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Vacancy complexes induce long-range ferromagnetism in GaN

Zhenkui Zhang, Udo Schwingenschlöggl,^{a)} and Iman S. Roqan^{a)}

Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

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By means of density functional theory, we argue that ferromagnetism in GaN can be induced by vacancy complexes. Spin polarization originates from the charge compensation between neutral N and Ga vacancies. Defect formation energy calculations predict that a vacancy complex of two positively charged N vacancies and one doubly negative Ga vacancy is likely to form. This defect complex induces a net moment of $1 \mu_B$, which is localized around the negative Ga center and exhibits pronounced in-plane ferromagnetic coupling. In contrast to simple Ga vacancy induced ferromagnetism, the proposed picture is in line with the fact that N vacancies have a low formation energy. Formation energies indicate mutual stabilization of the intrinsic defects in GaN. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4901458>]

INTRODUCTION

After the prediction that GaN can become a room temperature ferromagnetic (FM) semiconductor,¹ a large number of experimental efforts have been devoted to achieve diluted ferromagnetic GaN by introducing $3d$ ions,² $4f$ ions,^{3,4} and p defects.^{5,6} A special case is Gd-doped GaN, for which colossal magnetic moments have been reported.³ Subsequent studies found the Gd atoms to behave paramagnetically and showed only weak indications of moment formation for the Ga atoms.^{4,7} Complexes of Gd with Ga vacancies have been predicted to support ferromagnetism,⁸ similar to complexes of Gd with N and O interstitials.⁹ Though defect complexes are likely to be related to the observed magnetic behavior,¹⁰ understanding the exact mechanism remains a challenge.

Room temperature ferromagnetism through p impurities and defect engineering has been realized in Refs. 11 and 12. In these studies, the p defects, such as Zn vacancies, lead to local moments and mediate the exchange interaction. In this context, a picture of Ga vacancy (V_{Ga}) induced ferromagnetism was developed for GaN based on results from density functional theory (DFT),¹³ ignoring the lower formation energy of the N vacancy (V_N).¹⁴ Experiments also have attributed the ferromagnetism in undoped GaN to V_{Ga} , but found V_N to be unavoidable to be introduced.⁵ Besides magnetically active complexes involving Ga vacancies in pristine GaN,⁶ also GaN vacancies (V_{GaN}) in Mg and Er doped GaN and GaN vacancy complexes have been confirmed.^{15,16} In this work, we will demonstrate long-range ferromagnetism induced by vacancy complexes in wurtzite GaN, incorporating both V_{Ga} and V_N , rather than the previously proposed V_{Ga} induced ferromagnetism. The magnetic interaction is found to be pronounced in the ab -plane and rather weak in the c -direction.

COMPUTATIONAL METHODOLOGY

All calculations are performed using the VASP code¹⁷ with projector augmented wave pseudopotentials¹⁸ and an

energy cutoff of 400 eV. The valence shells are $2s^2 2p^3$ for N and $3d^{10} 4s^2 4p^1$ for Ga, where the semicore d states are explicitly included for Ga. The Perdew-Burke-Ernzerhof flavor of the generalized gradient approximation is employed, with an on-site Coulomb repulsion to account for electronic correlation effects.¹⁹ A value of $U_{eff} = 5$ eV is adopted for both the Ga d and N p states. The optimized lattice parameters ($a = 3.129$ Å, $c/a = 1.627$) of wurtzite GaN agree with the experimental values ($a = 3.19$ Å, $c/a = 1.627$), while the calculated band gap of 2.88 eV underestimates the experimental value of 3.44 eV. All defective structures are fully relaxed until the forces per atom have declined to less than 0.04 eV/Å. The method of Gaussian smearing (ISMEAR = 0) was selected for electron occupations with a width of 0.08 eV for 192-atom and its doubled supercells and 0.04 eV for 300-atom supercells and its doubled supercells. An energy convergence of 5×10^{-5} eV is achieved. For 192 and 300-atom supercells $2 \times 2 \times 1$ k-meshes are found to be sufficient, while denser k-meshes are used for smaller supercells. For the 128-atom supercell the ion positions are allowed to relax together with the size and shape of the supercell. For the 192- and 300-atom supercells, we observe that the vacancy defects have a very slight effect on the lattice constant due to a very low concentration. Therefore, the ion positions are relaxed only as the size of supercell remains unchanged. The concerned magnetic properties are found to be independent of volume relaxation in the cases of 192- and 300-atom supercells.

RESULTS AND DISCUSSION

Supercells of different sizes containing one V_{GaN} are found to converge to a spin-polarized ground state with a magnetic moment of $2 \mu_B$. The results in Table I refer either to an onsite repulsion on both the Ga d and N p states ($U_{d,p}$) or to one on the Ga d states only (U_d), which corrects the energetic position of the Ga d states as well as the hybridization with the N p states to enhance the electronic structure description.²⁰ Comparing the results obtained by the two

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: Udo.Schwingenschlöggl@kaust.edu.sa and Iman.Roqan@kaust.edu.sa

TABLE I. Effects of the supercell size and onsite repulsion on the magnetic moments on the N (M_N) and Ga (M_{Ga}) neighbors of V_{GaN} . M_N and M_{Ga} (in μ_B) are obtained by extrapolating the sum of moments over all the atoms to the total $2\mu_B$ moment. $M_{N(i)}$ ($i = 1, 2, 3$) indicates the local moment spreading on the first, second, and third nearest N neighbors of the V_{Ga} center, respectively. M_{Ga} indicates the local moment on the first Ga neighbors of the V_N center. E_{spin} (in meV) is the energy difference between the spin degenerate and the spin-polarized state, indicating the stability of spin polarization. E_{mag} (in meV) is the energy difference between AFM and FM states, calculated by doubling the supercells.

	128		192		300	
	U_d	$U_{d,p}$	U_d	$U_{d,p}$	U_d	$U_{d,p}$
$M_{N(1)}$	0.38	0.54	0.47	0.55	0.47	0.54
$M_{N(2)}$	0.04	0.04	0.04	0.04	0.04	0.04
$M_{N(3)}$					0.00	0.00
M_{Ga}	0.05	0.01	0.01	0.00	0.01	0.00
E_{spin}	273	818	328	802	318	825
E_{mag}	92	-9	-28	-6	-10	-2

models ($U_{d,p}$ and U_d) allows us to check whether electron correlations in the N p states are important (so far, an open question^{21,22}). The results for the U_d model with a 128-atom supercell show differences to those for the $U_{d,p}$ model, which gives rise to consistent values for all supercell sizes (indicating that in this case the defect states are more localized). We conclude that the 192-atom supercell is sufficiently large to describe a V_{GaN} . The local moment extends to the second nearest N neighbors, as for the 300-atom supercell we obtain a negligible moment on the third nearest neighbors.

We have studied various configurations with different distances of the V_{Ga} and V_N and find a moment of $2\mu_B$ for every case except for two situations that have the Ga and N dangling bonds overlap directly. In these cases, the absence of spin polarization is a result of electron-hole compensation by the bonding between the dangling states of Ga and N. This bonding is accompanied by enhanced distortions. It is also found that V_{GaN} (V_{Ga} and V_N are nearest neighbors) is energetically favorable over configurations with larger separation. The binding energy needed to form V_{GaN} from V_{Ga} and V_N in neutral states is 2.3 eV, indicating a strong tendency of aggregation.

To demonstrate the origin of the $2\mu_B$ magnetic moment, we schematically present the electronic structures of isolated V_{Ga} and V_N (Fig. 1), based on our calculations that are in qualitative agreement with previous DFT studies.^{14,23,24} A neutral V_{Ga} extracts three electrons from the direct N neighbors and gives rise to a_1 and triplet-like defect states, which hereafter are referred to as t states. The spin-up t states are filled and are part of the valence band, whereas the spin-down t states are empty (Fig. 1(a)). A neutral V_N releases three electrons to its Ga neighbors. Two of them form a filled a_1' state, which is located within the valence band, whereas the remaining electron occupies t' states next to the conduction band (Fig. 1(b)).²³ Consequently, when V_{Ga} interacts with V_N this high-energy electron from V_N is released to V_{Ga} , forming a $V_{Ga}^- - V_N^+$ pair, leading to the net moment

FIG. 1. Energy diagram of defective GaN containing an isolated (a) V_{Ga} and (b) V_N . The left (right) part refers to the spin-up (spin-down) channel.

of $2\mu_B$. This charge transfer agrees with the argument that V_N^+ is the energetically most relevant defect.^{13,23,25}

For V_{GaN} and separated V_{Ga} and V_N (separation 8.5 Å), the total density of states (DOS) and the DOS projected on the N and Ga nearest neighbors are plotted in Fig. 2 (192-atom supercell). For V_{GaN} the insulating character is maintained with a reduced band gap of 0.53 eV. The in-gap states are due to the N nearest neighbors (mainly $p_x + p_y$) and are spin polarized. The Ga neighbors contribute to the defect states near the conduction band minimum (CBM), see Fig. 2, where hybridization of the Ga p and N p states appears at the valence band maximum (VBM). On the other hand, for separated V_{Ga} and V_N , we always find a half-metallic character. Changing U from 3 to 7 eV on the N p states has essentially no influence on the electronic structures.

Fig. 3(a) illustrates the spatial extension of the two holes trapped at the N neighbors of V_{GaN} , mainly in the ab -plane (three direct N neighbors). The first N neighbors of the V_{Ga} center exhibit displacement away from the vacancy center, while the Ga neighbors of the V_N side show displacement approaching the vacancy center. Similar behaviors are also found in the separated vacancy complexes, as will be demonstrated below. Fig. 3(b) shows that the distribution of the separated vacancies (distance between the centers of V_{Ga}^- and V_N^+ is 8.5 Å) remains predominantly planar around the V_{Ga} , with moments of $0.46\mu_B$ on each of the three in-plane N neighbors, despite a significant spin density on the single out-of-plane N neighbor ($0.26\mu_B$). The V_N does not trap holes. Fig. 3(c) is analogous to Fig. 3(b) but for the case of a single hole, i.e., an additional electron is introduced. The in-plane character is very pronounced and the bonds to the three in-plane N neighbors are elongated (1.821 Å) to even exceed that of the out-of-plane neighbor (1.806 Å). In Fig. 3(d) we address a single hole trapped in a $V_{Ga}-2V_N$ complex, again showing the pronounced in-plane character. The distance between V_{Ga}^- and the second V_N^+ is 7.6 Å in Fig. 3(d), whereas that between the two V_N^- centers is 5.4 Å. The

FIG. 2. Total and partial DOS of (a) V_{GaN} and (b) $V_{\text{Ga}}^{2-}-V_{\text{N}}^{2+}$ complex. The partial DOS refers to the N (magenta) and Ga (blue) neighbors of the defect.

discussed in-plane distribution of the holes is distinct from the isotropic distribution reported for zinc-blende GaN,¹³ showing that the magnetic interaction is much more anisotropic in the present wurtzite case.

We calculate the total energies for antiferromagnetic (AFM) and FM ordering between neighboring complexes in various charge states by doubling the 192 and 300-atom supercells along the a -axis. Table II gives the energy differences $E_{\text{mag}} = E_{\text{AFM}} - E_{\text{FM}}$ and the magnetic moments. The FM ordering is found to be favorable for a distance of 12.4 Å, except for neutral V_{GaN} and V_{Ga} , and is likely to survive at room temperature (about 23.5 meV (Ref. 26)), given the large energetic preference (E_{mag}). The ordering of two neutral V_{Ga} can only be AFM, because the t orbital is occupied by three electrons with parallel spin (see Fig. 1(a)). The same picture applies to neutral V_{GaN} , because the states around the Fermi energy (E_F) in Fig. 2(a) are fully spin

polarized. Charging V_{Ga} by either introducing an additional electron or creating V_{N} shifts E_F upwards in energy to partially occupy the defect states (see Fig. 2(b)). In this case, FM alignment between the local moments of neighboring complexes is possible (see Table II). This argument is also valid for negatively charged V_{GaN} , for which E_{mag} is larger than found in previous DFT studies of zinc-blende bulk and the surface of wurtzite GaN.^{13,27} It is noted that the absolute value of E_{mag} in the U_d model is considerably larger than that in the $U_{d,p}$ model (see Table I), demonstrating the role of electronic correlations in the N p orbital.

The magnetic interaction is found to be substantial at a separation of 12.5 Å between two $V_{\text{Ga}}^{2-}-V_{\text{N}}^{2+}$ complexes, but it declines quickly at a separation of 15.5 Å (see Table II). This picture is confirmed by the spin density maps in Fig. 4, which show overlap between the two defects at a separation of 12.5 Å but not at 15.5 Å. An additional configuration

FIG. 3. Spin density of (a) a neutral V_{GaN} (2 holes), (b) a neutral $V_{\text{Ga}}^{2-}-V_{\text{N}}^{2+}$ complex (2 holes), (c) a negatively charged $V_{\text{Ga}}^{2-}-V_{\text{N}}^{2+}$ complex (1 hole), and (d) a neutral $V_{\text{Ga}}^{2-}-2V_{\text{N}}^{2+}$ complex (1 hole). The isosurface level is $0.002 e/\text{\AA}^3$. Larger and smaller spheres represent the Ga and N atoms, respectively.

TABLE II. Total magnetic moment (M_{tot}) and E_{mag} (for two separations d) in various charge states. The moments are given in μ_B , the energies in meV, and the separations in Å. The d indicates the distance between two V_{Ga} centers arising from two vacancy complexes, while the distance between the two V_{N} centers is ignored as there is no spin polarization surrounding their centers. For the complex $V_{\text{Ga}}^- - V_{\text{N}}^+$, the distance between V_{Ga}^- and V_{N}^+ is 8.5 Å. For the $V_{\text{Ga}}^{2-} - 2V_{\text{N}}^+$ complex, the distance between V_{Ga}^{2-} and the second V_{N}^+ is 7.6 Å, whereas that between two V_{N}^- centers is 5.4 Å.

Defect	Charge	M_{tot}	E_{mag}	
			$d = 12.4 \text{ Å}$	$d = 15.5 \text{ Å}$
V_{GaN}	0	2.0	−6	−2
	−1	1.0	87	5
$V_{\text{Ga}}^- - V_{\text{N}}^+$	0	2.0	67	−1
	−1	1.0	70	14
$V_{\text{Ga}}^{2-} - 2V_{\text{N}}^+$	0	1.0	57	11
V_{Ga}	0	3.0	−8	−1
	−1	2.0	127	−1
	−2	1.0	54	2

has been examined with the two V_{Ga} in adjacent Ga layers in a distance of 11.2 Å. In this case, the FM and AFM states are energetically degenerate, suggesting paramagnetism, due to negligible overlap of the spin of the defect states. A dominantly in-plane magnetic coupling agrees with the anisotropic character of the magnetism in wurtzite ZnO after carbon-doping.²⁸

Fig. 5 gives formation energies for V_{GaN} , V_{Ga} , and V_{N} as a function of the Fermi energy, using $E_{\text{form}}[D^q] = E_{\text{tot}}[D^q] - E_{\text{tot}} + \sum n_i \mu_i + q[E_F + E_V]$,²⁹ where E_{tot} and $E_{\text{tot}}[D^q]$ are the total energies of the non-defective and defective (with charge q) supercells, respectively, n_i denotes the number of atoms introduced to ($n_i < 0$) or subtracted from ($n_i > 0$) the pristine supercell, μ_i is the chemical potential, and E_F denotes the Fermi energy (measured with respect to the pristine VBM, varying from zero to the experimental band gap). The chemical potentials, μ_{Ga} (Ga-rich/N-poor)

and μ_{N} (N-rich/Ga-poor), are calculated from metallic Ga and the N_2 molecule, respectively. In Ga-poor/N-rich environment, for example, $\mu_{\text{Ga}} = \mu_{\text{GaN}} - \mu_{\text{N}}$, where μ_{GaN} is given by the energy of a formula unit of GaN and μ_{N} by half of the energy of a N_2 molecule. According to Fig. 5(a), V_{N} has 3+, 1+, and 0 states as E_F varies from the VBM to the CBM, whereas the 2+ state is unstable, behaving as a negative- U defect. These results and the value of E_{form} at the VBM (−1.14/0.31 eV in N-poor/N-rich environment) agree with a recent hybrid functional study.²⁹ V_{GaN} has 0, 1-, and 2-states, consistent with Ref. 14, where E_{form} falls in between that of V_{Ga} in Ga-rich and Ga-poor environments. E_{form} does not depend on μ_{Ga} or μ_{N} , but on μ_{GaN} , as a formula unit of GaN is removed. The small stability range of the 1-state reduces the possibility that ferromagnetism is induced by V_{GaN} .

V_{Ga} can have charge states 0 and 2-, whereas the 1-state is metastable and the 3-state is unstable. This result contradicts previous studies (finding the existence of 0, −1, −2, and −3 states) in which the onsite Coulomb interaction of the Ga d states was not taken into account.^{14,30} To verify its influence, we have calculated E_{form} of V_{Ga} using the U_d model with $U_{\text{eff}} = 5 \text{ eV}$ to Ga d states, see Fig. 5(b), confirming a 2- state over a wide energy range and an unstable 3-state. Interestingly, plain GGA calculations using the $U_{d,p}$ converged structures qualitatively reproduce the wrong trend of Refs. 14 and 30 (see Fig. 5(c)). We therefore conclude convincingly that the discrepancy arises from electronic correlations in the Ga d orbitals. The experimental observation³¹ showed that negatively charged Ga vacancy of 2- state is more stable than that of 3- state, which supports our finding that this state is stable. The stability of V_{N}^+ and V_{Ga}^{2-} let us expect ferromagnetism in GaN when the ratio of V_{Ga} to V_{N} approaches 0.5, because V_{Ga}^{2-} captures two electrons from two V_{N} (leaving V_{N}^+). During this process, V_{Ga} and V_{N} are mutually stabilized with respect to their neutral states. As a consequence, long-range in-plane ferromagnetism is formed

FIG. 4. Spin density for ((a) and (c)) FM and ((b) and (d)) AFM ordering between two $V_{\text{Ga}}^{2-} - V_{\text{N}}^+$ complexes with one trapped hole. Yellow (blue) refers to spin-up (spin-down), for an isosurface level of 0.001 e/Å^3 .

FIG. 5. (a) Formation energies of V_{GaN} , V_{Ga} , and V_{N} in various charge states as functions of the Fermi energy, which is calculated using the $U_{d,p}$ model, namely, applying the onsite repulsion U to both N p and Ga d states ($U_{\text{eff}} = 5$ eV for the N p and Ga d states). The results of the formation energy of V_{Ga} calculated for (b) the onsite repulsion are only applied to Ga d states ($U_{\text{eff}} = 5$ eV) and (c) for plain GGA-PBE, without onsite repulsion on either N p or Ga d states.

between the Ga defects in a wide range of $1.0 \leq E_F \leq 2.5$ eV (see Fig. 5(a)).

In conclusion, we predict long-range ferromagnetism induced by vacancy complexes in GaN at distances up to about 13 Å. The distance corresponds to a vacancy complex concentration of about 1%, which is a realistic amount. The ferromagnetism turns out to be of remarkably strong in-plane character. The spin polarization originates from the charge compensation between neutral V_{N}^0 and V_{Ga}^0 forming a complex that consists of two V_{N}^{+} and one V_{Ga}^{2-} with a net moment of $1 \mu_B$ localized on V_{Ga}^{2-} . This charge transfer leads to a sharp mutual stabilization of the cation and anion vacancies according to the calculated defect formation energies. For example, $E_{\text{form}}[V_{\text{Ga}}^{2-}] + 2E_{\text{form}}[V_{\text{N}}^{+}] - E_{\text{form}}[V_{\text{Ga}}^0] - 2E_{\text{form}}[V_{\text{N}}^0] = 3$ eV for $E_F = 1$ eV in the N-rich environment. In fact, V_{N}^{+} and V_{Ga}^{2-} are the most relevant defects over a large range of E_F . Our findings provide a new understanding of the role of intrinsic defects in the ferromagnetism in GaN.

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