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Increasing flatness of surface bands of multilayer rhombohedral graphite with crystal thickness

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Flat bands, where Coulomb repulsion dwarfs bandwidth, hold the potential to realize many correlated electron states in a material. Rhombohedral graphite (RG) hosts an intrinsic flat band near the Fermi level localized on its top and bottom surfaces, in which the density of states is predicted to increase sharply with increasing crystal thickness. Here, we study rhombohedral graphite samples of multiple thicknesses using scanning tunneling microscopy and spectroscopy. We observe a van Hove singularity (vHs) in the density of states of all samples as well as additional peaks corresponding to the onsets of higher-energy bands that have been pushed away from the Fermi level due to interlayer hopping. The relative height of the central vHs to the higher-energy peaks increases with crystal thickness, a result that agrees quantitatively with our tight-binding (TB) calculations. We study the boundary between RG and hexagonal graphite and observe splitting of the flat surface band, an effect which can be described by the inclusion of a stacking fault into our TB model.

Introduction

Flat bands in the electronic structure of a material, where low band dispersion and a small bandwidth relative to the Coulomb interaction energy manifest as a sharp peak in the density of states, potentially host correlated electron states such as ferromagnets, superconductors, and charge-density waves. In van der Waals heterostructures of two-dimensional (2D) materials, researchers have exploited the “twist” degree of freedom to create moiré superlattices that can have a large effect on their electronic properties, for example, to engineer flat bands, such as in magic-angle twisted bilayer graphene [1, 2] and twisted homo- and heterobilayers of transition-metal dichalcogenides [3, 4]. Rhombohedral graphite (RG), a thermodynamically metastable phase of graphite accounting for $\sim 15\%$ of graphite found in nature [5], hosts intrinsically flat surface bands that grow flatter with increasing graphite thickness [6, 7]. It has been theoretically shown the surface bands host a low energy dispersion of the approximate form $E \propto p^N$ where p is the in-plane momentum and N is the total number of graphite layers, leading to a sharp peak in the density of states near $E = 0$. The bulk of RG is insulating, acquiring a gap as a result of an interlayer hopping γ_1 similar to that in bilayer graphene. The γ_1 hopping connects opposite sublattices on neighboring RG layers (Figure 1d), creating a staggered chain of intralayer γ_0 and interlayer γ_1 hopping pathways that connect the top and bottom surfaces of RG. This chain is analogous to the Su-Schrieffer-Heeger model for a one-dimensional chain [8], and thus RG can be thought of as being composed of parallel SSH chains. The end states of these chains hybridize to form a flat band that is localized on one of the sublattices on the surface (Fig. 1g) [8, 9]. RG thus offers an intrinsic flat band system that does not require moiré engineering.

RG’s intrinsic flat bands have been predicted to host a variety of correlation-driven ground states, including a high-temperature surface superconductivity state [10–12] and a weakly spin-polarized ferrimagnetic state [13, 14]. Recent measurement of RG trilayers revealed a superconducting transition in a narrow range of density and perpendicular displace-

ment field [15] occurring at the cusps of magnetic transitions in the system [16]. Attempts to further confine the intrinsic flat bands using alignment to a hexagonal boron nitride (hBN) substrate yielded a gate-tunable correlated Chern insulator that displays a magnetic hysteresis [17, 18], as well as signatures of a superconducting transition in this system [19]. Recently, pentalayer ($N = 5$) RG aligned to hBN showed evidence that it was a zero-field fractional Chern insulator (FCI) [20], a vivid demonstration of electron correlations and topology, though the precise role of the hBN moiré is not fully understood. For these moiré systems, alignment of the RG and hBN lattices is a difficult technique, where crystal lattice directions must first be characterized, and care must be taken that stacking does not cause a change in RG phase to the thermodynamically-stable hexagonal graphite [21]. From the perspective of device fabrication, a simpler approach to flatten the bands is to increase the thickness of RG [7], a route to enhancing electron-electron correlations that does not require difficult alignment of atomic lattices. Additionally, the flat bands are on the surface of the material instead of being trapped at the interface with hBN, making them available for proximity effects with other 2D materials and open for study using scanning probe techniques.

To date, while many studies have focused on trilayer RG [16–18, 22–25], there have been relatively few experimental studies on multilayer RG (defined here as $N > 3$) [20, 26–32] and, to the extent of our knowledge, no direct confirmation that the surface bands become flatter as the number of layers increases. In this paper, we present a spectroscopic characterization of the surface band in RG multilayer samples. The density of states of the flat surface band relative to that measured at the band edges of higher valence bands shows an increase with layer number N , for $N = 5, 9$, and 14 layer samples, and the results agree quantitatively with tight-binding (TB) calculations. We study the boundary between HG and RG graphite and observe that the flat surface band splits, an effect that we can describe by introducing a stacking fault into our TB calculation. A natural interpretation of the splitting of the flat surface band is in terms of electronic correlations [31, 32]; here, we highlight this alternative mechanism for peak splitting, which is of increased importance near physical or struc-

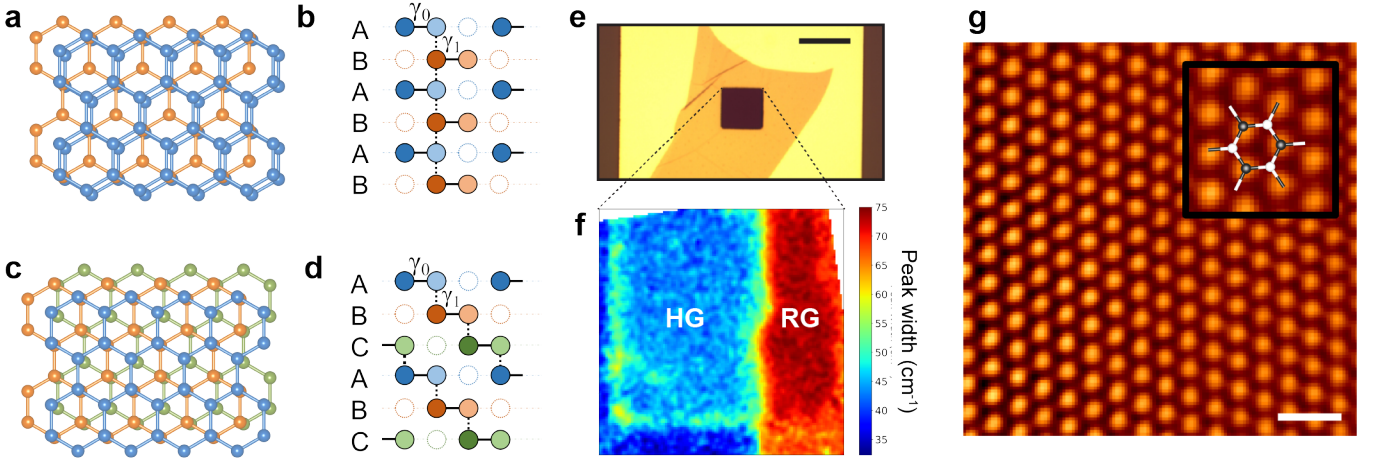


Figure 1. (a) Top-down and (b) side view of hexagonally-stacked graphite (HG). Intralayer hopping γ_0 and interlayer hopping γ_1 are shown. (c) Top-down and (d) side view of rhombohedrally-stacked graphite (RG). (e) Optical micrograph of 14L graphite sample on gold with a rectangular hole exposing the SiO_2/Si substrate. Scale bar is $10\ \mu\text{m}$. (f) Map of the Raman 2D peak width, showing an RG region on the right and an HG region on the left. Image is $12 \times 12\ \mu\text{m}^2$. (g) Atomic-resolution STM topograph of the RG surface, showing the trigonal symmetry of the lattice. Scale bar is $5\ \text{\AA}$. Inset: detailed view of the lattice with an atomic model overlaid.

tural phase boundaries.

Fabrication and Characterization

Graphite flakes of multiple thicknesses were mechanically exfoliated on $300\ \text{nm}\ \text{SiO}_2/\text{heavily doped Si}$ substrates. Initially, the flake thicknesses were characterized optically, and flakes with thicknesses 5-15 layers were chosen. Cr/Pd/Au electrodes were pre-fabricated on $300\ \text{nm}\ \text{SiO}_2/\text{Si}$ substrates and graphite flakes were placed partially on the SiO_2 and partially on the metal electrode using standard dry-transfer techniques (Fig. 1e). It is well known that this transfer technique can alter the stacking order of RG, causing a mechanical shift in the layers and converting it to thermodynamically-favored hexagonal graphite (HG) phase [21], and so the graphite phase was characterized post-transfer to verify that rhombohedral portions remained on the finished device. Sample thicknesses were determined by STM topography.

Raman spectroscopy was used to characterize stacking order of graphite flakes. Raman spectra for both graphite phases are shown in Supplementary Figure S2, acquired using an NT-MDT Spectra AFM/Raman equipped with $532\ \text{nm}$ laser calibrated on polystyrene $1001.4\ \text{cm}^{-1}$ peak. Both RG and HG exhibit a peak in the Raman spectrum at $2700\ \text{cm}^{-1}$ [33]. However, the hexagonal phase has a right-skewed peak and the rhombohedral phase has almost no skew. The width of this peak can be used to classify areas of the graphite flake into one of these phases, or a mixture of the two. A map of the 2D peak width is shown in Figure 1f, and a clear line dividing the two phases is observed. The peak width of the rhombohedral phase is consistent with previous measurements for fully-rhombohedral graphite stacks [21].

Devices were then annealed at 350°C under a flow of ~ 5

scm of forming gas (5% H_2 / 95% Ar) for 20 hours to remove polymers from the transfer process and clean the surface for STM measurements. This annealing step does not destroy the rhombohedral portions of the flake, as confirmed by subsequent characterization of graphite phase. The devices were then loaded into the ultrahigh vacuum, low temperature scanning tunneling microscope. All measurements are taken on a commercial CreaTec low-temperature STM, with a helium bath temperature of $4\ \text{K}$, and resulting STM temperature of $4.7\ \text{K}$. The STM is equipped with an electrochemically etched tungsten tip, which was indented into gold before and between measurements. The lock-in frequency was set to $869\ \text{Hz}$ in all dI/dV measurements.

A constant-current topographical image of an RG sample is shown in Figure 1g. Bright spots with an apparent trigonal symmetry are observed, with spacing $a = 2.46\ \text{\AA}$ as expected for graphite. The inset in Figure 1g shows a detailed view of the lattice with an atomic model of graphene overlaid. One sublattice appears bright while the other appears dark. This symmetry is expected for both HG and RG, and is the result of the interlayer hopping γ_1 pushing states originating from these atoms away from the Fermi level.

Turning now to the spectroscopic analysis of RG, Figure 2a shows a comparison of dI/dV measurements for a five-layer ($N = 5$) sample of both rhombohedral and hexagonal phases. While HG shows a slow increase in dI/dV as bias is increased, RG displays a sharp enhancement of the dI/dV signal at positive bias voltage, around approximately $+100\ \text{mV}$. This peak corresponds to the van Hove singularity in the surface states of RG, and is completely absent in the hexagonal phase. In addition to this peak, a gap feature between approximately $\pm 65\ \text{mV}$ about the Fermi level is observed in both spectra. This gap results from a phonon-mediated in-

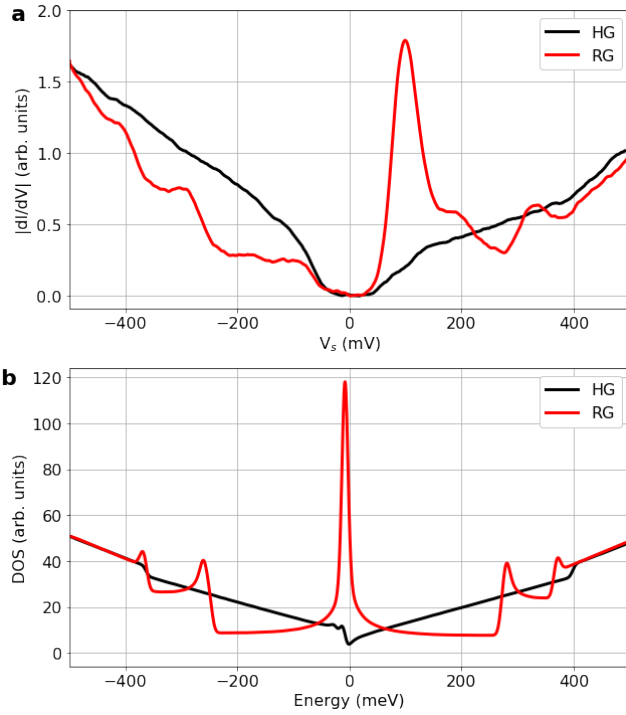


Figure 2. **(a)** dI/dV measurement for 5-layer RG vs 5-layer HG. A sharp dI/dV peak is seen at positive bias in RG, indicative of the flat surface bands. Tunneling current setpoints were 0.113 nA and 0.099 nA, respectively. **(b)** Density of states for RG and HG calculated using a tight-binding model.

elastic tunneling mechanism in graphene, which enhances all tunneling above or below the 67 meV out-of-plane graphene acoustic phonon mode at the K/K' points [34, 35]. This effectively shifts the position of all spectroscopic features by ± 67 mV, depending on whether the feature is above or below the Fermi level, and has previously been observed in graphene and graphite tunneling spectra [34, 36–39]. We observe this gap in some devices and do not observe it in others, and find that its presence is correlated with flow rate of forming gas during our anneal, and thus related to the presence of hydrogen at the surface. This has recently been demonstrated in controlled STM experiments as well [38].

The shift of the van Hove singularity to positive bias, which is expected to be centered around $E = 0$, may be explained by the following. First, the phonon gap previously mentioned shifts the peak by +67 mV. However if the peak were truly centered around $E = 0$, this would shift half of the peak to +67 mV and the other half to -67 mV. Instead, an apparent p-doping of the sample is observed, which shifts the van Hove singularity such that its entire width is found at positive bias. The magnitude of this doping changes between samples, and varies spatially across a single sample. We attribute this shift to adsorbed oxygen contaminants at the substrate interface that act as hole donors. Spontaneous hole doping in ambient conditions has been widely reported in graphene. Our fabrication techniques have been shown to further reinforce

this type of interfacial contamination [40, 41]. This behavior has been observed in STM measurements of trilayer RG with similar cleaning processes as this study [24]. Accounting for both p-doping and the presence of the phonon gap, these measurements qualitatively match dI/dV measurements of three, four and five-layer RG measured previously [24, 25, 27, 31].

In addition to the van Hove singularity, several shoulders in the density of states at negative bias voltages are observed. These shoulders correspond to onsets of electronic bands that have been pushed away from the Fermi level due to interlayer hopping γ_1 between opposite sublattices on adjacent layers, giving rise to the gapped bulk of RG. Similar shoulders are observed at positive sample bias, but these features do not align well with calculated conduction band edges. It is more likely that these features arise from tip-induced band bending, where the bands shift upwards at positive sample bias and cause the Fermi level to move into the first valence band, giving rise to an increased tunneling current and a peak in the dI/dV spectrum. This affects positive sample bias more strongly than negative bias due to the apparent p-doping of the sample surface, causing the corresponding downward band bending at negative sample bias to be suppressed by the large density of states of the surface flat band (for further discussion see the Supplemental Material [33] and references [42–48] therein). Because of this, conduction band peaks are not considered in further analysis.

To better understand our STS results, we use a tight-binding model that accounts for both intralayer and interlayer hoppings, γ_0 and γ_1 respectively, as well as several higher-order interlayer hopping pathways $\gamma_2 - \gamma_4$. These hopping pathways are detailed in Supplementary Figure S3, and hopping parameters used in this model have been calculated in previous studies [16, 33]. The resulting density of states calculated for a five-layer stack of RG, shown in Figure 2b, bears many similar qualities to our measurement. The sharp van Hove singularity resulting from the flat surface bands is observed close to zero. In dI/dV measurements, this peak is shifted to positive energy by both the phonon gap and an overall p-doping, which combine constructively to push the peak to large positive bias. The lower energy valence band onsets are observed as peaks at negative energies. In dI/dV measurements at negative bias, the combined effects of the p-doping and phonon gap counter one another, resulting in the calculated density of states peaks nearly aligning with the shoulders in the dI/dV measurements, with a small overall offset. With these effects in consideration, the density of states calculation agrees well with dI/dV measurements.

Thickness Analysis

We now turn our attention to a comparison of these spectroscopic features as a function of graphite thickness. Flakes of three different thicknesses ($N = 5, 9$ and 14 layers) were measured, and the resulting spectra are shown in Figure 3a. The sharp density of states peak is observed in every spec-

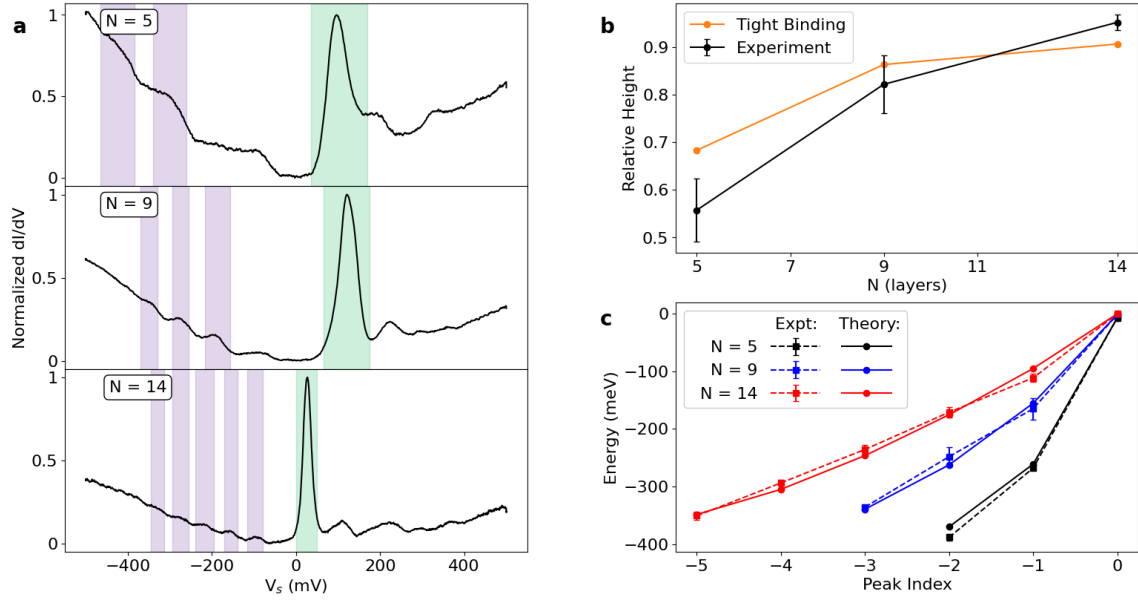


Figure 3. **(a)** Comparison of $N = 5, 9$, and 14 layer graphite samples. The surface flat band is highlighted in green, while the higher energy band onsets are highlighted in purple. The $N = 5$ spectrum was acquired using a different tip than that shown in Figure 2. **(b)** Relative peak height from experiment and from tight-binding model. “Relative” compares the height of the central peak to that of the first valence band peak. The spectra were normalized to the height of the central peak, with 0 being the minimum measured density of states between the first valence peak and central peak. The relative height was found by subtracting the height of the first valence peak from that of the central peak in the normalized data. **(c)** Energies of higher-order valence band peaks vs. peak index (relative to the van Hove singularity) for each device thickness. Dashed lines with square symbols indicate experimental data, while solid lines with circular symbols are calculated using the tight-binding model.

trum, highlighted in green, and grows in height as sample thickness is increased. The absolute density of states calculated from a dI/dV measurement depends on both the tip density of states and the true tip-sample separation distance, both of which are unknown. This makes quantitative comparison of feature heights between dI/dV measurements on different samples difficult. Consequently, between samples of different N we instead compare the relative height of the central peak to that of the first valence band. This comparison is shown in Figure 3b, averaged for multiple different tips and sample areas. The relative height grows as sample thickness increases, indicating the van Hove singularity is growing sharper. A similar calculation was performed using the density of states from the tight-binding model and is shown in Figure 3c, and the lineshape and magnitude qualitatively matches that from experiment. The observed spontaneous p-doping has no effect on the separation between the first valence band and central peak and reflects a simple spectroscopic shift of visible features.

Additionally, the lower energy valence band peaks (onsets), highlighted in purple in Figure 3a, become more numerous and more tightly spaced as thickness increases. This result is also seen in tight-binding models for the system, where each additional layer adds one valence band and one conduction band. The peak energy vs. peak position relative to the van Hove singularity (called “peak index” here) is shown in Figure 3d where it is compared to calculations for the tight-binding

model. The energies of these peaks have been adjusted to account for both the presence of the phonon gap and overall p-doping in the system. We see good agreement between the experiment and model.

Characterization of RG/HG boundary

Figure 1f shows the boundary between the HG and RG phases of the graphite sample which appears to be well-defined on a length scale set by the spatial resolution of the Raman spectrometer (a few hundred nanometers). The boundary demarcates a domain of RG that is several microns large, rendering it useful for incorporation into mesoscopic devices [30]. We investigated the HG/RG boundary in the $N = 14$ sample using STM/STS, as it is expected to harbor topological edge states due to the presumed topological nature of the RG graphite surface state [31]. A topographic STM image is shown in Figure 4a, showing a weak delineation between the hexagonal phase on the left and the rhombohedral phase on the right. 1D stacking solitons have been previously observed at this boundary in trilayer graphene [49]. A line scan showing the density of states across this boundary is shown in Figure 4b, aligned to the topographic image above.

Approaching the boundary from the RG side, the van Hove singularity splits into two peaks that slowly decay in height. The splitting of the vHs can indicate the opening of

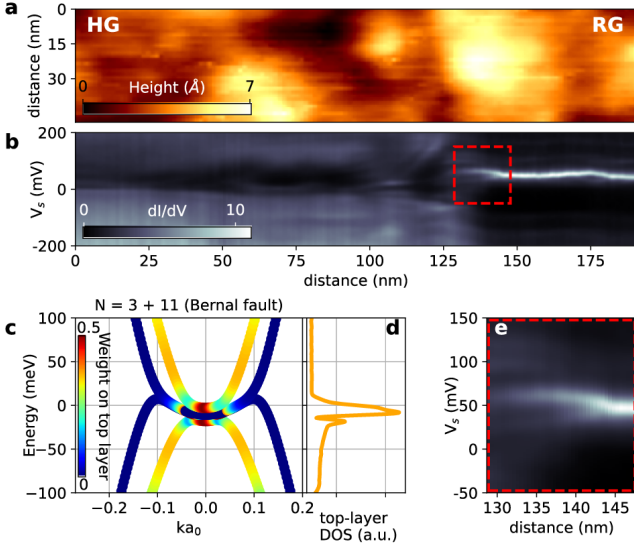


Figure 4. (a) Topograph across the HG/RG boundary shown in Fig. 1f. Topograph taken at 158 mV bias and 0.1 nA tunneling set-point. (b) dI/dV spectra along a line perpendicular to the boundary depicted in a). The van Hove singularity in RG splits as it approaches the HG region (red dashed box). (c) Calculated band structure for an RG stack with a Bernal fault between the 3rd and 4th layer, resulting in a $N = 3 + 11$ stack. The weight of the wavefunctions ($\sum_{\sigma=A,B} |\psi_{\sigma 1}|^2$, σ = sublattice), on the top layer is represented by the color bar. (d) Top-layer density of states calculated from (c). (e) Detail of dI/dV across the RG/HG boundary, showing more clearly the splitting of the van Hove singularity over a length scale of ~ 15 nm.

an interaction-induced gap, which could be due to the appearance of a magnetically-ordered state [32] or another type of electronic order, such as charge-transfer order [31]. Ref. [32] explored such effects using STS by exploiting locations with the RG sample where the Fermi level (i.e. zero bias) was located within the surface flat band and concluded that the surface electrons formed a structure of alternating gapped domains with antiferromagnetic order and gapless, paramagnetic domains. However, we note that in Fig. 4, the vHs is at a sample bias of ~ 50 mV, indicating the sample p-doping we observe consistently throughout our samples (in fact, we did not observe n-doping or zero doping at any location in any of our three samples).

We thus present an alternative interpretation of our observation of the vHs splitting: it is possible that it is the result of a particular change in the stacking order as the flake transitions from rhombohedral to hexagonal. Figure 4c shows a tight-binding calculation of the electronic structure of 14 layers of RG but including a Bernal stacking fault after between the third and fourth layer (counting down from the top surface). The accompanying DOS calculation shows that this stacking fault introduces a splitting of the van Hove singularity whose features are similar to those observed in experiment: the splitting is around ~ 20 meV and asymmetric, with more weight

in the peak on the positive-bias side. Additional information related to the tight-binding calculation for a stacking fault in a 14-layer sample is presented in Supplementary Figures S4 and S5 [33].

It's reasonable to predict the occurrence of a stacking fault within the first three atomic layers on the material's surface, considering the 10 nm width of the domain boundary and the tendency of the surface layers to decouple from the bulk in HOPG [50–52]. Additionally, it is improbable that the surface density of states would be substantially affected by stacking faults located deeper within the material. This is because any perturbations from such deeper faults would have a diminished impact on the surface. Bulk-sensitive techniques are needed to conduct a more thorough analysis of the stacking order. We note here that we cannot definitively report the observation of a topological edge state at the boundary, as was observed in Ref. [31] at the boundary between ABAB- and ABCA-stacked domains in twisted double-bilayer graphene. A reason may be, as discussed above, that in our samples the Fermi level does not reside within a gap (topological or otherwise).

Conclusions

In this work, we performed a spectroscopic study of the surface flat band of rhombohedral graphite. The central finding was the increase in the flatness of the surface band of rhombohedral graphite as the number of layers was increased from $N = 5$ to 9 to 14, consistent with the theoretical result that this surface band disperses like $E \sim k^N$. We characterized the flatness of the band by measuring the peak height ratio of the flat band to the first valence band, a metric that allowed us to directly compare different samples studied with different STM tips. This ratio, as well as the energy locations of all of the higher valence bands, agreed well with tight-binding calculations. At a boundary between hexagonal and rhombohedral graphite, we observed the splitting of the surface band. This effect was likely not due to interactions, since the Fermi level is not in the flat band, but rather due to a stacking fault. Furthermore, the inability to gate our samples to bring the Fermi level into the flat band meant that we were unable to verify certain predicted topological effects at the boundary. However, this limitation also enabled us to exclude the possibility of correlations influencing the peak splitting at the boundary. Since observable peak splitting is frequently examined in connection with correlated states, our tight-binding predictions indicate that further analysis is necessary to explain its occurrence. The ease of fabrication of rhombohedral graphite devices and access to the flat surface band implies that many more STM experiments exploring electron interactions [32] and topological properties [31], perhaps exploiting doping, lower temperatures, magnetic and electric fields, and quasiparticle interference, will be fruitful.

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