# Sample-Size Effects in the Magnetoresistance of Graphite

J. C. González, M. Muñoz, and N. García*

*Laboratorio de Física de Sistemas Pequeños y Nanotecnología, Consejo Superior de Investigaciones Científicas, E-28006 Madrid, Spain*

J. Barzola-Quiquia, D. Spoddig, K. Schindler, and P. Esquinazi†

*Division of Superconductivity and Magnetism, Universität Leipzig, Linnéstraße 5, D-04103 Leipzig, Germany*

(Received 20 June 2007; published 20 November 2007)

Conduction electrons in graphite are expected to have micrometer large de Broglie wavelength as well as mean free path. A direct influence of these lengths in the electric transport properties of finite-size samples was neglected in the past. We provide a direct evidence of this effect through the size dependence of the magnetoresistance, which decreases with the sample size even for samples hundreds of micrometers large. Our findings may explain the absence of magnetoresistance in small few graphene layers samples and ask for a general revision of the experimental and theoretical work on the transport properties of this material.

DOI: 10.1103/PhysRevLett.99.216601 PACS numbers: 72.20.My, 72.80.Rj, 75.47.Pq, 81.05.Uw

It belongs to physics' basics that the wave nature of the electrons must be invoked via the de Broglie wavelength $\lambda_{\rm dB} = h/p$ when they are confined in regions of the order of $\lambda_{\rm dB}$ ($p$ is the particle momentum). Similarly to the role that the atomic lattice constant plays to electron diffraction phenomena, the size of the sample is of importance for defining the properties of the system if it becomes of the order of $\lambda_{\rm dB}$. In usual metals this happens in the nanometer range. Graphite, however, is extraordinary because the de Broglie wavelength for massless Dirac fermions $\lambda_{\rm dB} \sim h v_F/E_F$ ($v_F \simeq 10^6$ m/s is the Fermi velocity and $E_F \lesssim 100$ K the Fermi energy) or for massive carriers $\lambda_{\rm dB} = h/\sqrt{2m^\star E_F}$ (with effective mass $m^\star \lesssim 0.01m$) as well as the two-dimensional Fermi wavelength $\lambda_F = (2\pi/n)^{1/2}$, are of the order of microns due to the low carrier density $n \lesssim 10^{10}$ cm$^{-2}$ and low effective mass.

In the semiclassical description of the electronic transport properties of metals à la Boltzmann, widely applied to graphite, the electrons are treated as particles of mass $m^\star$ with a group velocity $\vec{v} = \hbar^{-1}\vec{\nabla}_k E(\vec{k})$ of a fairly well "localized" wave packet. However, semiclassical theory may not be applicable when the coherence length, the Fermi wavelength, as well as the mean free path of the carriers are of the order of the sample size. In these conditions Boltzmann's transport theory may not be a good approximation and all kinds of finite-size effects should appear. For example, what is the meaning of the classical cyclotron radius $r_c \simeq m^\star v_F/eB \sim 0.05$ $\mu$m at $B \sim 1$ T when the wavelength of the electrons $\lambda_{{\rm dB},F} \sim 1$ $\mu$m? The Onsager quantization that gives rise to the de Haas-van Halphen and Shubnikov-de Haas oscillations also needs to be reconsidered because now the wave vector might not be a continuum for micrometer size samples. We note that electrons in graphite give us the unusual possibility to study electron optics phenomena in macroscopic samples.

Apparently, the question of what happens when the graphite sample size is reduced has not been correctly addressed in the past and the experimental data may need a new interpretation. The aim of this Letter is to analyze experimentally the behavior of the ordinary magnetoresistance (OMR) in highly oriented pyrolytic graphite samples upon their macroscopic size and the effects of a constrained region. We found that the smaller the size of a graphite sample or a constraint in it, the smaller the OMR is. Surprisingly, the effect is already noticeable at hundred-of-microns-large samples providing an unequivocal evidence for the huge mean free path (or elastic coherence length) and wavelength of the carriers in this material.

In order to carry out a systematic study we have performed experiments in different highly oriented pyrolytic graphite (HOPG) samples from Advanced Ceramics or Structure Probe, Inc., with mosaicities $0.4° \pm 0.1°$, $0.8° \pm 0.15°$, and $3.5° \pm 0.4°$. The smaller the mosaicity, the higher the orientation of the crystallites is, but their size remains practically similar for the mosaicity range used here. The results presented in this Letter are from HOPG samples with mosaicities of 0.4° and 0.8°. Results for larger mosaicity will be presented elsewhere. The advantage of using HOPG of good quality is that due to the perfection of the graphene layers and low coupling between them, a low two-dimensional carrier density $n \sim 10^{10}$–$10^{11}$ cm$^{-2}$ is obtained [1–3]. This value is much smaller than in typical few graphene layers (FLG) samples [4] probably due to lattice defects generated by the used method to produce FLG samples and/or surface doping. Other advantage of using HOPG samples is that the preparation procedure for macroscopic sample size (from mm to $\mu$m) is rather simple enhancing the reproducibility and also the possibilities of checking different geometries.

The graphite samples of thickness between $\sim$10 $\mu$m and $\sim$40 $\mu$m were prepared by peeling from HOPG using double sided tape. The samples were then glued with varnish onto silicon substrates. Electrical contacts were made by using silver loaded cryogenic epoxy in the usual four-point arrangement for resistance measurements. The used current was between 1 $\mu$A to 100 mA. The sample width was reduced by cutting the sample with a diamond tip (wide cuts). Also we changed the voltage electrode distance without changing the sample size. For small constrictions we used a FEI Novalab 200 dual beam scanning electron microscope (SEM) with a crossing focus ion beam (FIB). This setup allows us well-defined production of rectangular constraints of different lengths and widths between the voltage electrodes and to study their influence on the OMR. We have produced constrictions of micrometer size and not in the nanometer range because we are interested to know at what sample size or constriction width one starts observing size effects. Part of the experimental studies were done at room temperature and 77 K and a few samples were cooled down to 4 K. The magnetic field was applied always perpendicular to the graphene planes of the HOPG samples.

Electron backscattering diffraction (EBSD) was performed with a commercially available device (Ametek-TSL). In this setup the sample under investigation was illuminated by the SEM beam and the diffracted electrons were detected by a fluorescence screen and a digital camera. The TSL software was used to calculate the orientation of the HOPG surface as function of the electron beam position. Figures 1(a) and 1(b) show the same $600 \times 200\ \mu\mathrm{m}^2$ area of a HOPG sample. Figure 1(b) shows the distribution of the $c$ axis of the hexagonal unit cell at the graphite surface depicted by the spreading of the (red) color. The grain distribution can be also seen in Fig. 1(a) where the in-plane orientation is recognized by the (blue-green) color distribution. In Fig. 1 we see that the typical

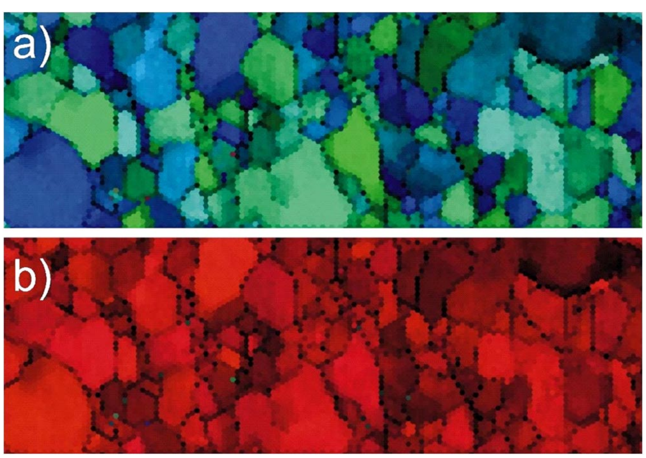


FIG. 1 (color online). Inverse pole figures maps from EBSD measurements of the HOPG surface showing the in-plane (a) and the $c$-axis orientation (b) of the crystallites on the sample surface. The scan size is $\sim 600 \times 200\ \mu\mathrm{m}^2$; the size of the domain patterns matches the results of EFM measurements [16].

crystal size in HOPG (0.4°) is of the order of several micrometers. Upon defect concentration in the crystals and their influence on the effective carrier density, one estimates $\lambda_{\mathrm{dB},F} \gtrsim 1\ \mu$m. Therefore, we expect that size effects might be seen at relatively large sample or constriction size. All these numbers already suggest a situation very different from that found in metals, where size effects in the magnetoresistance may start to be seen when the sample size reduces to $\sim$20 nm or less.

We would like to note also the following. The electron mean free path $L_e$ that is relevant to our measurements is due to inelastic processes because the resistance is measured, although we cannot exclude that part of it is due to an elastic change of momentum. Usually, size effects are expected when $L_e$ is comparable to or larger than the crystallites size, which in our case is $\lesssim 10\ \mu$m, see Fig. 1. The results presented below indicate, however, that sample-size effects on the OMR start to be seen at sample sizes 2 orders of magnitude larger than the classically estimated $L_e \simeq m^\star v_F \mu / e \gtrsim 1\ \mu$m, taking into account a mobility $\mu \sim 10^6\ \mathrm{cm}^2/\mathrm{V\,s}$ [5], a value 10–$10^2$ larger than those found in typical FLG. Comparing our results and these estimates we realize that due to the extraordinary large carrier wavelength $\lambda_{F,\mathrm{dB}}$, phenomena as wave diffraction and interference should play a significant role in the electronic conduction, and size effects might be seen at sample sizes much larger than any classically estimated value of $L_e$. In other words, if the results obtained in these studies for graphite apply also for FLG one would expect a measurable size effect for samples of micrometer size and $L_e \gtrsim 0.1\ \mu$m. In fact, quantum oscillations have been seen in experiments and explained in terms of quantum effects [6].

Figure 2 shows the dependence of the OMR defined as $[R(0.5\ \mathrm{T}) - R(0)]/R(0)$ with the sample width measured at 300 K (●, □) and 77 K ($*$) (right axis). Note that the sample width changes between 1 cm and 80 $\mu$m. The OMR clearly decreases from $\sim$40% for a macroscopic sample to $\sim$20% for a still relatively large constricted sample of 80 $\mu$m. The data (●) also indicate that the OMR saturates for a sample width $\gtrsim$1000 $\mu$m. In Fig. 2 there are points for another HOPG sample (□) prepared similarly, which shows the same trend. The decrease of OMR is also clearly observed at 77 K ($*$). This result is quite spectacular because the reduction is a factor of 2 at 300 K and nearly a factor 10 at 77 K, even if the sample size is $\sim$20–100 times the (estimated) mean free path or the Fermi wavelength.

One may speculate that due to the method used to reduce the width of the sample we are introducing defects and this is the reason for the observed decrease of the OMR. To check that this is not the case we have done two more experiments that are described below. The reason is that by reducing temperature the mean free path increases and quantum, nonclassical effects start to affect larger areas

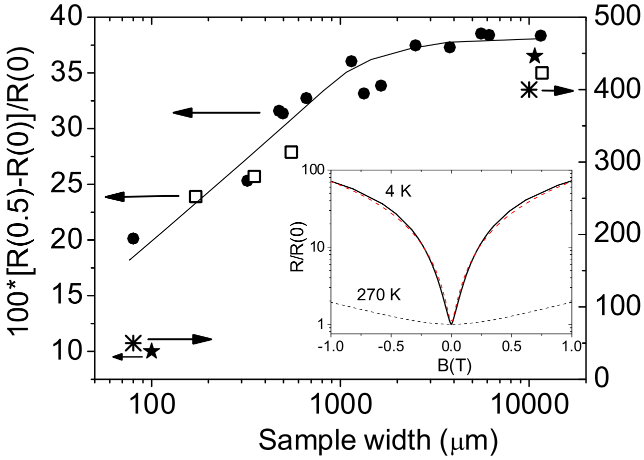


FIG. 2 (color online). Magnetoresistance as a function of sample's width size in micrometers. The data were taken from three HOPG samples of mosaicity 0.4° at 300 K (●, □, ★), left axis, and a sample of 0.8° at 77 K ( * ), right axis. The width of the samples described by the points (●, □, *) were changed using a diamond tip. The line is only a guide to the eye. The width values of the sample described by the symbol (★) mean the distance between the voltage electrodes without changing the sample dimensions. Inset: magnetoresistance $R(B)/R(0)$ vs applied field for a HOPG sample with a constraint width of 16 $\mu$m at 270 K and 4 K. The dashed (red) line follows the function $70|B|^{1.4} + 1$.

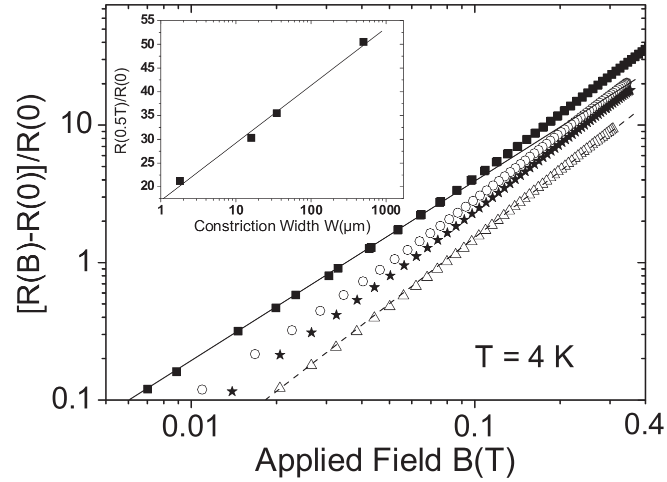


FIG. 3. Magnetoresistance of a HOPG sample (0.4°) as a function of applied magnetic field at different widths of a constraint localized in the middle of the voltage electrodes, at 4 K. The constraint widths were (1.8, 16, 35, 500) $\mu$m corresponding to the symbols: (△, ★, ○, ■). The straight line has a field dependence $B^{1.2}$ and the dashed line $B^{1.7}$. Inset: magnetoresistance defined as $R(0.5)/R(0)$ vs constriction width. The line is a logarithmic fit to the data.

of the sample. Note that HOPG samples have Dirac and massive electrons [3] and the former have a tremendously large mean free path (several tens of microns) and these are likely the ones that reduce the OMR at large sample size.

In the same Fig. 2 we show the change of OMR at 300 K for a HOPG sample changing only the distance between voltage electrodes from ~1 cm to ~100 $\mu$m (★). The same tendency is observed, i.e., the OMR decreases nearly logarithmical with the sample width or electrode distance. This phenomenon is also observed if we produce a rectangular constraint of small length ~2 $\mu$m, much smaller than the sample width ≃ 500 $\mu$m, and located at the middle between the voltage electrodes (distance ~500 $\mu$m) on a HOPG sample (0.4°), see Fig. 3. The constraint length is so small that in principle one does not expect any change in the OMR. In fact, at 270 K the value obtained for the OMR for this sample is ≃ 0.30 (at $B = 0.5$ T, see inset in Fig. 2), in agreement with the data shown in Fig. 2. In other words, at this temperature we measure the OMR coming from the sample bulk. The inset in Fig. 2 shows the parabolic behavior of the OMR at 270 K for the sample with a constraint width of 16 $\mu$m; this behavior remains independent of the constraint width in the measured range.

However, at lower temperatures, due to the increase of the mean free path the influence of the constraint might be not negligible anymore. In agreement with this expectation, we observed a clear dependence of the OMR with constraint width at 4 K, see Fig. 3. The inset in this figure shows the magnetoresistance defined as the resistance ratio $R(0.5)/R(0)$ versus the width of the constraint where a logarithmic dependence is clearly observable. Two important details of these results are worth to mention. The observed influence of the constraint remains even for macroscopic large widths, see inset in Fig. 3. Note that the measured magnetoresistance is given by two contributions, one coming from the sample bulk, which remains as a constant background, and the other due to the influence of the constraint.

All the results presented above point out to phenomena that in a metal do not happen at least at the scale of the graphite samples. Our results show that reducing the sample size the OMR reduces. If we extrapolate the overall sample size to a few micrometers or below we expect a negligible OMR, as has been experimentally observed for graphite samples of size of the order of ~50 $\mu$m to less than 100 nm [7,8]. We note also that the reported OMR data in FLG samples indicate practically the absence of OMR [9–11] in comparison with that observed in bulk HOPG, which is of the order of 5000% at ~0.5 T and at low temperatures [1], see Fig. 3. Apparently, the sample size in the experiments with FLG's is what strongly reduces the OMR and not their thickness, even if the classically estimated $L_e$ would remain much smaller than the typical FLG lateral size.

There is still a behavior that we would like to remark about the OMR. At 270 K the OMR increases quadratically with field (see inset in Fig. 2) while at temperatures below ~100 K it behaves quasilinearly (see Fig. 3 and inset in

Fig. 2). This is an experimental fact that is well-known for graphite and other semimetals. Abrikosov [12,13] suggested that this phenomenon takes place in the Landau level quantization regime of the Dirac fermion system, i.e., above a certain minimum field. However, note that this quasilinear OMR is also observed at very low fields [$\lesssim$0.01 T, see, for example, the data (■) in Fig. 3]. Our explanation is again in terms of electron mean free path and the role played by the platelets of $\sim$10 $\mu$m size approximately conforming HOPG (see Fig. 1). When the mean free path of the electrons is of the order or larger than the platelets size, then electrons reflect and are being transmitted coherently at the borders of the platelets and quantum currents circulate creating Hall-like potentials. This circulation of quantum currents at the platelets edges (see Fig. 1) produces a quasilinear behavior with field of the OMR. A similar picture has been discussed to interpret experiments done with a Corbino disk geometry in HOPG [14] and disordered semiconductors [15]. This is the same thing that happens in optics with the reflection of waves between different media. At room temperature the mean free path is smaller than the platelets size and the quantum currents at the border of the platelets do no exist. In this case we recover the classical parabolic Ohmic behavior of the OMR. This appears to be the explanation for the two regimes of OMR at low and high $T$. Temperature dependent measurements of the resistance with constraints provide an estimate of the mean free path and its temperature dependence $L_e \sim 1$–$4 \times 10^3 T^{-1.5}$ $\mu$m K$^{1.5}$ for $T > 10$ K.

The OMR 4 K data for different constraint widths shown in Fig. 3 indicate that the low-field exponent increases from 1.2 to 1.7 decreasing the size of the constraint. This behavior is due to electron localization at small fields that shows a OMR dependence of the type $\sim B^{-0.5}$. The change of slope in Fig. 3 is a clear manifestation of this effect. Localization effects are reflected also in a noise behavior of the OMR at low fields.

In conclusion, our studies reveal a rather spectacular size effect in the transport properties of graphite, specially in its magnetoresistance. The influence is observable up to macroscopic sample size of the order of several hundreds of micrometers, orders of magnitude larger than the estimated mean free path. We suggest that this is due to not only the large mean free path but also the Fermi wavelength of the carriers (Dirac as well as massive electrons) in graphite. Our results indicate that when the sample size is of the order or smaller than the Fermi wavelength or mean free path, the classical Boltzmann transport theory becomes gradually not valid, in particular, when the estimated classical cyclotron orbits are much smaller than $\lambda_F$, $L_e$. For these sizes the wave vector of the carriers might conform a discrete set of quantum numbers and therefore the quantization of orbits requires to have this into account. Our observations provide a possible answer to the almost absence of OMR in FLG's reported in the literature.

This work was done with the support of the DFG under ES No. 86/11 and of the Spanish CAICyT. One of us (J. B.-Q.) is supported by the EU under Ferrocarbon.

*nicolas.garcia@fsp.csic.es
†esquin@physik.uni-leipzig.de

[1] Y. Kopelevich, P. Esquinazi, J. H. S. Torres, R. R. da Silva, and H. Kempa, in *Advances in Solid State Physics*, edited by B. Kramer (Springer-Verlag, Berlin, 2003), Vol. 43, pp. 207–222.
[2] Y. Kopelevich, J. H. S. Torres, R. R. da Silva, F. Mrowka, H. Kempa, and P. Esquinazi, Phys. Rev. Lett. **90**, 156402 (2003).
[3] I. A. Luk'yanchuk and Y. Kopelevich, Phys. Rev. Lett. **93**, 166402 (2004).
[4] M. I. Katsnelson, Mater. Today **10**, 20 (2007).
[5] M. S. Sercheli, Y. Kopelevich, R. R. da Silva, J. Torres, and C. Rettori, Solid State Commun. **121**, 579 (2002).
[6] N. García, arXiv:0706.0135.
[7] E. Dujardin, T. Thio, H. Lezec, and T. W. Ebbesen, Appl. Phys. Lett. **79**, 2474 (2001).
[8] X. Zhang, Q. Z. Xue, and D. D. Zhu, Phys. Lett. A **320**, 471 (2004).
[9] K. S. Novoselov, A. K. Geim, S. V. Morozov, S. V. Dubonos, Y. Zhang, and D. Jiang, Science **306**, 666 (2004).
[10] K. S. Novoselov, A. K. Geim, S. V. Morozov, S. V. Dubonos, Y. Zhang, and D. Jiang, Nature (London) **438**, 197 (2005).
[11] Y. Zhang, Y.-W. Tan, H. Störmer, and P. Kim, Nature (London) **438**, 201 (2005).
[12] A. A. Abrikosov, Phys. Rev. B **60**, 4231 (1999).
[13] A. A. Abrikosov, Europhys. Lett. **49**, 789 (2000).
[14] H. Kempa, P. Esquinazi, and Y. Kopelevich, Solid State Commun. **138**, 118 (2006).
[15] M. M. Parish and P. B. Littlewood, Nature (London) **426**, 162 (2003).
[16] Y. Lu, M. Muñoz, C. S. Steplecaru, C. Hao, M. Bai, N. García, K. Schindler, and P. Esquinazi, Phys. Rev. Lett. **97**, 076805 (2006). See also the Comment by S. Sadewasser and Th. Glatzel, Phys. Rev. Lett. **98**, 269701 (2007); and the accompanying Reply by Y. Lu *et al.*, Phys. Rev. Lett.**98**, 269702 (2007).