Magnetism in 2D BN$_{1-x}$O$_x$ and B$_{1-x}$Si$_x$N: polarized itinerant and local electrons

Ru-Fen Liu$^\dagger$ and Ching Cheng$^\dagger$

Department of Physics, National Cheng Kung University, 1 University Road, Tainan 70101, Taiwan

We use density functional theory based first-principles methods to study the magnetism in a 2D hexagonal BN sheet induced by the different concentrations of oxygen and silicon atoms substituting for nitrogen (O$_N$) and boron (Si$_B$) respectively. We demonstrate the possible formation of three distinct phases based on the magnetization energy calculated self-consistently for the ferromagnetic (ME$_{FM}$) and antiferromagnetic (ME$_{AFM}$) states, i.e. the paramagnetic phase with ME$_{FM}$=ME$_{AFM}$, the ferromagnetic phase with ME$_{FM}$>ME$_{AFM}$ and finally the polarized itinerant electrons with finite ME$_{FM}$ but zero ME$_{AFM}$. While the O$_N$ system was found to exist in all three phases, no tendency towards the formation of the polarized itinerant electrons was observed for the Si$_B$ system though the existence of the other two phases was ascertained. The different behavior of these two systems is associated with the diverse features in the magnetization energy as a function of the oxygen and silicon concentrations. Finally, the robustness of the polarized itinerant electron phase is also discussed with respect to the O substitute atom distributions and the applied strains to the system.

PACS numbers: 75.75.+a, 71.10.Pm, 71.10.Ca, 61.72.-y

I. INTRODUCTION

The theoretical model of the two-dimensional (2D) homogeneous electron gas (HEG), which considers the electrons moving in a 2D uniform positive charge background, serves as an important model system for studying the fundamental many-electron behavior in 2D systems. These physical properties are closely connected to the operations of conduction electrons in the layered semiconductor devices as well as the recently synthesized 2D periodic systems. The most creditable method considered presently for studying the 2D HEG is the quantum Monte Carlo (QMC) method. The recent QMC studies found no region of stability for a ferromagnetic fluid in the 2D HEG. The phases were found to transit directly from a polarized Wigner crystal to the normal fluid (paramagnetic state). However, it would be interesting to explore the parallel phase diagram for real materials, i.e. systems of electrons moving in a neutralizing background formed by a 2D lattice of nuclei, and study the corresponding magnetic property as a function of the electron density.

Inspired by the exciting experimental works on the discovery and synthesisization of hexagonal boron nitride (h-BN) in low-dimensional structures as well as the possible formation of magnetism in these systems through creations of defects, here we present Density Functional Theory (DFT) based first-principles studies on the magnetic properties of a 2D hexagonal BN sheet induced by the oxygen and silicon atoms substituting for the N and B atoms respectively (denoted as O$_N$ and Si$_B$ hereafter), i.e. BN$_{1-x}$O$_x$ and B$_{1-x}$Si$_x$N. We demonstrate the possible formation of polarized itinerant electrons in the O$_N$ system. The stable phases are identified as, in increasing substitute atom concentration $x$, the paramagnetic phase, the ferromagnetic phase and finally the polarized itinerant electrons. In addition, the Si$_B$ system which though supports the formation of ferromagnetic phase displays no tendency to the stabilization of the polarized itinerant electrons, i.e. resembling the QMC result for a 2D HEG.

II. COMPUTATION METHOD

The DFT calculations employed in the present study use the generalized gradient approximation (GGA) for the exchange-correlation energy functional and the projector augmented-wave (PAW) method for describing the interaction between core and valence electrons as implemented in the VASP code. To simulate the systems with the substitute atom concentration $x$ ranging from 1/55 to 1/4, the supercells with distance (denoted as $d_{nn}$) of $\sim$17.5Å, 13.3Å, 10Å, 7.5Å and 5Å between nearest-neighbor substitute atoms were constructed. A vacuum distance larger than 12Å was used in the calculations to remove the interaction between layers. The numerical convergence was accomplished by using k-points meshes of (7 7 1) generated from Monkhost-Pack method for the supercell consisting of $2 \times 2$ unit cells (and the similar density of k-points meshes for the supercells of other sizes), and the kinetic-energy cut-off of 400eV (with tests at 500 eV) for expanding the single electron Kohn-Sham wavefunctions in plane-wave basis. The atomic forces calculated by Hellmann-Feynman theorem were relaxed to less than 0.02eV/Å in all calculations. Furthermore, the volume and shape were...
Hamiltonian, the net magnetic moments in these magnetic systems can be approximated from the exchange energy $J$, i.e. $ME = \sum J S_i S_j$, then the interaction among the local magnetic moments is confirmed by the corresponding density of states (DOS) of these systems. The magnetization energy $ME_{FM}$ for both $O_N$ and $Si_B$ is given in the unit of per substitute atom. (All the magnetic related quantities discussed here are set up with antiparallel local moments of equal magnitude and then followed by the spin-density relaxation in the self-consistent calculations.

III. RESULTS

The calculated magnetizations for both $O_N$ and $Si_B$ stay as $1 \mu_B$ per substitute atom throughout the systems of fractional $x$’s studied in this work. The magnetic moment found in both systems can be attributed to the $p_z$-electrons of $B$ atoms. When the $O$ or $Si$ substitute atom concentration is increased, both systems develop into the ferromagnetic phase with finite $J$. The values of $4J$ can be as high as 42meV for $Si_B$ at $x = 1/4$, which corresponds to a Curie temperature estimated with the mean field approximation ($T_{CMF}$) of 80K and 44meV for $O_N$ at $x = 1/9$, to a $T_{CMF}$ of 83K. Note that these ferromagnetic systems consist of no magnetic elements like Fe, Co, Ni, or rare-earth elements.

As the substitute atom concentration is increased, both systems develop into the ferromagnetic phase with finite $J$. The values of $4J$ can be as high as 42meV for $Si_B$ at $x = 1/4$, which corresponds to a Curie temperature estimated with the mean field approximation ($T_{CMF}$) of 80K and 44meV for $O_N$ at $x = 1/9$, to a $T_{CMF}$ of 83K. Note that these ferromagnetic systems consist of no magnetic elements like Fe, Co, Ni, or rare-earth elements.

The calculated magnetizations for both $O_N$ and $Si_B$ stay as $1 \mu_B$ per substitute atom throughout the systems of fractional $x$’s studied in this work. The magnetic moment found in both systems can be attributed to the $p_z$-electrons of $B$ atoms. When the $O$ or $Si$ substitute atom concentration is increased, both systems develop into the ferromagnetic phase with finite $J$. The values of $4J$ can be as high as 42meV for $Si_B$ at $x = 1/4$, which corresponds to a Curie temperature estimated with the mean field approximation ($T_{CMF}$) of 80K and 44meV for $O_N$ at $x = 1/9$, to a $T_{CMF}$ of 83K. Note that these ferromagnetic systems consist of no magnetic elements like Fe, Co, Ni, or rare-earth elements.

As the substitute atom concentration is increased, both systems develop into the ferromagnetic phase with finite $J$. The values of $4J$ can be as high as 42meV for $Si_B$ at $x = 1/4$, which corresponds to a Curie temperature estimated with the mean field approximation ($T_{CMF}$) of 80K and 44meV for $O_N$ at $x = 1/9$, to a $T_{CMF}$ of 83K. Note that these ferromagnetic systems consist of no magnetic elements like Fe, Co, Ni, or rare-earth elements.

The calculated magnetizations for both $O_N$ and $Si_B$ stay as $1 \mu_B$ per substitute atom throughout the systems of fractional $x$’s studied in this work. The magnetic moment found in both systems can be attributed to the $p_z$-electrons of $B$ atoms. When the $O$ or $Si$ substitute atom concentration is increased, both systems develop into the ferromagnetic phase with finite $J$. The values of $4J$ can be as high as 42meV for $Si_B$ at $x = 1/4$, which corresponds to a Curie temperature estimated with the mean field approximation ($T_{CMF}$) of 80K and 44meV for $O_N$ at $x = 1/9$, to a $T_{CMF}$ of 83K. Note that these ferromagnetic systems consist of no magnetic elements like Fe, Co, Ni, or rare-earth elements.

As the substitute atom concentration is increased, both systems develop into the ferromagnetic phase with finite $J$. The values of $4J$ can be as high as 42meV for $Si_B$ at $x = 1/4$, which corresponds to a Curie temperature estimated with the mean field approximation ($T_{CMF}$) of 80K and 44meV for $O_N$ at $x = 1/9$, to a $T_{CMF}$ of 83K. Note that these ferromagnetic systems consist of no magnetic elements like Fe, Co, Ni, or rare-earth elements.

The calculated magnetizations for both $O_N$ and $Si_B$ stay as $1 \mu_B$ per substitute atom throughout the systems of fractional $x$’s studied in this work. The magnetic moment found in both systems can be attributed to the $p_z$-electrons of $B$ atoms. When the $O$ or $Si$ substitute atom concentration is increased, both systems develop into the ferromagnetic phase with finite $J$. The values of $4J$ can be as high as 42meV for $Si_B$ at $x = 1/4$, which corresponds to a Curie temperature estimated with the mean field approximation ($T_{CMF}$) of 80K and 44meV for $O_N$ at $x = 1/9$, to a $T_{CMF}$ of 83K. Note that these ferromagnetic systems consist of no magnetic elements like Fe, Co, Ni, or rare-earth elements.
The establishment of the polarized itinerant electrons in O\textsubscript{N} at \( x = 1/4 \) is further supported through the charge distribution for the states in CBs just below \( E_F \) around \( \Gamma \) point in the non-spin-polarized calculation. In O\textsubscript{N}, the charges distribute mainly on the B atoms surrounding the O impurity (a rather extending distribution) which is further joined by the charges distributing above the more distant N atoms. Therefore the charges distribute as connected charge sheet throughout the system for the isosurface of density less than 0.324\( \text{e} \). This result contrasts to that in the Si\textsubscript{B} system whose charges distribute mostly around the substitute Si atoms (a more local distribution) and the connected isosurface occur only when the density is less than 0.213\( \text{e} \).

The \( x \)-dependence ME’s are also very different for Si\textsubscript{B} and O\textsubscript{N}. In Si\textsubscript{B}, both the ME\textsubscript{FM} and ME\textsubscript{AFM} decreases monotonically with respect to increasing \( x \) (decreasing \( d_{nn} \)). However, in O\textsubscript{N}, the two \( x \)-dependence ME’s diverge at values of \( x \) larger than 1/16, i.e. the decreasing and approaching zero ME\textsubscript{FM} versus an increasing ME\textsubscript{FM}. We should emphasize here that the behavior of ME\textsubscript{FM} for O\textsubscript{N} differs not only from that for Si\textsubscript{B} but also from that for the systems carrying localized moments formed by other non-magnetic substitute atoms in the BN sheet. Examples are the 2D BN sheet with carbon atoms substituting for either B or N atoms, Si atoms for N atoms, as well as the vacancies created by removing either B or N atoms\textsuperscript{10}. The exceptional behavior of ME\textsubscript{FM} together with the vanishing ME\textsubscript{AFM} in O\textsubscript{N} provides a prominent feature for this 2D system as developing into the polarized itinerant electron phase.

IV. ROBUSTNESS OF THE POLARIZED ITINERANT ELECTRONS IN O\textsubscript{N}

In order to examine how the establishment of the polarized itinerant electrons in O\textsubscript{N} at \( x = 1/4 \) depends on the oxygen distributions, different supercells consisting of O atoms with the same nearest-neighbor distance \( d_{nn} \sim 5\text{Å} \) but different numbers and distributions are studied. They include a) a \( 6\times6 \) supercell but with only eight instead of nine O substitute atoms, b) a \( 4\times4 \) supercell but with only three instead of four O atoms c) a rectangular instead of a \( 4\times2 \) hexagonal supercell with two O substitute atoms. All these examined systems were found to be still stabilized in the polarized itinerant electron phase with less than 4meV changes in ME\textsubscript{FM}. Regarding the substitute atom concentration \( x \), the highest \( x \) of magnetic O\textsubscript{N} system we considered is 1/3, i.e. \( d_{nn}=4.3\text{Å} \). At this concentration, the system remains stabilized in the polarized itinerant electron phase. However, we should emphasize that the role of N atoms in O\textsubscript{N} is essential as magnetism would disappear if all N atoms are replaced by O atoms, i.e. the BO sheet is in fact a normal metal. When mapping into the 2D HEG, this corresponds to the paramagnetic fluid at high electron density.

FIG 3 shows the \( x \)-dependence formation energy for
where \( E_{0N} \) (Si) to eliminate numerical errors, \( E_{BN\text{sheet}} \) calculated by using exactly the same supercell as 1/64, i.e. \( d_{\text{in}}=20\text{Å}. \)

\( E_{\text{Form}} \equiv E_{\text{ON(SiB)}} - E_{\text{BN\text{sheet}}} + E_{\text{N(B)}} - E_{\text{O(Si)}}, \)

where \( E_{\text{ON(SiB)}} \) and \( E_{\text{BN\text{sheet}}} \) are the energies for the \( \text{ON} \) (\( \text{SiB} \)) system (ferromagnetically polarized ones) and the BN sheet calculated by using exactly the same supercell to eliminate numerical errors, \( E_{\text{N}} \) (\( E_{\text{B}} \)) and \( E_{\text{O}} \) (\( E_{\text{Si}} \)) are the energies for the removed N (B) and the added O (Si) atoms respectively. The formation energy for the system of \( x = 1/64 \), i.e. the system with no interaction among the substitute atoms, is taken as the reference zero in the figure. Unlike the repulsive interactions in SiB at \( x \leq 1/9 \), the O atoms introduced for substituting N atoms in the BN sheet exhibit attractive interaction once \( x \) becomes larger than 1/32. Besides, by employing a very large supercell (11×10) with only two substitute atoms (SA) created at the distance \( d_{\text{SA-SA}} \) in the cell, it is shown (see the insert in FIG 3) that for both systems the substitute atoms tend to aggregate to form the system of \( x = 1/4 \).

FIG. 3: The \( x \)-dependence formation energy for \( \text{ON} \) and SiB, where the reference zero is chosen as the formation energy at \( x = 1/64 \), i.e. \( d_{\text{in}}=20\text{Å}. \)

\( \text{O}_N \) and \( \text{Si}_B \), which is defined as

\( E_{\text{Form}} \equiv E_{\text{ON(SiB)}} - E_{\text{BN\text{sheet}}} + E_{\text{N(B)}} - E_{\text{O(Si)}}, \)

where \( E_{\text{ON(SiB)}} \) and \( E_{\text{BN\text{sheet}}} \) are the energies for the \( \text{ON} \) (\( \text{SiB} \)) system (ferromagnetically polarized ones) and the BN sheet calculated by using exactly the same supercell to eliminate numerical errors, \( E_{\text{ON}} \) (\( E_{\text{BN\text{sheet}}} \)) and \( E_{\text{O}} \) (\( E_{\text{Si}} \)) are the energies for the removed N (B) and the added O (Si) atoms respectively. The formation energy for the system of \( x = 1/64 \), i.e. the system with no interaction among the substitute atoms, is taken as the reference zero in the figure. Unlike the repulsive interactions in SiB at \( x \leq 1/9 \), the O atoms introduced for substituting N atoms in the BN sheet exhibit attractive interaction once \( x \) becomes larger than 1/32. Besides, by employing a very large supercell (11×10) with only two substitute atoms (SA) created at the distance \( d_{\text{SA-SA}} \) in the cell, it is shown (see the insert in FIG 3) that for both systems the substitute atoms tend to aggregate to form the system of \( x = 1/4 \).

Considering the possible experimental fabrication of this 2D system supported on a substrate, our study show that the system with polarized itinerant electrons can sustain an external applied tensile and compressive strain of up to 0.1, i.e. a change of 10% in lattice constant. Similar study for SiB, on the contrary, leads to a nonmagnetic state when the system is under compressive strain.

V. CONCLUSION

In summary, we have explored the possible magnetic phases in the \( \text{ON} \) and \( \text{SiB} \) systems using first-principles methods. The polarized itinerant electron phase was found in the \( \text{BN}_{3/4} \text{O}_{1/4} \) system while in the \( \text{SiB} \) system only the paramagnetic phase at low silicon concentrations and ferromagnetic phase at high silicon concentrations were identified. The different magnetic properties in \( \text{ON} \) and \( \text{SiB} \) were discussed through the \( x \)-dependence magnetization energy, the band structures, and the charge-density distributions. The robustness of the formation of the polarized itinerant electron phase was also discussed with respect to the O substitute atom distributions and the applied strain to the system.

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] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Proc. Natl Acad. Sci. USA 102, 10451 (2005).
[2] Chuanhong Jin, Fang Lin, Kazu Suenaga, and Sumio Iijima, Phys. Rev. Lett. 102, 195505 (2009).
[3] D. M. Ceperley, Nature, 397, 386 (1999).
[4] B. Tanatar and D. M. Ceperley, Phys. Rev. B, 39, 5005 (1989).
[5] C. Attaccalite, S. Moroni, P. Gori-Giorgi, and G. B. Bachelet, Phys. Rev. Lett., 88, 256601 (2002).
[6] N. D. Drummmond and R. J. Needs, Phys. Rev. Lett. 102, 126402 (2009).
[7] E. P. Wigner, Phys. Rev. 46, 1002 (1934).
[8] N.G. Chopra, R.J. Luyken, K. Cherrey, V.H. Crespi, M.L. Cohen, S.G. Louie, and A. Zettl, Science 269, 966 (1995).
[9] Zhi-Gang Chen, Jin Zou, Gang Liu, Feng Li, Yong Wang, Lianzhou Wang, Xiao-Li Yuan, Takashi Sekiguchi, Hue-Ming Cheng and Gao Qing Lu, ACS Nano 2, 2183 (2008).
[10] Ru-Fen Liu and Ching Cheng, Phys. Rev. B 76, 014405 (2007).
[11] Veronica Barone and Juan E. Peralta, Nano Lett. 8, 2210 (2008).
[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] Vienna ab initio Simulation Package, G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993); 49, 14251 (1994); G. Kresse and J. Furthmuller, Comput. Mater. Sci. 6, 15 (1996); Phys. Rev. B 54, 11169 (1996).
[17] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
[18] H. Hellmann, Einführung in die Quantenchemie (Deuticke, Leipzig, 1937), pp.61 and 285; R. P. Feynman, Phys. Rev. 56, 340 (1939).
[19] A class of the doped systems involving only 2s- and 2p- electrons in the host 2D BN sheet has been studied previously[10], in which two types of magnetic moments are identified, i.e. the planer one formed by sp2-electrons and the perpendicular one formed by pz-electrons. The structure likely undergoes distortions for the systems with planer magnetic moments, besides we further found that their moments tend to vanish at $x = 1/4$; while that for the systems with perpendicular magnetic moments likely stays in the three-fold symmetry.
[20] Contrary to the invariable magnetic moments of $1\mu_B$ by the substituted O and Si atoms in a BN sheet, the magnetic moments by substituting B and N atoms in graphene disappear at low substitution concentration[21]. This could be attributed to the unusual linear dispersion $\pi$ and $\pi^*$ bands joined at the K symmetry point in reciprocal space in graphene.
[21] Ranber Singh and Peter Kroll, J. Phys.: Condens. Matter, 21, 196002 (2009).
[22] X. Blase, Angel Rubio, Steven G. Louie, and Marvin L. Cohen, Phys. Rev. B 51, 6868 (1995).
[23] B. Arnaud, S. Lebègue, P. Rabiller, and M. Alouani, Phys. Rev. Lett., 96, 026402 (2006).
[24] The distance between two layers in the bulk hexagonal BN, i.e. 3.3Å, were used to determine the isocharge density.
[25] There are probably more appropriate choices for $E_{N(B)}$ and $E_{O(Si)}$, e.g. half of the energy of O2 for E0. However, as we are discussing the formation energy relative to that of the systems with $x = 1/64$, the systems with those terms are cancelled out and play no role here.