



Tuning the electronic and magnetic properties of borophene by 3d transition-metal atom adsorption



J.Y. Li ^{a,b,1}, H.Y. Lv ^{a,1}, W.J. Lu ^{a,*}, D.F. Shao ^a, R.C. Xiao ^{a,b}, Y.P. Sun ^{a,c}

^a Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China

^b University of Science and Technology of China, Hefei, 230026, China

^c High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei, 230031, China

ARTICLE INFO

Article history:

Received 12 July 2016

Received in revised form 28 September 2016

Accepted 28 September 2016

Available online 30 September 2016

Communicated by R. Wu

Keywords:

Low-dimensional materials

Itinerant-electronic system

Density functional theory

ABSTRACT

The electronic and magnetic properties of borophene functionalized by 3d transition metal (TM) atom adsorption are investigated by using first-principles calculations. The results show that the 3d TM atoms can be adsorbed on borophene with high binding energies ranging between 5.9 and 8.3 eV. Interestingly, the originally nonmagnetic borophene tends to be ferromagnetic when Ti, V, Cr, Mn, and Fe atoms are adsorbed, and the magnetic moments are dominated by the TM atoms. The origin of the ferromagnetism is discussed based on the Stoner criterion. Our results indicate that the magnetic properties of borophene can be effectively tuned through the adsorption of 3d TM atoms, which could have promising applications in spintronics and nanoelectronics.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Inspired by the huge success of graphene [1], two dimensional (2D) materials, such as silicene [2], phosphorene [3], and transition metal dichalcogenides [4] have drawn lots of attention in the past few years. These 2D materials exhibit remarkable properties, including large I_{on}/I_{off} ratio [5], high carrier mobility [3], etc., which indicate the promising applications in future nanodevices [6]. Besides manipulating of the charge degree of freedom, due to the great progress in spintronics [7], there are also many efforts focused on modulating the spin characteristic of 2D materials by means of the transition metal doping [8], geometry reconstruction [9] or surface functionalization [10]. These methods have already achieved great success in the fields such as diluted magnetic semiconductor, but only few works concentrate on the metallic substrate [11].

Most recently, a new 2D material borophene was successfully synthesized which was grown on Ag (111) surface and exhibits anisotropic metallic characteristic [12]. Such newly emerging material soon attracts much attention and many studies have been done to explore its potential applications. Using first-principles calculation, Jiang et al. predicted that borophene could be a promising anode material for lithium-ion batteries, due to its high specific

capacity and high rate capability [13]. With respect to the spintronic applications, Meng et al. have investigated the edge effect on the magnetic properties of quasi-1D borophene nanoribbons and the systems with the zigzag edge configuration are found to exhibit ferromagnetic ground state [14]. However, to the best of our knowledge, few results have been reported on the robust ferromagnetism properties of 2D borophene. If we could introduce robust ferromagnetism in this 2D system, this newly emerging 2D material may have wider applications in the spintronics.

In this work, we aim to investigate the electronic and magnetic properties of 3d transition metal (TM) adsorbed borophene. The results show that the magnetic properties of borophene could be effectively tuned by 3d TM atom adsorption. When the adatoms are Ti, V, Cr, Mn, and Fe, the borophene tends to be ferromagnetic with the magnetic moment dominated by the TM atoms. Using Stoner criterion, such magnetic ground states can be explained by the itinerant ferromagnetic theory. Such robust ferromagnetism characteristic in borophene is highly desirable for the 2D spintronics.

2. Methods

All the calculations were performed with the projected augmented wave (PAW) formalism [15] as implemented in the ABINIT package [16,17]. The local density approximation (LDA) [18] was adopted to deal with the exchange and correlation energy. The B 2s/2p and the TM 3d/4s electrons were treated as valence electrons. The energy cutoff of 700 eV was employed and the Brillouin

* Corresponding author.

E-mail address: wjlu@issp.ac.cn (W.J. Lu).

¹ The authors contributed equally to this work.

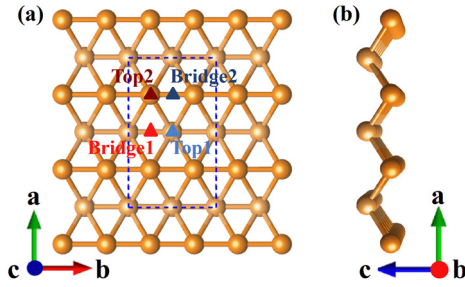


Fig. 1. (a) Top and (b) side views of borophene. The blue rectangle represents the supercell used in our calculation. The “Bridge” and “Top” sites denoted in (a) represent the sites on top of the boron atom (in the bottom layer) and the one in the middle of the bond between two boron atoms (in the bottom layer), respectively. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

zone was sampled with a $12 \times 8 \times 1$ Monkhorst–Pack $\mathbf{k}$ -mesh. A vacuum of 15 Å was added to ensure no interaction between borophene sheet. Structure optimization was performed until the force acting on the TM atom was less than 0.025 eV/Å. During the structure optimization, the lattice parameters and the internal coordinates of borophene were fixed to the experimental results ($a = 3.4$ Å, $b = 5.8$ Å) [12], while the TM atoms were fully relaxed.

3. Results and discussions

The top and side views of borophene are shown in Figs. 1(a) and (b), respectively. The borophene sheet is buckled, with the top and bottom layers of boron atoms in dark and light color, respectively. As denoted by the blue rectangle in Fig. 1(a), a $2 \times 2 \times 1$ supercell with the doping concentration of 12.5% is considered in this work. The 3d TM atoms (from Sc to Cu in the periodic table) are adsorbed on the surface of the borophene sheet.

Firstly, the energetically more favorable positions are determined by calculating the binding energy (E_b) of the TM atom adsorbed borophene, which is defined as $E_b = E(\text{TM}) + E(\text{borophene}) - E(\text{borophene} + \text{TM})$, where $E(\text{TM})$, $E(\text{borophene})$ and $E(\text{borophene} + \text{TM})$ are the energies of the isolated TM atom, the pristine borophene and the TM atom adsorbed borophene, respectively. We have considered different adsorption sites, including “Top1” (T1), “Bridge1” (B1), “Top2” (T2), and “Bridge2” (B2) sites as indicated in Fig. 1(a). The calculated binding energies with respect to these sites are listed in Table 1. The results show that the TM atoms will occupy either the T1 or the B1 sites, depending on the corresponding binding energies listed in Table 1. We can see that the Sc, Ti, V and Mn atoms tend to adsorb on the B1 site, while Cr, Fe, Co, Ni, and Cu atoms prefer T1 site. Moreover, due to the large binding energies, all the TM atoms bind tightly with the substrate of borophene sheet, which means that the structures are very stable when the atoms are adsorbed on the surface of borophene. On the other hand, we have also checked the possibility of segregation of the adsorbed TM atoms. To keep the adsorption concentration unchanged, we doubled the supercell and let the two adsorption atoms move closer to each other gradually. The results show that the energy of the system increases as the distance of two TM atoms is decreased, indicating that the segregation is not energetically favorable. In Table 1, we also listed the distances between TM atoms and the nearest-neighboring boron atoms. We can see that for each case, the distance when the TM atom is at the T1 site is relatively larger than that when it is at the B1 site.

In Fig. 2, we display the binding energies and magnetic moments of the TM atoms for different adatoms at their most stable absorption sites. We can see that from Sc to Cu, the binding energy (in red color) reaches its maximum at Ti atom while suddenly drops to its minimum at Cr, and then it increases again, reaching

Table 1

Binding energies E_b when the TM atoms are adsorbed on top of the four different sites of borophene, and distance d between TM atom and the nearest-neighboring boron atom.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$E_{b,T1}$	7.09	8.03	7.11	5.94	7.14	7.42	7.93	7.83	6.10
$E_{b,B1}$	7.22	8.28	7.26	5.90	7.27	7.41	7.82	7.59	5.91
$E_{b,T2}$	6.08	6.45	5.06	3.48	4.89	4.99	5.76	6.32	5.45
$E_{b,B2}$	7.04	7.97	7.03	5.85	7.19	7.34	7.86	7.78	6.06
d_{T1} (Å)	2.36	2.26	2.15	2.11	2.08	2.06	2.02	2.04	2.10
d_{B1} (Å)	2.18	2.06	1.97	1.90	1.87	1.84	1.83	1.88	2.03
d_{T2} (Å)	2.07	1.99	1.94	1.89	1.86	1.82	1.78	1.79	1.90
d_{B2} (Å)	2.32	2.08	2.05	1.98	1.96	1.93	1.90	1.90	2.00

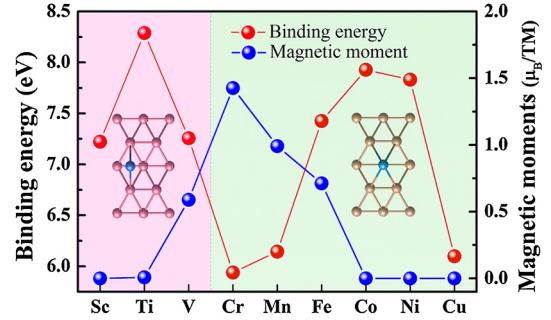


Fig. 2. Binding energy (in blue color) and magnetic moment around the TM atom (in red color) for different TM atom adsorbed borophene at the most stable absorption site. For Sc, Ti, and V atoms, the binding energies and magnetic moments are calculated when they are adsorbed on the B site (light pink region), while for Cr, Mn, Fe, Co, Ni, and Cu atoms, the values are calculated when the TM atoms are adsorbed on the T site (light blue region). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the other peak at Co atom. The binding energies range from 5.9 to 8.3 eV, indicating that the TM atom adsorbed systems are very stable. It is worth noting that the trend of the binding energy is the same as in the case of the TM doped carbon nanotube [19]. The overall shape of the binding energy indicates that the binding energy is related to the number of unpaired 3d electrons of TM atom. The systems with the 3d shell of the TM atoms half-filled (Cr and Mn: $3d^5$) and fully-filled (Cu: $3d^{10}$) have much smaller binding energies. On the other hand, the trend of the magnetic moment of the TM atom (blue line) is opposite to that of the binding energy. It is interesting to note that for Ti, V, Cr, Mn and Fe atoms, the system tends to be ferromagnetic. The Ti adsorbed borophene has the smallest magnetic moment of 0.22 μ_B/TM , and the maximum magnetic moment of 1.43 μ_B/TM is obtained for the Cr adsorbed borophene. To check the possibility of antiferromagnetic state, we have doubled the supercell, which has two TM atoms in it and the spins of the two atoms are aligned antiparallel to each other. For the above cases, the energies of the antiferromagnetic configurations are all relatively higher than those of the ferromagnetic state, indicating that the ferromagnetic states are energetically more favorable. More complex antiferromagnetic configurations are beyond the scope of the present work.

To investigate the origin of the magnetic properties, we calculate the corresponding density of states (DOS) for different systems, which are shown in Fig. 3. For the pristine borophene, as shown in Fig. 3(a), there are finite number of states at the Fermi energy, reflecting its metallic ground state. The perfect symmetry between the spin up and spin down channels reveals that the pristine borophene is nonmagnetic. The results for the Sc, Co, Ni, and Cu adsorbed systems are similar, that is, they are all nonmagnetic metals. For the Ti, V, Cr, Mn, and Fe adsorbed borophene (see Figs. 3(b)–(f)), which are ferromagnetic, the results show that they all remain metallic. The spin up and spin down channels are asymmetry, indicating that there exist exchange split-

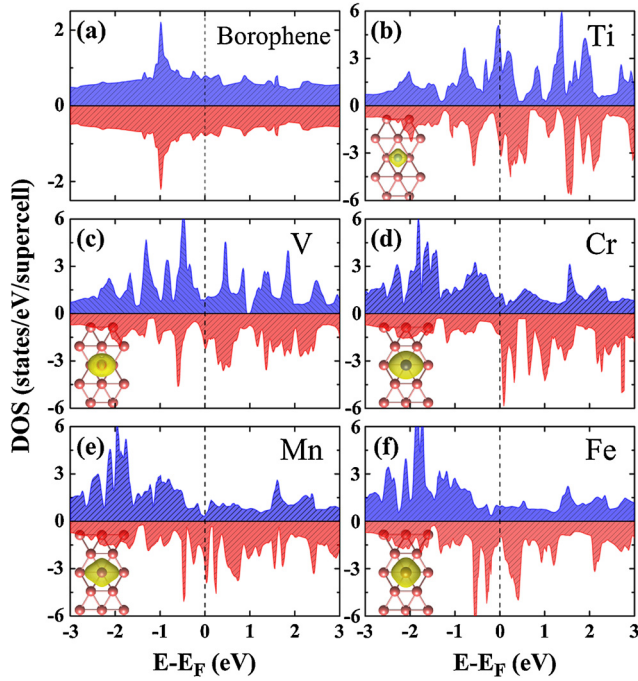


Fig. 3. Density of states (DOS) of (a) pristine, (b) Ti, (c) V, (d) Cr, (e) Mn, and (f) Fe adsorbed borophene. The insets in (b)–(f) are the corresponding spin density ($\rho_{\uparrow} - \rho_{\downarrow}$) isosurface distributions (0.01 eV/Å³).

ting energies in these systems, so these TM doped borophene are spin-polarized. Moreover, the results of the spin densities (see the insets in Figs. 3(b)–(f)) indicate that the magnetism is mainly localized around the TM atoms. The volume inside the isosurface is largest for the Cr-doped system while smallest for the Ti-doped one, which is consistent with the result that the magnetic moment is largest around the Cr atom while smallest around the Ti atom.

The origin of the ferromagnetism can be roughly explained by the Stoner criterion, which is defined as $N(E_F) \times I > 1$, where $N(E_F)$ donates the average number of states between spin up channel and spin down channel at the Fermi energy for the nonmagnetic case and I is the Stoner exchange parameter. For the system that exhibits obvious ferromagnetism, the Stoner exchange parameter I was calculated by the formula [20]

$$\Delta E_{ex} = m \times I, \quad (1)$$

where m and ΔE_{ex} are the magnetic moment and exchange splitting energy, respectively. For the nonmagnetic system, the Stoner exchange parameter I was calculated based on the relation [20]

$$E(m) - E(0) = \frac{1}{2} \chi^{-1} m^2, \quad (2)$$

where $E(m)$ is the energy when the moment was constrained to m , $E(0)$ is the energy of nonmagnetic case and χ is the enhanced susceptibility given by

$$\chi = \frac{2\mu_B^2 N(E_F)}{1 - N(E_F)I}. \quad (3)$$

In Table 2, we summarize the calculated $N(E_F)$, I and $N(E_F) \times I$ for the different TM atom adsorbed borophene. We can see that the Stoner criterion is satisfied for Ti, V, Cr, Mn, and Fe cases, therefore upon adsorption, these systems tend to be ferromagnetic. The results also indicate the itinerant ferromagnetism in these systems.

To further investigate the electronic and magnetic properties of the TM atom adsorbed borophene, we plot in Fig. 4 the partial density of states (PDOS) of the ferromagnetic systems. Here we

Table 2

Density of states at the Fermi energy $N(E_F)$ in nonmagnetic state and the Stoner parameter I along with the values of $N(E_F) \times I$ for the TM atom adsorbed borophene.

Element	$N(E_F)$ (states/eV/spin)	I (eV)	$N(E_F) \times I$
Sc	1.98	0.50	0.99
Ti	3.45	0.36	1.24
V	3.76	0.47	1.76
Cr	2.47	0.53	1.31
Mn	3.69	0.52	1.92
Fe	3.81	0.66	2.51
Co	1.26	0.50	0.63
Ni	1.34	0.23	0.31
Cu	0.82	0.34	0.28

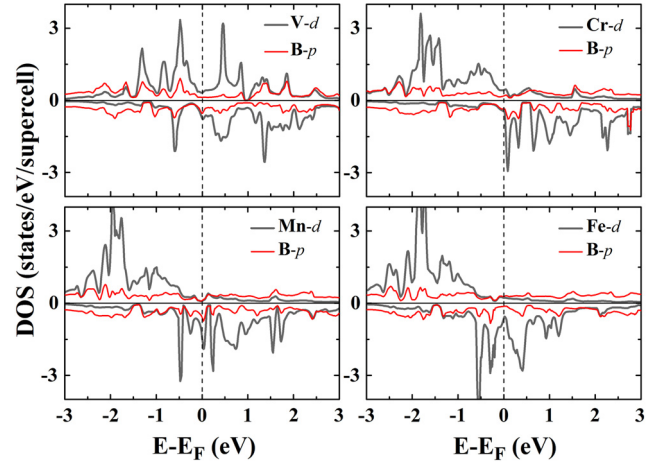


Fig. 4. Partial density of states (PDOS) of (a) V, (b) Mn, (c) Cr, and (d) Fe adsorbed borophene. The gray lines donate the 3d orbitals of the TM atoms while the red lines donate the 2p orbitals of boron. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

only show the four cases with relatively larger magnetic moments. For all the cases, the TM 3d orbital exhibits strong hybridization with the boron 2p orbital, which indicates the chemical adsorbing characteristic of the TM atoms. Furthermore, the 3d orbitals of the TM atoms are much more spin-polarized than those of the boron 2p orbitals, therefore the magnetism was mainly dominated by the 3d orbital of the TM atoms. Also, we can see that for the Cr doped system (see Fig. 4(c)), the PDOS of the 3d state was mainly dominated by the spin up channel, so the Cr adsorbed borophene exhibits a large magnetic moment. For Mn and Fe doped systems, the spin polarizations are relatively smaller than that of the Cr doped one, while much larger than that of the V doped system.

4. Conclusion

In summary, we have systematically studied the electronic and magnetic properties of the 3d TM atom adsorbed borophene by using the first-principles calculations. All the TM atoms considered in our calculations bind tightly on the surface of borophene. The 3d orbitals of the TM atoms show strong hybridization with the 2p orbitals of boron atoms, indicating the chemical adsorbing nature. Moreover, the system tends to be ferromagnetic when the adatoms are Ti, V, Cr, Mn, and Fe, with the magnetism dominated by the 3d orbital of the TM atoms. Based on the Stoner criterion, the origin of the ferromagnetism in the doped systems is discussed. Our results indicate that this novel material borophene could have promising applications in the fields of spintronics and nanoelectronics, which deserves further investigations in experiments.

Acknowledgements

This work was supported by the National Key Research and Development Program under Contract No. 2016YFA0300404, the National Natural Science Foundation of China under Contract Nos. 11404340, 11274311, U1232139, Anhui Provincial Natural Science Foundation under Contract No. 1408085MA11, and Youth Innovation Promotion Association, CAS (2012310). The calculations were partially performed at the Center for Computational Science, CASHIPS.

References

- [1] M.J. Allen, V.C. Tung, R.B. Kaner, *Chem. Rev.* 110 (2009) 132.
- [2] P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M.C. Asensio, A. Resta, B. Ealet, G. Le Lay, *Phys. Rev. Lett.* 108 (2012) 155501.
- [3] H. Liu, A.T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, P.D. Ye, *ACS Nano* 8 (2014) 4033.
- [4] Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, *Nat. Nanotechnol.* 7 (2012) 699.
- [5] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nat. Nanotechnol.* 6 (2011) 147.
- [6] G. Fiori, F. Bonaccorso, G. Iannaccone, T. Palacios, D. Neumaier, A. Seabaugh, S.K. Banerjee, L. Colombo, *Nat. Nanotechnol.* 9 (2014) 768.
- [7] S.A. Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S. Von Molnár, M.L. Roukes, A.Y. Chtchelkanova, D.M. Treger, *Science* 294 (2001) 1488.
- [8] J. He, K. Wu, R. Sa, Q. Li, Y. Wei, *Appl. Phys. Lett.* 96 (2010) 082504.
- [9] H. Zhang, X.B. Li, L.M. Liu, *J. Appl. Phys.* 114 (2013) 093710.
- [10] D.C. Elias, R.R. Nair, T.M.G. Mohiuddin, S.V. Morozov, P. Blake, M.P. Halsall, A.C. Ferrari, D.W. Boukhvalov, M.I. Katsnelson, A.K. Geim, et al., *Science* 323 (2009) 610.
- [11] H.Y. Lv, W.J. Lu, D.F. Shao, Y. Liu, Y.P. Sun, *Phys. Rev. B* 92 (2015) 21.
- [12] A.J. Mannix, X.F. Zhou, B. Kiraly, J.D. Wood, D. Alducin, B.D. Myers, X. Liu, B.L. Fisher, U. Santiago, J.R. Guest, *Science* 350 (2015) 1513.
- [13] H. Jiang, Z. Lu, M. Wu, F. Ciucci, T. Zhao, *Nano Energy* 23 (2016) 97.
- [14] F. Meng, X. Chen, J. He, *arXiv:1601.05338*, 2016.
- [15] P.E. Blöchl, *Phys. Rev. B* 50 (1994) 17953.
- [16] X. Gonze, J.M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, *Comput. Mater. Sci.* 25 (2002) 478.
- [17] X. Gonze, B. Amadon, P.M. Anglade, J.M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Cote, *Comput. Mater. Sci.* 180 (2009) 2582.
- [18] W. Kohn, L.J. Sham, *Phys. Rev.* 140 (1965) A1133.
- [19] E. Durgun, S. Dag, V.M.K. Bagci, O. Gülseren, T. Yildirim, S. Ciraci, *Phys. Rev. B* 67 (2003) 920.
- [20] H. Rosner, R. Weht, M. Johannes, W. Pickett, E. Tosatti, *Phys. Rev. Lett.* 88 (2001) 027001.