Defect-Induced Intrinsic Magnetism in Wide-Gap III Nitrides

Pratibha Dev, Yu Xue, and Peihong Zhang

Department of Physics, University at Buffalo, State University of New York, Buffalo, New York 14260, USA

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Cation-vacancy induced intrinsic magnetism in GaN and BN is investigated by employing density-functional theory based electronic structure methods. The strong localization of defect states favors spontaneous spin polarization and local moment formation. A neutral cation vacancy in GaN or BN leads to the formation of a net moment of $3\mu_B$ with a spin-polarization energy of about 0.5 eV at the low density limit. The extended tails of defect wave functions, on the other hand, mediate surprisingly long-range magnetic interactions between the defect-induced moments. This duality of defect states suggests the existence of defect-induced or mediated collective magnetism in these otherwise nonmagnetic sp systems.

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The search for room temperature dilute magnetic semiconductors (DMS) [1] has inspired a new wave of inquiry into one of the most fundamental problems of solid state physics: local moment formation and collective magnetism. Traditionally, local magnetic moment formation in solids has been associated with elements containing partially filled $3d$ or $4f$ subshells. The strongly localized nature of the $3d$ and $4f$ states, coupled with their high degree of degeneracy, favors spin-polarized electron configurations and leads to the formation of local moments. Collective magnetism is then a result of the coupling between these local moments.

However, there are no fundamental reasons against the possibility of local moment formation from localized sp states. In fact, there has been increasing evidence that localized defect states (or surface or edge states) in sp materials may form local moments and exhibit collective magnetism. Ferromagnetism in various carbon structures, mostly highly defective, has been observed [2–8] and investigated theoretically [9–14]. In addition, weak ferromagnetism in many supposedly nonmagnetic oxides has been reported [15–21]. In this Letter, we show that not only can cation vacancies in wide-gap nitrides (GaN and BN) promote the formation of local magnetic moments but also the magnetic coupling between these intrinsic defects induced moments is surprisingly long-ranged. This intrinsic defect derived and mediated long-range magnetic interaction opens a new route toward designing high T_c DMS through defect manipulation [22–25].

Our calculations are based on density-functional theory (DFT) within the local (spin) density approximation [L(S)DA] using the PARATEC code [26]. *Ab initio* norm-conserving pseudopotentials [27] are used. The plane-wave energy cutoff is set at 80 Ry to ensure the convergence of the calculations. We present only the results for the zinc blende structure. The subtle difference between the zinc blende and wurtzite phases of GaN does not affect our main conclusion here.

Localization of defect states and moment formation.— The top valence states of BN or GaN are derived from the fairly localized nitrogen p states. Acceptor (e.g., cation vacancy) states in GaN (or BN) are substantially more localized than those in GaAs. This localization of defect states may favor spontaneous spin polarization and the formation of local magnetic moments [28]. In the cubic crystal field (T_d symmetry), defect states associated with an isolated neutral Ga (or B) vacancy are split into an a_1 singlet and a t_2 triplet. The a_1 state is fully occupied; the remaining three electrons occupy the t_2 triplet. This partial filling of the triplet may lead to a net local moment M of $3\mu_B$ if the spin splitting is greater than the broadening of the defect levels.

Indeed, our DFT-based first-principles calculations for a neutral cation vacancy in both 64-atom and 216-atom cubic supercells confirm that spontaneous spin polarization develops with a $3.0\mu_B$ local moment for both GaN and BN systems (Table I). All structures studied are relaxed within the L(S)DA while keeping the lattice parameters fixed at their experimental bulk values. After the relaxation, the residual forces on atoms are smaller than 5×10^{-4} Ry/a.u. Nitrogen atoms surrounding the neutral Ga vacancy move outward by about 0.24 Å whereas the length of the first-shell N-Ga bonds shrinks from 1.95 to 1.90 Å. These results are in good agreement with those reported previously [29,30].

The calculated relaxation energies (ΔE^{relax}) are about 0.8 and 0.7 eV for a neutral cation vacancy in BN and GaN, respectively. The spin-polarization energies E^{pol} (energy difference between the spin-polarized and spin-

TABLE I. Magnetic and electronic properties of a neutral cation vacancy in GaN and BN.

System	Local moment (μ_B)	ΔE^{pol} (eV)	$\Delta\epsilon_\Gamma$ (eV)	ΔE^{relax} (eV)
$B_{31}(V_B)N_{32}$	3.0	0.21	0.74	0.80
$B_{107}(V_B)N_{108}$	3.0	0.54	0.72	0.80
$Ga_{31}(V_{Ga})N_{32}$	3.0	0.35	0.66	0.69
$Ga_{107}(V_{Ga})N_{108}$	3.0	0.53	0.61	0.70

unploarized states) listed in Table I suggest that the spin-polarized state should be stable well above room temperature. The splitting between the majority- and minority-spin t_2 states at the zone center [$\Delta\epsilon_\Gamma = \epsilon(t_2^\uparrow) - \epsilon(t_2^\downarrow)$] is also substantial, ranging from 0.61 eV for $Ga_{107}(V_{Ga})N_{108}$ to 0.72 eV for $B_{107}(V_B)N_{108}$.

Figure 1 shows the spin-resolved density of states (DOS) of a 64-atom GaN supercell containing a Ga vacancy [$Ga_{31}(V_{Ga})N_{32}$]. The strong spin polarization results in a complete separation of the majority- and minority-spin t_2 triplet and the formation of a local moment of $3.0\mu_B$. The localization of the defect states in these systems can also be visualized by plotting the defect states charge density in the real space. Figure 2 shows an isosurface ($\rho^0 = 8.5 \times 10^{-3}\ e/\text{a.u.}^3$ or $5.7 \times 10^{22}\ e/\text{cm}^3$) plot of the charge density of the majority-spin t_2 states in $Ga_{31}(V_{Ga})N_{32}$. It is evident that these defect states are strongly localized near the four nitrogen atoms surrounding the Ga vacancy (located at the center of the cell); about 60% of the defect-state (majority-spin t_2 triplet) charge is contained within the isosurface. It is this strong localization of defect wave functions that leads to a spin-polarized ground state and the formation of local moments in these systems.

Existence of local magnetic moments does not necessarily result in collective magnetism. For defect states to play a significant role, they must also display long-range magnetic interactions. Therefore, two important questions remain to be answered: (1) Do these defect-induced moments couple ferromagnetically (FM) or antiferromagnetically (AFM)? (2) Is this coupling long- or short-ranged? A long-range magnetic coupling is critical for achieving high temperature magnetism at low defect concentrations. If the coupling is short-ranged, then an impractically high defect concentration may be required to promote collective magnetism [23].

Extended tails of defect wave functions and long-range magnetic interaction.—Compared to the strongly localized $3d$ or $4f$ electrons of magnetic ions, defect states are far more extended even in wide-gap semiconductors such as GaN and BN. This *duality* (localization versus extension) of the defect wave functions opens up the possibility of defect-induced long-range magnetic couplings in these systems. When magnetic ions are introduced into the system, these defect states might also play an important role in mediating their interactions [25,31–34].

To illustrate this extended nature of defect wave functions, we plot in Fig. 3 the charge density isosurface ($\rho^0 = 7.8 \times 10^{-4}\ e/\text{a.u.}^3$ or $5.0 \times 10^{21}\ e/\text{cm}^3$) of defect states associated with a Ga vacancy in a 216-atom supercell [$Ga_{107}(V_{Ga})N_{108}$]. The isosurface contains about 85% of the charge of the majority-spin t_2 triplet. This plot clearly shows both the localized nature and the extended tail of the defect wave functions; the tails of the defect wave function extend well beyond the size of the 216-atom supercell ($a = 25.6$ a.u.). Therefore, we expect that defect wave functions overlap substantially at and beyond this separation. It is this slowly decaying tail of the defect wave functions that mediates the long-range magnetic coupling between defect-induced local moments as discussed below.

In order to study the magnetic coupling between these vacancy-induced local moments, we double the size of the supercells by placing two 64-atom or 216-atom cells side by side. Each supercell [$X_{62}(V_X)_2N_{64}$ or $X_{214}(V_X)_2N_{216}$; X = Ga, B] now contains two cation vacancies. Depending on the initial conditions of the self-consistent calculations, two stable magnetic structures are obtained: one is ferromagnetic, the other antiferromagnetic. (Note that this AFM structure shall not be considered as a realistic AFM ordering. This structure is studied only for obtaining the magnetic interaction.) The magnetic interaction can be conveniently studied by mapping the total energies of the systems with different magnetic (FM or AFM) orderings to a Heisenberg model: $H = -\sum_{\langle ij\rangle} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$. Within the nearest-neighbor Heisenberg model, the energy difference between the FM and AFM phases is $\Delta E^{\mathbf{M}} = E^{\text{AFM}} - E^{\text{FM}} = 4J_0(\mathbf{R})S^2$, where S is the net spin of the defect states and $J_0(\mathbf{R})$ is the nearest-neighbor

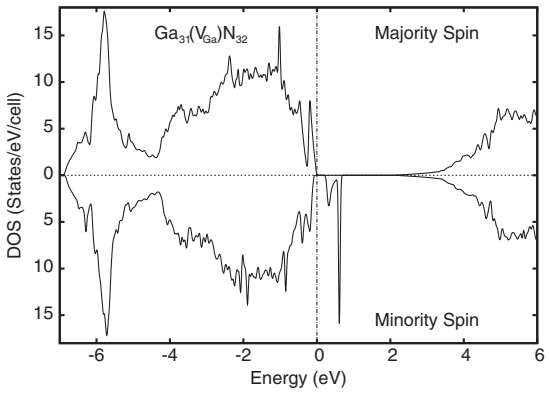

FIG. 1. Spin-resolved density of states of a Ga vacancy in a 64-atom GaN supercell. The strong spin polarization results in a complete separation between the majority- and minority-spin t_2 states. The nitrogen $2s$ states are not shown.

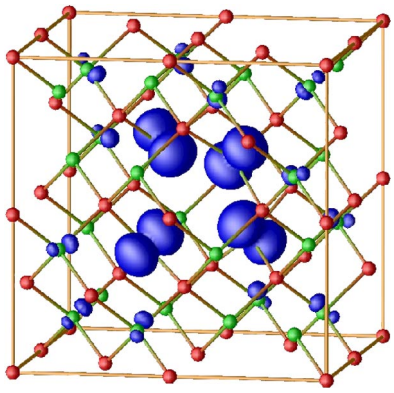

FIG. 2 (color online). Isosurface charge density plot ($\rho^0 = 8.5 \times 10^{-3}\ e/\text{a.u.}^3$) of the majority-spin t_2 states associated with a neutral Ga vacancy in a 64-atom GaN supercell, showing the localized nature of defect states. About 60% of the t_2 state charge is contained within the isosurface.

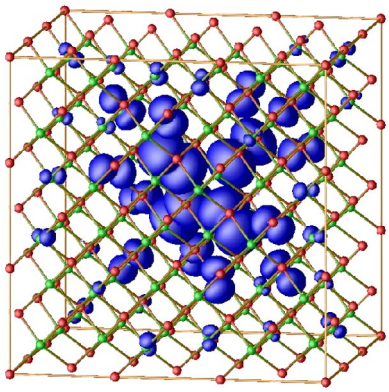

FIG. 3 (color online). Isosurface charge density plot ($\rho^0 = 7.8 \times 10^{-4}\ e/\text{a.u.}^3$) of the majority-spin t_2 states associated with a neutral Ga vacancy in a 216-atom GaN supercell, showing both the localized nature and the extended tails of the defect wave functions.

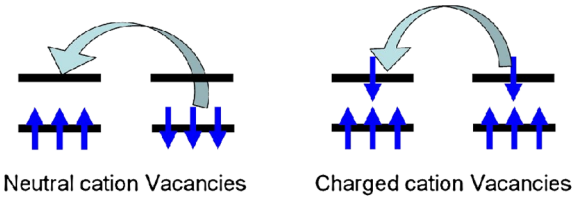

FIG. 4 (color online). Schematic of the exchange mechanism. For neutral cation vacancies, virtual hopping results in an AFM ground state; the same mechanism leads to a FM coupling between charged vacancies.

exchange coupling. Comparing this expression with the calculated energy difference between the FM and AFM phases, we obtain the nearest-neighbor magnetic coupling J_0 as a function of defect separation $\mathbf{R}$ (Table II). Since cation vacancies in these systems are likely to be (partially) compensated and become charged defects [35], our study also includes (negatively) charged defects. Interestingly, partial compensation of the cation-vacancy acceptors is actually favorable for promoting a long-range ferromagnetic coupling as shown in Table II.

Not surprisingly, neutral vacancies couple antiferromagnetically (see Table II). This is because the defect state (t_2 triplet) of a neutral cation vacancy is exactly half filled, virtual hopping is allowed in the AFM arrangement but not allowed in the FM configuration (shown in Fig. 4), resulting in a lower energy AFM state. The situation is quite the opposite for negatively charged cation vacancies. We obtain FM coupling for both (-1) and (-2) charge states (Table II). With extra electrons occupying the acceptor levels, virtual hopping is now allowed for FM arrangements (Fig. 4). These results can also be explained within the molecular orbital theory [36].

Our results also indicate that the coupling between these cation-vacancy induced local moments is fairly long-ranged. With a defect separation $\mathbf{R} = 17.1$ a.u., the calculated ferromagnetic exchange parameters for V_{Ga}^{-1} and V_{Ga}^{-2} are 30.5 and 27.1 meV, respectively. Even at $\mathbf{R} = 25.6$ a.u. (corresponding to a defect concentration of 0.9%), we still obtain a sizable ferromagnetic coupling for negatively charged vacancies. This is in contrast with previous results for Ca vacancy in CaO [23]; the exchange coupling between two Ca vacancies vanishes if the separation between defects is greater than $1.75d_0 = 15.9$ a.u., where d_0 is the lattice constant of CaO.

It is now known that the LSDA turns to delocalize the wave functions. The generalized gradient approximation (GGA) [37], on the other hand, has been shown to improve the quality of the calculated wave functions [38]. Therefore, it would be interesting to compare the LSDA results with the GGA ones. We also carry out calculations for the $\text{Ga}_{62}(\text{V}_{\text{Ga}})_2\text{N}_{64}$ system within the GGA using the Perdew-Burke-Ernzerhof functional [39]. We find that the GGA results agree qualitatively with the LSDA ones. The magnetic coupling J between negatively charged Ga vacancies changes from 30.5 meV within the LSDA to 32.8 meV within the GGA. The antiferromagnetic exchange J between neutral Ga vacancies is -3.0 meV within the GGA, to be compared with -5.8 meV within the LSDA. Although we believe that the LDA or GGA describes qualitatively well the electronic structure of these sp materials, higher-level calculations beyond the LDA or GGA and experimental verification are much needed.

The sensitivity of the exchange coupling to the charge state of defects suggests an experimentally viable way for controlling magnetism in these systems. For example, electrons may be introduced by charge injection or (optical or thermal) ionization of the trapped holes. If the acceptor

TABLE II. Magnetic coupling between cation-induced local moments in GaN and BN. The coupling is antiferromagnetic between two neutral vacancies. Upon charging the defect with electrons, the coupling becomes ferromagnetic.

	$X_{62}(\text{V}_X)_2\text{N}_{64}$				$X_{214}(\text{V}_X)\text{N}_{216}$			
	$X = \text{Ga}$		$X = \text{B}$		$X = \text{Ga}$		$X = \text{B}$	
Charge state	ΔE^M (meV)	J_0	ΔE^M (meV)	J_0	ΔE^M (meV)	J_0	ΔE^M (meV)	J_0
0	−52.6	−5.8	−164.6	−18.3	−2.7	−0.30	−3.8	−0.42
−1	122.2	30.5	155.0	38.8	13.0	3.3	19.9	5.0
−2	27.1	27.1	38.2	38.2	6.9	6.9	10.0	10.0
R (a.u.)	17.1		13.6		25.6		20.3	

states are fully compensated, local moments disappear. In this case, the extended tails of defect states may still play an important role in mediating the interaction between magnetic impurities in DMS.

So far we have only discussed the magnetic properties of one type of intrinsic point defects (cation vacancy). Localized defect states arising from nonmagnetic impurities and defect complexes (e.g., V_{Ga}-O_N) may also lead to formation of local moments and exhibit collective magnetism. Ferromagnetism in carbon-doped ZnO has been reported recently [21]. In addition, the observed [40,41] colossal magnetic moment ($\sim 4000 \mu_B$/Gd) and the surprisingly high Curie temperature (up to 800 K) in Gd doped GaN may also be explained by moment formation arising from defects. It is plausible that in the process of introducing Gd into GaN massive amounts of defects are created. The defect density may be significantly higher than the Gd concentration and some of the defects may carry local moments. It would be very interesting to investigate the magnetic coupling between the defect-induced moments and those of extrinsic magnetic impurities in these systems.

In summary, we have investigated local moment formation arising from cation vacancies in GaN and BN using DFT-based first-principles electronic structure methods. The strongly localized nature of the acceptor wave functions favors a spin-polarized ground state and the formation of local moments. The extended tails of defect wave function, on the other hand, promote long-range magnetic coupling between these defect-induced moments. The magnetic coupling is studied by mapping the calculated total energy with a nearest-neighbor Heisenberg model. The coupling is antiferromagnetic between neutral cation vacancies but becomes ferromagnetic upon charging the defect states with electrons. This sensitivity of the magnetic coupling to the defect charge state raises interesting possibilities of controlling the magnetism in these systems by charge injection or ionization of trapped holes.

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