Size dependence of the Josephson critical behavior in pyrolytic graphite TEM lamellae

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Abstract
We have studied the transport characteristics of TEM lamellae of different widths obtained from a graphite sample with electrical contacts at the edges of the embedded interfaces. The temperature dependence of the resistance, as well as the current-voltage characteristics, are compatible with the existence of Josephson-coupled superconducting regions. The transition temperature at which the Josephson behavior sets in decreases with a decreasing interface width and vanishes for widths below 200 nm. This interface-size dependence provides an explanation for differences observed in the transport behavior of graphite-based samples with interfaces, and it appears to be related to the influence of weak localization effects on the superconducting critical temperature.

Keywords: graphite interfaces, size effects, granular superconductivity

The possibility of high-temperature superconductivity at surfaces and interfaces has attracted the attention of the physics community since the earliest 1960s [1]. Superconductivity has been found at the interfaces of narrow-gap semiconducting superlattices, e.g., PbTe/SnTe, whose origin appears to be related to arrays of edge dislocations found when there is a lattice mismatch of the used semiconducting components [2, 3]. Interfaces in pure as well as doped Bi bicrystals can show superconductivity up to \( T_c \approx 21 \text{ K} \) [4, 5], although Bi as bulk is not a superconductor. Superconductivity was also found at the interfaces between oxide insulators [6] or between metallic and insulating copper oxides with critical temperature \( T_c \gtrsim 50 \text{ K} \) [7]. In all those experiments, the appearance of superconductivity was determined mainly by conductivity measurements. This is because conductivity is extremely sensitive to the superconducting properties of the interfaces, especially if they compete with the rest of the non-superconducting matrix.

The existence of high-temperature superconductivity embedded in disordered graphite grains was speculated on 40 years ago [8]. Since then, different studies were published in (not intercalated) graphite [9] as well as in doped disordered carbon samples [10] providing indications of high transition temperatures. The existence of quasi two-dimensional (2D) interfaces found in highly oriented pyrolytic (HOPG) and Kish graphite samples was known long time ago [11], but their extraordinary properties were reported only recently after contacting the edges of the embedded interfaces found in transmission electron microscope (TEM) graphite lamellae [12], see figure 1(b) as example. These interfaces are formed between slightly rotated Bernal graphite blocks around the \( c \)-axis. Several experiments indicate that the metalliclike behavior of the resistivity of graphite is mainly due to the parallel contribution from the interfaces; otherwise, a semiconducting behavior is observed [13, 14]. Evidence for granular superconductivity in graphite flakes has been independently observed in the field hysteresis and field periodic oscillations in high-resolution magnetoresistance measurements, as well as in SQUID magnetization measurements of HOPG samples with interfaces; for a review see [9].

The (granular) superconductivity at the interfaces between twisted graphite blocks by a small angle may be related to the existence of an array of line or screw dislocations that produce flat bands in the carrier band structure [15].
similar to what may happen at the interfaces between two different narrow-gap semiconductors [16]. We note further that high-temperature superconductivity has been predicted to occur at topologically protected flat bands on the surface [17] or at certain rhombohedral-Bernal interfaces [18, 19] in graphite [20]. Inclusions of rhombohedral graphite ordered regions have been found embedded in bulk Bernal graphite [21] as well as in exfoliated multilayer graphene films [22], both taken from HOPG samples. They thus provide an alternative mechanism for the formation of high-temperature superconductivity at the interfaces to that due to the array of defects. However, we do not yet have direct evidence of the presence or absence of such defects or rhombohedral stacking at the interfaces reported here. They thus require further study.

If the conditions for high-temperature superconductivity at some of the observed 2D interfaces exist, for example at a small enough twist angle between the graphite Bernal blocks as suggested in [15], we may expect that in real samples those superconducting regions are rather localized in space. We note that the topological protected conditions at the interface can be sensitively changed by different doping conditions (different amount of embedded hydrogen at the interface, for example) or due to existing defects like vacancies [23]. As we describe later, within the existing experimental evidence, it is possible to provide a rough estimate of the size of those regions. Following the experimental evidence for the existence of Josephson coupling through a normal graphene layer and between superconducting regions several hundreds of nm apart [24], a Josephson-like coupling between the superconducting patches localized at certain interface regions does appear highly possible. Figure 1(c) shows a rough sketch of what we may expect at certain interfaces.

In this work we report on a phenomenon that has not yet been reported for graphite and it is related to the transition temperature $T_c$ characteristic of the Josephson effect found at graphite interfaces [12]. We observed that this $T_c$ decreases with the width of the 2D interface regions. The observed behavior may clarify the origin of the differences in the temperature dependence of the resistance, especially the temperature at which the resistance shows a maximum $T_{\text{max}}$, in bulk graphite samples and in small graphite flakes with interfaces. At least part of these differences are related to the thickness of the measured lamellae, and therefore the area of the embedded interfaces where superconductivity exists. We expect that there exists a correspondence between the true superconducting critical temperature, the temperature $T_c$ (at which the Josephson behavior starts to be measurable), and that $T_{\text{max}} \sim T_c$.

TEM lamellae with a thickness between 80 nm and 800 nm were fabricated with the Ga+ beam of a dual-beam microscope (FEI Nanolab XT 200) from the same bulk HOPG sample grade ZYA ($0.4^\circ$ rocking curve width). We previously covered the sample surface with a tungsten-carbide (WC) film, deposited using electron beam induced deposition (EBID), to avoid the penetration of the Ga+ ions in the graphite structure of the lamella [12]. The lamella thickness corresponds to the width of the graphene planes and therefore to the width of the internal interfaces as they run parallel to the graphene planes; see figure 1(b) and the TEM images in [11, 12]. Moreover, electron backscattering diffraction (EBSD) measurements showed the existence of grains of several micrometers in the $ab$-plane [11, 25]. The transport measurements were done using a four-probe electrode technique in the conventional configuration; see figure 1(a).

Figure 2 shows the temperature dependence of the voltage for four TEM lamellae measured at a constant input current of 1 nA. For clarity and taking into account the differences in the absolute resistance between the samples, we present the voltages normalized to their maxima. Figure 2(a) shows the results obtained for three samples with 200, 300, and 500 nm thickness. The normalized voltage vs. temperature curve obtained from a bulk piece of HOPG (from which the lamellae were extracted) is shown as well (right y-axis). The normalized voltage behavior as a function of temperature of a fourth lamella, which is the thinnest we could fabricate (80 nm), is shown in figure 2(b). Note that the measurements of the four lamellae presented in figure 2 were done using 1 nA current because the observed transitions shift to lower
temperatures the larger the input current, as expected in a system with Josephson-coupled superconducting grains.

In Figure 2 we recognize clear drops of the voltage at different temperatures for lamellae with thickness $d \geq 200 \text{ nm}$, while for a thinner lamella ($d = 80 \text{ nm}$), a semiconducting-like behavior is observed to $2 \text{ K}$, the lowest measured temperature. A similar semiconducting-like dependence is measured for bulk graphite or multilayer graphene samples without interfaces, independently of the lateral size of the sample [14]. For lamellae with thickness $d \geq 200 \text{ nm}$, the measured voltage at low enough temperatures and currents fluctuates around zero within $\leq \pm 20 \text{ nV}$. The finite sensitivity of the electronics and the noise do not allow, strictly speaking, the observance of a zero resistance state below $T_c$. For that purpose, one needs to show the existence of persistent currents, as done in [27], for example. The current-voltage ($I - V$) characteristic curves obtained for the studied lamellae are consistent with the existence of Josephson junctions, as Figure 3 shows for an 800-nm-thick lamella at different temperatures.

Figure 2. (a) Normalized voltage measured at 1 nA current vs. temperature of three lamellae with different thicknesses, namely 200, 300, and 500 nm ($\pm 20 \text{ nm}$) for blue dots, black squares, and red triangles, respectively. The right $y$-axis indicates the corresponding values obtained for the original bulk HOPG sample, from which the lamellae were obtained, for an input current of $1 \mu \text{A}$ (empty purple circles). Note that this $1 \mu \text{A}$ current is necessary to get a good signal to noise ratio because of the very small base-plane resistance of HOPG samples of high grade. Due to the usual input current position of the electrodes and the large mean free path of the graphene layers in HOPG [26], only a very small fraction, i.e., $\leq 0.001$ of that input current goes through the interfaces. (b) Normalized voltage vs. temperature at 1 nA current measured for a lamella with thickness 80 $\pm 10 \text{ nm}$, where a semiconducting behavior is shown.

Figure 3. Current vs. voltage characteristic curves at different temperatures for one of the studied lamellae (thickness $d = 800 \text{ nm}$, $T_c \sim 87 \pm 3 \text{ K}$). The inset blow out the data at low currents and low voltages. The continuous lines were calculated following [28] with the critical Josephson current $I_c$, as the only free parameter; see text.

Early theoretical work provides an adequate framework to understand the measured $I - V$ curves, including the influence of thermal fluctuations on Josephson junctions [28, 29]. It is found that there is always a finite resistance, even below the critical current $I_c$, due to thermally activated phase processes. Using the differential equation proposed in [28], we fit the measured $I - V$ curves with $I_c(T)$ the only free parameter. To present the results in actual units of current and voltage, the values of the resistance in the normal state $R_n$ have been used, obtained from the slopes of the $I - V$ curves well above $I_c(T)$ once the linear regime was reached. From the fits to the $I - V$ curves shown in Figure 3 we obtained $I_c(\mu \text{A}) = 0.162, 0.158, 0.091, \text{ and } 0.013$ at $T = 40, 50, 70, \text{ and } 85 \text{ K}$, respectively. The crossing of the $I - V$ curves at large voltages (see Figure 3), is due to the transition from the metallic- to a semiconducting-like temperature dependence at large currents, similar to the magnetic-field driven metal-insulator transition (MIT) in HOPG with interfaces [30]; see Figure 4.

It was already reported that a magnetic field of the order or larger than of a few kOe, applied normally to the interfaces, destroys the observed Josephson coupling for lamellae with large area interfaces [12, 31]. In this communication we would like to compare the effect of the input current and that of a magnetic field applied normal to the interfaces. Figure 4 shows the MIT at different magnetic fields obtained for the bulk HOPG sample (with contacts at the top) and the corresponding current-induced MIT in a lamella obtained from the same HOPG sample with contacts at the interface edges at zero field. The similarity is expected for granular superconductivity; the measured giant field anisotropy [12, 32] indicates that the superconductivity is located at the 2D interfaces.

Let us analyze the orders of magnitudes of the critical magnetic field and low-temperature critical currents obtained.
from the data in figures 3 and 4. The critical magnetic field of the order of 50 mT corresponds to a single magnetic flux quantum \( \frac{h}{2e} \) over an area \( \sim 4 \times 10^{-14} \text{ m}^2 \) or \( \sim 200 \text{ nm} \). On the other hand, typically in short Josephson junctions with junction resistance \( R_J \), the low-temperature critical current and the critical temperature are related by \( eI_J/k_B T_c = cR_J \), where \( c \) is a number of the order of unity. For \( I_J \approx 0.16 \mu\text{A} \) and \( T_c \approx 85 \text{ K} \), we hence get \( R_J \approx 46 \text{ k}\Omega \), or twice the (normal-state) quantum of resistance \( h/e^2 \). Since it is likely that a region of size \( \sim 200 \text{ nm} \) contains several quantum channels, the Josephson junctions are probably of the tunneling type, i.e., transmission between the superconducting regions is relatively low.

Figure 2(a) (right y-axis) shows the temperature dependence of the normalized voltage of a bulk piece of the HOPG (ZYA) sample, of the same bulk piece from where all the lamellae here studied were obtained. The voltage shows a maximum at \( T \approx 150 \text{ K} \). This maximum is not universal, but depends on the internal structure of the graphite sample. Our hypothesis is that the position of the temperature of the resistance maximum is directly related to the existence of interfaces and their properties. Following transport results in graphite flakes [9, 14] and an interpretation of the magnetic-field driven MIT in graphite [30], we argue that the maximum in the electrical resistance indicates the temperature below which a Josephson-like coupling between the superconducting regions within the interfaces starts to be measurable. In this case, one possible reason for the change in the temperature dependence of the resistance would be the size of the superconducting regions or the superconducting/normal ratio.

Figure 5(a) shows \( T_c \) obtained at 1 nA vs. the lamella thickness \( d \). We observe that the defined \( T_c \) decreases nearly linearly with decreasing \( d \) and extrapolates to zero at a finite thickness \( d \sim 160 \text{ nm} \). Curiously, this is of the same order of magnitude as the size scale obtained from the critical magnetic field. To check whether this decrease of \( T_c \) is not due to an increase in the current density related to the change in the lamella geometry, we have measured also the current density dependence of \( T_c \) in two TEM lamellae. Figure 5(b) shows \( T_c \) as a function of the current density changing the input current for constant geometry. One sees clearly a much weaker dependence than the one obtained changing the lamella thickness.

The behavior of the granular superconductivity at graphite interfaces is certainly not simply due to inhomogeneously distributed superconducting strength within the graphite interfaces due to, e.g., differences in the doping or
As the mean free path \( \ell \) is the critical temperature is
\[ T_c(d) = T_{\infty} e^{-t_0/(a/d)} \quad (1) \]

Independent measurements done in graphite flakes without (or with much less influence of) interfaces provide \( t \sim 3 \mu m \) at \( T < 100 \, K \) and therefore \( D \sim 1.5 \times 10^3 \, cm^2/s \). Note that this is four orders of magnitude larger than the one used in [33], meaning that the effect is relevant in far thicker samples or at much higher temperatures than in Nb/Al multilayers with \( T_c \lesssim 10 \, K \). We use this diffusion constant and \( T_{\infty} \approx 150 \, K \), i.e., the temperature of the maximum resistance measured in the bulk HOPG (see figure 2). The obtained numerical solution of equation (2) is plotted as the continuous green line in figure 5. The semiquantitative agreement is remarkable, as well as the estimated cut-off \( d_{\min} = \ell_0/(T_c) \approx 0.38 \, \mu m \), below which equation (2) has no solution.

We note that using either the theory of [34] or the model used in [33] to describe our results has many shortcomings: for interface superconductivity, we expect screening to be strongly inhomogeneous, whereas [34] assumes homogeneous superconductors and in [33] the metals did not differ very much. Moreover, even the use of the conventional weak-coupling theory in describing our results is questionable because of the high critical temperatures. One possible explanation of this high critical temperature is associated with the flat bands emerging at the interfaces due to either the presence of line or screw dislocations [15] or inclusions with rhombohedral stacking [17, 18]. However, a prediction of the screening effect on such flat band superconductivity does not yet exist.

Finally, it should be noted that some evidence for the formation of charge density waves (CDW) was found in CaC\(_6\) at \( \sim 250 \, K \), whereas its \( T_c = 11.5 \, K \) [37]. We note that this phenomenon is in many systems antagonistic to superconductivity [38], although coexistence with superconductivity has been reported in some systems, e.g., NbSe\(_2\) [39]. On the other hand, doping the surface of bulk graphite samples with Ca atoms showed hints of superconductivity of \( T \sim 200 \, K \) [40]. Future experiments should try to check whether CDW are also formed in HOPG interfaces and their possible relation with the size effect reported in this study.

In conclusion, we have found that the temperature at which the Josephson behavior in TEM lamellae sets in decreases with the size of the interfaces. This behavior provides a way to understand differences in the temperature dependence of the resistance in graphite samples with interfaces. Weak localization effects appear to be a possible origin for the here reported phenomenon.
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