Spin-Dependent Electron Scattering at Graphene Edges on Ni(111)

A. Garcia-Lekue,^{1,2} T. Balashov,³ M. Olle,³ G. Ceballos,³ A. Arnau,^{1,4,5} P. Gambardella,^{3,6,7}

D. Sanchez-Portal,^{1,4} and A. Mugarza³

¹Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, E-20018 San Sebastián, Spain

² IKERBASQUE, Basque Foundation for Science, E-48011 Bilbao, Spain

³Catalan Institute of Nanoscience and Nanotecnology (ICN2), UAB Campus, E-08193 Bellaterra, Spain

⁴Centro de Física de Materiales CFM - MPC, Centro Mixto CSIC-UPV, Paseo Manuel de Lardizabal 5, E-20018, San Sebastián, Spain

⁵Dpto. de Física de Materiales UPV/EHU, Facultad de Quimica, Paseo Manuel de Lardizabal 3, E-20018, San Sebastián, Spain

⁶Instituciò Catalana de Recerca i Estudis Avancats (ICREA), E-08193 Barcelona, Spain

⁷Department of Materials, ETH Zurich, Hönggerbergring 64, CH-8093 Zurich, Switzerland

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We investigate the scattering of surface electrons by the edges of graphene islands grown on Ni(111). By combining local tunneling spectroscopy and *ab initio* electronic structure calculations we find that the hybridization between graphene and Ni states results in strongly reflecting graphene edges. Quantum interference patterns formed around the islands reveal a spin-dependent scattering of the Shockley bands of Ni, which we attribute to their distinct coupling to bulk states. Moreover, we find a strong dependence of the scattering amplitude on the atomic structure of the edges, depending on the orbital character and energy of the surface states.

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Understanding electron scattering at graphene edges and domain boundaries is fundamental to control transport and quantum confinement in graphene-based electronic devices [1-3]. Edges and boundary defects play an important role in electron transport across multidomain, mesoscopic graphene layers [4,5], as well as in inducing energy gaps [6,7] and magnetic order [8] in graphene nanostructures.

A particularly relevant issue for the performance of nanodevices is the scattering of electrons at the interface between graphene and metal contacts, which determines the charge and spin injection efficiency into graphene. Weakly interacting metal contacts simply dope the Dirac bands [9,10]. In such a case, scattering depends only on the energy match between undistorted graphene and metal states. The interface with more reactive metals, however, is usually characterized by significant electronic reconstruction, which defines a complex scenario for scattering. The graphene-Ni interface represents an interesting case where the interaction with the ferromagnetic substrate opens hybridization gaps [11-14] and induces magnetic moments [15]. Consequently, graphene is predicted to behave as a perfect spin filter in contact with a magnetic Ni electrode [13,14], as suggested also by the high spin injection efficiency measured in Ni₈₀Fe20/graphene/Si heterostructures [16]. Previous studies focused on electron injection perpendicular to the interface, whereas edge scattering in the most common current-in-plane geometry, remains unexplored.

In this Letter, we investigate electron scattering at the edges of graphene on a Ni(111) substrate. We grow graphene nanoislands with well-defined edge geometries in order to simultaneously probe the electronic structure of

the vertical and lateral graphene interfaces and compare it with that of the pristine Ni surface. We find clear signatures of spin- and edge-dependent electron scattering revealed by local tunneling spectroscopy measurements combined with spin-polarized ab initio electronic structure calculations. This behavior is attributed to the strong distortion of the electronic structure at the interface, where the Ni surface states significantly shift in energy and space due to the confinement induced by the graphene layer, and to the different coupling to bulk states of majority and minority Ni states. We further demonstrate that edge scattering is strongly structure dependent, with asymmetries in the reflection amplitude of up to 30% for reconstructed and nonreconstructed zig-zag edges. These results suggest the possibility of lateral spin filtering for graphene layers, and demonstrate the importance of designing nanostructures with well-defined edges to control electron or spin transport and confinement in graphene.

The experiments were performed using a scanning tunneling microscope (STM) operated at 5 K in ultrahigh vacuum. The Ni(111) single crystal was cleaned by cycles of Ar^+ sputtering and annealing to 925 K. Graphene nanoislands were grown from the catalytic decomposition of propene (C₃H₆) on a clean Ni(111) single crystal. Islands with straight edges and either triangular or hexagonal shape were obtained by controlling the reaction temperature and annealing conditions, following the method presented in Ref. [17]. Spectroscopic measurements were performed by STM using the lock-in technique, with a bias voltage modulation of frequency 3 kHz and amplitude 1 mV_{rms} for the dI/dV spectra, and of 15 mV_{rms} for the dI/dV maps. The *ab initio* calculations of the electronic structure were



FIG. 1 (color online). (a) Topographic profile and constant height dI/dV spectra taken along the yellow line that crosses the hexagonal island in the STM image shown on the right. The standing waves arising from scattering of the S_1 and S_2 surface states are indicated by green lines. Setpoint values: I = 4 nA, $V_b = -3.0$ V. (b) dI/dV spectra of the Ni surface (black), graphene island (red), and of a Ni impurity in the island (dotted grey). (c) Calculated density of states of majority and minority states, projected onto C (red areas) and Ni (black line) atoms. Graphene bands are labeled as $G_{u/l}^{\uparrow/\downarrow}$ for spin up/down (\uparrow/\downarrow) and upper and lower band (u/l). For visualization purposes, the PDOS of Ni has been divided by 50.

carried out using density functional theory, as implemented in the SIESTA code [18]. We use a supercell description of the system, consisting of a slab containing 13 layers of Ni(111), covered by a single graphene layer on each side. For pristine Ni(111), we employ a 19-layer slab in order to avoid interactions between surface states on the two opposite sides. Further details on the calculations are given in the Supplemental Material [19].

We investigate first the local electronic structure of the graphene islands and surrounding Ni surface, focusing on how the electronic states of both graphene and Ni are mutually perturbed at the interface. Figure 1(a) shows a series of dI/dV spectra taken along a line that crosses a hexagonal graphene island and contains one impurity [arrow in Fig. 1(a)]. The impurity consists of one or more Ni atoms that get trapped during the formation of the graphene islands [17]. Representative dI/dV spectra of the Ni surface, Ni impurity, and graphene nanoisland are shown in Fig. 1(b). The spectrum acquired on graphene



FIG. 2 (color online). (a) Topographic ($V_b = 0.1$ V) and (b) constant current dI/dV maps simultaneously acquired at different energies, showing the interference patterns of the S_1 surface state scattered from graphene islands. Setpoint current: I = 0.3 nA. Image size: 30×37 nm². (c) Topographic and dI/dV profiles along the yellow line in (b), illustrating the absence of interference patterns inside the island.

shows two prominent peaks around E_F followed by a weaker and broad hump centered at about +0.80 eV. First principles calculations assign them to graphene π states [Fig. 1(c)], which split into spin-polarized gapped bands $G_{u/l}^{\uparrow/\downarrow}$ due to the strong hybridization with Ni *d* bands [13,14,19–21]. The spin-split Ni *d* bands can be clearly identified as the two sharp peaks d^{\uparrow} and d^{\downarrow} in the impurity spectrum; on the Ni surface such peaks are masked by the dominant contribution of surface states, which we label as S_1 and S_2 following the nomenclature of previous studies [22–24] (further information on the electronic structure of the surface states can be found in Fig. S2 of the Supplemental Material [19]).

In the following we will examine how the Ni surface states are affected by the interaction with graphene, and how this interaction is determinant for scattering at the graphene edge. The strong spatial variations of the dI/dV intensity outside the graphene island [green lines in Fig. 1(a)] are due to the quantum interference between incident and reflecting surface electrons. The interference patterns formed by S_1 at different energies are clearly visible in the dI/dV maps and profile shown in Fig. 2. This shows that the Ni surface states are very sensitive to the presence of graphene edges. Moreover, contrary to graphene nanoislands grown on Ir(111) [25,26], the wave patterns are absent inside the islands. Our *ab initio* calculations attribute this effect to the significant modification of the S_1 surface state below the graphene layer, which



FIG. 3 (color online). (a) Energy of the majority IFS as a function of the graphene-Ni distance. The energy of the S_1 state for pristine Ni(111) is represented by the red line. (b) Planar average of the density associated with the majority IFS at the equilibrium graphene-Ni distance (2.1 Å). (c) Topographic and constant current dI/dV maps simultaneously acquired at the energy of the IFS. Setpoint current: I = 1.2 nA. Image size: 9.7×9.7 nm². (d) Topographic profile and constant current dI/dV spectra taken along a line that goes from Ni to a graphene island [yellow line in (c)], showing the IFS and the higher lying FERs. Setpoint values: I = 1 nA, $V_b = 0.1$ V.

leads to a large energy mismatch of the surface state inside and outside the island. Such an energy mismatch depends strongly on the graphene-metal separation, as illustrated by the calculations reported in Fig. 3(a) for the majority electrons. As graphene is brought to the equilibrium distance of 2.1 Å with respect to the Ni surface plane, the S_1 state shifts in energy from slightly below E_F up to about 2.5 eV above E_F , and its spectral weight shifts towards the graphene-Ni interface [Fig. 3(b)]. This means that rather than being quenched, as concluded in Ref. [21], the surface state evolves into an interface state (IFS), as found for graphene-covered Ru(0001) [27]. The IFS can easily be identified in the constant current dI/dV spectra of Fig. 3(d). Here, field emission resonances (FERs) that originate from the tip-induced Stark shift of image states are recognized by their upward energy shift when going from graphene to Ni, due to the higher work function of the latter [27,28]. In contrast, the peak at 2.45 V is localized on the graphene island [Fig. 3(c)] and can thus be associated with the IFS predicted by our calculations at this energy. Such large energy shifts of the surface state only occur when graphene and metal states strongly hybridize and result in highly reflecting graphene edges. This is opposed to the case of less reactive metals such as Ir(111), where significant transmission of surface electrons across a graphene edge is possible due to the large energy overlap of states at the two sides [26].

The scattering of spin-split Ni surface states can lead to a lateral spin filtering effect similar to that mediated by bulk d states in the transport perpendicular to the graphene-Ni interface [13,14]. We investigate this effect by analyzing the Fourier transform of the standing wave patterns shown



FIG. 4 (color online). (a) Dispersion relation obtained from the standing wave periodicity. A parabolic curve is included as a guide (dashed line), with onset at -0.110 eV, as obtained from the dI/dV spectra. (b) Planar average density of the majority and minority S_1 states at the Γ point.

in Fig. 2(b) [29]. We find a single dispersion curve [Fig. 4(a)] with no evidence for exchange-split bands. This curve is assigned to the majority S_1^{\uparrow} sate, in agreement with all the band structure calculations reported to date, which predict S_1^{\uparrow} to be partially occupied in clear contrast to the minority S_1^{\downarrow} [19,22,23,30,31]. Another strong argument for such assignation is provided by the different surface character of majority and minority S_1 bands, as depicted in Fig. 4(b). The minority band, lying much closer to bulk states [19], presents a substantially shorter lifetime and a larger penetration into the bulk, illustrated in Fig. 4(b) by the density profile of each of those bands at Γ . At this point, S_1^{\downarrow} overlaps with bulk bands and assumes a surface resonance character. Scattering to bulk states at the graphene edge further reduces the lifetime of S_1^{\downarrow} electrons. This explains the dominant contribution of the majority states to the standing waves and supports the identification of the experimental curve in Fig. 4(a) with the dispersion of the S_1^{\uparrow} band. The overall effect is a spin-dependent scattering that is mainly due to the different absorption to bulk states at the graphene edges, as opposed to the spin-dependent transmission in the scattering of Ni d states perpendicular to the interface [13,14].

Finally, we investigate the influence of the edge geometry on electron scattering. Hexagonal islands are ideal for this purpose, since edges on adjacent sides present a distinct atomic structure, as shown in Fig. 5(a). The two different edge types correspond to an unreconstructed zig-zag edge (*n*) and a reconstructed edge (*r*) with double periodicity that is related to the so-called "57" reconstruction [32], in which the outermost hexagons are replaced by pentagons and heptagons [2]. The asymmetry in the scattering amplitude at two opposite edges is evident in Figs. 5(b) and (c). From the spectroscopic images shown in (c) we observe that reconstructed edges produce weaker dI/dV oscillations at most energies. At +1.6 V, intensity modulations also appear at the graphene side of the edge, which could either



FIG. 5 (color online). (a) Atomically resolved topographic image of the boundary of a graphene island, where reconstructed edges (*r*) exhibit twice the periodicity of the nonreconstructed ones (*n*). (b) Constant height dI/dV maps measured on a 50 × 50 grid on the hexagonal island of Fig. 1. Setpoint values: I = 4 nA, $V_b = -3.0$ V. (c) Topographic and dI/dV profiles taken along the green line in (b). For better visualization, the profiles are normalized by subtracting the dI/dV intensity of the Ni surface and divided by the intensity at the center of the island. (d) Asymmetry of the scattering intensity of n/r edges for the S_1 (black) and S_2 (red) surface state, as defined in the text. Error bars indicate the standard deviation of data obtained from different edges of the hexagon.

indicate asymmetric scattering of the graphene bands in this energy range (see Fig. S3 in Ref. [19]) or the presence of edge states. The asymmetry effect can be better quantified by measuring the dI/dV intensity $(I_{n,r})$ at the first maximum of the standing wave as a function of energy, indicated by ticks in Fig. 5(b). Both edges are excellent reflectors for the S_1 states due to the large energy shift of this band in the graphene covered region, which effectively inhibits transmission. Therefore, the peak intensity ratio for the two edge types is mainly determined by the differences in the reflection/absorption ratio [33]. Absorption here means both elastic and inelastic scattering into bulk states. Figure 5(d)shows the edge scattering asymmetry defined as the ratio $(I_n - I_r)/(I_n + I_r)$. Positive values $(I_n > I_r)$ thus imply larger absorption at reconstructed edges. We see that, for S_1 , the asymmetry increases as we go higher in energy (away from the Γ point), saturating at a value of about 30% at +0.8 V. The increment of the asymmetry is consistent with the periodicity doubling of the r edge that, due to band folding, is likely to increase the absorption into bulk. On the other hand, the downwards dispersing S_2 band shows a more complex behavior, with a negative asymmetry at Γ that changes sign at lower energy. Therefore, the edge type, electron energy, and orbital composition of the surface state concur in determining the scattering asymmetry.

In conclusion, graphene nanoislands with well-defined edge geometry grown on Ni(111) allowed us to study the scattering of two-dimensional electrons parallel to the graphene-metal interface. The strong interaction between C and Ni atoms induces a significant energy mismatch of the surface bands inside and outside graphene, quenching the transmission through the graphene edge. In the case of the S_1 surface state of Ni, this effect is modulated by the different degree of coupling to bulk states of each spin-split band, leading to pronounced spin-dependent scattering that favors the reflection of majority electrons. The atomic edge structure has a significant influence on the scattering amplitude, leading to a scattering asymmetry for the majority S_1 band of up to 30%. These results elucidate the complex scattering properties of graphene-metal interfaces and are important for the control of electron transport and quantum confinement in lateral graphene junctions with spin-polarized electrodes.

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Supplementary information for "Spin-dependent electron scattering at graphene edges on Ni(111)"

A. Garcia-Lekue,^{1,2} T. Balashov,³ M. Ollé,³ G. Ceballos,³ A.

Arnau,^{1,4,5} P. Gambardella,^{3,6,7} D. Sanchez-Portal,^{1,4} and A. Mugarza³

¹Donostia International Physics Center (DIPC),

Paseo Manuel de Lardizabal 4, E-20018 San Sebastian, Spain

²IKERBASQUE, Basque Foundation for Science, E-48011, Bilbao, Spain

³Catalan Institute of Nanoscience and Nanotecnology (ICN2), UAB Campus, E-08193 Bellaterra, Spain

⁴Centro de Física de Materiales CFM - MPC, Centro Mixto CSIC-UPV, Apdo. 1072, San Sebastian, Spain
⁵Dpto. de Física de Materiales UPV/EHU, Facultad de Química, Apdo. 1072, San Sebastian, Spain
⁶Instituciò Catalana de Recerca i Estudis Avancats (ICREA), E-08193 Barcelona, Spain

⁷Department of Materials, ETH Zurich, Schafmattstrasse 30, CH-8093 Zurich, Switzerland

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Corresponding author: A. Mugarza (aitor.mugarza@icn.cat)

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I. FIRST-PRINCIPLES SIMULATIONS

A. Computational details

The SIESTA calculations were done using the generalized gradient approximation for exchange-correlation [1] and a cutoff of 200 Ry for the real-space grid integrations. The basis set consisted of double-zeta plus polarization orbitals for all the atomic species. A $14 \times 14 \times 1$ Monkhorst-Pack mesh was used for the k-point sampling of the three-dimensional Brillouin zone. For the graphene islands on Ni(111), we employed a supercell description of the system, made up of a slab containing 13 layers of Ni(111), covered with a single graphene layer on each side and with a vacuum region of more than 10Å between both surfaces. According to previous works [2, 3], the most stable geometry for graphene on Ni(111) is the top/fcc-hollow configuration, where half of the C atoms are located on top of the Ni atoms of the first layer while the other half are at positions of the Ni atoms of the third layer (fcc hollow sites). In this work, we used this configuration for all graphene/Ni(111) calculations with a graphene/metal distance of ~ 2.1Å. For the calculations of pristine Ni(111), a supercell containing 19 layers of Ni(111) was used in order to avoid interactions among surface states localized in different surfaces.



FIG. S1. (a) Top and (b) side views of the top/fcc-hollow configuration of graphene-Ni(111) used in the calculations. For visualization purposes, only the first three Ni layers are shown in (b).

B. Electronic band structure of pristine Ni(111)

In Fig. S2(a) we have represented the band structure of Ni(111) for majority and minority bands. As previously reported [2, 3], majority d bands lie below Fermi level, whereas the minority d bands are higher in energy and cross the Fermi energy. Regarding surface states, at the Γ point the S_1 majority state is located below Fermi level but it does not hybridize with d bands, so that it has a pure surface state character. The minority state instead is above Fermi energy and strongly hybridizes with d bands, thus becoming a surface resonance state rather than a pure surface state. For this reason, whereas the majority S_1 state at the Γ point can be easily distinguished, further inspection of the electronic band structure is required for the detection of the minority S_1 state. With this purpose, we have looked at the band structure projected on Ni s and p orbitals. As expected, the majority S_1 state has a strong sp character and it is clearly identified at the Γ point. For the minority bands, although the S₁ state is not a pure sp state at the Γ point due to the strong hybridization with d bands, it recovers its sp character as we move away from the Γ point. In this way, and with the additional information provided by the analysis in Fig. S2(b), we are able to identify both majority S_1 surface state and minority S_1 resonance state at the Γ point shown by arrows in Fig. S2(a). The position of the S_1 state is found to be quite sensitive to the calculation method, as concluded from the spread in values reported in previous calculations [2, 4–6]. An uncertainty of at least 200 meV depending on the details of the calculations is observed, although in all cases the bottoms of the majority and minority S_1 bands are, respectively, occupied and unoccupied. However, despite this uncertainty, our overall description of the surface electronic structure is found to be in very good agreement with existing theoretical and experimental information for Ni(111)[2, 4-6]. The planar averaged density of states of S_1 states at the Γ point is exhibited in Fig. 4(b) of the manuscript.

Majority and minority S_2 surface states, on the other hand, are both located well below Fermi level and, due to their strong hybridization with d bands around the Γ point, they are not easily trackable in Fig. S2(a). For this reason, we have represented the band structure of Ni(111) along the Γ M direction projected onto the surface Ni atoms, as shown

in Fig. S2(b). This projection allows a straightforward identification of majority and minority S_2 states around the Γ point, in good agreement with previous works [5, 6].



FIG. S2. (a) Majority (left panel) and minority (right panel) electronic band structure of Ni(111) system. The color of the lines represent the Ni-s (blue) or Ni-d (black) character of each electronic state. S_1 majority surface state and S_1 minority resonance state at the Γ point are highlighted by red arrows. (b) Zoomed-in view of the Ni(111) band structure within the selected area depicted by green rectangles in (a). The color of the lines is related with the surface character of each band: red lines represent bands fairly localized at the surface (dominant weight from surface atoms), whereas gray lines represent bands with small weight on surface atoms. S_1 majority surface and minority resonance states, as well as S_2 majority and minority resonance states at the Γ point are highlighted by red labels.

C. Electronic band structure of graphene/Ni(111)

Figure S3 shows the majority and minority electronic band structure of graphene/Ni(111) for different graphene-Ni distances (d_{G-Ni}). As d_{G-Ni} increases (see Fig. S2a), the band structures of isolated graphene and Ni(111) are gradually recovered. In particular, we observe the shift in the energy of the interface state and the closing of the Dirac bands. For $d_{G-Ni} = 4.5$ Å, we basically regain the superimposed band structures of graphene and pristine Ni(111).



FIG. S3. Majority (left panel) and minority (right panel) electronic band structure of graphene-Ni(111) system for d_{G-Ni} equal to (a) 4.5Å, (b) 3.3Å, (c) 2.7Å and (d) 2.1Å. The radius of the red circles represent the C character and the color of the lines the Ni-s (blue) or Ni-d (black) character of each electronic state. In Fig. S3(d), the IFS at the Γ point is highlighted by a green arrow.

II. EFFECT OF NI IMPURITIES ON THE ELECTRONIC PROPERTIES OF GRAPHENE

At the temperature where graphene nanoislands are formed, namely at 450° C, Ni atoms diffuse and some of them get trapped in the nanoislands. Whereas their presence during the chemical reaction can play an important role in the nucleation of the islands, the effect on the electronic structure is very local, limited to the impurity site, as shown in Fig. S4. Here we reproduce the dI/dV series of Fig. 1a of the main text, taken along an impurity, and compare it with another series acquired at the same island, but which does not cross any impurity. The lack of any variation in the spectral signal of the latter along the whole island reflects the homogeneity of the electronic structure away from impurities. The range of the electronic perturbation induced by the impurity can be quantified by plotting the spatial distribution of the dI/dV signal around the Ni impurity at the energy of the majority d level (-0.5 eV). This is done in Fig. S4(d), where the topographic profile at the same location is added for comparison. The extension of the spectroscopic signal, 6 Å FWHM, is comparable to the topographic signal coming from the impurity, of 5.5 Å, which is in turn a typical value for the width of single atom impurities measured by STM.



FIG. S4. Topographic profile and constant height dI/dV spectra taken along a line without (a) and with (b) impurities. The lines are indicated in the topographic image of (c). Set point values: I = 4 nA, $V_b = -3.0$ V. (d) Spatial distribution around the impurity of the dI/dV signal at -0.5 eV [purple line in (b)], and the corresponding topographic signal.

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