# Towards Molecular Dynamics Studies of Hydrogen Effects in Fe-Cr-Ni Stainless Steels

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# Fe-Ni-Cr Potential

## Five criteria for "Good" Fe-Ni-Cr potential

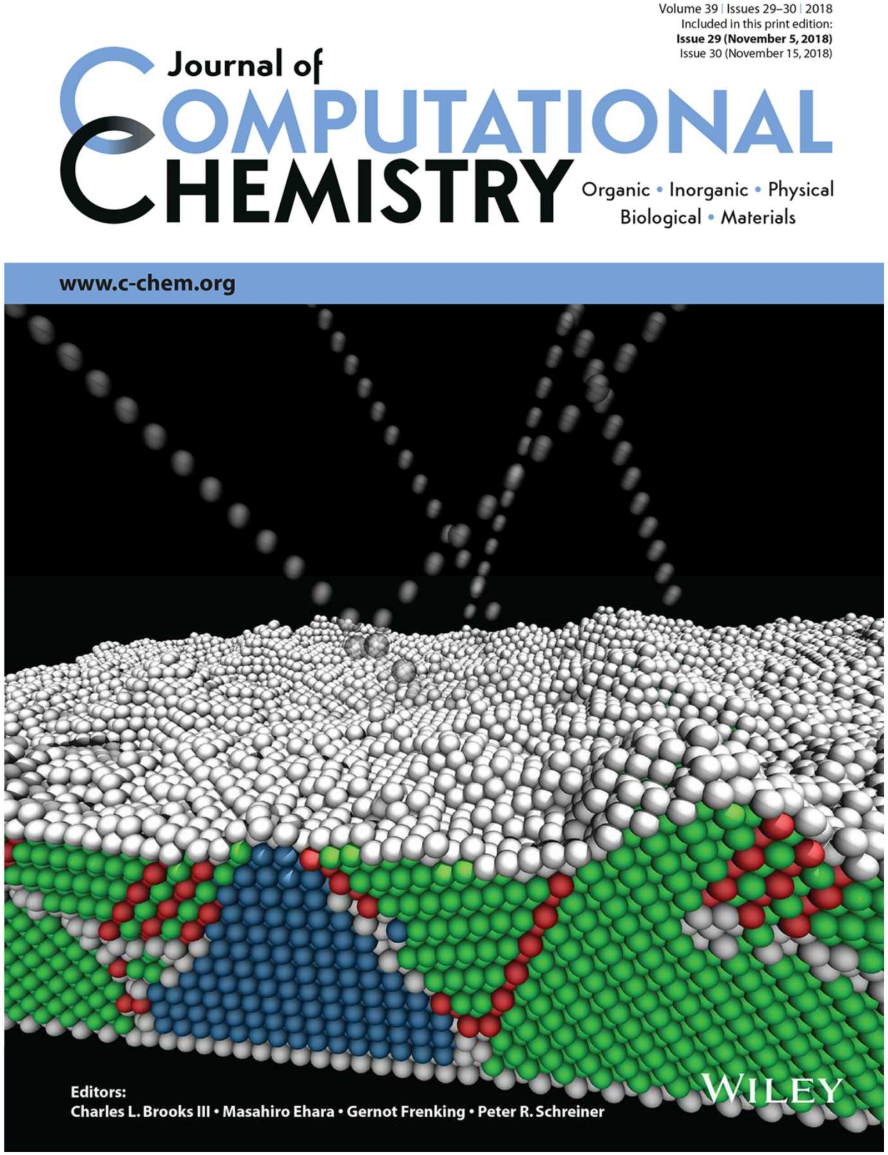
1. Give reasonable energy and volume for various compositions
2. Permit stable MD simulations of austenite
3. Prescribe well the elastic constants
4. Capture the correct stacking fault energy ($\gamma_{sf}$)
5. Pass stringent MD validation tests

# Status of Literature Fe-Ni-Cr Potentials

1. Our old potential (CALPHAD 1993, 17, 383) did not consider the four criteria
2. Smith and Was' potential (PRB 1989, 40, 10322) was fitted to effective atoms and did not consider stacking fault energy
3. The 2013 version of Bonny et al's potential (MSMSE 2013, 21, 085004) incorrectly predicts phase separation

4. The 2011 version of Bonny et al's potential (MSMSE 2011, 19, 085008) incorrectly predicts negative slope of stacking fault energy with Ni composition
5. Tong et al's potential (Mol. Sim. 2016, 42, 1256) incorrectly predicts large negative stacking fault energy (~ -200 mJ/m$^2$)
6. The 2018 version of Bonny et al's potential (MSMSE, 2018, 26, 065014) is based on the 2013 version

# We Developed an Fe-Ni-Cr EAM Potential



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## An Fe-Ni-Cr Embedded Atom Method Potential for Austenitic and Ferritic Systems

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Fe-Ni-Cr stainless-steels are important structural materials because of their superior strength and corrosion resistance. Atomistic studies of mechanical properties of stainless-steels, however, have been limited by the lack of high-fidelity interatomic potentials. Here using density functional theory as a guide, we have developed a new Fe-Ni-Cr embedded atom method potential. We demonstrate that our potential enables stable molecular dynamics simulations of stainless-steel alloys at high temperatures, accurately reproduces the stacking fault energy—known to strongly influence the mode of plastic deformation (e.g., twinning vs. dislocation glide vs. cross-slip)—of these alloys over a range of compositions, and gives reasonable elastic constants, energies, and volumes for various compositions. The latter are pertinent for determining short-range order and solute strengthening effects. Our results suggest that our potential is suitable for studying mechanical properties of austenitic and ferritic stainless-steels which have vast implementation in the scientific and industrial communities. Published 2018. This article is a U.S. Government work and is in the public domain in the USA.

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### Introduction

Fe-Ni-Cr stainless-steels have superior mechanical and corrosion-resistive properties, but are more expensive than many other steels. A science-based design of new material compositions with a reduced cost requires a fundamental understanding of mechanical properties including dislocation characteristics (e.g., core structure, energy, and mobility), deformation mode (e.g., dislocation motion vs. twinning vs. phase transformation), and decohesion of interfaces such as grain boundaries. One way to achieve such an understanding is through molecular dynamics (MD) simulations. Such simulations require a high-fidelity Fe-Ni-Cr ternary interatomic potential. For simulations of mechanical properties, by "high-fidelity" we refer specifically to four criteria: (1) permit stable MD simulations of alloys (e.g., no artificial phase or solute segregation at elevated temperatures); (2) capture the correct stacking fault energy ($\gamma_{sf}$) known to strongly influence twinning and dislocation cross-slip; (3) accurately reproduce the elastic constants; and (4) give reasonable energies and volumes for relevant compositions and phases.

To our knowledge, five Fe-Ni-Cr interatomic potentials have been published.[1–5] The potential we published in 1993[1] was not targeted at meeting the four criteria, therefore, it was not considered. We also did not consider the potential published by Smith and Was in 1989[2] for two reasons: (1) the Ni-Fe and Ni-Cr components of their potential were fitted approximately where different species were not distinguished but were rather treated as identical "effective" atoms and (2) the fitted and tested properties did not include the stacking fault energy. We did however test the other three literature potentials. Interestingly, we found that with the 2013 version of the potential developed by Bonny et al.,[4] Cr is unstable in solution in the austenite phase and separates out at elevated temperatures. This is inconsistent with the experimental observation that austenite is a stable, homogeneous phase at elevated temperatures. The 2011 version of the potential developed by Bonny et al.[3] does enable stable MD simulations of austenitic stainless-steels, and should be a more appropriate potential than the 2013 version for studying mechanical properties. However, we find that the 2011 potential predicts a decreasing stacking fault energy with increasing Ni content, a behavior that is inconsistent with experimental evidence and density functional theory (DFT) calculations.[6] The potential developed by Tong et al.[5] predicts large negative values of stacking fault energy. This suggests that a face centered cubic (fcc) austenite crystal may not be as stable as a hexagonal close packed (hcp) crystal with this potential. In summary, the 2011 version of Bonny et al.'s potential would be our first choice for studying mechanical properties, although, there is an issue with the trend in stacking fault energy with increasing Ni concentration. The other potentials are less appropriate for studying mechanical properties, but may be suitable for other applications.

To advance MD simulations of mechanical properties of stainless-steels, we have developed a new Fe-Ni-Cr embedded atom method (EAM) potential[7] with focus on satisfying the four criteria outlined above. In addition, our potential captures the lowest energies for the equilibrium elemental crystals—body-centered-cubic (bcc) for Fe and Cr and fcc for Ni—and enables stable simulations of both austenitic (fcc) and ferritic (bcc) alloys. This represents an improvement over the other literature potentials, which can usually be used only for austenitic

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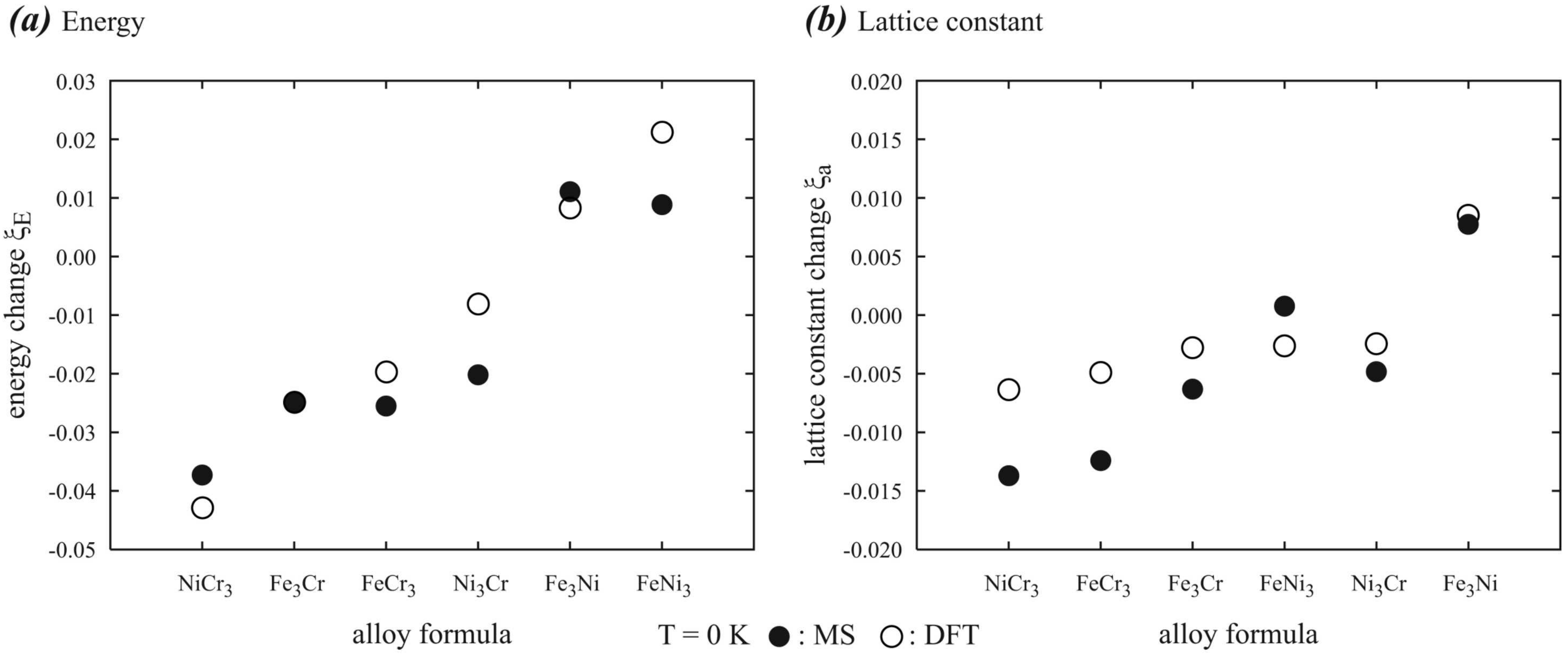
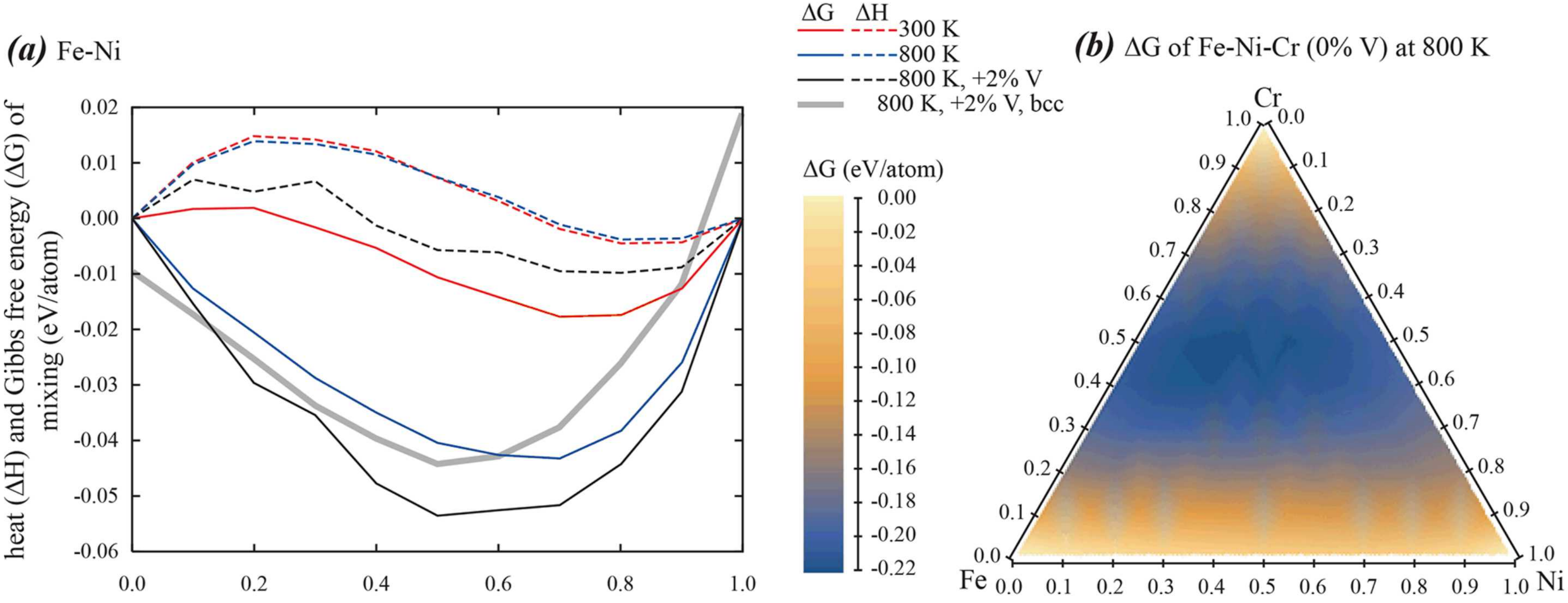
# Fe-Ni-Cr Criterion 1: Energy and Volume Trends



Calculated swelling for Ni and Cr in bcc Fe are 10% and 8% respectively, compared to 5% and 4% experimental values (King, J. Mater. Sci., 1, 79, 1966)

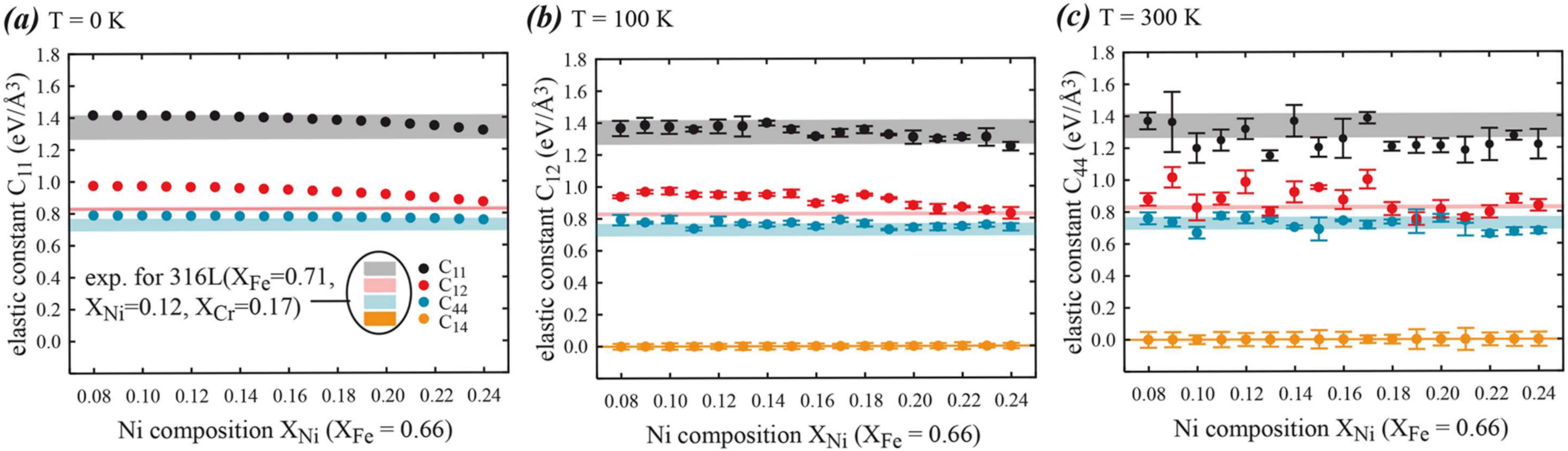
# Fe-Ni-Cr Criterion 2: Stable Austenite

## Overview of Gibbs free energy of mixing



# Fe-Ni-Cr Criterion 3: Elastic Constants

## Time averaged MD over 24 ns

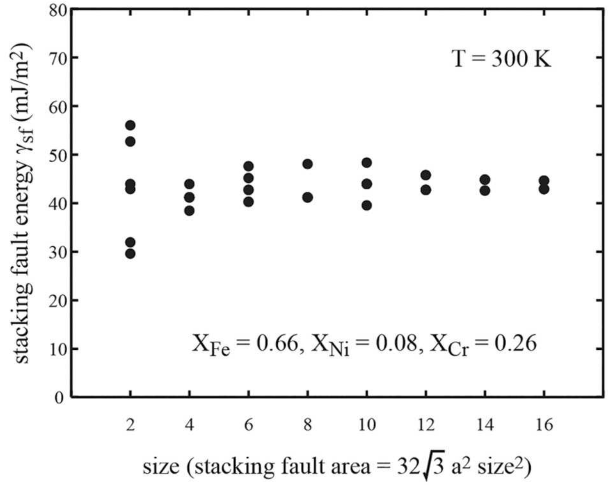


Experimental data for 316L from **(1)** Ledbetter, Ultrasonics 1985, 23, 9; **(2)** Bonny et al, MSMSE 2011, 19, 085008; **(3)** Bonny et al, MSMSE 2013, 21, 085004.

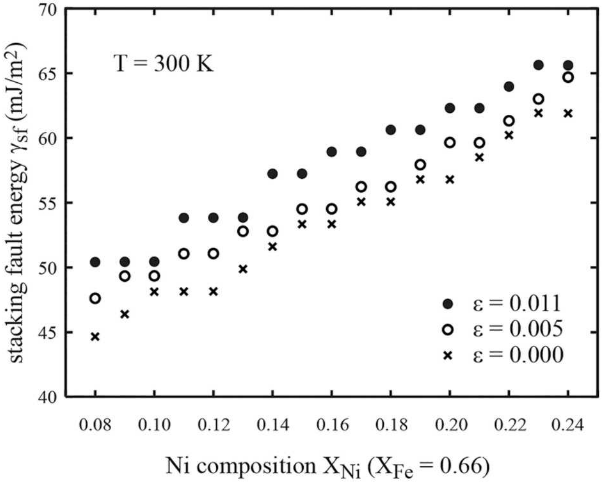
# Fe-Ni-Cr Criterion 4: Stacking Fault Energy

## Time averaged MD over 0.4 ns

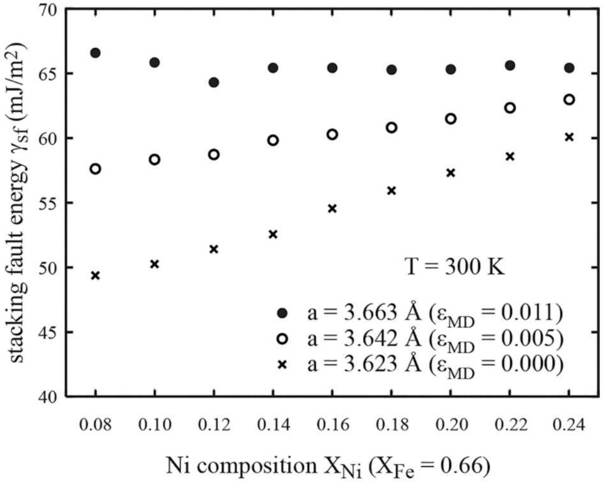
*(a)* Convergence of MD stacking fault energy



*(b)* Converged MD stacking fault energy vs. $X_{Ni}$



*(c)* DFT (EMTO-CPA) stacking fault energy vs. $X_{Ni}$



maximum area ~ 1000 nm$^2$

The predicted stacking fault energies match well with experimental results (see, for example, Vitos et al, PRL 2006, 96, 117210, and references therein).

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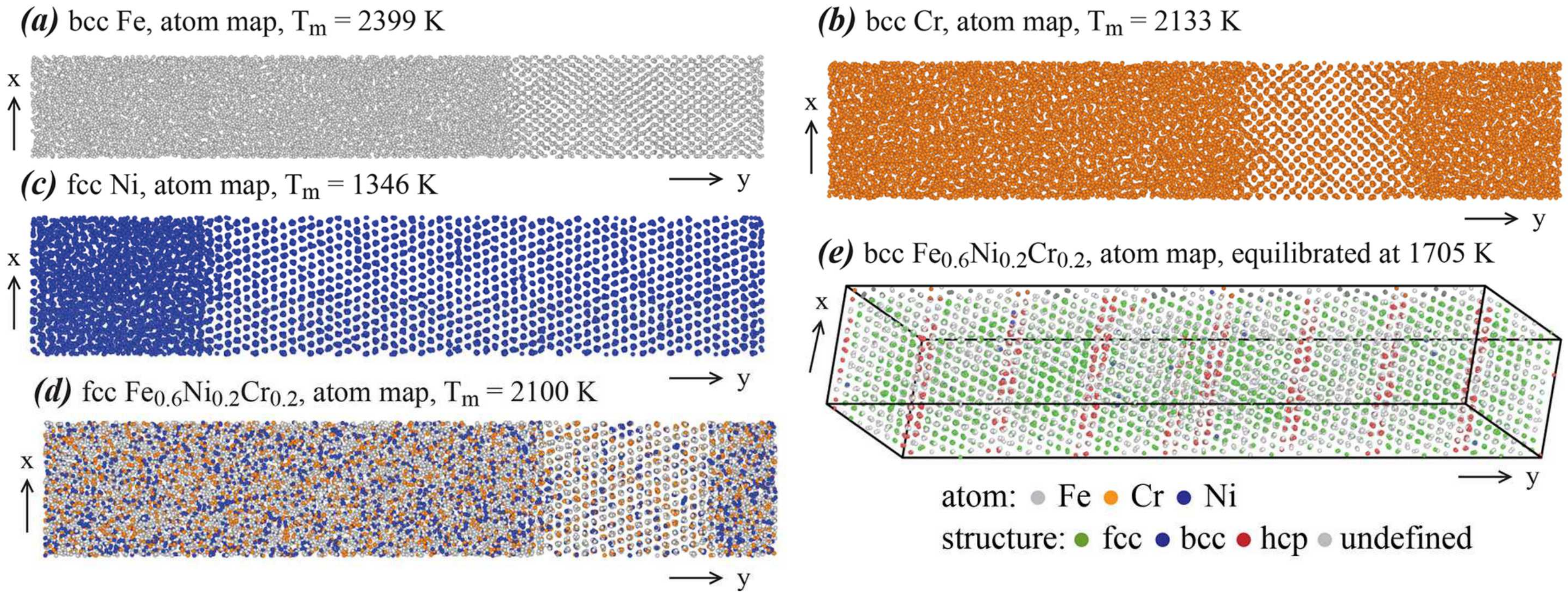
# Fe-Ni-Cr Criterion 5: Stringent MD Melting Tests



*(a)* bcc Fe, atom map, $T_m = 2399$ K

*(b)* bcc Cr, atom map, $T_m = 2133$ K

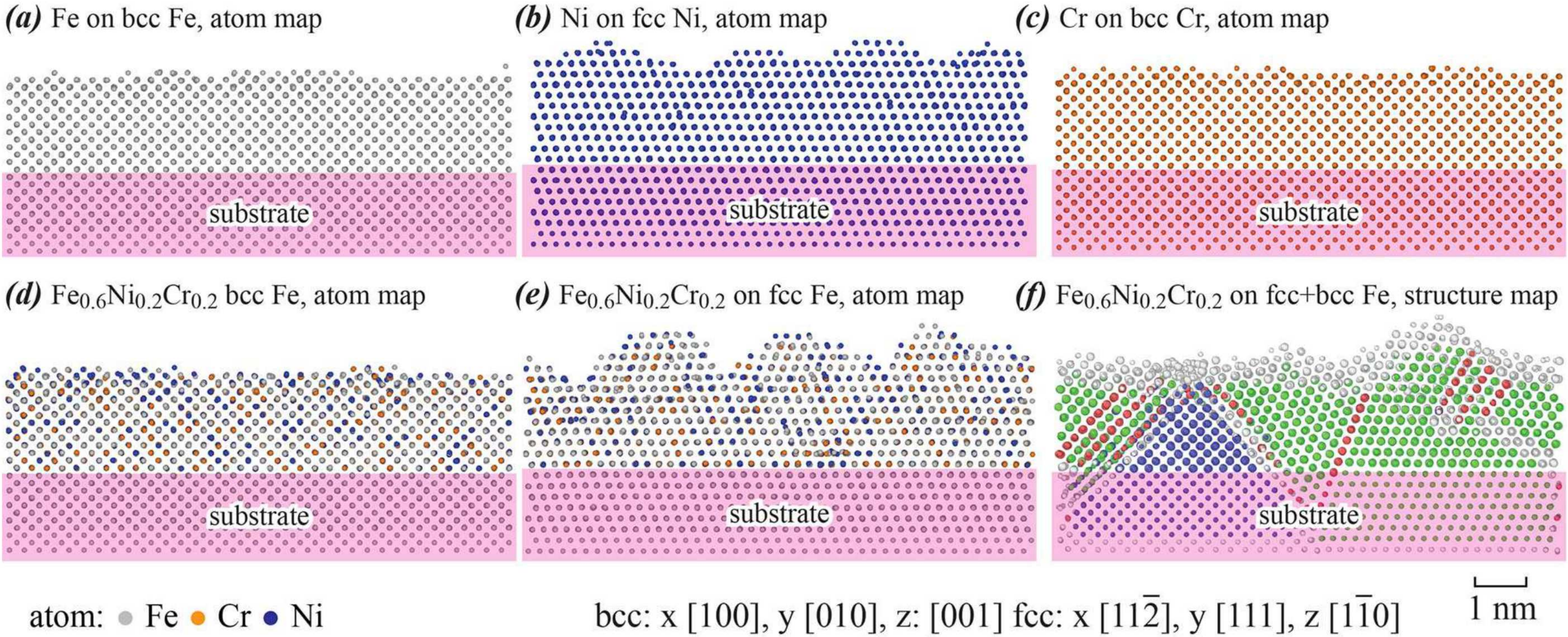
*(c)* fcc Ni, atom map, $T_m = 1346$ K

*(d)* fcc $Fe_{0.6}Ni_{0.2}Cr_{0.2}$, atom map, $T_m = 2100$ K

*(e)* bcc $Fe_{0.6}Ni_{0.2}Cr_{0.2}$, atom map, equilibrated at 1705 K

**Note Bonny et al's 2013 version gives:**

# Fe-Ni-Cr Criterion 5: Stringent MD Growth Tests



*(a)* Fe on bcc Fe, atom map

*(b)* Ni on fcc Ni, atom map

*(c)* Cr on bcc Cr, atom map

*(d)* $Fe_{0.6}Ni_{0.2}Cr_{0.2}$ bcc Fe, atom map

*(e)* $Fe_{0.6}Ni_{0.2}Cr_{0.2}$ on fcc Fe, atom map

*(f)* $Fe_{0.6}Ni_{0.2}Cr_{0.2}$ on fcc+bcc Fe, structure map

atom: ● Fe ● Cr ● Ni

structure: ● fcc ● bcc ● hcp ● undefined

bcc: x [100], y [010], z: [001] fcc: x $[11\bar{2}]$, y [111], z $[1\bar{1}0]$

T = 300 K, $E_i$ = 0.1 eV, R ~ 0.5 nm/ns

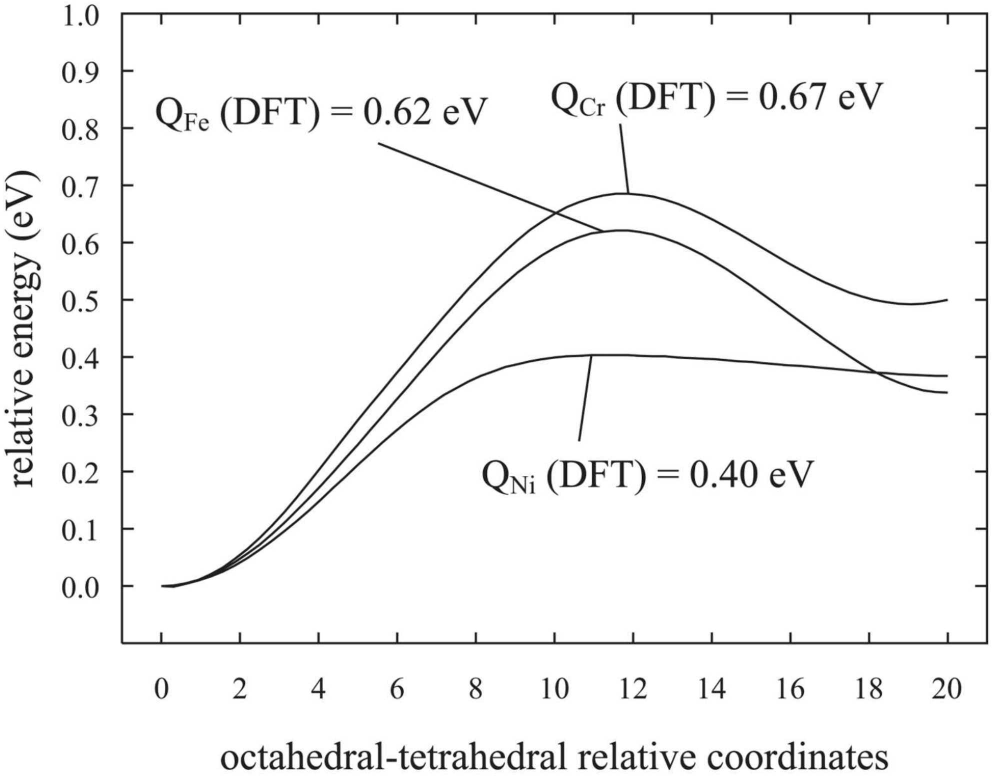
# Fe-Ni-Cr-H Potential

## Five more criteria for "Good" potential

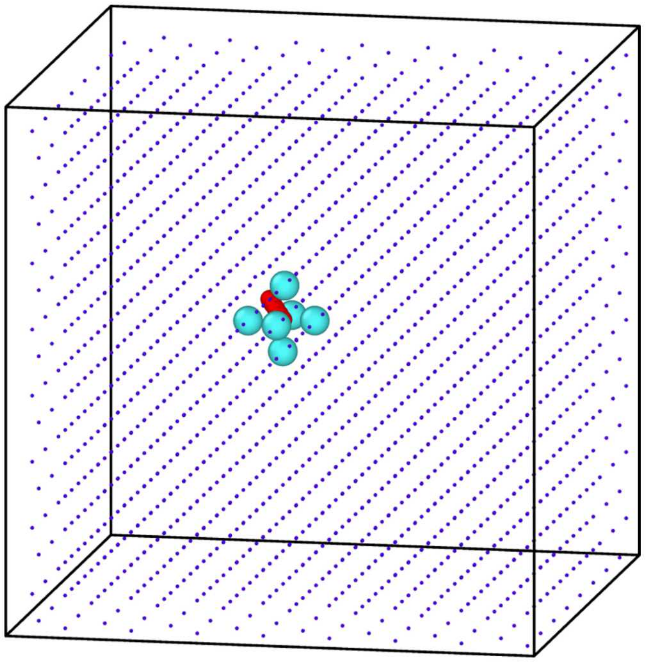
1. Give good diffusion barriers in Fe, Ni, Cr
2. Prescribe well Fe-H, Ni-H, Cr-H energy trends
3. Capture correct swelling volumes in Fe, Ni, Cr
4. Match negative H-H energies from DFT
5. Pass stringent MD validation tests

# H Criterion 1: Diffusion Energy Barriers

## Diffusion energy profiles



## Method for fcc Cr



Small blue: Fe; big blue: Cr; red: H

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# H Criteria 2-4: H Swelling and H-H Energy Trends

## Swelling volume/energy trends in Fe, Ni, Cr

## H-H energy trends in Fe, Ni

Table I. H swelling volume $\Omega_H$, relative H binding energy under local M environment $\Delta E_{H(M)}$, and H-H interaction energy under local M environment $\Delta E_{H\text{-}H(M)}$. Matrix is either fcc Fe or fcc Ni

| property | M = Fe (in fcc Fe) | | M = Ni (in fcc Ni) | | M = Cr (in fcc Fe) | |
|---|---|---|---|---|---|---|
| | MD | DFT | MD | DFT | MD | DFT |
| $\Omega_H$ (Å$^3$) | 2.11 | 2.16 | 2.44 | 2.23 | 1.90 | 1.95 |
| $\Delta E_{H(M)}$ (eV) | 0.00 | 0.00 | -0.19 | -0.14 | -0.36 | -0.29 |
| $\Delta E_{H\text{-}H(M)}$ (eV) | -0.015 | -0.010 | -0.053 | -0.028[1] | ----- | ----- |

1. von Pezold et al, Acta Mater. 2011, 59, 2969.

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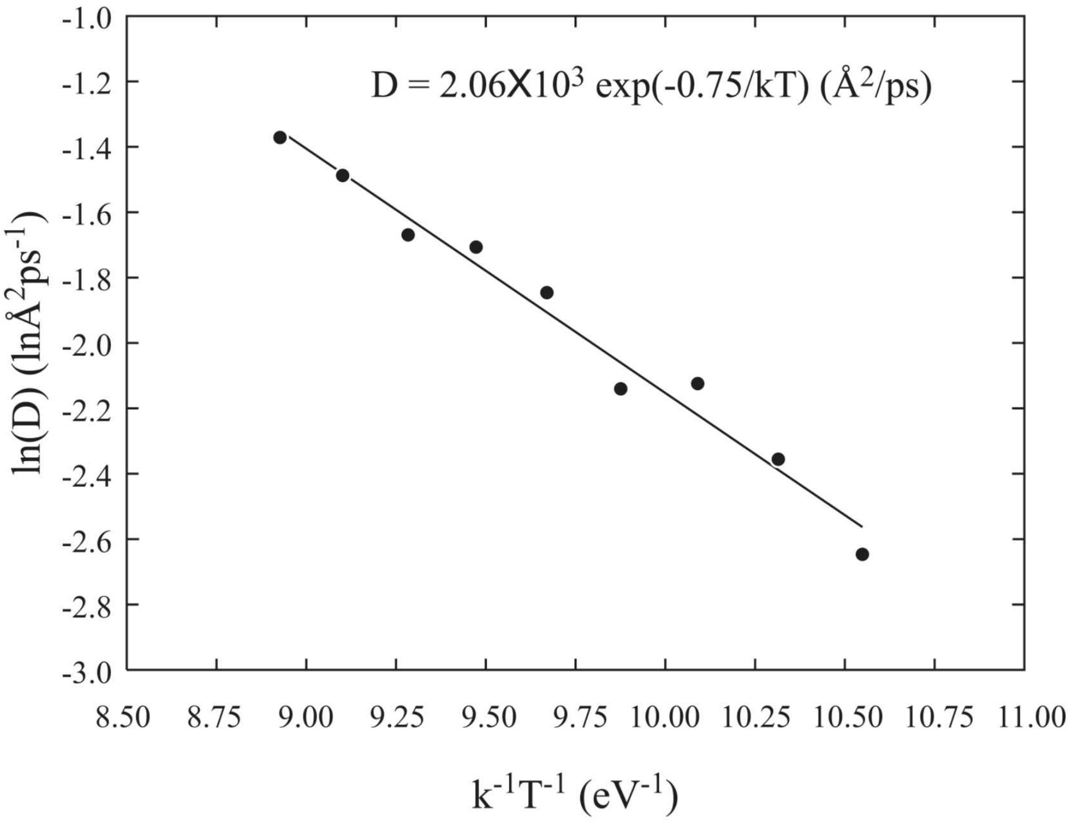
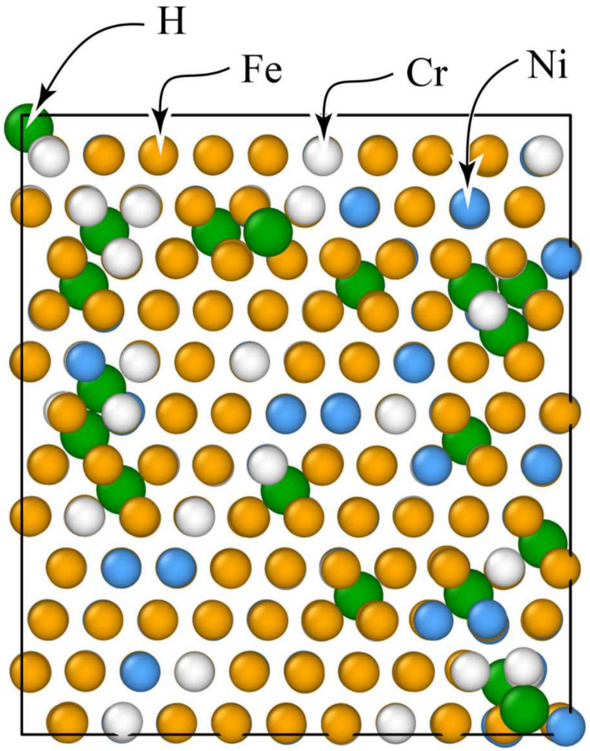
# H Criterion 5: Stringent MD Tests

## Arrhenius plot from MD



## Configuration from MD

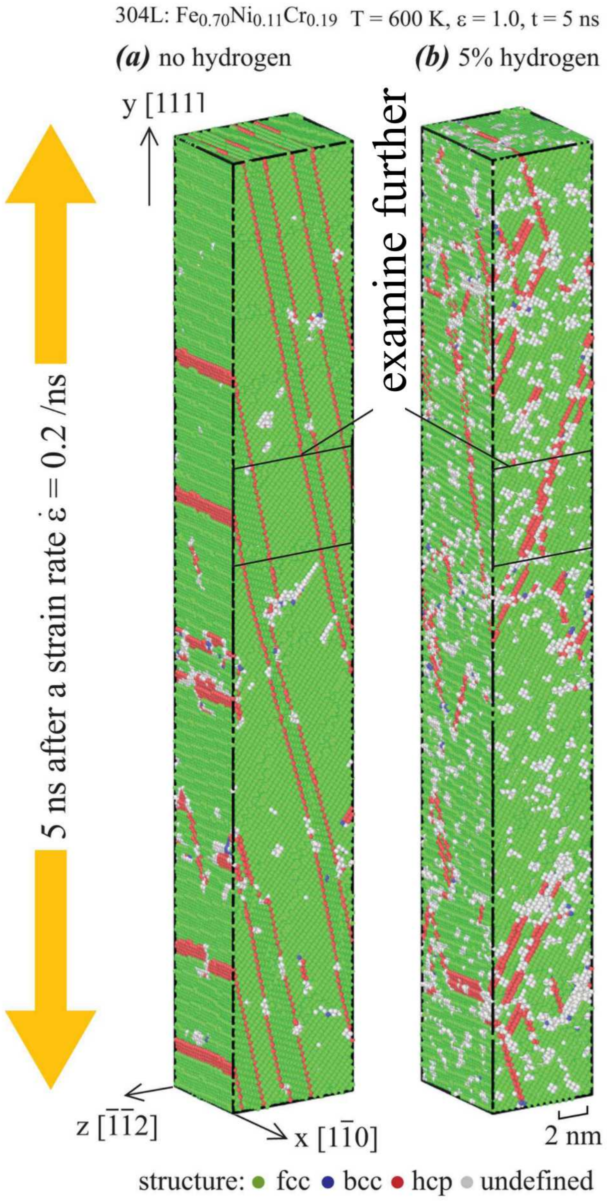


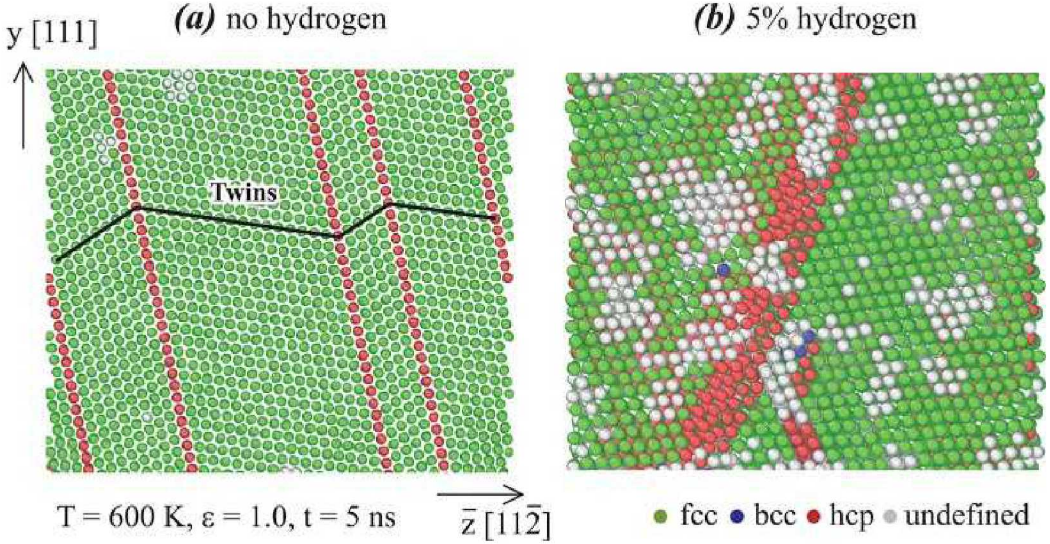
T = 1300 K, t = 23 ns

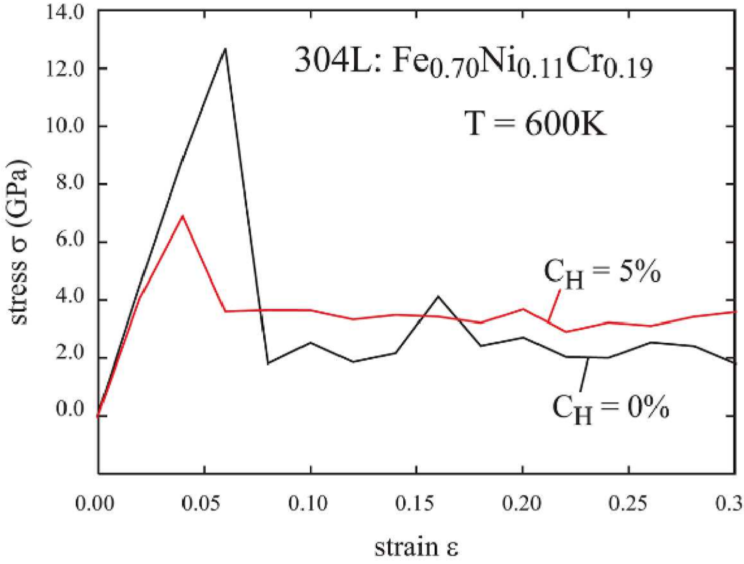
# Working in Progress

1. Our potential predicts hydrogen-vacancy interaction energies of -2.3, -2.4, and -1.7 eV in fcc Fe, Ni, and Cr
2. The corresponding values from our DFT calculations are -0.36, -0.22, and -4.4 eV
3. We are working to address this issue

# MD Tensile Test Simulations







Stress-strain curves

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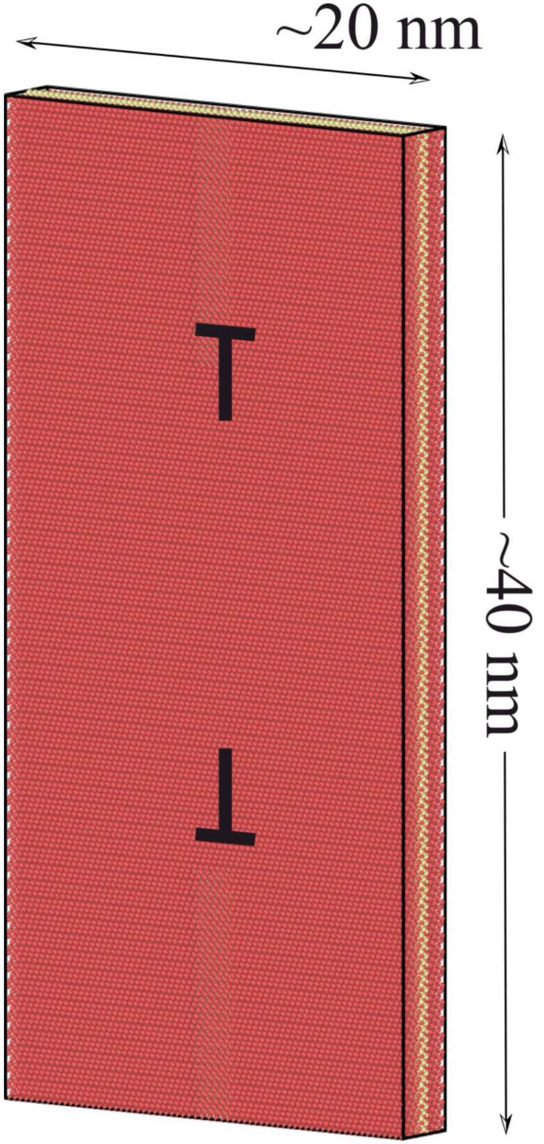
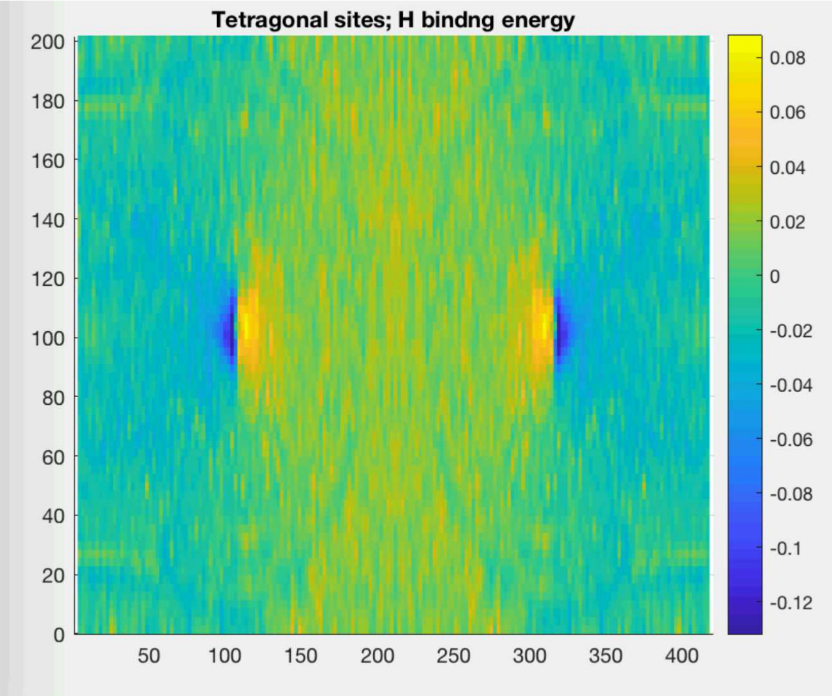
# Opportunities: Al-H Example



## Hydrogen Cottrell atmosphere from energy calculation

1. Unlike literature Monte Carlo methods which statistically sample hydrogen sites, our energy maps exhaustively calculate all 50760 sites
2. Well behaved hydrogen Cottrell atmosphere is obtained



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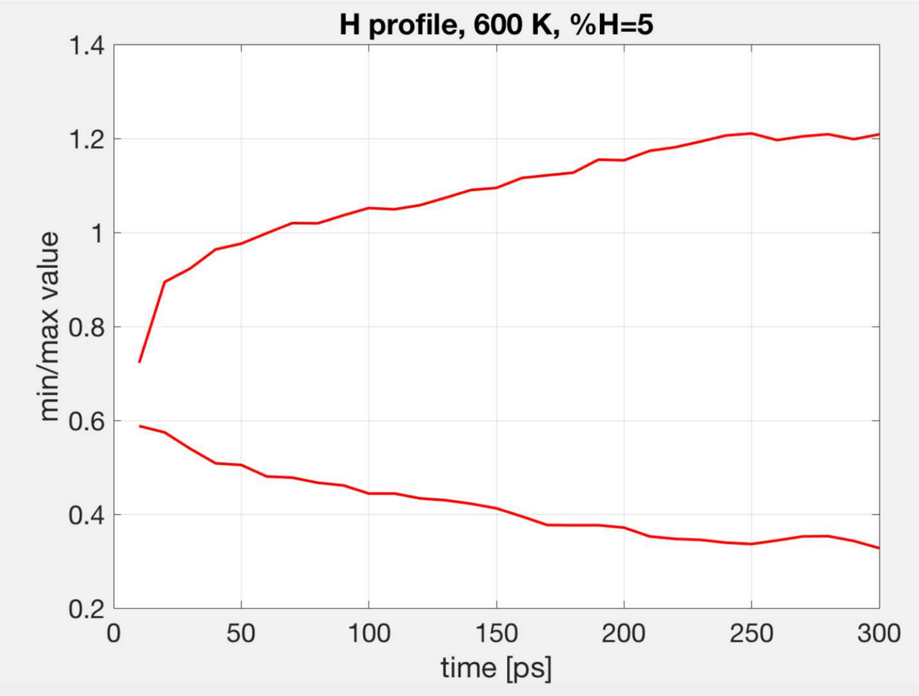
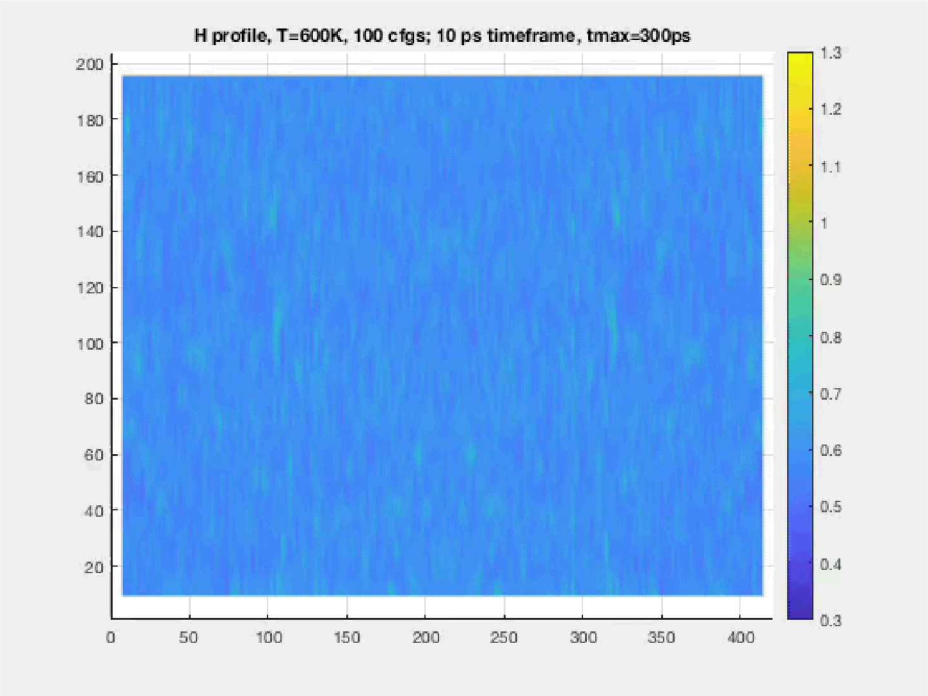
# Opportunities: Al-H Example

## Hydrogen Cottrell atmosphere from time averaged MD calculation

1. Demonstrate that MD can produce meaningful Cottrell atmosphere results

2. This is significant as MD provide time information





# Conclusions

- ☐ Our Fe-Ni-Cr potential
  - ➢ Gives reasonable energy and volume for various compositions
  - ➢ Permits stable MD simulations of austenite
  - ➢ Prescribes well the elastic constants
  - ➢ Captures the correct stacking fault energy
  - ➢ Passes stringent MD validation tests
- ☐ Our H-metal potential
  - ➢ Gives good diffusion barriers in Fe, Ni, Cr
  - ➢ Prescribes well Fe-H, Ni-H, Cr-H energy trends
  - ➢ Captures correct swelling volumes in Fe, Ni, Cr
  - ➢ Matches negative H-H energies from DFT
  - ➢ Passes stringent MD validation tests