Uncertainty quantification for solute transport modeling

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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.

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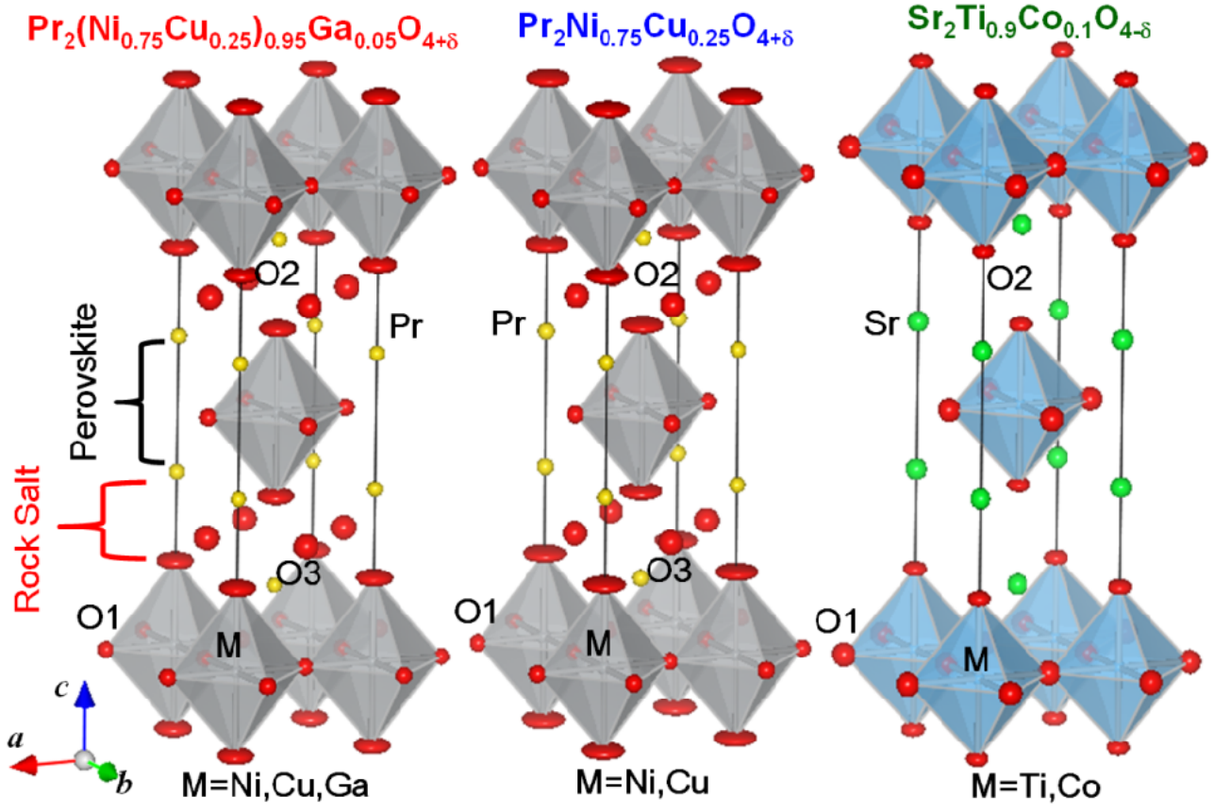
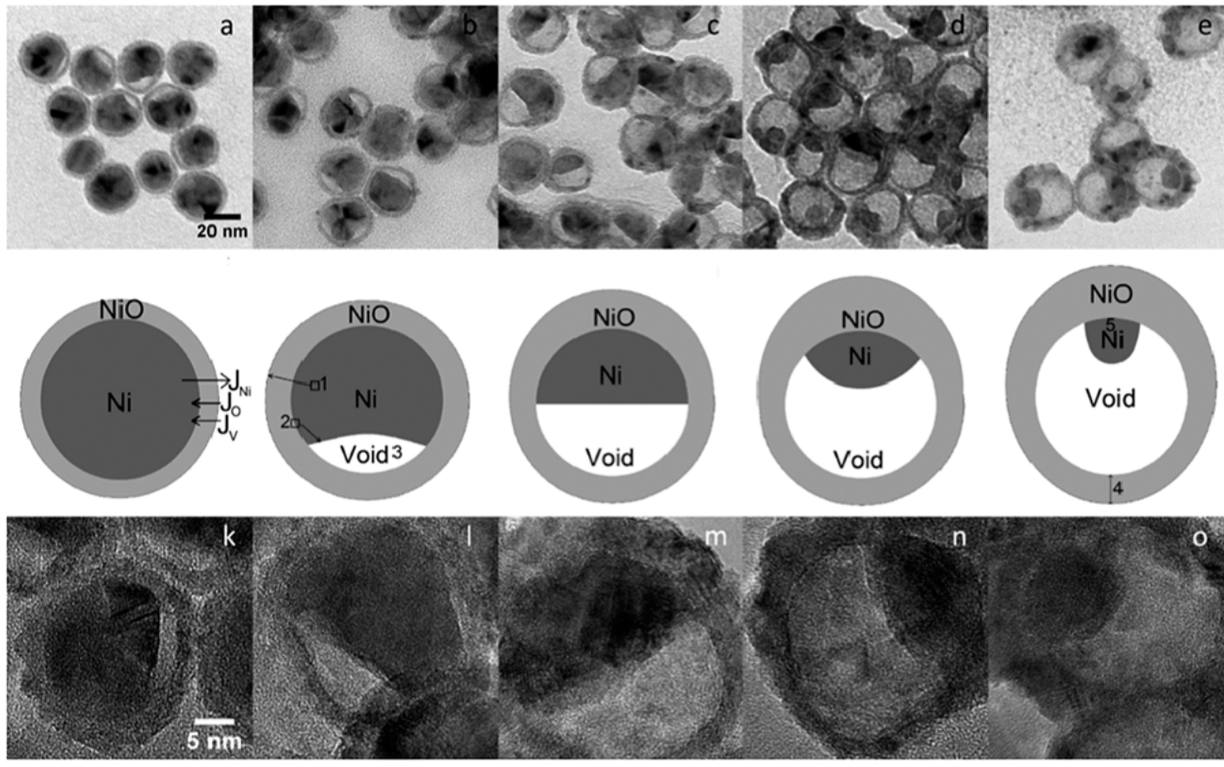
Mass transport

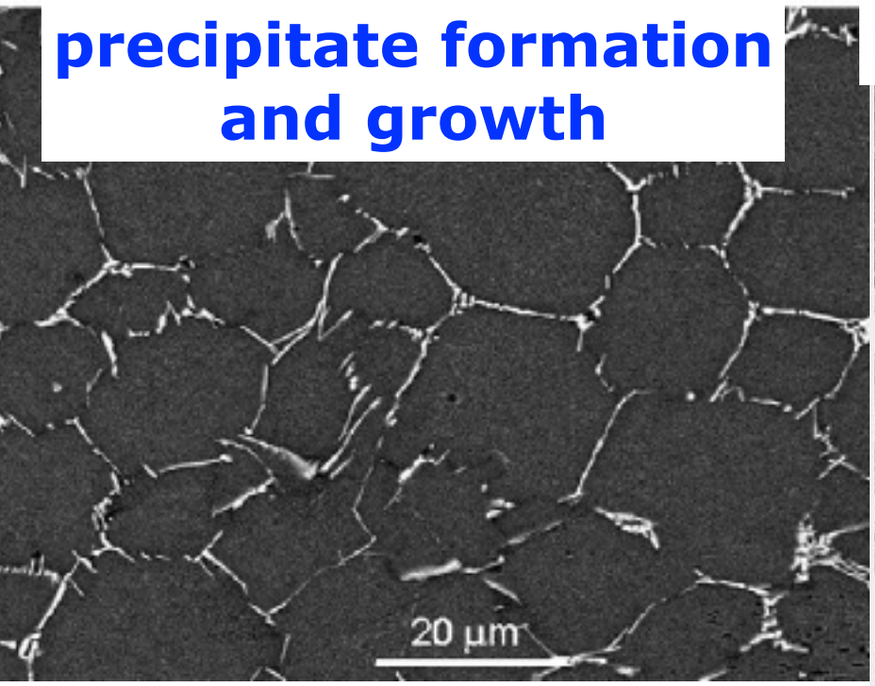
ion transport



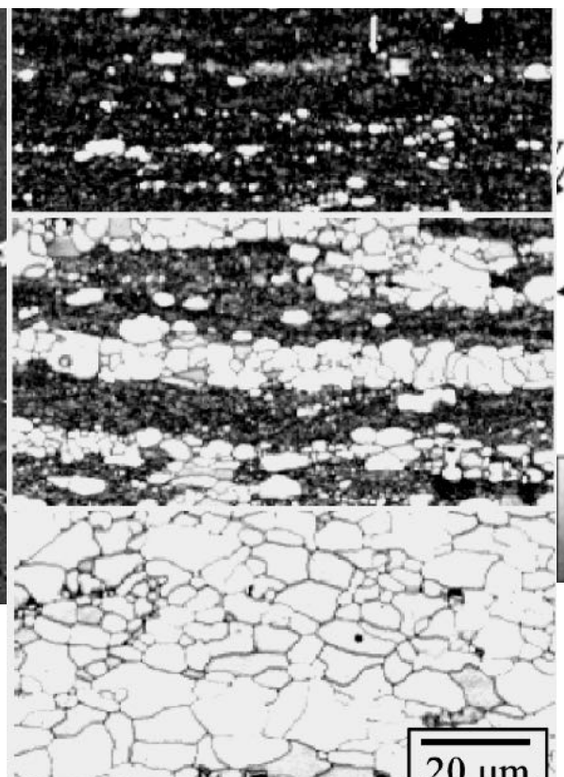
(nano) Kirkendall effect



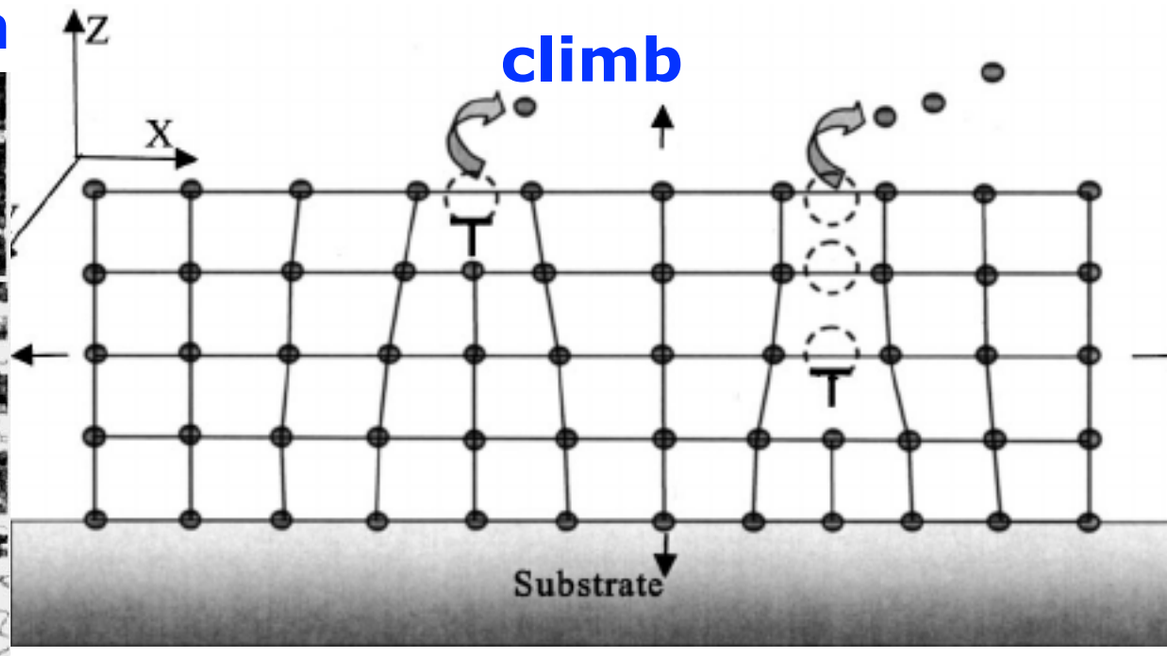
precipitate formation and growth



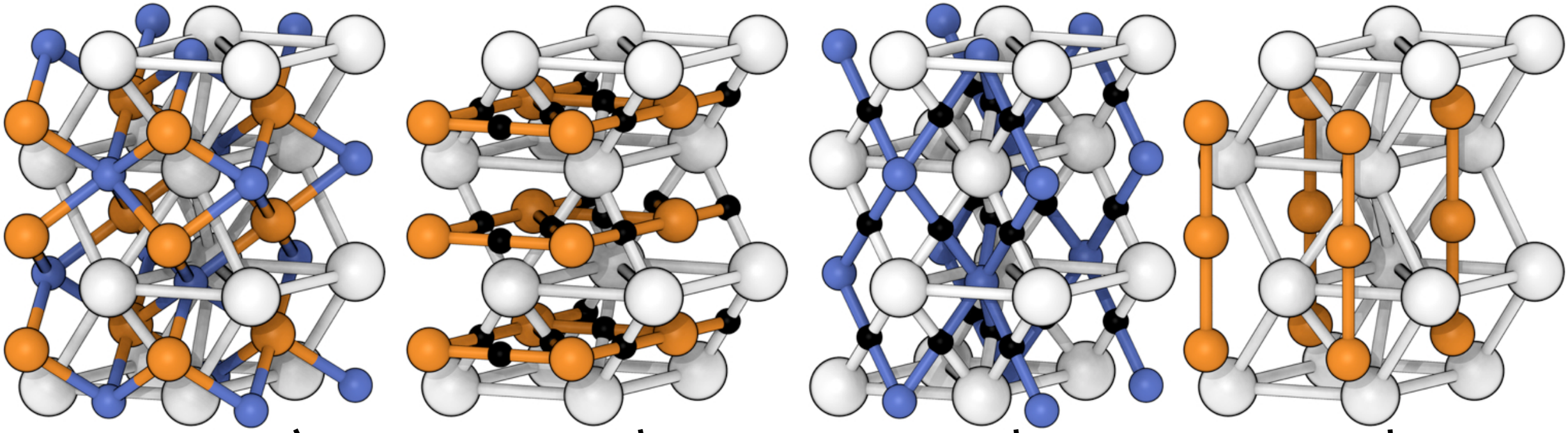
recrystallization



climb



Oxygen diffusion constant in HCP Ti



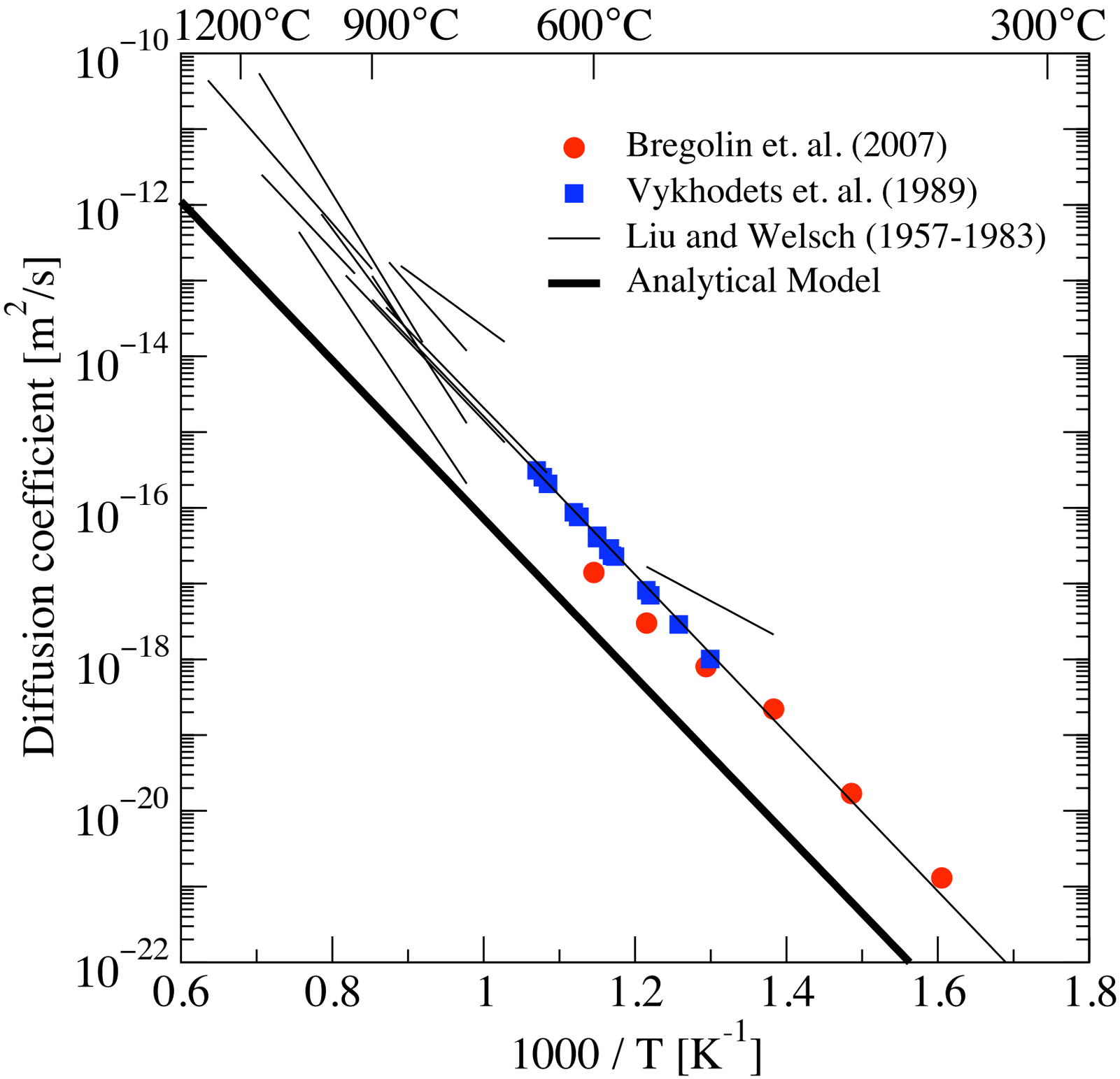
$$D_{basal} = a_{Ti}^2 \left[\lambda_{oh} + \frac{3}{4}\lambda_{oc} + \frac{1}{4}\lambda_{hc}\left(\frac{\lambda_{oh}}{\lambda_{ho}}\right) + 0\lambda_{oo} \right]$$

$$D_{c\text{-}axis} = c_{Ti}^2 \left[\frac{3}{8}\lambda_{oh} + 0\lambda_{oc} + \frac{3}{8}\lambda_{hc}\left(\frac{\lambda_{oh}}{\lambda_{ho}}\right) + \frac{1}{4}\lambda_{oo} \right]$$

Oxygen diffusion separates into the sum of the single networks.

H.H. Wu and D.R. Trinkle, Phys. Rev. Lett. **107**, 045504 (2011)

Oxygen diffusion constant in HCP Ti



Analytical results a factor of 10 lower than experimental observations.

Analytical barriers match well to experiments.

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

H.H. Wu and D.R. Trinkle, Phys. Rev. Lett. **107**, 045504 (2011)

Interstitial sites in HCP Mg

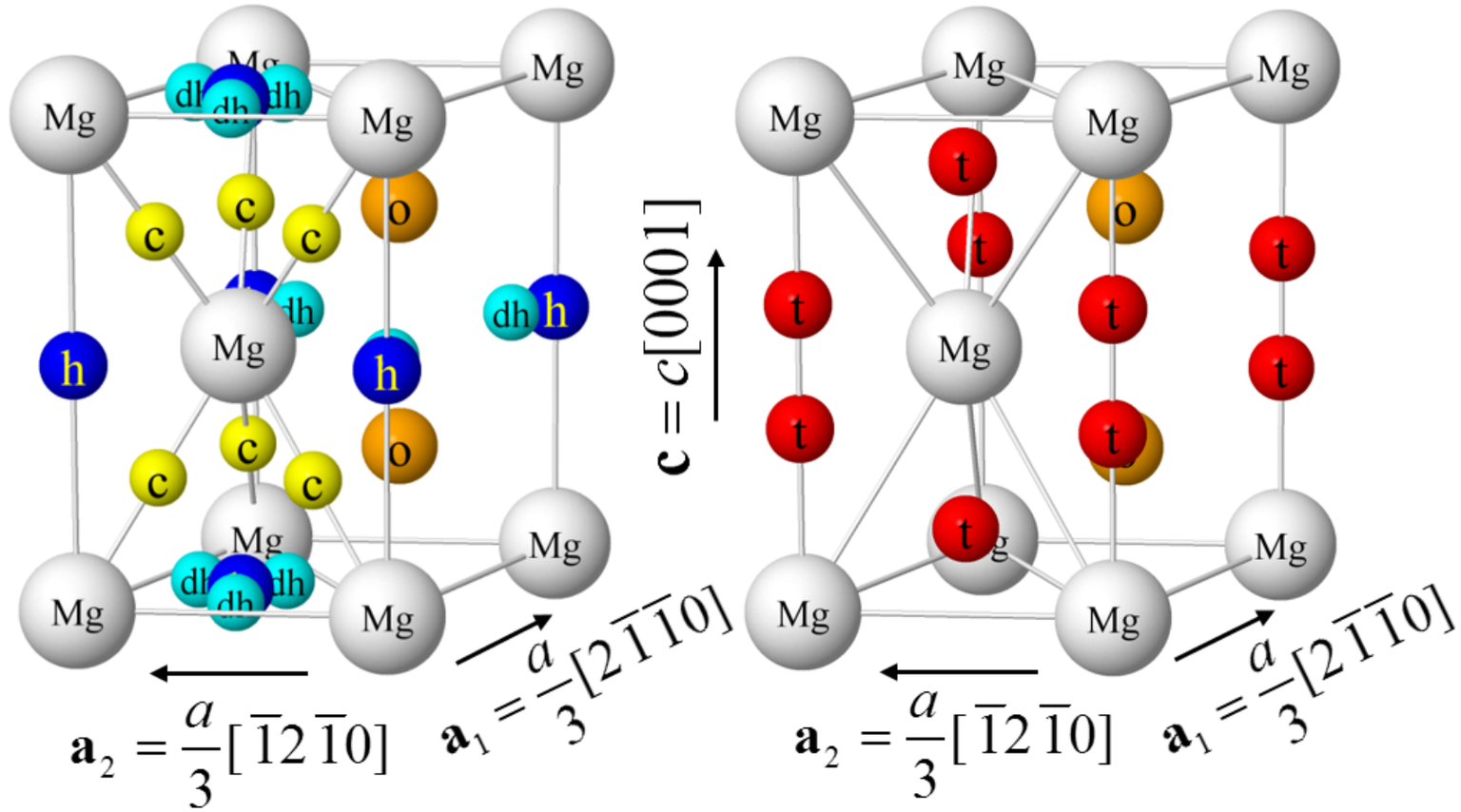
Tetrahedral (t)

Octahedral (o)

Hexahedral (h)

Crowdion (c)

Distorted Hexahedral (dh)

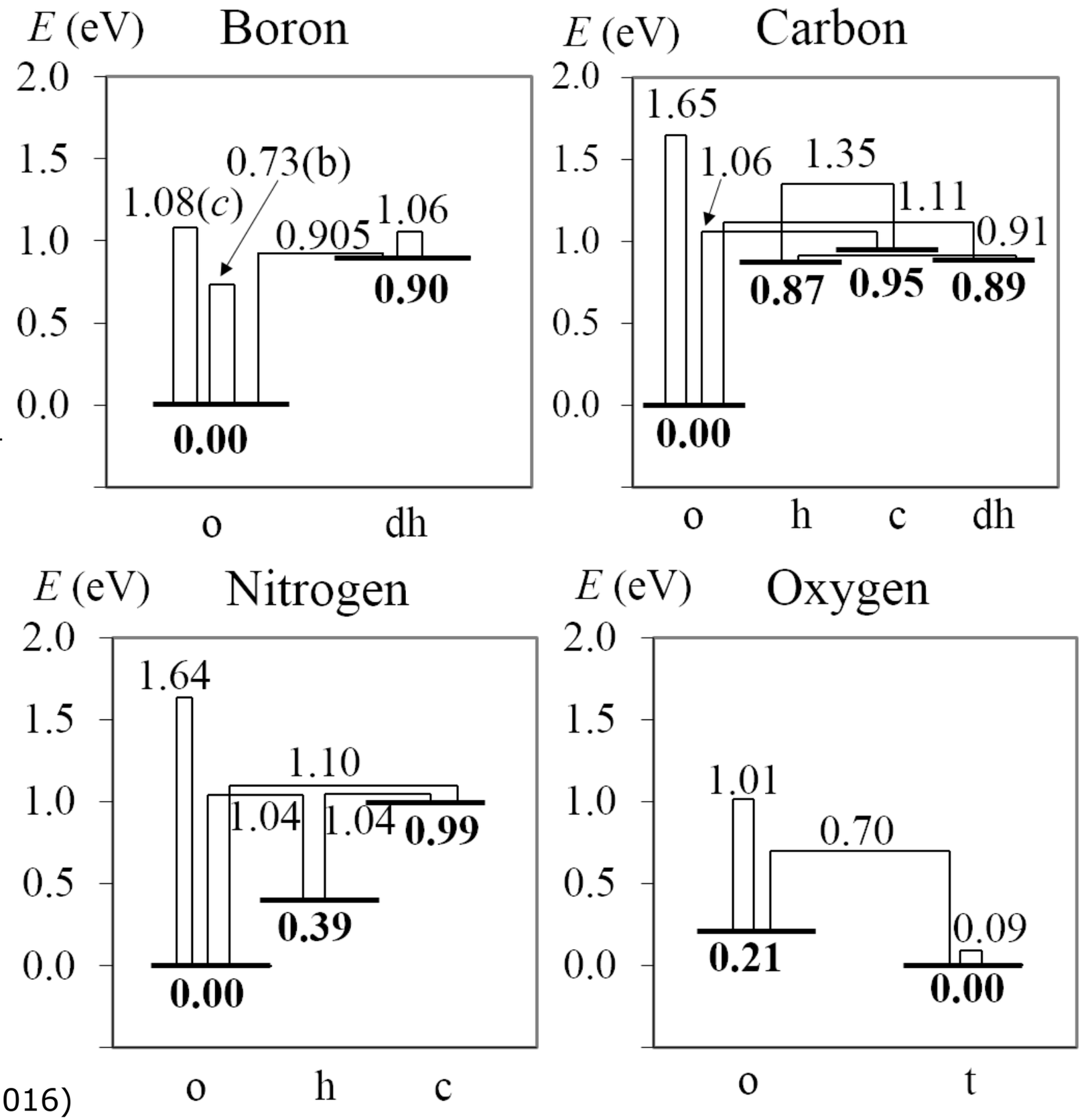


Solute	Ground state	Metastable (energy in eV over ground state) $3s^2$	Metastable (energy in eV over ground state) $3s^2 2p^6$
Boron	Octahedral	dh (0.90)	dh (0.89)
Carbon	Octahedral	h (0.87), dh (0.89), c (0.94)	h (0.87), dh (0.88), c (0.94)
Nitrogen	Octahedral	h (0.39), c (0.99)	h (0.39), c (0.99)
Oxygen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

Agarwal and Trinkle, *Phys. Rev. B* **94** (2016)

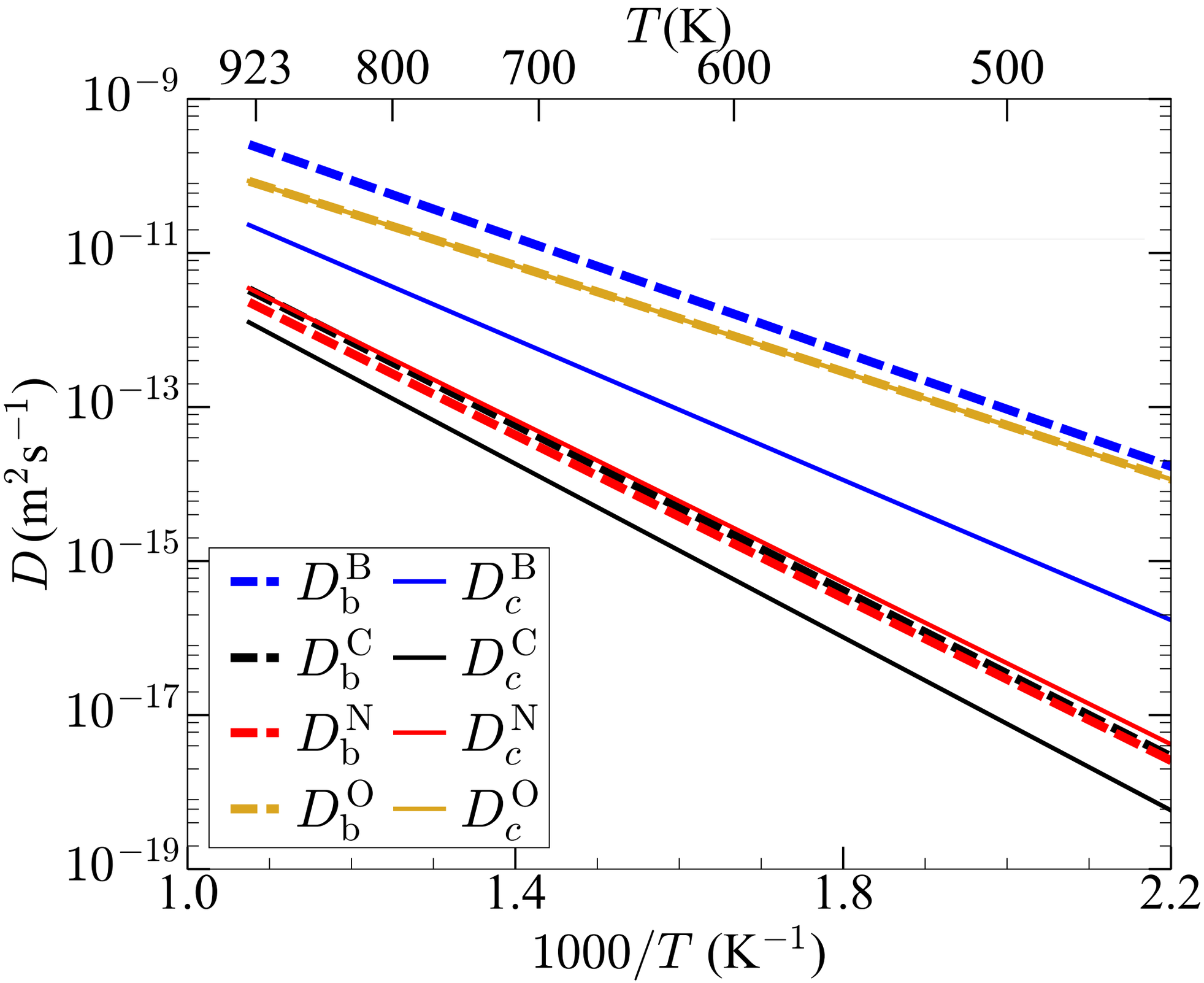
Migration barriers in HCP Mg

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



Agarwal and Trinkle, *Phys. Rev. B* **94** (2016)

Diffusivity in HCP Mg



Agarwal and Trinkle, *Phys. Rev. B* **94** (2016)

Exp: Zotov and Tseldkin, Sov. Phys. J. **19**, 1652 (1976).

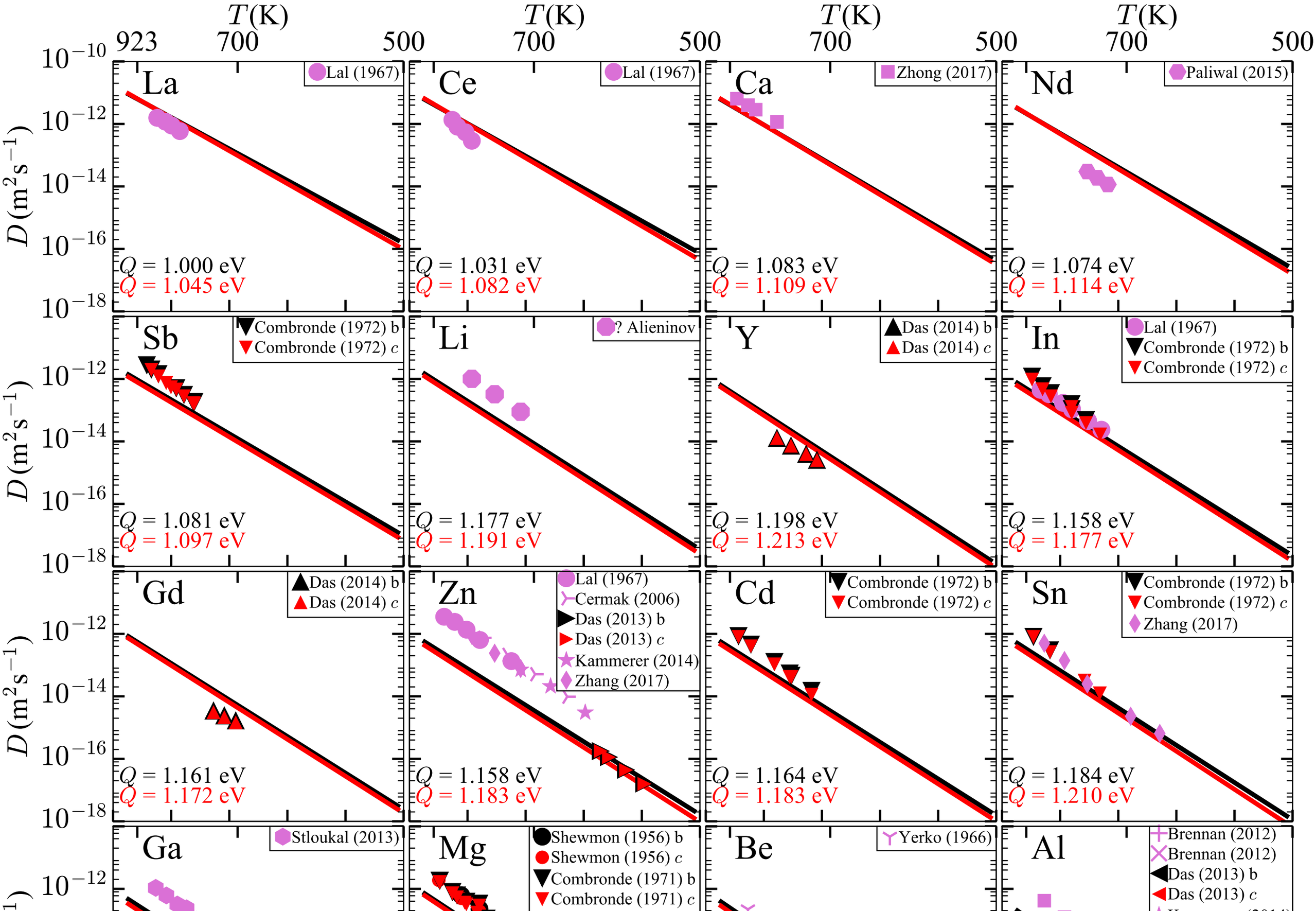
Vacancy mediated diffusion in Mg

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

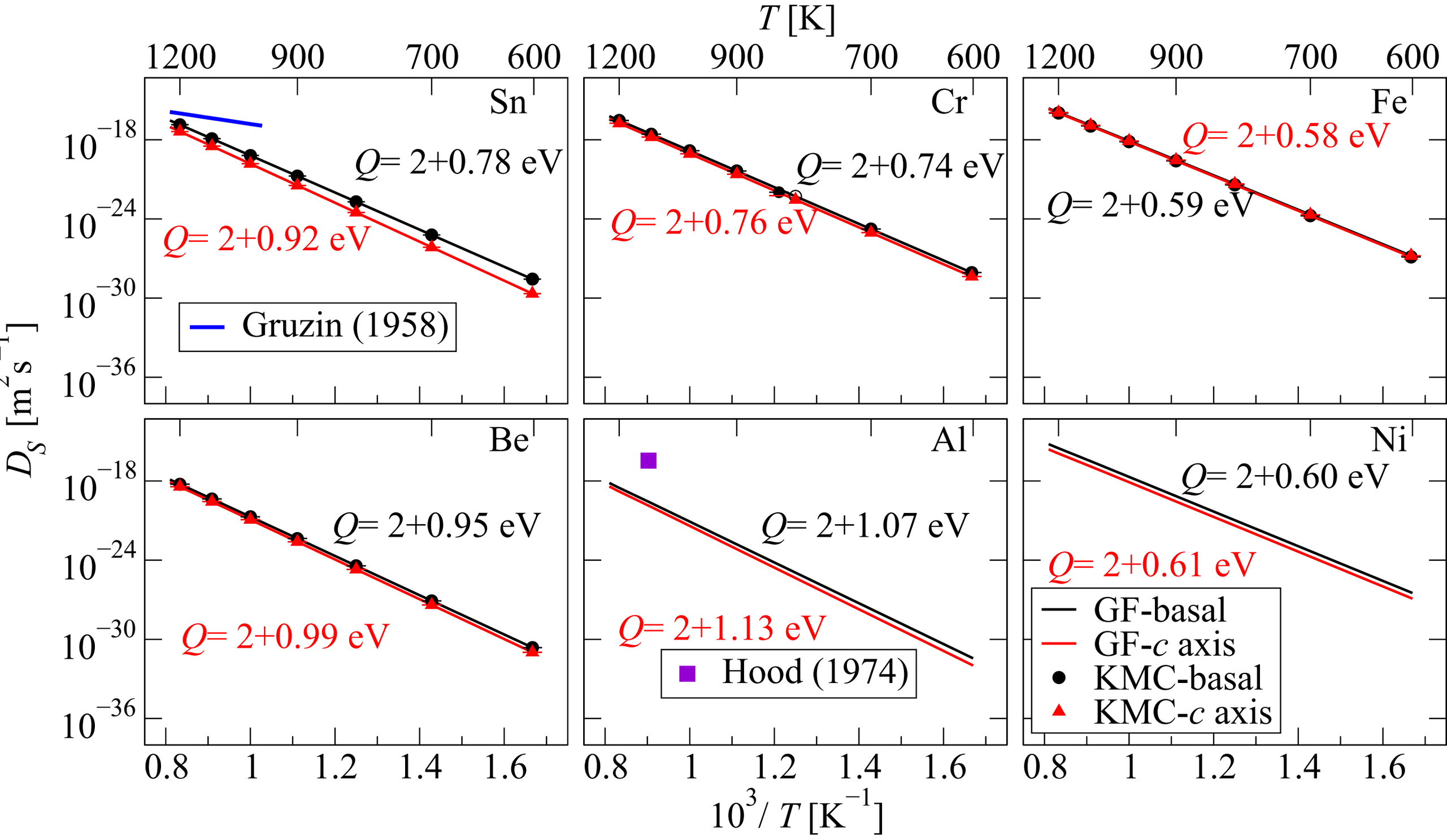
Solute	8-freq. (Q)	GF (Q)	Exp. (Q)	GF (T_{cross})	8-f (T_{cross})
Nd	1.18 | 1.20	1.08 | 1.13	1.16 (Paliwal2015)	529 | 422	< 0 K
Ce	1.14 | 1.15	1.03 | 1.09	1.82 (Lal1966)	648 | 589	252 | 287
La	1.10 | 1.11	1.00 | 1.04	1.06 (Lal1966)	746 | 714	415 | 452
Gd	1.24 | 1.26	1.16 | 1.17	0.82 | 0.85 (Das2014)	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

Agarwal and Trinkle, *Phys. Rev. Lett.* **118,** 105901 (2017)

Vacancy mediated diffusion in Mg

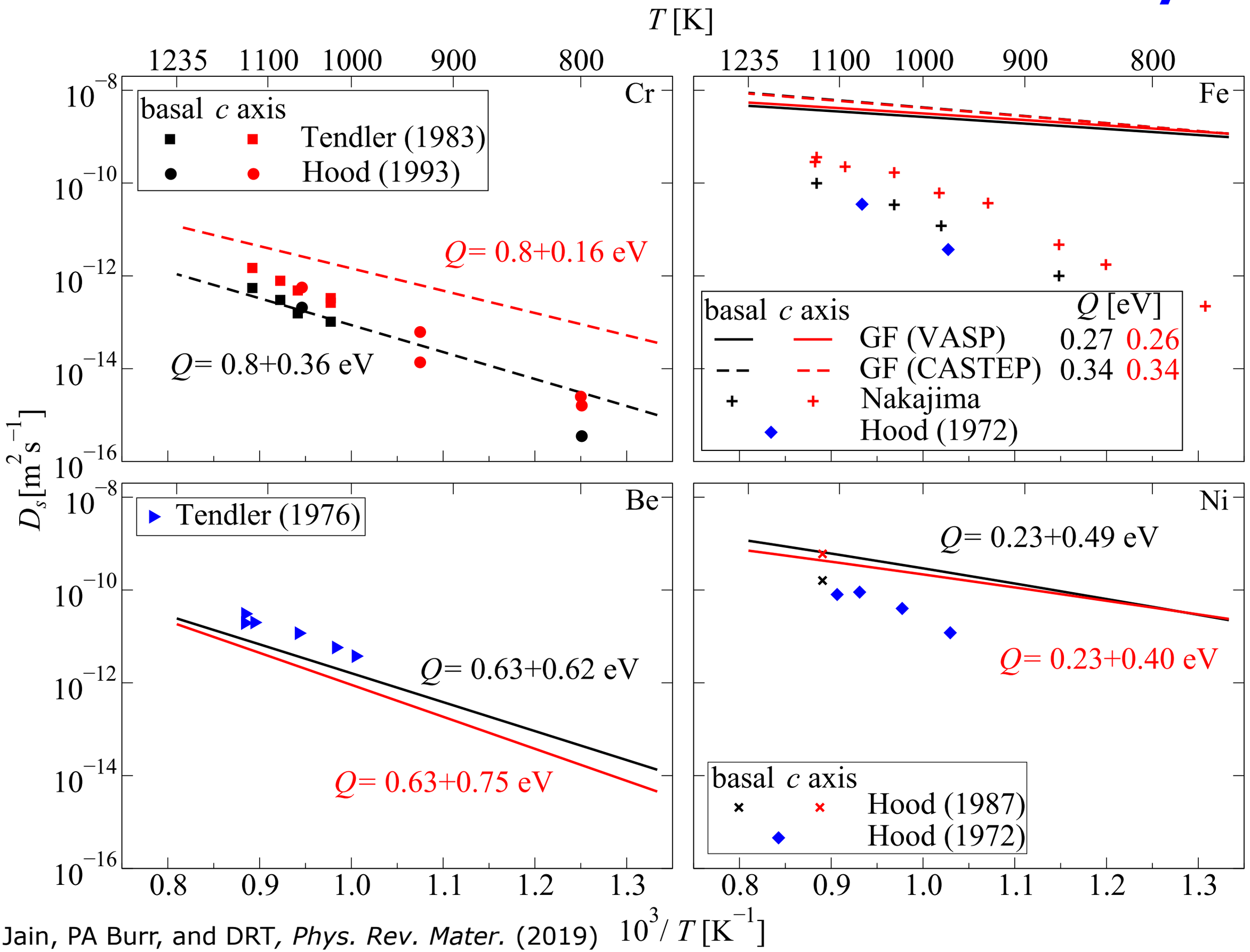


Vacancy mediated diffusion in Zr: solute diffusivity



ACP Jain, PA Burr, and DRT, *Phys. Rev. Mater.* In press (2019)

Interstitial diffusion in Zr: solute diffusivity



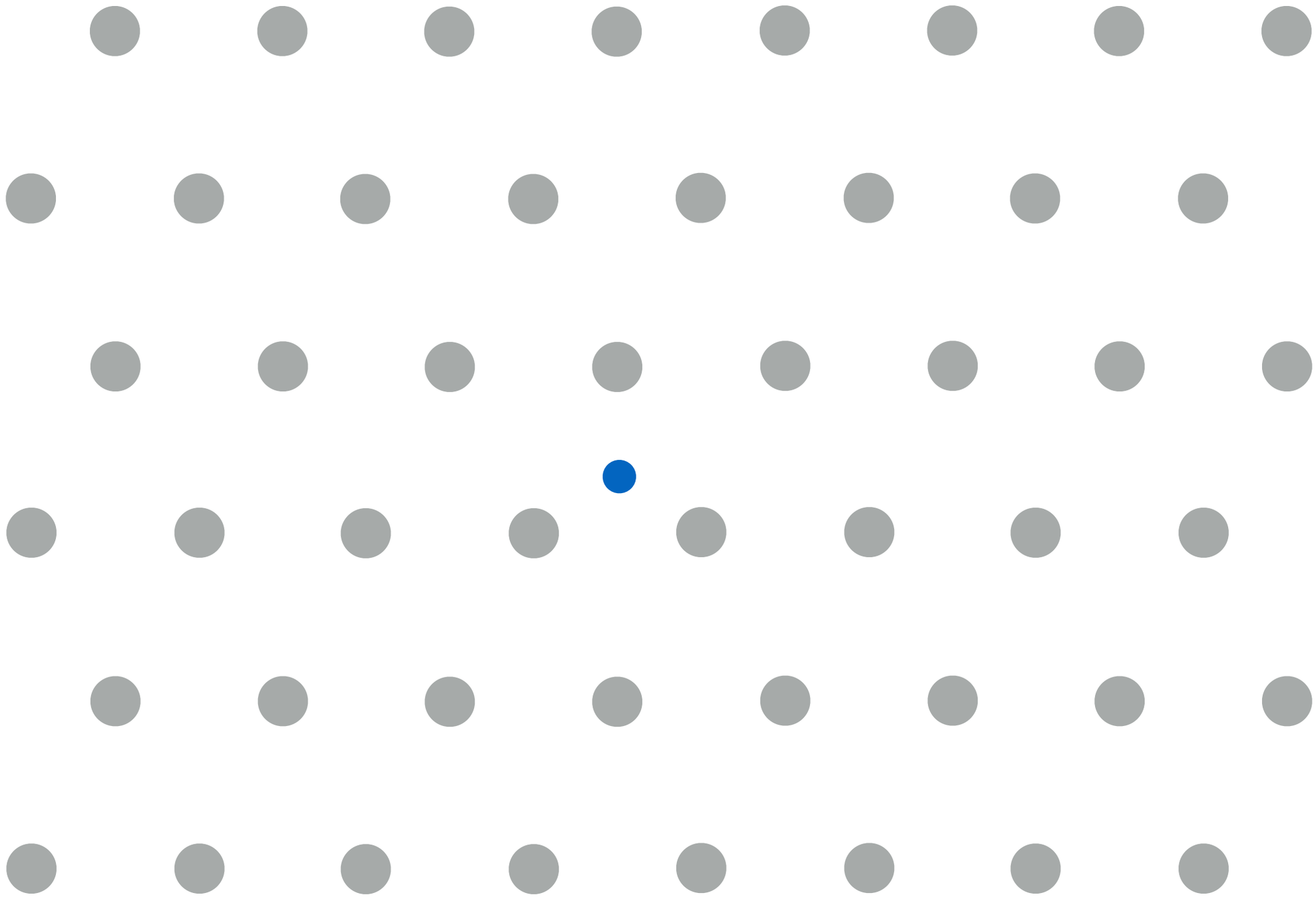
ACP Jain, PA Burr, and DRT, *Phys. Rev. Mater.* (2019)

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



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

Atomistic mechanism for diffusivity: substitutional solute

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

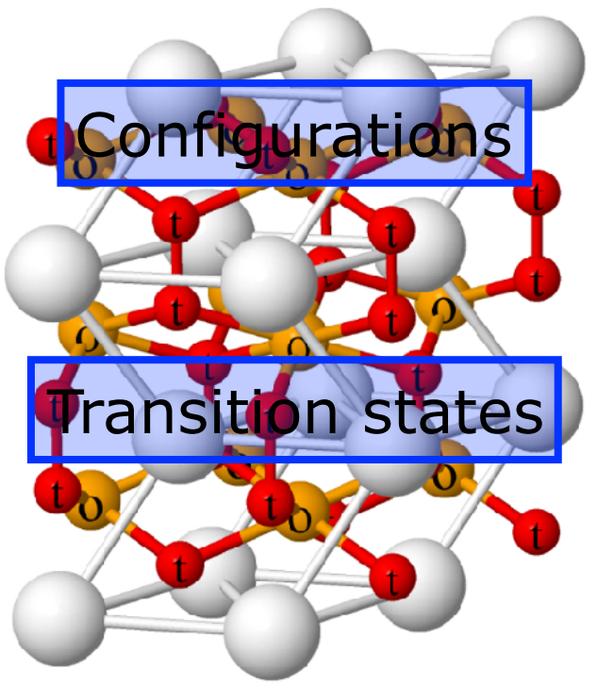
Replacing trajectories with probabilities: Master equation

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

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

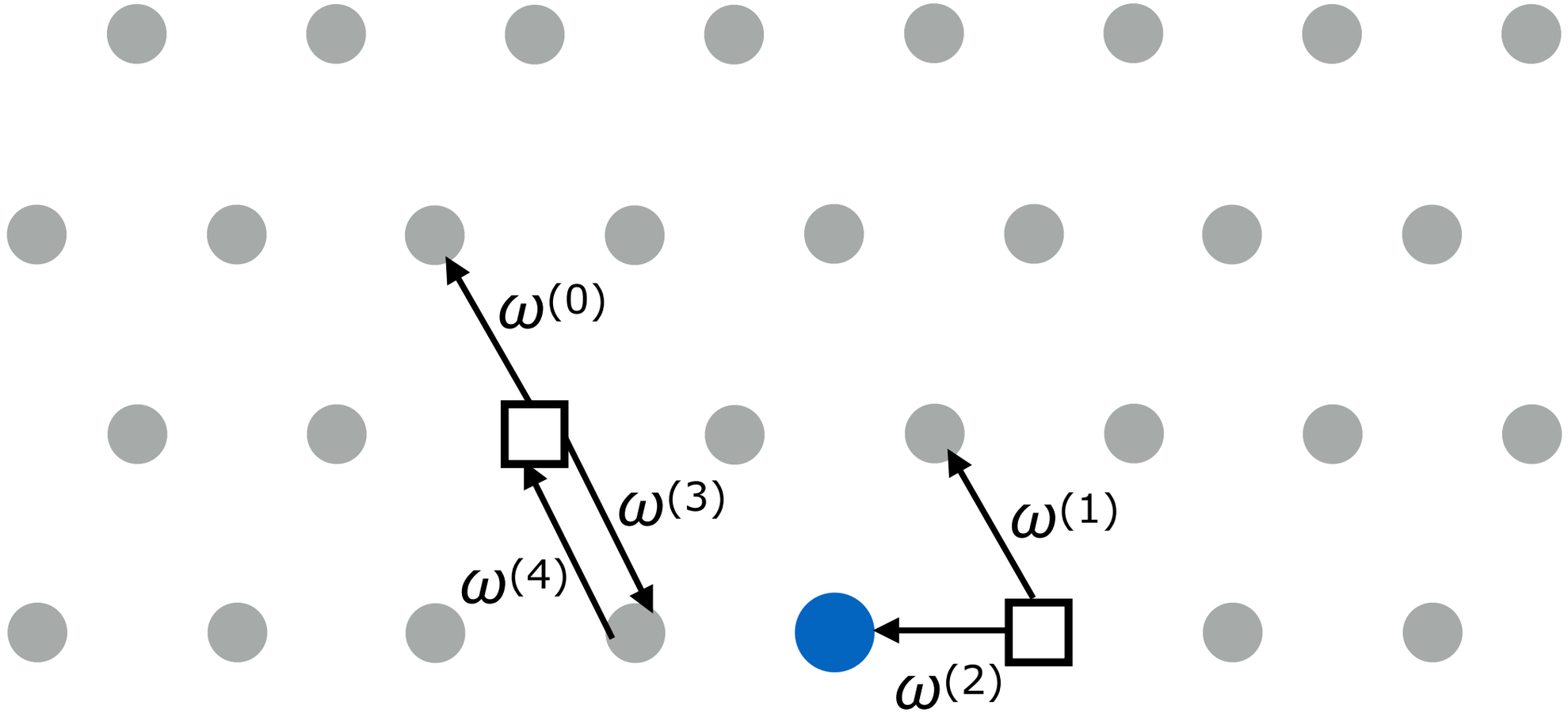
configuration $\underline{\chi}$, probability $P(\underline{\chi},t)$

- **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)



Software: dallastrinkle.github.io/Onsager
Interstitials: Trinkle, Phil. Mag. **96** (2016)
Vacancy-mediated: 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

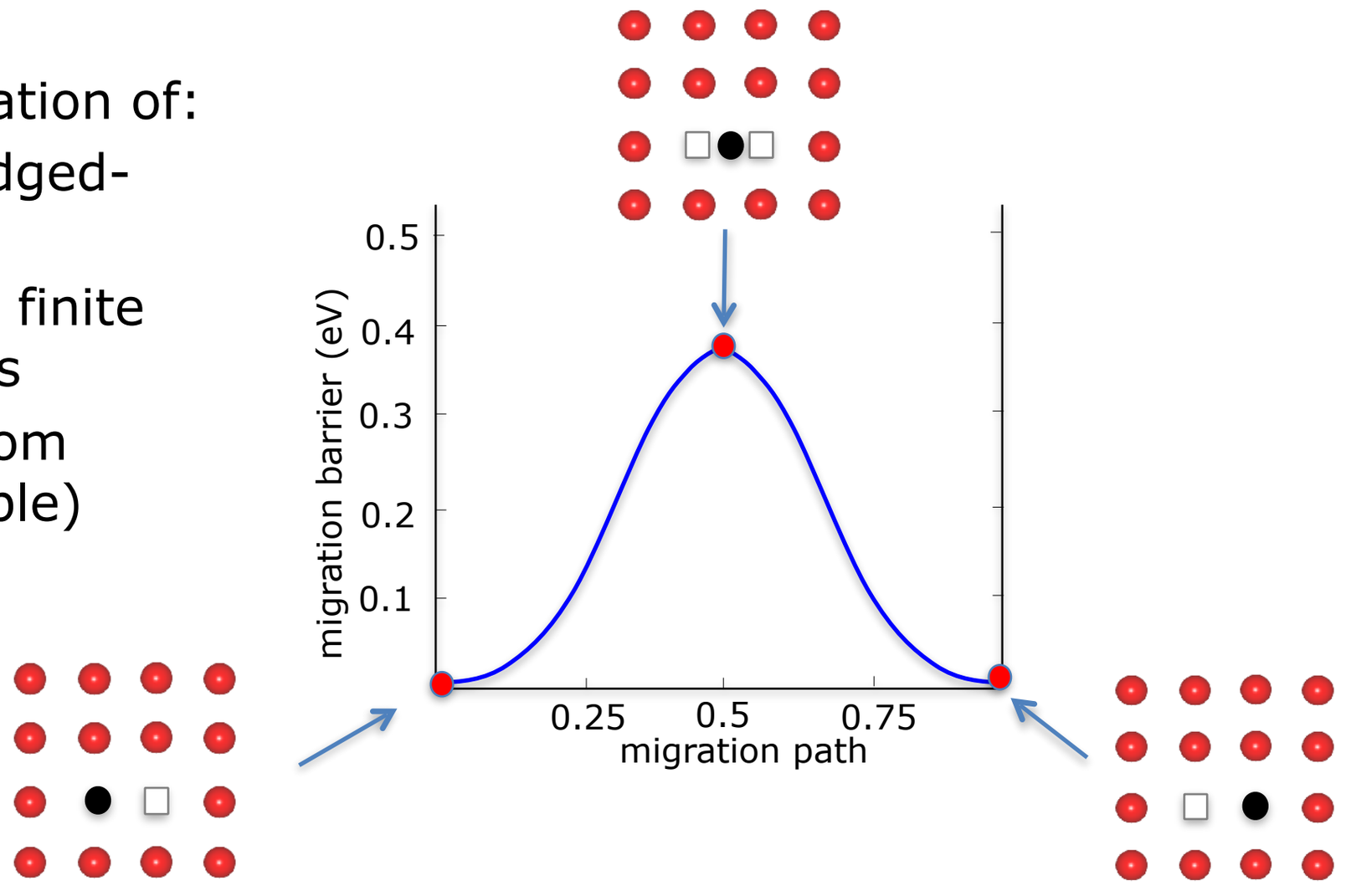
Jump frequencies: harmonic transition state theory

atomic jump rate: $$\omega = \frac{\prod_{3N} \nu^{(\text{initial state})}}{\prod_{3N-1} \nu^{(\text{final state})}} \exp\left(-\frac{\Delta F^{(\text{TS–IS})}_{\text{elec}}}{k_{\text{B}}T}\right) \exp\left(-\frac{\Delta H^{(\text{TS–IS})}_{\text{mig}}}{k_{\text{B}}T}\right)$$

phonon frequency

enthalpy of migration

- 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

$$\mathbf{x}(t) - \mathbf{x}(0) = \sum_n \delta\mathbf{x}_n$$

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 Carlo[1] (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 poorly[2]

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

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

Computing diffusivity: Direct solution of master equation

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

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

$$P_0(\underline{\chi})W(\underline{\chi} \to \underline{\chi}') = P_0(\underline{\chi}')W(\underline{\chi}' \to \underline{\chi})$$ equilibrium (no flux)

$$\sum_{\underline{\chi}'} P_{\mathrm{ss}}(\underline{\chi})W(\underline{\chi} \to \underline{\chi}') = \sum_{\underline{\chi}'} P_{\mathrm{ss}}(\underline{\chi}')W(\underline{\chi}' \to \underline{\chi})$$ steady state (constant flux)

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

$$\mathbf{b}^\alpha(\underline{\chi}) := \sum_{\underline{\chi}'} W_{\underline{\chi}\underline{\chi}'}\delta\mathbf{x}^\alpha(\underline{\chi} \to \underline{\chi}') \qquad g_{\underline{\chi}\underline{\chi}'} := W^+_{\underline{\chi}\underline{\chi}'} \text{ (pseudoinverse)}$$

$$\underline{\mathrm{L}}^{\alpha\beta} = \frac{1}{k_\mathrm{B}T\Omega}\sum_{\underline{\chi}\underline{\chi}'}\frac{1}{2}P_0(\underline{\chi})W_{\underline{\chi}\underline{\chi}'}\delta\mathbf{x}^\alpha(\underline{\chi} \to \underline{\chi}') \otimes \delta\mathbf{x}^\beta(\underline{\chi} \to \underline{\chi}')$$ "bare" mean-squared displacement

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

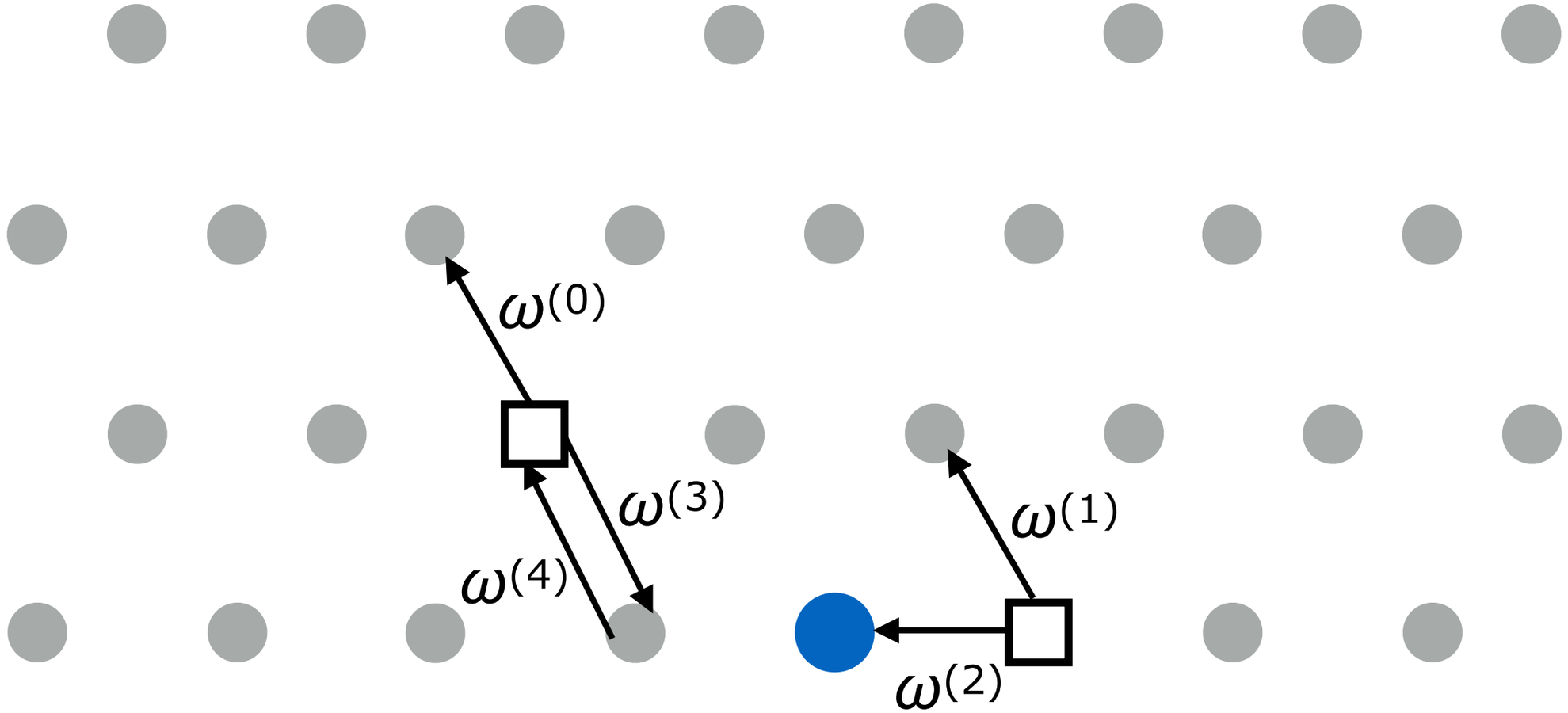
Example: vacancy-mediated diffusion in magnesium

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:
     $\Delta E = -\mathbf{f}\cdot(D^{-1})\cdot\mathbf{f}/2$
   - 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”



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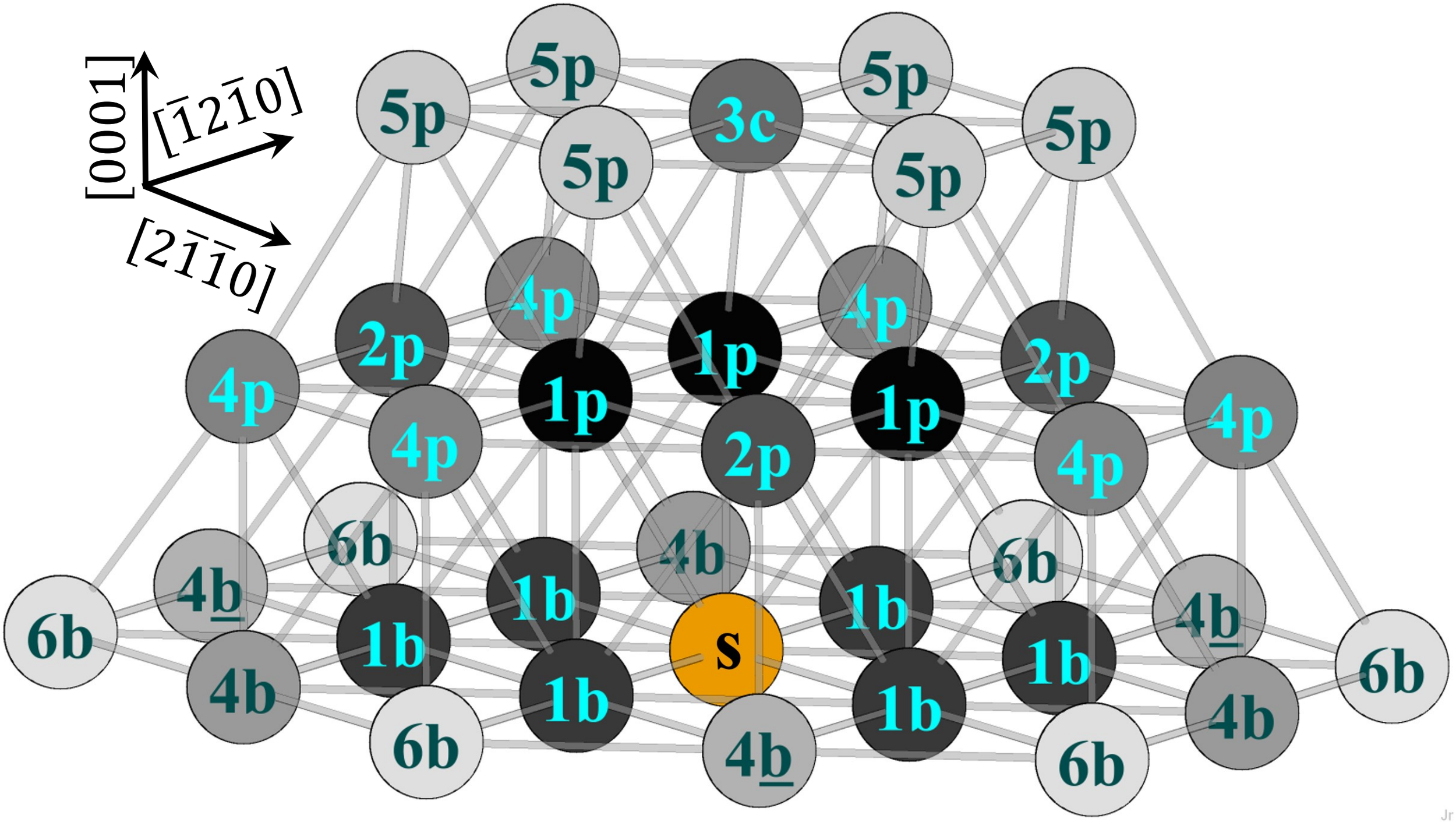
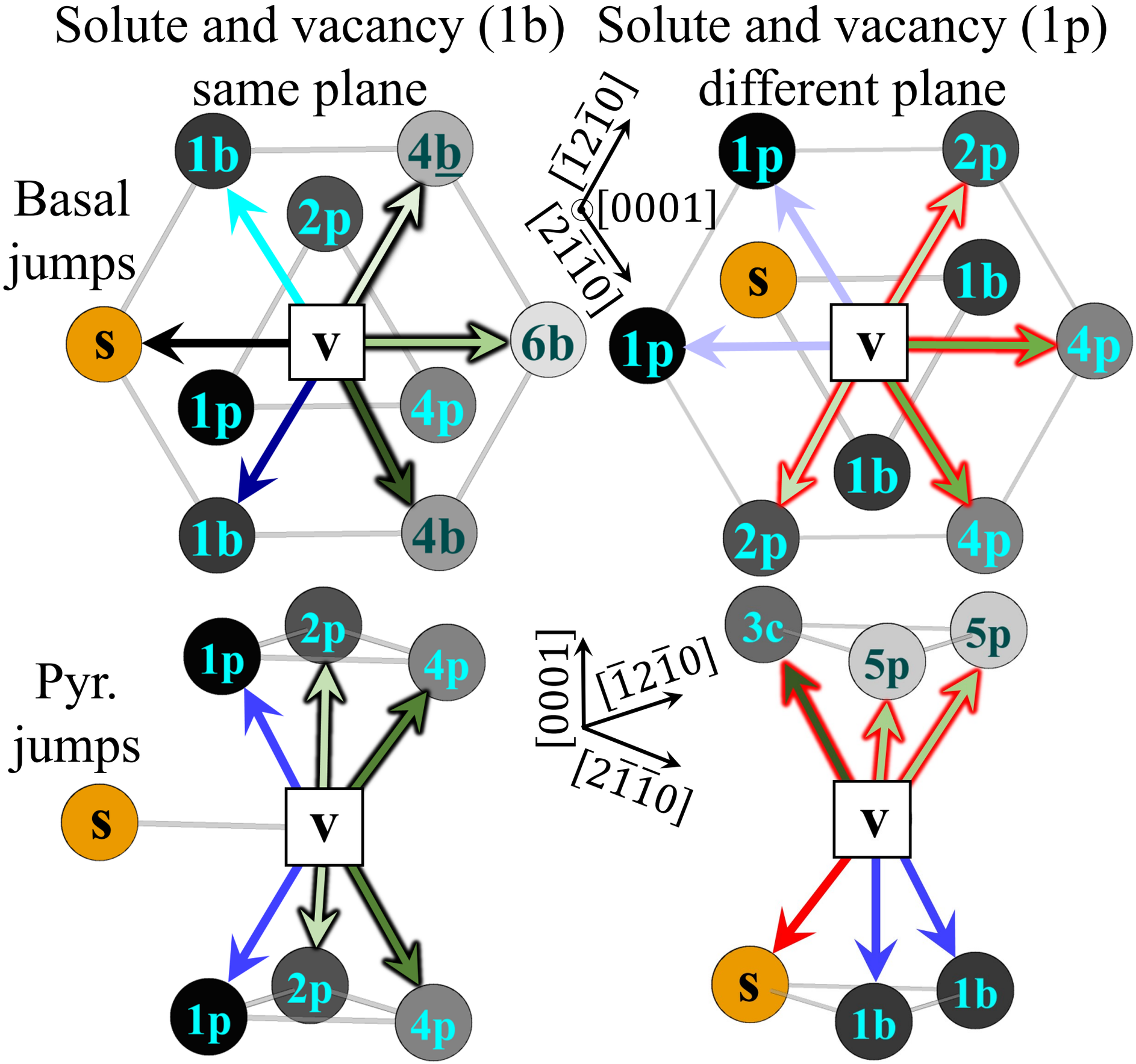
Vacancy-solute complexes in HCP

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



Agarwal and Trinkle, *Phys. Rev. Lett.* **118,** 105901 (2017)

Vacancy jumps near a solute in HCP



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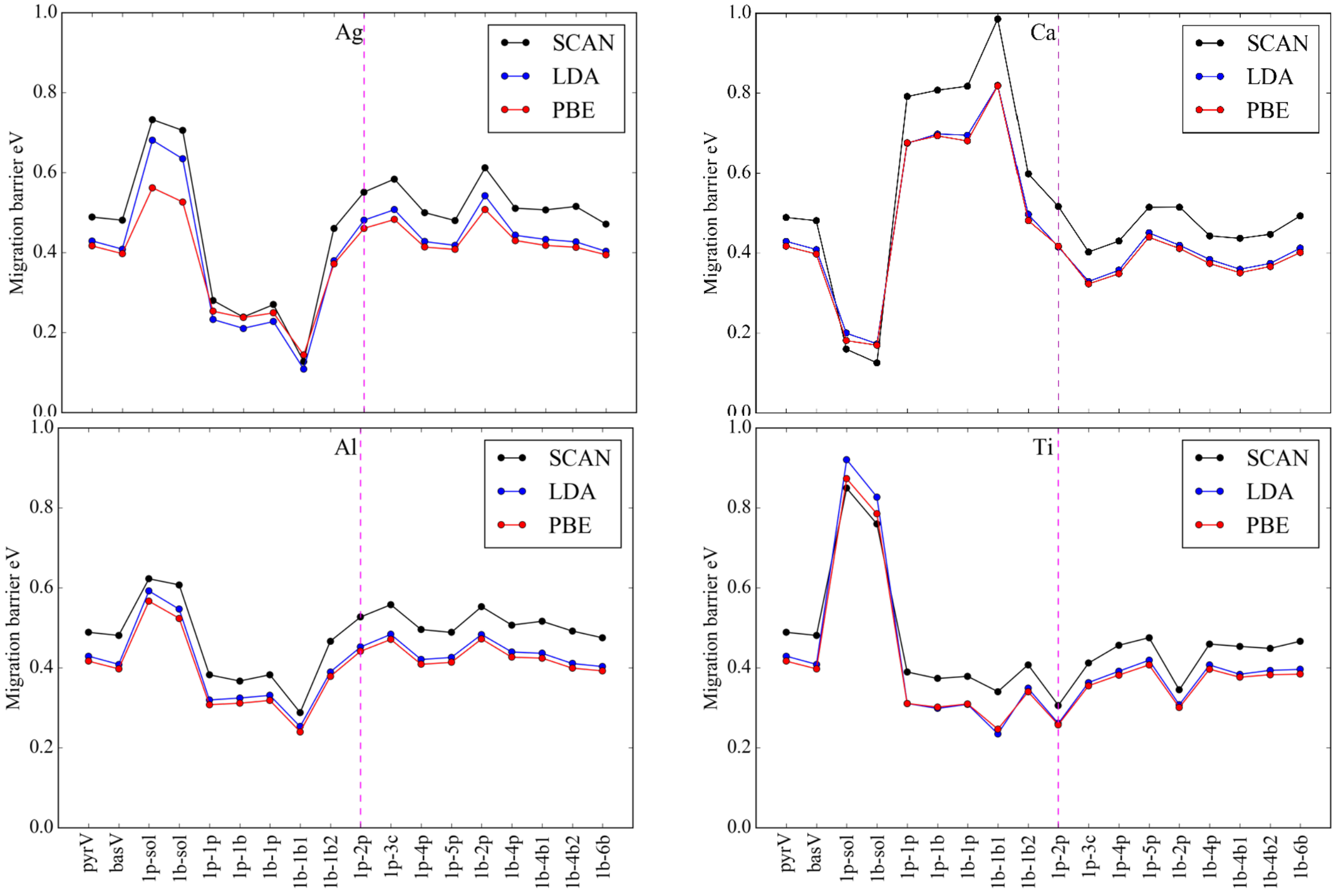
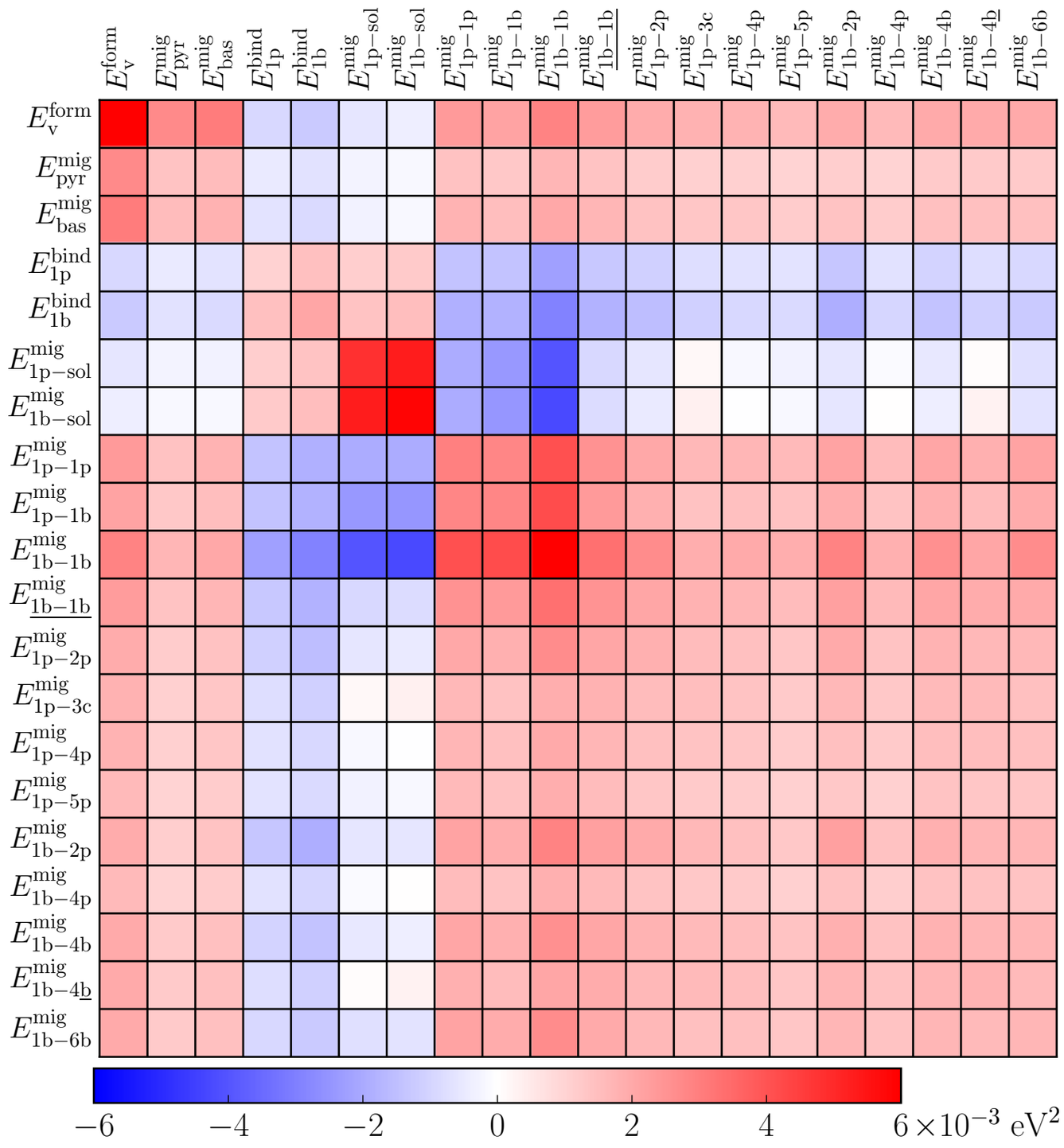


Uncertainty in DFT input data for Mg

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



Agarwal and Trinkle, *Uncertainty Quantification in Multiscale Modeling* (2020)

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 ($\underline{\theta}$)

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

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

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

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^{SV}/L^{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

$$\theta = \begin{pmatrix} \theta^{V} \\ \theta^{S} \end{pmatrix}, \quad \Sigma = \begin{pmatrix} \Sigma^{VV} & \Sigma^{VS} \\ \Sigma^{SV} & \Sigma^{SS} \end{pmatrix} \qquad P(\theta) = P^{V}(\theta^{V}) P^{S}(\theta^{S}|\theta^{V})$$

Uncertainty in diffusivity

3. Computational details:
   - Use Gaussian-Hermite quadrature for vacancy parameters for computational efficiency
   - Multivariate normal distribution samples for solute-vacancy parameters

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

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

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

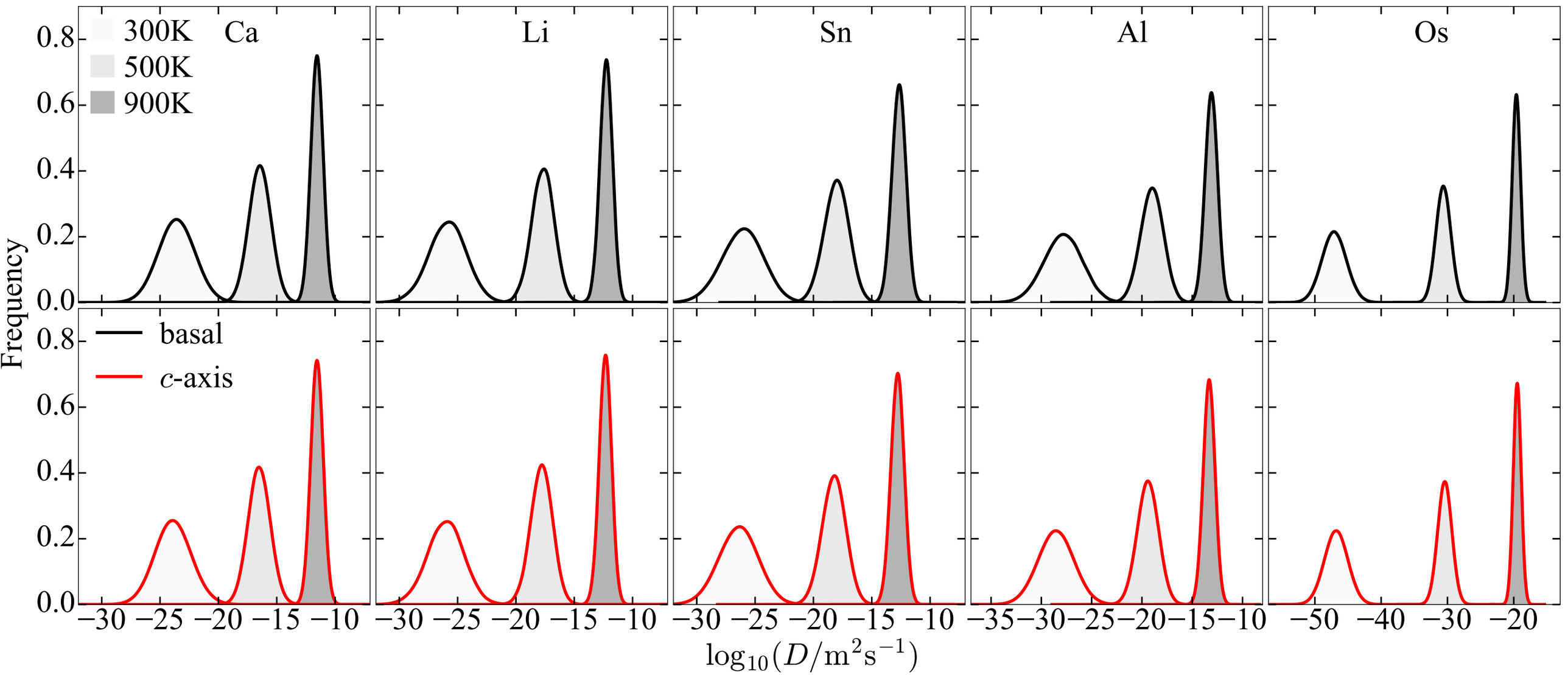
$$\text{covariance}: \quad \Sigma^{\mathrm{ss}} - \Sigma^{\mathrm{sv}} (\Sigma^{\mathrm{vv}})^{-1} \Sigma^{\mathrm{vs}}$$

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

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

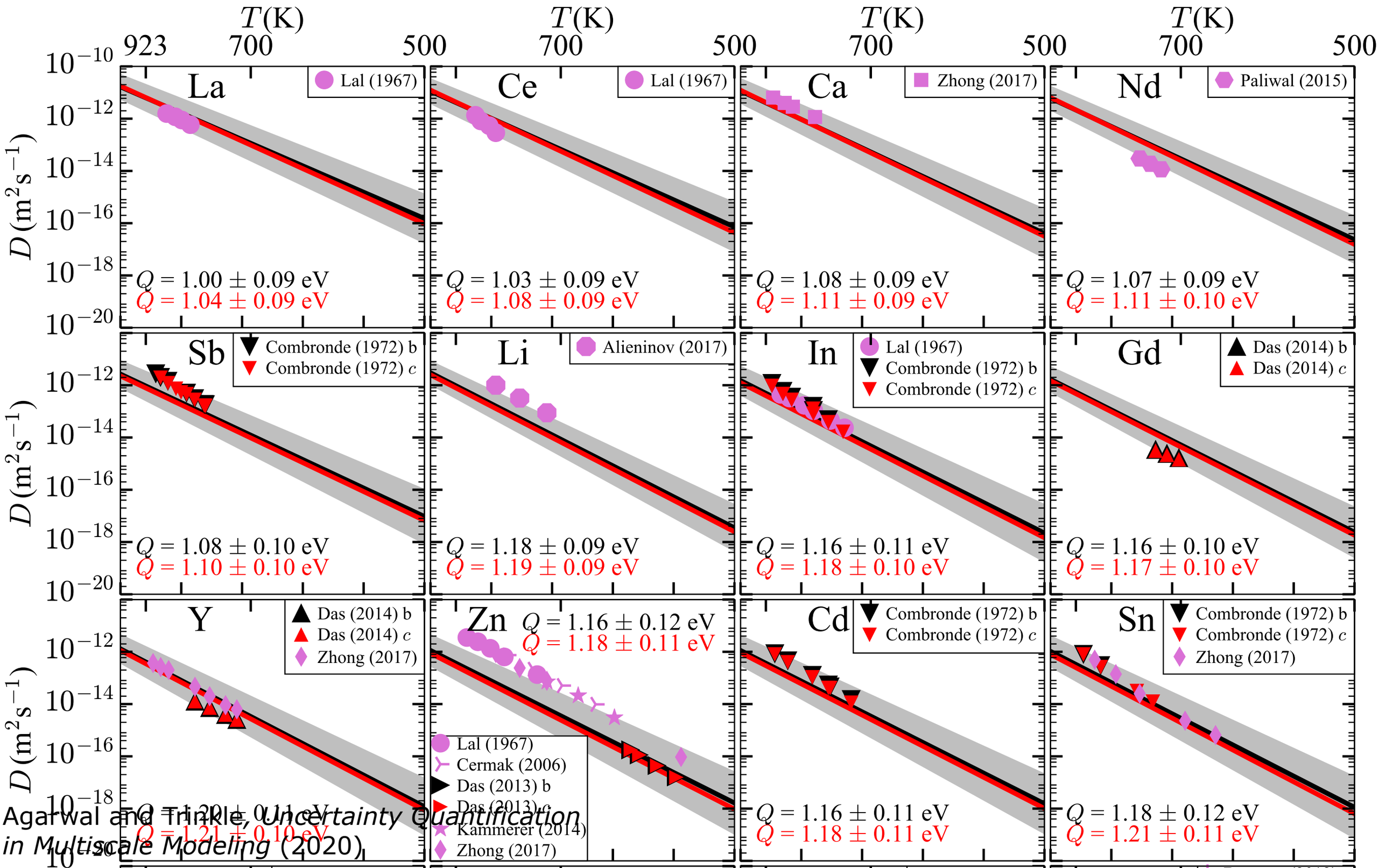
Uncertainty in diffusivity: histograms of X-Mg

1. Take variability in DFT input parameters and *sample* possible DFT data
   - Bayesian inference approach
   - Assume multivariate normal distribution: empirical covariances and mean values



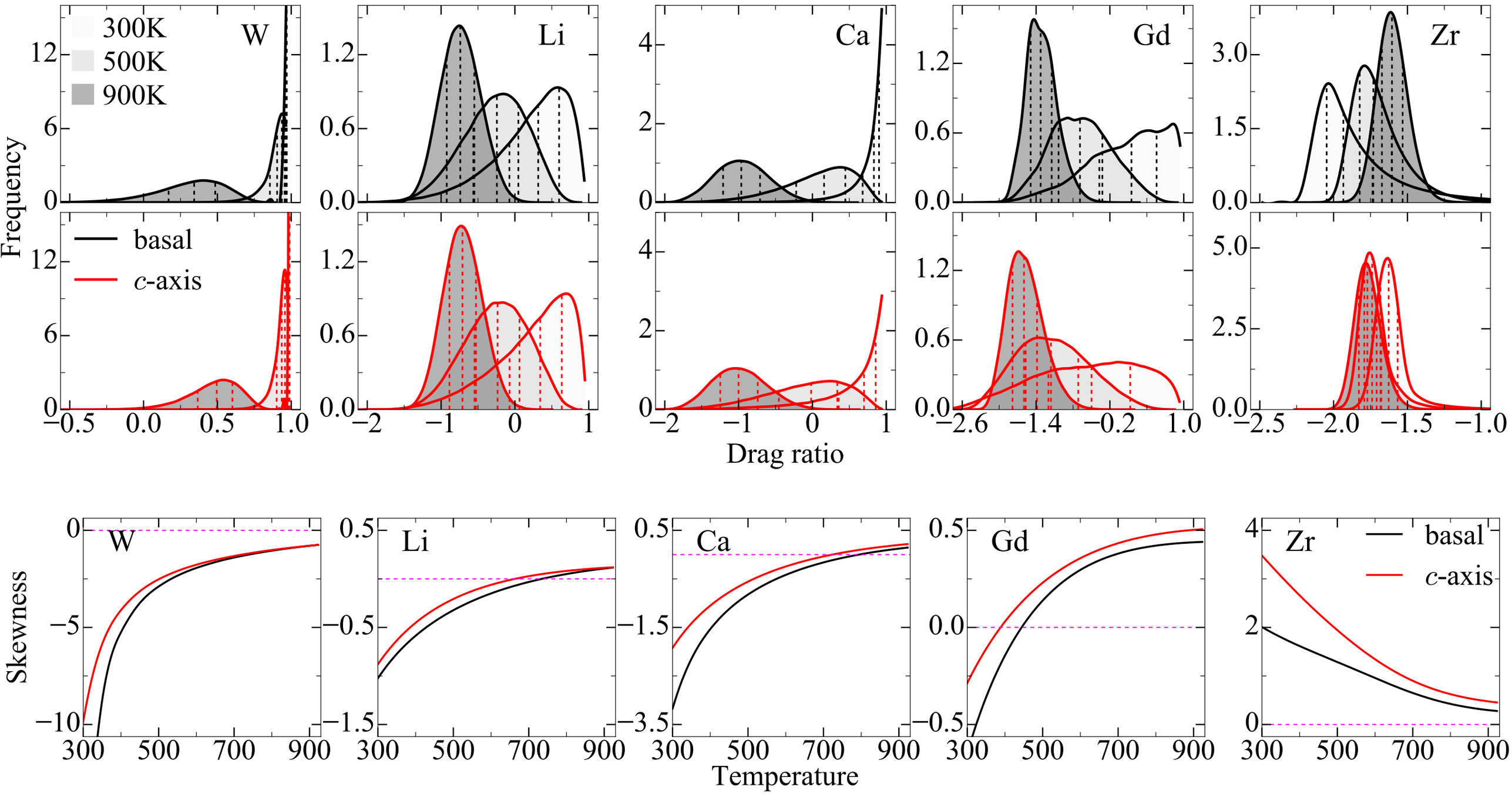
Agarwal and Trinkle, *Uncertainty Quantification in Multiscale Modeling* (2020)

Uncertainty in diffusivity: X in Mg vs. experiment



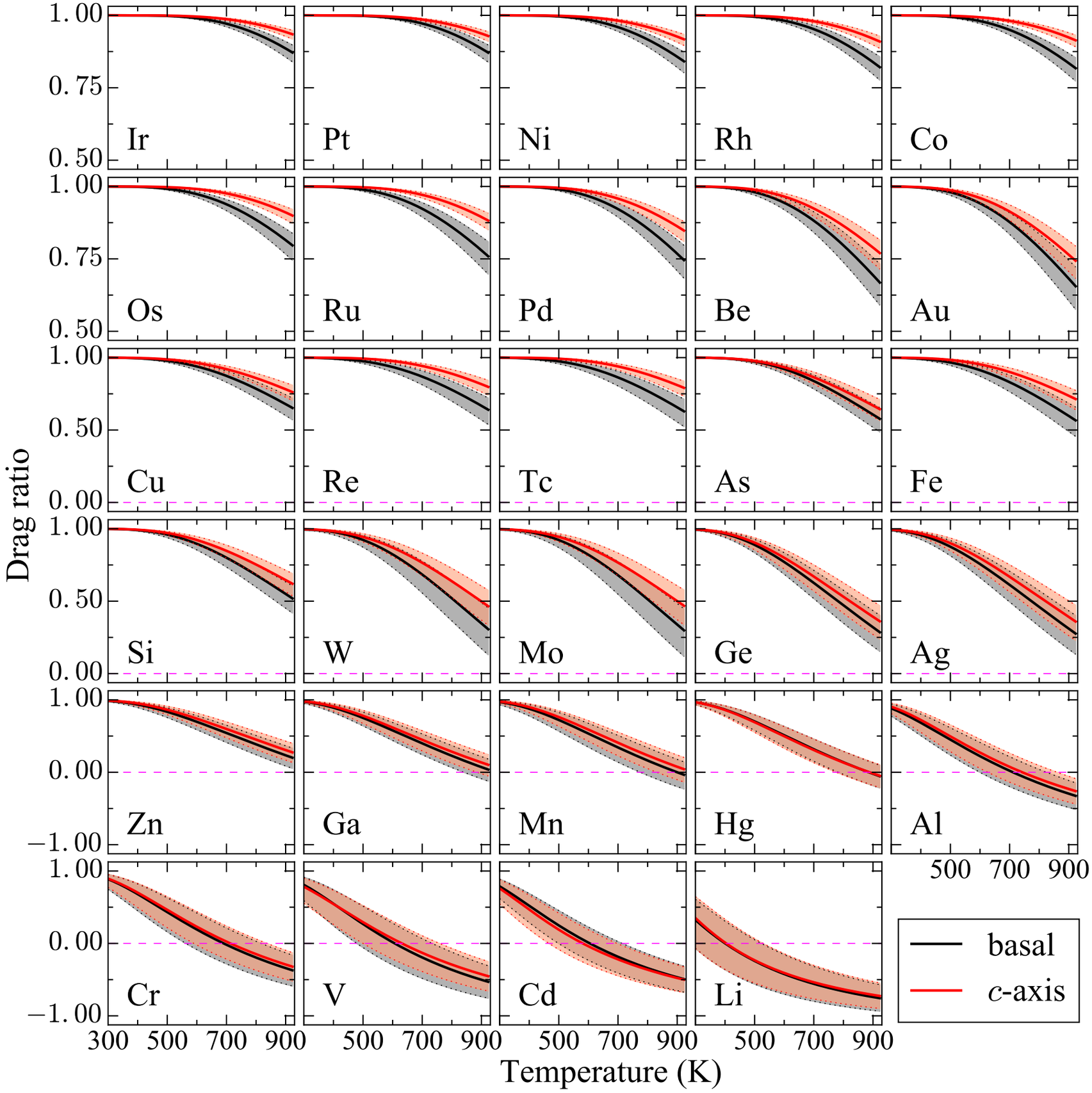
Agarwal and Trinkle, *Uncertainty Quantification in Multiscale Modeling* (2020)

Uncertainty in drag: histograms of X-Mg

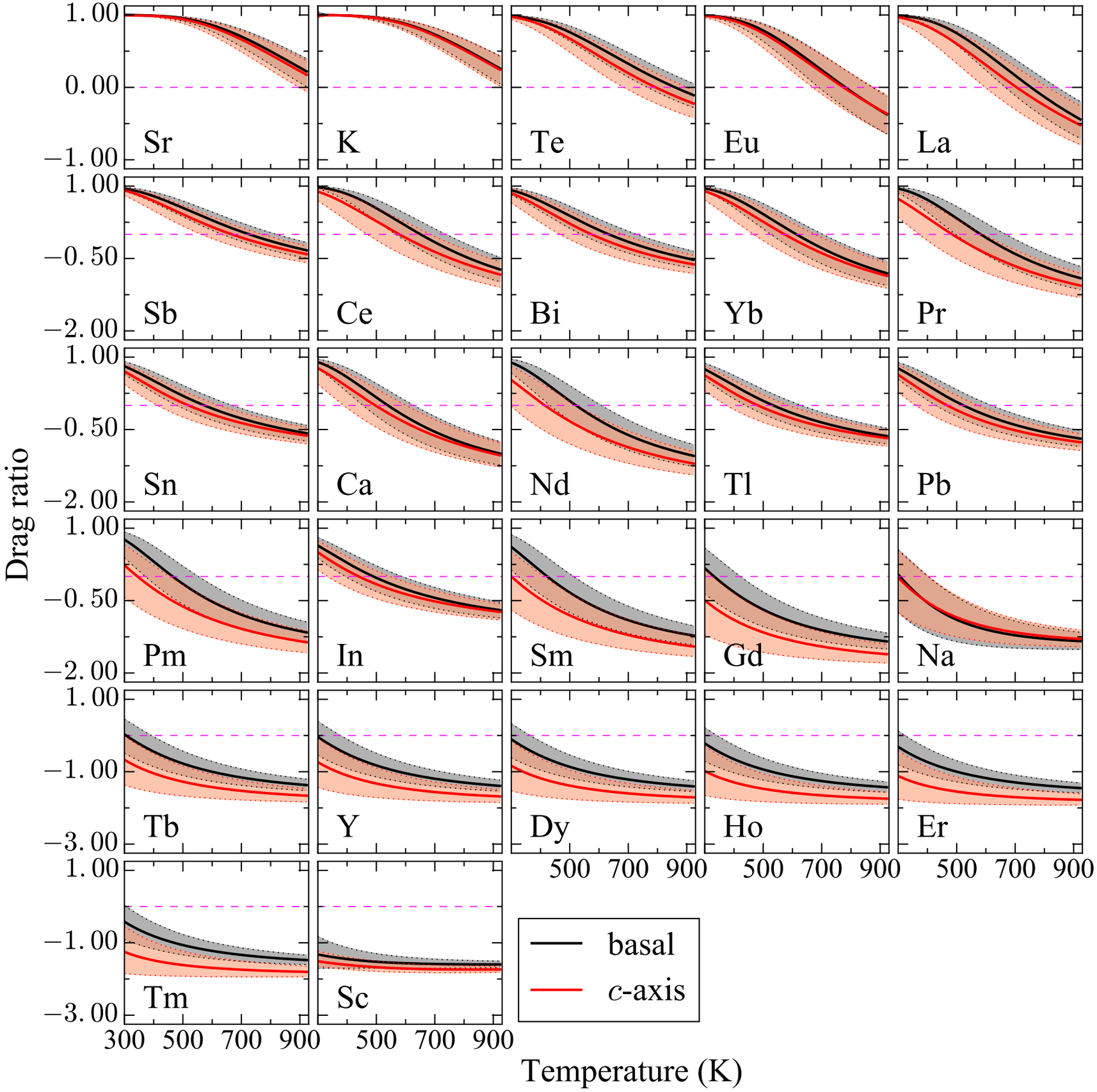


Agarwal and Trinkle, *Uncertainty Quantification in Multiscale Modeling* (2020)

Uncertainty in drag: X-Mg



Uncertainty in drag: X-Mg



Uncertainty quantification for solute transport modeling

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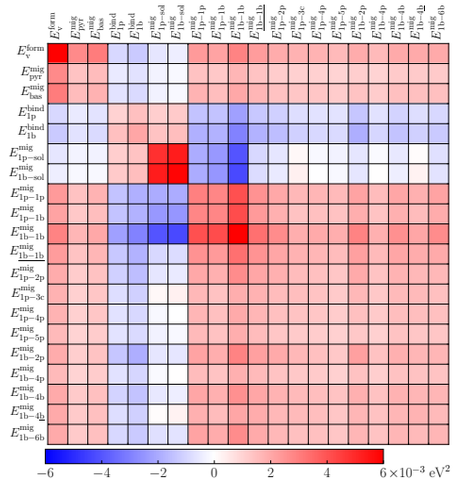
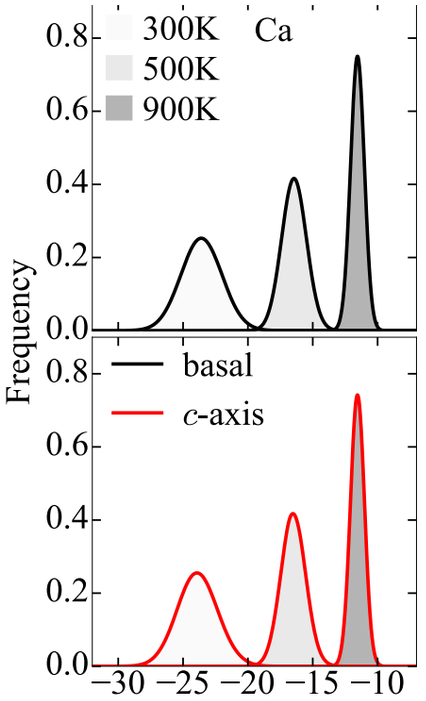
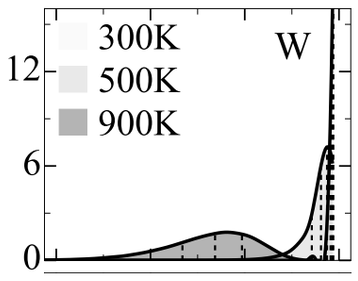
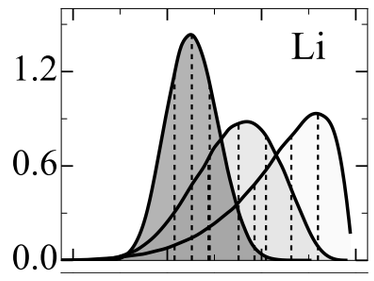
Motivation: who do we blame when experiments and theory don't agree?

- **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

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