Rhombohedral Multilayer Graphene: A Magneto-Raman Scattering Study

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Supporting Information

ABSTRACT: Graphene layers are known to stack in two stable configurations, namely, ABA or ABC stacking, with drastically distinct electronic properties. Unlike the ABA stacking, little has been done to experimentally investigate the electronic properties of ABC graphene multilayers. Here, we report on the first magneto optical study of a large ABC domain in a graphene multilayer flake, with ABC sequences exceeding 17 graphene sheets. ABC-stacked multilayers can be fingerprinted with a characteristic electronic Raman scattering response, which persists even at room temperatures. Tracing the magnetic field evolution of the inter Landau level excitations from this domain gives strong evidence for the existence of a dispersionless electronic band near the Fermi level, characteristic of such stacking. Our findings present a simple yet powerful approach to probe ABC stacking in graphene multilayer flakes, where this highly degenerated band appears as an appealing candidate to host strongly correlated states.

KEYWORDS: Graphene, Raman spectroscopy, rhombohedral graphite, electronic Raman scattering, magnetic field

Tailoring the electronic and optical properties of layered materials by controlling the layer orientation or their stacking order is an important possibility offered by the physics of two-dimensional systems. Graphene is the first isolated two-dimensional crystal,1 and the properties of graphene stacks, from mono- to multilayers (N-LG), have been intensively investigated in the past decade.2 The thermodynamically stable stacking of multilayer graphene is the Bernal stacking, where the A sublattice in one layer comes right below the B sublattice in the other layer.3 It was not until recently that experiments on rhombohedral stacking, with an ABC layer sequence, have been reported. ABC trilayer graphene, the simplest rhombohedral N-LG, has been successfully isolated and presents a tunable band gap4,5 as well as chiral quasi-particles as evidenced from their unconventional quantum Hall effect.6−8

To our knowledge, there are yet no investigations of ABC graphene multilayers thicker than 6 layers. This is mainly because of the low abundance of this stacking in real samples (∼15%)9 and because the two different stackings coexist within the same flakes, as revealed by recent optical and near field microscopy studies.10−14 Hence, tracing the evolution of the electronic properties of ABC-stacked multilayers, when increasing the number of layers, remains challenging. One intriguing predictions about the electronic properties of ABC-stacked multilayers is that they are expected to host surface states (localized mainly on the top and bottom layers) with a flat dispersion near the corners of the Brillouin zone, and bulk states with a band gap. When increasing the number of ABC-stacked layers, the extend of the flat dispersion of the low energy bands increases, while the size of the bulk band gap decreases.15,16

Notably, the surface states of ABC-stacked graphene multilayers have been reported as topologically protected, due to the symmetry of this material,16 and may thus resemble those well-known surface states of 3D topological insulators.17−20 Interestingly, due to weak spin−orbit interaction in carbon-based systems, an even closer analogy is found with the surface states of topological crystalline insulators.21 Nevertheless, in contrast to these two families of topological insulators, the bulk band gap of ABC-stacked graphene multilayers gradually closes with the increasing number of atomic sheets and bulk rhombohedral graphite may behave as a 3D topologically protected semimetal.22 The expected high degeneracy of the flat bands could lead to exotic electronic ground states, such as magnetically ordered phases or surface superconductivity.23−25 Experimental signatures of these flat bands has been recently observed in scanning tunnelling spectroscopy (STS) and angular-resolved photo emission spectroscopy (ARPES) investigations of nanometer scale

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domains of ABC-stacked graphene multilayers (5 layers) grown on 3C-SiC.26

In this Letter, we demonstrate, using Raman scattering techniques, that ABC-stacked multilayers (N > 5) can be found within exfoliated N-LG flakes. They have characteristic signatures in their Raman scattering response, which allow for their identification at room temperature. These signatures include a change of the 2D band feature line shape,27 together with an additional Raman scattering feature which we attribute to electronic Raman scattering (ERS) across the band gap in the bulk. ABC-stacked domains can thus be identified by spatially mapping the Raman scattering response of different flakes. Experiments performed with an applied magnetic field (B) reveal two distinct series of electronic inter Landau level excitations, involving the low energy flat bands, and the gapped states, respectively. Experimental results are explained in the frame of a tight binding (TB) model of the electronic band structure of rhombohedral N-layer thin graphite layers.28,29

Model and Experiment. The seven-parameter TB model developed by Slonczewski-Weiss and McClure30,31 for bulk graphite can be simplified by only considering the two first intra- and inter- nearest neighbors hopping parameters \( \gamma_0 \) and \( \gamma_1 \), respectively (Figure 1e–h). The calculated low energy band structure of ABC N-LG is shown in Figure 1a–c, for \( N = 3, 8, \) and 15 layers. Two characteristic evolutions when increasing the number of ABC-stacked layers arise from these calculations: (i) the flat part of the low energy \( E_{2g}^{15} \) bands (red bands in Figure 1a–c) extends over a larger \( k \)-space region, and (ii) the energy separation \( E_g \) between the \( E_{2g}^{0} \) (green bands in Figure 1a–c), decreases and ultimately closes for rhombohedral graphite (see Figure 1d).

A natural way of exploring electronic band structures of solids is to apply a magnetic field in order to induce Landau quantization and to trace the evolution of inter Landau level excitations with a magneto-spectroscopy techniques, such as magneto-Raman scattering spectroscopy. The evolution with magnetic field of the four lowest in energy bands of a \( N = 15 \) ABC stacked sequence is presented in Figure 1i. One can note that Landau levels are formed from the flat bands (red lines) and that their energies grow nearly linearly with the magnetic field, but starting from a finite onset magnetic field.32 For \( N = 15 \), the onset field is close to \( B \approx 3 \) T, as indicated by blue bar in Figure 1i. As a consequence, inter-Landau level excitations within the flat bands (red arrows), in the first approximation, evolve linearly with the applied magnetic field, however with a rather unusual extrapolated negative energy offset (see Supporting Information). We anticipate that this will be the magneto-Raman scattering signature of electronic states with such dispersion. Landau levels in the \( E_{2g}^{0} \) and \( E_{2g}^{1} \) bands (green lines in Figure 1i) also show a nontrivial evolution when increasing the magnetic field. From \( \pm \gamma_1 \) eV at the K-point, their energies first decrease (increase) with the magnetic field until they reach \( \pm E_g / 2 \), respectively. For higher magnetic fields, their energies increase (decrease) with a quasi linear evolution. Thus, inter Landau level excitations involving these states (green arrows) are expected to first decrease in energy down the gap value, and then to grow in a linear way for higher magnetic fields.

Figure 1. (a–c) Electronic dispersions for \( N = 3, 8, 15 \) layers obtained from the low energy effective Hamiltonian, respectively. The dashed horizontal red lines and the arrows indicate the energy gap. (d) Evolution of the energy gap as a function of the number of ABC-stacked layers. (e, f) Schematics of the crystal structure of ABA and ABC N-LG. Open circles and black dots are carbon atoms of the A and B sublattices, respectively. (g, h) Side views of the unit cells of ABA and of ABC N-LG. (i) Calculated dispersion of the 20 first Landau levels for the flat band (red) and for the lowest energy bands in the bulk (green), as a function of B, for \( N = 15 \) ABC-stacked layers.
enhanced due to an optical interference effect in the substrate.\textsuperscript{12,32} The N-LG flake covers five different holes labeled h0 to h4, where it is suspended. The flake has been characterized by atomic force microscopy (AFM) measurements which indicate a thickness of 15−17 layers (see Supporting Information). Raman scattering spectra are then measured at room temperature with 50× objective and a $\lambda = 632.8$ nm laser excitation, or at liquid helium temperature in a solenoid using a homemade micromagneto-Raman scattering (MMRS) spectroscopy setup with a $\lambda \sim 785$ nm laser excitation (see Methods). In both experiments, piezo stages are used to move the sample with respect to the laser spot and to spatially map the Raman scattering response of the flake, or to investigate specific locations.

**Experimental Results.** Two characteristic Raman scattering spectra measured at h0 (black curve) and at h4 (orange curve) are presented in Figure 2b. One can recognize on these spectra the characteristic phonon response of sp$^2$ carbon, including the G band feature around $\sim 1580$ cm$^{-1}$, and the 2D band feature observed around $\sim 2700$ cm$^{-1}$ when measured with 632.8 nm excitation. If the spectrum measured at h0 corresponds to that of thin AB-stacked layers,\textsuperscript{33} the spectrum measured at h4 is notably different, even though the thicknesses of the layer at these two locations are similar: (i) the G band energy at h4 is blue-shifted by 2−3 cm$^{-1}$ with respect to that measured at h0 (see Figure 2c), (ii) the 2D band line shape is more complex with two additional contributions indicated by arrows in Figure 2d, and (iii) an additional broad feature is observed at h4 around 1805 cm$^{-1}$ with a full width at half-maximum (fwhm) of $\sim 180$ cm$^{-1}$ (see Figure 2e). These are the three main Raman scattering signatures of ABC-stacked graphene multilayers.

To study the homogeneity of the N-LG flake, we have performed spatial mappings of the Raman scattering response at room temperature, with 2 μm spatial steps. When scanning the surface of the flake, it appears that the broad Raman scattering feature is observed in a large domain and that its central position can change from one location to another (see

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**Figure 2.** (a) Optical microscope image of the measured flake deposited over a silicon substrate covered with 6 μm regularly spaced circular holes. The freestanding parts are labeled h0 to h4. (b) Room temperature Raman scattering spectra from h0 (black line) and h4 (orange line). (c, d, e) Zoom on details of b: G band, 2D band and on the two blue boxes depicting the low intensity spectrum, respectively. (f) Raman scattering spectra measured at two random locations on the ABC-stacked domain (red and blue lines) and on the AB-stacked domain (black line). (g, h) False color maps of the scattered intensity in the energy range within the 2D band feature boxed in d, and in the energy range boxed in e corresponding to the ERS for a $N = 15$ ABC-stacked layers, respectively.
Figure 2f). As will be clarified in the following by the magneto-Raman scattering measurements, we interpret this feature as arising from an electronic excitation between two $E_1^\pm$ bands of the band structure of ABC N-LG. Similar to metallic carbon nanotubes,34 to graphene35 and to bulk graphite,36,37 electronic excitations do contribute to the $B = 0$ Raman scattering response of ABC-stacked N-LG. The different locations on the flake where this ERS signal is observed are presented in the form of a false color spatial map in Figure 2h. The modified line shape of the 2D band is also observed at different locations on our flake, shown in Figure 2g. The correlation between these two false color maps is a strong indication that the observation of the ERS feature and of the modified 2D band line shape are signatures of the same, ABC stacking. This flake is hence composed of two distinct domains: the first is ABA-stacked and is extending over $h_0$, $h_1$, and $h_2$, while the other is ABC-stacked, extending over $h_3$ and $h_4$. The energy of this ERS (i.e., the bulk band gap in Figure 1a–c) depends on the number of ABC-stacked layers, and taking the extreme values of the ERS energy from the measured Raman spectra all over the ABC domain, we estimate the number of ABC-stacked graphene layers to vary from $\sim 12$ to $\sim 17$ over the whole flake. This feature is also observed at low temperature, as can be seen in Figure 3a. An intrinsic, interaction induced, band gap has been observed in the transport properties of ABC-stacked trilayer graphene, with a magnitude ranging between 6 meV6 and 42 meV.38 In the present configuration, our optical experiment only probes energies higher than 75 meV, and no effect of this possible gap is observed. Would a band gap exist in our sample, its magnitude would be lower than $\sim 40$ meV, and its proper description is beyond the scope of the present manuscript.

Characteristic MMRS spectra measured at $h_4$ are presented in Figure 3b, for different values of $B$. The central position of the broad ERS feature increases with increasing magnetic field and its intensity seems to vanish for $B > 15$ T. The fact that magnetic fields can influence so much the energy and amplitude of this feature is in line with an electronic origin for this excitation. Above $B > 5$ T a series of sharp features,
dispersing with the magnetic field, appears in the Raman
scattering response. They have a symmetric line shape, in
contrast to electronic excitations observed in bulk graphite.36

The evolution of the Raman scattering response with
magnetic field, measured at h4 and h3, are presented in
Figures 3c–d, respectively, in the form of false color maps of
the scattered intensity. These two locations show a similar
response. The observed electronic excitation spectrum in
magnetic field is composed of a series of features linearly
dispersing with increasing magnetic field and of the ERS
observed at B = 0, that acquires a fine structure at finite B. The
linearly dispersing features, in line with magneto-Raman
scattering selection rules in graphene39 or in graphite,36 can
be attributed to symmetric (ΔmL = 0, where n is the Landau
level index) inter Landau level excitations within the
E2g bands, and they represent the strongest contribution to the electronic
Raman scattering spectrum in magnetic field. Optical-like
excitations (ΔmL = ±1) are not directly seen, but they
effectively couple to the G band. They give rise to the
magneto-phonon resonance and to the associated anticrossings
when they are tuned in resonance with the G band energy.36,40
Such anticrossings are indicated by black arrows in the B-
differentiated color map of h4, presented in Figure 3e. The
detailed analysis of the magneto-phonon resonance in ABC N-
LG is beyond the scope of this paper. Of much weaker
intensity, Raman scattering features with an energy decreasing
when increasing the magnetic field are observed (red marked
regions in Figure 3c–d). These features are better seen in
Figure 3e that shows the B-differentiated false color map of h4.
They correspond to symmetric (ΔmL = 0) inter Landau level
excitations within the lowest E1g bands in the bulk. The energy
of such excitations first decreases with the magnetic field as
long as the Landau levels are confined in the cone of the
corresponding band structure at B = 0 (Figure 1c), and then,
when the inter Landau level energy spacing reaches the value of
the energy gap in the bulk, they merge with the broad ERS
feature.

The evolution of these two families of electronic excitations
with increasing magnetic field is grasped by our tight-binding
analysis. We first determined the central positions of the
different observed excitations using Lorentzian functions and
searched for the parameters entering the model to best describe
our data. From this modeling, we can determine the number of
layers to be N = 14 and 15 for h3 and h4, respectively (Figures
4a–b), while we set γ0 = 3.08 eV and γ1 = 0.39 eV, as observed
in bulk graphite.36,41−43 In a simple approach (see Supporting
Information), we calculated the electronic excitation spectrum39,44,45
and its evolution when applying a magnetic field. These results are compared to the experimental evolution in
Figure 4c–d for h4. The model reproduces the main observed
features. In particular, the electronic excitation observed at B = 0
is reproduced and arises indeed from an inter band electronic
excitation that loses its spectral weight when the magnetic field
is increased, transforming into inter Landau level excitations
with their characteristic negative energy dispersion.

Conclusion. We report on the observation of electronic
excitations in N-LG system, which includes a large domain of
~15 ABC-stacked layers. The analysis of its low energy
electronic excitations with magnetic field can be understood in
the frame of a tight-binding model with three parameters, the
number of ABC-stacked layers and the intra- and interlayer
nearest neighbors hopping integrals γ0 and γ1. Such stacking has
a unique signature in its Raman scattering response at B = 0, in
the form of a low energy electronic excitations across the band

Figure 4. (a–b) Evolution of the inter Landau level excitations as a function of the magnetic field (red circles and blue squares) together with the corresponding calculated excitation spectra for locations h3 with N = 14 and h4 with N = 15, respectively. Experimental errors are smaller than the symbol size. (c) False color map of scattered intensity at h4 as a function of the magnetic
field. (d) Calculated electronic excitation spectrum from both the flat bands and the gapped bands, as a function of the magnetic
field.
gap in the bulk. The ERS response is also observed at room temperature. The central position of the ERS is related to the number of ABC-stacked layers which can then be deduced using simple Raman scattering spectroscopy. Our findings underscore the rich physics hidden in graphene multilayers with ABC stacking, namely, the existence of electronic bands with a flat dispersion (diverging density of states) localized on the surface, and of electronic states in the bulk with an energy gap that depends on the number of layers. These results represent an impetus for other studies targeting the highly correlated surface states, which may lead to emergent exotic electronic ground states on this system, such as magnetic order or superconductivity.

Methods. The measured flake was obtained from the mechanical exfoliation of natural graphite. It was then transferred nondeterministically on top of a undoped SiO2(90 nm)/Si substrate on top of which an array of holes (~6 μm diameter) was etched by means of optical lithography techniques. Room temperature Raman characterization is performed on the flake, using a helium–neon laser source of λ = 633 nm (i.e., E = 1.95 eV). To probe the Landau levels dispersion in our ABC-NLG flake, we used an experimental setup comprising a homemade micro-Raman probe that operates at low temperatures and high magnetic fields. The excitation source was provided by a solid state titanium-doped monomode optical fiber. The end of the Raman probe hosts a miniaturized optical table comprising a set of filters and lenses in order to clean and focalize the laser spot. A high numerical aperture lens is used to focalize the laser light on the sample, which is mounted on X–Y–Z piezo stages, allowing us to move the sample relative to the laser spot with sub-micrometer accuracy. The nonpolarized backscattered light is then injected into a 50 μm multimode optical fiber coupled to a monochromator equipped with a liquid nitrogen cooled charge coupled device (CCD) array. The excitation laser power was set to ~1 mW and focused onto a ~ 1 μm diameter spot. The resulting intensity is sufficiently low to avoid significant laser-induced heating and subsequent spectral shifts of the Raman features. The probe is then placed in a resistive magnetic equipped with a liquid He cryostat at 4 K. The evolution of the Raman spectrum with magnetic field was then measured on the freestanding parts by sweeping the values of the magnetic field. Each spectra was recorded for a ΔB = 0.15 T in order to avoid any significant broadening of the magnetic dependent features line-widths. The details of the theoretical description of the LLs and the magneto-Raman spectrum are given in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

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Electronic band structure of ABC-stacked thin layers, model for electronic Raman scattering, evolution of the electronic excitation spectrum as a function of the number of layers, mixed ABA-ABC stacking, AFM measurements (PDF)
Supplementary information for “Observation of electronic excitations in rhombohedral multilayer graphene”

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THE ELECTRONIC STRUCTURE

Taking into account only the nearest neighbor intra \((\gamma_0 \simeq 3.08 \text{ eV})\) and inter \((\gamma_1 \simeq 0.39 \text{ eV})\) layer hopping terms, the low energy Hamiltonian for ABC-stacked N-LG graphene (around the K point) is given by:

\[
H_{ABC} = \begin{pmatrix}
0 & v_{FP_-} & 0 & 0 & v_{FP_-} \\
v_{FP_+} & 0 & \gamma_1 & 0 & \gamma_1 \\
0 & v_{FP_-} & 0 & \gamma_1 & 0 \\
\gamma_1 & 0 & \gamma_1 & 0 & \gamma_1 \\
\ldots & \ldots & \ldots & \ldots & \ldots
\end{pmatrix},
\]

where we used the basis \([\phi_A_1, \phi_B_1, \phi_A_2, \phi_B_2, \ldots, \phi_B_N]^T\).

The corresponding low energy band structure for ABC-stacked 3, 6, 15-LG is shown in Figure 1. The spectrum consists of a set of \(2N\) bands, two of them touching each other at the Dirac point \(K\) with a flat dispersion and the rest at an energy \(\pm \gamma_1\) at \(k = 0\).

FIG. 1: Energy spectrum of ABC N-LG for \(N = 3, 6, 15\) layers, respectively. The red lines indicate the low energy bands obtained with the \(2 \times 2\) effective approximation [1–4].
The flat bands at the charge neutrality can be described by an effective Hamiltonian \([1-4]\)
\[
H_{\text{eff}} = -\gamma_1 N+1 \begin{pmatrix}
0 & (v_F p_-)^N \\
(v_F p_+)^N & 0
\end{pmatrix},
\]
(2)
which is written in the basis \([\phi_A, \phi_B]^T\), that is, involving only the \(A\) and \(B\) sites of the bottom and top layers, respectively.
This leads to the following energy dispersion \([1,3]\):
\[
\varepsilon_k = \pm \gamma_1 N+1 (\hbar v_F k)^N \sim p^N,
\]
(3)
shown by red lines in Figure \([1\]. However, the effective Hamiltonian \([2\] is valid only in the interval \([-p_D, p_D]\), with
\[
p_D = \frac{\hbar v_F}{2 c}\]. Outside this interval the surface subbands are no longer flat and the effective approximation diverges drastically as seen in Figure \([1\).

INELASTIC LIGHT SCATTERING AT ZERO MAGNETIC FIELD

For the sake of completeness here we closely follow Ref. \([5\] to briefly present the theoretical description of the electronic Raman process. The interaction of the electrons with photons is included in the Hamiltonian \([1\] by replacing \(p\) by the canonical momentum \(\mathbf{\Pi} = p + \frac{\varepsilon}{c} \mathbf{A}(r)\) where \(\mathbf{A}\) is the vector potential associated with the light field and it is given by
\[
\mathbf{A} = \sum_{l,q,z} \frac{\hbar c}{\sqrt{2\Omega}} \left( \mathbf{e}_{l}(qr-\Omega t)/\hbar b_{l_{q}z} + h.c. \right).
\]
(4)
The latter includes the annihilation operator \(b_{l_{q}z}\) for a photon with in-plane momentum \(q\), energy \(\Omega\) (which determines its out-of-plane momentum component \(q_z = \sqrt{\Omega^2 - q^2}\)) and polarization \(l\). Expanding the (full) Hamiltonian up to the second order in the vector potential, we obtain the interaction part
\[
H_{\text{int}} = \frac{ev_F}{c} \mathbf{J} \cdot \mathbf{A} + \frac{e^2}{2c^2} \sum_{l,j} \left( \partial^2_{l_{j}p_{j}} H \right) A_{l} A_{j},
\]
(5)
where \(v_F \mathbf{J} = \nabla_p H\) is the current vertex and \(\frac{e^2}{2c^2} \left( \partial^2_{l_{j}p_{j}} H \right)\), with \(i = \{x, y, z\}\), is the two photon contact interaction tensor \([5\]. Thus, there are two contributions to the inelastic light scattering amplitude: a one-step process \(R_\omega\) (contact interaction) and a two-step process \(R_D\) involving an intermediate virtual state. The latter consists of an absorption (emission) of a photon with energy \(\Omega(\Omega)\) transferring an electron with momentum \(p\) from an occupied state in the valence band into a virtual intermediate state, followed by another electron emission (absorption) of the second photon with energy \(\Omega(\Omega)\), which moves the electron to the final state with momentum \(p + q - \tilde{q}\) and given by \([5,6]\)
\[
R_D = \frac{(e\hbar v_F)^2}{2 \sqrt{\Omega \Omega}} \left[ (\mathbf{J}_q \cdot \mathbf{l}) G^A_{\Omega + \varepsilon_i} \left( \mathbf{J}_{-\mathbf{q}} \cdot \mathbf{l}^* \right) + (\mathbf{J}_{-\mathbf{q}} \cdot \mathbf{l}^*) G^A_{\Omega + \varepsilon_f} (\mathbf{J}_q \cdot \mathbf{l}) \right].
\]
(6)
Here \(\mathbf{J}_q\) denotes \(\mathbf{J}(q)\) and \(G^A_{\Omega + \varepsilon_i}\) is the advanced Green function for electrons with energy \(\Omega + \varepsilon_i(f)\) where \(\varepsilon_i(f)\) correspond to the energy of initial (final) electronic state. The energy difference \(\omega = \Omega - \Omega = \varepsilon_f - \varepsilon_i\) is the Raman shift. The contact interaction process, due to the terms quadratic in the electron momentum \(p\), is
\[
R_\omega = \frac{(e\hbar v_F)^2}{2 \sqrt{\Omega \Omega}} \left( \partial^2_{l_{j}p_{j}} H \right) l_j^z \delta_{p_{p}+q_{\tilde{q}}}. \]
(7)
In our case, \(\mathbf{J} = (\sigma_y \otimes I, \sigma_y \otimes I, \sigma_z \otimes I)\) with \(I\) the \(N \times N\) identity matrix and \(\sigma_i\) the \(2 \times 2\) Pauli matrices. Considering \(v_F p \ll \Omega\) \((G^A_{\Omega + \varepsilon_i} = 1/\Omega\) and \(G^A_{-\Omega + \varepsilon_f} = -1/\Omega\) the dominant contributions to the Raman scattering amplitude is
\[
R_D = \frac{(e\hbar v_F)^2}{\Omega \Omega} \left( -i \left( \mathbf{l} \times \mathbf{l}^* \right)_z J_z \right)
\]
(8)
whereas the contact interaction take the form
\[
R_\omega = \frac{(e\hbar)^2}{6 \Omega \Omega} \left( \varepsilon^z \times \mathbf{J} \right) \cdot \mathbf{d}
\]
(9)
with \(\mathbf{d} = (l_x \varepsilon_x + l_y \varepsilon_y + l_z \varepsilon_z - l_y \varepsilon_y)^N\). The transition amplitude \(R = R_D + R_\omega\) is analogous to what was obtained for monolayer graphene \([8\].
THE LANDAU LEVEL SPECTRUM AND RAMAN SHIFT

In the presence of an external magnetic field $B$ the canonical momentum $p$ must be replaced by $\Pi = p + e/c \mathbf{A}(r)$ where $\mathbf{A}(r)$ is the vector potential describing a magnetic field perpendicular to the graphene layers [8]. We use units such that $h \equiv 1 \equiv c$. The components of the gauge-invariant momentum obey the commutation relation $[\Pi_x, \Pi_y] = -i/l_B^2$, where $l_B \simeq 26nm/\sqrt{B[T]}$ is the magnetic length. This allows us to introduce the harmonic oscillator operators $\hat{a} = (l_B/\sqrt{2}) \Pi_-$ and $\hat{a}^\dagger = (l_B/\sqrt{2}) \Pi_+$ with $[\hat{a}, \hat{a}^\dagger] = 1$ where $\Pi_\pm = \Pi_x \pm i\Pi_y$. Then the Hamiltonian takes the form

$$H_{ABC} = \begin{pmatrix}
0 & \epsilon_0 \hat{a} & \epsilon_0 \hat{a}^\dagger & \gamma_1 & \gamma_1 & \ldots & \gamma_1 \\
\epsilon_0 \hat{a}^\dagger & 0 & \gamma_1 & \epsilon_0 \hat{a} & \gamma_1 & \ldots & \gamma_1 \\
\gamma_1 & \epsilon_0 \hat{a}^\dagger & 0 & \gamma_1 & \ldots & \ldots & \gamma_1 \\
\gamma_1 & \gamma_1 & \epsilon_0 \hat{a}^\dagger & 0 & \ldots & \ldots & \gamma_1 \\
& & & \ldots & \ldots & \ldots & \ldots \\
& & & & \ldots & \ldots & \ldots \\
& & & & & \ldots & \ldots & \ldots \\
& & & & & & \ldots & \ldots & \ldots \\
\end{pmatrix}_{2N \times 2N}$$

(10)

where $\epsilon_0 = \sqrt{2} \hbar v_F/l_B \simeq 36\sqrt{B[T]}$ meV is the cyclotron energy in monolayer graphene. The $2N$-components eigenstates corresponding to Hamiltonian (10) have the following structure

$$|\psi_n^\alpha\rangle = [c_{A_1}^\alpha \varphi_{n-1}, c_{B_1}^\alpha \varphi_n, c_{A_2}^\alpha \varphi_{n+1}, c_{B_2}^\alpha \varphi_{n+1}, c_{A_3}^\alpha \varphi_{n+2}, \ldots]^T$$

(11)

where $\varphi_n \equiv \varphi_{n,k} (x, y) \sim e^{iky} e^{-z^2/2} H_n(z)$ is the wave function of harmonic oscillator with $z = (x - kf_B^2)/l_B$ and $H_n(z)$ is the Hermite polynomial. As in the usual one-dimensional harmonic oscillator

$$\hat{a} \varphi_n = \sqrt{n+1} \varphi_{n+1}$$

(12)

$$\hat{a}^\dagger \varphi_n = \sqrt{n} \varphi_{n-1}$$

(13)

Then, for each value of $n$, one needs to diagonalize the following matrix

$$\begin{pmatrix}
0 & \epsilon_0 \sqrt{n} & \gamma_1 & \epsilon_0 \sqrt{n+1} & \gamma_1 & \ldots & \gamma_1 \\
\epsilon_0 \sqrt{n} & 0 & \gamma_1 & \epsilon_0 \sqrt{n+1} & \gamma_1 & \ldots & \gamma_1 \\
\gamma_1 & \epsilon_0 \sqrt{n+1} & 0 & \gamma_1 & \ldots & \ldots & \gamma_1 \\
\gamma_1 & \gamma_1 & \epsilon_0 \sqrt{n+1} & 0 & \ldots & \ldots & \gamma_1 \\
& & & \ldots & \ldots & \ldots & \ldots \\
& & & & \ldots & \ldots & \ldots \\
& & & & & \ldots & \ldots & \ldots \\
& & & & & & \ldots & \ldots & \ldots \\
\end{pmatrix}_{2N \times 2N}$$

(14)

in order to obtain a set of $2N$ Landau levels (LLs) and the corresponding coefficients $\{c_{A_1}^\alpha, c_{B_1}^\alpha\}$ that determine the eigenstates $|\psi_n^\alpha\rangle$ with $\alpha = 1, \ldots, 2N$. In Eq. (14), the index $n$ is required to be positive. However, we note that Eq. (10) supports eigenstates with the following structure

$$|\psi_0\rangle = \begin{pmatrix}
c_{B_1} \varphi_0 \\
c_{A_2} \varphi_0 \\
c_{B_2} \varphi_1 \\
c_{A_3} \varphi_1 \\
c_{B_3} \varphi_2 \\
c_{A_4} \varphi_2 \\
c_{B_4} \varphi_3 \\
\vdots \\
\end{pmatrix}, |\psi_{-1}\rangle = \begin{pmatrix}
c_{B_1} \varphi_0 \\
c_{A_2} \varphi_0 \\
c_{B_2} \varphi_1 \\
c_{A_3} \varphi_1 \\
c_{B_3} \varphi_2 \\
c_{A_4} \varphi_2 \\
c_{B_4} \varphi_3 \\
\vdots \\
\end{pmatrix}, |\psi_{-2}\rangle = \begin{pmatrix}
c_{B_1} \varphi_0 \\
c_{A_2} \varphi_0 \\
c_{B_2} \varphi_1 \\
c_{A_3} \varphi_1 \\
c_{B_3} \varphi_2 \\
c_{A_4} \varphi_2 \\
c_{B_4} \varphi_3 \\
\vdots \\
\end{pmatrix}, \ldots, |\psi_{-N+1}\rangle = \begin{pmatrix}
\vdots \\
\varphi_0 \\
\end{pmatrix}.$$ 

(15)

These eigenstates can be obtained from (11) by extending the range of possible values of $n$ to $n \geq -N + 1$ and using the rule that harmonic oscillator wavefunction with negative subindices must be replaced by zero. The corresponding eigenvalues can be obtained by applying $H_{ABC}$ to these states and solving for the nontrivial part of the eigenvalue
FIG. 2: a-g), Inter-Landau level transitions ($\Delta n = 0$) from the surface subbands, for $N = 3, 8, 10, 14, 17$, respectively. The red line in each plot indicate a linear fitting for a given transition.

equation. For each one of the different form of the eigenstates in Eq. (15) there is always one eigenstate with zero energy while the remaining possible states appear around $\sim \pm \gamma_1$ for small magnetic field. Hence, there are $N$ nontrivial eigenstates with zero energy for ABC-stacked $N$-layers graphene [1]. Notice that this result can also be obtained from the effective Hamiltonian (2).

To find the electronic Raman spectrum in the presence of an external magnetic field, we calculate transition amplitude (matrix elements of the operator $R = R_D + R_\omega$) between the initial $|\psi_\alpha^\alpha n\rangle$ and final $|\psi_\beta^\alpha m\rangle$ states. This procedure leads to the selection rules $n = m$ and $\alpha = \beta$ for the $R_D$ process as in monolayer graphene where the ones allowed by $R_D$ correspond to a symmetric optically active inter-LL excitations (transitions with $\Delta n = 0$ in the usual Landau notation for monolayer graphene). Transitions with $m \neq n$ are also possible, due to processes represented by $R_\omega$, but in this case with intensities considerably lower. In order to compare our theoretical calculations with the false color maps of the magneto-Raman scattering spectrum (Figures 4c-d of the main text) we assign a gaussian function to each possible transitions line with height equal to $|\langle \psi_\beta^\alpha m | R | \psi_\alpha^\alpha n \rangle|^2$ and standard deviation $\sigma \approx 0.004$ eV to simulate a possible Landau level broadening in the real sample.

LANDAU LEVEL EVOLUTION AS A FUNCTION OF NUMBER OF LAYERS

Figure 2a-g shows a series of plots of the B-evolution of the inter-band Landau level transitions from the surface subbands, for different number of layers $N$. The slope of these lines increases with the number of layers until reaching a maximum value for the bulk limit. As we discussed in the main text, the evolution of these lines is quasi-linear in the energy range were we performed the magneto-Raman measurements. However, the modeling of these data shows that these lines will depart from the linear regime and ultimately curve at very low energy to reach the zero energy value at $B = 0$, reproducing the flat part of the surface subband at $B = 0$ (see Figure 1). From the evolution of the Landau level transitions with the number of layers, we can extract the value of the intercept for each line by performing a linear fitting $A x + E_0$, where $E_0$ is the value of the energy at $B = 0$ obtained from the extrapolation of the Landau level transition lines for a given number of layers $N$. Figure 3 is a plot of $E_0$ as a function of $N$, from 3 to 17 layers. By performing magneto-Raman measurements of the electronic excitations in ABC stacked N-LG, one can estimate the number of layers on the flake from $E_0$, by a linear fitting of the B-evolution of the electronic excitations from the surface subbands in the linear regime (i.e., from 600 to 2800 cm$^{-1}$ or from 0.08 to 0.35 eV).
CASE OF MIXED STACKING OF GRAPHENE LAYERS

For the sake of comparison, we also performed magneto-Raman measurements on h2, a region where no ERS at $B = 0$ is observed (boxed region in Figure 4a). A comparison between the observed electronic excitations in h2 and those observed in h3 and h4 is shown in Figure 4b, for different values of the magnetic field, after subtraction of the $B = 0$ spectrum. At first glance, the electronic excitations observed in h2 have rather asymmetric line shapes, if compared to the well symmetric features observed on the ABC stacked suspended parts (h3, h4). The electronic excitation spectrum obtained at h2 is shown in Figure 4c as a false color map of the Raman scattering intensity as a function of the magnetic field. Different electronic excitations are observed, with a quasi linear evolution with increasing magnetic field. The energy of the large majority of these excitations converge to zero when the magnetic field tends to $B = 0$, which is characteristic of the magneto-Raman response of ABA stacked N-LG. Nevertheless, we observe at least three excitations, that extrapolate to a finite $B$ in a similar way to the observed excitations from h3 and h4, reported in the main text. Of much weaker intensity, these three excitations are better seen in the $B$-differentiated false color map of h2, they are indicated by red arrows in Figure 4d.

In order to illustrate the difference in the dispersion of the electronic excitations with magnetic field between h2 (where the ABA stacking dominates) and h3 or h4 (where there is pure ABC stacking), we performed a spatial mapping of our N-LG flake at fixed magnetic field $B = 17$ T. Figure 5a shows two Raman spectra taken from this map at h2 (red curve) and h4 (black curve). These two Raman spectra show an electronic excitation at different energies, hence the two suspended parts have distinct electronic excitations spectra. The false color map in Figure 5b is obtained by plotting the Raman scattering intensity of the difference in the electronic excitation dispersion all over the flake. From the conspicuous contrast in Figure 5b, we reveal again, thanks to magneto-Raman spectroscopy, the two domains with different stacking configurations.

The evolution with magnetic field of the electronic excitations in h2 can be understood by considering a tight-binding model for N-LG system with a mixed stacking of its graphene layers. In this case, the Hamiltonian contains an ABA-stacked 8 layers graphene coupled to 7 layers with an ABC sequence. The low energy electronic band structure corresponding to the ABABABAB-ABCABCA stacked 15-LG is shown in Figure 6a. The best fit for h2 yields $N = 15$ with $\gamma_0 = 3.15$ eV and $\gamma_1 = 0.4$ eV (Figure 6b-c). Where the three excitations observed in h2 that extrapolate at finite $B = 0$ originate from the symmetric (i.e., $\Delta|n| = 0$) inter-band Landau level transitions within the flat bands at the charge neutrality in Figure 6a. While the almost parabolic bands in Figure 6a give rise to the remaining complex electronic excitations spectrum observed in h2. The main conclusion is that while the suspended parts h3 and h4 that have been discussed in the main text, have a rather pure ABC stacking, h2 on the other hand is interpreted as being inhomogeneous and exhibits both ABA and ABC stacking configurations. It is interesting to emphasize the striking difference in complexity that both cases present, while the mixed stacking case (h2) presents a rather complicated magneto-Raman spectrum, the pure ABC stacking situation (h3 and h4) shows a clean and simple one.
FIG. 4: Observation of low temperature electronic excitations from N-LG with a mixed stacking of graphene layers. a), Optical microscope image of the N-LG, the suspended part where magnetic dependent magneto-Raman spectra have been recorded, labelled h2, is boxed in red square. b), $B = 0$ subtracted Raman spectra from h2, and the previously measured h3, and h4 respectively, for different values of the magnetic field. c), False color map of the micro-Raman scattering intensity spectra as function of magnetic field from h2. d), $B$-differentiated false color map of (b), the three excitations that extrapolate at finite $B$ are indicated by red arrows.

FIG. 5: Contrast in electronic excitations spectrum from the two domains. Raman spectra recorded at $B = 17$ T from h2 and h4. The contrast in the scattering intensity between the two domains is shown in (b) in the form of a false color map of the micro-Raman scattering intensity from the N-LG flake at $B = 17$ T, showing the contrast in the Raman scattering intensity as a function of the stacking configuration (i.e., ABA or ABC).
FIG. 6: **Modeling of the data from the magneto-Raman experiment on h2.** By considering a single tight-binding Hamiltonian that contains the stacking configuration ABABABAB-ABCABCA, we plot its low energy band structure in (a). The fitting of the electronic excitations observed in h2 is obtained by considering the symmetric inter Landau level transitions of an ABC stacked 7 layer graphene, indicated by green colored data in (b), coupled with an ABA stacked 8 layer graphene, indicated by blue colored data in (c).

**ATOMIC FORCE MICROSCOPY MEASUREMENTS**

To investigate the thickness of the flake, we performed atomic force microscopy (AFM) on three different edges as seen in Figure 7a. The thickness was estimated from the edges by assuming a thickness for the first monolayer sheet on top of the silicon dioxide layer equal to 0.529 nm (as measured under nominally the same conditions for a reference graphene flake). The atomic interlayer distance in graphite is taken to be 0.335 nm, this gives a thickness that varies from 15 to 17 layers, in accordance with the number of layers we used in the tight binding model to fit the experimental data.

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FIG. 7: a), Optical microscope image of the flake, the colored arrows indicate the sections where AFM measurements were performed. b), Plot of the edges profile (a) obtained from the AFM. The thickness varies from 15 to 17 graphene monolayers.