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Migration Processes of the As Interstitial in GaAs and InGaAs

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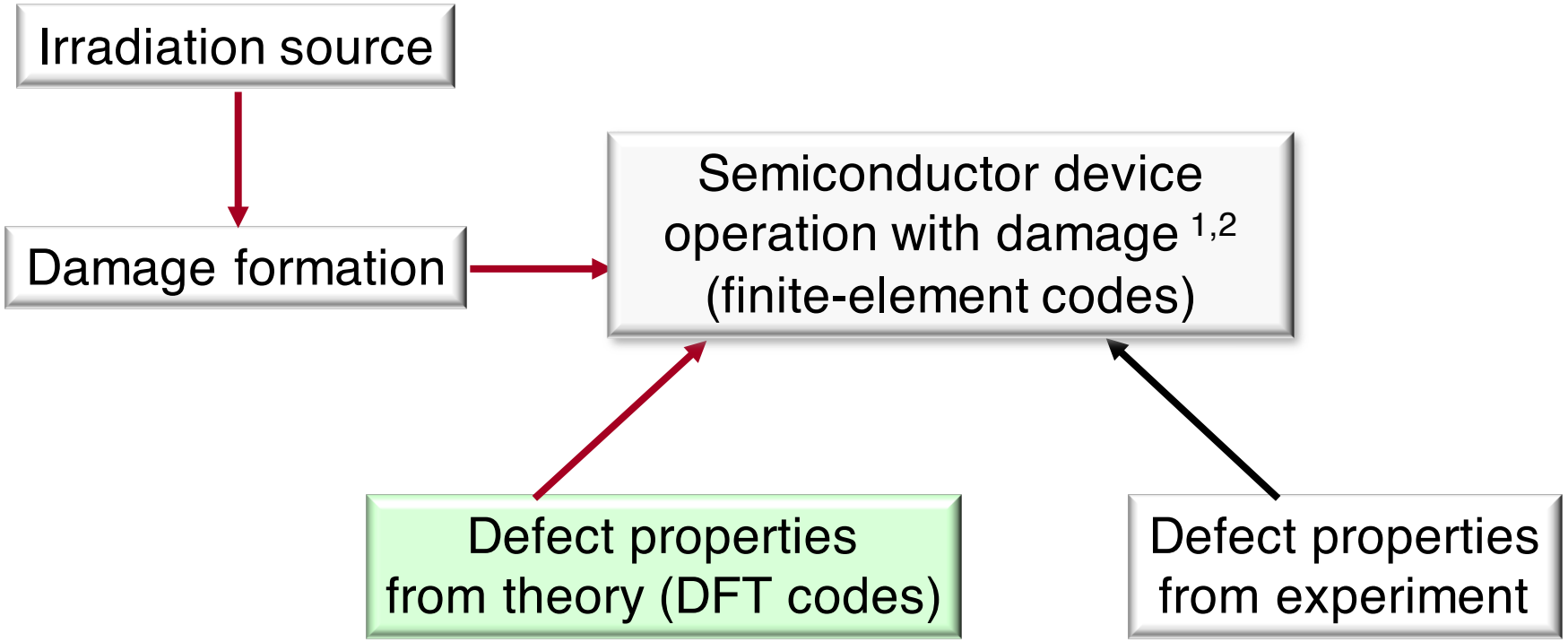
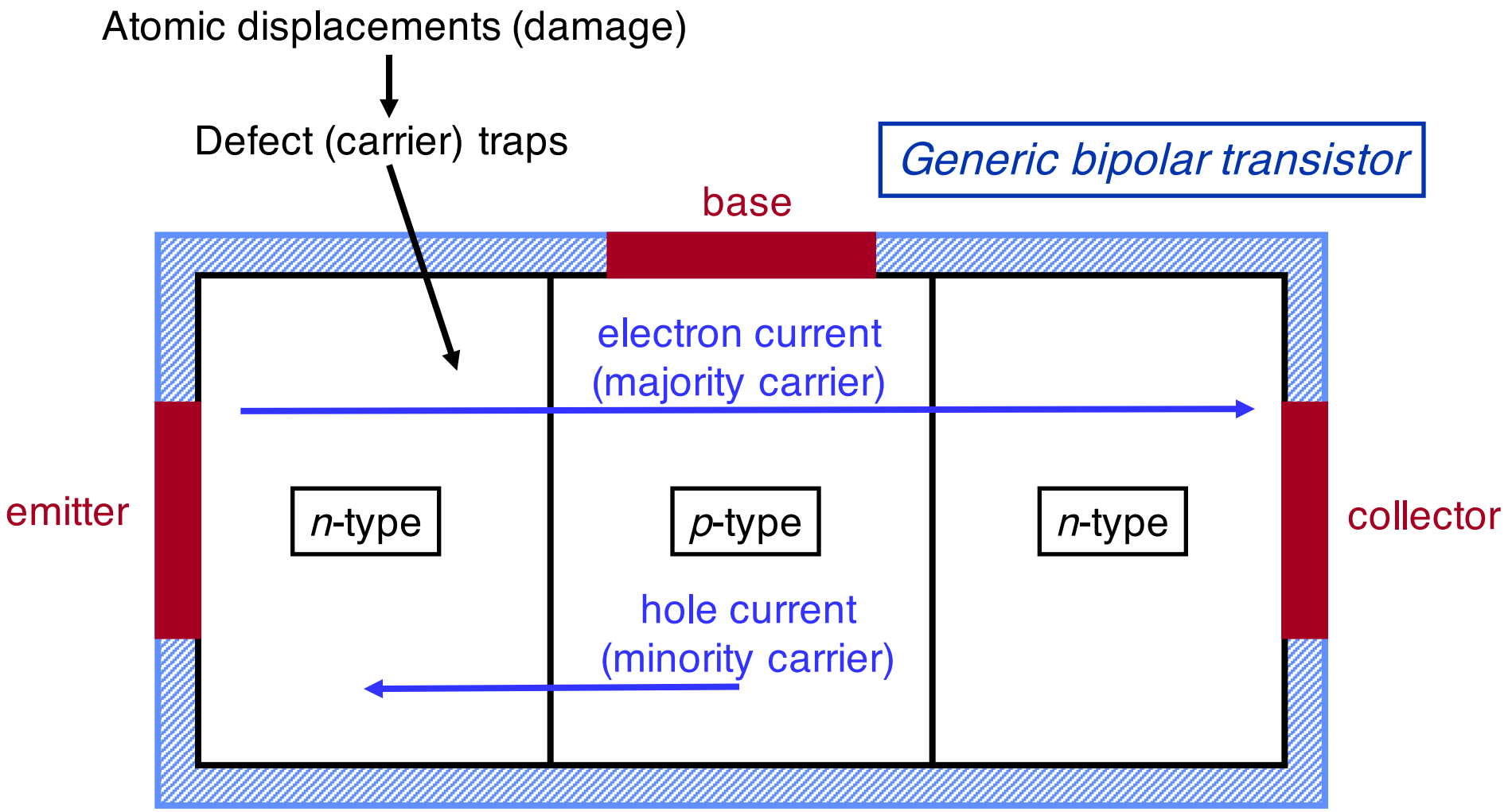
Motivation

Sandia is developing new capabilities for predictive simulation of neutron-irradiated semiconductor devices, involving multiple loosely-coupled codes and including both thermal and current-induced annealling of the damage



1. S. M. Myers, P. J. Cooper and W. R. Wampler, J. Appl. Phys. **104**, 044507 (2008)
2. W. R. Wampler and S. M. Myers, J. Appl. Phys. **117**, 045707 (2015)

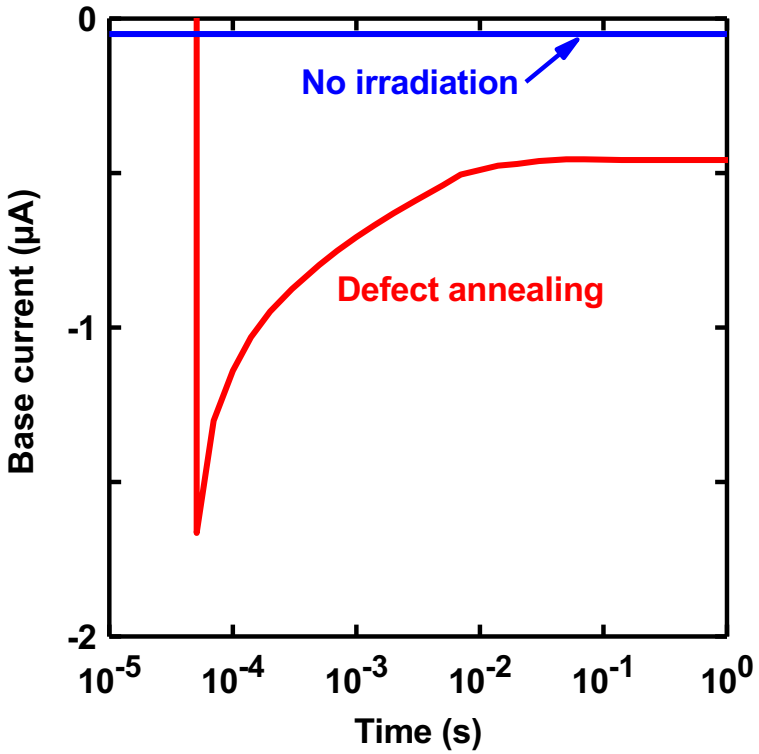
Background



Rapid gain changes occur due to the formation and subsequent annealling of defect traps, which cause carrier recombination and increased base current

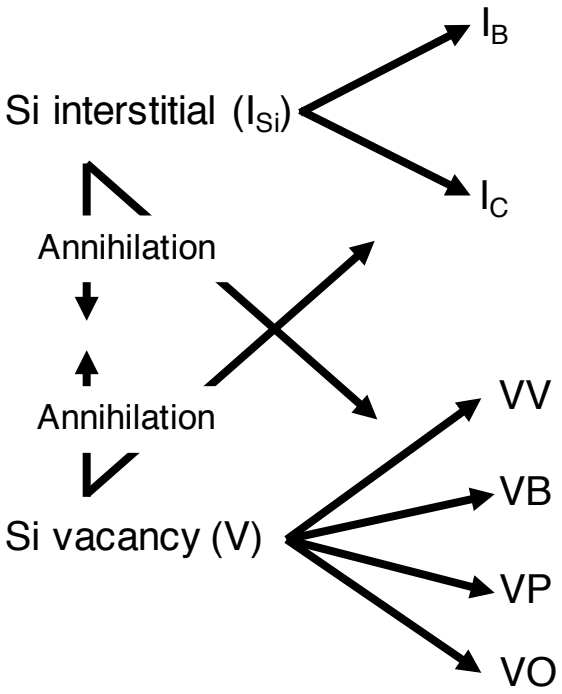
Background

Experimental data for a Si bipolar transistor



Defect traps in Si and their evolution

Primaries Secondaries… and so on



The recovery toward the pre-irradiation base current is largely due to migration of the Si interstitial and its reactions with other defects, dopants and impurities

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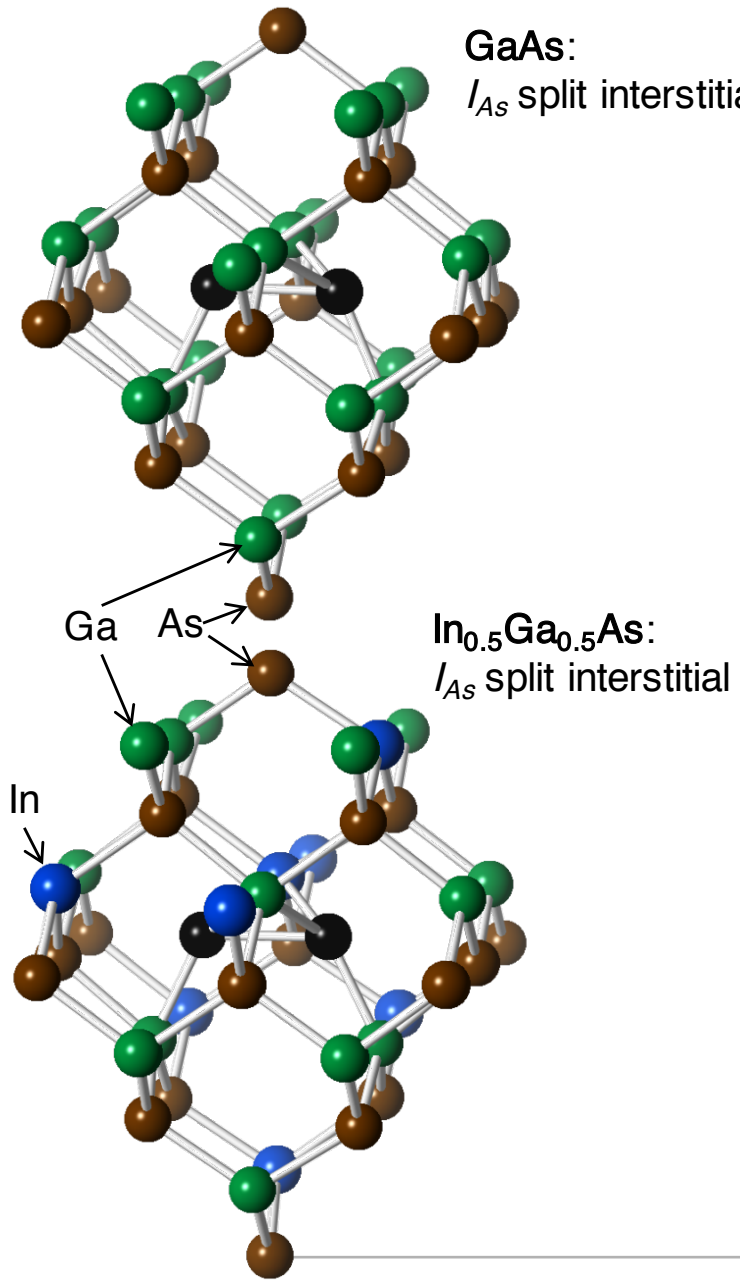
The As interstitial (I_{As}) in GaAs and InGaAs



Sandia has developed simulation capabilities for both Si and GaAs-based devices

The Si-device capability employs our earlier DFT/LDA results for Si interstitial migration

The GaAs-device capability uses our recent DFT/LDA results for I_{As} migration in GaAs

Current work is focused on understanding and predicting I_{As} migration in an $In_{0.5}Ga_{0.5}As$ alloy where configurational complexity fundamentally alters its behavior

Characteristics of I_{As} in GaAs

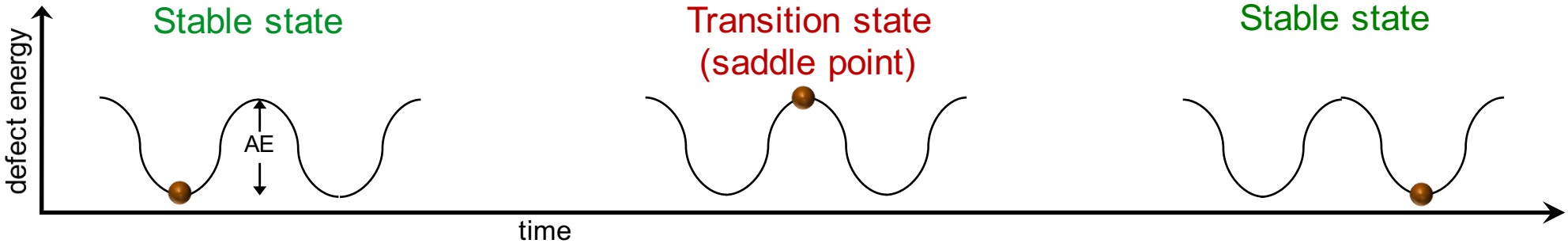
The structure and energy of I_{As} depend on its *charge state* (q)

I_{As} has multiple charge states and *levels* (denoted q-1/q), which are defined as the Fermi levels at which its charge-state changes

The charge states and levels of I_{As} control its relative carrier capture and emission rates (under study by Normand Modine), and thus its influence on device performance

I_{As} is believed to migrate via both *thermal* and *carrier-induced* [3] processes

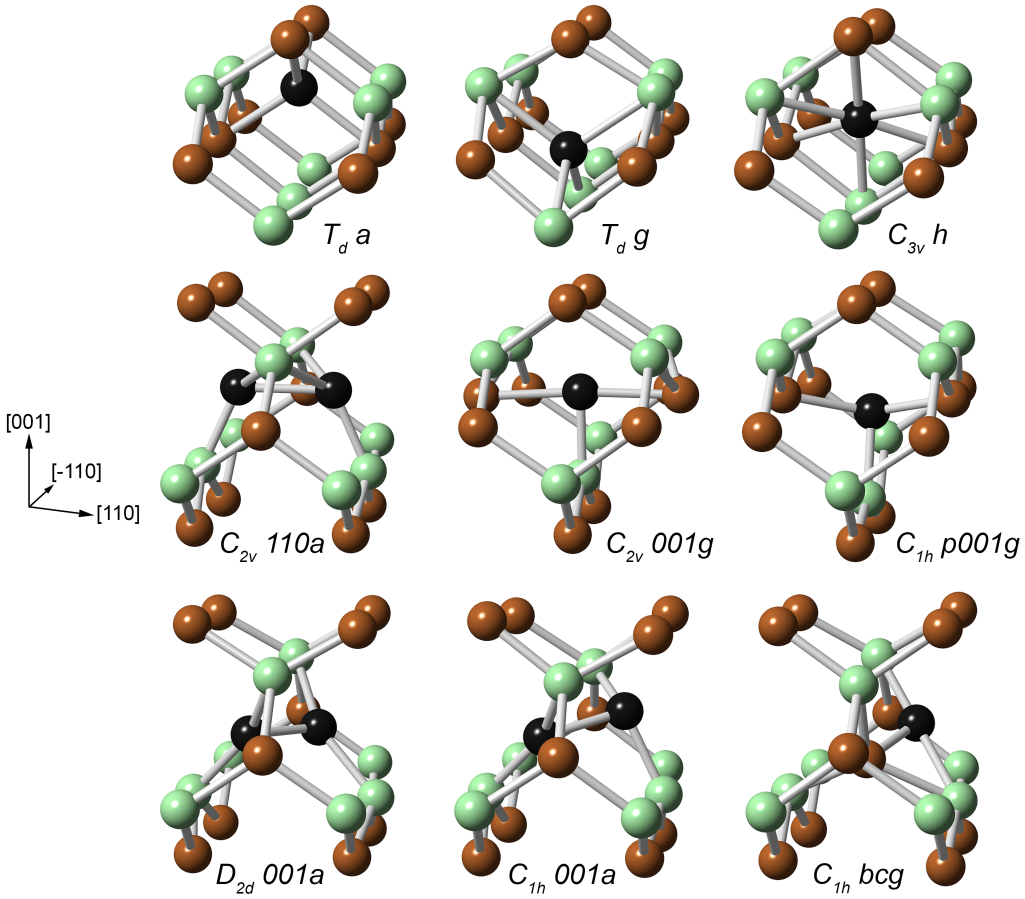
Thermal migration process with a site-independent activation energy (AE)



3. The first report of carrier-induced annealling in GaAs was from Sandia's Radiation Sciences Center:
C. E. Barnes, Phys. Rev. B **1**, 4735 (1970)

Identifying the migration processes

Candidate configurations



Procedure

- A *bounds analysis* [4] was used to identify the charge states of each candidate configuration
- For each charge state, the *dimer method* [5] was used to search for stable and transition states
- For each transition state, the dimer configura configurations were relaxed to the associated stable states
- For each transition-state/stable-state pair, the AE was calculated from their formation energies
- Cell-size effects were removed by extrapolating formation energies from 216-, 512- and 1000-atom supercells to the infinite-cell-size limit [6]

4. N. A. Modine, A. F. Wright and S. R. Lee, Comput. Mater. Sci. **92**, 431 (2014)
5. G. Henkelman and H. Jonsson, J. Chem. Phys. **111**, 7010 (1999)
6. G. Makov and M. C. Payne, Phys Rev. B **51**, 4014 (1995)

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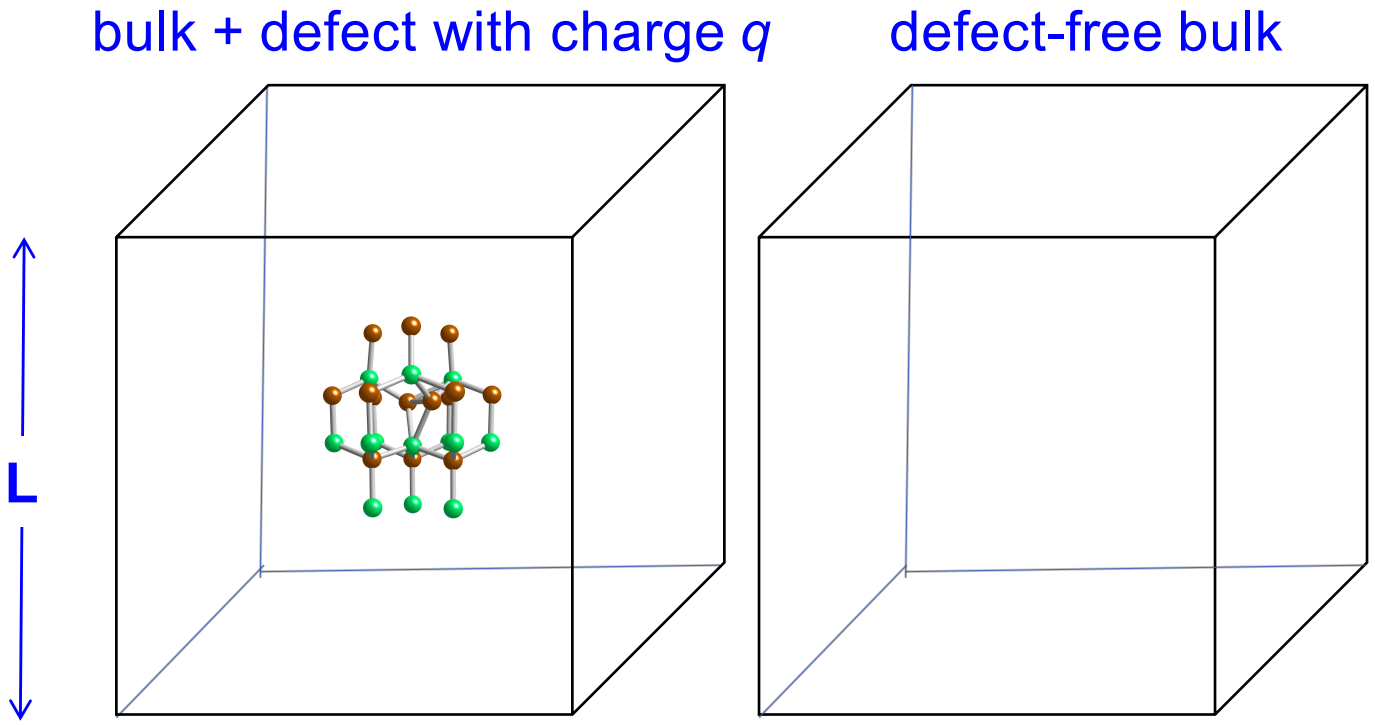
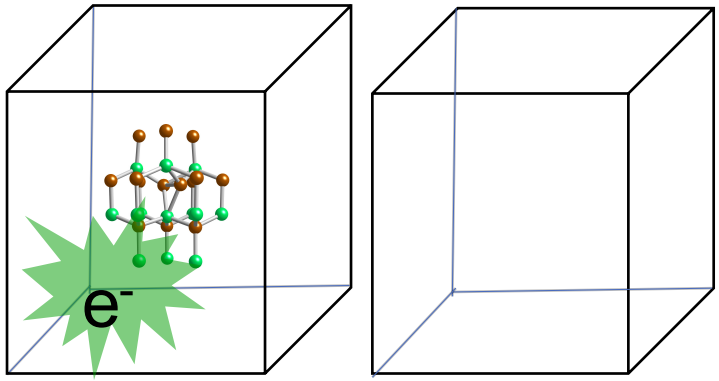
Bounds on DFT Defect Levels

Consider the combined energy of two independent, finite-sized cells…

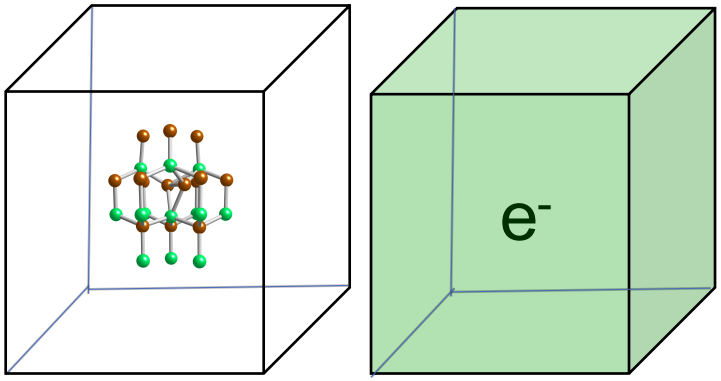


Bounds on DFT Defect Levels

Add an extra electron to one or the other of the cells…



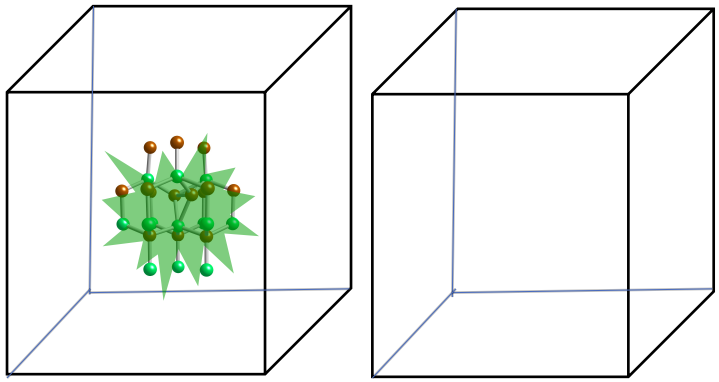
$$E^D(q-1,L) \quad + \quad E^B(0,L)$$



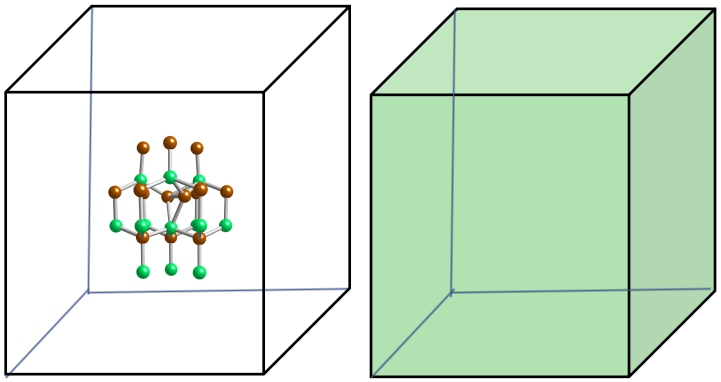
$$E^D(q,L) \quad + \quad E^B(-1,L)$$

Bounds on DFT Defect Levels

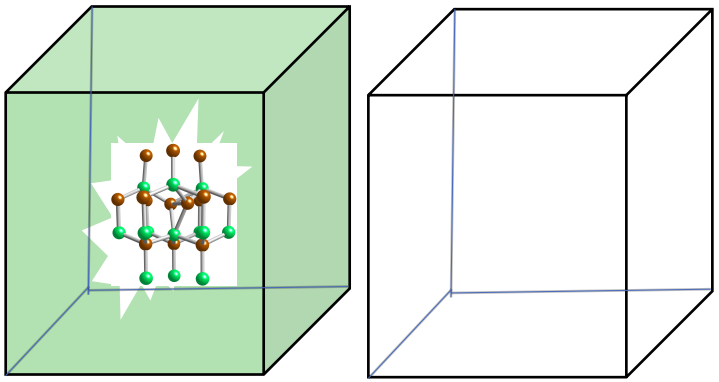
If the electron is attracted to the defect;



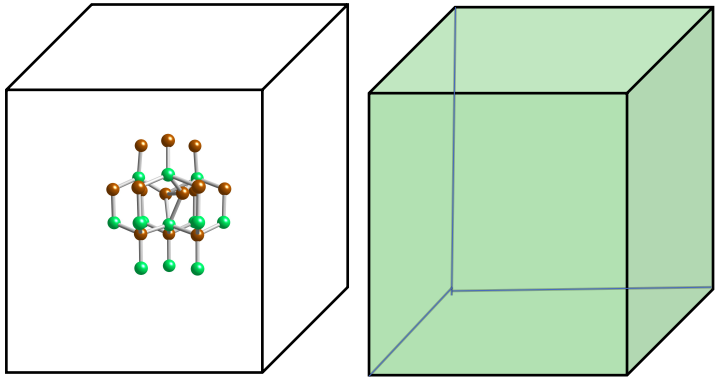
$$E^D(q-1,L) + E^B(0,L) < E^D(q,L) + E^B(-1,L)$$



If the electron is repelled by the defect;



$$E^D(q-1,L) + E^B(0,L) < E^D(q,L) + E^B(-1,L) + \delta(L)$$



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Bounds on DFT Defect Levels

Rearranging, we get an approximate *upper bound* on the defect level:

$$\Delta^D(q-1/q,L) \le \Delta^B(-1,L) + \delta(L)$$

Where the bound is the negative of the electron affinity:

$$\Delta^B(-1,L) \equiv E^B(-1,L) - E^B(0,L)$$

And the bound is exact in the limit of an infinite-sized cell:

$$\delta(L) \to 0 \quad \text{as} \quad L \to \infty$$

Similarly, adding an extra hole gives a *lower bound*:

$$\Delta^D(q+1/q,L) \ge \Delta^B(+1,L) - \delta(L)$$

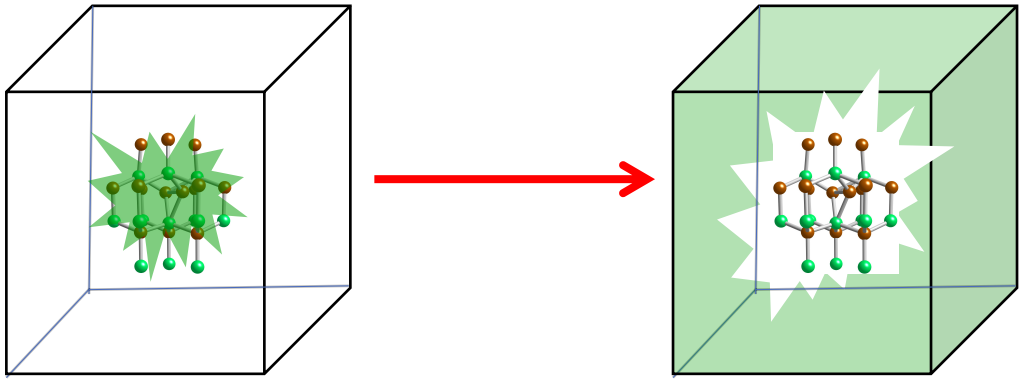
Where the bound is the negative of the ionization energy:

$$\Delta^B(+1,L) \equiv E^B(0,L) - E^B(+1,L)$$

Physical Meaning of the Bounds

If the *q-1/q* defect level matches the upper bound, then the energy of the defect in charge state *q-1* is the same as the energy of the defect in charge state *q* plus an extra electron in the bulk. This is unlikely to happen by accident.

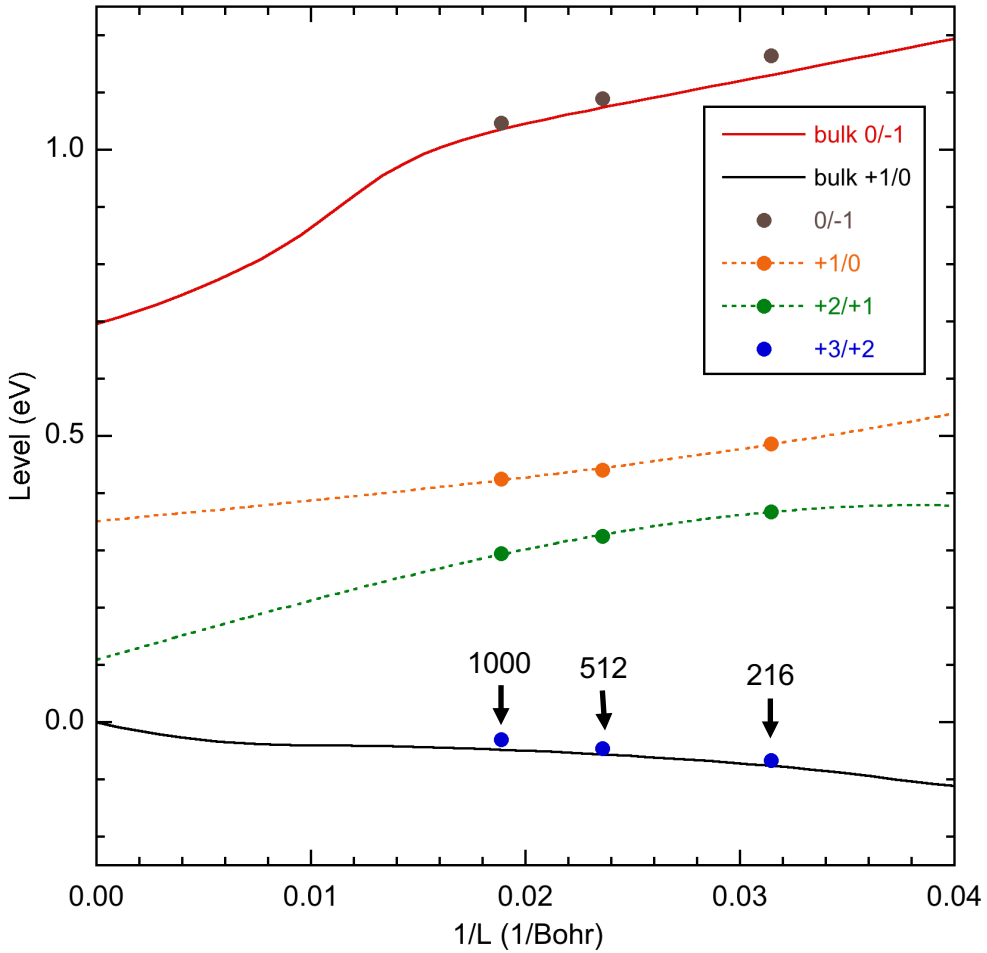
Instead, the defect in charge state *q-1* is unstable and spontaneously converts to charge state *q* losing an electron to the bulk!



Likewise, if the *q+1/q* level matches the lower bound, then the defect in charge state *q+1* is unstable and spontaneously converts to charge state *q* losing a hole to the bulk.

Bounds analysis of the As antisite (As_{Ga}) in GaAs

The bounds are seen to limit the charge states (and levels) of As_{Ga}



- The plots are As_{Ga} 0/-1, +1/0, +2/+1 and +3/+2 levels and Makov-Payne fits
- Results for the 0/-1 and +3/+2 levels are close to the bounds, meaning…
  - ✓ the (proposed) q = -1 state is q = 0 plus an electron in the conduction band
  - ✓ the (proposed) q = +3 state is q = +2 plus a hole in the valence band

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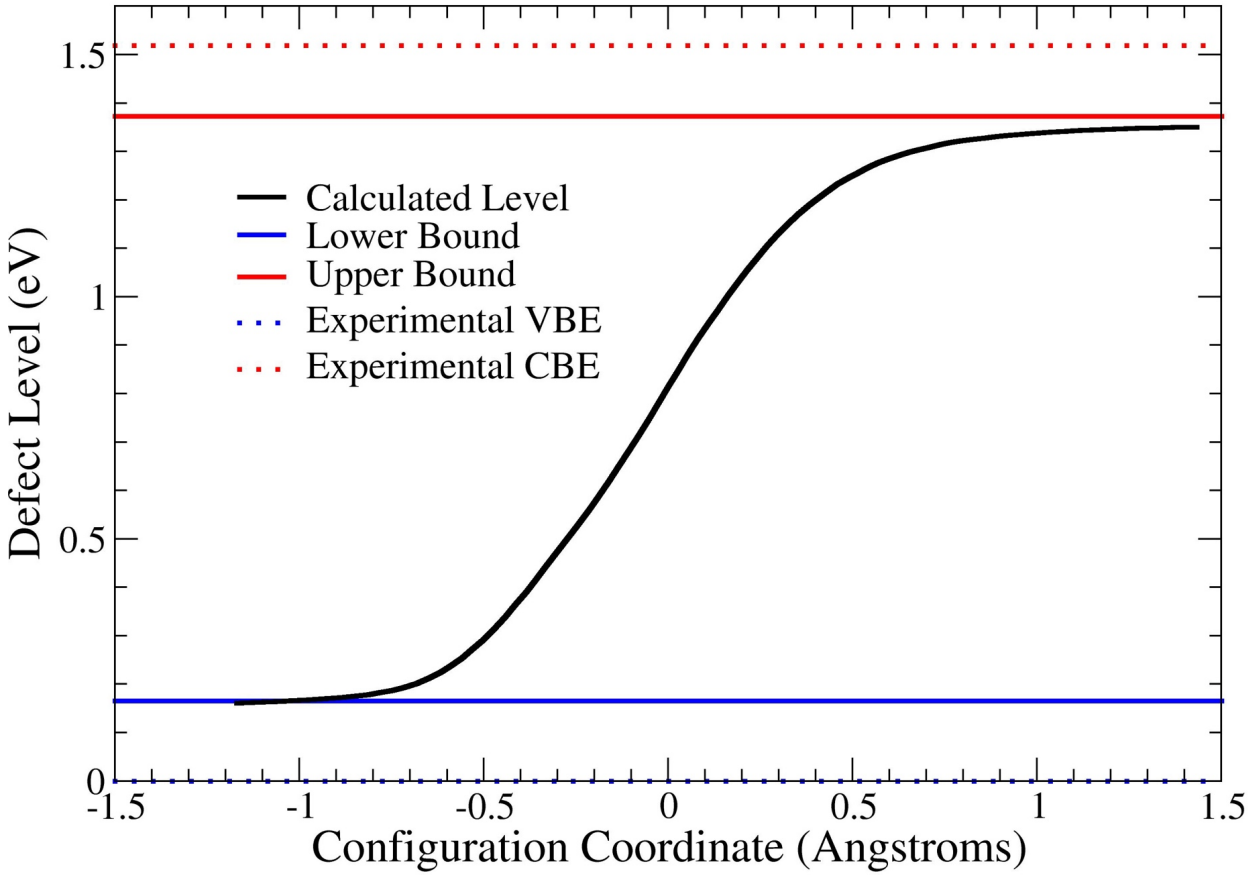
Further evidence of the limiting-role of the bounds

The bounds limit the allowed movement of the As_{Ga} +1/0 level due to ionic distortions (relevant to studies of non-radiative carrier capture)[7]



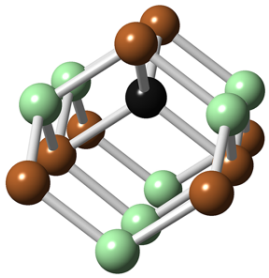
7. N. A. Modine, unpublished

Some Conclusions about the Bounds

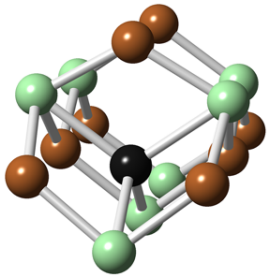
- *Help explain why DFT calculations with finite supercells can give good defect levels despite the band-gap problem*
- *Are a powerful tool to determine when a defect charge state is unstable (using a particular supercell and functional)*
- *Demonstrate (yet again) why more advanced functionals are needed for defect calculations*

Stable states

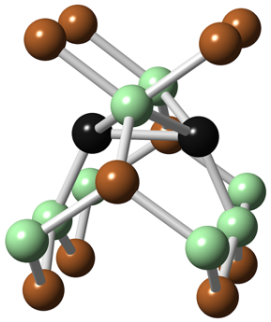
Stable-state configurations



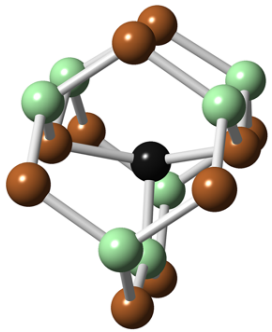
T_d *a : q = +3*



T_d *g : q = +3*

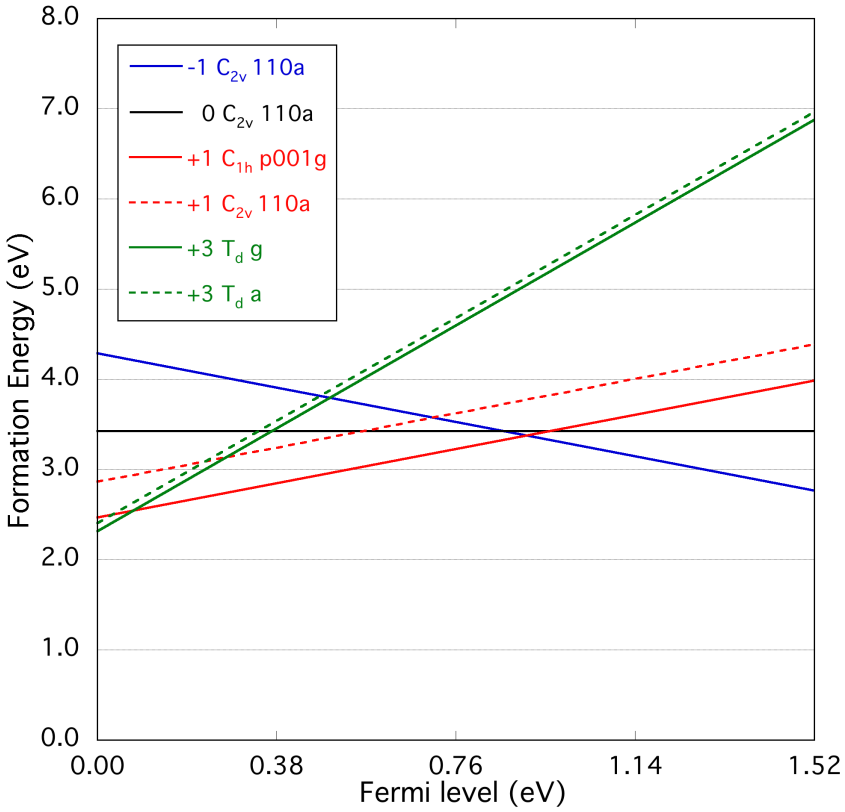


C_{2v} *110a : q = -1, 0, +1*



C_{1h} *p001g : q = +1*

Fermi-level dependence of the stable-state formation energies



(solid lines are ground states, dashed lines are metastable states)

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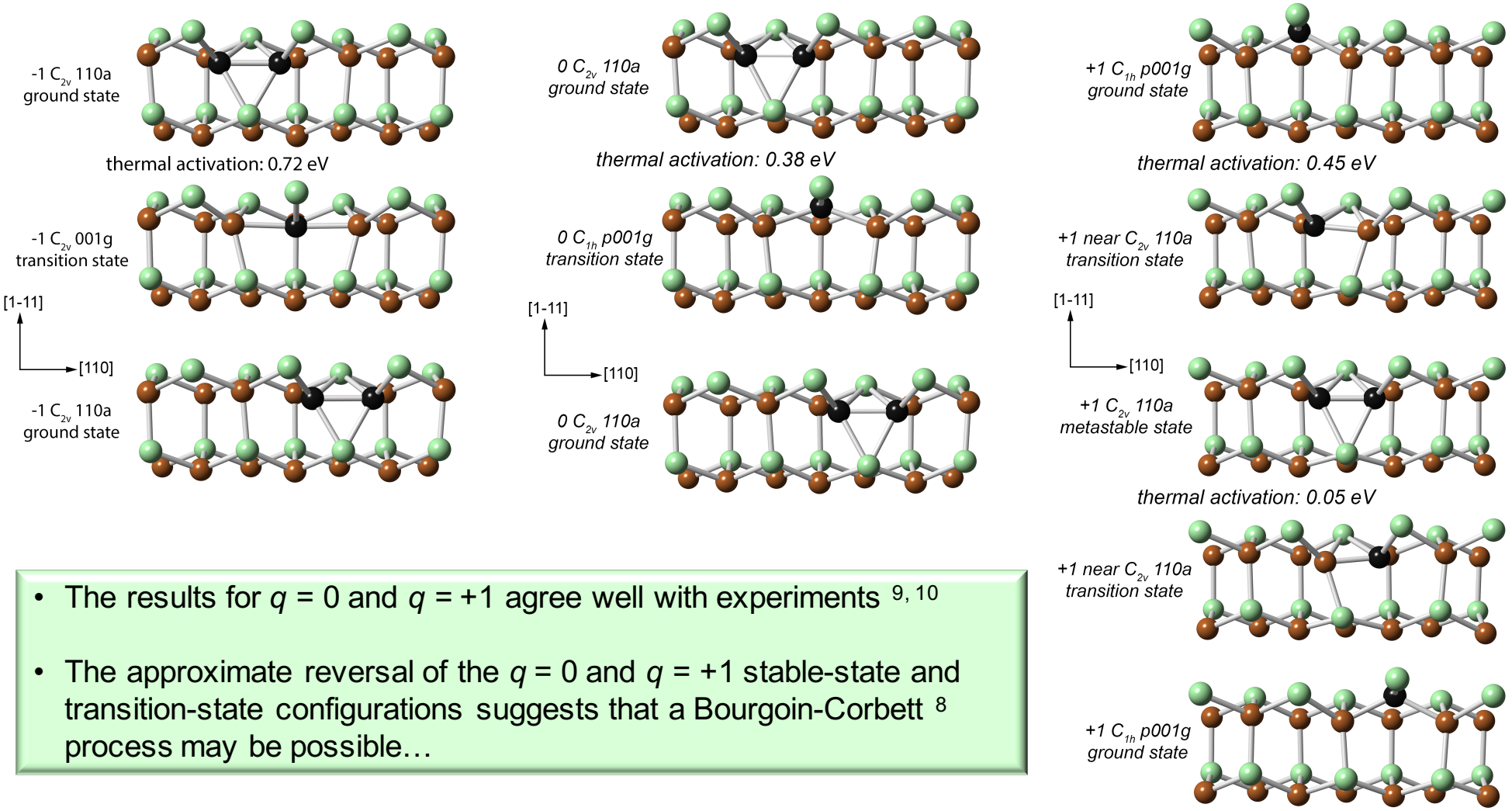
Lowest-energy thermal migration processes

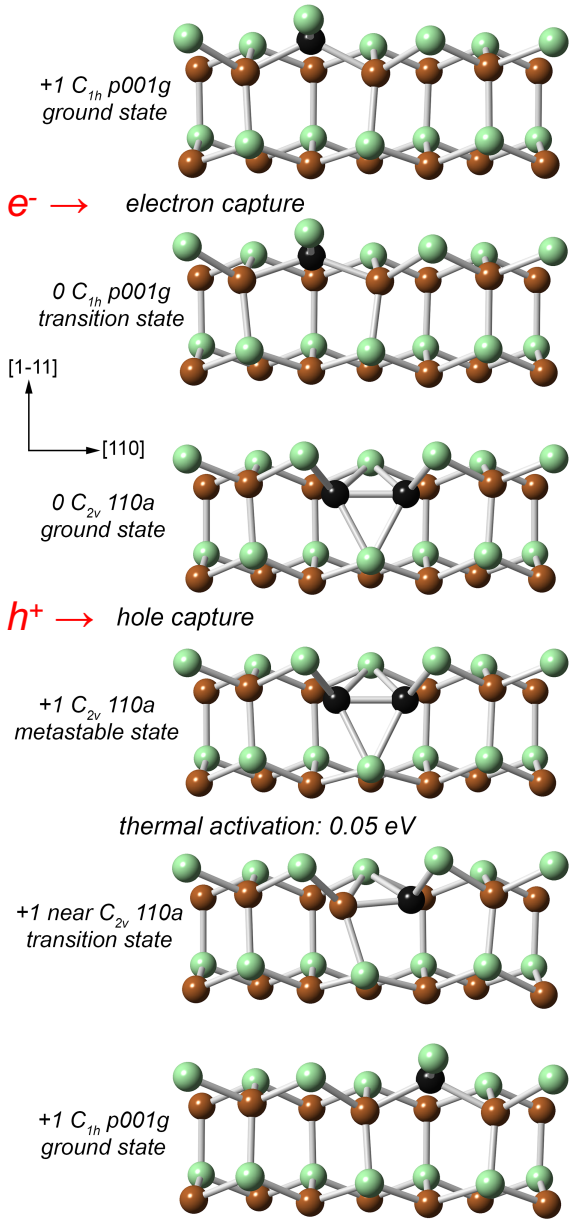


- The results for q = 0 and q = +1 agree well with experiments [9, 10]
- The approximate reversal of the q = 0 and q = +1 stable-state and transition-state configurations suggests that a Bourgoin-Corbett [8] process may be possible…

8. J. C. Bourgoin and J. W. Corbett, Radiation Effects **36**, 157 (1978)
9. R. F. Scholz and U. Gosele, J. Appl. Phys. **87**, 704 (2000)
10. D. Stievenard, X. Boddaert and J. C. Bourgoin, Phys. Rev. B **34**, 4048 (1986)

Bourgoin-Corbett migration processes

- Alternating capture of an electron and a hole is predicted to produce (nearly) athermal migration with a residual AE of 0.05 eV
- This result is consistent with the observation of carrier-induced annealling in gamma-irradiated GaAs diode by Barnes [8]



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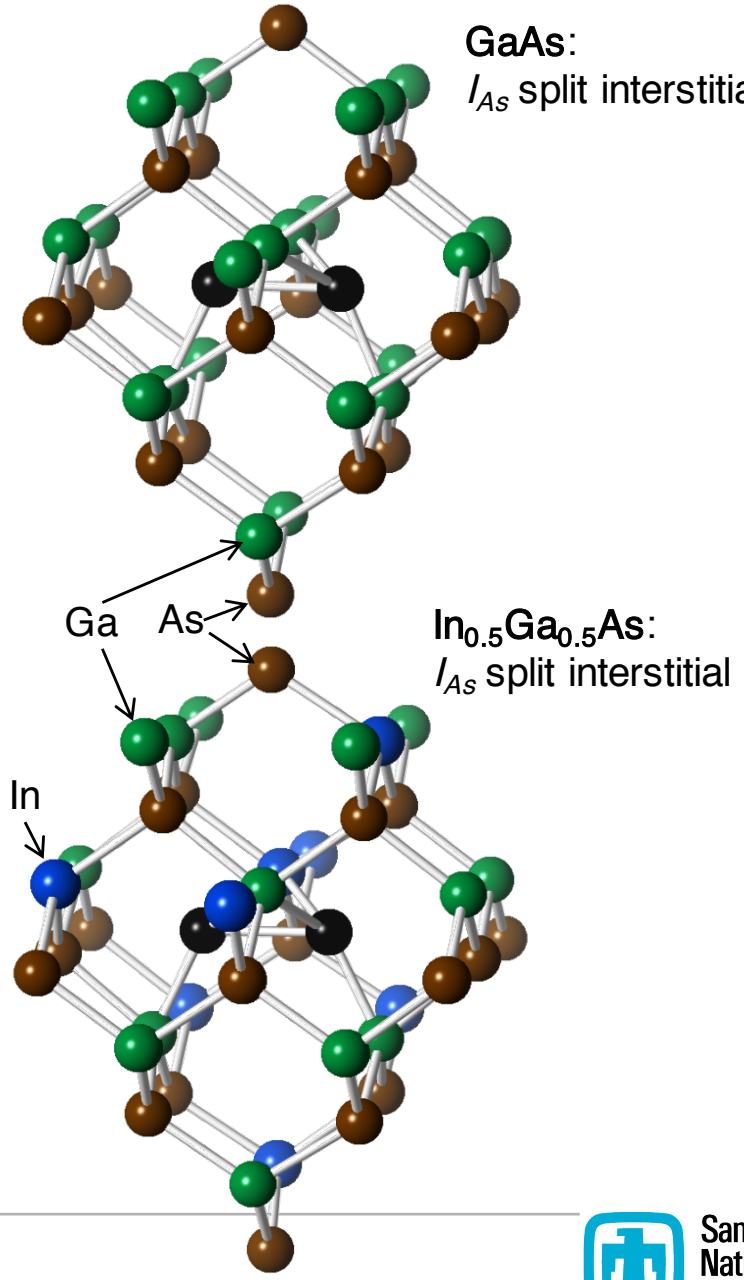
New capability to simulate diffusion in an alloy

Why is this challenging? – Configurational complexity fundamentally alters defect energies and behavior – computational burden rises exponentially

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



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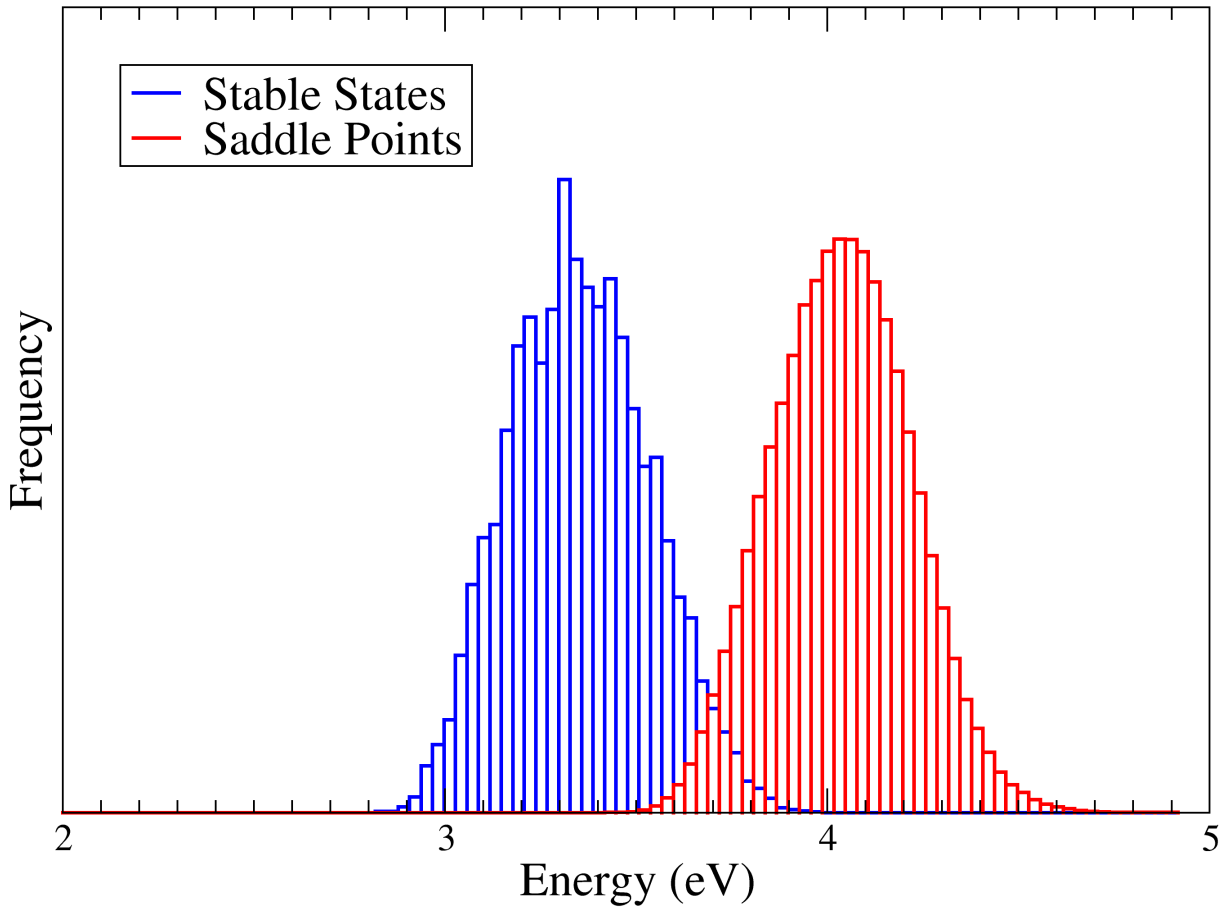
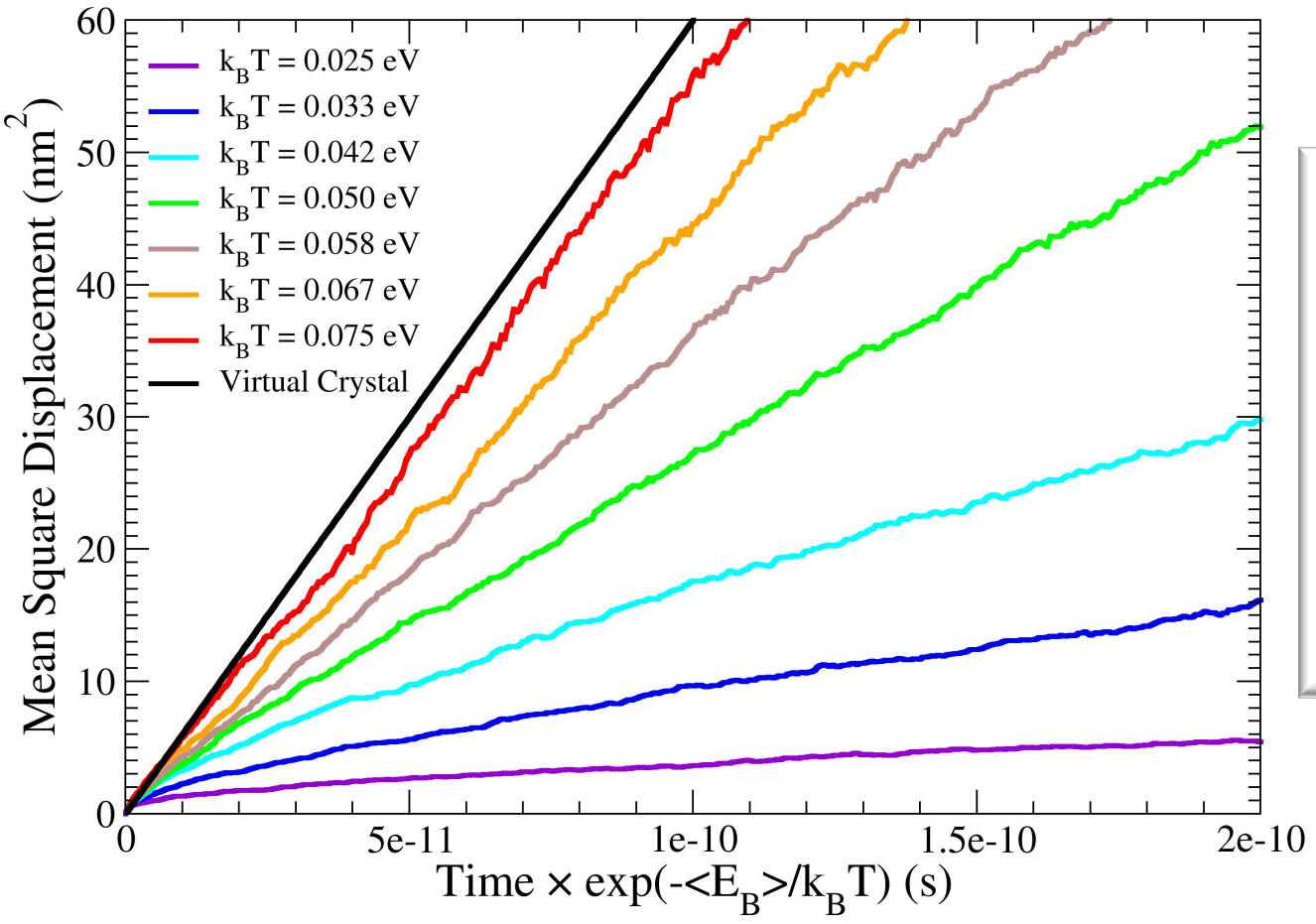
Results from Cluster Expansions (q = -1)

Histograms of stable-state and saddle-point energies



- Similar distributions for saddle point and stable state energies
- The difference between the average saddle point and stable state energies is similar to the barrier in GaAs (0.7 eV)
- The fact that the energies have distributions has a profound effect on defect diffusivities!

Temperature Dependence of Thermal Diffusion



- We compare diffusion at different temperatures (T) by rescaling time
- In a homogeneous system, the rescaled rate of diffusion is then independent of T (labeled Virtual Crystal in the plot)
- In contrast, diffusion in the alloy is slowed by a large, T dependent factor

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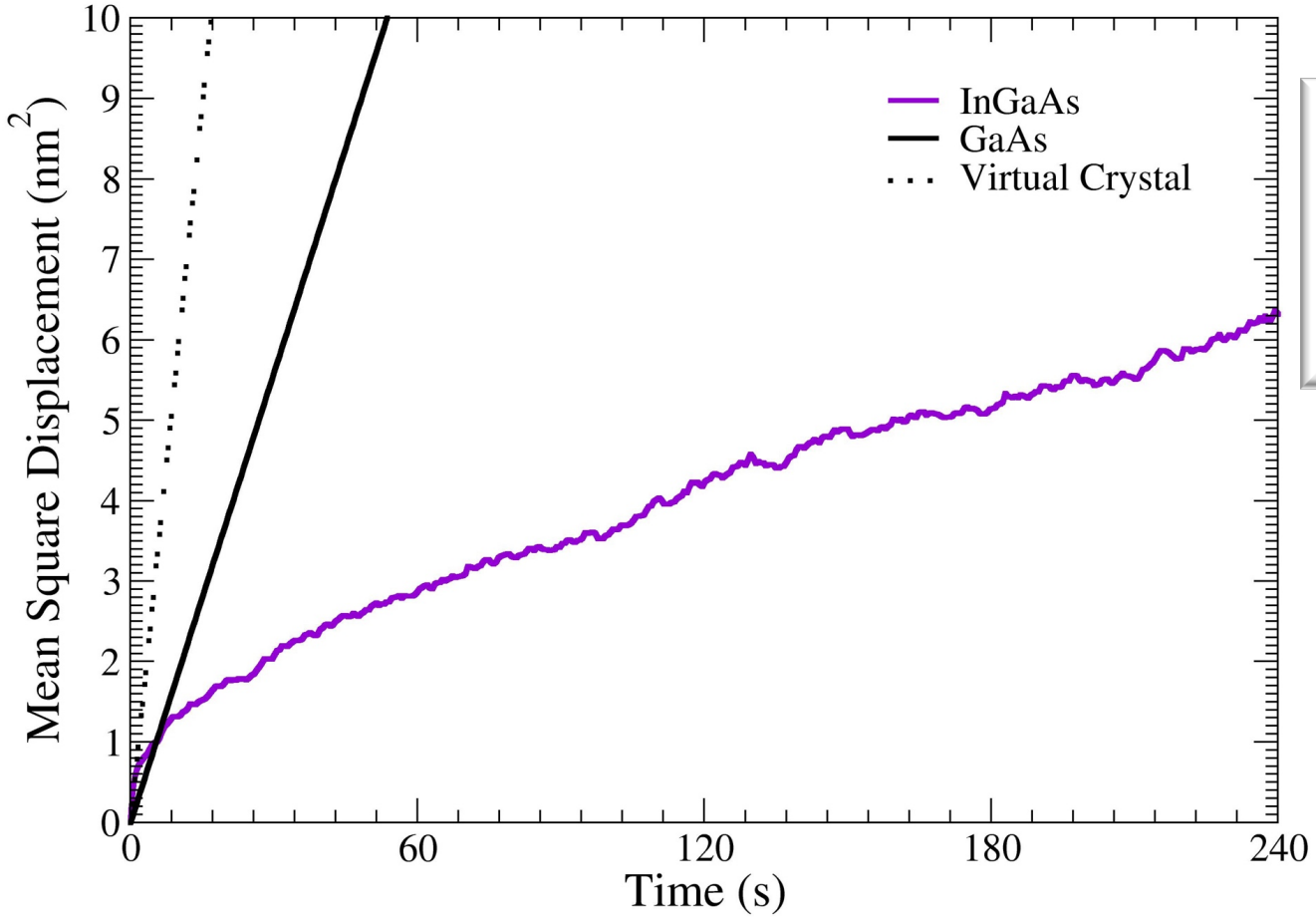
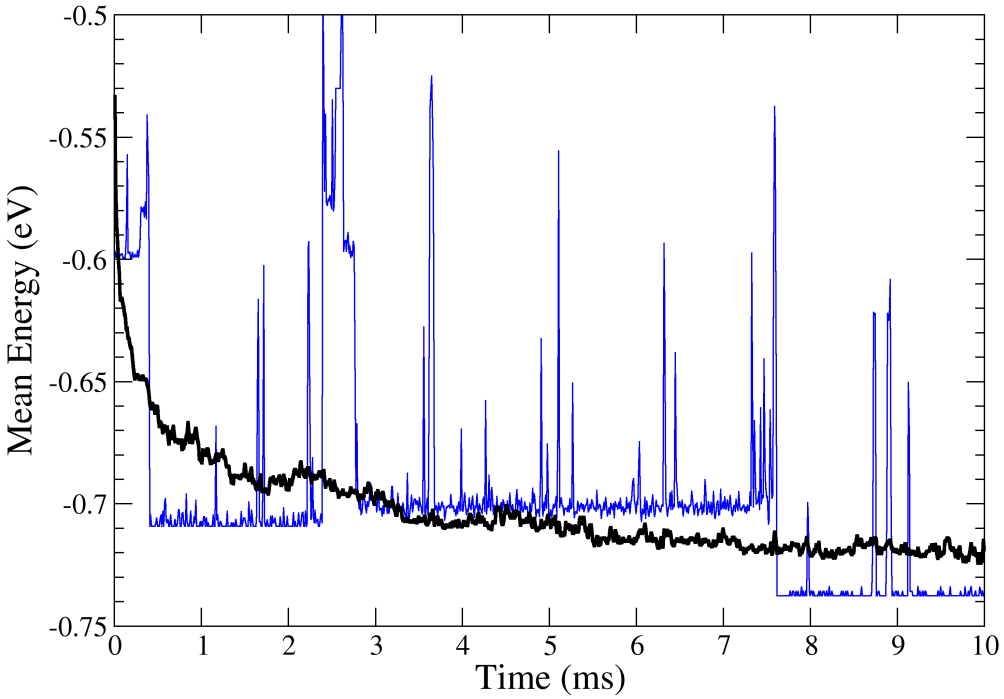
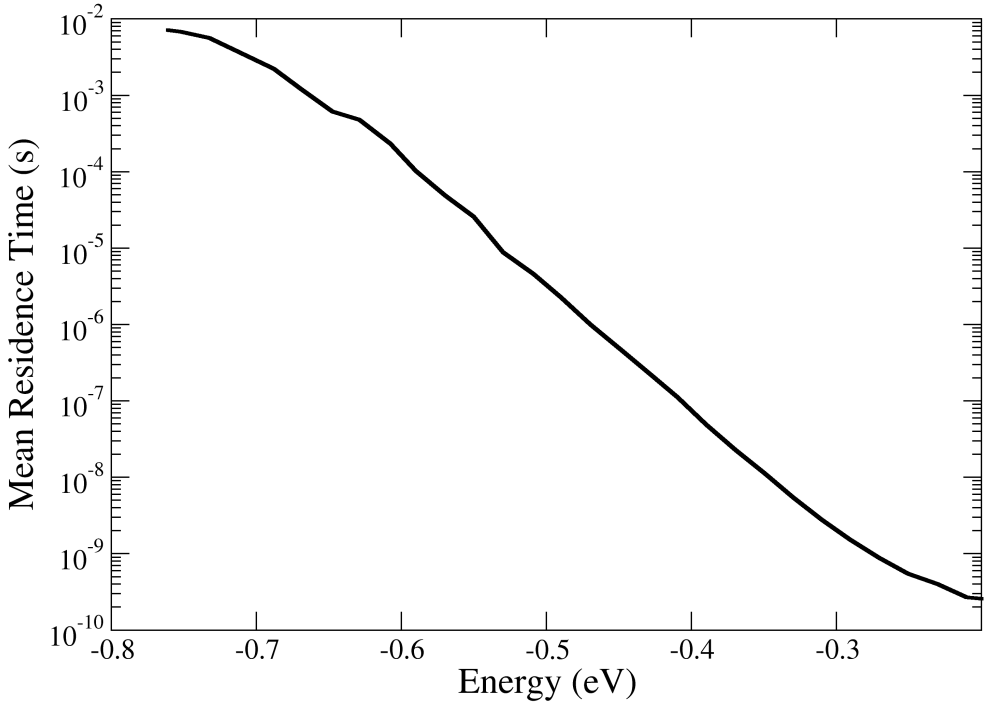
Temperature Dependence of Thermal Diffusion



- If we look closer, we see that the diffusion slows down with time
- This is not something that can be modeled with a single activation energy

Why Does Diffusion Slow Down?





- As the defect diffuses, it finds lower energy sites in the alloy.
- Lower energy sites trap the defect for (exponentially) longer times.
- The fact that there is a distribution of stable-state energies fundamentally alters the diffusion of I_{As} in InGaAs.

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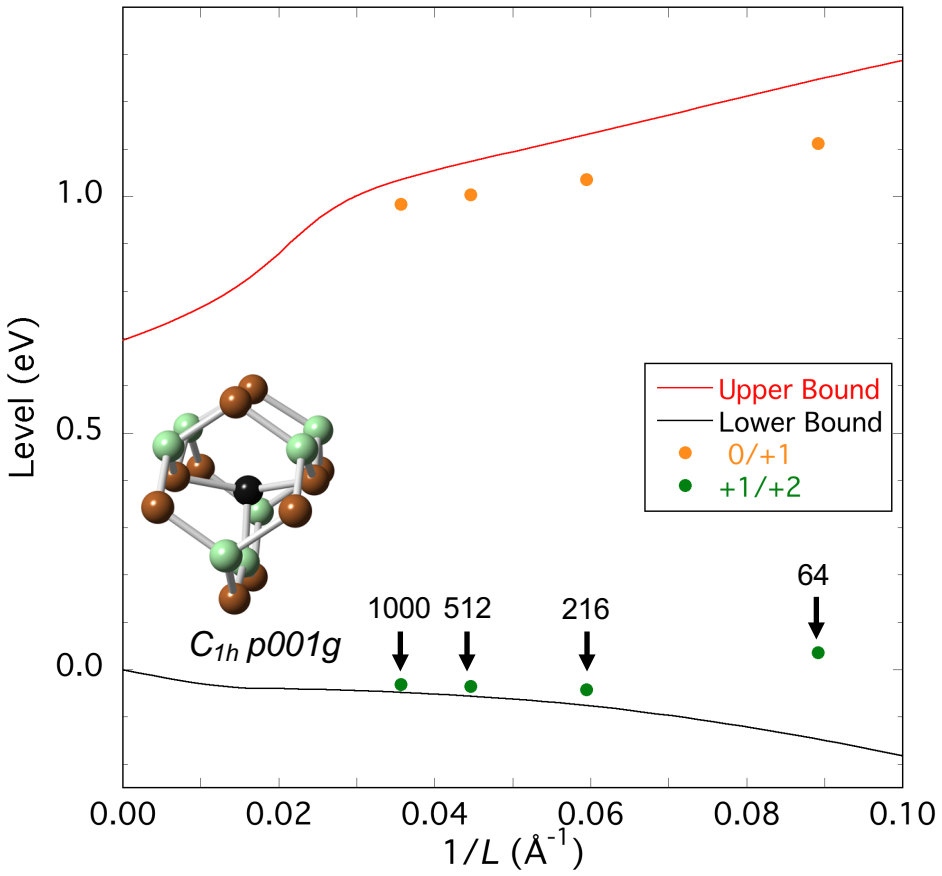
Conclusions

- DFT calculations, even using functionals such as the LDA, are able to provide useful information about defects in binary semiconductors and enable predictive simulations of gain-degradation and recovery in semiconductor devices
- We have combined DFT with Cluster Expansions, and KMC to gain new insights into defect diffusion in semiconductor alloys
- A notable insight is that diffusion at normal temperatures will require explicit consideration of the alloy-site dependence of the stable-state defect energies

Why is there no *q* = +2 state?



- The bounds analysis clearly identifies a +1 charge state for C_{1h} *p001g*
- When an electron is added to the +1 state, it becomes partially de-localized (~25%) in the conduction band, allowing an estimate to be made of its formation energy
- When an electron is removed from the +1 state, the hole is mostly de-localized in the valence band (~55% in the 216-atom cell, ~70% in the 512-atom cell, and ~80% in the 1000-atom cell), not allowing an estimate to be made
- In a 64-atom cell, the +2 state is stable