Directional-dependent spin exchange between divacantly substituted Fe in graphene

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In this study, we investigate the isolated magnetic interactions between two identical Fe atoms divacantly-substituted into graphene. Using density functional theory, we simulated the electronic and magnetic properties for a supercell of graphene with spatial variation of the Fe atoms along either the armchair or zig-zag directions. Overall, we find that the exchange interaction between the two Fe atoms fluctuates from ferromagnetic to antiferromagnetic as a function of the spatial distance in the armchair direction. Given the induced magnetic moment and increased density of states at the Fermi level by the surrounding carbon atoms, we conclude that an RKKY-like interaction may characterize the exchange interactions between the Fe atoms. Furthermore, we examined the same interactions for Fe atoms along the zig-zag direction in graphene and found no evidence for an RKKY interaction as this system shows standard superexchange between the transition-metal impurities. Therefore, we determine that Fe-substituted graphene produces a directional-dependent spin interaction, which may provide stability to spintronic and multifunctional devices and applications for graphene.

I. INTRODUCTION

Even after over a decade of high-profile research, graphene continues to provide fascinating results and phenomena1–3 ranging from semiconductor physics and superconductivity to magnetic properties and magic angles3–5. The interest in graphene and other two-dimensional (2D) materials is due to their possible technological applications stemming from their electronic properties and high tensile strength, which makes 2D materials excellent candidates for many applications, such as flexible supercapacitors or as a highly sensitive gas detectors3–7.

The interest in graphene comes from its ability to conduct electrons through a stable and robust honeycomb lattice (shown in Fig. 1(a)), where its unique electronic structure and tensile strength strongly suggests electronic applications in memory and logic devices and processes5–11. These properties have enabled the use of graphene nanoribbons (GNRs) in field-effect transistors, which provide viable technological applications in suitable logic devices5–9. Through the utilization of GNRs in quantum dot technology, a large band gap can be introduced producing the possibility of a logic switch12–13.

While nanoscale logic devices are a practical use of graphene, they only take advantage of one degree of freedom of the electron, charge. However, in the last decade, there has been a significant push for 2D materials in the realm of spintronics14,15, where the ability for a spintronic device to take advantage of the coupling between magnetic moment and conduction electrons can open new avenues for technological applications14,15. Such a device could be utilized to create a logic device or memory storage unit, which is of great interest in the technology sector due to graphene’s inexpensive and practical fabrication.

Graphene has been shown to gain magnetic moment when a vacancy is introduced into the material, giving rise to the prospect of spin-based memory storage devices16–18. Additionally, the introduction of magnetic impurities onto and into graphene have been shown to induce magnetism that could be controlled19–28. Furthermore, studies on graphene have shown to produce a Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between two magnetic impurities introduced into a

FIG. 1: Comparison of the (a) normal graphene structure and the (b) single vacant and (c) di-vacant Fe substitutions. Below shows the range of substituted Fe dimers along the (d) armchair and (e) zigzag directions.
FIG. 2: The change in energy between ferromagnetic (positive) and antiferromagnetic (negative) configurations for the (a) armchair and (b) zigzag directions as a function of separation distance. The change in energy is directly proportional to the exchange interaction. Here, the armchair configuration seems to be dominated by a RKKY-like interaction, which is characterized by the oscillatory nature of the spin exchange, while the zigzag configuration seems to only be dominated by superexchange.

single-atomic-layer \[20, 29, 30\], where an RKKY interaction occurs when two magnetic atoms coupling in a non-magnetic material through the conduction electrons\[31–33\]. In this case, one of the impurities interacts with the conduction electrons of the graphene, which induces a small spin polarization in the carbon atoms around the magnetic impurity. This effect has been shown via density functional theory (DFT) calculations that the magnetic spin of the metal impurities in graphene changed inversely proportional to the cube of the separation between the two metal impurities \[29\].

Recently, it was shown that direct substitution of two transition-metal impurities in place of individual carbon atoms in graphene (shown in Fig. \[1\](b)) resulted in an RKKY interaction\[20\]. This study was then pushed further to show that these interactions could be used to display the potential of a graphene spintronic device by showing that they could change the magnetic spin of the substituted impurities in a graphene nanoribbon by applying a bias voltage \[30\]. However, experimental studies have shown that a divacant substitution (Fig. \[1\](c)) of metal impurities is the energy-favorable structure over the single vacant substitution\[11, 28\]. Therefore, it is essential to extend the work of Crook et al.\[20\] and examine the exchange interactions in the divacant configuration.

In this study, we examine the spatial dependence of electronic and magnetic properties of two magnetic Fe atoms in graphene. Using density functional theory, we present the electronic band structure, density of states, electron density, and Mulliken population for Fe atoms separated along both the armchair and zig-zag directions. We find that the exchange mechanism between the atoms is directionally dependent, where the two Fe atoms seem to couple through an RKKY-like interaction along the armchair direction and a superexchange in the zig-zag direction. We argue that this directionality of exchange coupling may help provide an experimental realization of a spintronic device.

II. METHODS

Calculations were performed using Density Functional Theory (DFT) through the utilization of Atomistix Toolkit (ATK) by Quantumwise\[34–36\]. Starting with a 12x12 supercell of graphene (216 atoms), two C atoms were replaced by a single Fe atom. Another Fe atom was then inserted into graphene in the same manner at varying distances from the original Fe atom. This spatial distance was performed along both the zig-zag and armchair directions, shown in Figure 1(d) and (e), respectively. Using a geometry optimization, the supercell was relaxed to find the ground state configuration.

Using a Spin-polarized Generalized Gradient Approximation (SGGA) in the Perdew, Burke, and Ernzerhof (PBE) functional was applied using a 10x10x1 k-point sampling, and an applied Hubbard potential of 4 eV was placed on the Fe 3$d$-orbitals to produce localized magnetic moments\[36\]. The electronic band structure, density of states (DOS), Mulliken population, and electron density were determined. Through an examination of the total energy for the ferromagnetic and antiferromagnetic configurations, the ground state was established. With the ground state known, we then analyzed the electronic structure to determine the nature of the exchange coupling.

III. RESULTS AND DISCUSSION

To understand the magnetic and electronic properties of Fe atoms divacantly substituted into a supercell of graphene, the exchange characteristics of the magnetic dimer in graphene can be considered by a standard spin Hamiltonian,

$$H = -J \mathbf{S}_1 \cdot \mathbf{S}_2,$$

\[\text{(1)}\]
FIG. 3: The electron density difference between the spin up and down channels for the Fe dimer interactions along the armchair and zigzag directions. At large separation distances, the armchair configuration seems to transition from a RKKY dominated interaction to that of a superexchange. This is characterized by a shift in the orbital interactions.

where J is the superexchange interaction between the two spins. In a standard quantum spin dimer, you get two energy levels of $3/4J$ and $-1/4J$. Therefore, the change in energy between the two states $J > 0$ and an AFM ground state for $J < 0$. Therefore, through an examination of the energy difference of the FM and AFM configurations, one can determine the ground state configuration and estimate the exchange interaction.

Figure 2 shows the change in energy between the FM and AFM configurations. For the armchair configuration (Fig. 2(a)), the change in energy shows a distinct oscillation between FM and AFM ground states, where the zig-zag configuration (Fig. 2(b)) is consistently below zero and indicates constant AFM exchange. This difference in exchange shows a directionally-dependent exchange in graphene, where the armchair configuration is consistent with that of an RKKY interaction, which has been shown in the single vacant case as well. However, the zig-zag configuration only produces a standard superexchange between the impurity atoms.

To examine these interactions further, we calculated electronic properties using density functional theory. Figure 4 shows the electronic band structure and density of states (DOS) for the divacant substitution of graphene with Fe dimers along the armchair direction, where the band structure contains both spin up (black) and spin down (red) bands for the 2 (a), 6 (c), and 10 (e) carbon separated impurities. This separation is due to the ferromagnetic (FM) polarization of the ground state. The 4 (b) and 8 (d) carbon separated impurities only show the spin up bands since the antiferromagnetic (AFM) nature of the system makes the spin up and down bands degenerate. The DOS for each configuration is paired alongside the band structure, where we present the total and partial DOS, as well as the local DOS (LDOS) for C, and the LDOS of Fe (moving left to right).

An analysis of the electronic structure and local density of states for the carbon atom indicates a slight metallicity between the two Fe impurities. Therefore, given alternating magnetic ground state shown in Fig. 2(a) and the modest density of states in the linking carbon atoms, it is likely that an RKKY interaction exists between Fe impurities along the armchair direction, which is in agreement with previous calculations on metal impurities substituted in graphene.

Figure 3 shows the electron density difference for the Fe atoms substituted along the armchair and zig-zag directions that shows the magnetic spin of the Fe atoms and their influence on the surrounding carbon atoms as the two Fe atoms are separated along both directions. In the armchair case, we find that the orbital interactions between the magnetic impurities changes and magnetic moment alternates between FM and AFM. However, this interaction is different for the zig-zag direction, which only has AFM magnetic interactions. Furthermore, the electron distribution in the 2 and 4 carbon separation cases for the armchair also produce a different pattern.
FIG. 4: The electronic band structure and density of states for the dimer interactions along the armchair direction with (a) 2 (FM), (b) 4 (AFM), (c) 6 (FM), (d) 8 (AFM), and (e) 10 (FM) carbon separations and exchanges.

than the others. Therefore, there is a competition between RKKY interactions and a standard Heisenberg interaction. As the RKKY is weakened, the standard interaction takes over and indicates the competition between conduction electron mediated exchange and the standard superexchange.

Along the zig-zag direction, the configuration of the two metal impurities does not seem to exhibit the same characteristics to that of an RKKY interaction, which is already clear in Fig. 3. The orbital configurations of electron density difference indicates why zig-zag direction is not conducive for an RKKY interaction. Furthermore, an examination of the ground state energy between FM and AFM interactions (Fig. 2(b)) shows the constant AFM ground state with decreasing superexchange coupling with increasing spatial distance, which provides no evidence of an RKKY interaction along that direction.

Figure 5 shows the electronic band structure and density of states (DOS) for the divacant substitution of graphene with Fe dimers along the zig-zag direction, where the band structure contains both spin up (black) and spin down (red) bands for the 3 (a), 5 (b), 7 (c), and 9 (e) carbon separated impurities. However, unlike the armchair band structure, there are only black bands in the zig-zag, which is caused by the spin degeneracy between spin up and spin down bands. The electronic band structure and DOS suggests that the zig-zag direction only contains an antiferromagnetic (AFM) nature in the system. The DOS for each configuration is paired alongside the band structure, where we present the total and partial DOS, as well as the local DOS (LDOS) for C, and the LDOS of Fe (moving left to right).

A study of the electronic band structure for the zig-zag configuration, represented in Figure 5 shows that there is no indication of a change of spin in the bands as the two impurities are separated, which suggests that there is not an RKKY interaction between the two Fe atoms when substituted along the zig-zag direction. The DOS, however, show that graphene behaves as a metal in the zig-zag direction as there are states near the Fermi level which indicates that there are conduction electrons when Fe atoms are divacantly-substituted in the zig-zag direction. However, the band structure suggests that there is only a superexchange instead of an RKKY interaction.

Figure 3 shows the magnetic spin of the Fe atoms as they are separated along the zig-zag direction. This figure directly indicates that the magnetic spin of the Fe atoms remain the same throughout the separation
A. V. Krasheninnikov and R. M. Nieminen, Attractive through their conduction electrons and remain in the same state throughout.

IV. CONCLUSION

In this study, Fe atoms were divacantly substituted into a graphene sheet and along either the armchair or zig-zag directions. Using density functional theory, the electronic and magnetic properties for the Fe atoms were determined for various spatial separations. An analysis of the exchange energy shows that graphene produces a directional dependent magnetic exchange, where interactions along the zig-zag direction seem to be governed by a standard superexchange while the interactions along the armchair direction produce an RKKY exchange interaction. This dichotomy of interactions may provide an avenue that graphene can be used in the development of a spintronic device or logic switch.

The prospect for spintronic devices utilizing graphene is a highly sought after in the technology industry. This study provides results suggesting a directional dependence of the magnetic exchange in graphene may be utilized in a device setup that takes advantage of the effects of both a standard superexchange and an RKKY interaction. It may be possible to influence electrons through voltage gates and take advantage of the magnetic spin of the impurities. However, these device applications warrant and require further investigation into the construction of a spintronic device using these types of magnetic configurations.

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