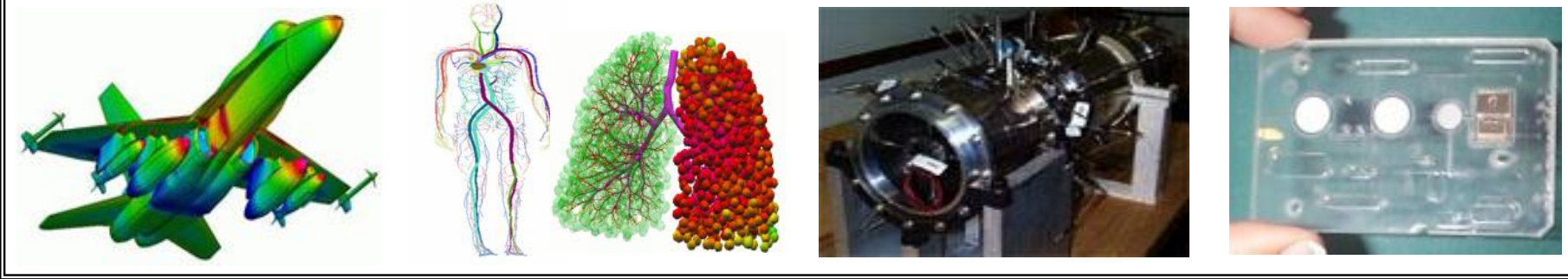
Delivering Breakthrough Solutions

AB-INITIO AND MULTI-SCALE STUDY OF Al-Ni-Fe ALLOY SYSTEMS



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DE-FE0005867 award
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1st Year Project Presentation

March, 2012

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AGENDA

- OBJECTIVES
- "THE TEAM"
- SIGNIFICANT FINDINGS: YEAR 1

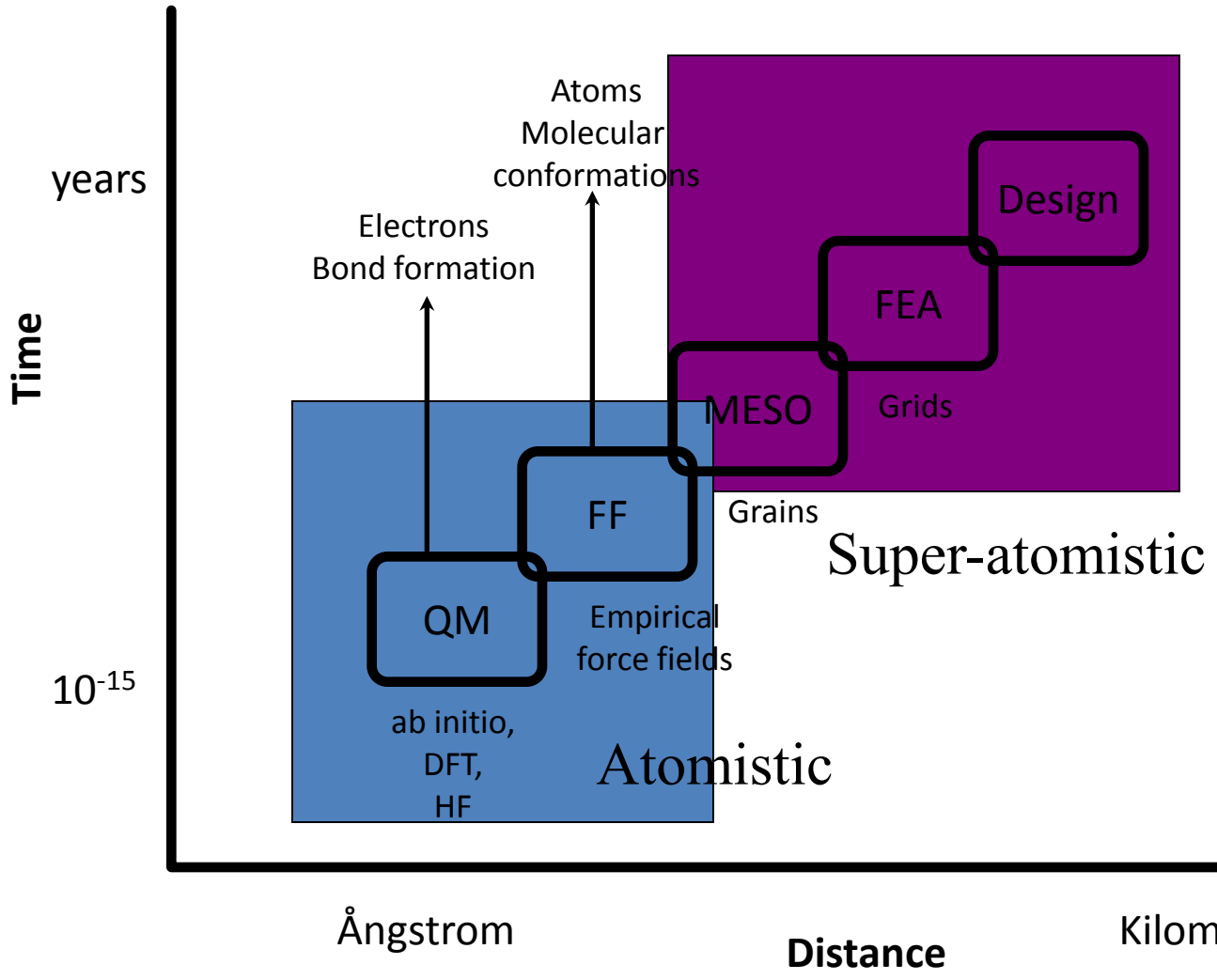
  - REAXFF FORCE FIELD DEVELOPMEMT FOR Fe/Ni/Al/S

  - APPLICATION: MULTISCALE ANALYSIS OF ALLOY SYSTEMS
- SUMMARY
- QUESTIONS AND DISCUSSION

MATERIALS FOR A CLEAN ENERGY ECONOMY

- New materials with micro-to-nano features (e.g., grain shape and size distribution, grain boundary character, grain orientation, and texture) are of vital importance for a clean energy economy.
- However, the current trial-and-error material development methodology is expensive (> $10M) and time consuming (10 to 20 years).
- Activity and excitement over new materials have enhanced, driven by government investment (http://www.whitehouse.gov/blog/2011/06/24/materials-genome-initiative-renaissance-american-manufacturing).
- Increasing trend is to use the advances in multi-scale simulations and high-throughput screening.
- CFD Research Corporation (CFDRC) and Pennsylvania State University (PSU) have teamed in this project to develop, demonstrate, and validate computational capabilities for predictive analysis of interactions at the grain boundary of refractory alloys.

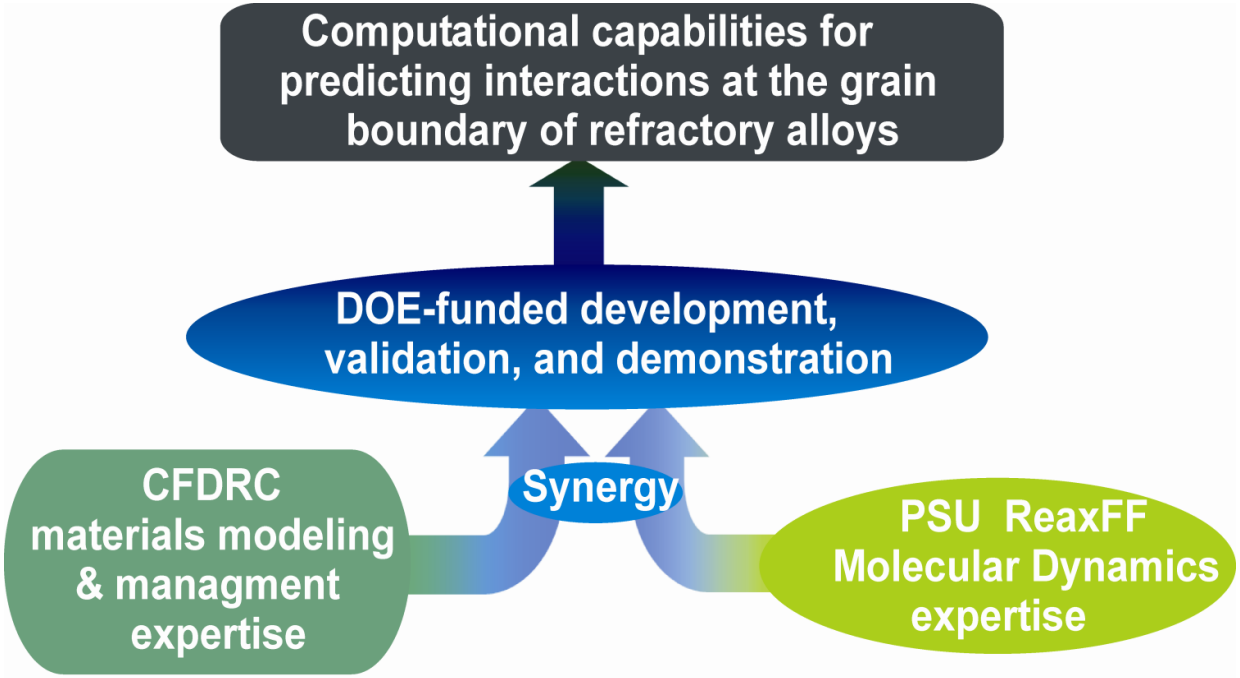
MULTISCALE MODELING FRAMEWORK



QM methods:
- Fundamental
- Expensive, only small systems

FF methods
- Empirical; need to be trained
- Much cheaper than QM, can be applied to much larger systems

OVERALL PROJECT OBJECTIVES



- **The overall objectives of the proposed project are:**
  - **Develop computational capabilities for predictive analysis of grain boundary interactions using large-scale ReaxFF-Molecular Dynamics (MD) simulations**
  - **Assess degradation mechanisms, and**
  - **Design approach to limit segregation at the grain boundaries of refractories for coal gasification and related processes**

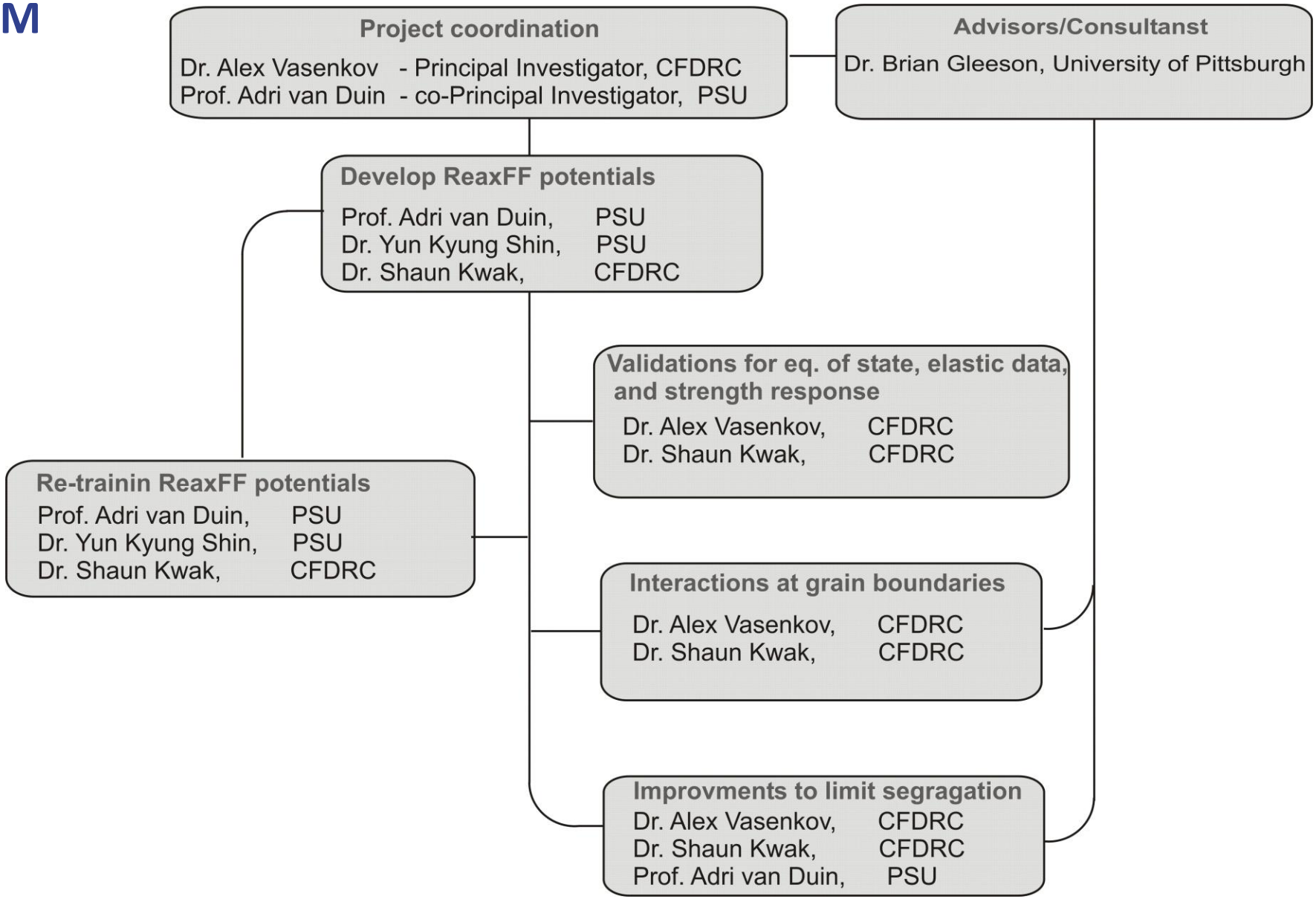
SPECIFIC PROJECT OBJECTIVES

- **More specific Year 1 technical objectives are:**

  - **Demonstrate the feasibility by developing ReaxFF parameters for Ni/Fe/Al/O/S interactions and reproducing trends observed for elemental segregation.**

  - **Validate ReaxFF potentials against literature data for equation of state and elastic data.**

TEAM


Project coordination
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Prof. Adri van Duin - co-Principal Investigator, PSU
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Develop ReaxFF potentials
Prof. Adri van Duin, PSU
Dr. Yun Kyung Shin, PSU
Dr. Shaun Kwak, CFDRC
Validations for eq. of state, elastic data, and strength response
Dr. Alex Vasenkov, CFDRC
Dr. Shaun Kwak, CFDRC
Re-trainin ReaxFF potentials
Prof. Adri van Duin, PSU
Dr. Yun Kyung Shin, PSU
Dr. Shaun Kwak, CFDRC
Interactions at grain boundaries
Dr. Alex Vasenkov, CFDRC
Dr. Shaun Kwak, CFDRC
Improvments to limit segragation
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CFD Research Corporation

Advanced Technology and Service Company

- Supporting Federal Agencies and global businesses since 1987
- Over 70% staff with advanced degrees
- 50+ patents (awarded & pending)

CFDRC develops cutting-edge technologies and provides innovative solutions for:

- **Energy & Materials**
- **Biomedical & Life Sciences**
- **Aerospace & Defense**

HQ – Huntsville, AL

Bio-Laboratories
HAIB, Huntsville, AL

Engineering T&E
Scottsboro, AL

Gov't Sites

MSFC, Huntsville, AL

USAARL,Ft. Rucker, AL

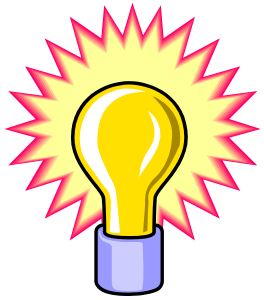
Why CFDRC? *Valuable Technology Partner*

Pioneering Physics-based Simulations

Coupled Multi-physics, Multi-scale, Multi-fidelity simulations of fluid, thermal, chemical, mechanical, electrical and biological phenomena for **real world** applications.

→ ***Better insights and better decisions for:***

- new concepts and designs
- improved operations and safety
- reduced development time and cost



Complimentary Design, Fabrication, T&E Expertise and Facilities for:

- Combustion, Propulsion and power systems
- Biomedical and Energy devices

→ ***Facilitates better products & better systems.***

SIGNIFICANT FINDINGS: YEAR 1

A. REAXFF DEVELOPMENT – Fe/Ni/Al/S

ALLOY MODELING FROM FIRST PRINCIPLES

Method: Plane-wave Basis Density Functional Theory (DFT)

- All DFT calculations were performed using **VASP 4.6**.

- 0 K electronic structures were calculated by solving the Kohn-Sham equation using plane-wave basis set.

- Structures were optimized by decoupling the quantum representation of electrons from the classical representation of nuclei (Born-Oppenheimer approximation).

More calculation details:

- Projector-augmented-wave (PAW) method for ion-electron potential
- Perdew-Burke-Ernzerhof (PBE) exchange correlation functional
- Plane-wave cut off energy of 400 eV (standard for oxides and sulfides)
- Interval in momentum space for k-point sampling: 0.20 $Å^{-1}$ – 0.25 $Å^{-1}$
- Spin polarization considered for all calculations

VALIDATION OF THE FIRST-PRINCIPLES METHOD

- **Validation was performed over five different cubic crystal structures and different alloying compositions (three example cases are shown below).**

Color code: **Experiment**
Theory (ab initio); All-electron FLAPW (very accurate and much more expensive)
Theory (ab initio); Pseudopotential or PAW DFT (similar to this work)

	Lattice parameter a_0 (Å)		Magnetic moment (μ_B/atom)		Formation enthalpy (eV/atom)	
	This work	Previous work	This work	Previous work	This work	Previous work
FeNi ($L1_0$)	3.556	3.547[a]/3.568[f]/ **3.582**[c]/3.556[g]	1.660	1.606[a]/1.63[f]/ **1.70**[c]/**1.630**[g]	-0.069	-0.057[a]/**-0.067**[g]
Fe_3Ni ($L1_2$)	3.591	3.560[a]/3.588[f]/ **3.578**[g]	2.067	1.834[a]/1.97[f]/ **2.066**[g]	0.040	0.054[a]/**0.048**[g]
$FeNi_3$ ($L1_2$)	3.551	3.5[a]/3.560[f]/ **3.553**[c]/**3.545**[g]	1.265	1.18[a]/1.13[f]/ **1.15**[c]/**1.202**[g]	-0.088	-0.080[a]/**-0.089**[g]

Good agreement with experiments and other first-principles calculations

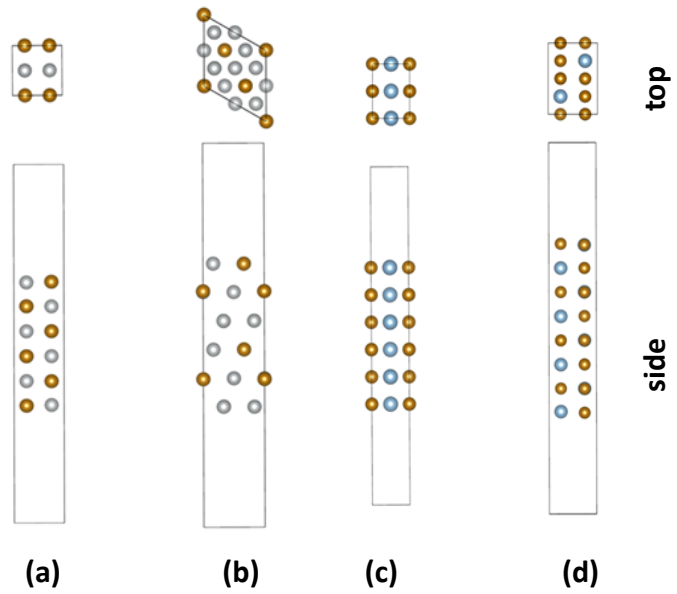
STRUCTURE-ENERGY (SE) RELATIONSHIPS FROM FIRST PRINCIPLES

- SE database is constructed for Fe-Ni-Al binary slab surface systems (4 example structures are shown)
- Energy information

Bulk composition	Surface Index	Formula	E_{Total} (eV)	E_s (eV/atom)
(a) FeNi ($L1_0$)	(100)	$(FeNi)_6$	-80.319	0.946
(b) Fe_3Ni ($L1_2$)	(111)	$(Fe_3Ni)_6$	-176.040	0.672
(c) FeAl (B2)	(110)	$(FeNi)_6$	-73.501	0.698
(d) Fe_3Al (DO_3)	(110)	$(Fe_3Al)_6$	-229.547	0.126

All calculation results are stored as database for reactive force field

- Structure information

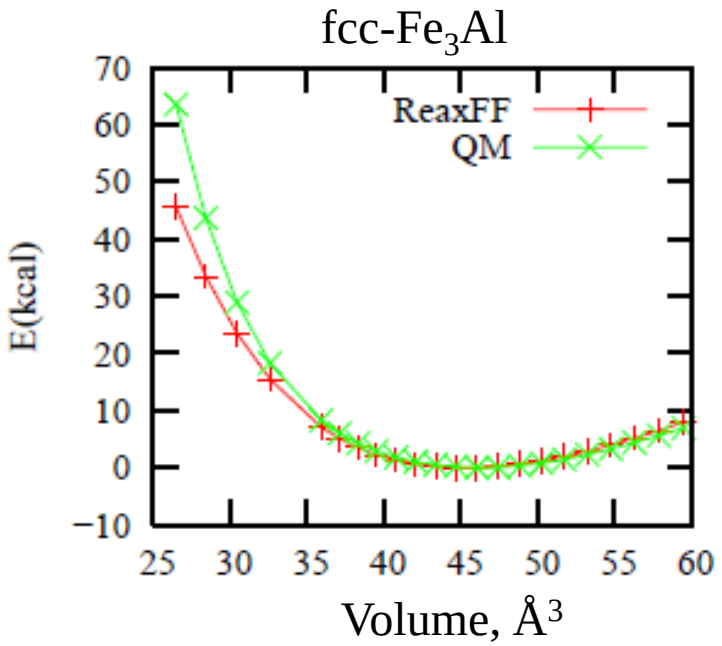


DEVELOPMENT OF REAXFF POTENTIALS FOR FE/AL/NI ALLOY

First-principles QM data included in the training set to describe diffusion, alloy formation, mechanical properties…

Volume(pressure) equation of state: the relation between volume change and energy

Fe-X (X= Ni,Al), Ni/Al binary alloys with X concentration up to 75 at. %.

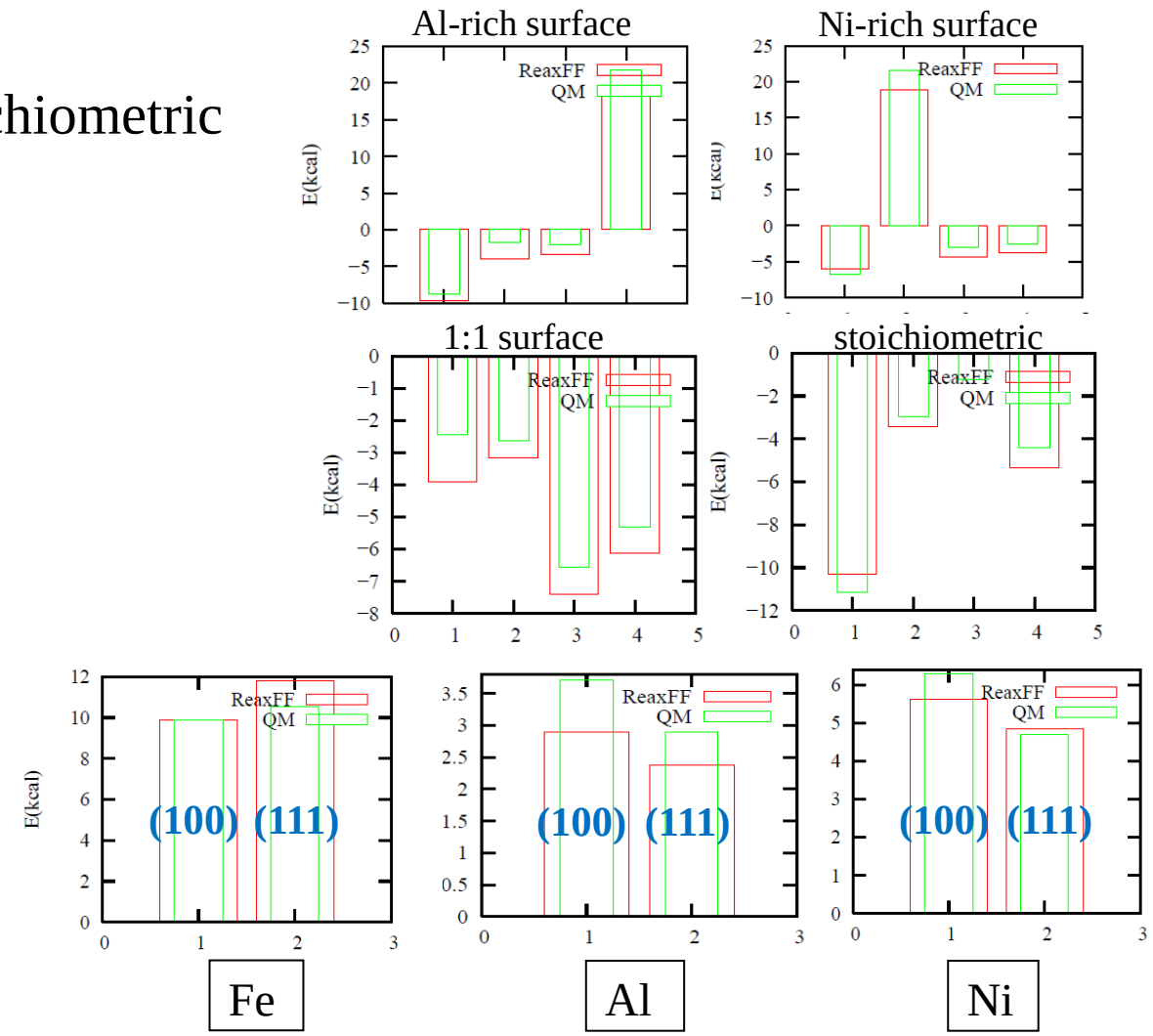


SURFACE ENERGY OF ALLOY SLAB SURFACES

Stoichiometric/Non-Stoichiometric surface:

NiAl(100,001,011)
Ni_3Al(001,0111)
$NiAl_3$(001,011)

Pure metal surface:
Fe/Al/Ni(100,111)



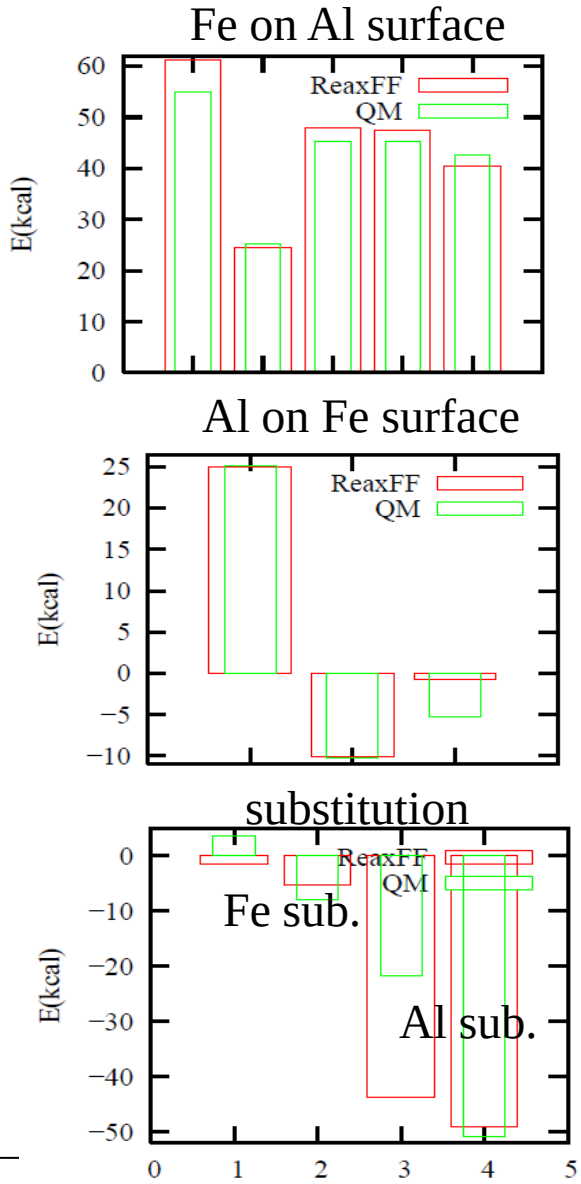
BINDING ENERGIES ON METAL SURFACES

Fe on Al surface

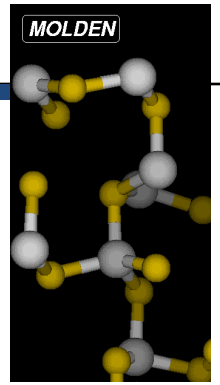
- bridge on Al(001)
- hollow on Al(001)
- fcc on Al(111)
- hcp on Al(111)
- substitution on (001,111) surface

Al on Fe surface

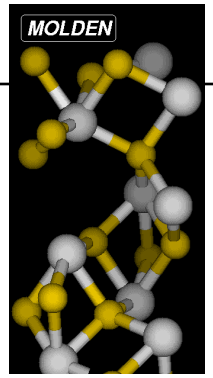
- bridging on Fe(001)
- hollow on Fe(001)
- substitution on (001,111) surface



EOS OF α-AL_2S_3 AND CORUNDUM



α–Al_2S_3



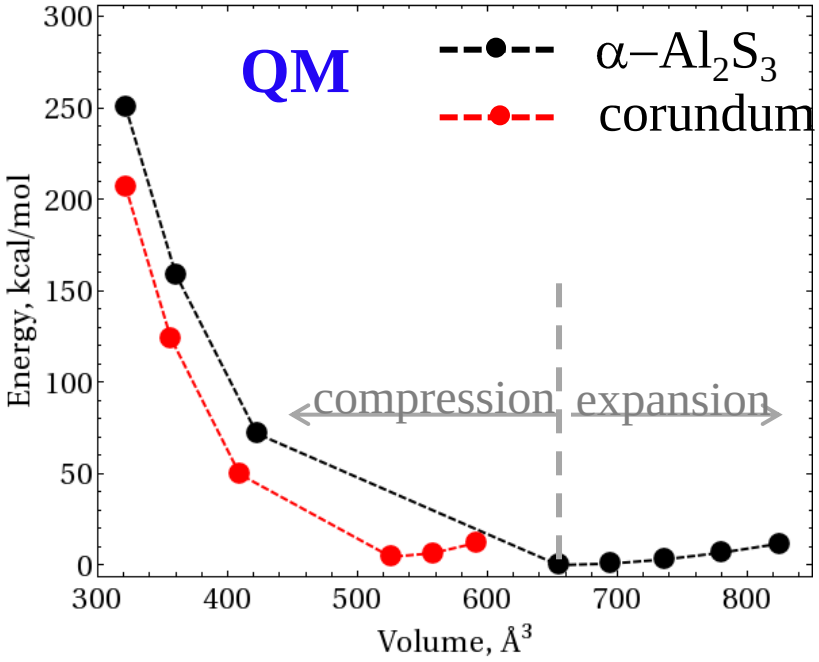
corundum

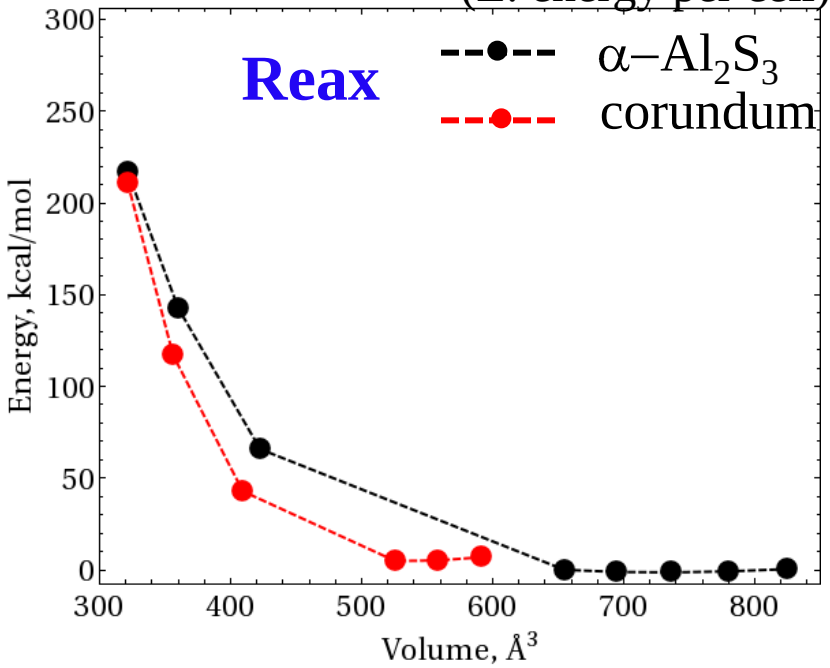
Al

S

Phase transition of α-Al_2S_3 to corundum phase at low pressure region

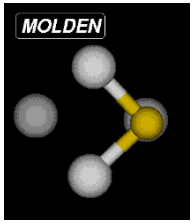
(E: energy per cell)

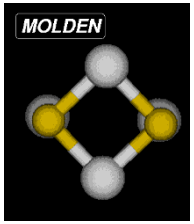


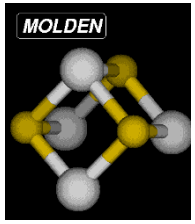


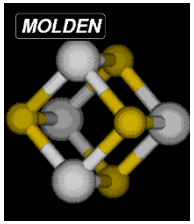
THERMODYNAMIC STABILITY OF S-DOPED AL CRYSTAL

Sulfur at the interstitial of octahedral site in Al(fcc)





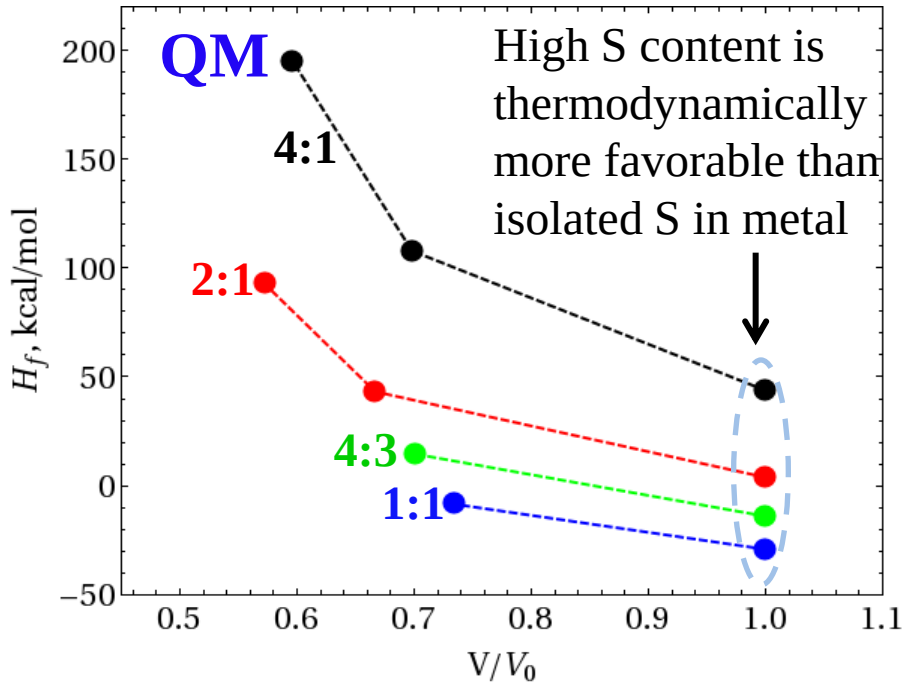


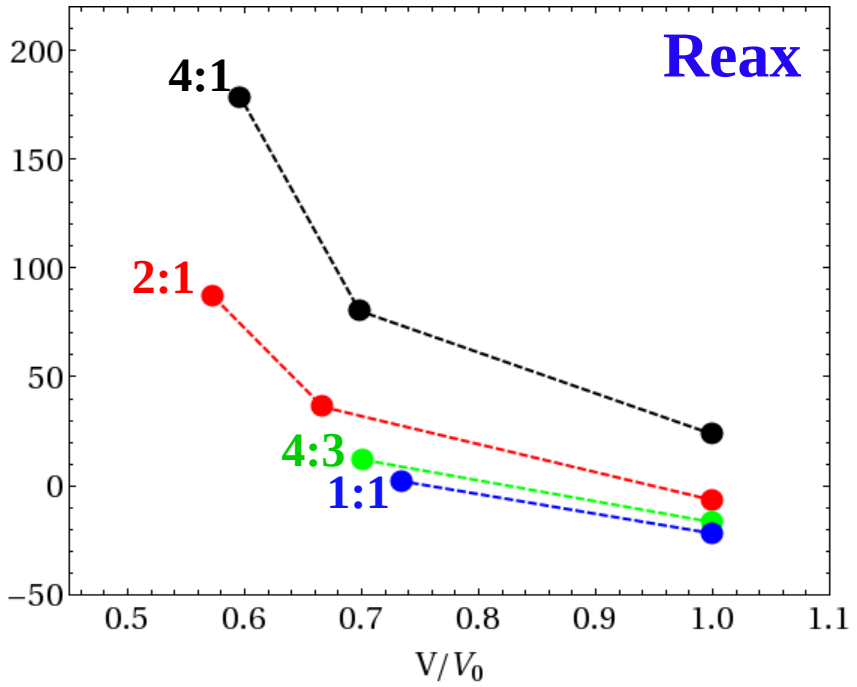


Al:S= 4:1 2:1 4:3 1:1

$$H_f = \frac{1}{nS}(E_{system} - E_{fcc-Al} - nS \cdot E_{\alpha-sulfur})$$

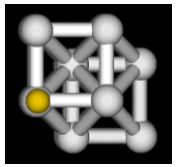
(*nS*: N. of sulfur in the crystal)

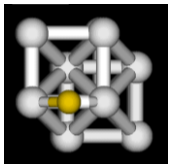




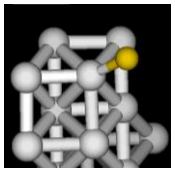
BINDING ENERGY OF S AT FCC-AL(100,111) SURFACE SITES

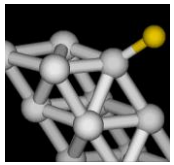
$$E = \frac{1}{nS}\left(E_{slab} - E_{fcc-Al,slab} - nS \cdot E_{\alpha-sulfur}\right)$$

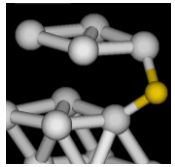

top


bridge

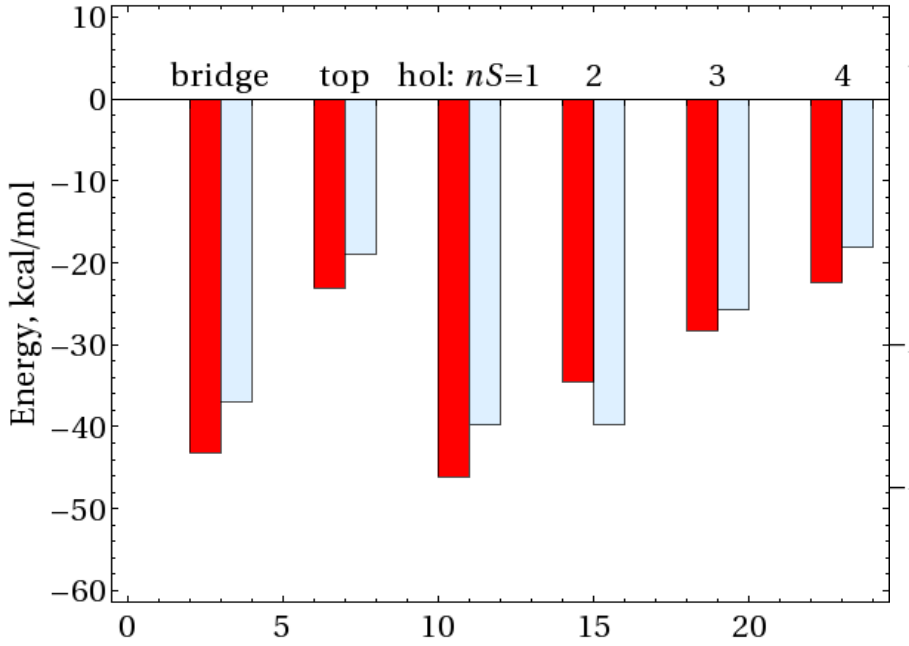

hollow


fcc

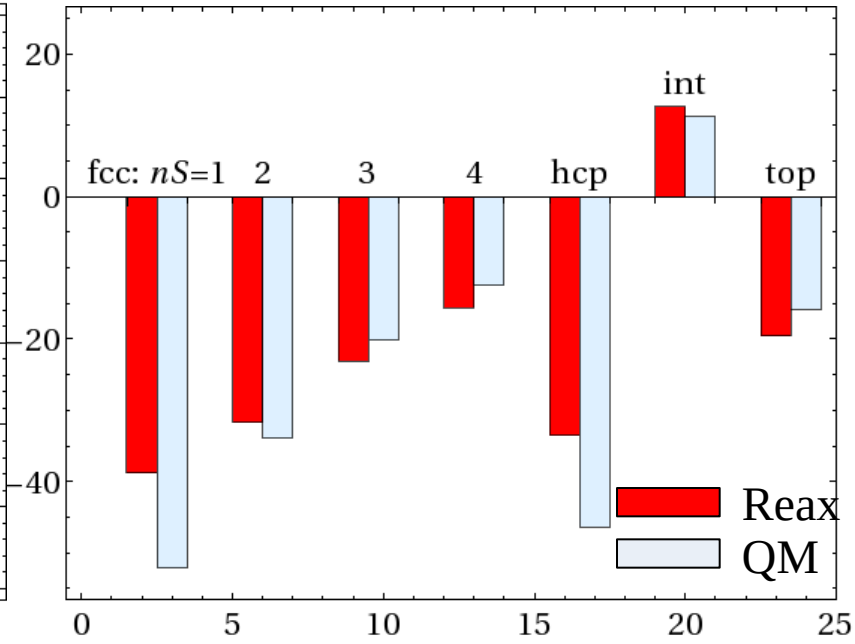

hcp


interstitial at subsurface

Al(100)



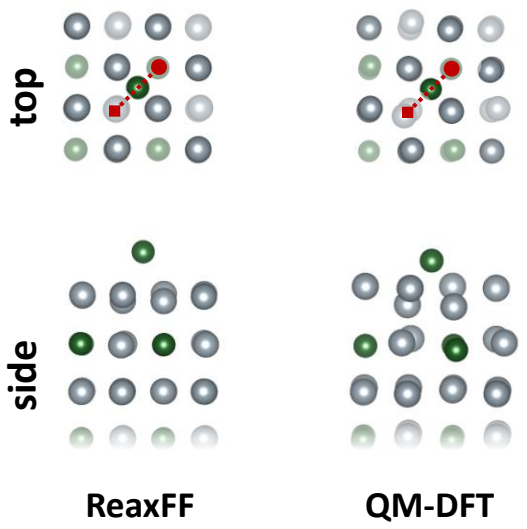
Al(111)

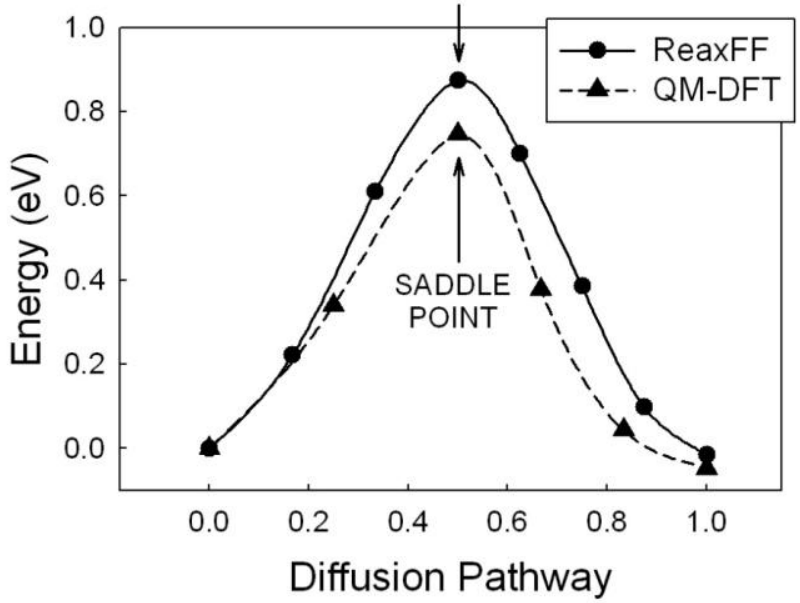


TRANSITION STATE PREDICTIONS FROM REAXFF

- The *ab initio* trained ReaxFF force fields can also illustrate the kinetics of atomistic-scale processes with fair accuracy.
- Such processes include diffusion, adsorption, and dissociation at alloy surfaces.

Aluminum diffusion on Fe_3Al (100) surface:





SIGNIFICANT FINDINGS: YEAR 1

B. DEMONSTRATION – FEASIBILITY OF REAXFF-BASED MODELING

REAXFF PREDICTIONS FOR ELASTIC CONSTANTS

- **Three independent elastic constants for cubic systems – C_{11}, C_{12}, and C_{44}.**

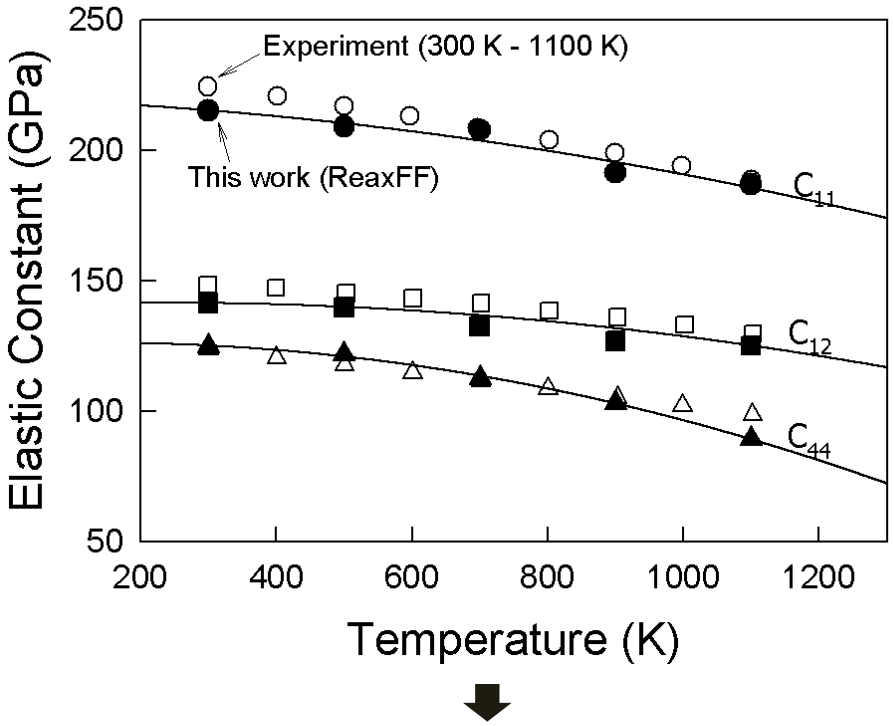
From the stress-strain relationship:

$$\boldsymbol{\varepsilon} = \mathbf{C} \cdot \boldsymbol{\sigma}$$

$$\begin{aligned} \sigma_{xx} &= C_{11}\delta \\ \sigma_{yy} + \sigma_{zz} &= 2C_{12}\delta \\ P_{110} &= \frac{1}{2}(C_{11} + C_{12} + 2C_{44})\delta' \end{aligned}$$

δ and δ' – deformation parameters.

Ni_3Al (FCC, single crystal)

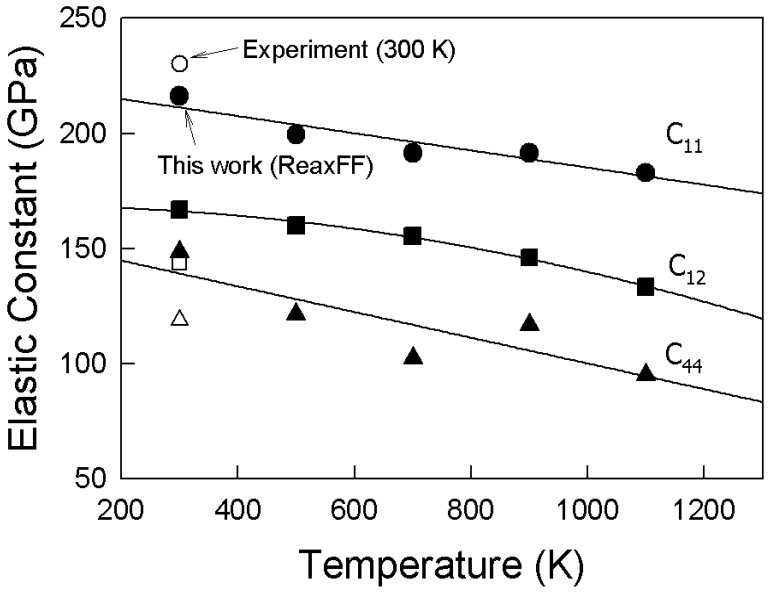


- **Comparison between ReaxFF predictions and experimental measurements for the elastic constants of Ni_3Al ($L1_2$) single crystal in the temperature range of 300 K – 1100 K.**
- **Experimental data from Prikhodko, S., et al., *Metall. Mater. Trans. A*, 30, 2403 (1999).**

REAXFF PREDICTIONS FOR ELASTIC CONSTANTS (CONT.)

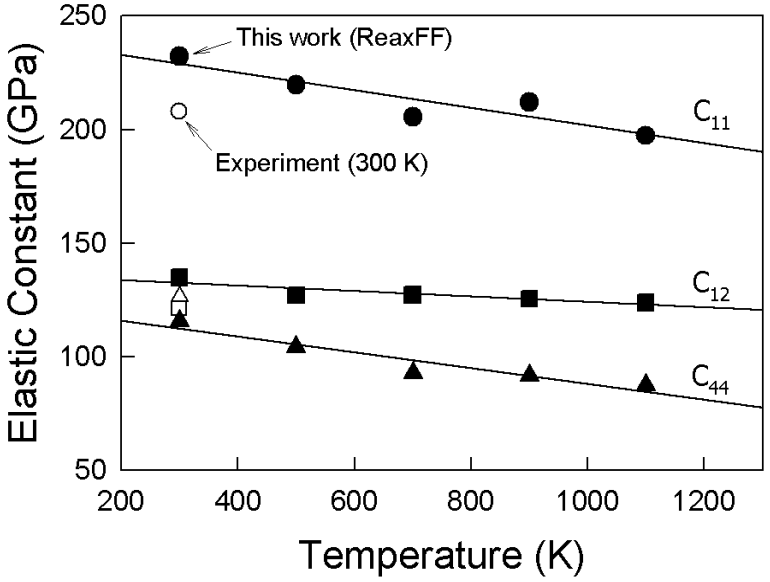
FeAl (BCC, single crystal)

Experiment data at 300 K from Einspruch and Claiborne, *J. Appl. Phys.* 35, 175 (1964)



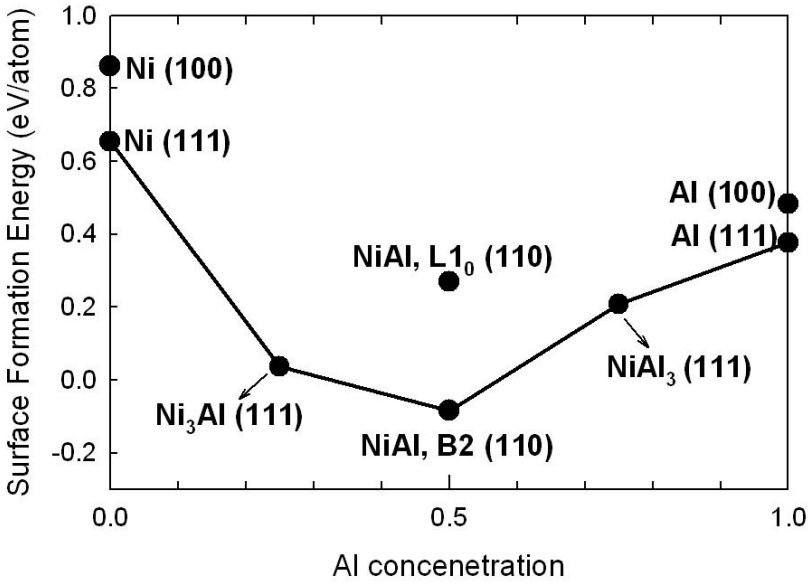
Ni_3Fe (FCC, single crystal)

Experiment data at 300 K from *"Single crystal elastic constants and calculated aggregate properties: a handbook"* 1971: M.I.T. Press



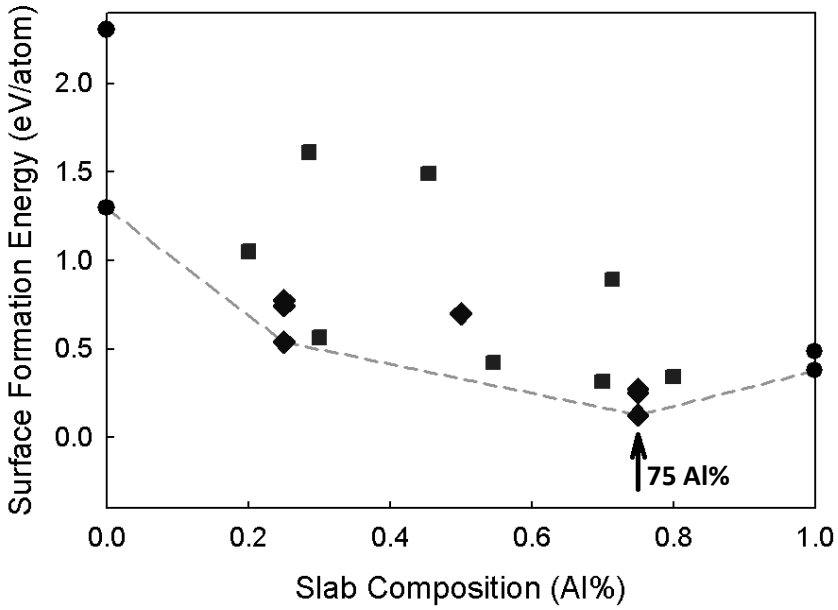
A short series of ReaxFF-MD simulations can provide temperature-dependent mechanical properties of ANY alloy systems of interest.

SURFACE COMPOSITION PREDICTIONS FROM DFT



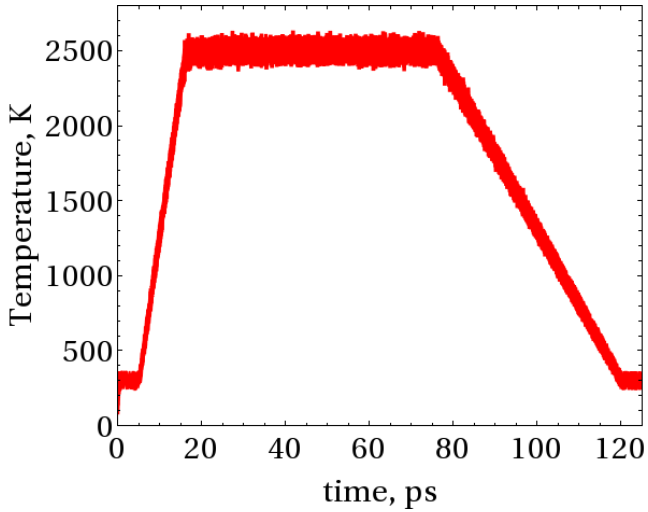
- **Surface formation energy vs. alloying composition at Ni-Al alloy surfaces**

- **Surface formation energy vs. alloying composition at Fe-Al alloy surfaces**



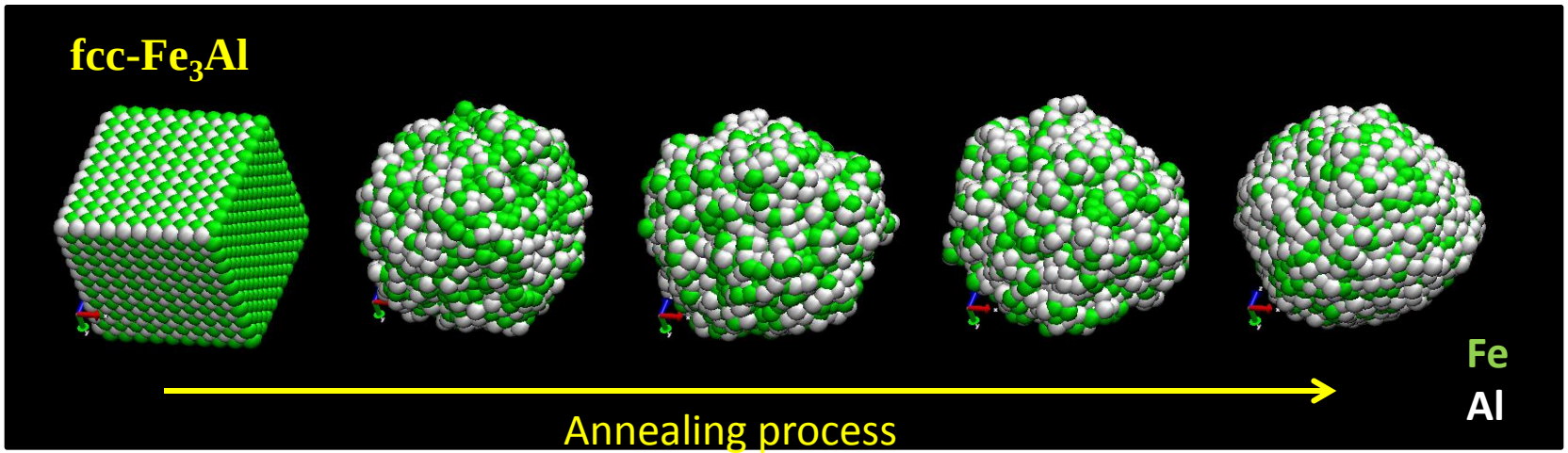
QM-DFT not only provides DB for force field development but also provide key physical insights.

RECONSTRUCTION OF BINARY ALLOY SURFACE DURING ANNEALING

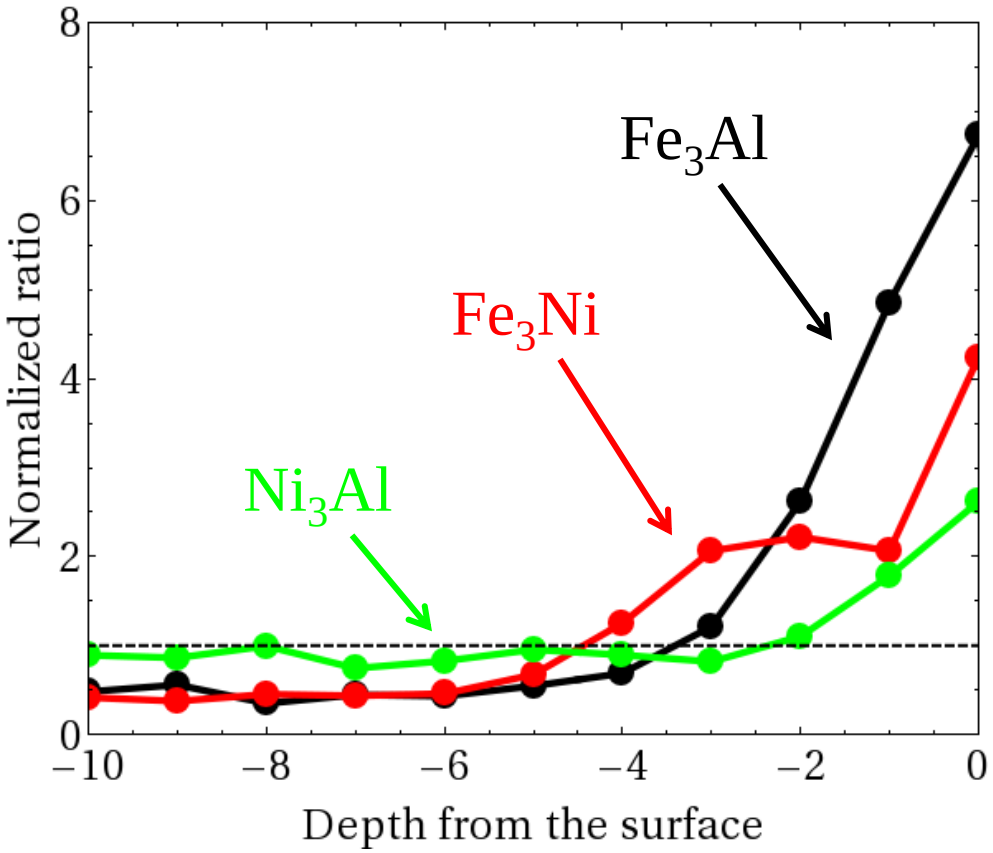


Cluster (fcc-Fe_3Al, Fe_3Ni and Ni_3Al) consisting of ~4000 atoms, ~35x35x35 Å

Heating up to 2500 K with temperature gradient 0.05 K/step and cooling to 300 K with 0.0125 K/step



COMPOSITION PROFILE AFTER COOLING TO 300 K

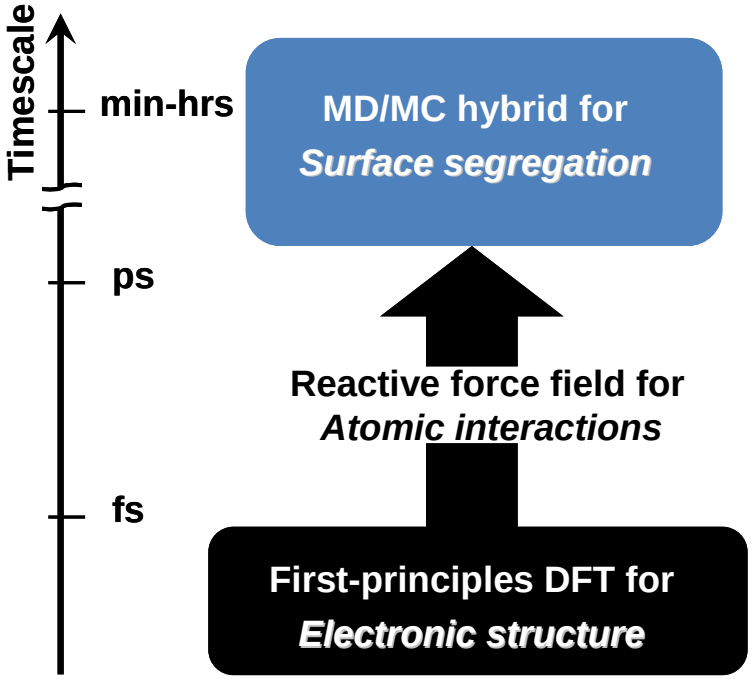


Weak segregation of Al in Ni_3Al and strong segregation in Fe_3Al : segregation of NiAl is energetically less favorable due to high heat of formation. (L. Hammer *et al.*, *Surface Science*, 412/413 (1998))

Deeper subsurface segregation of Ni in Fe_3Ni, ~4.5 Å

AL SEGREGATION AT FE-AL ALLOY SURFACES: MULTISCALE MODELING

- MD simulations are typically limited to a nanosecond time scale – not usually applicable for segregation-diffusion processes which occurs in sec – hrs.



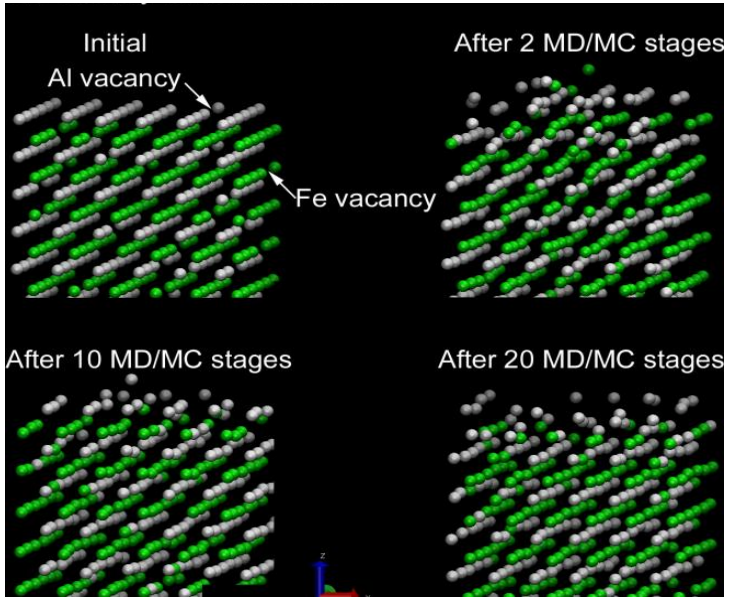
- We employed MD-Monte Carlo (MC) hybrid scheme along with the first-principles trained ReaxFF force fields.
- MC simulation stages were iterated with the short bursts of atomistic MD simulation stages:
  - MC steps "perturb" the structure to stimulate the rare occurring events such as nearest neighbor hops.
  - MD steps "relax" the structure to bring the realistic representation of the system at the equilibrium temperature.

ReaxFF-based MD-MC hybrid scheme is ready for segregation studies.

AL SEGREGATION WITH AND WITHOUT VACANCY-RELATED DEFECTS

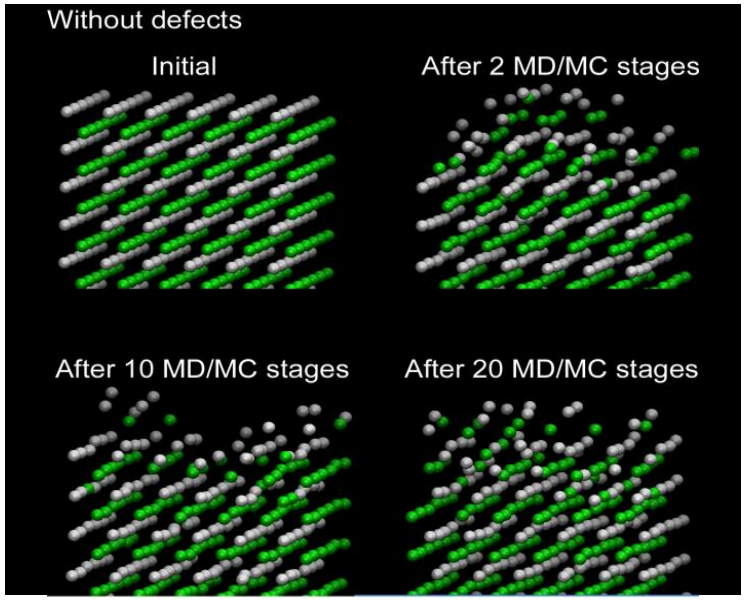
Assessment of the initial vacancy concentration

I. Vacancy assisted segregation (8% vacancy defects)



➢ Representation of ideal cases where <u>maximum segregation occurs</u>

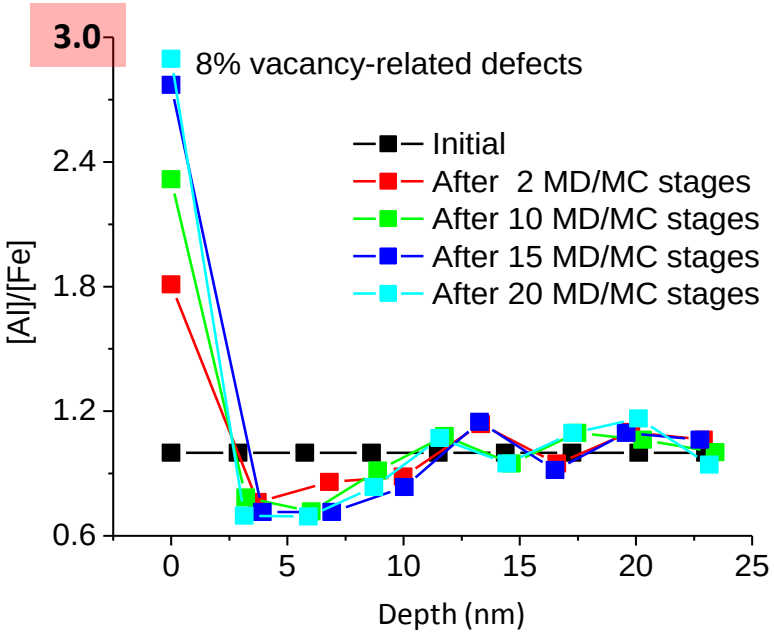
II. Segregation at pristine surface (no defects)

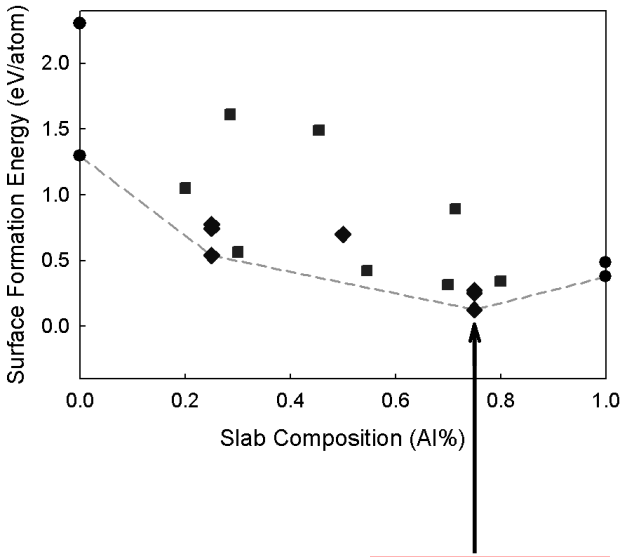


➢ Representation of experimental condition where <u>segregation occurs on annealed surfaces</u>

AL SEGREGATION WITH AND WITHOUT DEFECTS (CONT.)

▪ **Spatial depth profile of Al/Fe ratio (I): Ideal case with maximum segregation**

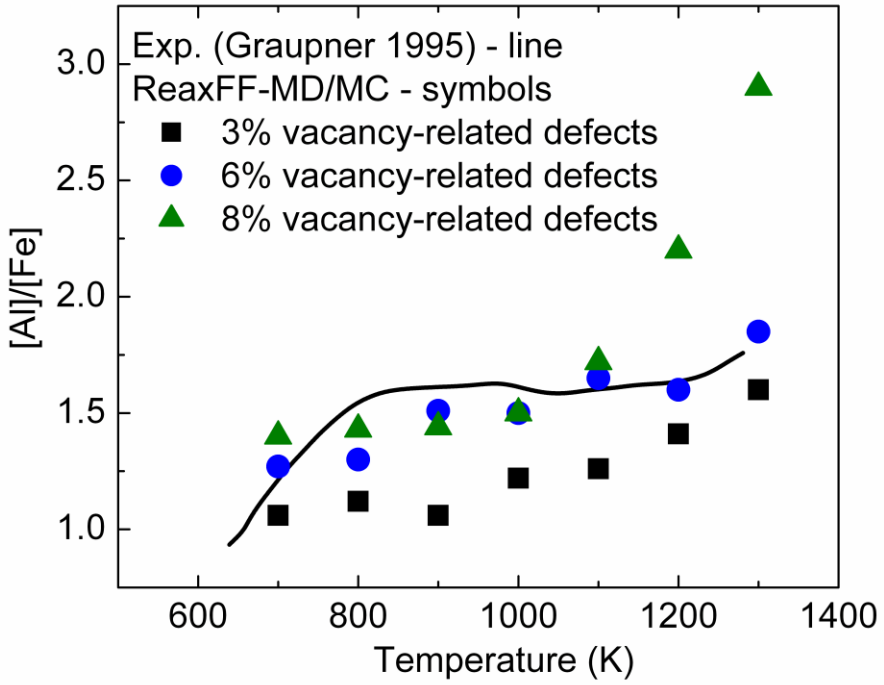




- **Maximum segregation leads to the theoretical limit predicted from DFT.**

MD-MC results are consistent with DFT predictions.

AL SEGREGATION: DIRECT COMPARISON WITH EXPERIMENT

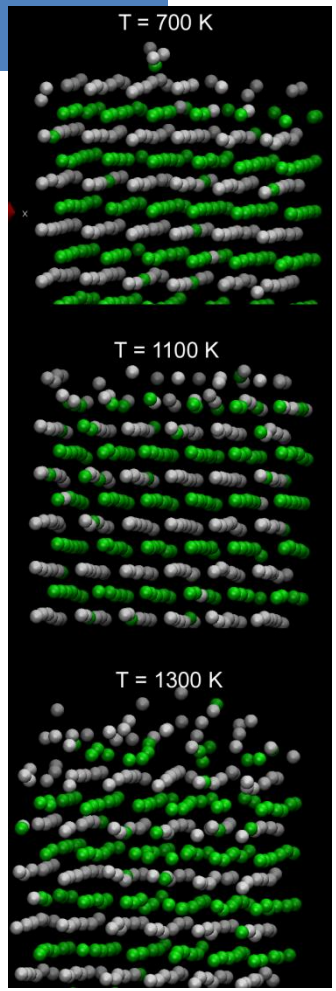


- **Simulation with 6% vacancy concentration yields a close agreement with sputtering-annealing experiment on FeAl surfaces [Graupner et al., Surf. Sci. 322, 103 (1995)].**
- **In the 700 K to 1100 K range, Al/Fe ratio slowly rises with the increased concentration of vacancy sites.**
- **In contrast, at temperatures above 1100 K, Al/Fe quickly grows with the increased vacancy concentration.**

- **The ReaxFF-MC/MD predictions point to the competition between the vacancy-driven bulk and surface diffusion.**

Direct comparison with segregation experiment shows a good agreement.

AL SEGREGATION: DIRECT COMPARISON WITH EXPERIMENT



- We relate this drastic change with the enhanced surface diffusion, whose activation barrier was estimated at ~0.1 eV.
- The surface diffusion is responsible for disordering of the surface and massive formation of vacancy sites at the surface.
- Increase in annealing temperature over 1100 K leads to disordered surfaces accelerating the Al diffusion.
- This is the first time when first-principles-based computational model is used to provide quantitative insight to the mechanism of segregation.

Illustration of competition between the vacancy-driven bulk and surface diffusion.

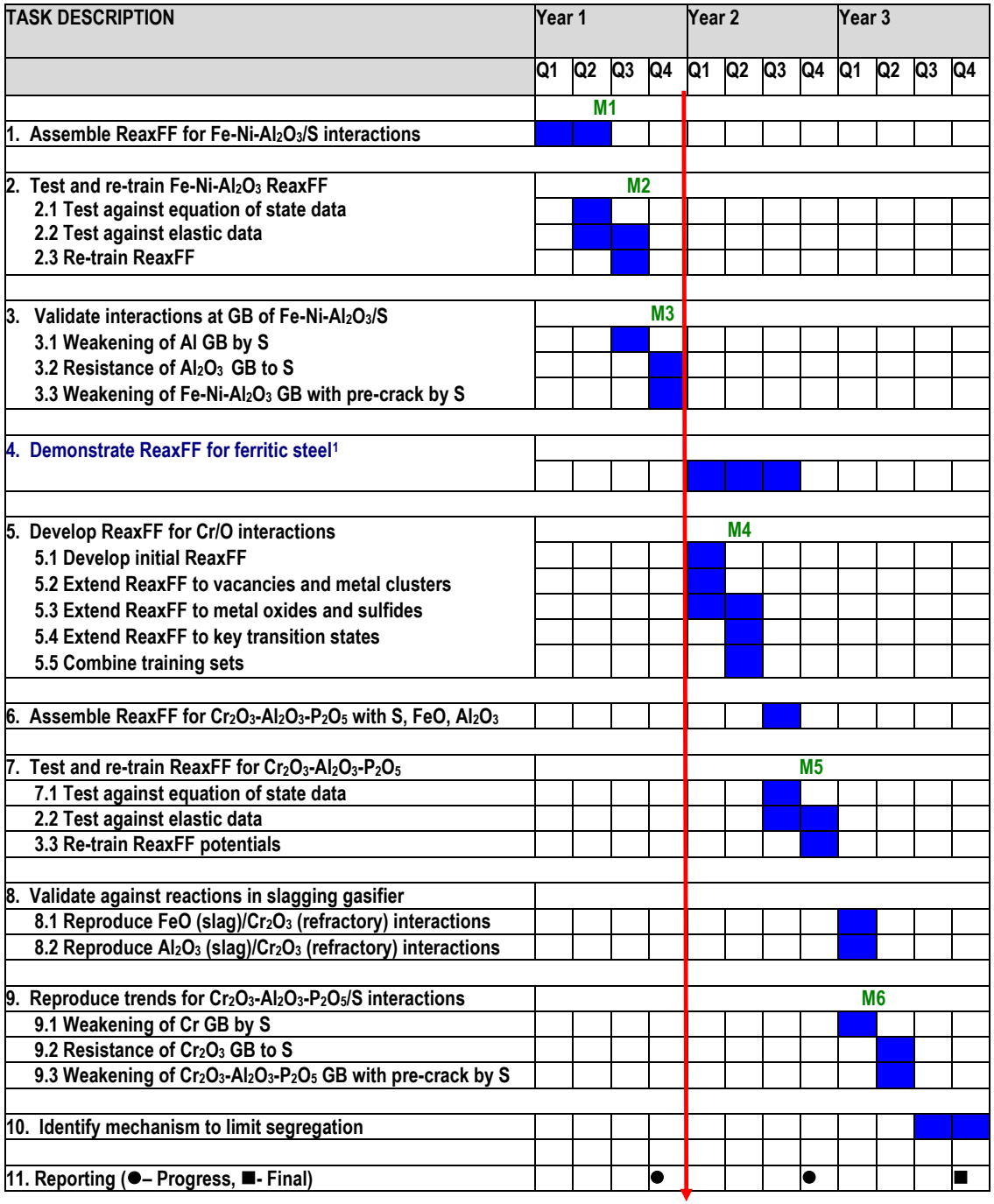
CONCLUSIONS

CONCLUSIONS

- ReaxFF potentials for Ni/Fe/Al/O/S interactions have been developed and validated against first-principles energetics information based on QM calculations.
- Developed ReaxFF potentials for Fe-Ni-Al alloy systems were shown to be reliable to the scale of 3 kcal/mol for heat of formation and 20% of elastic properties.
- A short series of ReaxFF-based MD simulations demonstrate the feasibility of the method towards predicting the thermodynamic and kinetic properties of the alloy systems.

CONCLUSIONS (CONT.)

- Successful implementation of MD/MC hybrid scheme to the ReaxFF method enables a direct comparison with experiment on segregation in Fe-Al surfaces in a temperature range from 400°C to 1000°C.
- Owing to the nature of force field methods, the method provides a straight forward extension to multi-component alloy systems with an expected level of accuracy comparable to QM-based analysis.



(3/13/2012)

Year 1 Milestones

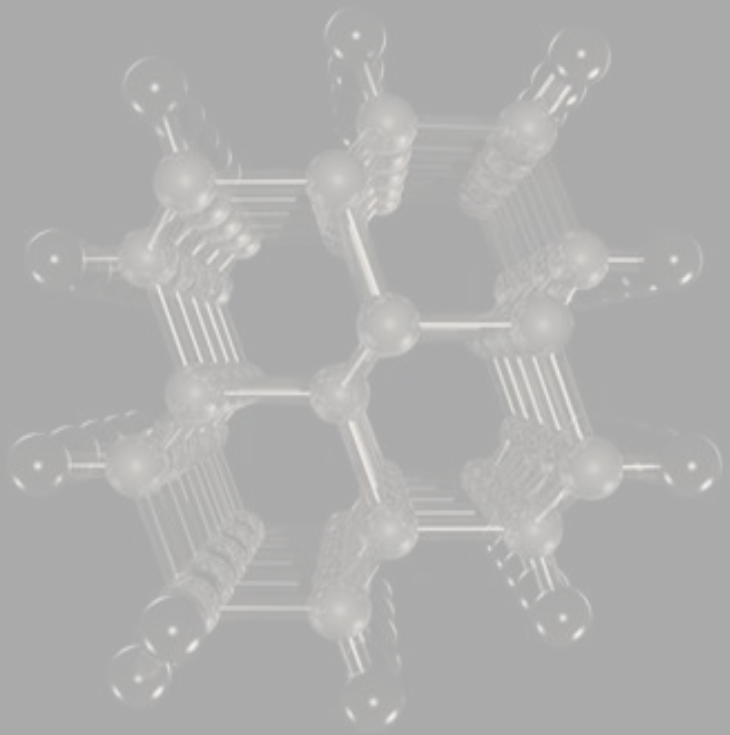
100% M1 ReaxFF potentials for Al/O/X clusters (X=S, Fe, and Ni) are tested to reproduce QM-binding low-energy sites within 3 kcal/mol

100% M2 ReaxFF potential for Fe/Ni/Al/O interactions are tested to reproduce equation of state and elastic data from the literature with an accuracy of 10% and 20%, respectively

60% M3 ReaxFF potentials for interactions of Fe-Ni-Al and Fe-Ni-Al2O3 GB with S are tested to reproduce trends from the literature

30% M4 ReaxFF potential for Cr, Cr/O, and Cr/S are tested to reproduce QM-binding energies for low-energy sites within 3 kcal/mol

[1]This task was added to incorporate modeling of ferritic steels with simple compositions



THANK YOU