Ab initio Studies of the Possible Magnetism in BN Sheet by Non-magnetic Impurities and Vacancies

Ru-Fen Liu and Ching Chen
Department of Physics, National Cheng Kung University, 70101, Tainan, Taiwan

We performed first-principles calculations to investigate the possible magnetism induced by the different concentrations of non-magnetic impurities and vacancies in BN sheet. The atoms of Be, B, C, N, O, Al and Si are used to replace either B or N in the systems as impurities. We discussed the changes in density of states as well as the extent of the spatial distributions of the defect states, the possible formation of magnetic moments, the magnitude of the magnetization energies and finally the exchange energies due to the presence of these defects. It is shown that the magnetization energies tend to increase as the concentrations of the defects decreases in most of the defect systems which implies a definite preference of finite magnetic moments. The calculated exchange energies are in general tiny but not completely insignificant for two of the studied defect systems, i.e. one with O impurities for N and the other with B vacancies.

PACS numbers: 75.75.+a, 73.22.-f, 67.57.Pq, 61.72.Ji

I. INTRODUCTION

The magnetism involving only s- and p-electron elements continues to attract much attention due to the potential of extensive applications as well as the urge to understand its physical origins. Recently, some experimental groups have discovered either weak or strong ferromagnetism in fullerences and graphite systems. A few theoretical studies attempting to find magnetism in some potential non-magnetic systems have also been carried out previously. However, the origin of ferromagnetism in those systems is still under debate on both experimental and theoretical sides. The mechanism for forming magnetic ordering in solids, such as ferromagnetism, antiferromagnetism, etc., can be referred to the direct or indirect exchange interactions among magnetic moments. Therefore, a strong enough exchange interaction should be the crucial criterion to determine this possibility. The Subsec. A will present the electronic properties of BN sheet by the analysis of orbital-projected partial density of states (DOS). We shall demonstrate that there exist mostly very weak interactions among these defect-induced magnetic moments except two cases.

BN can form three different bulk structures which are hexagonal BN(h-BN), cubic BN(c-BN) and wurtzite BN(w-BN). Of these three structures, h-BN is the room temperature phase. Similar to graphite, h-BN is quasi-2D with weak interaction between layers. Nevertheless, different from the delocalized \( \pi \) electrons in graphite, the stronger electronegativity of N than that of B causes \( \pi \) electrons to distribute more around N. This strong directional effect of bonding confines the motion of \( \pi \)-electrons and thus results in a gap in h-BN. BN is the lightest III-V compound of those that are isoelectronic with III-V semiconductors such as GaAs, but with wider band gap. The Subsec. B includes the effects on DOS due to defects in BN sheet. The GDOS and SEEDOS are in Sec. II. In this section, the Subsec. A will present the electronic properties of BN sheet by the analysis of orbital-projected partial density of states (DOS). The Subsec. B includes the effects on DOS due to defects, i.e. the location of the defect states in DOS, as well as the extent of the spatial distribution of these defect states.

Our plans for this article are as the followings: Sec. II summarizes the computational methods in this work. The results of non-spin-polarized calculations are presented in Sec. III. In this section, the Subsec. A will present the electronic properties of BN sheet by the analyzed orbital-projected partial density of states (DOS). The Subsec. B includes the effects on DOS due to defects, i.e. the location of the defect states in DOS, as well as the extent of the spatial distribution of these defect states. All the results of spin-polarized calculations

---

*Electronic address: fmliu@phys.ncku.edu.tw
†Electronic address: ccheng@phys.ncku.edu.tw
are presented in Sec. IV. In the Subsec. A, we will investigate the possible formation of finite magnetic moments induced by defects while the results of exchange energies and the corresponding Curie temperatures will be presented in the Subsec. B. Finally, the conclusions are in Sec. V.

II. COMPUTATION METHOD

Our calculations are based on density functional theory (DFT) with generalized gradient approximation (GGA) of Perdew and Wang for the exchange-correlation energy functional. The PAW method implemented by Kresse and Joubert is used to describe the core-valence electrons interactions. There are 2, 3, 4, 5, 6, 3 and 4 valence electrons included here for Be, B, C, N, O, Al and Si respectively. The one-electron Kohn-Sham wavefunctions are expanded by the plane-wave basis with kinetic energy cut-off ($E_{\text{cut}}$ hereafter) of 400 eV. The sampled k-points in the Brillouin zone (BZ) are generated by the Monkhorst-Pack technique with gamma centered grids for hexagonal lattice. All calculations are carried out by Vienna ab initio simulation package (VASP).

The calculated lattice constants of h-BN are $a = 2.5\,\text{Å}$ and $c = 6.36\,\text{Å}$ with $13 \times 13 \times 5$ k-point grids and compared with the experimental results ($a = 2.5\,\text{Å}$ and $c = 6.66\,\text{Å}$) are reasonably well. The supercells composing of $4 \times 4 \times 1$ primitive unit cells of BN sheet are used to simulate systems with defects (See FIG. 1). The vacuum distance between BN sheets (taken as along the z direction) was chosen to be around $13\,\text{Å}$ which was tested with $3 \times 3 \times 1$ k-point grids to be large enough to avoid interactions between the sheets.

Of all the relaxed configurations in this work, the atomic forces calculated by Hellmann-Feynman theorem were smaller than 0.02 eV/Å. In the spin-polarized calculations, we performed the above atomic relaxations again to ensure the relaxed configurations. The DOS and magnetic moments of the final relaxed structures were then evaluated. The larger supercells of $8 \times 4$ and $8 \times 8$ were used to study the possible finite magnetic moments induced by defects, as well as the variation of the magnetization energy (denoted as $E_M$ hereafter) and the exchange energy $J$ with respect to the distances between defects, i.e. defect concentrations.

III. NON-SPIN-POLARIZED CALCULATIONS: DENSITY OF STATES

A. BN sheet

The orbital-projected partial DOS of $B$ and $N$ in BN sheet are presented in FIG. 2. The colors of blue, yellow, green and red in the figures represent the $s$-, $p_x$-, $p_y$- and $p_z$-orbital-projected partial DOS respectively. The spiky feature of the DOS is due to the dimensional reduction from 3D bulk h-BN to 2D planar structure of BN sheet. Two valence bands (shorted as VB hereafter) and the lowest 3eV range of the conduction band (shorted as CB hereafter) are included in the figure for discussion. The DOSs in the same energy range for BN sheets with defects will be used in the following discussion for comparison and the bottom of the CB is taken as the zero of the energy for convenience in discussing the splitting of the electronic bands from the two VBs as well as the CB due to the presence of defects. The two VBs in BN sheet are well-separated as those in the bulk h-BN. The lower-energy VB (VB1 hereafter) contains 2 electrons: one is from the $s$-electron of $N$ and the other is from the hybridized $s$- and $p$-electrons ($sp^2$-electrons hereafter) of $B$. The higher-energy VB (VB2 hereafter) contains 6 electrons, i.e. three $sp^2$-electrons and one $p_z$-electron from $N$ and two $sp^2$-electrons from $B$. From FIG. 2 we see that the nature of the two VBs for $B$ is mainly hybridized $sp^2$-orbitals while that for $N$ is $s$-like orbitals in VB1 and hybridized $sp^2$-like orbitals in VB2. Near the top of VB2 and the bottom of CB, the DOS’s are mostly $p_z$-orbital.
FIG. 3: (Color online) The DOS’s for the BN sheet with defects. The upper pannel shows defects on B while the lower one shows defects on N. (a)-(f) are the results of the defect systems with impurities Be, N, B, C, O, Al and Si atoms respectively. The defect systems with B and N vacancies are shown in (g). All dashed lines cut at $E_F$.

in nature. However, the dominant contribution switches from the $p_z$-orbital on N atoms near the top of VB2 to the $p_z$-orbital on B atoms near the bottom of CB. That is the electronic excitation in BN sheet would involves displacement of electron distribution from the $p_z$-orbital around N atoms to the $p_z$-orbital around B atoms.

**B. Effect of defects**

In the present section, we discuss the effect of defects on the DOS of BN sheet when the spin-polarization is not yet switched on. We shall demonstrate that the effect of defects on the DOS can be generally categorized into two groups according to the chemical properties of the defects. The $4 \times 4$ supercell was employed in all the results presented in this section which corresponds to a doping of $1/32$ ($\sim 3\%$) of the defects in the system and a distance of $10.03\AA$ between the neighboring defects. The possible interaction between defects will be discussed in the following section when the exchange energy is investigated. However, the results presented in the present section are applicable to the systems with low-density dopings of defects as we shall demonstrate in the following section that the interaction between defects is already quite small in the present configurations. The effect of C impurity on the DOS of BN sheet will be discussed in details first and then followed by the results for the series of defects we studied. For simplicity, we denote, e.g. $C_B$, as the defect system which consists of an impurity of C atom substituting one of B atoms in the original super-cell of BN sheet and $V_B$($V_N$) as the system consisting of a vacancy replacing one of the original B(N) atoms.

One of the effects of the impurities is to introduce electronic states into the energy regions which originally have no DOS in the BN sheet. We present the total DOS of all the defect systems considered in this study in FIG.3. In the case of $C_B$ (FIG.3(c)), the defect states split from the original three bands and move to the lower energy region. This is due to the stronger bonding ability of C ions for electrons compared to that of B ions. On the contrary, in the case of $C_N$, the bonding ability of C ion is weaker than that of N ion for electrons such that the defect bands move to the higher-energy positions compared to the original three bands. Therefore, the locations of defect bands is determined by the bonding ability of the defects compared to the substituted host atoms.

The effects of defects on the DOS’s can be summarized into two types as outlined schematically in FIG.4. For $N_B$, $C_B$, $O_B$, $O_N$ and $Si_B$, the bonding abilities of the impurities are stronger than the substituted host atoms. We name these as type I. For $Be_B$, $Be_N$, $B_N$, $C_N$, $Al_N$ and $Si_N$, which are named as type II, the three defect bands all move to the region of higher energy than the original three bands.

Of these studied defect systems, some consist of odd
number of electrons in the supercell, i.e. Be$_B$, Be$_N$, C$_B$, C$_N$, O$_B$, O$_N$, Si$_B$, Si$_N$, V$_B$ and V$_N$, such that there is an unpaired electron occupying the defect state located between the VB2 and CB for Be$_N$, C$_B$, C$_N$, O$_B$, Si$_N$ and V$_N$, the top of VB2 for Be$_B$ and V$_B$ as well as the bottom of CB for O$_N$ and Si$_B$. We denote DB as the state that the unpaired electron occupies hereafter. We shall show in the next section that magnetic moments are likely to form for those cases with partially occupied DBs. In case the partially occupied defect bands which form definite magnetic moments are also extended in nature, the long-range magnetic order can develop. Hence, it is expected that for Be$_B$, O$_N$, Si$_B$ and V$_B$ whose defect states locating at the edge of the original extended bands, the defect bands are more likely to be extended in nature and then more likely to lead to larger exchange energies as will be presented in the next section.

In order to determine the properties of the partially-filled DBs, the extent of the states in space is established from summing over the contributions of the orbital-projected partial DOS of the DBs for the neighboring atoms of the defects as presented in FIG.5. For Be$_B$, Be$_N$, O$_B$ and O$_N$, we see that the electrons of the DBs distribute more on the nearest neighboring atoms of the impurity than the impurity itself. This is contrary to the C$_B$, C$_N$, Si$_B$ and Si$_N$ systems in which most of the electrons of the DBs distribute around the impurity atoms. These results demonstrate that the electrons of the defect states due to impurities do not have to distribute mostly on the impurities themselves. About the spatial extent of the defect states, FIG.4 shows that only three systems, i.e. Be$_B$, O$_N$ and V$_N$, reach beyond 5Å. However, the defect states for all the defect systems considered in the present study are confined in a distance of 6Å around the defects no matter whether the partially-filled defect states are at the edge of the extended bands or not. Finally, we should emphasize that FIG.5 also reveals two categories of DBs: one is formed by the sp$^2$-hybridized orbitals, e.g. s, p$_x$ and p$_y$, and the other is p$_z$ in nature. These orbital-projected-DOS analyses imply the difference of the electronic distributions of the magnetic moments (detail discussions in the next section) formed by the unpaired electrons in DB, e.g. the moments are distributed on the plane of BN sheet for Be$_N$, O$_B$ and V$_B$ while the moments are distributed perpendicularly to the plane of BN sheet for Be$_B$, C$_B$, C$_N$, O$_N$, Si$_B$, Si$_N$ and V$_N$ systems.

IV. SPIN-POLARIZED CALCULATIONS: THE EFFECTS OF DEFECTS

In this section, we present the results of spin-polarized calculations to investigate the possible formation of finite magnetic moment in the BN sheets containing defects as well as the possible long-range magnetic ordering in these systems.

![FIG. 5: (Color online) The ratio of the orbital-projected partial DOS summing over the ith nearest neighbours of the defect of the system with partially-filled DB. There are 1(the defect), 3, 6, 3, 6, 3 and 1 atoms contributing to each bars in sequence. $a$ is the lattice constant 2.5Å.]

A. The possible formation of magnetic moments

To identify the possible magnetic moments due to defects as well as the extent of the magnetic moments, the 4 × 4 and 8 × 8 supercells consisting of only one defect were employed to simulate the BN sheet with defect concentrations of 3.125% and 0.78% respectively, i.e. corresponding to a distance of 10.03Å and 20.05Å between nearest-neighbour defects (denoted by $d_B$ hereafter). In order to obtain the relevant physical quantities for the cases within the range between $d_B = 10Å$ $\sim$ 20Å, we create a rectangular supercell as shown in FIG.5. By
FIG. 6: (Color online) The rectangular supercell with cell dimensions 20.05 Å and 17.37 Å. The distance between the two defect sites is 13.26 Å. The supercell contains 64 primitive cells of BN sheet.

FIG. 7: (Color online) The calculated magnetic moments with respect to \( d_D \), the distance between the nearest-neighboring defects.

FIG. 8: (Color online) The magnetization energy \( E_M \) v.s. \( d_D \).

FIG. 9: (Color online) The relaxed structure for the defect system of \( OB \). The impurity, \( O \) atom, was relaxed and moved toward two of the three neighboring \( N \) atoms to open up one of the original \( N - O \) bonds. The spin-polarized energy for this configuration with unequal \( N - O \) bond lengths is lower than that with equal \( N - O \) bond lengths by 111 meV.

FIG. 10: (Color online) The calculated magnetic moments of the systems with respect to \( d_D \) are presented in FIG. 7. For \( Nb, BN, AlB \) and \( AlN \) which have even number of electrons in the supercell and completely-filled DBs, there exist no magnetizations and they are therefore excluded from the following discussions. The calculated magnetic moments in \( BeB \) and \( VB \) were found to vary as \( d_D \) increases. However, their magnitudes converge to 1 \( \mu_B \) as \( d_D \) increases to 17.37 Å. For \( BeN, CB, CN, OB, ON, SiB, SiN \) and \( VN \), the calculated magnetic moments are always found to be 1 \( \mu_B \) and independent of \( d_D \). Note that for all the defect systems possessing finite magnetic moments, the defect bands are always partially occupied. The 1 \( \mu_B \) of magnetizations in these defect systems should be attributed to the unpaired electron occupying the defect states.

To understand how stable these finite moments in BN sheet are, the magnetization energies, i.e. \( E_M \), obtained from the total-energy difference between the systems with and without spin-polarized configuration were calculated. The results are plotted in FIG. 8. Firstly, the \( E_M \)s of these systems tend to increase as \( d_D \)s increase. This suggests a definite preference of finite magnetic moments for these defect systems with distant non-magnetic defects. Secondly, the corresponding \( E_M \) for these defect systems with distant defects can be determined by the saturated values in the figure, e.g. 360 meV for \( VB \), 300 meV for \( OB \), 220 meV for \( BeN \) etc., and then are found to be in the wide energy distribution (from 16 meV of \( BeB \) to 360 meV of \( VB \)). We notice that the defect systems with metal-like electronic properties (\( BeB, ON, SiB \) and \( VB \)), i.e. with fermi level at the edge of either VB2 or CB, do not necessarily lead to large \( E_M \). For example, the \( E_M \) of \( BeB \) is very small, i.e. 16 meV which is even smaller than the room temperature thermal energy of 25 meV. However, the \( E_M \) of \( VB \) is the largest, i.e. 360 meV, of all the systems we considered. We should mention that, when the defect distance is increased, the
metal-like DOS does not always hold. The bandwidth of the defect bands might become smaller due to localization such that they eventually separate from the original VB2 or CB bands. Of the studied systems with metalization such that they eventually separate from the original VB2 or CB bands, the defect bands might become smaller due to localization such that they eventually separate from the original VB2 or CB bands. Of the studied systems with metalization such that they eventually separate from the original VB2 or CB bands, the defect bands might become smaller due to localization.

Finally, for those systems with $p_z$-like magnetic moments, the bond lengths between defect and neighboring host atoms were found relaxed but preserving the threefold symmetry. However, we found that, the relaxed bond lengths of $Be_N$, $O_B$ and $V_B$ which have planar distributions in the magnetic moments (the $sp^2$-hybridized electron in DB) undergo structural distortions and break the threefold symmetry of the original BN systems after the spin-polarization calculation is switched on (John-Teller (JT) effect). FIG. 9 shows the relaxed structure of $O_B$. The impurity, $O$ atom, moved toward two of the neighboring $N$ atoms to open up one of the three original $N-O$ bonds. The total energy of this distorted structure with spin-polarization is lower than that of the structure with equal $N-O$ bond length by 111meV, similarly for $Be_N$ by 33meV and for $V_B$ by 47meV. The effect of JT distortion are also responsible for the consequences of relatively larger magnetization energy of $Be_N$, $O_B$ and $V_B$ with planarly distributed moments compared to those with $p_z$-like moments.

B. The exchange energy

From the above analyses, we have demonstrated that the non-magnetic defects can induce finite magnetic moments in BN sheet. To identify the possible long-range magnetic ordering in these systems, the Heisenberg-type of spin couplings is employed to model the interaction ($J$, i.e. the exchange energy) between the nearest-neighbor magnetic moments due to defects. The exchange energy $J$ is determined from the total-energy difference between two spin configurations, i.e. one with antiparallel and the other with parallel spin configuration whose energy are denoted as $E_{AFM}$ and $E_{FM}$ respectively hereafter. For simulating two defects distancing 10.03Å, we employed either the 8 × 4 supercell with two defect sites in each sub-supercells of 4 × 4 or the 8 × 8 supercell with those in the two diagonal sub-supercells of 4 × 4 to generate different spin configurations. In the antiferromagnetic configuration, the 8 × 4 supercell describes a configuration of six nearest neighbours ($d_D = 10.03Å$) in which four are antiparallel- and two are parallel-spin to the centered defect while the 8 × 8 supercell describes a configuration of two antiparallel-spin nearest neighbours ($d_D = 10.03Å$) and a $d_D = 17.37Å$ for the four next-nearest neighbours. The rectangular supercell in FIG. 8 with defects on both sites is also used to simulate the two spin configurations for the systems with defect distance of 13.26Å. In the rectangular supercell, there are four nearest neighbours for a defect and all are antiparallel-spin neighbours in the antiferromagnetic configuration. We have used both 8 × 4 and 8 × 8 supercells for the $V_B$ and $O_N$ systems and the exchange energy obtained from the 8 × 8 supercells were considered in the discussion as they correspond more to the low-doping conditions we would like to consider. The different values of the exchange energies obtained from using 8 × 4 and 8 × 8 supercells indicate that the simple pair-wise Ising interaction is not a good enough model to describe the energies of these systems of $d_D = 10.03Å$. We notice that both $V_B$ and $O_N$ have DB at the edge of either CB or VB2. The 8 × 8 supercells were also used on a few of the other defect systems, but all lead to similar results as those obtained from the 8 × 4 supercells.

Our results are summarized in FIG. 10 where the lines are to guide the eyes. From the previous magnetization energy calculations, our computational accuracy can recognize meaningful energy difference of 5meV and larger values between configurations. For those systems of $Be_B$, $Be_N$, $C_B$, $O_B$ and $Si_N$, the calculated 8Js which are less than 5meV are too small to determine whether the systems are ferro-(8J > 0) or antiferro-magnetic (8J < 0). For $O_N$, $V_B$ and $Si_B$, they are found to be ferromagnetic, and for $C_N$ and $V_N$, anti-ferromagnetic at $d_D = 10.03Å$. We should mention that the relaxed spin configurations of all the systems discussed here remained anti-ferromagnetic at the end of the calculations if with initial antiparallel-spin configurations. The exchange energies for $O_N$, $V_B$ and $Si_B$, which possess metal-like DOS, are relatively larger at $d_D = 10.03Å$, but not for

FIG. 10: (Color online) The exchange energy $8J$ v.s. defect distances where $J \equiv \frac{1}{2}(E_{AFM} - E_{FM})$. The energy range from $-5$meV to $5$meV is the estimated region where the magnitude of $8J$ is too small to be used to identify the sign of $8J$ in our calculations. The dashed line indicates the value of exchange energy respected to $50K$ of Curie temperature ($T_{C}^{MF}$) under mean-field approximation.
the case of $Be_B$ whose $E_M$ is tiny anyway. Although the magnetization energy of $V_B$ can be as large as 200 meV at $d_B = 10.03\AA$, the exchange energy is considerably much smaller (5.6 meV), similarly for $Si_B$ whose $E_M \sim 90$ meV while $J$ is smaller than 2 meV. (Note FIG.10 shows the data of 8 times the exchange energy $J$.) This contrast is much reduced in the case of $O_N$ whose $E_M \sim 17$ meV and $J \sim 9.4$ meV at $d_D = 10.03\AA$. When the $d_D$ is increased to 13.26Å, the magnitude of exchange energies for all the above systems decrease. At the end, there are only two systems, i.e. $O_N$ and $V_B$, which have large enough exchange energies to be identified numerically as the magnetically ordered systems.

Within the framework of Heisenberg spin model, it is possible to estimate the Curie temperatures ($T_c$) of these systems. The mean-field result is given by

$$k_B T_c^{MF} = \frac{2}{3} J_0,$$

(1)

where $J_0$ is the on-site exchange parameter reflecting the exchange field created by all the neighbouring magnetic moments.\[24\] Note that the $T_c$ determined by Eq.(1) is regarded as an overestimated values.\[25\] Since the $J_0$ is regarded as an overestimated values\[25\]. Hence, the estimated $T_c$ (denoted as $T_c^{MF}$ hereafter) by just simply substituting $J$ in FIG.10 into the $J_0$ in Eq.(1) is expected as an upper-bound of $T_c^{MF}$ for a given system. For $O_N$, $V_B$ and $Si_B$ with relatively large $J_S$ at $d_D = 10.03\AA$, the $T_c^{MF}$s are $72K$, $43K$ and $13K$ respectively. However, they reduce to around 20K for $O_N$ and $V_B$, below 5K for $Si_B$ when $d_D$ is increased to 13.26Å. In addition, the $T_c^{MF}$s of the defect systems with exchange energies smaller than 5 meV are all below 5K in different concentrations. Therefore, one can conclude that the effect of the long-range magnetic ordering is very weak in all the defect systems considered here except for the defect systems of $O_N$ and $V_B$. However, our calculations suggest that the systems of $Be_B$, $C_B$, $C_N$, $O_B$, $O_N$, $Si_B$, $Si_N$, $V_B$ and $V_N$ all have finite magnetic moments and are therefore at least paramagnetic.

V. CONCLUSIONS

Different concentrations of non-magnetic impurities and vacancies in BN sheet were studied using first-principles methods to investigate the possible magnetism in these systems involving only $s$- and $p$-electron elements. We firstly studied the effects of these defects on DOS and analyzed the characters as well as the spacial extent of these defect states. The magnetization energies, possible magnetic moments as well as the exchange energies for these defect systems in different concentrations were evaluated. We demonstrated that all the defect systems with partially-filled defect bands exhibited a definite preference for finite magnetic moments. The calculated exchange energies for low-density defect systems are all tiny except for the $O_N$ and $V_B$ whose exchange energies are not completely insignificant with an estimated $T_c$ of 20K.

Acknowledgments

This work was supported by the National Science Council of Taiwan. Part of the computer resources are provided by the NCHC (National Center of High-performance Computing). We also thank the support of NCTS (National Center of Theoretical Sciences) through the CMR (Computational Material Research) focus group.

[1] T. L. Makarova et al., Nature(London), 413, 716 (2001); However, retraction in T. L. Makarova et al., Nature(London), 440, 707 (2006) and references within.
[2] M. Tamura et al., Chem. Phys. Lett. 186, 401 (1991); P. M. Allemand et al., Science, 253, 301 (1991); Y. Murakami and H. Suematsu, Pure Appl. Chem. 68 A163, (1996); F. J. Owens, Z. Iqbal, L. Belova, K. V. Rao, Phys. Rev. B 69, 033403 (2004); O. E. Kvyatkovskii, I. B. Zakharova, A. L. Shelankov, T. L. Makarova, Phys. Rev. B 72, 214426 (2005).
[3] P. Esquinazi et al., Phys. Rev. B 66, 024429 (2002) and Phys. Rev. Lett., 91, 227201 (2003); Y. Kopelevich et al., J. Low Temp. Phys., 119, 601 (2000).
[4] Yong-Hyun Kim, J. Choi, K. J. Chang, D. Tomanek, Phys. Rev. B 68, 125420 (2003); Yuchen Ma et al., New J. Phys. 6 68, (2004); H. J. Xiang et al, New J. Phys., 7, 39 (2005); Hong Seok Kang, J. Phys. Chem. B 110, 4621 (2006); R. Q. Wu et al., J. Phys.: Condens. Matter 18 569 (2006); M. S. Si and D.S.Xue, Europhys. Lett., 76(4), 664 (2006).
[5] A. N. Andriotis, M. Menon, R. M. Sheetz, L. Chernozatskii, Phys. Rev. Lett., 90, 026801 (2003); P. Esquinazi et al., Phys. Rev. Lett., 91, 227201 (2003); P. O. Lehtinen, A. S. Foster, Y. Ma, A. V. Krasheninnikov, R. M. Nieminen, Phys. Rev. Lett., 93, 187202 (2004).
[6] S. L. Rumyantsev et al., in "Properties of Advanced SemiconductorMaterials GaN, AlN, InN, BN, SiC, SiGe". Edited by M. E. Levinstein, S. L. Rumyantsev, M. S. Shur, John Wiley and Sons, Inc., New York, 2001, p67-92.
[7] J. Cumings and A. Zettl, Chem. Phys. Lett. 316, 211 (2000); E. Bengu and L. D. Marks, Phys. Rev. Lett., 86, 2385 (2001); W. Mickelson, S. Aloni, W. Han, J. Cumings, and A. Zettl, Science 300, 467 (2003); F. F.
Xu, Y. Bando and D. Golberg, New J. Phys. 5 118 (2003).
[8] X. Blase, A. Rubio, S. G. Louie, and M. L. Cohen, Europhys. Lett. 28, 335 (1994).
[9] J. Osorio-Guillén, S. Lany, S. V. Barabash, A. Zunger, Phys. Rev. Lett., 96, 107203 (2006).
[10] D. M. Edwards and M. I. Katsnelson, J. Phys.: Condens. Matter 18, 7209 (2006).
[11] A. N. Andriotis, R. M. Sheetz and M. Menon, J. Phys.: Condens. Matter 17 L35-L38 (2005).
[12] P. Hohenberg and W. Kohn, Phys. Rev., 136, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev., 140, A1133 (1965).
[13] J. P. Perdew in 'Electronic Structure of Solids ’91, edited by P. Ziesche and H. Eschrig (Akademie-Verlag, Berlin, 1991); J. P. Perdew et al., Phys. Rev. B 46, 6671 (1992).
[14] P.E. Blöchl, Phys. Rev. B 50, 17953 (1994).
[15] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
[16] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
[17] G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993); 49, 14251 (1994); G. Kresse and J. Furthmüller, Comput. Mater. Sci. 6, 15 (1996); Phys. Rev. B 54, 11169 (1996).
[18] N. Ooi, A. Rairkar, L. Lindsley and J. B. Adams, J. Phys.: Condens. Matter 18 97 (2006).
[19] The lattice constants calculated from LDA with $E_{\text{cut}} = 400$eV are $a = 2.48\AA$ and $c = 5.9\AA$ and become $a = 2.5\AA$ and $c = 6.23\AA$ when $E_{\text{cut}}$ is increased to 500eV. However, the GGA results of $c$ become $7\AA$ at $E_{\text{cut}} = 500$eV. Similar results of overestimation for $c$ in hexagonal BN from GGA has been documented in [13, 20].
[20] A. Janotti, S.-H. Wei and D. J. Singh, Phys. Rev. B 64, 174107 (2001).
[21] H. Hellmann, Einführung in die Quantenchemie (Deuticke, Leipzig, 1937), pp.61 and 285; R. P. Feynman, Phys. Rev. 56, 340 (1939).
[22] With Heisenberg Hamiltonian: $H = -2J \sum_{i,j} S_i \cdot S_j$, we have $\xi \equiv E_{AFM} - E_{FM}$, where $\xi$ is effective coupling pairs.
[23] K. Sato, P. H. Dederics and H. Katayama-Yoshida, Europhys. Lett., 61(3), 403 (2003).
[24] J. Kudrnovský et al., Phys. Rev. B 69, 115208 (2004).
[25] G. Bouzerar, T. Zimman and J. Kudrnovský, Europhys. Lett., 69(5), 812 (2005).