Effect of rotational stacking faults on the Raman spectra of folded graphene

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The Raman spectral signature of folded graphene layers for one to six layers was studied. Folding allows realization of rotational disorder in otherwise perfect samples. We show that the two-dimensional Raman band of the folded sample is up shifted compared to the unfolded sample. The evolution of the spectral signature with increasing number of layers is discussed.

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I. INTRODUCTION

Graphene, defined as a two-dimensional (2D) honeycomb lattice of carbon atoms, has recently attracted major attention from the physics research community.[1,2] Part of the interest lies in the nature of the electronic band structure which permits carriers to behave as massless Dirac fermions with a vanishing density of states at the Fermi level.[3] These properties are destroyed as soon as two graphene layers are stacked in Bernal *AB* configuration (referred in the following as Bernal bilayer) as the electronic dispersion curve is no longer linear.[4,5] In a recent publication Latil *et al.*[6] claimed that non-*AB* stacking of two graphene layers (referred to as misoriented layers in our paper) conserves the linear electronic band structure. According to their paper, a rotational stacking fault decouples the electronic structure of the two consecutive misoriented layers. Within the framework of this theory, a four-layer sample made of two misoriented Bernal bilayers will have an electronic structure close to that of one Bernal bilayer.

To experimentally address this issue, one should measure independently the number of layers, their stacking configuration, and their electronic properties. The number layers can be determined by atomic force microscopy (AFM).[7] This measurement will be independent of the stacking because the interlayer distance is almost identical for Bernal and misoriented layers (0.35 nm).[8] The stacking configuration can be determined from electron-diffraction experiments.[9] Electronic properties can be determined from point scanning tunneling spectroscopy (STS).[10]

Carrying out all these measurements on the very same sample is a difficult task, particularly for sample preparation for transmission electron microscopy (TEM). We will show that these constraints can be avoided to a great extent by the choice of particular samples and by the use of Raman spectroscopy.

It has been demonstrated that Raman spectroscopy is useful to probe the electronic band structure.[11] Since the work of Ferrari,[9] Raman is routinely used to identify graphene and samples of few Bernal layers even if the spectral signature of samples with more than five layers is still being discussed.

The samples we have chosen to study are accidentally and randomly partially folded on themselves. This folded configuration has two clear interesting aspects: both fundamental

as well as practical. From the fundamental point of view the random folding will generate a rotational stacking fault. For example, a Bernal trilayer (*ABA*) will generate after folding on itself a hexalayer sample with a rotational fault (*ABA A′B′A′*). We then obtain a sample in which the stacking configuration is perfectly known except for the rotation angle between the two misoriented consecutive layers. From the practical point of view, the thickness of the folded part can be measured independently of the substrate which gives access to the number of layer with better accuracy. Indeed, even if we do not know exactly the detailed interaction of the tip-graphite contact, we can postulate that it will be identical on both fold and unfolded parts so the height difference will be purely topographic.

The work we present here has been carried out on well-identified graphene and few Bernal stacked layers, namely, one, two, three, five, and six layers (our efforts have not yet produced a four-layer sample) and their folded parts.

II. EXPERIMENTAL SETUP

Graphene layers were prepared by using mechanical exfoliation of graphite[12] deposited on Si/SiO$_2$ substrates with 290–295 nm thermally grown oxide (commercially available at IBS).[13] This oxide thickness allows rapid localization of interesting pieces with an optical microscope. We then select pieces of various thicknesses that show clearly a folded part (see Fig. 1 as example). Finally, AFM (tapping mode, 300 kHz cantilever with 40 N/m spring constant) measurements were carefully done across the folded edge to extract topological information.

Raman spectra were recorded using two spectrometers. For 488 nm (2.54 eV) and 514.5 nm (2.41 eV) excitation wavelengths, we use a Jobin-Yvon T64000 spectrometer operating in triple configuration (1800 gr/mm grating mode) coupled with a liquid-nitrogen-cooled charge-coupled device (CCD) camera. For 633 nm (1.96 eV) excitation wavelength, we use a Jobin-Yvon Aramis spectrometer (1800 gr/mm grating configuration) with a Peltier-cooled CCD camera. Excitation laser light was focused on the substrate using a confocal microscope with a 1 μm typical spot size. The laser beam power was set to 3.5 mW impinging on the sample for all studied wavelengths.
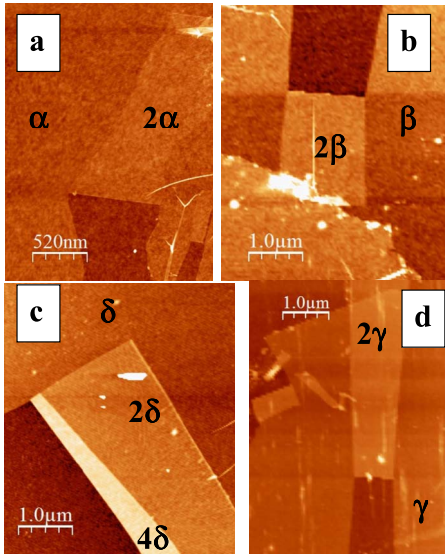
FIG. 1. (Color online) (a) Graphene (α) and folded part (2α). (b) Bernal bilayer (β) and folded part (2β). (c) Bernal trilayer (δ), folded part (2δ), and refolded (4δ) part. (d) Bernal hexalayer (γ) and folded part (2γ).

III. RESULTS

Figure 1 display the AFM images of some configurations probed and discussed in this paper. The first observation is that, except for graphene, the torn edges are neat and straight, whatever their thickness is. When a ribbon is folded [Figs. 1(b) and 1(d)], the two sides are almost parallel.

By analyzing[14] AFM images, we can directly measure the thickness of the folded layer(s) perpendicularly to the torn edge on top of a graphitic plane (thus regardless of the substrate interaction). The result allows unambiguous assignation of the number of layers. Raman spectra were then recorded on folded and nonfolded areas. On a useful sample, both folded and nonfolded areas should be larger than the micro-Raman laser spot (about 1 μm diameter). This has been achieved in all configurations except one: folded graphene. We did not find a piece of folded graphene large enough; thus, the spectrum of folded graphene will be a superposition of graphene and folded graphene spectra. However, as we will see, this will be enough to demonstrate that there is an effect of the folding on the Raman response.

We observed that when reducing the excitation energy, Raman spectra of the 2D bands are more detailed and easier to identify as their internal structure spreads over a wider energy span. Graphene exhibits a unique peak whose position is wavelength dependent. A Bernal bilayer has a more structured 2D band composed of four components. The Bernal trilayer has at least five components and spreads over 150 cm^{-1} for 633 nm excitation wavelength. The spectra spreading almost stops at the Bernal pentalayer for which the 2D band stops and the internal structure cannot be resolved even at 633 nm. For the Bernal hexalayer, all structure is lost except for two main components. We report here only the results obtained for 633 nm. See Refs. 9 and 15 for more details on the excitation energy dependence.

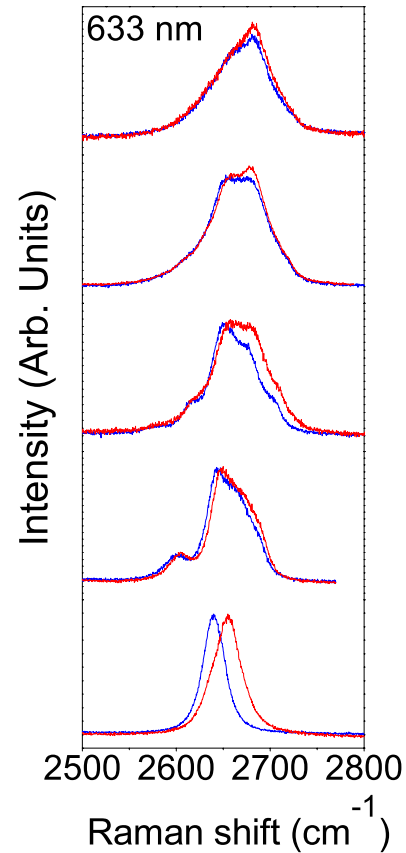Figure 2 shows the 2D Raman spectra of the unfolded part

FIG. 2. (Color online) 2D Raman spectra of graphene and two, three, five, and six Bernal stacked layers (black) and their folding (red). The folding does not, as expected, give a Bernal configuration, i.e., a sample of two misoriented graphene layers does not have the same signature as a Bernal bilayer, the two misoriented Bernal trilayer system does not behave like a Bernal hexalayer, etc. See Table I for the 2D blueshifts.

of well-identified Bernal n layers ($n=2, 3, 5$, and 6) and their folded counterparts. Concerning the G peak, beside a small down shift between graphene and folded graphene comparable to the one observed between graphene and Bernal bilayer,[7] we did not observed any significant novelties and thus spectra will not be shown.

Focusing on the two main peaks of the 2D band of graphene n layers ($n=2-6$), namely, the one at high energy (around 2680 cm^{-1} at 633 nm) and the one at low energy (around 2650 cm^{-1} at 633 nm), we found that the intensity of the high-energy peak is monotonously increasing with the number of layers.

Concerning the folded part, we will detail measurements on a folded graphene (total of two layers), a folded Bernal bilayers (total of four layers), a folded Bernal trilayers (total of six layers), a folded Bernal pentalayer (total of ten layers), and a folded Bernal hexalayer (total of 12 layers). We will thus be able to compare spectra of two different systems with six layers; the only difference has been a rotational stacking fault ($ABABAB$ compared to $ABAB'A'B'$).

We have explained that folding should allow creation of rotational disorder as the two pieces will be misoriented with respect to each other (the probability of an accidental AB
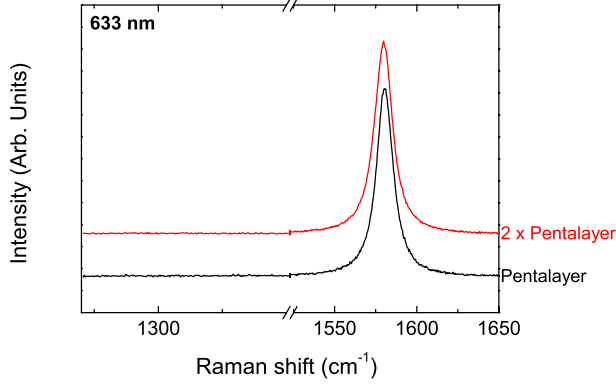
FIG. 3. (Color online) Comparative spectra for Bernal penta-layer and folded Bernal pentalayer normalized to the G peak intensity. (a) $1270-1400$ cm^{-1} area showing the absence of D band. (b) The G peak positions are similar with no significant shift observed.

stacking after a random folding approaches zero). We should first check that no faults or defects are created.

We have then measured the D and G peaks for all the folded samples. Except for graphene in which the torn edge of the folded part is probed [see Fig. 1(a) and recall that the laser spot has a diameter of about 1 μm], we did not observe any increase in the D component after folding. The Bernal pentalayer is shown as a typical example (Fig. 3). This result shows that as expected the rotational stacking fault does not create point defects that lead to the so-called D band. The Raman spectra of D and G lines do not present any particularities and are not shown.

We will now focus on the 2D band area of the folded samples (Fig. 2). The first observation is that, even up to six layers, the folding changes the spectra. (i) For folded graphene, the peak is clearly up shifted (about 15 cm^{-1}) compared to graphene and appears broader. (ii) For the Bernal bilayer, the folding also gives an up shift (4 cm^{-1}) of the structure. The profile of the 2D band is however almost unchanged. (iii) For the folded Bernal trilayers, there is still a small up shift and relative increase in the 2680 cm^{-1} component. (iv) For folded Bernal pentalayer and Bernal hexalayers, the up shift is hardly visible but the relative increase in the 2680 cm^{-1} component is clearly observed. Despite apparent discrepancies, we can extract some common trends. Folding with rotational stacking fault lead as predicted[6] to identical Raman signatures than unfolded sections except for two details. First, there is a global up shift, dependent on the excitation energy, which seems to be inversely proportional to the sample thickness. Second, we note a constant increase in the 2680 cm^{-1} component each time a sample is folded. This second effect is particularly visible on the folded Bernal trilayer and beyond. It might even be present to a smaller extent for the Bernal bilayer. The 2D blueshift measured

TABLE I. Measured blueshift (cm^{-1}) of 2D band upon folding of a n-layer Bernal (excitation wavelength of 633 nm).

Number of Bernal layers	1	2	3	5	6
Blueshift (cm^{-1})	14.2	4.6	5.3	2.3	−0.2

upon folding versus number of layers is reported in Table I.

The folded graphene system has been already observed on a large sample[16] as well as two independent graphene overlappings.[17] The result is that misoriented bilayer graphene exhibits a single 2D peak as graphene, with a small blueshift. In the present paper, we will focus on the n-graphene folded samples and the evolution of their spectra.

The analysis of the 2D spectra on folded sample shows that, as expected, rotational fault decouples the electronic structures of the graphene layers: in the first approximation, the two pieces can be treated independently. The blueshift might come from a different phonon dispersion curve in the folded configuration compared to the unfolded piece as we have proposed for overlapping graphene[17] although Ni et al.[16] proposed a reduced Fermi velocity as explanation.

The origin of the increase in the 2680 cm^{-1} contribution with the folding is not fully understood. It is noteworthy that in turbostratic graphite, there is a single 2D contribution around 2680 cm^{-1}, although the full width at half maximum (FWHM) is about 40 cm^{-1}.[18]

Two simple hypotheses can be made. The first is that it is a signature of the rotational fault stacking. The second will be that this evolution of the spectra reflects the increase in the number of layers, independently of their stacking order.

For the first hypothesis folded graphene and folded Bernal bilayer should exhibit the same effect, which is contrary to what is measured (only a global up shift of the 2D spectra is observed in both cases). If the second hypothesis is true, folded three layers should look like a Bernal hexalayer, which is again not what we observed. To explain this feature, a precise understanding of the 2D band structure of graphite is required, which is beyond the scope of this paper.

In a recent publication, Cançado et al.[19] showed that the 2D band of graphite evolves from a single peak for turbostratic graphite [presented as a purely two-dimensional system with no three-dimensional (3D) order] to the usual two-peak feature (called G'_{3DA} and G'_{3DB} in the paper) for HOPG. The relative intensity of IG'_{3DB}/IG'_{3DA} is a measure of the three-dimensional order in highly ordered pyrolytic graphite (HOPG).

Our results contradict this picture as the 2680 cm^{-1} peak (G'_{3DB} in the paper of Cançado et al.) increases with thickness, relative to the G'_{3DA} peak, even for a constant 3D order (as the random folding decouples the total thickness increase from the vertical order). To go further, we need to study thicker sample with several foldings. We believe that such folded samples will help us to understand the building up of the 2D band by probing precisely known sequences of stacking and purely rotational fault graphitic system.

IV. CONCLUSION

We have demonstrated that folded samples are very convenient tools to probe known sequences of Bernal and non-Bernal graphene stacking. One result is that the Raman signature of Bernal n layer is meaningful up to six layers. More important, the misorientation of two consecutive layers has, as expected, a strong effect on Raman spectra. First the Raman spectra of a n-layer folded sample are closer to the

unfolded spectra than from the 2*n*-layer spectra, beside a small global up shift. Second the 2680 cm^{-1} contribution seems to be more sensitive to the total thickness of the sample rather than to the stacking configuration. These folding configurations are, we believe, important tool to decipher the building up of the 2D band of graphite.

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