



Quest for magnetism in graphene via Cr- and Mo-doping: A DFT approach



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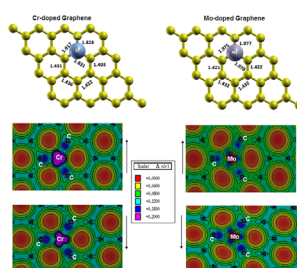
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HIGHLIGHTS

- Cr-/Mo-doping in graphene results halfmetallic/metallic state.
- Fermi level is tuned by Cr-/Mo-doping in graphene to open up magnetic channel.
- Unpaired Cr/Mo-d electrons are responsible for inducing magnetism in doped graphene.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to find signature of magnetism in graphene via Cr-/Mo-doping, full potential report based on density functional theory (DFT) of electronic and magnetic properties of pristine and Cr- and Mo-doped graphene has been presented. The Fermi level (E_F) is tuned via both doping such that zero band gap of graphene is overcome and magnetic channel gets induced. The Cr-/Mo-doping brings graphene from semimetallic to half metallic/metallic state. The local environment nearby to the dopant changes drastically and many carbon atoms become non equivalent and show induced magnetism. However, the main contributor in total moment of resultant nanomaterials is transition metal (Cr/Mo) atom. The origin of magnetism is analyzed on the basis of (i) p-d hybridization among C-p and Cr/Mo-d states and (ii) spin-polarized valence electron density. The resultant nanomaterials due to high spin polarization may be promising candidates for spin based technological applications.

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1. Introduction

Graphene, a single layer of carbon atoms in a honeycomb structure is the famous nanomaterial on which focused attentions

have been paid right from its discovery in 2004 [1]. It is one of the most recent nanomaterial with astonishing electronic, mechanical, optical and transport properties [2]. Geim and Novoselov were awarded the Nobel Prize in Physics in 2010 for ground breaking synthesis of the 2D material; graphene using mechanical exfoliation technique. Graphene is the building block of other Carbon based materials, e.g. graphite, which results from stacked

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graphene and carbon nanotubes which can be obtained by rolling up one or more graphene sheets. After its successful fabrication, graphene has become a rising star in the field of materials science and nanotechnology for its potential use in both, electronic [3–6] as well as spintronic [7–10] applications. Nato et al. [11] by using tight binding model showed that the valence and conduction bands in graphene touch at Fermi level (E_F) which makes it a zero band gap semiconductor. The unique zero gap of graphene leads to some limitations in the real electronic device fabrications. To make it useful for realistic applications, it is desirable to modify the bandstructure of graphene as per need. Doping (to introduce impurities such as adsorbing or substitutional atoms) is the efficient way to tune the physical properties of graphene.

Several efforts have been made to check the induction of magnetic properties in graphene layer by doping with suitable transition metals. Doping of many transition metals in graphene may induce the magnetism. Gan et al. [12] studied the migration of Au and Pt atoms in graphene layer using high resolution transmission electron microscopy (HRTEM) and showed that these metal atoms strongly interact with carbon present in graphene. Santos et al. [13] calculated structural, electronic and magnetic properties of graphene containing 3d transition metals and noble metals as substitutional impurities. These impurities provide an important route to add functionalities or to tune the response of devices based on graphenic materials. Transition-metal atoms (Sc–Zn, Pt and Au) embedded in single and double vacancies (SV and DV) in a graphene sheet were simulated using density functional theory (DFT) approach by Krasheninnikov et al. [14]. They showed that for most embedded metals, the bonding is strong and the metal–vacancy complexes exhibit interesting magnetic behavior.

The induced magnetic properties via diffusion of adatoms in a graphene sheet were observed by Lehtinen et al. [15]. They analyzed the role of adatoms in diffusion over surfaces and found a magnetic moment of $\sim 0.5 \mu_B$ on graphene. The ferromagnetic property of Mn-doped graphene was investigated by Min et al. [16]. They found that magnetic moment of doped material varies with dopant concentrations. Wu et al. [17] examined the role of Mn-3d orbital for inducing magnetic moment of $3.00 \mu_B$ in Mn-doped graphene using GGA and GGA+U formalism. Mandel et al. [18] observed the remarkable effect of half metallicity in graphene nanosheets with 90% change in magnetoresistance at room temperature. Naji et al. [19] studied the electronic and magnetic properties of Co and Ni adatom adsorption on the graphene material using DFT. They found the magnetic/nonmagnetic behavior for Co/Ni adsorption and estimated the Curie temperature (T_c) in case of Co adsorption around 438 °K.

Doping of transition metal (TM) may lead to remarkable magnetic properties and huge spin polarization in graphene which can found intriguing place in nanoelectronic devices and spintronic applications. Keeping the literature work and potential of doped graphene nanomaterials in the mind, we are highly motivated to study the electronic properties and magnetic response of Cr- and Mo-doped graphene for finding the signature of magnetism and/or half metallicity. The paper is organized as follows: Section 2 describes the computational details of methodology used. Important results of electronic and magnetic properties of present nanomaterials are described in Section 3. Finally in Section 4, the results of present work are summarized and conclusions are drawn.

2. Computational details

The full potential linearized augmented plane wave (FP-LAPW) method as implemented in WIEN2k [20] and based on DFT [21] was employed for the calculations of electronic and magnetic properties of present systems. In this method, core states were

treated fully relativistically, whereas, a scalar relativistic approximation was used for the valence states. The gradient generalized approximation (GGA) formalism within Perdew–Burke–Ernzerhof (PBE) parameterization [22] was used to construct the exchange and correlation (XC) potentials. The radii of muffin-tin (MT) sphere (R_{MT}) for various atoms were taken in the present calculations to ensure the nearly touching spheres. The plane wave cut off parameters were decided by $R_{mt}K_{max} = 7$ (where K_{max} is the largest wave vector of the basis set) and $G_{max} = 12 \text{ a.u.}^{-1}$ (for Fourier expansion of potential in the interstitial region). The doped system consists of (4×4) supercell of graphene (32 C atoms) in which one Cr/Mo atom substitutes one C atom, corresponding to 3% doping. To avoid the interaction between graphene layers, a vacuum layer of 20 Å was added along the normal to graphene sheet in all calculations. The \mathbf{k} -space integration was carried out using the modified tetrahedron method [23] with a \mathbf{k} -mesh of $8 \times 8 \times 1$ in the irreducible Brillouin zone (IBZ) to obtain self-consistency. All atoms were allowed to be relaxed until the calculated Hellmann Feynman force on each atom became smaller than 0.02 eV \AA^{-1} .

3. Result and discussion

The substitutional doping in graphene where a single metal atom (Cr or Mo) has been replaced by one carbon atom in proposed supercell of graphene layer is mainly focused. There exists experimental evidence for this kind of defect as reported by Gan et al. [12]. Thus, this type of theoretical investigation is of prime importance. Before performing the final calculations, the geometrical optimization of pristine and doped graphene sheets allowing all C atoms and dopant to relax, is required essentially. The significant bondlengths in optimized geometry are mentioned in Fig. 1. The presence of heavier atoms; Cr/Mo in doped systems substantially influences the various C–C bondlengths. The C–Cr/C–Mo bondlength gets increased to at least 1.837 Å/1.977 Å due to larger atomic radius of Cr/Mo atom as compared to C atom. A similar change in bondlengths has also been observed by Ullah et al. [24] for Be doping and Be, B co-doping in graphene. Further, due to larger atomic radius, the Cr/Mo atom does not fit exactly in graphene planar geometry and moves up from the graphene plane at a perpendicular distance of 0.068 Å/0.074 Å. The actual position of dopant (Cr/Mo) can be easily identified in perpendicular view of Fig. 1.

The stability of doped systems has been verified by binding energy [$E_b = E_{doped} - (E_{vacancy} + E_{Cr/Mo})$], where $E_{doped}/E_{vacancy}$ is the equilibrium energy of graphene, with dopant/vacancy and $E_{Cr/Mo}$ is the equilibrium energy of an isolated Cr/Mo atom. The binding energies are found to be -7.1 eV and -6.8 eV in Cr- and Mo-doped graphene, respectively, which are in accordance to experimental range; -8.0 eV to -6.0 eV for TMs doping in graphene [14].

By analyzing total density of states (DOS) of electrons in pristine, Cr- and Mo-doped graphene (Fig. 2), it is observed that on substituting C atom with Cr/Mo atom, the total DOS gets altered and localized levels start to appear, especially in the vicinity of E_F . Further, the inspection of total DOS manifests complete spin polarization and half metallic characteristics with small energy gap in minority spin channel (MIC) of Cr-doped graphene. On the other hand, partial spin polarization and metallic behavior among both spin channels has been observed in Mo-doped graphene. In other words, the Cr-/Mo-doping in pristine graphene results in a transition from semimetal to half metal/metal. The empirical relation of degree of spin polarization (P) in a material at E_F , although it is quite difficult to measure [25], is given by:

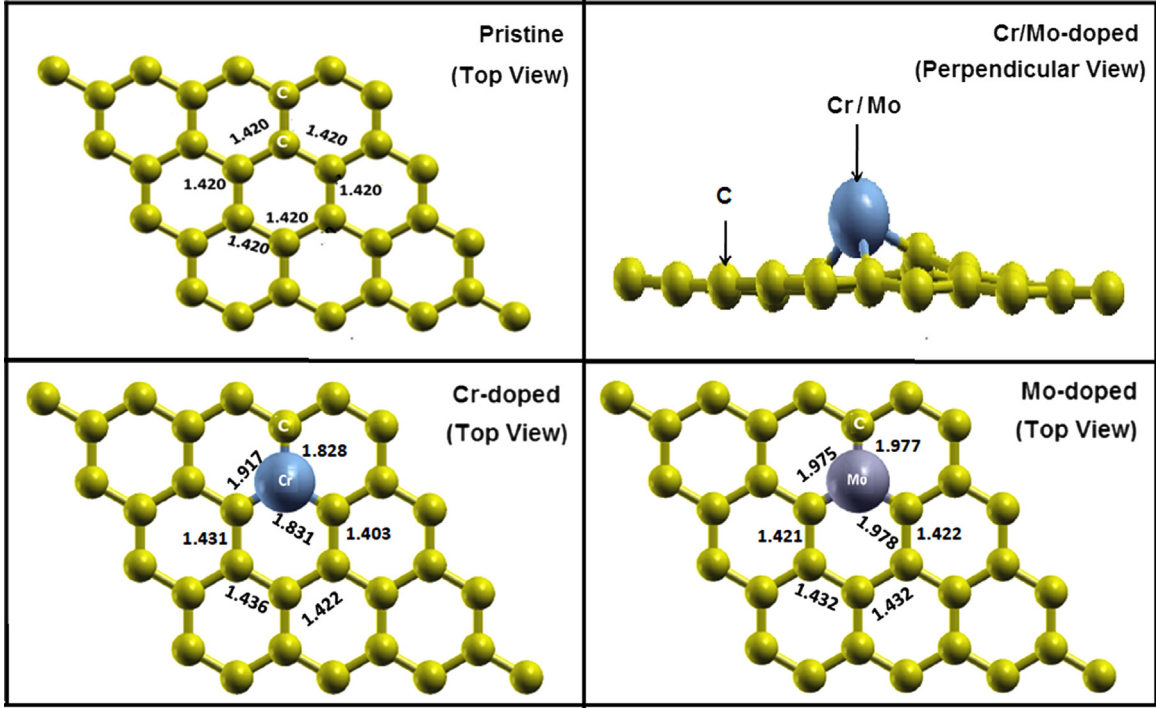


Fig. 1. A 4×4 unit cell of graphene doped with (a) Cr atom and (b) Mo atom.

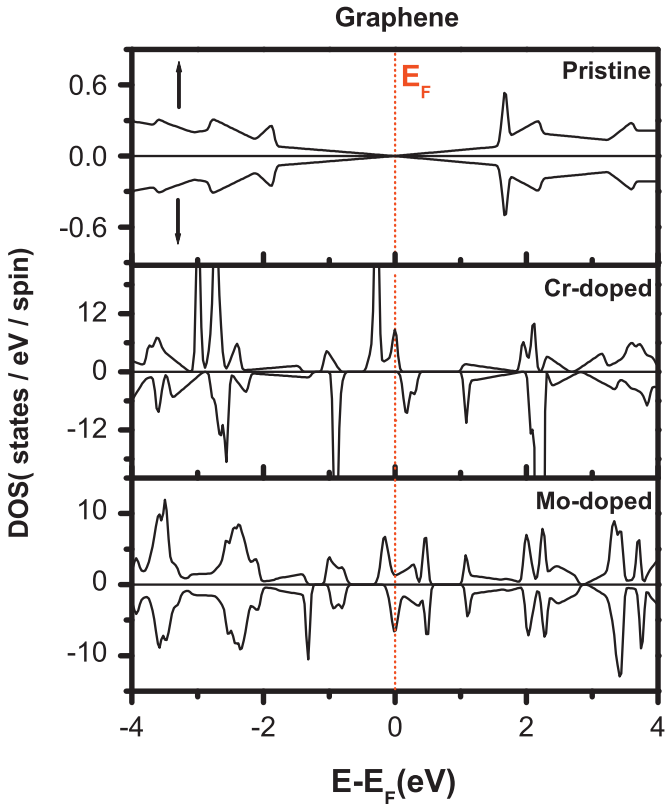


Fig. 2. Calculated spin polarized total Density of States (DOS) of Pristine, Cr-doped and Mo-doped graphene.

$$P = \frac{N_{\uparrow}(E_F) - N_{\downarrow}(E_F)}{N_{\uparrow}(E_F) + N_{\downarrow}(E_F)} \quad (1)$$

where $N_{\uparrow}(E_F)$ and $N_{\downarrow}(E_F)$ represent DOS of majority (\uparrow) and minority (\downarrow) spin electrons at the E_F , respectively. As mentioned in Table 1,

Table 1

Calculated Band gap and/or HM gap, Spin density of states at E_F and polarization for pristine and Cr-/Mo-doped graphene.

Graphene	Band gap (eV)	Half-metallic gap (eV)	Nature	$N_{\uparrow}(E_F)$	$N_{\downarrow}(E_F)$	P (%)
Pristine	0.00	–	Semimetal	0.00	0.00	–
Cr-doped	0.87	0.10	Half-metal	8.71	0.00	100.0
Mo-doped	–	–	Metal	1.36	6.55	65.6

Cr-doping produces complete 100% spin polarization at E_F whereas for Mo-doping, relatively low spin polarization (65.6%) has been found. However, the calculated value of Mo-doped graphene is still appreciable for spintronic applications.

The existence of half metallic (HM) gap i.e. a minimal gap for spin excitation in MIC is a striking feature of a material. This gap is of unique importance for creating a hole and an electron in MIC. It is defined as

$$E_{HM} = \text{Min} \{ (E_F - E_V^{\text{top}}), (E_C^{\text{bot}} - E_F) \} \quad (2)$$

where E_V^{top} and E_C^{bot} represent the energy corresponding to top of valence band (VB) and bottom of conduction band (CB), respectively. A true HM ferromagnet is governed by a non zero HM gap instead of band gap in any spin channel. Thus, it has to be calculated for clear understanding of half metallicity of the material. Table 1 manifests that only Cr-doped graphene shows half metallic gap (0.10 eV) and energy band gap (0.87 eV) in MIC whereas these gaps do not exist in Mo-doped graphene due to the absence of complete spin polarization.

To explore the contribution of various states in total DOS, the partial DOS of present systems are investigated (Fig. 3) which reveals that in Cr-doped graphene, the majority spin Cr-d and C-p states are located at E_F . These states are responsible for generating localized magnetism and half metallic character. Further, the contribution of C-s states towards total DOS is almost zero which justifies that C-s electrons remain isolated and are not responsible for any bonding. On the other hand, in Mo-doped graphene, a

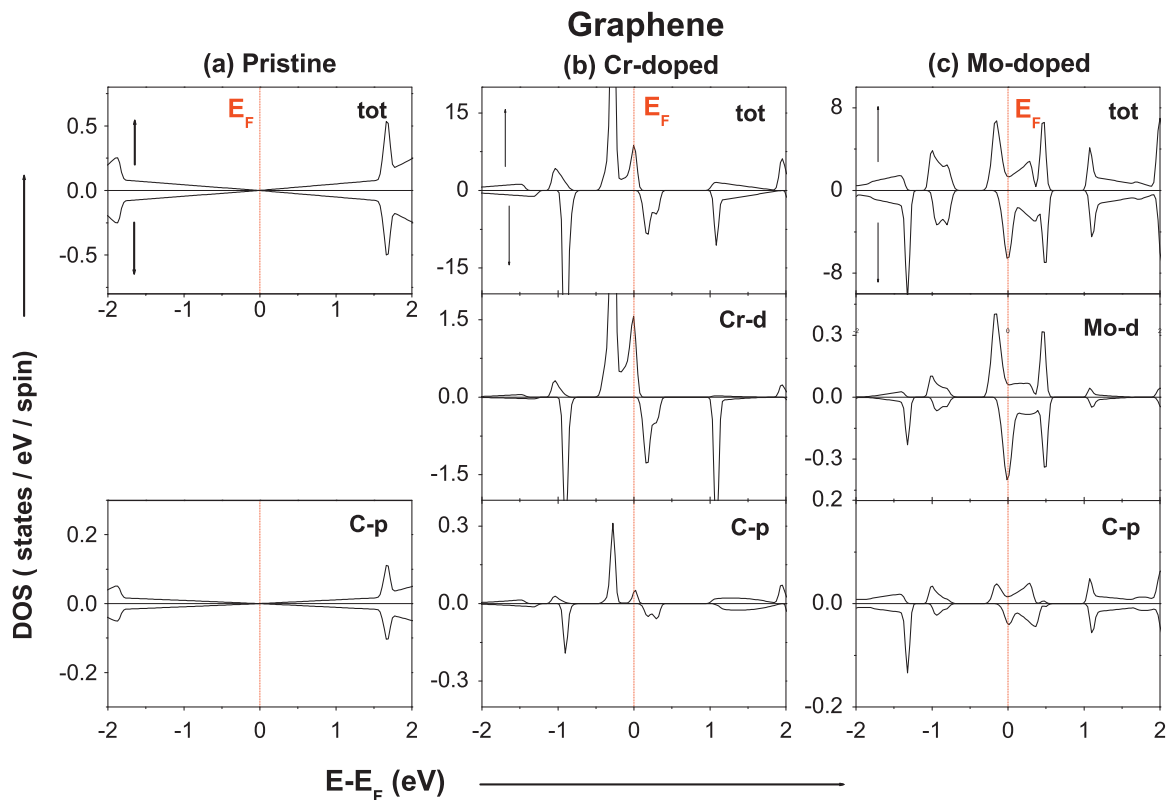


Fig. 3. Calculated atom resolved partial Density of States (PDOS) of Pristine, Cr-doped and Mo-doped graphene.

suitable amount of DOS is available for Mo-d and C-p states at and in the vicinity of E_F for both spin channels. Thus, energy bands of graphene which were just touching at E_F , intersect now due to p-d interactions in both spin channels. This leads to transition of semimetallic state of graphene into metallic ones on Mo-doping. The dissimilar behavior of Mo-doped graphene (metallic) as compared to Cr-doped graphene (half metallic) can be explained on the basis of different characteristics of 3d and 4d orbitals of Cr and Mo atoms, respectively. Relatively large size of Mo-4d orbital is responsible for weak covalent bonding in case of Mo-doped graphene which generates the metallic behavior rather than half metallic with a low magnetic moment. Here also, contribution of C-s states towards total DOS is almost negligible. The p-d exchange mechanism between C-p and Cr-d/Mo-d orbitals is solely responsible for the origin of half-metallic/metallic behavior in Cr-/Mo-doped graphene. The Cr-/Mo-doping is suitable way to tune the E_F and to generate magnetic ordering in graphene.

Pristine graphene has zero magnetic moment; however on doping with Cr or Mo atom, magnetism can be attained. The total moment is proportional to net difference of DOS of electrons in two spin channels. Therefore, an appreciable moment of $2.00 \mu_B$ has been found in Cr-doped graphene whereas Mo-doped graphene, due to small difference of DOS in the vicinity of E_F , witnesses a small moment (i.e. $0.45 \mu_B$). This can also be confirmed by checking the moment on individual Cr and Mo atoms (Table 2)

Table 2

Calculated total (M_{tot}), atom resolved ($M_{Cr/Mo/C1/C2}$) and interstitial (M_{int}) magnetic moments of pristine and Cr-/Mo-doped graphene. ($M_{C1/C2}$ represents induced moment on first/second nn C-atoms to TM atom).

Graphene	M_{tot} (μ_B)	$M_{Cr/Mo}$ (μ_B)	M_{C1} (μ_B)	M_{C2} (μ_B)	M_{int} (μ_B)
Pristine	0.000	0.000	0.000	0.000	0.000
Cr-doped	2.000	1.213	-0.052	0.025	0.871
Mo-doped	0.420	0.100	-0.004	0.015	0.230

which are the main contributor of the total moment. Doping of these atoms, makes many C atoms non-equivalent and surprisingly, some fractional induced moment also gets appeared due to p-d hybridization on first and second nearest neighbors (nn) C atoms to dopant. For other C atoms away from dopant, this type of induction is almost negligible. The remaining moment is found to be distributed evenly in the interstitial region among C atom.

Total valence electronic charge densities, $n(r)$ over graphene monolayer for both spins have been investigated in Fig. 4 to clarify further different magnetic response for both doped samples of graphene sheets. Fig. 4(a) and (b) shows that the electronic densities in both spin of pristine graphene are identical and electronic charge is equally shared between p-orbitals of two adjacent atoms through out the monolayer which confirms a clear covalent bonding via sp^2 hybridization. Concentrating now on Fig. 4(c) and (d) for Cr-doped graphene, it can be noticed that the valence electronic charge densities of Cr atom in majority and minority spins are dissimilar. Here, Cr atom abruptly influences the local environment and due to charge transfer from it to nearby C atoms (as indicated by blue color in Fig. 4(c) and (d) with a stipulation that larger charge accumulation is shown by violet and blue colors only according to thermometer scale), some induced moments get appeared on nearby C atoms also and Cr-C bonds become slightly polar covalent. In majority spin, the charge distribution around Cr tends to be spherical whereas for minority spin, the charge contours around Cr atom are non-spherical. As a result, different DOS for majority and minority spins appears which generates appreciable magnetic moment on Cr-doped graphene. Finally for Mo-doped graphene (Fig. 4(e) and (f)), the Mo-4d orbital has a radial node so it has different electron density than that of Cr-3d orbital. Due to the presence of this node, the p-d hybridization becomes weaker and valence electronic charge density in majority and minority spin of Mo doped graphene seems to be almost identical. This can lead to small magnetic moment only in graphene on Mo doping.

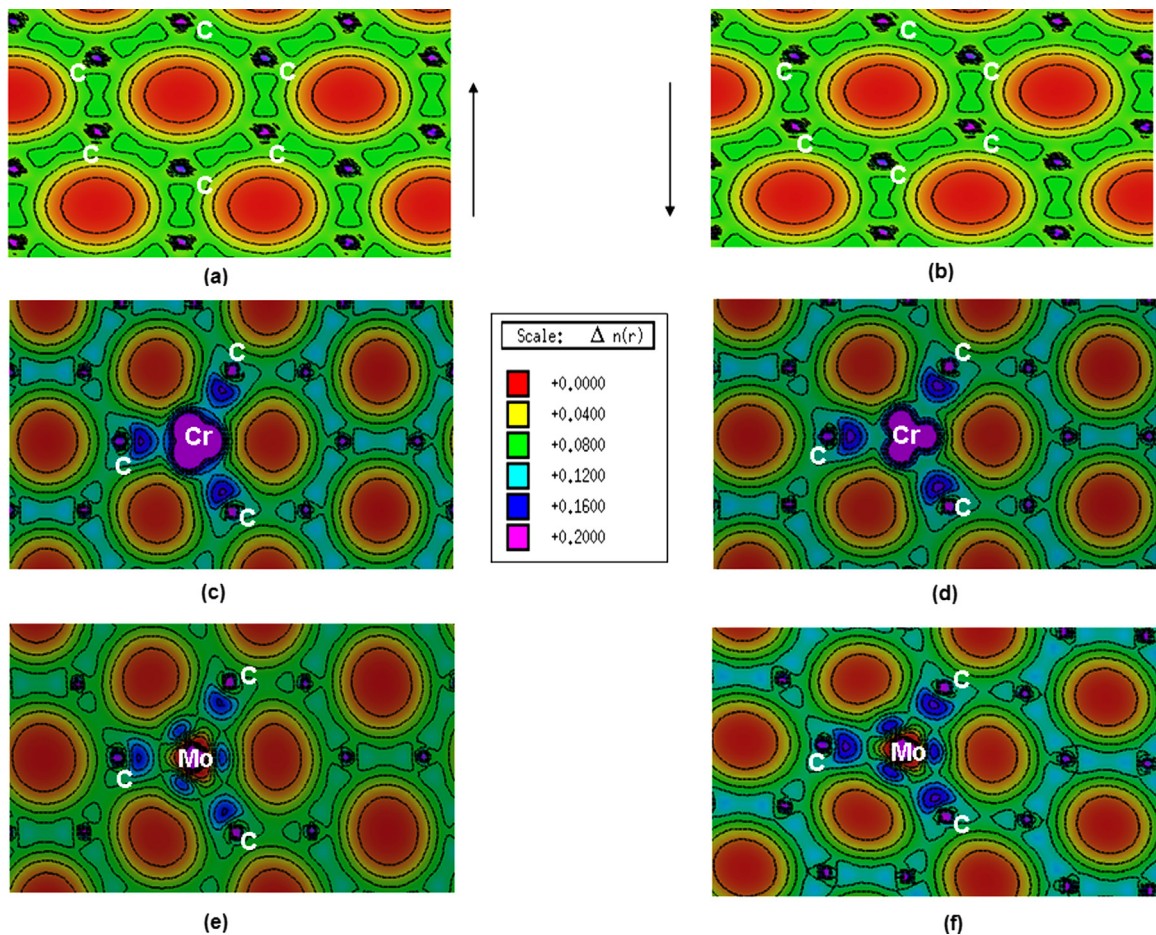


Fig. 4. Spin polarized total valence electron charge density, $n(r)$ over the graphene plane in units of $e/\text{\AA}^3$ for (a), (b) Pristine, (c), (d) Cr-doped and (e), (f) Mo-doped grapheme. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

To quantify the actual charge transfer, Bader charge analysis [26] was performed. As Cr has 6 vacancy and 5.59e charge is retained by Cr atom whereas the difference of charge i.e. 0.41e gets transfer to nearby C atoms in Cr-doped grapheme. Further, for Mo-doped grapheme, relatively less i.e. 0.04e charge gets transferred to C atoms as the maximum amount of charge (5.96e out of 6e) remains accumulated on Mo-atom. The large/small charge transfer from Cr/Mo to C atoms can be understood by observing the electronegativity difference between Cr/Mo and C atoms. The small charge transfer for Mo-doping leaves the graphene with less magnetic moment.

The existence of half-metallic/metallic behavior in Cr-/Mo-doped graphene can open a viable route for spintronic applications such as spin-current generator, spin based devices i.e. hard disk drives, magnetic random access memory (MRAM), magnetic inks and tapes, spin qubits for quantum computing and magnetic tunnel junctions (MTJ).

4. Summary and conclusion

The electronic and magnetic properties of Cr- and Mo-doped graphene at 3% doping concentration have been investigated using full potential DFT approach. Both TM atoms create magnetism in graphene by shifting the energy levels at E_F and opens up a magnetic channel for graphene to be used in real nanoscale spintronic devices. In actual, Cr-doped graphene is found to be true half metallic ferromagnet whereas in Mo-doped graphene, the half metallicity is not observed due to less spin polarization.

The unpaired d-electrons of Cr/Mo atom are responsible for inducing magnetism on doped graphene sheet. The DOS of C-p and Cr-/Mo-d states in doped graphene are asymmetric near the E_F . Therefore, the magnetic properties mainly arise due to exchange mechanism between C-p and Cr-/Mo-d orbitals. The magnetic ordering created in graphene in this way makes it suitable for recording media, magnetic sensors, magnetic inks and spintronic devices.

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References

- [1] A.K. Geim, K.S. Novoselov, *Nat. Mater.* 6 (2007) 183.
- [2] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I. V. Grigorieva, S.V. Dubonos, A.A. Firsov, *Nature* 438 (2005) 197.

- [3] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov, A. K. Geim, Proc. Nat. Acad. Sci. USA 102 (2005) 10451.
- [4] Y. Zhang, Y.W. Tan, H.L. Stromer, P. Kim, Nature 438 (2005) 201.
- [5] Y.W. Son, M.L. Cohen, S.G. Louie, Nature 444 (2006) 347.
- [6] T.O. Wheleng, K.S. Novoselov, S.V. Morozov, E.E. Dovin, M.I. Katsnelson, A. K. Geim, A.I. Lichtenstein, Nano Lett. 8 (2008) 173.
- [7] K.S. Novoselov, A.K. Geim, S.V. Morozov, Y. Zhang, D. Jiang, S.V. Dubonos, I. V. Grigorieva, A.A. Firsov, Science 306 (2004) 666.
- [8] A.K. Geim, F. Schedin, S.V. Morozov, E.W. Hill, P. Blake, M.I. Katsnelson, K. S. Novoselov, Nat. Mater. 6 (2007) 652.
- [9] K.S. Novoselov, A.K. Geim, Science 315 (2007) 1379.
- [10] P. Avouris, Z. Chen, V. Perebeinos, Nat. Technol. 2 (2007) 605.
- [11] A.H. Castro Neto, et al., Rev. Mod. Phys. 81 (2009) 109.
- [12] Y. Gan, L. Sun, F. Banhart, Small 4 (2008) 587.
- [13] (a) E.J.G. Santos, D.S. Portal, A. Ayuela, Phys. Rev. B 81 (2010) 125433;
(b) E.J.G. Santos, D.S. Portal, A. Ayuela, New J. Phys. 12 (2010) 053012.
- [14] A.V. Krashenninnikov, P.O. Lehtinen, A.S. Foster, Phys. Rev. Lett. 102 (2009) 126807.
- [15] P.O. Lehtinen, A.S. Foster, A. Ayuela, A.V. Krashenninnikov, R.M. Nieminen, Phys. Rev. Lett. 93 (2004) 187202.
- [16] L.T. Min, J.J. Liu, Y.M. Zhang, H. Guo, Z.Y. Zhang, Chin. Phys. B 22 (2013) 117502.
- [17] M. Wu, E.Z. Liu, M.Y. Ge, J.Z. Jiang, Appl. Phys. Lett. 4 (2009) 102505.
- [18] S. Mandal, M. Barkey, S.K. Saha, Carbon 61 (2013) 254.
- [19] S. Naji, A. Belhaj, H. Labrim, M. Bhihi, A. Benyoussef, A. El. Kenz, J. Phys. Chem. C 118 (2014) 4924.
- [20] P. Blaha, K. Schwarz, G. Madsen, D.K.J. Luitz, Wien2k, An Augmented Plane Wave plus Local Orbitals Program for Calculating Crystal Properties, Vienna University of technology, Austria, 2001, ISBN: 3-9501031-1-2.
- [21] M. Weinert, E. Wimmer, A.J. Freeman, Phys. Rev. B 26 (1982) 4571.
- [22] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [23] P.E. Blöchl, O. Jepsen, O.K. Andersen, Phys. Rev. B 49 (1994) 16223.
- [24] S. Ullah, A. Hussain, W.A. Syed, M.A. Saqlain, I. Ahmad, O. Leenaerts, A. Karim, RSC Adv. 5 (2015) 55762.
- [25] R.J. Soulen Jr., J.M. Byers, M.S. Osofsky, B. Nadgorny, T. Ambrose, S.F. Cheng, P. R. Broussard, C.T. Tanaka, J. Nowak, J.S. Moodera, A. Barry, J.M.D. Coey, Science 282 (1998) 85.
- [26] R. Bader, Atoms in Molecules: A Quantum Theory, Oxford University Press, New York, 1994.