

Uncertainty quantification for solute transport modeling

Dallas R. Trinkle and Ravi Agarwal / Materials Science and Engineering
Univ. Illinois, Urbana-Champaign

Motivation: who do we blame when experiments and theory don't agree?

... or: how can we agree if we don't know what we're agreeing to?

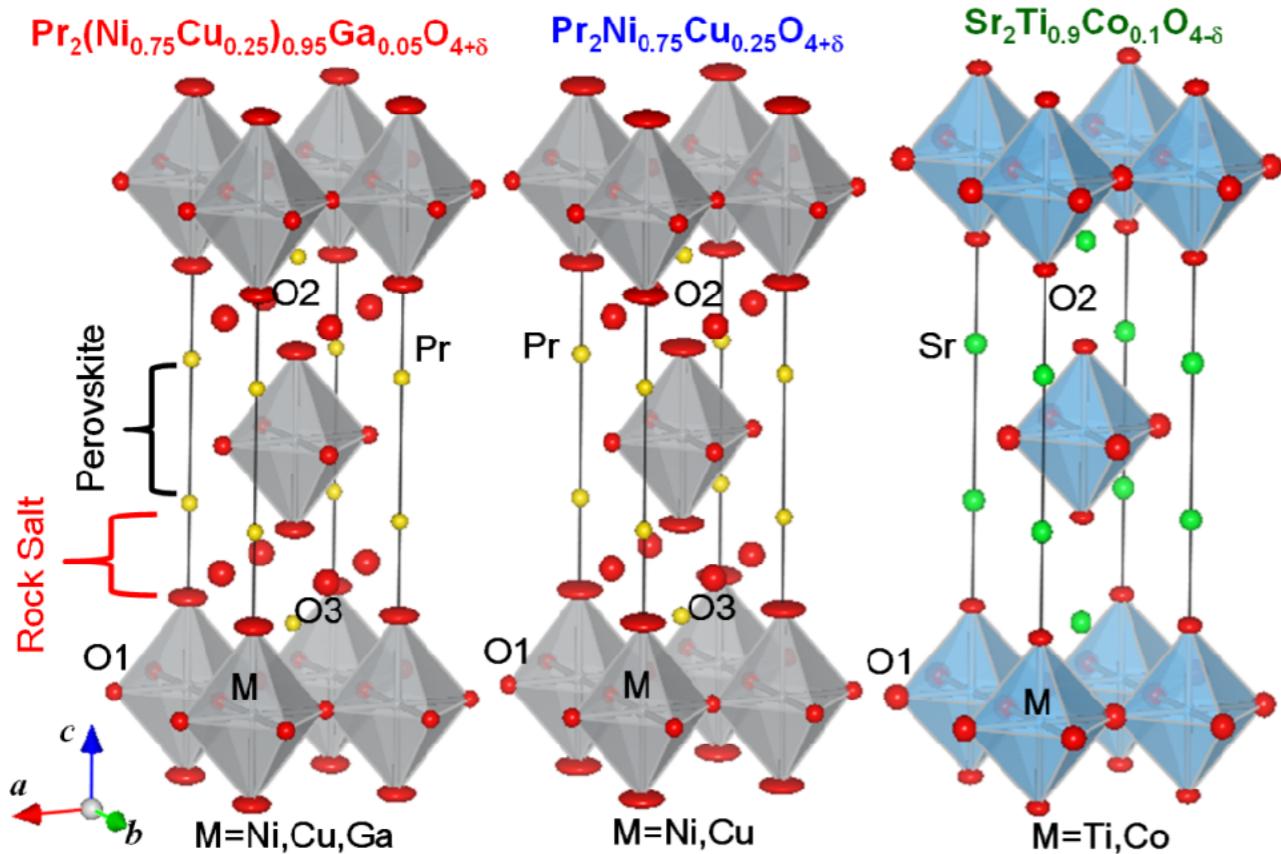


Propagating uncertainty from first-principles calculations via analytic models of mass transport can quantify uncertainty in diffusivity predictions.

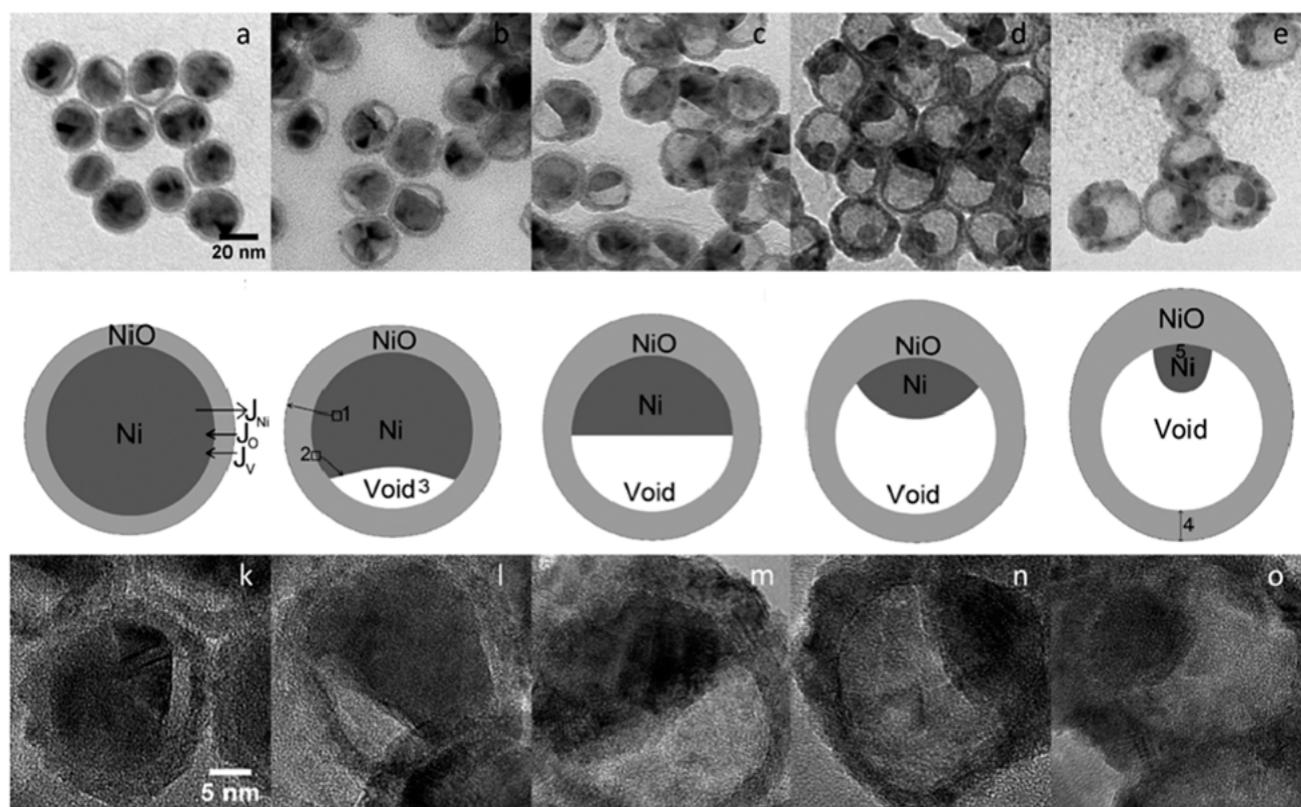


Mass transport

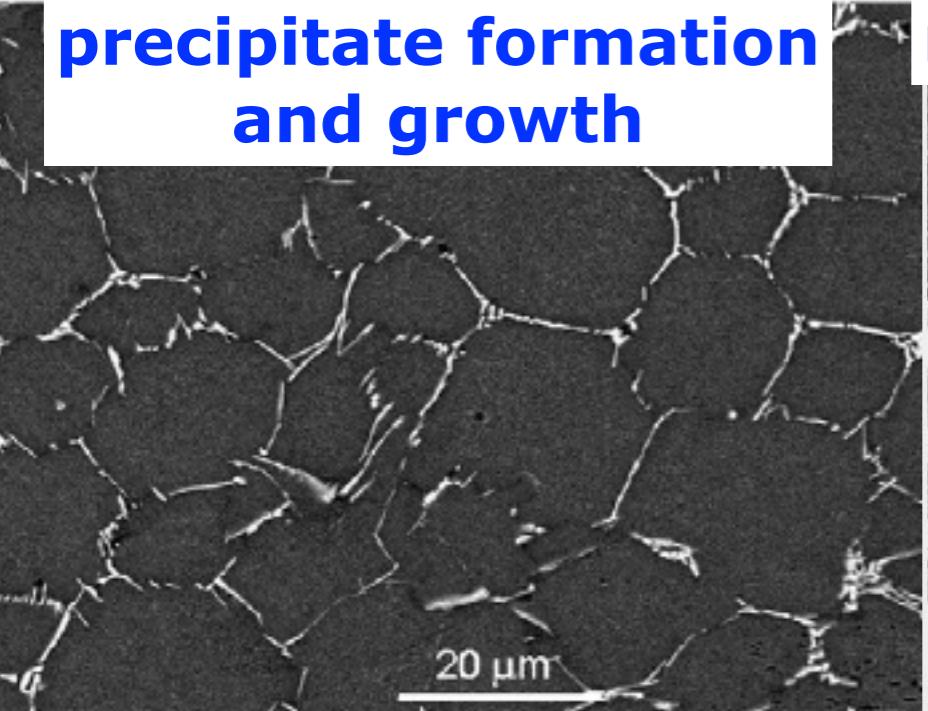
ion transport



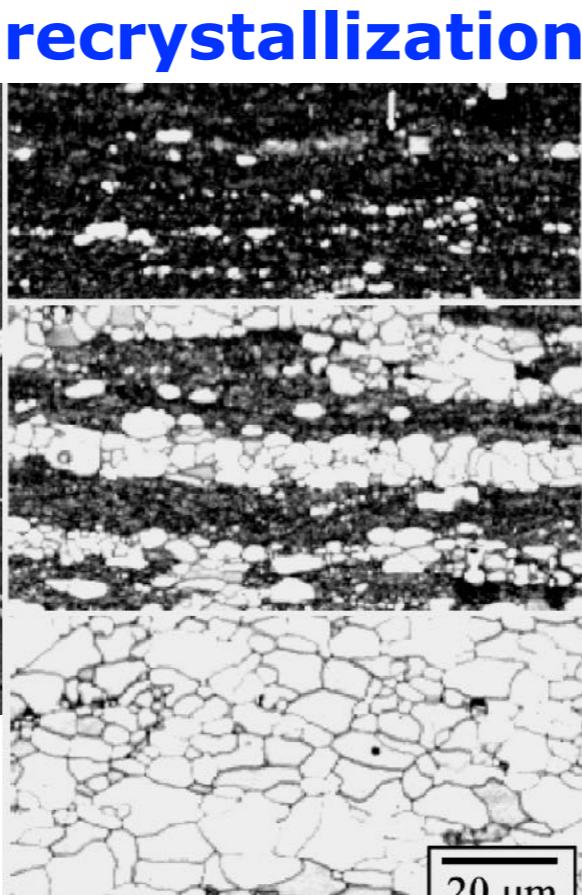
(nano) Kirkendall effect



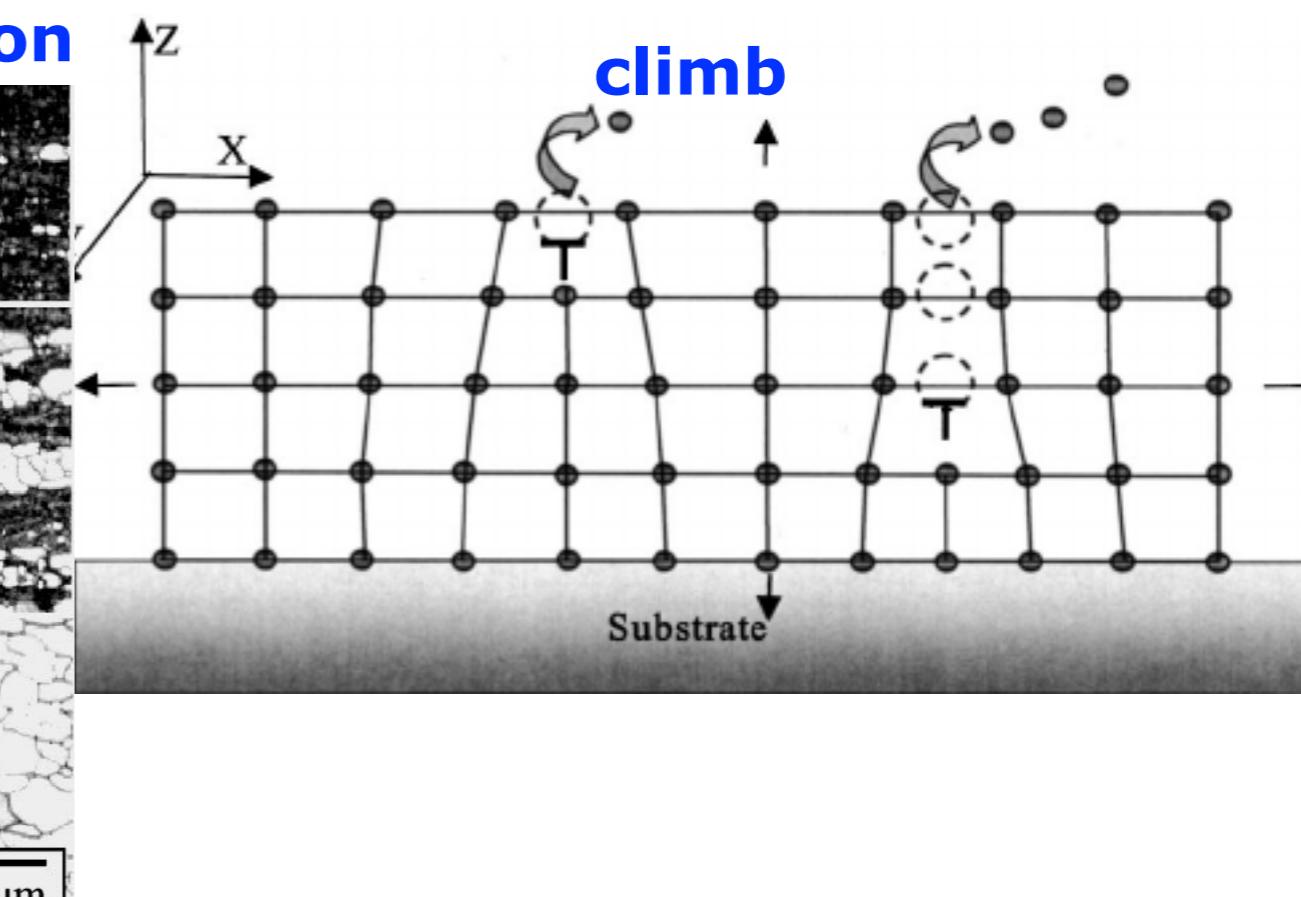
precipitate formation and growth



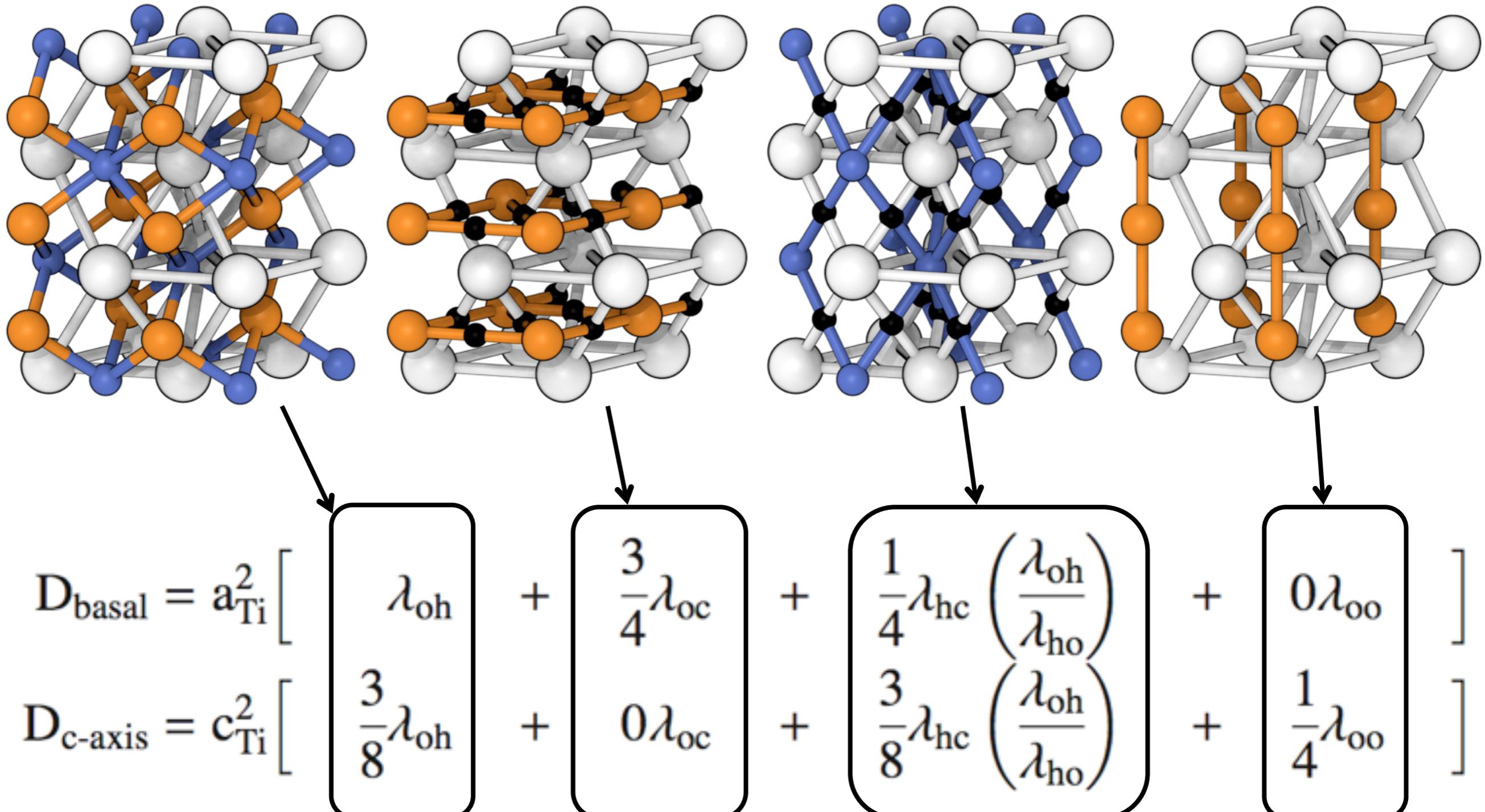
recrystallization



climb

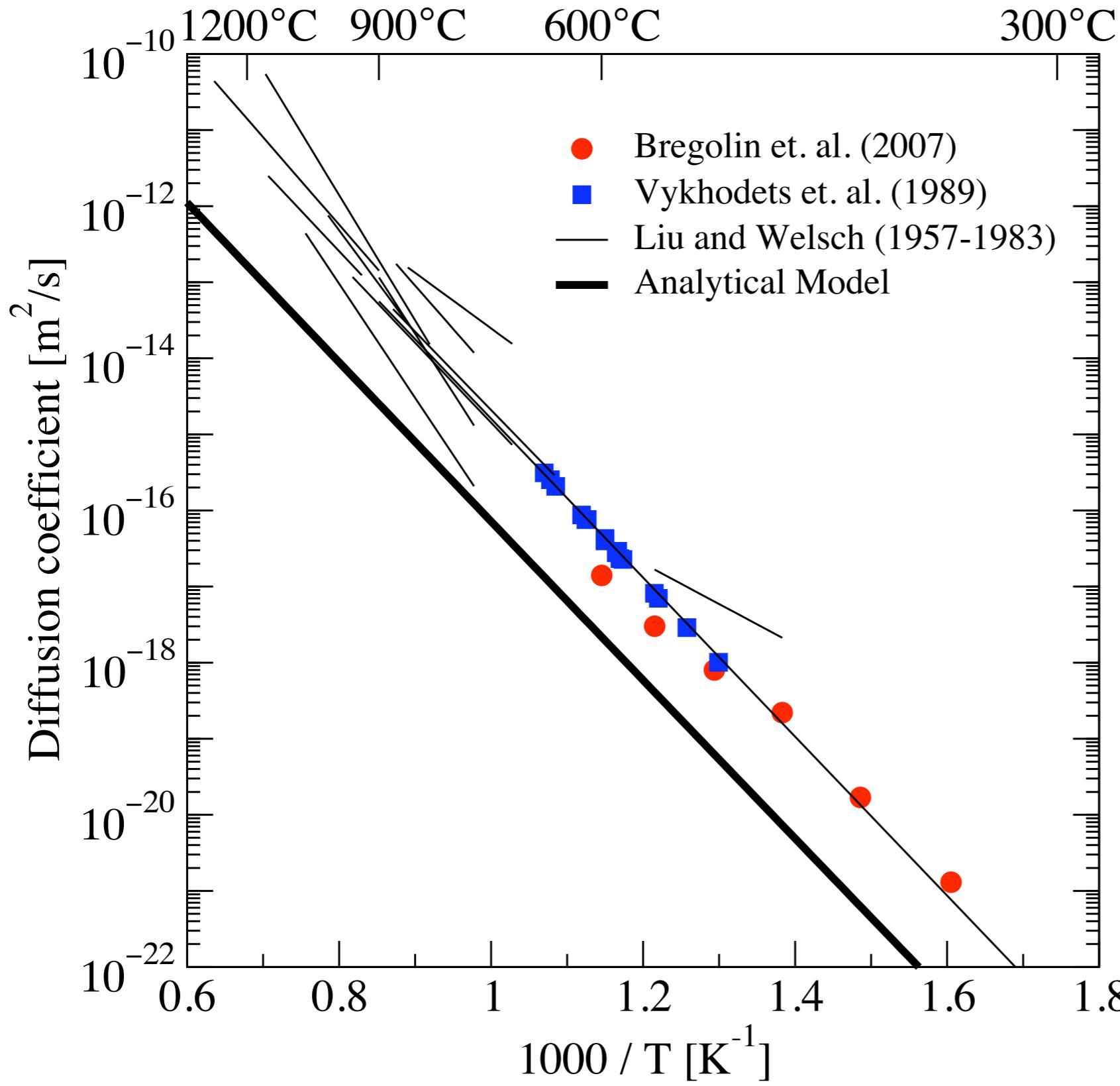


Oxygen diffusion constant in HCP Ti



Oxygen diffusion separates into the sum of the single networks.

Oxygen diffusion constant in HCP Ti



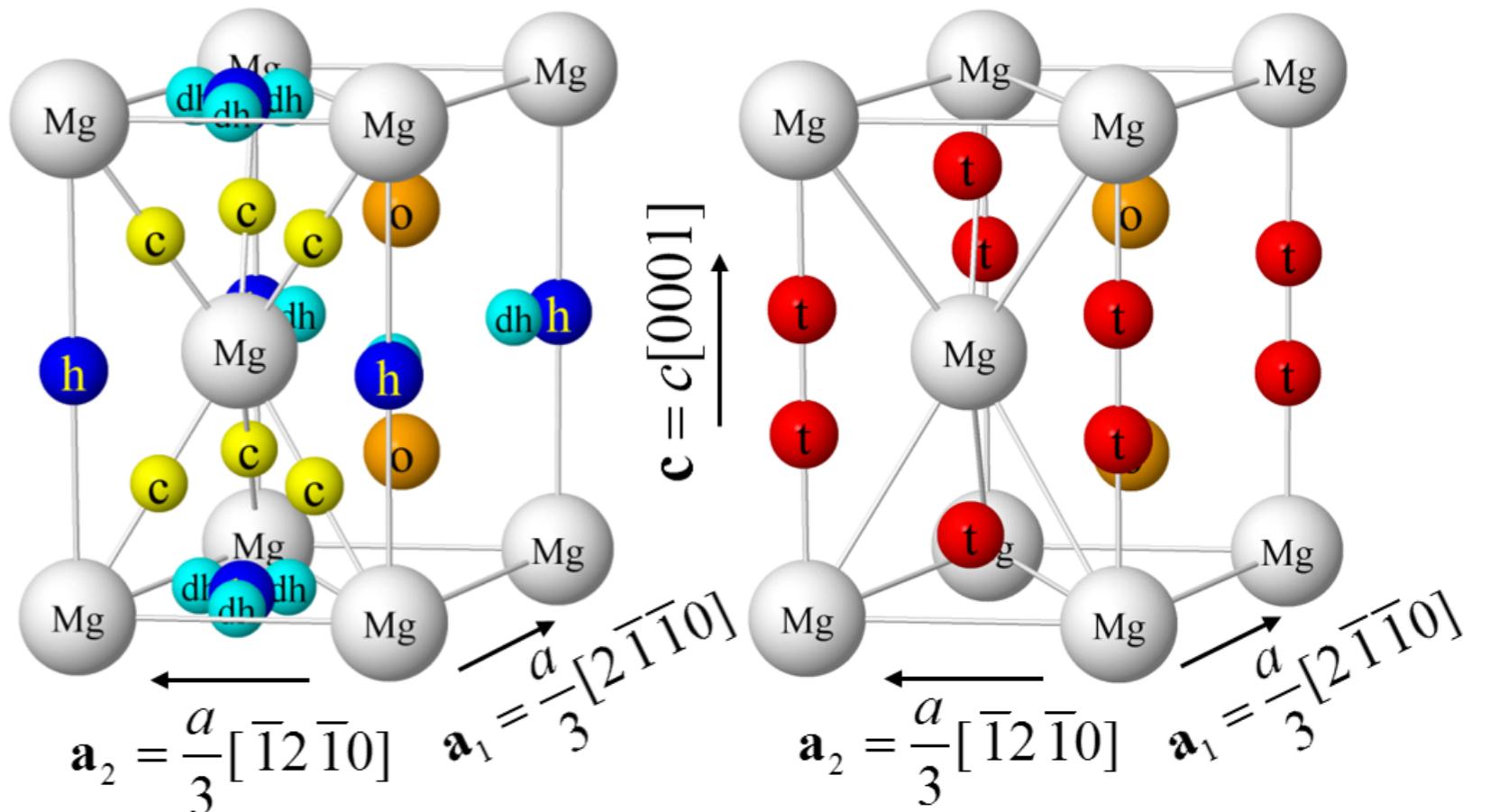
Analytical results are a factor of 10 lower than experimental observations.

Analytical barriers match well to experiments.

$$D_0 = 2.18 \times 10^{-6} \text{ m}^2\text{s}^{-1}$$
$$E_a = 2.08 \text{ eV}$$

Interstitial sites in HCP Mg

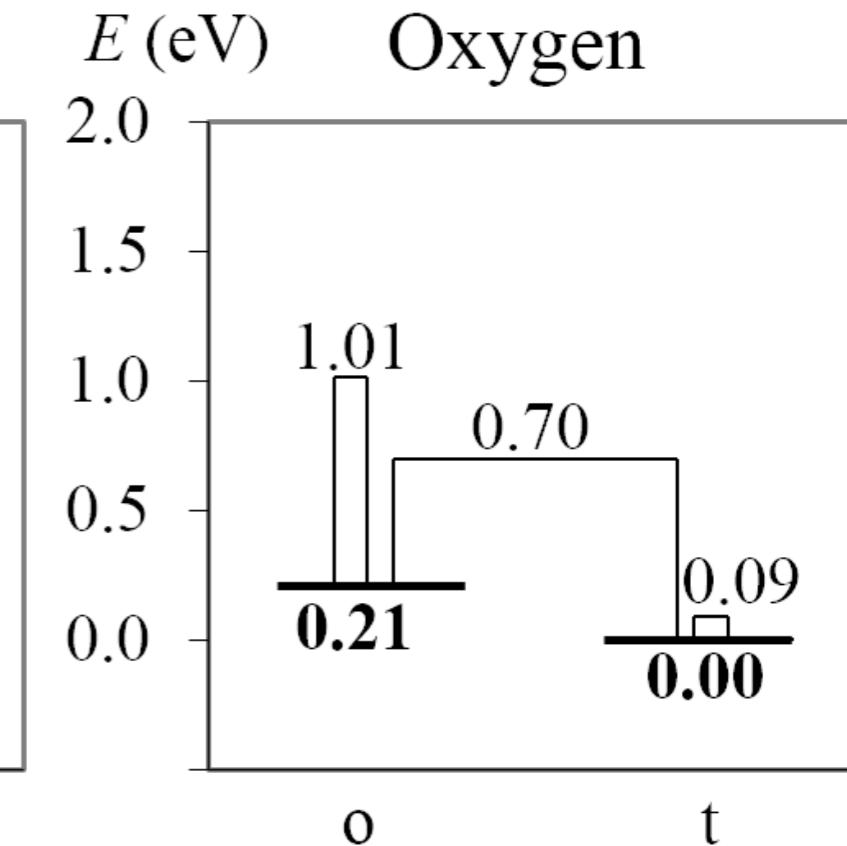
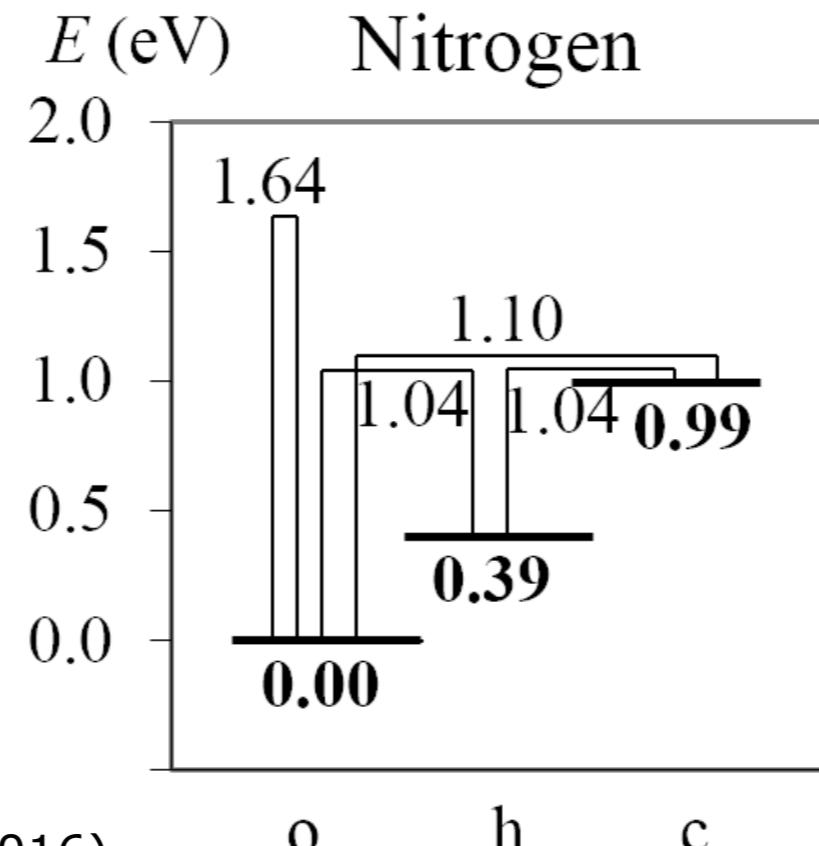
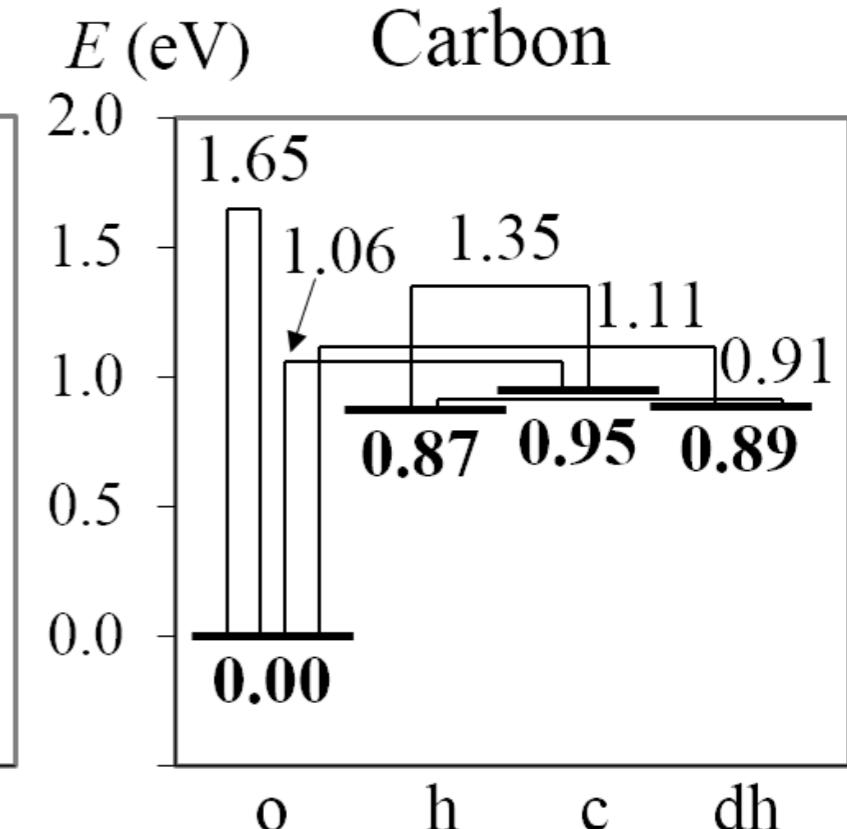
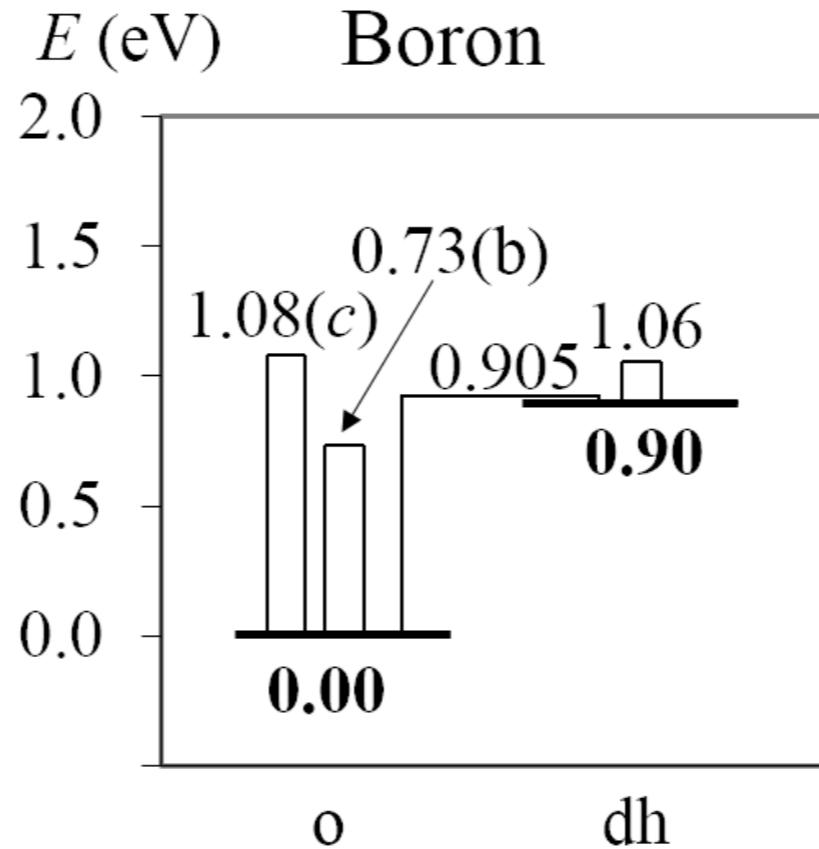
Tetrahedral (t)
 Octahedral (o)
 Hexahedral (h)
 Crowdion (c)
 Distorted Hexahedral (dh)



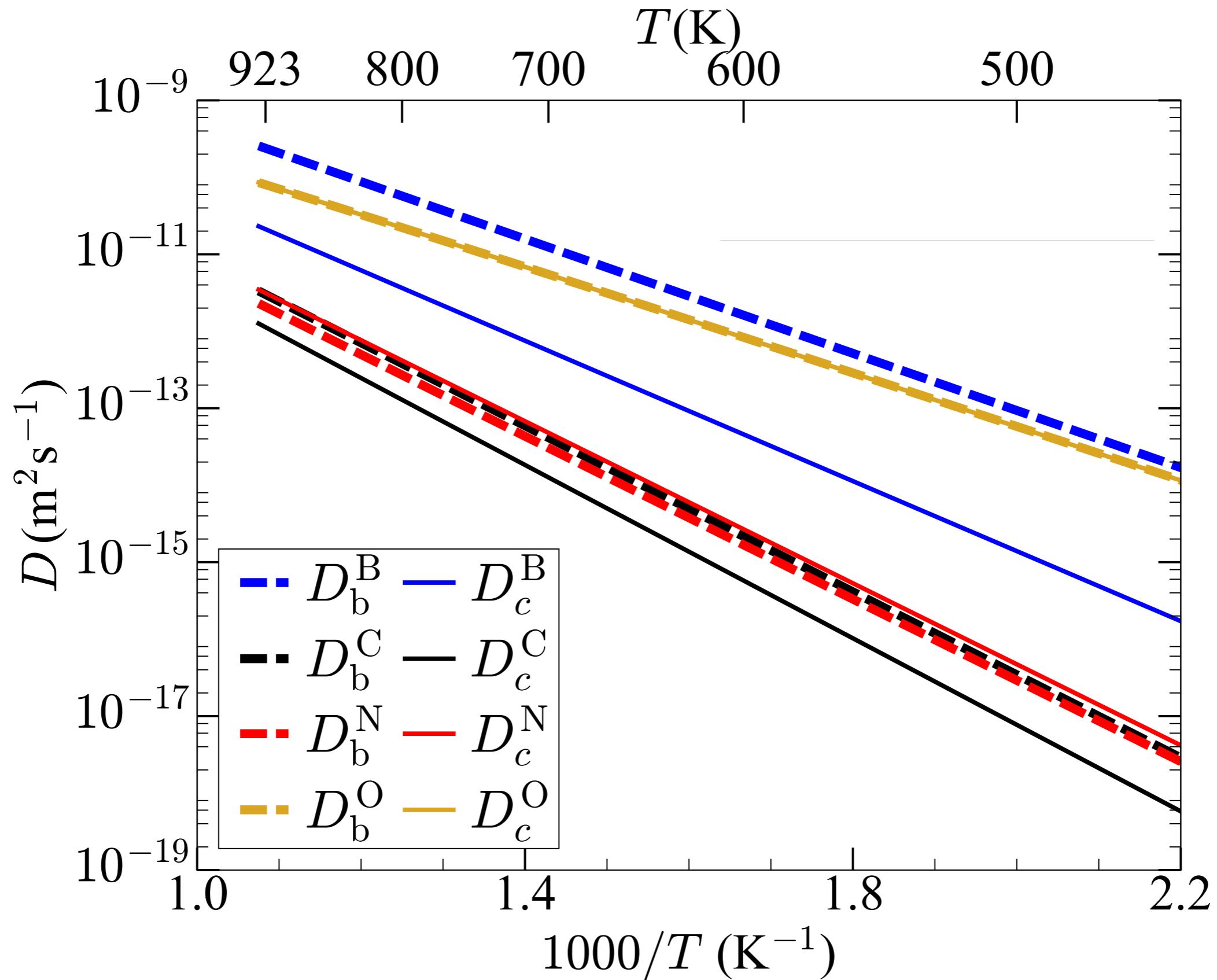
Solute	Ground state	Metastable (energy in eV over ground state) $3s^2$	Metastable (energy in eV over ground state) $3s^22p^6$
Boron	Octahedral	dh (0.90)	dh (0.89)
Carbon	Octahedral	h (0.87), dh (0.89), c (0.94)	h (0.87), dh (0.88), c (0.94)
Nitrogen	Octahedral	h (0.39), c (0.99)	h (0.39), c (0.99)
Oxygen	Tetrahedral	o (0.21)	o (0.19)

Migration barriers in HCP Mg

- Rate of migration $\sim e^{-E_b/kBT}$
- Migration barrier from CI-NEB with one intermediate image



Diffusivity in HCP Mg

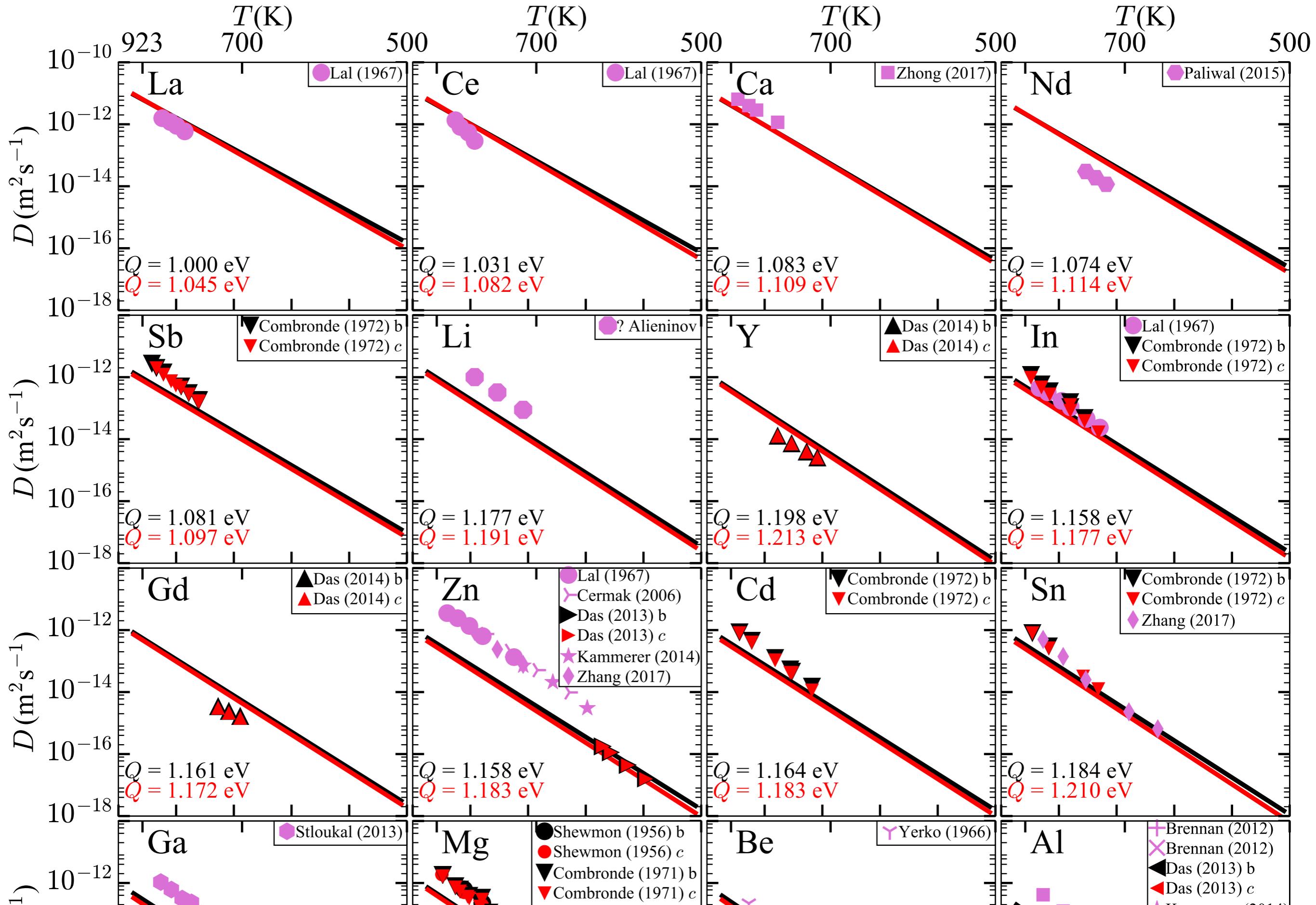


Vacancy mediated diffusion in Mg

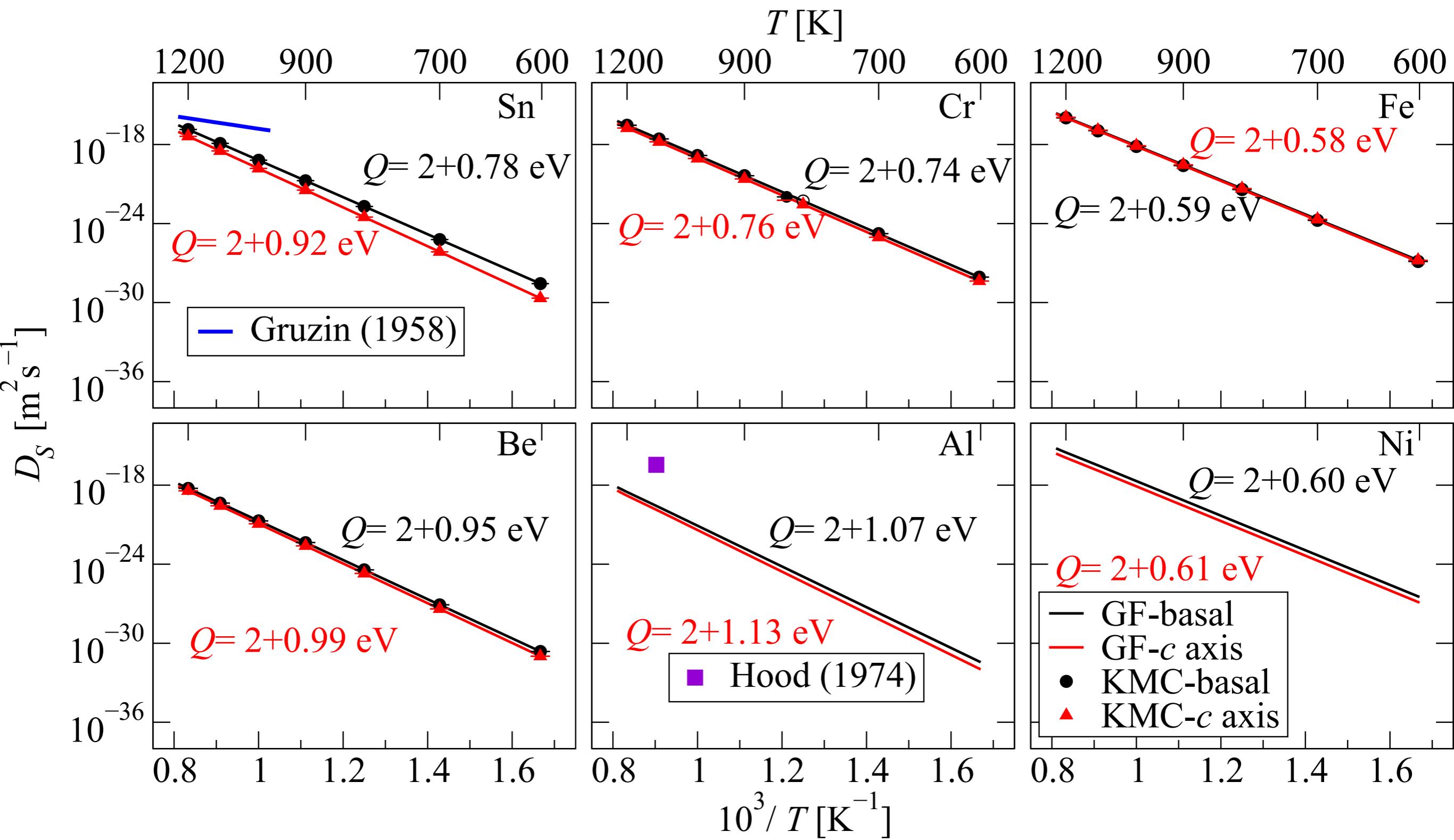
- Differences of ~0.1 eV in activation energies for rare-earth solutes
- Significant differences in crossover temperatures

Solute	8-freq. (Q)	GF (Q)	Exp. (Q)	GF (T_{cross})	8-f (T_{cross})
Nd	1.18 1.20	1.08 1.13	1.16 (Paliwal2015)	529 422	< 0 K
Ce	1.14 1.15	1.03 1.09	1.82 (Lal1966)	648 589	252 287
La	1.10 1.11	1.00 1.04	1.06 (Lal1966)	746 714	415 452
Gd	1.24 1.26	1.16 1.17	0.82 0.85 (Das2014)	341 218	> 923 K
Y	1.25 1.27	1.20 1.21	1.01 1.02 (Das2014)	271 190	> 923 K
Ca	1.12 1.14	1.08 1.11	1.07 (Zhong2017)	538 501	309 343

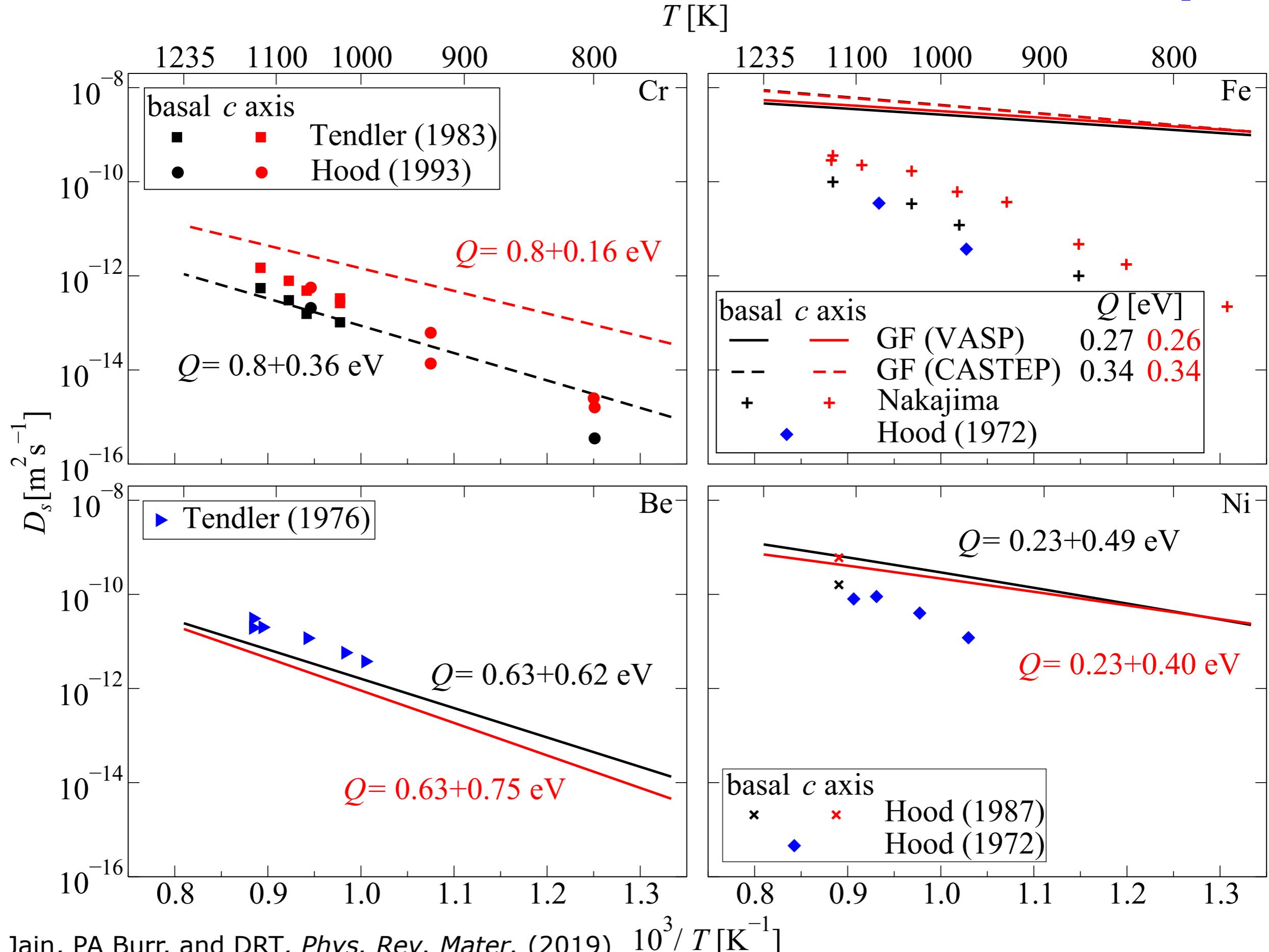
Vacancy mediated diffusion in Mg



Vacancy mediated diffusion in Zr: solute diffusivity



Interstitial diffusion in Zr: solute diffusivity

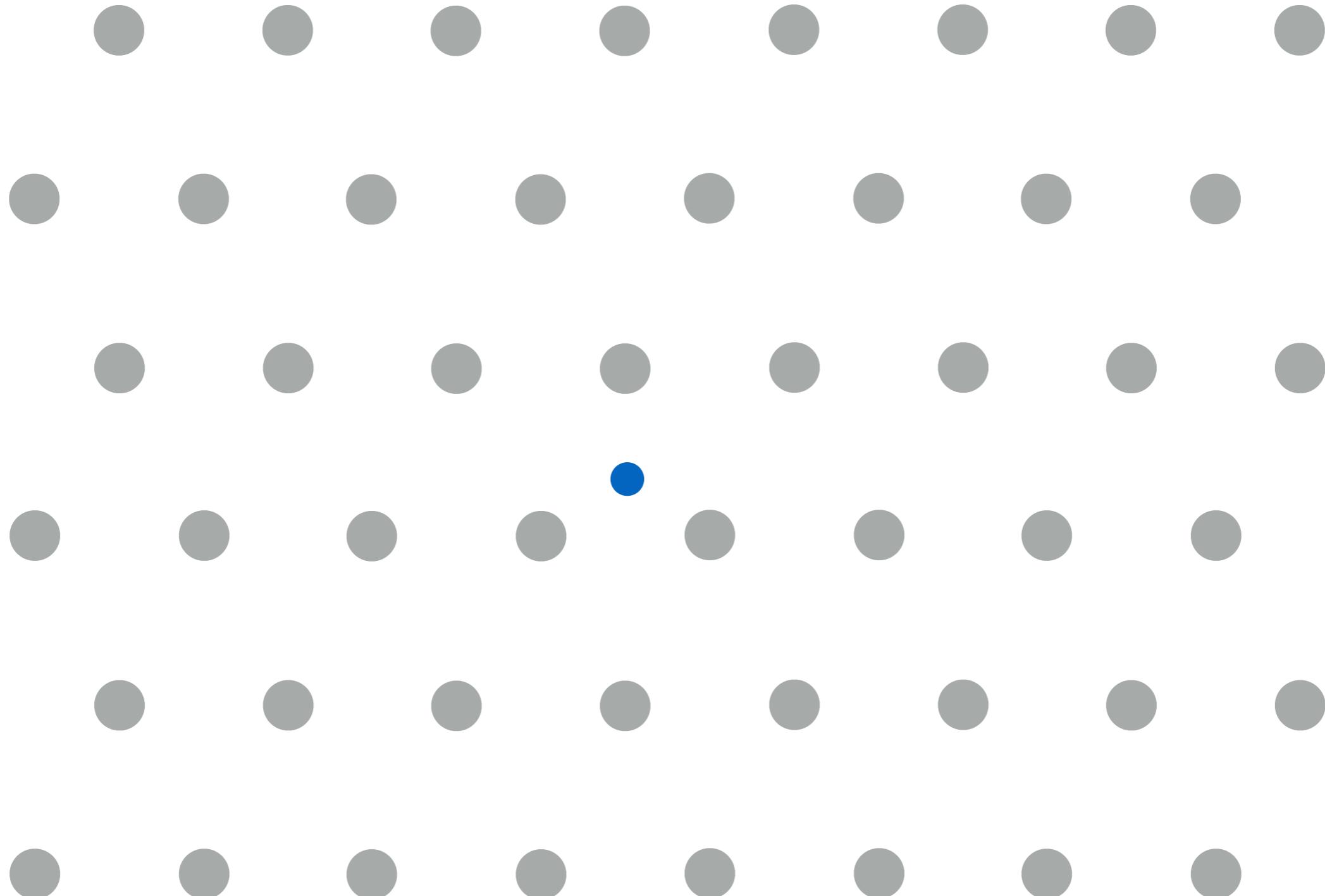


What's the disagreement all about?

- Are there experimental issues?
 - Adequate thermal control?
 - Are point defects at equilibrium?
 - Is the species transport compositionally insensitive?
- Are there computational issues?
 - Do we have the proper diffusion mechanism?
 - Is DFT incorrect?
- Are our expectations wrong?
 - What sort of agreement should we be expecting?

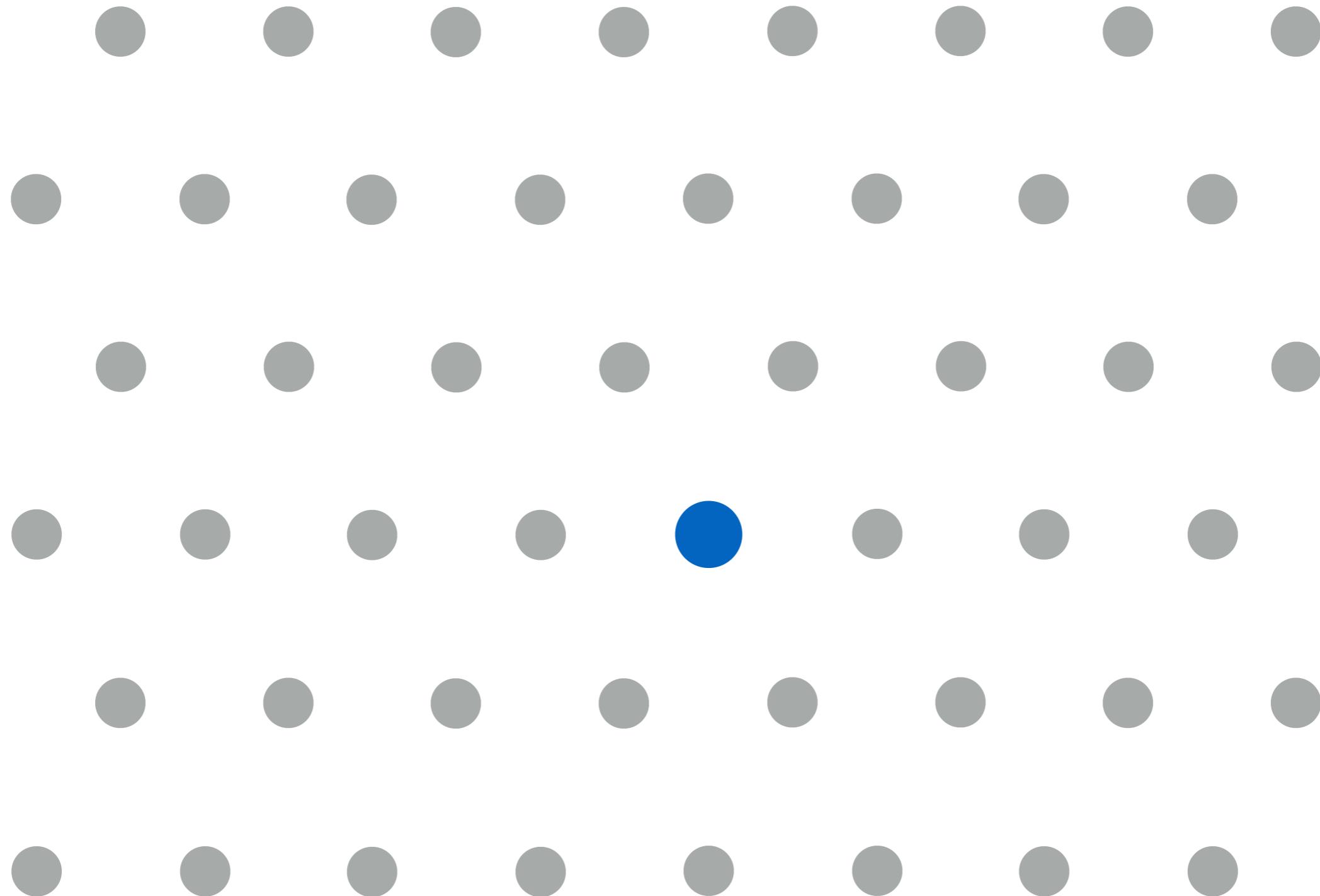
Can we (1) quantify DFT uncertainty and
(2) propagate that forward to quantify
transport modeling uncertainty?

Atomistic mechanism for diffusivity: interstitial solute



$$\lim_{t \rightarrow \infty} \left\langle \frac{(x_i(t) - x_i(0))(x_j(t) - x_j(0))}{2t} \right\rangle = D_{ij}$$

Atomistic mechanism for diffusivity: substitutional solute



$$\lim_{t \rightarrow \infty} \left\langle \frac{(x_i^A(t) - x_i^A(0))(x_j^B(t) - x_j^B(0))}{2t \Omega k_B T} \right\rangle = L_{ij}^{AB}$$

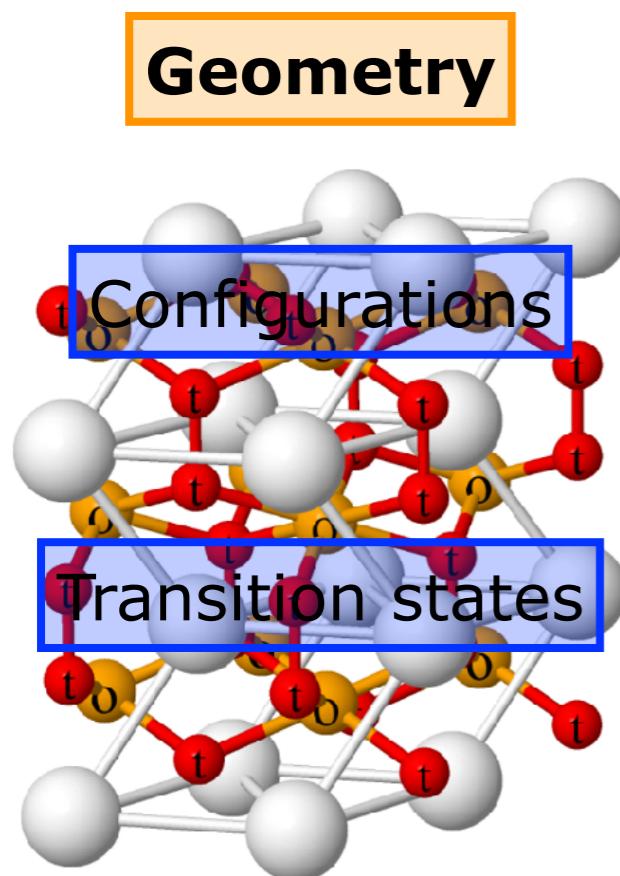
Replacing trajectories with probabilities: Master equation

$$\frac{dP(\underline{\chi}, t)}{dt} = \sum_{\underline{\chi}'} P(\underline{\chi}', t) W(\underline{\chi}' \rightarrow \underline{\chi}) - P(\underline{\chi}, t) W(\underline{\chi} \rightarrow \underline{\chi}')$$
$$= \sum_{\underline{\chi}'} P(\underline{\chi}', t) W_{\underline{\chi}' \underline{\chi}}$$

configuration $\underline{\chi}$, probability $P(\underline{\chi}, t)$

- **Master equation:**

- Well-defined states that thermalize before next transition
- Markovian process (no memory)
- Equilibrium: detailed balance (no fluxes)
- Steady state: balance (constant fluxes, no time evolution)



Computational evaluation

DFT: supercell
relaxation + NEB

Data output

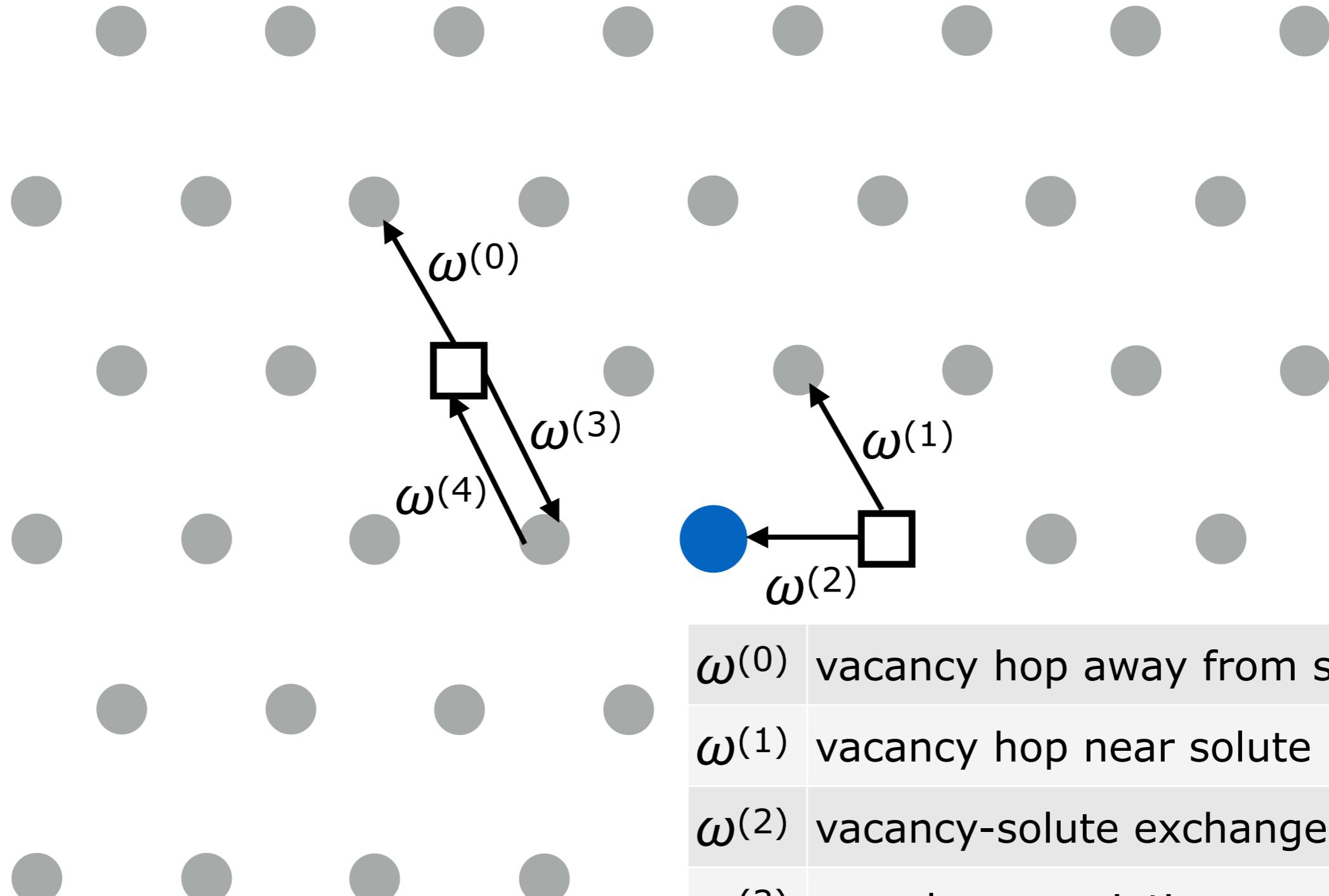
Configuration
energies + entropies

Transition
energies + entropies

Software:
Interstitials:
Vacancy-mediated:

dallastrinkle.github.io/Onsager
Trinkle, Phil. Mag. **96** (2016)
Trinkle, Phil. Mag. **97** (2017)

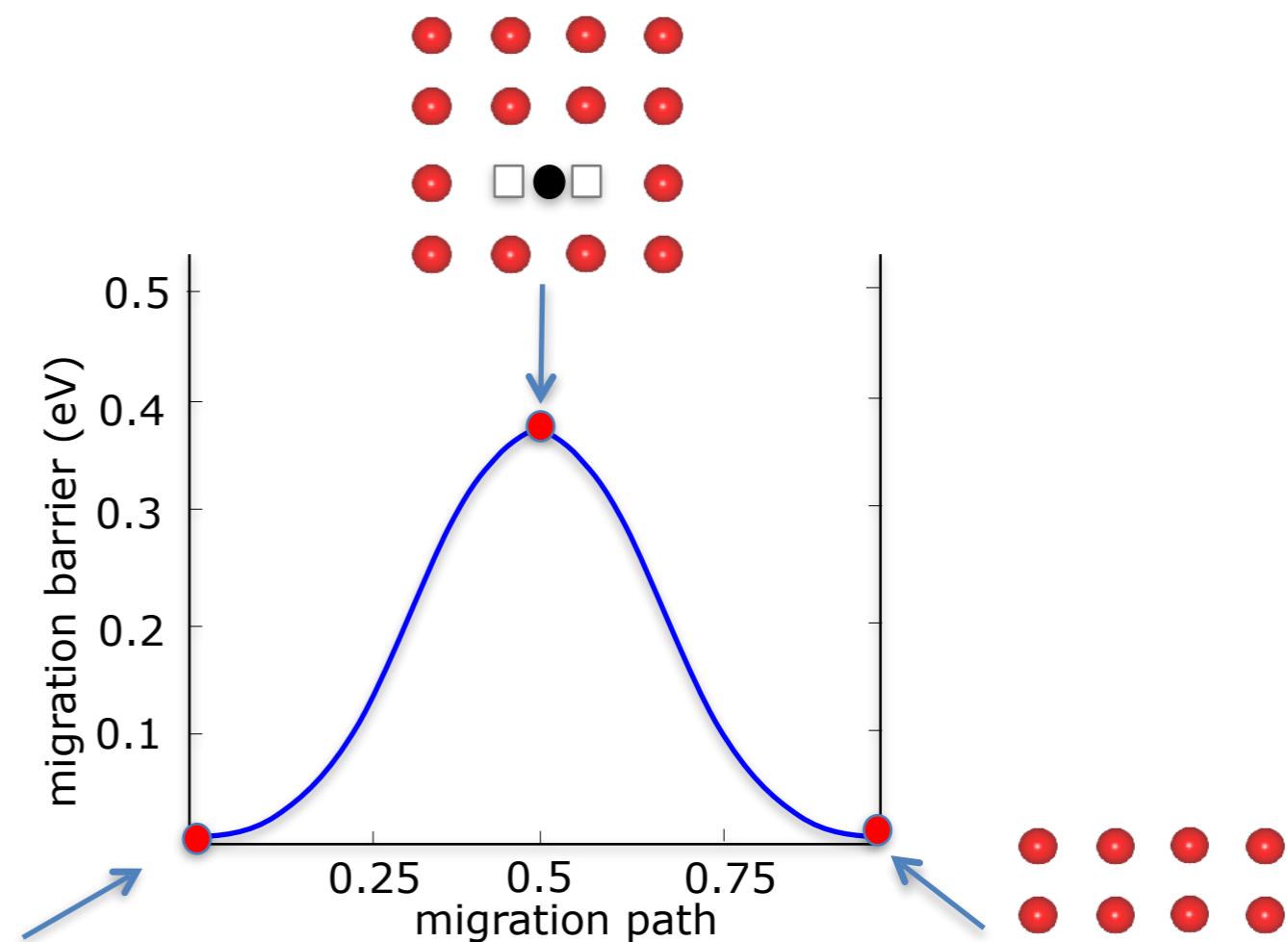
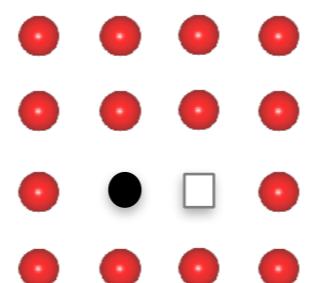
Atomistic mechanism for diffusivity: “five frequency model”



$\omega^{(0)}$	vacancy hop away from solute
$\omega^{(1)}$	vacancy hop near solute
$\omega^{(2)}$	vacancy-solute exchange
$\omega^{(3)}$	complex association
$\omega^{(4)}$	complex dissociation

Jump frequencies: harmonic transition state theory

- First-principles (DFT) calculation of:
 - transition state using nudged-elastic band
 - phonon frequencies from finite difference force constants
 - electronic contribution from density of states (ignorable)



Computing diffusivity: random walk

$$\mathbf{x}(t) - \mathbf{x}(0) = \sum_n \delta \mathbf{x}_n \quad \text{Atomic jumps}$$

$$(\mathbf{x}(t) - \mathbf{x}(0)) \otimes (\mathbf{x}(t) - \mathbf{x}(0)) = \sum_{nn'} \delta \mathbf{x}_n \otimes \delta \mathbf{x}_{n'}$$

$$= \sum_n \left\{ \delta \mathbf{x}_n \otimes \delta \mathbf{x}_n + 2 \sum_{m=1}^{\infty} \delta \mathbf{x}_n \otimes \delta \mathbf{x}_{n+m} \right\}$$

“bare” mean-squared displacement

correlation

- Stochastic methods:
 - Molecular dynamics (including accelerated approaches)
 - Kinetic Monte Carlo¹ (including on-the-fly)
- *Multiple issues:*
 - **Stochastic:** increasing number of trajectories to reduce variance
 - **Correlation:**
 - increasingly long trajectories to reduce error
 - increasingly size cells to reduce error
 - poor convergence for systems with large rate anisotropy
 - Evaluating derivatives with respect to strain converges poorly²

¹G. E. Murch, *Diffusion in Crystalline Solids*, (1984) Chap. 7

²Li and Trinkle, Phys. Rev. E **96** (2016)

Computing diffusivity: Direct solution of master equation

$$\frac{dP(\underline{\chi}, t)}{dt} = \sum_{\underline{\chi}'} P(\underline{\chi}', t) W(\underline{\chi}' \rightarrow \underline{\chi}) - P(\underline{\chi}, t) W(\underline{\chi} \rightarrow \underline{\chi}')$$

$$= \sum_{\substack{\underline{\chi}' \\ \underline{\chi}}} P(\underline{\chi}', t) W_{\underline{\chi}' \underline{\chi}}$$

configuration $\underline{\chi}$, probability $P(\underline{\chi}, t)$

$$P_0(\underline{\chi}) W(\underline{\chi} \rightarrow \underline{\chi}') = P_0(\underline{\chi}') W(\underline{\chi}' \rightarrow \underline{\chi}) \quad \text{equilibrium (no flux)}$$

$$\sum_{\substack{\underline{\chi}' \\ \underline{\chi}}} P_{ss}(\underline{\chi}) W(\underline{\chi} \rightarrow \underline{\chi}') = \sum_{\substack{\underline{\chi}' \\ \underline{\chi}}} P_{ss}(\underline{\chi}') W(\underline{\chi}' \rightarrow \underline{\chi}) \quad \text{steady state (constant flux)}$$

$$\mathbf{J}^\alpha = \frac{1}{2\Omega} \sum_{\underline{\chi}\underline{\chi}'} \left\{ P_{ss}(\underline{\chi}) W_{\underline{\chi}\underline{\chi}'} - P_{ss}(\underline{\chi}') W_{\underline{\chi}'\underline{\chi}} \right\} \delta \mathbf{x}^\alpha(\underline{\chi} \rightarrow \underline{\chi}') = - \sum_{\beta} \underline{\mathbf{L}}^{\alpha\beta} \nabla \mu_\beta$$

$$\mathbf{b}^\alpha(\underline{\chi}) := \sum_{\substack{\underline{\chi}' \\ \underline{\chi}}} W_{\underline{\chi}\underline{\chi}'} \delta \mathbf{x}^\alpha(\underline{\chi} \rightarrow \underline{\chi}') \quad g_{\underline{\chi}\underline{\chi}'} := W_{\underline{\chi}\underline{\chi}'}^+ \quad (\text{pseudoinverse})$$

$$\underline{\mathbf{L}}^{\alpha\beta} = \frac{1}{k_B T \Omega} \sum_{\underline{\chi}\underline{\chi}'} \frac{1}{2} P_0(\underline{\chi}) W_{\underline{\chi}\underline{\chi}'} \delta \mathbf{x}^\alpha(\underline{\chi} \rightarrow \underline{\chi}') \otimes \delta \mathbf{x}^\beta(\underline{\chi} \rightarrow \underline{\chi}')$$

"bare" mean-squared displacement

$$+ \frac{1}{k_B T \Omega} \sum_{\underline{\chi}\underline{\chi}'} P_0(\underline{\chi}) \mathbf{b}^\alpha(\underline{\chi}) g_{\underline{\chi}\underline{\chi}'} \mathbf{b}^\beta(\underline{\chi}')$$

correlation

Interstitials:

Trinkle, Phil. Mag. **96** (2016)

Vacancy-mediated: Trinkle, Phil. Mag. **97** (2017)

Quantifying uncertainty in DFT

- **Density functional theory is not exact**
 - Controlled approximations: basis size, supercell size, k -point integration
 - Uncontrolled approximations: exchange-correlation potential
- **No more than one exchange-correlation treatment is correct**
 - Local-density approximation (LDA): Ceperley-Alder
 - Generalized gradient approximation (GGA): PBE
 - Meta-GGA: SCAN
 - Hybrid functionals
 - ... and many, many more
- **How can we quantifying uncertainty in DFT?**
 - Bayesian approach: sample over different exchange-correlation treatments, weighted by likelihood (e.g., *PRL* **95**, 216401 (2005))
 - Empirical estimate from variability in results

Example: vacancy-mediated diffusion in magnesium

Uncertainty in DFT input data for Mg

1. Use three distinct exchange correlation treatments:

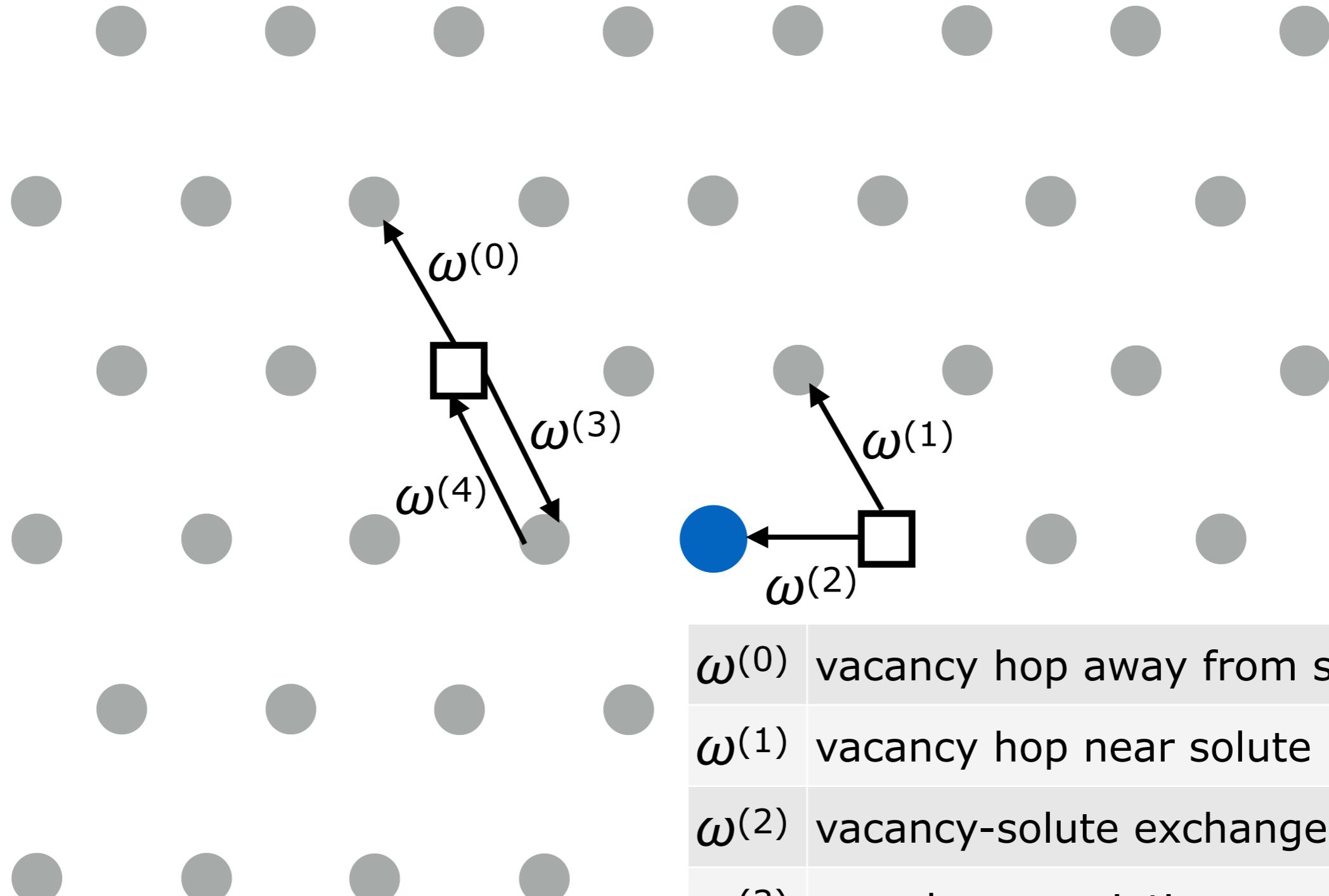
- Local-density approximation (LDA): Ceperley-Alder
- Generalized gradient approximation (GGA): PBE
- Meta-GGA: SCAN

2. Use PAW-PBE relaxed positions as initial guess

- Scale supercell dimensions to LDA or SCAN lattice constants
- Compute energy and forces
- Approximate relaxation energy with PBE lattice Green function:
$$\Delta E = -\mathbf{f} \cdot (\mathbf{D}^{-1}) \cdot \mathbf{f} / 2$$
- Gives correct energies with < 5 meV error

Energy [eV]	PBE	LDA	SCAN
Vacancy formation energy	0.814	0.852	0.948
Pyramidal activation energy	0.417	0.429	0.489
Basal activation energy	0.397	0.409	0.481

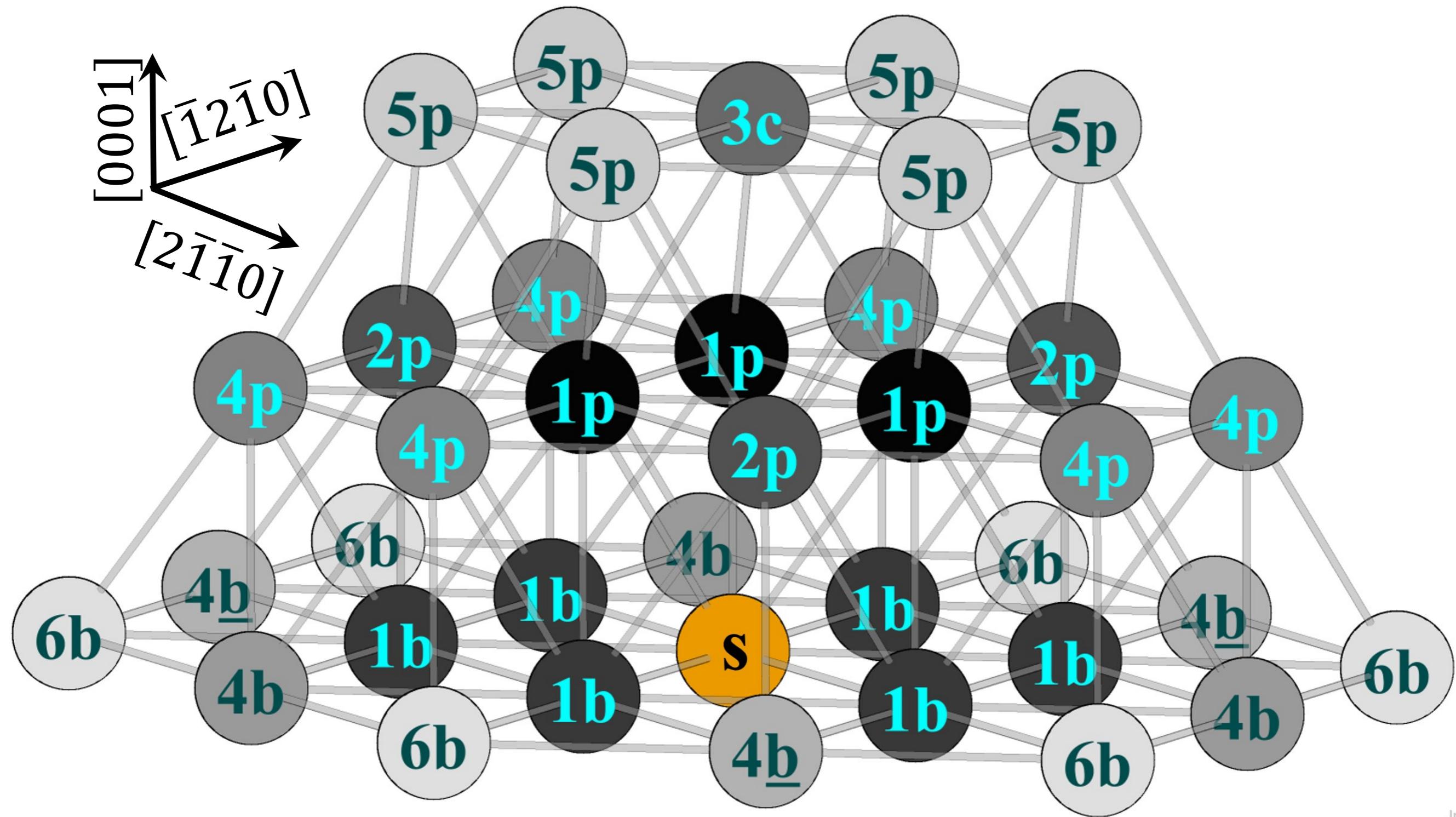
Atomistic mechanism for diffusivity: “five frequency model”



$\omega^{(0)}$	vacancy hop away from solute
$\omega^{(1)}$	vacancy hop near solute
$\omega^{(2)}$	vacancy-solute exchange
$\omega^{(3)}$	complex association
$\omega^{(4)}$	complex dissociation

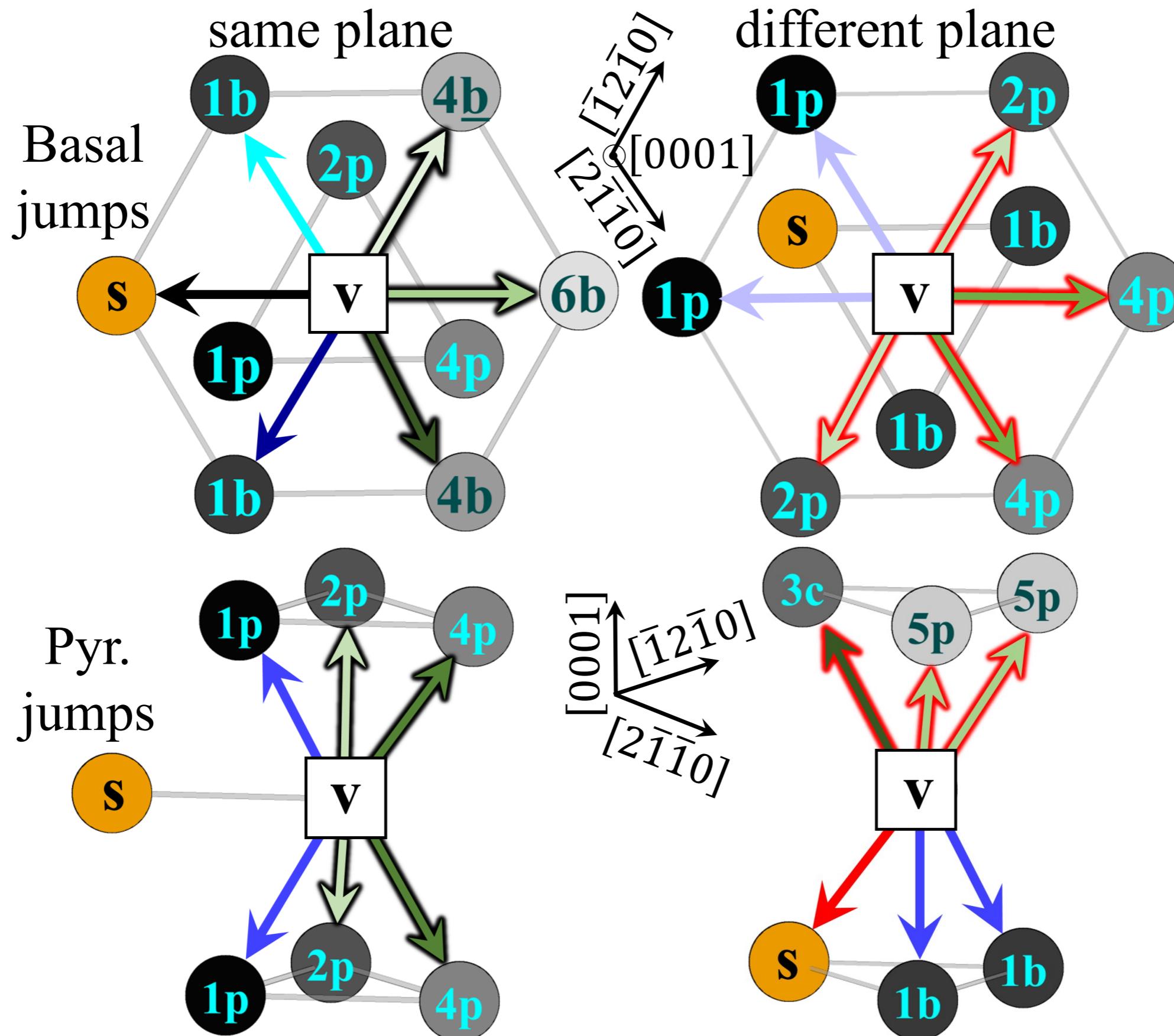
Vacancy-solute complexes in HCP

- 2 different first-neighbor complexes: 1b 1p
- 7 different “next jump” complexes: 2p 3c 4b 4b 4p 5p 6b



Vacancy jumps near a solute in HCP

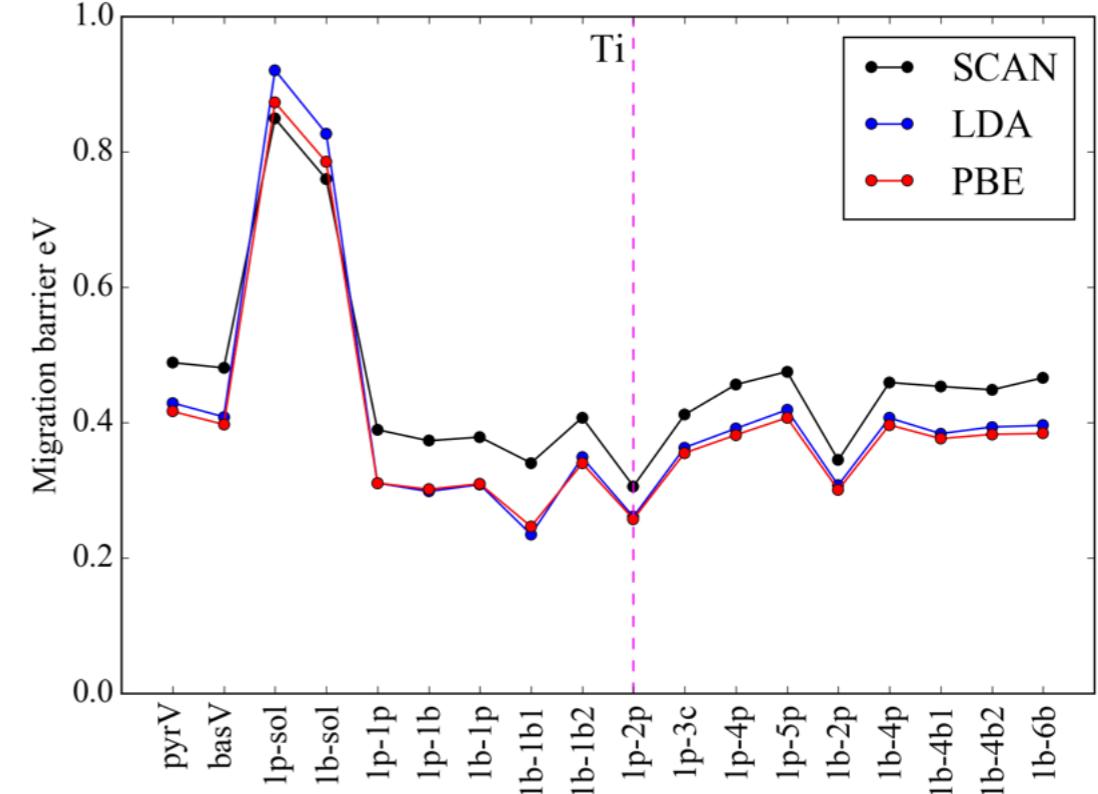
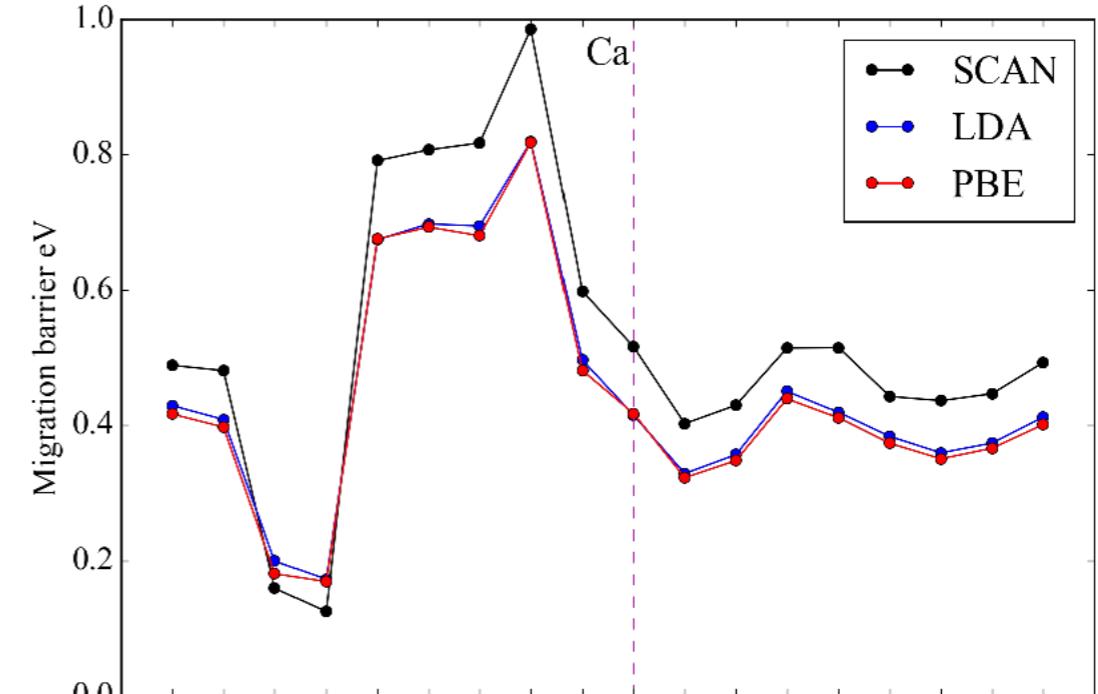
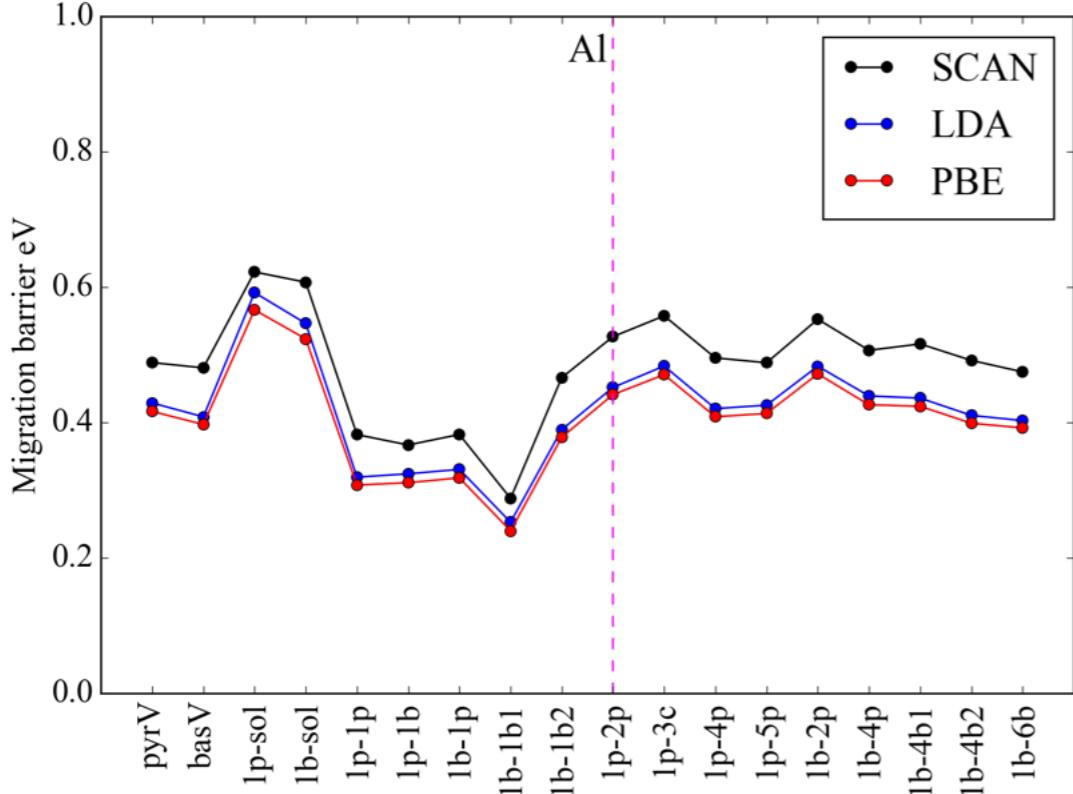
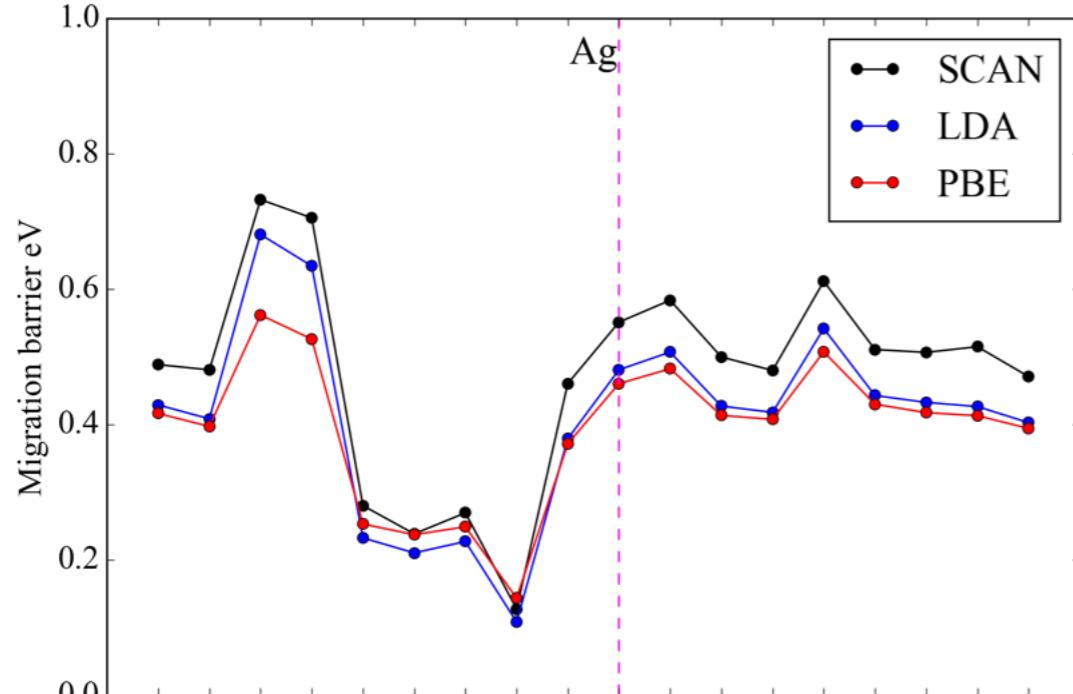
Solute and vacancy (1b) Solute and vacancy (1p)



Uncertainty in DFT input data for Mg

1. Use three distinct exchange correlation treatments:

- Local-density approximation (LDA): Ceperley-Alder
- Generalized gradient approximation (GGA): PBE
- Meta-GGA: SCAN



Uncertainty in DFT input data for Mg

1. Use three distinct exchange correlation treatments:

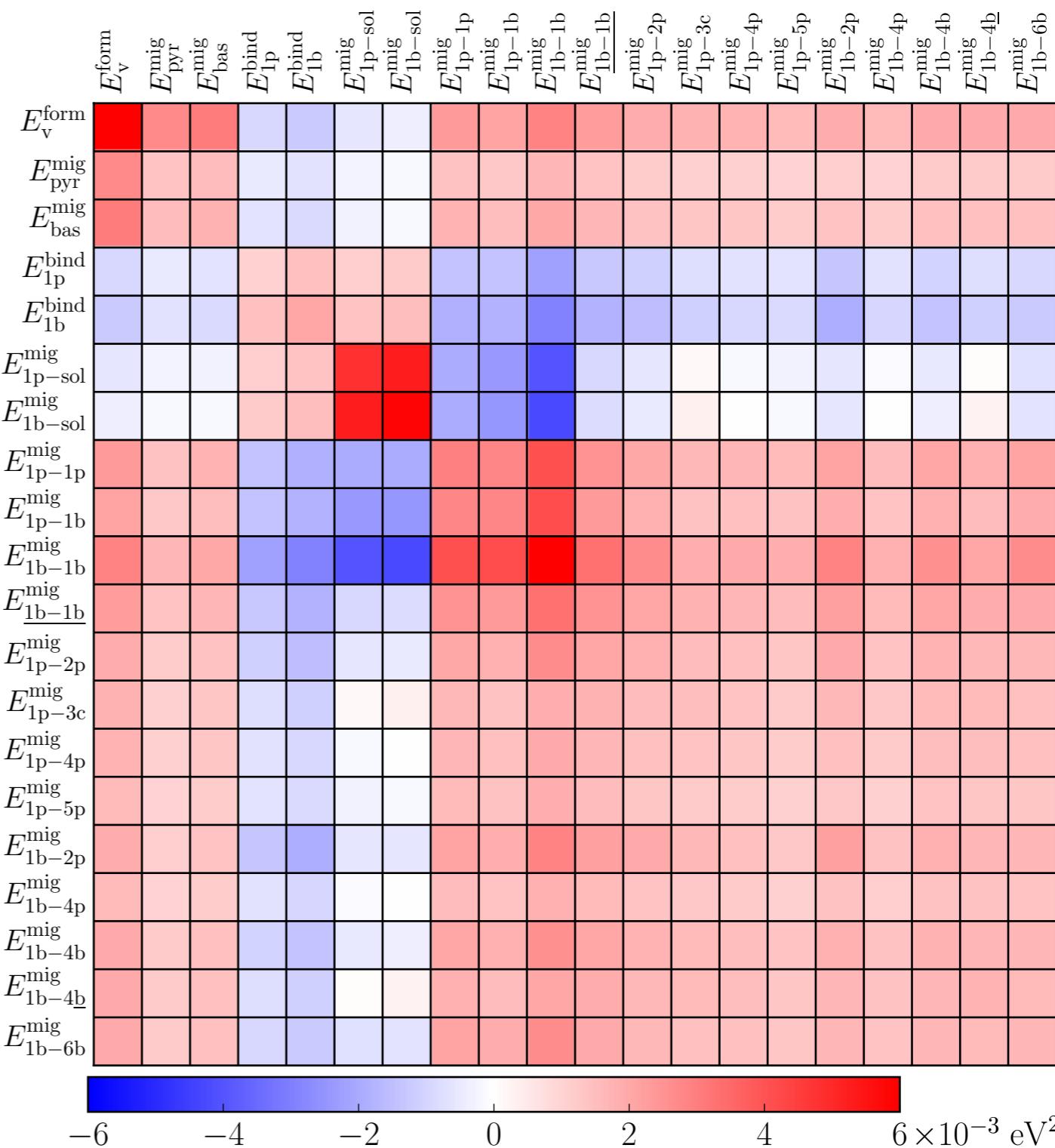
- Local-density approximation (LDA): Ceperley-Alder
- Generalized gradient approximation (GGA): PBE
- Meta-GGA: SCAN

2. Differences due to XC similar for different chemistries:

treat as random variation

Covariance matrix:

- Diagonal: variance around mean
- Off-diagonal: (anti)correlation between quantities across different chemistries
- Source of variability: solute chemistry and exchange-correlation treatment



Uncertainty in diffusivity

1. Take variability in DFT input parameters and *sample* possible DFT data

- Bayesian inference approach
- Assume multivariate normal distribution: empirical covariances (Σ) and mean values ($\bar{\theta}$)

$$P(\theta) = \det(2\pi\Sigma)^{-1/2} \exp\left[-\frac{1}{2}(\theta - \bar{\theta})\Sigma^{-1}(\theta - \bar{\theta})\right]$$

mean value of f : $\langle f(\theta; T) \rangle = \int_{\theta} d\theta P(\theta) f(\theta; T)$

probability distribution of f : $P^f(f_0; T) = \int_{\theta} d\theta P(\theta) \delta(f_0 - f(\theta; T))$

Uncertainty in diffusivity

1. Take variability in DFT input parameters and *sample* possible DFT data
 - Bayesian inference approach
 - Assume multivariate normal distribution: empirical covariances (Σ) and mean values ($\underline{\theta}$)
2. Distribution of predictions:
 - Diffusivities follow approximately log-normal distributions
 - Drag ratios ($L^{\text{SV}}/L^{\text{SS}}$) follow more complex distribution
3. Computational details:
 - Use Gaussian-Hermite quadrature for vacancy parameters for computational efficiency
 - Multivariate normal distribution samples for solute-vacancy parameters

$$\theta = \begin{pmatrix} \theta^v \\ \theta^s \end{pmatrix}, \quad \Sigma = \begin{pmatrix} \Sigma^{vv} & \Sigma^{vs} \\ \Sigma^{sv} & \Sigma^{ss} \end{pmatrix} \quad P(\theta) = P^v(\theta^v)P^s(\theta^s|\theta^v)$$

Uncertainty in diffusivity

3. Computational details:

- Use Gaussian-Hermite quadrature for vacancy parameters for computational efficiency
- Multivariate normal distribution samples for solute-vacancy parameters

$$\theta = \begin{pmatrix} \theta^v \\ \theta^s \end{pmatrix}, \quad \Sigma = \begin{pmatrix} \Sigma^{vv} & \Sigma^{vs} \\ \Sigma^{sv} & \Sigma^{ss} \end{pmatrix} \quad P(\theta) = P^v(\theta^v)P^s(\theta^s|\theta^v)$$

- Both $P^v(\theta^v)$ and $P^s(\theta^s|\theta^v)$ are multivariate normal distributions.
 - P^v has mean $\bar{\theta}^v$ and covariance Σ^{vv}
 - P^s mean depends on θ^v but covariance is independent:

$$\text{mean : } \bar{\theta}^s + \Sigma^{sv}(\Sigma^{vv})^{-1}(\theta^v - \bar{\theta}^v)$$

$$\text{covariance : } \Sigma^{ss} - \Sigma^{sv}(\Sigma^{vv})^{-1}\Sigma^{vs}$$

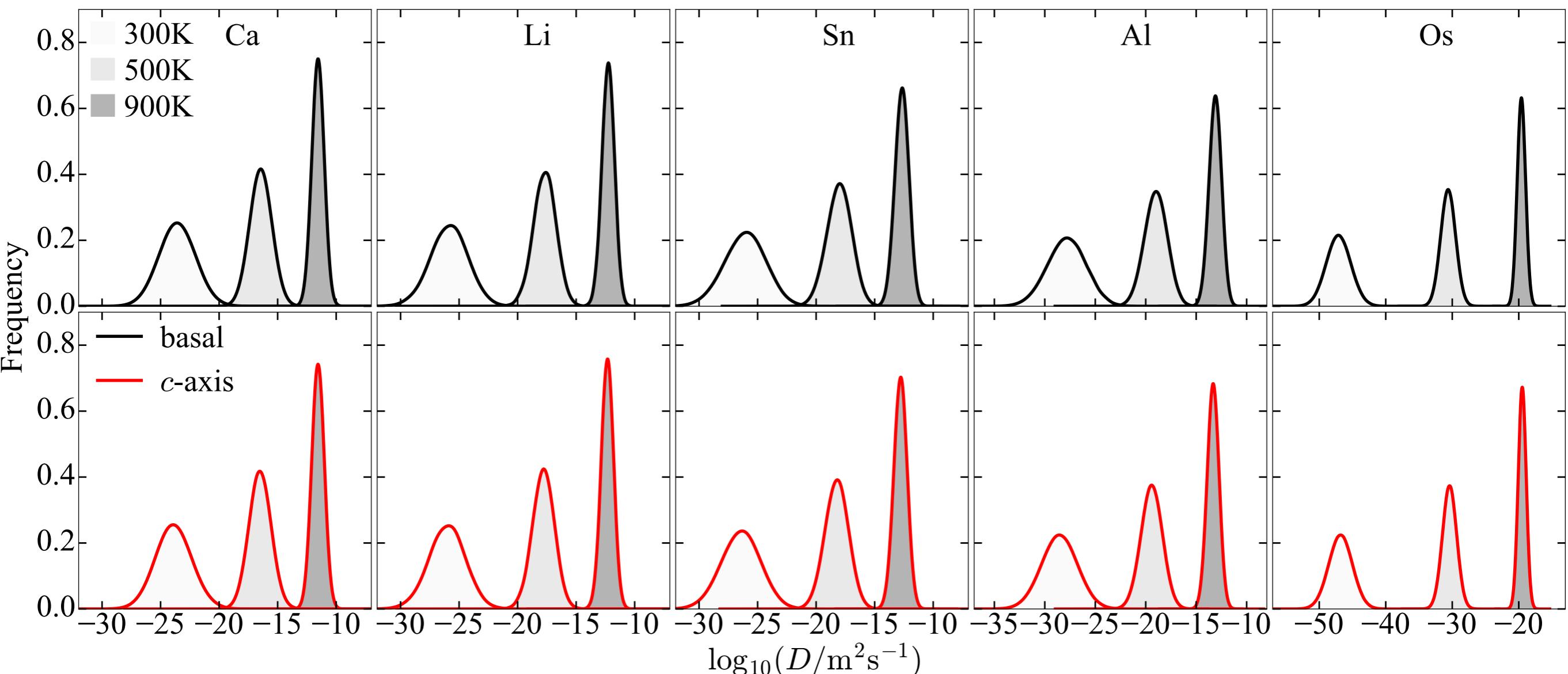
$$\langle f(\theta^v, \theta^s; T) \rangle = \int_{\theta^v} d\theta^v P^v(\theta^v) \left[\int_{\theta^s} d\theta^s P^s(\theta^s|\theta^v) f(\theta^v, \theta^s; T) \right]$$

$$\langle f(\theta^v, \theta^s; T) \rangle \approx \sum_{i=1}^{N_{GH}} \frac{w_i}{N} \sum_{j=1}^N f(\theta^{v,i}, \theta^{s,j}; T)$$

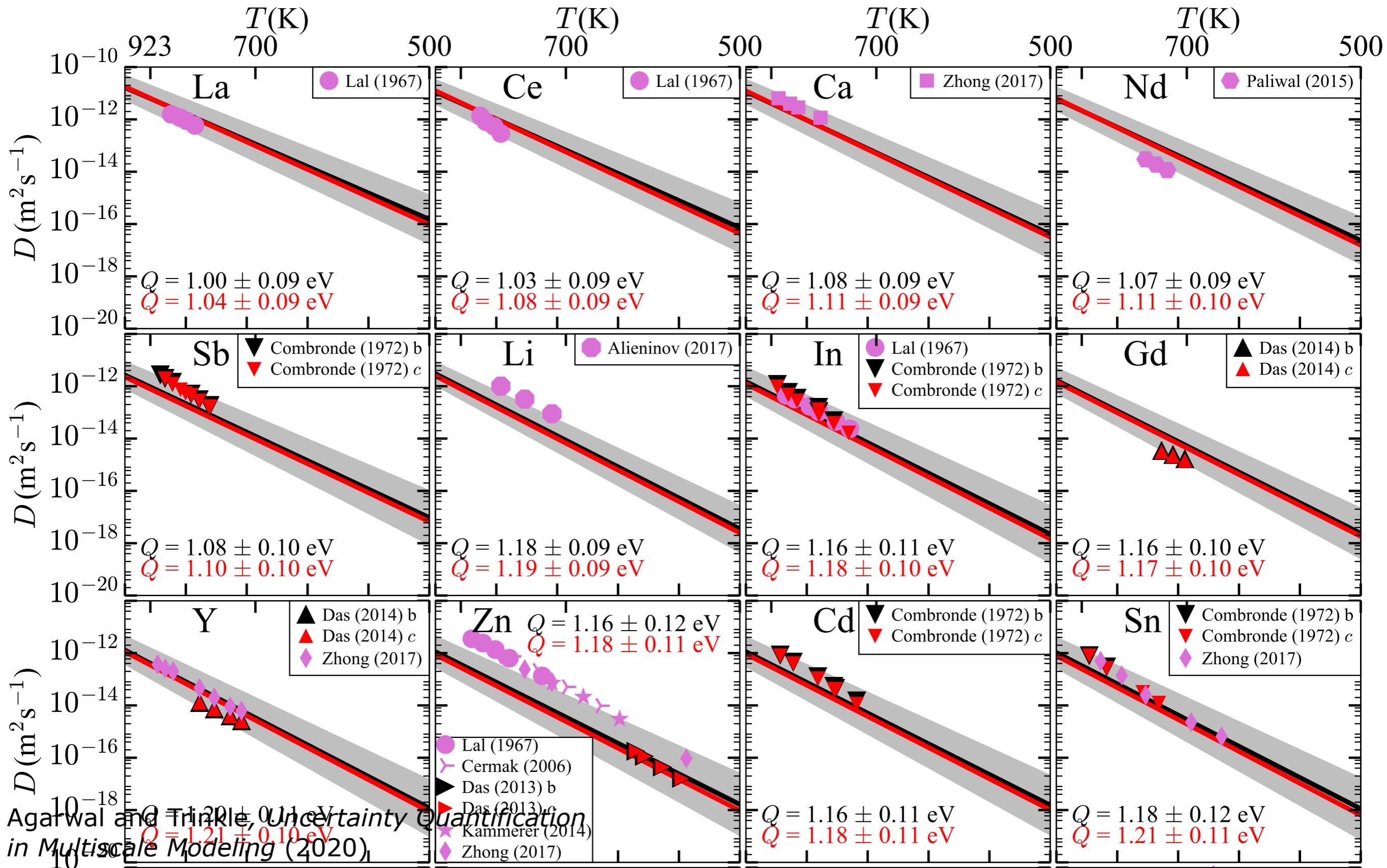
Uncertainty in diffusivity: histograms of X-Mg

1. Take variability in DFT input parameters and *sample* possible DFT data

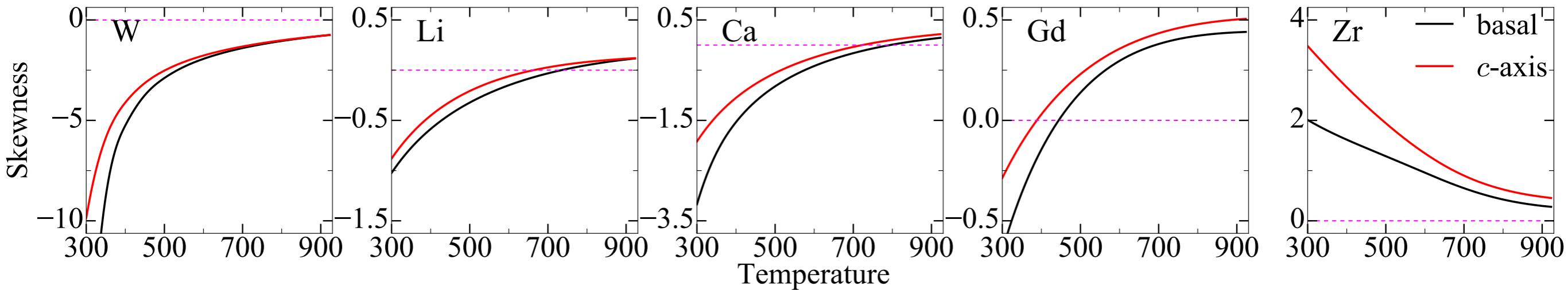
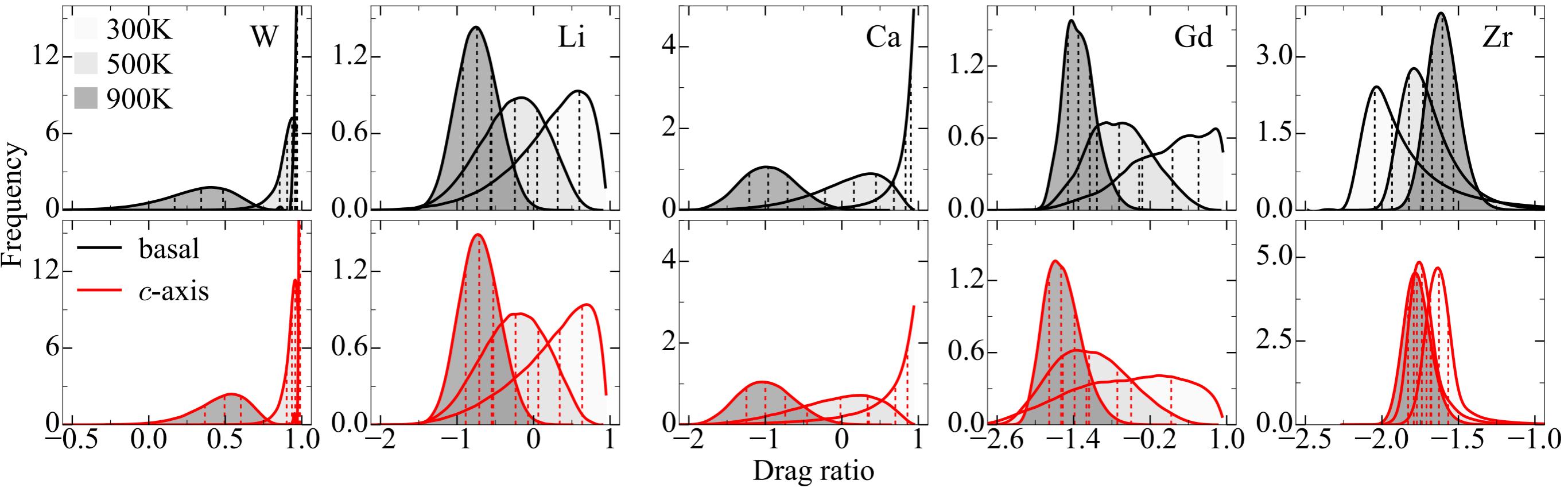
- Bayesian inference approach
- Assume multivariate normal distribution: empirical covariances and mean values



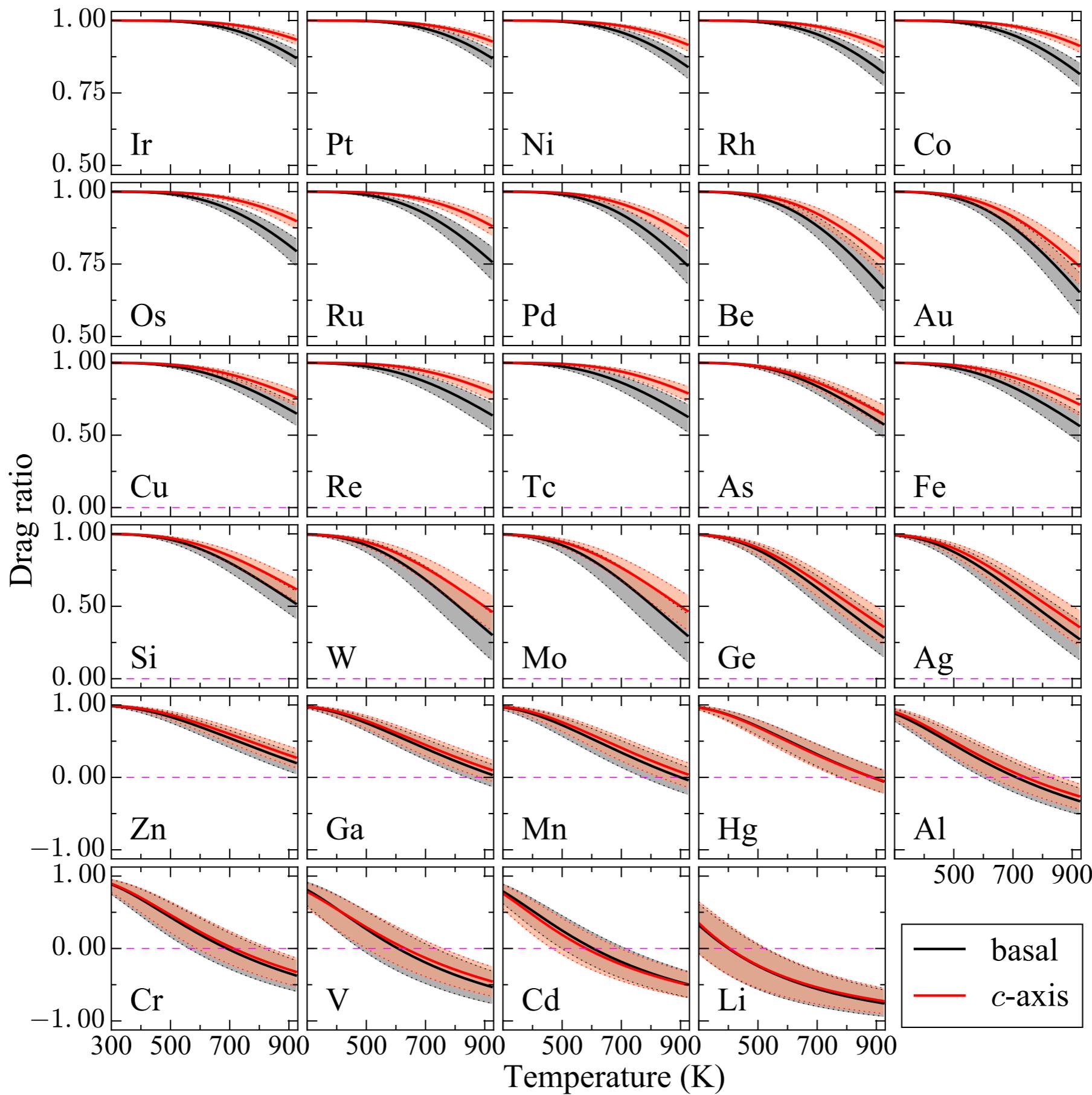
Uncertainty in diffusivity: X in Mg vs. experiment



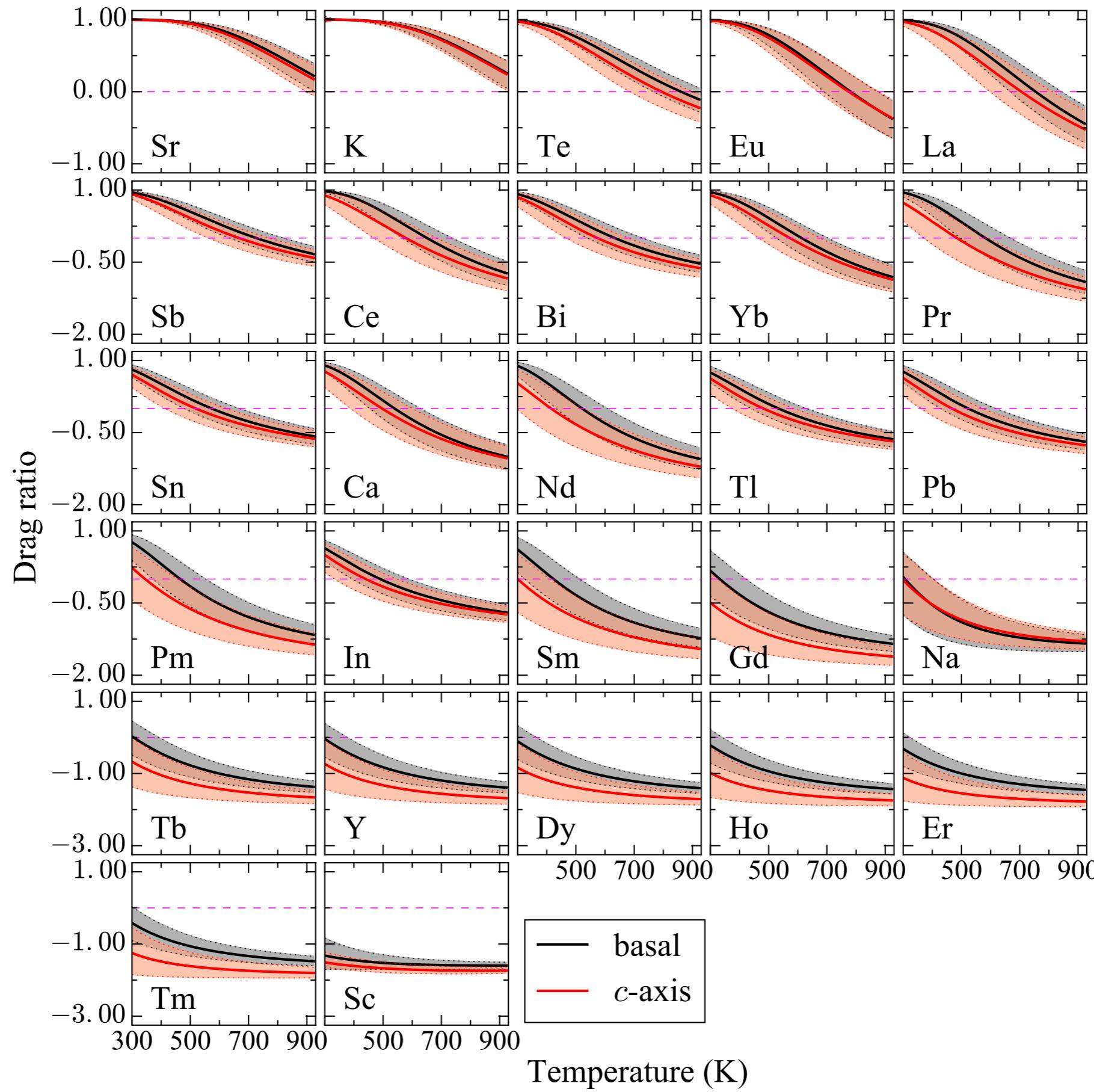
Uncertainty in drag: histograms of X-Mg



Uncertainty in drag: X-Mg



Uncertainty in drag: X-Mg



Uncertainty quantification for solute transport modeling

Dallas R. Trinkle and Ravi Agarwal / Materials Science and Engineering
Univ. Illinois, Urbana-Champaign

Motivation: who do we blame when experiments and theory don't agree?

- **Vacancy-mediated diffusivity**

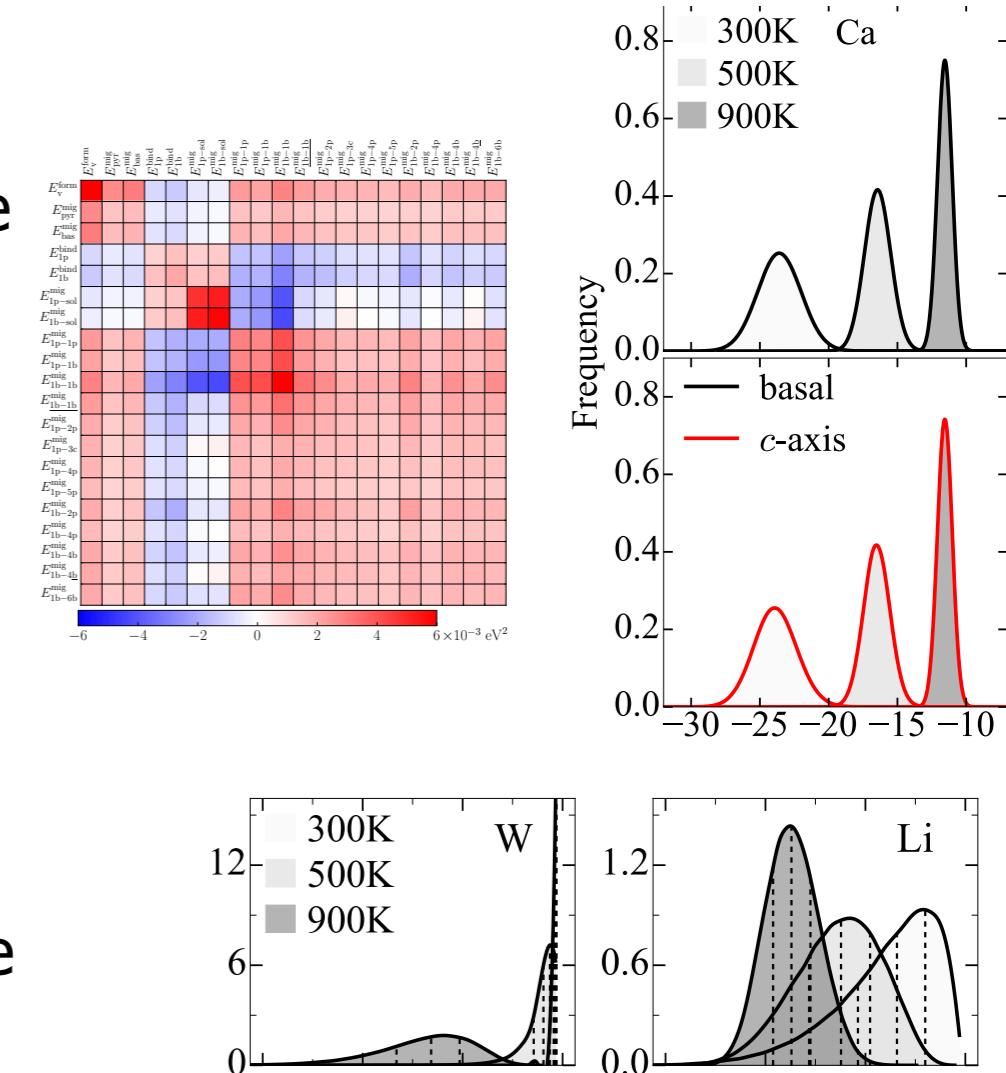
- Quantifying uncertainty in DFT values
- Quantifying uncertainty in diffusivity when there are multiple activated processes at play

- **Applying error bars to DFT predictions**

- Future calculations can include DFT errors
- Derivatives sufficient for diffusivity UQ

- **Possible correlations across solutes**

- Fast substitutional solute diffusivity dominated by vacancy processes: may look like systematic errors
- Slow substitutional solutes and interstitial solute diffusivity dominated by solute processes



Propagating uncertainty from first-principles calculations via analytic models of mass transport can quantify uncertainty in diffusivity predictions.



Computational resources from Turing@UIUC, NSF/Teragrid, DOE/NERSC
DOE/BES (DE-FG02-05ER46217), ONR N000141210752, NSF/CDSE 1411106

dtrinkle.matse.illinois.edu

MSE
at
Illinois