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Magnetic properties of vacancies in a graphitic boron nitride sheet by first-principles pseudopotential calculations

M. S. Si and D. S. Xue*

Key Laboratory of Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, Lanzhou 730000, People's Republic of China

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We use *ab initio* methods to calculate the magnetic properties of vacancies in a graphitic boron nitride sheet (g-BN). By applying a full spin-polarized description to the system, we demonstrate that the nitrogen vacancy (V_N) or the boron vacancy (V_B) can induce spontaneous magnetization. The magnetic nature of these intrinsic vacancies suggests that it is important to understand their role in the recently observed magnetism in the metal-free materials.

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As the techniques for growth and preparation of light-element nanostructures have developed, the list of feasible applications has seen rapid increases.[1,2] However, concurrent to this growth of technological possibilities has been an increase in the demand for atomic-scale understanding of the processes which determine light-element nanostructure properties. Studies of radiation effects[3] in graphite and other carbon nanostructures and experiments on as-grown nanotubes[4] have demonstrated that intrinsic vacancies are a common phenomenon in standard samples. Understanding the properties of these intrinsic vacancies has become an essential part of such diverse processes in light-element materials such as strain,[5] lithium storage in nanotube based batteries,[6] catalytic growth,[7] junctions,[8] and quantum dot creation.[4,9] Possibly even more importantly, the recent experimental demonstrations of magnetism in a pure carbon system[10–14] have ignited speculation that carbon could offer the tantalizing prospect of a zero-gap, high-temperature, ferromagnetic semiconductor. Several studies have speculated that intrinsic carbon vacancies could be responsible for the observed magnetic properties.[10,15] Much of recent research activity is based on carbon-related materials. Until now the g-BN material with vacancies revealing the $d0$ ferromagnetism phenomena has not been reported experimentally. Also, there are only a few theoretical studies concerning electronic structure[16,17] and magnetic properties[18] of defects in BN systems.

In this paper, we report results of our density functional theory (DFT) and local spin-density approximation (LSDA) studies on the electronic and magnetic properties of the V_N and V_B defects in g-BN. This system is interesting because g-BN has a melting temperature >1700 K, which makes it suitable for high temperature applications, and the g-BN can form different nanoscale structures such as nanotubes,[19] fullerenes,[20] and fullerites.[21] The BN-based magnetic nanostructures can be used as molecular magnets. Therefore, the basic theoretical studies on the source of magnetization in connection with vacancies in g-BN will certainly be important.

Our calculation is based on the density functional theory and the local spin density functional formalism. The calculation is carried out using the SIESTA code.[22,23] The valence electrons are described by a linear combination of numerical atomic-orbital basis set (LCAO) (Refs. 24 and 25) and the atomic core by norm-conserving pseudopotentials. The pseudopotentials generated using the Troullier and Martins scheme[26] are used to describe the interaction of valence electrons with atomic core, and their nonlocal components are expressed in the fully separable form of Kleinman and Bylander.[27,28] The generalized gradient approximation correction in the form of Perdew *et al.*[29] is adopted for the exchange-correlation potential. The double-zeta plus polarization atomic orbital basis set is employed in the calculation. The Hamiltonian matrix elements are calculated by charge density projection on a real space grid with an equivalent plane wave cutoff energy of 300 Ry. Periodical boundary condition is employed and the adjacent layers are separated by a vacuum region 12 Å. The conjugate gradient algorithm[30] is adopted to fully relax the structure of the graphitic sheet until the maximum force on a single atom is within 0.02 eV/Å. A supercell consisting of a graphitic-BN sheet made of $5\times5\times1$ unit cell is used in the calculations. For this 49-atom supercell the total energy is converged to 10^{-5} eV with a Monkhorst-Pack[31] k-point mesh of $5\times5\times1$. The structure and electronic properties of g-BN are calculated using similar parameters. The equilibrium lattice constant (which equals the nearest-neighbor N-N or B-B distance) of 2.52 Å and the band-gap of 4.60 eV for g-BN are in good agreement with those obtained by similar calculations.[18,32] Upon V_N or V_B in g-BN of the 49-atom supercell, we calculate the total energies for both the spin-polarized and the non-spin-polarized states. The results suggest that in each case spin polarization is favored by 0.03 eV over nonpolarization from the total energy. To study the properties of the vacancies, we consider a g-BN supercell of 50 atoms with a single nitrogen or boron atom removed. Our test calculations show that the vacancies placed in any position in the supercell lead to the same results. Our calculations also show that the equilibrium atomic structure (see Fig. 1) of the V_N or V_B type vacancy in the g-BN crystal is similar to that of the pristine g-BN, in the sense that the N and B atoms are still located in a plane, after the introduction of the vacancy. This geometry is not similar to the previous works on carbon-related materials.[15,33,34] In the case of the V_N defect [Fig. 1(a)], the three boron atoms closest to the vacancy move closer to each other, forming a regular trianglelike structure. The distance between any two of those boron at-

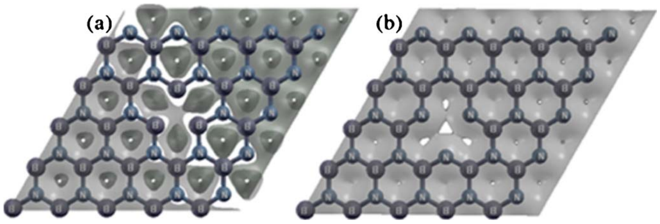

FIG. 1. (Color online) The atomic structures and the charge density isosurfaces of the V_N (a) and V_B (b) defects in the g-BN with both isovalues of 0.01 $e/Å^3$.

oms is 2.28 Å, whereas the nearest-neighbor N-N or B-B distance in the perfect g-BN is ~2.52 Å. The formation energy[35] of the V_N defect was 8.33 eV. The formation energy of the vacancy at the site i (i=N,B) in the pristine g-BN crystal, is given by the expression

$$E^f[V_i^0] = E_{\rm tot}[V_i^0] - E_{\rm tot}[g\text{-BN,pristine}] + \mu_i, \tag{1}$$

where $E_{\rm tot}[V_i^0]$ is the total energy of the supercell containing the vacancy defect, $E_{\rm tot}$ [g-BN, pristine] is the total energy of the corresponding pristine g-BN supercell (without any defects), and μ_i is the chemical potential of atom i. Equation (1) is a special case of Eq. (2) of Ref. 36, in a sense that in our case we deal with neutral defects ($q=0$) and the number of atoms removed from the supercell in order to create a vacancy defect at the site i, is exactly one ($n_i=-1$). Contrary to the V_N defect case, in the case of the V_B defect, the three atoms closest to the vacancy, i.e., the three nitrogen atoms, move further apart from each other, forming a regular trianglelike structure [Fig. 1(b)] whose side has a length of 2.62 Å. The formation energy was 9.99 eV. By comparing the two formation energies above, it seems that the V_N defect is more likely to form than the V_B one. The isosurfaces of the charge density around the N and B vacancies (Fig. 1), with the isovalue of 0.01 $e/Å^3$ for both defect cases (V_N and V_B), demonstrate clearly the presence of the charge distribution between any two atoms closest to the vacancy, indicating the formation of a weak covalent bond.

The ground state of the V_N is spin-polarized with a magnetic moment of $1.0\mu_B$, and the isosurface of spin density with isovalue of 0.005 $e/Å^3$ is shown in Fig. 2(a). After the removal of one nitrogen atom, each of the three neighboring boron atoms now has one unpaired electron. From the regular local symmetry of the atomic structure and the spin density distribution closest to the nitrogen vacancy, we predict that the three boron atoms should produce exactly identical magnetic moments. Further, qualitative analysis on the distribution of the magnetic moment and the unpaired electron has been studied. From the standard Mulliken population analysis[37] on the charges of the atoms we found that the spin polarization mainly comes from the $2p_z$ orbital of each boron atom with value about $0.25\mu_B$, the spin density isosurface being the projection on the xy plane. Moreover, these polarized boron atoms closest to the vacancy also make the six near-neighbor boron atoms polarized and they altogether provide a magnetic moment ~$0.25\mu_B$ [cannot be seen in Fig. 2(a)]. In the case of the V_B defect, the magnetic moment is $3.0\mu_B$, and the isosurface of spin density with isovalue of 0.0048 $e/Å^3$ is shown in Fig. 2(b). Concerning each nitrogen atom closest to the vacancy, the counting of the five valence electrons is as follows: two electrons participate in the covalent bond with the borons. The remaining three electrons make the magnetic properties more complicated. Due to the low-dimensional effects and the broken local symmetry,[38,39] the remaining electrons will be newly assigned from that of perfect g-BN. From the three remaining electrons, one goes to the $2p_x$, $2p_y$, or $2p_z$ orbital, the magnetic moment is only provided by $2p_x$ or $2p_y$ orbitals from the standard Mulliken population analysis, and these orbitals of each nitrogen atom altogether offer the magnetic moment around $0.75\mu_B$. The other magnetic moments come from six near-neighbor nitrogen atoms polarized by the nitrogen ones closest to the vacancy as shown in Fig. 2(b), and each one has a magnetic moment ~$0.125\mu_B$. The second electron goes to the pseudodangling sp^3 bond (the sp bonds are not identical in the g-BN with vacancies, for distinguishing the standard sp bond we add the modificatory word "pseudo" here). The third electron is shared between pseudodangling sp^3 bond and any two nitrogen atoms nearest to the vacancy forming a weak covalent bond as shown in Fig. 1(b). The pseudodangling sp^3 bond will also probably be very slightly spin polarized, but this effect is negligibly small and cannot be seen in Fig. 2(b).

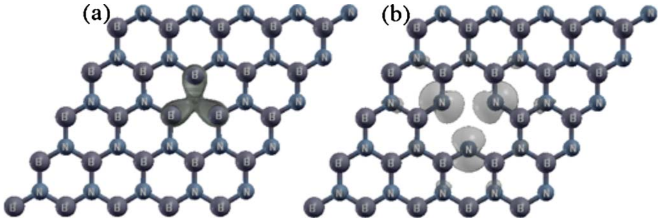

FIG. 2. (Color online) The spin-density isosurface at the isovalue of 0.005 $e/Å^3$ (0.0048 $e/Å^3$) of the V_N defect (a) [V_B defect (b)] in the g-BN.

We want to point out that the magnetic state is not dependent on the size of the cell, since it is consistently the ground state for the 72 and 98 atom slabs. However, we also find that the total energy difference between nonmagnetic and magnetic as a function of the cell size contains oscillations as obviously observed by Lehtinen *et al.*[38] This oscillatory behavior[38,40] points to a RKKY interaction between the vacancies in the g-BN. The spin-polarized band structures of pristine g-BN, the V_N and V_B in the g-BN are given in Fig. 3. In the band structure of pristine g-BN, we can see that all states are in twofold degeneracy, indicating no spin polarization. The nitrogen vacancy results in a lift-up of the Fermi level of the system and emergence of a flat band near the Fermi level, which is due to the fact that the vacancy obtained by removing a nitrogen atom acts as an n-type vacancy. All bands with energies lower than −3.0 eV are fully occupied and thus do not contribute to spin polarization. However, the flat band near Fermi level is split into two branches. The spin-up branch is occupied and the spin-down branch is left empty, leading to a spontaneous polarization with a net magnetic moment of $1.0\mu_B$. The case of the V_B defect appears to have a different behavior, the Fermi level

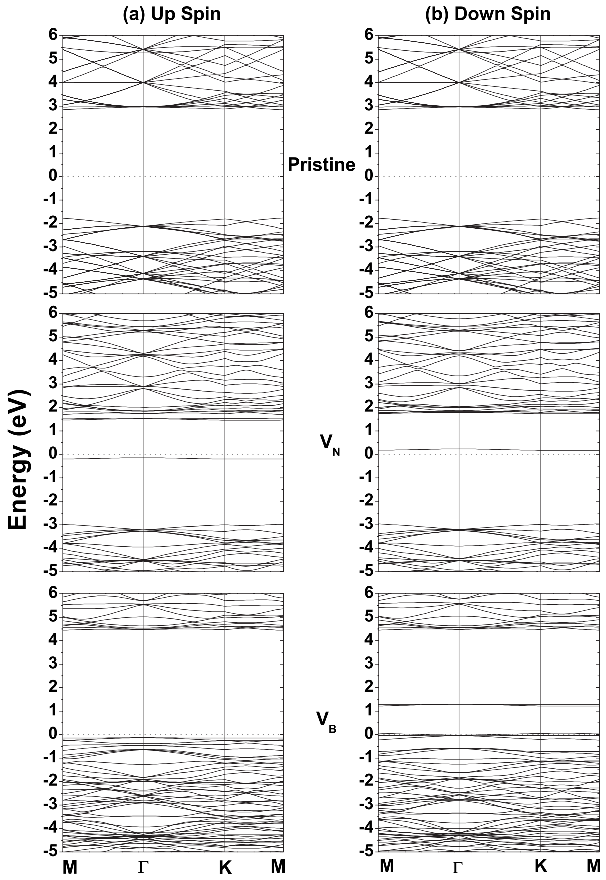

FIG. 3. The band structures of pristine g-BN, the V_N and V_B defects in the g-BN along symmetry directions. The Fermi level is set to zero.

being pushed down since the lost boron atom forms a p-type vacancy. Below the Fermi level the occupied bands of spin-up are more than that of spin-down, inducing a spontaneous polarization with a net magnetic moment of $3.0\mu_B$. Moreover, there are some occupied states of spin-down at the Fermi level, and the states of spin-up disappear at the Fermi level, revealing half-metallic behavior.

In Fig. 4 we present the majority and minority densities of states (DOS) of the three systems. In the case of the V_N defect [Fig. 4(b)], we can see that the majority DOS exceeds the minority DOS by the occupied peak just below the Fermi level. On the contrary, in the case of the V_B defect [Fig. 4(c)] the majority DOS vanishes at the Fermi level, while a peak in the minority DOS emerges at the Fermi level. The result appears to have the desired half-metallic behavior leading to a complete, i.e., 100%, spin polarization of the conduction electrons.

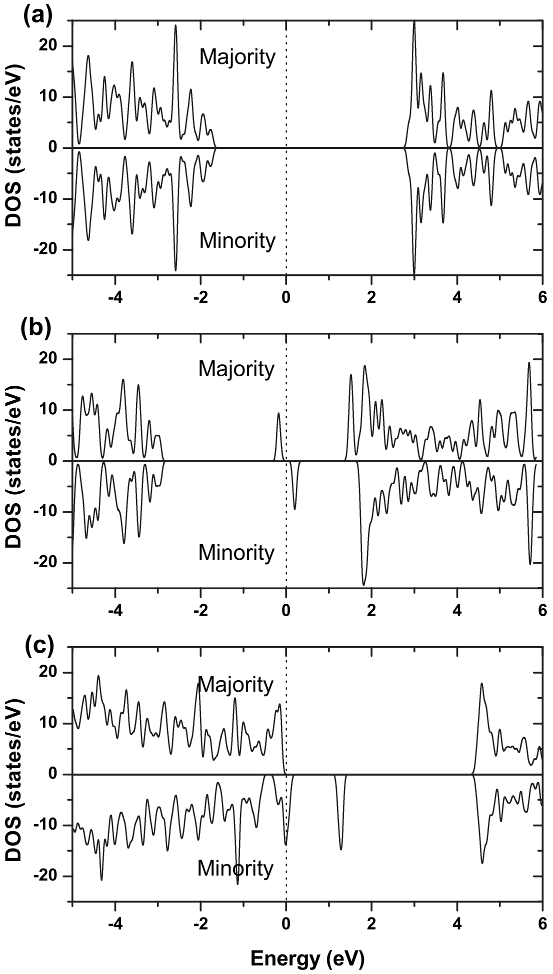

FIG. 4. The calculated majority and minority DOS of (a) pristine g-BN, (b) the V_N defect in the g-BN, and (c) the V_B defect in the g-BN. The Fermi level is denoted by the vertical dotted lines.

In summary, we have performed first-principles pseudopotential calculation with double-zeta plus polarization atomic-orbital basis set to study the electronic and magnetic properties of single vacancies in g-BN. The results show that the vacancies can induce spontaneous magnetization. More interestingly, the V_B in g-BN appears to have desired half-metallic behavior. The similar magnetic moment induced by defects was reported[41] in AlN nanotube and this also proves our results.

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*Electroic address: xueds@lzu.edu.cn

[1] R. Saito, M. Fujita, G. Desselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College London Press, London, 1998).

[2] P. M. Ajayan, Chem. Rev. (Washington, D.C.) **99**, 1787 (1999).

[3] F. Banhart, Rep. Prog. Phys. **62**, 1181 (1999).

[4] M. Bockrath, W. J. Liang, D. Bozovic, J. H. Hafner, C. M. Lieber, M. Tinkham, and H. Park, Science **291**, 283 (2001).

[5] G. G. Samsonidze, G. G. Samsonidze, and B. I. Yakobson, Phys. Rev. Lett. **88**, 065501 (2002).

[6] V. Meunier, J. Kephart, C. Roland, and J. Bernholc, Phys. Rev. Lett. **88**, 075506 (2002).

[7] Y. H. Lee, S. G. Kim, and D. Tománek, Phys. Rev. Lett. **78**, 2393 (1997).

[8] M. Ouyang, J. L. Huang, C. L. Cheung, and C. M. Lieber, Science **291**, 97 (2001).

[9] M. T. Woodside and P. L. McEuen, Science **296**, 1098 (2002).

[10] T. L. Makarova, B. Sundqvist, R. Höhne, P. Esquinazi, Y. Kopelevich, P. Scharff, V. A. Davydov, L. S. Kashevarova, and A. V. Rakhmanina, Nature (London) **413**, 716 (2001).

[11] S. Bandow, F. Kokai, K. Takahashi, M. Yudasaka, and S. Iijima, Appl. Phys. A: Mater. Sci. Process. **73**, 281 (2001).

[12] P. Esquinazi, A. Setzer, R. Höhne, C. Semmelhack, Y. Kopelevich, D. Spemann, T. Butz, B. Kohlstrunk, and M. Lösche, Phys. Rev. B **66**, 024429 (2002).

[13] R. A. Wood, M. H. Lewis, M. R. Lees, S. M. Bennington, M. G. Cain, and N. Kitamura, J. Phys.: Condens. Matter **14**, L385 (2002).

[14] J. M. D. Coey, M. Venkatesan, C. B. Fitzgerald, A. P. Douvalis, and I. S. Sanders, Nature (London) **420**, 156 (2002).

[15] Y. Ma, P. O. Lehtinen, A. S. Foster, and R. M. Nieminen, New J. Phys. **6**, 68 (2004).

[16] W. Orellana and H. Chacham, Phys. Rev. B **63**, 125205 (2001).

[17] T. M. Schmidt, R. J. Baierle, P. Piquini, and A. Fazzio, Phys. Rev. B **67**, 113407 (2003).

[18] R. Q. Wu, G. W. Peng, L. Liu, and Y. P. Feng, J. Phys.: Condens. Matter **18**, 569 (2006).

[19] N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, and A. Zettl, Science **269**, 966 (1995).

[20] D. Golberg, Y. Bando, O. Stephan, and K. Kurashima, Appl. Phys. Lett. **73**, 2441 (1998).

[21] V. V. A. Pokropivny, V. V. Skorokhod, G. S. Oleinik, A. Kurdyumov, T. S. Bartnitskaya, A. V. Pokroprivny, A. G. Sisonyuk, and D. M. Sheichenko, J. Solid State Chem. **154**, 214 (2000).

[22] P. Ordejón, E. Artacho, and J. M. Soler, Phys. Rev. B **53**, R10441 (1996).

[23] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).

[24] J. Junquera, O. Paz, D. Sánchez-Portal, and E. Artacho, Phys. Rev. B **64**, 235111 (2001).

[25] E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García, and J. M. Soler, Phys. Status Solidi B **215**, 809 (1999).

[26] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[27] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[28] D. M. Bylander and L. Kleinman, Phys. Rev. B **41**, 907 (1990).

[29] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[30] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *New Numerical Recipes* (Cambridge University Press, New York, 1986).

[31] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[32] Y. N. Xu and W. Y. Ching, Phys. Rev. B **44**, 7787 (1991).

[33] A. A. El-Barbary, R. H. Telling, C. P. Ewels, M. I. Heggie, and P. R. Briddon, Phys. Rev. B **68**, 144107 (2003).

[34] R. H. Telling, C. P. Ewels, A. A. El-Barbary, and M. I. Heggie, Nat. Mater. **2**, 333 (2003).

[35] G. X. Qian, R. M. Martin, and D. J. Chadi, Phys. Rev. B **38**, 7649 (1988).

[36] K. Laaksonen, H.-P. Komsa, E. Arola, T. T. Rantala, and R. M. Nieminen, J. Phys.: Condens. Matter **18**, 10097 (2006).

[37] A. Szabo and N. S. Ostlund, *Modern Quantum Chemical* (McGraw-Hill, New York, 1989).

[38] P. O. Lehtinen, A. S. Foster, A. Ayuela, A. Krasheninnikov, K. Nordlund, and R. M. Nieminen, Phys. Rev. Lett. **91**, 017202 (2003).

[39] M. S. Si and D. S. Xue, Europhys. Lett. **76**, 664 (2006).

[40] P. Bruno and C. Chappert, Phys. Rev. B **46**, 261 (1992).

[41] M. Simeoni, S. Santucci, S. Picozzi, and B. Delley, Nanotechnology **17**, 3166 (2006).

[42] A. Kokalj, Comput. Mater. Sci. **28**, 155 (2003).