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Effect of vacancies on ferromagnetism in GaN:Mn dilute magnetic semiconductors from first-principles

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In spite of considerable interest in ferromagnetism of the dilute magnetic semiconductor GaN:Mn, the nature of the ferromagnetism is still quite controversial. Experimental values for the Curie temperature T_C vary widely depending upon the details of the growth conditions which might affect the impurity concentrations and possibly the magnetic properties. In order to gain insight into the effects of the impurities, we have performed *ab initio* density functional studies of the magnetic interactions in GaN in the presence of vacancies. Both nitrogen and gallium vacancies have been considered. The nitrogen vacancy releases electrons in the system which changes the Mn d^4 state to a half-filled Mn d^5 state, so that the antiferromagnetic superexchange becomes dominant. Previous studies have found the nitrogen vacancy has the lowest formation energy, so the presence of these vacancies is predicted to lower T_C. The naive picture of Ga vacancies is the release of holes into the system which should increase ferromagnetism due to the increased hole concentration compared to the vacancy-free material. However, we find an antiferromagnetic interaction for the Ga vacancy as well, in agreement with Mahadevan's work. This can be attributed to the localized nature of the hole states which do not participate in the transport. The effects of localization of the holes from the Ga vacancy has been demonstrated using the virtual crystal approximation. Thus both the nitrogen and gallium vacancy are found to impede ferromagnetism.

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I. INTRODUCTION

Many materials are currently being investigated for spintronics applications. The dilute magnetic semiconductors (DMS) combine functionalities of semiconductors and magnetic materials for many new applications.[1] A few years ago, Dietl *et al.*[2] investigated a series of materials predicted to have a Curie temperature (T_C) larger than room temperature using a Zener model. While GaAs:Mn (Refs. 3–9) may be the most studied of these materials, GaN:Mn[5–13] has received considerable attention as well in search of higher values of T_C than found in GaAs:Mn. Experimentally, there are still questions as to the nature of the ferromagnetism in GaN:Mn. Values of T_C range from well below liquid nitrogen temperatures (10 K[14]) to well above room temperature [940 K (Ref. 15)] depending on the growth conditions, with the magnetism believed to arise from the Mn d moments which lie at the Ga sites. Up to $\sim 1-8\%$ doping can be incorporated into the structure, depending on annealing, growth conditions, and thickness of samples.[1,15–17]

Most theoretical studies of GaN:Mn, including electronic structure calculations, have investigated the interactions between Mn in the wurtzite[9,10,13,16,18–24] (and sometimes zincblende[9,10,12,20]) unit cell. However, as in all semiconductors, the native defects in the material change the properties from those seen in the pure samples. The nature of these native defects has been studied previously, but their importance to ferromagnetism in GaN:Mn has not been addressed systematically up to this point. The magnetic properties of Ga vacancies in Mn-doped GaN was investigated by Mahadevan and Mahalakshmi,[25] but that work only looked at the effects for the nearest-neighbor Mn configuration. Our results will show that the interactions between Mn do change depending on their relative positions with respect to the Ga vacancy. No investigations have studied the effects of N vacancies on magnetism. The presence of these N and Ga vacancy defect states along with Mn is a form of codoping of the materials which may enhance or suppress the ferromagnetic nature of the dopant Mn in the material. A better understanding of how such defects affect the magnetic properties of Mn-doped GaN is necessary to predict which growth conditions will be best to use this material for spintronics applications.

II. METHOD OF CALCULATION

To address these issues, electronic structure calculations were performed within density functional theory[26] using the full-potential linearized augmented plane wave (FP-LAPW) program WIEN2K.[27] The unit cell consists of a $2\times2\times2$, 32 atom supercell where the number of the **k** points in the irreducible Brillouin zone (IBZ) varied from 20 to 120 to obtain the band structure and exchange interaction coefficients. Increasing the number of **k** points beyond this provided marginal changes to the calculated parameters. As is well known, this method separates space into muffin-tin spheres surrounding the atoms and an interstitial region between the spheres. The magnetic moments arising from the calculation are distinguished by the moments connected to each atom within the muffin-tin sphere and the moment from the interstitial region which is not associated with any specific atom. The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof[28] was employed where the lattice parameters were relaxed to find $a=6.405$ Å and $c=10.634$ Å compared to the experimental values of $a=6.384$ Å and $c=10.392$ Å, a 3% increase in volume, typical for GGA calculations. This crystal structure remains unchanged in the calculations for configurations including Mn (which go to the Ga site[23]) or including N or Ga vacancies.

III. RESULTS

A. Electronic structure

1. GaN with Ga and N vacancies

Calculation of the energies of defects in GaN has been studied extensively by Limpijumnong and Van de Walle.[29] Their calculations focused on the formation energies of a series of native defects. These included nitrogen (V_N) and gallium (V_{Ga}) vacancies and antisite defects of nitrogen on the gallium site or gallium on the nitrogen site as well as N or Ga on interstitial sites. The formation energies for each of these defects were calculated as a function of the Fermi energy (E_F). The lowest lying defect states are N vacancies[29,30] and, at larger values of E_F, Ga vacancies under the typical Ga-rich growth conditions. Ganchenkova and Nieminen[30] claim similar results, though the N vacancy has lower energy than the Ga vacancy for all values of E_F.

The calculated band gap in GaN of 1.4 eV [Fig. 1(a)] is smaller than the experimental band gap of ~3.4 eV,[31] typical of density functional electronic structure calculations. The Ga *s* and *p* states below E_F are well separated from the N *s* and *p* states above. A N vacancy in $Ga^{3+}N^{3-}$ [Fig. 1(b)] provides three extra electrons. An electronic structure calculation for GaN with this type of vacancy gives a paramagnetic state. Using the band structure of GaN [Fig. 1(a)] as a reference, the three electron states are distributed so that two form near the top of the valence band while the other one crosses E_F near the bottom of the conduction band. A closer analysis of these bands reveals that the two deeper bands reside around the N vacancy while the higher energy electron moves to the neighboring Ga sites. This distribution of electrons is consistent with the valence picture as a function of E_F put forward by Limpijumnong and van de Walle[29] where the charge state changes from 3+ to 1+ as the Fermi level crosses the two N character bands near the original valence band edge and remains unchanged up to the conduction band edge. The sharp feature just above E_F corresponds to broken bonds in nearest-neighbor Ga sites around the N vacancy.

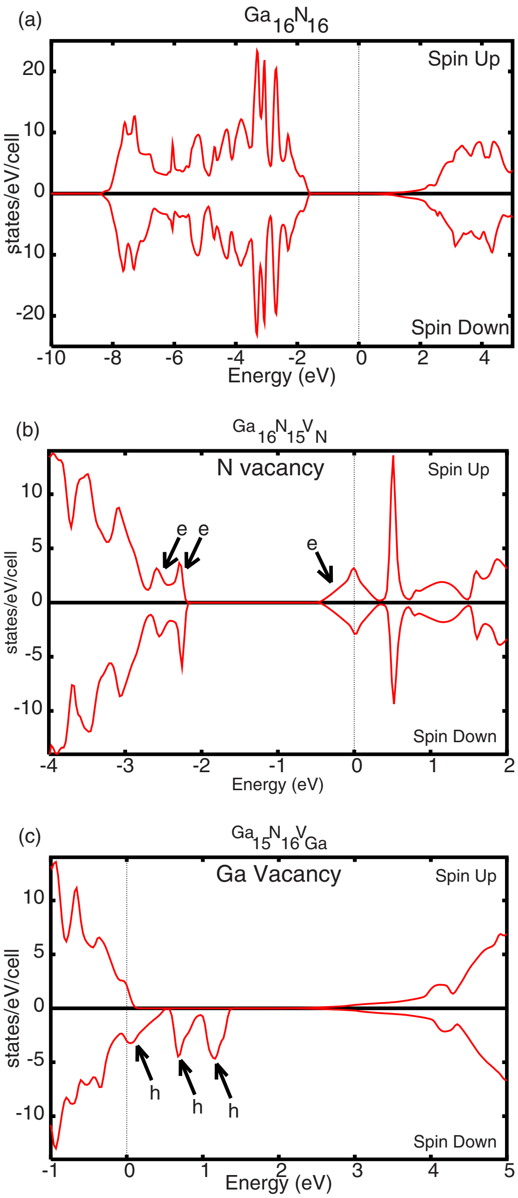

FIG. 1. (Color online) Density of states for GaN (a) without any vacancy, (b) with one N vacancy (which adds three electrons), and (c) with one Ga vacancy (which adds three holes). The positions of the extra electron states from the N vacancy and the extra hole states from the Ga vacancy are indicated by the arrows.

On the other hand, the Ga vacancy in $Ga^{3+}N^{3-}$ yields three extra holes. Mahadevan and Mahalakshmi[25] has previously noted that a Ga vacancy in GaN should be spin-polarized due to Hund's rule. Unlike in the paramagnetic case of a N vacancy, electronic structure calculations for a Ga vacancy in GaN finds a ferromagnetic ground state. Non-spin-polarized calculations of GaN and GaN with a N vacancy find a lower energy than the spin-polarized calculations by 60 meV/unit cell and 50 meV/unit cell, respectively. However, the spin-polarized calculation for GaN with a Ga vacancy has a lower energy by 420 meV/unit cell compared to the non-spin polarized result. The three Ga holes are shared by the four neighboring N atoms forming three distinct spin-polarized states near the top of the valence band just above E_F [Fig. 1(c)]. The magnetic moment on each of the N sites surrounding the vacancy is $\sim 0.5\mu_B$. (The remaining portion of magnetic moment is associated with the interstitial region.) Again, this is consistent with the valence picture as a function of E_F put forward by Limpijumnong and van de Walle[29] where the charge state changes quickly from 0 to 3− as the Fermi level crosses the three bands just above the original valence band edge and remains unchanged to the conduction band edge. This type of ferromagnetic state in the absence of any magnetic atoms is referred to as "d^0 ferromagnetism."[32] Several oxide systems, including CaO,[33] ZnO,[34] ZrO_2,[35,36] In_2O_3,[34] TiO_2,[34,37] and HfO_2,[34,38–40] have been predicted to have this property. The lack of experimental evidence to this point has been attributed to the formation energy for the defects necessary to have this d^0 ferromagnetism being too large to form a percolation cluster of such

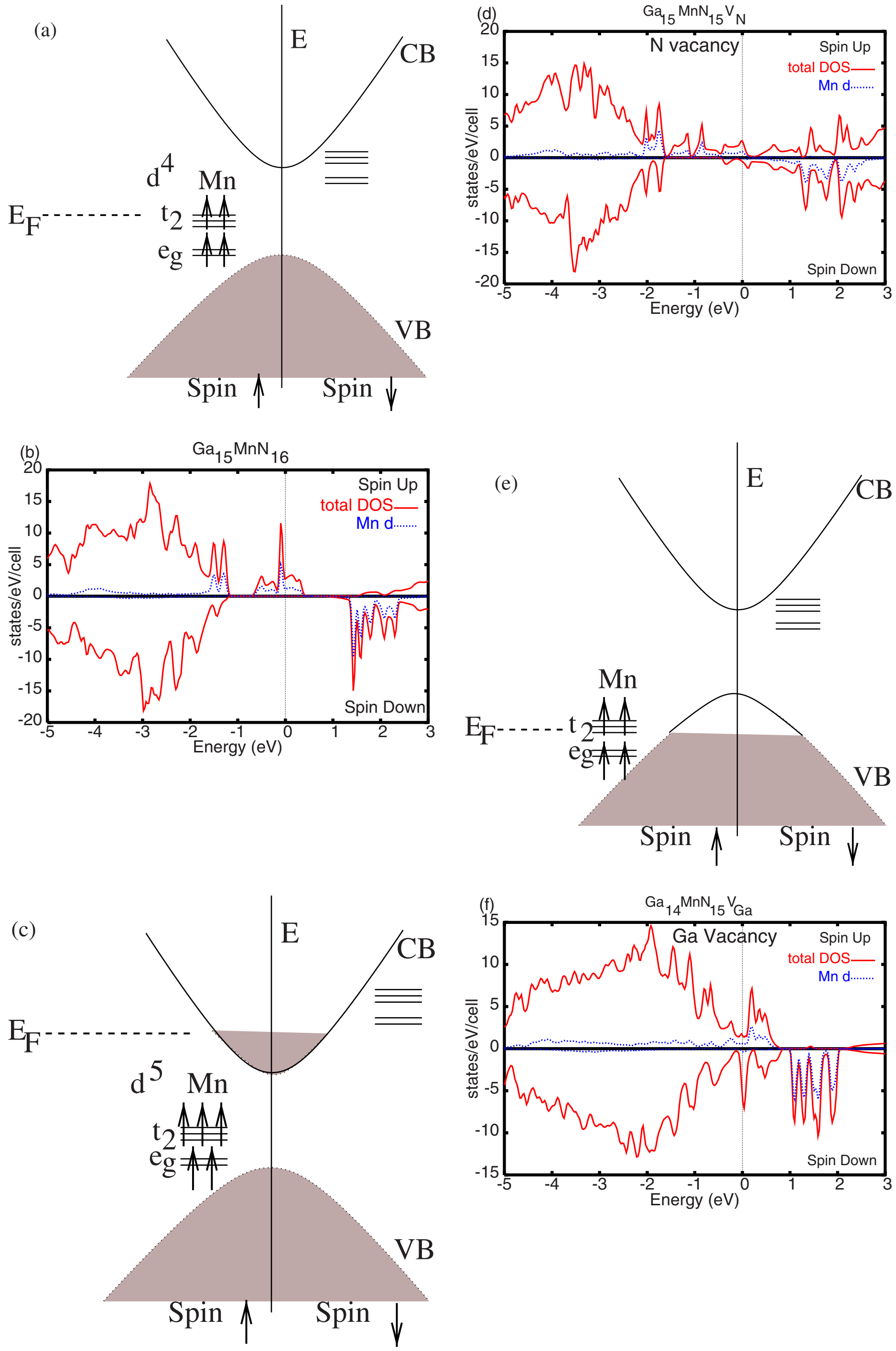

FIG. 2. (Color online) Electronic structure and schematic diagram of the position of the Mn *d* levels with respect to the conduction band (CB) and valence band (VB) in GaN (a),(b) with no vacancies, (c),(d) with a N vacancy, and (e),(f) with a Ga vacancy. The Mn *d* states and their occupancies (consistent with the calculated Mn moments as discussed in the text) are indicated in the schematic figures on the left.

defects necessary for bulk ferromagnetism.[33] We will leave the discussion of whether a sufficient Ga hole concentration is necessary for a percolation cluster in GaN for another time. In the interest of this paper, the spin-polarization for Ga vacancies are important for understanding the nature of the magnetic interaction in GaN:Mn when Mn is added.

2. GaN with Ga and N vacancies plus Mn

The position of the Mn states in GaN:Mn has been studied previously,[23] but some of the main details are recounted [Figs. 2(a) and 2(b)] here for better understanding of what happens when Ga and N vacancies are introduced. For GaN:Mn the empty Mn *d* states lie just below the conduction band edge while the partially filled Mn e_g states lie just below the t_{2g} levels just above the valence band edge. Since Mn replaces Ga in $Ga^{3+}N^{3-}$, Mn has a d^4 configuration so that E_F lies in the middle of the t_{2g} band. The d^4 configuration has been confirmed experimentally.[41] The position of the Mn *d* states coming from density functional calculations has been improved upon[42] by moving them closer to their experimental positions using such methods as SIC-LSD (self-interaction correction-local spin density). This has been shown to improve the estimation of T_C in some materials. However, since we are interested in the general features of how the ferromagnetism changes with Ga and N vacancies, which has not been studied in detail before, we will leave these corrections for a later time.

As mentioned earlier, a N vacancy introduced into GaN releases three electrons, two of which form deep states just above the valence band edge with the other one forming near the bottom of the conduction band [Fig. 1(b)]. When Mn is introduced to the system, the d^4 state forms somewhere in the middle of the gap, below the high-lying N vacancy state. The extra electron from this level gets transferred to the Mn level which fills the Mn t_{2g} to form a d^5 state. The Mn level moves down in energy to that of the other two N vacancy states at the top of the valence band [Figs. 2(c) and 2(d)], so no further charge transfer takes place. The N states remain spin unpolarized, so the total moment from the system comes only from Mn. The experimental measurement of the coexistence of an observed dominant Mn^{2+} (d^5) and a smaller Mn^{3+} (d^4) component in GaN:Mn has been attributed to N vacancies,[43] unlike what would be expected for simple Mn substitution for Ga.

As mentioned earlier, the Ga vacancy adds three holes to the system which are spin-polarized and lie on the neighboring N atoms [Fig. 1(c)]. Addition of Mn does not change the electron distribution significantly as the Mn d^4 levels settle near the position of the Ga vacancy states just above E_F [Figs. 2(e) and 2(f)]. The spin-polarized states arising from the Ga vacancy remain spin-polarized and interact strongly with the Mn moment. When the Mn atom is the shortest distance to any of the four N atoms neighboring the Ga vacancy (1.96 Å), the magnetic moment on the N atom reverses while the other N atoms further from Mn remain aligned parallel to each other, revealing a strong short-range antiferromagnetic interaction between Mn and the Ga vacancy. Placing these N at more than this nearest-neighbor distance from Mn appears to have no effect on the N moments. The average hole moment on the N atoms is $\sim 0.4\mu_B/\mathrm{N}$, slightly reduced from before Mn was added.

The localized Mn spins cross E_F to give a moment of $3.3\mu_B$ in the muffin-tin sphere, consistent with previous calculations which range from 3.1 to $3.8\mu_B$.[6,7,10,13,16,18,21,23,24,49] The total moment of $4.0\mu_B$ includes the contribution from the interstitial region not included in the muffin-tin spheres. For GaN:Mn+V_N three electrons are added and we expect a filled band, where we find the Mn moment increases to $3.6\mu_B$ with a total moment in the cell of $4.7\mu_B$, consistent with a filled shell value of $5.0\mu_B$. As mentioned before, the V_N electron states are paramagnetic, so the moment in the cell all comes from Mn. For GaN:Mn+V_{Ga} which adds extra holes, the holes lie on the N sites surrounding V_{Ga} and are spin-polarized. As mentioned in the previous paragraph, the polarized N sites align antiferromagnetically with Mn when they are nearest neighbors (1.96 Å). When the Mn-N separation is larger than this distance, the total moment in the cell is $5.1\mu_B$ which is a combination of the Mn moment of $2.8\mu_B$ and the total of the polarized Ga vacancy electrons which reside on neighboring N sites of $0.38\mu_B$ each. When the Mn-N distance is nearest neighbor, the closest N atoms reverse their sign with a reduction of $\sim 0.2\mu_B$ on Mn.

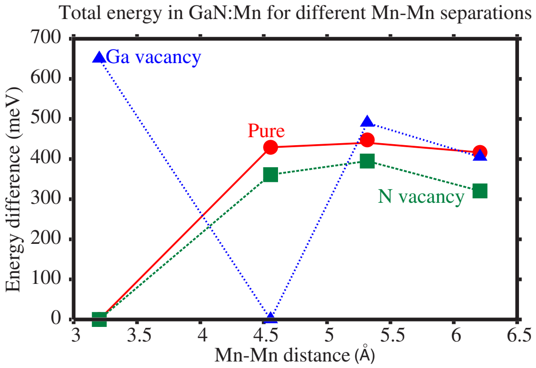

FIG. 3. (Color online) Total energy of GaN:Mn_2 with the lowest energy configuration for each case is set to zero for the three cases studied: No vacancy, one N vacancy, and one Ga vacancy. One Mn and the N or Ga vacancy are in nearest-neighbor positions with the other Mn atom moved around the unit cell. Configurations with larger Mn-vacancy distances are found to have higher energies.

B. Exchange parameter *J*

In order to calculate the exchange parameter J, two Mn atoms must be placed in the unit cell. The total energies for ferromagnetic and antiferromagnetic configurations were calculated in order to find J at a variety of Mn-Mn separations. However, this also provides information about which Mn-Mn separation has the lowest energy. With no vacancies, the Mn atoms prefer to be close to each other with all other distances having ~500 meV higher energy (Fig. 3), in agreement with a similar calculation by Uspenskii *et al.*[8] Similarly, in the presence of a single N vacancy, the lowest energy is when the N vacancy lies between the two nearest-neighbor Mn atoms [Fig. 4(a)]. The Mn and N vacancy are nearest neighbors (1.96 Å) for each of these configurations with the position of the second Mn atom varying in the unit cell. The configurations with Mn further apart are about ~400 meV higher in energy. Every possible relative position between the N vacancy and the Mn have not been studied, of course, but a few test cases not shown here with larger Mn-V_{N} separations found larger energies. (These are not the formation energies as the lowest energy configuration is set to zero, so the configuration with no vacancy cannot be compared to that with a vacancy.)

In the case of the Ga vacancy, the results are much different for the nearest- (3.20 Å) and next-nearest-neighbor (4.55 Å) Mn distances from those cases with no vacancy or with a N vacancy (Fig. 3). While all configurations were not considered, each configuration had one Mn and the Ga vacancy at nearest-neighbor positions (3.20 Å) with the second Mn position varied throughout the unit cell [Fig. 4(b)]. As with the N vacancy, all possible configurations have not been studied, but those other configurations which were studied with larger Mn-V_{Ga} separations not shown here had larger energies. The nearest-neighbor Mn configuration has higher energy than the lowest energy next-nearest-neighbor Mn configuration by ~650 meV. The third-nearest- and fourth-nearest-neighbor configurations have energies similar to those of GaN:Mn and GaN:Mn+V_{N}. These energies do not describe the experimental positions of the atoms in the unit

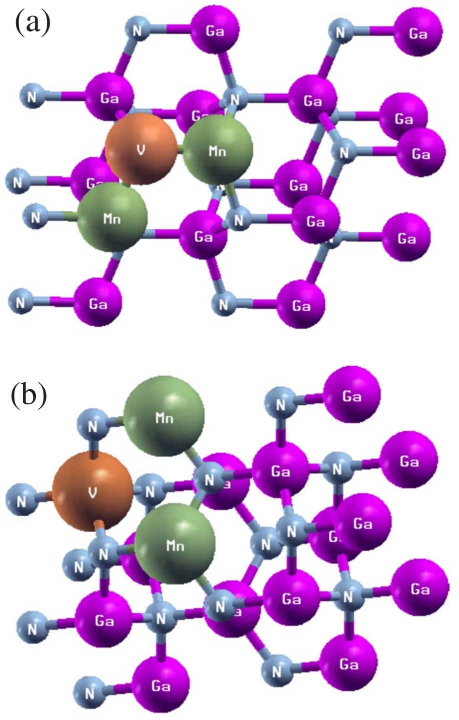

FIG. 4. (Color online) Atomic positions for GaN with two nearest-neighbor Mn and (a) a single N vacancy and (b) a single Ga vacancy (Ref. 50). The Mn and vacancy sites are made larger for emphasis.

cell in that the Mn atoms never reach equilibrium, but this indicates that the interaction between the Mn and the Ga vacancy holes on the N sites acts differently when the Mn atoms are close to each other.

The magnetic exchange parameter, J, of course depends upon the concentration of Mn within the unit cell. As mentioned earlier, the experimental concentration of Mn in GaN can be at most 1–8 %.[1,15–17] Small concentrations require very large unit cells which are computationally very challenging, mainly in terms of the time to run such a calculation. To understand the effect of Mn concentration on J, we have calculated J for concentrations in $\mathrm{Ga}_{1-x}\mathrm{Mn}_x\mathrm{N}$ ranging from x equals 100% (containing four atoms in the unit cell) to 6.25% (containing 64 atoms in the unit cell) (Fig. 5). (Of course, this does not represent the correct crystal structure or lattice constants for MnN, but we are primarily interested in the small Mn concentration limit.) The magnetic exchange interaction parameter, J, is the energy gain per Mn atom comparing the ferromagnetic and antiferromagnetic configurations so is defined $J=(E_{\mathrm{AFM}}-E_{\mathrm{FM}})/2$ which makes J positive for a ferromagnetic ground state. Between 12.5% (32 atom unit cell) and 6.25% (64 atom unit cell), the value of J decreases only about 3%, which is near the margin of error for the calculation of J anyway. Therefore, all of our calculations are performed using the 32 atom unit cell which is much easier computationally and should obtain most the proper physics of the larger unit cells (and smaller concentrations) with only a small correction to the value of J.

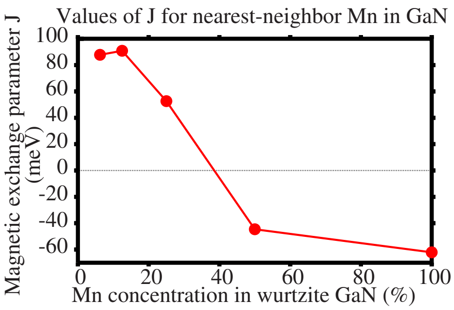

FIG. 5. (Color online) Magnetic exchange parameter J for nearest-neighbor Mn atoms in GaN:Mn as a function of Mn concentration using the lattice structure and lattice parameters of GaN.

Before discussing the values of the magnetic exchange interaction parameter, J, it is important to note what is expected for each vacancy. According to the calculations of the DOS for GaN with the two types of vacancies, different behavior is expected for each vacancy. For the N vacancy, the three extra electrons mostly go to the neighboring Ga or Mn sites but remains paramagnetic [Fig. 1(b)]. The N vacancy adds one electron to the d^4 state to make it d^5. The extra three electrons from the N vacancy lie on the neighboring Ga atoms, farther from the Mn atoms than the N vacancy itself [Fig. 4(a)]. The filled Mn d shell is expected to interact antiferromagnetically which should cause a reduction of J. On the other hand, the Ga vacancy provides three extra holes [Fig. 1(c)] which should provide extra carriers to enhance ferromagnetism and increase J. In our calculation, the three extra holes lie on the neighboring N atoms which are closer to Mn than the Ga vacancy itself [Fig. 4(b)].

The N and Ga vacancies have a striking effect on the magnetic exchange interaction. In GaN:Mn J begins $\sim$90 meV/Mn for nearest-neighbor Mn distances before dropping to below 10 meV/Mn for second- and third-nearest neighbors before increasing to $\sim$15 meV/Mn for the fourth-nearest neighbor (Fig. 6). These results are consistent with other calculations of the exchange interaction for GaN:Mn.[20,24,44–47]

Experiments confirm that the Mn prefers to lie on Ga sites near N defect sites.[48] The inclusion of a N vacancy next to the Mn site changes J from positive to negative indicating that an antiferromagnetic ground state is favored with $J\sim$

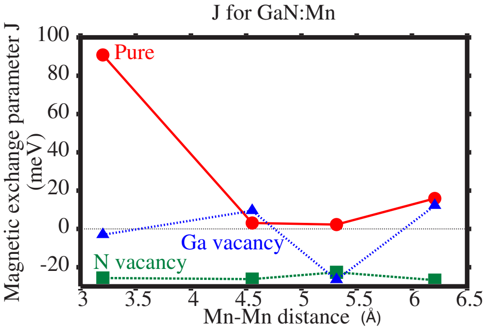

FIG. 6. (Color online) Magnetic exchange parameter J as a function of Mn-Mn distance for GaN:Mn with no vacancies, with one N vacancy, and with one Ga vacancy. As before, one Mn and the N or Ga vacancy are in nearest-neighbor positions with the other Mn atom moved around the unit cell.

−10 to −20 meV/Mn with little dependence on distance between Mn atoms (Fig. 6). This can be understood by remembering that the additional electrons produced from the N vacancy changes the Mn d^4 to a d^5 state. While the hole in the Mn d^4 state could interact ferromagnetically with other Mn atoms by the double exchange mechanism, the filled d^5 state interacts with other Mn atoms by antiferromagnetic superexchange. While there are two Mn atoms in the unit cell, both appear d^5 in character meaning only 1 electron goes to the conduction band.

As in the case of N vacancies, Mn atoms prefer to lie near Ga vacancy sites.[47] We have further shown that the second-nearest neighbor to the Ga vacancy is preferred to the nearest neighbor since the Ga vacancy can then lie between two Mn atoms (Fig. 3). The exchange parameter J changes as a function of distance between the Mn atoms, from nearest-neighbor to fourth-nearest-neighbor, to an extent that the Ga vacancy's effect on J cannot be understood by simply studying a single point. The nearest-neighbor Mn (3.20 Å) has a negative $J \sim -3$ meV/Mn which shows that the AFM state is slightly favored. A similar value of the exchange parameter was noted by Mahadevan and Mahalakshmi,[25] with differences in the values attributable to the methods used and the relative positions of the Mn atoms with respect to the Ga vacancy. The second-nearest-neighbor Mn (4.55 Å), on the other hand, has a $J \sim 9$ meV/Mn which is slightly larger than that of GaN:Mn with no vacancy. The AFM state is again stronger with $J \sim -26$ meV/Mn for the third-nearest-neighbor Mn (5.32 Å) The fourth-nearest-neighbor Mn (6.21 Å) is again ferromagnetic with $J \sim 12$ meV/Mn, slightly smaller than for the pure compound. The distance between the Mn atoms, which implies the relative position of the Ga vacancy with respect to the Mn atoms, profoundly changes the magnetic properties of GaN:Mn+V_{Ga}.

It is very difficult to make a general theory explaining the variation in the magnetic exchange parameter, J, for GaN:Mn with the Ga vacancy. Neither the ferromagnetic nor the antiferromagnetic configurations are favored for all distances, as in the case of GaN:Mn with no vacancies or with a N vacancy. The values can be above, below, or almost the same as those in GaN:Mn with no Ga vacancy. What is clear, however, is that the naive expectation that the Ga vacancy will provide extra hole carriers to mediate the Mn magnetism through the lattice is wrong.

The naive picture of Ga vacancies in GaN:Mn is that the Mn remains in a d^4 state with the Ga vacancy providing three extra holes. These holes would then delocalize and provide extra carriers for the ferromagnetic Mn d states which should improve the ferromagnetic properties of GaN:Mn. The problem with the naive picture of the Ga vacancy in GaN:Mn is that the three holes which arise from a Ga vacancy do not spread evenly over the lattice and provide extra holes for the Mn atoms but remain mostly localized on the N atoms directly neighboring the Ga vacancy. The extra holes do not contribute to the transport but remain localized within the lattice.

C. Virtual crystal comparisons

It is possible to understand this situation by using the virtual crystal approximation (VCA).[51] One can change the atomic charge and valence on specific atoms to model the effects of mixed valency or localized electron or hole states in the crystal. Here, we start with the GaN:Mn unit cell with two Mn atoms at nearest-neighbor distances and no vacancies. A fixed total concentration of extra holes, consistent with that expected from removing one Ga atom, are distributed in the unit cell at different sites (Fig. 7). The purpose of changing the valence at different sites is to find a qualitative rather than a quantitative understanding of how localization changes J.

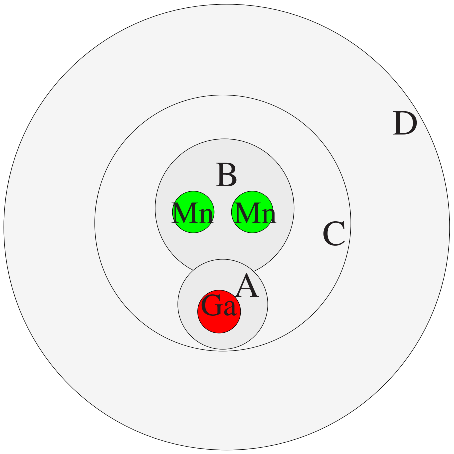

FIG. 7. (Color online) Schematic diagram for GaN:Mn with nearest neighbor Mn of regions where the holes are distributed in the virtual crystal approximation. In the first case, the Ga vacancy is simulated by adding holes to the N sites surrounding where Ga had previously been removed, indicated as region A. Region B describes the same concentration of holes distributed on the N atoms nearest to each Mn atom. Region C is an expansion of region B to include both the N and Ga atoms closest to Mn. Region D is the entire unit cell.

We will compare the results of the virtual crystal approximation with the value of J in GaN:Mn for nearest-neighbor Mn with no vacancies (Table I) for reasons which will become clear later. Region A (Fig. 7) attempts to model the results found in our electronic structure calculations for a single Ga vacancy. The extra holes were added only to the N sites surrounding the position of the Ga vacancy (the Ga atom is still here now, of course) [Fig. 4(b)]. The magnetic

TABLE I. Calculated values of J using the virtual crystal approximation. $Ga_{14}Mn_2N_{16}$ was studied with the same total extra hole concentration expected from a Ga vacancy distributed over different sites. The different configurations are described schematically in Fig. 7.

System	Radius of hole localization region (Å)	J (meV)
$Ga_{14}Mn_2N_{16}$ (no VCA)		91
A	1.97	38
B	2.38	116
C	3.08	73
D	6.23	81

exchange parameter, J (Table I), is now substantially decreased. When the extra holes are very localized around this Ga site, ferromagnetism is suppressed which could be the result of the localized state taking electrons away from Mn. Region B moves the extra holes to the N sites surrounding the two Mn atoms. Here, J has increased, so if the hole states have close contact with the Mn atoms, they can act as carriers between the Mn and enhance the ferromagnetism. This is consistent with the naive picture which has not been borne out in our calculations. Region C spreads the extra holes out further to not just the closest N atoms but also the closest Ga atoms surrounding the two Mn sites. The J is slightly smaller than when no holes are introduced, but can be interpreted as the holes are no longer close enough to the Mn sites to enhance ferromagnetism, but are not so localized to significantly reduce it either. Region D is found by spreading the extra hole states to all but the Mn atoms in the unit cell. J now approaches that found with no vacancy, so having hole states everywhere has almost no effect on the magnetism between the Mn atoms. What can be taken from these VCA calculations is that extreme localization of the holes around the Ga vacancy, as seen in our electronic structure calculations, will suppress ferromagnetism. If the holes could congregate around the Mn atoms, ferromagnetism could be increased as in the naive picture, but spreading the hole states out further neither significantly helps nor hinders ferromagnetism.

IV. SUMMARY

In conclusion, electronic structure calculations of the N and Ga vacancies in GaN:Mn show that the presence of these defects significantly reduces its ferromagnetic properties. N vacancies add three electrons which changes the Mn d^4 to d^5 and adds electron carriers which stay mostly on the Ga sites, far away in both position and energy from the Mn d states. The Mn d^4 states which interact ferromagnetically by double exchange in GaN:Mn are changed to d^5 which interact antiferromagnetically by superexchange in GaN:Mn+V_N. Ga vacancies, on the other hand, add three extra holes which one would naively provide extra carriers. However, these hole states are spin-polarized and aligned antiferromagnetically with the Mn d in a short-range interaction (1.96 Å). The holes from the Ga vacancy are localized on the four nearest-neighbor N atoms so do not act as carriers. Virtual crystal approximation (VCA) calculations show that if the holes would be somewhat less localized and remain around the Mn atoms, the ferromagnetism would be enhanced, but the hole states from the Ga vacancy localize very close to this vacancy. This reduces the exchange parameter J possibly by pulling electrons away from Mn. This work suggests that improvements in the ferromagnetic properties can be achieved by eliminating both N and Ga vacancies in GaN:Mn to produce more perfect crystals.

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