First-Principles Studies of Tritium Species Diffusivity Across the Interface of Nickel-Plated Zircaloy-4

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Disclaimer

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Scope of Work

Three Subtasks

- **Task 1**: *Exploring ^3H diffusion across pure Ni-Zr interface*. The diffusion pathway will be obtained and serves as our baseline for the following tasks. **Completed**
- **Task 2:** *Calculating the ^3H diffusion pathways across the Ni-Zr interface when $NiO_x/Ni(OH)_x$ appeared in the Ni side of the interface region*. Based on the pure Ni-Zr interface model from Task 1, we will introduce $NiO_x/Ni(OH)_x$ clusters on the Ni side closer to the interface. Then, the ^3H diffusion pathways and barriers from Ni side to the zircalory-4 will be explored. We will investigate how $NiO_x/Ni(OH)_x$ affects the ^3H diffusion across the interface. **Completed**
- **Task 3**: *Exploring the effects of impurities on ^3H diffusion in Ni-plated Zircaloy-4 getter*. Based on the model constructed in Task 2, we will introduce impurities (e.g., Sn, Fe, C, defects) on the Zr side of the interface. Then, the pathways and barriers of ^3H diffusion from Ni side to the zircalory-4 will be calculated. From this task, we will determine whether the impurity can help or hinder the ^3H diffusion into Zircalory-4 getter to form Zr^3H_x phases for ^3H storage. **Completed**

NETL's supercomputer was shutdown from February through June.

Milestones/Deliverables

Tasks & Milestones	Schedules (Months)										
	11	12	1	2	3	4	5	6	7	8	9
Task1: Exploring ^3H diffusion across pure Ni-Zr interface											
Milestone 1: Obtain ^3H diffusion pathway across Ni-Zr interface											
Task2: Calculating the ^3H diffusion pathways with $NiO_x/Ni(OH)_x$ cluster in interface											
Milestone 2: The effects of $NiO_x/Ni(OH)_x$ on ^3H diffusion pathways & barriers											
Task3: Exploring the effects of impurities on ^3H diffusion in Ni-plated Zircaloy-4 getter											
Milestone 3: The impurity effects on ^3H diffusion pathways & barriers											
Milestone 4: Wrap up the calculations into manuscript and submit final report											
M: monthly report; **S:** semi-year report; **F:** final report	M	M	M	M	M	S	M	M	M	M	F

FY2024 Accomplishments

Publications

(1) H. P. Paudel, T. Jia, W. A. Saidi, D. Senor, A. Casella, Y. Duan, "*First-principles density functional study of tritium diffusion in alpha-Zirconium with C and Sn impurity,*" **Journal of Physical Chemistry C 127**(26)(2023)12435-12443.

(2) D. N. Tafen, Morgan Redington, H. P. Paudel, Y. Duan, "*First-Principles Studies of Tritium Species Dissociability and Diffusivity Across the Interface of Nickel-Plated Zircaloy-4 Getters,*" **Tritium Science Program FY23 Final Report**, DOE/NETL-2023/3931, Dec. 2023. doi:10.2172/2279020.

(3) D. N. Tafen, H. P. Paudel, D. J. Senor, A. M. Casella, Y. Duan, "*Solubility and Diffusivity of Tritium Species in Interface of Nickel-Plated Zircaloy-4: First Principles Density Functional Study,*" **Phys. Chem. Chem. Phys.** (2024) submitted.

(4) Morgan Redington, H. P. Paudel, D. N. Tafen, Daniel P. Miller, Eva Zurek, Y. Duan, "*Tritium Adsorption and Absorption on (100) and (001) Surfaces of Pure and Tin Defective Zirconium,*" **J. Phys. Chem. C** (2024) to be submitted.

(5) H. P. Paudel, D. N. Tafen, D. J. Senor, A. M. Casella, Y. Duan, "*First-Principles Studies of Tritium Species Diffusivity Across the Interface of Nickel-Plated Zircaloy-4*", (2024) under preparation.

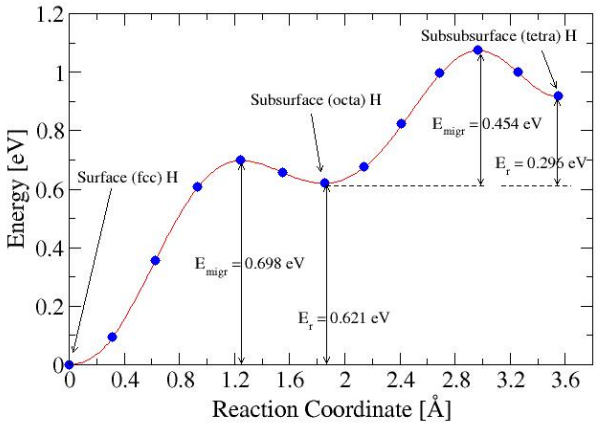
Presentations

(1) Y. Duan, H. Paudel, D. N. Tafen, T. Jia, D. Senor, A. M. Casella, "*First-principles study of the tritium formation in γ-$LiAlO_2$ pellets and diffusion into Zircaloy-4 getter,*" **APS March Meeting**, Mar.03-08, 2024, Minneapolis, MN.

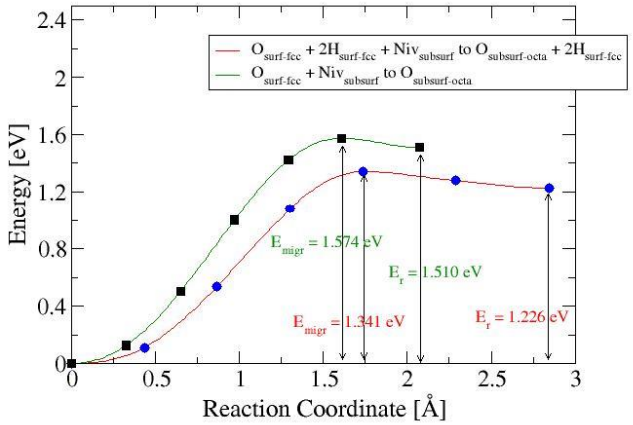
Review from 2023: Tritium Diffusion in Ni (111) Surface

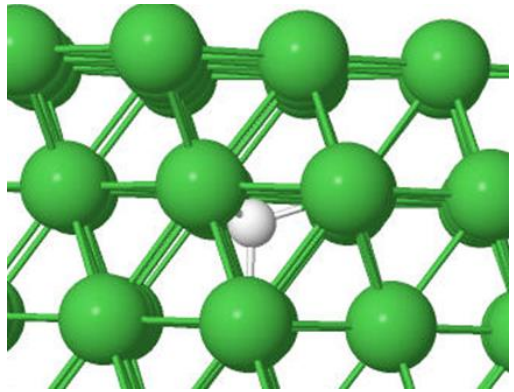
NATIONAL ENERGY TECHNOLOGY LABORATORY

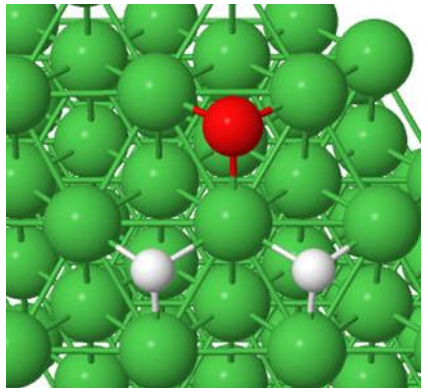
Diffusion of H from Ni(111) surface to bulk

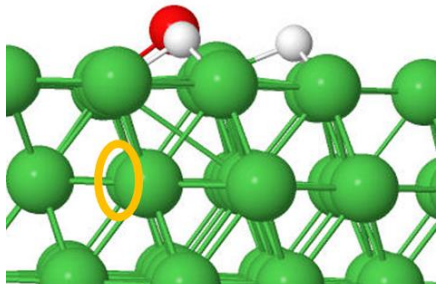


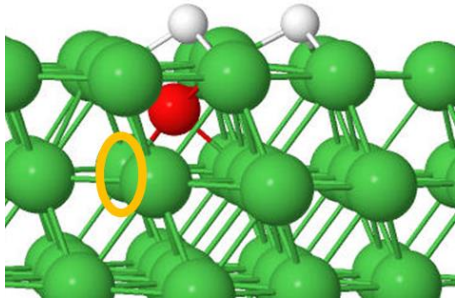
H migration from surface to subsurface



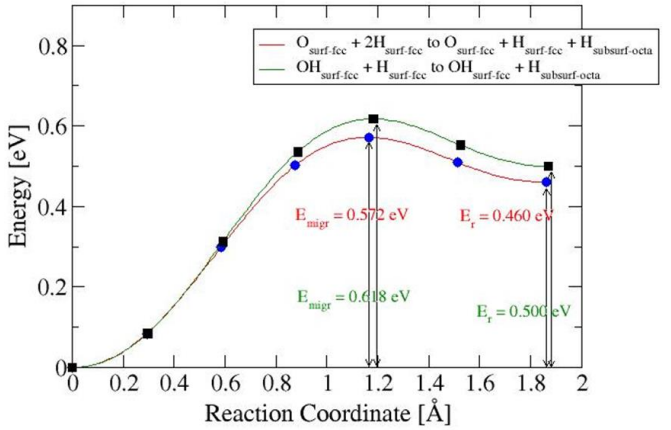








- Explored $^3H_2$ and ^3H_2O binding sites and their dissociation on the (111) surface of $^3H_2O \rightarrow O^3H + ^3H \rightarrow O + ^3H + ^3H$, and $^3H_2 \rightarrow ^3H + ^3H$.
- Formation of NiO_x or $Ni(O^3H)_x$ and higher diffusion energy barrier for O as compared to that of ^3H.
- Only ^3H diffuses through Ni layer and reaches Ni-Zircalory-4 interface to form metal hydrides.

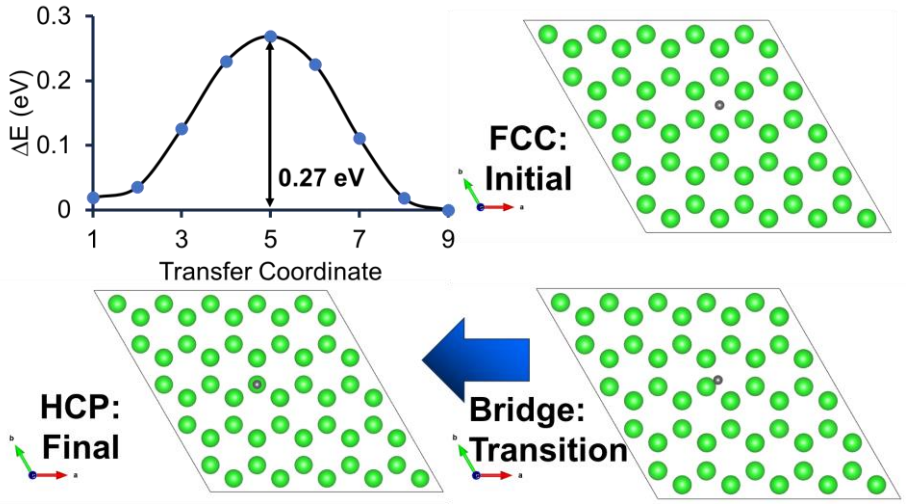


Review from 2023: Tritium Diffusion in Zr (0001) Surface

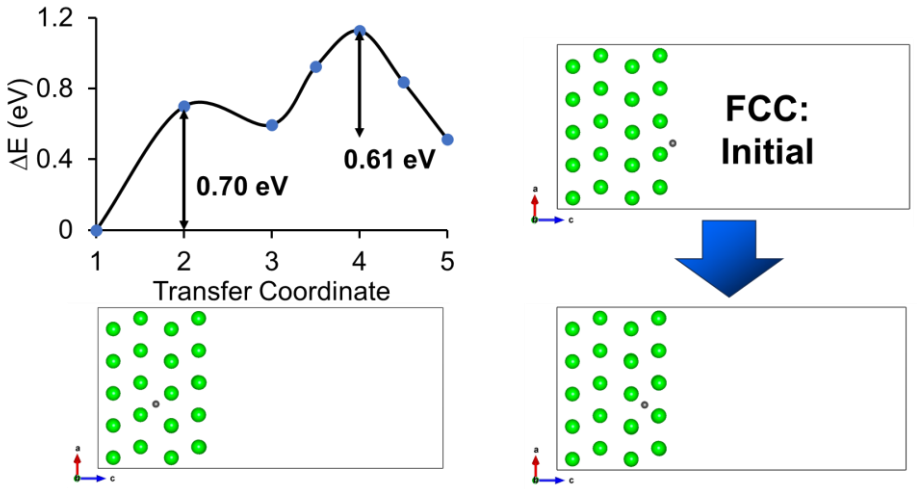
(Completed by Morgan Redington, SUNY Buffalo: 2023 Summer Intern)

The surface-surface and surface to subsurface diffusion barriers for ^{3}H on these surfaces were calculated. The effect of Sn on ^{3}H was shown to have a strong repulsive effect on these surfaces.

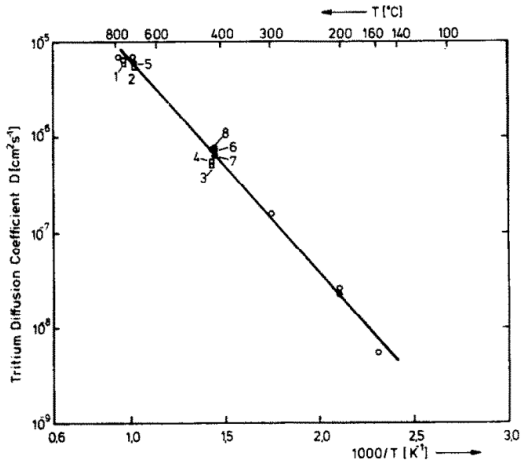
Zr(100) Surface Transfer



Zr(001) Surface to Bulk Transfer



J. of Nuc. Mats. 88 (1980) 15-22



$D_0 = (1.04^{+0.28}_{-0.17}) \times 10^{-3}$ $[cm^2 \cdot s^{-1}]$,

$E_A = -42.1 \pm 1.1$ $[kJ \cdot mol^{-1}]$

~0.43 eV

- The largest diffusion coefficient on the surface was found to be 9.53 x 10^{-10} m^2/s at 600 K.
- A surface-subsurface diffusion coefficient of 5.14 x 10^{-13} m^2/s at 600 K was calculated, with Sn impurities determined to reduce this by up to 9 orders of magnitude.

Creating Zr/Ni Interface Models

Lattice Parameters Mismatch Minimization

Ni-Ni bond length = 2.457 Å
Zr-Zr bond length = 3.170 Å

5*2.457 = 12.28 Å
4*3.170 = 12.68 Å

Parameter ratio a_{Ni}/a_{Zr} = 1.070

Minimize the stress in xy plane!

Ni(111): 9 x 9 22.113 Å
Zr(0001): 7 x 7 22.190 Å

Parameter ratio ~ 0.996

Lattice aspect ratio ~ 1

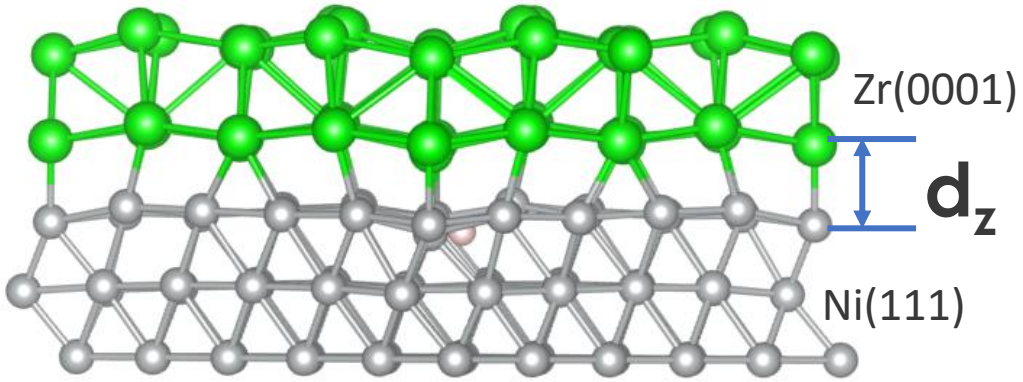
Ni(111): 5 x 5 12.28 Å
Zr(0001): 4 x 4 12.68 Å

Parameter ratio ~ 1.070

Zr/Ni Interface Models

Ni(111)/Zr(0001) Interfaces and Model Optimization

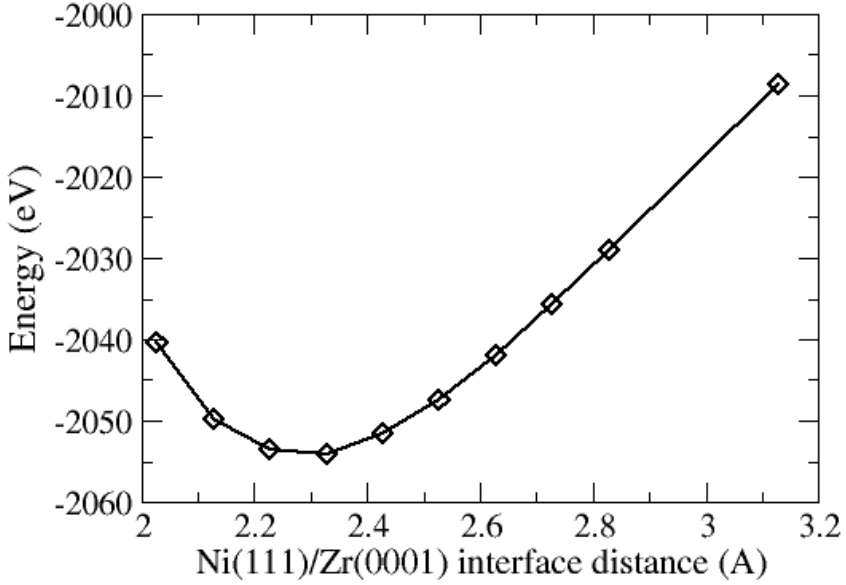
Five-Layer Ni()/Zr Interface Model



5*2.457 = 12.28 Å
4*3.170 = 12.68 Å

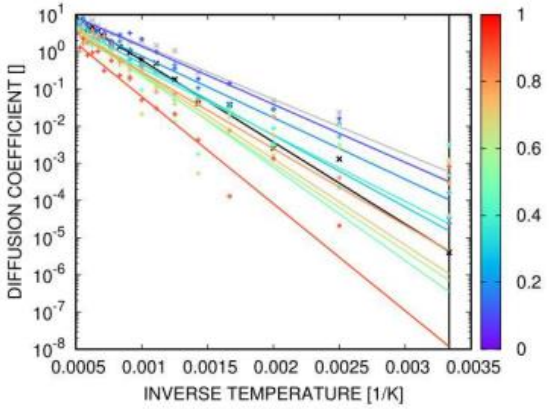
New ratio a_{Ni}^*/a_{Zr}^* = 1.032

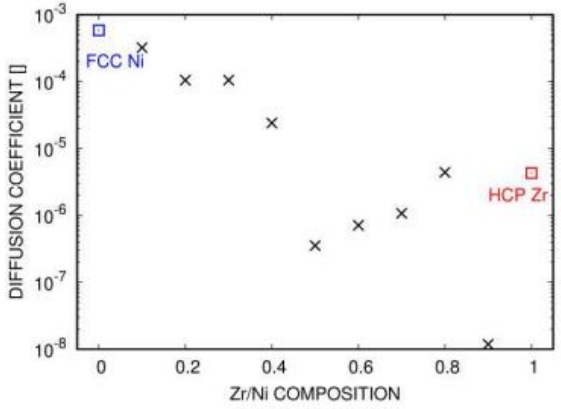
Interface Optimization

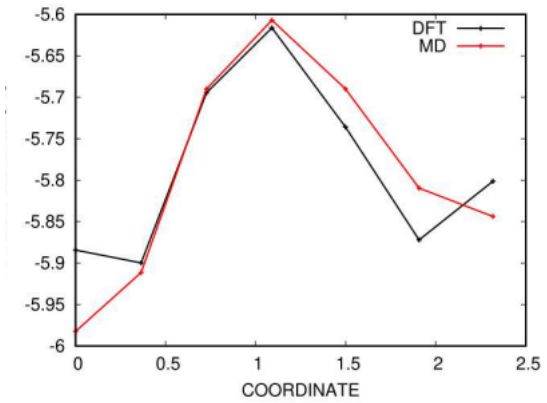


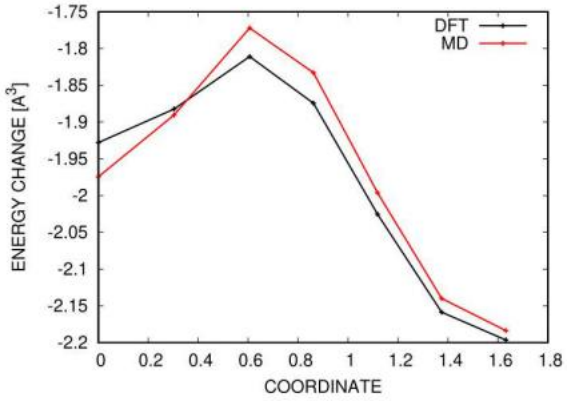
$d_{opt} = 2.32$ Å

Literature Reviews









Jones et al., SAND2019-15034R

- Ni atoms diffuse crossing the interface more easily and deeply into Zr side than Zr atoms into Ni side.
- The activation energies of Ni and Zr are 1.25 and 1.28 eV for Ni(100)//Zr(0001) interface, 1.33 and 1.42 eV for Ni(110)//Zr(0001) interface at the temperature range of 950–1100 K.
- The interdiffusion for case of Ni(110)//Zr(0001) interface is easier than that of Ni(100)//Zr(0001) interface.

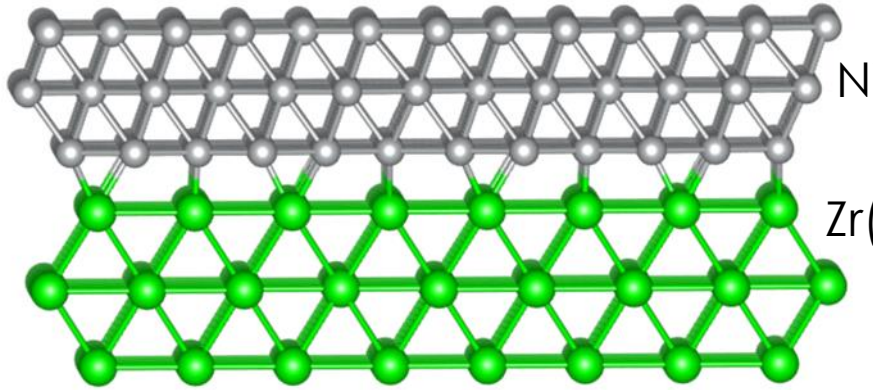
Ni(111)/Zr(0001) Interface Model

Six Layers Ni(111)Zr(0001) Interface Model

On Ni side:

- Bond distance varies d_{Ni-Ni}= 2.5-2.65 Å
- More displacement along a-axis
- Minimal displacement along c-axis

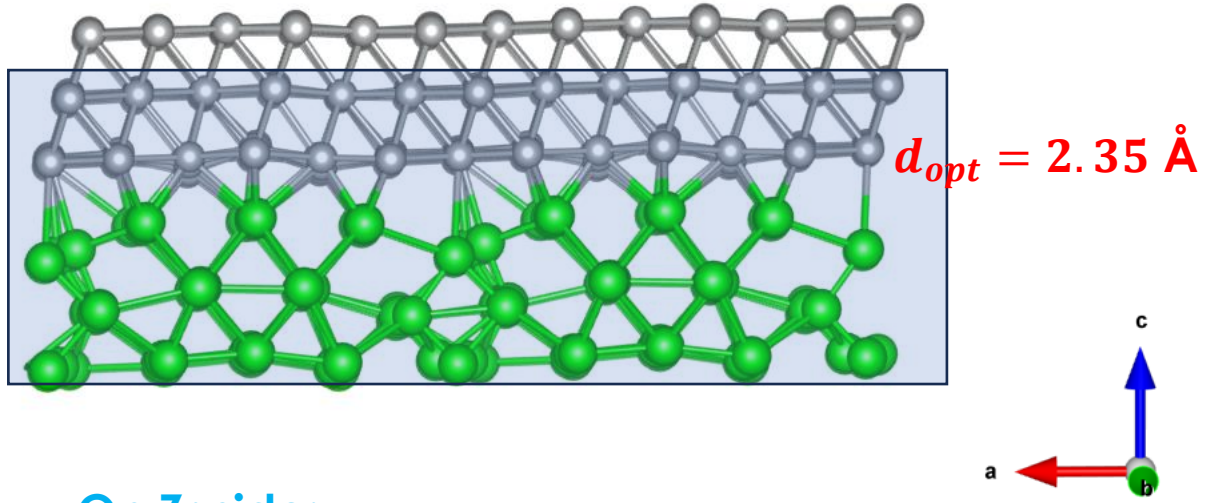
d_{Ni-Ni} = 2.45 Å



Ni(111)

Zr(0001)

d_{Zr-Zr} = 3.24 Å

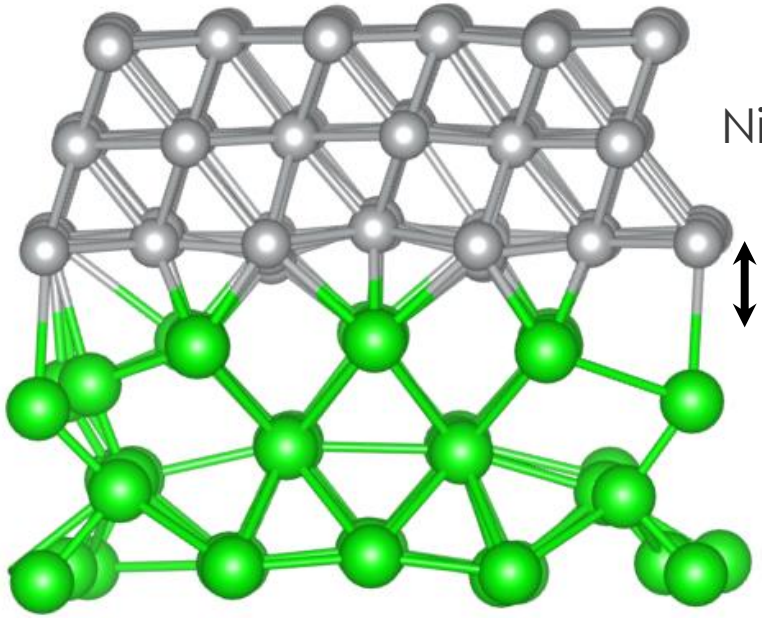


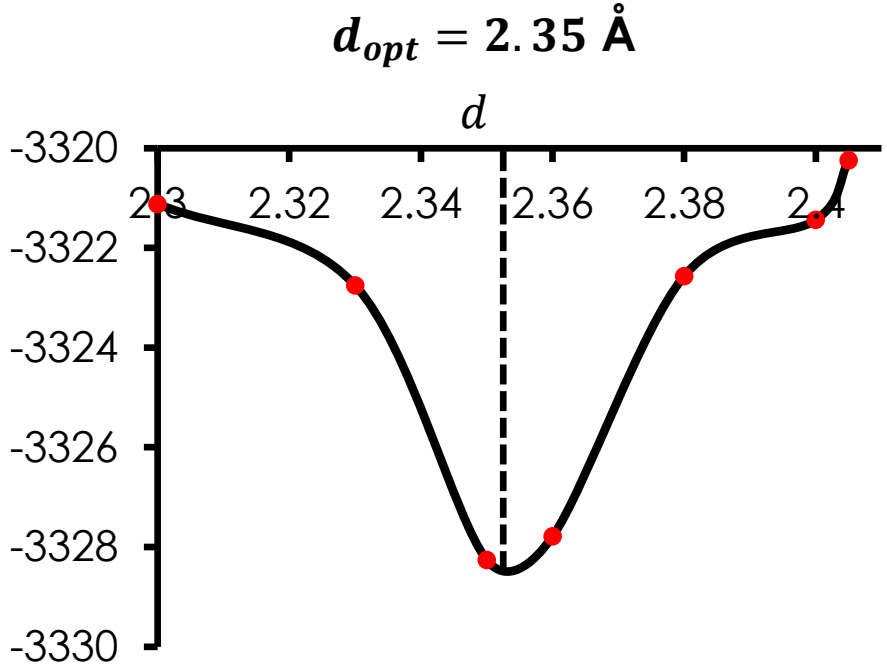
On Zr side:

- More displacement along a-axis
- Boundary atoms are more displaced
- Displacement of some atoms by more than an Å

Ni(111)/Zr(0001) Interface Model

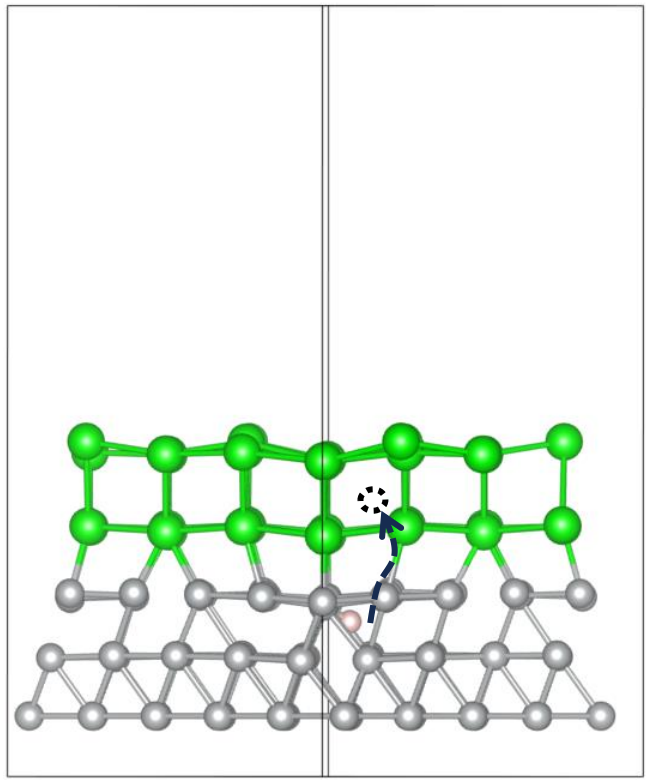
Six Layers Ni(111)Zr(0001) Model Optimization



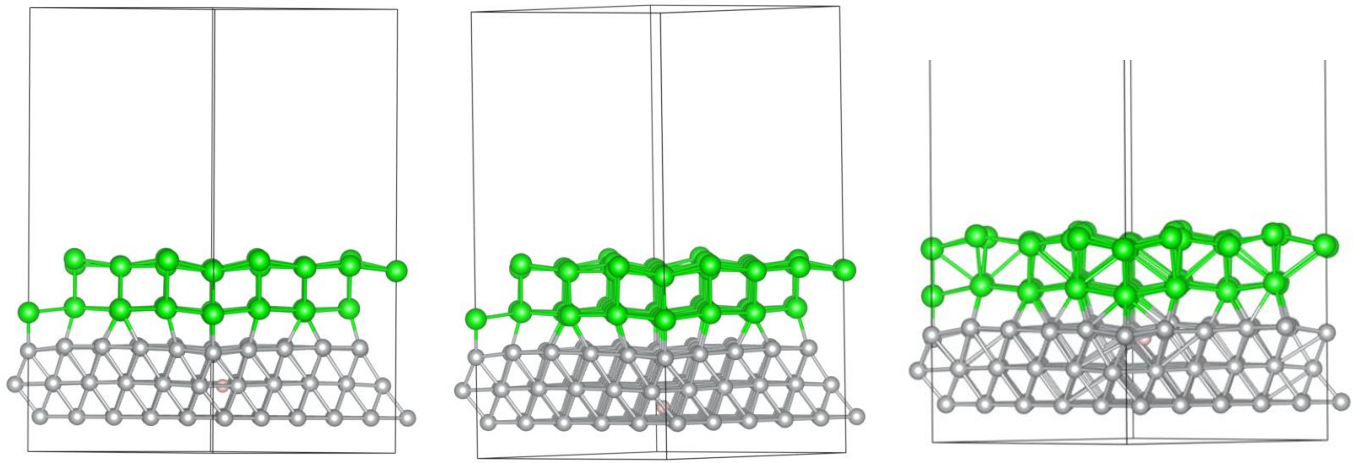


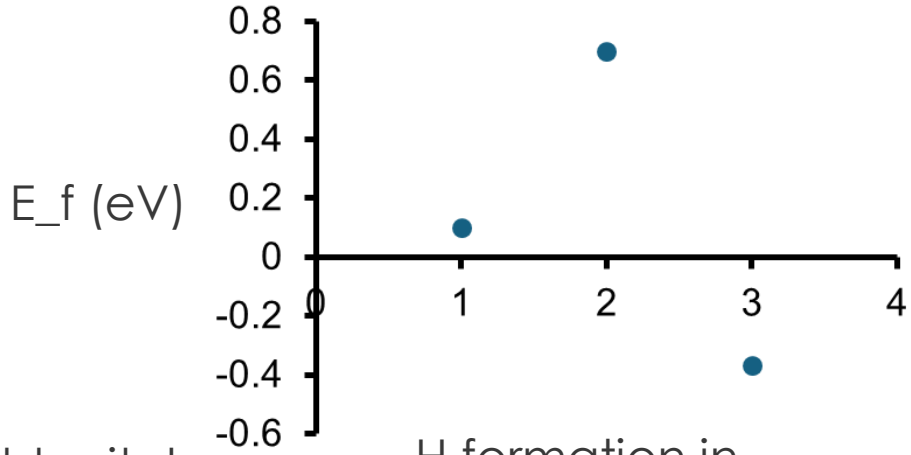
Ni(111)/Zr(0001) Interface Model

Tritium Formation at Ni (111)/Zr(0001) - Initial State Optimization



Top site



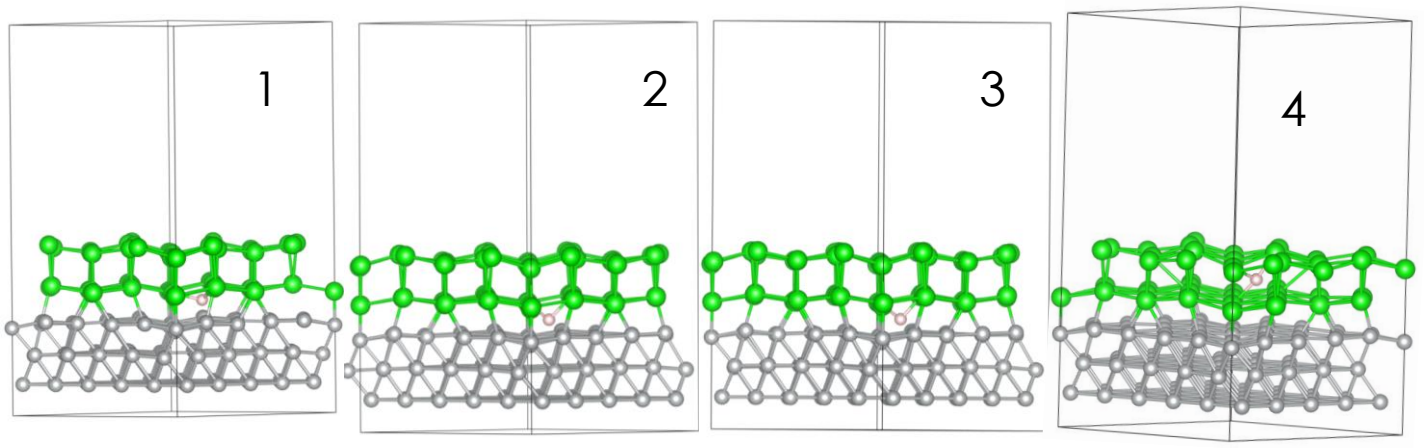


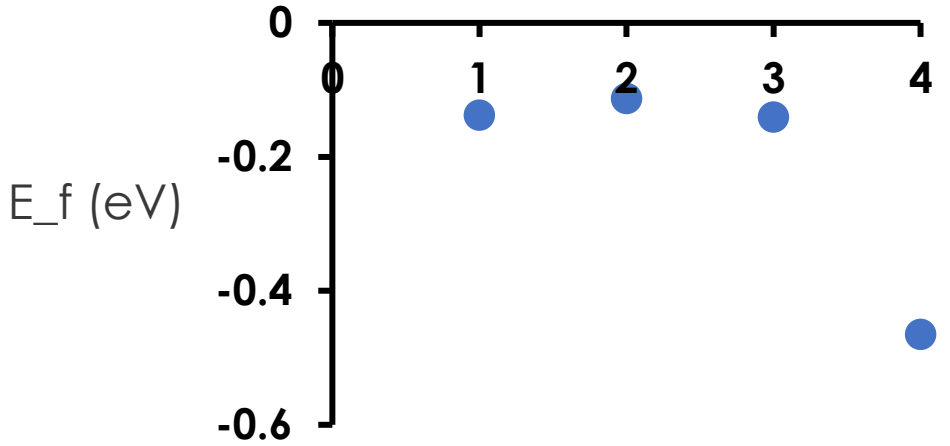
Many local minima, challenging to accurately predict the ^{3}H stable site!

H formation in Ni site = -0.36 eV

Ni(111)/Zr(0001) Interface Model

Tritium Formation at Ni (111)/Zr(0001) - Final State Optimization





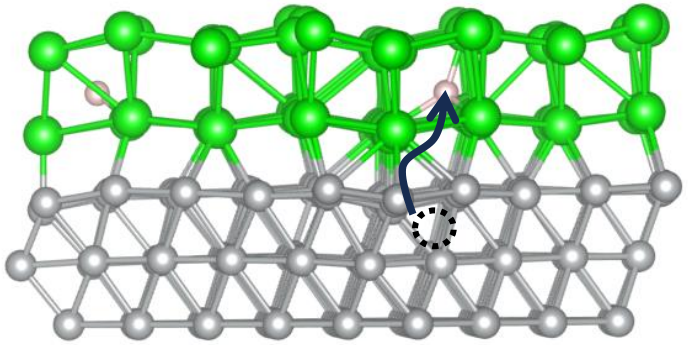
H formation in
Zr site = -0.46 eV

Many local minima, challenging to accurately predict the ^{3}H stable site!

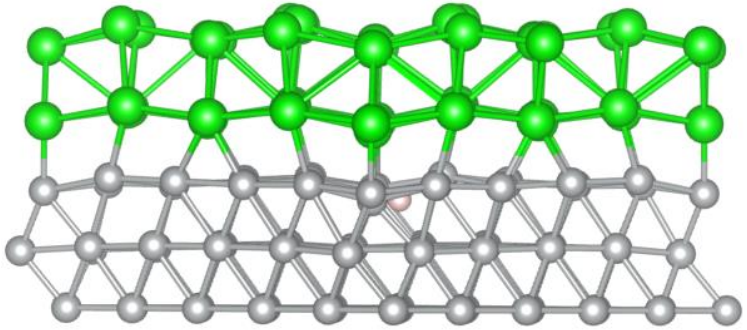
Ni(111)/Zr(0001) Interface Model

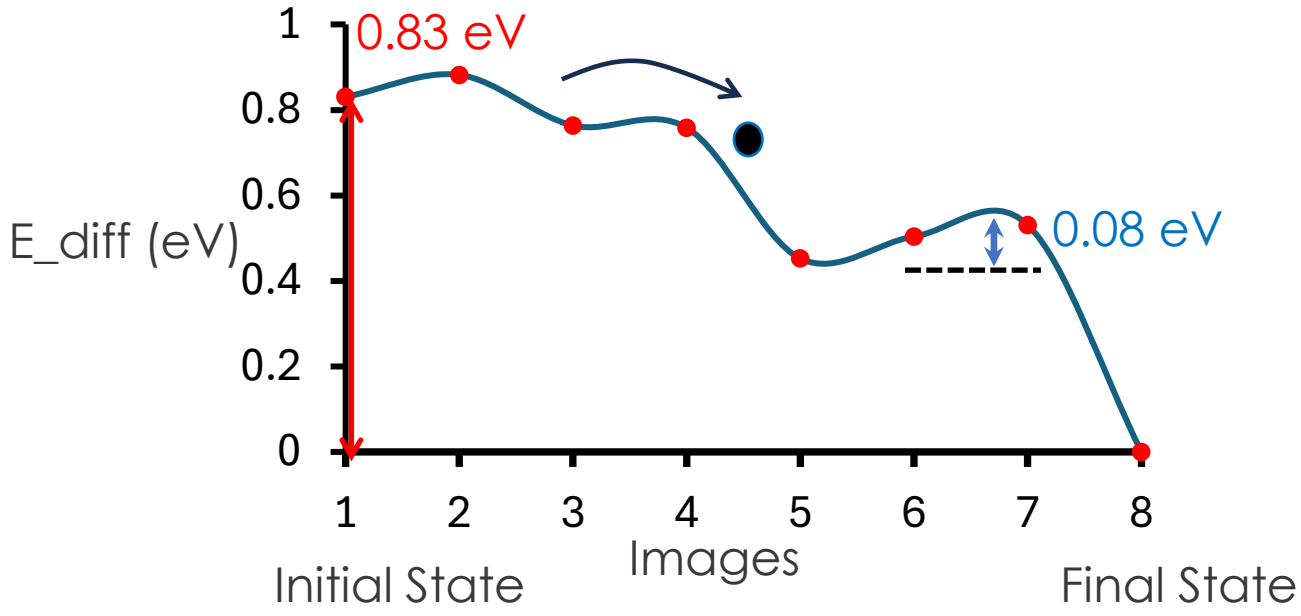
Tritium Diffusion Across Ni(111)/Zr(0001) Interface

Final State



Initial State

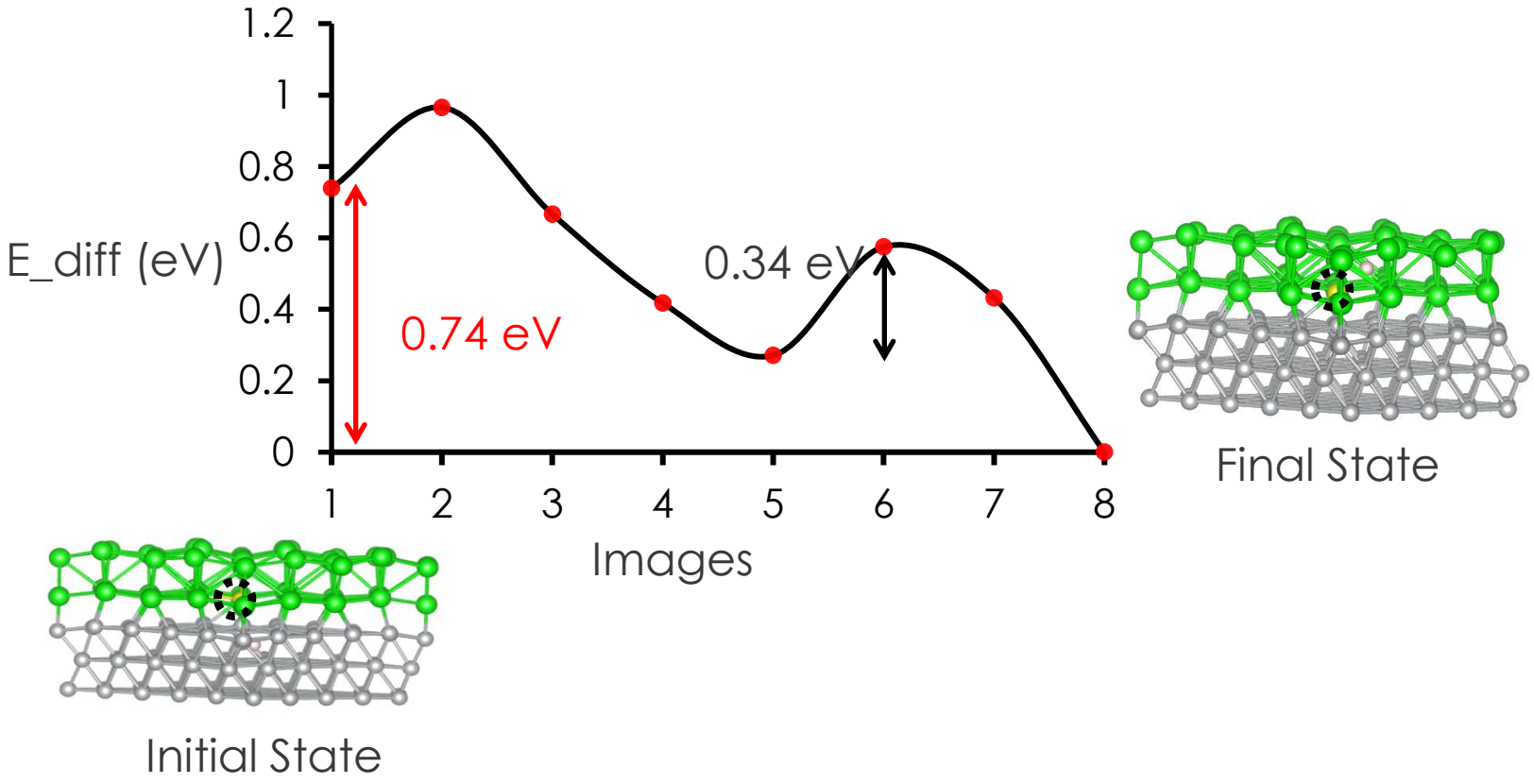




Zr (0001) site for ^{3}H is 0.83 eV lower than Ni (111) site.

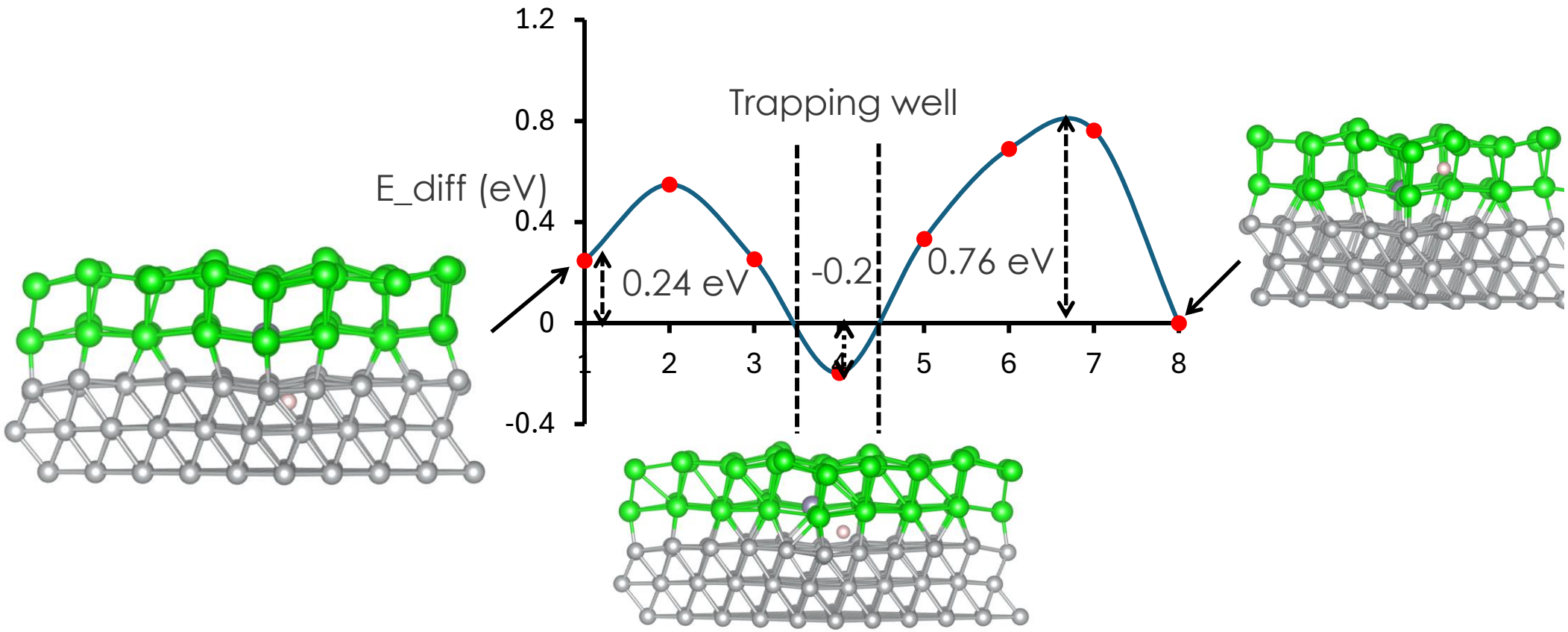
Ni(111)/Zr(0001) Interface Model

Tritium Diffusion Across Ni(111)/Zr(0001) Interface: With One Zr Vacancy



Ni(111)/Zr(0001) Interface Model

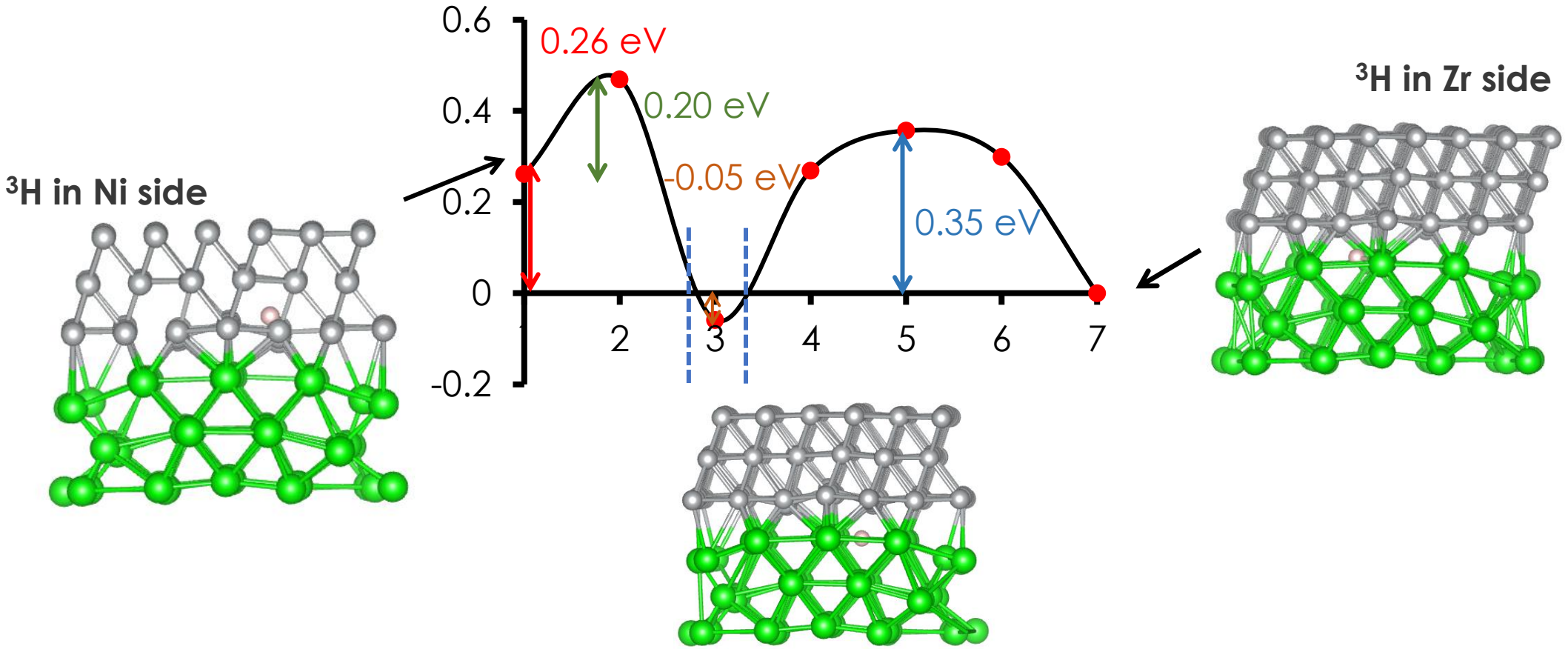
Tritium Diffusion Across Ni(111)/Zr(0001) Interface: With a Sn Impurity



With a Sn impurity, small ^{3}H trapping well was found at the interface.

Ni(111)/Zr(0001) Interface Model

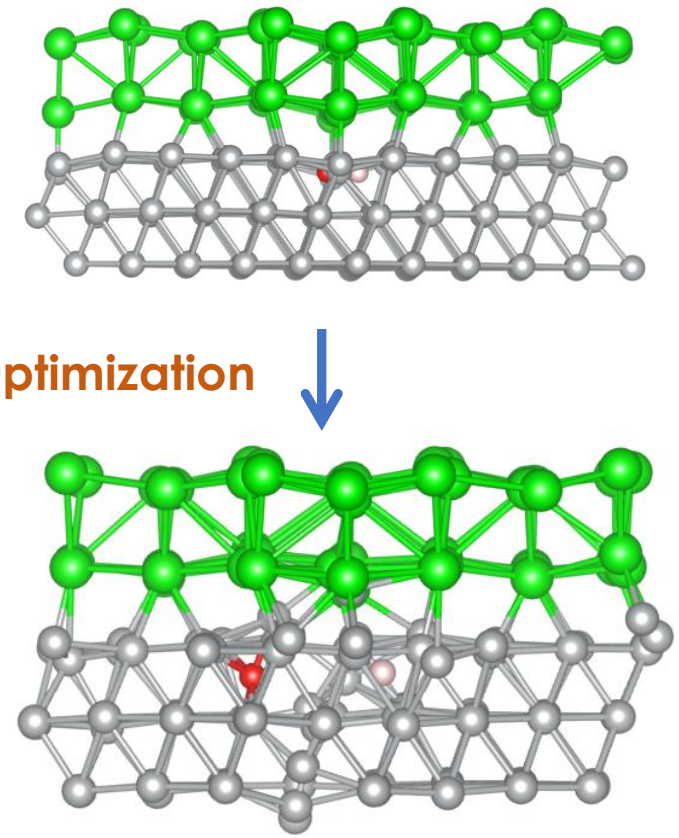
Diffusion of H in Ni(111)/Zr(001) Six Layers



3H is more stable by 0.26 eV in Zr region than in Ni!

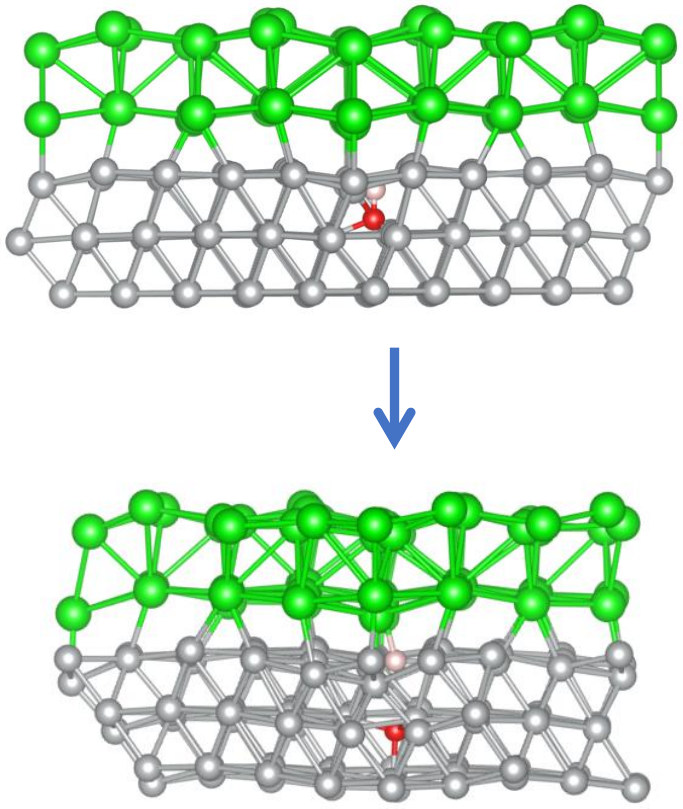
Ni(111)/Zr(0001) Interface Model

Introducing Ni(OH) at the Interface

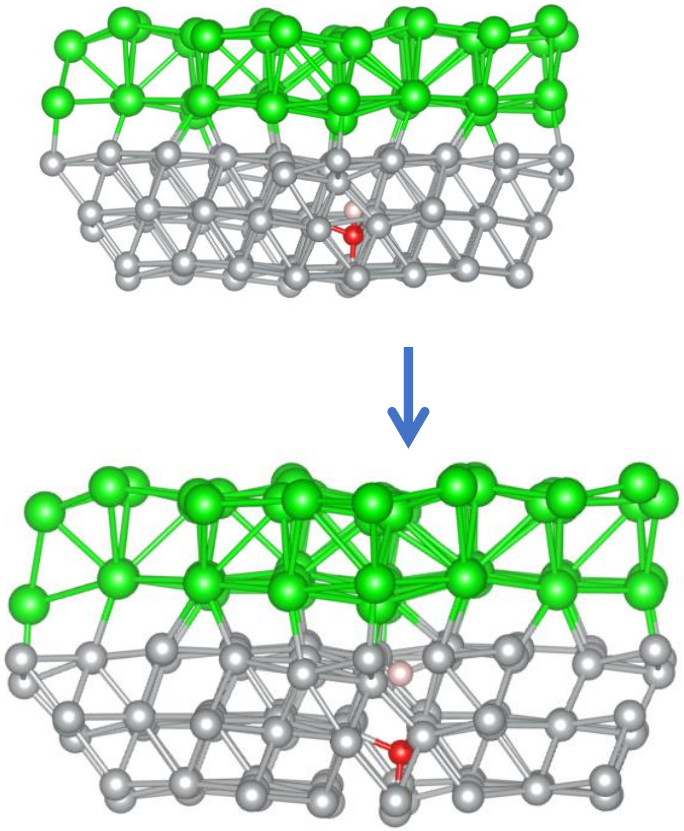


Optimization

^{3}H Formation -4.87 eV



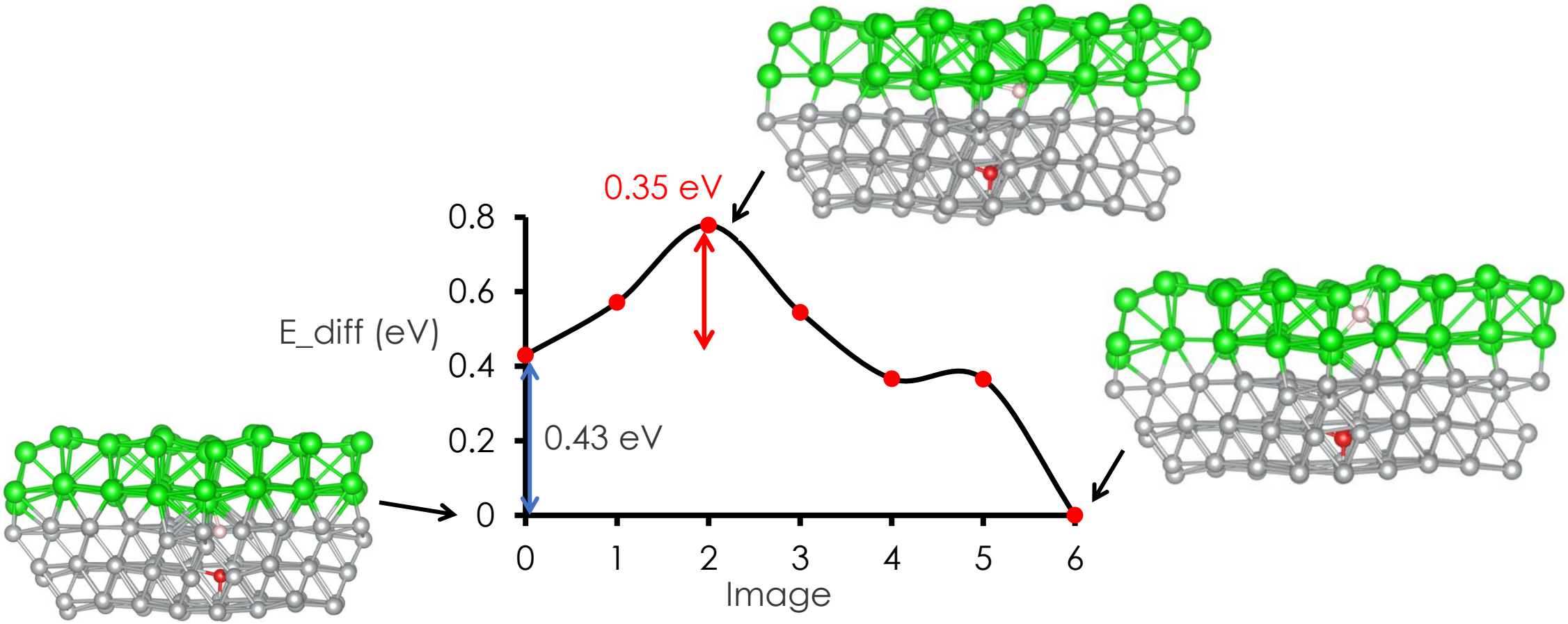
-6.64 eV



-6.59 eV

Ni(111)/Zr(0001) Interface Model

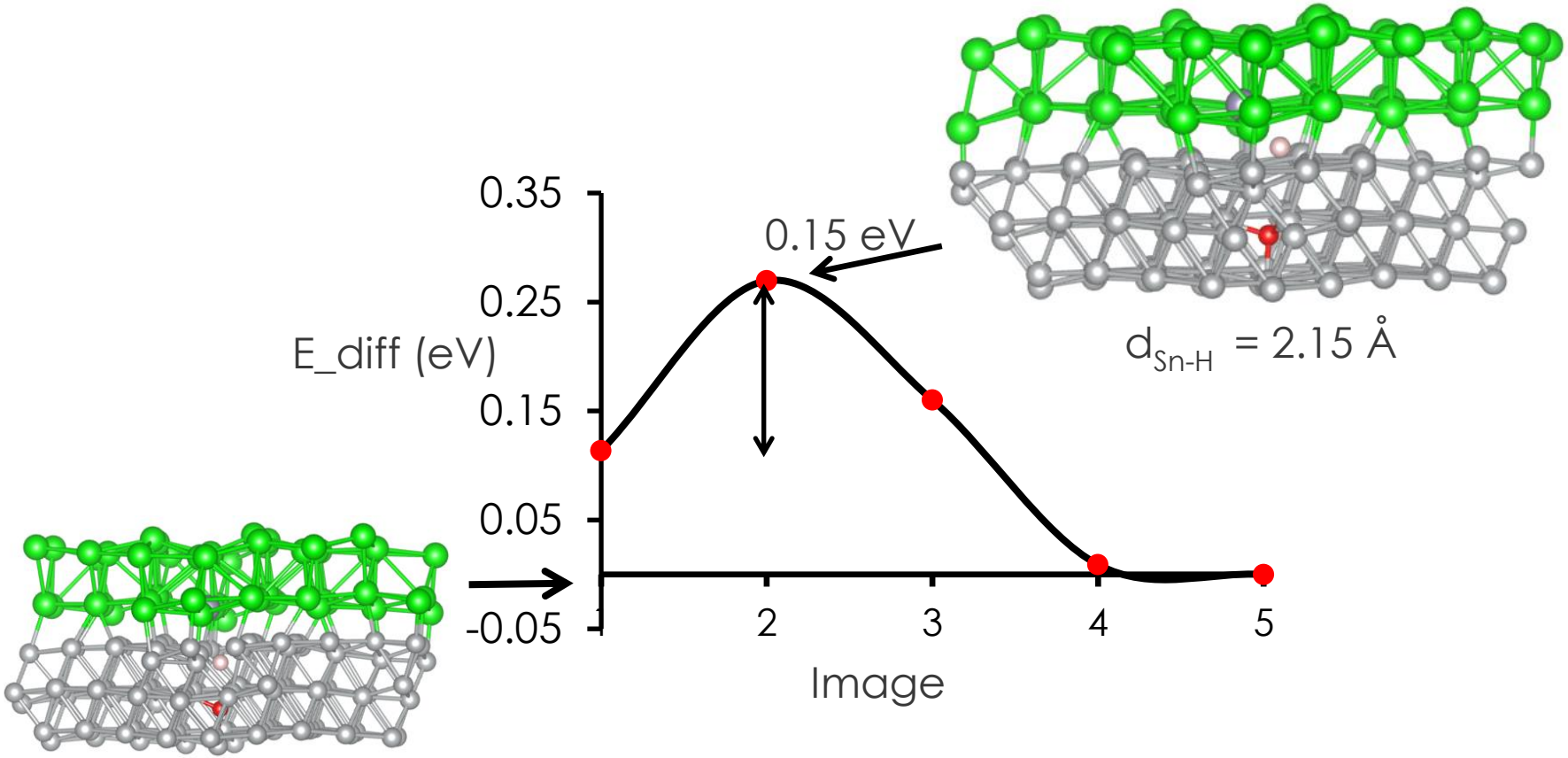
Introducing Ni(OH) at the Interface: Diffusion of ^{3}H



Initial energy barrier height for tritium diffusion in presence of O in Ni (111) was found to be 0.35 eV, almost 0.25 eV higher than with no O impurity but 3H is more stable by 0.43 eV in Zr region.

Ni(111)/Zr(0001) Interface Model

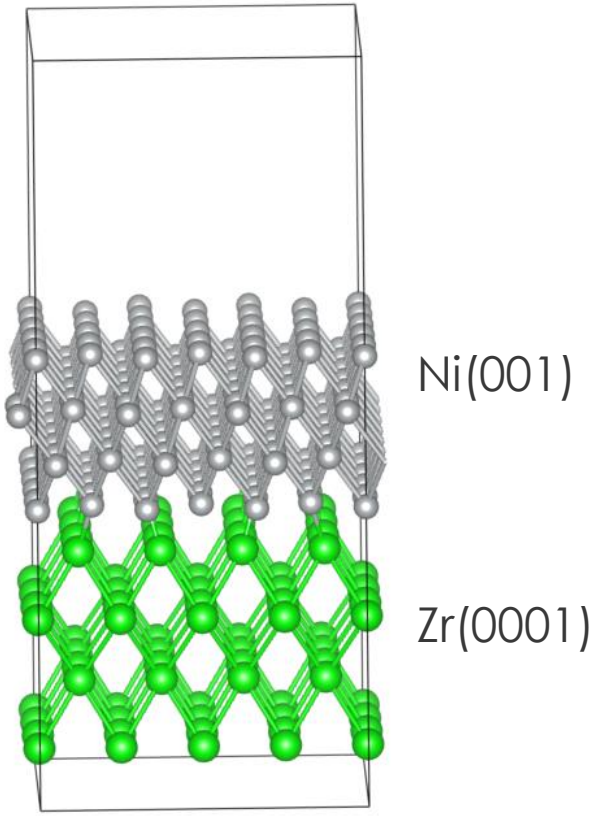
Introducing Sn and Ni(OH) at the Interface: Diffusion of ^3H



The ^3H stability in Zr region is reduced by 0.2 eV with Sn and Ni(OH) as compared to with Ni(OH) only.

Ni(111)/Zr(0001) Interface Model

Ni(001)/Zr(0001) Interface Model



This model provides a more realistic picture for the ^{3}H diffusion at Ni/Zr interface. However, it requires intensive computational resources for the diffusion property calculations.

Ni/Zr Alloy Interface Development

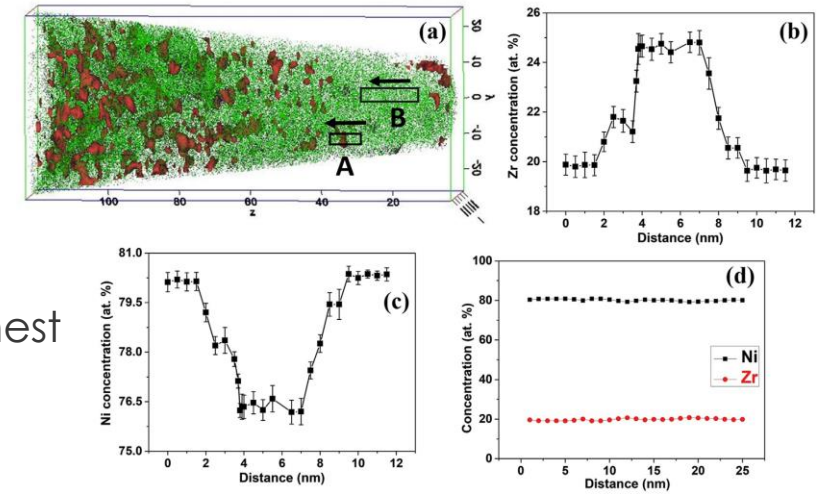
Simple Toy Model for Ni(111)/Zr(0001) Alloy at the Interface

Ni-Ni bond length = 2.457 Å
Zr-Zr bond length = 3.170 Å

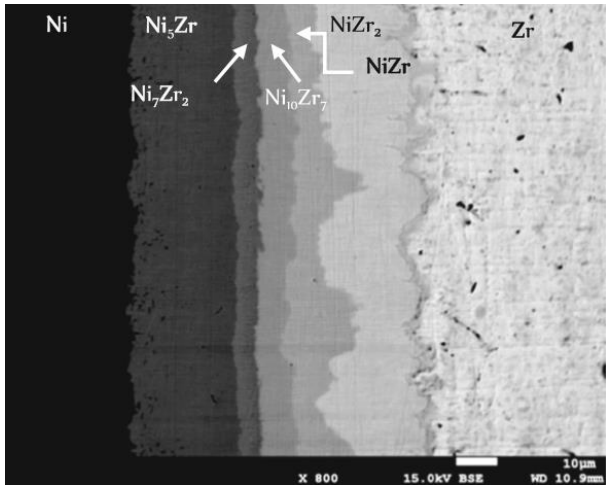
Five intermetallic compounds, Ni_5Zr, Ni_7Zr_2, $Ni_{10}Zr_7$, NiZr and $NiZr_2$ are found to grow in the interdiffusion zone.

Activation energy is found to be lowest for $Ni_{10}Zr_7$ (178 ± 8 kJ/mol) and highest for NiZr (323 ± 6 kJ/mol).

In amorphous NiZr smaller atoms are the predominant diffusing species.



Machine learning assisted computational model for complex interfacial Ni/Zr alloy with varying elemental composition.



TEM studies for microstructure evolution of the as-deposited film (EDXS spectrum showing the Ni and Zr elements).

Back-scattered electron (BSE) image of the interdiffusion zone.

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Summary and Conclusions

- We created Ni/Zr interface models with different Ni and Zr surfaces.
- We optimized the interface models for Ni(111)/Zr(0001) with total of five and six layers and studied the tritium diffusion pathways.
- Ni-Zr bond length was optimized and was found to be 2.32 Å for five layer and 2.35 Å for six layers interface systems.
- In Ni/Zr interface model, ^{3}H was found to be relatively more stable by 0.83 eV in Zr (0001) region than Ni (111) region.
- With a substitutional Sn in in Zr-site, the relative stability was found to be 0.24 eV higher in Zr(0001) region.
- ^{3}H was found to trap by an energy 0.2 eV at the interface region with Sn impurity.
- Initial energy barrier height for tritium diffusion in presence of O in Ni (111) was found to be 0.35 eV, almost 0.25 eV higher than with no O impurity but ^{3}H was more stable by 0.43 eV in Zr region.
- The ^{3}H stability in Zr region was reduced by 0.2 eV with Sn and Ni(OH) as compared to with Ni(OH) only.

Thank You!

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