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Band structures of defective graphenes

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ABSTRACT

Band structures of defective graphenes are analyzed by crystal orbital method. In laterally slipped faults, there appear σ bands consisting of weakly interacted dangling bonds. The peculiar σ bands cross with frontier π bands, and the resultant double occupation leads to the disappearance of ferromagnetic interactions. On the other hand, in longitudinally slipped faults, there are no crossings of the σ bands within the frontier levels, and the ferromagnetic interactions result from polycarbene-type spin alignment.

1. Introduction

Since 2004, science of graphenes has been rapidly developed toward tunable electronic properties. In the field of physics, high mobility of carriers and pseudo-relativistic effects have been reported [1,2]. In graphene science, scanning tunneling microscope (STM) technique made it possible to observe the network structures and various edge states. Some graphenes are expected to exhibit magnetic ordering characteristic of the unique edge states. For example, while so-called acene (zigzag) edges lead to spin alignment at the non-bonding sites due to the half occupation of semi-flat bands at $|k| > 2\pi/3$ [3–6], the so-called phenanthrene (arm-chair) edges do not have flat bands. In addition, methylene-substituted graphene edges (Klein edges) are also predicted to show ferromagnetic interactions, because the systems become non-Kekulé polymers with completely degenerate flat bands [7–11]. Recently, the Wannier functions of the flat bands have been found to span common atoms between each adjacent cell, which lead to ferromagnetic interactions of the systems [11]. The exchange integrals result from reduction in Coulomb repulsions between the electrons with parallel spin, which cannot span the same atomic site due to the Pauli principle. Thus, the existence of flat bands is essential to design and analyze for magnetism of graphenes. The mechanism for the ferromagnetic interactions resembles those of organic ferromagnets such as non-Kekulé polymers in which the direct exchange interactions between the flat-band electrons mainly contribute to the stability of magnetic states. This situation has been well established by the Wannier functions localized at each unit cell [12,13]. That is, in organic polyradicals, itinerant characters of the non-bonding electrons cause direct exchange interactions between the adjacent cells.

Recently, ferromagnetic interactions have been observed in highly oriented pyrolytic graphite (HOPG) even at the room temperature [14–17]. The magnetism has been established as one of the purely organic ferromagnetism, which has not come from any metal impurity [14]. In these materials, the observed magnetization curves show narrow hysteresis, which is applicable to soft ferromagnetic materials. These magnetisms probably originate from defective structures in the graphene plane. Point defects in graphitic materials cause impurity levels within the band gaps [18,19]. The non-bonding levels lead to paramagnetism with small spin-quantum numbers. However, magnetic ordering such as ferromagnetism should be attributed to geometric ordering of the defects. Intuitively, dangling bonds in grain boundaries give narrow σ bands, and the resultant flat bands lead to possible ferromagnetism. The amplitudes of the Bloch functions should spread over the grain boundaries. In 2009, Červenka et al. [14] proposed schematic models for grain boundaries that lead to spin alignment in longitudinally slipped faults. They observed magnetic force microscopy (MFM) image of grain boundaries in HOPG and recorded the topographies. They proposed longitudinally slipped graphene sheets, which look like a fault (dislocation) caused by earthquake. If the grain has the acene edges with zigzag carbon atomic array, this model is reasonable in that flat π bands may be conserved due to two weakly interacted edges in the fault. However, the electronic states of these grain boundaries are not clear yet. The band structures are worth analyzing in which the flatness of the magnetic bands and the half occupations should determine the ferromagnetic interactions. In this article, the origin of magnetism in defective graphenes is clarified by the crystal orbital method. As simple models for the grain boundaries, one-dimensional defective

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graphenes are considered. As shown in Fig. 1a and b, we consider laterally and longitudinally slipped graphenes, which lead to two types of faults. In the laterally slipped model, there appears a σ band consisting of the dangling bonds. The peculiar σ band crosses with frontier π bands, and the resultant double occupation leads to the disappearance of ferromagnetic interactions. In longitudinally slipped model, there are no crossings of σ bands within the frontier levels, and the possible ferromagnetic interactions should be converted into those of polycarbenes with increase in the displacements.

2. Model compounds and computations

As it is well known, the band structures of acene-edged graphenes have already been analyzed as ladder-like polymers, of which frontier bands are flat at the wavenumber region $|k| > 2\pi/3$ [3,4]. In this region, the Bloch functions have non-bonding characters, of which amplitudes mainly spread at the edge carbons. As a grain boundary model, we consider defective graphenes as shown in Fig. 2, where **1** and **2** are acene-edged graphene ribbons with 3 and 19 ladders, respectively. We first consider a simplest fault model by using graphene ribbon with 3 ladders **1**. In this article, both sides are monohydrogenated for simplicity. The effects of hydrogenation are qualitatively not so important, because both-sided dangling bonds do not interact with frontier π crystal orbitals. The faults are made in the central ladder, as shown in Fig. 2. One is laterally slipping mode, and another is longitudinally slipping mode. Next, more reasonable model with enough large scale is considered by graphene ribbon with 19 ladders **2**. The faults are also made in the central ladder, as schematically shown in Fig. 2. In both laterally and longitudinally slipped models, the systems are regarded as quasi-one-dimensional polymers, of which unit cells contain monohydrogen-terminated acene edges at both sides and hydrogen-free faulted points at the center of ladders. The original C – C bondlengths were fixed to 1.40 Å, and the C – C – C bond angles were fixed to 120.0°. As shown in Fig. 2, laterally slipping displacements Δx (> 0) were made from 0.00 to 1.21 Å (1.40 Å $\times \cos(\pi/6)$). We note that the laterally slipping displacements over 1.21 Å are reduced to smaller displacements due to the periodic properties. Longitudinally slipping displacements Δz (> 0) were also made from 0.00 to 1.20 Å. In the calculations, the steps of displacements were set to be ca. 0.4 Å in both modes. The one-dimensional period a was set to be 2.425 Å.

The band structures were calculated by the crystal orbital method under the extended Hückel approximation [20]. The extended Hückel method is suitable for the estimation of the overlap integral S_{ij} between the ith and jth atomic orbitals. S_{ij} is reflected to the resonance integral β_{ij} ($\beta_{ij}=(K/2)S_{ij}(I_i+I_j)$ [20]),

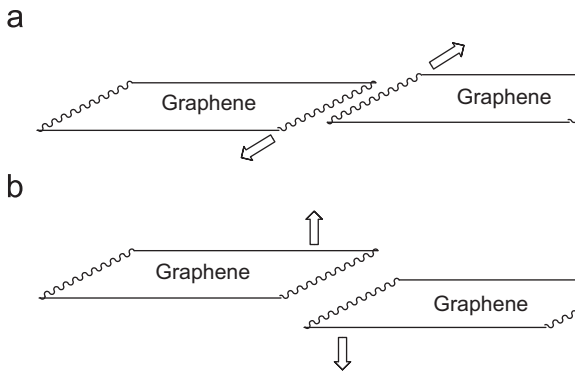

Fig. 1. Two types of slipping modes in graphenes: (a) laterally slipping mode and (b) longitudinally slipping mode. Both sides are regarded as acene edges.

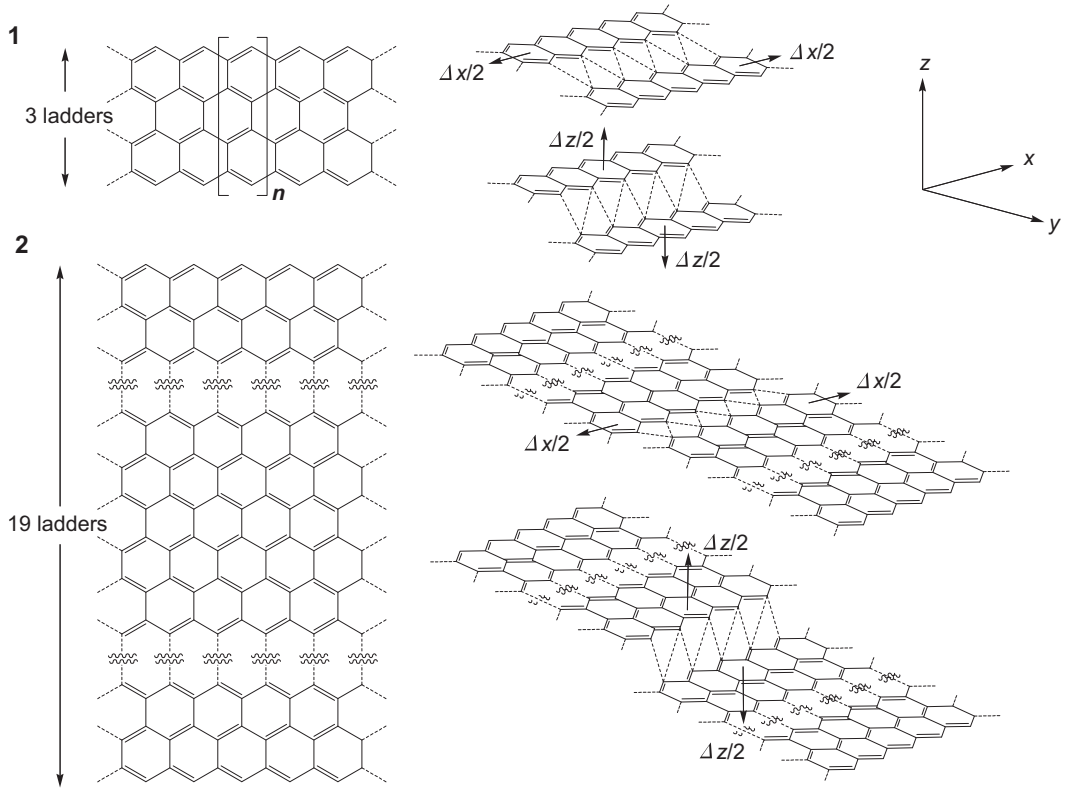

Fig. 2. Model compounds for defective graphenes. **1** has 3 ladders with acene edges and **2** has 19 ladders with acene edges. The slipping modes are also shown with definition of the displacements.