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Vacancy Induced Magnetism and Spin Filtering in 2D GaN Monolayer

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Exotic properties functionalized by Ga or N atom vacancies in two-dimensional GaN monolayer have been predicted for the first time. A detailed ab-initio study of the structural, electronic, magnetic and optical properties of a 2D–GaN monolayer containing Ga or N atom vacancies has been performed. In the present study, we make two refinements in the density functional theory. At first, long range dispersion interactions not discussed so far have been accounted for. Further, norm-conserving pseudopotentials and plane waves are employed in generalized gradient approximation in contrast to earlier workers who have used soft or ultra-soft pseudopotentials. One observes that the strength of induced magnetism depends not on the separation of Ga-vacancies but on the number of Ga atom vacancies. The magnetism induced by N-atom vacancies is either zero or quite small. Spin filtering has been observed in many configurations. A strong continuous absorption from the far infrared region to the deep visible region is seen in some systems. It may be useful for development of photo-emitting devices which will emit in various regions of energy spectrum including visible emission. The emission of 2D-GaN monolayer lying in deep ultraviolet region may be used for sterilization, water purification etc.

Keywords: Ab-initio study, 2D-GaN monolayer, Dispersion forces, Vacancies, Magnetism, Spin filter, Optical absorption.

1 Introduction

Presently, III-V binary gallium nitride (GaN) compound has become very important material for the development of the laser diodes and light emitting diodes. The performance of the electronic devices using GaN materials has improved substantially. For the production of the nano-optoelectronic devices, the band gap of GaN may be tuned both in visible and ultraviolet energy regions by doping the GaN materials with the other kinds of atoms. GaN based devices in addition to their opto-electronic applications have also been utilized in several other fields *e. g*., solar cells, water splitting devices *etc.*

Magnetism has been found in many functionalized graphene materials. The experimental investigations of the 2D-GaN monolayer are scarce. Some workers have prepared 2D-GaN crystal using different experimental techniques[1-3]. Recently, Gonzalez *et al.*.[4] have reported the structural and electronic properties of single vacancy in pure 2D-GaN monolayer using ultra-soft potentials in quantum espresso package. However, they ignored the long range dispersion interactions in their study. The magnetic behaviour of 2D-GaN monolayer has not been explored much. In the present article, we have made a comprehensive ab-initio study of the structural, electronic, magnetic and optical properties of the 2D-GaN-monolayer induced by several vacancies and observed high magnetism, spin filtering and optical absorption for the first time in the literature.

2 Method

We consider the long range dispersion interactions (LRDI) as considered by Grimmes[5] in the ABINIT package in the present study. These long range interactions have been ignored in earlier studies. Further, most of the earlier workers have employed soft or similar pseudopotentials *e.g*. Vanderbilt or PAW etc. which are not norm-conserving ones for the study of the 2-D systems. We have used norm-conserving pseudopotentials which are expected to predict more reliable results. The present *ab-initio* study uses the norm-conserving pseudopotentials and the plane waves. For the conversion of the wave function between the real and reciprocal lattices, we employ an efficient fast Fourier-transform algorithm[6]. We calculate the wave function in a fixed potential according to state by state or band by band by using conjugate gradient algorithm[7,8]. The non-local norm-conserving pseudopotential of Troullier and Martin[9] within a separable approximation has been considered. An exchange-functional of Perdew *et. al.*[10] produced by FHI code [11] has been used.

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We have performed spin-polarised, self-consistent calculation and optimised the various structures by relaxing both the lattice constants and the atomic positions simultaneously in contrast to the other usually used ab-initio softwares *e.g.* Quantum-espresso where the optimisation for the lattice vector and atomic positions are done separately. A convergence of 10^{-5} eV for the total system energy was achieved. Hellmann-Feynman forces lesser than 5×10^{-2} eV/Å were obtained. A two-dimensional super cell of 4x4x1 containing 32 atoms was chosen. A grid of 10×10×1 k-points in Brillouin zone within the Monkhorst-Pack scheme and a plane wave cut-off energy of 80 Ry have been used for achieving the convergence. The long range dispersion interactions (LRDI) as considered by Grimmes[5] in the ABINIT package have been included in the present study. These long range interactions have been ignored in earlier studies.

We define ' buckling ' as the maximum difference in the heights of the atoms normal to the monolayer plane. In all the figures depicting the electronic structures, the Fermi level (E_F) has been set at the zero of the energy.

3 Results and Discussion

3.1 Pure 2D-GaN monolayer

For the pure 2D-GaN monolayer, the atomic configuration is shown in Fig. 1(a). The optimised value of the lattice parameter is 3.07 Å. A small buckling of 0.074 Å is seen. The cohesive energy per Ga-N pair for pure 2D-GaN monolayer is obtained as 8.38 eV. Other theoretical workers have obtained values of the cohesive energy which are different from our results. As an example, Sahin *et al.*.[13] have reported a lattice parameter of 3.20 Å but a cohesive energy of 12.74 eV after using projected augmented wave potential and a cut off kinetic energy of 500 eV using VASP software. The other workers, Gonzalez *et al.*[4] who have employed ultra-soft potential in quantum espresso package have reported a lattice parameter of 3.21 Å and a cohesive energy of 7.68 eV. In fact, the inclusion of LRDI in the present study contracts the GaN monolayer which results in a smaller lattice constant and higher electron energy band gap as will be seen later.

The computed electronic structure for the pure 2D-GaN monolayer has been depicted in Fig. 1(b). A perusal of Fig. 1(b) reveals that the valence band maximum (VBM) lies at the symmetric point, K whereas the conduction band minimum (CBM) occurs at the symmetric point Γ of the Brillouin zone (BZ). The value of the indirect band gap is 2.93 eV. A lower value of 2.27 eV has been reported by Sahin *et al.*[13]. A direct band gap of 2.11 eV has been shown by Gonzalez *et al.*[4]. The result of the occurrence of the direct band gap in GaN monolayer obtained by Gonzalez *et al.* arises because of their use of ultra-soft potential in Quantum Espresso method. The total and the projected density of states (PDOS) at Ga and N atoms are not presented in graph for brevity. A high PDOS appears at the VBM which is mainly comprised of the p - orbitals of N atoms. There occurs small PDOS at the CBM which has contributions mainly from the s- orbitals of both the host atoms. There appear high DOS of the N- p states around -1.0 eV in the valence band and at 4.7 eV in the conduction band regions. Fig. 1(c) depicts the absorption spectrum for the pure 2D-GaN monolayer. No absorption is seen in the visible region but small absorption is observed in the near ultraviolet region. The strongest absorption occurs in the energy range, 5.4 - 6.4 eV with a peak at 5.7 eV. It originates from the occurrence of high DOS both in the valence band

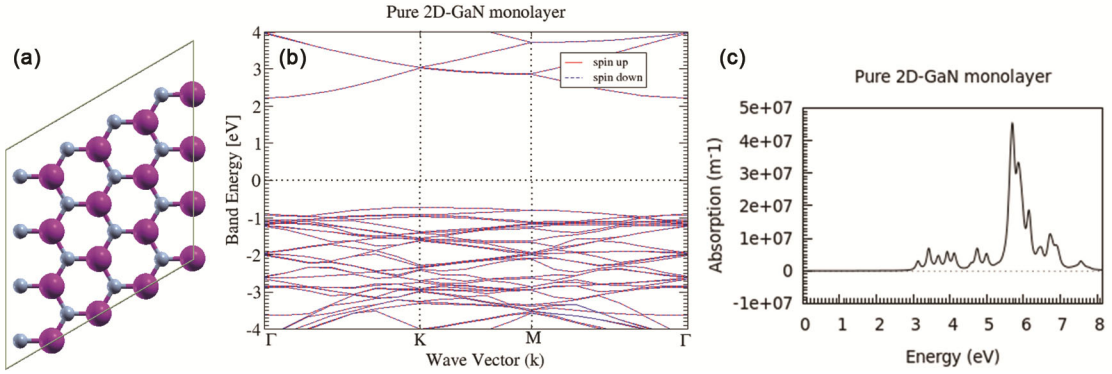

Fig. 1 — Pure 2D-GaN monolayer (a) atomic configurations having Ga (purple), N (grey) (b) electronic band structure (c) optical absorption.

region and in the conduction band region as stated above. Tian *et al.*[12] have obtained this peak at 5.24 eV. The occurrence of the absorption in the ultraviolet energy region can be utilized in various applications e.g., optoelectronic devices, sterilization and water filtering etc.

3.2 Ga vacancies in pure 2D-GaN monolayer

In future calculations, the spin up and spin down charge densities on all the atoms have been computed. The difference between the spin up and down charge densities is called as the net spin charge density which is indicative of the magnitude of the magnetic moment at different positions of the space.

3.2.1 One Ga vacancy

For 1-Ga vacancy in pure 2D-GaN monolayer, the optimised atomic configurations and the net spin charge density are presented in Fig. 2(a). The optimised value of the lattice parameter is found to be 3.29 Å which is larger by 7% of 3.07 Å obtained earlier for the pure 2D-GaN monolayer. A small buckling of 0.12 Å is observed.

The electronic structure for this system is depicted in Fig. 2(b). A perusal of Fig. 2(b) reveals that the Ga-N monolayer with one Ga vacancy remains an insulator. For a neutral Ga vacancy, Gonzalez *et al.*[4] have also found the monolayer semiconducting. The VBM lies at the Γ–point and the CBM occurs between the Γ– and K-point symmetry points of the BZ. Thus, one observes an indirect band gap of 0.39 eV. There appear several narrow bands both in the VBM and CBM energy regions. These bands correspond to the N-p orbitals and possess spin down character. The system will obstruct the flow of electron having spin up direction and will behave like a spin filter. High PDOS of the N-p orbitals exists on either side of the E_F. The absorption for this system is shown in Fig. 2(c). One observes that the main peak in the pure 2D-GaN monolayer observed at 5.24 eV is red-shifted to 5.15 eV. A quite strong doublet occurs at 6.81 eV. Quite small optical absorption occurs in the infrared energy region but appreciable one in the visible and near ultraviolet energy regions which may give rise to electromagnetic radiation in the broad energy range from infra-red to far ultraviolet. A Ga vacancy creates a magnetic moment of 3.12 μ_B per unit cell. A value equal to 3.0 μ_B has been reported by Gonzalez *et al.*[4]. One notes the occurrence of the major part of the magnetic moment on the three neighbouring N atoms of the vacancy (Fig. 2a). A magnetic moment equal to 0.55 μ_B exists on each N atom and the remaining one on the distant atoms and in the interstitial space.

3.2.2 Near 2-Ga vacancy

The GaN monolayer containing two second-neighbouring Ga vacancies in the pure 2D-GaN monolayer is investigated. The optimised atomic configuration and the net spin charge density are shown in Fig. 3(a). The lattice parameter of this system is found to be 3.26 Å. The N atoms which are the immediate neighbours of the Ga-vacancy are shifted out of the GaN-monolayer plane by different magnitudes. The buckling is quite high and the maximum N-atom displacement is 0.98 Å.

Fig. 3(b) shows the electronic structure for this system. The VBM lies below the E_F at -0.037 eV at the Γ–point and at 0.011 eV above the E_F at the K-point. Thus, the Fermi level lies within a very narrow band and the system is metallic. The CBM occurs between the K- and M - points at 0.725 eV. Thus, the separation between the VBM and CBM is indirect equal to 0.71 eV. Both the edges of the indirect band gap possess the spin down character and the system will behave as a spin filter for the electrons having

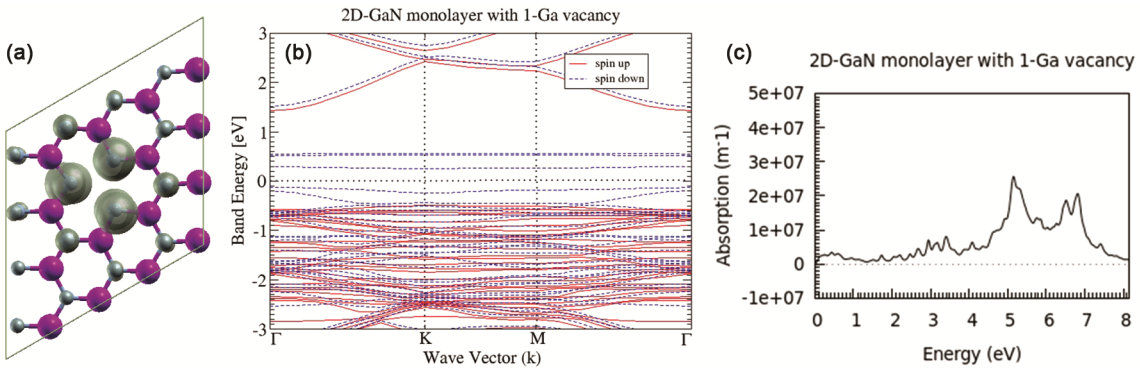

Fig. 2 — 2D-GaN monolayer with 1-Ga vacancy (a) atomic configuration and isosurface of net spin charge density of 10^{-3} e/Å (b) electronic band structure (c) optical absorption.

spin up. The PDOS is seen to be quite high for the N-p orbitals in the vicinity of the E_F. The absorption for this system is shown in Fig. 3(c). The absorption is quite similar to the absorption seen earlier for 1-vacancy except two differences. The absorption is enhanced in the infrared energy region but reduced in the ultraviolet region without a doublet. The total magnetic moment for this system is obtained as 6.56 μ_B per unit cell. Each of the four nearest neighbouring N atoms possesses magnetic moment equal to 0.55 μ_B. The N atom which is the common neighbour of the two near Ga-vacancies has a magnetic moment of 1.17 μ_B. The remaining part of the magnetic moment is distributed in the interstitial space.

3.2.3 Far 2-Ga vacancy

The 2D-GaN monolayer possessing two Ga-vacancies which are far apart has been studied. The optimised atomic configuration and the net spin charge density on the atoms are presented in Fig. 4(a). The optimised value of lattice parameter is 3.26 Å which is same as seen for the GaN-monolayer containing two near Ga-vacancies. There appears large bucking of 0.66 Å in the GaN monolayer.

The electronic structure for this system is depicted in Fig. 4(b). The system is semi-conducting. The VBM occurs at the Γ–point whereas the CBM appears between the Γ- and M- points at energy 0.047 eV. This gives rise to an indirect gap of 0.05 eV. Both the VBM and CBM possess the spin down character. The system will behave like a spin filter for the filtering of electron having spin up direction. Large PDOS of the N-p orbitals constitute the two ends of the indirect gap. Fig. 4(c) depicts the absorption for this system. The absorption is quite similar to those seen earlier for the 2 Ga-vacancies except that the absorption is somewhat enhanced in the low energy region in the infrared. The system may give rise to strong emission in the far infrared region. The total magnetic moment for this system is 6.48 μ_B per unit cell. The magnetic moment is comprised of an averaged 0.57 μ_B at each of the four nearest N atoms, 1.17 μ_B on the common neighbor N atom and the remaining one on the far atoms and inside the interstitial space.

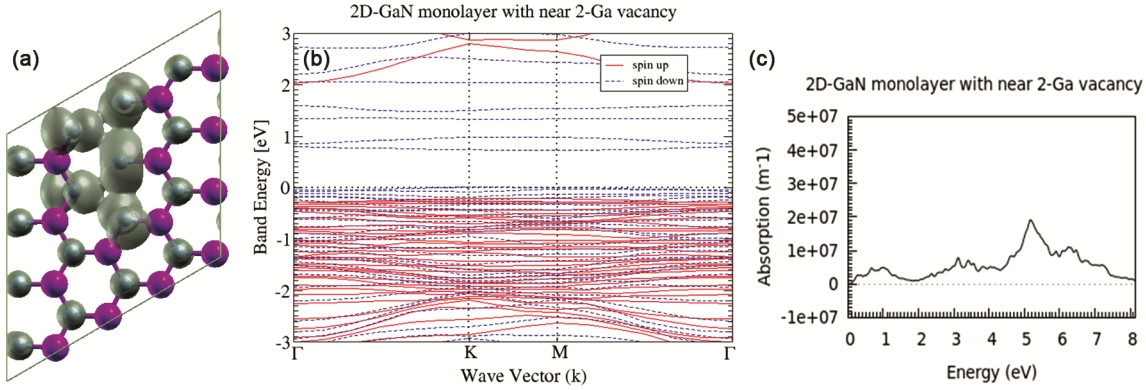

Fig. 3 — 2D-GaN monolayer with near 2-Ga vacancy (a) atomic configuration and isosurface of net spin charge density of 10^{-3} e/Å (b) electronic band structure (c) optical absorption.

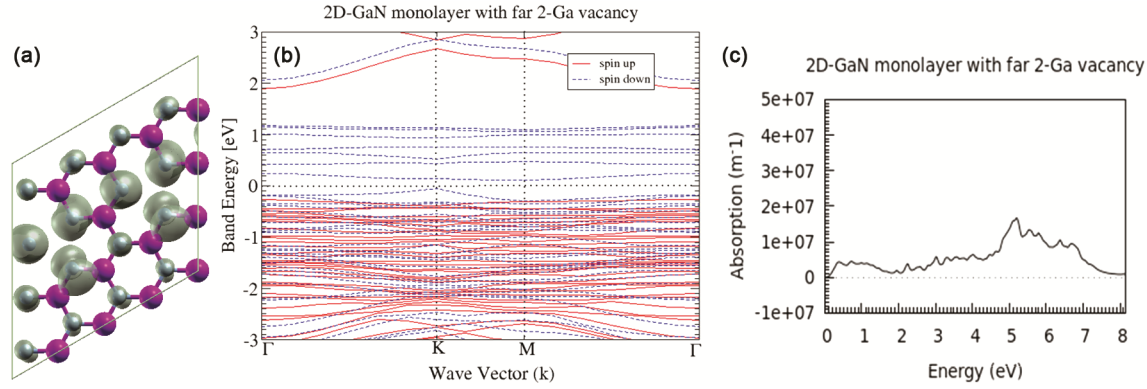

Fig. 4 — 2D-GaN monolayer with far 2-Ga vacancy (a) atomic configuration andisosurface of net spin charge density of 10^{-3} e/Å (b) electronic band structure (c) optical absorption.

3.2.4 3-Ga vacancy

For a cluster of three nearest-neighbouring Ga vacancies in the pure 2D-GaN monolayer, the optimised atomic configuration and the net spin charge densities are shown in Fig. 5(a). The value of the lattice parameter is 3.18 Å. The buckling is also reduced to 0.12 Å. The atoms are less relaxed as compared to those seen in the GaN-monolayer containing 2 Ga- vacancies.

Fig. 5(b) contains the electronic structure for this system. This atomic configuration is seen to be semi-conducting. The VBM appears at the Γ–point and the CBM at the K-point. The indirect band gap turns out to be 0.45 eV. Again, as both the boundaries of the indirect band gap are formed by the states having spin down nature, the monolayer will allow the transport of electrons having spin down only and work as spin filter. The PDOS is again large for the N-p orbitals in the vicinity of the E_F. The absorption as shown in Fig. 5(c) is appreciable from the infrared to the far ultraviolet electromagnetic energy region except in the visible region. The absorption in the far ultraviolet region contains now two strong peaks at 5.0 and 5.5 eV. The total magnetic moment for this system is obtained as 9.15 μ_B per unit cell. Each of the three nearest neighbouring N atom possesses 1.15 μ_B whereas each of the three next –nearest neighbouring N atom contains a magnitude of 0.55 μ_B.

3.3 N vacancies in pure 2D-GaN monolayer

3.3.1 One N vacancy

For 1-N vacancy in the pure 2D-GaN monolayer, Fig. 6(a) contains the optimised atomic configurations and the net spin charge density. The optimised value of the lattice parameter is 3.07 Å just equal to that of the pure GaN-monolayer. The buckling is also small equal to 0.08 Å.

Fig. 6(b) shows the electronic structure for the 1-N vacancy in the 2D-GaN monolayer. The GaN-monolayer becomes conducting. The E_F lies within a band having spin up character. The nearest valence states occur about 1.78 eV below the metallic band at E_F. The monolayer will allow only the transport of spin up electrons behaving as a spin filter. One observes large PDOS corresponding to the Ga-s,p and N-p orbitals in the vicinity of the E_F. Fig. 6(c) depicts

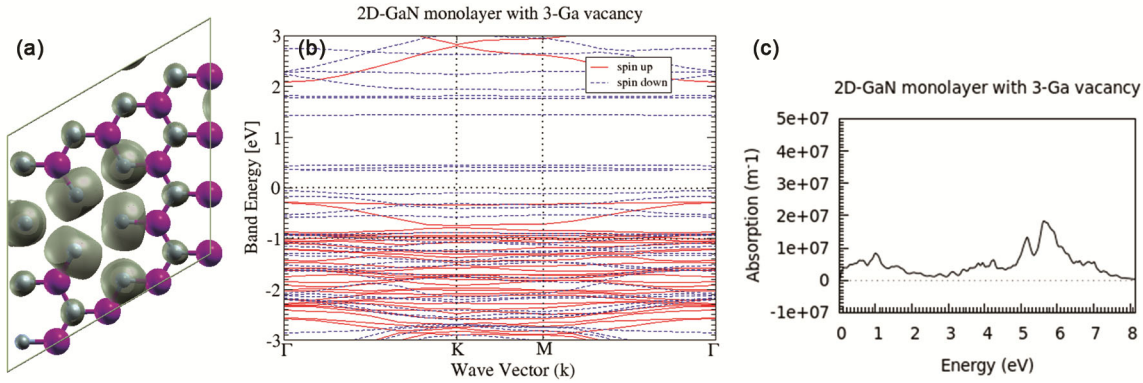

Fig. 5 — 2D-GaN monolayer with 3-Ga vacancy (a) atomic configuration and isosurface of net spin charge density of 10^{-3} e/Å (b) electronic band structure (c) optical absorption.

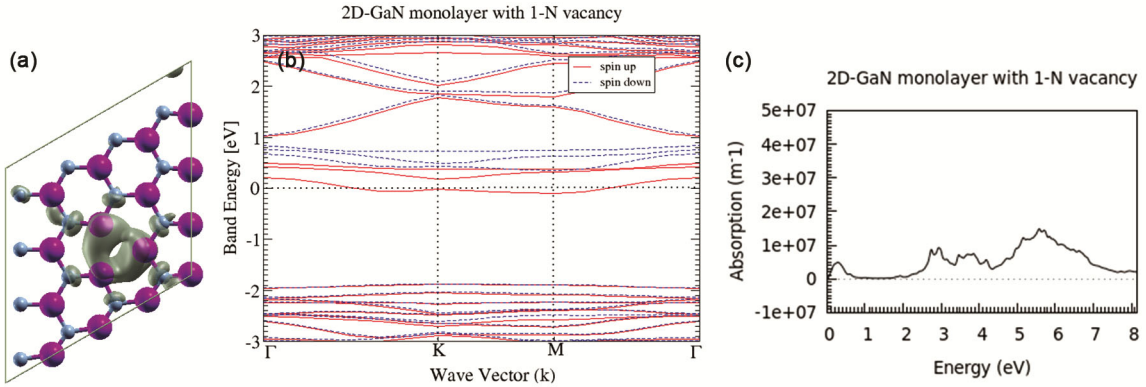

Fig. 6 — 2D-GaN monolayer with 1-N vacancy (a) atomic configuration and isosurface spin charge density of 10^{-3} e/Å (b) electronic band structure (c) optical absorption.

the absorption spectra for this system Weak absorption appears in the far infrared region. No absorption is seen in the visible region. The total magnetic moment for this system is obtained as 0.97 μ_B per unit cell. This magnetic moment is comprised of 0.19 μ_B on each of the three nearest Ga atoms and the remaining part on the far atoms and in the interstitial space.

3.3.2 Near 2-N vacancy

Fig. 7(a) presents the optimised atomic configuration alongwith the net spin charge density for the two near N vacancies in the pure 2D-GaN monolayer. The lattice parameter of this system is found to be 3.28 Å A small buckling of 0.14 Å is present in the GaN monolayer.

The electronic structure for this system is shown in Fig. 7(b). One observes that there is no splitting between the spin up and down states and it leads to zero magnetic moment. The system is semi-conducting with an indirect band gap of 0.71 eV. A large PDOS of Ga-s,p states is seen in the vicinity of the E_F. The absorption for this system is shown in Fig. 7(c). There is large absorption above 2.0 eV. Strong absorption peaks appear in the ultraviolet region. This atomic configuration will give strong emission both in the visible and the far ultraviolet energy regions.

3.3.3 Far 2-N vacancy

Fig. 8(a) contains the optimised atomic configuration and the net spin charge density for two far N-vacancies in pure 2D-GaN monolayer. The lattice parameter is again enhanced to 3.24 Å . Also, the buckling is seen to be small equal to 0.11 Å.

The electronic structure for this system is shown in Fig. 8(b). There is no splitting between the spin up and spin down states. The system is metallic. There is large PDOS of N-p and Ga-s,p states in the vicinity of The lattice parameter is 3 the E_F. Fig. 8(c) depicts the absorption for this system. There occurs strong absorption above 2.1 eV which will lead to emission in the visible region also.

3.3.4 3-N vacancy

For the 3-N vacancies in the pure 2D-GaN monolayer, the optimised atomic configuration and the computed net spin charge density are shown in Fig. 9(a). The lattice parameter is 3.13 Å. A quite

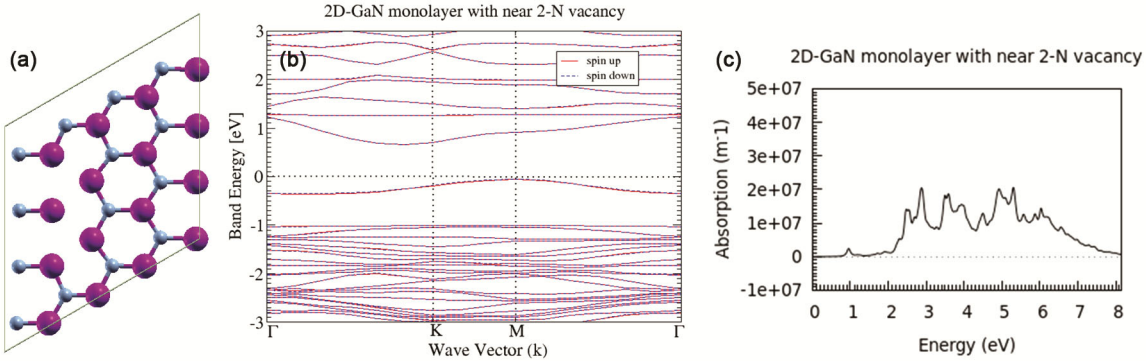

Fig. 7 — 2D-GaN monolayer with near 2-N vacancy (a) atomic configuration and isosurface spin charge density of 10^{-3} e/Å (b) electronic band structure (c) optical absorption.

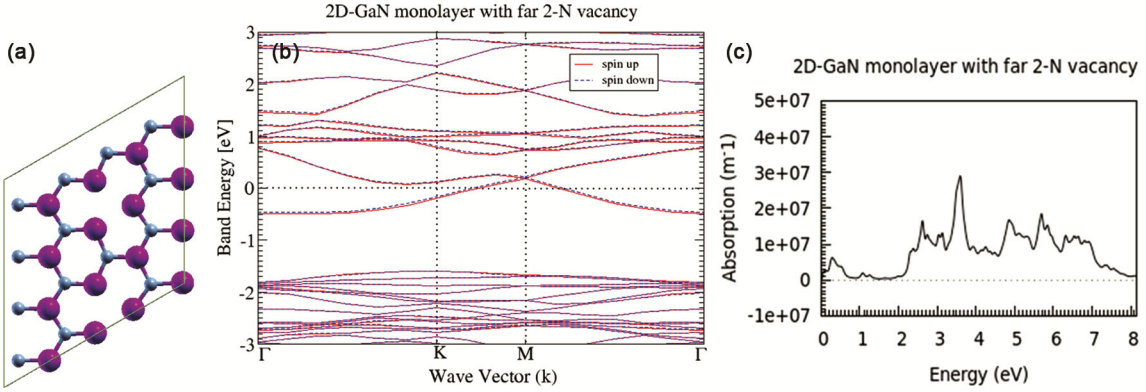

Fig. 8 — 2D-GaN monolayer with far 2-N vacancy (a) atomic configuration and isosurface spin charge density of 10^{-3} (b) electronic band structure (c) optical absorption.

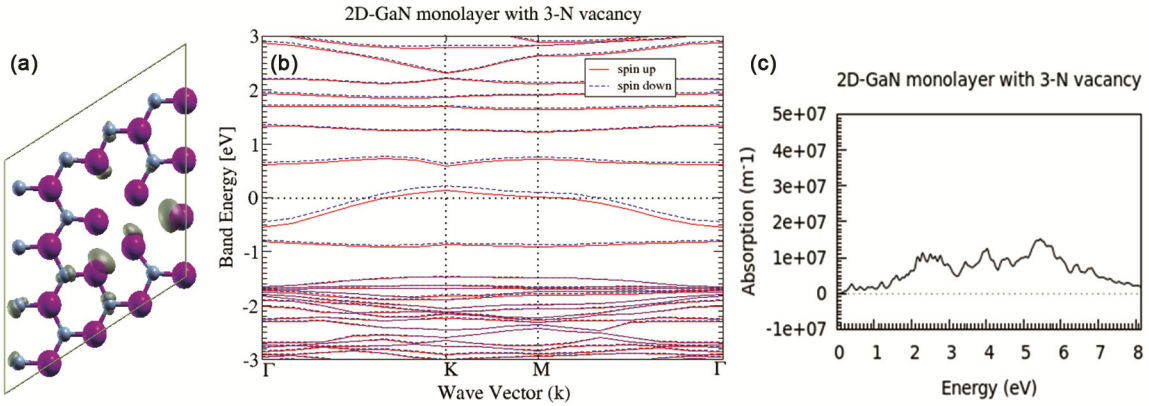

Fig. 9 — 2D-GaN monolayer with 3-N vacancy (a) atomic configuration and isosurface of net spin charge density of 10^{-3} e/Å (b) electronic band structure (c) optical absorption.

Table 1 — The details for each system including the lattice parameter, magnetic moment, nature, band gap and spin filtering are given.

System	Lattice constant (Å)	Net magnetic moment (μ_B)	Nature of system with band gap and spin filter if present
Pure 2D-GaN monolayer	3.07	0.0	semiconductor with an indirect bad gap of 2.93 eV
2D-GaN monolayer with 1-Ga vacancy	3.29	3.12	semiconductor with an indirect bad gap of 0.39 eV and spin filter
2D-GaN monolayer with near 2-Ga vacancy	3.26	6.56	Metallic and spin filter
2D-GaN monolayer with far 2-Ga vacancy	3.26	6.01	Semiconductor with an indirect band gap 0.16 eV and spin filter
2D-GaN monolayer with 3-Ga vacancy	3.18	9.15	semiconductor with an indirect band gap of 0.45 eV and spin filter
2D-GaN monolayer with 1-N vacancy	3.07	0.97	Metallic and spin filter
2D-GaN monolayer with near 2-N vacancy	3.28	0.0	semiconductor with an indirect band gap of 0.71 eV
2D-GaN monolayer with far 2-N vacancy	3.24	0.0	metallic
2D-GaN monolayer with 3-N vacancy	3.13	0.23	metallic

high buckling of 0.70 Å is found in the GaN monolayer.

The electronic structure for this system is shown in Fig. 9(b). One observes that this system is metallic. The bands possessing both the spin up and spin down characters are present around the E_F. Large PDOS of the states belonging to the Ga-s,p orbitals are seen around the E_F. The absorption is shown in Fig. 9(c). There occurs continuous absorption above 1.5 eV. Weak absorption is observed in the infrared region. The total magnetic moment for this system is obtained as 0.23 μ_B per unit cell. This magnetic moment is comprised of 0.04 μ_B on each of the six nearest Ga atoms and the remaining part on the far atoms and in the interstitial space.

The details for each system including the lattice parameter, magnetic moment, nature, band gap and spin filtering are given in Table 1. The GaN monolayer is dilated by the creation of the vacancies except one case. A non-localized magnetic moment of about 3 μ_B is present because of the occurrence of one Ga–atom vacancy. This magnetic moment is enhanced as multiple of three times of the number of the Ga- vacancies irrespective of their separation. About 50% of these systems are metallic and the remaining ones are semi-conductors possessing indirect band gaps.

4 Conclusions

A detailed *ab-initio* study has been made for the structural, electronic, magnetic and optical properties of 2D-GaN monolayer by creating several Ga or N atom vacancies. The norm-conserving pseudopotentials have been employed in this ab-initio calculation in contrast to other earlier workers who have used soft or ultra-soft pseudopotentials. We predict the occurrence of the continuous emission of electromagnetic radiation from the infra-red to the deep ultraviolet region in some systems. It has been found that the strength of the induced magnetism is independent of the separation of Ga- vacancies but does depend on the number of the Ga - atom

vacancies. The magnetism induced by the N- atom vacancies is quite small. The spin filtering has been observed in many of the studied configurations. These systems may therefore be useful for the development of photo-emitting devices which will emit in the various regions of energy spectrum including white emission. The emission of 2D-GaN monolayer lying in the deep ultraviolet region may also be used for the sterilization, water purification etc. No experimental data is available for comparison. Intensive experimental investigations of the above studied Ga or N atom vacancies in 2-D GaN monolayer need to be verified experimentally the presently predicted exotic properties.

Acknowledgements

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