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QUALIFICATION ALTERNATIVES TO SPR

SAND2011-1791C

First Principles Defect Chemistry for Modeling Irradiated GaAs and III-V's

- Getting electrons and atoms into QASPR

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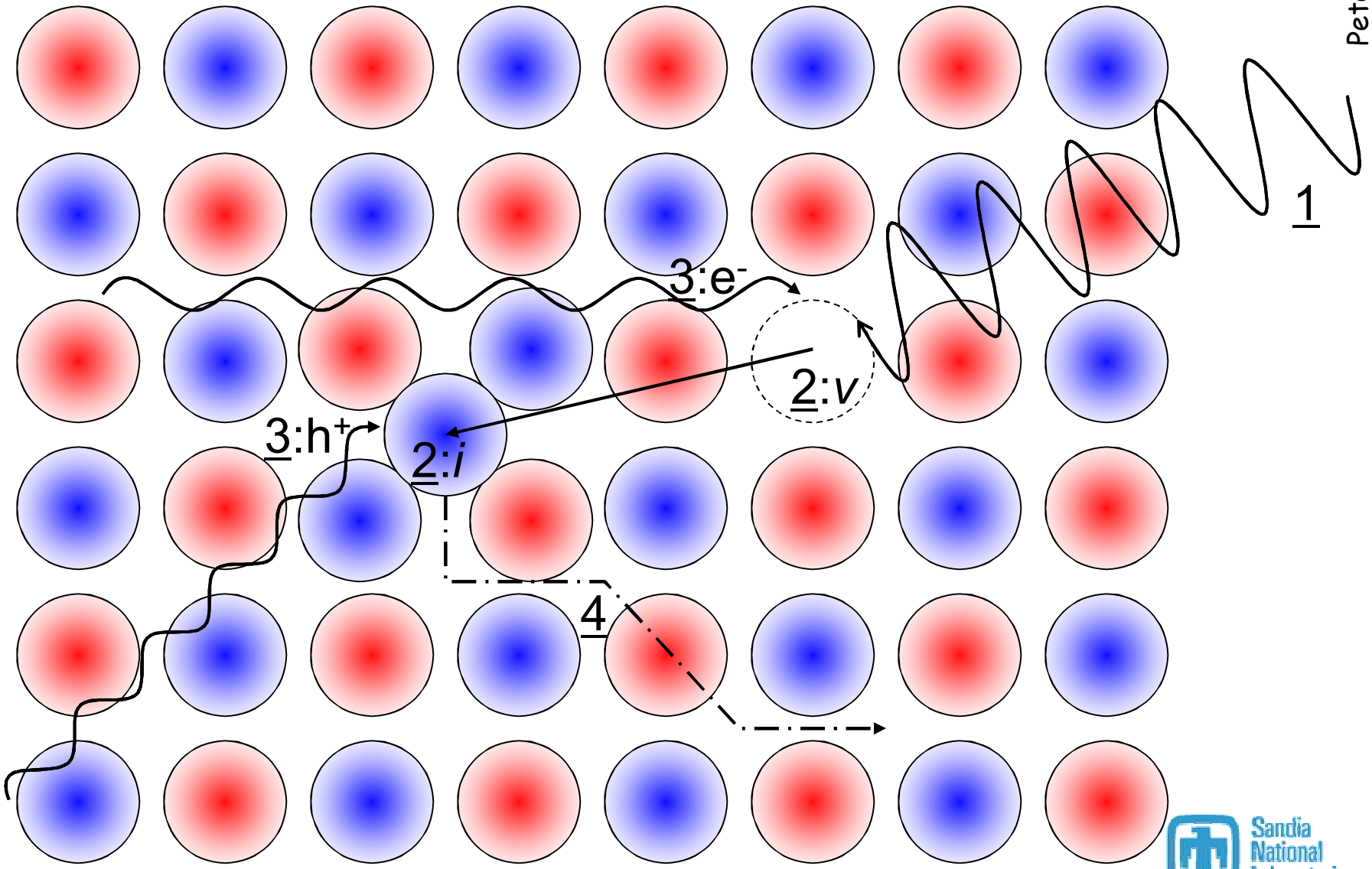
It begins with displaced atoms …



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Modeling Radiation Response - QASPR

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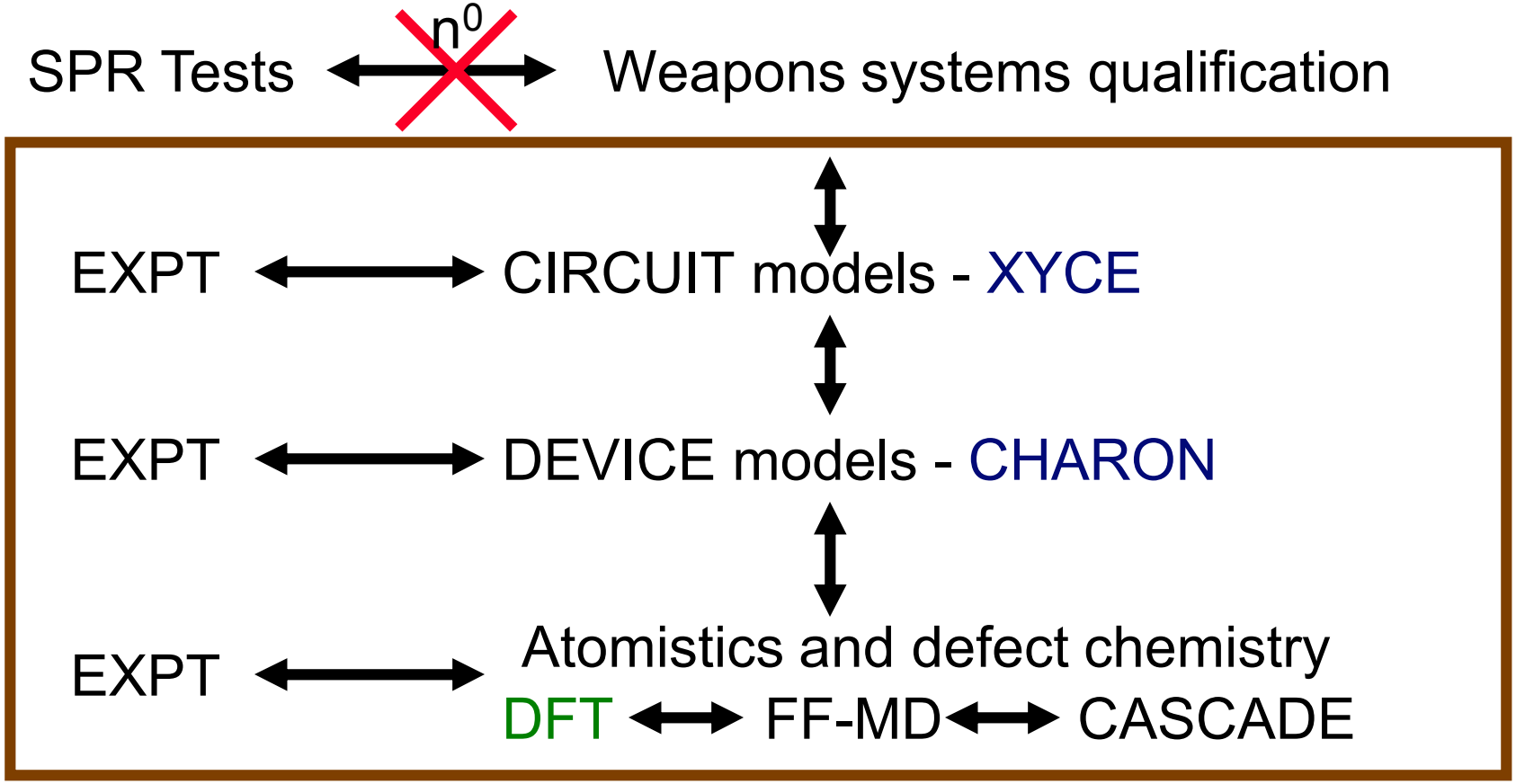

QASPR charter: replace SPR tests with expt'l-comp'l system

Atomistic density functional theory (DFT) gives defect chemistry

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Radiation defects chemistry: Si

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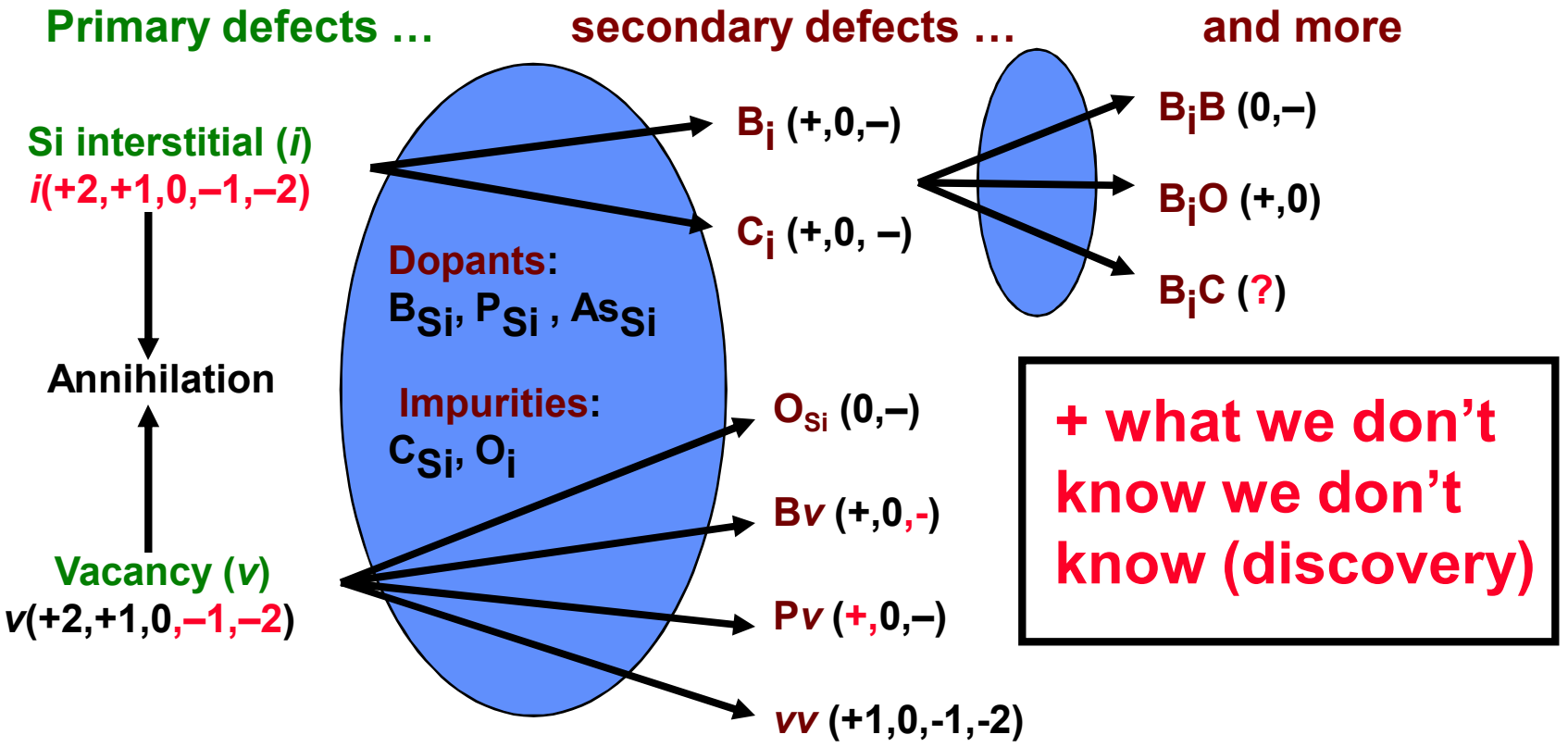

Need to know defects species, charge states, levels, chemical networks …
DFT most accurate (sometimes only) probe of defect behavior
This chemistry map almost entirely blank in GaAs, III-V's - unknown

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HBT model needs more than Si, or even GaAs

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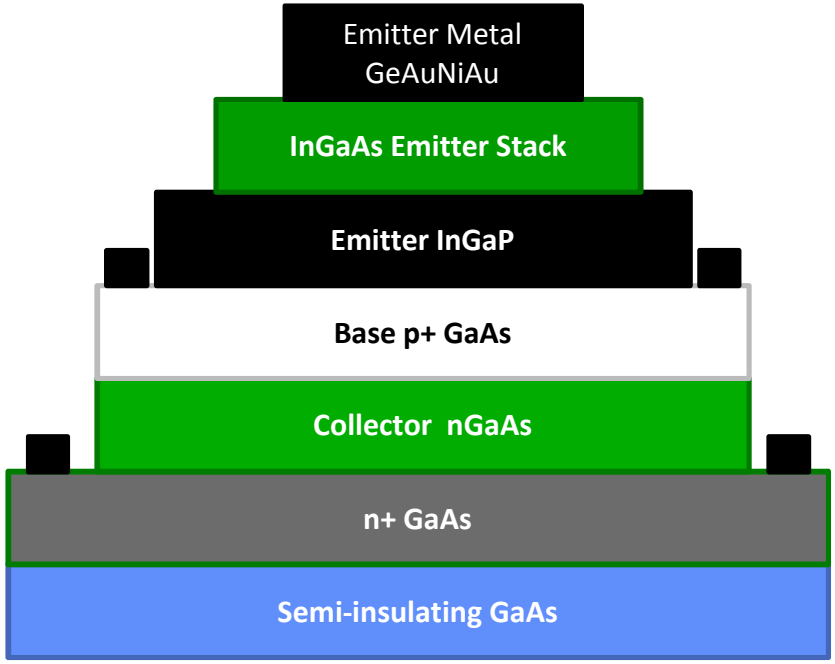
Example HBT stack



(Thanks: Don King and Gary Patrizi)

AlGaAs and InGaP
are important in HBT devices

Need defect physics for:
InP and GaP, AlAs

Then need to extend that
defect physics to ternary alloys.

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The sequence of physics challenges

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- **Silicon: lots of good data**
  - Expt: DLTS (levels) + EPR (chemical identity)
  - Need DFT to fill key gaps in QASPR defect package:
    - interstitial, vacancies(-q), reactions/migration energies
    - Unknown unknowns (P*v*, B*v*)
- **GaAs: more complex system, very little good data**
  - DLTS (levels) + EPR(chemical identity)
  - Only defect characterized is EL2 (As_{Ga}), no radiation-defects
  - DFT must take place of EPR to identify chemistry
  - **Validation challenge**
- **HBT's: other III-V's and ternary alloys, even less good data**

Strategy: (1) comprehensive quantitative validation in Si
(2) extend into GaAs, validate and predict
(3) lather, rinse, repeat: dopants in GaAs, III-V, …

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Computational challenges

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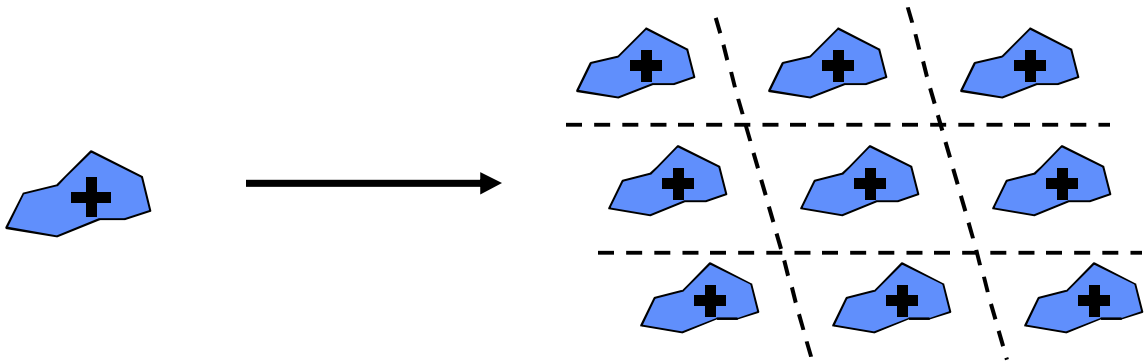
- **Conventional DFT failed for defect levels in semiconductors**
  - (1) Physical accuracy: "band gap problem"
  - (2) Computational model convergence – model size limitations
  - (3) Lack of good and sufficient data for validation (esp. III-V's)
  - (4) Supercell problem for charged defects:



Finite charged defect

Ill-defined (Coulomb divergence)

- lots of "point solutions" with DFT, but no robust, predictive method

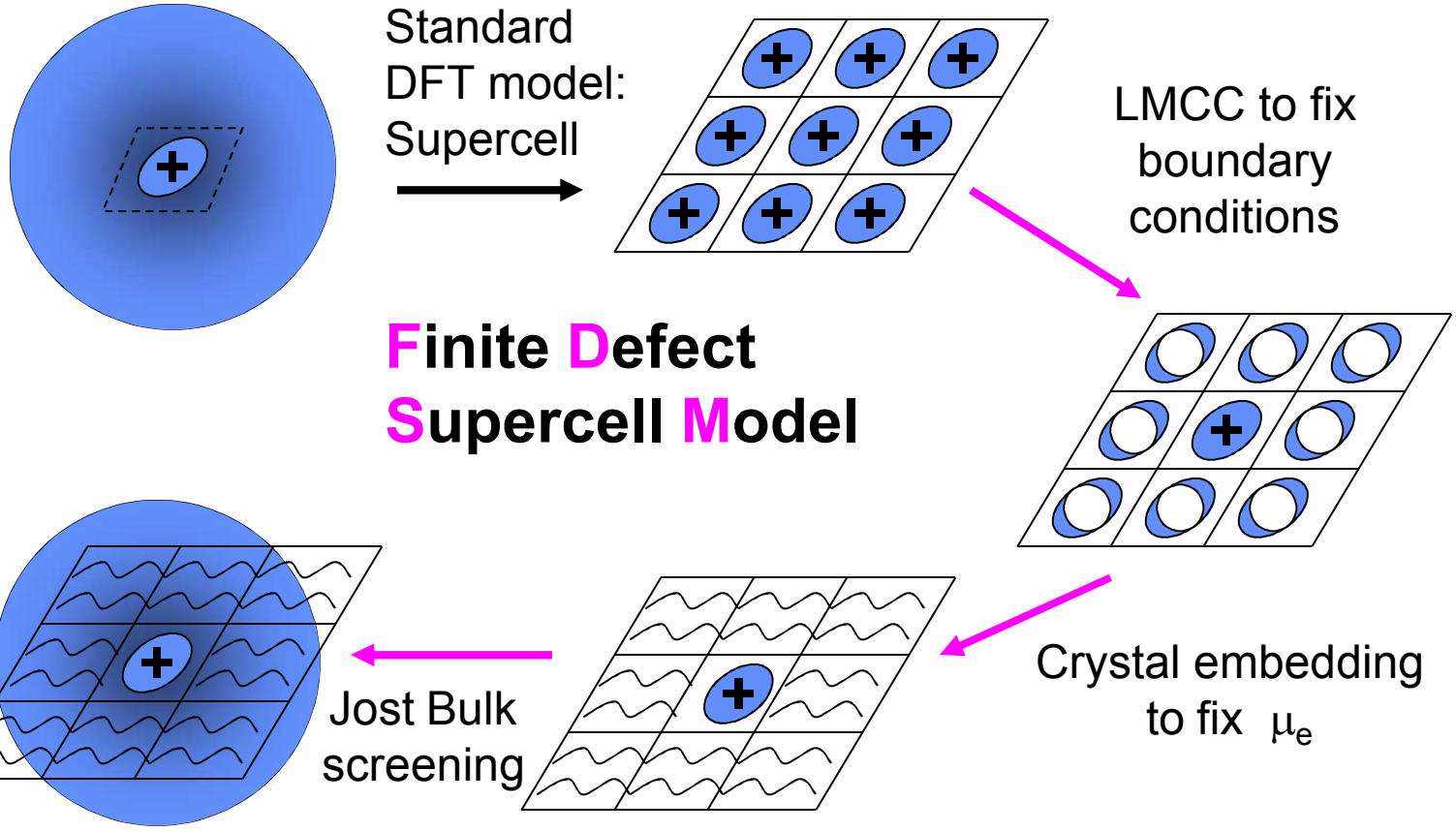
- **Need to build and justify new approaches, apply to new problems**

Strategy: incrementally build/test, V&V defect models

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

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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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Si: DFT/PBE vs. Experimental Levels

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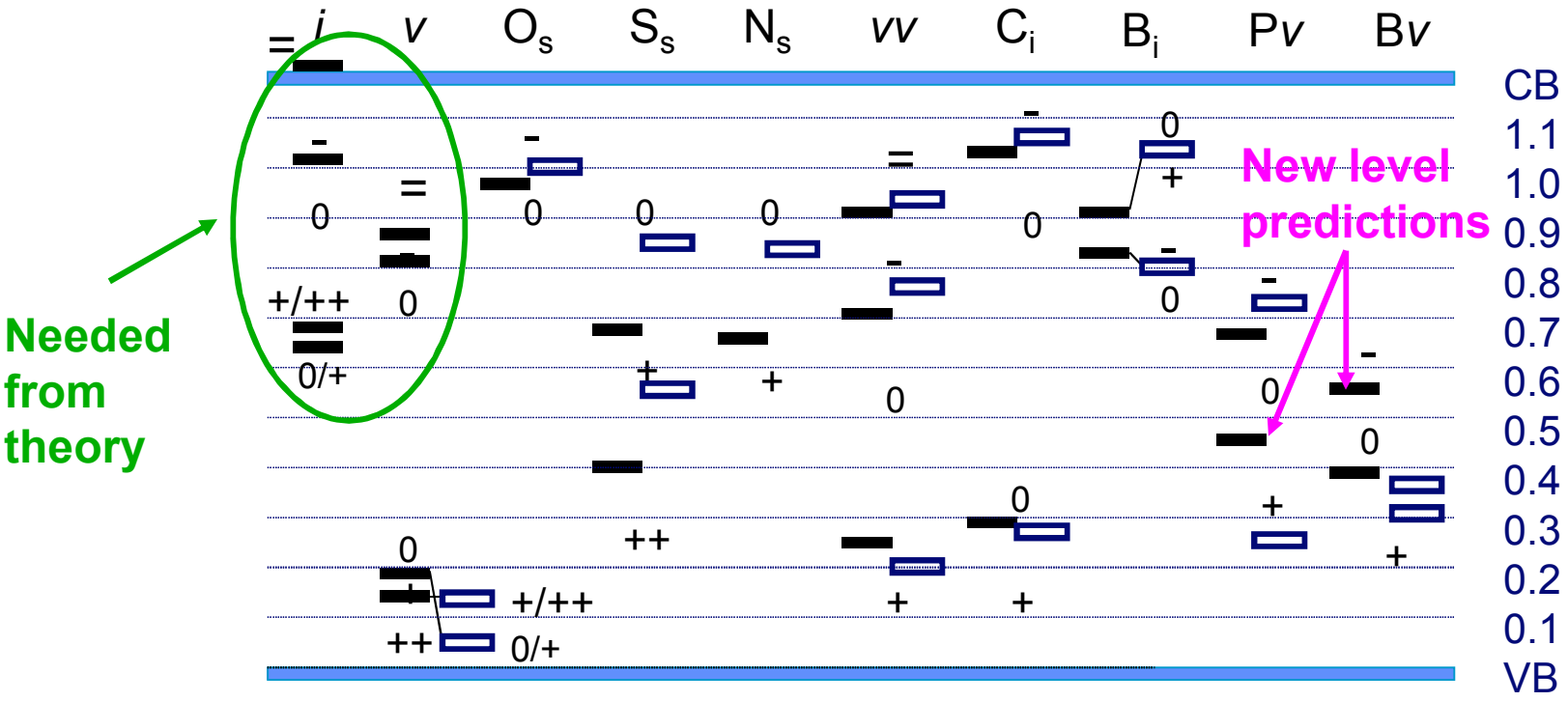


… and $v_2P(=/-/0/+)$,$vP_2(-/0)$,$v_2O(=/-/0/+/2+)$,$v_2O_2(=/-/0/+/2+)$,$H_i(-/0/+)$ … O_i, P_s, B_s, C_s,

DFT "defect gap" matches experiment – no band gap problem.
DFT/PBE max error=0.20 eV, mean |error|=0.10 eV – VALIDATION

DFT gives verified, validated results with good uncertainties

Simple intrinsic defects in GaAs: LDA

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

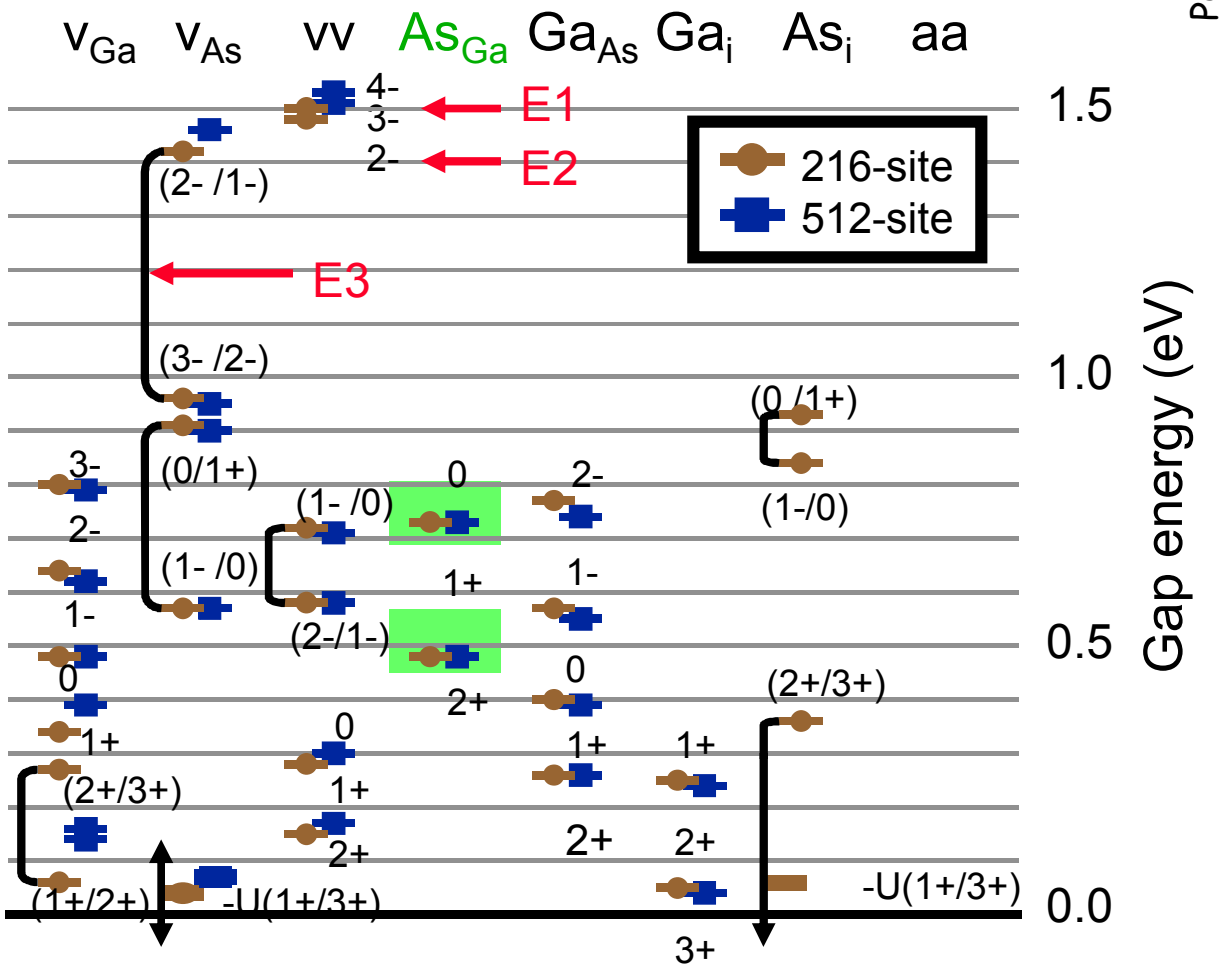
216-site results = 512-site
Verification: cell-converged

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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Transients: Identify mobile species in GaAs

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- **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 also 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

- **No other mobile species (e.g. vacancies are stationary)**
  - consistent with, and roughly validated by experimental analyses

Transient effects dominated first by As_i, second by Ga_i

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GaAs transient defect chemistry network

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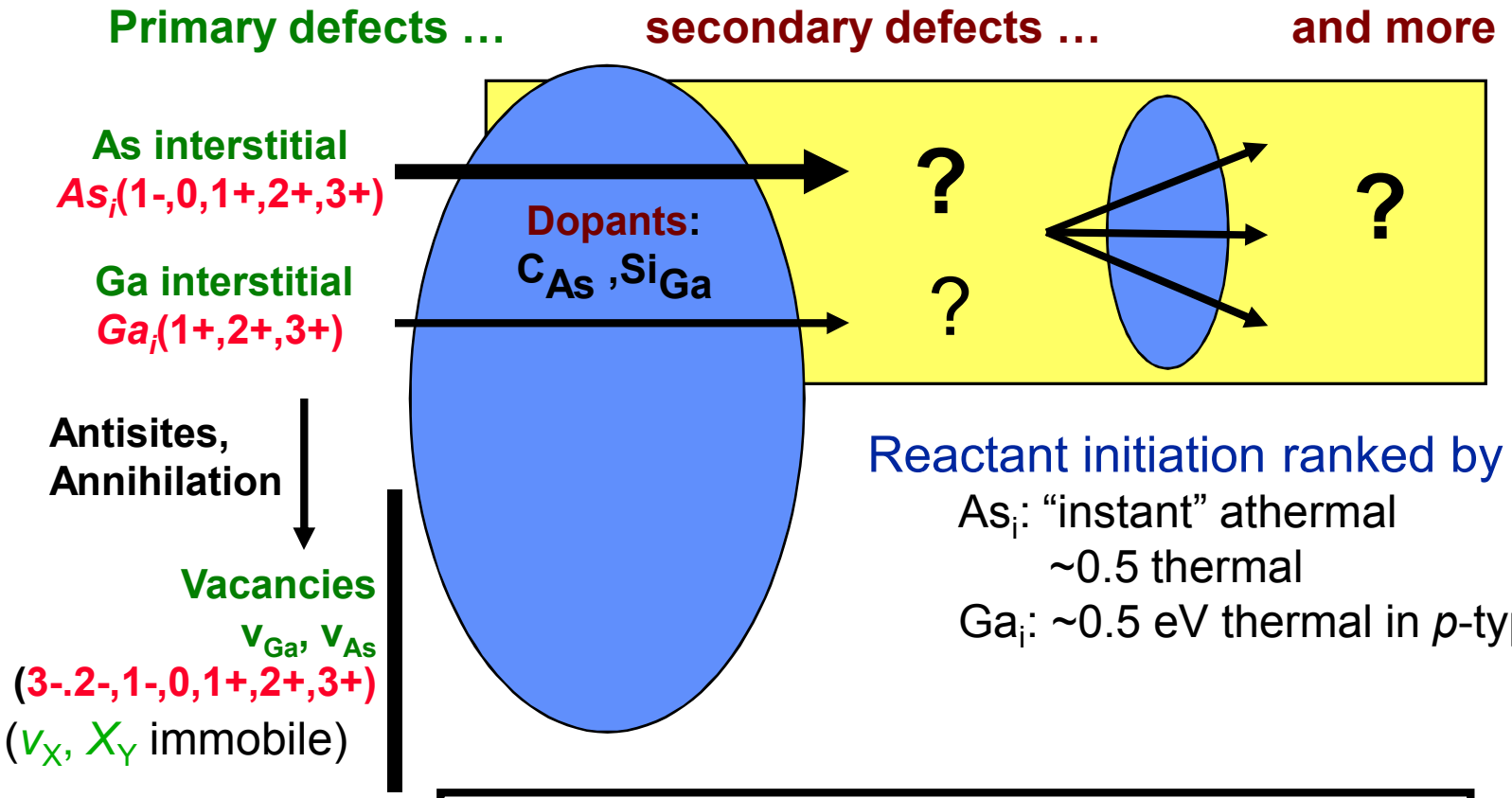

Reactant initiation ranked by mobility:

As_i: "instant" athermal
~0.5 thermal

Ga_i: ~0.5 eV thermal in *p*-type

Likely reactant targets of mobile interstitials:

p-type … C_{As} - in *p*-type

n-type … Si_{Ga} (Si_{As}) - in

Interstitial-defect reactions and energies

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Thermodynamic (non-charge conserving)

As interstitial:

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

Ga interstitial:

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

GaP: Simple intrinsic defects

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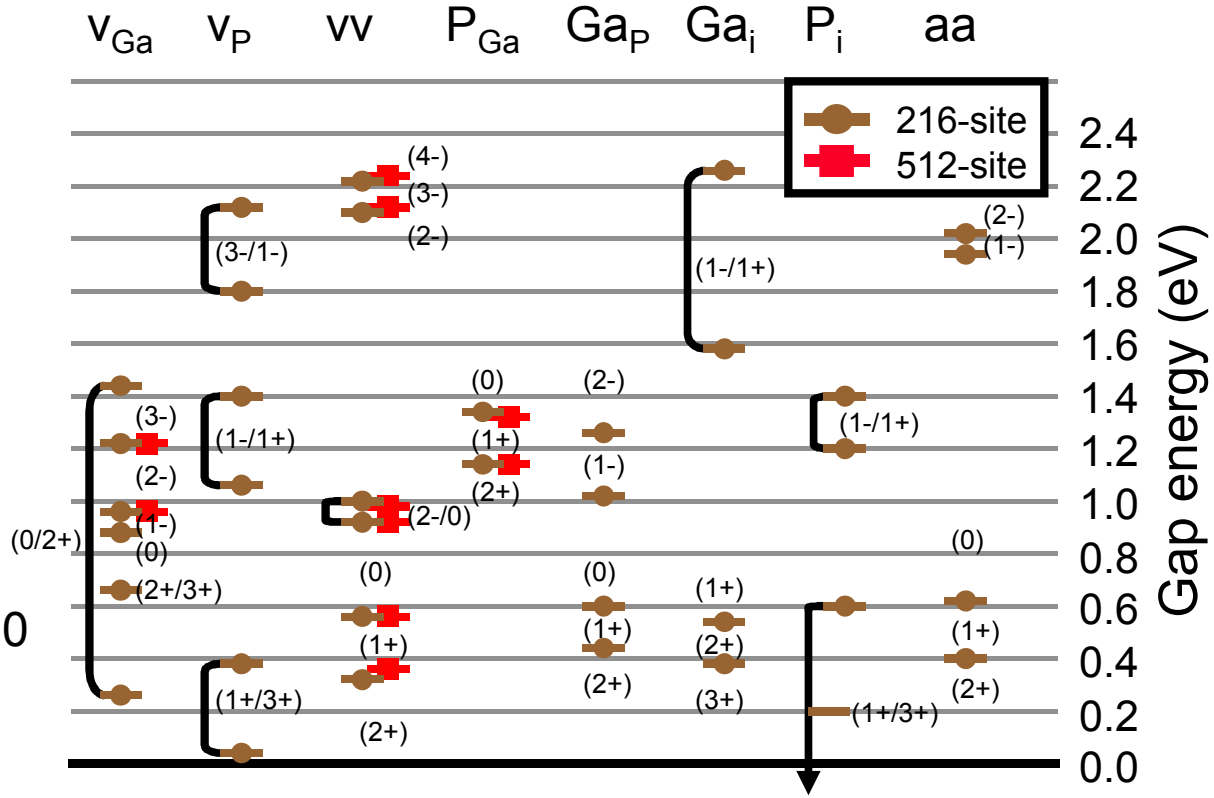
SeqQuest version dev2.62/j, LDA, Ga(Z=3) PP

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

SeqQuest version dev2.62/j, LDA, In(Z=3) PP

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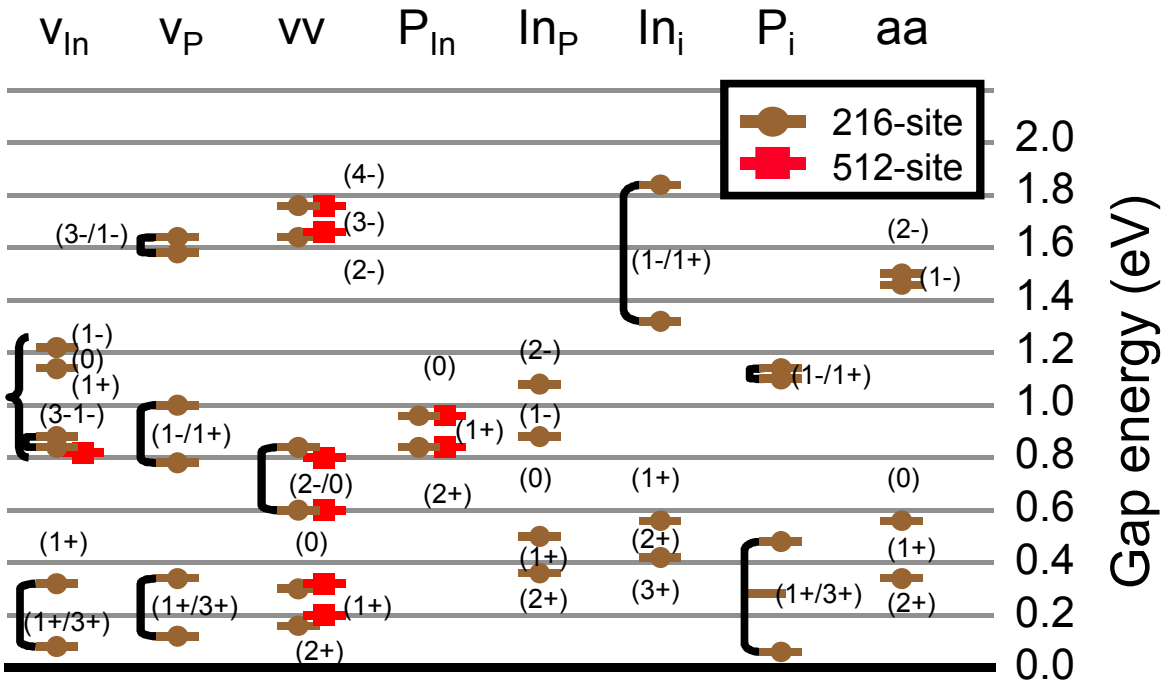
216-site results = 512-site
Verification: cell-converged

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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Path forward for defect chemistries

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- Impurity-defect chemistry in GaAs - Si (*n*-type), C (*p*-type)
  - clean up chemical networks, need experiment to filter possibilities
- Set up baseline defect physics for other III-V - get ahead of engineering needs
  - identify mobile species, and begin to scope radiation chemistry networks
  - scope issues for extending to HBT-relevant alloys, e.g. InGaP
- Ternaries? Looks like InGaP ~ GaP + InP …
- Need to figure out physics in GaAs (U-band)
- Need experiment in InP, GaP, InGaP for model development, validation
- Need to develop validated defect-aware device models

DFT has achieved accuracy necessary for device model needs
DFT studies can meet (lead) engineering timeline constraints

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- Extra slides -

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V&V: EL2 and the As antisite

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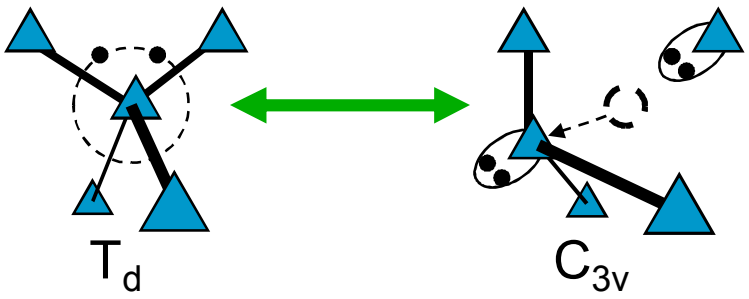
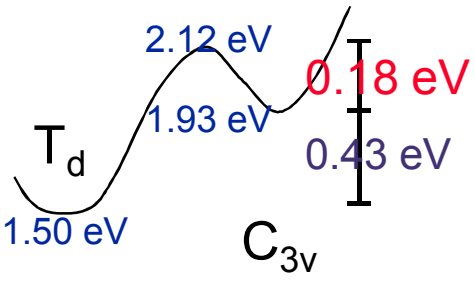
EL2 = antisite $As_{Ga}(0)$





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

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 Si-complexes
$(SiAs)_{Ga}$ [2-], [1-] states thermodynamically inaccessible

Levels can be used to extend defect physics package in GaAs

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

The polarization model and verification

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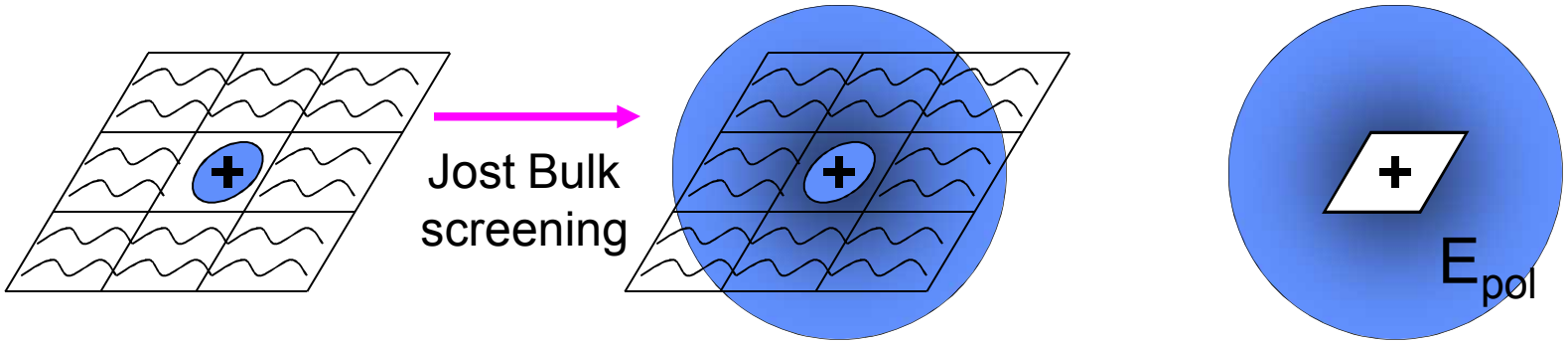
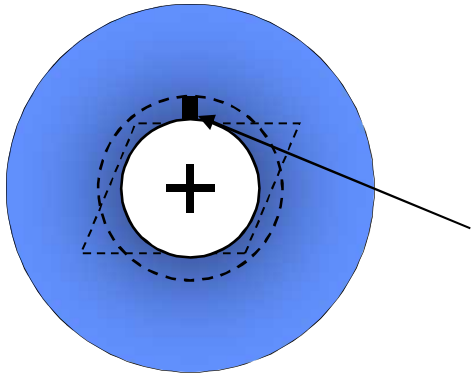


For extrapolation to infinite cell, need energy of screening outside of cell. E_{pol}

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

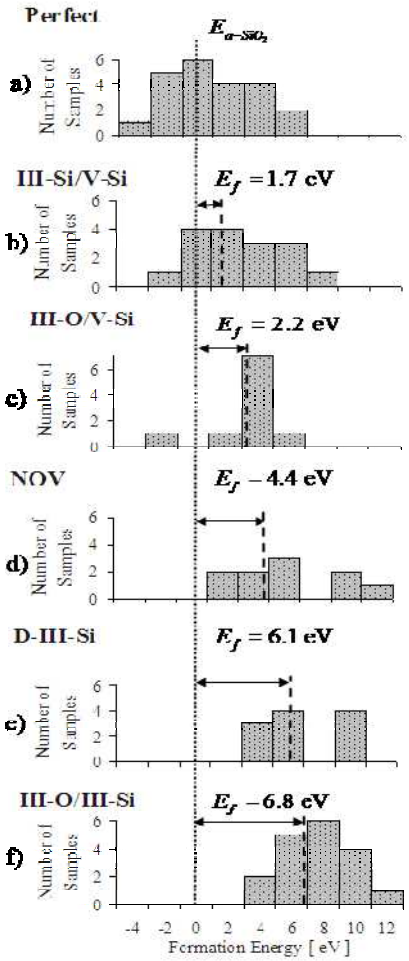
R_{skin} = unscreened volume **inside** cell.
fit: =1.5(1) bohr

ε_0 = static dielectric constant - expt

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

Enabling progress on oxides

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 interfaces

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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