Rare-earth defect pairs in GaN: LDA+U calculations

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The structural and electronic properties of rare-earth (RE) (Eu, Er, and Tm) related defect pairs in GaN have been investigated theoretically. Based on LDA+U total-energy calculations, their possible role in the luminescence process is discussed. In all charge states, the lanthanides show a strong preference for the Ga-lattice site, either as isolated substitutional or complexed with intrinsic defects. With respect to the electronic valence, a proper description of correlation effects of the strongly localized 4f electrons is shown to be crucial, especially if the RE_{Ga} is paired with donors like the Ga interstitial or the N vacancy. The pairs formed by RE_{Ga} substitutionals and vacancies or interstitials lower the symmetry and are found to locally distort the environment. By this, they are quite effective in relaxing the selection rules for the luminescent intra-4f-shell transitions. While for n-type GaN, the next-nearest-neighbor pair $RE_{Ga}V_{Ga}$ pair is energetically favored, for p-type GaN, the $RE_{Ga}V_N$ pair provides the most stable configuration and introduces shallow levels close to the conduction band, which can act as assistant levels in the luminescence process.

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I. INTRODUCTION

Rare-earth (RE) doped nitrides have been already successfully used for the realization of light emitting devices.[1,2] In particular Eu, Er, and Tm dopings in GaN leads to the emission of visible light in narrow bands in the red, green, and blue, respectively. For this reason, the RE ions can be used as primary color sources and/or mixed opportunely to obtain the full visible spectrum.[3] Moreover, GaN suffers less from the temperature quenching of the luminescence than other hosts with smaller band gap.[4] It is thus possible to realize high brightness light emitters with outstanding durability and long lifetime. The next step toward the mass production of GaN:RE-based devices exploiting this technology is the optimization of the device itself, i.e., the realization of efficient devices. This means that (1) the energy transfer from the host to the rare-earth dopants and (2) the efficiency of the luminescent transitions (i.e., the radiative/nonradiative decay ratio) have to be optimized.

The first issue requires the understanding of the excitation mechanism of the RE ions in the host. However, the electronic structure of the RE luminescent centers as well as their excitation and emission mechanisms are still under debate.[5] The screening of the outer shells makes a direct excitation of the f electrons difficult; nonetheless, the presence of nearby intrinsic defects[6] or the formation of structured isovalent traps[7] may help this process. In any case, the exact microscopic structure of the RE impurity is not known but crucial for a better understanding of the observed efficiency luminescence. The responsible intra-4f-shell transitions are actually forbidden in the free ions by the Laporte selection rules. However, these selection rules are relaxed in the crystal due to the admixture of states of opposite parity induced by the crystal field of the surrounding. The lattice location of the rare earths and their neighborhood determine the symmetry of their environment and are therefore crucial to the emission. Despite many efforts, no luminescence band has been definitively assigned to a particular lattice site or a specific microscopic structure. Even if the lanthanide ions seem to prefer the Ga-lattice site[5] and generate emission spectra compatible with axial C_{3v} symmetry,[8] the signatures of different centers with distinct optical properties has been found in the emission spectra of RE-doped GaN samples,[9,10] raising the question about a varying environment of the lanthanide ions. Uedono *et al.*[11] put the luminescence from Eu samples in relation with an aggregation of Ga vacancies. By means of positron annihilation, the presence of Ga vacancies or even larger vacancy clusters is shown suggesting Eu-V_{Ga} pairs or Eu ions complexed with vacancy clusters as dominant defects in Eu-implanted GaN samples. However, an exact determination of the microscopic structure was not possible and requires further investigations, e.g., total-energy calculations to find out the best candidates for the luminescent centers.

There have been different attempts to investigate rare-earth ions in GaN theoretically from first principles. Using the local-density approximation (LDA) of density-functional theory (DFT), Filhol *et al.* adopted the so-called frozen-core approximation[12] (i.e., treating a fixed number of 4f electrons as core electrons) to investigate Eu, Er, and Tm dopings in hexagonal GaN, while Svane *et al.* used a self-interaction corrected (SIC) approach beyond LDA-DFT to investigate the RE_{Ga} substitutionals in cubic GaN.[13] In the first work, the isolated substitutionals of all the investigated rare-earth impurities are found to be electrically inactive, while in the SI-corrected work, the Eu ion was found to induce a gap state, indicating that a frozen-core LDA approach may not be appropriate to describe the electronic structure for all the possible positions of the Fermi level. The present LDA+U approach was already shown to be well suited to cover both topics: the correlation effects beyond LDA-DFT and the full lattice relaxation.[14]

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In this work, we investigate by means of spin-polarized LDA+U total-energy calculations defect structures which can be created during the growth or implantation of GaN:RE. The investigated defects range from the isolated substitutionals RE_{Ga}, RE_N, and interstitials RE_{int} to the defect pairs built up with neighboring vacancies (e.g., $RE_{Ga}V_N$ and $RE_{Ga}V_{Ga}$). On the basis of their geometric and electronic structure, formation energy and electronic valence, we discuss if they can play a role in the luminescence process. The main focus of our work is on the analysis of all the possible charge states of the defect complexes, whereby a reliable description of the correlation effects beyond usual LDA-DFT is shown to be crucial to determine the electronic valence. This paper is organized as follows. In Sec. II we illustrate the theoretical aspects of this work, in particular, the LDA+U method and the calculation of the charge transition states via the Slater-Janak transition state model, as well as the realization of the approach via a DFT-based tight-binding approach (DFTB). In Secs. III and IV, we show and discuss the results of our simulations of different defect pairs and finally, in Sec. V, we summarize the findings we have come to in the proceeding sections.

II. METHODS

A. Spin-polarized LDA+U

The simulation of strongly correlated systems like the rare-earth ions requires techniques beyond the LDA usually employed for the simulation of solid-state systems. Examples of these methods are LDA+U (Ref. 15) and the SIC.[16] In this work, we adopt the LDA+U calculation scheme as implemented in the density-functional-based tight-binding tool DFTB.[17] The choice of the calculation scheme is due to the necessity to scan a lot of structural and electronic configurations and to handle the huge cells needed to reproduce the dilute concentration of RE ions in the GaN host used in the experiments. Both the DFTB method and its LDA+U extensions have been thoroughly discussed elsewhere.[14] We restrict ourselves to outline the main features of the LDA+U approach, essential to describe the f-electron properties.

The LDA+U correction to the total energy (spin-unpolarized case) is given by

$$E = E_{\mathrm{LDA}} - \sum_{\mathcal{M}} \left[\frac{1}{2}\overline{U_{\mathcal{M}}} N_{\mathcal{M}}(N_{\mathcal{M}}-1) - \frac{1}{2}\sum_{i\neq j \in \mathcal{M}} U_{ij}\eta_i\eta_j \right],$$

with the Coulomb integral

$$U_{ij} = \langle i,j | V_{ee} | i,j \rangle \tag{1}$$

and

$$\overline{U_{\mathcal{M}}} = \frac{1}{N_{\mathcal{M}}^2}\sum_{i,j\in\mathcal{M}} U_{ij} = \frac{1}{(2l+1)^2}\sum_{i,j\in\mathcal{M}} U_{ij}, \tag{2}$$

whereby the U_{ij} vanish if i and j are belonging to different localized manifolds $\mathcal{M}$, containing $N_{\mathcal{M}}=\Sigma_{i\in\mathcal{M}}=2l+1$ strongly interacting electronic orbitals. As a consequence, each Kohn-Sham level is corrected by an amount

$$\varepsilon_i = \frac{\partial E_{\mathrm{LDA}+U}}{\partial \eta_i} = \varepsilon_{iLDA} + U_{ii}\left(\frac{1}{2} - \eta_i\right), \tag{3}$$

i.e., an orbital-dependent linear correction $U_{ii}(\frac{1}{2}-\eta_i)$ is provided. Occupied orbitals ($\eta_i=1$) are shifted downward and unoccupied orbitals ($\eta_i=0$) upward by an energy $\frac{1}{2}U_{ii}$, in order to recover the correct separation between the upper and lower Hubbard bands.

In the spin-polarized case (see Refs. 14 and 15 for the derivation), an additional spin-polarized exchange parameter J_l^σ enters the formulation. Assuming the same correction for the two spin channels σ, the Kohn-Sham levels are shifted by an amount $\frac{1}{2}(U_l-\bar{J}_l)$, where $\bar{J}_l$ is the spin-averaged exchange integral and the index l is the orbital label. For a given angular momentum, $U-\bar{J}$ is often treated as a single effective parameter called U_{eff}. The U_{eff} values used in this work have been determined by means of self-consistent calculations as described in Ref. 18. Thereby, we neglect the (nearly vanishing) influence of the host matrix and use the same value of U_{eff} for the f electrons of each lanthanide in all investigated system: 6.8 eV for Eu, 7.6 eV for Er, and 7.3 eV for Tm. These values are in agreement with the $(U_f-\bar{J}_f)$ used in similar calculations.[19]

B. Slater-Janak transition state

The Slater-Janak transition state model[20] allows a calculation of charge transition levels by analyzing the Kohn-Sham eigenvalues of the density-functional theory.[21,22] In particular, in connection with the LDA+U approach and the supercell method (i.e., periodic boundary conditions), the Slater-Janak transition state model has been proven to be a powerful tool.[18] It circumvents a comparison of the total energy for differently charged systems that in finite supercells is often affected by some uncertainties due to the artificial Coulomb interactions between the periodic images of the charged supercells.[23,24] The Slater-Janak model, on the other hand, requires, besides a sufficiently reliable prediction of the energetical position with respect to the band edges, a linear dependence of the Kohn-Sham eigenvalues on their occupation numbers. The linearity of the energy eigenvalues has been carefully checked for each of the investigated systems as described in Ref. 18. The second requirement, reliable values for the fundamental gap is achieved via an empirical correction as described in the following subsection.

C. Computational

In the DFTB (Ref. 17) calculation scheme, the electronic wave functions are linear combinations of a localized basis of Slater-type orbitals, which is well suited for the simulation of the strongly localized f electrons. The method gives us the possibility to investigate solid-state systems in a very efficient way. In particular with the use of very large supercells (256 and 512 atoms), the spurious interaction of defects with their periodic images can be reduced significantly. In addition, the DFTB code allows for an empirical correction of the fundamental gap to the experimental value by optimizing the on-site Hubbard-U that enters the tight-binding Hamiltonian.

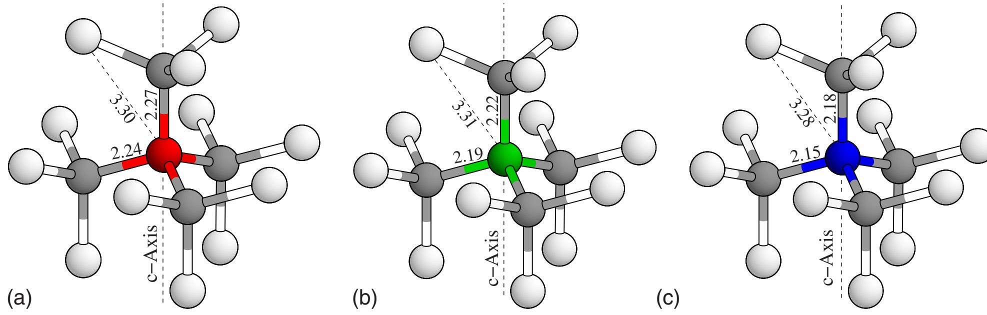


FIG. 1. (Color online) The RE_{Ga} substitutionals in hexagonal GaN. Ga atoms are white, nitrogen atoms light gray. Eu (left-hand side), Er (center), and Tm (right-hand side) are the darker atoms at the center of each picture. The numbers show the bond lengths in Å.

This correction is crucial for a proper prediction of the one-particle levels in the band gap. All the results shown here were obtained by spin-polarized DFTB calculations within the LSDA+U approach. The spin configuration, which minimizes the total energy, was determined by comparing the ground state of all possible subspaces with different spin. Supercells containing one impurity (corresponding to a distance of 17.5 Å between defects in neighboring cells) were relaxed using the Γ-point approximation until the residual forces were lower than 10^{-4} eV/atom. The error bars arising from the physical and numerical approximations used in the present study concerning the charge transition values amount to about 10% of the gap size; bond lengths can be assumed to be accurate within about 2%.

III. LATTICE LOCATION OF THE RARE-EARTH IONS

Before investigating pairs with intrinsic defects, the preferred lattice site for an incorporation of isolated RE ions in the lattice is discussed. In principle, there are three possibilities, the Ga site, the N site, or an interstitial position. We mainly focus our investigation on the effects of RE doping in hexagonal GaN. If not explicitly specified (as, e.g., the case for the RE_{Ga}), our results refer to simulations of the hexagonal host.

A. Isolated substitutionals

Selected rare-earth substitutionals have been already investigated as an example application of the present LSDA +U calculation scheme, namely, Er and Eu at the Ga sublattice in hexagonal GaN and substitutional Eu_{Ga} in cubic GaN.[14,18] In this section, we summarize the main features of these defects, which are needed to understand the behavior of the defect pairs and extend our calculation to Tm_{Ga}. In our simulation, the RE_{Ga} isolated substitutionals have the C_{3v} symmetry with bond lengths reported in Fig. 1.[25] They cause a relatively small lattice relaxation (whose extent reflects the atomic size of the lanthanide) and are in the neutral charge state isovalent with the substituted Ga (RE^{3+}). This means that the number of localized f electrons is 6 for Eu (total spin 3), 11 for Er (total spin 3/2), and 12 for Tm (total spin 1). The charge residing on the N ligands does not differ significantly (less than 1.5%) from the charge residing on the N atoms in bulk GaN. The effect of the atomic relaxation in this calculation turns out to be quite important despite its moderate extent, as it shifts the position of the charge transitions to smaller values of the Fermi energy: in the case of cubic GaN, we find a (0/−) transition level for Eu, Er, and Tm at 1.53, 2.01, and 2.10 eV above the valence band, respectively. We found a very similar behavior in the case of hexagonal GaN, where the charge transition levels are lowered by about 0.8 eV by the relaxation (see Table I). For unrelaxed cubic supercells, we find the (0/−) charge transition level only for Eu_{Ga} substitutionals at 2.53 eV above the valence band and for Er just below the conduction band edge (i.e., 3.30 eV above the valence band). No charge transition (0/−) was observed for Tm. These results are readily comparable and in nice agreement with the SI-corrected results in Ref. 13, where within unrelaxed supercells of cubic GaN only Eu undergoes a (0/−) charge transition at 2.44 eV above the valence band.

In order to compare our results with the calculations of Filhol *et al.*,[12] Eu, Er, and Tm isolated substitutionals have also been investigated within a L(S)DA approach treating the f shells as core states. In this case, no charge transition levels are found (neither for relaxed nor for unrelaxed supercells), showing again the importance of going beyond LDA to describe the electronic structure of rare-earth ions.

Furthermore, our theoretical investigation confirms the preferred incorporation of the rare-earth ions at the Ga lattices cite being already evident from experimental investigations.[5] For substitutional Eu_N, Er_N, and Tm_N at the nitrogen sublattice, we find that the RE ion does not stay on site, causing a serious lattice distortion in the host. For each of the examined lanthanides, the formation energy of the

TABLE I. Charge transition $\epsilon(0/-)$ levels calculated for different RE_{Ga} substitutionals. The levels are given in eV above the valence band.

Syst.	Ref. 13	Ideal	Relaxed
(cub.) Eu_{Ga}	2.44	2.53	1.53
(cub.) Er_{Ga}	none	3.30	2.01
(cub.) Tm_{Ga}	none	none	2.10
(hex.) Eu_{Ga}		2.40	1.58
(hex.) Er_{Ga}		3.11	2.35
(hex.) Tm_{Ga}		3.20	2.48

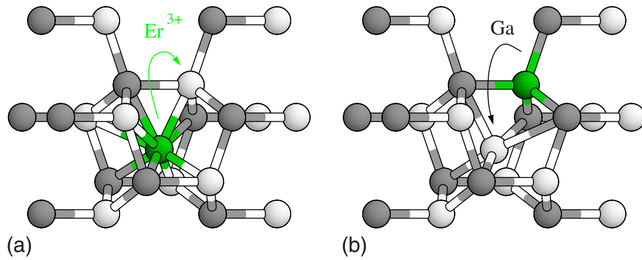


FIG. 2. (Color online) The RE interstitials in hexagonal GaN. Rare-earth ions will not stay in the interstitial configuration (left-hand side) but will rather take the place of a neighboring Ga atom, which is shifted in the interstitial site (right-hand side). N atoms are black, Ga white, and Er green.

RE_N substitutional lies at least 20 eV above the formation energy of the related RE_{Ga}, indicating that this kind of defect will not appear in significant concentrations, independent of its charge state.

B. Rare-earth interstitials I_{RE}

According to our total-energy calculations, the interstitials of all the three investigated ions (Eu, Er, and Tm) in hexagonal GaN are less favorable than a configuration with the RE ion at the Ga site and the substituted Ga atom occupying an interstitial site, independent from the starting positions of the RE ion (see Fig. 2). We have investigated all the starting position for the RE ions proposed in Refs. 26 and 27 as stable positions for the interstitial Ga in GaN. The kick-out process is favored for all the investigated RE by more than 0.5 eV, with Eu showing the largest energy gain. In principle, this particular behavior is not surprising since Ga_{int} is one of the dominant intrinsic defects in GaN.[28] It can be also explained with the size of the impurity ions: while very small impurity atoms like hydrogen prefer the interstitial site,[29] big ions like the lanthanides do not fit into the space between the lattice sites and prefer regular lattice sites. This explains why for Eu, the largest RE, the kick out process is even more favorable than for Er and Tm.

In the final configuration of the resulting $RE_{Ga}Ga_{int}$ pair, the C_{3v} symmetry of the single substitutionals is broken by the nearby Ga_{int}. Due to the such distorted crystal field, the RE ion is displaced by 0.09 Å (Eu and Er) and 0.08 Å (Tm) into the direction of the Ga interstitial. Thereby, the kicked-out Ga atom is shifted from the octahedral interstitial site at the center of the hexagonal channel occupied by isolated Ga_{int} in hexagonal GaN.[26,27] Even if isolated Ga_{int} in GaN are highly mobile defects,[26] we find them to be bound to the lanthanide. The calculated binding energy of 1.00 eV (Eu), 0.57 eV (Er), and 0.44 eV (Tm) is somehow higher (specially for Eu) than the LDA values reported in Ref. 12 and can be explained by the formation of a stabilizing Coulomb interaction between the Ga^{+}_{int} and the RE^{-}_{Ga}. Analyzing the occupation of the LSDA+U one-particle levels, the formation of RE substitutionals and Ga interstitials can be interpreted as

$$RE^{0}_{int} \rightarrow RE^{-}_{Ga} + Ga^{+}_{int}.$$

For the defect pairs in the neutral charge state, the rare-earth ions in the interstitial configuration keep all their f electrons and promote only the two electrons of the 6s shell to the host (RE^{2+} ions), while the gallium interstitial results positively charged. In other words, in the neutral charge state the aggregate includes the RE ion in divalent configuration in contradiction of the assumption in Ref. 12 of an overall trivalent incorporation of RE ions. We find a (+/0) charge transition toward the trivalent configuration (i.e., the pair is positively charged) slightly below that of the isolated RE_{Ga}. In addition, the 2+ and − charge states of the $RE_{Ga}Ga_{int}$ pair are predicted to be possible in highly p-type and highly n-type wurzite GaNs, respectively.

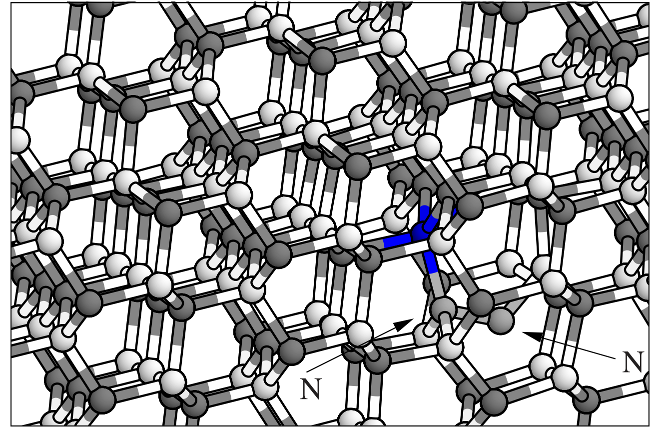


FIG. 3. (Color online) Complexes formed by RE substitutionals and N interstitials in hexagonal GaN result in the so-called *N split-interstitial* configuration. Dark gray in the picture: The Tm impurity occupying the Ga place. The arrows indicate the two N atoms sharing a lattice site.

Isolated RE interstitials have been observed in other RE-doped semiconductors, such as GaAs and Si (Ref. 30), but so far not in GaN. Our results agree with this fact but seem to be at, first view, in contradiction with Refs. 31 and 32, in which it is proposed to identify some emitting center in Er-doped GaN with Er^{3+} ions in interstitial positions near defects created introducing the dopants into the lattice as observed for GaAs:Er^{3+}. Because of its high formation energy (above 20 eV for all investigated ions), the complex $RE_{Ga}Ga_{int}$ in wurtzite GaN will hardly be formed under equilibrium conditions indeed. However, it can be formed by nonequilibrium processes such as the ion implantation. Besides $RE_{Ga}Ga_{int}$ pairs, also $RE_{Ga}N_{int}$ pairs are possible products of an interstitial incorporation of the RE ions (see Fig. 3). These pairs present characteristics similar to the $RE_{Ga}Ga_{int}$ interstitials. The lanthanide ion is slightly displaced from the ideal Ga site (by 0.15, 0.12, and 0.11 Å for Eu, Er, and Tm, respectively), whereby the N_{int} is found in the so-called split-interstitial configuration: the interstitial nitrogen forms a rather short N-N bond with one of the host nitrogen atoms with whom it shares the lattice site (see Fig. 3). In the neutral charge state, the N-N distances are 1.551, 1.570, and 1.567 Å for Eu, Er, and Tm, respectively. This is well beyond the N-N distance in N_2 molecules (1.121 Å in DFTB) but shorter than the N-N distance in solid N (hcp structure, N-N distance 3.861 Å in DFTB). The formation energy of these complexes (13.34, 11.54, and 9.95 eV for Eu, Er, and Tm, respectively, in the neutral charge state, LSDA

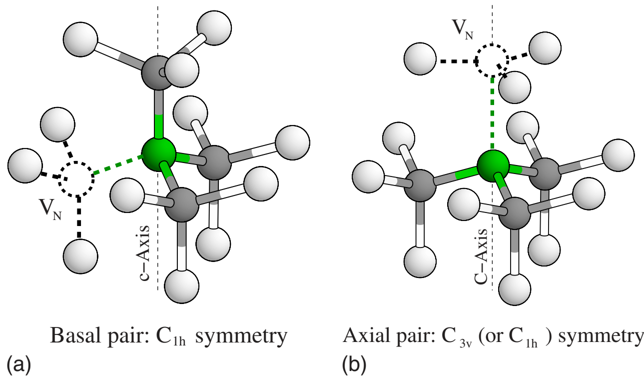


FIG. 4. (Color online) Defect pairs formed by Er_{Ga} substitutionals and V_N in hexagonal GaN. Because of the inequivalent N sites in hexagonal GaN (the Er-N bond along the c axis is longer than the other three), the complexes can be formed in two configurations. The basal configuration (left-hand side) has C_{1h} symmetry, whereas the ideal axial configuration (right-hand side) has the C_{3v} symmetry, or the C_{1h} if a Jahn-Teller distortion occurs.

calculation) is lower than the formation energy of the $RE_{Ga}Ga_{int}$ pairs, whereby the calculated binding energy (1.33, 0.94, and 0.92 eV for Eu, Er, and Tm, respectively) is comparable with their binding energy. Just like the $RE_{Ga}Ga_{int}$ pairs, all investigated $RE_{Ga}N_{int}$ pairs can occur in different charge states and possess deep gap levels. The RE has valence +2 and does not lend any f electron to the lattice, exactly like in the case of the related $RE_{Ga}Ga_{int}$ complexes, which probably excludes a role in high-energy fluorescent transitions.

IV. LANTHANIDE ENVIRONMENT

Our calculations confirmed that the lanthanide ions in GaN prefer the Ga site. However, it remains the issue of the RE environment. The lattice distortion introduced by the isolated RE_{Ga} substitutionals is relatively small and confined to the first neighbors' shell. As the luminescent intra-f transitions are due to a crystal symmetry breaking, we want to examine defect configurations, which introduce more lattice distortion in the host. Therefore, we simulate how the presence of neighboring vacancies influences the structural and electronic properties of isolated substitutional RE ions in hexagonal (wurzite) GaN.

A. $RE_{Ga}V_N$

Assuming that the RE ion is incorporated at a Ga site, the defect pair can be created by removing one of the three equivalent N ligands or the one along the crystal c axis. In the first case, the $RE_{Ga}V_N$ complex (basal pair) will have the C_{1h} symmetry; in the second case, the complex (axial pair) can have the higher (axial) C_{3v} symmetry or the C_{1h} symmetry if a Jahn-Teller distortion occurs (Fig. 4). We found the Jahn-Teller distorted axial pairs to be energetically slightly favored upon the basal pairs, with a formation energy in the neutral charge state lower by 0.04, 0.07, and 0.01 eV for Eu, Er, and Tm, respectively. Both in the case of the axial and

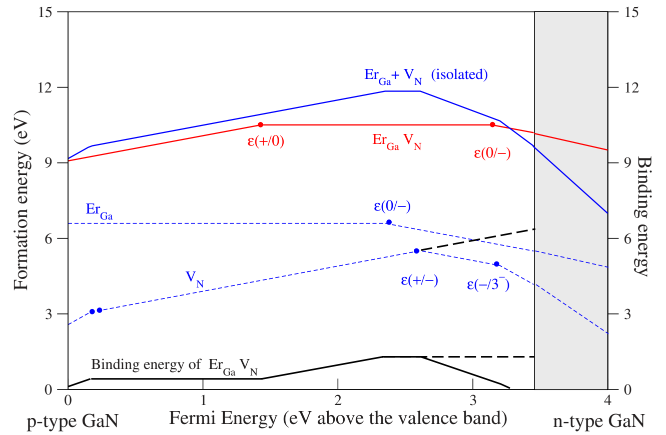


FIG. 5. (Color online) Formation energy and binding energy of the $Er_{Ga}V_N$ pair as a function of the Fermi energy in hexagonal GaN. Dotted lines are the calculated formation energies of the isolated Er_{Ga} and V_N, the solid lines are their sum (blue), the formation energy of the $Er_{Ga}V_N$ pair (red) and its binding energy (black), given as difference of the two curves.

basal pairs, we observe a quite pronounced relaxation of the structure. The lanthanide is slightly displaced from the crystal c axis (0.14, 0.11, and 0.10 Å for Eu, Er, and Tm in the ionized state, respectively). A somewhat larger displacement of Eu was also found with the help of LDA calculations reported in Ref. 12, where the displacement is quantified in 0.23, 0.21, and 0.20 Å for Eu, Er, and Tm for $RE_{Ga}V_N$ pairs, which we assume to be in the axial configuration.

In Fig. 5, the binding energy of the $Er_{Ga}V_N$ pairs is shown as a function of the Fermi energy. The formation energy of the complex is reported in the same figure. A charge transition $(0/-)$ close to the conduction band was found for all the investigated rare earths by means of the Janak transition state. The transition takes place at 3.14, 3.14, and 3.15 eV above the valence band for Eu, Er, and Tm, respectively, i.e., almost independent of the RE, as the charge transition occurs in the N vacancy. In moderately n-type GaN, the $RE_{Ga}V_N$ pairs are therefore neutral or positively charged. An f-electron related charge transition $(+/0)$ is calculated at 0.27, 1.43, and 1.59 eV above the valence band for Eu, Er, and Tm, respectively (see also Table II). Below these values, the RE ion is trivalent. We want to remark here that the existence of the negative charge states of the isolated V_N vacancy is still under debate (see Refs. 26 and 33). We report

TABLE II. Trivalent to divalent charge transitions for the lanthanide ions within different environments. Note that trivalent is the valence state of the lanthanide contributing to the luminescence. The transitions are given in eV above the valence band and include the effect of the lattice relaxation.

RE ion	RE_{Ga} $(0/-)$	$RE_{Ga}V_N$ $(+/0)$	$RE_{Ga}V_{Ga}$ $(3-/4-)$
Eu	1.58	0.27	2.59
Er	2.35	1.43	cond. band
Tm	2.48	1.59	cond. band

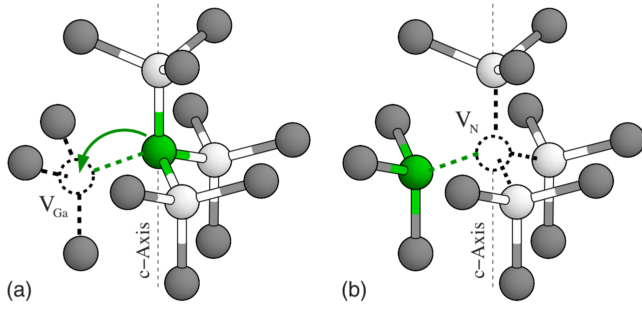
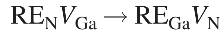


FIG. 6. (Color online) The lanthanide in $\mathrm{RE_N}V_{\mathrm{Ga}}$ pairs in hexagonal GaN (left-hand side) leaves the N site to occupy the Ga site ($\mathrm{RE_{Ga}}V_{\mathrm{N}}$, right-hand side).

therefore in Fig. 5 the binding energy of the $\mathrm{RE_{Ga}}V_{\mathrm{N}}$ pair assuming that the isolated V_{N} vacancy will not occur in negative charge state (dashed lines). In this case, the defect would be bound for strongly *n*-type material too. If the isolated V_{N} vacancy can be negatively charged, the resulting defect level can act as an assistant level in the luminescence process.

In principle, $\mathrm{RE_N}V_{\mathrm{Ga}}$ pairs can be considered as competing alternative. However, independent of the starting configuration (axial or basal), we observe that these pairs are not formed at all. The rare earth in fact leaves the N site moving into the V_{Ga} *without any barrier* in between the migration path. This spontaneous transformation (Fig. 6)



$$\mathrm{RE_N}V_{\mathrm{Ga}} \rightarrow \mathrm{RE_{Ga}}V_{\mathrm{N}}$$

shows again that the RE ions prefer the Ga sublattice, either as isolated substitutionals or forming pairs with native defects.

B. $\mathrm{RE_{Ga}}V_{\mathrm{Ga}}$

An isolated $\mathrm{RE_{Ga}}$ substitutional in hexagonal GaN is surrounded by a first shell of four nitrogen neighbors, which have, in turn, each three gallium neighbors. Each $\mathrm{RE_{Ga}}$ substitutional has also 12 s neighbors, which are not all equivalent (hexagonal lattice). Removing one of these second neighbors originates a $\mathrm{RE_{Ga}}V_{\mathrm{Ga}}$ complex, as illustrated in Fig. 7. If the vacancy lies in the plane defined by the *c* axis and a basal RE ligand, or if the missing Ga is one of the neighbors of the axial RE ligand, the pair has symmetry C_{1h} (like in the upper part of Fig. 7); otherwise, it has the lowest

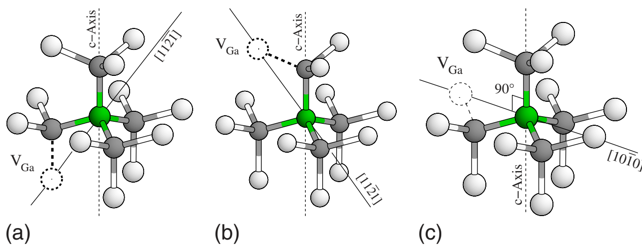


FIG. 7. (Color online) $\mathrm{Er_{Ga}}V_{\mathrm{Ga}}$ pairs in hexagonal GaN. Because of the inequivalent Ga sites in hexagonal GaN, the complexes can have different symmetry. The configurations (a) and (b) have the C_{1h} symmetry, while the configuration (c) has the C_1, i.e., has no symmetry.

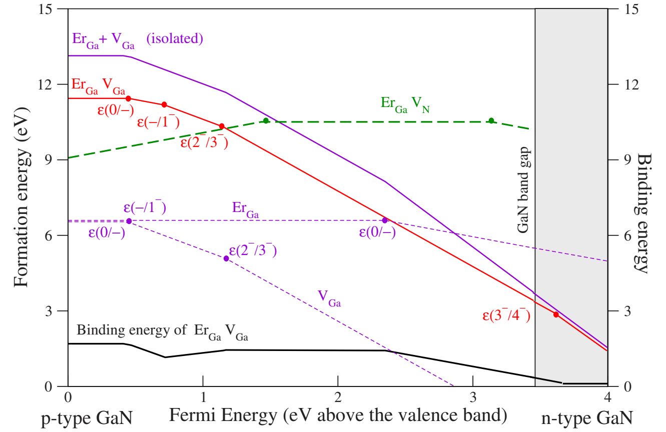


FIG. 8. (Color online) Formation energy and binding energy of the $\mathrm{Er_{Ga}}V_{\mathrm{Ga}}$ pair as a function of the Fermi energy in hexagonal GaN. Dotted lines are the formation energies of the isolated $\mathrm{Er_{Ga}}$ and V_{Ga}, the solid lines are their sum (blue), the formation energy of the $\mathrm{Er_{Ga}}V_{\mathrm{N}}$ pair (red) and its binding energy (black), given as difference of the two curves. The formation energy of the $\mathrm{Er_{Ga}}V_{\mathrm{N}}$ pair (dashed line) is reported for comparison (see also Fig. 5).

symmetry C_1. According to our total-energy calculations, however, these configurations differ by a very small energy (0.003 eV) and can be considered energetically degenerate. We will present, thus, only the results of the C_1 configuration (see also lower part of Fig. 7). This configuration is *statistically* more probable because of the larger number of equivalent configurations (6 to 3 with respect to the configuration within C_{1h} symmetry). Furthermore, it provides the lowest symmetry, i.e., will be more effective in breaking the hexagonal crystal-field symmetry, crucial for an efficient luminescent transition.

Isolated $\mathrm{V_{Ga}}$ in GaN behave as triple acceptors,[26] with the acceptor levels localized in the lowest third of the band gap. According to our LSDA+U total-energy calculations also $\mathrm{RE_{Ga}}V_{\mathrm{Ga}}$ pairs (RE=Eu,Er,Tm) behave as triple acceptors, with common charge transitions around 0.5 eV (0/−), 0.7 eV (−/2−), and 1.1 eV (2−/3−) above the valence band (see Fig. 8). These charge transition take place in the vacancylike one-particle states and are, thus, very close to that of the isolated V_{Ga} in hexagonal GaN and independent of the given RE ion. Moreover, we investigate the possibility of a further transition to the charge state 4− for the $\mathrm{RE_{Ga}}V_{\mathrm{Ga}}$ pair. For Er and Tm, we found the charge transition to take place above the conduction band minimum in the conduction bands. Er and Tm ions near the Ga vacancies are therefore trivalent, independent of the charge state. In the case of $\mathrm{Eu_{Ga}}V_{\mathrm{Ga}}$ pairs, in contrast, a further charge transition involving the *f* states is introduced in the fundamental gap at 2.59 eV above the valence band (see Table II). As a result, in highly *n*-type GaN, Eu is incorporated divalently within the $\mathrm{Eu_{Ga}}V_{\mathrm{Ga}}$ pair. Both for isolated $\mathrm{RE_{Ga}}$ substitutionals and for $\mathrm{RE_{Ga}}V_{\mathrm{Ga}}$ pairs, the trivalent-divalent charge transitions for Er and Tm take place at similar energies, approximately 1 eV higher than the corresponding Eu transitions. In this sense, our calculation confirms the empirical model of Dorembos and Van der Kolk to estimate the location of the lanthanide impurity energy levels in GaN and other semiconductor alloys.[34] Assuming

thermal activation, these transition levels are too deep in the gap (more than 1 eV below the conduction band edge) to serve as *self-assistant* levels for luminescent transitions.

$RE_{Ga}V_{Ga}$ pairs do not involve directly neighboring lattice sites but a lattice site and one of its second neighbors. This does not mean, however, that the complex is not bound, or that the binding energy is particularly low. The $RE_{Ga}V_{Ga}$ are bound for every position of the Fermi energy within the band gap (see Fig. 8). Their large binding energy around 2 eV makes these pairs one of the dominant defects pairs in RE-doped GaN. This is due to the strong coupling between Er_{Ga} and V_{Ga} mediated by the displaced N ligand accompanied by a huge relaxation energy as high as 6–10 eV, depending on the lanthanide. The N atom between the vacancy and the rare-earth ion moves toward the missing atom. The RE ion follows, maintaining a similar distance from all N ligands. This relaxation is more pronounced for Eu than for Er and Tm. The displacement of the RE ions from the Ga site is of 0.51, 0.29, and 0.25 Å for Eu, Er, and Tm, respectively. It is important to note that assuming $RE_{Ga}V_{Ga}$ pairs as defect model, the pronounced displacement for Eu could explain why recently Eu has been indicated by Rutherford back-scattering spectroscopy measurements to be the only RE laying off site.[35,36]

The mean distance of the nitrogen ligands to the rare earth in the $RE_{Ga}V_{Ga}$ complexes has been considered an important parameter in the luminescence process. Uedono *et al.*[11] suggested that in the case of Eu-doped GaN, the presence of Eu-V_{Ga} complexes would stretch the lengths of Eu-N bonds and therefore enhance the transition rate of its $4f$ electrons. Our calculations reveal that even if the lanthanide is displaced from the Ga-lattice site and its environment undergoes a heavy relaxation with symmetry breaking, the mean RE-N bond length (2.29, 2.14, and 2.12 Å for Eu, Er, and Tm) is not substantially different from that of the single RE_{Ga} substitutionals (2.28, 2.16, and 2.14 Å for Eu, Er, and Tm).

V. SUMMARY

The effect of rare-earth doping in GaN has been investigated by means of LDA+U calculations. The structural and electronic properties of different rare-earth related defect pairs, such as RE_{Ga} and vacancies (V_N, V_{Ga}) or interstitials (N_{int}, Ga_{int}), which have been previously proposed as candidate emitting centers, have been calculated and discussed. In all their possible charge states, the lanthanides show a strong preference for the Ga-lattice site, either as isolated substitutional or complexed with intrinsic defects. With respect to the electronic valence, a proper description of correlation effects of the strongly localized $4f$ electrons is shown to be crucial especially if the RE_{Ga} is paired with intrinsic donors, such as the N vacancy, for which the charge transition toward a divalant electronic configuration is found at considerably lower Fermi levels if compared with the isolated substitutionals. Among the investigated configurations, the RE_{Ga} vacancy pairs have a prominent position because of their formation energy and because they are bound for almost all the values of the Fermi energy. While for p-type GaN, the $RE_{Ga}V_N$ pair is energetically favored, for n-type GaN, the next-nearest-neighbor pair $RE_{Ga}V_{Ga}$ provides the most stable configuration. Both configurations are quite effective in breaking the crystal symmetry and by this in relaxing the selection rules. They therefore allow the intra-$4f$ electronic transitions responsible for the observed luminescence. Furthermore, $RE_{Ga}V_N$ pairs introduce shallow levels, which can act as assistant levels in the luminescence process. Regarding the stability of divacancies in the material,[33] the set of possible models can be straightforward extended to RE complexes involving $V_{Ga}V_N$ divacancies, providing further candidates to explain the luminescent transitions. With the exception of nearest $RE_{Ga}V_N$ pairs, the lanthanides are always fourfold coordinated, with RE-N bond lengths, which do not strongly depend on the local environment of the rare-earth ion. This fact is important for the interpretation of most of the existing experiments. They provide only an averaged fingerprint of the surrounding and are, thus, not sensible to the local atomic ordering around the lanthanide. Further experimental investigations, e.g., electron-paramagnetic-resonance measurements are necessary to achieve more detailed information about the exact microscopic structure surrounding the RE_{Ga} ions.

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