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# Interstitial-nitrogen- and oxygen-induced magnetism in Gd-doped GaN

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The observed ferromagnetism in Gd-doped GaN appears to arise from lattice defects incorporated along with Gd rather than from Gd itself. A previous model, invoking Ga vacancies as the primary defect responsible for the magnetism is here argued to be unlikely because Ga vacancies have a high energy of formation in the neutral charge state that carries magnetic moment. Interstitial nitrogen as well as oxygen in octahedral sites next to Gd are shown to be a more likely source of defect induced magnetism. They not only support magnetic moments and ferromagnetic coupling in semi-insulating conditions but are also energetically attracted toward the Gd and energetically more likely to form in the presence of Gd.

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Gadolinium-doped GaN is one of the most intriguing dilute magnetic semiconductors. After the initial findings of ferromagnetism above room temperature by Asahi *et al.*,[1,2] it was found by Dhar *et al.*[3,4] that even in concentrations as dilute as $10^{15}$ $cm^{-3}$ magnetism survived up to high temperatures, and moreover, in this dilute regime, it was claimed that the net magnetization of the sample normalized per Gd is much larger than the nominal magnetic moment ($7\mu_B$) of a $Gd^{3+}$ ion: up to $4000\mu_B$/Gd. They called this "colossal magnetic moments." This surprising finding was found to occur even stronger in samples with implanted Gd rather than Gd incorporated during growth.[5,6] Hite *et al.*[7] reported similar findings and found an increased effect with Si codoping but a quenching of the magnetism by proton irradiation,[8] which was however reversible by annealing. Others[9,10] found traces of secondary phases, none of which, however, can quite explain the ferromagnetism above room temperature. Paramagnetic/ferromagnetic resonance studies by Kammermeier *et al.*[11] found no conclusive signals that could account for the high temperature magnetism although some evidence for either Gd or GdN clusters.

While initially it was suggested[3,12] that the origin of this colossal magnetic moment arose from polarization of the surrounding host medium, later studies increasingly point to a defect origin for the magnetism in this system. The fact that implantation leads to even higher magnetization but annealing reduces it somewhat[5,6] strongly suggests that defects are responsible. X-ray magnetic circular dichroism (XMCD) studies[13,14] show that the Gd $L_3$ edge XMCD signal does not follow the hysteresis observed by superconducting quantum interference device measurements, indicating that the main origin of the magnetism does not arise from Gd itself.

Several theoretical models have been proposed to explain these observations. Dalpian and Wei[15] proposed that *sf* coupling in the tetrahedral environment leads to a conduction band spin splitting. Ionization of donor electrons, arising for example from oxygen shallow donors, known to be present in the sample in concentrations exceeding that of Gd by a factor 1000 in the most Gd-dilute samples, could then fill the spin-split-off band and thereby potentially be a source of the large magnetic moment.[16] However, our calculations[17] show that the splitting of the conduction band decreases linearly with concentration and becomes negligible in the dilute limit of $10^{15}$ Gd/$cm^3$.

Recently, Liu *et al.*[18] proposed that Ga vacancies are responsible for this magnetism. They showed that Ga vacancies give rise to 3 empty minority spin states slightly above the valence band giving rise to $3\mu_B/V_{\mathrm{Ga}}$ aligned parallel to the Gd-4*f* induced moments and promoting fairly strong ferromagnetic interactions between Gd. In contrast, the exchange interactions between Gd in otherwise pure GaN were found to be antiferromagnetic by Dalpian and Wei.[15] Their result that *n*-type doping would change this interaction into a ferromagnetic coupling, was not supported by our own calculations.[17] Although it might be viewed as consistent with the fact that oxygen and Si are both shallow donors and could be involved in the magnetism, the material in which the magnetism is found is generally semi-insulating rather than *n* type.[4] The Ga-vacancy model is consistent with our finding that *p*-type doping weakly promotes ferromagnetism.[17] It is also consistent with the results by Dev *et al.*[19] suggesting that Ga vacancies on their own without even any Gd can lead to ferromagnetism and exhibit rather strong and long-range couplings between them. The Ga-vacancy model was recently further explored by Gohda and Oshiyama[20] who showed that by adding increasingly more vacancies per Gd, magnetic moments as large as $220\mu_B$ could be obtained for 71 Ga vacancies per Gd.

None of the previous works however addressed the question of the cause of such large concentrations of vacancies. Here we first consider this question based on data available in the literature on native defects in GaN (Refs. 21–23) and show that this analysis makes the model of Ga vacancies rather implausible. We then propose two alternative defects: nitrogen and oxygen octahedral interstitials and provide evidence that they could also promote magnetism and furthermore are energetically more likely to occur.

The calculations presented here are carried out within the LSDA+U (local spin density functional with orbital-dependent Coulomb corrections) formalism[24] and using the full-potential linearized muffin-tin orbital (FP-LMTO) method.[25] Based on our extensive studies of Gd compounds,[26–29] we use both $U_f$ and $U_d$ Coulomb interactions on the Gd. Fully relaxed supercell models with 64 atoms based on the zincblende structure are used. One does not expect the magnetism observed in these systems to be specific to the wurtzite or zincblende structure.

We begin by reviewing the Ga-vacancy model. At first,

 

one might think that Ga vacancies might be introduced as a strain relief mechanism to compensate for the introduction of the large Gd atoms. A calculation of the increase in lattice constant per Gd substitution and of the decrease in lattice constant of GaN per Ga vacancy indicates that of order 20 Ga vacancies per Gd would be required to keep the lattice constant unchanged. However, there is no *a priori* reason why Gd incorporation would have to maintain the lattice strain free. In fact, there are experimental indications from x-ray diffraction that Gd implantation does increase the lattice constant.[5]

Considering the energy of formation of Ga vacancies as reported by Limpijumnong and Van de Walle[23] shows that the Ga vacancy in the neutral charge state, i.e., the charge state that carries the $3\mu_B$ per vacancy has the largest energy formation of all native defects, about 9 eV. Ga vacancies become favorable in *n*-type material but would then occur in the triple negative charge state. Even down to about midgap, corresponding to the known semi-insulating nature of the samples, the triple negative charge state is favored. This invalidates this model as the origin of magnetism because that charge state does not carry magnetic moment because the minority spin states would become filled.

The reason for magnetic moments for the neutral charge state of GaN is the presence of nitrogen dangling bonds near such defects. N-2*p* orbitals are much more localized than later row group V *p* orbitals. In fact, they are nodeless and hence resemble a 3*d* orbital in terms of their radial wave function. It is precisely this localized nature of the *p* orbitals of first row elements that could give rise to magnetism because magnetic moments arise from intra-atomic Coulomb interactions. By keeping the spins parallel, one reduces the net Coulomb repulsion because of the exchange effect. This gives clues of possible alternatives which could promote magnetism: we should look for defects that involve N nonbonded orbitals. Clearly, N vacancies or Ga interstitials or antisites do not satisfy this requirement while N interstitials do.

Based on Limpijumnong and Van de Walle's[23] results, for midgap Fermi levels, the two defects with lowest energy for formation are the nitrogen vacancy and the nitrogen interstitial in a neutral charge state. We thus investigate whether the latter supports a magnetic moment. The lowest energy for interstitial nitrogen in wurtzite GaN is a split-interstitial configuration.[23] However, even in the split interstitial, the N atoms form only weak bonds with each other. For simplicity, we here consider instead the octahedral interstitial site in zincblende GaN. Furthermore, we consider primarily the interstitial adjacent to a Gd atom. The additional idea introduced here is that because Gd prefers octahedral bonding, interstitials such as N and O may be attracted toward Gd.

Figure 1 shows the partial and total density of states for a N and O octahedral interstitial placed as nearest neighbor to a Gd atom in a 64 atom GaN supercell containing one $Gd_{Ga}$ substitution. We can see that, similar to the Ga vacancy, a spin splitting occurs for the defect states. The majority spin states (spin down) are filled and occur below midgap whereas the minority states (spin up) occur closer to the conduction band or even above it. The total density of states helps us locate the valence band maximum (VBM). We can

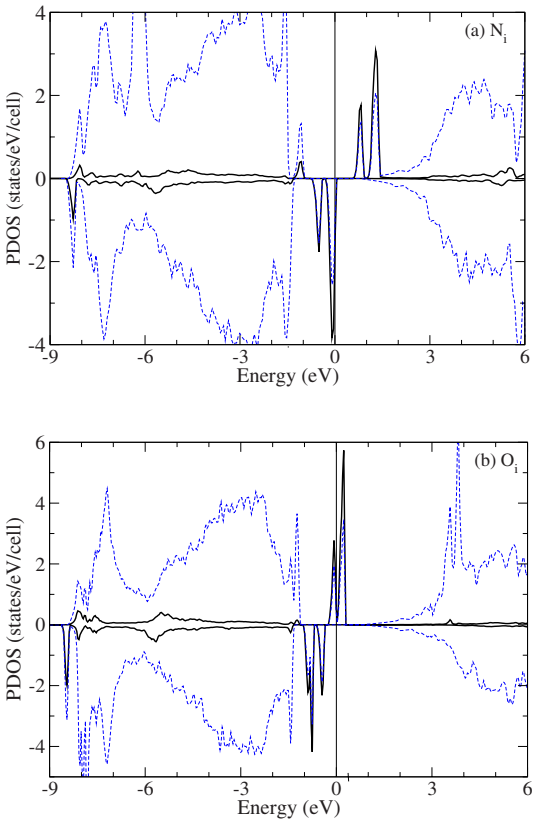


FIG. 1. (Color online) Partial and total densities of states of (a) octahedral interstitial N and (b) octahedral interstitial O, each placed next to a Gd in Gd-doped GaN [$GdGa_{31}N_{32}$:(N/O) cell]. Dashed (blue) line: total DOS (scaled), thick solid (black): PDOS on interstitial site. The zero of energy is the Fermi energy of the supercell.

see evidence of a state weakly localized on the $N_i$ just above the VBM, indicating some bonding to the Gd. The large spin splitting and energy position in the gap results from the nonbonding character of these states, derived primarily from the N or O-2*p* orbitals. The spin splitting leads to a net magnetic moment of $3\mu_B$ for the N case and $2\mu_N$ for the oxygen case for the neutral charge state. One can clearly see that one of the minority spin states takes the one extra electron in the O case and hence leads to one less $\mu_B$. This establishes the formation of additional magnetic moment by such interstitials, which is the first condition for them to play a role in the magnetism. Second we find that this magnetic moment is parallel to that of the Gd-4*f* states. This is slightly surprising because in GdN, the induced magnetic moments on N are actually antiparallel to Gd and much smaller.[27] In fact, this indicates that at least with only one interstitial N or O nearby, the Gd does not give up its tetrahedral bonding with the other N and the additional interstitial nitrogen basically has nonbonding *p* orbitals. This then is consistent with the high magnetic moment of the $N_i$.

Next, we examine whether these interstitials will promote ferromagnetic coupling between Gd. To this end, we perform calculations for a 64 atom cell with two $Gd_{Ga}$ atoms placed, as either first, second, third or fourth nearest neighbors from each other and with a N or O interstitial as nearest neighbor to one of the Gd atoms. Figure 2 shows that the antiferro-

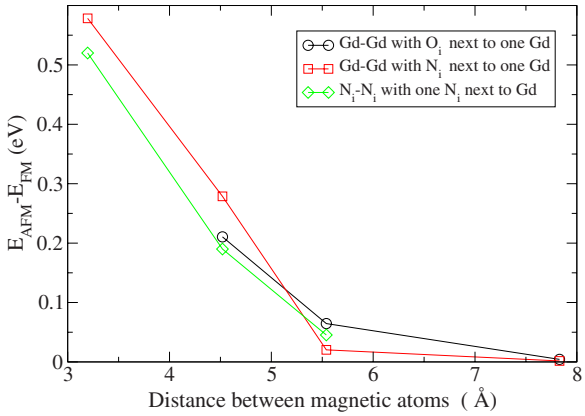


FIG. 2. (Color online) Energy difference between antiferromagnetic or ferromagnetic coupling for magnetic atom pairs in Gd-doped GaN as function of the distance between the magnetic atoms.

magnetic configuration of the Gd spins in each of those cases has higher energy than the ferromagnetic configuration. The exchange interaction $J_i$ is the corresponding energy difference divided by two and is quite large for first and second nearest Gd neighbors. This is qualitatively consistent with a high Curie temperature. Next, we consider the coupling between N interstitials. Two N interstitials are placed in the cell, one of them next to the single Gd in the cell and the other one farther away at three possible distances. We show these results in the same Fig. 2. We find comparably strong ferromagnetic coupling between $N_i$ and Gd. This indicates, similar to the Ga-vacancy case, that the defect states, while obtaining their magnetism from the localized nature of the N $p$ or O $p$ nonbonding states on the central atom, have a sufficiently long-range tail to interact ferromagnetically with other N or O interstitials further away from the Gd. The range of these interactions is comparable to that between Ga vacancies.

Thus far, we have shown that magnetism is promoted by N or O octahedral interstitials next to the Gd. We now address the question why N or O is expected to migrate close to the Gd. To this end we first compare the energy of formation of a $Gd_{Ga}$-$N_i$ pair with that of a separated $Gd_{Ga}$ and $N_i$ defect, each of the latter being calculated in isolation without the other defect present. We find that the $N_i$ is attracted toward the $Gd_{Ga}$ by a binding energy of 1.4 eV, thus providing a strong driving force for interstitial N, once it has been formed, to move toward Gd. We have also performed calculations with a cell containing both a remote N vacancy and a N interstitial adjacent to Gd and found that the N vacancy had negligible effect on the electronic structure of the $Gd_{Ga}$-$N_i$ pair and magnetic coupling between Gd was equally favored. Since the formation of Frenkel pairs ($V_N$, $N_i$ pairs) is likely to occur, in particular under Gd implantation conditions, it seems likely that some $N_i$ are present in the system. In fact, Dhar *et al.*[5] reported that interstitials and vacancies are expected to be dominant in different implantation zones with, in particular, N interstitials accumulating in the deepest zone.

For oxygen, we can make an even stronger statement by considering the reaction between a remote oxygen substitutional defect $O_N$, with a $Gd_{Ga}$ defect to form a $Gd_{Ga}$-$O_i$ pair,

$$N + \frac{1}{2}GaN{:}Gd_{Ga} + \frac{1}{2}GaN{:}O_N \rightarrow GaN{:}Gd_{Ga} - O_i. \quad (1)$$

Here, we assume that the nitrogen vacancy left behind by the oxygen leaving its substitutional site, known to be the favored site in otherwise pure GaN, is filled by a N from the gas reservoir. The energy for this reaction is $\Delta H = -1.75\ \text{eV} - \mu_N$, with $\mu_N$ the chemical potential of nitrogen. For molecular $N_2$ gas, the chemical potential is about $-4.94$ eV,[30] leading to an unfavorable positive value. However, under growth conditions with a plasma source we may assume $\mu_N$ to approach the atomic value $\mu_N = 0$ leading to a favorable negative value. While the results do not support formation of a strong octahedral bond, it does support the idea of a migration of O impurities toward Gd in a growth environment with high chemical potential of N. This is also consistent with the well-known chemical affinity of Gd for oxygen. The high levels of O incorporation in Gd-doped samples by themselves give evidence for this affinity.

In conclusion, we have shown that both N and O octahedral interstitials are more plausible candidates for defect induced magnetism in Gd-doped GaN than Ga vacancies. Like Ga vacancies, they form defects states in the gap, which support a magnetic moment of $2-3\mu_B$, and have sufficiently extended tails to experience relatively long-range ferromagnetic coupling among each other and with Gd. Unlike Ga vacancies, however, they can support a neutral charge and magnetic state for midgap Fermi levels consistent with semi-insulating conditions because their defect levels occur at higher energies in the gap. They also have significantly lower energy of formation. $N_i$ is likely to occur as the result of formation of Frenkel pairs in nonequilibrium growth or implantation conditions. We showed furthermore that it is favorable for $N_i$ to migrate toward Gd. For O, which is also known to be amply present in the samples, we showed that even substitutional O can lower its energy by migrating to an octahedral interstitial site next to Gd as long as the N chemical potential is high enough as expected in a GaN growth environment. While these defects do add additional magnetic moment beyond the nominal $Gd^{3+}$ one, it is unlikely that they can explain truly colossal moments in the ultradilute limit. This would require a large number of such defects to form per Gd. It does however support the possibility of ferromagnetism at modest concentrations of Gd and interstitials.

In future work, it would be of interest to examine if more than one interstitial N or O can move close to Gd and whether this would further strengthen the effect. For a quantitative study of this defect induced magnetism, it will be necessary to further map out the distance dependence of the exchange interactions between these interstitials and between them and Gd. Extending the study to wurtzite lattices would also be of obvious interest.

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