How Perfect Can Graphene Be?

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We have identified the cyclotron resonance response of the purest graphene ever investigated, which can be found in nature on the surface of bulk graphite, in the form of decoupled layers from the substrate material. Probing such flakes with Landau level spectroscopy in the THz range at very low magnetic fields, we demonstrate a superior electronic quality of these ultralow density layers ($n_0 \approx 3 \times 10^9$ cm⁻²) expressed by the carrier mobility in excess of 10^7 cm²/(V · s) or scattering time of $\tau \approx 20$ ps. These parameters set new and surprisingly high limits for intrinsic properties of graphene and represent an important challenge for further developments of current graphene technologies.

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The fabrication of graphene structures has triggered a vast research effort focused on the properties of twodimensional systems with massless Dirac fermions. Nevertheless, further progress in exploring this quantum electrodynamics system in solid-state laboratories seems to be limited by the insufficient electronic quality of manmade structures, and the crucial question arises as to whether existing technologies have reached their limit or major advances are in principle possible. The substrate, and more generally any surrounding medium, has been recently identified as a dominant source of extrinsic scattering mechanisms, which effectively degrade the electronic quality of currently available graphene samples [1,2]. Despite significant advances in technology, including the fabrication of suspended specimens [3,4], the realistic limits of the scattering time and mobility in graphene, achievable after elimination of major extrinsic scattering sources, remain an open issue. Experiments call for higher quality samples, which are almost certainly crucial for possible verification of interesting predictions concerning basic phenomena of quantum electrodynamics (e.g., Zitterbewegung) or observation of the effects of interactions between Dirac fermions, (resulting, e.g., in the appearance of the fractional quantum Hall effect). Even more simple effects such as lifting the degeneracy of the spin and/or pseudospin degree of freedom in very high magnetic fields indicate the strong influence of the sample quality on the information that can be deduced from experiments [5,6].

Recently, well-defined graphene flakes have been discovered in the form of sheets, decoupled from, but still located on the surface of bulk graphite which naturally serves as a well-matched substrate for graphene [7]. In this Letter, we report on response from these flakes in microwave magneto-absorption experiments and show that their Dirac-like electronic states are quantized into Landau levels (LLs) in magnetic fields down to 1 mT and at elevated temperatures up to 50 K. The deduced unprecedented quality of the studied electronic system sets surprisingly high limits for the intrinsic scattering time and the corresponding carrier mobility in graphene.

The cyclotron resonance (CR) has been measured in a high-frequency EPR setup in double-pass transmission configuration, using the magnetic-field-modulation technique. A flake of natural graphite was placed in the variable temperature insert of the superconducting solenoid and via quasioptics exposed to the linearly polarized microwave radiation emitted by a Gun diode at frequencies 283.2 or 345 GHz (1.171 or 1.427 meV). The absorbed radiation has been followed by either heterodyne detection (283.2 GHz) or by the bolometer (345 GHz). To enhance the relatively weak response of graphene flakes, the modulation amplitude ($\Delta B \sim 0.5$ mT) had to be chosen close to the CR width, which broadens resonances observed at lower fields. All spectra have been corrected for the remanent field of the magnet.

Our main experimental finding is illustrated in Fig. 1. The traces in this figure represent the magneto-absorption response of the natural graphite specimen at different temperatures, measured as a function of the magnetic field at fixed microwave frequency. They correspond to the derivative of the absorption strength with respect to the magnetic field since the field modulation technique has been applied. Strong at 7.5 K, but rapidly vanishing with temperature lines marked with numbered arrows in Fig. 1 can be easily recognized as CR harmonics of K point electrons in bulk graphite. A possible origin of the temperature dependent transition marked with the star will be discussed later on. The features of primary interest, which we argue are due to decoupled graphene sheets on the graphite surface, are seen at very low fields, within the yellow highlighted area of Fig. 1.

The interpretation of these low-field data is schematically illustrated in Fig. 2. The observed spectral lines



FIG. 1 (color online). Magneto-absorption spectra (detected with field modulation technique) of natural graphite specimen taken in the temperature interval 7.5–50 K at fixed microwave energy $\hbar \omega = 1.171$ meV. The response of low electron concentration graphene layers decoupled from bulk graphite is seen within the yellow highlighted area. High CR harmonics of K point electrons in bulk graphite [21], with basic CR frequency ω_c corresponding to the effective mass $m = 0.054m_0$ [20] are shown by numbered arrows. The origin of features denoted by stars is discussed in the text.

[Fig. 2(a)] are assigned to cyclotron resonance transitions between adjacent LLs ($|\Delta n| = 1$) with energies: $E_n =$ $\operatorname{sign}(n)\tilde{c}\sqrt{2e\hbar B|n|} = \operatorname{sign}(n)E_1\sqrt{B|n|}$ [8,9], characteristic of massless Dirac fermions in graphene sheets with an effective Fermi velocity \tilde{c} . This velocity is the only adjustable parameter required to match the energies of the observed and calculated CR transitions. A best match is found for $\tilde{c} = (1.00 \pm 0.02) \times 10^6 \text{ m} \cdot \text{s}^{-1}$ in fair agreement with values found in multilayer epitaxial graphene [10,11] or exfoliated graphene on Si/SiO₂ substrate [12– 14]. As can be seen from Figs. 2(b) and 2(c), the multimode character of the measured spectra is directly related to thermal distribution of carriers among different LLs. The intensity of a given transition is proportional to the difference in thermal occupation of the involved LLs. Roughly speaking, the strongest transitions imply LLs in the vicinity of the Fermi level, which fixes E_F at around 6–7 meV from the Dirac point.

To reproduce the experimental data, we assume the absorption strength is proportional to the longitudinal con-



FIG. 2 (color online). Magneto-absorption spectrum (after removing a weak linear background seen in the raw data of Fig. 1) measured at T = 25 K and microwave frequency $\hbar \omega = 1.171$ meV (a) in comparison with the LL fan chart (b), where the observed cyclotron resonance (CR) transitions are shown by arrows. The occupation of individual LLs is given by the Fermi-Dirac distribution plotted in the part (c). For simplicity, we considered only *n*-type doping with $E_F = 6.5$ meV. The dashed lines show positions of resonances assuming $\tilde{c} = 1.00 \times 10^6 \text{ m} \cdot \text{s}^{-1}$.

ductivity of the system:

$$\sigma_{xx}(\omega, B) \propto (B/\omega) \sum_{m,n} M_{m,n} \frac{f_n - f_m}{E_m - E_n - (\hbar\omega + i\gamma)},$$

where f_n is the occupation of the *n*-th LL, and $M_{m,n} = \alpha \delta_{|m|,|n|\pm 1}$ with $\alpha = 2$ for *n* or *m* equal to 0, otherwise $\alpha = 1$ [10,15]. The calculated traces in Fig. 3 have been drawn taking $\gamma = 35 \ \mu eV$ for the line broadening, $\tilde{c} = 1.00 \times 10^6 \text{ m} \cdot \text{s}^{-1}$ and $E_F = 6.5 \text{ meV}$. To directly simulate the measured traces, the derivative of the absorption with respect to the magnetic field has been calculated taking account of the field modulation $\Delta B = 0.5 \text{ mT}$ used in the experiment. In spite of its simplicity, our model is more than in a qualitative agreement with our experimental data, see Fig. 3. The calculation fairly well reproduces the experimental trends: the multimode character of the spectra, the intensity distribution among the lines, as well as its evolution with temperature; and it allows us to estimate the characteristic broadening of the CR transitions.

Our modeling could be further improved but at the expense of additional complexity which we want to avoid here. Assuming magnetic-field and/or LL index dependence of the broadening parameter γ and taking into account the possible fluctuation of the Fermi level within



FIG. 3 (color online). Background-removed magnetoabsorption spectra from experiment at T = 25 and 40 K (black curves) in comparison to the response at the microwave frequency $\hbar\omega = 1.171$ meV calculated for parameters $\tilde{c} = 1.00 \times 10^6 \text{ m} \cdot \text{s}^{-1}$, $\gamma = 35 \ \mu\text{eV}$, and $E_F = 6.5 \text{ meV}$. The dashed lines show the calculated positions of the CR transitions.

the ensemble of probed flakes would improve the agreement between experiment and theory, particularly at low temperatures. Comparing both, the measured and simulated traces, we are also more confident in the spectacular observation of the CR transition (involving the n = 0 LL) at a magnetic field as low as 1 mT. Bearing in mind the small value of the extracted broadening parameter, one may conclude that LL quantization should survive in studied graphene layers down to the field of B = $(\gamma/E_1)^2 \approx 1 \ \mu$ T. Hence, the magnetic field of the Earth of ~50 μ T is no longer negligibly small. Instead, it can open an energy gap at the Dirac point up to $\Delta \approx 0.3$ meV, depending on the sample orientation.

To crosscheck our interpretation, we have also measured the spectra using a different (higher) microwave energy $\hbar\omega = 1.427$ meV, see Fig. 4. Despite the weaker sensitivity of the experimental setup at this frequency, we can clearly identify the same set of inter-LL transitions simply shifted to higher magnetic fields.

The finite Fermi energy $E_F \approx 6-7$ meV, corresponding to a carrier density of $n_0 \approx 3 \times 10^9$ cm⁻², indicates that the probed layers are in thermodynamical contact with the surrounding material, which supplies these carriers. On the other hand, we find no signs of electrical coupling of these graphene layers to bulk graphite. Our experiments show that any possible energy gap opened due to this interaction at the Dirac point cannot exceed a few hundred μ eV. The absence of this gap convincingly confirms that we are indeed dealing with decoupled graphene and not with the *H* point of bulk graphite, where Dirac-like fermions are also present [16] but a (pseudo)gap of a few meV is expected [17] and indeed observed [18]. The temperature evolution of the measured spectra is another important



FIG. 4 (color online). Positions of CRs at microwave energies $\hbar \omega = 1.171$ and 1.427 meV. Each position represents an average value obtained at different temperatures. One background-removed CR spectrum at each microwave frequency with a high number of observed CRs is shown in the inset. The grey curves show positions of CRs for $\tilde{c} = 1.00 \times 10^6 \text{ m} \cdot \text{s}^{-1}$.

indication allowing us to discriminate between the graphene and bulk graphite contributions. No (or very weak) temperature broadening of CR transitions is expected for graphene [3,11,19], whereas the response of bulk graphite should follow the relatively strong decrease of the carrier scattering time, expressed by the average mobility, which reaches up to $10^6 \text{ cm}^2/(\text{V} \cdot \text{s})$ at low temperatures, but falls down by 1 order of magnitude at $T \approx 50$ K [20]. Indeed, this behavior is observed in Fig. 1. Whereas the CR harmonics of K point electrons in bulk graphite [21] seen in the spectra at $|B| \ge 20$ mT, disappear very rapidly upon increasing T, the graphenelike features survive and their intensity is simply following the vanishing difference in the occupation between the adjacent LLs. It is worth noticing that the graphenelike signal, although always substantially weaker then the response from bulk graphite, has been observed for a number of different specimens of natural graphite. Mechanical scratching of the sample surface and the fast thermal cooling have been found to enhance the signal from decoupled graphene compared to bulk graphite, likely helping in detaching graphene sheets from the graphite crystal.

Since the well-defined LL quantization in our graphene flakes is observed down to |B| = 1 mT, see Fig. 2, we obtain via the semiclassical LL quantization condition $\mu B > 1$ the carrier mobility $\mu > 10^7$ cm²/(V · s), almost 2 orders of magnitude higher in comparison with suspended [2–4] or epitaxial graphene [11]. The LL broadening γ , obtained via comparison of our experiment with the simulated traces, allows us to estimate the scattering time $\tau \approx 20$ ps ($\tau = \hbar/\gamma$), which significantly exceeds those reported in any kind of man-made graphene samples,

see, e.g., Refs. [2,3], and gives an independent estimation for the mobility $\mu = e\tau \tilde{c}^2/E_F \approx 3 \times 10^7 \text{ cm}^2/(\text{V} \cdot \text{s})$ in good agreement with the estimate above. Even though we cannot verify this estimate by a direct electrical measurement, a near correspondence of the scattering time derived from CR measurements and transport scattering time was recently verified on samples with a significantly lower mobility [12]. Moreover, the estimated mobility should not decrease with temperature, as no broadening of CRs is observed up to T = 50 K, when CR intensities become comparable with the noise. This extremely high value of mobility combines two effects: the long scattering time τ and a very small effective mass $m = E_F / \tilde{c}^2 \approx$ $2 \times 10^{-4} m_0 E_F$ [meV]. Remarkably, the same scattering time in a moderate density sample $(n_0 = 10^{11} \text{ cm}^{-2})$, would imply the mobility still remaining high, around $\mu \approx$ 5×10^6 cm²/(V · s), and comparable to best mobilities of two-dimensional electron gas in GaAs structures at these densities.

The model we used here to describe the magnetoabsorption response of Dirac fermions is amazingly simple, based on a one-particle approximation, and it is perhaps surprising that it is so well applicable to simulate the experimental data, particularly in context of the outstanding quality of the electronic system studied. At first sight, the observation of collective excitations, due to, e.g., magneto-plasmons, could be expected in our experiments, and only preliminary theoretical work addresses the surprising approximate validity of Kohn's theorem in graphene [22,23]. Also, size-confined magneto-plasmons are apparent in the microwave-absorption spectra of twodimensional gas of massive electrons [24], but apparently not seen in our experiments on graphene. This perhaps points out the qualitative difference in the plasmon behavior in systems with quadratic and linear dispersion relations [25,26]. On the other hand, we speculate that the transition, marked with stars in Fig. 1, has a character of a collective excitation. The energy of this excitation softens with temperature and can be deduced to scale roughly as B/T, which points towards its magnetic origin. For example, B/T energy scaling is typical of a ferromagnetic resonance, see, e.g., Ref. [27]. Nevertheless, the origin of this spectral feature remains an intriguing puzzle. We see this feature repeatedly on different samples, but at slightly different energies, each time however characteristically evolving with temperature. With its apparent magnetic characteristics, one should seek its origin in impurities [28], structural defects [29], or edge states [30] in graphene, but possibly also on the surface of bulk graphite [31].

To conclude, graphene layers decoupled from bulk graphite have been probed in CR experiment, which offers unambiguous evidence of extremely high carrier mobility in graphene exceeding $10^7 \text{ cm}^2/(\text{V} \cdot \text{s})$. This measurement significantly shifts the limits of intrinsic mobility in gra-

phene [19] and poses a quest for further development in the technology of its fabrication. Graphene samples with mobilities comparable to the best GaAs samples [32] thus seem to be achievable.

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