Tuning the valence and concentration of europium and luminescence centers in GaN through co-doping and defect association

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Defect physics of Eu-doped GaN is investigated using first-principles hybrid density-functional defect calculations. This includes the interaction between the rare-earth dopant and native defects (Ga and N vacancies) and other impurities (O, Si, C, H, and Mg) unintentionally present or intentionally incorporated into the host material. While the trivalent Eu$^{3+}$ ion is often found to be predominant when Eu is incorporated at the Ga site in wurtzite GaN, the divalent Eu$^{2+}$ is also stable and found to be predominant in a small range of Fermi-level values in the band-gap region. The Eu$^{2+}$/Eu$^{3+}$ ratio can be tuned by tuning the position of Fermi level and through defect association. We find co-doping with oxygen can facilitate the incorporation of Eu into the lattice. The unassociated Eu$_{Ga}$ is an electrically and optically active defect center and its behavior is profoundly impacted by local defect–defect interaction. Among the Eu-related defects, we identify complexes such as Eu$_{Ga}$O$_{N}$, Eu$_{Ga}$Si$_{Ga}$, Eu$_{Ga}$H$_{H}$, Eu$_{Ga}$Mg$_{Ga}$, and Eu$_{Ga}$O$_{N}$Mg$_{Ga}$ as efficient defect-related Eu$^{3+}$ centers for non-resonant excitation. This work calls for a re-assessment of certain assumptions regarding specific defect configurations previously made for Eu-doped GaN and further investigation into the origin of the photoluminescence hysteresis observed in (Eu,Mg)-doped samples.

I. INTRODUCTION

Rare-earth (RE) doped III-nitrides are of interest for optoelectronic and spintronic applications [1]. Thanks to their 4f-electron core, which is well shielded by the outer 5s$^2$ and 5p$^6$ electron shells, these RE dopants offer very sharp intra-f optical transitions at wavelengths from the infrared to ultraviolet. GaN doped with trivalent europium (Eu$^{3+}$), for example, emits visible light in the red spectral region and is considered as a promising candidate for light-emitting diodes (LEDs) [2, 3]. In general, a RE luminescence center can be optically excited by resonant (direct) or non-resonant (indirect) excitation. In the former the excitation energy is directly absorbed into the 4f-electron core, whereas in the latter it is indirectly transferred from the host. The non-resonant excitation mechanism is believed to be mediated by defects which act as carrier traps. An electron (hole) trapped at a defect level can then recombine non-radiatively with a hole (electron), e.g., from the valence (conduction) band, and the recombination energy is transferred to the 4f-core.

RE-related defects are of interest in particular because of the close proximity of the RE ion to the carrier trap which enhances energy transfer efficiency. A detailed understanding of defect physics in RE-doped III-nitrides is thus essential to understanding their properties and to designing materials with improved performance.

Experimentally, while the trivalent Eu$^{3+}$ ion was found to be predominant in Eu-doped GaN samples and multiple Eu$^{3+}$ luminescence centers were observed [4, 12], the divalent Eu$^{2+}$ has also been found or suspected to be present [13, 20]. In addition to being of interest for its magnetic properties [14, 15, 20], Eu$^{2+}$ can offer useful luminescence centers in its own right. Mahalingam et al. [15], for example, attributed the blue emission in Eu-doped GaN/SiO$_2$ nanocomposites to the presence of Eu$^{2+}$. Mitchell et al. [19] reported a thorough work on the control of the Eu$^{2+}$/Eu$^{3+}$ ratio in GaN through co-doping and by tuning the growth conditions and were able to achieve high Eu$^{2+}$ concentrations using O and/or Si as co-dopants and suitable experimental conditions. Oxygen was found to play a critical role in the incorporation of Eu into GaN and the quality of Eu-doped GaN samples prepared by organo-metallic vapor phase epitaxy (OMVPE) [19, 21] and lead to sharp and uniform emission spectra and improved energy transfer efficiency [19, 21, 22]. Significant enhancement of the luminescence intensity were also found in GaN co-doped with Eu and Mg [23, 27] or Si [28]. Notably, Mg-containing Eu-doped GaN samples were reported to exhibit thermally activated photoluminescence (PL) hysteresis through the so-called “hysteretic photochromic switching” [24, 32]. Altogether the luminescence in Eu-doped GaN can be characterized by its complexity with the presence of multiple optically active centers and the dependence on the growth conditions. The interpretation of experimental observations and the discussion in terms of specific defect configurations have been, however, largely speculative.

On the theory side, calculations for Eu-doped GaN were carried out by several research groups using density-functional theory (DFT) based methods, including the local-density approximation (LDA) or self-interaction corrected LDA, the generalized gradient approximation (GGA), and GGA+$U$, and LDA+$U$ within a DFT-based tight-binding approach [33–41]. These studies provided useful information on the structural and electronic properties but limited data on defect structure and energetics. Besides, the computational methods employed in these
previous studies are known to have limited predictive power, especially in determining defect energy levels \[42\]. A more rigorous theoretical and computational approach is needed for the study of defect physics in Eu-doped GaN. In such an approach, the employed methods should possess the ability to overcome the “band-gap problem” encountered in standard DFT/DFT+U calculations and, at the same time, provide a reasonable description of the RE 4f states in the RE-doped system. In addition, all orbitals in the system should be treated on equal footing.

Here, we present a first-principles investigation of defect physics in Eu-doped GaN using hybrid density-functional defect calculations. The hybrid DFT/Hartree-Fock method \[43\] employed here has been shown to be successful in the study of defects in semiconductors in general \[42\] and RE-doped materials in particular \[44\]. Specific calculations are carried out for the substitutional Eu impurity, native point defects (Ga and N vacancies), and impurities (O, Si, C, H, and Mg) in both the unassociated (i.e., isolated defect) form and the associated (i.e., defect complex) form. These impurities are selected as they are common unintentional or intentional co-dopants in GaN. Based on the results, we discuss the tuning of Eu-related defects as optically active defect centers. Efficient Eu3+ luminescence centers are identified and the reported photoluminescence hysteresis is discussed.

II. METHODOLOGY

We model defects in the GaN host using a supercell approach in which a defect is included in a periodically repeated finite volume of the host material. Note that we often use “defect” as a generic term, referring to not only native point defects (intrinsically to the materials) but also impurities (i.e., extrinsic point defects; not to be confused with “impurity phases”), and defect complexes; impurities can be intentionally incorporated (i.e., dopants) or unintentionally present. The formation energy of a defect X in effective charge state q (i.e., with respect to the host lattice) is defined as \[42\] \[45\]

\[
E^f(X^q) = E_{\text{tot}}(X^q) - E_{\text{tot}}(\text{bulk}) - \sum_i n_i \mu_i + q(E_v + \mu_e) + \Delta^q, \tag{1}
\]

where \(E_{\text{tot}}(X^q)\) and \(E_{\text{tot}}(\text{bulk})\) are the total energies of the defect and bulk supercells; \(n_i\) is the number of atoms of species \(i\) that have been added (\(n_i > 0\)) or removed (\(n_i < 0\)) to form the defect; \(\mu_i\) is the atomic chemical potential, representing the energy of the reservoir with which atoms are being exchanged. \(\mu_e\) is the electronic chemical potential, i.e., the Fermi level, representing the energy of the electron reservoir, referenced to the valence-band maximum (VBM) in the bulk \(E_v\). Finally, \(\Delta^q\) is the correction term to align the electrostatic potentials of the bulk and defect supercells and to account for finite-size effects on the total energies of charged defects, calculated following the procedure of Freysoldt et al. \[46\] \[47\].

In thermodynamic equilibrium, the formation energy of a defect directly determines the concentration \[45\]:

\[
c = N_{\text{sites}}N_{\text{config}} \exp \left( -\frac{E^f}{k_B T} \right), \tag{2}
\]

where \(N_{\text{sites}}\) is the number of high-symmetry sites in the lattice (per unit volume) on which the defect can be incorporated, \(N_{\text{config}}\) is the number of equivalent configurations (per site), and \(k_B\) is the Boltzmann constant. Clearly, at a given temperature, a defect that has a lower formation energy will be more likely to form and occur with a higher concentration. Note that, when a material is prepared under non-equilibrium conditions, excess defects can be frozen-in and the equilibrium concentration estimated via Eq. \[2\] is only the lower bound \[48\].

While the Fermi level in Eq. \[1\] can be treated as a variable, it is not a free parameter. The actual Fermi-level position can be determined by solving the charge-neutrality equation \[45\]:

\[
\sum_i c_i q_i - n_e + n_h = 0, \tag{3}
\]

where \(c_i\) and \(q_i\) are the concentration and charge, respectively, of defect \(X_i\); \(n_e\) and \(n_h\) are free electron and hole concentrations, respectively; and the summation is over all possible defects present in the material.

From defect formation energies, one can calculate the thermodynamic transition level between charge states \(q\) and \(q'\) of a defect, \(\epsilon(q/q')\), defined as the Fermi-level position at which the formation energy of the defect in charge state \(q\) is equal to that in charge state \(q'\) \[42\], i.e.,

\[
\epsilon(q/q') = \frac{E^f(X^q; \mu_e = 0) - E^f(X^{q'}; \mu_e = 0)}{q' - q}, \tag{4}
\]

where \(E^f(X^q; \mu_e = 0)\) is the formation energy of the defect X in charge state q when the Fermi level is at the VBM \(\mu_e = 0\). This \(\epsilon(q/q')\) level [often referred to as the \((q/q')\) level], corresponding to a defect energy level (or simply defect level), would be observed in, e.g., deep-level transient spectroscopy (DLTS) experiments where the defect in the final charge state \(q'\) fully relaxes to its equilibrium configuration after the transition. Note that these defect levels are not the same as the Kohn-Sham levels obtained in a band-structure calculation such as those associated with the so-called “defect states” that may be observed in the electronic density of states (DOS) of a system in the presence of a defect. In fact, the Kohn-Sham levels cannot be directly identify with any levels that can be observed in experiments \[42\] \[45\].

Our total-energy calculations are based on DFT with the Heyd-Scuseria-Ernzerhof (HSE) functional \[43\], the projector augmented wave method \[49\], and a plane-wave basis set, as implemented in the Vienna \textit{Ab Initio} Simulation Package (VASP) \[50\]. The Hartree-Fock mixing
parameter is set to 0.31 and the screening length to the default value of 10 Å. These parameters result in a band gap of 3.53 eV for GaN, very close to that (~3.5 eV) reported in experiments. Defects in GaN are simulated using a 96-atom supercell and a 2×2×2 Monkhorst-Pack k-point mesh for the integrations over the Brillouin zone. In defect calculations, the lattice parameters are fixed to the calculated bulk values but all the internal coordinates are relaxed. The Eu 4f electrons are included explicitly in the calculations since in Eu-doped GaN the 4f states are present in the band gap and play an important role in the material’s defect physics. This is different from, e.g., the case of erbium (Er) doped GaN in which Er 4f electrons can be treated as core states [51]. In all calculations, the plane-wave basis-set cutoff is set to 400 eV and spin polarization is included. All structural relaxations are performed with the HSE functional and the force threshold is chosen to be 0.04 eV/Å or smaller.

The chemical potentials of Ga, N, Eu, H, C, O, Si, and Mg are referenced to the total energy per atom of bulk Ga, N, H2 at 0 K, bulk Eu, H2 at 0 K, bulk C (diamond), O2 at 0 K, bulk Si, and bulk Mg, respectively. μGa and μN vary over a range determined by the formation enthalpy of GaN such that μGa ± μN = ΔH(GaN) (calculated to be −1.26 eV at 0 K). We will examine defect landscape in GaN in two extreme limits: Ga-rich (μGa = 0) and N-rich (μN = 0) conditions. Specific values of the Eu, H, C, O, Si, and Mg chemical potentials are determined by assuming equilibrium with EuN (ΔH = −1.20 eV at 0 K), H2 at 0 K, bulk C, β-Ga2O3 (−10.07 eV), β-Si3N4 (−9.17 eV), and Mg3N2 (−4.16 eV), respectively. It should be noted that the transition level ϵ(q/q’) [Eq. ⅱ] is independent of the choice of the atomic chemical potentials.

III. RESULTS

A. Unassociated native defects and impurities

In bulk (i.e., perfect and undoped) GaN (wurtzite, space group P63mc), each Ga is coordinated with four N atoms: one along the c-axis and three in the basal (ab) plane. There is a small C3v distortion at the Ga lattice site with the Ga–N bond length calculated for the axial N atom (1.958 Å) slightly different from that for the basal N atoms (1.952 Å). For comparison, the experimental values for the axial and basal Ga–N bond lengths are 1.956 Å and 1.949 Å [52], respectively. In the presence of a defect, the lattice environment in the defect’s vicinity can be further distorted, and such a local distortion is often different for different charge configurations.

Figure ⅱ shows the calculated formation energies of various unassociated (i.e., isolated) native point defects and impurities in GaN. The substitutional Eu impurity (EuGa) is found to be stable as EuGa0 (i.e., Eu3+ at the Ga3+ lattice site, with a calculated magnetic moment of 6 μB; spin S = 3) and/or EuGa+ (i.e., Eu2+ at the Ga3+ site, with a magnetic moment of 7 μB; spin S = 7/2), depending on the Fermi-level position. EuGa introduces two defect levels in the bulk band gap: the (+/0) level at 0.22 eV above the VBM and the (0/−) level at 3.09 eV (i.e., 0.44 eV below the CBM). It should be noted, however, that “EuGa3+” is not a true charge state of EuGa. It is, in fact, a defect complex consisting of EuGa0 and an electron hole (h+; spin S = 1/2) localized on one of the neighboring basal N atoms. In the EuGa0 (EuGa) configuration, the Eu–N bond length is 2.233 Å (2.321 Å) for the axial N atom and 2.197–2.208 Å (2.283–2.297 Å) for the basal N atoms. The local distortion at the Ga lattice site where the Eu dopant is incorporated is thus more pronounced and slightly deviates from the C3v symmetry. The result is also consistent with the fact that the ionic radius of Eu3+ is smaller than that of Er3+.

The electronic behavior of Eu is thus different from that of erbium (Er) in GaN. Er was found to be stable only as Er3+, and the isolated ErGa does not introduce any defect levels [51]. The origin of the difference can be traced back to the difference in their electronic structure.

For the results of the nitrogen vacancy (VN), gallium vacancy (VGa), hydrogen interstitial (H), and substitutional carbon (CN) and oxygen (ON) were already reported and discussed in detail in Ref. [51] but are included in Fig. ⅱ for easy reference since in the next sections we will discuss defect complexes consisting of EuGa and these native point defects and impurities. VN introduces the (3+) defect.
FIG. 2. Formation energies of defect complexes consisting of Eu\(_{\text{Ga}}\) and native defects in GaN, Eu\(_{\text{Ga}}\)-V\(_{\text{N}}\) and Eu\(_{\text{Ga}}\)-V\(_{\text{Ga}}\), plotted as a function of Fermi level from the VBM to the CBM, under the Ga-rich and N-rich conditions. For each defect, only segments corresponding to the lowest-energy charge states are shown. Large solid dots connecting two segments with different slopes mark the defect levels. V\(_{\text{N}}\) can be at the basal or axial N site with respect to the Eu\(_{\text{Ga}}\) component. The (0\/-) level of Eu\(_{\text{Ga}}\)-V\(_{\text{N}}\) is right above the CBM. Level at 0.53 eV above the VBM and the (+/0) level at 0.27 eV below the CBM. V\(_{\text{Ga}}\) has four defect levels in the band gap: (+/0) at 1.03 eV and (0/-) at 1.67 eV above the VBM, and (-/2-) at 1.29 eV and (2/-3-) at 0.71 eV below the CBM. H\(_{\text{i}}\) is amphoteric [i.e., positively (negatively) charged in the p-type (n-type) GaN] and its (+/-) level occurs at 0.50 eV below the CBM. C\(_{\text{N}}\) has two defect levels: (+/0) at 0.31 eV and (0/-) at 1.02 eV above the VBM. O\(_{\text{N}}\) is a shallow donor and only stable as O\(_{\text{N}}^+\) [51]. We find that Si\(_{\text{Ga}}\) is also a shallow donor, being stable only in the Si\(_{\text{Ga}}^+\) configuration. Si (O) thus readily donates one electron to the lattice and becomes a positively charged defect when incorporated at the Ga (N) lattice site in GaN. The result for Si\(_{\text{Ga}}\) is in agreement with that reported by Matsubara and Bellotti [53].

B. Defect complexes of Eu and native defects

Some of the unassociated defects discussed in Sec. III A can come close and form defect complexes. Such defect association often changes the local lattice environment and defect energetics and can lead to important implications. Figure 2 shows the formation energies of defect complexes consisting of Eu\(_{\text{Ga}}\) and native defects V\(_{\text{N}}\) and V\(_{\text{Ga}}\). Eu\(_{\text{Ga}}\)-V\(_{\text{N}}\) and Eu\(_{\text{Ga}}\)-V\(_{\text{Ga}}\) have been widely speculated in the literature as possible luminescence centers in Eu-doped GaN [2, 3, 5, 11, 40]. In the case of Eu\(_{\text{Ga}}\)-V\(_{\text{N}}\), the V\(_{\text{N}}\) part can be at the basal or axial lattice site with respect to Eu\(_{\text{Ga}}\); see Fig. 3. We find that Eu\(_{\text{Ga}}\)-V\(_{\text{N}}\) introduces four defect levels in the band gap region: (3+/2+) at 0.76 eV, (2+/+) at 0.90 eV, and (+/0) at 1.86 eV above the VBM, and (0/-) at 0.07 eV above the CBM. A careful inspection shows that in going from (Eu\(_{\text{Ga}}\)-V\(_{\text{N}}\))^0 to (Eu\(_{\text{Ga}}\)-V\(_{\text{N}}\))^- the additional electron stays in the vicinity of the void formed by V\(_{\text{N}}\); (Eu\(_{\text{Ga}}\)-V\(_{\text{N}}\))^0 is a defect complex consisting of Eu\(_{\text{Ga}}\) and V\(_{\text{N}}^+\) whereas (Eu\(_{\text{Ga}}\)-V\(_{\text{N}}\))^- is a complex of Eu\(_{\text{Ga}}\) and V\(_{\text{N}}^0\); see also Table I. The extra electron is thus captured by the V\(_{\text{N}}\) part of the complex and the substitutional Eu at the Ga site remains Eu\(_{\text{Ga}}^{2+}\). The axial geometric configuration, i.e., Eu\(_{\text{Ga}}\)-(V\(_{\text{N}}\))\(_{\text{axial}}\) has a higher formation energy than the basal one in all the stable charge states; its defect transition levels are also slightly shifted as seen in Fig. 2 e.g.
the (0/−) level is now at 0.02 eV above the CBM. Eu$_{\text{Ga}}$-$V_{\text{Ga}}$, on the other hand, has six defect levels: (3/−/2+) at 0.95 eV, (2+/+) at 1.35 eV, (0+/0) at 1.77 eV, (0/−) at 1.92 eV, (−2/−) at 2.17 eV, and (2−/−) at 2.61 eV above the VBM. The highest defect level associated with this complex is thus 0.92 eV below the CBM.

The electronic behavior of Eu$_{\text{Ga}}$-V$_N$ in GaN. Er$_{\text{Ga}}$-(V$_N$)$_{\text{basal}}$ was also reported to have the (0/−) level at 0.02 eV above the CBM [51]. Our results for Eu$_{\text{Ga}}$-V$_N$ and Eu$_{\text{Ga}}$-V$_{\text{Ga}}$ are, however, qualitatively different from those reported by other groups [35, 37], which can be ascribed to the different methods used in the current work and the previously reported studies.

The local lattice environment is changed significantly due to defect–defect interaction. For example, in (Eu$_{\text{Ga}}$-V$_N$)$^0$, Eu moves off-center and closer to the vacancy by 0.27 Å; see Fig. 3(a). The binding energy of the complex with respect to its isolated constituents, Eu$_{\text{Ga}}$ and V$_N^-$, is 2.20 eV. In the other stable charge states of the basal configuration, (Eu$_{\text{Ga}}$-V$_N$)$^q$ with $q = +$, 2+, and 3+, the displacement is 0.19 Å, 0.27 Å, and 0.38 Å, respectively. Similar local lattice distortion is observed in the axial geometric configurations; for example, the displacement of Eu in (Eu$_{\text{Ga}}$-V$_N$)$^0$ is 0.25 Å along the c-axis and toward the vacancy; see Fig. 3(b). The local distortion is even larger in the case of (Eu$_{\text{Ga}}$-V$_{\text{Ga}}$)$^q$ where Eu moves closer to the vacancy by 0.78 Å ($q = 0$), 0.32 Å ($q = 1$), 0.49 Å ($2−$), and 1.33 Å ($3−$). The position of their neighboring atoms is also slightly shifted as seen in Figs. 3 and 4.

The structure and energetics of a defect complex, in general, can be expressed in terms of those of its isolated constituents which are usually elementary defects acting as basic building blocks [51, 52]. The example involving Eu$_{\text{Ga}}$-V$_N$, given above is an illustration of such an analysis. In Table I we list the characteristics of all Eu-related defect complex configurations, including the valence state of Eu, constituent defects, and binding energy of the complexes with respect to the isolated constituents. Note that the decomposition of (Eu$_{\text{Ga}}$-V$_{\text{Ga}}$)$^q$ with $q = 0, +, +2, +3$ into basic building blocks is not straightforward due to the very strong local lattice distortion which makes it difficult to identify constituent defects. For example, due to the large displacement, Eu might be regarded as being incorporated as an interstitial defect (Eu$_i$) instead of the substitutional Eu$_{\text{Ga}}$.

The results summarized in Table I show that Eu is stable as Eu$^{3+}$ in all the stable charge states of the complexes with Ga or N vacancies, except (Eu$_{\text{Ga}}$-V$_N$)$^q$ ($q = 0, −$) and (Eu$_{\text{Ga}}$-V$_{\text{Ga}}$)$^q$ ($q = 0, +$) in which Eu is stable as Eu$^{2+}$. Compared to the unassociated Eu$_{\text{Ga}}$, the association between Eu$_{\text{Ga}}$ and V$_N$ is found to extend the range of Fermi-level values below the CBM under which Eu$^{2+}$ is energetically more stable than Eu$^{3+}$, from 0.44 eV in the former (see Fig. 1) to 1.67 eV in the latter (Fig. 2). The binding energy of Eu$_{\text{Ga}}$-V$_N$ is relatively large, suggesting that it can exist as a defect complex in real samples. Eu$_{\text{Ga}}$-V$_{\text{Ga}}$, on the other hand, has a much smaller binding energy; see Table I. Together with the high calculated formation energy (Fig. 2), Eu$_{\text{Ga}}$-V$_{\text{Ga}}$ is unlikely to be stable or occur with a high concentration as a complex under thermodynamic equilibrium growth conditions (see further discussion in Sec. IV A).

### C. Defect complexes of Eu and other impurities

In addition to the native point defects, Eu$_{\text{Ga}}$ can also form complexes with impurities that are unintentionally present in the growth environment or intentionally incorporated into the host material as co-dopants. Figure 5 shows the formation energies of defect complexes Eu$_{\text{Ga}}$-H$_N$, Eu$_{\text{Ga}}$-C$_N$, Eu$_{\text{Ga}}$-O$_N$, and Eu$_{\text{Ga}}$-Si$_{\text{Ga}}$. Eu$_{\text{Ga}}$-H$_N$ has one defect level in the bulk band gap: (+/0) at 1.36 eV below the CBM. The (Eu$_{\text{Ga}}$-H$_N$)$^0$ configuration is a defect complex consisting of Eu$_{\text{Ga}}$ and H$_N^+$, whereas (Eu$_{\text{Ga}}$-H$_N$)$^+$ is a complex of Eu$_{\text{Ga}}^0$ and H$_N^+$; see also Table I. The valence state of Eu in the complex thus changes as one crosses the transition level (+/0). In these defect complexes, the H interstitial is bonded to one of the nearest N neighbors of Eu. In (Eu$_{\text{Ga}}$-H$_N$)$^{0+}$, the N–H distance is 1.00 Å (1.02 Å) and the distance between Eu and the N atom in the NH unit is 2.34 Å (2.30 Å); see Fig. 6(a).

Eu$_{\text{Ga}}$-C$_N$ has two geometric configurations associated with two possible positions of C$_N$ with respect to Eu$_{\text{Ga}}$. Eu$_{\text{Ga}}$-C$_N$ introduces two defect levels: (+/0) at 0.33 eV (0.17 eV) above the VBM and (0/−) at 1.08 eV (1.17 eV) below the CBM for the basal (axial) configuration. The distance between the two defects in the complex is
TABLE I. Eu-related defects in Eu-doped GaN: The stable valence state of the rare-earth (RE) ion, constituent defects, binding energy \( E_b \), magnetic moment \( M \), and defect levels \( \epsilon(q/q') \), with respect to the VBM \( E_v \), at 0 eV, or the CBM \( E_c \), at 3.53 eV). Note that \( h^+ \) is an electron hole localized at an N lattice site. Spin-polarized defects in a complex are found to interact ferromagnetically; the magnetic moment of the complex is thus equal to the sum of those of the constituents. The values in the parentheses are for the axial (with respect to Eu) configurations.

| Defect | RE ion | Constituents | \( E_b \) (eV) | \( M \) (µB) | Defect levels (eV) |
|--------|--------|--------------|----------------|-------------|------------------|
| Eu\(_{Ga}^+\) | Eu\(^{3+}\) | Eu\(^{3+}\) \(_{Ga}\) + \( h^+ \) | 1.58 (1.08) | 6 | \( \epsilon(+/0) = E_v + 0.22 \) |
| Eu\(_{Ga}^-\) | Eu\(^{3+}\) | Eu\(^{2+}\) \(_{Ga}\) | 1.37 (1.07) | 7 | \( \epsilon(2+/+0) = E_v + 0.90 (0.81) \) |
| (Eu\(_{Ga}-\text{V}N\))\(^{3+}\) | Eu\(^{3+}\) | Eu\(^{0}\) \(_{Ga}\) + V\(^{3+}\) \(_N\) | 0.16 | 8 | \( \epsilon(-2/-3) = E_c - 1.36 \) |
| (Eu\(_{Ga}-\text{V}N\))\(^{2+}\) | Eu\(^{3+}\) | Eu\(^{0}\) \(_{Ga}\) + V\(^{2+}\) \(_N\) | 0.23 | 7 | \( \epsilon(-/0) = E_c - 1.08 (1.17) \) |
| (Eu\(_{Ga}-\text{V}N\))\(^+\) | Eu\(^{3+}\) | Eu\(^{2+}\) \(_{Ga}\) + V\(^{3+}\) \(_N\) | 0.45 | 6 | \( \epsilon(+0) = E_c - 1.36 \) |
| (Eu\(_{Ga}-\text{H}O\))\(^+\) | Eu\(^{3+}\) | Eu\(^{0}\) \(_{Ga}\) + H\(^+\) \(_O\) | 1.25 | 6 | \( \epsilon(+0) = E_c + 0.33 (0.17) \) |
| (Eu\(_{Ga}-\text{H}O\))\(^0\) | Eu\(^{2+}\) | Eu\(^{1+}\) \(_{Ga}\) + H\(^+\) \(_O\) | 2.17 | 7 | \( \epsilon(0/-0) = E_c - 0.92 \) |
| (Eu\(_{Ga}-\text{C}N\))\(^+\) | Eu\(^{3+}\) | Eu\(^{0}\) \(_{Ga}\) + C\(^+\) \(_N\) | 0.61 (0.50) | 8 | \( \epsilon(-/0) = E_c - 1.08 (1.17) \) |
| (Eu\(_{Ga}-\text{C}N\))\(^0\) | Eu\(^{3+}\) | Eu\(^{0}\) \(_{Ga}\) + C\(^0\) \(_N\) | 0.58 (0.63) | 7 | \( \epsilon(0/-0) = E_c - 0.92 \) |
| (Eu\(_{Ga}-\text{O}N\))\(^+\) | Eu\(^{3+}\) | Eu\(^{0}\) \(_{Ga}\) + O\(^2-\) \(_N\) | 0.76 (0.62) | 6 | \( \epsilon(0/-0) = E_c - 1.26 (1.23) \) |
| (Eu\(_{Ga}-\text{Si}Ga\))\(^+\) | Eu\(^{3+}\) | Eu\(^{0}\) \(_{Ga}\) + Si\(^+\) \(_Ga\) | 1.59 (1.41) | 7 | \( \epsilon(0/-0) = E_c - 1.14 \) |
| (Eu\(_{Ga}-\text{Si}Ga\))\(^0\) | Eu\(^{2+}\) | Eu\(^{1+}\) \(_{Ga}\) + Si\(^+\) \(_Ga\) | 0.92 | 7 | \( \epsilon(0/-0) = E_c - 1.04 \) |
| (Eu\(_{Ga}-\text{Mg}Ga\))\(^0\) | Eu\(^{3+}\) | Eu\(^{0}\) \(_{Ga}\) + Mg\(^+\) \(_Ga\) + \( h^+ \) | 0.48 (0.40) | 7 | \( \epsilon(0/-0) = E_v + 0.97 (0.85) \) |
| (Eu\(_{Ga}-\text{Mg}Ga\))\(^-\) | Eu\(^{3+}\) | Eu\(^{0}\) \(_{Ga}\) + Mg\(^+\) \(_Ga\) | -0.10 (-0.06) | 6 | \( \epsilon(0/-0) = E_c - 0.78 \) |
is a complex of Eu$_{Ga}$ and Si$_{Ga}^+$, whereas (Eu$_{Ga}$-Si$_N$)$^+$ is a complex of Eu$_{Ga}^0$ and Si$_{Ga}^+$. The Eu–Si distance is 3.25 Å (3.27 Å) in the 0 (+) charge state; see Fig. 6(d).

The electronic behavior of Eu$_{Ga}$-C$_N$ is thus similar to that of Er$_{Ga}$-C$_N$ [51]. Other defect complexes are different. For example, Er$_{Ga}$-O$_N$ is a shallow donor and thus has no defect levels in the bulk band gap; Er$_{Ga}$-H$_i$ introduces the (+/−) level [51] instead of (+/0) like in the case of Eu$_{Ga}$-H$_i$. This, again, illustrates the difference between Er and the mixed-valence Eu in GaN.

D. Defect complexes of Eu, O, and Mg

We now focus on possible interaction between Eu, Mg, and O in GaN. Figure 7 shows the calculated formation energy of Mg-related defects. The unassociated Mg$_{Ga}$ has the (0/−) level at 0.39 eV above the VBM, in reasonable agreement with previous studies [56, 57]. It is noted that “Mg$_{Ga}^0$” is not a true charge state of Mg$_{Ga}$, but a defect complex consisting of Mg$_{Ga}$ and an electron hole (h$^*$) localized on one of the basal N atoms. The Mg–N distance is 2.22 Å for the N atom that hosts h$^*$ and 2.00–2.01 Å for the other N atoms. The axial configuration of Mg$_{Ga}^0$ is 10 meV higher in energy than the basal one. A metastable configuration of Mg$_{Ga}^0$, in which the hole is delocalized over all N atoms is 0.19 eV higher in energy than the ground-state one. In this configuration, all the Mg–N distances are almost equal (2.02–2.04 Å).

Eu$_{Ga}$-Mg$_{Ga}$ has a defect level, (0/−), at 0.97 eV or 0.85 eV above the VBM, see Fig. 6, depending on specific geometric configurations. (Eu$_{Ga}$-Mg$_{Ga}$)$_0^0$ is a complex consisting of Eu$_{Ga}^0$, Mg$_{Ga}$, and h$^*$, whereas (Eu$_{Ga}$-Mg$_{Ga}$)$^−$ is a complex of Eu$_{Ga}^0$ and Mg$_{Ga}^-$. Figure 6(a) shows the lowest-energy configuration of (Eu$_{Ga}$-Mg$_{Ga}$)$_0^0$ in which h$^*$ resides on the N atom that is basally (axially) bonded to Eu (Mg). Other configurations, such as that shown in Fig. 6(b), are 38–75 meV higher in energy. In the basal (with respect to Eu) configuration, see Figure 6(a), the distance between Mg and the N site that bridges Mg and Eu is 2.12 Å (2.02 Å) when the complex is in the 0 (−) charge state. The presence of h$^*$ on that N atom thus slightly elongates the Mg–N bond. The Eu–N distance is also longer for the N atom that hosts h$^*$ [2.23 Å, compared to 2.25 Å (2.18 Å) for the axial (other basal) Eu–N bonds in (Eu$_{Ga}$-Mg$_{Ga}$)$_0^0$]. In the axial configuration, see Figure 6(b), the distance between Mg and the N site that bridges Mg and Eu is also longer when h$^*$ is on that N atom: the Mg–N bond length is 2.09 Å (2.01 Å) in (Eu$_{Ga}$-Mg$_{Ga}$)$^0^0$ (−). The calculated binding energy of (Eu$_{Ga}$-Mg$_{Ga}$)$^0^0$ is almost zero, suggesting that Eu$_{Ga}$-Mg$_{Ga}$ may be not stable as a complex when incorporated under n-type, thermodynamic equilibrium growth conditions (see also discussion in Sec. IV A).

Note that, unlike Mg$_{Ga}^0$, a metastable state of (Eu$_{Ga}$-Mg$_{Ga}$)$_0^0$ in which the hole is delocalized over the N atoms cannot be stabilized (even at the DFT-GGA level of the calculations where the electronic states tend to be over-delocalized). This is due to the local lattice distortion caused by the presence of Eu in the complex.

Finally, we consider a complex consisting of Eu$_{Ga}$, O$_N$, and Mg$_{Ga}$. Eu$_{Ga}$-O$_N$-Mg$_{Ga}$ introduces one defect level
in the band gap: \((0/−)\) at 0.78 eV below the CBM; see Fig. 7. The neutral charge state, \((\text{Eu}_{\text{Ga}}−\text{Mg}_{\text{Ga}})^{0}\) [(a) and (b)] and \((\text{Eu}_{\text{Ga}}−\text{O}_{\text{N}}−\text{Mg}_{\text{Ga}})^{0}\) [(c) and (d)]. Large spheres are Eu, medium Ga/Mg, and small N/O. Charge densities associated with the localized hole \(h^*\) in the \((\text{Eu}_{\text{Ga}}−\text{Mg}_{\text{Ga}})^{0}\) configuration are visualized as (yellow) isosurfaces; the isovalue for the isosurface is set to 0.05 \(\text{e/Å}^3\).

IV. DISCUSSION

A. Tuning the Eu valence and concentration

Our results clearly show that Eu can be stable as \(\text{Eu}^{2+}\) and/or \(\text{Eu}^{3+}\) in GaN. Figure 8 highlights the dependence of the \(\text{Eu}^{2+}/\text{Eu}^{3+}\) ratio on the position of Fermi level \(\mu_e\). For \(\mu_e < E_c − 0.44\) eV, the formation energy of \(\text{Eu}_{\text{Ga}}^0\) is lower than that of \(\text{Eu}_{\text{Ga}}^{2+}\). At position A, for example, the concentration of \(\text{Eu}_{\text{Ga}}^0\) is much larger than that of \(\text{Eu}_{\text{Ga}}^{2+}\) and hence \(c(\text{Eu}^{2+})/c(\text{Eu}^{3+}) < 1\). At \(\mu_e = E_c − 0.44\) eV (i.e., position B), \(\text{Eu}_{\text{Ga}}^0\) and \(\text{Eu}_{\text{Ga}}^{2+}\) have equal concentrations; i.e., \(c(\text{Eu}^{2+})/c(\text{Eu}^{3+}) = 1\). For \(\mu_e > E_c − 0.44\) eV, \(\text{Eu}_{\text{Ga}}^{−}\) is energetically more stable than \(\text{Eu}_{\text{Ga}}^{0}\); at position C, e.g., \(c(\text{Eu}^{2+})/c(\text{Eu}^{3+}) \gg 1\). Even a small shift in the Fermi-level position (hence a small change in the formation energy of \(\text{Eu}_{\text{Ga}}^{−}\)) can lead to a large change in the Eu\(^{2+}\) concentration; see Eq. 4.

As shallow donors, O and Si can make GaN n-type or, at least, shift the Fermi level toward the CBM as the charge neutrality condition [Eq. (1)] is re-established. When the Fermi level moves closer to the CBM, the n-type carrier concentration increases. In the case of Eu-doped GaN, O and/or Si co-doping can be employed to control the charge state of \(\text{Eu}_{\text{Ga}}\) and thus the valence state of Eu. For example, with an appropriate concentration of the co-dopants, the Fermi level of the material can be “pinned” near or above \(E_c − 0.44\) eV where the concentration of \(\text{Eu}^{2+}\) is high. Donor-like defects such as the positively charged configurations of \(\text{V}_N\) and \(\text{H}_i\) can have similar effects, although they are expected not to be as effective as the shallow donors in shifting the Fermi level. We emphasize that these are global effects since those defects do not need to be close to \(\text{Eu}_{\text{Ga}}\) for the Fermi-level shift to happen; the defect–defect interaction takes place only indirectly via the interaction with the common electron reservoir [i.e., \(\mu_e\) in Eq. (1)].

The effects of defect association and thus local defect–defect interaction are investigated by considering defect complexes explicitly, as presented in Sec. III. Overall, we find that the electronic behavior of complexes is significantly different from that of their unassociated constituents; see Table II. Defect levels associated with the complexes are shifted, compared to those associated with the isolated ones, and additional levels may form as a result of strong local elastic and electrostatic interactions between constituents in the complexes. Notably, the valence state of Eu can be controlled through defect association. For example, \(\text{Eu}^{2+}\) is found to be more stable in complexes with \(\text{V}_N\), \(\text{H}_i\), \(\text{O}_N\), and \(\text{Si}_{\text{Ga}}\) under n-type con-
ditions. In complexes with $V_{Ga}$ (at least under n-type conditions), $C_N$, and $Mg_{Ga}$, Eu is stable only as $Eu^{3+}$; see Table II. Defect association also changes the formation energy and can thus affect defect incorporation during growth. Complexes of $Eu_{Ga}$ and $O_X$ or $Si_{Ga}$ can have a much lower formation energy than the isolated $Eu_{Ga}$, indicating that co-doping with O and/or Si makes it easier to incorporate Eu into GaN. The formation energy is significantly lower in the case of $Eu_{Ga}$-$O_N$-$Mg_{Ga}$.

The results summarized in Table II also show that the binding energy varies significantly from one defect complex to another. Having a positive calculated binding energy, however, does not mean that the defect complex will readily form. As discussed in Ref. 45, under thermodynamic equilibrium, the binding energy needs to be greater than the larger of the formation energies of the isolated constituent defects for the complex to have significant concentration since it can still form under non-equilibrium growth conditions and get trapped inside the material. (Eu,Mg)-doped GaN, for example, has often been made by ion-implanting with Eu fluences or prepared by molecular-beam epitaxy (MBE). Defect complexes such as $Eu_{Ga}$-$Mg_{Ga}$ thus can still exist even when having a very small binding energy. Overall, one should expect that defects are present in the material in both the unassociated and associated forms.

Our results showing $Eu^{2+}$ stable only in a small range of Fermi-level values near the CBM, see Fig. II or III, thus explain why $Eu^{3+}$ is often found to be predominant in Eu-doped GaN samples. A significant $Eu^{2+}$ concentration occurs only when prepared under certain conditions. Mitchell et al. [19, 20], for example, were able to achieve $c(Eu^{2+})/c(Eu^{3+}) > 1$ when using both O and Si as co-dopants and suitable experimental conditions. The relatively low temperature (e.g., 700°C instead of 1030°C) used during growth via OMVPE also appeared to play a key role in increasing the $Eu^{3+}$ concentration [19, 20, 22]. This is likely because decreasing the temperature leads to an increase in the concentration of complexes and a decrease in the concentration of their isolated constituents; see a detailed discussion in Ref. 45. In other words, it is easier to incorporate Eu into GaN in the form of complexes such as the low-formation-energy $Eu_{Ga}$-$O_N$ at lower growth temperatures. The temperature, of course, cannot be too low as the concentration of thermally activated defects is still governed by Eq. (2).

B. $Eu$-related defects as luminescence centers

We now focus on the electronic behavior of the $Eu$-related defects and discuss their possible role as luminescence centers. As reported earlier, the isolated $Eu_{Ga}$ has defect levels in the bulk band gap. The $(0/-)$ level can act as an electron trap. The electron-capturing defect configuration is $Eu^0_{Ga}$, which is essentially $Eu^{3+}$. When $Eu^0_{Ga}$ captures an electron from the conduction band (e.g., previously excited from the valence band to the conduction band under band-to-band excitation) and becomes $Eu^-_{Ga}$ (assuming that the system has enough time to relax to its equilibrium configuration), the valence state of Eu changes from trivalent to divalent ($Eu^{2+}$). The captured electron in $Eu^0_{Ga}$ then recombines non-radiatively with a free hole from the valence band or a hole at some acceptor level and transfer the recombination energy to the $Eu^{2+} \rightarrow 4f$-core. The $(+/0)$ level can act as a hole trap. Compared to $Eu$-related defect complexes discussed below, the isolated $Eu_{Ga}$ trap is expected to be less effective since there is no Coulomb attraction between the carrier and the carrier-capturing defect configuration ($Eu^0_{Ga}$). Note that the carrier capture cross section can decrease by orders of magnitude in going from Coulomb attractive defect centers (e.g., $\sim 10^{-12}$–$10^{-15}$ cm$^{-2}$) to neutral centers (e.g., $\sim 10^{-15}$–$10^{-17}$ cm$^{-2}$) repulsive centers (e.g., $\sim 10^{-22}$ cm$^{-2}$). The relatively small energy separation between the defect level and the band edge may also increase the likelihood of the captured carrier being thermally re-excited into the band.

Experimentally, the isolated $Eu_{Ga}$ is believed by many to be the dominant $Eu^{3+}$ center in $Eu$-doped GaN samples. The luminescence center is often characterized by its high relative abundance (up to more than 97% of the incorporated Eu) and a low-efficiency energy transfer from the GaN host to the $Eu^{3+}$-4F-core (the effective excitation cross section $\sim 1.2 \times 10^{-17}$ cm$^2$) and strong thermal quenching. These descriptions appear to be consistent with the characteristics of the isolated $Eu_{Ga}$ center reported in this work.

For $Eu_{Ga}$-$V_N$, the $(+/0)$ level can act as a deep electron trap. An electron is likely to be captured at the $V_N^+$ part of the carrier-capturing defect configuration ($Eu_{Ga}$-$V_N^+$), due to the Coulomb attraction. This trap is 1.86 eV above the VBM, slightly smaller than the separation (2.12 eV) between the $7F_0$ and $5D_0$ levels of Eu ions. Note, however, that the error bar in our calculation of the defect level ($q/q'$) is expected to be about 0.1 eV; thus the trap may actually be higher and the energy obtained from a non-radiative recombination of the trapped electron at the $(+/0)$ level and a hole may be large enough to excite an electron from $7F_0$ to $5D_0$. In other words, we cannot completely rule out the role of $Eu_{Ga}$-$V_N$ as an electron trap and an efficient defect center for the $5D_j \rightarrow 7F_j$ transitions, although it is also likely that the complex has a limited role in high-energy luminescent transitions. The defect levels nearer to the VBM, $(3+/2+)$ and $(2+/+)$, may act as hole traps; however, their hole-capture efficiency should be very low given the Coulomb repulsion between the carrier and the positively charged ($V_N^{2+}$ or $V_N^+$) part in the hole-capturing defect configuration of $Eu_{Ga}$-$V_N$. The role of the $(0/-)$ level, approximately at the CBM, is not clear at this point.

For $Eu_{Ga}$-$V_{Ga}$, the defect levels nearer to the VBM and CBM may act as hole and electron traps, respec-
tively. However, they are unlikely to be efficient due to the Coulomb repulsion between the carrier and certain parts of the carrier-capturing defect configurations; see Fig. 4. The traps formed by $\text{EuGa}_0\text{C}_0$ are also expected not to be very efficient because the carrier-capturing defect configuration $(\text{EuGa}_0\text{C}_0)^0$ is all neutral; see Fig. 4(b).

The $(+/0)$ level of $\text{EuGa}_0\text{H}_i$, $\text{EuGa}_0\text{ON}_i$, and $\text{EuGa}_0\text{Si}_{\text{Ga}}$ is expected to be an efficient electron trap. An excited electron from the conduction band is likely to be captured at the positively charged $(H_i^+, O_{\text{N}}, \text{or Si}_{\text{Ga}}^+)$ part of the carrier-capturing defect configuration, due to the Coulomb attraction; see Fig. 4(a), 4(c), and 4(d). In the case of $\text{EuGa}_0\text{ON}_i$, for example, since the neutral charge state of $O_{\text{N}}$ is energetically unstable, the captured electron is likely transferred to the $\text{EuGa}_0^0$ part and transforms it into $\text{EuGa}_0^0$, assuming the system is allowed to relax to its equilibrium configuration, and hence $(\text{EuGa}_0\text{ON}_i)^+$ becomes $(\text{EuGa}_0\text{ON}_i)^0$ which then recombines with a hole and the energy is transferred to the Eu $4f$-core.

Regarding the Mg-containing defect complexes, the $(0/-)$ level of $\text{EuGa}_0\text{Mg}_{\text{Ga}}$ can act as a deep hole trap. A hole from the valence band (e.g., previously created by exciting an electron from the valence band to the conduction band) can be efficiently captured at the negatively charged $(\text{Mg}_{\text{Ga}}^-)$ part of the carrier-capturing defect configuration $(\text{EuGa}_0\text{Mg}_{\text{Ga}}^-)$; see Table 1. Finally, the $(0/-)$ level of $\text{EuGa}_0\text{ON}_i\text{Mg}_{\text{Ga}}$ can act as an electron trap with the carrier likely being captured at the $O_{\text{N}}^-$ part of $(\text{EuGa}_0\text{ON}_i\text{Mg}_{\text{Ga}})^0$. The behavior of this neutral configuration should be similar to that of $(\text{EuGa}_0\text{ON}_i)^+$ described above.

Altogether we find that $\text{EuGa}_0\text{ON}_i$, $\text{EuGa}_0\text{Si}_{\text{Ga}}$, $\text{EuGa}_0\text{H}_i$, $\text{EuGa}_0\text{Mg}_{\text{Ga}}$, $\text{EuGa}_0\text{ON}_i\text{Mg}_{\text{Ga}}$, and possibly $\text{EuGa}_0\text{V}_{\text{N}}$ are efficient defect-related Eu$^{3+}$ centers for non-resonant excitation. The significant local distortion around the Eu$^{3+}$ ion should help relax the Laporte selection rules and allows for bright emission. As discussed above, they are efficient carrier traps and thus likely to have high carrier capture cross sections. The energy transfer from the GaN host to the Eu$^{3+}$ $4f$-core is also expected to be efficient, given the close proximity of the carrier-capturing part to the Eu$^{3+}$ ion in the carrier-capturing defect configuration. Experimentally, it was shown that efficient energy transfer to the Eu $4f$-core and a high concentration of the Eu-related defect centers is key to enhanced emission intensity. Our findings are thus consistent with experimental observations showing that the Eu$^{3+}$ PL emission was significantly enhanced in GaN co-doped with Eu and O, Si, or Mg.

Finally, we now comment on the PL hysteresis observed in (Eu,Mg)-doped GaN, believed to involve hysteretic photochromic switching (HPS) between two defect configurations, namely “Eu0” and “Eu1(Mg)”, in which the Eu$^{3+}$ ion experiences slightly different local crystal fields. The authors identified “Eu0” and “Eu1(Mg)” with the so-called “shallow transient state” (STS) and “deep ground state” (DGS), respectively, proposed by Lany and Zunger for Mg$_{\text{Ga}}$ in Mg-doped GaN. The DGS is equivalent to the Mg$_{\text{Ga}}^0$ configuration consisting of Mg$_{\text{Ga}}^0$ and $h^+$ in our work and the STS can be identified with the metastable configuration mentioned in Sec. III D. One assumption made by O’Donnell et al. was that, in (Eu,Mg)-doped GaN, Eu could be regarded as a “spectator ion”. This may not be the case as we find that, e.g., the $(0/-)$ level of $\text{EuGa}_0\text{Mg}_{\text{Ga}}$ is shifted by $\sim 0.5$ eV from that of Mg$_{\text{Ga}}$ and the local lattice environment and hence the ability to stabilize a metastable state is different for $(\text{EuGa}_0\text{Mg}_{\text{Ga}})^0$ and Mg$_{\text{Ga}}^0$; see Sec. III D. Note that Mg in (Eu,Mg)-doped GaN is expected to be present both as the isolated Mg$_{\text{Ga}}$ and in Eu$_{\text{Ga}}$-Mg$_{\text{Ga}}$. It is not clear at this point if the perturbation is strong enough to cause the observed PL hysteresis when Mg$_{\text{Ga}}$ and Eu$_{\text{Ga}}$ are far apart such that the metastable configuration of Mg$_{\text{Ga}}^0$ can be stabilized. Besides, the total-energy difference between the stable and metastable configurations is rather large (0.19 eV).

In (Eu,O,Mg)-doped GaN, Cameron et al. observed another Eu$^{3+}$ center denoted as “Eu0(0x)” in addition to “Eu1(Mg)” and “Eu0”. Eu0(0x) was found to be stable over a prolonged excitation time and a wide temperature range, unlike the other two Eu$^{3+}$ centers. The center can be identified with the Eu$_{\text{Ga}}$-O$_{\text{N}}$-Mg$_{\text{Ga}}$ complex in our calculations which should co-exist with smaller defect complexes such as Eu$_{\text{Ga}}$-Mg$_{\text{Ga}}$ and the unassociated defects. With its low formation energy, the complex is expected to occur with a significant concentration. The main difference between Eu$_{\text{Ga}}$-Mg$_{\text{Ga}}$ and Eu$_{\text{Ga}}$-O$_{\text{N}}$-Mg$_{\text{Ga}}$ is that upon capturing a hole the negatively charged state of the former becomes $(\text{EuGa}_0\text{Mg}_{\text{Ga}})^0$ with a localized hole residing at the bridging N atom, whereas upon capturing an electron the neutral state of the latter becomes $(\text{EuGa}_0\text{ON}_i\text{Mg}_{\text{Ga}})^-$ with the valence change occurring on the Eu ion; all assuming the system is allowed to relax to its equilibrium configuration.

V. CONCLUSIONS

We have carried out a study of defects in Eu-doped GaN using hybrid density-functional calculations. The material is found to exhibit rich defect physics resulting from the ability of Eu to be mixed-valence and the interaction between the rare-earth dopant and native point defects and (intentional or otherwise) impurities. Eu can be stable as divalent and/or trivalent when incorporated at the Ga lattice site in GaN, and the Eu$^{2+}$/Eu$^{3+}$ ratio is dependent on the position of Fermi level and thus the growth conditions. We have discussed the tuning of the Eu valence state and concentration in terms of global and local effects caused by indirect and direct defect–defect interactions through co-doping and defect association, respectively. Based on a detailed analysis of the defects’ local lattice environment and electronic behavior, the isolated Eu$_{\text{Ga}}$ is identified as an optically active Eu$^{3+}$ center. Eu-related defect complexes such as Eu$_{\text{Ga}}$-O$_{\text{N}}$, Eu$_{\text{Ga}}$-Si$_{\text{Ga}}$, Eu$_{\text{Ga}}$-H$_i$, Eu$_{\text{Ga}}$-Mg$_{\text{Ga}}$, and Eu$_{\text{Ga}}$-O$_{\text{N}}$-Mg$_{\text{Ga}}$ are, however, more efficient Eu$^{3+}$ centers for non-
resonant (band-to-band) excitation. Eu\textsubscript{Ga}V\textsubscript{N} can also be an efficient Eu\textsuperscript{3+} center, although it may have a limited role in high-energy luminescent transitions. Eu\textsubscript{Ga}V\textsubscript{GaN}, on the other hand, is unlikely to be an efficient center.

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