Fundamental Studies of Complex Precipitation Pathways in Lightweight Alloys*

** Subtask 1A1 under the Powertrain Materials Core Program (PMCP)*

Dongwon Shin (PI)
Contributors: Amit Shyam, Matt Chisholm, Larry Allard, Jon Poplawsky, Balasubramaniam Radhakrishnan, and J. Allen Haynes
Oak Ridge National Laboratory

Arun Devaraj and Bharat Gwalani - Pacific Northwest National Laboratory

Lianghua Xiong and Dileep Singh - Argonne National Laboratory

June 4th, 2020

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Program Overview: VTO Powertrain Materials Core Program

Timeline/Budget

- Budget: $30M/5 years
- Program Start: Oct 2018
- Program End: Sept 2023
- 30% Complete

Barriers

- Increasing engine power densities & higher efficiency engines; resulting in increasingly extreme materials demands (increased pressure and/or temperature)
- Affordability of advanced engine materials & components
- Accelerating development time of advanced materials
- Scaling new materials technologies to commercialization

FY20 Program Research Thrusts	FY20 Budget	Participating Labs
1. Cost Effective LW High Temp Engine Alloys	**$1.05M**	**ORNL**
2. Cost Effective Higher Temp Engine Alloys	$1.525M	ORNL, PNNL
3. Additive Manufacturing of Powertrain Alloys	$1.075M	ORNL
4A. Advanced Characterization	$1.025M	ORNL, PNNL, ANL
4B. Advanced Computation	$0.60M	ORNL
5. Exploratory Research: Emerging Technologies	$0.75M	ORNL, PNNL, ANL

Partners

- Program Lead Lab
  - Oak Ridge National Lab (ORNL)
- Program Partner Labs
  - Pacific Northwest National Lab (PNNL)
  - Argonne National Lab (ANL)

Program structure includes three alloy development thrusts (1-3), a foundational support thrust (4), and a thrust for one-year exploratory projects (5).

Project Overview: Subtask1A1: Fundamental Studies of Complex Precipitation Pathways Pathways

Timeline/Budget

- Project start: Oct 2018
- Project end: Sep 2021
- Percent complete: 30%
- **1A1 Budget**
  - **FY19: $350k**
  - **FY20: $350K**

Barriers

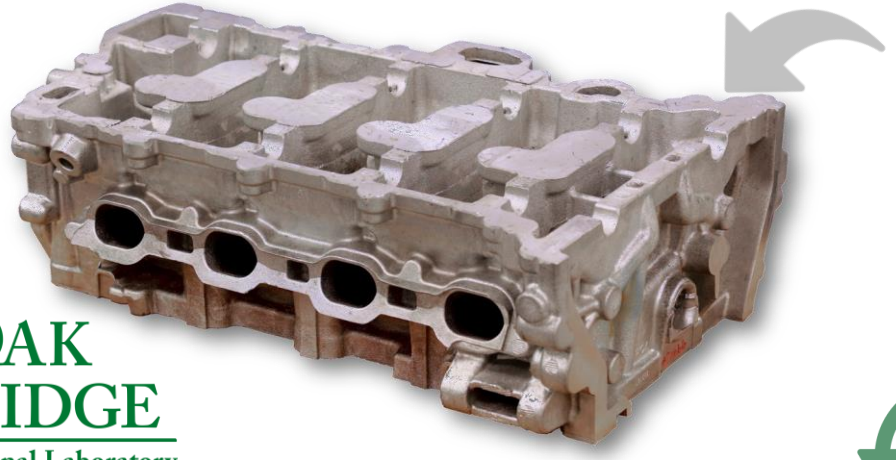
- Fundamental precipitation/growth/coarsening mechanisms of key precipitates in lightweight alloys are not well understood.
- Thermodynamic equilibrium and diffusion kinetics of lightweight alloys are not readily available.
- Processing-structure-property relationship in lightweight alloys are not yet completely understood/established.

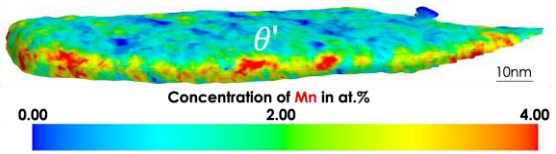
Thrust 1: Tasks/Subtasks	TRL	PI(s)	FY19	FY20
Task 1A. New Al Alloys with Improved High Temperature Performance				
• 1A1. Fundamental studies of complex precipitation pathways	**Low**	**Shin**	**$350k**	**$350k**
• 1A2. New higher performance Al alloys (>400C)	Low	Shyam	$400k	$375k
Task 1B. New AlCuMnZr alloy variants with tailored performance				
• 1B1. Intermediate temperature variants of cast ACMZ alloys	Mid	Shyam	$300k	$225k
• 1B2. Commercial collaborations for ACMZ alloys	Mid	Shyam	$125k	$100k
		Subtotals	**$1,175k**	**$1,050k**

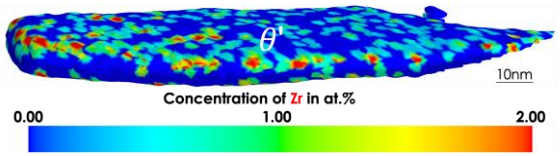
Partners

- Subtask 1A1 Lead
  - Oak Ridge National Lab (ORNL)
- Thrust 4
  - Oak Ridge National Lab (ORNL)
  - Argonne National Lab (ANL)
  - Pacific Northwest National Lab (PNNL)

Developing advanced lightweight high-temperature alloys to increase the efficiency of internal combustion engines







ORNL developed **Al**Cu**M**n**Z**r alloy in **4 years** from a concept to full engine testing **by identifying key mechanism for stabilizing** meta-stable θ'-Al_2Cu at high-temperatures.

Alloy Development (Thrust 1) – Chemistry and Heat Treatment

Atomistic Behavior → *Microstructural Evolution* → *Mechanical Property Prediction*

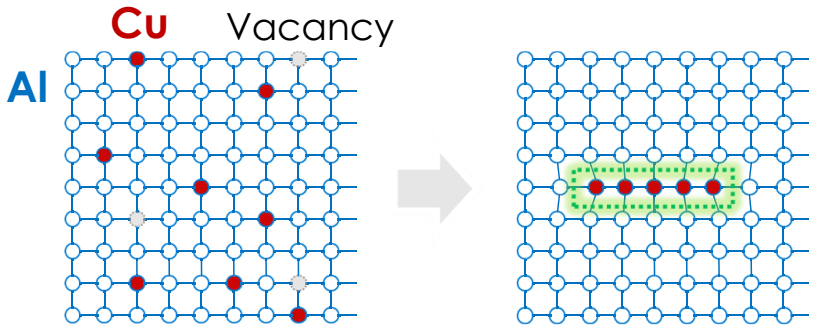
Task 1A1 (MAT187)
This presentation

Task 1A2

Task 1B (MAT188)
Next presentation

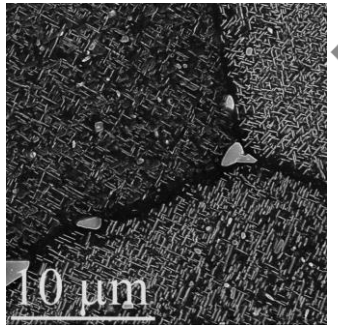
Fundamental research to unveil the underlying mechanisms of complex precipitation pathways in lightweight alloys is required.

Retaining desirable θ'-Al_2Cu at elevated temperatures to increase the operation temperature of internal combustion engines

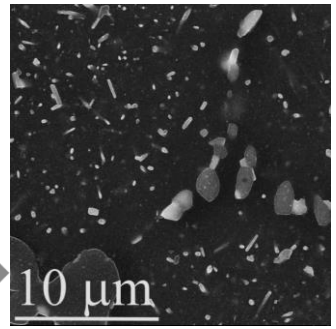


supersaturated solid solution (extra Cu)

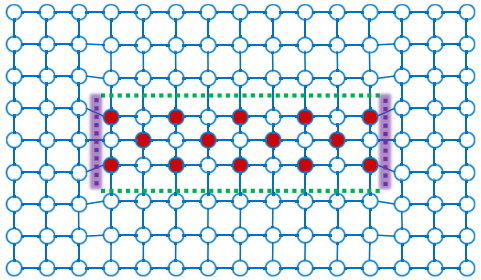
GP zone
coherent interface



high strength w/ thin θ'



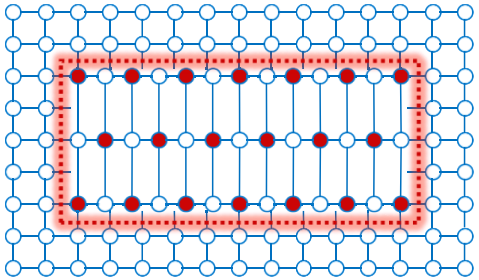
low strength w/ equiaxed θ



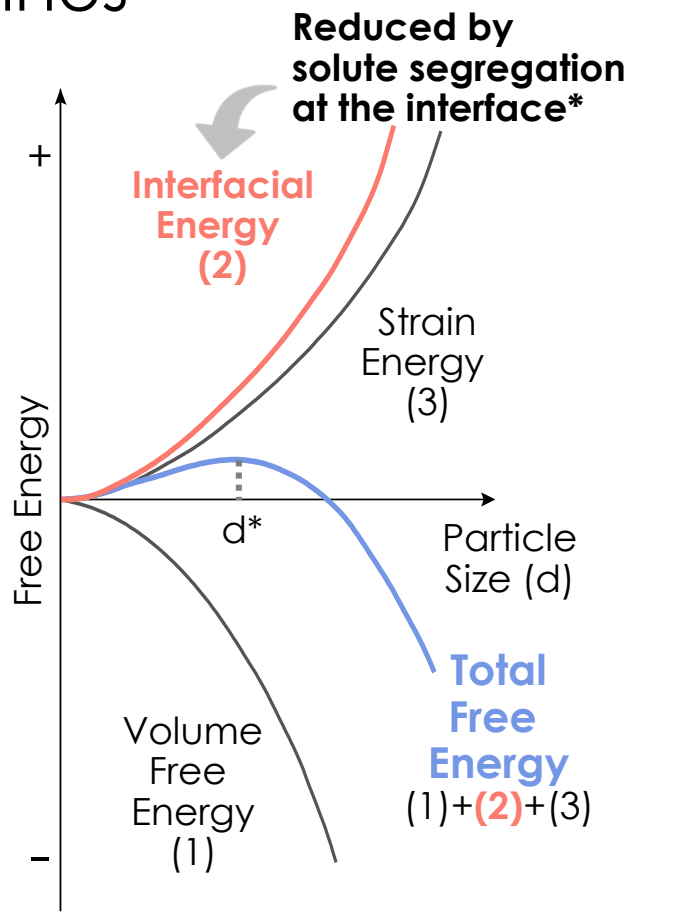
θ'-Al_2Cu
semi-coherent interface

detrimental phase transformation

accelerate with high temp



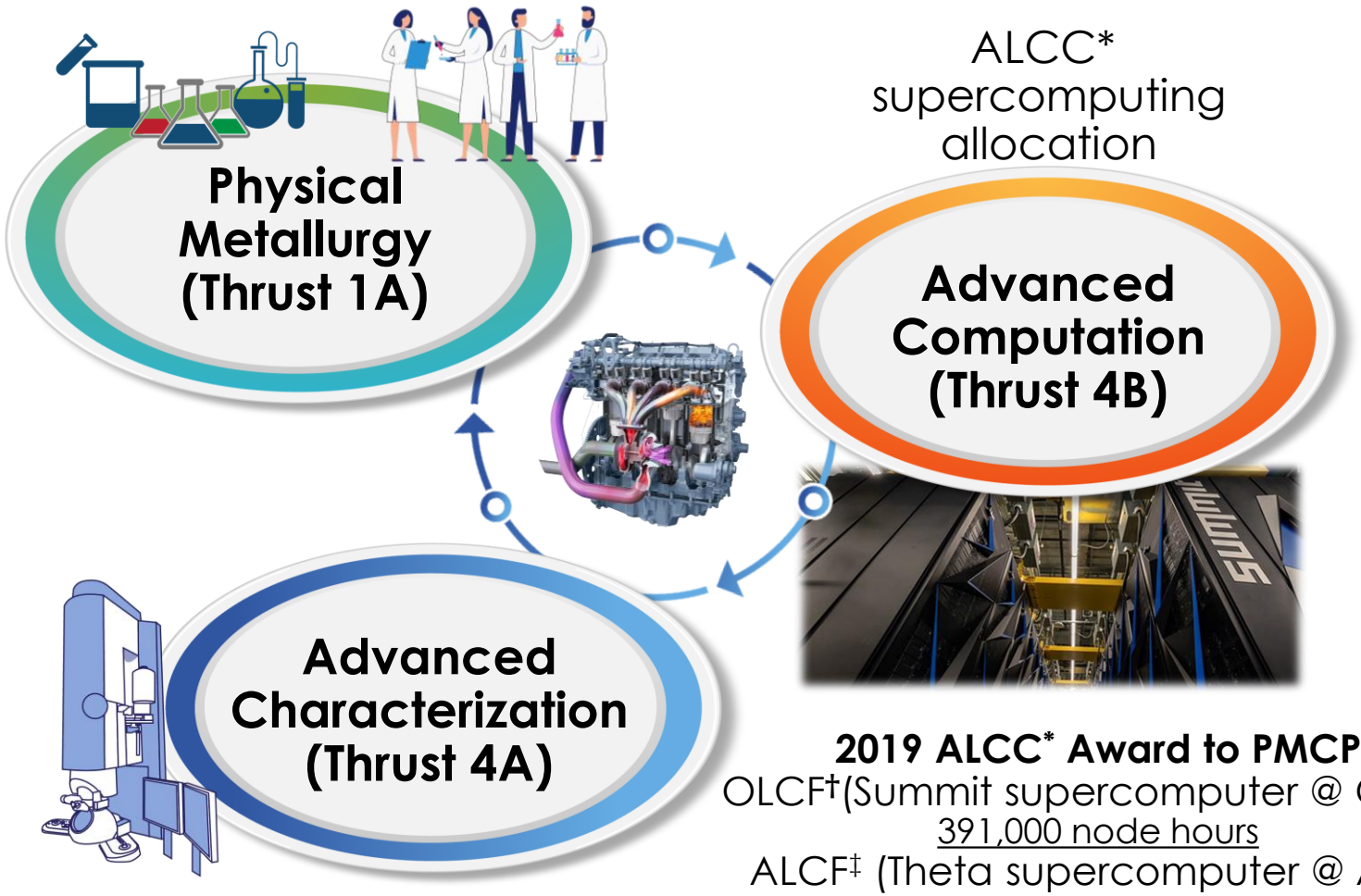
θ-Al_2Cu
Incoherent interface



*Shyam et al., Mater. Sci. Eng. A 765 (2019), 138279
Shin et al., Acta Mater. 141 (2017), 342

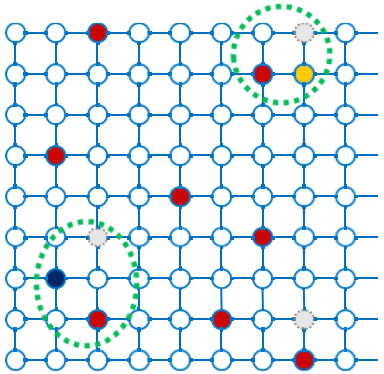
Atomistic-level engineering to harness the stability of θ'-Al_2Cu at high temperatures

Accelerated exploration of high-temperatures alloys with modern characterization and supercomputing between three labs - to unravel complex precipitation pathways in lightweight alloys

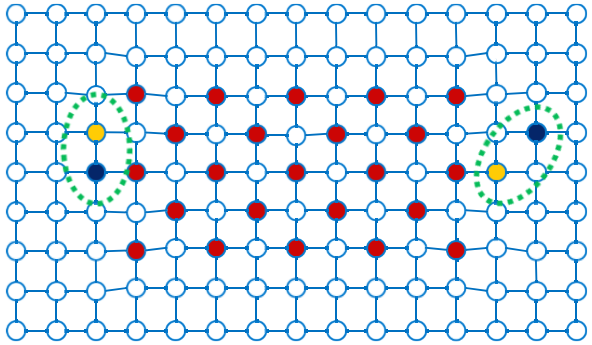


2019 ALCC* Award to PMCP
OLCF†(Summit supercomputer @ ORNL)
391,000 node hours
ALCF‡ (Theta supercomputer @ ANL)

Precipitation pathways in Al-alloys



Clustering behavior among key alloying elements and vacancies



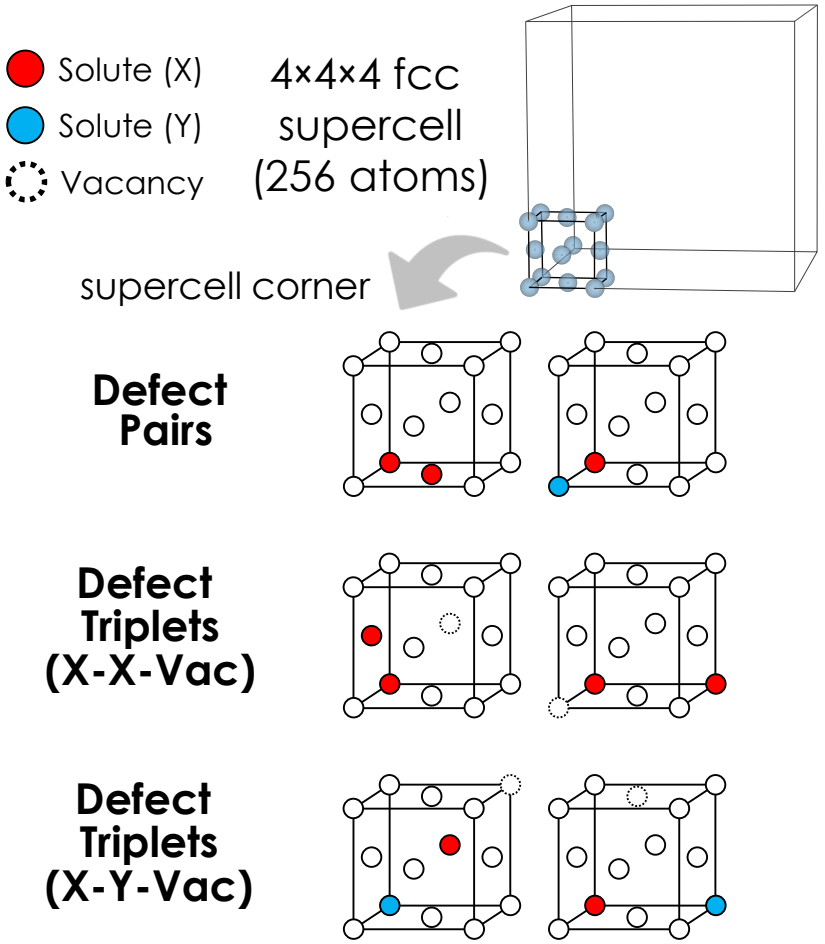
Solute segregation behavior to stabilize key precipitates

*ASCR Leadership Computing Challenge, †Oak Ridge Leadership Computing Facilities, ‡Argonne Leadership Computing Facilities

Milestones for Thrust 1A

Due	Milestone Description	Status
FY20 Q1	Submit joint experimental and theory publication on non-equilibrium interfacial solute segregation.	**Completed**
FY20 Q2	Finish creation of a solute-vacancy segregation energy database for aluminum alloys.	**Completed**
FY20 Q3	Comparison of neutron diffraction data with crystal plasticity predictions in a high temperature aluminum alloy.	**Completed**
FY20 Q4	Submit manuscript on neutron diffraction analysis of deformation in an aluminum alloy. (Go/No Go)	**On Track**

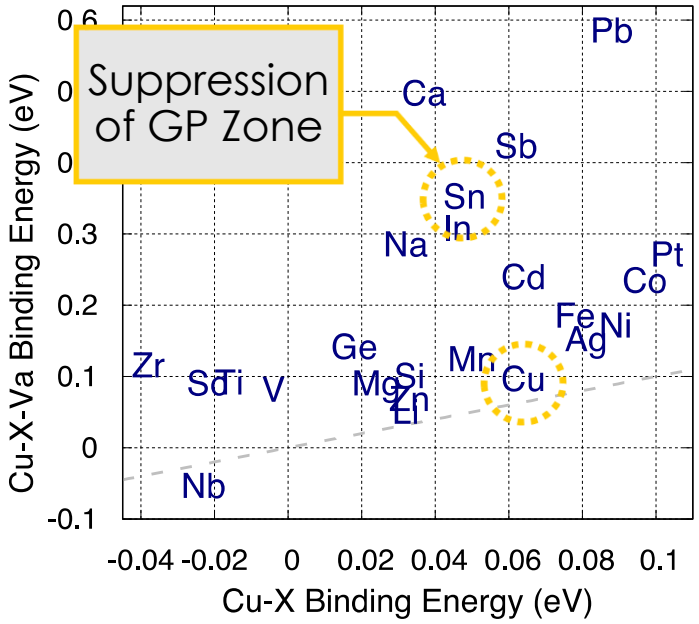
Solute-vacancy clustering in Al is important in understanding precipitation and alloy heat treatment, but largely unknown

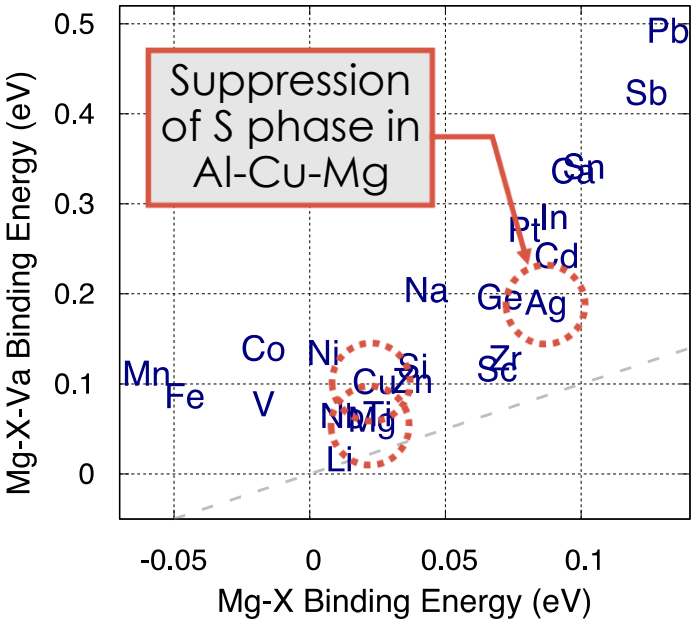


Select configurations are shown

High-throughput density functional theory (DFT) scaled to a petascale supercomputer allowed quantitative simulation of affinities between solute clusters and vacancies in the aluminum matrix – to explain early stage nucleation and growth/coarsening of key precipitates

The higher, the more favorable binding with vacancies

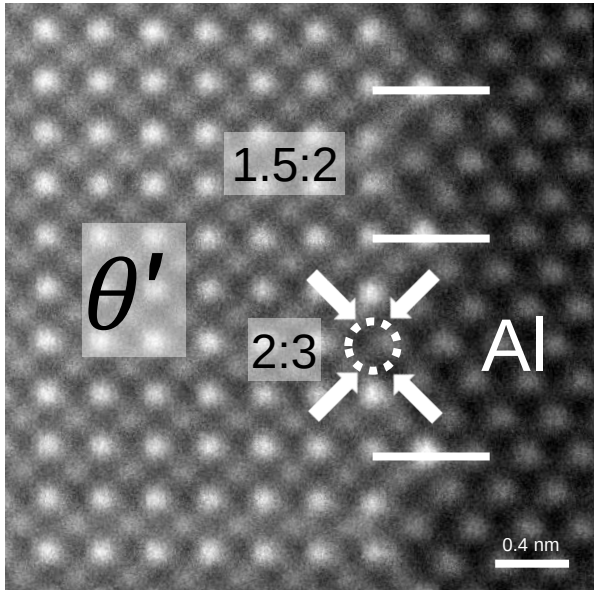


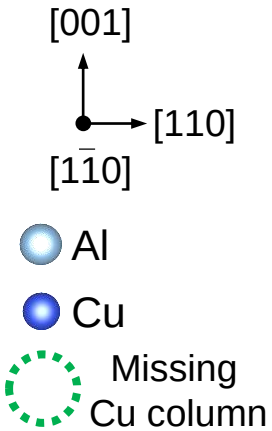


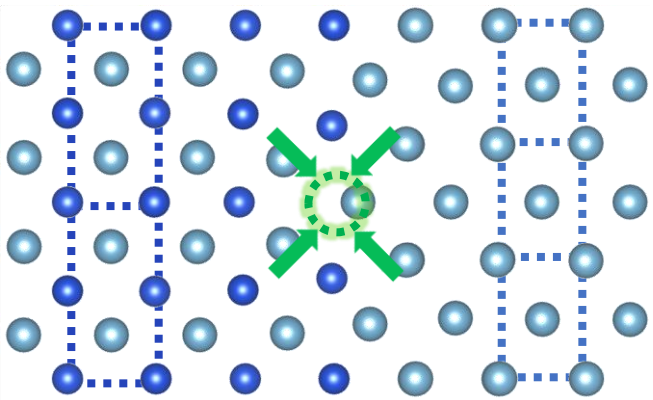
First-principles total energies of 1,621 supercells were computed on ORNL Summit in a few days

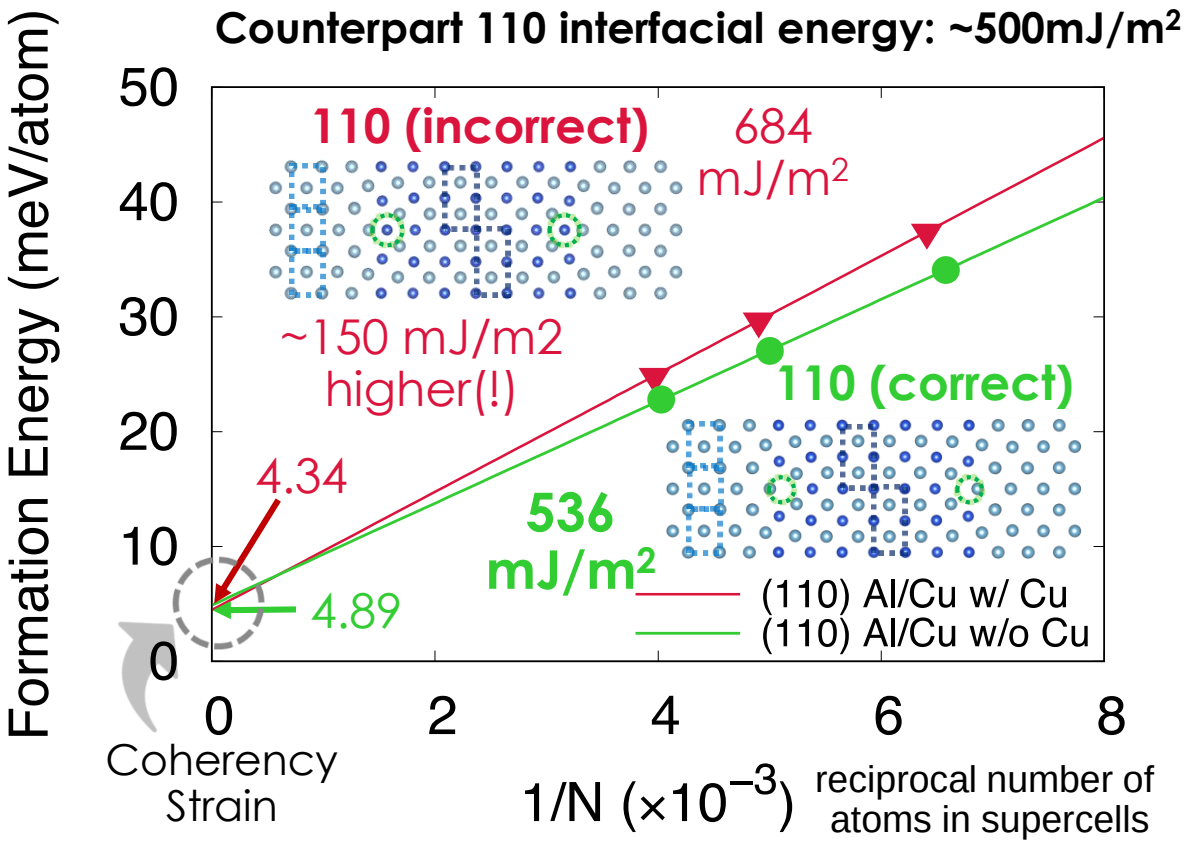
STEM* guided supercell construction of previously under-investigated 110 Al/θ'-Al_2Cu semi-coherent interface

The highest resolution microscope at ORNL





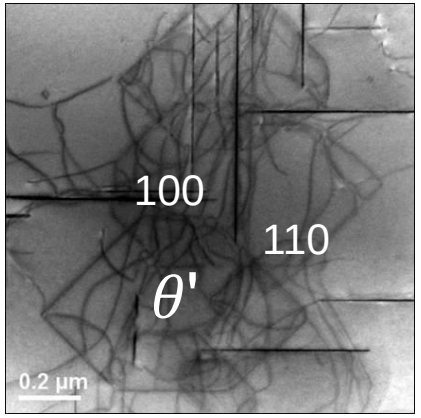


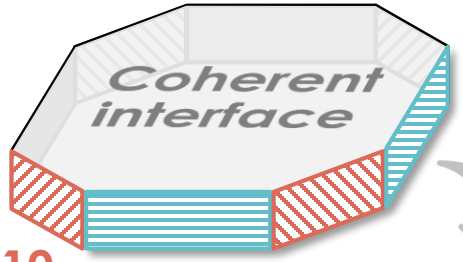


An atomistic model that represents a key semi-coherent interface between Al and θ'-Al_2Cu has been developed - using the actual interface structure from STEM

*STEM: Scanning Tunneling Electron Microscopy

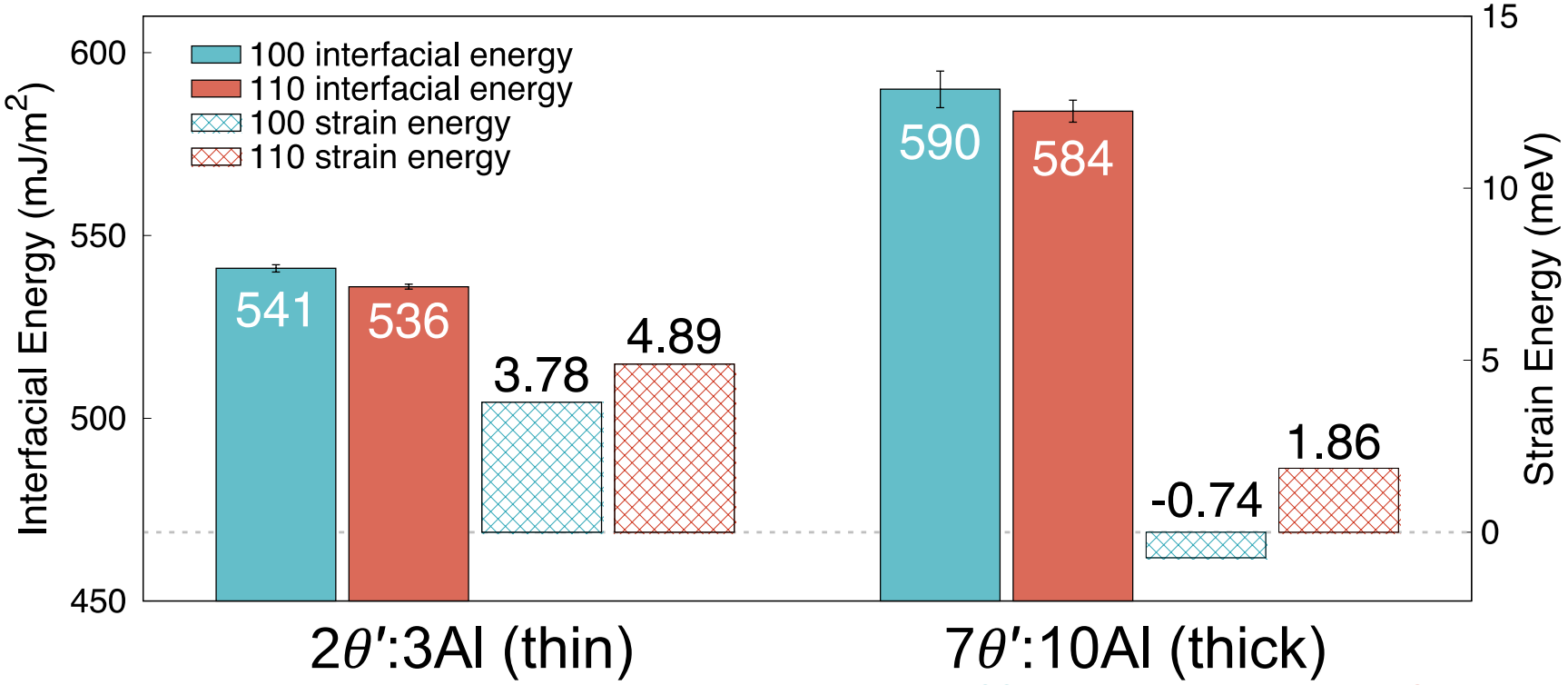
STEM and DFT identified the interplay between interfacial and strain energies of 100 and 110 orientations of Al/θ' semi-coherent interface

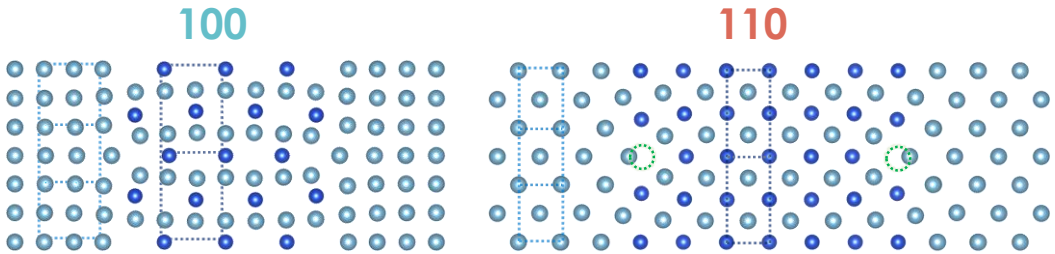


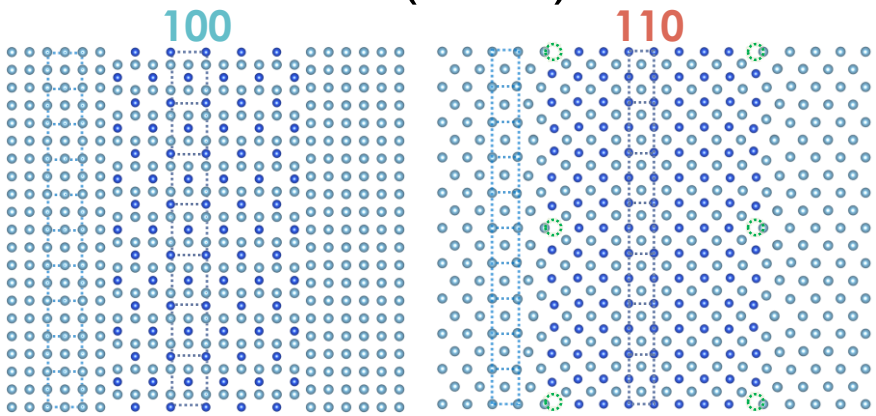


110 100

Semi-coherent interface



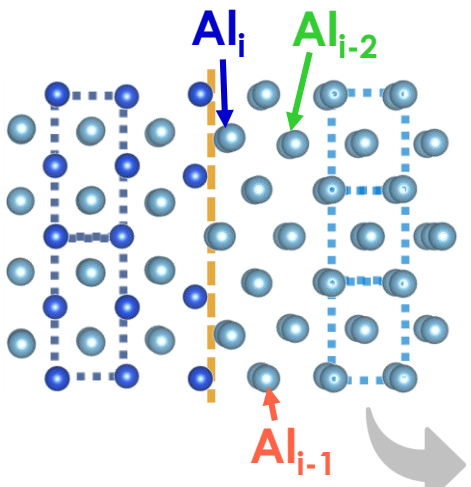




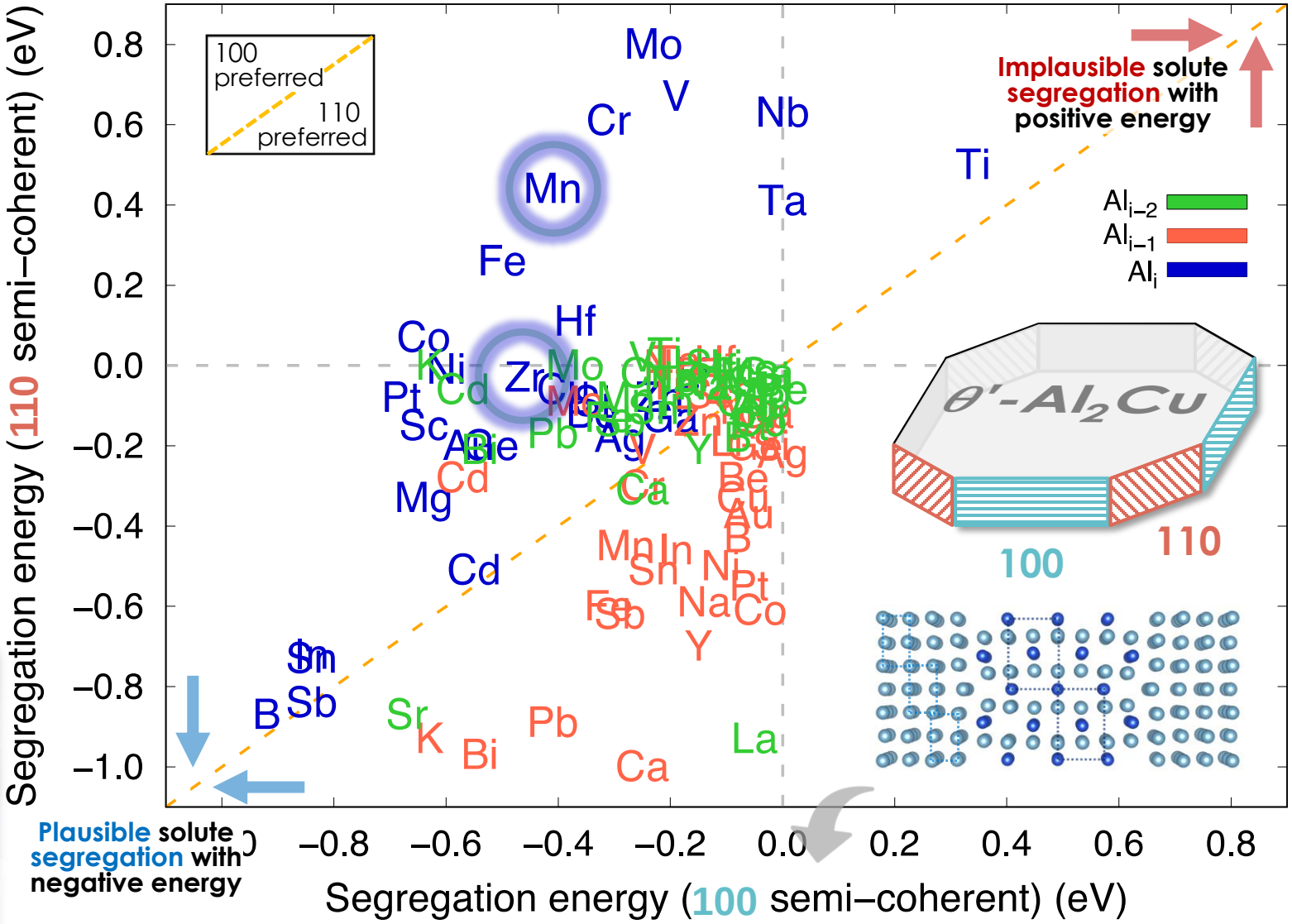
Al Cu Missing Cu column

Theory predicted solute segregation of semi-coherent interface that affects precipitate morphology is largely different depends on the orientation

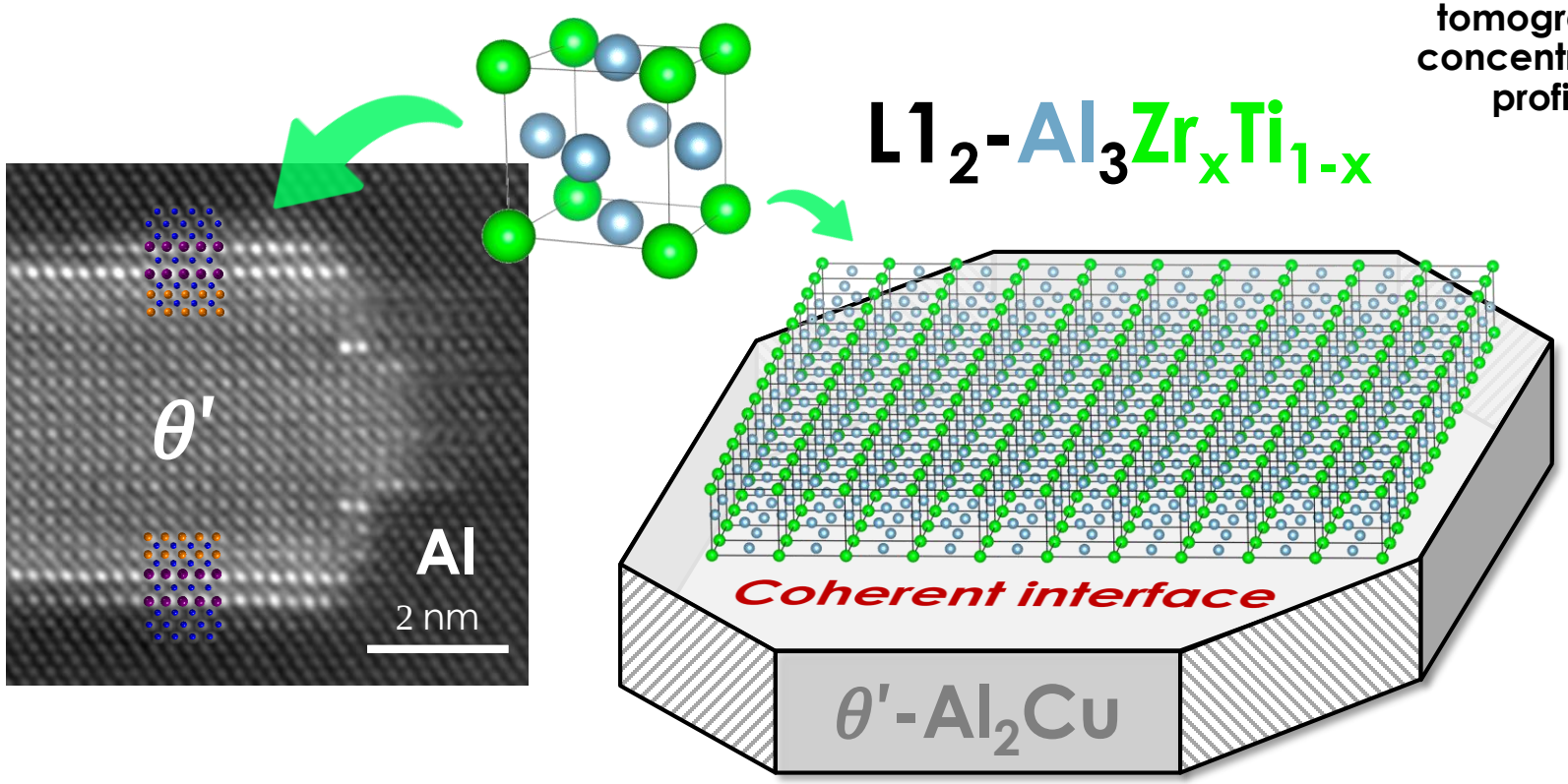
STEM-guided supercell model



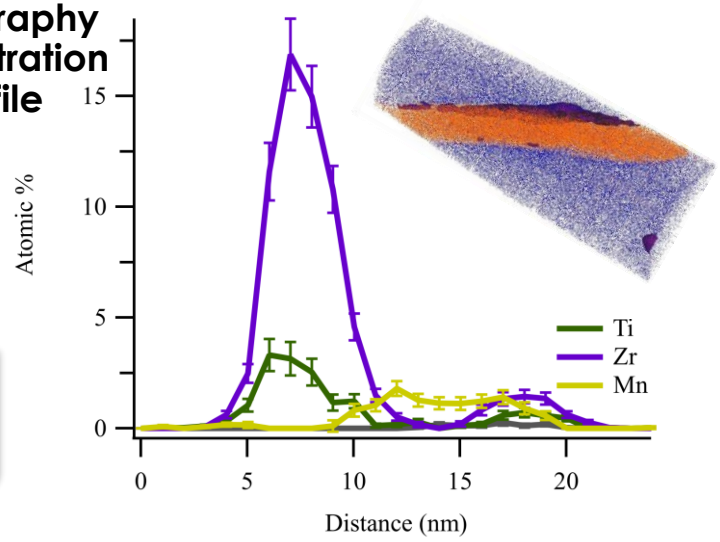
Rapid construction of solute segregation energy database using world #1 supercomputer at Oak Ridge National Laboratory



STEM and APT* reveals the formation of $L1_2$-Al_3X phase on Al/θ'-Al_2Cu coherent interface



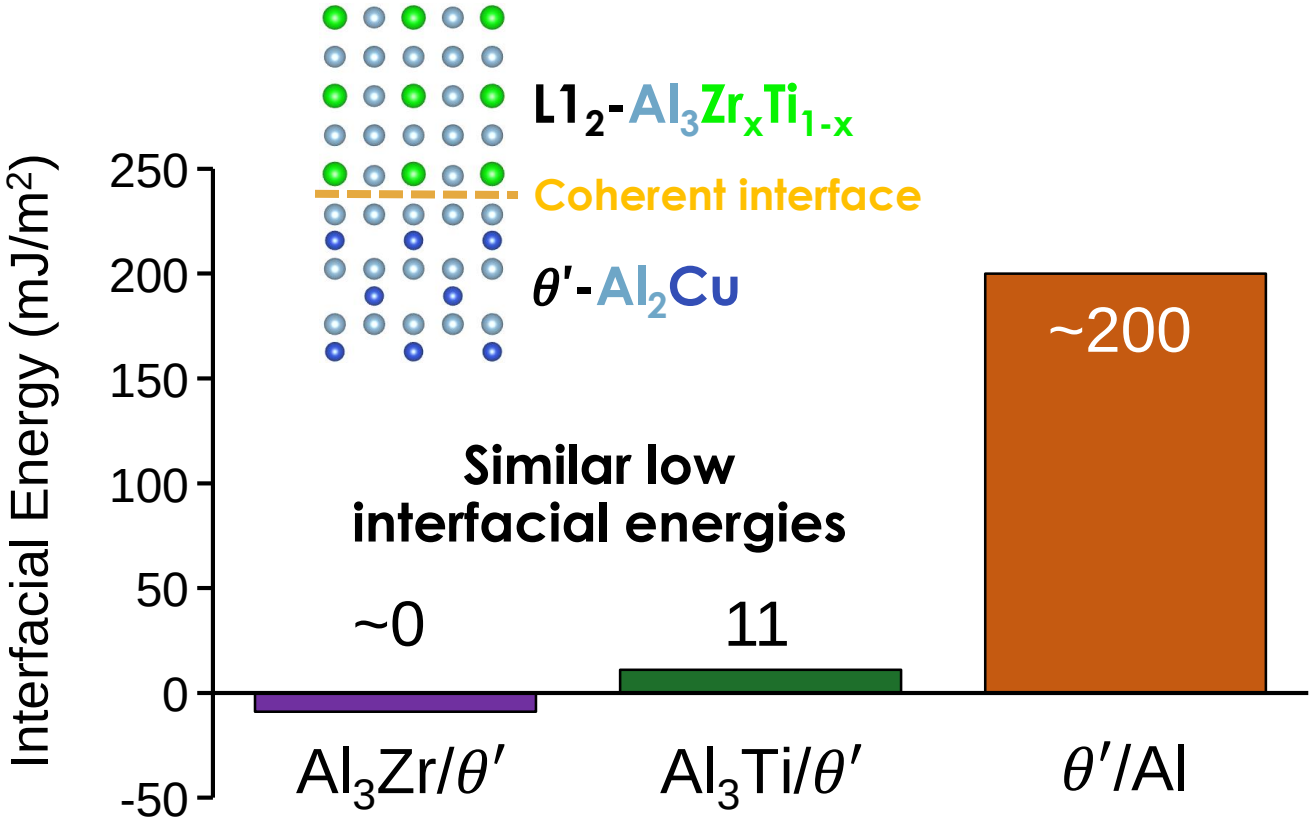
*atom probe tomography concentration profile

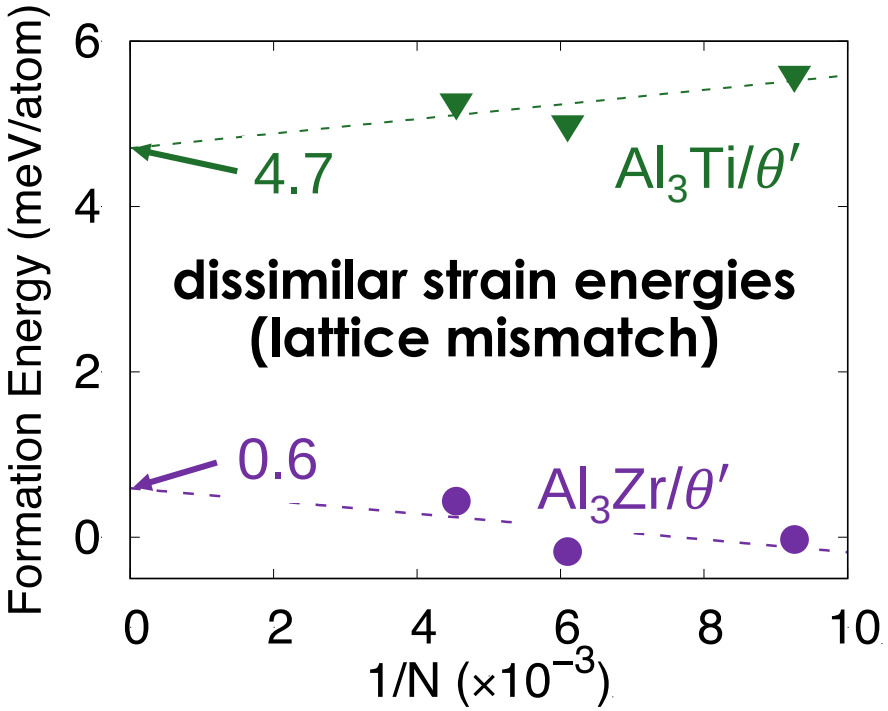


- Zr and Ti add up to 25 at%
- Synergistics effect between Zr/Ti and Mn
- Mn: **faster** diffusion, **low** temp
- Zr,Ti: **slow** diffusion, **high** temp

Multiple mechanisms to stabilize θ' at elevated temperatures: co-precipitation of $L1_2$-Al_3(Zr,Ti) at the Al/θ' coherent interface provides an additional alloy design strategy for higher-temperature strengthening

Theoretical calculations (via DFT) reveal very low interfacial energy between θ'-Al_2Cu and $L1_2$-$Al_3(Zr,Ti)$ at the coherent interface





Newly identified underlying mechanism of stabilizing θ'-Al_2Cu at high temperatures via $L1_2$ co-precipitation

Collaboration and Coordination with Other Institutions

Pacific Northwest NATIONAL LABORATORY

Argonne NATIONAL LABORATORY

OAK RIDGE National Laboratory | CENTER FOR NANOPHASE MATERIALS SCIENCES

OAK RIDGE National Laboratory | LEADERSHIP COMPUTING FACILITY

OAK RIDGE National Laboratory | SPALLATION NEUTRON SOURCE

PennState

THE UNIVERSITY OF TENNESSEE KNOXVILLE

- **Thrust 1: Experimental Validation**
- **Thrust 4A: Advanced Characterization**
- **Thrust 4B: Advanced Computation**

Remaining Challenges and Barriers

- Complex mechanisms of nucleation, growth, and coarsening of key precipitates in lightweight alloys have not been fully understood.
  - Significant experimental investigation and theoretical exploration efforts are desirable.
- Fundamental experimental data, e.g., equilibrium thermodynamics and diffusion kinetics, of lightweight alloys are largely missing.
  - High-throughput experimental measurements and computations from high-fidelity models are needed.

Response to Previous Year Reviewers' Comments

- Project was not reviewed last year

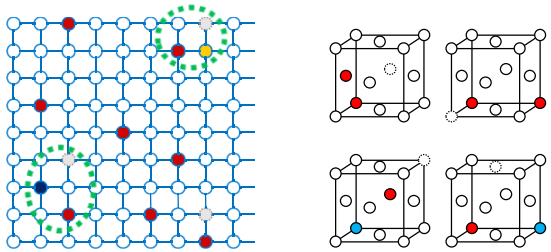
Proposed Future Research

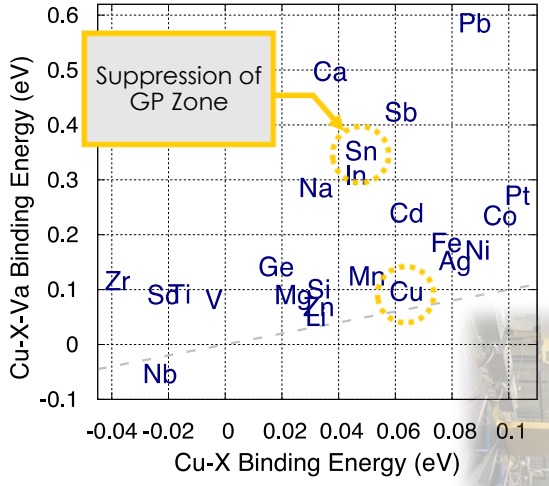
- Solubility of alloying element within θ'-Al_2Cu
  - Temperature dependency of solute partitioning in θ'
  - First-principles cluster expansion approach to construct DFT phase diagram
- Simulation of multiple solute segregation at the interface
  - Synergetic/detrimental effect as a function of solute composition
  - High-throughput DFT to populate training dataset for machine learning
- Thermodynamic stability investigation of key precipitate in Al-Ni system

Any proposed future work is subject to change based on funding levels.

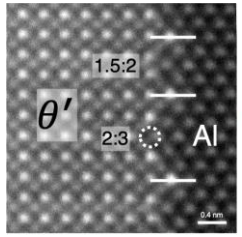
Subtask 1A1 promoted fundamental scientific understanding of lightweight alloys via advanced characterization and computation (Thrust 4A/4B) to support accelerated alloy design (Thrust 1)

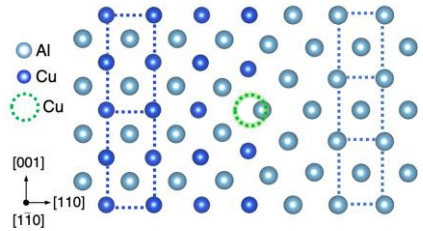
Solute-vacancy clustering in Al

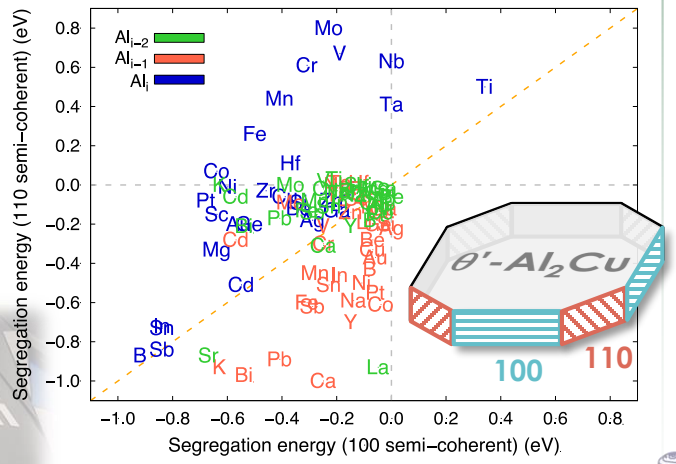




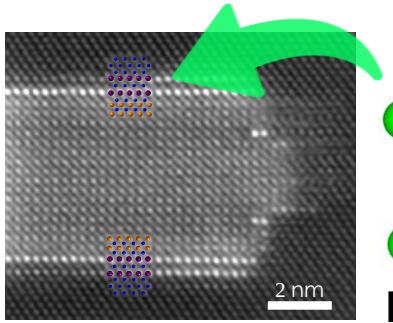
Solute segregation of 110 interface

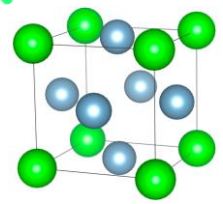




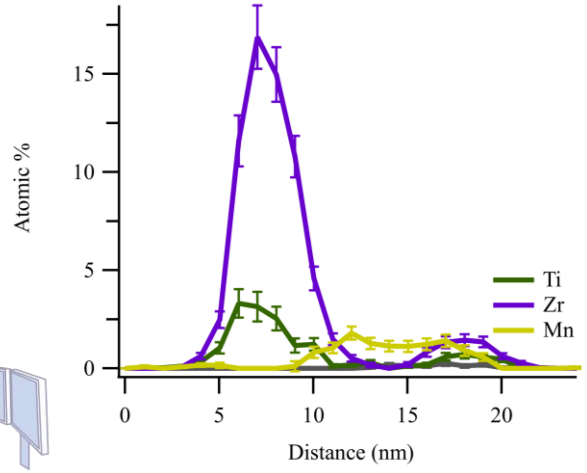


Co-precipitation of $L1_2$ at θ'-Al_2Cu





$L1_2$-$Al_3Zr_xTi_{1-x}$



Technical Back-Up Slides

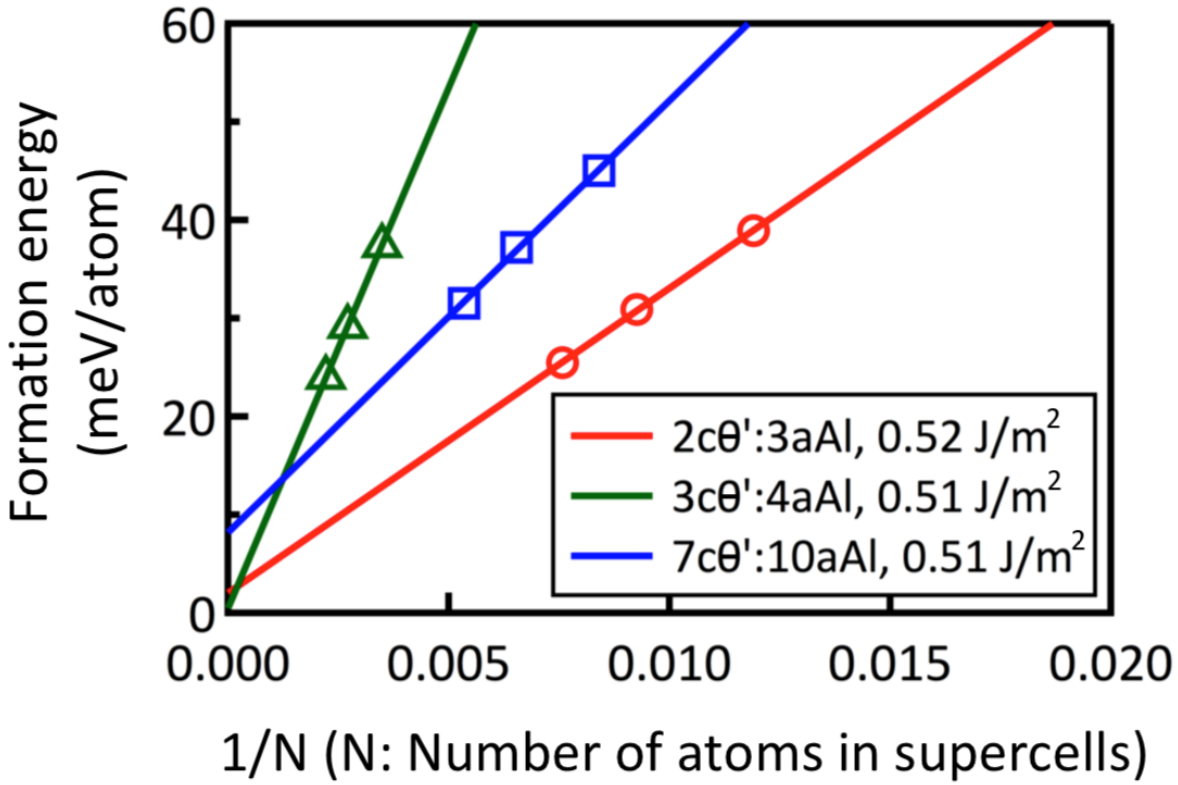
Size-variant interfacial energy calculations with strain

Energetic **penalty** to create interfaces w.r.t. reference states

$$\Delta E_f = [E_{\mathrm{Al_{a+2b}Cu_b}(\alpha,\theta')} - E_{\mathrm{Al_a}(\alpha)} - E_{\mathrm{Al_{2b}Cu_b}(\theta')}]/N$$

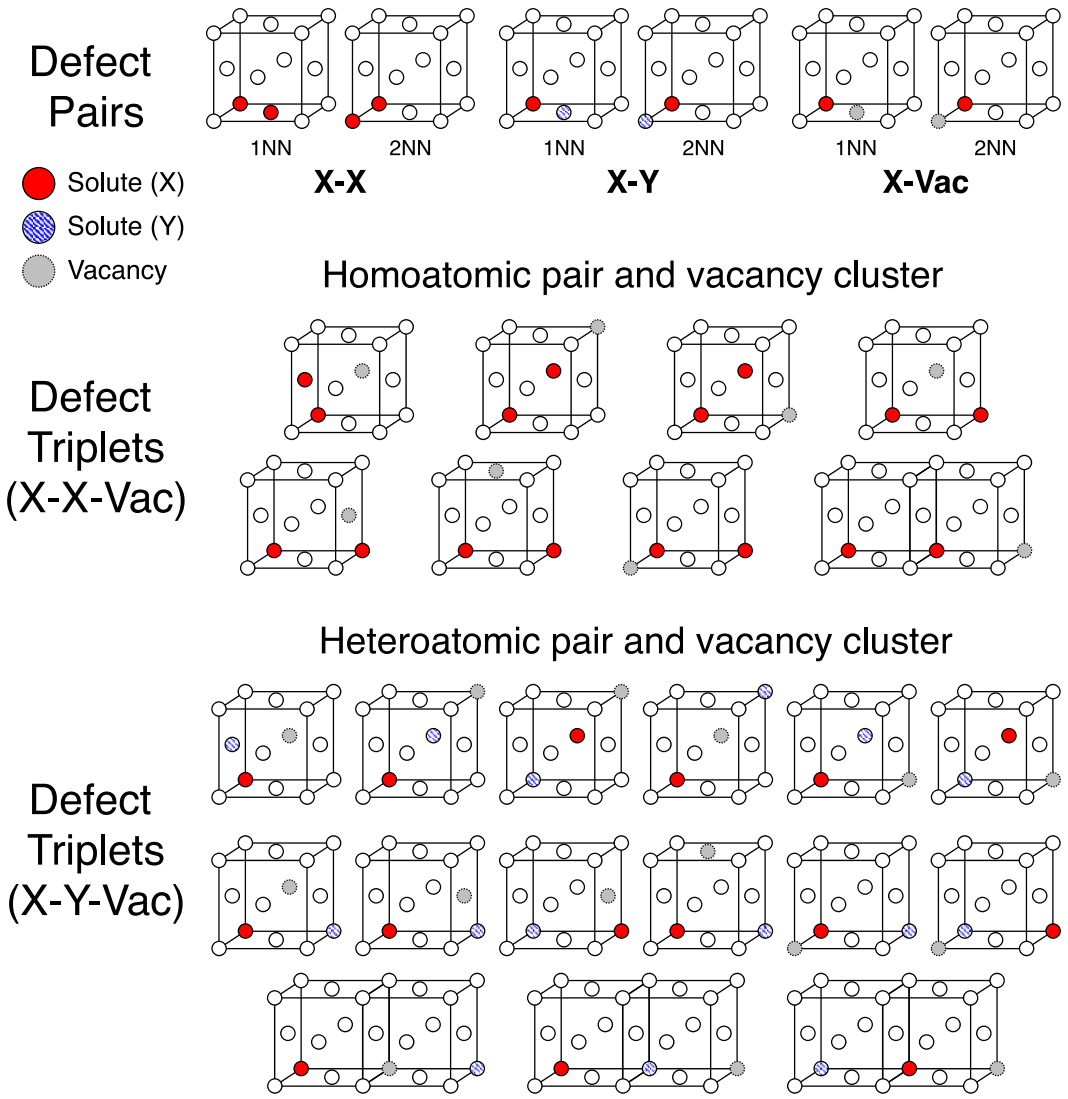
$$\Delta E_f = \boxed{\delta E_{cs}}(\alpha,\theta') + \frac{2\boxed{\sigma}A}{N}$$

E: total energy
N: total number of atoms
***E_{cs}*: coherency strain**
σ: interfacial energy
A: area



Kim, K.; Zhou, B. C.; Wolverton, C. Interfacial Stability of θ'/Al in Al-Cu Alloys. *Scr. Mater.* **2019**, *159*, 99–103.

Solute-vacancy clustering in Al is important in understanding precipitation and heat treatment, but largely unknown



$$-E_{bind}(X\text{-}X) = E(Al_{254}X_2) + E(Al_{256}) - 2E(Al_{255}X)$$

$$-E_{bind}(X\text{-}Y) = E(Al_{254}XY) + E(Al_{256}) - E(Al_{255}X) - E(Al_{255}Y)$$

$$-E_{bind}(X\text{-}\bullet) = E(Al_{254}X\bullet) + E(Al_{256}) - E(Al_{255}X) - E(Al_{255}\bullet)$$

$$-E_{bind}(X\text{-}Y\bullet) = E(Al_{253}XY\bullet) + E(Al_{256}) - E(Al_{254}XY) - E(Al_{255}\bullet)$$

$$= E(Al_{253}XY\bullet) + E(Al_{256}) - E(Al_{254}X\bullet) - E(Al_{255}Y)$$

$$= E(Al_{253}XY\bullet) + 2E(Al_{256}) - E(Al_{255}X) - E(Al_{255}Y) - E(Al_{255}\bullet)$$

Positive sign for favorable binding

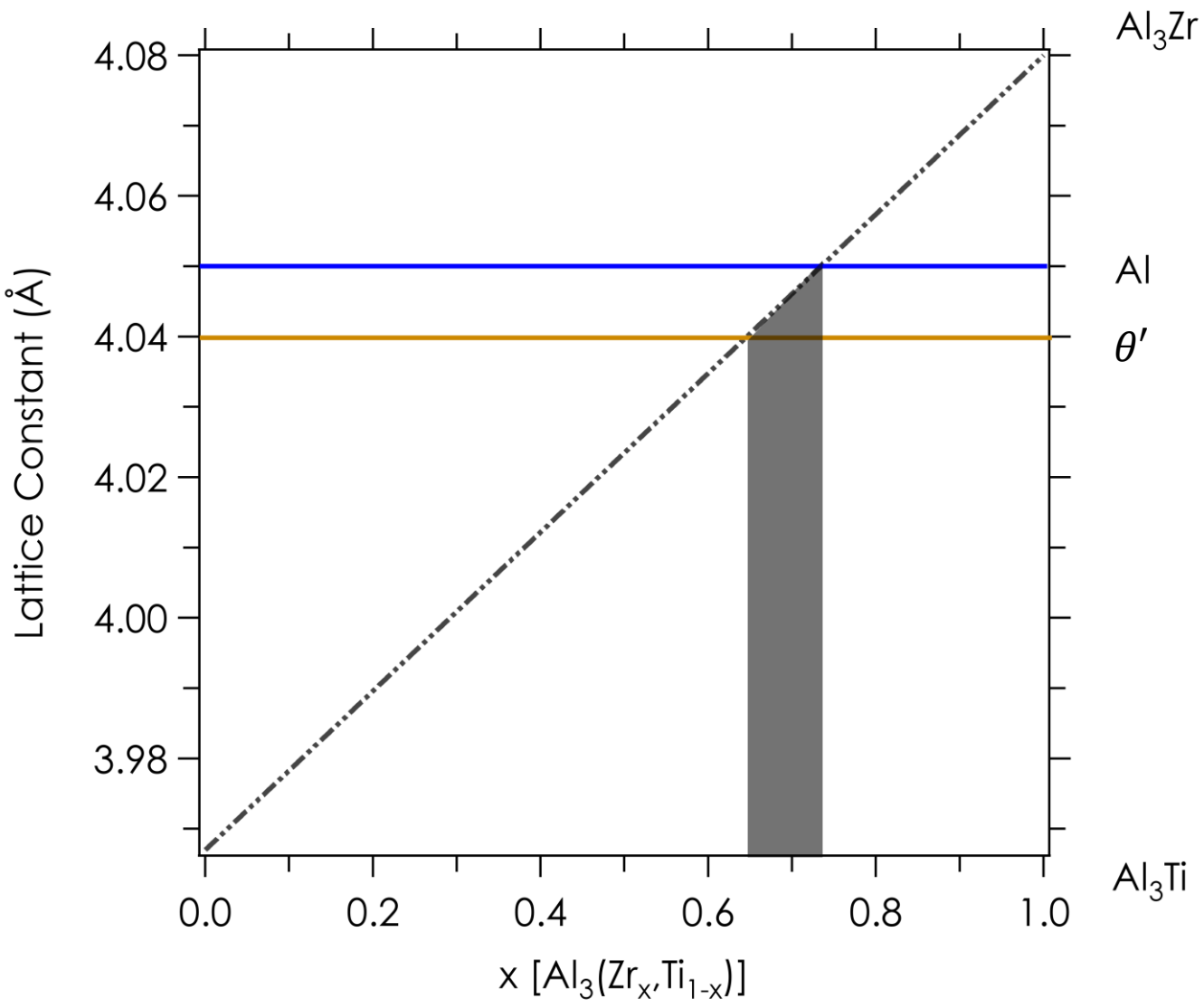
First-principles total energies of 1,621 supercells were computed on a DOE supercomputer

θ'/$L1_2$ Strain Energy – Vegard's Law

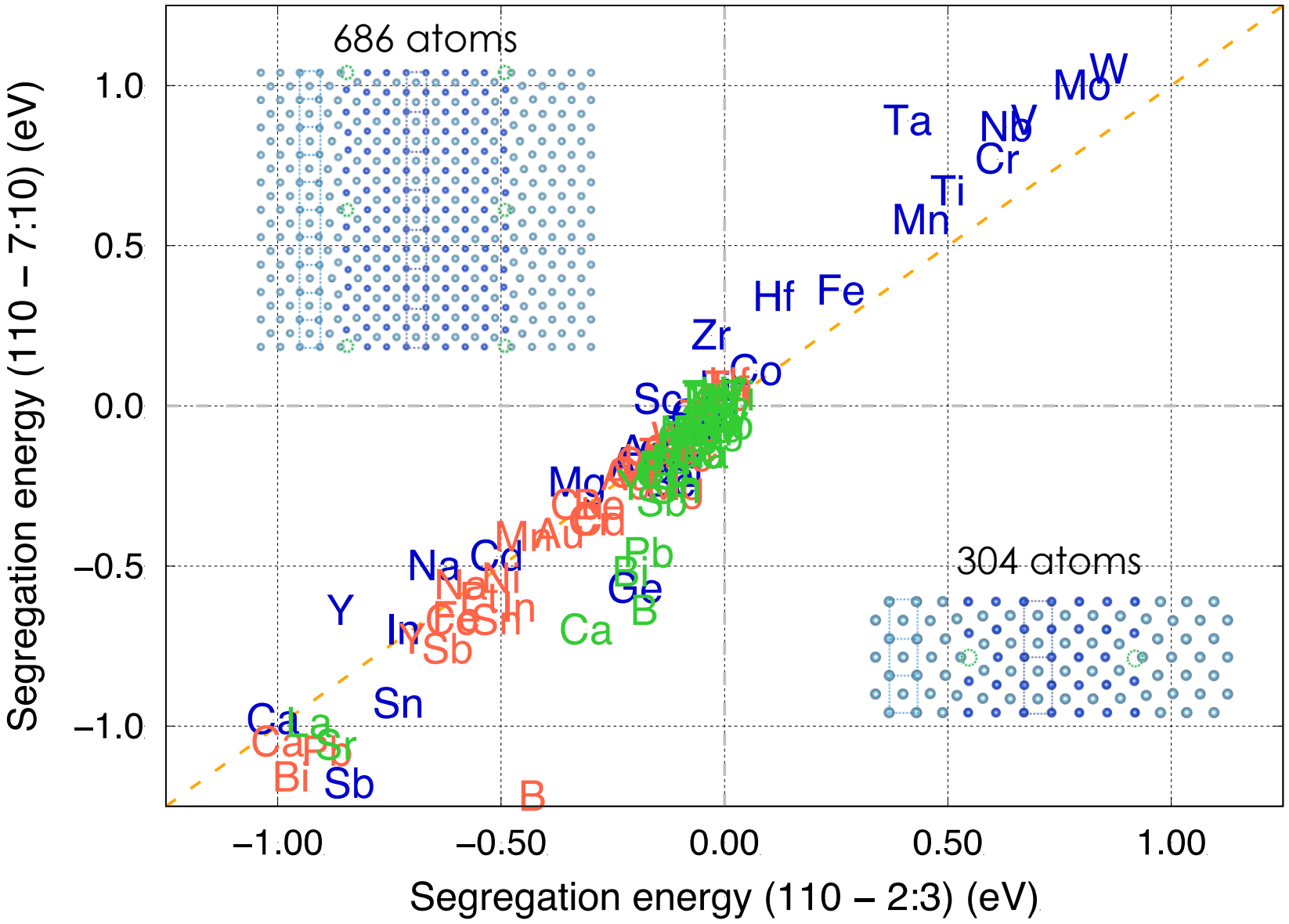
- $E_{Ti_s} = 4.7$ meV
- $E_{Zr_s} = 0.6$ meV

- Al_3Zr has a much lower strain energy than Al_3Ti
- Al_3Zr lattice constants (a)
  - $L1_2$ = 4.08 Å
  - $D0_{23}$ = 4.01 Å
- Al_3Ti lattice constants (a)
  - $L1_2$ = 3.97 Å
  - $D0_{22}$ = 3.85 Å
- α-Al = 4.05 Å
- θ' = 4.04 Å (001)

*Knipling, K. E. *et al.* DOI:10.3139/146.101249



Ideal range: x ~ 0.65-0.73

Isotropic solute segregation behavior between 2:3 and 7:10 models

Much larger supercell was required to correctly capture the 7:10 stacking ratio between θ' and fcc Al