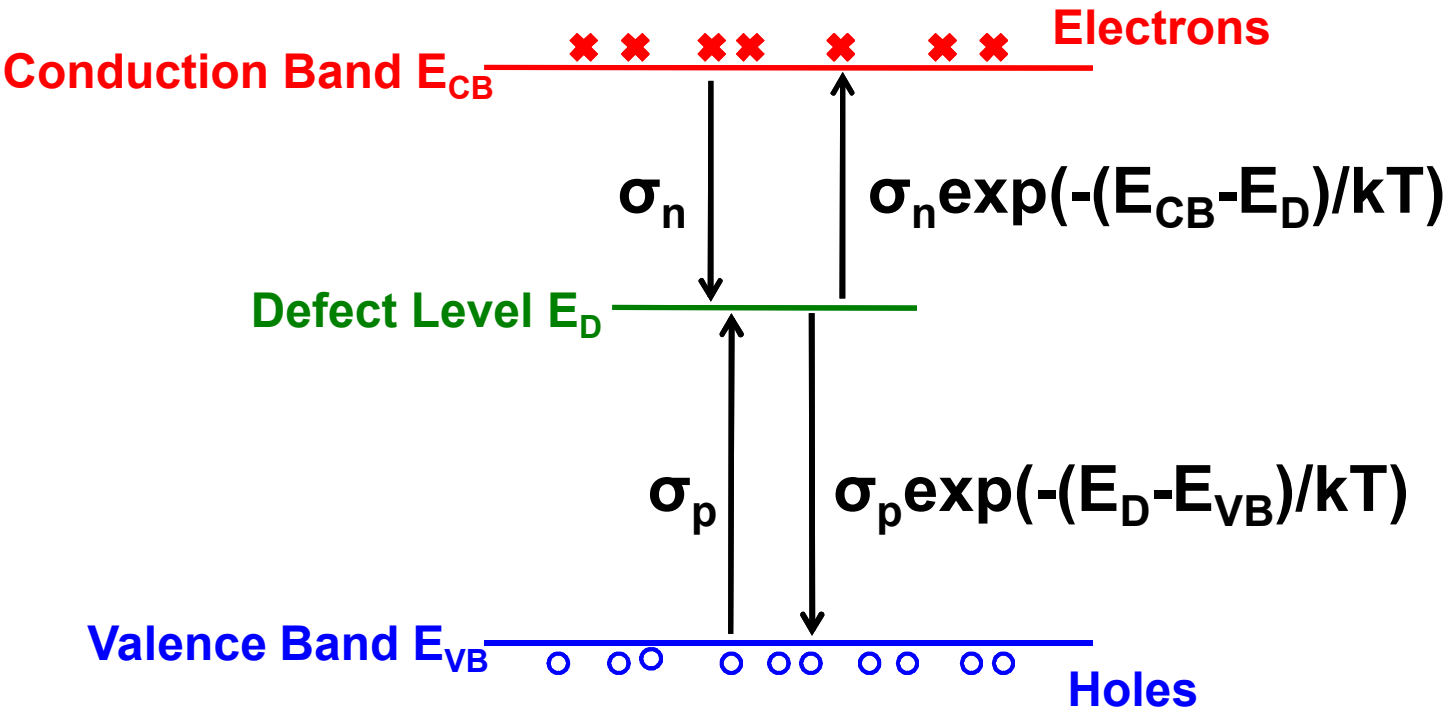
SAND2015-5053C

DFT Calculations of Activation Energies for Carrier Capture by Defects in Semiconductors



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How Much Do Real Cross-Sections Vary?

Henry and Lang, PRB 1977 studied
13 cross-sections in GaAs and GaP

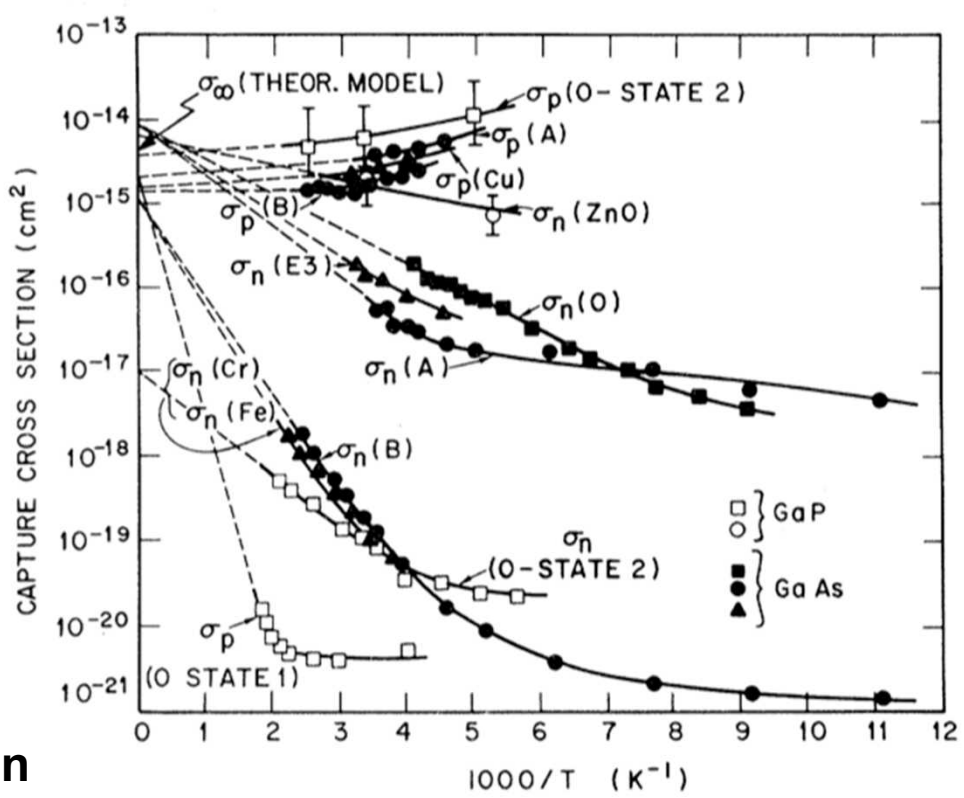
Wide variation at room-temperature

Extrapolate to similar values at high-T

Generally, have the high-T form

$$\sigma(T) = \sigma_\infty \exp(-E_B/kT)$$

Henry and Lang's theory of Multiphonon Emission explains this result



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Henry and Lang Theory of Carrier Capture

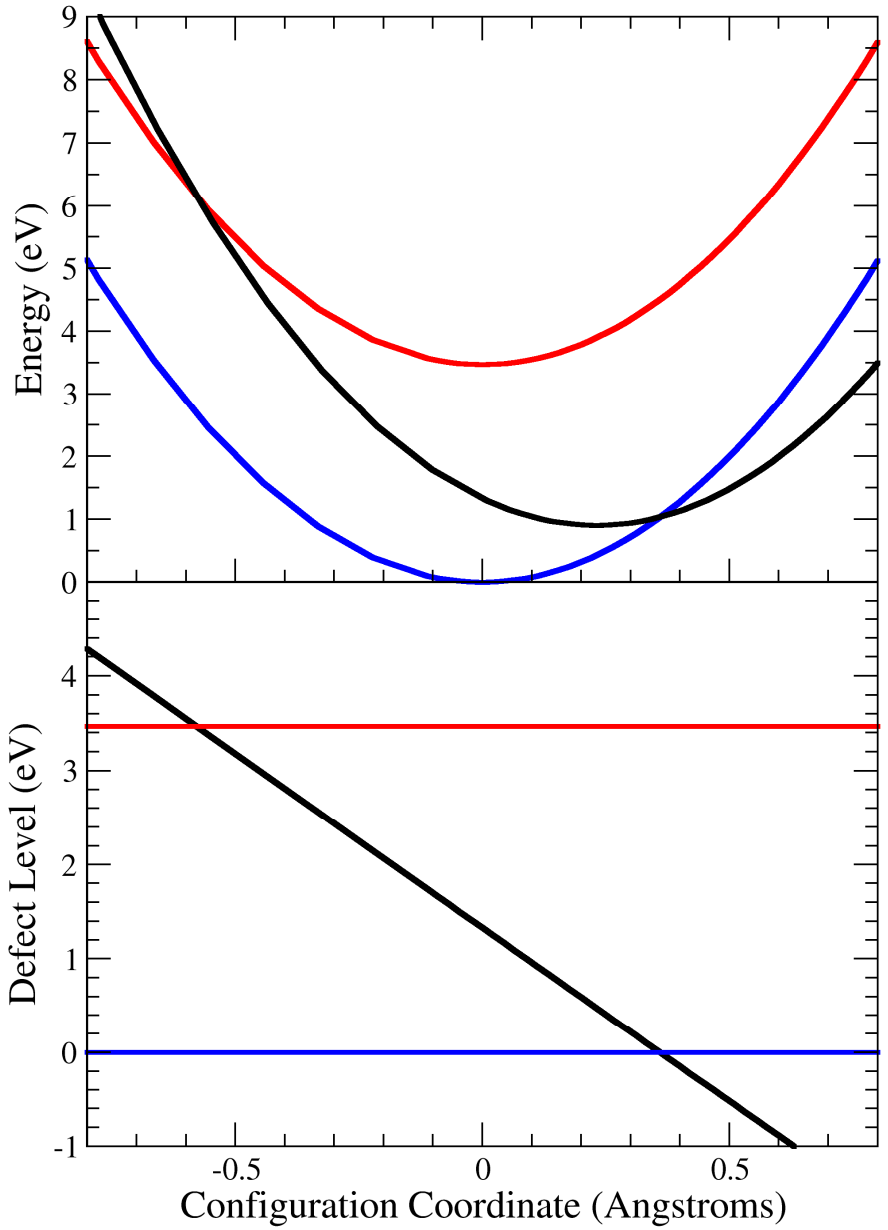
Assume a configuration coordinate λ

Upper Panel: λ-Dependent Energies
Blue Line: Q_D=q with no carriers
Black Line: Q_D=q-1 with a hole
Red Line: Q_D=q with hole and electron

Lower Panel: λ-Dependent Defect Level
Black Line:q-1/q defect level
Blue Line: Valence band
Red line: Conduction band

Nonradiative capture/emission occurs near level crossings when energy can be conserved

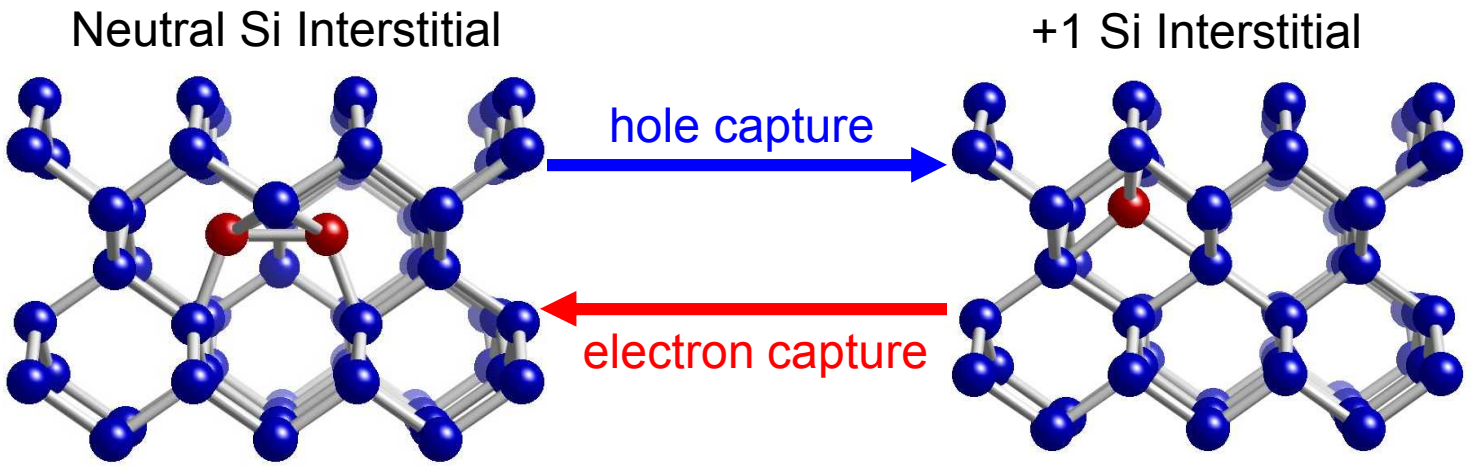
Activation energies given by differences between crossing-points and minima



First-Principles Calculations of Carrier Capture

Detailed theories based on DFT perturbation theory (L. Shi and L.-W. Wang, PRL 2012; A. Alkauskas et al., PRB 2014) have been developed to calculate capture cross-sections when the harmonic approximation holds

Instead, we have considered the anharmonic case:



So far, we have focused on carrier capture activation energies and the high-T behavior

DFT w/ Assumed Configuration Coordinate

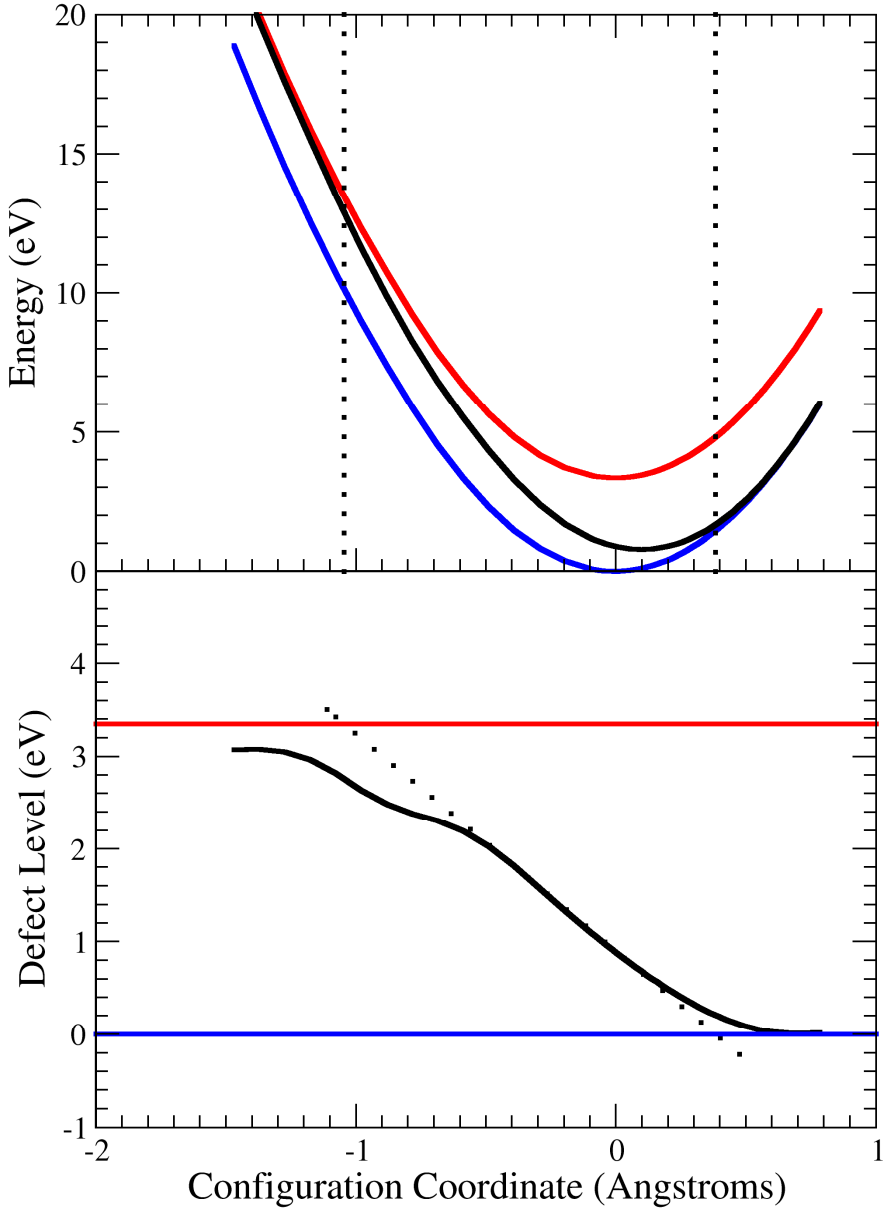
V_{Ga} -2/-3 level in GaN – Possibly associated with yellow luminescence

Extrapolated configuration coordinate from difference in relaxed structures

Upper Panel:
Blue Line: Q_D=-2 with no carriers
Black Line: Q_D=-3 with a hole
Red Line: Q_D=-2 with hole and electron

Lower Panel:
Black Line:-3/-2 defect level
Blue Line: Lower Bound
Red line: Upper Bound

Extrapolation Gives:
0.89 eV activation energy for holes
10.1 eV activation energy for electrons



Configuration Coordinate Optimization

We have developed a new algorithm inspired by transition state finding methods

For a given defect level, perform a constrained minimization of the defect energy over configurations consistent with that level

Consider the pathway of such configurations as the level is varied

Several useful properties:

- We get the same result by minimizing the energy of either charge state
- The pathway passes through both ground state configurations
- We expect the pathway to be piecewise continuous

If “diabatic” energies were used, the pathway would pass through the transition states for carrier capture

The minimization is easily accomplished by mixing Newton steps parallel to the force difference vector with perpendicular relaxation steps

DFT w/ Optimized Configuration Coordinate

For hole capture, optimization doesn't change the results very much

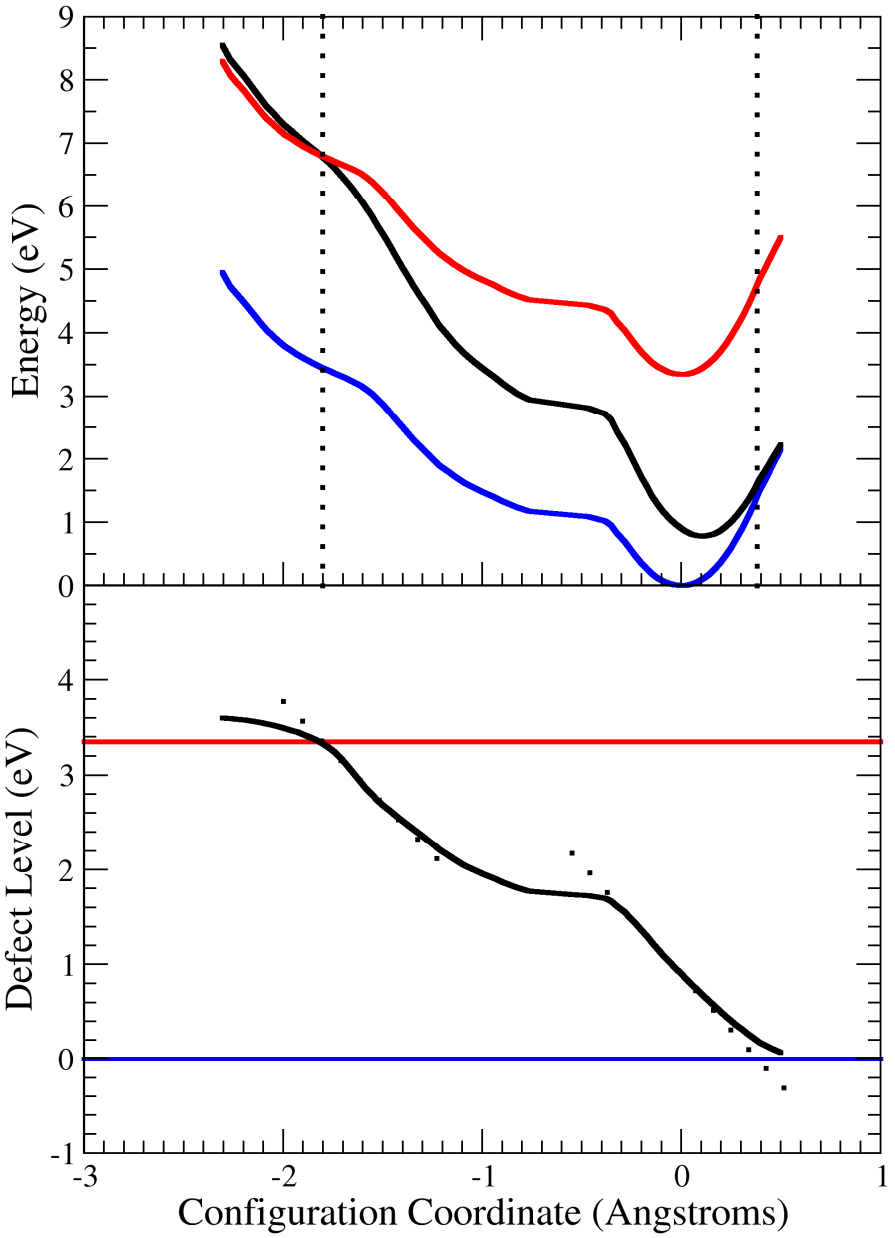
For electron capture, a complex, symmetry breaking distortion is observed beyond about 0.4 A

This distortion converts an N dangling bond into a Ga dangling bond releasing two electrons

Extrapolation gives:

0.83 eV activation energy for holes

3.45 eV activation energy for electron



Comparison of Our Calculated Barriers for V_{Ga} to Experiments on Yellow Luminescence

Experiment suggests electron capture barrier > 0.6 eV

We get 3.45 eV. Good!

Experiment suggest hole capture barrier < 0.3 eV

We get 0.83 eV. Not good!

Some possible explanations:
Convergence with respect to supercell size and/or BZ sampling
Better functionals (e.g., hybrids) might be needed
V_{Ga} must be in a defect complex to contribute to YL
Some other defect (e.g., C_N) is solely responsible for YL

Next Steps For This Work

Study more defects looking for cases where direct comparison with experiment is possible

Extend our procedures to the full temperature range: S and ω are easily calculated near the ground state configurations, but how do we smoothly patch together our anharmonic, multidimensional results for high temperature with the harmonic theory for low temperatures?

In general, we probably have to solve the anharmonic Schrodinger equation for vibration along the configuration coordinate.