First-principles Study of the Tritium Species Diffusion Across Ni-Zircaloy-4 Getter Interface

NATIONAL ENERGY TECHNOLOGY LABORATORY

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APS March Meeting, Mar. 20, 2026

Contributors of this Work

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  - Dr. Yueh-Lin Lee
  - Dr. Morgan Redington (summer intern)
- **PNNL**
  - Dr. David Senor
  - Dr. Andrew Casella

Disclaimer

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Tritium & Its Application

- Tritium is a radioactive isotope of hydrogen for commercial and military applications.
  - Tracer for chemical structures, geological water, medical diagnostics, sign illumination, vision device.
  - boost the yield of both fission and thermonuclear weapons
- Half-life of 12.3 years and low concentration (<20 kg) on Earth.
- So, to maintain certain amount of ^{3}H, we need to produce ^{3}H.

To produce tritium:

$$^{6}_{3}\mathrm{Li} + \mathrm{n} \rightarrow \, ^{4}_{2}\mathrm{He} + \, ^{3}_{1}\mathrm{H} + 4.8\ \mathrm{MeV}$$

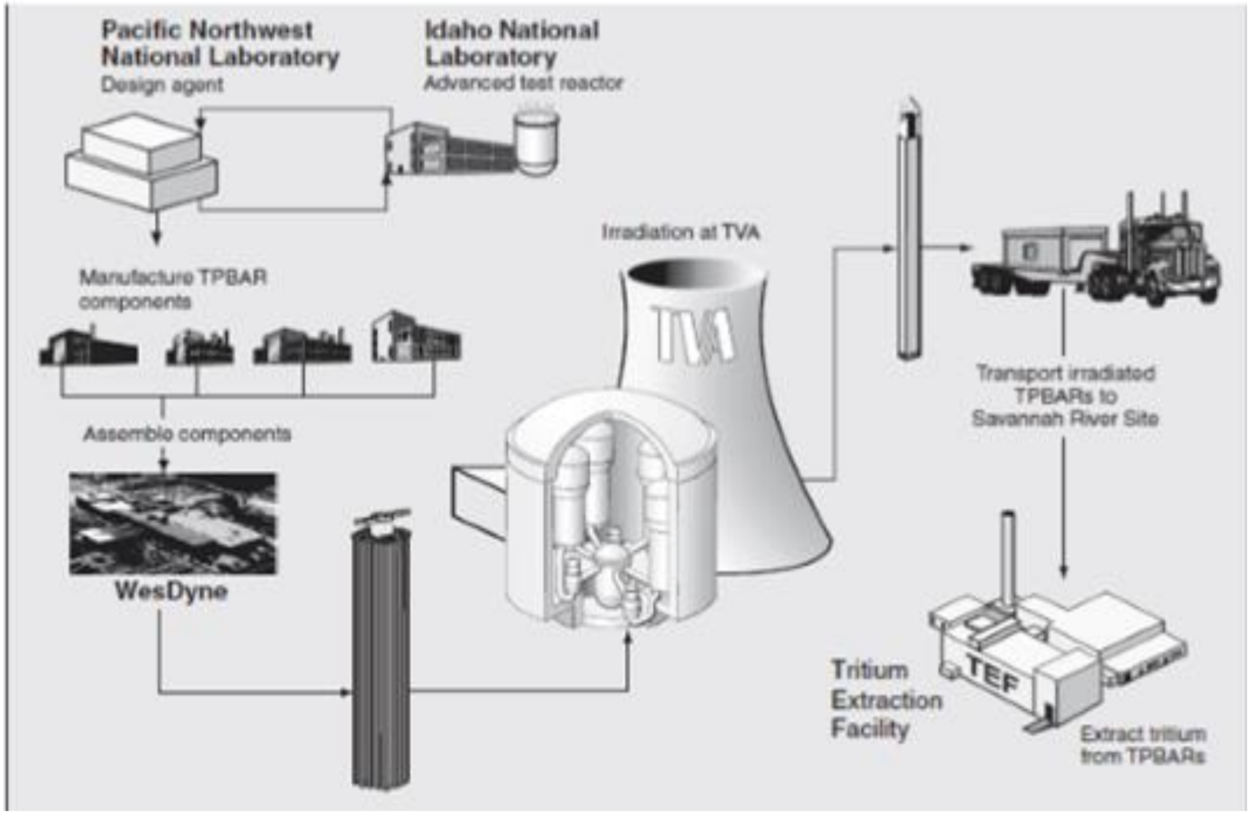
$$^{10}_{5}\mathrm{B} + \mathrm{n} \rightarrow 2\, ^{4}_{2}\mathrm{He} + \, ^{3}_{1}\mathrm{H}$$

$$^{3}_{2}\mathrm{He} + \mathrm{n} \rightarrow \, ^{1}_{1}\mathrm{H} + \, ^{3}_{1}\mathrm{H}$$

$$^{14}_{7}\mathrm{N} + \mathrm{n}\ (\text{cosmic rays} > 4\mathrm{MeV}) \rightarrow \, ^{12}_{6}\mathrm{C} + \, ^{3}_{1}\mathrm{H}$$

TPBAR producing tritium

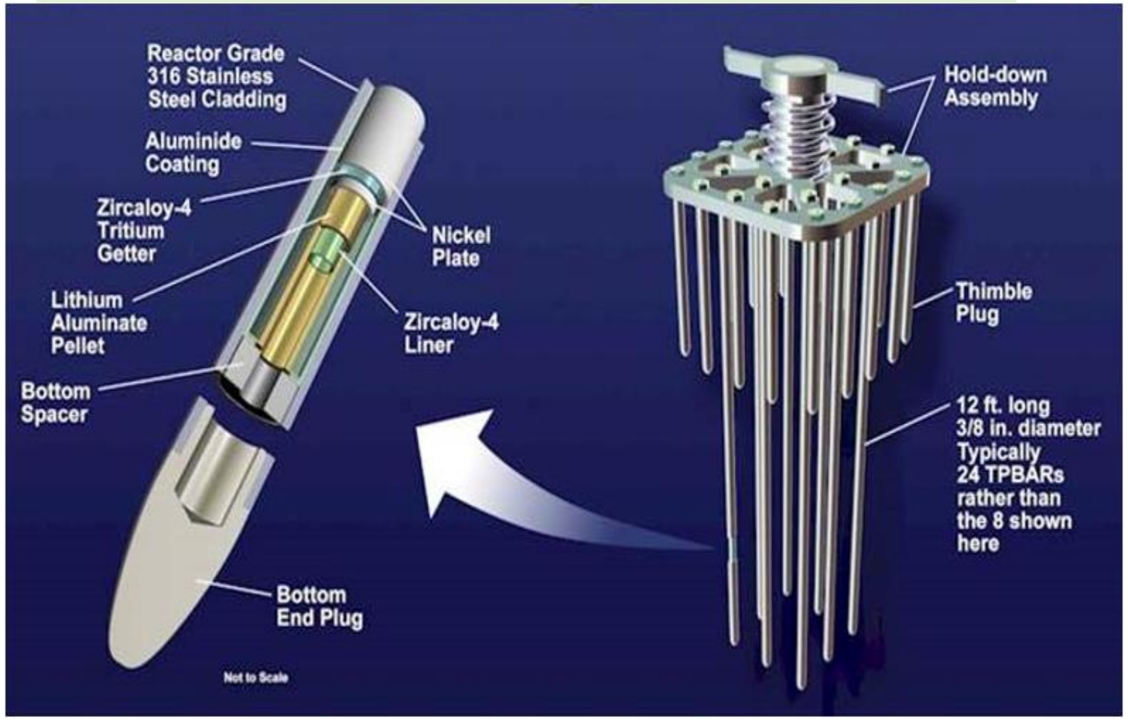
DOE/NNSA's Tritium Modernization Program



- Senor, D.J., *Recommendations for Science and Technology in Support of the Tritium Sustainment Program, PNNL-27216*. 2017, PNNL

Tritium-Producing Burnable Absorber Rod (TPBAR) in light water reactor to produce tritium through

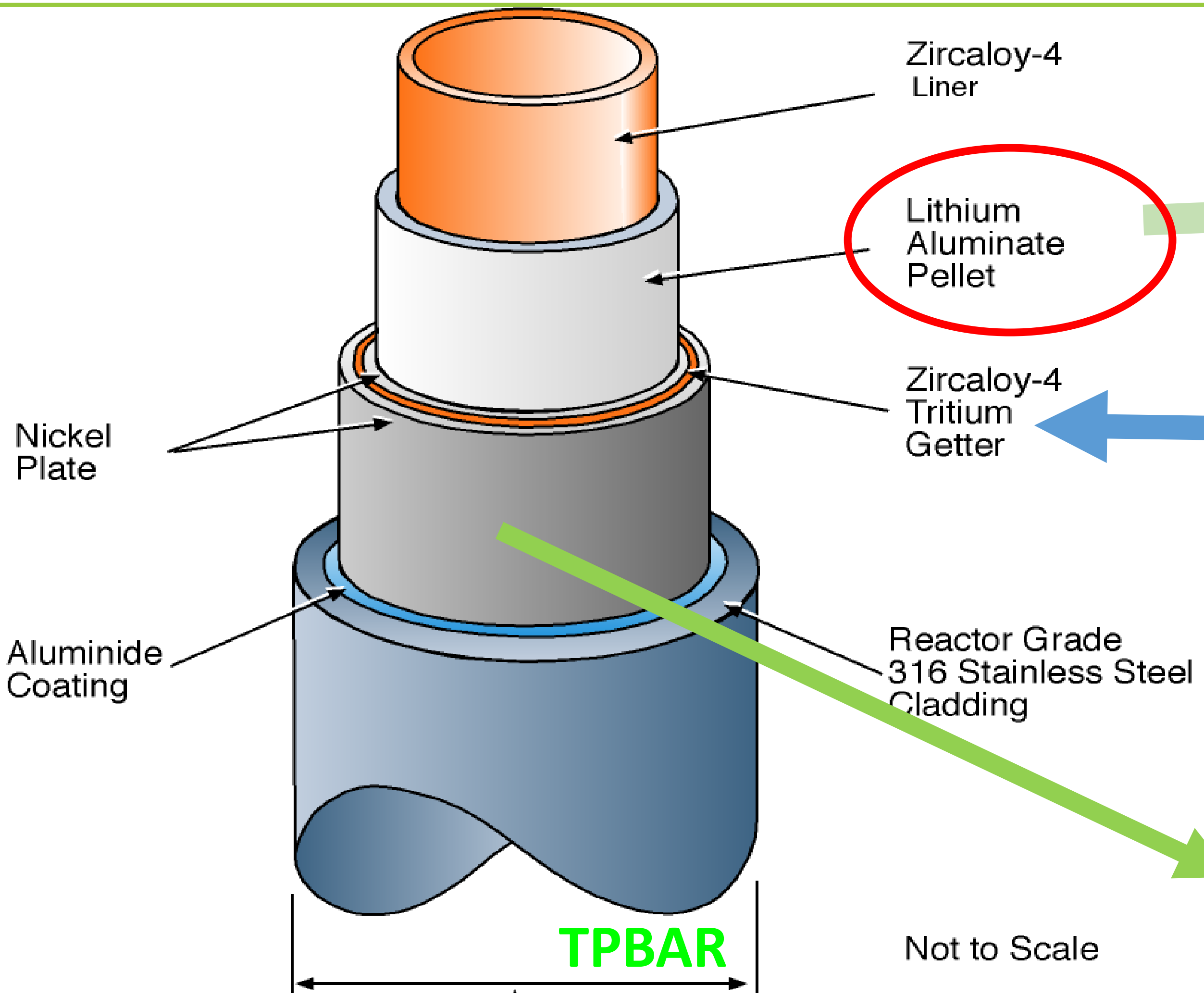
$$^{6}_{3}\mathrm{Li} + \mathrm{n} \rightarrow \ ^{4}_{2}\mathrm{He} \ + \ ^{3}_{1}\mathrm{H} + 4.8\ \mathrm{MeV}$$



One TPBAR produces ~1.0 g $^{3}H_2$ over 1.5 years. Typically arranged in 17x17 array

- Anderson, E. S., *et al*, PNNL-14401, (2003), doi:10.2172/15010654

Tritium production from r-$LiAlO_2$ Pellet



We found

$$^{6}_{3}\mathrm{Li} + \mathrm{n} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{H} + 4.8\ \mathrm{MeV}$$

Main product

$^{3}H_2$, $^{3}H_2O$

Now we focus on:

- T_2 & T_2O diffusion on nickel plate & across Ni-Zircalcoy-4 to form metal hydrides.
  - The role of Nickel Plate. Can the O stay in Ni layer to form NiO_x or $Ni(O^3H)_x$?
  - ^3H species get off the surface & diffusion into getter to form metal hydrides.
  - Impurity effects on ^3H diffusion and metal hydrides formation.

- Paudel, *et al*, **Comput. Mater. Sci. 181**(2020)109748; **193**(2021)110419; **J. Phys. Chem. C 122**(2018)9755-65, 28447-5;, **127**(2023)12435-43
- T. Jia, *et al*, **J. Nucl. Mater. 555**(2021)153111; **540**(2020)152394, **522**(2019)1-10; **Appl. Surf. Sci. Adv. 5**(2021)100114

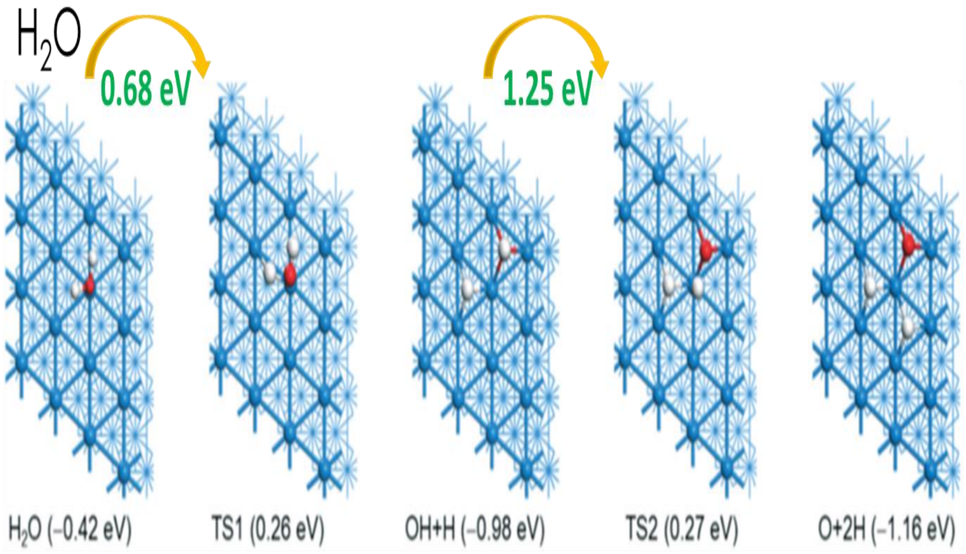
T_2 or T_2O on Ni (111) Surface & subsurface

Our focus:

- If O can stay in the Ni layer to form NiO_x or $Ni(OH)_x$
- Only ^3H pass through Ni layer to get into Getter to form metal hydrides.

Literature review

- H_2O



$H_2O \rightarrow OH + H$

$OH \rightarrow O + H$

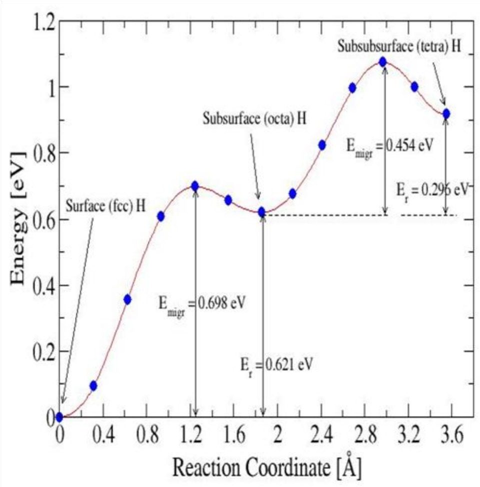
- H_2 (g) $\rightarrow$ H + H

Size	Method	E_a(eV)	E_r(eV)
4 x 4	PBE+vdW	0.09* (0.25ML)	-0.60
4 x 4	PBE+vdW	0.03** (0.125ML)	-0.75
4 x 4	PBE+vdW	0.13** (0.25ML)	-0.74

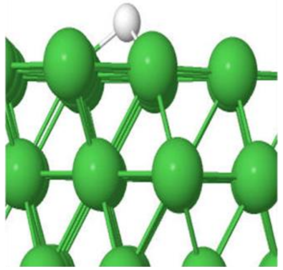
Zhu et al. Catal. Sci. Technol. 2019, **9**, 199.
Shirazi et al. Phys. Chem. Chem. Phys. 2017, **19**, 19150.

*Both H-atoms located at the fcc and hcp sites adjacent to each other. **fcc and hcp sites opposite to each other.

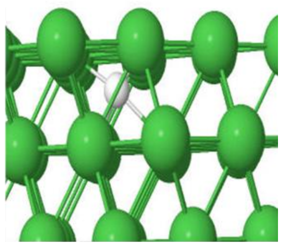
Diffusion of H from Ni(111) surface to bulk



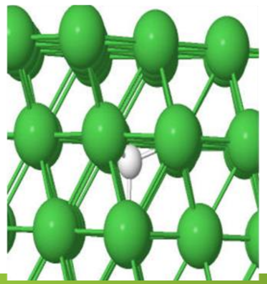
H: fcc



H: octahedral



H: tetrahedral



White: H
Green: Ni
Red : O

Chemical Potential Domains for $Ni(OH)_2$

Thermodynamic Basis

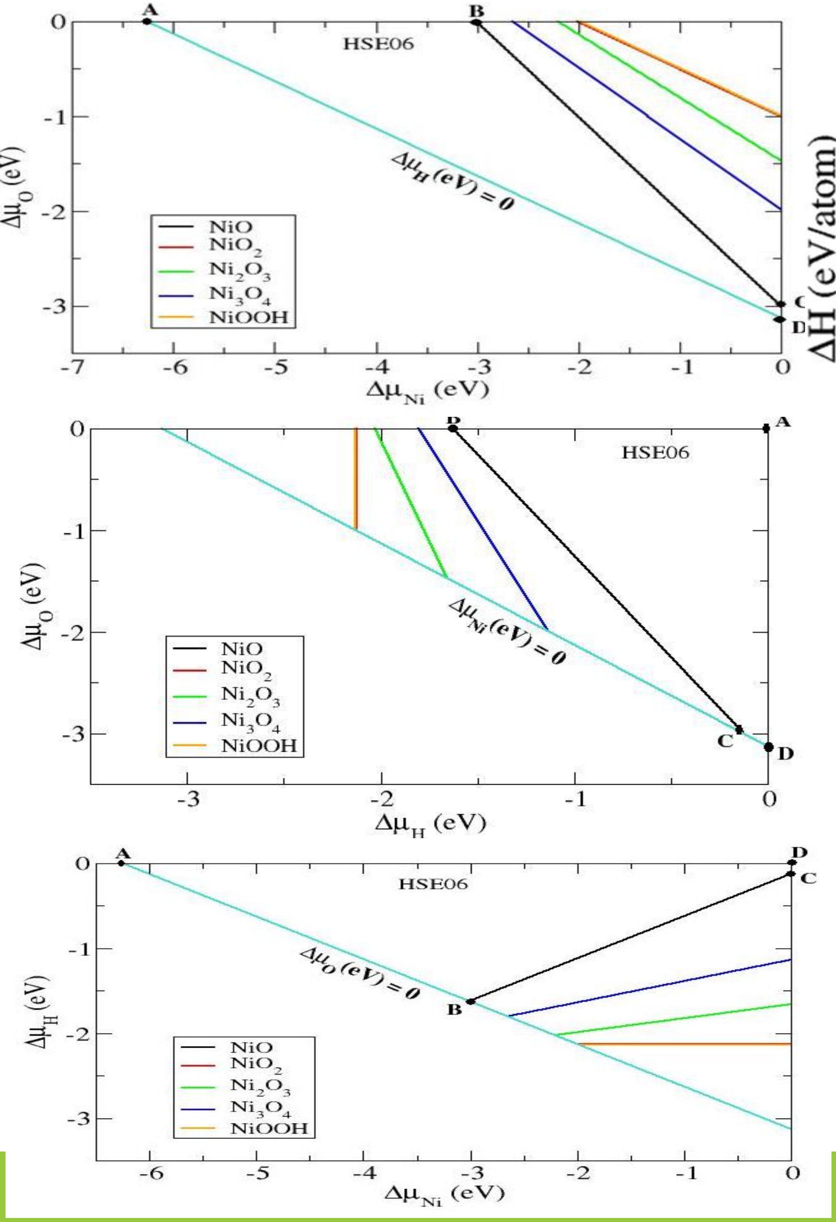
- Stability requires smaller atomic chemical potential than corresponding elemental solid, i.e., $\mu_i \le \mu_i^{solid/gas}$

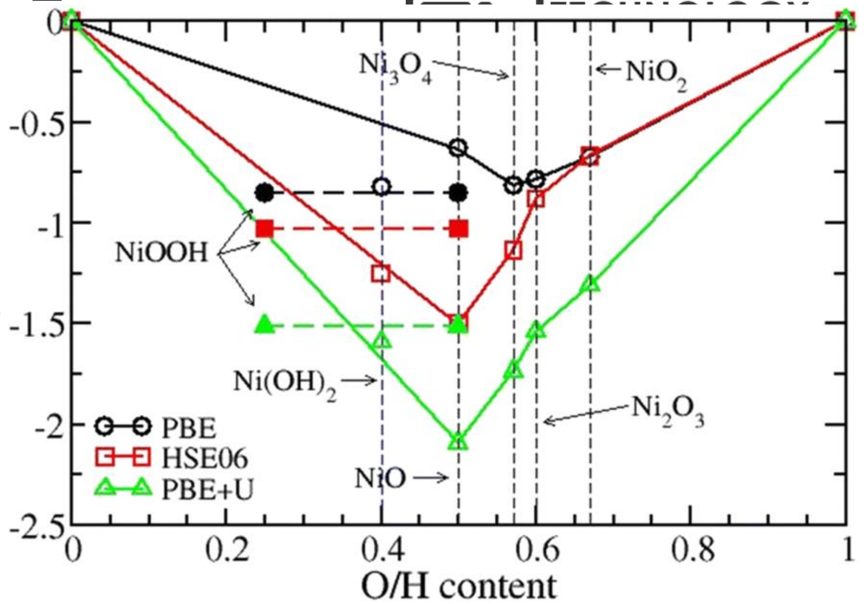
  and

$$\Delta\mu_{Ni} + 2\Delta\mu_O + 2\Delta\mu_H = \Delta H(Ni(OH)_2)$$
$$\Delta\mu_i = \mu_i - \mu_i^{solid/gas}$$
$$\Delta\mu_i \le 0, \qquad i = Ni, O, H$$

- Constraints on $\Delta\mu_i$ to avoid the formation of other competing pha considering the existing solids NiO, Ni_2O_3, Ni_3O_4, NiO_2, NiOOH

$$\Delta\mu_{Ni} + \Delta\mu_O \le \Delta H(NiO)$$
$$\Delta\mu_{Ni} + 2\Delta\mu_O \le \Delta H(NiO_2)$$
$$2\Delta\mu_{Ni} + 3\Delta\mu_O \le \Delta H(Ni_2O_3)$$
$$3\Delta\mu_{Ni} + 4\Delta\mu_O \le \Delta H(Ni_3O_4)$$
$$\Delta\mu_{Ni} + 2\Delta\mu_O + \Delta\mu_H \le \Delta H(NiOOH)$$



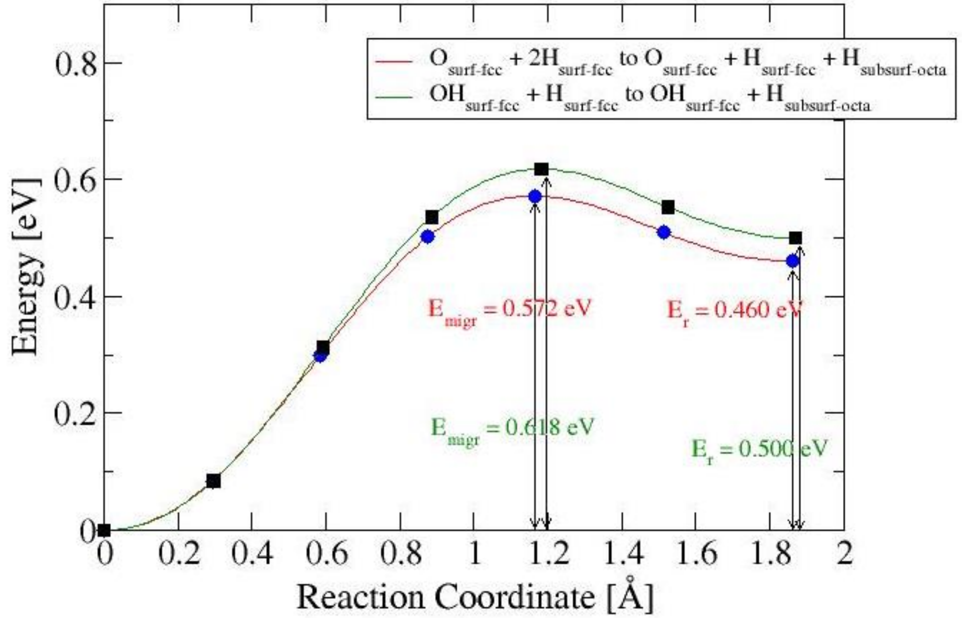


- Stable chemical potential region of the bulk Ni(O[3]H)$_2$ in terms of the chemical potentials $\Delta\mu_O, \Delta\mu_{Ni}$, and $\Delta\mu_H$ using PBE functional.
- Points A, B, C, and D define the limiting stable conditions, the allowed chemical potential range for Ni(O[3]H)$_2$ to be a stable phase.

- Tafen, *et al*, **PCCP 27**(2025)481-489
- Redington, *et al*, **PCCP 27**(2025)7893-7904

H and O Diffusion thru Ni(111) Surface

H migration from surface to subsurface



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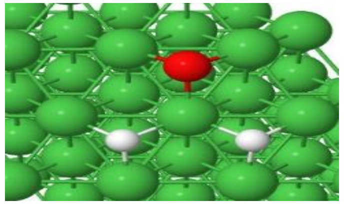

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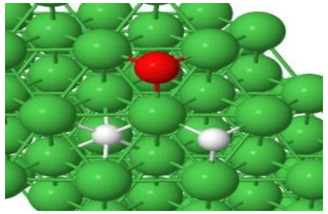

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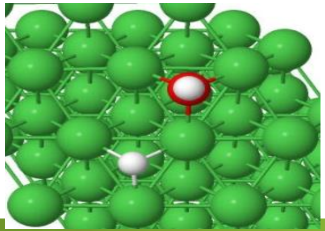

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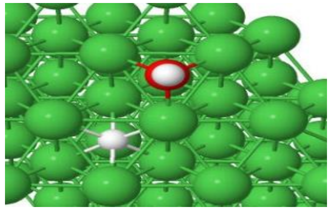
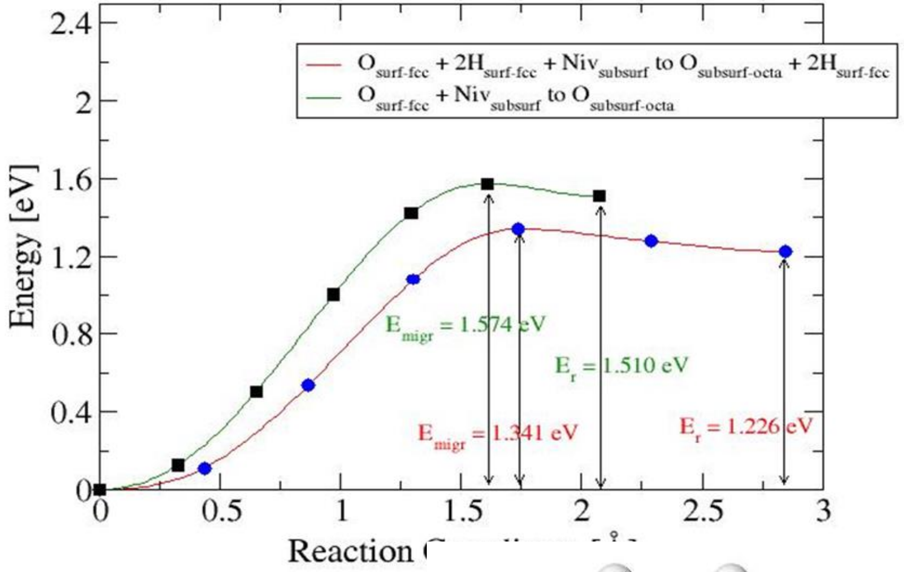
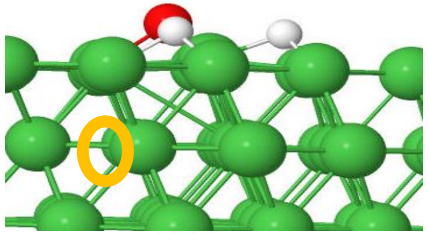


O migration from surface to subsurface



O = Niv, Ni vacancy

IS



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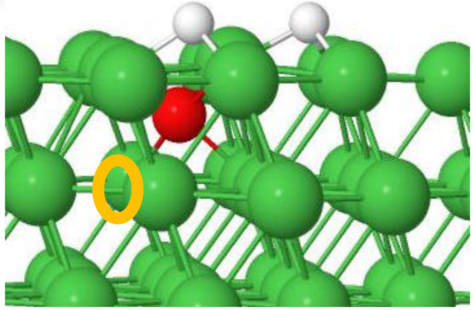

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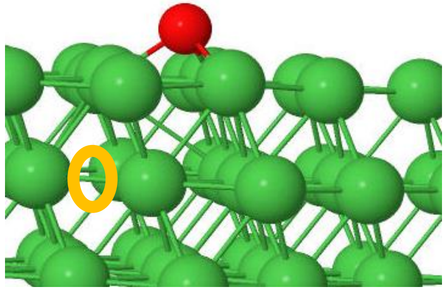

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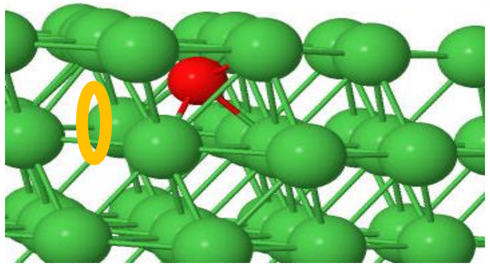

Formation of $Ni(O^3H)_x$

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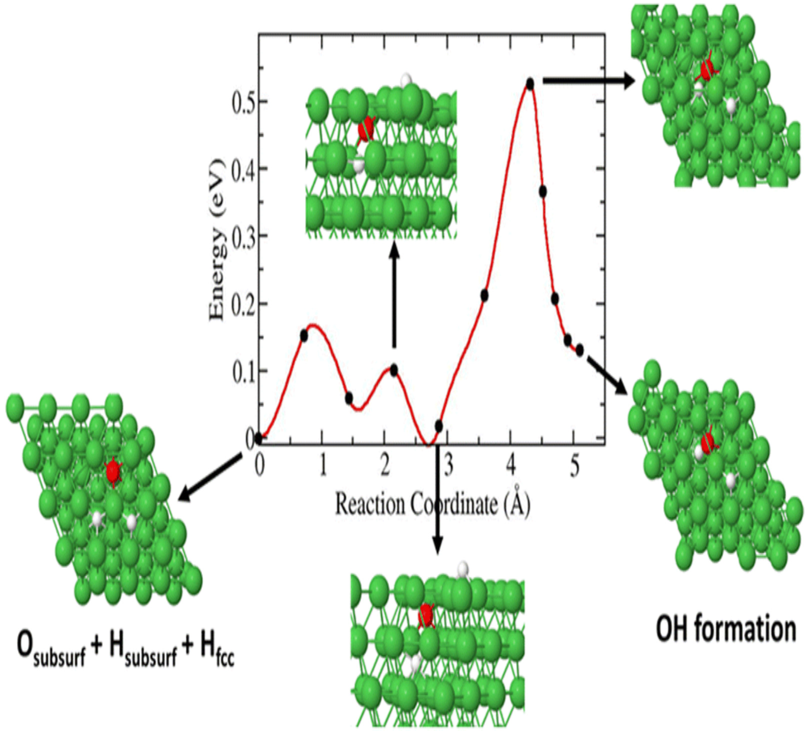
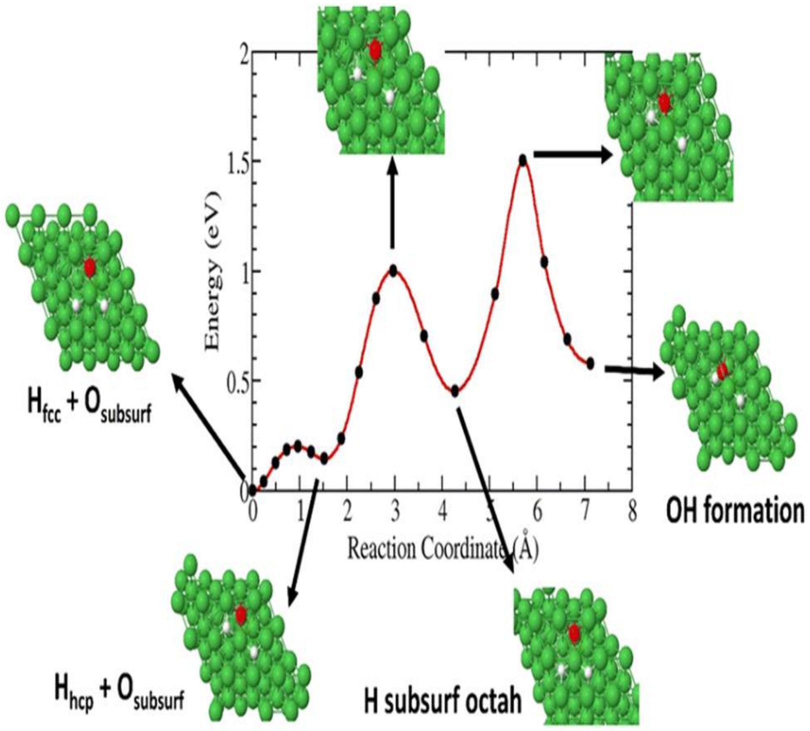
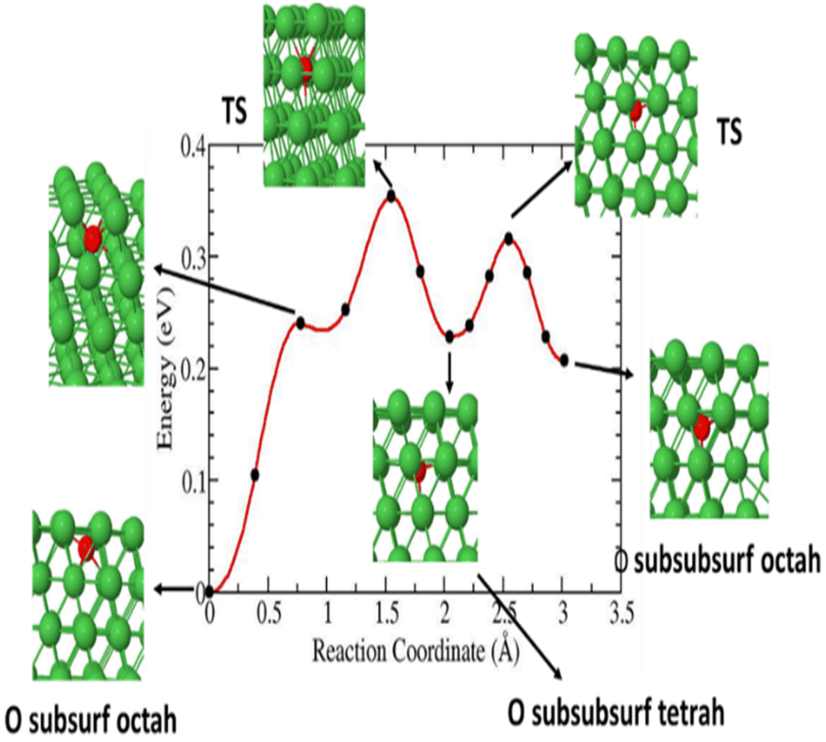


through diffusion of a subsurface H species



through diffusion of a surface ^3H species



O species from a subsurface octahedral to a sub-subsurface octahedral.

Preliminary results:

- Tafen, *et al*, **PCCP 27**(2025)481-489; Redington, *et al*, **PCCP 27**(2025)7893-7904

- ^3H is much easier to diffuse from surface to sub-surface than O;
- O prefers to diffuse into V_{Ni} site to form NiO_x or $Ni(O^3H)_x$ due to its high diffusion energy barrier compared to that of ^3H;
- Formation of NiO_x or $Ni(O^3H)_x$ phase in Ni subsurface layer is limited by O diffusion energy barrier and Ni vacancy defects.

Zr/Ni Interface models

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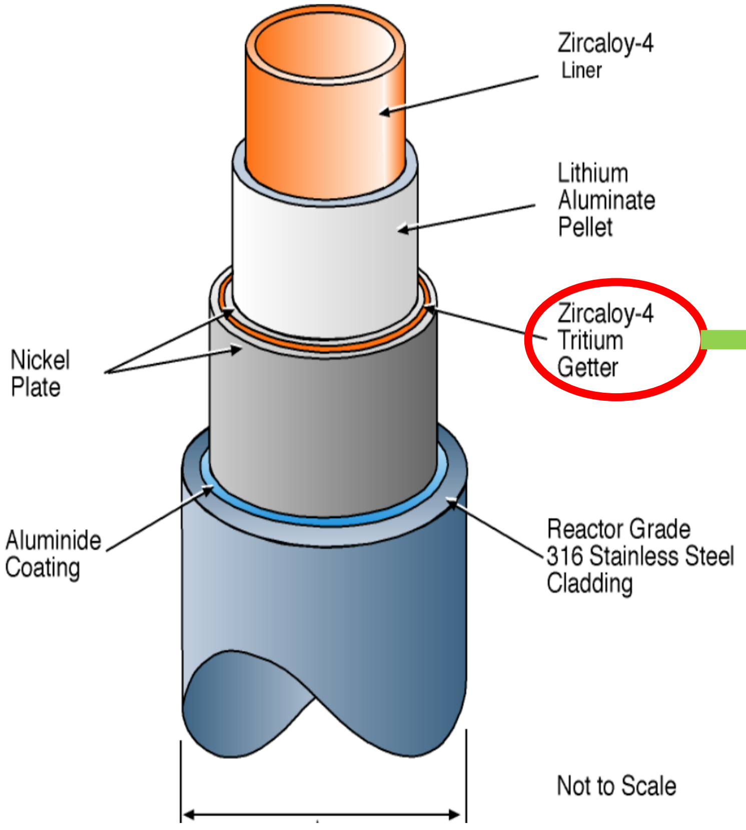
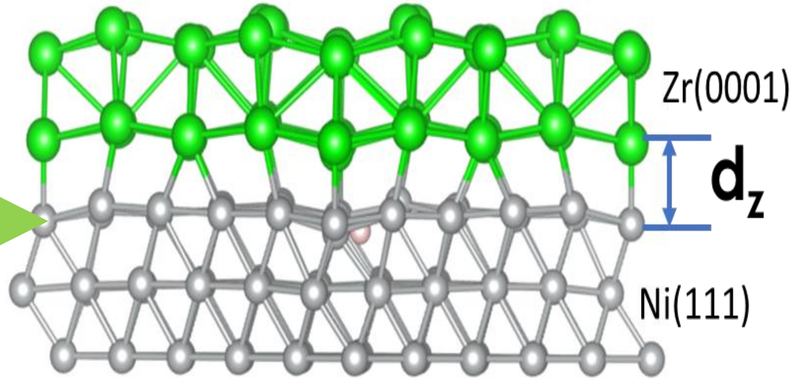
Ni(111)/Zr(0001) interfaces and model optimization



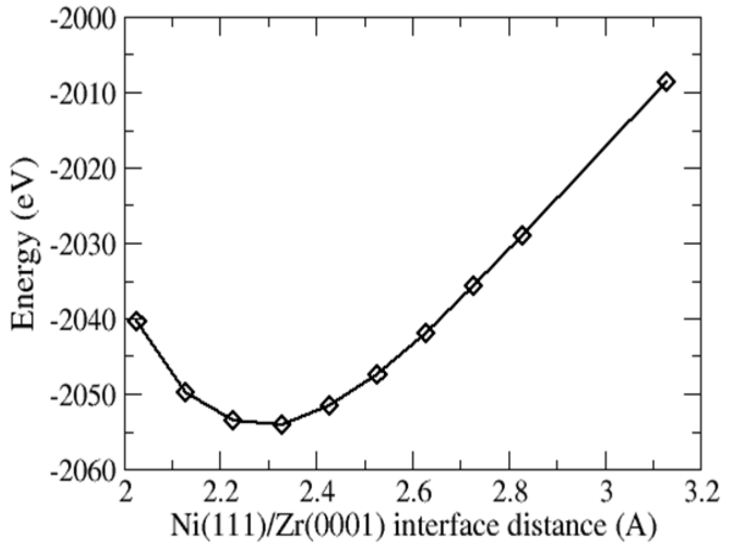
Five-layer Ni()/Zr interface model



5*2.457 = 12.28 Å
4*3.170 = 12.68 Å

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

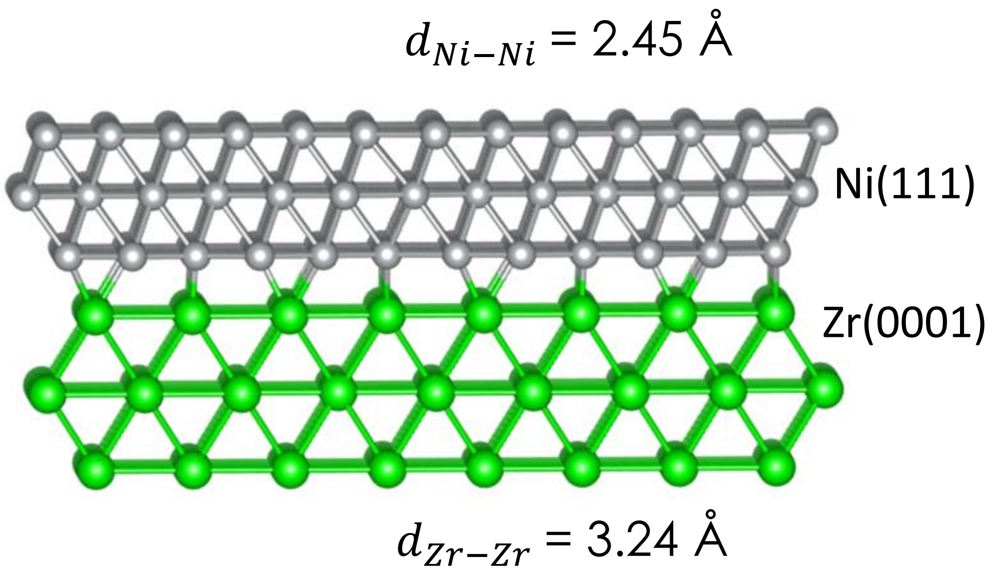
Interface Optimization



$d_{opt} = 2.32$ Å

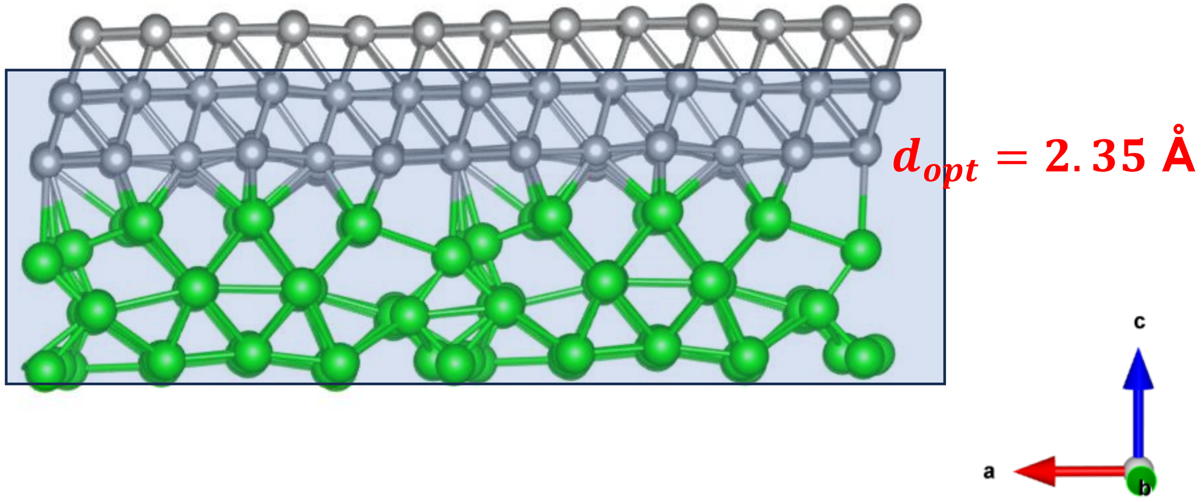
Ni(111)/Zr(0001) Interface model

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



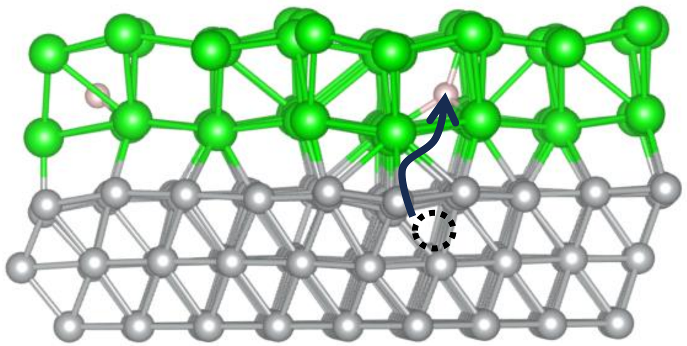
On Zr side:

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

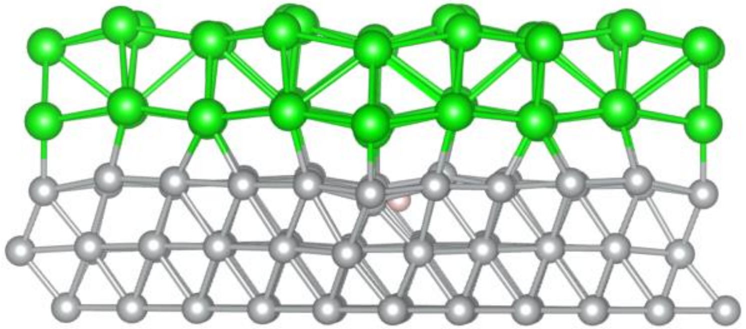
Ni(111)/Zr(0001) Interface model

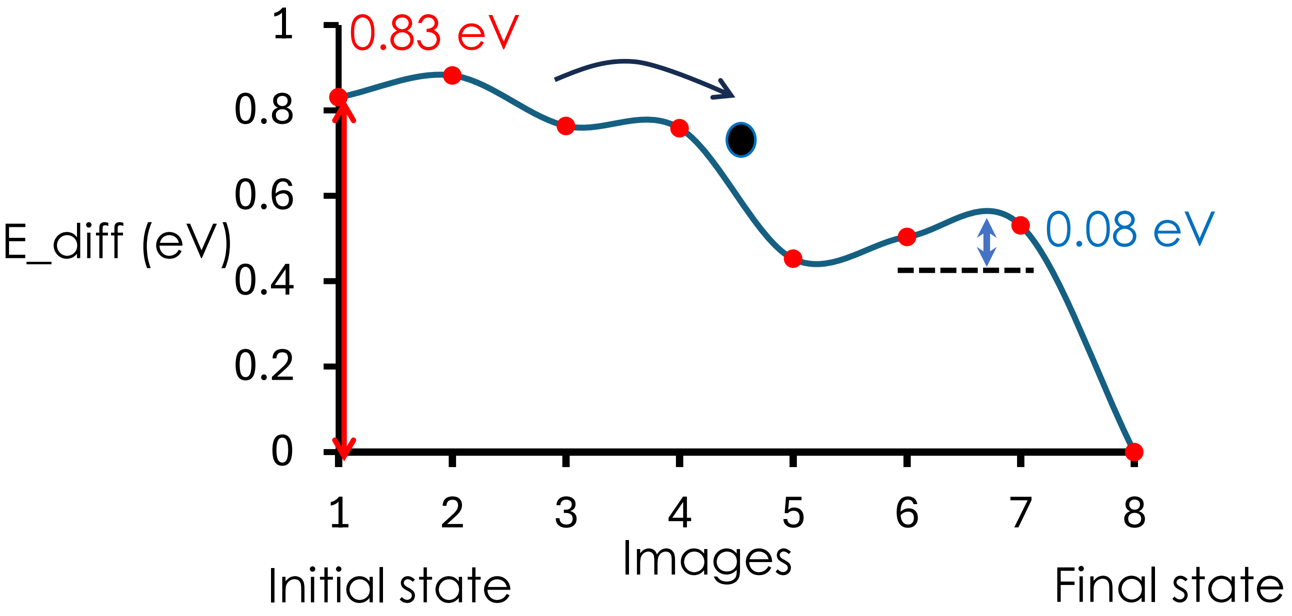
Tritium diffusion across Ni(111)/Zr(0001) Interface

Final state



Initial State

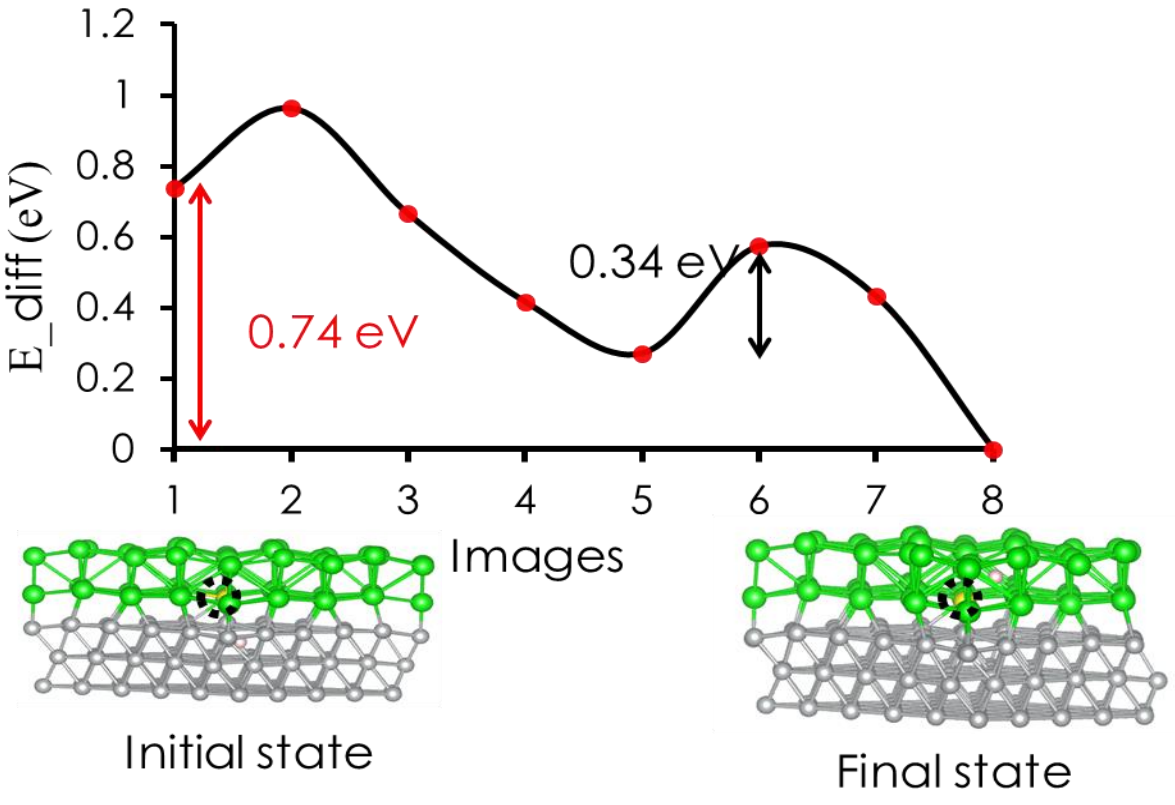




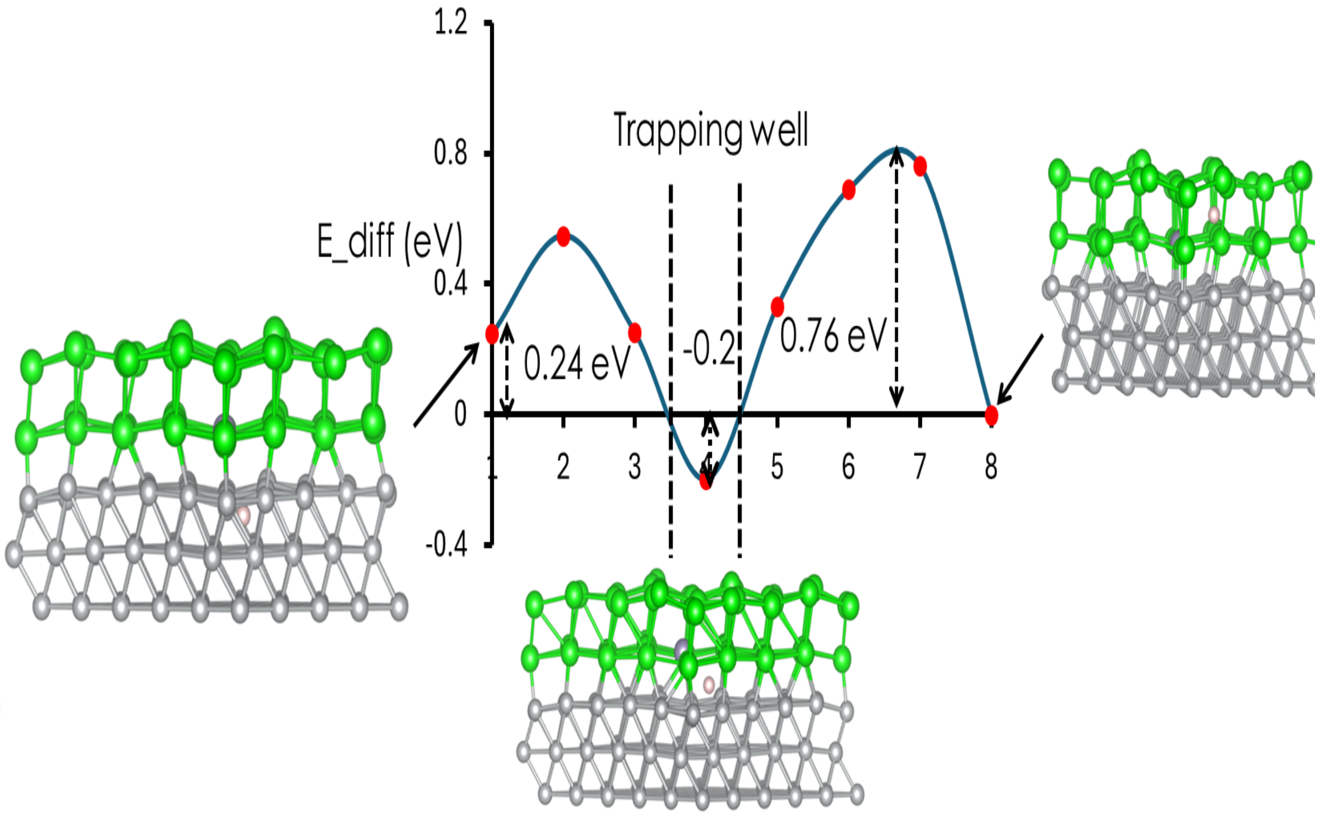
Zr (0001) site for ^{3}H is 0.83 eV lower than Ni (111) site.

Ni(111)/Zr(0001) Interface model

Tritium diffusion across Ni(111)/Zr(0001) Interface: With one Zr vacancy



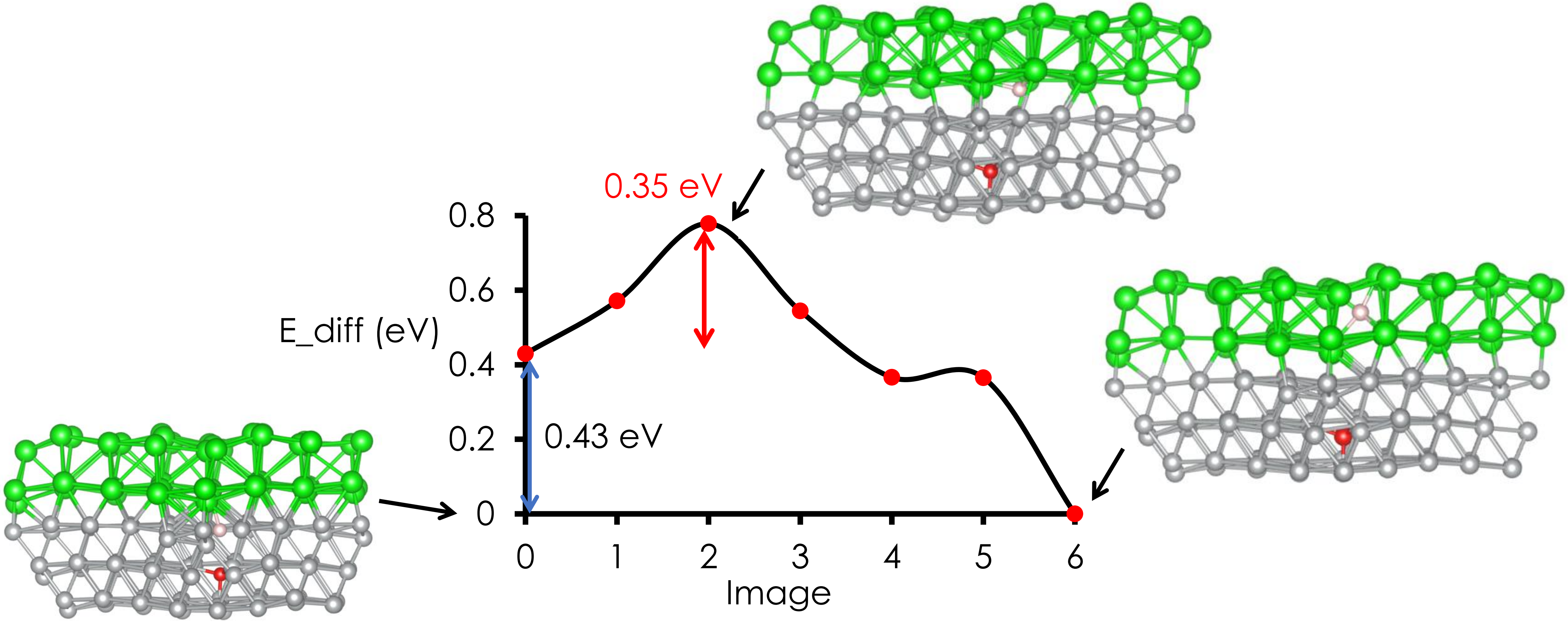
Tritium diffusion across Ni(111)/Zr(0001) Interface: With a Sn impurity



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

Ni(111)/Zr(0001) Interface model

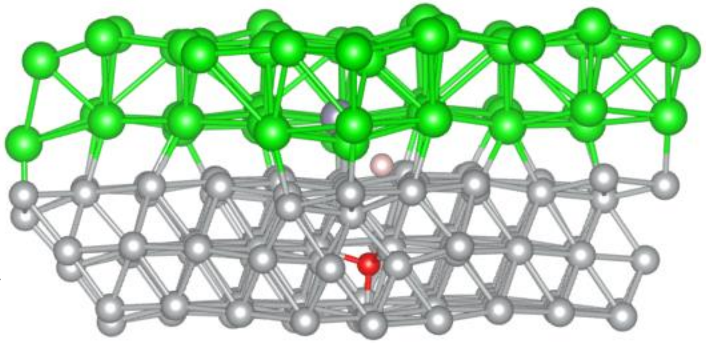
Introducing Ni(OH) at the interface: Diffusion of ^3H

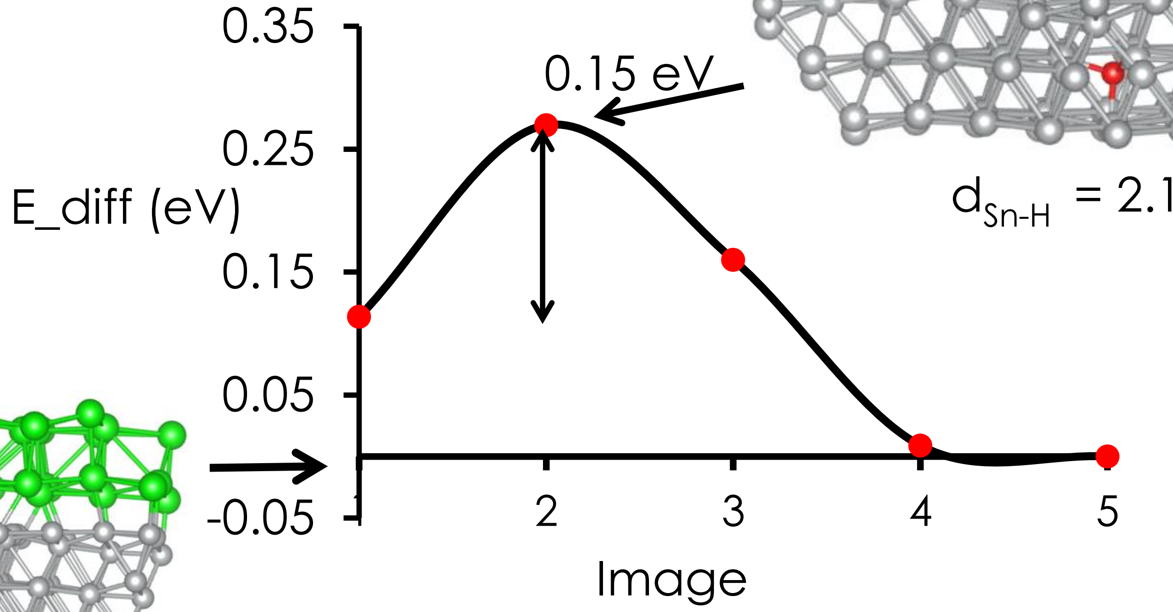


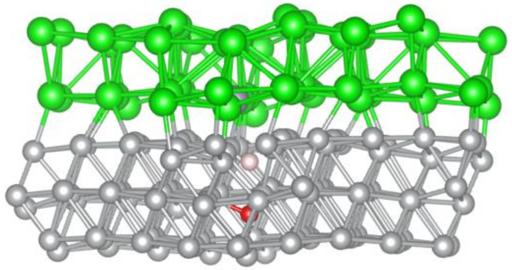
Initial energy barrier height for tritium diffusion in presence of O in Ni (111) was found to be 0.35 eV, almost 0.25 eV higher than with no O impurity but ^3H is more stable by 0.43 eV in Zr region.

Ni(111)/Zr(0001) Interface model

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







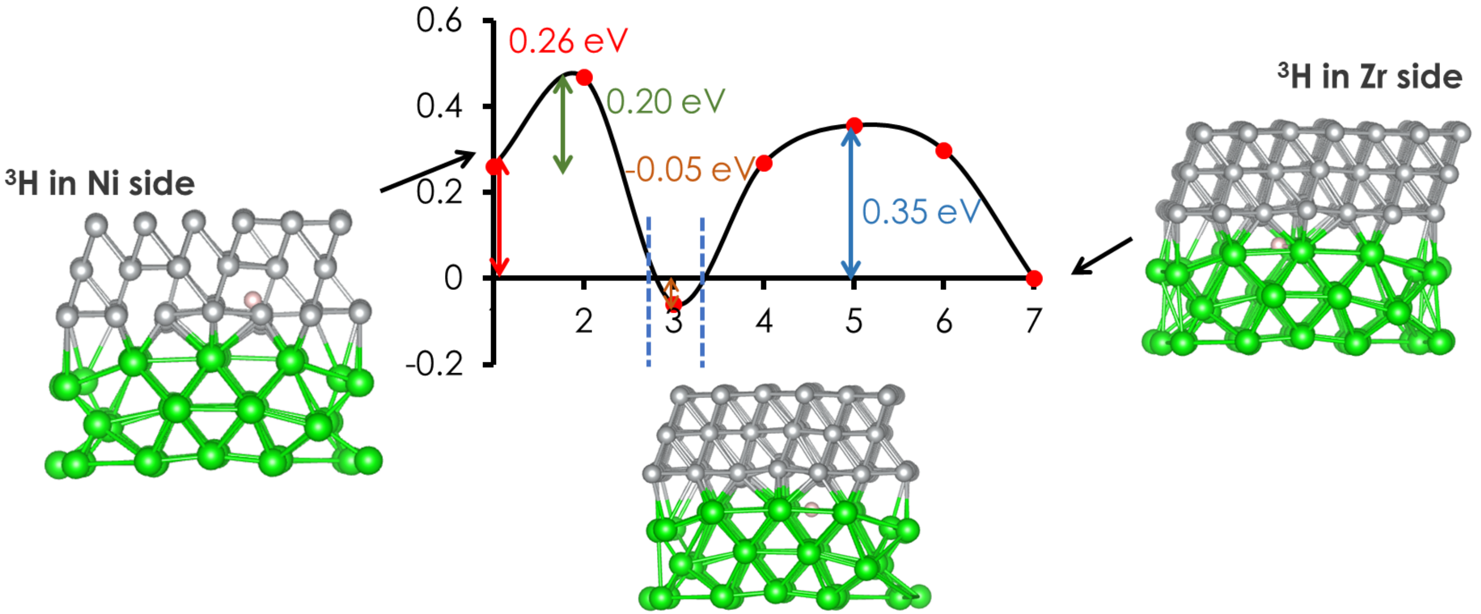
$d_{Sn\text{-}H}$ = 2.15 Å

$d_{Sn\text{-}H}$ = 2.13 Å

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

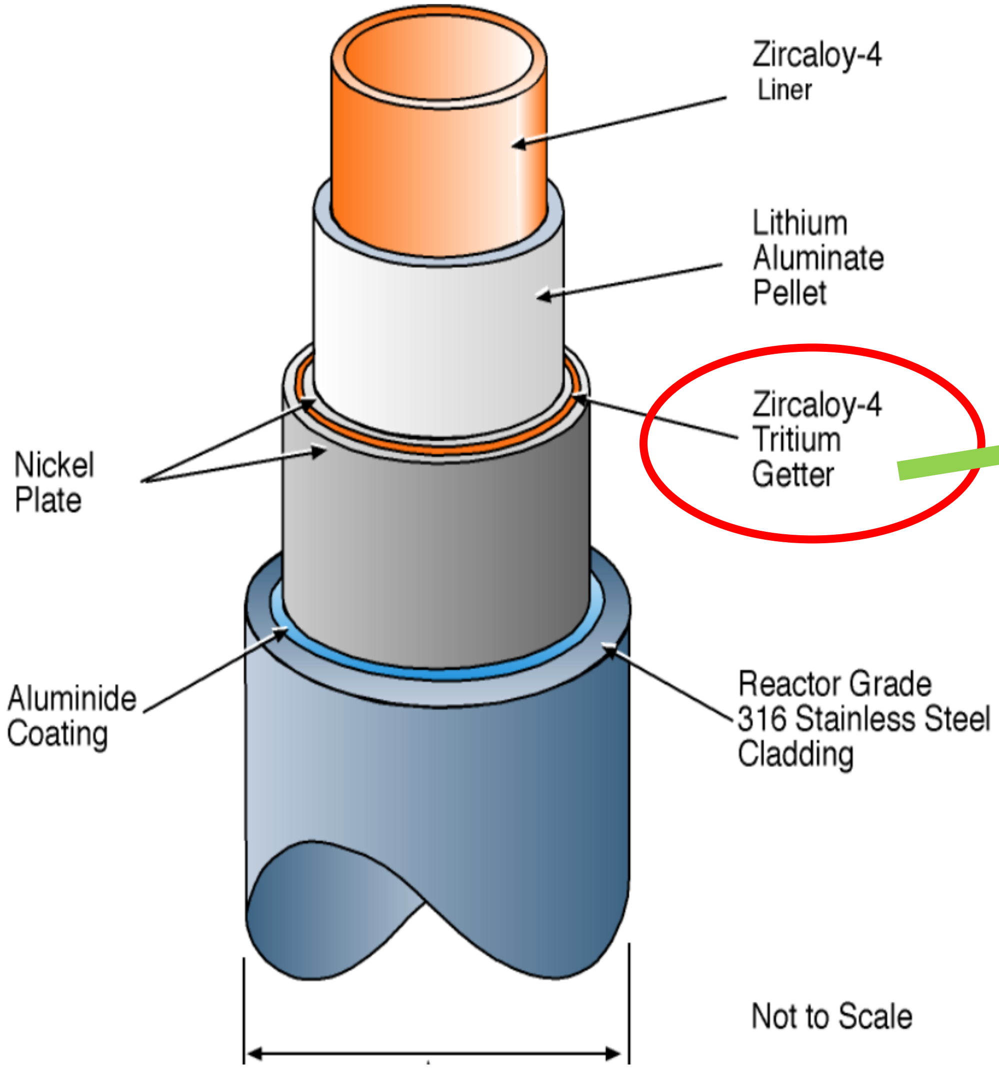
Tritium Diffusion Across Ni (111)/Zr (0001) Interface

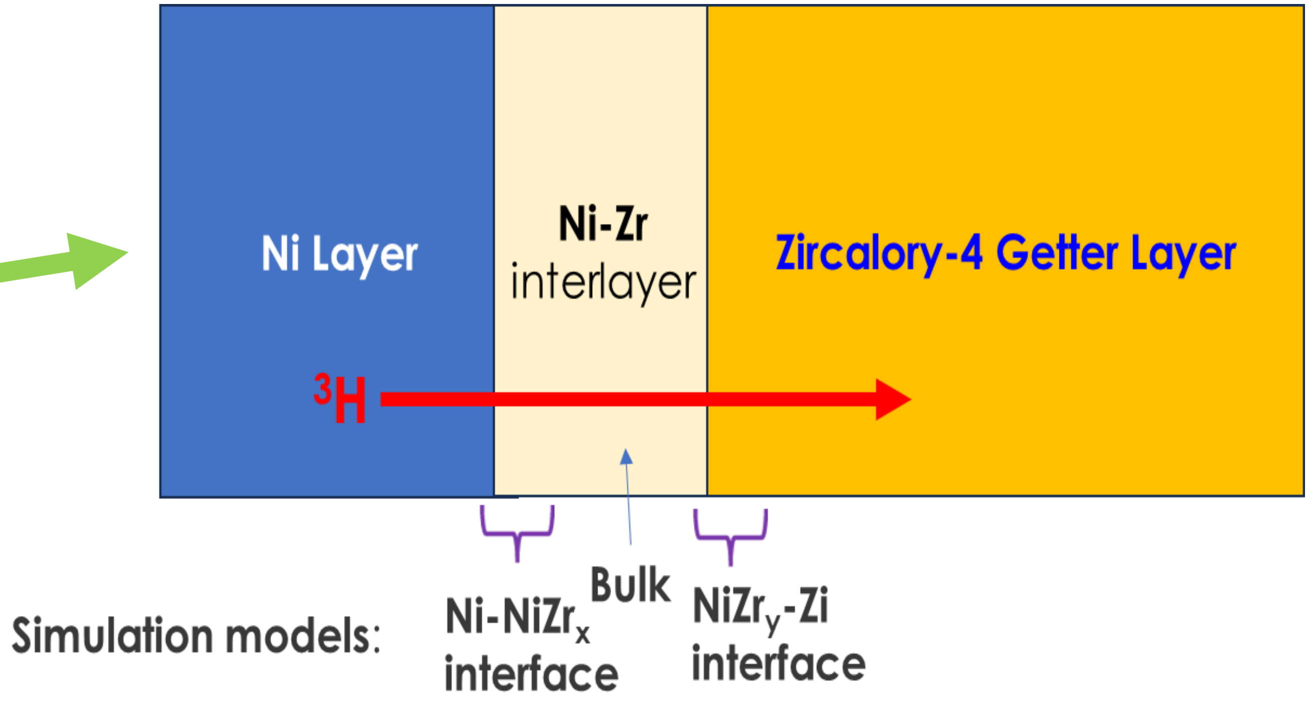


^{3}H is more stable by 0.26 eV in Zr region than in Ni.

- 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.
- 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.

Ni/ZrNi/Zr Getter Model





Ni/NiZr/Zr Alloy Interface Modeling

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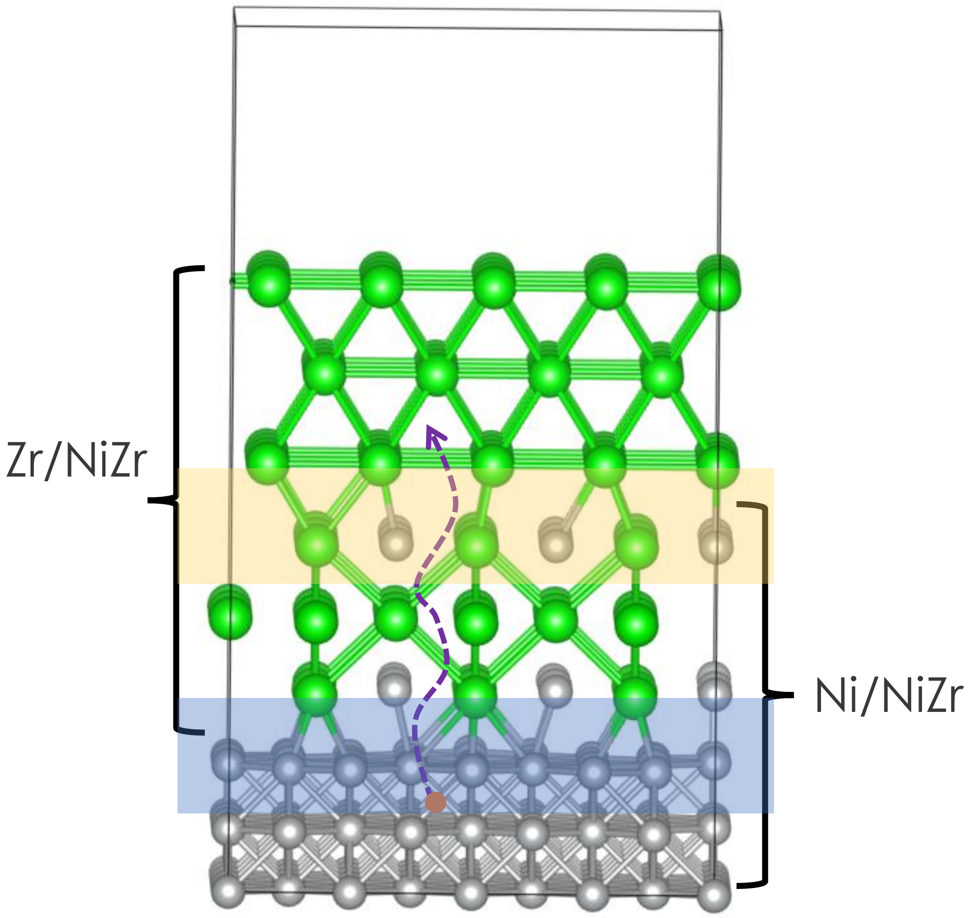
Objective

- **Calculate the solubility and diffusion behavior for T at the Ni/NiZr/Zr interface.**

Challenges

- Design two interface models: Ni/NiZr and NiZr/Zr.
- Adsorption and diffusion of T across the complex interfaces.



Ni/NiZr/Zr interface

Ni/Zr Alloy Complex Interface Development

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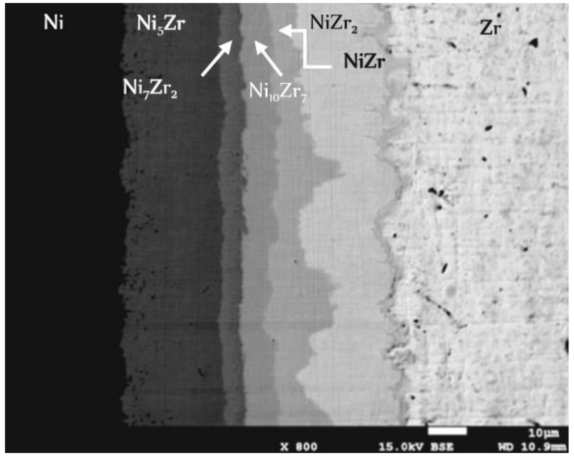
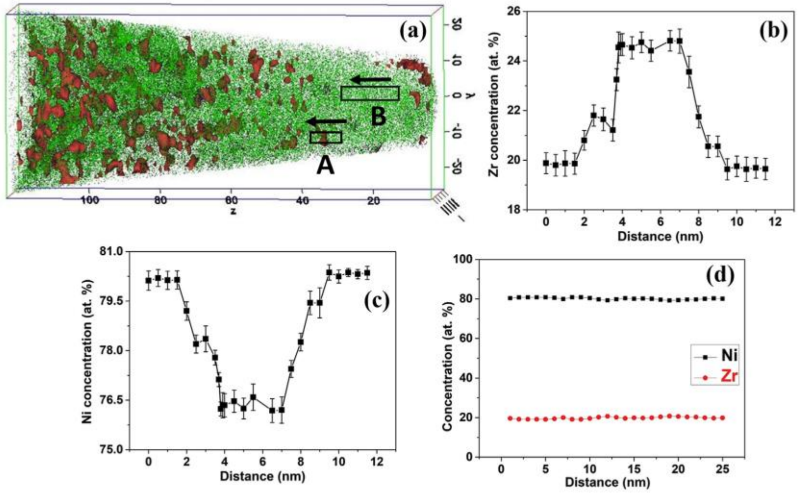
Simple Toy Model for Ni (111)/Zr (0001) Interface

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.



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



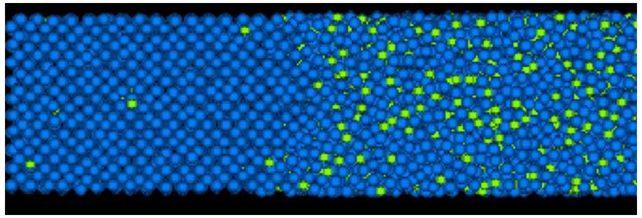
TEM images and concentration profile for microstructure evolution of the as-deposited film; the energy dispersive X-ray spectroscopy (EDXS) spectrum showing the Ni and Zr elements.

Journal of Alloys and Compounds 844 (2020) 156078.
Journal of Phase Equilibria and Diffusion 36, 4, 2015.

Experimental Facts on NiZr Interface

Modeling of Binary Intermetallic Compound $Ni_{0.5}Zr_{0.5}$

- Ordered $Ni_{0.5}Zr_{0.5}$ and $Ni_{0.33}Zr_{0.67}$ intermetallic compounds indicate that amorphization may be initiated by destroying the long-range order in the system by introduction of antisite defects.
- It is in fact possible to fabricate the "metallic glass" (solid alloys that are non-crystalline and have a glass-like structure) over a wide continuous range from $Ni_{0.2}Zr_{0.8}$ to $Ni_{0.3}Zr_{0.7}$ above the crystallization temperature T_C.
- The sharp drop in Tc for the Zr-rich alloy $Ni_{20}Zr_{80}$ is due to the formation of the high-pressure ω-Zr phase.



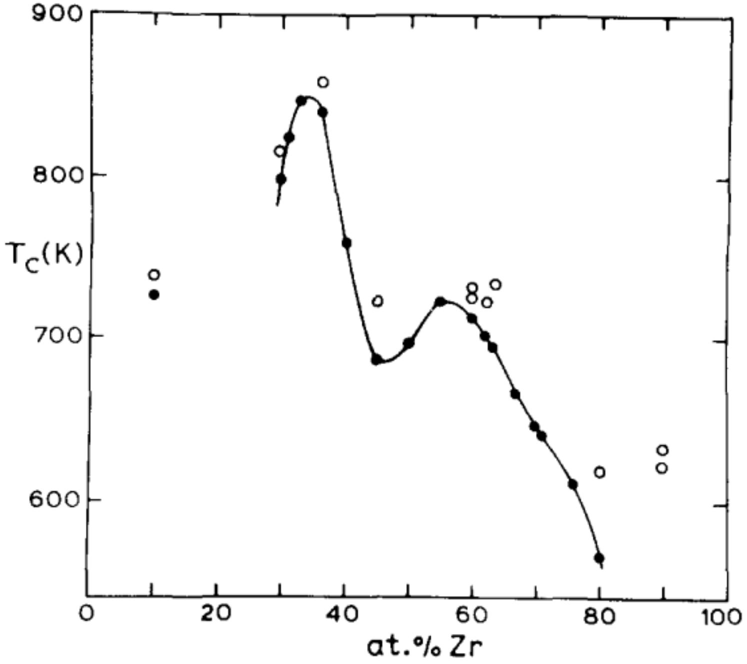
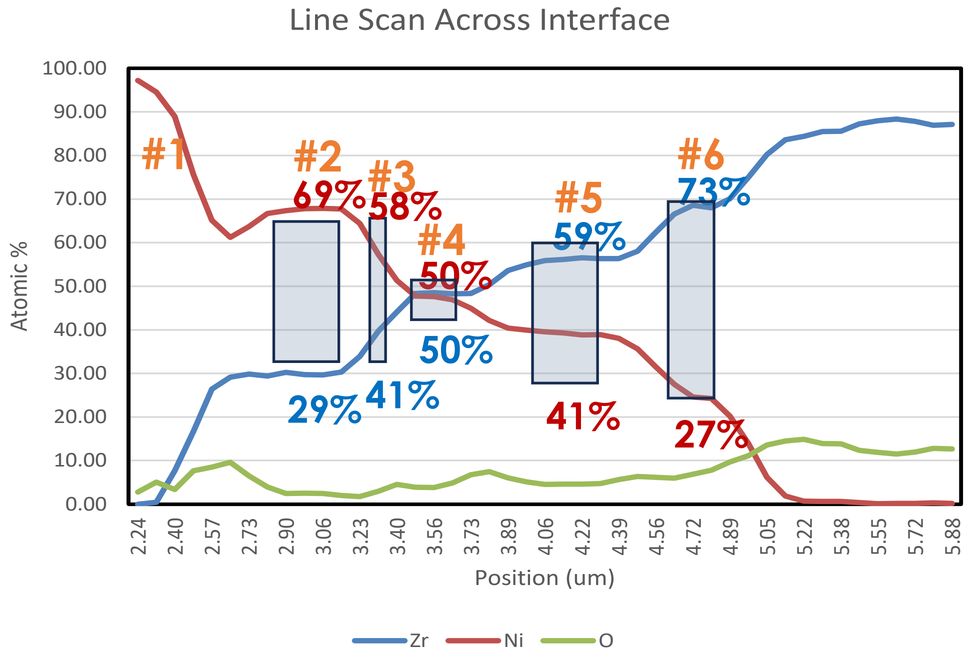


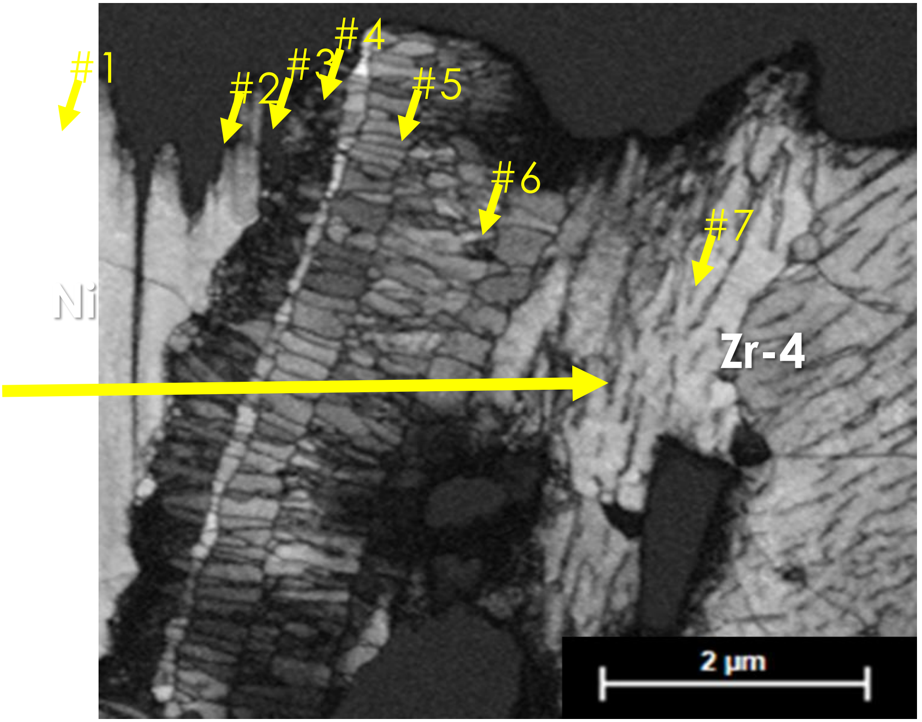
FIG. 2. The crystallization temperatures (solid circles) for Ni-Zr taken from DSC measurements at 10 K/min heating rate. The open circles give the temperatures of subsequent peaks in the DSC scan.

- Altounian, Z.; Guo-hua, T., **J Appl Phys** 1983, **54** (6), 3111-3116.

Experimental Facts on Ni_xZr_{1-x} Interface

Information Provided by PNNL





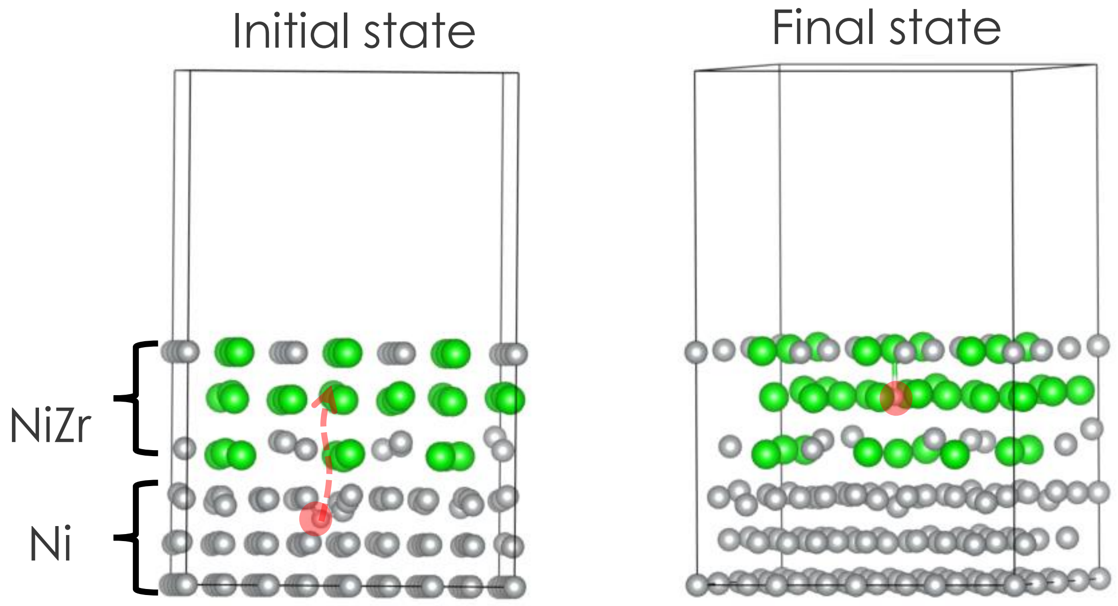
Unirradiated Getter: Transmission Kikuchi Diffraction (TKD) Map of FIB TEM Foil from OD.

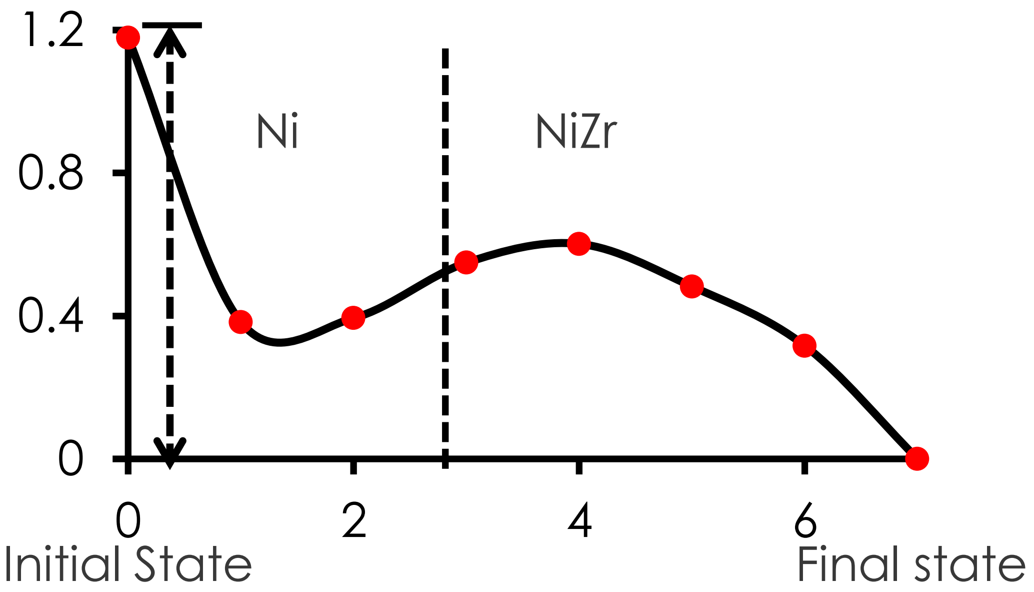
Note the complexity of the interface.

Thanks to Dan Edwards and Josh Silverstein.

$Ni\text{-}Ni_1Zr_3$ Interface Model

Diffusion of ^3H Across Ni- Ni_1Zr_3 Interface



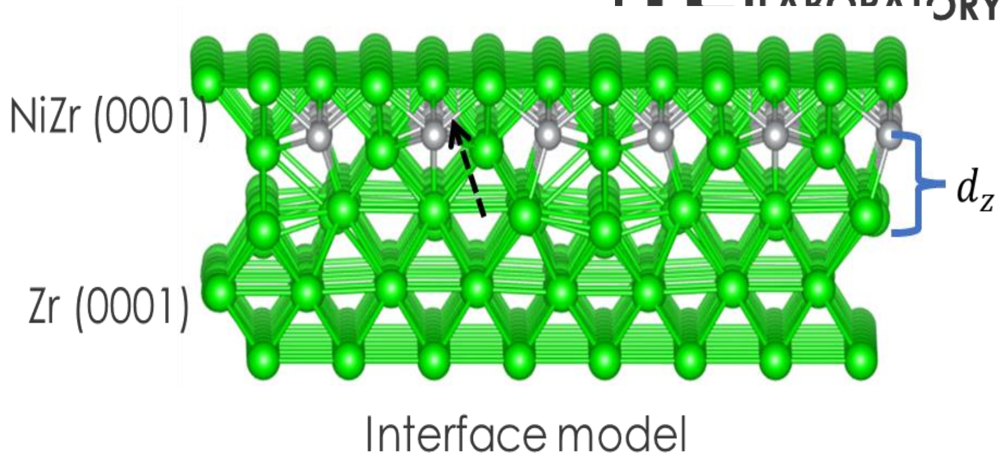


Final state energy is higher than initial state by nearly 1.2 eV; T formation at Ni_1Zr_3 side is higher than Ni side.

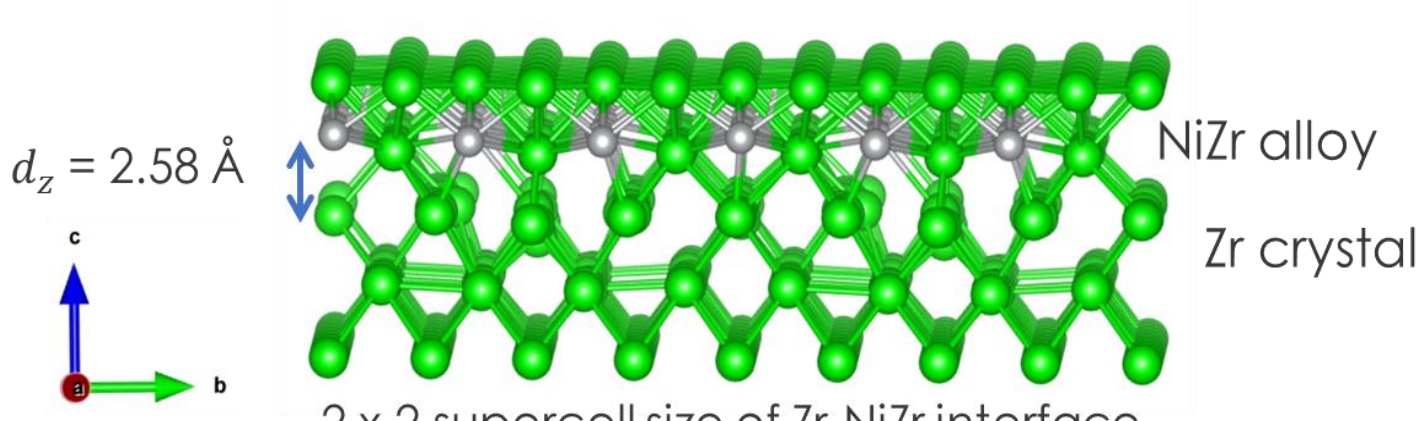
Modelling of Zr- Ni_1Zr_3 Interface: Calculation Steps

Calculation Steps

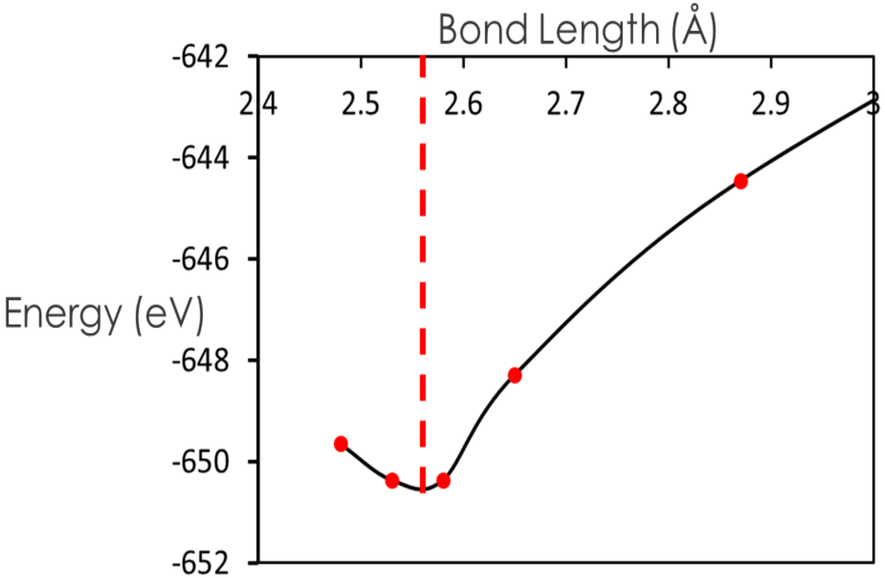
- Optimize Ni/NiZr/Zr interface.
- Calculate the diffusion barriers across the alloy interface for ^{3}H.
- Introduce Sn impurity and vacancies.
- Calculate the diffusion barriers for ^{3}H in the presence of impurities and vacancies, and without Sn impurity and vacancies.



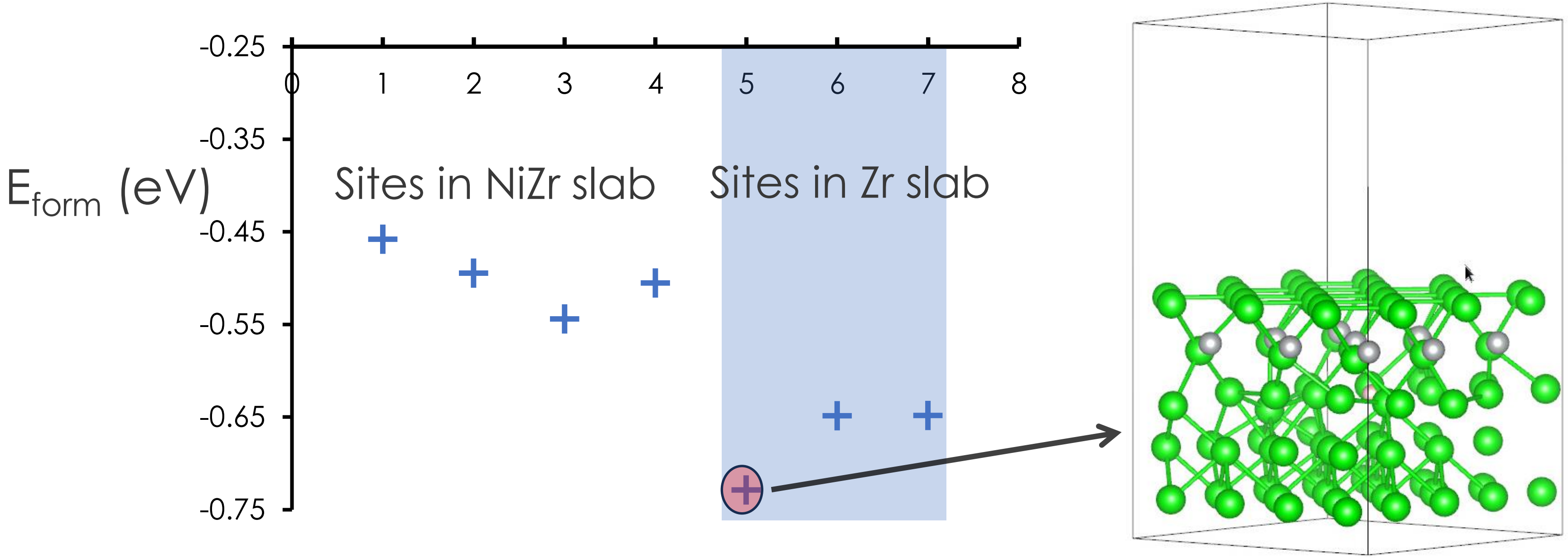
Interface model



2 x 2 supercell size of Zr-NiZr interface.

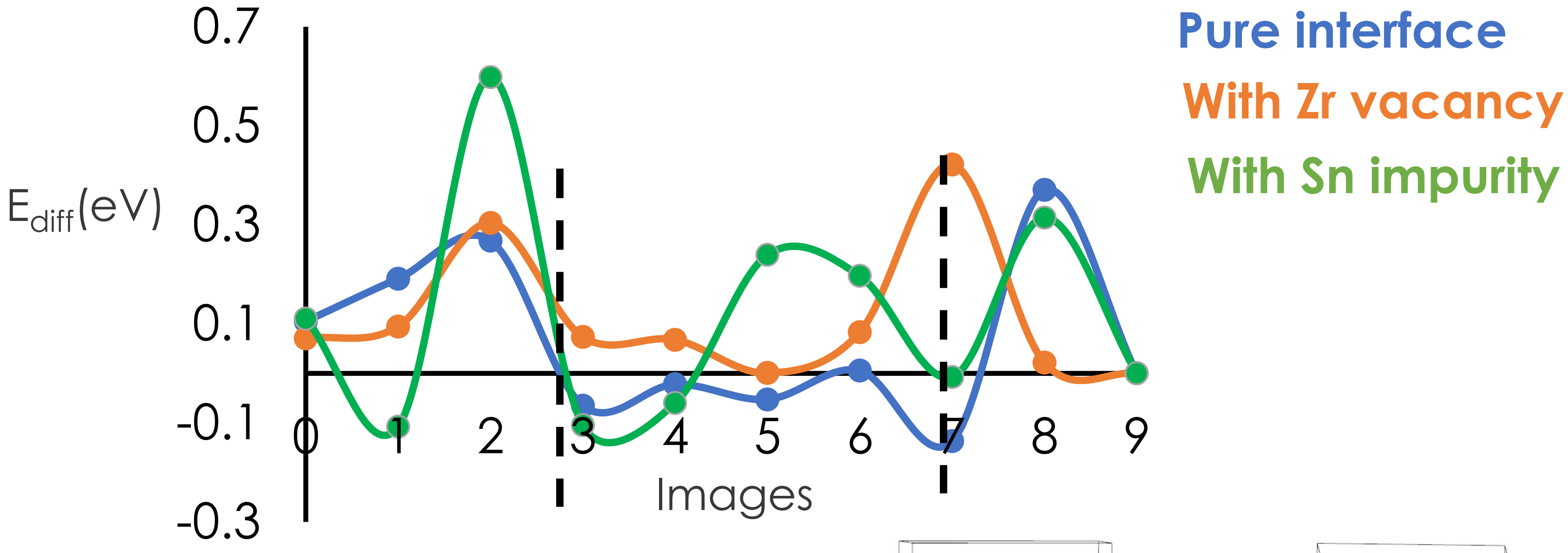


T Optimization in Zr-Ni_1Zr_3 Interface

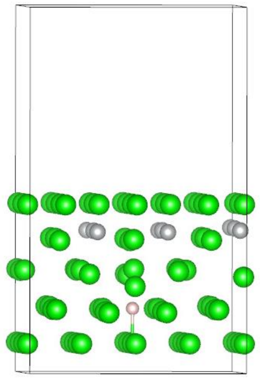


T formation was found to be relatively higher in the Zr slab. This leads to T to diffuse with no barrier on the Zr side of the interface.

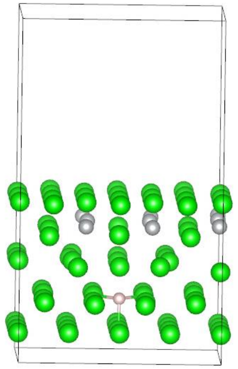
T Diffusion Across Zr-Ni_1Zr_3 Interface



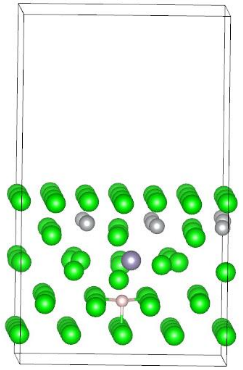
- In pure interface and one with Sn impurity interface, T is found to have trapping barrier.
- This result is consistent with the T trapping at the interface found in pure interface model.
  (D. Tafen et al' 2024)



Pure interface



With Zr vacancy



With Sn impurity

Summary & Conclusions

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- Our predicted $^3H_2$ and ^3H_2O molecules from γ-$LiAlO_2$ pellet verify the experimental findings. The dominated product is $^2H_2$.
- The $^3H_2$ and ^3H_2O will be dissociated on the surface of Ni and diffuse into subsurface. It's likely the Ni-O could be formed, indicates NiO_x & $Ni(O^3H)_x$ phase could be formed, Only ^3H diffused into getter to form metal hydrides (Zr^3H_x).
- ^3H can be easily diffused through Ni(111)/Zr(0001) interface. Sn & O present could hinder ^3H diffusion.
- More complicated Ni/$NiZr_x$/Zr interface models were built. The complete ^3H diffusion pathways across these interfaces were calculated. The effects of impurities and defect along the ^3H diffusion path were investigated.
  - The minimum Ni-Zr bond length in each interface was fully optimized and was found to be 2.58 Å for Zr/ Ni_1Zr_3 and 2.19 Å for Ni/ Ni_1Zr_3 .
  - The T diffusion barriers in Zr/ Ni_1Zr_3 were found to be 0.5, 0.42, and 0.62 eV, respectively, in pure interface, with Zr vacancy and with Sn impurity. However, a trapping well of 0.13 eV was found in the Zr/Ni_1Zr_3 interface with a Sn impurity.
  - The ^3H stability in Ni_1Zr_3 alloy region was found to be higher by more than 1 eV than in Ni system.

Thank You !

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