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Modeling Point Defect Diffusion in Compound Semiconductor Alloys

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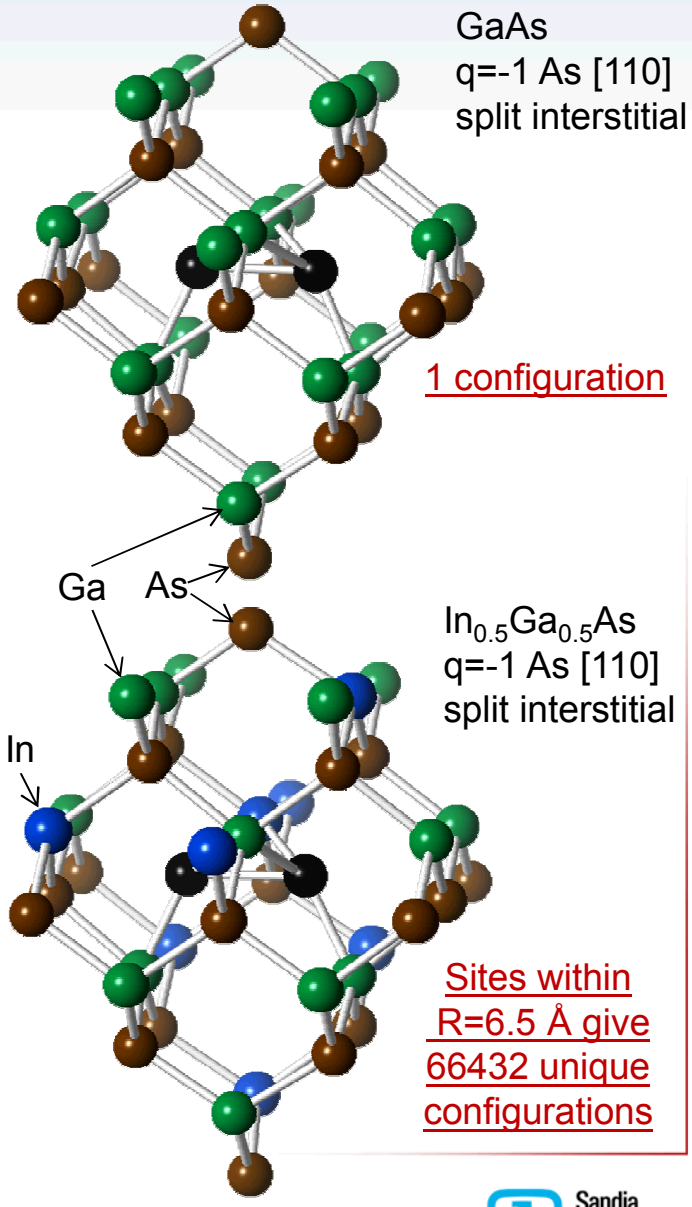
Objective and Approach

Develop a new capability to simulate diffusion of point-defects in semiconductor alloys (InGaAs) with density-functional-theory accuracy

Why is this challenging? – Configurational complexity fundamentally alters defect energetics & behavior – Computational burden rises exponentially

- Kinetic Monte Carlo (KMC) simulations of point-defect diffusion in an alloy require rapid evaluation of defect energies at all relevant locations in the alloy
- Density-functional-theory (DFT) defect energies are sufficiently accurate to produce physically realistic simulations, but the computation time needed for DFT is orders of magnitude too large for direct use
- Cluster Expansions (CE) allow rapid evaluation of defect energies in an arbitrary local alloy environment
- We obtain the CE coefficients by fitting to a training set of defect energies calculated using DFT



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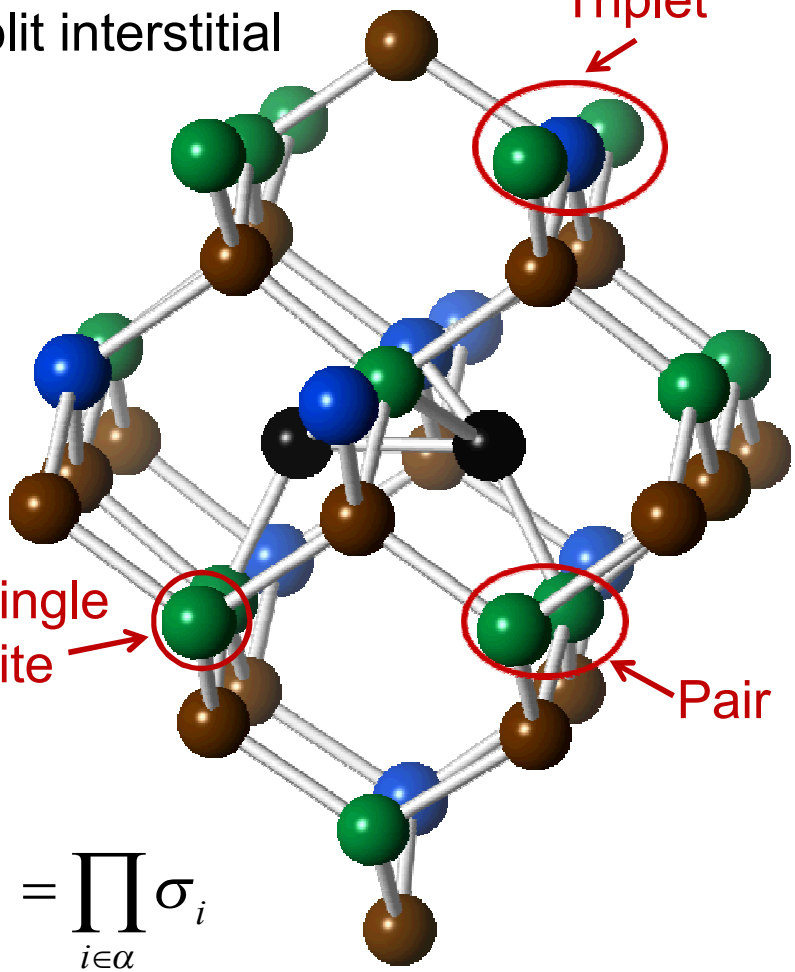
Cluster Expansions For Defects In Alloys

q=-1 As [110] split interstitial



$$\varphi_\alpha = \prod_{i \in \alpha} \sigma_i$$

$$E(\vec{\sigma}) = E_0 + \sum_\alpha V_\alpha \cdot \varphi(\vec{\sigma})$$

- Performed cluster-expansion for the formation energy of the q=-1 As [110] split interstitial
- Used a modified version of the *CHASM* code developed in Anton Van der Ven's group
- Calculated a 258 configuration training set using Socorro DFT software
- The occupations of 18 Group-III sites near the defect are represented by Ising-like variables
- Products of these Ising-like variables give terms in the cluster expansion
- Current CE includes 6 single-site terms, 7 pair terms, & 26 triplet terms
- The 18 site CE models 66432 unique local environments for the defect
- Hence, direct simulations by DFT would be nearly impossible

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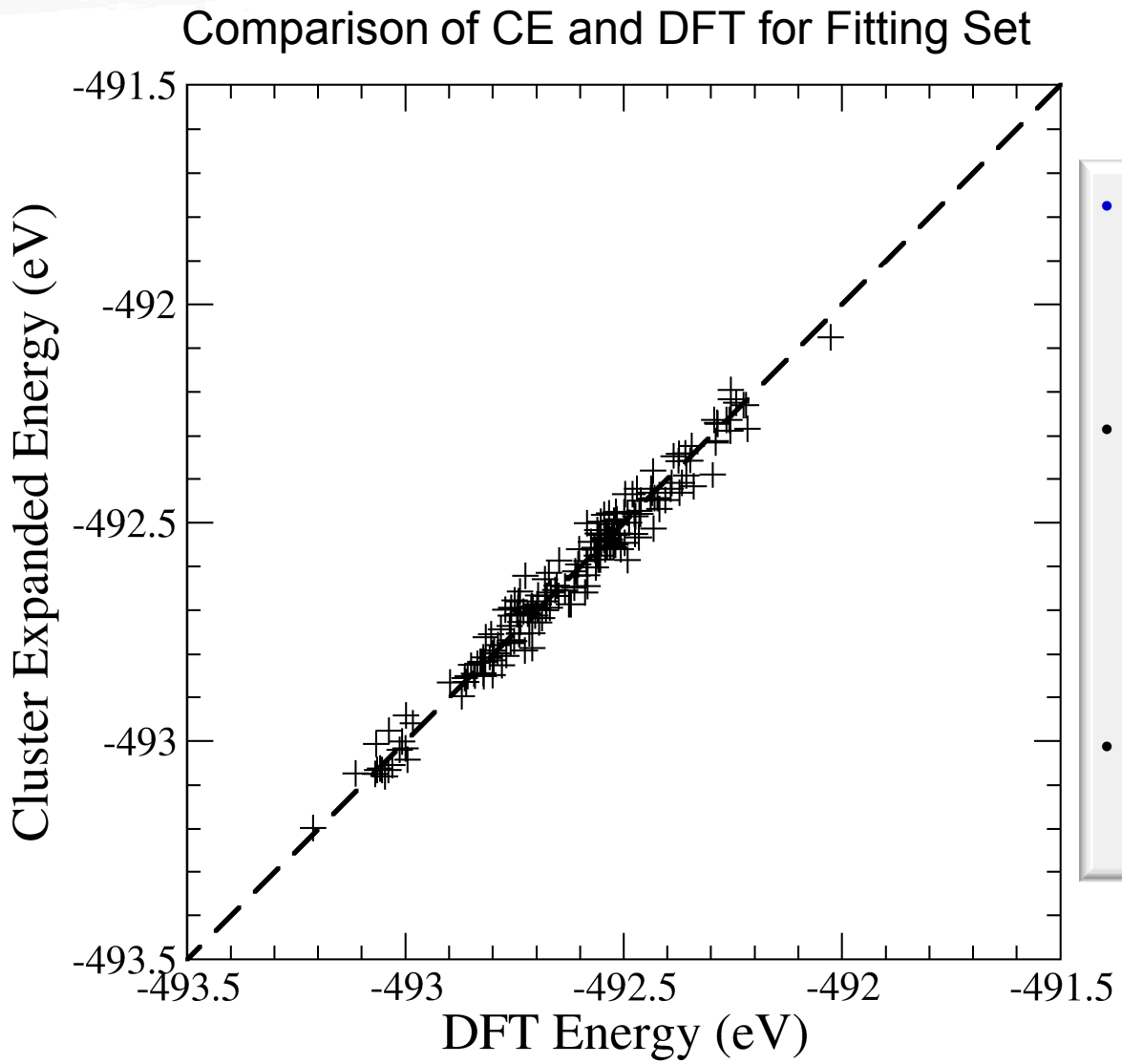
Accuracy of the Cluster Expansion



- Identified key procedures to optimize the sites and interactions included in the CE and improve the accuracy of the CE
- The cluster expansion for the q=-1 As [110] split interstitial captures over 90% of the energy variance:
  - Training set rms error = 0.036 eV
  - Training set max error = 0.105 eV
  - Cross-validation error = 0.047 eV
- The optimized CE errors are less than typical DFT errors for defects in semiconductors

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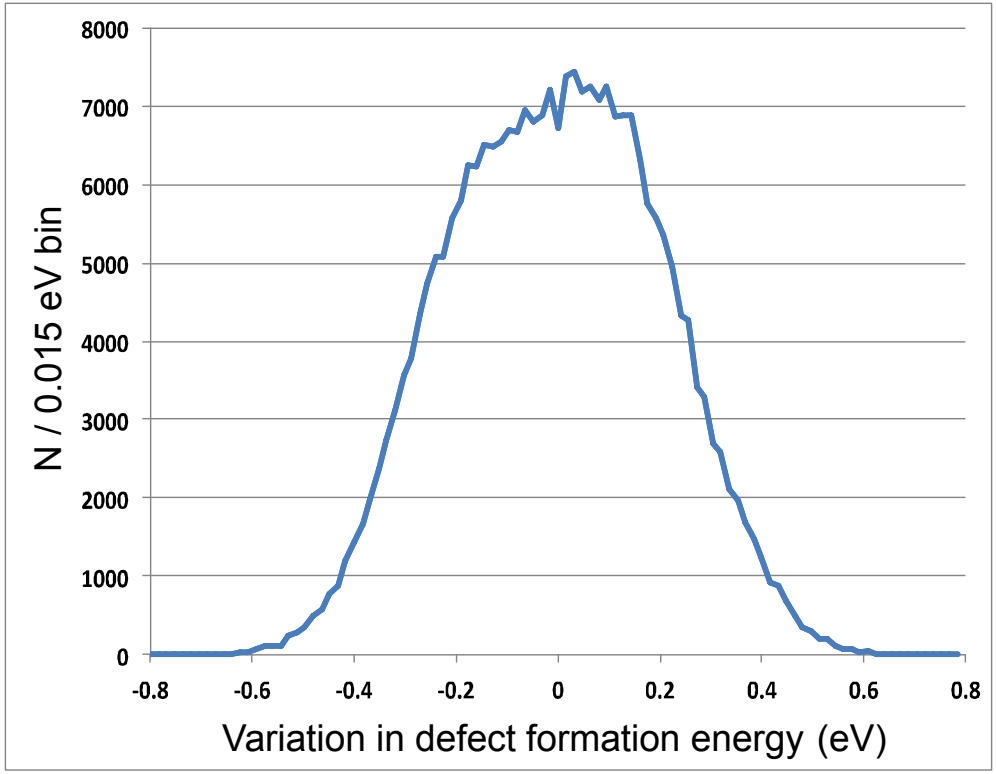
Defect Properties Strongly Dependent on Local Alloy Environment

Histogram of Defect Energies Obtained from the Cluster Expansion



The range of predicted formation energies for the q=-1 As [110] split interstitial energies exceeds 1 eV!

- In the alloy, the energy of the defect depends strongly on position
- This energy variation is large compared to the diffusion barrier in GaAs and should have a major impact on diffusion
- The variations in defect energy are correlated from site to site and have a non-linear dependence on alloy composition
- In order to explore these effects, we have incorporated our CE into a Kinetic Monte Carlo (KMC) model of diffusion

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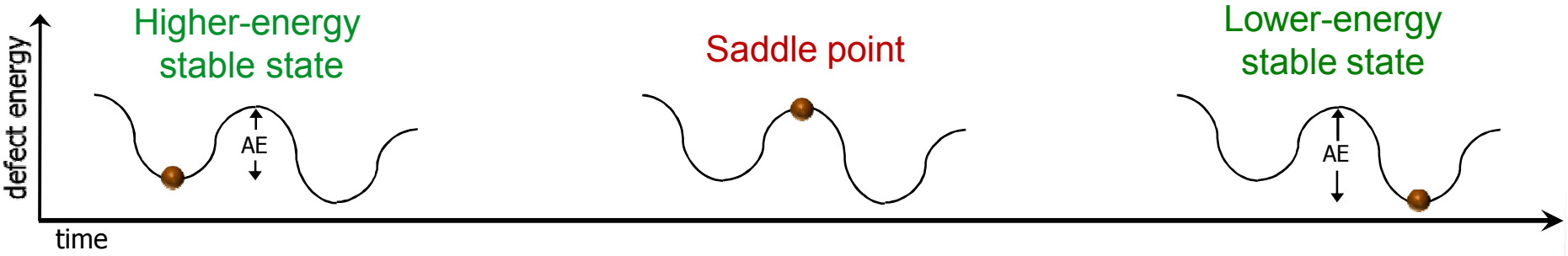
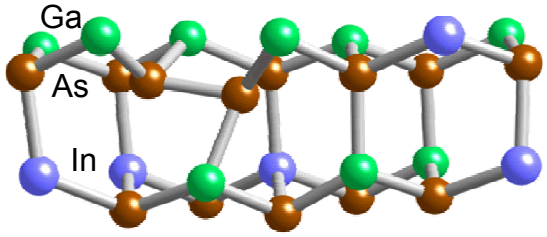
Thermal Diffusion of the q=-1 As Interstitial

Thermal-diffusion with a site-dependent energy (AE = Activation Energy)

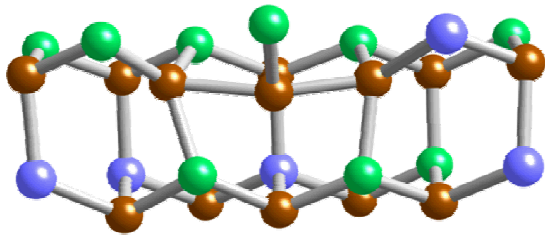


Atomistic configurations obtained from DFT (Relaxation and Dimer Method)

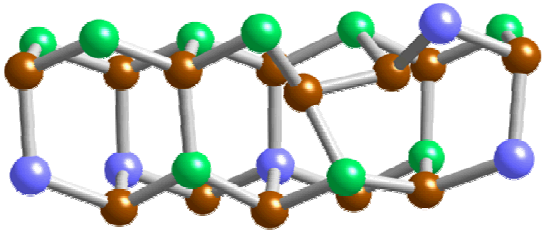
[110] split with
local environment A



"C_{2v}-001g" saddle point with
local environment A+B



[110] split with
local environment B



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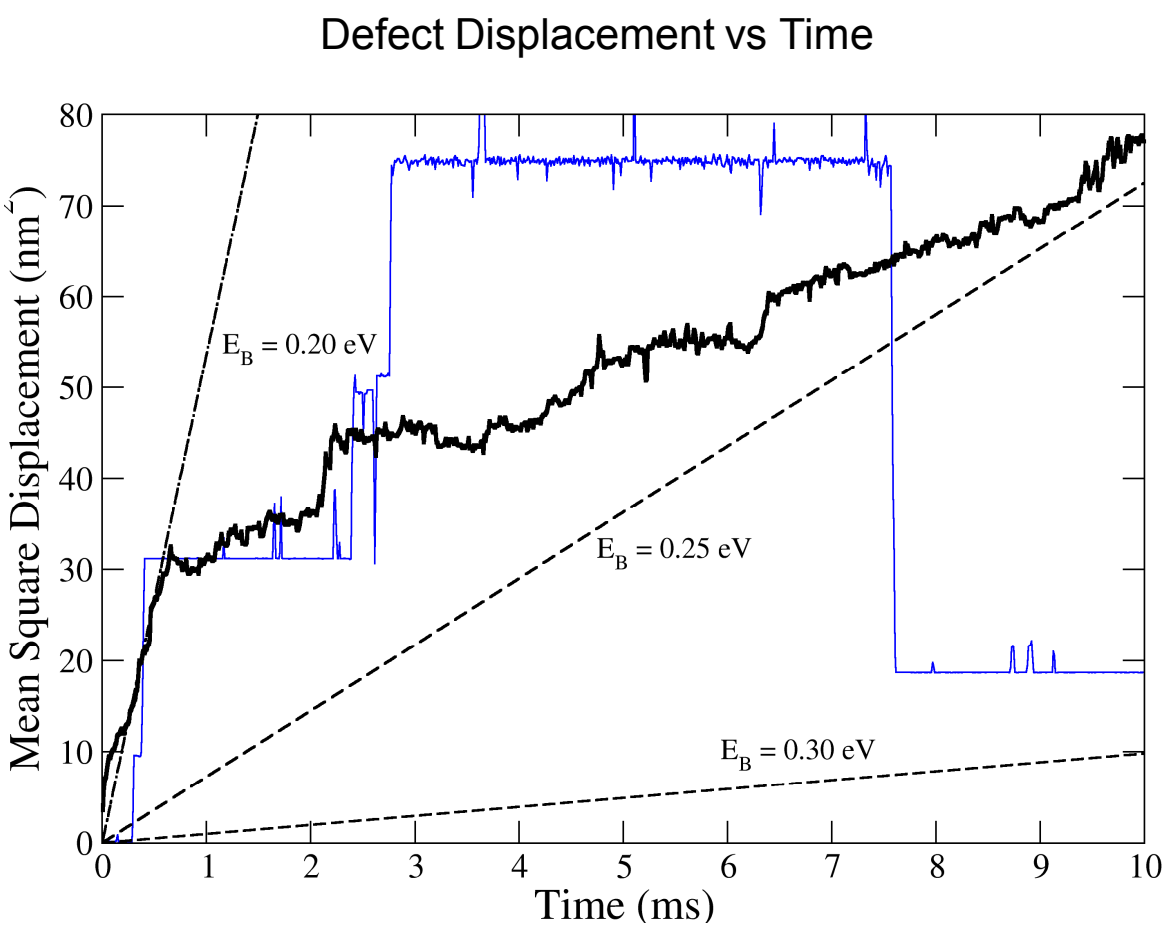
Kinetic Monte Carlo (KMC) for Thermal Diffusion



- KMC simulation of a single thermally diffusing q = -1 As interstitial in InGaA
- Use cluster expansion for position-dependent stable-state energies
- Approximate saddle-point energies chosen to give a small constant barrier for the higher energy stable state
- Room temperature simulation with an attempt rate of 10^9 s^{-1}
- Blue line is averaged over time bins for a single trajectory; Black line is averaged over time bins and 96 independent trajectories

The rate of diffusion decreases dramatically with time!

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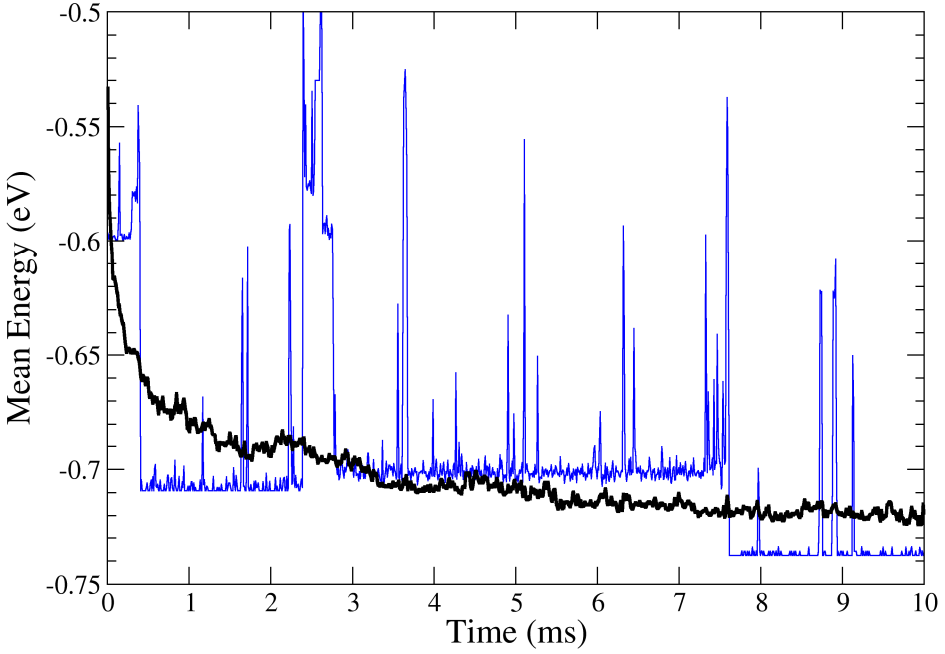
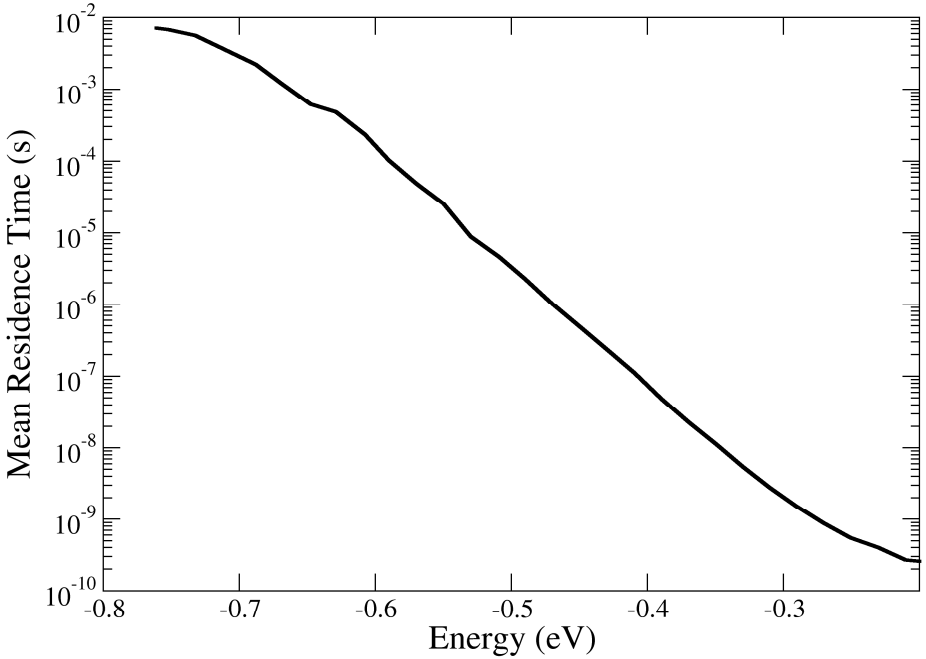
Why Does Diffusion Slow Down?

Defect Energy vs Time



Residence Time vs Energy



- As the defect diffuses, it finds lower energy sites in the alloy.
- Lower energy sites trap the defect for (exponentially) longer times.

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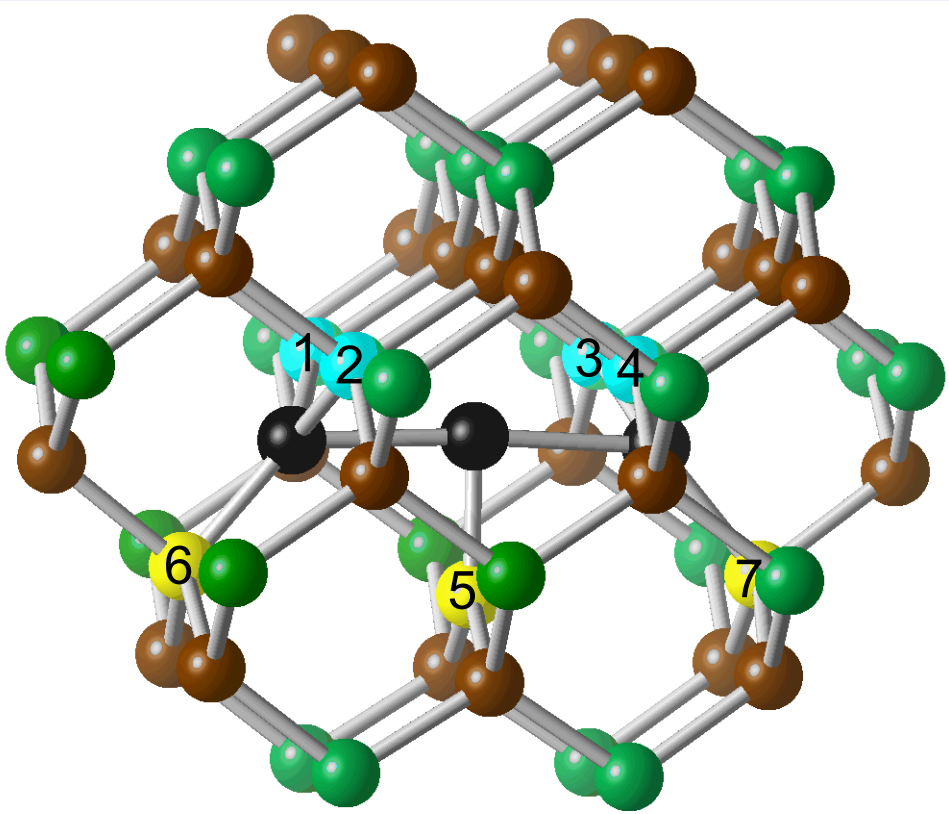
Preliminary Work on CE for Saddle Point Energies



- Saddle-point structure has 7 nearest-neighbor sites and 31 next-nearest-neighbor sites
- Constructed a 358-configuration training set using DFT and the dimer method
- Initial CE built using the 7 nearest neighbor sites and a 48 configuration training set

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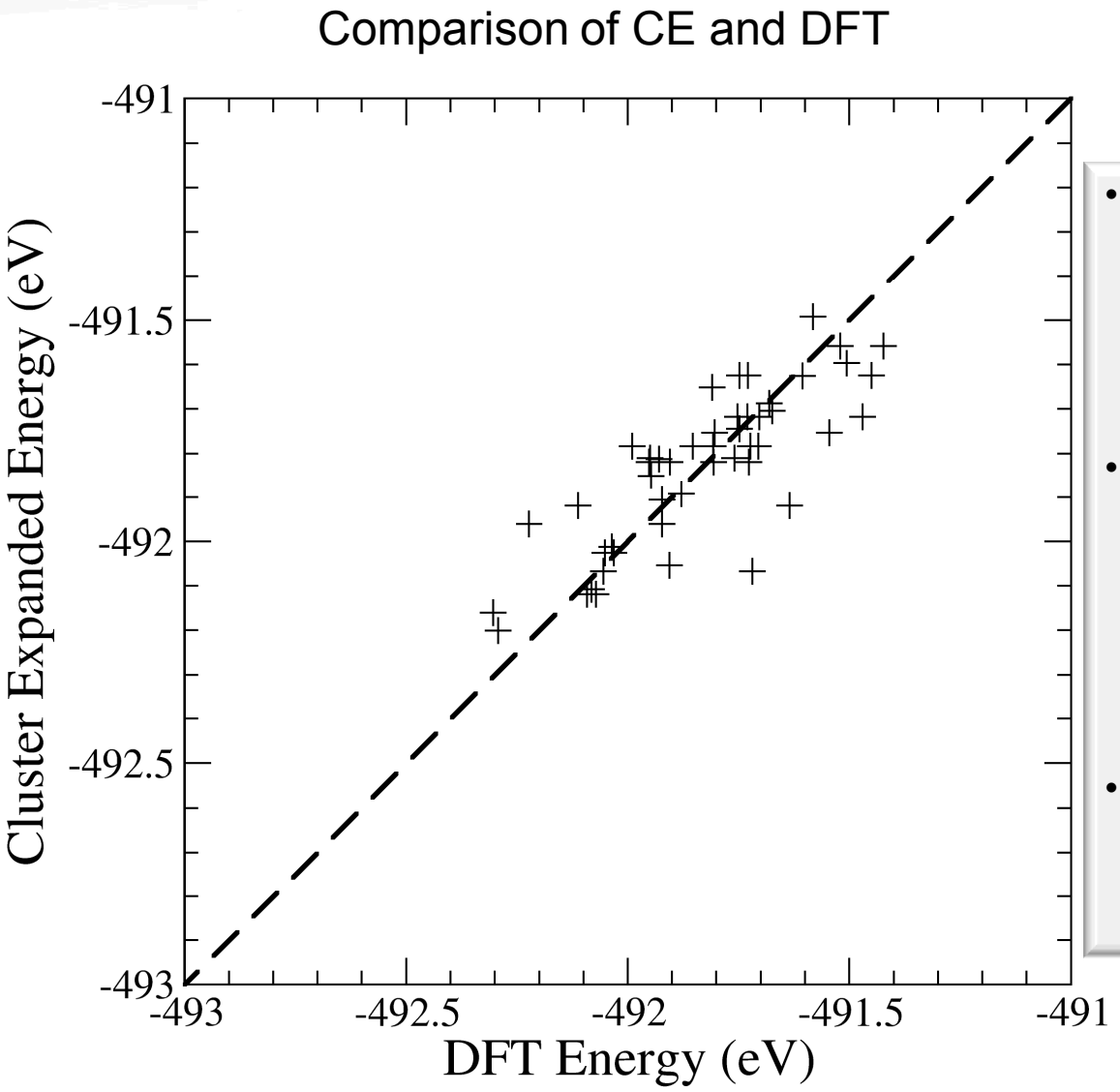
Accuracy of Our Preliminary Cluster Expansion for the Saddle Points



- Our initial cluster expansion for the saddle points is similar in accuracy to initial cluster expansions for the stable states that used only nearest neighbors
- It is not as accurate as our final, optimized cluster expansion for the stable states:
  - Training set rms error = 0.123 eV
  - Training set max error = 0.348 eV
  - Cross-validation error = 0.143 eV
- We will need to identify the next-neighbor sites responsible for this inaccuracy and include them in our cluster expansion

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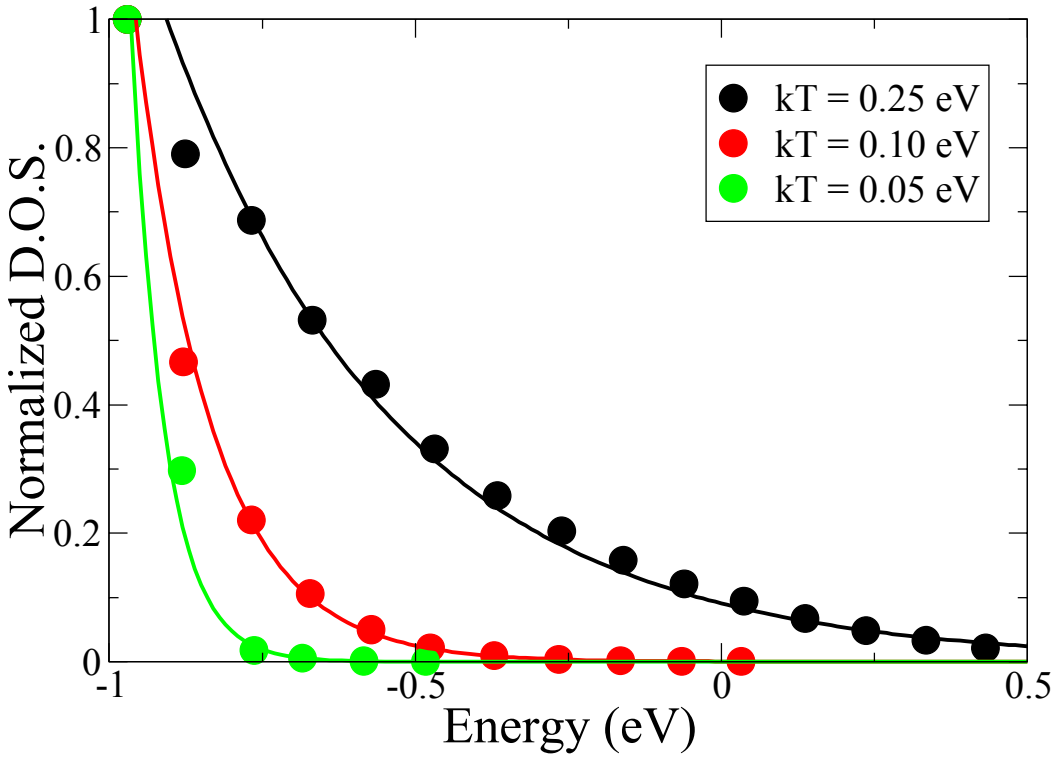
Conclusions

- We have combined DFT, Cluster Expansions, and KMC to simulate thermal diffusion of point defects in semiconductor alloys
- We have applied our approach to the q=-1 As interstitial in InGaAs
- The energy of a defect can vary dramatically (> 1eV) with position due to changes in the local environment
- Defects can become trapped in progressively lower energy sites leading to a slowing of defect diffusion with time
- We are continuing to work on cluster expansions for saddle point energies and the stable-state energies of other charge states with the goal of treating both thermal and athermal (Bourgoin-Corbett-like) diffusion

Key Accomplishments:
Analyzed Initial KMC Simulation Results for Thermal Diffusion

Density of Defect States (DOS) in $In_{0.5}Ga_{0.5}As$
vs
Stable-State Defect Energy

(for As split-interstitial, C_{2v}-110a, q=-1)



- The DOS are computed by sorting the sequence of defect energies encountered as the defect moves through the lattice during a single KMC simulation. The resulting distribution is normalized by the population frequencies (slide 6) to remove the biasing effect of population statistics
- The KMC algorithm should "seek out" the lowest energy configurations, such that the defect spends more time in them than in higher-energy states (all else being equal)
- As expected, the observed density of states show that low-energy stable states are very strongly favored, especially at lower temperatures

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