Ferromagnetic- and superconducting-like behavior of the electrical resistance of inhomogeneous graphite flake

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Abstract

We have measured the magnetic field and temperature dependence of the resistivity of several micrometers long and heterogeneously thick graphite sample. The magnetoresistance results for fields applied nearly parallel to the graphene planes show both a granular superconducting behavior as well as the existence of magnetic order in the sample.

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The possible existence of high-temperature superconductivity in highly oriented pyrolytic graphite (HOPG) has been speculated 10 years ago from resistivity and SQUID measurements \[1\]. For fields parallel to the c-axis of the HOPG samples and after subtraction of the huge diamagnetic background, the magnetization showed superconducting-like, sample-dependent hysteresis loops \[1\]. Strikingly, SQUID measurements indicated also the presence of high-temperature magnetic order in graphite. Both behaviors appeared to depend on the sample and its thermal treatment. The intrinsic origin of the ferromagnetic signals in HOPG in virgin as well as in irradiated HOPG found convincing evidence through SQUID, x-ray magnetic circular dichroism (XMCD) and anisotropic magnetic resistance (AMR) measurements, see Ref. \(2\) and Refs. therein. There is consent that this phenomenon is related to defects in the graphite structure, including non-magnetic ad-atoms as hydrogen \[3, 4, 5, 6, 7\].

Regarding the existence or not of superconductivity in graphite several studies provided some but still not conclusive support for its existence, see Ref. \(1\) and Refs. therein. Theoretical work that deals with possible superconducting states in graphite as well as in graphene has been published in recent years. For example, \(p\)-type superconductivity has been predicted to occur in inhomogeneous regions of the graphite structure \(8\) or \(d\)-wave high-\(T_c\) superconductivity in graphite based on resonance valence bonds \(9\). Following the BCS approach in two dimensions (with anisotropy) critical temperatures \(T_c \sim 60\) K have been estimated if the density of conduction electrons per graphene plane is \(n \sim 10^{14}\) cm\(^{-2}\), a density that might be induced by defects and/or hydrogen ad-atoms \(10\). Predictions for superconductivity in graphene were also published \(11, 12\) supporting the idea that \(n > 10^{13}\) cm\(^{-2}\) in order to reach \(T_c > 1\) K. In contrast to the basically 3D superconductivity in intercalated graphitic compounds, see e.g. Ref. \(13\), it is speculated that \(T_c\) in the graphene layers of graphite may be much larger because of the role of the high-energy phonons of the 2D graphite structure itself \(10\).

Recently published high-resolution measurements of the magnetoresistance (MR) of micrometer small and several tens of nanometers thick graphite samples suggest the existence of inhomogeneous, granular superconductivity with critical temperature \(T_c \gtrsim 25\) K \(14\). The claim of granular superconductivity in graphite is based on three main observations: (a) the existence of anomalous hysteresis loops of resistance versus magnetic field applied parallel to the \(c\)-axis that indicate the existence of Josephson-coupled superconducting grains, (b) the observation of oscillatory behavior in the magnetoresistance vs. field that can be related to
Andreev reflections of Copper pairs at the interfaces of superconducting and semiconducting regions, similar to a phenomenon observed recently in conventional superconducting-normal junctions \[15\], and (c) the phenomena observed in (a) and (b) vanish at \(T > T_c\), where \(T_c\) denotes the temperature at which the resistance \(R(T)\) reaches a maximum, i.e. \(R(T < T_c)\) shows metallic behavior with an anomalous large magnetoresistance. The observed phenomena support the view that HOPG is a system with non-percolative superconducting domains immersed in a semiconducting-like matrix \[14\].

Recent experimental study suggests that the internal interfaces between \(\sim 50\) nm thick (in the c-axis direction) crystalline graphite regions running parallel to the graphene planes might be the regions where superconductivity is located \[16\]. These interfaces may have enough carrier density to trigger granular superconductivity with different critical temperatures, keeping the quasi-two dimensional behavior. This phenomenon is actually not new but already observed at the interfaces between Bi crystals where superconductivity up to \(\simeq 20\) K was found, although pure Bi is not superconducting \[17\].

The aim of this work is to check whether transport measurements could provide further evidence for a granular superconducting-like behavior. For this purpose we need to locate the voltage electrodes nearer those internal interfaces. Simultaneously, we search for ferromagnetic-like behavior in the MR, which should exist in virgin HOPG samples according to SQUID results for fields applied parallel to the graphene planes \[2\]. Our experimental work demonstrates that a heterogeneously thick and several micrometers long graphite flake shows superconducting as well as ferromagnetic-like behaviors in the MR. The prevailing behavior depends on the measured region on the sample.

The sample we show in this study was obtained from a HOPG sample with 0.4° rocking curve width. The impurity levels of metallic elements are below 5 \(\mu\)g/g with the exception of V (16 \(\mu\)g/g). The preparation of the MG samples is simple and based on exfoliation of pieces of the HOPG sample. We have used ac current \(I\) of amplitude \(\lesssim 1\) \(\mu\)A. Current dependent behavior has been observed at \(I \gtrsim 3\) \(\mu\)A but because self heating effects can play a role, we will not discuss this in this work. Note also that the current does not flow only through the interfaces and therefore the interpretation of current dependence in the MR is not simple.

Figure \(\Pi(a)\) shows an optical microscope picture of the measured \(\sim 200\) nm thick sample without electrodes (sample S2A). The pictures in Fig. \(\Pi(b)\) show the AFM signals measured
at two different regions (see line scans in (a)). In the lower sample region the AFM scan shows several steps of $\sim 30$ nm height each. Taking into account the internal structure of HOPG, see the TEM picture in Fig. 1(c) and also Ref. 16, some of the steps are related to the interfaces between crystalline regions than run inside the sample parallel to the AFM plateaus. From the lower to the upper part of the sample (path 2 in (a)) there is an increase of thickness of $\sim 100$ nm, see upper AFM scan in Fig. 1(b). Therefore, we decided to put two pairs of voltage electrodes at the lower and upper parts of the sample, labeled CH3 and CH4 and the electrodes for current at the two extrema $I_+, I_-$, see Fig. 1(d). In Fig. 1(c) we have drawn schematically the positions of the CH3 electrodes as well as some of the expected granular superconducting regions (red straight lines parallel to the graphene planes and the interface region) separated by semiconducting regions (gray lines) at one of the interfaces. The measurements presented below were done on the longitudinal channels CH3 and CH4. The other channels CH5 and CH6 show a mixture of usual Hall, planar Hall effect features and longitudinal resistance behavior, as observed in CH3 and CH4 when the field is applied nearly parallel to the sample surface, and will not be further discussed here.

Figure 2 shows the temperature dependence of the normalized resistance $R(T)$ measured at CH3 and CH4. This dependence is typical for MG samples of this thickness [14, 16], i.e. $R(T)$ shows a semiconducting behavior with a sample and position dependent resistance maximum. The semiconducting behavior of $R(T)$ is basically intrinsic of graphite; it is affected by lattice defects and in particular by the interfaces between crystalline regions [16]. In the inset of the same figure we show $MR = R(B) - R(0)/R(0)$ at two temperatures for CH3 and for fields applied normal to the graphene planes of the sample. Although the zero-field resistances at 4 K and 100 K are equal, the MR’s differ each other in disagreement with Kohler’s rule. This indicates that there is an extra electronic mechanism that increases by $\sim 25\%$ the MR(8T) at 4 K with respect to 100 K.

Taking into account previous results [14, 16], we interpret the decrease of $R$ below $\sim 50K$ for CH3 as due to weakly coupled superconducting regions. Decreasing temperature the phases of the order parameters of individual superconducting regions become correlated decreasing the total resistance. Within this hypothesis the whole behavior of $R$ depends on the single grains condensation energy and the strength of the intergrain Josephson coupling energy. Global superconductivity is established via Josephson tunneling if there is sufficiently long-range phase coherence. If the superconducting regions are localized at the boundaries
FIG. 1: (a) Optical picture of the MG sample. The lines 1 and 2 give the scan directions of the AFM line scans shown at (b). (c) Electron transmission microscope picture of a 200 nm thick lamella obtained from the same bulk HOPG sample as the MG sample. The \( c \)-axis of the graphite structure runs normal to the interfaces. The thickness of the single crystalline regions (defined by the homogeneous gray color regions) is between 20 nm to \( \sim \) 70 nm. At the top of this picture we draw schematically the positions of the CH3 and current electrodes. In case superconducting regions exist between the CH3 electrodes, e.g at the red lines depicted in the picture, separated by semiconducting regions (gray lines), we expect to see some evidence in the voltage drop. (d) Optical microscope photo of the sample with its electrode distribution.

or interphases between crystalline graphite regions, see Fig. 1(c), even in the case a long range macroscopic phase coherence would exist at the interfaces, it is clear that due to the \( c \)-axis resistance a zero-resistance state can never be measured between the electrodes of CH3.
FIG. 2: Temperature dependence at zero applied field of the normalized resistance for the two longitudinal channels CH3 and CH4. The inset shows the magnetoresistance $MR$ at two temperatures for CH3 and fields applied normal to the graphene planes of the sample.
If our assumption of granular superconductivity below $\sim 50$ K for the region measured by CH3 is correct, the MR results shown in Fig. 2 suggest that the contribution to the MR due to granular superconductivity is overwhelmed by a large background, whatever its origin. Because our aim is to search for a more obvious hint for superconductivity in the MR, it should be clear that we need to decrease the MR background substantially. This is possible reducing the field component normal to the graphene layers [19] in such an amount that the applied field will still be able to influence the order parameter of the superconducting grains and/or the coupling between them.

Figure 3 shows the MR measured at CH3 (a) and CH4 (b) at different temperatures below 50 K. The magnetic field was applied parallel to the main area of the sample within $\pm 3^\circ$. The MR of CH3 shows an unique behavior not yet reported so far for graphite. At low $T$ the MR increases abruptly at $B \gtrsim 0.25$ T and saturates at $B \gtrsim 0.75$ T. According to recently done theoretical estimates, the carrier density as well as the effective mass of the carriers in HOPG can have a strong influence on its $T_c$ [10]. Therefore, we expect a distribution of $T_c$ at the interfaces. We interpret the broadening of the transition at higher $T$ as related partially to the expected distribution of $T_c$, to the increasing phase fluctuations with $T$ but also to a Hall component, which is the origin of the field asymmetry in the MR clearer observed at higher $T$, see Fig. 3(a).

At low enough $T$ the overall behavior of the MR measured at CH3 resembles that found in different granular superconductors. The negative and small MR observed at low fields and the change to a positive MR, see Fig. 3(a), are features strikingly similar to that observed in, e.g. fractal Pb films [20, 21], Al nanowires [22], or Sn stripes close to the global $T_c$ [23]. Several interpretations about the origin of the negative MR have been published, as e.g. non-equilibrium charge imbalance at normal-superconducting interfaces produced by localized phase-slip centers [22, 23], quenching of the pair-breaking effect by the applied field on Kondo impurities localized at the interfaces [20], increase of the local critical current (determined by the interference between regions of different superfluid densities) with field [20] or to the coexistence of two superconducting phases [21]. In our case, however, the negative MR at low fields and temperatures has a different origin, as we demonstrate below.

The MR of CH4, measured simultaneously with that of CH3, shows a qualitatively different behavior, see Fig. 3(b). This is compatible with those observed in many ferromagnetic materials. This negative MR is accompanied by a hysteresis at low fields, see Fig. 4 that
FIG. 3: (a) Magnetoresistance measured at CH3 vs. magnetic field applied parallel to the graphene planes within $\pm 3^\circ$ at different temperatures. (b) The same but for CH4. The current was applied at an angle of 55$^\circ$ with respect to the magnetic field. The saturation of the MR is observed up to 8 T, the highest field applied.

gets smaller the higher the temperature. This fact reveals the existence of magnetic order similar to the one reported recently for irradiated HOPG sample [2, 24]. Note that at low fields the negative MR is practically identical for both channels, see Fig. 4(a), and that this vanishes for $T \to 50$ K for CH4. We can estimate the change of ferromagnetic magnetization at saturation $M_s$ assuming that $M_s \propto MR^{1/2}$ at high enough fields. Using the data obtained at 7 T for the MR at CH4, we obtain a linear decrease of $M_s$ with $T$ with an effective critical Curie temperature $T_C \sim 50$ K, see Fig. 4(b). This linear decrease with $T$ of $M_s(T)$ agrees with the quasi two-dimensional magnetic order in proton- [25] as well as carbon-bombarded HOPG samples [26]. We note, however, that this Curie temperature is an effective one since
FIG. 4: (a) Magnetoresistance of CH3 and CH4 at 4 K for magnetic fields applied parallel to the sample graphene planes and at an angle of 55° from the applied current direction. (b) Temperature dependence of the square root of the magnetoresistance at saturation ($B = 7$ T) that is proportional to the ferromagnetic moment at saturation obtained for CH4. The linear behavior agrees with that observed in virgin and irradiated graphite samples and it is compatible with 2D magnetic order [2, 25].

the electrodes measure in parallel both ferromagnetic as well as non-ferromagnetic regions that could have lower resistivity at high $T$ and therefore affect the measured voltage. We may conclude therefore that in the sample region measured by CH4 the ferromagnetic signal overwhelms.

In conclusion we have measured the temperature and magnetic field dependence of the resistivity of an inhomogeneous, mesoscopic HOPG sample. The behavior depends on the sample region. In particular in sample regions where the electrodes pick up the response
of interfaces between crystalline regions inside the sample, the behavior of the MR resembles that of granular superconductors. In agreement with SQUID measurements done in virgin HOPG samples for fields normal to the c-axis, our transport measurements reveal a ferromagnetic behavior, which is the origin of the negative MR.

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