

Modeling neutral defects in III-V ternary alloys with a special quasirandom structure: Analysis of As- and III-site point defects in InGaAs

Peter A. Schultz ^{*}

Sandia National Laboratories, Albuquerque, New Mexico 87185-1322, USA



(Received 23 June 2025; revised 25 August 2025; accepted 2 September 2025; published 22 September 2025)

While first-principles density functional theory modeling has become a vital tool to investigate defect properties in semiconductors, the lack of crystalline periodicity in pseudobinary random composition alloys, such as $\text{In}_{1-x}\text{Ga}_x\text{As}$, complicates such analyses. We present a simulation strategy to systematically take into account the variability in the local defect environment in order to predict statistical properties of neutral intrinsic defects in $\text{In}_{1-x}\text{Ga}_x\text{As}$. We use a comprehensive sampling from a modest-sized 64-atom special quasirandom structure (SQS) to define a statistically representative set of defects, and use a 512-atom hypercell, a $2 \times 2 \times 2$ supercell of SQS supercells, to achieve cell-size convergence. We articulate an equivalent site principle and describe how it constrains atomic chemical reference energies in computation of defect formation energies in pseudobinary alloys. A simple protocol for estimating reference energies for the Ga and In atoms sharing the III site succeeds in obtaining the equivalence of defects at Ga-sites and In sites in the SQS supercell, (<30 meV differences in average formation energies). For III-site defects, such as the As antisite As_{III} , the statistical variability in formation energies is modest, $\approx 0.1\text{--}0.2$ eV. The variability in formation energy at As-site defects, such as the As vacancy v_{As} , can be much larger, >1 eV. The As antisite is shown to be a low-energy defect and the most likely to be present in as-grown materials, just as in GaAs. All other defects are higher-energy defects unlikely to be important in native material, but potentially important in radiation-damaged material. With a strong variability in defect energies, especially on the As-site, explicit consideration of statistical variability due to compositional randomness will be imperative for meaningful and quantitative comparisons to experiment.

DOI: [10.1103/7lsb-t719](https://doi.org/10.1103/7lsb-t719)

I. INTRODUCTION

Defect behavior in III-V semiconductors is important for understanding the performance of as-grown materials but is particularly crucial for the response of III-V based devices subjected to radiation-induced displacement damage. $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, commonly referred to as InGaAs, is a promising pseudobinary III-V material for electronics (because of its increased electron mobility) and sensors (because of its sensitivity to crucial infrared wavelengths) in space applications. Displacement damage—point defects formed after atoms are knocked out of their lattice sites by incident radiation—has been implicated as responsible for “dark current” and degradation of InGaAs-based devices in radiation environments [1–5], but very little is definitively known about as-grown or radiation-induced atomic-scale defects in InGaAs. In this paper I describe a first-principles-based approach to model defects in a pseudobinary alloy such as $\text{In}_{1-x}\text{Ga}_x\text{As}$ that takes full account of the statistical nature of defect properties

within a random local chemical environment and apply it to simple neutral defects in InGaAs.

First-principles investigations of point defects using density functional theory can probe where experiments are often blind and offer more confident identification and characterization of technologically important defects where experiments alone are inconclusive. The unambiguous identification of the *EL2* in GaAs as the arsenic antisite, As_{Ga} (arsenic substitutional, replacing a gallium atom in the lattice), was guided by theory [6,7]. The reassignment of prominent GaAs radiation centers *E1-E2* and *E3* [8] to the divacancy vv and As vacancy v_{As} , respectively, was accomplished through theory only recently, after careful reanalysis founded upon quantitative predictions of GaAs defect levels [9,10] reconciled a number of seemingly contradictory experimental observations. The use of density functional theory (DFT) within supercell approximations on ever more powerful computer platforms has made first principles modeling an invaluable component of defect physics studies in Si and binary semiconductors.

Understanding of defects and their behavior in technologically important ternary alloys such as InGaAs lags far behind that in binary III-V semiconductors. With the identification and characterization of simple primary defects (initial knock-out defects: vacancies and interstitials) in the end-member binary GaAs still evolving—and almost nonexistent in the end-member InAs—after decades of study, it is no surprise that the understanding of defects in the pseudobinary InGaAs bridging between GaAs and InAs remains in

^{*}Contact author: paschul.xnl@gmail.com

its infancy. Random occupation of In and Ga on the III site in InGaAs complicates defect identification and characterization. A defect of a given type, e.g., a vacancy, will not have a single discrete energy as it will in a crystalline binary. Defect formation energies and defect energy levels (electronic charge transitions—trap levels—within the band gap) will vary depending upon the compositional variations in the local chemical environment surrounding any defect site. Defect diffusion behavior, e.g., of interstitials, expresses new spatial and temporal complexities [11] not encountered in crystalline GaAs. The nature and magnitude of that variability is an intrinsic, unavoidable, and a crucial aspect of characterizing defect behavior in ternary semiconductors. In the face of this complexity, there is a clear need for computational modeling to accompany experiment to help understand defect behavior in InGaAs.

First-principles DFT computational studies of defects in InGaAs are relatively few, inconclusive, and generally examine anecdotal examples rather than embrace the full statistical variability of defects in InGaAs. The early studies of Bonapasta and Giannozzi [12] examined a single Ga vacancy and a single As vacancy, and both a Ga and an As antisite defect selected from a 64-atom supercell with cation III sites randomly (and equally) populated with Ga atoms and In atoms, using the local density approximation (LDA). Komsa and Pasquarello [13], again with a small 64-atom supercell with random Ga and In site occupations, used hybrid functionals to present gap levels for also only one example of each of these simple defects. Murphy *et al.* [14], using a generalized gradient approximation [15], instead did a sampling of sites from random 64-site InGaAs supercells to describe the statistical variability of a defect formation energy, but only for the neutral As vacancy v_{As} . Small supercells with only 64 atoms can be unreliable; they predict the structure of the silicon self-vacancy incorrectly and have been shown to be inadequate even to resolve elastic interactions between defects [16]. Larger computational models are needed to reduce finite-size effects, due to spurious defect-defect interactions. A more recent DFT study from Vedel *et al.* [17] examined a wider selection of defects and charge states in larger random supercells up to 432 atoms, reducing size-effect errors, but again probed defects at only a few select sites in these larger supercells. Using statistical sampling of defect sites within a larger random-composition 216-site InGaAs supercell, Lee *et al.* [11] performed a detailed study of As interstitials (As_i) in InGaAs, toward understanding diffusivity of As_i in InGaAs.

Following the early example of Lee and Chang [18], some recent defect modeling studies in InGaAs ignored the compositional variability to examine defects in an ordered InGaAs crystal structure as a proxy for defects in the random lattice [19–22]. This expedience of using an ordered CuAu-I structure to examine defects in InGaAs was rationalized using evidence of long-range order in as-grown InGaAs [19,20]. Kulish *et al.* asserted that the effects of randomness were small [21,22]. As cautionary counterexamples, however, Murphy *et al.* [14] presented results showing ≈ 1 eV variations—not small—in the v_{As} formation energy obtained from sampling a random-composition model. Lee *et al.* [11] described a similar variability in As_i formation energies, with profound consequences for As_i

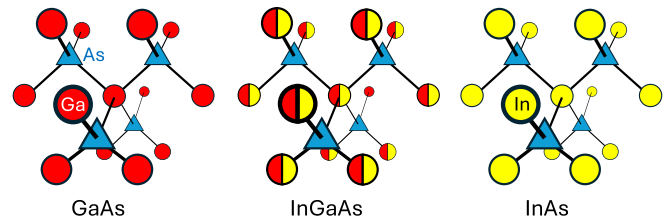


FIG. 1. A schematic depiction of the local chemical structure of GaAs, InGaAs, and InAs.

diffusion, leading to markedly different behavior in InGaAs than in crystalline GaAs.

In this article, I present a first-principles analysis of vacancy and antisite defects on both the As and III sites in $In_{0.5}Ga_{0.5}As$ using a generalized gradient approximation [15] to DFT. The statistical variability in the neutral defect formation energies in the random alloy is explored through a comprehensive sampling of candidate defects sites within a 64-atom special quasirandom structure (SQS) [23], a supercell conformal to a $2 \times 2 \times 2$ supercell of the conventional 8-atom cubic unit cell of the zinc blende lattice. Use of an SQS (or otherwise random composition) supercell model to calculate defect formation energies places new constraints on the specification of atomic chemical potentials for the Ga and In cations. A means to specify those atomic energies in $In_{0.5}Ga_{0.5}As$ is proposed that yields a consistent description of III-site defects regardless of whether a Ga or an In atom occupied the original site in the SQS supercell. Finite-size effects and convergence to asymptotically dilute defects are assessed through use of a 512-atom “hypercell”: a $2 \times 2 \times 2$ supercell of this 64-atom SQS supercell. This 512-site hypercell, conformal to a $4 \times 4 \times 4$ conventional cubic zinc blende lattice, is large enough to reliably quantify defect energies in the dilute bulk limit, with comprehensive defect statistics obtained sampling from the subset of unique sites defined by the 64-atom SQS primitive subcell. Characterization of charged defects and defect levels will be considered separately in a future study, where challenges—and controversies—of accurately accounting for charge in supercells and the band-gap problem are distinct issues, and where the focus will shift to reaching for constructive coordination with experiment to decipher the defect physics in InGaAs.

II. CONCEPTUAL CHALLENGES TO MODELING PSEUDOBINARY ALLOYS

The III-V semiconductors GaAs and InAs adopt a zinc blende structure in their ground states, composed of interpenetrating fcc lattice of As atoms and fcc lattice of Ga or In atoms to form a lattice where each atom is coordinated with four atoms of the other type in a perfect tetrahedron, as illustrated in Fig. 1. An $In_{1-x}Ga_xAs$ random alloy adopts the same zinc blende chemical structure, where the III site is randomly occupied by either a Ga atom or an In atom. Every III site (In or Ga) in InGaAs remains surrounded by four As atoms in an approximate tetrahedral orientation, as in the binary end-members GaAs ($x = 1$) and InAs ($x = 0$). The four III sites around each As atoms are occupied by either four Ga atoms and zero In atoms (4:0), three Ga and one In atoms

(3:1), two Ga and two In (2:2), (1:3), and (0:4). The tetrahedral space-group symmetry of the lattice is lost, but InGaAs retains the macroscopic cubic structure of the end-member binaries.

InGaAs can be grown with different proportions of In and Ga [24]. The specific composition given by $x = 0.47$ (more precisely [25,26], $x = 0.468$), $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, is technologically useful because it makes a perfect lattice match with the InP used as a substrate. With the lattice-matching Ga-In composition split nearly evenly, DFT studies of defects (see above) typically use an even 50-50 mix in their modeling for convenience and clarity. This evenly balanced composition is adopted here as well, for simplicity and to facilitate direct comparisons to previous results. Ultimately, a 3% departure in composition from experiment will not lead to meaningful differences in the defect analyses.

In the binary GaAs (or InAs), there is but a single unique defect site for each defect such as v_{As} , all other sites are equivalent by translational symmetry of the crystalline lattice. In InGaAs, there is no translational symmetry. Every atomic site has a different chemical environment determined by the random occupations of Ga and In on the III sites around it, e.g., every v_{As} will be different depending on the occupation of the four III sites around it (to lowest order) and the occupations of more distant III sites. How much do different defect properties vary as a function of the local chemical environment? What aspects of the local chemical environment are these defects properties sensitive to? How to describe that statistical variability in the defects to meaningfully and usefully compare with experiment? This variability can be significant [11,14]. In the following I describe the design of the modeling approach employed to tackle modeling of defects in InGaAs.

A. Accuracy and uncertainties in density functional theory

A crucial consideration in designing any modeling study is a diligent, quantitative understanding of the accuracies and uncertainties in the methods being used. The uncertainties (quantified description of errors) are dependent upon both physical and numerical accuracy. The physical accuracy is limited principally by the accuracy of the density functional approximation. The numerical precision is limited by the implementation of the computational models. In previous studies of defects in Si [27,28], GaAs [9], and 3d-doped GaN [29], comprehensive comparisons to experimental data revealed an average accuracy of 0.1 eV (with maximum variances of 0.2 eV). Hence for InGaAs, 0.1–0.2 eV is the expected limit of physical accuracy due to the DFT approximation alone. The development of the approach described below is informed by these accuracy expectations.

B. Special quasirandom structures for statistical sampling

To generate a representative sample of candidate defect site environments in compositionally random InGaAs, I use a 64-atom cubic zinc blende cell, conformal with a $2 \times 2 \times 2$ replication of the conventional 8-atom cubic supercell, where the occupancies of Ga and In on the fcc III-sublattice are specified by an SQS. This SQS supercell offers 32 chemically unique As sites on the V sublattice, and 16 chemically unique Ga and In sites (each) on the III sublattice. In the following, I

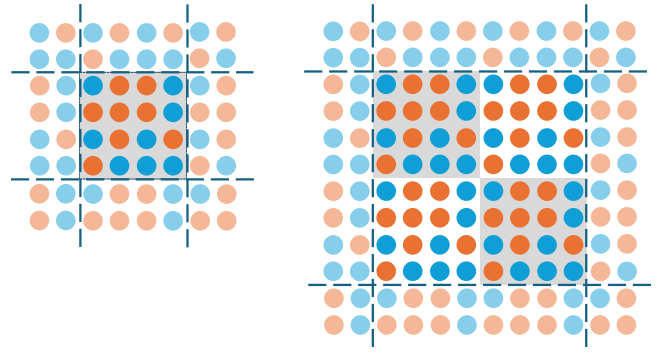


FIG. 2. An idealized representation of the hypercell concept in two-dimensions; a 2×2 supercell of a base supercell.

comprehensively sample each defect type from every unique site in the SQS supercell and use the collective results from this sampling to analyze the statistical nature of each defect.

A sampling from an SQS supercell with this few sites proves sufficient to numerically resolve the statistical variability that is meaningful within the physical uncertainties of the DFT, and offers a sufficient coverage of the interesting local environments that are physically important for the defects. I note a crucial distinction between using this SQS as a template for generating candidate defect sites, from using this SQS as an accurate model of the undefected material. The latter would depend on this SQS supercell being representative of bulk InGaAs, which might not be as random as the SQS and might depend on processing conditions (it is plausible to believe certain growth methods might favor some ordering or closer local balance between In and Ga). Use of this SQS supercell is meant only to obtain defect properties correlated with local environments and is not meant to predict the overall macroscopic structure of the material.

C. Hypercells for size scaling

A 64-atom SQS supercell might be sufficient to yield a representative statistical sample of local defect environments but will be inadequate to eliminate or assess finite-size errors. In GaAs, we had determined that at least a $3 \times 3 \times 3$ 216-atom supercell was needed for semiquantitative accuracy [9,28], while for InAs defects, it proves necessary to expand to even larger models, to $5 \times 5 \times 5$ 1000-atom supercells, to fully resolve localized defects from the delocalized band edges in that narrow-gap semiconductor [30]. $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ has a band gap (0.81 eV [25,26,31]) intermediate between GaAs (1.52 eV) and InAs (0.42 eV), indicating that an intermediate $4 \times 4 \times 4$ 512-atom supercell is likely needed for accurate defect calculations in InGaAs.

A comprehensive sampling of all defect sites within a fully random larger 216- or 512-atom supercell is computationally impractical. Moreover, sampling from just a single supercell size, of whatever size, finite-size errors cannot be precluded nor rigorously assessed. Conveniently, a $2 \times 2 \times 2$ supercell of the 64-atom SQS supercell—a hypercell—produces a 512-atom supercell conformal with a conventional $4 \times 4 \times 4$ supercell of the desired larger size. The hypercell concept is illustrated in Fig. 2.

The chemical environment for each site in the 64-atom SQS supercell is exactly identical to the chemical environment in the larger 512-atom hypercell through translational symmetry between the different SQS subcells. A comprehensive sampling of defects on the 64 unique sites (corresponding to sites in the SQS subcell) in this 512-atom hypercell is computationally practical. Thus, a direct assessment of finite-size errors can be computed for a defect in the same chemical environment in the 64-site supercell and the 512-site hypercell. Moreover, this hypercell approach has the computational benefit that the relaxed atomic configuration of a defect in the smaller 64-atom supercell can be used to construct a partially converged starting configuration in the large cell, accelerating its structural energy optimization. This strategy is commonly used in supercell size sequences of defects in crystalline semiconductors, e.g., GaAs from 64- to 216-site supercells and from 216- to 512-atom supercell, to accelerate structural relaxations in the larger, more computationally expensive cells.

D. Equivalent site principle for defining atomic reference-state energies

The formation energy Ω_D of a neutral defect D is conventionally defined with respect to atomic reference state energies described as chemical potentials μ_i :

$$\Omega_D = E_D - \sum_i n_i \mu_i, \quad (1)$$

where E_D is the computed total energy of the defect supercell and the n_i are the number of each atom type i in the calculation. This leaves aside net charge and its associated ambiguities of defining a Fermi energy ϵ_F and supercell correction terms. As noted by Van Vechten [32], observing that physicists historically had used isolated neutral atoms as their reference, obtaining a cohesive energy, and chemists used elemental standard states, thus obtaining heats of formation: the choice of reference state is, in principle, arbitrary, any consistent choice might do. The choice should be made on the basis of accuracy and simplicity of the calculations and clarity of presentation.

Exploiting this flexibility, Zhang and Northrup (ZN) [33] introduced a particularly useful and popular convention based upon equilibrium constraints. The primary constraint is that the sum of chemical potentials of the components of the perfect bulk system equals the energy of the combined bulk system, such that the formation energy Ω_{bulk} , the reference supercell for the defect calculations, is zero. Applying this to InGaAs, this constraint is expressed in Eq. (2):

$$\mu_{\text{In}_{1-x}\text{Ga}_x\text{As}} = (1-x)\mu_{\text{In}}^x + (x)\mu_{\text{Ga}}^x + \mu_{\text{As}}. \quad (2)$$

The subordinate constraint is that the chemical potentials of the constituents are bounded by thermodynamic limits. In the In-Ga-As chemistry, these are typically taken as the elemental standard states: for an As-rich convention the μ_{As} is set to the energy per atom in the A7 bulk As crystal structure, while for the III atoms, a Ga-rich convention will use the Ga energy in its A11 ground-state structure for μ_{Ga} and an In-rich convention its energy in its ground state body centered tetragonal structure for μ_{In} . In the GaAs or InAs binary end members, choosing one of these fully determines all atomic chemical

potentials. The As-rich convention ($\mu_{\text{As}} = \mu_{\text{As}}^{\text{A7}}$) is most commonly adopted—and most useful: bulk As precipitates are a competing phase in synthesis—such that

$$\begin{aligned} \text{GaAs: } \mu_{\text{Ga}}^{\text{GaAs}} &= \mu_{\text{GaAs}} - \mu_{\text{As}}^{\text{A7}}, \\ \text{InAs: } \mu_{\text{In}}^{\text{InAs}} &= \mu_{\text{InAs}} - \mu_{\text{As}}^{\text{A7}}, \end{aligned} \quad (3)$$

but it is also common practice also to quote formation energies—redundantly, and less usefully—in the III-rich limit. Redundantly, in that the As- and III-rich limits are trivially related through the bulk formation energy of the III-V from its elemental components [33], and unusefully, because neither bulk Ga nor bulk In are realistic competing thermodynamic phases in the growth. Indeed, growing bulk Ga is a significant technical challenge (even leaving aside that Ga is liquid at room temperature) [34].

For the ternary InGaAs, selecting the As-rich convention leaves an ambiguity for the definition of the In and Ga chemical reference energies in Eq. (2). This ambiguity is moot if the III-particle numbers are unchanged in the defect, as in removing an As atom in the calculations of v_{As} reported by Murphy *et al.* [14]. Vedel *et al.* [17] examined defects involving both As site and III sites but focused on charge transition energies rather than reporting meaningful absolute defect formation energies—they used elemental standard states for the chemical reference of all the atoms. Kulish *et al.* [21] fit As, Ga, and In atomic reference energies to a variety of $\text{In}_x\text{Ga}_y\text{As}_z$ alloy formation energies, claiming an accuracy of $O(0.1 \text{ eV})$ —estimates insufficient to satisfy accuracy requirements for use in defect formation energies here. The ambiguity in atomic reference energies for InGaAs is not resolved satisfactorily nor consistently in this literature; every study has adopted a different approach.

Resolution of this ambiguity follows from observing that InGaAs is not just a ternary compound, it is a true pseudobinary, with a III-lattice site that has a fully random occupation of either Ga or In. For the infinite bulk system (and in the limit of large supercell models), a missing atom on the III site is agnostic about whether a Ga or an In atom is missing from the lattice, as illustrated in Fig. 3. The chemical environment about every III site is statistically equivalent to every other III site. The missing atom could be, in principle, either an indium atom or a gallium atom, in proportion to the mixing parameter x . Using this equivalent site principle (ESP), the formation energy of an atom removed, or replaced, from a III site (a vacancy, or an As antisite) should be independent of supercell site. This provides the additional constraint to disambiguate the relative In and Ga chemical potentials in the SQS basis supercell. In the limit of large supercells, the In and Ga vacancies (or As antisites on either Ga or In sites) in SQS hypercell models should yield the same formation energy, on average.

A simple chemical insight provides a workable and sufficiently accurate estimate for the relative In and Ga chemical potentials. The In and Ga atoms in InGaAs have four nearest-neighbor As atoms, just as in their end-member binary alloys InAs and GaAs. Operating in the As-rich limit defined by Eq. (3), the heat of formation of InGaAs from InAs and GaAs can be written

$$\Delta H_f^x = E(\text{In}_{1-x}\text{Ga}_x\text{As}) - [(1-x)E(\text{InAs}) + (x)E(\text{GaAs})], \quad (4)$$

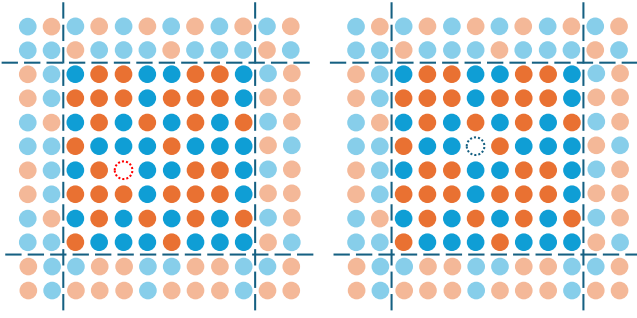


FIG. 3. Illustration of the equivalent site principle applied to a lattice defect in a pseudobinary lattice. An empty site in a random lattice (pseudobinary) is agnostic concerning what type of atom is missing. Note that the two vacancy configurations could be generated from the same base supercell, but removed atom of one type on one side and an atom of a different type on the other. In the limit of large supercells, a supercell calculation should similarly be agnostic about which type is removed, so that the formation energy of the vacant site should be the same, statistically averaged, regardless of the identity of the atom in the undefected supercell.

which can be recast in terms of atomic reference potentials [using Eq. (3)] as

$$\Delta H_f^x = (1-x)[\mu_{\text{In}}^x - \mu_{\text{In}}^{\text{InAs}}] + (x)[\mu_{\text{Ga}}^x - \mu_{\text{Ga}}^{\text{GaAs}}], \quad (5)$$

where the heat of formation for InGaAs is expressed in terms of the In and Ga atomic reference energies. Because Ga and In are isoelectronic in chemically identical environments and not directly bonded to each other, the energy of mixing should be dominated by III-As bond strains around the atoms caused by the change in lattice constant in going to InGaAs from either InAs or GaAs. For the 50-50 alloy, that strain energy will be approximately the same for the Ga and In atoms in the lattice, so that to obtain the primary equilibrium condition in Eq. (2), the heat of formation should be evenly shared between the In and the Ga atoms, defining:

$$\begin{aligned} \mu_{\text{In}}^{\text{InGaAs}} &= \mu_{\text{In}}^{0.5} = \mu_{\text{In}}^{\text{InAs}} + \Delta H_f^{0.5}, \\ \mu_{\text{Ga}}^{\text{InGaAs}} &= \mu_{\text{Ga}}^{0.5} = \mu_{\text{Ga}}^{\text{GaAs}} + \Delta H_f^{0.5}. \end{aligned} \quad (6)$$

The $\mu_{\text{Ga}}^{\text{InGaAs}}$ and $\mu_{\text{In}}^{\text{InGaAs}}$ are not arbitrary, instead, their relative values are determined by the ESP and require only the formation energies of the bulk alloys. This hypothesis will be tested and assessed in the following.

For the specific 50-50 alloy investigated in this paper, this simple equipartition of the formation energy is straightforward and shown to be sufficiently accurate. For general nonequal compositions x , this partition is less straightforward. In the limit of small x , the removal of the atom from a supercell model will resemble a vacancy in the majority end member binary, whether the atom removed in the hypercell was originally either the dominant or minority atom. This mandates the partition of the heat of the formation into the atomic chemical potentials must be skewed toward the minority specie. A III atom from the lattice has a $(1-x)$ likelihood to be a majority atom and an x likelihood to be a minority atom. A plausible approach to satisfy this small- x limit and the equipartition limit in Eq. (3) is to partition the heat of formation to each species using that ratio: $(1-x)\Delta H_f^x$ to the

minority species energy and $(x)\Delta H_f^x$ to the majority species energy, and then spread that partition among the (x) minority atoms and among the $(1-x)$ majority atoms:

$$\begin{aligned} \mu_{\text{In}}^x &= \mu_{\text{In}}^{\text{InAs}} + \frac{x}{(1-x)} \Delta H_f^x, \\ \mu_{\text{Ga}}^x &= \mu_{\text{Ga}}^{\text{GaAs}} + \frac{(1-x)}{x} \Delta H_f^x. \end{aligned} \quad (7)$$

This more general hypothesis is not tested herein.

III. COMPUTATIONAL DETAILS

The computational methods follow generally the same approach as described previously for defect calculations in GaAs [9]. The first-principles density functional theory calculations of defects in InGaAs are executed with the SEQQUEST code [35] using pseudopotentials and contracted Gaussian basis sets. The Perdew-Burke-Ernzerhof (PBE) flavor of the generalized gradient approximation [15] is used as the density functional, including spin-polarization where appropriate.

Formulating satisfactory pseudopotentials (PP) for these atoms can be challenging because of the shallowness of the d states, particularly for Ga [36]. All atoms are represented with “large-core,” Hamann-type generalized norm-conserving pseudopotentials [37], generated using the FHI98PP code [38] with custom atomic settings optimized to maximize transferability. We had previously determined that $3d$ -core and $3d$ -valence PP yielded defect results that did not meaningfully differ in GaAs [28]. We use five valence electrons for As and three valence electrons for both Ga and In. Their respective semicore d^{10} shells are treated as core electrons in the pseudopotential, and the nonlinear core density effects on the valence exchange-correlation potentials are included through a partial core correction [39]. A linear combination of atomic orbitals basis is used in the calculations. A double- ζ plus polarization (DZP) contracted Gaussian $2s2p1d$ basis describes the three valence electrons for Ga and In, and five valence electrons for As: two radial degrees of the freedom for the strongly occupied s and p functions, adding a single d function for angular polarization. In vacancy defect calculations, this atomic-centered basis is augmented by a $1s1p1d$ “ghost atom” at vacated sites (single Gaussian functions of 0.12, 0.14, and 0.16/bohr² for the s , p , and d functions, respectively).

Calculations for the 64-atom SQS supercell [23], conformal to a $2 \times 2 \times 2$ supercell of the conventional 8-atom cubic base supercell, uses a regular $3 \times 3 \times 3$ k -grid offset from Γ to sample the Brillouin zone. The 512-atom hypercell uses an offset $2 \times 2 \times 2$ k grid. Tests with a $4^3 k$ -grid in the SQS cell changed As antisite formation energies by $\lesssim 3$ meV from the 3^3 results, below any meaningful resolution of the defect analysis (e.g., far less than the ≈ 30 meV reductions in the antisite formation energy seen in going to the larger 512-atom hypercell). With no spatial symmetries (only time reversal) this leads to 14 and $4k$ points in the irreducible Brillouin zone, respectively. A single lattice parameter (5.964 Å) is optimized for the SQS constrained to a cube. This cubic lattice parameter is held fixed to this equilibrium bulk value in all subsequent defect calculations. A fully unconstrained cell-shape optimization of the SQS supercell shows only

TABLE I. Nearest-neighbor analysis at As sites in SQS.

Near neighbors:	4Ga:0In	3Ga:1In	2Ga:2In	1Ga:3In	0Ga:4In
Number of As sites	2	8	12	8	2

negligible deviations from this ideal cubic shape. The atomic positions are relaxed until the forces on all atoms are less than 0.0002 Ry/bohr (5 meV/Å), sufficient to converge the defect energy to less than 1 meV. This structural optimization uses a modified Broyden method due to Johnson [40] in cases with well-behaved (near-harmonic) potential wells and uses an efficient accelerated steepest descent in less-well-behaved potential wells to negotiate more complicated paths to a minimum-energy structure.

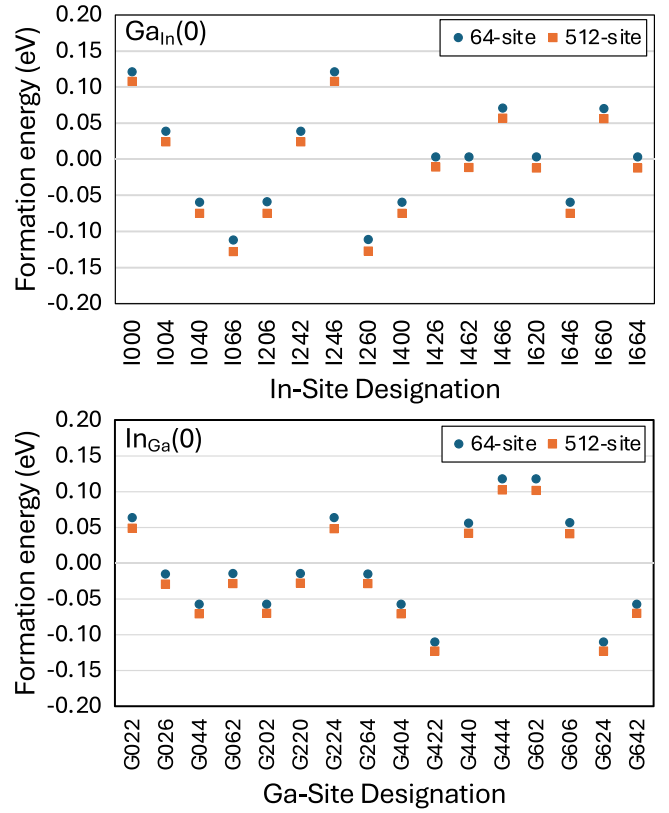
A discrete defect occupation (DDO) [27] is imposed to enforce state occupations consistent with the infinitely dilute defect limit. Correspondingly, the electronic temperature is zero, as the DDO sets defect occupations to integers. In those isolated cases where “sloshing” between (near-)degenerate states or with band-edge states impedes convergence, a small (typically 0.0001 Ry) artificial electronic temperature in a Fermi-Dirac scheme to occupy orbital eigenstates *within* each k point would be used to stabilize the self-consistency, a temperature kept small enough to have negligible effect on the total energy.

I sample defects from a 64-atom SQS structure as the base supercell (tabulated coordinates are in the Supplemental Material [41]). The most impactful and important aspect of the occupation randomness on the III site in the SQS is the number of Ga and In nearest neighbors around each of the 16 As sites. As shown in Table I, this distribution within the SQS exactly matches the 1:4:6:4:1 proportions of an ideal binomial distribution. This is evidence of balanced randomness in the SQS and offers good sampling statistics for each type of site.

The atomic chemical potentials are obtained from the computed thermochemistry of bulk calculations for GaAs, InAs, and the SQS supercell model for InGaAs, as summarized in Table II. The PBE lattice parameters overestimate experiment by $\approx 2\%$. The quoted a_0 for InGaAs, 5.964 Å, is used in all the defect supercell calculations. The PBE computed enthalpy of mixing, $\Delta H_f^{0.5} = 36$ meV/(III-As formula unit), agrees well with previous results (33 meV) [14]. The endothermic energy indicates that the alloy is less stable than the separate binary phases. This $\Delta H_f^{0.5} = 36$ meV completes the

TABLE II. Structural properties of GaAs, $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$, and InAs: lattice constant a_0 , and computed average III–As bond distance (Å), bulk modulus B , heat of formation ΔH /(III-As formula unit) with respect to elemental standard states, calculated (PBE) and experiment (Expt.).

	a_0 (Å)		$\overline{R}_{\text{Ga-As}}$		B (GPa)	ΔH (eV)
	Expt.	PBE	PBE	PBE		
GaAs	5.65	5.739	2.485		59.6	0.787
InGaAs	5.858	5.964	2.514	2.655	49.8	0.601
InAs	6.059	6.187		2.679	47.2	0.487

FIG. 4. Computed formation energy (in eV) for Ga_{In} and In_{Ga} isosite substitutions over unique SQS sites in the 64-site SQS supercell (blue circles) and 512-site hypercell (red squares).

specification of the atomic reference potentials via Eq. (2), used in constructing the defect formation energies reported in this paper. The average Ga–As bond distance in the InGaAs SQS (ranging from 2.47 to 2.55 Å) is stretched by ≈ 0.03 Å from GaAs while the average In–As bond distance (ranging from 2.62 to 2.69 Å) is compressed by a comparable amount from InAs, qualitatively consistent with the hypothesis of roughly equal balance of bond strain between the Ga and In atoms.

IV. RESULTS

A. Isosite substitution

The defect analysis begins with isosite defects, a Ga substituted on an In site or vice versa. Being isoelectronic, cross substitutions of Ga and In are chemically inert and electrically inactive, they induce no changes to the bonding and produce no levels in the band gap, and therefore allow tests of size effects and direct probes of local site energies without complicating factors. The formation energies of the (neutral) Ga_{In} and In_{Ga} isosite substitutions is charted in Fig. 4, and a statistical breakdown is presented in Table III.

The isosite can be used as an indirect probe of the local strain around each site, in how easily a given Ga site can accommodate a larger In atom and vice versa. The formation energies for both the Ga isosite and the In isosite range from -0.1 to $+0.1$ eV, indicating that elastic effects alone yield significant variation of more than 0.2 eV in defect-formation

TABLE III. Statistical analysis of isosite substitutional formation energies, minimum (Min.), maximum (Max.), average (Ave.), and standard deviation (St. Dev.), in meV.

	Min.	Max.	Ave.	St. Dev.
$\text{Ga}_{\text{In}}(0)$				
64 site	-112	+121	+0.9	74
512 site	-128	+108	-13.9	74
Relaxation	13.4	16.1	14.8	0.8
$\text{In}_{\text{Ga}}(0)$				
64 site	-110	+118	-1.9	73
512 site	-122	+102	-15.9	72
Relaxation	12.2	16.2	14.0	1.2

energy. This variability in local environment must be considered in any assessment of defects in InGaAs.

Statistically averaged over all sites (in the 512-atom hypercell), the Ga isosite and In isosite show a small stabilization, ≈ 15 meV, with respect to the unmodified hypercell. This is consistent with a positive (endothermic) mixing energy for InGaAs [14] peaking at $x = 0.50$. Consistent, but not definitive; note that the standard deviation of the isosite formation energy, >70 meV, is much larger than this margin.

The site-resolved results presented in Fig. 4 show how the hypercell approach can be used effectively to assess finite-site errors. The 512-site hypercell results closely follow the 64-site SQS results at each site. The larger 512-site supercell accommodates a small, uniform 12–16 meV of additional relaxation over the smaller 64-site, a cell-size sensitivity much smaller than the statistical variability due to local chemical environment. The Ga isosite has the same cell-size energy lowering—strain relief—as the In isosite, supporting the notion of equipartition of the heat of formation into the chemical potentials for each atoms based upon bond strain.

It is interesting to note that an In isosite substitution in the 50-50 64-site SQS cell creates a $\text{In}_{17}\text{Ga}_{15}\text{As}_{32}$ system, which, coincidentally, has the same composition as the technological relevant alloy, $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$. In principle, a 64-atom SQS cell could be fashioned with this composition to directly model defects in $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$.

B. As antisite As_{III}

The arsenic antisite As_{Ga} —As replacing a Ga atom in the lattice—is a technologically important defect in GaAs. Developing growth strategies to eliminate the midgap *EL2* center, identified as the As_{Ga} [6,7], was crucial to making GaAs a useful electronic material. The As_{Ga} has a low formation energy in GaAs (<1.3 eV using PBE [9]), reduced to near zero in *p*-type material taking into account two donor states, and is easily generated during growth of GaAs. Given the chemical similarity to GaAs, the As antisite is expected to exhibit similar behavior and to be similarly important in InGaAs.

The As antisite in InGaAs is a spin-0 defect, just as in GaAs. Figure 5 shows the *k*-sampling dependence of the neutral As antisite formation over all III sites. With a defect state in the Kohn-Sham band gap (these calculations indicate that the As antisite will be a double donor), this represents a

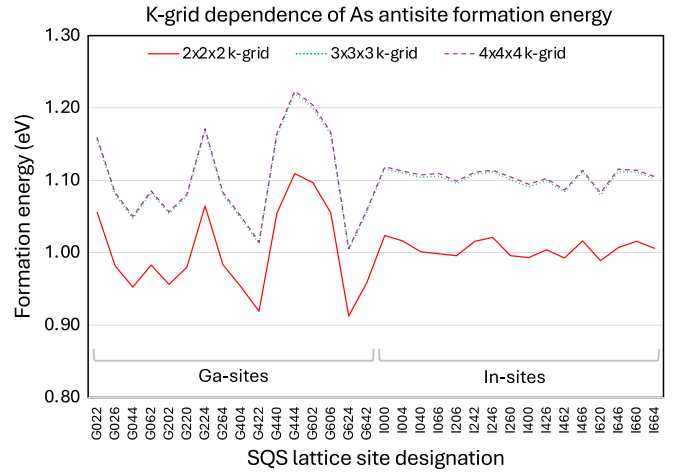


FIG. 5. Formation energy of As_{III} antisite over unique sites in the 64-site SQS, as a function of *k*-point sampling: $(2 \times 2 \times 2)$ *k* grid (red solid line), $(3 \times 3 \times 3)$ *k* grid (green dotted line), $(4 \times 4 \times 4)$ *k* grid (purple dashed line). The $(3 \times 3 \times 3)$ and $(4 \times 4 \times 4)$ almost perfectly overlay each other.

meaningful test of the convergence of the calculations with respect to *k* points. The $(2 \times 2 \times 2)$ *k*-grid results are clearly unconverged, systematically yielding values 0.1 eV too small, while the $(3 \times 3 \times 3)$ *k*-grid results are well converged, within <3 meV of the $(4 \times 4 \times 4)$ *k*-grid results.

For the InGaAs defect calculations, the As antisite can replace either a Ga site or an In site in the SQS model. According to the ESP, this substitution should yield the statistically same result on either site of the SQS, and the computed formation energies of the As antisite in the 512-site hypercell charted in Fig. 6 show this. The formation energy of substitution on the Ga sites exhibits much greater scatter (>0.2 eV, standard deviation = 66 meV), than substitution on the In sites which are confined to narrow range around 1.086 eV (St. Dev. = 11 meV). Notably, the variability in antisite forma-

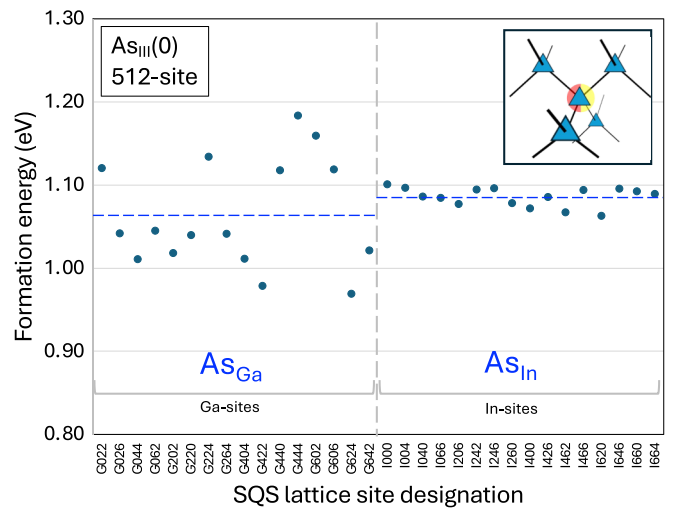
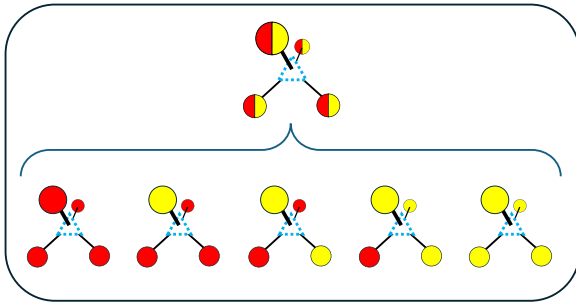


FIG. 6. Computed formation energy (in eV) of the As antisite As_{III} on the 16 unique Ga sites and 16 In sites in the 512-atom hypercell. The average antisite formation energy over the Ga sites is 1.063 eV, over the In sites is 1.086 eV.

FIG. 7. The simple arsenic vacancy v'_{As} in InGaAs.

tion energies over the different Ga sites closely echoes the variability for In isosite formation energies on the same Ga sites as depicted in Fig. 4. This indicates that accommodating bond strain due to a larger atom (As antisite, In isosite) is responsible for this variability. The As antisite roughly mimics in size the In lattice atom it replaces, and hence shows minimal variability in its formation energy.

The low 1.1 eV formation energy of the As antisite in InGaAs, 0.2 eV less than the corresponding antisite in GaAs, suggests that this will be an easily formed defect during InGaAs growth, just as it is in GaAs. With two donor states, the same as the antisite in GaAs, the formation energy will be further reduced (to near zero) in p -type doped InGaAs. The As antisite is likely to be an important defect in InGaAs devices.

C. As vacancy v_{As}

The arsenic vacancy in InGaAs can take five different local chemical structures distinguished by the relative occupations of Ga and In in the four nearest-neighbor III-atom sites, as illustrated in Fig. 7. With five different local chemistries—five cohorts—the As vacancy could be expected to manifest as five different defects.

The computed formation energy of the simple neutral As vacancy $v'_{\text{As}}(0)$ is charted in Fig. 8, resolved over unique SQS sites segregated into cohorts defined by (Ga:In) nearest neighbors. Just as in GaAs [9], the site-shifted v_{As}^* —a III-site nearest-neighbor hopping into the vacated As site—is not stable for the neutral As vacancy in InGaAs. The formation energies range from 1.9 eV (for the two vacancy sites in the SQS with all-In neighbors) to 3.2 eV (for the two vacancy sites with all-Ga neighbors). This wide breadth of formation energies prominently illustrates one major difference between the random alloy and GaAs. This 1.3 eV variability highlights the hazards of using an anecdotal approach to model defects in InGaAs. Sampling a single defect site to model a defect in InGaAs could be significantly in error with respect to the representative defect.

Notwithstanding this expanded range, the formation energy is quite large, in contrast with the As antisite above. Arsenic vacancy populations will be negligible in as-grown InGaAs. While the v_{As} , with its large formation energy, is unlikely to be important for native as-grown material, it is likely to be an important primary displacement damage defect for irradiated InGaAs just as it is for irradiated GaAs. In GaAs, the prominent $E3$ defect center [8] was identified through DFT calculations [9,10] as the v_{As} .

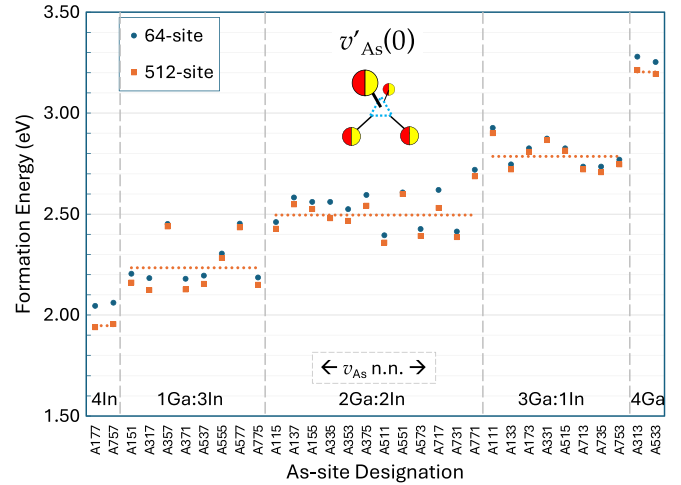


FIG. 8. Computed formation energy (in eV) of the neutral simple As vacancy v'_{As} sorted by numbers of (Ga:In) nearest neighbors, from (0Ga:4In) at the left to (4Ga:0In) at the right. The dotted lines mark the average within the nearest-neighbor-resolved groups (for the 512-site hypercell).

Murphy *et al.* [14] had observed in their calculations that the formation energy of the simple neutral As vacancy v'_{As} exhibited a strong dependence upon the (In:Ga) occupations of the immediate nearest-neighbor III sites, with the formation energy decreasing with increasing number of indium nearest neighbors [14]. This strong dependence is echoed in the current results. The results in Fig. 8 are segregated into cohorts with different (Ga:In) nearest-neighbor ratios, starting from all-In neighbors on the left and incrementally proceeding through to all-Ga neighbors on the right. An unmistakable increase in formation energy can be discerned with increasing number of Ga neighbors vs In neighbors.

The average formation energies within these cohorts are listed in Table IV. With each increased Ga neighbor the average formation energy monotonically increases by >0.25 eV. Despite this large average separation, the neighbor-resolved cohorts are not totally disjoint; the variability within each cohort is large enough to allow some overlap of formation energies of individual sites between cohorts. For a simple measure of this variability, the standard deviation of formation energies within the 12 (2Ga:2In)-site vacancies is large, 0.10 eV. This is the most important cohort, being the most populous cohort in a fully random alloy by a binomial distribution. This plurality of the (2:2), a more homogenous local stoichiometry, is likely further reinforced in any realistic growth process.

As seen in Table IV, the variability in the $v_{\text{As}}(0)$ formation with the local III stoichiometry is dominated by the local chemistry. The increase in formation energy from (4In:0Ga) to (0In:4Ga) in InGaAs parallels the same increase in formation energy for $v_{\text{As}}(0)$ from InAs (4:0) to GaAs (0:4). The larger In atoms are more effective at bonding across the vacancy than the smaller Ga atoms, and it is these bonding interactions that lead to the stratification of formation energies in the different cohorts. The defects in InGaAs take advantage of the compositional randomness and distorted local environments to further lower their energy—the 4-Ga neighbor formation

TABLE IV. Average formation energy (As-rich, in eV) of the neutral simple arsenic vacancy $v'(0)_{\text{As}}$ as a function of cohort defined by the relative number of Ga and In neighbors. Alongside the results for InGaAs, the formation energy of the $v_{\text{As}}(0)$ in the end-member binaries InAs (on the left) and GaAs (on the right) is also presented.

	InAs	InGaAs					GaAs
		(0Ga:4In)	(1Ga:3In)	(2Ga:2In)	(3Ga:1In)	(4Ga:0In)	
E_{form}	2.49 eV	1.95	2.23	2.50	2.79	3.20	3.40 eV

energy in InGaAs is 0.2 eV lower than for the analogous defect in GaAs (3.49 eV), and the 4-In neighbor vacancy in InGaAs is also lower, by 0.5 eV, than its analog in InAs (2.49 eV)—but the dominant trend of increasing formation energy with increasing Ga neighbors is predominantly due to changing local bonding chemistry.

In making these comparisons, it is instructive to note that the $v'_{\text{As}}(0)$ is not thermodynamically stable in the GaAs end-member binary, lying within a negative- U ($1-/1+$) charge transition (between an isotropic $T_d(1+)$ configuration and a Ga-Ga pairing $D_{2d}(1-)$ configuration). In this intermediate neutral charge state, the vacancy induces only a weak D_{2d} distortion itself (and fails to induce that distortion from the ideal T_d in the smaller 64-site supercell due to finite-size effects, i.e., defect-defect electronic interactions). For InGaAs, the random local environments already impose the necessary distortions, so orbital degeneracies—and the associated Jahn-Teller distortions—are avoided.

In the InAs end-member binary, the D_{2d} structure of the $v'_{\text{As}}(0)$ cannot be stabilized. The necessary degeneracy in the partially occupied single-particle (Kohn-Sham) e states cannot be sufficiently split to bring the occupied defect state below the conduction band-edge state. With the lack of symmetry due to the composition disorder in InGaAs, it can be challenging to discriminate a band-edge state from a defect state, even in the larger 512-site hypercell. Nonetheless, there were only a small number of sites in InGaAs where the $v_{\text{As}}(0)$ occupied single-particle state was not cleanly within the Kohn-Sham band gap. The disorder-induced distortions in the bonding brought an occupied vacancy orbital into the Kohn-Sham band gap. The $v_{\text{As}}(0)$ is a valid local state. The compositional disorder appears to enhance localization in defect states, and perhaps reduce the consequences of finite cell errors.

D. Cation vacancy v_{III}

A simple vacancy on the cation site, v'_{III} , whether from removal of a Ga or an In atom from the SQS model, leaves behind a cavity with four As nearest neighbors, as illustrated in Fig. 9. In the neutral vacancy, the missing III atom takes three electrons with it, leaving behind three holes in the As lone pairs (the dangling bonds pointing into the vacancy). In the ideal Ga T_d simple vacancy in GaAs, these holes are distributed into three degenerate p -like combinations of these dangling bonds. By Hund's (first) rule, this should result in a quartet $S = 3/2$ state, and it indeed does prefer a quartet in those GaAs calculations, but is only favored over the doublet $S = 1/2$ in the GaAs $v'_{\text{Ga}}(0)$ calculations in the very largest (1000 atom) supercells. In InGaAs, with compositional

disorder destroying the local site symmetry, and using only 512-site cells, the $v'_{\text{III}}(0)$ calculations all favor the doublet $S = 12$ spin state over the $S = 3/2$.

The computed formation energies of the III-vacancies across all the unique SQS sites are charted in Fig. 10. Focusing first on the simple $v'_{\text{III}}(0)$ formation energies, the 512-site hypercell results closely parallel the 64-site supercell results, with a modest 66 ± 10 meV lowering, $\Delta E(512; 64)$, resulting from expanding the relaxation into the larger supercell. This indicates at least semiquantitative size-convergence in even the small 64-site supercell.

Focusing further upon the 512-site results, the overall average formation energy for $v'_{\text{III}}(0)$ is 2.541 eV. In accordance with the ESP, the average formation energy on sites originally occupied by Ga atoms in the SQS, 2.552 eV, is nearly identical to the average formation energy on sites originally occupied by In atoms, 2.530 eV, considering the site-variability of the formation energy (standard deviation: 100 meV). The vacancies descending from the Ga sites and In sites in the SQS structure are indistinguishable, consistent with the ESP.

The simple onsite structure $v'_{\text{III}}(0)$ proves not to be the ground-state structure of the III-site vacancy, the neutral III vacancy favors the site-shifted $v^*_{\text{III}}(0)$ illustrated in Fig. 9. In GaAs, the site-shift vacancies were crucial for a correct description of both the As and Ga vacancies [9,10,42,43]. For GaAs: $v_{\text{As}}(0)$, the site-shift was entirely unstable [9], and this instability is echoed in the current results for InGaAs. For GaAs: $v_{\text{Ga}}(0)$, the site-shift vacancy $v^*_{\text{Ga}}(0)$ was metastable but the simple vacancy $v'_{\text{Ga}}(0)$ was lower in energy; it was only for the positive charge states that the site-shifted v^*_{Ga} became the ground states. For InGaAs, there are four symmetry-distinct As nearest-neighbor atoms that could possibly shift into each unique vacant SQS III site. These site shifts are seen to have widely varying formation energies, from 1.8 to nearly 3.3 eV,

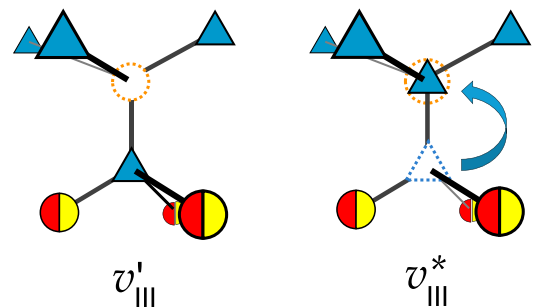


FIG. 9. Schematic diagram of the atomic configuration around a III-site vacancy in InGaAs: the simple vacancy v'_{III} and the site-shift vacancy v^*_{III} .

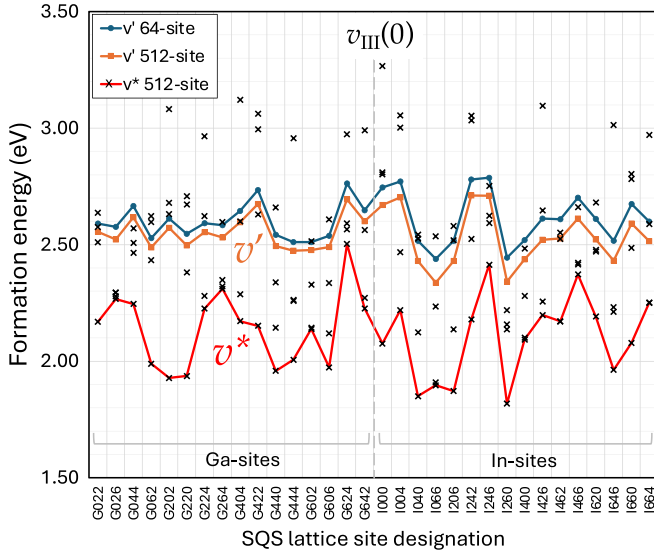


FIG. 10. Computed formation energy (in eV) of the neutral III-site vacancy $v_{\text{III}}(0)$ at each SQS lattice site. The 64-site SQS supercell results for the simple vacancy $v'_{\text{III}}(0)$ are marked by blue circles, and the 512-site hypercell results for the simple vacancy $v'_{\text{III}}(0)$ are marked by amber squares. The lines are included only to guide the eye across a series. The site-shifted results, where one of the four neighboring As atoms shifts into the vacated III site are marked by a (black) x, and a red solid line guides through the lowest-energy site-shift at each site.

as plotted in Fig. 10. The distortions created by the random local chemical environment lead to large differences in site-shift energies.

In a significant and notable departure from GaAs, a site-shifted $v_{\text{III}}^*(0)$ is lower energy than the metastable $v'_{\text{III}}(0)$, by more than 0.4 eV (on average). This will have important ramifications for the defect level analysis. The lowest-energy site-shift almost always has the nearest of the four As atom to the original III site hop into the vacant site, the As atom with the shortest, most compressed bond to the III atom in the SQS model.

Moreover, the lowest energy site-shift structures, all those with formation energy less than 2.0 eV, leave behind a v_{As} with three In atoms in neighboring sites to the shift-created vacancy. For the sites where the lowest site-shift energy is larger than 2.3 eV, none of the four site-shift configurations leaves behind three In neighbors. Just as for the simple v_{As} there appears to be a stratification of formation energies based upon the relative occupation of In and Ga in the neighboring sites to the As vacancy site, that is apparently

magnified from the ≈ 0.25 eV spacing seen in the simple vacancy.

A summary of the $v_{\text{III}}(0)$ formation energy statistical analysis is presented in Table V. The significant findings from this defect analysis are (1) there are large statistical variations in defect energies due to compositional disorder, larger than cell-size errors; (2) that site shifts need to be incorporated into a defect analysis, especially where calculations in the end-member binaries indicate a susceptibility to large configurational changes; (3) the ESP is valid, vacancies originating at Ga-site and In sites in the SQS are statistically indistinguishable; (4) there is a strong stratification in vacancy energies depending on III-atom neighbors and, finally (5) even with the large site-shift stabilization, the III-site vacancies remain high-energy defects unlikely to form in significant numbers during growth. As a primary defect generated in initial displacement damage, the v_{III} will be a crucial component in any analysis of radiation effects.

E. Divacancy vv

The divacancy, a nearest-neighbor pair of vacancies, has been determined to be an important primary damage defect in GaAs [9,10] responsible for the $E1$ - $E2$ defect traps observed in irradiated GaAs [8]. It is plausible to presume that it would be similarly prominent in irradiated InGaAs.

A schematic of a divacancy structure in the lattice is depicted in Fig. 11. From the SQS supercell, there are 128 possible unique divacancy pairs, straightforwardly counted by noting that a divacancy pair $v_{\text{As}}-v_{\text{III}}$ has an arsenic atom at one side, and there are 32 unique arsenic sites in the 64-site SQS, and each arsenic atom is bonded to four distinct III-site atoms. All 128 unique vv defect structures in the SQS are sampled in these calculations.

The computed overall average formation energy over the 128 distinct vv defects is 3.166 ± 0.078 eV, a high formation energy within a relatively narrow range of scatter. Separated into cohorts where the v_{III} originated with a Ga atom in the SQS and with a In atom in the SQS, the resolved averages are within 1 meV of this combined average, upholding to exceptionally fine precision the validity of the ESP. This high formation energy indicates that vv will take negligible populations in grown materials. The importance of vv in InGaAs will be as a primary defect in irradiated material.

The $vv(0)$ formation energies are charted in Fig. 12, segregated into cohorts resolved by Ga:In occupations of the three III-site atoms around the As vacancy. There appears to be an overall trend of increasing formation energy with increasing number of Ga neighbors (vs In neighbors) in this chart. The plotted averages within cohorts, the values also

TABLE V. Formation energy (As rich, in eV) of the neutral III-site vacancy $v_{\text{III}}(0)$, with standard deviations ($\pm$).

Average	64 site	512 site			
	v'_{III}	$\Delta E(512; 64)$	v'_{III}	v_{III}^*	$\Delta E(v'; v^*)$
III site	2.607 ± 0.098	0.066	2.541 ± 0.100	2.120 ± 0.170	0.421 ± 0.122
Ga site	2.599 ± 0.076	0.047	2.552 ± 0.069	2.137 ± 0.162	0.415 ± 0.129
In site	2.615 ± 0.118	0.085	2.530 ± 0.126	2.102 ± 0.182	0.428 ± 0.119

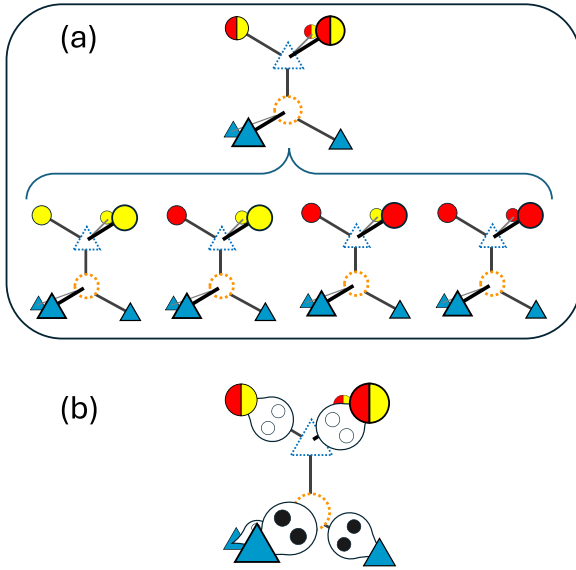


FIG. 11. Schematic of the structure and bonding around divacancy defect in InGaAs, where neighboring As and III sites are vacated. (a) Three As atoms neighbor the vacant III site, while three III atoms neighbor the vacant As site. The vv can take four different chemical forms, from 3In:0Ga through 0In:3Ga. (b) The qualitative chemical bonding description of the neutral $vv(0)$: the As dangling-bond orbitals become fully occupied lone pairs, and the III-site dangling bonds all become empty.

listed in Table VI, support this interpretation. However, the cohort-resolved differences are much smaller than the cohort-dependent differences identified above for the $v_{As}(0)$. While the stepwise differences between III-neighbor cohorts for $v_{As}(0)$ were larger than 0.25 eV, the entire difference between the (0Ga:3In) to (3Ga:0In) cohorts is only 0.14 eV, and only the initial step from (0Ga:3In) to (1Ga:2In) at 0.07 eV is clearly discernible within the scatter of formation energies.

Given the magnitude of the III-neighbor dependence for $v_{As}(0)$, why is there minimal III-neighbor dependence in $vv(0)$? The difference can be rationalized by the chemical nature of the bonding illustrated in Fig. 11(b). The four III-atom dangling bonds around an isolated $v_{As}(0)$ are occupied by three electrons, and the ground-state energy incorporates bonding interactions between them. Those occupation energies and bonding interactions will be strongly dependent upon the chemical identity of those atoms. The three III-dangling bonds around the v_{As} side of the divacancy are unoccupied because all six electrons left behind in dangling bonds fill the three As lone pairs around the v_{III} side. This interpretation, just as it was for GaAs: $vv(0)$, is supported by the atomic structure. The three III atoms in $vv(0)$ retreat away from the vacancy toward a more planar sp^2 configuration with their bonding As neighbors. With no occupied bonding states shared by these retreated III-neighbors, the formation energy is only weakly dependent upon the chemical identity of the III neighbors. Notably, this will change as the vv captures electrons and begins to occupy the III-atom dangling orbitals.

This chemical description also explains another seeming oddity in the results: the defect formation energy of a vv in the larger 512-atom hypercell is universally *larger* than its defect formation in the 64-atom SQS supercell. The $vv(0)$ defects are a relatively uniform ≈ 80 meV higher in energy in the larger hypercell. Similar behavior had been observed in GaAs: $vv(0)$ as well [9], as listed in Table VI, where the supercell-size-dependence could be more finely resolved than in InGaAs. Elastic effects cannot be responsible. Relaxations expanded into the larger volume afforded in the larger supercell would lead strictly to a decrease in energy. Electronic effects, defect banding and state degeneracies, are also not responsible. In silicon, the $v_{Si}(0)$ is famously and erroneously seen to favor a symmetric T_d structure over the correct D_{2d} distortion in small supercells due to electronic effects, a consequence of defect banding among degenerate states. There are no such state degeneracies in the $vv(0)$ to cause such an error. That

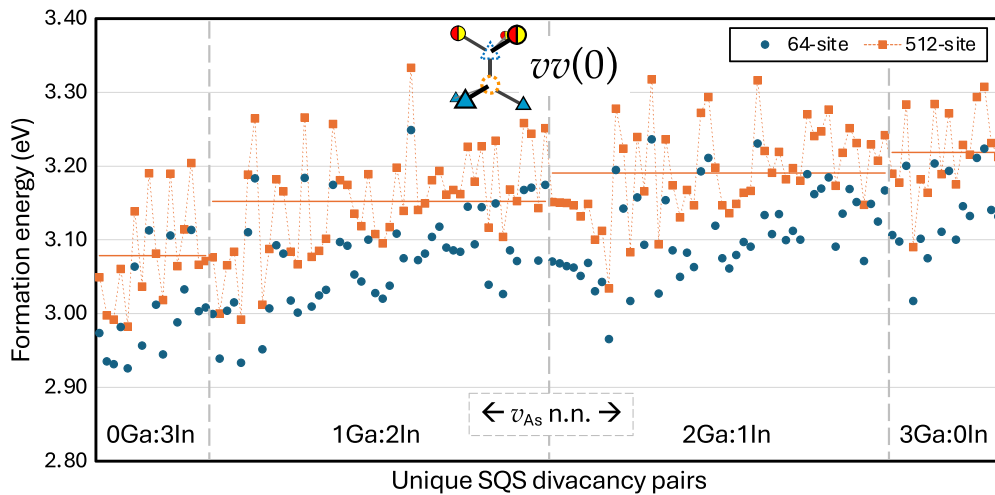


FIG. 12. Computed formation energy (in eV) of the divacancy $vv(0)$ at each SQS lattice site. The 64-site SQS supercell results for the divacancy are marked by (blue) circles, and the 512-site hypercell results for the divacancy are marked by (amber) squares (connected by dashed lines to guide the eye). The solid (amber) lines are the average across a cohort defined by the number of Ga vs In nearest neighbors to the v_{As} (noting that the fourth nearest-neighbor III site is vacant).

TABLE VI. Average formation energy (As rich, in eV) of the divacancy $vv(0)$.

Supercell	GaAs	InGaAs				
		Total	(0Ga:3In)	(1Ga:2In)	(2Ga:1In)	(3Ga:1In)
64 site	3.509	3.088 ± 0.073	3.006	3.076	3.111	3.147
216 site	3.592					
512 site	3.615	3.160 ± 0.078	3.079	3.152	3.191	3.219
1000 site	3.627					
$\Delta E(512; 64)$ (meV)	+106	$+78 \pm 8$	$+73 \pm 10$	$+76 \pm 8$	$+79 \pm 6$	$+82 \pm 5$

leaves electrical effects, finite-size Coulomb effects, as the last possible culprit. That charged defects incur severe Coulombic electrical finite-size errors in supercell calculations is commonplace lore. But $vv(0)$ has no net charge.

The bonding depiction in Fig. 11(b) offers a physical mechanism for this effect. The electrons in the divacancy leave the III-atom dangling bonds on one end of the $vv(0)$ to fill the As dangling bonds to form full lone pairs on the other. This transfer of electrons from the III atom to the As atom across the divacancy forms a strong local dipole within the $vv(0)$. This periodic array of 111-oriented defect dipoles interact attractively. The spurious dipole-dipole terms lower the energy, Coulombic interactions that scale as $1/L^3$ with cell size [44]. This leads to an energy increase with increase in supercell size, a uniform increase that is only dependent upon the supercell size, not the defect structure. The magnitude of the dipole-dipole error is slightly reduced in InGaAs from GaAs. In GaAs, the increase in $vv(0)$ formation energy from 64-site calculations to 512-site calculations is 0.11 eV. This formation-energy increase from the 64-site SQS to the 512-site hypercell is reduced to 0.07 eV in InGaAs. This reduction is largely attributable to the larger lattice constant (and larger effective L) for InGaAs with respect to GaAs.

A crude $1/L^3$ fit of the variation in $vv(0)$ formation energies across the GaAs supercell sizes (64, 216, 512, 1000 site) suffers only <4 meV deviations across the collection of cell sizes. With this fit, the 512-site formation energy is only 20 meV less than the infinite bulk limit. By analogy, the computed InGaAs $vv(0)$ formation energy in the 512 hypercell is within 10 meV of the infinite-bulk limit, well within the margin of error given by the accuracy of DFT (as discussed above). The 64-site formation energy is almost 0.1 eV in error due the supercell-size electrostatics, with respect to the bulk limit, comparable to the intrinsic accuracy of the DFT itself, a magnitude that could potentially compromise the accuracy of predictions. The larger 512-atom hypercells are needed to accurately obtain the neutral $vv(0)$ formation energy.

F. Cation antisites Ga_{As} and In_{As}

The neutral cation antisites are the last of the defects considered in this paper, where a gallium atom or an indium atom replaces an arsenic atom in the lattice, as illustrated in Fig. 13. The As antisite, an arsenic replacing a gallium or indium atom in the lattice, is a low-energy defect that is potentially generated in growth conditions (see above), and it is conceivable that the Ga antisite might be also.

The III atom has two fewer valence electrons than the As atom it replaces, so the neutral III-antisite leaves two holes in the bonds to its neighbors naturally leading to a double acceptor state, i.e., the defect will readily take up two electrons to fill the holes in the bonds. In GaAs, the Ga_{As} was determined to be a deep rather than shallow defect [45], and the two holes (from three degenerate p -like states) coupled into a triplet spin state (Hund's rule) and inducing a symmetry-lowering distortion because of the associated Jahn-Teller instability.

For InGaAs, the compositional randomness eliminates all symmetry around the $\{\text{III}\}_{\text{As}}$. The defects start in a symmetry-lowered configuration, and there are no exact state degeneracies, so the favored ground-state spin—either a spin-singlet or a spin-triplet coupling of the two holes—cannot be guessed *a priori*. In a reversal from the GaAs where the triplet is favored, the results for InGaAs indicate that the spin-triplet is universally *higher* than the spin-singlet, for both the Ga and In antisites at all As sites in the lattice, by significant margins (between 0.01 and 0.20 eV). The local atomic distortions are significant enough to stabilize a singlet-spin in preference to a triplet-spin.

Gallium and indium antisites formation energies for the spinless neutral charge state are charted in Fig. 14. While the $\text{In}_{\text{As}}(0)$ exhibits greater scatter [± 98 meV vs ± 59 meV for $\text{Ga}_{\text{As}}(0)$], the average formation energies for $\text{Ga}_{\text{As}}(0)$ and $\text{In}_{\text{As}}(0)$ are nearly identical, at 2.676 and 2.674 eV, respectively. This is not a (direct) consequence of an ESP. The insertion of a new atom into the lattice (rather than removal or replacement of an existing site-equivalent atom pre-existing in the lattice) might, in principle, be expected to lead to chemically differentiated formation energies for steric reasons, if nothing else—the In is a much larger atom than Ga. However,

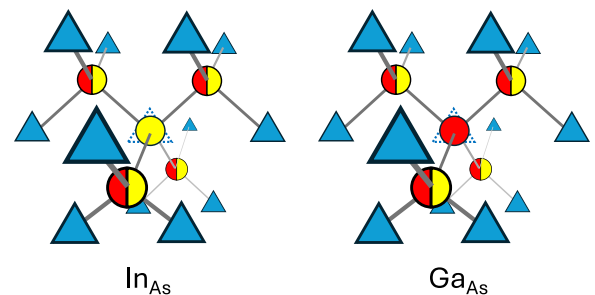


FIG. 13. Schematic of the structure and bonding around a cation antisite defect, where an As atom in the lattice is replaced by a III atom, either In or Ga. The antisite is surrounded by four other III cations in the lattice, forming a local cluster of five III atoms.

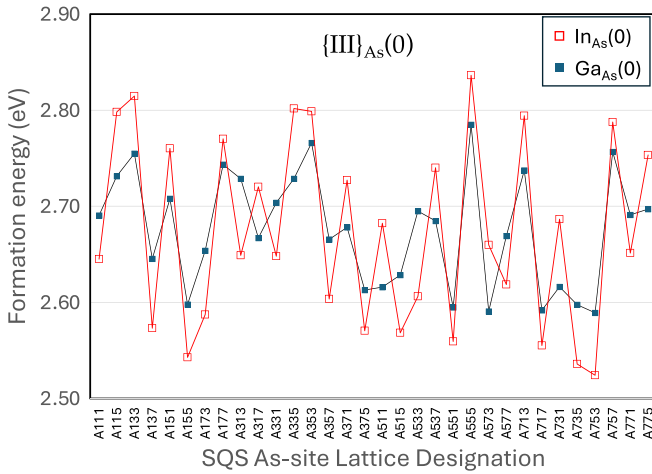


FIG. 14. Computed formation energy (in eV) of the cation antisites $\{\text{III}\}_{\text{As}}(0)$ across SQS sites, for the 64-atom SQS supercell and the spinless $S = 0$ ground state. The $\text{Ga}_{\text{As}}(0)$ formation energies are marked by (blue) filled squares, and the $\text{In}_{\text{As}}(0)$ formation energies are marked by (red) open squares. The lines are solely to guide the eye across each series, as the average formation energy is approximately the same for the two defects.

like for the isosite substitution above (where the difference between $\text{Ga}_{\text{In}}(0)$ and $\text{In}_{\text{Ga}}(0)$ energies was small), this steric effect is minimal. In the case of the antisite any steric-induced energy is spread over a cluster of five III atoms reducing long-range strain effects. Furthermore, the Ga-antisite and In antisite have significant overlap in Ga : In cohort populations, counting the number of Ga and In atoms within the 5-atom cluster of III atoms around the antisite.

With such large formation energies, ranging from 2.52 to 2.84 eV, the cation antisites are unlikely to be formed in as-grown material. The cation antisite is not a primary defect like a vacancy or interstitial, so neither would it be formed in the initial displacement damage consequent to irradiation. The cation antisite could only be generated via ensuing reactions between primary defects, a mobile Ga or In finding and filling an As vacancy. Vacancies and As antisites will certainly be much more important, these more prevalent and prominent defects are more likely to be observed. Note that a Ga antisite has not (yet, at least) been definitively observed in GaAs [45]. The cation antisites are unlikely to be important in the deciphering of the defect physics in InGaAs.

V. DISCUSSION

The defects in InGaAs presented here were selected to test and assess the approaches adopted to address the conceptual challenges defined in Sec. concepts. I also include those that will be crucial for deciphering defect physics in InGaAs in coordination with experiment, that either might be low-energy defects that could be incorporated during growth (e.g., antisites), or are primary defects that would be generated during displacement damage and later observed in experiment (e.g., vacancies).

Interstitials are generated in displacement damage, but their (static) structure and defect levels are immaterial in the

early stages of a coordinated theory-experiment investigation of defect physics in InGaAs. Interstitials are never observed in III-V semiconductors (in GaAs or InAs, at least) and are generally believed to be highly mobile (such as the GaAs:As_i [8]), so that their diffusion and reactive behavior is the crucial aspect—beyond the scope of this study. Additionally, because of the configurational complexity of interstitials even in crystalline GaAs [9,46,47], exacerbated by the compositional complexity of InGaAs, undertaking a investigation of interstitial behavior in InGaAs is a massive undertaking deserving its own study [11].

Di-antisite pairs are also potentially common displacement damage defects in irradiated GaAs and presumably InGaAs, where a III site has an As sitting in it and the neighboring As site has a III atom sitting in it. Modeling of di-antisites would be more readily accomplished in the SQS model than interstitials, with a computational challenge comparable to the modeling the divacancy—one would simply swap (instead of remove) every one of 128 distinct As-III atom pairs. However, di-antisite pairs have never been identified in experimental studies in GaAs. In the presence of more populous and highly visible vacancies, di-antisites are unlikely to be useful in deciphering defect physics in InGaAs.

The results indicate that, just as in GaAs, the most important defects in a campaign to decipher defect physics in InGaAs will be the simple As antisite (its low formation energy will make As_{III} a common defect in growth) and the vacancies (which are immobile primary defects in radiation-caused displacement damage)—defects that are seen to have single-particle states in the gap and likely possess defect levels that could be observed in experiments. Calculations for these charge states and the associated defect levels will be presented in a separate work.

These formation energy results for neutral defects document the importance of incorporating the statistical variability due to the compositional randomness in InGaAs. Even for simple, electronically inert defects such as isosite substitutions, the formation energy can vary by more than 0.1 eV about a statistical average—where the compositional randomness appears only at second-nearest neighbors. Any anecdotal (single or few candidate defects) would have at least this magnitude of potential error. Where the random III-site occupation neighbors the site, such as $v_{\text{As}}(0)$, the formation energies can span a range of 1.3 eV. The larger part of this variation is between cohorts of differing (Ga:In) neighbor occupations, but even ignoring the >0.25 eV differences between neighbor-resolved cohorts and restricting to within only the most populous (2Ga:2In) cohort, the variability in the $v_{\text{As}}(0)$ formation energy is ≈ 0.1 eV around its average value, due to composition variations in the *third*-nearest-neighbor shell. Comparable to or larger than the estimate of the DFT accuracy (and reasonable expectations of experimental accuracy), this statistical variability must be accounted for in any predictive analysis of defects in InGaAs.

Nearest-neighbor occupations of the III site dominate the variability in defect formation energy in InGaAs. This is prominently expressed in the large energy steps between nearest-neighbor-resolved cohorts for $v_{\text{As}}(0)$. Consideration of nearest-neighbor occupations around a defect will be most important in computational defect studies. Interestingly, the

formation energy of the $vv(0)$ seemed largely indifferent to the (Ga:In) makeup of the nearest neighbors to the v_{As} side of the vacancy. Variability in chemical composition in second- or third-nearest-neighbor shells causes smaller (ca. 0.1 eV) but still non-negligible variations in defect energies. Consideration of longer-range compositional randomness should not be completely ignored but is less vital. As a corollary, the 64-site SQS supercell has sufficient variability in chemical environments to quantitatively assess this statistical variability. It is also sufficient to assess and verify the validity of the ESP in these defect calculations to high accuracy. This vindicates the hypercell approach to use the compositional randomness with the smaller SQS supercell to obtain adequate statistics, and a supercell-of-SQS-supercells to minimize finite-size errors in the larger hypercell.

Notably, these statistical variations for many (most) defects are larger than finite-size errors as measured by the difference between the 64-site SQS supercell and 512-site hypercell. Adequate statistical composition sampling is more important than supercell finite-size errors for evaluation of defect properties, at least for neutral defects. For charged defects, the much larger charge-charge interactions between cells and their dependence upon size will change this balance. Stronger localization in defect states appears to be another consequence of compositional randomness. The finite-size effects (supercell size dependence) are reduced for InGaAs in comparison to GaAs.

The Makov-Payne [44] multipole analysis has been a bedrock foundation for understanding long-range electrostatic errors in supercell calculations, used to rationalize corrections to calculations of charged defects. These results here for the $vv(0)$ in InGaAs (and GaAs) provide the first documented evidence that dipole-dipole interaction can also be important in calculations of defects in bulk semiconductors. The cell-size-scaling results give credible estimates for their magnitude. For the GaAs and InGaAs, the dipole-dipole finite-size error is $O(0.1 \text{ eV})$ from 64-site supercells, and $<20 \text{ meV}$ from 512 site supercells, perhaps acceptable within the accuracy expected from DFT. For III-V's with smaller lattice constants (smaller L , and larger $1/L^3$) such as nitrides, this dipole-dipole finite-size error could be a more significant concern.

VI. CONCLUSIONS

This paper has introduced a strategy for modeling defects in random composition pseudobinary alloys and applied it to a deliberately curated selection of neutral defects in InGaAs, to assess the importance and effectiveness of different components of that strategy and to gain preliminary insight to identify the crucial aspects of the defect physics in as-grown and radiation-damaged InGaAs.

The statistical variability in defect properties due to compositional randomness on the III site is shown to be substantial, generally comparable to the intrinsic physical error expected of DFT, and potentially much larger than DFT errors for As-site defects such as the v_{As} . Differing numbers of Ga and In nearest neighbors lead to large differences in (cohort-average) formation energies. Comprehensive sampling of defects from a relatively small SQS (64 atom)

supercell proves sufficient to adequately assess this statistical variability, while use of a $2 \times 2 \times 2$ hypercell of SQS supercells conveniently allows for directly assessing finite-size effects for each sampled defect in a 512-atom supercell that is largely size-converged. Given the nature of the statistical variability, dominated by near-neighbor interactions, $O(0.25 \text{ eV})$ and more modest $O(0.1 \text{ eV})$ variability due to longer-range compositional randomness, the formal sophistication of an SQS is almost certainly excessive. A simply randomized structure (such as adopted in early InGaAs studies by Bonapasta and Giannozzi [12], or Komsa and Pasquarello [13]) is likely sufficient to offer adequate sampling of the important cohorts of local environments. But in any computational study of InGaAs defects, explicit consideration of statistical variation due to compositional randomness within a randomized model will be vital for quantitatively credible comparisons to experiment.

Curiously, defect calculations in the smaller 64-site supercells in the random alloy appear to be better converged with respect to cell size than their counterparts in the crystalline III-V binary semiconductors such as GaAs or InAs, at least for the neutral defects considered here. The compositional randomness leads to stronger localization and reduced defect-defect interactions, the energy lowering in larger cells mostly due to strain relaxation within the larger volume of the larger supercell.

An equivalent site principle articulates the notion that Ga-site and In-site defects should have the same (statistically) behavior. The invocation of the ESP in SQS-based defect calculations in InGaAs imposes a constraint on the relative chemical reference potentials of the In and Ga atoms on the III site in the pseudobinary, removing an arbitrariness in their definition. A simple (and easily computed) prescription is proposed to define the chemical potentials of Ga and In, dividing the heat of formation of InGaAs from its end-member binary proportionately between the Ga and In atoms. This partition is shown to be broadly effective at upholding the ESP in all the defects considered here. The precision with which the results verify the validity of the ESP is additional evidence that the 64-atom SQS model is large enough and adequately samples the statistical variability of the full infinite bulk random alloy.

The results for this selection of defects in InGaAs mostly parallel the conclusions concerning analogous defects in GaAs. The As antisite, analogous to the $EL2$ center in GaAs, is the only low-energy defect that is likely to be found in as-grown material. The neutral $As_{III}(0)$ has an occupied state in the DFT gap, suggesting it will be a double donor. The single vacancies $v_{As}(0)$ and $v_{III}(0)$ are both stable, but while a v_{Ga} will be indistinguishable from a v_{In} (agnostic in a pseudobinary via the ESP), it is the $v_{As}(0)$ that will express as multiple different defects depending upon its III-atom neighbors, with sufficiently separated cohorts that might conceivably be resolved in experiments. In addition, the results indicate it will be crucial to include site-shifts in full description of the vacancy, the disordered composition in InGaAs leads to a much stronger preference for a site shift in v_{Ga} than in GaAs, where site-shifts proved essential for accurate interpretations of experimental observations [10]. The single vacancies—and the divacancy—are higher-energy defects unlikely to be seen

in as-grown material, but as primary displacement damage defects, will have significant populations (and presumably become visible to experiment) in irradiated InGaAs.

ACKNOWLEDGMENTS

I am grateful to Su-Huai Wei and Alex Zunger for graciously providing the 64-atom SQS structure used in this study. I thank Harold P. Hjalmarsen and Arthur H. Edwards for frequent illuminating discussions of basic issues in modeling defects in random-composition alloys over the many years of this effort. I acknowledge useful guidance from conversations with Evan M. Anderson concerning making constructive connections between the theory effort with the larger experimental project he leads. I am grateful to Boris Kiefer and Arthur Edwards for constructive technical critiques of the paper, and I am also grateful to Austin Shipley and Marcos Calva for providing their valuable perspectives. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under Contract No. DE-NA0003525. This work was partially supported by a Laboratory Directed Research and Development (LDRD) project

(No. 233119). This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government. This paper is authored by an employee of National Technology & Engineering Solutions of Sandia, LLC under Contract No. DE-NA0003525 with the U.S. Department of Energy (DOE). The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a nonexclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this article or allow others to do so, for United States Government purposes. The DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan [48].

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

-
- [1] G. J. Shaw, S. R. Messenger, R. J. Walters, and G. P. Summers, Radiation-induced reverse dark currents in $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ photodiodes, *J. Appl. Phys.* **73**, 7244 (1993).
 - [2] S. Barde, R. Ecoffet, J. Costeraste, A. Meygret, and X. Hugon, Displacement damage effect in InGaAs detectors: Experimental results and semi-empirical model prediction, *IEEE Trans. Nucl. Sci.* **47**, 2466 (2000).
 - [3] O. Gilard, L. S. How, A. Delbergue, C. Inguibert, T. Nuns, J. Barbero, J. Moreno, L. Bouet, S. Mariojouis, and M. Boutillie, Damage factor for radiation-induced dark current in InGaAs photodiodes, *IEEE Trans. Nucl. Sci.* **65**, 884 (2018).
 - [4] G. T. Nelson, G. Uoin, S. J. Polly, K. B. Wynne, A. W. Haberl, W. A. Lanford, R. A. Lowell, and S. M. Hubbard, *In situ* deep-level transient spectroscopy and dark current measurements of proton-irradiated InGaAs photodiodes, *IEEE Trans. Nucl. Sci.* **67**, 2051 (2020).
 - [5] M. Benfante, J.-L. Reverchon, O. Gilard, S. Demiguel, C. Virmondois, C. Durnez, T. Dartois, and V. Goiffon, Electron-field-enhanced generation current in proton irradiated InGaAs photodiodes, *IEEE Trans. Nucl. Sci.* **70**, 523 (2023).
 - [6] J. Dabrowski and M. Scheffler, Theoretical evidence for and optically inducible structural transition of the isolated as antisite in GaAs: Identification and explanation for the *EL2*, *Phys. Rev. Lett.* **60**, 2183 (1988).
 - [7] D. J. Chadi and K. J. Chang, Metastability of the isolated arsenic-antisite defect in GaAs, *Phys. Rev. Lett.* **60**, 2187 (1988).
 - [8] J. C. Bourgoin, H. J. Bardeleben, and D. Stiévenard, Native defects in gallium arsenide, *J. Appl. Phys.* **64**, R65 (1988).
 - [9] P. A. Schultz and O. A. von Lillienfeld, Simple intrinsic defects in gallium arsenide, *Modell. Simul. Mater. Sci. Eng.* **17**, 084007 (2009).
 - [10] P. A. Schultz, The *E1-E2* center in gallium arsenide is the divacancy, *J. Phys.: Condens. Matter* **27**, 075801 (2015).
 - [11] S. R. Lee, A. F. Wright, N. A. Modine, C. C. Bataille, S. M. Foiles, J. C. Thomas, and A. Van der Ven, First-principles survey of the structure, formation energies, and transition levels of As-interstitial defects in InGaAs, *Phys. Rev. B* **92**, 045205 (2015).
 - [12] A. A. Bonapasta and P. Giannozzi, Effects of strain and local charge on the formation of deep defects in III-V ternary alloys, *Phys. Rev. Lett.* **84**, 3923 (2000).
 - [13] H.-K. Komsa and A. Pasquarello, Comparison of vacancy and antisite defects in GaAs and InGaAs through hybrid functionals, *J. Phys.: Condens. Matter* **24**, 045801 (2012).
 - [14] S. T. Murphy, A. Chroneos, R. W. Grimes, C. Jiang, and U. Schwingenschlögl, Phase stability and the arsenic vacancy defect in $\text{In}_x\text{Ga}_{1-x}\text{As}$, *Phys. Rev. B* **84**, 184108 (2011).
 - [15] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
 - [16] P. A. Burr and M. W. D. Cooper, Importance of elastic finite-size effects: Neutral defects in ionic compounds, *Phys. Rev. B* **96**, 094107 (2017).
 - [17] C. D. Vedel, T. Gunst, S. Smidstrop, and V. P. Georgiev, Shockley-Read-Hall recombination and trap levels in $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ point defects from first principles, *Phys. Rev. B* **108**, 094113 (2023).
 - [18] S. G. Lee and K. J. Chang, Energetics and hydrogen passivation of carbon-related defects in InAs and $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$, *Phys. Rev. B* **53**, 9784 (1996).
 - [19] J. Wang, B. Lukose, M. O. Thompson, and P. Clancy, Ab initio modeling vacancies, antisites, and Si dopants in ordered InGaAs, *J. Appl. Phys.* **121**, 163102 (2017).

- [20] M. Reveil, J. Wang, M. O. Thompson, and P. Clancy, Preferred diffusional pathways of intrinsic defects and silicon dopants in an ordered phase of $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$: A first principles study, *Acta Mater.* **140**, 39 (2017).
- [21] V. Kulish, W. Liu, and S. Manzhos, A model for estimating chemical potentials in ternary semiconductor compounds, *MRS Adv.* **2**, 2909 (2017).
- [22] V. Kulish, W. Liu, F. Benistant, and S. Manzhos, Dopant-dopant interactions in beryllium doped indium gallium arsenide: An *ab initio* study, *J. Mater. Res.* **33**, 401 (2018).
- [23] A. Zunger, S.-H. Wei, L. G. Ferreira, and J. E. Bernard, Special quasirandom structures, *Phys. Rev. Lett.* **65**, 353 (1990).
- [24] A. C. Irvine and D. W. Palmer, First observation of the *EL2* lattice defect in indium gallium arsenide grown by molecular-beam epitaxy, *Phys. Rev. Lett.* **68**, 2168 (1992).
- [25] K.-H. Goetz, D. Bimberg, H. Jürgensen, J. Selders, A. V. Solomonov, G. F. Glimski, and N. Razeghi, Optical and crystallographic properties and impurity incorporation of $\text{Ga}_x\text{In}_{1-x}\text{As}$ ($0.44 < x < 0.49$) grown by liquid phase epitaxy, vapor phase epitaxy, and metal organic chemical vapor deposition, *J. Appl. Phys.* **54**, 4543 (1983).
- [26] C. P. Kuo, S. K. Vong, R. M. Cohen, and G. B. Stringfellow, Effect of mismatch strain on band GaP in III-V semiconductors, *J. Appl. Phys.* **57**, 5428 (1985).
- [27] P. A. Schultz, Theory of defect levels and the “band gap problem” in silicon, *Phys. Rev. Lett.* **96**, 246401 (2006).
- [28] P. A. Schultz and A. H. Edwards, Modeling charged defects inside density functional theory band gaps, *Nucl. Instrum. Methods Phys. Res. Sect. B* **327**, 2 (2014).
- [29] P. A. Schultz, A. H. Edwards, R. M. Van Ginhoven, H. P. Hjalmarson, and A. M. Mounce, Theory of magnetic 3d transition metal dopants in gallium nitride, *Phys. Rev. B* **107**, 205202 (2023).
- [30] P. A. Schultz, In InAs, with a 0.42 eV band gap, every defect is a shallow defect, within 0.2 eV of a band edge, that requires large supercells to be resolved (unpublished).
- [31] E. Towe, Photoluminescence of undoped $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}$ grown by the vapor phase epitaxy technique, *J. Appl. Phys.* **53**, 5136 (1982).
- [32] J. A. Van Vechten, A simple man’s view of the thermochemistry of semiconductors, in *Handbook on Semiconductors*, Vol. 3: *Materials Properties and Preparation*, edited by S. P. Keller (North-Holland, Amsterdam, 1988), pp. 1–111.
- [33] S. B. Zhang and J. E. Northrup, Chemical potential dependence of defect formation energies in GaAs: Application to Ga self-diffusion, *Phys. Rev. Lett.* **67**, 2339 (1991).
- [34] S. Chakravarty, D. J. Sharar, and P. J. Shamberger, Heterogeneous nucleation of gallium with lattice-matched cubic carbide and nitride phases, *J. Appl. Phys.* **130**, 125107 (2021).
- [35] P. A. Schultz, SEQQUEST code, <https://dft.sandia.gov/Quest/>.
- [36] O. A. von Lilienfeld and P. A. Schultz, Structure and band gaps of Ga-(V) semiconductors: The challenge of Ga pseudopotentials, *Phys. Rev. B* **77**, 115202 (2008).
- [37] D. R. Hamann, Generalized norm-conserving pseudopotentials, *Phys. Rev. B* **40**, 2980 (1989).
- [38] M. Fuchs and M. Scheffler, *Ab initio* pseudopotentials for electron structure calculations of polyatomic systems using density functional theory, *Comput. Phys. Commun.* **119**, 67 (1999).
- [39] S. G. Louie, S. Froyen, and M. L. Cohen, Nonlinear ionic pseudopotentials in spin-density-functional calculations, *Phys. Rev. B* **26**, 1738 (1982).
- [40] D. D. Johnson, Modified Broyden’s method for accelerating convergence in self-consistent calculations, *Phys. Rev. B* **38**, 12807 (1988).
- [41] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/7lsb-t719> for tabulated coordinates of atoms in the reference SQS supercell.
- [42] G. A. Baraff and M. Schlüter, Bistability and metastability of the gallium vacancy in GaAs: Actuator of the *EL2*? *Phys. Rev. Lett.* **55**, 2340 (1985).
- [43] S. Pöykkö, M. J. Puska, M. Alatalo, and R. M. Nieminen, Metastable defect complexes in GaAs, *Phys. Rev. B* **54**, 7909 (1996).
- [44] G. Makov and M. C. Payne, Periodic boundary conditions in *ab initio* calculations, *Phys. Rev. B* **51**, 4014 (1995).
- [45] P. A. Schultz, Discriminating a deep gallium antisite defect from shallow acceptors in GaAs using supercell calculations, *Phys. Rev. B* **93**, 125201 (2016).
- [46] A. F. Wright and N. A. Modine, Migration processes of the As interstitial in GaAs, *J. Appl. Phys.* **120**, 215705 (2016).
- [47] G. Zollo, Y. J. Lee, and R. M. Nieminen, Properties of intrinsic di-interstitials in GaAs, *J. Phys.: Condens. Matter* **16**, 8991 (2004).
- [48] <https://www.energy.gov/downloads/doe-public-access-plan>.