In-Plane Magnetization and Quantum Anomalous Hall Effect in BiFeO$_3$/Graphene Superlattice

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Abstract

We predict the presence of quantum anomalous Hall effect (QAHE) in the artificial superlattice of graphene embedded in (111)-oriented BiFeO$_3$ layers based on first-principles calculations. Due to the electron transfer and the proximity effect at the BiFeO$_3$/graphene interface, we find that the magnetic moments of the Fe atoms near the graphene layer were slightly less than that of bulk Fe atoms. Regarding the ferromagnetic moment orientation of Fe atoms in perovskite BiFeO$_3$, we reveal that the in-plane magnetization gives the ground state. The QAHE band gap depends on the magnetization direction, and the separation between the graphene layer and the perovskite BiFeO$_3$ slab as well, which might be adjusted by applying external uniaxial stress in experiment. Our results provide a route for designing hybrid 2D materials with emerging properties that are not available in single materials alone.
In 1879, the Hall effect was discovered when a perpendicular magnetic field was applied to an electric current in metal sheet, in which the Lorentz force was generated onto the electrons. In clean samples of low-density two-dimensional electron gas, discrete Landau levels are created by strong magnetic field leading to the quantized Hall conductance, known as the “quantum Hall effect” (QHE). Such intriguing effect is important not only for the fundamental breakthrough to bring topology to the condensed matter physics, but also for its potential practical application in dissipationless electronic devices. However, the prerequisite of strong magnetic field limits the application of QHE. In 1988, Haldane suggested the possibility to realize QHE in the absence of magnetic field by introducing staggered magnetic flux in a hexagonal honeycomb lattice system. To distinguish it from the traditional QHE from strong external magnetic field, this phenomenon is named as “quantum anomalous Hall effect” (QAHE).

Nevertheless, the staggered magnetic flux is also difficult to be achieved experimentally that hinders the observation of QAHE. Over the past decades, great progress has been made in exploring how to achieve QAHE in realistic two-dimensional materials both theoretically and experimentally. The proposals mainly focus on two categories, i.e., magnetically doped topological insulator thin film and magnetized narrow-gapped two-dimensional atomic-layer crystals. In experiments, the former strategy has been realized experimentally in magnetically doped topological insulator film Cr-doped (Bi, Sb)$_2$Te$_3$ sample by using the molecular beam epitaxy growth. However, the observations are made under extremely low temperature limited by the low Curie temperature and small energy gap. To take advantage of QAHE in the dissipationless electronic devices, the presence of QAHE at higher temperature is strongly demanded, which is still a difficult challenge awaiting to be solved.

Graphene provides another possible solution as a unique two-dimensional material. Graphene has attracted tremendous attention because of its superior mechanic, thermal, optical, electrical properties, including the linear Dirac dispersion relationship, and extremely high carrier mobility. Although the pristine graphene is gapless and does not possess either magnetization or strong spin-orbit coupling, QAHE might be induced by the externally tunable magnetization and Rashba spin-orbit coupling. To introduce magnetization and Rashba spin-orbit coupling, one may try doping magnetic metal atoms on graphene or by placing the graphene on magnetic substrates. Although the atomic adsorption is a simple and straightforward scheme,
the metal atoms are likely to form clusters on the surface of graphene\textsuperscript{14-16}, which is detrimental to graphene-based electronic transport. On the other hand, it has been reported that the magnetism in the topological insulators can be induced by the proximity coupling with the magnetic insulators\textsuperscript{17-22}. For example, Xiao \textit{et al.} predicted that the bilayers of perovskite-type transition-metal oxides grown along the [111] crystallographic axis are potential candidates for two-dimensional topological insulators\textsuperscript{23}. Weng \textit{et al.} found the gap opening of Dirac cone by the spin-orbit coupling, with nontrivial topological magnetic phase corresponding to the quantum anomalous Hall effect from LaMnO\textsubscript{3} (111) bilayer sandwiched in LaScO\textsubscript{3} barriers\textsuperscript{24}; they further proposed strong magnetoelectric couplings for the electric field control the magnetization in BiFeO\textsubscript{3} (BFO) bilayer sandwiched in SrTiO\textsubscript{3} along the [111] axis\textsuperscript{25}. Therefore, the antiferromagnetic perovskite oxide BiFeO\textsubscript{3} is an ideal choice of substrate as such insulating substrate does not affect the electronic transport properties of graphene. Moreover, the Fe atoms on (111) surface is intra-layer ferromagnetic, but inter-layer antiferromagnetic, resulting a local magnetic moment but a vanishing overall magnetization. The orbital hybridization of graphene and substrate can also induce a substantial spin-orbit coupling effect, which benefits the presence of a QAHE band gap. However, the energy gap is located far away from Fermi level as reported in previous work in heterostructure interface of graphene and multiferroic BFO\textsuperscript{11, 26-29}.

Here, we constructed the superlattices of graphene and BFO\textsuperscript{26-29} in this work. Such hybrid system can be assembled by using the frontier fabrication technology of layer-by-layer construction in a precisely controlled sequence\textsuperscript{26, 31}. The multiferroic perovskite BFO\textsuperscript{32} with a band gap about 2.7 eV\textsuperscript{33}, is both ferroelectric (Curie temperature \( T_c \approx 1103 \) K) and antiferromagnetic (Néel temperature \( T_N \) is approximately 643 K)\textsuperscript{34}. At the room temperature, the space group of BFO is R3c with the lattice constants \( a = 5.58 \) Å, \( c = 13.87 \) Å\textsuperscript{35}. The structure can be described as rhombohedral deformation of cubic perovskite cells with both ferroelectricity and oxygen octahedral tilting along (111) axis. BFO is a G-type antiferromagnet at room temperature, in which Fe\textsuperscript{3+} ions have large magnetic moment. Along the (111) direction, the Fe ions of same atomic layer have the same direction of magnetic moment and the adjacent layers of Fe ions have opposite directions of magnetic moment. Therefore, we construct a (111) terminated BFO/graphene superlattice, which may induce both exchange field and Rashba spin-orbit coupling. People can prepare heterojunctions of graphene and BFO,
with the help of state-of-the-art techniques. Recently, Katiyar et al. successfully deposited pure phase BFO films on Pt/TiO$_2$/SiO$_2$/Si substrates by using pulse laser deposition$^{36}$, and Wu et al. stacked BFO nanoplates on monolayer graphene over a Si substrate with a 285 nm SiO$_2$ layer$^{37}$.

We found that in the relaxed BFO/graphene superlattice, the average distance between graphene and the Fe atomic layer is about 2.94 Å, and the spacing between graphene and Bi layer is approximately 3.75 Å. The Fe atoms near the graphene layer have magnetic moment (3.97 $\mu_B$) that is slightly smaller than the other Fe atoms (4.16 $\mu_B$). Later we illustrate the charge density difference of the BFO/graphene superlattice to check the magnetic change and electron transfer. We have also studied the electronic band structures with and without spin-orbit coupling (SOC) for the BFO/graphene superlattice. Through our previous work, it has been proved that there is a quantized anomalous Hall conductance in BFO/graphene heterostructures$^{11}$. Therefore, in this work we pay more attention to the influence of in-plane magnetization strength on the quantum anomalous Hall effect in the following. We revealed the effect of the magnetization of Fe atoms in perovskite BFO on the QAHE located at the interface of the BFO/graphene superlattice system. The SOC band gaps $\delta$ of about 1.65 meV, 1.11 meV and 1.30 meV are found at the K and K' valleys, when the magnetization directions are respectively along the X-axis, Y-axis and Z-axis. By rotating the in-plane magnetization we confirmed that the system is in the ground state when the direction of the magnetic moment is in-plane, as shown in Table S1 and Figure S1 in SI. Finally, we demonstrated how to enhance the Rashba SOC and QAHE gap in graphene by reducing the distance between graphene and the BFO.

Our density functional theory (DFT)$^{38}$ calculations employed the Perdew-Burke-Ernzerhof (PBE) method as implemented in the Vienna Ab initio Simulation Package (VASP)$^{39}$. The electron exchange–correlation interaction was described by the generalized gradient approximation (GGA) plus the on-site Coulomb interaction (GGA + U) approach$^{40}$. The effective value of Hubbard U was chosen to be 4 eV on the Fe atoms, and we also considered the van der Waals interaction by using the D3 and optB86b vdW functional in the DFT calculation$^{41}$. The kinetic energy cutoff was chosen as 550 eV for the plane wave basis set and the first Brillouin-zone integration was $3 \times 3 \times 2$ Monkhorst-Pack grids. The convergence of electronic energy was set to $10^{-6}$ eV in the self-consistent calculations. During structural optimization, all atoms in the BFO/graphene superlattice were allowed to relax along any direction, and the
interatomic forces were converged to less than 0.01 eV/Å.

In our calculations, periodic boundary conditions are applied when we construct the BFO/graphene superlattice by inserting a $4 \times 4$ supercell of graphene into the $\sqrt{3} \times \sqrt{3}$ supercell of six-layer (111)-orientated BFO, as shown in Figure 1 (a). The lattice parameters of graphene and BFO allow that the lattice mismatch between graphene and BFO in our calculation is only about 1.78%. The relaxed distance between graphene and the Fe atoms is found to be $d_0 = 2.94$ Å, and that between the graphene and the Bi atomic layer is approximately 3.75 Å as shown in Figure 1 (b). There are three Fe atoms located beneath graphene per unit cell: one below the honeycomb hole (H-site Fe), and the other two are below A-site and B-site Fe, as illustrated in Figure 1 (c).

To show the variation of charge density before and after the insertion of graphene,
we plot the charge-density difference of the BFO/graphene superlattice in Figure 2 (a). We can find that the electrons tend to transfer toward the Fe atoms near the graphene layer. Moreover, the electron transfers around the three types of Fe atoms are found to be different in detail. As shown in Figure 2 (b) and (c), the top and side views of charge-density difference illustrate the visualization of electron accumulation and depletion (yellow and cyan respectively) between A, B and H-site Fe atoms and graphene. More importantly, the proximity effect from magnetized Fe layer is expected to efficiently magnetize the graphene layer.11

Figure 2. (a) The charge density difference of the BFO/graphene superlattice, where the yellow and cyan colors indicate electron accumulation and depletion, respectively. Red and blue arrows represent the directions of the magnetic moments of Fe. (b) Top view and (c) side view of the charge density difference show the difference of charge transfer for Fe atoms at A-site, B-site, and H-site.

Then we study the QAHE of BFO/graphene superlattice by calculating the band structure along the path Γ-Κ'-Κ-Γ of the Brillouin zone, as illustrated in Figure 3. Figure 3 (a) shows the spin-resolved band structure of the superlattice without including the SOC effect. We find that the band structure is basically formed by the superimposition of graphene and perovskite BFO. However, the spin-majority and spin-minority bands of graphene are split as indicated by red and blue, respectively. Figure 3 (b) shows the zoom-in of the spin-polarized band structure around Dirac point near the K with an
exchange splitting $M \sim 33.11$ meV. Because of the magnetic Fe atoms below the graphene layer, the spin-split $\pi$ bands of graphene have the majority (minority)-spin energy band shifting upward (downward). It is noteworthy that the crossings of the majority-spin and minority-spin bands are located exactly at the Fermi level, which may necessarily facilitate the practical realization of QAHE. We also note that due to the perturbation of staggered A and B sublattice potential in the graphene, at K point the gaps (11.32 and 15.48 meV) are seen for the same majority or minority spin bands.

Figure 3. The electronic band structures of the BFO/graphene superlattice. (a) and (b) are spin-resolved electronic band structures where the red and blue lines are for the majority-spin and minority-spin electrons. (c) and (d) are the band structures when SOC is included, for the magnetization along X-axis. The zoom-in energy dispersion near the K point are shown in (b) and (d). The dashed horizontal line at 0 eV indicates the Fermi level in all panels.
When spin-orbit coupling is further included, the global band gaps $\delta$ are opened at the intersections of spin-majority and spin-minority bands. The global gap values are 1.65 meV, 1.11 meV and 1.30 meV for the magnetization directions of perovskite BFO aligned in the X-axis, Y-axis and Z-axis respectively, as illustrated in Figures 3 and 4. Figure 3 (d) shows the zoom-in the energy dispersion near the K point of Figure 3 (c), clearly indicating that the Fermi level is inside the SOC-induced QAHE gap and all the band gaps form a ring area around the K point. We have further explored that for BFO/graphene superlattice, the magnetic moment orientation of Fe atoms has a great influence on the QAHE at the interface in the system. The magnetic moments tend to be aligned in-plane, and when the magnetization direction is the X-axis, the system has the largest global band gap of 1.65 meV. From a symmetry point of view, it is not forbidden that an in-plane magnetization can induce a Hall effect\(^{42}\). In our present superlattice, the magnetic order leads to broken time-reversal symmetry, and the insertion of graphene also destroys both in-plane mirror symmetries. Therefore, our DFT calculations yield a nonzero anomalous Hall effect.

The QAHE induced by magnetization and Rashba SOC can be understood using the following model Hamiltonian\(^{11}\):

$$H(k) = -v_f\eta(\sigma_x k_x + i \sigma_y k_y)I_z + MI_y S_z + \frac{2\eta}{2}(\eta \sigma_x S_y - \sigma_y S_x) + U \sigma_z I_z \quad (1)$$

where $v_f = 3v_f/2$ is the Fermi velocity with hopping energy $t \sim 2.60$ eV, $\eta = \pm 1$ are for K and K' points, respectively. Pauli matrices $\sigma$ and $s$ stand for sublattice and spin degrees of freedom, respectively. The first term in Eq. (1) describes the Hamiltonian of the pristine graphene, the second term gives the $\pi$-electron exchange coupling to magnetic Fe ions, and the third term corresponds to the Rashba SOC\(^{43}\). The last term represents the staggered sublattice potential. Both terms of exchange splitting and Rashba SOC play key roles\(^{44-46}\) in the formation of QAHE thanks to the interface effect of BFO and graphene. The former term arises from the proximity exchange coupling by magnetic Fe atoms and the latter term originates from the breaking the mirror symmetry of the single layer graphene\(^{11}\). The staggered sublattice potential mentioned before would not affect the size of the band gap $\delta$. We can extract the values of the model parameters by fitting Eq. (1) to the first principles band structure near the Dirac points in Figure 3 (b) and (d). For example, the magnetic exchange field in the second term in Eq. (1) for the present BFO/graphene superlattice is estimated to be $M \sim 32.76$ meV, 32.96 meV and 33.6 meV, when the magnetic moments of perovskite BFO lie in
X-axis, Y-axis and Z-axis, respectively. From the third term, we obtain that the Rashba SOC strength is \( \lambda_R \approx 1.94 \text{ meV}, 1.31 \text{ meV} \) and \( 1.53 \text{ meV} \), respectively.

Figure 4. The relationship between the SOC band gap and the in-plane magnetizations’ rotation angle \( \theta \) of Fe atom. The six kinds of symbols indicate the data calculated along the different K-path in the Brillouin zones as shown in the inset. The red dashed line represents the SOC band gap of the BFO/graphene superlattice when the magnetization direction is along the Z-axis.

The above calculations show that the magnetization orientation of the BFO/graphene superlattice tends to be in-plane. In order to explore its effect on the QAHE of the superlattice system, we take the X-axis as the initial direction in the XY plane, rotate the magnetization direction of the Fe atoms counterclockwise, and use the parameter \( \theta \) to indicate the angle between the magnetization and initial direction, i.e., when \( \theta \) is 0°, the magnetization orientation is the X-axis, and 90° is for the Y-axis. We can see that the QAHE gap is dependent on the in-plane magnetization angle \( \theta \), being symmetric with respect to the X-axis, as illustrated in Figure 4. From the X-axis to the -X-axis of the system, the band gap gradually decreases, reaching a minimum of 0.43 meV for -X-axis. This is due to the broken spatial inversion symmetry owing to the insertion of the graphene layer in the perovskite BFO. Using this special result, one can
control the QAHE gap quantitatively at the graphene layer by adjusting the in-plane magnetization orientation of the Fe atoms.

To further enlarge the energy gap, we try to enhance the proximity effect between graphene and BFO slab by simply reducing the spacing between graphene and the perovskite BFO since both the exchange field and the Rashba SOC are caused by hybridization between them. In experiment, one can control the distance between the graphene and the BFO slab by applying an external uniform stress perpendicular to the graphene layer. Here we used a way to simulate the effect of stress on BFO-graphene superstructure, in the case, we move only the graphene layer to the adjacent Fe atomic layer, while keeping all other atomic layer fixed.

![Figure 5](image.png)

Figure 5. The first-case calculated (a) local magnetic moments of Fe and (b) total magnetic moments as a function of the displacement \(d_0 - d\) in the BFO/graphene superlattice \(d_0\) represents the relaxed distance between the graphene layer and the underlying Fe atoms obtained after the geometry optimization).

We plot in Figure 5 for the magnetic moment of three different types of Fe atoms (A, B, and H-sites), and total magnetic moment for the whole BFO/graphene...
superlattice as a function of distance change (d₀-d). When the separation between the graphene layer and the Fe atomic layer is reduced by 0.8 Å, we find that the A, B and H-site Fe magnetic moments decreases by 0.081 µB, 0.050 µB, and 0.019 µB, respectively. The total magnetic moment increases by 0.116 µB for the whole system. As the graphene monolayer gets closer to the Fe atomic layer, enhanced electron charge transport from graphene to the Fe layer results in the slight reduction of Fe atomic magnetic moments. Consistent with our analysis of the charge density difference, the hybridization between graphene and A-site Fe is most affected, and the H-site Fe is least influenced by the distance change.

Figure 6. (a) Band gap δ, (b) the Rashba SOC strength λₑ, and (c) the exchange field M vs the decrease of BFO/graphene distance with three different magnetizations. The red square, blue diamond and yellow sphere symbols indicate the data calculated by shifting graphene toward the Fe atoms with magnetizations aligned in X-axis, Y-axis and Z-axis,
respectively.

We further explore the dependence of energy gap \( \delta \), the Rashba SOC strength \( \lambda_R \), and the exchange field \( M \) on the BFO-graphene distance \((d_0-d)\) as shown in Figure 6. We find that when the interlayer distance is reduced, the values of \( \delta \), \( \lambda_R \) and \( M \) are all increased monotonically. It is noteworthy that, when we reduce the Fe - graphene layer distance by 0.8 Å with magnetization along X-axis, i.e., interlayer distance \( d = 2.14 \) Å, the band gap \( \delta \), the Rashba SOC strength \( \lambda_R \), and the exchange field \( M \) can reach 2.89 meV, 3.40 meV, and 125.63 meV, respectively. When we set the Fe atomic magnetic moments in Y-axis and reduce the Fe - graphene layer separation by 0.8 Å, the band gap \( \delta \), the Rashba spin-orbit coupling constant \( \lambda_R \), and the exchange field \( M \) increase to 2.15 meV, 2.53 meV, and 125.53 meV, respectively. From comparison of these model magnetizations, we find obvious enhancement effect on the QAHE at the graphene layer inside the BFO/graphene system regardless of the Fe atoms' magnetization direction.

Although there are slight differences between the parameters obtained using these three kinds of methods to modeling stress, both simulations show that the stress can effectively enhance the magnetization strength, Rashba SOC, and thus the energy gap. The most stress sensitive parameter is the magnetization strength that changes dramatically as a result of an interlayer distance reduction of 0.8 Å. As a final remark, we further considered the van der Waals interaction, the distance between graphene and the Fe atomic layer (Bi atomic layer) can be slightly decreased from \( d_0 = 2.94 \) Å (3.75 Å) to \( d_0 = 2.60 \) Å (3.28 Å), which simply helps us obtain the larger QAHE band gap \( \delta \) and the Rashba spin-orbit coupling \( \lambda_R \).

In summary, we studied the QAHE in a BFO/graphene superlattice where the graphene monolayer is embedded between the slabs of antiferromagnetic BiFeO\(_3\) with (111) planes. By calculating the charge density difference and the magnetic properties, we discovered the electron charge transfer from the graphene to Fe atomic layer leading to the magnetization of graphene with Fermi energy lies at the intersect points between spin-majority and minority bands. The magnetization direction of the superlattice system is more likely to align in-plane, and the presence of interfacial Rashba SOC opens QAHE band gaps of about 1.65 meV, 1.11 meV and 1.30 meV with the Fermi level located inside the band gap and the magnetic moment of Fe atoms in the X-axis, Y-axis and Z-axis respectively, which benefits the observation of intrinsic QAHE.
without external voltage gate tuning. It is noteworthy that further consideration of the van der Waals interaction may reduce the distance between graphene and the Fe atomic layer from $d_0 = 2.94$ Å to $d_0 = 2.60$ Å in the absence of stress, which helps to obtain the larger QAHE band gap $\delta$. Our work strongly validates the presence of intrinsic QAHE in the BFO/graphene superlattice, which might be seen in similar superlattices of honeycomb lattices with many other antiferromagnetic perovskites.

**Supplementary Material**

See the supplementary material for the total energy with three different magnetization directions and the magnetic anisotropy energy (MAE) within $xoy$ plane of BFO/graphene superlattice.

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**References**

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Figure (a) shows the magnetic moment $M$ (in $\mu_B$) as a function of the distance $d_0 - d$ (in Å). The graph compares different sites of Fe: H-site Fe (squares), A-site Fe (circles), and B-site Fe (triangles). The data points are connected with lines to illustrate the trend.

Figure (b) presents the total magnetic moment (in $\mu_B$) as a function of $d_0 - d$ (in Å). The data points are represented by red circles, and a line is drawn to connect them, indicating the increase in magnetic moment with the decrease in distance.
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