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SAND2010-7997P

# Radiation defect chemistry in GaAs and III-V's

## Density functional theory (DFT): SeqQuest

**Thursday, November 18, 2010, 10:00-10:30am**

**Peter A. Schultz**
**Multiscale Dynamic Materials Modeling Dept 1435**

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NNSA National Nuclear Security Administration

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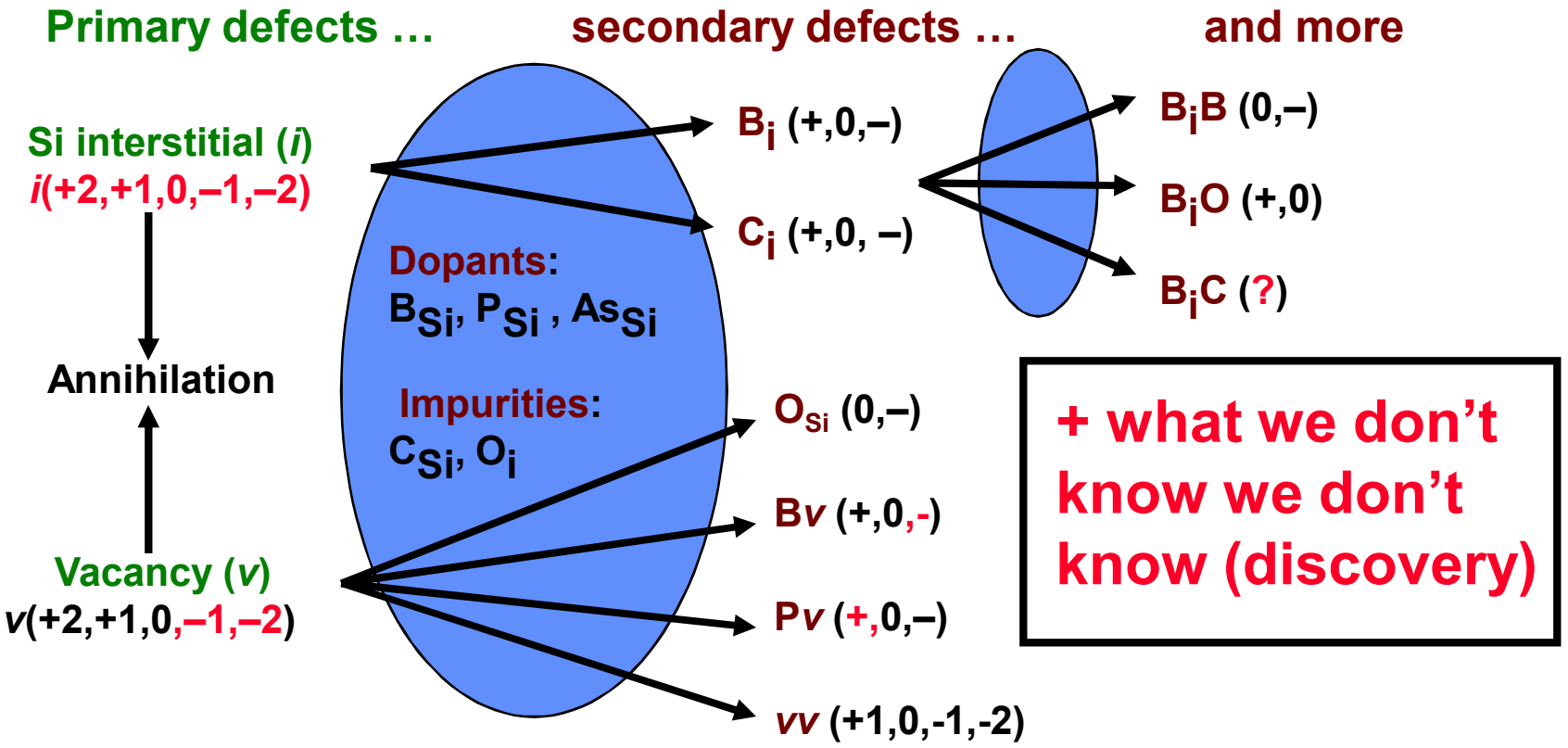
# Radiation defects chemistry: Si




Need to know defects species, levels, chemical evolution …
DFT most accurate (sometimes only) probe of defect behavior
This chemistry map almost entirely blank in GaAs, III-V's - unknown

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# Requirements for defect levels

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- **Experimental uncertainties for defect levels 0.03 eV - 0.1 eV - unknown**
  - Ideally kT=0.03 eV - Si: A-center, vv(+/0/1/2-), v(2+/1+/0)
  - Typically larger, 0.1 eV - Si: $B_i$(-/0)/0.08 eV, Bv: a mess(U>0.1eV), etc
  - Sometimes “infinite” - Si: P*v*(0/+) only recently identified in experiment
  - In GaAs, few levels <0.1 eV, mostly unknown (unknowable?) defects
- **Some numerical evidence from device simulations for 0.1-0.2 eV**
  - Sensitivity Analysis: results not strongly dependent on levels
  - Device simulations already use less accurate data (MD, BCA)
- **Required accuracy: 0.1-0.2 eV (awaiting refined guidance from SA)**
  - Matches accuracy of typical experimental data
  - Improves on existing device simulation practice

Need systematic numerically-driven SA guidance

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# DFT challenges

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- **Conventional DFT failed for defect levels in semiconductors**
  - (1) "band gap problem" - DFT Kohn-Sham band gaps are awful
  - (2) defect level problem
    - reference level for charge unknown
    - location of band edges cf levels (related to band gap problem)
    - e.g.: 10 theory calculations for $v_{Ga}$ levels = 10 different results
  - (3) unknown (and unassessable) accuracy
    - accuracy of functionals unknown
    - accuracy of pseudopotentials unproven (e.g. 3d: core vs. valence)
  - (4) computational limitations - cell size inadequate to isolate defects
  - (5) lack of good and sufficient data for validation (esp. III-V's)
    - lots of "point solutions" with DFT, but no robust, transferable methods
- **Need to build and justify new approaches, apply to new problems**

Strategy: incrementally build verified, validated models



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# Incremental development of DFT models

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**(1) Silicon: lots of good data, with some gaps and unknowns**

- develop robust methods for defects (FDSM)
- verify models, validate against comprehensive defect data

  DFT/SeqQuest with FDSM gives 0.1 eV average, 0.2 eV max error in levels
- predict gaps (interstitials, vacancies), discover unknowns (P*v*,B*v*)

**(2) GaAs: more complex system, less good data**

- verify models (e.g., PP, cells), learn how to validate with less data
- identify primary radiation defects, predict properties

  Verified and validated same accuracy as Si, redefined defect assignments
- identify mobile species, and develop and quantify chemical networks

**(3) III-V's: even less good data**

- verify models (e.g., PP, cells), adapt validation
- identify primary radiation defects, predict properties
- identify mobile species, and develop and quantify chemical networks

**(4) Alloys, oxides and other materials important in HBT's.**



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# Computational methods - GaAs and III-V's

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- **General purpose DFT code SeqQuest** (http://dft.sandia.gov/Quest)
  - Version 2.61j, and development Version dev-2.62/j (equivalent to 2.61j)
  - well-converged (Gaussian-based) local orbital basis
  - both LDA and PBE functionals
  - converged norm-conserving pseudopotentials (Ga,In with both $Z_{val}$=3,10)
  - full force-relaxed (<1 meV total energies)
  - full FDSM … robust control of boundary conditions

- **Large bulk simulation supercells**
  - $a_0$=$a_0$(theory) (GaAs:5.60Å(LDA),5.63Å(3d),5.74Å(PBE); $a_0$(expt)=5.65 Å)
  - 216-, 512- and some 64-site (+defect) cubic III-V cells
  - k-sampling: ($2^3$ for 216- and 512-cells, $3^2$ for 64-site cell)
  - real-space grids: 64/$96^3$, 216/$144^3$, 512/$192^3$ ($96^3$, $144^3$,$192^3$ for GaAs-d0)
  - fully calibrated, verified polarization model
  - all these computational parameters are tested for convergence

Comparable method to Si that yielded 0.1 eV accuracy



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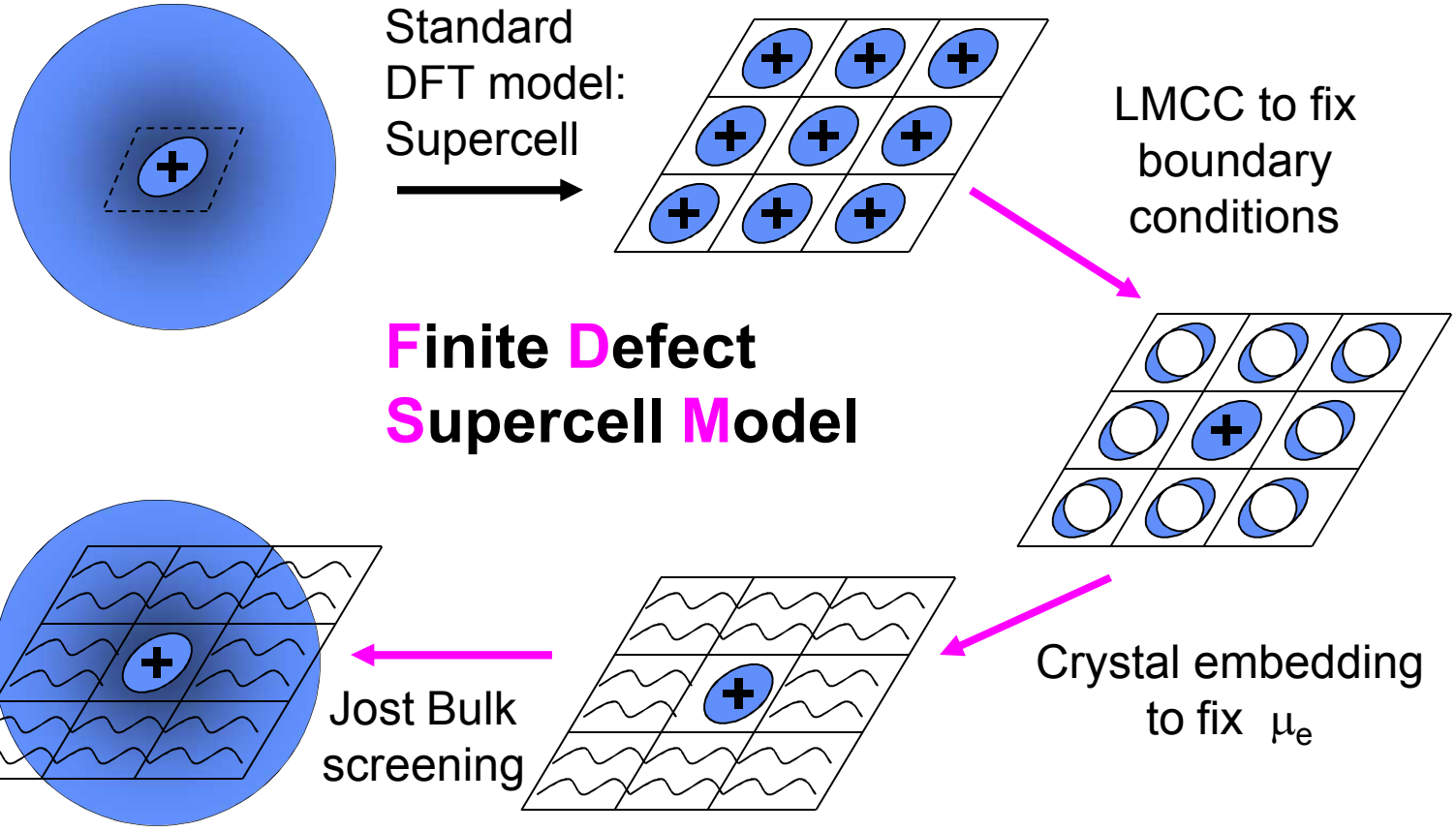
# A supercell theory of defect energies

Peter A. Schultz

Peter A. Schultz, Phys. Rev. Lett. **96**, 246401 (2006).




FDSM - breakthrough for robust calculations of defect levels

# Simple intrinsic defects in GaAs: LDA

P.A. Schultz and O.A. von Lilienfeld, MSMSE **17**, 084007 (2009), 35pp.

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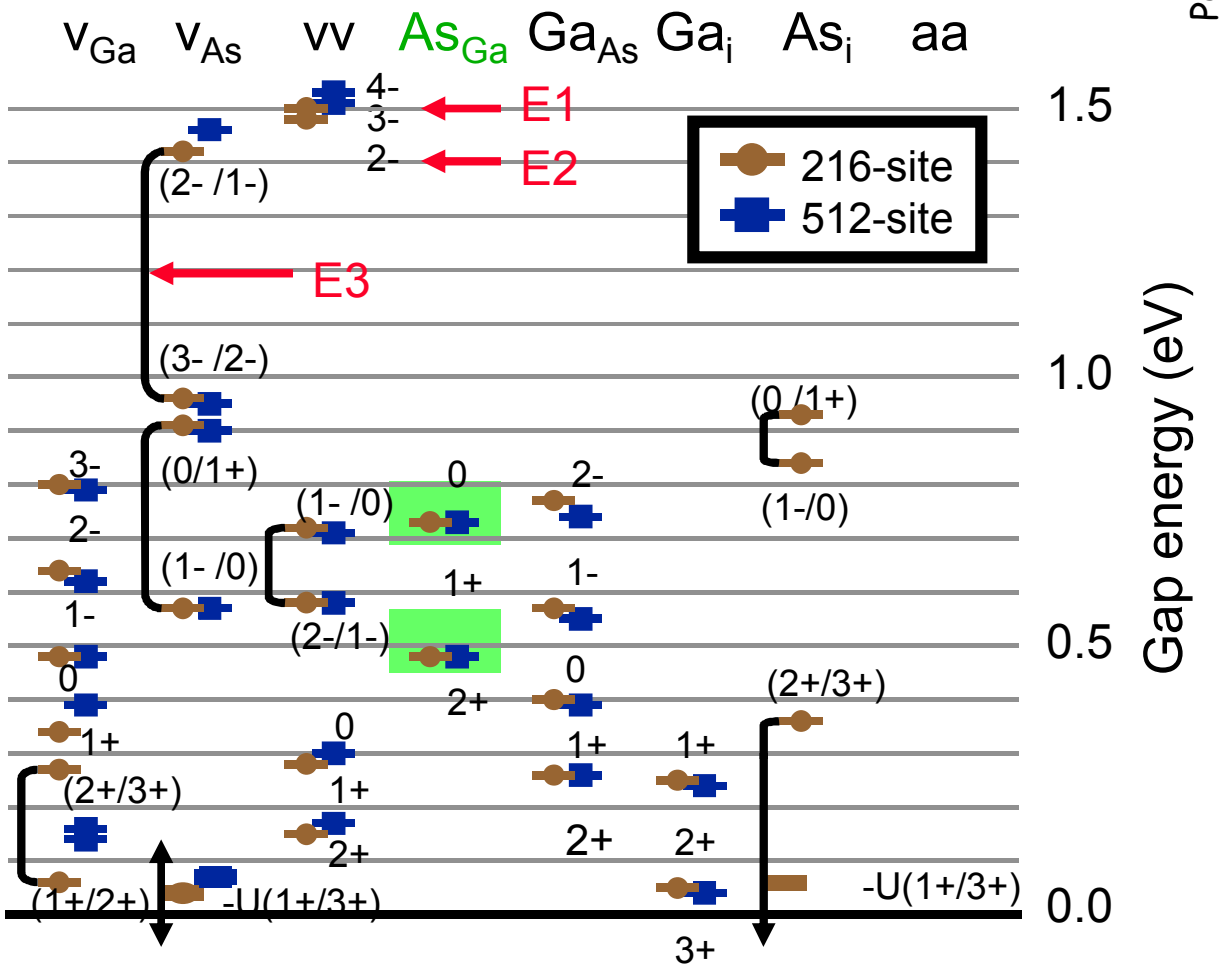
216-site results = 512-site
Verification: cell-converged

LDA-3d = LDA to ≤0.1eV
Verification: PP converged

Defect band gap = ~1.54 eV
Validation: band gap (1.52)

$As_{Ga}$ levels = EL2 levels
vGa levels below midgap
Validation: levels < 0.1 eV

DFT/SeqQuest-FDSM
V&V accuracy ~0.1 eV




Pure prediction: a GaAs radiation defects Rosetta Stone

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# Mobile species: interstitials

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- **Unlike in Si, *v*:GaAs are (both) immobile**
  - experiment observes these to be stable (until something else annihilates them)
  - "simple" nearest-neighbor hops leave trail of high-energy antisites
  - second-neighbor hops require strong bond breakings (high-energy)
    - $v_{Ga}$: El-Mellouhi & Mousseau, PRB **74**, 205207 (2006)
    - $v_{As}$: El-Mellouhi & Mousseau, Appl. Phys. A **86**, 309 (2007)
  - while FDSM results contradict levels, they do not contradict lack of mobility

- **$Ga_i$ is *thermally* mobile in *p*-type**
  - migration barriers, T-H-T: $Ga_i$[1+] 1.1 eV, $Ga_i$[2+] 0.8 eV, $Ga_i$[3+] 0.5 eV,
- **$As_i$ is *thermally* mobile in *p*-type, likely in *n*-type**
  - *p*-type migration barriers, T-H-T: $As_i$[3+], $As_i$[2+] <0.5 eV (~validated)
  - *n*-type: flat (<1 eV) structural energy variations in other charge states
- **$As_i$ is a*thermally* mobile in *p*-type (~validated), just as in Si**
  - e.g., T [3+] + $e^-$ —> H[2+] + $h^+$ —>T'[3+] + $e^-$
  - recombination-enhanced diffusion through bistabilities in other charge states

Transient effects dominated first by $As_i$, second by $Ga_i$



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# GaAs transient defect chemistry network

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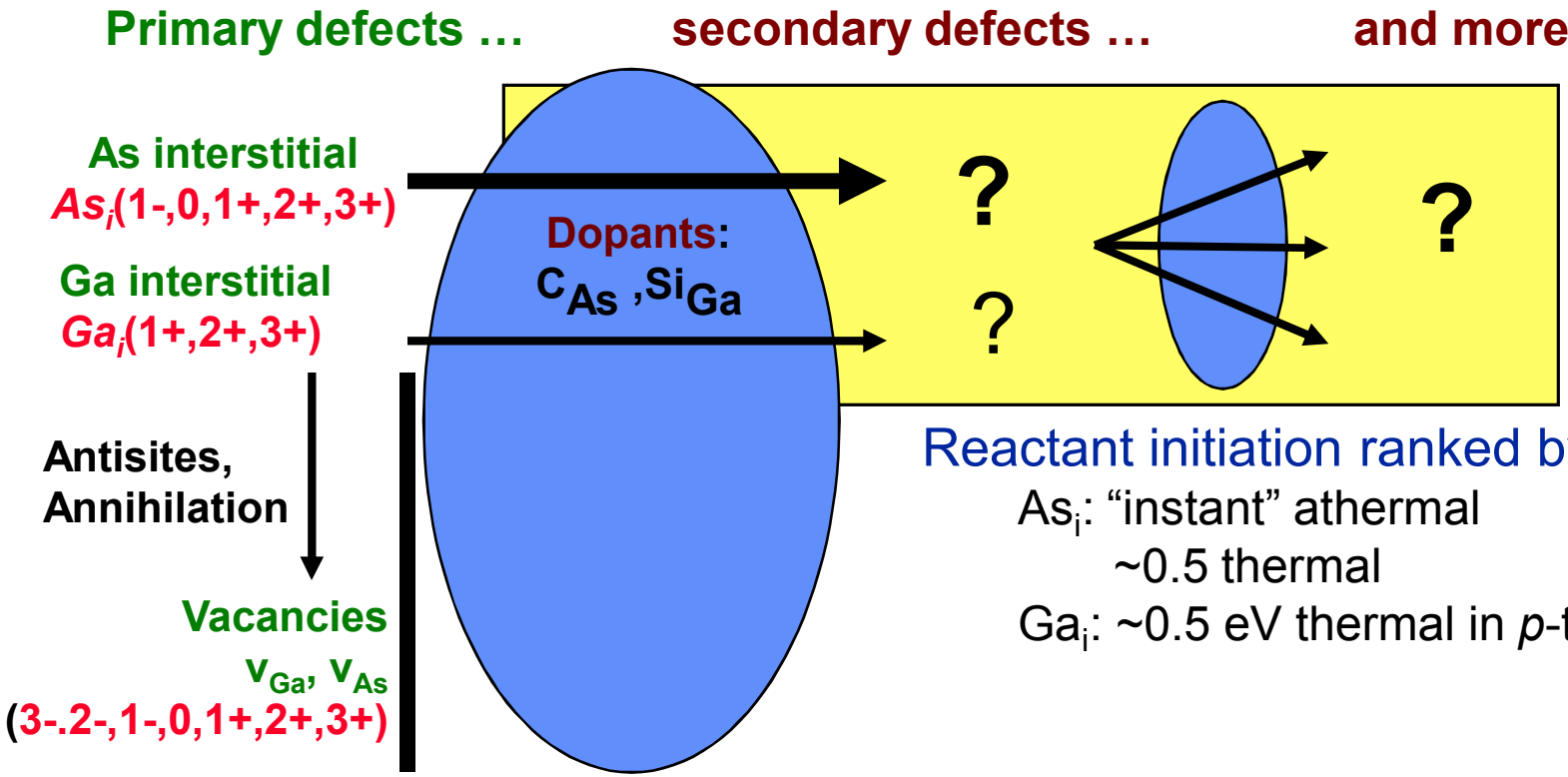


Reactant initiation ranked by mobility:

$As_i$: "instant" athermal
~0.5 thermal
$Ga_i$: ~0.5 eV thermal in *p*-type

Reactant target ranked by concentrations:

$C_{As}$ - in *p*-type
$Si_{Ga}$ ($Si_{As}$) - in *n*-type
Ignore 2nd order (i-i, clusters) for now

# The dopants - C:GaAs, Si:GaAs

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SeqQuest version dev2.62/j, LDA, Ga(Z=3) PP, 216-site cell

| | $C_{As}$[1-] | $C_{Ga}$[1+] | $Si_{As}$[1-] | $Si_{Ga}$[1+] |
|---|---|---|---|---|
| **Formation Energy** | | | | |
| (eV) | | | | |
| at CB (*n*-type) | 1.42 | 4.56 | 0.34 | 0.95 |
| at VB (*p*-type) | 2.96 | 3.02 | 1.88 | -0.59 |
| **Energy Levels** | | | | |
| (eV, cf. CB; n/x=not exist) | | | | |
| E(1-/0) | n/x | -0.28 | n/x | n/x |
| E(0/1+) | n/x | -0.44 | n/x | n/x |

Carbon exclusively on As site

Si is amphoteric (dopant on Ga site, acceptor on As)

Consistent with experiment (and previous DFT)

Sanity check - not *quantitative* validation

# Defect reactions and energies

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Thermodynamic (non-charge conserving)

## As interstitial:

| | | Reaction energy |
|---|---|---|
| p-type: | $As_i + C_{As} \longrightarrow C_i$ | -1.35 eV |
| (VB edge) | $C_i + C_{As} \longrightarrow (C_2)_{As}$ | -3.23 |
| | $(C_2)_{As}$ is terminus of chemistry | |
| n-type: | $As_i + Si_{Ga} \longrightarrow (SiAs)_{Ga}$ | -0.70 |
| (CB edge) | $(SiAs)_{Ga}$ is terminus of chemistry | |
| | but perhaps source of delayed release of $As_i$ | |
| | e.g. $(SiAs)_{Ga} \longrightarrow As_{Ga} + Si_i$ | +2.20 |
| | $(SiAs)_{Ga}$ is strongly bound vs. dissociation to $Si_i$ | |

## Ga interstitial:

| | | |
|---|---|---|
| n-type: | $Ga_i + Si_{Ga} \longrightarrow Si_i$ | -0.92 |
| (CB edge) | $Si_i$ will be mobile (just as in Si), not a terminus | |

# Defect complex energy levels

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| (in eV) | $C_i$ (cf VB) | $(C_2)_{As}$ (cf VB) | $Si_i$ (cf CB) | $(SiAs)_{Ga}$ (cf CB) |
|---|---|---|---|---|
| E(2-/1-) | +1.23 | n/x | -0.14 | -0.33 |
| E(1-/0) | +1.04 | +1.18 | -0.03 | +0.71 |
| E(0/1+) | +0.53 | +0.97 | -0.71 | -1.03 |
| E(1+/2+) | +0.32 | n/x | -0.40 | -1.35 |

Complexes have complicated structures, bistabilities
Lead to -U transitions in several places
$(SiAs)_{Ga}$[2-], [1-] states thermodynamically inaccessible

Levels can be used to extend defect physics package in GaAs

# HBT model need more than GaAs

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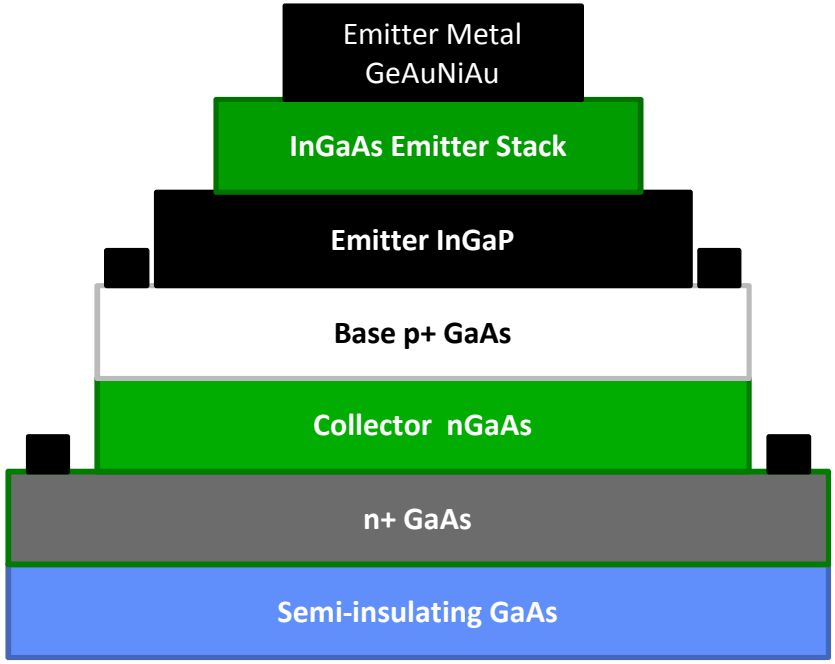
## HBT stack




AlGaAs and InGaP
are important in HBT devices

Need defect physics for:
InP and GaP, AlAs

Then need to extend that
defect physics to alloys.

# GaP: Simple intrinsic defects

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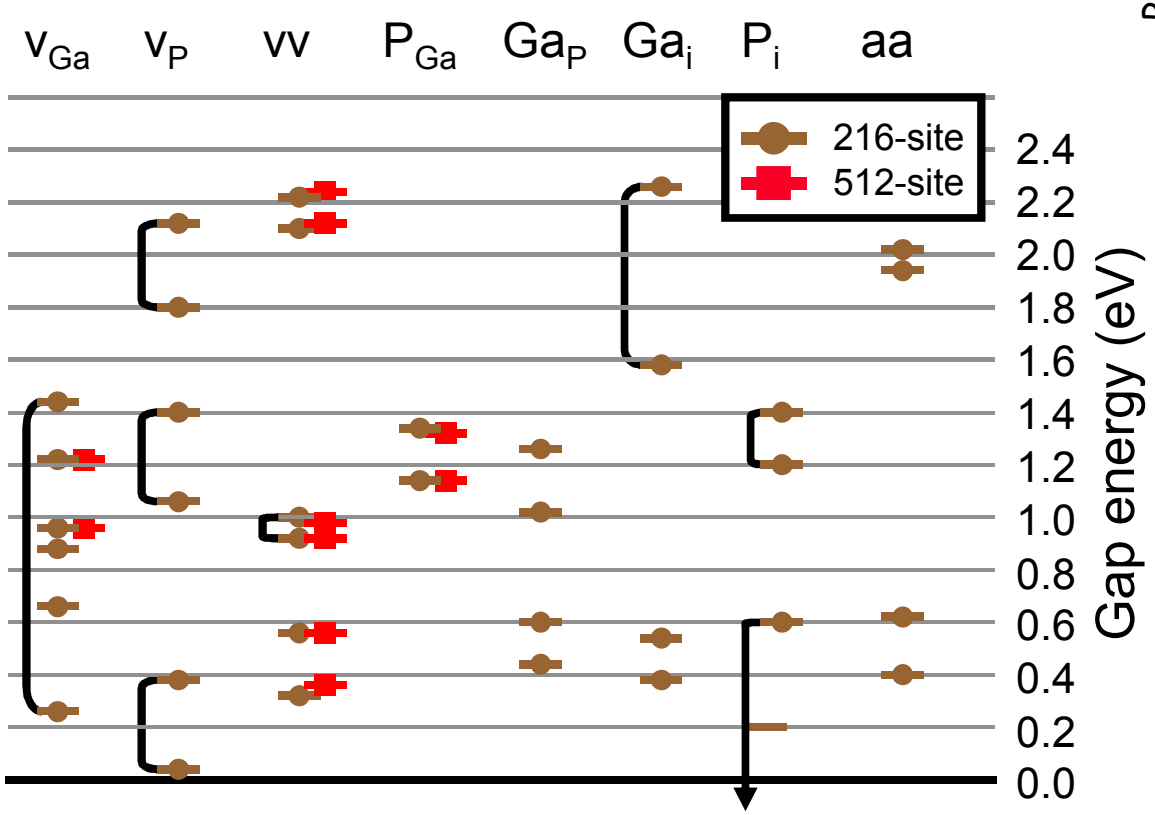
216-site results = 512-site
Verification: cell-converged

Defect band gap = ~2.4 eV
Validation: band gap (2.35)

Mobile species:
$P_i$, thermal (~0.5 eV)
and athermal p-type
$Ga_i$, migration barriers ~1.0




Similar to GaAs …
… with some differences

Pure prediction: defect physics of GaP almost unknown

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# InP: Simple intrinsic defects

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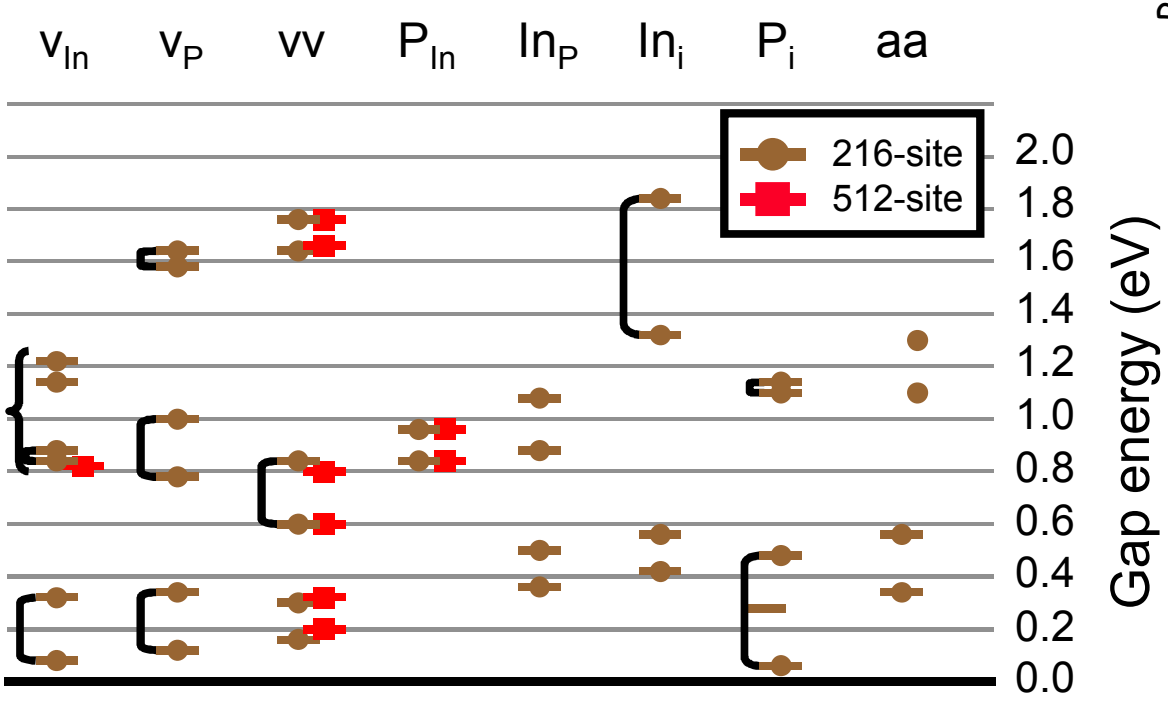
216-site results = 512-site
Verification: cell-converged

Defect band gap = ~1.7 eV
Validation: band gap (1.42)

Mobile species:
$P_i$, thermal (~0.5 eV)
and athermal p-type
$In_i$, barriers > 0.7 eV




Similar to GaAs, GaP
Some difference, but same mobile species -> similar defect chemistries

InGaP alloy within reach, intermediate between InP, GaP?



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# Enabling progress on oxides

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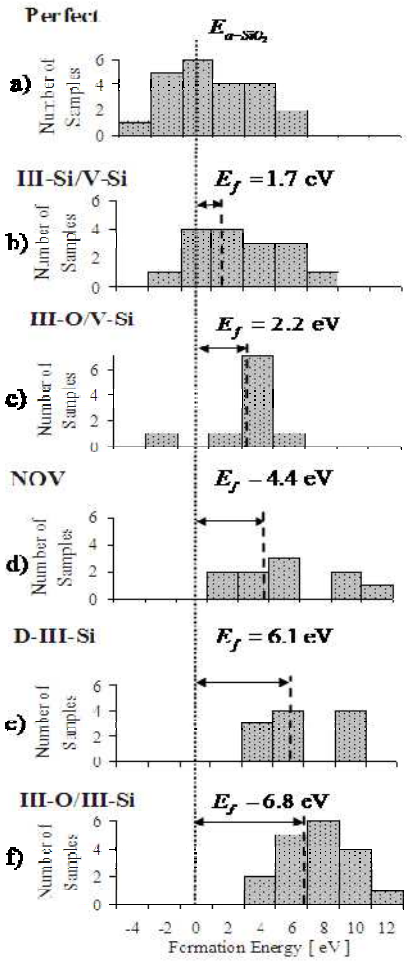
Collaboration with Purdue (ASC/PSAAP program) and PNNL
N. Anderson, R. Vedula, A. Strachan (Purdue), R. Van Ginhoven (PNNL)




## Strategy:

(1) MD (ReaxFF) to generate **many** hi-fidelity samples
both stoichiometric and O-deficient (60 each)
(2) DFT (SeqQuest/PBE) to screen structures
(3) identify non-artifact "defects", compute energies
(4) model charge states, diffusion and surfaces

Advance: accurate, statistical approach for a-$SiO_2$
Prediction: isolated III-Si (E' centers), without $v_O$

Advance: FDSM approach for amorphous systems
New capability: defect levels (charge traps) in oxides

Progress made outside of QASPR
Methods now enable quantitative studies of oxides

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# Path forward

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- Impurity-defect chemistry - Si (*n*-type), C (*p*-type)
  - clean up chemical networks, need experiment to filter possibilities
  - submitted to HEART-2011, to be submitted to peer-reviewed journal - March?
- Set up baseline defect physics for other III-V - get ahead of engineering needs
  - write/publish GaP/InP defect physics - Spring?
  - AlAs defects submitted to MRS 2011 Spring Meeting
  - identify mobile species, and begin to scope radiation chemistry networks
  - scope issues for extending to HBT-relevant alloys, e.g. InGaP
- Nurture oxide collaborations: ASC/PSAAP, AFRL, quantum computing
  - $SiO_2$ bulk and $SiO_2$/Si interfaces (PRL submitted, more papers coming)
- Comprehensive VV-UQ plan for DFT for defect physics - Fall 2011?
  - methods now sufficiently developed to enable meaningful plan

DFT has achieved accuracy necessary for engineering needs
DFT studies can meet engineering timeline constraints



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# - extra slides -

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# The polarization model and verification

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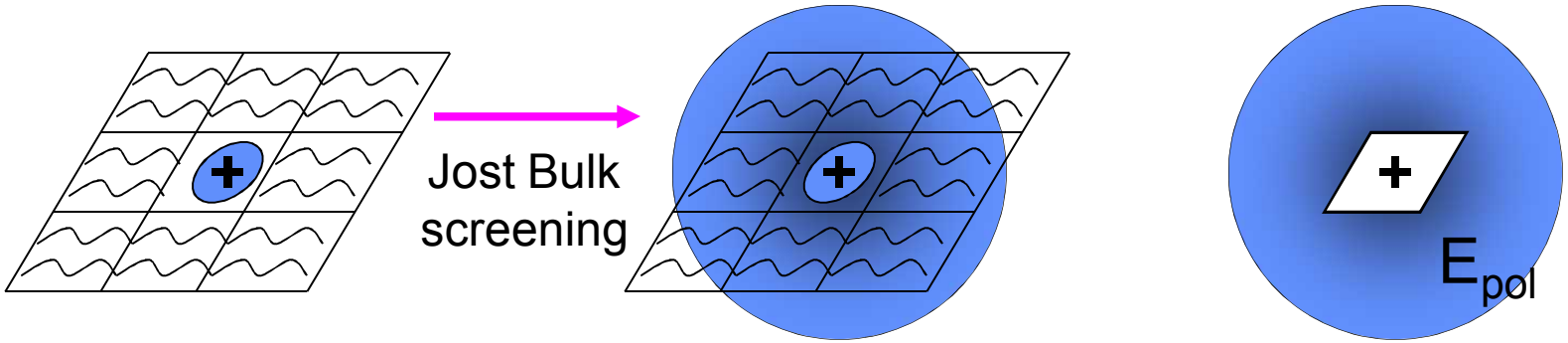
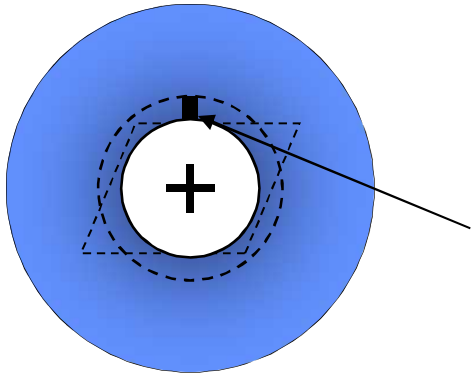



For extrapolation to infinite cell, need energy of screening outside of cell. $E_{pol}$

Jost model: $$E_{pol} = \frac{(1 - 1/\varepsilon_0)\, q^2}{R_{jost}}$$

$R_{jost} = R_{vol} - R_{skin}$
q = charge on defect
$R_{jost}=R_{vol} - R_{skin}$
$R_{vol}$ = radius of volume sphere



Two parameters for any material

$R_{skin}$ = unscreened volume **inside** cell.
fit: =1.5(1) bohr

$\varepsilon_0$ = static dielectric constant - expt

| Si | GaAs | InP | GaP | AlAs | InAs |
|---|---|---|---|---|---|
| 11.8 | 13 | 12.5 | 11.2 | 10.1 | 15.15 |

# III-V: The DFT Defect Gap

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- Usual band gap definition: CB to VB energy
  - cannot compute directly in DFT (Kohn-Sham (KS) gap is wrong predictor)
- Defect band gap: range of transition energies for local defects

| **Si** | **1.17 eV** | |
|---|---|---|
| | KS | Defect |
| lda | 0.49 | 1.2 |
| pbe | 0.62 | 1.2 |

| **AlAs** | **2.16$^{i}$ eV** | |
|---|---|---|
| | KS | Def. |
| lda | 1.37 | 2.2 |
| pbe | 1.53 | **n/a** |

$\varepsilon_0 = \varepsilon_0$(expt)
$R_{skin} = 1.6(1)$
Verified polarization model

| **GaAs** | **1.52 eV** | |
|---|---|---|
| | KS | Def. |
| lda | 0.83 | 1.54 |
| lda-3d | 0.47 | 1.51 |
| pbe | 0.45 | 1.44 |
| pbe-3d | 0.13 | **n/a** |

| **GaP** | **2.35 eV** | |
|---|---|---|
| | KS | Def. |
| lda | 1.51 | 2.3 |
| lda-3d | 1.47 | **n/a** |
| pbe | 1.74 | **n/a** |
| pbe-3d | 1.52 | n/c |

| **InP** | **1.42 eV** | |
|---|---|---|
| | KS | Def. |
| lda | 0.67 | 1.7 |
| lda-3d | 0.66 | 1.7 |
| pbe | 0.47 | **n/a** |
| pbe-3d | 0.46 | n/c |

DFT: defect band gap accurate for interesting III-V

# Si: DFT/PBE vs. Experimental Levels

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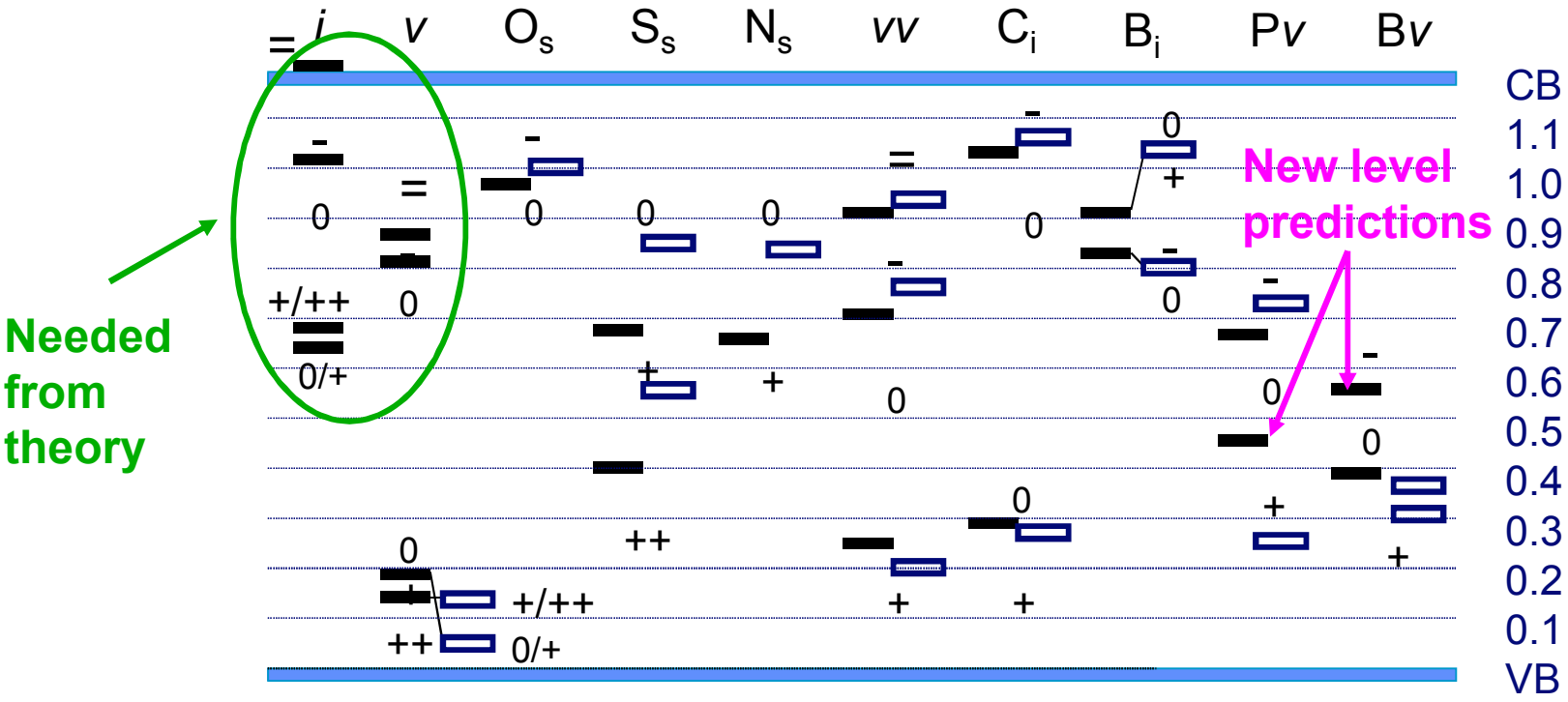



… and $v_2P(=/-/0/+)$,$vP_2(-/0)$,$v_2O(=/-/0/+/2+)$,$v_2O_2(=/-/0/+/2+)$,$H_i(-/0/+)$ … $O_i$, $P_s$, $B_s$, $C_s$,

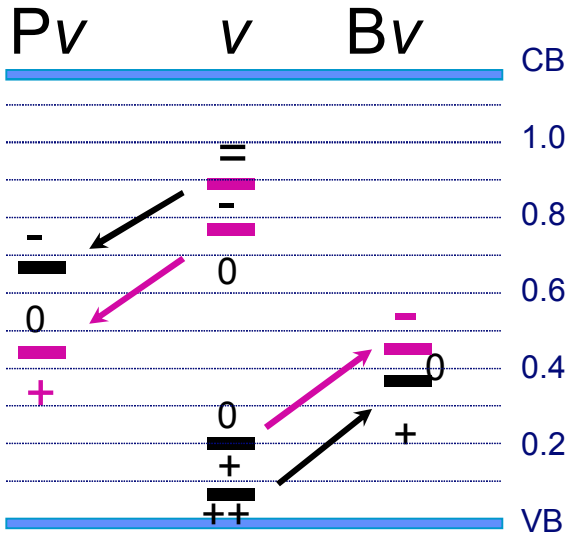
DFT “defect gap” matches experiment.
DFT/PBE max error=0.20 eV, mean |error|=0.10 eV - VALIDATION
Band gap problem not seen in **total-energy-based** defect levels

# Si: new P-v and B-v charge states



- Silicon level calculations - over 15 defects with levels

  *i*(=/-/0/+/++), *v*(=/-/0/+/++), *vv*(=/-/0/+), $C_i$(-/0/+), $B_i$(-/0/+), P*v*, B*v*
  $O_s$(A-center), $O_i$, $N_s$, $S_s$, $v_2O$, $v_2O_2$, $H_i$, $vP_2$, $v_2P$, …
  DFT "defect band gap" matches experiment (1.2 eV)
  DFT: mean |error| = 0.10 eV, max error~0.2 eV




Task: Theory quantified v(=/-), v(-/0)

Discovery: Theory *predicted* Pv(+) and Bv(-)

"Absolute prediction"
new levels >0.4 eV from band edge
validation error: 0.2
P*v*(0/+) subsequently confirmed in experiment
[Larsen, et al PRL 97, 106402 (2006)]

VALIDATION is key to quantitative DISCOVERY - GaAs is ALL discovery

# V&V: EL2 and the As antisite

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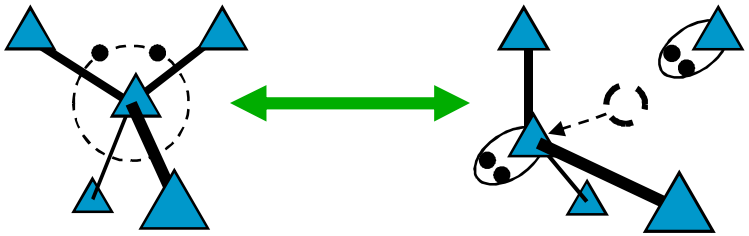
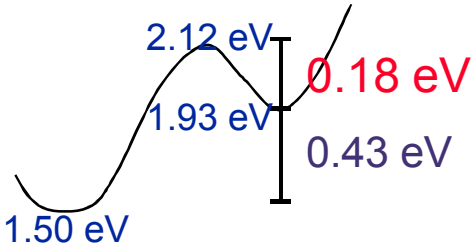
## EL2 = antisite $As_{Ga}(0)$






216-site =
512-site
(~ 64-site)

| | **Experiment -EL2** | **SeqQuest/FDSM - $As_{Ga}$** |
|---|---|---|
| EL2(0/1+) | $E_c$ -0.74 eV | $E_c$ -0.81 eV |
| EL2(1+/2+) | $E_v$+0.54 eV | $E_v$ +0.48 eV |
| Splitting: | 0.24 eV ($E_g$=1.52) | 0.25 eV |
| EL2* | no donor states | no donor states |
| Reorientation: | ~0.3 eV | ~0.2 eV |

Verification: 64-216-512-site supercell results match
Validation: DFT matches experiment for EL2 w/in 0.1eV

# The divacancy is the E1-E2 radiation center



P.A. Schultz, PRL, submitted

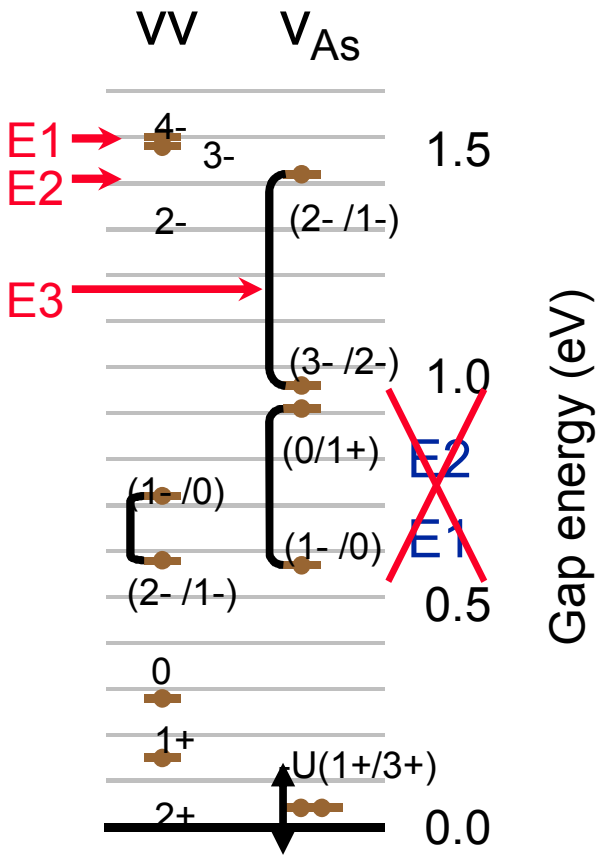
## Rewriting radiation physics in GaAs

Old (experimental) lore, back to 1988:

- E1, E2 center = $v_{As}$(-/0), $v_{As}$(0/+)
- E3 = $v_{As}$+ *i*
- *vv* is dismissed

New results:

- $v_{As}$(-/+) is mid-gap negative-U (only *one* level)
- $v_{As}$(3-/1-) is upper-gap -U (*one* level)
- *vv*(4-/3-/2-) near conduction band
- Re-analysis of expt (positron, displacement)




vv is major radiation defect: E1-E2

vAs(3-/1-) transition is the E3

Differential diffusion of $Ga_i$ and $As_i$ is crucial element

First identified radiation defects in GaAs (EL2 was non-rad)

# GaAs defects: principal findings (thus far)

Peter A. Schultz

- "Simple" intrinsic defects very complicated
  - more charge states, bi/meta-stabilities, negative-U … need theory
- Mono-vacancies have global site-shift bistability, $v_X \leftrightarrow v_Y Y_X$
  - bistability must be included in unified description of vacancy
- Simple chemical motifs described bonding in ground state
  - As-pyramid (lone-pair), trivalent-Ga, weak Ga-Ga pairs across *v*
- Interstitials have low thermal barriers for diffusion
  - $Ga_i$: 1 eV, $As_i$: <0.5 V, these will be active species
- The $As_i$ will also diffuse athermally
- The divacancy is important radiation defect (so is $v_{As}$)

DFT-SeqQuest/FDSM levels good enough to identify GaAs defects strictly on quantitative defect level calculations

# $Ga_i$ - gallium interstitial

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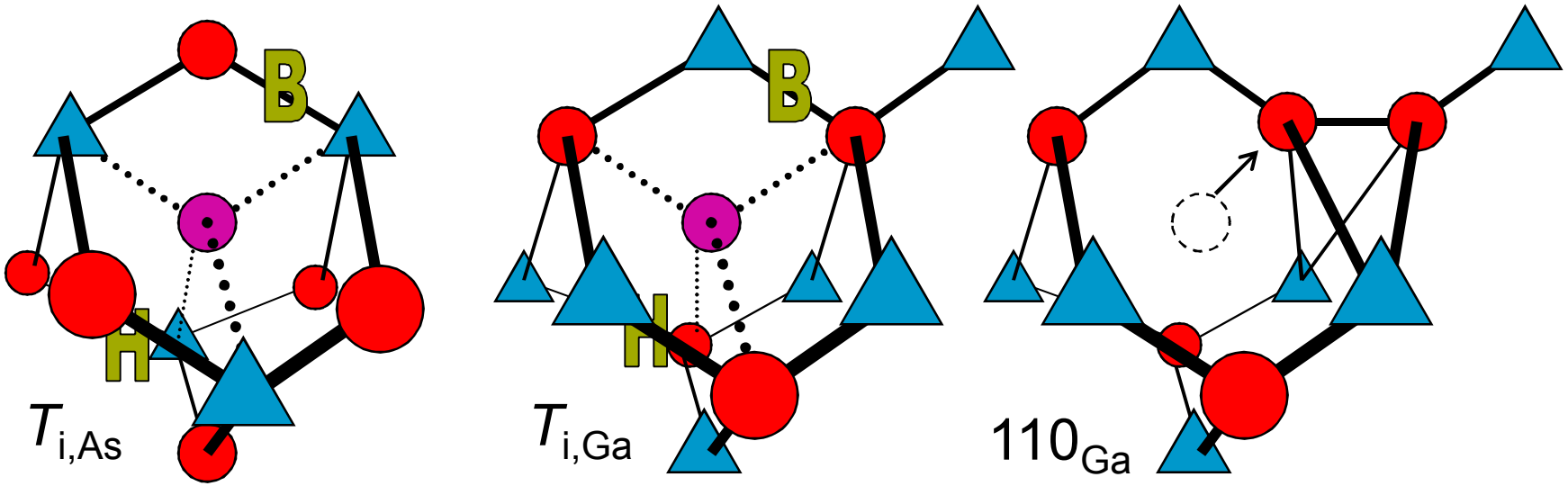
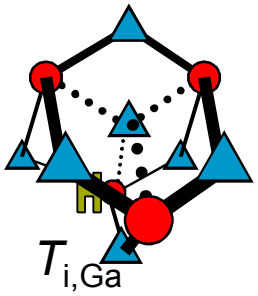
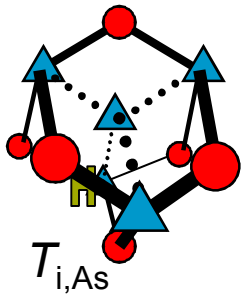


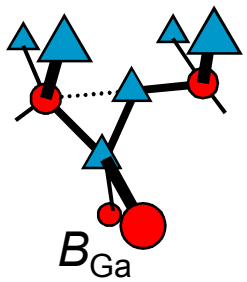

$Ga_i$ only thermodynamically stable (1+) to (3+); no stable $Ga_i(0)$
Off-network $T_{i,Ga}$ is ground state, (1+) across full band gap
Off-network $T_{i,As}$ is 0.27 eV higher, through 1.15(10) eV *H*-site barrier
$T_{i,As}$ takes charge states from (1+) to (3+)

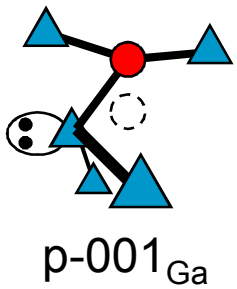
$Ga_i$ electrically active (may be visible), thermally mobile (0.5-1.1 eV)

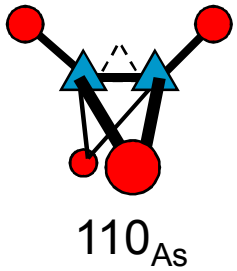
# $As_i$ - arsenic interstitial




...

| $As_i$(q) | ground state | next | barrier |
|---|---|---|---|
| (1-) | $110_{As}$ | $B_{Ga}$(+0.5 eV) | >0.5 eV |
| (0) | $110_{As}$ | $B_{Ga}$(+0.2) | >0.2 eV |
| (1+) | p-$001_{Ga}$ | $H$(+0.3); $B_{Ga}$(+0.4) | >0.4 eV |
| (2+) | $H$ ~ $B_{Ga}$ | $T_{i,Ga}$(+0.2);$T_{i,As}$(+0.4) | ~0.4 eV |
| (3+) | $T_{i,Ga}$~$T_{i,As}$ | $H$(+0.4) | ~0.4 eV |

Charge states from (1-) to (3+)
Multiply metastable, bistable from in-network(-) to off-network(+)
Low thermal barriers for diffusion: < 0.5 eV
Athermal diffusion (esp. p-type), e.g.: $T$(3+) - $H$(2+) - $T$(3+)

$As_i$ active, thermally mobile (<0.5 eV), athermal diffusion

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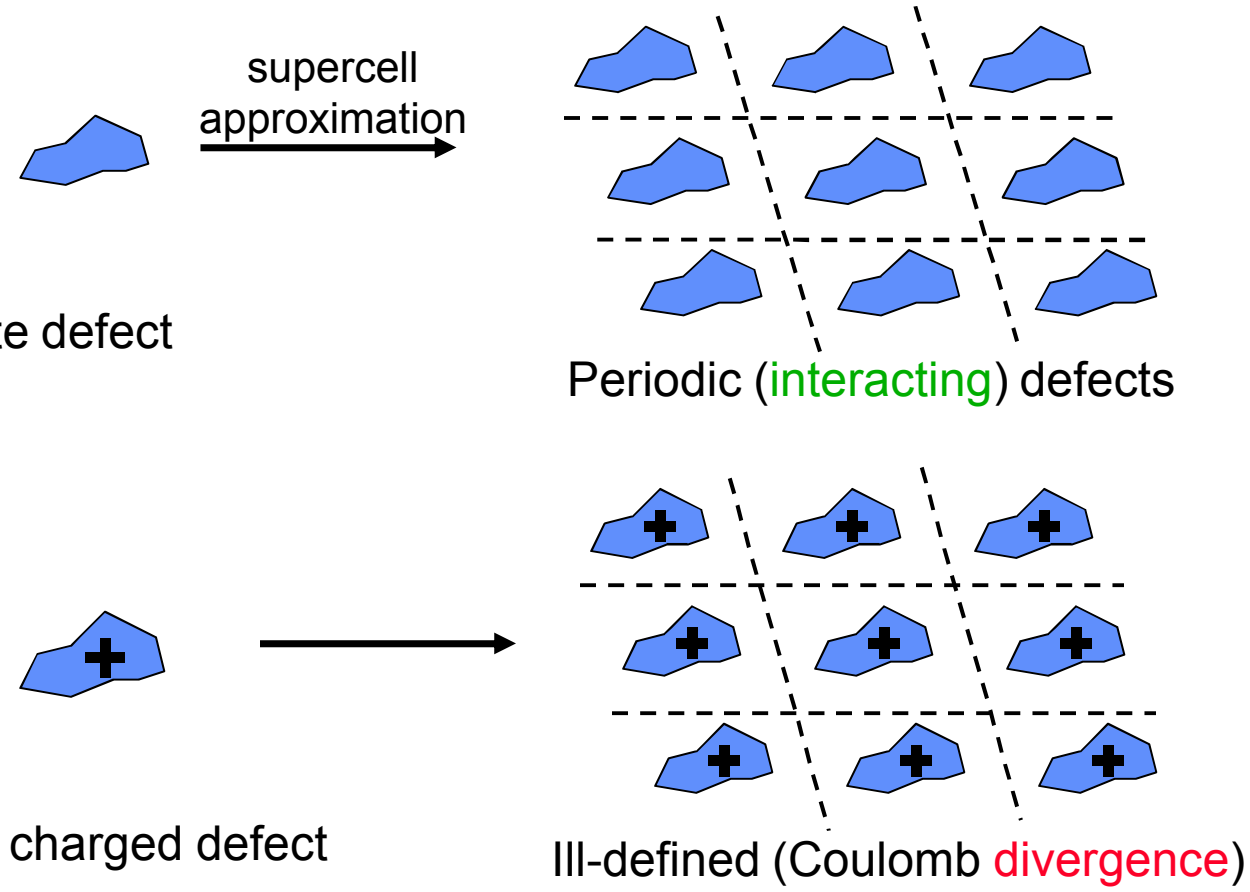
# The supercell approximation




Interactions and divergence are key issues

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