

Role of vacancies in the magnetic and electronic properties of SiC nanoribbons: An *ab initio* study

Juliana M. Morbec^{1,*} and Gul Rahman^{2,†}

¹*Instituto de Ciências Exatas, Universidade Federal de Alfenas, 37130-000 Alfenas, MG, Brazil*

²*Department of Physics, Quaid-i-Azam University, Islamabad 45320, Pakistan*

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Using *ab initio* calculations based on density functional theory, we investigate the effects of vacancies on the electronic and magnetic properties of zigzag SiC nanoribbons (Z-SiCNR). Single (V_C and V_{Si}) and double ($V_{Si}V_{Si}$ and $V_{Si}V_C$) vacancies are observed to induce magnetism in Z-SiCNRs. The presence of a single V_{Si} does not affect the half-metallic behavior of pristine Z-SiCNRs; however, a single V_C leads to a transition from half-metallic to metallic behavior in Z-SiCNRs due to the edge Si p orbitals and the atoms surrounding the vacancy. The interactions of vacancies with foreign impurity atoms (B and N) are also investigated, and it is observed that $V_{Si}N_C$ not only suppresses the oscillatory type magnetism of $V_{Si}V_C$ but also retains the half-metallic character of the pristine Z-SiCNRs. The defect formation energies of vacancies can be reduced by substitutional B and N atoms. We believe that ferromagnetism is expected if Z-SiCNRs are grown under suitable conditions.

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I. INTRODUCTION

Silicon carbide (SiC) is an attractive material for numerous technological applications, mainly in harsh environments. Bulk SiC is known to possess outstanding properties (such as high thermal conductivity, high breakdown electric field, high electronic mobility, excellent chemical and physical stability, good radiation resistance, and wide band gap)^{1,2} which make it a suitable semiconductor for high-power, high-temperature, and high-frequency devices. Furthermore, SiC nanowires and nanotubes, which have already been synthesized,^{3,4} exhibit excellent characteristics and are good candidates for applications ranging from hydrogen storage media⁵ and gas sensors⁶ to optical⁷ and field-emission devices.⁸

In the last few years, the successful synthesis of SiC nanotubes³ and, recently, the theoretical prediction of the stability of two-dimensional SiC monolayers with honeycomb structure^{9,10} have stimulated increasing interest in SiC nanosheets and nanoribbons (NRs). According to recent theoretical studies, SiC nanosheets and armchair SiC-NRs (A-SiCNRs) behave as nonmagnetic wide-band-gap semiconductors,⁹⁻¹¹ whereas zigzag SiCNRs (Z-SiCNRs) are magnetic (with very small magnetic moments)^{11,12} and can present metallic or semiconducting character, depending on the width of the nanoribbon¹¹⁻¹³ (half-metallicity was predicted for Z-SiCNRs narrower than 4 nm,¹¹ which makes these NRs promising candidates for spintronic applications). However, *ab initio* investigations have recently shown that these characteristics can be modified by the presence of some impurities and defects. For example, it has been observed that (i) substitutional B, N, As, and P impurities induce magnetism in SiC sheets,¹⁰ (ii) half-metallic Z-SiCNRs become metallic when doped with N atoms,¹⁴ and (iii) B (N) substituting an edge Si (C) atom transforms semiconducting Z-SiCNRs into half-metallic systems.¹⁵ In addition, Si vacancy has been shown to induce magnetism in nonmagnetic SiC sheets^{10,16} and A-SiCNRs.¹⁰

Intrinsic defects, especially vacancies, have been suggested to be related to the origin of magnetism in SiC structures: besides the aforementioned studies of vacancies in SiC sheets and A-SiCNRs (Refs. 10 and 16), there is experimental evidence

that defects dominated by Si + C divacancies can induce room-temperature ferromagnetism in diamagnetic SiC crystals.^{17,18} Despite the great potential of Z-SiCNRs for spintronics, the role of intrinsic defects (vacancies) and their interactions with foreign impurities in these NRs have not, to our knowledge, been investigated so far. In this work we investigated, by means of *ab initio* calculations, the effects of vacancies on the electronic and magnetic properties of Z-SiCNRs, and the interactions of vacancies with foreign impurity atoms. Our extensive results indicate that the presence of one C (V_C) or Si (V_{Si}) vacancy per supercell, as well as two vacancies ($V_{Si}V_{Si}$ or $V_{Si}V_C$), can induce large magnetic moments in Z-SiCNRs. The defect formation energy of V_{Si} is decreased when the interactions with B and N impurities are considered.

II. COMPUTATIONAL DETAILS

Spin-polarized calculations were performed within the framework of the density functional theory (DFT),¹⁹ as implemented in the SIESTA code,²⁰ employing the generalized gradient approximation of Perdew, Burke, and Ernzerhof²¹ (GGA-PBE) for the exchange-correlation functional and norm-conserving Troullier-Martins pseudopotentials²² to describe the electron-ion interactions. We used an energy cutoff of 200 Ry for the real-space mesh and a double- ζ basis set with polarization functions for all atoms. We considered Z-SiCNR with width $W = 6$ (6Z-SiCNR), as depicted in Fig. 1. The 6Z-SiCNR was simulated within the supercell approach with 84 atoms in the unit cell (including H atoms to passivate the edge dangling bonds) and vacuum regions of 17 and 20 Å along the y and z directions, respectively. Additional test calculations were also carried out for large supercells (12Z-SiCNR) containing 156 atoms to see the convergence of our numerical results. All atomic positions were fully relaxed until the forces on each atom were smaller than 0.05 eV/Å. The Brillouin zone was sampled using Monkhorst-Pack k -point meshes of $11 \times 1 \times 1$ and $121 \times 1 \times 1$ for the total-energy and electronic-structure calculations, respectively. Using the Mulliken population analysis, the local magnetic moment was calculated by $m = \rho^\uparrow - \rho^\downarrow$, where ρ^\uparrow (ρ^\downarrow) represents the spin-up (spin-down) valence electrons of an atom.

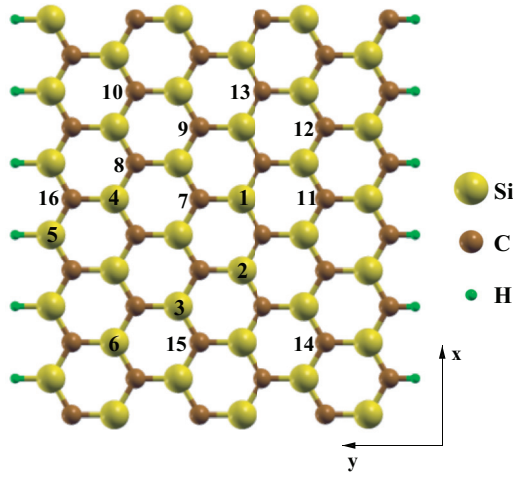


FIG. 1. (Color online) Structural model of 6Z-SiCNR. Labels 1, 2, ..., 16 indicate the positions of the vacancies or impurities.

In this work, we investigated the presence of single (one V_C or V_{Si} per supercell) and double ($V_{Si}V_{Si}$ and $V_{Si}V_C$) vacancies in 6Z-SiCNR. The energetic stability of these systems was examined by calculating their defect formation energies E_f . We used

$$E_f = E[V_X/6Z\text{-SiCNR}] - E[6Z\text{-SiCNR}] + \mu_X \quad (1)$$

for single vacancy ($X = \text{Si}$ or C) and

$$E_f = \frac{1}{n} \{ E[V_{Si}V_X/6Z - \text{SiCNR}] - E[6Z - \text{SiCNR}] + \mu_{Si} + \mu_X \} \quad (2)$$

for double $V_{Si}V_X$ ($n = 2$ if $X = \text{Si}$, and $n = 1$ if $X = \text{C}$). Here, $E[6Z\text{-SiCNR}]$ is the total energy of pristine 6Z-SiCNR, and $E[V_X/6Z - \text{SiCNR}]$ and $E[V_{Si}V_X/6Z - \text{SiCNR}]$ are the total energies of 6Z-SiCNR with single V_X and double $V_{Si}V_X$, respectively. The chemical potential of the atomic specie X is μ_X . In equilibrium conditions,

$$\mu_{Si} + \mu_C = \mu_{SiC}^{NR} = \mu_{Si}^{\text{bulk}} + \mu_C^{\text{bulk}} - \Delta H_f. \quad (3)$$

μ_{Si} and μ_C characterize the growth conditions: in the Si-rich limit, the system is assumed to be in thermodynamic equilibrium with the bulk Si and $\mu_{Si} = \mu_{Si}^{\text{bulk}}$ (in this case, $\mu_C = \mu_{SiC}^{NR} - \mu_{Si}^{\text{bulk}}$); in the C-rich limit, $\mu_C = \mu_C^{\text{bulk}}$ and $\mu_{Si} = \mu_{SiC}^{NR} - \mu_C^{\text{bulk}}$. We considered diamond structures in the calculation of μ_C^{bulk} and μ_{Si}^{bulk} . ΔH_f is the heat of formation of the SiCNR. We found $\Delta H_f = -1.214$ eV, which compares well with the heat of formation of SiC nanotubes $[-1.2$ and -1.3 eV for (6,6) and (8,0) SiC nanotubes, respectively].²³ To check the quality of the pseudopotentials and computational parameters which are used in the present calculations, we also calculated the heat of formation of bulk 3C-SiC; we found $\Delta H_f = 0.679$ eV, which is in good agreement with the experimental value of 0.72 eV.²⁴

III. RESULTS AND DISCUSSION

First, we examined the electronic and magnetic properties of pristine 6Z-SiCNR. The electronic band structure [Fig. 2(a)] and the density of states [Fig. 3(a)] show that 6Z-SiCNR

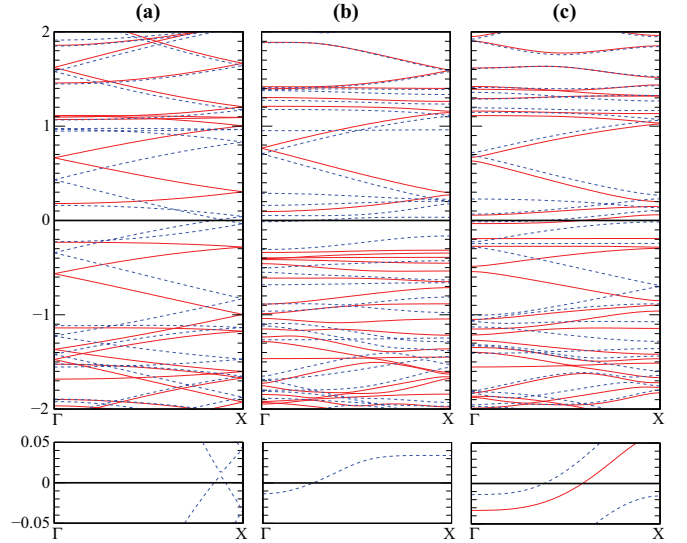


FIG. 2. (Color online) Electronic band structure of (a) pristine 6Z-SiCNR, (b) $V_{Si}/6Z\text{-SiCNR}$, and (c) $V_C/6Z\text{-SiCNR}$. The band structure of each system is presented in two ranges: $|E - E_F| \leq 2.0$ eV (top panel) and $|E - E_F| \leq 0.05$ eV (bottom panel). Solid red and dashed blue lines indicate spin-up and spin-down bands, respectively. The Fermi level is set to zero and is indicated by the solid black line.

exhibits half-metallic behavior: the spin-up channel is semi-conducting (with a direct band gap of about 0.41 eV at the Γ point), whereas the spin-down channel is metallic. As can be

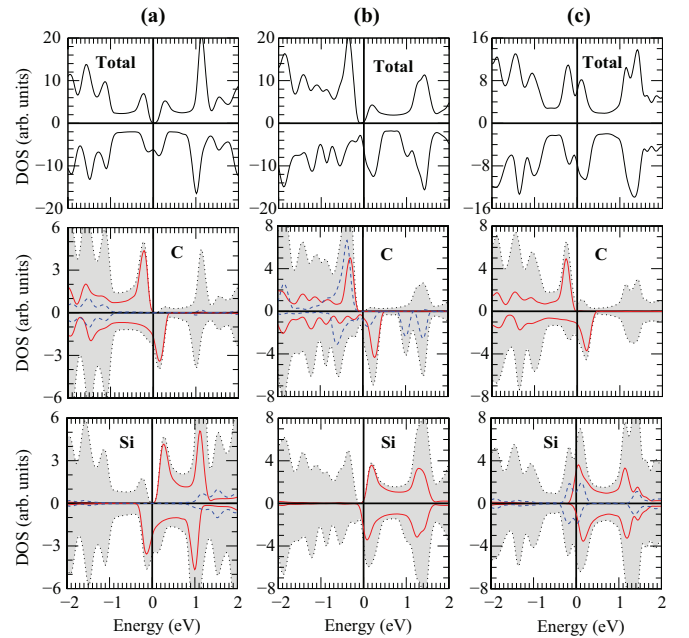


FIG. 3. (Color online) Density of states (DOS) of (a) pristine 6Z-SiCNR, (b) $V_{Si}/6Z\text{-SiCNR}$, and (c) $V_C/6Z\text{-SiCNR}$. In the middle (bottom) panels the shaded regions indicate the DOS of the C (Si) atoms; solid red lines show p orbitals of the edge C (Si) atoms, and dashed blue lines show p orbitals of the three C (Si) atoms around Si^I (C^I) in (a) and V_{Si}^I (V_C^I) in (b) [(c)]. The Fermi level is set to zero and is indicated by the solid black line. We considered a Gaussian broadening of 0.1 eV for the DOS diagrams.

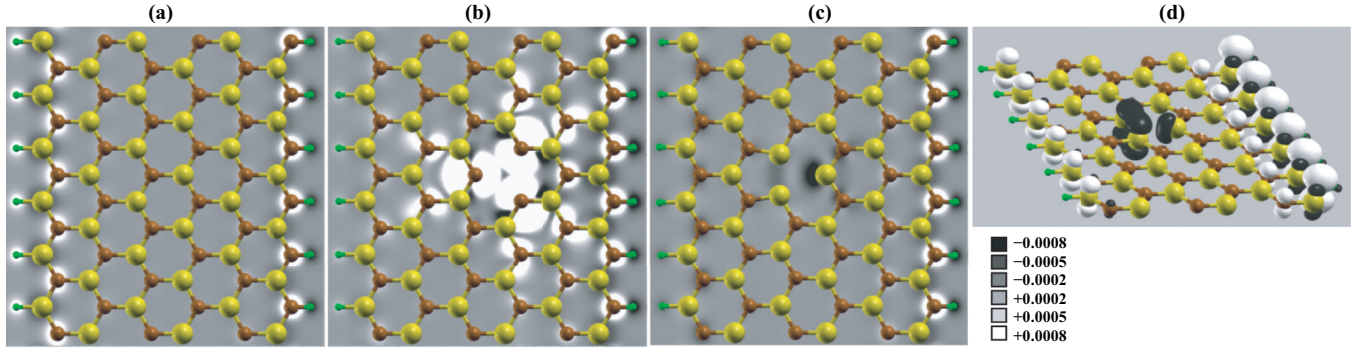


FIG. 4. (Color online) Contour plot of spin-density distribution of (a) pristine 6Z-SiCNR, (b) $V_{\text{Si}}/6\text{Z-SiCNR}$, and (c) $V_{\text{C}}/6\text{Z-SiCNR}$. (d) For comparison purposes the spin-density isosurface of $V_{\text{C}}/6\text{Z-SiCNR}$ system is also shown at $8.0 \times 10^{-4} e/\text{bohr}^3$.

seen in Fig. 3(a), the partially occupied spin-down electronic state is mainly composed of p orbitals of the edge C and Si atoms. The 6Z-SiCNR also has a very small magnetic moment, about $0.03\mu_B$ per supercell. Our results are in agreement with a previous theoretical work¹¹ which reports magnetic moment of $0.023\mu_B$ per cell in 6Z-SiCNR and predicts half-metallicity in Z-SiCNRs narrower than 4 nm. The spin-density distribution of pristine 6Z-SiCNR [Fig. 4(a)] shows that the magnetic moments are mainly localized on the edge atoms, and their orientations are parallel at each edge and antiparallel between the two edge atoms. Each edge C (Si) atom has a local magnetic moment of about $0.16\mu_B$ ($-0.17\mu_B$), while the total magnetic moment of the other C (Si) atoms is about $0.29\mu_B$ ($-0.20\mu_B$). The strong contribution of the edge C and Si atoms to the magnetization of 6Z-SiCNR can also be seen in Fig. 3(a): the spin-up p states of the edge C atoms are completely occupied, whereas the spin-down states are partially occupied; for the edge Si atoms, we note that their spin-down p states have a small occupation, whereas their spin-up states are empty.

A. Single vacancy

We have investigated the effects of vacancies on the electronic and magnetic properties of 6Z-SiCNR. We considered initially one V_{Si} or V_{C} per supercell, which corresponds to a defect concentration of 2.78%. V_{Si} and V_{C} were created at the center of the nanoribbon by removing Si and C atoms labeled 1 and 7 (see Fig. 1), respectively. The presence of a single V_{Si} and V_{C} induces magnetic moments of $4.19\mu_B$ and $1.19\mu_B$ per supercell, respectively. We found that one V_{Si} per supercell leads to an increase, from $0.03\mu_B$ to $4.19\mu_B$, in the magnetic moment of 6Z-SiCNR, which is similar to that reported for SiC sheets and A-SiCNRs in previous *ab initio* studies where a single V_{Si} was found to induce a large magnetic moment of $4.0\mu_B$ in nonmagnetic SiC sheets^{10,16} and A-SiCNRs.¹⁰ On the other hand, V_{C} appears to play different roles in the magnetism of Z-SiCNRs, A-SiCNRs, and SiC sheets: while we found a magnetic moment of $1.19\mu_B$ induced by a single V_{C} in 6Z-SiCNRs, recent theoretical works have reported that the presence of a single V_{C} does not give rise to any magnetic moment in SiC sheets^{10,16} and A-SiCNRs.¹⁰ This suggests that 6Z-SiCNR, where magnetism can be tuned either by Si or C vacancies, can be a promising candidate for spintronics. In the following paragraphs we will discuss the origin of the magnetism in the $V_{\text{C}}/6\text{Z-SiCNR}$ system,

showing that it is almost entirely due to the magnetization of the edge C atoms. As we have shown, $V_{\text{C}}/6\text{Z-SiCNR}$ system is magnetic. To be more confident about the magnetism of $V_{\text{C}}/6\text{Z-SiCNR}$, we also carried out calculations using a large supercell (156 atoms) and created a carbon vacancy and relaxed all the atoms. Interestingly, we found that this system also leads to magnetism in SiCNR and the magnetism is mainly originated from the edge C atoms. Therefore, we confirm that the magnetism of $V_{\text{C}}/6\text{Z-SiCNR}$ is not due to structural relaxation but to the C edge atoms.

Figure 4(b) presents the distribution of spin density in 6Z-SiCNR with a single V_{Si} ($V_{\text{Si}}/6\text{Z-SiCNR}$). We note that the spin density is mostly localized around the vacancy and on the edge C atoms: the local magnetic moment of each edge C atom varies from $0.233\mu_B$ to $0.287\mu_B$, while the three C atoms surrounding the V_{Si} have magnetic moments of $0.435\mu_B$, $0.865\mu_B$, and $0.865\mu_B$. This can also be seen in Fig. 3(b), which shows that the spin-up p states of the edge C atoms and of the C atoms around the V_{Si} are completely occupied, whereas their spin-down states are partially occupied. The presence of a single V_{Si} destroys the complete occupation of p orbitals of the C atoms surrounding the vacancy, giving rise to empty spin-down states above the Fermi level. The local magnetic moment of each edge Si atom is about $-0.04\mu_B$, which suggests that the C atoms and the Si atoms couple antiferromagnetically. Such types of magnetic coupling are also observed in the other defect-driven magnetic systems.^{25–28} The smaller magnetization of the edge Si atoms in $V_{\text{Si}}/6\text{Z-SiCNR}$ compared to that observed in pristine 6Z-SiCNR (where we found magnetic moments of about $-0.17\mu_B$ for each edge Si atom) can also be seen in Fig. 3; by comparing Figs. 3(a) and 3(b) we note that the occupation of spin-down p states of the edge Si atoms is larger in pristine 6Z-SiCNR [Fig. 3(a)] than in $V_{\text{Si}}/6\text{Z-SiCNR}$ [Fig. 3(b)]. Such changes in the occupation of spin-down p states also decrease the exchange splitting of the edge Si atoms, which results in small magnetic moments. On the other hand, the exchange splitting is large in the edge C atoms.

In the $V_{\text{C}}/6\text{Z-SiCNR}$ system we found that the magnetic moment comes mainly from the edge C atoms [see Figs. 3(c), 4(c), and 4(d)]. Each edge C atom has a magnetic moment of about $0.20\mu_B$, whereas the Si atoms surrounding the V_{C} have magnetic moments of $-0.04\mu_B$, $-0.07\mu_B$, and $-0.07\mu_B$. It is interesting to see that both the Si and C atoms

are isoelectronic, where one could expect the same magnetism in both Si and C vacancies. However, we observed a quite different nature of magnetism; e.g., atoms surrounding V_{Si} (V_{C}) have large (small) local positive (negative) magnetic moments. This behavior can be understood due to different natures of the wave functions of the p orbitals. Usually, cation/anion vacancies induce spin-positive polarization on the surrounding atoms, but $V_{\text{C}}/6\text{Z-SiCNR}$ shows the spin density of the Si atoms is larger in the spin-down states.

The electronic band structure [Fig. 2(b)] and the density of states [Fig. 3(b)] of $V_{\text{Si}}/6\text{Z-SiCNR}$ show that the presence of a single V_{Si} does not affect the half-metallic character of pristine 6Z-SiCNR ; in this system, the spin-down channel is metallic, whereas the spin-up channel is semiconducting, with an indirect band gap of 0.41 eV. In contrast, we found that a single V_{C} transforms the half-metallic 6Z-SiCNR into a metallic system [see Figs. 2(c) and 3(c)]. Note that the half-metallicity is mainly destroyed by the p orbitals of the edge atoms and the atoms surrounding the vacancy. Figure 3(c) shows that the partially occupied spin-up electronic state consists mainly of p orbitals of the edge Si atoms and of the Si atoms surrounding the vacancy, with no contribution from p orbitals of the edge C atoms. This shows that the electronic structure can easily be tuned either by creating holes (simply based on electron counting), i.e., V_{C} , or by electron doping, i.e., N doping.¹⁴ We attribute this electronic phase transition to hole doping.²⁹ The electronic phase transition is mainly due to Si p orbitals which are delocalized compared with the C p orbitals. The total densities of states in Figs. 3(a)–3(c) show that the population of density of states (within an energy range of ± 0.5 eV) in spin-up states of electrons increases as we move from the pristine to the V_{C} system. This increment is mainly caused by the edge Si atoms and Si atoms surrounding the vacancy.

The energetic stability of single V_{Si} and V_{C} in 6Z-SiCNR was examined by comparing E_f of the $V_{\text{Si}}/6\text{Z-SiCNR}$ and $V_{\text{C}}/6\text{Z-SiCNR}$ systems. Our results for E_f , obtained using Eq. (1), are listed in Table I. As can be seen, the occurrence of a single V_{C} in Z-SiCNRs is energetically favored over single V_{Si} . This behavior is similar to that observed in bulk SiC,³⁰ SiC sheet,¹⁶ and SiC nanotubes,³¹ where V_{C} has also been reported to be more stable than V_{Si} .

B. Double vacancies

In order to study the interactions of V_{Si} and V_{C} , we also investigated the presence of two vacancies per supercell. Since V_{Si} appears to play a more important role on the magnetism of Z-SiCNR than V_{C} , we considered configurations with (i) two Si vacancies, $V_{\text{Si}}^1 V_{\text{Si}}^i$, and (ii) Si + C vacancies, $V_{\text{Si}}^1 V_{\text{C}}^i$. The index i in V_X^i indicates the position of the X vacancy (see Fig. 1).

The formation energies and the total magnetic moments per supercell for $V_{\text{Si}}^1 V_{\text{Si}}^i$ and $V_{\text{Si}}^1 V_{\text{C}}^i$ in 6Z-SiCNR are presented in Table I [the defect formation energies were calculated using Eq. (2)]. These results show that the presence of double Si vacancies can give rise to large magnetic moments in Z-SiCNRs (for example, we found magnetic moments of about $3.9\mu_B$ in $V_{\text{Si}}^1 V_{\text{Si}}^3/6\text{Z-SiCNR}$ and $V_{\text{Si}}^1 V_{\text{Si}}^4/6\text{Z-SiCNR}$). However, the formation of these magnetic $V_{\text{Si}}^1 V_{\text{Si}}^i/6\text{Z-SiCNR}$ systems is quite unlikely since they have very high formation energies

TABLE I. The calculated formation energies in Si-rich and C-rich conditions and total magnetic moments per supercell M for single (V_{Si} and V_{C}) and double ($V_{\text{Si}}^1 V_{\text{Si}}^i$ and $V_{\text{Si}}^1 V_{\text{C}}^i$) vacancies in 6Z-SiCNR . The index i in V_X^i indicates the position of the vacancy (see Fig. 1). Single V_{Si} (V_{C}) is localized on site 1 (7).

	M (units of μ_B)	Formation energies (eV)	
		Si rich	C rich
Single vacancy			
V_{Si}	4.19	8.053	9.267
V_{C}	1.19	4.419	3.205
Two Si vacancies			
$V_{\text{Si}}^1 V_{\text{Si}}^2$	−0.02	2.806	4.020
$V_{\text{Si}}^1 V_{\text{Si}}^3$	3.86	7.836	9.050
$V_{\text{Si}}^1 V_{\text{Si}}^4$	3.88	7.439	8.653
$V_{\text{Si}}^1 V_{\text{Si}}^5$	2.99	7.999	9.213
$V_{\text{Si}}^1 V_{\text{Si}}^6$	3.81	7.481	8.695
Si + C vacancies			
$V_{\text{Si}}^1 V_{\text{C}}^7$	0.06	6.764	6.764
$V_{\text{Si}}^1 V_{\text{C}}^8$	1.34	4.682	4.682
$V_{\text{Si}}^1 V_{\text{C}}^9$	0.14	8.149	8.149
$V_{\text{Si}}^1 V_{\text{C}}^{10}$	1.91	10.214	10.214
$V_{\text{Si}}^1 V_{\text{C}}^{11}$	1.99	11.198	11.198
$V_{\text{Si}}^1 V_{\text{C}}^{12}$	−0.93	3.842	3.842
$V_{\text{Si}}^1 V_{\text{C}}^{13}$	−0.57	4.486	4.486
$V_{\text{Si}}^1 V_{\text{C}}^{14}$	4.03	12.005	12.005
$V_{\text{Si}}^1 V_{\text{C}}^{15}$	2.30	9.281	9.281
$V_{\text{Si}}^1 V_{\text{C}}^{16}$	3.47	11.198	11.198

(see Table I). It is also noticeable that the $V_{\text{Si}}-V_{\text{Si}}$ interactions reduce the magnetic moments compared with the single- V_{Si} system. The formation of $V_{\text{Si}}^1 V_{\text{C}}^i$, which also induces magnetic moments in 6Z-SiCNRs , is energetically favorable when compared with a single V_{Si} and double $V_{\text{Si}}^1 V_{\text{Si}}^i$. For instance, $V_{\text{Si}}^1 V_{\text{C}}^8$, $V_{\text{Si}}^1 V_{\text{C}}^{12}$, and $V_{\text{Si}}^1 V_{\text{C}}^{13}$ have formation energies smaller than 4.7 eV and induce magnetic moments of $1.34\mu_B$, $-0.93\mu_B$, and $-0.57\mu_B$ in 6Z-SiCNR , respectively (see Table I). It is worth mentioning here that recent experimental works have shown that defects created in 6H-SiC bulk by neutron or ion irradiations are mainly formed by $V_{\text{Si}} V_{\text{C}}$ divacancies and induce room-temperature magnetism in diamagnetic SiC crystals.^{17,18} Such experimental results illustrate that $V_{\text{Si}} V_{\text{C}}$ are the stable intrinsic defects in 6H-SiC , and we also found that $V_{\text{Si}} V_{\text{C}}$ -type defects are easily formed in NR compared with V_{Si} . Table I clearly shows that $V_{\text{Si}} V_{\text{C}}$ divacancies have an oscillatory-type magnetism where the magnetic moments oscillate and strongly depend on the location of the C vacancy. This rise and fall of magnetic moments in $V_{\text{Si}} V_{\text{C}}$ divacancies system is similar to bulk SiC crystal.¹⁸ Comparing the defects, we note that this rise and fall of magnetic moments is suppressed by filling the C vacant site with N, which will be discussed in the following paragraphs.

Figures 5 and 6 present the electronic band structures (Fig. 5) and the spin-density distributions (Fig. 6) for some representative magnetic systems with two vacancies per supercell, viz., $V_{\text{Si}}^1 V_{\text{Si}}^4/6\text{Z-SiCNR}$ and $V_{\text{Si}}^1 V_{\text{C}}^8/6\text{Z-SiCNR}$. As can be

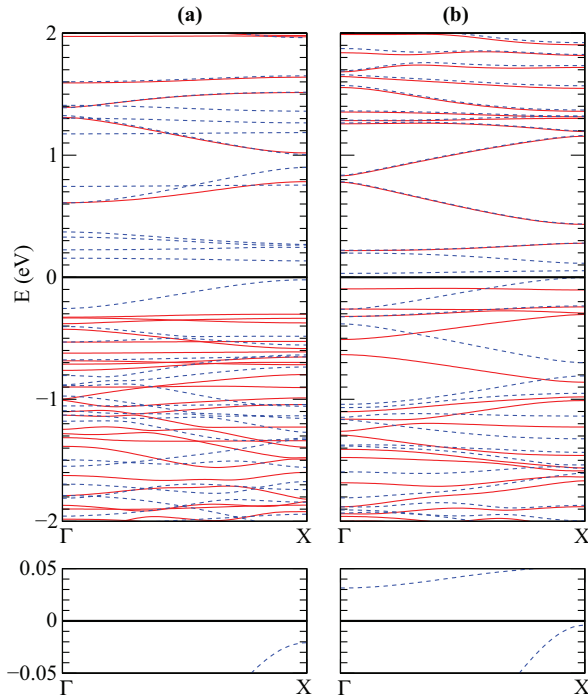


FIG. 5. (Color online) Electronic band structure of the (a) $V_{\text{Si}}^1 V_{\text{Si}}^4 / 6\text{Z-SiCNR}$ and (b) $V_{\text{Si}}^1 V_{\text{C}}^8 / 6\text{Z-SiCNR}$ systems. The band structure of each system is presented in two ranges: $|E - E_F| \leq 2.0$ eV (top panel) and $|E - E_F| \leq 0.05$ eV (bottom panel). Solid red and dashed blue lines indicate spin-up and spin-down bands, respectively. The Fermi level is set to zero and is indicated by the solid black line.

seen in Fig. 5, both $V_{\text{Si}}^1 V_{\text{Si}}^4 / 6\text{Z-SiCNR}$ and $V_{\text{Si}}^1 V_{\text{C}}^8 / 6\text{Z-SiCNR}$ systems exhibit semiconducting character, with band gaps of 0.91 eV (0.15 eV) and 0.31 eV (0.04 eV) for the spin-up (spin-down) channels of $V_{\text{Si}}^1 V_{\text{Si}}^4 / 6\text{Z-SiCNR}$ and $V_{\text{Si}}^1 V_{\text{C}}^8 / 6\text{Z-SiCNR}$, respectively. These results indicate that the presence of double vacancies ($V_{\text{Si}} V_{\text{Si}}$ or $V_{\text{Si}} V_{\text{C}}$) can transform half-metallic Z-SiCNRs into semiconducting systems. As we increased the vacancy concentrations to $\sim 5.56\%$ (in double-vacancy systems), half-metal to semiconductor phase transition was observed. This phase transition is due to holes which are localized on the dangling bonds around the vacancies and also have some contribution from the edge atoms. Usually, when a vacancy is created, some states around the Fermi level, which are occupied in the pristine system, are removed, and

such a removal of states creates holes around the Fermi energy which changes the electronic structure of the material.^{28,32-34} In Fig. 2(a) we see some states just below the Fermi level; however, when a Si vacancy is created, some missing states (near the X point) can be seen [see Fig. 2(b)]. Similar holes were also observed in the SiC monolayer with a Si vacancy.¹⁶ In 6Z-SiCNR, the electronic and magnetic structures are modified not only by the atoms surrounding a vacancy but also by the edge atoms¹² [also see Fig. 4(d)]. This makes 6Z-SiCNR different from other materials where magnetism is caused by vacancies. Our results teach us that the electronic band structure of Z-SiCNRs can easily be engineered by V_{Si} or V_{C} . The distribution of spin density in $V_{\text{Si}}^1 V_{\text{Si}}^4 / 6\text{Z-SiCNR}$ [Fig. 6(a)] shows that the magnetic moments are mostly localized on the C atoms surrounding the Si vacancies. The C atoms around V_{Si}^4 have magnetic moments of $0.23\mu_B$, $0.88\mu_B$, and $0.88\mu_B$, while the C atoms around V_{Si}^1 have magnetic moments of $1.06\mu_B$, $0.91\mu_B$, and $0.91\mu_B$. On the other hand, in $V_{\text{Si}}^1 V_{\text{C}}^8 / 6\text{Z-SiCNR}$ [Fig. 6(b)] we observe that the C atoms surrounding V_{Si}^1 move to form new C-C bonds; thus the dangling bonds of these atoms are recombined, leading to almost zero local magnetic moments. In this system the magnetic moments are mostly localized on edge C atoms: we found magnetic moments between $0.16\mu_B$ and $0.21\mu_B$ for each edge C atom.

As we can see, in the $V_{\text{Si}}^1 V_{\text{Si}}^4$ system one of the Si vacancies lies close to the edge [see Fig. 6(a)]. To ignore the edge effect (if it has some effect on the electronic and magnetic properties of SiCNRs) we also carried out some test calculations for $V_{\text{Si}}^1 V_{\text{Si}}^4$ by considering a large supercell (12Z-SiCNR). In this case, we kept the same distance between V_{Si}^1 and V_{Si}^4 that we used in the small supercell. The calculated magnetic moment (per supercell and per Si vacancy) is $\sim 3.50\mu_B$. We must note that the small difference in the magnetic moments ($3.88\mu_B$ in 6Z-SiCNR and $3.50\mu_B$ in 12Z-SiCNR) is due to the difference in the total number of atoms in the two NRs.

Our studied systems induce magnetism due to vacancies and the magnetic moments are not carried by conventional magnetic elements (Fe, Ni, or Co) where one can also calculate the true ground magnetic state of a material. Thus, either V_{Si} or V_{C} in 6Z-SiCNR distorts the bond lengths, which can give different atomic magnetic moments at different atomic sites. To get a qualitative analysis of magnetism in 6Z-SiCNR, we also carried out calculations by considering the antiferromagnetic (AFM) and ferromagnetic (FM) types of $V_{\text{Si}} V_{\text{Si}}$ interactions. We studied the FM and AFM interactions between the Si vacancies by considering the FM and AFM coupling between the atoms surrounding the vacancies. We solved the Kohn-Sham equation³⁵ in the FM and AFM states and compared their total energies to get the ground-state magnetic structure. We found that the FM state is more stable than the AFM state by ~ 0.14 eV per cell, which is much larger than room temperature. Therefore, room-temperature magnetism is expected in 6Z-SiCNR. The FM stability against AFM was also confirmed through fixed-moment calculations. It is emphasized that this kind of magnetic coupling strongly depends on the distance between the vacancies.^{28,36} Some of the selected cases were also reinvestigated using a large supercell to consider the FM/AFM coupling between the Si vacancies. We noticed that FM is still expected.

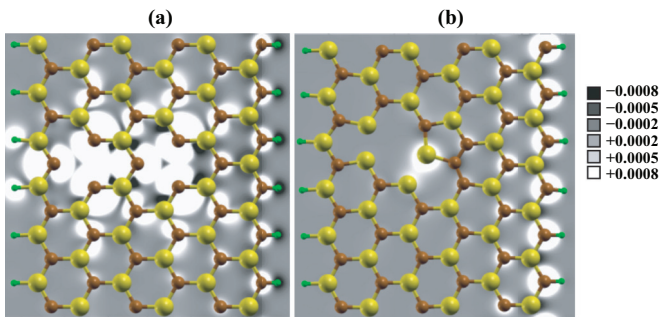


FIG. 6. (Color online) Spin-density distribution in (a) $V_{\text{Si}}^1 V_{\text{Si}}^4 / 6\text{Z-SiCNR}$ and (b) $V_{\text{Si}}^1 V_{\text{C}}^8 / 6\text{Z-SiCNR}$.

TABLE II. Calculated formation energies in Si-rich and C-rich conditions and total magnetic moments per supercell M for 6Z-SiCNR with a single V_{Si} and B (N) at the Si (C) site. The index i in $V_{\text{Si}}^1 B_{\text{Si}}^i$ and $V_{\text{Si}}^1 N_{\text{C}}^i$ indicates the substitutional Si or C site for the B or N impurity (see Fig. 1).

		Formation energies (eV)	
	M (units of μ_B)	Si rich	C rich
B at Si site			
$V_{\text{Si}}^1 B_{\text{Si}}^2$	2.86	6.904	9.332
$V_{\text{Si}}^1 B_{\text{Si}}^3$	4.90	8.235	10.663
$V_{\text{Si}}^1 B_{\text{Si}}^4$	2.24	7.058	9.486
$V_{\text{Si}}^1 B_{\text{Si}}^5$	4.61	8.611	11.039
$V_{\text{Si}}^1 B_{\text{Si}}^6$	4.81	7.565	9.993
N at C site			
$V_{\text{Si}}^1 N_{\text{C}}^7$	0.63	5.133	5.133
$V_{\text{Si}}^1 N_{\text{C}}^8$	3.06	8.246	8.246
$V_{\text{Si}}^1 N_{\text{C}}^9$	3.07	7.662	7.662
$V_{\text{Si}}^1 N_{\text{C}}^{10}$	3.01	8.583	8.583
$V_{\text{Si}}^1 N_{\text{C}}^{11}$	2.38	7.188	7.188
$V_{\text{Si}}^1 N_{\text{C}}^{12}$	3.12	7.417	7.417
$V_{\text{Si}}^1 N_{\text{C}}^{13}$	3.12	7.682	7.682
$V_{\text{Si}}^1 N_{\text{C}}^{14}$	3.09	7.660	7.660
$V_{\text{Si}}^1 N_{\text{C}}^{15}$	3.04	8.212	8.212
$V_{\text{Si}}^1 N_{\text{C}}^{16}$	2.95	8.956	8.956

C. Interaction of vacancies with substitutional B and N impurities

Among the defects investigated, single V_{Si} was found to induce the largest magnetic moment (see Table I), which suggests that this defect can play an important role in the magnetism of Z-SiCNR. However, the formation of single V_{Si} in Z-SiCNR is expected to be energetically unfavorable due to its high defect formation energy. To explore this system, we need to reduce its defect formation energy, and for this reason the role of substitutional B and N impurities in 6Z-SiCNR is also investigated. Since Costa and Morbec¹⁴ recently reported that B prefers to occupy a Si site whereas N preferentially substitutes a C atom, we examined configurations with single V_{Si} at position 1 and (i) B at Si site $i = 2, \dots, 6$ (see Fig. 1), $V_{\text{Si}}^1 B_{\text{Si}}^i/6\text{Z-SiCNR}$, or (ii) N at C site $i = 7, \dots, 16$, $V_{\text{Si}}^1 N_{\text{C}}^i/6\text{Z-SiCNR}$. The energetic stability of these systems was determined from their formation energies,

$$E_f = E[V_{\text{Si}}^1 Y_X^i/6\text{Z-SiCNR}] - E[6\text{Z-SiCNR}] + \mu_{\text{Si}} + \mu_X - \mu_Y, \quad (4)$$

where $X = \text{Si}$ and $Y = \text{B}$ for the $V_{\text{Si}}^1 B_{\text{Si}}^i/6\text{Z-SiCNR}$ systems and $X = \text{C}$ and $Y = \text{N}$ for $V_{\text{Si}}^1 N_{\text{C}}^i/6\text{Z-SiCNR}$. We used α -boron bulk and N_2 molecules to obtain B and N chemical potentials, respectively.

The formation energies (in Si-rich and C-rich conditions) and the total magnetic moments per supercell for $V_{\text{Si}}^1 B_{\text{Si}}^i/6\text{Z-SiCNR}$ and $V_{\text{Si}}^1 N_{\text{C}}^i/6\text{Z-SiCNR}$ systems are listed in Table II. From these results, we note that some $V_{\text{Si}}^1 B_{\text{Si}}^i/6\text{Z-SiCNR}$ and $V_{\text{Si}}^1 N_{\text{C}}^i/6\text{Z-SiCNR}$ configurations are energetically

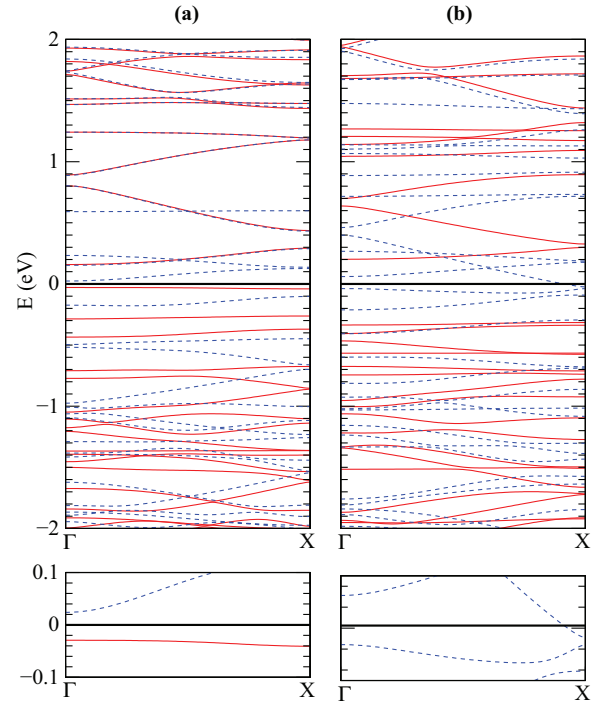


FIG. 7. (Color online) Electronic band structure of the (a) $V_{\text{Si}}^1 B_{\text{Si}}^4/6\text{Z-SiCNR}$ and (b) $V_{\text{Si}}^1 N_{\text{C}}^8/6\text{Z-SiCNR}$ systems. The band structure of each system is presented in two ranges: $|E - E_F| \leq 2.0$ eV (top panel) and $|E - E_F| \leq 0.1$ eV (bottom panel). Solid red and dashed blue lines indicate spin-up and spin-down bands, respectively. The Fermi level is set to zero and is indicated by the solid black line.

more favorable than $V_{\text{Si}}^1/6\text{Z-SiCNR}$ (for example, $V_{\text{Si}}^1 B_{\text{Si}}^2$ and $V_{\text{Si}}^1 B_{\text{Si}}^4$ are more favorable than $V_{\text{Si}}^1/6\text{Z-SiCNR}$ at Si-rich and stoichiometric conditions). This indicates that one B atom occupying a Si site as well as one N atom occupying a C site can stabilize a single V_{Si} in Z-SiCNR. In addition, we observe that the $V_{\text{Si}}^1 B_{\text{Si}}^i/6\text{Z-SiCNR}$ and $V_{\text{Si}}^1 N_{\text{C}}^i/6\text{Z-SiCNR}$ systems have large magnetic moments (except for $V_{\text{Si}}^1 N_{\text{C}}^7/6\text{Z-SiCNR}$, whose magnetic moment is $0.63\mu_B$). This smallest magnetic moment can be expected in $V_{\text{Si}}^1 N_{\text{C}}^7/6\text{Z-SiCNR}$ based on the separation between V_{Si}^1 and N_{C}^7 , which is 1.81\AA . We found magnetic moments larger than $2\mu_B$ for all other configurations with $V_{\text{Si}} B_{\text{Si}}$ or $V_{\text{Si}} N_{\text{C}}$. However, the $V_{\text{Si}} N_{\text{C}}/6\text{Z-SiCNR}$ systems are more interesting than $V_{\text{Si}} B_{\text{Si}}/6\text{Z-SiCNR}$. When N is doped at the vacant C site in $V_{\text{Si}} V_{\text{C}}/6\text{Z-SiCNR}$, then the C- V_{Si} -type interactions increase the magnetization. So we believe that N in 6Z-SiCNR has two roles; it not only stabilizes the intrinsic defects but also increases the magnetization of 6Z-SiCNR. From all the thermodynamic data, it is summarized that those systems with low magnetic moments have smaller formation energies.

The electronic band structures for the $V_{\text{Si}}^1 B_{\text{Si}}^4/6\text{Z-SiCNR}$ and $V_{\text{Si}}^1 N_{\text{C}}^8/6\text{Z-SiCNR}$ systems are depicted in Fig. 7. As can be seen, the semiconducting character of $V_{\text{Si}}^1 V_{\text{Si}}^4/6\text{Z-SiCNR}$ is maintained when B is doped at the vacant Si^4 site: both the spin-up and spin-down channels of $V_{\text{Si}}^1 B_{\text{Si}}^4/6\text{Z-SiCNR}$ [Fig. 7(a)] are semiconducting with band gaps of 0.19 and 0.13 eV, respectively. However, the presence of a N atom occupying a vacant C site can lead semiconducting $V_{\text{Si}} V_{\text{C}}/6\text{Z-SiCNR}$ systems to turn into half-metallic ones.

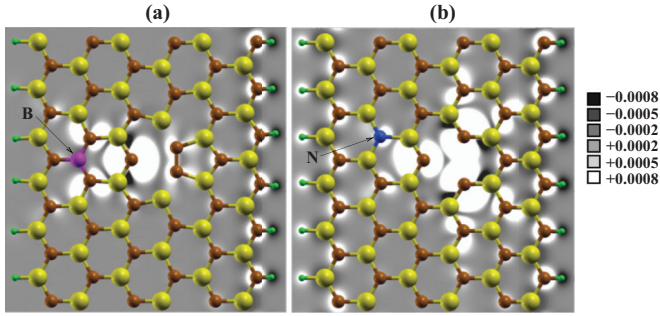


FIG. 8. (Color online) Spin-density distribution in (a) $V_{\text{Si}}^1 B_{\text{Si}}^4 / 6Z\text{-SiCNR}$ and (b) $V_{\text{Si}}^1 N_{\text{C}}^8 / 6Z\text{-SiCNR}$.

Figure 7(b) shows that the $V_{\text{Si}}^1 N_{\text{C}}^8 / 6Z\text{-SiCNR}$ system is a half metal: while its spin-down channel is metallic, the spin-up channel is semiconducting, with a band gap of 0.52 eV. It is interesting to note that $V_{\text{Si}}^1 B_{\text{Si}}^i / 6Z\text{-SiCNR}$ remains semiconducting, consistent with our picture of hole-induced electronic phase transition. When a vacant V_{Si}^i site is filled with boron in the bivacancy $V_{\text{Si}}^1 V_{\text{Si}}^i$ system, it means that we are filling the empty orbitals (holes) created by V_{Si}^i . However, the $V_{\text{Si}}^1 B_{\text{Si}}^4$ system has sufficient holes compared with the pristine 6Z-SiCNRs and remains semiconducting, as expected. Boron mainly induces impurity states near the Fermi level in both spin-up and spin-down channels [see Fig. 7(a)]. On the other hand when N is doped at the V_{C}^i site in the $V_{\text{Si}}^1 V_{\text{C}}^i$ system, electrons are injected into $V_{\text{Si}}^1 V_{\text{C}}^i$, and we have sufficient electrons to fill the empty states. These electrons are mostly in the spin-down states and have sufficient energy to cross the Fermi energy, and $V_{\text{Si}}^1 N_{\text{C}}^8$, e.g., transforms to a half metal compared with $V_{\text{Si}}^1 V_{\text{C}}^8$. Such reentrant behavior of 6Z-SiCNR is ascribed to electron doping.

The spin-density maps presented in Fig. 8 show that the presence of a B (N) impurity filling a vacant Si (C) site strongly affects the distribution of spin density in $V_{\text{Si}}^1 V_{\text{Si}}^i / 6Z\text{-SiCNR}$ ($V_{\text{Si}}^1 V_{\text{C}}^i / 6Z\text{-SiCNR}$). When a B atom occupies the vacant Si^4 site [see Fig. 8(a)], the dangling bonds of the C atoms surrounding V_{Si}^4 are saturated, leading the magnetic moments of these C atoms to decrease from $0.23\mu_B$, $0.88\mu_B$, and $0.88\mu_B$ in $V_{\text{Si}}^1 V_{\text{Si}}^4 / 6Z\text{-SiCNR}$ to $0.004\mu_B$, $0.039\mu_B$, and $0.039\mu_B$ in $V_{\text{Si}}^1 B_{\text{Si}}^4 / 6Z\text{-SiCNR}$. In addition, two of the three C atoms surrounding V_{Si}^1 move closer to each other to form a C-C bond, which leads to a decrease (from $0.91\mu_B$ in $V_{\text{Si}}^1 V_{\text{Si}}^4 / 6Z\text{-SiCNR}$ to $0.02\mu_B$ in $V_{\text{Si}}^1 B_{\text{Si}}^4 / 6Z\text{-SiCNR}$) in the magnetic moments of these atoms; the third C atom surrounding V_{Si}^1 (labeled 7 in Fig. 1) has a magnetic moment of about $0.80\mu_B$. On the other hand, Fig. 8(b) shows that bond reconstructions in the vicinity of V_{Si}^1 , which were observed in $V_{\text{Si}}^1 V_{\text{C}}^8 / 6Z\text{-SiCNR}$, do not occur when N is doped at the vacant C^8 site. Such a process results in an increase in the local magnetic moments of the C atoms surrounding V_{Si}^1 (we found magnetic moments of $0.17\mu_B$, $0.87\mu_B$, and $0.90\mu_B$ in these atoms) and, consequently, in an

increase in the magnetization of the system ($V_{\text{Si}}^1 V_{\text{C}}^8 / 6Z\text{-SiCNR}$ has a magnetic moment of $1.34\mu_B$, while $V_{\text{Si}}^1 N_{\text{C}}^8 / 6Z\text{-SiCNR}$ has a magnetic moment of $3.06\mu_B$).

Before summarizing our DFT calculations, we would like to comment on the shortcomings of DFT-PBE calculations. It is an accepted fact in the DFT community that DFT local-density approximation (LDA)/GGA calculations do not reproduce the experimental band gap of insulators and semiconductors. The band gap of SiC can be recovered using either LDA/GGA + U or Hedin's GW approximation (GW) or self-interaction correction (SIC) calculations.^{37–39} However, there are DFT + U calculations which clearly demonstrate that defect (vacancy)-induced magnetism does not change using either DFT or DFT + U calculations.^{40–42} Indeed, DFT + U calculations will affect the electronic structure of materials. We believe that DFT + U /SIC/GW calculations will not change the magnetism of SiC NRs.

IV. CONCLUSIONS

Ab initio calculations were performed to investigate the magnetism of pristine and defective Z-SiCNRs. Single (V_{Si} and V_{C}) and double ($V_{\text{Si}} V_{\text{Si}}$ and $V_{\text{Si}} V_{\text{C}}$) vacancies were considered to probe the electronic structures of Z-SiCNRs. Our results indicate that these native defects can induce large magnetic moments in Z-SiCNRs. While the half-metallic character of the pristine Z-SiCNR is maintained in the presence of a single V_{Si} , we found that a single V_{C} leads to a transition from half-metallic to metallic behavior in Z-SiCNRs, and double $V_{\text{Si}} V_{\text{Si}}$ and $V_{\text{Si}} V_{\text{C}}$ can transform half-metallic Z-SiCNRs into semiconducting systems. Such electronic phase transitions were discussed in terms of hole doping. Single V_{Si} induced the largest magnetic moment among the defects investigated, but this defect has higher formation energy and is energetically unfavorable when compared with the single V_{C} and double $V_{\text{Si}} V_{\text{C}}$. The ferromagnetic ground state was shown to be more stable than the antiferromagnetic state; therefore room-temperature ferromagnetism was also speculated in defective Z-SiCNRs. To reduce the defect formation energy of single V_{Si} and realize it experimentally, the interactions of substitutional B and N impurities with this native defect were also studied. We found that a B atom substituting a Si atom as well as a N atom substituting a C atom in the presence of vacancies leads to a considerable reduction of the defect formation energy of V_{Si} . Therefore, we believe that light elements are beneficial for the realization of room-temperature magnetism in defective Z-SiCNRs.

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*jmmorbec@gmail.com

†gulrahman@qau.edu.pk

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