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Evidence for semiconducting behavior with a narrow band gap of Bernal graphite

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Abstract. We have studied the resistance of a large number of highly oriented graphite samples with areas ranging from several mm² to a few µm² and thickness from ∼10 nm to several tens of micrometers. The measured resistance can be explained by the parallel contribution of semiconducting graphene layers with low carrier density < 10⁹ cm⁻² and the one from metallic-like internal interfaces. The results indicate that ideal graphite with Bernal stacking structure is a semiconductor with a narrow band gap $E_g \sim 40$ meV.

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1. Introduction

The study of the transport properties of graphite has been the object of discussion for more than 60 years [1–6]. The work of Slonczewski and Weiss [4] as well as that of McClure [5, 6]—both a continuation of the work of Wallace [1] on the band structure of graphene—introduced several (free) coupling parameters within a tight binding calculation and the k.p. method to obtain the graphite band structure. The parameters were then fixed using as the reference the transport results obtained in bulk graphite samples with carrier density per graphene layer \( n(T \to 0) = n_0 \gtrsim 10^{10} \text{cm}^{-2} \). The apparent existence of a relatively large carrier density seemed to be compatible with the relatively small and metallic-like resistivity measured in several bulk graphite samples [7]. All these early results obtained for the graphite structure were resumed later within the so-called two-band model for graphite developed by Kelly [7]. After that, many band structure calculations using the local density as well as other approximations [8] reached the same conclusions and claimed to fit well the experimental results; see, e.g., [9, 10]. Note, however, that all these calculations depend on parameters that are being fixed to fit experimental data. If those experimental results do not reflect the intrinsic properties of ideal graphite, clearly those calculations as well as the obtained parameters cannot be taken as intrinsic to the graphite structure.

A different approach to obtain the binding energy between the planes of graphite has been proposed using the Lennard-Jones potential and assuming that the binding between graphene layers is due to van der Waals forces [11–13]. These forces represent a very weak interaction and therefore it is rather clear that this approach will not give a similar band structure for graphite as the one proposed with large coupling between the graphene planes. From an experimental point of view, we may now doubt that the large number of reported data, e.g. \( n(T) \), reflect ideal graphite. The exhaustive experience accumulated in gapless or narrow gap semiconductors [14] indicates already that care should be taken with the measured carrier density because it can easily be influenced by impurities and/or defects in the graphite/graphene lattice [15, 16].

We believe that the multigrain morphology of real oriented graphite samples has not been taken into account appropriately in the literature, especially its influence on the carrier density and other transport phenomena. For example, electron backscattering diffraction (EBSD) reveals the typical size of the grains to be a few microns in the \( a, b \) plane within highly oriented pyrolytic graphite (HOPG) samples (see [17]), a size that limits the carrier mean free path at low temperatures [18]. Moreover, the contribution to the transport properties of internal two-dimensional (2D) interfaces found recently between single-crystalline regions inside the HOPG samples [19] was apparently never taken into account in the existing literature on graphite. Why can these interfaces be of extreme importance in graphite? As the results from various semiconductors show (e.g. \( n\)-Ge bicrystals [20, 21], p-\( \text{InSb} [22] \) as well as in \( \text{Hg}_{1-x} \text{Cd}_x \text{Te} \) grain boundaries [23]), internal interfaces lead to the formation of confined quasi-2D carrier systems with \( n_0 \sim 10^{12}–10^{13} \text{cm}^{-2} \) and clear signs of the quantum Hall effect [21]. Recent studies have demonstrated the large sensitivity of the resistivity of graphite samples to the internal interfaces that exist between crystalline regions of \( \sim 30–100 \text{nm} \) thickness, a few microns long and running mostly parallel to the graphene planes [19]. These results indicate that the earlier reported values of \( n(T) \) as well as the metallic-like behavior of the resistivity \( \rho(T) \) are not intrinsic to the graphite Bernal structure but are due, to a large extent, to the contribution of internal interfaces and defects.
The aim of this work is to propose a simple model to explain the experimental longitudinal resistance data obtained in different oriented graphite samples of different thickness and area. The rather complicated behavior of the longitudinal resistivity can be explained assuming the parallel contribution of regions with semiconducting graphene layers and the one from the interfaces between them, as transmission electron microscopy (TEM) studies reveal [19].

2. Sample characteristics

All the graphite samples were taken from the same Bernal-type HOPG sample from Advanced Ceramic of high purity (see, e.g., [24]) and with a rocking curve width of $(0.35 \pm 0.1)^\circ$. As shown by Bernal [25], this structure has the usual ABABABA... stacking of the single graphene layers inside graphite. This is the stable graphite structure, which is obtained by suitable annealing treatments eliminating also the possible rhombohedral modification that results from deformation of the original hexagonal structure. The internal structure of the used samples is shown in the TEM picture in figure 1. As shown in [19], this picture reveals single crystalline regions of graphene layers, of thickness between 30 nm and $\sim$100 nm. These regions are clearly recognized in figure 1 through the different grayscale and have a slight different orientation between each other, e.g. different angle misalignments. We note that a rotation up to 30° between the graphene layers from neighboring graphite regions has been observed by high resolution TEM (HRTEM) in few-layer graphene sheets in [26].

Of importance for understanding the measured behavior of the resistance of graphite samples is the existence of well-defined interfaces between the single-crystalline regions. As we mentioned in the introduction, interfaces between crystalline regions in semiconductors with different orientations, for example [20–23], lead to confined quasi-2D carrier systems with a much larger carrier density than the bulk matrix. We assume therefore that these interfaces running parallel to the graphene layers of the graphite structure are the origin of metallic-like resistivity as well as of the apparent large carrier density measured in bulk samples, i.e. $n_0 \gtrsim 10^{10}$ cm$^{-2}$, an assumption that is supported by the change in absolute resistivity with thickness [19].

Taking into account the internal microstructure of the graphite samples, it is clear that it is necessary to measure the resistance of samples of small enough thickness in order to get the intrinsic transport of the graphite structure with its weak coupled graphene layers. The micrometer small samples with thickness below 100 nm were prepared by a rubbing method [19]. The resistivity data were obtained with four contacts by checking the ohmic behavior at room temperature. The deposited Pd/Au contacts on the micrometer large graphite flakes were prepared by electron lithography, and micro-Raman characterization was used to check for the sample quality [19], as the inset in figure 2 demonstrates. Following the characterization work of [27], the Raman spectra confirm similar stacking between the bulk and thin graphite samples. The micrometer large mean free path at 300 K and the low carrier density [28, 29] are further proof of the high quality of the thin graphite flakes discussed in this work.

3. Temperature dependence of the carrier density

We start with the temperature dependence of the carrier density $n(T)$ obtained from a 40 nm thin and several micrometers large graphite flake sample. It is important to recognize that
due to the large mean free path of the carriers $\ell$ in the graphene layers within the graphite structure, ballistic and not diffusive transport has to be taken into account [18, 29]. To obtain the mean free path or the intrinsic carrier density of the graphene layers inside graphite, one cannot use straightforwardly the Boltzmann–Drude approach to interpret the longitudinal and transverse resistances. Due to the large mean free path of the carriers in the weakly coupled graphene layers within the graphite structure, it is possible to use experimental methods where the ballistic transport is clearly revealed. One possible experimental method is the constriction method based on the measurement of the longitudinal resistance $R$ as a function of the width $W$ of a constriction located between the voltage electrodes. When $\ell \gtrsim W$ the ballistic contribution overwhelms the diffusive ones and allows us to obtain $\ell(T)$ and $n(T)$ without the need for free parameters or arbitrary assumptions [18, 28]. Another experimental method is by the measurement of the length dependence of the resistance. If ballistic transport is important, then a finite resistance is extrapolated at zero sample length, a value that can be used to obtain directly the mean free path without free parameters or arbitrary assumptions [29]. Both independent methods provide similar large carrier mean free paths as well as a much lower carrier density than those found in the literature for bulk graphite samples.

Figure 2 shows $n(T)$ for a thin graphite sample; it follows an exponential dependence with an activation energy or energy gap $E_g \sim 46$ meV. Due to the small gap and from figure 2, it is not obvious that the experimental curve is exponential and not linear at temperatures above the saturation region. A simple way of identifying that is by calculating the temperature derivative. In case of linear temperature behavior, we expect a saturating upper derivative value at high temperatures but a shallow maximum for the exponential function at intermediate temperatures. The bottom right inset shows the calculated derivative for both curves, the experimental and the
Figure 2. Carrier density per graphene layer obtained using the constriction method [18] for a graphite sample of size $9 \times 3 \times 0.040\,\mu\text{m}^3$. The continuous line is a fit to the data and follows $n(T)\, [10^8\,\text{cm}^{-2}] = 2.7 + 12.4 \exp(-540/2T[K])$. We estimate a $\sim30\%$ error in the absolute value of the carrier density, mainly due to sample geometry errors, as well as in the constriction widths. The upper left inset shows the Raman (514 nm) spectra of: (o) bulk graphite (figure 2(a)) and (red line) a multigraphene sample (similar to that of figure 3(a)). The absence of a D-peak indicates the absence of a significant number of defects. The bottom right inset shows the temperature-dependent derivative of the carrier density (circles) and of the fitting curve shown in the main panel. Note the maximum in the derivative at $\sim125\,\text{K}$ present in both derivatives. The horizontal straight line is only a guide to the eyes.

It is clear that the exponential function provides the correct temperature dependence of the carrier density. The shallow minimum in $R(T)$ (the main panel of figure 2) at $T < 50\,\text{K}$ is an artifact due to interfaces, at least the one between the substrate and sample and/or the sample free surface. The finite value of $n(T \to 0)$ can be due to this interface contribution or due to lattice defects [15] including a very small amount of impurities such as hydrogen; note that $n = 10^8\,\text{cm}^{-2}$ would mean of the order of a single hydrogen atom or C-vacancy in a $1\,\mu\text{m}^2$ graphene area.

One may be surprised to get such a low carrier density in comparison with the usual values reported in the literature for graphite, e.g. $n_0 \gtrsim 10^{10}\,\text{cm}^{-2}$ [7, 9, 10]. Firstly, we note that the measured graphite sample has a thickness less than 50nm and therefore much less contribution of interfaces. Secondly, the measured carrier density of graphite reported in the literature was obtained mostly for bulk samples with an unknown concentration of interfaces as well as defects. Further independent evidence that supports an intrinsic low carrier density in graphite is given by the vanishing of the Shubnikov–de Haas (SdH) oscillations in the magnetoresistance the thinner the graphite sample, an experimental fact already reported in 2001 that to our knowledge remained without explanation [30]. Note that earlier publications reported SdH oscillations of very large amplitude, e.g. [31], in comparison with the rather weak
amplitudes, if observed at all, found nowadays in better quality samples or thin enough graphite samples. A clear demonstration that these SdH oscillations are actually non-intrinsic to ideal graphite is given by their appearance in thin graphite samples upon introducing defects by irradiation as shown in [15, 32].

4. Temperature dependence of the resistance of different graphite samples

Following the results from [19] as well as the semiconducting behavior of \( n(T) \), see figure 2, obtained for a thin graphite sample, we assume therefore that the graphene layers inside each graphite sample are semiconducting and their signal between the voltage electrodes is given by an effective resistance of the type

\[
R_s(T) = a(T) \exp\left(\frac{+E_g}{2k_BT}\right).
\]

(1)

The prefactor \( a(T) \) depends basically on the mobility, i.e. the mean free path, and on details of the carriers band structure (e.g. effective mass). If we take into account in \( a(T) \) the temperature dependence of the mean free path recently obtained for similar samples, i.e. \( \ell(T) \approx (3)^{-1} + (6.4 \times 10^3/\ell^2)^{-1} \) (\( \ell \) in \( \mu \text{m} \) and \( T \) in K), we obtain \( E_g \) obtained from the fits to the data remains the same within the confidence limits of 35%. For simplicity we will take \( a(T) \) as a temperature-independent parameter as well as the energy gap \( E_g \). The absolute value of the prefactor \( a \) (as well as of other prefactors) will change from sample to sample; note that we estimate the resistance of a given sample and not its resistivity.

For samples with thickness larger than \( \sim 50 \text{ nm} \) and of several micrometers length, there is a larger probability of having interfaces, whose signals will be picked up by the voltage contact electrodes (usually several micrometers apart). Therefore, in parallel with \( R_s(T) \) we simulate the contribution from the interfaces through the resistance:

\[
R_i(T) = R_0 + R_1T + R_2 \exp\left(-\frac{E_a}{k_BT}\right),
\]

(2)

where the coefficients \( R_1, R_2 \) as well as the activation energy \( E_a \) are free parameters. The temperature-independent term in equation (2) represents the residual resistance measurable at low enough temperatures. The unusual thermally activated term as well as the, in general weak, linear one will be discussed at the end. The total resistance \( R_T(T) \) is given by the parallel contributions of \( R_s \) and \( R_i \) as \( R_T(T) = [R_s(T)^{-1} + R_i(T)^{-1}]^{-1} \). Clearly, by changing the parameters one can obtain all types of behavior for \( R(T) \). We will see that a consistent description of the data can indeed be reached and that the main free parameter \( E_g \) is similar for all samples.

Figures 3 and 4 show the normalized resistance versus temperature and the fits with the parallel resistance model described above of six different samples with different weights between the intrinsic semiconducting and the non-intrinsic interface contribution. That is why the pre-factors of the main terms in \( R_T(T) \) must change from sample to sample, i.e. \( R_1/R_0, R_2/R_0 \) and \( a/R_0 \), because we do not fit the resistivity but the resistance. From all the obtained data and within the confidence limits of the fitting, we obtain an energy gap \( E_g = 40 \pm 15 \text{ meV} \), independently of the sample geometry, i.e. a similar energy gap is obtained for very thin as well as thick graphite samples if the contribution of the interfaces does not shortcircuit completely that from the graphite crystalline regions. This fact indicates that we are not dealing here with a special graphite structure found only in a few tens of nanometers thick samples. This is the main result of this study.
but for samples with geometry and thickness as well as in the high-temperature part where one recognizes the slight increase of resistance just below follows \( R_i(T)/R_0 = 1 + 0.2 \times 10^{-3}T[K] + 0.7 \exp(-38/T[K]) \) and \( R_s(T)/R_0 = 2.35 \exp(260/2T[K]) \). The dashed curve above follows \( R_i(T)/R_0 = 1 + 2.17 \times 10^{-3}T[K] + 0.7 \exp(-38/T[K]) \) and \( R_s(T)/R_0 = 2.35 \exp(400/2T[K]) \). The inset in (c) is a magnified view of the high-temperature part where one recognizes the slight increase of resistance at \( T > 200 \text{K} \), an increase that can be obtained by changing slightly the used parameters, as the lower curve shows.

![Figure 3](http://www.njp.org/)

**Figure 3.** Normalized resistance \( R/R_0 \) versus temperature for three HOPG samples with thickness, length (between voltage electrodes), width and \( R_0 \): (a) \( \simeq 20 \mu m, 2 \text{ mm}, 1 \text{ mm}, 0.003 \ \Omega \); (b) \( \simeq 10 \mu m, 1 \text{ mm}, 1 \text{ mm}, 0.013 \ \Omega \); (c) \( \simeq 50 \text{ nm}, \sim 3 \mu m, \sim 3 \mu m, 15 \ \Omega \). The (red) lines through the experimental data are obtained from the parallel contributions given by equations (1) and (2): (a) \( R_i(T)/R_0 = 1 + 2.2 \times 10^{-3}T[K] + 5.2 \exp(-48/T[K]) \); (b) \( R_i(T)/R_0 = 1 + 2.2 \exp(-33/T[K]) \) and \( R_s(T)/R_0 = 3.4 \exp(662/2T[K]) \); (c) \( R_i(T)/R_0 = 1 + 2 \times 10^{-3}T[K] + 0.7 \exp(-38/T[K]) \) and \( R_s(T)/R_0 = 2.35 \exp(340/2T[K]) \). Note that the curves obtained are very sensitive to small changes in parameters. For example, in (c), the continuous curve just below follows \( R_i(T)/R_0 = 1 + 2.41 \times 10^{-3}T[K] + 0.7 \exp(-38/T[K]) \) and \( R_s(T)/R_0 = 2.35 \exp(260/2T[K]) \). The dashed curve above follows \( R_i(T)/R_0 = 1 + 2.17 \times 10^{-3}T[K] + 0.7 \exp(-38/T[K]) \) and \( R_s(T)/R_0 = 2.35 \exp(400/2T[K]) \). The inset in (c) is a magnified view of the high-temperature part where one recognizes the slight increase of resistance at \( T > 200 \text{K} \), an increase that can be obtained by changing slightly the used parameters, as the lower curve shows.

![Figure 4](http://www.njp.org/)

**Figure 4.** Similar to figure 3 but for samples with geometry and \( R_0 \): (a) \( \simeq 13 \text{ nm}, 14 \mu m, 10 \mu m, 490 \ \Omega \); (b) \( \simeq 20 \text{ nm}, 5 \mu m, 10 \mu m, 32 \ \Omega \); (c) \( \simeq 37 \text{ nm}, 27 \mu m, 6 \mu m, 69 \ \Omega \). The lines through the experimental data are: (a) \( R_i(T)/R_0 = 1 - 6.2 \times 10^{-4}T[K] \) and \( R_s(T)/R_0 = 1.18 \exp(480/2T[K]) \); (b) \( R_i(T)/R_0 = 1 + 0.096 \exp(-24/T[K]) \) and \( R_s(T)/R_0 = 0.82 \exp(350/2T[K]) \). (c) \( R_i(T)/R_0 = 1 + 0.0044 T[K] + 0.47 \exp(-12/T[K]) \) and \( R_s(T)/R_0 = 0.73 \exp(400/2T[K]) \).

We stress that the interfaces as well as the single-crystalline regions are restricted in thickness as well as in the \( a, b \) plane parallel to the graphene layers. This fact supports the use of the simple parallel resistance model. For thick enough graphite samples (thickness \( t \gtrsim 1 \mu m \)),
the contribution of the interfaces is overwhelming and the measured resistance will be mainly given by equation (2), as the results for the bulk HOPG sample show, see figure 3(a). The exponential term with an activation energy $E_a/k_B = 48 \pm 2$ K is of the same order as that reported in [33] for similar samples. To fit the data shown in figure 3(a), a relatively small linear-temperature term contributes at high temperatures.

In general, the semiconducting behavior starts becoming clearly visible in thinner samples due to the decrease in the number of interfaces; obviously, there is no sharp thickness threshold because the properties of the interfaces as well as the defects and carrier concentrations vary from sample to sample, affecting the relative weight between the two parallel contributions. The results shown in figures 3(b) and (c) are examples where the two contributions $R_i$ and $R_s$ compete. For samples thinner than $\sim 40$ nm, the semiconducting behavior starts overwhelming that from the interfaces; see figure 4.

Note that this semiconducting behavior is observed for a range of about five orders of magnitude in sample area and that the width or length of the samples overwhelms the intrinsic Fermi wavelength of the graphene planes inside the sample [28], $\lambda_F \lesssim 1$ $\mu$m. Therefore, the semiconducting behavior is not due to a quantum confinement shift, as observed in Bi nanowires [34] of small diameter $d < \lambda_F$. We stress that our results should not be interpreted as a metallic-to-semiconducting transition as a function of thickness, but only the weight between the two parallel contributions changes upon sample thickness. Because at least the sample–substrate and sample–surface interfaces remain, as for the sample of figure 4(a), both parallel contributions are always present. We note that the $T$ dependence of the $c$-axis resistivity of graphite with pressure [35] shows similar characteristics as the ones for the resistivity in plane shown here. The $c$-axis resistivity behavior was basically interpreted with a tunnel barrier for the electrons between planes and crystallites.

5. Discussion

We would like to discuss the question of the existence of an energy gap taking into account the results from the literature and whether this intrinsic semiconducting behavior has been observed in the past.

(a) As we discussed above and taking into account the contribution of the interfaces bulk graphite samples have, it is clear that the behavior obtained in transport measurements of those samples is not intrinsic. Therefore, we cannot consider those experimental results to be a proof of the apparent metallicity of graphite.

(b) One would expect that infrared (IR) measurements show somehow the semiconducting behavior. However, those measurements, as for example in [36], were made in bulk samples (several mm$^2$ area and several hundreds of micrometers thick) that show clear SdH oscillations [37] with the usual carrier density above $10^{10}$ cm$^{-2}$ per graphene layer and therefore do not represent intrinsic graphite. Note that the internal interfaces (see figure 1), due to their large carrier density in comparison with the crystalline regions, are those regions that provide a shielding to the electromagnetic wave used in IR measurements. In general, we remark that spectroscopy methods are not completely reliable when one wants to resolve a gap of 40 meV in samples that are inhomogeneous for the reasons discussed above. Therefore, we believe that the intrinsic properties of the single-crystalline graphite regions are not actually seen by this technique. Also other experimental techniques (see,
e.g., [38]) would have problems in recognizing an electronic band structure with an energy gap of the order of 40 meV if the carrier density is much larger than the intrinsic one of ideal, defect-free graphite.

(c) We may ask about the results on graphite using angle-resolved photoemission spectroscopy (ARPES) published several times in the past. There are three points that we should take into account about ARPES results. Firstly, this technique is surface sensitive, although we may expect to see to some extent a vestige of the bulk band edge. Secondly, different samples may provide different results. A clear correlation between sample quality and its other characteristics with the ARPES results is difficult, because one does not always find the necessary information in the reported studies. Finally, the scanned sample area and the energy resolution of the usual spectroscopy systems. We know from other techniques such as EBSD [17] or electron force microscopy (EFM) [39] that homogeneous regions of graphite appear to be in the region of 10 µm (parallel to the planes) or smaller. Regarding the energy resolution, we find, for example, in the ARPES work of [40] a resolution of 15–65 meV, in [41] it is from 15 to 40 meV and in [42] it is 40 meV. This resolution appears to be too low to clearly resolve an energy gap of the order of 30–50 meV in bulk graphite. A better energy resolution between 4 and 15 meV has been achieved in [9, 43] by using kish and natural graphite samples, respectively. Interestingly, in [43] an energy gap of 25 meV between the and bands at the K(H) point was reported, whereas in an energy gap of 37 meV has been inferred from the band fits near the H point, although the used sample had apparently an average carrier density of 6 × 10^{11} cm^{-2} (at 25 K). Clearly, higher energy resolution, smaller scanned areas and clearer sample quality aspects are necessary in future experiments using this technique.

(d) In general, we note that techniques that are sensitive to the surface do not necessarily provide the intrinsic properties of graphite. Apart from the extra doping graphite surfaces may have due to defects and added atoms or molecules, we note that the surface itself may have a different electronic structure than the graphene layers inside the Bernal structure due to the total absence of coupling with a graphene layer above it. Therefore, scanning tunnelling microscopy (STM) experiments on the graphite surface do not necessarily provide the intrinsic behavior of graphite with certainty. However, there are STM experiments that suggest the existence of an energy gap of the same magnitude as the one obtained in this work. This energy gap appeared in a few graphene layers [44] from ‘unidentified states’ or levels that at zero magnetic field do not coalesce, a result supported by Hubbard calculations with a constant potential [45]. Clearly, if a few graphene layers show an energy gap, there seems to be no simple reason to rule out that graphite should not have it. Note also that in [44], other electronic contributions, partially due to Dirac fermions, have been obtained at the surface. This fact suggests that the resistance of this interface (or between the sample and the substrate) will provide a different conduction path in parallel with the semiconducting one from the internal graphene layers. This gives a simple explanation for the saturation in resistance measured at low temperatures.

(e) In order to compare the results of the temperature dependence of the resistance $R(T)$ obtained in single- or few-layer graphene samples with our results, one should compare the one obtained at the lowest carrier density possible. This has been done in, e.g., [46], where it was recognized that at the lowest carrier density reached near the neutrality point (the former Dirac point) the resistance does not behave like a metal but rather as a semiconductor. With increasing the carrier density only slightly with the bias voltage,
the resistance starts showing signs of metallicity [46]. Further semiconducting behavior in $R(T)$ has been seen in [47] and [48].

(f) Last but not least, we would like to point out the recently performed optical pump–probe spectroscopy experiments on 30 nm thick graphite flake [49], a sample geometry relevant for comparison with our study. Even for excitation densities ten times as large as that one of our samples, these experiments suggest a renormalization of the band gap by $\sim 30 \text{ meV}$, which is nearly constant during the first picosecond. The authors of [49] conclude that carrier equilibration in graphite is similar to that in semiconductors with a non-zero band gap.

The interaction between graphene planes in graphite is of the van der Waals type, which gives a binding energy of $\lesssim 400 \text{ K}$. This means that each graphene layer should be very slightly affected and therefore the electron–electron interaction may also be active in graphite as in ideal single graphene. This cannot be excluded because the data obtained in the literature are for large $n$ and therefore any gap of the magnitude we obtain here will not be so easily measurable. Electron interactions are large and for a small enough carrier density the expected screening will be very weak, promoting therefore the existence of an energy gap. This is what is observed in Monte Carlo simulations for the unscreened Coulomb interaction in graphene with different Dirac flavors [50].

Before concluding we would like to discuss the possible origin of the exponential function in equation (2) because this is not the usual one that one expects for metals or semimetals and cannot be understood within the usual electron–phonon interaction mechanisms also in two dimensions. We note that this function has already been used to describe the increasing resistance of bulk graphite samples with temperature and is speculated to be related to some superconducting-like behavior in graphite [33]. We note further that a similar dependence has been observed in granular Al–Ge [51], which shows for a particular Al concentration a semiconductor–superconductor transition practically identical to that in figure 4(c). The thermally activated behavior in equation (2) can be understood on the basis of the Langer–Ambegaokar–McCumber–Halperin (LAMH) model [52, 53] that applies to narrow superconducting channels in which thermal fluctuations can cause phase slips. The value of the activation energy $E_a$ obtained from the fits depends on the measured sample and is between 10 and 40 K for a large number of measured samples.

Although we do not claim that this exponential function is due to granular superconductivity embedded within the interfaces shown in figure 1, this speculation matches a series of experimental hints obtained recently. We would like to mention that the possible existence of high-temperature superconductivity in non-percolative regions within the internal interfaces found in highly oriented pyrolytic graphite has recently been proposed [19]. The experimental hints are quite diverse and all of them point in the same direction: (i) huge magnetic field-driven metal–insulator transition in bulk graphite [54, 55]. This transition vanishes for thin enough samples because of the lack of internal interfaces. (ii) Superconducting-like hysteresis loops in the magnetization of pure HOPG samples ([56, 57] and references therein). (iii) Anomalous hysteresis in the magnetoresistance of mesoscopic graphite samples, similar to that found in granular superconductors [58, 59]. (iv) Quantum oscillations in the magnetoresistance in multigraphene samples based on the Andreev scattering mechanism [58]. (v) Superconducting-like magnetic field-driven transition in the resistance of an internal interface of a graphite flake [60]. (vi) Finally, Josephson-like $I/V$ characteristic curves found in thin graphite lamellas [61].
Since most of the theoretical predictions emphasize that superconductivity should be possible under the premise that the carrier density per graphene area \( n > 10^{13} \text{ cm}^{-2} \) in order to reach \( T_c > 1 \text{ K} \), it is then appealing that regions at the internal interfaces within the graphite structure may have superconducting patches due to the much higher carrier density. We note that interfaces in some semimetal materials such as Bi can be superconducting [62, 63].

The weak linear term in equation (2) provides a typical metallic dependence of the resistance, which may come from the metallic regions within the interfaces. This small term is not always necessary to obtain a reasonable fit to the data and can even be negative (or may follow a weak variable range hopping dependence) as appears to be the case for the sample–substrate and/or sample–surface interfaces; see figure 4(a). Even in the case of the total absence of internal interfaces, as for example for thin enough samples, it is clear that the semiconducting behavior of the intrinsic graphite regions cannot be observed at low enough temperatures due to the parallel contributions of the surface and/or substrate/sample.

In conclusion, the temperature dependence of the electrical resistance of oriented graphite samples can be quantitatively understood assuming the parallel contribution of semiconducting and normal metallic (and/or granular superconducting) regions. The semiconducting contribution clearly indicates that Bernal graphite is a semiconductor with a narrow gap of the order of 40 meV. We may speculate that what we observe in graphite may also apply to other semimetals and a material with strictly zero band gap probably does not exist in nature.

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