On the origin of the electric carrier concentration in graphite

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We investigate the dependence of the electrical resistivity and magnetoresistance of single crystalline micrometer-sized graphite samples of a few tens of nanometers thick on the defect concentration produced by irradiation at low fluences. We show that the carrier density of graphite \( n \) is extremely sensitive to the induced defects for concentrations as low as \( \sim 0.1 \) ppm and follows \( n \sim 1/R_v^2 \) with \( R_v \) the distance between defects in the graphene plane. These and Shubnikov-de Haas oscillations results indicate that at least a relevant part of the carrier densities measured in graphite is not intrinsic.

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The electronic properties of ideal graphite are actually not well known simply because defect-free graphite samples do not exist. In the last fifty years scientists flooded the literature with reports on different kinds of electronic measurements on graphite samples, providing evidence for carrier (electron plus hole) densities per graphene layer at low temperatures \( n_0 \sim 10^{10} \ldots 10^{12} \text{ cm}^{-2} \), see e.g. Refs. \([1,2,3]\). Taking into account that: (1) an exhaustive experience accumulated in gapless semiconductors - whose density of states should be similar to its counterpart in a semiconductor - indicates so far that the measured \( n_0 \) is most probably due to impurities \([4]\), and (2) the expected sensitivity of \( n_0 \) in graphite on lattice defects and impurities or adatoms \([2,5]\), a fundamental question remains unanswered, namely, how large is the intrinsic \( n_0 \) of ideal graphite? Why \( n_0 \) is so important? Let us recapitulate some fundamental band structure theoretical results for the graphite structure \([2]\). Two-dimensional (2D) calculations assuming a coupling \( \gamma_0 \) between nearest in-plane neighbors C-atoms give a carrier density (per C-atom) \( n(T) = (0.3 \ldots 0.4)(k_B T/\gamma_0)^2 \) (\( \gamma_0 \approx 3 \text{ eV} \) and \( T \) is the temperature). Introducing a coupling \( (\gamma_1 \sim 0.3 \text{ eV}) \) between C-atoms of type \( \alpha \) in adjacent planes one obtains \( n(T) = a(\gamma_1/\gamma_0)^2 + b(T/\gamma_0)^2 + c(T^3/\gamma_0^3 \gamma_1) + \ldots \) (\( a, b, c, \ldots \) are numerical constants). In both cases \( n(T \to 0) \to 0 \). Neither in single layer graphene nor in graphite such \( T \)-dependences were ever reported \([6]\), i.e. a large density background \( n_0 \) was always measured and assumed as “intrinsically” without taking care of any influence from lattice defects (including edge effects \([2]\) or impurities. To fit experimental data and obtain a finite Fermi energy \( E_F \), up to seven free parameters were introduced in the past, whereas in the simplest case \( E_F \propto \gamma_1 \) \([2,6]\).

Clearly, any evidence that speaks against an intrinsic origin of - even a part of - the measured \( n_0 \) in graphite samples would cast doubts on the relevance of related electronic band structure parameters obtained in the past and will help significantly to clarify observed transport phenomena. As in the case of gapless semiconductors \([4]\) this requires a formidable experimental task. For example, to prove that the measured \( n_0 = 2 \times 10^8 \text{ cm}^{-2} \) in Ref. \([3]\) is due to vacancies/interstitials requires a vacancy resolution better than 0.05 ppm. Although nowadays the concentration of impurities in graphite can be measured with \( \sim 0.1 \) ppm resolution there is no experimental method that allows us to determine with such a precision the number of vacancies or C-interstitials. In spite of that and because of this situation we would like to start the discussion on the origin of \( n_0 \) postulating that at least part of it cannot be intrinsic. The studies presented here provide answers to: (1) Can a single vacancy/interstitial provide \( \sim \) one carrier into the conduction band even if they are several hundreds of nm apart (ppm concentration)? This is a relevant issue specially because we expect that the Fermi wavelength in graphite \( \lambda_F \gtrsim 1 \mu \text{m} \) \([10]\). (2) Can the resistivity of graphite change with such small defect concentrations? (3) How reliable are band structure parameters of graphite obtained from the field-induced quantum oscillations in the resistivity (or magnetization)? (4) Why there is an apparent maximum value for \( n_0 \sim 10^{12} \text{ cm}^{-2} \) in graphite samples?

In this study we measured the change of the electrical resistance of thin crystalline graphite samples as a function of defect concentrations between \( \sim 0.1 \) to \( \sim 10^6 \text{ ppm} \). To do this we irradiated three \( \sim 60 \text{ nm} \) thick and tens square micrometer samples under ambient conditions with a focused proton microbeam of 2.25 MeV energy scanned over the samples. A photo of sample 1 can be seen in Fig. 1. Particle induced x-ray emission measurements were done in situ and revealed a total concentration of \( \sim 20 \mu \text{g/g} \) of non-magnetic impurities except hydrogen of concentration \( 0.5 \pm 0.3\% \) \([11]\). The magnetoresistance of a fourth sample of size \( 11 \times 2 \times 0.015 \text{ mm}^3 \) was measured at three different parts, each of length \( \approx 1.6 \mu \text{m} \) and irradiated with 30 keV Ga\(^+\) ions. In this sample Shubnikov-de Haas (SdH) oscillations were measured at 4K before and after irradiation and also for the corresponding bulk sample. Further details on the electron-beam spectroscopy and Raman techniques and the exfoliation and ultrasonic procedures used to characterize and prepare the crystalline thin graphite flakes from bulk samples will be published elsewhere.

Figure 2(a) shows the relative change of the resistance
The carrier density is of two the initial value at 297 K before irradiation for weakly-coupled graphene sheets [12]. Within a factor \( n \) the dashed lines are obtained assuming a Fermi energy \( E_F = E_0 + k_B T \) and a \( T^{-2} \) dependence for the mean free path, see text for details. The inset shows an optical microscope picture of sample 1 with gold electrodes on top.

FIG. 1: Temperature dependence of the resistance of sample 3 in the as-prepared state and after proton irradiation with a fluence of \( 9 \times 10^{13} \) cm\(^{-2} \) (continuous lines). Note the large change in \( R(T) \) after inducing only \( \sim 3 \) ppm vacancy density. The dashed lines are obtained assuming a Fermi energy \( E_F = E_0 + k_B T \) and a \( T^{-2} \) dependence for the mean free path, see text for details. The inset shows an optical microscope picture of sample 1 with gold electrodes on top.

The resistances obtained at different initial relaxed conditions after irradiation of 3.1, 4.0, 4.3, 6.4, 7.2, 9.0 \( \times 10^{13} \) protons per cm\(^{-2} \), corresponding to the curve numbers 7, 9, 10, 14, 16, 19, from top to bottom. The small oscillations in the resistance observed during irradiation are an artifact due to the overlapping of the proton current and the ac current of the resistance bridge.

(b) Change of resistance relative to its value in the virgin state \( R_0 \) vs. time. The time scale is taken from the time at which the beam does not hit the sample anymore, i.e. the minimum in \( \Delta R/R(0) \) in (a). Note the decrease of resistance with irradiation for the first three curves (1-3 from bottom) even in the relaxed states (after 1 hour). As in (a) the different curves are taken from the sample at different initial states irradiated with fluences \( (1, 2, ..., 19) = (1, 1.5, 2.0, ..., 9) \times 10^{13} \) protons/cm\(^2\).

We assume graphite as a structure composed of weakly-coupled graphene sheets [12]. Within a factor of two the initial value at 297 K before irradiation for the carrier density is \( n_i \sim 6 \times 10^{10} \) cm\(^{-2} \) and for the mean free path \( l_i \sim 50 \) nm [13]. The smallness of \( l \) at 297 K in comparison to the sample size allows us to use the Boltzmann-Drude semiclassical approach. This is important because for our sample sizes and at \( T \lesssim 150 \) K there is no straightforward theoretical approach that includes ballistic and diffusive scattering that allows us to obtain in a simple way \( n(R_V) \) from the resistance. Hall effect measurements are not necessarily preferred to obtain \( n(R_V) \) since: - the Hall signal depends on at least six unknown parameters \( (n, l, m^* \) for electrons and holes independently) that change with defect concentration and \( T \); - conventional multiband approaches appear to be inadequate for graphite [13]; - added to these difficulties, the Hall signal of graphite can be anomalous at \( T < 150 \) K [13].

Following SRIM simulations [14] the produced defect concentration at a proton fluence of \( 10^{13} \) cm\(^{-2} \) would be \( n_V \sim 10^9 \) cm\(^{-2} \). Assuming that each defect in the graphene plane increases by one the carrier number, the increase in carrier density after irradiating such fluence...
The relative change of resistance vs. fluence for sample 2 (open symbols) and sample 3 (close symbols). The upper x-axis corresponds to the corresponding scales as average defect distance within a graphene plane $R_V$ and the defect density in parts per million (ppm). The triangles represent the change of the resistance in the relaxed state after irradiation to the virgin state $R_0$, i.e. $R(t \geq 1h)/R_0 - 1$. The circles are obtained from $R_{min}/R_0 - 1$ and the squares $R_{min}/R(t \geq 1h)-1$. The curves were obtained with Eq. (1) with the following parameters: $n_V = 0.1/R_V^2$, $l_i = 50$ nm (long dashed); $0.1/R_V^2$, 20 nm (dot); $1/R_V^2$, 50 nm (continuous); $3/R_V^2$, 150 nm (red dash-dot); $3/R_V^2$, 50 nm (dash-double dot). The short-dash curve was obtained assuming the usual 3D relation $R \propto 1/ln$ and with $n_V = 0.9/R_V^2$, $l_i = 150$ nm. Note that with this 3D relationship no minimum in the measured range is obtained within a broad variation of parameters.

At 297 K, the produced defects by irradiation are metastable [15], see Fig. 2. Therefore, we plot in Fig. 3 the relative change of the resistance just at the end of the irradiation $R_{min}$ with respect to the virgin state $R_0$, i.e. $R_{min}/R_0 - 1$ (close and open circles in Fig. 3). Another possibility is to plot the relative change with respect to the resistance taken one hour after irradiation $R_{rel}$, i.e. $R_{min}/R_{rel} - 1$ (close and open squares in Fig. 3). Both ways minimize the influence of annealing effects and provide a similar behavior. These relative changes indicate that the resistance reaches a minimum $\sim 90\%$ of its initial value at $R_V = 20 \ldots 30$ nm, see Fig. 3. At higher fluences the resistance increases because the decrease of $l$ starts to overwhelm the increase in $n$.

A quantitative description of these data can be done taking into account the two dimensional resistivity [10] $\rho = 2/\pi e^2 r_F^2 N(E_F)\tau_F$, where $v_F$, $E_F$, $\tau_F$ are the Fermi velocity, the Fermi energy and the scattering relaxation time at Fermi energy. Using $N(E_F)$ for clean graphene [8], the expression for $E_F = h v_F k_F$ and $\tau_F = l/v_F$, one arrives at the simple expression $\rho = (\pi/2)^{1/2}(\hbar/e^2) l^{-1} n^{-1/2}$. Furthermore, the carrier density increases as $n = n_i + n_V$, where $n_V = 1/R_V^2$ for one carrier per defect. Following Mathiessen’s rule, the mean free path is given by $l^{-1} = l_i^{-1} + l_V^{-1}$, where $l_i$ is the initial value due to all scattering centers before irradiation and $l_V$ the mean free path due to the produced defects. The relative change of resistance can be written as

$$R - R_0 \over R_0 = \left(1 + l^{-1} \over 1 + (n_V/n_i) l^{-1} l_V^{-1}ight)^{1/2} - 1. \quad (1)$$

The solid curve shown in Fig. 3 is obtained with $l_V = 1.15 \times 10^6 [\text{cm}^{-1}] R_V^2 [\text{cm}^2]$ for $l_i = 50$ nm and $n_V = 1/R_V^2$. Within logarithmic corrections, the obtained $l_V(R_V)$ function agrees quantitatively with that found in Ref. [8].

In Fig. 3 we show also other curves obtained using other values for $l_i$ and pre-factors for $n_V(R_V)$ as well as assuming the usual 3D relationship $R \propto 1/n$ instead of $1/n^{1/2}$. The comparison indicates that within a factor of two $n_V$ is indeed given by $1/R_V^2$ (for $R_V > 10$ nm) and that the usual 3D relationship for $R$ cannot describe the observed behavior within a reasonable range of parameters.

The remarkable increase in $R(T < 300$ K) and the observed change in the temperature dependence of graphite after inducing only $\sim 3$ ppm defect density ($R_V \sim 100$ nm) is mainly given by the decrease of $E_F \approx E_F(0) + k_B T \propto \sqrt{n(T)}$ with temperature. As shown in Ref. [8], $E_F$ is basically determined by thermal electrons (note that $E_F \sim 330$ K for $n = 6 \times 10^{10}$ cm$^{-2}$) and its $T$-dependence overwhelms that of $l(T)$. With $E_F(T)$,
The stopping and range of ions in matter \(l_i(T) \propto T^{-2}\) \cite{3} and the parameters obtained from Fig. 3 in Eq. (1) one can understand the observed temperature dependence of the resistance above \(\sim 100\,\text{K}\), see Fig. 1; at lower temperature the Boltzmann-Drude approach looses its validity.

The band parameters of graphite were obtained mostly on macroscopic samples and usually from magneto-optical studies, SdH and de Haas-van Alphen oscillations, cyclotron resonance, etc. We doubt that in graphite samples the defect density is negligible and therefore we expect that the carrier density is neither small nor homogeneously distributed. Within the 11 \(\mu\text{m}\) length of sample 4 we measured the magnetoresistance at 4 K and calculate its first derivative in different parts of similar area. The SdH oscillations depend on the sample position, see Fig. 4, indicating clearly inhomogeneities in the carrier concentration within micrometers in agreement with EFM results that revealed sub-micrometer domain-like carrier density distributions in graphite surfaces \cite{17}.

For the measured sample area that gives curve (a) in Fig. 4 and within experimental resolution there are no SdH oscillations up to a field \(B \simeq 1.8\,\text{T}\) in clear contrast to the bulk sample, see Fig. 4. This fact can be understood assuming that in most of this sample part \(n_0 \lesssim 10^8\,\text{cm}^{-2}\). Then, the corresponding Fermi wavelength \(\lambda_F \gtrsim 0.8\,\mu\text{m}\) is of the order of the sample size and larger than the cyclotron radius \(r_c = m^*v_F/eB\) for \(B > 0.07\,\text{T}\) assuming \(m^* = 0.01m\) (\(m\) is the free electron mass). In this case we do not expect to observe any SdH oscillations. However, for \(B \simeq 1.8\,\text{T}\) and 2.8 T two maxima are observed. From the measured “period” \(P\) in \(1/B\) as well as from the first field at which the first maximum appears we estimate the existence of domains of size \(\lesssim 100\,\text{nm}\) in which \(\lambda_F \lesssim 50\,\text{nm}\), i.e. domains with \(n_0 \gtrsim 10^{11}\,\text{cm}^{-2}\) within a matrix of much lower carrier concentration. This indicates that the description of the SdH oscillations in real graphite samples can be achieved only within the framework of inhomogeneous 2D systems \cite{15, 19}, an issue rarely studied in the past.

The selected \(\text{Ga}^+\) irradiation produced an average defect concentration of \(\sim 10^{12}\,\text{cm}^{-2}\), i.e. \(\sim 10^3\,\text{ppm}\) (Ga implantation \(\lesssim 1\,\text{ppm}\) in the thin graphite sample, “homogenizing” its carrier density distribution. After irradiation the SdH oscillations are clearly observed for \(B \gtrsim 0.7\,\text{T}\), see Fig. 4. Their period \(0.16\,\text{T}^{-1} \leq P \leq 0.23\,\text{T}^{-1}\) is within the range found in literature \cite{2, 20} and indicates \(n_0 \sim 3 \times 10^{11}\,\text{cm}^{-2}\).

Finally, if a relevant part of the reported carrier concentration in graphite is due to defects, why does it appear to saturate at \(n_0 \sim 10^{12}\,\text{cm}^{-2}\) (\(\sim 3 \times 10^{-4}\) carrier per C-atom)? We note that such saturation is also observed in gapless semiconductors with increasing donor concentration \cite{4}. We might therefore expect it when the average distance between defects is of the order of the range of modification of the electronic structure produced by, e.g. a single vacancy, found experimentally to be \(\sim 3\,\text{nm}\) \cite{21} implying \(n_0 \lesssim 10^{13}\,\text{cm}^{-2}\).

Concluding, the obtained results indicate that a concentration of defects (or impurities) of \(\sim 0.2\,\text{ppm}\) can generate a carrier density \(\sim 10^9\,\text{cm}^{-2}\) affecting the transport properties. This is an extraordinary sensitivity taking into account the large distances between defects these concentrations imply. Taking into account that, in best case, we have an impurity concentration \(\lesssim 20\,\text{ppm}\), except for hydrogen \(\lesssim 1\%\), plus an unknown concentration of vacancies and interstitials, we should doubt about the assumed “intrinsic” origin of the measured carrier concentrations in graphite. The behavior of SdH oscillations in micrometer-sized graphite regions and their changes after introducing defects support the above statement and indicate that real graphite is composed by an inhomogeneous distribution of carrier density.

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dence (Fig. 2) shows that this is governed by interstitial migration processes \[22\] and single vacancy diffusion \[23\] with activation energies \(\sim 0.87\) eV and \(\sim 0.93\) eV, respectively. The migration processes annihilate partially the produced defects and at fluences (for sample 3) \(\gtrsim 2 \times 10^{13}\) cm\(^{-2}\) the relaxed resistance increases indicating that the graphite structure remains with a certain amount of defects decreasing the overall carrier mobility.

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