High-Throughput and Ab Initio Molecular Dynamics approaches for Developing Alloy Diffusion Databases (with an Application to Radiation Induced Segregation in Ni-Cr Alloys)

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Multicomponent Diffusion Data and Its Impact on the Materials Design Process: Data Needed; Data Acquisition; and Data Application

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Outline

- Some thoughts on Ab-Initio Diffusion Calculations
- Simple Diffusion in Elements/Dilute alloys
  - High-throughput approaches
- Screening for Fast Oxygen Migration in Perovskites
  - High-throughput and datamining
- Ni-Cr Radiation Induced Segregation
  - Ab initio MD approach
- Summary

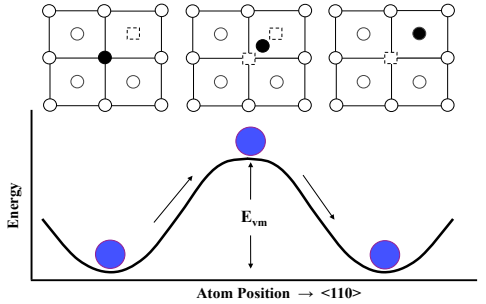
Some Thoughts on Opportunities in Ab-Initio Diffusion Calculations

- Simple diffusion (no or limited structural/chemical disorder)
  - Pure elements, pure sublattices in ordered phases, dilute impurities, simple surfaces, …
  - Ab initio (CNEB + Phonons) + Analytic models => D
  - Opportunities for high-throughput/datamining approaches
- Complex diffusion (structural/chemical disorder)
  - Concentrated alloys, grain boundaries, interfaces, clusters, …
  - Ab initio (CNEB + Phonons) + Kinetic Monte Carlo => D
  - Molecular Dynamics (for “low” barriers ~0.5 eV) => D

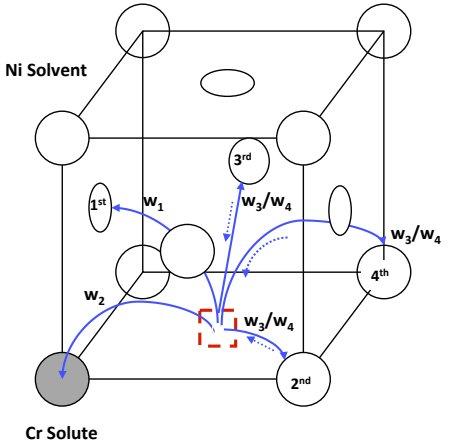
Simple Diffusion in Elements/Dilute Alloys: High-Throughput Approaches

Basic Vacancy Diffusion for Pure Elements, Dilute Alloys

- **Diffusion in pure elements:**
  - Dominated by a single defect formation and migration energy taking ~10 hours to predict
- **Diffusion in dilute alloys:** multi-frequency models can predict D accurately
  - Dominated by ~5 defect and migration energies taking few days to predict



$$D = a^2 f \nu \exp\left(-\left(E_{vf} + E_m\right)/kT\right)$$



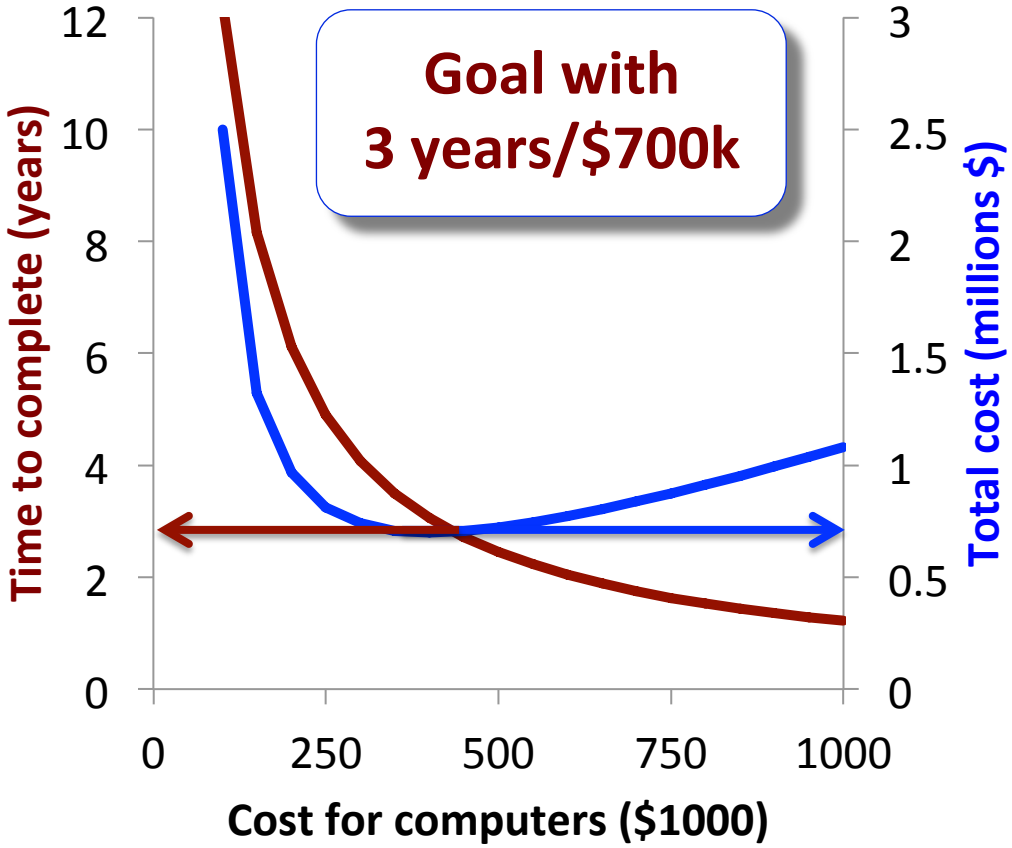
Opportunity for database development with high-throughput calculations

High-Throughput for Pure Elements, Dilute Alloys – A Materials Genome Opportunity

Determine D* for pure A and $A_{1-x}B_x$ (x<<1) for all elements in the FCC, BCC, and HCP crystal structures

Resource needs

- ~40 viable pure elemental systems in each structure ➔ 2,500 alloy-structure systems
- 1 system takes ~5 day on 100 cores (= $20k).
- So need about 3,500 Core-Years, 1 postdoc.



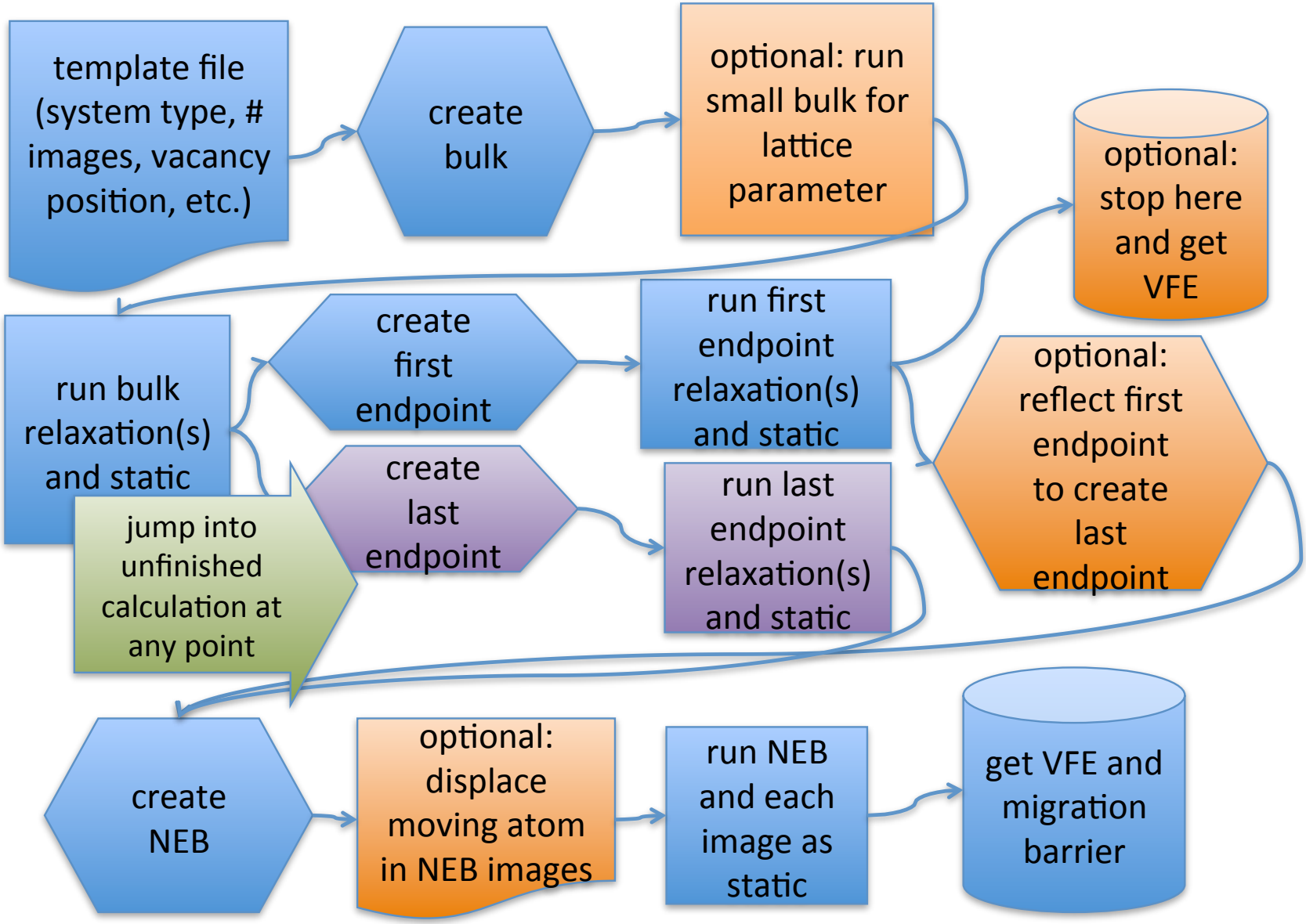
Present Efforts: High-Throughput for Pure Elements

Evaluate diffusion activation energy for all pure elements in all three crystal structures (HCP, BCC, FCC)

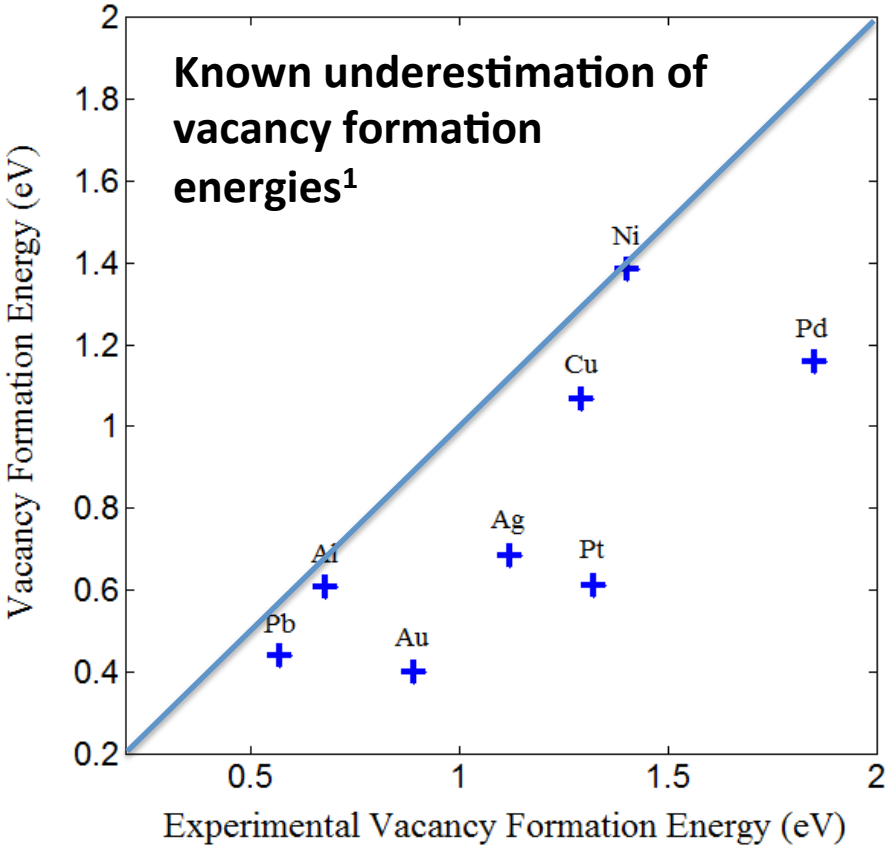
Status

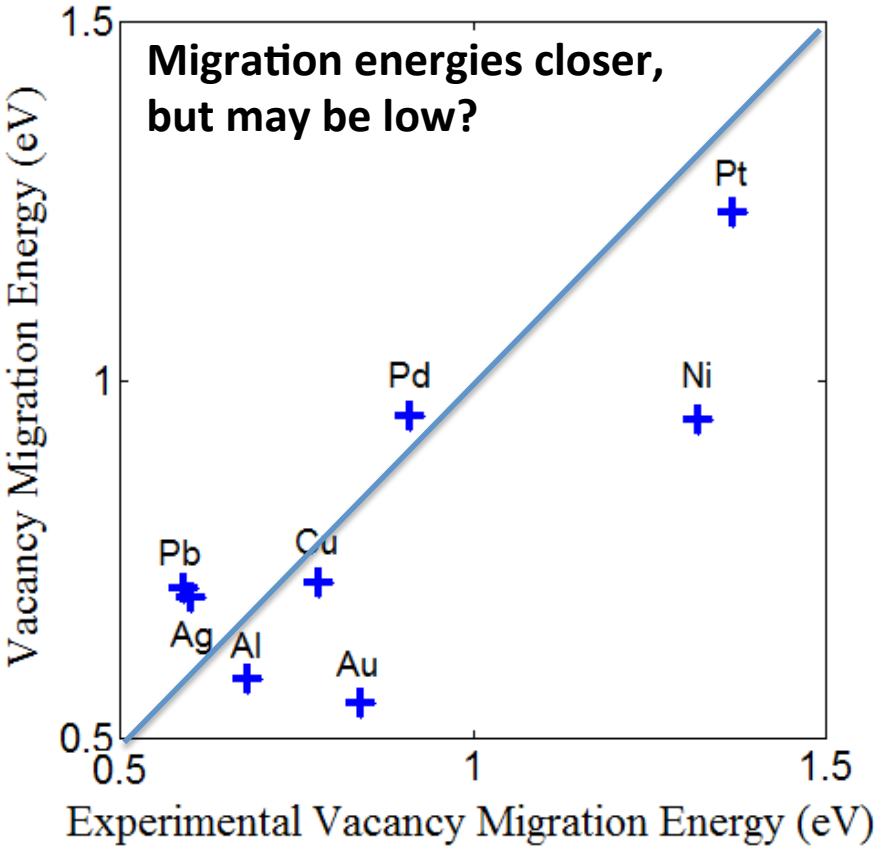
- Written automation codes to perform high-throughput computations
- # Completed Evac calculations = 47 hcp + 48 fcc = 95
- # Completed Emig calculations = 24 hcp + 43 fcc = 67
- Rate of Completion has been ~ 1 system/day on 100 cores
- All calculations with DFT from VASP, GGA, PAW
- **Work done with one undergraduate guided by a graduate student**

High-Throughput Diffusion Calculations – Python Codes



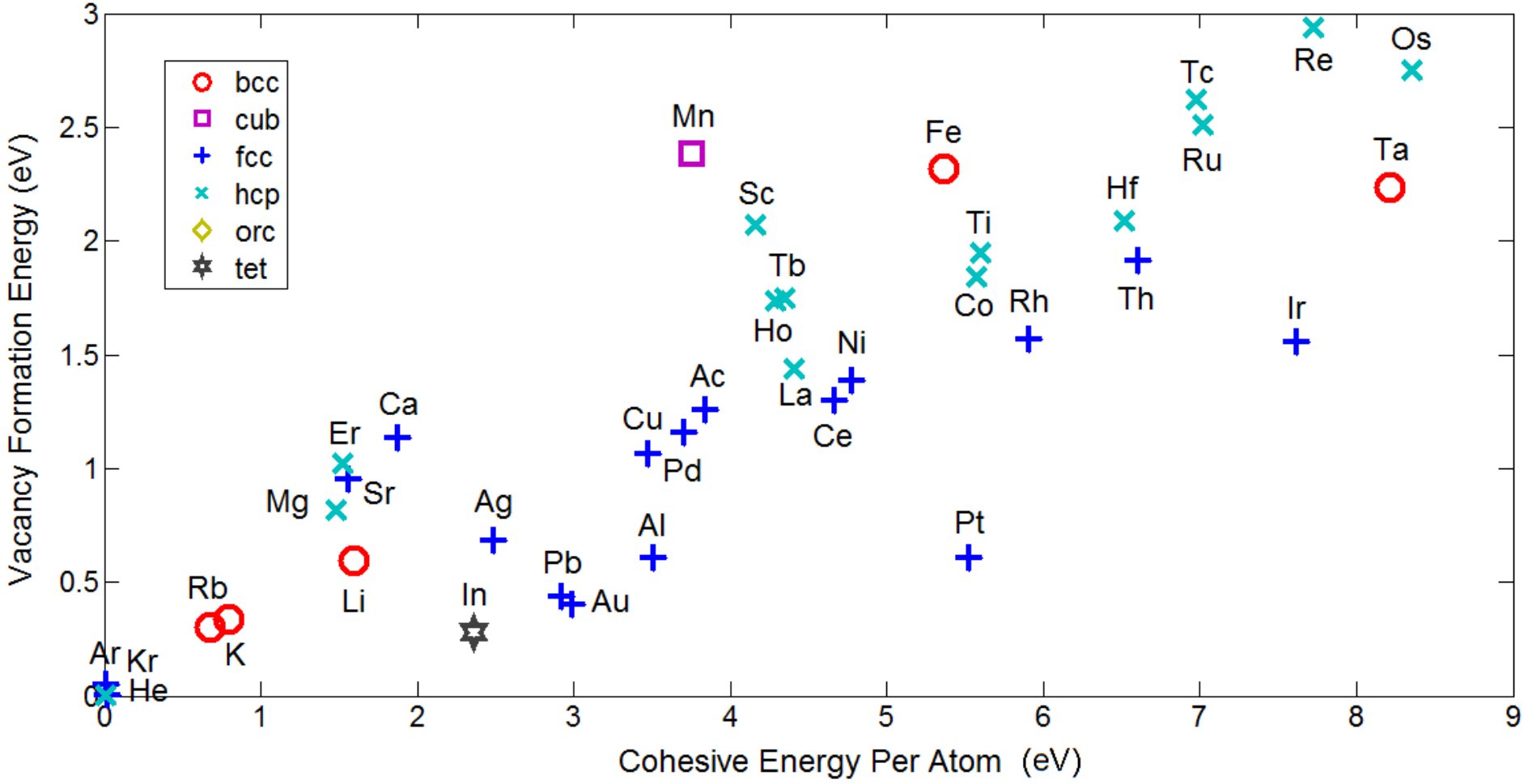
Trends vs. Experiment



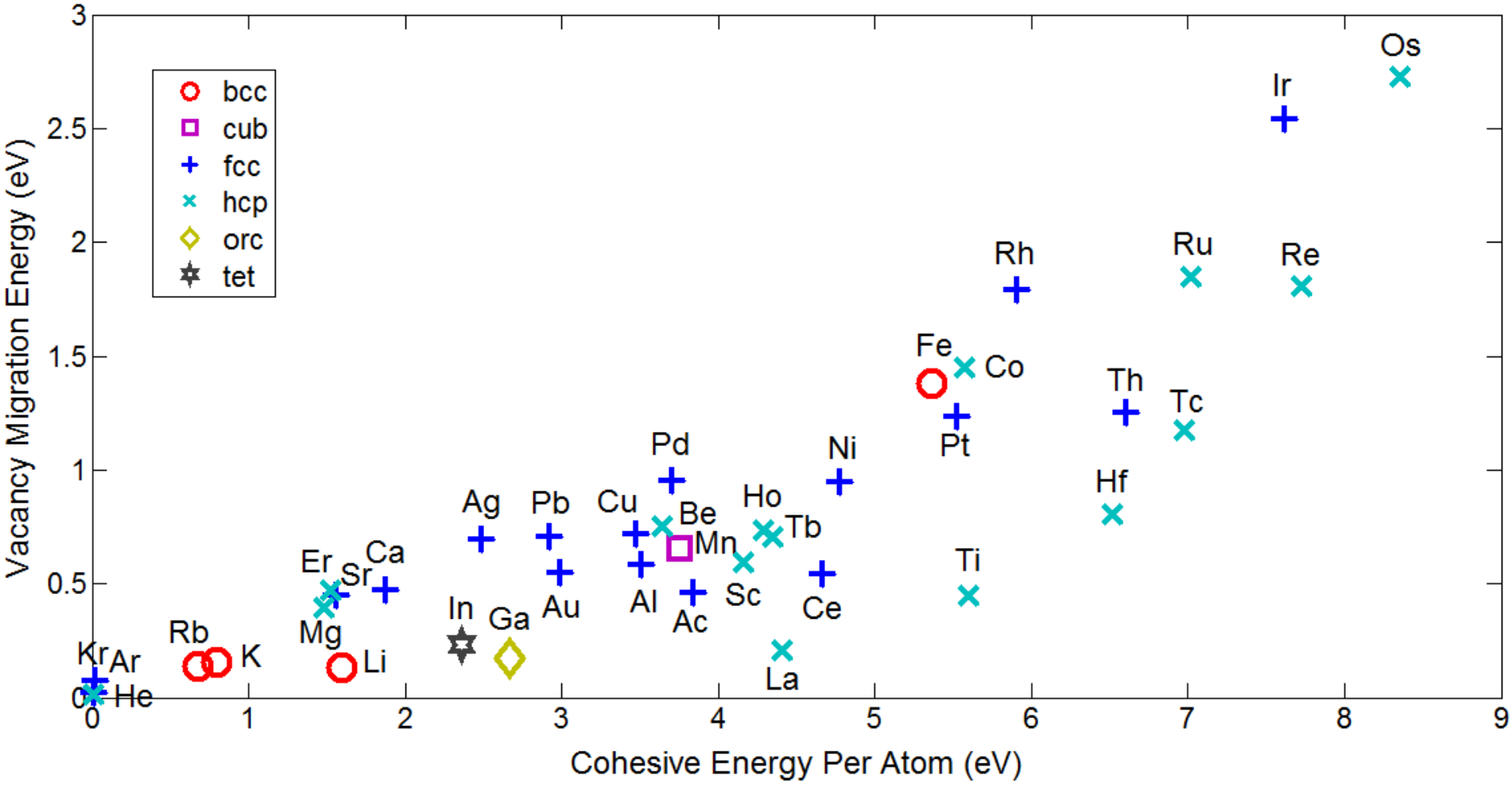


[1] A. Mattsson, et al., PRB (2002)

FCC Evac versus Ecoh/atom



FCC Emig versus Ecoh/atom



Summary of Simple Diffusion in Elements/Dilute Alloys

- High-throughput approaches can enable comprehensive databases – Large scale impact for small scale costs
  - Scale of 3 years/$700k.
  - Addition of phonons for attempt frequencies, thermal expansion (See Chelsea Zacherl talk for efficient methods) and interstitial diffusion also practical.
- Provide critical data for CALPHAD models, trend identification.
- Have written software and are running initial database at UW.

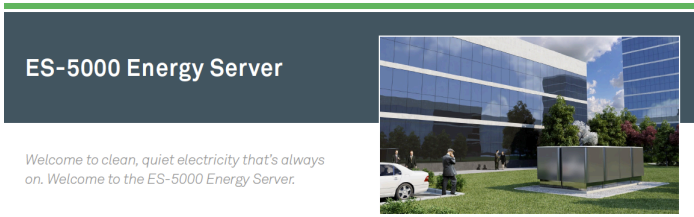
Screening for Fast Oxygen Migration in Perovskites

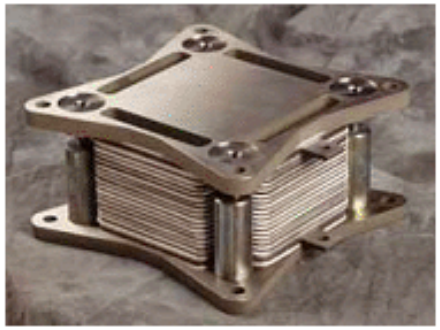
Motivation

- Oxygen diffusion is important in
  - solid oxide fuel cells (esp. low T)
  - sensors (response time)
- Fast diffusion characterized by high diffusion coefficient

$$D \propto exp\left(-\frac{E_m}{kT}\right)[V_O^{++}]$$

- Fast diffusion corresponds with low migration barrier $\mathbf{E_m}$



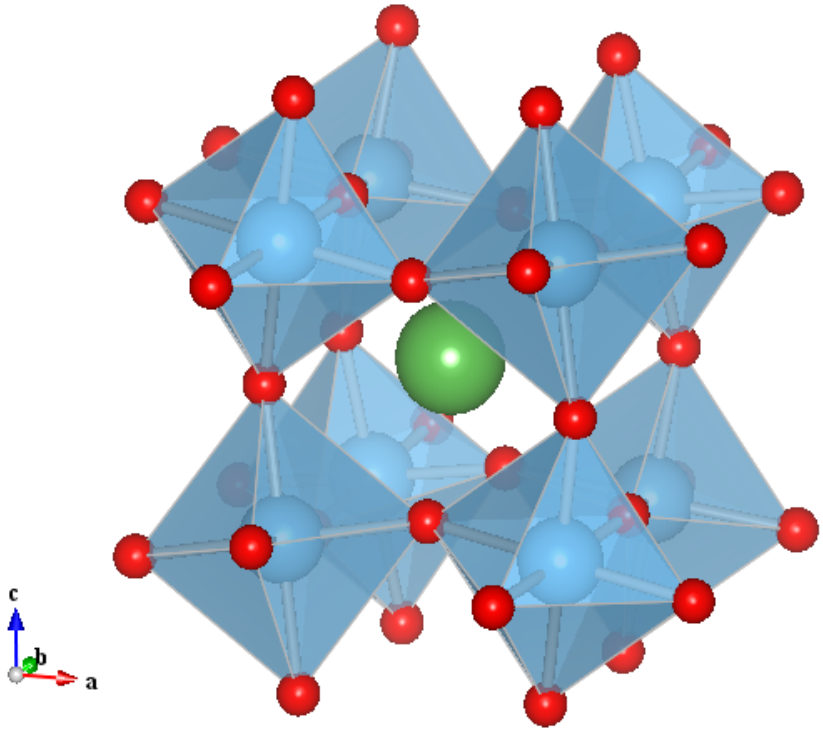


Planar SOFC - Courtesy of Siemens Westinghouse Power Corp.

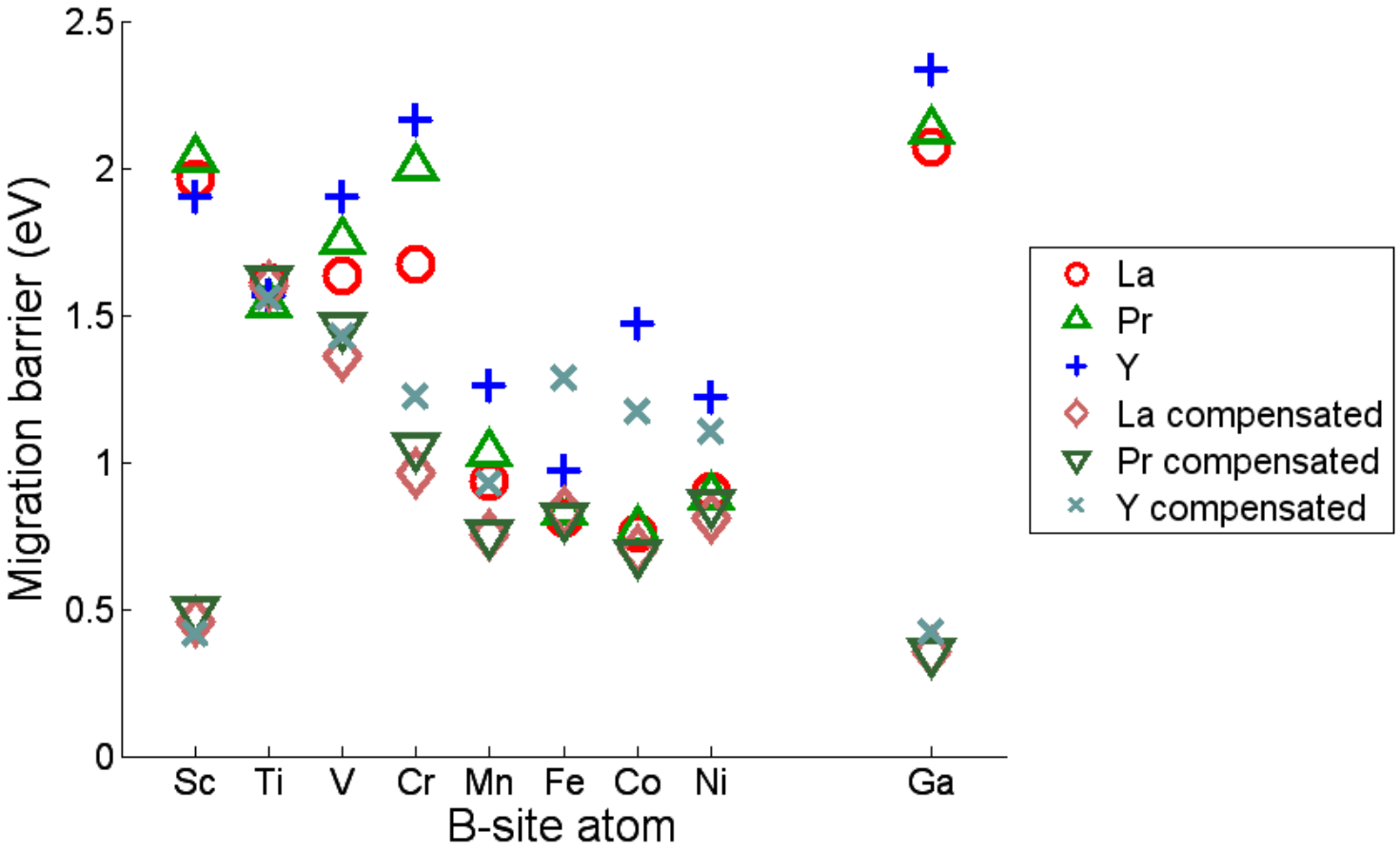
Oxygen sensor for fuel injection system
http://www.rockauto.com

Modeling Perovskite Oxygen Migration Barriers

- Perovskites: $A^{3+}B^{3+}O_3$
- [A = La, Pr, Y][B = 3d transition metal, Sc, Ga]O_3 = 27 systems, 54 barriers (compensated and uncompensated)
- Using VASP with PAW-GGA, PW-91, High-throughput NEB scripts
- 40-atom supercell with 4x4x4 Monkhorst-Pack kpoint mesh
- Climbing Image Nudged Elastic Band method, 3 images
- Using only one position and jump direction gives 100-200 meV error
- High-spin ferromagnetic start (high temperature operation above magnetic transition temperature)



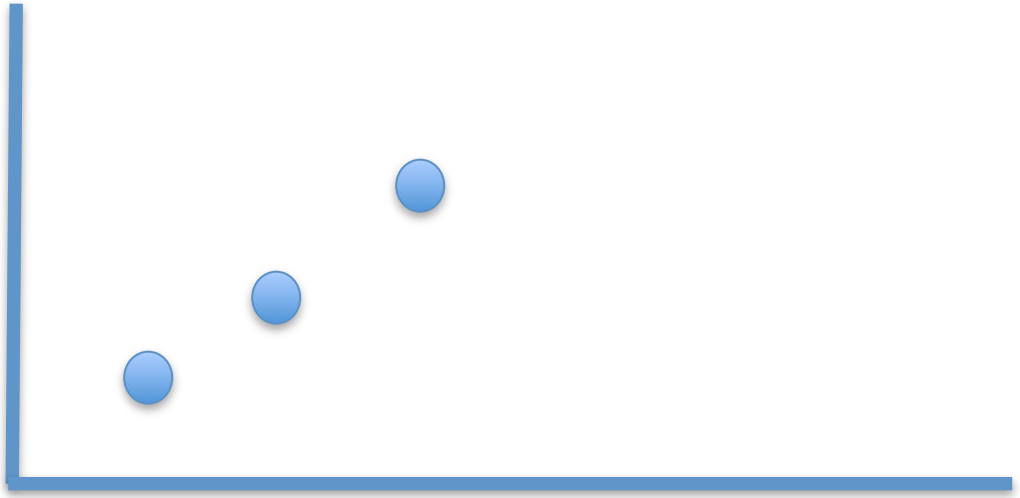
Perovskite Migration Energies



- Wide range, from 0.4-2.4 eV
- Challenging to explore whole perovskite space (>10,000 systems with A and B site alloying)
- Can we identify easy to determine descriptors to understand and predict these values?

Do Migration Barriers Trend with any Bulk or Endpoint Characteristics (Descriptors)?

Slow Calculations: NEB-calculated migration barrier



Fast calculations: Descriptors derived solely from the bulk and vacancy

Search for Descriptors with Partial Least Squares (PLS) Regression

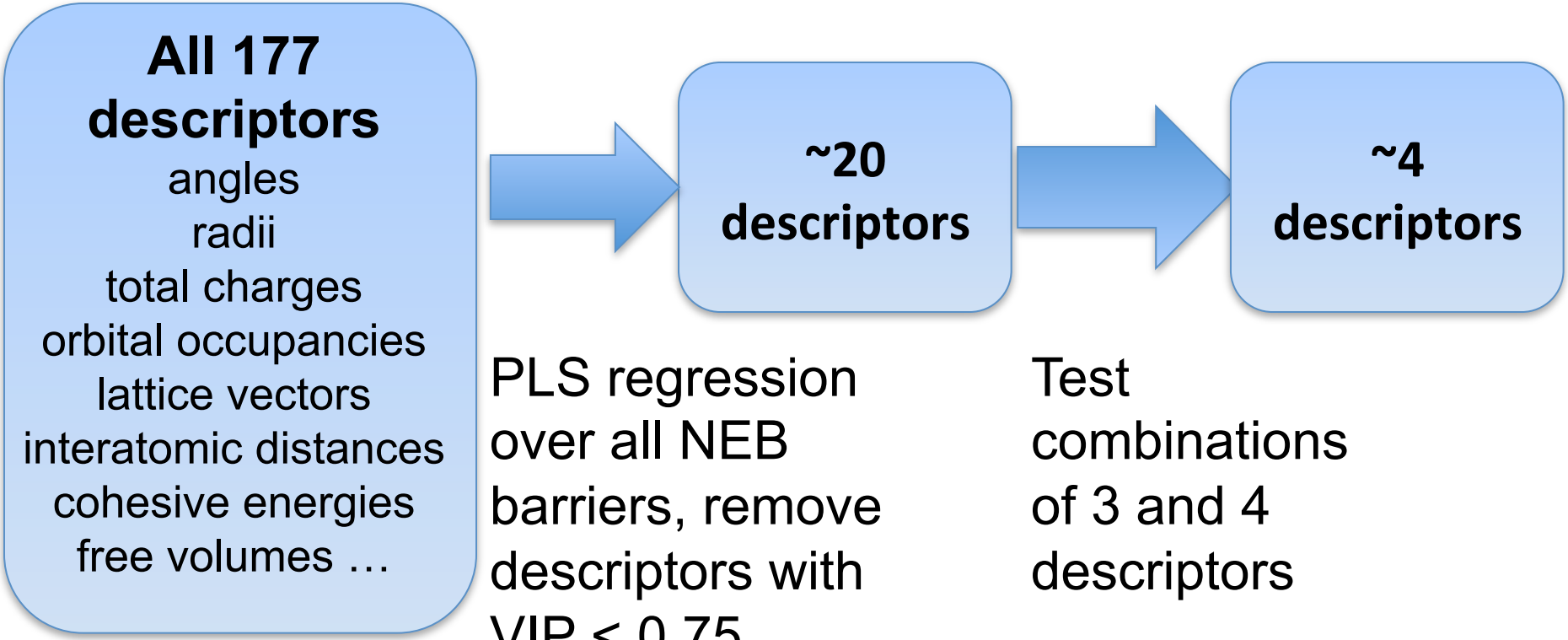
- PLS is a linear regression on descriptors

$$\textit{PLS barrier} = c_0 + c_1*(\textit{value of descriptor 1}) + c_2*(\textit{value of descriptor 2}) + c_3*(\textit{value of descriptor 3}) + \ldots$$

- Also returns a Variable Importance for the Projection (VIP) for each descriptor.

de Jong, Chemometrics and Intelligent Laboratory Systems ***18****, 251-263 (1993).*

Choosing Descriptors



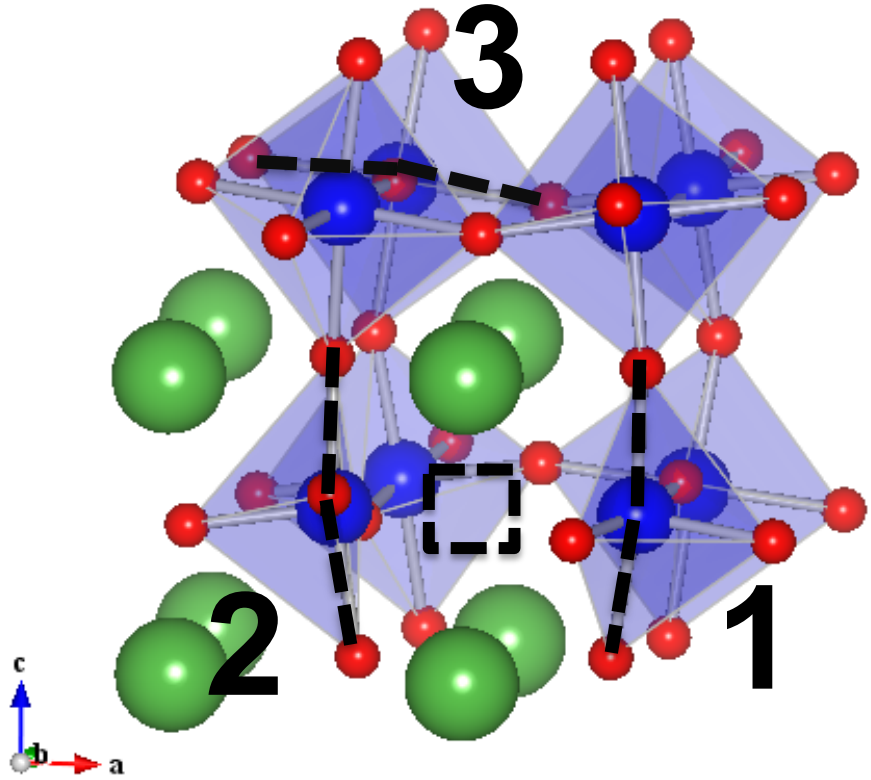
PLS regression over all NEB barriers, remove descriptors with VIP < 0.75, repeat until

Test combinations of 3 and 4 descriptors

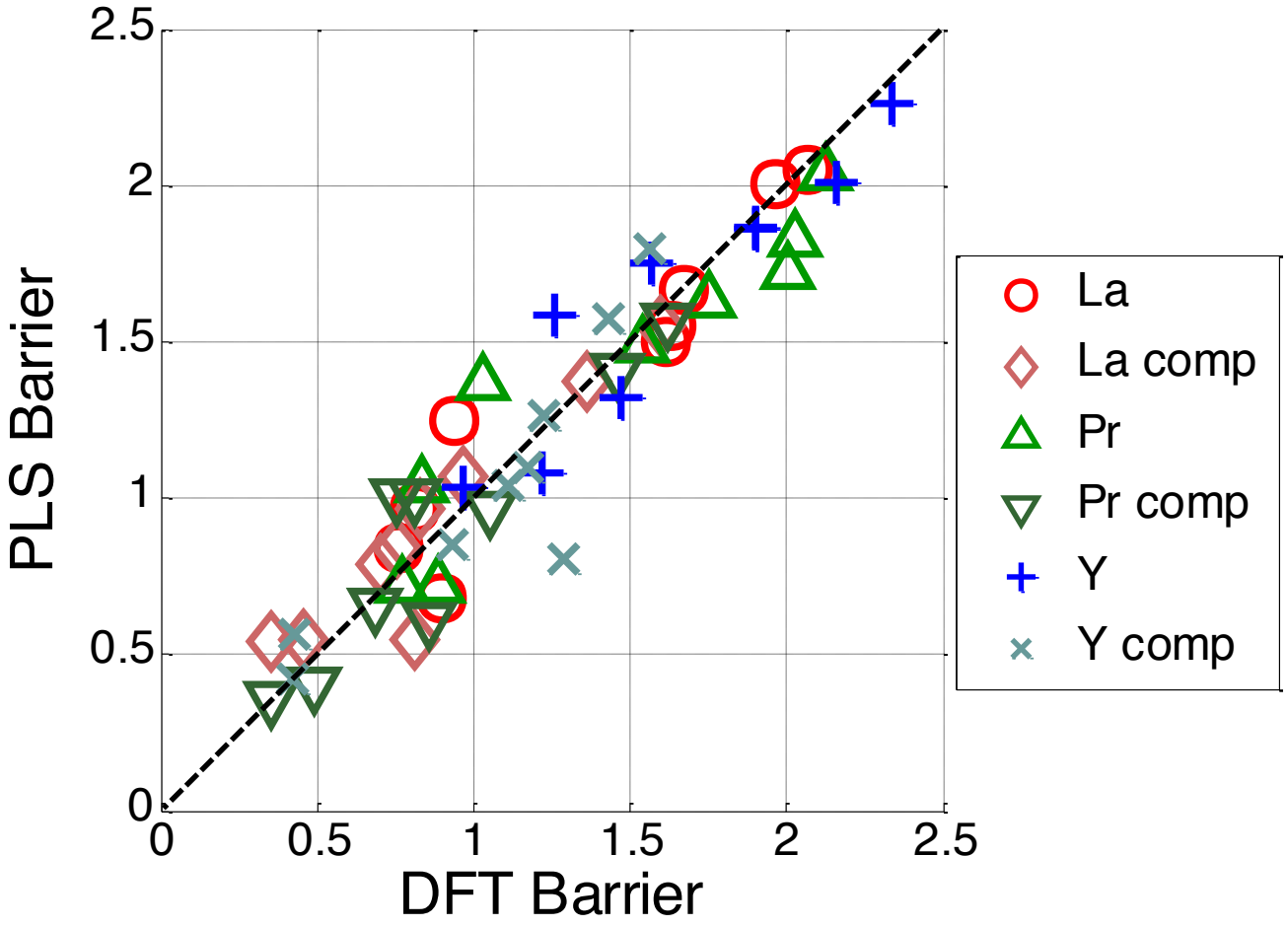
Non-rigorous method, but fruitful

PLS Derived Descriptors

VIP	Coeff.	Description
0.00	-45.613	Intercept
1.42	0.127	O-B-O 1
1.07	-0.074	O-B-O 2
0.80	0.239	O-B-O 3
0.71	-0.030	Bulk avg. B-O-B

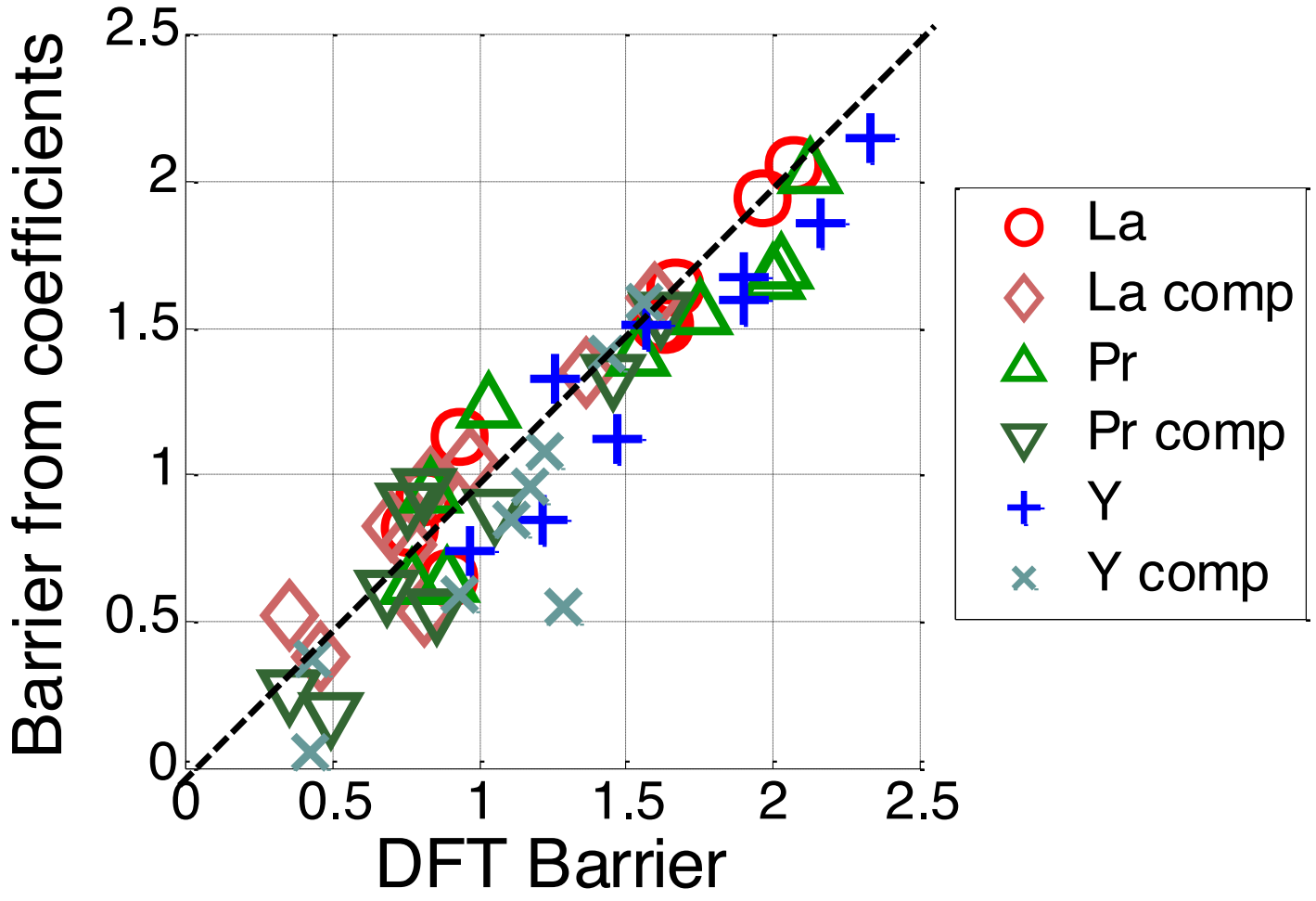


PLS Regression on All Data



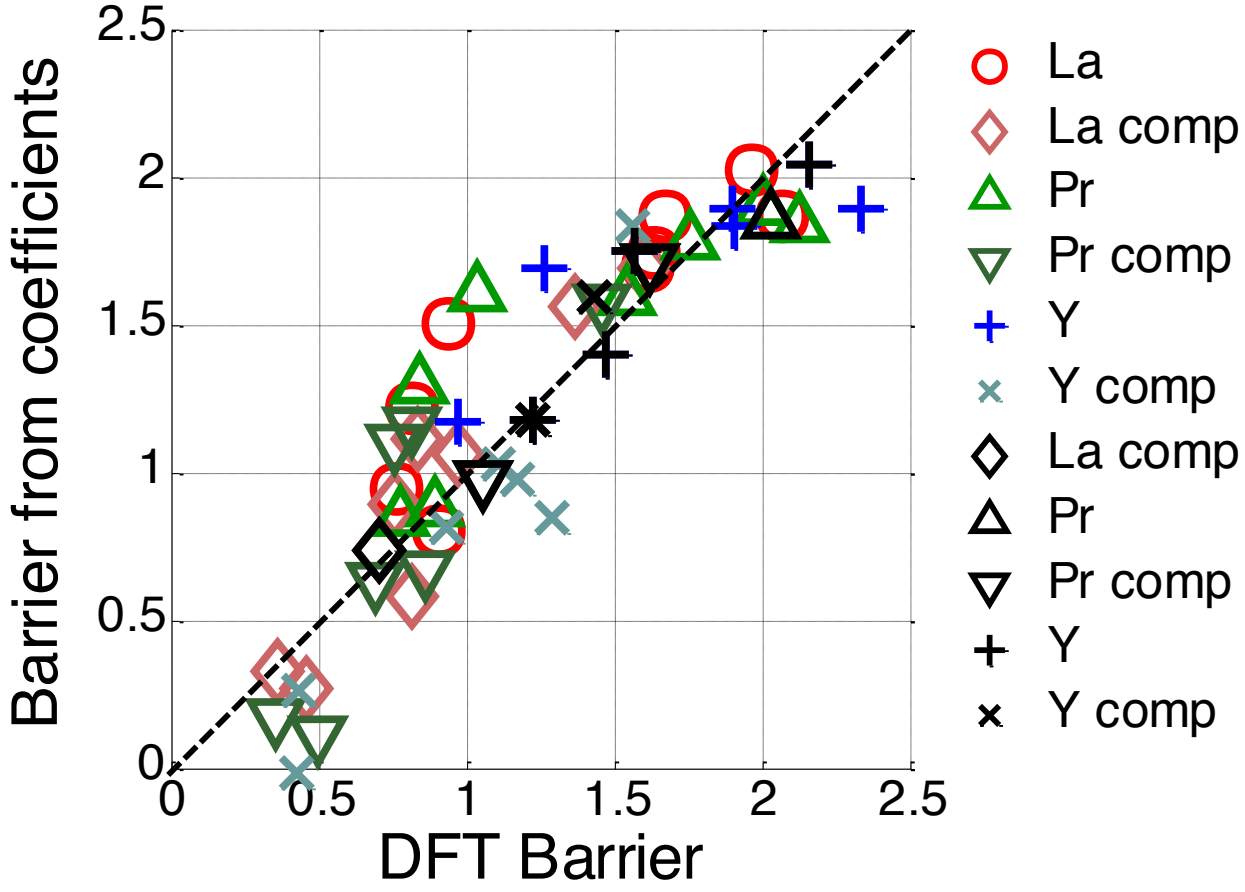
Max error: 0.50 RMS: 0.16

Predicting $PrBO_3$ and YBO_3 from $LaBO_3$



Max error: 0.73 RMS: 0.22

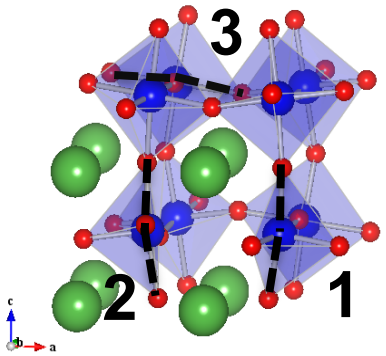
Predicting All Data from Random Subset (Fit to 10 systems)

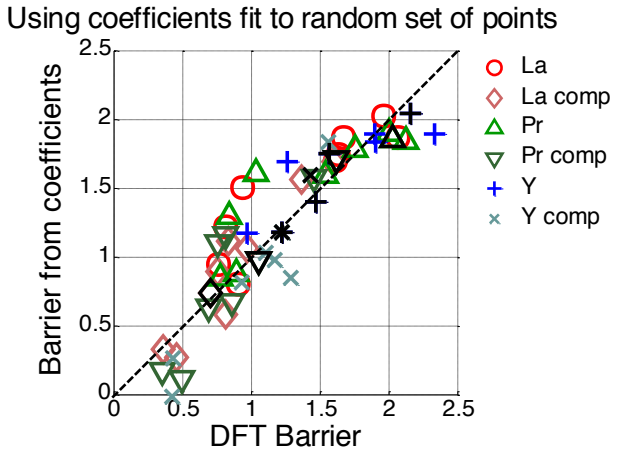


Max error: 0.58 RMS: 0.24

Summary of Screening for Fast Oxygen Migration in Perovskites

- Migration barriers of 54 ABO_3 perovskites can be represented with only
  - three O-B-O bond angles in the first endpoint
  - the average relaxed B-O-B bond angle in the bulk
- **Data from bulk and vacancy can now be used to screen for low barriers.**
- May be many similar ways to accelerate migration energy calculations on complex structures with **mining of descriptors.**





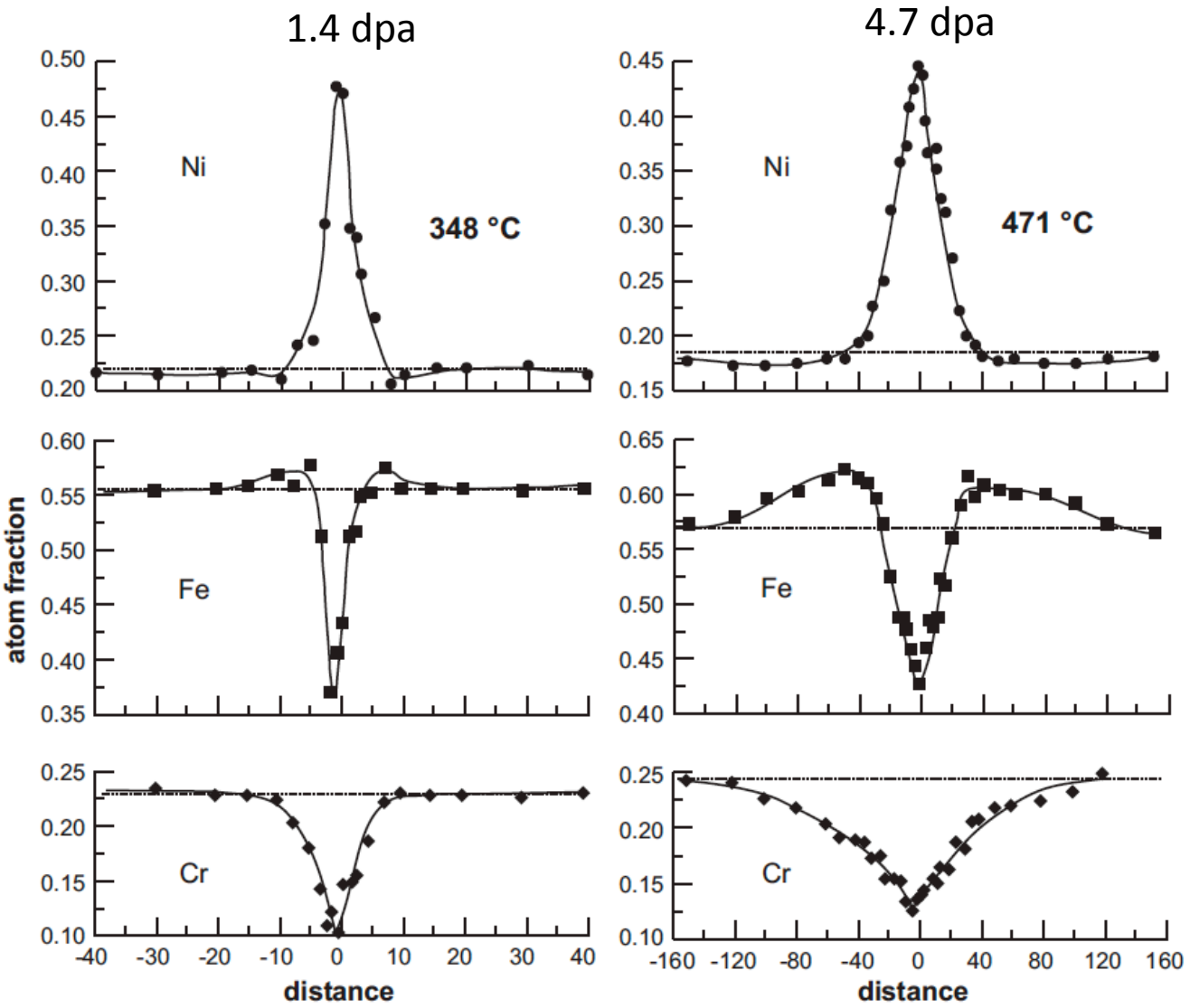
Ni-Cr Radiation Induced Segregation
Ab initio Molecular Dynamics Approach

What is Radiation Induced Segregation (RIS)?

A change in composition at a defect sink (grain boundary, void, dislocation, surface, …) due to unequal transport of species to the sink by radiation induced defects

RIS in Fe-Cr-Ni Steels

Austenitic (fcc) steel: Fe-20Cr-25Ni-0.8Nb (wt%)

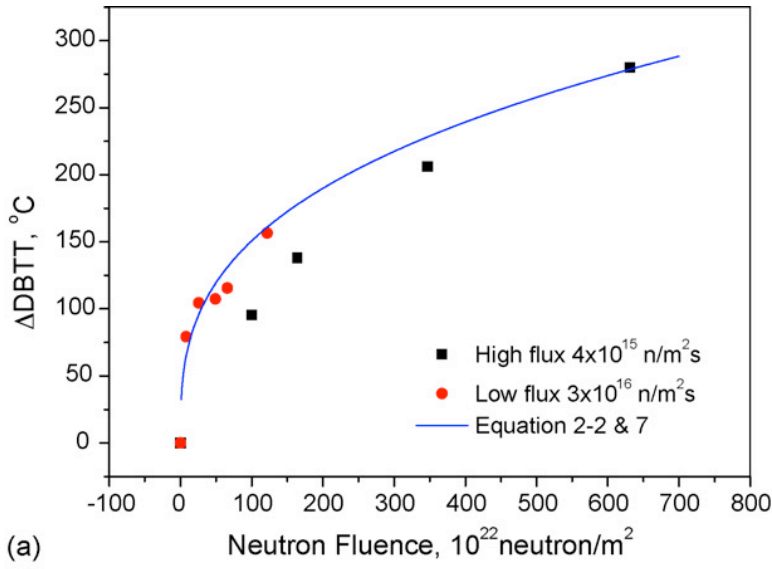


Norris, et al., ASTM STP 1125 '92; Ashworth, et al. JNM '92; Ardell, *Materials Issues for Generation IV Systems '08*

Why Does RIS Matter?

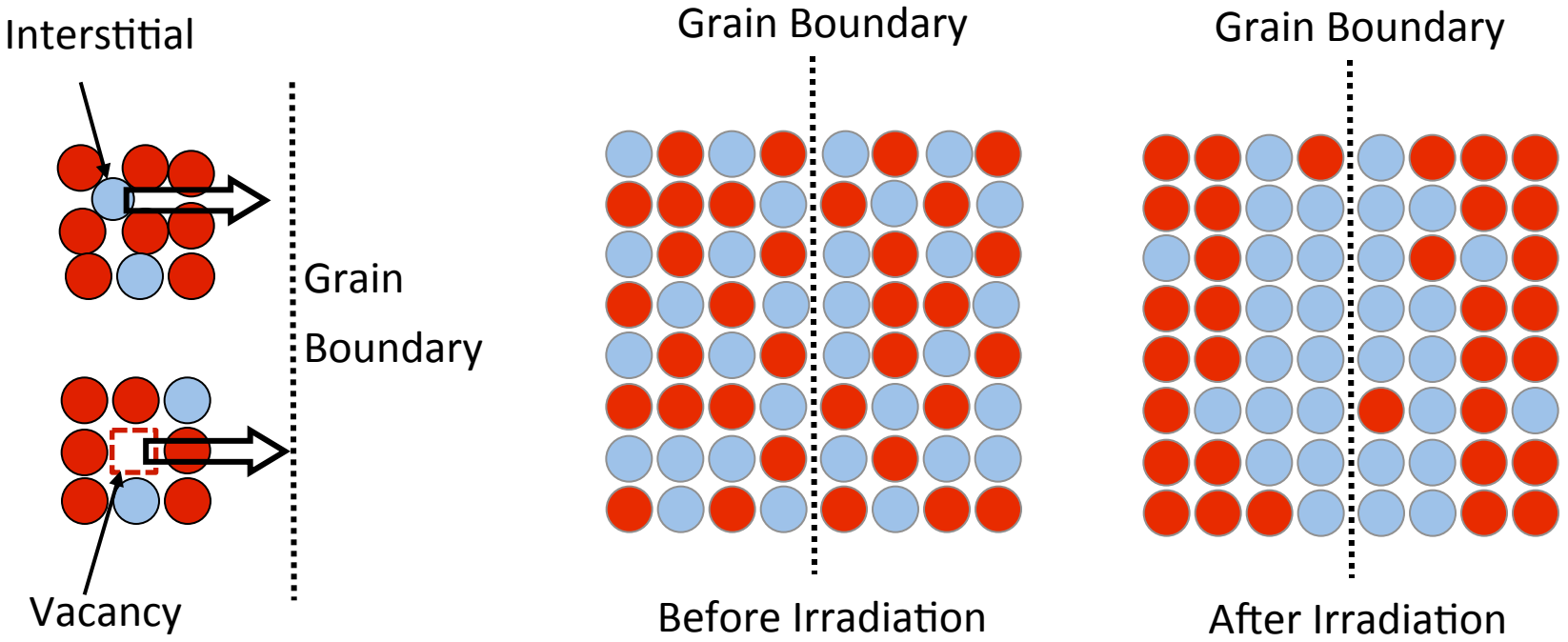
- Linked to Radiation Induced Precipitation (RIP)
- Linked with intergranular failure and void swelling
- Potentially contributes irradiation assisted stress corrosion cracking (IASCC)
- Particular interest in Cr RIS in steels as Cr is key for corrosion protection

Lu, et al, *MSE* '06



RPV Steel DBTT due to P RIS

The Atomic Level View of RIS



Possible RIS Mechanism to Enrich Blue

- Migrates preferentially as interstitials
- Exchanges preferentially with vacancies
- Defect-solute interaction, e.g. vacancies drag species to sink

$$D^{I}_{Blue} > D^{I}_{\mathrm{Re}\,d}$$

$$D^{V}_{Blue} < D^{V}_{\mathrm{Re}\,d}$$

$$D_{VBlue} > 0$$

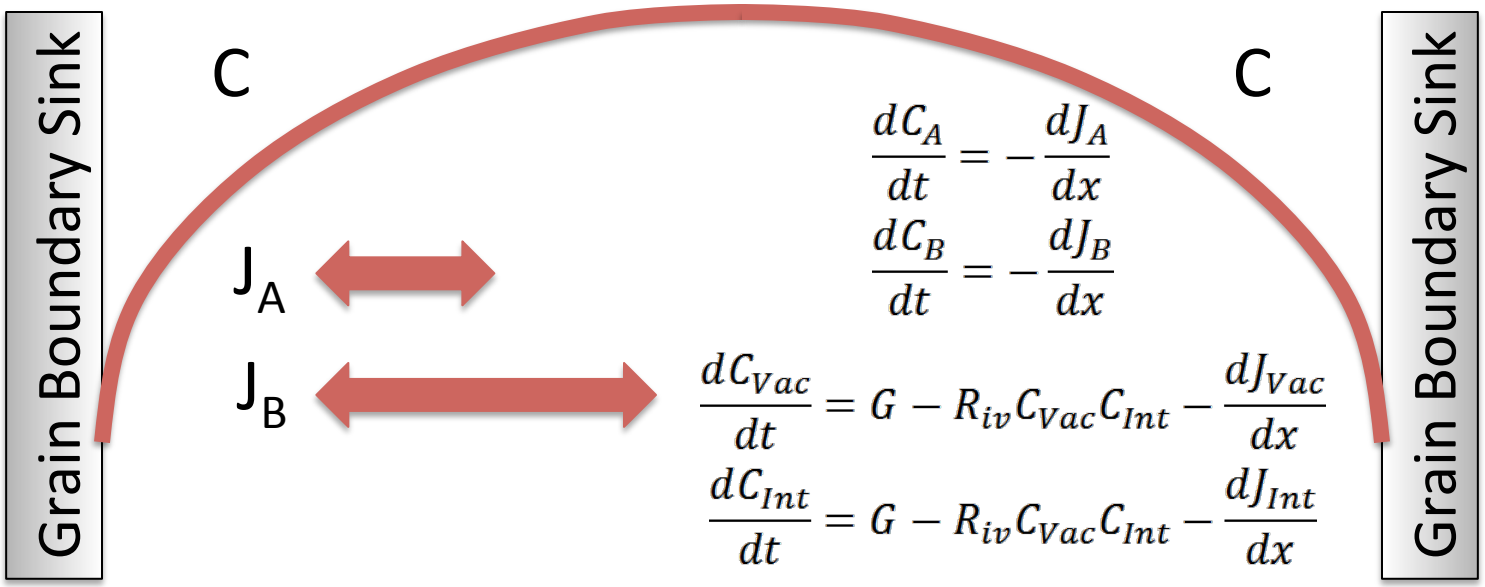
Modeling RIS

Obtain flux from diffusion coefficients

$$J_i = -\sum_{j=1}^{N} D_{ij} \nabla n_j$$

Wiedersich, et al., J. Nucl. Mater. '79

Solve for time evolution of concentrations with standard generation/annihilation terms and perfect sink boundary



Existing RIS Models for FCC Steels

- Many existing Cr RIS models in steels
- Mixed success in quantitative agreement on RIS prediction
- Poor qualitative agreement on mechanism
  - **Ni-solute interstitial binding:** N. Q. Lam, *Proceedings of the Symposium on Radiation Damage Analysis for Fusion Reactors* (1983)
  - **Vacancy exchange mechanism:** J.M. Perks and S.M. Murphy (BNES, London, 1987)
  - **Vacancy exchange mechanism:** S. Watanabe, et al., *J. Nucl. Mater.* (1995):
  - **Cr-Interstitial repulsion:** R.G. Faulkner, *International Workshop on Defect Production, Accumulation and Materials Performance in an Irradiation Environment* (1997)
  - **Vacancy exchange mechanism, concentrations dependent D:** T.R. Allen and G.S. Was, *Acta Materialia* (1998)
  - **Vacancy-Cr binding for TNES:** E. P. Simonen and S. M. Bruemmer (MRS Proceedings, 1999)
- **Present best model is vacancy exchange mechanism (Inverse Kirkendall)* but more fundamental understanding of active mechanisms is needed**

*G.S. Was, et al. JNM (2012)

Dilute Diffusion from Multifrequency Models

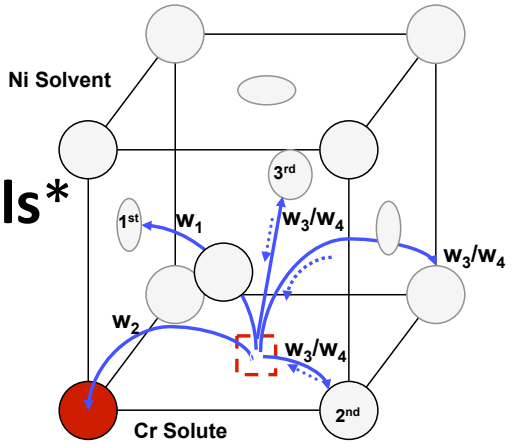
Ab Initio Energetics (E_V)

Thermodynamics (stat. mech. Models)
Kinetic rates (transition state theory)

Atomic scale concentrations, rates

$$C_V = e^{-E_{Vf}/kT} \quad R_V = \nu e^{-E_{Vm}/kT}$$

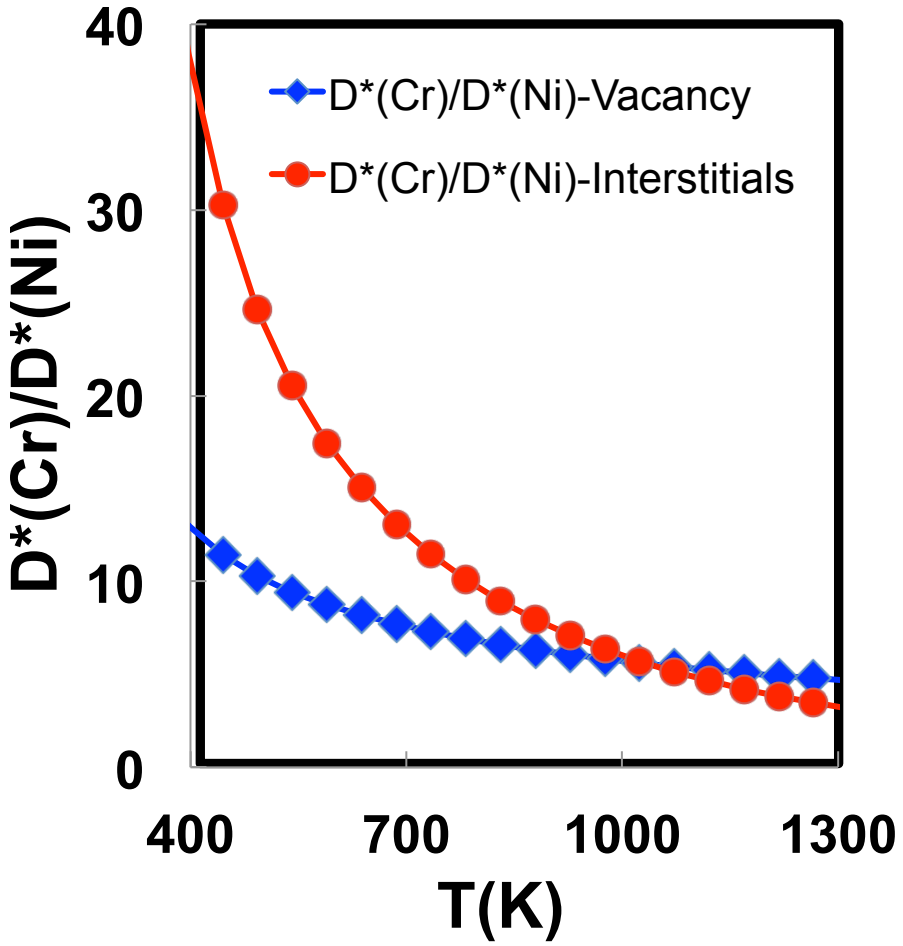
Multifrequency models*



Kinetic Coefficients (D)

*A.R. Allnatt and A.B. Lidiard, *Atomic Transport in Solids*, '96

Ratio of Tracer Diffusion Coefficients

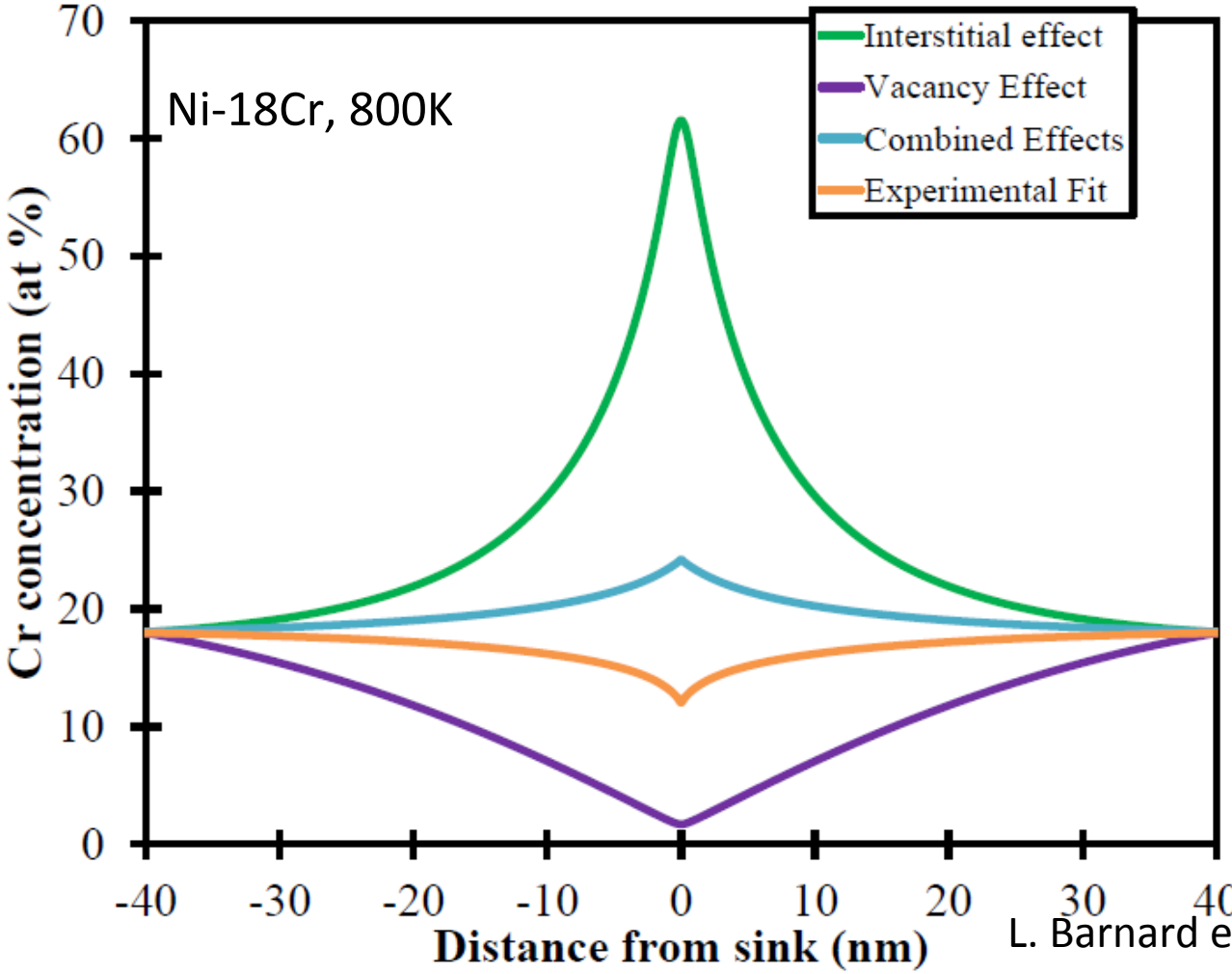


- For vacancies D*(Cr)/D*(Ni) ~ 8 (700K), typically ~ 2-3 from models. Cr much faster than expected!
- First insight into species dependent interstitials flux. Cr must faster!
- Suggest new idea
  - Vacancies deplete / Interstitial enrich Cr
  - Cr RIS a balance of vacancy and interstitial contributions

$$\Delta c_{Cr} \sim \left\{ -\frac{D^*_{Cr,Vac}}{D^*_{Ni,Vac}} + \frac{D^*_{Cr,Int}}{D^*_{Ni,Int}} \right\}$$

J.D. Tucker, R. Najafabadi, T.R. Allen, D. Morgan, *J. Nuclear Materials* (2010)

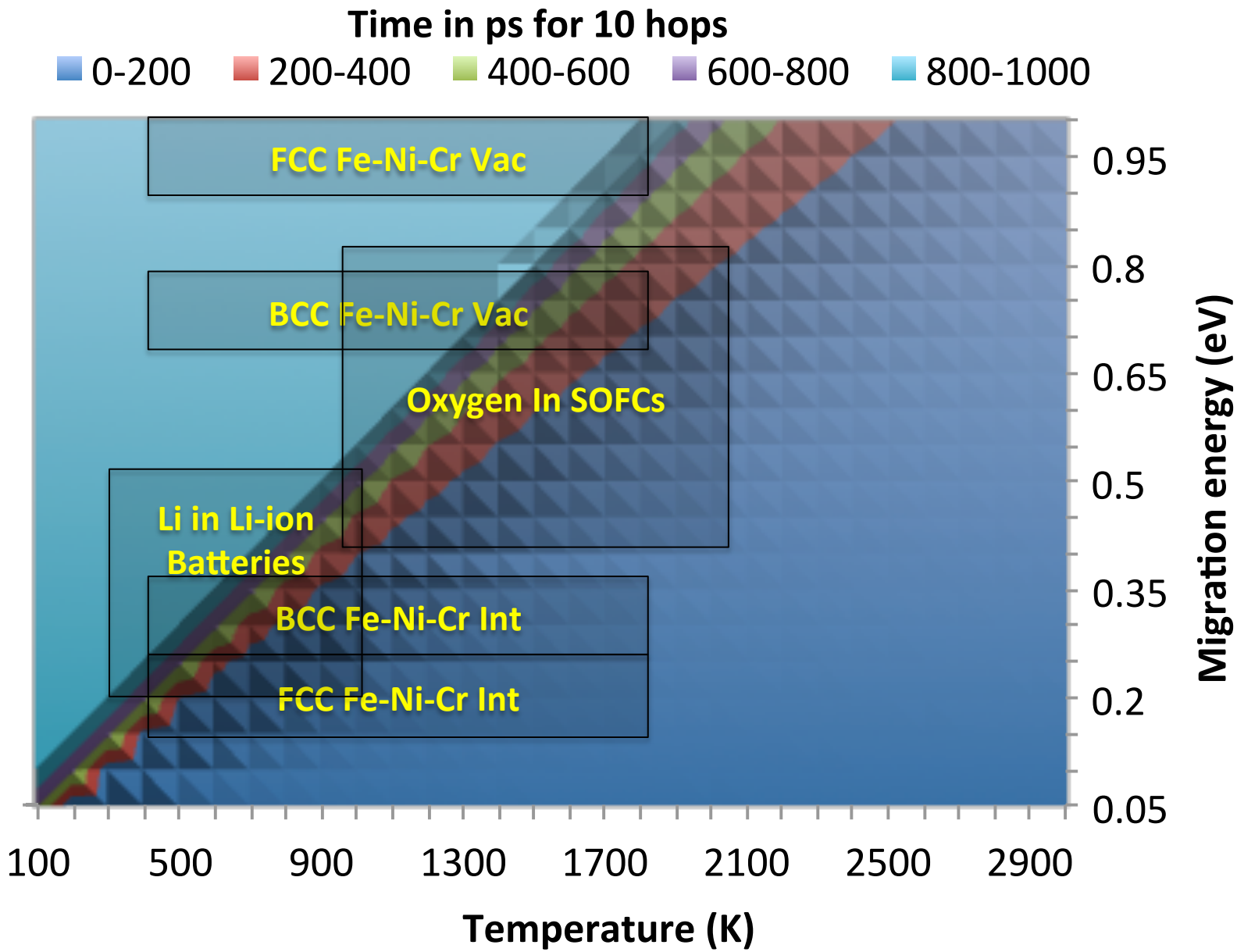
Interstitial vs. Vacancy Contributions to RIS



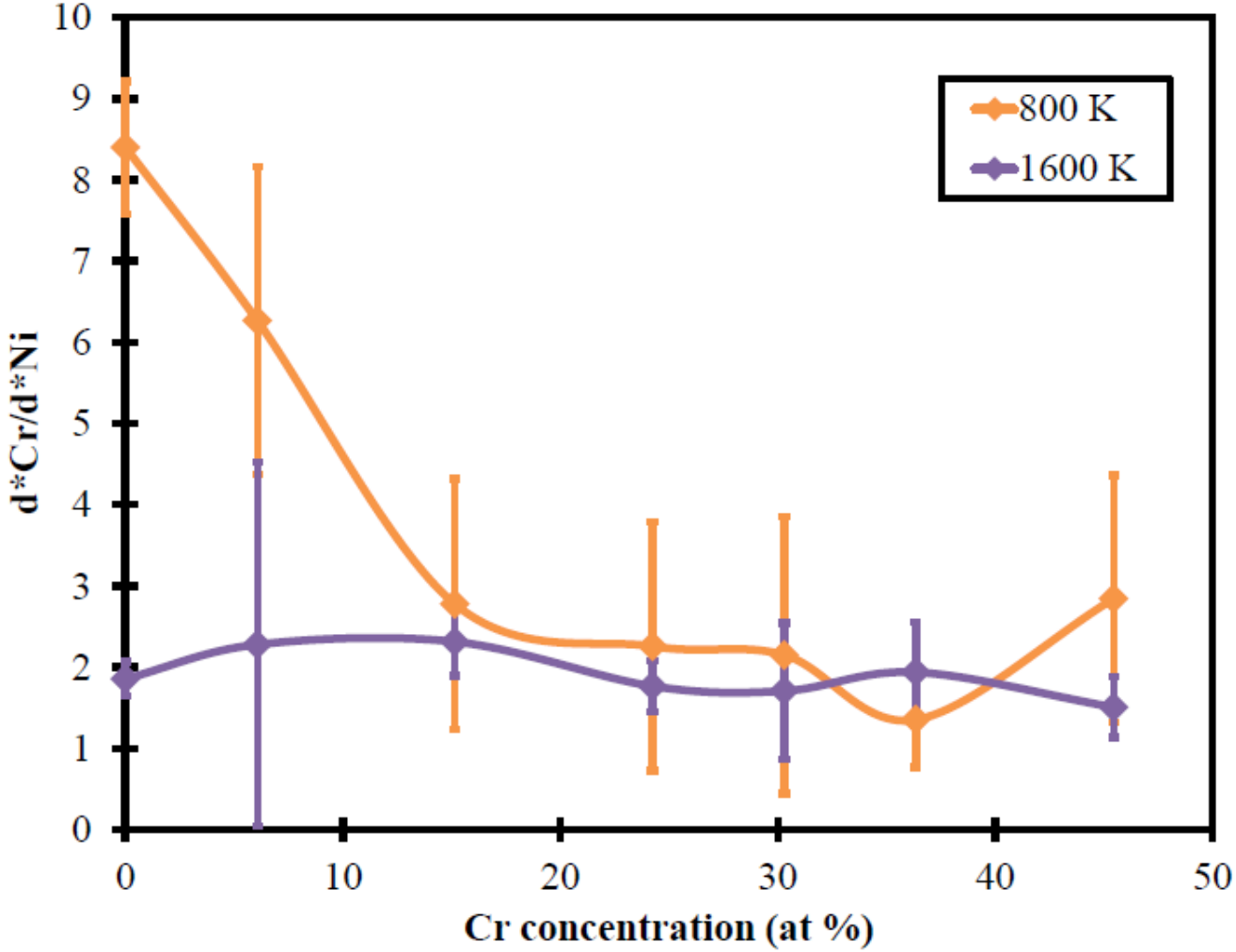
L. Barnard et al., *JNM* (2012)

- Vacancy values consistent with experiments but too strong
- Interstitials seem to be far too strong
- Missing composition dependence of interstitials!

Systems Accessible to Ab Initio Molecular Dynamics (AIMD)

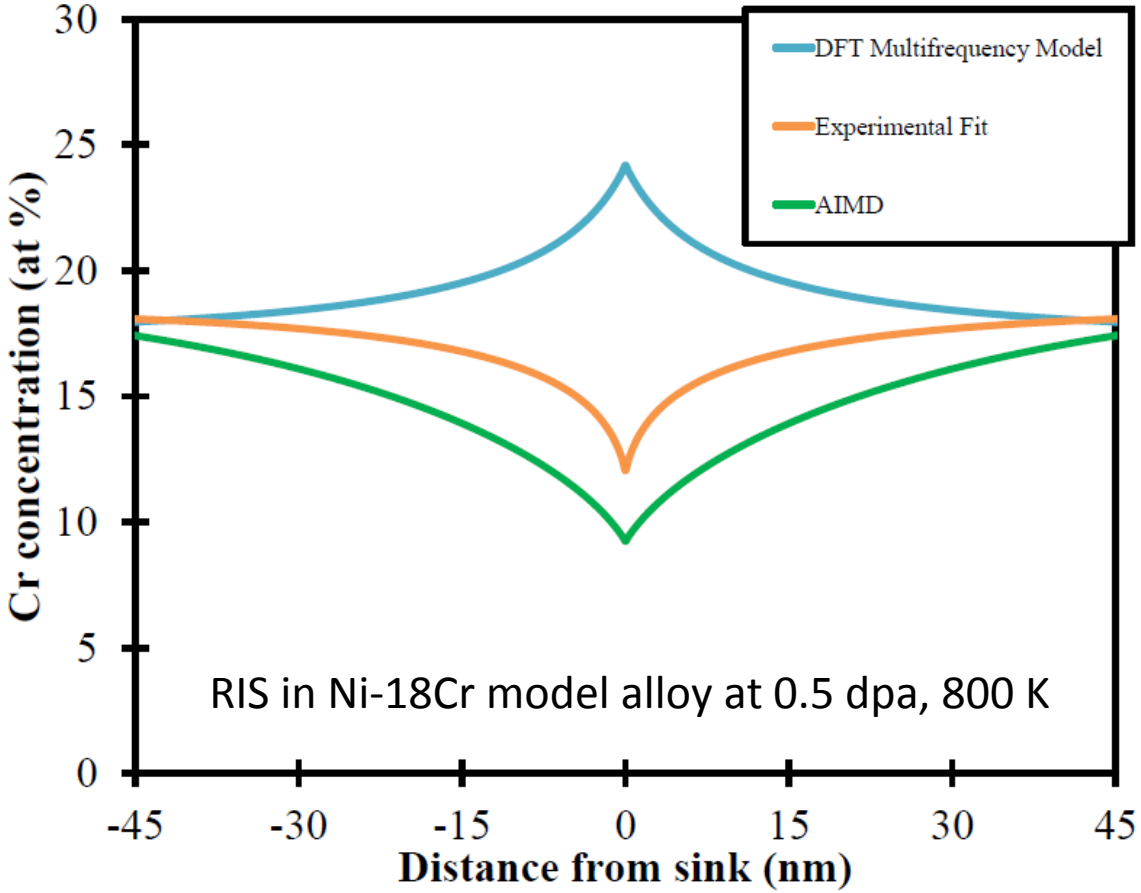


Cr and Ni Interstitial Diffusion in Ni-Cr Alloys



- Dramatic change in interstitial D_{Cr}/D_{Ni} with composition, cannot use dilute values!
- Perhaps dip seen near Ni_2Cr phase (forms experimentally at 863 K)

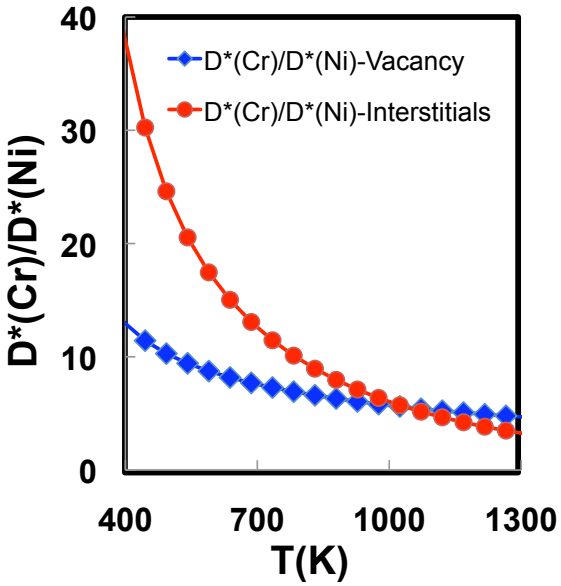
RIS Prediction from AIMD Result

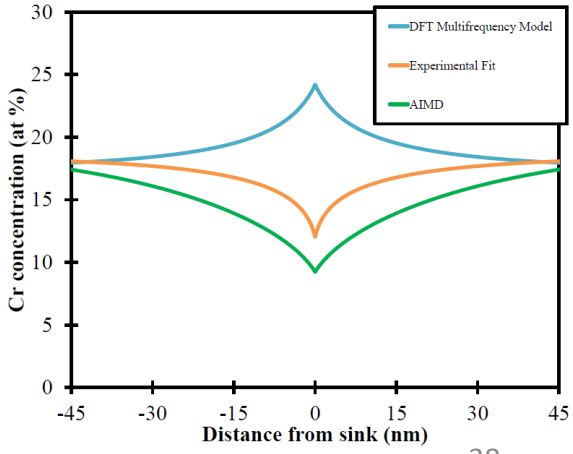


- Semi-quantitative agreement with experiments.
- Validates ab initio informed model that shows coupled effect of interstitials and vacancies.
- Further fitting to experiment can yield quantitative model

Summary of Ni-Cr RIS: Ab initio Molecular Dynamics Approach

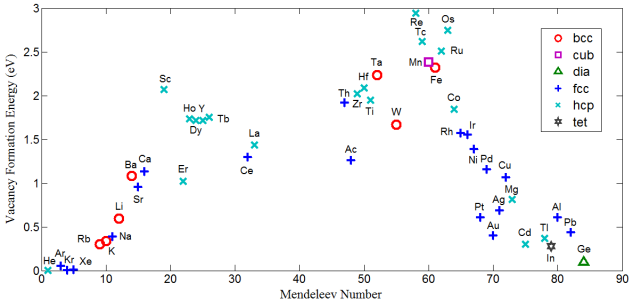
- Ab initio based model provides **new insights** for Ni-Cr RIS
  - Vacancy mechanism: Cr much faster than Ni than previously thought.
  - Interstitial mechanism: Strong interstitial bias for Cr over Ni – not previously included in any model.
  - **Observed Cr RIS in steels likely a balance of strong interstitial and vacancy RIS tendencies**
- Concentration dependent diffusion coefficients obtained from ab initio molecular dynamics – powerful tool for low-barrier systems (~0.5eV)

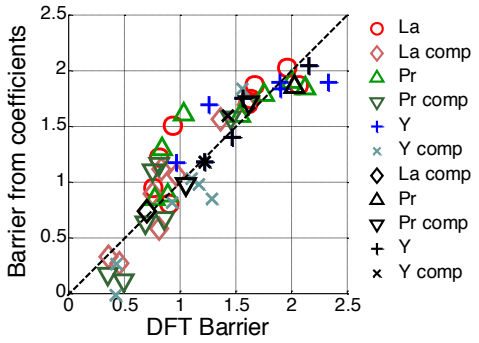


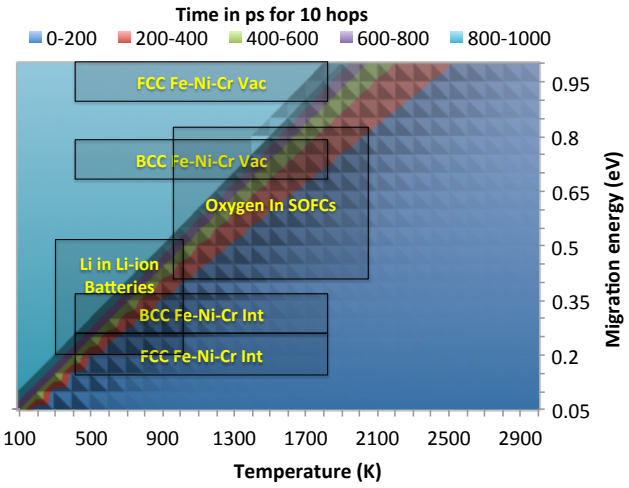


Overall Summary

- **High-throughput** ab initio simulations can provide massive diffusion coefficient databases at fraction of the cost of experiment
  - DFT accuracy an issue
  - Level of detail of simulation (attempt frequencies, G_{mig} vs. E_{mig})
- Diffusion in simple systems is now accessible to **high-throughput and datamining approaches**
  - Database of Evac, E_{mig} in dilute alloys in standard structures (3 years/$700k)
  - Perovskites – predicting of E_{mig} with just 4 descriptors can speed searches
- Diffusion in alloys amenable to **direct ab initio MD** for low barrier systems ~(0.5 eV)
  - Demonstrated semi-quantitative model for RIS
  - Could enable straightforward database development with enough computing time







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COMPUTATIONAL MATERIALS GROUP

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* Brian Puchala * Mehdi Benhassine
* Ming-Jie Zheng * Narasimhan Swaminathan
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http://matmodel.engr.wisc.edu/

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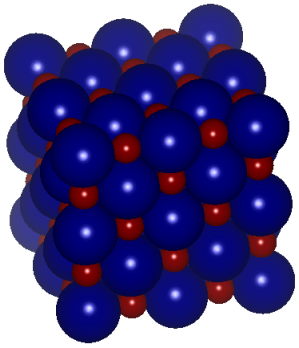
Backup Slides

Integrating with Other Tools

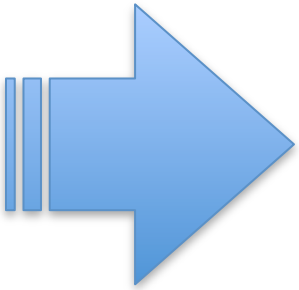
Perform job-specific functions



Use ASE[1], aconvasp[2], or other code to:

- Generate crystal structures
- View and manipulate supercells
- Interpolate NEB images
- Extract and compare energies

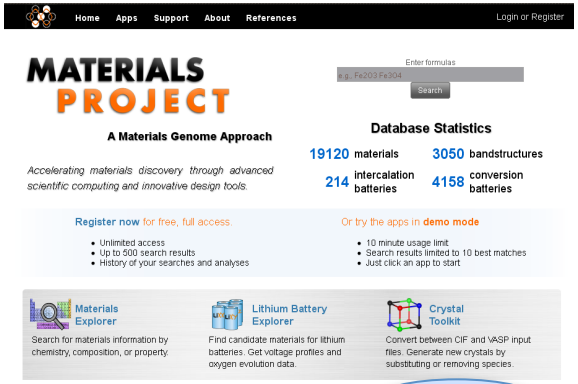
Manage sequence of jobs



Use our code to:

- Queue jobs
- Monitor jobs
- Call job-specific functions as needed
- Advance job sequence
- Restart unfinished sequence at any step

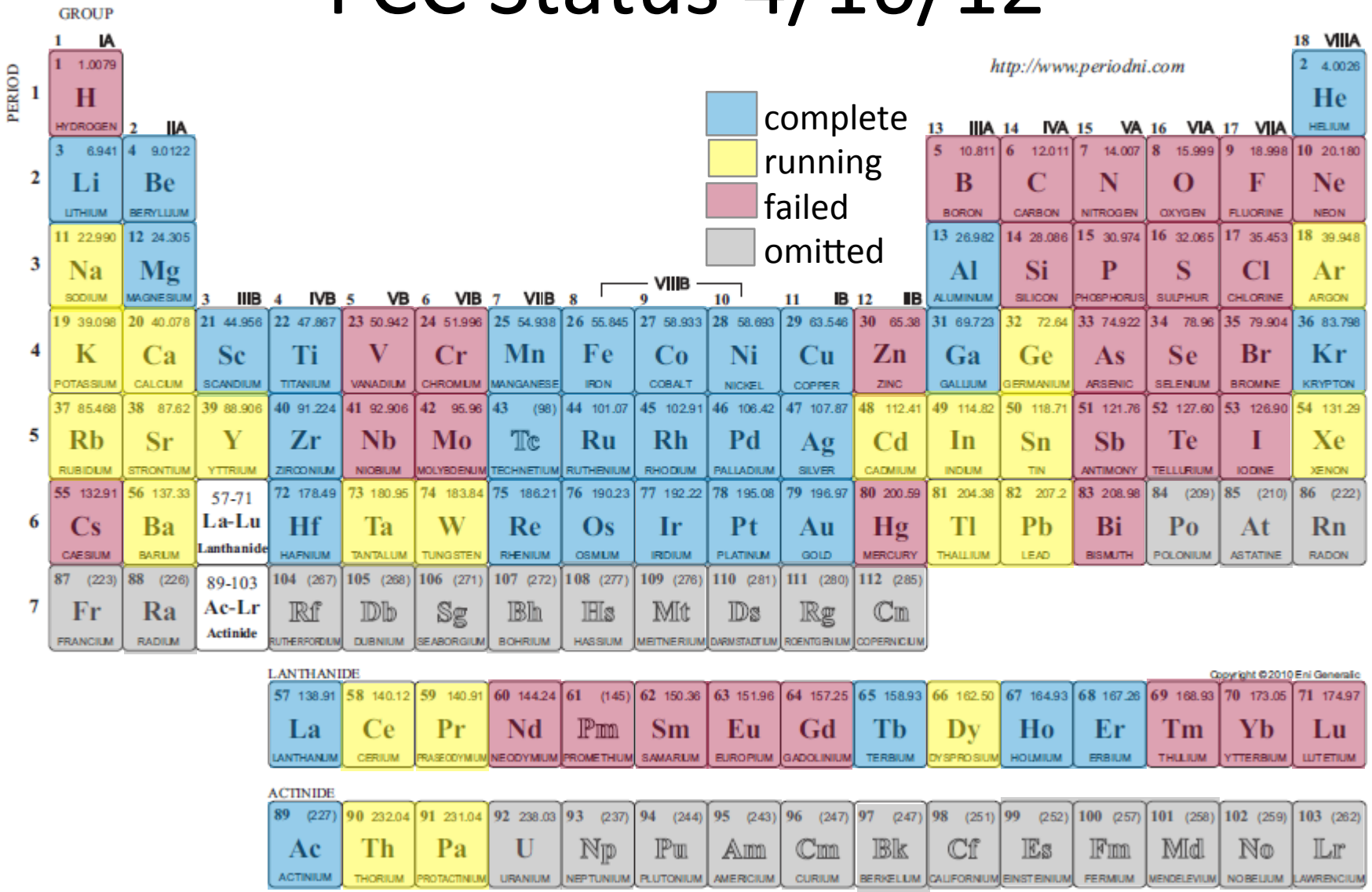
Obtain and store migration barriers and VFEs



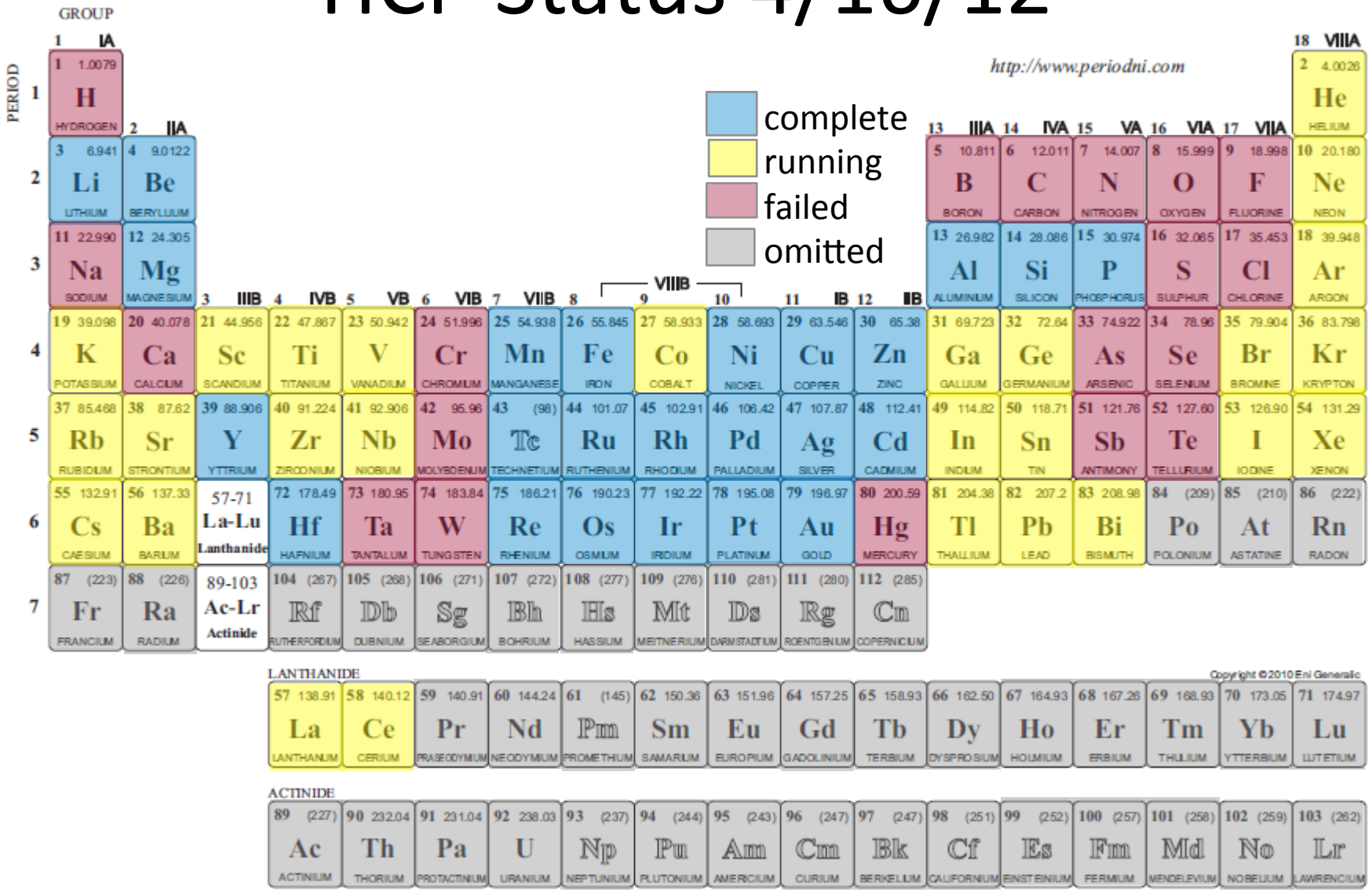
Integrate results with another database project (Materials Project)[3] or present them in a common format (Computational Materials Repository)[4]

[1]Atomic Simulation Environment: S. R. Bahn and K. W. Jacobsen, *Comput. Sci. Eng.* (2002); [2]S. Curtarolo, et al., *Comp. Mat. Sci.* (2012); [3]http://www.materialsproject.org/; [4]https://wiki.fysik.dtu.dk/ase/, Computational Materials Repository at https://wiki.fysik.dtu.dk/cmr/

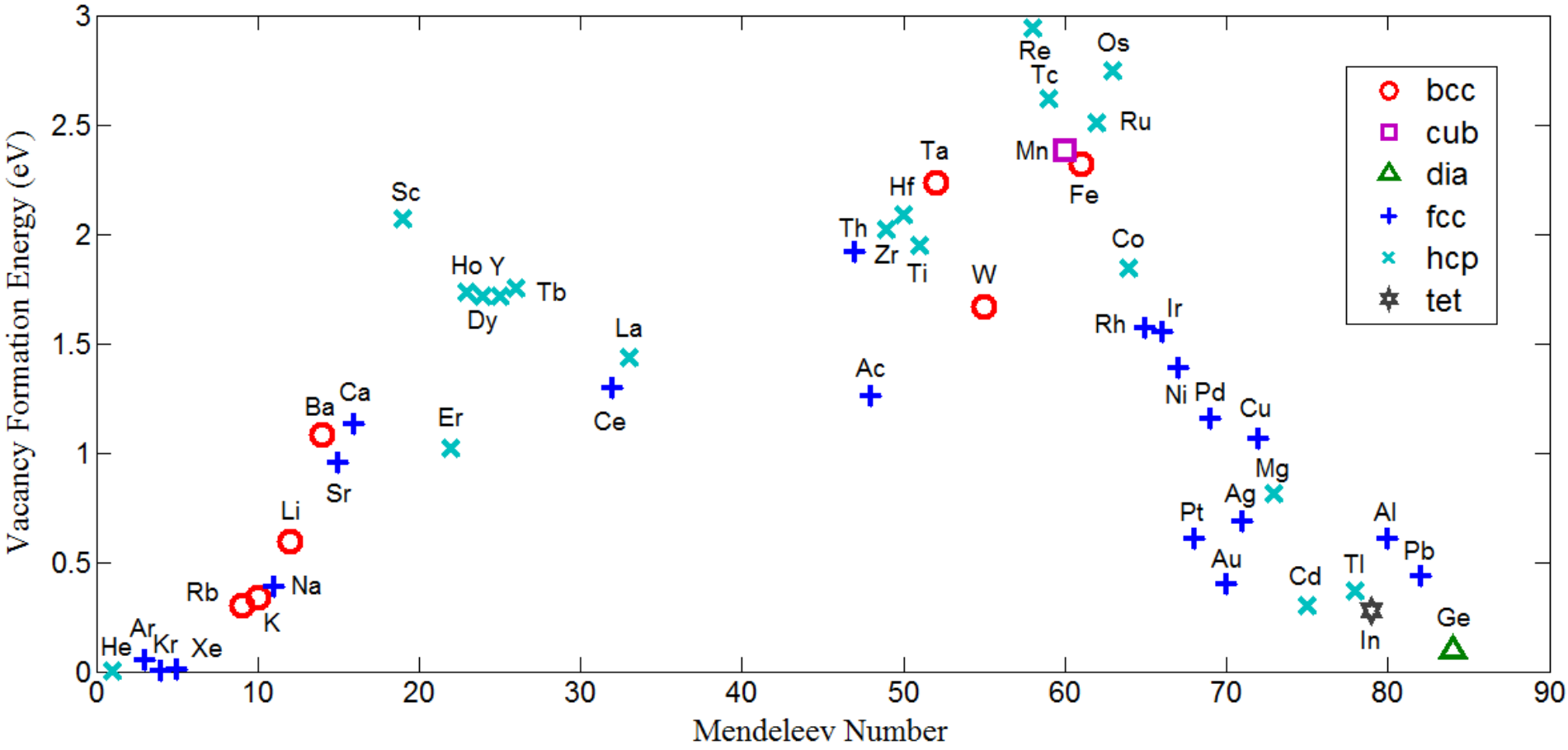
FCC Status 4/16/12



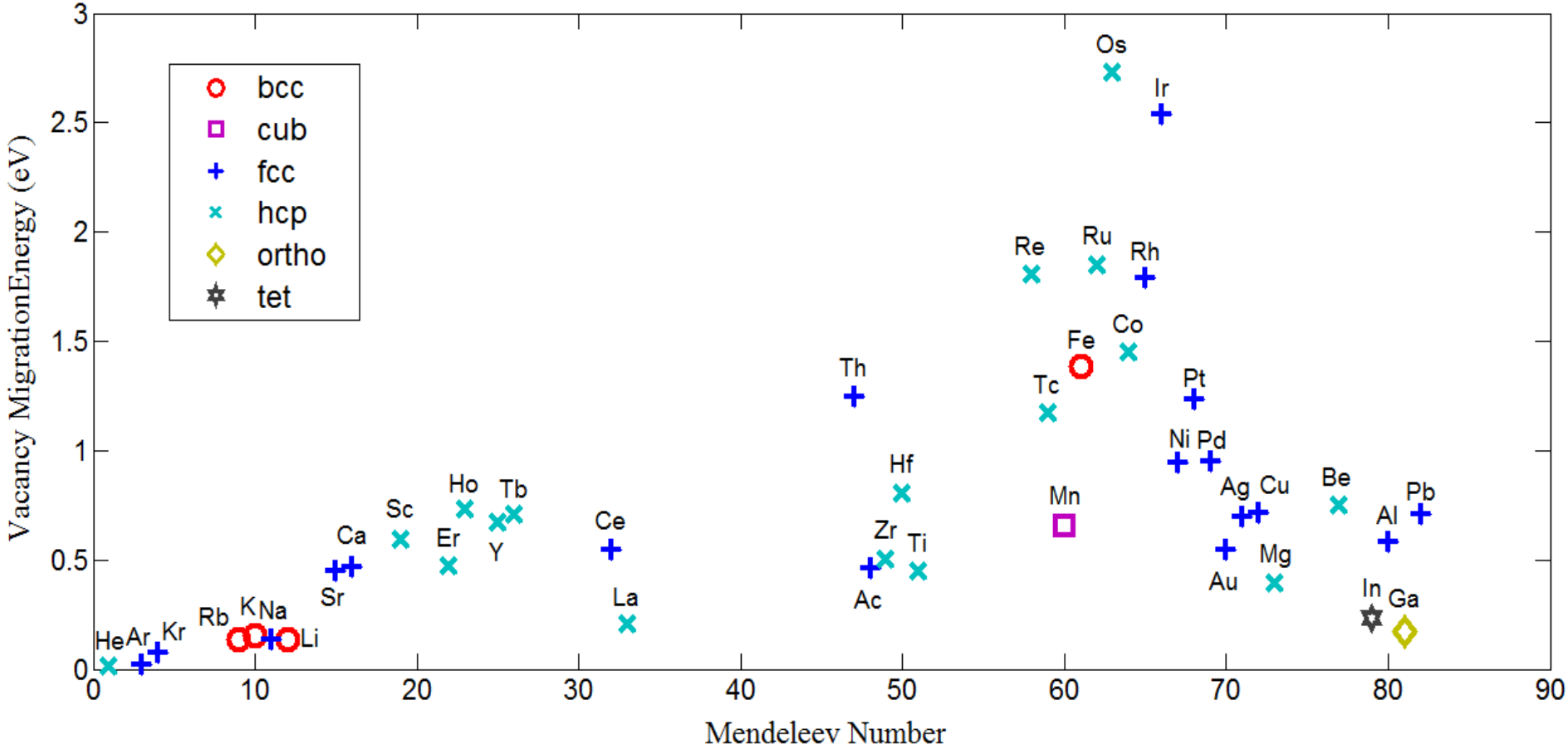
HCP Status 4/16/12



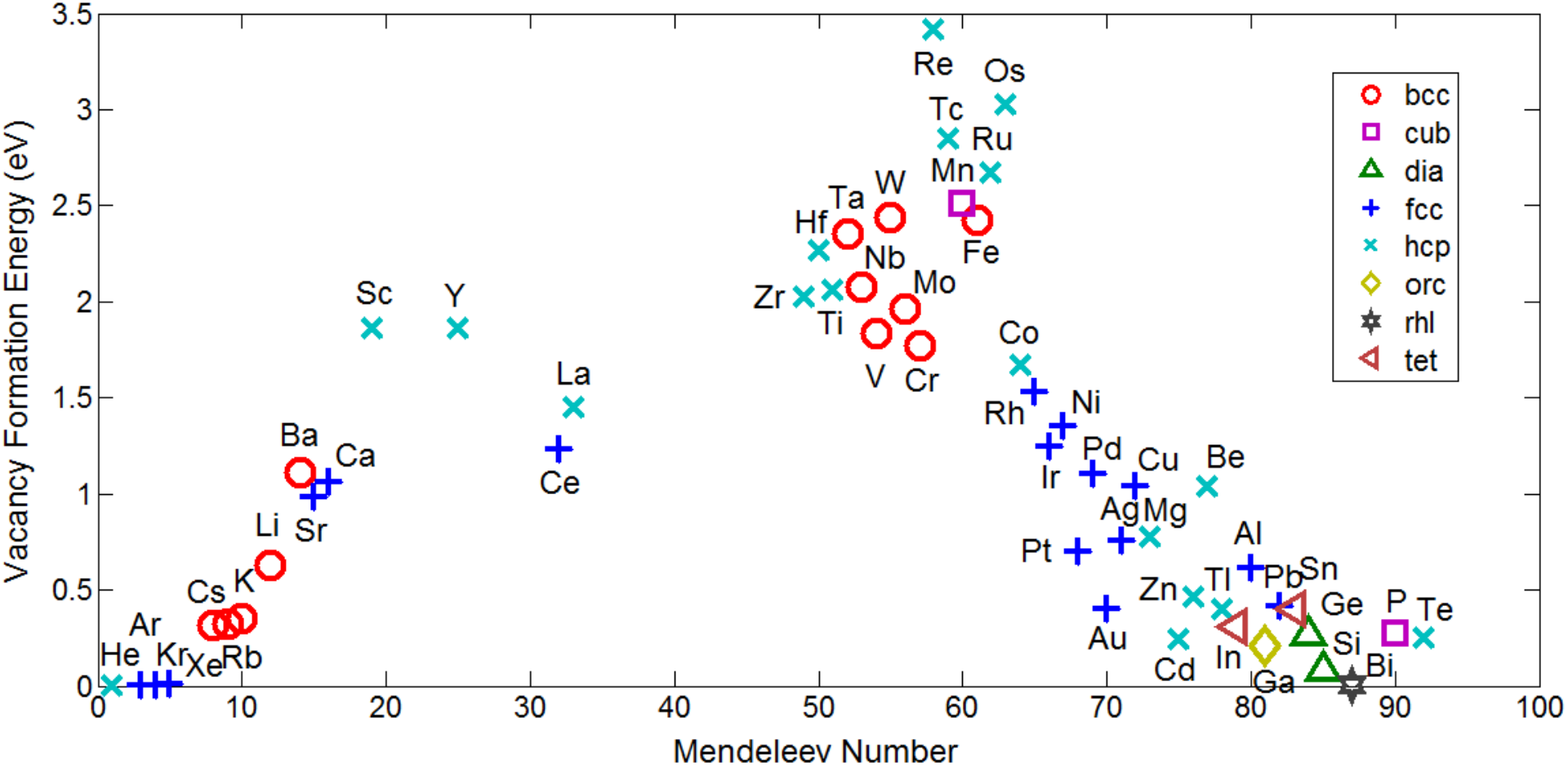
Trends with Descriptors: FCC H_{vf} Vs. Mendeleev Number



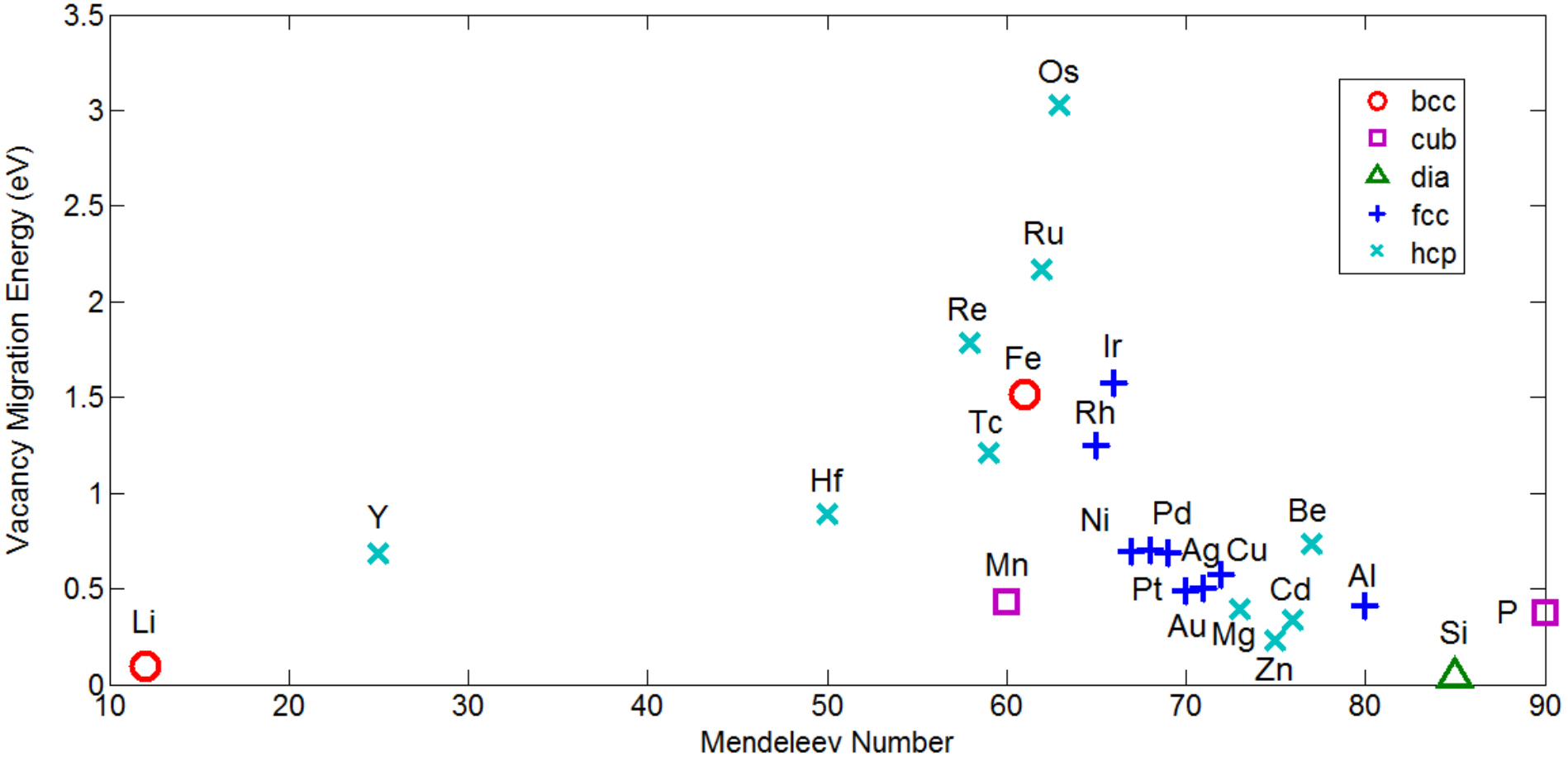
Trends with Descriptors: FCC H_{mig} Vs. Mendeleev Number



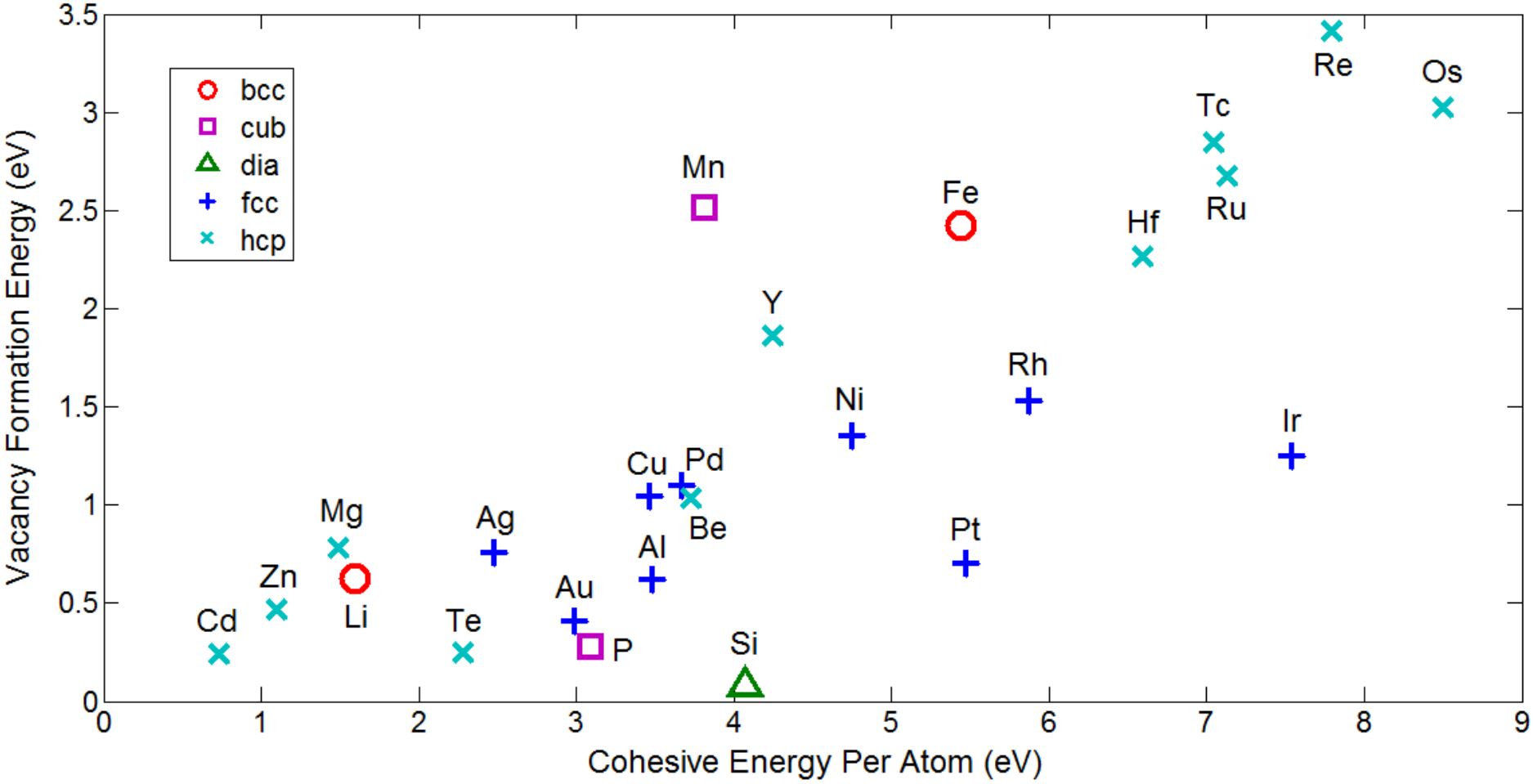
Trends with Descriptors: HCP H_{vf} Vs. Mendeleev Number



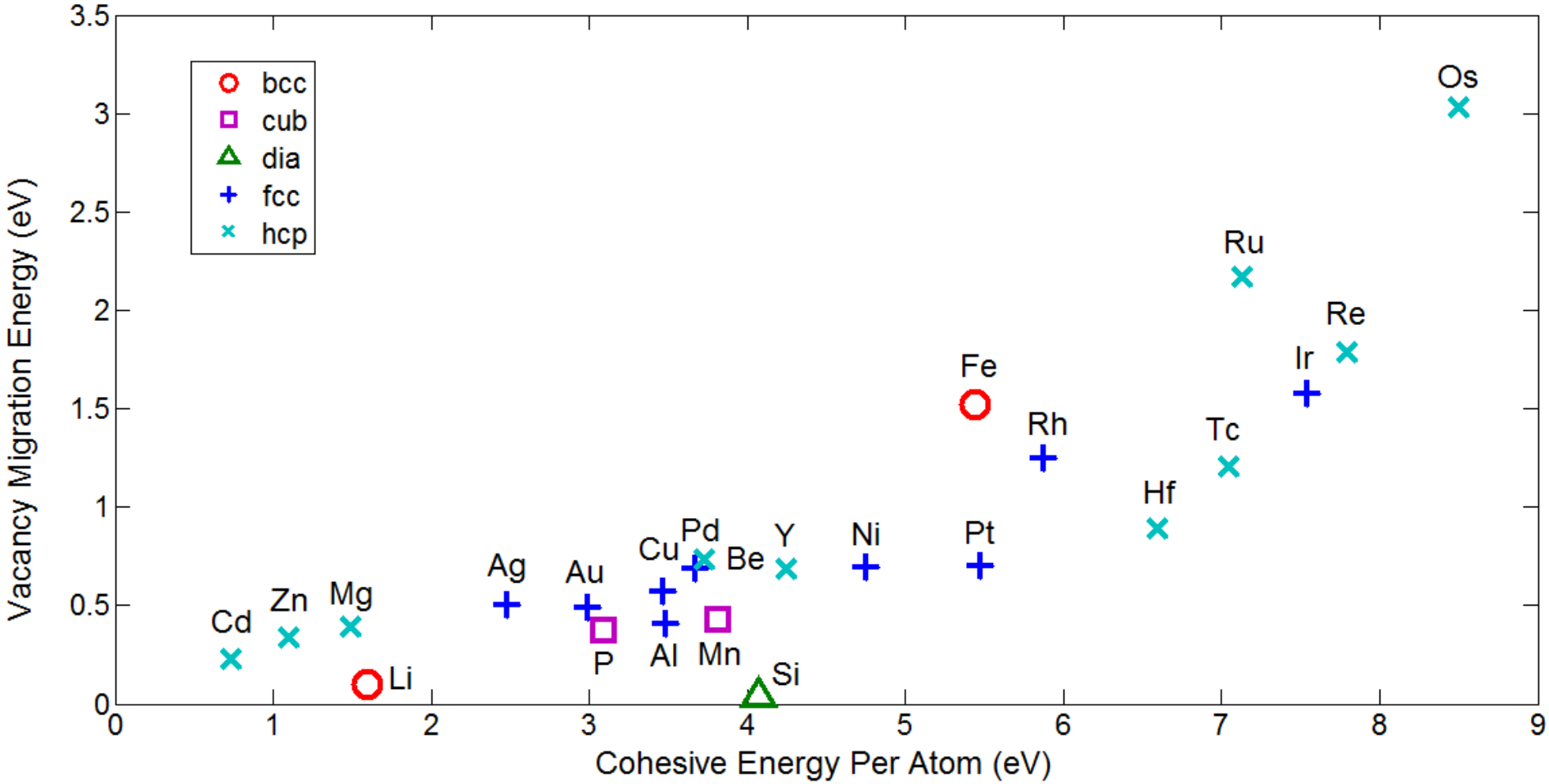
Trends with Descriptors: HCP Basil H_{mig} Vs. Mendeleev Number



HCP Evac versus Ecoh/atom

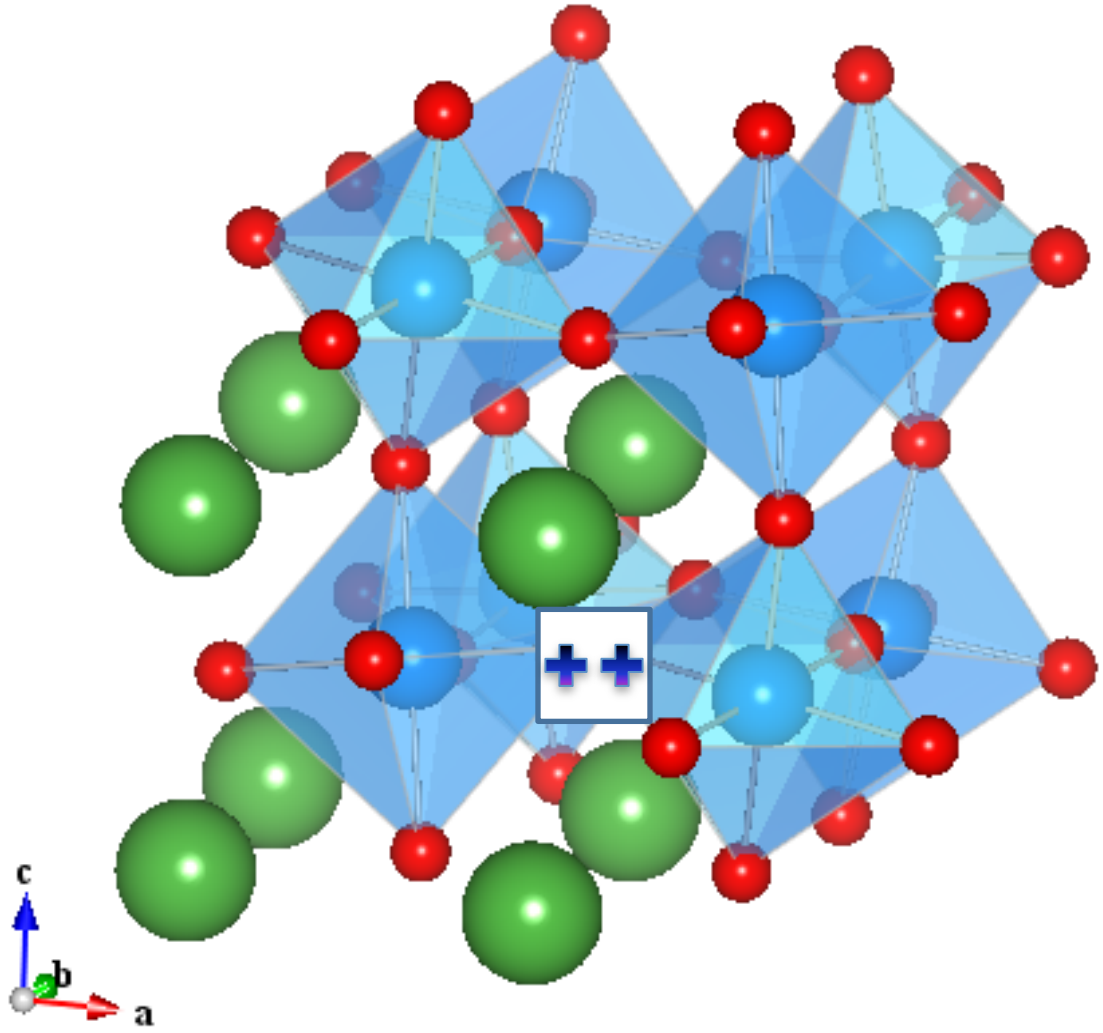


HCP Emig versus Ecoh/atom



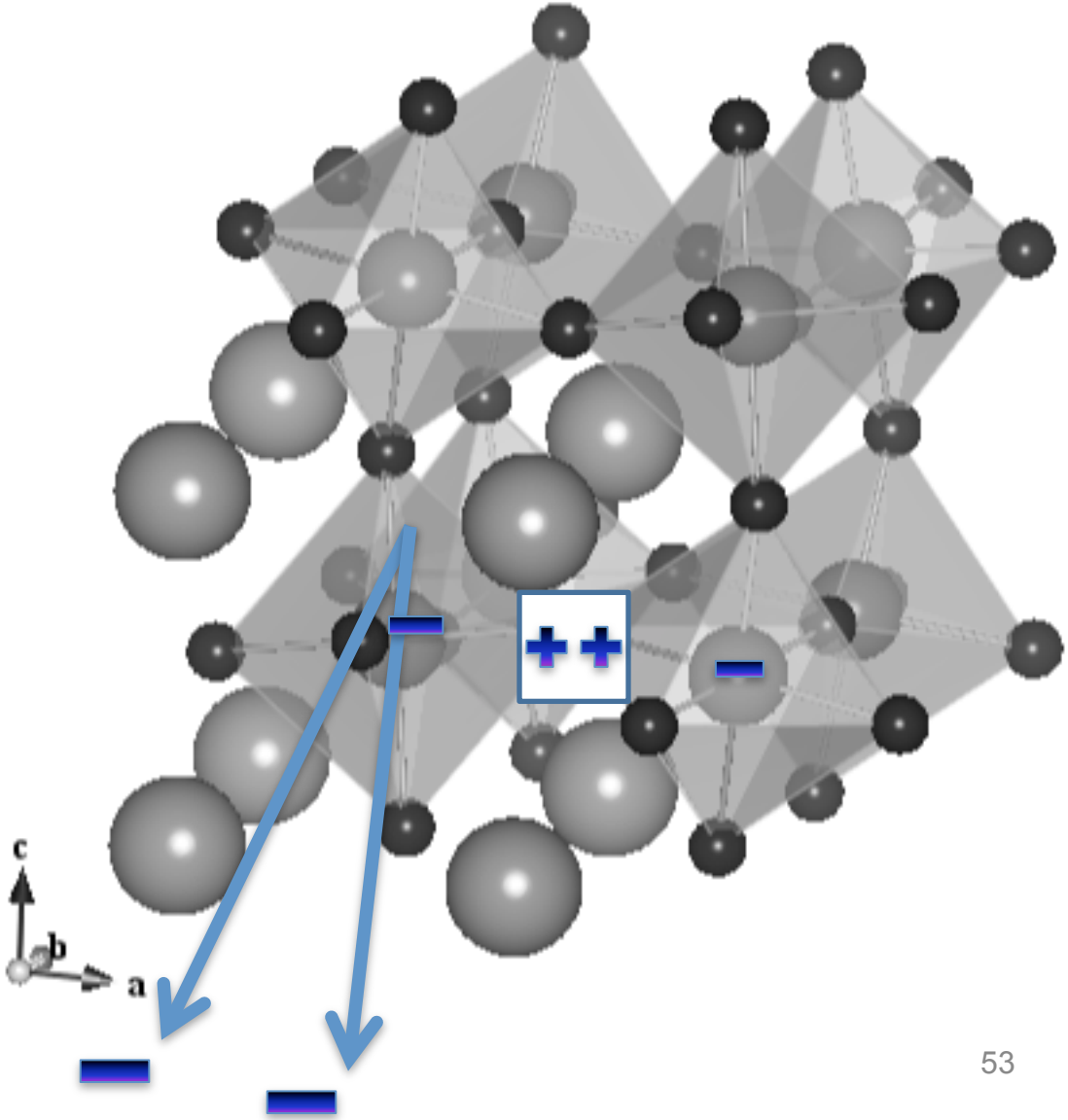
Modeling the vacancy

- The crystal expects an O^{2-} at the vacancy site,
- so the vacancy is a ‘positive’ defect with a +2 charge.
- For charge neutrality, the creation of each vacancy requires the handling of two extra electrons, or two ‘negative’ defects.

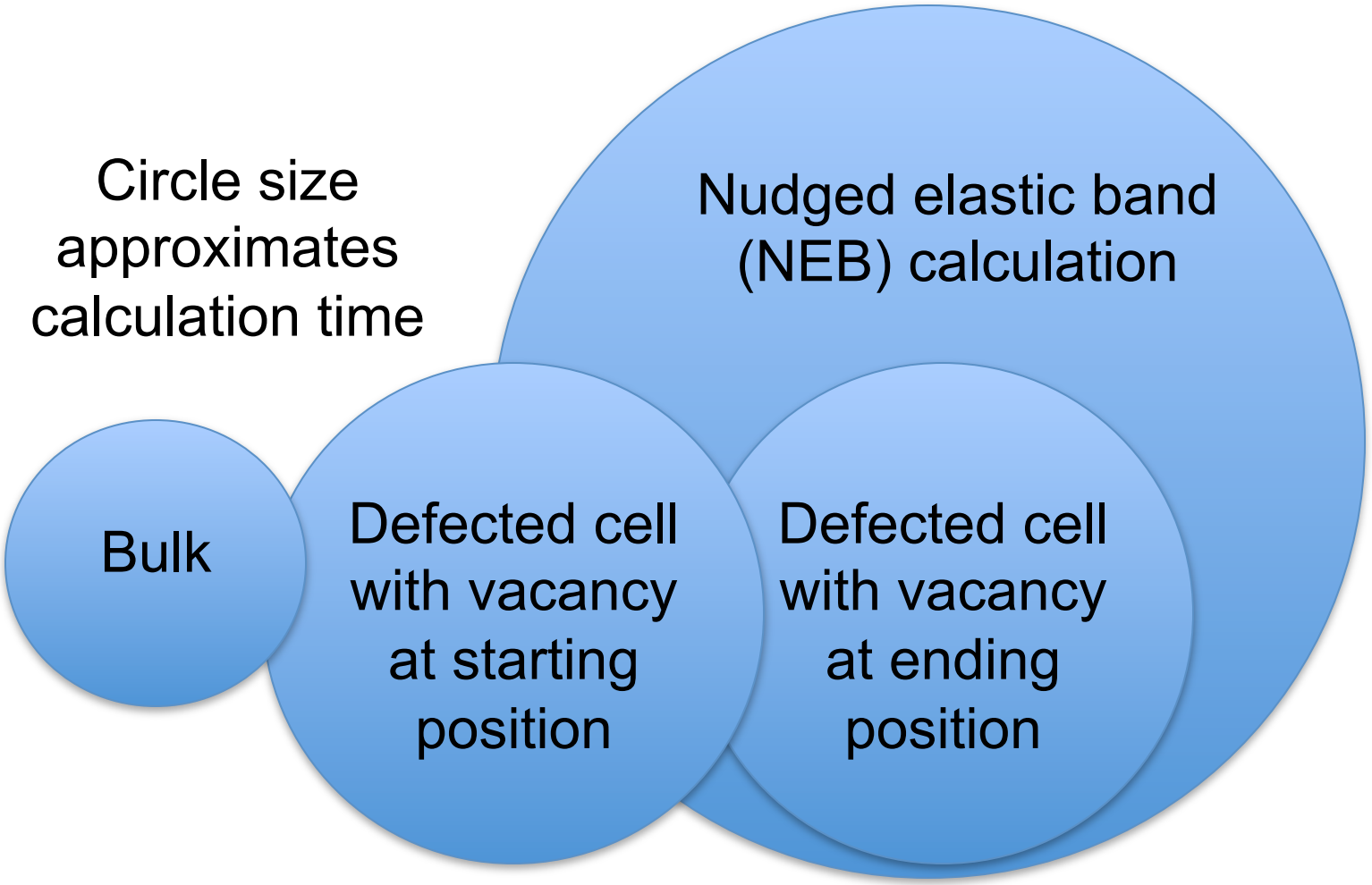


Modeling the vacancy

- We model the ‘negative’ defects by:
- 1) Removing two electrons to simulate defects outside the supercell: “compensated”
- 2) Letting the supercell produce negative defects: “uncompensated”



Can we screen for low barriers before doing a complete barrier calculation?

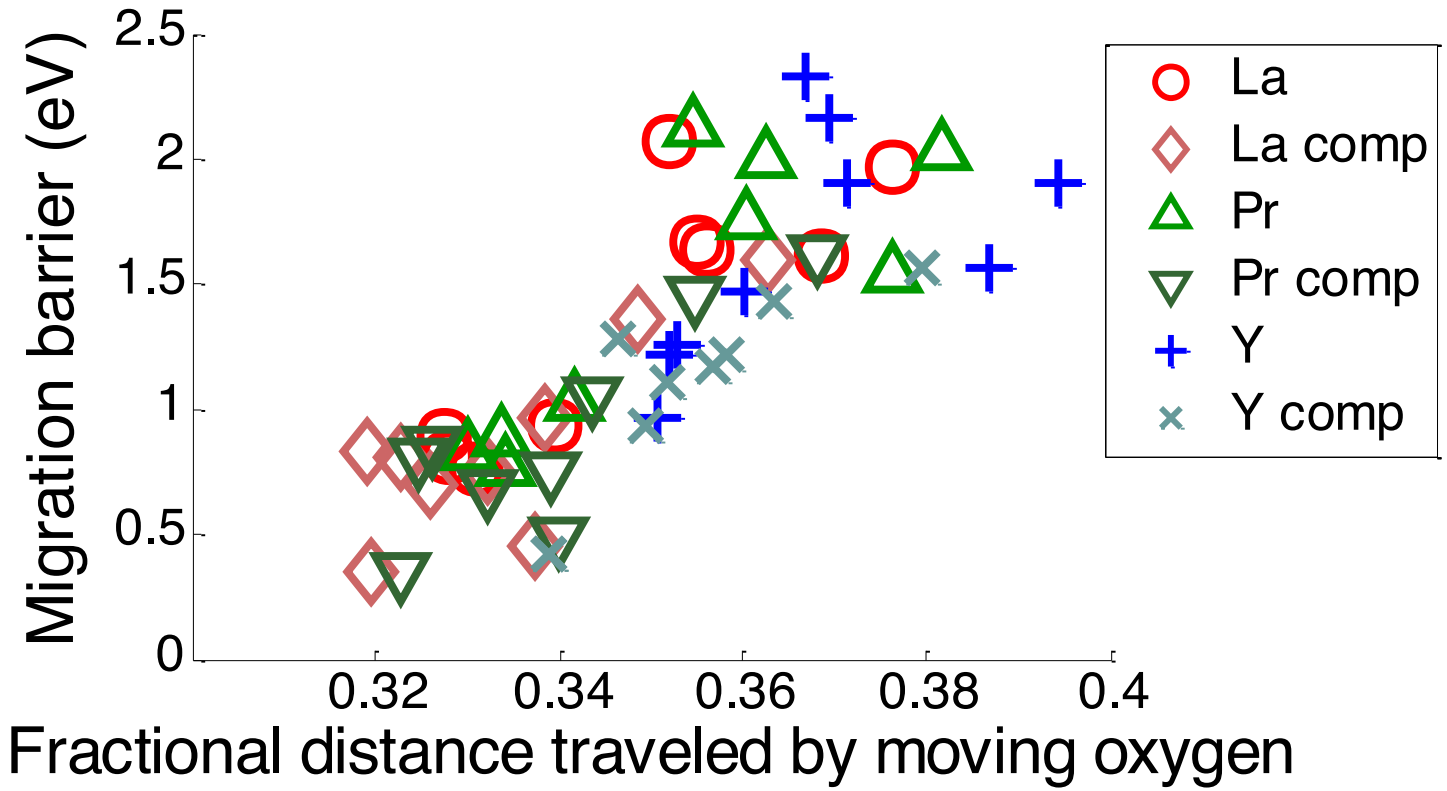


Descriptors That Did Not Correlate with Barrier

- Goldschmidt tolerance factor (cubic quality of unit cell, ability to form perovskite) and bulk cubic quality measures
- Kilner critical radius (defines triangle for oxygen to ‘squeeze’ through)
- B-site cation radius or electronegativity...
- But, some integrated effect of these and other factors may contribute to what we did find...

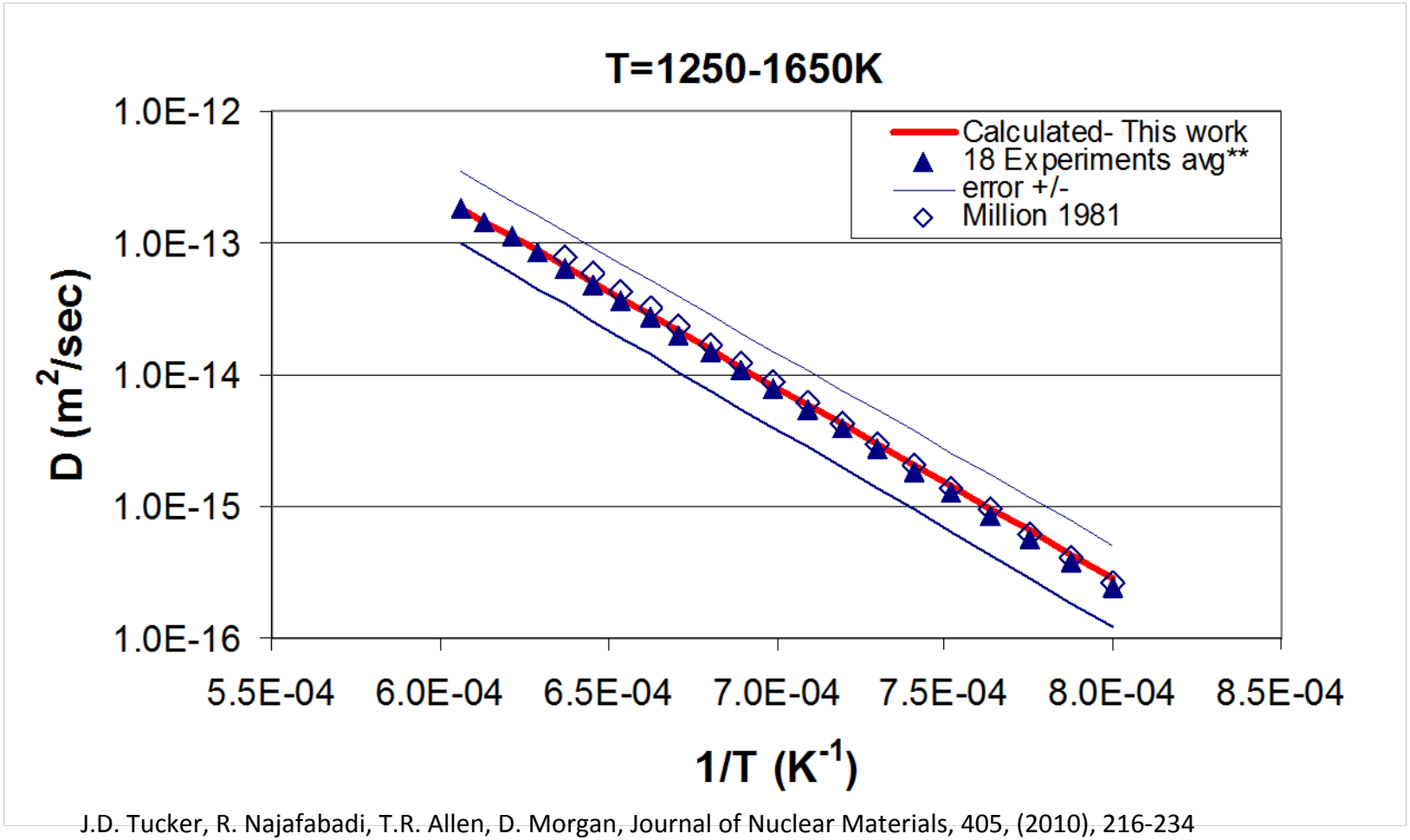
*Sammells et al., Solid State Ionics **52**, 111-123 (1992).*
*Mogensen et al., Solid State Ionics **174**, 279-286 (2004).*

Shorter Travel Distance Correlates with Lower Barriers



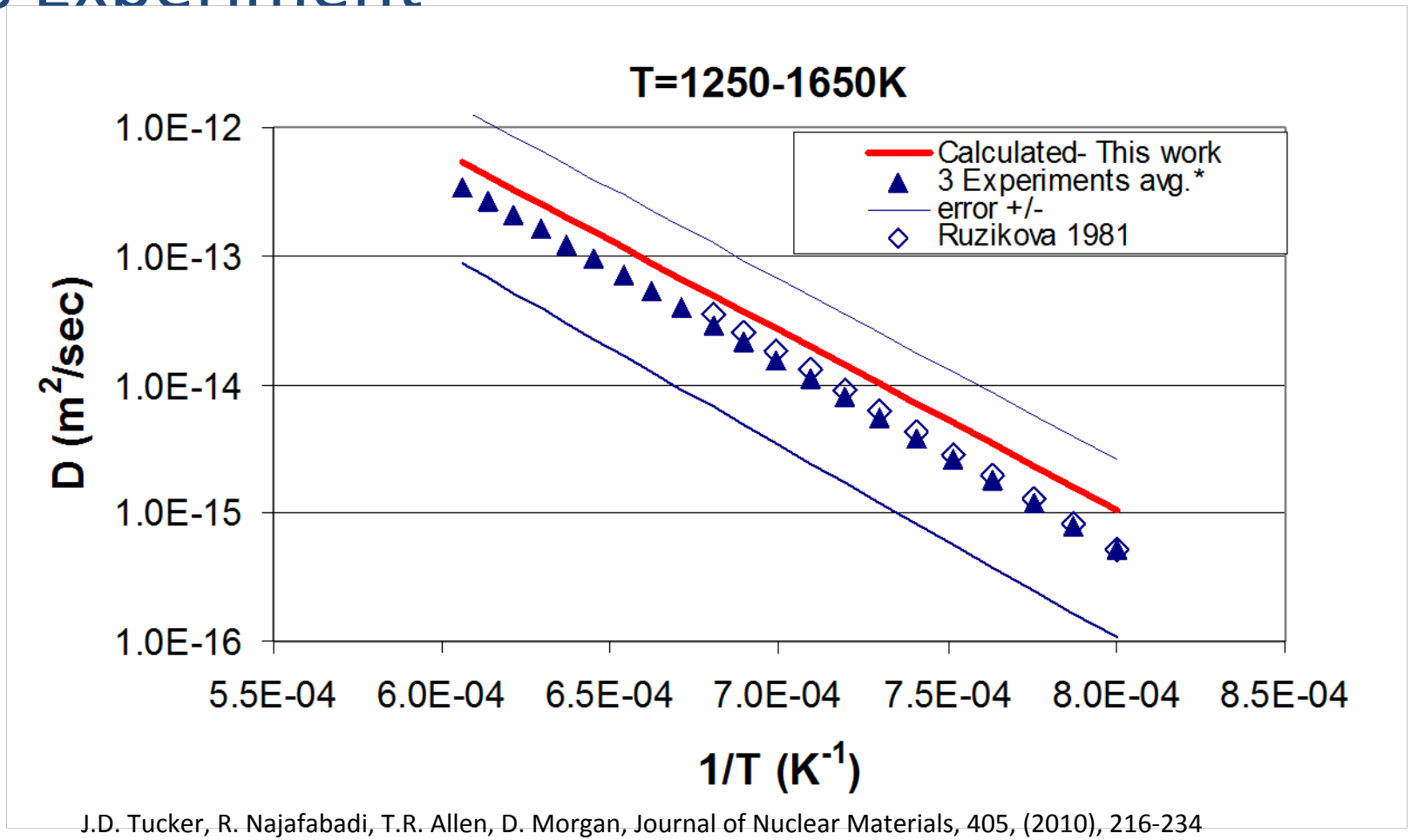
- Shows that structural geometry is playing a key role.
- But path length is no easier to get than Emig, so need a descriptor easier to calculate.

Ni Vacancy Self Diffusion – *Ab initio* vs Experiment



J.D. Tucker, R. Najafabadi, T.R. Allen, D. Morgan, Journal of Nuclear Materials, 405, (2010), 216-234

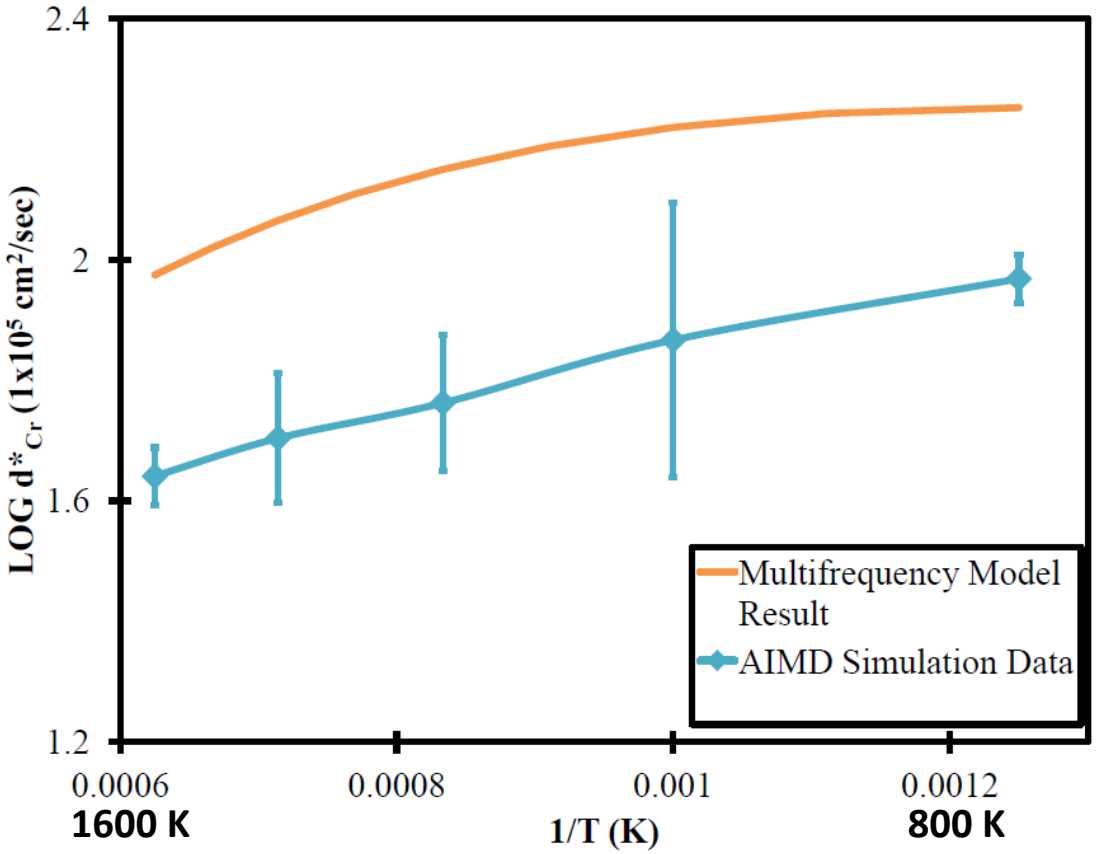
Cr Vacancy Impurity Diffusion in Ni – *Ab initio* vs Experiment



J.D. Tucker, R. Najafabadi, T.R. Allen, D. Morgan, Journal of Nuclear Materials, 405, (2010), 216-234

- For Ni self diffusion and Cr impurity diffusion, the *ab initio* values agree well with experiment.

Dilute Cr Interstitial Diffusion in Ni: Multifrequency vs AIMD



- Excellent agreement – discrepancy due to attempt frequency being approximated in multifrequency model
- The unusual T dependence of D_{Cr} in the dilute limit is reproduced.