Electronic structure and magnetic properties of substitutional transition-metal atoms in GaN nanotubes*

Zhang Min(张 敏)[a] and Shi Jun-Jie(史俊杰)[b]†

[a] College of Physics and Electron Information, Inner Mongolia Normal University, Inner Mongolia Key Laboratory for Physics and Chemistry of Functional Materials, Hohhot 010022, China
[b] State Key Laboratory for Mesoscopic Physics and Department of Physics, Peking University, Beijing 100871, China

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The electronic structure and magnetic properties of the transition-metal (TM) atoms (Sc–Zn, Pt and Au) doped zigzag GaN single-walled nanotubes (NTs) are investigated using first-principles spin-polarized density functional calculations. Our results show that the bindings of all TM atoms are stable with the binding energy in the range of 6–16 eV. The Sc- and V-doped GaN NTs exhibit a nonmagnetic behavior. The GaN NTs doped with Ti, Mn, Ni, Cu and Pt are antiferromagnetic. On the contrary, the Cr-, Fe-, Co-, Zn- and Au-doped GaN NTs show the ferromagnetic characteristics. The Mn- and Co-doped GaN NTs induce the largest local moment of $4\mu_B$ among these TM atoms. The local magnetic moment is dominated by the contribution from the substitutional TM atom and the N atoms bonded with it.

Keywords: transition-metal atom doping, electronic structure, magnetic property, spin-polarized density-functional calculation

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1. Introduction

One-dimensional nanomaterials, such as nanowires (NWs), nanotubes (NTs) and nanoribbons (NRs), have attracted a great deal of attention due to their interesting geometries (small size and large surface-to-volume ratio), novel physical properties (strong quantum confinement and large surface effects) and potential device applications. Recently, BN[1] and AlN[2] nanostructures, SiC NTs,[3] GaN NTs[4] together with NWs[5] and NRs,[6] ZnO NTs and NRs[7] and InGaN NWs[8] have been synthesized successfully. Those works have paved a new way for us to explore compound nanomaterials.

It is well-known that GaN is a natural semiconductor material in blue and ultraviolet light emitting and in high-power electronic devices. Hence, the GaN NTs have become an active research field in recent years. The stabilities and electronic structures of single-walled GaN and InN NTs have been studied by using first-principles calculations.[9,10] Compared with bulk materials, some novel physical properties have been found in the GaN NTs. For example, according to the recent calculations of exciton states in GaN NTs, the excitation energy can be reduced by decreasing dimensions.[11] The successful synthesis of perfect single crystal GaN NTs by an "epitaxial casting" method[4] gives rise to a possibility to fabricate GaN NT-based functional materials for creating a new class of spintronic semiconductor devices by embedding a transition-metal (TM) atom in GaN NTs due to the spin degree of freedom from the d electrons of the TM atom.

In recent years, many experimental and theoretical investigations have been focused on the dilute magnetic semiconductor nanomaterials (doped with TM atoms), which are very useful in developing future nanoscale spintronic semiconductor devices due to their unique characteristics on electron-spin polarization.[12–21] Kitchen *et al.*[15] substituted Mn for Ga atoms using a scanning tunneling microscope (STM) with a controlled bias voltage and investigated the interaction between the Mn acceptors at the atomic scale. Dietl *et al.*[16] found that the Curie temperature for the Mn doped GaN and ZnO exceeds room temperature. The electronic and magnetic properties of ZnO doped with Mn[17] and (Mn,C)[18] have also been further investigated. Xie *et al.*[19] successfully synthesized the Zn-doped GaN NTs with a zigzag morphology by a chemical vapor deposition method. Liu *et al.*[20] observed the ferromagnetism in the Cr-doped GaN and AlN thin films above 900 K and investigated their structural, electrical and magnetic properties. Based on first-principles spin-polarized density functional calculations, the electronic structure and magnetic properties of the Mn-doped GaN NTs have been investigated.[14] Wang *et al.*[12] investigated the structure and magnetic properties of the Cr clusters in Cr-doped GaN NTs as a function of the Cr concentration and found that the coupling between two Cr atoms is ferromagnetic (FM), no matter whether the GaN NTs are single-walled or multi-walled. To avoid controversies regarding the FM ordering, an alternative choice instead of the TM-atom doping in GaN is to use nonmagnetic elements, such as Cu or Au. Rosa *et*

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†Corresponding author. E-mail: jjshi@pku.edu.cn

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al.[22] employed density functional theory (DFT) within the generalized-gradient approximation (GGA) to study the structural and electronic properties of pure Cu-doped GaN bulk material and found a weak FM behavior. The Cu doping has been further investigated in GaN and ZnO.[22–25]

To the best of our knowledge, in spite of several investigations on the magnetic properties of doping GaN materials, it is still unclear whether the substitutional TM atom in the single-walled GaN NTs has a magnetic moment. Both the electronic structure and magnetic properties of the substitutional TM atoms in GaN NTs have not been studied systemically. Our purpose here is to present a detailed first-principles study for the structural, electronic and magnetic properties of the zigzag GaN NTs doped with the TM atoms (Sc–Zn, Pt and Au). We find that the Sc and V doped GaN NTs exhibit a nonmagnetic behavior. The GaN NTs doped with Ti, Mn, Ni, Cu and Pt are antiferromagnetic (AFM). On the contrary, the Cr, Fe, Co, Zn and Au doped GaN NTs show the FM characteristics.

2. Calculation method

We use the spin-polarized DFT implemented in the Cambridge Sequential Total Energy Package (CASTEP) code,[26] which can give accurate valence band structures and ground state properties of semiconductors.[27] For reducing the numerical cost, we adopt a $1 \times 1 \times 1$ 20-atom supercell of the zigzag (5,0) GaN NTs and use a plane wave basis set with the cutoff energy of 350 eV and ultrasoft pseudopotentials.[28] Considering the periodic requirement of the CASTEP code, we construct a single-walled GaN NT array arranged in a square lattice with a vacuum layer (the distance between the two nearest neighbor NT surfaces) of ~ 12 Å, which is equivalent to a lattice constant of ~ 18 Å including the NT diameter ~ 6 Å. The Monkhorst–Pack k-point grid is chosen to be $1 \times 1 \times 11$.[29,30] The GGA with Perdew–Burke–Ernzerhof's (PBE) exchange–correlation potential is adopted.[31] The Ga ($3d^{10}4s^24p^1$), N ($2s^22p^3$) and the d- and s-electrons of the doped TM atom are treated as the valence electrons. Convergence with respect to the plane wave cutoff energy and k-point sampling have been carefully checked. Our calculations for the local distortions resulting from different covalent radii of Ga and doped TM atoms are based on reducing the magnitude of the calculated forces and stresses until they become smaller than the chosen convergence tolerances. The structures of GaN NTs have been optimized here by minimizing the total energy and the Hellmann–Feynmann force with respect to the atomic coordinates of the NTs doped with the TM atoms. In our following calculations, the total energy converges to less than 10^{-6} eV/atom. All atoms in the supercell are fully relaxed with the maximum force acting on each atom smaller than 0.03 eV/Å. The maximum stress is less than 0.05 GPa. The maximum displacement is less than 0.001 Å.

In order to investigate the magnetic coupling of the local magnetic moments induced by the TM atoms, we double the size of the supercell by placing two 20-atom cells with two TM atoms along the NT axis. Their magnetic interaction can thus be studied by calculating the total energies of the structures with different magnetic orderings, i.e., the FM state with parallel spin and the AFM one with antiparallel spin in the $1 \times 1 \times 2$ 40-atom supercell including two TM atoms. Our calculation method is similar to the one adopted in Ref. [32].

3. Results and discussion

A graphitic-like GaN sheet can be rolled into a cylinder to form a GaN single-walled NT like the construction of the silicon carbide NTs.[33] After the structural optimization, we find that the initial polygon structure of the NT is transformed into a perfect cylindrical NT, which is consistent with the results of Refs. [9] and [14]. Our calculations show that the zigzag GaN NT has a direct band gap at the Γ point. For the (5,0) GaN NT, our calculation results for the band gap E_g, the vertical and horizontal bond lengths a_v and a_h, the length of a unit cell along the tube axis L and the tube diameter d together with the previous theoretical results are summarized in Table 1. The good agreement with the previous theoretical calculations indicates that our first-principles calculations are accurate and believable.

Table 1. Comparison of the band gap E_g, the vertical and horizontal bond length a_v and a_h, the length of a unit cell along the tube axis L and the tube diameter d with the previous theoretical results for the (5,0) GaN single-walled NT.

	E_g/eV	a_v/Å	a_h/Å	L/Å	d/Å
Other calculation[34]	1.816			5.44	5.31
This work	1.720	1.865	1.885	5.48	5.35

In order to study the preferred magnetic coupling of the TM-atom doped GaN single-walled NTs, we calculate the total energies for both FM and AFM states with full geometry optimization for all configurations. The optimized nearest vertical and horizontal distances between the TM and N atoms d^v_{TM-N} and d^h_{TM-N}, and the length of a unit cell along the tube axis L, as well as the energy difference ΔE between the AFM and FM states for the TM-atom doped GaN NTs are summarized in Table 2. We can see from Table 2 that the optimized vertical (horizontal) distances between the TM and N atoms are in the range from 1.782 Å (Fe-doped) to 2.128 Å (Au-doped) (1.774 Å (Cr-doped) to 2.170 Å (Au-doped)). All of the TM–N bond lengths are modified significantly in the TM-atom doped GaN NTs due to the atomic relaxation. For example, the Sc–N bond lengths d^v_{TM-N} and d^h_{TM-N} are calculated to be 2.026 Å and 2.008 Å, which approximately extend by

8.63% and 7.67%, respectively, compared with the original Ga–N bond lengths in the pristine GaN NTs.

Table 2. The optimized nearest vertical and horizontal distances between the TM and N atoms $d^{\rm v}_{\rm TM-N}$ and $d^{\rm h}_{\rm TM-N}$, the length of a unit cell along the tube axis L and the energy difference $\Delta E(=E_{\rm AFM}-E_{\rm FM})$ for the GaN single-walled NTs doped with the TM atoms. The last column denotes the magnetic coupling characteristics of the ground state.

TM atom	$d^{\rm v}_{\rm TM-N}$/Å	$d^{\rm h}_{\rm TM-N}$/Å	L/Å	ΔE/eV	Coupling
Sc	2.026	2.008	5.478	0	–
Ti	1.910	1.881	5.488	−0.064	AFM
V	1.802	1.831	5.502	0	–
Cr	1.787	1.774	5.487	0.009	FM
Mn	1.826	1.819	5.474	−0.051	AFM
Fe	1.782	1.778	5.446	0.084	FM
Co	1.803	1.845	5.428	0.111	FM
Ni	1.796	1.862	5.492	−0.061	AFM
Cu	1.859	1.892	5.491	−0.064	AFM
Zn	1.946	1.923	5.505	0.093	FM
Pt	2.023	2.048	5.427	−0.024	AFM
Au	2.128	2.170	5.412	0.002	FM

In order to determine the preferred magnetic ground state, the total energies for both the FM and AFM states have been calculated for all TM-atom doped GaN NTs after the geometry optimization. We find from Table 2 that the Sc- and V-doped GaN NTs are nonmagnetic. The Cr-, Fe-, Co-, Zn- and Au-doped GaN NTs exhibit the FM characteristics, while the Ti-, Mn-, Ni-, Cu- and Pt-doped GaN NTs have an AFM behavior. For example, the Co-doped GaN NT is found to have an FM ground state, which is 0.111 eV below the AFM state in energy. On the contrary, the Mn-doped GaN NT has an AFM ground state with energy 0.051 eV below the FM state.

The local magnetic moments of the substitutional TM atoms doped in the GaN NTs are shown in Fig. 1(a). We can see from Fig. 1(a) and Table 2 that the substitution of the TM atoms has a significant influence on the magnetic properties of the GaN NTs. It is interesting to note that the Sc or V atom doped in a single-walled GaN NT is nonmagnetic, while the Mn or Co atom has the largest local magnetic moment ($\sim 4\mu_{\rm B}$). Compared with the case of the TM atom embedded in graphene,[35,36] the local magnetic moments of the substitutional TM atoms doped in the GaN NTs (see Fig. 1(a)) are different. Hence, the TM-atom properties can be effectively modified by its surrounding. Following the tradition for the TM-atom doped issues,[35,36] we further calculate the binding energy (see Fig. 1(b)), instead of the formation energy, for the substitutional TM atoms in the GaN NTs. The binding energy is defined as the energy difference between the initial structure (an isolated TM atom together with a reconstructed GaN NT supercell with a Ga vacancy) and the corresponding TM-atom doped GaN NT supercell. Generally, the binding energy is closely related to the bond characteristics, for example, the bond length between the N and TM atoms and their hybridization. We can find from Fig. 1(b) that the binding energies are in the range of 5.8–16.4 eV, which indicates that the TM-atom doped GaN NTs are stable. Comparing Fig. 1(b) with the binding energy (2–8 eV) of the TM atom doped in graphene (mainly determined by the covalent bond between the TM and C atoms[35,36]), we know that the results in Fig. 1(b) are reasonable due to the strong ionic and covalent bonds between the TM and N atoms. Figure 1(b) also shows that the binding energy has a complicated variation when the d-electron number increases. The binding energy increases with increasing d-electron number (≤ 5) from Sc to Cr. A maximum is obtained for the Cr-doped GaN NT, which has the half-filled d orbital. Then, the binding energy decreases with increasing d-electron number (≥ 5). In particular, the small binding energies for the GaN NTs doped with Cu, Zn and Au with a fully-filled d shell are 8.19 eV, 6.83 eV and 5.82 eV, respectively. The physical reason can be analyzed as follows. The increase of the binding energy from Sc to Cr is due to the decrease of the TM–N bond length (see Table 2), which increases the TM–N interaction and the binding energy. The binding energy decreasing from Mn to Au is because of the strong hybridization of the TM and its nearest-neighbor N atoms (please refer to Fig. 4).

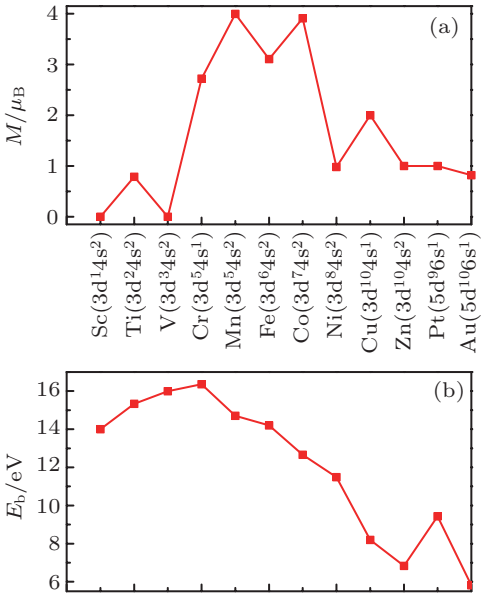


Fig. 1. (color online) (a) Magnetic moment M and (b) binding energy $E_{\rm b}$ of the single-walled zigzag GaN NTs doped with the substitutional TM atoms. The lines guide the eye.

As a representative of the nonmagnetic GaN NTs, both the electronic band structure and the spin-polarized partial densities of states (PDOS) for the spin-up and spin-down electrons are plotted in Fig. 2 for the optimized V-doped GaN NT. The Fermi level, indicated by the horizontal dashed line, is set to zero energy. We can see from Fig. 2 that there is no difference for the occupancy of the spin-up and spin-down electrons. The V-doped GaN NT induces one impurity band near

the Fermi level in the band gap, which has a δ-like sharp PDOS peak and mainly comes from the 3d orbital of the V atom with the valence electron configuration $3d^3 4s^2$ (see Fig. 2(b)). We know that the V atom occupying the cation site in the V-doped GaN NT donates its three electrons to compensate the three electrons of the substituted Ga atom. The impurity band has thus been occupied by the two 3d electrons of the V atom with different spins, which directly leads to the nonmagnetic property of the V-doped GaN NT. Moreover, the inset of Fig. 2 shows that the electron states of the impurity band, mainly arising from the 3d electrons of the V atom, are localized around the V atom. The V-doped GaN NT has thus no magnetism.

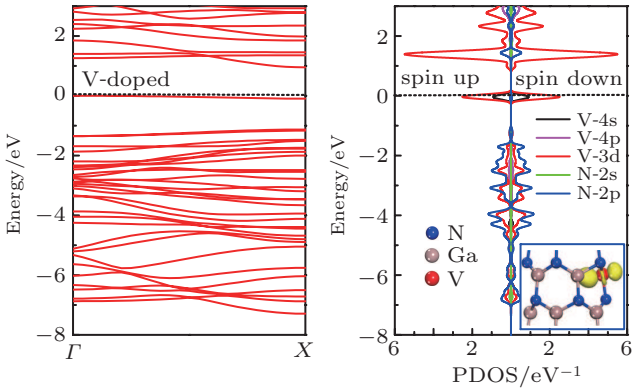


Fig. 2. (color online) Typical electronic structure of the GaN NT doped with the V atom. (a) Band structure and (b) spin-polarized PDOS of the V and its nearest N atoms in the V-doped GaN NT. The inset shows the isosurface of the total magnetization density. Here the zero energy corresponds to the Fermi energy.

Based on the above analysis, we know that the TM atoms, substituted the Ga atoms in GaN NTs, dominate the formation of the local magnetic moment. As a typical structure of the AFM GaN NTs with the TM-atom doped, we investigate the electronic structures and spin-polarized PDOS of the Mn-doped GaN NT here. Our results for the spin-up and spin-down electrons are plotted in Fig. 3 for the optimized Mn-doped GaN NT. We can see from Fig. 3(a) that the Mn atom induces four impurity energy levels in the band gap due to the spin-splitting effects. When the Mn atom occupies the cation site, it donates three electrons to compensate the three electrons of the substituted Ga atom and leaves the four unpaired d electrons to form the local magnetic moment. Hence the strong spin polarization results in a complete separation of the spin-up and the spin-down channels and the formation of a local magnetic moment of $4\mu_B$, which is in excellent agreement with the results in Ref. [13]. The spin-polarized PDOS of the Mn and its nearest-neighbor N atoms are shown in Fig. 3(b). We can see from Fig. 3(b) that there are some sharp PDOS peaks in the vicinity of the Fermi level due to the strong hybridization between the Mn 3d and N 2p states. The localization of the impurity states in the Mn doped GaN NT can also be visualized by plotting the impurity state charge density in the real space. The isosurface plots of the total magnetization density of the Mn-doped GaN NT is illustrated in Fig. 4(a). We can see from Fig. 4(a) that these spin states are strongly localized around the Mn and its nearest three N atoms. It is this strong localization of the electron wave functions that leads to a spin-polarized AFM ground state and the formation of the local magnetic moment in the Mn doped GaN NT.

In order to understand the FM property of the TM-atom doped GaN NTs, we plot the band structure and the spin-polarized PDOS for the optimized Zn-doped GaN NT in Fig. 5. We can find from Fig. 5(a) that the Zn-doped GaN NT has two almost-degenerate half-filled impurity bands crossing over the Fermi level. Our results clearly show that, when the Zn atom is doped in the GaN NT, it is polarized and donates its three electrons to the neighboring N atoms. Moreover, we can see from Fig. 5(b) that the 2p electrons of the neighboring N atoms occupy the impurity bands. The $1\mu_B$ local magnetic

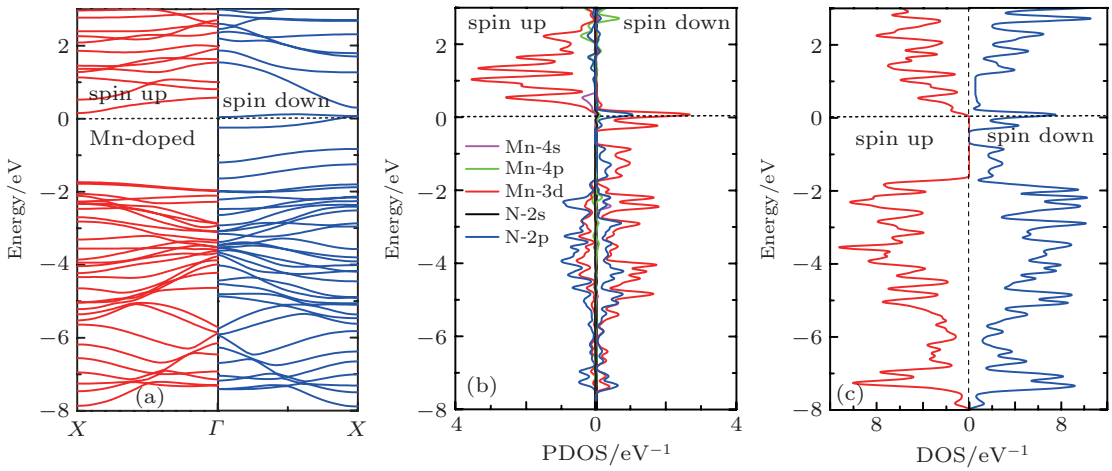


Fig. 3. (color online) Typical electronic structure of the GaN NT doped with the Mn atom: (a) band structure, (b) spin-polarized PDOS of Mn and its nearest N atoms and (c) the total DOS. The zero energy corresponds to the Fermi level.

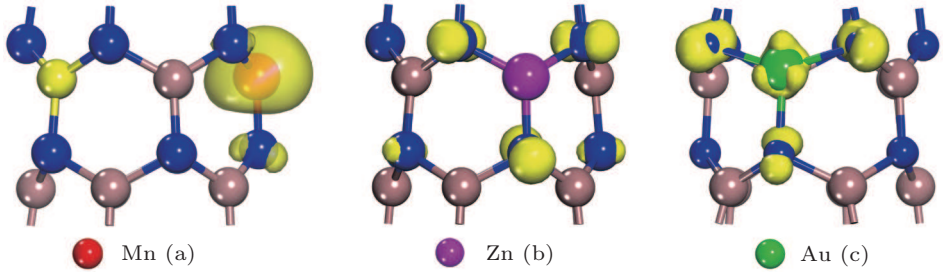


Fig. 4. (color online) Our calculation results for the isosurface of the total magnetization density for the (a) Mn-, (b) Zn- and (c) Au-doped GaN NTs after relaxation. We can obtain the spin-up and spin-down magnetization densities of the AFM state for the Mn-doped NT by using different colors in a $1 \times 1 \times 2$ 40-atom supercell, i.e., doubling the cell in panel (a) along the NT axis. The magnetization density of the FM state (parallel spin) for the Zn- or Au-doped NTs can be obtained by simply doubling the cell in panel (b) or (c).

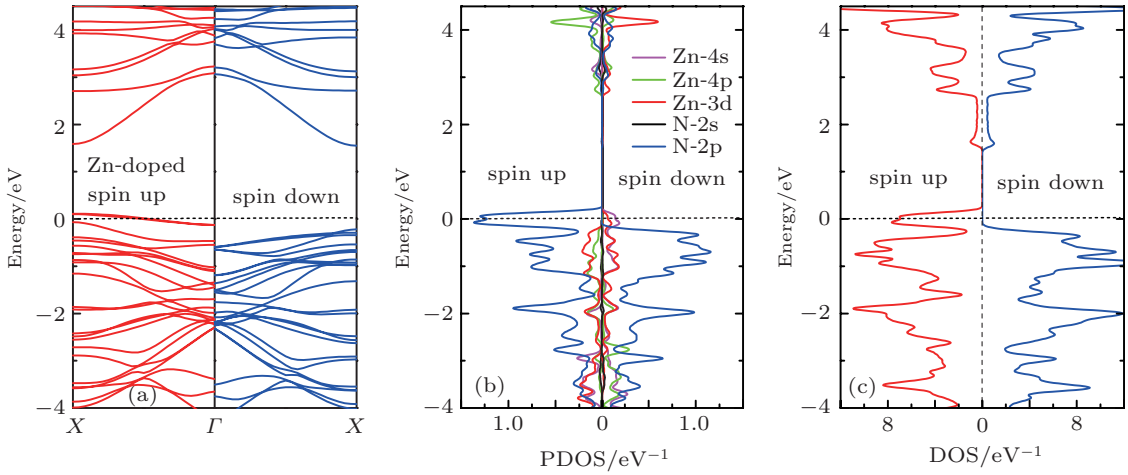


Fig. 5. (color online) Typical electronic structure of the Zn-doped GaN NT: (a) band structure, (b) spin-polarized PDOS of Zn and its nearest N atoms and (c) the total DOS.

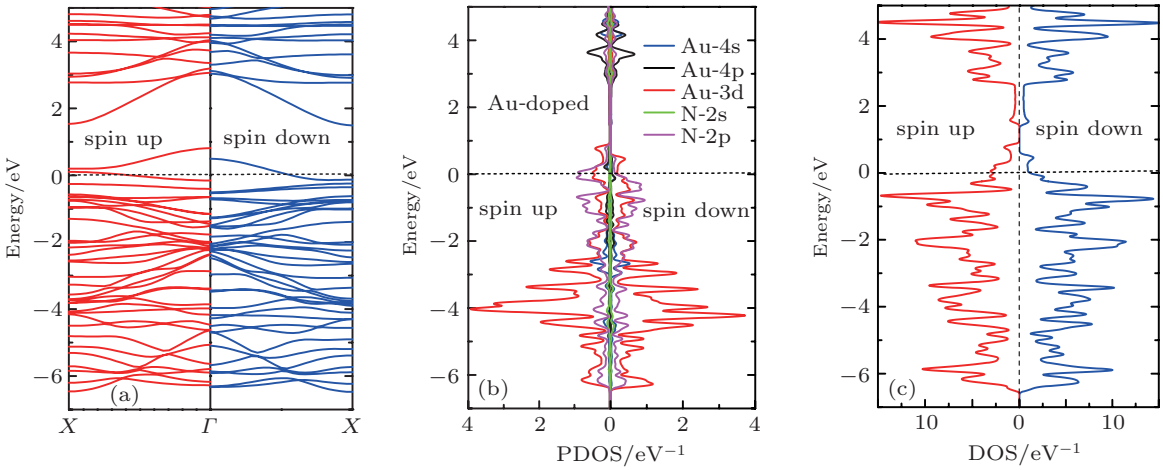


Fig. 6. (color online) Typical electronic structure of the Au-doped GaN NT: (a) band structure, (b) spin-polarized PDOS of Au and its nearest N atoms and (c) the total DOS.

moment (see Fig. 1(a)) originates from the half-filled almost-degenerate impurity bands in the Zn-doped GaN NT. The isosurface of the total magnetization density for this structure is presented in Fig. 4(b). We can see from Fig. 4(b) that the spin state is mainly localized around the N atoms bonded with the Zn atom. This picture clearly explains the origin of the local magnetic moment and the FM characteristics of the Zn-doped GaN NT.

We further investigate the electronic structure and the spin-polarized PDOS for the optimized Au-doped GaN NT in Fig. 6. We can see from Fig. 6(a) that the Au-doped GaN NT

induces six impurity bands in the band gap. There are two impurity bands crossing over the Fermi level and the other four bands are under the Fermi level. Our results show that, when the Au atom is doped in the GaN NT, it is polarized and donates its three electrons to the neighboring three N atoms. Moreover, there is a strong hybridization among the 5d electrons of the Au atom, the 2s and 2p electrons of the neighboring N atoms, which approximately introduces $1\mu_B$ local magnetic moment in the Au doped GaN NT. We can see from Fig. 6(b) that the N atoms bonded with the substitutional Au atom have the most important contribution to the impurity bands. The isosurface of the total magnetization density for this structure is shown in Fig. 4(c). We can see from Fig. 4(c) that the spin state is mainly localized around the doped Au atom and the N atoms bonded with the Au atom, which illustrates the origin of the local magnetic moment and the FM ground state of the Au-doped GaN NT.

4. Conclusion

In this paper, we perform first-principles spin-polarized DFT calculations for the electronic structures and magnetic properties of the TM-atom doped single-walled GaN NTs. Our calculations show that the binding energy of the TM atoms (Sc–Zn, Pt and Au) doped in the GaN NTs is large (6–16 eV), which indicates that the binding is stable. The doped TM atoms, except for the Sc and V atoms, give rise to a spin-polarized ground state and lead to the formation of a local magnetic moment. The Mn- and Co-doped GaN NTs have the largest local moment of $4\mu_B$ among these TM atoms. The local magnetic moment is mainly due to the contribution from the substitutional TM atom and the N atoms bonded with it. The GaN NTs doped with Ti, Mn, Ni, Cu and Pt exhibit the AFM characteristics, while the Cr, Fe, Co, Zn and Au doped GaN NTs have the FM behavior. The TM-atom properties can vary widely in different hosts. Our results strongly contribute to the understanding of the TM-atom doped single-walled GaN NT properties and pave a new way to modulate its magnetic characteristics.

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