Point-defect complexes and broadband luminescence in GaN and AlN

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We have employed the plane-wave pseudopotential method to study point defect complexes in GaN and AlN. The results reveal that defect complexes consisting of dominant donors bound to cation vacancies are likely to be formed in both materials. The position of the electronic levels in the band gap due to these defect complexes is shown to correlate well with the experimentally commonly observed broadband luminescence both in GaN and in AlN. The origin of the large bandwidth of the luminescence spectrum is discussed. [S0163-1829(97)03115-9]

I. INTRODUCTION

The III-V nitrides have recently gained considerable interest due to their optoelectronic material properties, characterized by the wide band gaps (e.g., 3.4 eV for w-GaN and 6.2 eV for w-AlN), which enable applications emitting short wavelength (blue/UV) light. Defect-induced electronic states in the band gap can significantly alter the optical performance. This fact becomes extremely important in laser devices, where parasitic components in the emission spectrum are highly undesirable. Two infamous examples of defect-induced phenomena are the commonly observed broadband emissions in luminescence spectra of both GaN and AlN. In GaN this emission is located in the yellow part of the spectrum (centered at 2.2–2.3 eV with a linewidth of $\sim$ 1 eV).[1–4] Correspondingly in AlN this band is located $\sim$ 1 eV higher in the spectrum (near UV) (with a linewidth of 1.0–1.5 eV).[5] For brevity, in the following we refer to these broadband emissions as yellow luminescence (YL) in GaN and violet luminescence (VL) in AlN.

Several models for the origin the YL in GaN have been proposed. However, there is no consensus even about the qualitative nature of electronic levels participating in the YL process. A transition from a shallow donor level to a deep acceptor level has been suggested,[6] while another model proposes a transition between a deep double donor and a shallow acceptor.[2] The cathodoluminescence studies have revealed that emission of YL is enhanced at extended defects.[7] In principle, the extended defects themselves could induce suitable gap states for YL, but point defects trapped or incorporated at these extended defect structures present another alternative.

In a study by Youngman and Harris,[5] VL in AlN was seen to correlate with oxygen incorporation, which has led to the suggestion that aluminium-vacancy–oxygen-donor complexes are related to the origin of the VL. The cathodoluminescence studies in AlN (Ref. 5) show a clear correlation between the VL intensity and extended defects that are known to contain substantial amounts of oxygen.[8,9]

In our earlier theoretical studies,[10] GaN and AlN were found to be nearly identical with respect to the character of interatomic bonding, as clearly demonstrated by the similar formation energetics of the typical point defects in the two materials. However, the obvious difference in the physical properties is the band gap, which is nearly twice as wide in AlN compared to GaN. This directly affects the formation energetics of *charged* defects and leads to the appearance of ionization levels that are present in the AlN band gap while nonexistent in GaN.[10]

The similar line shape of the broadband luminescence in GaN and AlN suggests that it could originate from the same kind of defects present in both materials. Keeping the similar materials properties for GaN and AlN in mind, our aim in this paper is to theoretically investigate point defects and defect complexes that could serve as the common origin of the two luminescence bands. We show that cation-vacancy-related complexes are energetically very favorable defects in both materials and induce gap states that are very likely to take part in the YL/VL emission. Furthermore, the demonstrated fundamental difference related to donor levels in GaN and AlN provides a logical explanation for the shift in the emission energy between the YL and the VL. Our theoretical predictions are shown to be consistent with recent experimental data related to YL/VL emission. Our calculations are also in good agreement with those recently carried out for GaN by Neugebauer and Van de Walle,[11] and give further evidence that cation-vacancy complexes are indeed closely related to the origin the of the luminescence phenomena in question.

II. METHODS

Our plane-wave pseudopotential calculations are based on density-functional theory (DFT) in the local-density approximation (LDA). We employ the Vanderbilt-type non-norm-conserving pseudopotentials[12] for N and O and the standard norm-conserving pseudopotentials[13] with the nonlinear core-valence exchange-correlation scheme[14] for Ga, Al, and Si. The plane-wave basis is expanded up to a 25-Ry kinetic-energy cutoff. Supercells containing 32 atoms and a $2 \times 2 \times 2$ k-point mesh[15] are found to give convergence with respect to system size. Further details of the calculational procedures can be found in a previous publication,[10] and will therefore not be repeated here.

The well-known tendency for band-gap underestimation in DFT/LDA calculations is clearly present in the wide-band-gap materials such as GaN and AlN.[16] For this reason the single-particle eigenvalues do not provide reliable infor-
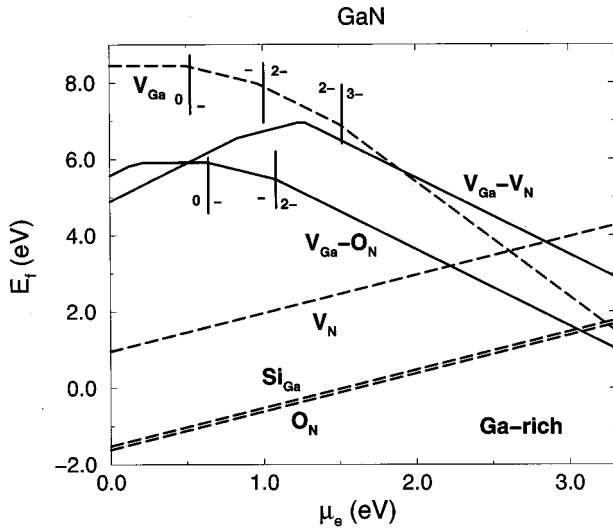
FIG. 1. Formation energies and ionization levels for the studied defects in GaN for the Ga-rich case. The experimental band-gap value (3.3 eV) is used to give the upper limit for the electron chemical potential. The dashed lines correspond to isolated point defects and the solid lines to defect complexes, respectively.
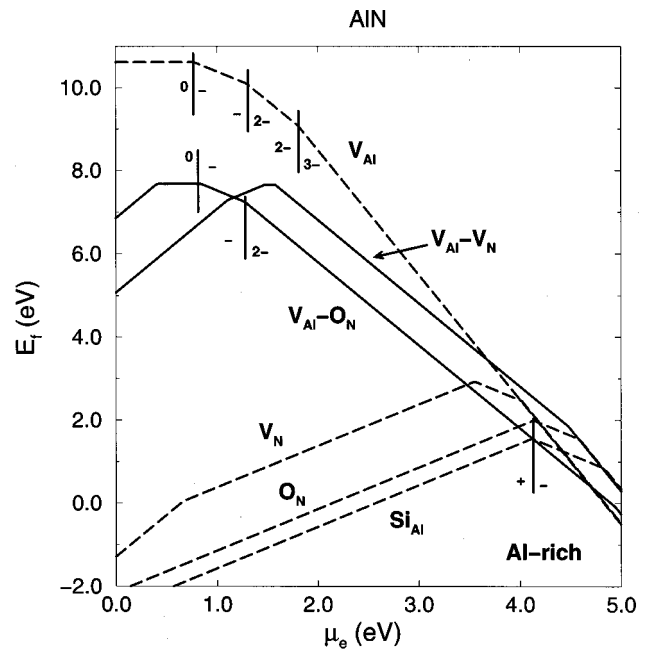

FIG. 2. Formation energies and ionization levels for the studied defects in AlN for the Al-rich case. An estimated experimental band-gap value (5.0 eV) is used to give the upper limit for the electron chemical potential. The dashed lines correspond to isolated point defects and the solid lines to defect complexes, respectively.

mation on optical transition energies between the electronic levels in the band gap. The most trustworthy information given by the calculations are the *total* energies. The standard formation energy analysis[17,10] uses these total-energy values to determine the most stable charge states as a function of the electron chemical potential (the Fermi level) in the band gap. The experimental band-gap value is commonly used to give bounds for the accessible electron chemical potential. We emphasize that this is not a severe approximation since only total energies are involved in the analysis. Ionization levels are identified as Fermi level positions at which the stablest charge state of a defect is changed. These levels appear as changes in the slopes of the formation energy curves (see, e.g., Figs. 1 and 2 below). The differences between ionization levels bear a clear connection to optical transition energies. For instance, the energy difference between the $(+/0)$ donor level and the $(0/-)$ acceptor level indeed provides an energy estimate for the corresponding donor-acceptor pair (DAP) transition. Since the ionization levels are derived using total energies associated with fully relaxed atomic configuration, the calculated energy difference corresponds to the zero-phonon transition.

The calculations are principally performed in the zinc-blende structure and for consistency the band-gap values are chosen accordingly in the results presented (3.3 eV for GaN and 5.0 eV for AlN).[10] However, for completeness we have repeated some of the calculations for the wurtzite structure and we will refer to those calculations below when appropriate. Our general observation is that the results obtained for the zinc-blende phase are to a large extent valid also in the hexagonal wurtzite structure, as the comparison with other independently obtained results[11,18–20] further confirms.

The results presented correspond to Ga-rich (Al-rich) growth conditions typical for the two nitrides. The atomic chemical potentials for the impurity species (O and Si) were determined using the relevant alloys in each case (Ga$_2$O$_3$ and Al$_2$O$_3$ for O and Si$_3$N$_4$ for Si).[10]

III. RESULTS

A. Isolated point defects

The formation energies and ionization levels for the most relevant *isolated* point defects in GaN and AlN are represented in Figs. 1 and 2 by dashed lines. We find the cation vacancies (V_{Ga}, V_{Al}) to be the most easily created *negatively* charged defects; the dominant charge state for these vacancies is the triply negative one that leads to low formation energies when the position of the electron chemical potential is higher than at the midgap (n-type conditions). The ionization levels for the cation vacancies are in the range of ~ 0.5–1.7 eV above the valence-band maximum, which shows that these defects act as deep acceptors.

In Figs. 1 and 2 three potential donors are also considered: V_N, O_N, and Si_{Ga} (Si_{Al} in AlN). The immediate observation is that there is a fundamental difference in the character of these donors between the two materials: In GaN the principal charge state for these defects is the singly positive one for nearly all Fermi-level positions. The ionization level between the singly positive and neutral charge state lies slightly below the conduction-band edge, i.e., these defects act as shallow donors in GaN, which is consistent with experimental results.[22] In contrast, in AlN two ionization levels appear well below the conduction-band edge, which means that the shallow character encountered in GaN is transformed into a deep one.

The formation energies for O_N and Si_{Ga} (Si_{Al} in AlN) are strikingly low, while V_N is found energetically clearly less favorable. The results for GaN are in good agreement with the calculations by Neugebauer and Van de Walle.[11,18–20] However, our calculations show that the formation energies for O_N and Si_{Ga} are nearly equal in GaN, while in the calcu-

lations by Neugebauer and Van de Walle Si_{Ga} was found to lie about 0.6 eV lower in energy than O_N.[11,20] We associate this discrepancy with the differing Ga $3d$-electron description in the two calculations[21] and also with the general accuracy obtainable in plane-wave pseudopotential studies for the impurity related defects. In AlN we find that Si_{Al} is slightly preferred over O_N.

Undoped GaN is typically found to be heavily n type.[23] This means that there must be a large concentration of shallow donors present and consequently that the Fermi level is high in the band gap. There is still an active ongoing debate on the shallow defect(s) responsible for the measured free-carrier concentrations. Nitrogen vacancies have been widely suggested to be the dominating defect.[24] However, recent careful secondary ion mass spectroscopy (SIMS) measurements[22,25] have revealed that the impurity (Si and O) concentrations are large enough to explain the free-electron concentration. As shown above, the easy formation of Si and O related substitutional donors compared with the formation of nitrogen vacancies agrees well with these SIMS results. Thus we conclude that in typical n-type conditions isolated nitrogen vacancies are likely to exist in appreciable concentrations only in the absence of *both* oxygen and silicon impurities from the growth process. The relative concentration of Si and O donors is a much more subtle question and is difficult to solve quantitatively using theoretical predictions. We rather think that the relative abundance of the two impurity species in the growth process principally determines the donor responsible for the background carrier concentration. The high position of the Fermi level in GaN suggests that gallium vacancies should act as effective compensating centers for the shallow donors and should therefore exist in a large concentration. However, it is evident from the background carrier concentration in undoped samples that Ga vacancies cannot fully compensate the dominant donors. Direct experimental evidence for the existence of Ga vacancies or Ga-vacancy-related defect complexes in n-type GaN is provided by the very recent positron annihilation measurements[26] that reveal positron trapping at a negatively charged vacancylike defect.

The deep donor character of V_N, O_N, and Si_{Al} in AlN has important consequences. While the shallow donors in GaN easily contribute to the free-carrier concentration, the corresponding deep donors in AlN are very unlikely to behave similarly. This is consistent with experimental observations: The typically large oxygen content in AlN does not lead to n-type conduction, but the material remains insulating.[23,5] For charge neutrality the easily incorporated donors are compensated by the Al vacancies, which, in principle, requires one triply negative Al vacancy for three singly positive donors. Our results thus agree with the earlier suggestion of oxygen compensation by metal vacancies in AlN.[5]

B. Defect complexes

Given the information of the most favorable isolated point defects in GaN and AlN, the obvious questions are whether they would bind together and what are the properties and formation probabilities of such defect complexes. The most logical constituents for a defect complex are the positively charged donorlike defects and negatively charged cation va-

cancies with acceptor character, which are likely to attract each other on electrostatic grounds. In Figs. 1 and 2 we show with solid lines the formation energies and the related ionization levels for V_{Ga}-V_N and V_{Ga}-O_N (V_{Al}-V_N and V_{Al}-O_N) defect complexes in GaN (AlN). The important observation for V_{Ga}-O_N and V_{Al}-O_N complexes is that their formation energy is clearly lower than that of an isolated cation vacancy. This confirms that the complex formation between cation vacancies and substitutional oxygen donors is indeed a very likely process in the two nitrides, as suggested in our earlier publication.[10] The formation energy for divacancies is seen to be clearly higher than for the oxygen-related complexes. Thus the preference found for isolated point defects is repeated for defect complexes that they constitute. The atomic structures found for the investigated defect complexes and the constituent point defects are described in the Appendix.

The dominant charge state for the investigated defect complexes is found to be the doubly negative one, which is an obvious sum of the typically triply negative cation vacancy and the singly positive donor. The position of the ionization levels reveal that the properties of these defect complexes are largely set by the cation vacancy. However, small shifts are observed as illustrated in Figs. 1 and 2; there is about 0.5 eV difference in the $(2-/3-)$ ionization level for the isolated cation vacancy and the $(-/2-)$ ionization level for the defect complex with oxygen bound to the vacancy. Furthermore, when the Fermi level approaches the bottom of the band gap the role of the anion vacancies in the complex can be seen in the appearance of the positive charge states. In AlN we also see the effect of the nitrogen vacancies in the ionization levels close to the conduction-band edge: A transition occurs from the doubly negative to the four times negative-charge state.

Since the dominant Si donors occupy a cation site, they cannot exist as nearest neighbors to cation vacancies as in the case of the V_{Ga}-O_N complexes. We therefore estimate that the binding energies for Si-related defect complexes should be lower than for oxygen-related complexes.[27]

IV. DISCUSSION

As regards the type of electronic transition relevant for YL in GaN, two recent experimental results strongly speak for a transition from a shallow effective-mass-like donor level to a deep acceptor level. The high-pressure studies by Suski *et al.*[3] show that the position of the center of the YL spectrum rises as a function of applied pressure almost at the same rate as the conduction-band edge. This behavior is characteristic for shallow effective-mass donors following the conduction-band edge rather closely, whereas the pressure dependence of deep gap states is generally much smaller.[3] Thus the observed pressure dependence of YL is very difficult to explain with a model based on a transition between a deep initial state and a shallow final state, but is consistent with the shallow-donor-to-deep-acceptor model. In a recent light-induced electron spin resonance experiment by Reinacher *et al.*,[28] a signal due to the deep defect involved in YL was seen with excitation energies larger than 2.6 eV. This means that the position of the deep defect is around $E_c - 2.6$ eV, which verifies that the final state is in-

deed a deep and not a shallow acceptor. Our calculations provide very logical candidates for both the shallow and the deep defects: Si_{Ga} and O_N were found to be dominant shallow donors. Gallium vacancies were found to be compensating acceptors that are likely to form complexes with substitutional oxygen donors. The ionization levels associated with the defect complexes are indeed close to the experimentally observed position of the deep acceptor level.

In AlN the incorporation of oxygen is experimentally observed to bear a clear connection to the VL.[5] The involvement of V_{Al}-O_N complexes has been suggested in several experimental studies.[5] Our calculations were indeed shown above to give firm support to the presence of these complexes in AlN. Furthermore, our calculations predict that these complexes possess a deep acceptor level about 1 eV above the valence-band maximum. On the other hand, oxygen donors were found to have a deep character with the first ionization level $(+/-)$ about 3 eV above the level related to the V_{Al}-O_N complex. This value correlates with the observed energy[5] (3.2–3.3 eV) of the VL in AlN and suggests that the VL transition is from the oxygen-induced deep donor level to Al-vacancy-related deep acceptor level. We get an even better agreement with the VL transition energy from our calculations for O_N in wurtzite-AlN: the ionization level between the singly positive- and negative-charge states is about 0.3 eV higher in the gap than in the zinc-blende phase.

Thus we suggest that the broadband luminescences in GaN and AlN have essentially the same origin. The initial state in the transition is a donor-induced level, which is shallow in GaN and deep in AlN. The final state is the deep acceptor state related to a cation vacancy complex.

Further evidence supporting this luminescence model comes from the high-pressure experiments. Suski *et al.*[3] found in their study concerning the YL in GaN that the energy position of the YL saturates at 2.8 eV when the applied pressure was over 20 GPa. They suggested that the saturation is due to a deep level that at this crossover point enters the gap. The deep character of this level means that the initial level of the luminescence no longer follows the rising conduction-band edge (as the shallow effective-mass level did) and this causes the saturation in the position of the luminescence band. This is precisely what a comparison of our results between GaN and AlN predicts: When the band gap increases (due to either increasing Al content or applied external pressure) and a value of about 4 eV is exceeded, the negative-charge states of the dominant donors (O and Si) become stable and the related deep levels appear in the gap. We also note that in the high-pressure studies[30,29] a freezeout in the free-electron concentration is observed at high pressures that are comparable to the values for YL saturation. This confirms the entering of the donor level in the gap. The YL was observed to saturate at a value of 2.8 eV in GaN, while the VL in AlN has energy that is typically $\sim$ 0.5 eV higher. We relate this difference to two facts. In GaN the measured shift in the YL position before saturation is about 25% smaller than the shift in the conduction-band edge.[3] This is presumably due to the fact that the position of the final state in the YL (acceptor level) is also affected by the applied pressure and shifts upward in the gap.[3] On the other hand, we are making a comparison between two materials with differing cation species; while there is qualitative agreement on the luminescence mechanism, small quantitative differences are likely to arise simply due to differences in the cation vacancy properties.

Evidence for the presence of cation vacancies in the luminescence processes also comes from the experimental results for GaN by Zhang *et al.*[31] They found that the intensity of YL was greatly reduced in *p*-type conditions (Mg doping) or when Ga was made more abundant in the growth process. Both observations are consistent with the calculated acceptor character of gallium vacancies or related defect complexes.

Finally, we will address the origin of the broad line shape of the YL and of the VL. Gaussian line shapes are commonly detected in luminescence experiments when a strong coupling to ionic degrees of freedom is associated with the DAP transition.[32,33] Such emissions are typical for materials with pronounced polar character such as II-VI compounds. For instance, in ZnS or ZnTe transitions from donor levels to zinc-vacancy–halogen-impurity-complex acceptor levels are known to induce broad luminescence bands with a Gaussian line shape.[32] This obviously bears close similarity to our model for the origin of YL (VL) luminescence in GaN (AlN). The rather polar character of GaN and AlN, compared, e.g., with GaAs, further supports the analogy with the emission in II-VI compounds. The large lattice relaxations associated with the cation-vacancy ends of the defect complexes with varying electronic occupation (Appendix) provide explanation for the strong phonon coupling necessary for the Gaussian line shape.

Another factor affecting the line shape of a DAP transition is the Coulomb interaction between the ionized donors and acceptors in the final state. This interaction is generally known to lead to the appearance of satellite peaks in the emission spectrum[33] and should lead to asymmetric broadening of the line shape.

We also note that Youngman and Harris[5] suggest that the inhomogeneity in the defect structures can lead to broadening of the impurity levels and subsequent widening of the luminescence spectrum. Both in GaN and AlN the broadband luminescence is seen to correlate with the extended defects in the cathodoluminescence studies.[7,5] We think that trapping of point defects and defect complexes at these extended defects is likely to occur and provides variations in the local environment leading to electronic state broadening. Also, since both Si and O are likely donors in GaN and AlN, participation of donor levels with slightly differing environments acts as a possible additional source for defect level broadening. Furthermore, our calculations demonstrate that the dominant deep acceptors have multiple ionization levels in the range $\sim$ 0.5–1.7 eV above the valence-band maximum. Participation of these levels, in addition to the highest one, to the luminescence process provides another logical source for the broad line shape.

Since both YL and VL spectra are generally lacking any clear structure, the separate contribution from each of the broadening factors outlined above is difficult to solve quantitatively. We suggest that a careful recording of the luminescence spectra with improved resolution could reveal important features that could be identified as due, e.g., to Coulombic interaction or phonon replicas, generally exhibiting qualitatively well separable character.

In our earlier study[34] we have suggested the involvement

TABLE I. Details of the atomic configuration for Si_{Al} in AlN for two dominant charge states. d_i denotes the bond length between the Si atom and the nearest-neighbor Al atoms. The bond length values are given in units of the nearest-neighbor distance of the perfect lattice.

Defect	d_1	d_2	d_3	d_4
Si_{Al}^+	0.94	0.94	0.94	0.94
Si_{Al}^-	1.12	0.96	0.96	0.96

of nitrogen antisite defects in the YL process in GaN due to the large lattice relaxations observed. In the light of the present results, we observe that the electron states due to nitrogen antisites can certainly contribute to the yellow emission, but the antisites are not likely to be the principal defect behind the YL. The formation energy of nitrogen antisites is higher than for the defects investigated in the present study, which suggests that in equilibrium they are not present in large enough concentrations to explain the observed luminescence.

V. CONCLUSION

Our calculations give firm support to the donor-acceptor origin of the parasitic luminescence in GaN and AlN. The initial state of the luminescence transition is most evidently a level formed by shallow donors in GaN, while in AlN the involved donors have a deep character. Substitutional Si and O impurities are found to be most likely candidates for the donor defects. The final state of the luminescence is provided by the deep acceptor levels related to cation vacancy complexes. We find clear evidence for complex formation between the positively charged donors and negatively charged cation vacancies. The broadband luminescence spectrum and its origin are found to be analogous with the DAP transitions in II-VI compounds. The coupling between the electronic and ionic degrees of freedom, level broadening due to inhomogeneity in the defect structures, and participation of several acceptor levels are suggested to be principal contributing factors behind the wide line shape.

APPENDIX: DETAILS OF ATOMIC RELAXATION

When the Al fraction in $Al_xGa_{1-x}N$ compounds is increased, the conduction-band edge rises. With sufficient Al

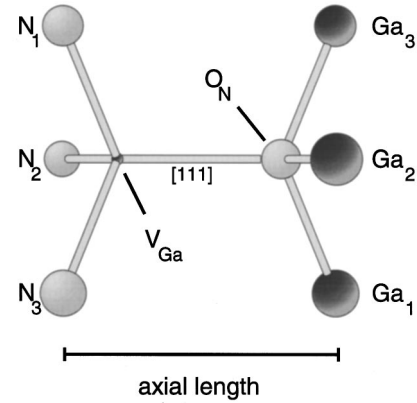FIG. 3. Atomic geometry of the defect complexes investigated. Shown is the $V_{Ga(Al)}$ -O_N complex. The atomic geometry related to divacancy can be obtained simply by the removal of the oxygen atom from the structure.

concentration the negative-charge states for the donors finally become stable.[10] For oxygen in the negative-charge states we have found off-center displacement from the substitutional position in AlN.[10] In a similar way in the present study, Si_{Al} in AlN is found to be displaced along the [111] direction in the negative-charge states as shown in detail in Table I. Thus off-center displacements are reported to be typical also for substitutional Si in $Al_xGa_{1-x}N$, in addition to O_N.

The nearest-neighbor nitrogen atoms of isolated cation vacancies (V_{Ga} and V_{Al}) are found to relax about 10% outward with the relaxation being largest (12%) for the neutral charge. The relaxation modes for isolated anion vacancies (V_N) are rather sensitive to the charge state; the outward relaxation for positive-charge states changes to an inward relaxation with increasing negative charge.

The atomic geometry of the defect complexes studied is illustrated in Fig. 3. The general observation regarding the atomic relaxation of the defect complexes is that their configurations largely follow the combined features of the constituent defects. The cation vacancy ends are seen to considerably relax outward in all charge states and the difference between the various charge states is clearly enhanced when compared with the isolated vacancy. The anion vacancy end of a divacancy relaxes outward in the positive-charge states and slightly inward in the negative-charge states. Oxygen at the nitrogen site stabilizes the nitrogen vacancy end of the defect complex and maintains a nearly constant distance to the three neighboring Ga atoms. In the most negatively charged defects in AlN distortions from the axial symmetry are observed. No radical changes in the axial length of the defect complexes are detected, but a nearly constant few percent increase in the axial length is found for all charge states.

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