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## Simple Intrinsic Defects in GaP: Numerical predictions

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# **Simple intrinsic defects in GaP: Numerical predictions**

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## **Abstract**

This Report presents numerical tables summarizing properties of intrinsic defects in gallium phosphide, GaP, as computed by density functional theory, intended for use as reference tables for a defect physics package in device models.

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## NOMENCLATURE

CBE	conduction band edge
DFT	density functional theory
eV	electron Volt
FDSM	finite defect supercell model
GGA	generalized gradient approximation
IP	ionization potential
LDA	local density approximation
LMCC	local moment countercharge
MSMSE	Modelling and Simulation in Materials Science and Engineering
n/c	not computed
n/x	not exist
PAS09	Article: P.A. Schultz and O.A. von Lilienfeld, MSMSE <b>17</b> , 084007 (2009).
PBE	Perdew/Burke/Ernzerhof, a “flavor” of GGA
PP	pseudopotential
SNL	Sandia National Laboratories
VBE	valence band edge

# 1. INTRODUCTION

The numerical results for density functional theory (DFT) calculations of properties of simple intrinsic defects in gallium phosphide, GaP, are presented. The results of the defect calculations are summarized into a series of numerical Tables containing the parameters needed to populate defect physics packages needed for device simulations. In addition, a summary of the GaP-specific verification and validation evidence and needs is discussed that provides a basis for estimating an overall uncertainty in predicted defect energy levels of the same size as for earlier simulations of silicon defects [1] and GaAs defects [2] (henceforth “PAS09”), namely, 0.1-0.2 eV accuracy/uncertainty.

## 1.1. Computational methods

The details of the computational methods are comprehensive described previously (as applied to GaAs) [2], and will only be briefly summarized here. The DFT calculations were performed with the SEQQUEST code. [3] The defect calculations were performed using both the local density approximation (LDA) [4] and the Perdew-Burke-Ernzerhof (PBE) flavor of the generalized gradient approximation [5], this comparison being a partial assessment of the physical uncertainties within DFT functionals [6]. Calculations with both  $3d$ -core and  $3d$ -valence pseudopotentials (PP) were used for the gallium atom, to test (verify) the convergence in the PP construction for defect properties.

The calculations of charged defects used the Finite Defect Supercell Model (FDSM) [1] to incorporate rigorous boundary conditions for the solution of the electrostatic potential in a charged supercell [7] and extrapolate the computed defect energies to the infinitely dilute limit. Defect calculations were performed using 64-atom, 216-atom, and 512-atom cubic supercells. The 216-site supercell calculations proved to be sufficiently converged to achieve the required accuracy and are the default production calculations listed in this Report.

These simulation contexts are labeled in the following as: LDA64, LDA, and LDA512, for 64-site, 216-site, and 512-site, respectively, supercell calculations using LDA and the  $3d$ -core ( $Z=3$ ) PP for Ga; PBE for the 216-site supercells using PBE and  $3d$ -core PP; and LDA-3d and PBE-3d for the 216-site supercells with  $3d$ -valence ( $Z=13$ ) PP for the Ga atoms.

## 1.2. Verification and validation

The defect level calculations all used SEQQUEST and the FDSM, the same methods used in DFT calculations of defects in silicon and GaAs, which yielded mean absolute errors of 0.1 eV and maximum absolute error of 0.2 eV for defect levels over a wide sampling of different defects. This is the expected accuracy (uncertainties) of the methods for these defect level calculations in GaP, and the limit of the physical accuracy of the DFT approximations used in this analysis.

The phosphorus PP has been described previously [8], and are the same used in the silicon defect calculations [1]: a standard  $s^2p^3$  valence atom, added a  $d$ -potential with  $R_c=1.08$  Bohr to use as the local potential. The gallium PP were the same as those used in the GaAs calculation, as described in PAS09, were extensively verified in Ref. [8], and validated for the bulk crystalline calculations. The PP used in this study were further tested here, all defect calculations were performed with both the  $3d$ -core and  $3d$ -valence PP for Ga. While the absolute formation energies of neutral defects differed by as much as 0.36 eV (for the Ga antisite, the differences in

formation energies were typically much smaller. The largest difference in computed defect level below was only 0.09 eV, usually much less (notably, for the Ga antisite), indicating an effective cancellation of errors was occurring. Hence, while uncertainties in the absolute formation energies might be as large as 0.4 eV, but the (3*d*-core) defect levels, obtained as differences in formation energies, have much smaller uncertainties, of 0.1 eV, with respect to pseudopotential construction.

The bulk properties for GaP obtained within these simulations contexts is are presented in the following Table.

**Table 1. Computed bulk GaP properties**

Simulation context	Lattice parameter (Å)	Bulk Modulus (GPa)	Kohn-Sham Band gap (eV)	Formation energy (eV)
<b>Experiment</b>	5.447 (a)	88.8 (b)	2.34 (c)	0.91 (d)
<b>LDA</b>	5.397	87.7	1.51	0.896
<b>LDA-3d</b>	5.419	86.0	1.47	0.785
<b>PBE</b>	5.506	76.0	1.74	1.020
<b>PBE-3d</b>	5.532	75.4	1.52	0.909

(a) Ref. [9].

(b) Ref. [10].

(c) Ref. [11].

(d) Ref. [12].

Comparisons of experimental formation energies to computed formation energies are problematic for phosphides, both because DFT has difficulties with the van der Waals part of the bonding in some bulk phosphorus allotropes, and because experimental assessments are also complicated by the uncertainties in relative formation energies of different phosphorus allotropes [13]. The listed values, experimental and theoretical, use black phosphorus as the elemental reference (although the experiment uses the *A17* structure and the DFT the *A7* structure). The apparent good agreement between experiment and the simulations should be regarded skeptically and as somewhat fortuitous.

### 1.2.1. Extrapolation model

The total energy calculations for the charged defects used a modified-Jost model [14, 1] to evaluate the missing charge polarization (screening) energy outside the finite volume of the supercell:

$$E_{\text{pol}} = (1 - 1/\epsilon_0) q^2/R_{\text{Jost}} \quad (1)$$

where  $\epsilon_0$  is the static dielectric constant, and  $R_{\text{Jost}} = (R_{\text{sphere}} - R_{\text{skin}})$  is the radius of a sphere with a volume equal to the volume of the supercell,  $R_{\text{sphere}}$ , less the skin depth,  $R_{\text{skin}}$ , of an unscreened surface region within the sphere.  $R_{\text{skin}}$  must be calibrated (fit) once for each material system.

The *extrapolation model* was *calibrated* via calculations of negative charge states of the gallium vacancy, in unrelaxed tetrahedral structures for the (1-), (2-), and (3-) charge states.

The *extrapolation model* was then *verified* using the (0/1+) and (1+/2+) transitions of the P<sub>Ga</sub> antisit, via comparisons of defect levels extrapolated to infinitely dilute defects from 64-site, from 216-site, and from 512-site supercell calculations. 216-site cells were assessed to be necessary to meet required level of quantitative confidence. The *vv* divacancy (as an example of a low-symmetry defect expected to have large spatial extent) with 216-site supercells was repeated using 512-site supercells as a further verification test. The differences in any defect level between the 216-site and 512-site results was always less than 0.04 eV, even for extreme charge states (of the *vv*).

The *extrapolation model* was *validated*. The experimental GaP dielectric constant, 11.1 [15], for  $\epsilon_0$  and a physically reasonable unpolarized “skin depth” ( $R_{\text{skin}}$ ), 1.5 bohr, led to a converged extrapolation, and these parameters are also consistent with extrapolation models in multiple other III-V defect calculations such as GaAs, AlAs, and InP (all using experimental  $\epsilon_0$  and  $R_{\text{skin}}=1.5(2)$ )

The quantities defining the extrapolation model are summarized in the next Table.

**Table 2. Supercell extrapolation energies,  $\epsilon_0=11.2$ ,  $R_{\text{skin}}=1.5$  bohr.**

Context:	LDA64	LDA512	LDA	LDA-3d	PBE	PBE-3d
$a_0(\text{\AA})$	5.397	5.397	5.397	5.419	5.506	5.532
IP(VBE) (eV)	5.42	5.61	5.51	5.45	5.17	n/c
Charge	External polarization energy (eV), Eq. 1					
$ q  = 1$	1.1110	0.5205	0.7089	0.7058	0.6937	0.6902
$ q  = 2$	4.4441	2.0821	2.8356	2.8230	2.7748	2.7607
$ q  = 3$	9.9993	4.6846	6.3802	6.3518	6.2432	6.2115
$ q  = 4$	17.7765	8.3282	11.3425	11.2920	11.0991	11.0427

### 1.2.2. Verification and validation of GaP defect results

There is little experimental data available to quantitatively validate GaP defect level results. The span of computed defect levels approximately matches the experimental band gap, suggesting the total energy calculations underlying the defect level calculations are broadly accurately representing the defect physics, and the overall uncertainties in the defect level calculations would be consistent with the 0.1-0.2 eV uncertainties (accuracy) observed for computed defect levels in silicon [1] and GaAs [2]. There is good experimental evidence that the phosphorus antisite P<sub>Ga</sub>(2+/1+) transition is located at 1.10 eV above the valence band edge (VBE), with the first donor level (1+/0) being located somewhere in the upper half of the band gap [16]. This midgap state is roughly reproduced in both the LDA and PBE calculations, but is insufficient to serve as validation. For one thing, the position of the VBE and CBE needs to be calibrated using data. There is a need to acquire more detailed definitive experimental data to better assess these uncertainties, and also to better calibrate the inferred positions of the VBE and CBE on the scale of ionization potentials corresponding to defect charge transition energies.

The SEQQUEST DFT calculations of relaxed defect structures and defect levels all passed their internal verification checks, and the 216- and 512-site FDSM result comparisons verified the convergence of the extrapolation model to infinitely dilute bulk. The SEQQUEST results for GaP defects roughly match results from several years ago [17], in those particulars where a meaningful comparison could be ventured—symmetries of relaxed structures, formation energies of neutral defects—indicating a “weak” verification of the results by comparison to results of another code (VASP).

## 2. RESULTS

The section contains the Tables that summarize the numerical results for DFT simulations of defects in GaP.

### 2.1. Defect atomic structures

The following Tables list the ground state structures for the simple intrinsic defects in GaP as a function of charge state. The bonding structures are all illustrated (for GaAs) in PAS09. In the vacancies, note the discriminating nomenclature:  $v'$  refers to the simple vacancy, and  $v^*$  refers to the site-shifted form of the vacancy (where a nearest-atom to the vacancy hops into the vacant site, thus creating a vacancy-antisite pair).

**Table 3. Ground state structure designations for vacancy and antisite defects.**

Charge state	$v' = v_{\text{Ga}} \leftrightarrow v^* = v_{\text{P}}\text{P}_{\text{Ga}}$	$v' = v_{\text{P}} \leftrightarrow v^* = v_{\text{Ga}}\text{Ga}_{\text{P}}$	$vv$	aP	aGa
(4-)	-	-	$C_{1h}\text{-pair}(\text{Ga})$	-	-
(3-)	$v'/T_d$	$v^*/C_{3v}$	$C_{1h}\text{-pair}(\text{Ga})$	-	-
(2-)	$v'/\sim T_d$	$v'/\text{pair-}D_{2d}$	$\sim C_{3v}\text{-in}(\text{Ga})$	$*C_{3v}$	$T_d$
(1-)	$v'/\sim T_d$	$v'/\text{pair-}D_{2d}$	$\sim C_{3v}\text{-in}(\text{Ga})$	$*C_{3v}$	res- $D_{2d}$
(0)	$v^*/C_{1h}\text{-pair}(\text{Ga}) \}$	$v'/\text{pair-}D_{2d}$	$C_{3v}\text{-out}(\text{Ga})$	$T_d$	res- $D_{2d}$
(1+)	$v^*/C_{3v}\text{-in}(\text{Ga}) \sim v^*/C_{1h}\text{-pair}(\text{Ga})\{\text{pbe}\}$	$v'/T_{2d}\text{-in}(\text{Ga})$	$\sim C_{3v}\text{-out}(\text{Ga})$	$T_d$	res- $D_{2d}$ $C_{2v} \{\text{pbe}\}$
(2+)	$v^*/C_{3v}\text{-out}(\text{Ga})$	$v'/T_d\text{-out}(\text{Ga})$	$\sim C_{3v}\text{-out}(\text{Ga})$	$T_d$	$\sim T_d$ pair- $D_{2d}$ {pbe}
(3+)	$v^*/C_{3v}\text{-out}(\text{Ga})$	$v'/T_d\text{-out}(\text{Ga})$	-	-	$T_d$
(4+)	-	-	-	-	$T_d$

**Table 4. Ground state structure designations for the interstitials and di-antisite.**

Charge state	$\text{Ga}_i$	$\text{P}_i$	$aa^{(a)}$
(2-)	-	-	$C_{3v}$
(1-)	$C_{2v} \text{ split-}(110)_{\text{Ga}}$	$C_2\text{-twisted split-}110_{\text{P}}$	$C_{3v}$
(0)	$C_{2v} \text{ split-}(110)_{\text{Ga}}$	$^{(b)}C_{2v} \text{ split-}110_{\text{P}} \{\text{lda-3d,pbe}\} \sim C_2\text{-twisted split-}110_{\text{P}} \{\text{lda}\}$	$C_{3v}$
(1+)	$T_{i,\text{Ga}} \{\text{lda}\}$	$C_{1h} \text{ p-}(001)_{\text{Ga}}$	$C_{3v}$
(2+)	$T_{i,\text{P}}$	$C_{3v} \text{ H-site}$	$C_{3v}$
(3+)	$T_{i,\text{P}}$	$T_{i,\text{P}}$	-

(a) Symmetry-reducing distortions (to  $C_{1h}$ ) yield negligible (<11 meV) energy lowering.

(b) The  $C_2$  twisted split- $110_{\text{P}}$  is only 2 meV higher for LDA context, 7 meV lower for LDA-3d, and 19 meV lower for PBE.

## 2.2. Defect charge transition energy levels

This section presents the defect charge transition levels of the simple intrinsic defects in GaP, in eV, along with neutral formation energies. The defect level calculations are the primary result of the Report, the later formation energies are all derived from these values.

**Table 5. Defect levels for the gallium vacancy, in eV, referenced to the VBE:  $v_{\text{Ga}}(v') \leftrightarrow v_{\text{P}}-\text{P}_{\text{Ga}}(v^*)$**

$V_{\text{Ga}}$ Context	Neutral formation energy	Defect levels (eV), cf. VBE						
		(3+/2+)	(2+/1+)	(1+/0)	(0/1-)	(1-/2-)	(2-/3-)	(3-/4-)
<b>Unrelaxed <math>T_{\text{d}}-v'</math> (for polarization calibration)</b>								
LDA64	3.998	n/c	n/c	n/c	0.896	1.305	1.755	n/x
LDA	4.112	n/c	n/c	n/c	0.954	1.342	1.802	n/x
LDA512	4.186	n/c	n/c	n/c	0.949	1.342	1.811	n/x
<b>Relaxed thermodynamic levels</b>								
LDA	3.63	0.75	0.36	1.54	0.99	1.07	1.33	n/x
LDA-3d	3.53	0.75	0.35	1.49	0.97	1.07	1.31	n/x
PBE	3.48	0.88	0.45	1.58	0.95	1.00	1.28	n/x
PBE-3d	n/c	n/c	n/c	n/c	n/c	n/c	n/c	-

**Table 6. Defect levels for the phosphorus vacancy, in eV, referenced to the VBE:  $v_{\text{P}}(v') \leftrightarrow v_{\text{Ga}}-\text{Ga}_{\text{P}}(v^*)$**

$V_{\text{P}}$ Context	Neutral formation energy	Defect levels (eV), cf. VBE						
		(3+/2+)	(2+/1+)	(1+/0)	(0/1-)	(1-/2-)	(2-/3-)	(3-/4-)
LDA	3.76	0.48	0.15	1.51	1.17	2.24	1.90	n/x
LDA-3d	3.64	0.50	0.16	1.44	1.12	2.15	1.81	n/x
PBE	3.76	0.65	0.28	1.54	1.20	2.19	1.82	n/x
PBE-3d	n/c	n/c	n/c	n/c	n/c	n/c	n/c	-

Table 7. Defect levels for the divacancy, in eV, referenced to the VBE:  $vV = v_P - v_{Ga}$

Context	Neutral formation energy	Defect levels (eV), cf. VBE						
		(3+/2+)	(2+/1+)	(1+/0)	(0/1-)	(1-/2-)	(2-/3-)	(3-/4-)
LDA512	5.02	n/x	0.47	0.68	1.09	1.04	2.24	2.35
LDA	4.99	n/x	0.44	0.67	1.10	1.03	2.21	2.33
LDA-3d	4.86	n/x	0.46	0.65	1.11	1.02	2.13	2.24
PBE	4.45	n/x	0.38	0.62	1.40	1.00	2.19	2.28
PBE-3d	n/c	-	n/c	n/c	n/c	n/c	n/c	n/c

Table 8. Defect levels for the phosphorus antisite, in eV, referenced to the VBE:  $aP = P_{Ga}$

Context	Neutral formation energy	Defect level (eV), cf. VBE						
		(3+/2+)	(2+/1+)	(1+/0)	(0/1-)	(1-/2-)	(2-/3-)	(3-/4-)
LDA64	2.016	n/x	1.258	1.438	-			
LDA512	2.018	n/x	1.254	1.442	-			
LDA	2.015	n/x	1.253	1.438	2.20	2.24		
LDA-3d	2.04	n/x	1.26	1.44	2.19	2.24		
PBE	1.76	n/x	1.18	1.34	2.25	2.22		
PBE-3d	n/c	-	n/c	n/c	-			

Table 9. Defect levels for the gallium antisite, in eV, referenced to the VBE:  $aGa = Ga_P$

Context	Neutral formation energy	Defect level (eV), cf. VBE						
		(4+/3+)	(3+/2+)	(2+/1+)	(1+/0)	(0/1-)	(1-/2-)	(2-/3-)
LDA	3.88	-0.01	0.19	0.54	0.71	1.12	1.37	n/x
LDA-3d	3.52	0.01	0.20	0.58	0.74	1.11	1.34	n/x
PBE	4.09	0.01	0.18	0.51	0.68	1.10	1.34	n/x
PBE-3d	n/c	n/c	n/c	n/c	n/c	n/c	n/c	-

Table 10. Defect levels for the di-antisite, in eV, referenced to the VBE:  $aa = \text{Ga}_P - \text{P}_{\text{Ga}}$

$aa$ ( $C_{3v}$ ) Context	Neutral formation energy	Defect levels (eV), cf. VBE						
		(4+/3+)	(3+/2+)	(2+/1+)	(1+/0)	(0/1-)	(1-/2-)	(2-/3-)
LDA	2.94	0.06	0.21	0.50	0.73	2.05	2.13	n/x
LDA-3d	2.66	0.12	0.26	0.52	0.73	2.04	2.12	n/x
PBE	3.03	0.02	0.19	0.48	0.72	1.99	2.04	n/x
PBE-3d	n/c	-	-	-	-	-	-	-

Table 11. Defect levels for the gallium interstitial, in eV, referenced to the VBE:  $i\text{Ga} = \text{Ga}_i$

$\text{Ga}_i$ Context	Neutral formation energy	Defect levels (eV), cf. VBE						
		(3+/2+)	(2+/1+) <sup>(a)</sup> ( $T_{i,\text{Ga}}[+]$ )	(1+/0) <sup>(a)</sup> ( $T_{i,\text{Ga}}[+]$ )	(0/1-)	(3+/2+)	(2+/1+) <sup>(b)</sup> ( $T_{i,\text{P}}[+]$ )	(1+/0) <sup>(b)</sup> ( $T_{i,\text{P}}[+]$ )
LDA	4.92	0.49	0.64	2.37	1.68	0.49	0.78	2.23
LDA-3d	4.87	0.39	0.61	2.37	1.64	0.39	0.66	2.32
PBE	5.13	0.51	0.69	2.36	1.68	0.51	0.77	2.29
PBE-3d	n/c	n/c	n/c	n/c	n/c	n/c	n/c	n/c

(a) Thermodynamic levels traversing charge state ground states:  $T_{i,\text{Ga}}(1+) - T_{i,\text{P}}(2+) - T_{i,\text{P}}(3+)$ .

(b) Levels of the  $\text{Ga}_i$  trapped in the  $T_{i,\text{P}}$  site (i.e., excluded from  $T_{i,\text{Ga}}(1+)$  ground state).

Table 12. Defect levels for the phosphorus interstitial, in eV, referenced to the VBE:  
 $i\text{P} = \text{P}_i$

$\text{P}_i$ Context	Neutral formation energy	Defect levels (eV), cf. VBE						
		(3+/2+)	(2+/1+)	(1+/0)	(0/1-)	(1-/2-)	(2-/3-)	(3-/4-)
LDA	3.83	0.61	0.00	1.50	1.27	n/x		
LDA-3d	3.11	0.63	0.06	1.47	1.27	n/x		
PBE	3.72	0.61	-0.12	1.53	1.26	n/x		
PBE-3d	n/c	n/c	n/c	n/c	n/c	-		

### 2.3. Defect formation energies

The ground state defect formation energies, as a function of charge state are trivially obtained by simple arithmetic from the neutral formation energies and the computed defect charge transition energy levels in the previous section. The defect formation energies in these Tables are presented in the phosphorus-rich (A7-structure) limit. The formation energies of the charged defects are presented with the Fermi level at the VBE. The Tables present the formation energies of all the simple intrinsic defects, segregated by simulation context.

The gallium interstitial quotes two formation energies for the (1+) charge, the first is the ground state of the (1+) in the non-bond tetrahedral interstitial site with Ga nearest neighbors:  $T_{i,Ga}$ . The  $T_{i,P}$  has charge states from (1+) through (3+), and is the ground state for the (2+) and (3+), and therefore its formation energy is also quoted.

**Table 13. Formation energies of GaP defects at VBE, in eV, context = LDA.**

Charge state	vGa	vP	vv	aP	aGa	aa	iGa $T_{i,Ga}; T_{i,P}$	iP
(4-)	-	-	11.66	-	-	-	-	-
(3-)	7.02	9.06	9.34	-	-	-	-	-
(2-)	5.69	7.16	7.12	6.45	6.37	7.12	-	-
(1-)	4.62	4.93	6.09	4.22	5.00	4.99	6.60	5.10
(0)	<b>3.63</b>	<b>3.76</b>	<b>4.99</b>	<b>2.02</b>	<b>3.88</b>	<b>2.94</b>	<b>4.92</b>	<b>3.83</b>
(1+)	2.09	2.25	4.32	0.58	3.17	2.21	2.56;2.69	2.33
(2+)	1.73	2.10	3.89	-0.67	2.63	1.71	1.92	2.33
(3+)	0.97	1.62	-	-	2.44	1.49	1.43	1.73
(4+)	-	-	-	-	2.45	1.43	-	-

**Table 14. Formation energies of GaP defects at VBE, in eV, context = LDA-3d.**

Charge state	vGa	vP	vv	aP	aGa	aa	iGa $T_{i,Ga}; T_{i,P}$	iP
(4-)	-	-	11.36	-	-	-	-	-
(3-)	6.88	8.72	9.13	-	-	-	-	-
(2-)	5.57	6.91	6.99	6.47	5.97	6.82	-	-
(1-)	4.50	4.76	5.97	4.23	4.63	4.70	6.51	5.08
(0)	<b>3.53</b>	<b>3.64</b>	<b>4.86</b>	<b>2.04</b>	<b>3.52</b>	<b>2.66</b>	<b>4.87</b>	<b>3.81</b>
(1+)	2.04	2.19	4.21	0.60	2.78	1.93	2.50;2.55	2.34
(2+)	1.69	2.04	3.75	-0.65	2.21	1.41	1.89	2.29
(3+)	0.94	1.53	-	-	2.00	1.15	1.50	1.66
(4+)	-	-	-	-	1.99	1.03	-	-

Table 15. Formation energies of GaP defects at VBE, in eV, context = PBE.

Charge state	vGa	vP	vv	aP	aGa	aa	iGa $T_{i,Ga}; T_{i,P}$	iP
(4-)	-	-	11.31	-	-	-	-	-
(3-)	6.72	8.97	9.04	-	-	-	-	-
(2-)	5.44	7.15	6.84	6.23	6.54	7.06	-	-
(1-)	4.44	4.96	5.85	4.01	5.19	5.02	6.81	4.98
<b>(0)</b>	<b>3.48</b>	<b>3.76</b>	<b>4.45</b>	<b>1.76</b>	<b>4.09</b>	<b>3.03</b>	<b>5.13</b>	<b>3.72</b>
(1+)	1.91	2.22	3.83	0.42	3.41	2.32	2.77;2.84	2.19
(2+)	1.46	1.94	3.45	-0.76	2.90	1.83	2.08	2.32
(3+)	0.58	1.29	-	-	2.72	1.64	1.57	1.71
(4+)	-	-	-	-	2.71	1.62	-	-

## 2.4. Defect migration energies

Only two intrinsic defects are potentially mobile: the  $\text{Ga}_i$  and  $\text{P}_i$ . All other defects will be immobile at room or operating temperature (certainly for the time scales of interest for radiation damage). In addition to potential thermal diffusion, the  $\text{P}_i$  is predicted to exhibit athermal diffusion [18] (via carrier-driven Bourgoin-Corbett diffusion [19]) in  $p$ -type GaP, and potentially recombination-enhanced diffusion in  $n$ -type GaP.

### 2.4.1. Gallium interstitial – thermal diffusion

For the Ga interstitial in GaP, the DFT calculations find thermodynamically stable states for the same (1+), (2+), and (3+) charge states seen for the Ga interstitial in GaAs, and additionally (0) and (1-) charges states in the split-(110)<sub>Al</sub> interstitial now are stable defects in the gap. The positive interstitials strongly favor non-bonded tetrahedral interstitial positions over all other structures, and both  $T(0)$  defects are deeply embedded in the conduction band.

The gallium interstitial can potentially migrate thermally in  $p$ -type GaP, through either the hexagonal site (via a  $T_{i,P}-H-T_{i,Ga}-H-T_{i,P}$  path) or through a split-(110)<sub>Ga</sub> site (via a kick-out mechanism). The barriers through both sites are comparable to each other, and somewhat higher than the barriers in GaAs. The  $\sim 1$  eV barriers in  $p$ -type suggest perhaps limited thermal mobility in GaP. The  $n$ -type diffusion was not characterized, but with the non-bonded interstitial sites not available for migration the neutral or negatively charged Ga interstitial (high in the conduction band), thermal diffusion is probably very slow in  $n$ -type.

**Table 16. Diffusion barriers (thermal) for the gallium interstitial, in eV.**

Pathway:	Hexagonal site ( $H$ )			Split-(110) <sub>Ga</sub> site		
	$\text{Ga}_i(1+)$	$\text{Ga}_i(2+)$	$\text{Ga}_i(3+)$	$\text{Ga}_i(1+)$	$\text{Ga}_i(2+)$	$\text{Ga}_i(3+)$
<b>Context</b>						
<b>LDA</b>	1.24	0.96	0.87	0.98	1.04	1.23
<b>LDA-3d</b>	1.20	0.96	0.80	0.99	1.04	1.13
<b>PBE</b>	1.15	0.93	0.90	0.94	1.03	1.19
<b>PBE-3d</b>	n/c	n/c	n/c	n/c	n/c	n/c

### 2.4.2. Phosphorus interstitial – thermal diffusion

Migration paths and barriers for the P interstitial were only obtained for  $p$ -type GaP, an incidental byproduct of a comprehensive search for ground state structures. The thermal barrier for migration for the  $\text{P}_i(3+)$  migration is likely 0.5-0.6 eV via a non-bonded  $T_{i,P}-H-T_{i,Ga}$  pathway, the hexagonal ( $H$ ) site being the saddle point between the lower-energy  $T$  sites. The thermal barrier for  $\text{P}_i(2+)$  diffusion is less than 0.7-0.8 eV, along the same pathway, except that the  $H$ -site is the ground state, and the  $T$ -sites are the barriers. Evaluating the DFT thermal barrier for migration of the  $\text{P}_i(3+)$  is complicated by  $H$ -site descending (very slightly) into the VBE. The energy of the mixed VBE-defect state at the  $H$ -site slightly underestimates the true barrier that would for a pure defect state. The data in brackets in the following Table indicates energies that are likely slightly ( $<0.1\text{eV}$ ) underestimated, as this is the self-consistent calculation of the

delocalized state embedded in the VBE rather than the localized defect state it is almost degenerate with.

**Table 17. Diffusion barriers (thermal) for the phosphorus interstitial, in eV.**

Context	P <sub>i</sub> (2+) <0.8 eV				P <sub>i</sub> (3+) ~0.6 eV		
	B <sub>g</sub>	T <sub>i,P</sub>	H	T <sub>i,Ga</sub> (barrier)	T <sub>i,P</sub>	H <sup>(a)</sup> (barrier)	T <sub>i,Ga</sub>
LDA	+0.25	+0.40	0	+0.74	0	>[0.52]	0.48
LDA-3d	+0.31	+0.36	0	+0.74	0	>[0.48]	0.58
PBE	+0.23	+0.50	0	+0.81	0	>[0.34]	0.64
PBE-3d	n/c	n/c	n/c	n/c	n/c	n/c	n/c

(a) The values in brackets are approximate; the calculated state is a mixed delocalized-defect state where the defect eigenstate has dipped into the VBE.

### 2.4.3. Athermal and recombination enhanced diffusion: phosphorus interstitial

The phosphorus interstitial will likely diffuse athermally in *p*-type. One obvious Bourgoin-Corbett migration path driven by capture of carriers is:



as the tetrahedral interstitial ground state captures an electron and collapses downhill, without a barrier, to the *H*-site, which, in turn, re-emits the electron, and collapses downhill, without a barrier back into a *T* site. There are further paths that capture yet more electrons and then insert into the lattice, and then re-emerge into different *T*-site upon re-emitting their electrons. The relatively flat landscape and multiple bistabilities and changes in structure for the (1-), (0), and (1+) charge states further suggest that recombination enhanced diffusion is likely among these charge states of the phosphorus interstitial.

### 3. CONCLUSIONS

The parameters needed to describe the defect properties of simple intrinsic defects in GaP are tabulated.

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