Electronic properties of rhombohedral graphene multilayers with a twin boundary

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Thin films of rhombohedral graphite are becoming a popular platform for the studies of strongly correlated states of electrons in 2D materials, due to topologically protected flat bands on their surfaces. In this work, we study rhombohedral graphite with a twin boundary stacking fault, where the low-energy dispersion is comprised of four bands strongly localised at the surfaces and at the twinned interface. We derive an effective 4-band low energy model, where we implement the full set of Slonczewski-Weiss-McClure (SWMcC) parameters, and analyse the semimetallic properties of low-energy bands and their topological properties. We find the conditions for the bands to be localised at the twin boundary, protected from the environment-induced disorder that is screened by the surface states. This protection together with a high density of states at the charge neutrality point, in some cases – due to a Lifshitz transition, makes this system a promising candidate for being a strongly-correlated material.

I. INTRODUCTION

In the recent years, multilayer graphenes were found to host various correlated phases of matter driven by electron-electron interactions: superconductivity \cite{1-5}, ferromagnetism \cite{6, 7}, nematic state \cite{8}, and Mott insulator \cite{9-11}. The electron correlation effects in these systems are promoted by the characteristically flat low-energy bands \cite{12-15}. Among all these systems, few-layer rhombohedral (ABC) graphenes are the only ones which can be grown using chemical vapour deposition \cite{16} without the need to assemble twistronic structures with a high precision of crystallographic alignment. The low-energy bands in ABC films are set by topologically protected surface states, hence, it is affected by external environment. As a result, their dispersion depends both on the number of layers in the film, encapsulation and vertical electric bias, so that the ABC graphenes may behave both as compensated semimetals and gapful semiconductors \cite{14}.

A rhombohedral graphitic film with one stacking fault such as as twin boundary, Fig. 1 also host low-energy flat bands \cite{17, 18}: four rather than two specific for ABC graphene. The additional two bands come from the twin boundary inside the film, hence, they can be protected from the environmental influences due to screening by the surface states. Here, we study the low-energy spectra of thin films of twinned ABC graphene such a ‘mABAn’ multilayer sketched in Fig. 1 where the twin boundary appears as a Bernal (ABA) trilayer buried inside the film with $n$ and $m$ rhombohedral (ABC and CBA) layers above and underneath it. In Fig. 1 we also present four low-energy bands in a 9-layer film (3ABA3) with a twin boundary at the middle layer, which illustrates that such systems are semimetals and that - in some of these systems - there might be at least one low energy band located at the twinned interface. Moreover, we notice that a neutral (undoped) 3ABA3 multilayer has an additional feature: the electron Fermi energy in it is close to the Lifshitz transition \cite{19-21}, marked by the van Hove singularity in the density of states, Fig. 1.

The presented-below analysis of band structure of twinned multilayers of ABC graphene is based on the hybrid $k\cdot p$ - tight binding theory which accounts for the full set of Slonczewski-Weiss-McClure (SWMcC) parameters for graphite \cite{22-24}, in section II. Taking all SWMcC parameters into account appear to be important, as (similarly to what has been found in monolithic ABC films \cite{14}) the next-neighbour/layer hoppings and coordination-dependent on-carbon potentials lift an artificial degeneracy of band edges predicted by the minimal model accounting for only closest neighbour hopping \cite{18, 25}. In Sec. III we develop and test an effective 4-band model for rhombohedral structures with one twin boundary, which improves the low-energy Hamiltonian.
II. SWMCC MODEL FOR MULTILAYERS WITH VARIOUS STACKINGS

In the basis of sublattice amplitudes for electron states in a mABAn multilayer, \( \Psi^\ell = (\psi_{A_1}, \psi_{B_1}, \cdots, \psi_{A_N}, \psi_{B_N})^\ell \), the Hamiltonian, which will be used to describe the subbands in it, is written as

\[
\mathcal{H} = \begin{pmatrix}
H_g^s & V & W & \cdots & 0 & \cdots & 0 & 0 & 0 \\
V^\dagger & H_g^b & V & \cdots & 0 & \cdots & 0 & 0 & 0 \\
W^\dagger & V^\dagger & H_g^s & \cdots & 0 & \cdots & 0 & 0 & 0 \\
0 & 0 & 0 & \cdots & \mathcal{H}_{ABA} & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \cdots & H_g^s V^\dagger & W^\dagger & \cdots & 0 & 0 \\
0 & 0 & 0 & \cdots & V & H_g^b V^\dagger & \cdots & 0 & 0 \\
0 & 0 & 0 & \cdots & 0 & 0 & W V^\dagger & H_g^s \\
\end{pmatrix},
\]

\( H_g^s = H_g + (\Delta_1^s 0 0) + \Delta_2^s \hat{s}_2, \quad H_g^b = H_g + \Delta_1^b \hat{s}_2, \quad H_g = v \begin{pmatrix} 0 & \pi_\xi^s \\ \pi_\xi^s & 0 \end{pmatrix}, \quad V = \begin{pmatrix} -v_4 \pi_\xi & \gamma_1 \\ -v_3 \pi_\xi & -v_4 \pi_\xi \end{pmatrix}, \quad W = \begin{pmatrix} 0 & 0 \\ \gamma_2/2 & 0 \end{pmatrix} \quad \hat{W} = \begin{pmatrix} \gamma_5/2 & 0 \\ 0 & \gamma_2/2 \end{pmatrix}. \)

Here, \( \hat{s}_2 \) is a 2 \times 2 unit matrix, \( \pi_\xi \equiv \xi p_x + ip_y \), with \( P = (p_x, p_y) \) being the valley momentum measured from \( h \mathbf{K}_\xi = h \mathbf{K}_\xi \pm \mathbf{a}_3 \), \( 1,0 \), and, below we use the following values of parameters implemented in Eq. (1): \( v = 1.02 \times 10^6 \) m/s, \( v_3 = 0.102 \times 10^6 \) m/s, \( v_4 = 0.022 \times 10^6 \) m/s, \( \gamma_1 = 390 \) meV, \( \Delta_1^s = 25 \) meV, \( \gamma_2 = -17 \) meV, \( \gamma_5 = 38 \) meV. In addition, we account for energy shift, \( \Delta_\xi \), of the surface orbitals which captures the influence of the encapsulation and other environmental conditions.

In the Hamiltonian for the band energies around the centre of \( K_\pm \) valleys, parameter \( \gamma_1 \) sets the largest energy scale. As a consequence, in rhombohedral graphite with a twin boundary, we observe a clear spectral separation of the bands in the dispersion, where a set of \( m + n + 1 \) conduction (valence) bands are split by \( \pm \gamma_1 \) from the two isolated pairs of conduction and valence bands with dispersions illustrated in Fig. 2 for several exemplary multilayers. These four bands determine the low-energy physics of the system, and in the next section, we develop an effective 4 \times 4 model for the Hamiltonian that describe them.

III. EFFECTIVE 4-BAND MODEL FOR TWINNED RHOMBOHEDRAL FILMS

To study the low-energy dispersion, we employ degenerate perturbation theory [27], which allows us to construct an effective 4 \times 4 Hamiltonian out of the low-energy basis, highlighted in red in Fig. 4. This basis consists of three sublattice amplitudes of the non-dimer orbitals, \( \psi_{B_1}, \psi_{A_{m+2}} \) and \( \psi_{B_N} \), and the antisymmetric combination of sublattice amplitude of orbitals dimerised with the layer at the twin boundary, \( \psi_0 = (\psi_{A_{m+3}} - \psi_{A_{m+1}})/\sqrt{2} \). In turn, the high-energy basis encompasses the rest of \( p_z \) orbitals the dimer sites and a symmetric orbital \( \psi_s = (\psi_{A_{m+3}} + \psi_{A_{m+1}})/\sqrt{2} \). The matrix elements of the low-energy effective Hamiltonian can be determined from the degenerate perturbation theory [27] around the valley \( h \mathbf{K}_\xi \) point,

\[
\langle \psi_i | \mathcal{H}_{\text{eff}} | \psi_j \rangle = \langle \psi_i | H_g \left\{ Q [ -H_{\perp,X}^{-1} ] Q H_g \right\}^{n-1} | \psi_j \rangle, \tag{2}
\]

where \( H_{\perp,X} (X = R \text{ or } T) \) is the high energy Hamiltonian acting on the high-energy basis of B-A dimer bonds inside the two rhombohedral stacks,

\[
H_{\perp,R}^{-1} \approx \begin{pmatrix}
-\Delta'/\gamma_1^2 & 1/\gamma_1 \\
1/\gamma_1 & -\Delta'/\gamma_1^2
\end{pmatrix}, \tag{3}
\]

or between the high-energy basis around the twin-boundary, \( \{ \psi_{B_{m+2}}, \psi_s \} \),

\[
H_{\perp,T}^{-1} \approx \begin{pmatrix}
-(2\Delta' + \gamma_5)/(4\gamma_1^2) & 1/(\sqrt{2} \gamma_1) \\
1/(\sqrt{2} \gamma_1) & -\Delta'/\gamma_1^2
\end{pmatrix}, \tag{4}
\]

in the high-energy basis adjacent to the twin-boundary. In Eq. (2), \( Q \) is a projector onto the subspace spanned by the low-energy basis.

Then, for \( n, m > 0 \), the low-energy Hamiltonian, written in the basis of \( \{ \psi_{B_1}, \psi_a, \psi_{B_N}, \psi_{A_{m+2}} \} \), takes the form

\[
\begin{pmatrix}
H_g^a & V & W & \cdots & 0 & \cdots & 0 & 0 & 0 \\
V^\dagger & H_g^b & V & \cdots & 0 & \cdots & 0 & 0 & 0 \\
W^\dagger & V^\dagger & H_g^a & \cdots & 0 & \cdots & 0 & 0 & 0 \\
0 & 0 & 0 & \cdots & \mathcal{H}_{ABA} & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \cdots & H_g^a V^\dagger & W^\dagger & \cdots & 0 & 0 \\
0 & 0 & 0 & \cdots & V & H_g^b V^\dagger & \cdots & 0 & 0 \\
0 & 0 & 0 & \cdots & 0 & 0 & W V^\dagger & H_g^a \\
\end{pmatrix},
\]

of the bands in the dispersion, where a set of \( m + n + 1 \) conduction (valence) bands are split by \( \pm \gamma_1 \) from the two isolated pairs of conduction and valence bands with dispersions illustrated in Fig. 2 for several exemplary multilayers. These four bands determine the low-energy physics of the system, and in the next section, we develop an effective 4 \times 4 model for the Hamiltonian that describe them.
FIG. 2: Top 4 rows: Comparison between the full SWMcc (left) and effective 4-band model (right) for the low-energy band dispersion’s for various nABAm films (middle) within $\pm 30$ meV near the Fermi level in undoped structures; the Fermi-energy contours are plotted with a broadening of $\pm 1$ meV. The background behind the Fermi contours indicates the total probability to find the carriers of the 4 low-energy bands on the 4 low energy orbitals: this demonstrates that the range of validity of 4-band model extends over the range of momentum space fully accommodating the Fermi energy cuts of the bands. Bottom row: The influence of the surface orbitals energy shift, $\Delta_s$, on the distribution of wave function weight between the surface (green) and twin boundary (red) for a 3ABA3 film. Images in this row should be compared to the spectra and wave function weights displayed in Fig.1 for $\Delta_s = 0$. 

3ABA3, $\Delta_s = -5$ meV

3ABA3, $\Delta_s = 5$ meV
\[ H_{\text{eff}} = \begin{pmatrix}
\frac{p^2}{2m_e} + \Delta_s & -\gamma_1 X_{n+1} & 0 & -\gamma_1 X_{n+2} - \nu_3 \pi_e X_n + \nu_2 X_{n-1}/2 \\
-\gamma_1 X_{n+1} & \frac{p^2}{2m_e} + \Delta' - \gamma_2 & 0 & -\gamma_1 X_{n+2} - \nu_3 \pi_e X_n + \nu_2 X_{n-1}/2 \\
0 & \gamma_1 X_{n+1}/\sqrt{2} & \frac{p^2}{2m_e} + \Delta_s & 0 \\
\frac{1}{2} X_m + 3 & \nu_3 \pi_e X_n + \gamma_2 X_{n-1}/2 & 0 & \frac{p^2}{2m_e} + \Delta' - \gamma_2 
\end{pmatrix}, \]

where \( p = |\pi_\xi| \), the sum in \( X_n \) is extended to all positive integers \( n_1, n_2, \) and \( n_3 \) satisfying \( n_1 + 2n_2 + 3n_3 = n \), \( m_e = \left( \frac{4m_e + 2D'}{\gamma_1} \right)^{-1} \), and \( m_e' = \left( \frac{4m_e + \pi^2 (\gamma' + \gamma_2/2)}{\gamma_1} \right)^{-1} \). For a special case of \( m = 0 \) (and/or \( n = 0 \)), we substitute \( m_e \) in the on-site energy of \( \psi_{B_1} \) (and/or \( \psi_{B_N} \)) with \( 2m_e' \), and, for the case of ABA trilayer, \( m = n = 0 \), there is a direct \( \gamma_2/2 \) hopping between \( B_1 \) and \( B_3 \).

In Fig. 2, we present a comparison between band structures obtained by diagonalising the full Hamiltonians \( \text{Eq.}(1) \) and \( \text{Eq.}(2) \) for four different stacking configurations. The two sets of low-energy dispersions almost coincide, as well as, the Fermi contours at charge neutrality. We also present the Fermi contour at charge neutrality (broadened by \( \pm0.5 \) meV), to highlight the existence of both electron and holes pockets. Interestingly, for 4ABA1 and 3ABA3 films, the Fermi level lies very close to the Lifshitz transition point, which enhances the density of states. To estimate the range of validity of the low-energy model in Eq.\( (3) \), we use the second column of Fig. 2 to indicate with the background color the sum of the squared amplitudes of the eigenvectors of the 4 low-energy bands on the low-energy orbitals, computed using the full SWMCC model. We note that the electron states near the Fermi surface at charge neutrality are located mostly on the low-energy orbitals, so that the effective model is applicable.

When \( m = n \), the structure of the film is mirror-symmetric with respect to the twin boundary, so that the low energy Hamiltonian decouples into two \( 2 \times 2 \) blocks in the basis \( \{ \psi_{B_1} + \psi_{B_N}, \psi_{A_{n+2}}, \psi_{B_1} - \psi_{B_N}, \psi_a \} \) of mirror-symmetric (s) and anti-symmetric (as) bands,
FIG. 3: Low-energy bands in nABAn and nABA films with colours indicating the distribution of valley-asymmetric topological g-factor.

points are weakly gapped by

$$\delta_s = 2 |d_{s,z}(p_D)| = \left| \frac{p_D^2}{4 \gamma_1} (2 \Delta' - \gamma_5) + \Delta_s \right|$$

$$+ \left[ \frac{\gamma_2}{2} - v^2 \frac{p_D^2}{4 \gamma_1} \left( 4 \gamma_1 \frac{v}{v_4} + \gamma_5 \right) \right] \delta_{n,0}$$

$$\delta_{as} = 2 |d_{as,z}(p_D)| = \left| \frac{\gamma_5}{2} - \Delta' \right|$$

$$- \left[ \frac{\gamma_2}{2} + v^2 \frac{p_D^2}{4 \gamma_1} \left( 4 \gamma_1 \frac{v}{v_4} + \gamma_5 \right) \right] \delta_{n,0}.$$

To mention, for $\Delta_s = 0$, the gaps for symmetric bands vanish, $\delta_s = 0$, due to the imposed a degeneracy of non-dimer orbitals on the twinned interface. The environment, such as encapsulation, would influence the energies of surface orbitals, lifting the mentioned degeneracy and introducing the energy separation of surface and twin boundary bands. Low-energy band dispersions for $\Delta_s \neq 0$ are shown in the bottom panels of Fig. 2, where we also indicate by colours the bands which are localized on the surface or on the twin boundary.
IV. BERRY CURVATURE AND TOPOLOGICAL VALLEY G-FACTORS OF THE LOW-ENERGY BANDS

The use of the effective 4-band model is convenient to study the topological characteristics of rhombohedral graphite with a twin-boundary stacking fault. This includes Berry curvature of the bands and the associated magnetic moments, described in the literature in terms of valley g-factors. Large magnetic moment affects the transport measurements, quantum dot spectra [26, 28–30], valley-polarised currents [31], or an anomalous contribution to the Hall conductivity [14]. Such an analysis is particularly easy to perform for mirror-symmetric nA-BAn films, where the $4 \times 4$ Hamiltonian is reduced to a pair of effective $2 \times 2$ Hamiltonians, one for mirror-symmetric (s) and the other for mirror-antisymmetric (as) bands. In this case the topological valley g-factor due to the Berry curvature of conduction (+) and valence (−) bands read [14]

$$g_{\nu}^{\pm} = 2\frac{\Omega_0^{\pm}}{d} ; \Omega_{\pm} = \mp \frac{\hbar^2}{2d^3} \mathbf{d}_\beta : \left[ \partial p_x \mathbf{d}_\beta \times \partial p_y \mathbf{d}_\beta \right]. \quad (9)$$

Note that this magnetic moment and Berry curvature have opposite signs in the $K_{\pm}$ valleys, so that $g_{\nu}$ would directly quantify the valley splitting in out-of-plane magnetic field.

The band structures around $K_+$ of three mirror-symmetric films, coloured according to valley g-factor, are presented on the left-hand side panels of Fig. 3 for $\Delta_s = 0$. On the right-hand side panels of Fig. 3 we plot the valley g-factor for several mirror-asymmetric structures, computed with the Hamiltonian in Eq.(5). The topological features in these two pairs of bands are concentrated near the band edges, with valley g-factor reaching $g_{\nu} \sim 100$ at the hot-spots near Dirac points. For the structures with a small number of layers, there are well-articulated Dirac points with large orbital magnetic moment concentrated at them and $g_{\nu} \sim 10^3$, like observed earlier in ABA graphene trilayer [26]. To mention, magnetic moments of mirror-symmetric bands are controlled by the environment-induced surface energy, $\Delta_s$, and can be tuned across the range $g_{\nu} \sim 10$ to $d_{\nu} \sim 10^3$, in contrast to the mirror-antisymmetric bands. Similarly to rhombohedral graphite, individual Dirac points become almost indiscernible with a growing number of layers [14], the magnetic moment spreads over a broader range of momenta with the maximum $g_{\nu} \sim 100$ shifting away from the $K_\pm$ points.

V. CONCLUSIONS

Overall, the presented study offers an effective model for thin films of rhombohedral graphite with a twin-boundary stacking fault. In particular, we show that all of such structures are semimetals, hence, feature high density of states which potential to promote the formation of strongly correlated states of electrons. Moreover, for several systems, such as 4ABA1 and a twinned 9-layer ABC film, 3ABA3, we notice that the Fermi level is very close to the Lifshitz transitions in the low-energy bands spectrum. From thicker films, we find that some bands have states localized at the twin boundary, which would make their flat band and possible correlated states less vulnerable to disorder effects form the environment.
