Evidence for Disorder Induced Delocalization in Graphite

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We present electrical transport measurements in natural graphite and highly ordered pyrolytic graphite (HOPG), comparing macroscopic samples with exfoliated, nanofabricated specimen of nanometer thickness. Nano-samples exhibit a very large c-axis resistivity $\rho_c$ – much larger than expected from simple band theory – and non-monotonic temperature dependence, similar to macroscopic HOPG, but in stark contrast to macroscopic natural graphite. A recent model of disorder induced delocalization is consistent with the data. Micro-Raman spectroscopy reveals clearly reduced disorder in exfoliated samples and HOPG, as expected within the model – therefore presenting further evidence for a novel paradigm of electronic transport in graphite.

Graphite is a paradigmatic layered material and has been investigated intensively for many decades. The in-plane resistivity $\rho_{ab}$ is rather well described by a simple Drude model. However, the resistivity $\rho_c$ along the c-axis, perpendicular to the graphite basal planes, as well as its temperature dependence $\rho_c(T)$, are not described by the simple band structure model $\rho_{ab}$, and currently lack theoretical understanding despite extended efforts. The resistive anisotropy $R_A = \rho_c/\rho_{ab}$ is a convenient dimensionless parameter characterizing transport properties.

Carbon atoms in the graphite basal planes are strongly bound by covalent bonds, while much weaker Van der Waals forces bind the graphene sheets along the c-axis. Non-trivial disorder such as stacking faults and crystalline grains result in a mosaic angle and complicate electronic transport. Simple band theory predicts $R_A = m_c/m_{ab} \sim 140$, the ratio of the corresponding band masses, which holds in presence of isotropic disorder. This agrees well with measurements in natural graphite (NG) $\rho_{ab}$ and $\rho_c$. In highly oriented pyrolytic graphite (HOPG), the anisotropy was found to be much larger, even exceeding 10'000 in some experiments $\rho_{ab}$ and $\rho_c$. Moreover, band theory $\rho_{ab}$ predicts a monotonic metallic temperature dependence for both $\rho_{ab}$ and $\rho_c$, resulting in a temperature independent anisotropy $R_A$. This is seen in NG $\rho_{ab}$, but not in HOPG, where $\rho_c$ is non-monotonic with a maximum around 40 K $\rho_{ab}$, similar to $\rho_c$ in other layered materials, such as NaCo$_2$O$_4$ $\rho_{ab}$ and Cuprates $\rho_{ab}$. A large anisotropy far exceeding 100 combined with the non-metallic temperature dependence – together referred to as anomalous behavior – are currently not understood and present a fundamental problem in condensed matter physics.

In this Letter, we use exfoliation and nano-fabrication techniques to investigate electrical transport in graphite flakes (see Fig. $\rho_{ab}$), comparing samples with thicknesses in the nanometer range with macroscopic samples and further comparing HOPG with Indian and Madagascar NG. Surprisingly, while conforming to the band-structure results in macroscopic NG flakes, NG displays anomalous behavior in nanostep samples – namely a large resistive anisotropy as well as a non-metallic temperature dependence. HOPG, on the other hand, shows no size dependence, behaving anomalously in all samples. We note that there are no previous $\rho_c$ data for nanometer thickness specimen, to the best of our knowledge. Interestingly, the in-plane resistivity of all samples is in good agreement with reported values $\rho_{ab}$, and shows no size-dependence, making it clear that the large anisotropies in the anomalous samples are to be attributed to a large $\rho_c$. These measured anisotropies appear consistent with a recent model based on disorder induced delocalization by Maslov et al. $\rho_{ab}$, further corroborated by a disorder characterization of our samples using micro-Raman spectroscopy. Conduction path mixing due to a finite mosaic angle can account for the non-monotonic temperature dependence $\rho_{ab}$, altogether presenting first experimental evidence for a novel paradigm of electrical transport in graphite.

FIG. 1: Nano-graphite samples. (a) Device schematic. Ti/Au contacts (yellow) for 4-wire measurements are patterned on each plateau, isolated from the graphite walls by a SiO$_2$ layer (purple). AFM picture (b) and optical microscope image (c) of an HOPG flake with two plateaus. (d) Cross section along the blue line in (b), giving plateau heights.
To produce nanostep samples, we use the design shown in Fig. 1(a). We exfoliate graphite onto a SiO$_2$/Si wafer and identify suitable flakes with two plateaus differing in height using an optical microscope. The lower plateau height $d$ and the step height $h$ are determined from an AFM image and cross-sections, see Fig. 1(b,d), giving heights between 14 and 150 nm. To extend the range to larger step heights, we use e-beam lithography and oxygen-plasma etching to carve steps up to $h = 450$ nm.

For contacting the plateaus, we first cover parts of the exterior edges of both plateaus with SiO$_2$ of at least 80 nm thickness in order to prevent short-circuiting the $c$-axis. Contacts (typically a few hundred nanometers in width) and bonding pads are patterned in a final e-beam step, evaporating a Ti/Au layer thicker than 110 nm (SiO$_2$ thickness plus 30 nm). A typical device is shown in Fig. 1(c). All resistances are measured with a standard 4-wire lock-in technique. This layout allows measurements of both $\rho_{ab}$ and $\rho_c$ on the same device, as needed to obtain the anisotropy, but requires resistivity corrections due to geometry inherent conduction path mixing.

The in-plane resistivity $\rho_{ab} = R_{ab}A_{ab}/l_{ab}$ is estimated from the 4-wire resistance $R_{ab}$ with current and voltage probes on the same plateau and assuming a simple rectangular shape of the graphite sample, with voltage probe distance $l_{ab}$ and total graphite cross section $A_{ab}$ (see Fig. 1(a)). This is a good approximation for thin samples, if the anisotropy is smaller than $l_{ab}/d \sim 250$. For large anisotropy – as seen in most samples – the extracted $\rho_{ab}$ presents an upper bound due to an effectively thinner conduction layer, since the current cannot penetrate easily along the highly resistive $c$-axis. The $\rho_{ab}$ extracted here (see Table I) agree rather well with literature, typically giving $\rho_{ab} \sim 1 \mu\Omega$ m. Moreover, $\rho_{ab}$ appears independent of the graphite thickness and is similar for NG and HOPG samples, as seen in Fig. 2 open symbols.

Next, we determine the $c$-axis resistivity $\rho_c$. Since $l_c$, the contact to contact distance across the step, is much larger than the step height $h$ (see Fig. 1(a)), we need to subtract the in-plane contributions to the measured resistance $R_c$ to obtain the corrected resistance $R_{corr}$ using

$$R_{corr} = R_c - \rho_{ab} \cdot \left( \frac{l_{cl}}{w_l \cdot d} + \frac{l_{cu}}{w_u \cdot (d + h)} \right),$$

with upper/lower contact to step distance $l_{cl/au}$ and corresponding plateau widths $w_l/w_u$. $\rho_c$ is then obtained from $\rho_c = R_{corr}A_u/h$, where $A_u$ is the upper plateau area. We note that as previously for $\rho_{ab}$, we again overestimate the thickness $d$ for large anisotropy. However, here, this effectively cancels the overestimated $\rho_{ab}$, making the extracted $\rho_c$ quite robust. The correction is often substantial, reducing $\rho_c$ and the anisotropy by a large factor (see Table I). The resulting $\rho_c$ are displayed in Fig. 2 as a function of height (filled symbols), giving very large $\rho_c$ and correspondingly large anisotropy $R_A$ for all nanographites, both NG and HOPG. Interestingly, a power-law fit (linear fit on the log-log graph, slope $-1 \pm 0.4$) through all NG nanostep $\rho_c$ data points seems to indicate a trend reducing $\rho_c$ with increasing step height towards the macroscopic $\rho_c$ value in NG samples. HOPG nanostep data is excluded from the fit, since HOPG has no apparent size dependence when going from macroscopic to nanostep samples (filled red diamonds). However, the wide spread of the data and the resulting error bars on the fit-slope are significant; to make a more definite statement, samples with step heights between 1 $\mu$m and 100 $\mu$m might give more insight.

![Graph of ρc vs. thickness](image)

**Fig. 2**: Influence of graphite thickness on $\rho_c$ (solid markers) and $\rho_{ab}$ (empty markers) at room temperature, comparing HOPG (red) with Madagascar NG (green) and Indian NG (blue). For $\rho_{ab}$, the abscissa value used is $d + h$, the overall flake thickness, see Table I. Previous measurements of macroscopic samples (black) were added for both HOPG (stars) and NG (open markers). Dashed horizontal lines indicate literature values $\rho_{ab REF}$ for $\rho_{ab}$ and $\rho_c REF$ for $\rho_c$. Further, the best power-law fit to all NG nanostep data (dotted line, linear fit on log data, slope of $-1.0 \pm 0.4$) is added to indicate a potential trend, see text.

To allow a comparison with previous experiments, we also investigate macroscopic NG and HOPG samples, again measuring both $\rho_{ab}$ and $\rho_c$. Due to the geometry used, corrections are small and not necessary for the macroscopic samples. The values obtained are also added to Fig. 2 together with typical values from literature. We find decent agreement between our macroscopic data and previous measurements, reproducing here again the large discrepancy in $\rho_c$ between HOPG and NG in macroscopic samples.

Next, we turn to the temperature dependence $\rho_c(T)$ of the macroscopic samples. For HOPG, we find a non-metallic $\rho_c$ at high $T$ ($d\rho_c/dT < 0$), see Fig. 3(a). Around 40 K, $\rho_c$ displays a rather shallow maximum,
TABLE I: Nano-sample parameters, see text for definitions, and Fig. 1 for an illustration. Samples listed here are represented in Figs. 2 and 3. Fig. 2 includes data from additional exfoliated Madagascar samples.

| Material     | $\rho_{ab} [\mu \Omega \text{m}]$ | $d [\mu \text{m}]$ | $h [\mu \text{m}]$ | $w_e [\mu \text{m}]$ | $w_a [\mu \text{m}]$ | $\xi [\text{nm}]$ | $R_{\text{corr}} [\%]$ | $A_{\text{corr}} [\mu \text{m}^2]$ | $\rho_c [\text{m} \Omega \text{m}]$ | $R_A$ |
|--------------|----------------------------------|---------------------|--------------------|------------------------|----------------------|-------------------|--------------------------|-------------------------------|-------------------------------|-------|
| HOPG 1       | 1.22                              | 11.5                | 4                  | 25                     | 2.5                  | 35                | 30                       | 14                           | 2.3                           | 361   |
| HOPG 2       | 0.78                              | 12.1                | 6                  | 20                     | 2                   | 20                | 30                       | 24                           | 2.9                           | 57    |
| Madagascar 1 | 1.45                              | 27.4                | 1.2                | 10                     | 2.3                  | 10                | 16                       | 80                           | 13.1                          | 248   |
| Madagascar 2 | 0.60                              | 26.0                | 4.2                | 8                      | 3.3                  | 5                 | 14                       | 37                           | 5.6                           | 95    |
| India 1      | 0.71                              | 18.9                | 1                  | 20                     | 3                   | 20                | 15                       | 17                           | 10.7                          | 100   |
| India 2      | 5.27                              | 37.0                | 2.4                | 20                     | 2                   | 15                | 20                       | 150                          | 1.27                          | 88    |

FIG. 3: Temperature dependence of resistivities. $\rho_c(T)$ in macroscopic HOPG (a) and macroscopic Indian (b) NG, $\rho_{ab}(T)$ in nanoscale samples for HOPG (red) and NG India (blue) and Madagascar (green). Two samples are presented for each graphite type, corresponding to Table I (solid, sample 1; dashed, sample 2) (d) $\rho_c(T)$ for the same samples.

In macroscopic NG.

Motivated by an anisotropy far exceeding the band structure expectation, we consider a recent theory by Maslov et al. [13]. A similar effect was also previously observed for photons [14]. Within this theory, c-axis transport is strongly suppressed in samples with weak bulk disorder due to 1D Anderson localization along the c-axis induced by randomly spaced barriers (e.g. stacking faults). This gives a very large $\rho_c$ and anisotropy $R_A$, as observed in the anomalous samples. In samples with sufficiently strong bulk disorder, however, c-axis localization is destroyed by bulk scattering out of the c-axis direction, leading to reduced $\rho_c$ and smaller $R_A$, as seen in the macroscopic NG samples. Interestingly, here, disorder can suppress Anderson localization, rather than enhancing it, as is usually the case. Therefore, HOPG and nanostep samples are expected to have weak bulk disorder, whereas macroscopic NG specimen either have significantly more bulk disorder (suppressing c-axis localization), or fewer c-axis barriers, insufficient for localization (barriers spacing exceeding coherence length).

To characterize disorder, we have measured spatially resolved micro-Raman spectra, see Fig. 4. We plot $\xi = I_D/I_G$, the ratio of the G-peak intensity $I_G$ and D-peak intensity $I_D$ after background subtraction, obtaining an intensity independent characterization of disorder. For graphite, $0 \leq \xi \lesssim 1$. A large $\xi$ indicates a high degree of disorder (large $I_D$). Due to a finite integration time, $\xi$ has measurement noise of $\sim 1/50$, i.e. $\xi \lesssim 1/50$ indicates an invisible D-peak and weak disorder. We note that for macroscopic samples, the Raman measurements probe only a thin surface layer. For the nanostep samples, on the other hand, a significant depth is characterized, presenting a good measurement of graphitic bulk disorder.

In macroscopic and nanostep HOPG, disorder is very low ($\xi \lesssim 1/50$ essentially everywhere, not shown), while macroscopic Madagascar NG samples are clearly more dirty, consistent with expectations from the model. Micron sized regions of strong disorder mix with cleaner areas in pristine NG, see Fig. 5(a) for a typical scan. A histogram is adjacent to the scan, revealing a broad distribution extending up to $\xi \sim 1/3$. In contrast, an exfoliated Madagascar flake displays significantly reduced disorder, see Fig. 5(b). Several exfoliated NG samples

in good agreement with previous HOPG measurements [3]. In contrast, macroscopic Indian NG behaves weakly metallic and monotonic down to 4 K (shown in Fig. 3(b)), also in agreement with previous NG data [3]. Overall, our data from macroscopic samples fully agrees with the literature, giving us confidence that a comparison of the exfoliated samples with literature is appropriate.

The temperature dependence of the exfoliated nano-graphite samples are shown in Fig. 3 (c) and (d), normalized to the high-T value. In most samples, $\rho_{ab}(T)$ is metallic and monotonic, as expected, and in agreement with macroscopic data [3, 20]. In two specimens, $\rho_{ab}$ is weakly non-monotonic. This seems to occur occasionally in nanoscale samples, as previously reported [21, 22]. Interestingly, $\rho_c(T)$ of all nanostep samples is qualitatively the same, showing a non-metallic and non-monotonic temperature dependence, qualitatively identical to macroscopic HOPG, and clearly different from the macroscopic NG data. We emphasize that the non-metallic $\rho_c(T)$ combined with the large anisotropy $R_A$ constitutes anomalous behavior for all nanoscale samples. In contrast, only macroscopic HOPG is anomalous, not
were inspected, all exhibiting $\xi$ significantly smaller than in macroscopic NG samples.

We note that exfoliating macroscopic NG only once already results in strongly reduced disorder. Clearly, exfoliating somehow acts expose clean surfaces \cite{24} and to remove bulk disorder, though the mechanism is not clear. This could potentially explain the size dependence mentioned in Fig. 2; thinner samples tend to require more exfoliation steps, therefore becoming cleaner, more localized, and obtaining a larger $\rho_c$. Ultimately, for sufficiently small $h$, 1D localization should break down and $\rho_c$ decrease strongly – not visible in the present data, presumably because $h$ is still too large. Overall, the Raman data is in good agreement with the predictions of the model, namely weak disorder in all exfoliated and all HOPG samples, as opposed to strong disorder in NG macroscopic samples.

Finally, we turn to the anomalous temperature dependence of $\rho_c$. If the c-axis resistivity $\rho_c$ is very large, the c-axis conductance path could easily be mixed with the ab-conductivity $\sigma_{ab}$ due to the finite mosaic angle $\theta$, effectively short circuiting the intrinsic c-axis conductivity $\sigma_c$. Assuming small tilting $\theta \ll 1$, the measured conductivity $\tilde{\sigma}_c$ can be written as \cite{15}

$$\tilde{\sigma}_c(T) = \sigma_c(T) + \langle \theta^2 \rangle \cdot \sigma_{ab}(T),$$

where $\langle \theta^2 \rangle$ is the variance of $\theta$. In low bulk-disorder samples at low temperatures, the intrinsic $\sigma_c$ is very small (strongly localized) and $\tilde{\sigma}_c(T)$ obtains a significant component from $\sigma_{ab}$, including the (weakly) metallic temperature dependence $\sigma_{ab}(T)$, leading to a slight increase of $\rho_c(T)$ upon increasing $T$. At higher $T$, localization is weakened (due to phonon scattering, equivalent to increasing bulk disorder for increasing $T$), $\sigma_c$ is enhanced and becomes increasingly more dominant, leading to a decreasing $\rho_c$ above some cross-over $T$. For a mosaic angle of about $0.8^\circ$ (values between $0.2^\circ$ and $2^\circ$ were measured, not shown), the crossover would occur around 40 K, in agreement with the data. For disordered samples, on the other hand, the intrinsic $\sigma_c$ is dominating $\tilde{\sigma}_c(T)$ since localization is already lifted by disorder, resulting in the usual metallic temperature dependence, as seen in macroscopic NG \cite{7}.

In conclusion, we observe anomalous behavior, namely high $\rho_c$ and non-monotonic $\rho_c(T)$, in both NG and HOPG exfoliated samples. This is in stark contrast to macroscopic samples, where the anomalous behavior is only seen in HOPG, consistent with previous experiments. A recently proposed transport theory \cite{13} can consistently explain this convergence on the nanoscale, the macroscopic data, and the temperature dependence. Further, finding indeed low disorder in exfoliated and HOPG samples, and high disorder in macroscopic NG, as expected within the model. We note additionally that neutron irradiation experiments \cite{5,11} inducing bulk disorder also give consistent results, namely reduced $\rho_c$ after irradiation of HOPG, further corroborating the model. We therefore present first, clear evidence of disorder induced delocalization as a new paradigm of electronic transport in graphite.

Though beyond the scope of the present work, it would be very interesting to subject the model to further scrutiny: studying intermediate steps filling the thickness gap in Fig. 2 but also even smaller thicknesses, ultimately down to few- or bi-layer graphene, potentially revealing the localization length. This might be facilitated by bottom contacts with layers deposited on top, followed by top contacts. We note that the minimum thickness in the present samples is 14 nm, corresponding to about 50 graphene layers. Further, a characterization of graphite disorder would be of great interest, e.g. investigating stacking faults and angles, intercalation, grain and boundary formation, aiming at identifying the localization mechanism, leading ultimately to a microscopic understanding of electrical transport in graphite. The results presented here were obtained in graphite, but it would be intriguing to learn if similar arguments apply to some of the numerous other layered materials.

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Disorder characterization with micro-Raman spectroscopy. Ratio $\xi = I_D/I_G$ of the D-peak and the G-peak intensities, scanned (resolution $\sim 0.5 \mu m$) on (a) macroscopic Madagascar NG and (b) exfoliated Madagascar flake, plotted on the same color-scale, as indicated. White is off the graphite flake. Corresponding histograms of $\xi$ gathered over the shown scan areas are shown to the right of each scan.}
\end{figure}
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