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Magnetic properties of gadolinium and carbon co-doped gallium nitride

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ABSTRACT

Investigations have been carried out to study the ferromagnetic properties of Gadolinium (Gd) Carbon (C) co-doped wurtzite Gallium Nitride (GaN) using full-potential linear augmented plane wave (FP-LAPW) method within the density functional theory. The system shows half-metallic nature when single Gd is substituted in $Ga_{36}N_{36}$ supercell. The presence of carbon in GaN supercell is found to generate weak magnetic moment (M_s) in the neighbouring atoms. When Carbon is codoped in the Gd-GaN, it increased the total magnetic moment of the system (M_{tot}). The cause of ferromagnetism in the Gd and C co-doped GaN has been explained by Zener's *p-d* exchange mechanism. The role of defects in the magnetic property of this system is also investigated. The results indicate the gallium vacancy influences the magnetic moment of the Gd and C codoped GaN more than the nitrogen vacancy. The presence of holes is effective than electrons in achieving the ferromagnetism in the considered system.

1. Introduction

Spintronics, which utilizes the spin of an electron along with that of a charge has lead to the development of new age electronics devices and is extensively researched [1–7]. The principle target for the realization of spintronics is to add magnetic functionality to non-magnetic semiconductors i.e. Dilute magnetic semiconductors (DMS). GaN is one of the promising semiconductors researched for this purpose. The pursuit of developing room temperature DMS has led to study of doping additional elements with transition material in GaN. Wang *et al.* [8] reported the carbon co-doping in the GaMnN has increased the ferromagnetism in the system. In this, Mn, C co-doped GaN, the carbon in GaN matrix favour the nitrogen sites over the Gallium sites and Mn, C co-doping in GaN matrix is reported to be energetically more favourable. The preference for the ferromagnetic coupling over the anti-ferromagnetic coupling between the two doped Mn sites is enhanced by carbon co-doping. Munawar Basha *et al.* [9] observed that on adding small amount of carbon with cobalt to the GaN system there is considerable change in their magnetic moment and electronic behavior. Dhar *et al.* [10] observed large magnetic moment in Gadolinium (Gd) doped Gallium Nitride (GaN) and the material found to exhibit ferromagnetism above room temperature even with a Gd concentration less that 10^{16} cm^{-3}. Hence, to generate spin-polarised electrons(holes) in the conduction band (valence band) GaN:Gd may be easily doped with donors (acceptors) with a concentration exceeding that of Gd. Gustavo *et al.* [11] found that $Ga_{1-x}Gd_xN$ system exhibits some unique behavior that is drastically different from TM-doped GaN. By means of theoretical techniques, Simone *et al.* [12] investigated the behavior of rare earth (RE) dopant in GaN. Ga site is preferred over N-site by lanthanide ions. The RE_{Ga} V_N (Nitrogen vacancy) pairs are the most promising candidates as luminescent centers. The influence of defects in observing magnetism in Gd-GaN have been highlighted in the experimental studies [13,14]. In a computational study, Tawinan *et al.* [15] showed that the under equilibrium conditions, for the Gd doped GaN it is unlikely for the Gd atom to be on Nitrogen site since the energy of formation for Gd on anti-sites is extremely high. Rather than isolated substitutional Gd, Ga vacancies is expected to have long range coupling. Gohda and Oshiyama [16] observed energetically stable ferromagnetic configuration among spins of Ga vacancies (V_{Ga}) and Gd atom. When Ga vacancies are increased the magnetic moment increases monotonically. Lei Liu *et al.* [17] performed the first principle calculations of the electronic structure and magnetic interaction of GaN: Gd. It is predicted that holes are more effective than electrons in contributing to the observed colossal magnetic moment of Gd ions. At most magnetic moment of 7 μ_B is supplied from the 4*f* electrons of Gd atom replacing a Ga atom in GaN: Gd. Dev *et al.* [18] investigated cation vacancy induced intrinsic magnetism in GaN and BN, and found that strong localization of defect states favours

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spontaneous spin polarization and local moment formation. Dev and Zhang [19] observed ferromagnetic coupling between magnetic moments for cation vacancies in ZnO. Potassium substituted GaN, is one such a case. Both non-magnetic and magnetic impurities may contribute to observed magnetism for oxide and nitride based DMS. Lin Yu *et al.* [20] observed that with high carbon concentration weak ferromagnetism is observed in Carbon doped GaN. Martin Roever *et al.* [21] observed co-doping Oxygen along with Gd in GaN promotes ferromagnetism. In our literature survey, we have found no report on the theoretical calculations on the Gadolinium and Carbon co-doped GaN. In this paper, the possible magnetism in Gd and C co-doped GaN system has been investigated. The role of defects in the Gd, C – GaN system in achieving magnetism is also studied.

2. Computational details

In the present work, full-potential linear augmented plane wave (FP-LAPW) method as implemented in the WIEN2k code has been used [22]. It is based on the density functional theory for the exchange correlation potential. To calculate the exchange correlation potential LDA+U has been employed. There is a failure on the part of conventional DFT to describe the system with strongly correlated *d* and *f* electrons. The use of GGA/LDA for the estimation of exchange-correlation potential will underestimate the bandgap values. The effective on-site coulomb parameters, U and J, affect the placement of d and f electron states significantly. They are often adjusted to reach with experimental value in some sense. Here we use DFT+U method for the correction of U and J, and employed Hubbard potential U =6 eV an J =0 eV for 4*f* electrons of Gd as already reported by Sabirianov *et al.* [23] and Harmon *et al.* [24]. We have constructed the hexagonal unit cell of GaN bulk, and then we built 3×3×2 supercells with Ga/N atoms substituted appropriately with Gd/C according to the requirement of the doping.

GaN crystallizes in wurtzite structure in the space group *P*63*mc* (space group no:186). The lattice parameter of GaN are a =3.186 Å and c =5.186 Å [25].

In this, the internal parameter z determines the position of the atom along c-axis in the hexagonal structure and will vary for different compounds. The calculated z value is 0.376 and it is used as initial structural parameter.

3. Results and discussion

In the GaN, the valence band maximum is composed primarily from the N *p* orbital with the Ga orbitals taking part to a lesser extent. Very minor contributions are made by the d orbitals to the top of the valence band as most of them are deep inside. In the band dispersion curve, the band gap of GaN is found to be direct between Γ–Γ directions with the value of 1.92 eV. Earlier report of Wang *et al.* [26] show the band gap of GaN to be 1.58 eV with GGA while thee experimental band gap of GaN is 3.4 eV [27].

The schematic representation of unit cell for Wurtzite GaN used in our calculation is shown in Fig. 1. Ga and N are represented by violet and light blue balls. Gd, C, V_{Ga} (Ga vacancy), and V_N (N vacancy) are represented by grey, yellow, light green and dark blue balls respectively.

According to the requirement of the doping, Ga positions are replaced with Gd atoms, N positions are replaced with C atoms, and Ga or N vacancies are introduced. One atom of Ga is replaced by one atom of Gd to obtain dopant concentration of 2.7% ($Gd_{01}Ga_{35}N_{36}$) as shown in Fig. 1(a). The spin magnetic moment (M_s) of Gadolinium is found to be 6.71 μ_B. Band gap for spin up state is 1.66 eV and spin down is 1.7 eV.

The partial density of states (PDOS) of Gd 4*f* orbitals without 'U' (Hubbard potential) and with U is as shown in Fig. 2(a) and (b). When the calculations are performed without 'U', the Gd 4*f* levels are found to occupy the top of the valence band very close to Fermi level as shown in figure. With the inclusion of 'U' the Gd 4*f* levels are found to be lying in the region −3 to −4.2 eV. Previous studies by Alexander et al. indicated that 4*f* levels of Gd lie at about 4 eV relative to fermi level [28]. So the possible interaction of Gd 4*f* with N 2*p* which is in the top of the valence band, has been ruled out.

The density of states for 2.7% Gd doped GaN ($Gd_{01}Ga_{35}N_{36}$) is shown in Fig. 3(a).

Two Gallium atoms have been replaced with two gadolinium atoms to obtain 5.5% atomic doping concentration as shown in Fig. 1(b). The band gap for the system $Gd_{02}Ga_{34}N_{36}$ for spin up and spin down is found to be 1.72 eV and 1.73 eV respectively. The M_s of two Gadoliniums is found to be around 6.7 μ_B respectively.

The PDOS Ga 4*p*+5*d*, N 2*p*, and Gd 5*d* is shown in Fig. 3(b), (c), & (d) respectively. From the Fig. 3, it can be seen that 5*d* orbital of Gd appears at the highest occupied level. In the case of Fig. 3(a), for spin up states, there is no impurity orbital level above the Fermi level. For spin down state, there is an impurity orbital level, which arises due to the Gd dopant at Fermi level. Hence the system is ferromagnetic with half metallic character. From the Fig. 3, it can be seen that Gd 5*d* overlaps with N 2*p* orbitals. The 5d electron of Gd couples with 2*p* electron of nearest neighbouring nitrogen atom to form tetrahedral bonding. The magnetic moment of the Gd-GaN is due to the *p-d* exchange interactions.

The system $C_{01}Ga_{36}N_{35}$ of single Carbon doped in GaN supercell is as shown in the Fig. 1(k). The total DOS and PDOS for the system $C_{01}Ga_{36}N_{35}$ is shown in Fig. 3(e), (f), (g). When the Carbon atom is introduced in GaN supercell, M_s is generated in the equidistant nearest neighbouring Ga atoms. M_s for the three nearest neighbouring Ga atoms at the distance 1.976 Å from C atom is 0.015 μ_B. M_s of the C is 0.18 μ_B and M_{tot} is 0.92 μ_B. For both the spin up and down state the impurity orbital level is above the Fermi level. The system seems to exhibit the metallic character, since the introduction of carbon in the GaN creates the acceptor impurity level above the valance band. Weak magnetic moment is observed as there is possibility of *p-d* exchange interaction due to hybridization between Ga *p-d* and C *p* orbitals.

One atom of Ga is replaced with one atom of Gd and one atom of Nitrogen is replaced with one atom of C to get 2.7% Gd – 2.7% C co-doped GaN ($Gd_{01}C_{01}Ga_{35}N_{35}$). In the addition of carbon in Gd-GaN system two positions for carbon is considered – i) carbon is bonded with Gd (Fig. 1(c)) and ii) carbon is far away from Gd (Fig. 1(d)). The Carbon atom is shown as yellow ball.

In the latter case, for Gd bonded away from C in a GaN supercell, M_{tot} is 7.69 μ_B/Cell. M_s of Gd is found to be 6.65 μ_B and that of the carbon is found to be 0.14 μ_B. The impurity level for both the spin up and down state is above the Fermi level and hence the system $Gd_{01}C_{01}Ga_{35}N_{35}$ (Gd bonded away from C) is metallic in nature. In the first case, for Gd bonded to C in the $Gd_{01}C_{01}Ga_{35}N_{35}$ system, M_s of Gd is found to be 6.82 μ_B and that of C is found to be 0.38 μ_B. M_{tot} is 8 μ_B/cell. It can be seen that the M_{tot} also increases from 7.69 μ_B/cell to 8 μ_B/cell, M_s of the Gd atom increases from 6.65 μ_B to 6.8 μ_B, and M_s of C increases from 0.13 μ_B to 0.38 μ_B. Total DOS, PDOS of C 2*p*, Gd 5*d*, nearest neighbour of C atom i.e., Ga 4*p*+3*d*, and the second nearest neighbour N 2*p* of $Gd_{01}C_{01}Ga_{35}N_{35}$ is shown in Fig. 4(a),(b),(c),(d) & (e). For this system (Gd bonded to C in GaN supercell), the energy range exists between −1 and 0 eV below the Fermi level. In the case of the system in which Gd is bonded to C, the increase in the magnetic moment can be explained by Zener's *p-d* exchange mechanism [29,30]. Zener *p-d* exchange mechanism dominates if the '*d*' states of the impurity are localized as in the case of (Ga, Mn) Sb [29]. The majority '*d*' states are localized. With the introduction of C near Gd atom, in the ferromagnetic state, hybridization takes place between the Gd '*d*' levels and C '*p*' states. C-state hybridized Gd 5*d* shells are stronger than Ga- and N- states. Such interaction is not possible in the case where C is bonded away from Gd. Also as a result, impurity levels appear in the spin up state as shown in Fig. 4. For both spin up and spin down state,

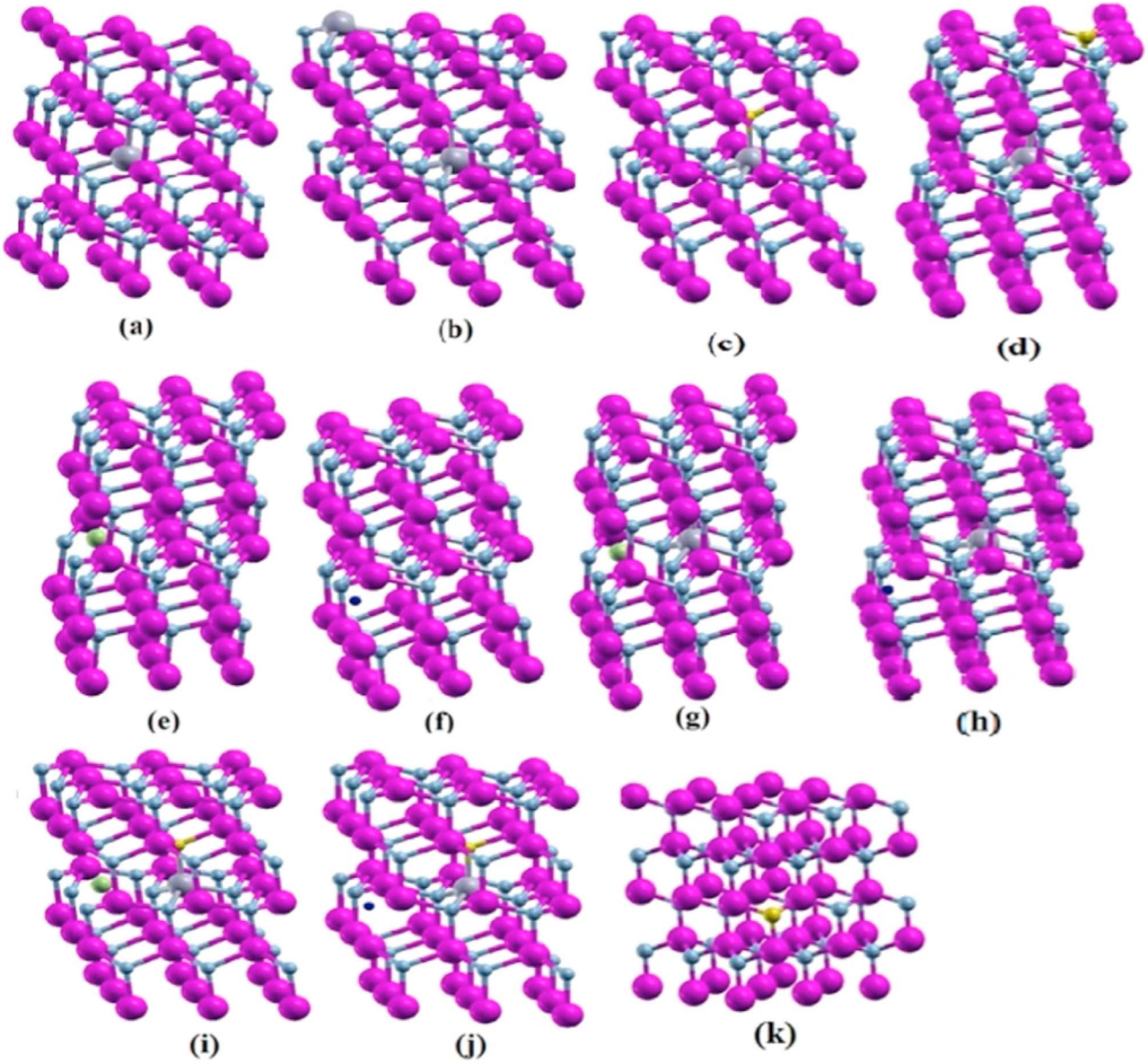

Fig. 1. (a) Single Gd doped GaN (b) Double Gd doped GaN (c) Single Gd bonded to Carbon in a GaN supercell (d) Single Gd bonded away from Carbon (e) GaN supercell with Gallium vacancy (f) GaN supercell with Nitrogen vacancy (g) Single Gd with Ga Vacancy (h) Single Gd with N vacancy (i) Gd – C codoped with Ga vacancy (j) Gd – C codoped with N vacancy (k) C doped in GaN supercell.

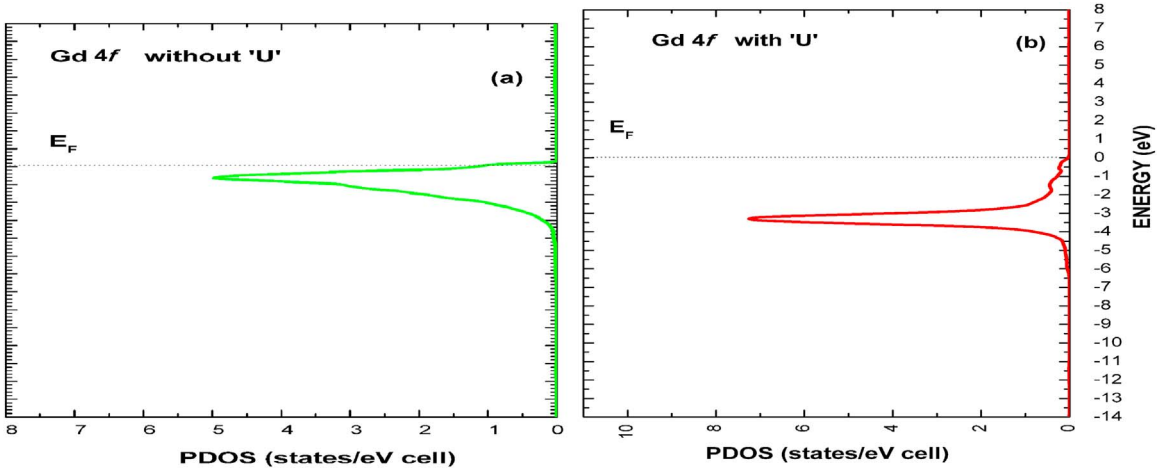

Fig. 2. PDOS of $Gd_{01}Ga_{35}N_{36}$ showing Gd-4*f* (a) without 'U' and (b) with 'U'.

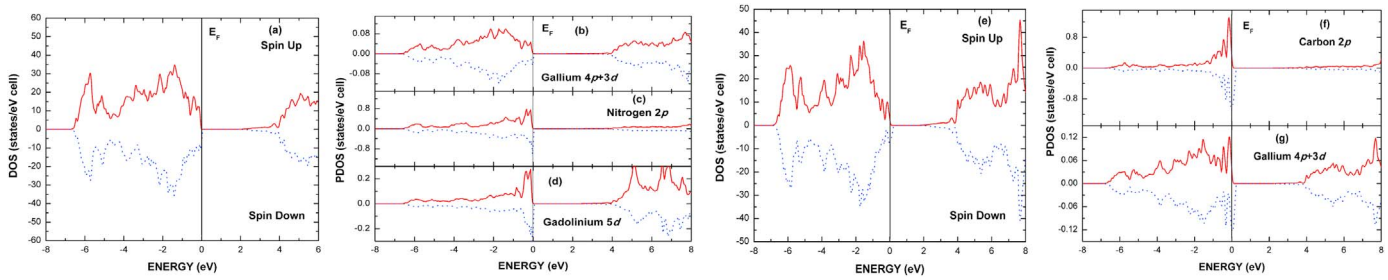

Fig. 3. $Gd_{01}Ga_{35}N_{36}$ (a) Total DOS, PDOS of (b) Gallium 4*p*+3*d* (c) Nitrogen 2*p* (d) Gadolinium 5d and Carbon doped GaN – $C_{01}Ga_{36}N_{35}$ (e) Total DOS, PDOS of (f) Carbon 2*p* (g) Gallium 4*p*+3*d*.

there is impurity level above the Fermi level. Hence the system $Gd_{01}C_{01}Ga_{35}N_{35}$ (Gd bonded to C) is metallic in nature Table 1.

Ga (V_{Ga}) and N (V_N) vacancy are simulated by removing a Ga ($V_{Ga}Ga_{35}N_{36}$) or N ($V_NGa_{36}N_{35}$) atom in GaN as shown in Fig. 1(e) & (f). The Ga vacancy is shown as green ball and N vacancy as blue ball. For co-doped GaN with Ga and N vacancy, Gd and C atoms are introduced along with removal of Ga or N appropriately as specified in the before shown simulations according to the requirement of the doping. The systems are shown in Fig. 1(g), (h), (i), & (j). The M_{tot} for all the vacancy systems is listed in Table 2. By the introduction of Ga and N vacancy, there is no change in the M_s of Gd and C in the system. There is increase in M_{tot} of the system when Ga vacancy is introduced. The three surrounding N atoms which are at the distance of 1.976 Å have localized M_s of 0.45 μ_B in $V_{Ga}Ga_{35}N_{36}$ system. M_{tot} for $V_{Ga}Ga_{35}N_{36}$, $V_{Ga}Gd_{01}Ga_{34}N_{36}$ and $V_{Ga}Gd_{01}C_{01}Ga_{34}N_{35}$ are 3 μ_B , 9.99 μ_B and 11 μ_B respectively. There is only a slight decrease in M_{tot} when N vacancy is introduced. For $V_NGa_{36}N_{35}$, $V_NGd_{01}Ga_{35}N_{35}$, and $V_NGd_{01}C_{01}Ga_{35}N_{34}$, the M_{tot} are 0.64 μ_B, 6.46 μ_B and 7 μ_B respectively. This is slightly less than M_{tot} for $Gd_{01}Ga_{35}N_{36}$ and $Gd_{01}C_{01}Ga_{35}N_{35}$ which is 7 μ_B and 8 μ_B respectively.

Fig. 5 (a) & (b) shows the total DOS of Gallium and vacancy induced GaN. The removal of one Ga atom introduces three holes in the Gd-GaN system with minority spin which leads to spin polarization of N 2*p* electrons. It is clearly seen in the difference in the DOS of Fig. 5 near the Fermi level of spin-up and spin-down states. There is a strong *p*-*d* exchange coupling between the *p*-like top GaN valence bands and Ga 3*d* orbitals. Similarly, each missing N atom donates three conduction electrons to the system which leads to shift in the Fermi level in the DOS. But not much difference in DOS is noted in spin-up and spin-down states. The lower part of conduction band has significant *d* bands which leads to *s*-*d* coupling but it is weak so there is no significant raise in total magnetic moment of created nitrogen vacancy Gd-GaN systems.. This *s*-*d* exchange coupling is reported to be anti-ferromagnetic in nature [17]. So, the nitrogen vacancy will not affect much on the magnetic moment of the system. The experimental observation [31] of paramagnetism in *n*-type GaN films also confirms the predictions. Hence, holes are more effective than electrons in contributing to the observed magnetic moment in the system.

Table 1
M_s of Gd, and C, and M_{tot} of the system.

S.no	System	M_s of Gd (μ_B)	M_s of C (μ_B)	M_{tot} (μ_B)
1	$Gd_{01}Ga_{35}N_{36}$	6.71	–	7
2	$Gd_{02}Ga_{34}N_{36}$	6.71	–	13.99
3	$C_{01}Ga_{36}N_{35}$	–	0.18	0.92
4	$Gd_{01}C_{01}Ga_{35}N_{35}$ (Gd bonded away from C)	6.65	0.14	7.69
5	$Gd_{01}C_{01}Ga_{35}N_{35}$ (Gd bonded to C)	6.82	0.38	8

Table 2
M_{tot} for vacancy (Ga and N) in GaN, Gd doped GaN, Gd-C co-doped GaN.

S.no.	System	M_{tot} (μ_B/Cell)
1	$V_{Ga}Ga_{35}N_{36}$	3
2	$V_NGa_{36}N_{35}$	0.64
3	$V_{Ga}Gd_{01}Ga_{34}N_{36}$	9.99
4	$V_NGd_{01}Ga_{35}N_{35}$	6.46
5	$V_{Ga}Gd_{01}C_{01}Ga_{34}N_{35}$	11
6	$V_NGd_{01}C_{01}Ga_{35}N_{34}$	7

4. Summary

In summary the theoretical calculations are carried out to investigate the effect of Gadolinium and Carbon co-doping in GaN system.

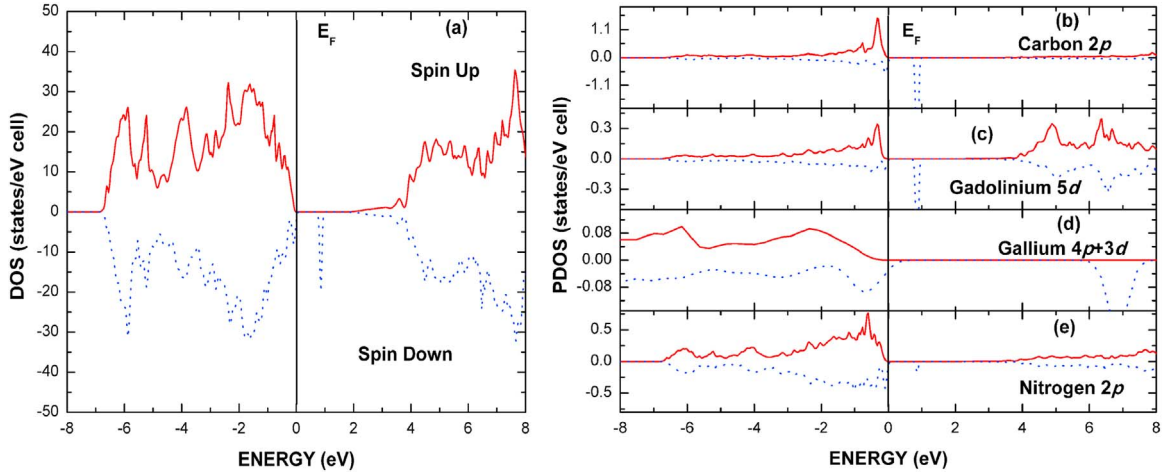

Fig. 4. $Gd_{01}C_{01}Ga_{35}N_{35}$ (Gd bonded to C) (a) Total DOS, PDOS of (b) Carbon 2*p* (c) Gadolinium 5d (d) Gallium 4*p*+3*d* (e) Nitrogen 2*p*.

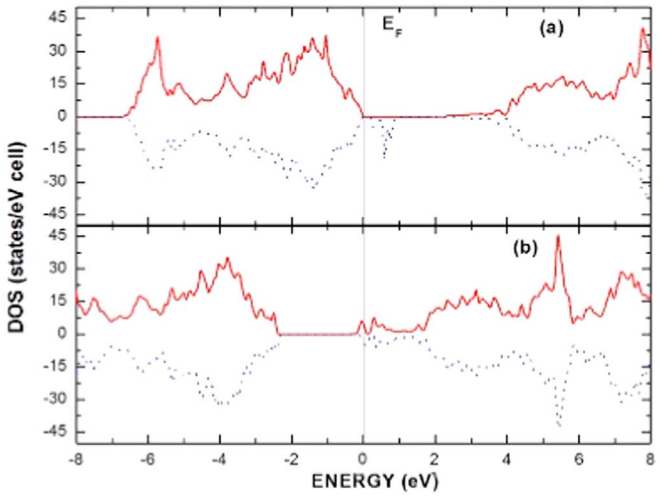

Fig. 5. Total DOS of (a) Gallium vacancy induced GaN (b) Nitrogen vacancy induced GaN.

When single Gd is added in GaN supercell, the system exhibits half-metallic nature. With only C doped in GaN supercell, the system becomes metallic in character. The presence of C in GaN supercell generates weak M_s in the neighbouring atoms. When Gd and C are co-doped at different sites in GaN supercell, the system remains metallic. The system retains the metallic character when Gd and C are bonded together. When C is bonded to Gd the M_s of Gd and C, and M_{tot} is greater compared to the system in which Gd and C are bonded at different sites in GaN supercell because of Zener *p-d* exchange mechanism. From the introduction of vacancy, it is observed that N vacancy system does not affect the M_{tot} much, while Ga vacancy system influences both M_s of neighbouring atoms as well as M_{tot}. Hence, holes are more effective than electrons in contributing to the observed magnetic moment in the system.

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