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Valley-polarized massive charge carriers in gapped graphene

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The lifting of the fourfold degeneracy of the zeroth Landau level in graphene under high magnetic fields has been the subject of numerous experimental studies, and attributed to various mechanisms such as pure spin splitting, spin splitting combined with subsequent valley splitting, or the formation of a quantum Hall insulator. Unexplored, however, is the influence of an energy gap on the quantum Hall effect (QHE) states in graphene. Here we demonstrate, using measurements of the magnetoresistance of graphene antidot lattices (GALs) in magnetic fields up to 30 T and temperatures between 2 and 100 K, that gap opening in these samples is accompanied by valley polarization and a change from linear to parabolic band structure at low carrier energies. The emergence of a massive character of the carriers profoundly alters the transport characteristics of the zeroth Landau level, which manifests itself in a linear increase of the activated gap with magnetic field. Furthermore, samples of the highest quality display spin splitting on top of the valley splitting, albeit of significantly smaller magnitude.

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I. INTRODUCTION

Graphene’s remarkable electronic properties arise from its peculiar lattice structure with two different sublattices, which leads to a linear energy dispersion wherein the valence and conduction band meet at the charge neutrality point (CNP).1 As a characteristic feature of graphene, its $N = 0$ Landau level (LL) is equally shared by electrons and holes, with the fourfold degeneracy originating from the spin and sublattice symmetry (pseudospin). High magnetic fields can lift the degeneracy,2–4 which has mainly been ascribed to electron-electron interactions4,5 or the Zeeman effect.2,3,6,7 Recently, the issue of whether the symmetry breaking favors “spin-first, valley-later” splitting or vice versa has attracted increasing attention. Preferential valley splitting could for example provide access to a valley Hall effect, wherein carriers in different valleys flow to opposite transverse edges upon application of an in-plane electric field. The valley Hall effect belongs to the same category of Berry-phase supported topological transport phenomena as its counterpart, the spin Hall effect.9

Despite the progress in exploring the zeroth LL of pristine graphene, only little is known about the impact of an energy gap on the LL splitting hierarchy in graphene. Addressing this question requires a method to reliably introduce a band gap.10 One possible strategy is to introduce lateral confinement in the form of a graphene antidot lattice (GAL).11 According to theory, GALs have a fundamental band gap that scales inversely with the neck width between the nanoholes, akin to graphene nanoribbons.12–14 From the experimental side, a transport gap, whose magnitude increases with decreasing neck width,15 has been observed, although unequivocal proof for the presence of a fundamental band gap has remained elusive so far.16 Theory furthermore predicts that an isolated graphene antidot in a magnetic field causes breaking of the electron-hole symmetry in the individual valleys.17 Here we present magnetotransport data acquired from GALs of different geometry, demonstrating that the antidot confinement potential opens a gap which induces a parabolic dispersion for electrons and holes. The associated valley-split lowest LLs are found to be attached to this parabolic, and accordingly the actual gap measured is composed of the zero-field gap plus the cyclotron energy.

II. EXPERIMENTAL RESULTS AND DISCUSSION

A. Experiment

An example of the investigated GALs, electrically contacted in Hall bar geometry, is displayed in Fig. 1(a). A series of pristine graphene and GAL devices were fabricated either on a Si/SiO2 substrate or freely suspended, following a previously described procedure.18 The CNP of the samples typically ranged between $V_{\text{CNP}} = 5$ and 20 V, while for the suspended flakes it was located close to zero gate voltage ($V_{\text{CNP}} = 0$ V) after current annealing. Electrical measurements were performed by standard ac lock-in techniques with an input impedance of 100 MΩ down to $T = 1.4$ K and under external magnetic fields up to 30 T. We investigated a total of 13 devices on 7 different substrates, with a maximum carrier mobility of 5.000 cm²/V s reached for GALs on SiO2, and up to 20.000 cm²/V s for suspended devices.

B. Divergence of magnetoresistance

In Fig. 1(a) the magnetic field-dependent electrical resistance at the CNP and $T = 1.4$ K is depicted for nonstructured graphene and two different GALs with a nanohole spacing of 100 and 200 nm, respectively. The pristine graphene exhibits a monotonous positive magnetoresistance at low magnetic fields, most likely arising from spatial carrier mobility fluctuations.20 Under higher $B$ fields (>10 T), in the quantum Hall regime, the resistance increase becomes more pronounced, indicative of degeneracy lifting of the zeroth
LL. By comparison, the GAL with 100 nm nanohole spacing features a quasilinear negative magnetoresistance up to \( \sim 1 \) T, ascribable to a change of the hopping probability between localized states in this regime.\(^{18,21-23}\) At higher \( B \) fields, the sample displays a diverging, positive magnetoresistance. A similar behavior has been observed for several other 100 nm spacing samples, and also for the GAL with 200 nm nanohole spacing, albeit with a weaker resistance increase in the latter case. Figure 1(b) reveals that for the \( B \) field range between 6 and 25 T, the minimum conductivity of a 100 nm spacing GAL as a function of inverse temperature can be well fitted by the Arrhenius equation\(^ {24}\) \[ \sigma \propto \exp(-E_a/2k_B T), \]
where \( E_a \) is the activation gap.

To further analyze the diverging magnetoresistance we explore the carrier concentration dependence of both the Hall and longitudinal resistance. The Hall resistance of a 10 nm spacing GAL device (\( V_{\text{CNP}} = 15.5 \) V) is depicted in Fig. 2(a) as a function of the voltage \( V = V_G - V_{\text{CNP}} \), with the back gate voltage \( V_G \). The resistance plateaus observed at \( R_{xy} = \{\pm 2h/e^2, \pm 6h/e^2, \ldots\} \) corresponding to filling factors \( \nu = \{\pm 2, 6, \ldots\} \) are characteristic of the LL pattern of pristine graphene. At temperatures above 30 K, there is a smooth zero transition of \( R_{xy} \) between the \( \nu = -2 \) and \( \nu = +2 \) plateaus, even at the highest \( B \) field (see data at 88 K).

This behavior is similar to pristine graphene, and testifies a finite, equal density of electrons and holes near the CNP.\(^ {25}\) However, below 30 K, \( R_{xy} \) diverges at small charge carrier densities \( q \), and does not cross zero anymore for magnetic fields above 10 T. The divergence of the Hall resistance follows a \((\pm 1/q)\) dependence away from the quantized \( \nu = \pm 2 \) plateaus, and occurs at higher absolute voltages \( |V_G - V_{\text{CNP}}| \) with increasing \( B \) field. Correspondingly, the longitudinal (\( \sigma_{zx} \)) and transverse (\( \sigma_{yx} \)) conductivity flatten into a zero plateau toward the CNP upon crossing from filling factor \( \nu = -2 \) to \( \nu = +2 \) [see Fig. 2(b)]. Close to the CNP no current could be detected within the digitalization limit, revealing the presence of an insulating state. The Hall data, taken together with the temperature dependent conductivity and diverging magnetoresistance, prove the presence of a fundamental energy gap in the GALs.

**FIG. 1.** (Color online) (a) Lateral four-probe magnetoresistance of GALs with 100 nm (solid green line) and 200 nm spacing (dashed red line), and a pristine graphene device (short dashed black line). Right inset: Zoom of the magnetoresistance in the main panel. Left inset: Scanning electron micrograph (scale bar is 1 \( \mu \)m) of a typical Hall bar device with 100 nm nanohole spacing. The current leads and Hall probe contacts are colored yellow and green, respectively. (b) Arrhenius plot of the conductivity at the CNP of the 100 nm spacing sample for magnetic fields between 6 and 25 T.

**C. Valley-first splitting of the \( N = 0 \) LL**

The Hall resistance data in Fig. 2(a) provide direct access to the electron and hole density via the inverse Hall coefficient \( \nu = (e/2h)R_{xy} \), where \( R_{xy} \) is the Hall resistance. For \( T < 4 \) K, \( R_{xy} \) diverges, while outside the insulating region the usual graphene QHE plateaus occur at filling factors \( \nu = \{\pm 2, \pm 6, \pm 10, \ldots\} \) (dashed gray horizontal lines). (b) Longitudinal and transverse conductivity of the same sample. The shaded area indicates the insulating regime. (c) Concentration of electrons (positive values) and holes (negative values), as determined from the Hall data. At \( T = 88 \) K (dash-dotted red line \( B = 15 \) T; dashed red line \( B = 30 \) T) electrons and holes coexist at the CNP. At \( T = 4 \) K (solid blue line \( B = 15 \) T; dashed blue line \( B = 30 \) T), the gap region emerges. The three light gray curves (solid bold, solid fine, and dashed) are ideal curves representing pure electron or hole conduction outside the gap for different gap sizes.

**FIG. 2.** (Color online) (a) Hall resistance measured at \( V_{\text{CNP}} = 15.5 \) V for \( T = 4 \) K and \( T = 88 \) K, each at magnetic fields of \( B = 15 \) T and \( B = 30 \) T. For temperatures above the band gap (\( T = 88 \) K), the Hall resistance shows a smooth, monotonous zero crossing around the CNP. Below the band gap (\( T = 4 \) K), the Hall resistance diverges, while outside the insulating region the usual graphene QHE plateaus occur at filling factors \( \nu = \{\pm 2, \pm 6, \pm 10, \ldots\} \) (dashed gray horizontal lines). (b) Longitudinal and transverse conductivity of the same sample. The shaded area indicates the insulating regime. (c) Concentration of electrons (positive values) and holes (negative values), as determined from the Hall data. At \( T = 88 \) K (dash-dotted red line \( B = 15 \) T; dashed red line \( B = 30 \) T) electrons and holes coexist at the CNP. At \( T = 4 \) K (solid blue line \( B = 15 \) T; dashed blue line \( B = 30 \) T), the gap region emerges. The three light gray curves (solid bold, solid fine, and dashed) are ideal curves representing pure electron or hole conduction outside the gap for different gap sizes.
For a semiconductor with two types of charge carriers, the densities are related to the Hall coefficient by:

\[ \frac{1}{R_H} = B/R_{xy}, \]

where \( n \) and \( p \) are the electron and hole densities, and \( \mu_n \) and \( \mu_p \) are the corresponding mobilities. This simple two-carrier model is applicable to graphene despite the presence of electron-hole puddles since tunneling between the corresponding areas can occur. In the present samples, the conductance of massive charge carriers approaches a density of \( q = n + p \), while the hole density \( p \) approaches zero (vice versa for the \( n \)-type regime). At the CNP the carrier density is \( q = n + p \), whereas the spin degeneracy is preserved, as illustrated in Fig. 3. Support for this conclusion derives from the fact that \( R_{CNP} \) depends only on the perpendicular \( B \)-field component rather than the total \( B \) field (see Fig. 4). In these measurements, the sample was rotated out-of plane by an angle \( \theta \) relative to the sample orientation perpendicular to the external field. As exemplified for constant total fields of \( B_{tot} = 1, 6, 12, \) and \( 14 \) T, the angle-dependent resistance at these magnetic fields coincides with the values recorded at zero angle, where \( B_{tot} (\theta = 0^\circ) = B_{perp} (\theta) \). Moreover, the minimum resistance remains unchanged upon keeping the perpendicular field constant at different values of \( B_{tot} \) (see inset), with corresponding angle \( \theta \) \([B_{perp} = B_{tot} \cos(\theta)]\). Both data sets confirm that the gap is not related to Zeeman splitting.

\[ \Delta V = \alpha V - \Delta q, \]

resulting in \( n \)-type conduction with \( p = 0 \) and \( n = q \).

Since valley-first splitting is a necessary and sufficient condition for the occurrence of a diverging Hall resistance, it follows that the gap separates electrons and holes into two valley split \( N = 0 \) LLs, whereas the spin degeneracy is preserved. In the present samples, the zero crossing has vanished (see Fig. 2(a)), indicating that the gap is not related to Zeeman splitting.

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assuming a parabolic dispersion (Zeeman term the LL positions. The red dashed lines represent the LLs in pristine graphene ($E_g$ gap values representing linear fits. The dashed lines correspond to the calculated suspended (blue triangles) spacing samples, with the full lines for the 100 nm (black squares), 200 nm (red circles), and 100 nm broadening by the antidot lattice.13–15 Under an applied magnetic field, tentatively explained on the basis of a small band gap introduced (see Fig. 3). In the QHE regime, the two levels indicate that the gap opening in GALs is accompanied by the emergence of a parabolic energy dispersion in vicinity of the gap13–15 (see Fig. 3). In the QHE regime, the two levels originating from the $N = 0$ LL reside within this parabolic dispersion region, whereas the higher ($N \neq 0$) LLs remain in the linear dispersion regime and are hence expected to mirror the LL structure of pristine graphene. The parabolic dispersion regime can be described by

$$E(k) = \pm \frac{\hbar^2 k^2}{2m} + \frac{E^0_g}{2},$$

where $m$ is the mass, $E^0_g$ is the zero-field band gap originating from the antidot lattice, and the $\pm$ sign accounts for electrons and holes, respectively. The energy of the two $N = 0$ LLs is therefore given by

$$E_\pm = \pm \frac{1}{2} \left( \hbar \omega_c + E^0_g \right),$$

with the cyclotron frequency $\omega_c = eB/m$. The magnetic field dependent band gap is thus given by $E_g = E_+ - E_- = \hbar eB/m + E^0_g$, where $m = m_{\text{eff}}m_e$, with $m_e$ as the free electron mass. The LL energies can be related to the experimentally accessible gate voltages by rewriting Eq. (3) in terms of the gate voltage by using $V = q/\alpha = k^2/2\pi \alpha = E_m/\pi h^2 \alpha$, which leads to

$$V_\pm = \pm \frac{1}{2} \left( \frac{eB}{\alpha \pi \hbar} + \frac{m_{\text{eff}}m_e}{\alpha \pi \hbar^2} E^0_g \right),$$

where $V = V_G - V_{\text{CNP}}$. Thus, in a parabolic dispersion $V$ depends linearly on the magnetic field. Note that in the linear dispersive regime, the gate voltage positions of the $N \neq 0$ LLs also depend linearly on $B$ field. This is apparent from the conversion of $E = \sqrt{\left(2e\hbar^2/\pi B\right)N}$ to gate voltage positions using $V = q/\alpha = E^2/[\pi \hbar^2 (\pi f)^2 \alpha]$, which yields $V_\pm = \pm 2eB|N|/(\pi \hbar \alpha)$.

The $B$-field dependent LL positions for the 100 nm spacing sample are visualized in the LL fan diagram of Fig. 6(a), where the first derivative of the inverse Hall resistance $-d(1/R_{xy})/dV$ is plotted as a function of both gate voltage and magnetic field. The maxima within the green regions in the fan diagram mark the transitions from one QHE plateau to the following, and therefore represent the center of a LL. The black lines are fits to Eq. (4), which yield an effective mass $m_{\text{eff}} = 0.08$ and a zero-field gap $E^0_g = 22.0$ K. The latter value is in good agreement with the estimated gap size of $E^0_g \approx 15$ K for similar GALs at zero magnetic field.23 A gate coupling factor of $\alpha = 8.5 \times 10^{10}$ cm$^2$ V$^{-1}$ was extracted from the slope of the higher LLs (red dash-dotted lines). The slightly increased $\alpha$ results most likely from inhomogeneous electric field effects,
analogous to observations made on graphene nanoribbons. In the same manner, values of \( E_g^0 = 14.5 \text{ K}, \alpha = 7.2 \times 10^{10} \text{ cm}^{-2} \text{ V}^{-1} \), and \( m_{\text{eff}} = 0.10 \) were obtained for the 200 nm spacing sample, and \( E_g^0 = 33.0 \text{ K}, \alpha = 5.0 \times 10^{10} \text{ cm}^{-2} \text{ V}^{-1} \), and \( m_{\text{eff}} = 0.08 \) for the suspended 100 nm spacing sample.

Combining the extracted values of \( m_{\text{eff}} \) and \( E_g^0 \) with Eq. (3) provides the \( B \)-field dependent gap between the two \( N = 0 \) LL center positions. In Fig. 5 this actual LL gap (dashed lines) is compared to the activation gaps (symbols). Since the activation gap is the distance between the mobility edges of the two broadened LLs, the difference between the activation gap and the actual gap corresponds to the LL broadening (see right part of Fig. 3). The extent of the LL broadening differs depending on the amount of disorder. From the plot, the LL broadening is estimated to be \( \Gamma = (90 \pm 10), (120 \pm 10), \) and \( (30 \pm 10) \text{ K} \) for the 100, 200, and suspended 100 nm spacing sample, respectively. The latter broadening is appreciably smaller than the value of \(~100 \text{ K} \) reported for pristine (nonsuspended) graphene at low temperatures. It is furthermore noteworthy that a linear instead of parabolic energy dispersion could not account for the observed magnetic field behavior. In fact, this would result in a quite weak, square-root-like dependence of the energy gap on the field,1

\[
E_g^0 = \left( 1 - \frac{E}{g^*} \right) \sqrt{2\pi \Gamma}. 
\]

When spin splitting is included, the estimated LL broadening decreases to \( \Gamma = 60 \text{ K} \) for the 200 nm spacing sample, and \( \Gamma = 20 \text{ K} \) for the suspended 100 nm spacing sample, as derived from the field at which the spin splitting becomes visible. This results in respective exchange energies of \( E_{\text{gs}}^0 = 100 \text{ K} \) and \( E_{\text{gs}}^0 = 30 \text{ K} \), which correspond well with \( E_{\text{gs}}^0 = 130 \text{ K} \) reported for pristine graphene.

### III. Conclusion

The observed QH insulator behavior points toward valley-first splitting in the GALs provided that the charge carriers would be associated with different valleys in the lowest LL, similar to the case of pristine graphene. Due to the possibility of sizable intervalley scattering, however, the situation might be more complicated than for unstructured graphene, such that further studies are needed to determine the effect of the periodic nanohole array on the quasiparticle properties. From an application perspective, valley-first splitting could be exploited for graphene-based valleytronic devices such as gate-tuned valley filters or beam splitters. To this end, GAL devices of improved mobility (e.g., by use of BN) would be highly beneficial. In addition, the emergence of a massive character of the charge carriers is relevant for all graphene semiconductor applications that rely upon a band gap introduced by spatial confinement, like in, e.g., nanoribbons. In fact, the introduction of a charge carrier mass at low carrier densities might alter other properties unique to graphene.

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