Molecular Dynamics Simulations of Radiation-Enhanced Permeation of Hydrogen Isotopes In Ni

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TPBAR Project Review

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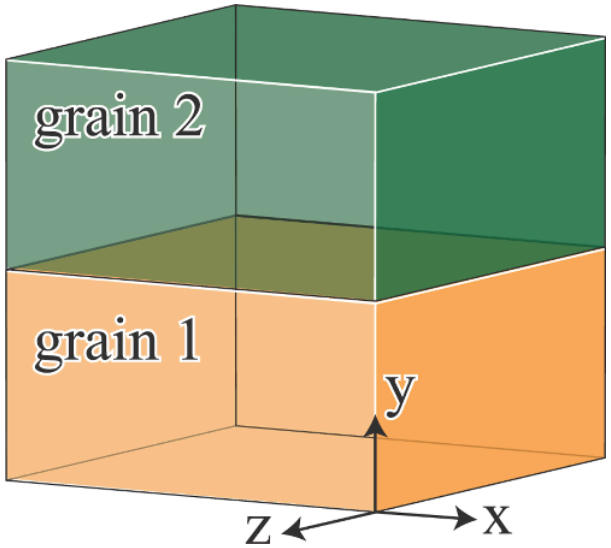
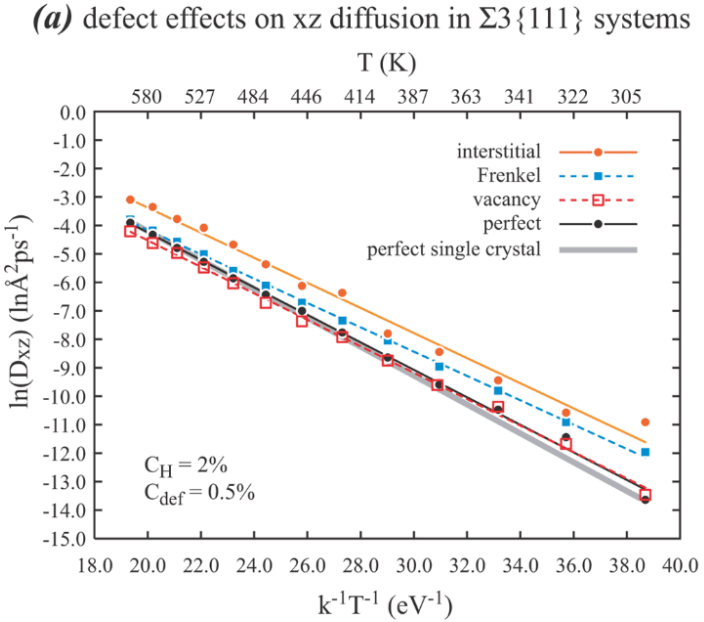
Incorporating Grain Boundaries



Incorporating Statistics



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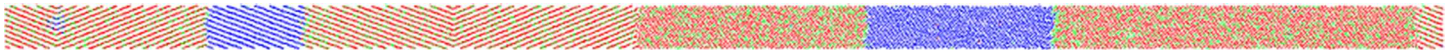
Motivation

- The TMIST-2 irradiation experiment at the Advanced Test Reactor at Idaho National Laboratory measured a tritium permeation enhancement in 316 stainless steel by a factor of ~2 to 5 relative to ex-reactor results
- Grain boundaries and irradiation-induced defects may be both responsible
- Statistics of diffusion cannot be captured by DFT calculations. Molecular dynamics (MD) simulations are required to understand this
- The only literature stainless steel potential (Bonny et al, MSMSE, 21, 85004, 2013) incorrectly predicts phase separation



- We therefore use Ni as an exemplar to perform extensive MD simulations on hydrogen diffusion in Ni to elucidate the tritium permeation enhancement in 316 stainless steels

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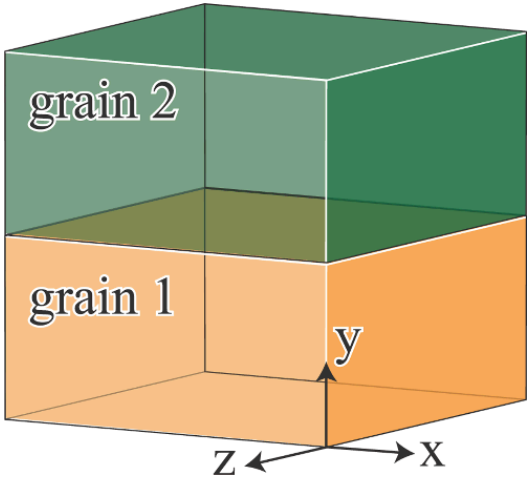
Molecular Dynamics Method



- Grain boundaries parallel to xz plane are simulated with bi-crystals under periodic boundary conditions
- Single crystal and Σ3{111}, Σ5{100), Σ11{311} grain boundaries are studied
- Systems with and without point defects are both considered. Three different point defects (interstitials, vacancies, and Frenkel pairs) are independently simulated. Defect concentration is fixed at contain $C_{def} = 0.5\%$
- Systems contain a hydrogen concentration of $C_H = 2\%$
- Ni-H potential from Angelo et al, MSMSE, 3, 289, 1995
- MD simulations are performed at 13 temperatures 300 K, 325 K, …, 575 K, 600 K for a period of $t_{MD} = 440$ ns (after 1 ns pre-equilibration)

Diffusion Analysis

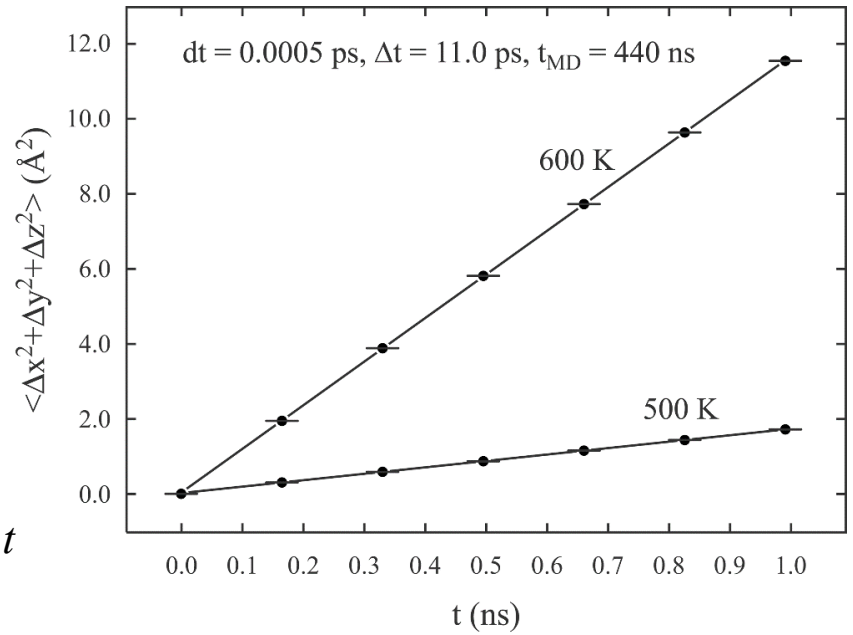
- The coordinates $\alpha_i(t)$ of N hydrogen atoms (i = 1, 2, …, N), are recorded on a time interval of Δt, i.e., at times of $t = j\Delta t$, j = 1, 2, …, m ($m = t_{MD}/\Delta t$), where Δt can be any multiple of the time step size dt used in the MD simulations.
- m+1-k measurements can be made for the displacement of a hydrogen atom i over a $k\Delta t$ period: $\Delta\alpha_{i,j}(k\Delta t) = \alpha_i(j\Delta t - \Delta t + k\Delta t) - \alpha_i(j\Delta t - \Delta t)$ where j = 1, 2, …, m+1-k.
- This allows us to calculate mean square displacement (MSD):

$$\left\langle \left[\Delta\alpha(k\Delta t)\right]^2 \right\rangle = \frac{\sum_{i=1}^{N}\sum_{j=1}^{m+1-k}\left[\Delta\alpha_{i,j}(k\Delta t)\right]^2}{N(m+1-k)}$$

- MSD can be fitted to diffusivities D:

$$\left\langle \left[\Delta\alpha(k\Delta t)\right]^2 \right\rangle = 2D_\alpha t$$
$$\left\langle \left[\Delta x(k\Delta t)\right]^2 \right\rangle + \left\langle \left[\Delta z(k\Delta t)\right]^2 \right\rangle = 4D_{xz} t$$
$$\left\langle \left[\Delta x(k\Delta t)\right]^2 \right\rangle + \left\langle \left[\Delta y(k\Delta t)\right]^2 \right\rangle + \left\langle \left[\Delta z(k\Delta t)\right]^2 \right\rangle = 6D_{xyz} t$$

MSD convergence figure



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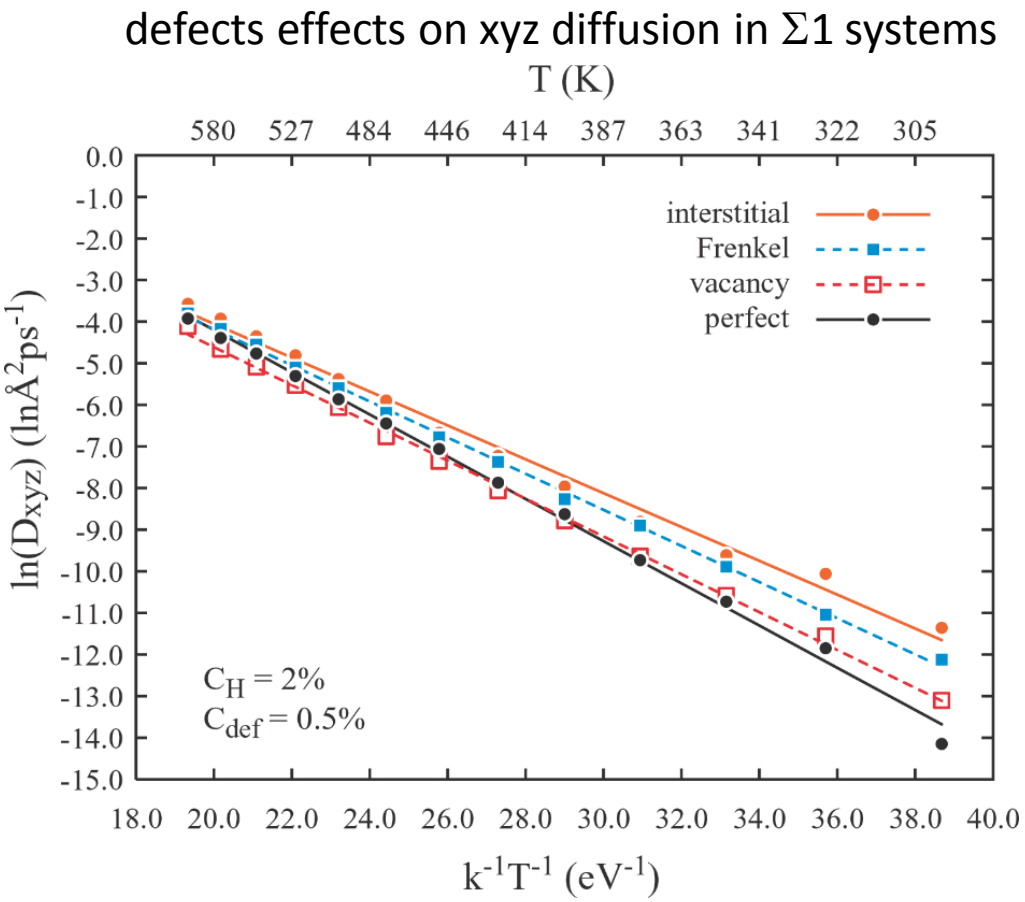
Defect Effects on H Diffusion in Ni Single Crystals



- Diffusivities are close with and without vacancies
- At the simulated interstitial concentration of 0.5%, interstitial increases diffusivities by 16.3 times at 300 K and 1.4 times at 600 K as compared with perfect crystals
- Activation energy of diffusion for perfect crystals is predicted to be 0.51 eV, as compared to the experimental value of 0.40 eV*

*L. Katz, M. Guinan, and R. J. Borg, Phys. Rev. B, 4, 330 (1971)

t = 440 ns

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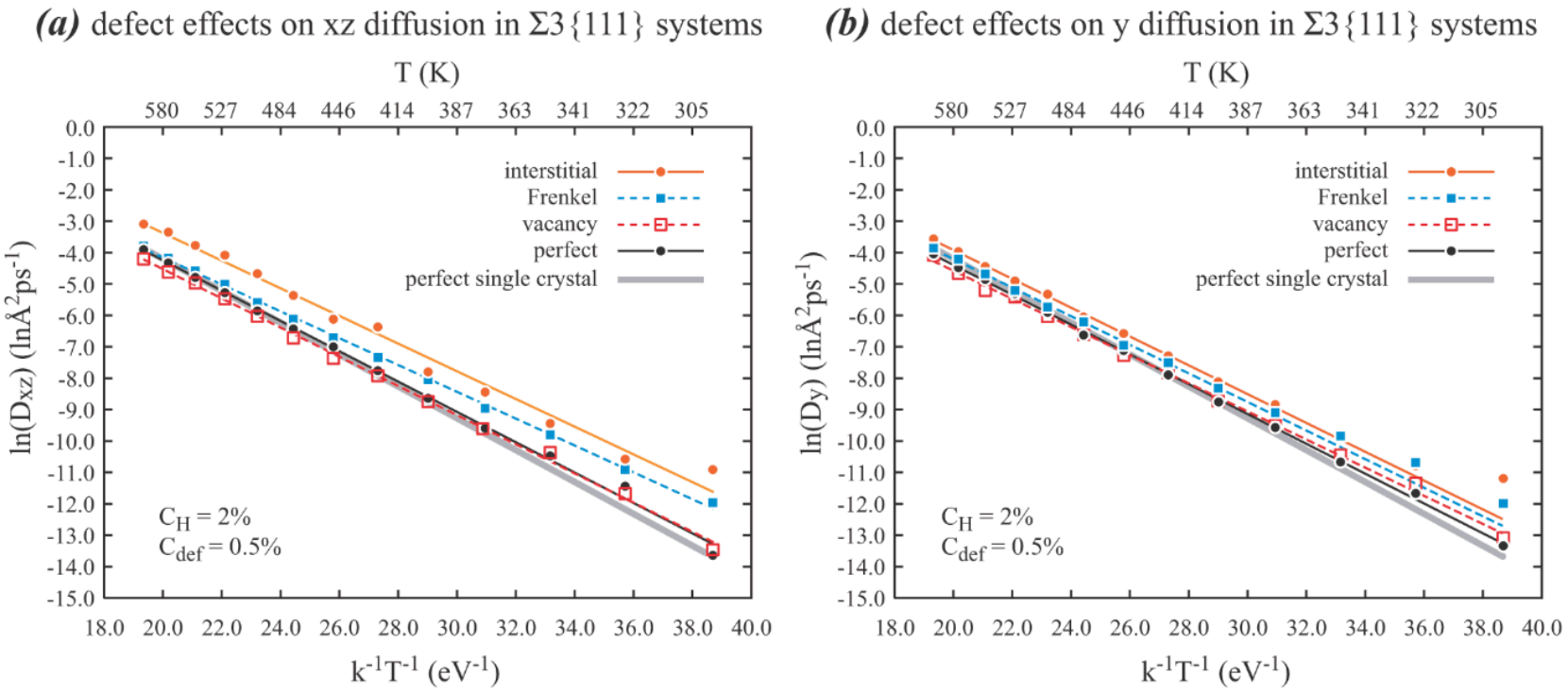
Defect Effects on H Diffusion in Ni with the Σ3{111} GB



- The coherent twin boundary almost has no effects on diffusivities with different defects except in the interstitial case
- Interstitial increases on-plane diffusivities by 15.3 times at 300 K and 2.3 times at 600 K as compared with perfect crystals
- Out-plane diffusivities are close to single crystals, indicating insignificant grain boundary trapping

t = 440 ns

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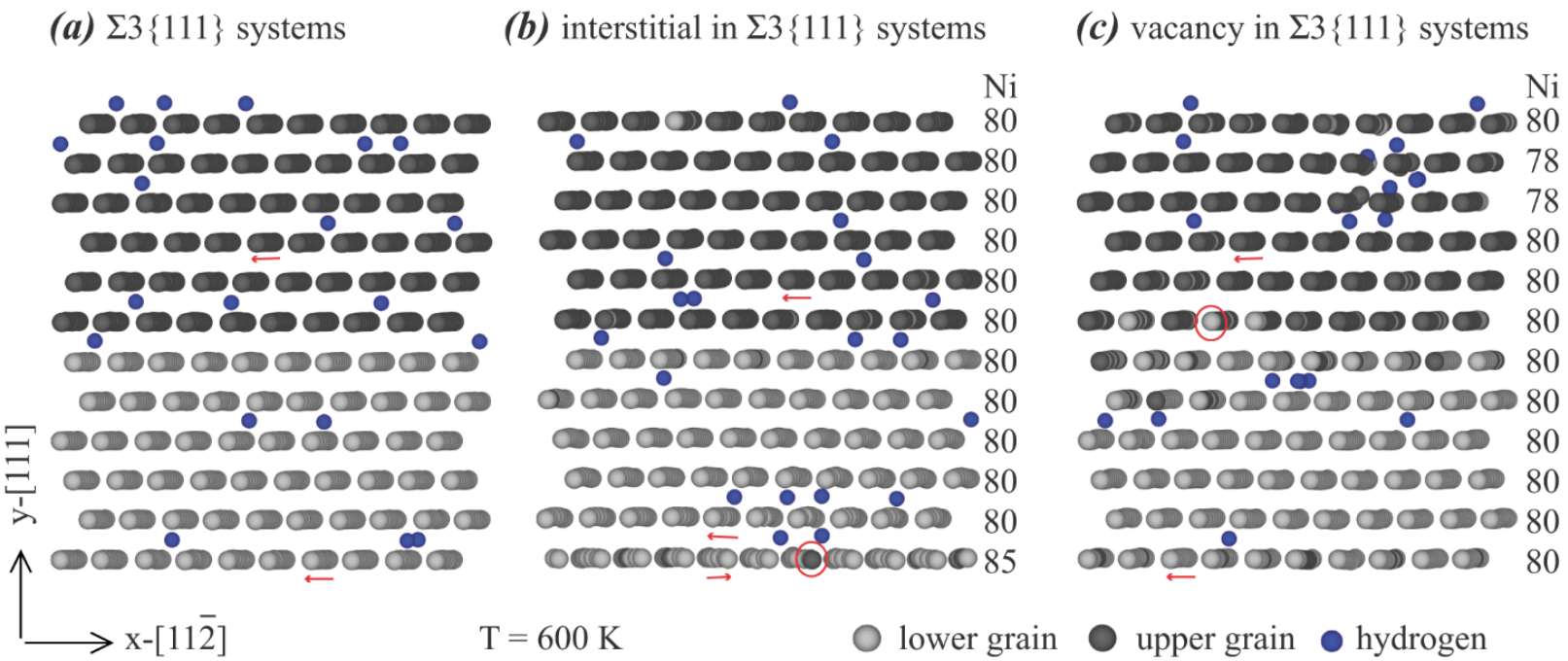
Visualization of Σ3{111} Grain Boundary

$C_H = 2\%$
$C_{def} = 0.5\%$



- Hydrogen does not segregate, but Ni interstitials and vacancies segregate at grain boundary
- Ni diffusion only occurs at the presence of interstitials and vacancies
- Interstitials cause reconstructions of atomic rows

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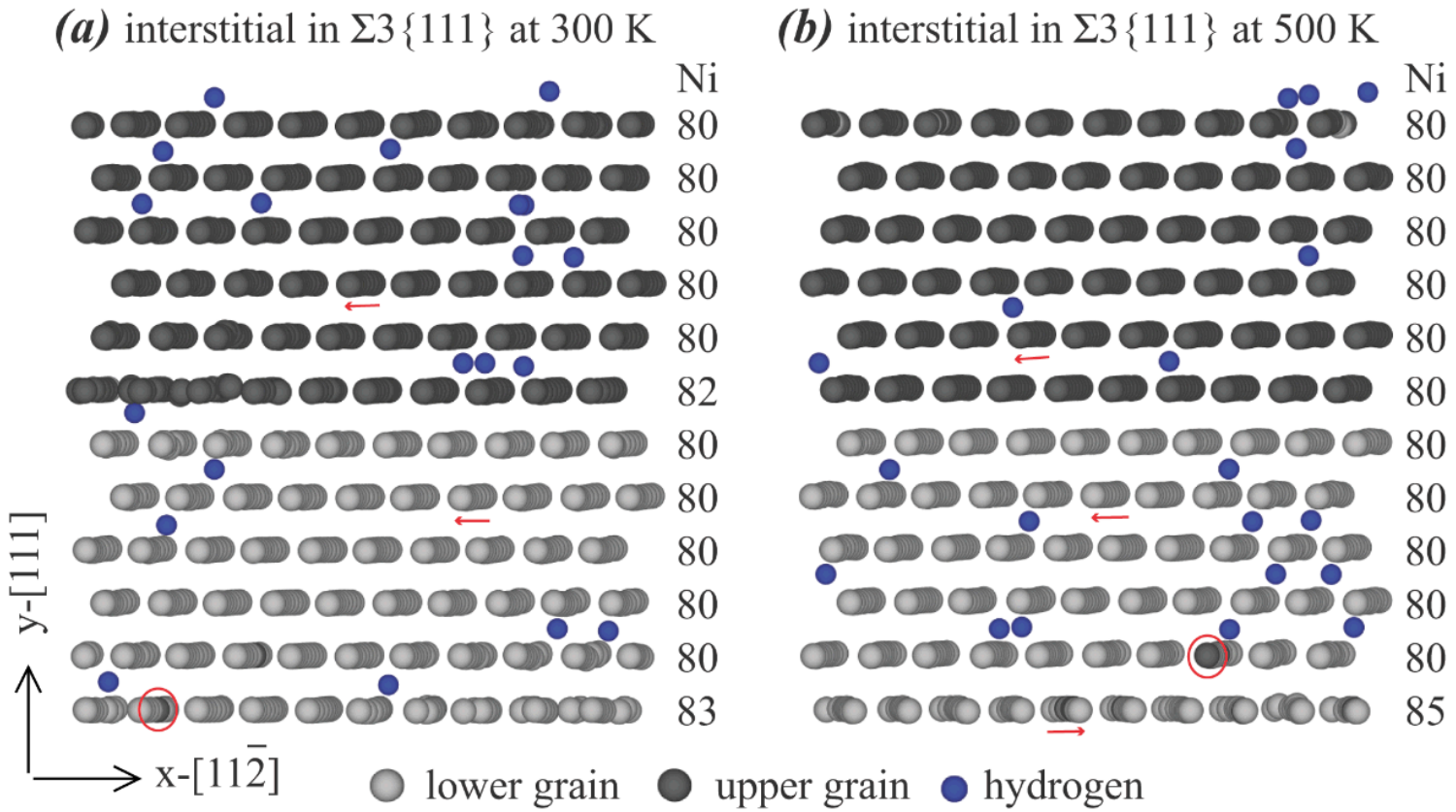
Observation of Two Σ3{111} Grain Boundary Reconstructions due to Interstitials



- The 300 K reconstruction is similar to the one shown above, but the atomic rows in the 500 K reconstruction are different

$C_H = 2\%$,
$C_{def} = 0.5\%$

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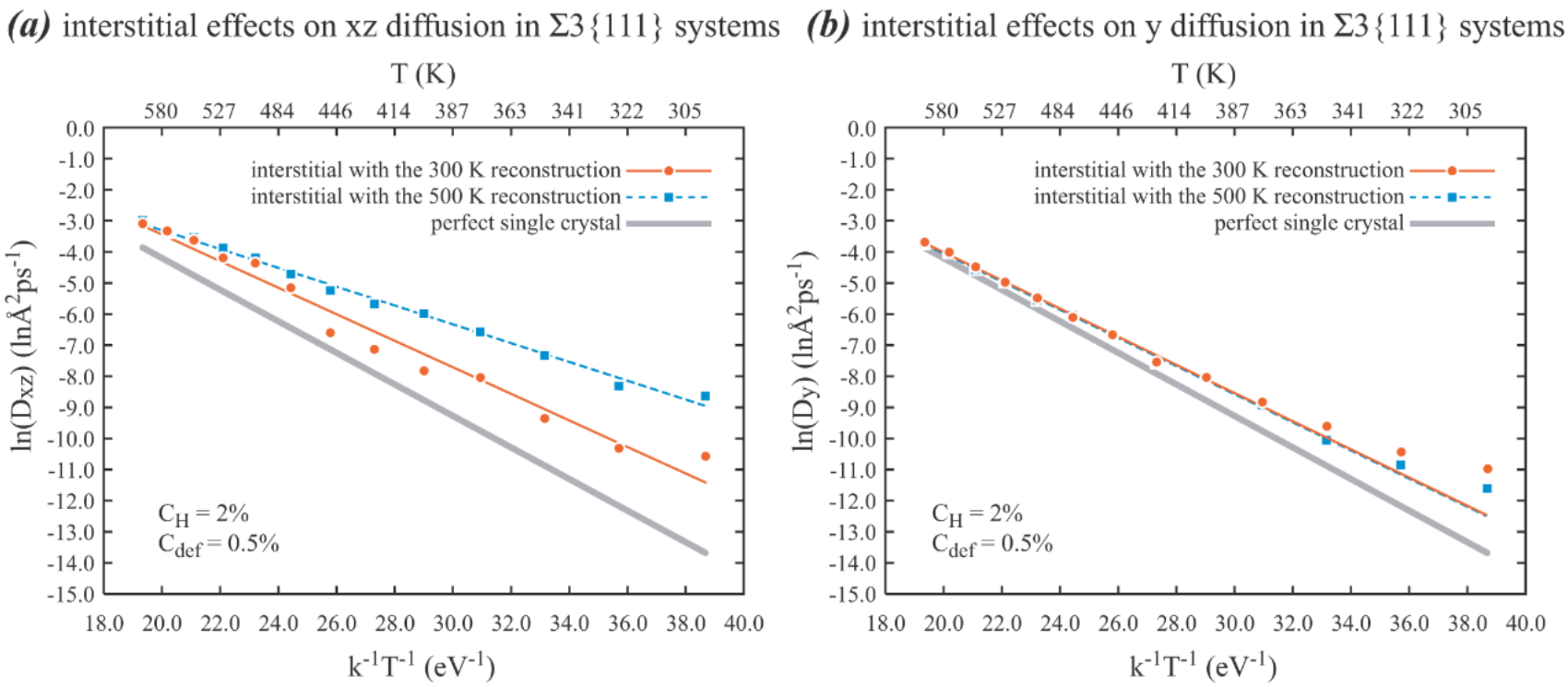
Statistical Effects of Initial Σ3{111} GB Reconstructions



- Depending on reconstruction, the combination of interstitials and the Σ3{111} grain boundary may significantly increase the on-plane diffusivities
- Interstitial increases on-plane diffusivities by 146.7 times at 300 K and 2.4 times at 600 K as compared with the boundary alone case
- Out-plane diffusivity is not significantly affected

t = 440 ns

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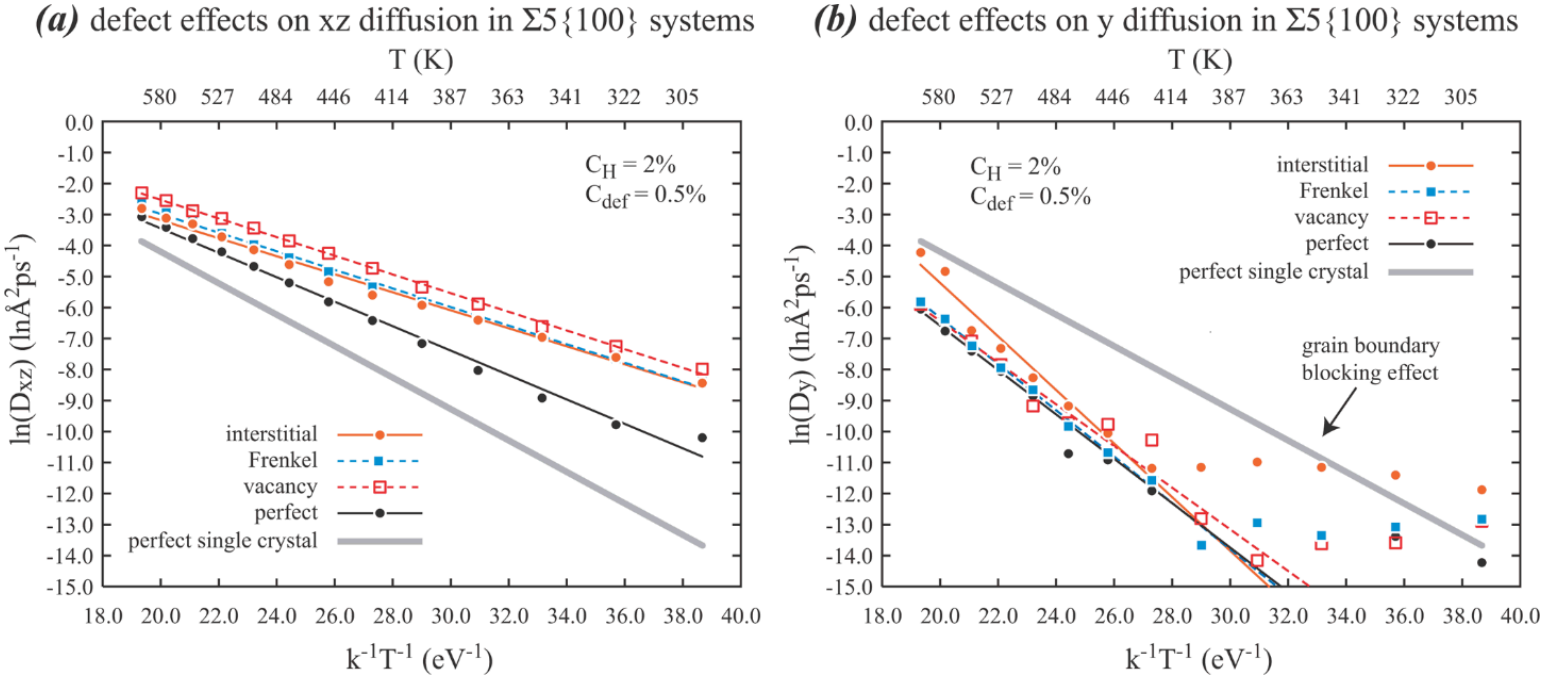
Defect Effects on H Diffusion in Ni with Σ5{100} GB



- The Σ5{100} GB itself significantly increases the on-plane diffusion (relative to single crystal)
- All defects increase the on-plane diffusivities, especially vacancies (in single crystals, interstitials have the biggest effects and vacancies have negligible effects)
- Vacancy increases on-plane diffusivities by 9.2 times at 300 K and 2.2 times at 600 K as compared with the boundary alone case
- The out-plane diffusivities are significantly reduced as compared to bulk diffusion, indicating boundary trapping that is confirmed by the two segments

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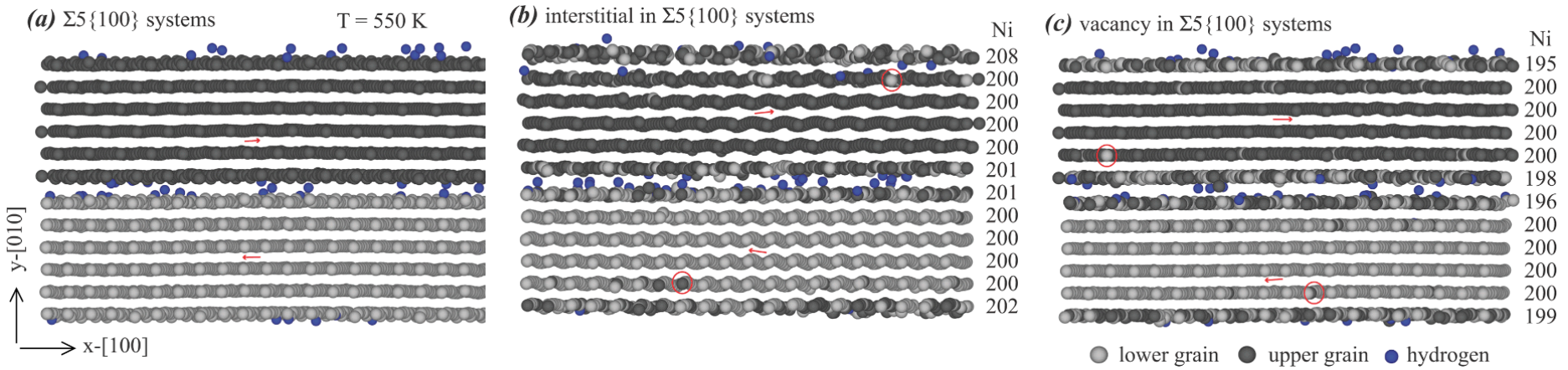
Visualization of Σ5{100} Grain Boundary

$C_H = 2\%$
$C_{def} = 0.5\%$



- Hydrogen atoms strongly segregates at the GB
- Ni interstitials and vacancies strongly segregate at the GB
- No change in the orientation of atomic rows
- Ni diffusion only occurs when ether interstitials or vacancies are present
- No statistical effects of initial configurations on diffusivities were found

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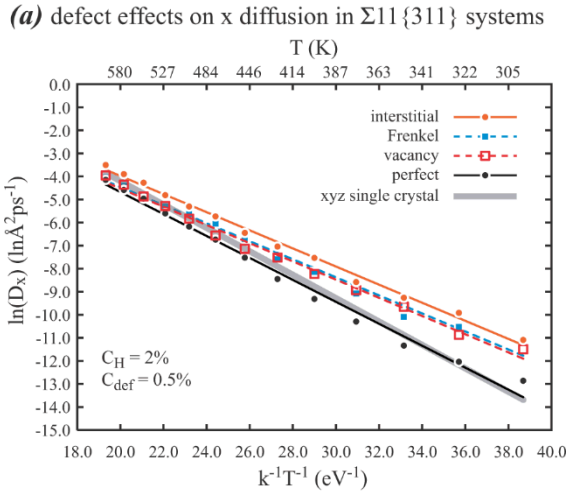
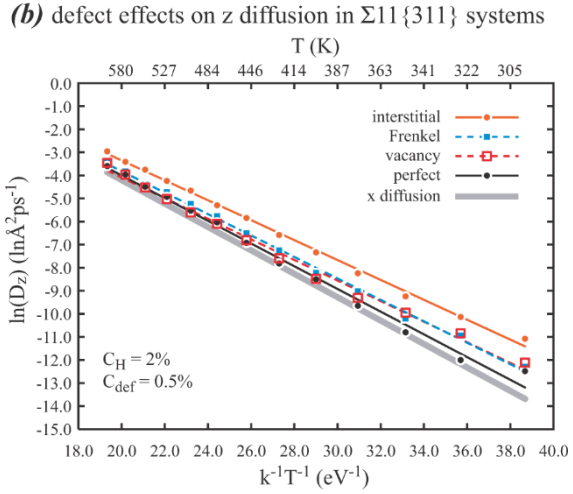
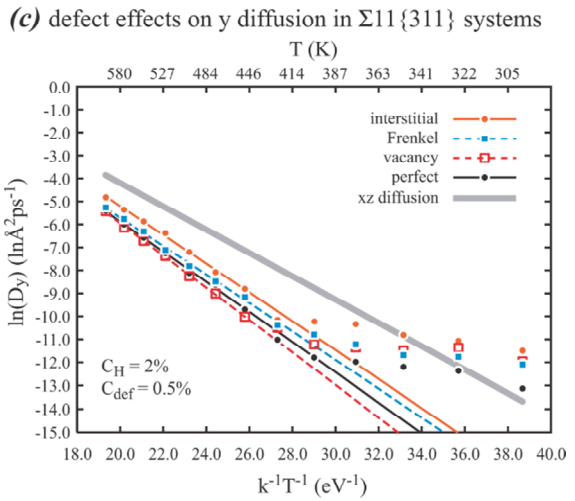
Defect Effects on H Diffusion in Ni with Σ11{311} GB







- Diffusivities in the two on-plane directions slightly differ
- Defects increase on-plane diffusivities especially at low temperatures
- Interstitials most significantly increase on-plane diffusivities
- In the x- direction, interstitials increase diffusivities by 5.9 times at 300 K and 1.9 times at 600 K as compared with the boundary alone case
- In the z- direction, interstitials increase diffusivities by 4.1 times at 300 K and 1.9 times at 600 K as compared with the boundary alone case
- The out-plane diffusivities are significantly reduced as compared to bulk diffusion, indicating boundary trapping that is confirmed by the two segments

t = 440 ns

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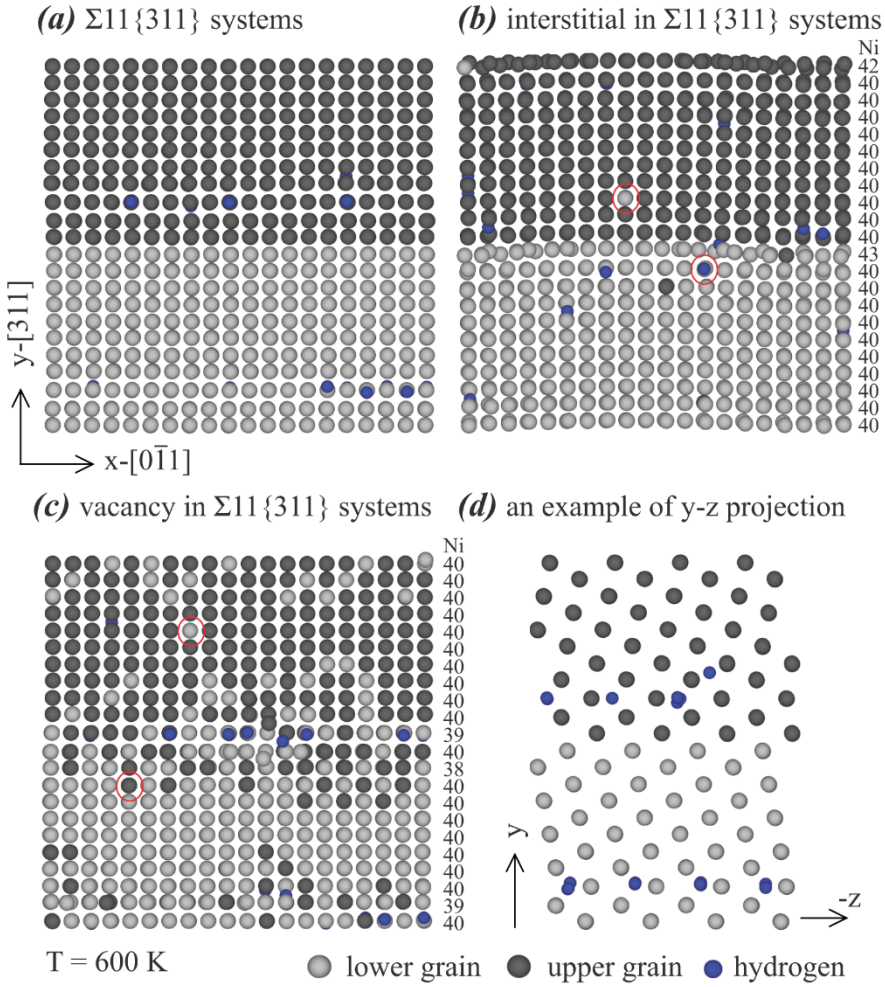
Visualization of Σ11{311} Grain Boundary



- Hydrogen atoms strongly segregates at the GB
- Ni interstitials and vacancies strongly segregate at the GB
- No change in the orientation of atomic rows
- Ni diffusion only occurs when ether interstitials or vacancies are present
- No statistical effects of initial configurations on diffusivities were found

$C_H = 2\%, C_{def} = 0.5\%$

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Activation Energy and Pre-exponential Factors

Table I. Activation energies Q and pre-exponential factors D_0 for different cases. Note that subscript "xyz" indicates isotropic bulk diffusion, "y" indicates out-plane diffusion, "xz" indicate isotropic in-plane diffusion, "x" and "z" indicate that the anisotropic in-plane diffusion is further split into two directions.

	No defects	Vacancies	Interstitials		Frenkel pairs
	Single crystals				
Q_{xyz} (eV)	0.508	0.455	0.407		0.435
$D_{0,xyz}$ (Å^2/ps)	3.835×10^{2}	8.925×10^{1}	5.959×10^{1}		9.075×10^{1}
	Σ3{111}				
Q_{xz} (eV)	0.483	0.465	0.441	0.302	0.427
$D_{0,xz}$ (Å^2/ps)	2.283×10^{2}	1.190×10^{2}	2.336×10^{2}	1.553×10^{1}	8.116×10^{1}
Q_y (eV)	0.475	0.448	0.459	0.453	0.455
$D_{0,y}$ (Å^2/ps)	1.666×10^{2}	8.089×10^{1}	1.941×10^{2}	1.503×10^{2}	1.352×10^{2}
	Σ5{100}				
Q_{xz} (eV)	0.395	0.301	0.291		0.300
$D_{0,xz}$ (Å^2/ps)	8.623×10^{1}	3.376×10^{1}	1.413×10^{1}		2.073×10^{1}
Q_y (eV)	0.716	0.672	0.864		0.747
$D_{0,y}$ (Å^2/ps)	2.289×10^{3}	1.116×10^{3}	1.767×10^{5}		5.497×10^{3}
	Σ11{311}				
Q_x (eV)	0.476	0.395	0.393		0.391
$D_{0,x}$ (Å^2/ps)	1.271×10^{2}	2.907×10^{1}	4.808×10^{1}		2.888×10^{1}
Q_z (eV)	0.493	0.447	0.432		0.465
$D_{0,z}$ (Å^2/ps)	3.474×10^{2}	1.262×10^{2}	1.983×10^{2}		2.420×10^{2}
Q_y (eV)	0.655	0.703	0.627		0.620
$D_{0,y}$ (Å^2/ps)	1.388×10^{2}	3.342×10^{2}	1.528×10^{2}		8.077×10^{2}

$C_H = 2\%$

$C_{def} = 0.5\%$

Point defects + grain boundaries can reduce on-plane diffusion energy barrier, in agreement with experiments*

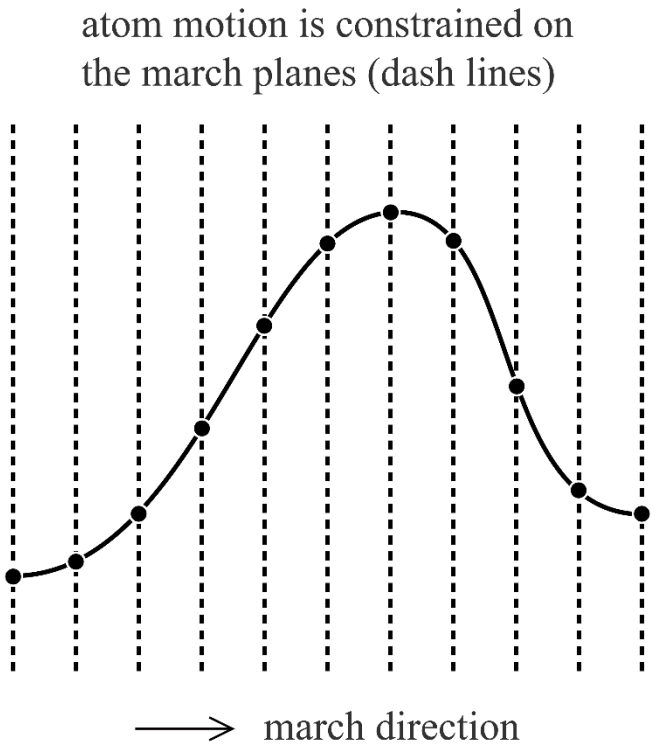
*A. Qudriss, J. Creus, J. Bouhattate, E. Conforto, C. Berziou, C. Savall, and X. , Acta Mater., 60, 6814 (2012).

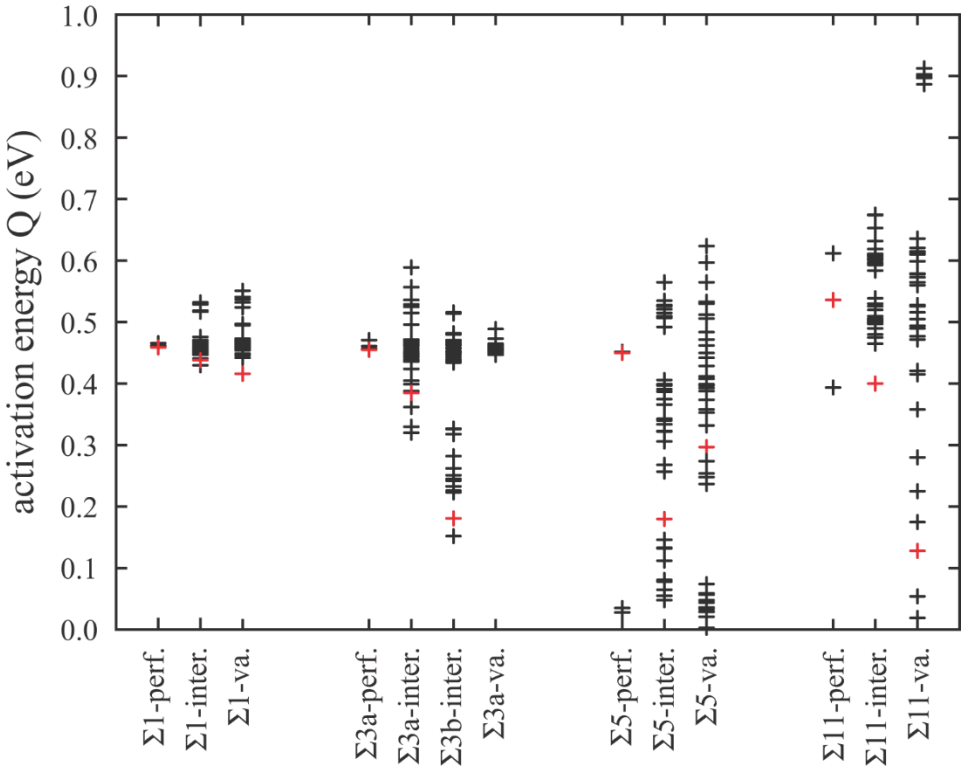
Table II. Hydrogen-defect interaction energy (eV).

Point defects		Grain boundaries		
Vacancies	Interstitials	Σ3{111}	Σ5{100}	Σ11{311}
-0.18	-0.12	-0.03	-0.20	-0.24

By placing hydrogen at different locations, MD simulations at 100 K are used to calculate time-averaged interaction energies between hydrogen and various defects

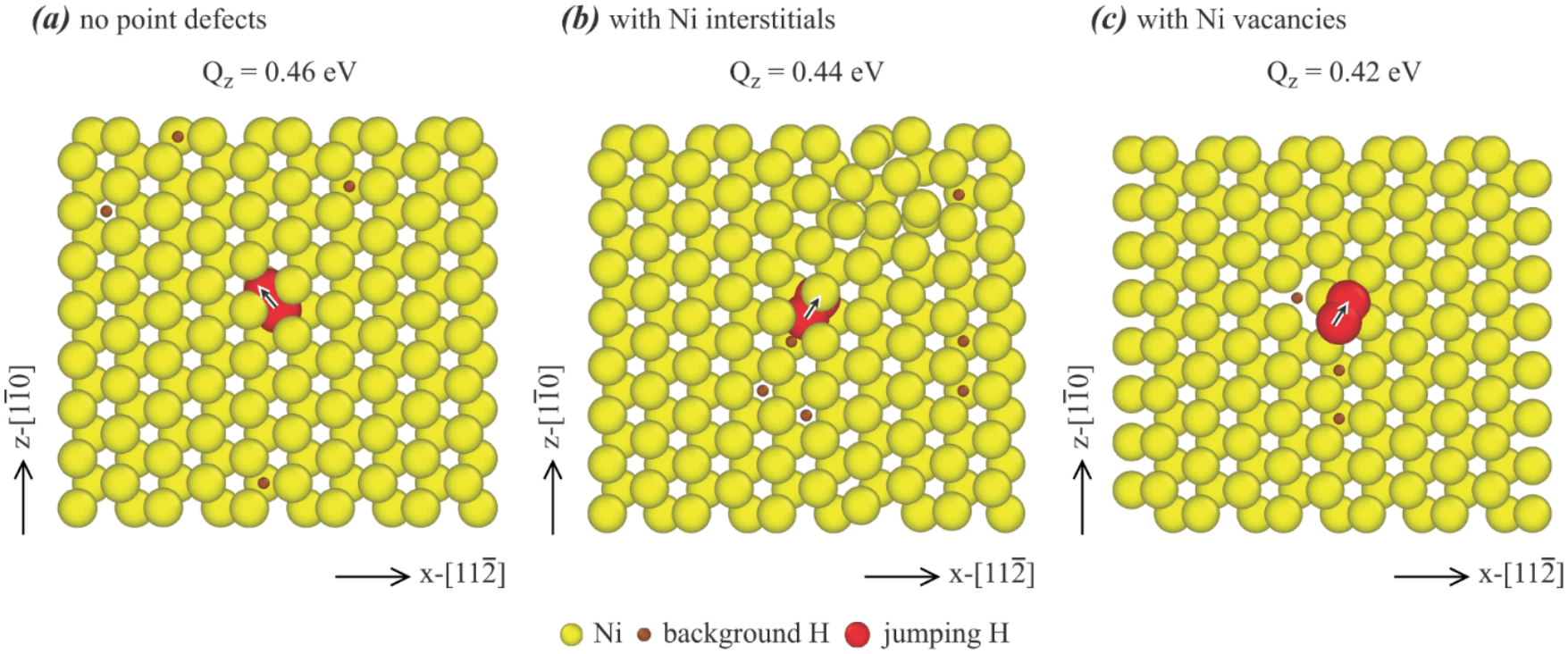
Activation Energy of Individual Jumps





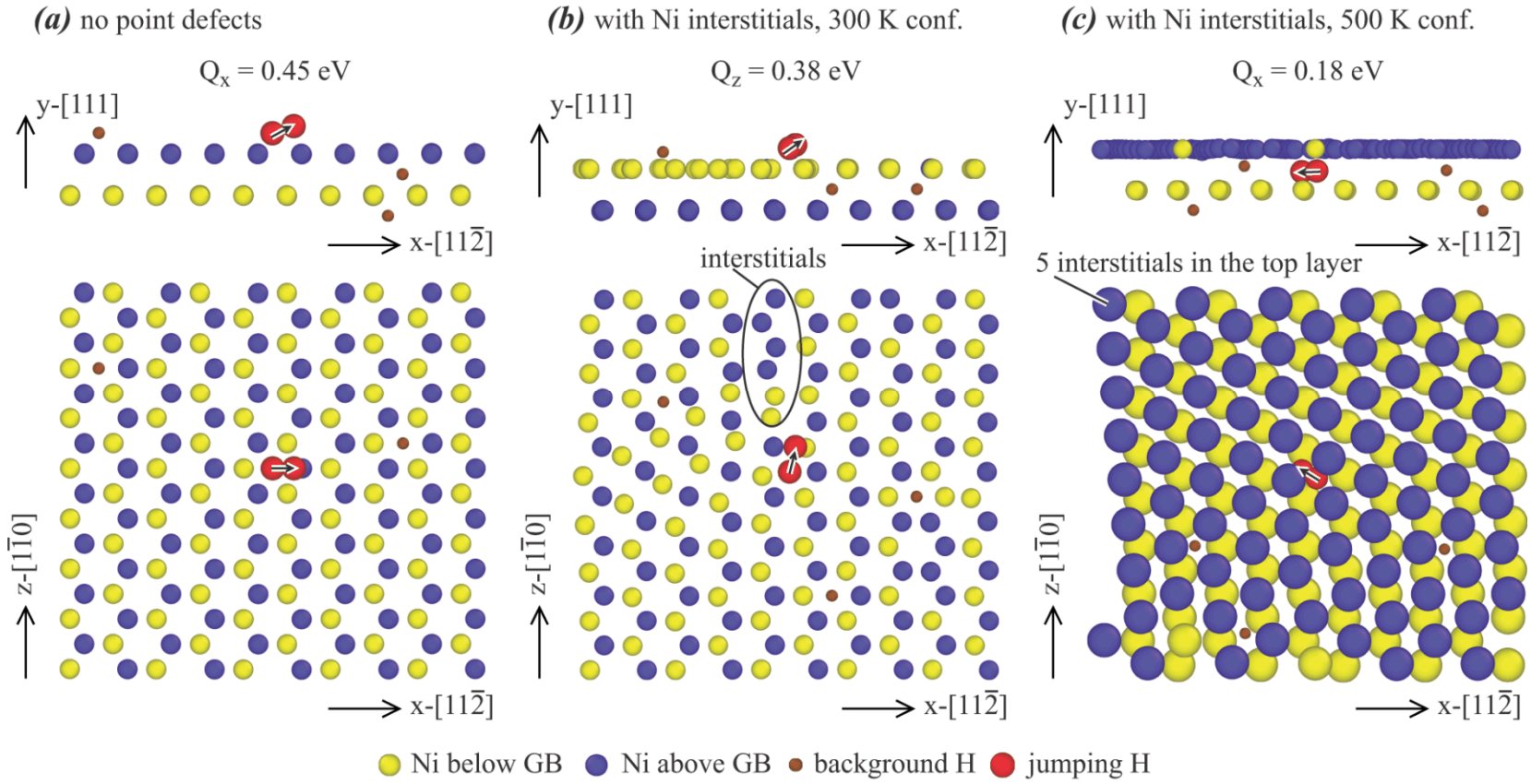
- By sequentially marching the hydrogen atoms in the three coordinate directions and relaxing the structure with the marching atom constrained on the marching plane, molecular statics can be used to calculate the energy barrier of atomic jumps
- This method can be easily automated to calculate a variety of atomic jumps

Visualization of Atomic Jumps in Single Crystal



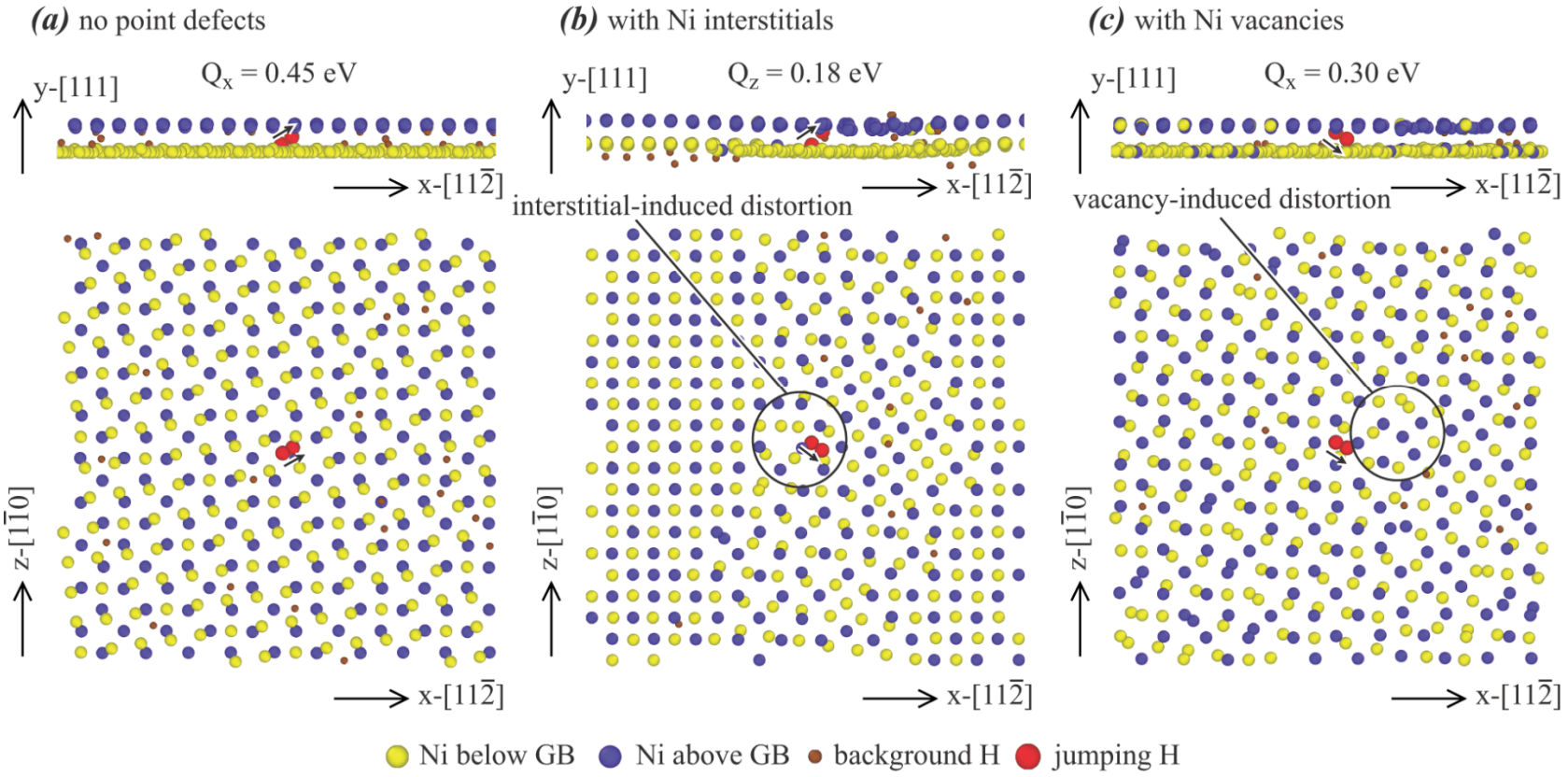
Presence of nickel interstitials or vacancies can reduce the energy barrier of some hydrogen jump paths, but not too much

Visualization of Atomic Jumps near the Σ3 GB



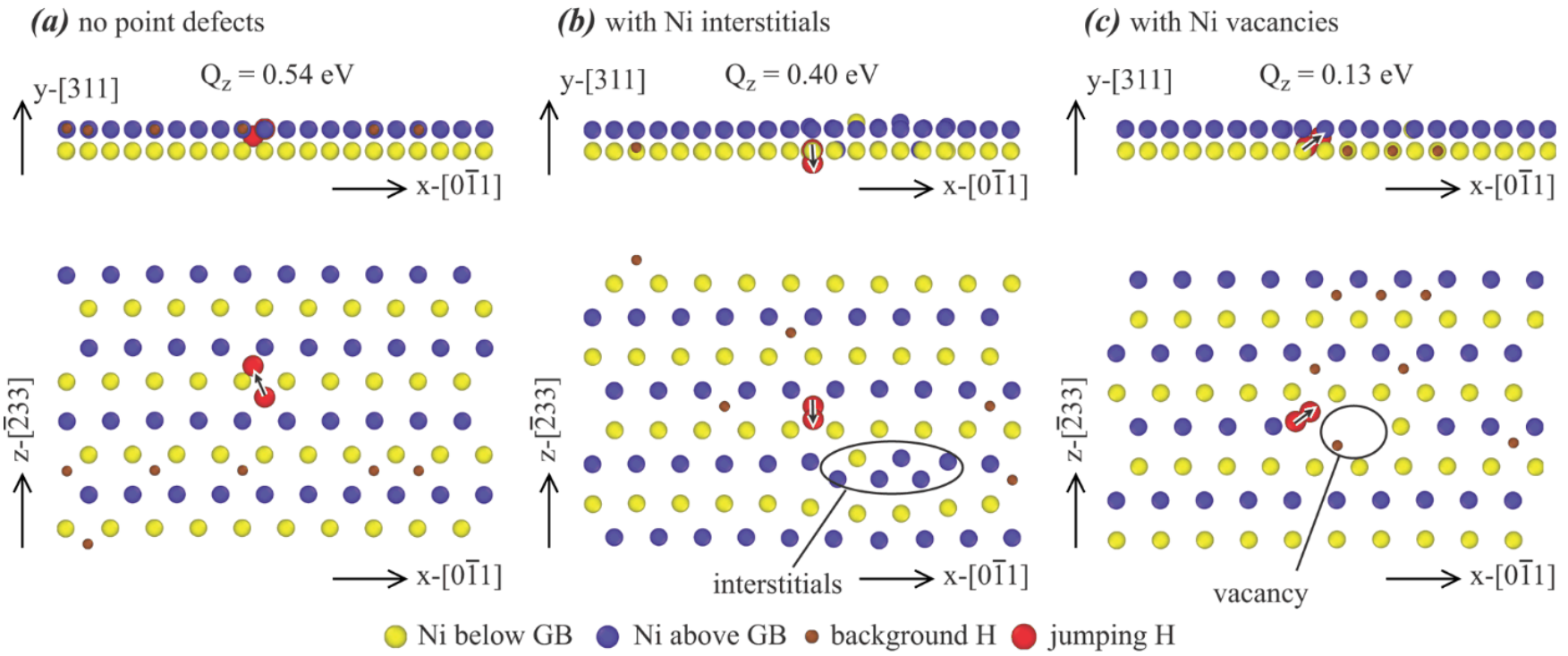
- Presence of nickel interstitials or vacancies can reduce the energy barrier of some hydrogen jump paths further from GB effects alone
- The 500 K initial configuration more effectively reduces the energy barrier because the 5 nickel interstitials are uniformly distributed

Visualization of Atomic Jumps near the Σ5 GB



- Presence of nickel interstitials or vacancies can reduce the energy barrier of some hydrogen jump paths further from GB effects alone
- Both interstitials and vacancies cause local distortion

Visualization of Atomic Jumps near the Σ11 GB



- Presence of nickel interstitials or vacancies can reduce the energy barrier of some hydrogen jump paths further from GB effects alone
- Local interstitials and vacancies are more clearly defined than the Σ5 grain boundary case

Major Conclusions

1. Robust MD diffusion simulation methods have been developed to account for statistical interactions between diffusion species, grain boundaries, and irradiated defects. Highly converged results with almost no statistical errors are demonstrated
2. The predicted activation energy of H diffusion in defect-free single crystal Ni, 0.51 eV, compares well with the experimental value, 0.40 eV
3. For single crystals, 0.5% interstitial increases H diffusivities by 16.3 times at 300 K and 1.4 times at 600 K as compared with perfect crystals. Vacancy does not sensitively change diffusivities
4. Interstitials cause different reconstructions of $\Sigma 3\{111\}$ grain boundaries. Some reconstructions may have significantly increased on-plane H diffusivities: by 146.7 times at 300 K and 2.4 times at 600 K as compared with the boundary alone case
5. Defects significantly increase on-plane H diffusivities on $\Sigma 5\{100\}$ grain boundary
6. $\Sigma 5\{100\}$ and $\Sigma 11\{311\}$ grain boundaries have significant H trapping effects, leading to significantly reduced out-plane H diffusivities
7. Molecular statics calculations of energy barriers of individual jumps help understand the mechanisms of diffusivity changes

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