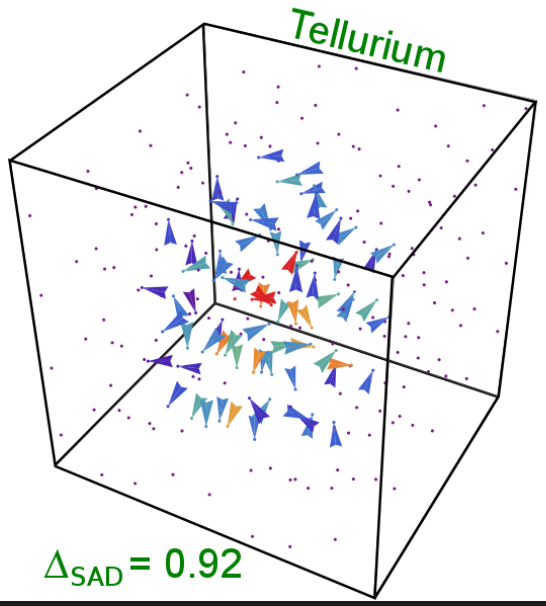
Computational Methods – Single Atom Distortion

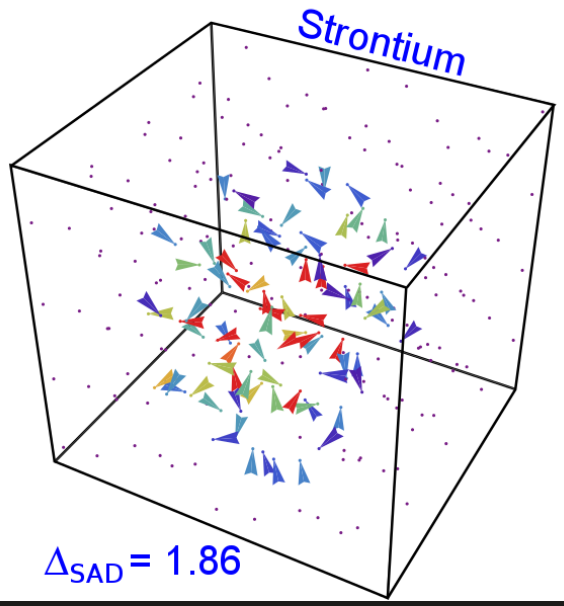


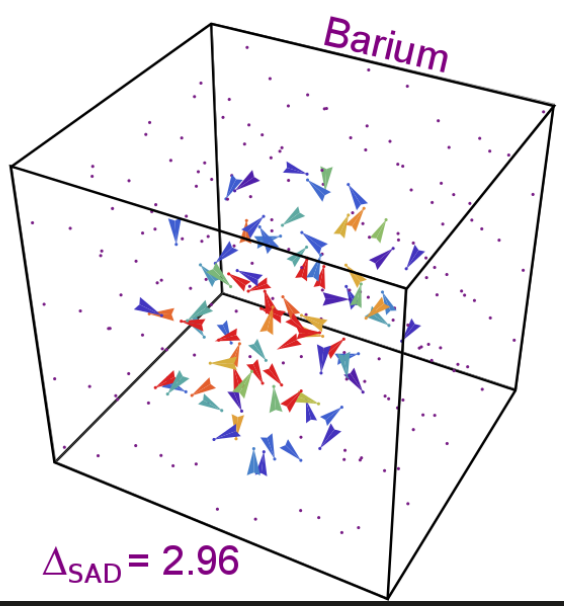
Computational Methods – Single Atom Distortion

$$\Delta_{SAD} = \sum_{i=1}^{N} |\vec{r}_{Alloy,i} - \vec{r}_{SnSe,i}|$$









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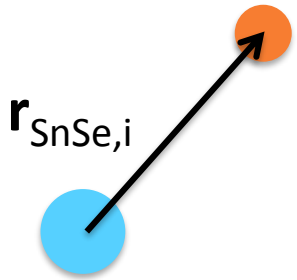

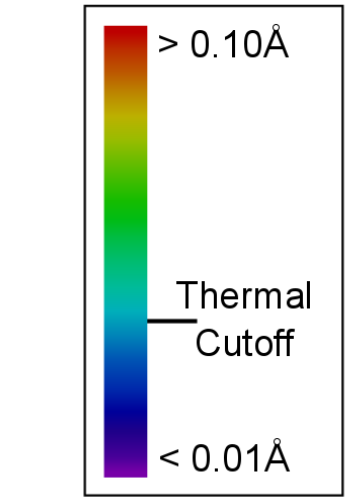

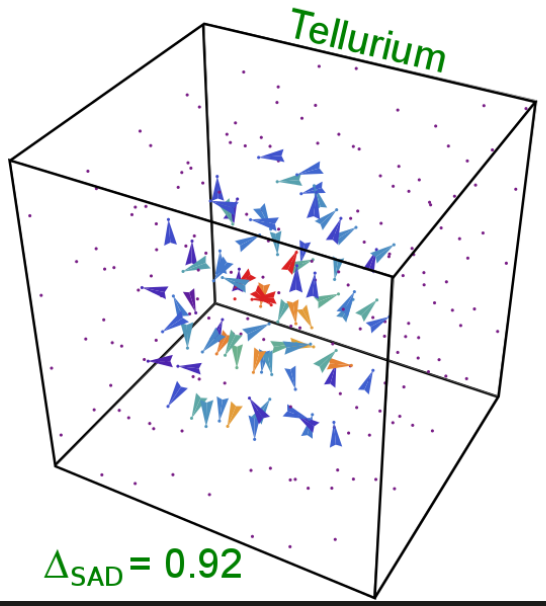

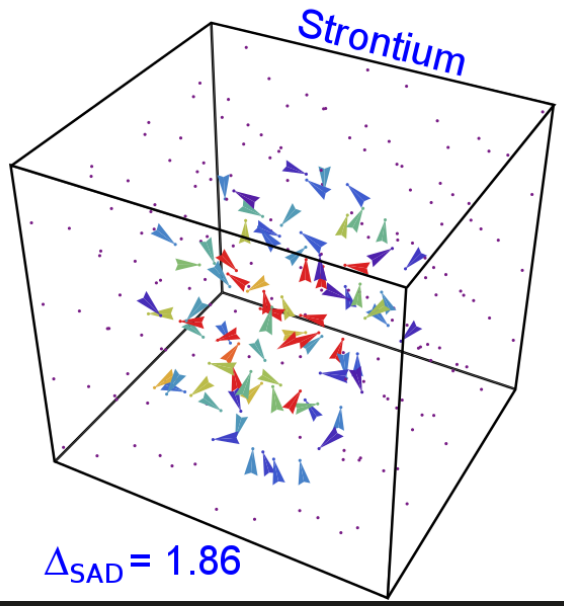

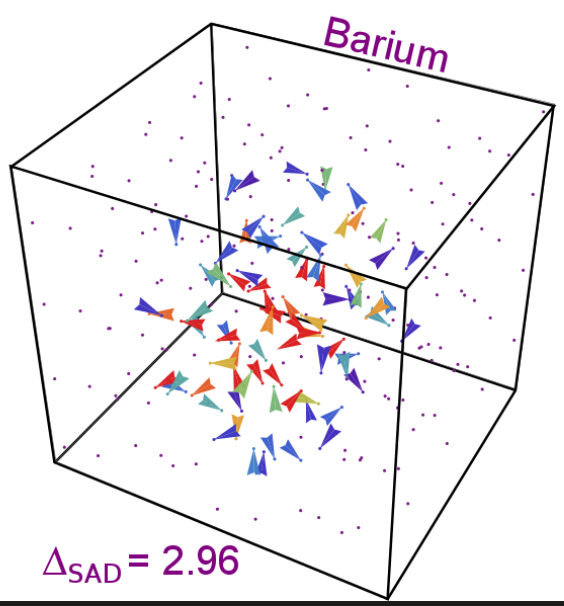

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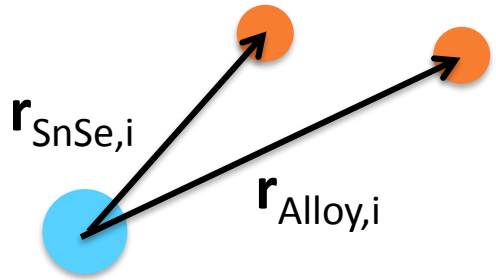

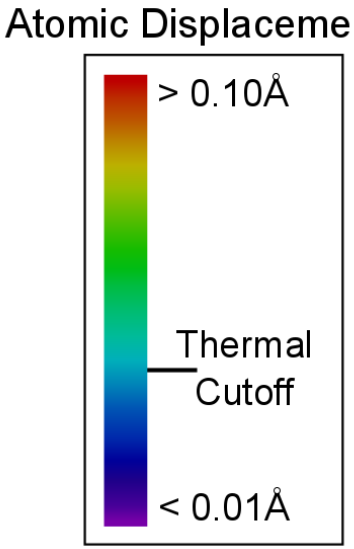

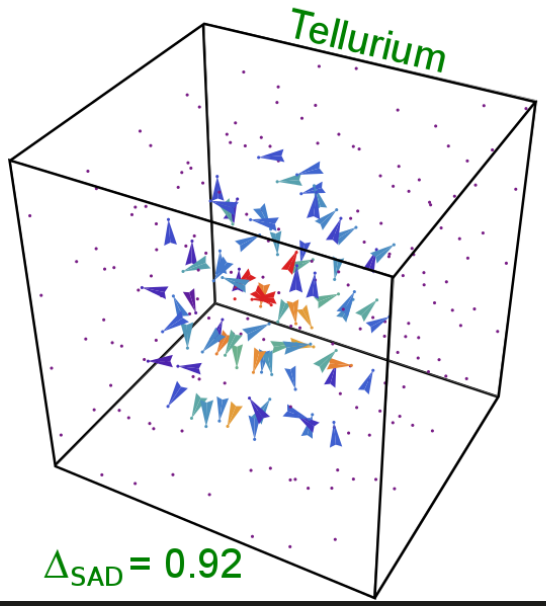

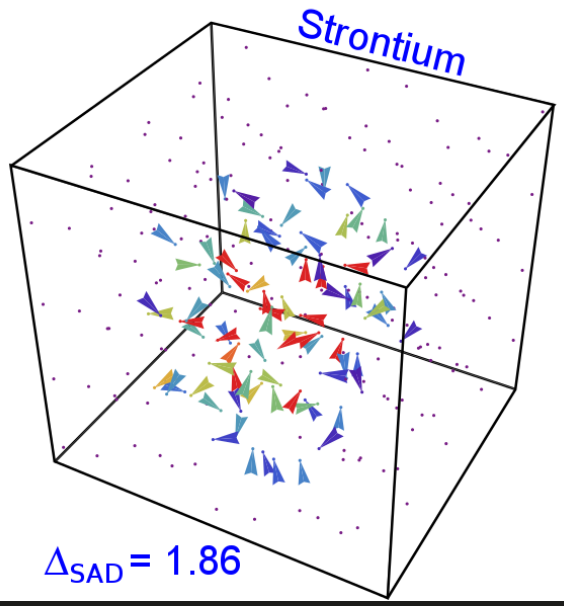

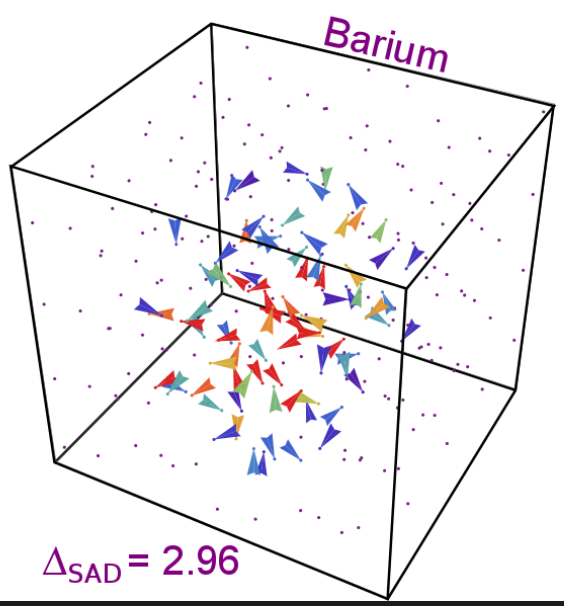

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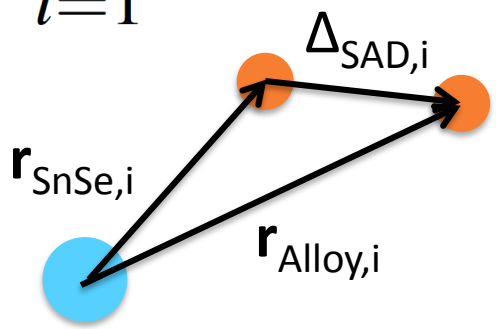

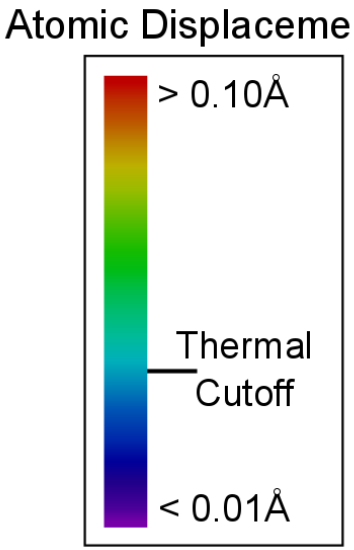

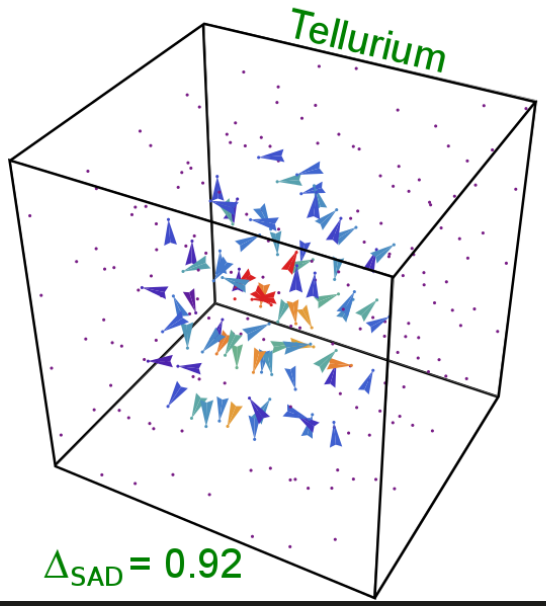

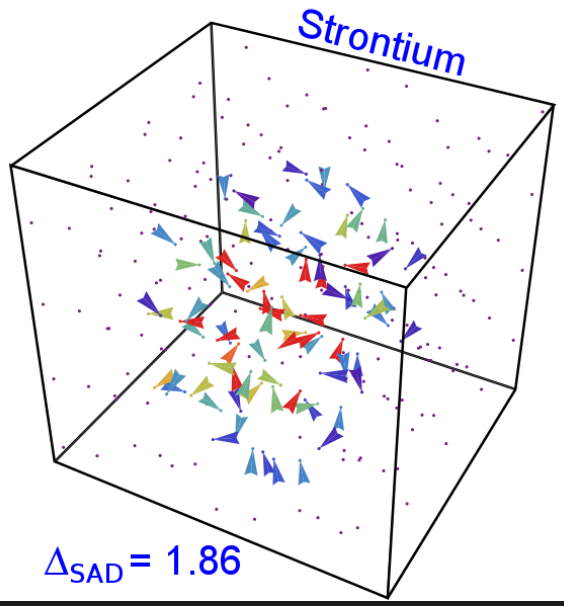

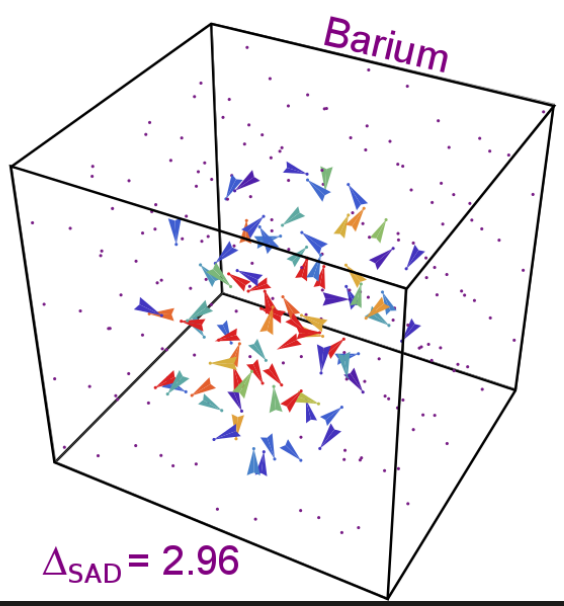

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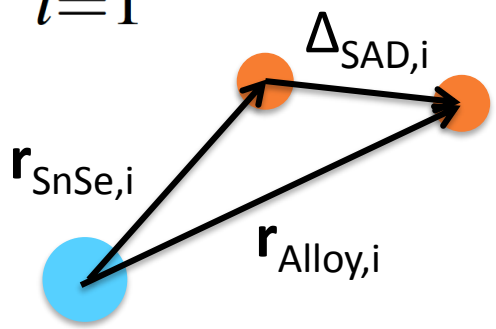
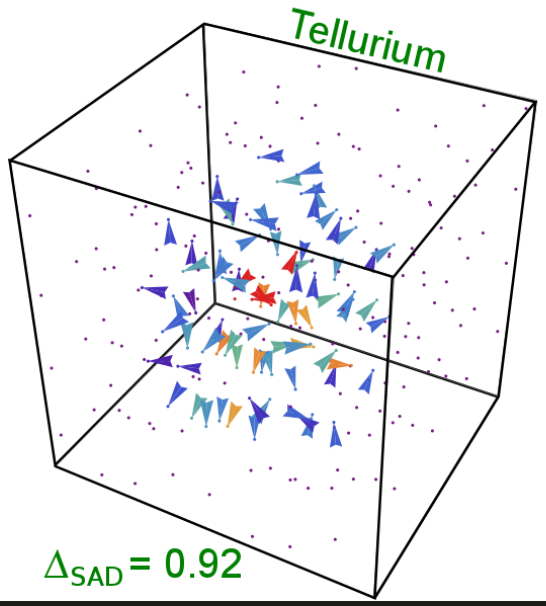
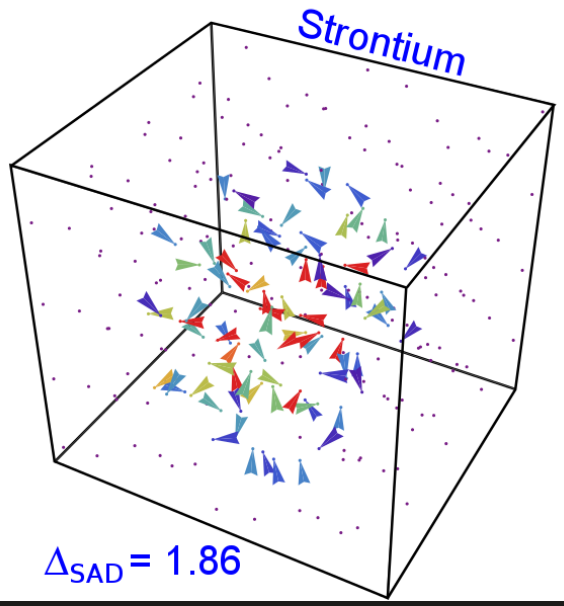
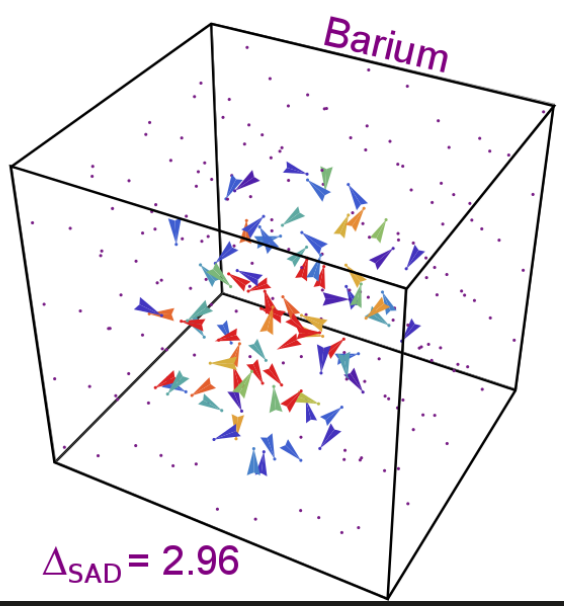


Alloy	Δ_{SAD} (Å)
SnSe	0
S	0.38
Ge	0.54
Te	0.92
Sr	1.86
Ba	2.96







Computational Summary

Approach 3: Bulk Modulus (Supercell)

Standard calculation of total energy in DFT (LDA) as a function of cell volume…

Fitting of the Murnaghan equation of state to E(Ω)

$$E(\Omega) = E_0 + \frac{B_0\Omega}{B_0'}\left(\frac{(\Omega_0/\Omega)^{B_0'}}{B_0'-1}+1\right) - \frac{B_0\Omega_0}{B_0'-1}$$

Alloy	B_0 (GPa)
SnSe	42.2
S	40.8
Ge	39.9
Te	38.1
Sr	34.3
Ba	31.5

Hybridization of Experimental and Computation

Do experiment and computation agree?

Alloy	B_0 (GPa)	Δ_{PDF} (Å)	Δ_{SAD} (Å)
SnSe	42.2	0	0
S	40.8	1.62	0.38
Ge	39.9	2.69	0.54
Te	38.1	2.89	0.92
Sr	34.3	3.74	1.86
Ba	31.5	4.14	2.96

Alloy	Γ_s/Γ_m	Γ_s'
S	0	0
Ge	1.73	0.0063
Te	1.99	0.0168
Sr	17.8	0.0297
Ba	85.0	0.0491

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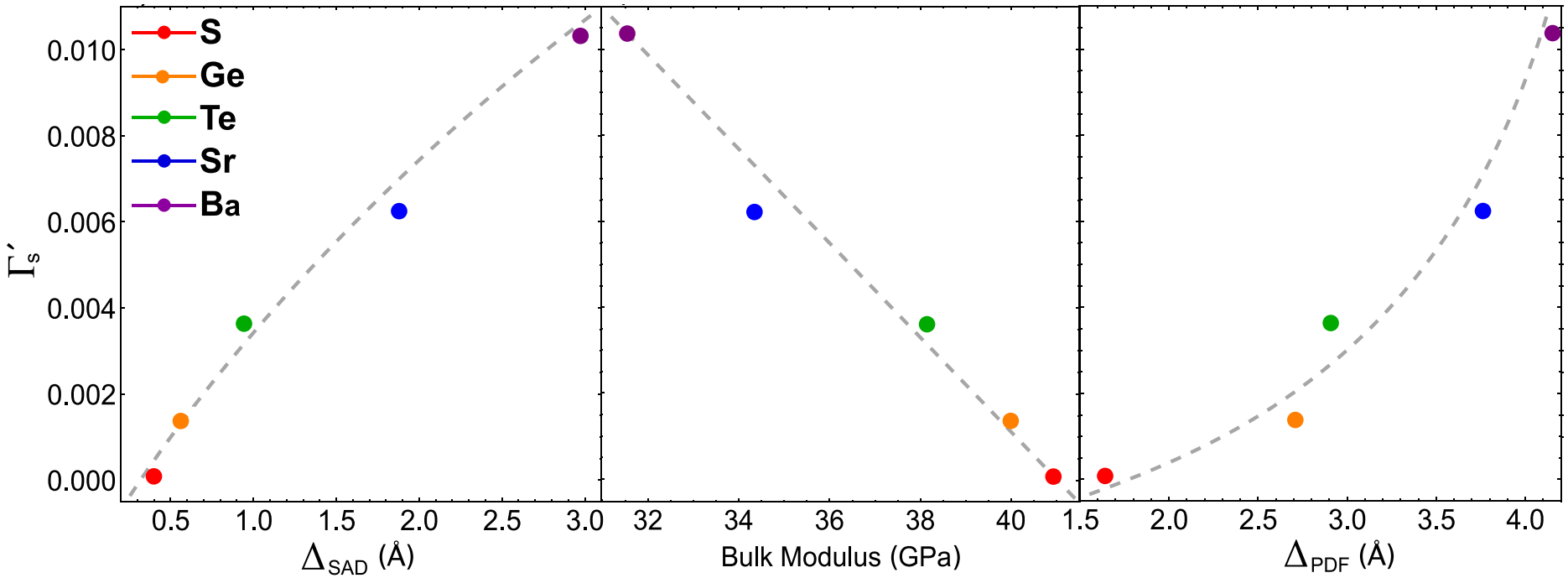

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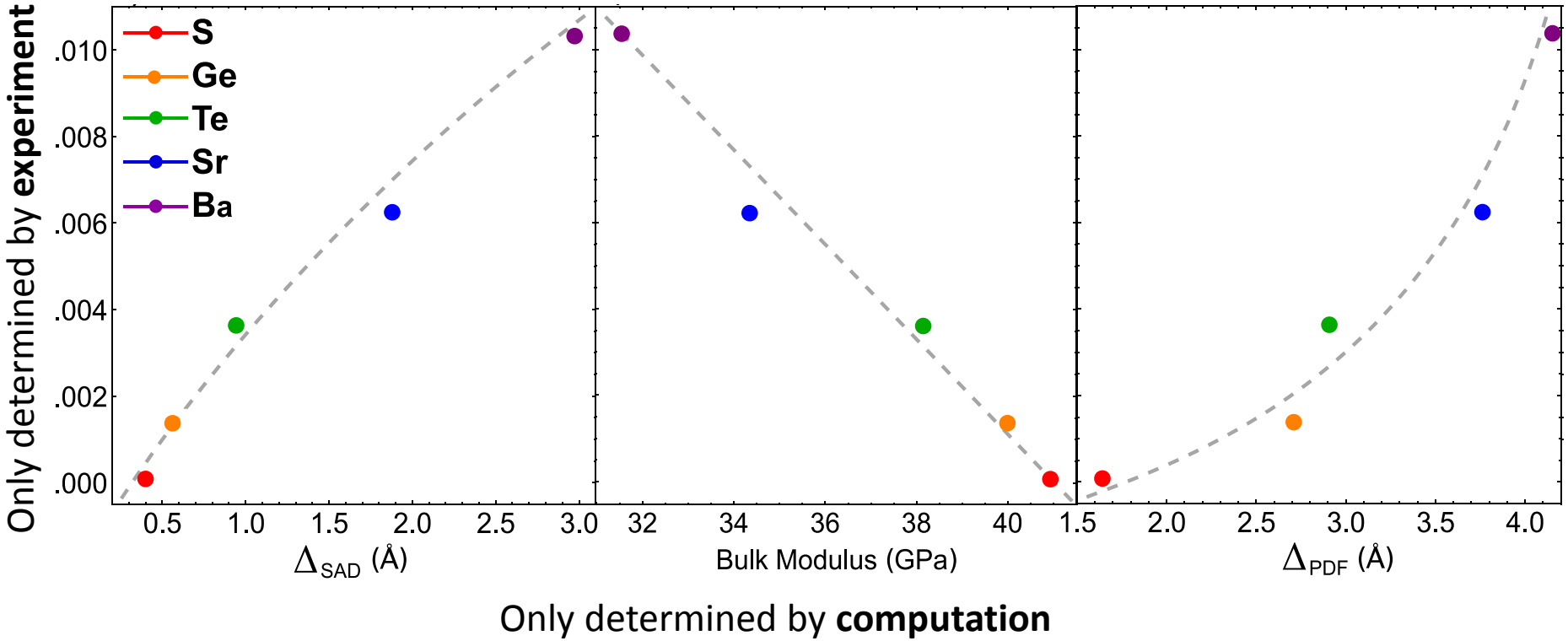

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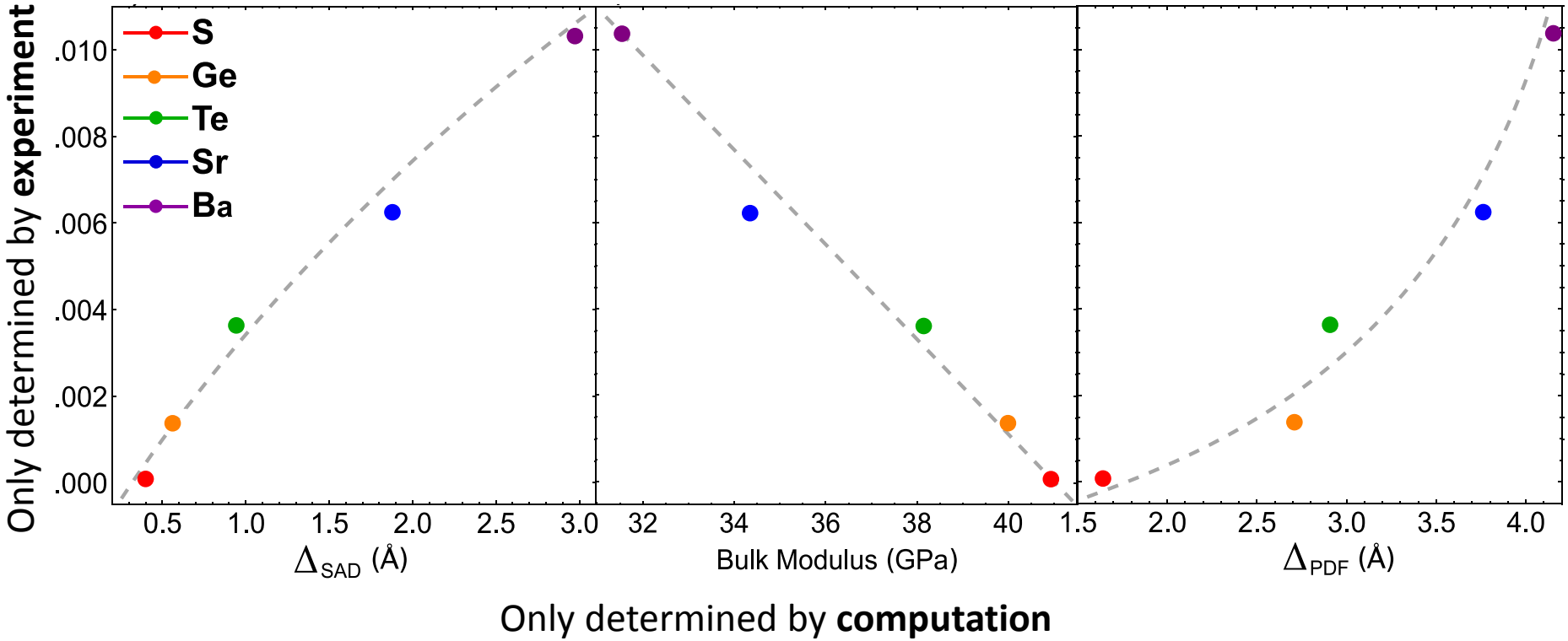
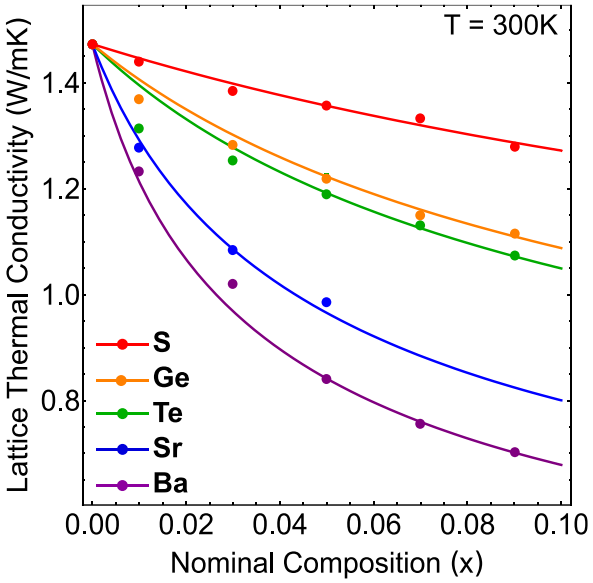
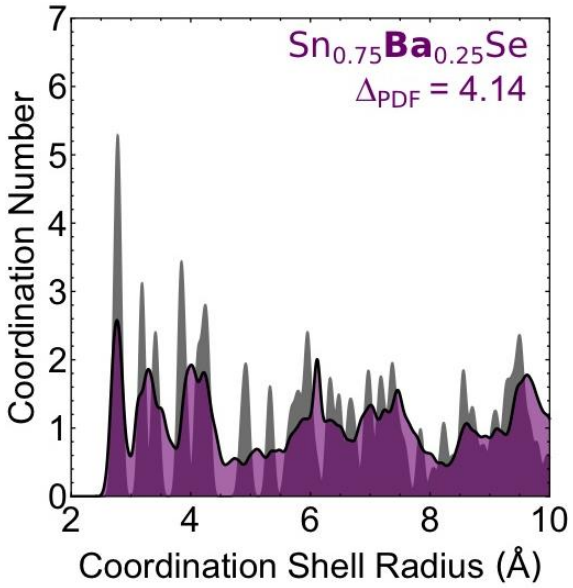


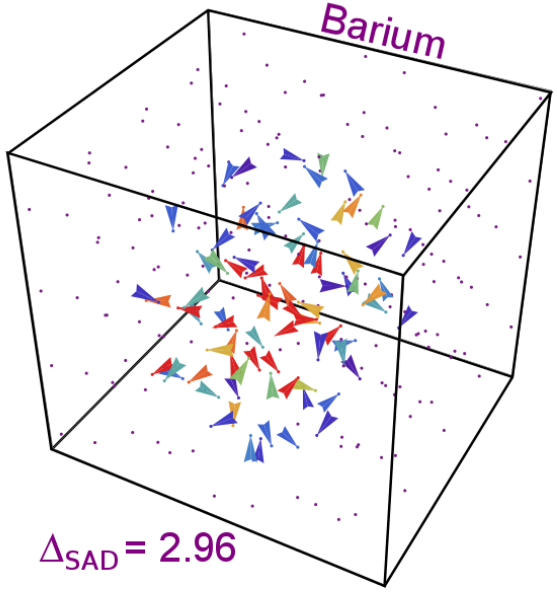
Yes!

Computation successfully ranks relative changes in strain and transport by proxy.

Conclusion

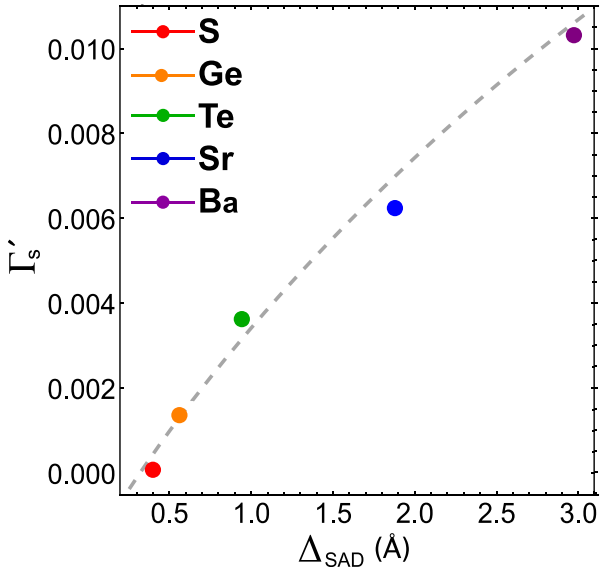






Presented inexpensive, conceptually transparent methods to visualize alloying in SnSe.

Strain effects can be observed far from host lattice site.

Computational ranking successful as proxy for experiment.

Possible down-selection of effective alloying agents.