

Importance of finite-size corrections for accurate *ab initio* modeling of carrier capture at semiconductor defects: A case study of substitutional C_N in GaN

S. R. Lee^{✉,*}, N. A. Modine^{✉,†} and W. R. Wampler*Sandia National Laboratories, Albuquerque, New Mexico 87185, USA*

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In *ab initio* studies of carrier-capture processes in defective semiconductor materials, the single-effective-mode formalism and the static-coupling approximation have become the predominant theoretical approaches for determining carrier-capture coefficients. The single-mode formalism relies on accurate nonequilibrium defect energies obtained from density-functional theory (DFT), where required inputs are a series of configurationally displaced, defect-containing supercells obtained using an interpolative ansatz, and where the DFT outputs are corresponding total energies that have traditionally been postprocessed *using a long-established ground-state formulation of finite-size corrections* and defect-formation energies. This formulation remains commonly used even though the defects that form a configuration-coordinate (CC) diagram typically exist as structures that are displaced from the ground state. To remedy this inconsistency, Kumagai has recently proposed novel methods for implementing finite-size corrections specifically intended for DFT calculations of the defect energies used to construct CC diagrams and implement the single-mode formalism [Y. Kumagai, *Phys. Rev. B* **107**, L220101 (2023)]. Kumagai's approach builds on the latest finite-size-correction methods introduced to describe vertical charge-state transitions for charge-localizing point defects in semiconductors and insulators [T. Gake *et al.*, *Phys. Rev. B* **101**, 020102 (2020); S. Falletta *et al.*, *ibid.* **102**, 041115 (2020)]. The newly identified finite-size artifact treated in these studies is the polarization charge induced on a configurationally frozen defect and its subsequent interaction with a vertical transition in charge state. In this work, we evaluate Kumagai's proposed methodology by applying it in a high-precision DFT study of carrier capture by substitutional C_N in GaN, a well-characterized and technologically relevant defect and material. We have rigorously calculated C_N defect energies across various supercell sizes for each defect configuration and charge state on the hole-capture CC diagram of $C_N(q = -1)$, enabling a direct comparison of the slopes of the defect energies versus inverse cell size with those predicted by Kumagai. The most consequential prediction of Kumagai's method is that these slopes distinctly vary as the square of the linear-interpolation parameter used to construct the nonequilibrium defect configurations. Our results quantitatively support this prediction. Moreover, with these new finite-size corrections and multiple-cell-size DFT calculations in place, we find that the classical energy barrier for hole capture by $C_N(q = -1)$ in GaN decreases to 0.092–0.127 eV. This finding confirms the recent ≈ 0.1 eV prediction of Reshchikov based on the weak temperature dependence for hole capture observed in photoluminescence experiments [M. A. Reshchikov, *J. Appl. Phys.* **129**, 121101 (2021)]. These results stand in stark contrast to previously calculated barriers of 0.486 and 0.73 eV, which also used the single-mode formalism but were obtained by instead using ground-state-based finite-size corrections. Our reduced classical barrier for capture increases the temperature-dependent hole-capture coefficient of a $C_N(q = -1)$ defect by *more than two to four orders of magnitude* for temperatures of 100–600 K, compared to the previous 0.486 eV results. While other defects may not be as dramatically affected as here, we suggest that incorporating proper finite-size corrections for the vertical-transition-like states embedded within CC diagrams is an essential, yet previously unrecognized, component of accurate modeling of carrier-capture when using the single-effective-mode formalism.

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I. INTRODUCTION

Semiconductor materials have enabled numerous technological advances in power electronics, microelectronics, and optoelectronics—with these technologies underpinning further broad advances in information technology and software, robotics, and of late, artificial intelligence. Motivated by the increasingly central importance of these materials in our lives—and with the age of semiconductors having begun some 76 years ago with the first demonstration of Ge transistors [1]—the study of point defects, impurities, and their

*Contact author: srlee@sandia.gov†Contact author: namodin@sandia.gov

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complexes within semiconductors has been widely pursued, with researchers seeking to further advance physical understanding, improve semiconductor-materials performance, and assure device reliability. Through such work, we have come to understand that one of the most important defect-associated mechanisms altering electronic-device performance is nonradiative recombination of carriers at defect sites [2,3], wherein a free carrier is captured by an electrically active defect, and multiple phonons are emitted to dissipate the carrier annihilation energy [4–9].

The associated development of multiple-phonon-emission (MPE) theories for describing nonradiative-recombination processes in semiconductors has evolved over several decades, with many of the foundational principles established in early research dating from the 1950s [2–13], following soon after the aforementioned first transistors. A second period of more focused MPE-theory development occurred in the 1970s and later [6–9,14–18], during which time it became better established that MPE was a dominant mechanism for nonradiative recombination [9]. Materials-enabled device developments were again motivating, with GaP, GaAs, and other III-V compound-semiconductors having become prominent because of the intense research interest that followed the first demonstration of GaAsP-based visible-emitting semiconductor lasers in 1962 [19].

Similarly, the latest surge in the development of MPE theory followed the emergence of III-nitride materials and high-efficiency blue-light-emitting diodes in 1994 [20]. Because density-functional theory (DFT) had also become prominent by this time [21], this later research has sought to couple MPE theories to DFT, with a goal to capture the complete atomistic details of a given defect, thereby producing higher-fidelity calculations for specific defects and materials of interest [22–48]. These newer treatments have pursued multiple paths, reflecting both the complexity of antecedent MPE theories and their varying tractability within modern DFT. In this regard, Shi and Wang have pursued an explicit DFT treatment of multiple phonon modes [23], which they have used to comprehensively revisit several of the major conceptual variants of earlier MPE theory [26], with some (e.g., classical Marcus theory [49]) even having separate, related roots in molecular chemistry. Of the variants studied, those based upon the static-coupling approximation [5,8,9,11] have been argued by Shi *et al.* to be most important to MPE studies of semiconductors [26]. Barmparis *et al.* and Nichols *et al.* have also pursued extensive treatments of multiple phonon modes, while further including the option to model nonequilibrium, athermal processes arising from semiconductor-device operation, with their enhanced modeling enabled by either Monte Carlo [27] or time-dependent DFT (TDDFT) approaches [45]. Yet-other modern efforts have also pursued TDDFT [46,47], where improved modeling of the many-body nature of the electron-hole interaction of a defect's excited states has been sought. Finally, Green's-function methods [48] have recently been developed, again with emphasis on nonequilibrium effects, and where one avoids altogether the finite-size effects caused by periodic supercells that emerge as the primary interest herein.

In contrast to the multiple-phonon-mode treatments, Schanovsky *et al.* [22], Alkauskas *et al.* [24,25,29,30], and

more recently many others [33–44], have pursued a simpler formalism for DFT-based modeling of carrier capture, wherein a linear interpolation connects the atomic positions of the pair of configurationally relaxed point-defect structures that define the excited and relaxed defect states associated with capture. In such efforts, the resulting family of interpolated (and if desired, extrapolated) defect structures define a *single-effective-phonon mode* that implicitly captures the multiple-mode character. For this single-effective-mode model, only the prevailing static-coupling variant of MPE theory has been pursued. The relative simplicity of the single-mode model when implemented in combination with static coupling has recently led to software developed by Turiansky *et al.* that systematizes this formalism [35]. In a paper detailing their efforts, these authors have reassessed certain aspects of the single-mode model, with a goal to improve the accuracy and broaden the pursuit of carrier-capture modeling. The topics discussed include (i) numerical vs analytical calculations of the Sommerfeld effect, (ii) an interpolative method for computing more reproducible, accurate phonon-phonon matrix elements, and (iii) a new, PAW-based (projector-augmented wave function) formalism for calculating electron-phonon matrix elements, among others.

Apart from these refinements, Kumagai [50] has more recently pointed out that one of most important factors influencing the accuracy of the single-mode formalism—*finite-size effects arising from modeling the unrelaxed ionic configurations of defects when using periodically replicated supercells*—has still not been thoroughly examined. Building upon the latest finite-size correction methods introduced to describe defect-formation energies for vertical charge-state transitions [51–53], Kumagai has gone forward to propose a new finite-size-correction method for the DFT calculations specifically used to construct the configuration-coordinate (CC) diagrams used within the single-mode formalism. Most recently, Zhang *et al.* have further commented that Kumagai's finite-size-correction method has not yet been applied to actual calculations of the carrier-capture coefficient [54]. While finite-size corrections suitable for use with the defect-formation energies used in CC diagrams may at first appear to be only an insubstantial detail, the situation may instead be much like that for DFT studies involving the formation energy of the ground states of charged defects, where the earlier introduction, refinement, and assessment of proper finite-size corrections *specifically designed for the fully relaxed configurations of charged defects* has led to almost-revolutionary improvements in defect-modeling accuracy [55–77].

The present work thus revisits the single-mode static-coupling formalisms for modeling the carrier-capture process, with a primary focus on the largely unexamined finite-size effects noted by Kumagai [50]. In doing so, we utilize the well-known 0/–1 hole-capture transition for C substituting on a N site in GaN (herein, C_N) as the exemplar for our study. This defect is of particular interest for multiple reasons: First, it is optically and electronically one of the most important, well-studied defects found in devices made from GaN materials [78–112], which are now grown on an industrial scale by metalorganic chemical-vapor deposition for use in solid-state lighting and power electronics. Second, the hole-capture and electron-capture coefficients of C_N in GaN

have been extensively investigated multiple times by both *ab initio* modeling [24,25,29,30,35,43,44] and experimental measurements [95–97,99,103,104], providing rare and clear benchmarks for comparison. Third, these thorough-going theoretical and experimental benchmarks at times surprisingly disagree, most especially regarding the almost-constant hole-capture coefficients that have been found in experiments spanning 100–600 K [95–97,99,104], versus DFT calculations that have found this coefficient to vary by ~ 2 –3 orders of magnitude for the same temperature range [25,29,30,35], with theory underestimating the experimental capture coefficients at all measured temperatures. We resolve these discordant results by exhaustively recalculating the CC-diagram, the associated classical thermal barrier to hole capture, and the hole-capture coefficient as a detailed function of supercell size, thereby demonstrating the critical importance of properly correcting for finite-size effects when modeling carrier capture by using the single-mode formalism.

As the present work approached completion, we found that Nichols *et al.* have also recently addressed the above-noted discrepancy between experiment and theory for equilibrium hole capture by substitutional $C_N(q = -1)$ in GaN by instead using a multiple-phonon-mode treatment [45]. As found here, their results eliminate most of the discrepancy previously seen at higher temperatures ($T > 500$ K), but unlike here, they leave in place differences that still approach an order of magnitude at lower temperatures ($T < 200$ K). While these authors attribute their substantial improvement in modeling accuracy to the use of a multiple-mode formalism in place of the prevailing single-mode formalism, this inference omits a second crucial difference—varying treatments of the finite-size effects. In most existing multiple-mode carrier-capture studies, explicit finite-size corrections are typically omitted [23,26–28,45], and *this practice inconspicuously replaces the incorrect finite-size corrections presently used in almost all single-effective-mode studies*. Herein, we find that single-mode theory reproduces multiple-mode theory (to within reasonable computational uncertainties) when *both* are done without any finite-size corrections. This last result strongly suggests that it is the multiple-mode theory’s fortuitous omission of incorrect finite-size corrections that primarily improves the accuracy of their treatment of hole capture by $C_N(q = -1)$ compared to previous single-mode results. Hence, it is probably not the detailed inclusion of multiple-phonon-mode physics that is pivotal, as stated in Ref. [45].

II. THEORY AND METHODS

A. Construction of carrier-capture defect configurations

The single-mode formalism for investigating carrier capture rests upon linear interpolation (and at times, extrapolation) of the two relaxed (ground-state) atomic configurations of the defect undergoing a capture event, with the interpolation yielding a series of atomically displaced defect configurations that enable modeling of the carrier-capture event. The formalism appears to have been first used in conjunction with DFT by Schanovsky *et al.* for a study of carrier capture by point defects in quartz [22], with Alkauskas *et al.*

subsequently using the method to study both photoluminescence (PL) line shapes and carrier-capture processes in studies of point defects in GaN and ZnO [24,25]. Drawing upon Refs. [22] and [24], the interpolated atomic configurations needed to construct the CC diagram can be defined by

$$R_{\kappa j}(\alpha) = R_{\kappa j}^e + \alpha \Delta R_{\kappa j}, \quad (1)$$

$$\Delta R_{\kappa j} = R_{\kappa j}^r - R_{\kappa j}^e, \quad (2)$$

where $R_{\kappa j}^e$ and $R_{\kappa j}^r$ are the atomic-position coordinates for the defect-containing supercell when at the structurally relaxed configuration for each of the two defect charge states, q_e and q_r , defining the capture event. The subscript κ labels each of the atoms located within the defect-containing supercell, where $j = \{x, y, z\}$ is the atom’s position, and where x, y , and z designate Cartesian components of the position.

To facilitate the development of finite-size corrections, we take q_e as the charge state of the defect when on the excited-state “branch” (i.e., the total-energy parabola) of a CC diagram, and we take q_r as the charge state of the defect when on the relaxed-state branch. The charge state q_r is equal to q_e plus the charge of the captured carrier. The linear interpolation parameter, taken as $\alpha = \alpha_e$ for Eqs. (1) and (2), advances the defect configuration from $\{R_{\kappa j}^e\}$ at $\alpha_e = 0$ to $\{R_{\kappa j}^r\}$ at $\alpha_e = 1$. By reversing the roles of $R_{\kappa j}^r$ and $R_{\kappa j}^e$ in Eqs. (1) and (2), with the interpolation parameter now taken $\alpha = \alpha_r$, we define a second interpolation that oppositely advances from $\{R_{\kappa j}^r\}$ to $\{R_{\kappa j}^e\}$. The resulting *local interpolation parameters*, α_e and α_r , specific to each branch of the CC diagram will prove convenient to use when applying finite-size corrections to the DFT calculations used to form each corresponding branch.

As usual, one connects the interpolated defect configurations to phonon properties by introducing the configuration coordinate, $Q(\alpha) = \alpha Q_0$, where Q_0 is defined in terms of the initial- and final-state atomic positions of the defect through a mass-weighted sum over all atoms:

$$Q_0 = \left[\sum_{\kappa, j} m_{\kappa} \Delta R_{\kappa j}^2 \right]^{1/2} = M^{1/2} R_0, \quad (3)$$

where m_{κ} is the atomic mass of atom κ , M is the modal mass, and $R_0 = [\sum_{\kappa, j} \Delta R_{\kappa j}^2]^{1/2}$. To construct the CC diagram, one calculates $\{R_{\kappa j}(\alpha)\}$, Q_0 , and $Q(\alpha)$ by applying Eqs. (1)–(3) for each α of interest, *where, unlike the finite-size corrections to come*, only one of the two local interpolation parameters has traditionally been needed. DFT calculations then follow for each interpolatively distorted defect structure, $\{R_{\kappa j}(\alpha)\}$, using each of the two relevant defect charge states of the carrier-capture event. The energy of the carrier that will be captured is then added to the energy of the defect in charge state q_e to obtain the total energy of the initial excited-defect-plus-carrier system that appears in the CC diagram. We note that Turiansky *et al.* have recently developed a library of open-source Python software, named *NonRad*, that implements application of Eqs. (1)–(3) and other helpful calculations supporting DFT studies of carrier capture [35,113].

B. Defect-formation energies of vertical-transition states

In the single-effective-mode carrier-capture calculations to date, the needed defect energies have been calculated from DFT supercell data by routinely applying the standard defect-formation-energy and finite-size-correction formulations originally developed for defect ground states [25,29,30,34–44]. However, research by Gake *et al.* [51], Falletta *et al.* [52], and Kumagai [50] has recently revealed that the use of the ground-state formulation is incorrect because the defect energies forming the CC diagram essentially result from a series of vertical-transition-like states. In the present work, we have therefore set aside the ground-state formulations and instead pursue the new formulation for defect-formation energies developed to describe the defect state produced by a vertical charge-state transition, $q' \rightarrow q$ [51,52].

The term “vertical transition” denotes a defect state where *only* the electronic structure relaxes when the defect changes to some final charge state, q , while the defect’s ionic positions are held fixed at the ground-state atomic configuration, $\mathbf{R}_{q'}$, determined for some other initial charge state, q' . In terms of the previous section’s notation, the present quantities, q' and $\mathbf{R}_{q'}$, represent either of the two defect ground states defined by q_e and $\{R_{\kappa j}^e\}$, or q_r and $\{R_{\kappa j}^r\}$, in the CC diagram. Following Ref. [52], the defect-formation energy of a defect that has undergone a vertical transition can be written:

$$E_f(q, \mathbf{R}_{q'}) = E_d(q, \mathbf{R}_{q'}) - E_b(0, \mathbf{R}_0) + q(\epsilon_F + \epsilon_v) - \sum_i n_i \mu_i + E_{\text{cor}}(q, \mathbf{R}_{q'}), \quad (4)$$

where $E_d(q, \mathbf{R}_{q'})$ is the total energy of the defect-containing supercell in its final state, and $E_b(0, \mathbf{R}_0)$ is the total energy of the corresponding, defect-free, bulk supercell. Equation (4) limits to the standard expression for a defect’s ground-state formation energy whenever $q = q'$ such that the vertical transition vanishes. Just as in the standard ground-state formulation of the defect-formation energy [114], the parameters ϵ_F (the Fermi level), ϵ_v (the valence-band-edge energy), n_i (the number of atoms of type i , added or removed from the bulk supercell), and μ_i (the chemical potential for atoms of type i) specify the electronic- and chemical-potential reservoirs used to form the defective supercell from the bulk supercell. Because q and q' differ for a vertical transition, one must use a reformulated finite-size correction, $E_{\text{cor}}(q, \mathbf{R}_{q'})$, that accounts for fundamental changes in the correction energy arising from the modified electrostatic response of the defect following the transition $q' \rightarrow q$.

Moving beyond notational changes, most of the complexity of the reformulated defect-formation energy rests with the determination of $E_{\text{cor}}(q, \mathbf{R}_{q'})$ for the vertical transition. In Ref. [52], Falletta *et al.* have shown that the total correction energy may be written as a sum of three distinct *model-charge-distribution-based* energy-correction terms, where each term shares a similar functional form, $E_m(q^*, \epsilon_*)$, given by an assumed charge-distribution model. While these “model terms” all resemble a ground-state correction in their mathematical form, each term is uniquely delineated by some applicable charge state, q^* , and dielectric constant, ϵ_* , where these defining parameters are chosen to represent each of the conceptual steps that make up the ver-

tical transition. Employing this representation, the summed contributions to the finite-size correction of a vertical transition may be written [52] as

$$E_{\text{cor}}(q, \mathbf{R}_{q'}) = E_m(q', \epsilon_0) - E_m(q' + q'_{\text{pol}}, \epsilon_\infty) + E_m(q + q'_{\text{pol}}, \epsilon_\infty), \quad (5)$$

with q'_{pol} given by

$$q'_{\text{pol}} = -q' \left(1 - \frac{\epsilon_\infty}{\epsilon_0} \right), \quad (6)$$

where ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, respectively. The ionic polarization charge, q'_{pol} , is the effective charge on a configurationally relaxed defect in charge state q' that arises from the ionic polarization response of the material to the electric field created by the periodically repeated charged defect. The ionic polarization charge *necessarily arises because of a nonzero divergence of the polarization field* near a charged defect that is configurationally relaxed [52], and this process is physically responsible for the difference between ϵ_0 and ϵ_∞ . While q'_{pol} has always been present on a charged defect that is configurationally relaxed, we have typically accounted for it through the static dielectric constant of the material alone, such that it remains implicit.

In contrast, for a vertical transition, the fixed ionic configuration produced by q' determines the ionic polarization, but the electronic polarization, which physically is responsible for ϵ_∞ , responds to both the new defect charge state and the fixed ionic polarization charge. Thus, one must account for both the fixed ionic polarization and the high-frequency dielectric constant to correctly model the complex *mixture of electronic and ionic screening* that occurs in a vertical transition. In Eq. (5), the first term on the right represents the standard finite-size correction for a defect when fully relaxed (both electronically and ionically) at its ground state, $\mathbf{R}_{q'}$, while at its *initial charge state*, $q^* = q'$, such that the applicable dielectric constant is $\epsilon_* = \epsilon_0$. The second term in essence removes the ground-state correction, but *now with the ionic polarization charge explicitly included*, $q^* = q' + q'_{\text{pol}}$, and the ionic configuration now held fixed at $\mathbf{R}_{q'}$, such that $\epsilon_* = \epsilon_\infty$. The third term represents the finite-size correction of the defect when electronically (but not ionically) relaxed while at its *final net charge state*, $q^* = q + q'_{\text{pol}}$, with the ionic configuration still fixed such that again, $\epsilon_* = \epsilon_\infty$.

For interested readers, Falletta *et al.* [52] offer a concise, conceptual derivation of Eqs. (4)–(6), along with a more detailed and rigorous discussion than offered here. Alternatively, Gake *et al.* [51] offer an earlier, groundbreaking, and more mathematical elaboration of the same physics, where the focus is on the portion of the finite-size correction associated with the vertical transition alone, denoted $\mu_{\text{cor}}(q' \rightarrow q, \mathbf{R}_{q'})$, which is just Eq. (5) with the well-known ground-state term omitted.

To apply Eq. (5) to DFT calculations, one must define the stipulated model-dependent energy-correction function, $E_m(q^*, \epsilon_*)$. Gake *et al.* [51] and Falletta *et al.* [52] have repurposed the ground-state finite-size correction method of Freysoldt, Neugebauer, and Van de Walle (herein, the FNV

method) [65–67], which allows them to define $E_m(q^*, \varepsilon_*)$ as follows:

$$E_m(q^*, \varepsilon_*) = \frac{M(q^*)^2}{2L\varepsilon_*} + q^* \Delta V(q^*, \varepsilon_*), \quad (7)$$

$$\begin{aligned} \Delta V(q^*, \varepsilon_*) &= -\frac{2\pi Q_m^*}{3L^3\varepsilon_*} = \frac{2\pi}{3L^3\varepsilon_*} \int dr^3 \rho^{q^*}(\mathbf{r})r^2 \\ &= I[\rho^{q^*}(\mathbf{r})]/\varepsilon_*. \end{aligned} \quad (8)$$

In Eq. (7), the term $M(q^*)^2/2L\varepsilon_*$ is the magnitude of the Madelung energy of a periodic array of defects when approximated as point charges, q^* , immersed in a uniform background of charge-neutralizing jellium [55,56]. Here, M is the Madelung constant, V_s is the supercell volume, and $L = V_s^{1/3}$. The term $q^* \Delta V(q^*, \varepsilon_*)$ is the higher-order correction produced by the alignment potential, $\Delta V(q^*, \varepsilon_*)$, as defined by FNV [65–67].

By recalling Makov and Payne’s groundbreaking work on electrostatic finite-size effects in periodic supercells, Komsa *et al.* have shown that $\Delta V(q^*, \varepsilon_*)$ may alternatively involve Q_m^* , which, as seen in Eq. (8), is the quadrupole moment of the radial charge distribution, $\rho^{q^*}(\mathbf{r})$, where ρ^{q^*} is defined as a difference of the defect-charge distribution and the model-charge distribution used to assess finite-size effects [56,69,70]. Equations (7) and (8) prove useful when manipulating Eq. (5) for comparison to its various alternative forms in the literature. The notable charge-density differencing method introduced by Makov and Payne presages the potential-difference-based alignment approach used in the later FNV method. In practice, the *sxdefectalign* code used to implement the FNV method redefines the alignment potential as $-\Delta V(q^*, \varepsilon_*) = C$ [65–67], which is not to be confused with our use of C below for the capture coefficient.

By using Eqs. (7) and (8) to expand the model functions in Eq. (5), one obtains the finite-size correction of a vertical transition in a less symbolic, more useful form. As a notational convenience, we partition the expanded correction into contributions arising from the Madelung energies (which are first-order in $1/L$ and denoted by E_{cor}^M) and contributions arising from potential alignment (which are third order in $1/L$ and denoted by E_{cor}^A). The partitioning yields the following expanded results for Falletta *et al.* [52]:

$$E_{\text{cor}}^M(q, \mathbf{R}_{q'}) = \frac{M}{2L} \left[\frac{(q')^2}{\varepsilon_0} - \frac{(q' + q'_{\text{pol}})^2}{\varepsilon_\infty} + \frac{(q + q'_{\text{pol}})^2}{\varepsilon_\infty} \right], \quad (9)$$

$$\begin{aligned} E_{\text{cor}}^A(q, \mathbf{R}_{q'}) &= q' \Delta V(q', \varepsilon_0) - (q' + q'_{\text{pol}}) \Delta V(q' + q'_{\text{pol}}, \varepsilon_\infty) \\ &\quad + (q + q'_{\text{pol}}) \Delta V(q + q'_{\text{pol}}, \varepsilon_\infty). \end{aligned} \quad (10)$$

If the localized defect charge is assumed to be pointlike, the Madelung-energy contribution of Eq. (9) is readily seen to be algebraically equivalent to other results obtained earlier by Gake *et al.* [51] (see Ref. [53] for a proof) and later by Kumagai [50]. In Kumagai’s case, the Madelung correction has been adroitly simplified by defining an effective dielectric constant for a vertical transition given by

$$1/\varepsilon_{\text{eff}} = 1/\varepsilon_\infty - 1/\varepsilon_0. \quad (11)$$

The use of Eq. (11) along with Eq. (6) allows Eq. (9) to be tersely recast as follows:

$$E_{\text{cor}}^M(q, \mathbf{R}_{q'}) = \frac{M}{2L} \left[\frac{q^2}{\varepsilon_0} + \frac{(q - q')^2}{\varepsilon_{\text{eff}}} \right], \quad (12)$$

where we have modified Kumagai’s results (originally developed for a CC diagram) to apply in general for a vertical transition. We find that all these existing treatments of the point-charge Madelung energy [50–53] are also exactly reproduced in direct calculations done using the *sxdefectalign* code’s implementation of the Madelung-energy-related finite-size correction for a vertical transition state [67].

In contrast to these Madelung-related finite-size corrections, we find that direct calculations of the corresponding alignment-related corrections vary quite noticeably (see the computational results and discussion in Sec. III B 3) for each of the published formulations that utilize a summed series of pseudo-ground-state corrections to describe the correction of a vertical transition state [50–53]. In practice, one may avoid any unintended variations introduced by the original pseudo-ground-state approaches by using the finite-size correction capability recently implemented within the *sxdefectalign* code to describe a vertical transition state [67]. In Eq. (16) of the *sxdefectalign* code manual, Freysoldt has simplified the alignment portion of the finite-size correction to read as follows [67]:

$$\begin{aligned} E_{\text{cor}}^A(q, \mathbf{R}_{q'}) &= [q_1 + q_2] \mathcal{C}_{\text{vt}} = q \Delta V_{\text{vt}}(q', q - q', \varepsilon_0, \varepsilon_\infty) \\ &= q \Delta V(q - q', \varepsilon_{\text{eff}}), \end{aligned} \quad (13)$$

where, as we discuss below, the code takes $q_1 + q_2 = -q$, and where herein, the subscript vt designates that the true vertical-transition-state capability of *sxdefectalign* has been used. The last term of Eq. (13) reflects another observation of Kumagai’s where he has noted that the value of $-\mathcal{C}_{\text{vt}}$ given by *sxdefectalign*’s vertical-transition-state capability can be alternatively calculated using the code’s ground-state capability by using $(q - q', \varepsilon_{\text{eff}})$ as pseudo-ground-state input parameters. When correcting vertical transitions using the FNV method, we prefer to use the intended vertical-transition-state capability implemented within *sxdefectalign*—in place of the various manually summed, pseudo-ground-state formulations built around the code’s earlier ground-state capability—because the intended path gives the vertical transition state’s finite-size correction using a single, consistently applied, electrostatic-modeling step.

To apply Eqs. (12) and (13) to the DFT-based defect energies used to construct a CC diagram, we must next relate a vertical transition’s charge states, q and q' , to the charge states and configuration coordinates that define the diagram.

C. Finite-size corrections within CC diagrams

While Gake *et al.* have alluded to CC diagrams and their associated optical transitions as exemplars motivating the development of the above-discussed finite-size corrections for vertical transition states [51], Kumagai’s recent work is the first to consider in detail how to implement related corrections within a CC diagram [50]. Here, we will further explicate Kumagai’s groundbreaking results by appealing to the linearity of electrostatic theory and dielectric screening.

Indeed, long-range electrostatic interactions primarily cause the spurious finite-size artifacts found in DFT calculations of defect formation energies, and these interactions prominently degrade the accuracy of not only configurationally relaxed defects, but also the unrelaxed, configurationally interpolated defects that compose a CC diagram. These electrostatic interactions depend on the net charge of the supercell, q , localized on the defect, the dielectric properties of the surrounding material, and the ionic displacement field of the defect when embedded within a periodic supercell. For typical semiconductors and insulators (ferroelectrics and unusual, highly nonlinear materials are excluded) and realistic electric field strengths, we can assume that the dielectric response of both the ions and electrons in a material is linear [115]. *In particular, we can assume a linear relationship between the displacement of the ions associated with ionic screening and the resulting ionic polarization field of the material.*

Thus, when the supercell's ionic positions are linearly interpolated along the configuration coordinate, $Q(\alpha)$, the resultant ionic polarization field and its associated polarization charge, q'_{pol} , must also vary linearly with α . At the configurationally relaxed end points, Eq. (6) determines q'_{pol} from the defect charge q' that controls the long-ranged dielectric response, and a straightforward linear interpolation determines q'_{pol} for each of the interpolated defect configurations. We can then invert Eq. (6) to determine that the effective charge, q' , must also vary linearly with α . The needed finite-size corrections for the CC diagram immediately follow by substitution of the interpolated values of q'_{pol} and q' into either Eq. (5) or its subsequent variations, Eqs. (9)–(13). While q' emerges here as a parameter derived from the linear electrostatic response of the displaced ions, and while no linkage of q' to configurationally relaxed defect states proves necessary—except for those resting at the CC diagram's interpolative end points—Eq. (5) *et seq.* still formally apply.

Because q'_{pol} has been eliminated from Eqs. (9)–(13), we ultimately need to consider only q' , which we write in terms of the above-described linear interpolation in α :

$$q' = q_e \pm \alpha_e \Delta q_c, \quad (14)$$

$$q' = q_r \mp \alpha_r \Delta q_c. \quad (15)$$

In Eqs. (14) and (15), the upper sign applies for hole capture, the lower sign applies for electron capture, and the choice of which equation to use is determined by the branch of the CC diagram under consideration when performing the DFT calculations. Finally, Δq_c determines the ultimate sign of α , as Δq_c depends on the type of capture:

$$\Delta q_c = q_r - q_e = \pm 1. \quad (16)$$

With Eqs. (14)–(16) in hand, we see that the total finite-size correction given by summing Eqs. (12) and (13) reduces further when making finite-size corrections within a CC diagram:

$$E_{\text{cor}}(q, \mathbf{R}_{q'}) = \frac{M}{2L} \left[\frac{q^2}{\epsilon_0} + \frac{(\alpha \Delta q_c)^2}{\epsilon_{\text{eff}}} \right] + q \Delta V_{\text{vt}}(q', q - q', \epsilon_0, \epsilon_{\infty}). \quad (17)$$

Here, the first-order Madelung-energy correction term is that of Kumagai [50], while the third-order potential-alignment term is that of Freysoldt [67], and not that of Refs. [50–52]. In Eq. (17), the parameter Δq_c appears to formally convert the dimensionless units of α to those of charge.

To implement Eq. (17) using *sxdefectalign*, one uses the vertical-transition-state capability available in the software, where the input parameters for correcting DFT-based CC diagrams involve ϵ_0 , ϵ_{∞} , q , and q' [now calculated per Eqs. (14)–(16)]. Importantly, the software uses recast charges q_1 and q_2 given by

$$q_1 = -q' \quad \text{and} \quad q_2 = -(q - q'), \quad (18)$$

where the leading negative signs support the atomic units used for charge in the code's input files [67]. In closing, we reiterate that application of Eqs. (14)–(18) requires the use of q and α taken as the local values, (q_e or q_r) and (α_e or α_r), appropriate for the type of capture and branch of interest on the CC diagram.

D. Benchmarking of finite-size correction methods

To obtain benchmark finite-size corrections for comparison to the potential-alignment approach detailed in the previous two sections, we have used a hybrid approach that retains the above-described Madelung energies for a neutralized point-charge array, while replacing the potential-alignment step with a physically motivated curve-fitting step. This less-common method requires multiple supercell sizes and builds upon simpler, related models used in Refs. [116–121]. The laborious use of multiple supercells is of particular interest not only because it provides a means for independently benchmarking alignment-based finite-size corrections, but also because it provides a means to directly assess the validity of the first-order portion of the correction scheme proposed by Kumagai [50].

In practice, our hybrid approach entails least-squares fitting of a set of uncorrected defect-formation energies, $E_f(1/L)$, to an expression of the form

$$E_f(1/L) = E_0 - \frac{M}{2L} \left\{ \frac{q^2}{\epsilon_0} + \frac{(\alpha \Delta q_c)^2}{\epsilon_{\text{eff}}} \right\} + \frac{a_3}{L^3} + \frac{a_5}{L^5} + \dots + d e^{-\mu L}, \quad (19)$$

where again, $L = V_s^{1/3}$. For hexagonal supercells, $V_s = (\sqrt{3}/2)a_s^2 c_s$, where $a_s = ma$, $c_s = nc$, and the supercells consist of $m \times m \times n$ primitive cells of wurtzite GaN having lattice constants a and c . Importantly, the second term of Eq. (19) derives from the known Madelung energy given by the first term on the right in Eq. (17) *and is not a fitted quantity*. The first and third terms of Eq. (19) involve the primary fitting parameters, E_0 and a_3 , where E_0 is the fully corrected defect energy and a_3/L^3 serves as a generalized replacement for the potential-alignment correction. Because of the unusually large range of cell sizes examined in the present work, we also include an optional, higher-order, fitted term, c_5/L^5 . In addition, we introduce an optional exponential term describing k -point-sampling-dependent finite-size errors arising from wave-function overlap, where these errors are parametrized

by a prefactor, d , and a linear attenuation coefficient, μ . This last term stems from Freysoldt *et al.*'s tight-binding study of the scaling behavior of wave-function-overlap errors [76]. As will be discussed in Sec. III, we have deployed Eq. (19) in multiple, coupled forms to investigate and visualize the interdependent effects of k -point-sampling and supercell-size convergence.

Least-squares fitting of finite-size nonlinearities in $1/L$ by using Eq. (19) advantageously captures certain $1/L^3$ contributions and other nonlinearities that potential alignment alone cannot. Such contributions may include (i) elastic interaction of the periodic array of defects [55,122–128], (ii) the above-noted wave-function overlap errors [76], and perhaps other electrostatic effects [129]. The obvious tradeoff of the less used fitting approach is the significantly increased computational cost of the multiple defect calculations, necessarily done at high numerical accuracy for a wide range of supercell sizes to realize high-quality results sufficient for benchmarking purposes.

E. Carrier-capture coefficients

To calculate the carrier-capture coefficient, C , we used the single-effective-mode static-coupling approximation as developed in Refs. [8,14–16,22,25,35], with C as recently expressed in Ref. [35]:

$$C = f \frac{2\pi}{\hbar} g V_s W_{if}^2 \sum_m w_m \sum_n |\langle \chi_{im} | \hat{Q} - Q_o | \chi_{fn} \rangle|^2 \times \delta(\Delta E + m\hbar\Omega_i - n\hbar\Omega_f), \quad (20)$$

where

$$\begin{aligned} W_{if} &= \langle \psi_i | \frac{\partial \hat{H}}{\partial Q} | \psi_f \rangle \\ &= (\varepsilon_f - \varepsilon_i) \left\langle \psi_i \left| \frac{\partial \psi_f}{\partial Q} \right. \right\rangle \\ &= (\varepsilon_f - \varepsilon_i) \frac{\partial}{\partial Q} \langle \psi_i | \psi_f \rangle. \end{aligned} \quad (21)$$

In Eq. (20), f is a product of correction factors f_s and f_c , where f_s is the temperature-dependent Sommerfeld scaling factor that corrects for enhancement or suppression of the capture rate due to Coulomb attraction or repulsion [16,25,35], and f_c is a separate scaling factor that corrects for spurious wave-function interactions of the charged defect with valence-band-edge states [25,35]; g is the degeneracy of the final atomic configuration of the defect; V_s is the supercell volume used to determine W_{if}^2 ; and W_{if} are electron-phonon matrix elements. The double summation over phonon quantum numbers, m and n , in Eq. (20) involves the harmonic-oscillator wave functions, χ_{im} and χ_{fn} , representing the initial and final vibrational states, where the weight factor w_m is the thermal occupation of initial state m , and where Q_o is the difference in Q for the initial and final ground-state configurations of the defect. Finally, in the δ -function argument of Eq. (20), ΔE is the energy of the defect's charge-state transition level, taken here with reference to the band edge supplying the captured free carrier, and $\hbar\Omega_{i,f}$ (or elsewhere herein $\hbar\Omega_{e,r}$) are the initial- and final-state (or elsewhere herein, the excited- and relaxed-state) phonon energies.

Turning to Eq. (21), we have departed slightly from Ref. [35] as the present expression defining W_{if} applies for norm-conserving pseudopotentials (NCPs). Here, ψ_i and ψ_f are Kohn-Sham electronic wave functions for the defect-containing supercell in its initial and final states, $\hat{h}$ is the Kohn-Sham Hamiltonian, and $\varepsilon_f - \varepsilon_i$ represents a difference of the electronic wave functions' eigenvalues. An analogous expression for calculating W_{if} using the projector-augmented-wave (PAW) method, which produces smooth, non-norm-conserving wave functions and requires the introduction of an overlap operator, is given in Ref. [35]. Further in-depth discussion of the derivation and usage of Eqs. (20) and (21) appears in Refs. [25] and [35].

F. Computational details

DFT calculations were primarily performed using the SOCORRO electronic-structure code [130], semilocal norm-conserving pseudopotentials, and the hybrid-functional of Heyd, Scuseria, and Ernzerhof (HSE06) [131,132] as implemented within LIBXC [133]. Pseudopotentials for Ga, N, and C were either obtained from ABINIT [134] or built by using the FHI98PP software package [135]. Resulting FHI98PP data were converted in format for use in Socorro with a final representation in the Kleinman-Bylander format [136]. An 816-eV cutoff was used to define the plane-wave basis for the Kohn-Sham orbitals and the Kleinman-Bylander projectors, while a 3265-eV cutoff was used to define the plane-wave basis for the electron density and local potentials. Substitutional C_N defects were constructed from hexagonal bulk-GaN supercells having sizes of 16, 128, 432, and 1024 atoms, with the supercell aspect ratio fixed at $c_s/a_s \cong 0.812$. Additional supporting calculations have used supercells constructed from either hexagonal cells having a size of 192 atoms, or orthohexagonal cells [137] having a size of 96 atoms [138]. Sampling meshes in the Brillouin zone were constructed using the mean-value (Baldereschi) technique [139,140] and the Monkhorst-Pack (MP) technique [141], where even-index MP basal-plane-mesh components were shifted off the Γ point. The maximum MP mesh size was varied inversely with cell size, as detailed in Sec. III A. Occupation of the Kohn-Sham orbitals was calculated using a Fermi distribution with $kT = 25.7$ meV. The energy-change tolerance for self-consistent-field (SCF) electronic-structure iterations was $< 3 \times 10^{-5}$ eV, while the maximum force tolerance (rms) for structural-relaxation iterations of atomic coordinates was $< 3 \times 10^{-3}$ eV/Å. For SOCORRO, the exact-exchange mixing parameter for HSE06 was set to 0.27 to reproduce the low-temperature band gap of GaN [142].

Supporting DFT calculations used for ground-state or other benchmarking purposes were performed by using the VASP code [143], the PAW method [144], and the HSE06 functional as natively implemented in VASP. In this case, the Ga pseudopotentials treated the Ga-3d electrons first as core and then as valence, producing two distinct sets of results. A 520- or 526-eV cutoff was used to define the plane-wave basis for calculations for the core or valence treatments, respectively. The occupations of the Kohn-Sham orbitals were calculated using Gaussian distributions with $\sigma = 25$ meV. The SCF energy tolerance was $< 1 \times 10^{-5}$ eV, while the maximum force

TABLE I. Comparison of calculated and measured bulk properties of GaN. The measured lattice parameters, internal-distortion parameter, and band gap of GaN have been taken from experiments reported in Refs. [148,149], and [142], respectively.

Pseudopotential type	Ga-3d treatment	a (Å)	c (Å)	u (Å)	E_g (eV)
NCP	core	3.178	5.163	0.3776	3.467
PAW	core	3.193	5.186	0.3776	3.512
PAW	valence	3.178	5.166	0.3773	3.481
Exp.		3.189	5.186	0.377	3.503

tolerance (per atom) was <0.01 eV/Å. Supercell sizes and Brillouin zone sampling were as above. For VASP, the mixing parameter for HSE06 was set to 0.30 or 0.29 for the core or valence treatments, respectively. For calculations done using both VASP and SOCORRO, nonaliased FFTs and reciprocal-space projectors were both used to further ensure accuracy.

All our finite-size corrections have used recent, high-quality, experimental quantities for the static and high-frequency dielectric constants of GaN [145]. These experiments differ by <0.5 – 1.2% from precise DFT calculations done using either the local-density-approximation [146,147] or the HSE06 hybrid-functional [110]. The somewhat anisotropic dielectric response of GaN has been included by suitable averaging of the dielectric-tensor components [67,71,72], giving $\bar{\epsilon}_0 = 9.587$ and $\bar{\epsilon}_\infty = 5.303$.

Table I shows calculated benchmarking results for the lattice parameters, a and c , the internal-distortion parameter, u , and the band gap, E_g , of bulk GaN obtained using the above computational methods. For both SOCORRO and VASP, we observe very good agreement between our calculations and the experimental results also shown in the table [142,148,149].

III. RESULTS AND DISCUSSION

A. Ground states of C_N

Previous hybrid-functional DFT studies have extensively investigated the ground states of C_N in GaN [25,35,106–112], wherein it is widely agreed that there are three possible strongly localized charge states ($q = -1, 0$, and $+1$) and two resulting defect levels within the band gap of GaN, with the defect possibly exhibiting deep-acceptor or deep-donor behavior, depending on the Fermi level. For the $q = -1$ ground state of C_N , the defect has C_{3v} symmetry, no spin polarization, nearly equal C–Ga bond lengths for all four nearest-neighbor bonds, and moderate, uniform bond strains ($\Delta l/l = -0.02$) [106]. For the $q = 0$ ground state, two possible defect structures have been mentioned in the literature [106,110], with the reported structures found to have similar formation energies. The first structure reported (designated as the $\perp$ configuration) retains near- C_{3v} symmetry [106], where the C–Ga bond oriented perpendicular to the basal plane becomes very elongated ($\Delta l/l = +0.08$), and the other three C–Ga bonds are near the bulk bond length ($\Delta l/l = +0.01$) with their bond-axes oriented partially parallel to the basal-plane. The second structure (designated as the $\parallel$ configuration) breaks symmetry by lowering to C_{1h} , and a very elongated C–Ga bond again appears [110]. In this case, however, the longest bond becomes one of the three orientations resting partially parallel to the basal plane. The other three bonds are again nearer the

bulk length [110] but are of slightly unequal length in accord with the broken symmetry. For both $q = 0$ structures there is one unpaired spin. Finally, for the $q = +1$ ground-state, the defect symmetry is C_{1h} , there are two unpaired spins, and the structure exhibits much less bond-length variation than $q = 0$.

Here, we have recalculated the C_N ground states as a function of supercell size with two goals in mind: the first was to find the fully relaxed defect structures necessary for constructing supercell-size-dependent CC diagrams; the second was to further benchmark our computational methods against established work. While most of our results for ground states and CC diagrams were obtained by using NCPs and the SOCORRO code, with Ga- d electrons treated as core, we later revisited the C_N ground states using VASP. The latter effort produced two sets of additional ground-state results, one with Ga- d electrons treated as core, and one with them treated as valence. The use of multiple codes, pseudopotential types, d -electron treatments, and finite-size correction methods facilitated deeper comparisons to previous work.

Table II summarizes our results for the transition levels of C_N in GaN and compares these to the levels seen in previous hybrid functional studies; we see relatively good agreement between the present work and all previous hybrid functional work, in contrast to similar comparisons for some of the native point defects in GaN. This agreement results in part for two reasons. First, the convergence of C_N is relatively fast with respect to k -point sampling, with Γ -point sampling giving unusually useable accuracy even for smaller, 96- and 128-atom supercells. Indeed, the Group-averaged defect levels shown in Table II differ by <0.15 eV when moving from the lowest-rigor (Group A) to the highest-rigor (Group C) combinations of k -point sampling and cell size. Second, the removal of finite-size effects for C_N places only modest demands on the correction methods because no ground states of C_N are multiply charged, and because the observed $1/L^3$ nonlinearities for $E_f(1/L)$ are atypically small. In Table II, we have averaged this work’s defect-level values involving the $\perp$ and $\parallel$ configurations of the $C_N(q = 0)$ defect, as the defect levels of the two configurations differ by only 3–24 meV. Comparing the various 0/–1 levels in Table II to the published measurements summarized in Table III, we see that the hybrid-functional theory and the experiments span a similar range of values, 0.89 – 1.1 eV vs 0.87 – 1.04 eV, respectively. Aptly, the most rigorously performed calculations (Table II, this work, Group C) show excellent agreement with the most accurate experiments (Table III, PL-ZPL and TC results), further demonstrating the thoroughness of our computational methods.

While the theory and experiments generally agree, it nevertheless proves useful to further scrutinize Table II. By comparing the computational parameters and average defect

TABLE II. Computational parameters and charge-state transition levels, E_t , for hybrid-functional studies of substitutional C_N in GaN. The tabulated results have been divided into groups according to the methods used for k -point sampling and finite-size corrections. “Bald.” indicates the mean-value k -point of Baldereschi [139,140].

Referenced work	Ga-3d treatment	Finite-size method	No. of atoms	k -point sampling	w.f. cutoff (eV)	Force tolerance (eV/Å)	$E_t(0/-1)$ (eV)	$E_t(+1/0)$ (eV)
Demchenko <i>et al.</i> [107]	core	mLZ	128	Γ point	400	0.05 max	1.04	0.48
Deák <i>et al.</i> [111]	valence	mFNV	128	Γ point	420	0.02 max	1.1	0.3
Group A {						average:	1.070	0.390
						std dev:	± 0.042	± 0.127
Alkauskas <i>et al.</i> [25]	core	FNV	96	Bald.	400	0.005 max	1.02	
Turiansky <i>et al.</i> [35]	core	FNV	96	Bald.	400		1.06	
Lyons <i>et al.</i> [106]	core	FNV	96	$2 \times 2 \times 2$	300		0.90	0.35
Lyons <i>et al.</i> [112]	core	FNV	96	$2 \times 2 \times 2$	400		0.90	0.30
Matsubara <i>et al.</i> [110]	valence	FNV	96	$2 \times 2 \times 2$	425	0.05 max	0.89	0.26
Group B {						average:	0.954	0.303
						std dev:	± 0.080	± 0.045
This work, by NCP	core	hyb. fit	varied:	varied:	816	0.003 rms	0.936	0.298
This work, by PAW	core	hyb. fit	16 to	$5 \times 5 \times 5$ to	520	0.01 max	0.948	0.304
This work, by PAW	valence	hyb. fit	1024	Γ point	526	0.01 max	0.904	0.269
Group C {						average:	0.929	0.290
						std dev:	± 0.023	± 0.019

levels shown for each Group in Table II, one may observe a correlation of the defect levels with some of the computational parameters that have been used. Still focusing on the 0/−1 level central to the present carrier-capture modeling, we see that this level’s Group-averaged value decreases from 1.070 eV down to 0.929 eV as the k -point sampling progressively improves and as the chosen finite-size correction methodology evolves. As regards the latter, Group A in Table II has used modified versions of the standard Lany-Zunger [63] and FNV correction methods [65,66] (designated as “mLZ” and “mFNV” in Table II); Group B has used the FNV method without modification; and finally, Group C has

TABLE III. Experimental results for the 0/−1 charge-state transition level of substitutional C_N in GaN. Tabulated results were measured using deep-level optical spectroscopy (DLOS), deep-level transient spectroscopy (DLTS), photoluminescence (PL) spectroscopy, and transient capacitance (TC). For the DLOS, the reported Frank-Condon shift has been removed, giving the thermodynamic level in the table. ZPL represents the energy of the zero-phonon line.

Experimental method	Temp. (K)	$E_t(0/-1)$ (eV)
DLOS [104]	298	0.89
DLTS [90,94]	298	0.86, 0.87
Optical-current DLTS [83]	370	0.940
PL activation energy [78]	>480	0.86 ± 0.04
PL activation energy [87]	>590	1.04
PL upper threshold [78]	4.2	0.910
PL of the ZPL [97]	18	0.916 ± 0.003
TC in p - n diode [104]	298	0.89 ± 0.02

used our hybrid-fitting method described in Sec. IID (designated “hyb. fit” in Table II).

The correlated downward trend in the values of the 0/−1 level becomes notable in the present context because of the original work on $C_N(q = -1)$ hole capture by Alkauskas *et al.* [25]. These authors have proposed that if their 0/−1 level were corrected downwards by only 0.13 eV (from 1.02 eV for their 0 K DFT, to an estimated 0.89 eV for the 400–600 K used in experiment [95]) they would obtain a much-improved agreement between theory and experiment for their calculated hole-capture coefficients for C_N . The 0/−1 level of 0.936 eV found here (Table II, Group C, NCP, which enters our CC diagrams below) moves substantially in the suggested direction, but primarily for computational reasons, and not thermal ones as originally argued. Regardless, the reduced level found here at 0 K indicates that our revisited hole-capture coefficients for C_N should tend towards correctly higher values—even in the absence of any finite-size-correction improvements in the CC diagrams still to come.

B. Finite-size correction of configuration-coordinate diagrams

1. Defect energies corrected using hybrid-fitting

Figure 1 shows the application of our hybrid finite-size correction method (Sec. IID) to defect energies for substitutional C_N calculated for use within a CC diagram according to Eq. (4) [but sans $E_{\text{cor}}(q, \mathbf{R}_{q'})$] for selected defect configurations constructed according to Eqs. (1)–(3). Figure 1(a) for $C_N(q = 0)$ is immediately seen to be quite striking—even before discussing the fitting of the data—in that the asymptotic slopes of $E_f(1/L)$ as $1/L \rightarrow 0$ clearly rise monotonically with Q , and do not remain constant at zero as seen for the

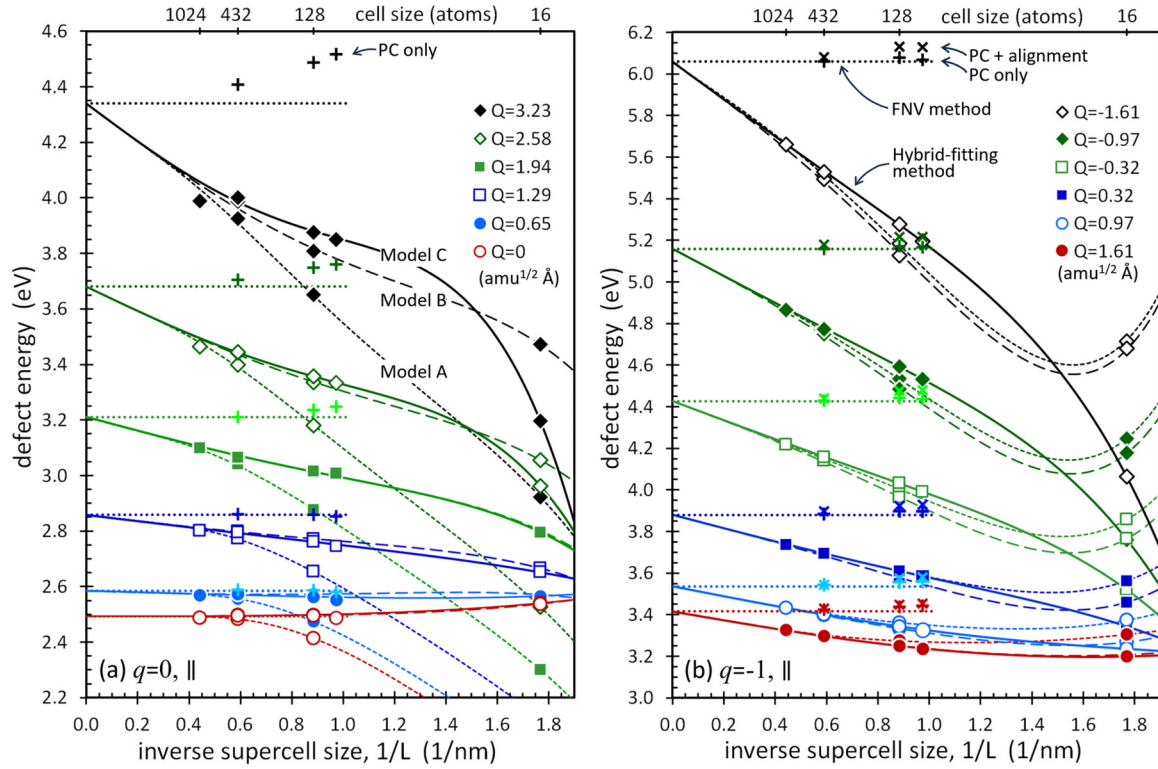


FIG. 1. Defect-formation energies for substitutional C_N plotted vs inverse supercell size for selected configuration coordinates, Q , where (a) $q = 0$ and (b) $q = -1$. Larger plotted symbols show DFT-based defect energies for the $\parallel$ configuration of C_N prior to application of any finite-size corrections. Corresponding plotted curves show least-squares fitting results for a linked hybrid-fitting method, where the linked model components (A, B, and C) are described in the main text. Separate sets of smaller symbols (+ and $\times$) plotted adjacent to horizontal reference lines show defect energies after FNV-method finite-size corrections have been independently applied to the same uncorrected defect energies, where the two differing FNV treatments (labeled “PC” and “PC + alignment”) are also described in the main text. For those interested in a clearer view of the fitted data, simplified plots of the fitted curves and data sets are separately shown for each of the contributing Model components (A, B, and C) in the Supplemental Material [150].

$q = 0$ relaxed-defect configuration [Fig. 1(a), $Q = 0$]. This immediately refutes the validity of typically used finite-size corrections for relaxed configurations, which instead predict a constant slope of zero.

Delving further into Fig. 1, we see that for each Q , the associated plot of $E_f(1/L)$ has three distinct curves fitted to the uncorrected defect energies, which are plotted as the larger symbols. The three curves represent three corresponding models [designated here as Models A (fine-dashed lines), B (coarse-dashed lines), and C (solid lines)] that are parametrically linked to each other to define a global least-squares fitting model, which we apply to three corresponding sets of defect energies calculated for each value of Q . Model A consists of Eq. (19) in full, where the fitted defect energies are initial Γ -point-sampled DFT calculations done for all values of Q and all cell sizes of interest. The exponential term in Eq. (19) is necessarily included because of the large wave-function-overlap errors produced by our intentional use of Γ -point sampling [76] within the linked analysis. Model B is again Eq. (19), with the exponential term now omitted. Here, the fitted defect energies result from taking the Γ -point-sampled ionic configurations from Model A and rerunning each of them for a single SCF electronic-structure iteration cycle at some improved k -point sampling, without any ionic relaxation allowed. For Models A and B, the fitting parameters

E_0 , a_3 , and a_5 in Eq. (19) are shared when jointly fitting these models’ respective defect energies. The differences between the two modeled data sets enables an embedded estimate of the previously unexamined wave-function overlap error term, $de^{-\mu L}$. Model C resembles Model B, but the only shared fitting parameter is E_0 , which joins all three models. For Model C, the fitted defect energies are all fully converged with respect to k -point sampling, with the sampling density increasing as cell size decreases. Because the ionic configurations differ from those for the earlier, uniformly applied Γ -point sampling, the fitting parameters a_3 and a_5 differ from those in Models A and B. Use of the parametrically linked models provides enhanced quantitative information on the combined convergence with respect to k -point sampling and cell size, while also facilitating improved estimates of the likely uncertainty in the final defect energy because of the finite-size correction methodology.

As seen in both Figs. 1(a) and 1(b), the linked fits are excellent, with the Kumagai-predicted charge states and the associated fixed-configuration ($Q \neq 0$) Madelung energies giving visually satisfying predictions of the slopes of the uncorrected DFT defect formation energies. If we focus on the fitted curves seen for Model A versus Model B, we see that differences between the two models and their fitted data are captured quite well by the approximate exponential term

described by Freysoldt [76]. If we instead focus on the fitted curves for Model C, we see that nonlinearities in the plots of $E_f(1/L)$ are on the whole quite modest, excepting extreme cases where large values of Q and very small cell sizes coexist to drive a more noticeable local curvature. The only notable fitting failures appear at the largest cell size (1024 atoms) as Q exceeds $1.94 \text{ amu}^{1/2} \text{ \AA}$ for the neutral-defect energies shown in Fig. 1(a). These deviations result from a cell-size-dependent band-structure effect (as detailed below) and are not a failure of either Eq. (19) or Kumagai's new approach to finite-size corrections for CC diagrams.

We have assessed the uncertainty of the finite-size-corrected defect-formation energies produced by the hybrid-fitting approach by refitting the uncorrected defect energies for three additional cases using either subsets of the originally fitted data, or subsets of the globally linked model. Case 1 used the original model but omitted all the 1024-atom supercell data; case 2 used linked Models A and B only; and case 3 used Model C only, with the latter cases fitted to all cell sizes. For the refitting of $C_N(q = -1)$ defects in the parallel configuration, the mean absolute error (MAE) of the refitted values of $E_f(1/L = 0)$ relative to the corresponding originally fitted values was found to be only 0.0025 eV, where the MAE was calculated across all three refitted cases for all 16 values of Q . A similarly calculated MAE for $C_N(q = 0)$ defects gave 0.0030 eV. In the latter case, invalid DFT data sets for the three largest values of Q have been omitted because of the band-structure effects alluded to just above. On the whole, the hybrid-fitted results are quite stable for reasonable variations in both the range of fitted data and the selected model.

Because the uncertainty of the finite-size corrections accomplished using the hybrid-fitting procedure appears to be quite small, the overall uncertainty for *differences of defect energies* calculated in this work is likely dominated by more fundamental considerations like the pseudopotential implementations, the Ga-3d-electron treatments, and the selection and tuning of the hybrid-functionals. These latter sources of errors are suggested to be significantly less than $\pm 50 \text{ meV}$ by (i) the small standard error ($\pm 23 \text{ meV}$) observed among the differing DFT treatments used within the Group-C results shown in Table II and (ii) the fact that the mean of these treatments (0.929 eV) nearly equals the most accurate experimental results available for the $-1/0$ level (0.916 eV).

2. Defect energies corrected using Madelung energies and potential alignment

To assess differences between our hybrid-fitted results for $E_f(1/L = 0)$ and finite-size-corrected results obtained using Madelung energies and potential-alignments, we separately calculated $E_f(1/L = 0)$ for each of our 96-, 128-, and 432-atom results by using the *sxdefectalign* code in conjunction with the charge states defined in Eqs. (14)–(16) and Eq. (18), as described at the end of Sec. II C. For comparison, these corrections have been obtained using the Madelung point-charge (PC) energies alone [“+” symbols labeled as “PC only” in Figs. 1(a) and 1(b)] and using the Madelung energies along with potential alignments [“x” symbols labeled as “PC + alignment” in Fig. 1(b)]. The difference in the energy of each plotted symbol and the plotted reference line determined by

the hybrid-fitting method (horizontal dotted lines in Fig. 1) indicates the estimated error of the FNV approach as a function of $1/L$.

For the $C_N(q = 0)$ defects in Fig. 1(a), the FNV PC-only results for $E_f(1/L = 0)$ lie on the reference lines defined by the fitting for $Q \leq 1.61 \text{ amu}^{1/2} \text{ \AA}$, indicating the two methods closely agree for these Q . This agreement is essentially by construction, as the hybrid-fitted curves and the FNV-corrected data points intentionally use identical Madelung-energies, and the alignment term vanishes here for all Q because $-q = q_1 + q_2 = 0$. In contrast, the FNV PC-only results increasingly rise above the reference lines as Q exceeds $1.61 \text{ amu}^{1/2} \text{ \AA}$. In this regime, the defect charge is thought to become partly delocalized for reasons to be discussed below, in which case, neither of the applied finite-size corrections is truly valid, and the disagreement is irrelevant.

For the $C_N(q = -1)$ defects in Fig. 1(b), the PC-only FNV results rest near the reference lines for all values of Q , again indicating close agreement of the methods. However, we see that this agreement degrades when potential alignment has been included, which is unusual compared to typical ground-state behavior, where the alignment corrections are usually observed to be beneficial to accuracy. Even so, this increased disagreement remains $< 0.071 \text{ eV}$ for all Q , which is in accord with published studies of the accuracy of the FNV method when applied to defect ground states [72].

3. Pseudo-ground-state formulations of the potential-alignment correction

Figure 2 compares selected alignment corrections obtained in the previous section using the vertical-transition-state capability of *sxdefectalign*, to similar, less-refined corrections obtained using the summed, pseudo-ground-state approaches developed to obtain a first understanding of proper finite-size corrections for vertical transition states [51,52] and CC diagrams [50]. To calculate the pseudo-ground-state-based alignment corrections, we have used Eq. (13) of Ref. [51], Eq. (6) of Ref. [50], and Eq. (10) herein, which is taken from Ref. [52]. When applying these formulations, we at times observed a discontinuous change in ΔV as the DFT calculations moved into the configurationally extrapolated regions of the CC diagram ($Q < 0$ and $Q > 1.524 \text{ amu}^{1/2} \text{ \AA}$). As later discussed, these discontinuities appear to arise from unintended delocalization of the applied charge. To produce Fig. 2, such discontinuities have been removed by linear extrapolation of valid ΔV values selected from within the well-behaved configurationally interpolated region of the diagram ($0 < Q < 1.524 \text{ amu}^{1/2} \text{ \AA}$). All results in Fig. 2 are for the $q = -1$, $\parallel$ configuration of substitutional C_N when modeled using 96-atom supercells.

Figure 2 reveals several informative aspects of the alignment corrections. First, all the formulations yield the same result at the configuration coordinate, $Q = 0$, of the $q = -1$ branch of the underlying CC diagram, where the only true one-electron vertical transition occurs. Second, three of the formulations also correctly limit to the $q = -1$ ground-state correction located at $Q = 1.524 \text{ amu}^{1/2} \text{ \AA}$, with only the formulation of Gake *et al.* deviating. Third, for any given value of Q , the corrections agree with each other to within less than

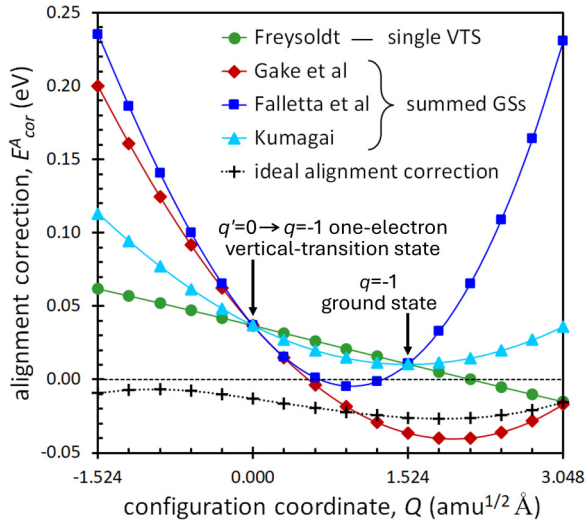


FIG. 2. Comparison of the potential-alignment corrections obtained using each of four differing published formulations to best estimates of the ideal alignment correction. The corrections have all been calculated for the defect-formation energies of the $q = -1$, $\parallel$ configuration of substitutional C_N when modeled using 96-atom supercells as a function of the configuration coordinate associated with the $-1/0$ defect level [see Fig. 1(b)]. The results labeled “Freysoldt” use the vertical-transition-state (VTS) capability of the *sxdefectalign* code, as discussed in the previous section. The results labeled “Gake *et al.*” [51], “Falletta *et al.*” [52], and “Kumagai” [50] use approaches that sum a series of pseudo-ground-state-based corrections (GSs). The “ideal” corrections result from differencing each of the fully corrected hybrid-fitting results with its corresponding 96-atom result corrected using the Madelung energy alone [see PC-only data, no alignment correction, Fig. 1(b)].

60 meV whenever Q lies within the configurationally interpolated region of the CC diagram. However, the corrections increasingly differ as Q moves into the adjacent extrapolated regions of the CC diagram. Fourth, all three of the pseudo-ground-state formulations feature a clearly quadratic dependence on Q (or equivalently, α), whereas the vertical-transition-state results from *sxdefectalign* are purely linear in Q . Last, the linear results of *sxdefectalign* best approximate the ideal corrections estimated from the hybrid-fitted results.

As further seen in Fig. 2, two clearly different curves appear for the alignment corrections of Gake *et al.* [51] and Falletta *et al.* [52], which is at first surprising because Falletta *et al.* have proved these formulations to be equivalent [53]. In successfully repeating their proof in our Supplemental Material [150], we have come to realize that the differing results in Fig. 2 arise because of a significantly restrictive assumption of the proof, which requires the quantity $B \equiv [\epsilon_*/q^*]\Delta V(q^*, \epsilon_*)$ to be a constant for all relevant pairings of (q^*, ϵ_*) . Because this assumption fails to hold for the various values of $\Delta V(q^*, \epsilon_*)$ calculated from the electrostatic potentials of auxiliary DFT calculations needed to implement the alignment formulas given in Refs. [51] and [52], these formulations prove to be unequal when directly calculated (excepting $Q = 0$ in Fig. 2).

Finally, the distinctly parabolic corrections seen in Fig. 2 arise because q' depends on α through Eq. (14) or (15),

and each pseudo-ground-state formulation contains q' (and/or q'_{pol}) in both the prefactor and the argument of ΔV for one or more of the formulation’s terms, giving the corrections’ dependence on α^2 (or Q^2). This contrasts with the vertical-transition-state formulation implemented in *sxdefectalign*, where only q appears as the prefactor to ΔV_{vt} in Eq. (13), and where q is constant for all local values of α defining the CC diagram. Because $q-q'$ still appears within the argument of ΔV_{vt} in Eq. (13) through the defect’s ionically frozen configuration previously determined at q' , the alignment corrections exhibit only linear dependence on α . This latter formulation of *sxdefectalign* seems to be more consistent with our existing understanding of the alignment potential [65,69,73], wherein only the external charge applied to the charge-neutral defect-containing supercell requires an alignment-potential correction—basically, because only that charge originates from an external reservoir where a “misalignment” exists between the DFT calculation and the reservoir needed to conserve charge.

4. Analysis of the finite-difference slopes of $E_f(1/L)$

Figure 3 further examines the slopes of the $E_f(1/L)$ curves shown in Fig. 1 by comparing a series of finite-difference slopes to the model-defined slopes expected for three specific categories of model-based finite-size corrections, where all slopes are plotted as a function of α . The finite-difference slopes in Fig. 3 are given by $m_{\text{fd}} = \Delta E_f(1/L)/\Delta(1/L)$, using pairs of uncorrected, fully k -point-converged, defect energies calculated for 128- and 432-atom supercells, and for 432- and 1024-atom supercells. The model-based slopes in Fig. 3 are given by $m_{\text{mod}} = L \times E_M(1/L)$, where $E_M(1/L)$ is the Madelung energy applicable to each of the model categories to be discussed next.

Several notable points appear in the figure. First, neither ground-state models [55,56,65,66] nor one-electron vertical-transition-state models [51,52] have slopes with any dependence on α [or $Q(\alpha)$], whereas both the $q = 0$ and -1 finite-difference slopes in the figure clearly do. In contrast, the model proposed by Kumagai [50] for use with CC diagrams does have α -dependence through the magnitude of the defect’s structurally induced polarization charge, $\alpha \Delta q_c$, with this charge entering quadratically into the Madelung energy, as seen in Fig. 3.

Moreover, we see that the finite-difference slopes substantially follow the parabolic slopes from Kumagai’s theory, albeit inexactly because some higher-order curvature remains present at the differenced cell sizes. Notably, the slopes for the larger cell-size pairs (432- and 1024-atom cells) show the best agreement with Kumagai’s predicted asymptotic slopes, consistent with an improving cell-size convergence. While we are unable to run supercells that are large enough to more exactly converge the finite-difference slopes, it is already clear from Fig. 3 that the first order ($1/L$) finite-size corrections predicted by Kumagai’s are essentially correct.

Even so, there are some notable disagreements between Kumagai’s predicted slopes and the finite-difference slopes. In Fig. 3(b) where $q = 0$, the marked tendency for the plotted finite-difference slopes to depart from the predicted parabolic trendline for $\alpha_r > 1$ (or $Q > 1.659 \text{ amu}^{1/2} \text{ Å}$) corresponds

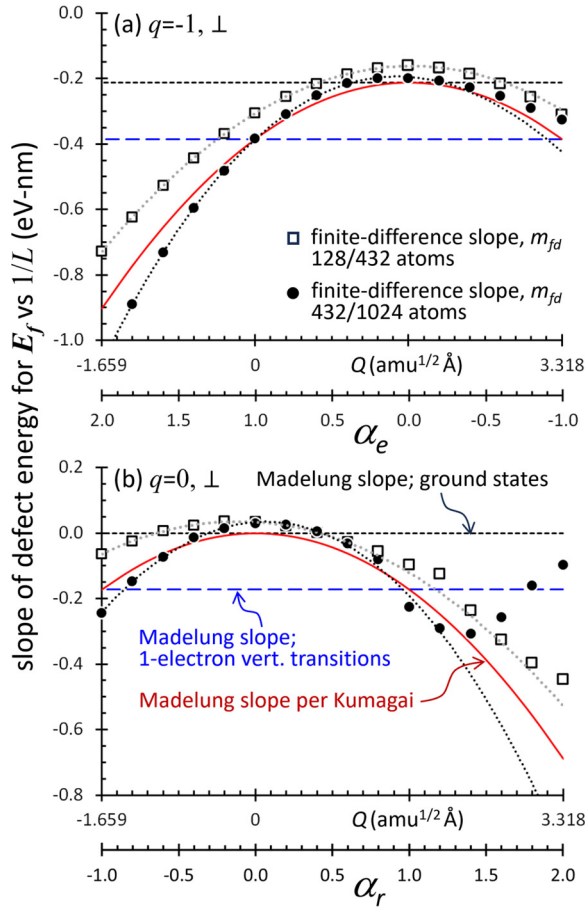


FIG. 3. Comparison of the theoretical Madelung-energy slopes predicted by finite-size methods for plots of $E_f(1/L)$ [plotted as lines only, one for each of the three different categories of finite-size-correction methods labeled in panel (b)] to finite-difference DFT slopes calculated directly from plots of uncorrected defect-formation energies vs $1/L$ (plotted as symbols with dotted trendlines). All slopes are plotted vs the local interpolation parameter, α_e or α_r , used to construct the interpolated C_N defect structures and calculate the defect energies for (a) $q = -1$ and (b) $q = 0$.

with the somewhat poorly fit data previously noted in Fig. 1(a) for $Q > 1.89 \text{ amu}^{1/2} \text{ Å}$. The cause is the same for both—the evolution of the defect’s band structure with structural distortion, discussed next—which causes defect-energy anomalies that manifest more sensitively for the slopes in energy.

5. Dependence of defect band structure on the configuration coordinate

To understand the above-noted anomalies in the nonequilibrium-defect energies seen at larger Q , we examined the defect bands (eigenvalues) of substitutional $C_N(q = -1)$ that result as a function of Q , where early-in-the-study DFT calculations were done using 192-atom supercells and Γ -point Brillouin-zone sampling to obtain the eigenvalues of interest. The results are shown in Fig. 4, where we see three DFT defect bands grouped together within the gap (the red, green, and yellow solid lines), and possibly, one DFT defect band located quite near the valence band maximum (turquoise line). For $C_N(q = -1)$, all four defect bands are

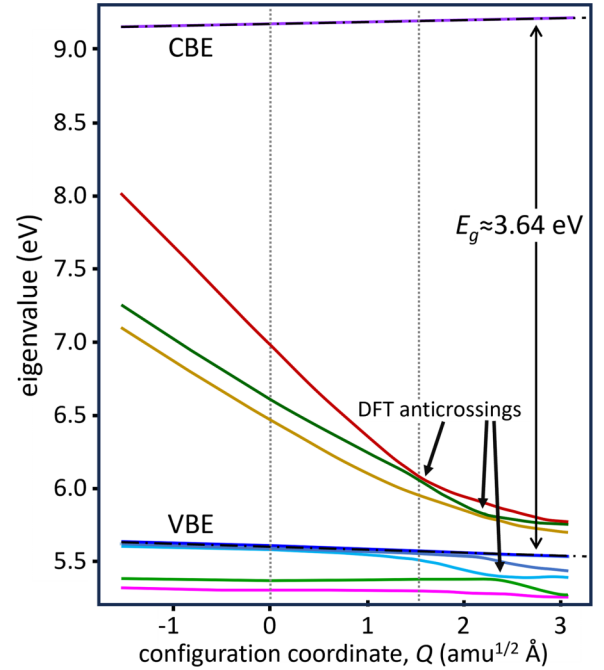


FIG. 4. Plot of band eigenvalues vs Q for DFT calculations of the relaxed electronic structure of interpolated configurational states of substitutional $C_N(q = -1)$ in GaN. The DFT was initial work done using 192-atom supercells with C_N in the perpendicular configuration. VBE denotes the valence-band edge. CBE denotes the conduction-band edge.

doubly occupied, and the defect has no spin polarization. At lower values of Q , the upper three defect bands reside near midgap. These bands move downward in energy with increasing Q and eventually approach the valence-band edge as Q exceeds $1.5 \text{ amu}^{1/2} \text{ Å}$.

This approach to the band edge is accompanied by multiple anticrossings of the defect bands (with two anticrossings clearly seen in the gap, and one possibly seen below the band edge). For the smaller defect supercells used here, the DFT band gap is enlarged to $\approx 3.64 \text{ eV}$ because of finite-size effects, as annotated in the figure. Consequently, the upper defect bands tend to remain marginally separated from the valence-band edge even at higher Q . For larger supercells (not shown), the DFT band gap decreases towards the bulk value and the small defect/valence-band separation seen in Fig. 4 tends to vanish. As a result, the defect bands increasingly interact with the valence-band edge for both larger cell sizes and larger values of Q . Notably, similar band-crossing effects have previously been reported by Kim *et al.* in Ref. [33], where the visualization of defect band structure near to and within the band gap was similarly found to be informative.

Returning to the finite-difference slopes shown in Fig. 3, we see that the described valence-band interaction quite likely alters the defect energies and associated slopes for the larger-supercell data [black dots in Fig. 3(b)], causing the expected parabolic trend of these slopes to breakdown as Q exceeds $1.5 \text{ amu}^{1/2} \text{ Å}$. The interaction is much stronger for $q = 0$ than for $q = -1$ because there is one unpopulated defect band in the gap for $q = 0$, which tends to incorrectly fill as it moves into the valence-band edge. Consequently, we see

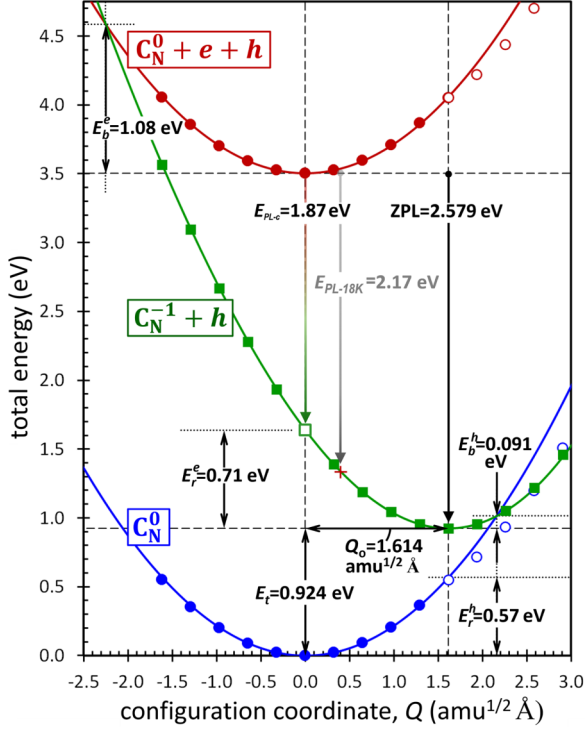


FIG. 5. Configuration-coordinate (CC) diagram for hole capture and electron capture at substitutional C_N sites in GaN (red, green, and blue solid-line curves) obtained using the $\parallel$ configuration of $C_N(q = 0)$. The CC diagrams are constructed from well-converged defect-formation energies and accurate finite-size corrections based on Kumagai’s method [50] as implemented within this work’s hybrid-curve-fitting scheme.

much stronger deviations in slope for Fig. 3(b) where $q = 0$, as compared to Fig. 3(a) where $q = -1$.

These unintended band-structure effects produced by interpolated (and extrapolated) defect structures may limit the useful range of the CC-diagram’s defect energies not only here, but also for other defects showing unusual, anharmonic-like behavior when implemented using the single-mode formalism. In contrast to our findings, recent studies of carrier capture by others have reported quite substantial anharmonicities attributed to real violations of Hooke’s law [33,37–39]. A hallmark of these studies has been the modeling of defects with very high Q_0 values ($Q_0 \sim 5 - 15 \text{ amu}^{1/2} \text{ Å}$, versus only $\approx 1.6 \text{ amu}^{1/2} \text{ Å}$ herein), where one may increasingly expect true anharmonicity because of the high configurational distortion of the defects. Because the cause of nonparabolicity within CC diagrams may be ambiguous, we suggest that *apparent* deviations from harmonic behavior may often require further assessment to establish their status as either genuine data, or misleading artifacts.

C. Configuration-coordinate diagrams and MPE theory parameters

1. CC diagrams obtained using hybrid fitting

Figure 5 shows an example analysis of CC diagrams calculated for hole capture (green and blue solid-line curves) and electron capture (red and green solid-line curves) for

the parallel configuration of C_N in GaN, where the finite-size-corrected defect energies have been obtained using the hybrid-fitting approach shown in Fig. 1. Our $C_N(q = 0)$ data (filled blue circles) are well fitted in the harmonic approximation while our $C_N(q = -1) + h$ data (filled green squares) are clearly anharmonic and well fitted by a cubic model. For hole capture, the anharmonicity has been approximately handled by refitting the $C_N(q = -1) + h$ data over a restricted range of Q using the harmonic approximation, which we write in a conveniently modeled form as $E_{\text{tot}} = 119.61(\hbar\Omega)^2 Q^2$ by suppressing the offsets E_i and Q_0 . Here, the total energy, E_{tot} , and the effective phonon energy, $\hbar\Omega$, have units of eV, and Q has units of $\text{amu}^{1/2} \text{ Å}$. For $C_N(q = 0)$, the data for $Q \geq 1.614 \text{ amu}^{1/2} \text{ Å}$ (open circles, Fig. 5) are omitted from the CC-diagram curve-fitting analyses because of the already discussed degraded accuracy of this data. Because these data are excluded, calculation of the barrier for hole capture requires a careful extrapolation of the fitted $C_N(q = 0)$ curve up to the intersection with the $C_N(q = -1) + h$ curve. The resulting hole-capture barrier energy, $E_b^h = 0.091 \text{ eV}$, has been found to be only moderately sensitive to the range of the fitted harmonic $C_N(q = 0)$ data. Indeed, E_b varies by only $\pm 0.013 \text{ eV}$ for several differently implemented curve fits utilizing from 3–10 of the valid $C_N(q = 0)$ data points, with the fitted data centered at $Q = 0$ and spanning a ΔQ range as small as $0.646 \text{ amu}^{1/2} \text{ Å}$ and as large as $2.91 \text{ amu}^{1/2} \text{ Å}$.

The example results described in the preceding paragraph and in Fig. 5 feed into the upper section of Table IV, where we summarize the MPE theory parameters for hole capture that result from the various CC-diagrams ($\hbar\Omega_e^h$, $\hbar\Omega_r^h$, E_b^h , E_r^h , E_r^e) and ground-state analyses (E_i , Q_0) developed in this course of this work. In the headings of Table IV, $\hbar\Omega$ denotes the phonon energy associated with the effective mode; E_b denotes the barrier energy for capture; E_r denotes the relaxation energy for capture; superscripts h and e designate hole capture and electron capture, respectively; and subscripts e and r again designate the excited and relaxed states of capture. In the middle section of Table IV, we show previous theoretical results [25,35] for comparison to present work, while in the bottom section of Table IV, we show previous measurements [78,95,96,103]. Finally, on the right side of Table IV, we summarize the classical PL peak positions ($E_{\text{PL-C}} = E_g - E_i - E_r^e$) estimated for the radiative electron capture that follows hole capture. The table’s *unindented headings* under “Referenced work” (and adjacent row entries) designate primary data for comparing theory and experiment, as discussed next, while the *indented headings* (and adjacent row entries) designate secondary data to be discussed later.

Inspecting the unindented, primary data rows shown in Table IV, several notable points emerge. First and most important, this work’s barriers for hole capture obtained by extensive hybrid fitting, $E_b^h = 0.091$ and 0.094 eV , agree quite well with the value inferred from the thorough PL studies of Reshchikov *et al.* [103], where $E_b^h \approx 0.1 \text{ eV}$ was estimated. As has been discussed by Reshchikov *et al.* [103], this small barrier is necessary to reproduce the nearly temperature-independent hole-capture coefficients that have been measured at 100 K [99], 300 – 325 K [104], and 400–600 K [95,96]. In sharp contrast, the previous DFT-based results shown for Alkauskas *et al.* [25] and Turiansky *et al.*

TABLE IV. Multiphonon-emission-theory parameters for hole capture by substitutional $C_N(q = -1)$ in GaN. Previous theoretical results are taken from Refs. [25]^a and [35]^b, where Ref. [25] has recommended substantial post-DFT adjustments to E_t and E_b that are shown within square brackets. Previous measurements are taken from Refs. [103]^c and [78]^d, where the E_r^e , E_r^h , and Q_0 values within braces have been calculated using the referenced table entries. Rows labeled as “Benchmarks” summarize calculations done at a supercell size of 96 atoms to replicate previous work. ^aThe original anharmonic-fitting results are shown. [†]The harmonic approximation has been applied. [§]The values shown are Γ_{PL} or Γ_{PLE} , where $E_r^e \approx \Gamma_{PL}$ and $E_r^h \approx \Gamma_{PLE}$. ^{*}For Ref. [78]^d, the reported PL-emission-threshold result at 4.2 K for E_t has been used in place of their activation-energy measurements at 480 K for consistency with 0 K DFT. The labels “d-c” and “d-v” designate whether Ga-3d electrons were treated as core or valence for the work. All symbols are defined within the main text.

Referenced work	Q_0 (Å√amu)	E_t (eV)	E_b^h (eV)	$\hbar\Omega_r^h$ (meV)	$\hbar\Omega_e^h$ (meV)	E_r^h (eV)	E_r^e (eV)	E_{PL-c} (eV)
This work:								
$C_N \perp$, hyb. fit, d-c	1.659	0.948	0.094	42.2	51.3 [†]	0.575	0.758 [§]	1.80
$C_N \parallel$, hyb. fit, d-c	1.614	0.924	0.091	42.5	50.7 [†]	0.567	0.714 [§]	1.87
432 atoms, d-v	1.519	0.904	0.127	42.9 [†]	50.4 [†]	0.494 [§]	0.629 [§]	1.97
Benchmark A, d-c	1.524	0.967	0.091	45.8 [†]	53.1 [†]	0.585 [§]	0.726 [§]	1.81
Benchmark B, d-c	1.524	0.956	0.086	45.8 [†]	53.2 [†]	0.582 [§]	0.701 [§]	
Alkauskas <i>et al.</i> ^a	1.61	1.02	0.73	36	42	0.37	0.49	2.11
[as adjusted] ^a		[0.89]	[0.23]					
Benchmark C, d-c	1.571	0.954	0.760	36.1	45.6 [†]	0.366	0.512 [§]	1.95
Turiansky <i>et al.</i> ^b	1.69	1.06	0.486	33.6	37.5	0.386	0.480	2.05
Benchmark D, d-c	1.571	0.954	0.478	36.1	43.4 [†]	0.366	0.512 [§]	2.00
Reshchikov <i>et al.</i> ^c		0.916	≈ 0.1	56	56	0.44 [§]	0.44 [§]	
{inferred herein}	{1.130}	0.916	{0.1}	56	56	{0.479}	{0.479}	{2.11}
Ogino and Aoki ^d		0.91 [*]		40	41	0.55	0.51	
(using $E_r \approx \Gamma_{PL,PLE}$)						0.40 [§]	0.43 [§]	
{inferred herein}	{1.592}	0.91 [*]	{0.1}	40	41	{0.485}	{0.510}	{2.08}

[35] instead find $E_b^h = 0.73$ (when unadjusted) and 0.486 eV, respectively. In these earlier works, the DFT was conducted without benefit of (the not yet invented) finite-size corrections for the unrelaxed defect configurations found in CC diagrams. This unintended shortcoming yielded abnormally large barriers to capture that caused the resulting capture coefficient to vary by orders of magnitude over 100–600 K.

Second, this work’s relaxation energies for electron capture, $E_r^e = 0.714$ and 0.758 eV, fall notably above those of the previous DFT studies, $E_r^e = 0.49$ and 0.48 eV, and further disagree with the smaller-yet value suggested by the experiments of Reshchikov *et al.*, which have assumed that $E_r \approx dFC \approx \Gamma_{PL} = 0.44$ eV, where dFC is the Frank-Condon shift. In contrast, Ogino and Aoki have directly measured E_r^e and find 0.51 eV, in slightly better agreement with our results. Third, this work’s relaxation energies for hole capture, $E_r^h = 0.567$ and 0.575 eV, are also seen to rise above previous theory, but less strongly than for E_r^e . In this case, our agreement with the previous DFT, $E_r^h = 0.37$ and 0.386 eV, is marginal. More importantly, the experiments exhibit generally better agreement with our E_r^h values, as PLE (PL-excitation) peak-width results again suggest $E_r^h \approx dFC \approx \Gamma_{PLE} = 0.44$ eV per Reshchikov *et al.* [103], while Ogino and Aoki [78] directly measure a clearly higher result, $E_r^e = 0.55$ eV, which rests quite close to results herein. Thus, the striking improvements found here for E_b^h , and to a lesser degree, E_r^h , appears to entail degraded fidelity for the excited-state relaxation energy, E_r^e . The foregoing observations all tend to result from the significantly increased curvatures of the defects’ total energy curves produced by the newly applied finite-size corrections.

Using the standard definition of the Huang-Rhys parameter, $S^{e,h} = E_r^{e,h}/\hbar\Omega$, and inserting Table IV data, we find

that $S^{e,h} = 14.4, 13.5$ herein, when averaging results for the hybrid-fitted MPE data sets. These results are somewhat larger than previous theory, which finds $S^{e,h} = 10.3, 11.7$ [25] and $S^{e,h} = 11.5, 12.8$ [35], with our result for S^e showing more disagreement because of our larger E_r^e . More notably, previous experiments report $S^{e,h} = 12.8, 13.4$ [78] and $S = 7.8$ [103], where the early work of Ogino and Aoki [78] agrees relatively well with all of the theory, including ours, while the much later, quite thorough work of Reshchikov [103] significantly disagrees with all theory.

Finally, this work’s separately determined results for the $\parallel$ and $\perp$ configurations of $C_N(q = 0)$ are seen to be nearly equal for all reported MPE values in Table IV, confirming the assumption of previous DFT studies that consideration of just a single configuration with an assigned degeneracy of $g = 4$ suffices.

As an exploratory aside, we additionally analyzed the CC-diagram data in Fig. 5 to obtain nominal MPE parameters for electron capture. The resulting untubulated values are: $\hbar\Omega_e^e = 42.2$ meV, $\hbar\Omega_r^e = 45.3$ meV, and $E_b^e = 1.08$ eV, with $\Delta E = E_g - E_t = 2.579$ eV and $Q_0 = 1.614$ amu^{1/2} Å. Some of these parameters differ somewhat from related, complementary values found in Table IV for hole capture because we have fitted the anharmonic $C_N(q = -1)$ total-energy data to a harmonic approximation differing from that used for hole capture. To be specific, the harmonic approximation has been selected in each case to exactly reproduce the applicable barrier energy, as this energy (and not the implicitly adjusted relaxation energy) most strongly effects the harmonic phonon matrix-element calculations in Eq. (20). The fitted electron-capture barrier is somewhat tentative because the constructed series of extrapolated defect configurations used to approach

the barrier's crossing point extend far outside the interpolative region of the CC diagram (with $\Delta Q_{\text{extrap}} = -2.25 \text{ amu}^{1/2} \text{ \AA}$ here, versus only $+0.55 \text{ amu}^{1/2} \text{ \AA}$ for hole capture) and thus involves a less-studied regime.

2. CC diagrams obtained using FNV

To further examine finite-size correction techniques and resulting hole-capture computational fidelity, we have assessed differences in the CC diagrams and MPE-theory parameters that result when we replace our hybrid-fitted approach for finite-size corrections with the more-typical FNV approach executed using a single, smaller supercell size. In contrast to previous work, the FNV corrections herein have been properly implemented for the distorted defect configurations found in CC diagrams. In the present test study, we have used the $C_N \parallel$ defect configuration, 96-atom supercells, shifted $2 \times 2 \times 2 k$ -point sampling, and the *sxdefectalign* code to implement Eq. (17), with the needed charge states taken from Eqs. (14)–(16) and (18). The CC-diagram curve-fitting methods and data-fitting ranges used to determine MPE parameters were like those of the previous section. The resulting MPE parameters are shown in the indented, upper section of Table IV, on the row labeled as Benchmark A. Comparing to the hybrid-fitted results two-rows up in the table, we see that more noticeable (but still minor) differences arise for the ground-state-determined values of E_t and Q_0 , with the CC-diagram-determined MPE parameters either showing noticeably less change (E_b^h , E_r^h , and E_r^e), or showing moderate changes driven primarily by the change in Q_0 ($\hbar\Omega_i^h$ and $\hbar\Omega_f^h$). Importantly, we find that the barrier for hole capture, $E_b^h = 0.091 \text{ eV}$, equals that from our extensive hybrid-fitted calculations. This agreement results in part because the reduced value of Q_0 cannot alter the barrier height, as it only acts to set the absolute scale of the configuration coordinate. Overall, we see that the small-supercell FNV-corrected results for the MPE-theory parameters agree quite well with our hybrid-fitted calculations discussed earlier, once all the unrelaxed configurations in the CC diagram are properly finite-size corrected.

If we remove the FNV alignment term from the Benchmark-A finite-size corrections and recalculate the MPE parameters, we obtain the Benchmark B results in Table IV. The Benchmark B results hardly differ from those of Benchmark A, such that both benchmarks agree with the hybrid-fitted results. We noted earlier that the tendency of the FNV alignment procedure is to somewhat overestimate the needed corrections for the present defects' total energies. Even so, we see here that the modestly over-corrected FNV alignments only slightly alter the resulting MPE-theory parameters. In agreement with our findings, Kumagai has similarly noted that “the [FNV] alignment terms do not exhibit a significant effect” in his separate initial test calculations [50]. These observations, while intriguing, may not be entirely generalizable without further studies of carrier capture for a wider palette of defects and charge states – preferably using defects with larger, significant alignment corrections for the underlying ground states.

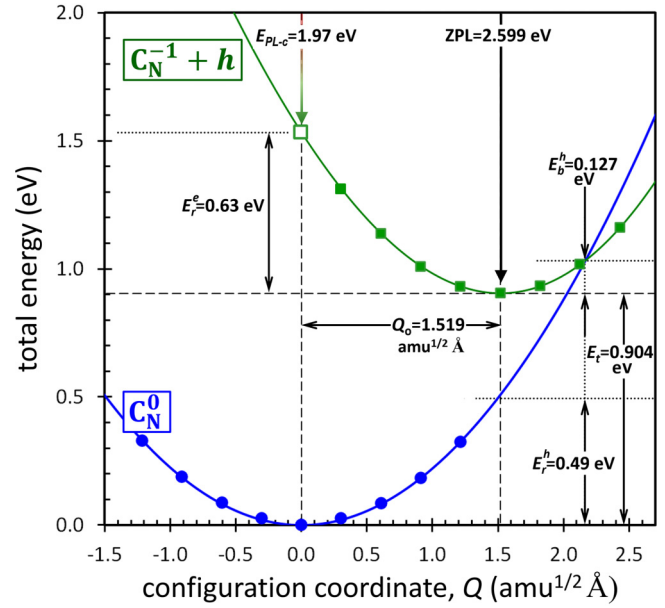


FIG. 6. Configuration coordinate (CC) diagram for hole capture at substitutional C_N sites in GaN as determined by DFT with Ga-3d electrons treated as valence.

3. CC diagrams with Ga-3d electrons treated as valence

Because of the marginal agreement between our above-calculated relaxation energies ($E_r^e = 0.714 \text{ eV}$) and the reported experimental values ($E_r^e \approx dFC \approx \Gamma_{PL} = 0.44 \text{ eV}$ [103] and $E_r^e = 0.51 \text{ eV}$ [78]), we have performed two additional studies seeking possible explanations. In the first of these, we investigated whether treating Ga-3d electrons as valence rather than as core yields a substantially different CC diagram. To this end, the CC diagram for hole capture was recalculated using 432-atom supercells, Γ -point sampling of the Brillouin zone, high-accuracy SCF and force convergence (as above), and d -valence PAW pseudopotentials as implemented within VASP. For finite-size corrections, we used only the point-charge-based Madelung energies of Eq. (17) when calculating the corrected defect energies, E_0 , with the charge states again from Eqs. (14)–(16). The nonlinear in $1/L$ finite-size contributions in Eq. (17) were omitted given their nearly negligible effect at larger cell sizes, as seen for our d -core results in Fig. 1(b). We summarize the resulting d -valence MPE-theory parameters on the row labeled “432 atoms, d -v” shown in the upper, indented section of Table IV.

Figure 6 shows the CC diagram resulting from the d -valence study. For the d -valence results, we find a beneficial reduction of relaxation energies, with E_r^h decreasing from 0.567 to 0.494 eV for d -core versus d -valence, respectively. Similarly, E_r^e decreases from 0.714 to 0.629 eV. These improved relaxation energies are accompanied by a modest change in the hole-capture energy barrier, which rises from 0.091 up to 0.127 eV, with the effect on the hole-capture coefficient to be examined below. The corresponding Huang-Rhys parameters fall to $S^{e,h} = 11.5, 12.5$, bringing our results closer to the mean of the experiments, while now moving below the higher, early results stated by Ogino and Aiko.

4. Supplemental reanalysis of experimental CC diagrams

The second reexamined source of disagreement rests with approximations sometimes made when first constructing the experimental CC diagrams. Such approximations can be self-consistently refined as new experimental observations come to light, as described next. Because experiments have at times reported only approximate values in the form $E_r \approx \Gamma_{\text{PL}} \approx d\text{FC} = 0.44$ eV, as in Ref. [103], and because experiments do not report absolute values for Q_0 , we have performed a supplemental reanalysis of the experiments to estimate *experimentally self-consistent, absolute values for E_r and Q_0* for further comparison to theory. This reanalysis is enabled by Reshchikov's recent and pivotal observation that the nominal value of the barrier for hole capture rests near 0.1 eV [103]. By (i) assuming that the barrier energy in fact equals 0.1 eV in the experiments, (ii) by further assuming harmonic total energies versus Q , and (iii) by using the existing experimental results for $\hbar\Omega_i^h$, $\hbar\Omega_f^h$, E_t , and E_g , one may reconstruct the experimental CC diagrams while also solving for the values of Q_0 , E_r^h , and E_r^e consistent with each experiment. The reanalysis results for the two reported experimental CC diagrams appear enclosed within braces in the bottom, indented sections of Table IV.

As seen in Table IV, further-improved agreement between experiment and theory emerges from the supplemental analysis. First, E_r^h rises to 0.479–0.485 eV for the two experiments, becoming almost identical to the d -valence theoretical results at 0.494 eV. Second, E_r^e rises to 0.479–0.510 eV for the experiments, with the d -valence results for E_r^e now much more reasonably positioned only 0.12–0.15 eV above the reanalyzed experiments. Using these revised E_r values, the experimental Huang-Rhys factor becomes $S^{e,h} = 12.4, 12.1$ for Ref. [78] versus $S = 8.6$ for Ref. [103], somewhat reducing differences here as well. As expected, the derived relaxation energies now end up exceeding the reported values for $\Gamma_{\text{PL}} \approx d\text{FC}$ by 40–70 meV, with E_r no longer assumed equal to Γ_{PL} for the reanalyzed results. These small nominal shifts arise because the phonons mediating the underlying radiative-recombination process raise the actual PL peak (or the line-shape-modeled peak [24]) to an energy slightly above the position classically estimated from the CC diagram alone.

In Table IV, the values of Q_0 found for the reanalyzed experiments disagree with each other. However, this observation simply reflects the already noted differences in $\hbar\Omega$ for the older experimental work of Ogino and Aoki in Ref. [78] and the more recent work of Reshchikov summarized in Ref. [103]. Reshchikov has previously discussed this notable experimental difference in Ref. [102]. In essence, the differing results arise from the much wider ($\approx \sqrt{2}\times$) temperature-dependent PL peak widths measured in Ref. [78] versus Refs. [101,102]. The differing widths cause the phonon energies, which are obtained by fitting the same theoretical model to the PL-peak widths versus temperature [78,101,102], to inversely differ by a similar relative amount. Reshchikov attributes the wider PL peaks seen in Ref. [78] to a possible “increased contribution from transitions in the near-surface depletion region of GaN:C powder studied in that work.” Our results ($\hbar\Omega_{e,r} = 42.9, 50.4$ meV) rest in between Reshchikov's more recent experiments

($\hbar\Omega = 56$ meV [101,102]) and Ogino and Aoki's earlier experiments ($\hbar\Omega_{e,r} = 40, 41$ meV [78]). In contrast, previous DFT results ($\hbar\Omega_{e,r} = 33.6, 37.5$ meV [35] and $\hbar\Omega_{e,r} = 36, 42$ [24,25]) rest on average somewhat below the early experiments [78] and significantly below the more recent experiments [101,102]. (Here, the subscript attributions for the excited- and relaxed-state phonon energies, $\hbar\Omega_{e,r}$, describe radiative electron capture, as that process leads to the yellow luminescence studied in the cited PL experiments.)

Another potential source of disagreement between theoretical and experimental CC diagrams involves temperature effects. To adjust DFT results obtained for 0 K for comparison to experiments performed at elevated temperatures, corrections may be needed to account for the temperature dependence of the band gap and the defect levels, as described in Refs. [25,30]. These effects are not an issue here because the cited experimental CC diagrams were determined using optical methods advantageously performed at low temperatures (4.2–18 K) [78,95,96,103], where these corrections become negligible.

5. Benchmark testing of DFT methodology

To demonstrate that our DFT methodology reproduces previous work (when analyzed with conventional finite-size corrections designed for relaxed defect configurations), we repeated the CC-diagram calculations of both Alkauskas *et al.* [25] and Turiansky *et al.* [35] by using the $C_N \parallel$ defect configuration along with their k -point sampling (Baldereschi), finite-size correction method (FNV with defects corrected as though ground states), CC-diagram curve-fitting ranges (which varied between the two previous works), and cell size (96 atoms), but while using our NCPs and the SOCORRO code. We show results for the repeated calculations as the indented, secondary data in the middle section of Table IV, on the rows labeled as Benchmarks C and D. By comparing these benchmarking results to the above-adjacent previous works in the table, we find that we can reproduce the previous DFT results to a good approximation using our separate computational machinery. Thus, our new results for the classical barrier to capture, and our differing CC-diagram details, mostly arise from the newly applied finite-size correction methods of Kumagai [50] and, to a lesser degree, from our reduced 0/−1 level for C_N —and not from extraneous computational differences.

The various MPE parameters reported above for hole-capture and electron-capture enter our capture-coefficient calculations below in Sec. III E. Before turning to those calculations, we revisit the electron-phonon matrix elements for carrier capture.

D. Electron-phonon matrix elements

Following the procedure established in Ref. [25] and elaborated in Ref. [35], we calculated the electron-phonon matrix elements, W_{if} , relevant to hole capture by the $q = -1$ charge state of the substitutional C_N defect in GaN by using the expression at the end of Eq. (21). The needed slope of the wave-function overlap, $\partial\langle\psi_i|\psi_f\rangle/\partial Q$, was evaluated numerically using a series of neutral-defect configurations spaced at

TABLE V. PAW-based calculations of electron-phonon coupling constants for substitutional C_N in GaN. The coupling constants are expressed as the product $V_s W_{if}^2$ yielding units of $\text{eV}^2 \text{\AA}/\text{amu}$. The calculations used the $C_N(q=0)$ defect in its $\parallel$ configuration.

Referenced work	Ga-3d treatment	Relaxation k -point	$V_s W_{if}^2$			
			1024 atoms	432 atoms	128 atoms	96 atoms
This work	<i>core</i>	Γ	6.3	6.8	7.5	5.5
	<i>valence</i>	Γ		7.6		
Turiansky <i>et al.</i> [35]	<i>core</i>	Bald.				2.8
Benchmark E	<i>core</i>	Bald.				3.8
w/skipping	<i>core</i>	Bald.				4.6

values of α_r that ranged from -0.25 to $+0.25$ in increments of 0.05 . The choice to displace about the configurationally relaxed neutral-defect state appropriately describes matrix elements even for hole-capture at $C_N(q=-1)$ while removing certain unwanted Coulomb interactions, as explained in Refs. [25] and [35]. To compare results for PAW- and NCP-pseudopotentials, the phonon-electron matrix elements were calculated using CC diagrams obtained using each type of potential, with the PAW results for W_{if} calculated using VASP in combination with the *NONRAD* code, V1.2.0, developed by Turiansky *et al.* [35,113]. The NCP results were calculated using our own modifications to the Socorro code. In the slope calculations, the final state was taken as the unoccupied defect band found within the band gap of the spin-down channel, while the initial states were taken as the three valence-band-edge states of GaN appearing within the same spin channel of the defect calculation [25,35]. Because occupied defect bands possibly interleave with the initial states of interest at the band edge, band-structure plots were constructed to visualize the structure of the near-band-edge region, allowing us to differentiate defect bands from bulk bands. In comparisons of the defect's spin-down band structure with the bulk band structure, two defect bands (identified by their almost flat, weakly linear character) were observed within the five spin-down defect bands located nearest the valence-band edge. These defect bands were skipped over when selecting the three valence bands to be used as initial states, in contrast to Refs. [25] and [35], which assumed that the valence-band-edge states are the three bands directly below the unoccupied defect band.

In practice for substitutional C_N , one matrix element between the defect state and a valence-band-edge state is quite large compared to the others, so the contribution from this matrix element, which is included in both our calculations and previous work, dominates the final answer. Nonetheless, our findings suggest that proper identification of the band-edge states in the presence of resonant defect states may be important for other defects. As in Refs. [25] and [35], we took the rms average of the individual W_{if} values for the selected final bands as the nominal value of W_{if} , which was then used to calculate $V_s W_{if}^2$. Such calculations were performed as a function of supercell size using 96, 128, 432, and 1024-atom cells having approximate volumes of 1099, 1466, 4946, and $11\,724 \text{\AA}^3$. Tables V and VI summarize the results obtained for $V_s W_{if}^2$ using the PAW and NCP pseudopotentials.

Comparisons of the electron-phonon coupling constants in Tables V and VI reveal several interesting observations. First,

the PAW and NCP results are nearly equivalent, exhibiting coupling constants with quite similar magnitudes and trends with cell size, even though the DFT-code implementations of the overlap calculations are completely independent, and the pseudopotential treatments of the atomic-potential core region are conceptually different. Second, the coupling constants at the smallest 96-atom cell size are noticeably smaller than all other cell sizes, with the coupling abruptly rising upon moving up to a still-small 128-atom cell size, followed by a weaker declining trend in the coupling as the cell size rises to 432 atoms and then 1024 atoms. Third, comparison of the limited coupling results seen in the tables for d -valence versus d -core treatments show the differing treatments to yield approximately the same coupling, with the directly comparable 432-atom PAW results in Table V differing by only 11%. Given this small difference and considering the generally wider variability in coupling with cell size and other factors (discussed below), we elected to use the best-available, 1024-atom coupling results in Table V when calculating all hole-capture-coefficient results.

An unsatisfying aspect of the coupling-constant results shown in Table V is the factor-of-2 difference seen between this work ($5.5 \text{ eV}^2 \text{\AA}/\text{amu}$) and that of Turiansky *et al.* ($2.8 \text{ eV}^2 \text{\AA}/\text{amu}$) for nominally similar calculations performed using 96-atoms cells. To investigate this difference, we computed Benchmark E shown at bottom in Table V, where Benchmark E (initially done without defect-band skipping) was a thorough effort to reproduce the $V_s W_{if}^2$ results of Turiansky *et al.* [35] by using related online information and input files available at GitHub [113] and NOMAD [151]. As seen by comparing Benchmark E results ($3.8 \text{ eV}^2 \text{\AA}/\text{amu}$) to those of Turiansky *et al.* ($2.8 \text{ eV}^2 \text{\AA}/\text{amu}$) in Table V, we failed to reproduce Ref. [35] results. This discrepancy was subsequently traced to our use of V1.2.0 of the *NonRad* code, rather than V1.0.0 originally used to obtain the results in Ref. [35]. Two specific problems stem from the V1.0.0 code package: First, there is a coding bug wherein the final-state eigenvalue is omitted from the W_{if} calculations, which was corrected in V1.0.1 and all subsequent code versions. Second, as seen in the archived tutorial for *NonRad* V1.0.0 (which appears to be written based on calculations done for Ref. [35]), the wave functions at the Baldereschi k -point were used to calculate the matrix elements in the last step of the W_{if} calculations. This differs from the intended calculation of matrix elements using the wave functions at the zero-weight Γ point described in Ref. [35]. When we reintroduce these

TABLE VI. NCP-based calculations of electron-phonon coupling constants for substitutional C_N in GaN. The coupling constants are expressed as the product $V_s W_{if}^2$ yielding units of $\text{eV}^2 \text{\AA}/\text{amu}$.

Referenced work	C_N type	Ga-3d treatment	Relaxation k -point	$V_s W_{if}^2$		
				432 atoms	128 atoms	96 atoms
This work	$\parallel$	<i>core</i>	Γ	7.3	7.6	
Alkauskas <i>et al.</i> [25]	$\perp$	<i>valence</i>	Bald.			4.5

two errors while using V1.2.0 of *NonRad*, the Benchmark E results fall to $2.77 \text{ eV}^2 \text{\AA}/\text{amu}$, exactly as expected. The remaining differences between Benchmark E and this work's best 96-atoms results arise from our use of defect-band skipping (which raises the coupling from 3.8 to $4.6 \text{ eV}^2 \text{\AA}/\text{amu}$), and our use of Γ -point sampling at all steps in the electron-phonon coupling calculations, along with use of a later version of the VASP pseudopotential library (which together raise the coupling from 4.6 to $5.5 \text{ eV}^2 \text{\AA}/\text{amu}$).

Based on our coupling-constant studies, we recommend use of the following methods for improving accuracy and reproducibility of electron-phonon overlap calculations: (1) Use only Γ -point sampling for the DFT calculations used to determine W_{if} (alternatively, during the initial ionic-relaxation step, one might use a regular k -point mesh that does not itself unduly promote symmetry breaking, unlike the single Baldereschi k -point sometimes used); (2) use supercell sizes substantially larger than 100 atoms; and (3) use carefully selected initial- and final-state bands based on comparative visualizations of calculated band structures for both the defect and bulk supercells. (Higher k -point sampling remains important for separately obtaining accurate defect-formation energies as needed for constructing reliable CC-diagrams.)

E. Carrier-capture coefficients

1. Hole-capture coefficients for $C_N(q = -1)$

The rate coefficient for a nonradiative carrier-capture reaction can be evaluated using the multiphonon emission model shown in Eqs. (20) and (21), which assume the defect vibrational states are those of harmonic oscillators. This formulation uses values for the phonon energies of the excited and relaxed states, $\hbar\Omega_e^h$ and $\hbar\Omega_r^h$, the difference between the defects' configurationally relaxed ground-state energies, E_t , and the corresponding difference between the defects' configuration coordinate, Q_0 , whose values are all obtained from DFT calculations discussed above. We evaluate the phonon transition matrix elements by direct integration of the harmonic-oscillator wave-function overlap integrals, where the cubic-spline interpolation scheme of Turiansky *et al.* has been used to remove the δ functions appearing in Eq. (20) and convert the summations to integrations [35]. In addition to the defect parameter values listed in Table IV, we use $V_s W_{if}^2 = 6.3 \text{ eV}^2 \text{\AA}/\text{amu}$ from Table V for $C_N(q = 0)$ in a 1024-atom supercell. The dashed-red curve in Fig. 7 shows calculated hole-capture coefficient values obtained using our *d-core* MPE-theory results (see Table IV, row labeled " $C_N \parallel$, hyb. fit, *d-c*") for the case of no Sommerfeld correction, such that $f_s = 1$ in Eq. (20).

For comparison in Fig. 7, the corresponding dashed-blue curve shows calculated values instead obtained using our *d-valence* MPE-theory results (see Table IV, row labeled "432 atoms, *d-v*"). The solid-blue and dot-dashed-blue curves show calculated values with nontrivial Sommerfeld corrections applied for effective masses of 0.18 and 1.0, as were used in Refs. [35] and [25], respectively. The selected masses are approximately those for the light- and heavy-hole valence bands in GaN. The calculations of f_s followed Eq. (13) of Ref. [35]. Finally, the black curves in Fig. 7 show recalculated values obtained using the defect parameters reported in Ref. [35], while the black crosses show previous results taken directly from Fig. 6 of Ref. [35]. The good agreement between our recalculated values (solid-black curve) and those extracted from Ref. [35] (black crosses) verifies

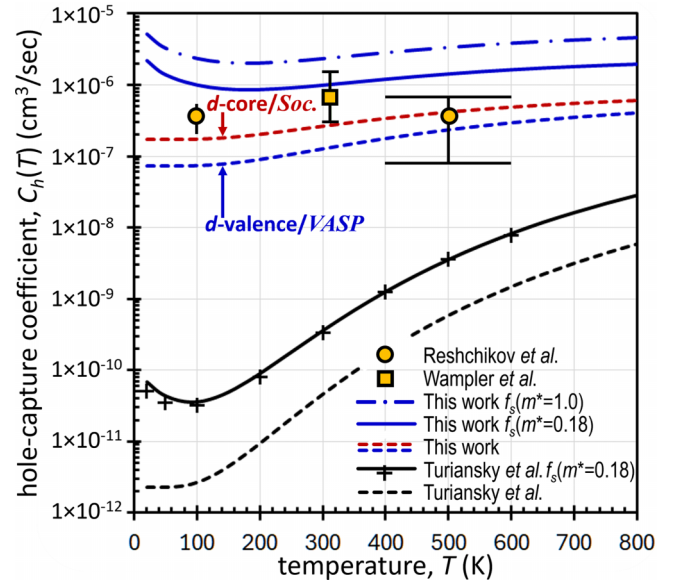


FIG. 7. Rate coefficients for nonradiative hole-capture by substitutional $C_N(q = -1)$, calculated using Eq. (20) with defect-parameter values from Table IV (this paper) and from Turiansky *et al.* [35]. The calculated values are shown with and without the Sommerfeld scaling factor (excepting our *d-core/SOCORRO* results), $f_s(m^*)$, where f_s has been calculated using two previous choices for the reduced mass, m^* [25,35]. The calculated results are compared to the experiments of Reshchikov *et al.* [95–97,99] and Wampler *et al.* [104]. The experiments' error bars are as-reported, except for the 500 K datum, which shows the mean and standard deviation calculated herein for five samples measured at high temperature [95,97]. The lateral extent of the error bars indicates the temperature ranges over which the measurements were made.

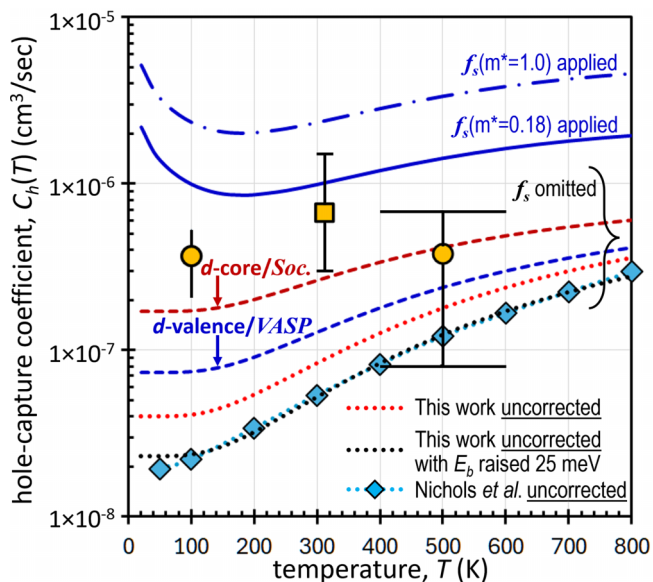


FIG. 8. Comparison of this work’s *finite-size-corrected* rate-coefficient calculations for nonradiative hole-capture by substitutional $C_N(q = -1)$ and experimental results (each as already defined in Fig. 7), to three different additional results obtained *without finite-size corrections*: (i) This work’s single-mode *d-core* calculation of $C_h(T)$ performed using only 96-atom supercells (light-red dotted line), (ii) the preceding case with E_b raised by 25 meV by similarly raising E_i (black dotted line), and (iii) the multiple-mode modeling results of Nichols *et al.* [45], which also used 96-atom cells and *d-core* calculations (turquoise dotted line and diamond symbols).

that our implementation of Eq. (20) reproduces previous work.

Figure 7 also shows experimental values for hole capture rate coefficients determined from recent measurements of transient capacitance from thermal emission of holes $C_N(q = 0) \rightarrow C_N(q = -1) + h$ in the temperature range from 300 to 325 K [104], and from measurements of PL at 100 K [99] and in the temperature range from 400 to 600 K [95–97]. As seen in figure, the experimental values of the hole-capture coefficient are nearly independent of temperature and are in good agreement with the calculated values when using the MPE-parameter values obtained in the present work. In contrast, hole-capture coefficients calculated using the parameters from Ref. [35] give a temperature dependence much larger than observed experimentally, with the values at room temperature too small by about three orders of magnitude. The differing accuracy and temperature dependence is largely due to the difference in barrier energy for our *d-core* and *d-valence* treatments, $E_b = 0.091$ and 0.127 eV, respectively, versus 0.486 eV in Ref. [35]. The high capture barriers previously found by DFT have been previously noted by Reshchikov *et al.*, who reported an insignificant temperature dependence for hole capture and thus suggested a barrier energy $E_b \approx 0.1$ eV [103].

Very recently, striking calculations of the hole-capture coefficient of $C_N(q = -1)$ have been carried out by Nichols *et al.* by using a multiple-phonon-mode treatment [45]. Their results are shown by the diamond-shaped symbols in Fig. 8, where for a more detailed comparison, we have reproduced an

enlarged plot of our results shown in Fig. 7. Figure 8 shows that the multiple-mode treatment eliminates most of the modeling discrepancies previously seen at higher temperatures ($T > 500$ K) but leaves in place discrepancies that still approach an order of magnitude at lower temperatures ($T < 200$ K). This contrasts with the present work, where we find a more nearly temperature-independent hole-capture coefficient that reproduces all existing experiments to within an order of magnitude or better.

As seen by further inspecting Fig. 8, the Sommerfeld scaling factors, f_s , which are traditionally applied ad hoc to the purely DFT-based capture coefficients, may also have a significant effect on the accuracy of the calculated carrier-capture coefficients. In Fig. 8, the omission or inclusion of f_s causes differences in the capture coefficients that often exceed an order of magnitude, with the results resting below experiments when omitted and above them when applied. These corrections, which are intended to correct for the Coulomb interaction of a spatially extended free carrier as it approaches a charged defect during capture, originate from work first reported by Sommerfeld in 1931 [152], and then Pässler in 1976 [16], and remain in use even now with little subsequent modification [25,35] (excepting recent rederivations done to accommodate low-dimensional materials [153]). One readily infers that such corrections may be less evolved and tested than the present-day DFT-based MPE-theories they are intended to correct.

Interestingly, Nichols *et al.* [45] and some other multiple-mode practitioners [23,26,27] have omitted use of the traditional Sommerfeld scaling factors altogether, unlike various single-mode practitioners [25,35,36,40]. [Even so, Nichols *et al.* do discuss the need for a “Sommerfeld factor to correct for small supercell effects,” which appears to instead correspond to a separate Coulomb-related effect specifically attributed to an interaction of the band-edge wave function with the charged defect when a finite-size supercell is used for electron-phonon matrix-element calculations, as described in Ref. [35]. This latter effect is designated f_c herein, per the discussion following Eq. (20). It plays no role in the works under discussion because the electron-phonon matrix elements associated with f_c have all been calculated by displacing the *neutral* defect configuration such that f_c (quite unlike f_s) is unity.] Given the historical character, the large magnitude, and the ambiguous author-dependent inclusion or omission of the traditional Sommerfeld scaling factor [16], further studies to test, clarify, and improve such scaling appear to be needed. In Ref. [40], Singh *et al.* have discussed some of the underpinning assumptions of Pässler’s treatment [16] of the Sommerfeld effect [152], which may be a starting point for such studies. While further study of the Sommerfeld factor has merit, the prevailing view nonetheless holds that *some form* of Sommerfeld-like correction remains appropriate—basically, because the modest supercell sizes typically used within DFT for describing the wave-function overlap of defect states and free-carrier states [per Eq. (21)] essentially omit the longer-range Coulomb interactions present at the onset of capture [16,153].

The relatively small dispersion of the five results shown at the bottom of Fig. 8, where in each case the Sommerfeld scaling factors have been omitted, results from our efforts

to briefly investigate the relative performance of the single-mode and multiple-mode formalisms when applied under similar circumstances. Nichols *et al.* [45] have understandably attributed their substantial improvement in modeling accuracy (diamond symbols, Fig. 8) to their use of the multiple-mode formalism in place of the single-mode formalism used in Refs. [25] and [35] (black curves, Fig. 7). However, as shown by the bottom-most three curves in Fig. 8, we can closely replicate the results of multiple-mode theory by simply recalculating the single-mode theory under conditions similar to Ref. [45] (i.e., by using only small, 96-atom supercells and shifted $2 \times 2 \times 2$ k -point sampling when determining the CC-diagram's potential energy curves) provided that we make one critical and surprising change to our current approach: *the intentional omission of all finite-size corrections.*

The resulting MPE parameters ($\hbar\Omega_e^h = 46.3$ meV, $\hbar\Omega_r^h = 37.8$ meV, $Q_0 = 1.524$ amu^{1/2} Å, and $E_t = 0.752$ eV) produce the hole-capture coefficients in Fig. 8 (light-red dotted line) resting less than a factor of 2 above the multiple-mode results (diamond symbols) shown for Ref. [45]. Moreover, if we raise the calculated E_t by only 25 meV, we find that the resulting hole-capture coefficients in Fig. 8 (black dotted line) then fall directly on top of the multiple-mode results shown for Ref. [45]. The corresponding thermal barriers to hole capture for this work's two single-mode calculations done without finite-size corrections are $E_b = 0.159$ and 0.184 eV, where the latter value may be viewed as a precise fit to the thermal barrier implicitly present in the multiple-mode results. The small, 25 meV difference between these thermal barriers probably arises from variations in underlying methodological factors used herein versus in Ref. [45]. Such factors include the hybrid-functional implementations (LIBXC vs VASP), the pseudopotential selection and type (NCPs vs PAWs), and the DFT codes (SOCORRO vs VASP). Because the present *uncorrected* single-mode work closely reproduces the multiple-mode work done in Ref. [45] where finite-size corrections have been necessarily omitted (presumably because of formalistic complications), we can conclude that it is the multiple-mode theory's *fortuitous omission of the incorrect finite-size corrections* used in the previous single-mode modeling [25,29,35] that primarily improves the accuracy of the multiple-mode treatment of hole capture by $C_N(q = -1)$. It is not the detailed inclusion of multiple-phonon-mode physics that is pivotal, as stated in Ref. [45]. Instead, the correct conclusion is that the single-mode and multiple-mode models are quite similar in modeling accuracy, at least for the present case of hole capture by $C_N(q = -1)$ in GaN.

During peer review of the present work, we found one more noteworthy, but less-noticed, multiple-phonon-mode study of hole capture by $C_N(q = -1)$ in GaN done by Zhang *et al.* [154]. Surprisingly, these multiple-phonon results forerun those of Nichols *et al.* by nearly seven years yet find similarly large hole-capture coefficients that vary from about 1×10^{-7} cm³/s near 20 K up to 4×10^{-7} cm³/s near 800 K, when Sommerfeld scaling factors are omitted. Proceeding as above, we have inferred the difference between the thermal barrier implicit in Zhang *et al.*'s multiple-mode results and that of our uncorrected, 96-atom, single-mode results in Fig. 8. In this case, the hole-capture barrier of Zhang *et al.* rests

approximately 45 meV lower than ours, instead of 25 meV higher as seen above for Nichols *et al.* Because the differences between these three hole-capture barriers remain quite modest, we interpret Zhang *et al.*'s results as further reinforcing our conclusion regarding the similarity of results for single-mode and multiple-mode models.

The above comparisons yield an important corollary. To wit, when performing carrier-capture calculations using the single-mode approach, the use of no finite-size corrections at all is far superior for determining E_b (which is the single most important MPE-theory parameter to get right) than an inconsistent use of the incorrect traditional corrections designed for configurationally relaxed defects. The traditional corrections strictly apply at the two parabolic energy minima of the CC diagram, but not anywhere else. The problem created by the traditional corrections is that they correctly raise E_t , thus shifting the separation of the diagram's parabolas, but fail to simultaneously increase the curvature of the parabolic potential-energy curves that define the phonon energies. The resulting internal inconsistency of the two sets of defect energies within the CC diagram manifests as a shift-induced error in the parabolic crossover point, such that finite-size correction ends up *unintentionally enhancing* the post-correction error in E_b . Without this enhanced error, the carrier-capture coefficient without finite-size corrections is only about five times too low at low temperature (see red-dashed line versus red-dotted line in Fig. 8), and not more than four orders of magnitude too low as in Fig. 7 (see red-dashed line versus black-dashed line in Fig. 7).

2. Electron-capture coefficients for $C_N(q = 0)$

Figure 9 shows the rate coefficient for nonradiative electron capture by neutral C_N (black curve), calculated using Eq. (20) and the MPE-theory parameters given at the close of Sec. III C 1. The calculations also use a value for $V_s W_{if}^2 = 0.363$ eV² Å³/amu, which was calculated much as described above for hole capture, with the needed wave functions and band eigenvalues again calculated for configurational displacements about $C_N(q = 0)$. For electron capture, however, the states involved are redefined such that the spin-down defect band within the gap becomes the initial state, and a single, nondegenerate band at the conduction-band edge becomes the final state. In Fig. 9, the very small, calculated values for *nonradiative* capture by MPE are caused by the large barrier, $E_b = 1.08$ eV, determined by the electron-capture CC diagram shown in Fig. 5. In contrast, the measured and calculated rates for *radiative* capture shown for comparison in Fig. 9 are much larger and independent of temperature [34,98]. Hence, the radiative electron-capture process completely dominates at low and intermediate temperatures, giving the ubiquitous YL1-band luminescence signature of carbon impurities in GaN.

Figure 9 further compares our nonradiative electron-capture results to both computational results recently reported by Zhao *et al.* [44] and measurements of the thermal quenching of YL1-band PL at higher temperatures reported by Reshchikov [105]. As seen above for hole capture, our results for the nonradiative electron-capture coefficient for $C_N(q = 0)$ in GaN also rest orders of magnitude above previous results

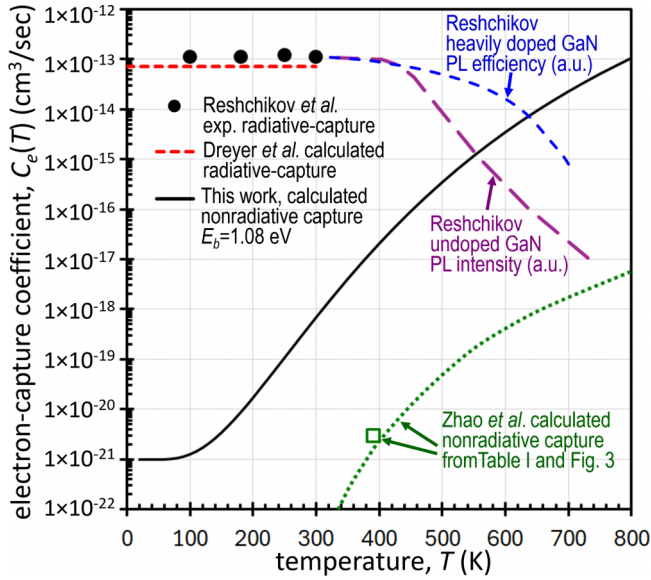


FIG. 9. Rate coefficients vs temperature for nonradiative electron capture by $C_N(q=0)$ calculated herein are compared to those of Zhao *et al.* [44]. Also shown are measured values (Reshchikov *et al.* [98]) and calculated values (Dreyer *et al.* [34]) for radiative capture giving YL1-band luminescence, as well as measurements of the quenching of YL1-band luminescence with rising temperature (Reshchikov [105], Figs. 2 and 10 therein). We have renormalized the PL measurements of Ref. [105] to match the experimental radiative-capture coefficients shown at lower temperatures.

[44]. As one may infer, this occurs because Ref. [44] has continued to use the traditional but incorrect, ground-state-centric finite-size corrections in their CC diagrams whereas we again apply the new finite-size correction suggested by Kumagai [50]. Comparing to Reshchikov's PL-quenching measurements in Fig. 9 (dashed curves), we see that our rapidly rising results for nonradiative electron-capture (solid-line curve, where $E_b \approx 1.08$ eV) remain just low enough at intermediate temperatures for the thermal emission of holes (from neutral C_N defects to the valence band, where the activation energy is $E_A \approx 0.85$ eV) to completely dominate the YL1-band PL quenching observed beyond 400–450 K in GaN [105].

IV. CONCLUSIONS

To conclude, we have thoroughly demonstrated the importance of the new finite-size corrections recently proposed for use in CC diagrams by Kumagai [50]. In doing so, we have pursued a refined understanding of the underlying electrostatic phenomena and the resulting finite-size corrections originally articulated by Gake *et al.* [51] and Falletta *et al.* [52] within a context appropriate to CC diagrams. We have then extensively applied the resultant finite-size correction schemes to studies of carrier capture by substitutional C_N in GaN to investigate their efficacy and compare to previous work.

The application of the finite-size corrections of Kumagai [50] within probative recalculations of the carrier-capture coefficients for C_N in GaN yields several novel results of

basic relevance to accurate studies of MPE theory when using the single-effective-mode formalism. Most notably, we find through our efforts to construct CC diagrams as a detailed function of supercell size that *even defects residing in charge-neutral supercells require significant, Madelung-like, finite-size corrections that are first order in $1/L$ once the defect's configuration displaces away from its fully relaxed state.* Moreover, the uncorrected defect-formation energies *exhibit Madelung-energy-related slopes that vary parabolically with the interpolation parameter, α , used to construct the displaced defect configurations that form the CC diagrams, which is exactly as predicted by Kumagai [50].* For a defect within a supercell of net charge q , the surprising parabolic behavior observed for a neutral defect persists, but now in conjunction with a configuration-independent Madelung energy that varies traditionally as q^2 .

Moving beyond the described first-order Madelung-energy contributions, we have additionally examined the finite-size contributions within CC diagrams of order $1/L^3$ by comparing a benchmark-quality hybrid-fitting approach with the potential-alignment approach originally popularized by FNV [65,66], which has been recently modified to correctly include vertical transitions [67]. Our primary findings here are twofold. First, the accuracy of the higher-order, potential-alignment component of the FNV-derived finite-size correction as now implemented for vertical transitions [67] performs with an accuracy similar to that established when appropriately applied at defect ground states [72]. However, the substitutional C_N defect in GaN presents only weak nonlinearities in $E_f(1/L)$ and thus offers an undemanding, almost benign test case. Further studies of the FNV method's alignment-correction accuracy within CC diagrams, if done by using defects with higher charge states and larger nonlinearities in $E_f(1/L)$, would better establish applicability in this new realm.

Second, for alignment corrections separately calculated using formulations that sum a series of ground-state-like contributions, as was done to first understand finite-size corrections for vertical transitions [50–53], we find noticeable disagreement between these formulations when specifically applied to CC diagrams, with their results also tending to disagree with the fully integrated vertical-transition-state formulation implemented within the *sxdefectalign* code [67]. This observation contrasts with the corresponding Madelung-energy corrections, where all formulations agree even when applied to CC diagrams. The integrated *sxdefectalign* formulation best agrees with our more rigorous hybrid-fitting approach, while uniquely exhibiting characteristics in accord with our current understanding of alignment corrections, where only the externally applied charge q of the final state requires alignment. We therefore recommend the vertical-transition-state capability of *sxdefectalign* as the preferred approach for those using the FNV method to implement finite-size corrections for any DFT calculations used to construct CC diagrams.

Finally, we have assessed the modeling fidelity attainable when Kumagai's finite-size corrections are properly applied within recalculations of carrier-capture coefficients for C_N in GaN. Recapitulating those results, we find that proper finite-size corrections raise the hole-capture coeffi-

cients of $C_N(q = -1)$ by *two to four orders of magnitude* relative to those of Ref. [35]. Moreover, these new results rest adjacent to *either the lower, or the upper*, standard-error bounds of the available temperature-dependent experimental measurements [95–97,99,104] when the somewhat-debated Sommerfeld scaling factors have been correspondingly *either omitted from, or applied to*, the purely DFT-based results. The venerable Sommerfeld factor itself [16] thus emerges as an additional post-DFT correction that may partly limit overall carrier-capture modeling accuracy. Our efforts to repeat the hole-capture calculations for $C_N(q = -1)$ within small, 96-atom supercells and without applying finite-size corrections has revealed two final insights. Firstly, we have found that the use of no finite-size corrections at all is strongly preferred over present-day use of the mostly incorrect ground-state-based finite-size corrections, especially when determining the barrier energy to capture. Lastly, by comparing the small-cell-size hole-capture coefficients calculated herein using the *single-effective-mode* formalism to those recently calculated using a *multiple-phonon-mode* formalism [45,154], we have found that these differing formalisms give essentially equivalent calculated carrier-capture coefficients—once *all* finite-size corrections are omitted in both formalisms. The noted equivalence would prove interesting to explore across a broader range of defects and materials, as the present finding is specific to hole capture by $C_N(q = -1)$ in GaN.

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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.

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