Electronic structure of substitutionally Mn-doped graphene

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\textbf{Abstract.} The electronic structure and magnetism of manganese (Mn)-doped graphene has been studied using the density functional theory. It was found that the electronic structure was sensitive to the value of the on-site energy for the Mn 3d orbital. Thus, it was crucial to accurately account for the electron correlation in the calculation. By using the self-consistent \textit{U} method, we were able to determine the specific \textit{U} value in this chemical environment to be 5.39 eV, and we found that the system is a charge transfer insulator with a bandgap of about 0.2 eV. The Mn strongly binds with the carbon atoms, causing the localization of the $\pi$ orbital near the Fermi level. The crystal field splits the Mn d orbitals and leads to 3.00$\mu_B$ magnetic moment at the ground state. The Mn-doped graphene acquires macroscopic antiferromagnetism when the doping density reaches a threshold between 3 and 5%.

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1. Introduction

Graphene, a single layer of graphite with carbon atoms tightly packed into a honeycomb lattice, has attracted much interest from both experimentalists and theorists because of its novel two-dimensional (2D) structure. A number of unusual properties, such as zero-gap band structure, massless charge carrier and anomalous quantum Hall effect, have been reported in graphene. Besides its great meaning as a landmark for material science and for continuing fundamental experimental and theoretical research, potential applications of the novel 2D material in extensive fields such as energy materials, microelectronics, sensors and superconductors are expected.

For a defect-free graphene layer, no magnetic ordering is expected from theoretical calculations. Thus, the magnetic properties experimentally observed in graphene are often explained by the existence of different kinds of defects, which can easily be created by the absorption of adatoms during sample preparation or electron and ion radiation treatments, etc. Due to its potential applications in nanoelectronics, the interactions between the metal atoms and graphene have been investigated theoretically, in which the stable geometric structure, the electronic structure and the magnetic properties are often addressed. Concerning the magnetic properties of transition metal atom-doped graphene, the on-site energy should be correctly considered for the system with localized (strongly correlated) d and f electrons. However, this point has often been ignored in many studies. In this work, we report our first-principles calculation results of graphene doped with the Mn atom. We are particularly interested in the Mn adatom because the ground state configuration of an isolated Mn atom is $3d^54s^2$, with a magnetic moment of $5\mu_B$ according to Pauli’s exclusion principle. Thus, it is considered as a good candidate of magnetic dopants in nanomagnetic applications because of its unusually high magnetic moment. In order to account for the large Coulomb on-site energy of the Mn 3d orbitals, we have employed the density functional theory (DFT) + $U$ method. The rest of this paper is as follows. In the next section, we briefly describe the method and calculation details. We then present our results together with detailed discussions, including the $U$ dependency of the electronic structure, the electronic structure under a self-consistent $U$ method and the effect of the Mn doping density. Finally, we summarize our paper and draw a conclusion.
2. Method and calculation details

Two codes, VASP [17] and PWSCF [18], were employed for comparison purposes. For the VASP calculations, we used a series of $U$ values ($U = 0, 4$ and $8$ eV) to study the dependence of the electronic structure on $U$. For these calculations, we employed the projector augmented wave (PAW) method [19, 20], with the Perdew, Burke and Ernzerhof (PBE) [21] exchange-correlation function. The Kohn–Sham orbitals were expanded with a set of plane-wave basis up to $550$ eV. The Brillouin zone is sampled with a $5 \times 5 \times 1$ Monkhorst–Pack $k$-point grid [22].

For the PWSCF calculations, we employed the Vanderbilt ultrasoft pseudopotentials [23], and the plane-wave energy cutoff was chosen to be $58$ Ryd. The sampling of the Brillouin zone was done using a $3 \times 3 \times 1$ Monkhorst–Pack grid, while a $19 \times 19 \times 1$ Monkhorst–Pack grid was used for the calculation of the density of states (DOS). The $U$ parameter used in PWSCF calculations was self-consistently determined using the method proposed by Cococioni and co-workers [24, 25]. In these calculations, we used a $5 \times 5$ supercell in the $x$–$y$ plane and a vacuum layer of $15$ Å in the $z$-direction to simulate an isolated adatom on graphene. All calculations were performed in a spin-unrestricted manner. The Mn atom was initially placed $1.20$ Å above the vacancy site of the graphene. Thus the initial distance between the dopant atom and the nearest carbon atoms was about $1.86$ Å, which was close to the sum of their covalent radius. Geometry optimization was then performed such that all the internal coordinates were relaxed while the lattice parameter was fixed at the perfect graphene value until the Hellmann–Feynman forces were less than $0.03$ eV Å$^{-1}$. All the relative energies for different magnetic configurations were converged within $5$ meV with respect to the energy cutoff and $k$-point grid. Note that, due to the different pseudopotentials used in our calculations with these two codes, the lattice parameters for the minimum total energy were consequently different, i.e. $a_{\text{VASP}} = 1.430$ Å and $a_{\text{PWSCF}} = 1.427$ Å for the perfect graphene. Figure 1(a) shows the configuration used. A Mn atom was doped in the graphene by substituting a carbon atom in the lattice. It can also be regarded as a Mn atom being adsorbed on a vacancy site in the graphene sheet.

DFT + $U$ is a method that includes the electron–electron on-site correlation effect described by a Hubbard-like Hamiltonian within the DFT framework [16], and therefore the $U$ value is
Figure 2. Result of the self-consistent field calculation of parameter $U$. Through a linear fit of the data, the value of $U = 5.39\,\text{eV}$ is obtained for the present system. $U_{\text{in}}$ and $U_{\text{out}}$ have the same meaning with respect to [21].

sensitive to the chemical environment and the geometric structure. However, as in the VASP calculations that we performed, $U$ was always a phenomenological parameter, and its value was not determined. It was then identified by Cococionni and Gironcoli [24] that the $U$ value is related to the unphysical curvature behavior of the DFT functional [23] and can be calculated from first principles. In our PWSCF calculations, we employed their method and determined the value of $U$ as $5.39\,\text{eV}$ through a linear fitting procedure, as shown in figure 2.

3. Results and discussion

3.1. Structure and energetic properties

The strength of the bonding between the Mn adatom and the graphene is determined by the binding energy, e.g. a larger binding energy means stronger binding of the dopant atom to the nearest carbon atoms. The binding energy $E_b$ is defined as $E_b = E_{\text{vac-graphene}} + E_{\text{Mn}} - E_{\text{total}}$, where $E_{\text{total}}$, $E_{\text{vac-graphene}}$ and $E_{\text{Mn}}$ stand for the spin-polarized total energy of the system, the total energy of the graphene with a monovacancy and the energy of an isolated Mn atom, respectively. We show the parameters for the relaxed structures in table 1. A schematic diagram is shown in figures 1(a) and (b) to represent the relaxed geometries. After the relaxation, the three nearest carbons to the Mn atom were raised to about $0.37\,\text{Å}$ in both VASP and PWSCF calculations and the bonding lengths of Mn–C were 1.834 and 1.826 Å in VASP and PWSCF, respectively, which was close to the sum of their covalent radius $1.94\,\text{Å}$. The binding energies were 6.39 and $6.22\,\text{eV}$ in VASP and PWSCF, respectively. Both the bond length and the magnitude of the bonding energy indicate a covalent bonding feature between the Mn atom and the nearest carbon atoms. The covalent bonding character can also be observed in the charge distribution image, as shown in figures 1(c) and (d).
Table 1. Parameters for Mn-doped graphene. \( a \) is the lattice parameter for perfect graphene. \( E_b \) is the binding energy, \( m \) is the total magnetic moment, charge (Mn) is the charge transfer between the Mn atom and the graphene, \( h \) is the height of the related atom above the graphene plane and \( d \) (Mn–C) is the bonding length between the Mn atom and the three nearest C atoms.

| \( U \) (eV) (VASP) | \( a \) (Å) | \( E_b \) (eV) | \( m \) (\( \mu_B \)) | Charge (Mn) (e) | \( h \) (Mn) (Å) | \( h \) (C1,C2,C3) (Å) | \( d \) (Mn–C) (Å) |
|-----------------|---------|----------|-----------------|----------------|-----------|----------------|---------|
| 0 eV (VASP)     | 1.430   | −6.39    | 3.00            | −0.90          | 1.37      | 0.37           | 1.834   |
| 4 eV (VASP)     | 1.427   | −6.22    | 3.00            | −0.97          | 1.39      | 0.37           | 1.826   |
| 8 eV (VASP)     | 1.427   | −6.22    | 3.00            | −0.47          |           |                |         |
| 0 eV (PWSCF)    | 1.427   | −6.22    | 3.00            | −0.93          | 1.37      | 0.37           | 1.834   |
| 5.39 eV (PWSCF) | 1.427   | −6.22    | 3.00            | −0.97          | 1.39      | 0.37           | 1.826   |

Figure 3. DOS of the system, together with PDOS. (a,b,c) DOS for VASP calculations with \( U = 0, 4 \) and \( 8 \) eV, respectively, together with the PDOS of 4s, 4p and 3d orbitals of the Mn atom.

3.2. Electronic structures and magnetic properties

The inclusion of the on-site energy has limited effect on the magnetic property of the Mn-doped graphene, as shown in table 1, column \( m \). All calculations reported a 3\( \mu_B \) staggered magnetic moment per unit cell induced by the dopant Mn atom. In addition, the spatial charge distributions from all calculations are similar to each other. Therefore, we show only the spatial charge distribution from the \( U = 8 \) eV calculation in VASP in figures 1(c) and (d).

However, the on-site energy \( U \) substantially modified the electronic structure of the Mn-doped graphene. Figure 3 shows the DOS of the system and the projected DOS (PDOS) onto Mn 3d, 4s and 4p orbitals with \( U = 0 \), 4 and 8 eV for VASP calculations. The results clearly show the trend of electronic structure change when \( U \) is increased. For \( U = 0 \) eV, the system has a metallic or semimetallic character with finite DOS at the Fermi energy level. However, for \( U = 4 \) and 8 eV, the 3d orbitals of the Mn atom were pushed below the Fermi level when the value of \( U \) increased, as expected. Consequently, the system opens a gap at the Fermi level and becomes a semiconductor. Interestingly, the magnitude of the bandgap does not sensitively depend on the \( U \) values, and both \( U = 4 \) and 8 eV yield a bandgap of about 0.2 eV. A closer
Figure 4. DOS for PWSCF calculation with $U = 5.39$ eV, together with the PDOS of 2p orbital of C atoms (C1, C2 and C3) and 4s, 4p and 3d orbitals of the Mn atom.

(examination of PDOS indicates that the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) were dominated by the 2p orbital of C atoms. This shows the criticality of Mn 3d orbitals, which is extremely sensitive to the value of $U$. In other words, the GGA + $U$ method is necessary for studying the Mn-doped graphene system in the present work. Therefore, it is essential to accurately determine the $U$ value in the specific chemical environment.

The self-consistent $U$ calculation result is shown in figure 4. It can be found that the inclusion of the on-site energy has also opened a bandgap of about 0.2 eV. The PDOS of Mn 3d orbitals mainly locate 0.06 eV below the highest occupied band energy. Both the HOMO and the LUMO were primarily contributed by C 2p orbitals and Mn 4p3d orbitals, indicating that the Mn-doped graphene studied here is a charge transfer insulator. Since the inclusion of on-site energy opens the gap, it is obvious that the electron localization effect is important and is the main reason for the electronic structure change. The electron localization effect can also be observed from the local density of states (LDOS) around the Fermi level (figure 5).

Figure 5. Local charge distribution around the Fermi level. (a) Local charge distribution for perfect graphene. (b) Local charge distribution for Mn-doped graphene. The blue balls are C atoms and the green part is the local charge around the Fermi level.)
Figure 6. (a) Spin-polarized charge density ($\rho_{\text{spin-up}} - \rho_{\text{spin-down}}$) of the system. The isosurface corresponds to a value of $0.002 \text{ eÅ}^{-3}$. The yellow balls are C atoms. The green part is the minority spin charge and the red part is the majority spin charge. (b) A scheme for Mn d orbital splitting.

Figure 7. Plot of the magnetic moments with different supercells. The solid line is used to guide the eyes.

Nevertheless, the localization does not affect the magnetic properties much, and the total magnetic moment remains at $\sim 3.00 \mu_B$ for all the calculations, regardless of the $U$ value used. Lowdin's charge analysis shows that the Mn atom loses $\sim 0.5$ electron after doping, and the d orbital is occupied by $\sim 5.5$ electrons. Due to the trigonal symmetry of the crystal field around the Mn atom, the fivefold degeneracy of the original d orbitals is lifted and the $d_{z^2}$ orbital becomes fully occupied under low crystal fields (figure 6(b)). Hence, the 5.5 electrons yield $3.5 \mu_B$ local magnetic moment for the Mn atom. The three nearest-neighbor C atoms are also slightly polarized, each possessing $0.27 \mu_B$ magnetic moment antiparallel to the magnetic moment of the Mn atom. The polarization of the remaining part of the graphene can be neglected compared to the three nearest C atoms, as shown in figure 6(a). Thus, the magnetic moment is localized around the Mn dopant atom.

3.3. Magnetic coupling

Finally, we discuss the relationship between magnetic coupling and Mn doping density. Because of computational limits, we have studied two Mn dopant atoms on (i) $4 \times 8$ and (ii) $3 \times 6$ graphene supercells. We argue that the same self-consistent $U$ value (5.39 eV) can be applied to these two systems since the effect of the Mn dopant on the graphene is quite localized. We verify this by showing the calculated magnetic moment (figure 7) and the spin density...
Figure 8. Configurations of two Mn atoms doped graphene. (a,b) Configurations AA and AB with a 4 × 8 supercell, with the dopant distance larger than 9 Å. (c,d) Configurations AA and AB with a 3 × 6 supercell. (e,f) Configurations AA and AB with a 4 × 8 supercell, with the dopant distance less than 7 Å. AA and AB represent two Mn atoms substituting two C atoms on the same sublattice and different sublattice, respectively. The numbers behind ‘AA’ and ‘AB’ represent the dopant distance.

Figure 9. Plot of relative total energies with different dopant distances, configurations and spin configurations. The energy of the FM solution in the AA configuration was taken as the reference. The five-pointed star represents the FM spin configuration and the open circle represents the AFM spin configuration.

However, it should be noted that when the dopant concentration is decreased to about 1% (one dopant atom in a 6 × 6 supercell), the bandgap disappears and the semimetallic character of pure graphene is preserved. The explanation is as follows. With a low dopant concentration, carbon atoms that were far away from the dopant atom were hardly affected.
by the localized state induced by the dopant atom. Thus, these carbon atoms dominate the electronic state at the Fermi level and preserve the semimetallic character of pure graphene. Two possible structural configurations were considered for each supercell size in our calculations, i.e. two Mn atoms substitute two C atoms on the same sublattice (AA) or on a different sublattice (AB), as shown in figure 8. For each structural configuration, there are also three possible spin configurations for the Mn dopant, i.e. spin-parallel (ferromagnetic or FM), spin-antiparallel (antiferromagnetic or AFM) and paramagnetic (PM). We show the relative total energies of AFM and FM states in figure 9, and the ground state should be regarded as the PM state if the energy difference between the AFM and FM states is sufficiently small. For the 4 × 8 supercell systems with two Mn atoms far away from each other (figures 9(a) and (b)), the total energy is insensitive to the spin configuration, and thus the ground state should be regarded as PM, since the two atoms are too far apart to induce spin interactions. Nevertheless, if the two Mn atoms occupy the same sublattice (AA configuration), the distance between each of the two Mn atoms is exactly the lattice constant for the supercell, which achieves maximum symmetry, and hence is energetically much more favorable than the AB configuration. However, for the smaller 3 × 6 supercell systems, the total energy is an interplay between the structural symmetry and the super-exchange between the two Mn atoms, since the distance between them is close enough to induce magnetic interactions. This can be demonstrated by 3 × 6 panels in figure 10, because the spin polarization becomes non-negligible on the C atoms between the Mn atoms. It was found that the super-exchange between the Mn atoms in AB configuration favors an AFM solution with an energy difference of about 38 meV; however, the AA configuration favors a PM solution, since the AA configuration causes spin frustration due to C3v symmetry. The AB configuration eliminated this frustration by bringing the two Mn atoms closer together and breaking the C3v symmetry, and it is therefore
favored by the $3 \times 6$ supercell. To evaluate the distance dependence of the magnetic coupling strength, we also performed simulations using two Mn atoms in the $4 \times 8$ supercell (figures 9(e) and (f)). With such a small distance between the dopant atoms, the large defect–defect interaction dominates the coupling between the dopants. Thus, in both AA and AB configurations, the AFM solution is more stable than the FM solution. The energy difference is 28 meV for the AA configuration and 41 meV for the AB configuration. This result is similar to that of Co-doped graphene, i.e. the system always converged to the same spin solution when at a small distance between the dopants [26]. These results suggest that, when the dopant concentration is sufficiently small such that the distance between the dopants is sufficiently large (>10 Å), the super-exchange interaction is very weak and the system does not show magnetism (PM state) macroscopically; the FM state is never favored in the AA configuration, which is the opposite to the Co-doped graphene. The inter-dopant magnetic coupling will be negligible at sufficiently small distance (<7 Å) when the system becomes the AFM state macroscopically. Unlike the disordered graphene or the substitutionally Co-doped graphene [26, 28], the total magnetic moment in this system cannot be interpreted with Lieb’s theorem for bipartite lattices [27], since the magnetic coupling does not favor the FM (AFM) solution in the AA (AB) configuration and the total magnetic moment of the system does not follow the equation $S = |N_A - N_B|$, where $N_{A(B)}$ is the number of Mn dopants in A(B) sublattices.

4. Conclusions

In conclusion, we have investigated the geometric structure and electronic structure of Mn-doped graphene by the GGA and GGA + $U$ methods. The calculation using the VASP code with different values of $U$ yields very different electronic structure, showing the importance of the on-site energy term in this system. Using the self-consistent $U$ method, we were able to determine the $U$ value to be 5.39 eV for this chemical environment. It was found that single Mn atom-doped graphene with a concentration larger than 1% is a charge transfer semiconductor with a bandgap of about 0.2 eV. The doping induces 3.00 $\mu_B$ magnetic moment around the dopant, which mainly comes from the Mn 3d orbitals. By Mn doping, when the doping concentration reaches a threshold between 3 and 5%, i.e. with a mean dopant distance of less than 7 Å, graphene can acquire macroscopic AFM.

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References

[1] Hashimoto A, Suenaga K, Gloter A, Urita K and Iijima S 2004 Nature 430 870
[2] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 Nature 438 197
[3] Novoselov K S, Jiang D, Schedin F, Booth T J, Khotkevich V V, Morozov S V and Geim A K 2005 Proc. Natl Acad. Sci. 102 10451
[4] Zhang Y, Tan Y-W, Stormer H L and Kim P 2005 Nature 438 201
[5] Son Y-W, Cohen M L and Louie S G 2006 Nature 444 347
[6] Wehling T O, Novoselov K S, Morozov S V, Vdovin E E, Katsnelson M I, Geim A K and Lichtenstein A I 2008 Nano Lett. 8 173
[7] Geim A K and Novoselov K S 2007 Nat. Mater. 6 183
[8] Yoo E J, Kim J, Hosono E, Zhou H-S, Kudo T and Honma I 2008 Nano Lett. 8 2277
[9] Tombros N, Jozsa C, Popinciuc M, Jonkman H T and van Wees B J 2007 Nature 448 571
[10] Schedin F, Geim A K, Morozov S V, Hill E W, Blake P, Katsnelson M I and Novoselove K S 2007 Nat. Mater. 6 652
[11] Uchoa B and Castro Neto A H 2007 Phys. Rev. Lett. 98 146801
[12] Yazeyev Oleg V and Helm L 2007 Phys. Rev. B 75 125408
[13] Chan K T, Neaton J B and Cohen M L 2008 Phys. Rev. B 77 235430
[14] Wu M, Liu E-Z, Ge M Y and Jiang J Z 2009 Appl. Phys. Lett. 94 102505
[15] Krasheninnikov A V, Lehtinen P O, Foster A S, Pyykkö P and Nieminen R M 2009 Phys. Rev. Lett. 102 126807
[16] Anisimov V I, Zaanen J and Andersen O K 1991 Phys. Rev. B 44 943
[17] Kresse G and Hafner J 1994 J. Phys.: Condens. Matter 6 8245
[18] http://www.quantum-espresso.org
[19] Blöchl P E 1994 Phys. Rev. B 50 17953
[20] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758
[21] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[22] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
[23] Vanderbilt D 1990 Phys. Rev. B 41 7892
[24] Cococcioni M and de Gironcoli S 2005 Phys. Rev. B 71 035105
[25] Kulik H J, Cococcioni M, Scherlis D A and Marzari N 2006 Phys. Rev. Lett. 97 103001
[26] Santos E J G, Sánchez-Portal D and Ayuela A 2010 Phys. Rev. B 81 125433
[27] Lieb E H 1989 Phys. Rev. Lett. 62 1201
[28] Yazyev O V 2008 Phys. Rev. Lett. 101 037203