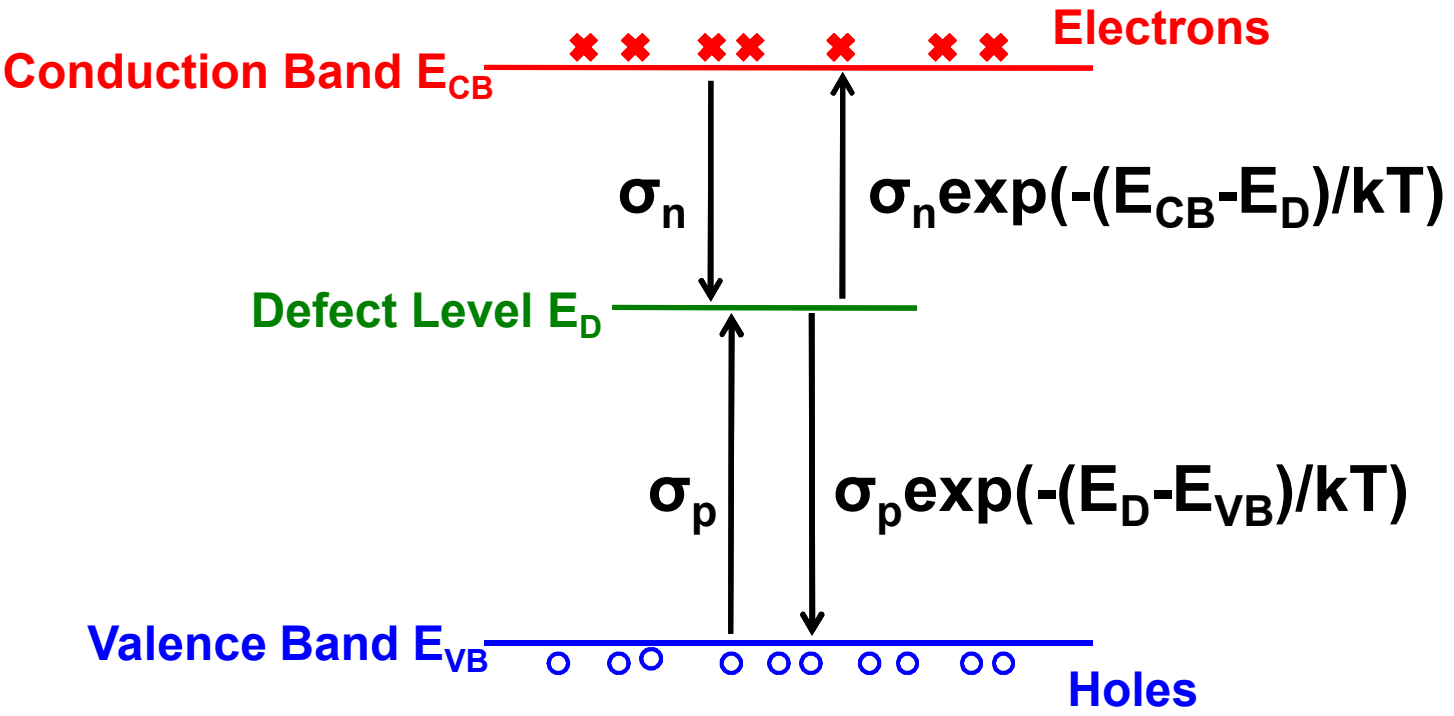
SAND2016-3843C

DFT Calculations for Carrier Capture by Defects in Semiconductors



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Why Study the EL2 Level in GaAs?

- Rare opportunity to validate models of carrier capture
- Generally believed to be the 0/+1 level of the As antisite in GaAs
- Electron capture cross-sections were measured as a function of temperature by Lang and Logan (1980)
- Henry and Lang's Multiphonon Emission Theory (1977) fits the results with 4 parameters

E_t = 0.75 eV

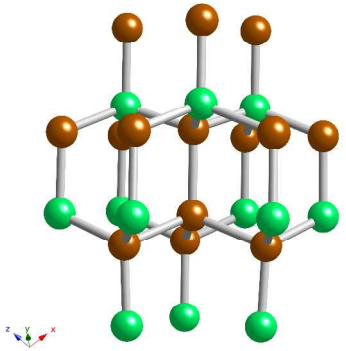
E_r = 0.24 eV

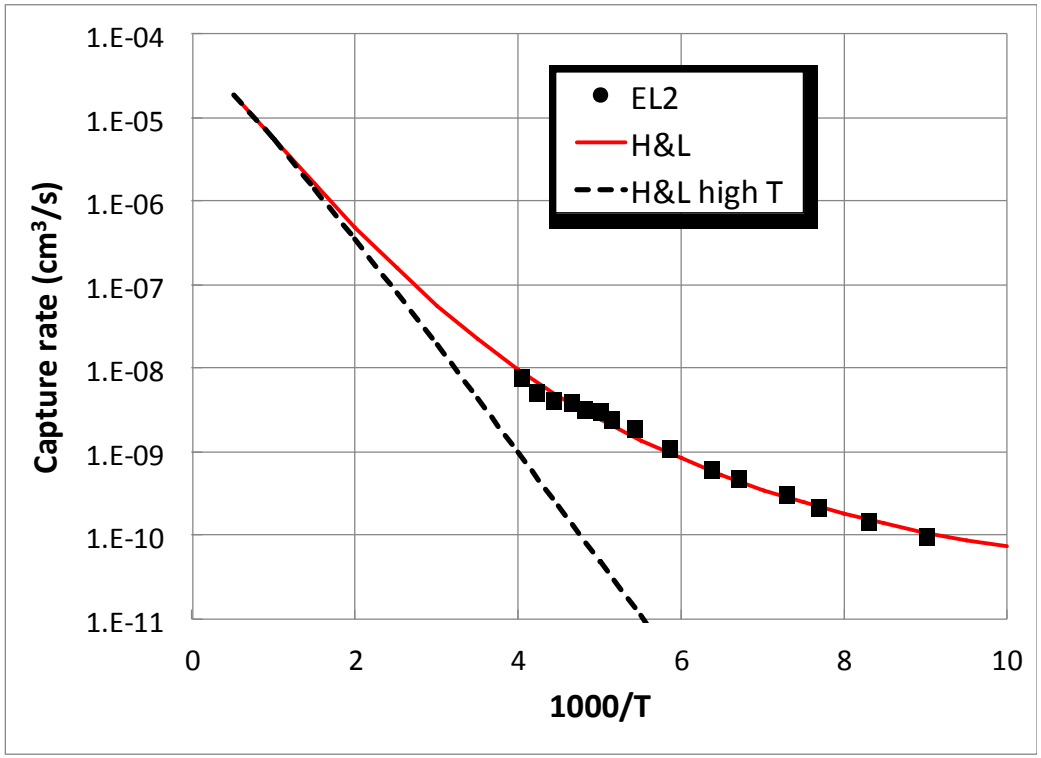
$\hbar\omega$ = 0.021 eV

A = 6.3×10^{-5} cm^3/s

- High-T slope given by carrier capture activation energy

$E_b = (E_t - E_r)^2 / (4E_r)$ = 0.27 eV





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Henry and Lang MPE Theory

Assume a configuration coordinate λ

Energies depend on charge q and λ
Red Line: $E_{q=0}(\lambda)$
Blue Line: $E_{q=+1}(\lambda) + E_{CB}$
Black Line: $E_{q=+1}(\lambda) + E_{VB}$

Physical Meaning of Parameters

Trap depth E_t: From DFT or independe measurements (DLTS)

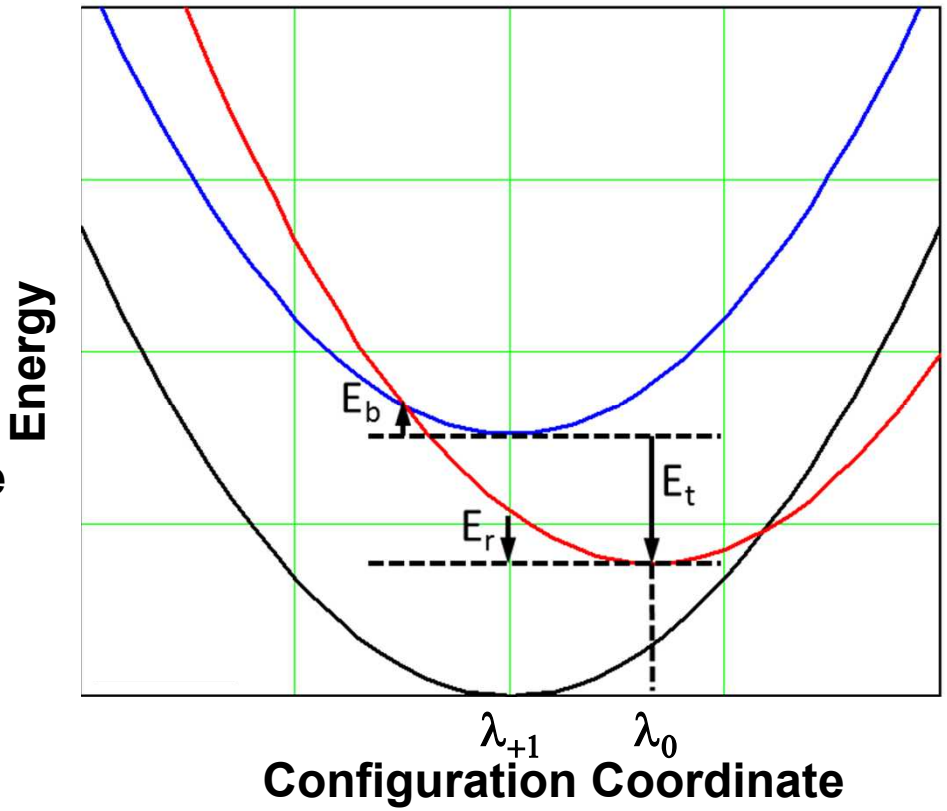
Relaxation energy E_r: From DFT

$E_{q=0}(\lambda_{+1}) - E_{q=0}(\lambda_0)$

$E_{q=+1}(\lambda_0) - E_{q=+1}(\lambda_{+1})$

Phonon frequency $\hbar\omega$: From DFT second derivative of $E(\lambda)$

Prefactor A: Experiments suggest 10^{-6} to 10^{-4} cm^3/s; Other groups (Alkauskas et al, L.-W. Wang et al) working on DFT-based calculations



Activation energy E_b is energy to reach crossing points where energy can be conserved during a non-radiative capture process

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DFT Calculations of the EL2 Relaxation Energy

Computational Details:

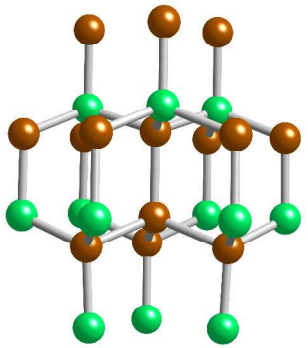
216 atom supercells

LDA and PBE functionals

Norm-conserving pseudopotentials

40 Rydberg plane-wave cutoff

Up to -4X-4X-4 k-point sampling



T_d

	$E_{q=0}(\lambda_{+1}) - E_{q=0}(\lambda_0)$	$E_{q=+1}(\lambda_0) - E_{q=+1}(\lambda_{+1})$	E_b
LDA	0.076 eV	0.075 eV	1.49-1.52 eV
PBE	0.077 eV	0.076 eV	1.47-1.49 eV

Calculated EL2 relaxation energies differ by a factor of 3 from the value obtained by fitting to experiment: E_r = 0.24 eV

As a result, the calculated activation energies differ by a factor of 6 from the experimental activation energy: E_b = 0.27 eV

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Anharmonic, Multidimensional Theory for E_b

Can we generalize Henry and Lang's ideas to arbitrary energies $E_{q=0}(\Lambda)$ and $E_{q=+1}(\Lambda)$ in high dimensional configuration space Λ?

The activation energy E_b controls high-T behavior, and thus getting an accurate E_b is essential to capturing experimental behavior

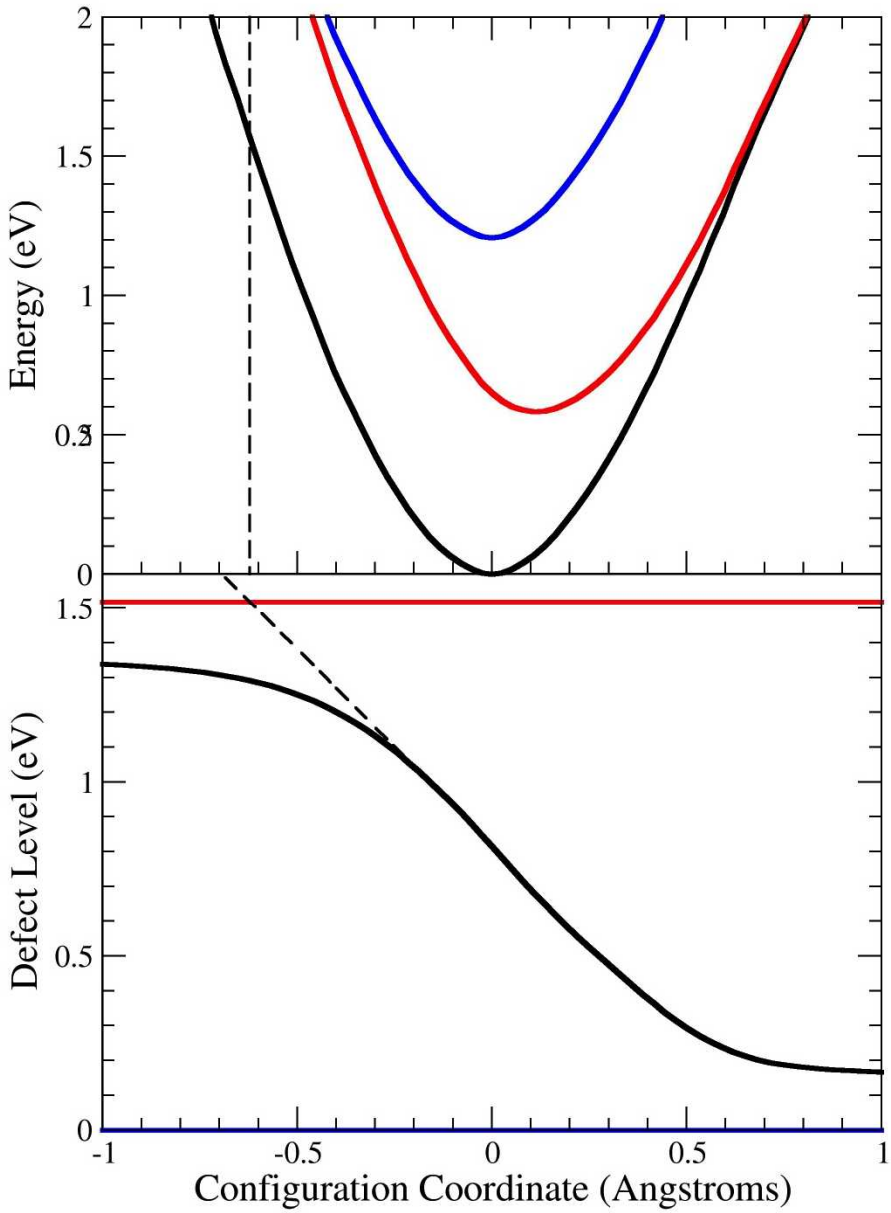
From the correspondence principle and transition state theory, non-radiative carrier capture at high-T should be dominated by a "carrier-capture transition state" defined as the lowest energy state where energy can be conserved during the capture process

Energy can be conserved during electron capture when the vertical defect level reaches the conduction band, i.e., $\Delta(\Lambda) = E_{q=0}(\Lambda) - E_{q=+1}(\Lambda) = E_{CB}$

We have developed a new algorithm that does a constrained minimization of the energies $E_{q=0}(\Lambda)$ and $E_{q=+1}(\Lambda)$ over configurations Λ that are consistent with a given level $\Delta(\Lambda)$

When we apply this algorithm to the level $\Delta(\Lambda) = E_{CB,}$ we obtain the "carrier-capture transition state" and E_b

Does Anharmonicity Change Our EL2 Result?



We have applied our anharmonic, multdimensional approach to E2 using the LDA functional

We calculated obtain an optimized configuration coordinate by varying the target $\Delta(\Lambda)$

The energies and defect levels are plotted along this coordinate

By processing the data to remove artifacts of the LDA band gap problem, we obtain E_b= 1.57 eV

This is in good agreement with the harmonic theory (1.49 – 1.52 eV), but not with experiment

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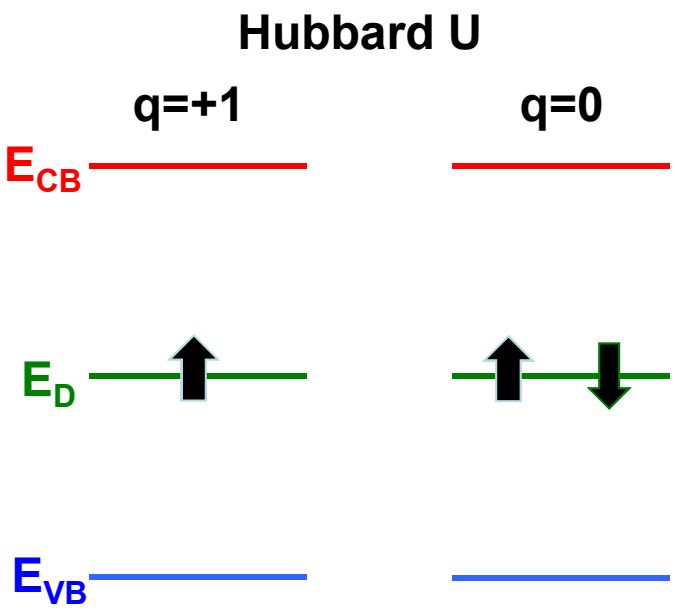
How About Hybrid Functionals?



Computational Details:

216 atom supercells

-2X-2X-2 K-point sampling

Atomic positions relaxed with the hybrid

Sandia's Socorro software

Performed during Trinity Phase 1 Open Science Period at LANL

	$E_{q=0}(\lambda_{+1}) - E_{q=0}(\lambda_0)$	$E_{q=+1}(\lambda_0) - E_{q=+1}(\lambda_{+1})$	E_b
PBE23%	0.122 eV	0.112 eV	0.81-0.91 eV
HSE06	0.114 eV	0.108 eV	0.89-0.95 eV

The calculated E_r and E_b are closer to experiment (E_r = 0.24 eV, E_b = 0.27 eV), but still off by factors of about 2 and 4, respectively.

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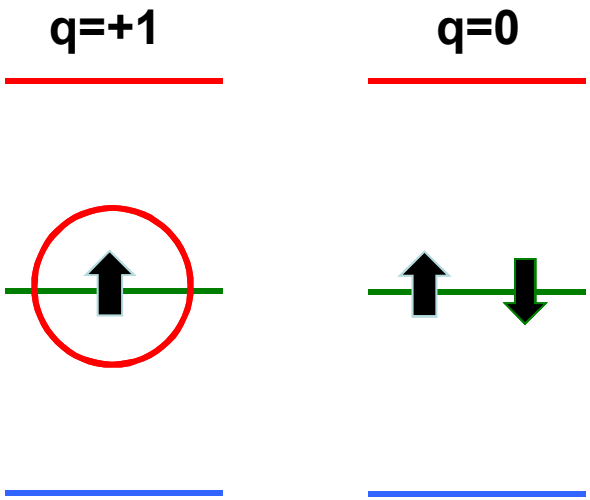
How About Spin-Polarization?



	E_r Without Spin	E_r With Spin
LDA	0.076 / 0.075 eV	0.074 / 0.074 eV
PBE	0.077 / 0.076 eV	0.074 / 0.073 eV
PBE23%	0.122 / 0.112 eV	0.109 / 0.099 eV
HSE06	0.114 / 0.108 eV	0.102 / 0.094 eV

Including spin polarization for the q=+1 state actually lowers the calculated relaxation energy and increases the discrepancy with experiment

Conclusions and a Challenge

These results leave us with a puzzle!

Possible resolutions:

Unexpected coupling between hybrids and anharmonicity?

An intermediate electronic state?

Something missing in our calculations?

Something missing in the Henry and Lang MPE theory?

EL2 is not what we think it is?

I challenge researchers working on DFT calculations for carrier capture to see whether their methods give better results for EL2!

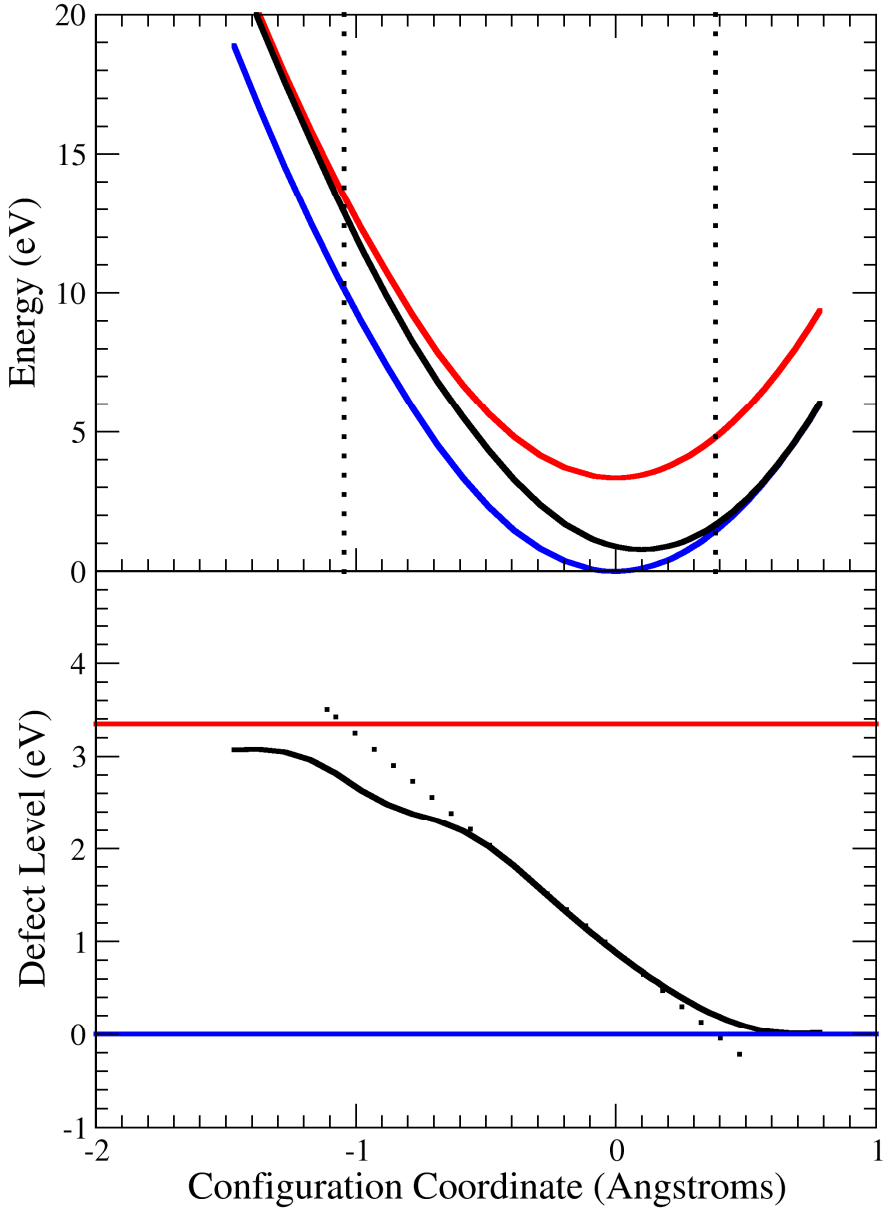
DFT w/ Assumed Configuration Coordinate

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



DFT w/ Optimized Configuration Coordinate

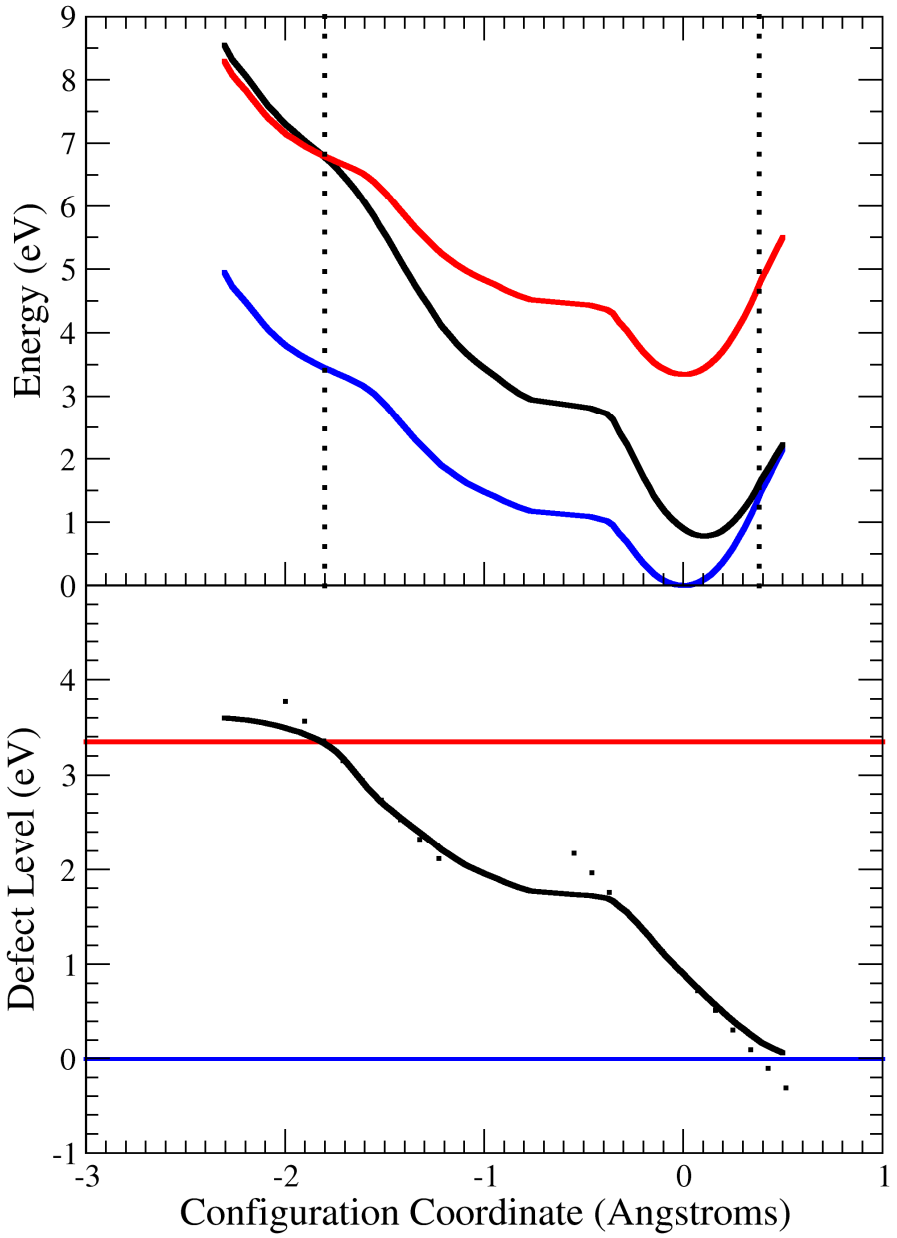
For hole capture, optimization doesn't change the results very much

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

Extrapolation Gives:

3.45 eV activation energy for electron capture which is consistent with yellow luminescence – Good!

0.83 eV activation energy for hole capture – Maybe too large?



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.

Do These Classical Activation Energies Generally Control the High Temperature Behavior?

Henry and Lang obtained the same result from the high-T limit of the fully quantum expressions in the harmonic case

Quantum and classical results should agree at high-T based on the Correspondence Principle

We have checked two cases carefully:

- Does the classical barrier give the high-T slope for small relaxation energies? YES
- Does the classical barrier give the high-T slope when you consider thermal excitation of the band edge carriers? YES

Thanks for help from Audrius Alkauskas and Bill Wampler!

Model for Calculating Capture Cross-Sections

Q is an ionic configuration coordinate

U_v is the energy of neutral system with defect

U_c is the energy with extra electron in CB

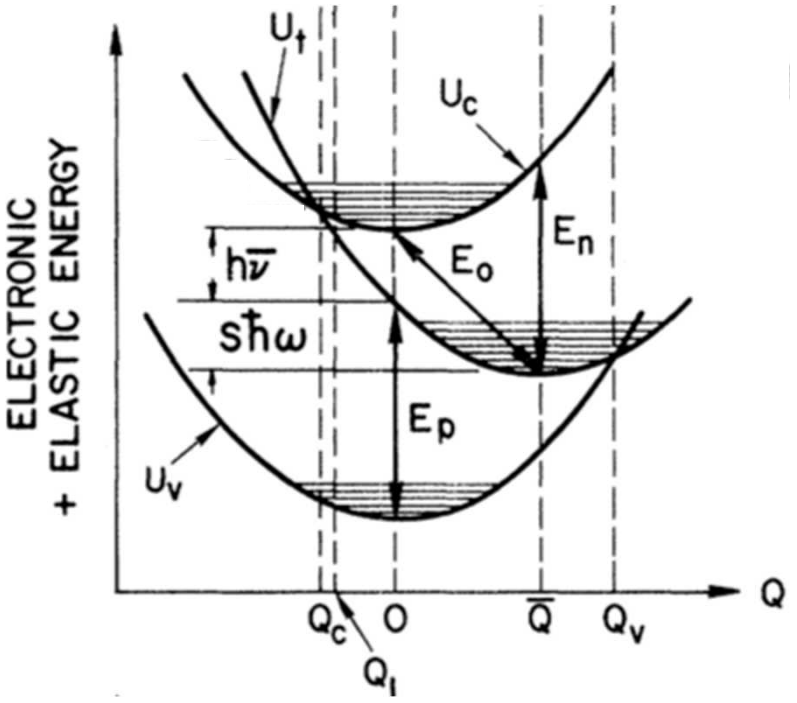
U_t is the energy with extra electron on defect

Q=0 is the minimum for neutral defect

$Q=\bar{Q}$ is the minimum for charged defect

U_c and U_t cross at $Q=Q_c$

U_v and U_t cross at $Q=Q_v$



E_p is the optical excitation threshold from VB

E_n is the optical excitation threshold from defect

$h\bar{\nu}$ is the zero-phonon emission line from CB

$S\hbar\omega$ is the relaxation energy for the charged defect

E_0 is the thermodynamic defect level (relative to the CB)

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Model for Calculating Capture Cross-Sections

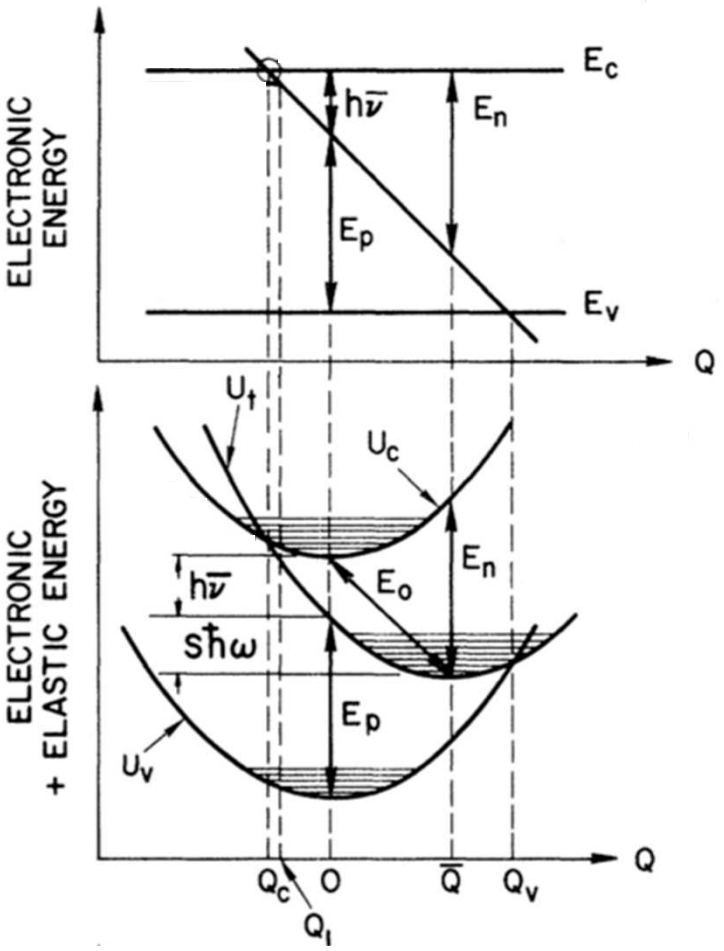
Normally, the defect level is defined as the difference of relaxed charge state energies

Alternatively, we can define a Q dependent defect level for charge states at the same Q

This defect level crosses into the CB at $Q=Q_c$ and the VB at $Q=Q_v$

These level crossing regions dominate the thermal capture and emission of carriers

We can define Q_1 as the point where the adiabatic approximation begins to break down



Q_1 is taken to be 0.06 eV from the crossing in Henry and Lang

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Calculating Nonradiative Capture Cross-sections

Perturbation theory for the transition rate gives

$$w = \frac{2\pi}{\hbar}\,\mathrm{ave}_{n_c}\sum_{n_t}\left|\langle tn_t|\mathcal{H}|cn_c\rangle\right|^2\delta(\mathcal{E}_c-\mathcal{E}_t)$$

Where $|n_c\rangle$ and $|n_t\rangle$ are vibrational states,

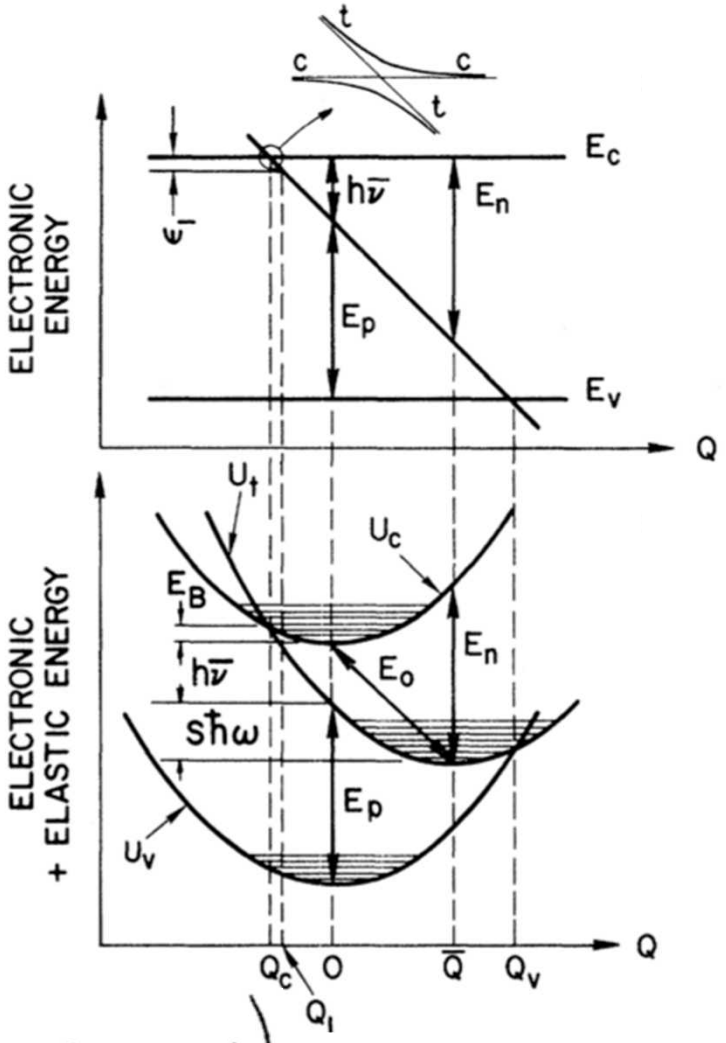
$$\mathcal{E}_c = n_c\hbar\omega\text{, and }\mathcal{E}_t = n_t\hbar\omega - E_0$$

Result is dominated by level crossing region, so assume that $|c\rangle$ and $|t\rangle$ are constant

$$|c\rangle = u_c(r, Q_1),\quad |t\rangle = u_t(r, Q_1)$$

Then, defining $\Delta V(r, Q) = V(r, Q) - V(r, Q_1)$

$$w = \frac{2\pi}{\hbar}\left|\langle t|\Delta V|c\rangle\right|^2\left(\mathrm{ave}_{n_c}\sum_{n_t}\left|\langle n_t|n_c\rangle\right|^2\delta(\mathcal{E}_c-\mathcal{E}_t)\right)$$



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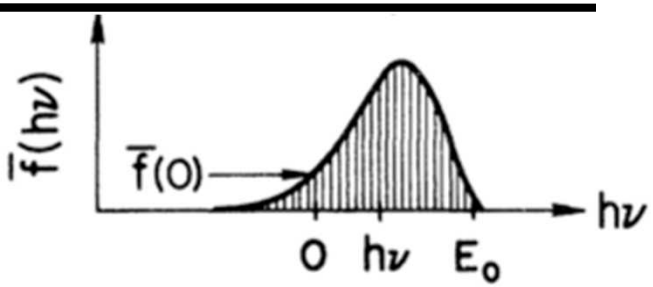
Calculating Nonradiative Capture Cross-sections

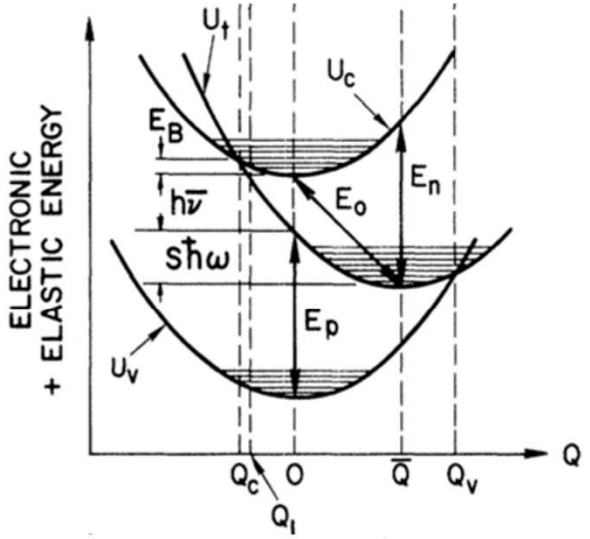
Defining the "Normalized Line Shape"

$$f(h\nu) = \mathrm{ave}_{n_c} \sum_{n_t} |\langle n_t | n_c \rangle|^2 \, \delta(\mathcal{E}_c - \mathcal{E}_t - h\nu)$$



And using $\sigma_c = (\Omega / \langle v \rangle) w$ **, we get**

$$\sigma_c = \underbrace{(2\pi\Omega / \hbar\langle v \rangle) |\langle c | \Delta V | t \rangle|^2}_{\text{Weakly Varying}} \underbrace{f(0)}_{\text{Strongly Varying}}$$



For Radiative Recombination, similar arguments give

$$\frac{dw^{\mathrm{rad}}}{d(h\nu)} = \frac{2\pi}{\hbar} \mathrm{ave}_{n_c} \sum_{n_t} |\langle u_t \, n_t | H_{\mathrm{rad}}(r) | u_c \, n_c \rangle|^2 \, \delta(\mathcal{E}_c - \mathcal{E}_t - h\nu) \rho_{\mathrm{rad}}$$

$$= \frac{2\pi}{\hbar} \rho_{\mathrm{rad}} |\langle \varphi_t | H_{\mathrm{rad}} | \varphi_c \rangle|^2 f(h\nu) \sim (h\nu)^3 f(h\nu)$$

where φ_c **and** φ_t **are evaluated at** $Q = 0$ **(the Condon Approximation)**

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Observations about the Normalized Line Shape

If we assume simple harmonic oscillators with the same frequency, we get the Huang and Rhys line shape, a function of E_0 $\hbar\omega$ **and** S

$$f(h\nu) = \sum_{p=-\infty}^{\infty} \delta(E_0 - p\hbar\omega - h\nu) W_p$$

Where

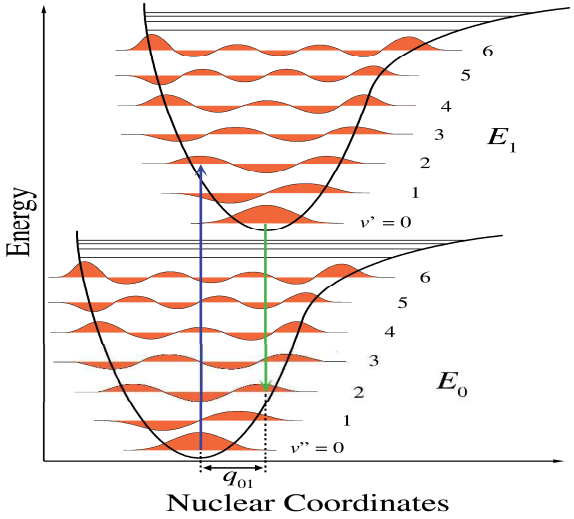
$$W_p = \exp[-(2n+1)S][(\bar{n}+1)/\bar{n}]^{p/2} \times I_p(2S[(\bar{n}+1)\bar{n}]^{1/2})$$

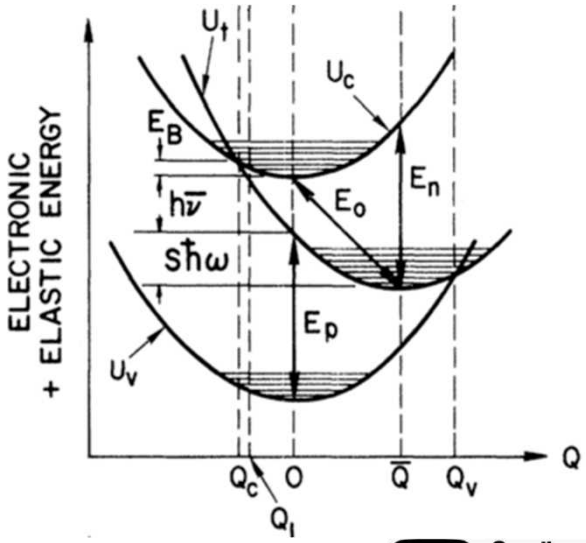
I_p **is a modified Bessel function, and**

$$\bar{n} = [\exp(\hbar\omega/kT) - 1]^{-1}$$

At high temperature, we obtain

$$\sigma_c = \left(\frac{4\pi E_B}{kT}\right)^{1/2} \frac{\Omega |\langle t|\Delta V|c\rangle|^2}{\hbar\langle v\rangle h\bar{\nu}} e^{-E_B/kT}$$





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

Experiment suggests electron capture barrier > 0.6 eV

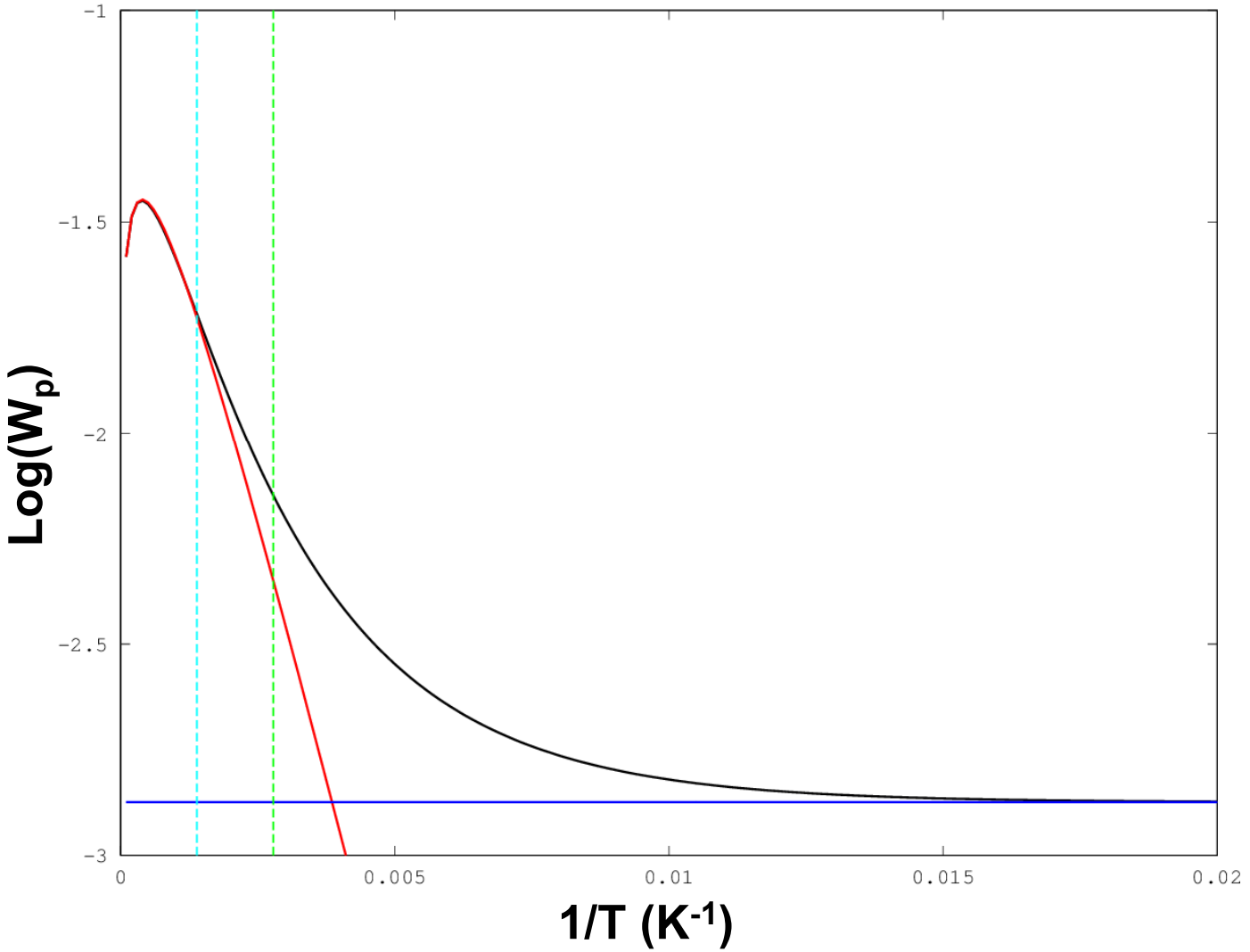
We get 3.45 eV. Good!

However, the hole capture barrier 0.83 eV would suggest that non-radiative capture of holes would be slower than observed

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

Is This High Temperature Limit Generally Valid?

Evaluate exact W_p (Black) and Approximate W_p (Red) including the $T^{-1/2}$ factor for E_0=0.31eV, hω=0.031 eV, and S=3.226



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How Much Do Real Cross-Sections Vary?

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

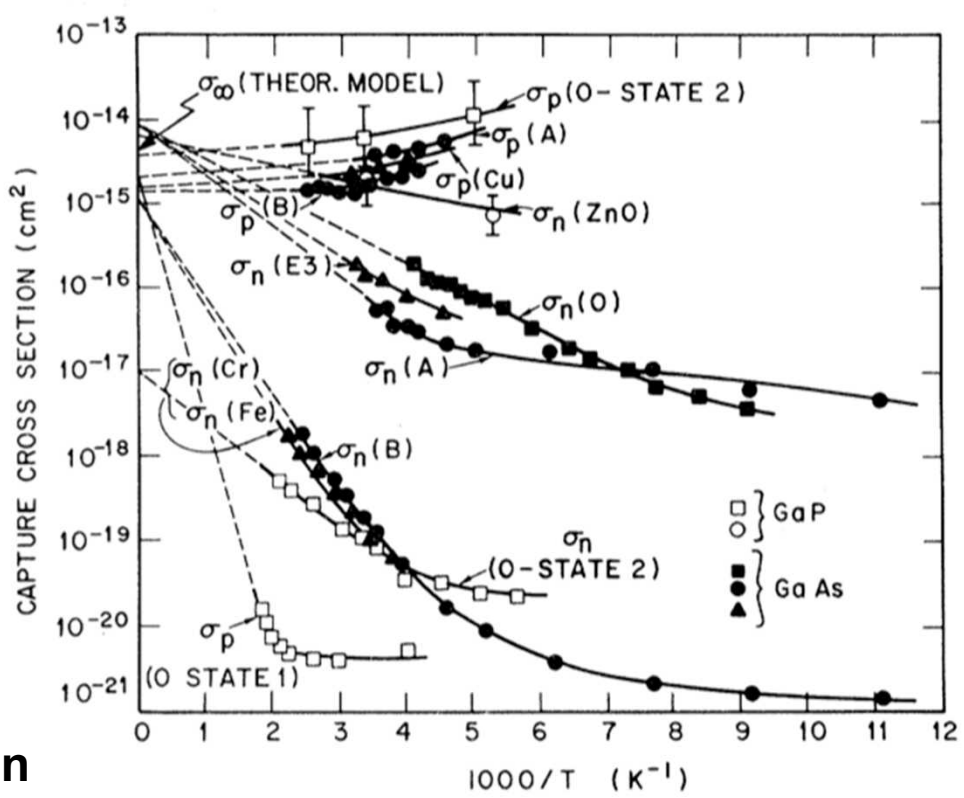
Wide variation at room-temperature

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

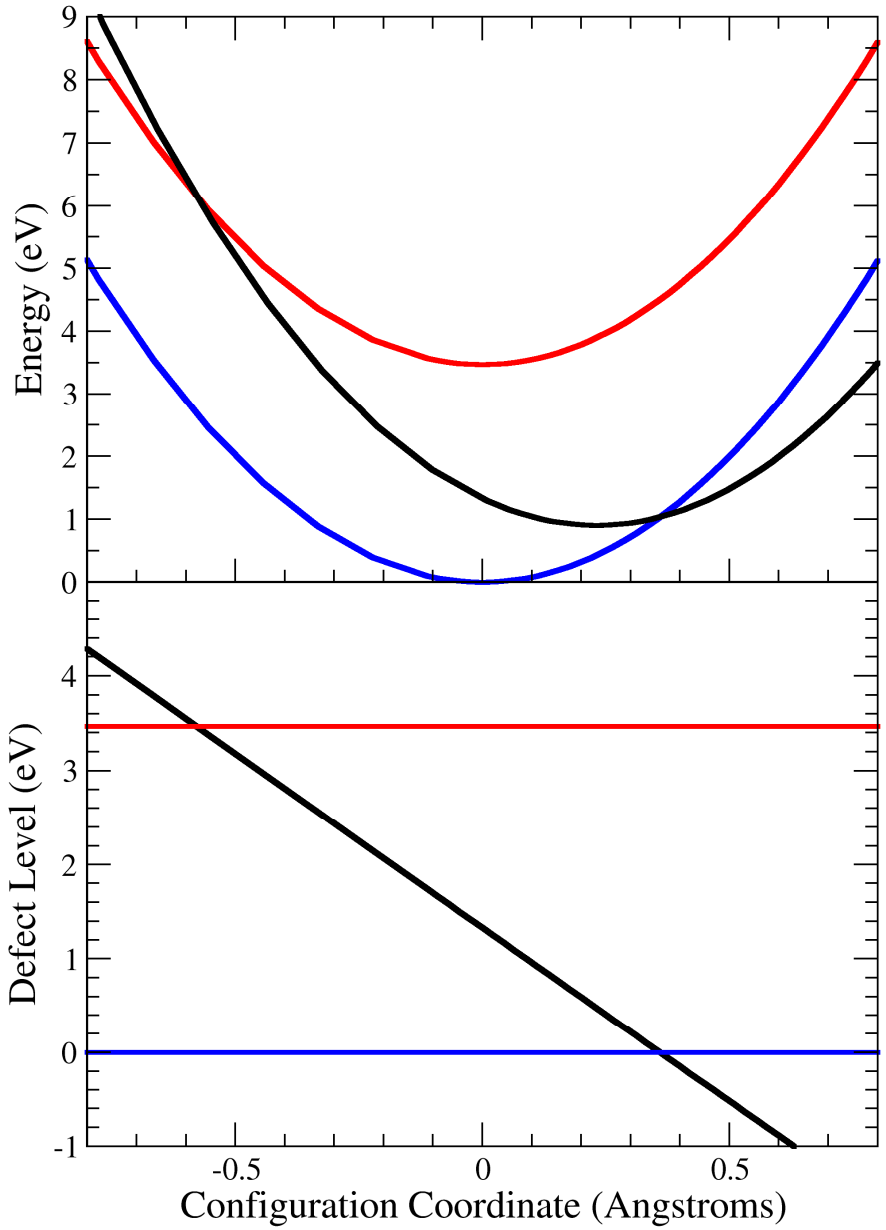
Assume a configuration coordinate λ

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

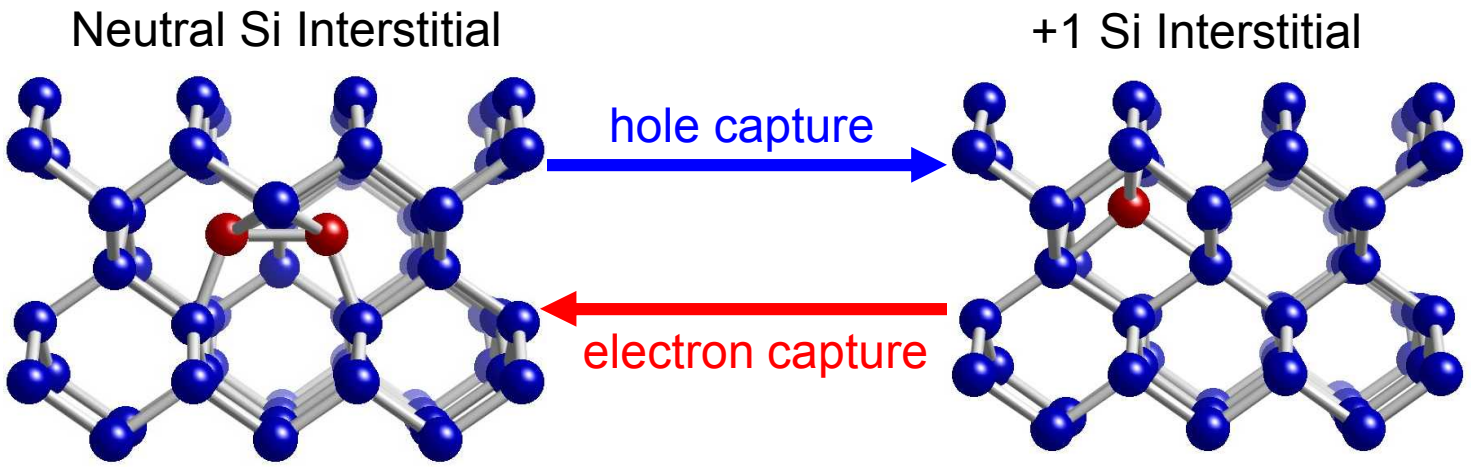
Activation energies given by differences between crossing-points and minima



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