Macroscopic-ranged proximity effect in graphite

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Abstract

We report proximity-induced superconducting features over macroscopic lengths in highly oriented pyrolytic graphite. The phenomenon is triggered when electrical currents are injected in the material through superconducting electrodes, few millimeters apart from each other. Such a large range is anomalous, as proximity-induced features in normal conductors hardly surpass few micrometers. The results can be explained as due to the presence of pre-existing superconductivity in graphite on small, localized regions.

Keywords: graphite, superconductivity, proximity effect, Dirac

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

When superconducting (S) and normal (N) materials are brought together, Cooper pairs from the S region drift into N. This is known as the superconducting proximity effect (PE), which causes a region of N close to the S–N interface to present superconductivity (SC). The effect occurs over distances of the order \( \xi_N \), the normal coherence length in N. This value depends on the ratio between the superconducting coherence length in S (\( \xi_s \)) and the mean-free path of carriers in N (\( l \)). For the limiting cases \( l \gg \xi_s \) and \( l \ll \xi_s \)—the clean and dirty limits—, \( \xi_N \) assumes the form \( \xi_N = \frac{\hbar v_F}{2\pi k_B T} \), respectively, [1] with \( v_F \) the Fermi velocity in N.

Although usually confined to regions tenths or hundredths of nanometers near the S–N interface, in some cases, the PE can occur over several thousand times the length \( \xi_N \). This is observed in selected S–N–S systems, and is related mostly to the properties of the N material. In underdoped cuprates, for example, such a behavior has been tentatively attributed [2–4] to the occurrence of superconducting fluctuations above \( T_c \). In clean transition-edge sensors, on the other hand, the survival of the PE over scales thousands of times higher than \( \xi_N \) is thought to happen due to the presence of nonequilibrium SC [5, 6]. In addition, geometrical quantization of superconducting excitations in clean N materials can protect supercurrents over length scales much above \( \xi_N \) (see, e.g. [7, 8]).

One possibility to obtain the PE over macroscopic scales, hence, is to study the properties of S–N–S sandwiches with...
clean N materials possessing both large $\xi_N$ and indications of superconducting fluctuations. A promising candidate satisfying both conditions is graphite, which can be described as a quasi-compensated layered semimetal. In this material [9–11], $\rho_i/\rho_s < 10^{-4}$, $I \lesssim 10 \mu m$ and $v_F \approx 10^6$ m s$^{-1}$. These values lead to large estimated normal coherence lengths at low temperatures $\xi_N(T = 4 \text{ K}) = h v_F/2\pi k_B T \approx 2 \mu m$. It also presents various indications of SC, reported across the literature. Among them, are the presence of switching features in magnetoresistance akin to Josephson junction arrays [12–15], signatures of a Bose-metal phase [16, 17] (also seen in Bi) and the existence of superconducting-like magnetization hysteresis loops even at high temperatures [17]. In addition, very recently, percolative ($R = 0$) SC has been measured in twisted bi- [18] and multi-layer [19] graphenes.

Given these signatures, it is conceivable that the superconducting PE in graphite can have a far longer reach than $\xi_s \approx 1 \mu m$, possibly reaching macroscopic scales. So far, however, no such a phenomenon has been observed. Instead, most available reports on the literature focus on nanometer-sized devices [20–24]. Here, we studied the electrical transport characteristics of millimetric samples outfitted with superconducting current-injection leads. Results revealed signatures of a long-range PE in our devices, persisting above 700 $\mu m$ (200–300 $\xi_N$) from the superconducting electrodes—an unusually long distance in bulk systems.

This work is organized as it follows: In section 2.1, the sample preparation and geometry are described. In section 2.2, the characterization of pristine graphite and the superconducting alloy are presented. Section 2.3 contains the main results of the manuscript, whereas sections 2.4 and 2.5 discuss the possibility of experimental artifacts by presenting scanning tunneling microscopy (STM) and Hall measurements. A discussion about the experimental results is carried out in section 2.6.

2. Results and discussion

2.1. Sample preparation

All our samples were extracted from a commercially-available highly oriented pyrolytic graphite (HOPG) crystal with 0.3° mosaicity [11]. Its room-temperature in-plane resistivity was, approximately, $5 \mu \Omega$ cm. The devices had typical in-plane dimensions of 5 mm $\times$ 1 mm and thicknesses varying between 0.15 mm and 0.4 mm.

Samples were either contacted in a standard four-probe configuration for electrical transport measurements, or in a six-probe Hall bar configuration for simultaneous Hall and longitudinal resistance measurements. Samples contacted in a four-probe configuration had voltage electrodes covering the whole sample’s surface width, as is schematized in the inset of figure 1. This was done to mitigate possible effects of current distribution in the material. Voltage electrodes of samples contacted in the six-probe Hall bar configuration were spread across the whole height of the sample, for the same reasons (see figure 5).

Additional devices were prepared in an eight-probe longitudinal/Hall-bar hybrid configuration. In it, electrodes were placed at the surface and edges of the samples. This geometry was realized to verify possible current distribution issues. In these devices, edge electrodes covered the whole sample height (as for devices with 6 probes), whereas top electrodes were point-like (see figure 8).

In total, ten samples were studied (labeled GS1 to GS10). With a single exception (GS8), all devices presented similar properties. Results representative of samples GS1, GS2, GS6 and GS10 can be found throughout the main text (figures 1, 2, 5 and 8, respectively). Additional results for sample GS1, as well as data for samples GS3–GS5 are shown on sections B and D of the supplementary material (https://stacks.iop.org/JPCM/33/495602/mmedia). Only a single sample did not exhibit a 4-probe transition within experimental accuracy. Its results are not shown here.

2.2. Control samples and the superconducting alloy

Control samples had all electrodes made of silver paste and were characterized in the interval $2 \text{ K} \leq T \leq 10 \text{ K}$. Measurements revealed a smooth metallic-like behavior, typical of well-graphitized HOPG [25–27]. Results are presented in figure 1.

Subsequent samples were contacted as indicated in the cartoon of figure 1, with two outermost electrodes composed of a superconductor (SC) and the remaining ones of silver paste. The distance between adjacent electrodes was approximately 0.7 mm to 1 mm. We refer to them by the numbers shown in figure 1.

The electrical resistivity of our devices was probed with DC and low-frequency AC measurements (up to $f \approx 5 \text{ Hz}$), which yielded the same results. Experiments were simultaneously performed in two-and four-probe configurations. Two-probe measurements ($2p$) were achieved by applying current
and measuring voltage between superconducting electrodes 1 and 4. Experiments in the four-probe configuration (4p) were performed by applying electrical current between (superconducting) contacts 1 and 4 and measuring the potential between the (normal) probes 2 and 3.

The superconductor chosen for the current electrodes was an alloy of In/Pb (50% in volume each) with critical temperature \( T_c \approx 6.8 \) K and critical magnetic field \( B_c(0) < 1.8 \) T (see the supplementary material for details). The alloy was connected to the edges of our samples with a soldering iron (see the supplementary material for details). The alloy was measured parallel to the graphene planes.

### 2.3. Transport measurements

The main result of the present work is illustrated in figure 1. In it, resistance vs temperature plots of the sample GS1 are shown. Measurements were carried out prior and after connecting SC current-injection leads to the device. While no anomaly was observed for a sample with only N electrodes, the injection of electrical currents through SC contacts induced a superconducting-like transition in 4p measurements. This occurred despite voltage probes being distant ca 0.7 mm–1 mm from the SC contacts (two orders of magnitude above \( \xi_c \)). Such a behavior was shared by all our devices.

The details of the 4p feature, however, were sample-dependent. In eight of our devices, the transition manifested as a sharp decrease of the 4p resistance \( R_{4p} \equiv V_{4p}/I \) at the applied current) below \( T_c \). In one sample, it manifested as a sharp increase. One device did not present signatures of the 4p transition, within experimental uncertainty. When a decrease was observed, it accounted for, at most, 10% of the sample resistance at the center of the transition. Its general behavior was similar to the one observed in 2p measurements \( R_{2p} \equiv V_{2p}/I \), which are undoubtedly associated to the SC at the SC electrodes. The large distances between the normal and superconducting contacts in the 4p configuration, however, do not allow for the same interpretation. In what follows, we consider data of the majority of devices, showing a sharp decrease in \( R_{4p}(T < T_c) \). The discussion, however, can also be applied to the case when a sharp increase manifests.

Figure 2 shows the behavior of sample GS2 in the presence of in-plane magnetic fields \((B \parallel c)\) for the 2p and 4p configurations. This orientation was chosen to suppress the high orbital magnetoresistance of graphite, which can reach 1000% for relatively low \((\approx 0.1 \) T) magnetic fields along the material’s \( c \)-axis [11]. Because the phenomenon of interest was superimposed to this response, the chosen geometry ensured the best possible experimental resolution. Similar results were obtained for \( B \parallel c \) and are shown in the supplementary material. In the sample, the electrical current leads presented a contact resistance \( R_C \approx 12.5 \) m\( \Omega \) at \( T = 2 \) K, while graphite \( (R_{2p} - 2R_C) \) had a resistance of approx. 32.3 m\( \Omega \). Two-probe measurements revealed a clear superconducting transition with \( T_c \approx 6.8 \) K, accounting for up to 6% of the total sample resistance at zero magnetic field. A transition was also observed in 4p measurements in the same temperature range, albeit accounting for up to 3% of the measured signal.

The amplitude of the 4p transition, defined as \( \Delta R_{4p} \equiv |R_{4p}(T \lesssim T_c) - R_{4p}(T \gtrsim T_c)| \) (see figure 3), did not vary monotonically as a function of \( B \). Instead, it increased with the applied magnetic field, reaching saturation above 0.1 T (see figure 3). This behavior can be understood by considering the creation of a low-resistance channel below \( T_c \), which operates in parallel with graphite. The equivalent circuit is represented as a cartoon in figure 3. In it, the low resistance channel (denoted by \( R_L \)) acts as a shunt resistor, which carries a fraction \( I_L \) of the total electrical current \( I_0 \) applied to the system. Assuming that \( R_{4p} \) senses mostly the dissipative channel of graphite, the measured resistance below \( T_c \), can be expressed as a function of \( I_s \) by

\[
R_{4p}(T < T_c) \equiv \frac{V_{4p}(T < T_c)}{I_0} = \frac{R(T) \times (I_0 - I_s) + I_s}{I_0}, \tag{1}
\]

where \( V_{4p}(T < T_c) = R(T) \times (I_0 - I_s) \) corresponds to the actual measured voltage drop between normal electrodes on the sample, and \( R(T) \) is the resistance of pristine graphite.

Above \( T_c \), \( R_{4p}(T) \) should match the resistance of the pristine sample, as the low resistance channel ceases to exist \( (I_s = 0) \). In this case \( R_{4p}(T > T_c) = R(T) \times I_0 \) and, through equation (1), we obtain a simple expression for the amplitude of the 4p transition

\[
\Delta R_{4p} \equiv R_{4p}(T \lesssim T_c) - R_{4p}(T \gtrsim T_c) \approx R(T_c) \times \frac{I_s}{I_0}. \tag{2}
\]

Considering the weak slope on the \( R(T) \) behavior of pristine graphite (see figure 1), \( R(T_c) \) is approximated by \( R(T_c) \approx R_{4p}(T \gtrsim T_c) \). The expression (2) can then be normalized, resulting in

\[
\frac{\Delta R_{4p}}{R_{4p}(T \gtrsim T_c)} \approx \frac{I_s}{I_0} \propto I_s \tag{3}
\]

and providing a link between \( \Delta R_{4p} \) and \( I_s \).

We first consider the behavior of \( \Delta R_{4p}/R \) at weak magnetic fields \( B < 0.1 \) T (see figure 3(c)). In this field range,
by assuming a low resistive channel, after the subtraction of a polynomial resistance background \( R_0(T) \). \( \Delta R_{4p} \) is chosen at the point indicated by an arrow in the figure. This value corresponds to the intersection between the maximum slope during the transition and a linear extrapolation of the \( R_{4p} \) behavior above \( T_c \). This value corresponds to the intersection between the maximum slope during the transition and a linear extrapolation of the \( R_{4p} \) behavior above \( T_c \). The inset shows the derivative of the 2\( p \) resistance as a function of temperature. The maxima in such curves were chosen as the transition temperature.

\[
B_c(T) = B_c(0) \left( 1 - \frac{T_c}{T_c^{0}} \right),
\]

which correlates the transition temperature \( T_c \) with the applied field \( B_c \). In the equation, \( B_c(0) \) corresponds to the critical magnetic field at \( T = 0 \) K, and \( T_c^{0} \) the critical temperature at zero magnetic field.

The \( B_c(T) \) diagrams for sample GS2 are shown in figure 4. They revealed that the 4\( p \) feature happened at lower temperatures and magnetic fields in relation to the 2\( p \) transition. This result suggests the 4\( p \) transition as a consequence of the 2\( p \) one. Indeed, both 2\( p \) and 4\( p \) measurements revealed two transitions occurring in close proximity, which can be linked to the existence of two phases in the SC electrodes, with similar \( T_c \)’s (see the supplementary material). The persistence of these features in 4\( p \) measurements indicate that the suppression of the 4\( p \) transition by magnetic fields is closely related to the suppression of SC at the current electrodes [29]. This is also reinforced by the fact that the \( B_c \) vs \( T \) diagram for the 4\( p \) transition remains unchanged after modifying the magnetic field orientation relative to the sample’s c-axis (see the supplementary material). Such a result strengthens the hypothesis of superconducting electrodes as the objects inducing the phenomenon at hand. It also shows that the magnetic flux through the regions of HOPG responsible for the 4\( p \) transition does not depend on the magnetic field orientation. In a highly anisotropic system such as graphite, the latter can be explained by a low resistance channel confined to low-dimensional (quasi-1D or quasi-0D) sites/structures within the material.

The existence of these regions/structures would also explain the behavior of \( R_{4p}(T) \) in our devices, which did not show a continuous drop below \( T_c \) when compared with pristine samples (see figure 1). Such a result is at odds with the conventional superconducting PE. In it, the 4\( p \) resistance should
change linearly with $\xi_N$, roughly $[1, 30]$ as $R_{4p}(T) \propto R_0(1 - \kappa_N/T)$. Instead, our $R(T)$ results suggest that an eventual proximity-induced state seen in 4$p$ must be confined to a fixed fraction of the sample volume, as also inferred from measurements performed at $B \perp c$ and $B \parallel c$. This hypothesis is further supported by measurements in samples contacted in the 6$p$-Hall configuration, see figure 5. On them, the resistance drop below $T_c$, observed in the longitudinal resistance, was larger than on other configurations (about 10% of the total measured signal). Meanwhile, a negligible change in the Hall effect was observed in the same temperature range. Such results are consistent with the induction of the phenomenon at small, localized puddles on the sample, which usually do not contribute to the material’s Hall conductivity.

The absence of the conventional superconducting PE in our samples is further evidenced by experiments in asymmetric devices with a single superconducting electrode. Measurements in this configuration did not present any anomaly (see figure 6). These results also weight against experimental artifacts due to the distribution of electrical currents. Had this been the case here, the presence of a single superconducting electrode should suffice to prompt changes near at least one of the voltage probes, therefore, triggering the same effect as seen in 4$p$.

2.4. Surface characterization

We proceed to verify if our observations could be an artifact caused by the diffusion of superconducting material throughout graphite, originating from the current electrodes, or due to the dispersion of a ‘cloud’ of superconducting particles across the sample surface during soldering.

Both possibilities are unlikely due to the characteristic time lengths involved in the soldering process (few seconds) and to the fact that no flux is used (hence, no ‘particle cloud’ should form). For confirmation, scanning electron microscopy (SEM) measurements and extensive low-temperature scanning tunneling spectroscopy (STS) at different points across sample surfaces were carried out. Superconducting dust splattered during soldering should be observable in SEM images as small particles. Diffusion of superconducting material throughout graphite should manifest as superconducting gaps of amplitude $\approx 1$ meV (the same one of lead) on scanning tunneling spectra measured over large sections of HOPG. Neither of these features were observed. In particular, STM measurements in HOPG did not show qualitative differences above and below its electrode’s $T_c$. Combined, these observations categorically discard In/Pb diffusion or localized foreign superconducting islands as the source of our observations. Examples of SEM images of the sample surface, together with typical STM spectra are shown in figure 7.

Despite not showing signatures of SC, STS did reveal features similar to those of graphite/graphene. These include occasional regions with linear, graphene-like spectra, periodic peaks on the density of states as a function of bias voltage, and small pseudo-gap-like features, with energies in the range of 10 meV (see figures 7(c) and (d)). The latter have been previously observed and were associated with van-Hove singularities caused by the twisting of adjacent graphene layers. The obtained gap width (10 meV) corresponds to a rotation between layers $[31]$ around 1.13’. This value is close to the ‘magic angles’ for which bilayer graphene has been recently reported to present SC $[32]$. Such a result provides a candidate for the localized regions subject to induced SC in our samples.

Additionally, STM measurements made in the contact regime (i.e., the probing tip was touching graphite’s surface) presented zero bias conductance peaks in some regions of the sample surface. They manifested as a nearly two-fold enhancement of the local differential conductance in graphite. Such a feature was well-described within the Blonder–Tinkham–Klapwijk model for a direct ballistic N–S point contact junction $[33]$. This feature, which is shown in the
supplementary material, will be discussed in more detail elsewhere. Such results suggest the possibility of Andreev reflections of quasiparticles in a ballistic microstriction between a normal metal tip and a superconducting region, occurring during measurements in different parts of the sample.

2.5. Current distribution

In anisotropic materials (such as graphite), contact placement can aggravate current distribution issues. These, in turn, can cause artifacts that compromise measurements. In this work, we minimize possible artifacts arising from current distribution by choosing different contact configurations/geometries, by measuring several devices, and by probing different samples.

As explained in section 2.1, samples were contacted with three different probe configurations. Two of those are represented in figures 1 and 5. Namely, samples with four probes were measured as schematized in the insert of figure 1, with electrodes spanning the whole width of the sample. Conversely, samples contacted in the six-probe Hall configuration (figure 5) had voltage electrodes placed only at the sample’s edges, covering its entire height. Yet, in both cases, a clear transition to a lower resistance state was observed below $T_c$ (see figures 1, 2 and 5).

The same qualitative behavior in both four-probe and six-probe-Hall geometries indicate that our samples are not subject to current distribution issues. Otherwise, qualitatively different results would be expected, hinging on contact positioning. This argument is supported by measurements performed in samples containing a single superconducting electrode. Results for one of these devices are shown in figure 6. All samples measured in this configuration (three in total, see the supplementary material) did not present transitions below $T_c$. Had the origin of the $4p$ transition been associated with current distribution caused by the SC electrodes, it should also manifest on those samples.

Despite all our samples being prepared using the same raw materials, measurements performed on the four-probe and six-probe-Hall configurations, as shown in figures 2 and 5, were realized on different devices. To account for this, a sample was prepared in an eight-probe hybrid configuration. This geometry was a combination of the four-probe and six-probe Hall geometries, thus allowing the simultaneous measurement of the longitudinal $4p$ sample resistance at the top and along the edges of the sample. A schematic is shown on the inset of figure 8. Due to conservation of charge, current distribution issues on this device would require qualitatively different behaviors to be observed on different electrodes. Instead, similar measurements were obtained for both top and edge electrodes, corroborating the results presented in figures 2 and 5. Such a result further discards current inhomogeneities as the source of the $4p$ transition reported here.
The overall behavior of the $4p$ transition triggered in graphite supports the presence of induced superconducting features in our devices in ranges above those of the conventional superconducting PE. Its characteristics, however, do not point towards a bulk-related phenomenon. As discussed in section 2.3, the properties of our samples can be described by the existence of two independent transport channels acting in parallel: a high- and a low-resistance one. The high resistance channel seems to be related to transport through pristine graphite, whereas the low resistance channel is unambiguously associated to the presence of superconducting electrodes in the device. The fact that Hall measurements remain unchanged above and below $T_c$, whereas the sample’s longitudinal resistance shows variations as large as 10%, strongly suggests that transport through the low resistance channel occurs along small localized grains in graphite, which should not contribute to its Hall resistance.

Suitably, the occurrence of the conventional superconducting PE does not justify the $4p$ transition. As previously presented, the lack of features in samples with a single SC electrode, the null dependence on $T$, the increasing transition amplitude with magnetic fields, and the long range of the phenomenon (up to 700 $\mu$m – 1 mm distant from the superconducting electrodes, whereas $\xi_N \approx 1–2$ $\mu$m [1, 9–11, 36–38]) all attest against such a hypothesis.

Instead, all our results can be accounted for by considering the pre-existence of mesoscopic, superconducting-prone islands in graphite. This hypothesis is consistent with previous reports in the literature, which indicate localized superconducting domains in the material [12, 14–16, 39]. In this context, the presence of superconducting leads can act as a trigger for global coherent transport along such a pre-existing channel. In addition to overall sample behavior, superconducting puddles can be justified by point contact measurements performed during our STM study. These provided strong indications of Andreev reflections across graphite’s surface, signaling the existence of superconducting regions in bulk HOPG with dimensions above the superconducting coherence length [40].

Pristine samples, however, showed no superconducting-like transitions, in agreement with most reports to date [11, 17, 21, 41, 42]. Such an observation requires that the transfer of charge from bulk graphite to the hypothesized superconducting regions must be forbidden under normal conditions. This can be justified self-consistently by considering the superconducting islands in graphite as objects with reduced dimensions embedded in a low-conductance quasi-2D electron gas (2DEG). This hypothesis has been suggested on previous STM, magnetization and transport studies in different types of pristine graphite [12, 14–16, 26], as well as inferred from our measurements.

Indeed, considering the typical $4p$ sample resistivity around $\sigma \approx 5$ $\mu$Ω cm (see figure 1) and assuming a homogeneous current distribution across the sample volume, our devices show a conductance per graphene layer of the order $\sigma_L = \sigma c_0 / t \approx 4.6 \times 10^{-4} \approx 6G_0$. In it, $c_0 = 0.335$ nm is the interplane spacing in graphite, $t \approx 0.2$ mm the sample thickness and $G_0 = 2e^2 / h$. In this case, the system could be roughly described as an array of superconducting islands at $T \ll T_c$, embedded in a quasi-2DEG with local conductance close to the conductance quantum. This situation is similar to a graphene film decorated with superconductors, tuned near the charge neutrality point [29]. Under such circumstances, the Coulomb blockade impeding the introduction of carriers into the superconducting islands is expected to decrease with the conductivity of the 2DEG, following $\exp(-\pi^2G_0/8)$, $G_0$ the conductance of the metallic matrix [43, 44]. Such an enhanced Coulomb blockade at low conductances (approaching a few kilo Ohms) can lead to a weak charge quantization in the superconducting grains. This forbids charge transfer to/from the superconducting regions. The phenomenon effectively disables the superconducting channel in the material by fixing the number of Cooper pairs in the system ($\Delta N = 0$), which results in large phase fluctuations destroying the macroscopic superconducting order [43].

However, the introduction of superconducting leads in the sample acts as a reservoir of Cooper pairs, bypassing the weak quantization constraint and effectively delocalizing carriers ($\Delta N \neq 0$). This re-enables transport by this network of

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**Figure 8.** Normalized $R_{4p}(T)/R_{4p}(T = 2\,K)$ measurements for a sample prepared with 8 electrodes (GS10), as represented in the inset of the figure. The current electrodes were made of a Pb/In alloy, whereas all voltage electrodes were composed by Ag paste. $R_1$, $R_2$ and $R_3$ correspond to the respective electrode pairs shown in the inset. The normalizing factors were $R_{4p}(T = 2\,K) = 7$ $\mu$Ω, 3 $\mu$Ω and 13 $\mu$Ω for $R_1$, $R_2$ and $R_3$, respectively. $R_1$ and $R_3$ were measured along the sample edges, whereas $R_2$ was measured at the sample top. Curves have been shifted vertically for clarity.

Finally, we verified possible instabilities of the instrumentation used during the experiments. For this, a piece of copper was probed under the same conditions as used for graphite samples. Results did not reveal any transitions (see the supplementary material), discarding instrumentation artifacts from current sources, amplifiers and voltmeters as the source of our observations in graphite.

**2.6. Discussion**

The overall behavior of the $4p$ transition triggered in graphite supports the presence of induced superconducting features in our devices in ranges above those of the conventional superconducting PE. Its characteristics, however, do not point towards a bulk-related phenomenon.
superconducting islands—thus resulting in the observed behavior in 4p measurements.

Our interpretation is also consistent with previous analysis of the magnetic-field-induced metal–insulator transition taking place in HOPG, which indicated intrinsic 2e carriers in the material [13]. In particular, the characteristic magnetic field \( B_0 \approx 0.13 \) T related to the suppression of the 4p transition (figure 3), is very close to the critical magnetic field \( B_{\text{crit}} \approx 0.11 \) T associated with the suppression of the bosonic character of carriers in the system [13]. The presence of paired electrons in the absence of a coherent superconducting phase entails the existence of localized superconducting puddles. Hence, if the 4p transition is to be related to small superconducting-prone regions, its suppression should occur in tandem with the suppression of the Bose-metal phase discussed for graphite [13].

This is indeed suggested by the similarity between \( B_0 \) obtained here and the parameter \( B_{\text{crit}} \) of reference [13]. In the context of thick S–N–S junctions, the characteristic magnetic field \( B_0 \approx 0.13 \) T (see figure 3 and the associated discussion) can be further related to a distance \( L \) between superconducting regions within graphite. This distance can be estimated as \([28] L = 2\sqrt{\pi/\left(2\pi e B\right)} \approx 100 \) nm. Such a value is justified by considering that low magnetic fields (prior to the suppression of SC at the electrodes) disrupt the interaction between superconducting grains within graphite, rather than a macroscopic weak link between the two superconducting electrodes. Random in nature, such grains are to present a sample-dependent distribution. Hinging on their size and coupling, their network can act either as a low- or a high-resistance channel for carriers, akin to observations in homogeneous and highly granular superconducting thin films, respectively [45].

Although not showing signs of a superconducting gap, STM measurements allow for a second, upper limit estimation of the average distance between such grains. A proximity-induced superconducting gap in an N layer of thickness \( L \) is expected to be at least 3 times larger than the structure’s Thouless energy \([46, 47]E_{\text{Th}} = \hbar D/L^2.\) In it, \( D \) is the electronic diffusion coefficient on N. For graphite with electronic mobility \([11] \mu \approx 10^6 \) cm² V⁻¹ s⁻¹, \( D \approx 100 \) cm² s⁻¹ at \( T = 1 \) K. Assuming \( E_{\text{Th}} \lesssim 5 \times 10^{-4} \) meV (our STM experimental resolution) results in an estimated distance between superconducting puddles on graphite of the order \( L \approx 1 \) μm. In multigraphenes, proximity phenomena have been shown to surpass these distances [48].

The remaining issue becomes, then, the identification of such regions. The absence of clear evidence of superconducting gaps in STM scans seem to discard most of the features commonly found in the surface of graphite (e.g. wrinkles, folds, bubbles, impurities and grain boundaries) as possible candidates for hosting the proposed superconducting-prone regions. We are not able to eliminate, however, regions with gap-like structures in their STS (see figure 7). These can be associated with the twisting of adjacent graphene layers by small angles [31]. Such regions have been demonstrated to host SC at low temperatures. However, STM measurements specifically designed to probe their properties are yet to reveal clear evidence of superconducting gaps at temperatures as low as 1 K (see e.g. references [49, 50]).

Additionally, experiments performed by us in samples contacted at their lateral edges (see figure 5) have shown resistance drops below \( T_c \) amounting for about 10% of the total measured signal. Transitions on this geometry were better-defined and larger than those observed on samples contacted at the top surface—figures 2 and 5. Edge regions are more susceptible to deformations during the sample cutting process, which generates different types of irregularities. Enhanced transitions observed along them further indicate lattice distortions as possible candidates for the phenomenon at hand. Unfortunately, due to the disordered nature of graphite’s edges, we are currently unable to probe their differential conductance (as done for the remainder of the sample surface).

In short, we demonstrated the induction of a macroscopic, long-range, superconducting-like PE in bulk graphite outfitted with superconducting current leads. The phenomenon manifests as SC-like transitions on graphite’s resistance, which was probed 700 μm–1 mm away from the superconducting electrodes (much above \( \xi_N \approx 1–2 \) μm). The suppression of these transitions is closely related to the breakdown of SC on the current probes, thus suggesting that an unconventional superconducting PE is at play. Our work supports the existence of intrinsic superconducting correlations in low-dimensional, localized regions of pristine graphite. Unfortunately, structural traits responsible for such properties could not be pinned from our measurements. However, results seem to discard features commonly found in the surface of graphite as their source. Our observations open routes toward superconducting electronic circuitry in bulk materials regardless of their volumetric conductivity.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.
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