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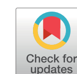
Communication

Magnetism in monolayer InSe by nonmetal doping: First-principles study



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ABSTRACT

To develop InSe-based spintronics devices, introducing magnetism into monolayer InSe is essential. In this work, the electronic and magnetic properties of nonmetal (NM) doped (H, B, C, Si, N, P, As, O, S, Te, F, Cl, Br and I) monolayer InSe were investigated by first-principles calculations. The results indicate that atoms from VA, VIA and VIIA groups are possible to substitute Se atoms under In-rich condition. Second, we have found that only the InSe doped with NM acceptors with odd number of valence electrons possesses magnetism. Especially B doped InSe is a half-metal. However, VIIA group doped InSe does not exhibit magnetism due to the In-In covalent bond. This work provides an important guidance for developing spintronic devices on monolayer InSe.

1. Introduction

Bulk InSe is a layered material with strong covalent in-plane interatomic bonds and weaker van der Waals (VDW) interlayer bonds. Monolayer InSe with a unique quadruple layer structure consists of two Se layers and two In layers in the sequence of Se-In-In-Se (Fig. 1b) [1,2]. Recently, InSe has stimulated considerable worldwide attention due to its unique electronic properties such as optical anisotropic [3,4], small effective mass [5–8], and high electron mobility [9,10]. However, native InSe is non-magnetic, which limits its application in the emerging field of spintronics. Thus introducing magnetism in monolayer InSe is essential.

Doping is a promising method to modulate the magnetic properties of layered materials [11–13]. Experimentally, transition metals (Fe, Co), which fill In vacancies, have demonstrated ferromagnetism at room temperature [14], similar to diluted magnetic semiconductors and ferromagnetic topological insulators [15–17]. Moreover, there is evidence that doping with NM atoms can also introduce magnetism [18,19]. Experimentally it would be easier to synthesize NM atoms doped InSe, because the dominant defects in monolayer InSe are Se vacancies [20–22]. Thus, a comprehensive study of magnetism arising from NM dopants is need.

In this work, using first-principles calculations, we have studied the geometrical structure, formation energy, electronic and magnetic properties of doped monolayer InSe with a series of NM atoms, ie, IA (H), IIIA (B), IVA (C and Si), VA (N, P and As), VIA (O, S and Te) and VIIA (F, Cl, Br and I) groups. We have found that for doped InSe to gain magnetism, the NM acceptor needs to have an odd number of valence electrons. Especially the B doped system becomes half-metallic. But there is an exception that VIIA group atoms with odd number of valence electrons cannot induce magnetism due to the In-In covalent bond.

2. Computational methods

The first-principles calculations based on density functional theory using the Vienna Ab-initio Simulation Package (VASP) with Projected augmented wave (PAW) pseudopotentials, and The exchange-correlation potentials are treated by Perdew-Burke-Ernzerhof (PBE) function of the generalized gradient approximation (GGA) [23,24]. A $4 \times 4 \times 1$ monolayer InSe supercell with a 15 Å vacuum layer is adopted. One Se atom is substituted by NM atoms in all doped systems (Fig. 1). The cutoff energy for the plane-wave basis was set at 500 eV and an $8 \times 8 \times 1$ k-point sampling grid was applied for integration over the first Brillouin zone. The structural optimization is continued until the convergence tolerance of energy and maximum force was less than 1.0×10^{-5} eV/atom and 1.0×10^{-3} eV/Å, respectively. Moreover, the spin-orbit coupling (SOC) has been considered for all systems.

We have calculated the formation energy (E_f) of all the doped systems to assess the stability of different NM dopants:

$$E_f = E_{doped} - E_{undoped} + \mu_{Se} - \mu_{NM} \quad (1)$$

E_{doped} and $E_{undoped}$ are the total energy of the monolayer InSe with

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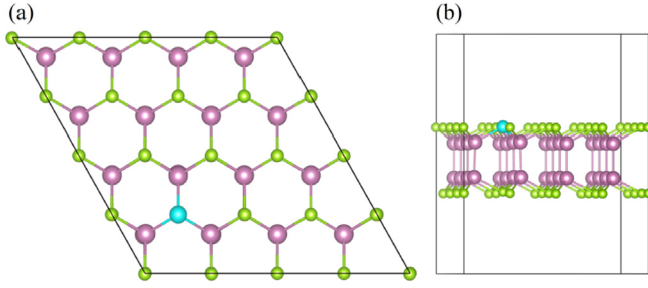

Fig. 1. (a) Top view and (b) side view of the crystal structure of a doped $4 \times 4 \times 1$ supercell monolayer InSe. The lavender, green and blue spheres denote the In, Se and NM atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and without NM atom, μ_{NM} is the NM chemical potential, calculated using it's the most stable structure in nature [25]. Because the synthesis of InSe is a dynamic process, the E_f is unfixed and changing from In-rich condition to Se-rich condition. The chemical potentials of In and Se atoms satisfy the equations:

$$\mu_{In} + \mu_{Se} = \mu(InSe) \tag{2}$$

Under Se-rich condition, μ_{Se} is the chemical potential of bulk Se, and μ_{In} is obtained by Eq. (2). Under In-rich condition, μ_{In} is the chemical potential of In bulk, and μ_{Se} calculated by Eq. (2). Negative E_f suggests that NM atom is energetically favorable to substitute Se atom.

3. Results and discussion

3.1. Formation energies and optimized structures

Table 1 lists the calculated supercell lattice constants and E_f of the doped systems. The lattice constants of undoped InSe ($a = b = 4.100$ Å) are almost identical to the previous theoretical ($a = b = 4.090$ Å) and experimental results ($a = b = 4.050$ Å) [18,26]. It is found that for all of them, the E_f is lower under the In-rich condition than that under the Se-rich condition. This indicates that the NM atoms prefer to substitute the Se atoms under In-rich conditions, since more Se vacancies are present in this case. Therefore, only the E_f under In-rich conditions will be discussed in the following. Overall, VIA group doped systems have negative E_f ($-0.40 \sim -2.65$ eV), which is explained by the similar electronic structure to Se. Second, the E_f of VA and VIIA group doped

Table 1
The equilibrium lattice constants a, with unit Å. E_f are the formation energy under In-rich and Se-rich conditions. M_{tot}, M_{NM}, M_{In} and M_{Se} are the total magnetic moments, local magnetic moments of NM, In and Se atoms, with unit μ_B.

Dopant	a	E_f		M_{In}	M_{Se}	M_{NM}	M_{tot}
		In-rich	Se-rich				
H	4.085	2.26	3.32	0.20	0.12	−0.01	0.35
B	4.103	3.53	4.59	0.21	0.20	0.11	0.53
C	4.093	3.91	4.97	–	–	–	–
Si	4.116	1.53	2.59	–	–	–	–
N	4.087	1.76	2.82	0.05	0.17	0.35	0.58
P	4.108	0.70	1.76	0.09	0.15	0.17	0.41
As	4.113	−0.65	0.41	0.10	0.17	0.15	0.43
O	4.077	−2.65	−1.59	–	–	–	–
S	4.094	−1.07	−0.01	–	–	–	–
undoped	4.100	–	–	–	–	–	–
Te	4.109	−0.40	0.66	–	–	–	–
F	4.089	−2.34	−1.28	–	–	–	–
Cl	4.104	−0.68	0.38	–	–	–	–
Br	4.108	−0.34	0.72	–	–	–	–
I	4.113	0.14	1.20	–	–	–	–

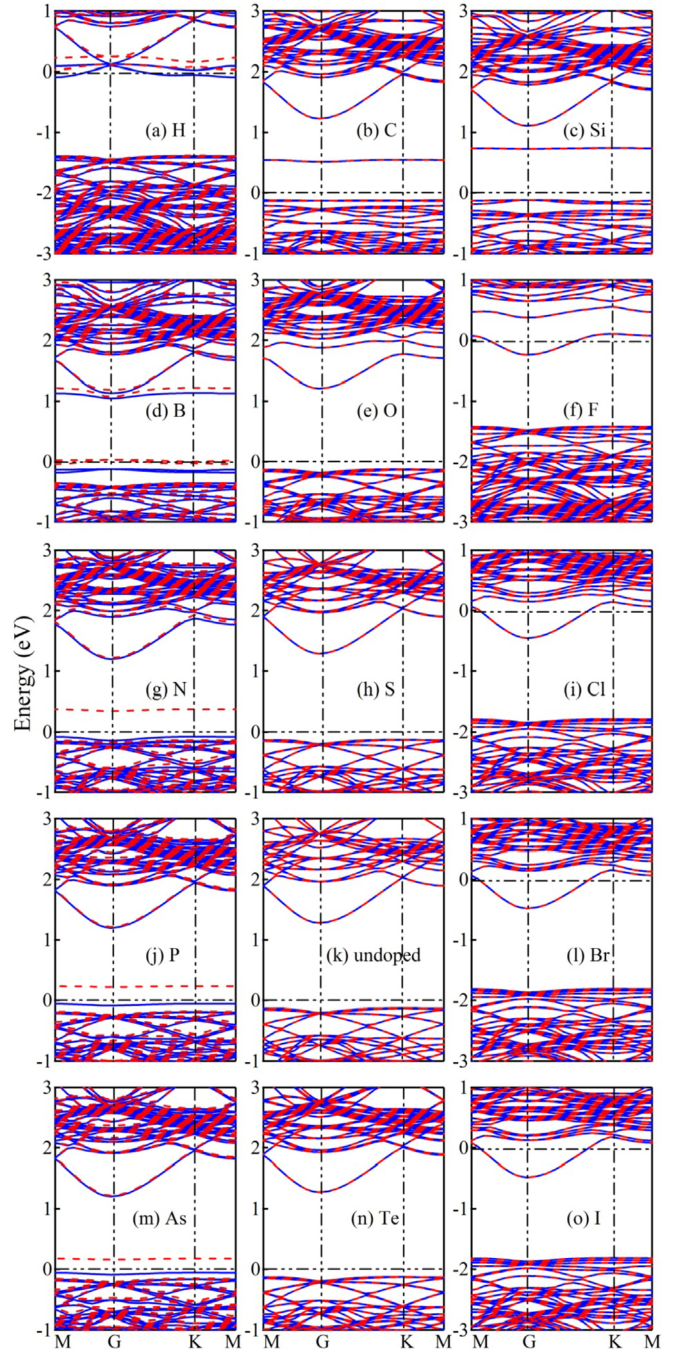

Fig. 2. Band structure of undoped and doped monolayer InSe; blue solid (red dotted) line represent spin up (spin down) states, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

InSe is around zero, this is because the number of valence electronics is only one electron away from Se. Thus, doping InSe by atoms from VA, VIA and VIIA groups is possible by thermal-dynamically preferred methods. On the other hand, IA, IIIA and IVA group doped InSe possess large E_f (1.53–3.91 eV) which makes them harder to be synthesized. However, experimentally it is still possible to synthesize doped materials with E_f higher than 1 eV through non-equilibrium methods such as molecular beam epitaxy (MBE) and low-energy ion irradiation [27,28].

3.2. Electronic and magnetic properties

Fig. 2 illustrates the band structure of all systems. We have found

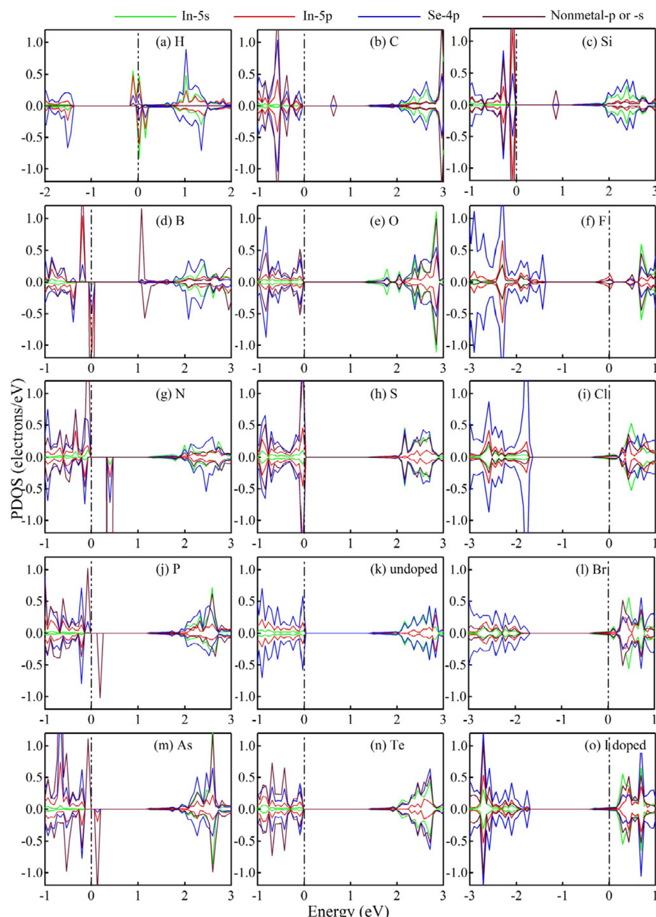

Fig. 3. The PDOS of undoped and NM doped systems. Only the NM acceptor dopants with an odd number of valence electrons can induce magnetism.

that only the IA, IIIA and VA group doped systems gain magnetism as the spin up and spin down states are asymmetric around the Fermi level. More interestingly, B doped systems acquire the half-metallic property because the Fermi level only crosses the spin down impurity level, and this causes 100% spin polarization at the Fermi level. To understand the mechanisms of NM dopants modulating the electronic and magnetic properties of monolayer InSe, we calculated the average partial density of states (PDOS) of In, Se and NM atoms for all doped systems, as shown in Fig. 3, respectively.

For undoped monolayer InSe, the conduction band (CB) is mostly composed of In-5*s* and Se-4*p* states, while the valence band (VB) is composed of In-5*p* and Se-4*p* states. And it has an indirect band gap (E_g) of 1.41 eV. Moreover, the band structure of monolayer InSe with SOC is same as that without SOC, and is consistent with previous theoretical and experimental results [3,7,18]. On the other hand, SOC is important for determining the actual electronic structure of the impurity state with energy close to the VBM [29,30]. However, we found that SOC slightly affects the band structure of doped systems, due to the impurity state with energy larger to the VBM. Therefore, SOC is not considered in this work.

For VIA (O, S and Te) group doped system, the electronic properties are similar to undoped one. However, IVA (C and Si) group doped systems have additional symmetric deep empty impurity level (mostly composed of IVA-*p* states) within the band gap due to the missing pair of valence electrons. Therefore, NM dopants with an even number of valence electrons cannot induce magnetism.

For IA group doped InSe, the spin up and spin down impurity state (mostly composed of Se-4*p*, In-5*s* and In-5*p* states) near the Fermi level is asymmetric (Fig. 3a). For IIIA group doped InSe, the Fermi level only

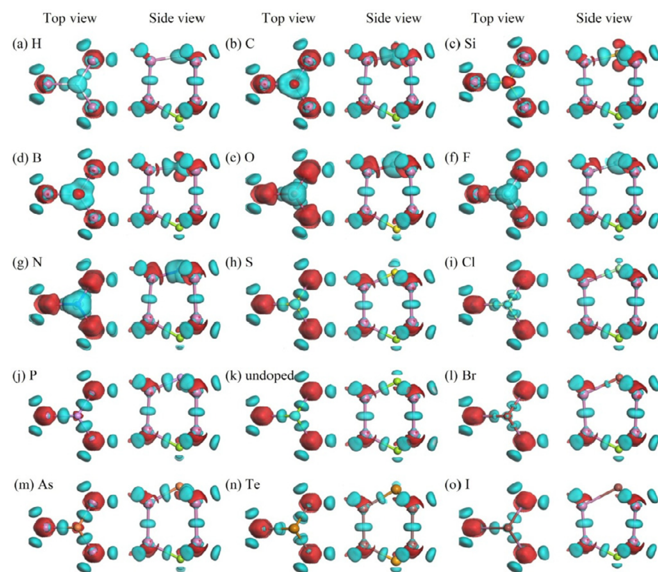

Fig. 4. The electron density difference of undoped and NM doped systems, isosurface value was taken at 0.05 e/Å^3.

crosses the spin down impurity level, indicating half-metallic behaviour (Figs. 2d and 3d). VA (N, P and As) group doped systems have a spin splitting of about 0.33, 0.09 and 0.06 eV. This decreases as the atomic number increase (Fig. 3g, j and m). Therefore the NM dopants with odd number of valence electrons can induce magnetism, due to each substitutional NM atom will cause odd holes and form asymmetric impurity levels around the Fermi level. Similar results have been reported in NM doped $MoSe_2$ [31–33].

However, the dopants from VIIA (F, Cl, Br and I) group cannot induce magnetism. It is found that each provides an additional electron and from a donor impurity level (mostly composed of VIIA-*p* states) below the CB, and their spin-up and spin-down states are symmetrical. Next, we have calculated electronic density difference of each doped system based the atomic electronic density and shown in Fig. 4. The azure (or red) regions indicate the electron accumulation (or loss), and the azure regions between the two atoms indicate that they form a covalent bond. Each In atom forms three covalent bonds with the neighboring Se atoms and another bond with the other In atom along the z axis (Fig. 4k). The two covalently bonded In atoms can be regarded as a dimer [20]. Then, the electron sea between the two In layers acts as an electron reservoir. And, there is a difference between electrons and holes aborted by the electron seas formed between the two In layers. Meanwhile, we found that the VA-*p* state and VIIA-*p* state are located above and below the Fermi level, respectively, as shown in the band structure in Fig. 2. Therefore, the electrons injected by the VIIA dopants will be easily dispersed in the existing electronic sea. So, this electron will be dispersed in the existing electron sea and will not be localized on one In atom (Fig. 4f, i, l and o). This process reduces the overall energy of the system. It is for this reason that no local magnetic moment at/around the dopant and this explains the non-magnetism in VIIA group doped monolayer InSe. In contrast, when electrons jump out of the electron sea to occupy the position of the hole on the impurity level (such as VA group), the total energy of the system is increased. Therefore, the holes introduced by the dopant are localized around the dopant and In atoms. Then, dopants with odd number of valence electrons can induce magnetism, except for those in group VIIA.

In order to quantify the contribution of the magnetic moment from each atom [34], the spin density of NM doped InSe has been calculated and shown in Table 1 and Fig. 5. It is found that the local magnetic moment in all doped systems is mainly from the NM atoms and the six nearest In atoms and the thirteen nearest neighboring Se atoms. In

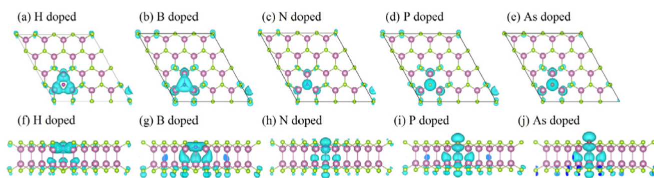

Fig. 5. Spin density of NM doped monolayer InSe, isosurface value was taken at 0.001 e/$Å^3$. The pale blue (red) regions represent spin up (down) electron density, and the magnetic moment are almost from the dopant atoms and the nearest In and Se atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

addition, the spin density distribution of all doped systems has three-fold symmetry and the spins of all atoms are parallel.

4. Conclusions

In summary, using first-principles calculations, we found that doping InSe with atoms from VA, VIA and VIIA groups can be realized by thermal-dynamically preferred methods under In-rich condition. More importantly, only NM acceptor dopants from IA, IIIA and VA groups with odd number of valence electrons can induce magnetism, while dopants from VIIA group cannot.

Acknowledgements

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References

[1] A. Amokrane, F. Proix, S.E. Monkad, A. Cricenti, C. Barchesi, M. Eddrief, K. Amimer, C.A. Sebenne, J. Phys. Condens. Matter 11 (1999) 4303.
[2] S.J. Magorrian, V. Zólyomi, V.I. Falko, Phys. Rev. B 94 (2016) 245431.
[3] V. Zolyomi, N.D. Drummond, V.I. Falko, Phys. Rev. B 89 (2014) 205416.
[4] J. Camassel, P. Merle, H. Mathieu, A. Chevy, Phys. Rev. B 17 (1978) 4718.
[5] N. Kuroda, Y. Nishina, Solid State Commun. 34 (1980) 481.
[6] E.K. Rogers, R.J. Nicholas, J.C. Portal, A. Chevy, Solid State Commun. 44 (1982) 379.
[7] C. Sun, H. Xiang, B. Xu, Y.D. Xia, J. Yin, Z.G. Liu, Appl. Phys. Exp. 9 (2016) 035203.
[8] J.E. Padilha, R.H. Miwa, A.J.R. da Silva, A. Fazzio, Phys. Rev. B 95 (2017) 195143.
[9] S. Sucharitakul, N.J. Goble, U.R. Kumar, R. Sankar, Z.A. Bogorad, F.C. Chou, Y.T. Chen, X.P. Gao, Nano Lett. 15 (2015) 3815.
[10] D.A. Bandurin, A.V. Tyurnina, G.L. Yu, A. Mishchenko, V. Zólyomi, S.V. Morozov, R.K. Kumar, R.V. Gorbachev, Z.R. Kudrynskyi, S. Pezzini, Z.D. Kovalyuk, U. Zeitler, K.S. Novoselov, A. Patanè, L. Eaves, I.V. Grigorieva, V. Falko, A.K. Geim, Y. Cao, Nat. Nanotechnol. 12 (2017) 223.
[11] Q. Yue, S.L. Chang, S.Q. Qin, J.B. Li, Phys. Lett. A 377 (2013) 1362.
[12] R.F. Liu, C. Cheng, Phys. Rev. B 76 (2007) 014405.
[13] S.L. Xiao, W.Z. Yu, S.P. Gao, Surf. Sci. 653 (2016) 107.
[14] J.J. Ning, G.J. Xiao, C.Z. Wang, B.B. Liu, G.T. Zou, B. Zou, CrystEngComm 15 (2013) 3734.
[15] X.F. Kou, M.R. Lang, Y.B. Fan, Y. Jiang, T.X. Nie, J.M. Zhang, W.J. Jiang, Y. Wang, Y.G. Yao, L. He, K.L. Wang, ACS Nano 7 (2013) 9205.
[16] A. Ramasubramaniam, D. Naveh, Phys. Rev. B 87 (2013) 195201.
[17] F. Tsui, L. He, L. Ma, A. Tkachuk, Y.S. Chu, K. Nakajima, T. Chikyow, Phys. Rev. Lett. 91 (2003) 17.
[18] X.P. Li, C.X. Xia, X.H. Song, J. Du, W.Q. Xiong, J. Mater. Sci. 52 (2017) 7207.
[19] Y.N. Sun, X.F. Wang, M.X. Zhai, A.L. Yao, J. Phys. D Appl. Phys. 50 (2017) 215003.
[20] D. Wang, X.B. Li, H.B. Sun, Nanoscale 9 (2017) 11619.
[21] A.A. Kistanov, Y.Q. Cai, K. Zhou, S.V. Dmitriev, Y.W. Zhang, J. Mater. Chem. C 6 (2018) 518.
[22] D.W. Ma, T.X. Li, D. Yuan, C.Z. He, Z.W. Lu, Z.S. Lu, Z.X. Yang, Y.X. Wang, Appl. Surf. Sci. 434 (2018) 215.
[23] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[24] D.R. Hamann, M. Schluter, C. Chiang, Phys. Rev. Lett. 43 (1979) 1494.
[25] http://www.webelements.com.
[26] I.A. Kibirev, A.V. Matetskiy, A.V. Zotov, A.A. Saranin, Appl. Phys. Lett. 112 (2018) 191602.
[27] Q. Ma, M. Isarraraz, C.S. Wang, E. Preciado, V. Klee, S. Bobek, K. Yamaguchi, E. Li, P.M. Odenthal, A. Nguyen, D. Barroso, D.Z. Sun, G.V.S. Palacio, M. Gomez, A. Nguyen, D. Le, G. Pawin, J. Mann, T.F. Heinz, T.S. Rahman, L. Bartels, ACS Nano 8 (2014) 4672.
[28] L. He, F.X. Xiu, X.X. Yu, M. Teague, W.J. Jiang, Y.B. Fan, X.F. Kou, M.R. Lang, Y. Wang, G. Huang, N.C. Yeh, K.L. Wang, Nano Lett. 12 (2012) 1486.
[29] Z.B. Aziza, V. Zólyomi, H. Henck, D. Pierucci, M.G. Silly, J. Avila, S.J. Magorrian, J. Chaste, C.Y. Chen, M. Yoon, K. Xiao, F. Sirotti, M.C. Asensio, M.E.E. Lhuillier, V.I. Falko, A. Ouerghi, Phys. Rev. B 98 (2018) 115405.
[30] S.J. Magorrian, V. Zólyomi, V.I. Falko, Phys. Rev. B 96 (2017) 195428.
[31] X. Zhao, X.N. Zhang, T.X. Wang, S.Y. Wei, L. Yang, Rsc Adv. 7 (2017) 26673.
[32] H.P. Li, S.L. Huang, Q. Zhang, Z.P. Zhu, C.S. Li, J. Meng, Y. Tian, Chem. Phys. Lett. 692 (2018) 69.
[33] Y.F. Zhao, W. Wang, C. Li, Y.B. Xu, L. He, Solid State Commun. 281 (2018) 6.
[34] P. Venezuela, R.B. Muniz, A.T. Costa, D.M. Edwards, S.R. Power, M.S. Ferreira, Emergence of local magnetic moments in doped graphene-related materials, Phys. Rev. B 80 (2009) 241413.