First-principles study on electronic properties of twisted bilayer borophene

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Abstract. Borophene has received considerable investigations in recent five years that it is reported to possess a series of marvelous properties. However, most of the researches are about its monolayer form, the bilayer borophene, especially the twisted bilayer form which is a hot topic recently, has not been studied in detail. Herein, the first-principles calculations based on the density functional theory (DFT) method was performed to study the electronic properties of three kinds of twisted bilayer borophene that each kind of bilayer borophene is twisted to a certain angle in the plane. For the consideration of structural stability and calculation cost, the bilayer borophene are optimized to be 32.2°, 58.0° and 83.6° using an algorithm based on crystal matching theory. The charge density of relaxed twisted bilayer borophene shows the proximity of boron atoms. The analysis of band structure reveals that the twisted bilayer structure could separate the degenerate band and transform the bands to direct type, thus, modulating the resistance. In addition, a near-zero density of states could be found when bilayer borophene is twisted. This research could provide a basis for the applications of borophene, such as integrated electronic devices and micro/nano electronics.

1. Introduction
The twisted two-dimensional (2D) van der Waals (vdW) materials, in which the parts of its structure are stacked by van der Waals forces with a twisted angle, is a hot research interest recently. And the effect of twisted angle to 2D material is gradually developed to be a branch of the burgeoning 2D materials researches. As graphene is the first 2D materials to be synthesized, the first twisted bilayer structure study is also carried out on graphene by Cao Yuan et al. [1, 2]. In the works by Cao Yuan, the twisted bilayer graphene could be modulated and produced using the exfoliation process. And at a certain angle, that 1.1°, the twisted bilayer graphene possesses intrinsic superconductivity and near-zero flat bands, in which the zero corresponds to the Fermi energy. This excellent work astonished and inspired researchers to further study the superconducting materials.

Borophene is also a new-born 2D material that its first synthesis can trace back to 2015. Since then, borophene has walked into the sight of researchers formally and considerable studies about basic properties and potential application of borophene have been conducted. As borophene is reported to have a high strength [3] and unique electronic properties [4, 5], it is always taken comparison with graphene and could be a powerful rival. However, different from graphene, borophene is a highly anisotropic material and has a quasi-planar structure. Besides, borophene has abundant allotropes. [6] These characteristics make the properties of borophene more diverse and the analysis more complicated. However, it means more useful applications remains to be discovered. As for bilayer and
few-layer borophene, to the best of our knowledge, there are still rare studies about this topic. The work by Ihsan Boustani [7] could be the first to talk about the bilayer boron sheet using theoretical calculations. The center atom of the bilayer boron sheet in the hexagonal cell is close to each other and forms a pyramid shape. And then, Hongxia Zhong et al. [8] studies the mechanical and electronic properties of few-layer borophene using first-principles calculations. The vdW force is also adopted in that work, and it is found that the energy band will split at $\Gamma$ point which indicates the interaction between layers is stronger than other few-layer semiconductors. Up to now, a few materials, such as graphene and GaN [9] have been studied the twisting effect. However, the twisted bilayer borophene has not been investigated.

For the analysis of twisted materials by theoretical calculation, one difficult point is the cell match. [10] The cell match will introduce the match strain and result in large amounts of computation. In this work, a cell match algorithm for the 2D orthorhombic system which is based on cell math theory was used. Another difficult point is the analysis of electronic properties. Here we combine charge density, band structure and density of states to analyze the electronic properties. After the introduction of the background of our work, in the next chapter, we illustrate the calculations details and our original twisted bilayer structures of borophene. And then, the relaxed structures with charge density are represented. We mainly focus on the band structure to explain the twisting effect for bilayer borophene, and at last, the density of states also reflects the twisting effect to a certain degree.

2. Model and methods

All the calculations, including structure optimization, self-consistent calculation, band structure and density of states (DOS), were performed by the Vienna ab initio package (VASP) software, employing the density functional theory plane wave basis set and the generalized gradient approximation (GGA) exchange-correlation functional using Perdew-Burke-Ernzerhof (PBE). The projector augmented wave method with a 450eV cut-off energy was employed. The energy convergence accuracy for wavefunction is calculated to less than $10^{-5}$ eV, while the limited maximum ionic step for atomic force is set to 0.01 eV/Å. For each twisted bilayer borophene, in the Z direction, a more than 15 Å vacuum layer was built to avoid the image-image interaction. Taking the van der Waals (vdW) into account, the optPBE-vdW model was adopted. The 20x10, 20x3 and 3x20 k points mesh size was set in the Brillouin zone, respectively. For the calculations on band structure of twisted bilayer borophene with vdW force, a $\Gamma-Y-M-X-\Gamma$ k-point path was set, in which the sampled 50 points were set along each high-symmetry line.

![Fig.1](image)

Fig.1 Top view of (a) 32.2°, (b) 58.0°, (c) 83.6° twisted bilayer borophene. The red dashed line and blue dashed line represents the armchair direction of two layers, respectively.

As shown in Fig.1, we build the twisted bilayer borophene for three different angles, that 32.2°, 58.0° and 83.6°, by a geometric matching method based on reference [10-12]. It should be noted that we choose 2-Pmmn borophene to build a bilayer structure since the 2-Pmmn borophene has the most
anisotropic structure among all of the allotropes. The dashed red and blue line represents the armchair direction of two layers, respectively. According to the cell match algorithm, each twisted bilayer structure has a certain shear strain due to the cell match error. And we distribute the shear strain to each layer, which the total mismatch error will reduce by half. For 32.2°, 58.0° and 83.6°, the shear strains are 0.76°, 0.73° and 0.42°, respectively. For 32.2°, the original lattice constants a and b is 5.95 Å and 10.10 Å. And they are 3.29 Å and 23.90 Å for 58.0° and 19.29 Å for 83.6°. The numbers of boron are 52, 68 and 72. All the structure is the orthorhombic system, which means α=β=γ=90°. The initial interlayer spacing is set to 3 Å before structural relaxation.

3. Results and discussion

The charge density of relaxed twisted bilayer borophene with 32.2°, 58.0° and 83.6° are shown in Fig.2 a-c. After the relaxation, the atomic configuration of twisted bilayer borophene has some changes. The averaged interlayer spacings are 2.93 Å, 3.065 Å, 2.655 Å, which indicates our initial interlayer spacing settings are rational. In fact, according to the reference [8], the non-twisted bilayer borophene reaches its minimum system total energy at about 3.05 Å. The twisting angle and shear strain should be other factors to influence the interlayer spacing. And with the twisting angle increasing, from 32.2° to 58.0°, the interlayer spacing increasing, while from 58.0° to 83.6°, it decreases. Meanwhile, there exists a regular atom closing between two layers, as the isosurface of charge density is set to 0.07 e, the closing boron atoms form a columnar shape. This behavior is similar to previous studies of bilayer borophene, these pyramids could be owing to π bonds between layers. The closing boron atoms forms π-π interaction and this structure could lead to an energetic stability for twisted bilayer borophene. Except for the atomic configuration, a delocalized charge distribution can be derived from the blue charge density isosurface, the charge is diffuse in the whole structure. The charge density section at the boundary also shows by the green-yellow-red diagram. We can conclude that the interlayer bonding of twisted bilayer borophene is π-bond type, resulting in the pyramids structure.

To further study the electronic properties of twisted bilayer borophene, the electronic band structures for 32.2°, 58.0° and 83.6° angle with vdW force are calculated and shown in Fig.3 a-c. Besides, for a purpose of cross comparison, we also calculated the band structure of the 83.6° twisted bilayer borophene without vdW force, showing in Fig.3d, where the structure without vdW force is relaxed independently. In Fig.3a, different from the monolayer borophene and few-layer borophene with zero twisted angles [8] that no energy bands cross the Fermi energy level until tri-layer, there exist two cross-Fermi energy bands in Γ-Y k point path of 32.2° twisted bilayer borophene. In Y-M,
the bands open up and a bandgap appears. In M-X, a degenerate band crosses Fermi level, that is, several bands in X-Γ. It should be noted that the Γ-Y-M-X-Γ k points path of twisted bilayer borophene differed in each angle, which means the axis direction of the lattice is different from the armchair direction when there exists a twisted angle, while the armchair direction corresponds to axis direction in non-twisted situation. Despite the difference in expression, the twisting angle still has a significant effect on the modulation of the band structure of bilayer borophene. When the twisting angle increases, the band structure also transforms. In Fig.3b, for 58.0° twisted bilayer borophene, the energy bands become steep and the degenerate bands split, and when the quasi-vertexes are derived with the splitting degenerate bands. In Fig.3c, for 83.6° twisted bilayer borophene, the energy bands split more evidently. And when focus on the red and black bands near the Fermi level, several vertexes could be found. Especially in the Y point, the energy bands transform to the direct type near the vertex. Therefore, we can conclude that the twisting angle could split the energy bands and transform the bands to direct type, thus, modulate the electronic properties of bilayer borophene. Furthermore, in Fig.3d, the band structure of 83.6° twisted bilayer borophene without vdW force shows a bandgap and a Dirac-like cone appears. This phenomenon is interesting and the twisted bilayer borophene without vdW force remains further investigations.

Fig.3 Band structure of (a) 32.2°, (b) 58.0°, (c) 83.6° twisted bilayer borophene with van der Waals force and (d) 83.6° twisted bilayer borophene without van der Waals force. The Fermi level corresponds to zero.

Except for the band structure, we also calculated the density of states (DOS) for the three kinds of twisted bilayer borophene. As shown in Fig.4a-c, the Fermi level corresponds to zero which is marked by the dashed red line and the dashed-dot blue line represents the zero DOS. On the whole, DOS in Fermi level of all the twisting angles is not zero, indicating the twisted bilayer borophene is metallic. Moreover, with the twisting angle increases, the DOS moves up and a gorge-like DOS under Fermi level appears, which is marked by the green circle. The marked DOS is near zero which can be another argument for the modulation effect of twisting angle.
Fig. 4 Density of states (DOS) for (a) 32.2°, (b) 58.0°, (c) 83.6° twisted bilayer borophene. The Fermi level corresponds to zero. The near-zero DOS are marked by the green circle.

4. Conclusion
In this work, we studied the electronic properties of twisted bilayer borophene with 32.2°, 58.0° and 83.6° angles, respectively, by first-principles calculation. The charge density of relaxed twisted bilayer borophene is analyzed and found that the behavior of atoms closing between layers. The analysis of band structure reveals that the twisted bilayer structure could separate the degenerate band and transform the bands to direct type, thus, modulating the resistance of bilayer borophene. And a near-zero density of states could be found when bilayer borophene is twisted.

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