CONDENSED
MATTER

Ab Initio Study on Nonmetal and Nonmagnetic Metal Atoms Doped Arsenene[1]

M. Luo[a], *, Y. E. Xu[b], and Y. X. Song[c]

[a] *Department of Physics, Shanghai Second Polytechnic University,
Shanghai, 201209 People's Republic of China*

[b] *Department of Electronic Engineering, Shang Hai Jian Qiao University,
Shanghai, 201306 People's Republic of China*

[c] *Key Laboratory of Polar Materials and Devices, East China Normal University,
Shanghai, 200241 People's Republic of China*

*e-mail: luomin@sspu.edu.cn

Received August 4, 2017

The structural, electronic, and magnetic properties of arsenene doped with a series of nonmetals (B, C, F, N, and O) and nonmagnetic metals (Al, Ga, Li, Mg, and Na) are investigated using density functional theory. Magnetism is observed in the case of C. Among all the cases, the C-doped system is the most stable formed system. Hence, we study the ferromagnetic interaction in two-C-doped arsenene. Interestingly, both nonmagnetic (NM) and antiferromagnetic (AFM) states have been observed. As the increasing C−C distance, the magnetic coupling between the moments induced by two C is found to be AFM and the origin of the coupling can be attributed to the $p−p$ hybridization interaction involving polarized electrons.

1. INTRODUCTION

Novel functional two-dimensional (2D) materials with unique and unpredictable features have become a hot for recent years. Typically, the discovery of graphene [1] has gained much interest due to its exotic physics and potential applications in nanoelectric devices [2, 3]. Furthermore, many research efforts have also sought for other 2D materials with natural band gap in recent years [4, 5]. A potential 2D atomic crystal, namely phosphorene, displays excellent mechanical, thermoelectric, optical and electronic properties [6−9].

Recently, a new elemental 2D material has been identified based on theoretical calculations [10−12], namely grey arsenic, which is the structural counterpart of blue phosphorus. Zhang et al. [13] predicted that although the bulk phase of gray arsenic is typically semimetal, it can transform into an indirect band-gap semiconductor as thin as a monolayer (arsenene), which is different from planar graphene, silylene, and puckered phosphorene. Interestingly, it can transform from indirect gap to direct gap semiconductor under biaxial strain. Arsenene as a new 2D semiconductor shows a wide band gap of 1.49 eV and gets lots of attention [14, 15]. As is well known, it has been verified that transition metal (TM) atoms could induce magnetism,

scattering and superconduction at a low doping concentration and modify the electronic structure obviously [16]. In contrast to the magnetic moment based the d electrons of TM atoms, the magnetism induced by the sp states of nonmetal elements has much stronger long-range exchange coupling interactions without clustering of magnetic ions [17−19]. However, to the best of our knowledge, less interest has been gained to the electronic and magnetic properties of nonmetals and nonmagnetic metals doped arsenene.

Therefore, in this work, we focus on the electronic and magnetic properties of X-doped arsenenes (X = B, C, F, N, O, Al, Ga, Li, Mg, and Na) using ab initio method. The magnetic states are observed in the case of C. Among them, the C-doped arsenene has the largest binding energy. Then, we studied the interaction in the two-C-doped arsenene. Both nonmagnetic and ferromagnetic states were observed. Our results indicated that the antiferromagnetic (AFM) coupling is originated from the $p−p$ hybridization mechanism.

2. METHOD

Our calculations are performed by the ab initio method based on density functional theory (DFT) within the generalized gradient approximations (GGA-PBE) [20] as implemented in the VASP package [21]. The projector augmented-wave (PAW) [22]

---

[1] The article is published in the original.

pseudopotential method is used and the cut off energy is 450 eV. The $5 \times 5 \times 1$ k-points were used. The lattice parameter and buckling height of arsenene is 3.60 and 1.39 Å, respectively [17, 18]. The separation between two layers is 15 Å. In the relaxation procedures of the electron and ion degrees of freedom, the convergence tolerances of the total (free) energy are 0.1 and 1.0 meV, respectively.

3. RESULTS AND DISCUSSIONS

3.1. Electronic and Magnetic Properties of X Doped Arsenene

Firstly, in order to judge the stability of structures, we calculated the binding energy of the each case. Table 1 shows geometric and magnetic features of X-doped (X = B, C, F, N, O, Al, Ga, Li, Mg, and Na) arsenene. Here, the binding energy is estimated as $E_b = (E_G + E_{TM}) - E_T$, where E_G and E_T are the total energy of arsenene with one vacancy and with a TM dopant, respectively, E_{TM} is the energy of a TM atom. From our calculations, for nonmetals dopants, the values of E_b are in the range of 4.09–5.406 eV, which are close to the case of phosphorene. For nonmagnetic metals, the values are in the range of 2.469–4.532 eV. It is obvious that the average binding energy of nonmetals doped systems is much larger than that of nonmagnetic metals cases, as shown in Fig. 1, which indicates the strong bonding strength in nonmetal-doped arsenene.

Now, we studied the magnetic properties of X-doped (X = B, C, F, N, O, Al, Ga, Li, Mg, and Na) arsenene. Nonmagnetic states are observed in above cases except for C. A magnetic moment of $0.99\mu_B$ is shown in the case of C. To estimate the effect of nonmetal atoms on the electronic properties of arsenene, the band structures of one-X-doped arsenene of the $4 \times 4 \times 1$ supercell are first investigated, as shown in Fig. 2. From Fig. 2a, for the pure arsenene, the spin-up and spin-down components are symmetric, such that there are no magnetic properties. While the X dopant is doped, in the band gap there are some impurity channels from all atoms. However, for B, F, N, O, Al, Ga, Li, Mg, and Na, the spin-up and spin-down parts in the above cases are identical, and there are still no magnetic properties in these systems. With the one-C-doped arsenene, as shown in Fig. 2c, the C atom induces impurity states in the band gap. These impurity states in spin-up component are below the Fermi level (E_F) and that is above E_F in the spin-down component. Hence, the two parts are asymmetric, indicating the system is magnetic.

As shown in Fig. 3, we investigate the magnetism distributions of C-doped arsenene by analysis of the spin density. It is noticeable that the magnetic moments mainly concentrated on C and its neighboring three As atoms. The three surrounding atoms, As1,

Table 1. Binding energy (E_b), total magnetic moment (μ_{total}), and X-As bond lengths (L) of the X-doped $4 \times 4 \times 1$ arsenene (X = B, C, F, N, O, Al, Ga, Li, Mg, and Na)

| Nonmetals	B	C	F	N	O
E_b, eV	5.021	5.406	4.09	4.705	4.729
μ_{total} (μ_B)	0.0	0.99	0.0	0.0	0.0
L (Å)	2.057	1.971	2.347	1.950	2.079
Nonmagnetic metals	Al	Ga	Li	Mg	Na
E_b, eV	4.532	4.318	3.006	3.255	2.469
μ_{total} (μ_B)	0.0	0.0	0.0	0.0	0.0
L, Å	2.443	2.443	2.647	2.604	3.025

As2, and As3 have equal contribution to the magnetic moment. Next, we analyze the origin of the magnetic behavior and the doping effects of element C, as shown in Fig. 4, we calculated the total density of states (TDOS) and projected density of states (PDOS) of C-doped arsenene. As we discussed in Fig. 2c, there are obviously asymmetry spin spitting around the E_F in spin-up and spin-down densities. Corresponding PDOS discussions further reveal that these asymmetric impurity states in the band gap are mainly originated from the $2p$ electrons of C and $4p$ orbitals of adjacent As atoms, which demonstrated the hybridization of C and its surrounding As atoms. Similar analysis has been reported in the other study [23, 24].

3.2. Magnetic Coupling in C-substituted Arsenene

In the following, we come to investigate the interaction between two C dopants, and several possible configurations are shown in Fig. 5b. We fix one C dop-
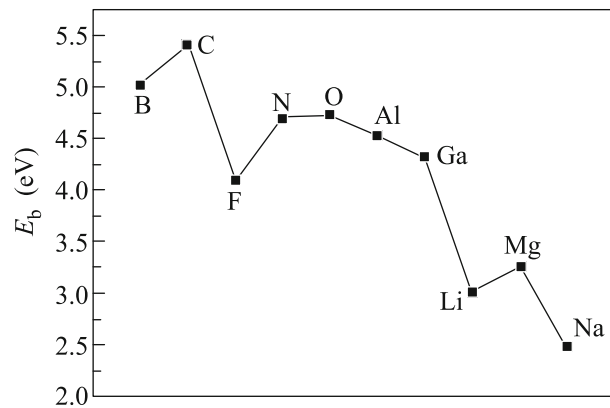
Fig. 1. Binding energies of different nonmetals and nonmagnetic metals doped in the $4 \times 4 \times 1$ AsX (X = B, C, F, N, O, Al, Ga, Li, Mg, and Na) monolayer.
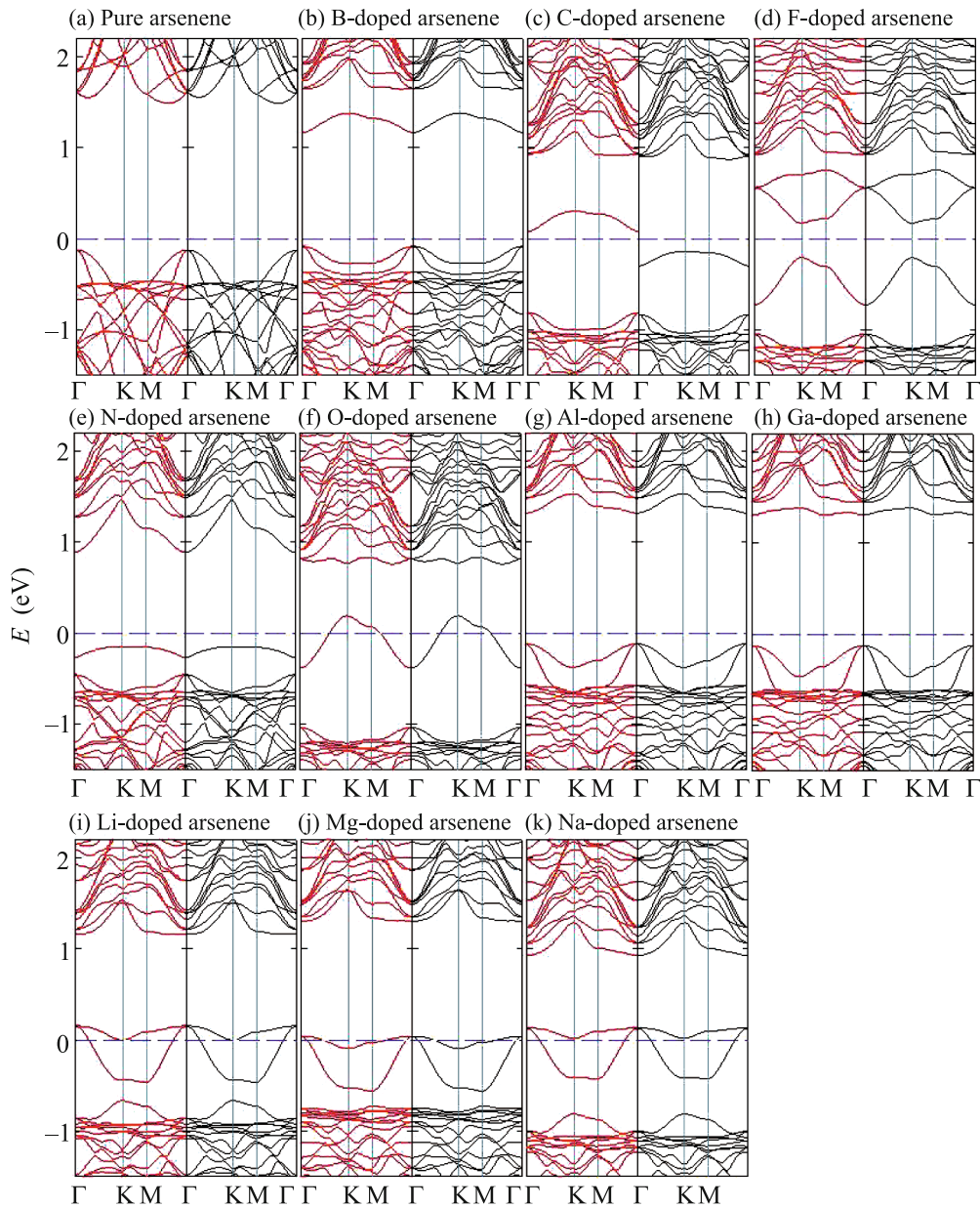
**Fig. 2.** (Color online) Band structures of nonmetals and nonmagnetic metals doped arsenene (AsX). The red and black lines represent the spin-up and spin-down components, respectively, where the Fermi level is indicated by the dotted line.

ant [denoted 0] and use i to denote another dopant C $(0, i)$, $i = 1–4$. From our calculations, the ferromagnetic coupling depends on C–C distance, as shown in Table 2.

In addition, we calculate the total energy difference ($\Delta E = E_{\mathrm{AFM}} - E_{\mathrm{FM}}$) between the AFM and ferromagnetic (FM) states for each configuration. While the C–C distance is not too large in the cases of $(0, 1)$, $(0, 2)$, and $(0, 3)$, ranging from 1.375 to 5.780 Å, ΔE keeps zero, which means that there no magnetic coupling between two C dopants. As the C–C distance

increasing to 7.20 Å [case $(0, 4)$], ΔE gets a value of -0.050 eV, implying an AFM coupling between two C. Note that a much larger C–C distance is considered in the $6 \times 6 \times 1$ supercell, as listed in Table 2, the total energy difference between the FM and AFM states is -0.061 eV. Then, we can expect that the AFM state is the favor state in the C-doped arsenene.

To further understand the different magnetic states, the TDOS and PDOS for case $(0, 3)$ and $(0, 4)$ are shown in Figs. 6 and 7, respectively. From Figs. 6b and 6c, we can see the spin-up and spin-down compo-
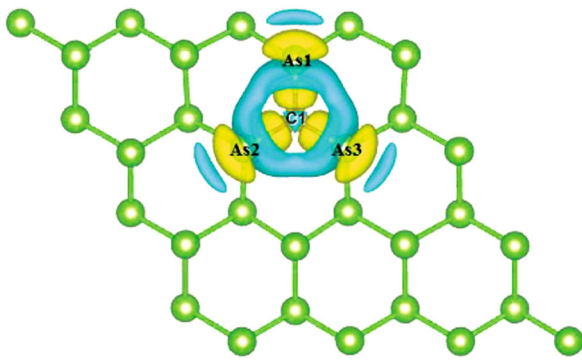
Fig. 3. (Color online) Calculated spin density distribution of one-C-doped arsenene. Yellow and cyan isosurfaces represent positive and negative spin densities (0.002 e/Å^3), respectively.
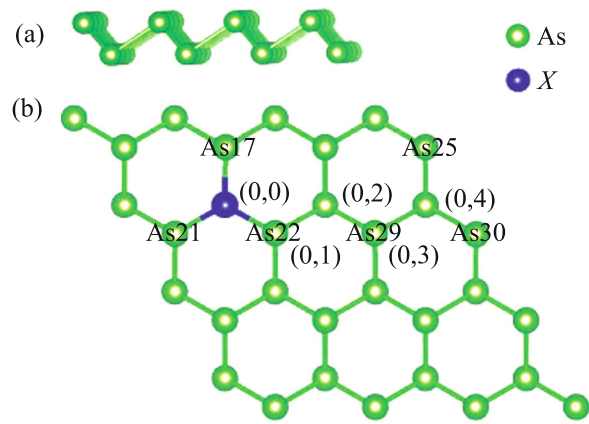
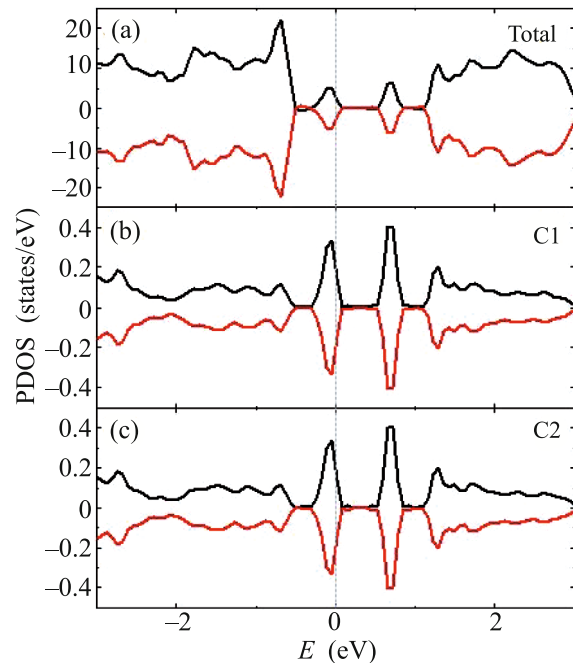**Fig. 5.** (Color online) (a) Schematic structure showing side view of pristine arsenene. (b) Top view of X-doped $4 \times 4 \times 1$ arsenene (X = B, C, F, N, O, Al, Ga, Li, Mg, and Na).
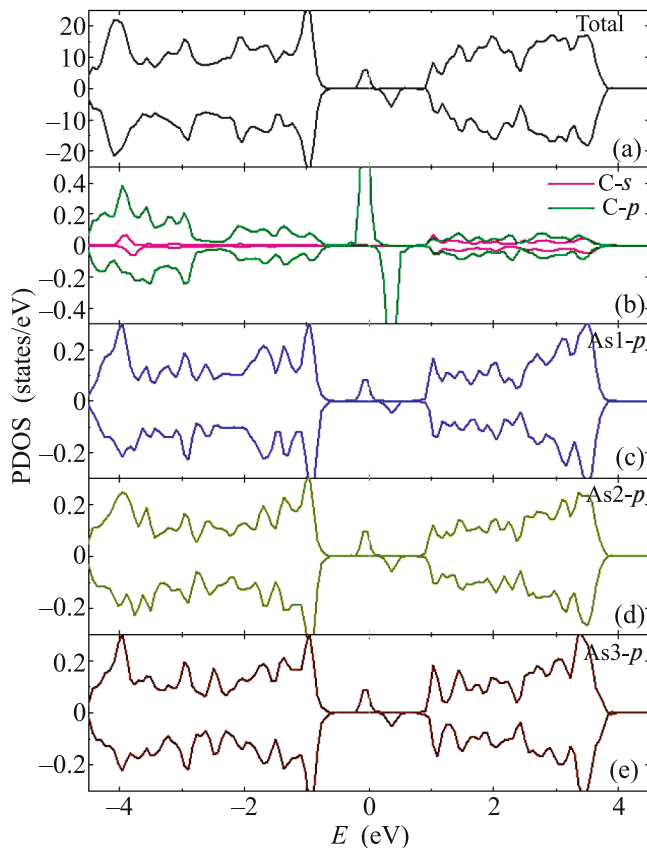
Fig. 4. (Color online) (a) Total density of state (TDOS). (b) Projected density of state (PDOS) of one-C-doped system C atom. (c−e) Three As atoms around C. The vertical dashed line indicates the Fermi level E_F.

Fig. 6. (Color online) (a) TDOS of two-C-doped system [case (0, 3)], (b, c) two C. The ground state is nonmagnetic (NM). The black and red lines represent the spin-up and spin-down states, respectively. The Fermi level E_F is noted by dashed line.

nents of each C are identical, implying that the total spin polarizations of one C dopant is zero. Hence, no magnetic property is expected. As is shown in Figs. 7b and 7c, it is obvious that the $2p$ states of dopant C

hybridize with $4p$ states of their neighboring As atoms near E_F. The spin of p electrons of the C atom aligns parallel to neighboring As atoms through the $p-p$ hybridization interaction. The majority-spin p states
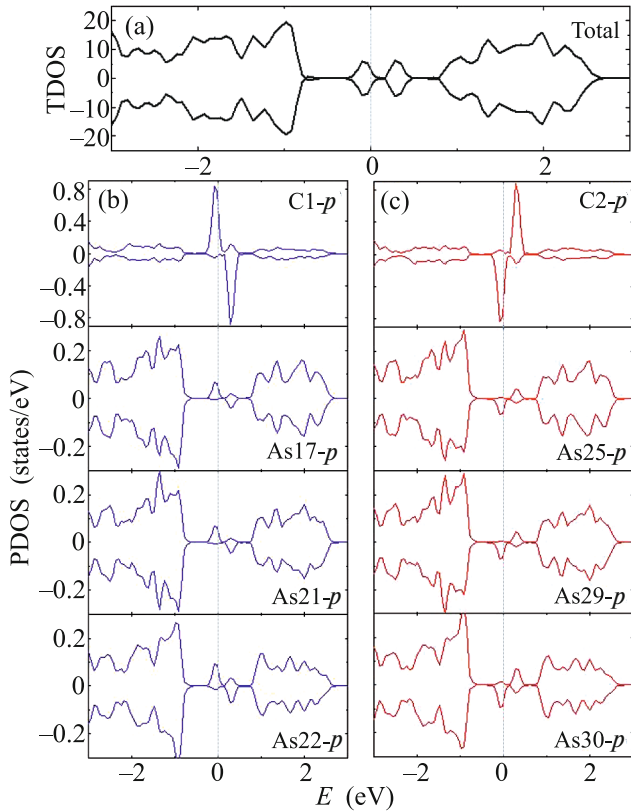
Fig. 7. (Color online) (a) TDOS of two-C-doped system [case (0, 4)]; (b, c) two C and their neighboring three As atoms (marked in Fig. 1b). The ground state is antiferromagnetic (AFM).

of the C atom near E_F are completely filled, where as the higher energy minority-spin p states of the C atom are empty. Consequently, when the spin of the two C atoms are antiparallel to each other, the spin-conserving hopping for electrons from the p orbitals of one C atom to the p orbitals of other C atom lower energy of system due to the strong intra-atomic exchange interaction between the electrons in p level, while such

Table 2. Optimized C−C distance (d_{C-C}), the total energies (E_{tot}), the energy differences (ΔE) between AFM and FM. The configurations of C atoms are as shown in Fig. 1b

System	Configuration	d_{C-C}, Å	E_{tot}, eV	ΔE, eV	Ground state
$As_{30}C_2$ (4 × 4 × 1)	1	1.375	−154.585	0.0	NM
	2	3.271	−152.698	0.0	NM
	3	5.780	−152.538	0.0	NM
	4	7.200	−152.341	−0.050	AFM
$As_{70}C_2$ (6 × 6 × 1)		10.800	−339.491	−0.061	AFM

hopping is not allowed when the spins are parallel to each other [25], thus resulting in a AFM coupling between magnetic moments induced by two dopants in C-doped arsenene.

4. CONCLUSIONS

Using ab initio methodology, the structural, electronic, and magnetic properties of nonmetals and nonmagnetic metals doped arsenene, including B, C, F, N, O, Al, Ga, Li, Mg, and Na, are theoretically investigated in this paper. Magnetic states are observed in the case of C. From our calculations, the C-doped arsenene is the most stable system among them. Then, the FM coupling in two-C-doped arsenene was studied and both NM and AFM states were observed. The results show that the AFM order could be explained by the $p-p$ coupling between C and its neighboring As atoms. Our study suggests that nonmetal dopant might be a possible approach to tune electronic and magnetic properties of arsenene, which opens an alternative way for future spintronic applications.

REFERENCES

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science **306**, 666 (2004).
2. A. K. Geim and K. S. Novoselov, Nat. Mater. **6**, 183 (2007).
3. A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. **81**, 109 (2009).
4. K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. **105**, 136805 (2010).
5. B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, Nat. Nanotech. **6**, 147 (2011).
6. S. Rodin, A. Carvalho, and A. H. Castro Neto, Phys. Rev. Lett. **112**, 176801 (2014).
7. T. Low, A. S. Rodin, A. Carvalho, Y. Jiang, H. Wang, F. Xia, and A. H. Castro Neto, Phys. Rev. B **90**, 075434 (2014).
8. R. Fei, A. Faghaninia, R. Soklaski, J. A. Yan, C. Lo, and L. Yang, Nano Lett. **14**, 6393 (2014).
9. A. Ramasubramaniam and A. R. Muniz, Phys. Rev. B **90**, 085424 (2014).
10. J. C. S. Levy, J. Magn. Magn. Mater. **373**, 2 (2015).
11. C. Kamal and M. Ezawa, Phys. Rev. B **91**, 085423 (2015).
12. L. Kou, Y. Ma, X. Tan, T. Frauenheim, A. Du, and S. Smith, J. Phys. Chem. C **119**, 6918 (2015).
13. S. L. Zhang, Z. Yan, Y. F. Li, Z. F. Chen, and H. B. Zeng, Angew. Chem. Int. Ed. **54**, 3112 (2015).
14. D. C. Wang, L. Chen, C. M. Shi, X. L. Wang, G. L. Cui, P. H. Zhang, and Y. Q. Chen, Sci. Rep. **6**, 28487 (2016).

15. F. Ersan, E. Aktürk, and S. Ciraci, J. Phys. Chem. C **120**, 14345 (2016).

16. A. Hashmi and J. Hong, J. Phys. Chem. C **119**, 9198 (2015).

17. O. V. Yazyev and L. Helm, Phys. Rev. B **75**, 125408 (2007).

18. L. Shen, R. Q. Wu, H. Pan, G. W. Peng, M. Yang, Z. D. Sha, and Y. P. Feng, Phys. Rev. B **78**, 073306 (2008).

19. J. J. Attema, G. A. de Wijs, G. R. Blake, and R. A. de Groot, J. Am. Chem. Soc. **127**, 16325 (2005).

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

21. G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

22. G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

23. P. Wu, M. Huang, W. J. Cheng, and F. L. Tang, Physica E **81**, 7 (2016).

24. L. Kou, Y. Ma, X. Tan, T. Frauenheim, A. Du, and S. Smith, J. Phys. Chem. C **119**, 6918 (2015).

25. P. Dev and P. H. Zhang, Phys. Rev. B **81**, 085207 (2010).