INL/CON-24-76904-Revision-0

Vacancy-mediated transport and segregation tendencies of solutes in FCC Ni under diffusional creep

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Idaho National Laboratory

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Vacancy-mediated transport and segregation tendencies of solutes in FCC Ni under diffusional creep

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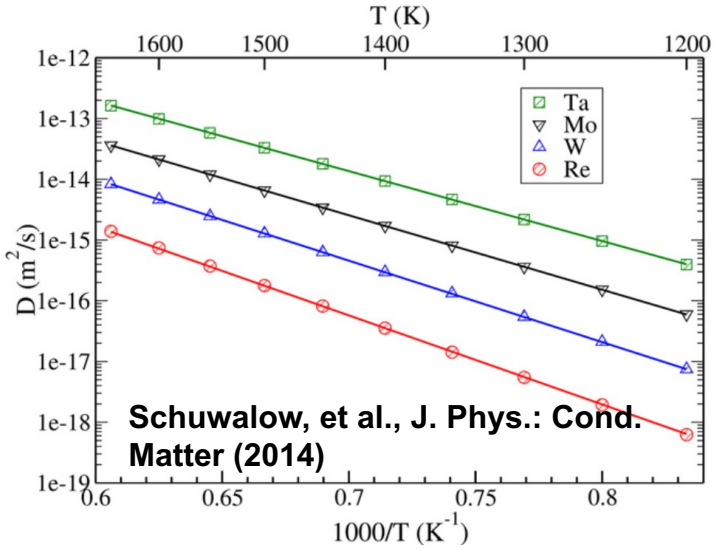
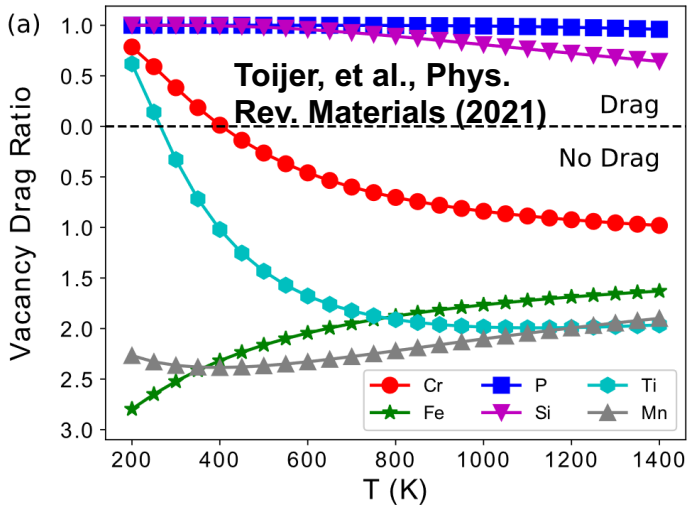
Literature

Several DFT studies on solute diffusion in FCC Ni

- DFT + five-frequency model:
  - interactions limited to the 1st nn.
  - Tucker, et al., J. Nucl. Mater. (2010): Cr and Fe solutes
  - Hargather et al., Acta Materialia (2018): diffusivities of 26 solutes in FCC Ni
- DFT + KMC :
  - Schuwalow et al. calculated diffusivities of Mo, Re, W, and Ta solutes in FCC Ni
- DFT + SCMF :
  - taking into account kinetic correlations to calculate Onsager transport coefficients.
  - Toijer et al. studied the solute-point defects interaction in FCC Ni using DFT (solutes: Cr, Fe, Si, Al, P, and Mn): vacancy drag and segregation tendencies





Methodology

- **In this work:**
  - we adopt the methodology of **DFT+SCMF** to investigate the segregation tendencies of Co, Cr, Mo, Re, W, and Ta solutes in Ni-based superalloys
  - we extend this model to include the segregation tendencies **under strain** using the linear elasticity theory as implemented in the KineCluE code

- Using density functional theory (DFT):
  ➔vacancy-solute interactions: formation, binding and migration energies
  ➔phonon calculations to obtain attempt frequencies (diffusion prefactors) and vacancy formation entropy
- Using self-consistent mean field theory (SCMF):
  ➔cluster transport coefficients and partition functions

T. Schuler, et al., Comp. Mater. Sci. 171 (2020) 109191
L. Messina, et al., Acta Materialia 191 (2020) 166--185

DFT Computational Details

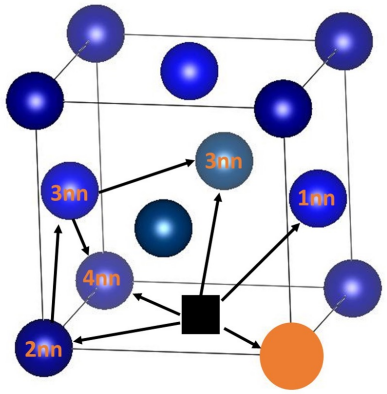
- PAW pseudopotentials as implemented in VASP
  - GGA-PBE exchange-correlation functionals
  - 108-atom and 192-atom supercells
- Climbing-image NEB to get the saddle point energy for atomic jumps
  - One intermediate image
- Frozen phonons method to calculate the attempt frequencies
  - 0.02 Å atomic displacements to get force constants

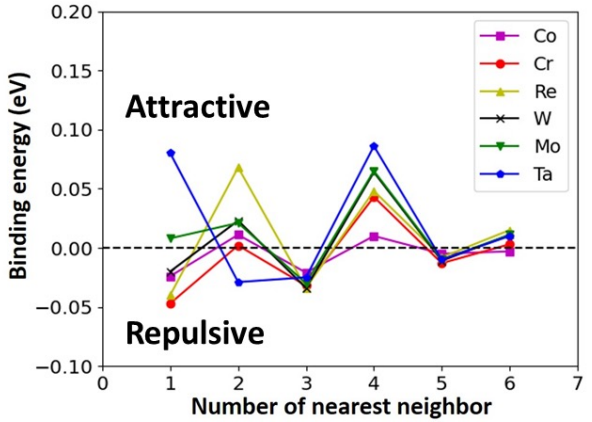
Vacancy-Solute Interactions

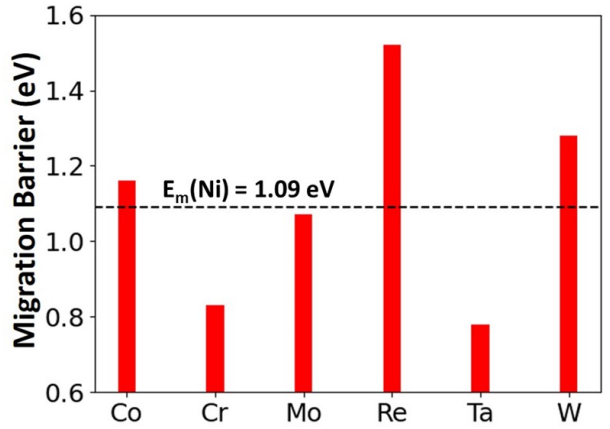
- Vacancy-solute interactions up to the 4th nn are considered
- For each solute, the migration barrier for 8 jumps are calculated:
  - vacancy-solute exchange
  - 7 vacancy jumps (dissociation/association and reorientation) (1nn➔1nn, 1nn➔2nn, 1nn➔3nn, 1nn➔4nn, 2nn➔3nn, 3nn➔3nn, 3nn➔4nn)

Findings:

- Ta, Cr, and Mo are relatively fast diffusers
- Co, W, and Re are relatively slow diffusers.







SCMF Computational Details

$$\begin{pmatrix} J_V \\ J_B \end{pmatrix} = \frac{-1}{k_B T} \overbrace{\begin{pmatrix} L_{VV} & L_{VB} \\ L_{VB} & L_{BB} \end{pmatrix}}^{\text{Onsager matrix}} \begin{pmatrix} \nabla \mu_V \\ \nabla \mu_B \end{pmatrix}$$

- Cluster expansion:

$$\begin{pmatrix} L_{VV} & L_{VB} \\ L_{VB} & L_{BB} \end{pmatrix} = C\Big(f_V \underbrace{\begin{pmatrix} L_{VV}^{(V)} & 0 \\ 0 & 0 \end{pmatrix}}_{\text{Contribution from clusters with vacancies}} + f_{VB} \underbrace{\begin{pmatrix} L_{VV}^{(VB)} & L_{VB}^{(VB)} \\ L_{VB}^{(VB)} & L_{BB}^{(VB)} \end{pmatrix}}_{\text{Contribution from clusters with vacancy-solute pairs}}\Big)$$

- f_V and f_{VB} are the fractions of vacancies and vacancy-solute pairs, respectively, and are obtained from the SCMF partition functions
- Kinetic range (r_{kin}) = 4 lattice constants (after performing convergence tests)
- Dilute limit: maximum solute concentration [B] using this cluster size is 0.1 at. %

Cluster fractions

$$f_V = \frac{C_V - C_{corr}}{C}, f_{VB} = \frac{C_{VB}}{C}$$

$$C_V = Z_V[V] = Z_V e^{\frac{-E_{form}^{vac}}{k_B T}} e^{\frac{S_{form}^{vac}}{k_B T}}$$

$$C_{VB} = Z_{VB}[V][B]$$

Z_{VB} : pair partition function

$$Z_{VB} = \sum_i e^{\frac{E_{bind}^i}{k_B T}}$$

$$C_{corr} = Z_{VB}^0[V][B]$$

(sites that single vacancies cannot occupy because of the geometrical definition of the vacancy-solute pair)

Z_{VB}^0: non-interacting cluster partition function (# of possible pair configurations within r_{kin}.

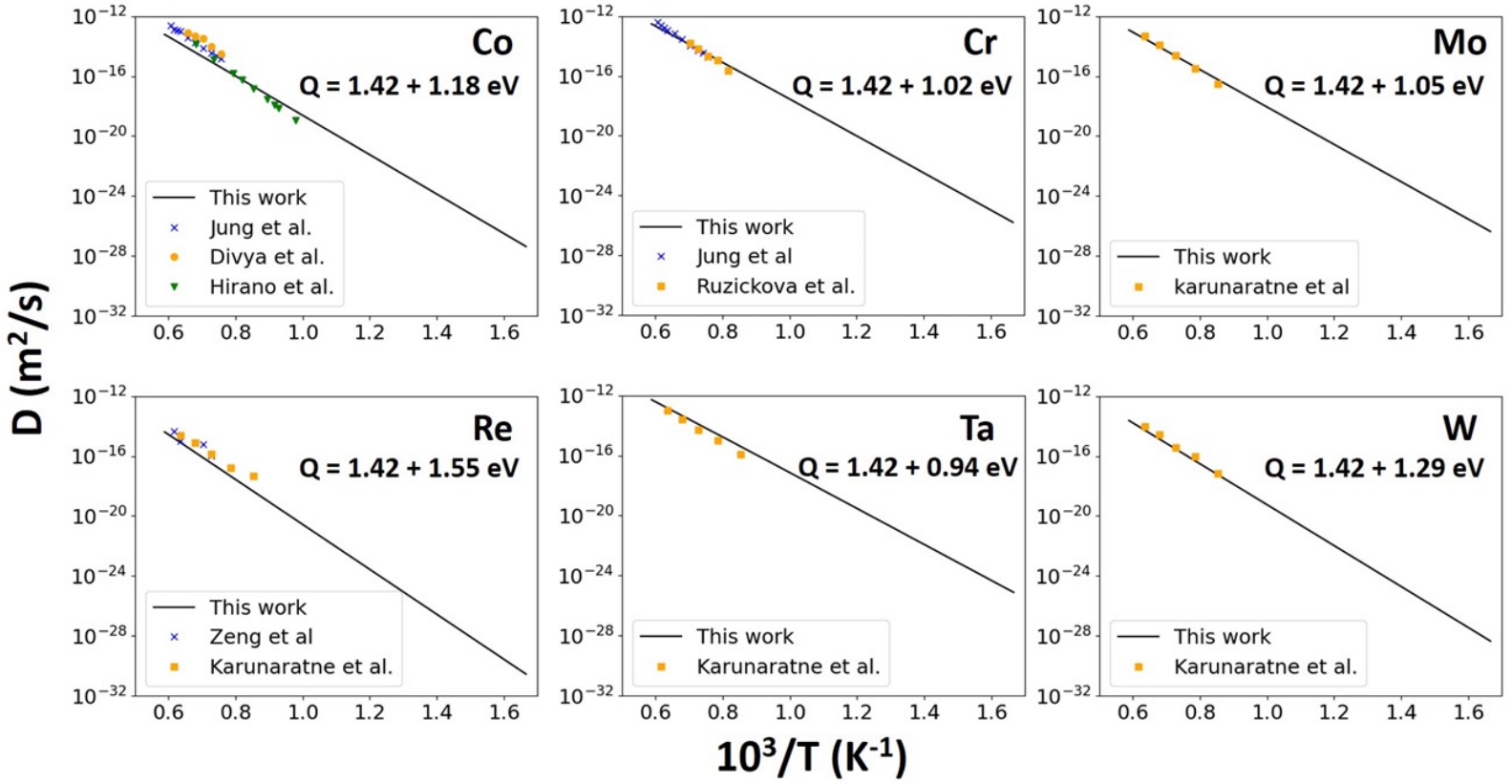
L. Messina et al., Acta Materialia 191 (2020) 166--185

Solute Diffusivities

- In the dilute limit:

$$D_B = \frac{L_{BB}}{[B]}$$

- Good agreement of calculations with experimental data



Solute vacancy drag and partial diffusion coefficient ratio

We analyze flux coupling from transport coefficients

➔Vacancy drag ratio (G) indicates if a solute
- follows the vacancy in its migration **(G>0)** or
- diffuses in the opposite direction **(G<0)**

$$G = \frac{L_{VB}^{(VB)}}{L_{BB}^{(VB)}}$$

➔PDC ratio describes the diffusion of solute atoms relative to matrix atoms
- **-ve PDC ratio: vacancy drag ➔** solute enrichment at sinks
- **+ve PDC ratio: inverse Kirkendall**
  - PDC ratio > 1 : solute depletion at sinks (favorable solute-vacancy exchange)
  - 0 < PDC ratio < 1 : solute enrichment (slower than the host atoms, so effectively enriched)

$$PDC = \frac{1-C_B}{C_B}\frac{L_{VB}}{L_{AV}}$$

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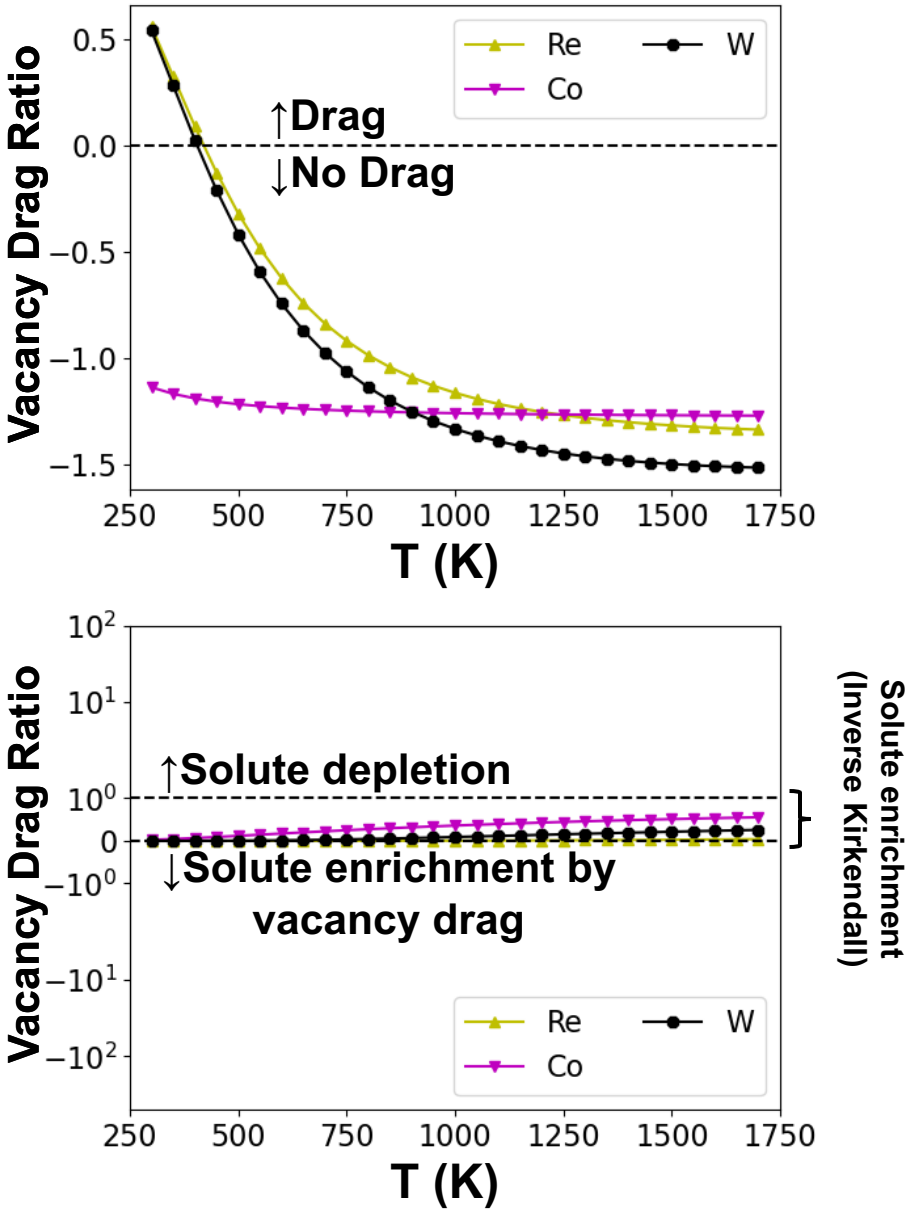
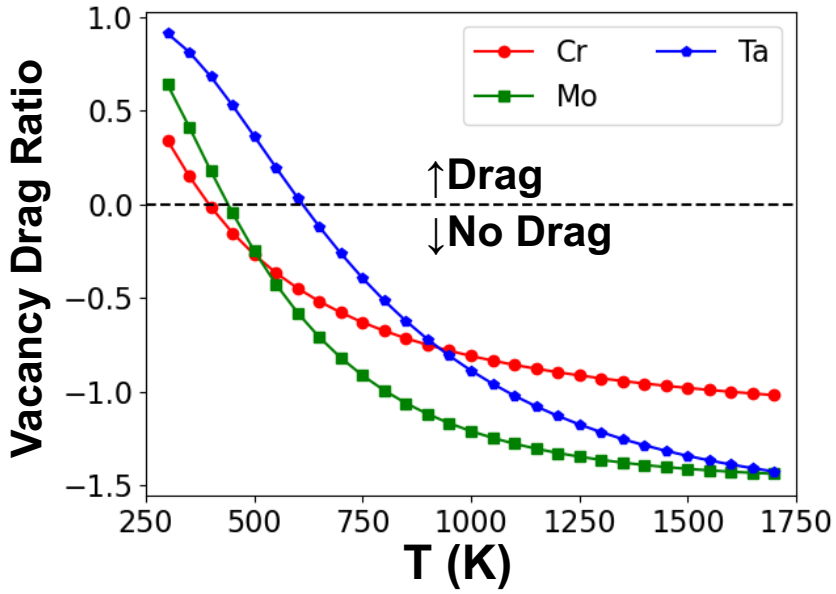
Segregation Tendencies
(A) Slow diffusers

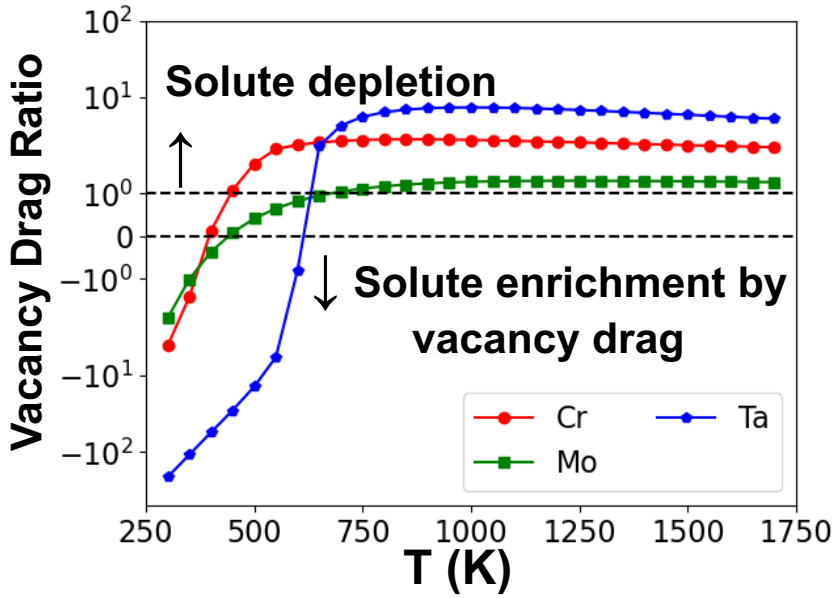
- Re and W :
  - dragged by vacancies at low temperature below ~400 K
  - At higher temperatures, they move opposite to the vacancy flux but are enriched (inverse Kirkendall mechanism)
- Co:
  - not dragged by vacancies at any temperature due to weak binding
  - Enrichment by inverse Kirkendall mechanism



Segregation Tendencies (B) Fast diffusers

- Cr and Mo:
  - dragged by vacancies at low temperature below ~400 K (enriched)
  - Cr depletion at T > 500 K
  - Mo depletion at T > 600 K
- Ta:
  - Dragged by vacancies up to 600 K due to strong binding
  - Ta depletion above 650 K





Strain Effects

Linear elasticity theory approach

- Instead of repeating DFT calculations on strained supercells:
- The binding and migration energies under strain tensor ε_{ij} :

$$E_b^x(\varepsilon = \varepsilon_{ij}) = E_b^x(\varepsilon = 0) + P_{ij}^x \varepsilon_{ij}$$

$$E_m^{x1\Rightarrow x2}(\varepsilon = \varepsilon_{ij}) = E_m^{x1\Rightarrow x2}(\varepsilon = 0) - P_{ij}^{ts(x1\Rightarrow x2)} \varepsilon_{ij}$$

- P_{ij}^x is the DFT elastic dipole tensor of a defect configuration (x)
- $P_{ij}^{ts(x1\Rightarrow x2)}$ is the DFT elastic dipole tensor of a transition state between two configurations x1 and x2
- In this work, we are only considering a tensile hydrostatic strain $\begin{pmatrix} +e & 0 & 0 \\ 0 & +e & 0 \\ 0 & 0 & +e \end{pmatrix}$

E. Clouet, et al., Comp. Mater. Sci. 147 (2018) 49--63
T. Schuler, et al., Comp. Mater. Sci. 171 (2020) 109191

Segregation Tendencies Under Strain

- Two factors control the sensitivity of strain effect on the segregation tendency

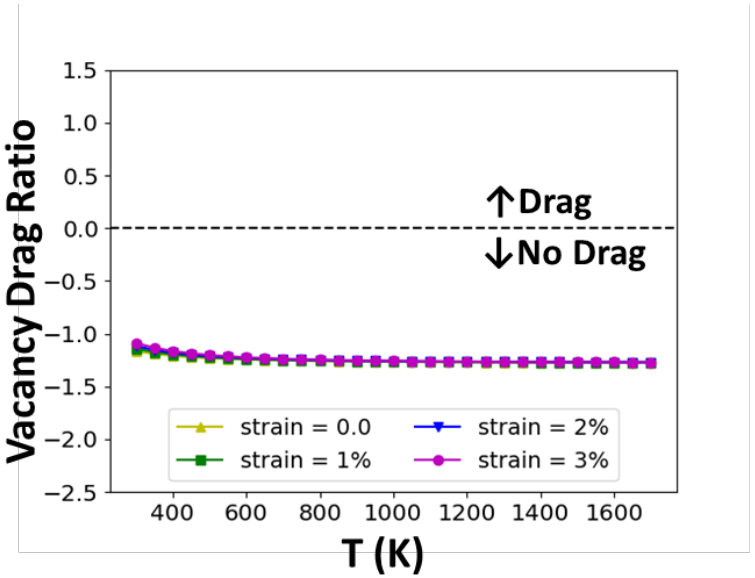
1. **Relative mobility of the solute**
   - The segregation tendency of slow diffusers (Co, W, Re) is not affected by strain (even if the vacancy drag ratio changes)
   - The segregation tendency of fast diffusers (Mo, Cr, Ta) is significantly affected by strain
2. **The stress introduced by the solute in the lattice (relaxation volume)**
   - The vacancy drag of solutes with higher residual stresses have higher sensitivity to strain

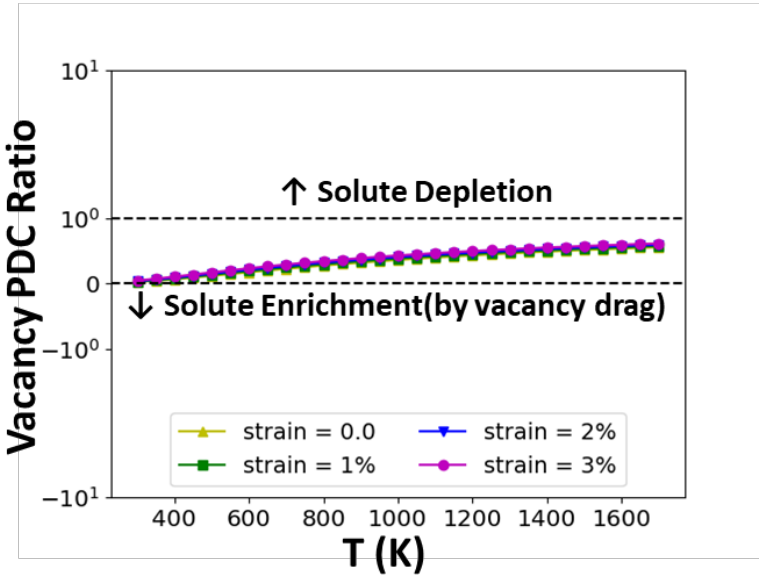
Segregation Tendencies Under Strain: (A) Slow diffusers

(1) Co
(Slow diffuser, zero residual stress)

- No change in vacancy drag
  (because of the zero elastic dipole tensor)
- No change in segregation tendency

	E_m (eV)	Stress (eV)	Solute-vacancy pair stress (eV)
Vacancy	1.09	-4.6 /	-
Co	1.16	0.0 / *(No residual stress)*	$\begin{pmatrix} -4.7 & 0 & 0 \\ 0 & -4.6 & 0.11 \\ 0 & 0.11 & -4.6 \end{pmatrix}$



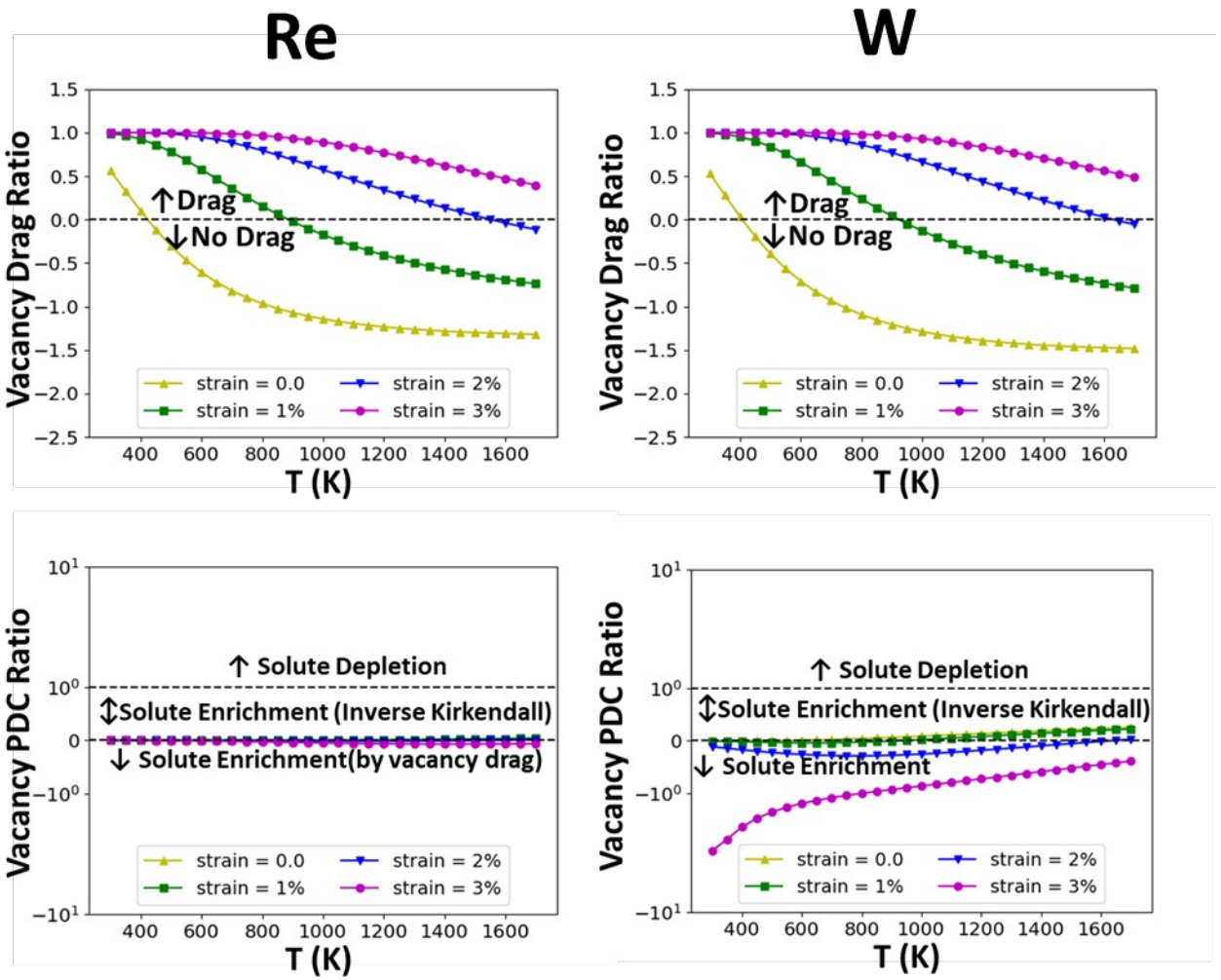


Segregation Tendencies Under Strain: (A) Slow diffusers

(2) Re and W
(Slow diffusers,
non-zero residual stress)

- Although vacancy drag increases with tensile strain, Re enrichment is minimally affected
  (**too slow to be strongly dragged)**
- W enrichment increases by vacancy drag mechanism
  (faster than Re)

	E_m (eV)	Stress (eV)
Re	1.52 (slowest)	5.0 /
W	1.28	5.5 /

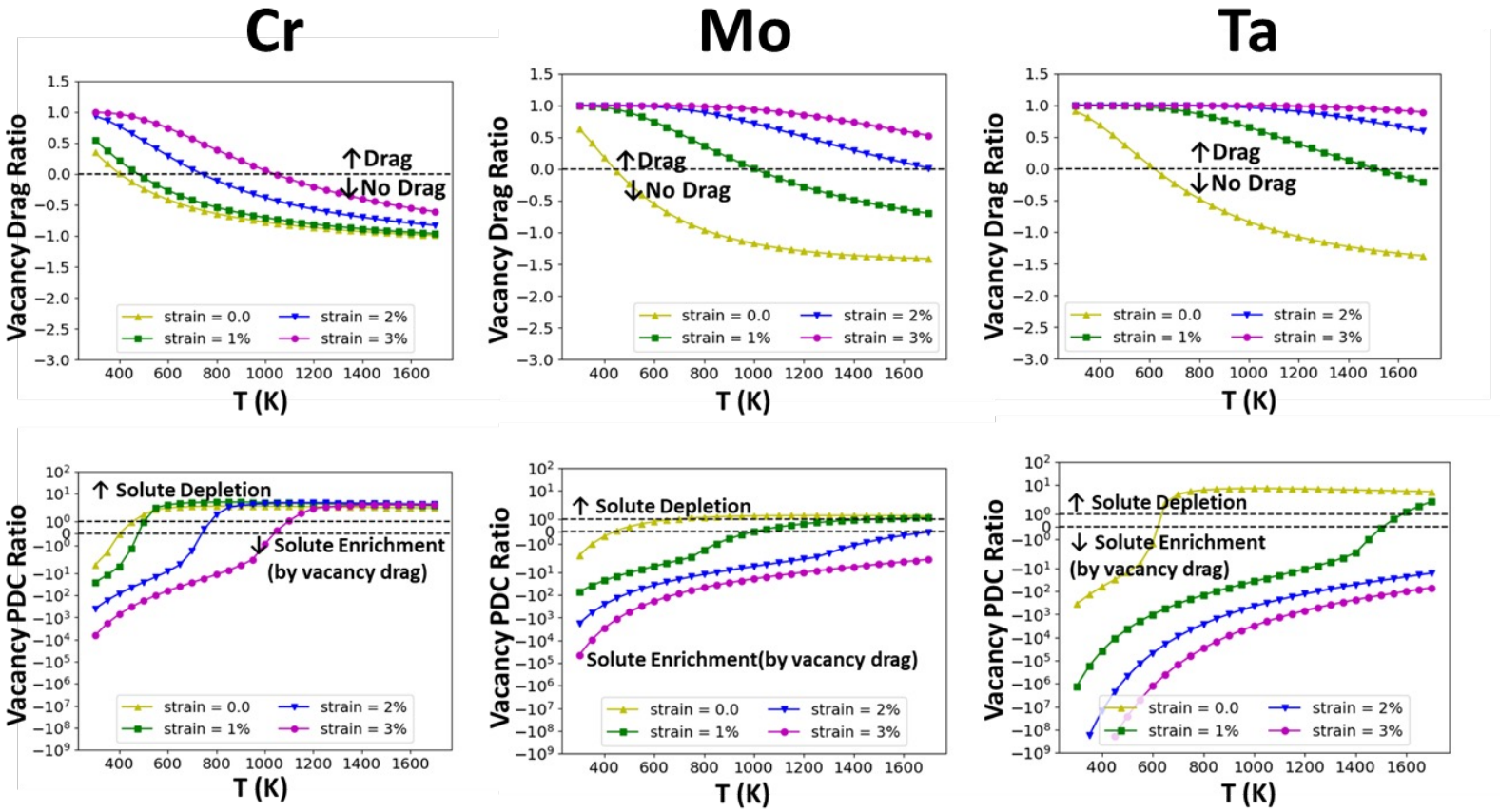


Segregation Tendencies Under Strain: (B) Fast diffusers

(3) Cr, Mo, and Ta (fast diffusers)

- Multiple orders of magnitudes changes in PDC ratio
- The increase of enrichment tendency is the highest for Ta (fastest & highest residual stress)

	E_m (eV)	stress (eV)
Mo	1.07	5.4 /
Cr	0.84	2.7 /
Ta	0.78	7.9 /



Summary and Conclusions

- Solute-vacancy defect energetics in FCC Ni were calculated using first-principles calculations (DFT)
- The Onsager transport coefficients were evaluated using the SCMF approach
- Fast diffusers (Ta, Cr, and Mo)
  - depleted at sinks due to favorable vacancy-solute exchange (inverse Kirkendall) at high temperatures
  - enriched at sinks by vacancy drag at low temperatures
- Slow diffusers (Co, Re, and W)
  - Enriched at sinks by the inverse Kirkendall mechanism
- The segregation tendency of fast-diffusing solutes is more sensitive to strain

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